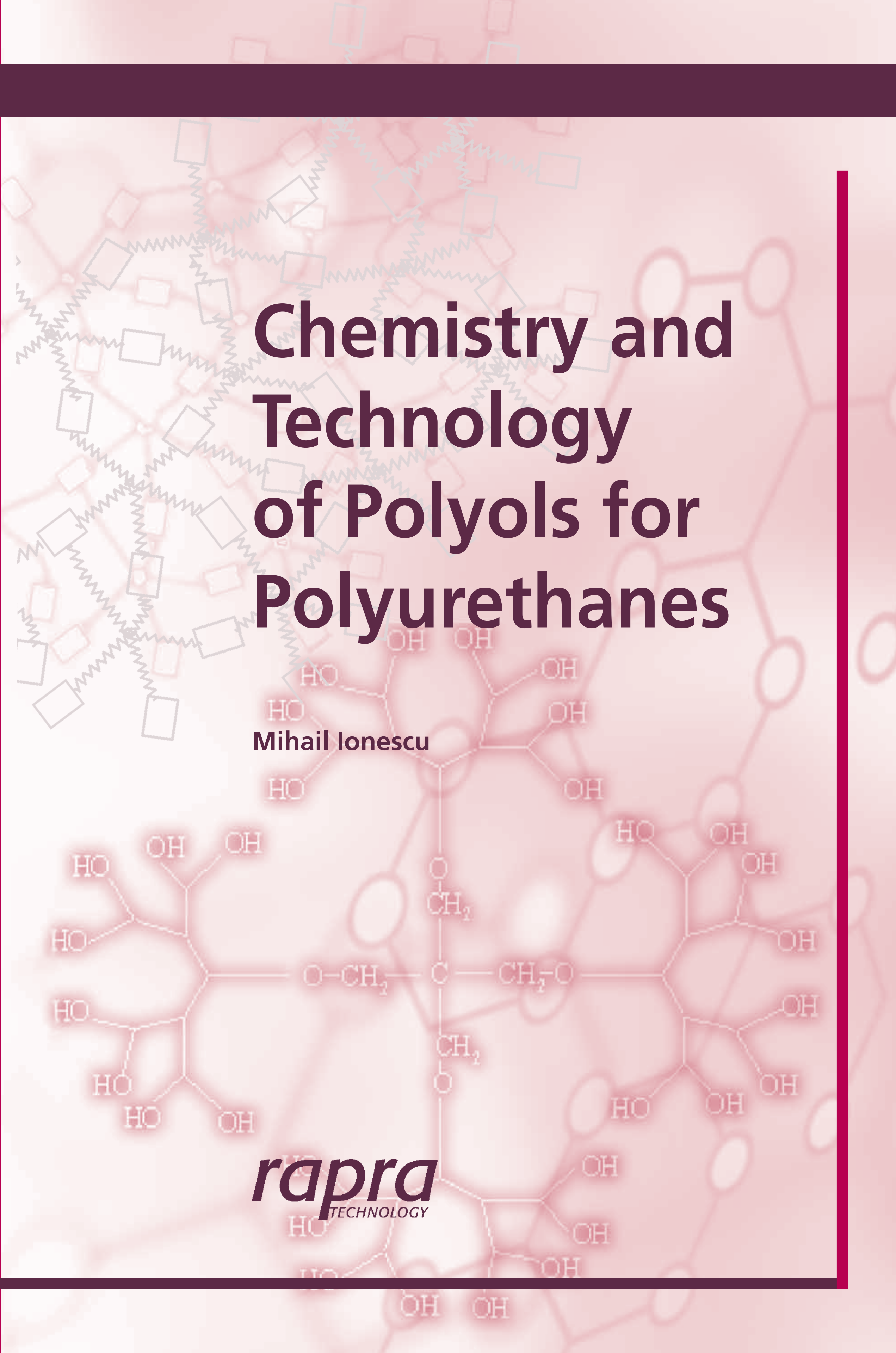
Chemistry and Technology of Polyols for Polyurethanes

Mihail Ionescu



rapra TECHNOLOGY

Chemistry and Technology of Polyols for Polyurethanes

Mihail Ionescu

Rapra Technology Limited

Shawbury, Shrewsbury, Shropshire, SY4 4NR, United Kingdom
Telephone: +44 (0)1939 250383 Fax: +44 (0)1939 251118
http://www.rapra.net

First Published in 2005 by

Rapra Technology Limited
Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK

A catalogue record for this book is available from the British Library.

ISBN: 978-1-84735-035-0

Typeset, printed and bound by Rapra Technology Limited

This book is dedicated to the memory of Dr Jack Buist, an exceptional personality in the field of polyurethane chemistry and technology. His vision on the advanced technologies in the polyurethane industry, his brilliant scientific activity leading to unanimous worldwide recognition, the exceptional career at ICI Polyurethanes, his work as founding editor of the international journal, *Cellular Polymers and Progress* has had great impact on the general worldwide development of polyurethane chemistry and polyurethane technology in the last five decades of the twentieth century. Dr Jack Buist will be forever, one of polyurethane's great men and has truly earned his place alongside Professor Otto Bayer, Professor Kurt C Frisch, Dr Adnan AR Sayigh, Dr Carlo Fiorentini and Dr Guenter Oertel in the Polyurethane's Hall of Fame.

Chemistry and Technology of Polyols for Polyurethanes

Contents

Preface

The first polyurethane synthesised by Dr Otto Bayer, in 1937, at IG Farbenindustrie (Germany), by the reaction of a polyester diol with a diisocyanate, opened a new way in macromolecular chemistry: that is the synthesis of polymers by a new reaction, called polyaddition reaction.

Polyurethanes, having a relatively short history, of slightly more than 65 years, became one of the most dynamic groups of polymers, and their use covers practically all the fields of polymer applications - foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibres and so on. Polyurethanes are used in nearly every aspect of daily life, changing the quality of human life. Furniture, bedding, seating for cars, shoe soles, thermoinsulation for refrigerators and buildings, wood substitutes, packaging, and coatings, are only a few common examples of polyurethane use in every day life.

Polyurethanes are obtained by the reaction of an oligomeric polyol (low molecular weight polymer with terminal hydroxyl groups) and a diisocyanate (or polyisocyanate). The structure of the oligomeric polyol used for polyurethane manufacture has a very profound effect on the properties of the resulting polymer.

The present monograph is dedicated to these very important raw materials used to build the polyurethane polymeric architecture: and covers chemistry and technology of oligomeric polyol fabrication, properties of these hydroxyl terminated oligomers and the effects of the oligomeric polyol structure on the resulting polyurethane properties.

So as not to be confused over the term ‘polyol’ some explanations are necessary. Generally, the term ‘polyol’ is used, in organic chemistry, for low molecular weight organic substances, very clearly identified as molecular entities, having more than two hydroxyl groups, such as: glycerol, propylene glycol, sorbitol and so on. The term ‘polyol’, is frequently used in relation to polyurethane fabrication, for all polyhydroxylic intermediates used. To be very clear, the present monograph is a study exclusively focused on oligomeric polyols, particularly low molecular weight polymers with terminal hydroxyl groups, covered by the general term of ‘oligo-polyols’. These oligo-polyols are not unique molecular species, being similar to all the polymers: a mixture between homologue species with various molecular weights (they have a molecular weight distribution). These oligo-polyols have an average molecular weight, by contrast with the low molecular weight of the polyols from organic chemistry which have a clear and unique molecular weight. In the text of this monograph, if the chemical nature of oligo-polyol is known, before the name ‘polyol’ is used the chemical name of the oligomeric chain, such as: polyether polyols, polyester polyols, polycarbonate polyols, acrylic polyols, Mannich polyols and so on. If the oligomeric polyols, are discussed generally, the term used will be ‘oligo-polyol’.

Many excellent monographs have been dedicated to polyurethanes and, of course, the oligo-polyols were described there, but in a very general manner. The present monograph goes into the details of oligo-polyols synthesis in depth, and explains the chemical and physico-chemical subtleties of all oligo-polyol fabrications.

A large variety of chemical reactions for the synthesis of oligo-polyols to build the chemical architecture of oligo-polyols are used, such as: ring opening polymerisation of cyclic monomers by anionic, cationic or coordinative mechanisms, polycondensation reactions (polyesterification, transesterification, Mannich reactions, phenol-aldehydes condensations and so on), alkoxylation, radical polymerisation, transformation of double bonds in hydroxyl groups, such as: epoxydation-hydrolysis, hydroxylation, hydroformylation, ozonolysis-reduction and so on), oxidation and amidation reactions. These varieties of chemical reactions need serious knowledge of organic and macromolecular chemistry and the author tries to explain, in a very simple and accessible manner, the very complex phenomena involved in oligo-polyol fabrication.

The scientific literature dedicated to oligo-polyols is really impressive and the majority of information is based on the patent literature. The scientific literature, dedicated exclusively to oligo-polyols for polyurethanes is unexpectedly scarce. As an immediate consequence, the present monograph is based especially on the patent literature and on the personal experience of the author, who has worked for more than 30 years, on the synthesis of oligo-polyols for polyurethanes. As mentioned before, there are excellent books dedicated to polyurethanes and an excellent book dedicated to the chemistry and technology of isocyanates. The present monograph, dedicated to the second very important component of polyurethane fabrication, oligo-polyols, tries to complete this series of monographs in a logical manner.

This book attempts to link in a general concept, organised in a systematic manner, the most important knowledge, data and information concerning the chemistry and technology of oligo-polyols for polyurethanes. This general point of view resulting from the fact that all oligo-polyols used for polyurethanes have many things in common, will be presented, in detail, in this monograph. In order not to provide too much information, and to avoid presentation of confidential data, the commercial names of the oligo-polyols are not mentioned. Thus, each oligo-polyol is identified by the chemical structure or by the chemical name. At the same time and for the same reasons, the names of companies which developed and produced the various types of common oligo-polyols are not mentioned. The commercial name and the company name is specified exceptionally, only for the unanimously accepted very important developments in the area of oligo-polyols (e.g., PHD-polyols of BAYER and so on).

Of course, it is totally impossible to cover all the aspects and to describe all the oligo-polyol structures created as a consequence of the impressive worldwide creative effort of research laboratories from companies, universities, research centers and institutes, but I am sure that the most important aspects of oligo-polyol manufacture are presented.

The present monograph is addressed to all specialists working in the area of oligo-polyols for polyurethanes: students, researchers, scientists, engineers, professors, experts from: industry, universities, research centers and research institutes.

I hope that the monograph will be the start for new and original and developments in the area of oligo-polyols for polyurethanes, including creation of totally new oligo-polyols, with a new design and new chemical architecture, and of course for new technologies and unconventional manufacturing technologies.

Good luck!

I express my profound gratitude to my wife Adriana for her continuous and unconditional help and support.

I am grateful to, and I thank very much Ms Frances Powers, Senior Commissioning Editor, Rapra Technology, for her tenacity, patience, attention, high competency and professionalism to review and correct each page, each table, each formula, each sentence, each reference, each word, each sign and to produce the book to such standard. I am also grateful to Frances, for the fact that all the time she believed in me, and in my capability to finish the book.

I would also like thank very much to the following members of Rapra's Publishing Department: Ms Claire Griffiths and Mrs Hilary Moorcroft (editorial assistants) and Mrs Sandra Hall for typesetting the book and designing the cover, all of whom have done a remarkable job, in producing such a high quality book.

Mihail Inonescu
August 2005

1

Polyols

1.1 Introduction

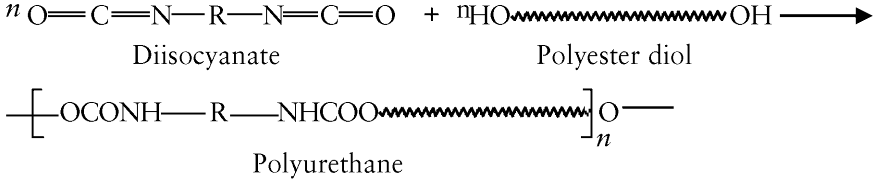
The polyurethanes are a special group of heterochain polymers, characterised by the following structural unit [1-33]:

$$\left[\!\!-\text{OCONH}-\text{R}-\text{NHCOO}-\text{R}'-\right]_n$$

The urethane groups -NH-COO- are esters of carbamic acid, an hypothetically unstable (and impossible to obtain under normal conditions) acid [R-NH-COOH]. It is possible to synthesise the urethane groups by various methods [22], but the most important one is the reaction between an isocyanate and an alcohol [1-33]:

$$\underset{\text{isocyanate}}{\text{R}-\text{N}=\text{C}=\text{O}} + \underset{\text{alcohol}}{\text{HO}-\text{R}'} \longrightarrow \underset{\text{urethane}}{\text{R}-\text{NHCOO}-\text{R}'}$$

The first urethane was synthesised, by this route, as early as 1849 by Wurtz [6, 16, 22, 30]. In 1937, following very systematic and intensive research works at IG Farbenindustrie, in Germany, Dr. Otto Bayer synthesised the first polyurethane, by the reaction of a diisocyanate with a polyester having two terminal hydroxyl groups (called polyester diol, in fact an α,ω–telechelic polymer with terminal hydroxyl groups) [1, 2]:



In fact, Bayer invented a new method for the synthesis of macromolecular compounds: the polyaddition reaction, which is a special case of polycondensation, with the difference that the reaction product is exclusively the polymer. In the classical polycondensation reactions, the products are: the polycondensation polymer and a low molecular weight (MW) compound (water, alcohols, and so on). The fact that in the polyaddition reactions the product is only the polymer is of great technological importance, especially for the purity and the morphology of the resulting macromolecular compound.

In the slightly more than 65 years of the existence of polyurethanes, the growth of the polyurethanes was constant and the prediction for the future is very optimistic due to the new markets opened in Eastern Europe, Asia and South America [34].

In **Figure 1.1**, one can see the growth of polyurethane consumption, between 2000-2004.

Figure 1.2 shows the world consumption of polyether polyols and polyester polyols for polyurethanes in the period of time 2000-2004.

Polyurethanes represent only 5% of the worldwide polymer consumption (**Figure 1.3** shows around 10.6 million metric tonnes in 2004), but the dynamics of their growth is constantly high, around 4-6% [35].

The main field of polyurethane application is the furniture industry, around 30% of the total polyurethanes produced worldwide is used for the production of mattresses from flexible slabstock foams. Automotive manufacture is the second important application for flexible and semiflexible polyurethanes (seat cushioning, bumpers, sound insulation, and so forth). Rigid polyurethane foams are used in thermal insulation of buildings and refrigerators, cold stores, pipe insulation, refrigerated transport, thermal insulation in chemical and food industries. The polyurethane elastomers are used for shoe soles,

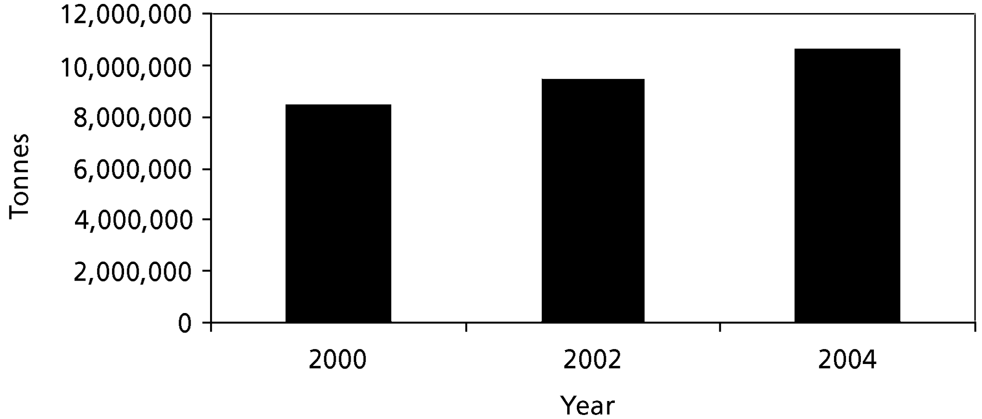


Figure 1.1 World consumption of polyurethanes (2000-2004)

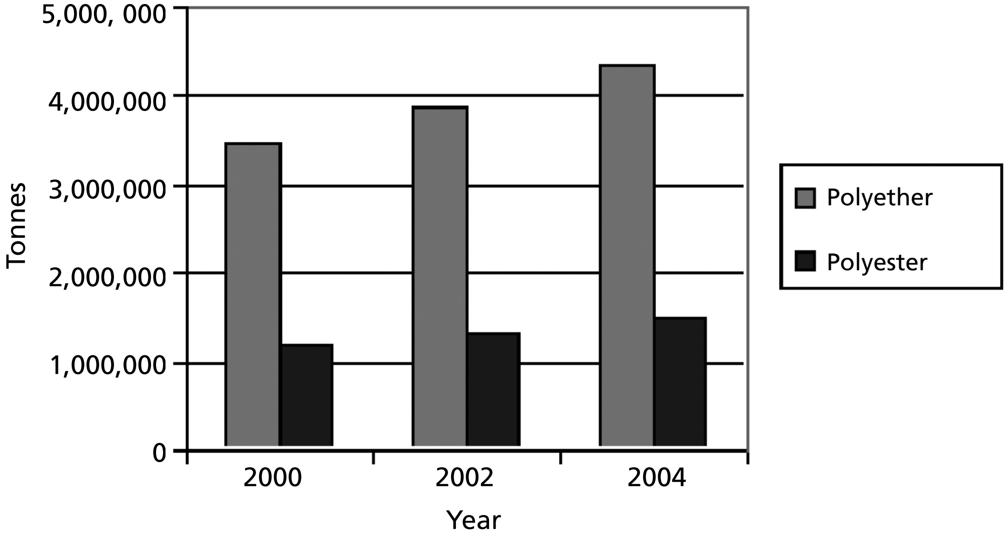


Figure 1.2 World consumption of polyether and polyester polyols for polyurethanes between 2000-2004

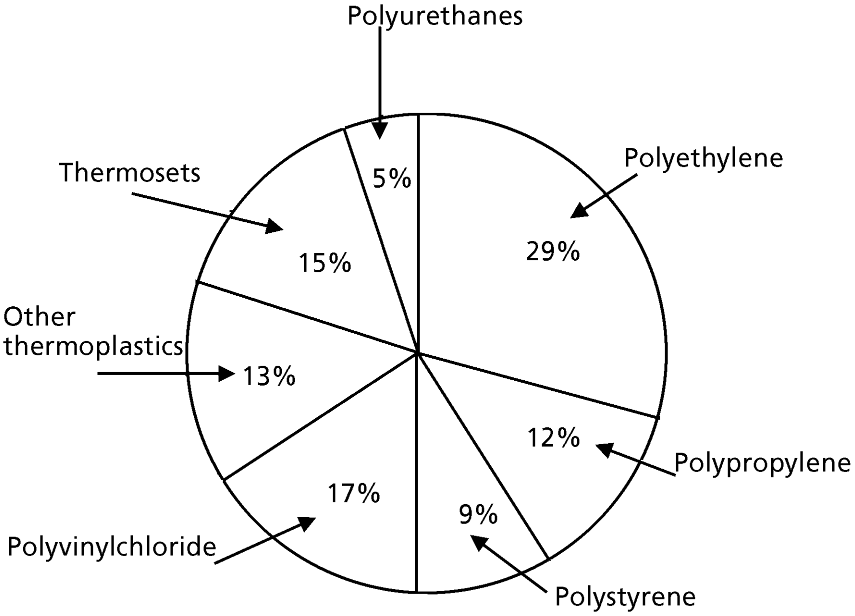


Figure 1.3 Polyurethanes and world production of plastics

footwear, athletic shoes, pump and pipe linings, industrial tyres, microcellular elastomers, etc. Polyurethane adhesives, sealants, coatings and fibres represent another group of polyurethanes with specific applications. The main applications of polyurethanes are presented in **Figure 1.4** [35].

Figure 1.5 shows that the majority of polyurethanes used worldwide are foams (flexible, semiflexible, rigid foams), around 72% from the total polyurethanes.

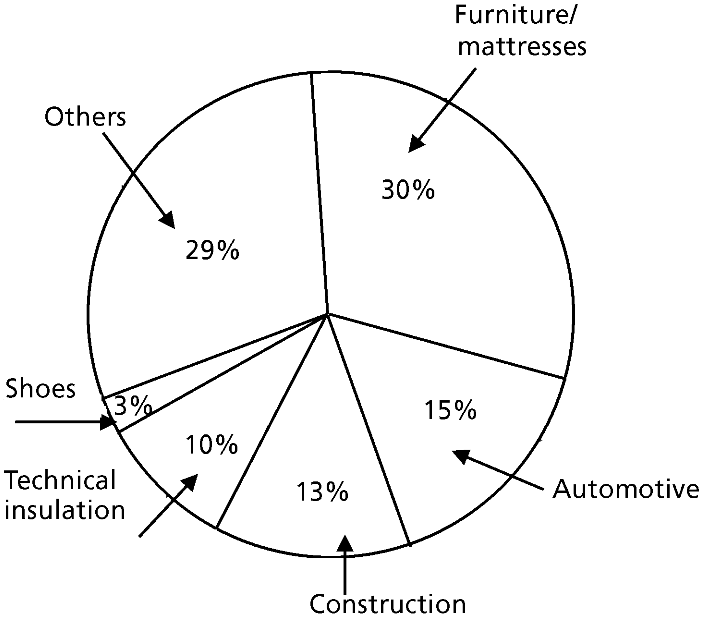


Figure 1.4 The main applications of polyurethanes

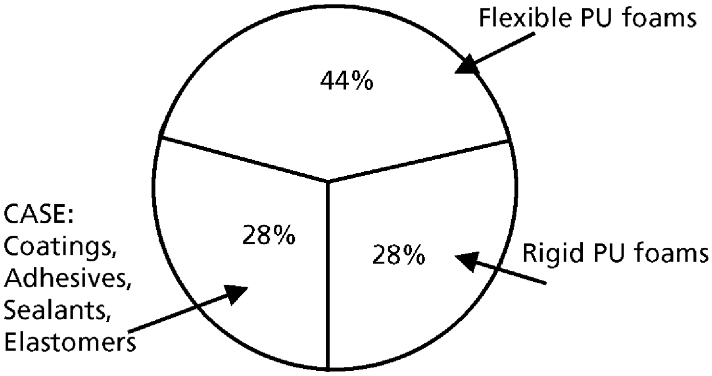


Figure 1.5 World consumption of polyurethanes, by products (2000-2002)

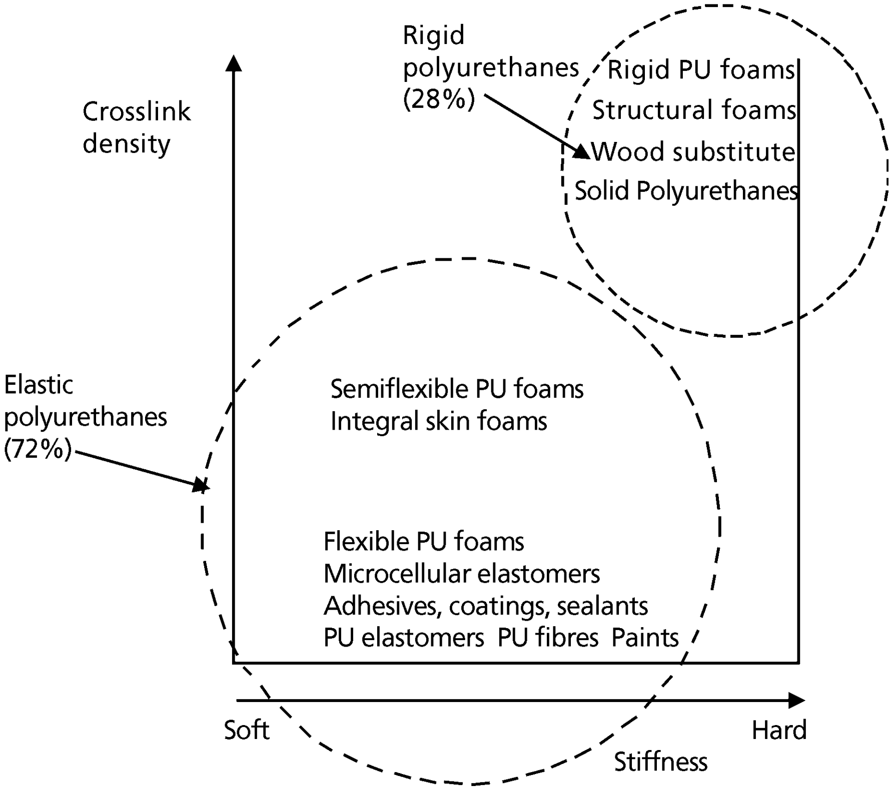
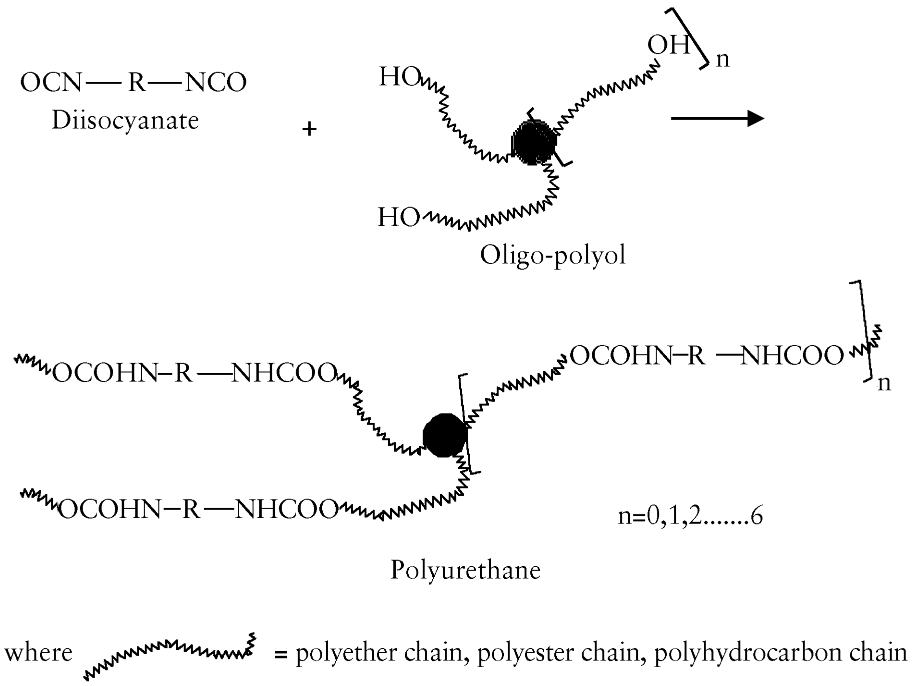


Figure 1.6 Classification of polyurethanes as function of crosslink density and stiffness

It is well known that a foam is a composite solid-gas material. The continuous phase is the polyurethane polymer and the discontinuous phase is the gas phase. Polyurethanes are an extremely versatile group of polymers, produced in a wide range of densities, crosslink densities and stiffnesses, from very soft to very hard structures, as shown in **Figure 1.6**.

Considering the practical and applicative reasons, the polyurethanes can be divided into two main categories: elastic polyurethanes, e.g., flexible foams, elastomers, coatings, adhesives, fibres etc., and rigid polyurethanes, e.g., rigid polyurethane foams, structural foams, wood substitutes, solid polyurethanes, etc. This common classification of polyurethanes in elastic and rigid polyurethanes is mainly based on the oligo-polyol structure. Thus, the general reaction for the polyurethane synthesis is:



The MW of the oligo-polyols used in polyurethane synthesis varies between 300-10000 daltons, in the region of low MW polymers (oligomers), the number of hydroxyl groups/molecule of oligo-polyol (the oligo-polyol functionality) being generally in the range of 2-8 OH groups/mol.

A polyol of low functionality, having around 2-3 hydroxyl groups/mol and with a high MW of 2000-10000 daltons, leads to an elastic polyurethane and on the contrary, a low MW oligo-polyol of 300-1000 daltons, with a high functionality of around 3-8 hydroxyl groups/mol leads to a rigid crosslinked polyurethane.

A diisocyanate reacted with a high MW diol (for example polyether or polyester diol of MW of 2000-4000) leads to very elastic linear polyurethanes (polyurethane elastomers) [3, 6, 13, 14, 24, 25]. The urethane linkages (and urea linkages), because of the possibility of association by hydrogen bonds, generate the ‘hard domain‘ or ‘hard segment‘ of a polyurethane elastomer. The high mobility of high MW polyol chains represent the ‘soft domain’ or ‘soft segment’ and assures the high elasticity of the resulting polyurethane elastomer (**Figures 1.7** and **1.8**).

This structure is in fact an interesting, virtually crosslinked structure by secondary bonds (hydrogen bonds). At higher temperatures, the hydrogen bonds are destroyed and it is

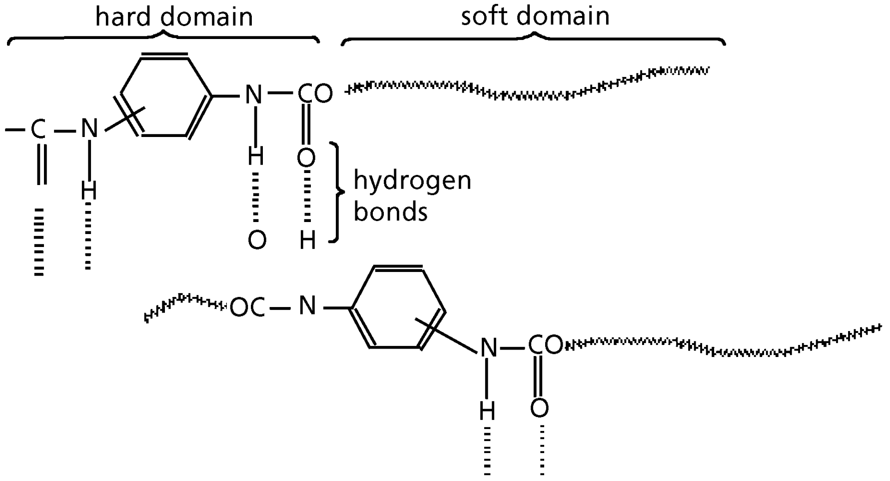


Figure 1.7 The 'hard domains' and 'soft domains' of polyurethane elastomers

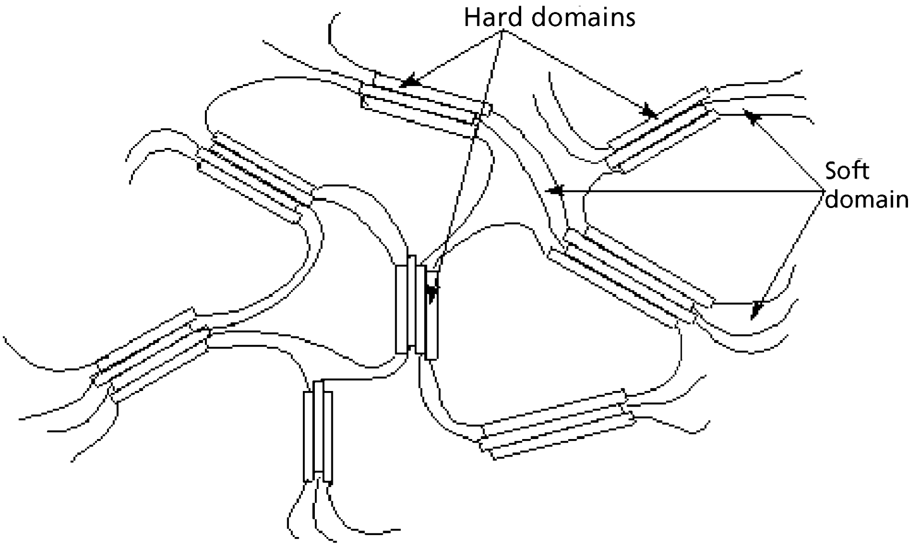


Figure 1.8 'Virtually' crosslinked polyurethane elastomers

possible to process the linear polyurethane elastomer in the melt state, similarly to all common thermoplastics (thermoplastic elastomers) [3-10, 23-25, 29].

A polyol of high MW (3000-6500 daltons) and of low functionality, of around 2-3 hydroxyl groups/mol, if reacted with a diisocyanate, leads to a low crosslinked, flexible polyurethane structure. This structure is characteristic of flexible polyurethane foams. Because the resulting structure is a crosslinked one, the MW of the resulting polyurethane is infinite in value. Only linear polyurethanes have a finite and determinable MW.

In **Figure 1.9** one can see an hypothetical crosslinked structure of a flexible polyurethane foam resulting from an oligo-triol of MW of 3000-6500 daltons and a diisocyanate [3-16, 20].

The rigid polyurethane structures are created by using low MW polyols (150-1000 daltons) which have high functionalities, of around 3-8 hydroxyl groups/mol. By reacting these low MW oligo-polyols of high functionality with a diisocyanate or polyisocyanate (having 2-3 –NCO groups/mol), a hard, rigid polyurethane structure is obtained. This high rigidity is an immediate consequence of the high crosslink density of the resulting polyurethane polymer [3-6, 10, 11, 14, 36].

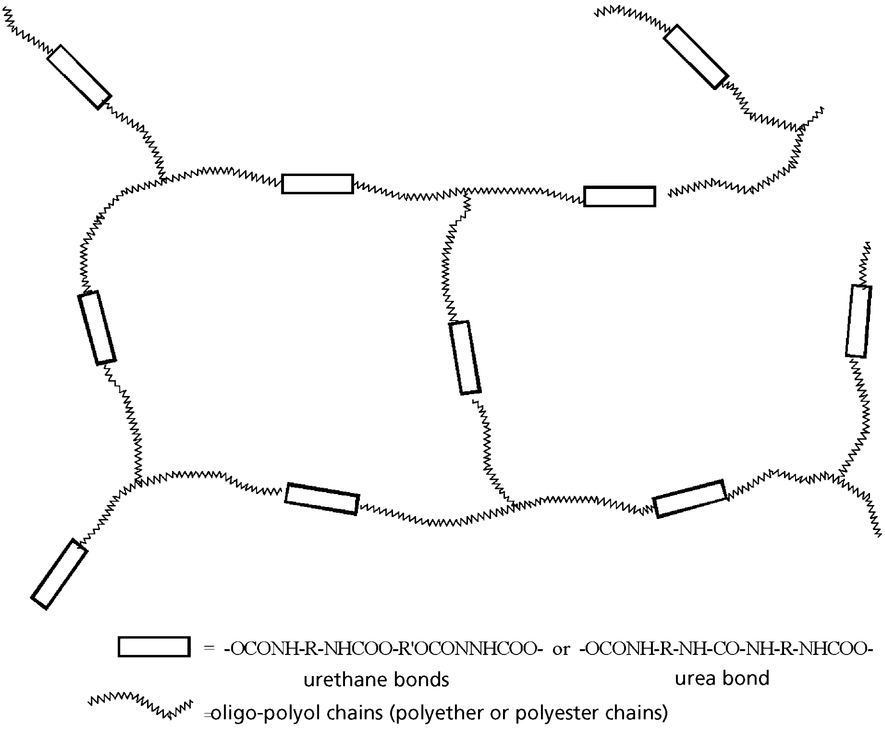


Figure 1.9 Hypothetical crosslinked structure of a flexible polyurethane foam

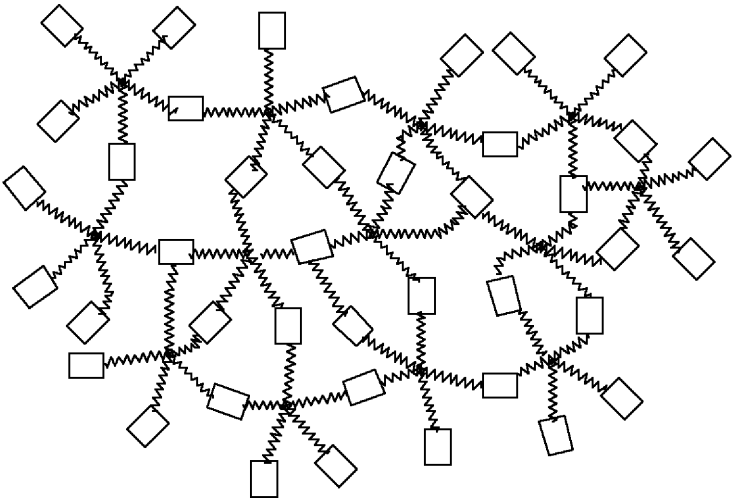


Figure 1.10 Crosslinking in rigid polyurethane foams

Figure 1.10 shows an hypothetical, highly crosslinked structure of a rigid polyurethane.

Several aspects of the profound influence the oligo-polyol structure has on the properties of the resulting polyurethanes have been discussed in this chapter. In order to fully understand the role of the polyol structure on the properties of polyurethanes, the method of chemical insertion of oligo-polyol into the polyurethane macromolecules, will be discussed in Chapter 2, with the most important aspects of the chemistry of polyurethanes. After that, the general and common characteristics of oligo-polyols for polyurethanes will be presented. The later chapters will deal with a detailed presentation of the main types of oligo-polyols for polyurethanes, the chemistry and technology of these oligo-polyols including their manufacture. The oligo-polyols are presented in two main groups: oligo-polyols for elastic polyurethanes and oligo-polyols for rigid polyurethanes. Finally, a short chapter which is a generalisation of all the knowledge concerning the oligo-polyols, describes the relations between oligo-polyols structure and the properties of the final polyurethanes.

References

1. O. Bayer, *Angewandte Chemie*, 1947, **A59**, 257.

2. O. Bayer, *Modern Plastics*, 1947, **24**, 149.

3. *Polyurethane Technology*, Ed., P.F. Bruins, Interscience Publishers, London, UK, 1969.

4. *The ICI Polyurethanes Book*, Second Edition, Ed., G. Woods, John Wiley & Sons, Chicester, UK, 1990.

5. *Telechelic Polymers, Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Boca Raton, FL, USA, 1989, p.203.

6. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999.

7. *Advances in Polyurethane Technology*, Eds., J.M. Buist and H.A. Gudgeon, Maclaren and Sons, London, UK, 1968.

8. S.D.Gagnon in *Kirk-Othmer Encycopedia of Chemical Technology*, Fourth Edition, Ed., J.I. Kroschowitz, John Wiley & Sons, New York, NY, USA, 1996, Volume 19, p.722.

9. H. Ulrich in *Kirk-Othmer Encyclopedia of Chemical Technology*, Ed., J.I. Kroschowitz , Fourth Edition, John Wiley & Sons, New York, NY, USA, 1997, Volume 24, p.695.

10. J.H. Saunders and K.C. Frisch, *Polyurethanes: Chemistry and Technology*, *Part I, Chemistry,* Interscience Publishers, New York, NY, USA, 1962.

11. J.H. Saunders and K.C. Frisch, *Polyurethanes: Chemistry and Technology*, *Part II, Technology*, Interscience Publishers, New York, NY, USA, 1964.

12. *Handbook of Polymeric Foams and Foam Technology*, Eds., D. Klempner and K.C. Frisch, Hanser, Munich, Germany, 1991

13. *Plastic Foams,* Eds., K.C. Frisch and J.H. Saunders, Marcel Dekker, New York, NY, USA, 1972.

14. *Polyurethane Handbook*, Ed., G. Oertel, Hanser Verlag, Munich, Germany, 1985.

15. *Developments in Polyurethanes - I*, Ed., J.M. Buist, Applied Science Publishers, London, UK, 1978.

16. *Flexible Polyurethane Foams*, Second Edition, Eds., R. Herrington and K. Hock, Dow Chemical Company, Midland, MI, USA, 1997.

17. H. Ulrich in *Reaction Polymers*, Eds., W.F. Gum, W. Riese and H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.50.

18. A.A.R. Sayigh, H. Ulrich and W.J. Farrisey in *Condensation Monomers*, Eds., J.K. Stille and T.W. Campbell, Wiley Interscience, New York, NY, USA, 1972, p.231.

19. *Analytical Chemistry of the Polyurethanes*, Eds., D.J. David and H.B. Staley, Wiley-Interscience, New York, NY, USA, 1969, Volume 16, Part III, High Polymers.

20. G.W. Woods, *Flexible Polyurethane Foams, Chemistry and Technology*, Applied Science Publishers, Englewood, NJ, USA, 1982.

21. H. Ulrich in *Encyclopedia of Polymer Science and Engineering*, Ed., J.I. Kroschowitz, John Wiley & Sons, Inc., New York, NY, USA, 1987, Volume 8, p.448.

22. H. Ulrich, *Chemistry and Technology of Isocyanates*, J. Wiley and Sons, Chichester, UK, 1996.

23. G. Woods, *Polyurethanes, Materials, Processing and Applications*, Rapra Review Report No.15, Volume 2, No.3, Rapra Technology, Shrewsbury, UK, 1988.

24. A.F. Johnson, P.D. Coates and M.W.R. Brown, *Reactive Processing of Polymers*, Rapra Review Reports No.73, Volume 7, No.1, Rapra Technology, Shrewsbury, UK, 1994.

25. J.A. Brydson, *Thermoplastic Elastomers: Properties and Applications*, Rapra Review Report No.81, Volume 7, No.9, Rapra Technology, Shrewsbury, UK, 1995.

26. *MDI and TDI: Safety, Health and the Environment - A Source Book and Practical Guide*, Eds., D.C. Allport, D.S. Gilbert and S.M. Outterside, Wiley Publishers, Chichester, UK, 1998.

27. R.M. Evans, *Polyurethane Sealants, Technology and Applications*, 2nd Edition, Technomic Publishing, Lancaster, PA, USA, 1993.

28. B.A. Dombrow, *Polyurethanes*, 2nd Edition, Reinhold Publishing Corporation, New York, NY, USA, 1965.

29. *Kunststoff-Handbook, Volume 7, Polyurethane*, Eds., R. Vieveg and A. Höchtlen, Carl Hanser Verlag, Munich, Germany, 1966. (In German)

30. *Houben Weyl: Methoden der Organische Chemie*, Volume 14, Part 2, Eds., E.Muller, O.Bayer, H.Meerwein and K.Ziegler, Georg Thieme Verlag, Stuttgart, Germany, 1963, p.57. (In German)

31. *Ullmanns Encyclopädie der Technischen Chemie*, 4th Edition, Eds., E. Bartholome, E. Biekart, H. Hellman, H. Ley, M. Wegert and E. Weise, Verlag Chemie, Munich, Germany 1980, Poly(alkylene glycole), p.31.

32. *Ullmanns Encyclopädie der Technischen Chemie*, 4th Edition, Eds., E. Bartholome, E. Biekart, H. Hellman, H. Ley, M. Wegert and E. Weise, Verlag Chemie, Munich, Germany 1980, Polytetrahdrofuran, p.297.

33. *Ullmanns Encyclopädie der Technischen Chemie*, 4th Edition, Eds., E. Bartholome, E. Biekart, H. Hellman, H. Ley, M. Wegert and E. Weise, Verlag Chemie, Munich, Germany 1980, Urethane Polymers, p.302.

34. *Proceedings of an International Symposium on 60 Years of Polyurethanes*, 1998, Detroit, MI, USA.

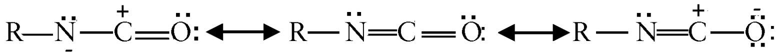
35. *Kunststoffe Plast Europe*, 1997, **87**, 9, 6.

36. S.G. Entelis, V.V. Evreinov and A.I. Kuzaev, *Reactive Oligomers*, Brill Publishers, Moscow, Russia, 1988.

2

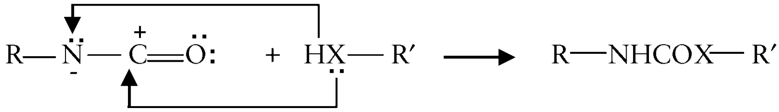
Basic Chemistry of Polyurethanes

The high reactivity of the isocyanate group with hydrogen active compounds can be explained by the following resonance structures [1-3]:



$$R{-}\overset{..}{\underset{-}{N}}{-}\overset{+}{C}{=}\ddot{O}{:} \longleftrightarrow R{-}\ddot{N}{=}C{=}\ddot{O}{:} \longleftrightarrow R{-}\ddot{N}{=}\overset{+}{C}{-}\overset{-}{\underset{..}{\ddot{O}}}{:}$$

Electron density is higher at the oxygen atom, while the carbon atom has the lowest electron density. As an immediate consequence, the carbon atom has a positive charge, the oxygen atom a negative one and the nitrogen atom an intermediate negative charge. The reaction of isocyanates with hydrogen active compounds (HXR) is in fact an addition at the carbon - nitrogen double bond [1-25]:



$$R{-}\overset{..}{\underset{-}{N}}{-}\overset{+}{C}{=}\ddot{O}{:} \quad + \quad H\underset{..}{X}{-}R' \longrightarrow R{-}NHCOX{-}R'$$

The nucleophilic centre of the active hydrogen compounds (the oxygen atom of the hydroxyl groups or the nitrogen atoms in the case of amines), attacks the electrophilic carbon atom and the hydrogen adds to the nitrogen atom of the -NCO groups. Electron withdrawing groups increase the reactivity of the -NCO groups and on the contrary, the electron donating groups decrease the reactivity against hydrogen active compounds. Aromatic isocyanates (R = aryl) are more reactive than aliphatic isocyanates (R = alkyl). Steric hindrance at -NCO or HXR´ groups markedly reduces the reactivity.

2.1 Reaction of Isocyanates with Alcohols

The reaction between isocyanates and alcohols, the most important reaction involved in polyurethane synthesis, is an exothermic reaction and leads, as mentioned before, to production of urethanes [1-26]:

$$R{-}N{=}C{=}O + HO{-}R' \longrightarrow R{-}NHCOO{-}R' + \Delta H \text{ (24 Kcal/mol)}$$

Isocyanate Alcohol Urethane Reaction heat

2.2 Reaction of Isocyanates with Water

The reaction between isocyanates and water leads to production of gaseous carbon dioxide and an urea group. This reaction is a very convenient source of a gas necessary to generate the cellular structure of polyurethane foams [1-26]:

$$\underset{\text{Isocyanate}}{R{-}N{=}C{=}O} + \underset{\text{Water}}{HOH} \longrightarrow \underset{\substack{\text{Unstable}\\ \text{carbamic acid}}}{\left[R{-}NHCOOH\right]} \longrightarrow \underset{\text{Amine}}{R\text{-}NH_2} + CO_2\uparrow$$

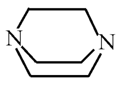
The amine reacts very rapidly with other isocyanate molecules and generates a symmetrical disubstituted urea [1-3, 6-24]:

$$\underset{\text{Isocyanate}}{R{-}N{=}C{=}O} + \underset{\text{Amine}}{H_2N{-}R} \longrightarrow \underset{\text{Disubstituted urea}}{R{-}NH\,CONH{-}R'}$$

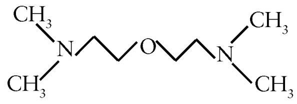
The reaction of isocyanate with water is more exothermic than the reaction with alcohols and the total heat release per mole of water is about 47 kcal/mol [1-3]. It is evident that one mole of water reacts with two -NCO groups, which is very important in order to calculate the correct quantity of isocyanate needed for polyurethane formulations.

Water is considered, in polyurethane foam manufacture, as a chemical blowing agent, because the gas generation is a consequence of a chemical reaction.

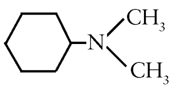
The reaction between isocyanates and alcohols or water is catalysed by tertiary amines with low steric hindrance, and some tin, lead or mercury compounds such as [1-3, 6-23]:



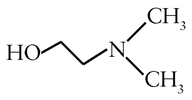
Triethylenediamine



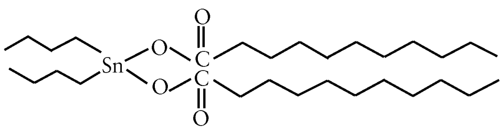
Bis(2-dimethylaminoethyl) ether



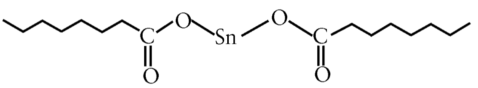
N,N dimethyl cyclohexylamine



N,N dimethylethanolamine



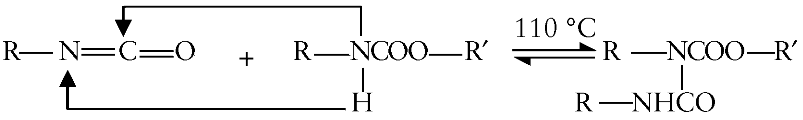
Dibutyiltin dilaurate



Stannous octoate

2.3 Reaction of Isocyanates with Urethanes

Urethane groups may be considered hydrogen active compounds, due to the hydrogen atom linked to the nitrogen atom. By the reaction of an isocyanate with an urethane group an allophanate is formed [1, 3, 6-18, 21, 23-25]:



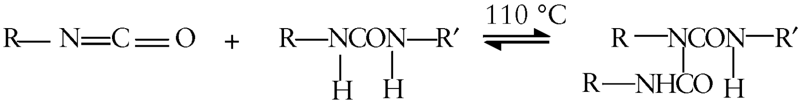
$$R{-}N{=}C{=}O \;+\; R{-}\underset{\displaystyle H}{\underset{|}{N}}COO{-}R' \;\underset{}{\overset{110\ ^\circ C}{\rightleftharpoons}}\; R{-}\underset{\displaystyle R{-}NHCO}{\underset{|}{N}}COO{-}R'$$

Isocyanate Urethane Allophanate

Due to the electron withdrawing effect of the carbonyl groups, the urethane group has a much lower reactivity than the aminic -N-H groups and in order to promote the allophanate formation higher temperatures are necessary: greater than 110 °C. It is important to mention that the allophanate formation is a reversible reaction.

2.4 Reaction of Isocyanates with Urea Groups

Similarly to the allophanate formation, the -N-H groups of urea react with isocyanates, to generate a biuret [1, 3, 6-18, 21, 23-25]:



$$R{-}N{=}C{=}O \;+\; R{-}\underset{\displaystyle H}{\underset{|}{N}}CO\underset{\displaystyle H}{\underset{|}{N}}{-}R' \;\overset{110\ ^\circ C}{\rightleftharpoons}\; R{-}\underset{\displaystyle R{-}NHCO}{\underset{|}{N}}CO\underset{\displaystyle H}{\underset{|}{N}}{-}R'$$

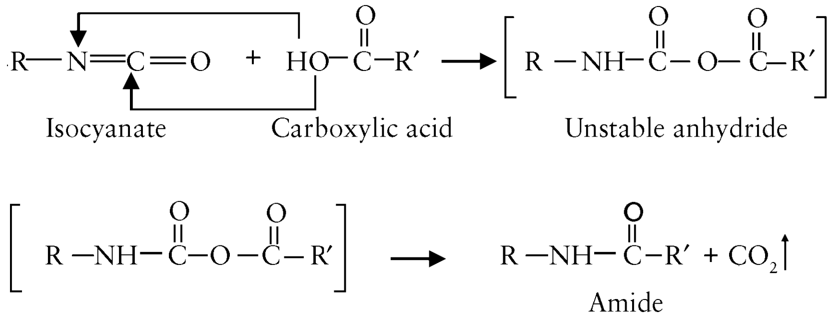
Isocyanate Disubstituted urea Biuret

Also similarly to the allophanate formation, the reaction between urea and isocyanates is an equilibrium reaction and needs higher temperatures too (> 110 °C).

Formation of allophanates and biurets in polyurethane chemistry, especially when an excess of isocyanate is used, is in fact a supplementary source of crosslinking.

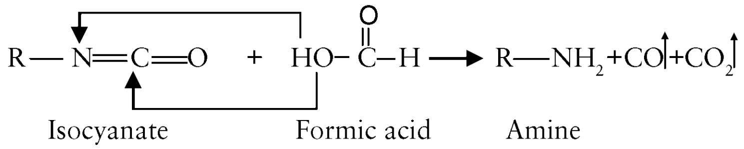
2.5 Reaction of Isocyanates with Carboxylic Acids

The reactivity of isocyanates toward carboxylic acids is much lower than the one with amines, alcohols and water. The final product is an amide and gaseous carbon dioxide [1-3, 13]:



$$R{-}N{=}C{=}O + HO{-}\overset{O}{\overset{\|}{C}}{-}R' \longrightarrow \left[R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'\right]$$

$$\left[R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'\right] \longrightarrow R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}R' + CO_2\uparrow \qquad (2.1)$$



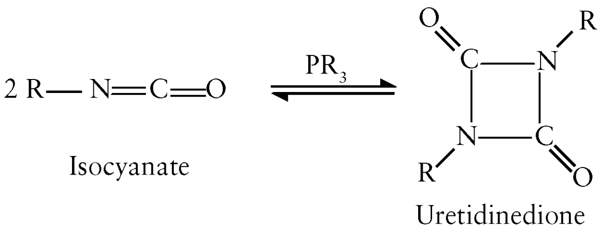
$$R{-}N{=}C{=}O + HO{-}\overset{O}{\overset{\|}{C}}{-}H \longrightarrow R{-}NH_2 + CO\uparrow + CO_2\uparrow \qquad (2.2)$$

A special case is the reaction of an isocyanate group with formic acid. One mol of formic acid generates two mols of gases: one mol of carbon dioxide and one mol of carbon monoxide. Formic acid is considered, like water, to be a reactive blowing agent (see Equations 2.1 and 2.2).

Isocyanates have some important reactions without the participation of active hydrogen compounds. These reactions, of real importance in polyurethane chemistry are: dimerisation, trimerisation, formation of carbodiimides and reaction with epoxides and cyclic anhydrides.

2.6 Dimerisation of Isocyanates

Isocyanates give two types of dimerisation reactions: formation of uretidinediones and of carbodiimides [1, 3, 12, 13, 15, 23-25]:

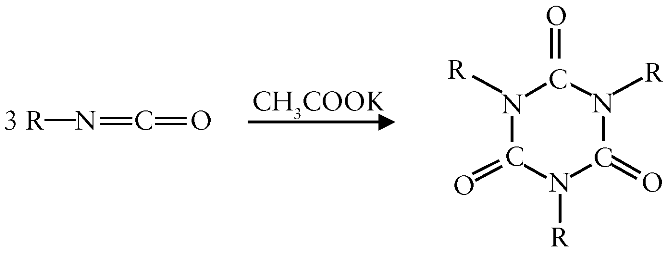


$$2\,R{-}N{=}C{=}O \longrightarrow R{-}N{=}C{=}N{-}R + CO_2$$

Isocyanate Carbodiimide

2.7 Trimerisation of Isocyanates

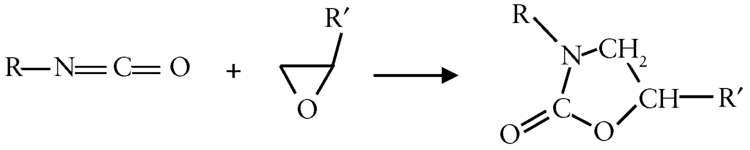
Trimerisation of isocyanates is an important reaction of -NCO groups that takes place in the presence of special catalysts, (e.g., potassium acetate, tris [dimethylaminomethyl] phenol and others), with the formation of heterocyclic isocyanurate compounds [1, 3, 12, 13, 15, 23-25]. The reaction is used for the manufacture of isocyanuric foams and urethane-isocyanuric foams, in the presence of excess isocyanates (isocyanate index = 200-600). Highly crosslinked structures are formed. Urethane groups are present in the resulting structure obtained from the reaction of NCO groups with the oligo-polyol hydroxyl groups as well as isocyanuric rings resulting from the trimerisation of isocyanate groups:



Isocyanate Isocyanurate

2.8 Reaction of Isocyanates with Epoxide Compounds

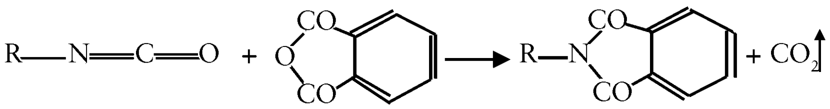
The reaction of -NCO isocyanate groups with epoxidic rings, in the presence of special catalysts, leads to the formation of cyclic urethanes (oxazolidones) [1, 3, 12, 13, 23-25]:



Isocyanate Epoxide Oxazolidone

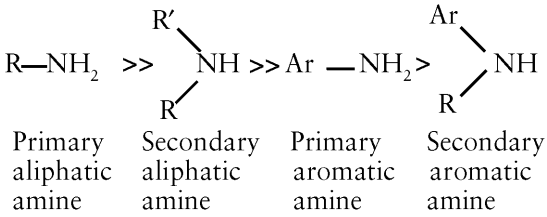
2.9 Reaction of Isocyanates with Cyclic Anhydrides

Isocyanates react with cyclic anhydrides to form cyclic imides [1, 3, 15]:

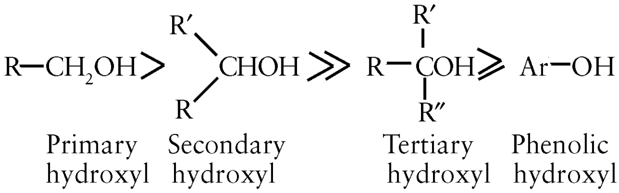


Isocyanate Phthalic anhydride Phthalimide

Table 2.1 shows the relative reaction rates of isocyanates against different hydrogen active compounds. All the amines are much more reactive than the hydroxyl compounds, the relative order being as follows:



Primary hydroxyl groups are more reactive than secondary hydroxyl groups and much more reactive than tertiary or phenolic hydroxyl groups:



Primary hydroxyl groups are around three times more reactive than secondary hydroxyl groups and 200 times more reactive than tertiary hydroxyl groups.

In order to understand the effect of polyol structure on the properties of polyurethanes a minimum amount of information about the structure and reactivity of isocyanates is

Table 2.1 The relative reactivities of isocyanates against different hydrogen active compounds [2, 25]

Hydrogen active compound	Formula	Relative reaction rate (non-catalysed, 25 °C)
Primary aliphatic amine	$R\text{-}NH_2$	2500
Secondary aliphatic amine	$R_2\text{-}NH$	500-1250
Primary aromatic amine	$Ar\text{-}NH_2$	5-7.5
Primary hydroxyl	$R\text{-}CH_2\text{-}OH$	2.5
Water	HOH	2.5
Carboxylic acid	R-COOH	1
Secondary hydroxyl	$R_2\text{-}CH\text{-}OH$	0.75
Urea	R-NH-CO-NH-R	0.375
Tertiary hydroxyl	$R_3\text{-}C\text{-}OH$	0.0125
Phenolic hydroxyl	Ar-OH	0.0025-0.0125
Urethane	R-NH-COOR	0.0025

needed. Oligo-polyols for polyurethanes are commercialised in a large number of types and structures. However, in practice, limited types of isocyanates are used. The most important isocyanates, covering the majority of polyurethane applications are aromatic isocyanates: toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Aliphatic isocyanates such as hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) or 4,4′ dicyclohexyl diisocyanate (HMDI) are used to a much lesser extent, and only for special applications. TDI is commercialised using a mixture of the 2,4 and 2,6 isomers (TDI 80/20 having 80% 2,4 TDI and 20% 2,6 TDI and TDI 65/35 having 65% 2,4 TDI and 35% 2,6 toluene diisocyanate) or 2,4 TDI as pure isomer. The most important application of TDI is in flexible polyurethane foam manufacture. The structures of commercial TDI are presented in **Figure 2.1** [1-3, 6, 12, 13, 23, 27, 28]:

The second most important aromatic isocyanate is MDI, commercialised in various forms and functionalities, the most important being: pure MDI, ‘crude’ MDI and polymeric MDI (PAPI) [1-3, 6-25, 27].

Pure MDI, having two -NCO groups/mol, is commercialised mainly as 4,4′ isomers, but it is possible to use 2,4 and 2,2 isomers. The main applications of pure MDI (especially the 4,4′ isomer) are: polyurethane elastomers, microcellular elastomers and some flexible foams. The structures of pure MDI isomers are presented in **Figure 2.2**.

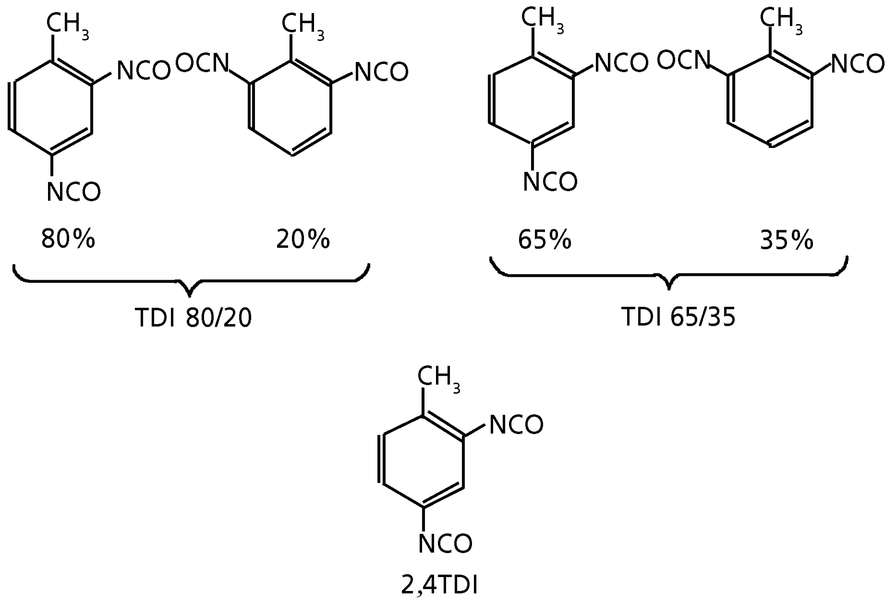


Figure 2.1 The chemical structures of commercial TDI

'Crude' MDI is a mixture of 4,4′ MDI isomer (around 48-50%) and high molecular weight (MW) isomers having 3, 4, 5 and higher numbers of aromatic rings, with functionalities in the range of 2-3 -NCO groups/mol (see **Figure 2.3**).

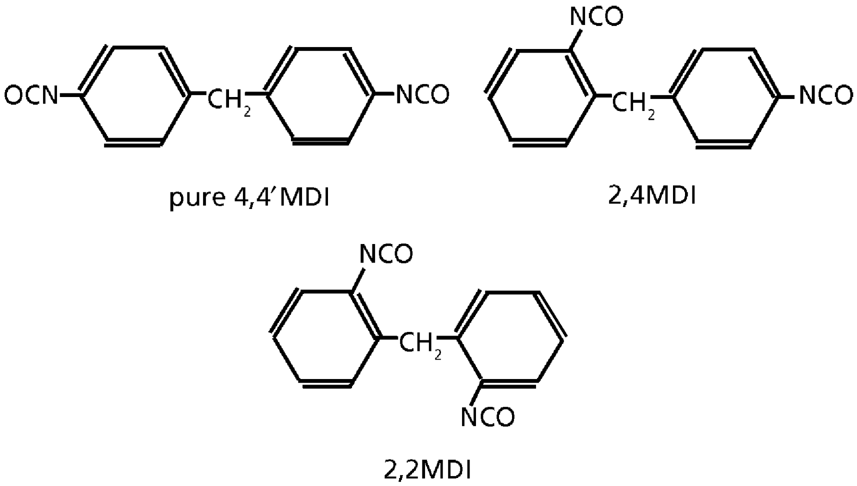


Figure 2.2 The chemical structures of pure MDI

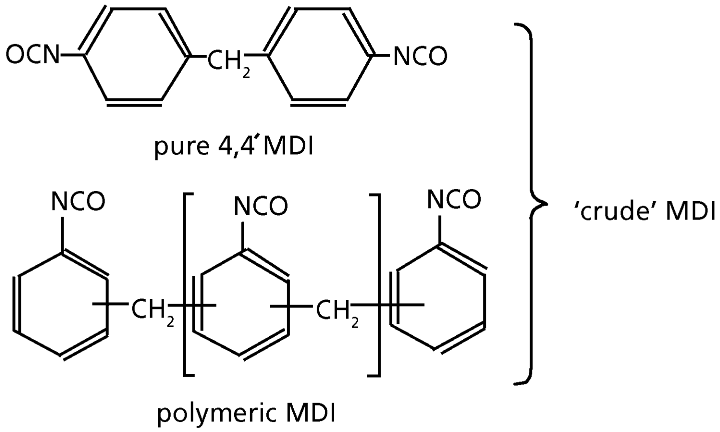


Figure 2.3 The chemical structure of 'crude' MDI

A high functionality polymeric MDI (called PAPI), obtained after the distillation of one part of pure 4,4′ MDI isomer, has a high functionality, close to three -NCO groups/mol (see **Figure 2.4**).

'Crude' MDI and PAPI are especially used in highly crosslinked polyurethanes, such as rigid polyurethane foams. Polymeric MDI have lower vapour pressures than TDI. Mixtures of TDI with polymeric MDI are also used in many applications, (e.g., in high resilience flexible foams). Aliphatic diisocyanates have a much lower reactivity than aromatic isocyanates. The most important aliphatic diisocyanates are presented in **Figure 2.5** [1-3, 6, 23-25]:

The characteristics of commercial TDI are presented in **Table 2.2** and the characteristics of commercial MDI in **Table 2.3**.

The reactivity of isocyanates toward active hydrogen compounds is a much more complex problem. As a general rule, the -NCO groups of a diisocyanate have different reactivities, in spite of the perfect symmetry of the molecule. The explanation of this effect is simple: after the reaction of the first molecule of the hydrogen active compound (an alcohol for

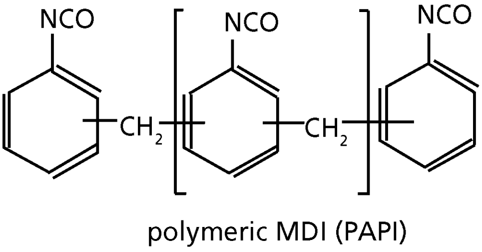


Figure 2.4 The chemical structure of polymeric MDI (PAPI)

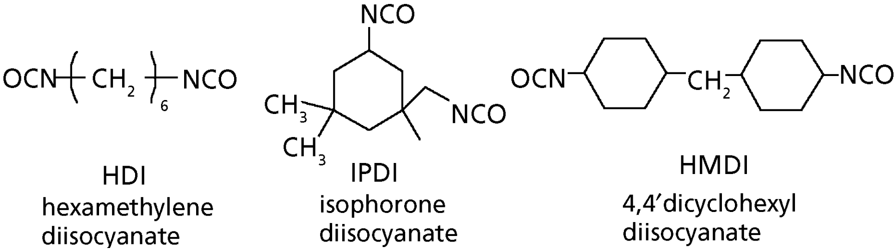


Figure 2.5 The chemical structures of some aliphatic diisocyanates

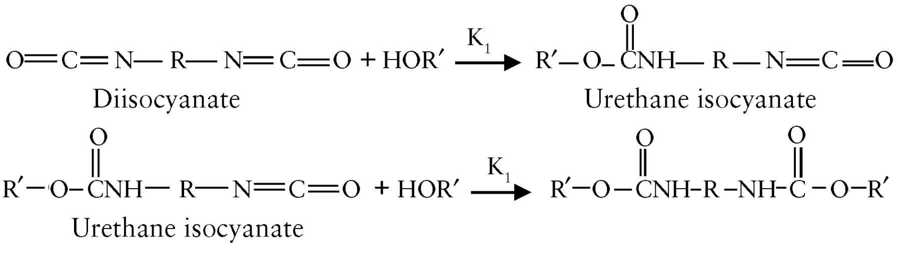
Table 2.2 The main characteristics of commercial TDI

Property	TDI 80/20	TDI 65/35	2,4 TDI
Form	liquid	liquid	liquid
Molecular weight, g/mol	174.16	174.16	174.16
Equivalent weight g/OH group	87.08	87.08	87.08
Boiling point, °C, at 0.101 MPa	251	251	251
Freezing point, °C	14.0	8.5	21.4

Table 2.3 The main characteristics of two commercial MDI

Property	pure MDI	polymeric MDI
Form	solid	liquid
Molecular weight, g/mol	250	>450
Functionality, -NCO groups/mol	2	2-3
Equivalent weight, g/OH group	125	>225
Boiling point, °C, at 665 Pa	194	-

example), the diisocyanate is first transformed into a urethane isocyanate. The second isocyanate group has a much lower reactivity than the first -NCO group, because the urethane group, due to its electron releasing effect, decreases the reactivity (Equations 2.3).



$$O{=}C{=}N{-}R{-}N{=}C{=}O + HOR' \xrightarrow{K_1} R'{-}O{-}\overset{\overset{O}{\|}}{C}NH{-}R{-}N{=}C{=}O$$

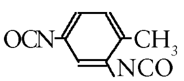
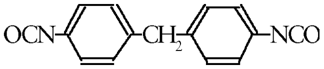
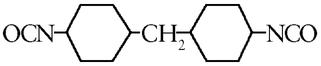
$$R'{-}O{-}\overset{\overset{O}{\|}}{C}NH{-}R{-}N{=}C{=}O + HOR' \xrightarrow{K_1} R'{-}O{-}\overset{\overset{O}{\|}}{C}NH{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R' \quad (2.3)$$

$$K_1 > K_2$$

This interesting effect is presented in **Table 2.4**. The difference between the values of K_1 and K_2 and the higher reactivity of aromatic isocyanates (TDI and MDI) is shown, as compared to aliphatic isocyanates (HDI and HMDI).

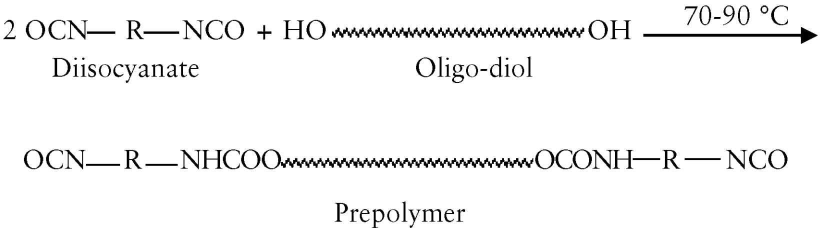
In polyurethane fabrication, some special techniques are used, such as: prepolymer technique, quasiprepolymer technique and ‘one shot’ technique.

Table 2.4. The different reactivities of -NCO groups in some aromatic and aliphatic diisocyanates against hydroxyl groups

Diisocyanate	R	K_1	K_1 / K_2
2,4 TDI		400	12.121
Pure MDI		320	2.909
HDI	$\mathrm{OCN{-}(CH_2)_6{-}NCO}$	1	2.000
HMDI		0.57	1.425

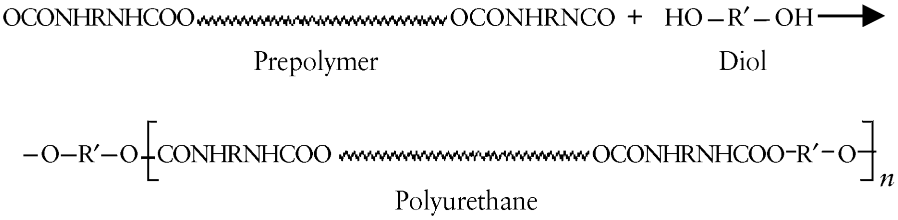
2.10 Prepolymer Technique

Prepolymers are formed by the reaction of a diisocyanate with an oligo-polyol, at the molar ratio [diisocyanate]/[OH group] of 1/1, in fact only one group of diisocyanate reacts with one hydroxyl group of the polyol. A structure with free terminal -NCO groups called 'prepolymer' is produced (see Equation 2.4):



$$\underset{\text{Diisocyanate}}{2\,\mathrm{OCN{-}R{-}NCO}} + \underset{\text{Oligo-diol}}{\mathrm{HO}\sim\sim\sim\sim\sim\mathrm{OH}} \xrightarrow{70\text{-}90\ ^\circ\mathrm{C}} \underset{\text{Prepolymer}}{\mathrm{OCN{-}R{-}NHCOO}\sim\sim\sim\sim\sim\mathrm{OCONH{-}R{-}NCO}} \tag{2.4}$$

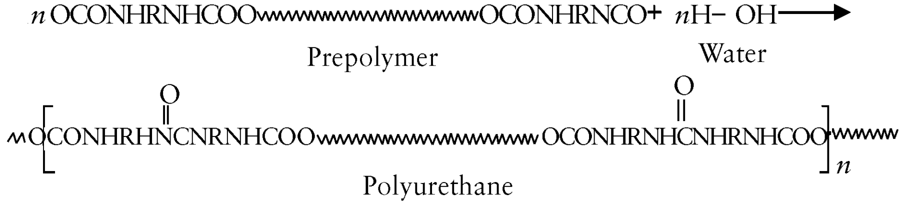
By the reaction of a prepolymer with a chain extender such as: ethylene glycol, diethylene glycol, 1,4 butane diol or a diamine, the high molecular weight polyurethanes are formed (see Equation 2.5).



$$\underset{\text{Prepolymer}}{\mathrm{OCONHRNHCOO}\sim\sim\sim\sim\sim\mathrm{OCONHRNCO}} + \underset{\text{Diol}}{\mathrm{HO{-}R'{-}OH}} \longrightarrow \underset{\text{Polyurethane}}{-\mathrm{O{-}R'{-}O}\left[\mathrm{CONHRNHCOO}\sim\sim\sim\sim\sim\mathrm{OCONHRNHCOO{-}R'{-}O}\right]_n} \tag{2.5}$$

This 'prepolymer' technique is frequently used in the manufacture of polyurethane elastomers, coatings, sealants, flexible foams, monocomponent polyurethanes, etc.

In the special case of monocomponent polyurethanes, the single partner of the reaction is the prepolymer. The prepolymer is extended to a high MW polymer by reaction with water present in the atmosphere. Water, is in fact, a chain extender and the resulting high MW polymer has both bonds: urethane and urea bonds:



$$n\,\text{OCONHRNHCOO}\sim\!\sim\!\sim\!\sim\text{OCONHRNCO} + n\text{H}-\text{OH} \longrightarrow$$

$$\sim\left[\text{OCONHRHN}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NRNHCOO}\sim\!\sim\!\sim\!\sim\text{OCONHRNH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NHRNHCOO}\right]_n\sim\!\sim$$

If a prepolymer derived from an oligo-triol or an oligo-polyol, having three or more terminal -NCO groups is used, if it is in contact with atmospheric humidity, crosslinked polyurethanes are obtained.

2.11 Quasiprepolymer Technique

Quasiprepolymers are obtained in a similar way to the prepolymers, with the difference that the reaction between oligo-polyol and the isocyanates is developed in the presence of a large excess of isocyanate. Quasiprepolymers are a mixture of prepolymers and free isocyanates (around 16-32% free isocyanates):

$$\left.\begin{array}{c}\text{OCNRNHCOO}\sim\!\sim\!\sim\!\sim\text{OCONHRNCO}\\ \text{Prepolymer}\\ \\ \text{OCN}-\text{R}-\text{NCO}\\ \text{Free diisocyanate}\end{array}\right\}\text{Quasiprepolymer}$$

Quasiprepolymers are frequently used to transform a solid isocyanate, (e.g., pure MDI), into a liquid, and are used in flexible PU foams, in microcellular elastomers and in other PU applications.

2.12 One Shot Technique

One of the most used techniques to obtain polyurethanes is the one-shot technique, which consists of the very efficient mixing, in one step only, in a short time, of all the raw materials involved in polyurethane fabrication: isocyanate, oligo-polyol, chain extenders or crosslinkers, silicon emulsifiers, blowing agents, catalysts, such as tertiary amines and tin or stannous catalysts and other auxiliary raw materials (flame retardants, fillers). The ‘key’ to the ‘one shot’ technique is extremely efficient mixing, in a very short time. At this initial stage, the reactions between isocyanates and active hydrogen compounds are insignificant and the reaction mixture is liquid.

In order to simplify the procedure of using too many components, a ‘masterbatch’, that is a mixture of the components that do not react with each other, (e.g., oligo-polyol, water, chain extender, catalysts, etc.), is made before foaming. Then it is possible to use only two components: one is the polyolic component (called component A or formulated polyol, containing a mixture of all raw materials except for the isocyanate, in the proportions needed) and the second component is the isocyanate (called component B or isocyanate component). The polyurethane that results is a consequence of the very efficient contact between the isocyanate component and the polyolic component. Usually, in rigid PU foams only two components are used. In flexible foams, the polyolic component is divided into two components, especially in order to avoid the contact of some hydrolysable component with water, (e.g., stannous octoate). The gravimetric ratio between the components is verified before the foaming process and if necessary, it is corrected.

Modern foaming machines permit a simultaneous dosing of many components, (e.g., seven components, three different oligo-polyols). The correct ratio between the components is assured by the perfectly controlled flow of each component. In this manner, it is possible to use a large range of formulations by simply changing the component flow. This facility assures a high flexibility in the foaming process.

All the previous information regarding the general chemistry of polyurethanes and the structure of isocyanates have a role in the better understanding of how the oligo-polyols get chemically inserted in the high MW polyurethane structure and to understand the role played by the polyol structure in the properties of the resulting polyurethanes.

2.13 Several Considerations on the Polyaddition Reaction

As mentioned previously, the synthesis of polyurethanes, by the reaction of a diisocyanate (or polyisocyanate) with oligo-diols (or oligo-polyols), is a polyaddition reaction (or step-addition polymerisation), a particular type of polycondensation reaction. There is a great difference between the polycondensation and the polyaddition reactions and the classical radical polymerisation or ionic (living) polymerisation reactions. In radical polymerisations (typical chain reactions), the high MW polymer is formed at the beginning of polymerisation. The reaction system is constituted from monomer and high

MW polymer. The radical polymerisations are characterised by strong transfer reactions, simultaneous with the polymerisation reaction.

Living ionic polymerisations are characterised by a linear increase of the MW in the resulting polymer, with the conversion. In the reaction system there are: the monomer and the polymer. In living ionic polymerisations, the termination reactions are absent.

In our particular type of step-addition polymerisation, monomers, dimers, trimers, oligomers and polymers are the reactive species which participate in the chain growth. Initially, the monomers react with monomers and give dimers, dimers react with monomers and dimers and give trimers and tetramers, respectively. The high MW polymer is formed only in the last stages of the polyaddition reaction, at high conversion rates. Chain transfer and termination reactions are absent.

In **Figure 2.6** one can compare, the MW growth of polymers in radical, living anionic and step-addition polymerisation reactions.

As in all polycondensation reactions, in polyaddition reactions (for example in polyurethane synthesis), the molar ratio between the reactive group (in our case between [-NCO]/[hydroxyl groups]), has a very strong influence on the MW of the resulting polyurethane polymer. The maximum MW is obtained at an equimolecular ratio [-NCO]/[OH] = 1 [29]. A small excess of one reactant (isocyanate or hydroxyl groups), drastically reduces the MW of the resulting polyurethane (**Figure 2.7**).

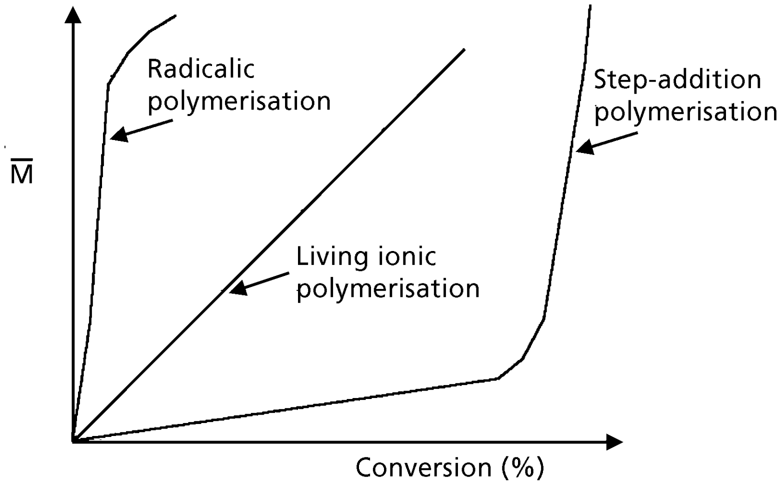


Figure 2.6 Molecular weight growth in radical, living ionic and step-addition polymerisations

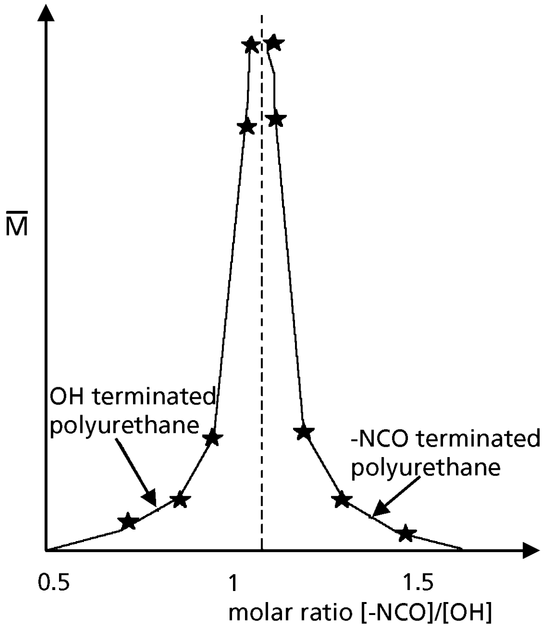


Figure 2.7 The effect of the molar ratio [-NCO]/[OH] on MW of the polyurethanes

References

1. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999.

2. *Flexible Polyurethane Foams*, Second Edition, Eds., R. Herrington and K. Hock, Dow Chemical Company, Midland, MI, USA, 1997.

3. *MDI and TDI: Safety, Health & Environment, A Source Book and Practical Guide*, Eds., D.C. Allport, D.S. Gilbert and S.M. Outterside, Wiley Publishers, Chichester, UK, 1998.

4. O. Bayer, *Angewandte Chemie*, 1947, **A59**, 257.

5. O. Bayer, *Modern Plastics*, 1947, **24**, 149.

6. *Polyurethane Technology*, Ed., P.F. Bruins, Interscience Publishers, London, UK, 1969.

7. *The ICI Polyurethanes Book*, Second Edition, Ed., G. Woods, John Wiley & Sons, Chicester, UK,1990.

8. *Telechelic Polymers, Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Boca Raton, FL, USA, 1989, p.203.

9. *Advances in Polyurethane Technology*, Eds., J.M. Buist and H.A. Gudgeon, Maclaren and Sons, London, UK, 1968.

10. S.D. Gagnon in *Encyclopedia of Polymer Science and Technology*, 2nd Edition, Ed., J.I. Kroschowitz., John Wiley & Sons, Inc., New York, NY, USA, 1986, p.273.

11. H. Ulrich in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Edition, Ed., J.I. Kroschowitz, John Wiley & Sons, New York, NY, USA, 1997, Volume 24, p.695.

12. J.H. Saunders and K.C. Frisch, *Polyurethanes, Chemistry and Technology*, *High Polymers, Volume 14, Part I*, Chemistry, Interscience Publishers, New York, NY, USA, 1962.

13. J.H. Saunders and K.C.Frisch, *Polyurethanes, Chemistry and Technology, High Polymers, Volume 14, Part II, Technology*, 1964, Interscience Publishers, New York, NY, USA.

14. *Handbook of Polymeric Foams and Foam Technology*, Eds., D. Klempner and K.C. Frisch, Hanser, Munich, Germany, 1991.

15. *Plastic Foams,* Eds., K.C. Frisch and J.H. Saunders, Marcel Dekker, New York, NY, USA, 1972.

16. *Polyurethane Handbook*, Ed., G. Oertel, Hanser Verlag, Munich, Germany, 1985.

17. *Developments in Polyurethanes, I*, Ed., J.M. Buist, Applied Science Publishers, London, UK, 1978.

18. H. Ulrich, *Reaction Polymers*, Hanser Publishers, New York, NY, USA, 1992.

19. A.A.R. Sayigh, H. Ulrich and W.J. Farrisey in *Condensation Monomers*, Eds., J.K. Stille and T.W. Campbell, Wiley Interscience, New York, NY, USA, 1972, p.231.

20. *Analytical Chemistry of the Polyurethanes*, Eds., D.J. David and H.B. Staley, Wiley Interscience, New York, NY, USA, 1969, Volume 16, Part III, High Polymers.

21. G.W. Woods, *Flexible Polyurethane Foams, Chemistry and Technology*, Applied Science Publishers, Englwood, NJ, USA, 1982.

22. H. Ulrich in *Encyclopedia of Polymer Science and Engineering*, Ed., J.I. Kroschowitz, John Wiley & Sons Inc., New York, NY, USA, 1987, Volume 8, p.448.

23. *Kunststoffe Plast Europe*, 1997, **87**, 9, 6.

24. S.G. Entelis, V.V. Evreinov and A.I. Kuzaev, *Reactive Oligomers*, Brill Publishers, Moscow, Russia, 1988.

25. W.D. Vilar, *Chemistry and Technology of Polyurethanes*, 3rd Edition, Vilar Poliuretanos Ltd., Lugoa, Rio de Janeiro, 2002. *www.polyuretanos.com.br/*.

26. A.F. Johnson, P.D. Coates and M.W.R. Brown, *Reactive Processing of Polymers*, Rapra Review Reports No.73, Volume 7, No.1, Rapra Technology, Shrewsbury, UK, 1994.

27. G. Wegener, M. Brandt, L. Duda, J. Hofmann, B. Klesczewski, D. Koch, R-J. Kumpf, H. Orzesek, H-G. Pirkl, C. Six, C. Steinlein and M. Weisbeck, *Applied Catalysis*, 2001, **221**, 1-3, 303.

28. *Houben Weyl: Methoden der Organische Chemie*, Eds., E. Müller, O. Bayer, H. Meerwein and K. Ziegler, Georg Thieme Verlag, Stuttgart, Germany, 1963, Volume 14, Part 2, p.57.

29. C.V. Oprea and V. Bulacovschi, *Polimeri, Teoria Proceselor de Sinteza (Polymers: Theory of Synthesis Processes)*, Editura Tehnica, Bucharest, Romania, 1986, p.399. [In Romanian]

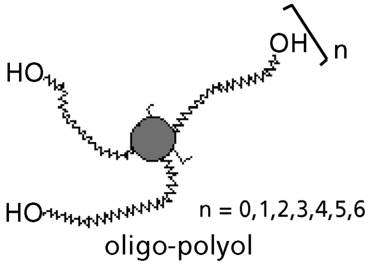
3

The General Characteristics of Oligo-Polyols

Polyols used in polyurethane manufacture are divided from the structural point of view in two groups. In the first group there are the low molecular weight (MW) polyols, very well described in organic chemistry, having unitary and concrete MW, such as: propylene glycol, ethylene glycol, dipropylene glycol, diethylene glycol, 1,4 butanediol, neopentyl glycol, triethanolamine, glycerol, etc. These polyols are currently used in the polyurethane fabrication as chain extenders (the polyols with two hydroxyl groups/mol called diols) or as crosslinkers (the polyols with more than two hydroxyl groups/mole such as triols, tetraols, etc.). Because these polyols are very well characterised and the chemistry and technology of these compounds is well known [1, 2], this chapter does not cover this group.

The second group of polyols for polyurethane contains low MW polymers (oligomers with a maximum MW of 10,000 daltons) with terminal hydroxyl groups (hydroxy telechelic oligomers), called oligo-polyols, characterised by an average molecular weight and having a molecular weight distribution (MWD) of homologous species. The present chapter is dedicated exclusively to this second group of oligo-polyols for polyurethanes, which together with isocyanates are the most important raw materials to build the complex architecture of a polyurethane polymer [3-12].

The general formula of an oligo polyol for polyurethane is shown in **Figure 3.1**:



where:

● = a chemical organic structure, aliphatic, cycloaliphatic, aromatic, heterocyclic etc.

∿∿∿ = oligomeric chain (polyether chain, polyester chain, polyhydrocarbon chain, polysiloxane chain etc.)

∿ OH = terminal hydroxyl group

n = the number of chains derived from one hydroxyl group

f = n + 2 (the total number of hydroxyl groups/mol=functionality)

Figure 3.1 The general formula of oligo-polyols for polyurethanes

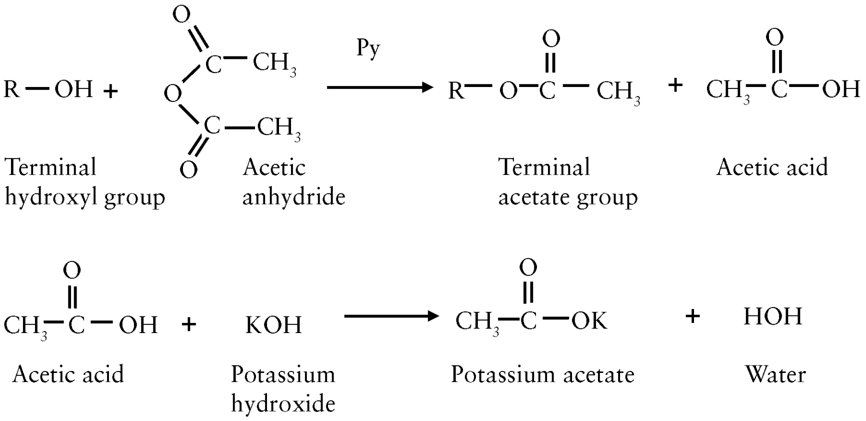
An oligo-polyol for polyurethanes, may have two, three, four, five, six, seven or a maximum of eight hydroxyl groups/mol. Polyols with a higher number of hydroxyl groups/mol are rarely used (for example dendritic polyols). Oligo-polyols with only one hydroxyl groups/mol are present in all the polyether polyols based on propylene oxide (see Chapters 4.1.1-4.1.4).

Irrespective of the chemical structure of the oligomeric chain, the oligo-polyols have general and common characteristics and these characteristics are determined by the same analytical methods. These first common elements permit an unitary and general point of view on all oligo-polyols for polyurethanes.

3.1 Hydroxyl Number

The first common characteristic of oligo-polyols for polyurethanes is the presence of terminal hydroxyl groups [13-17]. The hydroxyl number is defined as the quantitative value of the amount of hydroxyl groups available for the reaction with isocyanates. The hydroxyl number (or hydroxyl index) is expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mg KOH/g). The most important analytical method for hydroxyl number determination (OH#) is the reaction of the terminal hydroxyl groups with organic anhydrides (acetic anhydride or phthalic anhydride). The acidic carboxyl groups resulting from this reaction are neutralised with the equimolecular quantity of potassium hydroxide.

The reaction with acetic anhydride is presented in reaction 3.1.

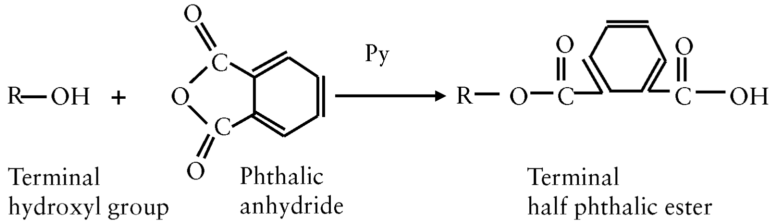


$$R{-}OH + (CH_3CO)_2O \xrightarrow{Py} R{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH$$

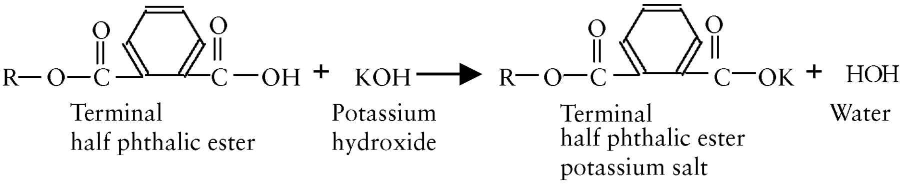
$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH + KOH \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}OK + HOH$$

(3.1)

The reaction with phthalic anhydride is shown in reaction 3.2.



(3.2)



Reactions 3.1 and 3.2 show that for one hydroxyl group, one mole of KOH (56,100 mg of KOH), is consumed in the neutralisation process. Consider the MW of an oligo-polyol, M_n, and the number of hydroxyl groups/mol, f (f = functionality). The hydroxyl number of this oligo-polyol is calculated as follows: for 1 mole of oligo-polyol, having f hydroxyl groups/mole, f x 56,100 mg of potassium hydroxide are needed. In order to obtain the hydroxyl number (OH#) expressed in mg KOH/g, the total mg KOH used should be divided by the M_n of oligo-polyol:

$$OH\# \frac{f \bullet 56100}{M_n} \tag{3.3}$$

Equation 3.3 is a fundamental equation in oligo-polyol chemistry, having very important practical applications. The number average molecular weight, M_w, of an oligo-polyol is easily calculated with this formula, if the functionality and the OH# are known:

$$M_n = \frac{f \bullet 56100}{OH\#} \tag{3.4}$$

where:

OH# = hydroxyl number of oligo-polyol in mg KOH/g,

M_n = number average molecular weight (g/mol),

f = functionality, the number of OH groups/mol, and

56,100 = equivalent weight of KOH, in milligrams.

The method for hydroxyl group determination, using acetic anhydride, is described in detail in ASTM E222 [15] and the method using phthalic anhydride, including the rapid determination of hydroxyl groups using imidazole as a catalyst, are described in detail in ASTM D4274 [16] and ISO 14900 [18]. An interesting method for hydroxyl number determination, using the reaction of terminal hydroxyl groups with *p*-toluenesulfonyl isocyanate, which does not interfere with acidic species, is described in ASTM E1899 [17].

The rapid determination of hydroxyl number by near infrared spectroscopy has been described by Turley and Pietrantonio[14].

3.1.1 Hydroxyl Percentage

Hydroxyl percentage (%OH) is another form of expressing the concentration of hydroxyl groups in any polyol. The sum of the atomic weights in the OH groups is 16 + 1 = 17 g/OH group.

Hydroxyl percentage is defined as the gravimetric percentage of all the hydroxyl groups in an oligo-polyol molecule:

$$\%\mathrm{OH} = \frac{f \bullet 17}{M} = \frac{f \bullet 17}{\dfrac{f \bullet 56100}{\mathrm{OH}\,\#}}$$

$$\%\mathrm{OH} = \frac{\mathrm{OH}\,\#}{33}$$

The hydroxyl percentage is easily obtained by dividing the hydroxyl number (OH#) by 33. The hydroxyl number is then calculated from the equation:

$$\mathrm{OH\#} = (33) \bullet (\%\mathrm{OH})$$

An oligo-polyol with an hydroxyl number of 56 mg KOH/g, for example, has 1.6969% hydroxyl groups and a polyol with an OH# of 400 mg KOH/g has 12.12% hydroxyl groups.

3.2 Functionality

Functionality is the second important characteristic of an oligo-polyol and is defined as the number of hydroxyl groups/molecule of oligo-polyol. The functionality of an oligo-polyol is not very easy to determine. An old method is based on the determination of the conversion at the gel point (p) of a reaction between a polyol and a diisocyanate [19]. The functionality is determined by using the well known equation of Flory $p = 2/f$, where p is the conversion at gel point and f is the medium functionality of the reaction system [19].

For polyether polyols an NMR method was elaborated for functionality determination [20]. The most usual and practical method for functionality determination is based on the assessment of the MW of an oligo-polyol, by a method applicable to low MW compounds (MW < 10,000 daltons), such as vapour pressure osmometry (VPO) or gel permeation chromatography (GPC), together with hydroxyl number determination. The functionality is calculated by using the fundamental equation 3.4:

$$M_n = \frac{f \bullet 56100}{OH\#} \tag{3.4}$$

In the case of a mixture of two oligo-polyols with different functionalities (f_1 and f_2), the equivalent functionality, fe, of the oligo-polyol mixture is calculated using the general formula:

$$fe = x_1 \cdot f_1 + x_2 \cdot f_2 \tag{3.5}$$

where x_1 and x_2 are the molar ratios of each oligo-polyol in the mixture and f_1 and f_2 are the functionalities of the corresponding oligo-polyols. The general structure of oligo-polyols having various functionalities are shown in **Figures 3.2-3.8**.

Figure 3.2 General structure of a monol (oligo polyol with only one hydroxyl group/mol)

Figure 3.3 General structure of a diol (oligo-polyol with two hydroxyl groups/mol)

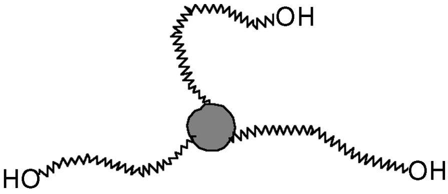


Figure 3.4 General structure of a triol (oligo-polyol with three hydroxyl groups/mol)

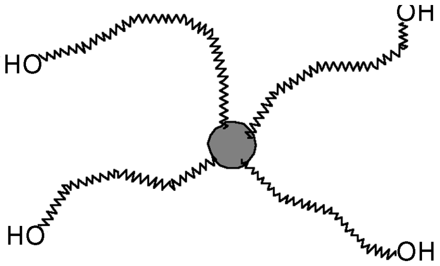


Figure 3.5 General structure of a tetraol (oligo-polyol with four hydroxyl groups/mol)

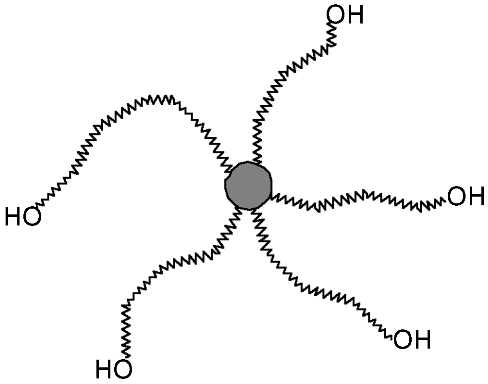


Figure 3.6 General structure of a pentol (oligo polyol with five hydroxyl groups/mol)

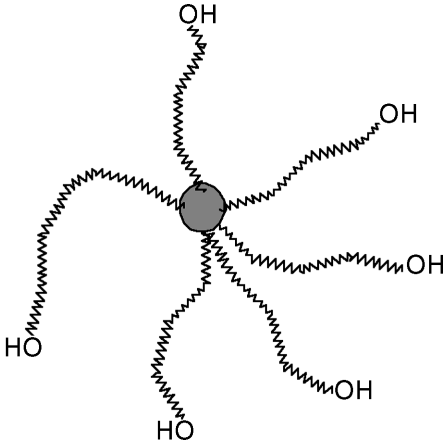


Figure 3.7 General structure of a hexol (oligo-polyol with six hydroxyl groups/mol)

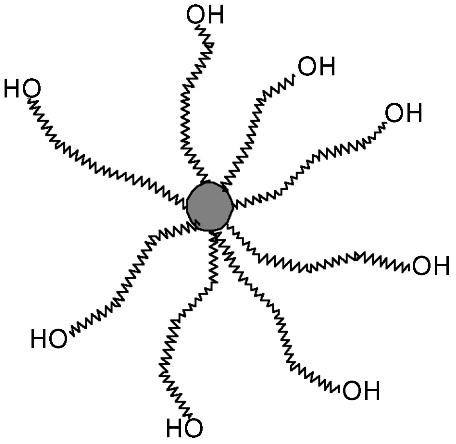


Figure 3.8 General structure of an octol (oligo-polyol with eight hydroxyl groups/mol)

The average functionality of a complex mixture of polyols may be calculated in a simple manner, by dividing the total number of hydroxyl groups by the total number of molecules.

$$fe = \frac{\text{Total number of hydroxyl groups}}{\text{Total number of molecules}} \quad \text{(OH groups/mol)}$$

In the polyol composition are present:

n_1 = mols of polyol with the functionality f_1
n_2 = mols of polyol with the functionality f_2
n_i = mols of polyol with the functionality f_1

The average functionality fe of the polyol mixture is:

$$fe = \frac{n_1{}^*f_1 + n_2 {}^* f_2 + \ldots\ldots.+.n_i{}^*f_1}{n_1 + n_2 + \ldots\ldots. + n_i} \qquad (3.6)$$

Formula 3.6 is very easy to apply because it is not necessary to calculate the molar fractions of each component. As a practical example, the average functionality, fe, (or equivalent functionality), of a mixture of 1000 kg of glycerol and 3500 kg of sucrose will be calculated:

1000 kg of glycerol represents 1000 ÷ 92 = 10.86 mols

1000 kg of glycerol has 10.82 mols x 3 = 32.46 hydroxyl groups

3500 kg of sucrose represents 3500 ÷ 340 = 10.29 mols ($f_2 = 8$)

3500 kg of sucrose have: 10.29 mols x 8 = 82.32 hydroxyl groups

By using the formula 3.6 is possible to calculate easily the equivalent functionality (fe) of this polyolic mixture:

$$fe = \frac{\text{total number of OH groups}}{\text{total number of molecules}} = \frac{32.58+82.32}{10.86+10.29} = \frac{114.9}{21.15} = 5.43$$

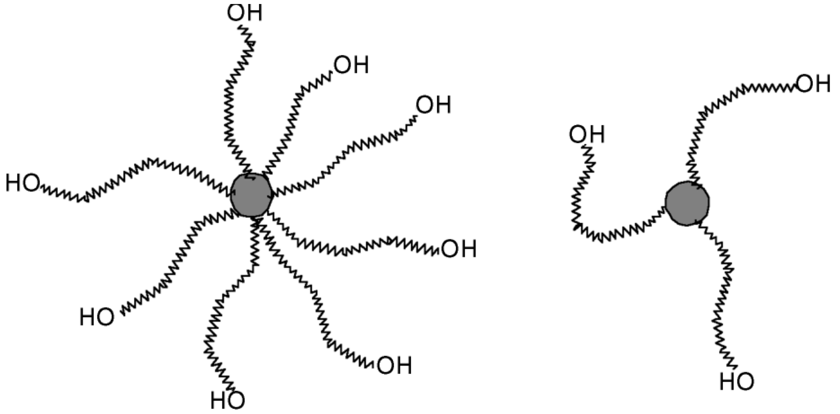
The mixture of 1000 kg glycerol with 3500 kg sucrose has an equivalent functionality of 5.43 OH groups/mol.

In fact, the general formula 3.5 is deduced easily from formula 3.6:

$$fe = \underbrace{\frac{n_1}{n_1+n_2+\ldots+n_i}}_{x_1} * f_1 + \underbrace{\frac{n_2}{n_1+n_2+\ldots+n_i}}_{x_2} * f_2 + \ldots + \underbrace{\frac{n_i}{n_1+n_2+\ldots+n_1}}_{x_i} * f_i \qquad (3.7)$$

$$fe = x_1 * f_1 + x_2 * f_2 + ..+ x_1 * f_1$$

In practice mixtures are frequently obtained between oligo-polyols of different functionalities, for example octol with triol or hexol with triol. For example an equimolecular mixture between an oligo-octol and an oligo-triol (see **Figure 3.9**) has the equivalent functionality of 5.5 OH groups/mol (calculated easily with formula 3.7):



1 mol oligo-octol

1 mol oligo-triol

Figure 3.9 General structure of a mixture of two different oligo-polyols (octol + triol, having an equivalent functionality (fe) of 3 < fe < 8)

$x_1 = 0.5$ and $x_2 = 0.5$. As an immediate consequence the equivalent functionality of this oligo-polyol mixture is:

$$fe = 0.5 \times 8 + 0.5 \times 3 = 4 + 1.5 = 5.5 \text{ hydroxyl groups/mol}$$

3.3 Molecular Weight and Molecular Weight Distribution

The MW of any oligo-polyol is calculated with formula 3.4 if the functionality (f) and the hydroxyl number (OH#) are known, in fact it is a particular case of MW determination by the quantitative analysis of the terminal functional groups, in our case the hydroxyl groups. Thus, a triol with an OH# of 27 mg KOH/g has a calculated MW of 6,233 daltons, but a tetraol having the same OH#, has a calculated MW of 8,311 daltons. **Table 3.1** gives the values of the MW for oligo-polyols of different functionalities.

The MWD is an important characteristic of oligo-polyols, differentiating the oligo-polyols from the unitary low MW polyols of organic chemistry. As in all polymers, the MW distribution of oligo-polyols is given by the ratio between weight average molecular weight MW (M_w) and the M_n, both being determined by GPC.

$$\mathrm{MWD} = \frac{M_w}{M_n} \begin{pmatrix} \text{polydispersity index or} \\ \text{molecular weight distribution} \end{pmatrix}$$

The oligo-polyol MWD curves are presented in **Figure 3.10**.

A broad MWD represents a large number of macromolecules which have a wide distribution of molecular weights. The MWD of oligo-polyols is currently determined by GPC using tetrahydrofuran as solvent [21].

Table 3.1 The oligo-polyols MW values function of the functionality (f)

Oligo-polyol type	MW value
Diols (f = 2)	112200/OH#
Triols (f = 3)	168300/OH#
Tetraols (f = 4)	224400/OH#
Hexols (f = 6)	336600/OH#
Octols (f = 7)	448800/OH#

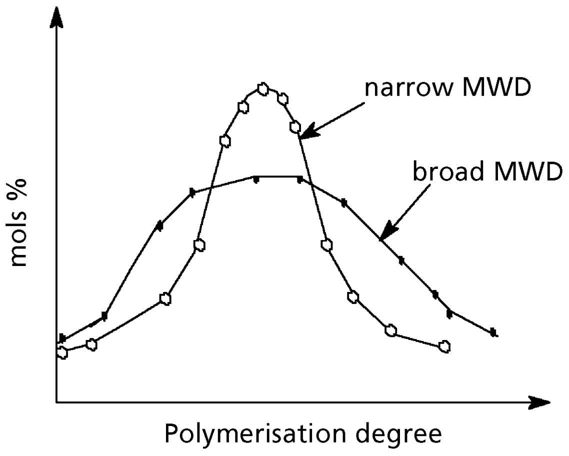


Figure 3.10 General aspect of the oligo-polyols MWD curves

A narrow MWD shows that the majority of molecular species are situated in a very narrow interval of polymerisation degree. The extremely narrow MWD polymers, called monodisperse polymers (all the macromolecules have the same molecular weight), are very difficult to obtain by synthetic methods. Real monodisperse polymers, such as: proteins, nucleic acids (DNA), etc., are produced only in Nature

The practice of polyurethane fabrication, proved that oligo-polyols with narrow MW distribution give much better physico-mechanical properties in the resulting polyurethane than the oligo-polyols with a broad MWD, especially in the area of elastic polyurethanes (elastomers, flexible foams, etc.), based on high MW oligo-polyols. The problem of MWD will be discussed for each oligo-polyol type separately. As a general rule, the oligo-polyols obtained by anionic, cationic or coordinative ring opening polymerisation (polyalkyleneoxide polyols, polytetrahydrofuran diols, etc.), have a narrower MWD (MWD = 1.05-1.3) than the oligo-polyols obtained by the polycondensation processes (MWD = 2.5-2.8).

3.4 Equivalent Weight

The equivalent weight (EW) [1, 22]of an oligo-polyol is defined as the oligo-polyol MW divided by its functionality:

$$\mathrm{EW} = \frac{M}{f} = \frac{\dfrac{f \bullet 56100}{\mathrm{OH} \neq}}{f}$$

$$\mathrm{EW} = \frac{56100}{\mathrm{OH} \neq} \tag{3.8}$$

Equation 3.8 for EW is very convenient for practical use because it does not depend on the functionality, which is very difficult to determine. The EW of an oligo-polyol is very useful for the required isocyanate quantity calculation. One equivalent weight of an oligo-polyol reacts with one equivalent weight of the diisocyanate (the MW of the isocyanate divided by the number of -NCO groups). The EW of polyols with the same OH# are identical, irrespective of the functionality. Thus a diol with an OH# of 56.1 mg KOH/g (MW = 2000) and a triol of the same OH# (MW = 3000), have the same EW of 1000.

The EW can also be calculated by using formula 3.9:

$$\mathrm{EW} = \frac{M}{f} = \frac{\dfrac{f \bullet 17}{\%\mathrm{OH}}}{f}$$

$$\mathrm{EW} = \frac{17}{\%\mathrm{OH}} \tag{3.9}$$

3.5 Water Content

The water content [23] is expressed as the percentage of free, nonchemically bound water in the oligo-polyol. The water content is determined by the classical Karl-Fischer method, described, in detail, for oligo-polyols in ASTM D4672 [23] and ISO 14897 [24]. As a general rule, the water content which is acceptable for the majority of oligo-polyols is between 0.05-0.1%.

3.6 Primary Hydroxyl Content

The terminal hydroxyl groups in the oligo-polyols for polyurethanes are only primary hydroxyl groups or secondary hydroxyl groups [22, 25-34]. Due to their lower reactivity with isocyanates, the oligo-polyols used for polyurethanes do not have terminal tertiary hydroxyl groups or phenolic end groups. As mentioned before, primary hydroxyl groups are around 3-3.3 times higher in reactivity than secondary hydroxyl groups, in the uncatalysed reactions with isocyanates (see Chapter 1).

As an immediate consequence, the oligo-polyols containing terminal primary hydroxyl groups are more reactive in the reaction with isocyanates than the oligo-polyols having only secondary hydroxyl groups. The primary hydroxyl content of an oligo-polyol is an important characteristic, because it is possible to determine the potential reactivity with isocyanates.

Due to the big similarity between the primary and secondary hydroxyl groups, it is difficult to determine practically, the primary hydroxyl content by a reaction with a specific chemical reagent. The chemical methods are generally based on the difference in reactivity of the previously mentioned hydroxyl species and are in fact analytical kinetic methods. The first method, called the method of the competitive reaction kinetics, is based on the second-order kinetics of the primary and secondary hydroxyl groups reaction with a common reagent, namely, acetic anhydride [25] or phthalic anhydride [27] (Hanna and Siggia method [25]). The graphical representation of the integrated form of second order kinetics is a straight line, in the case of an unique hydroxylic species, the slope of this line is proportional to the rate constant. In the case of a mixture of two different hydroxylic species having different reactivities (a mixture of primary and secondary hydroxyls), two straight lines are obtained with two different slopes. The first straight line is characteristic of the more reactive species which reacts first (in our case the primary hydroxyl) and the second straight line is characteristic of the species with lower reactivity, (in our case the secondary hydroxyl). This marked change of the straight line slope is used for determination of the primary hydroxyl content of polyether polyols [25].

In **Figure 3.11**, one observes the kinetic curves of the oligo-polyol reaction, having only secondary hydroxyl groups compared to oligo-polyols having primary and secondary hydroxyl groups.

The value of time, t_1, determined graphically, corresponds to b1 mols of hydroxyl groups reacted, which represents the total quantity of primary hydroxyl. The primary hydroxyl content is expressed as the ratio between the molar quantity of primary hydroxyl and the total quantity of hydroxyl groups as percentage:

$$\%\ \text{primary hydroxyl} = \frac{b1}{b} \times 100$$

Generally, in any oligo polyol there are the following relationships:

$$[OH_t]=[OH_1] + [OH_2]$$

$$\%[OH_1] = \frac{[OH_1]}{[OH_t]} \times 100$$

where:

$[OH_t]$ = total hydroxyl groups (mol/l),
$[OH_1]$ = primary hydroxyl groups (mol/l),
$[OH_2]$ = secondary hydroxyl groups (mol/l), and
$\%[OH_1]$ = percentage of primary hydroxyl.

A specific reagent for the primary hydroxyl group determination is triphenylchloromethane [22], which has a very reactive chlorine atom and a bulky substituent (triphenylmethyl). Due to the high steric hindrance of triphenylchloromethane, a selective reaction with primary hydroxyl groups takes place. Unfortunately, the precision is not very high because the secondary hydroxyl groups react only to a very small extent (8-10%). In order to make it a more precise method, it is necessary that before the determination, a calibration curve should be done and the real primary hydroxyl content is corrected by the decrease in the quantity of secondary hydroxyl reacted.

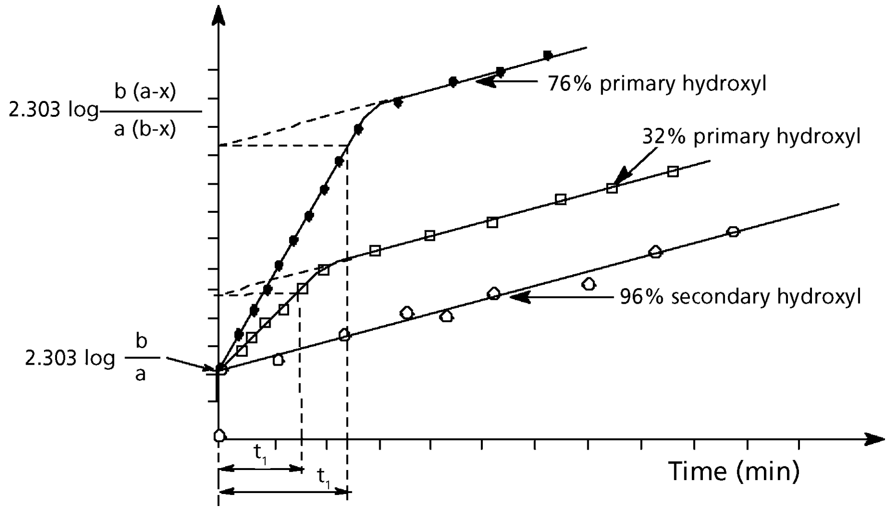
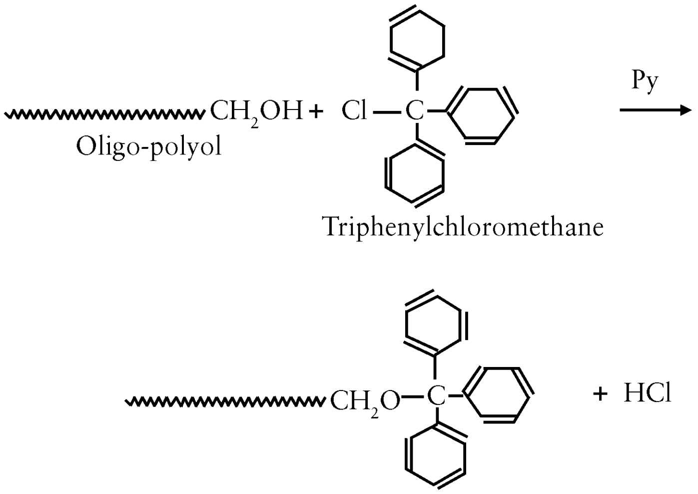
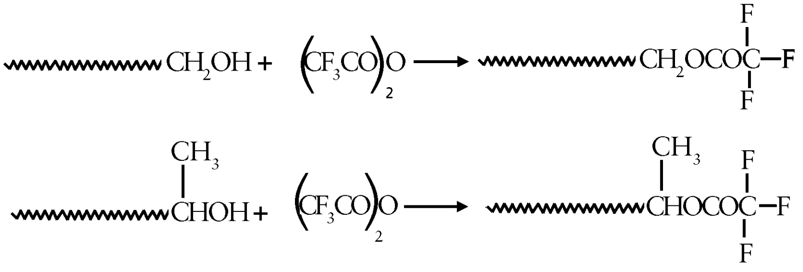


Figure 3.11 Graphical representation of second order kinetics of the oligo-polyols reaction with different primary hydroxyl contents with phthalic anhydride. *a: initial concentration of phthalic anhydride; b: initial concentration of hydroxyl groups;* t_1*: time for total consumption of primary hydroxyl; x: concentration of a or b reacted at time t. Temperature: 30 °C; Solvent: pyridine*



The method is extremely simple and needs only the neutralisation of the resulting hydrochloric acid with a strong base solution of a known concentration. Unfortunately, as mentioned previously, this method is not very accurate. The most accurate and usual methods for primary hydroxyl determination are two NMR spectroscopic methods: ^{19}fluorine NMR and ^{13}carbon NMR. Both methods are described in detail in ASTM D4273 [34].

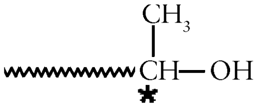
The Test method A, based on ^{19}fluorine NMR spectroscopy, is based on the derivatisation of terminal oligo-polyol groups with trifluoroacetic anhydride. The fluorine atoms of the trifloroacetic esters of primary hydroxyls have a totally different chemical shift as compared to the fluorine atoms of the secondary hydroxyl trifluoroacetic esters.



The ^{19}fluorine NMR method is one of the most accurate methods for primary hydroxyl determination. It is suitable for oligo-polyols (especially polyether polyols) with hydroxyl numbers in the range 24-300 mg KOH/g and primary hydroxyl percentages in the range of 2 to 98%.

Test Method B, ^{13}carbon NMR spectroscopy, is based on the difference of chemical shifts corresponding to the carbon atom linked to a primary hydroxyl (around 61-63 ppm, internal standard tetramethyl silane) as compared with the chemical shifts corresponding to the carbon atom linked to a secondary hydroxyl group (around 69-70 ppm with tetramethyl silane as internal standard). The ^{13}carbon NMR method is simple because it does not need any preliminary derivatisation. Unfortunately, the low concentration of carbon atoms linked to the terminal hydroxyl groups and the low natural abundance of the ^{13}C isotope (around 0.5%), mean that to obtain good precision in the determination, a sufficient number of repetitive pulses (500-1000) need to be accumulated by the spectrometer until the peaks of the primary and secondary hydroxyl carbons can be accurately measured by the spectrometer's integration system.

$\sim\!\sim\!\sim \underset{*}{C}H_2-OH$



$\sim\!\sim\!\sim \underset{*}{\overset{CH_3}{\overset{|}{C}}}H-OH$

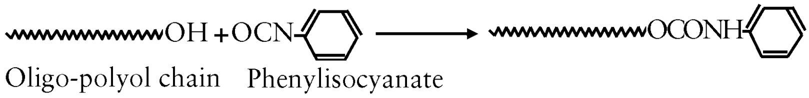
The ^{13}carbon NMR method is suitable for oligo-polyols with hydroxyl numbers in the range of 24-109 mg KOH/g and primary hydroxyl content in the range of 10-90% and has a lower precision than the ^{19}fluorine NMR method. In both NMR spectroscopic methods, the surface corresponding to the primary hydroxyls is divided by the sum of surfaces corresponding to primary + secondary hydroxyl groups and is expressed as a percentage. The integral curves assure a rapid calculation of surfaces and of the percentage of primary hydroxyls. Some examples of the hydroxyl content of oligo-polyols could be: polypropylene glycols and the triol homopolymers of propylene oxide which have practically only secondary hydroxyl groups (94-96%), the block copolymers propylene oxide – ethylene oxide, with terminal polyethylene epoxide block, which have both primary and secondary hydroxyl groups (30-85% primary hydroxyl groups) and polytetrahydrofuran and polyesters, based on diethylene glycols or polycaprolactone polyols which have 100% primary hydroxyls as terminal groups.

3.7 Reactivity

All the oligo-polyols are used to build the polyurethane high MW structure in a reactive process, as a consequence of the oligo-polyols terminal hydroxyl group reaction with polyisocyanates. The reactivity of oligo-polyols in polyurethane fabrication is a very important practical characteristic. Reactivity is a measure of the reaction rate of an oligo-polyol with an isocyanate in order to make the final polyurethane polymer. One practical method is the measurement of viscosity, in time, by Brookfield Viscosity Test (BVT), especially used to determine the reactivity of ethylene oxide capped polyether polyols. **Figure 3.12** shows the effect of the primary hydroxyl content upon the reactivity of ethylene-oxide capped polyether triols of MW of 5,000 daltons.

It is observed that the oligo-polyols with low reactivity (0% primary hydroxyl, i.e., having only secondary hydroxyls) have the lowest viscosity increase over time. By contrast, the very high reactivity polyols, having 85-100% primary hydroxyl content, have the highest viscosity increase over time. As a consequence, this method of evaluation of viscosity increase in time is a very simple and useful practical method to ascertain the reactivity of oligo-polyols.

A reliable method to determine the oligo-polyol reactivity is the study of the kinetics of the oligo-polyol's reaction with phenyl isocyanate, a model for the -NCO groups of toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI):



The advantage of using phenyl isocyanate is that it is possible to develop the reaction kinetics until 100% conversion, without gelation. Obviously the results are relative, but it is possible to determine the relative order of reactivity between two or three oligo-polyols [35].

Figure 3.13 shows the reaction kinetics curves (conversion against time) of the phenyl isocyanate reaction with oligo-polyols having various percentages of primary hydroxyls.

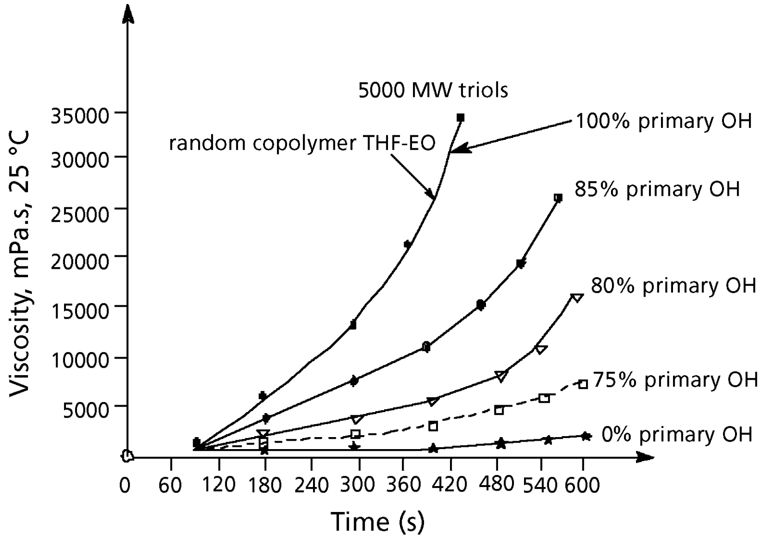


Figure 3.12 Effect of primary hydroxyl content on oligo-polyols reactivity. THF: tetrahydrofuran, EO: ethylene oxide

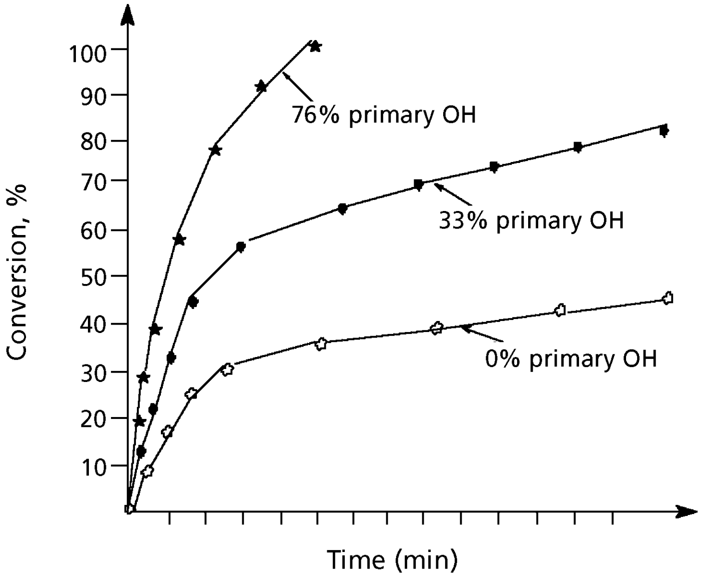


Figure 3.13 Kinetic curves of the phenyl isocyanate reaction with oligo-polyols having various primary hydroxyl contents. *[Phenyl isocyanate] = [OH] = 0.5 mol/l. Solvent: toluene; Catalyst: triethylamine; Temperature: 30 °C*

The marked increase of the reactivity with the primary hydroxyl content increase is obvious.

3.8 Specific Gravity

The specific gravity of oligo-polyols is determined by the classical method, using a pycnometer, at constant temperature (usually at 25 °C). The Standard Test Method for the specific gravity determination in polyols is ASTM D4669 [36].

3.9 Viscosity

The viscosity is an important characteristic of oligo-polyols [37]. A special characteristic of all oligo-polyols is the fact that practically all of them are liquid at room temperature or at low temperatures (40-60 °C). This fact is a really important technological advantage, because the high MW polyurethane polymer is obtained using only low viscosity or medium viscosity liquid intermediates, which are very easy to process. The viscosity gives an indication of the processability of an oligo-polyol.

The oligo-polyol's viscosity is determined using a Brookfield viscosimeter. The Standard Test Method for oligo-polyol viscosity determination is ASTM D4878 [37]. There are two test methods, A and B, applicable for viscosities between 0.01 to 1000 Pa-s, at 25 °C, or for solid polyols (such as polytetrahydrofuran), at 50 °C. Test method A is indicated for oligo-polyols of very high viscosities.

3.10 Colour

The Test Standard Method for oligo-polyol colour determination, Gardner and APHA colour, is ASTM D4890 [38]. Generally the APHA colour scale is used for very light coloured or colourless oligo-polyols, (e.g., high MW polyether polyols or polyester polyols). The Gardner colour scale is used for oligo-polyols having a more intensive colour, of yellow to brown colour (for example sucrose-based polyether polyols, *ortho*-toluene diamine based polyols). The light colour of oligo-polyols increases their commercial value and is an indication that the product was not degraded during the process of synthesis.

3.11 Acid Number

The reaction of an oligo-polyol with polyisocyanates is catalysed by tertiary amines. The presence of a residual acidity decreases the catalytic activity of the tertiary amines, by acid-base neutralisation. To avoid negatively affecting the reactivity in polyurethane synthesis it is very important to carefully control the acidity of oligo-polyols. Thus, the acid number is the amount of acidic groups in an oligo-polyol. The acid number is expressed as the number of miligrams of potassium hydroxide required to neutralise the acidity of one gram sample. Acid number is important to correct the value of hydroxyl number, in order to obtain the real value for OH# (for a good correction of the OH# value, the acid number is added to the determined value of OH#). Thus, for the majority of oligo-polyols, the maximum acidity accepted is around 0.05-0.1 mg KOH/g. For some polyols, such as polyester polyols or reactive flame retardants, the maximum acidity accepted is around 2 mg KOH/g. Acid number in polyols is determined according to ASTM D4662 [39].

To conclude, the common physico-chemical characteristics of oligo-polyols for polyurethanes determined by standard analytical methods are: hydroxyl number, hydroxyl percentage, primary hydroxyl content, molecular weight, equivalent weight, molecular weight distribution, viscosity, specific gravity, acidity and colour (See Chapters 3.1-3.11).

Of course, some oligo-polyols have specific and particular characteristics and these special characteristics will be presented in detail for each group of oligo-polyol. For example:

unsaturation and the content of ethylene oxide are characteristic for polyether polyols, and copolymers such as propylene oxide - ethylene oxide [39-43]. The phosphorus or bromine content is characteristic for reactive flame retardants, the aromaticity is characteristic for aromatic polyols.

Summarising, no matter what their chemical structure, oligo-polyols have some general and common characteristics such as:

- All oligo-polyols are low MW polymers, in the range characteristic for oligomers (MW < 10000 daltons).
- All oligo-polyols have terminal hydroxyl groups, being in fact telechelic, low MW polymers (hydroxyl terminated telechelic oligomers).
- All oligo-polyols have primary or secondary hydroxyl groups but not tertiary hydroxyl groups.
- All oligo-polyols have a functionality, a number of hydroxyl groups/mol, in the range 2-8 OH groups/mol.
- The transformation of all oligo-polyols in high MW polyurethane polymers is based on reactive processes, as a consequence of chemical reaction.
- All oligo-polyols are liquid at room temperature or at low temperatures (40-60 °C) and due to the low viscosities are very easy to process to high MW polyurethanes.
- All oligo-polyols are characterised by general and common physico-chemical characteristics (see Chapter 3), determined by common standard test methods.

As was mentioned previously, for practical reasons, the oligo-polyols are divided in the present book into two important groups: oligo-polyols for elastic polyurethanes and oligo-polyols for rigid polyurethanes.

The main oligo-polyol types described in detail in the present book are presented in **Table 3.2.**

Table 3.2 The main types of oligo-polyols

Oligo-polyols for elastic polyurethanes	**Oligo-polyols for rigid polyurethanes**
1. Polyalkylene oxide polyols (polyether polyols)	1. Polyether polyols
2. Polymer polyols (filled polyols)	2. Aminic polyols
3. Polytetrahydrofuran polyols	3. Polyols based on condensates
4. Polyester polyols	4. Polyester polyols
5. Polybutadiene polyols	5. Polyols from renewable resources
6. Acrylic polyols	6. Flame retardant polyols
7. Other oligo-polyols	7. New oligo-polyol structures
	8. Polyols by chemical recovery of polyurethane wastes

References

1. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, Chapter 6, p.1.

2. H.W. Bank and F.A. Stuber in *Reactive Polymers*, Ed., H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.107.

3. B.G. Hill, *Chemtech*, 1973, **10**, 613.

4. *Polyethers*, *Polyalkylene Oxides and Other Polyethers, Part I*, Ed., N.G. Gaylord, Interscience Publishers, New York, NY, USA, 1963.

5. J.H. Saunders and K.C. Frisch, *Polyurethanes: Chemistry and Technology, Part I*, Interscience Publishers, New York, NY, USA, 1962.

6. D.J. Sparow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.182.

7. F.E. Bailey, Jr., and J.V. Koleske, *Alkylene Oxides and Their Polymers*, Surfactant Science Series, Volume 35, Marcel Dekker, Inc., New York, NY, USA, 1991.

8. K. Schauerte, M. Dahm, W. Diller and K. Uhlig in *Polyurethane Handbook: Chemistry, Raw Materials, Processing, Application Properties*, Ed., H.Oertel, Hanser Verlag, New York, NY, USA, 1985, p.42.

9. Y.C. Yen, *Polyols from Ethylene Oxide and Propylene Oxide*, Process Economics Program Report No.45, Stanford Research Institute, Menlo Park, CA, USA, 1968.

10. Y.C.Yen and T.S. Tsao, *Polyols for Polyurethanes,* Process Economic Program Report No.45A, Stanford Research Institute, Menlo Park, CA, USA, 1982, p.119.

11. H.R. Friedly in *Reaction Polymers*, Eds., W.F. Gum, W. Riese and H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.66-91.

12. *Flexible Polyurethane Foams*, 2nd Edition, Eds., R. Herrington and K. Hock, Dow Chemical Company, Midland, MI, USA, 1997, Chapter 2, p.15.

13. M.A. Carey, S.L. Wellons and D.K. Elder, *Journal of Cellular Plastics*, 1984, **20**, 1, 42.

14. P.A. Turley and A. Pietrantonio, *Journal of Cellular Plastics*, 1984, **20**, 4, 274.

15. ASTM E222, *Standard Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation*, 2000.

16. ASTM D4274, *Standard Test Methods for Testing Polyurethane Raw Materials, Determination of Hydroxyl Numbers in Polyols*, 1999.

17. ASTM E1899, *Standard Test Method for Hydroxyl Groups Using Reaction with p-Toluenesulfonyl Isocyanate (TSI) and potentiometric titration with Tetrabutylammonium Hydroxide*, 2002.

18. ISO 14900, *Plastics - Polyols for use in the Production of Polyurethane - Determination of Hydroxyl Number*, 2001.

19. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, USA, 1983.

20. R.H. Carr, J. Hernalsteen and J. Devos, *Journal of Applied Polymer Science*, 1994, **52**, 8, 1015.

21. B.G. van Leuwen, D.G. Powell, J.E. Puig and F.S. Natoli in *Advances in Urethane Science and Technology*, Volume 2, Eds., K.C. Frisch and S.L. Reegen, Technomic Publishers, Westport, CT, USA, 1973, p.173.

22. J.G. Hendrickson, *Analytical Chemistry,* 1964, **36**, 1, 126.

23. ASTM D4672, *Standard Test Methods for Polyurethanes Raw Materials: Determination of Water Content in Polyols*, 2000.

24. ISO 14897, *Plastics - Polyols for use in the Production of Polyurethane - Determination of Water Content*, 2002.

25. J.G. Hanna and S. Siggia, *Journal of Polymer Science*, 1962, **56**, 164, 297.

26. W.B. Crummett, *Analytical Chemistry*, 1962, **34**, 9, 1147.

27. M.S. Budd, *Analytical Chemistry*, 1962, **34**, 10, 1343.

28. A. Mathias and N. Mellor, *Analytical Chemistry,* 1966, **38**, 3, 472.

29. S.L. Manatt, D.D. Lawson, J.D. Ingham, N.S. Rapp and J.P. Hardy, *Analytical Chemistry*, 1966, **38**, 8, 1063.

30. T. Groom, J.S. Babiec and B.G. van Lewen, *Journal of Cellular Plastics*, 1974, **10**, 1, 43.

31. D.A.R. Williams, R. Dyke, S. Malcomson and S. Massey, *Journal of Cellular Plastics*, 1983, **19**, 2, 121.

32. C.L. LeBas and P.A. Turley, *Journal of Cellular Plastics*, 1984, **20**, 3, 194.

33. J.R. Deily, *Journal of Cellular Plastics*, 1983, **19**, 2, 76.

34. ASTM D4273, *Standard Test Methods for Polyurethane Raw Materials: Determination of Primary Hydroxyl Content in Polyether Polyols*, 1999.

35. F. Stoenescu, M. Ionescu, V. Dumitriu and I. Mihalache, *Materiale Plastice,* 1981, **18**, 3, 155.

36. ASTM D4669, *Standard Test Method for Polyurethane Raw Materials: Determination of Specific Gravity of Polyols*, 2002.

37. ASTM D4878, *Standard Test Methods for Polyurethane Raw Materials: Determination of Viscosity of Polyols*, 2003.

38. ASTM D4890, *Standard Test Methods for Polyurethane Raw Materials: Determination of Gardner and APHA Color of Polyols*, 2003.

39. ASTM D4662, *Standard Methods for Polyurethane Raw Materials: Determination of Acid and Alkalinity Number of Polyols*, 2003.

40. M. Noshiro, Y. Jitsugiri, S. Kozawa and T. Shimada in *International Progress in Urethanes*, Volume 5, Eds., F. Ashida and K.C. Frisch, Technomic Publishers, Lancaster, PA, USA, 1988, p.28.

41. G. Wegener, M. Brandt, L. Duda, J. Hofmann, B. Klesczewski, D. Koch, R-J. Kumpf, H. Orzesek, H-G. Pirkl, C. Six, C. Steinlein and M. Weisbeck, *Applied Catalysis*, 2001, **221**, 1-2, 303.

42. F. Heatley, J. Ding, G. Yu and C. Booth, *Die Makromoleculare Chemie: Rapid Communications*, 1993, **14**, 12, 819.

43. G-E. Yu, A.J. Masters, F. Heatley, C. Booth and T.G. Blease, *Die Makromoleculare Chemie,* 1994, **195**, 5, 1517.

4 Oligo-Polyols for Elastic Polyurethanes

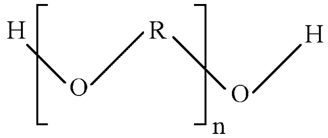
The oligo-polyols for elastic polyurethanes (PU) are characterised by a high molecular weight (MW), usually situated in the range of 2000-6500 daltons, and by a low functionality, of around 2-3 hydroxyl groups/mol. The high elasticity is given firstly by the high mobility of the oligo-polyol chains, which permits free rotation around the bonds of the main chain and, as general rule, these polymers have a low value for the glass transition temperature (T_g) in the range of –50 °C to – 86 °C. At room temperature, the oligo-polyols for elastic PU are situated in the highly elastic domain and conserve this important characteristic at lower temperatures (of course at negative temperatures higher than T_g). It is clear that the high elasticity of the resulting polyurethanes is given by the high MW and high mobility oligo-polyol segment and due to the low crosslink density, as a consequence of the low functionality of the oligo-polyols.

4.1. Polyalkylene Oxide Polyether Polyols [1-16]

The polyether polyols for elastic polyurethanes are low MW polymers, with terminal hydroxyl groups, characterised by the following general repeating unit (see **Figure 4.1**).

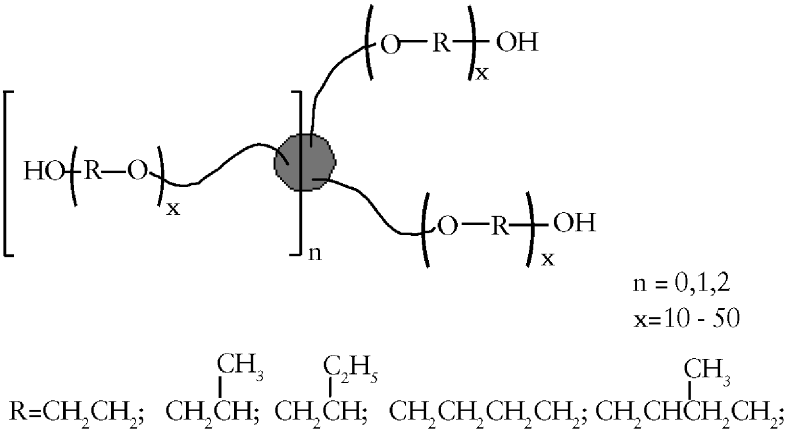
Because the functionality of an oligo-polyol for elastic polyurethane is 2-3 hydroxyl groups/mol, the general formula shown in **Figure 4.1** becomes the formula shown in **Figure 4.2**.

Polyalkylene oxide polyether polyols are the most important group of polyols for PU, representing around 80% of the total oligo-polyols production. The general formula of a polyalkylene oxide polyether polyol is presented in **Figure 4.3**.



R = alkyl group

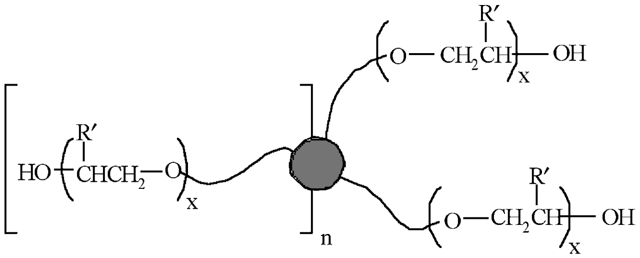
Figure 4.1



n = 0,1,2
x=10 - 50

$$R{=}CH_2CH_2;\ CH_2\overset{CH_3}{\overset{|}{C}}H;\ CH_2\overset{C_2H_5}{\overset{|}{C}}H;\ CH_2CH_2CH_2CH_2;\ CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2;$$

Figure 4.2

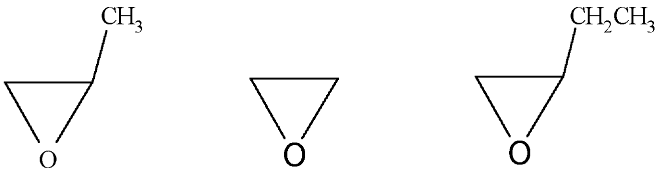


n = 0,1,2
x = 17 - 50

R′ = H, CH_3 , C_2H_5

Figure 4.3

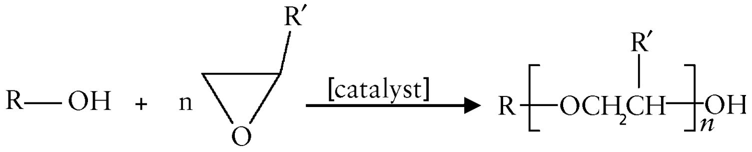
The polyalkylene oxide polyols are obtained by the polymerisation of alkylene oxides, initiated by different polyols called starters or chain initiators. The most important alkylene oxides (oxiranes or epoxides) used in oligo-polyols synthesis are propylene oxide (PO), ethylene oxide (EO) and butylene oxide (BO) (see **Figure 4.4**).



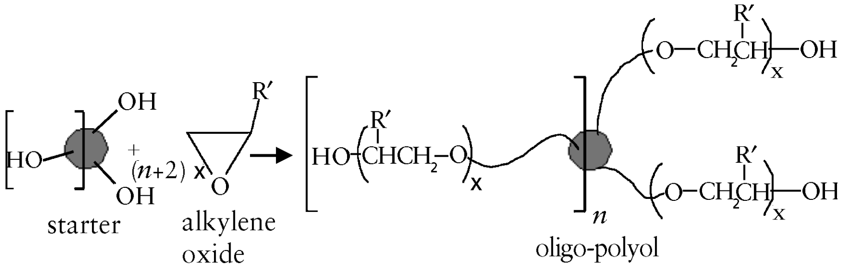
Propylene oxide (PO) Ethylene oxide (EO) Butylene oxide (BO)

Figure 4.4

The general polymerisation reaction of an alkylene oxide initiated by one hydroxyl group is:



The general polymerisation of an alkylene oxide, initiated by a polyfunctional starter, is:



The starter used in the synthesis of oligo-polyols for elastic PU usually has 2-3 hydroxyl groups/mol. Starters with a functionality of 4 hydroxyl groups/mol are seldom used. Starters having 5-8 hydroxyl groups/mol (for example, for high load bearing flexible foams used in carpet underlay) are used to a small extent, and only for special applications.

The starters used frequently in the synthesis of oligo-polyols for elastic PU and some important characteristics of these starters for PU chemistry are presented in **Table 4.1**.

The catalysts used for alkylene oxide polymerisation, initiated by hydroxyl groups, are:

- *Anionic catalysts:*

NaOH, KOH, CsOH, $Sr(OH)_2$, $Ba(OH)_2$, [17-29, 60, 69, 32, 33], calcium naphthenates, calcium octanoates, phosphazenium compounds [34-38].

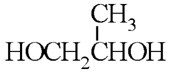
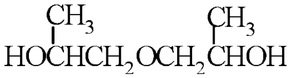
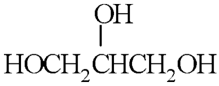
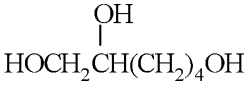
- *Cationic catalysts:*

Lewis acids and Brönstedt superacids such as BF_3, PF_5, SbF_5, HPF_6, HBF_4, $HSbF_6$, CF_3SO_3H (triflic acid), $Al(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, $Nd(CF_3SO_3)_3$ [39-41].

- *Co-ordinative catalysts:*

Aluminium and zinc alkyls and alcoholates [$Al(OR)_3$, $Zn(OR)_2$], aluminium and zinc tetraphenyl porphirinates [43-47], titanium alcoholates [$Ti(OR)_4$], dimetallic catalysts (DMC) based on $Zn_3[Co(CN)_6]_3$ [48].

Table 4.1 The most important starters used for the synthesis of oligo-polyols for elastic PU

Starter	f	Structure	Molecular weight (daltons)	Hydroxyl number (mg KOH/g)
Water	2	HOH	18	6233.3
Ethylene glycol	2	$HOCH_2CH_2OH$	62	1807.9
Diethylene glycol	2	$HOCH_2CH_2OCH_2CH_2OH$	106	1057.4
1,2 Propylene glycol	2	 $\mathrm{HOCH_2\overset{CH_3}{C}HOH}$	76.1	1474.6
Dipropylene glycol (DPG)	2	 $\mathrm{HO\overset{CH_3}{C}HCH_2OCH_2\overset{CH_3}{C}HOH}$	134.2	836.3
Glycerine	3	 $\mathrm{HOCH_2\overset{OH}{C}HCH_2OH}$	92	1829
Trimethylol propane	3	$CH_3CH_2C(CH_2OH)_3$	134.2	1254.1
1,2,6 Hexanetriol	3	 $\mathrm{HOCH_2\overset{OH}{C}H(CH_2)_4OH}$	134	1255
Triethanolamine	3	$N(CH_2CH_2OH)_3$	146	1152.7
Ethylenediamine	4	$H_2NCH_2CH_2NH_2$	60	3740
Pentaerythritol	4	$C(CH_2OH)_4$	136.15	1648.18

The most important catalyst used industrially for the synthesis of high MW polyethers is potassium hydroxide (KOH) [1-14, 17, 49-53]. The second catalyst group is the group of dimetallic catalysts based on a nonstoichiometric complex of $Zn_3[Co(CN)_6]_3{*}ZnCl_2$ (DMC) with various ligands. DMC catalysts are the highest performance catalysts known at this time for PO polymerisation, being around 1000 times more active than potassium hydroxide (see Chapter 4.9).

Unfortunately, DMC catalysts are not efficient for EO polymerisation, and it is practically impossible to obtain PO-EO block copolymers with this catalyst. Acidic catalysts are not used on an industrial scale for alkylene oxide polymerisation due to the formation of substantial amounts of cyclic ethers as side products. Acidic catalysts are used industrially only for the synthesis of polytetrahydrofuran polyols or, to a lesser extent, for tetrahydrofuran - alkylene oxide copolyether polyol fabrication (see Sections 7.1, 7.2 and 7.3) Other catalysts have a minor importance for large scale polyether polyol production.

Some of the other catalysts are excellent hydroxyl group alkoxylation catalysts but are very expensive, for example, polyphosphazenium catalysts [34-38], aluminium tetraphenyl porphine [42-47] and caesium hydroxide [18-24, 48].

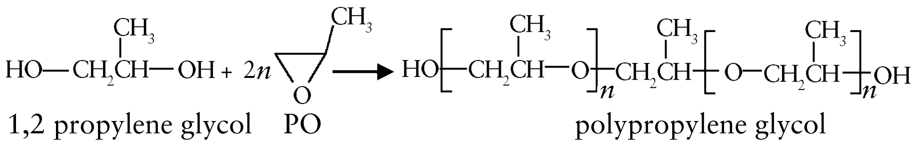
Catalysts for the polymerisation of alkylene oxides initiated by hydroxyl groups must have some general and very important qualities:

a) They are not destroyed by the presence of hydroxyl groups and are active in the presence of a large excess of hydroxyl groups. Some catalysts, such as aluminium or zinc alkyls, or methyl aluminoxanes, do not resist hydroxyl groups. Some catalysts are very efficient in the presence of monomer and nonprotic solvents, such as: µ-oxo-alkoxides [16] or Vandenberg catalysts (triisobutylaluminium - water - acetyl acetone) [16], but become totally inefficient in the presence of a large excess of hydroxyl groups.

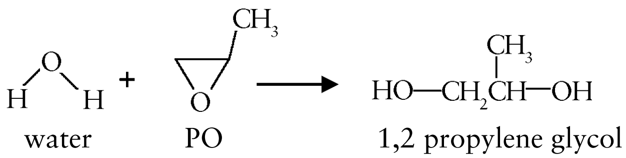
b) The resulting active centre (generally of the alcoholate type) rapidly reaches equilibrium with all the hydroxyl groups existing in the reaction system, and each hydroxyl group becoming a chain initiator.

c) They do not develop undesired side reactions, such as isomerisation, formation of cyclic oligomers and so on.

The polymerisation reaction of PO, initiated by a bifunctional starter such as 1,2 propyleneglycol, leads to the formation of polyether diols, each hydroxyl group generating a polyetheric chain, terminated by a hydroxyl group [1-13]:



Water is a difunctional starter. Thus, by the reaction of water with PO in the first step, 1,2 propylene glycol is formed by hydrolysis of the oxiranic ring. In the second step, the PO polymerisation is initiated by the 1,2 propylene glycol formed *in situ* [1-13]:



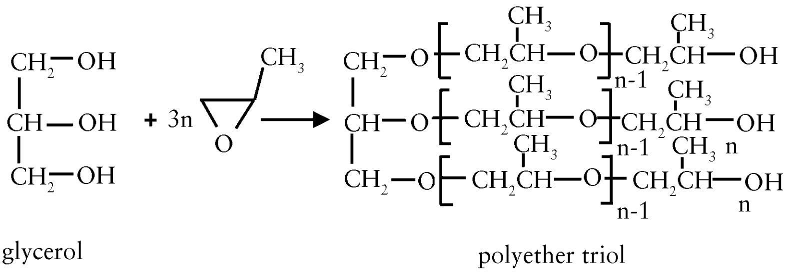
The presence of water in starters or in monomers (PO, EO or BO) always leads to polyether diols. The control of water content in the raw materials, used for polyether polyol synthesis, has a great practical importance for two reasons:

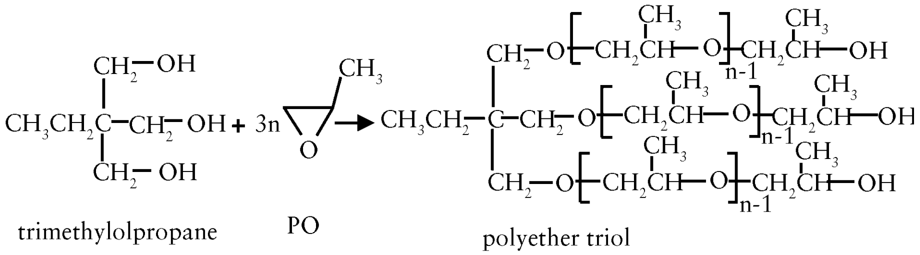
a) The presence of water decreases the functionality of the resultant polyether polyol in the case of polyols with a functionality higher than f = 2 , for example polyether triols;

b) It is impossible to obtain high MW polyethers (polyethers of low hydroxyl number) if the water content in monomers is high (water content > 0.05-0.1%). High MW diols (3000-4000 daltons) and high MW triols (5000-6500 daltons) can be synthesised only when the water content in oxiranic monomers is lower than 0.01%.

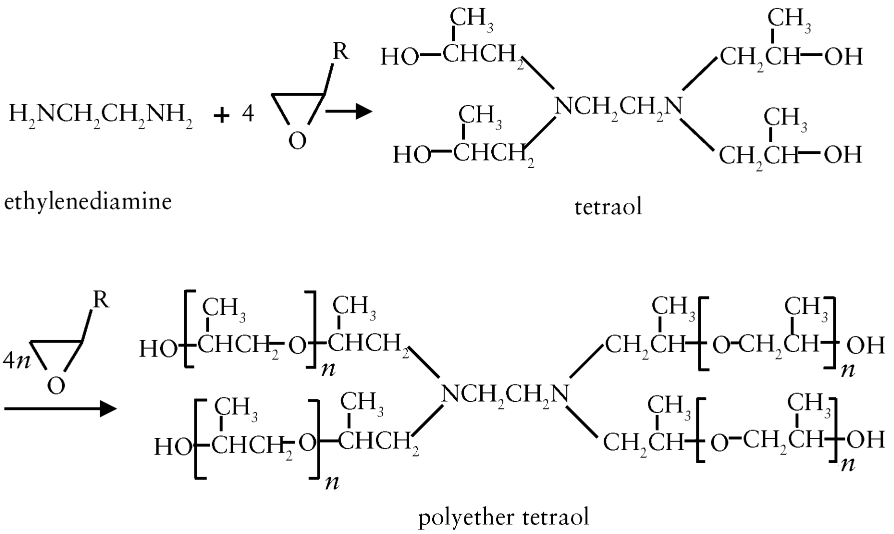
This behaviour is a consequence of the extremely high hydroxyl number of water (OH# = 6233.3 mg KOH/g). At higher levels of water, there is a tendency for the hydroxyl number of monomers to increase – it is practically impossible to obtain polyethers with low hydroxyl numbers such as 25-36 mg KOH/g. For higher MW polyethers, the ratio of monomers:starter is high and the cumulative quantity of water introduced into the reaction with monomers is high.

If trifunctional initiators such as glycerol or trimethylolpropane are used as starters for the alkylene oxides polymerisation, star-like polyether triols are formed [1-13, 15-17, 54, 60, 69, 75]:





Tetrafunctional starters (such as pentaerythritol and ethylene diamine) are used to a small extent for the synthesis of high MW polyethers. An interesting tetrafunctional starter is ethylene diamine. In the first step the alkylene oxide reacts with the -N-H groups forming a tetraol. By the polymerisation reaction of alkylene oxides initiated by the tetraol formed *in situ*, a high MW polyether tetraol is obtained:



By using two oxiranic monomers, such as PO and EO, it is possible to obtain a great variety of polyether polyols: homopolymers of PO, block copolymers PO-EO (with terminal or internal poly[EO] block) or random copolymers (heteropolyethers) of PO-EO, diols or triols of different MW.

Figure 4.5 shows some structural possibilities for polyether diols and polyether triols [1-13].

The polyether diols are used especially for PU elastomers, coatings adhesives and sealants.

The polyether triols are the most important class of polyether polyols and they are used in flexible PU foam fabrication. The majority of polyether triols used in flexible foams are copolymers of PO-EO. Random copolymers are used in continuous slabstock flexible foams and block copolymers (PO-EO), with terminal poly[EO] block, are used in moulded foams (hot moulding and cold cure moulding processes).

Tetraol or higher functionality polyether polyols are used to a lesser extent in flexible foams, especially when a high compression strength is required (for example in carpet underlay).

The high MW polyether triols, copolymers of PO-EO are the most important oligo-polyols for PU, having the biggest volume of industrial production. This is the reason why the synthesis of polyether triols, by polymerisation of PO and/or EO and initiated by glycerol, will be presented in detail.

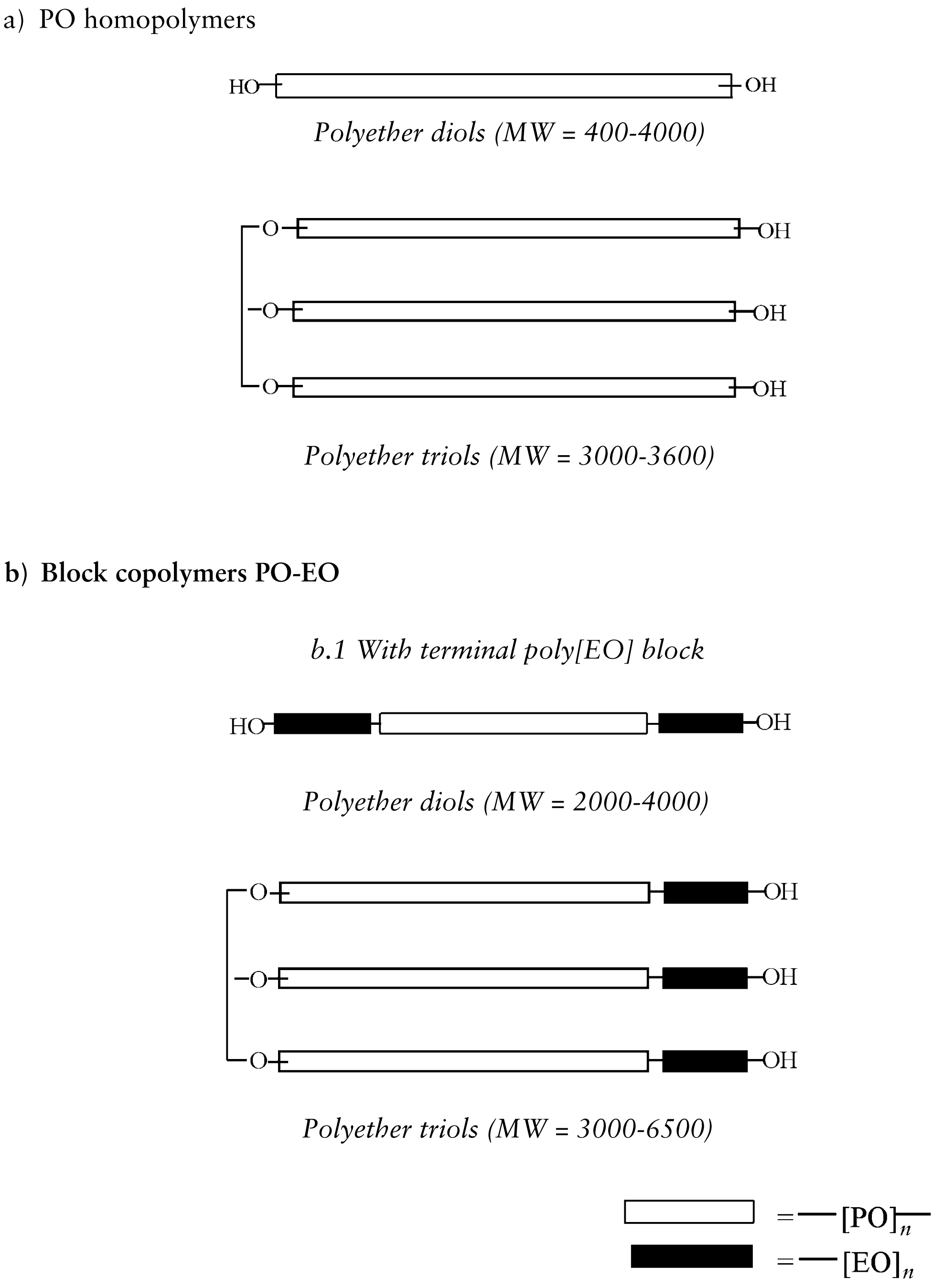
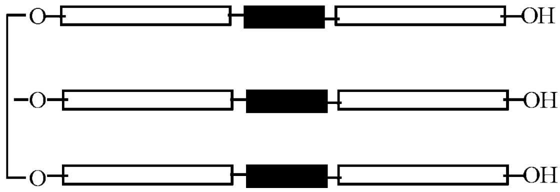


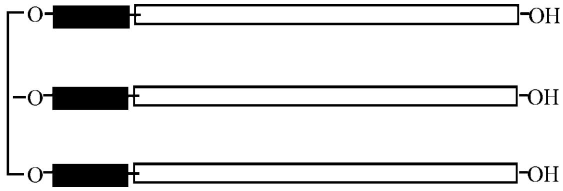
Figure 4.5 Various structures of polyether diols and triols

b.2 Block copolymers PO-EO with internal poly [EO] block

Polyether diols (MW = 2000-4000)



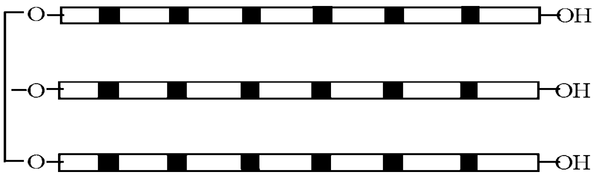
Polyether triols (MW = 3000-3600)



Polyether triols with poly[EO] block linked to the starter (MW = 3000-3600)

c) Random copolymers PO-EO (heteropolyethers polyols)

Polyether diols PO-EO random copolymers (MW = 2000-4000)



Polyether triols PO-EO random copolymers (MW = 3000-4000)

Figure 4.5 Continued ...

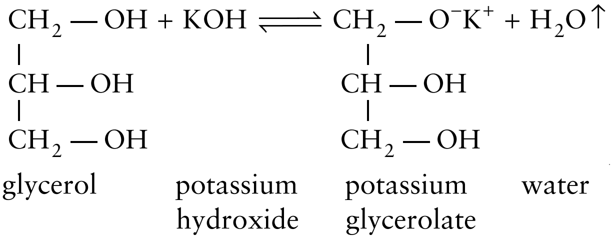
4.1.1 Synthesis of Polyether Triols Based on Glycerol Homopolymers of PO

The PO homopolymers (MW of 3000) initiated by glycerol are some of the most popular polyols for flexible PO slabstock. This structure is one of the oldest structures of a polyether used for flexible PU foams. In essence these polyether triols are obtained by the anionic polymerisation of PO initiated by glycerol and catalysed by KOH.

Between KOH and the hydroxyl groups there is a well known equilibrium reaction, with the formation of a potassium alcoholate and water [2, 4, 9-14, 49, 50, 52-54, 56-61]:

$$\underset{\text{hydroxyl}}{R\quad OH} + \underset{\substack{\text{potassium}\\\text{hydroxide}}}{KOH} \rightleftharpoons \underset{\substack{\text{potassium}\\\text{alcoholate}}}{RO^-K^+} + \underset{\text{water}}{H_2O}$$

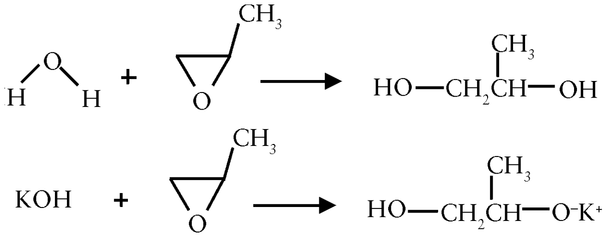
In the case of glycerol, potassium glycerolate and water are formed:



$$\begin{array}{llll} CH_2-OH + KOH & \rightleftharpoons & CH_2-O^-K^+ + H_2O\uparrow & \\ | & & | & \\ CH-OH & & CH-OH & \\ | & & | & \\ CH_2-OH & & CH_2-OH & \\ \text{glycerol} \quad \text{potassium hydroxide} & & \text{potassium glycerolate} & \text{water} \end{array} \qquad (4.1)$$

The equilibrium (4.1) is shifted right, towards the formation of potassium glycerolate, by distillation of the resulting water under vacuum, at 100-130 °C . A solution of potassium glycerolate in glycerol is formed.

Both KOH and water present in glycerol are sources of polyether diols which decrease the functionality of the polyether triol [2-13]:

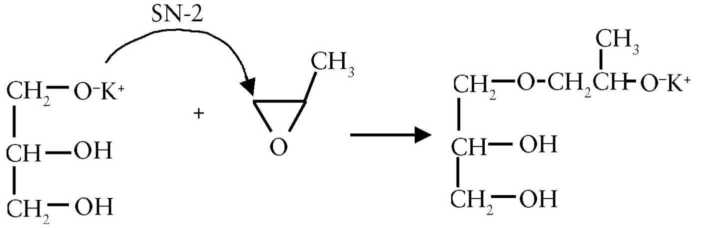


Thus, in order to obtain maximum functionality, the water resulting from reaction 4.1 must to be eliminated until the level of water is around 0.1%. For many industrial applications, water in the starter up to a maximum of 0.1-0.5% is accepted. Higher functionalities of polyethers lead to higher compression strengths of the resulting flexible PU foams.

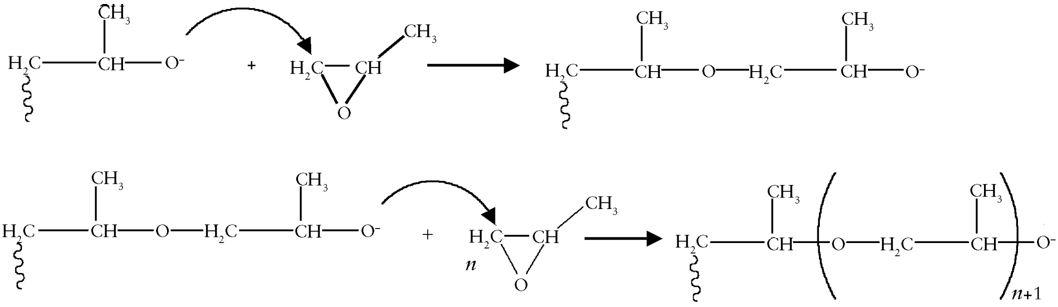
Polyether diols present in the mixture with polyether triols lead to an improvement of elongation and tensile strength, with a little sacrifice of the compression strength.

4.1.1.1 Anionic PO Polymerisation Reaction Initiated by Glycerol

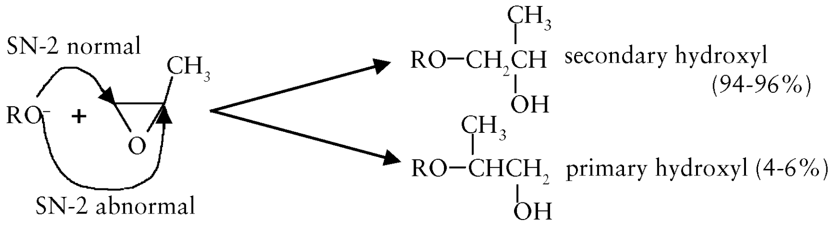
A PO polymerisation reaction initiated by glycerol hydroxyl groups is in fact a repeated second order nucleophilic substitution (SN-2 type) by the attack of the strongly nucleophilic alcoholate group on the carbon atoms of the oxiranic ring [1-15, 17, 49-54, 56-73]:



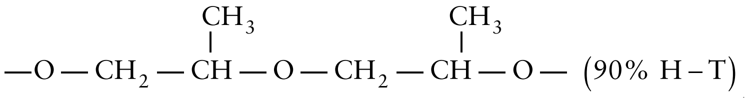
One observes that by ring opening the oxiranic cycle, an alcoholate group is formed too. These alcoholate groups again attack the oxiranic ring of other PO molecules, the chain is extended with new PO units, and the resultant chain end has the same catalytically active potassium alcoholate group. The MW increases stepwise during the polymerisation reaction, as a function of the ratio of PO quantity reacted/quantity of glycerol:



The SN-2 attack of the alcoholate anion take place preferentially at the α-carbon atom of the oxiranic ring (normal SN-2 attack), which is explained by the low steric hindrance of this atom and by the electron release effect of the methyl group, which increases the electron density at the carbon atom in the β position [2, 4, 5, 9-14, 17, 49-54]. An high electron density carbon atom is less susceptible to the attack of the anions. As an immediate consequence, the terminal hydroxyl groups are predominantly secondary, thus proving that this is a predominantly normal SN-2 attack [4, 74]:

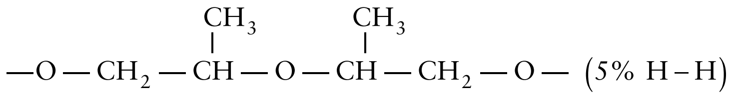


One can consider the anionic polymerisation of PO as a regiospecific polymerisation, because, due to the preferential attack of the α-carbon oxiranic ring atom, the microstructure of the chain is predominantly head-to-tail (H-T) type [4, 69, 74]:

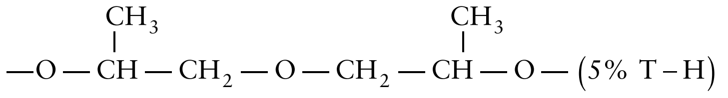


$$-O-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-O-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-O-\quad (90\%\ H-T)$$

^1H NMR and ^{13}C NMR studies have proved that the polypropyleneoxide obtained by PO anionic polymerisation have to a lesser extent head-to-head (H-H, around 5%) and T-H (around 5%), microstructures [72]:



$$-O-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-O-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-O-\quad (5\%\ H-H)$$

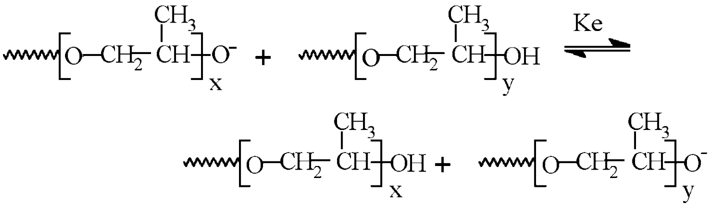


$$-O-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-O-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-O-\quad (5\%\ T-H)$$

Due to the high ring strain energy of the oxiranic ring, the polymerisation of PO and EO is strongly exothermic. Thus, the heat of PO polymerisation is 1500 kJ/kg [4-6, 9, 12] and of EO polymerisation is higher, 2100 kJ/kg [4-6, 9, 12].

4.1.1.2 Transfer Reactions in Anionic Polymerisation of Alkyleneoxides [2-14, 49-51, 53, 54, 60, 69, 73, 75-78]

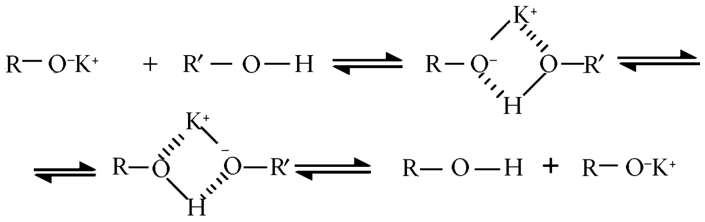
In the anionic polymerisation of alkyleneoxides, initiated by hydroxyl groups, transfer reactions occur. The first important transfer reaction is the equilibrium reaction of alcohol - alcoholate (4.2). This equilibrium means that each hydroxyl group from the reaction system is a chain initiator group, of equal probability.



$$\sim\!\left[O-CH_2-\overset{\overset{\large CH_3}{|}}{CH}\right]_x\!-O^- + \sim\!\left[O-CH_2-\overset{\overset{\large CH_3}{|}}{CH}\right]_y\!-OH \xrightleftharpoons{Ke} \sim\!\left[O-CH_2-\overset{\overset{\large CH_3}{|}}{CH}\right]_x\!-OH + \sim\!\left[O-CH_2-\overset{\overset{\large CH_3}{|}}{CH}\right]_y\!-O^-$$

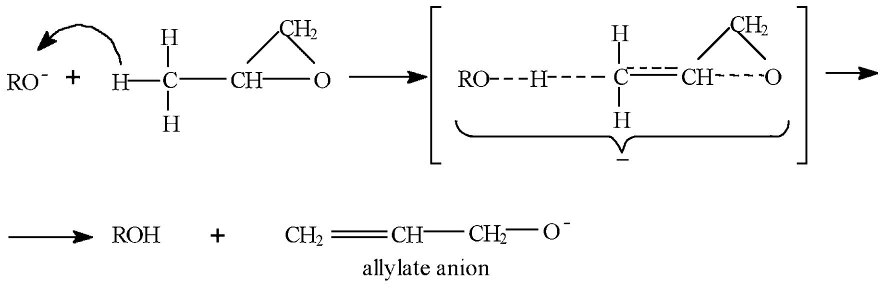
(4.2)

The equilibrium takes place by a quadricentric intermediary state, which is in fact a complex alcohol - alcoholate [5, 69, 79]:



This rapid equilibrium is the reason why the polyalkyleneoxides obtained by anionic polymerisation have a narrow molecular weight distribution (MWD). Another reason for the narrow MWD is the difference in reactivity of the active growing alcoholate species. Weybull and Nicander [80, 81] proved that lower MW species are more reactive than the higher MW species, react preferentially and narrow the MWD.

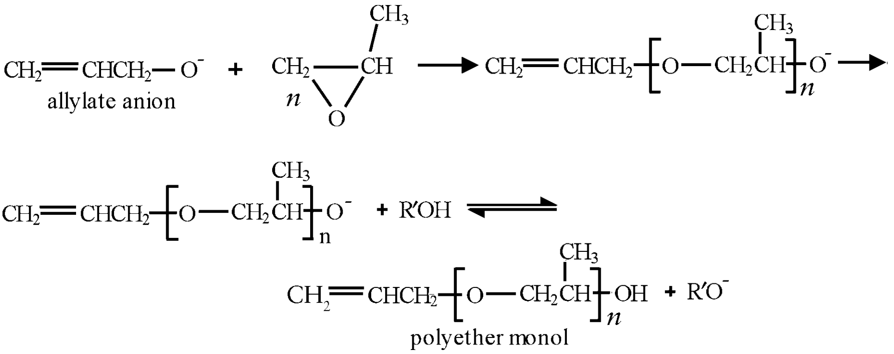
The second important transfer reaction, characteristic of PO anionic polymerisation, is the transfer with the monomer, which is in fact an E-2 elimination reaction (4.3). This reaction is based on the abstraction of a hydrogen atom from the methyl group of PO, which due to the neighbouring oxiranic ring has an acidity, but of course a very low acidity [2-14, 49-51, 53, 54, 60, 69, 73, 75-78]:



(4.3)

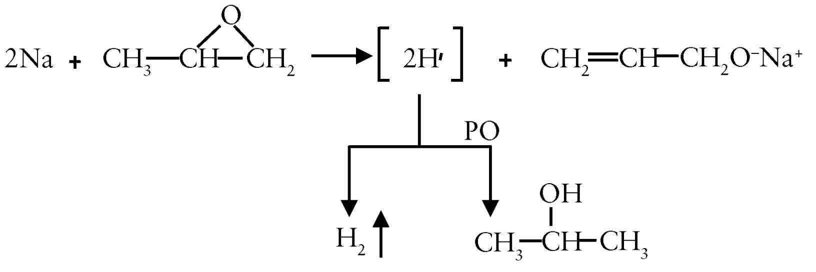
The resulting potassium allylate (the potassium alcoholate of allylic alcohol), initiates the anionic polymerisation of PO, with the formation of undesired polyether monols

(allyl alcohol having only one hydroxyl group is monofunctional). The resulting polyether monols have a terminal double bond and of course only one hydroxyl group:

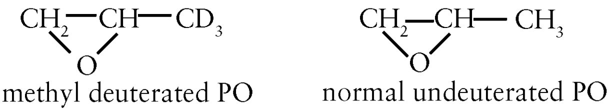


The fact that the transfer reaction takes place at the methyl group was proved directly by two experiments:

a) By the addition of metallic sodium to anhydrous PO, hydrogen was liberated, proving that the methyl group has acidity [77]:



b) The isotopic effect, PO having completely deuterated methyl groups, would give unsaturated bonds three times lower than the normal undeuterated PO [77]:



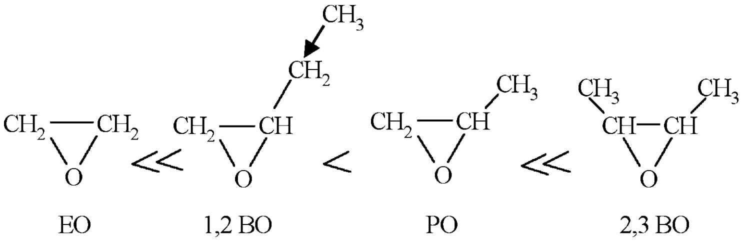
$$\frac{K_D}{K_H} \sim 3$$

K_D = rate of constant of rearrangement to allyl alcohol of methyl deuterated PO

K_H = rate constant of rearrangement to allyl alcohol of normal undeuterated PO

This side reaction of hydrogen abstraction from the monomer is impossible to avoid in anionic polymerisation of PO, but it is possible to minimise it. The formation of double bonds as a consequence of the transfer reaction with the monomer is more significant at higher polymerisation temperatures, with higher MW polyethers [2-5, 51, 124-126], with reactors with higher metallic surfaces [124] and, to a much lesser extent, at high catalyst concentrations [2-5, 51, 124-126].

EO, due to the absence of acidic methyl groups, doesn't give transfer reactions. It is very interesting that 1,2 butylene oxide gives the transfer reaction with the monomer, but only to a very low extent when compared with PO [82, 83]. The explanation of this behaviour is the decrease of the acidity of the hydrogen atoms linked to the carbon atom neighbouring the oxiranic ring, due to the electron release of the methyl group of the ethyl substituent. On the other hand, the isomeric 2,3 dimethyl oxirane (2,3 butylene oxide), because of the presence of two methyl groups linked to the oxiranic ring, has the highest unsaturation in anionic polymerisation (the highest transfer rate). The relative order concerning the capability of various oxiranes to develop the rearrangement reactions as a consequence of the transfer of the monomers is:



Due to these effects, the random copolymers EO - 1,2 BO have a very low unsaturation [82, 83]. For random copolymers of PO-EO, the unsaturation is much lower than for PO homopolymers because of the inability of EO to isomerise unsaturated compounds.

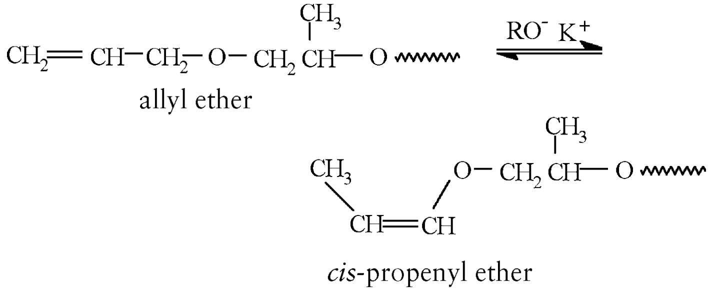
The rearrangement of PO to allyl alcohol in anionic polymerisation depends strongly on the nature of the alcoholate cation. The relative order of alcoholate reactivity in the transfer reaction with the monomer [9, 18-29, 48, 84, 85] is:

Li >> Na > K > Rb > Cs > Ca > Ba

Thus, with CsOH as catalyst instead of KOH, PO-based polyethers with very low unsaturation are obtained [18-24, 47, 79, 83-85], the maximum MW possible being 8000 daltons (as compared with a MW of 6500 daltons, which is the maximum MW it is possible to obtain in the presence of KOH). Very low unsaturations are obtained using strontium and barium hydroxides, and alkoxides as catalysts for PO anionic polymerisation [25-29, 79].

It is very interesting that in the presence of potassium alcoholates, the allyl ethers develop a rearrangement reaction (reaction 4.4) to propenyl ether [60, 77, 78], *cis*-propenyl ether type [77, 78] or a mixture of *cis*-and *trans*-propenyl ethers [88].

The formation of *cis*-propenyl ether is probably a consequence of a cyclic intermediary structure. The formation of *trans*-propenyl ether is probably a consequence of free rotation of bonds in the transition state. The rate of the transformation of allyl ether groups in propenyl ether groups is higher at higher temperatures (150-160 °C). This rearrangement of ally ethers to propenyl ether groups is catalysed not only by alkaline alcoholates [60, 77, 78] but also by some complex compounds of ruthenium (such as ruthenium dichloride-triphenylphosphine complex [89]):



$$CH_2{=}CH{-}CH_2{-}O{-}CH_2\overset{CH_3}{\overset{|}{C}H}{-}O\sim\sim \xrightleftharpoons{RO^- K^+} CH_3{-}CH{=}CH{-}O{-}CH_2\overset{CH_3}{\overset{|}{C}H}{-}O\sim\sim$$

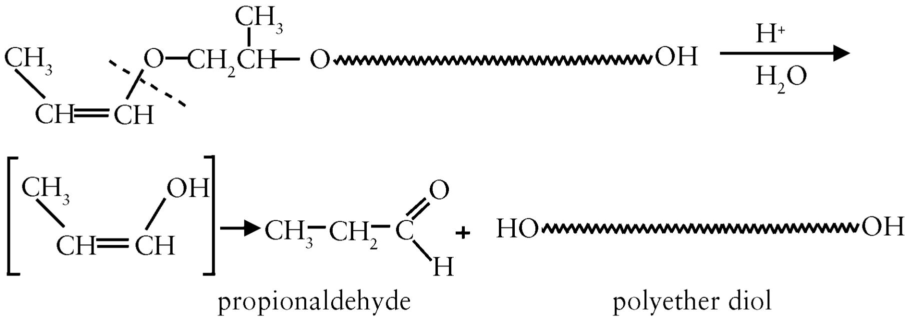
(4.4)

The nature of the alkali metal cation of the alcoholate group has a strong influence on the rate of isomerisation of allyl ether to propenyl ether, with reactivity in the following order [78]:

Li <<< Na << K << Rb < Cs

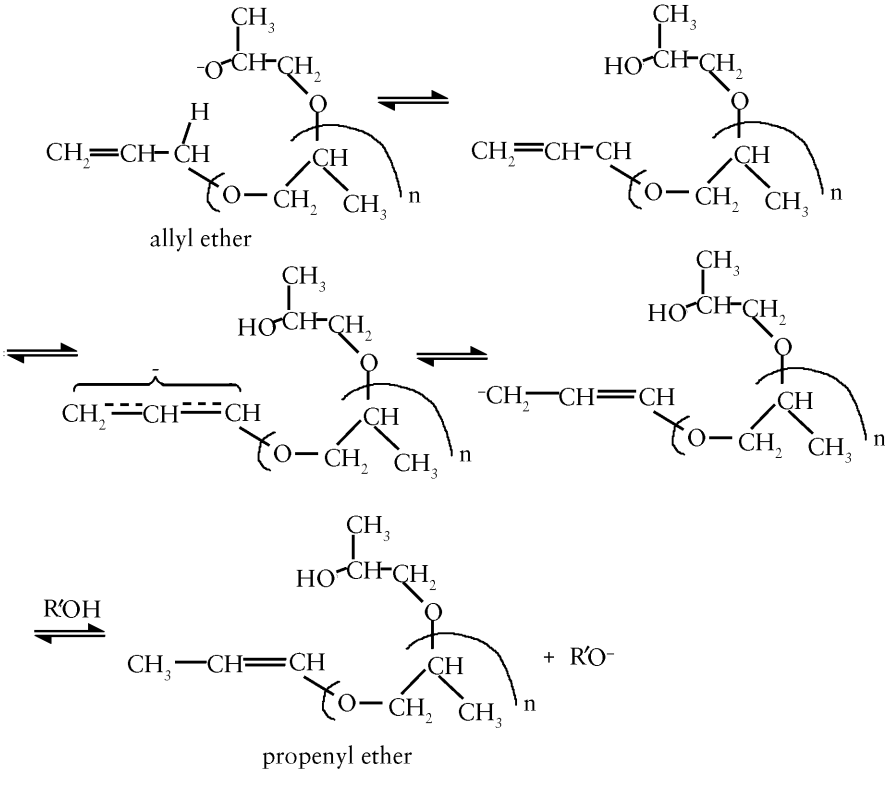
This relative order is exactly the same as the order of the dissociation degree of the resulting alkaline alcoholate. At lower dissociation degree (Li), the rate of rearrangement is very low, while at high dissociation degree (Rb or Cs), maximum reaction rates are obtained. Usually, caesium alcoholates give allyl ether to propenyl ether isomerisation rates of around 150-300 times higher compared to potassium alcoholates. In normal industrial PO anionic polymerisation conditions, the propenyl ether groups represent around 20-27% from total unsaturation. The ratio between allyl ether and propenyl ether groups is determined by IR [77], ^{1}H NMR and ^{13}C NMR techniques [54, 60, 69, 88].

This transformation of allyl ether terminal groups to propenyl ether terminal groups is very important in practice because during the purification step (the elimination of potassium ion), the propenyl ether is hydrolysed by the acids used for purification to propionaldehyde and a polyether diol [76, 90]:



This acidic treatment decreases markedly the PO-based polyether unsaturation, and the undesired monols are transformed into polyether diols.

The mechanism of the rearrangement of allyl-ether groups to propenyl-ether groups catalysed by alkaline alcoholates is [78]:



The kinetics of this rearrangement is described by the following simple second order law:

$$-\frac{d[\text{allyl}]}{dt} = K_r[\text{allyl}][\text{ROK}]$$

where:

[allyl] = concentration of terminal allyl groups;

[ROK] = concentration of potassium alcoholate;

K_r = second order reaction constant

The rearrangement rate constant of transformation of allyl ether to propenyl ether depends strongly on the polymerisation temperature [60]. For example at 90 °C, $K_r = 0.572 \times 10^{-5}$ l/mol/s, while at 130 °C it is much higher - $K_r = 28.1 \times 10^{-5}$ l/mol/s [60].

We can conclude that the polyether triols obtained by anionic polymerisation of PO initiated by glycerol consist of four polymeric species:

a) Polyether triols (resulting from the reaction of PO with glycerol).

b) Polyether diols (resulting from the reaction of PO with water from raw materials).

c) Polyether monols (allyl ether type, by PO rearrangement).

d) Polyether monols (propenyl ether type, by the rearrangement of allyl ether monols).

The polyethers obtained by the anionic polymerisation of PO initiated by glycerol are not trifunctional, having a lower functionality than 3, but usually in the range 2 < f < 3. The diols and monols decrease the functionality. The functionality is lower for high MW polyethers and for the polyethers obtained at higher polymerisation temperatures. In **Figure 4.6**, one observes the strong polyether triol functionality decrease as the polyether MW increases.

The polyether triol functionality as function of unsaturation and of diol content can be calculated using the following formula:

$$\text{Functionality} = \frac{(\%\ \text{OH})/1.7}{\text{unsaturation} + \dfrac{[(\%\text{OH})/1.7] - \text{unsaturation}}{\dfrac{\text{nominal}}{\text{functionality}} - \text{mol\% diol}}} \left(\text{OH groups/mol}\right)$$

where:

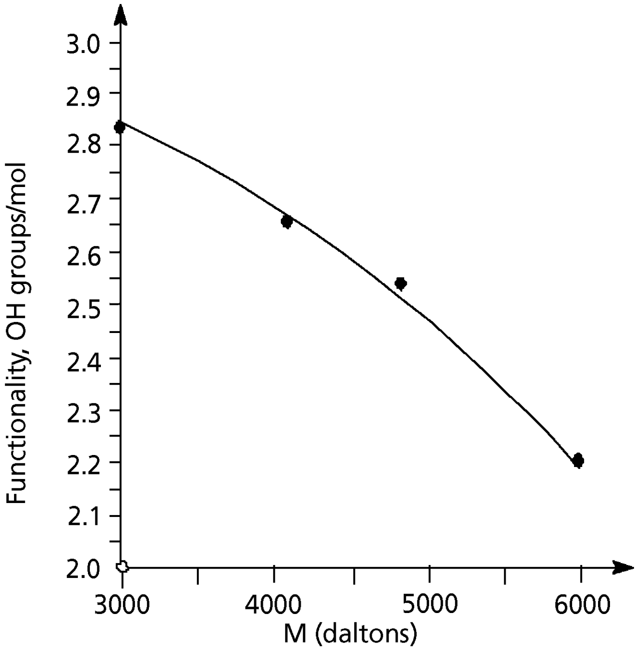


Figure 4.6 The real functionality of polyether triols, PO homopolymers, as function of the polyether MW

unsaturation is expressed in mequiv/g,

nominal functionality: f = 3, and

mol% diol is based on the total water content of raw materials.

Other formulas were deduced for the equivalent functionality of flexible triols.

Thus it is well known that the functionality of a system is defined as the total number of hydroxyl groups divided by the total number of molecules:

$$fe = \frac{\text{total number of hydroxyl groups}}{\text{total number of molecules}} \left(\text{OH groups/mol}\right)$$

In a polyether triol composition the following are present:

n_1 = mols of monols, of functionality $f_1 = 1$

n_2 = mols of diols, of functionality $f_2 = 2$

n_3 = mols of triols, of functionality $f_3 = 3$

The average functionality fe of a polyether triol is:

$$fe = \frac{(n_1 \times 1) + (n_2 \times 2) + (n_3 \times 3)}{n_1 + n_2 + n_3}$$

The average functionality of a polyether triol can be calculated with the following formula (deduced from the previous formula) [48]:

$$fe = \frac{OH\#/56.1}{\left[OH\#/56.1 - DB\right] \times (1/fn) + DB}$$

OH# = hydroxyl number of the polyol;

fn = nominal functionality of triol (fn = 3 OH groups/mol);

DB = double bond content (miliequiv./g)

In Section 4.1.1, the general mechanistic aspects of anionic polymerisation of alkylene oxides (especially PO) were discussed. The anionic polymerisation of PO initiated by hydroxyl groups is considered as a ‘pseudo living’ polymerisation. This type of polymerisation has some important aspects of living polymerisations: the active centre (alcoholate type) is stable and active, and during the polymerisation reaction the number of active alcoholate centres remains constant. This characteristic of living polymerisations is very important for the synthesis of block copolymers. For example if after the addition of PO to the living polymer EO (or BO) are added, then block copolymers are obtained.

Unfortunately other characteristics of living polymerisation are not applicable in the case of anionic PO polymerisation, due to the rearrangement of PO to allyl alcohol. Thus if the well known relationship shown in Equation 4.5 is applicable to the true living polymerisations is not possible to use it for PO anionic polymerisation, due to a nonlinear variation of the MW against the monomer consumed in the reaction:

$$D_n = \frac{[M]}{[I]} \tag{4.5}$$

where:

D_n = degree of polymerisation,

[M] = monomer concentration, and

[I] = initiator (starter) concentration.

As a general rule, in anionic polymerisation of PO catalysed by KOH, a maximum, limited MW of around 6000-6500 daltons can be obtained, as it is impossible to obtain higher MW at the normal polymerisation temperature (110 °C). With CsOH as catalyst, the maximum MW is around 8000 daltons. The graph of MW against mols of monomer consumed/mol of starter are not straight lines as in living polymerisations, but are curves with a tendency to a limited value (see **Figure 4.7**).

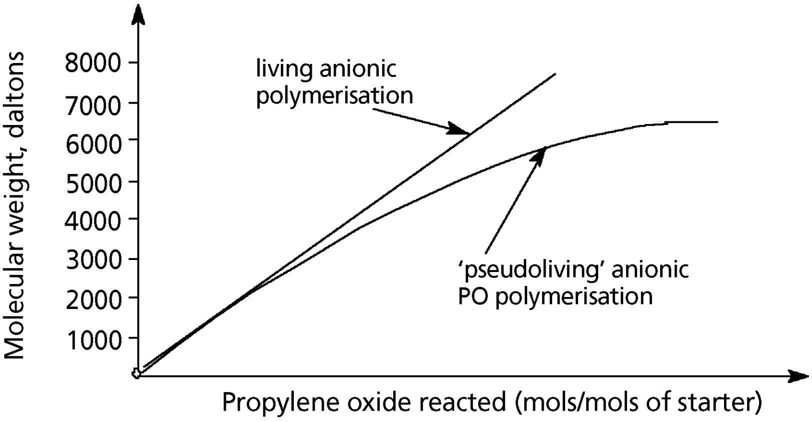
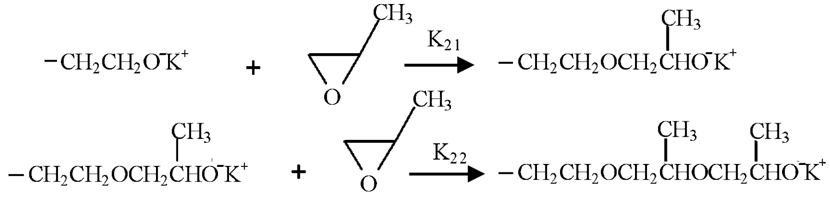


Figure 4.7 MW of polyether triols, PO homopolymers, as function of mols of monomer reacted/mol of starter

4.1.2 Kinetics of PO Addition to Glycerol [14, 49, 50, 52, 53, 62-71, 73, 77, 92-95]

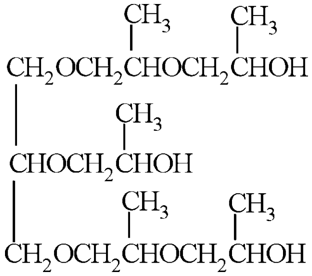
4.1.2.1 General Considerations

In the propoxylation of glycerol, the addition rate of PO to the hydroxyl groups of the starter is different when compared with the addition rate of PO to the formed secondary hydroxyl groups. It is observed that glycerol has two primary hydroxyl groups and one secondary hydroxyl group. In the studies of PO copolymerisation with EO, the ratio r between the reaction constant of PO with secondary hydroxyl (K_{22}) and the reaction constant with primary hydroxyl (K_{21}) is [56, 71]:



$$r = \frac{K_{22}}{K_{21}} = 0.36$$

PO reacts around three times more rapidly with primary hydroxyl groups than with secondary hydroxyl groups. In the particular case of glycerol, the first moles of PO react preferentially with the primary hydroxyl groups of glycerol. After the addition of around 5 moles of PO/mole of glycerol, all the hydroxyl groups of the resulting adduct are secondary hydroxypropyl groups, and the starter (glycerol) practically disappears from the reaction system [96]:



Santacesaria and co-workers [62-67, 92] studied propoxylation and ethyoxylation of various fatty alcohols, and these studies are very important for the mathematical simulation of the process. The study links the chemical process to the mass transfer process. The variation of the reaction mass density as a function of moles of alkylene oxide added to the starter, is a very important parameter to correct the variation of the reaction volume during the alkoxylation processes.

The solubility of alkylene oxides in the reaction mass is another important parameter, because the reaction takes place in the liquid phase and the gaseous monomer is transferred from the gas phase to the liquid phase. Because all the propoxylation and ethoxylation reactions are strongly diffusion dependent, the surface of the gas-liquid interface is a very important parameter for the mass transfer from the gas to liquid, and the real consumption of alkylene oxides depends strongly on this parameter. Between the alkoxylation of fatty alcohols and the alkoxylation of glycerol, there are many similarities if we use the Santacesaria kinetic model. Thus if RXH are considered to be the hydroxyl groups of the starter, the reaction rate of alkylene oxides addition is:

1. Reaction with hydroxyl groups of the starter (initiation reaction):

$$RXH + PO \xrightarrow{K_o} RX(PO)H$$

$$-\frac{d[PO]}{dt} = K_O\left[RX^-H^+\right]\times[PO]$$

2. Propagation reaction:

$$RX(PO)H + nPO \xrightarrow{K_p} RX(PO)_n H + nPO$$

$$-\frac{d[PO]}{dt} = K_p\left[RX(PO)_n^- K^+\right]\times[PO]$$

The global reaction rate of the propolylation process is:

$$-\frac{d[PO]}{dt} = K_O\left[RX^-H^+\right]\times[PO] + K_p\left[RX(PO)_n^- K^+\right]\times[PO]$$

It is well known that during anionic polymerisation of alkylene oxides, initiated by hydroxyl groups, there is a permanent equilibrium of alcohol - alcoholate. The distribution of alkylene oxide sequences/hydroxyl groups depends very much on the value of the equilibrium constant K_e which, in its turn, depends on the acidity of hydroxyl groups:

$$RX^-K^+ + RX(PO)H \overset{K_e}{\rightleftharpoons} RXH + RX(PO)^- K^+$$

$$K_e = \frac{[RXH]\times\left[RX(PO)^- K^+\right]}{\left[RX^-K^+\right]\times[RX(PO)H]}$$

The value of K_e depends strongly on the difference in acidities of the hydroxyl species involved. In the propoxylation of 1-octanol and 2-octanol values for K_e of 2.2 -2.5 are found [63].

In the propoxylation of glycerol, after the addition of 5 mols of PO/mol of glycerol, the concentration of the starter and of the alcoholate groups derived from the starter are practically zero [96], and the equation of the chemical process becomes the classical second order reaction:

$$-\frac{d[PO]}{dt} = K_O[\text{Catalyst}]\times[PO] \tag{4.6}$$

The addition of the alkylene oxide to the starter (glycerol) is important only in the earlier stage of the reaction. In the synthesis of high MW polyethers (3000-65000 daltons), the molar ratio PO:glycerol is around 84-110, much higher than the ratio of PO:glycerol which is 5, when glycerol disappears as a chemical entity. In the PO anionic polymerisation initiated by glycerol, for high molecular weight polyethers, the reaction with the starter has minor importance and is neglected. Thus, the general second order kinetic equation is representative for this process (Equation 4.6). The addition to the starter is important for the synthesis of short chain polyethers (see Chapter 12.1), where the polymerisation degree/hydroxyl group is low, around 0.5-2 PO units/OH group (1.5-6 PO units/mol of glycerol).

4.1.2.2 Kinetics of PO and EO Anionic Polymerisation (Propagation Reaction)

The anionic polymerisation of PO is characterised by two simultaneous reactions [4, 5, 14, 52, 53, 69, 73, 77, 94, 95]:

a) The rate of PO anionic polymerisation reaction (R_p = propagation reaction) is characterised by the classical second order kinetic equation of bimolecular nucleophilic substitution:

$$R_p = -\frac{d[PO]}{dt} = K_p[\text{Catalyst}] \times [PO] = K_p[RO^-K^+] \times [PO]$$

b) The rate of transfer to monomer (R_{tr} = the rate of the PO rearrangement to allyl alcohol) is characterised by a kinetic equation typical of E-2 elimination reactions:

$$R_{tr} = -\frac{d[PO]}{dt} = K_{tr}[\text{Catalyst}] \times [PO] = K_{tr}[RO^-K^+] \times [PO] = \frac{[>C=C<]}{dt}$$

PO is consumed in both reactions. Thus the global kinetic equation for PO consumption (R_g) is the sum of both reaction rates R_p and R_{tr}:

$$R_g = R_p + R_{tr}$$

$$R_g = K_p[RO^-K^+] \times [PO] + K_{tr}[RO^-K^+] \times [PO] = (K_p + K_{tr})[RO^-K^+] \times [PO]$$

$$\frac{R_{tr}}{R_g}=\frac{K_{tr}\left[RO^{-}K^{+}\right]\times\left[PO\right]}{\left(K_p+K_{tr}\right)\left[ROK^{-}\right]^{+}\times\left[PO\right]}=\frac{K_{tr}}{K_p+K_{tr}}=\frac{C_{tr}}{1+C_{tr}}$$

$$\frac{R_{tr}}{R_g}=\frac{\dfrac{\left[>C=C<\right]}{dt}}{-\dfrac{d\left[PO\right]}{dt}}=-\frac{\left[>C=C<\right]}{d\left[PO\right]}=\frac{C_{tr}}{1+C_{tr}}$$

Because C_{tr} <<1 it can be considered:

$$-\frac{\left[>C=C<\right]}{d\left[PO\right]}=C_{tr}$$

Gladkovski [73, 94] determined that the constant of transfer reaction (K_{tr}) is around 2000-4000 times lower than the constant of propagation reaction (K_p). Gladkovski found that for PO polymerisation, at 120 °C, the following values for K_p and K_{tr} were $K_p = 10.6 \times 10^{-3}$ l/mol/s and $K_{tr} = 2.65 \times 10^{-6}$ l/mol/s. An excellent study on the propagation and transfer in PO anionic polymerisation was developed at Manchester University [69]. The values found for C_{tr}, between 20-80 °C were 0.085×10^{-2} to 0.45×10^{-2} [61]. Becker found a value of C_{tr} of 0.004 for the PO anionic polymerisation at 110 °C [68].

The kinetic equation (4.6) for PO propagation reaction has been verified by many authors [4, 5, 14, 52, 53, 62-71, 73, 79, 92, 93, 95]. This equation was proved correct only at constant concentration of hydroxyl groups [14, 53, 93]. An interesting experimental observation was that the hydroxyl group concentration has a strong effect on the rate of PO consumption, and the rate constant of propagation reaction K_p is in fact a function of hydroxyl group concentration [14, 53, 93]. In accordance with the general theory of SN-2 substitution reaction, the hydroxyl groups solvate the anions (in our case the alcoholate anions) very strongly, and thus the nucleophilicity of the anions is diminished. As an immediate consequence the global reaction rate in the anionic PO polymerisation decreases [14, 53, 93].

Figure 4.8 shows the effect of hydroxyl group concentration on the propagation constant K_p values. At lower hydroxyl group concentrations the value of K_p is higher, and at higher hydroxyl group concentrations the value of K_p diminishes markedly. The inhibitory effect of hydroxyl groups in the anionic polymerisation of PO and EO is evident, with the observation that, at constant hydroxyl group concentration, EO is around three times more reactive than PO.

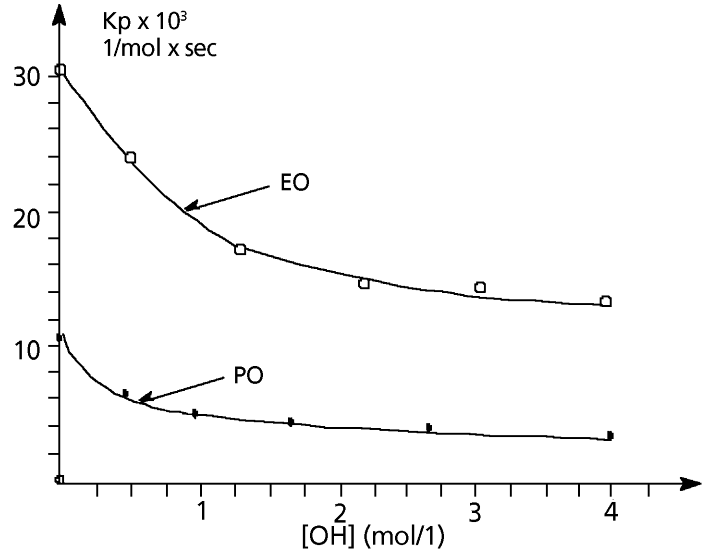


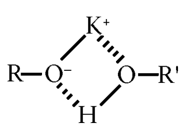
Figure 4.8 The value of propagation constant K_p as function of hydroxyl groups concentrations in anionic polymerisation of EO and PO

Using the kinetic equations and the forms of the catalyst in the reaction medium, one obtains a function, $K_p = f([OH])$.

In the reaction system of PO anionic polymerisation there are two different catalytic species [5, 69]:

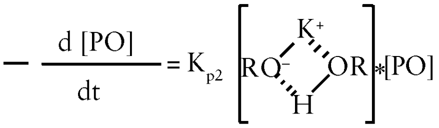
a) One is the potassium alcoholate (RO^-K^+);

b) The second is the quadricentric alcohol - alcoholate complex:



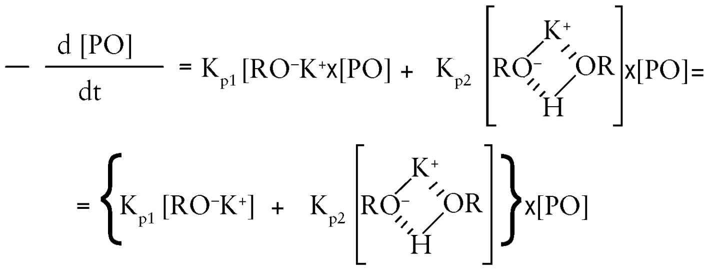
Each catalytic species leads to different reaction rates in the anionic PO polymerisation, the highest reaction rate being catalysed by the uncomplexed alcoholate:

$$-\frac{d\,[PO]}{dt} = K_{p1}\,[RO^{-}K^{+}] * [PO]$$



$$-\frac{d\,[PO]}{dt} = K_{p2}\left[\begin{matrix} & K^{+} & \\ RO^{-} & & OR \\ & H & \end{matrix}\right] * [PO]$$

The global rate of PO consumption is the sum of both reaction rates:

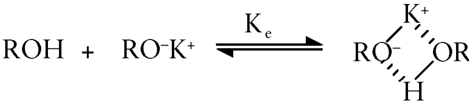


$$-\frac{d\,[PO]}{dt} = K_{p1}\,[RO^{-}K^{+}x[PO] + K_{p2}\left[\begin{matrix} & K^{+} & \\ RO^{-} & & OR \\ & H & \end{matrix}\right]x[PO] =$$

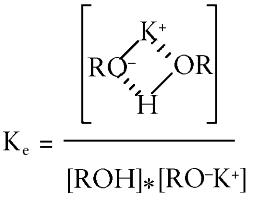
$$= \left\{K_{p1}\,[RO^{-}K^{+}] + K_{p2}\left[\begin{matrix} & K^{+} & \\ RO^{-} & & OR \\ & H & \end{matrix}\right]\right\}x[PO]$$

(4.7)

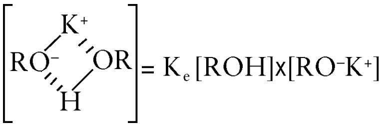
Between the hydroxyl groups and the alcoholate groups of the reaction system there is an equilibrium characterised by the equilibrium constant K_e:



$$ROH + RO^{-}K^{+} \overset{K_e}{\rightleftharpoons} \begin{matrix} & K^{+} & \\ RO^{-} & & OR \\ & H & \end{matrix}$$



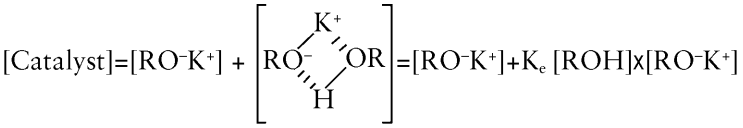
$$K_e = \frac{\left[\begin{matrix} & K^{+} & \\ RO^{-} & & OR \\ & H & \end{matrix}\right]}{[ROH] * [RO^{-}K^{+}]}$$



$$\left[\begin{matrix} & K^{+} & \\ RO^{-} & & OR \\ & H & \end{matrix}\right] = K_e\,[ROH]x[RO^{-}K^{+}]$$

(4.8)

The mass balance of all catalytic species gives:



$$[\text{Catalyst}]=[\mathrm{RO^-K^+}]+\left[\mathrm{RO^-}\underset{\mathrm{H}}{\overset{\mathrm{K^+}}{\cdots}}\mathrm{OR}\right]=[\mathrm{RO^-K^+}]+K_e\,[\mathrm{ROH}]\mathrm{x}[\mathrm{RO^-K^+}]$$

$$[\text{Catalyst}]=[\mathrm{RO^-K^+}](K_e\,[\mathrm{ROH}]+1) \qquad (4.9)$$

By replacing the value of the complex alcohol - alcoholate (4.8) in the general kinetic equation (4.7), one obtains:

$$-\frac{d[\mathrm{PO}]}{dt}=K_{p1}[\mathrm{RO^-K^+}]\times[\mathrm{PO}]+K_{p2}\times K_e[\mathrm{ROH}]\times[\mathrm{RO^-K^+}]\times[\mathrm{PO}]$$

$$-\frac{d[\mathrm{PO}]}{dt}=(K_{p1}+K_{p2}\times K_e[\mathrm{ROH}])\times[\mathrm{RO^-K^+}]\times[\mathrm{PO}] \qquad (4.10)$$

The value of alcoholate concentration is obtained from the relationship in 4.9:

$$[\mathrm{RO^-K^+}]=[\text{Catalyst}]/(K_e[\mathrm{ROH}]+1) \qquad (4.11)$$

By the introduction of the potassium alcoholate concentration (4.9) into Equation (4.10) one obtains:

$$-\frac{d[\mathrm{PO}]}{dt}=\left(\frac{K_{p1}+K_{p2}\times K_e[\mathrm{ROH}]}{K_e[\mathrm{ROH}]+1}\right)\times[\text{Catalyst}]\times[\mathrm{PO}]$$

$$-\frac{d[\mathrm{PO}]}{dt}=\left(\frac{K_{p1}}{K_e[\mathrm{ROH}]+1}+\frac{K_{p2}\times K_e[\mathrm{ROH}]}{K_e[\mathrm{ROH}]+1}\right)\times[\text{Catalyst}]\times[\mathrm{PO}] \qquad (4.12)$$

Equation 4.12 is the general equation of the anionic polymerisation of PO, representing a complex dependence on the hydroxyl group concentration. The value of K_p in the general equation 4.12 is a function of hydroxyl group concentration:

$$K_p=\frac{K_{p1}}{K_e[\mathrm{ROH}]+1}+\frac{K_{p2}\times K_e[\mathrm{ROH}]}{K_e[\mathrm{ROH}]+1}$$

Experimental determinations for PO polymerisation, at 120 °C and 0.4 MPa lead to the following values for the constants K_{P_1}, K_{P_2} and K_e [97]:

$K_{p_1} = 10 \times 10^{-3}$ l/mol/s

$K_{p_2} = 5.55 \times 10^{-3}$ l/mol/s

$K_e = 9$ l/mol

The anionic polymerisation of PO is in fact a competition of two simultaneous reactions: the propagation reaction (R_p) and the transfer reaction (R_{tr}). An interesting way to obtain it directly from the synthesis of low unsaturated polyether polyols, is to accelerate selectively the propagation reaction while the transfer reaction remains unchanged or lower. It is well known that low unsaturation of polyether polyols represents a low monol content and leads to better physico-mechanical properties in the resulting PU, because in the PU chemistry the monol (a monofunctional compound) is a chain stopper, (i.e., it stops the MW increase).

One practical way to obtain lower unsaturated polyether polyols directly from synthesis, is to develop the anionic polymerisation of PO at lower temperatures (see **Table 4.2**). This effect is based on the different activating energies of the propagation reaction (R_p) and of the transfer reaction (R_{tr}). The reaction with the highest activating energy has a more significant variation of temperature compared to the reaction with the lower activating energy.

Thus, the rate of transfer with a PO monomer with a much higher activation energy varies more with the temperature than the PO propagation reaction. As an immediate consequence, by the decreasing the polymerisation temperature from 110-120 °C to 80 °C [69], polyether polyols with much lower unsaturation are obtained. In order to get convenient reaction rates, the catalyst concentration was increased. **Table 4.3** shows the variation of propagation constant K_p of PO anionic polymerisation as a function of temperature.

One observes that, at 120 °C, the propagation rate constant is around 10 times higher than at 80 °C. By increasing the catalyst concentration 10 times (e.g., from 0.25% to

Table 4.2 The activation energy of propagation reaction (R_p) and transfer reaction (R_{tr}) in PO and EO anionic polymerisation

Reaction type	Activation energy, Kcal/mol PO	Activation energy, Kcal/mol EO
Propagation reaction (R_p)	17.4 [9, 95]	17.8 [9, 95]
Transfer reaction (R_{tr})	25.1 [95] 31.8 [73]	– *

* *No transfer reaction*

Table 4.3 Variation of propagation constant in PO anionic polymerisation, as a function of temperature [97]

Temperature, °C	K_p x 10^3, l/mol/s	Temperature, °C	K_p x 10^3, l/mol/s
70	0.43	115	3.79
80	0.50	120	5.1
90	0.84	125	6.55
100	1.58	130	8.53
110	2.85	–	–

2.5% as KOH against final polyol), approximately the same reaction rates as for 120 °C were obtained, with the beneficial effect of obtaining a low unsaturation (for example of 0.02-0.03 milliequivalents/g obtained at 80 °C, as compared with 0.06-0.07 obtained at 120 °C and at polyether MW of 5000 daltons) [97]. The increase of catalyst concentration does not have a significant effect on the unsaturation growth.

All the reaction constants discussed in this book have relative values and not absolute values, because the PO anionic polymerisation is strongly diffusion dependent and each polymerisation reactor has specific hydrodynamic properties.

Another way to accelerate the rate of propagation reaction (R_p) is by the complexation of the potassium cation of the alcoholate active centre. The electrical conductivity measurements [14, 53, 68] in crude alkaline polyether proved that the potassium alcoholate dissolved in the liquid polyether media is practically undissociated, the dissociation degree being very low – only 1.3-2% [53].

$$\underset{\text{ion pair}}{RO^-K^+} \xrightleftharpoons{K_D} \underset{\substack{\text{free}\\ \text{alcoholate}\\ \text{anion}}}{RO^-} + \underset{\substack{\text{free}\\ \text{cation}}}{K^+}$$

It is well known from many SN-2 nucleophilic substitution reactions that the free ions (in our case free anions) are much more reactive than the undissociated ion pairs [14, 53, 74].

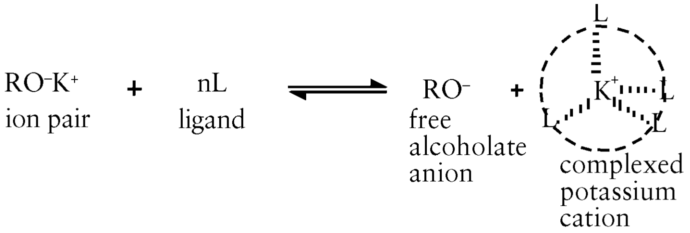
$$K_D = \frac{\left[RO^-\right]\left[K^+\right]}{\left[RO^-K^+\right]} = \left[C\right] \times \frac{a^2}{1-a}$$

K_D = dissociation degree

[C] = initial concentration of the catalyst

a = fraction of free ions

By the potassium cation complexation with specific ligands, the positive charge is screened and as an immediate consequence the electrostatic interaction between the anion and cation decreases and the dissociation degree increases [14, 53]:



It is well known that alkali and alkaline earth cations are very difficult to complex due to the configuration of the rare gas electronic structure of these ions. Fortunately, some specific ligands are known, such as aprotic dipolar solvents (dimethylformamide, sulfolane, dimethylsulfoxide, *N*-methyl pyrolidone and so on), aminoxides, phosphinoxides, glymes and polyethylene glycols, crown ethers and cryptates, bidentate amines (tetramethyl ethylene diamine, 1,10 phenanthroline, etc. [14, 53, 61, 68].

Figure 4.9 shows some complexes of potassium cations, with different ligands.

Figure 4.10 shows the accelerating effect of various ligands in PO anionic polymerisation [14, 53].

It is observed that the most efficient ligands are crown ethers and criptates, followed by aprotic dipolar solvents, polyethylene glycols, glymes and finally bidentate amines.

Representing the values of propagation constant K_p as function of the complexed potassium alcoholate, a perfectly straight line was obtained, characterised by the equation [14, 53]:

$K_p = K_- \times a + K_{+-} \times (1\text{-}a)$

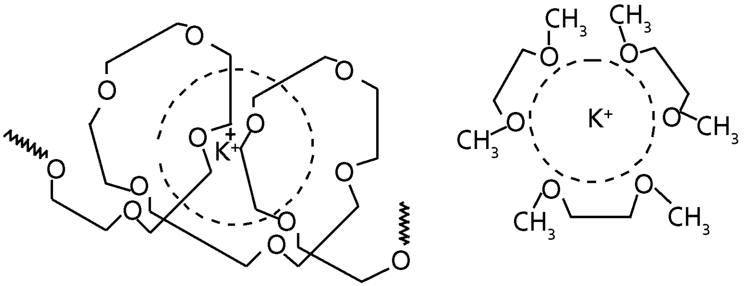
K_- = propagation constant characteristic to the free anion;

K_{+-} = propagation constant characteristic to the undissociated pair ions

Thus, in the case of PO anionic polymerisation with complexed potassium cations, the kinetic equation for propagation reaction (4.10) becomes:

$$-\frac{d[PO]}{dt}=\left[K_{-}\times a+K_{-+}(1-a)\right]\times\left[RO^{-}K^{+}\right]\times[PO]$$

Since, in practice, the dissociation constant of potassium alcoholate in liquid polyether is very low (a = 0.013-0.02), one considers that a = 0 and the equation then becomes the

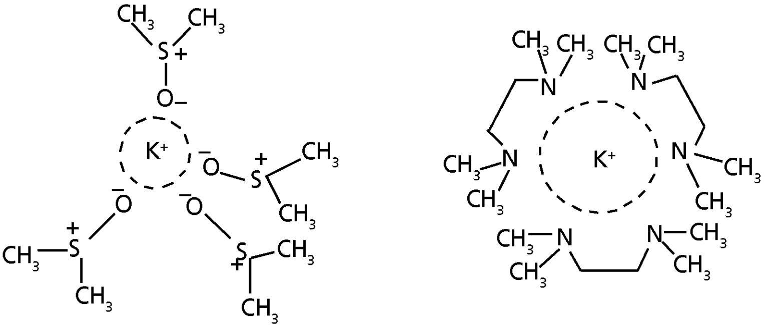


complex K+ - polyethylene glycols

complex K+ - glyme

complex K+ - 18-crown-6

complex K+ - cryptate [2,2,2]



complex K+ - DMSO

complex K+ -
tetramethylethylene diamine

Figure 4.9 Some potassium cation complexes with different ligands

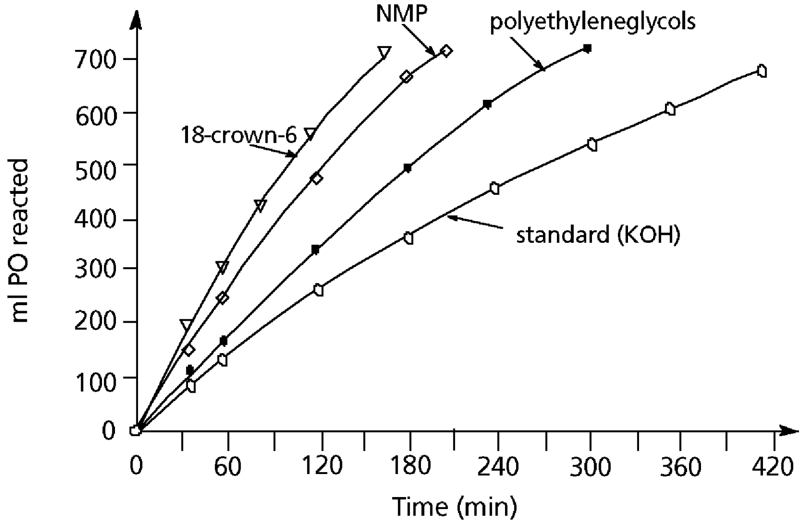


Figure 4.10 The effect of various ligands on the PO consumption rate in anionic PO polymerisation. Temperature: 110 °C; Pressure: 0.4 MPa; catalyst concentration: 0.0056 mol/l; NMP: *N*-methyl pyrolidone

classical equation 4.10 for anionic PO polymerisation, practically catalysed exclusively by the undissociated ion pairs:

$$-\frac{d\left[PO\right]}{dt}=K_{+-}\times\left[RO^{-}K^{+}\right]\times\left[PO\right]=K_{p}\left[Catalyst\right]\times\left[PO\right]$$

By replacing the value of K_{p_1} in the general equation of PO anionic polymerisation (4.10), one obtains a new equation (4.13), dependent on the hydroxyl group concentration:

$$-\frac{d\left[PO\right]}{dt}=\left(\frac{K_{-}\times a+K_{+\_}\times(1-a))}{K_{e}\left[ROH\right]+1}+\frac{K_{p2}\times K_{e}\left[ROH\right]}{K_{e}\left[ROH\right]+1}\right)\times\left[Catalyst\right]\times\left[PO\right]$$

$$K_{p}=\frac{K_{-}\times a+K_{+\_}\times\left(1-a\right)}{K_{e}\left[ROH\right]+1}+\frac{K_{p2}\times K_{e}\left[ROH\right]}{K_{e}\left[ROH\right]+1} \tag{4.13}$$

Equation (4.13) is a more general equation of the PO anionic polymerisation of PO, where the propagation constant is a function of the hydroxyl group concentration and of the dissociation constant of the alcoholate anion.

If the hydroxyl group concentration [OH] is constant and a = 0, we obtain the well known equation (4.6) for the propagation reaction R_p in anionic PO polymerisation.

The values for the propagation constant due to the free ions, and the propagation constant due to the pair ions, for PO anionic polymerisation at 120 °C and 0.4 MPa are presented next [14, 53]:

$$K_- = 5.8 \times 10^{-2} 1/\text{mol} \times \text{s}$$

$$K_{+-} = 5.0 \times 10^{-3} 1/\text{mol} \times \text{s}$$

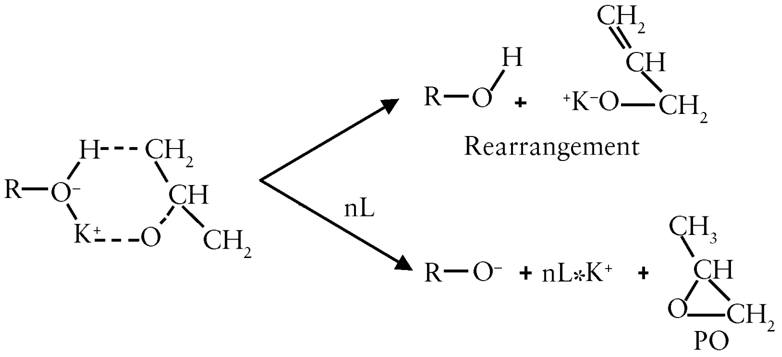
$$\frac{K_-}{K_{+-}} = 11.6$$

To conclude, at 120 °C and 0.4 MPa the propagation constant, due to the free ions, is around 11.6 times higher than the propagation constant characteristic of the undissociated ion pairs. Thus, by the simple addition of a specific ligand for potassium, without any modification of the reaction parameters, one can obtain a polyether polyol in a shorter time (around two to three times shorter) than for normal anionic PO polymerisation, without ligands for potassium. Becker [68, 70, 71] proved that in the complexation of a potassium cation with a crown ether, such as 18-crown-6, the reaction rate of PO polymerisation is ten times higher than at the normal polymerisation rate with an uncomplexed potassium ion. An increase in PO polymerisation rate from eight times at 120 °C to 30 times at 20 °C was determined by Price and co-workers [61].

It is interesting to note that the polyethers obtained by potassium complexed catalysts have two to four times lower unsaturation than the polyethers obtained by usual anionic PO polymerisation, with uncomplexed potassium cation.

Figure 4.11 shows the strong decrease of polyether polyols unsaturation by using different ligands for PO anionic polymerisation than potassium. The minimum unsaturation is obtained by using strong ligands for potassium, such as criptates and crown ethers [14, 53].

One explanation of this effect is the propagation reaction acceleration and the deceleration of the transfer reaction. The mechanism of PO rearrangement to allyl alcohol is based on a cyclic intermediary state, in fact a weak complex alcoholate-PO:



PO is a very poor ligand and the complex alcoholate - PO is very weak. By using a strong ligand for potassium, PO a soft ligand, is eliminated from the complex and the isomerisation to allyl alcohol is inhibited.

The explanation that, in the presence of a high concentration of hydroxyl groups, the unsaturation is very low, is based on the strong affinity of the alcoholate for hydroxyl groups. As an immediate consequence, hydroxyl groups being stronger ligands than PO are preferentially complexed and PO is eliminated from the complex alcoholate - PO. Of course the isomerisation of PO to allyl alcohol takes place to a much lesser extent:

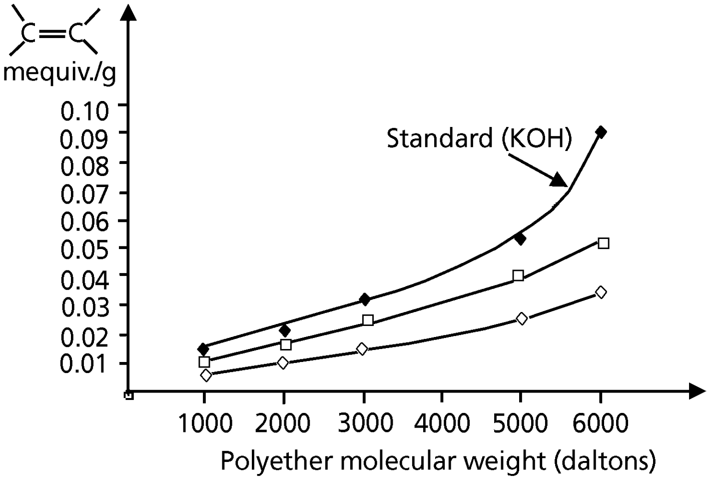
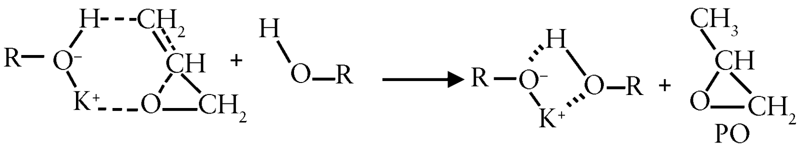


Figure 4.11 The effect of some ligands of potassium cation on the unsaturation of the polyether triols. Temperature: 110 °C; Pressure: 0.4 MPa; catalyst concentration: 0.0056 mol/l; Ligands: polyethylene glycol; MW = 2000 (❐) and 18-crown 6 (◊)



It is well known that in the case of polyethers used for rigid PU foams, having a high concentration of hydroxyl groups (OH# = 300-800 mg KOH/g), the resulting unsaturation is extremely low (0.005-0.01 mequiv/g). Conversely, the polyether for flexible PU foams, having a low concentration of terminal hydroxyl groups (OH# = 28-56 mg KOH/g), has a high unsaturation (0.04-0.09 mequiv/g. This is another explanation for the unsaturation of polyether polyols increasing with the MW increase.

The presence and quantitative determinations of polyether monols and polyether diols in polyether triols was realised by: thin layer chromatography (TLC) [97], column chromatography [73, 94], gel permeation chromatography [4] and NMR spectroscopy [88].

Thus, in **Figure 4.12** the thin layer chromatograms of PO homopolymers, triols and diols are presented. One observes that the polyether diols are mixtures of polyether diols and monols and the polyether triols are mixtures of polyether triols, diols and monols. The polyether monol was obtained by propoxylation of the allyl alcohol.

By using the optical density measurements of thin layer chromatograms, it was possible to obtain a clearer picture of the polyether triol composition, including the determination of the ratio between triols, diols and monols (**Figure 4.13**).

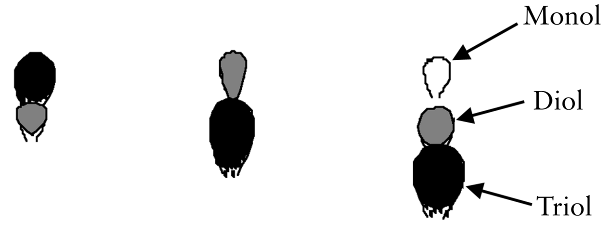


Figure 4.12 Comparative thin layer chromatograms of polyether triols, diols and monols, PO homopolymers

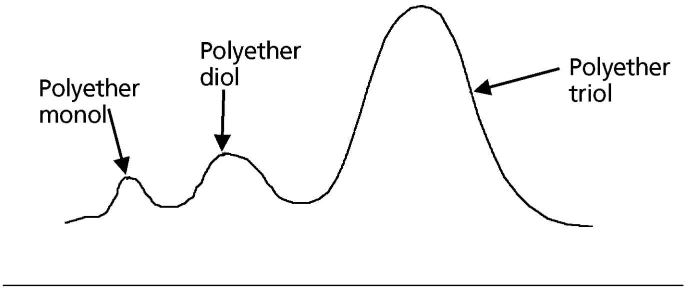


Figure 4.13 Optical density measurements of a thin layer chromatogram of polyether triol, PO homopolymer, of MW of 3000 daltons

The chemistry of the PO anionic polymerisation, initiated by glycerol, is presented in detail in Chapter 12.1.2. The resulting polyethers are triols, homopolymers of PO. Another triol starter used successfully instead of glycerol is trimethylolpropane (TMP). TMP has some advantages, such as a perfect symmetry and a structure with three reactive primary hydroxyl groups, and disadvantages such as its solid state with a melting point (mp) of 57 °C and the fact that it is more expensive than glycerol. Glycerol is liquid, easy to handle and transport, is a raw material from renewable resources (animal fats and vegetable oils), is cheaper than TMP, and therefore is used predominantly on the industrial scale, as a starter for flexible polyether triols production.

Polyether diols are obtained in the same way as polyether triols, with the difference that the starter is propylene glycol or DPG instead of glycerol or TMP. Because potassium hydroxide and water lead, by the reaction with PO, to polyether diols, it is not necessary to anhydrisate the initial mixture of starter - KOH (solid or aqueous solution). The polyether diols, homopolymers of PO, are obtained by direct propoxylation of a propylene glycol or DPG mixture with KOH (solid or aqueous KOH: 40-50% solution).

Generally, the high MW polyether diols (polypropylene glycols (PPG): MW 1000-4000 daltons) are rarely used in flexible PU foams. Sometimes, in order to increase the elongation and tensile strength of the flexible PU foams, polyether diols are used in the mixture together with polyether triols (80% polyether triols and 20% polyether diols [99]). High MW polypropylene glycols are frequently used in special PU applications, such as in PU elastomers, coatings, adhesives and sealants.

The most important characteristics of industrially produced polyether diols and triols homopolymers of propylene oxide are presented in **Tables 4.4** and **4.5**. All the polyether PO homopolymers, diols or triols have mostly secondary hydroxyls as terminal groups (94-96% secondary hydroxyls) (see **Figure 4.14**).

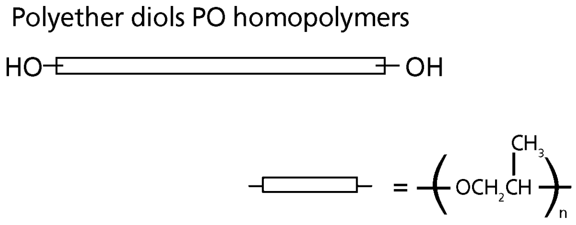


Figure 4.14

Table 4.4 The characteristics of polyether diols, PO homopolymers (polypropylene glycols)

Molecular weight, daltons	Hydroxyl number, mg KOH/g	Acidity, mg KOH/g	Water, %	Viscosity at 25 °C, mPa-s	Unsaturation, mequiv/g (functionality)
400	250	max. 0.05	max. 0.05	60-75	0.005 (1.999)
1000	112	max. 0.05	max. 0.05	140-150	0.01 (1.990)
2000	56	max. 0.05	max. 0.05	250-350	0.03 (1.94)
3000	37	max. 0.05	max. 0.05	550-590	0.06 (1.86)
4000	28	max. 0.05	max. 0.05	970-990	0.090 (1.69)

The most important polyether triol, PO homopolymer, is the glycerine based triol of MW of 3000 daltons, used in continuous slabstock PU foams (**Figure 4.15**).

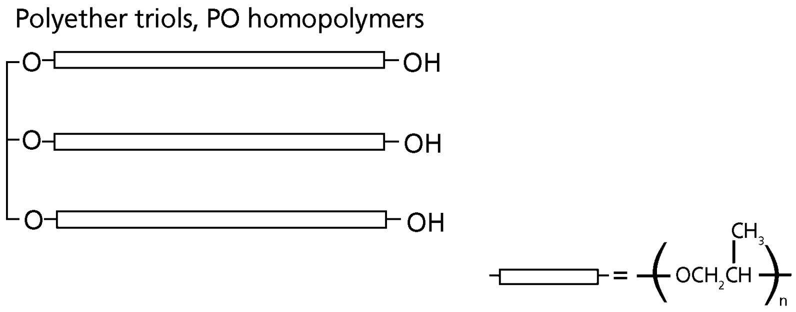


Figure 4.15

Table 4.5 The characteristics of polyether triol, PO homopolymer of MW of 3000 daltons

No.	Characteristic	Unit	Value
1	Molecular weight	daltons	3000
2	Functionality	OH groups/mol	3
3	Hydroxyl number	mg KOH/g	53-59
4	Unsaturation	mequiv/g	0.035-0.04
5	Viscosity, 25 °C	mPa-s	400-550
6	Acidity	mg KOH/g	max. 0.1
5	Water content	%	max. 0.1
6	Colour	APHA	max. 30-50

4.1.3 Random Copolyethers PO-EO (Heteropolyether Polyols) [1, 4, 9, 12, 56-58, 70, 71]

The random copolyether triols PO-EO, usually called heteropolyether polyols, with a MW of 3000-3600 daltons, are the most important polyether polyols for flexible PU slabstock foams, generally used in furniture industry. The worldwide consumption of flexible PU foams is presented in **Figure 4.16**.

It can be seen that moulded flexible PU foams using EO capped polyether polyols (block copolymers PO-EO with terminal poly[EO] block) represent only 22% of total worldwide consumption and that the majority of foams are flexible slabstock PU foams which use random copolyethers of PO-EO. It can therefore be concluded that the most important polyols for flexible PU foams production are in fact the random copolyethers PO-EO.

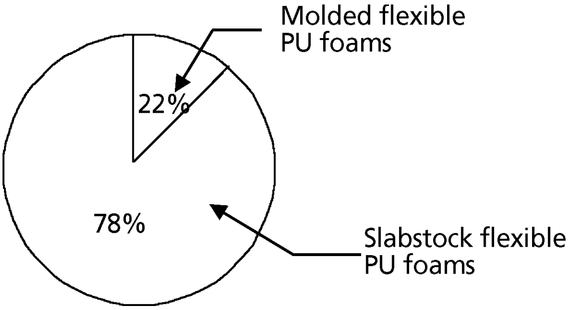


Figure 4.16 Worldwide consumption of flexible PU foam

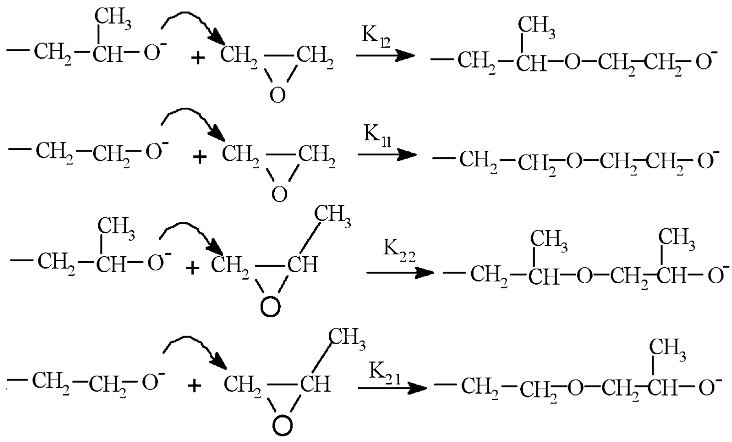
Practically, the synthesis of random copolyethers of PO-EO is very similar to the synthesis of polyether PO homopolymers, with the difference that the starter (mainly glycerol) is reacted with an homogeneous mixture of PO-EO, containing around 10-15% EO, instead of PO alone.

The resulting polyether polyols have EO units (minority units) and PO units (majority units) randomly distributed in the polyetheric chains. These random PO-EO copolyether polyols are considered 'internally activated' polyethers (all the polyethers having internal EO units are considered 'internally activated' polyethers) and have predominantly secondary terminal hydroxyl groups. This generally required characteristic in polyols for slabstock foams is explained by the high temperatures generated in the centre of the bun (around 150-170 °C) during the continuous foaming process, which assures enough activating energy for a high conversion of the reaction between diisocyanates and the lower reactivity terminal secondary hydroxyl groups of the random copolyether polyol.

The random copolyether polyols, due to the hydrophilic EO units, have a much better compatibility with water, used as blowing agent, dissolving a higher quantity of water than homopolymer triols. The result is a very uniform cellular structure and excellent physico-mechanical properties. The random PO-EO structure has an intrinsic surfactant effect and permits small errors in silicon emulsifier dosage, without negative effects on cellular structure or on physico-mechanical properties. The random PO-EO structure of polyether triols leads to better tensile strength and elongation, that for polyether triol PO homopolymers and conserves the compressive strength, especially at lower densities [100, 101].

For continuous flexible PU slabstock production, the heteropolyether triols PO-EO are considered universal polyols used in conventional soft and supersoft flexible PU foams, covering a large range of densities (12-40 kg/m^3) and load bearing properties.

In the random copolymerisation of PO with EO, the following four important reactions take place (EO is monomer 1 and PO is monomer 2):



All the copolymerisation reactions are characterised by the copolymerisation constant r_1 and r_2 defined as:

$$r_1 = \frac{K_{11}}{K_{12}} \text{ and } r_2 = \frac{K_{22}}{K_{21}}$$

These constants r_1 and r_2 represent the ratio between the reaction constant of the reaction of one monomer with the chain end derived from the same monomer unit, and the reaction constant of the reaction of the same monomer with the chain end derived from the second monomer unit.

Table 4.6 shows the values of K_{11}, K_{22}, r_1 and r_2 for the anionic copolymerisation of EO with PO, at different temperatures, in the presence of KOH as catalyst [57, 58, 70, 71]. For comparison the values of r_1 and r_2 for copolymerisation of EO with BO are also given [70, 71].

EO is observed to be much more reactive against the hydroxyethyl primary hydroxyl group (chain end derived from EO). That explains the preferential tendency of EO to react with another hydroxyethyl unit, forming microblock structures (...PO-EO-EO-PO-...) with a low tendency of alternation. It is observed, that by the temperature increase, the tendency to alternation increases and the tendency to form poly[EO] microblocks diminishes. Therefore at higher temperatures more uniform random structures are obtained than at lower temperatures. Other authors have proved that between 25-80 °C the reactivity ratios are identical to those obtained in copolymerisation of PO with EO [59].

Table 4.6 Reaction constants for copolymerisation of EO with PO and EO with BO at various temperatures

Bulk copolymerisation of EO with PO				
Temperature, °C	**K_{22}, l/mol/s**	**K_{11}, l/mol/s**	**r_1**	**r_2**
25	–	–	0.5	6.0 [57]
0-80	–	–	0.25-0.30	2.8-3.1 [58]
70	0.43×10^{-3}	0.24×10^{-2}	0.17	3.0 [70, 71]
90	1.70×10^{-3}	1.34×10^{-2}	0.26	2.5 [70, 71]
120	10.60×10^{-3}	9.00×10^{-2}	0.36	1.6 [70, 71]
Copolymerisation of EO with BO				
Temperature, °C	**K_{22}, l/mol/s**	**K_{11}, l/mol/s**	**r_1**	**r_2**
80	–	–	0.17	4.1 [59]

The ^{13}C NMR study of a heteropolyether polyol (MW: 3600 daltons) containing 15% EO units proved that 45% of total EO units have a microblock structure (...PO-EO-EO-PO..) and that 55% of total EO units are alternating sequences of PO-EO-PO units [97].

Figure 4.17 shows a typical curve for anionic copolymerisation of EO with PO. The curve represents the content (as molar fraction) of EO units (X_1) in the polyether chains, as function of the content of the unreacted EO (x_1) in the monomer mixture. The corresponding quantities of PO (x_2 and X_2) are calculated easily of course (x_2= 1-x_1 and X_2 = 1-X_1).

Figure 4.17 clearly shows that EO is the monomer that is consumed first, having a much higher reactivity than PO in anionic polymerisation.

It is not possible for EO to isomerise to the allyl structure. As an immediate consequence, the unsaturation of the random copolyethers, PO-EO, is lower than the unsaturation of analogue PO homopolymers, at the same MW [75].

The increased propagation rate, due to the presence of EO, a monomer more reactive than PO, is another explanation for the resulting lower unsaturation of random PO-EO copolyethers.

The polyether most used in practice for continuous free rise slabstock flexible PU foams are the triols, copolyethers PO-EO, containing around 10-15% EO randomly distributed (most used 10-12% EO), of MW in the range of 3000-3600 daltons (OH# = 42-60 mg KOH/g).

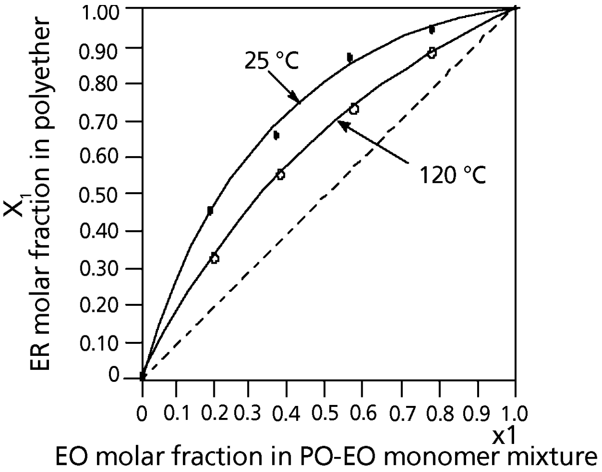


Figure 4.17 Composition diagram of PO-EO copolymerisation

The general structure of random copolymers of PO-EO and copolyether triols (PO-EO) is presented in **Figure 4.18**. The main characteristics of the random copolymers of PO-EO, heteropolyether triols, which are used most, are presented in **Table 4.7**.

A very interesting structure of random PO-EO copolyethers is a structure containing a high EO content, of around 75% EO (**Figure 4.19**). In this structure the majority of monomer units are EO units (mainly internal EO and terminal), and PO represents minority units of around 25%. This structure consists of microblocks of poly[EO] alternating with PO units and has two important applications:

a) As a cell opener polyol in flexible polyurethane foams, especially in high resilience foams);

b) As a softener polyol. The softening effect of these polyols is due to the solvation of urethane and urea bonds by the poly[EO] chains. Thus, the secondary hydrogen bonds attracting forces decrease and, as an immediate consequence, the compression strength decreases.

By using these random polyethers with high EO content (**Figure 4.19**), it is possible to obtain softer flexible PU foams without any auxiliary blowing agent (such as methylene chloride) [102-104].

A similar polyether polyol, having the same EO and PO content but in the form of a block copolymer (internal poly[EO] block and terminal poly[PO] block), gives a solid polyether in the form of a wax, probably due to the crystallisation of poly[EO] chains.

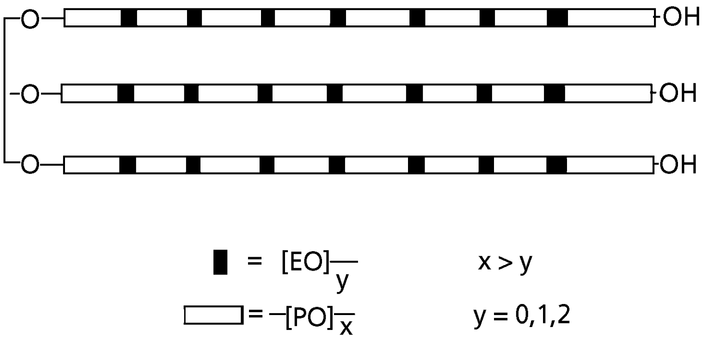


Figure 4.18 The general structure of random copolymers of PO-EO (heteropolyether triols)

By using a homogeneous mixture of PO-EO, containing 20-25% PO, the resulting PO-EO copolyether is liquid because the PO units perturb the regularity of the long poly[EO] chains which also disturbs their tendency to organise themselves into crystalline structures.

The main characteristics of random PO-EO copolyethers with high EO content are presented in **Table 4.8**. One observes that the PO-EO copolyether has a medium primary hydroxyl content, of around 50%, and that the EO units are not only internal groups but some of them are terminal groups too.

Table 4.7 The main characteristics of polyether triol random copolymers (PO-EO heteropolyether polyols)

Characteristic	Unit	MW = 3000 daltons	MW = 3600 daltons
Aspect	–	viscous liquid	viscous liquid
Hydroxyl number	mg KOH/g	53-59	42-49
Viscosity, 25 °C	mPa-s	450-650	500-700
Unsaturation	mequiv/g	0.03-0.04	0.035-0.045
Na + K	ppm	max. 5	max. 5
Acidity	mg KOH/g	max. 0.05-0.1	max. 0.05-0.1
Water content	%	max. 0.05-0.1	max. 0.05-0.1
EO content	%	10-15	10-15
Primary hydroxyl	%	low (4-15%)	low (4-15%)

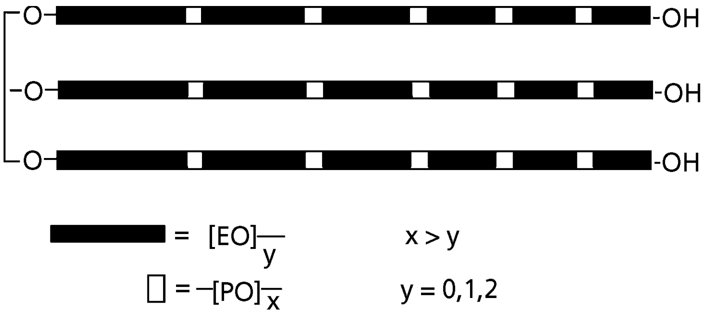


Figure 4.19 Polyether triols, EO-PO random copolymers, with high EO content

Table 4.8 Characteristics of random copolyether triols with high internal EO content

Characteristic	Unit	MW = 3000-5000 daltons
Aspect	–	viscous liquid sometimes turbid
Hydroxyl number	mg KOH/g	33-42
Viscosity, 25 °C	mPa-s	1100-2000
Unsaturation	mequiv/g	0.015-0.020
Na + K	ppm	max. 5
Acidity	mg KOH/g	max. 0.1
Water content	%	max. 0.1
EO content	%	75
Primary hydroxyl	%	~50

4.1.3.1 Other Random Copolyethers Obtained by Anionic Polymerisation

A very interesting group of random copolyethers is obtained by anionic copolymerisation of EO (a highly hydrophilic monomer) with BO (a highly hydrophobic monomer). Because EO does not isomerise to double bond structures and BO has a much lower tendency to isomerise to allyl structures than PO (see Chapter 12.2), the BO-EO copolyethers have a very low unsaturation level compared to PO homopolymers or even PO-EO copolymers [82]. This variant of polyether polyols synthesis in the form of BO-EO copolymers is a very interesting way to obtain low unsaturation polyether polyols directly from synthesis. Another group of low unsaturation polyether polyols, obtained directly from synthesis, are the tetrahydrofuran (THF)-EO and THF-PO copolymers synthesised with cationic catalysts (see Chapter 7.3).

In practice hybrid structures of polyether polyols for flexible PU such as (a, b and c structures) are frequently used [105]:

a) block [PO] - random *[PO-EO]* (**Figure 4.20**),

b) block [PO] - random *[PO-EO]* - block [EO] (**Figure 4.21**) or

c) block [PO] - random *[PO-EO]*-block [EO] - random *[PO-EO]* - block [PO] (**Figure 4.22**).

This polyether triol hybrid structure block [PO] - random [PO - EO]- block EO, with a MW of 3000 daltons, was used successfully for hot moulded flexible PU foams with

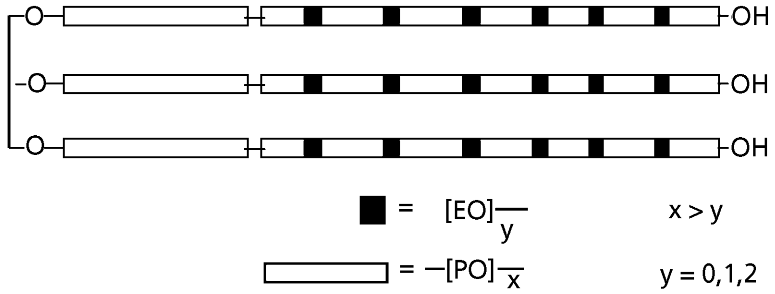


Figure 4.20 Polyether triol type block [PO] - random [PO-EO]

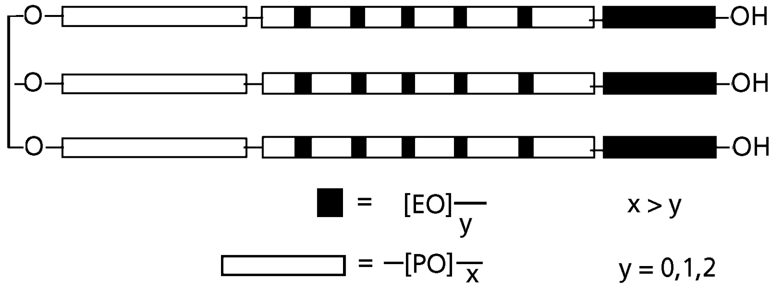


Figure 4.21 Polyether triol, block [PO] - random [PO - EO] - block [EO]

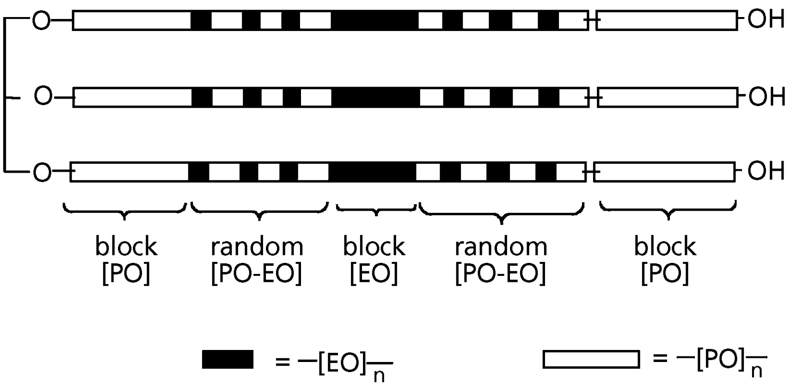


Figure 4.22 Polyether triols with the following succession of structures: block [PO], random [PO-EO], block [EO], - random [PO-EO], and block [PO]

enhanced flow properties. EO was randomly distributed (5-8%) and around 5% EO was terminal block, the primary hydroxyl content being around 30-35%. A similar structure was used for some polyether triols, with a MW of 5000-6000 daltons, with 3-5% randomly distributed EO (internal EO) and 13-15% EO as terminal block. By using this polyether type, high resilience PU foams, with better flow properties, low shrinkage and a high percentage of open cells are obtained.

An interesting hybrid structure [97] was obtained by an alternate PO and EO addition without any intermediary digestion or degassing. The resulting structure, block [PO]-random [PO-EO] - block [EO] - random [PO-EO] - block [PO], is shown in **Figure 4.22**.

This structure was used successfully for continuous slabstock flexible PU foams. The polyethers have a MW of 3000-3600 daltons (hydroxyl number of 46-56 mg KOH/g), a viscosity of 550-650 mPa-s, have practically only terminal secondary hydroxyl groups and contain around 10-12% EO internally distributed.

In this section the most important random copolyether PO-EO structures were presented. Considering the highest production volume, the random copolyethers PO-EO with a MW of 3000-3600 daltons are the most important polyether type produced worldwide, used in continuous flexible slabstock foams, with the highest volume of consumption (of around 78% from the total flexible foams).

4.1.4 Polyether Polyols Block Copolymers PO-EO [1, 4, 51, 52, 100, 101, 106, 108]

The 'pseudoliving' character of PO anionic polymerisation produces a large variety of block copolymers, by simply changing the nature of the oxirane monomer because the catalytic species (potassium alcoholate) remains active during and after the polymerisation reaction. Thus, if a polyether is synthesised first by anionic polymerisation of PO and the polymerisation continues with another monomer, such as EO, a block copolyether PO-EO with a terminal poly[EO] block is obtained. Another synthetic variant is to obtain a polyethoxylated polyether first by the anionic polymerisation of EO initiated by glycerol [108], followed by the addition of PO to the resulting polyethoxylated triol. A block copolyether PO-EO is obtained with internal poly[EO] block linked to the starter. Another possibility is to add the monomers in three steps: first PO is added to glycerol, followed by EO addition and finally by the addition of PO. A copolyether triol block copolymer PO-EO with the internal poly[EO] block situated inside the polyetheric chain between two poly[PO] blocks is obtained [4, 100, 101].

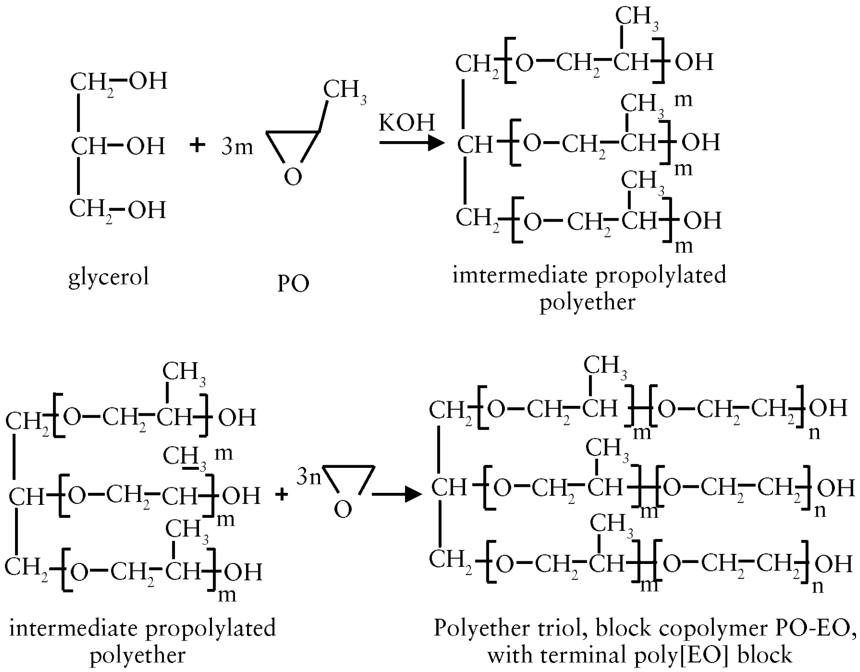
These three block copolyether PO-EO structures are presented in **Figure 4.28**. The most important structure of block copolyethers of PO-EO is the first structure with a terminal poly[EO] block, named EO capped polyols. These polyols are used to mould flexible PU foams, especially for car seats. The polyether diol block copolymers PO-EO, with terminal poly[EO] blocks, are successfully used for PU elastomers (microcellular elastomers, shoe soles and so on).

4.1.4.1 Synthesis of Polyether Polyols, Block Copolymers PO-EO with Terminal Poly [EO] Block [1, 4, 12, 51, 52, 106, 108]

The synthesis of polyether triols, block copolymers with terminal poly[EO] block is relatively simple: in the first step a propoxylated intermediate polyether is synthesised by the polyaddition of PO to the starter (glycerol or propylene glycol). After the addition of the required quantity of PO, the unreacted monomer is eliminated by vacuum distillation and the polymerisation continues by the addition of EO, the second monomer.

Generally, the quantity of EO used as a terminal block varies between 5-18%. At EO contents higher than 18-20%, the block copolymers become cloudy liquids or waxes due to the crystallisation of poly[EO] longer chains [106].

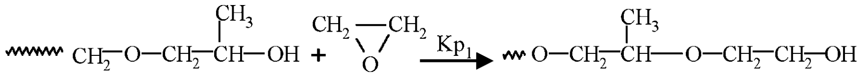
The reactions involved in the synthesis of EO capped polyether triols are:



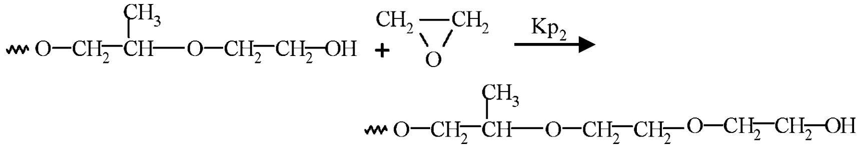
The most important characteristic of EO capped polyethers is the formation of terminal primary hydroxyl groups of hydroxyethyl type. It is well known that primary hydroxyl groups are around 3-3.3 times more reactive than secondary hydroxyl groups in the reaction with aromatic -NCO groups. In the catalysed reactions (for example catalysed by dibutyl tin dilaurate), the reactivity of primary hydroxyl groups is much higher, being around 21 times higher than that of secondary hydroxyl groups [17]. To conclude, due to the high primary hydroxyl content, the polyether polyols (diols or triols), block copolymers PO-EO with terminal poly[EO] block, are much more reactive than the corresponding polyether polyols PO homopolymers, in the fabrication of PU.

When EO reacts with the intermediate propoxylated polyether having secondary hydroxyl terminal groups, two competitive reactions take place:

a) The reaction of EO with the secondary hydroxyl groups:



b) The reaction of EO with the primary hydroxyl groups:



Unfortunately, EO reacts preferentially with the primary hydroxyl groups and as an immediate consequence the concentration of primary hydroxyl groups, as a function of EO content, is a nonlinear variation, practically a curve with a tendency to a limited value [4, 52, 108, 110].

Figure 4.23 shows the variation of primary hydroxyl content of a polyether triol with a MW of 5000 daltons against the EO content [52].

Based on kinetic considerations, an equation (4.16) was proposed which represents the variation of the primary hydroxyl content as function of the quantity of EO reacted [52]. This equation is very similar to the equation of Weybull and Nicander [80, 81] used to measure the distribution of EO sequences per hydroxyl group in ethoxylated nonionic surfactants (for example, ethoxylated fatty alcohols).

$$\frac{[\mathrm{EO}]}{[\mathrm{OH_t}]} = (1-\mathrm{K})\times \mathrm{r} - \mathrm{K}\times 2.303\times \log(1-\mathrm{r}) \tag{4.16}$$

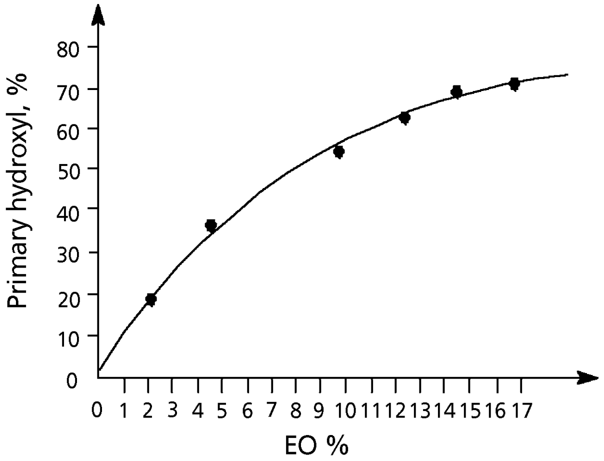


Figure 4.23 Variation of primary hydroxyl content as a function of EO content in polyether triols block copolymers [PO-EO] with terminal poly[EO] block; MW = 5000 daltons; catalyst: KOH - 0.0056 mol%

$$\frac{[EO]}{[OH_t] \times r} = (1-K) - \frac{K \times 2.303 \times \log(1-r)}{r} \qquad (4.17)$$

where:

[EO] = the quantity of EO needed (mol/l);

$[OH_t]$ = total concentration of hydroxyl groups (mol/l);

$[OH_1]$ = concentration of primary hydroxyl groups (mol/l);

$[OH_2]$ = concentration of secondary hydroxyl groups (mol/l);

$[OH_t] = [OH_1] + [OH_2]$ = the sum of concentrations of primary and secondary hydroxyl groups (mol/l);

$r = \frac{[OH_1]}{[OH_t]}$ = molar fraction of primary hydroxyl groups;

K = distribution constant

Representing graphically $\frac{[EO]}{[OH_t] \times r}$, as function of $\frac{2.303 \times \log(1-r)}{r}$, a perfectly straight line is obtained.

The distribution constant K is parameter characterised by the following equation:

$$K = C \times \frac{K_{p1}}{K_{p2}} \times \frac{A_1}{A_2}$$

where:

K_{p1} = the rate constant of the EO reaction with primary hydroxyl;

K_{p2} = the rate constant of the EO reaction with secondary hydroxyl

A_1 = the acidity of primary hydroxyl group;

A_2 = the acidity of secondary hydroxyl group;

C = a constant dependent on the hydrodynamic regime of the reactor, on the conditions of mass transfer and on the particular working conditions.

The intersection of the resulting straight line with the y-axis (**Figure 4.24**) gives the value of 1-K, and then the value of distribution of constant K can be immediately determined.

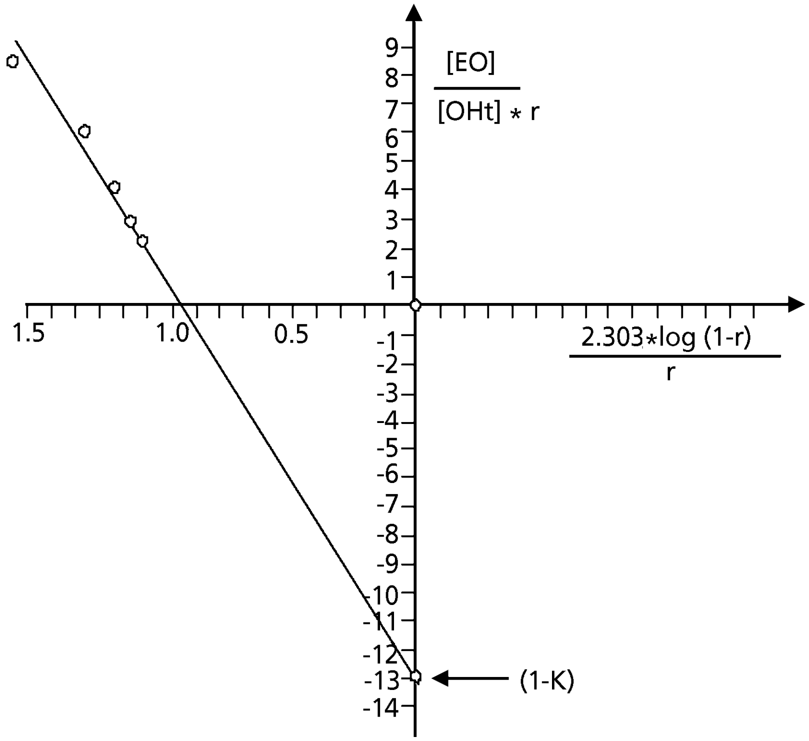


Figure 4.24 Graphical representation of Equation 4.17 in the form of a straight line, at polyether triols of MW of 5000 daltons, block copolymers PO-EO with terminal poly[EO] block; Distribution constant K = 14

Practical experience of many ethoxylation reactions proved that in two different reactors, with different hydrodynamic conditions, at the same EO concentration different primary hydroxyl percentages are obtained.

In ideal conditions, the constant C = 1, but in real conditions C > 1.

If the reaction conditions are maintained at constant, the distribution constant K is an important characteristic of the ethoxylation process. If for a given ethoxylation reaction the distribution constant K is determined at any moment, it is possible to appreciate the quantity of EO necessary to obtain the desired primary hydroxyl content for the synthesised EO capped polyether polyol.

An important aspect of the ethoxylation reaction is that the primary hydroxyl content depends strongly on the hydroxyl number of the intermediate propoxylated polyether polyol. If a polyol is ethoxylated, an intermediate propoxylated polyether with an high hydroxyl number is obtained; if the ethoxylation is done with a lower primary hydroxyl content with the same quantity of EO, an intermediate propoxylated polyether with a lower hydroxyl number is obtained (see **Table 4.9**).

The explanation of this behaviour is clear: if EO units are distributed on a high number of hydroxyl groups, the primary hydroxyl groups are lower compared to the situation in which the same quantity of EO is distributed on a low number of hydroxyl groups. This important dependence is easily observed from the data in **Table 4.9**.

The dependence between [EO], [OHt] and r is reflected by equation 4.16.

$$\frac{[\mathrm{EO}]}{[\mathrm{OH_t}]} = (1-\mathrm{K})\times \mathrm{r} - \mathrm{K}\times 2.303\times \log(1-\mathrm{r}) \tag{4.16}$$

Table 4.9 The effect of the hydroxyl number of the intermediate propoxylated polyether polyol on the primary hydroxyl content (EO concentration was around 10% against final polyol) [50]

No.	OH# of intermediary propoxylated polyether, mg KOH/g	OH# of ethoxylated polyether, mg KOH/g	Primary hydroxyl content of ethoxylated polyether, %
1	437	402	16
2	54	48.5	43
3	36	33	58
4	32	29	71

The rearrangement of equation 4.16 terms leads to equation: of [EO] = f (r):

$$\left[EO\right] = \underbrace{\left[OH_t\right] \times (1-K)}_{a} \times r - \underbrace{\left[OH_t\right] \times K \times 2.303}_{b} \times \log(1-r)$$

$$\left[EO\right] = a \times r + b \times \log(1-r) \tag{4.18}$$

Equation 4.18 is in fact the analytical form of the curves in Figures 4.23 and 4.25.

In practice, it is very important to obtain a high primary hydroxyl content with minimum EO quantity. A high EO content leads to turbid polyether polyols because longer poly[EO] chains are insoluble in liquid polypropylene oxide. The flexible PU foams made with highly ethoxylated polyols have poor humidity/ageing/degradation characteristics and a lower compression strength.

Some important parameters which have an influence on the percentage of primary hydroxyl (at the same EO content) have been experimentally identified, such as:

a) Catalyst concentration,

b) The rate of EO addition,

c) The ethoxylation temperature,

d) The nature of the catalyst, and

e) The presence of traces of unreacted PO.

4.1.4.1.1 The Effect of the Catalyst Concentration on the Primary Hydroxyl Content

The active centres in the anionic polymerisation of alkylene oxides are the alcoholate groups in the presence of a high concentration of hydroxyl groups. If the number of the alcoholate groups is higher, the EO is distributed on a high number of active centres and, as an immediate consequence, the resulting primary hydroxyl content is higher. Thus, by increasing the catalyst concentration from 0.2-0.25 to 0.5% (as KOH), an increase of the primary hydroxyl content of around 10% is observed (**Figure 4.25**).

The same effect of catalyst concentration (catalyst: NaOH) on the distribution of EO sequences/hydroxyl groups was observed in the synthesis of nonionic surfactants of polyethoxylated fatty alcohol types. Thus, by the transformation of 60-100% of the

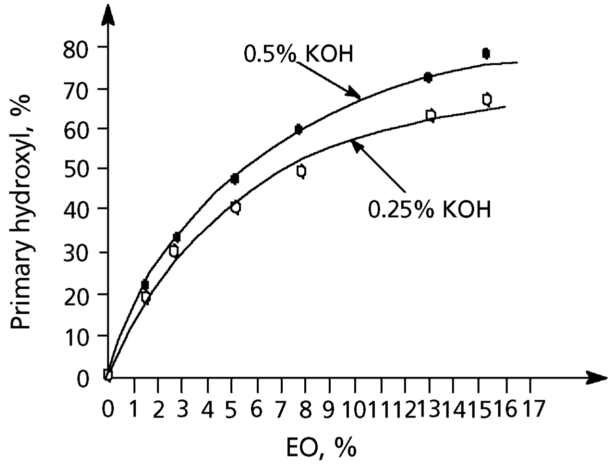


Figure 4.25 The effect of catalyst concentration on the primary hydroxyl content; MW = 4700-5000 daltons; Ethoxylation temperature: 130 °C

hydroxyl groups in the alcoholate groups (high catalyst concentration), there is a very narrow distribution of EO sequences per hydroxyl group, compared to the broad distribution obtained in the presence of catalytic quantities of NaOH.

If all or the majority of hydroxyl groups are transformed in alcoholate groups, the alcohol-alcoholate equilibrium does not takes place any more and the difference in acidity is not important. In conclusion, a convenient method to increase the percentage of primary hydroxyl groups is to increase the catalyst concentration. In practice, especially for high MW capped polyether polyols, in order to obtain a higher primary hydroxyl content, the concentration of catalyst used is 0.3-0.35%, higher than the usual catalyst concentration of 0.2-0.25% (as KOH) used for PO homopolymers or random PO-EO copolyethers [107].

4.1.4.1.2 The Effect of EO Addition Rate on the Primary Hydroxyl Content

As mentioned before, the rate of anionic EO polymerisation is around three times higher than the rate of anionic PO polymerisation under the same reaction conditions.

It was observed experimentally that if the EO addition rate is high (in fact a high ethoxylation pressure), cloudy polyols and low primary hydroxyl content are formed [51]. The explanation of this behaviour is that if the rate of EO addition is too high, the equilibrium of alcohol - alcoholate does not have enough time to get established and the polyethylene oxide chains grow on a limited number of hydroxyl groups. As an immediate consequence, longer poly[EO] chains are formed, which have a tendency to crystallise and cause the polyether to become cloudy.

A low EO addition rate (in fact a low ethoxylation pressure), leads to perfectly clear capped polyols, because the alcohol - alcoholate equilibrium has enough time to get established and, as an immediate consequence, the same quantity of EO is distributed on a high number of hydroxyl groups. Shorter poly[EO] chains derived from a high number of hydroxyl groups are formed and the primary hydroxyl content is higher. To conclude, in order to obtain a high primary hydroxyl content, the rate of EO addition has to be low [51]. For example, for a polyol of MW of 4700-5000 daltons and 15% EO as terminal block, an addition of EO in around three-five hours at 130 °C is a convenient way to obtain a primary hydroxyl content of 70-75%.

4.1.4.1.3 The Effect of Ethoxylation Temperature on the Primary Hydroxyl Content

The studies of PO copolymerisation with EO gives very important information concerning the reactivity of both monomers. The reactivity ratios in EO copolymerisation with PO, as

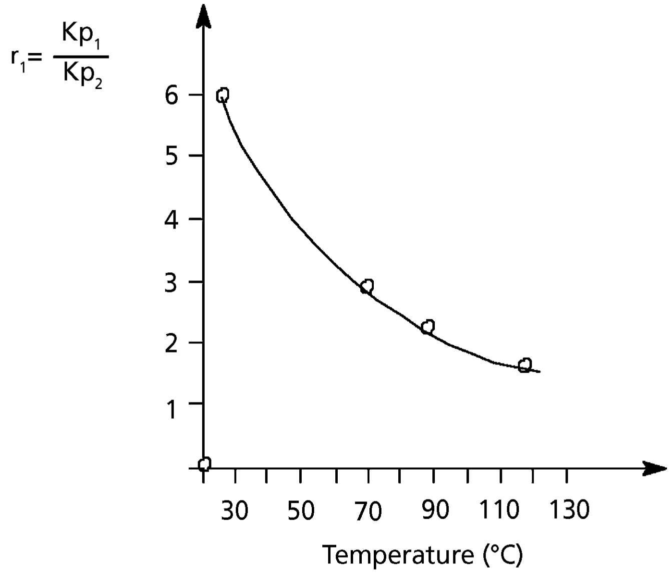


Figure 4.26 Variation of the reactivity constant r_1 *versus* temperature in ethoxylation of the propoxylated intermediate polyethers

a function of temperature, are presented in Section 4.1.3. **Figure 4.26** shows the variation of the reactivity constant r_1 *versus* temperature in the range 70-120 °C (r_1 represents the ratio between the reaction constant of EO with the primary hydroxyl K_{p1}, as per the reaction constant of EO with the secondary hydroxyl K_{p2}).

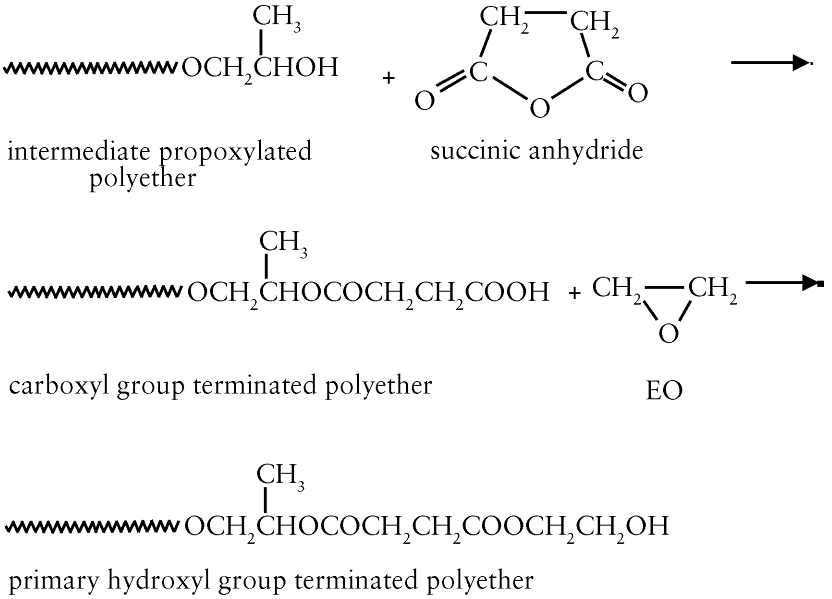
One observes that with temperature increase, the ratio between the reaction rate of EO with the primary hydroxyl, as per the reaction rate of EO with secondary hydroxyl, decreases. If at 70 °C, EO is three times more reactive in the reaction with the primary hydroxyl than with the secondary hydroxyl at 120 °C, EO is only 1.6 times more reactive in the reaction with the primary hydroxyl than in the reaction with the secondary hydroxyl. As an immediate consequence, by ethoxylation of propoxylated polyethers at higher temperatures (125-130 °C), a more uniform distribution of EO units per hydroxyl group takes place and the resulting primary hydroxyl content is higher than that resulting from ethoxylation at lower temperatures (90-105 °C). Of course, another beneficial effect of a higher ethoxylation temperature is that the equilibrium of alcohol - alcoholate is established more rapidly.

4.1.4.1.4 The Effect of the Catalyst Nature on the Primary Hydroxyl Content

In the synthesis of nonionic surfactants (ethoxylated fatty alcohols), it was observed that in acidic catalysis (HBF_4, BF_3 etherate, SbF_5, $HSbF_6$, HPF_6, $HClO_4$) a more uniform distribution of EO sequences per hydroxyl groups takes places, compared to the ethoxylation in anionic catalysis.

Figure 4.27 shows that by the ethoxylation of an intermediary propoxylated triol (MW of 4500 daltons) in the presence of a Lewis acid (BF_3) or a Brönstedt acid (HBF_4), a primary hydroxyl of around 10-15% higher than in anionic catalysis is obtained, at the same EO content.

An extremely high primary hydroxyl content is obtained by reacting a purified propoxylated polyether with a cyclic anhydride (for example succinic anhydride), followed by the reaction with EO (addition of EO to the carboxyl groups formed). A primary hydroxyl content of 60% is obtained, with only 5% EO as terminal block [85]:



It is very interesting that by using alkaline-earth catalysts in the ethoxylation reaction (Ca, Sr or Ba alcoholates or carboxylates), a narrower distribution of EO sequences per hydroxyl group resulted, compared to use of alkaline catalysts. For example, with barium alcoholate as catalyst around 80-85% primary hydroxyl, at 15% EO as terminal block, are obtained with polyether triols (MW of 5000 daltons), compared to 65-75% primary hydroxyl obtained in the presence of KOH. The explanation of this behaviour

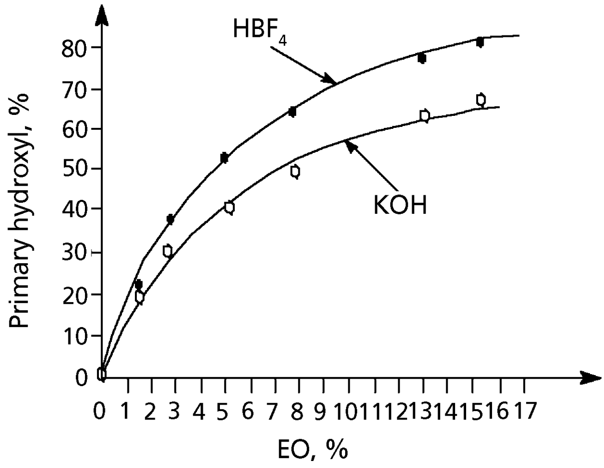
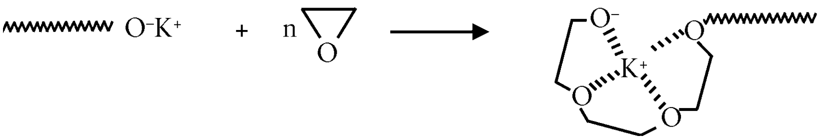


Figure 4.27 The effect of the catalyst nature on the primary hydroxyl content

is the occurrence of a template effect, by the complexation of the potassium cation with the poly[EO] chains formed:



The potassium cation is retained, by complexation, at the same chain end, the alcohol -alcoholate equilibrium is perturbed, and EO reacts preferentially with this template structure and the resulting primary hydroxyl content decreases. In the case of bivalent cations with two positive charges, the alcoholate anion is linked more strongly by electrostatic forces and the coordination of the cation with the formed poly[EO] chains takes place to a much smaller extent.

In conclusion, the ethoxylation catalyst nature has an important influence on the primary hydroxyl content. A higher primary hydroxyl percentage than in the classical reaction catalysed by KOH is obtained by the ethoxylation of the intermediate polyether polyols in acidic catalysis or with alkaline-earth alkoxides or carboxylates [25-29].

4.1.4.1.5 Removing PO before the Ethoxylation Reaction

The last step in the synthesis of the intermediary propoxylated polyether, before ethoxylation, is the degassing step, the elimination of the unreacted PO by vacuum distillation. It was observed experimentally that if the PO is not efficiently removed in the degassing step, the resulting primary hydroxyl content is lower. The explanation is very simple: EO is much more reactive than PO and reacts first. After the addition of the majority of EO, the remaining PO (the less reactive monomer), reacts at the end of chain, transforming part of the primary hydroxyls into secondary hydroxyls.

In conclusion, in order to obtain high percentage primary hydroxyls, it is necessary to remove very efficiently the remaining PO after the synthesis of the intermediate propoxylated polyether.

The polyether diols, block copolymers of PO-EO with terminal poly[EO] block are obtained absolutely identically to the previously described EO capped polyether triols, the difference being that the propoxylated intermediate is a propoxylated polyether diol.

The most important polyether, PO-EO block copolymer structures, having terminal poly[EO] block (structure a) and internal poly[EO] block (structures b and c), are presented in **Figure 4.28**.

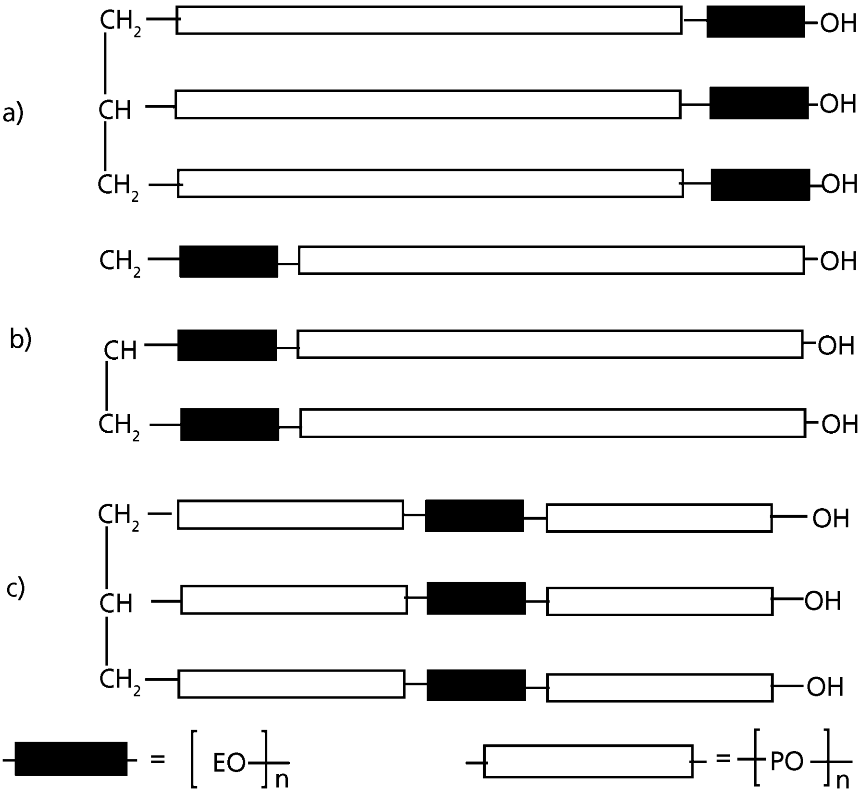


Figure 4.28 The structures of polyether triol block copolymers PO-EO: a) terminal poly[EO)] block; b) poly[EO] block linked to the starter; c) internal poly[EO] block

The most important polyether triol, PO-EO block copolymers with poly[EO] block, used in practice, are:

a) Polyether triols, based on glycerol, PO and EO (terminal block) with a MW of 3000 daltons (**Table 4.10**);

b) Polyether triols, based on glycerol, PO and EO (terminal block) with a MW of 5000 daltons (**Table 4.11**);

c) Polyether triols, based on glycerol, PO and EO (terminal block) with a MW of 6000 daltons (**Table 4.12**);

d) Polyether triols, based on glycerol, PO and EO (internal block) with a MW of 3600 daltons (**Table 4.13**).

Table 4.10 Characteristics of polyether triol, based on glycerol PO-EO block copolymers (terminal block) with a MW of 3000 daltons

Characteristic	Unit	Value
Aspect	–	Viscous liquid
Molecular weight	daltons	3000
Functionality	OH groups/mol	3
Ethylene oxide	%	5
Primary hydroxyl	%	30-35
Hydroxyl number	mg KOH/g	53-59
Viscosity, 25 °C	mPa-s	400-550
Unsaturation	mequiv/g	0.035-0.04
Acidity	mg KOH/g	max. 0.05-0.1
Water content	%	max. 0.05-0.1
Na + K	ppm	max. 5
Colour	APHA	max. 30-50
Application: Hot moulded flexible PU foams for car seating		

Table 4.11 Characteristics of polyether triol, based on glycerol PO-EO block copolymers (terminal block) with a MW of 4700-5000 daltons

Characteristic	Unit	Value
Aspect	–	Viscous liquid
Molecular weight	daltons	4700-5000
Functionality	OH groups/mol	3
Ethylene oxide	%	13-15
Primary hydroxyl	%	65-75
Hydroxyl number	mg KOH/g	33-39
Viscosity, 25 °C	mPa-s	750-1000
Unsaturation	mequiv/g	0.06-0.065
Acidity	mg KOH/g	max. 0.05-0.1
Water content	%	max. 0.05-0.1
Na + K	ppm	max. 5
Colour	APHA	max. 30-50
Applications: Cold moulded high resilience flexible PU foams for car seats, semiflexible and integral skin PU foams, high resilience slabstock flexible foams		

Table 4.12 Characteristics of polyether triol, based on glycerol PO-EO block copolymers (terminal block) with a MW of 6000-6500 daltons

Characteristic	Unit	Value
Aspect	–	Viscous liquid
Molecular weight	daltons	6000-6500
Functionality	OH groups/mol	3
Ethylene oxide	%	13-15
Primary hydroxyl	%	75-85
Hydroxyl number	mg KOH/g	27-29
Viscosity, 25 °C	mPa-s	1000-1200
Unsaturation	mequiv/g	0.08-0.09
Acidity	mg KOH/g	max. 0.05-0.1
Water content	%	max. 0.05-0.1
Na + K	ppm	max. 5
Colour	APHA	max. 30-50
Applications: cold moulded high resilience flexible PU foams, semiflexible and integral skin PU foams, microcellular elastomers (shoe soles)		

Table 4.13 Characteristics of polyether triol, based on glycerol PO-EO block copolymers (internal poly[EO] block) with a MW of 3400-3600 daltons

Characteristic	Unit	Value
Aspect	–	Viscous liquid
Molecular weight	daltons	3400-3600
Functionality	OH groups/mol	3
Ethylene oxide	%	10-12
Secondary hydroxyl	%	94-96
Hydroxyl number	mg KOH/g	450-650
Viscosity, 25 °C	mPa-s	500-650
Unsaturation	mequiv/g	0.045-0.055
Acidity	mg KOH/g	Max. 0.05-0.1
Water content	%	max. 0.05-0.1
Na + K	ppm	max. 5
Colour	APHA	max. 30-50
Application: continuous slabstock flexible PU foams		

The polyether triols (PO-EO block copolymers with terminal poly[EO] block) are very reactive polyols due to the presence of a high percentage of primary hydroxyls. These polyether polyols with terminal poly[EO] block, are used preferentially for moulded flexible PU foams.

The polyols with internal poly[EO] block, used sometimes in slabstock flexible PU foams, give flexible PU foams with lower compression strength than the random copolyether polyols PO-EO, having the same MW and EO content. The poly[EO] block has a softening effect due to the solvation of urea and urethane bonds. These polyethers with internal poly[EO] units are called 'internally activated' polyether polyols. In spite of the presence of terminal low reactivity, secondary hydroxyl bonds (94-96%), a reactivity increase takes place, explained by the catalytic effect of some urethane and urea bonds which are partially solubilised by the poly[EO] block. These urethane and urea groups have a well known catalytic effect on the reaction between isocyanate groups and hydroxyl groups, leading to a self-acceleration effect. As an immediate consequence, the polyether polyols with internal poly[EO] block are more reactive in the foaming process than the random copolyethers of PO-EO of the same MW and EO content.

As an example, a group of polyether diols (block PO-EO copolymers with terminal poly[EO] block) are the polyethers derived from propylene glycol (or DPG), PO and EO of MW of 2000 daltons and around 15-20% EO as a terminal block (**Figure 4.29**).

Table 4.14 Characteristics of polyether diols, block copolymer PO-EO, with terminal poly[EO] block, with a MW of 2000 daltons

Characteristic	UM	Value
Aspect	–	Viscous liquid
Molecular weight	daltons	2000
Functionality	OH groups/mol	2
Ethylene oxide	%	18-20
Primary hydroxyl	%	65-70
Hydroxyl number	mg KOH/g	53-59
Viscosity, 25 °C	mPa-s	400-550
Unsaturation	mequiv/g	0.03-0.04
Acidity	mg KOH/g	max. 0.05-0.1
Water content	%	max. 0.05-0.1
Na + K	ppm	max. 5
Colour	APHA	max. 30-50
Application: PU elastomers, microcellular elastomers (shoe soles)		

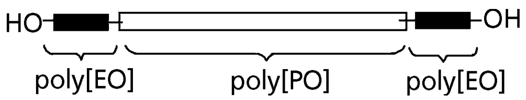
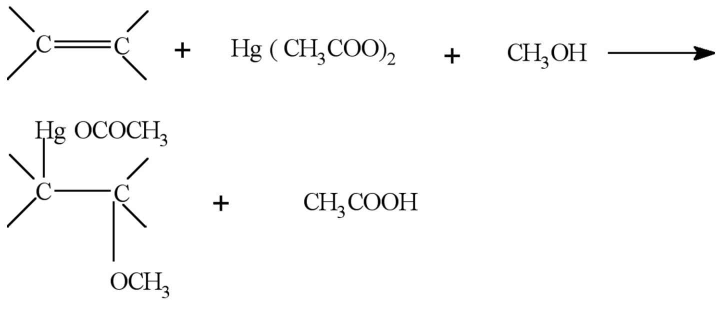


Figure 4.29

In Sections 4.1, 4.1.1, 4.1.2, 4.1.3 and 4.1.4, the chemistry of polyether polyol synthesis, the mechanism and kinetics of alkylene oxide polyaddition to hydroxyl groups and the most important structures of polyalkylene oxide polyether polyols for elastic polyurethanes – PO homopolymers, random PO-EO copolymers and PO-EO block copolymers – were discussed.

Tables 4.9-4.14 show some general characteristics of polyether polyol PO-EO block copolymers, such as MW, hydroxyl number, functionality, viscosity and colour, but also some other characteristics such as unsaturation, EO content, and potassium and sodium content which are specific for polyether polyols.

Unsaturation (standard test methods ASTM D4671 [111] and ISO 17710 [112] represents the amount of terminal double bonds in polyether polyols. One usual method is chemical determination of the double bond content based on the quantitative reaction of mercuric acetate with double bonds in methanol. The reactions involved are:



$$CH_3COOH + NaOH \longrightarrow CH_3COOK + H_2O$$

It is observed that one double bond generates one mol of acetic acid which is neutralised with an equivalent quantity of NaOH of known concentration. This stoichiometry permits an easier calculation of the double bond content.

The unsaturation is expressed in milliequivalents of double bonds per one gram of polyether (mequiv/g). Recent methods for determination of terminal unsaturation in polyether polyols are based on ^1H NMR and ^{13}C NMR spectroscopic methods [88].

In the ^{1}H NMR spectra of polyethers, the protons linked to the carbon atoms of allyl and propenyl double bonds have specific chemical shifts:

^{1}HNMR:		δ (ppm)
allyl end group	$CH_2{=}\overset{*}{C}H{-}CH_2O{-}$	5.70
allyl end group	$\overset{*}{C}H_2{=}CH{-}CH_2O{-}$	5.08; 4.99
propenyl end group	$CH_3{-}\overset{*}{C}H{=}CHO{-}$	4.21
propenyl end group	$CH_3{-}CH{=}\overset{*}{C}HO{-}$	5.81

In the ^{13}C NMR spectra, the chemical shifts specific to the allyl and propenyl double bonds carbon atoms are:

^{13}CNMR:		δ (ppm)
allyl end group	$CH_2{=}\overset{*}{C}H{-}CH_2O{-}$	134.7
allyl end group	$\overset{*}{C}H_2{=}CH{-}CH_2O{-}$	116.4
propenyl end group	$CH_3{-}\overset{*}{C}H{=}CHO{-}$	100.4
propenyl end group	$CH_3{-}CH{=}\overset{*}{C}HO{-}$	145.8

EO content: represents the amount of EO units ($-CH_2CH_2O-$) in copolyether polyols (PO-EO), and random and block copolymers. Determination of EO content is based on two NMR spectroscopic methods (Standard Test Method ASTM D4875 [113]): Method A (^{1}H NMR) and Method B (^{13}C NMR) which are used for an EO content greater or equal to 6%.

The determinations are based on the fact that in EO containing copolyethers the amount of methylene groups is higher than in PO homopolymers, normally because an EO unit has two methylene groups and a propylene oxide unit has one methylene group and one methynic group (CH). In Method A (based on ^{1}H NMR spectra), the ratio of the area corresponding to the CH_2 + CH groups ($\delta = 3.1$-3.5 ppm) per area which corresponds to the methyl groups ($\delta = 0.9$ ppm) is used to determine quantitatively the amount of EO in polyethers. Similarly in the ^{13}C NMR spectra, the area corresponding to CH_2 groups ($\delta = 73$ ppm) per area corresponding to CH_3 groups ($\delta = 18$ ppm) permits the calculation of the EO content in polyethers. The values of the corresponding area are obtained directly from the integral curves. As mentioned previously, the ^{13}C NMR spectra enable much information concerning the polyether structure, such as the primary hydroxyl content, to be obtained. The area corresponding to the carbon atoms linked to primary hydroxyls

(δ = 60.9-62 ppm) divided into the sum of the area corresponding to the carbon atoms linked to primary hydroxyls plus the area corresponding to the carbon atoms linked to secondary hydroxyls (δ = 66.2-66.9 ppm) leads to the direct determination of the primary hydroxyl content in PO-EO copolyethers. The values of the corresponding area are also obtained directly from the integral curves.

Sodium and potassium content in polyethers is determined by flame photometry from aqueous solutions of polyethers disaggregated before, or directly from solutions of polyethers in ethanol. The determinations are based on calibration curves made with solutions having known amounts of sodium and potassium ions. The maximum content of Na and K ions in polyethers was around a maximum of 5-10 ppm. In the polyether polyols used for prepolymer manufacture, the maximum limit for Na and K content is accepted as a maximum of 2 ppm in order to avoid the trimerisation and gelation of the prepolymer during storage.

Based on the knowledge of chemistry mentioned previously, section 4.1.5 now discusses the most important aspects of the technology for polyether polyols fabrication using alkaline catalysts.

4.1.5 Technology for Polyether Polyol Fabrication

The manufacturing process for polyether polyol synthesis using alkaline catalysts consists of the following characteristic steps:

a) Preparation of starter-catalyst solutions,

b) Anionic polymerisation of alkyleneoxides initiated by polyolic starters,

c) Digestion,

d) Degassing,

e) Polyether polyol purification (catalyst removal), and

f) Stabilisation (addition of the antioxidants).

The industrial processes currently used worldwide for polyether polyol synthesis by anionic polymerisation of alkylene oxides are discontinuous processes, a fact that is explained by the great number of polyether polyol types produced in the same reactor and by the relatively low reaction rate of the propoxylation reaction.

In the history of PU, some continuous processes for polyether polyol synthesis by anionic polymerisation were developed, but only at small scale (i.e., pilot plant). Tubular reactors with static mixing systems or a column with plate reactor types were used, but these technologies were not extended to industrial scale levels. The first continuous process for high MW polyether synthesis was developed by Bayer (IMPACT Technology) and is based on the very rapid coordinative polymerisation of alkylene oxides, especially PO, with dimetallic catalysts (DMC catalysts – see Chapter 5). A principle technological scheme of a polyether polyol fabrication plant is presented in **Figure 4.30**.

4.1.5.1 Preparation of Starter-Catalyst Solution

The starter polyol (glycerol, trimethylolpropane) is mixed with an aqueous solution of KOH (40-50% concentration) or with solid KOH (85-90% purity) in reactor 1. The water from the catalyst solution and from the equilibrium reaction with KOH is eliminated from the reaction system by vacuum distillation at 110-130 °C:

$$\mathrm{ROH} + \mathrm{KOH} \rightleftharpoons \mathrm{RO^{-}K^{+}} + \mathrm{H_2O}\uparrow$$

The nitrogen bubbling (generally containing less than 10 ppm oxygen), in the reaction mass greatly increases the efficiency of water distillation, shortening the distillation time. A final concentration of 0.1-0.5% water in the starter-catalyst mixture is acceptable and the water distillation is considered finished. The resultant starter-catalyst mixture is in fact a solution of an alcoholate derived from the starter (e.g., potassium glycerolate). The reason for water elimination is to avoid the formation of high quantities of polyether diols formed by the reaction of alkylene oxides with water, which decreases the functionality of the resulting polyether triols with a tendency to decrease some properties of flexible PU foams, such as compression strength. On the other hand polyether diols increase the elongation and tensile strength of the resulting flexible PU foams.

In polyether diol synthesis using as a starter propylene glycol or DPG, the water distillation is not necessary because water and KOH lead to polyether diols and the final functionality is not affected. The catalyst concentration is calculated to be around 0.2-0.3% (as KOH) against final polyether polyol (around one alcoholate group/10-50 hydroxyl groups). As an initial level, the concentration of KOH against the starter is around 11-15% (as KOH), (high MW polyethers with a MW of 5000-6500 daltons need higher catalyst concentrations compared to polyether polyols with a MW of 3000-3600 daltons.)

4.1.5.2 Anionic Polymerisation of Alkylene Oxides Initiated by Polyolic Starters

Anionic PO polymerisation consists of the PO addition to the starter, at 105-125 °C and 0.3-0.5 MPa. The flow of PO addition is the flow required to maintain the pressure and temperature of the reaction constant, in the stated range. PO, having a low boiling point (bp = 33.6 °C), is volatilised spontaneously by the simple contact with the hot reaction mass at 105-125 °C and generates a pressure. PO is consumed in the polymerisation reaction and a high volatile monomer, PO, is transformed into a compound with a very low volatility: the polyether. As an immediate consequence of PO consumption in the reaction, the pressure has a tendency to decrease and, in order to maintain the pressure constant, PO is continuously added. Of course the temperature is maintained within the required range by continuous elimination of the reaction heat by cooling.

An important technological problem is the volume increase from the starter to the final polyol. Thus, the volume increase from one mol of glycerol to one mol of polyether polyol with a MW of 3000 daltons is theoretically around 30 times, and to one mol of polyether with a MW of 5000-6000 daltons is around 54-65 times. Because the initial quantity of starter is too low to be well stirred, the polymerisation reaction is divided into two steps. In the first step an intermediary MW polyether is synthesised, by polyaddition of PO to the starter called prepolyether (MW = 550-700 daltons) which is stored separately. The synthesis of high MW polyether is very similar, the difference being that the starter is a part of the synthesised prepolyether. The synthesis of prepolyether is possible in a special reactor (reactor 3, **Figure 4.30**) or even in the polymerisation reactor for high MW polyether synthesis (reactor 3, **Figure 4.30**). In the first situation, one batch of prepolyether is calculated to be exactly the quantity for one batch of the final polyether polyol and thus it is not necessary to store quantities of the prepolyether. If the prepolyether is synthesised in the big reactor (reactor 3), a large quantity of prepolyether is obtained which it is necessary to store under nitrogen, in a special storage tank. This quantity of prepolyether is enough for 8-10 batches of final polyether polyols.

The anionic polymerisation of alkylene oxides initiated by different polyolic starters is the most important step of polyether polyol manufacture.

The polymerisation reaction takes place by the stepwise addition of the alkylene oxide to the starter, under an inert protective atmosphere of nitrogen (having less than 10 ppm oxygen), at 120-125 °C and 0.2-0.5 MPa. The inert atmosphere protects the labile polyetheric chain against an undesired thermo-oxidative degradation and, as a consequence, assures a final product with a good colour. The alcoholate groups are very sensitive to oxidation and, in the presence of air at higher temperature, rapidly give brown degradation products. On the other hand PO and EO are very flammable organic substances and in the presence of air are explosive mixtures. As an immediate consequence, a protective, inert atmosphere in polyether polyol synthesis is absolutely obligatory.

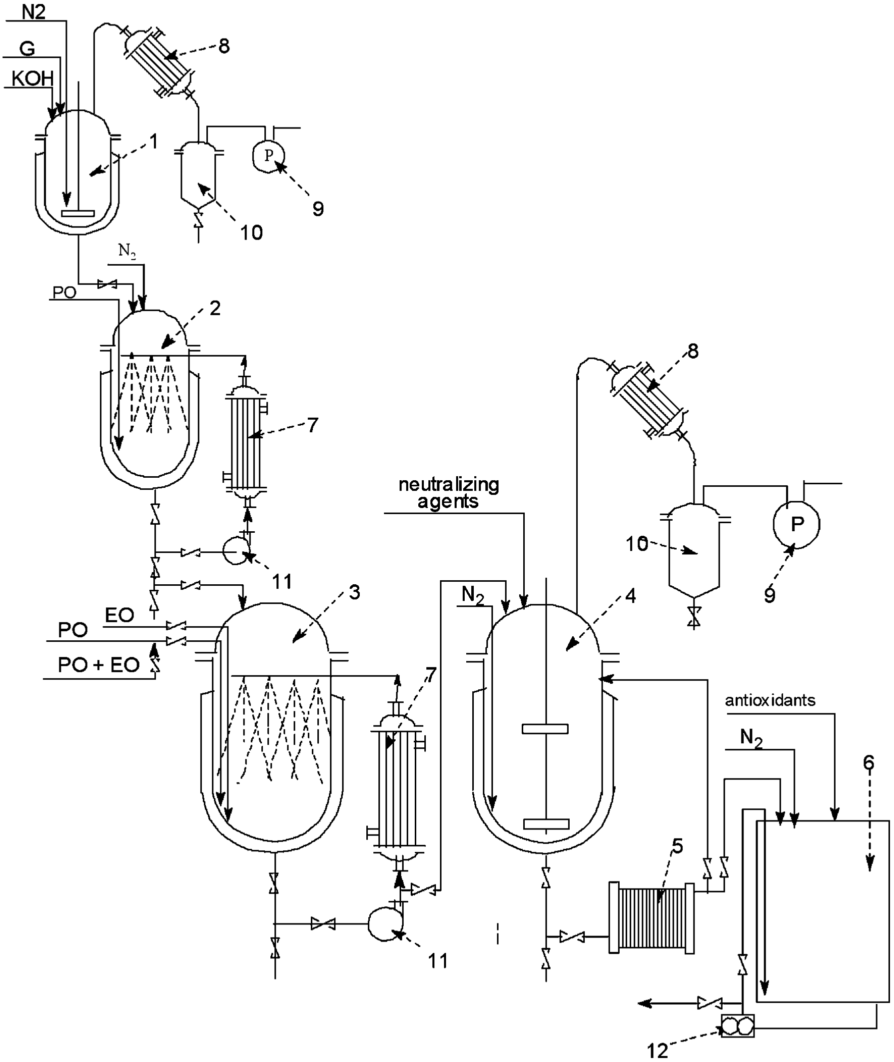


Figure 4.30 Scheme for polyether polyol fabrication by anionic polymerisation of alkylene oxides, initiated by glycerol or diols (variant). *1 - Reactor for potassium glycerolate synthesis; 2 - Reactor for prepolyether synthesis; 3 - Reactor for polyether synthesis; 4 - Reactor for purification; 5 - Filter press; 6 - Storage tank for final purified polyether; 7 - Heat exchangers for removal of the reaction heat; 8 – Condensers; 9 - Vacuum pumps; 10 - Vessels for distilled water; 11 - Recirculation pumps; 12 - Gear pump or screw (or double screw) pump*

The second problem in polyether polyol manufacture is that the oxirane ring opening reaction is very exothermic (22.7 kcal/mol for PO and 26.7 kcal/mol for EO). The reaction heat is eliminated continuously from the reaction mass by cooling with the external mantle and more efficiently by using a loop reactor, having an external heat exchanger on the recirculation flow. The rate of reaction heat elimination is one of the most important parameters which controls the total time of a polyether batch, but the most important is the time of alkylene oxide addition. An inefficient cooling system leads to a long total time of a polyether batch, because the addition of the monomer is frequently stopped in order to maintain the temperature in the required range.

The synthesis of polyether polyols by anionic polymerisation of gaseous monomers such as PO (bp 33.6 °C) and EO (bp 10.3 °C), at 100-125 °C, is a strong, diffusion dependent process. Of course the polymerisation reaction takes place in a liquid state, where the anionic catalyst is present.

The gaseous monomers are divided into two phases – a part in the gaseous phase and a part solubilised in the liquid phase. During the reaction in the liquid phase, the concentration of PO (or EO) decreases and, in order to continue the reaction, it is necessary to transfer the monomer from the gaseous phase to the liquid phase. This mass transfer from the gas phase to the liquid phase is one of the most important parameters which controls the rate of alkylene oxide consumption in this strong diffusion dependent process.

Thus, the reactors having only one stirrer, or stirrer and recirculation, give a low rate of PO or EO consumption. The modern reactors, based on the concept of an efficient gas-liquid contact, generate an extremely high surface (30,000-70,000 m^2/m^3 of reaction mass) by spraying the liquid reaction mass in very fine droplets [62-67, 92, 114-116]. This high contact surface considerably improves the mass transfer from the gas to liquid phase, and without any modification of the polymerisation reaction parameters (temperature, pressure, catalyst concentration), high rates of alkylene oxides consumption are obtained. Therefore, by using reactors of gas-liquid contactor type (spray type or ejector type), rates of alkylene oxide consumption of around three to four times higher are obtained, by the application of the engineering concept of an efficient gas-liquid mass transfer.

Thus, in normal reactors (with stirring or with stirring and recirculation) the rate of PO consumption is around 100 kg/m^3 x h and for EO around 400 kg/m^3 x h. In gas-liquid contactor reactors higher flows of 300-400 kg of PO/m^3 x h and for EO around 1200 kg/m^3 x h are obtained (see Scheme 4.19).

The time needed for one batch synthesis decreases considerably (around three times) and the reactor productivity increases substantially.

Due to the very high monomer consumption rate, it is possible to decrease the catalyst concentration considerably with major advantages for the quality of the final product (better colour, low unsaturation) which gives substantial help for the purification step (a lower quantity of catalyst necessary to be removed).

Thus, the general equation for mass transfer of PO from the gas phase to liquid phase is [62-67, 92]:

$$-\frac{d[PO]}{dt} = K_{mt} \times S \times ([PO_1]-[PO]) \tag{4.19}$$

where:

K_{mt} = mass transfer coefficient;

S = interface area gas-liquid, m^2;

$[PO_1]$ = concentration of PO at equilibrium in liquid polyether (the solubility of PO in polyether in the temperature and pressure conditions used for polymerisation), mol/l;

[PO] = momentary concentration of PO in the polyether, mol/l

The consumption rate of PO, as a consequence of polymerisation reaction in the liquid phase, is characterised by the well known kinetic equation:

$$-\frac{d[PO]}{dt} = K_{p*}[Catalyst] \times [PO]$$

Under the conditions of stationary state, the mass transfer rate of PO from gas to liquid is equal to the chemical consumption rate in the liquid phase:

$$K_{mt} \times S \times ([PO_1]-[PO]) = K_p \times [Catalyst] \times [PO]$$

$$K_{mt} \times S \times [PO_1] = K_{mt} \times S \times [PO] - K_p \times [Catalyst] \times [PO]$$

$$[PO] = \frac{K_{mt} \times S \times [PO_1]}{K_{mt} \times S - K_p \times [Catalyst]} \tag{4.20}$$

Equation 4.20 shows that mass transfer is a determining factor in anionic polymerisation of PO, a high surface area of the liquid reaction mass giving high rates of PO consumption. On the other hand, due to the very high efficiency of stirring, the gas-liquid contactor reactor type assures a very narrow MW distribution of the resulting polyether. For the ethoxylation of intermediate propoxylated polyethers (in block copolymers PO-EO synthesis), the spray technique assures a very narrow distribution of EO sequences in the hydroxyl groups.

The gas-liquid contactor type reactors are extremely safe and may be considered the best reactors for the synthesis of polyether polyols by anionic polymerisation of alkylene oxides, initiated by various polyolic starters (**Figure 4.31**).

Santacesaria deduced a unique rate expression for PO consumption, considering both chemical and mass transfer contributions (Equation 4.21) [62-67]:

$$\frac{1}{V_1} \times \frac{dn_{PO}}{dt} = \frac{K_L \times S \times [PO_1] \times \left(K_O\left[RMX^- M^+\right] + K_p \sum\left[RX(PO)^- M^+\right]\right)}{K_L \times S + K_O\left[RMX^- M^+\right] + K_p \sum\left[RX(PO)^- M^+\right]} \tag{4.21}$$

where:

V_1 = liquid volume;

n_{PO} = number of mols of PO in the liquid;

S = interfacial area;

K_L = liquid mass transfer coefficient without chemical reaction;

$[PO_1]$ = concentration of PO in bulk liquid at equilibrium;

K_O = reaction constant of PO with the starter;

K_p = reaction propagation constant

Due to the high efficiency of the mass transfer from the gas to liquid phase, the spray type reactors and the ejector type reactors are reactors without a stirrer. The total recirculation of the reaction mass with a high flow, together with the generation of a high interface gas-liquid are enough to assure a high mixing efficiency and rapid alkylene oxide consumption.

Excellent papers on the propoxylation and ethoxylation reactions of hydroxyl compounds, considering both the mass transfer and the PO consumption by chemical reaction, which proves the fundamental effect of the mass transfer in these diffusion dependent reactions, were published by Santacesaria and co-workers [62-67, 92] and Cramers and co-workers [117-119] and others [114-116].

An important problem in the case of a polyolic starter propoxylation is the calculation of the quantity of PO needed to be added to a known quantity of a polyolic starter, in order to obtain a desired hydroxyl number.

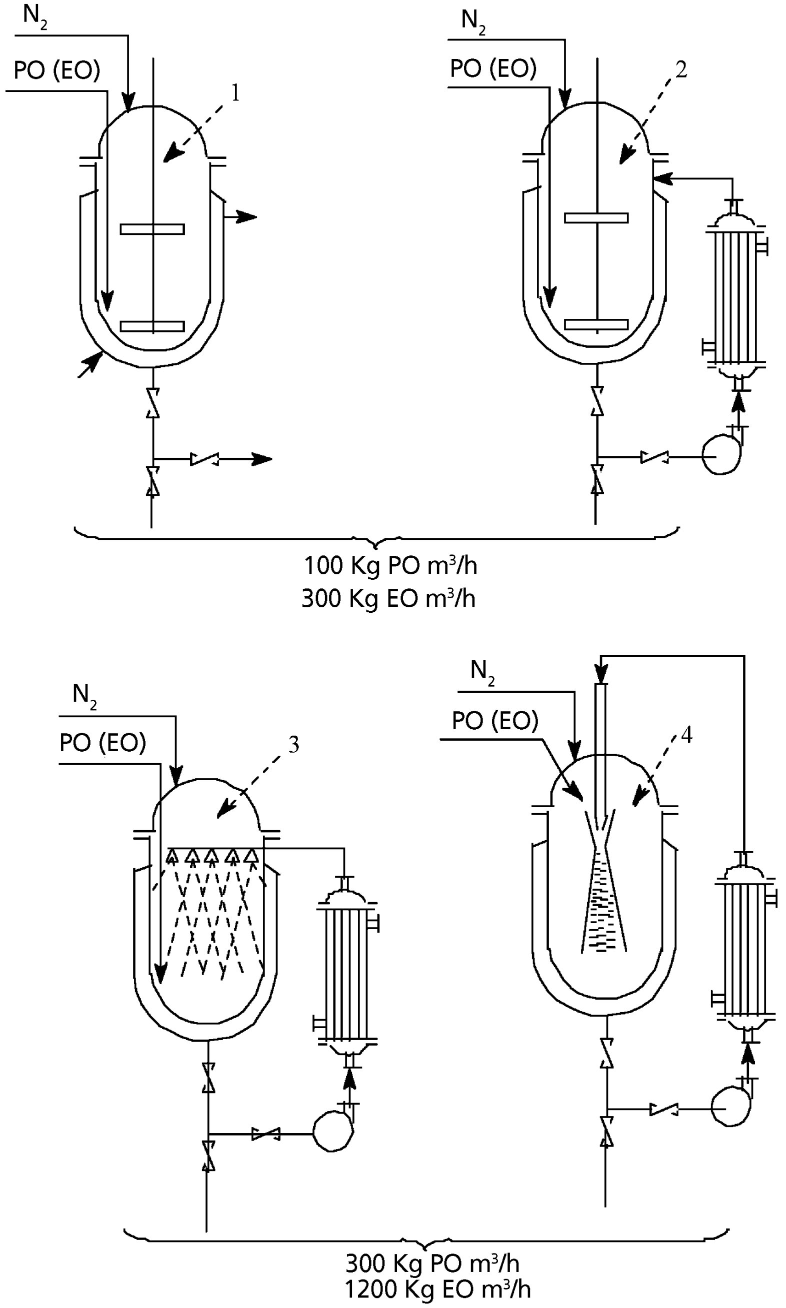


Figure 4.31 Reactor types used industrially for propoxylation and ethoxylation reactions

Based on the theoretical conservation of hydroxyl group number in the reaction system (during the polymerisation a monomer is added, i.e., PO or EO without hydroxyl groups), it is possible to obtain:

$$Q_i \times I_i = Q_f \times I_f$$

where:

Q_i = initial quantity of starter;

Q_f = the quantity of the resulting final polyether;

I_i = hydroxyl number of the starter;

I_f = hydroxyl number of the resulting final polyether

$$Q_f = Q_i + Q_{PO}$$

where:

Q_{PO} = the total quantity of PO needed to be added

$$Q_i \times I_i = \left(Q_1 + Q_{PO}\right) \times I_f$$

$$Q_1 + Q_{PO} = \frac{Q_i \times I_i}{I_f}$$

$$Q_{PO} = \frac{Q_i \times I_i}{I_f} = Q_1$$

$$Q_{PO} = Q_i \times \left(\frac{I_i}{I_f} - 1\right) \tag{4.22}$$

Equation 4.22 is a very useful equation, which is fundamental for the calculation of the theoretical quantity of PO (Q_{PO}) needed to be added to a quantity of starter (Q_i) in order to obtain a polyether with a desired I_f hydroxyl number.

Unfortunately, it was observed experimentally that Equation 4.22 is valid only for low MW PO homopolymers, of a maximum MW of 1000 daltons, such as for the synthesis of prepolyether by propoxylation of glycerol.

To obtain a high MW polyether (3000-6500 daltons), in fact polyethers with low hydroxyl numbers (OH# of 28-56 mg KOH/g), it was observed that a higher quantity of PO is necessary than the theoretical quantity calculated with Equation 4.22.

The excess of PO needed to obtain lower hydroxyl number polyethers is explained by two reasons:

a) The presence of small quantities of water in the starter and in PO leads to supplementary PO consumption. Water, having a very high hydroxyl number (OH# = 6233 mg KOH/g), in small quantities has a measurable effect on the hydroxyl number of the final polyether, and an excess of PO is necessary to obtain the desired final hydroxyl number.

b) The rearrangement of PO to allyl alcohol. PO, a substance without hydroxyl groups, generates a substance having hydroxyl groups (allyl alcohol) during the anionic polymerisation reaction. This transformation is more significant at higher polymerisation temperatures and for higher MW polyethers. The low hydroxyl number of the propoxylated intermediate used in block copolyether synthesis (of hydroxyl number 33-39 mg KOH/g) are very difficult to obtain and need a substantial, supplementary quantity of PO. Thus the real quantity of PO needed to obtain a polyether polyol with a specific hydroxyl number is:

$$Q_{POt} = Q_i \times \left(\frac{I_i}{I_f} - 1 \right) + Q_{POw} + Q_{POr}$$

where:

Q_{POt} = the real total quantity of PO needed;

Q_{POw} = the excess of PO due to the reaction with water;

Q_{POr} = the excess of PO due to the rearrangement of PO to allyl alcohol.

Q_{POr} is difficult to predict theoretically but is frequently determined experimentally. Q_{POr} depends on the reaction temperature history and on the final MW of the polyether.

As an initial level, at a polymerisation temperature range of 110-120 °C, the excess of PO needed is around 10-15% for a MW of 3000-3600 daltons, 20-30% for a MW of 4700-5000 daltons and 35-50% for a MW of 6000-6500 daltons. To obtain low unsaturation in conditions of convenient reaction rates, one considers that 105-110 °C is an optimum polymerisation temperature. Sometimes, for high MW polyethers (MW = 6000-6500 daltons), the final quantity of PO (around 35-40% from the total quantity of PO needed) is added at lower polymerisation temperatures of 90-105 °C or even 90-95 °C. It is a sacrifice for the polymerisation rate but results in an increase in the quality of the synthesised polyether, which will have a low unsaturation, corresponding to a low quantity of polyether monol in a polyether triol.

Because the PO polymerisation is the most important step in polyether polyol synthesis, the maintenance of the reaction parameter constants is extremely important, not only for the quality of the resulting polyethers, but for the safety of the plant as well. As an immediate consequence, sophisticated automation of PO addition, coupled with the automation of the cooling system, using process computers, was developed. Thus, at superior limits of temperature and pressure the PO addition is stopped and begun again when the parameters are once again in the required range of temperature and pressure. At inferior limits of the temperature, the PO addition is stopped to avoid the undesired accumulation of the monomer which leads to a very strong exothermal reaction impossible to control (runway reaction).

4.1.5.3 Digestion

After the addition of the calculated quantity of monomer, a very important step is the consumption of the unreacted monomer, by maintaining the reaction mass at the polymerisation temperature (100-125 °C), under continuous stirring or/and recirculation of the reaction mass. Because the PO addition was stopped, the pressure decreases from 0.35-0.45 MPa to less than 0.1 MPa, in 1.5-2 hours. This step is very important for the improvement of polyether yields and for the loss of a minimum quantity of monomer. The very intensive gas-liquid contactor reactors are extremely efficient in this step of digestion, because the remaining quantity of unreacted monomer decreases very much, in a short digestion time.

4.1.5.4 Degassing

The last traces of unreacted monomer are eliminated in two steps – in the first step by bubbling an inert gas (nitrogen) at the polymerisation temperature and then by application of a vacuum for around one hour, at 1333-26,664 Pa and for the same interval of temperature (100-125 °C).

4.1.5.5 Polyether Polyols Purification

The resulting crude, alkaline polyether contains around 0.2-0.3% of the KOH used as the catalyst. The idea of polyether polyol purification is to remove as much as possible of the alkaline ions until a very low level of 5-10 ppm (the requirements for industrial polyether polyols are < 5 ppm) is left.

A very low level of alkaline ions is needed because of the catalytic effect of these impurities in the reaction involving isocyanates:

a) Sodium and potassium ions catalyse the reaction of isocyanates with hydroxyl groups.

b) Alkaline ions catalyse the trimerisation reaction of isocyanate groups to isocyanurate rings. This reaction is extremely undesired for prepolymers (polyethers with isocyanate end groups), especially those used in elastomers and flexible foams (MDI based flexible PU foams). If the potassium content in the prepolymer is higher than 10-15 ppm, there is a marked tendency towards prepolymer gelification during storage. For some special applications, it is recommended that polyethers with a very low content of potassium ions [maximum 2 ppm (2 parts per million = 0.0002%)] are used in the prepolymer synthesis.

Many important characteristics of the final polyethers depend on the efficiency of the purification step, such as:

a) Sodium and potassium content: should be a maximum of 5 ppm,

b) Acidity: should be a maximum of 0.05-0.1 mg KOH/g,

c) Water content: should be a maximum of 0.05-0.1%, and

d) Colour, should be a maximum of 30-50 APHA.

Purification of 'crude', alkaline polyether polyols is by several methods, applied industrially, such as:

a) Neutralisation with acids of KOH, followed by the crystallisation of the resulting potassium salts and filtration.

b) Treatment with solid adsorbents.

c) Treatment with solid inorganic compounds.

d) Treatment with ion exchange resins.

e) Polyether polyol purification by extraction processes.

f) Other methods.

4.1.5.5.1 Neutralisation with Acids of KOH, Followed by the Crystallisation of the Resulting Potassium Salts and Filtration [4, 120-130]

The principle of polyether polyol purification by neutralisation with acids is simple: the alkaline polyether is neutralised with an aqueous solution of an acid (inorganic or organic) at moderate temperatures (50-90 °C) followed by crystallisation of the resulting potassium salts, anhydrisation by vacuum distillation and filtration.

The most important acids for polyether purification are orthophosphoric acid [120, 121, 129], hydrochloric acid [122], sulfuric acid [121, 131], formic acid [123], tartaric acid [124], oxalic acid [126], adipic acid [126] and carbon dioxide [127, 128, 130].

The presence of water is very important in the neutralisation step because it assures a good ion mobility in the organic media. An important step in this kind of purification is the 'maturation' step, a simple stirring of the polyether containing the resulting potassium salts, at the neutralisation temperature, in order to obtain big crystals which can easily be filtered. The addition of free solid crystals (as seeds), to the neutralised polyether (the same potassium salt resulting, by neutralisation, for example KH_2PO_4 when H_3PO_4 is used for neutralisation) helps the formation of big crystals.

4.1.5.5.2 Treatment with Adsorbents

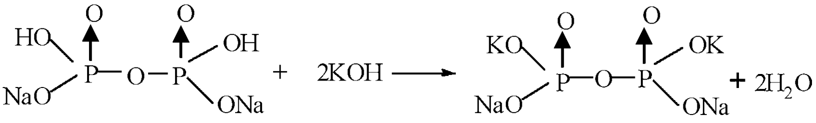
By the treatment of crude, alkaline polyethers, in the presence of water (1-2% against the polyether), with solid adsorbents (1-3% against the polyether) such as aluminium silicates (montmorillonite type, bentonites, activated Fuller's earth) and magnesium silicate (Magnesol) [132, 133], the potassium ion is efficiently retained on the solid surface by adsorption. The high surface area of these adsorbents, i.e., 100-250 m^2/g, helps the adsorption efficiency.

After the contact of the crude polyether with the adsorbents, in the presence of water, at 85-110 °C, for one to three hours, water is distilled under vacuum at 100-130 °C and the resulting solids are separated from the purified polyether by filtration, on a filter with high filtering surfaces (for example press filters). The purified polyether contains around 2-5 ppm of potassium ions, proving the high purification efficiency.

The advantage of this type of purification is the simplicity, but it produces a relatively high quantity of filtration cake which contains around 40-50% of polyether. In order to increase the yield of polyether, the filter is purged with nitrogen, under pressure. Another variant is a solvent extraction of the cake (e.g., with hexane or toluene or other similar solvents), followed by solvent distillation. The recovered polyether represents a yield increase of around 3-4%. The process of cake extraction with PO was developed [134] and the resulting solution of polyether in PO was used in the propoxylation step.

4.1.5.5.3 Treatment with Solid Inorganic Compounds

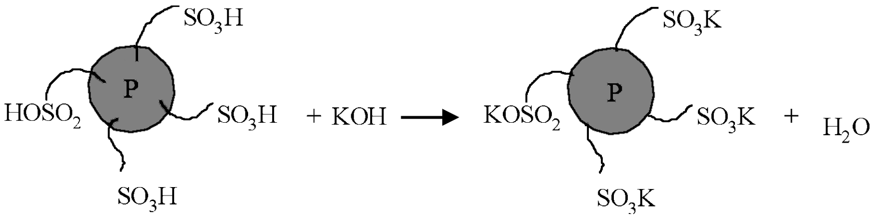
Inorganic, solid, acidic compounds, insoluble in polyethers, were used as efficient agents for the elimination of alkaline ions from the crude polyether polyols. The treatment of crude alkaline polyether, at 85-100 °C, with 1.5-2% of disodium acid pyrophosphate, in the presence of 1-2% water, leads to an efficient neutralisation of the catalyst-potassium ions being retained on the solid surface, by an ion exchange mechanism:



Water is removed by vacuum distillation and the resultant solid is separated from the purified polyether by filtration under pressure (0.4-0.6 MPa), at 80-100 °C. Similar results are obtained with calcium acid orthophosphate ($Ca(H_2PO_4)_2$) [97].

4.1.5.5.4 Treatment with Ion Exchange Resins [135]

The treatment of alkaline, crude polyether polyols with strongly acidic cation exchange resins (copolymer of styrene - divinylbenzene with sulfonic acid groups) is a very efficient purification method. The treatment is performed at moderate temperatures (for example 50-70 °C) in the presence of water or, better still, in the presence of a solvent such as methanol or a methanol-water mixture. The treatment may be static (by mixing the crude polyether with cation exchange resin in a reactor, followed by filtration) or, much better, in a dynamic system, in columns with cation exchange resins. The removal of alkaline cations is very efficient, sometimes less than 1 ppm of potassium ions being obtained:



The method has some disadvantages: the cation exchange resin needs to be regenerated by treatment with an aqueous solution of an acid, and a relatively high volume of wastewater results. This water contains potassium salts, acids and polyether which is not toxic but is not biodegradable either. For an efficient process, the solvent (methanol) needs to be recovered and recycled in the process. In spite of these disadvantages, the quality of the resulting polyethers is high., but this purification process is rarely used on an industrial scale.

4.1.5.5.5 Polyether Polyol Purification by Extraction Processes [130,136, 137]

Polyether polyols, homopolymers of PO, with high MW (2000-4000 daltons) are insoluble in water (the solubility of PO homopolymers in water is low, around 0.3%). By mixing a polyether polyol, PO homopolymer with water, after neutralisation with an acid, (polyether:water ratio = 1:3), at around 70 °C, two layers are formed: a superior polyether layer (with some water) and an inferior layer containing water and the potassium salt. After the efficient contact between these two layers by stirring, the stirring is stopped, the two layers are separated and the inferior layer is removed. After three washings with fresh water, polyether separation and water distillation, a polyether with a potassium content less than 10 ppm is obtained. The volume of water used is very high, and this is one disadvantage of this method. A second disadvantage is the fact that PO-EO copolyethers (block or random PO-EO copolymers) are impossible to purify by this method since emulsions, which are impossible or very difficult to separate into two layers, are obtained with water.

For PO-EO copolyethers, the extraction method may be used in the presence of a low density solvent for polyether, insoluble in water such as *n*-hexane (the ratio of polyether:hexane is 1:1).

After the neutralisation of the alkaline catalyst with an acid, the polyether is diluted with *n*-hexane. The polyether solution is contacted with water in counter flow using continuous centrifugal extractors. As a consequence of the extraction, two layers appear: the upper layer contains a solution of polyether in hexane and the lower layer contains water and the potassium salt. The upper layer is separated and the pure polyether is obtained by solvent vacuum distillation. The disadvantages of this process are a large volume of wastewater and the necessity of solvent recovery and recycling.

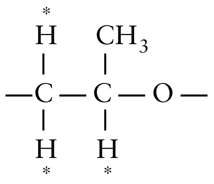
4.1.5.5.6 Other Methods of Polyether Purification

An interesting and efficient purification process for the polyether polyols is electrodialysis with ion exchange membranes [138]. Another unconventional purification method is the treatment of crude polyether with glycerol [139]. The purification is based on the fact that glycerol, with potassium alcoholates, gives an insoluble complex in polyether (probably potassium glycerolate). The solid complex of glycerol - potassium is filtered and reused as a starter, together with fresh glycerol, for a new polyether batch. The resulting polyether polyol has a low potassium content (< 10 ppm).

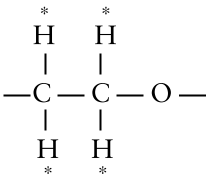
The most important processes for polyether polyol purification, used frequently on an industrial scale, are the first two processes: the neutralisation with acids followed by crystallisation of potassium salts, then filtration and the treatment with adsorbents.

4.1.5.6 Polyether Polyols Stabilisation [4, 9, 140, 141]

Polyethers being simple aliphatic ethers are very susceptible to auto-oxidation (self-oxidation), even by simple storage in air at room temperature. This behaviour is explained by the lability of the hydrogen atoms situated in the alpha position (attached to the carbon atoms linked to the etheric oxygen atoms of polyetheric chains):



$$-\underset{\substack{| \\ \mathrm{H} \\ *}}{\overset{\substack{* \\ \mathrm{H} \\ |}}{\mathrm{C}}}-\underset{\substack{| \\ \mathrm{H} \\ *}}{\overset{\substack{\mathrm{CH_3} \\ |}}{\mathrm{C}}}-\mathrm{O}-$$



$$-\underset{\substack{| \\ \mathrm{H} \\ *}}{\overset{\substack{* \\ \mathrm{H} \\ |}}{\mathrm{C}}}-\underset{\substack{| \\ \mathrm{H} \\ *}}{\overset{\substack{* \\ \mathrm{H} \\ |}}{\mathrm{C}}}-\mathrm{O}-$$

The tertiary hydrogen atom from the PO unit is very susceptible to radical attack.

The protection of polyether polyols against self-oxidation and thermo-oxidative degradation is realised by the addition, to the purified polyethers, of 2000-5000 ppm of antioxidants such as hindered phenols, substituted diphenylamines, phenothiazine, trialkyl phosphites and so on.

The stabilisation of polyether polyols has two objectives:

a) To protect the polyether chains during storage at room temperature.

b) To protect the polyether chains against thermo-oxidative degradation, especially in the PU processes where there are very high temperatures, such as in the continuous flexible PU slabstock process (antiscorching action).

The antioxidants are added to purified polyethers (not to alkaline polyethers which lead to the appearance of some undesired coloured compounds). The homogenisation with the polyethers is realised in storage tanks with an efficient mixing system, such as total recirculation or stirring with special stirrers, at low or moderate temperatures. The recirculation of polyethers at low temperatures is possible by using screw or double screw pumps or gear pumps especially designed for high viscosity liquids. Some examples of important antioxidant structures, commercialised by Ciba-Geigy are presented in **Figure 4.32**. The synergism between two or three antioxidants is noted, such as:

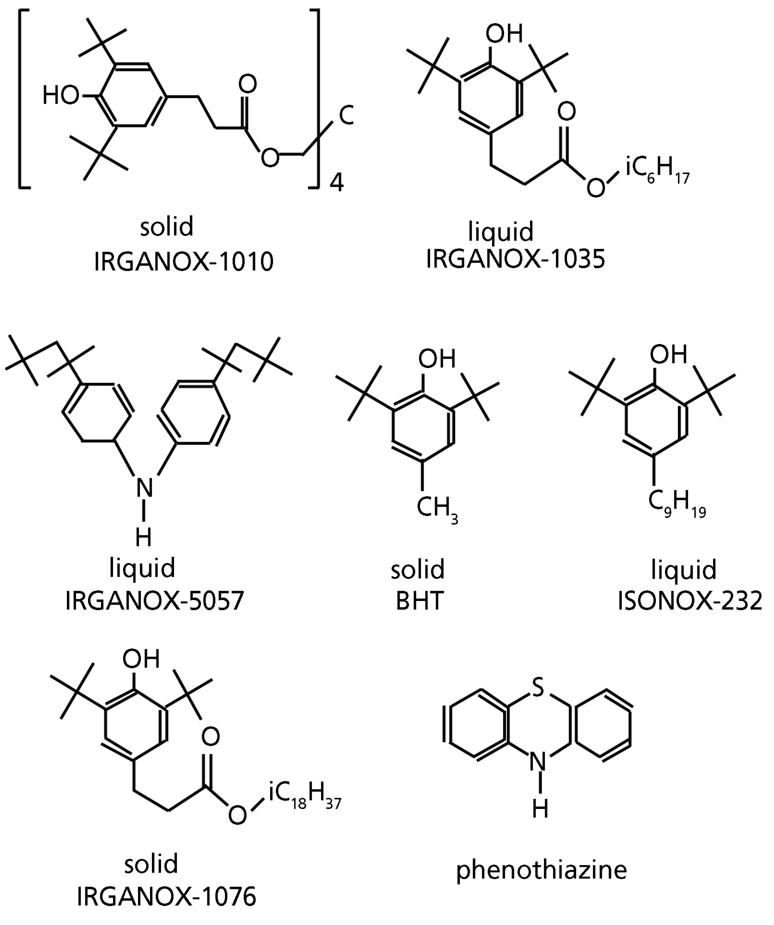
a) hindered phenols - alkylated diphenylamines,

b) hindered phenols - alkylated diphenylamines-phenothiazine, and

c) hindered phenols – phenothiazine.

Generally, liquid antioxidants are preferred, since they are more easily handled and homogenised with the polyethers.

The general flow diagram for the polyether polyol fabrication is presented in **Figure 4.33**.



solid
IRGANOX-1010

liquid
IRGANOX-1035

liquid
IRGANOX-5057

solid
BHT

liquid
ISONOX-232

solid
IRGANOX-1076

phenothiazine

Figure 4.32 Various antioxidant structures currently used in polyether polyol stabilisation

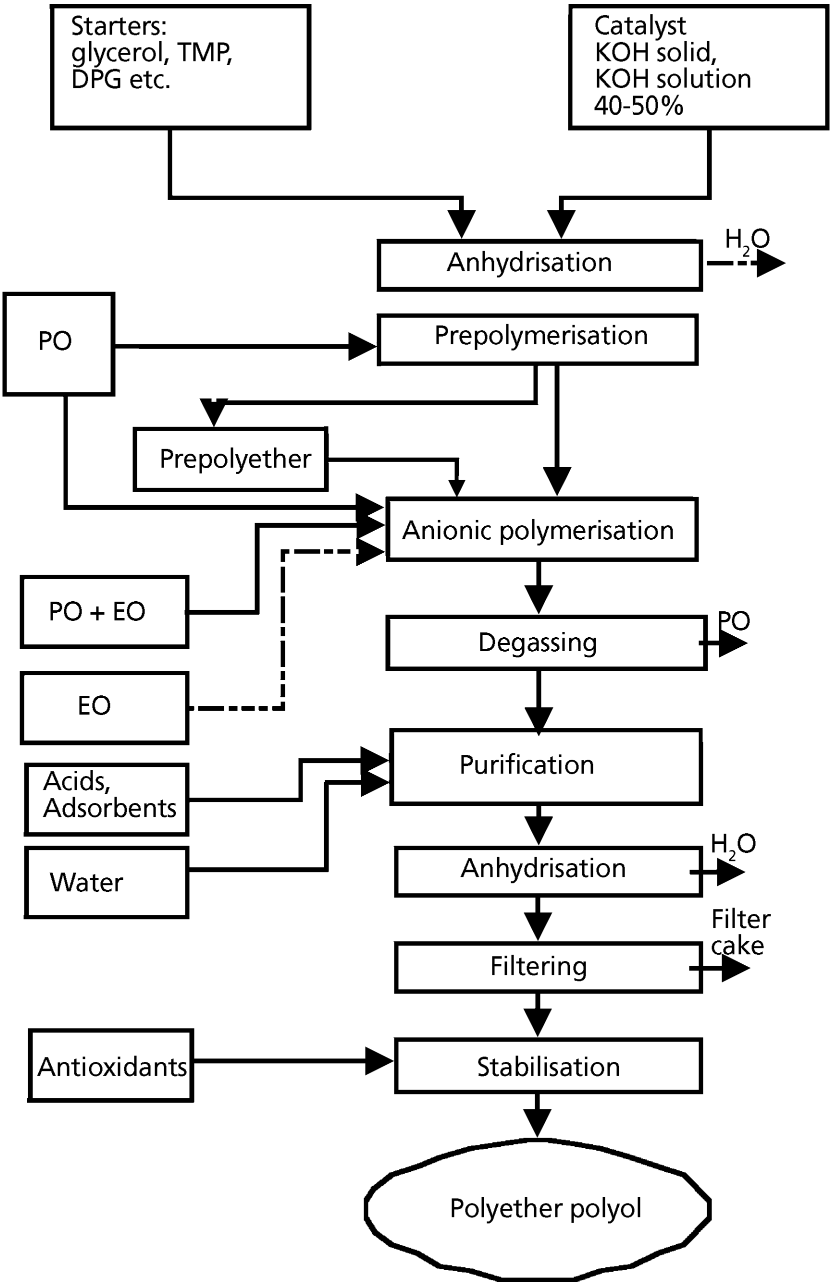


Figure 4.33 General technological flow for polyether polyol fabrication by anionic polymerisation

4.1.5.6.1 The Problem of the Presence of High MW Poly(propylene oxide) in PO Monomer

During the storage of PO, the formation of a high MW poly(propylene oxide) with a MW of 50,000-400,000 daltons and in very small quantities, as a consequence of the contact of liquid PO with the metal walls (carbon steel) of the storage tanks, was observed. The formation of this high MW polyether is explained by the co-ordinative anionic polymerisation of PO, catalysed by the oxides of aluminium, chromium, iron and nickel existing on the metallic surfaces.

This high MW poly(propylene oxide) (PPO) is a very dangerous contaminant. The polyether polyols obtained by using a PO with a content of high MW PPO (higher than 0.3-1 ppm), lead in the foaming process to very undesirable phenomena: the foam collapse with a low foam rise and substantial blow hole formation.

In order to avoid these extremely dangerous phenomena, methods of treatment of PO with adsorbents (active carbon, charcoal, attapulgite, diatomaceous earth) were devised. By the treatment at room temperature of PO with these adsorbents (0.1-1% adsorbent in liquid PO), after a short contact time of about 15 minutes the high MW polyether is almost quantitatively retained by adsorption. The PO resulting after the filtration of the solid adsorbent is practically free of high MW polymers, and the polyethers obtained with the treated PO can be used to manufacture resilient flexible foams which will not collapse, with high rise and free of blow hole formation.

The treatment of PO is made by classical methods: static bed percolation or dynamic flow through a bed of granular adsorbents or other methods.

Formation of this very high MW PPO is possible not only during PO storage but also during PO polymerisation with DMC catalysts, but never with anionic catalysts (see Section 4.9). The antifoaming effect is due to the precipitation of the high MW polymer during the foaming process, a phenomenon which doesn't appear with low MW PO homopolymers. The random copolymers PO-EO, with around 15-18% EO, eliminate this phenomenon, even at high MW, probably because the copolyether remains soluble in the foaming mixture.

In conclusion, to obtain a good, resilient, flexible PU foam without collapse, with high rise and free of blow holes, it is necessary that the PO used for the polyether synthesis be free of high MW PPO contaminants.

4.1.5.7 The Problem of Colour in Polyether Polyol Fabrication

The colour of polyether polyols is an important characteristic, the maximum value of colour accepted being around 50 APHA. For some polyether polyols, the maximum accepted value for colour is 30 APHA, which is practically a colourless product.

A low colour increases the commercial value and the polyether probably has an unaltered structure, without chain destruction and formation of new compounds, having labile groups such as aldehydes, ketones, esters or hydroperoxides. IR analysis of chromophoric groups in polyether polyols proved that colour is given mainly by carbonylic groups linked to double bonds [97]. Some important factors which have a strong influence on polyether polyol colour are discussed in Sections, 4.1.5.7.1, 4.1.5.7.2 and 4.1.5.7.3.

4.1.5.7.1 The Oxygen Content in the Inert Gas

The oxygen content of the inert gas (nitrogen) used in all steps of polyether fabrication, especially in the alkylene oxide anionic polymerisation step, has a very strong influence on the final colour of polyether polyol. It is well known that if the crude, alkaline polyether having alcoholate active groups, is in contact with air at the polymerisation temperature (100-125 °C), an intensive darkening of the reaction mass takes place. Good protection of the polyetheric chain during synthesis is assured using very pure nitrogen gas as an inert atmosphere, having a maximum oxygen content of 10 ppm.

4.1.5.7.2 The Propionaldehyde Content of PO Monomer (or Acetaldehyde in EO) and the Aldehyde Content of Starter

The propionaldehyde content of PO strongly affects the colour of the resulting polyether polyols, explained by an uncontrolled condensation of the aldehyde in the presence of an alkaline medium. A maximum of 10 ppm of propionaldehyde in PO of is perfect for a very good colour in the resulting polyether polyols. A maximum content of 50 ppm propionaldehyde is acceptable, but the crude polyether has a yellow colour, which fortunately is removed in the propoxylation step. A propionaldehyde level higher than 100 ppm leads to serious colour problems in polyether synthesis.

Utilisation of pure glycerol as a starter is very important for a good colour in polyether synthesis (called ‘urethane grade’ glycerol). The glycerol resulting by hydrolysis of fats or vegetable oils sometimes contains aldehydes (acrolein) which give colour problems. For polyether synthesis, a very pure glycerol of a minimum 99.5% purity, distilled in vacuum, without aldehydes or ester groups, is necessary to obtain polyether polyols with a good colour.

4.1.5.7.3 Effect of the Purification Step on the Polyether Polyol Colour

The purification step strongly improves the colour of final polyether polyols. Thus, by simple mixing of crude, alkaline polyether polyol with water, before neutralisation, in the presence of air, at 100 °C, a remarkable improvement in the colour takes place [42, 43]. In the absence of water, the colour deteriorates and the polyether becomes dark brown. Probably water participates chemically in complex reactions, by a mechanism which is not very clear.

The treatment of crude, alkaline, polyether polyol with adsorbents, in the presence of water (silicates of aluminium or magnesium having a big adsorption surface), at 80-100 °C, leads to a remarkable improvement in polyether polyol colour. Probably the polar chromophoric groups are adsorbed preferentially on the solid surface of the adsorbents.

Another experimental observation is that an acidic media always markedly improves the colour of polyether polyols. Thus by the addition to a crude polyether polyol, in the presence of water, of inorganic or organic acids, such as phosphoric, hydrochloric or adipic acids, a strong improvement in the colour takes place.

The addition of very small quantities of oxalic acid to a purified polyether polyol, improves the colour [97]; this is probably explained by the reducing capability of oxalic acid.

Another practical observation to be noted is that the simple storage of a purified polyether polyol, under air and at room temperature for one to two weeks leads to an evident enhancement of the colour.

The presence of antioxidants in polyethers has a negative influence on the colour. If the polyether is not very well purified and has a basic pH, the phenolic antioxidants are oxidised to quinonic chromophoric structures, which negatively affect the colour of polyether polyols. This is the reason why it is preferable to add antioxidants to the slightly acidic purified polyol and not to the alkaline polyether.

If traces of transitional metals are present accidentally (Fe^{3+}, Cr^{2+}, Ni^{2+}) in the polyether polyols, these ions interact with the antioxidants and give chromophoric substances by complexation with hindered phenols or with the alkylated diphenylamines.

It was proved experimentally that with polyether polyols having a high colour of 80-100 APHA, good flexible PU foams were obtained, with corresponding properties.

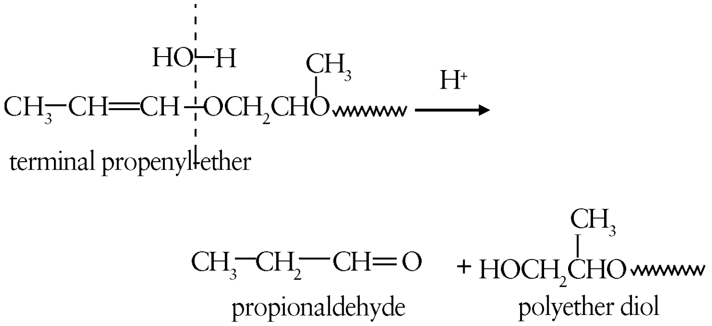
A good colour, less than 50 APHA, increases the commercial value of these products because it proves that the polyether chains have not been degraded during the fabrication process.

4.1.5.8 The Problem of Odour of Polyether Polyols [60, 90, 142]

The polyether polyols for flexible PU foams frequently have a distinct, unpleasant smell. In case of flexible slabstock foams where, in the centre of the PU bun, there are high temperatures (150-170 °C), an unpleasant odour appears during the foaming process which remains for a long time in the resulting PU foams.

The explanation for the existence of a polyether polyol odour is given by the presence of some low MW volatile impurities which in small concentrations give an intense and unpleasant odour.

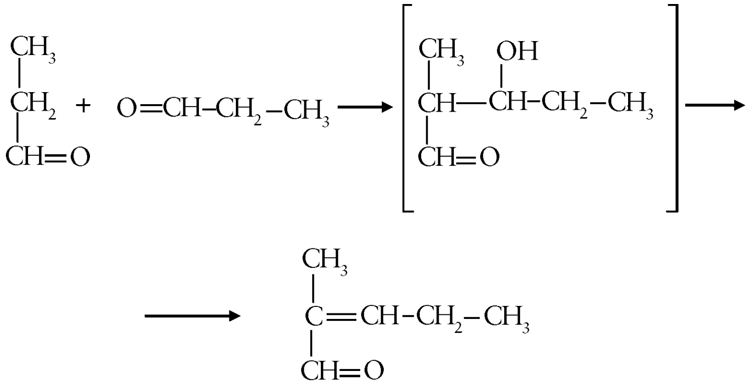
One impurity is propionaldehyde, which is found in PO used as monomer, but it is generated in the purification step by hydrolysis of the terminal propenyl-ether groups:



$$\underset{\text{terminal propenyl ether}}{CH_3-CH=CH-\overset{HO-H}{\vdots}OCH_2\overset{CH_3}{\overset{|}{C}}HO\sim\sim\sim} \xrightarrow{H^+} \underset{\text{propionaldehyde}}{CH_3-CH_2-CH=O} + \underset{\text{polyether diol}}{HOCH_2\overset{CH_3}{\overset{|}{C}}HO\sim\sim\sim}$$

(4.23)

The self-condensation of propionaldehyde by crotonic type condensation to 2-methyl-2 pentenal (4.24) is another possible source of compounds with an unpleasant odour in polyethers [142]:

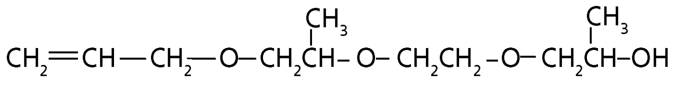


$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH=O \end{array} + O=CH-CH_2-CH_3 \longrightarrow \left[\begin{array}{l} CH_3 \quad OH \\ | \qquad\ \ | \\ CH-CH-CH_2-CH_3 \\ | \\ CH=O \end{array} \right] \longrightarrow \begin{array}{l} CH_3 \\ | \\ C=CH-CH_2-CH_3 \\ | \\ CH=O \end{array}$$

(4.24)

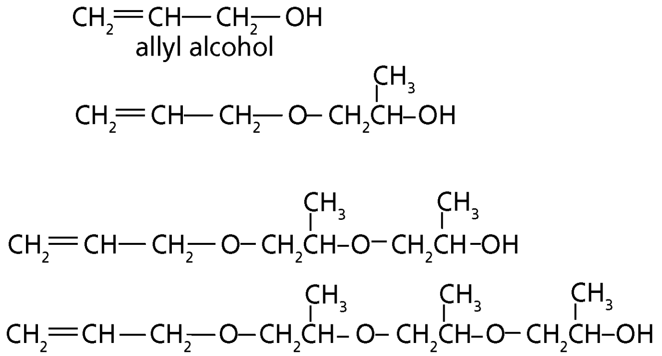
Another group of substances which give an unpleasant odour to polyether polyols is the allyl alcohol (formed by the rearrangement of PO) and its hydroxypropyl ethers formed by propoxylation of allyl alcohol during the anionic polymerisation process. By using a high vacuum distillation technique, the allyl ethers with one, two and three PO units were isolated (**Figure 4.34**).

In the case of random PO-EO copolyethers, a mixed allyl ether having both PO and EO units was identified by mass spectrometry:



$$CH_2{=}CH{-}CH_2{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}O{-}CH_2CH_2{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}OH$$

During the purification step, especially in the purification of polyethers with adsorbents (for example with aluminium silicates) a specific odour appears due to a cyclic compound, which was identified as cyclic acetal of dipropyleneglycol with propionaldehyde (2-ethyl-4,7-dimethyl-1,3,6-trioxacane) (**Figure 4.35**).



$$CH_2{=}CH{-}CH_2{-}OH$$

$$CH_2{=}CH{-}CH_2{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}OH$$

$$CH_2{=}CH{-}CH_2{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}OH$$

$$CH_2{=}CH{-}CH_2{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}O{-}CH_2\overset{\overset{CH_3}{|}}{C}H{-}OH$$

Figure 4.34 The structure of allyl alcohol and allyl ethers which gives the odour in polyether polyols

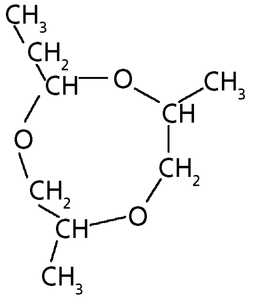
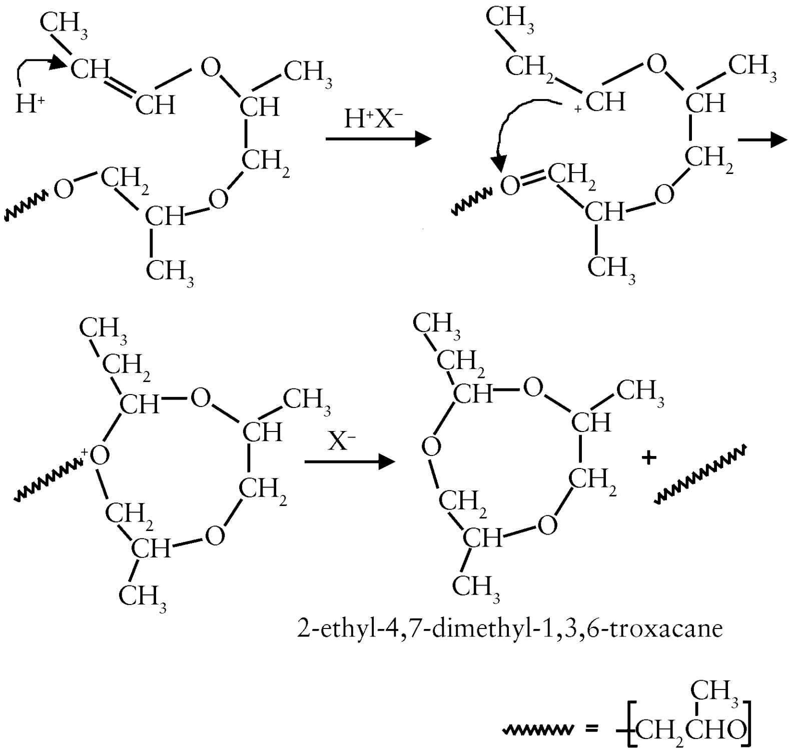


Figure 4.35 2-Ethyl-4,7-dimethyl-1,3,6-trioxacane

This compound proved to be the most powerful odorant agent in polyether polyols. Even in trace amounts, this substance confers an unpleasant odour to polyether polyols. The formation of this compound takes place in the purification step, in acidic media, involving the terminal propenyl-ether groups (in fact vinyl ether groups are very sensitive to acidic attack). The probable mechanism is the following cationic cyclisation:



2-ethyl-4,7-dimethyl-1,3,6-troxacane

The odour of polyether polyols is eliminated by several methods. One efficient method is to introduce into the liquid hot polyether polyol (at around 120 °C), under vacuum, fine drops of liquid water [142]. Water, of course, is transformed into a vapour, which is eliminated together with traces of substances that give the odour (some of these substances may give azeotropic mixtures with water, with a decrease in the boiling point).

Another efficient method is steam stripping. A flow of steam, at 110-125 °C, is introduced continuously, in counter flow, with a descending flow of polyether, in a classical column with plates, situated under vacuum [142] (**Figure 4.36**).

The resulting polyether, after water elimination by vacuum distillation, does not have any perceptible organoleptic odour.

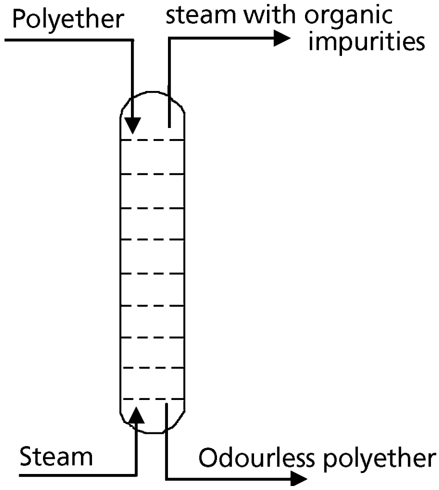
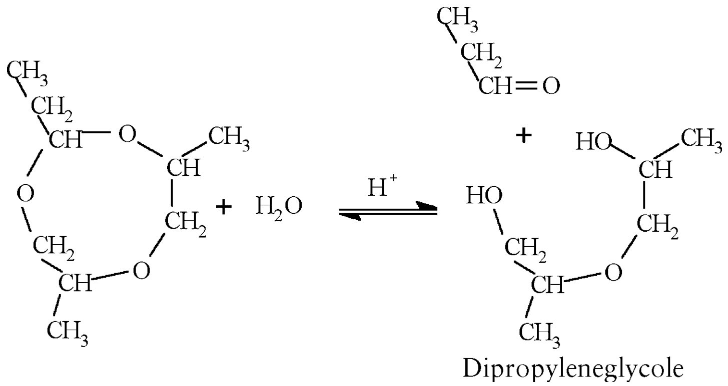


Figure 4.36 Steam stripping of polyether polyols in counter flow, in column with plates

The most interesting method of polyether polyol odour elimination is based on the acidic hydrolysis of the purified polyether [90]. Thus a polyether polyol is treated with 10% water in the presence of an acid (H_2SO_4 or HCl) at 90-100 °C, for one to two hours. The propenyl ether is hydrolysed to propionaldehyde and, instead of a double bond, a hydroxyl group is generated (reaction 4.23). At the same time the cyclic compound in **Figure 4.35**, formed during the purification step, is hydrolysed with the formation of propionaldehyde and dipropyleneglycol:



(4.25)

The main idea of the process is not to distil the water under acidic media, because reaction 4.25 is reversible and the cyclic compound in **Figure 4.35** can be regenerated, the reaction 4.25

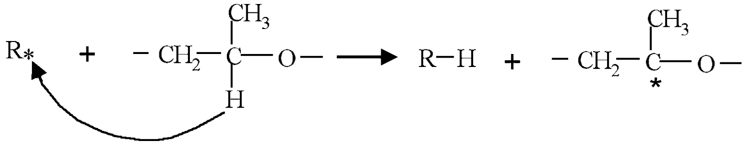
equilibrium being pushed to the left, by water elimination from the reaction system. Of course this reversible reaction takes place only in acidic catalysis (a general reaction of acetals). Under these circumstances, the acid catalyst is neutralised before water distillation, until the polyether becomes slightly basic. The water is distilled under vacuum, together with the propionaldehyde, and the polyether is purified again by normal procedures. The resulting polyether has no perceptible organoleptic odour and has the big advantage of the disappearance of the propenyl terminal double bonds. The total unsaturation of the resulting polyether decreases by 20-25%, compared to the initial polyether, before treatment.

4.1.5.9 Considerations of the 'Scorching' Phenomenon [140]

The thermo-oxidative degradation of the polyether chains is a classical chain reaction involving free radicals, characterised by the well known steps of initiation, propagation and termination [4, 9, 140]:

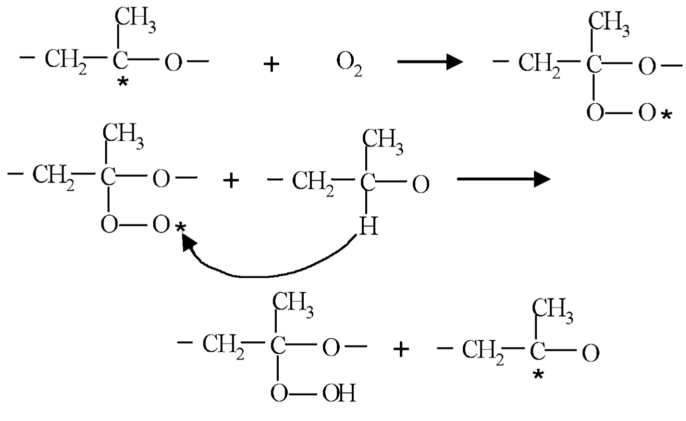
a) Initiation

A radical R* abstracts a hydrogen atom from the polyetheric chain generating a polymeric radical:



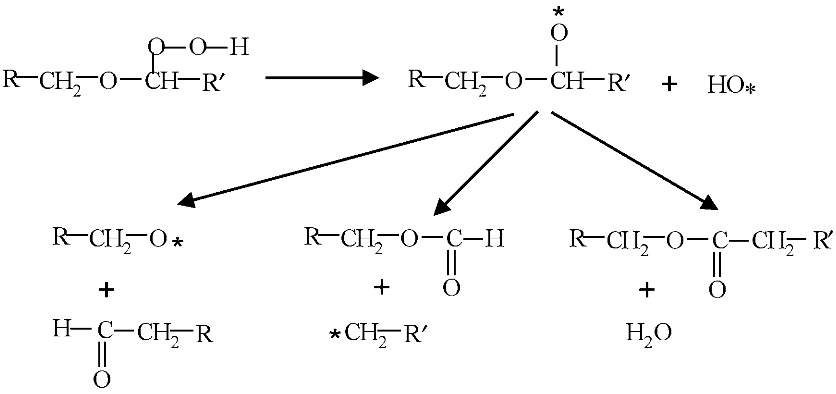
b) Propagation

The polymeric radical formed reacts readily with oxygen to form a peroxy radical, which by chain transfer, generates a labile hydroperoxy group:



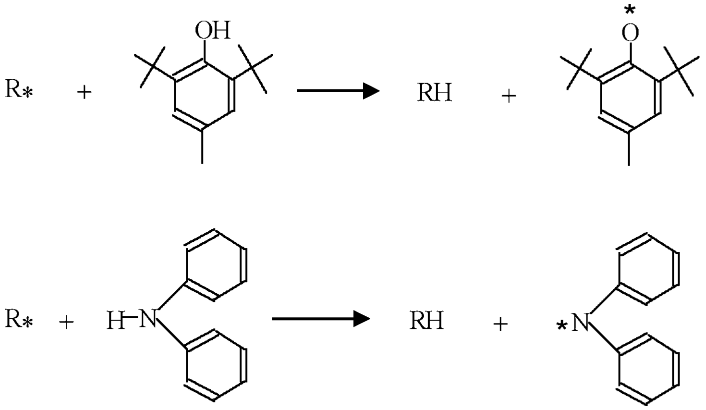
c) Termination

The hydroperoxide group decomposes to generate a very reactive alkoxy radical (RO*) and hydroxyl radicals (HO*), and finally aldehydes, ketones and esters are formed:



Because of the destruction of the polyether chain, the physico-mechanical properties of PU foams, based on these degraded polyols, are extremely poor.

The antioxidants added to the polyethers in the fabrication process, hindered phenols and diphenylamine types, act by a mechanism of 'chain breaking', by donation of hydrogen radicals to the very reactive radicals, formed during polyether thermo-oxidative degradation:



The very reactive radicals R* are blocked by being transformed into a neutral molecule (RH) and a radical of very low reactivity stabilised by conjugation. In that way the chain reactions are interrupted. Both antioxidants (hindered phenols and diphenylamines) are consumed after hydrogen radical donation (sacrificial antioxidants) [140].

In the fabrication of flexible slabstock PU foams, due to the very exothermic reaction between isocyanates with polyols and with water, the temperature in the centre of the polyurethane bun increases substantially. The PU foams, because of their cellular structure, have a poor thermal conductivity and the reaction heat is not eliminated. As an immediate consequence, the temperature in the centre of the bun becomes very high at around 150-170 °C. At this temperature, the labile polyetheric segment of the PU, in the presence of air, becomes the thermo-oxidative degradation. The air access is facilitated by the open cell structure of flexible PU foams. The PU foam develops a strong discoloration, more intensive in the centre of the bun, representing in fact a region of degraded polymer with poor physico-mechanical properties. This complex phenomenon of darkening and degradation in the centre of the bun of flexible slabstock PU foams is called ‘scorching’.

The scorching phenomenon is avoided by an adequate system of stabilisation. The efficient antioxidants used currently in polyether stabilisation were discussed previously. It is interesting that phenothiazine, in very small quantities (30-50 ppm) together with hindered phenols, have a very efficient antiscorching action. Unfortunately, phenothiazine and diphenylamines in high quantities have an effect of discolouring polyethers and are therefore used in small quantities. The most important antioxidants are hindered phenols of very low volatility used in combination with synergic quantities of dipenylamines or phenotiazine.

Butylated hydroxytoluene (BHT), or 2,6 di-*tert*-butyl-*p*-cresol, was used for many years as an excellent antioxidant in polyether polyols. Owing to its intrinsic volatility, BHT was eliminated as an antioxidant and a new type of polyether called ‘BHT free polyethers’ has appeared. The low volatility antioxidants give good fogging resistance, such as in interior automotive applications [140].

A new low volatility antioxidant with exceptional stabilising and antiscorching properties, with lactonic structure, was developed by CIBA [140] (**Figure 4.37**).

One of the most important methods to determine the thermo-oxidative resistance of a polyurethanic material is differential scanning calorimetry (DSC), a small-scale test. The

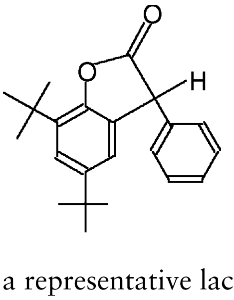


Figure 4.37 The structure of a representative lactonic type antioxidant [140]

temperature is increased at a rate of 5 °C/minute, between 50-220 °C. The temperature at the beginning of oxidation (strong exotherm) is a measure of the stabilising efficiency. At a constant temperature increase rate, a high temperature of oxidation at the beginning shows a high stabilising efficiency and on the contrary a low temperature of oxidation at the beginning shows a poor stabilising efficiency. **Figure 4.38** shows the temperature of oxidation beginning in an unstabilised polyether, a polyether stabilised only with a hindered phenol and a polyether stabilised with a synergic mixture of hindered phenol - diphenylamine type antioxidants. One observes that stabilised polyols have higher temperatures for oxidation beginning at around 180-200 °C compared to unstabilised polyether polyol (around 160 °C). A good antiscorching action is secured at a concentration of antioxidants in polyethers of around 4000-5000 ppm (0.4-0.5%).

Another DSC test is an isothermal test, carried out at a constant temperature (for example 170 °C). By maintaining the polyether sample at 170 °C, the oxygen absorption (as a consequence of oxygen consumption in oxidation of the polymeric material) is measured with a gas burette against time. The time needed for oxidation (beginning of oxygen absorption), is a direct measure of the stabilising efficiency of the polyether [this time is called oxygen absorption induction time (OIT)]. The longer OIT proved a good stabilisation. These DSC methods are indirect methods to determine the scorching resistance of a PU foam resulting from a stabilised polyether polyol, and they are very useful. For example, if the temperature at the start of polyether oxidation (190-200 °C) is higher than the temperature in the centre of the bun (160 °C), the PU foam will have

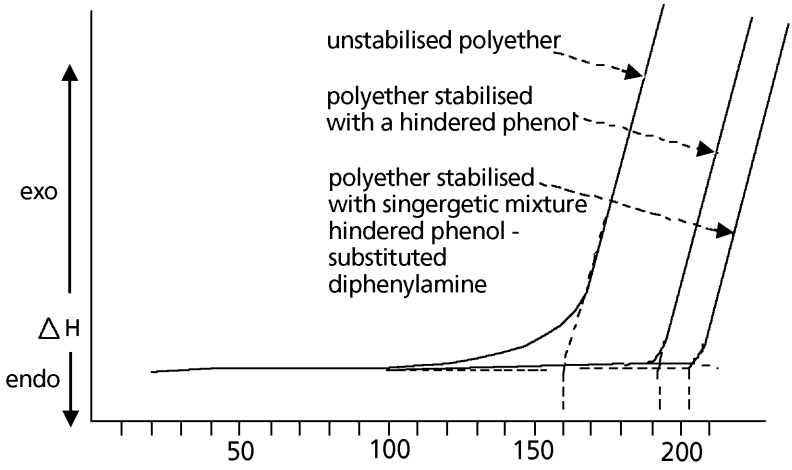


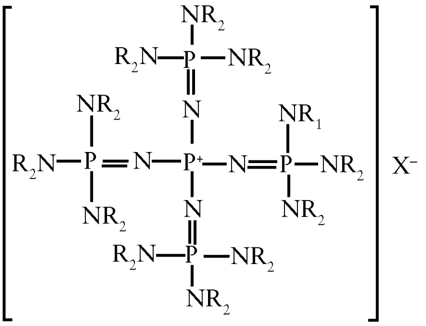
Figure 4.38 The DSC curves of an unstabilised polyether, a polyether stabilised with a hindered phenol and a polyether stabilised with a synergetic mixture hindered phenol - substituted diphenylamine

good resistance to scorching. Another method to determine the scorching phenomenon is the determination of the yellowness index of the PU foam, as function of temperature. A low yellowness index at higher temperatures proved good oxidative resistance and good resistance to scorching [140].

4.2 Anionic Polymerisation of Alkylene Oxides Catalysed by Phosphazenium Compounds

Phosphazenium compounds are a new class of catalyst that are extremely efficient in the anionic polymerisation of PO and EO, initiated by hydroxyl groups [34-38, 144-146].

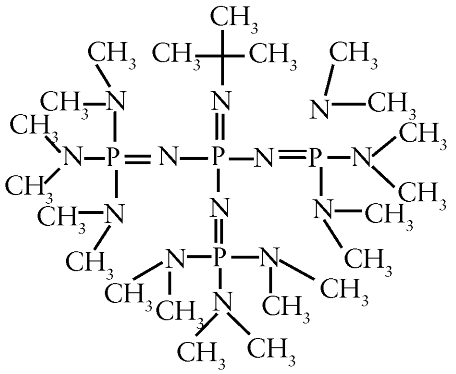
The general formula of a phosphazenium alkoxylation catalyst is:



The main characteristics of these phosphazenium compounds are a large volume of organic cations, excellent thermal and chemical stability of the cation and, as an immediate consequence of the large volume, a high degree of dissociation (practically 100%) of these salts in organic media. For good catalytic activity, the anion X$^-$ is preferably an alcoholate (RO$^-$) or hydroxide (HO$^-$). But the most important characteristic of phosphazenium catalysts is the very high basicity of these compounds (organic superbases), which makes them practically comparable with alkali hydroxides.

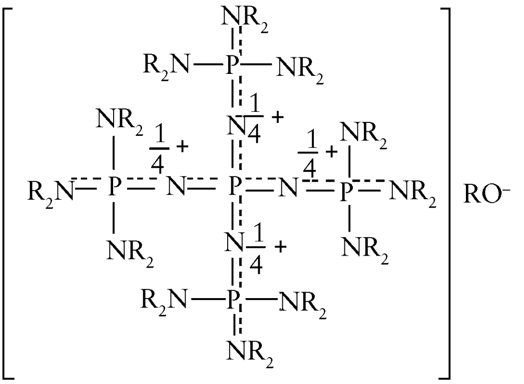
To explain the catalytic mechanism of the alkylene oxide polymerisation with phosphazenium compounds, several considerations concerning the peralkylated polyamino-phosphazenes should be made.

The reagent of the year in 1992 was one of the strongest organic bases, called the Schwesinger reagent [147]:



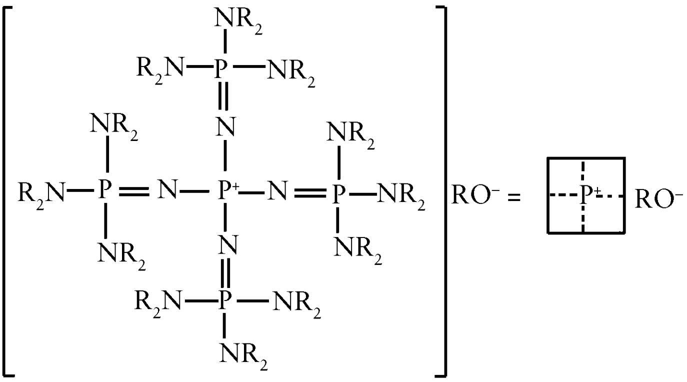
The question is: why are these phosphazene compounds very strong bases that are comparable with alkali hydroxides?

The answer is: that the high basicity is a consequence of an organic cation of great stability obtained by a special kind of conjugation called an *isovalent conjugation*. In this kind of conjugation the positive charge is distributed on a high number of atoms:

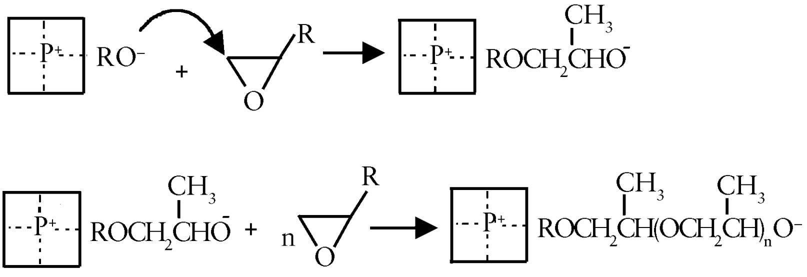


(4.26)

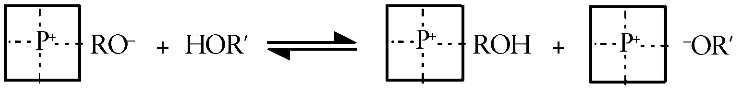
This special kind of conjugation increases considerably the stability of the organic cation which is very resistant at higher temperatures and resistant to basic media (the cation is not destroyed by alcoholate or hydroxide anions). The phosphazenium ion (structure 4.26) is much more stable than that of the quaternary ammonium hydroxides, alcoholates or salts. Owing to the very high dissociation degree in organic media (practically 100%), the phosphazenium alcoholates or hydroxides are very strong bases. The potassium alcoholates in the polyether media have a much lower dissociation degree, of around 1.3-2.0%. Based on this information, it is very easy to understand the mechanism of action of the phosphazenium catalyst. The formation of phosphazenium compounds is:



The PO polymerisation is reduced to the classical nucleophilic attack of the alcoholate anion on the α-carbon atom of the oxiranic ring, the counter ion being the big phosphazenium cation instead of the potassium cation:



The rapid alcohol - alcoholate equilibrium assures that each hydroxyl group in the reaction system is a chain initiator:



Phosphazenium hydroxides or alcoholates are very active catalysts for PO and EO anionic polymerisation initiated by glycerol, DPG or other starters, at lower temperatures of around 80-100 °C, giving colourless polyether polyols with very low unsaturation (around 0.02 mequiv/g at higher MW 5000-6000 daltons), which represents a very good performance in the synthesis of polyether polyols for PU.

Unfortunately the phosphazenium compounds are very expensive catalysts.

In **Table 4.15** the catalytic activities of phosphazenium catalysts are compared to other alkoxylation catalysts, at the same molar concentration.

Table 4.15 The catalytic activity of phosphazenium compounds as compared to other catalysts in PO polymerisation [134]

	Phosphazene P_5NMe_2OH	CsOH	DMC catalysts
PO polymerisation activity, g/mol/min	490	8.7	2100

For the catalytic efficiency in PO polymerisation the following relative order was established:

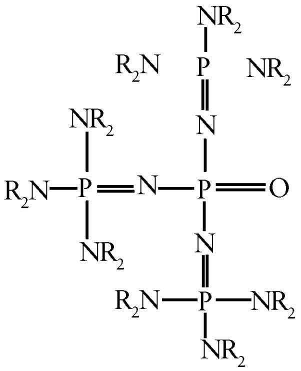
$$DMC >> P_5NMe_2OH >> CsOH > KOH$$

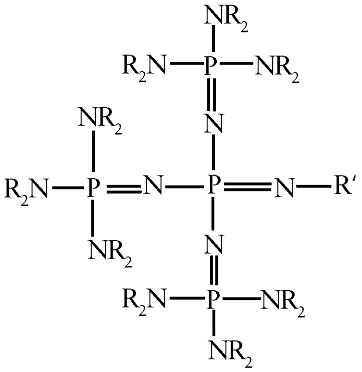
The advantage of phosphazenium catalysts, compared to DMC, is their capability to catalyse the anionic polymerisation of PO and EO and to be used successfully in the synthesis of PO-EO block copolymers with terminal poly[EO] block, without intermediate change of the catalyst nature.

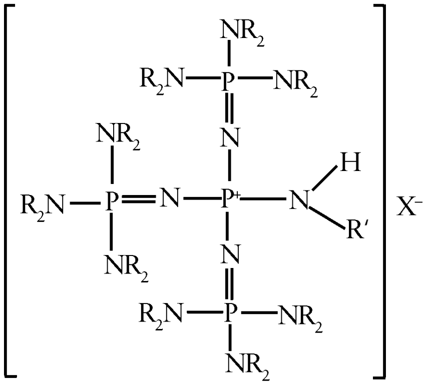
The polyethers made with phosphazenium catalysts are purified by conventional methods such as neutralisation with an acid in the presence of water (for example with orthophosphoric acid), anhydrisation and filtration in the presence of an adsorbent.

The MWD in polyethers made with phosphazenium catalysts is very narrow: M_w/M_n = 1.03-1.05.

The synthesis of phosphazenium compounds is based on the reaction of phosphorus pentachloride with various dialkyl and monoalkyl amines [34-38, 144-146]. Other phosphazenium compounds catalytically active in anionic PO and EO polymerisation, are:







4.3 High Molecular Weight Polyether Polyols Based on Polyamine Starters. Autocatalytic Polyether Polyols [148-152]

The freshly prepared, flexible PU foams, using tertiary amines as foaming catalysts, are well known to have an unpleasant odour, characteristic of amines. The staining of vinylic films or degradation of polycarbonate sheets is produced as a consequence of the aminic catalyst emission from PU foams. This problem is serious, especially in environments where there are elevated temperatures for long periods of time, for example in an automobile interior. These problems need a reduction of migratory amine catalyst emissions.

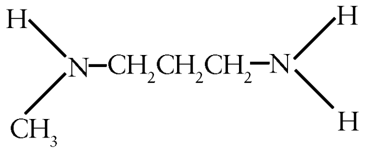
To solve these problems, polyols with self-catalytic activity and of course with low volatility were created, using polyamines as starters [148-152]. These polyols, with an intrinsic catalytic activity, are chemically incorporated in the PU structure. As an immediate consequence, the quantity of amines needed as the catalyst is reduced considerably and, of course, the amine emissions are also considerably diminished.

One of the first polyether polyols of this category was based on ethylenediamine (**Figure 4.39**). This polyol with a MW of around 7000 daltons, PO-EO copolyether (13-15% EO) with poly[EO] as terminal block, was used successfully for making cold cure high resilience moulding flexible PU foams. The self-catalytic effect of the polyol was not so important, but some beneficial effects emerge: a very attractive and uniform foam surface and a nonshrinking foam, with a high percentage of open cells.

One observes that the tertiary nitrogen atoms in the polyol structure shown in **Figure 4.39** have bulky substituents (the polyoxyalkylene chains with equivalent weight of around 1700-2000 daltons). This fact explains the modest catalytic activity in the foaming process.

A similar polyether polyol derived from triethanolamine with a MW of 5000 daltons, i.e., a PO-EO copolymer, with 15% poly[EO] as terminal block, gives flexible PU foams with poor physico-mechanical properties.

In order to increase the self-catalytic activity, high MW aminic polyols were created based on polyamines having one or two nitrogen atoms and low steric hindrance methyl groups (-N-CH_3 groups), such as [149-151]:



N-methyl-1,3-propylene diamine

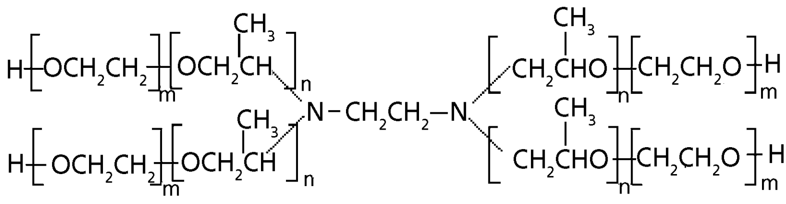
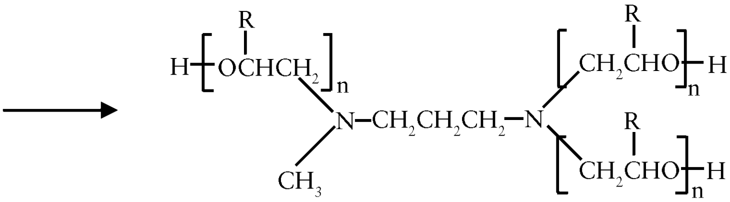
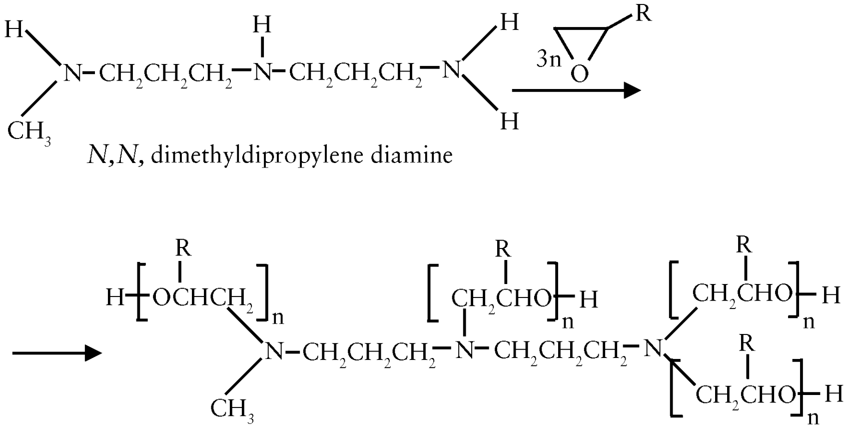


Figure 4.39 The structure of polyether tetraols, block copolymers PO-EO, based on ethylene diamine





All these polyols, based on *N*-methyl alkylated polyamines such as *N*-methylpropylenediamine, *N*,*N*-dimethyldipropylenediamine, *N*,*N* dimethyl trimethylolethane and other similar polyamines, have an improved self-catalytic activity and need only a low concentration of volatile tertiary amine catalysts in the foaming process. The resulting flexible PU foams have practically none of the unpleasant odours characteristic of the conventional flexible PU foams. The low amine emission in the foaming process diminishes the risk of workers exposed to the amines, and these polyether polyols may be considered to be more environmentally friendly.

The utilisation of the high MW aminic polyether polyols in the synthesis of polymer polyols [graft polyether polyols and polyisocyanate polyaddition (PIPA) polyols] is presented in Chapter 6 [148, 151].

The creation of the autocatalytic high MW aminic polyols based on *N*-methyl substituted polyamines, represents an important development in the area of polyether polyols for low-fogging flexible PU foams. The VORANOL VORACTIV polyols developed by DOW represent a revolutionary group of autocatalytic polyols with reduced volatile organic compounds (VOC) emissions in PU products, especially in high resilience foams for bedding and automotive seating [149, 150].

References

1. B.G. Hill, *Chemtech,* 1973, **3**, 10, 613.

2. *Polyethers*, *Polyalkylene Oxides and Other Polyethers, Part I*, Ed., N.G. Gaylord, Interscience Publishers, New York, NY, USA, 1963.

3. J.H. Saunders and K.C. Frisch, *Polyurethanes: Chemistry and Technology, Part I*, Interscience Publishers, New York, NY, USA, 1962.

4. D.J. Sparow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc. Boca Raton, FL, USA, 1989, p.182.

5. F.E. Bailey, Jr., and J.V. Koleske, *Alkylene Oxides and Their Polymers*, Surfactant Science Series, Volume 35, Marcel Dekker, Inc., New York, NY, USA, 1991.

6. K. Schauerte, M. Dahm, W. Diller and K. Uhlig in *Polyurethane Handbook: Chemistry, Raw Materials, Processing*, *Application, Properties*, Ed., G.Oertel, Hanser Verlag, New York, NY, USA, 1985, p.42.

7. Y.C. Yen, *Polyols from Ethylene Oxide and Propylene Oxide*, Process Economics Program Report No.45, Stanford Research Institute, Menlo Park, CA, USA, 1968.

8. Y.C. Yen and T.S. Tsao, *Polyols for Polyurethanes,* Process Economic Program Report No.45A, Stanford Research Institute, Menlo Park, CA, USA, 1982, p.119.

9. H.R. Friedly in *Reaction Polymers*, Eds., W.F. Gum, W. Riese and H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.66.

10. S. Gagnon in *Encyclopedia of Polymer Science and Engineering*, Volume 6, Eds., H.F. Mark, N. Bikales and C.G. Overberger, Wiley, New York, NY, USA, 1987, p.273-307.

11. N. Clinton and P. Matlok in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edition, Volume 6, Eds., R. Kirk and D.F. Othmer, Wiley Interscience Publishers, New York, NY, USA, 1986, p.225-273.

12. *Flexible Polyurethane Foams*, 2nd Edition, Eds., R.Herrington and K. Hock, Dow Chemical Company, Midland, MI, 1997, Chapter 2, p.6.

13. K. Schauerte, M. Dahm, M. Ditler and K. Uhlig in *Polyurethane Handbook*, Ed., G. Oertel Hanser, New York, NY, USA, 1985, p.42.

14. M. Ionescu, V. Zugravu, I. Mihalache and I. Vasile, Proceedings of the *4th Rapra International Conference on Cellular Polymers IV*, Shawbury, Shrewsbury, UK, 1997, Paper No.8.

15. R.A. Newton in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Volume 18, Eds., R. Kirk and D.F. Othmer, John Wiley & Sons, New York, NY, USA, 1982, p.645.

16. E.J. Vandenberg in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edition, Volume 8, Eds., R. Kirk and D.F. Othmer, John Wiley & Sons, New York, NY, USA, 1982, p.616.

17. *Polyurethane Technology*, Ed., P.F. Bruins, Interscience Publishers, New York, NY, USA, 1969.

18. J. Patton, Jr., *Chemtech,* 1976, **6**, 780.

19. T. Okamoto, S. Uemura and I. Hamo, inventors; Lion Corporation, assignee; JP 2000061304, 2000.

20. F. Yoshito and H. Tomoshi, inventors; Asahi Chemical Industries Co., Ltd., assignee; JP 9,040,796, 1997.

21. K. Ohkubo, Y. Sakaki, T. Tsutsui, T. Kunihiro, A. Nishikawa, T. Izukawa, K. Ueno, S. Sakai, Y. Tanaka, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 677,543A1, 1995.

22. H. Tsutsui, S. Yamazaki, Y. Hara and T. Izukawa, inventors; Mitsui Toatsu Chemicals, Inc., assignee; JP 9194589, 1997.

23. C.J. Reichel, T.L. Fishback and G. Aviles, inventors; BASF Corporation, assignee; EP 781,791A1, 1997.

24. C.J. Reichel, T.L. Fishback and G. Aviles, inventors; BASF Corporation, assignee; EP 946,625A1, 1999.

25. A.J. Heuvelsland, inventor; The Dow Chemical Company, assignee; EP 369,487B1, 1996.

26. A.J. Heuvelsland, inventor; The Dow Chemical Company, assignee; US 5,114,619, 1992.

27. A.J. Heuvelsland, inventor; The Dow Chemical Company, assignee; US 5,070,125, 1991.

28. D.E. Laycock and R.A. Sewell, inventors; The Dow Chemical Company, assignee; EP 737,221, 1996.

29. D.W. Cawlfield, J.J. Kaczur, H. Arabghani, inventors; Olin Corporation, assignee; US 5,254,227, 1993.

30. G-E. Yu, F. Heatley, C. Booth and T.G. Blease, *Journal of Polymer Science: Polymer Chemistry*, 1994, **32**, 6, 1131.

31. G-E. Yu, A.J. Masters, F. Heatley, C. Booth and T.G. Blease, *Macromolekulare Chemie*, 1994, **195**, 5, 1517.

32. J. Chavez, Jr., A.S. Farnum, V.M. Nace, R.A. Plepys, R.K. Whitmire, V.A. Kent, P.D. Bettge and H.R. Friedli, inventors; The Dow Chemical Company, assignee; US 5,342,541, 1994.

33. J.G. Perry and W.A. Speyng, inventors; BASF Corporation, assignee; US 4,985,551, 1991.

34. M. Kouno, K. Mizutani, T. Nobori and U. Takaki, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,763,555A2, 1996.

35. T. Nobori, T. Suzuki, S. Kiyono, M. Kouno, K. Mizutani, Y. Sonobe and U. Takaki, inventor; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,791,600A1, 1997.

36. S.H. Yamasaki, Y. Hara, S. Tamura, F. Yamazaki, H. Watanabe, M. Matsufuji, S. Matsumoto, A. Nishikawa, T. Izukawa, M. Aoki, T. Nobori and U. Takaki, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,916,686A1, 1998.

37. U. Takaki, T. Nobori, T. Izukawa and S. Yamasaki, inventors; Mitsui Toatsu Chemicals, Inc, assignee; EP 0,897,940A2, 1999.

38. T. Hayashi, K. Funaki, A. Shibahara, K. Mizutani, I. Hara, S. Kiyono, T. Nobori and U. Takaki, Mitsui Toatsu Chemicals, Inc., assignee; EP 0,950,679A2, 1999.

39. P. Kubisa and S. Penczek, *Progress in Polymer Science*, 1999, **24**, 10, 1409.

40. S. Penczek and P. Kubisa in *Ring-opening Polymerisation: Mechanisms, Catalysis, Structure, Utility*, Ed., D.J. Brunelle, Hanser Publishers, Münich, Germany, 1993.

41. S. Penczek, H. Sekiguchi and P. Kubisa in *Macromolecular Design of Polymeric Materials*, Eds., K. Hatada, T. Kitayama and O. Vogl, Marcel Dekker, New York, NY, USA, 1997.

42. E.A. Efford, inventor; The Dow Chemical Company, assignee; US 4,751,331, 1988.

43. T. Aida and S. Inoue*, Macromolecules*, 1981, **14**, 5, 1166.

44. S. Inoue and T. Aida in *New Methods for Polymer Synthesis*, Ed., W.J. Mijs, Plenum Press, New York, NY, USA, 1992, p.33.

45. S. Inoue and T. Aida in *Ring-Opening Polymerisation: Mechanisms, Catalysis, Structure, Utility*, Ed., D.J. Brunelle, Hanser Verlag, Münich, Germany, 1993, p.197.

46. T. Aida, *Progress in Polymer Science*, 1994, **19**, 3, 469.

47. H. Sugimoto and S. Inoue, *Advances in Polymer Science*, 1999, **146**, 39.

48. G. Wegener, M. Brandt, L. Duda, J. Hofmann, B. Klesczewski, D. Koch, R-J. Kumpf, H. Orzesek, H-G. Pirkl, C. Six, C. Steinlein and M. Weisbeck, *Applied Catalysis*, 2001, **221**, 1-2, 303.

49. C.W. Yost, C.A. Plank and E.R. Gerhard, *Industrial & Engineering Chemistry Product Research and Development,* 1967, **6**, 2, 113.

50. R.M. Guibert, C.A. Plank and E.R. Gerhard, *Industrial & Engineering Chemistry Process Design and Development,* 1971, **10**, 4, 497.

51. L.R. Christianson, M. Dheming and E.L. Ochoa, *Journal of Cellular Plastics,* 1977, **13**, 2, 111.

52. F. Stoenescu, M. Ionescu, V. Dumitriu and I. Mihalache, *Materiale Plastice,* 1981, **18**, 3, 155.

53. M. Ionescu, I. Mihalache, V. Dumitriu, F. Stoenescu and V. Ion, *Revista de Chimie*, 1988, **39**, 12, 1060.

54. F. Heatley, J-F. Ding, G-E. Yu, C. Booth and T.G. Blease, *Macromolekulare Chemie Rapid Communications,* 1993, **14,** 12, 819.

55. F. Heatley, J. Ding, G. Yu and C. Booth, *Die Makromoleculare Chemie: Rapid Communications*, 1993, **14**, 12, 819.

56. F. Heatley, G.Yu, C. Booth and T.G. Blease, *European Polymer Journal,* 1991, **27**, 7, 573.

57. A.K. Rastogi and L.E. St.Pierre, *Journal of Applied Polymer Science*, 1970, **14**, 5, 1179.

58. Y.L. Deng, J. Ding, G. Yu, R.H. Mobbs, F. Heatley, C. Price and C. Booth, *Polymer,* 1992, **33**, 9, 1959.

59. S. Dickson, G. Yu, F. Heatley and C. Booth, *European Polymer Journal*, 1993, **29**, 2-3, 281.

60. G-E. Yu, F. Heatley, C. Booth and T.G. Blease*, Journal of Polymer Science: Polymer Chemistry,* 1994, **32**, 6, 1131.

61. J.F. Ding, F. Heatley, C. Price and C. Booth, *European Polymer Journal*, 1991, **27**, 9, 895.

62. E. Santacesaria, M. Di Serio, L. Lisi and D. Gelosa, *Industrial & Engineering Chemistry Research*, 1990, **29**, 5, 719.

63. M. Di Serio, G. Vairo, P. Iengo, F. Felippone and E. Santacesaria, *Industrial & Engineering Chemistry Research,* 1996, **35**, 11, 3848.

64. E. Santacesaria, M. Di Serio, R. Garaffa and G. Addino, *Industrial &Engineering Chemistry Research*, 1992, **31**, 11, 2413.

65. M. Di Serio, R. Tesser, F. Felippone and E. Santacesaria, *Industrial & Engineering Chemistry Research,* 1995, **34**, 11, 4092.

66. E. Santacesaria, M. Di Serio, R. Garaffa and G. Addino, *Industral &Engineering Chemistry Research,* 1992, **31**, 11, 2419.

67. E. Santacesaria, M. Di Serio, P. Iengo in *Reaction Kinetics and the Development of Catalytic Process*, Eds., G.F. Froment and K.C. Waugh, Elsevier Science BV, Amsterdam, The Netherlands, 1999.

68. H. Becker and G. Wagner, *Acta Polymerica*, 1984, **35**, 1, 28.

69. G-E. Yu, A.J. Masters, F. Heatley, C. Booth and T.G. Blease, *Macromolecular Chemistry and Physics,* 1994, **195**, 5, 1517.

70. A. Stolarewiccz, H. Becker and G. Wagner, *Acta Polymerica*, 1981, **32**, 8, 483.

71. H. Becker, G. Wagner and A. Stolarewicz, *Acta Polymerica*, 1981, **32**, 12, 764.

72. J.F. Ding, C. Price and C. Booth, *European Polymer Journal*, 1991, **27**, 9, 891.

73. G.A. Gladkovski, L.P. Golovina, G.F. Vedeneeva and V.S. Lebedev, *Vysokomolekuliarnye Soedineniia,* 1973, **15A**, 6, 1221.

74. R.E. Parker and N.S. Isaacs, *Chemical Reviews,* 1959, **59**, 4, 737.

75. G-E. Yu, F. Heatley, C. Booth and T.G. Blease, *European Polymer Journal,* 1995, **31**, 589.

76. G.J. Dege, R.L. Harris and J.S. MacKenzie, *Journal of American Chemical Society*, 1959, **81**, 13, 3374.

77. D.M. Simons and J.J. Verbanc, *Journal of Polymer Science*, 1960, **44**, 144, 303.

78. E.C. Steiner, R.R. Peletier and R.O. Trucks, *Journal of American Chemical Society*, 1964, **86**, 21, 4678.

79. *Ring Opening Polymerisation*, Eds., K.C. Frisch and S.L. Reegen, Marcel Dekker, New York, NY, USA, 1969.

80. M.J. Schick, *Nonionic Surfactants*, Marcel Dekker, New York, NY, USA, 1967, p.8.

81. B. Weybull and B. Nicander, *Acta Chemica Scandinavia*, 1954, **8**, 847.

82. C.J. Reichel, T.L. Fishback and G. Aviles, inventors; BASF Corporation, assignee; EP 0781791B1, 1998.

83. F. Heatley, G-E. Yu, W-B. Sun, E.J. Pywell, R.H. Mobbs and C. Booth, *European Polymer Journal*, 1990, **26**, 5, 583.

84. J. Furukawa and T. Saegusa, *Polymerisation of Aldehydes and Oxides*, Interscience Publishers, New York, NY, USA, 1963, p.125.

85. C.J. Curtis, W.W. Levis, Jr., and L.C. Pizzini, inventors; BASF Wyandotte Corporation, assignee; US Patent 4,487,853, 1984.

86. M. Ionescu, C. Roibu, V. Preoteasa, S. Mihai, I. Bejenariu, E. Vaicumam and C. Stratula, inventors; SC OLTCHIM SA, assignee; RO 118,301, 2003.

87. M. Ionescu, C. Roibu, V. Preoteasa, I. Mihalache, V. Zugravu, S. Mihai, I. Bejenariu and I. Puscasu, inventors; SC OLTCHIM SA, assignee; RO 118,431, 2003.

88. R.H. Carr, J. Hernalsteen and J. Devos, *Journal of Applied Polymer Science*, 1994, **52,** 8, 1015.

89. T.L. Lambert, inventor; Huntsman Petrochemical Corp., assignee; US 5,962,748, 1999.

90. H.M.J. Brons and H. De Vos, inventors; Shell Oil Company, assignee; US 6,504,062, 2003.

91. A.W. Fogiel, *Macromolecules*, 1969, **2**, 6, 581.

92. E. Santacesaria, M. Di Serio and P. Iengo in *Reaction Kinetics and the Development of Catalytic Processes*, Eds., G.F. Froment and K.C. Waugh, Elsevier Science BV, Amsterdam, The Netherlands, 1999, p.267.

93. M.J. Béchet, *Bulletin de la Société Chimique de France*, 1971, **10**, 3953.

94. G.A. Gladkovskii, L.P. Golovina, G.F. Vedeneyeva and V.S. Lebedev, *Polymer Science USSR*, 1973, **15**, 6, 1370.

95. G. Gee, W.C.E. Higginson, K.J. Taylor and M.W. Trenholme, *Journal of the Chemical Society,* 1961, 4298.

96. U.H. Gibbson and Q. Quick, *Journal of Applied Polymer Science*, 1970, **14,** 41, 1059.

97. M. Ionescu, unpublished work.

98. R.J. Tuiman, T.L. Fischback, C.J. Reichel, inventors, BASF Corporation, assignee; US 6,344,494, 2003.

99. G. Woods, *Flexible Polyurethane Foams.Chemistry and Technology*, Applied Science Publishers, London, UK, 1982.

100. J.R. McConville and J.F. Wood, inventors; ICI, assignee; GB 1,111,383, 1968.

101. No inventors; Dow Chemical Company, assignee; GB 1,048, 312, 1966.

102. J. Fishbein, R.W.H. Bell, A.J. Clarke and P. Merriman, inventors; Dunlop Holdings Ltd., assignee; US Patent 3,857,800,1974.

103. S. Consoli and F. Galati, inventors; Montedison SpA, assignee; US 4,144,386,1979.

104. R. Petit and G. Repiquest, inventors; Naphtha Chimie, assignee; GB 1,236,858, 1971.

105. No inventors; Naphtha Chemie SA, assignee; GB 1,142,597, 1969.

106. D.G. Powell, J.E. Puig and B.G. van Leuwen, *Journal of Cellular Plastics,* 1972, **8**, 2, 90.

107. M. Ionescu, V. Dumitriu, I. Mihalache, F. Stoenescu, inventors; Institutul De Cercetari Chimice,Centrul De Cercetari Pentru Materiale Plastice, assignee; RO 93,252 , 1987.

108. R.J. Hartman, inventor; BASF Wyandotte Corporation, assignee; US 4,487,854, 1984.

109. E.M. Dexheimer, inventor, no assignee; US 2004254304, 2004.

110. A. Penati, C. Maffezoni and E. Moreti, *Journal of Applied Polymer Science*, 1981, **26**, 4, 1059.

111. ASTM D4671, *Standard Test Methods for Polyurethanes Raw Materials: Determination of Unsaturation of Polyols*, 1999.

112. ISO 17710, *Plastics - Polyols for use in the Production of Polyurethane - Determination of Degree of Unsaturation by Microtitration*, 2002.

113. ASTM D4875, *Standard Test Methods for Polyurethanes Raw Materials: Determination of the Polymerised Ethylene Oxide Content of Polyether Polyols*, 1999.

114. P. Straneo, C. Maffezoni and A. Marchegiano in *Proceedings of the World Surfactants Congress*, Munich, Germany, 1984.

115. W. Koering in *Proceedings of the 5th CESIO World Surfactants Congress*, Florence, Italy, 2000, p.11-23.

116. A.S. Padia and A.R. Bayne in *Proceedings of the 5th CESIO World Surfactants Congress*, Florence, Italy, 2000, p.111-120.

117. P.H.M.R. Cramers, A.A.C.N. Beenackers and L.L.van Dierendonck, *Chemical Engineering Science*, 1992, **47**, 13-14, 3557.

118. P.H.M.R. Cramers, L. Smit, G.M. Leuteritz, L.L.van Dierendonck and A A.C.M. Beenackers, *The Chemical Engineering Journal and the Biochemical Engineering Journal*, 1993, **53**, 1, 67-73.

119. P.H.M.R. Cramers, L.L. van Dierendonck and A.A.C.M. Beenackers, *Chemical Engineering Science*, 1992, **47**, 9-11, 2251.

120. A.C. Houston and E.J. Campbell, inventors; Shell Research, Ltd., assignee; GB 870,457, 1961.

121. A. Kohl, N. Schneider, G. Ley, W. Balz, M. Melzer and H. Jakusch, inventors; BASF AG; assignee; US 4,507,457, 1985.

122. W.D. Beauchamp, R.E. Booth and E.R. Degginger, inventors; Allied Chemical Corporation, assignee; US 3,016,404, 1962.

123. M. Wisner, H.P. Doerge and J.R. Peffer, inventors; Pittsburgh Plate Glass Company, assignee; US 3,299,151, 1967.

124. No inventors; ICI, assignee; GB 1,377,486, 1974.

125. R. Gehm and H.C. Vogt, inventors; BASF AG, assignee; DE 2,220,723, 1973.

126. G.P. Speranza, inventor; Jefferson Chemical Company, Inc., assignee; GB 3,000,963,1961.

127. T. John, Jr., and J.A. Muzzio, inventors; BASF Wyandotte Corporation, assignee; CA 1,060,480, 1979.

128. R.D.T. Gehm and J.D.T. Hutcison, inventors; BASF Wyandotte Corporation, assignee; US 3,833,669, 1974.

129. H. Müller, inventor; BASF AG, assignee; US 4,460,796, 1984.

130. J.A. Muzzio, inventor; BASF Wyandotte Corporation, assignee; US 4,137,398, 1979.

131. J. Louvar and N. Nicols, inventors; BASF Wyandotte Corporation, assignee; US 3,715,402, 1973.

132. J.A. Muzzio, inventor; BASF Wyandotte Corporation, assignee; US 4,029,879, 1977.

133. F. Stoenescu,M. Ionescu, V. Dumitriu and I. Mihalache, inventors; Centrul De Cercetari Pentru Materiale Plastice, assignee; RO 75,733, 1981.

134. M. Ionescu, V. Dumitriu, I. Mihalache, F. Stoenescu, N. Chiroiu and M. Talpasanu, inventors; Institutul De Cercetari Chimice,Centrul De Cercetari Pentru Materiale plastice, assignee; RO 92,858, 1987.

135. J.G. Perry and W.A. Spelyng, inventors; BASF Corporation, assignee; EP 376,157A3, 1990.

136. J.E. Tyre and F.G. Willeboordse, inventors; Union Carbide Corporation, assignee;US Patent 3,388,169, 1968.

137. H. Hetzel, P. Gupta, R. Nast, H. Echterhof andU. Brocker, inventors; Bayer AG, assignee US Patent 4,482,750, 1984.

138. K. Umemura, T. Shimodaira and H. Miyake, inventors; Asahi Glass, assignee; JP 8269190, 1996.

139. H.R. Parsons, D.C. Dunham, S.L. Schilling and K.J. Headley, inventors; Bayer Corporation, assignee; US Patent 5,962,749, 1999.

140. S.M. Andrew in *60 Years of Polyurethanes*, Eds., J.E. Kreston and E.W. Eldred, Technomic Publishing, Lancaster, PA, USA, 1998, p.101.

141. L.B. Barry and M.L. Richardson in Proceedings of 33rd SPI Annual Technical/ Marketing Conference, Orlando, FL, USA, 1990, p.468.

142. P. Gupta, G. Jacobs and J. Leuridan, inventors; Bayer AG, assignee; US 5,672,768, 1997.

143. S.H. Harris, P.E. Kreter and C.W. Polley in *Proceedings of Polyurethane World Congress: 50 Years of Polyurethanes*, Aachen, Germany, 1987, p.848.

144. M. Kuono, T. Nobori, K. Mizutani and U. Takaki, inventors; Mitsui Chemicals, Inc., assignee; US 5,952,457, 1999.

145. S. Yamasaki, Y. Hara, S. Tamura, F. Yamazaki, H. Watanabe, M. Matsufuji, S. Matsumoto, A. Nishikawa, T. Izukawa, M. Aoki, T. Nobori and U. Takaki, inventors; Mitsui Chemicals, Inc., assignee; US 6,207,794, 2001

146. S. Yamasaki, Y. Hara, T. Kunihiro, F. Yamazaki, M. Matsufuji, A. Nishikawa, S. Matsumoto, T. Izukawa, M. Isobe, K. Ohkubo, K. Ueno, inventors; Mitsui Chemicals, Inc., assignee; US 6,410,676, 2002.

147. R. Schwesinger and H. Schlemper, *Angewandte Chemie*, 1987, **99**, 1212.

148. D.R.L. Ramael, inventor; Huntsman International LLC, assignee, US 6,433,031,2002.

149. S. Waddington, J-M.L. Sonney, R.J. Elwell, F.M. Casati and A. Storione, inventors; The Dow Chemical Company, assignee; WO 0158976, 2001.

150. F.M. Casati, J. Gan, R.M. Wehmeyer, R.H. Whitmarsh, R.E. Drumright and J.W. Weston, inventors; Dow Global Technologies, Inc., assignee; WO 03055930, 2003.

151. W. Hinz, S. Adams, U. Koehler, C. Maletzko, K. Vorspohl and R. Zschiesche, inventors; BASF AG, assignee; US 5,476,969, 1995.

152. P. Horn, L. Jung, H. Larbig, R. Lebkucher and G. Lehr, inventors; BASF AG, assignee; US 5,672,636, 1997.

5

Synthesis of High Molecular Weight Polyether Polyols with Double Metal Cyanide Catalysts (DMC Catalysts)

Double metal cyanide catalysts (DMC catalysts) were developed 40 years ago by General Tire & Rubber [1]. These catalysts have the following general formula of a nonstoichiometric substance:

$$Zn_3\left[Co\left(CN\right)_6\right]_2 * ZnCl_2 * y\ Ligand * zH_2O \tag{5.1}$$

Instead of Co^{3+}, very active catalysts were obtained with cyanocobaltate complexes of Fe, Cr, Pt, Ir [1-7]. These catalysts have a very high efficiency for propylene oxide (PO) polymerisation, initiated by hydroxyl groups, leading to high molecular weight polyether polyols with very low unsaturation. The best DMC catalyst is based on zinc hexacyanocobaltate [2-7, 8-47], combining the efficiency with the accessibility and low cost of raw materials. The DMC catalysts with the structure 5.1 were obtained by the reaction of an aqueous solution of potassium hexacyanocobaltate $K_3[Co(CN)_6]$ [1-7, 9-34] or of an aqueous solution of hexacyanocobaltic acid [2, 3, 37], with an aqueous solution of $ZnCl_2$, at around 25-40 °C. The zinc hexacyanocobaltate precipitated as a white suspension:

$$3ZnCl_2 + 2K_3\left[Co\left(CN\right)_6\right] \rightarrow Zn_3\left[Co\left(CN\right)_6\right]_2 \downarrow + 6KCl$$

$$3ZnCl_2 + 2H_3\left[Co\left(CN\right)_6\right] \rightarrow Zn_3\left[Co\left(CN\right)_6\right]_2 \downarrow + 6HCl$$

A solution of ligand in water was added to the resulting suspension of $Zn_3[Co(CN)_6]_2$. The most important ligands used are: dimethyl ether of ethyleneglycol (glyme), dimethyl ether of diethyleneglycol (diglyme), 1,4 dioxane, *tert* butyl alcohol, ethyleneglycol mono *tert* butyl ether, diethylene glycol mono *tert* butyl ether, propylene glycol mono methyl ether, dipropylene glycol mono methyl ether, phosphorus compounds (phosphine oxides, phosphorus esters) dimethylsulfoxide, dimethylacetamide, *N*-methyl pyrolidone, polypropylene glycols, polyethylene glycols, polytetrahydrofuran, and polyester polyols [8-10, 12-29, 32-39, 48-50].

The resulting solid complex catalyst was separated by filtration (or by centrifugation). In order to eliminate as much as possible of the resulting potassium chloride, which has an inhibitory effect in PO polymerisation, the solid was reslurried in a mixture of ligand-water and finally in pure ligand and then filtered. The catalyst was dried at moderate temperatures (60-70 °C) and under vacuum (665-1330 Pa), for several hours. The catalytic activity of the catalyst increases substantially if the water content in the final catalyst is very low, water having an inhibitory effect on PO polymerisation. The analysis of the best catalysts proved that water is always present, around 0.5-1 mol of water/mol of catalyst ($z = 0.5-1$ in formula 5.1). The catalysts with the general formula shown in 5.1, synthesised with 1,2 dimethoxy ethane as ligand, were considered for many years a standard model for DMC catalysts [2, 51, 52]. The flow diagram for synthesis of DMC catalysts is presented in **Figure 5.1**.

The double bond content of polyether polyols synthesised with the standard DMC catalyst is very low, around 0.015-0.02 mequiv/g at a molecular weight of 6000-6500 daltons. Very high catalytic activity DMC catalysts were obtained using *tert*-butyl alcohol as ligand or with combinations of ligands such as: *tert*-butyl alcohol - polypropyleneglycol (MW = 1000-4000), *tert*-butyl alcohol - polyethyleneglycol (preferred MW = 2000), *tert*-butyl alcohol - sorbitans, *tert*-butyl alcohol - polytetramethyleneglycols, *tert*-butyl alcohol - *tert*-butoxy ethanol [17, 32], *tert*-butyl alcohol - hydroxyethyl pyrolidone, *tert*-butyl alcohol - poly (*N*-vinyl pyrolidone), *tert*-butyl alcohol - alkyl (polyglucosides) [8-10, 12-29, 32-39, 48-50].

These catalysts lead to an extremely low unsaturation, of around 0.005 mequiv/g, impossible to obtain with other catalysts.

In **Figure 5.2** one observes the unsaturation increase *versus* the polyether molecular weight for potassium hydroxide, compared with DMC catalysts.

A high unsaturation proved a high concentration in polyether monols and, as an immediate consequence, the functionality (f) of the resulting polyether triols is much lower than 3 OH groups/mol. Thus, a polyether triol of molecular weight of 6000 daltons, obtained with KOH, has a functionality of 2.14-2.21 OH groups/mol, much lower than that of polyether triols (2.94 OH groups/mol) obtained with DMC catalysts. The effect is very important in polyether diols. A polyether diol with a MW of 4000 daltons, obtained by anionic polymerisation has a functionality of 1.61 OH groups/mol, but a polyether diol obtained with DMC catalysts has a functionality close to the theoretical functionality ($f = 1.98-2.00$ OH groups/mol).

The PU elastomers obtained from polyether diols with DMC catalysts (Acclaim Polyols of Bayer) have a spectacular improvement in the majority of physico-mechanical properties when compared with PU elastomers made from the polyether diols, obtained by anionic catalysis.

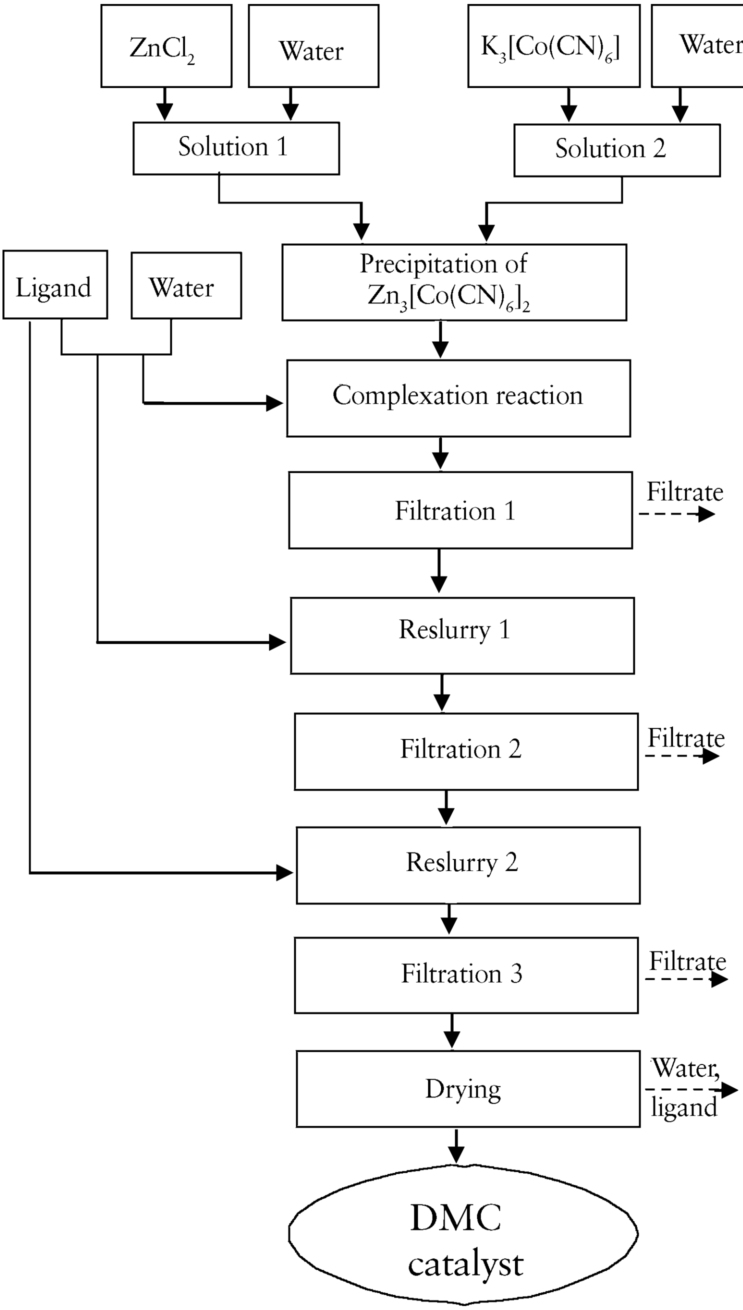


Figure 5.1 Flow diagram for synthesis of DMC catalysts

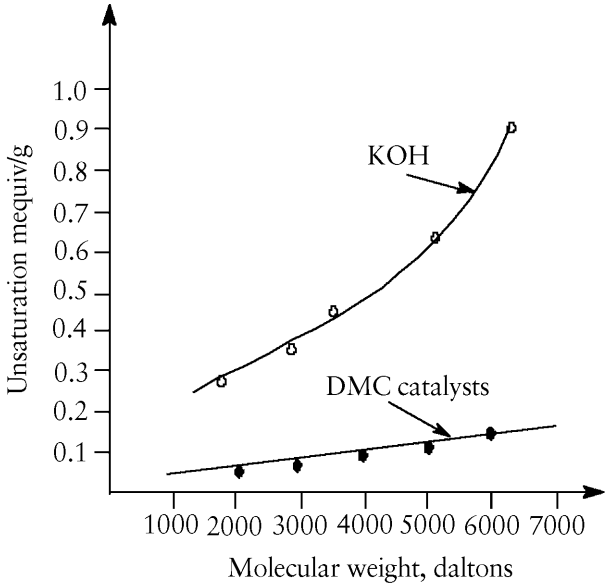


Figure 5.2 The polyether triol unsaturation obtained with DMC catalysts, compared with that obtained with potassium hydroxide

Table 5.1 shows the double bond content and the functionality of polyether triols, with a MW of 6000 daltons, synthesised with different catalysts.

DMC catalysts are real heterogeneous coordinative catalysts [2, 51, 52]. At the end of polymerisation, the catalyst is dispersed in the liquid polyether polyols in the form of small solid particles of around 200 nm (0.2 μm) diameter. By dilution with *n*-hexane and filtration, it is possible to achieve a quantitative removal of the DMC catalyst [51, 52].

Table 5.1 The double bond content of polyether triols synthesised with various alkoxylation catalysts

Catalyst	Mechanism	Unsaturation, mequiv/g	Functionality, OH groups/mol	References
KOH	anionic	0.09 - 0.1	2.14 - 2.21	[2]
CsOH	anionic	0.045 -0.055	2.46 - 2.55	[53]
$Ba(OH)_2$	anionic	0.03 - 0.04	2.60 - 2.68	[54-56]
Phosphazene	anionic	0.018 - 0.02	2.78 - 2.8	[57-61]
DMC	coordinative	0.005	2.94	[18-20]

It is very interesting that pure crystals of $Zn_2[Co(CN)_6]_2$ are catalytically inactive in PO polymerisation [6, 7]. It is only in the presence of an excess of $ZnCl_2$ and in the presence of ligands that the catalyst becomes very active catalytically.

X-ray diffraction studies proved that DMC catalysts, similar to many nonstoichiometric chemical substances, have many defects and vacancies in the crystalline structure [62]. These defects and vacancies are very strong co-ordination points. The oxiranic monomer is strongly co-ordinated by these centres at the oxygen atom and is transformed in a much more reactive structure than the uncoordinated monomer. This activation of the monomer by co-ordination explains the very high catalytic activity of DMC catalysts.

The alkylene oxide polymerisation, catalysed by DMC catalysts, is characterised by some specific points:

a) The first characteristic is an induction period that varies from 20-30 minutes to several hours. In this period of time, the consumption rate of PO is extremely low. After the induction period, the polymerisation rate of PO becomes extremely high and the catalyst is considered activated [1-52]. This behaviour is observed in **Figure 5.3**, where a typical curve for PO consumption in a PO polymerisation reaction catalysed by DMC catalyst is presented and compared with the reaction obtained with a classical KOH catalyst.

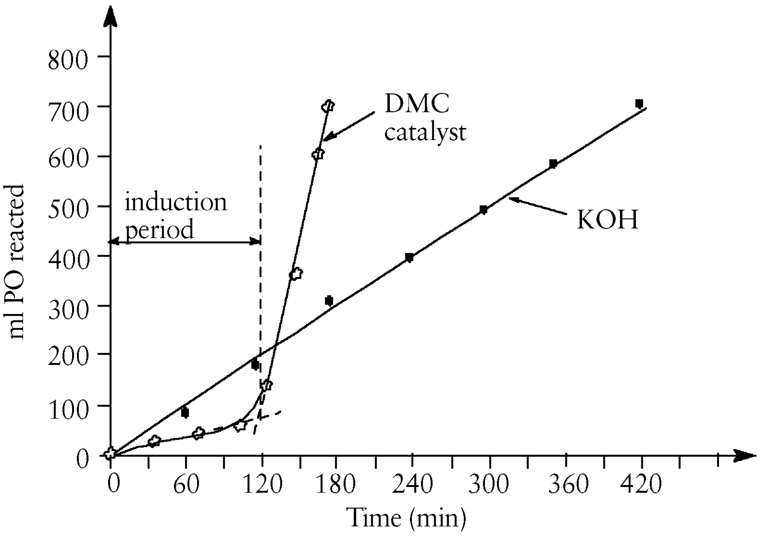


Figure 5.3 The PO consumption *versus* time in PO polymerisation with DMC catalysts and classical KOH catalyst. Temperature: 110 °C; pressure: 300 MPa; catalyst concentration: [KOH] = 0.25% and DMC catalyst: 200 ppm (0.02%)

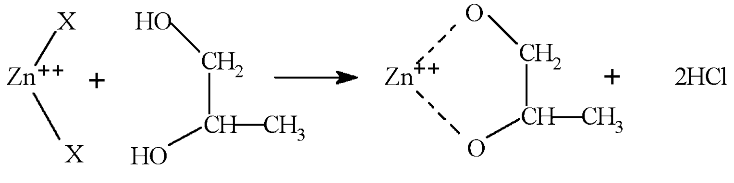
A possible explanation of the induction period is the substitution of the soft ligands from the crystalline structure with PO that are in excess. After the induction period, the PO polymerisation rate is so high that in one to three hours it is possible to add all the PO that is needed for the reaction. As a comparison, the polymerisation time, in the presence of KOH, is around 7-11 hours.

A very efficient method to avoid a long induction period is to obtain an 'activated masterbatch' of DMC catalyst. Thus, a quantity of DMC catalyst, 10-20 times higher than for normal PO polymerisation, is suspended in a purified polyether polyol used as starter (for example a polyether triol with a MW = 650-700 daltons) [51, 52]. To this suspension of DMC catalyst is added a quantity of PO, and the mixture is stirred under pressure (200-400 MPa), at 105-120 °C, until the pressure begins to decrease rapidly. A concentrated suspension of an 'activated' DMC catalyst was obtained. By using a part of this 'activated masterbatch' in normal PO polymerisation, the PO consumption starts immediately, without any induction period (see **Figure 5.4**).

With the synthesised 'activated masterbatch' of DMC catalyst it is possible to make 10-20 normal PO polymerisation reactions, leading to a considerable economy of time, due to the absence of the induction period, corresponding to each batch.

b) Another important characteristic of PO polymerisation with DMC catalysts is the impossibility of initiating the reaction by direct addition of PO to a starter such as glycerol or 1,2 propyleneglycol [1-7, 51, 52]. The explanation of this abnormal behaviour is given by the formation of very strong, stable and inactive zinc chelates, with the 1,2 glycol structure of the starters (reaction 5.2). This is explained by the fact that water has an inhibitory effect on PO polymerisation with DMC catalysts. During PO polymerisation, water reacts with PO and is transformed into 1,2 propyleneglycol, which blocks the activity of DMC catalyst by the formation of strong, catalytically inactive zinc chelates.

The formation of inactive zinc chelates mentioned before is shown in the following reaction:



(5.2)

The only possible way to initiate the PO polymerisation reaction catalysed by DMC catalysts is to use as starters, instead of pure polyols (e.g., glycerol, propylene glycol etc.), the low

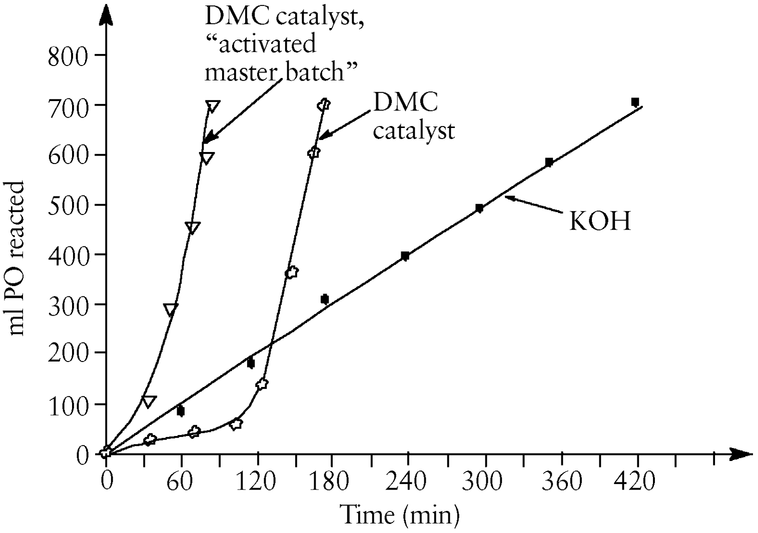


Figure 5.4 The elimination of the induction period in PO polymerisation using an 'activated masterbatch' of DMC catalyst. Temperature: 110 °C; pressure: 300 MPa; catalyst concentration: [KOH] = 0.25% and DMC catalyst: 200 ppm (0.02 %)

molecular weight PO adducts to these pure polyols. By propoxylating pure polyols with 1-3 PO units/hydroxyl groups, the possibility of 1,2 glycol structure generation disappears, because the distance between the new hydroxyl groups formed is too big to make a chelate. As an immediate consequence, the low molecular weight propoxylated polyethers, diols or triols, with a MW of 400-700 daltons are excellent initiators for PO polymerisation with DMC catalysts. There are some synthesis variants of these low molecular weight propoxylated starters, avoiding the purification step. One method is to use the PO polymerisation, initiated by glycerol and catalysed by magnesium oxide or by hydrotalcite followed by simple filtration [64]. Another variant is to obtain a low molecular weight adduct of PO for the polyolic starters, by cationic PO polymerisation catalysed with Lewis acids such as BF_3, SbF_5 or $Y(CF_3SO_3)_3$ [10, 38] or Brönstedt acids, such as CF_3SO_3H, HBF_4, HPF_6, $HSbF_6$ [39], but generally at lower temperatures. To the synthesised low molecular weight polyol, containing the acidic catalyst, the DMC catalyst is added and the co-ordinative PO polymerisation continues at higher temperatures (105-130 °C) to high molecular weight polyether polyols. It was observed that the acids (organic or inorganic) do not have any inhibitory effect on PO polymerisation with DMC catalysts [33, 41]. It is possible to start the PO polymerisation reaction with organic acids such as fumaric acid [63]. On the other hand, the basic substances such as: trialkylamines, alkali hydroxides and alkaly alcoholates strongly inhibit the catalytic activity of DMC catalysts.

The stepwise addition of starter together with PO is a practical method to obtain a high molecular weight polyether directly from glycerol or 1,2 propyleneglycol, without needing to first obtain a propoxylated oligomer [27-29]. This variant of continuous starter addition was proved not to markedly affect the molecular weight distribution of the resulting polyether, which is narrow [29].

Another variant is to use a very large excess of PO compared to the starter, to initiate the PO co-ordinative polymerisation directly from the starter, for example a gravimetric excess of 60-90 parts of PO/1 part of trimethylolpropane [41].

The fact that the acids do not inhibit the catalytic activity of DMC catalysts, and basic substances have a strong inhibitory effect, leads to the idea that the nature of PO polymerisation with DMC catalysts is cationic co-ordinative and not anionic co-ordinative.

It is possible to make an analogy between PO polymerisation by cationic mechanism (activated monomer mechanism, see Chapter 4.12) and PO polymerisation with DMC catalysts. Thus, in cationic polymerisation the monomer is activated by the formation of secondary oxonium cations by interaction with a proton and in DMC catalysts the monomer is activated by strong co-ordination (**Figure 5.5**).

In both PO activated structures, the electron density at the carbon atoms of the oxiranic ring decreases (in one case due to a neighbouring positive charge, in the second by co-ordination) and makes possible a nucleophilic attack of a weak nucleophile, such as the oxygen atom of hydroxyl groups. To conclude, the mechanism of PO polymerisation with DMC catalyst is based on the repeated nucleophilic attack of hydroxyl groups on the carbon atoms of PO, strongly activated by coordination (see **Schemes 5.3** and **5.4**).

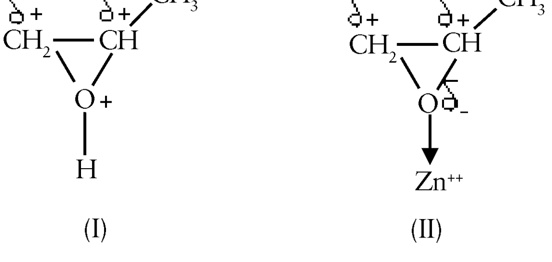
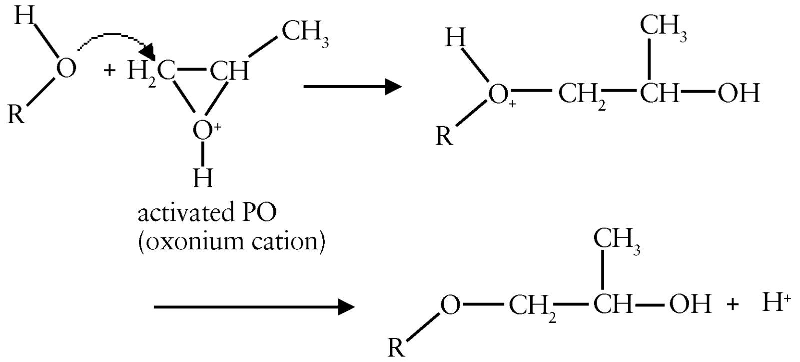


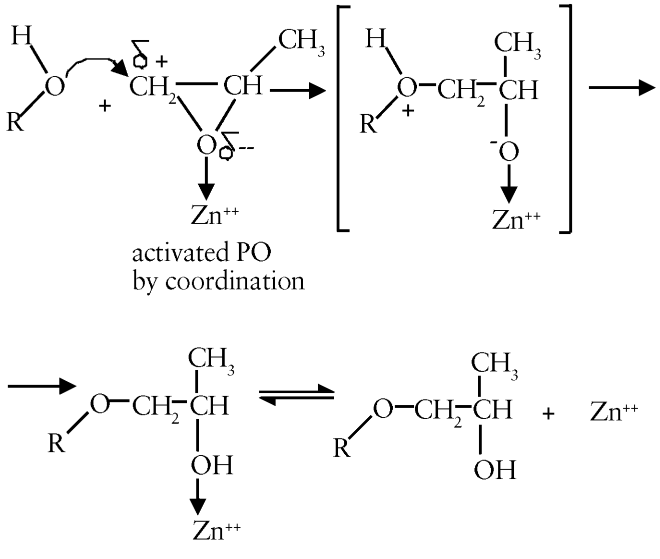
Figure 5.5 The activated monomer structures in cationic polymerisation (I) and in co-ordinative polymerisation with DMC catalysts (II)

Cationic polymerisation



Scheme 5.3

Coordinative polymerisation

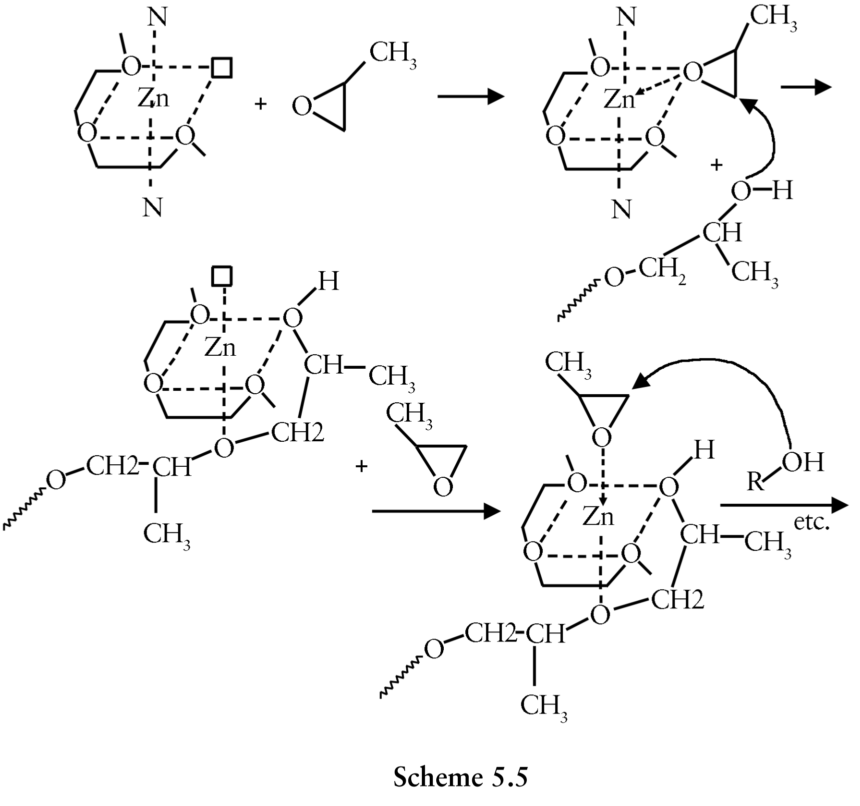


Scheme 5.4

A very similar mechanism for PO polymerisation with DMC catalysts was investigated by Xiaohua and co-workers [65] and Chen and co-workers [66, 67]. They proved that the co-ordination number of Zn^{2+} increases from 3 to 5.7 in the process of activation with PO. One considered that 5 oxygen atoms co-ordinate the Zn^{2+} ion and the sixth position is probably a vacancy of strong coordination power (reaction 5.5). The PO is activated by coordination in this position and the ring of the activated PO is opened by the reaction with hydroxyl groups (see **Scheme 5.5**).

An important characteristic of alkylene oxide polymerisation with DMC catalysts is the very low reaction rates obtained in EO coordinative polymerisation. EO, which is much more reactive than PO in anionic polymerisation, is less reactive than PO in the coordinative polymerisation [35, 68]. A possible explanation of this behaviour is the fact that PO is a more basic monomer than EO due to the electron release effect of the methyl substituent in the oxiranic ring (the electron density at the oxygen atom of the PO ring is higher than that in the EO ring). As an immediate consequence, PO, is more basic, and is more strongly co-ordinated (and more strongly activated too) to the active sites of DMC catalysts than EO, the less basic monomer.

The synthesis of block copolymers PO-EO with a terminal poly[EO] block is practically impossible, cloudy polyols always being formed, with a very low ethoxylation rate. The formation of cloudy polyols is because of an unfavourable (nonuniform) distribution of



Scheme 5.5

EO units per hydroxyl groups. As a consequence of this nonuniform distribution, longer poly[EO] chains (having more than 10 EO units) are formed, which are derived from some hydroxyl groups, which crystallise and precipitate at room temperature, as a separate phase, in the liquid polypropyleneoxide matrix and the polyether polyol becomes cloudy. The short poly[EO] chains, with less than 10 EO units per hydroxyl group, are liquid at room temperature and do not have any tendency to crystallise and as an immediate consequence the resulting polyether is transparent. The short poly[EO] chains are formed as a consequence of an uniform distribution of EO per hydroxyl group and depends on the catalyst nature (using KOH or CsOH as catalyst but not DMC catalysts).

Excellent PO-EO block copolyether polyols with terminal poly[EO] block, are formed by the addition, to the intermediate propoxylated polyether obtained with DMC catalysts, of an anionic catalyst (KOH or potassium alcoholates) followed by the addition of EO by classical technology, *via* an anionic mechanism. By this relatively complicated route, it is possible to obtain PO-EO block copolymers with high primary hydroxyl content and very low unsaturation.

Fortunately, the mixture PO-EO (having, for example, 10-20% EO) reacts quantitatively in the presence of DMC catalysts and it is possible to obtain random PO-EO copolyether polyols by this synthetic route.

An important characteristic of PO polymerisation with DMC catalysts is the formation of very high molecular weight polypropyleneoxides (MW = 100,000-400,000 daltons), in very small quantities (100-400 ppm) which have a dramatic antifoaming effect in flexible PU foams [33, 43]. The flexible PU foams made with polyether triols obtained with DMC catalysts, containing traces of very high molecular weight polypropyleneoxides, collapse. The formation of these very high molecular weight polypropyleneoxides is inhibited by the modification of DMC catalysts with some additives such as inorganic acids [33, 41] or chlorosilanes [43]. The explanation of the formation of these high molecular weight polyethers is the presence of small quantities of Zn-OH bonds in all DMC catalysts. By blocking these Zn-OH bonds with acids or with chlorosilanes, the formation of the very high molecular weight polyethers was inhibited:

$$—\mathrm{Zn}—\mathrm{OH}+\mathrm{HX}\rightarrow —\mathrm{Zn}—\mathrm{X}+\mathrm{H_2O}$$

$$—\mathrm{Zn}—\mathrm{OH}+\mathrm{Cl}—\mathrm{Si}(\mathrm{CH_3})_3\rightarrow —\mathrm{Zn}—\mathrm{O}—\mathrm{Si}(\mathrm{CH_3})_3+\mathrm{HCl}$$

The utilisation of a PO with EO mixture (e.g., with 17-18% EO) strongly diminishes the antifoaming effect of the very high molecular weight polyether formed.

The molecular weight distribution of propoxylated polyethers, obtained with DMC catalysts, is narrow. The molecular weight distribution is broader at higher molecular weight polyethers (MW = 10000-12000 daltons), but at a molecular weight of 5000-6000 daltons the molecular weight distribution is narrow (M_w/M_n = 1.02-1.2). A method to obtain a narrow molecular weight distribution is to use a very slow PO addition to the reaction mass (in fact a PO polymerisation at lower pressure). A high momentary excess of monomer (for example a polymerisation with all the PO at the beginning) leads to a broad molecular weight distribution of the resultant polyether [2].

The very high catalytic activity of DMC catalysts for PO co-ordinative polymerisation initiated by hydroxyl groups causes a substantial decrease of the catalyst concentration, until very low levels of around 25-50 ppm (0.0025-0.005%) are reached [21-26, 32]. At this level of catalyst concentration, reasonable reaction times are obtained including a reasonable induction period – as an immediate consequence the polyethers containing DMC catalysts can be used in polyurethanes (elastomers, sealants, adhesives, elastomers), without purification. The possibility of eliminating the purification step is of great technological importance. The plant and the process themselves are more simple and the yield in polyether is very high (98-99%).

DMC catalysts are considered to be the ones that perform best at this time for PO polymerisation initiated by hydroxyl groups. Bayer developed the first continuous process, with a very high productivity, for the synthesis of polyether polyols with DMC catalysts (IMPACT Catalyst Technology). In a short and simple production cycle, a large variety of polyether diols of very low unsaturation for elastomers, sealants, coatings and low monol content polyether triols destined for flexible polyurethane foams are obtained. This is one of the best developments in the last few years in the field of polyether polyol synthesis [2].

The very intensive research work carried out in recent years in the area of DMC catalysts by ARCO, Lyondell, BAYER, DOW, ASAHI, OLIN, ARCH and BASF represents fundamental and highly important contributions to the synthesis of high performance polyether polyols for polyurethanes.

References

1. J. Milgrom, inventor; The General Tire & Rubber assignee; US 3,278,457, 1966.
2. R.J. Herold and R.A. Livigni, *Polymer Preprints*, 1972, **13**, 1, 545.
3. R. Herold and R. Livigni in *Polymerisation Kinetics and Technology,* Ed., N.A.J. Platzer, Advances in Chemistry Series No.128, ACS, Washington, DC, USA, 1973, p.208.

4. J. Herold, *Macromolecular Synthesis*, 1974, **5**, 9.

5. R.A. Livigni, R.J. Herold, O.C. Elmer and S.L. Aggarwal in *Polyethers*, Ed., E.J. Vandenberg, American Chemical Society Symposium No.6, ACS, Washington, DC, USA, 1975.

6. J. Kuyper and G. Boxhoorn, *Journal of Catalysis*, 1987, **105**, 1, 163.

7. D.F. Mullica,W.O. Milligan, G.W. Beall and W.L. Reeves, *Acta Crystallography*,1978, **B34**, 12, 3558.

8. T. Hiromitsu, O. Shigeyuki, I. Masaki and Y. Shigeaki, inventors; Asahi Glass Co., Ltd., assignee; JP 3115430A2, 1919.

9. J.T. Ruszkay, inventor; Arco Chemical Technology, assignee; US 5,416,241, 1995.

10. J.W. Reisch, M.M. Martinez and M. Raes, inventors; Olin Corporation, assignee; US 5,144,093, 1992.

11. C. Smith, J.W. Reisch and J.M. O'Connor, *Journal of Elastomers Plastics*, 1992, **24**, 4, 306.

12. B. Le-Khac, inventor; Arco Chemical Technology, assignee; EP 654,302A1, 1995.

13. B. Le-Khac, P.T. Bowman and H.R. Hinney, inventors; Arco Chemical Technology, assignee; EP 743,093, 1996.

14. B. Le-Khac, H.R. Hinney and P.T. Bowman, inventors; Arco Chemical Technology, assignee; US 5,627,122, 1997.

15. J. Hoffmann, P. Gupta, H. Pielartzik, P. Ooms and W. Schäfer, inventors; Bayer, assignee; EP 892,002A1, 1999.

16. G.H. Grosch, H. Larbig, R. Lorenz, D. Junge, E. Gehrer and U. Trueling, inventors; BASF assignee; WO 99/16775, 1997.

17. Y. Kazuhiko and T. Hiromitsu, inventors; Asahi Glass, assignee; JP4,145123, 1990.

18. B. Le-Khac, inventor; Arco Chemical Technology, assignee; EP 700,949A2, 1996.

19. B. Le-Khac, inventor; Arco Chemical Technology, assignee; EP 761,708A3, 1997

20. B. Le-Khac, inventor; Arco Chemical Technology, assignee; European EP 894,108A1, 1999.

21. B. Le-Khac, inventor; Arco Chemie Technologie Nederland, assignee; WO 9816310A1, 1998.

22. B. Le-Khac, inventor; Arco Chemical Technology, assignee; US 5,693,584, 1997.

23. J. Hoffmann, P. Gupta, R-J. Kumpf, P. Ooms and W. Schäfer, inventors; Bayer, assignee; WO 9919062A1, 1999.

24. J. Hoffmann, P. Gupta, R-J. Kumpf, P. Ooms, W. Schäfer and M. Schneider, inventors; Bayer, assignee; WO 9919063A1, 1999.

25. J. Hoffmann, P. Ooms, P. Gupta, M. Schneider and W. Schäfer, inventors; Bayer AG, assignee; WO 99/33562A1, 1999.

26. J. Hoffmann, P. Ooms, P. Gupta and W. Schäfer, inventors; Bayer AG, assignee; WO 9946042, 1999.

27. P.T. Bowman, H.R. Hinney and R.L. Meeker, inventors; Arco Chemical Technology, assignee; US 5,714,639, 1998.

28. B. Le-Khac, H.R. Hinney and P.T. Bowman, inventors; Arco Chemical Technology, assignee; US 5,780,584, 1998

29. J.F. Pazos and T.T. Shih, inventors; Arco Chemical Technology, assignee; US 5,689,012, 1997.

30. *Plastics Technology*, 1999, **45**, 3, 67.

31. *Chemical Engineering*, 1999, **106**, 12, 94.

32. K. Sugiyama, H. Fukuda, A, Horie and H. Wada, inventors; Asahi Glass Company, assignee; EP 1022300B1, 2004.

33. B. Le-Khac, W. Wang and M.K. Faraj, inventors; Arco Chemical Technology, assignee; US 6,063,897, 2000.

34. R.M. Wehmeyer, inventor; Dow Global Technologies Inc., assignee; US 6,429,166, 2002.

35. K.S. Clement, L.L. Walker, R.M. Wehmeyer, R.H. Whitmarsh, D.C. Molzahn, W.P. Diaris and D.E. Laycock, inventors; Dow Global Technologies Inc., assignee; US 6,429,342, 2002.

36. P. Ooms, J. Hoffmann and P. Gupta, inventors; Bayer AG, assignee; US 6,468,939, 2002.

37. G.H. Grosch, H. Larbig, R. Lorenz, D. Junge and K. Harre, inventors; BASF AG, assignee; US 6,441,247, 2002.

38. J. Hoffmann and P. Gupta, inventors; Bayer AG, assignee; US 6,482,993, 2002.

39. K.B. Chandalia, J.W. Reisch and M.M. Martinez, inventors; Olin Corporation, assignee; US 5,391,722, 1995.

40. T. Watabe, H. Takeyasu, T. Doi and N. Kunii, inventors; Asahi Glass Company, Ltd., assignee; EP 0383333, 1990.

41. J.M. O'Connor and R.L. Grieve, inventors; Synuthane International Inc., assignee; WO 0183107A3, 2001.

42. L.E. Katz and J.W. Reisch, inventors; Olin Corporation, assignee; US 5,099,075, 1992.

43. M.K. Faraj, inventor; Arco Chemical Technology, assignee; US 6,051,680, 2000.

44. D.E. Laycok, K.L. Flagler and R.J. Gulotty, Jr., inventors; Dow Chemical Company, assignee; US 6,376,645, 2002.

45. D.E. Laycok and K.L. Flagler, inventors; Dow Chemical Company, assignee; US 6,358,877, 2002.

46. B. Le-Khac, inventor; Bayer Antwerp NV, assignee; US 6,211,330, 2001.

47. D.E. Laycok, K.L. Flagler and R.J. Gulotty, Jr., inventors; Dow Chemical Company, assignee; US 6,388,048, 2002.

48. E. Baum, S. Bauer, K. Harre, G. Tischer, G-H. Grosch, R. Pretzsch, T. Ostrowski, M.J. Pcolinski, S. Dinsch, I. Rotermund and R. Lorenz, inventors; BASF AG, assignee; DE 19949091, 2001.

49. J. Kim, J-T. Ahn, C.S. Ha, C.S. Yang and I. Park, *Polymer,* 2003, **44,** 11, 3417.

50. I. Kim, J-T. Ahn, I. Park and S. Lee in *Proceedings of the API Annual Technical/ Marketing Conference, Polyurethanes, 2002*, Salt Lake City, UT, USA, 2002, p.583.

51. J. Schuchardt and S. Harper in *Proceedings of the 32nd Annual Polyurethane Technical Marketing Conference,* San Francisco, CA, USA, 1989, p.360.

52. J.W. Reisch and D.M. Capone, *Elastomerics,* 1991, **123**, 4, 18.

53. Y. Fukazawa and T. Hashimoto, inventors; Asahi Chemical Industry Co., Ltd., assignee; JP 9040796, 1997.

54. A.J. Heuvelsland, inventor; The Dow Chemical Company, assignee; US 5,114,619, 1992.

55. A.J. Heuvelsland, inventor; The Dow Chemical Company, assignee; US 5,070,125, 1991.

56. W. Reich, E. Beck, E. Keil, U. Jager, M. Lokai, W. Fries and E. Ambach, inventors; BASF, assignee; EP737,121, 1997.

57. M. Kouno, K. Mizutani, T. Nobori and U. Takaki, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,763,555A2, 1997.

58. T. Nobori, T. Suzuki, S. Kiyano, M. Kouno, K. Mizutani, Y. Sonobe and U. Takaki, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,791,600A1, 1997.

59. S. Yamasaki, Y. Hara, S. Yamura, F. Yamazaki, H. Watanabe, M. Matsufuji, S. Matsumoto, A. Izukawa, M. Aoki, T. Nobori and U. Takaki, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,916,686A1, 1999.

60. M. Isobe, K. Ohkubo, S. Sakai, U. Takaki, T. Nobori, T. Izukawa, and S. Yamasole, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,897,940A2, 1999.

61. T. Hayashi, K. Funaki, A. Shibahara, K. Mizutani, I. Hara, S. Kiyono, T. Nobori and U. Takaki, inventors; Mitsui Toatsu Chemicals, Inc., assignee; EP 0,950,679A2, 1999.

62. F.E. Bailey, Jr., and J.V. Koleske, *Alkylene Oxides and Their Polymers*, Marcel Dekker, New York, NY, USA, 1991, p.76-79.

63. D.E. Laycock, R.J. Collacott, D.A. Skelton and M.F. Tchir, *Journal of Catalysis,* 1991, **130**, 2, 354.

64. J. Shen, K.G. McDaniel, J.E. Hayes, U.B. Holeschouskyu and H.R. Hinney, inventors; Arco Chemical Technology, assignee; US 5,990,232, 1999.

65. L. Xiaohua, K. Maoqing, W. Xinkui, *China Synthetic Rubber Industry*, 2001, **24**, 3, 147.

66. S. Chen and L. Chen in *Proceedings of the API Annual Technical and Marketing Conference, Polyurethanes 2002*, Salt Lake City, UT, USA, 2002, p.681.

67. S. Chen, N. Xu and J. Shi, *Progress in Organic Coatings,* 2004, **49**, 2, 125.

68. K.S. Clement, L.L. Walker, R.M. Wehmeyer, R.H. Whitmarsh, D.C. Molzahn, W.P. Diaris, D.E. Laycock, J.W. Weston and R.J. Elwell, inventors; Dow Global Technologies Inc., assignee; US 6,642,423, 2003.

6 Polymer Polyols (Filled Polyols)

Polymer polyols are defined as very fine and stable dispersions of solid polymers (vinylic polymers and copolymers, polyurea, polyurethanes) in liquid polyethers. Currently polymer polyols represent one of the most important group of polyolic intermediates for elastic polyurethanes [1-10].

The experience of flexible foam manufacture using polyols containing inorganic fillers ($BaSO_4$, $CaCO_3$), leads to the observation that fillers act as nucleating agents during the foaming process and aid cell opening at the end of the rise process, and the hardness or load bearing properties of the resulting filled flexible PU foams are markedly improved. Generally the inorganic fillers substantially increase the flexible foam density.

As with the inorganic fillers, the organic polymers can be successfully used as fillers. The preferred method is the synthesis of polymeric filler *in situ*, by radical polymerisation, polycondensation or polyaddition processes, developed in liquid polyether media [1-10].

These kind of polyether polyols containing polymeric fillers are called polymer polyols and are produced on a large industrial scale, because they are one of the most important group of polyols used for high performance flexible polyurethane (PU) foams and PU elastomers [8-12].

Polymer polyols are divided, by the nature of the polymer finely dispersed in the polyether matrix, into the following categories [8-10]:

a) Graft polyether polyols (the dispersed polymer is a carbocatenary vinylic polymer or copolymer obtained by radical polymerisation),

b) Poly Harnststoff Dispersion (PHD polyols; dispersions of polyurea),

c) Polyisocyanate poly addition (PIPA) polyols (polyurethane dispersions), and

d) Other polymer polyols (epoxy dispersions, aminoplast dispersions).

6.1 Graft Polyether Polyols

Graft polyether polyols are synthesised by *in situ* radical polymerisation of vinylic monomers in liquid polyethers, by batch, semi-continuous or continuous processes. The solid fraction varies between 10-50%, more frequently being between 10-40% [1-10].

The selected monomers are: acrylonitrile (ACN), styrene, α-methyl styrene methylmethacrylate, hydroxyalkyl acrylates and methacrylates, vinyl chloride and others [1-10, 13-18]. The most favoured monomers for industrial production of graft polyether polyols are ACN and styrene [1-10, 18-29]. The resulting products from the radical polymerisation of vinylic monomers in polyethers are opaque, generally white dispersions (except those derived from ACN, which are yellow dispersions). A graft polyether polyol has three polymeric components:

- the liquid polyether polyol (continuous liquid phase),
- linear ungrafted carbocatenary vinylic polymer, and
- grafted vinylic polymer on the polyether chains.

The third component, the graft species, acts as a nonaqueous dispersant (NAD), a compound having, in the same structure, polyetheric chains and vinylic polymer chains. This compound assures the stability of the resulting polymer dispersion and prevents sedimentation and coalescence of the vinylic polymer particles [1-5]. The mechanism of this dispersion stabilisation will be discussed later. The median diameter of solid particles for a performance polymer polyol is generally less than 1 μm, usually 0.2-0.5 μm [30].

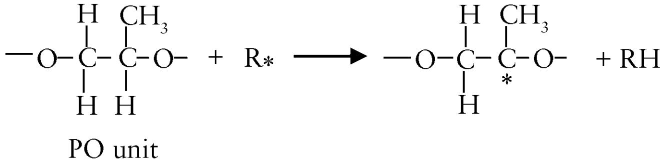
Practically, the process for the synthesis of graft polyether polyols consists of the addition of a mixture of polyether, vinylic monomer, radical initiator, and chain transfer agent to a polyether (or to a mixture of polyether and a nonaqueous dispersant) at high temperature (115-125 °C) [1-3]. Because the vinylic polymer is insoluble in the liquid polyether and precipitates during the grafting reaction, it is necessary to have very efficient stirring of the reaction mass (total recirculation of the reaction mass in loop reactors with high flow centrifugal pumps, turbine stirrers, sometimes use of static mixtures on the recirculation pipes), in order to obtain very fine particles. Because the radical polymerisation is a very rapid process, low efficiency of mixing leads to the formation of aggregates of big particles due to a local polymerisation, the vinylic monomers have not enough time to be homogenised with the reaction mass and so form aggregates.

Of course, a fundamental role in the formation of very fine particles plays the stabilising efficiency of the nonaqueous dispersant.

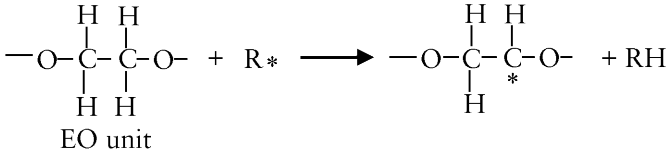
6.2 The Chemistry of the Graft Polyether Polyol Synthesis

The hydrogen atoms situated in the α position against the etheric oxygen atoms of the polyetheric chain are very susceptible to radical attack (hydrogen abstraction by radical mechanism), giving transfer reactions [1, 12, 18].

Thus, a propylene oxide unit in a polyether chain has 3 α-hydrogen atoms and an ethylene oxide (EO) unit has 4 α-hydrogen atoms:



$$-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-O- + R* \longrightarrow -O-\underset{H}{\overset{H}{C}}-\underset{*}{\overset{CH_3}{C}}-O- + RH$$



$$-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O- + R* \longrightarrow -O-\underset{H}{\overset{H}{C}}-\underset{*}{\overset{H}{C}}-O- + RH$$

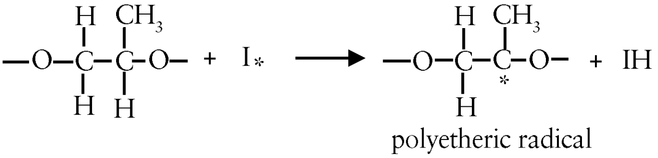
Due to the high number of α-hydrogen atoms, polyethyleneoxides are considered better transfer agents than propyleneoxides [2], in spite of the high lability of the tertiary hydrogen atom (hydrogen atom linked to the same carbon atom where is the methyl group) from the PO units.

The homopolymerisation and copolymerisation of vinylic monomers in liquid polyether polyols are typical chain reactions by radical mechanism and are characterised by: initiation, propagation and termination steps [31]:

a) Initiation reaction (thermal scission of the initiator in free radicals):

$$I—I \xrightarrow{\Delta} I* + I*$$

By the attack of the radical I* on a polyetheric chain, radical species situated at a carbon atoms of the polyetheric chains are generated by transfer reactions:

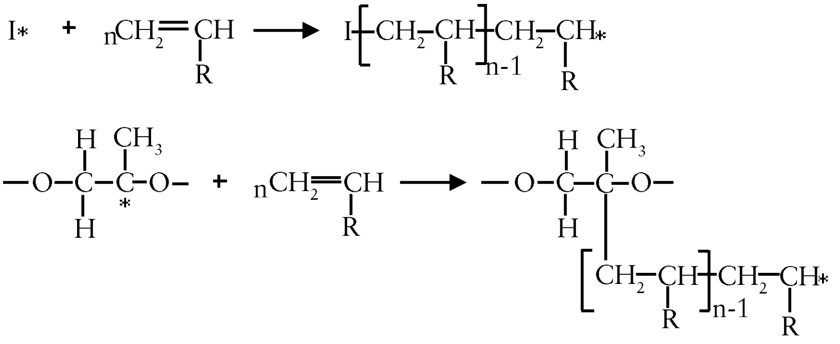


$$-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-O- + I* \longrightarrow -O-\underset{H}{\overset{H}{C}}-\underset{*}{\overset{CH_3}{C}}-O- + IH \quad (6.1)$$

(6.1)

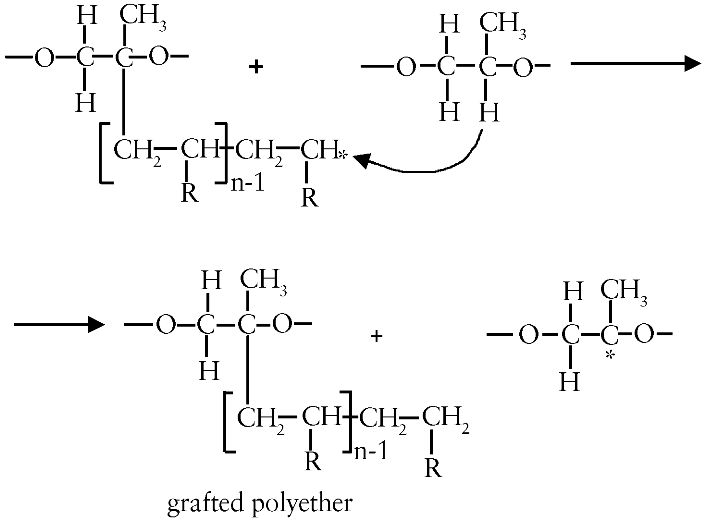
b) Propagation reaction:

Both radicals, I* and the radical generated on the polyetheric chains, initiate the radical polymerisation of vinylic monomers. The radical I* leads to the formation of ungrafted carbocatenary vinylic polymer. The polyetheric radical generates the formation of graft species:



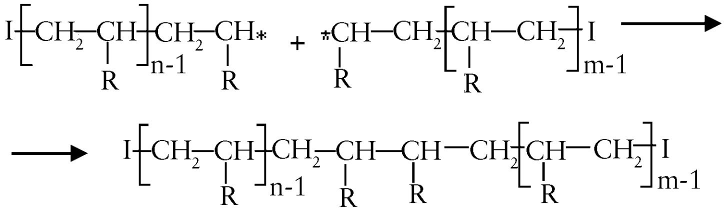
c) Termination reaction takes place by transfer, recombination or by disproportionation:

Termination by transfer:



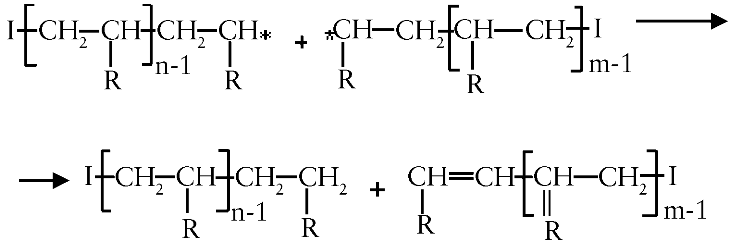
(6.2)

Termination by recombination (coupling of two macroradicals):



$$I\!-\!\left[CH_2-\underset{R}{CH}\right]_{n-1}\!-CH_2-\underset{R}{CH}{*} + {*}\underset{R}{CH}-CH_2-\left[\underset{R}{CH}-CH_2\right]_{m-1}\!-I \longrightarrow I\!-\!\left[CH_2-\underset{R}{CH}\right]_{n-1}\!-CH_2-\underset{R}{CH}-\underset{R}{CH}-CH_2-\left[\underset{R}{CH}-CH_2\right]_{m-1}\!-I$$

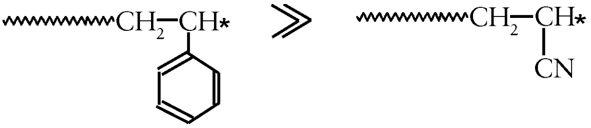
Termination by disproportionation:



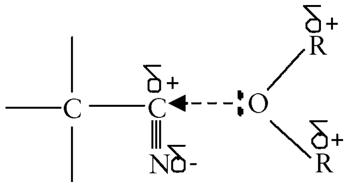
$$I\!-\!\left[CH_2-\underset{R}{CH}\right]_{n-1}\!-CH_2-\underset{R}{CH}{*} + {*}\underset{R}{CH}-CH_2-\left[\underset{R}{CH}-CH_2\right]_{m-1}\!-I \longrightarrow I\!-\!\left[CH_2-\underset{R}{CH}\right]_{n-1}\!-CH_2-\underset{R}{CH_2} + \underset{R}{CH}=CH-\left[\underset{R}{CH}-CH_2\right]_{m-1}\!-I$$

As mentioned before, the most important monomers for the industrial production of graft polyether polyols are: ACN and styrene.

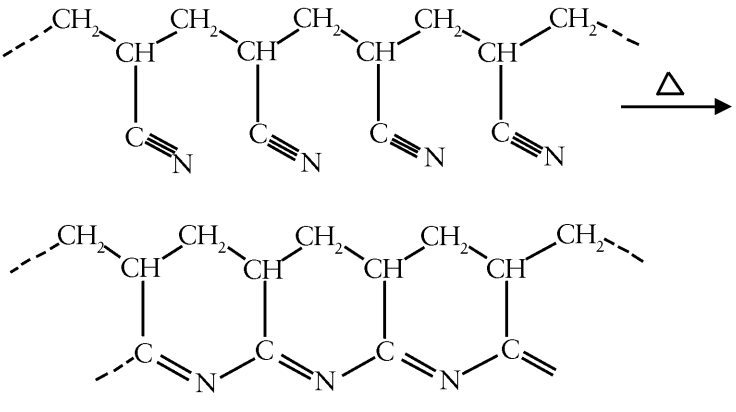
The stability of the macroradicals terminated in a styrene unit is much higher than the stability of the macroradicals terminated with an ACN unit [18]:



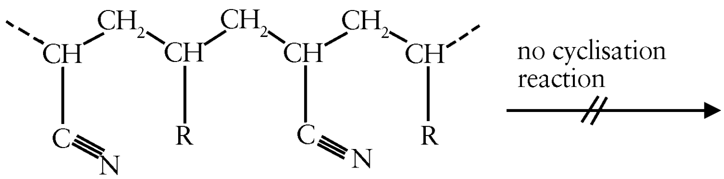
The order of this radical stability reverses the reactivity in the transfer reactions (reactions 6.1 and 6.2), that is the radical derived from ACN is much more reactive than the stable radical derived from styrene. This is the reason why the polymer polyols obtained exclusively with styrene give unstable polymeric dispersions (a sedimentation phenomenon, due to the absence of graft species appears, assuring the dispersion stability) [1, 3, 10]. On the contrary, the polymeric dispersions derived exclusively from ACN are extremely stable, due to the formation of grafted polyether polyol species which stabilise the dispersion very efficiently [1]. On the other hand, the interaction between -CN groups (electron acceptor groups) and the etheric groups (electron donating groups), leads to a supplementary contribution of the graft polyether polyols based on ACN stabilisation:



Unfortunately, ACN has a major disadvantage when used alone in grafting reactions, because the polymer polyols based exclusively on poly [ACN] are coloured products (light brown-yellow colour) and in the foaming process, at the higher temperatures used in continuous slabstock foams, at around 150-170 °C, a strong tendency to produce 'scorching' appears, a strong darkening in the centre of the polyurethane bun. This phenomenon is not a degradation of the polyetheric chain, it is in fact the formation of chromophoric groups due to an intramolecular cyclisation of two or more neighbouring -CN groups, which leads to a conjugate polycycloiminic polymer (6.3). This undesirable side reaction is avoided by using a comonomer together with ACN such as: styrene [1, 3-10], α-methyl styrene [18] or methyl methacrylate (MMA) [13]. The second monomer separates the ACN structural units, making the occurrence of intramolecular cyclisation impossible (reaction 6.4):



(6.3)



(6.4)

Thus, the most important commercial graft polyether polyols are based on ACN - styrene copolymers (styrene content 50-80%). The graft polyethers, having a high content of styrene, do not have a tendency to 'scorch'.

The polyether polyols based exclusively on ACN are commercialised because of their high glass transition temperature (T_g) of the polyacrylonitrile solid fraction. However, they are not used for production of slabstock foams, but for PU elastomers (microcellular elastomers for shoe soles) and integral skin foams.

Shell developed a special line of polymer polyols based exclusively on styrene [11], the stabilisation of the resulting dispersion of polystyrene in liquid polyether being given by special NAD [8, 9, 32, 33] and of course not to the graft species, which in the case of polystyrene are practically absent.

The graft polyether polyols, based exclusively on ACN or with a high ACN content (more than 50% ACN in the monomer mixture), do not need a special NAD due to the formation of graft species, the inevitable dispersion stabilisers formed *in situ*, the resulting dispersions being perfectly stable.

The stabilisation of polymeric dispersions in organic media is based on the principles of steric stabilisation [32, 33]. The steric stabilisation is assured by the presence of the NAD which have a very important characteristic: in the same chemical structure they have a segment with a strong affinity for the carbocatenary vinylic polymer and a second segment, a long polyetheric chain, with a strong affinity for the liquid polyether. The NAD is linked (chemically or physically adsorbed) on the surface of solid polymeric particles with the polymeric carbocatenary segment, the polyetheric chains at the exterior part of the polymeric particles are in the form of arms situated in the continuous polyetheric media, as shown in **Figure 6.1**.

The tendency to form the biggest particles by collapse (aggregation) of smaller diameter particles is avoided by the sterical repulsion between the external polyetheric arms (**Figure 6.2**) [32].

When two polymer particles are close to collapse, the concentration of polyetheric arms between the particles increases and an osmotic pressure spontaneously appears which forces the particles not to collapse [32].

For an improved stabilisation efficiency, the NAD which have longer polyetheric chains than the polyetheric chains of the polyether polyols are preferred for use as continuous phase [4, 6].

At this moment there are three ways to stabilise the polymeric dispersions in liquid polyethers with NAD:

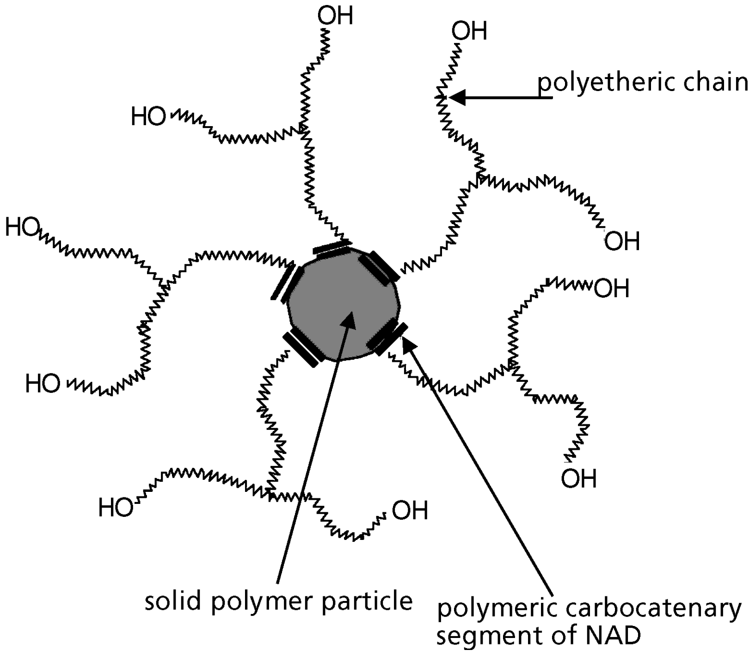


Figure 6.1 A solid polymer particle stabilised by NAD molecules

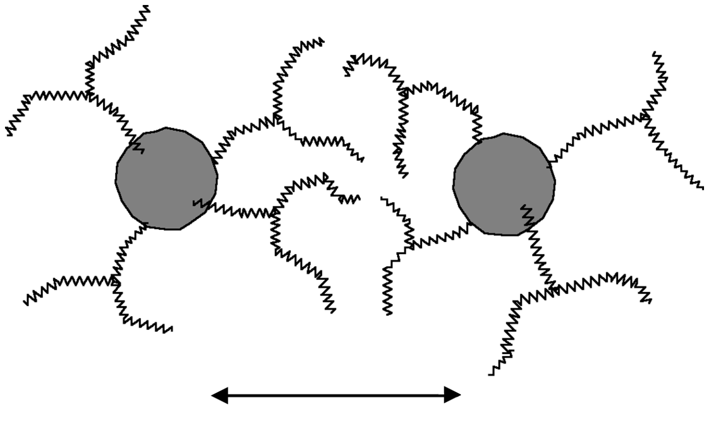


Figure 6.2 The sterical repulsion between two polymer particles

a) Generation *in situ* of the NAD by grafting reactions,

b) Utilisation in grafting reactions of macromers (surfmers – surfactant-monomer), in fact polyethers with polymerisable double bonds, and

c) Utilisation of nonreactive NAD (NAD without polymerisable double bonds).

6.2.1 Generation In Situ of NAD by Grafting Reactions

During the radical polymerisation of vinylic monomers in liquid polyether media, graft species (carbocatenary vinylic polymer chemically linked on the polyether) are formed, by chain transfer reactions, which play the role of a true NAD. For grafting reactions on polyether triols, the graft species have the following idealised structure (**Figure 6.3**).

It was mentioned previously that only the very reactive monomers (such as ACN and MMA), which form very reactive radicals, can generate these graft species, the true NAD being formed *in situ*. This is the reason that graft polyethers, based exclusively on ACN or with a high ACN content, do not need supplementary NAD. An alternative to generate graft species is to use radical initiators which generate radical species and give a strong transfer (strong ability of hydrogen abstraction) such as di-*tert*-butyl peroxide or *tert*-amyl peroxides [34].

In order to improve the chain transfer reaction with the polyether chains, a quantity of polyethers, having chemical groups which give very high transfer reaction rates such as -SH [35, 36], -S-S- [35, 36] or tertiary amine groups [37], were used in the mixture with polyethers used for grafting reactions.

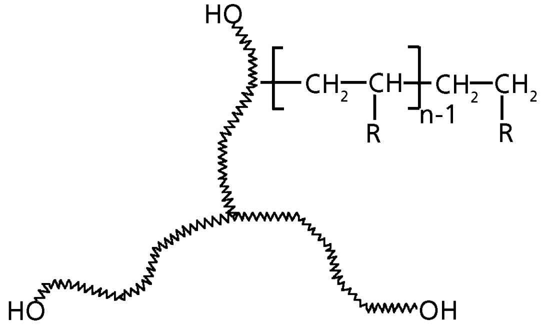
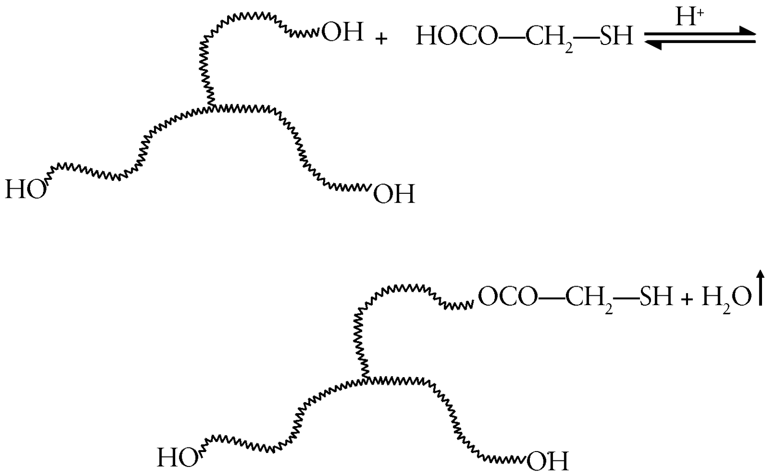
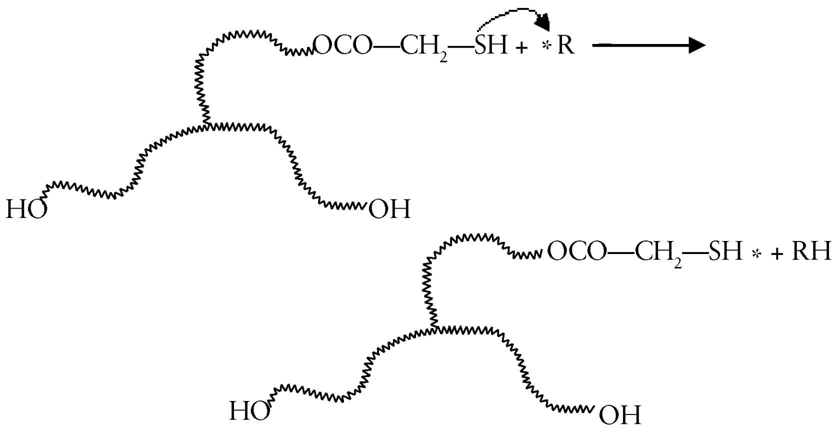


Figure 6.3 The structure of graft polyethers (NAD generated *in situ*)

Thus, the -SH group is very easy introduced as a terminal group in polyether polyols, by the esterification of terminal hydroxyl groups with thioglycolic acid in acid catalysis (reaction 6.5) [35, 36]. During the radical polymerisation of vinylic monomers in polyether media, the polyether with terminal -SH groups gives a very strong transfer (reaction 6.6).

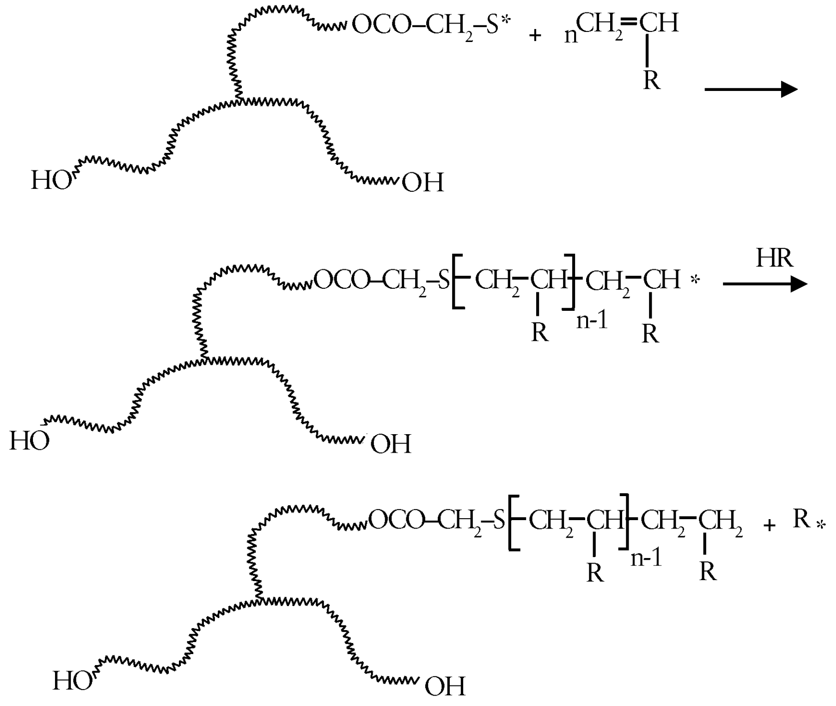


(6.5)



(6.6)

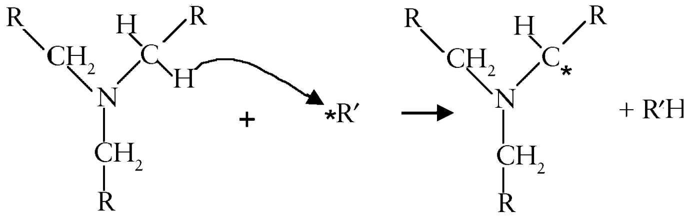
The radical generated at the sulfur atom initiates a new polymeric carbocatenary chain:



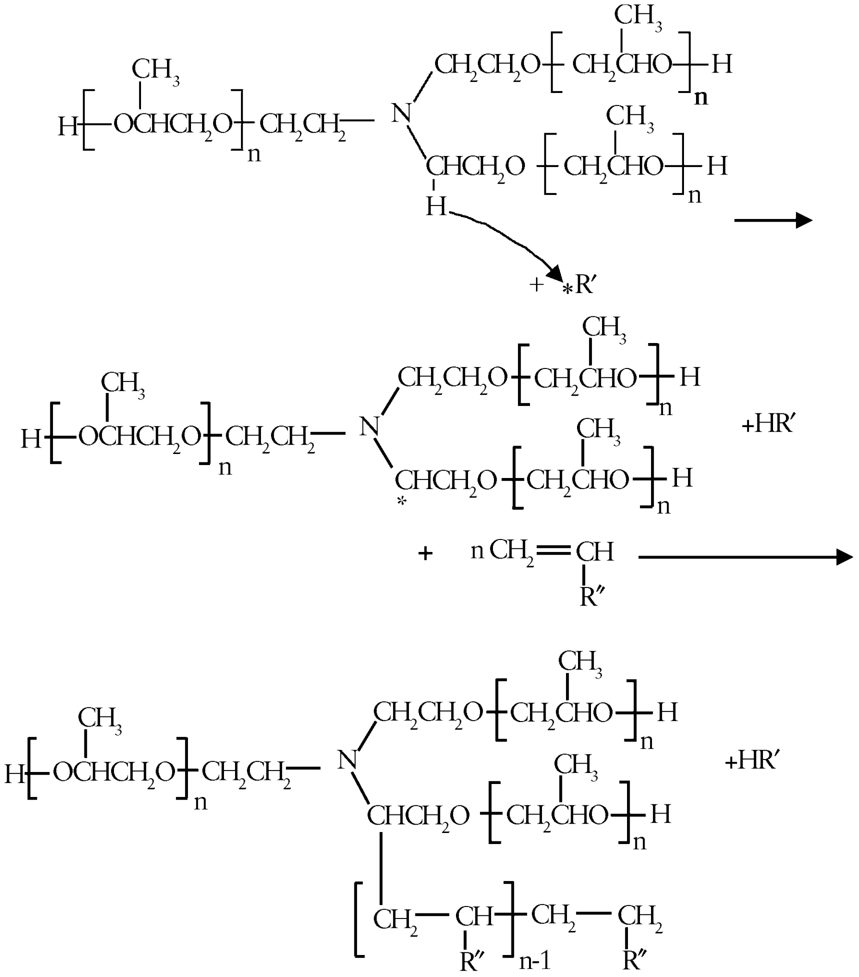
(6.7)

The resulting structure (6.7) is in fact a very efficient NAD obtained *in situ* by transfer reactions with terminal -SH groups [35, 36].

Another interesting group of substances, which give a very strong transfer in radical polymerisations, are trialkylamines. The hydrogen atoms situated in the α- position against the nitrogen atom are very labile and give very strong transfer reactions [37-39]:



The polyether polyols, initiated by triethanolamine or by the ethylene diamine with a molecular weight of 3000-7000 daltons, are polyethers having a tertiary amine structure with a high capability to give transfer reactions [37, 39]:



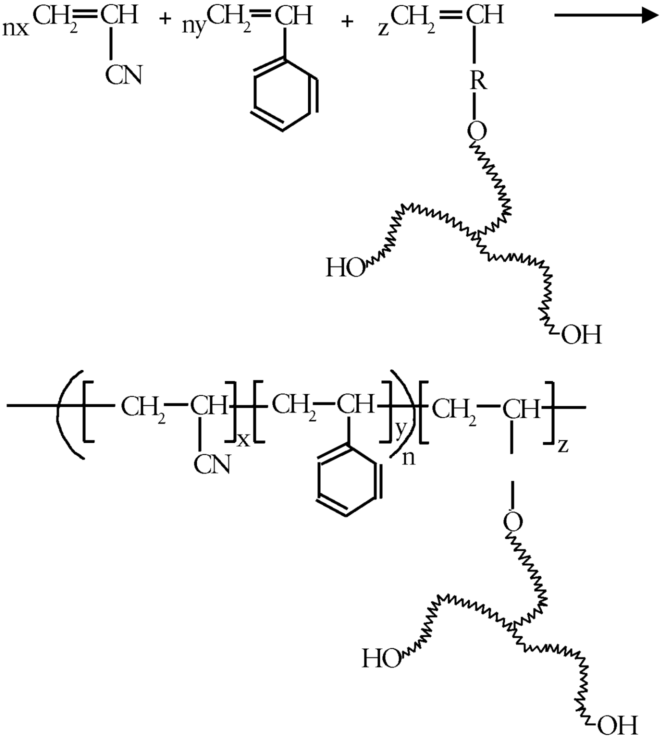
(6.8)

The structure (6.8) is another type of NAD formed *in situ* by transfer reaction with the tertiary amine type polyethers. Addition of a high molecular weight polyether initiated by an alkanolamine, ethylene diamine, *N*-methyl substituted propylene diamine, or *N*,*N* dimethyl dipropylene diamines in the polyether polyol used for grafting leads to the formation of very stable polymeric dispersions [37]. The solid fraction has particles of low median diameter (<1.5 μm). The resulting polymer polyols have low viscosities which give good stabilisation of the polymeric dispersion.

The dispersions obtained by copolymerisation of styrene with ACN, with low ACN content (ACN being around 25-30% in the monomer mixture), are more difficult to stabilise. For such low ACN content polymer polyols, or for polymer polyols based exclusively on styrene, more efficient NAD are necessary. These are discussed in the next chapters, i.e., macromers (reactive NAD) and nonreactive NAD.

6.2.2 Stabilisation of Polymer Dispersions in Polymer Polyols with Macromers (Reactive NAD)

The macromers used in the stabilisation of polymer dispersions are in fact polyether polyols with terminal double bonds, able to copolymerise with vinylic monomers (ACN, styrene) and to form graft species during the radical copolymerisation. The resulting graft polyether polyol, formed *in situ* by the copolymerisation process, is in fact a NAD:

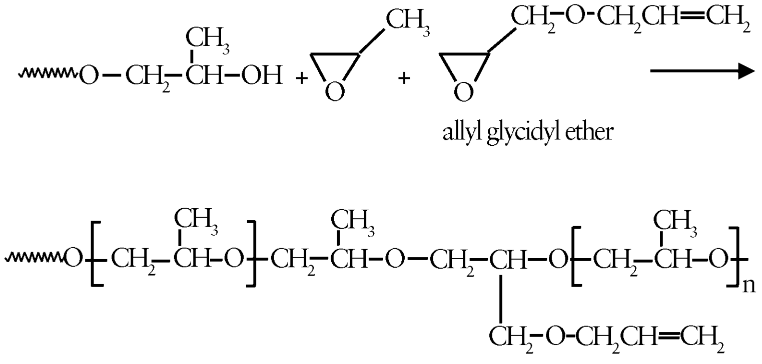


(6.9)

These graft species (6.9), artificially created by copolymerisation (not by transfer with polyetheric chains) assure an excellent stability of the polymeric dispersions in liquid polyether media. It is possible to obtain stable polymer dispersions by radical polymerisation of monomers which do not develop transfer reactions with the polyetheric chain, such as styrene. Due to their similarities to surfactants (one segment is lyophilic – the polyether chain and one segment is lyophobic – the carbocatenary polymer), the copolymers resulting from radical copolymerisation of vinylic monomers with the macromers are called 'surfmers'. The macromers used in the synthesis of polymer polyols by radical polymerisation lead to very fine polymeric dispersions (medium diameter < 1-1.5 μm), having lower viscosities with a high solid content.

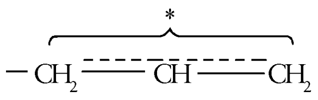
The most important way to synthesise macromers having polyetheric chains is to attach to the one terminal hydroxyl group a double bond (by various reactions of hydroxyl groups) or to introduce a double bond as a lateral group in the polyetheric chain [4, 8, 9, 11, 12, 40-56].

One of the older methods to obtain macromers is to add very small quantities of a monomer having a double bond and a polymerisable epoxy group in the same structure to propylene oxide, during the anionic polymerisation. A typical example of such a kind of monomer is allyl glycidyl ether. This monomer copolymerises anionically with PO, giving polyethers with small quantities of lateral double bonds (reaction 6.10).



(6.10)

The lateral allylic double bonds copolymerise with ACN and styrene, giving graft species *in situ*. This method has the advantage that the polyether used for grafting is made using the classical technology of anionic polymerisation, and then it is necessary to add only a small quantity of allyl glycidyl ether to the PO used for the synthesis. The disadvantage of this method is that the allyl group is not so reactive in radical polymerisation, because the radical derived from an allyl group is stable and of low reactivity, due to the well known conjugation:

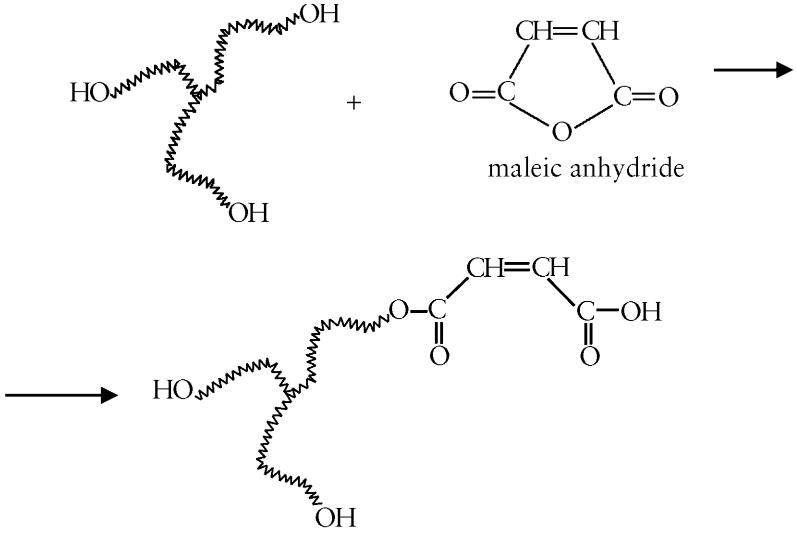


As an immediate consequence, only a part from the allylic groups participates in copolymerisation with vinylic monomers, to generate the 'graft species'.

The best way to obtain macromers with polyetheric chains is to use the reactions of polyether terminal hydroxyl groups with reagents containing double bonds.

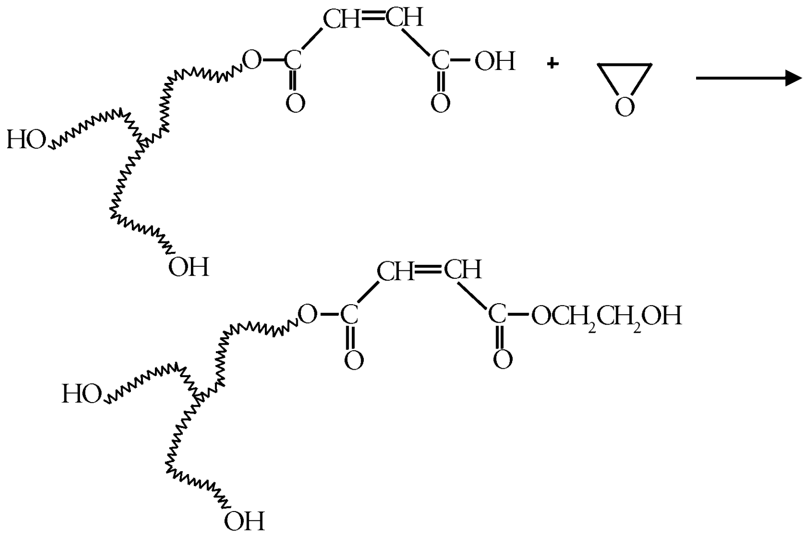
The most used reagent to generate double bonds, by the reaction with hydroxyl groups, is maleic anhydride (MA) [44-46, 55-57].

MA reacts quantitatively with hydroxyl groups at moderate temperatures (60-70 °C), with the formation of half esters of maleic acid (6.11).



(6.11)

So as not to increase the acidity of the resulting polymer polyol too much, the acidic carboxyl groups are esterified by the reaction with PO or EO (EO is preferred), for several hours at 120-130 °C:



(6.12)

The preferred polyether used in this reaction is a higher molecular weight triol of 5000-6000 daltons (preferred MW is 6000 daltons). By copolymerisation of the macromer (structure 6.12) with ACN and styrene, a NAD is obtained *in situ*, which is in fact a graft copolymer:

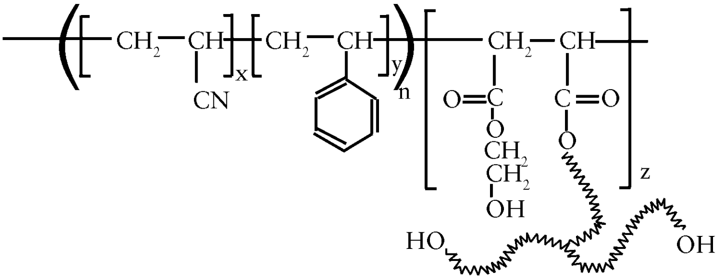


Figure 6.4 The structure of ternary copolymer ACN-styrene-maleic anhydride macromer, a NAD generated *'in situ'* by radical copolymerisation

It was observed experimentally that the *trans* isomer of maleic structures: the fumaric ester structures, are more reactive in copolymerisation with ACN and styrene than the maleic esters. The maleic esters (*cis* isomers, of structure 6.12) were rearranged to form fumaric esters (*trans* isomers, of structure, shown in **Figure 6.4**), in the presence of specific catalysts such as: calcium salts of organic acids (calcium naphthenate [55], calcium octanoate [55]) or morpholine [55]. The resulting very efficient and reactive macromer structure of the fumaric ester type is shown in **Figure 6.5**.

The concentration of these kinds of macromers, used in polymer polyol synthesis, is around 2-5% compared to the final polymer polyol. Higher concentrations lead to an undesired, substantial viscosity increase together with a decrease in median diameter of the resulting solid polymer particles. A lower concentration of macromer leads to poor stabilisation of the resulting polymer dispersion.

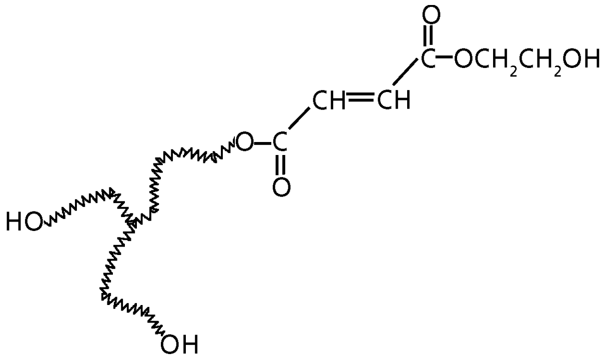
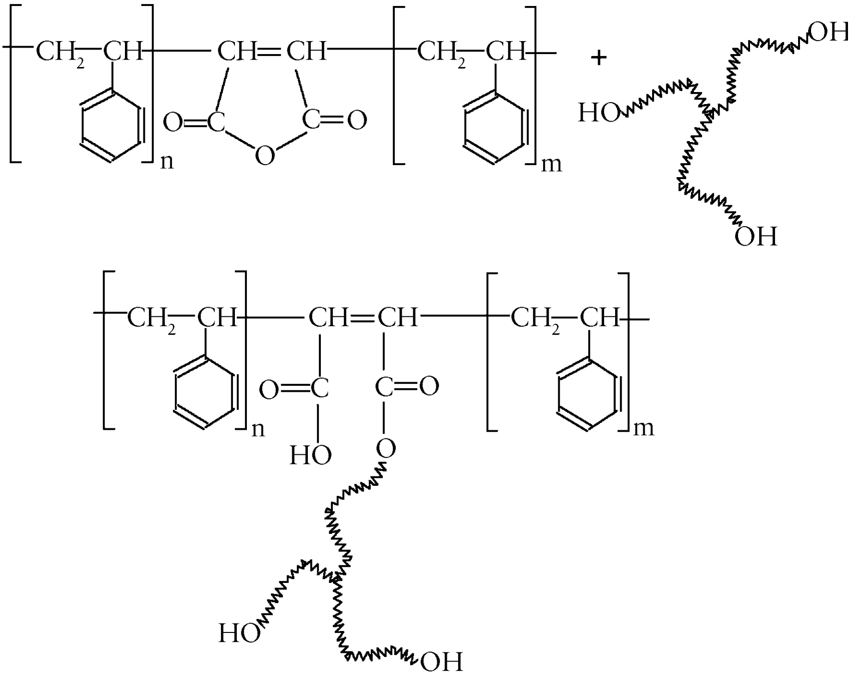


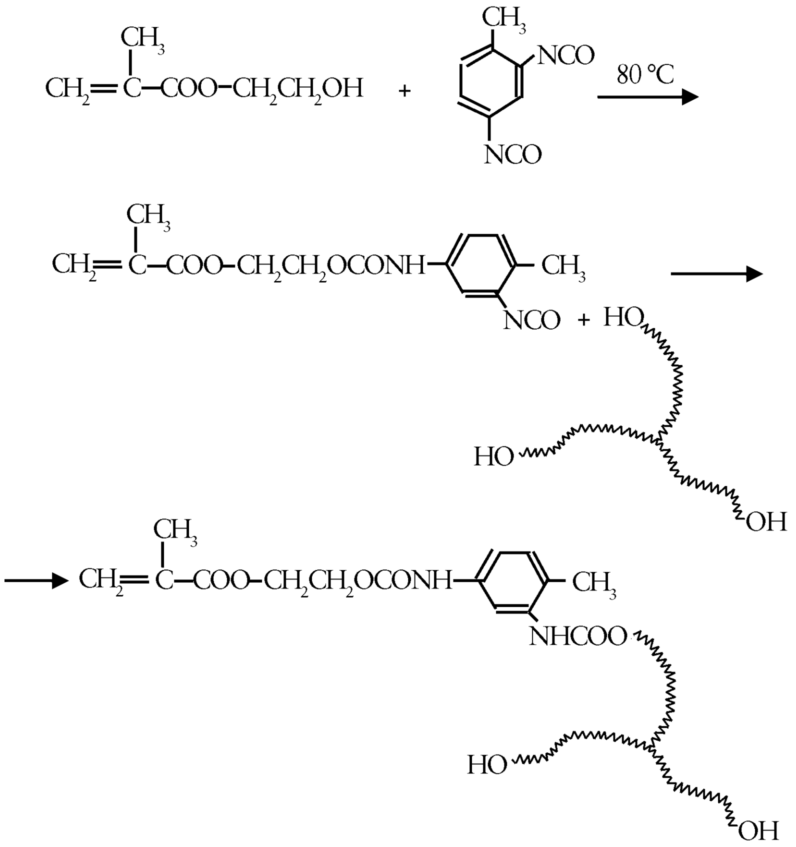
Figure 6.5 Macromer with fumaric ester structure

The presence of macromers in the synthesis of polymer polyols has another important technological advantage: it avoids the formation of crusts of vinylic polymer on the walls of the reactor used for radical copolymerisation.

MA can be used as comonomer together with the vinylic monomers (ternary copolymerisation ACN - styrene - MA) and the graft species is formed *in situ* by the reaction of the resulting copolymer ACN - styrene - MA with the polyether polyol, by its terminal hydroxyl groups. Another variant is to use a styrene - MA copolymer as NAD. This copolymer proved to be a very good NAD for high styrene content polymer dispersions in polyethers. Of course the real NAD is made by the reaction of a MA unit with the terminal hydroxyl group of the polyether [57].

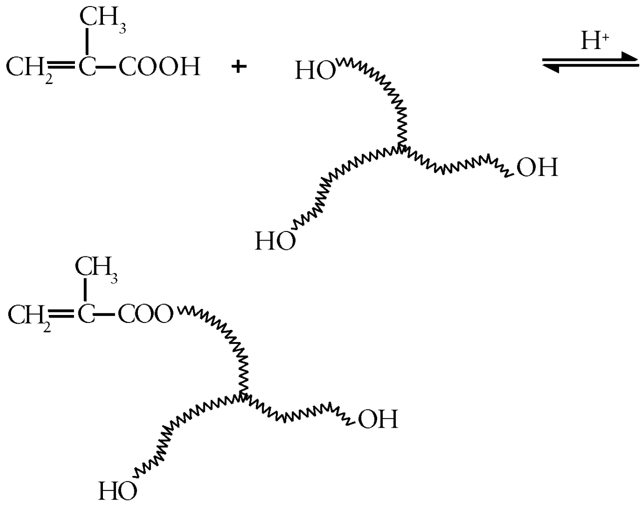


A very convenient method to obtain a macromer (structure 6.13) is by using an unsaturated isocyanate [50] or by using some accessible raw materials, by the reaction of a hydroxyalkyl acrylate or methacrylate with one -NCO group of a diisocyanate for example, 2,4 toluene diisocyanate (TDI) and to react the remaining -NCO group with the terminal hydroxyl group of a polyether polyol:



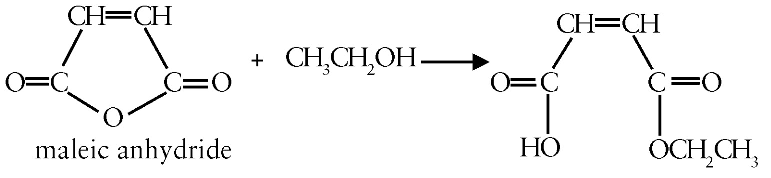
(6.13)

The simple esterification of acrylic or methacrylic acids, in acidic catalysis, with terminal hydroxyl groups of polyethers is a direct way to obtain macromers [47]:

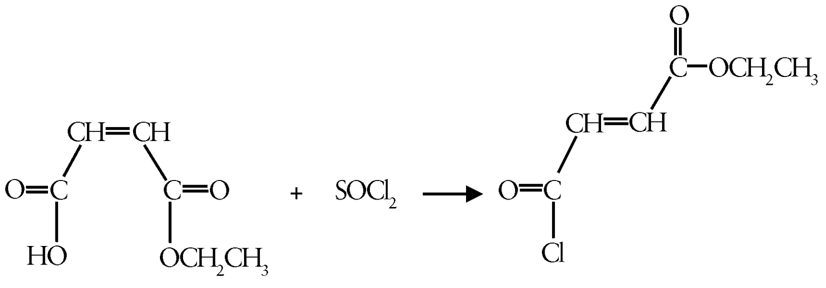


A simple and convenient method to obtain macromers useful for polymer polyols synthesis is based on the following succession of reactions (a-c) [52]:

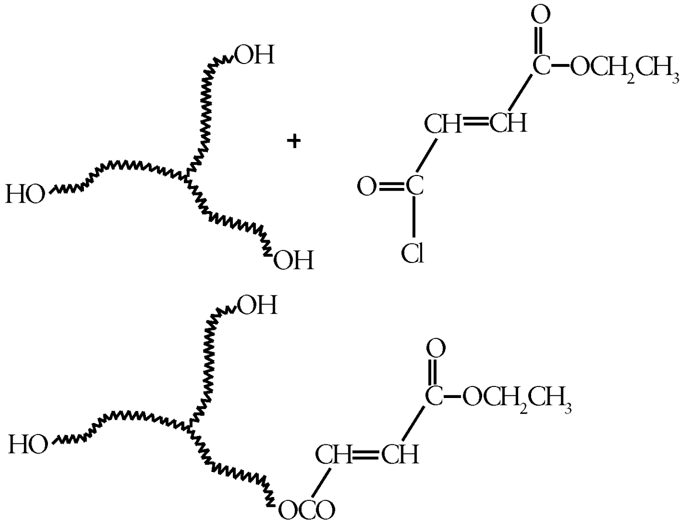
a) Reaction of MA with ethanol:



b) The half ester of MA is transformed in an acid chloride by the reaction with thionyl chloride ($SOCl_2$) together with a rearrangement to a fumaric acid structure:

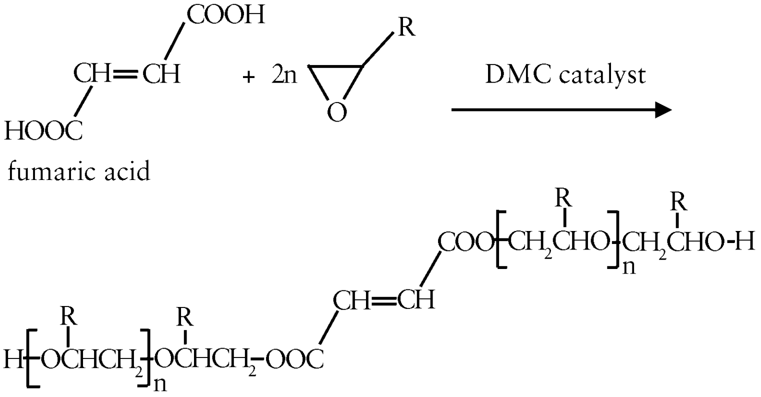


c) The resulting acid chloride of the fumaric acid half ester is reacted with the hydroxyl groups of polyethers, generating the terminal double bond of a macromer (structure 6.14), successfully used in polymer polyol stabilisation:



(6.14)

A direct method to obtain an efficient macromer useful as NAD for polymer dispersion stabilisation is the PO homopolymerisation or random PO-EO copolymerisation initiated by fumaric acid and catalysed by DMC catalyst [53]:



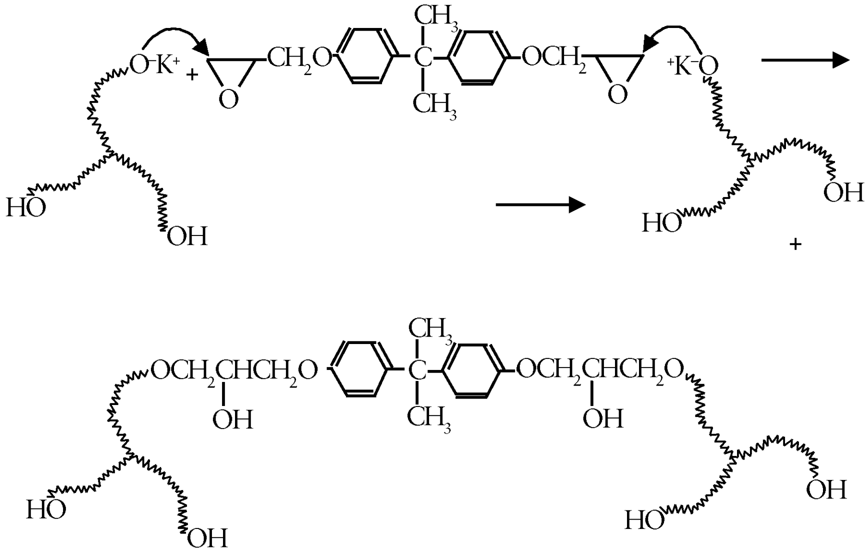
Of course there are many other reagents used to attach a double bond to polyether polyols such as: chloromethyl styrene (mixture of *meta* and *para* isomers), glycidyl acrylate and methacrylate [48] triethoxy or trimethoxy vinyl silanes [54].

6.2.3 Nonreactive Nonaqueous Dispersants

The nonreactive NAD are structures without polymerisable double bonds, but have a remarkable stabilisation effect on polymeric dispersions in polyether media. The main characteristic of such kinds of nonreactive NAD is to have an organic segment with high affinity for the carbocatenary vinylic polymer chemically linked to a high molecular weight polyether chain, which has a high affinity for the continuous liquid polyether matrix.

One such type of NAD is obtained by the reaction of a crude, alkaline, high molecular weight polyether of 6000 daltons, with a liquid epoxy resin having two epoxy groups (for example diglycidyl ether of bisphenol A).

After the reaction, developed in normal conditions of alkaline ring opening reactions, at 110-130 °C, the addition product is purified by classical methods, such as by treatment with adsorbents or by neutralisation - crystallisation techniques [58, 59].



(6.15)

The aromatic nuclei of the bisphenol A segment have a high affinity for the aromatic nuclei of styrene - ACN copolymer styrene units, the polyether chains having a strong interaction with the liquid polyether medium. As an immediate consequence, the structure 6.15 assures a good steric stabilisation of polymeric dispersions in liquid polyether polyols (see the structure in **Figure 6.6**).

A similar structure to the one in **Figure 6.6** is obtained by using instead of epoxy resins diphenylmethane diisocyanate (MDI pure or 'crude'). For example by using 'crude' MDI with the functionality of around 2.2-2.5 -NCO groups/mol, by the reaction with terminal groups of high molecular weight polyether triols (5000-6500 daltons), nonreactive NAD

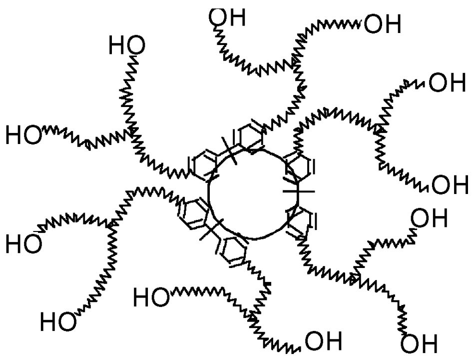
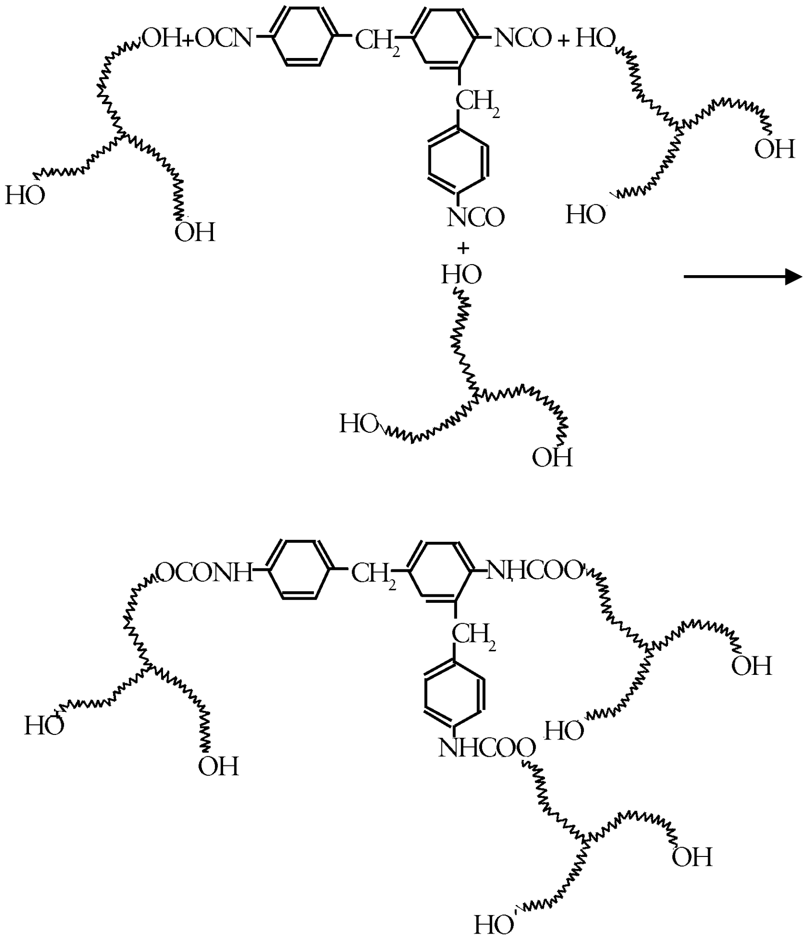


Figure 6.6 The structure of nonreactive NAD adsorbed on the vinylic polymer solid particle

are obtained with excellent capability to assure a good stabilisation of polymeric dispersions in liquid polyether polyols (reaction 6.16) [34-36, 60].

This kind of NAD, resulting from the reaction of 'crude' or pure MDI with high molecular weight polyether triols, is very efficient in stabilising copoly (ACN - styrene) dispersions or even polystyrene dispersions in polyether polyols.



(6.16)

Generally, the nonreactive NAD is used in higher concentrations, than the macromers in graft polyether polyols synthesis, of around 10-15% compared to the final polymer polyol.

Very efficient NAD (nonreactive from the point of view of radical polymerisation) are the very high molecular weight polyether polyols (e.g., a polypropylene glycol with a

MW of 120,000 daltons) [61]. In fact the nonreactive NAD presented before (structures 6.15 and 6.16) are polyethers with extended molecular weight, the chain extender being the epoxy resins or the diisocyanates (or polyisocyanates). As in the case of macromers, it is possible to obtain high, solid stable polymeric dispersions, of low viscosities, with nonreactive NAD too.

6.2.4 The Mechanism of Polymer Particle Formation in Polymer Polyols Synthesis by Radical Polymerisation [19]

The practical technique to obtain polymer polyols by radical polymerisation is to add an homogeneous mixture of vinylic monomer, initiator, chain transfer agent and a part of polyether polyol, to the rest of polyether polyol containing the NAD (macromer or nonreactive NAD), at 115-125 °C. The mechanism of solid polymer particle formation during radical polymerisation of vinylic monomers in liquid polyethers, in the presence of a nonreactive NAD, in the form of very stable dispersions, is described next.

By dissolving a nonreactive NAD in liquid polyether, NAD self organisation takes place in a spherical structure where the aromatic part is associated in the centre and the polyetheric chains are situated outside this sphere in the continuous polyether phase. The monomers have affinity for the aromatic part of this self-organised structure and are absorbed inside these ‘proto-particles’, of low diameter, of around 0.01-0.05 μm. This self-organisation structure is very similar to those of the micelle structure of surfactants in water. After consuming 3-5% of the total monomers the reaction mass turns from transparent to opaque white: this step is called the nucleation step. During the polymerisation of the remaining monomer quantity, no new particles appear and the polymerisation takes place inside the particles formed initially (**Figure 6.7**).

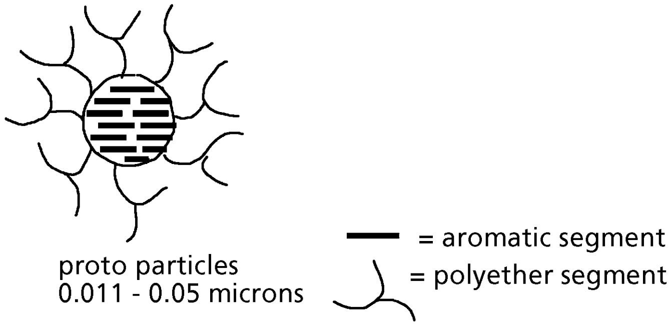


Figure 6.7 The structure of proto-particles, spherical self organised structures, with vinylic monomers surrounded by NAD

During the radical polymerisation process the median diameter of the particles increases from 0.01-0.05 to 0.2-0.6 μm. The final size is determined by the quantity of monomers and the number of particles. As a general rule, the number of polymer particles increases and the median diameter of particles decreases by increasing the quantity of NAD. Generally the particle size distribution is narrow and relatively monodisperse. Thus, the final polymer particle is around 10-20 times higher in diameter than the initial proto-particles (**Figure 6.8**).

When using a macromer as a NAD, a high macromer content copolymer, called a 'comb polymer', is formed first. After the consumption of 1-3% of the total quantity of vinylic monomers, the resulting high macromer content copolymer is self-organised in the similar spherical proto-particles, which turn the reaction mass from transparent to opaque, with the carbocatenary polymeric part situated inside the spheres and the polyetheric chain situated outside the sphere, in the continuous liquid polyether phase. The next steps are identical to those of nonreactive NAD. The particles formed remain constant in number but increase in particle diameter size, the final diameter being around 10-20 times higher than the initial proto-particle diameter, of around 0.3-1 μm.

It is possible to obtain a bimodal distribution of final particles median diameter (distribution with two maxima), by seeded radical polymerisation. For example, if a polymer polyol having particle diameter of 0.3-0.6 μm is added to the polyether before the radical polymerisation, after the normal polymerisation of the vinylic monomers, polymer polyols with a bimodal distribution of particles are obtained. As a general rule, a bimodal distribution leads to lower viscosities than an unimodal distribution of particle diameters, at the same solid content [32]. This is a method to obtain high, solid polymer

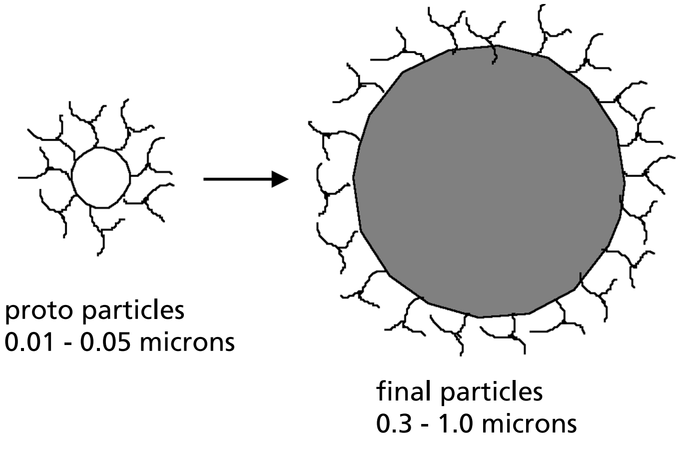


Figure 6.8 The final polymer particle stabilised by NAD

dispersions of lower viscosities [32]. The explanation for this interesting effect is that the small particles move into the large space between the big particles and this gives a superior utilisation of the volume, as shown in **Figure 6.9**.

A very important study on the effect of the distribution of median diameter solid polymer particles from graft polyether polyols on the properties of the resulting flexible polyurethane foams was made in 2002 [30]. It was observed that all the physico-mechanical properties of the resulting flexible PU foams are markedly improved, especially the hardness, if the median diameter is small, less than 0.5 μm (at the same solid content). At higher median diameter of particles (higher than 2-3 μm), all the properties have the tendency to decrease. The role of the polymer particles in the foaming process is to act as nucleating centres and as cell opening agents (by destruction of cells membranes during the foam rise). The second effect of the solid particles presence is to increase substantially the physico-mechanical properties of the resulting flexible PU foams, probably due to the supplementary secondary forces resulting from the interaction between the solid polymer particles and the PU matrix, especially the hardness, which is around 30-40% higher than that obtained with classical ungrafted polyether polyols.

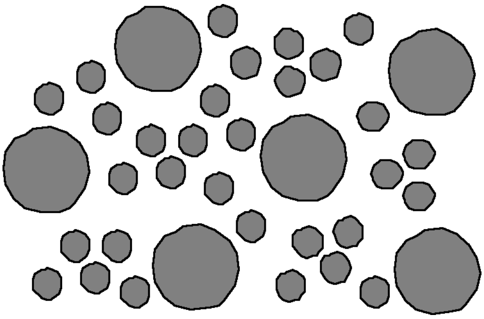


Figure 6.9 Bimodal distribution of polymer polyols particles with two different median diameters

6.3 The Technology of Polymer Polyols Manufacture by Radical Processes

One of the most common technologies for the synthesis of polymer polyols by a radical mechanism is based on the stepwise addition of a mixture of vinylic monomers (polyether polyol, initiator, transfer agent (mixture I)) to a second mixture (mixture II) of polyether polyol (identical with the polyether used for mixture I) and NAD (macromer or nonreactive NAD) under a nitrogen protective atmosphere, in the polymerisation reactor at 115-

125 °C. After the addition of all quantities in mixture I, the reaction mass is maintained at the same reaction temperature for around one hour for digestion, followed by the vacuum distillation of unreacted monomers or steam stripping and anhydrisation.

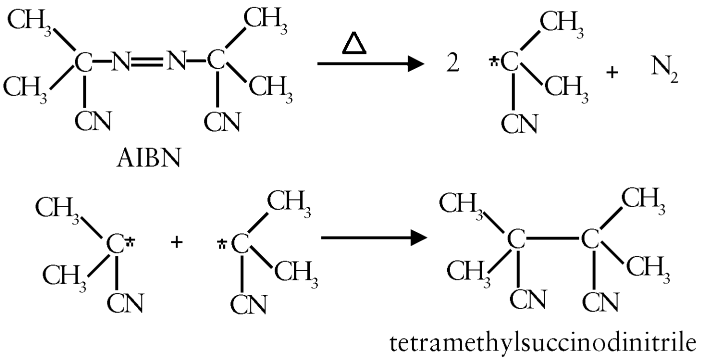
Of course, in order to increase the stability of mixture I, where vinylic monomers are in the presence of the initiator, the initiator is added separately, as a solution (for example as solution in the transfer agent), or as a suspension in the polyether.

The fabrication process of polymer polyols by radical mechanism is either a batch process, or a semi-continuous or continuous process.

A technological flow for a variant of semi-continuous process is presented in **Figure 6.10**.

The most important radical initiators used for polymer polyol synthesis are azoderivatives, such as azoisobutyrodinitrile (AIBN) [1, 3, 13, 22]. Other initiators used successfully are: peroxides (*tert*-amyl peroxides are very efficient), hydroperoxides and percarbonates, but the half life has to be lower than two minutes, at the polymerisation temperature (115-125 °C) [23-28].

AIBN leads to the formation of small quantities of tetramethylsuccinodinitrile, by coupling two radicals derived by AIBN scission:



When compared to normal radical polymerisations, in order to have a high level of hydrogen abstraction, the initiator concentration is considerably higher. For example, sometimes, in the grafting reactions with ACN and styrene, concentrations of AIBN of 2.5-4% against the sum of vinylic monomers (ACN + styrene) are recommended [8, 9].

After the radical polymerisation, there are around 0.3-0.5% unreacted monomers. ACN (bp = 77.3 °C) is very easy to eliminate by vacuum distillation, due to its low boiling point, but styrene (bp = 145.2 °C) is relatively difficult to eliminate and needs several

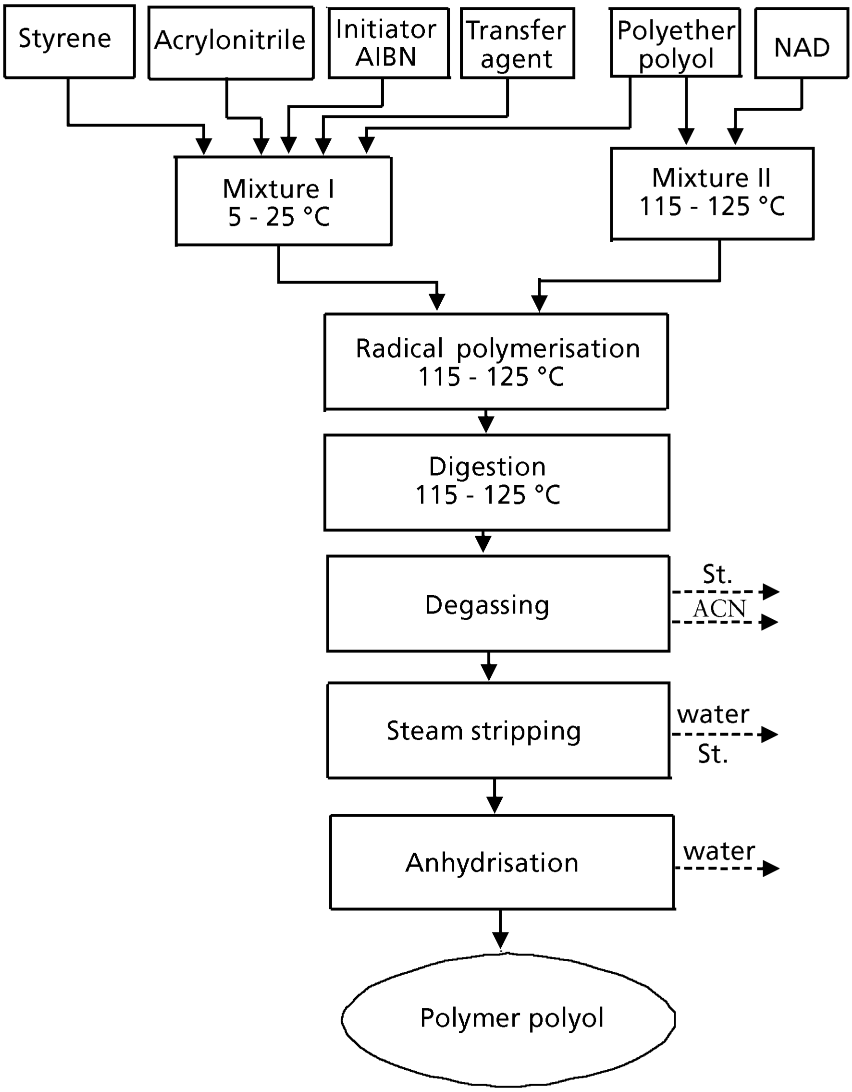
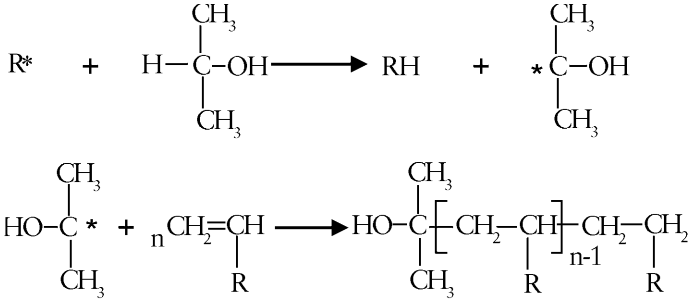


Figure 6.10 Technological flow for a semi-continuous fabrication of polymer polyols by radical mechanism; St: styrene; ACN: acrylonitrile

hours of vacuum distillation. Styrene, even in traces, confers an unpleasant odour to the synthesised polymer polyol, and some practical methods to solve this problem have been developed. One method is to add, at the end of copolymerisation reaction, an initiator of high scission temperature, such as *tert*-butylperbenzoate or *tert*-amyl peroxides. The last traces of styrene react with the radicals generated at the polymerisation temperature and lead to high volatility compounds. Another way is to add a small quantity of water, distilled during the vacuum distillation step. The azeotrope mixture of styrene - water having a lower boiling point than water and the excess of water used against the remaining traces of styrene, lead to the effective removal of the styrene from the synthesised polymer polyols. Another effective method is polymer polyol steam stripping directly in the polymerisation reactor, under vacuum or in a counter flow system, in classical columns with plates, similar to the elimination of odour from polyether polyols described before (see Chapter 4.6).

The utilisation of low molecular weight transfer agents, which control the molecular weight of the carbocatenary vinylic polymer, is a very effective way to obtain low viscosity polymer dispersions at high solid concentrations.

Thus, the transfer agents commonly used are: mercaptans (for example *tert*-dodecylmercaptane [62]), enol-ethers [63], carbon tetrachloride [64], isopropyl alcohol [56, 65], triethyl amine [38], and diethylamine, ethyl benzene toluene [66]. *Tert*-dodecylmercaptane is a very efficient transfer agent but, even used at very low concentrations (0.1-0.3%), generates an unpleasant odour (characteristic of mercaptans) in the final polymer polyol. This is the reason why other transfer agents, without unpleasant odour but with a modest transfer efficiency, are preferred, such as isopropyl alcohol, which needs to be used in higher concentrations (4-8% against final polymer polyol):



$$R^* + H-\overset{CH_3}{\underset{CH_3}{C}}-OH \longrightarrow RH + {*}\overset{CH_3}{\underset{CH_3}{C}}-OH$$

$$HO-\overset{CH_3}{\underset{CH_3}{C}}\,{*} + {}_{n}CH_2=\underset{R}{CH} \longrightarrow HO-\overset{CH_3}{\underset{CH_3}{C}}\left[CH_2-\underset{R}{CH}\right]_{n-1}CH_2-\underset{R}{CH_2}$$

The reactors used for radical polymerisation of vinylic monomers in polyether media need to have a very good and efficient mixing system, preferably by total recirculation with high flow centrifugal pumps, by using static mixers for recirculation, or by internal turbine stirrer with vertical baffles in the reactor.

The polymer polyols of low solid content are obtained by dilution of high solid content polyether polyols with ungrafted polyether polyol (the same polyol used for radical polymerisation). At the same solid content, the polymer polyols obtained by dilution of high solid content polymer polyols with ungrafted polyethers, always have a lower viscosity than the polymer polyols obtained by direct synthesis. Thus, a polymer polyol having 20% copoly (ACN - styrene) obtained by direct synthesis, has a higher viscosity

(2100-2400 MPa-s at 25 °C) than a polymer polyol having the same solid content, but obtained by the dilution of a polymer polyol with 40% solid content (viscosity after dilution: around 1800-2100 MPa-s).

The hydroxyl number of a polymer polyol is lower than the hydroxyl number of the initial polyether polyol used for grafting. The hydroxyl number decrease is a function of the polymer polyol solid content (generally the solid part has no hydroxyl groups). For the estimated hydroxyl number calculation at a known solid content, equation 6.17 is used:

$$Q_{Pe} * I_{Pe} = \left(Q_{Pe} + S_f\right) * I_f$$

$$I_f = \frac{Q_{Pe} * I_{Pe}}{Q_{Pe} + S_f} = \frac{I_{Pe}}{1 + \frac{S_f}{Q_{Pe}}} \qquad (6.17)$$

where:

Q_{Pe} = quantity of polyether polyol used for grafting

S_f = solid fraction, after grafting reaction

I_{Pe} = hydroxyl number of polyether polyol before grafting

I_f = hydroxyl number of polyether polyol before grafting

For example: what is the estimated hydroxyl number of a graft polyol obtained from 800 kg of polyether polyol of hydroxyl number 36 mg KOH/g, after a grafting reaction with 200 g of a mixture ACN - styrene (a 100% yield of radical reaction is assumed)? By using equation 6.17 one obtains:

$$S_f = 200 \text{ kg}$$

$$Q_{Pe} = 800 \text{ kg}$$

$$I_{Pe} = 36 \text{ mg KOH/g}$$

$$I_f = \frac{36}{1 + \frac{200}{800}} = \frac{36}{1 + 0.25} = \frac{36}{1.25} = 28.8 \text{ mg KOH/g}$$

Therefore, by grafting a polyether polyol with an OH# of 36 mg KOH/g with 20% vinylic monomers, the theoretical hydroxyl number of the resulting polymer polyol is 28.8 mg KOH/g.

Another simple formula of hydroxyl number calculation is shown in equation 6.18:

$$I_f = I_{Pe}\left(1 - Fp\right)$$
$$Fp = \frac{\text{weight of solid polymer}}{\text{weight of final polymer polyol}} \tag{6.18}$$

Fp (fraction of polymer) is the ratio between the weight of solid polymer from a known weight of final graft polyol.

The most important types of polymer polyols obtained by radical polymerisation (generally called graft polyether polyols) produced industrially are:

a) Polyether triol PO-EO block copolymer, with terminal poly [EO] block, of molecular weight of 4700-5000 daltons, having 65-75% primary hydroxyl content, grafted with 20-40% copoly (ACN - styrene, 50-75% styrene in the monomer mixture). These graft polyether polyols are used for manufacturing high resilience foams, by the cold cure moulding process, for semiflexible and integral skin PU foams.

b) Polyether triols, PO homopolymers or random PO-EO copolymers with 10-15% EO internally distributed, of molecular weight 3000-3600 daltons, grafted with 10-40% copoly (ACN - styrene, 70-75% St, even 100% styrene). These kinds of graft polyether polyols are used for flexible PU slabstock foams, to improve the hardness, especially at low or medium foam densities. In practice a polyol of 10-12% solid fraction is often used. This solid content is frequently obtained directly in the foaming machines by using a simultaneous flow of two polyols: one usual polyol for slabstock foams and one a polymer polyol of high solid content (40% solid content). The flow of each polyol is calculated to obtain the desired final solid content in the polyol mixture, or in the final PU foams.

c) Polyether diol with a molecular weight of 2000 daltons, PO homopolymers or PO-EO block copolymers with terminal poly[EO] block (15-20% EO), grafted with 10-20% copoly [ACN - styrene]. These grafted polyether diols are used for elastomers, especially for shoe soles. The resulting PU elastomers have a superior abrasion resistance, tensile and tear strength, as compared to PU elastomers made from ungrafted polyether diols.

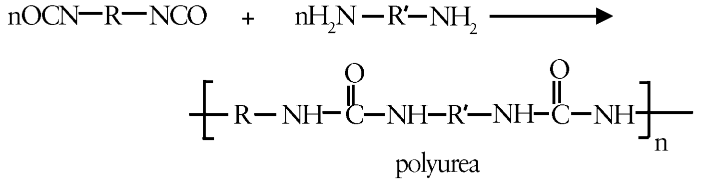
6.3.1 Synthesis of Polymer Polyols by Using Preformed Aqueous Polymeric Lattices

A very simple method to obtain polymeric dispersions in liquid polyethers is to make a mixture between a polyether polyol and a polymeric latex, such as the azeotropic copolymer styrene - ACN (StACN copolymer), obtained by emulsion copolymerisation, having around 20-40% solid content. The water is eliminated step-by-step by vacuum distillation and the solid polymer remains suspended in the liquid polyether medium. The resulting polymeric dispersion is probably stabilised by the surfactant used for the stabilisation during emulsion polymerisation. A large variety of lattices, such as: ACN - butadiene - styrene (ABS copolymers), polyvinylchloride or polystyrene can be used. To improve the stabilisation it is possible to add a small quantity of a NAD. Unfortunately, the quantity of water to be distilled is relatively large. The best procedure is to add the lattices step-by-step, to polyether under vacuum, at high temperatures of 100-130 °C. Thus, the latex is continuously added and water is continuously eliminated. The resulting polymer dispersion is relatively similar to the polymer polyols obtained by direct grafting reaction. The flexible PU foams based on these polymer polyols, obtained with polymeric lattices, have all the advantages of filled polyols, i.e., increased hardness, tensile strength and tear strength.

The advantage of the method is its simplicity: in fact it is a simple distillation. The disadvantages are that a large volume of water needs to be distilled, a large volume of waste water results, and there is a high energy consumption in the water distillation.

6.4 PHD Polymer Polyols (Polyurea Dispersions)

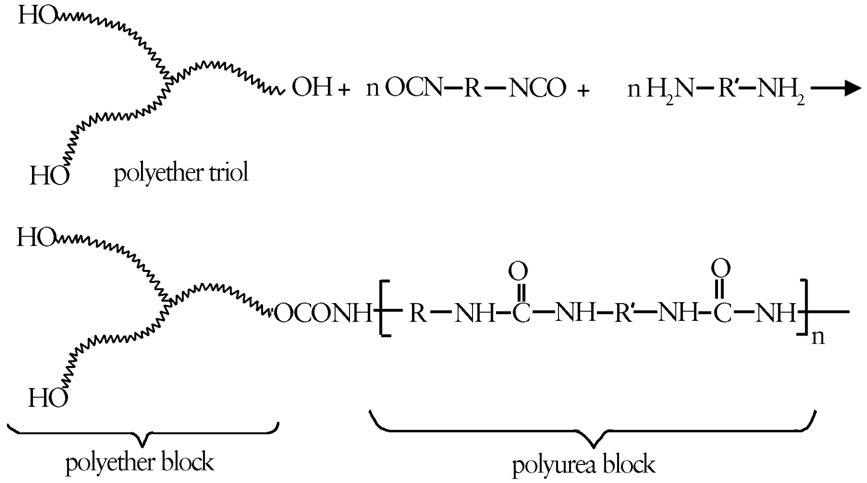
PHD polymer polyols are a special class of filled polyols developed successfully by Bayer, PHD being the abbreviation of the German name ‘polyharnstoff dispersion’ or polyurea dispersions [67-69]. PHD polyols contain organic urea, oligomeric or polymeric polyurea, finely dispersed in liquid polyether polyols [67-73]. The difference between PHD polyols and graft polyether polyols is the different nature of the solid polymer dispersed (it is a heterocatenary polymer – polyurea – instead of carbocatenary polymer) which is obtained by another synthetic procedure (polyaddition reaction between a diisocyanate and a diamine instead of radical polymerisation). The reaction between the diisocyanate and the diamine, takes place *in situ* (reaction 6.19), in liquid polyether. The resultant polyurea being insoluble in polyether, precipitates in the form of very fine particles:



$$nOCN{-}R{-}NCO + nH_2N{-}R'{-}NH_2 \longrightarrow \underset{\text{polyurea}}{\left[R-NH-\overset{O}{\overset{\|}{C}}-NH-R'-NH-\overset{O}{\overset{\|}{C}}-NH \right]_n}$$

(6.19)

A small part of the -NCO groups of diisocyanate reacts with the terminal hydroxyl groups of polyethers and forms a block copolymer structure, having a polyurea segment chemically linked to a polyether segment, which plays the role of a nonaqueous dispersant and assures the excellent stability of the resulting polyurea dispersion (reaction 6.20) [67, 68].



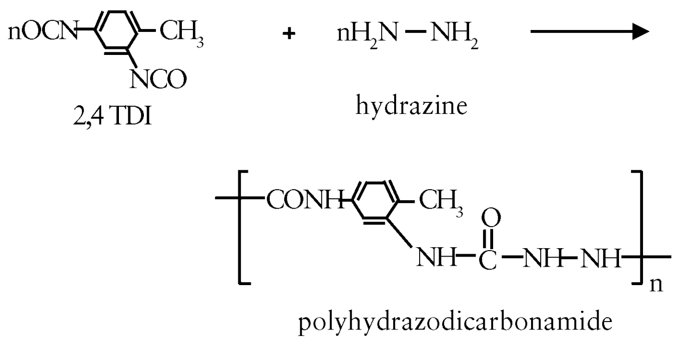
(6.20)

The concentration of this hybrid structure (polyether block linked to a polyurea block) is low, but it is enough to assure a good stability of the dispersion. This very reactive system is based on the big difference in reactivity between primary amines and hydroxyl groups and the -NCO groups of the diisocyanate. Thus the -NCO group reacts 3300 times more rapidly with primary amines than with secondary hydroxyl groups and around 1000 times more rapidly than with the primary hydroxyl groups.

This big difference in the reactivity of isocyanates, with primary amines and with hydroxyl groups results in the polyurea being formed preferentially – only a small part of the hydroxyl groups being reacted.

The presence of finely dispersed polyurea has two advantages: an increase of the interaction by secondary forces (mainly hydrogen bonds) between polyurea filler and the urethane and urea groups of the polyurethane matrix and, secondly, the polyurea reacts with diisocyanates in the polyurethane fabrication (biuret bond formation), leading to an increased crosslinking in the PU obtained. The global result is a substantial increase in hardness, tensile strength, tear strength and other properties as well, together with the beneficial cell opening ability of the solid polyurea filler.

The most favoured diamine used in practice is hydrazine [8-10, 69-73], as hydrazine hydrate (around 65% hydrazine and 35% water). By the reaction of hydrazine with TDI in liquid polyethers, a polyhydrazodicarbonamide is formed *in situ*, having a solid fraction of 5-40% (the preferred level is 10-20%), the median diameter of the solid particles being less than 1 μm.

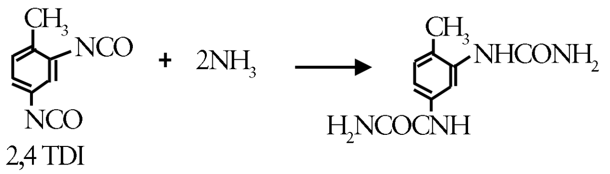


(6.21)

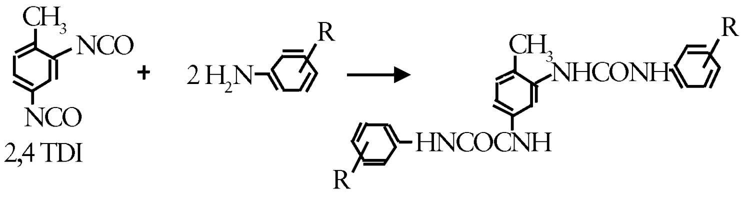
Because hydrazine hydrate contains water, after the polyaddition reaction 6.21 it is necessary to eliminate water by vacuum distillation. The reaction between hydrazine and TDI is very exothermic and the temperature increases rapidly in a short time, for example from room temperature to 50 °C to the reflux temperature (~ 100 °C or more) [7, 8, 67-73].

Usually the viscosity of PHD polymer polyols is higher than the viscosity of graft polyether polyols, at the same solids content. For example a graft polyether polyol, with a 20% solid fraction (copoly[ACN - styrene]), has a viscosity of 2000-3000 MPa-s at 25 °C, but a PHD polyol, with the same solids concentration has a viscosity of 3000-3500 MPa-s at 25 °C [10, 67-69]. This high viscosity is direct evidence of the intensive interaction, by secondary forces, between the polyurea filler and the continuous liquid polyether phase.

Very interesting PHD polyols are obtained by the reaction in polyether media of TDI with primary amines and, instead of polymeric polyurea, organic diurea compounds are generated, insoluble in polyethers, in the form of a very fine dispersion. Example of amines used include ammonia, anilines and substituted anilines, and fatty amines (reactions 6.22 and 6.23).



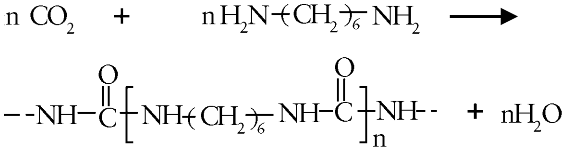
(6.22)



(6.23)

Other diamines used in PHD synthesis are: ethylenediamine, 1,6 hexamethylenediamine, alkanolamines or other diamines. From the industrial point of view, the most important diamine for PHD synthesis is hydrazine.

A very unconventional way to obtain a polyurea dispersion is to react gaseous carbon dioxide, at higher pressures (> 20 MPa) and at around 50 °C, with diamines dissolved in liquid polyether polyols [74]:



$$n\,CO_2 + n\,H_2N\text{-}(CH_2)_6\text{-}NH_2 \longrightarrow \text{--}NH\text{-}\overset{O}{\overset{\|}{C}}\left[NH\text{-}(CH_2)_6\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\right]_n NH\text{--} + nH_2O$$

From the practical point of view, in these very reactive systems, the most important thing is to assure a very high efficiency of stirring, to ensure a very rapid homogenisation of the raw materials, diamine, diisocyanate and polyether, in a very short time. In this manner the reaction between diamine and diisocyanate takes place rapidly, especially after the homogenisation of the reaction partners with the polyether, avoiding the formation of big particles and high polymer polyol viscosities characteristic of inefficient mixing.

This high efficiency mixing is realised in practice by using static mixers (Koenix or Schulzer) or high speed stirring chambers. Thus, if static mixers are used, a variant of the possible arrangement of hydrazine, diisocianate and polyether flows is presented in **Figure 6.11** (a variant).

In the first static mixer (1) a homogeneous mixture between polyether polyols and hydrazine is obtained, and in the second static mixer (2) a rapid homogenisation between TDI and polyether polyols takes place. The resultant solutions of hydrazine in polyether and of TDI in polyether enter the third static mixer at a rapid flow, to obtain a mixture between TDI and hydrazine in polyether, together with the beginning of the polyaddition reaction. The resulting suspension enters the final reactor, which has very good stirring capabilities (total recirculation and turbine stirrer), where the reaction is finished, until the -NCO groups react totally. Finally the water introduced together with hydrazine hydrate is removed by vacuum distillation, until the level of water is less than 0.1%.

Usually an equimolecular mixture diamine, TDI is used (a very small excess of TDI is frequently used to compensate for the consumption of TDI in reaction with hydroxyl groups), which normally leads to maximum molecular weight in the resultant polyurea. As a general observation, the molecular weight of solid polyurea from PHD polyols has a lower molecular weight than the copoly [ACN - styrene] obtained as filler in graft polyether polyols.

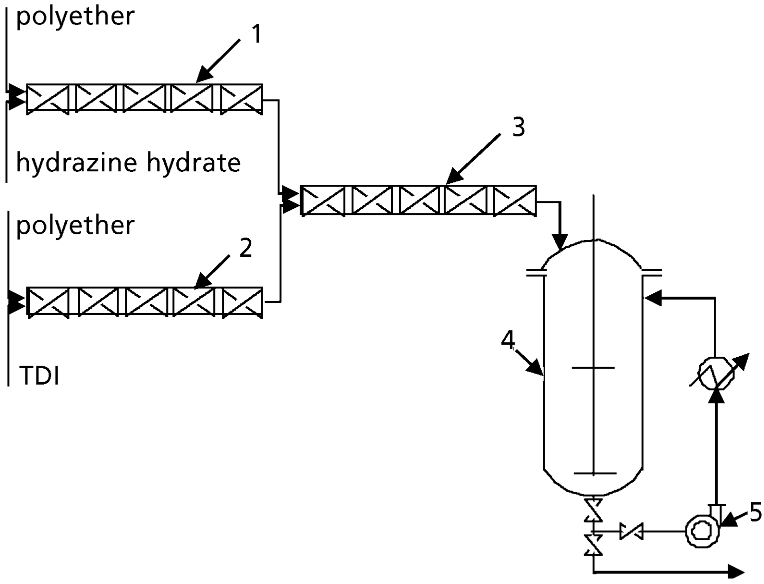


Figure 6.11 Technological scheme for PHD polyols synthesis (variant). 1) Static mixer for polyether with hydrazine; 2) Static mixer for polyether with TDI; 3) Static mixer for TDI-hydrazine reaction; 4) Loop reactor with total recirculation; 5) Recirculation centrifugal pump

Due to the presence of traces of unreacted reactive groups (for example -NH_2 groups), the number of determined hydroxyl groups are sometimes higher than the expected, theoretical hydroxyl number.

Generally, PHD polyols are obtained with 5-20% solid content (maximum 28%) and have a similar aspect with graft polyether polyols, i.e., white opaque dispersions, the median diameter of particles being < 1 μm.

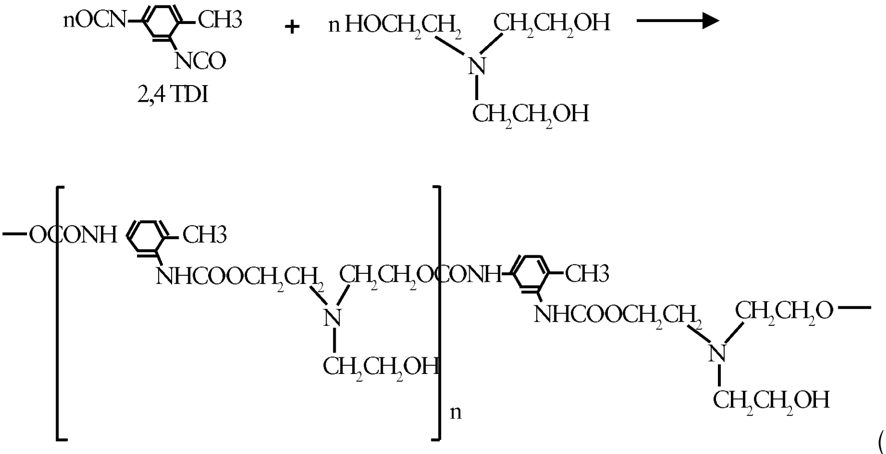
PHD polyols are successfully used for high resilience flexible PU foams (made by the cold cure process), for continuous slabstock flexible PU foams and for elastomers obtained especially by reaction injection moulding (RIM) technology.

6.5 Polyisocyanate Polyaddition (PIPA) Polymer Polyols [79-87]

The synthesis of polyisocyanate polyaddition (PIPA) polymer polyols is very similar to the synthesis of PHD polyols, with the difference that, instead of polyurea, a PU finely dispersed in liquid polyether polyol is obtained *in situ* [8-10]. The formation of PU results as a consequence of the TDI reaction with an alkanolamine or a diol in the liquid polyether polyol.

The preferred alkanolamines are triethanolamine and diethanolamine [8-10, 75-87], and the diisocyanates used are TDI and low functionality MDI (for example, pure MDI).

An ideal reaction for PIPA polyols synthesis is shown in reaction 6.24:



(6.24)

As a first observation, the difference in reactivity between the hydroxyl groups of triethanolamine and the hydroxyl groups of liquid polyether is not so high as that between amino groups and hydroxyl groups in reaction with a diisocyanate. In order to accelerate the reaction of diisocyanate with the primary hydroxyl groups of triethanolamine in PIPA production, specific catalysts such as dibutyl tin dilaurate or stannous octoate are used [79-87].

Generally, the synthesis of PIPA [86] consists of a rapid addition of all diisocyanate to a solution of triethanolamine (TEOA) in a polyether, in the presence of the previously mentioned catalysts (0.05-0.1%) at room temperature, with very efficient stirring. The reaction is very short (several minutes), and the temperature rises rapidly from room temperature to 40-70 °C (depending on the solid contents – at higher solid contents higher temperatures are obtained due to the higher quantity of diisocyanate reacted). After the addition of the diisocyanate (TDI or low functionality MDI), the reaction is maintained under very efficient stirring (one-two hours), for digestion, so that all the -NCO groups are reacted.

The polyether polyols used most frequently are PO homopolymers or random PO-EO copolymers (MW of 3000-3600 daltons) or PO-EO block copolymers with terminal poly[EO] block (MW of 4700-5000 daltons).

If a trifunctional compound (triethanolamine) is reacted with a difunctional diisocyanate (for example TDI), in order to avoid undesired crosslinking, formation of big particles or high viscosities, the molar ratio between TDI:TEOA is usually less or equal to 1:1. For high solid content, lower TDI:TEOA ratios (around 0.6:1), are used.

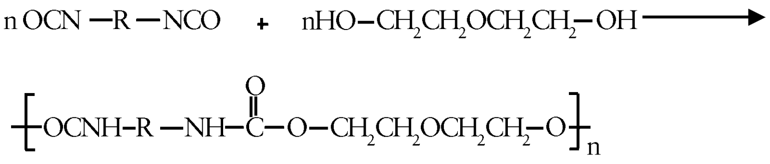
At a solids concentration of around 50%, the tertiary nitrogen atom of TEOA has enough self catalytic activity in the reaction with TDI and does not need the addition of a tin catalyst [78, 79, 88]. A tin catalyst is used for low solid contents of around 10-20% [86].

The solid fraction of PIPA polymer polyols has an appreciable concentration of hydroxyl groups (see formula 6.24). As an immediate consequence, the PIPA polyol frequently has a higher hydroxyl number than the initial polyol used as liquid medium for reaction 6.24. As a general rule, for better accuracy of hydroxyl number determination, for all polymer polyols, it is preferable to use the method of the reaction with *para* toluene sulfonyl isocyanate mentioned before (see Chapter 3).

These hydroxyl groups attached to the solid fraction can react with diisocyanate in the foaming process and can contribute to the crosslinking density increase in the resultant PU. Unfortunately, the presence of these hydroxyl groups at the surface of a separate solid phase makes the reaction with diisocyanates, at the solid - liquid interface, take place to a small extent only.

As was the case for graft and PHD polymer polyols, by using PIPA polyols, an increase in hardness, tensile strength and tear strength of the resultant flexible PU foams was observed, as compared to the PU foams made with unfilled polyether polyols.

Very interesting PIPA polyols are obtained by the reaction of diols having primary hydroxyl groups (e.g., diethyleneglycol), with TDI in polyether polyols having secondary hydroxyl groups (e.g., PO homopolymers of MW of 3000 daltons). PIPA polyols with 10-20% solid content are obtained. The difference in reactivity between the primary hydroxyl groups and secondary hydroxyl groups of polyethers is not very high (primary hydroxyls groups are around 21 times more reactive than secondary hydroxyl groups in the catalysed reaction with TDI). Under these conditions TDI reacts preferentially with diethylene glycol (DEG) (reaction 6.25) [63].



$$\mathrm{n\,OCN-R-NCO} + \mathrm{nHO-CH_2CH_2OCH_2CH_2-OH} \longrightarrow \left[\mathrm{OCNH-R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_2OCH_2CH_2-O}\right]_n$$

(6.25)

Unfortunately, the high viscosities of PIPA polyols obtained by the reaction of diisocyanates with glycols in polyethers, make the reaction with triethanolamine or diethanolamine preferred at industrial scale.

PIPA polyols are not commercialised. PIPA polyols are made generally by foam producers.

In a similar way with PHD polyols, PIPA polyols can be produced in very high efficiency stirred reactors or using the static mixers in series. A technological variant for PIPA polyol fabrication, by reaction of TEOA with TDI, is presented in **Figure 6.12**.

TEOA and polyether are continuously mixed in the first static mixer (1). The resulting mixture is contacted with TDI in the second static mixer (2), and the resulting mixture is introduced to the well stirred reactor (3) for digestion, in order to consume all-NCO groups.

As is the case for all polymer polyols, the main problem is to obtain high solid contents at lower viscosities. Two general phenomena linked to the viscosity of PIPA polyols are observed:

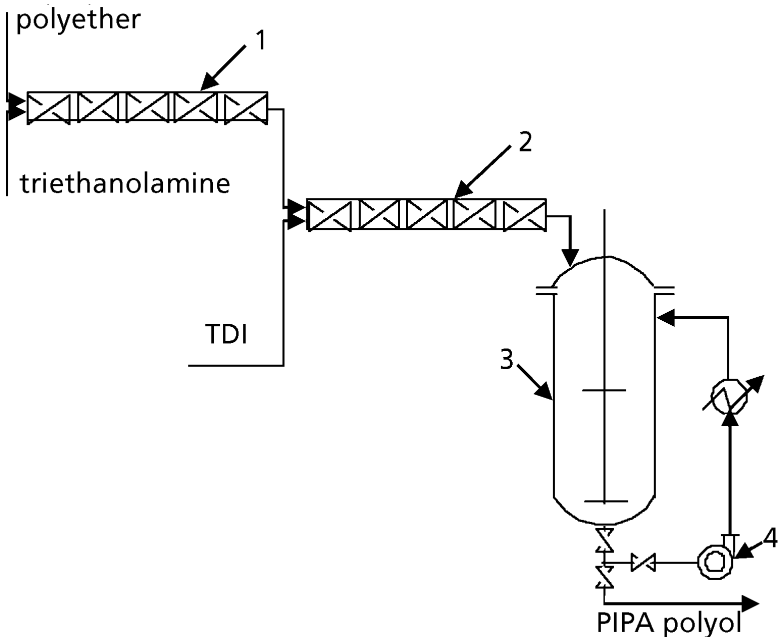


Figure 6.12 Technological scheme for PIPA polyols synthesis (variant). 1) Static mixer for polyether with triethanolamine (TEOA); 2) Static mixer for the reaction of TEOA with TDI; 3) Loop reactor with total recirculation; 4) Recirculation centrifugal pump

a) The viscosities of low solid content PIPA polyols are lower when they are obtained by dilution of high solid content PIPA polyols (e.g., with 50% solids) with unfilled polyether polyol, than in the case of PIPA polyols obtained by direct synthesis at the same solid content.

b) If the distribution of solid particles with median dimensions is bimodal (i.e., they have two different diameters), the viscosity of the resulting PIPA polyol is lower than that of a PIPA polyol with an unimodal distribution of solid particle with a median diameter (at the same solid content).

A PIPA polyol with a bimodal distribution of particle diameter is obtained by seeded polyaddition reaction [80].

If a PIPA polyol with 10% solids is used as initial polyol and to this polyol are added TEOA and TDI to obtain a PIPA polyol with 20% solids, a polymer polyol with a bimodal distribution of particle diameter is obtained. The solid particles from the initial polyol act as seeds and the diameter increases, beginning with the initial diameter of these particles and big particles result. By the reaction of TEOA with TDI new particles are also formed, which have smaller diameters. The global result is a bimodal distribution of particle diameters [80].

PIPA polyols, in spite of some disadvantages (tendency to foam shrinkage, and scorching), are used successfully for continuous slabstock flexible PU foams and high resilience foams (cold cure moulding process).

6.6 Other Polymer Polyols

In the practice, the most important polymer polyols are graft polyether polyols, PHD and PIPA polyols, but other good quality polymer dispersions in liquid polyethers have been created, which at this moment are not industrially important, such as:

a) Epoxy dispersions,

b) Polyamid dispersions,

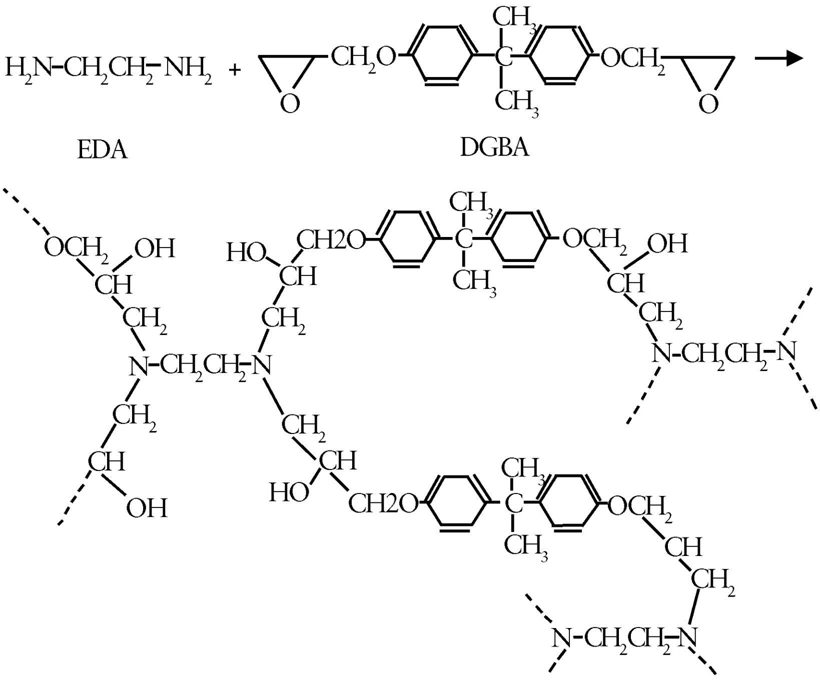
c) Aminoplast dispersions.

6.6.1 Epoxy Dispersions [89, 90]

A relatively new generation of filled polyols was obtained by the reaction of an epoxy resin with an epoxy hardener *in situ*, in liquid polyether media. Cured epoxy resins, finely dispersed in the liquid polyether (with around 20% solid content), are obtained.

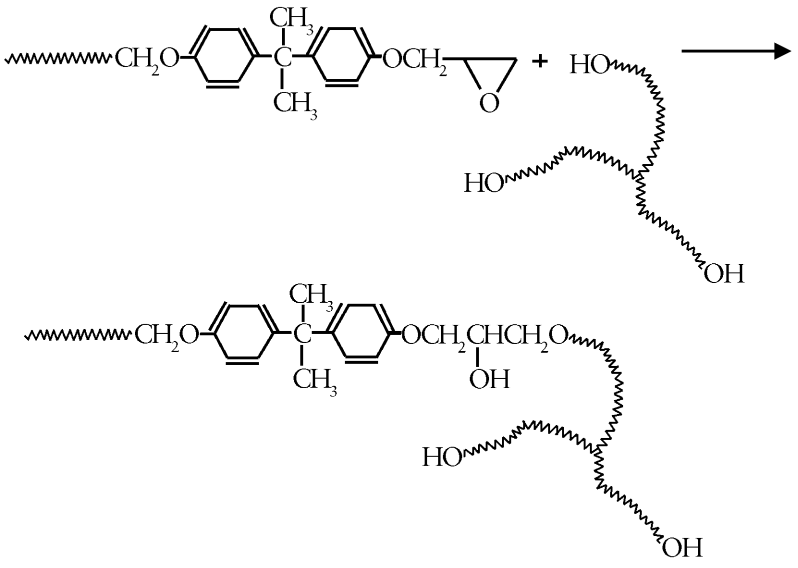
The preferred polyol is a polyether triol (MW of 4700-5000 daltons), with a terminal poly[EO] block (13-15% EO). The preferred epoxy resin is a liquid one, the diglycidyl ether of bisphenol A (DGBA), and the hardener is ethylenediamine (EDA). The molar ratio of epoxy resin:EDA is around 0.8-1:1.

The reaction of DGBA with EDA in polyether triols (reaction 6.26) takes place at 50-60 °C, and lasts 24-48 hours (a relatively long reaction time):



(6.26)

The resultant polymer dispersion of cured epoxy resin is stabilised by a NAD resulting *in situ* from the reaction of a small part of the hydroxyl groups in the polyether polyol, with the epoxy group of the epoxy resin (reaction 6.27) [89].

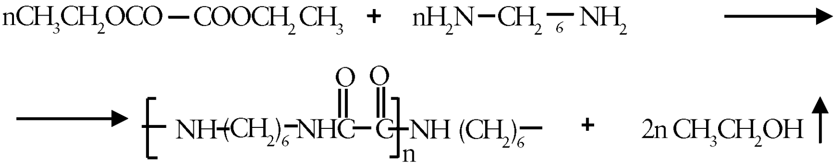


(6.27)

The aromatic bisphenolic structure has a great affinity for cured epoxy resin particles and the polyetheric arms have of course, a great affinity for the continuous polyetheric phase. This structure assures the steric stabilisation of this special kind of epoxy cured dispersion. By using these epoxy dispersions in high resilience cold moulded foams, a considerable increase in hardness, tear strength and tensile strength was noted. The disadvantages of these epoxy dispersions are the high price of epoxy resins and of EDA, and the very long reaction time needed for the crosslinking reaction.

6.6.2 Polyamide Dispersions [91]

An interesting way to make polymeric dispersions in liquid polyethers is the synthesis *in situ* of a polyamide by the polycondensation reaction between a dialkyl oxalate (for example, diethyl oxalate [91]) and a diamine, such as 1,6 hexamethylenediamine (reaction 6.28):

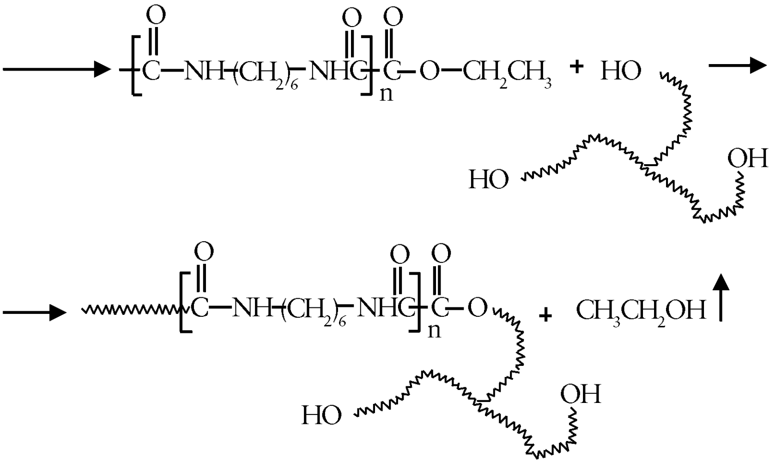


$$nCH_3CH_2OCO-COOCH_2CH_3 + nH_2N-(CH_2)_6-NH_2 \longrightarrow$$

$$\longrightarrow \left[NH-(CH_2)_6-NH\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C} \right]_n NH(CH_2)_6- \quad + \quad 2n\,CH_3CH_2OH\uparrow$$

(6.28)

A polymer polyol, consisting of an insoluble polyamide, finely dispersed in the liquid polyether polyols is obtained. The reaction is developed at 100-130 °C, under vacuum, for the elimination of the resulting ethanol. The stability of the resulting dispersions is probably assured by polyamide - polyether hybrid structures formed during the polycondensation reaction, by some transesterification reactions with hydroxyl groups of polyether polyols (reaction 6.29):

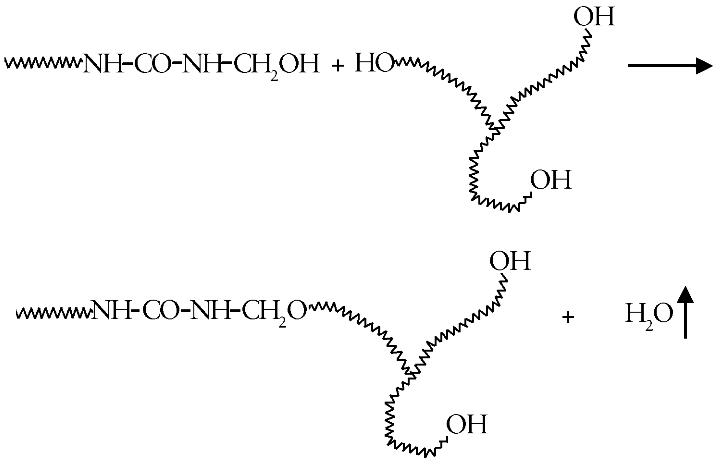


(6.29)

6.6.3 Aminoplast Dispersions [92-95]

Other polycondensation reactions which lead to finely dispersed polymers in liquid polyethers are the polycondensation reactions of urea and melamine with aqueous formaldehyde [92-95]. The reaction medium is usually polyether polyols, PO homopolymers or PO-EO copolymers (random or block copolymers), with MW of 3000-5000 daltons. During the polycondensation reaction, the aminoplast polymer precipitates, being insoluble in polyether and water (water from formaldehyde solution and reaction water), is eliminated by vacuum distillation. A variant of this reaction is to develop the polycondensation in water, and water containing the aminoplast polymer (as a viscous solution) is added to a polyether polyol, under vacuum, and at high temperature (100-130 °C), water being continuously eliminated from the reaction medium. The aminoplast insoluble polymer precipitates in the form of fine particles.

Some methylolic hydroxyl groups may react with terminal hydroxyl groups of polyether (etherification reaction). The resulting structure acts as a true NAD, having an aminoplast segment and a polyetheric segment (reaction 6.30).



(6.30)

A synthetic variant is to react firstly the polyether with a small quantity of TDI. The resultant extended polyether, containing urethane groups, participates together with urea groups in polycondensation reactions with aqueous formaldehyde. Thus a true nonaqueous dispersant is formed *in situ*, with an aminoplast block and a polyether block, which probably assures the efficient stabilisation of the resulting aminoplast dispersion.

Aminoplast dispersions, in spite of the accessibility and low cost of raw materials, are not produced industrially, due to the risk of toxic formaldehyde elimination, especially when the resulting aminoplast polymer polyol is used for slabstock foams and, of course, for moulded flexible foams used for seating or interior automotive parts.

References

1. W.C. Kuryla, F.E. Critchfield, L.W. Platt and P. Stamberger, *Journal of Cellular Plastics,* 1966, **2**, 2, 84.

2. K-H. Kahrs and J.W. Zimmerman, *Die Makromolekulare Chemie*, 1962, **58**, 75.

3. F.E. Critchfield, J.V. Koleske and D.C. Priest, *Rubber Chemistry and Technology*, 1972, **45**, 5, 1467.

4. R. Cloetens, W.A. Lidy, B.D. Phillips and D.B. Thomas in *Proceedings of the SPI/FSK Polyurethanes World Congress*, Aachen, Germany, 1987, p.480.

5. G.G. Ramlow, D.A. Heyman and O.M. Grace, *Journal of Cellular Plastics*, 1983, **19**, 4, 237.

6. J.H. Shears, C.G. Dam, J.C. Vandichel and H. Verstraete in *Proceedings of the 1996 SPI Polyurethanes Conference,* Las Vegas, NV, USA, 1996, p.150.

7. Y.C. Yen and T.S. Tsao, *Polyols for Polyurethanes*, Process Economics Program Report No.45A, Stanford Research Institute, Menlo Park, CA, USA, 1982, p.119.

8. K.R. Plowman in *Reaction Polymers*, Eds., W.F. Gum, W. Reise and H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.86-91.

9. D.J. Sparrow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.209-211.

10. *Flexible Polyurethane Foams*, Second Edition, Eds., R. Herrington and K. Hock, Dow Chemical Company, Midland, MI, USA, 1997, Chapter 2, p.10-14.

11. J.H. Shears, C.G. Dam, J.C. Vandichel and H. Verstraete, *Proceedings of Technical/Marketing Conference, Polyurethane Expo '96*, Las Vegas, NV, USA, 1996, p.150.

12. S. Hager, R. Schiffauer, J. Charron, D. Wardius and R. Skorpenske in *Proceedings of API Technical/Marketing Conference - Polyurethane Expo '99*, Orlando, FL, USA, 1999, p.267.

13. No inventors; ICI, assignee; GB 1,477,333, 1977.

14. R.C. De Wald, inventor; The Firestone Tire and Rubber company, assignee; US 3,655,553, 1972.

15. J. Jin III and J.C.H. Hua, inventors; Stauffer Chemical Corporation, assignee; US 3,925,506, 1975.

16. No inventors; ICI, assignee; GB 1,482,213, 1977.

17. W. Konter, J. Witte, P. Vehlewald and H-D. Block, inventors; Bayer AG, assignee; US 4,028,434, 1977.

18. M. Ionescu, K. Gosa, I. Mihalache, V. Zugravu and N. Carp, *Cellular Polymers*, 1994, **13**, 5, 339.

19. W.D.Vilar, *Chemistry and Technology of Polyurethanes*, Third Edition, 2002, Rio de Janeiro, Brazil, *http://www.poliuretanos.com.br/Ingles/Chapter1/14Polyethers.htm - polimerico*

20. D.C. Priest and R.A. Langdale-Smith, inventors; Union Carbide Corporation, assignee; US 4,208,314, 1980.

21. D.A. Heyman and O.M. Grace, *Journal of Cellular Plastics*, 1985, **21**, 2, 101.

22. F.E. Critchfield, D.W. Simroth and S.L. Watson, inventors, Arco Chemical Technology, assignee; US 5,496,894, 1996.

23. F.J. Preston, T.C. Kraus and K.B. Chandalia, inventors; Olin Corporation, assignee; US 4,153,643, 1979.

24. K.B. Chandalia, F.J. Preston and H.G. Barnowski, inventors; Olin Corporation, assignee; US 4,181,781, 1980.

25. J.E. Davis and P. Davis, inventors; BASF Wynadotte Corporation, assignee; US 4,161,468 , 1979.

26. No inventors; Union Carbide Corporation, assignee; GB 1,559,121, 1980.

27. No inventors; Union Carbide Corporation, assignee; GB 1,559,122, 1980.

28. No inventors; Union Carbide Corporation, assignee; GB 1,559,123, 1980.

29. No inventors; Union Carbide Corporation, assignee; GB 1,412,797, 1975.

30. A. Rath, W. Apichatachutapan, R. Gummaraju, R. Neff and D. Heyman in *Proceedings of API Technical and Marketing Conference – Polyurethanes '2002*, Salt Lake City, UT, USA, 2002, p.567.

31. *Free-Radical Polymerisation*, Eds., C.H. Bamford and C.F.H. Tipper, Elsevier, New York, NY, USA, 1976.

32. *Dispersion Polymerisation in Organic Media*, Ed., K.E.J. Barrett, John Wiley and Sons, London, UK, 1975.

33. D.H. Napper, *Polymeric Stabilisation of Colloidal Dispersions*, Academic Press, London, UK, 1983.

34. G.E. Corbett, E.L.S. Van Elderen-Van Dusseldorp, R. Van Klempen, inventors; Shell International Research Maatschappij BV, assignee; EP 0,495,551A3, 1992.

35. B.J. Breukel, E.L.S. Van Elderen-Van Dusseldorp, G.J. Hitchens, M.E. Martin and J.G. Rutten, inventors; Shell International Research Maatschappij BV, assignee; EP 0,786,480A1, 1997.

36. K. Lorenz, M. Dietrich, M. Brockelt, U. Scholz, R.J. Kumpf, J. Gronen and G. Jacobs, inventors; No assignee; US 6, 472,447, 2002.

37. H.R. van der Wal, F.M. Casati, R.M. Herrington and T.J. Woods, inventors; Dow Global Technologies, assignee; WO 03016373, 2003.

38. A. Nishikawa, T. Kunihiro, T. Izukawa and K. Asai, inventors; Mitsui Toatsu Chemicals, Inc., assignee; US 5,416,123, 1995.

39. M. Ionescu, C. Roibu, V. Preoteasa, I. Mihalache, S. Mihai Stanca, V. Zugravu, I. Bejenariu, I. Puscasu, inventors; SC OLTCHIM SA, assignee; RO 118,302, 2003.

40. J.E. Davis and D.A. Heyman, *Proceedings of the Polyurethanes World Congress*, Aachen, Germany, 1987, p.490.

41. O.M. Grace, S.E. Wujcik and D.A. Heyman, inventors; BASF Wyandotte, assignee; US 4,522,976, 1985.

42. O.M. Grace, S.E. Wujcik and D.A. Heyman, inventors; BASF Wyandotte, assignee; US 4,568,705, 1986.

43. P. Stamberger, inventor; Union Carbide Corporation, assignee; US 4,539,340, 1985.

44. P. Stamberger, inventor; Union Carbide Corporation, assignee; US 4,524,157, 1985.

45. K. Drake, K.L. Hoy and C.G. Seefried, Jr., inventors; Union Carbide Corporation, assignee; US 4,198,488, 1980.

46. G.G. Ramlow, D.A. Heyman, O.M. Grace, C.J. Reichel and R.J. Hartman, inventors; BASF Wyandotte, assignee; US 4,454,255, 1984.

47. D.K. Hoffman, R.F. Harris, N.B. Tefertiller and R.C. Rains, inventors; The Dow Chemical Company, assignee; US 4,460,715, 1984.

48. H.C. Vogt, M. Cneker, J.T. Patton., Jr., and B. Brizgys, inventors; BASF Wyandotte, assignee; US 4,261,877, 1981.

49. D.K. Hoffman, R.F. Harris, N.B. Tefertiller and R.C. Rains, inventors; The Dow Chemical Company, assignee; US 4,390,645, 1983.

50. T. Heinemann, M. Dietrich, G. Jacobs, M. Kratz, J. Sanders, U. Scholz and H. Woynar, inventors; Bayer AG, assignee; US 5,594,066, 1997.

51. M.B. Eleveld, W. Kazijn and R. Van Kempen, inventors; Shell Oil Company, assignee; US 6,403,667, 2002.

52. J.E. Davis, inventor; BASF Corporation, assignee; US 5, 254, 667, 1993.

53. J. Shen, K.G. McDaniel, J.E. Hayes, U.B. Holeschovsky and H.R. Hinney, inventors; Arco Chemical Technology, assignee; US 5,990,232, 1999.

54. G.D. Fogg, inventor; The Dow Chemical Company, assignee; US 5,990,185, 1999.

55. D.A. Heyman and J.A. Gallagher, inventors; BASF Corporation; assignee; US 5,919,972, 1999.

56. D.W. Simroth, inventor; Arco Chemical Technology, assignee; US 5,196,476, 1993.

57. J.E. Hayes and R.G. Gastinger inventors; Arco Chemical Technology, assignee; US 5,358,984, 1994.

58. R.E. Gastinger and J.E. Hayes, inventors; Arco Chemical Technology, assignee; US 4, 855,330, 1989.

59. P. Stamberger, inventor; Union Carbide Corporation, assignee; US 4,585,831, 1986.

60. R. Van Cleve, inventor; Union Carbide Corporation, assignee; US 4,357,430, 1982.

61. N.R. Shah, inventor; Union Carbide Corporation, assignee; US 4,119,586, 1978.

62. G.G. Ramlow, D.A. Heyman, O.M. Grace, C.J. Reichel and R.J. Hartman, inventors; BASF Corporation, assignee; US 4,689,354, 1987.

63. H. Alberts and G. Balle, inventors; Bayer AG, assignee; US 4,230,823, 1980.

64. J.F. Serratelli and M.A. Norton, inventors; The Dow Chemical Company, assignee; US 4,581,418, 1986.

65. J.E. Hayes, D.W. Simroth and X. Zhou, inventors; Arco Chemical Technology, assignee; US 5, 488,085, 1996.

66. M.R. Kratz, M. Dieterich, T. Heinemann, G. Jacobs, J. Sanders and H. Woynar, inventors; Bayer AG, assignee; EP 768324A1, 1997.

67. K.G. Spitler and J.J. Lindsey, *Journal of Cellular Plastics*, 1981, 17, 1, 43.

68. P. Vehlewald and R. Volland, *Kunststoffe*, 1983, 73, 8, 439.

69. M.A. Koshute and H.A. Freitag in *Proceedings of the SPI/FSK Polyurethanes World Congress*, Aachen, Germany, 1987, p.502.

70. E. Müller, inventor; Bayer AG, assignee; US 3,325,421, 1967.

71. K. Konig and M. Dietrich, inventors; Bayer AG, assignee; US 4,089,835, K. Konig and M. Dietrich, inventors; 1978.

72. No inventor; Bayer AG, assignee; US 4,761,434, 1988.

73. M. Cuscurida and G.P. Speranza, inventors; Texaco Inc., assignee; US 4, 296, 213, 1981.

74. T. Narayan and M.G. Kinnaird, inventors; BASF Corporation, assignee; GB 2,264,499, 1993.

75. A. Reischl, H. Müller and K. Wagner, inventors; Bayer AG, assignee; US 4,260,530, 1981.

76. J.P. Rowlands, inventors; Interchem International SA, assignee; US 4,374,209, 1983.

77. K. Pickin, *Urethanes Technology*, 1984, June, 23.

78. W.G. Carroll and P. Farley, inventors; ICI, assignee; US 4, 452,923, 1984.

79. W.G. Carroll, inventor; ICI, assignee; US 4,554,306, 1985.

80. J.M. Pal, J.P. Cosman and K. Tan, inventors; The Dow Chemical Company, assignee; US 5,068,280, 1991.

81. S.E. Wujcik, D.I. Christman and O.M. Grace, inventors; BASF Corporation, assignee; US 5,179,131, 1993.

82. K.J. van Keen and G.R. Blair, inventors; Woodbridge Foam Corporation, assignee; US 5,292,778, 1994.

83. E.L. Yeakley and M. Cuscurida, inventors; Arco Chemical Technology, assignee; US4,785,026, 1988.

84. M. Cuscurida, inventor; Texaco, Inc., assignee; US 4,518,778, 1985.

85. M.C. Raes, J.M. O'Connor and M.L. Rorin, inventors; Olin Corporation, assignee; US 4,497,913, 1985.

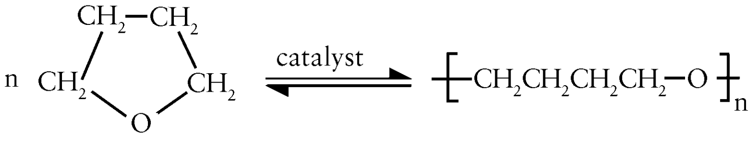
86. No inventor; J.C. Rowlands, assignee; GB2,072,204A, 1981.
87. M. Cuscurida, inventor; Texaco, Inc., assignee; US 4,293,470, 1981.
88. P. Farley and W.G. Caroll, inventors; ICI, assignee; EP 0,079,115, 1983.
89. H.R. van der Wal in *Proceedings of the SPI/FSK Polyurethanes World Congress*, Aachen, Germany, 1987, p.493.
90. O. Milovanovic-Levik, H.R. van der Wal and U. Tribelhorn, inventors; The Dow Chemical Company, assignee; US 4,789,690, 1988.
91. G.W. Speranza and R.L. Zimmerman, inventors; Texaco, Inc., assignee; US 4,452,922, 1984.
92. A. Reischl and A. Zenner, inventors; Bayer AG, assignee; US 4,184,990, 1980.
93. A. Reischl, inventor; Bayer AG, assignee; US 4,310,449, 1982.
94. A. Reischl, G. Jabs, W. Dietrich and A.C. Gonzalez-Dorner, inventors; Bayer AG, assignee; US 4,092,275, 1978.
95. M.C. Raes and O.J. Prolx, inventors; Olin Corporation, assignee; US 4,506,040, 1985.

7

Polyether Polyols by Cationic Polymerisation Processes

7.1 Polytetrahydrofuran (Polytetramethylene Glycols)

Polytetrahydrofuran (PTHF) is a polyether obtained by cationic ring opening polymerisation of tetrahydrofuran (THF), a five membered cyclic ether:



Tetrahydrofuran
THF

Polytetrahydrofuran
PTHF

The driving force of this polymerisation reaction is the ring strain of the THF cycle. The main contribution to this ring strain is not due to the deviation from the normal angle values of chemical bonds (angular tension), which is relatively low, but the most important contribution is due to the torsional repulsion forces between the hydrogen atoms situated in eclipsate positions (**Figure 7.1**). The angular tension of the THF cycle is small, around 0.556 kcal/mol [1-8], but the total ring strain is around 4.3 kcal/mol [7], 4-5 times higher than the angular tension. This ring strain of 4.3 kcal/mol is much lower than the ring strain of alkylene oxides, but is high enough to assure the ring opening polymerisation of THF.

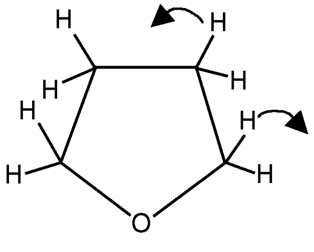


Figure 7.1 Torsional repulsion forces of hydrogen atoms in the tetrahydrofuran ring

The cationic catalysts used for THF polymerisation, with the general formula R^+X^- are: trialkyloxonium salts of superacids, esters of superacids, oxocarbenium salts, Lewis acid - oxirane complexes, superacid anhydrides, (e.g., triflic anhydride), and others [1-38] (**Figure 7.2**):

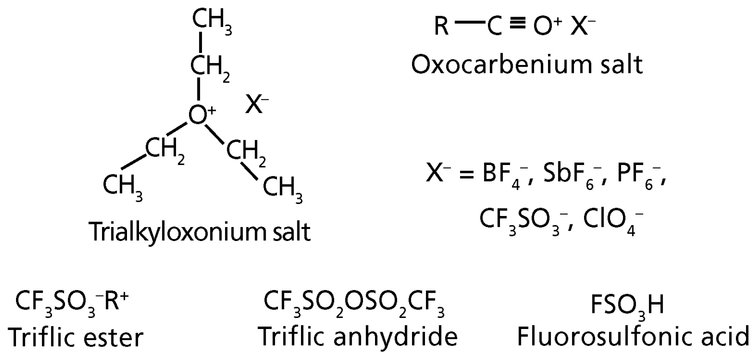
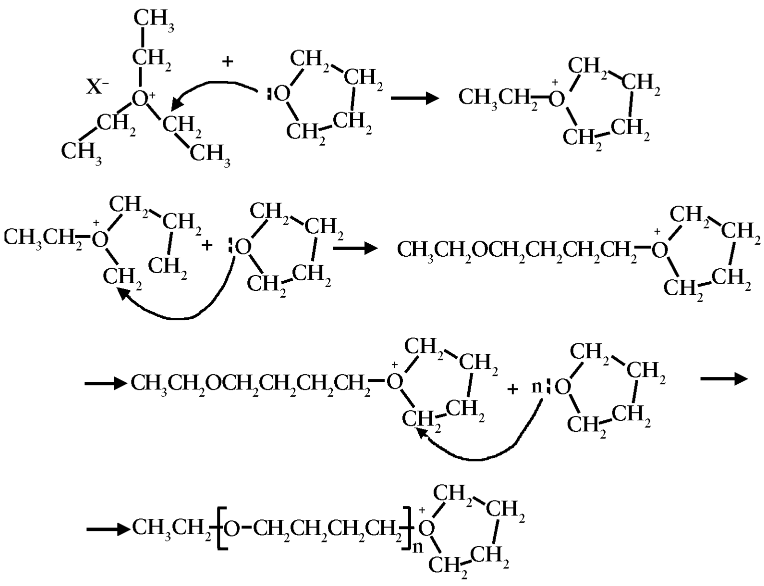


Figure 7.2 Cationic catalysts used in THF polymerisation

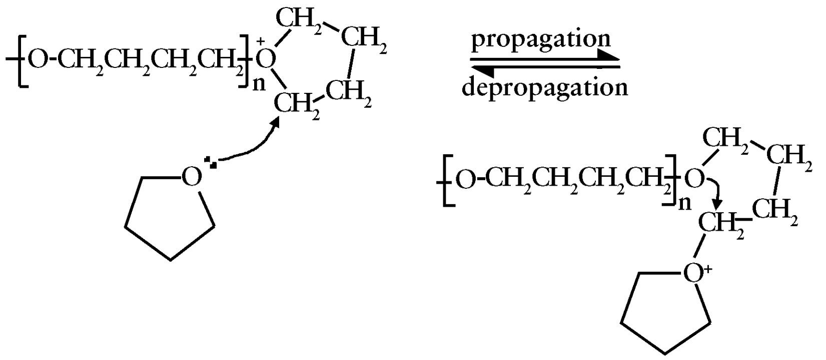
The ring opening polymerisation of THF has as active centres tertiary oxonium cations and is based on the nucleophilic attack of the oxygen atom of the THF monomer at the α-carbon atom of the oxonium cation. The α-carbon atom is activated by the presence of the neighbouring positive charge which decreases the electron density at this carbon atom. Thus, the nucleophilic attack of the oxygen atom of the monomer takes place at the activated α-carbon atom (reaction 7.1) [3, 7]:



(7.1)

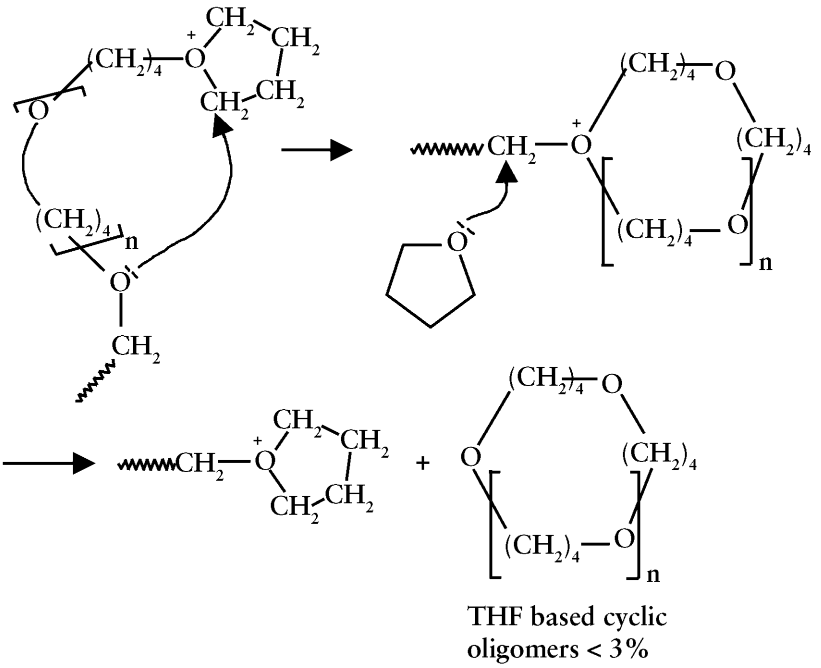
The polymerisation of THF is a typical example of equilibrium polymerisation, in which, during polymerisation, the monomer is always in equilibrium with the polymer, i.e., the propagation reaction rate is equal to the depropagation reaction rate [3, 7, 35, 36]. The mechanism of this kind of equilibrium polymerisation is based on the concurrence between SN2 nucleophilic attack of the monomer oxygen atom (propagation reaction) and the nucleophilic attack of the oxygen atom in the neighbouring structural unit, at the α-carbon atom of the trialkyloxonium chain end (depolymerisation reaction by 'back biting') as shown in reaction 7.2.

In the cationic polymerisation of THF, very small quantities of cyclic compounds (cyclic oligomers of THF) are formed (less than 3%), this is much lower than in alkyleneoxide cationic polymerisation [10, 11]. The cyclic oligomers are formed by the intramolecular nucleophilic attack of the etheric oxygen of the polymeric chains on the carbon atom from α position of the trialkyloxaonium chain end (reactions 7.2).



(7.2)

Formation of cyclic compounds [10, 11] is shown in reaction 7.3.



(7.3)

The ceiling temperature (T_c) of THF cationic polymerisation is around 83 °C [3, 7, 35, 36, 38]. Above the ceiling temperature the transformation of THF in PTHF is practically impossible from the thermodynamic point of view. T_c is the temperature at which the variation of the monomer to polymer transformation free energy is zero (it is well known that a transformation takes place only at a negative variation of free energy, $\Delta G < 0$). The value of T_c in polymerisation is given by relationship 7.4.

$$\Delta Gp = \Delta Hp - T * \Delta Sp$$

where:

ΔHp = variation of polymerisation enthalpy

ΔSp = variation of polymerisation entropy and,

ΔGp = variation of polymerisation free energy [4, 5].

if $\Delta Gp = 0$ one obtains: $\Delta Hp - T * \Delta Sp = 0$

$$T_c = \frac{\Delta Hp}{\Delta Sp} \qquad (7.4)$$

For equilibrium polymerisation, the value T_c is given by relationship 7.5. When the concentration of monomer at equilibrium (M_e) is 1, the relationship (7.5) becomes relationship (7.4) [3, 7, 35, 36].

$$T_c = \frac{\Delta Hp}{\Delta Sp + R\ \ln[M_e]} \tag{7.5}$$

For THF polymerisation it is possible to obtain polymer only under T_c, and the polymer yield at equilibrium increases markedly at lower temperatures. Thus, at –10 to –20 °C the polymer yield at equilibrium is around 60-75% and the monomer at equilibrium, always present in the reaction system, is around 25-40% from the initial monomer quantity. **Figure 7.4** shows the monomer concentration at equilibrium, in cationic THF polymerisation, as function of temperature.

The kinetics of THF polymerisation at equilibrium are described by the following kinetic equation [2, 3, 7, 35, 36] (equation 7.6):

$$-\frac{d[THF]}{dt} = Kp[I_O] * ([M] - [M_e]) \tag{7.6}$$

where:

Kp = propagation reaction constant

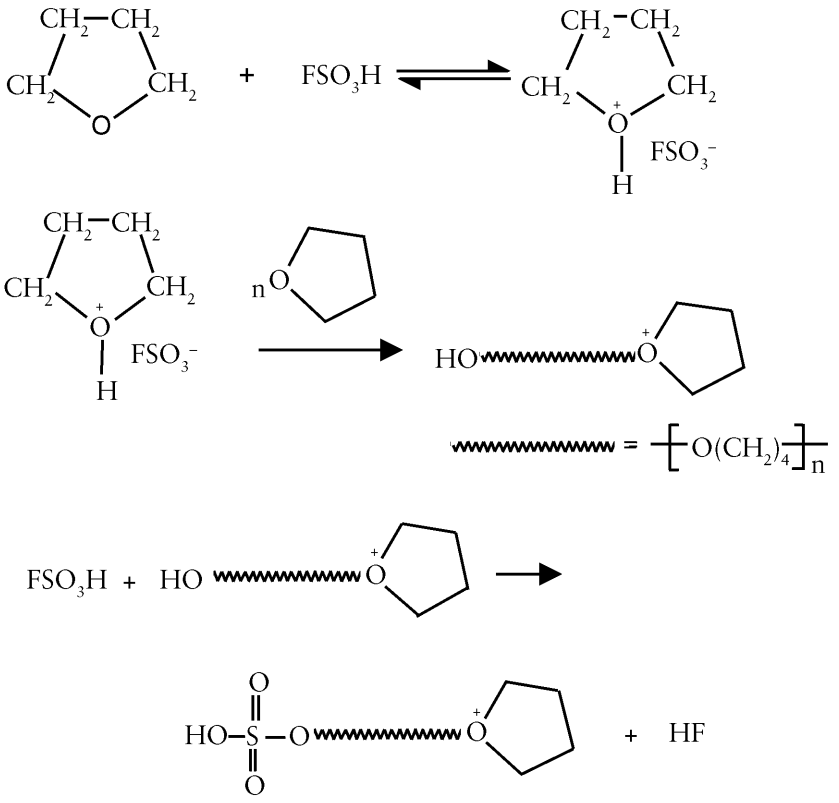
I_O = initial catalyst concentration

[M] = monomer concentration

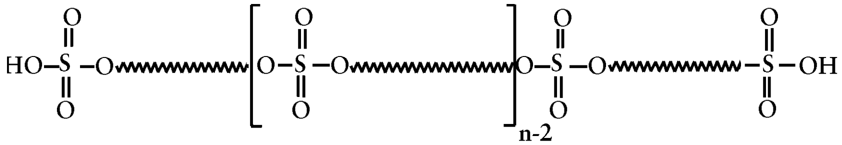
$[M_e]$ = monomer concentration at equilibrium.

From the polyurethane (PU) chemistry point of view, it is important to obtain α,ω telechelic PTHF, with terminal hydroxyl groups.

There are several methods for obtaining hydroxyl groups. One method, applied industrially, is the initiation of THF polymerisation with fluorosulfonic acid: FSO_3H [10, 11, 22, 35, 36]. The reaction takes place at -10 to 30 °C. Low molecular weight (MW) PTHF are formed which have monoakylsulfate and dialkylsulfate groups:



Finally a structure containing chains of PTHF linked by sulfate ester units, having terminal monoalkylsulfate units are obtained:



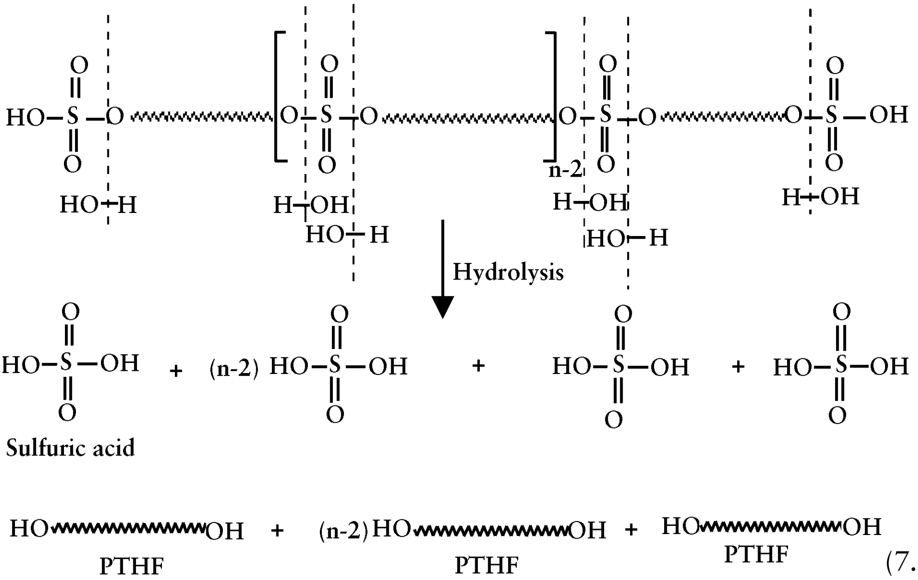
$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O\sim\sim\sim\left[O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O\sim\sim\sim\right]_{n-2}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O\sim\sim\sim-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

(7.7)

This sulfate group formation is irreversible under the reaction conditions and this kind of polymerisation is called ‘slowly dying’ polymerisation.

The telechelic PTHF, with terminal hydroxyl groups, is obtained by the hydrolysis of structure 7.7 with sulfate ester units (reaction 7.8). The products of hydrolysis are: sulfuric acid and hydroxy-telechelic PTHF with a practically theoretical functionality (f), of 2 OH groups/mol, without unsaturation. It is very important that the content of cyclic oligomers is extremely low, practically negligible.

A polymerisation variant is to use as catalyst oleum (a 30-60% solution of SO_3 in sulfuric acid), or better, in order to accelerate the reaction, a catalytic mixture of oleum-perchloric acid (or a perchlorate, such as magnesium perchlorate) [12, 16, 25, 28]. Similar structures with sulfate ester units (structure 7.7) are obtained. By the hydrolysis of the resulting structure the desired PTHF with terminal hydroxyl groups is obtained [13, 25, 28].



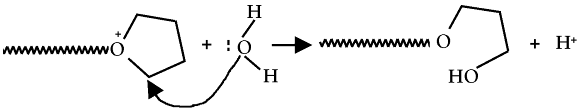
(7.8)

Addition of water is an excellent way to stop the cationic polymerisation reaction. Firstly, after the water addition, the unreacted THF is distilled and after that the hydrolysis reaction is developed at 90-95 °C.

PTHF is insoluble in water and separated as the upper organic layer. It is possible to promote this separation by addition of an inert solvent (benzene or toluene). The organic layer is separated, the solvent is distilled and polytetramethylene glycols (PTMG) of MW of 600-3000 daltons are obtained, in the form of white solid wax, with a low melting point (between 25-40 °C). For example a PTMG of MW of 2000 daltons has a melting point of about 35 °C. The magnitude of the MW depends on the ratio between the monomer and the FSO_3H or oleum catalysts - at a high ratio, higher MW are obtained.

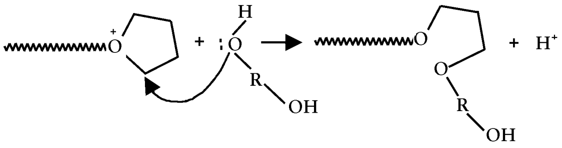
The active PTHF, with tertiary oxonium cation as the active group, easily develops transfer reactions with water, with alcohols and glycols, with anhydrides and with polymeric chains [2, 3, 7, 35, 36, 38]. All the transfer reactions mentioned are based on the nucleophilic attack of at the α carbon atom in the tertiary oxonium cation (reactions 7.9-7.12).

a) Transfer with water:



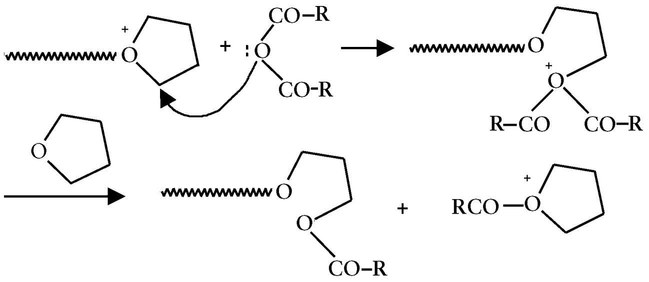
(7.9)

b) Transfer with glycols:



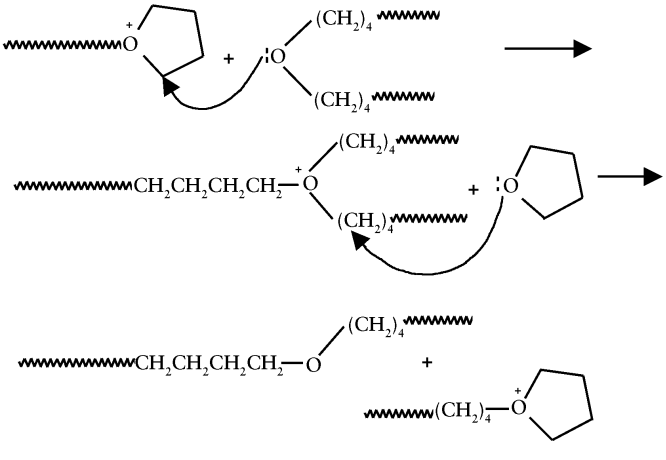
(7.10)

c) Transfer with anhydrides:



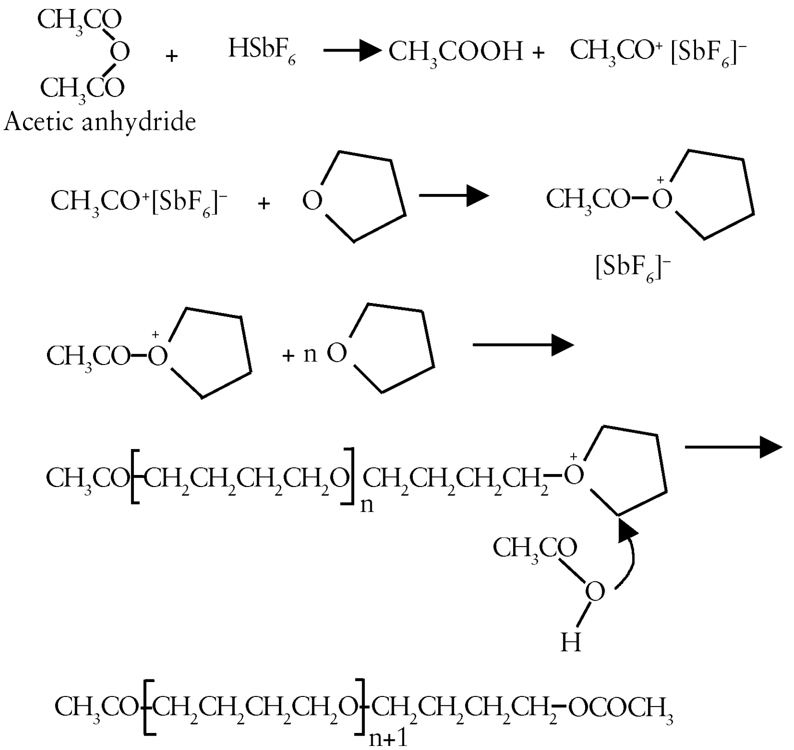
(7.11)

d) Transfer with the polymer chain:



(7.12)

Another industrial route to obtain α,ω hydroxy-telechelic PTHF is based on the transfer reaction with anhydrides (7.11). The polymerisation reaction is based on a mixture of anhydrides (usually acetic anhydride) and a superacid ($HSbF_6$, $HClO_4$, CF_3SO_3H or even in the presence of a polymeric superacid with -CF_2-CF_2-SO_3H groups (Nafion resins, solid analogue of triflic acid) [26, 27] or Lewis acids (BF_3, SbF_5) [20, 24], or solid acidic clays [29]. The real catalyst is the oxocarbenium salt formed by the reaction of acetic anhydride and the superacid :



(7.13)

A PTHF with acetoxy end groups (structure 7.13) is obtained. The monomer is consumed more rapidly than the anhydride, because it is much more basic and much more nucleophilic. The degree of polymerisation of the resulting PTHF is controlled by the ratio between the amount of monomer reacted and the sum of the anhydride and the superacid used in the initiation system (relationship 7.14) [2, 3, 7, 35, 36].

$$DP = \frac{[THFo] - [THFe]}{[Ac_2O] + [HA]} \quad (7.14)$$

where:

DP = degree of polymerisation

$[Ac_2O]$ = acetic anhydride concentration

[HA] = superacid concentration

[THFo] = initial quantity of THF

[THFe] = concentration of THF at equilibrium.

By hydrolysis, or much better by alcoholysis (with methanol), of PTHF having acetate end groups, α,ω hydroxy-telechelic PTHF is obtained (reaction 7.15). The catalyst used for alcoholysis is a hydroxide such as $Ba(OH)_2$ [20, 24, 26].

$$CH_3CO\left[CH_2CH_2CH_2CH_2O\right]_{n+1}CH_2CH_2CH_2CH_2{-}OCOCH_3 + 2CH_3OH \xrightleftharpoons{Ba(OH)_2}$$

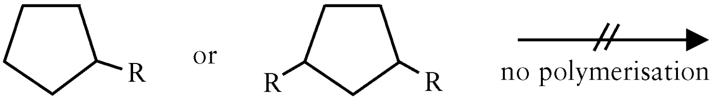
$$HO{-}\left[CH_2CH_2CH_2CH_2O\right]_{n+1}CH_2CH_2CH_2CH_2{-}OH + 2CH_3COOCH_3 \quad (7.15)$$

The unreacted THF, the excess of methanol and the resulting methyl acetate were removed by distillation and the α,ω hydroxy-telechelic PTHF remains as a solid wax at room temperature.

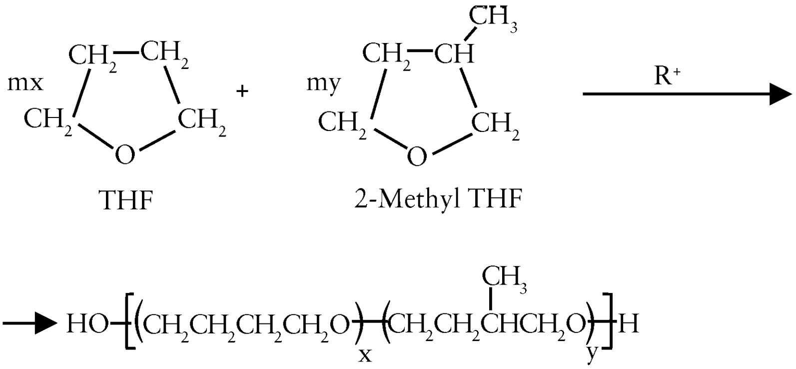
The characteristics of the most important PTMG used in practice are presented in **Table 7.1**.

The glass transition temperature (T_g) of PTHF is low, around –86 °C. This is the reason for its high elasticity at room temperature and at lower temperatures. The most important applications of PTMG are for making PU elastomers (cast elastomers, reaction injection moulding thermoplastic elastomers), and elastic fibres (‘spandex fibres’). The perfect bifunctionality of PTMG leads to higher performance PU elastomers, superior to those PU elastomers derived from polypropylene glycols obtained by anionic polymerisation, which have lower functionality than f = 2.

The THF substituted in the α position is impossible to polymerise because, during the propagation step, the attack of monomer is exactly in an α position against the oxygen atom of the THF cycle:



If the substituent R is in the β position, it is possible to obtain copolymers of THF-β substituted THF, which, fortunately, are liquid at room temperature, a very convenient property for PU applications. An interesting example of the liquid copolymer of THF-β substituted THF is the random copolymer THF-2-methyl-THF (reaction 7.16).



(7.16)

Table 7.1 The characteristics of the most important PTMG

Molecular weight	daltons	640-650	950-1050	1950-2110
Hydroxyl number	mg KOH/g	172-174	107-118	53-59
Softening point	°C	24-29	27-29.5	35-38
Viscosity, 40°C	mPa-s	120-180	240-280	1050-1250
Density, 40 °C	g/ml	0.978	0.974	0.972
Acidity	mg KOH/g	< 0.1	< 0.1	< 0.1
Water content	%	< 0.1	< 0.1	< 0.1

7.2 High Molecular Weight Polyalkylene Oxide Polyols by Cationic Polymerisation

Cationic polymerisation of alkylene oxides [polyethylene oxide (PO), ethylene oxide (EO), butylene oxide, epichlorohydrin and so on], initiated by hydroxyl groups, is catalysed by various Lewis acids, such as BF_3, BF_3-etherate, SbF_5, PF_5, $Al(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$ [3, 9, 35, 36, 39-44, 48-50] or Brönstedt superacids, such as: HBF_4, $HSbF_6$, HPF_6, CF_3SO_3H, $HClO_4$ [45-53], etc. The polymerisation rate of alkylene oxides in cationic catalysis is much higher than the polymerisation rate in anionic catalysis [48-53].

Thus, in **Table 7.2** the polymerisation rate constants of PO and EO in anionic and in cationic catalysis are compared.

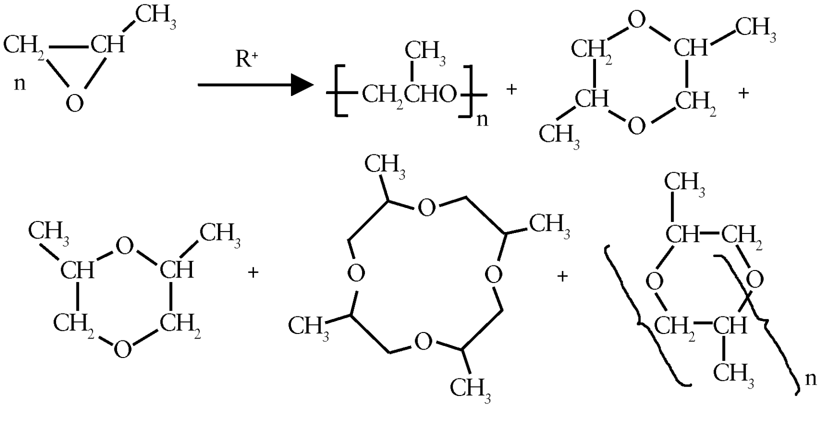
Table 7.2 The comparative rate constants of PO and EO polymerisation in anionic and cationic catalysis [54]

Monomer	Anionic catalysis K_p, l/mol x min	Cationic catalysis K_p, l/mol x min
EO (30 °C)	0.00021	0.162
PO (30 °C)	0.00011	8.100
EO (120 °C)	0.348	-
PO (120 °C)	1.044	-

Thus, PO is approximately 7500-8000 times more reactive in cationic catalysis than in anionic catalysis, at 30 °C and around 20-25 times more reactive in cationic catalysis, at 30 °C, than PO anionic polymerisation at 120 °C. It was observed that in cationic polymerisation, EO is around 50 times less reactive than PO, at 30 °C. However, in anionic catalysis there is a reversed order: EO is around 2-3 times more reactive than PO.

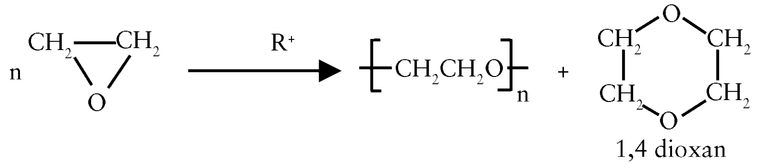
This very high PO polymerisation rate in cationic catalysis, at lower temperatures, is extremely attractive from the technological point of view.

Unfortunately, the cationic polymerisation of alkylene oxides leads to unpleasant side reactions: formation, together with the required polymer, of cyclic oligomers, of dioxane type and crown ether type (reaction 7.17) [3, 9, 35, 36, 45-53, 55].



(7.17)

For EO the desired polymer is formed and the main side product is 1,4 dioxane, which is a real advantage because 1,4 dioxane is a low boiling point (101 °C) cyclic oligomer (reaction 7.18) [45-47, 55].

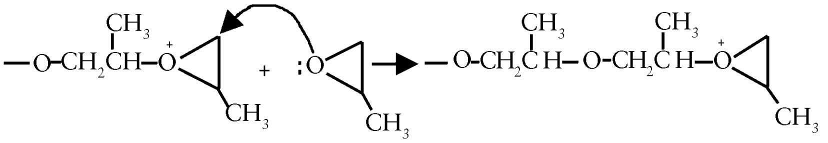


(7.18)

The formation of relatively high yield (15-25%) cylic oligomers, means that the cationic polymerisation of alkylene oxides cannot be used for high MW polyether polyol synthesis on an industrial scale [38, 56]. The cationic polymerisation process is only used industrially for producing PTHF- and THF-alkylene oxide copolymers [2, 3, 7, 35, 36, 54, 57, 58]. The cyclic oligomers are totally inert in the chemistry of PU formation because they do not have hydroxyl groups (are simple diluents) and confer a very unpleasant odour to the synthesised polyether polyols.

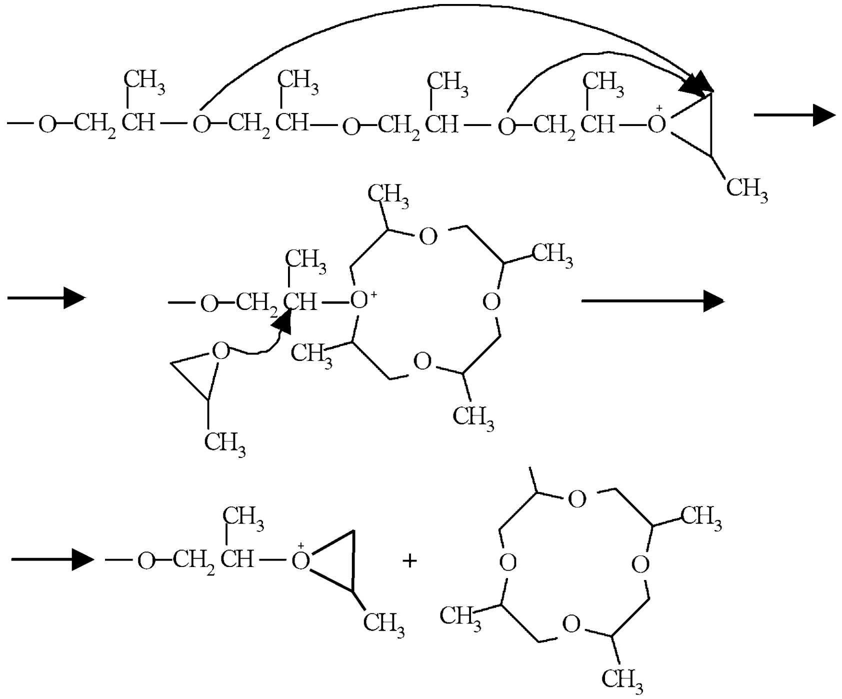
Penczek and co-workers discovered that the formation of cyclic oligomers is strongly suppressed in the cationic polymerisation of alkylene oxides, in the presence of a momentary high excess of hydroxyl groups ([OH] >> [alkylene oxide]) [45-49, 52-53, 55]. This discovery is one of the most important achievements in the cationic ring opening polymerisation of alkylene oxides. Practically, this concept may be realised by a very slow, step-by-step addition (at a very low alkylene oxide addition rate) to the polyolic starter-cationic catalyst mixture. Therefore, because of the very high reaction rate in cationic ring opening polymerisation, coupled with the very low addition rate, the momentary concentration of alkylene oxides in the reaction medium is very low and the hydroxyl groups are always in excess. Thus, by using this polymerisation technique, it was possible to obtain telechelic polyethers having terminal hydroxyl groups with a MW of 1000-2000 daltons, with a very low cyclic oligomer content (less than 1-2%).

Penczek [45-49, 52-53, 55] proved that the ring opening polymerisation mechanism of alkylene oxides in the presence of excess of hydroxyl groups is totally different from the cationic ring opening polymerisation in the absence of hydroxyl groups. In the classic mechanism of cationic polymerisation of alkylene oxides in the absence of hydroxyl groups, the cationic active centre is a tertiary oxonium cation at the end of the growing chain ([OH] = 0). This mechanism was called ‘activated chain end mechanism’ or ACE mechanism (reaction 7.19).



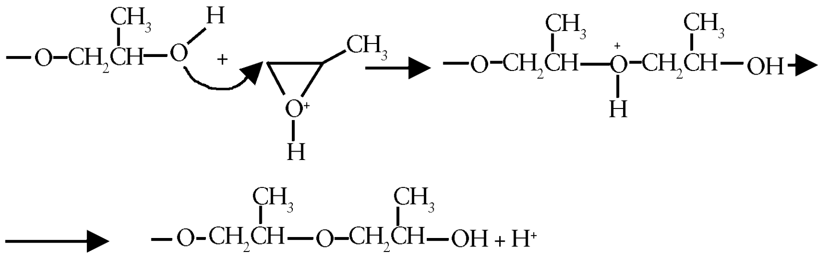
(7.19)

The ACE mechanism, developed in the absence of hydroxyl groups, leads to the formation of cyclic oligomers, at a high yield, by the ‘back biting’ mechanism (reaction 7.20).



(7.20)

The mechanism, developed by Penczek, in the presence of an excess of hydroxyl groups, is very similar to a solvolysis reaction [55] and is characterised by the presence of the active cationic centre to the monomer in the form of a secondary oxonium cation. The polymer chain extension takes place by the SN2 reaction of hydroxyl groups with the activated epoxide. This mechanism is called 'activated monomer' mechanism (AM mechanism), characterised by the relationship [OH] >> [PO] (reaction 7.21).



(7.21)

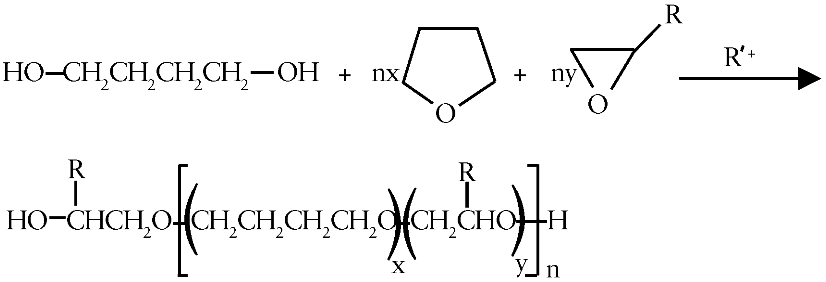
The polymerisation of PO initiated by hydroxyl groups and catalysed by aluminium triflate $Al(CF_3SO_3)_3$ [39, 44], or lanthanide triflates such as yttrium triflate $Y(CF_3(SO_3)_3$ [40] are some variants of cationic polymerisations developed at higher temperatures. The hydroxyl numbers obtained are generally high (the MW of the resulting polyethers is low).

It is hoped that the cationic polymerisation of alkylene oxides initiated by hydroxyl groups can be used, especially in the synthesis of high MW polyethers.

For low MW oligomers, (e.g., polyether triols initiated by glycerol with a MW of 600-1000 daltons), the cationic catalysis is used successfully especially in the synthesis of the starters/ precursors for coordinative polymerisation with dimetallic catalysts (DMC) (see Chapter 5).

7.3 Polyether Diols and Triols, Copolymers THF-alkylene Oxides

Cationic copolymerisation of THF with alkylene oxides (PO, EO) is another route to obtain copolyether diols or triols by a cationic mechanism. The copolymerisation of THF with PO and EO has been studied by many authors [3, 33-36, 54-59], generally being initiated by diols such as 1,4 butane diol. Copolyether diols with a MW of 1000-2000 daltons were obtained, which are viscous liquids at room temperature, compared with PTHF homopolymers which are solid waxes. The content of THF in these copolymers varies between 50-70%. The terminal groups in THF-PO copolymers are always derived from the alkylene oxide, secondary hydroxypropyl groups and the terminal groups in THF-EO copolymers are primary hydroxyethyl groups. Terminal groups derived from THF were not observed. The general reaction is in fact a random copolymerisation of THF with the alkylene oxides (reaction 7.22).



(7.22)

The cationic catalysts of this copolymerisation reaction are: Lewis acids (BF_3, SbF_5, PF_5) or superacids, such as (HBF_4, $HSbF_6$, HPF_6, CF_3SO_3H) [33-38, 54, 56-59].

In the presence of a polyolic compound used as starter, the Lewis acid generates *in situ* complex superacids:

$$BF_3 + HOR \rightleftharpoons [BFeOR]^- H^+$$

The big advantage of THF copolymerisation with alkyleneoxides is the fact that the equilibrium polymerisation characteristic of THF homopolymerisation is practically suppressed, at relatively high concentrations of alkylene oxides (30-50%). This behaviour leads to high yields of the resulting copolyether, THF-alkylene oxides, of around 85-90% (**Figure 7.3**).

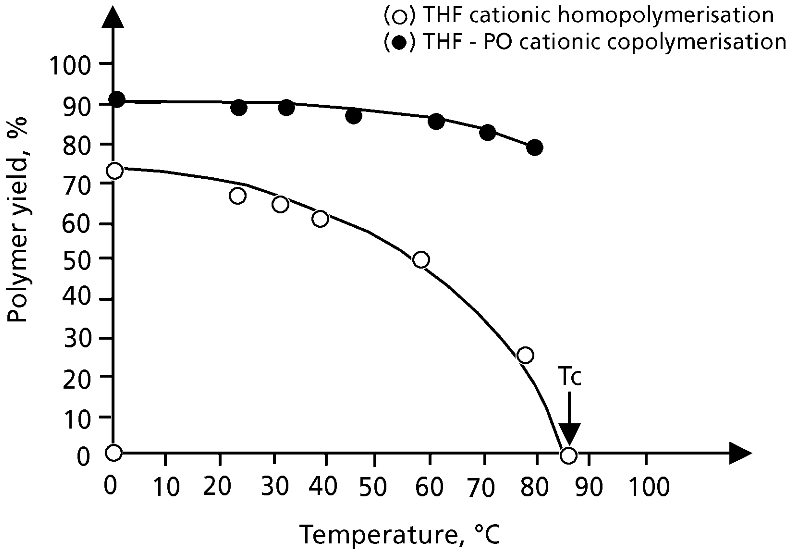


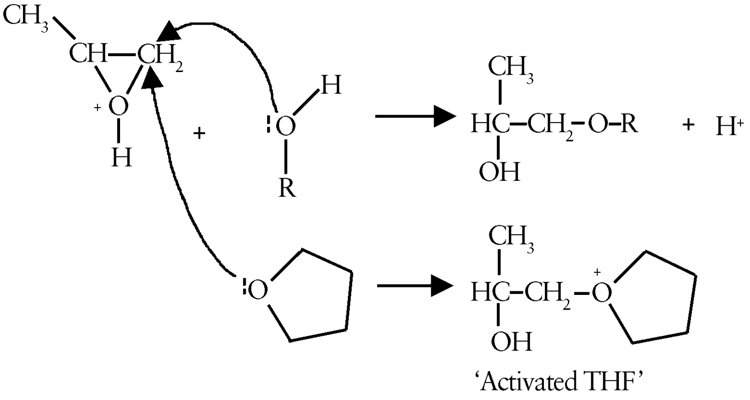
Figure 7.3 The variation of polymer yield *versus* temperature [54].

Reproduced with permission from Rapra Technology, Ltd. Copyright Rapra Technology, 1995

The copolymerisation of THF with alkylene oxides (PO, EO, epichlorohydrin and so on), catalysed by strongly acidic species, is perfectly explained by the 'activated monomer' mechanism presented before (Section 7.2).

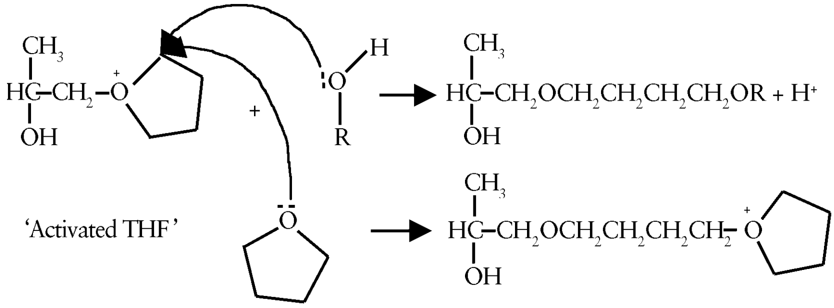
In the reaction medium there are two activated species: 'activated oxirane' and 'activated THF' [54, 55].

The most reactive species from the reaction system, the activated oxirane reacts with nucleophilic species from the reaction system (reaction 7.23):



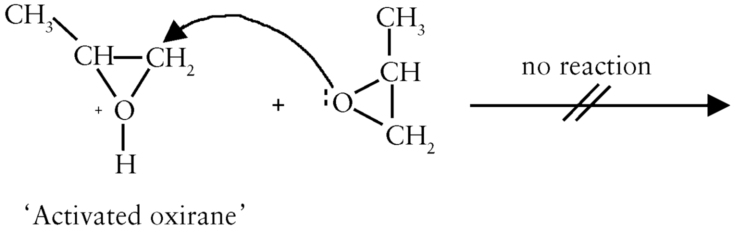
(7.23)

The activated THF reacts with the same nucleophilic species from the reaction system, similarly to the activated oxirane (reaction 7.24).

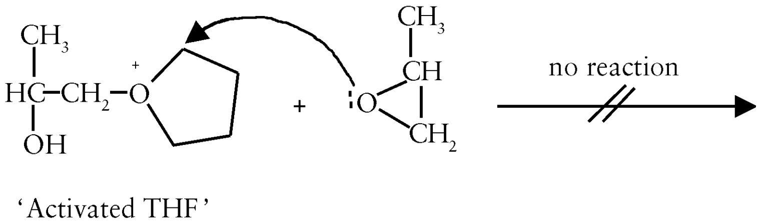


(7.24)

The oxygen atom of the PO or EO oxirane ring has a low nucleophilicity [3-5], compared to the hydroxyl groups of THF and probably does not react with activated monomer species (reactions 7.25 and 7.26).

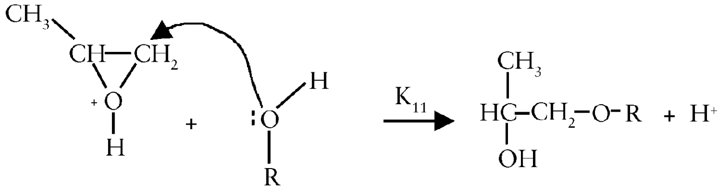


(7.25)

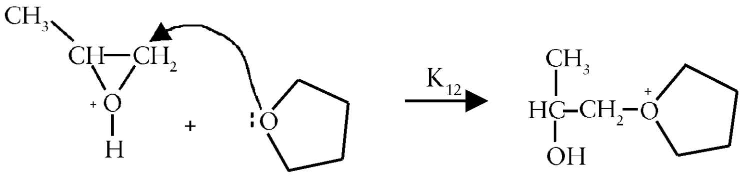


(7.26)

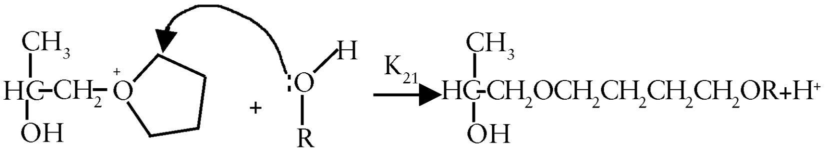
The random copolymerisation of THF with alkylene oxides by 'activated monomer' mechanism is characterised by reactions 7.27-7.30 [54].



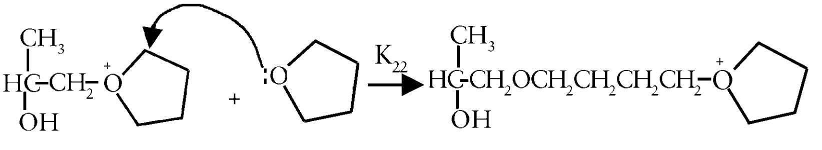
(7.27)



(7.28)



(7.29)



(7.30)

In the case of PO (monomer 1) copolymerisation with THF (monomer 2) in the presence of hydroxyl groups, the reactivity constants of copolymerisation r_1 and r_2 are:

$$r_1 = \frac{K_{11}}{K_{12}} = 1.8 \qquad r_2 = \frac{K_{21}}{K_{22}} = 0.6$$

It is clear that PO is much more reactive than THF in these copolymerisation reactions initiated by hydroxyl groups. It is highly probable that EO is more reactive than THF too, in the random copolymerisation of THF with EO, in the presence of hydroxyl groups. It is interesting that in the absence of hydroxyl groups, the monomer's reactivities are exactly in the reverse order: THF, the most basic monomer, is much more reactive than PO or EO.

Using the principles of cationic copolymerisation of THF with alkylene oxides by activated monomer mechanism, various polyethers diols or triols, copolymers THF-alkylene oxides were synthesised [5]. The diols are obtained by copolymerisation initiated by 1,4 butane diol or another diol [56-59]. The triols are obtained by copolymerisation initiated by glycerol (or other triol such as trimethylolpropane) [54].

The general copolymerisation procedure is relatively simple: to the mixture of THF, polyolic starter and catalyst (BF_3, SbF_5, HBF_4 $HSbF_6$), is added stepwise to the alkylene oxide (PO or EO), at a low temperature (0-30 °C), over several hours. After the reaction, the acidic catalyst is neutralised with a solid base, such as: CaO, $Ca(OH)_2$, hydrotalcite or weakly basic anion exchangers, followed by filtration and distillation of unreacted monomers [54].

By this procedure various copolymers THF-alkylene oxides, diols or triols, were synthesised with high yields (88-92%) with the following compositions [54]:

a) Copolymers THF-PO (Figure 7.4, Table 7.3);

b) Copolymers THF-EO (Figure 7.5, Table 7.4);

c) Copolymers THF-PO-EO (Figure 7.6, Table 7.5);

d) Copolymers THF-EO-PO (Figure 7.7, Table 7.6);

a) THF-PO copolymers:

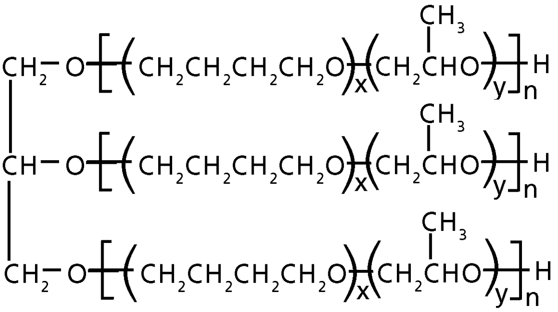


Figure 7.4 The structure of random copolymers of THF-PO

Table 7.3 The characteristics of polyether triols, random THF-PO copolymers (Figure 7.4)

Characteristic	Unit	MW = 3000	MW = 3600
THF	%	65	65
PO	%	35	35
Hydroxyl number	mg KOH/g	56.3	45.7
Primary hydroxyls	%	4-6	4-6
Acidity	mg KOH/g	0.35	0.4
Viscosity, 25 °C	mPa-s	1247	2470
Water content	%	0.04	0.032
Unsaturation	mEq/g	0.01	0.016
Cyclic oligomers	%	< 2	<2

b) THF-EO copolymers:

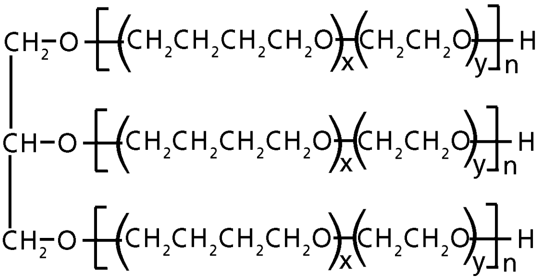


Figure 7.5 The structure of random copolymers of THF - EO

Table 7.4 The characteristics of polyether triols, random THF-EO copolymers (Figure 7.5)

Characteristic	Unit	MW = 3600	MW = 3800
THF	%	70	60
EO	%	30	40
Hydroxyl number	mg KOH/g	46.6	43.8
Primary hydroxyls	%	100	100
Acidity	mg KOH/g	0.35	0.40
Viscosity, 25 °C	mPa-s	2560	1070
Water content	%	0.035	0.04
Unsaturation	mEq/g	0.006	0.008
Cyclic oligomers	%	< 1	<1

c) THF-PO-EO copolymers:

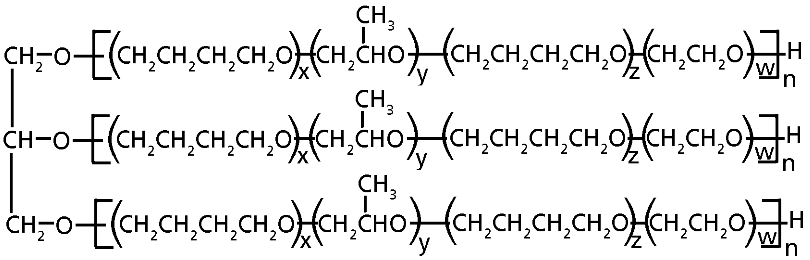


Figure 7.6 Structure of random copolymers of THF-PO-EO

Table 7.5 The characteristics of polyether triols, random THF-PO-EO copolymers (Figure 7.6)

Characteristic	Unit	MW = 4600	MW = 5000
THF	%	55	55
PO	%	30	30
EO	%	15	15
Hydroxyl number	mg KOH/g	36.9	33.5
Primary hydroxyls	%	63.8	64
Acidity	mg KOH/g	0.02	0.03
Viscosity, 25°C	mPa-s	5770	7600
Water content	%	0.03	0.04
Unsaturation	mEq/g	0.02	0.02
Cyclic oligomers	%	< 1	<1

d) THF-EO-PO copolymers:

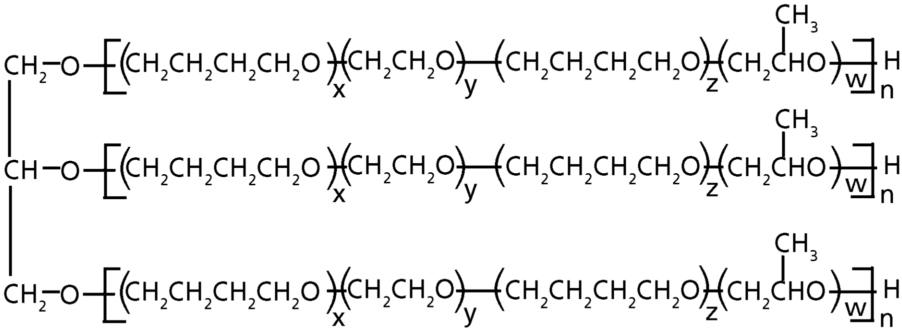


Figure 7.7 Structure of random copolymers of THF-EO-PO

Table 7.6 The characteristics of polyether triols, random THF-EO-PO copolymers (Figure 7.7)

Characteristic	Unit	MW = 4200
THF	%	55
PO	%	30
EO	%	15
Hydroxyl number	mg KOH/g	40
Primary hydroxyls	%	4-6
Acidity	mg KOH/g	0.04
Viscosity, 25 °C	mPa-s	8000
Water content	%	0.04
Unsaturation	mEq/g	0.018
Cyclic oligomers	%	< 2

The THF-PO copolyether has predominantly secondary hydroxyl groups, the terminal groups are derived from the alkylene oxide. Formation of primary hydroxyl groups by abnormal ring opening reaction of PO ring is also possible. The THF-EO copolyethers are very reactive, having exclusively primary hydroxyl groups (100% primary hydroxyl groups). The THF-PO-EO copolyethers (15% EO) have a primary hydroxyl content in the range 65-70%. The THF-EO-PO copolyethers have predominantly secondary hydroxyl groups. The cyclic oligomer content of these THF-alkylene oxides copolyethers is very low, less than 1-2%. The synthesised copolyether triols THF-alkylene oxides, have very low unsaturation, less than 0.02 mEq/g.

It was observed that the viscosities of the synthesised copolyethers THF-alkylene oxides are higher than the viscosities of polyalkylene oxide copolyether triols. The polyether triols, random copolymers of THF-alkylene oxides, give flexible PU foams with superior hardness, elongation, tear and tensile strengths compared to the flexible foams derived from classic polyalkylene oxide polyether triols.

The polyether diols, THF-alkylene oxide copolymers are used especially for preparing PU elastomers with high elastic properties (elongation, modulus, tear and tensile strength), superior to those of PU elastomers derived from polyalkylene oxide polyether diols (PO homopolymers or PO-EO copolymers).

The most important polyols obtained by cationic catalysis are PTHF homopolymers with a MW of 600-3000 daltons used for PU elastomers and ‘spandex’ fibres. The THF-alkylene oxide copolymers have a minor importance at this moment, being commercially insignificant.

The high price of THF has limited the penetration of polyether polyols based on THF and its copolymers with alkylene oxides in flexible PU foams area.

The most important area for PTHF and THF-alkylene oxides copolymers remains the PU elastomers area (including elastomeric fibres), the PTHF and the high THF content copolymers confer on the resulting PU elastomers specific properties, such as: excellent hydrolytic stability, resiliency, low temperature stability, elasticity at lower temperatures, and resistance to fungus attack [7, 35, 36, 37].

References

1. *Ullmann's Encyklopaedie Der Technischen Chemie*, 4th Edition, Volume 19, Ed., E. Bartholome, Verlag Chemie, Weinheim, Germany, 1972, p.297-299.
2. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Volume 18, Eds., M. Grayson and D. Eckroth, Wiley Interscience, New York, NY, USA, p.645-663.
3. K.C. Frisch and J.L. Reegen in *Ring Opening Polymerisation*, Eds., K.J. Ivin and T. Saegusa, Marcel Dekker, New York, NY, USA, 1969.
4. F.S. Dainton, F.R.S. Ivin and K.J. Ivin, *Quarterly Reviews*, 1958, **12**, 61.
5. P.A. Small, F.S. Dainton and T.R.E. Devlin, *Transactions of the Faraday Society*, 1955, **51**, 1710.
6. *Polyethers,* Ed., N.G. Gaylord, *High Polymers*, Volume 13, Part II, Wiley-Ineterscience, New York, NY, USA, 1963, p.298.
7. P.M. Dreyfuss and M.P. Dreyfuss in *Encyclopedia of Polymer Science and Technology*, Eds., H.F. Mark, N.G. Gaylord and N.M. Bikales, Volume 13, Interscience, New York, NY, USA, 1970, p.670-691.
8. J.D. Cox, *Tetrahedron*, 1963, **19**, 7, 1175.
9. J. Furukawa and T. Saegusa, *Polymerisation of Aldehydes and Oxides*, Interscience Publishers, New York, NY, USA, 1963.
10. J.M. McKenna, T.K. Wu and G. Pruckmayr, *Macromolecules*, 1977, **10**, 4, 877.

11. G. Pruckmyer and T.K. Wu, *Macromolecule*s, 1978, **11**, 1, 265.
12. G. Pruckmyer and T.K. Wu, *Macromolecules*, 1978, **11**, 4, 662.
13. K. Matsuda, Y. Tanaka, T. Sakai and J.P. Wakayama, inventors; Kao Soap Co. Ltd., assignee; DE 2,256,416A1, 1973.
14. G.E. Heinsohn, I.M. Robinson, G. Pruckmayr, W.W. Gilbert, inventors; E. I. Du Pont de Nemours and Company, assignee; US 4,163,115, 1979.
15. G.E. Heinsohn, G. Pruckmayr, I.M. Robinson, W.W. Gilbert, inventors; E.I. du Pont de Nemours and Co., assignee; DE 2,709,280A1, 1977.
16. K. Matsuda, Y. Tanaka and T. Sakai, inventors; Kao Soap Co. Ltd., assignee; DE 2,364,859A1, 1974.
17. S. Smith and A. Hubin, inventors; Minnesota Mining and Mfg Co, assignee; US 3,824,219, 1974.
18. S. Smith and A. Hubin, inventors; Minnesota Mining and Mfg Co, assignee; US 3,824,220, 1974.
19. N. Greif, R. Fikentscher, H. Bille and T. Simenc, inventors; BASF AG, assignee; DE 2,401,855B1, 1975.
20. N. Greif, R. Fikentscher, H. Bille and T. Simenc, inventors; BASF AG, assignee; DE 2, 624, 286A2, 1977.
21. B.E. Smart, inventor; DuPont de Nemours, assignee; US 3,963,767, 1976.
22. H. Tomomatsu, inventor; The Quaker Oats Corporation, assignee; US 3,980,672, 1976.
23. G.E. Heinsohn, G. Pruckmayr, I.M. Robinson, W.W. Gilbert, inventors; E. I. Du Pont de Nemours and Company, assignee; DE 2,709,280, 1977.
24. V. Leroy, C. Gaspard, J.J. Huet and L. Coheur, inventors; Centre de Recherches Metallurgiques - Centrum voor Research in de Metallurgie, and Centre d'Etude de l'Energie Nucleaire, CEN-SCK, assignees; DE 2,805,792A1, 1978.
25. H.E. Bellis, inventor; E. I. Du Pont de Nemours and Company, assignee; US 4,127,513, 1978.
26. G. Pruckmayr, inventor; E. I. Du Pont de Nemours and Company, assignee; US 4,153,786, 1979.

27. G.E. Heinsohn, I.M. Robinson, G. Pruckmayr and W.W. Gilbert, inventors; E. I. Du Pont de Nemours and Company, assignee; US 4,163,115, 1979.

28. T. Masuda, T. Takase, Y. Watanabe and F. Yamazaki, inventors; Mitsui Toatsu Chemicals, Inc., assignee; US 4,209,641, 1980.

29. H. Mueller, inventor, BASF AG, assignee; DE 3,402,027A1, 1985.

30. J.E. Kearnan, inventor; Stauffer Chemical Company, assignee; US 4,564,670, 1986.

31. L.A. Dickinson, *Journal of Polymer Science*, 1962, **58**, 166, 857.

32. N.E. Rustad and R.G. Krawiec, *Rubber Age*, 1973, **105**, 11, 45.

33. W. Meckel, W. Goyert and W. Wiester in *Thermoplastic Elastomers: A Comprehensive Review*, Eds., N.R. Legge, G. Holden and H.E Schröder, Hanser Publishers, Munich, Germany, 1987, p.13.

34. W.J. Murbach and A. Adicoff, *Industrial & Engineering Chemistry*, 1960, **52**, 9, 772.

35. *Telechelic Polymers, Synthesis and Applications*, Ed., E.J. Goethals, CRC Press Inc., Boca Raton, FL, USA, 1989, p.115.

36. *Telechelic Polymers, Synthesis and Applications*, Ed., E.J. Goethals, CRC Press Inc., Boca Raton, FL, USA, 1989, p.221.

37. *The ICI Polyurethanes Book*, Second Edition, Ed., G. Woods, John Wily & Sons, Chichester, UK, 1990.

38. K. Yasuda, Y. Yokoyama, S. Matsusta and K. Harada in *Cationic Polymerisation and Related Processes*, Ed., E.J. Goethals, Academic Press, London, UK, 1984, p.379.

39. M.J. Green, inventors; BP Chemicals Limited, assignee; EP 212,820A1, 1987.

40. H. Wolleb, A. Hafner, W.M. Rolfe, inventors; Ciba-Geigy AG assignee; EP 569,331A3, 1995.

41. D.R. Hollingsworth, J.F. Knifton, inventors; Texaco Chemical Company assignee; US 5,262,562, 1993.

42. N. Drysdale, inventor; E.I. Du Pont De Nemours and company assignee; WO 9502626A1, 1995.

43. N. Drysdale, inventor; E.I. Du Pont De Nemours and company assignee; WO 9613540A1, 1996.

44. J. Hofmann, P. Gupta and H. Pielartzik, inventors; Bayer AG, assignee; US 6,093,793, 2000.

45. K. Brezinska, R. Szymanski, P. Kubisa and S. Penczek, *Die Makromoleculare Chemie - Rapid Communications*, 1986, **7**, 1, 1.

46. S. Penczek, P. Kubisa and R. Szymanski, *Die Makromoleculare Chemie-Symposia*, 1986, **3**, 203.

47. M. Wojtania, P. Kubisa and S. Penczek, *Die Makromolekulare Chemie - Macromolecular Symoosia*, 1986, **6**, 201.

48. M. Bednarek, T. Biedron, P. Kubisa and S. Penczek, *Die Makromolekulare Chemie - Macromolecular Symposia*, 1991, **42/43**, 475.

49. M. Bednarek, P. Kubisa and S. Penczek*, Macromolecular Symposia,* 1996, **107**, 139.

50. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Advances in Urethane Science & Technology*, Eds., D. Klempner and K.C. Frisch, Technomic Publishers, Lancaster, PA, USA, 1998, **14**, 151.

51. P. Kubisa, *Die Makromolekulare Chemie - Macromolecular Symposia*, 1988, **13/14**, 203.

52. T. Biedron, R. Szymanski, P. Kubisa and S. Penczek, *Die Makromolekulare Chemie - Macromolecular Symposia*, 1990, **32**, 155.

53. M. Bednarek, P. Kubisa and S. Penczek, *Die Makromolekulare Chemie,* 1989, **15**, Supplement, 49.

54. M. Ionescu, I. Mihalache, V. Zugravu, S. Mihai and S. Sever, *Cellular Polymers*, 1995, **14**, 3, 203.

55. P. Kubisa and S. Penczek, *Progress in Polymer Science*, 1999, **24,** 10, 1409.

56. S.G. Entelis and G.V. Korovina, *Die Makromolekulare Chemie*, 1974, **175**, 4, 1253.

57. L.P. Blanchard and M.D. Baijal, *Journal of Polymer Science*, 1965, **A1**, 15, 2045.

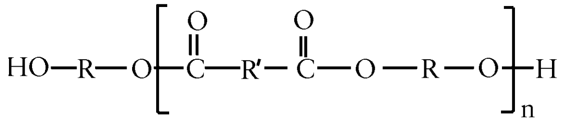
58. M.D. Baijal and L.P. Blanchard, *Journal of Polymer Science*, 1968, **23**, 157.

59. J.M. Hammond, J.F. Hooper and W.G.P. Robertson, *Journal of Polymer Science, Part A-1: Polmer Chemistry,* 1971, 2, 265.

8

Polyester Polyols for Elastic Polyurethanes

Polyester polyols for elastic polyurethanes (PU) are low molecular weight (MW) polymers (1000-4000 daltons) characterised by the presence of ester groups and terminal hydroxyl groups. The general formula of a polyester polyol is [1-8]:



$$HO-R-O\left[-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-O-R-O-\right]_n H$$

Polyester polyols are the second most important group of oligo-polyols for production of polyurethanes after polyether polyols. They represent around 18% of the polyols used globally in polyurethanes, corresponding to a total worldwide production of around 600,000 tones/year. About 60% of polyester polyols being produced in Europe [1].

Polyester polyols were the only polyols available to the polyurethanes industry at the beginning, but now, in spite of the leading position of polyethers in the total polyols usage in the polyurethane industry (around 80%), polyester polyols have stable and specific practical applications due to some superior characteristics of the resulting polyurethanes [1, 2, 3, 6-11].

The superior characteristics of polyester polyol based polyurethanes are explained by a better crystalline structure [1, 7] in the urethane segment, compared to the majority of polyether polyols which are amorphous [except polytetrahydrofuran (PTHF)], due to the superior secondary forces between the polyester chains [8] and also due to a superior thermal and fire resistance, compared to polyether polyol based polyurethanes. Polyester-based polyurethanes (flexible foams, coatings), have a superior solvent resistance compared to the polyether-based polyurethanes [8].

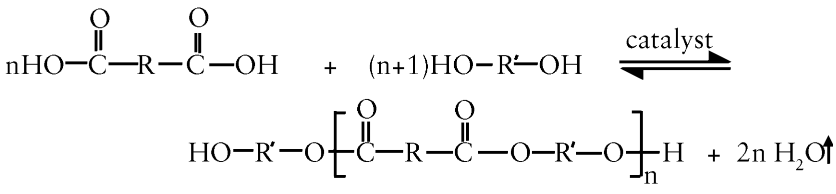
The most important segments of polyester polyol applications are those of polyurethane elastomers (43% of global polyester polyols consumption), flexible foams (15-18%), coatings, adhesives, rigid foams, synthetic leather, and sealants.

Polyester polyols have an intrinsic defect: they are liable to hydrolyse under high humidity/temperature conditions. To prevent the hydrolysis of polyester-based polyurethanes a worldwide research effort, led to the synthesis of polyester polyols with improved hydrolysis resistance [1, 6-8, 12, 13].

8.1 Chemistry of Polyester Polyol Synthesis

The polyester polyols are obtained by the polycondensation reactions between dicarboxylic acids (or derivatives such as esters or anhydrides) and diols (or polyols), or by the ring opening polymerisation of cyclic esters (lactones, cyclic carbonates).

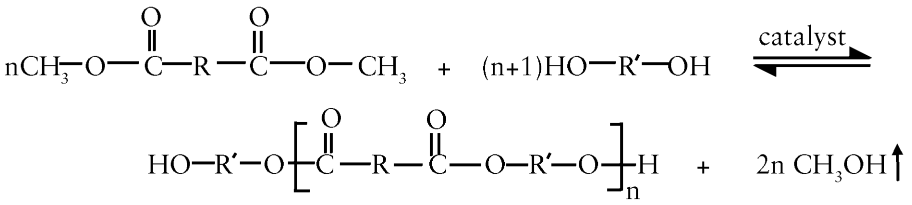
The polycondensation reaction between dicarboxylic acids and glycols is an equilibrium reaction, the equilibrium being shifted to the formation of polyester polyols by continuous elimination of water from the reaction system (reaction 8.1) [1-8, 12-27].



$$nHO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH + (n+1)HO-R'-OH \xrightleftharpoons{catalyst} HO-R'-O\left[\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O\right]_n H + 2n\,H_2O\uparrow \qquad (8.1)$$

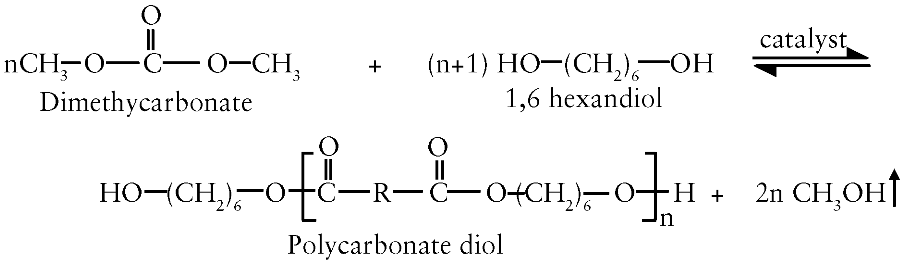
In order to generate terminal hydroxyl groups an excess of glycol is currently used. The reaction takes place in uncatalysed reaction conditions (self catalysis by the acidic carboxyl groups) but the best perfomances (low reaction time, low final acidity) are obtained in the presence of specific catalysts, such as: *p*-toluene sulfonic acid, tin compounds (stannous octoate), antimony, titanium (tetrabutyltitanate), zinc (zinc acetate), manganese (manganese acetate) or lead compounds and more recently enzymic catalysts (lipases) [1, 25].

The direct polyesterification reaction of diacids with glycols is the most important industrial synthetic route to polyester polyols. The second most important synthetic route is the transesterification reaction between dimethyl esters of dicarboxylic or dibasic acids (dimethyl adipate, dimethyl terephthalate, dimethyl carbonate or even polyethylene terephthalate) and glycols (reaction 8.2) [1, 3-8].



$$nCH_3-O-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-CH_3 + (n+1)HO-R'-OH \xrightleftharpoons{catalyst} HO-R'-O\left[\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O\right]_n H + 2n\,CH_3OH\uparrow \qquad (8.2)$$

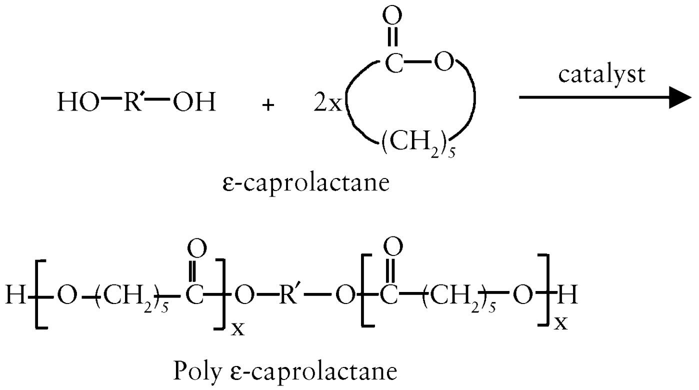
Aliphatic polycarbonates (polyesters of carbonic acid) are obtained by the transesterification reaction of dialkyl carbonates (for example dimethyl carbonate) with aliphatic diols. A typical example is the polycondensation of dimethyl carbonate with 1,6 hexanediol (reaction 8.3) [4-8]:



$$n\,CH_3{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3 + (n+1)\,HO{-}(CH_2)_6{-}OH \xrightleftharpoons{catalyst} HO{-}(CH_2)_6{-}O{-}\left[\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}O{-}(CH_2)_6{-}O\right]_n{-}H + 2n\,CH_3OH\uparrow$$

(8.3)

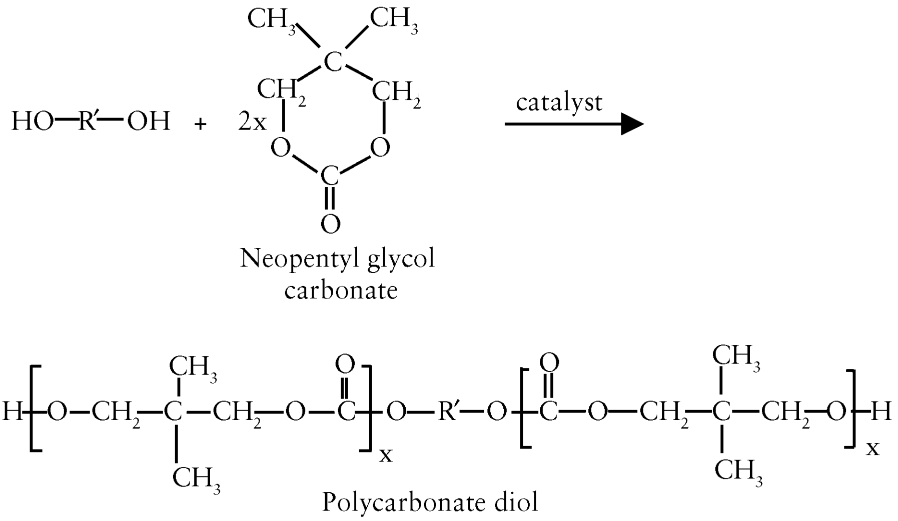
The third type of reaction for polyester polyols synthesis is the ring opening polymerisation of cyclic esters, such as ε-caprolactone (reaction 8.4) or cyclic carbonates, such as ethylene glycol carbonate, propylene glycol carbonate, neopentyl glycol carbonate, etc., (reaction 8.5) initiated by diols (or polyols) and catalysed by specific catalysts [7, 16].



(8.4)

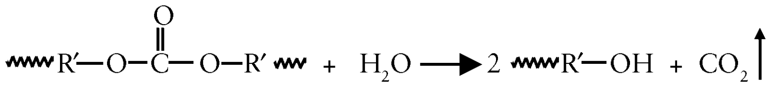
Polycaprolactone (PCL) polyols, due to the presence of a relatively long repeated hydrophobic segment -$(CH_2)_5$- are recognised as polyesters which lead to polyurethanes with good resistance to hydrolysis [7, 16].

Ring opening polymerisation of cyclic carbonates, initiated by glycols, leads to polycarbonate diols (reaction 8.5).



(8.5)

In spite of the aliphatic carbonate groups, hydrolytic labile, polycarbonate diols are recognised to give polyurethanes resistant to hydrolysis. The explanation of this resistance is given by the fact that, during the hydrolysis process, acidic groups are not formed (which catalyse strongly ester groups hydrolysis), but gaseous CO_2 is formed which is a very weak acid and is eliminated from the system (reaction 8.6) [14, 15].



$$\sim R'-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'\sim + H_2O \longrightarrow 2 \sim R'-OH + CO_2\uparrow \quad (8.6)$$

After this general presentation of the synthetic methods for obtaining polyester polyols, the direct polyesterification of dicarboxylic acids with glycols, the most important route to polyester polyols will be presented in detail.

Table 8.1 shows the most important polyols (diols and triols) and **Tables 8.2** and **8.3** show the most important dicarboxylic acids used as raw materials for direct polyesterification reactions.

By using the raw materials presented: diols, triols and dicarboxylic acids, it is possible to obtain a large variety of polyester polyol structures. For example to use one type of glycol and one type of dicarboxylic acid, but many other combinations are possible, such as using one dicarboxylic acid and two types of glycol or to use a glycol together with a small quantity of triol, to obtain a branched polyester polyol.

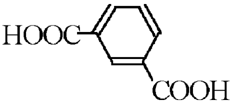
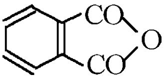
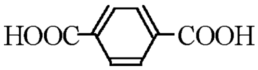
Table 8.1 The most important diols and triols used for polyester polyol synthesis

No.	Polyol	Formula	MW, daltons	Hydroxyl number, mg KOH/g
Diols				
1	Ethyleneglycol (EG)	$HOCH_2CH_2OH$	62.07	1807.6
2	Diethyleneglycol (DEG)	$(HOCH_2CH_2)_2O$	106.12	1057.2
3	1,2 Propyleneglycol (PG)	$HOCH_2CH(CH_3)OH$	76.10	1474.3
4	1,4 Butanediol (BD)	$HO–(CH_2)_4–OH$	90.12	1245.0
5	Neopentyl glycol (NPG)	$(CH_3)_2C(CH_2OH)_2$	104.0	1078.8
6	1,6 Hexanediol (HD)	$HO–(CH_2)_6–OH$	118.18	949.3
Triols				
1	Glycerol	$(HOCH_2)_2CHOH$	92.10	1827.3
2	Trimethylolpropane (TMP)	$(HOCH_2)_3CCH_2CH_3$	122	1379.5

Table 8.2 Aliphatic dicarboxylic acids used for polyester polyol synthesis

No.	Dicarboxylic acid	Formula	MW, daltons	Acid number, mg KOH/g
1	Adipic acid (AA)	$HOOC(CH_2)_4COOH$	146.14	767.78
2	Glutaric acid	$HOOC(CH_2)_3COOH$	132.12	849.2
3	Succinic acid	$HOOC(CH_2)_2COOH$	118.09	950.1
4	Sebacic acid	$HOOC(CH_2)_8COOH$	202.0	555.4
4	Azelaic acid	$HOOC(CH_2)_7COOH$	186.0	603.2

Table 8.3 Aromatic dicarboxylic acids and derivatives used for polyester polyol synthesis

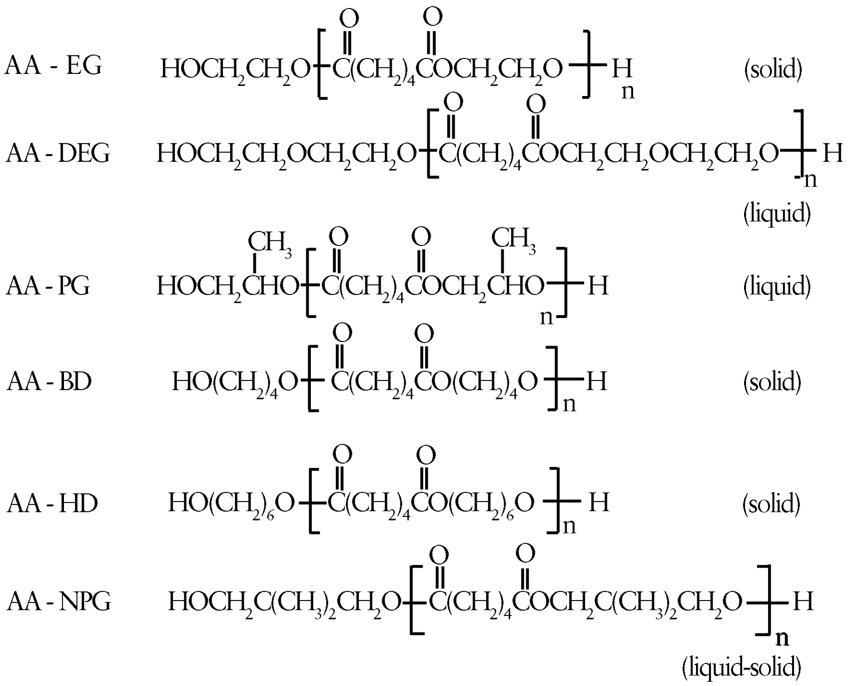
No.	Dicarboxylic acid	Formula	MW, daltons	Acid number, mg KOH/g
1	Isophthalic acid (IPA)		166.13	675.3
2	Phthalic anhydride		148.12	757.4
3	Terephthalic acid		166.13	675.3

AA is by far the most important dicarboxylic acid used for polyester polyol fabrication. The polyester polyols of MW of 2000 daltons, based on AA and each glycol (presented in **Table 8.2**) are well known (see **Figure 8.1**) [6, 8, 22-24].

It is possible to obtain polyester polyols based on AA and two different diols, such as: AA-EG/BD and AA-HD/NPG. Other possibilities are to develop the polyesterification with one glycol type and two different dicarboxylic acids, such as: AA/IPA-HD or AA/IPA-NPG/HD. These polyester polyols containing some aromatic groups of IPA are used on floor coatings and in adhesives.

By using, together with a diol, a triol such as TMP or glycerol it is possible to obtain polyesters with a functionality (f) higher than 2 OH groups/mol, situated in the range of 2-3 OH groups/mol. These polyester polyols are used for flexible PU foam fabrication. Flexible PU foams based on polyester polyols have a unique property: their clickability (capacity to be easily cut) and are used in laminates for textile industry.

Polyether polyols, especially polypropylene glycols, have lower functionality than is theoretically due to the presence of side reactions during synthesis (see details in



AA - EG $HOCH_2CH_2O\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_2CH_2O\right]_nH$ (solid)

AA - DEG $HOCH_2CH_2OCH_2CH_2O\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_2CH_2OCH_2CH_2O\right]_nH$ (liquid)

AA - PG $HOCH_2\overset{CH_3}{\overset{|}{C}}HO\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_2\overset{CH_3}{\overset{|}{C}}HO\right]_nH$ (liquid)

AA - BD $HO(CH_2)_4O\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}O(CH_2)_4O\right]_nH$ (solid)

AA - HD $HO(CH_2)_6O\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}O(CH_2)_6O\right]_nH$ (solid)

AA - NPG $HOCH_2C(CH_3)_2CH_2O\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_2C(CH_3)_2CH_2O\right]_nH$ (liquid-solid)

Figure 8.1 The structure of some representative polyester polyols used in polyurethane applications

Chapter 12.5). Polyester polyols in reality, have the theoretical functionality, which is a great advantage for many polyurethane applications. For polyester diols the functionality is 2 OH groups/mol. This structural aspect results in the polyester diols giving PU elastomers with excellent physico-mechanical properties, superior to all polypropylene glycols obtained by anionic PO polymerisation.

It is very clear, that the reaction between a dicarboxylic acid with a glycol always results in a polyester diol, the functionality being exactly 2 OH groups/mol. The functionality of a branched polyester polyol is calculated by the Chang equation [22]:

$$f = \frac{2}{1-(n-2)EW/Y}$$

where:

f = functionality of polyester polyol (OH groups/mol)

n = functionality of branched raw material (usually n = 3 OH groups/mol)

EW = equivalent weight of the polyester (M/number of OH groups)

Y = yield of the polyester based on one mol of branched modifier.

The equivalent weight is calculated using the well known formula:

$$EW = \frac{56100}{OH\#}$$

By polyesterification of AA, DEG and glycerol, a polyester was obtained with an hydroxyl number (OH#) of 46.75 mg KOH/g. By using one mol of branched modifier, the quantity (Y) of the resulting polyester is 3600 g. What then is the functionality of the polyester?

The equivalent weight is EW = 56100/46.75 = 1200

$$f = \frac{2}{1-(3-2)*\frac{1200}{3600}} = \frac{2}{1-0.333} = \frac{2}{0.667} = 2.998$$

The functionality of the resulting polyester is 2.998 OH groups/mol.

The polyesters derived from AA and DEG, and from AA and PG are liquid at room temperature. The branched polyesters based on AA-DEG/TMP or AA-DEG/glycerol are also liquid. The polyesters derived from AA-EG, AA-D, AA-HD and AA-NPG are solid at room temperature. It is very interesting that some polyester polyols based on AA and a mixture of glycols (which independently leads to solid polyesters), give by copolycondensation, liquid polyesters, for example the polyester AA-EG-(40-60%)BD [24].

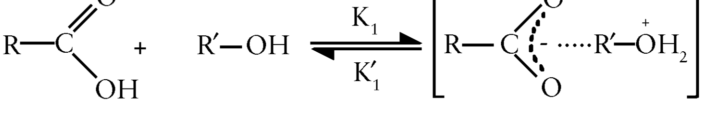
An important characteristic of polyester polyols is the final acidity. Due to the presence of unreacted terminal carboxyl groups, the acidity of polyester polyols is higher than the acidity of polyether polyols. The majority of commercial polyester polyols have a maximum acidity of 2 mg KOH/g, compared to the maximum acidity of 0.1 mg KOH/g for polyether polyols. It was observed with the polyester having a very low acidity (for example about 0.1 mg KOH/g), that the hydrolysis resistance of the resulting PU increases substantially, thus proving the catalytic activity of the free acidic groups in ester group hydrolysis reaction [14, 15]. Unfortunately to obtain an acidity lower than 0.1 mg KOH/g industrially is difficult and needs a long reaction time. In very efficient catalysed polyesterification reactions (with tin compounds), after 11 hours an acidity of about 0.4 mg KOH/g is obtained and in the uncatalysed polyesterification reaction, after 25 hours the acidity obtained is around 0.9-1 mg KOH/g. In conclusion, with an efficient catalyst it is currently possible to obtain, in a reasonable interval of time, a maximum acidity of 0.5 mg KOH/g.

Because many catalysts used in polyesterification reactions are liable to hydrolyse and thus lose their catalytic activity, frequently the first part of the polyesterification reaction (when water is massively eliminated from the reaction mass), is done without a catalyst (the catalysis is assured by the acidic carboxyl groups). After the distillation of the majority of water (3-6 hours) a specific catalyst is added (tin, titanium, lead or manganese catalyst, the best results being obtained with tin catalysts). Using a two-step polyesterification reaction, the catalyst is protected against hydrolysis and assures a good catalytic activity at the end of polyesterification reaction, when the concentration of carboxyl groups is very low, and it is very important to obtain a final low acidity.

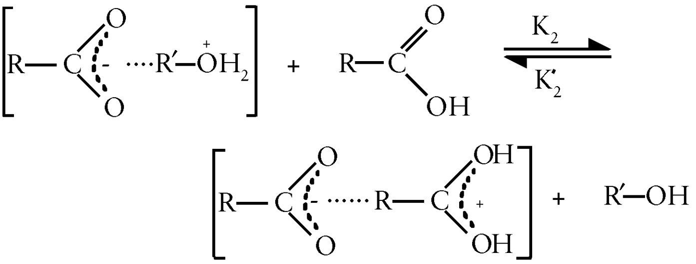
8.2 Consideration of the Kinetics of Polyesterification Reactions [18, 20, 21]

8.2.1 Self Catalysed Polyesterification Reactions (Without Catalyst)

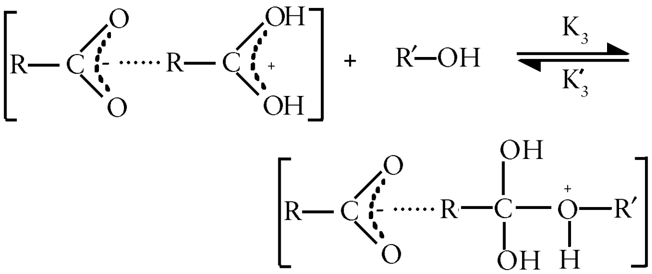
The mechanism of self catalysed polyesterification is described by the following four classical equilibrium reactions (reactions 8.7-8.10).



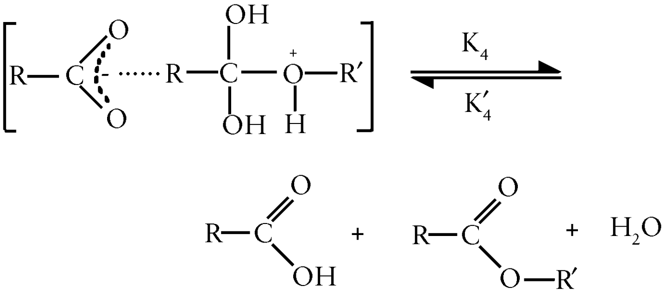
(8.7)



(8.8)



(8.9)



(8.10)

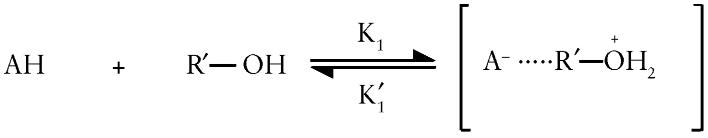
The 'key' to the succession of the reactions is the unstable complex between two acid groups (one group is transformed into an anion and one group into a cation) which react (reaction constant K_3) with one mol of alcohol (reaction 8.9) giving an unstable complex which is decomposed (reaction constant K_4) into one mol of ester, one mol of acid and one mol of water (reaction 8.10).

The general kinetic equation of the uncatalysed polyesterification is a third-order kinetic equation:

$$\frac{d[RCOOR']}{dt} = K_{III*}[RCOOH]^2 * [R'OH]$$

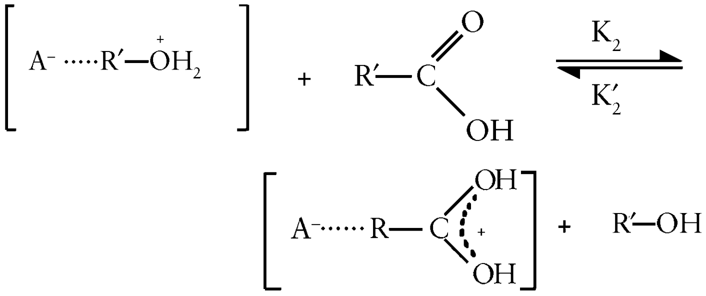
In fact one carboxyl group participates in the esterification and one carboxyl group plays the role of the acidic catalyst.

The mechanism of the acid-catalysed (AH = acid catalyst) polyesterification reaction (for example using *para* toluenesulfonic acid as the catalyst) is presented in the following equilibrium reactions (8.11-8.14). The mechanism is very similar to those of the self catalysed polyesterifications.

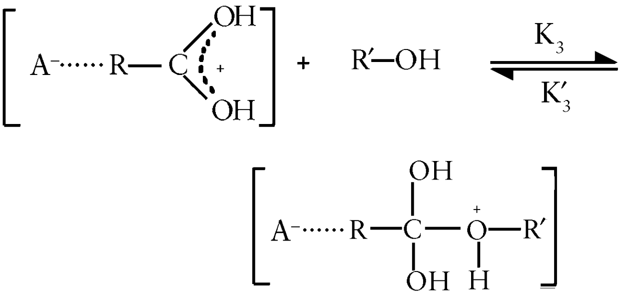


$$AH + R'{-}OH \underset{K'_1}{\overset{K_1}{\rightleftharpoons}} \left[A^- \cdots R'{-}\overset{+}{O}H_2 \right]$$

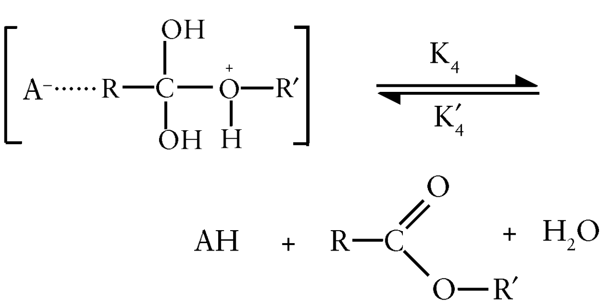
(8.11)



(8.12)



(8.13)



(8.14)

The third-order kinetic equation of the acid catalysed polyesterification is presented in equation 8.15.

$$\frac{d[RCOOR']}{dt} = K_{III} * [AH] * [RCOOH] * [R'OH] \tag{8.15}$$

In principle, the mechanism of acid catalysed polyesterification is similar to the mechanism of self catalysed polyesterification with the difference that the acidic carboxyl group used as catalyst is replaced by a strong acidic catalyst (AH).

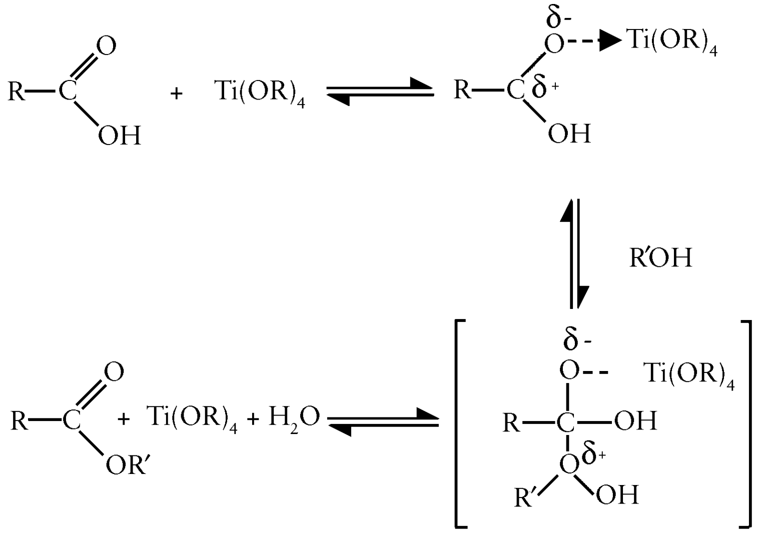
Hydrolysis of the ester (or reversed polyesterification reaction) is described by the following second-order kinetic equation (8.16):

$$-\frac{d[RCOOR']}{dt} = K_{II} * [AH] * [RCOOR'] * [HOH] \tag{8.16}$$

For the mechanism of polyesterification reactions catalysed by metallic derivatives (for example titanium or tin compounds) two variants (variant A and variant B) are discussed.

Variant A:

The carbonyl group of the acid is co-ordinated by the metallic compound [for example $Ti(OR)_4$] leading to a complex with charge polarisation (8.17). This complex reacts with the hydroxyl compound and gives a new unstable complex RCOOH - $Ti(OR)_4$ - R´OH, which is decomposed to ester, water and the regenerated catalyst (8.18).



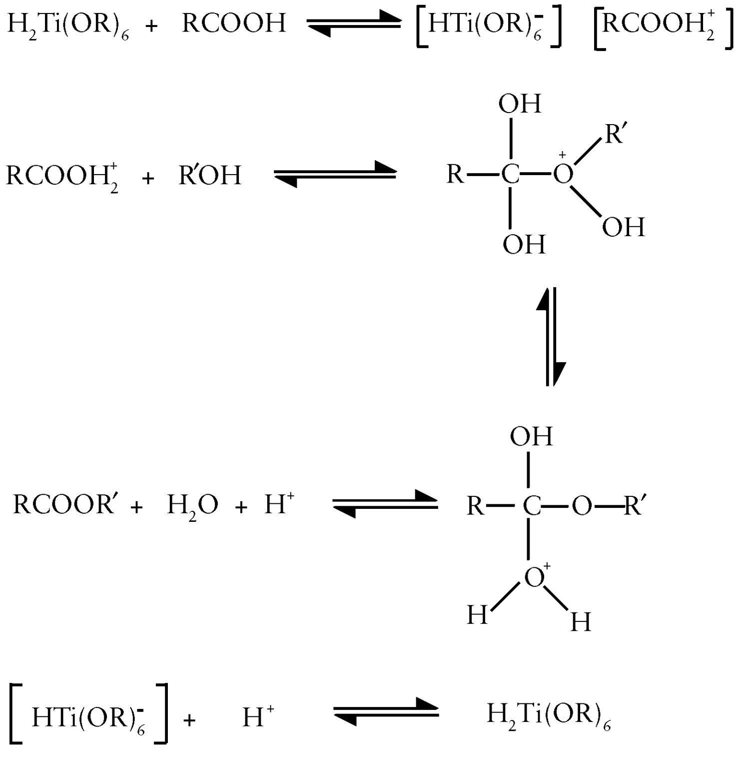
(8.17)

(8.18)

Variant B:

This variant is very similar to the mechanism of strong acid catalysed polyesterification. The strong acidic catalytic species is generated by the interaction of the hydroxyl group of glycol with the metallic compound (which is a Lewis acid) and the resulting complex reacts with the carboxyl groups, leading to a complex acid (reactions 8.19 and 8.20).

$$2ROH + Ti(OR)_4 \rightleftharpoons H_2Ti\,(OR)_6 \qquad (8.19)$$



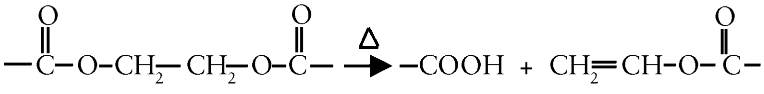
(8.20)

8.2.2 Side Reactions in Polyesterification

During the polyesterification reactions, especially at higher temperatures, it is possible to have some undesired side reactions take place, such as: formation of terminal double bonds, formation of aldehydes, formation of polyenes which lead to coloured polyesters and loss of functionality.

a) Terminal double bond formation:

$$-CH_2-CH_2-OH \xrightarrow{\Delta} -CH=CH + H_2O \quad (8.21)$$

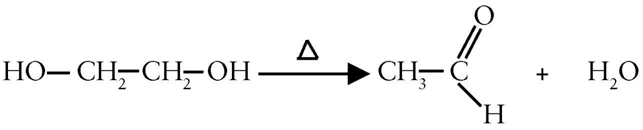


$$-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}- \xrightarrow{\Delta} -COOH + CH_2=CH-O-\overset{O}{\overset{\|}{C}}-$$

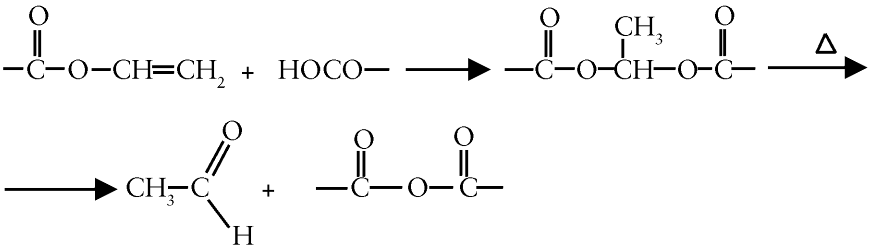
(8.22)

Reactions 8.21 and 8.22 lead to loss of functionality and reaction 8.21 to increase of acidity.

b) Aldehyde formation (reactions 8.23 and 8.24):

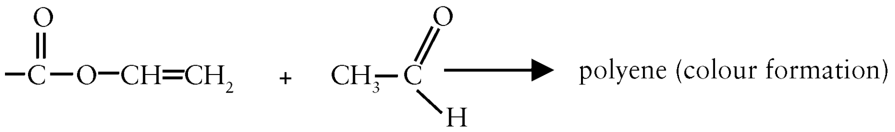


(8.23)



(8.24)

c) Polyene formation



The molecular weight distribution (MWD) of polyester polyols is broader than that of polyether polyols. The polydispersity index (PDI) of high MW polyester polyols (e.g., 2000 daltons) is around 2.8.

$$PDI = \frac{M_w}{M_n} = 2.8$$

where M_w is weight average molecular weight and M_n is the number average molecular weight.

The polyether polyols have a narrower MWD and a PDI of 1.02-1.2.

All polyester polyols have in their composition a very small quantity of low MW cyclic polyesters. Non-fogging polyesters for the automotive industry were obtained by thin film distillation in high vacuum of finished polyesters. In this way the low MW, volatile species and cyclic oligomers were eliminated [1].

8.2.3 Hydrolysis Resistant Polyester Polyols

The polyester chains and the resulting PU, due to the presence of hydrolytic labile ester groups, are susceptible to destroying the macromolecular chains by hydrolysis. As an immediate consequence, all the physico-mechanical properties of the polyester-based PU decrease markedly.

The hydrolysis susceptibility of a polyester or a polyester-based PU depends on the concentration of ester bonds, on the polyester polyol acidity, on the hydrophobicity of the glycol or dicarboxylic acid used for polyester synthesis, and on the steric hindrance around the ester groups. Low concentration of the ester bonds, low polyester acidity, high comonomer hydrophobicity and high steric hindrance around the ester groups confer hydrolysis resistance to the polyester-based PU.

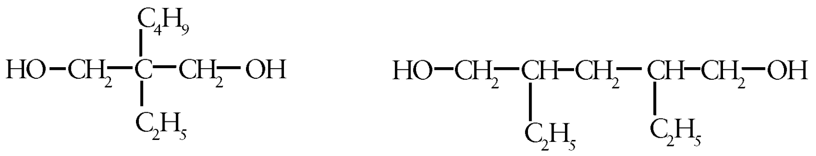
The intensive research done in the last few years proved that the hydrophobicity of the glycol or of the dicarboxylic acid used for polyester polyol synthesis is one of the most important parameters to improve the hydrolysis resistance of polyester-based PU.

Thus, the relative order of hydrolysis resistance of some usual polyester-based PU is presented next, which is exactly the order of hydrophobicity:

AA-HD > polycaprolactone > AA-BD > AA-DEG

New glycols were developed, which had hydrophobic groups and relatively high steric hindrances, which were used to improve the hydrolysis resistance of polyester-based PU - 2-butyl-2-ethyl 1,3 propanediol (BEPG; Kyowa Hakko Kogyo Co. Ltd.), (see **Figure 8.2**).

High performance in the synthesis of hydrolytically resistant polyurethanes was obtained by using in the polyesterification reaction, very hydrophobic fatty dimer acids and fatty dimer alcohols, products obtained from vegetable oils (see Chapter 12.5). The use of fatty dimeric acids and fatty dimeric alcohols (obtained by the hydrogenation of dimeric acids or dimeric esters) to build the polyester structure, creates an extremely high hydrophobic environment alongside a low concentration of labile ester bonds.



$HO{-}CH_2{-}\overset{\displaystyle C_4H_9}{\underset{\displaystyle C_2H_5}{C}}{-}CH_2{-}OH$

$HO{-}CH_2{-}\underset{\displaystyle C_2H_5}{CH}{-}CH_2{-}\underset{\displaystyle C_2H_5}{CH}{-}CH_2{-}OH$

2-ethyl-2-butyl-1,3-propane diol 2,4 diethyl-1,5-pentane diol

Figure 8.2 Diols with hydrophobic groups used in hydrolysis resistant polyester polyol synthesis

The synthesis of dimeric fatty acids is based on the reaction between a fatty acid with one double bond (oleic acid) and a fatty acid with two double bonds (linoleic acid) or three double bonds (linolenic acid), at higher temperatures in the presence of solid acidic catalysts (for example montmorillonite acidic treated clays). Dimerised fatty acids (C_{36}) and trimerised fatty acids (C_{54}) are formed. The dimer acid is separated from the trimeric acid by high vacuum distillation. By using fatty dimeric acids and dimeric alcohols in the synthesis of polyesters and of polyester polyurethanes, products are obtained with an exceptional resistance to hydrolysis, noncrystalline polymers with a very flexible structure and an excellent resistance to heat and oxygen (Chapter 12.5). Utilisation of hydrophobic dicarboxylic acids, such as sebacic acid and azelaic acid in polyesterification reactions leads to hydrolysis resistant polyurethanes.

The polyester polyurethanes based on polycarbonate diols and the intrinsic hydrolysis resistance of these special kind of polyurethanes were discussed before (Section 8.1).

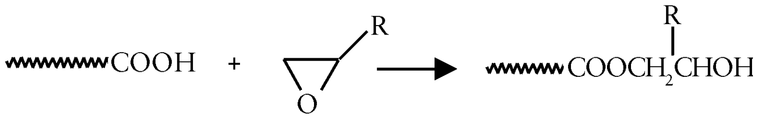
8.3 Technology for Polyester Polyols Fabrication [1, 2, 4, 5, 7, 9-11]

The synthesis of polyester polyols by a direct polyesterification reaction between diacids and glycols is operated under an inert atmosphere (nitrogen) in a conventional stirred stainless steel (corrosion resistant to acidic organic compounds, at higher temperatures of 200-240 °C) batch reactors. The volume of polyesterification reactors is around 20-50 m^3, less than the volume of reactors used in polyether synthesis which are 100 m^3 or more. The heating of polyesterification reactors is assured with high pressure steam, high thermoresistant fluids or by induction. Because the polyesterification reaction is an equilibrium reaction, the equilibrium is pushed to the polyester formation by continuous removal of water. The water is eliminated from the reaction system through a separation column, which assures a separation of water from the glycols. Glycols are returned back into the reactor and water is condensed and discharged for biotreatment. Thus, after charging the glycols and diacids, the temperature is increased and the reaction begins to be important at 135-140 °C. Water resulting from polyesterification is removed rapidly, generally under normal pressure. The temperature continues to be increased to 200 °C. Around 90% of the total water is distilled under these conditions. During this step, the concentration of carboxyl groups and of hydroxyl groups decreases substantially and the polyesterification reaction rate decreases rapidly, especially because the reaction becomes low in catalytic acid (carboxyl groups), the acidity being at this stage around 30 mg KOH/g.

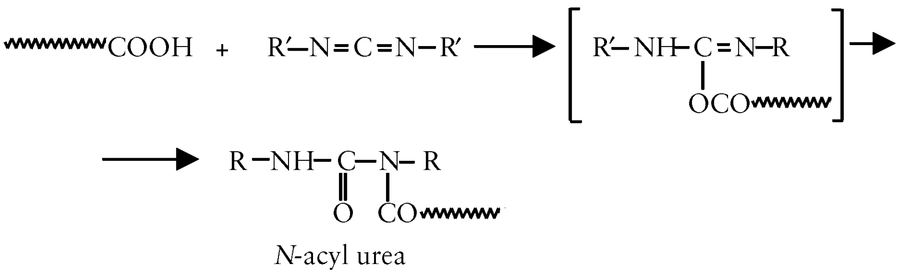
In the second stage of the polyesterification reaction the pressure is decreased to 400-200 Pa. In this second stage the polyesterification catalyst can be added, such as: *p*-toluene sulfonic acid, stannous octoate, titanium, lead or manganese compounds. Carrier gas or inert solvents, which give azeotropes with water (for example, xylene) may be used, to help the water elimination as much as possible.

The evolution of the polyesterification reaction is monitored by measuring the quantity of water distilled and by the determination of acid number, hydroxyl number and viscosity.

Finally, the resulting polyester polyol is filtered and sometimes stabilised with acid scavengers, such as epoxies or carbodiimides (reactions 8.25 and 8.26).



(8.25)



$$\sim\sim\sim\mathrm{COOH} + \mathrm{R'{-}N{=}C{=}N{-}R'} \longrightarrow \left[\mathrm{R'{-}NH{-}}\underset{\displaystyle \mathrm{OCO}\sim\sim\sim}{\underset{|}{\mathrm{C}}}\mathrm{{=}N{-}R} \right] \longrightarrow \mathrm{R{-}NH{-}}\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}}\underset{\displaystyle \mathrm{CO}\sim\sim\sim}{\underset{|}{\mathrm{N}}}\mathrm{{-}R}$$

(8.26)

A schematic showing polyester polyols production is presented in **Figure 8.3**.

Transesterification reactions between dialkyl esters of dicarboxylic acids and glycols are made using similar equipment.

Table 8.4 presents the main characteristics of some representative polyester polyols for elastic polyurethanes.

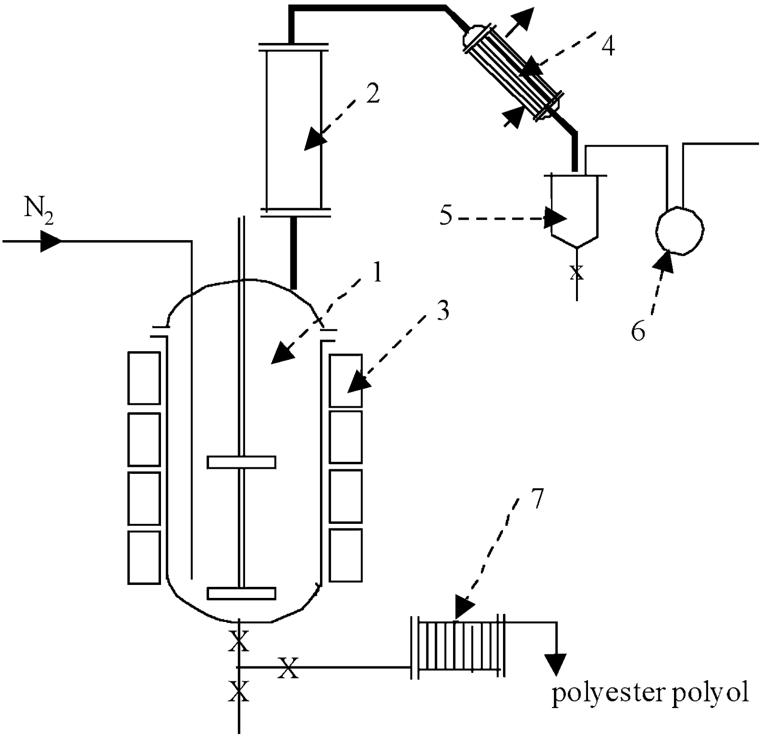


Figure 8.3 Installation for polyester polyols synthesis. *1) polyesterification reactor; 2) separation column; 3) induction elements for heating; 4) condenser; 5) vessel for condensed water; 6) vacuum pump; 7) filter*

The composition and structure of the polyester polyols lead to polyurethanes with distinct properties. These polyester-based polyurethanes have specific applications, as shown in **Table 8.5**.

8.4 Poly (ε-caprolactone) Polyols [28-54]

The lactones, the cyclic esters of hydroxy acids have been polymerised with various catalysts: anionic catalysts, cationic catalysts and organometallic catalysts [28, 29, 39, 45, 54]. Five member lactone rings are unpolymerisable. Four, seven or eight member lactones are polymerisable [28, 29, 39, 45, 54].

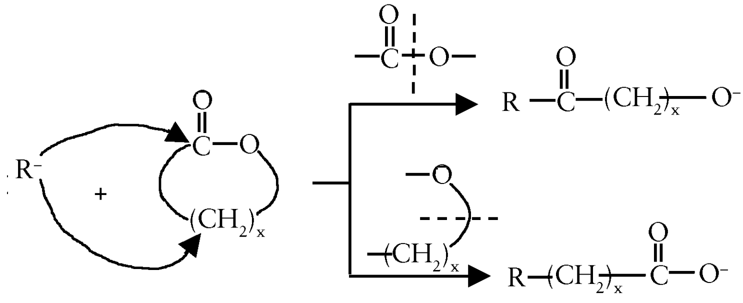
Table 8.4 The main characteristics of some polyester polyols for elastic polyurethanes [2]

Characteristic	AA-NPG	AA-DEG	AA-EG	AA-DEG/TMP
Structure	linear	linear	linear	branched
Functionality, f	2	2	2	2.4 - 3.0
MW, daltons	530	2900	2000	2700-3000
Hydroxyl number, mg KOH/g	200-220	35-45	52-58	50-60
Acidity, mg KOH/g	< 2	< 2	< 2	< 2
Water content, %	< 0.15	< 0.15	< 0.15	< 0.15
Density at 20 °C, g/cm^3	1.08	1.19	1.27	1.2
Viscosity at 70 °C, mPa-s	250	1100	450	1000-1500
Applications	Coating, lacquers	Flexible foams, elastomers	Elastomer, prepolymers, synthetic leather	Flexible foams, lacquers, coatings

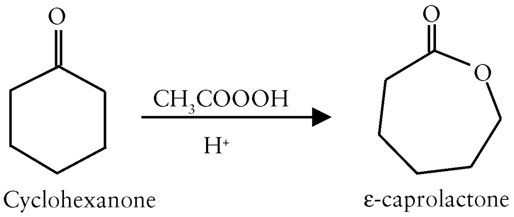
Table 8.5 Specific applications of polyester polyol composition and structure

Composition (structure)	Application
AA-DEG (linear)	Pigment carriers, soft elastomers, coatings, adhesives
AA-EG (linear)	Elastomers, thermoplastic polyurethanes, synthetic leather
AA-BD (linear)	Thermoplastic polyurethanes, adhesives, elastomers
AA-HD (linear)	Adhesives, coatings, thermoplastic polyurethanes, elastomers
AA-TMP/glycols (branched)	Flexible foams, microcellular elastomers, coatings
AA-glycerol/DEG (branched)	Flexible foams, coatings

By the attack of an anion to the lactone cycle (anionic polymerisation), carbonyl - oxygen scission and carbon - oxygen scission are possible:

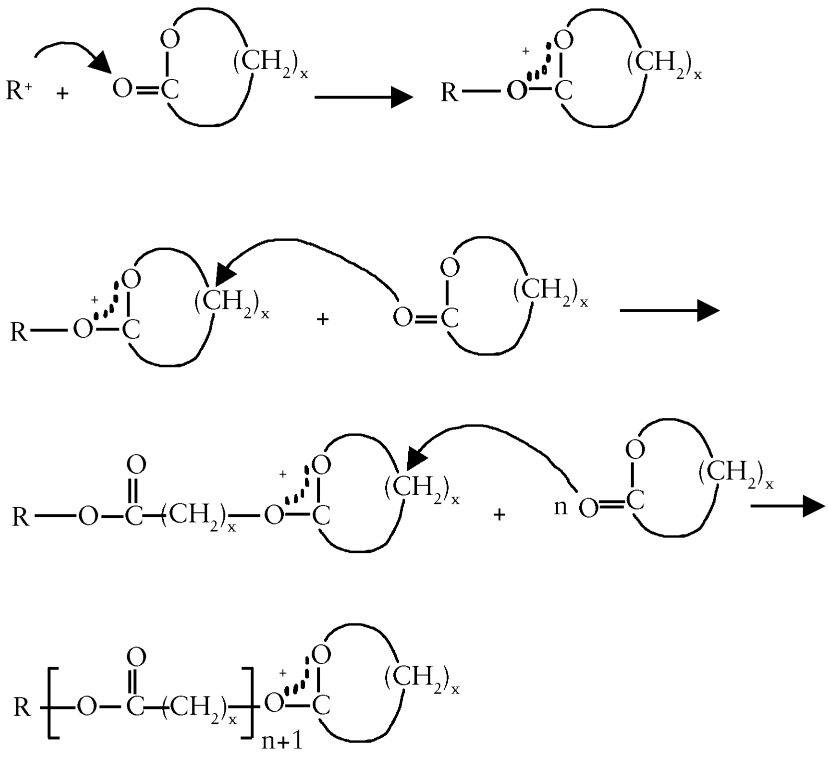


The carbon - oxygen scission leading to a carboxylate anion is possible only in highly strained ring lactones [30]. In the particular case of ε-caprolactone (CPL), the only way for ring scission is carbonyl - oxygen scission which always leads to terminal hydroxyl groups [28, 29, 39, 45, 54]. This fact is extremely advantageous for the synthesis of hydroxy-telechelic polyester polyols. CPL is obtained from cyclohexanone by the Bayer-Villiger reaction (reaction of cyclohexanone with peroxyacetic acid in acidic media, reaction 8.27):

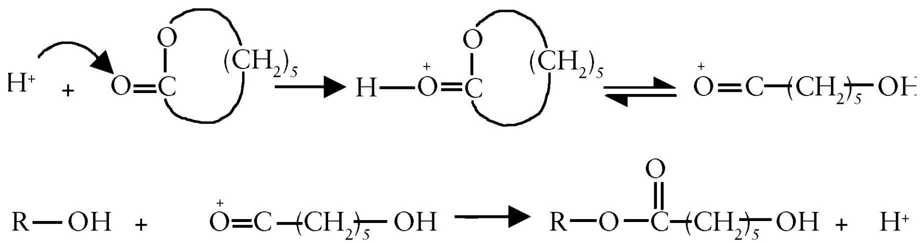


(8.27)

The cationic polymerisation of lactones takes place in the presence of the usual cationic catalysts (Lewis acids and Brönstedt superacids) and the active propagating species are oxonium cations, formed by the attack of the exocyclic oxygen atoms of lactone and the ring opening of the lactone cycle takes place by alkyl - oxygen bond scission [31]:



A very interesting variant of cationic polymerisation of CPL is based on the polymerisation initiated by hydroxyl compounds, at room temperature [42, 43, 44]. The mechanism called 'hydroxo-mechanism' is very similar to the 'activated monomer' mechanism developed for cyclic ethers. This kind of polymerisation is practically a living cationic polymerisation and in the particular case of CPL, using various polyols as starters, it is possible to obtain hydroxy-telechelic poly CPL) polyols, with various MW, depending on the molar ratio of CPL per polyol (reactions 8.28).



(8.28)

The MW of the resulting polyester polyols, in conditions of living polymerisation, is determined by the relationship given in 8.29.

$$M = \frac{n * 114 * x}{[ROH] * 100} \qquad (8.29)$$

where:

M = molecular weight of polycaprolactone polyol

n = number of mols of caprolactone reacted

114 = molecular weight of caprolactone

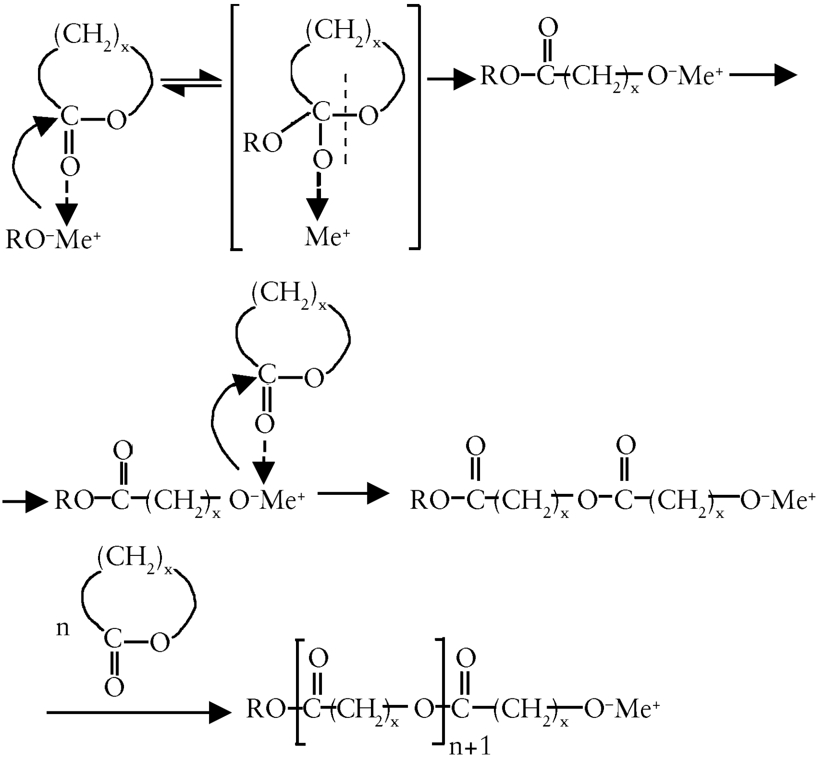
x = % conversion

ROH = mols of starter

Unfortunately, in the anionic polymerisation of lactones, a strong basic alcoholate attacks not only the ester group of the monomer, but also the ester groups of the resulting polyester, leading to a broadening of MWD and formation of cyclic oligomers by the 'back biting' mechanism. With alcoholates of potassium or lithium CPL polymerises in 1-5 minutes. At the beginning a narrow MWD is obtained, but due to the rapid inter- and intra-molecular ester exchange reactions, a broadening of the MWD eventually takes place.

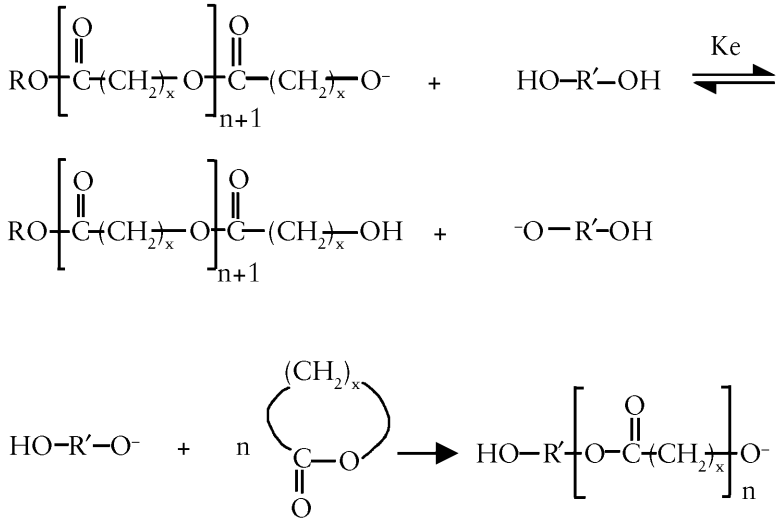
Using aluminium alcoholates such as: bimetallic oxo-alkoxides of aluminium and zinc $[(C_4H_9O)_4Al_2Zn]$ or aluminium porphyrinato alcoholates, living anionic polymerisation was observed. During the polymerisation there is a perfect relationship between the degree of polymerisation and conversion up to 100% conversion [41]. By using a polyol as starter it is possible to obtain perfectly controlled telechelic polymers, having 2-4 hydroxyl groups/mol.

The best catalysts for CPL polymerisation initiated by hydroxyl groups are the alcoholates of aluminium, titanium, zinc and lanthanides (the yttrium alcoholates are very efficient) [46-49] or tin salts (e.g., stannous octoate). The polymerisation with these catalysts is in fact an aniono-coordinative polymerisation, the monomer being activated by the coordination at the catalyst. The attack of the anionic species takes place at the carbonyl group (carbonyl - oxygen scission), as shown in the reactions in 8.30.



(8.30)

During the anionic or anionic coordinative polymerisation of lactones, there is a permanent equilibrium (8.31) between the alcoholate groups and hydroxyl groups from the reaction system:



(8.31)

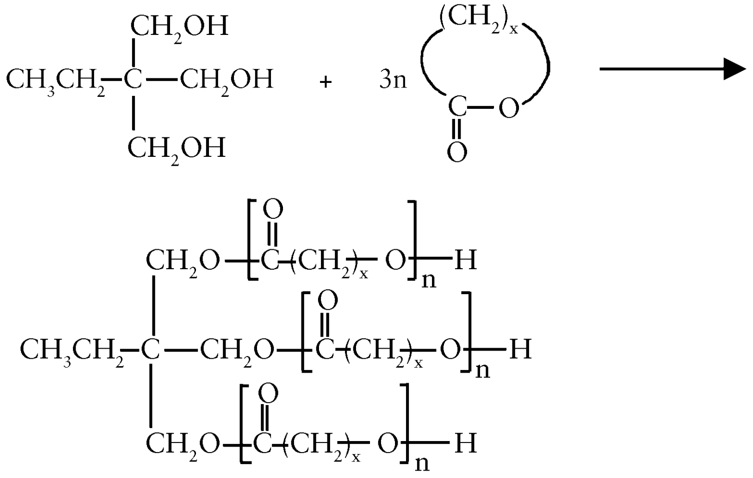
As a consequence of the equilibrium reaction (8.31), each hydroxyl group from the reaction system acts as a real transfer agent and as chain initiator. The catalysts with the general formula $(RO-)_nMe^{n+}$ may be for example aluminium tri (isopropylate), or tetrabutyl titanate, stannous octoate or similar catalysts.

The polymerisation of lactones initiated by hydroxyl groups is possible in the absence of any catalyst, but it needs higher reaction temperatures (160-180 °C).

The advantage of CPL-based polyester polyols is that the final functionality of the resulting oligo-polyol is identical to the functionality of the starter used and, generally, no side reactions were observed to markedly affect the functionality.

Generally, high MW polycaprolactone (PCL) polyols are in the form of solid waxes, but the corresponding low MW polyols are pastes or even liquids.

Representative PCL are the diols of MW of 2000-4000 daltons, used in hydrolytically stable PU elastomers. The diols used as starters are: DEG, 1,4 butanediol and NPG. The melting point of PCL, of MW of 2000 daltons, is in the range of 40-60 °C and of MW of 1000 daltons in the range of 30-40 °C. If a polyfunctional polyol is used as a starter, polyfunctional PCL polyols are obtained. Thus, by polymerisation of CPL initiated by trimethylolpropane (reaction 8.32) a polyester triol is obtained and initiated by pentaerythritol, a polyester tetraol is formed. It is interesting that some low MW PCL triols with a MW of 300-900 daltons are liquid at room temperature (melting points in the range of 6-16 °C). The viscosities of PCL polyols, at 60 °C, are 40-1600 mPa-s, depending on the polyol structure.



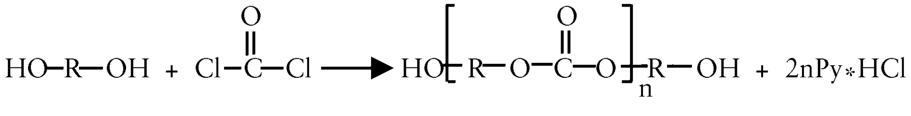
(8.32)

PCL polyols are used to produce hydrolysis and solvent resistant PU elastomers which are flexible at lower temperatures. A characteristic of these special polyester polyols is their uniform and fast reactivity due to the 100% primary terminal hydroxyl groups. A characteristic of elastic polyurethanes, based on PCL polyols, is the clickability and superior tear resistance.

8.5 Polycarbonate Polyols [11, 55-79]

Polycarbonate polyols have a structure, characterised by the aliphatic carbonic ester groups, as repeated units (**Figure 8.4**).

Initially, the polycarbonates were synthesised by the reaction of a diol with phosgene in the presence of an HCl acceptor, such as pyridine or alkali hydroxides [55]:



$$HO{-}R{-}OH + Cl{-}\overset{O}{\overset{\|}{C}}{-}Cl \longrightarrow HO\left[R{-}O{-}\overset{O}{\overset{\|}{C}}{-}O\right]_n R{-}OH + 2nPy{*}HCl$$

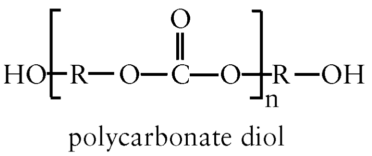
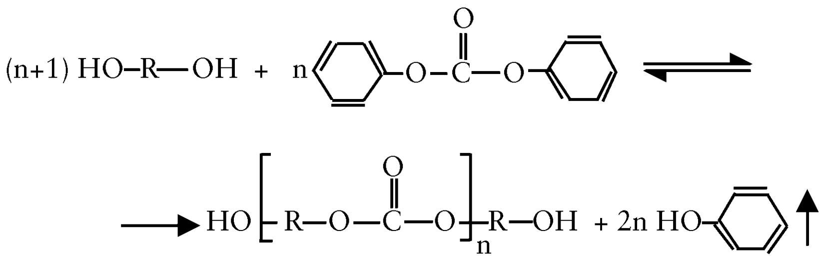


Figure 8.4 The general structure of polycarbonate diols

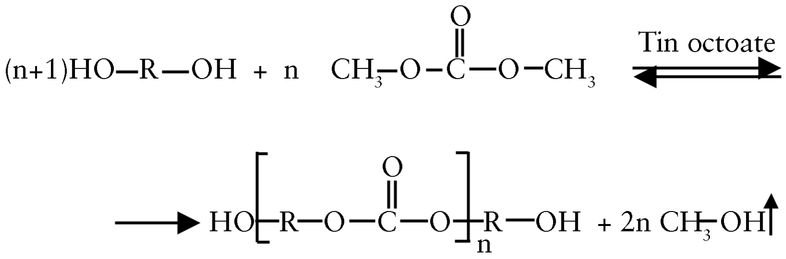
In order to obtain purer products, a process based on the transesterification of a glycol and a dialkyl or diaryl carbonates (reaction 8.33) was developed.



(8.33)

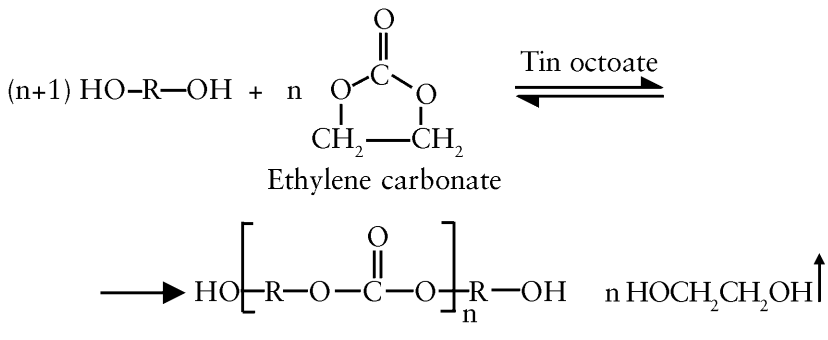
The process takes place at higher temperatures, up to 200 °C, and the equilibrium is pushed to the formation of polycarbonate, by vacuum distillation of phenol. Of course, like the synthesis of all polyesters, in order to generate hydroxyl groups an excess of glycol is needed. The reaction with diarylcarbonates (for example diphenylcarbonate) takes place without catalysts (reactions 8.34 and 8.35).

The dialkyl carbonates, such as dimethylcarbonate, or diethyl carbonate, or ethylene carbonate, need a catalyst (tin catalysts such as stannous octoate or sodium stannate trihydrate, or titanium catalysts) [11, 56-58].



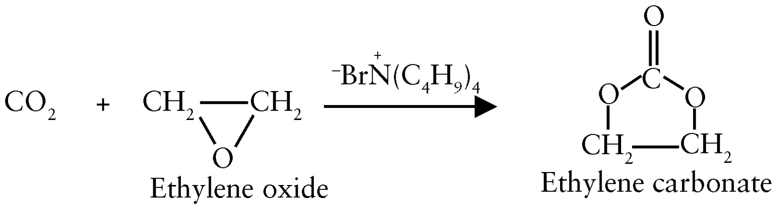
$$(n+1)HO-R-OH + n\ CH_3-O-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightleftharpoons{\text{Tin octoate}} HO\left[R-O-\overset{O}{\overset{\|}{C}}-O\right]_n R-OH + 2n\ CH_3OH\uparrow$$

(8.34)



(8.35)

Ethylene carbonate is produced industrially by the reaction of carbon dioxide with ethylene oxide (reaction 8.36), in the presence of a catalyst, such as tetrabutyl-ammonium bromide.

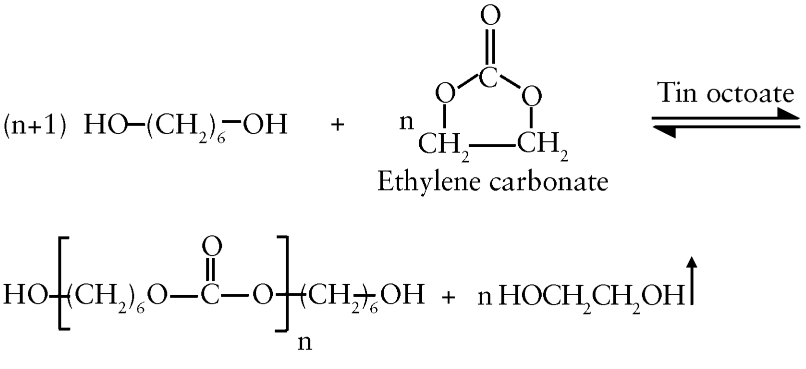


(8.36)

Ethylene carbonate has the advantage of a high boiling point (bp) (236 °C at 101 MPa) and it is possible to eliminate the resulting ethylene glycol (bp = 197.3 °C at 101 MPa) without major elimination of ethylene carbonate from the reaction system. Dimethyl carbonate has the advantage of elimination of a much lower boiling point product: methanol (bp = 64.7 °C at 101 MPa).

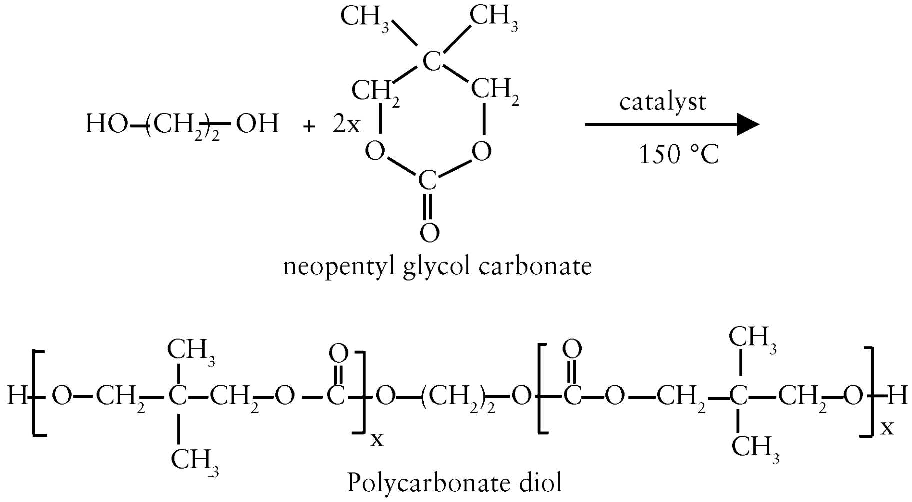
The preparation of polycarbonates is carried out in two stages. In the first stage a polycarbonate of lower MW is synthesised, at 150-200 °C, by distillation of EG resulting from reaction 8.35 under moderate vacuum (6.6-26.6 MPa). As for all polyesterification processes, a rectification column assures the elimination of EG and ethylene carbonate and the glycol used as the starter are returned to the reactor. In the second stage, the low MW polycarbonate is heated up to 250 °C under conditions of high vacuum (13-1333 Pa), and is condensed to a higher MW polycarbonate [11].

A representative polycarbonate is obtained by polycondensation reaction between 1,6 hexanediol and diphenyl carbonate or ethylene carbonate (reaction 8.37). The resulting 1,6 hexanediol polycarbonate, frequently synthesised at a MW of 2000 daltons, is a solid wax having a softening point of around 42-47 °C. Higher MW polycarbonates have higher softening points, of around 50-55 °C.



(8.37)

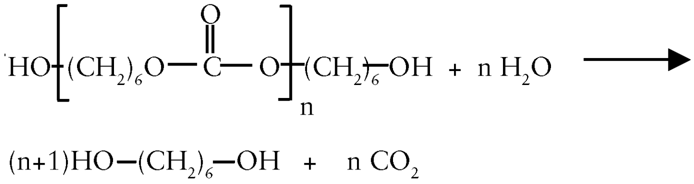
A second method for polycarbonate polyol synthesis is the ring opening polymerisation of cyclic carbonates of 5-6 members, initiated by various polyols as starters (reaction 8.38) [68-76].



(8.38)

The catalysts of this ring opening polymerisation reactions are: pyridinium salts (for example *N*-benzyl pyridinium *p*-toluene sulfonate [75]), *p*-toluene sulfonic acid [75], stannium or titanium compounds [68-74] etc. Other cyclic polymerisable cyclic carbonates are: ethylene carbonate and propylene carbonate [68-74].

Alkyl carbonates are relatively labile concerning the hydrolysis reaction. Surprisingly, polycarbonate polyols give PU that are extremely resistant to hydrolysis, superior to those PU derived from polyesters based on adipic acid and diethylene glycol. The explanation of this paradox, mentioned before, is that between the hydrolysis products of polycarbonate polyols, acidic groups which are able to further catalyse hydrolysis reactions are not formed. The products of polyester polyol hydrolysis are diacids and glycols. The products of polycarbonate polyols hydrolysis are carbon dioxide (a gas which is eliminated easily) and glycols [76]:



$$HO\left[(CH_2)_6O-\overset{O}{\overset{\|}{C}}-O\right]_n(CH_2)_6OH + n\,H_2O \longrightarrow$$

$$(n+1)HO-(CH_2)_6-OH + n\,CO_2$$

As an immediate consequence, the resistance to hydrolysis makes the hexanediol-polycarbonates and the resulting polyurethanes suitable for a long useful life. The specific applications for polycarbonate polyol based polyurethanes are: rollers for printing machines and textiles, cable sheaths, vibration dampers, coatings, adhesives for the shoe and packaging industry.

References

1. D. Reed, *Urethanes Technology*, 2000, **17**, 4, 41.

2. R. Becker in *Polyurethane*, VEB Fachbuchverlag, Leipzig, Germany, 1983, p.49.

3. Y.C. Yen and T.S. Tsao, *Polyols for Polyurethanes*, Process Economic Report No.45A, Stanford Research Institute, Menlo Park, CA, USA, 1982, p.192-212.

4. I. Goodman in *Encyclopedia of Polymer Science and Technology*, Volume 11, Eds., H.F. Mark, N.G. Gaylord and N.M. Bikales, Interscience, New York, NY, USA, 1969, p.62 and p.128.

5. G. Oertel, *Polyurethane Handbook*, Carl Hanser Verlag, Munich, Germany, 1985, p.54-62.

6. H.R. Friedly in *Reaction Polymers*, Eds., W.F. Gum, W. Riese and H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.80.

7. D.J. Sparrow and D. Thorpe in *Telechelic Polymers, Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.214.

8. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, Chapter 2, p.7, Chapter 3, p.10, Chapter 5, p.4-6.

9. R. Brooks, *Urethanes Technology*, 1999, **16**, 1, 34.

10. D. Reed, *Urethanes Technology,* 1999, **16**, 2, 40.

11. W.D. Vilar, *Chemistry and Technology of Polyurethanes*, Third Edition, 2002, Rio de Janeiro, Brazil, http://www.poliuretanos.com.br/Ingles/Chapter1/14Polyethers.htm - polimerico

12. Z.T. Ossefort and F.B. Testroet, *Rubber Chemistry and Technology*, 1966, **39**, 4, 1308.

13. G. Magnus, R.A. Dunleavy and F.E. Critchfield, *Rubber Chemistry and Technology*, 1966, **39**, 4, 1328.

14. C.S. Schollenberger and F.D. Stewart, *Journal of Elastoplastics*, 1971, **3**, 1, 28.

15. F.D. Stewart, inventor; The B.F.Goodrich Co., assignee; US3,463,758 1969.

16. R.A. Dunleavy and R.E. Critchfield, *Rubber World*, 1967, **156**, 3, 53.

17. S. Nakano, T. Morimoto, S-Y. Yamada, T. Fujiwa, H. Matsui and T. Tabuchi, inventors; Nippon Paint Co. Ltd., and Diacel Chemical Industries, Ltd., assignees; US5,446,110, 1995.

18. D.H. Solomon in *Polyesters*, Eds., I. Goodman and J.A. Rhys, Volume1, The Plastic Institute, London, UK, 1965, Chapter on Polyesterification, p.1.

19. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, USA, 1953.

20. S-A. Chen and J-C. Hsiao, *Journal of Polymer Science*, *Polymer Chemistry Edition*, 1981,**19**, 3123.

21. S-A. Chen and K-C. Wu, *Journal of Polymer Science, Polymer Chemistry Edition*, 1982, **20**, 7, 1819.

22. W.L. Chang, T. Baranowski and T. Karalis, *Journal of Applied Polymer Science*, 1994, **51**, 6, 1077.

23. W.L. Chang and T. Karalis, *Journal of Polymer Science*, *Part A*, 1993, **31**, 2, 493.

24. W.L. Chang, *Proceedings of Polyurethanes World Congress '97*, 1997, Amsterdam, The Netherlands, p.705.

25. A. Vonderhagen, inventor; Cognis Deutschland GmbH, assignee; WO 0034501A1, 2000.

26. J. Otton, S. Ratton, V.A. Vazner, and G.D. Markova, K.M. Nametov, V.I. Bakhmutov, S.V. Vinogradova and V.V. Korshak, *Journal of Polymer Science: Polymer Chemistry Edition*, 1989, **27**, 11, 3535.

27. G. Rafler, F. Tesch and D. Kunath, *Acta Polymerica*, 1988, **39**, 6, 315.

28. J.C. Park, inventor; B.F.Goodrich, assignee; GB 1,022,166, 1965.

29. D.B. Johns, R.W. Lenz and A. Lueke in *Ring-Opening Polymerisation*, Eds., K.J. Ivin and T. Saegusa, Elsevier, Amsterdam, The Netherlands, 1984, p.461.

30. H.K. Hall, Jr., and A.K. Schneider, *Journal of the American Chemical Society*, 1958, **80**, 23, 6409.

31. Y. Yamashita, T. Tsuda, H. Ishida, A. Uchikawa and Y. Kuriyama, *Die Makromolekulare Chemie,*1968, **113**, 139.

32. A. Hoffmann, R. Szymanski, S. Stomkowski, S. Penczek, *Die Makromolekulare Chemie*, 1984, **185**, 4, 655.

33. V. Jaacks and N. Mathes, *Die Makromolekulare Chemie*, 1970, **131**, 295.

34. W. Bergwerf and W.M. Wagner, inventors; Shell International Research, assignee; GB 1,133,293, 1968.

35. F.J. Franciscus and W.M. Wagner, inventors; Shell International Research, assignee; GB 1,133,294, 1968.

36. C. King, inventor; EI DuPont de Nemours, assignee; US 3,418,393, 1968.

37. R.W. Lenz, M. Dror, R. Jorgensen and R.H. Marchessault, *Polymer Engineering and Science,*1978, **18**, 12, 937.

38. K. Ito, Y. Hashizuka and Y. Yamashita, *Macromolecules*, 1977, **10**, 4, 821.

39. K. Ito and Y. Yamashita, *Macromolecules*, 1978, **11**, 1, 68.

40. M. Morton and M. Wu in *Ring-Opening Polymerisation: Kinetics, Mechanisms and Synthesis*, Ed., J.E. McGrath, ACS Symposium Series No.286, American Chemical Society, Washington, DC, USA, 1985, p.175.

41. A. Hamitou, T. Ouhadi, R. Jerome and P. Teyssie, *Journal of Polymer Science: Polymer Chemistry Edition,* 1977, **15**, 4, 865.

42. T. Aida, K. Sanuki and S. Inoue, *Macromolecules*, 1985, **18**, 6, 1049.

43. E.B. Ludvig and B.G. Belenkaya, *Journal of Macromolecular Science - Chemistry,* 1974, **A8**, 4, 819.

44. B.G. Belenkaya, E.B. Ludwig, A.L. Izumnikov and Y.I. Kulvelis, *Vysokomolekularnye Soedineniia, Seriia A.*, 1982, **24**, 288.

45. *Encyclopedia of Polymer Science and Technology*, 3rd Edition, Volume 11, Ed., J.I. Kroschwitz, Wiley-Interscience, Hoboken, NJ, USA, p.98.

46. R.D. Ludberg and E.F. Cox in *Kinetics and Mechanisms of Polymerisations, Volume2: Ring Opening Polymerisation*, Eds., K.C. Frisch and S.L. Reegen, Marcel Dekker, New York, NY, USA, 1989.

47. F. Hostettler, inventor; Union Carbide, assignee; US 2,933,477, 1960.

48. D.M. Young and F. Hostettler, inventors; Union Carbide, assignee; US 2,933,478, 1960.

49. C.F. Cardy, inventor; Interox Chemical, assignee; US 4,086,214, 1978.

50. W-H. Chang and V.G. Ammons, inventors; PPG Industries, assignee; USP 4,085,092, 1978.

51. Y. Shen, Z. Shen, Y. Zhang and Q. Hang, *Journal of Polymer Science: Polymer Chemistry Edition,* 1997, **35**, 8, 1339.

52. C. Miola-Delaite, E. Colomb, E. Pollet and T. Hamaide, *Macromolecular Symosia,* 2000, **153**, 275.

53. W.M. Stevels, P.J. Dijkstra and J. Feijen, *Trends in Polymer Science,* 1997, **5**, 9, 300.

54. M. Nishiura, Z. Hou, T-A. Koizumi, T. Imamoto and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 25, 8245.

55. E. Goethals in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.132-134.

56. *Polyurethanes Handbook*, Ed., G. Oertel, Hanser, Munich, Germany, 1985, p.17.

57. W. Heydkamp, K. König and H. Köpnick, inventors; Bayer AG, assignee; GB 1,263, 225, 1972.

58. K-H. Lai and H.N. Silvers, inventors; Beatrice Foods, assignee; US 4,131,731, 1978.

59. E. Müller, W. Kallert and J. Ivanyi, inventors; Bayer AG, assignee; US 3,544,524, 1970.

60. W. Thoma and E. Müller, inventors; Bayer AG, assignee; GB 1,165,830, 1969.

61. J. Ivanyi, W. Kallert and E. Müller, inventors; Bayer AG, assignee; GB 1,149,815, 1970.

62. M. Hamb and S. Gorman, *Urethanes Technology*, 1985, **2**, 2, 15.

63. E. Müller, W. Kallert and J. Ivanyi, inventors; Bayer AG, assignee; GB 1,179,222, 1970.

64. J. Ivanyi, W. Kallert and E. Müller, inventors; Bayer AG, assignee; GB 1,197,844, 1970.

65. K. König, W. Kallert, E. Müller and C. Muhlhausen, inventors; Bayer AG, assignee; GB 1,211,811, 1972.

66. K. König, U. Dobereiner, C. Muhlhausen and E. Müller inventors; Bayer AG, assignee; GB 1,270,077, 1973.

67. E. Bock and M. Dollhausen, inventors; Bayer AG, assignee; GB 1,224,350, 1971.

68. H.C. Stevens, inventors, Pittsburgh Plate Glass Company, assignee; US 3,248,414, 1966.

69. F. Hostettler and E.F. Cox, inventors, Union Carbide Company, assignee; US 3,379,693, 1968.

70. J. Rousell and G. Perrin, inventors; L'Air Liquide, assignee; US 3,869,090, 1975.

71. J.D. Malkemus, inventor; Jefferson Chemical Company, assignee; US 3,133,113, 1964.

72. H. Springmann and W. Dieterrich inventors; Chemische Werke Hüls AG, assignee; US 3,313,782, 1967.

73. R.F. Harris, inventor; The Dow Chemical Company, assignee; US 4,709.069, 1987.

74. D.G. Prier, inventor; The Dow Chemical Company, assignee; US 4,528,364, 1985.

75. S. Nakano, T. Morimoto, S-Y. Yamada, T. Fujiwa, H. Matsui and T. Tabuchi, inventors; Nippon Paint Co.Ltd., and Daicel Chemical Industries, Ltd., assignees; US 5,446,110, 1995.

76. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, Chapter 5, p.8-9, 13-14.

77. D.J. Sparow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Boca Raton, FL, USA, 1989, p.221-222.

78. E. Colomb, C. Novat and T. Hamaide, *Macromolecular Chemistry and Physics*, 1999, **200**, 11, 2525.

79. G. Rokicki, *Progress in Polymer Science*, 2000, **25**, 2, 259.

9 Polybutadiene Polyols

9.1 Polybutadiene Polyols by Radical Polymerisation of Butadiene

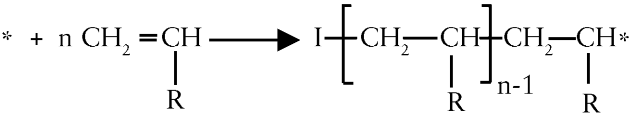
Radical polymerisation is used in the synthesis of oligo-polyols for polyurethanes (PU). One example is the synthesis of graft polyether polyols, but during radical graft polymerisation new hydroxyl groups are not created. Other examples of radical polymerisation used in the fabrication of oligo-polyols for PU is the synthesis of acrylic polyols (see Chapter 10). The hydroxyl groups of acrylic polyols are generated by using hydroxyalkyl acrylates or hydroxyalkyl methacrylates as comonomers, the hydroxyl groups being lateral substituents of the macromolecular chains and not terminal hydroxyl groups. One typical example of radical polymerisation with generation of terminal hydroxyl groups is the synthesis of hydroxy-telechelic polybutadiene. It is important that, for utilisation in elastic PU, the resulting carbocatenary chains with terminal hydroxyl groups, have a low glass transition temperature (T_g) of around –50 to –70 °C, such as: polybutadiene, polyisoprene, polybutylacrylate, etc.

It is well known that radical polymerisation is a chain reaction characterised by initiation, propagation and termination reactions [1]:

Initiation:

$$I{-}I \xrightarrow{\Delta} 2I^{*}{}_{\text{ch 1}}$$

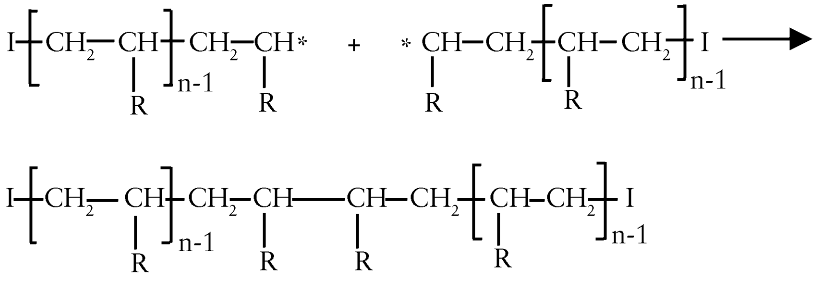
Propagation:



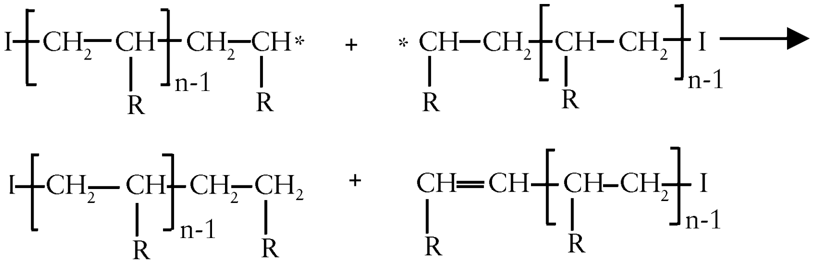
$$I^{*} + n\,CH_2{=}\underset{R}{\underset{|}{CH}} \longrightarrow I\left[CH_2{-}\underset{R}{\underset{|}{CH}}\right]_{n-1}CH_2{-}\underset{R}{\underset{|}{CH}}{}^{*}$$

Termination

a) By recombination:



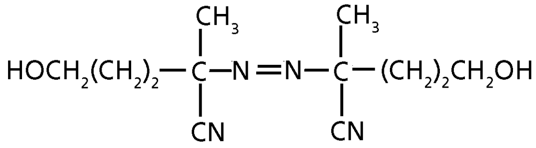
b) By disproportionation:



It is very clear that if the initiator has hydroxyl groups, and if the termination takes place exclusively by recombination then a polymeric diol is obtained [2, 3], which is ideal for polyurethane. If the termination takes place by disproportionation, only monofunctional compounds are obtained, which cannot be used in PU. The vinylic and dienic monomers used in practice have various termination mechanisms. Some monomers give only recombination reactions, such as styrene, acrylates (methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethyl hexyl acrylate), acrylonitrile and butadiene. Other monomers give both mechanisms of termination, around 65-75% disproportionation and 25-35% recombination, such as methacrylates (methyl methacrylate, ethyl methacrylate, butyl methacrylate etc.), substituted styrenes and other monomers [2, 3, 4].

It is very clear that only the first group of monomers, which lead to termination by recombination, can be used for synthesis of hydroxy-telechelic polymers which are useful in polyurethane fabrication and from the second group of monomers it is impossible to obtain oligo-polyols useful in PU.

Thus, the initiators which generate terminal hydroxyl groups are: hydrogen peroxide (HO-OH) and some special azo derivatives, such as 4,4 azobis (4-cyanopentanol), **Figure 9.1** [2, 3, 5-7]:



$$HOCH_2(CH_2)_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-(CH_2)_2CH_2OH$$

Figure 9.1 Structure of a typical azoderivative with hydroxyl groups

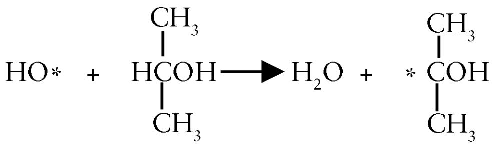
Hydrogen peroxide is decomposed to very reactive hydroxyl radicals either thermally or by a redox system [8]:

$$HO\ OH \xrightarrow{\Delta} 2HO^*$$

$$Fe^{2+} + HOOH \longrightarrow Fe^{3+} + HO^- + HO^*$$

In the presence of alcohols (used frequently as solvents), the very reactive hydroxyl radical gives transfer reactions (reactions 9.1 and 9.2) [2, 3].

$$HO* + CH_3OH \longrightarrow H_2O + *CH_2OH \qquad (9.1)$$



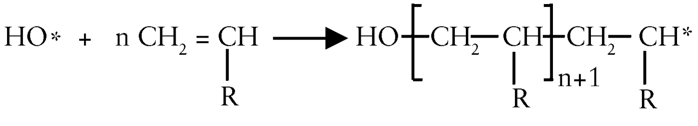
$$HO* + H\underset{CH_3}{\overset{CH_3}{C}}OH \longrightarrow H_2O + *\underset{CH_3}{\overset{CH_3}{C}}OH \qquad (9.2)$$

Thus, for radical polymerisation initiated by hydrogen peroxide of a monomer, which gives termination exclusively by recombination, it is possible to obtain good hydroxy-telechelic polymers, useful in polyurethane fabrication (reactions 9.3 and 9.4).

Initiation

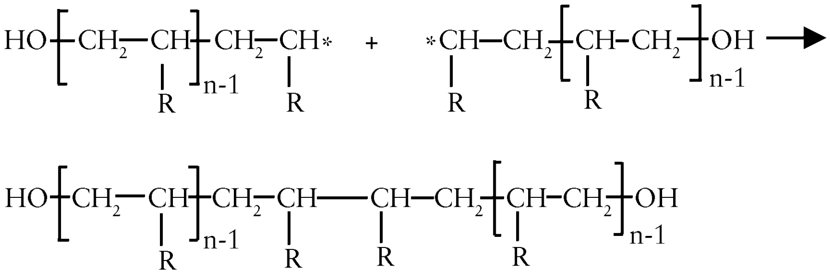
$$HO{-}OH \xrightarrow{\Delta} 2HO*$$

Propagation



$$HO* + n\,CH_2=\underset{R}{CH} \longrightarrow HO\left[CH_2-\underset{R}{CH}\right]_{n+1}CH_2-\underset{R}{CH^*} \qquad (9.3)$$

Termination



$$HO{-}\left[CH_2{-}\underset{R}{CH}\right]_{n-1}{-}CH_2{-}\underset{R}{CH}* \;+\; *\underset{R}{CH}{-}CH_2{-}\left[\underset{R}{CH}{-}CH_2\right]_{n-1}{-}OH \longrightarrow$$

$$HO{-}\left[CH_2{-}\underset{R}{CH}\right]_{n-1}{-}CH_2{-}\underset{R}{CH}{-}\underset{R}{CH}{-}CH_2{-}\left[\underset{R}{CH}{-}CH_2\right]_{n-1}{-}OH \qquad (9.4)$$

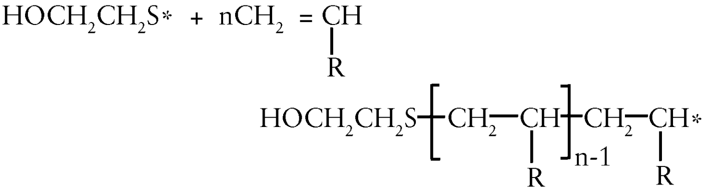
A very interesting way to obtain hydroxy-telechelic polymers by radical polymerisation is to use transfer agents, with high transfer capacity, containing hydroxyl groups such as mercaptoethanol ($HS\text{-}CH_2CH_2OH$) or bis hydroxyethyl bisulfide ($HOCH_2CH_2\text{-}S\text{-}S\text{-}CH_2CH_2OH$). Thus, in radical polymerisation, both sulfur compounds generate, by transfer reactions, the following radicals:

$$R* + HS{-}CH_2CH_2OH \longrightarrow RH + *S{-}CH_2CH_2OH$$

$$HOCH_2CH_2{-}S{-}S{-}CH_2CH_2OH \longrightarrow 2*S{-}CH_2CH_2OH \qquad (9.5)$$

The radical containing an hydroxyethyl group which is formed (9.5), initiates the formation of polymeric chains which, by recombination, give hydroxy-telechelic polymers (reactions 9.6 and 9.7). Based on the principles mentioned various hydroxy-telechelic polymers were obtained by radical polymerisation of styrene [9], acrylonitrile [10], butyl acrylate or butadiene [10-14]. Of course, the oligo-polyols derived from styrene and acrylonitrile are solid and difficult to use in PU, but butyl acrylate and butadiene lead to liquid polymers with terminal hydroxyl groups, which are useful in polyurethane manufacture.

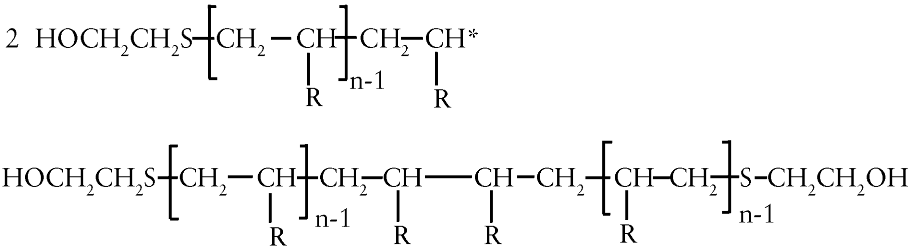
Propagation



$$HOCH_2CH_2S* + nCH_2 = \underset{R}{CH}$$

$$HOCH_2CH_2S{-}\left[CH_2{-}\underset{R}{CH}\right]_{n-1}{-}CH_2{-}\underset{R}{CH}* \qquad (9.6)$$

Termination



$$2\ \mathrm{HOCH_2CH_2S}\left[\mathrm{CH_2-\underset{R}{CH}}\right]_{n-1}\mathrm{CH_2-\underset{R}{CH}^*}$$

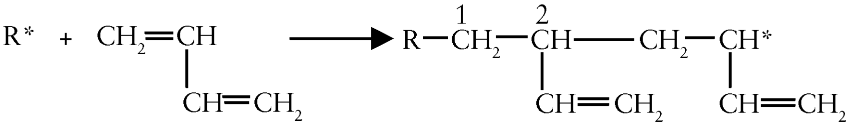
$$\mathrm{HOCH_2CH_2S}\left[\mathrm{CH_2-\underset{R}{CH}}\right]_{n-1}\mathrm{CH_2-\underset{R}{CH}-\underset{R}{CH}-CH_2}\left[\mathrm{\underset{R}{CH}-CH_2}\right]_{n-1}\mathrm{S-CH_2CH_2OH}$$

(9.7)

9.2 Synthesis of Polybutadiene Polyols by Radical Polymerisation of Butadiene [2, 3, 5-7, 9-15]

The most important oligo-polyol obtained by radical mechanism is hydroxyl terminated polybutadiene. Dienes (butadiene, isoprene), in conditions of radical polymerisation are special monomers because during radical polymerisation, which is a nonstereospecific polymerisation, several types of microstructures are generated in the same chain. Thus, in the particular case of butadiene the following types of microstructures are generated:

a*) 1-2 addition* (only one double bond of butadiene participates in radical polymerisation):



$$\mathrm{R^* + \underset{\displaystyle CH{=}CH_2}{CH_2{=}CH}} \longrightarrow \mathrm{R-\overset{1}{CH_2}-\underset{\displaystyle CH{=}CH_2}{\overset{2}{CH}}-CH_2-\underset{\displaystyle CH{=}CH_2}{CH}{}^*}$$

1,2 microstructure

b) 1-4 addition, characteristic for dienes:

$$\mathrm{R^* + CH_2{=}CH-CH{=}CH_2 \longrightarrow R-CH_2-CH{=}CH-CH_2{}^*}$$

$$\mathrm{R-CH_2-CH{=}CH-CH_2{}^* + CH_2{=}CH-CH{=}CH_2} \longrightarrow$$

$$\longrightarrow \mathrm{R-\overset{1}{CH_2}-\overset{2}{CH}{=}\overset{3}{CH}-\overset{4}{CH_2}-CH_2-CH{=}CH-CH_2{}^*}$$

1,4 microstructure

The 1,4 microstructures can be 1,4 *cis* or 1,4 *trans* microstructures (**Figure 9.2**).

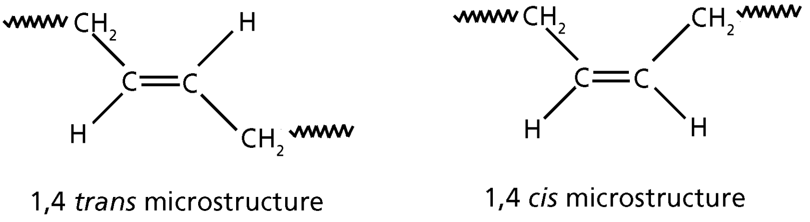
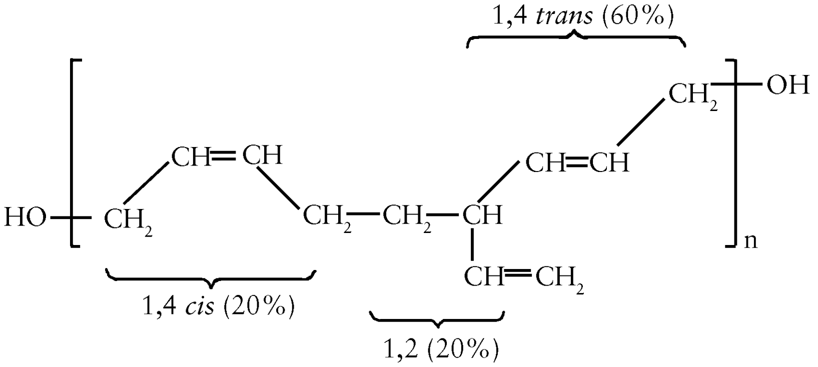


Figure 9.2 Microtructures of polybutadiene

Thus, the hydroxyl terminated polybutadiene, obtained by the radical polymerisation of butadiene initiated with hydrogen peroxide, has the following general structure [9-10, 15]:



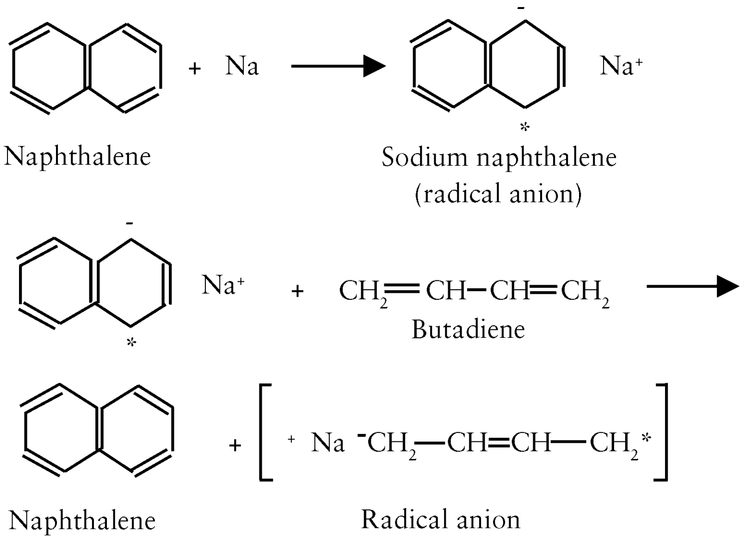
One observes that the majority microstructure is 1,4 *trans*. The terminal hydroxyl groups are exclusively primary hydroxyl groups of the allylic type (95%). The functionality (f) of these polybutadiene polyols is in the range of 2.2 - 2.6 OH groups/mol.

The fabrication process of hydroxyl terminated polybutadiene is based on the free radical polymerisation of butadiene, initiated by hydrogen peroxide at 100-150 °C, in the presence of a solvent such as: methanol [12], isopropanol [12], or in the presence of tricresyl phosphate [14]. The polymerisation in alcohols is used industrially.

The hydroxyl terminated polybutadienes lead to PU with physico-mechanical properties significantly lower than those of PU based on polyether or polyester polyols. The nonpolar polymeric chain and the extraordinary hydrophobicity mean that hydroxy terminated polybutadienes are used for special applications, due to their excellent electrical insulation properties which are equal or superior to epoxies or silicone elastomer systems. The hydrolytic stability of PU elastomers derived from hydroxyl terminated polybutadiene is superior to the majority of other types of PU. Thus, some specific applications of polyurethane elastomers based on hydroxyl terminated polybutadienes are: binder for solid propellents, encapsulating compounds, electrical insulation products and high performance hydrophobic and hydrolysis resistant elastomers [9, 10, 15].

9.3 Synthesis of Polybutadiene Polyols by Anionic Polymerisation of Butadiene [16-24]

Another variant for the synthesis of hydroxy telechelic polybutadiene is based on the anionic living polymerisation of butadiene, using sodium naphthalene as catalyst [16]. Sodium naphthalene generates, by reaction with butadiene, a radical anion (9.8). If two of these radicals are coupled together, they generate a dianion (9.9), which is an ideal bifunctional initiator for the synthesis of perfectly bifunctional polybutadiene by anionic polymerisation.



(9.8)

$$^{+}Na\ ^{-}CH_2—CH=CH—CH_2{}^{*} \quad + \quad {}^{*}CH_2—CH=CH—CH_2{}^{-}N^{+} \longrightarrow$$

$$^{+}Na\ ^{-}CH_2—CH=CH—CH_2——CH_2—CH=CH—CH_2{}^{-}Na^{+}$$

Dianion

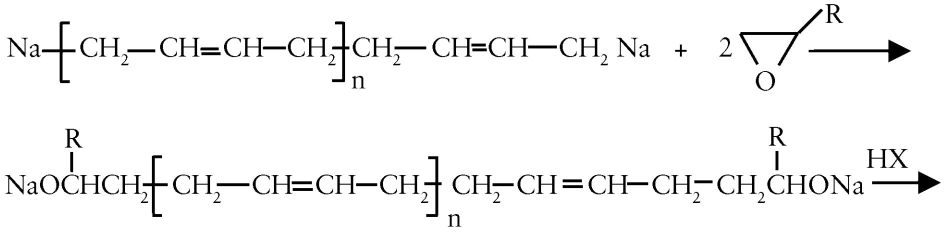
(9.9)

$$\text{Dianion} \quad + \quad n\ CH_2=CH-CH=CH_2 \longrightarrow$$
(9.9)

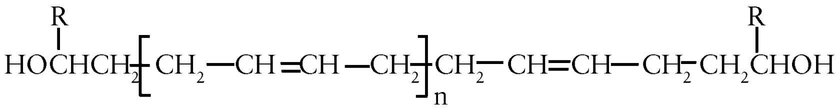
$$^{+}Na-^{-}CH_2-CH=CH-CH_2\left[CH_2-CH=CH-CH_2\right]_n CH_2-CH=CH-CH_2{}^{-}\ Na^{+}$$

Polybutadiene

The transformation of the anionic chain end in hydroxyl groups is made by the reaction of living anionic polybutadiene with propylene oxide or ethylene oxide, followed by hydrolysis or by neutralisation of the resulting alcoholate groups (reactions 9.10 and 9.11) [21-24].



(9.10)



$$HO\underset{|}{\overset{R}{C}}HCH_2-[CH_2-CH=CH-CH_2]_n-CH_2-CH=CH-CH_2-CH_2\underset{|}{\overset{R}{C}}HOH$$

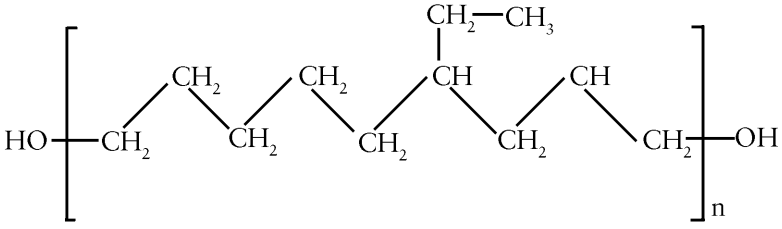
Polybutadiene diol

$R = H_2CH_3$ (9.11)

The resulting polybutadiene is a polymer with 1,4 *cis*, 1,4 *trans* and 1,2 microstructures. The resulting polybutadiene diol is perfectly linear having a high proportion of 1,2 microstructure (**Figure 9.3**). The functionality is very close to the theoretical functionality f = 2 OH groups/mol (92-93% bifunctional polybutadiene) [16-24].

The molecular weights (MW) of the commercial polyols are about 2000-5000 daltons and the molecular weight distribution is relatively narrow ($MW/M_n = 1.35$). The hydroxyl number varies from 21-51 mg KOH/g

The hydrogenated polybutadiene diols represent new polyhydroxylic hydrocarbon diols which are more resistant to oxidation due to the absence of double bonds (structure 9.12).



Hydrogenated polybutadiene diol

(9.12)

Polybutadiene diols and hydrogenated polybutadiene diols are used for producing thermoplastic polyurethane elastomers, hydrolytically stable PU elastomers, adhesives, sealants, coatings, encapsulation and electrical insulation polyurethanic products.

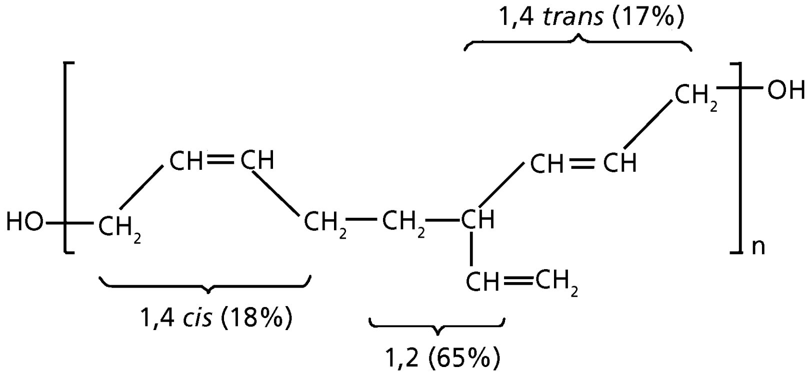


Figure 9.3 Structure of polybutadiene synthesised by anionic polymerisation where n~50

References

1. J.C. Bevington, *Radical Polymerisation*, Academic Press, New York, NY, USA, p.961.

2. W. Heitz in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.61-92.

3. D.J. Sparow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.222-223.

4. *Comprehensive Chemical Kinetics*, Volume14a, Eds., C.H. Bamford and C.F.H. Tipper, Elsevier, Amsterdam, The Netherlands 1976.

5. S.F. Reed, Jr., *Journal of Polymer Science*, Part A1, 1971, **9**, 7, 2029.

6. S.F. Reed, Jr., *Journal of Polymer Science*, Part A1, 1972, **10**, 3, 649.

7. S.F. Reed, Jr., *Journal of Polymer Science*, Part A1, 1973, **11**, 1, 55.

8. N. Uri, *Chemical Reviews*, 1952, **50**, 3, 375.

9. *Polybd Resins in Urethane Elastomers*, Atochem Technical Bulletin, Atochem North America, Philadelphia, PA, USA, 1990.

10. *Polybd, the Best of Two Worlds*, Arco Technical Bulletin, Arco Chemical Company, Newtown Square, PA, USA.

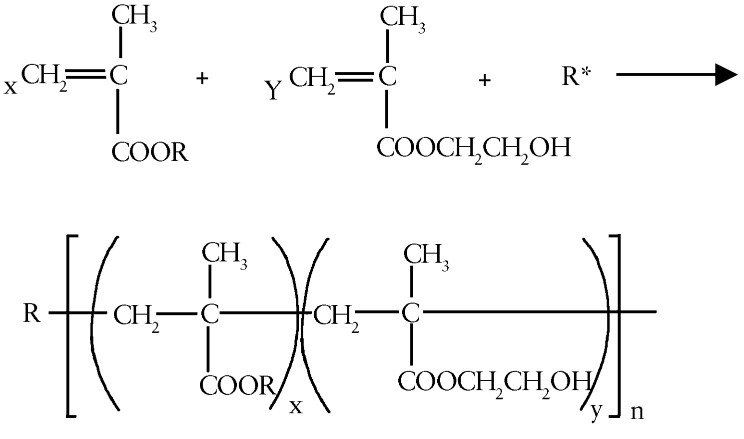
11. P.W. Ryan, *Journal of Elastoplastics*, 1971, **3**, 1, 57.
12. O.W. Burke, Jr., J.A.A Kizer and P. Davis, inventors; no assignee; US 3,673,168, 1972.
13. J.A. Verdol and R.W. Ryan, inventors; Atlantic Richfield, assignee; US 3,674,743, 1972.
14. J.A. Verdol and R.W. Ryan, inventors; Atlantic Richfield, assignee; US 3,808,281, 1972.
15. H.G. Hope and H.G. Wussow in *Polyurethane Handbook: Chemistry, Raw Materials, Processing, Applications, Properties,* Ed., G. Oertel, 2nd Edition, Hanser Publishers, Munich, Germany, 1994, p.421.
16. D.H. Richards, G.F. Eastmond and M.J. Stewart in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.33.
17. M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Processes*, Interscience, New York, NY, USA, 1968, p.62.
18. M. Morton, *Anionic Polymerisation: Principles and Practice*, Academic Press, New York, NY, USA, 1983.
19. K. Hayashi and C.S. Marvel, *Journal of Polymer Science*, Part A1, 1964, **2**, 6, 2571.
20. M. Morton, L.J. Fetters, J. Inomata, D.C. Rubio and R.N.Young, *Rubber Chemistry and Technology*, 1976, **49**, 2, 303.
21. J. Pytela and M. Sufcak in *Proceedings of the SPI Polyurethane World Congress*, 1997, Amsterdam. The Netherlands, September 1997, p.704.
22. H.B. Yokelson, P.O. Nubel, A. Sendijarevic, V. Sendijarevic and K.C. Frisch in *Proceedings of the SPI Polyurethanes 1995 Conference*, Chicago, IL, USA, 1995, p.100.
23. K.C. Frisch, A. Sendijarevic, V. Sendijarevic, H.B. Yokelson and P.O. Nubel in *Proceedings of the UTECH '96 Conference*, The Hague, The Netherlands, 1996, Paper No.42.
24. J. Pytela and M. Sufcak in *Proceedings of UTECH 2000 Conference*, The Hague, The Netherlands, 2000, Coatings,Adhesives, Sealants and Elastomer Session, Paper No.9.

10 Acrylic Polyols

Acrylic polyols represent a special group of amorphous polyols, of molecular weight (MW) of 8000-13000 daltons, obtained by radical copolymerisation of acrylic monomers (ternary or quaternary copolymers), such as acrylic or methacrylic acids and esters. The source of hydroxyl groups in these acrylic polyols is the utilisation in the radical copolymerisation reaction of hydroxyalkyl acrylates or hydroxyalkyl methacrylates [1, 2] as comonomers. The acrylic polyols are used in high performance polyurethane (PU) coatings.

The most important comonomers used as raw materials in acrylic polyols syntheses are shown in **Figure 10.1**.

The general radical copolymerisation reaction for synthesis of acrylic polyols is shown in reaction 10.1. It is obligatory that one of the comonomers is a hydroxyalkyl acrylate or hydroxyalkyl methacrylate (mainly hydroxyethylacrylate and hydroxyethylmethacrylate) in order to introduce hydroxyl groups (as lateral groups, not as terminal groups) available for the reaction with -NCO groups of diisocyanates (reaction 10.1).



$$x\,CH_2{=}C(CH_3)COOR + y\,CH_2{=}C(CH_3)COOCH_2CH_2OH + R^* \longrightarrow R\left[\left(CH_2-C(CH_3)(COOR)\right)_x\left(CH_2-C(CH_3)(COOCH_2CH_2OH)\right)_y\right]_n$$

(10.1)

Generally, the radical copolymerisation reactions of acrylic comonomers are performed in an adequate solvent, by dropwise addition of monomer - initiator (peroxides) mixture.

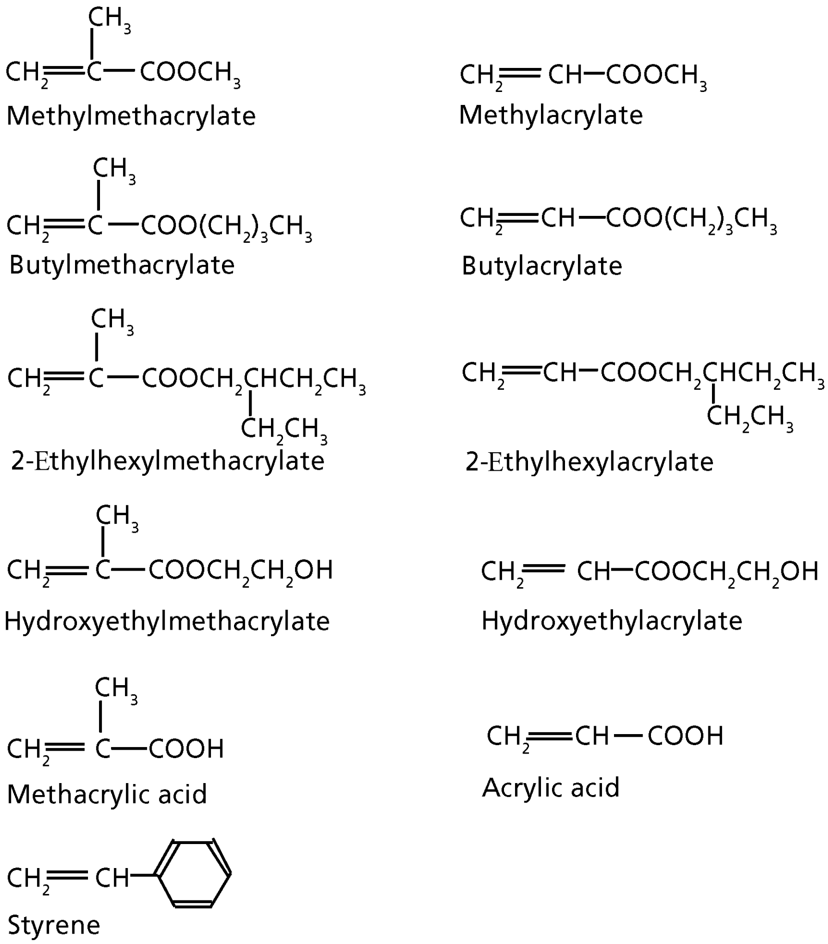


Figure 10.1 Comonomers used as raw materials for acrylic polyol syntheses

The resulting performances of acrylic polyol based PU coatings depend profoundly on the chemical nature of the monomers used. Thus, methylmethacrylate (MMA) confers exterior durability, excellent light stability, hardness and water resistance. Styrene confers hardness, water stability but, unfortunately, poor light stability. Butyl and 2-ethylhexyl acrylates and methacrylates confer flexibility and acrylic and methacrylic acids confer adhesion to metals and solvent/grease resistance.

Two representative acrylic polyols, quaternary copolymers of various acrylic monomers, are shown in **Figures 10.2** and **10.3**.

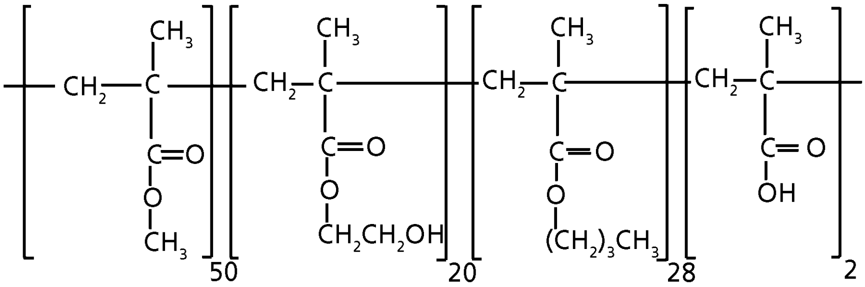


Figure 10.2 A representative structure of an acrylic polyol for hard PU coatings (with a high content of methylmethacrylate)

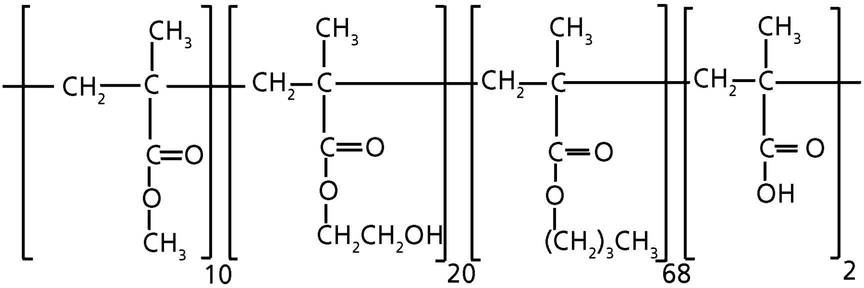


Figure 10.3 A representative structure of an acrylic polyol for elastic PU coatings (with a high content of butyl methacrylate)

The MW of the acrylic polyol (**Figure 10.2**) is around 13000 daltons and the glass transition temperature (T_g) is around 50 °C. The high content of methylmethacrylate confers hardness to the resulting PU coating.

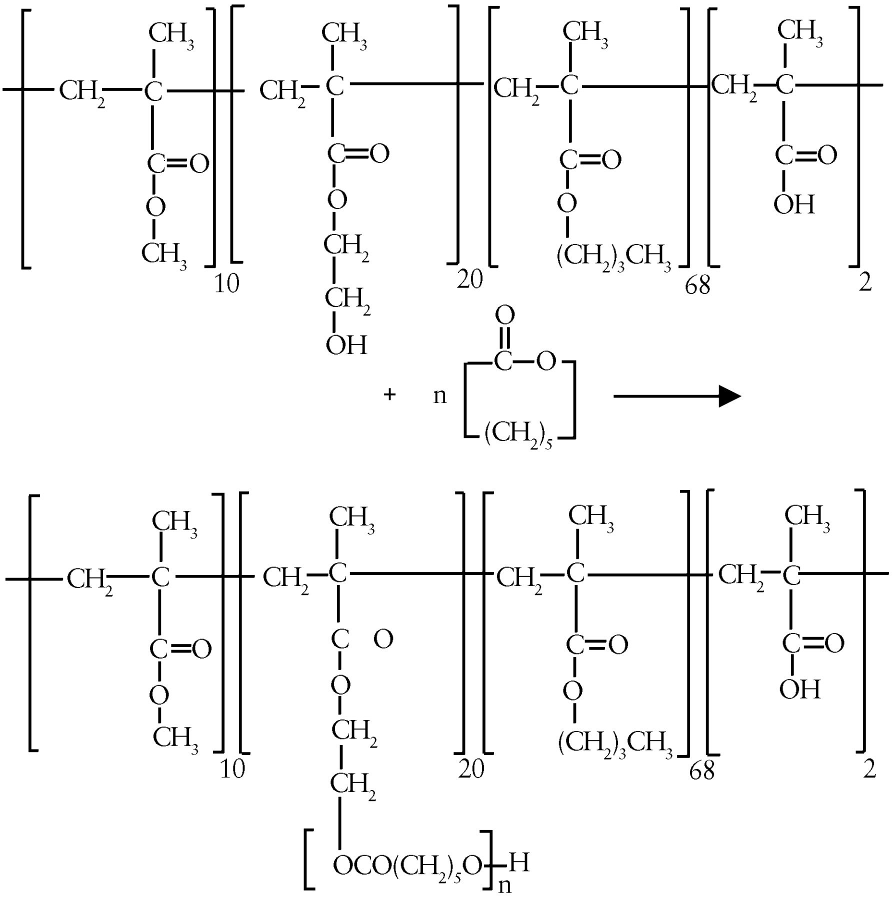
A more flexible structure is obtained by using a higher concentration of butyl acrylate or butyl methacrylate and a lower concentration of MMA (**Figure 10.3**).

The molecular weight of the acrylic polyol (**Figure 10.3**), used in elastic PU coatings, is around 11600 daltons. The T_g of the acrylic polyol (**Figure 10.3**) is around - 20 °C, proving its high flexibility at room temperature.

In both structures (**Figures 10.2** and **10.3**), the content of hydroxyl groups is around 20 mol%, the polyol having a very high functionality (f) of 20 OH groups/mol.

Generally, the acrylic polyols, which are amorphous solids at room temperature, are used as solutions (40-100% solids), in various solvents, but sometimes, special structures, which are liquid at room temperature, are used without solvents (for example the structures very rich in butyl esters). The most used solvents for acrylic polyols are: xylene, naphtha, butyl acetate, 1-methoxypropyl acetate, and butyl glycol. The viscosity of acrylic polyols varies from 1000-9000 mPa-s at 25 °C. The equivalent weight varies from 400-700 (OH number varies between 80-140 mg KOH/g). Due to the presence of acrylic acid units, the acidity of acrylic polyols is relatively high (2-5 mg KOH/g). Acrylic polyols have an excellent appearance, are very light in colour (they are practically colourless polyols), the Gardner colour frequently being < 1.

It is very interesting that acrylic polyols can be used as precursors to synthesise hybrid structures, such as acrylic - polyester polyols, by the polymerisation of some cyclic monomers such as ε-caprolactone, initiated by hydroxyl groups of acrylic polyols (reaction 10.2).



(10.2)

The resulting structure is a graft polyester which leads to high performance polyurethane coatings. In spite of the acrylic polyol's higher prices as compared to those of polyester polyols used in coatings, the high performance properties of the resulting PU coatings, such as: excellent appearance, hardness, superior gloss retention, excellent solvent resistance, ensure that there are many specific applications for acrylic polyols. One application is for automotive finishing because of the good chemical resistance and durability.

It is interesting that the systems containing acrylic polyols are readily dispersed in water after the neutralisation of -COOH groups with ammonia or with dimethylethanolamine [2]. The hydroxyl content is around 2-4% and the nonvolatile content around 40-45%, somtimes a cosolvent such as butyl glycol or naphtha (0-10%) is used. The viscosity of this kind of dispersion is low, around 200-1500 mPa-s at 25 °C.

References

1. R.T. Wojcik, *Polyurethane Coating: from Raw Materials to End-Products*, Technomic Publishing Company, Inc., Lancaster, PA, USA, 1999, p.78-82.

2. W.D. Vilar, *Chemistry and Technology of Polyurethanes*, 3rd Edition, Vilar Poliuretanos Ltd., Lugoa, Rio de Janeiro, 2002. www.polyuretanos.com.br/.

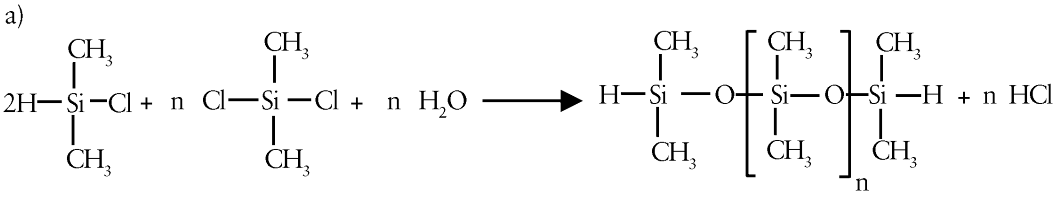
11

Polysiloxane Polyols

The very low glass transition temperature (T_g) of polysiloxane chains (T_g = –123 °C) is a very attractive property for using these kinds of polymeric chains to build an oligo-polyol structure with terminal hydroxyl groups [1]. The resulting structure called a polysiloxane polyol gives, after reaction with diisocyanates, polyurethane (PU) elastomers which conserve their high elasticity at very low temperatures [1].

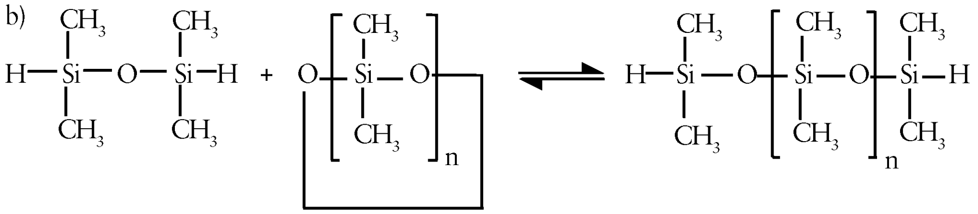
The synthesis of some experimental siloxane polyols is based on several reactions developed in two steps:

Step I: synthesis of a polysiloxane chain of molecular weight (MW) of 1000-3000 daltons, having terminal -Si-H bonds, by using classic reactions (reactions 11.1 and 11.2) [2-6]. These kinds of polysiloxanes with terminal -Si-H bonds are available commercially.



$$\text{a)}\quad 2\,H{-}Si(CH_3)_2{-}Cl + n\,Cl{-}Si(CH_3)_2{-}Cl + n\,H_2O \longrightarrow H{-}Si(CH_3)_2{-}O{-}\left[Si(CH_3)_2{-}O\right]_n{-}Si(CH_3)_2{-}H + n\,HCl$$

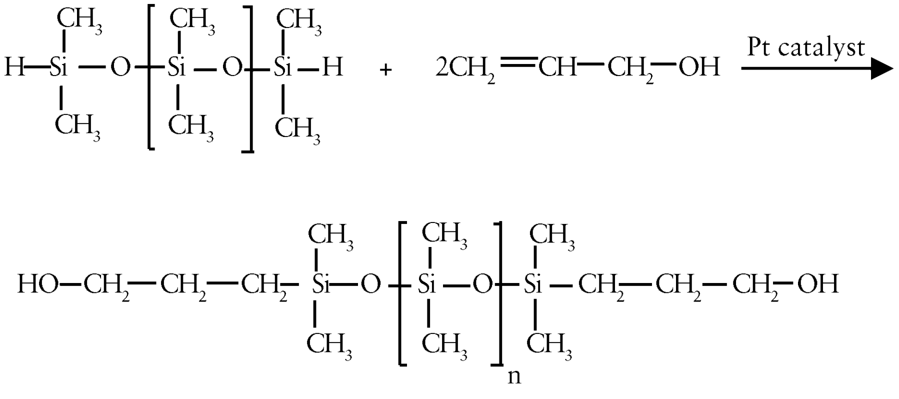
(11.1)



$$\text{b)}\quad H{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}H + \left[{-}O{-}Si(CH_3)_2{-}\right]_n\ (\text{cyclic}) \rightleftharpoons H{-}Si(CH_3)_2{-}O{-}\left[Si(CH_3)_2{-}O\right]_n{-}Si(CH_3)_2{-}H$$

(11.2)

Step II: The addition of the -SiH group to a compound having a double bond and a hydroxyl group (allyl alcohol or allyl alcohol based polyethers). The reaction is catalysed by platinum, palladium or rhodium catalysts (for example H_2PtCl_6, platinum complexes or even solid platinum supported catalysts). Hydrolysis resistant -Si-C- bonds (reactions 11.3 and 11.4.) are formed.

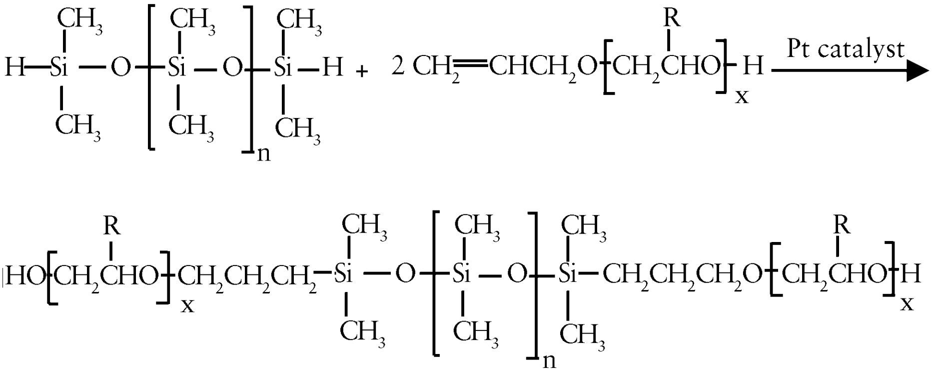


$$\mathrm{H{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\left[\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right]{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}H} + \mathrm{2CH_2{=}CH{-}CH_2{-}OH} \xrightarrow{\text{Pt catalyst}}$$

$$\mathrm{HO{-}CH_2{-}CH_2{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\left[\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right]_n{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_2{-}CH_2{-}CH_2{-}OH}$$

Polysiloxane diol

(11.3)



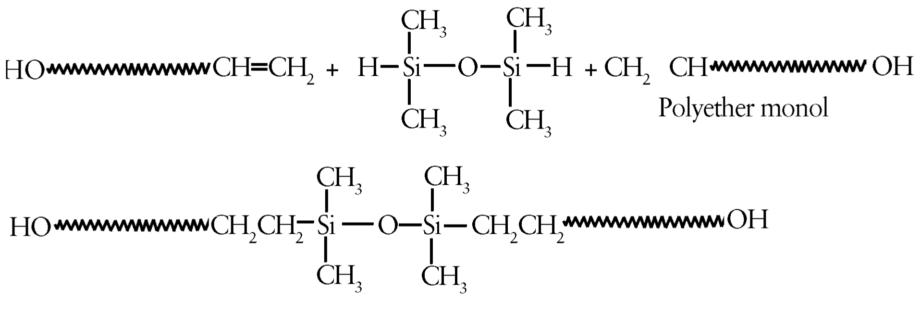
$$\mathrm{H{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\left[\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right]_n{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}H} + \mathrm{2\,CH_2{=}CHCH_2O\left[CH_2\overset{R}{C}HO\right]_x H} \xrightarrow{\text{Pt catalyst}}$$

$$\mathrm{HO\left[CH_2\overset{R}{C}HO\right]_x CH_2CH_2CH_2{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\left[\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right]_n{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_2CH_2CH_2O\left[CH_2\overset{R}{C}HO\right]_x H}$$

Polysiloxane diol

(11.4)

Reaction 11.4 is used to decrease the unsaturation of polyether polyols simultaneously with the functionality increase. Thus, by introducing a polyether polyol with high unsaturation (0.07-0.09 mequiv/g), a low molecular weight polysiloxane compound, having 2-3 Si-H groups/mol, together with a platinum catalyst, the polyether monol present in the polyether (in fact allyl ether based polyethers) is added to the polysiloxane compound and the monol is transformed into a diol or into a triol (reaction 11.5).

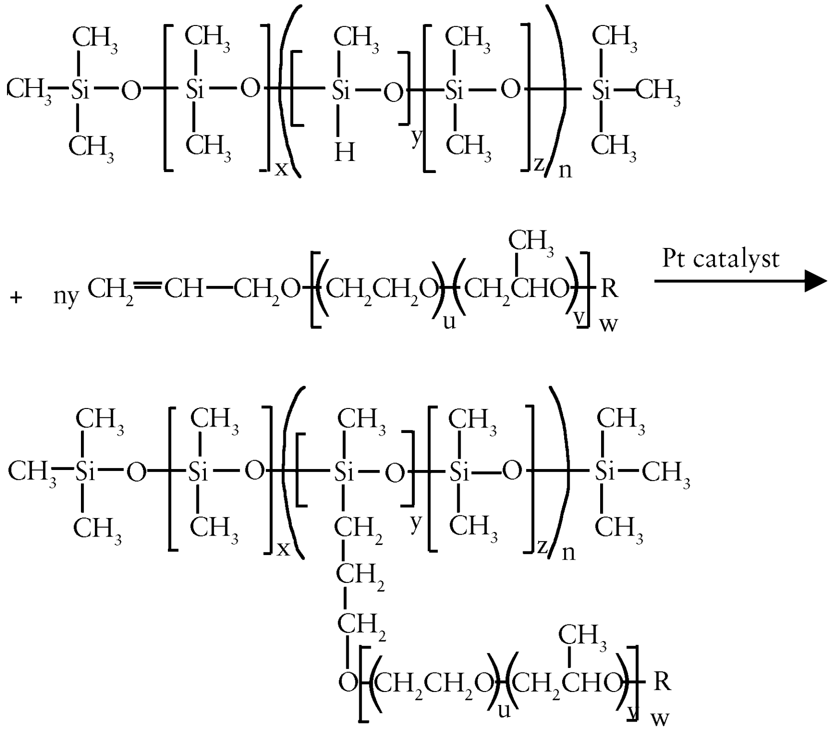


$$HO\sim\sim\sim CH{=}CH_2 + H-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-H + CH_2\ CH\sim\sim\sim OH$$

$$HO\sim\sim\sim CH_2CH_2-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2CH_2\sim\sim\sim OH$$

(11.5)

The same reaction (11.4) is currently used to obtain silicon emulsifier for flexible and rigid PU foams, by the reaction of polydimethylsiloxane of relatively high MW (3000-5000 daltons or more) having several -Si-H groups in the main polysiloxanic chain and a propylene oxide (PO) - ethylene oxide (EO) copolymer, block or preferably random copolymers, having minimum 50% EO units (reaction 11.6).



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_x\left(\left[\overset{CH_3}{\underset{H}{Si}}-O\right]_y\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_z\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

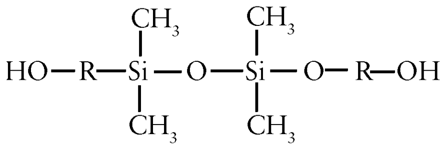
$$+\ ny\ CH_2{=}CH-CH_2O-\left[\left(CH_2CH_2O\right)_u\left(CH_2\overset{CH_3}{C}HO\right)_v\right]_w R \xrightarrow{\text{Pt catalyst}}$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_x\left(\left[\overset{CH_3}{\underset{CH_2CH_2CH_2O\left[\left(CH_2CH_2O\right)_u\left(CH_2\overset{CH_3}{C}HO\right)_v\right]_w R}{Si}}-O\right]_y\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_z\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Silicon emulsifier for PU foams

(11.6)

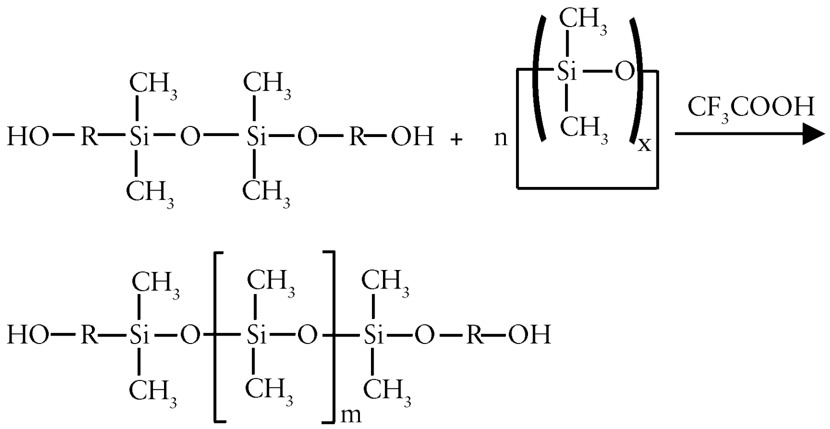
A second method for the synthesis of polysiloxane polyols is the equilibration of cyclic polydimethyl siloxanes with a compound of the following structure (11.7) [6, 7]:



$$HO{-}R{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}R{-}OH \qquad (11.7)$$

In the presence of an acidic catalyst (such as trifluoroacetic acid) polysiloxane diols (reaction 11.8) are formed [7].

The cyclic siloxanes at equilibrium (around 10%) are removed by vacuum distillation (after the acidic catalyst neutralisation). By this route, polysiloxane diols of MW in the range of 1000-6000 daltons are obtained [7].



(11.8)

The polyurethane elastomers based on these polysiloxane diols conserve their high elasticity at very low temperatures and have exceptional oxidative stability and electrical insulation properties [1, 9].

In Chapter 3, the chemistry and technology of the most important oligo-polyols used for elastic polyurethanes fabrication, in fact high MW oligomers (2000-12000 daltons) with terminal hydroxyl groups and low functionality (2-4 hydroxyl groups/mol) were discussed. Polyalkylene oxide polyols (homopolymers of PO or copolymers PO - EO, random or block copolymers), polytetrahydrofuran polyols, filled polyols (graft polyether polyols, poly Harnstoff dispersion - polyurea dispersions (PHD) and polyisocyanate polyaddition (PIPA) polyols), polybutadiene polyols and polysiloxane polyols were all discussed. The elastic polyurethanes represent around 72% of the total polyurethanes produced worldwide.

In Chapter 12, the oligo-polyols for rigid polyurethanes, having low MW (less than 1000 daltons) and high functionality (of around 3-8 hydroxyl groups/mol) will be discussed.

References

1. E.J. Goerthals in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Boca Raton, FL, USA, 1989.

2. P.V. Wright in *Ring-Opening Polymerization*, Eds., K.J. Ivin and T. Saegusa, Elsevier, Amsterdam, The Netherlands, 1984, p.1055.

3. G. Sauvet, J.J. Lebrun and P. Sigwalt in *Cationic Polymerization and Related Processes*, Ed., E.J. Goethals, Academic Press, New York, NY, USA, 1984, p.237.

4. S.W. Kantor, W. Grubb and R.C. Osthoff, *Journal of the American Chemical Society*, 1954, **76**, 20, 5190.

5. M.S. Beevers and J.A. Semlyen, *Polymer*, 1971, **12**, 6, 373.

6. P.M. Sermani, R.J. Minton and J.E. Mc.Grath in *Ring Opening Polymerization*, ACS Symposium Series No.286, Ed., J.E. McGrath, American Chemical Society, Washington, DC, USA, 1985, p.147.

7. I. Yilgor, J.S. Riffle and J.E. McGrath in *Reactive Oligomers*, ACS Symposium Series No.282, Eds., F.W. Harris and H.J. Spinelli, American Chemical Society, Washington DC, USA, 1985, p.161.

8. M. Ionescu, unpublished work.

9. J. Kozakiewicz, M. Cholinska, M. Skarzynski, S. Iwawska and Z. Czlonkowska-Kohutnicka in *Proceedings of the 35th Annual Polyurethane Technical/Marketing Conference*, *Polyurethanes '94*, Boston, MA, USA, 1994, p.101.

12

Polyols for Rigid Polyurethanes - General Considerations

In the previous chapters (Chapters 4-11) the chemistry and technology of oligo-polyols for elastic polyurethanes (PU; flexible and semiflexible PU foams, elastomers, adhesives, coatings, sealants, elastic fibres and microcellular elastomers) were presented. The elastic polyurethanes are the most important in commercial applications of polyurethanes, having around 72% of the global polyurethane market. Rigid polyurethanes, especially in the form of rigid polyurethane foams, wood substitutes, flotation and packaging materials represent, at this moment, around 28% of the global polyurethane market.

The oligo-polyols for rigid polyurethanes have two important characteristics: they are highly branched having a high functionality (around 3-8 hydroxyl groups/mol) and the chain derived from one hydroxyl group is short (the equivalent weight is low) [1-4]. As an immediate consequence of this special structure, reacting these polyols with aromatic diisocyanates [or polyisocyanates such as 'crude' diphenylmethane diisocyanate (MDI) or polymeric MDI (PAPI)] gives a highly crosslinked and very rigid polyurethane structure. The high density of urethane groups, as a consequence of their low equivalent weight, leads to strong and intensive interchain forces, by hydrogen bonds, and an increased rigidity. Thus, the oligo-polyols for rigid polyurethanes (mainly for rigid polyurethane foams), have a much higher hydroxyl number than the oligo-polyols for flexible polyurethanes, for the majority of oligo-polyols in the average range of 300-600 mg KOH/g (some special polyols have a hydroxyl number outside this range, e.g., 200-300 mg KOH/g and 600-800 mg KOH/g). The high concentration of hydroxyl groups leads to a high density of hydrogen bonds formed between these hydroxyl groups and as an immediate consequence to a strong interaction between the oligomeric chains that strongly increase the oligo-polyol viscosity. As a general rule, the viscosity of oligo-polyols for rigid PU is generally higher than the viscosity of oligo-polyols used for elastic PU, being in the range of 2,000 – 50,000 mPa-s at 25 °C.

The development of aromatic oligo-polyols for rigid polyurethanes, proved that the presence of aromatic nuclei (of low mobility and high rigidity), in the structure has a strong contribution to conferring rigidity to the resulting polyurethanes (see Chapter 21). For example, aromatic polyols with lower functionalities ($f = 2.3$-3 hydroxyl groups/mol;

Mannich polyols, aromatic polyester polyols, novolak-based polyols) lead, by the reaction with 'crude' MDI, to very rigid polyurethane structures [2] (see Chapter 15).

The cellular structure of rigid polyurethane foams (the majority of rigid polyurethanes) is generated in two ways: in a reactive manner using water as a reactive blowing agent (the reaction of isocyanates with water generates gaseous CO_2) or in an unreactive way with physical blowing agents which are low boiling point substances (such as pentanes, hydrofluorocarbons, etc.), which are evaporated by the exothermic reaction between the hydroxyl groups of the oligo-polyols with isocyanate groups, with the simultaneous formation of a polyurethane polymer, generating their cellular structure.

If the flexible foams have a predominantly open cell structure, the rigid polyurethane foams have a predominantly closed cell structure (more than 90% of the cells are closed), which confers to rigid PU foams excellent thermoinsulation properties. As a consequence the main applications of rigid PU foams are in thermoinsulation, at low and medium temperatures, for freezers, thermoinsulation in constructions and buildings, of storage tanks in the chemical and food industry, thermoinsulation, of pipes, elements for construction (sandwich panels), and so on. Rigid PU foams are the best materials known at this moment for thermoinsulation, having the lowest thermoconductivity constant (K factor) of all known materials. Utilisation of thermoinsulation with rigid PU foams leads to a considerable economy of energy, for example 90% for storage tanks for 'crude' oil and 50% for thermoinsulation of buildings [5].

The most important oligo-polyols for rigid polyurethanes are polyether polyols and aromatic polyester polyols [1-4, 6]. The aromatic polyether polyols, based on condensates of aromatic compounds with aldehydes, become very important polyols, especially after the introduction of new blowing agents (see Chapter 21).

Aminic polyols (aliphatic or aromatic) are a group of very reactive polyols with the structure of alkanolamines. The high reactivity is conferred by the self catalytic effect of tertiary nitrogen from the aminic polyol structure, in the reaction of hydroxyl groups with the -NCO groups (see Chapter 14).

By chemical recovery of polyester [poly(ethylene terephthalate) (PET)] (Chapter 16) and PU wastes, by alcoholysis or by aminolysis (Chapter 20), new polyols are obtained that can be used in rigid PU foam fabrication. The vegetable oil polyols, obtained by chemical transformation of the double bonds in vegetable oils in various hydroxyl groups are a very attractive route to obtain polyols from renewable resources (Chapter 17).

A special group of polyols for rigid PU foams is the group of reactive flame retardant polyols containing phosphorus, chlorine or bromine, which confer fire resistance to the resulting PU (Chapter 18).

The nature of the oligo-polyol structure has a profound effect on the physico-mechanical, thermal and fire proofing properties of rigid PU foams. Higher functionalities lead to a higher compression strength, improved dimensional stability and heat resistance, while tensile strength and elongation tend to decrease. The polyols with increased rigidity, having low mobility cycloaliphatic or aromatic structures tend to have better physico-mechanical and thermal resistance properties than the high mobility aliphatic polyols, with the same functionality and hydroxyl number (see Chapter 21). Dimensional stability and friability vary in opposite directions, function of hydroxyl numbers, since higher hydroxyl numbers give better dimensional stability and higher friability (see Chapter 21).

Generally, the polyether polyols for rigid PU foams give softer foams and superior hydrolysis resistance than polyester polyols. At the same time, polyester polyols lead to more thermoresistant and fire resistant rigid PU foams than the polyether polyols. Vegetable oil polyols confer onto the resulting rigid PU foams hydrophobicity and an excellent compatibility with pentanes, used as blowing agents (Chapter 20).

After this general presentation of oligo-polyols for rigid polyurethanes, each group of polyols will be presented in detail in the next few chapters, in order of importance, the most important being the group of polyether polyols, followed by the polyester polyols.

References

1. D.J. Sparrow and D. Thorpe, in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Boca Raton, FL, USA, 1989, p.207-209.

2. T.H. Ferrigno, *Rigid Plastic Foams*, 2nd Edition, Reinhold, New York, NY, USA, 1967.

3. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, 8, p.1-18.

4. W. Green, G.M.F. Jeffs and D.J. Sparrow, *Plastics & Rubber International*, 1984, 9, 5, 30.

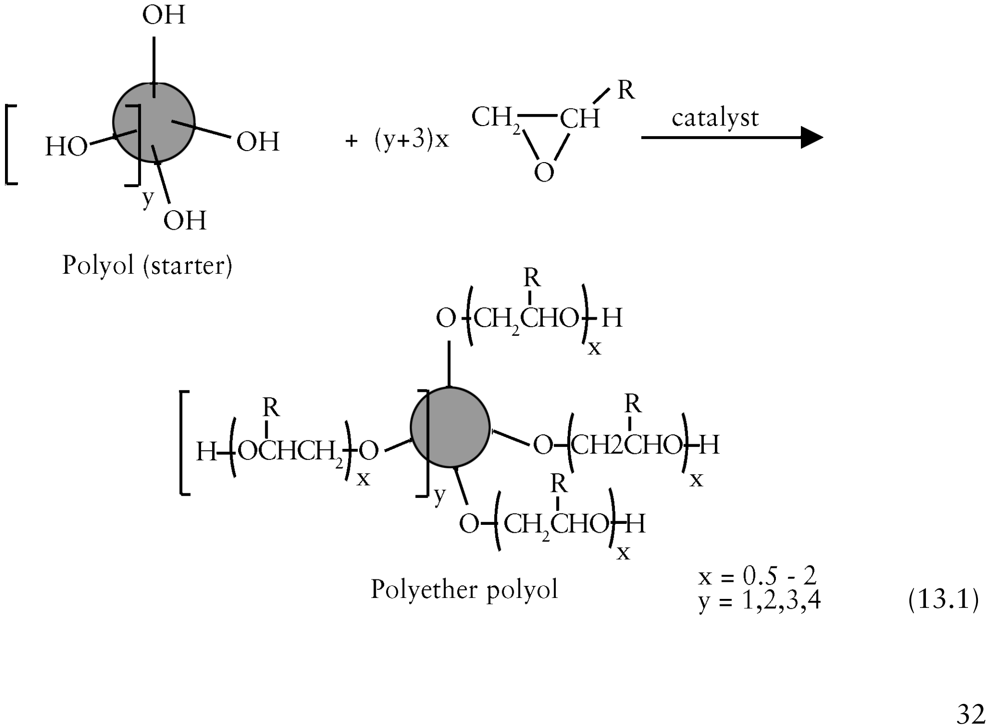
5. M. Ionescu, unpublished work.

6. K.C. Frisch and J.E. Kresta in *Sucrochemistry*, Ed., J.L. Hickson, ACS Symposium Series No.41, American Chemical Society, Washington, DC, USA, 1976.

13 Polyether Polyols for Rigid Polyurethane Foams

Polyether polyols for rigid polyurethane (PU) foams are low molecular weight (MW) adducts of propylene oxide (PO) [sometimes together with ethylene oxide (EO)] to polyols having 3-8 hydroxyl groups/mol or to polyamines having 2-3 amino groups/mol, the chain derived from one hydroxyl group being very short, around 0.5-2 alkylene oxide units. As mentioned previously, the hydroxyl number of these polyols is high, generally in the range 300 - 800 mg KOH/g [1-4] (rarely in the range 600-800 mg KOH/g). It is observed that the equivalent weight (EW) of polyether polyols for rigid foams is low, around 60 - 200, as compared with polyether polyols for flexible PU foams which have a much higher EW, of around 1000-2000.

The general synthesis reaction of polyether polyols for rigid PU foams by polymerisation of alkylene oxides (PO, EO) initiated by polyolic starters is presented in reaction 13.1.

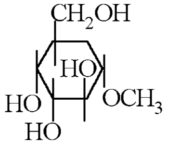
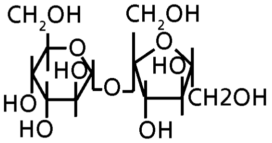


(13.1)

The most important low molecular weight polyols used as starters for polyether polyols destined for rigid PU foams synthesis are: glycerol, trimethylolpropane (TMP), triethanolamine, pentaerythritol, dipentaerythritol, α-methyl glucoside, xylitol, sorbitol and sucrose [1-27]. The main properties of these starter polyols, which are of interest for polyurethane chemistry, are presented in **Table 13.1**.

In **Table 13.1** one observes that some polyols used as starters have an aliphatic structure (glycerol, pentaeriythritol, xylitol, sorbitol) and others have cycloaliphatic structures (α-methyl glucoside and sucrose). As a general rule, the polyether polyols derived from polyols with a cycloaliphatic structure, due to their intrinsic low mobility and higher rigidity give rigid PU foams with superior physico-mechanical, thermal and fire resistance properties compared to the polyether polyols having aliphatic structures, at the same functionalities and hydroxyl numbers.

Table 13.1 Some characteristics of polyols used frequently as starters for polyether polyols for rigid PU foams

No.	Polyol used as starter	Formula	MW	f	Hydroxyl number, mg KOH/g
1	Glycerol	$HOCH(CH_2OH)_2$	92.10	3	1827.3
2	Trimethylol-propane	$CH_3CH_2C(CH_2OH)_3$	132.0	3	1275.0
3	Triethanolamine	$N(CH_2CH_2OH)_3$	149.19	3	1128.0
4	Pentaerythritol	$C(CH_2OH)_4$	136.0	4	1650.0
5	Dipentaerythritol	$(HOCH_2)_3CCH_2OCH_2—$ $—C(CH_2OH)_3$	254.0	6	1325.19
6	α-Methyl glucoside		194.19	4	1155.56
7	Xylitol	$HOCH_2(CHOH)_3CH_2OH$	152.0	5	1845.39
8	Sorbitol	$HOCH_2(CHOH)_4CH_2OH$	182.17	6	1847.7
9	Sucrose		342.30	8	1311.1

MW: molecular weight of polyol in daltons
f: functionality, OH groups/mol

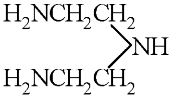
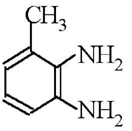
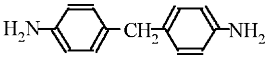
A second important group of starters used in the synthesis of polyether polyols for rigid PU foams is the group of polyamines, aliphatic or aromatic, having 2-3 amino groups/mol (primary or secondary amino groups) such as: ethylenediamine (EDA), diethylenetriamine (DETA), *ortho*-toluene diamine (o-TDA) and diphenylmethanediamine (MDA) [1, 2] (see Chapter 4.2). The main properties of these polyamines which are of interest in polyurethane chemistry are presented in **Table 13.2**.

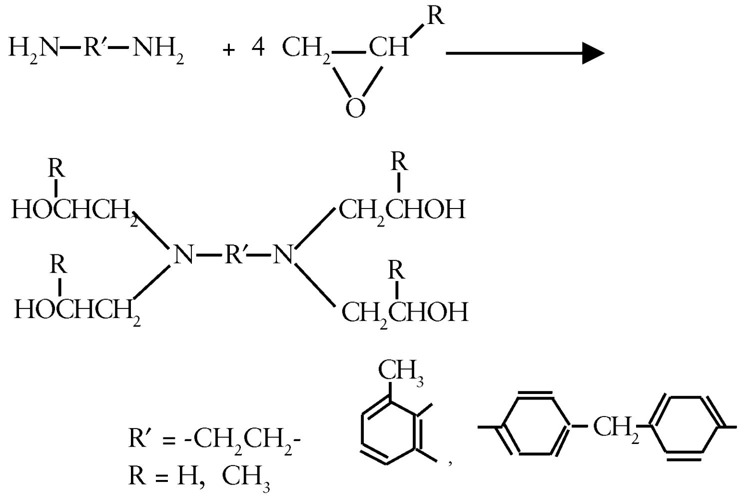
The amino groups ($-NH_2$) generated by the reaction with alkylene oxides (PO, EO) hydroxyalkyl groups, transforming the initial amine into an amino polyol (reaction 13.2).

The resulting amino polyols (structure 13.2) do not have a polyetheric structure, but if the addition of alkylene oxide continues by extension of the chains derived from hydroxyl groups, real structures of polyether polyols are formed (reaction 13.3).

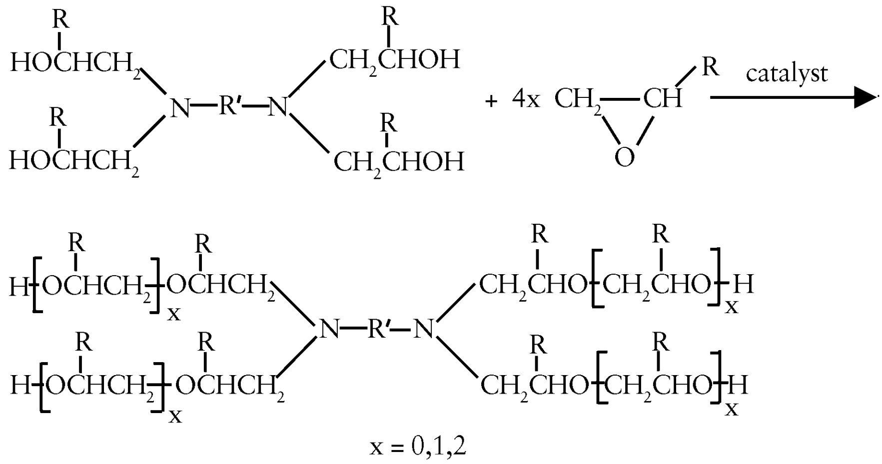
Of course the hydroxyl number presented in **Table 13.2** is a hypothetical one (the amines do not have hydroxyl groups), but it is very useful for the calculation of the final amino polyol hydroxyl number, after alkoxylation.

Table 13.2 Some characteristics of polyamines used frequently as starters for polyether polyols for rigid PU foams

No.	Polyamine used as starter	Formula	MW	f	Hydroxyl number, mg KOH/g
1	Ethylenediamine (EDA)	$H_2NCH_2CH_2NH_2$	60.10	4	3733.7
2	Diethylene triamine (DETA)	 $(H_2NCH_2CH_2)_2NH$	103.20	5	2718.0
3	*Ortho*-toluene diamine (2,3 and 3,4 isomers) (o-TDA)		122.16	4	1836.9
4	Diphenylmethane diamine (MDA)		198.27	4	1131.78



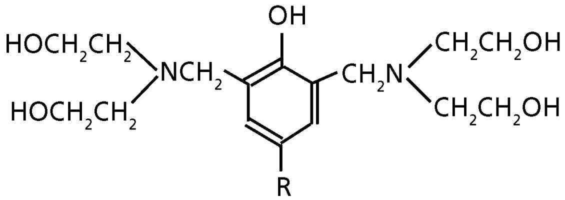
(13.2)



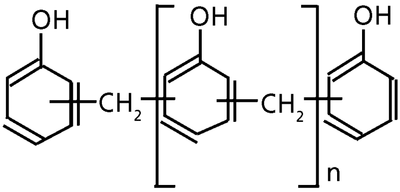
(13.3)

Both structures (13.2 and 13.3) are used successfully in rigid PU foams. Structure 13.2, having a high hydroxyl number, is used more frequently as crosslinker in many polyurethane applications (rigid PU foams, coatings).

A third group of starters, used in the synthesis of polyether polyols for rigid polyurethane foams, is the group of condensates of aromatic compounds (for example phenols) with aldehydes (for example formaldehyde) such as Mannich bases or novolaks (**Figure 13.1**). This group of starters is very important because, by their reaction with alkylene oxides, they give aromatic polyols which confer to the resulting rigid polyurethane foams excellent physico-mechanical, thermal, and fire proofing properties as well as dimensional stability (see details in Chapter 15).



Mannich base

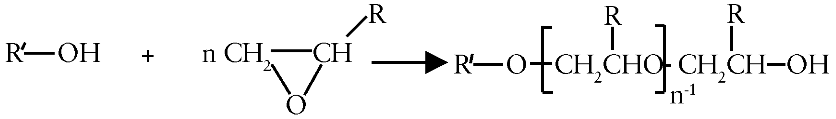


Novolak

Figure 13.1 Starters with aromatic structure (condensates of phenols with aldehydes)

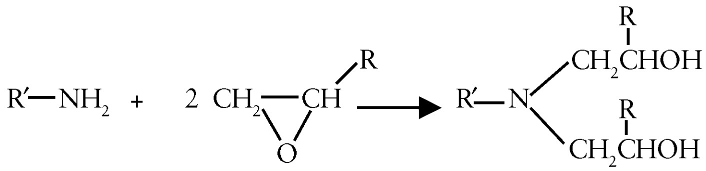
As a general observation, the main reactions involved in the synthesis of polyether polyols for rigid polyurethane foams are:

a) The polyaddition of alkylene oxides to hydroxyl groups (reaction 13.4):



$$R'{-}OH \;+\; n\,\underset{\diagdown O \diagup}{CH_2{-}CH}{-}R \longrightarrow R'{-}O{-}\left[CH_2\overset{R}{\overset{|}{C}}HO\right]_{n-1}{-}CH_2\overset{R}{\overset{|}{C}}H{-}OH \qquad (13.4)$$

b) The addition of alkylene oxides to amino groups (reaction 13.5):



$$R'{-}NH_2 \;+\; 2\,\underset{\diagdown O \diagup}{CH_2{-}CH}{-}R \longrightarrow R'{-}N\begin{cases} CH_2\overset{R}{\overset{|}{C}}HOH \\ CH_2\overset{R}{\overset{|}{C}}HOH \end{cases} \qquad (13.5)$$

13.1 The Polyaddition of Alkylene Oxides to Hydroxyl Groups

The polyaddition of alkylene oxides to hydroxyl groups is catalysed by the alkali hydroxides (KOH and NaOH) or low hindered tertiary amines or, to a much lesser extent, by acid catalysts [Lewis acids and Brönstedt superacids in order to generate short polyetheric chains, (see Chapter 7.2)]. Some heterogeneous basic catalysts are used to obtain short chain polyethers, such as: magnesium oxide, potassium fluoride on alumina [28] and hydrotalcite [29]. The most important catalysts used in industrial practice are alkaly hydroxides and the tertiary amines [1, 2, 30, 31].

It is well known that with the tertiary amines as catalysts it is impossible to obtain high molecular weight polyether chains (for example polyethers for flexible foams) but with short chain polyethers, having 1-3 alkylene oxide units, it is perfectly possible [31, 32].

The mechanism of alkylene oxide anionic polyaddition to hydroxyl groups, catalysed by alkali hydroxides, is discussed in chapters 4.1-4.1.5, the real active centre being the alkaline alcoholate, and the propagation reaction being the repeated SN-2 attack of the alcoholate anion on the α-carbon atom of the oxirane rings. The rapid equilibrium of the alcohol - alcoholate assures that each hydroxyl group from the reaction system is a chain initiator.

One major difference in PO polyaddition to hydroxyl groups was observed: since in the reaction system for producing polyether polyols for rigid foams (called rigid polyols) there is always a high concentration of hydroxyl groups, the rearrangement of PO to allyl alcohol is practically insignificant, the resulting unsaturation being very low, around 0.005-0.01 mequiv/g. As an immediate consequence, the functionality decrease in rigid polyether polyols is minor, due to the negligible quantity of polyether monol formed. As a conclusion, the unsaturation value of rigid polyols is not as important as the flexible polyol unsaturation, because it does not affect the properties of the resulting rigid PU foams.

13.1.1 The Mechanism of Alkylene Oxide Polyaddition to Hydroxyl Groups Catalysed by the Tertiary Amines [33-34]

The mechanism of alkylene oxide polyaddition to hydroxyl groups catalysed by the tertiary amines is much more complex [31]. The most efficient tertiary amines, used as catalysts in the addition of PO to hydroxyl groups, are the low hindered amines, having a minimum of two methyl groups/aminic nitrogen (see **Figure 13.2**) [30-35].

A special group of aromatic amines, of very high catalytic efficiency in the polyaddition reaction of PO to hydroxyl groups, is the imidazole group and the alkyl substituted imidazoles (**Figure 13.3**). Poly(*N*-vinyl imidazole) proved to have an important catalytic activity [31]. The amines of high steric hindrance to the nitrogen atom, such as: triethylamine, tripropylamine, tributylamine and triethanolamine, have a very poor catalytic activity [30, 31]. Triisopropanolamine has practically no catalytic activity [36]. *N*,*N*,*N*′,*N*′ tetrakis (hydroxypropyl) ethylenediamine (QUADROL) has no catalytic activity in PO polyaddition to hydroxyl groups [37].

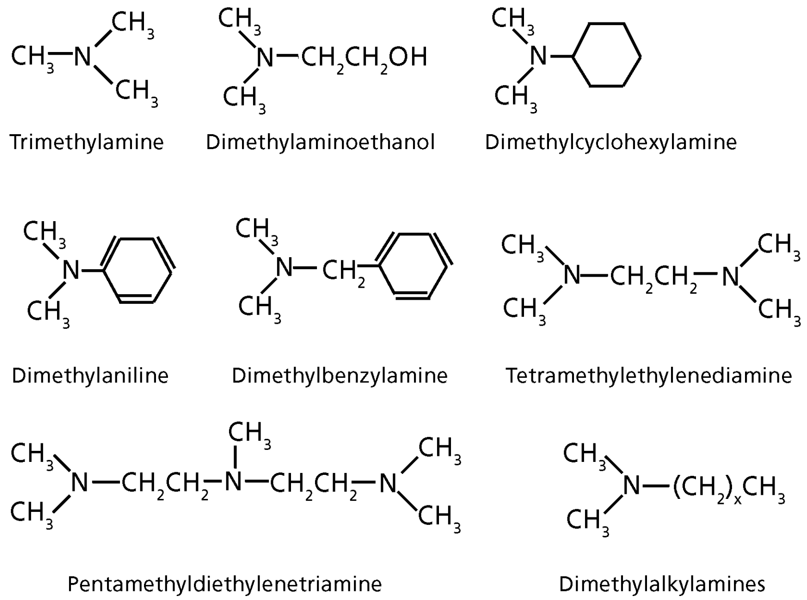


Figure 13.2 Tertiary amines with high catalytic activity in alkoxylation reactions

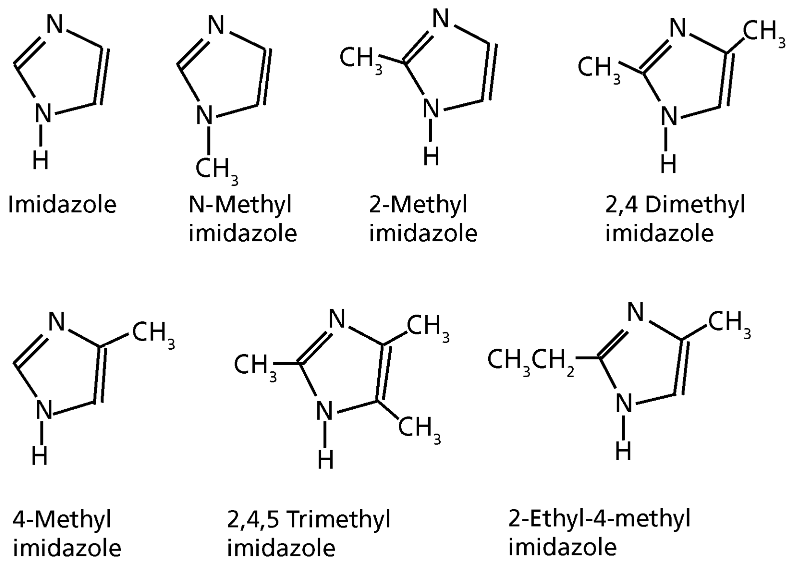
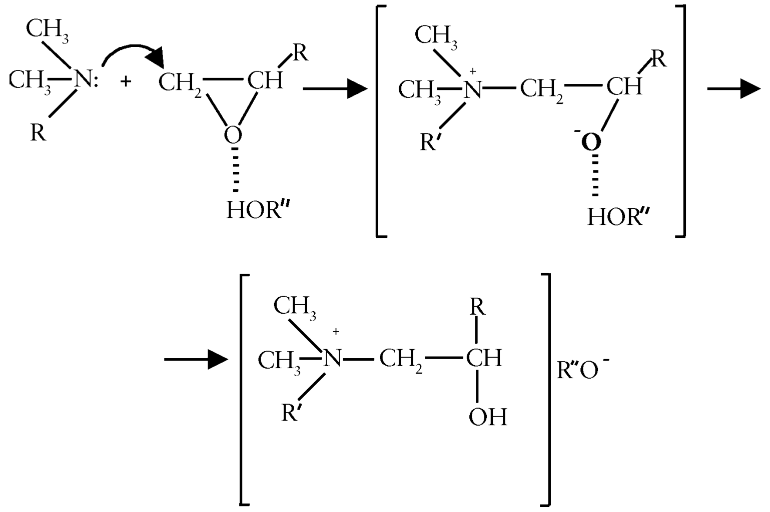


Figure 13.3 Imidazole and substituted imidazoles with high catalytic activity in alkoxylation reactions

The first step of PO addition to hydroxyl groups is the SN-2 attack of the tertiary nitrogen atom to the α-carbon atom of the oxiranic ring, activated by a hydrogen bond between the oxiranic oxygen and hydrogen atom of hydroxyl groups (reaction 13.6).

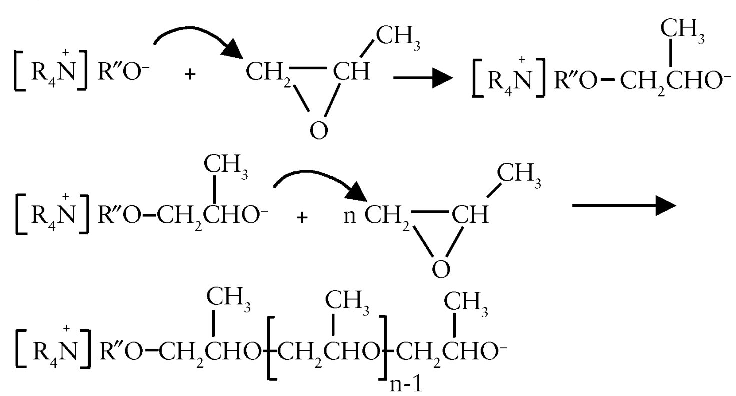


Quaternary ammonium alcoholate

(13.6)

In the absence of hydroxyl groups, reaction 13.6 does not take place. In the synthesis of polyether polyols for rigid PU foams there is a large excess of hydroxyl groups which assist the ring opening of PO. The weak hydrogen bond of around 3-5 kcal/mol, between the hydrogen of hydroxyl groups and the oxygen atom of epoxidic ring is enough to activate the alkylene oxide [3, 30, 38, 39].

The quaternary ammonium alcoholate (13.6) formed, develops the PO anionic polyaddition to hydroxyl groups in an identical manner to the potassium alcoholates, the single difference being that the potassium cations are replaced by quaternary ammonium cations (reaction 13.7).

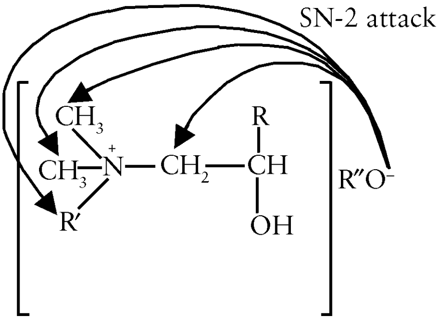


(13.7)

Unfortunately, the big difference between the potassium alcoholates and quaternary ammonium alcoholates is the fact that potassium alcoholate is perfectly stable at the polymerisation temperature, but the quaternary ammonium alcoholates are, on the contrary, not stable and are decomposed by two mechanisms (reactions 13.8 and 13.9) [31, 32]:

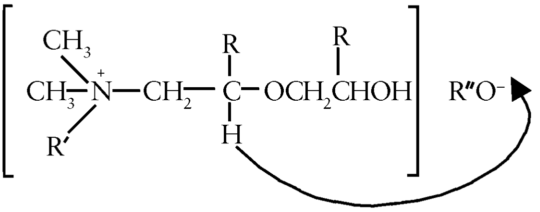
a) Intramolecular SN-2 nucleophilic substitution (reaction 13.8);

b) Hofmann degradation (β hydrogen abstraction, reaction 13.9);



Quarternary ammonium alcoholate

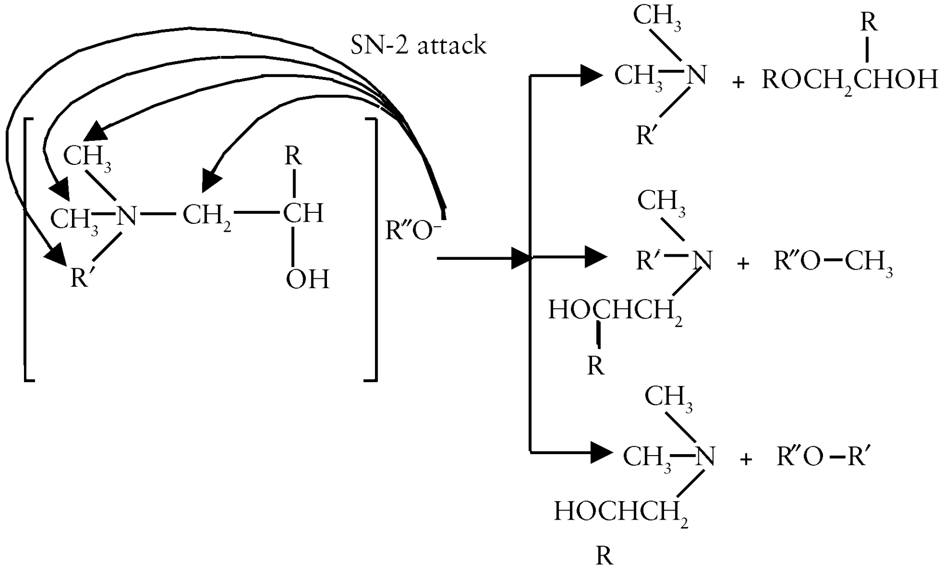
(13.8)



Quaternary ammonium alcoholate

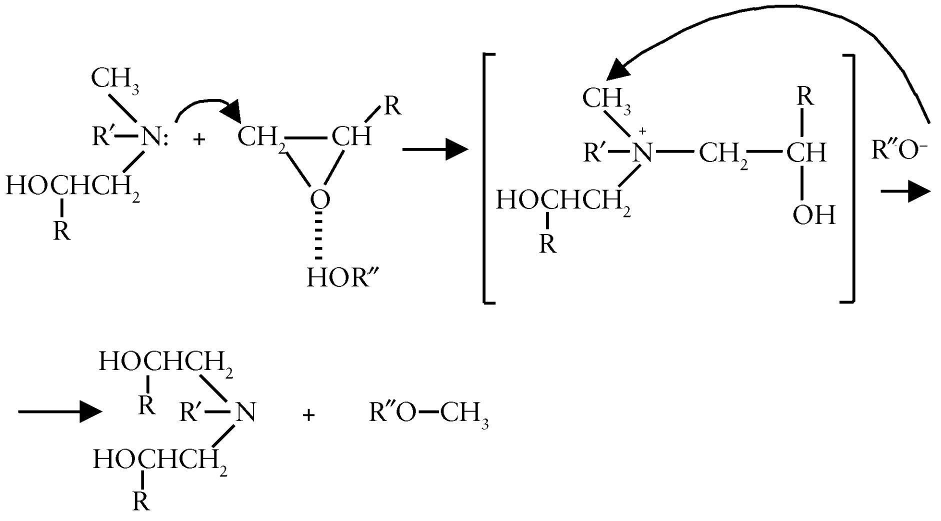
(13.9)

The intramolecular SN-2 nucleophilic substitution is based on the SN-2 attack of the alcoholate anion to the α-carbon atoms of the four alkylic substituents of the nitrogen atom, the α-carbon atoms being activated by the positively charged nitrogen atom present in the quaternary ammonium alcoholate (reactions 13.10).

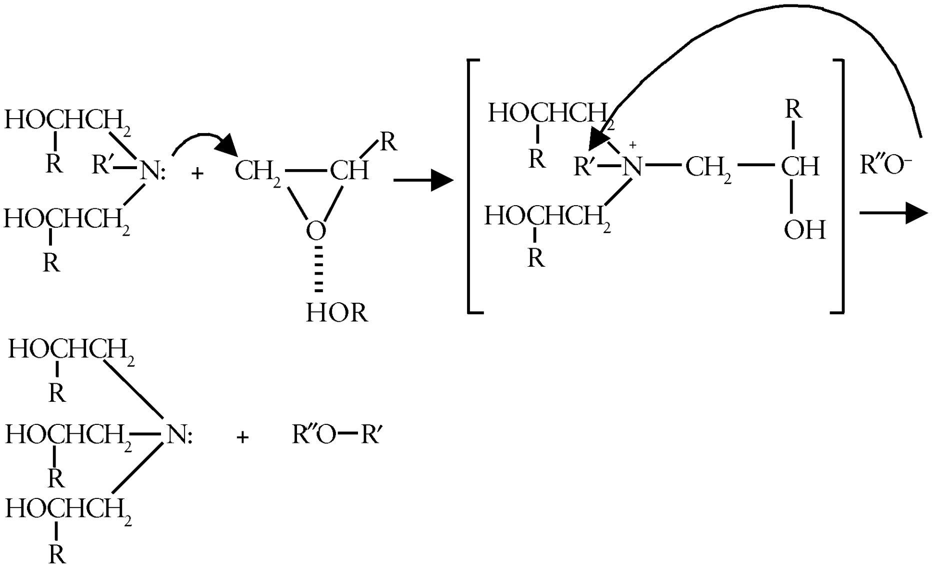


(13.10)

If the RO$^-$ anion attacks the carbon atom of the hydroxypropyl group an extension of the chain takes place and the initial amine is regenerated (first reaction 13.10). The regenerated tertiary amines again attack the oxiranic ring. This substitution type is very favourable to the polyaddition reaction. Unfortunately, the substitution reaction also takes place at the carbon atoms of the methyl groups, which are replaced, step-by-step, by hydroxypropyl groups (reactions 13.11 and 13.12).



(13.11)



(13.12)

By these successive reactions (13.10-13.12), the initial low hindered, very active amine is transformed into a low catalytic activity trialkanolamine, of high steric hindrance. It is important to obtain a meaningful conclusion: the initial tertiary amine does not remain identical at the end of reaction, it is transformed during alkylene oxide polyaddition into a new amine, a trialkanolamine of low catalytic efficiency. This change of the tertiary amine structure used as catalyst, during PO anionic polymerisation initiated by hydroxyl groups, explains the presence of two total different reaction rates of the PO consumption. Initially, the rate of PO consumption is very high and after a polyaddition of 65-75% of the PO needed, the rate of PO consumption suddenly becomes extremely low because the initial low hindered highly active amine is transformed into a trialkanolamine with low catalytic activity (reactions 13.10-13.13). This behaviour is clearly seen in **Figure 13.4**.

The point of the sudden change in the PO consumption rate is the moment of total transformation of the initial amine in a trialkanolamine of lower catalytic activity. Because of the low PO polymerisation rate in the second part of the reaction, at normal polymerisation temperatures of 110-120 °C, it is practically impossible to obtain, in the presence of tertiary amines as catalysts, polyether polyols with an hydroxyl number lower than 400 mg KOH/g.

The second side reaction is the Hofmann degradation, a destruction of the quaternary ammonium alcoholate by β hydrogen abstraction. This reaction takes place when the hydroxyalkyl group linked to the amine is longer, having a minimum of two PO units (reaction 13.13).

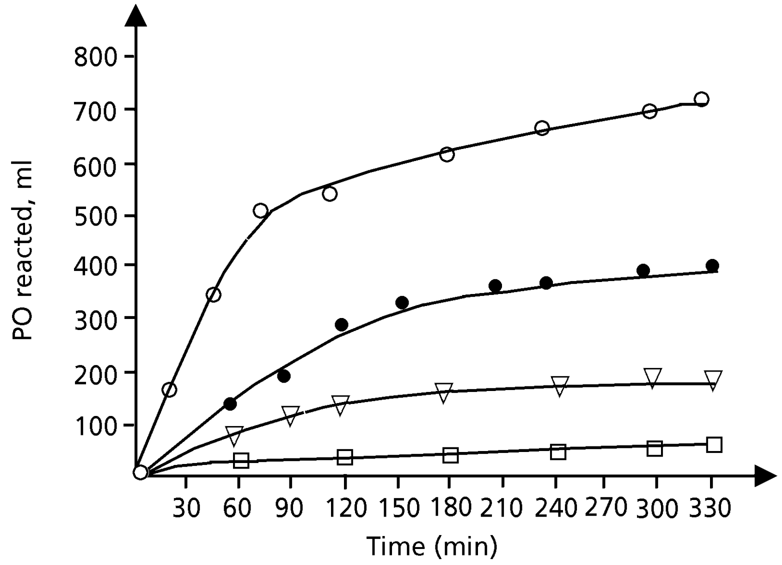
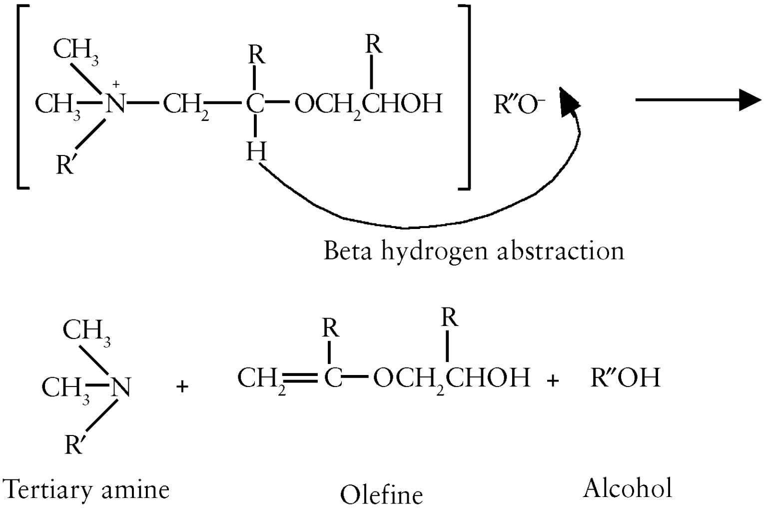


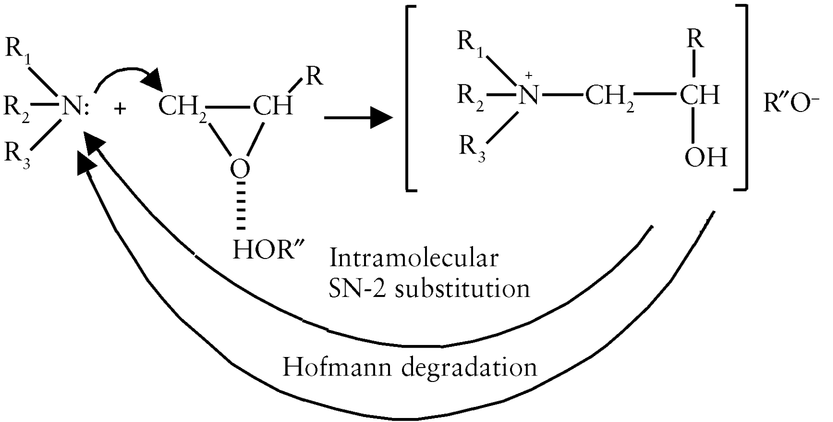
Figure 13.4 Volume of PO reacted *versus* time as function of the tertiary amine nature. Temperature: 120 °C; pressure: 0.35-0.4 MPa; catalyst: 0.0056 mol%; starter: sucrose:glycerol (3:1); dimethylaminoethanol (o); triethanolamine (●); tributylamine (∇); triisopropanolamine(❑)



(13.13)

The Hofmann degradation leads to a tertiary amine, an olefin and to the formation of a new hydroxyl group. Reaction 13.13 is predominant at higher temperatures. The resulting double bond increases the unsaturation of the polyether polyol. Generally, the unsaturation of rigid polyether polyols made with tertiary amines as catalysts is higher than the unsaturation of polyether polyols obtained with KOH as catalyst, being in the range of 0.05-0.06 mEq/g (as compared with the unsaturation of 0.005-0.01 mEq/g resulting in the case of rigid polyether polyols obtained in the presence of KOH).

It was observed that, if the polymerisation in the presence of tertiary amines is developed at lower polymerisation temperatures, of around 80-90 °C, paradoxally higher reaction rates of PO polyaddition are obtained than at higher polymerisation temperatures, (e.g., 120 °C). The explanation of this phenomenon is simple: at lower temperatures, the main catalytic species is the quaternary ammonium alcoholate, a very strong base and a very strong nucleophile, relatively stable, but at higher temperatures, the quaternary ammonium alcoholate is not resistant and it is decomposed into tertiary amines having a low basicity and being a weakly nucleophilic. In conclusion this behaviour is not in contradiction to thermodynamic rules, in fact it is a change of the active species nature: at lower temperatures there are more active species than at higher temperatures (see 13.14).

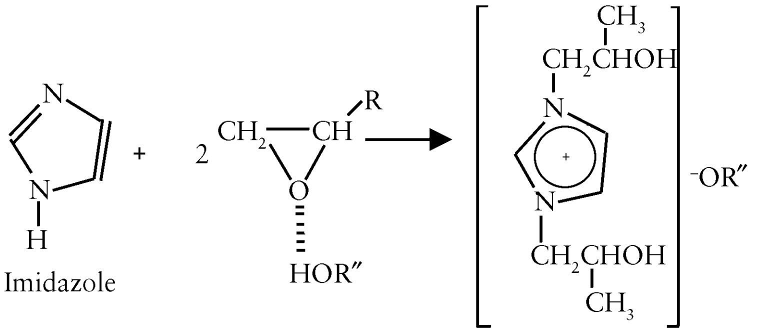


(13.14)

In conclusion, by using low hindered tertiary amines as catalysts for PO polymerisation, higher reaction rates and a low number of side reactions are obtained, at lower polymerisation temperatures (80-90 °C), where the strong base, quaternary ammonium alcoholate is stable and the predominant catalytic species.

In the case of imidazoles [32, 40], the situation is totally changed. With imidazoles and alkyl substituted imidazoles it is possible to develop PO polymerisation initiated by hydroxyl groups, without problems and without deactivation of the catalysts, even at

130-140 °C. The explanation of this behaviour is the formation of a very strong base and stable quaternary ammonium alcoholate, the cation being strongly stabilised by conjugation [32] (structure 13.15).



(13.15)

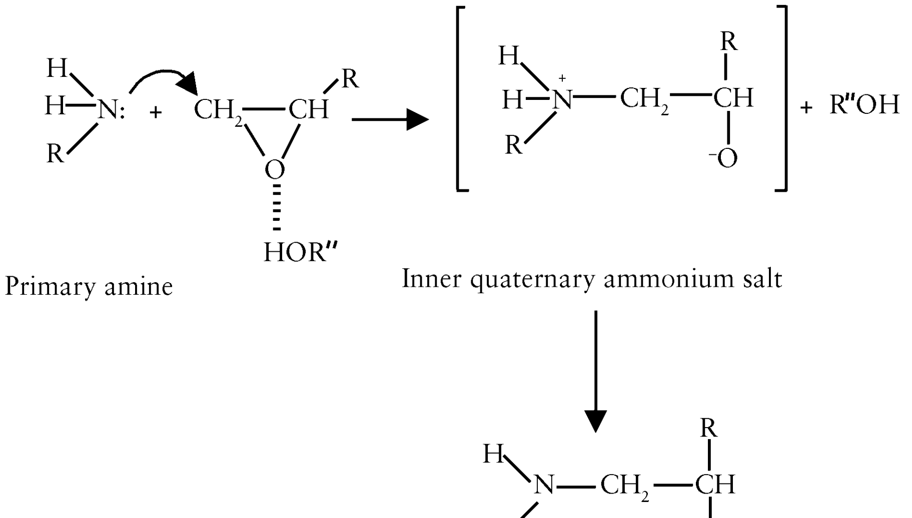
The dark colour of polyether polyols obtained in the presence of imidazoles as catalysts (Gardner colour > 18) can be improved substantially by the treatment with hydrogen peroxide (50% concentration) of around 0.1-0.3% against the polyol. The dark brown colour is the colour of the catalyst and it is not a consequence of polyether destruction. A better final colour is obtained using *N*-substituted imidazoles (such as *N*-methyl imidazole) [36].

Due to the complications generated by the catalysis with tertiary amines, at this moment the most widely used catalyst to obtain rigid polyether polyols is KOH, but some polyethers, especially of very high functionality, are obtained by tertiary amine catalysis.

Tertiary amines have a very important technological advantage: because the rigid PU foams obtained using tertiary amines as catalysts, do not require purification of the resulting polyether polyols. The traces of the tertiary amines, remaining in the polyols after PO polymerisation, have a catalytic effect in PU fabrication. In order to obtain the same reactivity in PU fabrication it is necessary to modify the composition of the formulated polyol, by decreasing the concentration of the amines used as foaming catalysts.

A very interesting catalyst used in the synthesis of polyether polyols for rigid PU foams is urea [41]. Sucrose polyether polyols obtained in the presence of urea as catalyst have a very light colour [41]. Unfortunately with urea it is possible to obtain lower molecular weight polyether polyols, with an hydroxyl number (OH#) higher than 500 mg KOH/g.

The addition of alkylene oxides to -NH_2 amino groups is based on the SN-2 nucleophilic attack of the nitrogen atom, at the α-carbon atom of the oxiranic cycle (reaction 13.16).



(13.16)

The presence of a compound with active hydrogen (water, alcohols, phenols) is obligatory [30, 31, 38, 39]. The weak hydrogen bond of 3-5 kcal/mol between the oxygen atom of oxiranic cycle and hydrogen atom of hydroxyl groups is enough to activate the oxiranic ring, and the nucleophilic attack of a weak nucleophile, such as a primary amine, takes place easily. In the absence of compounds with hydroxyl groups the reaction does not take place.

One observes that during the addition of oxirane compounds to the -NH- amino groups a lot of new hydroxyl groups are formed, which have a strong catalytic effect on reaction 13.16. Due to the increased concentration of hydroxyl groups formed during the reaction, a strong self acceleration of the alkylene oxide addition rate to the amino groups was observed [31]. When all the amino groups are reacted, the rate of alkylene oxide consumption decreases markedly and, in many cases, it is stopped. In order to increase the polymerisation degree/OH group it is necessary to add a catalyst (KOH or NaOH or a low hindered tertiary amine). As mentioned before, the tertiary amines with hydroxypropyl groups have no any catalytic activity in the extension of the chain with PO. It is impossible to continue the reaction with PO. Fortunately, it is possible to continue the polyoxyalkylation reaction, using EO as monomer. EO has a higher ring strain than PO and a lower steric hindrance (no substituents) and is much more reactive and it is possible to continue the reaction, in spite of the low catalytic efficiency of the tertiary amine formed by PO addition to the amino groups (reaction 13.16). Thus, using EO as monomer it is possible to add to the hydroxyl groups until there are 8-9 EO units/OH group (for PO it is only possible to react 1-2 PO units/OH group) [37].

Obviously, the extension of the polyetheric chain using KOH as catalyst needs a purification step. The advantage of using tertiary amines or the catalytic effect of the amino polyol is very important from the technological point of view because the purification step is eliminated, the production cycle is short and the yield in polyether polyol is very high.

13.2 Polyether Polyol Technologies for Rigid Foam Fabrication

Polyether polyols for rigid PU foams (called rigid polyether polyols) are obtained by a similar technology used for synthesis of high molecular weight polyether polyols and using the same installations. The difference is that polyether polyols for rigid foams having lower molecular weights than polyether polyols for elastic polyurethanes can be obtained in only one step (no need to synthesise an intermediate prepolyether, of intermediate molecular weight), because the volume increases from the initial starter mixture to the final polyol volume by a maximum of 3-7 times (as compared with 30-60 times volume increase in the case of polyether polyols for elastic polyurethanes). In fact, instead of glycerol or TMP, high functionality polyols or amines are used as starters - a similar propoxylation reaction takes place in principal, the molar ratio [PO]/[starters] being low, in the range 5-15/1.

Polyether polyols for rigid PU foams are obtained in the same type of polymerisation reactors as those used for high molecular weight polyether polyols, i.e., in stainless steel loop reactors, with an external heat exchanger, preferably with the possibility of generating a large surface of the liquid reaction mass, by a 'spray' technique or by an ejector technique (see Chapter 4.1.5).

Reactors used for the synthesis of rigid polyether polyols need an internal stirrer, because frequently high melting point polyols (such as pentaerythritol or sucrose) are used as starters and the initial reaction mass is a suspension of solid polyols in liquid.

Generally, the polymerisation conditions for polyfunctional polyol alkoxylation, with KOH as catalyst, to rigid polyether polyols are:

a) Temperature: 100-130 °C (usually 105-120 °C),

b) Pressure: 0.3-0.6 MPa (usually 0.35-0.45 MPa),

c) Catalyst concentration: 0.2-0.3% against final polyether polyol,

d) Alkoxylation time: 6-12 hours (depending on the stirring efficiency in the reactor, the heat elimination speed).

For alkoxylation in the presence of tertiary amines, lower alkoxylation temperatures of around 80-95 °C are recommended, because tertiary amines are more active at lower temperatures, as previously explained [31, 32]. The amine concentration varies from 0.3-0.6%, generally it is possible to use the same molar concentration as KOH, around 0.0056 mols to 100 g of final polyol.

At this moment the discontinuous batch processes are the most important processes used worldwide for the fabrication of rigid polyether polyols.

Continuous processes for the synthesis of rigid polyether polyols are discussed [42]. Generally a synthesis of a polyether polyol for rigid PU foams has the following steps:

a) Charge of starters and catalyst,

b) PO (or/and EO) polymerisation reaction,

c) Digestion,

d) Degassing,

e) Purification,

f) Filtration.

Of course for rigid polyether polyol synthesis in the presence of tertiary amines as catalysts, the purification step and sometimes filtration are eliminated, the fabrication process being shorter and simpler.

In order to decrease the total reaction time, a small reactor, with a stirrer, is linked to the polymerisation reactor, for the preparation of the initial starters - catalyst mixture. In this reactor, there are 1-3 polyols used as starters, the catalyst (KOH, NaOH or a tertiary amine) and sometimes, for solid polyols, an initial liquid medium (for example a part of an intermediary or final polyether polyol called ‘heel’, or an inert solvent). Generally, in the synthesis of polyether polyols for rigid foams it is preferred to avoid the utilisation of inert solvents, which need recycling and a more complicated installation.

The mixture of starters and catalyst (especially with solid starters, such as sucrose or pentaerythritol) is stirred for 1-2 hours, under nitrogen at 80-100 °C, to obtain a thermodynamic equilibrium (partial solid solubilisation, solvation of solid surfaces and so on). All these preparations can be made in the small reactor simultaneously with the PO polymerisation reaction. After the polymerisation step and after final polyether evacuation, the prepared mixture of starters with catalyst is added to the polymerisation reactor and the polymerisation reaction begins immediately. Of course, the catalyst can be added separately, directly into the reactor, after charging the starter mixture. After the creation of an inert atmosphere of nitrogen and the increase of reaction temperature in the range used for PO polymerisation, the PO polyaddition begins immediately. The addition of PO (or EO) happens automatically, with continuous removal of the reaction heat, with a cooling jacket and with the external heat exchanger.

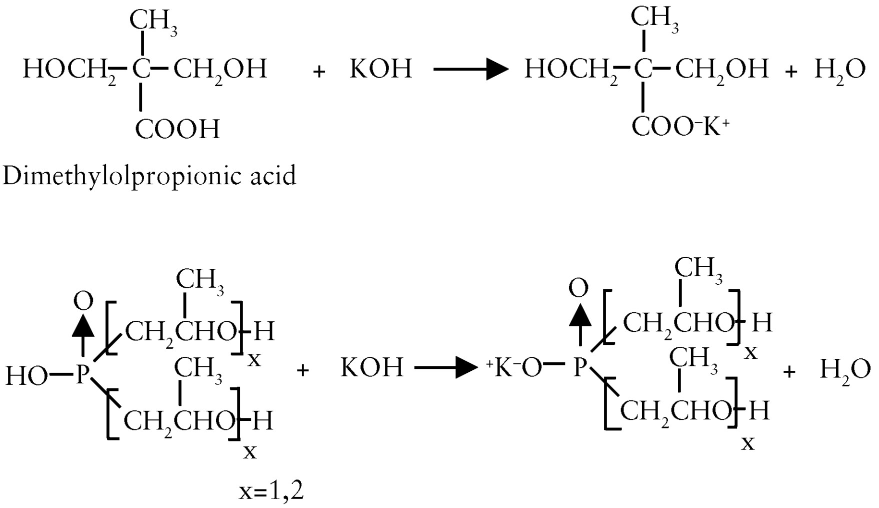
After the addition of all monomers (around 6-12 hours), a digestion takes place, the reaction mass being maintained at the reaction temperature, under stirring for around 1-2 hours. The unreacted PO is consumed and the pressure decreases from 0.35-0.45 MPa to less than 0.1 MPa. The last traces of unreacted PO are removed in two steps: first by nitrogen bubbling and finally by vacuum distillation. The degassing step of around 1-2 hours is considered to be sufficient for the efficient removal of unreacted monomer traces.

The removal of catalyst is not so important for rigid polyether polyols as for polyether polyols for flexible foams. Generally, the crude, alkaline polyether polyol is treated with adsorbents (aluminium or magnesium silicates) or is neutralised with an inorganic or organic acid (HCl, H_2SO_4, H_3PO_4, oxalic, tartaric or adipic acid) and the crystals of potassium salts formed in the polyether medium are filtered (see Chapter 4.1.5). Practically, the polyether polyols obtained are neutral, but the content of remnant ions (K^+ and Na^+) is much higher than for flexible polyols.

For example, in practice, polyethers with an alkaline ion content of 50-400 ppm are used successfully. This is possible because in rigid PU foam production the one shot technique is used predominantly. The prepolymer technique is used to a small extent for one component rigid PU foams, used as sealants or in coatings. In this case the polyol needs less than 2 ppm potassium ion (for example propoxylated glycerol), in order to avoid the gellification of the prepolymers, due to the trimerisation of -NCO groups catalysed by K^+ ions.

It is very interesting that it is possible to obtain rigid polyether polyols, with all potassium ions from the catalyst in the form of a soluble neutral potassium salt. The main condition is that the soluble potassium salt does not markedly catalyse the reaction between -NCO groups and hydroxyl groups. Thus, by using formic acid [43] or lactic acid [44] for neutralisation of the basic catalyst from crude polyethers, polyols are obtained with 2000-3000 ppm K^+ in the form of potassium formiate or potassium lactate, with a normal foaming behaviour, the resulting salt having only a minor catalytic effect on the reactions involved in polyurethane fabrication. On the other hand, by using dodecylbenzenesulfonic acid, oleic acid or acetic acid, it was observed that the resulting soluble potassium salts have an important catalytic effect in the reaction of -NCO groups with the hydroxyl groups and they are not recommended for neutralisation.

The utilisation of hydroxy acids as neutralising agents is based on the following principle: if the acid used for neutralisation has a minimum of 1-2 hydroxyl groups, the potassium salt is integrated in the rigid polyurethane structure and the mobility of potassium ions decreases markedly as does the possibility of catalysis. Hydroxy acids, such as, lactic acid, dimethylpropionic acid, or partially propoxylated phosphoric acid, were used successfully, for the neutralisation of crude, alkaline polyether polyols. The acidic groups are transformed with use of soluble potassium salts (reactions 13.17) and the hydroxyl groups of the resulting potassium salt, react with polyisocianates and are chemically inserted in the polyurethane structure [36].



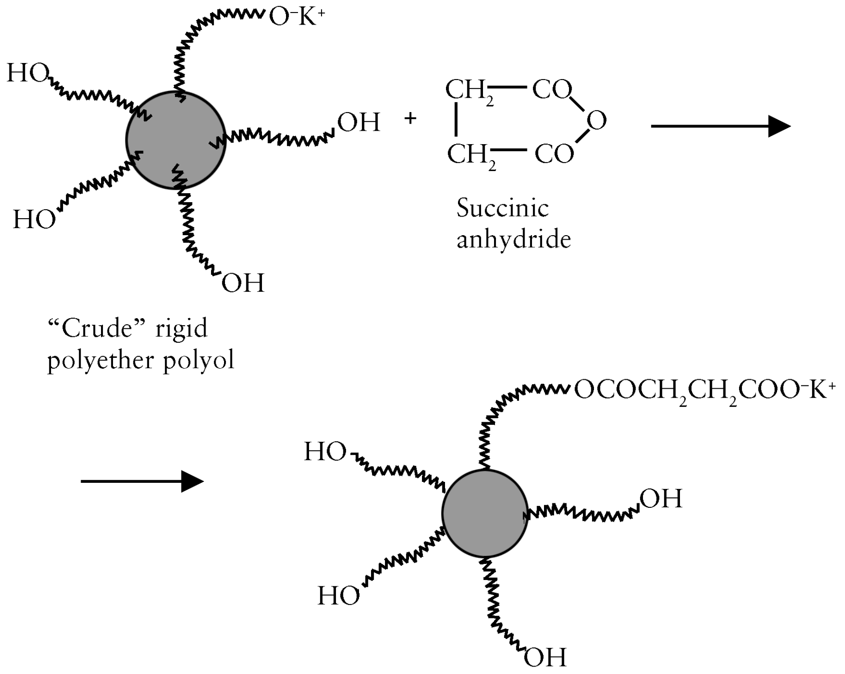
$$HOCH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}}-CH_2OH + KOH \longrightarrow HOCH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COO^-K^+}{C}}-CH_2OH + H_2O$$

Dimethylolpropionic acid

Partially propolylated phosphoric acid

(13.17)

A variant of the previously mentioned application is to make the neutralisation of the crude alkaline, rigid polyether polyol with a cyclic anhydride (for example with succinic or maleic anhydride). A structure is obtained in which the potassium salt is chemically linked to a rigid polyol structure (reaction 13.18) and which enters the polyurethane network during the foaming process. Unfortunately, phthalic anhydride, an easily available and cheap cyclic anhydride, leads to partially insoluble potassium salts [36].



(13.18)

Of course, by using a low steric hindrance tertiary amine as catalyst or by neutralisation with formic acid [43] or with hydroxyacids [44], the purification step is avoided, and the fabrication process is simpler, more productive and the necessary equipment simpler.

The technological flow for the rigid polyether polyols fabrication with KOH as catalyst and with tertiary amines as catalysts are presented in **Figures 13.5** and **13.6**, respectively.

Table 13.1 and **Table 13.2** show that the polyols and a polyamine used as starters for rigid polyols are divided in two categories:

a) polyols and polyamines which are liquids at the temperature of PO polyaddition reaction (the melting points are lower than the alkoxylation temperature) such as: glycerol, TMP, sorbitol (mp = 97.7 °C), xylitol and all the amines (o-TDA: mp = 63-64 °C, MDA: mp = 92-93 °C);

b) polyols which are solid at the PO polymerisation temperature, having higher melting points (mp > 130 °C) such as: pentaerythritol (mp = 253 °C), dipentaerythritol (mp = 222 °C), α-methyl glucoside (mp = 164-165 °C), sucrose (mp = 179-180 °C).

In the case of the first group of polyols (a), the PO polyaddition reaction takes place without problems because all the reaction partners are liquid in the reaction conditions.

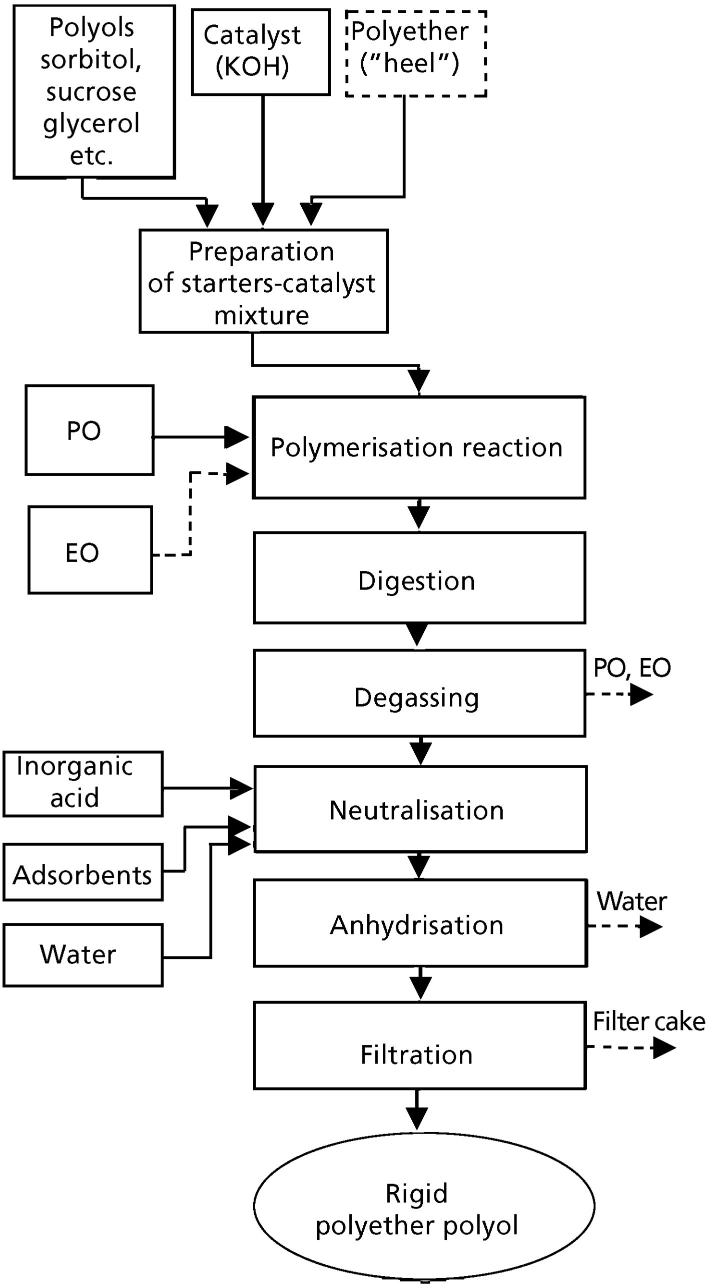


Figure 13.5 Flow diagram for rigid polyether polyol fabrication (catalyst: KOH)

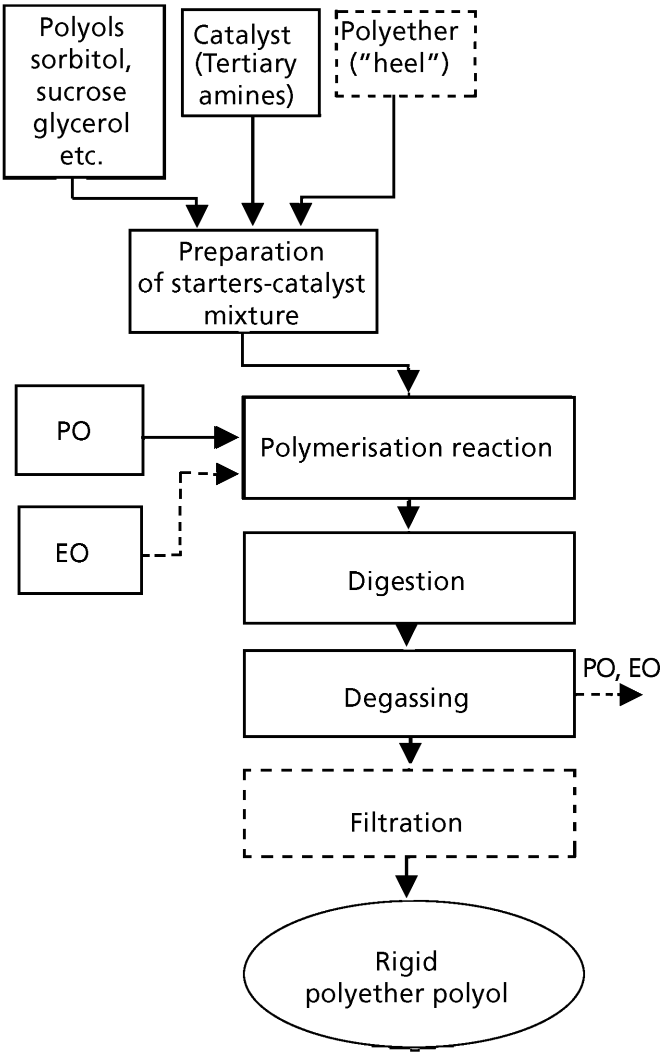


Figure 13.6 Flow diagram for rigid polyether polyol fabrication (catalyst: tertiary amines)

The second group of polyols, which are solid at the temperature conditions of PO polymerisation lead to very serious technological problems: how is it possible to efficiently react a solid polyol with a gaseous monomer (PO boiling point (bp) is 33.6 °C and the EO boiling point is 10.8 °C). This problem was solved in various ways and is discussed in detail in section 13.2.4.

13.2.1 Anionic Polymerisation of PO (or/and EO) Initiated by Polyols which are Liquid at the Reaction Temperature

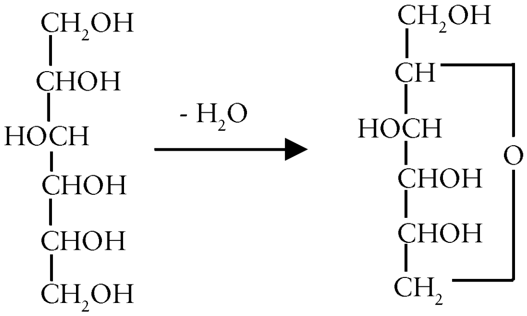
The synthesis of rigid polyether polyols, by polymerisation of PO or EO, initiated by polyols which are liquid under the conditions of the polymerisation temperature, is simple, and similar to the synthesis of the prepolyether by propoxylation of glycerol (see Chapters 4.1.1 and 4.1.5).

The polymerisation reactor is charged with a polyol - catalyst mixture and, under an inert atmosphere of nitrogen, PO (or EO) is added at the polymerisation temperature, preferable 105-125 °C for KOH or NaOH catalysts and 80-95 °C for tertiary amines.

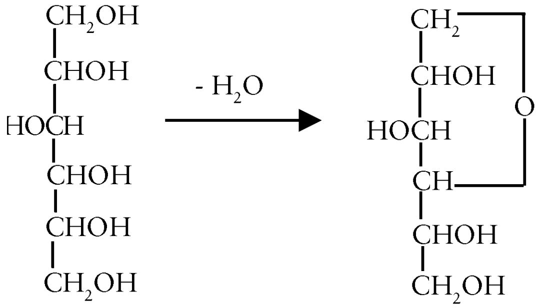
The single polyol from this group that needs special attention is sorbitol, which is delivered in the form of an aqueous solution of around 70%. It is possible to use solid sorbitol, which is delivered in the form of crystalline monohydrate, but it is much more expensive than liquid sorbitol (calculated as a dry substance) and more difficult to handle and melt. The polyols delivered as aqueous solutions need water distillation under vacuum, in order to limit the formation of polyether diols during the reaction with PO, which decreases the functionality of the resulting polyether polyols. There are two possibilities: to distill water until a relatively low level (0.1-0.5%) is reached or to make a controlled distillation of water, by stopping the distillation at a level of water which, together with sorbitol should lead to a functionality of 4.5-5 hydroxyl groups/mol.

It is well known that pure solid sorbitol gives polyether polyols with a very high viscosity, which are difficult to use in practice (higher than 50,000 mPa-s, at 25 °C). By using controlled quantities of water it is possible to decrease the functionality to a lower value, but this is perfectly acceptable. The equivalent functionality of 4.5-5 hydroxyl groups/mol leads to much lower viscosities in the resulting polyether polyols (5000-10000 mPa-s).

It is important to note that if the distillation of water from sorbitol solutions is conducted at too high a temperature, for example in excess of 140 °C, cyclic ethers called sorbitans are formed (by the intramolecular etherification of sorbitol), which have lower functionality than sorbitol (structures 13.19 and 13.20).



Sorbitol 1,5 cyclic sorbitan (13.19)



Sorbitol 1,4 cyclic sorbitan (13.20)

The most important polyether polyols from this first group of low melting point starters are sorbitol-based polyether polyols, which are considered to be the universal polyols for rigid PU foams. They can be used in all applications of rigid polyurethane foams, such as thermoinsulation, wood imitations, packaging, flotation materials and so on.

As mentioned previously, sorbitol is not used alone as starter, it is generally used in a mixture with a second polyol, such as, sorbitol - glycerol, sorbitol - dipropyleneglycol, sorbitol - water [19], or sorbitol - diethyleneglycol.

With a two polyol mixture it is very important to calculate the quantity of PO (Q_{PO}) needed to be added to a mixture of Q_1 (the quantity of first polyol) and Q_2 (the quantity of second polyol) in order to obtain the desired final hydroxyl number (I_f):

$$Q_1 * I_1 + Q_2 * I_2 = \left(Q_1 + Q_2 + Q_{PO}\right) * I_f$$

$$Q_1 * I_1 + Q_2 * I_2 = \left(Q_1 + Q_2\right) * I_f + Q_{PO} * I_f$$

$$Q_{PO} = \frac{Q_1 * I_1 + Q_2 * I_2 - \left(Q_1 + Q_2\right) * I_f}{I_f}$$

where:

Q_1 = quantity of polyol 1
Q_2 = quantity of polyol 2
Q_{PO} = quantity of PO
I_1 = hydroxyl number of $polyol_1$
I_2 = hydroxyl number of $polyol_2$
I_f = hydroxyl number of final polyether polyol

Usually, in practice the sum is calculated first (13.21) and the quantity of PO needed to obtain the desired final hydroxyl number is then easily calculated (13.22).

$$Q_1 + Q_2 + Q_{PO} = \frac{Q_I * I_1 + Q_2 * I_2}{I_f} \tag{13.21}$$

$$Q_{PO} = \frac{Q_1 * I_1 + Q_2 * I_2}{I_f} - \left(Q_1 + Q_2\right) \tag{13.22}$$

It is also important to calculate the equivalent functionality of the mixture of two polyols with different functionalities. The equivalent functionality (f_e), of a mixture of two polyols is calculated with the following general formula (relationship 13.23):

$$f_e = x_1 * f_1 + x_2 * f_2 \tag{13.23}$$

where:

f_e = equivalent functionality
f_1 = functionality of polyol 1
f_2 = functionality of polyol 2
x_1 = molar fraction of polyol 1
x_2 = molar fraction of polyol 2

$$x_1 = \frac{n_1}{n_1 + n_2} \qquad x_2 = \frac{n_2}{n_1 + n_2}$$

$$n_1 = \frac{Q_1}{M_1} \qquad n_2 = \frac{Q_2}{M_2}$$

where:

n_1 = number of mols of polyol$_1$
n_2 = number of mols of polyol$_2$
M_1 = molecular weight of polyol$_1$
M_2 = molecular weight of polyol$_2$

$$f_e = \left(\frac{\frac{Q_1}{M_1}}{\frac{Q_1}{M_1} + \frac{Q_2}{M_2}} \right) * f_1 + \left(\frac{\frac{Q_2}{M_2}}{\frac{Q_1}{M_1} + \frac{Q_2}{M_2}} \right) * f_2 \tag{13.24}$$

The relationship 13.24, is frequently used in practice, and after the rearrangement of terms, becomes relationship 13.25:

$$f_e = \left[\frac{1}{\frac{Q_1}{M_1} + \frac{Q_2}{M_2}} \right] * \left(\frac{Q_1}{M_1} * f_1 + \frac{Q_2}{M_2} * f_2 \right)$$

$$f_e = \frac{Q_1 * f_1 * M_2 + Q_2 * f_2 * M_1}{Q_1 * M_2 + Q_2 * M_1} \tag{13.25}$$

A practical problem, which appears frequently is to calculate the quantity of polyol 2 (Q_2) to be added to the quantity of polyol 1 (Q_1) in order to obtain the desired equivalent functionality (f_e). Of course the problem is solved by using relationship 13.24, but it is possible to use a more simplified relationship (13.26) deduced from relationship 13.25:

$$\begin{aligned} &Q_1 * M_2 * f_e + Q_2 * M_1 * f_e = Q_1 * f_1 * M_2 + Q_2 * f_2 * M_1 \\ &Q_1 * M_2 * (f_e - f_1) = Q_2 * M_1 * (f_e - f_2) \\ &Q_2 = \frac{Q_1 * M_2 * (f_e - f_1)}{M_1 * (f_e - f_2)} \end{aligned} \tag{13.26}$$

A practical example: what is the quantity (Q_2) of glycerol necessary to add to Q_1 (100 parts of sorbitol), to obtain an f_e of 5 hydroxyl groups/mol? By using the relationship 13.26 one obtains:

$$Q_2 = \frac{100 * 182 (5 - 6)}{92 * (3 - 5)} = 25.2 \text{ parts of glycerol}$$

13.3 Kinetic Considerations Concerning the Alkoxylation of Polyols to Rigid Polyether Polyols

For glycerol propoxylation to high molecular weight polyethers, the PO polyaddition to hydroxyl groups is characterised by two rate constants: K_i (constant of the initiation reaction, in fact the direct reaction with starter) and K_p (propagation constant, the reaction of PO with the formed hydroxypropyl groups). In the synthesis of high molecular weight glycerol-based polyethers, where the molar ratio between PO/glycerol is around 80-140/1, the most important step is the propagation reaction because, after the addition of 5 mols of PO/mol of glycerol, all the hydroxyl groups become hydroxypropyl groups and under these conditions the initiation step is neglected.

In case of rigid polyether polyols, where the polymerisation degree is low (maximum 6-16 PO units/mol of polyol), it is not possible to neglect the initiation step.

The model reaction kinetics for the propoxylation or ethoxylation of fatty alcohols and nonylphenol, for surfactant synthesis, was developed successfully by Santacesaria and co-workers [45-50]. Of course, it is clear that, in principle, there are many similarities between the propoxylation of a fatty alcohol and the propoxylation of polyols, but there are some small differences.

Unfortunately, it is a difference between a starter, such as nonylphenol, or a fatty alcohol, which have only one type of hydroxyl group and polyols. Some polyols used as starters for rigid polyether polyols have in the same molecule various types of hydroxyl groups (for example, primary hydroxyls and secondary hydroxyls) which do not have equivalent reactivities in the alkoxylation reactions. For example, sorbitol has two primary hydroxyls and four secondary hydroxyls, sucrose has three primary hydroxyls and five secondary hydroxyls. In both polyols, the secondary hydroxyls have different substituents and they are not totally equivalent. TMP, pentaeriythritol and dipentaerythritol have only one type of equivalent primary hydroxyl group. Thus, the initiation reaction (reaction of PO with hydroxyl groups of starter) is in fact the sum of the reactions of PO with each type of hydroxyl group of the starter:

$$\mathrm{Ro} = -\frac{d[\mathrm{PO}]}{dt} = K_i[\text{catalyst}]*[\mathrm{PO}] = K_{i1}[\mathrm{RX}_1^-][\mathrm{PO}] + Ki_2[\mathrm{RX}_2^-][\mathrm{PO}] + \\ + \,.........K_{in}[\mathrm{RX}_n^-][\mathrm{PO}]$$

$$\mathrm{Ro} = -\frac{d[\mathrm{PO}]}{dt} = \sum_{n-1}^{n} K_{in}[\mathrm{RX}_n^-][\mathrm{PO}]$$

RX_1^- , RX_2^- , RX_n^- are the alcoholate groups derived from each type of hydroxyl group from the starter.

The propagation reaction Rp is characterised by the following kinetic equation:

$$Rp = -\frac{d[PO]}{dt} = Kp\left[RX_i(PO)^-\right][PO]$$

$RX_i(PO)-$ = are the alcoholates derived from the formed hydroxypropyl groups

$$\sum_{n=1}^{n}\left[RX_{n-}^{-}\right]+\left[RX_i(PO)^-\right]=[\text{catalyst}]\ (\text{total catalyst concentration})$$

The global reaction rate Rt of propylene oxide polyaddition to various polyols is the sum between the initiation reaction (Ro) and propagation reaction (Rp):

$$Rt = Ro + Rp = -\frac{d[PO]}{dt} = \sum_{n=1}^{n} K_{in}\left[RX_{n-}^{-}\right][PO] + Kp\left[RX_i(PO)^-\right][PO]$$

Of course, the repartition of the anionic active centres on various hydroxyl groups in the reaction system is based on the following equilibrium reactions:

$$RX_n^- + R_iOH \overset{Ke}{\rightleftharpoons} RX_nH + R_iO^-$$

$$Ke = \frac{[RX_nH][R_iO^-]}{[RX_n^-][R_iOH]}$$

The polymerisation of PO and EO, initiated by polyfunctional starters, to make short chain polyether polyols is a reaction that is strongly dependent on diffusion. The consumption rate of PO or EO is given by two simultaneous factors: the rate of the chemical reaction in the liquid phase and the efficiency of the monomer mass transfer from the gaseous phase to liquid phase (see details in section 4.1.5). The PO (or EO) consumption rate, considering the mass transfer, is described by equation 13.27 [45-50]:

$$Rmt = -\frac{d[PO]}{dt} = K_L * S * \left([PO_b]-[PO_t]\right) \tag{13.27}$$

In pseudo steady-state Rmt-Rt:

$$K_L * S * \Bigg([PO_b]-[PO_t] = \sum_{n=1}^{n} K_{in}\left[RX_{n-}^{-}\right][PO] + Kp\left[RX_i(PO)^-\right][PO]$$

From the equation the $[PO_t]$ value is obtained:

$$\left[PO_t\right] = \frac{K_L * S * \left[PO_b\right]}{K_L * S + \sum_{n=1}^{n} K_{in}\left[RX_n^-\right] + Kp\left[RX_i(PO)^-\right]} \tag{13.28}$$

where:

K_L = mass transfer constant

S = surface of the gas-liquid interface

PO_b = solubility of PO in liquid reaction conditions

PO_t = concentration of PO in steady-state liquid

Equation 13.28 shows the very important role of the interface gas-liquid surface. Generally, a very high PO consumption rate is obtained if a reaction mass with a high surface area is generated, either by 'spray' reactor type or by ejector reactor type (described in detail in Chapter 4).

Details regarding the mathematical model of propoxylation or ethoxylation reactions are presented in the work of Santacesaria and co-workers [45-50].

The polymerisation reaction of PO takes place only in the liquid phase, where the catalyst is. The reaction rate depends on the concentration of monomer and catalyst in the liquid phase. Concentration of monomer in the liquid phase depends on the solubility of PO in the liquid reaction medium at the appropriate reaction conditions (temperature and pressure) which are variable during the polymerisation reaction. On the other hand, during PO polyaddition, the volume of the reaction mass increases continuously and, of course, the concentration of the anionic active centres decreases proportionally. As an immediate consequence one concludes that the reaction rate is variable during the PO or EO polymerisation reaction, i.e., it is not constant.

Unfortunately, in reality, at the beginning of the polymerisation reaction the solubility of PO in the polyolic starters (for example in molten sorbitol) is lower than in the adducts of PO to sorbitol. As an immediate consequence, an initial lower consumption rate of PO (in spite of the presence of two reactive primary hydroxyl groups in sorbitol) takes place (induction period). After the addition of 2-3 mols of PO/mol of sorbitol, the solubility of PO in the reaction mass increases substantially and the PO polymerisation reaction is strongly accelerated. **Figure 13.7** shows the PO consumption with time in the propoxylation of sorbitol at 120 °C. It is observed that after a short induction period of 40-60 minutes, the PO consumption is markedly accelerated.

On the contrary, by propoxylation of TMP, which has three equivalent primary hydroxyl groups, the reaction begins without an induction period and the PO consumption is rapid from the beginning. This behaviour is probably explained by the higher solubility of PO (hydrophobic monomer), in the molten starter, due to the presence of the hydrophobic ethyl group of TMP.

The polyether polyols for rigid PU foams based on polyols which are liquid under the conditions of alkylene oxides polymerisation are: glycerol and TMP polyether triols, of various molecular weights, sorbitol-based polyols (based on a mixture of sorbitol – glycerol, sorbitol – dipropyleneglycol, sorbitol – dithylene glycol) and xylitol-based polyether pentaols.

Table 13.3 shows some polyether triols, based on glycerol, with various hydroxyl numbers between 250-600 mg KOH/g. Generally, these polyols are not used alone in foaming formulations, because they lead to rigid PU foams of modest physico-mechanical properties. Since glycerol-based rigid polyether polyols have low viscosities, they are used in combination with high functionality polyols, to decrease the viscosity of the resulting formulations:

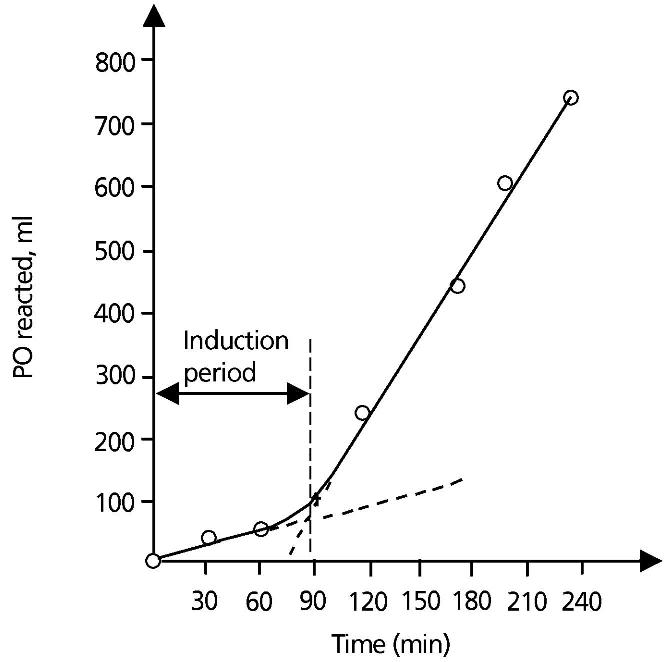
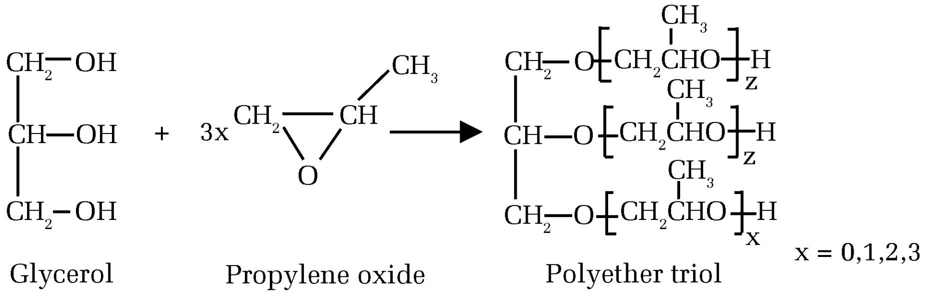


Figure 13.7 PO consumption *versus* time in sorbitol propoxylation. Temperature: 120 °C; pressure: 0.35-0.4 MPa; catalyst [KOH] = 0.0056 mol%



The glycerol-based rigid polyether triols are low viscosity liquids, nearly colourless and practically all the terminal groups are secondary hydroxyl groups. These polyols are frequently used as starters for the synthesis of high molecular weight polyether triols, with DMC catalysts (see Chapter 5). Some of these polyether triols are transformed into prepolymers, for example by the reaction with pure diphenylmethane diisocyanate (MDI) and then used for monocomponent rigid polyurethane foams (the hardening is a consequence of the -NCO groups of prepolymers reaction with the atmospheric humidity).

In **Table 13.4** the characteristics of some rigid polyether polyols based on a sorbitol - glycerol mixture are presented. The initial starter mixture is solution of sorbitol (70%) and glycerol. After water vacuum distillation, the mixture of sorbitol - glycerol containing 0.1-0.5% water, is propoxylated in the presence of a KOH catalyst, followed by the usual purification. These polyether polyols are transparent viscous liquids, which are colourless or slightly yellow polyols:

Table 13.3 The characteristics of some glycerol-based triols for rigid PU foams

Characteristic	**Unit**	**MW = 1000**	**MW = 550**	**MW = 400**	**MW = 300**
Functionality	OH groups/mol	3	3	3	3
Molecular weight	daltons	1000-1055	550	400	300
Hydroxyl number	mg KOH/g	158-162	300-310	420-430	550-600
Viscosity, 25 °C	MPa-s	270-280	300-310	410-430	730-750
Acid number	mg KOH/g	0.05-0.1	0.05-0.1	0.05-0.1	0.05-0.1
Water content	%	max. 0.05	max. 0.05	max. 0.05	max. 0.05

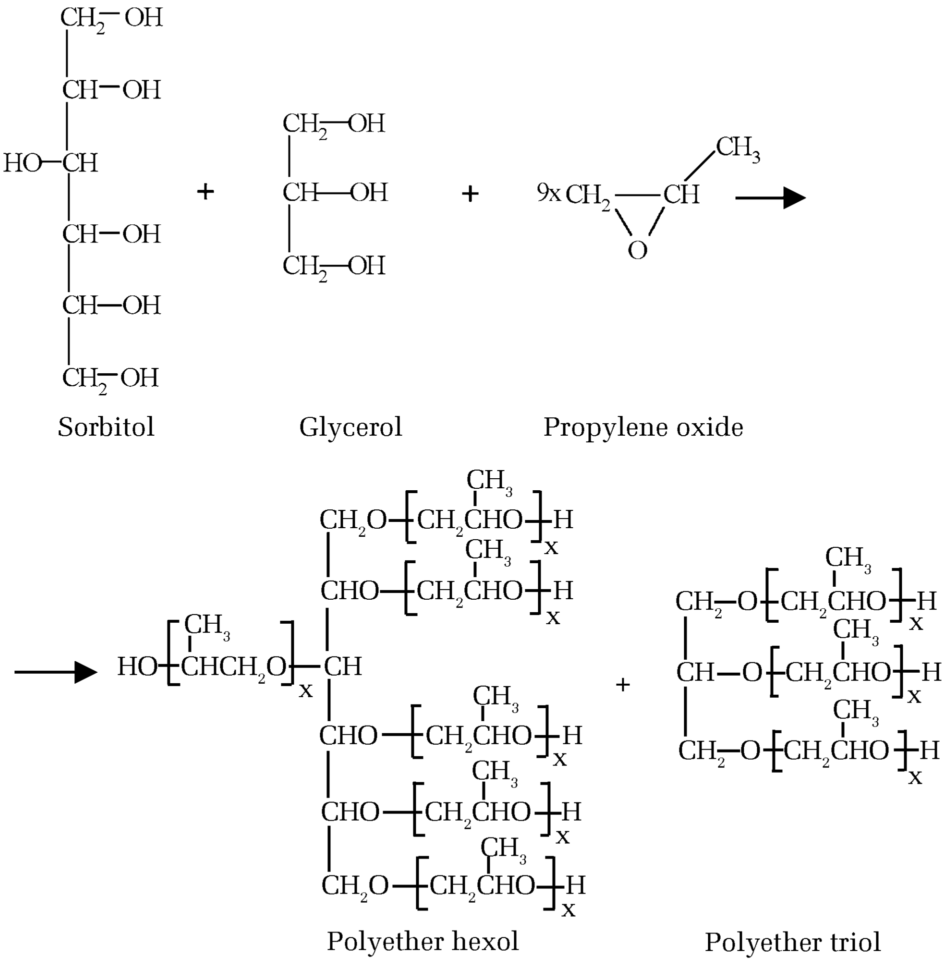
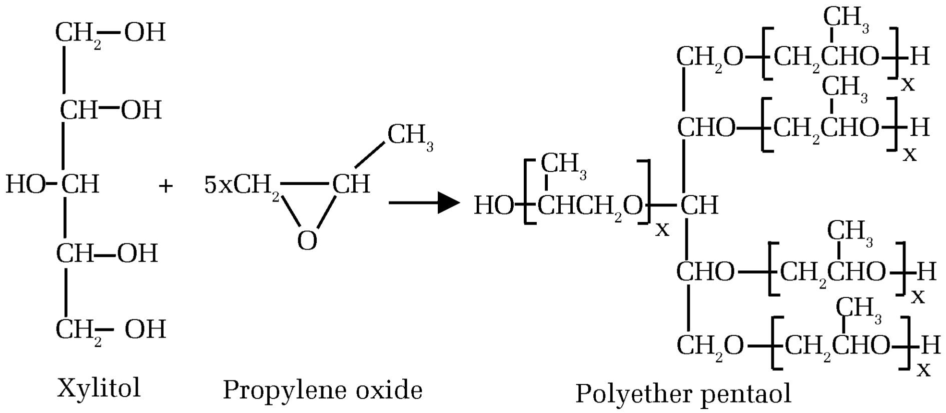


Table 13.4 The characteristics of some sorbitol-glycerol based rigid polyether polyols for rigid PU foams

Characteristic	Unit	Type I MW = 570-620	Type II MW = 510-520
Functionality	OH groups/mol	5	5
Molecular weight	daltons	570-620	510-520
Hydroxyl number	mg KOH/g	450-490	500-550
Viscosity, 25 °C	MPa-s.	4500-8000	20000-30000
Acid number	mg KOH/g	max. 0.1	max. 0.1
Water content	%	max. 0.1	max. 0.1
Density, 25 °C	g/ml	1.08-1.1	1.09-1.15
Na and K	ppm	max.50	max.50

Of course similar sorbitol polyols are obtained by direct propoxylation of the mixtures sorbitol - dipropyleneglycol (DPG), sorbitol - diethyleneglycol (DEG) and sorbitol-water.

A very interesting starter is xylitol, a polyol similar to sorbitol, with the difference that xylitol has five carbon atoms and five hydroxyl groups. Because its functionality is very convenient for rigid PU foams (functionality is 5 hydroxyl groups/mol), this polyol does not need any auxiliary polyol and is propoxylated directly, in the molten state (mp = 90-92 °C). All these starters: glycerol (from vegetable oils and fat hydrolysis), sorbitol (hydrogenation of glucose) and xylitol (hydrogenation of pentoses) have the advantage of being raw materials from renewable resources (see Chapter 4.8).



13.3.1 Anionic Polymerisation of PO (or/and EO) Initiated by High Melting Point Polyols which are Solid at the Reaction Temperature

Many important polyols used as starters for synthesis of rigid polyether polyols are solid in the conditions used for PO (or/and EO) polyaddition, having a melting point higher than 130 °C. Such polyols are: sucrose (mp = 179-180 °C), pentaerythritol (mp = 253 °C), dipentaerythritol (mp = 222 °C), α-methyl glucoside (mp = 164-165 °C) and other polyols. As mentioned previously, the main technical problem is to react a solid polyol with a gaseous monomer. This problem was solved by several practical solutions:

a) Using water as an initial reactive medium. The mixture of water - solid polyol is partially alkoxylated (in principal propoxylated) in the first step, followed by an intermediate distillation of water and the diols formed, and then a second alkoxylation (propoxylation) of the anhydrised reaction mass [14, 19];

b) To propoxylate a mixture between the solid polyol and a low melting point polyol such as: sucrose - glycerol [12, 30], sucrose - triethanolamine [9, 10], sucrose – diethylene glycol [51], sucrose-aromatic amines [25].

c) To use an inert solvent as liquid reaction medium such as: dimethylformamide (DMF) [35], toluene [52], xylene [15, 16, 53], dimethylsulfoxide, etc.

d) To use a polyether polyol as a liquid reaction medium, called ‘heel’. The solid polyol is suspended in a liquid polyether and is propoxylated [30, 54-56];

e) To use liquid propylene oxide or a mixture of propylene oxide - ethylene oxide as a reaction medium [17, 18].

In all the previous variants for propoxylation of solid polyols one thing is very important: the second substance added must solvate the solid polyol well. The reaction between gaseous monomer and solid polyol takes place at the surface, and partially, with the solvated polyol. Liquid adducts of PO to the solid polyol are formed. These adducts are solubilised into the liquid reaction medium and, step-by-step, all the solid is transformed in liquid polyether polyols. If the liquid reaction medium does not solvate the surface of the solid polyol well, a large quantity of unreacted polyol remains at the end of the propoxylation reaction.

Of course, in some variants, the solid polyols are partially solubilised, for example in water, in glycerol or in DMF. In these situations the reaction takes place without problems in the liquid phase and, at the same time at the well solvated surface of the high melting point solid polyol. Each variant for synthesis of rigid polyether polyols, based on high melting point polyols, will be described in detail.

a) Utilisation of water as reactive reaction medium [1, 14, 19]

One of the most popular technologies for synthesis of sucrose derived polyether polyols is based on the propoxylation of a mixture of sucrose - water (mixture very rich in sucrose). It is well known that water is the best solvent for substances having hydroxyl groups such as carbohydrates and polyols. Water is the best solvent for sucrose, one part of water is able to solubilise four parts of sucrose, at 100 °C.

Thus, a quantity of sucrose is added to a quantity of water, to obtain a stirrable mixture of sucrose in solution.

By propoxylation of this mixture of sucrose - water, in anionic catalysis (KOH or NaOH), propylene oxide (or EO) react not only with the hydroxyl groups of sucrose but react with water too, which is not an inert compound in this reaction (see Chapter 4). The reaction of PO with water causes diols (propyleglycol, dipropyleneglycol, etc.) to be formed, which decrease markedly the functionality of the resulting sucrose polyol. In order to minimise as much as possible, the diol formation, the propoxylation reaction of the sucrose - water mixture is divided into two steps:

(1) the initial reaction mass is reacted with a minimum quantity of PO, to transform all the initial reaction mass in a liquid (15-30% from the total quantity of PO). After that, the unreacted water and a part of the diols formed are vacuum distilled. The resulting reaction mass, which has in its composition low molecular weight PO adducts to sucrose and remaining undistilled oligopropylene glycols, is propoxylated with the rest of the PO and the final polyether polyol is thus obtained. The resulting polyether polyol is a mixture between octol polyether and a diol polyether, the functionality being in the range of 4.5-6 OH groups/mol, depending on the efficiency of the intermediate water and glycol distillation.

(2) The crude alkaline polyether is purified, a very popular variant being the purification by treatment with solid disodium acid pyrophosphate, in the presence of 1-2% water. After neutralisation of the alkaline catalyst, water is vacuum distilled and the polyether is filtered, at 0.4-0.6 MPa, using high surface pressure filters (for example a filter press). In order to facilitate the filtration, a small quantity of filter aids (for example diatomites) is added. Sometimes, for improving the sucrose polyether polyol colour, a small quantity of hydrogen peroxide (around 50% concentration) is added after the neutralisation step. A flow chart for polyol - water mixture propoxylation technology is presented in **Figure 13.8**.

The resulting filter cakes contain around 40-60% of polyether polyol. In order to improve the yield of the polyether, in some technologies the polyether is extracted with a solvent and, after the distillation of the solvent, 90-95% of the polyether retained in the filter cake is recovered. Low price solvents are used, such as *n*-hexane, hexane fractions, toluene, etc. A recovery method for polyether retained in the filter cakes, based on the extraction with PO in a closed system, was developed [57].

The resulting solutions of polyether in PO are used in the propoxylation step. By recovery of the polyether retained in the filter cakes, the global yield of the final polyether increases by around 3-4%.

The big disadvantages of this technology are: the long reaction time, many technological phases and the difficulty of establishing exactly the real final polyol functionality (the content of the diols remaining in the polyether after the intermediate vacuum distillation is difficult to measure accurately).

b) Rigid polyether polyols by propoxylation of the mixture of solid high melting point polyols - low melting point polyols [9-19, 30]

The representative examples are the synthesis of sucrose–based polyether polyols with a low melting point. Sucrose is well solvated by low molecular weight polyols such as glycerol, diethylene glycol, dipropylene glycol, triethanolamine and sorbitol. At the

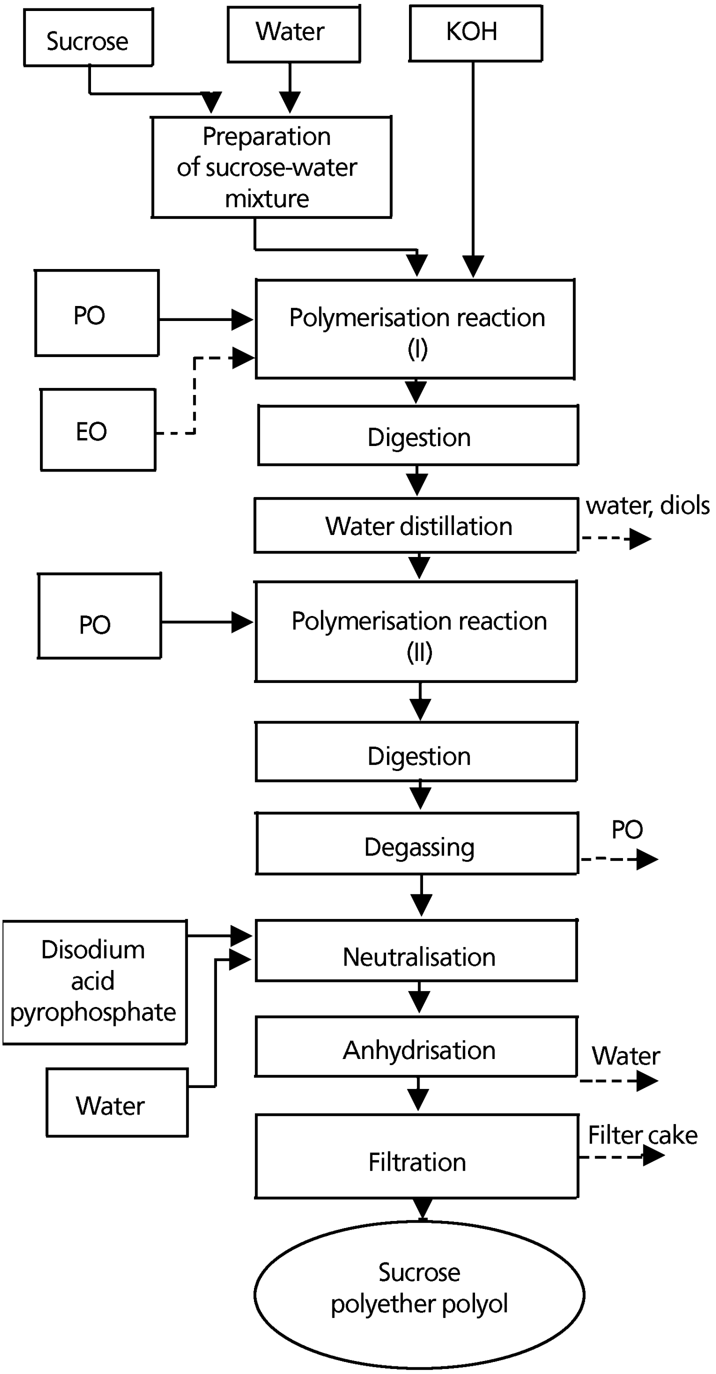


Figure 13.8 Flow chart for sucrose-water technology for polyether polyol fabrication

temperature of the propoxylation reaction part of sucrose is solubilised. For example, the solubility of sucrose in glycerol, at 120 °C is around 40-45% (40-45 parts of sucrose are solubility by 100 parts of glycerol). Triethanolamine has an exceptional effect on the solvating ability of solid sucrose. The same effect was observed with sorbitol. The molten sorbitol solvates very efficiently the solid sucrose and the propoxylation of the mixture of sucrose - sorbitol is a very efficient way to obtain a very high functionality polyether polyol (e.g., f = 7 OH groups/mol). Generally, the polyols having ethylene oxide units, have an exceptional solvating capacity for sucrose, superior to the propoxylated polyols. A very good co-polyol for sucrose from this category is diethylene glycol [51], which has a superior solvating capacity to dipropylene glycol.

The equivalent functionality of the resulting rigid polyether polyols is situated between the functionality of sucrose (f = 8 OH groups/mol) and the functionality of the second polyol (f = 2-3 OH groups/mol for glycols, glycerol or triethanolamine and 6 OH groups/mol for sorbitol). The equivalent functionality is calculated easily by using the formula 13.23.

The advantage of these types of processes: direct propoxylation of a mixture of high melting point polyol with a low melting point polyol, is the perfect control of the final functionality in the resulting polyether (function of the ratio of sucrose/second polyol), and the simplicity of the process with only one propoxylation step, without intermediate distillations.

Figure 13.9 shows the equivalent functionalities of different sucrose - polyol mixtures as a function of the gravimetric ratio of sucrose/second polyol. **Figure 13.9** shows that, except

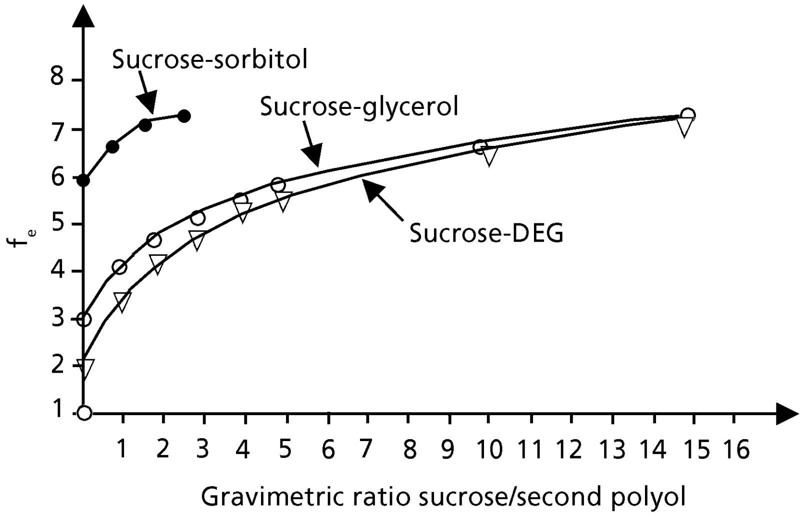


Figure 13.9 The equivalent functionalities (f_e) of mixtures of sucrose/second polyol as a function of the gravimetric ratio of sucrose:second polyol

for the mixture sucrose – sorbitol, very high functionalities (f = 6.5 – 7 OH groups/mol) are obtained only at very high ratios of sucrose/second polyol.

One observes that an f_e of 7 needs a mixture of sucrose - glycerol, very rich in sucrose (ratio of sucrose/glycerol around 15/1). For the sucrose - sorbitol mixture, the same functionality of 7 is obtained at a ratio of 1 mol/1 mol (sucrose/sorbitol), corresponding to a gravimetric ratio of around 1.86/1.

The mixtures rich in sucrose are practically impossible to stir. The mixtures of sucrose/glycerol (1-3/1) are easy to stir at 110-120 °C. Unfortunately, for higher ratios of sucrose/second polyol this variant of technology is impossible to apply.

The mixtures of sucrose - triethanolamine, usually of 1-1.5/1 (sucrose/triethanolamine) [9] are very stirrable mixtures, at the propoxylation temperature, and are frequently used in practice. Triethanolamine can be replaced by diethanolamine, monoethanolamine and even by ammonia [59]. The triol is formed *in situ* by the reaction of ammonia or primary or secondary ethanolamines with PO. The polyols based on sucrose – triethanolamine (**Table 13.6**) are frequently used to make rigid PU foams for thermoinsulation of freezers. The mixtures of sucrose - sorbitol lead easily to high functionality polyols, sorbitol having an excellent solvating capability for solid sucrose.

DEG is a very interesting copolyol for making sucrose-based rigid polyether polyols. Due to the high polarity of ethylene oxide units, DEG-sucrose mixtures [51] show an excellent stirrability of the initial reaction mass, but only for medium functionalities of around 4-5 OH groups/mol.

This method of direct propoxylation of mixtures between sucrose and a second polyol is often used in practice, the most important polyols being based on: sucrose - glycerol, sucrose - triethanolamine and sucrose - diethyleneglycol.

Table 13.5 shows the characteristics of some rigid polyether polyols, based on sucrose - glycerol and sucrose - triethanolamine.

The reactions (13.29 and 13.30), involved in the propoxylation of mixtures of sucrose - various polyols (glycerol, triethanolamine or DEG) lead to a mixture of two polyols, one is the polyether octol derived from sucrose and the second polyol is derived from the copolyol (triol or diol), the degree of polymerisation x/hydroxyl group being very short (x = 0, 1, 2, 3 PO units).

c) Utilisation of an inert solvent as liquid reaction medium

In the scientific literature processes are presented which use an inert solvent, as a liquid reaction medium for propoxylation (or/and ethoxylation) of high melting point polyols

Table 13.5 The characteristics of some sucrose - glycerol based rigid polyether polyols for rigid PU foams (structures I, II and III)

Characteristic	Unit	I	II	III
Functionality	OH groups/mol	4.3-4.5	5-5.5	6.5-7
Molecular weight	daltons	490-670	620-770	930-1090
Hydroxyl number	mg KOH/g	360-490	400-450	360-390
Viscosity, 25 °C	mPa-s	3400-7000	5000-10000	20000-35000
pH	-	6.5-8	6.5-8	6.5-8
Acid number	mg KOH/g	< 0.1	< 0.1	< 0.1
Water content	%	< 0.1	< 0.1	< 0.1

Table 13.6 The characteristics of a representative sucrose-triethanolamine-based rigid polyether polyol for rigid PU foams (structure I)

Characteristic	Unit	I
Functionality	OH groups/mol	4.6-4.7
Molecular weight	daltons	510-550
Hydroxyl number	mg KOH/g	480-500
Viscosity, 25 °C	mPa-s	6000-8000
Acid number	mg KOH/g	-
Water content	%	< 0.1
Density	g/ml	1.076
pH	-	9.5-10.5

such as: dimethyl formamide, toluene, xylene [15, 16, 35, 52, 53] etc. For example, dimethyl formamide, a modest solvent for sucrose and the propoxylation or ethoxylation of sucrose in DMF in the presence of tertiary amines as catalysts, gives very good polyols, with all the solid sucrose being reacted at the end of reaction [35]. The big disadvantages of the processes which use an inert solvent is the necessity of solvent recycling, in order to have an economic process. The corresponding plant is more complex because it needs storage tanks for solvent, pumps, etc., and the process has supplementary steps for solvent distillation and recycling. As in all the processes using solvents, the solvent recovery is partial and a part of the solvent always is lost. In conclusion, from the economic point of view, these processes using inert solvents do not perform very well and they tend not to be used industrially, in spite of the good quality of the resultant polyether polyols.

d) Utilisation of polyether polyols as liquid reaction medium [1, 30, 55]

Polyether polyols for rigid PU foams or intermediate polyether polyols (with a higher hydroxyl number than the final polyether) proved to be excellent reaction media for the propoxylation of solid polyols, especially to obtain very high functionality polyols. These polyether polyols, used as a liquid reaction medium, are called 'heel'. For example, at the PO polymerisation temperature (110-120 °C) a mixture of 60% sucrose and 40% sucrose-based polyether polyol is a perfectly stirrable mixture.

Of course the polyether polyol having terminal hydroxyl groups is not inert in propoxylation reactions. It was observed experimentally that, due to the presence of primary hydroxyl groups in all solid polyols, PO reacts preferentially with the solid polyol and not with the polyether which generally has only secondary hydroxyl groups. On the other hand, the superior reactivity of short chains, as compared with long chains, is another element which makes PO react preferentially with the solid polyol. For example, in the presence of amines used as catalysts, the polyether reacts with only 10-15% of the total PO used for synthesis.

Unfortunately when KOH is used as catalyst, a suspension of sucrose in polyether polyol cannot be propoxylated totally, a substantial part of sucrose always remains unreacted. Sometimes, a very unpleasant phenomenon appears during propoxylation of solid sucrose suspended in a liquid polyether polyol, in the presence of KOH as catalyst. An aggregation of solid particles of sucrose into big particles takes place, which makes stirring impossible. This proves that polyether is a modest agent for sucrose solvation.

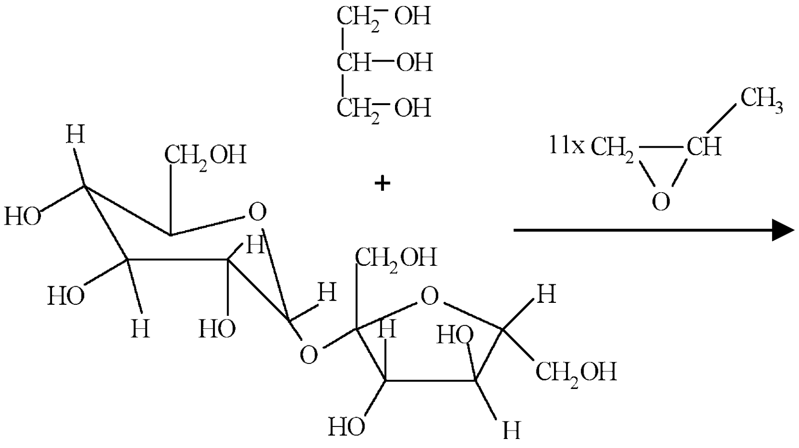
Fortunately, solid sucrose suspended in a liquid polyether is totally propoxylated in the presence of a tertiary amine used as catalyst. This effect is explained by the strong solvating ability of the tertiary amines.

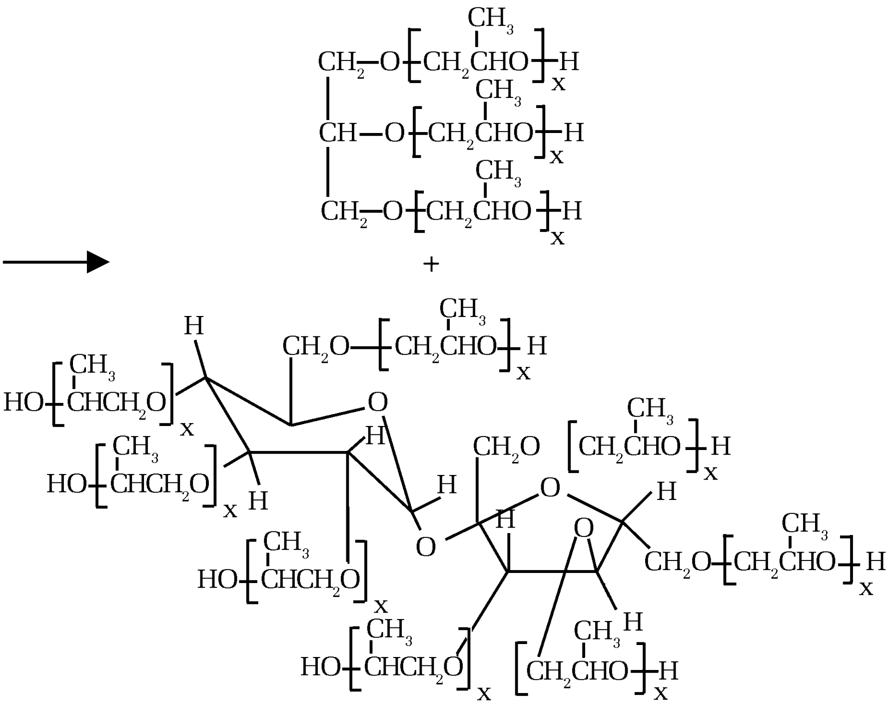
Thus, a mixture of a high concentration of sucrose, together with a small quantity of glycerol (sucrose/glycerol was around 15/1), suspended in a liquid polyether polyol is propoxylated totally in the presence of a tertiary amine, such as: dimethylaminoethanol, dimethylcyclohexylamine, or imidazoles. If the same mixture is propoxylated in the presence of KOH as catalyst, a large quantity of sucrose remains unreacted and is aggregated into big particles. As an immediate consequence, the resulting sucrose polyol has a lower viscosity and lower hydroxyl number than the expected values. The polyoxyethylene chains have a much stronger solvating effect on solid polyols, such as sucrose, than the polyoxypropylne chains. It was observed that if ethylene oxide is used in the first part of the alkoxylation (10-15% from the total monomers needed), the solid sucrose is totally consumed. The effect of sucrose solvation by the low molecular weight adducts of EO to sucrose was evident. By this technique it is possible to obtain low viscosity, very high functionality polyols (f = 6-7 OH groups/mol), but only in the presence of a tertiary amines as catalyst.

e) Utilisation of PO or a PO-EO mixture as reaction medium

Some processes [17, 18] describe the utilisation of PO as a reaction medium. A suspension of sucrose in PO or in PO-EO mixtures in the presence of a tertiary amine as catalyst (for example trimethylamine), leads to a total transformation of sucrose in liquid polyether polyols, at lower temperatures (80-95 °C). This process has the disadvantage of high pressures at the beginning of the reaction, which leads to some security problems due to the large excess of flammable and explosive monomers. Fortunately these problems are solved by conventional techniques. PO and EO are really excellent reaction media for alkoxylation of solid polyols, but only in the presence of tertiary amines and the resulting polyethers are of excellent quality. By this method it is possible to obtain a polyether polyol exclusively from sucrose and PO, a polyol with a functionality of 8 OH groups/mol. The viscosity of the resulting octol was very high, around 150,000 mPa-s at 25 °C. By analogy, a very interesting reactive liquid reaction media for propoxylation of solid polyols are the alkylene carbonates (ethylene carbonate or propylene carbonate) [36]. Thus, a suspension of sucrose in ethylene carbonate or propylene carbonate was propoxylated easily, in the presence of KOH as catalyst, at 110-120 °C. All the solid sucrose was transformed in liquid polyol. The resulting polyol had carbonate units from the reaction of hydroxyl groups with cyclic carbonates. The reactive solvent enters the polyol structure. Unfortunately, the resulting sucrose polyols obtained by using alkylene carbonates as solvents, are very dark in colour, probably because of a degradation of sucrose during the propoxylation reaction. Ethylene carbonate gives a more rapid transformation of solid sucrose in liquid polyol, proving a superior solvating capability [36].

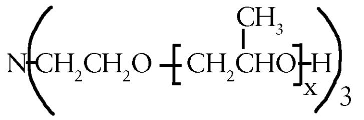
Some technologies use a sugar syrup (a solution of sucrose in water) instead of solid sucrose. Of course all the problems linked to the high melting point of polyols disappear but the problem of water elimination (the technology was described before) remains [14].





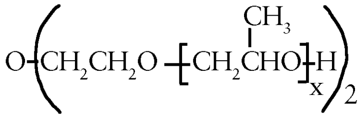
Polyether polyol based on sucrose-glycerol mixture

One can easily imagine that if the glycerol is replaced by triethanolamine [9, 10] or by DEG [51], the resulting polyols are of course a mixture of propoxylated sucrose with propoxylated triethanolamine or propoxylated DEG (13.29).



$$N\left(CH_2CH_2O-\left[CH_2\overset{CH_3}{\overset{|}{C}}HO\right]_x H\right)_3$$

Propoxylated triethanolamine



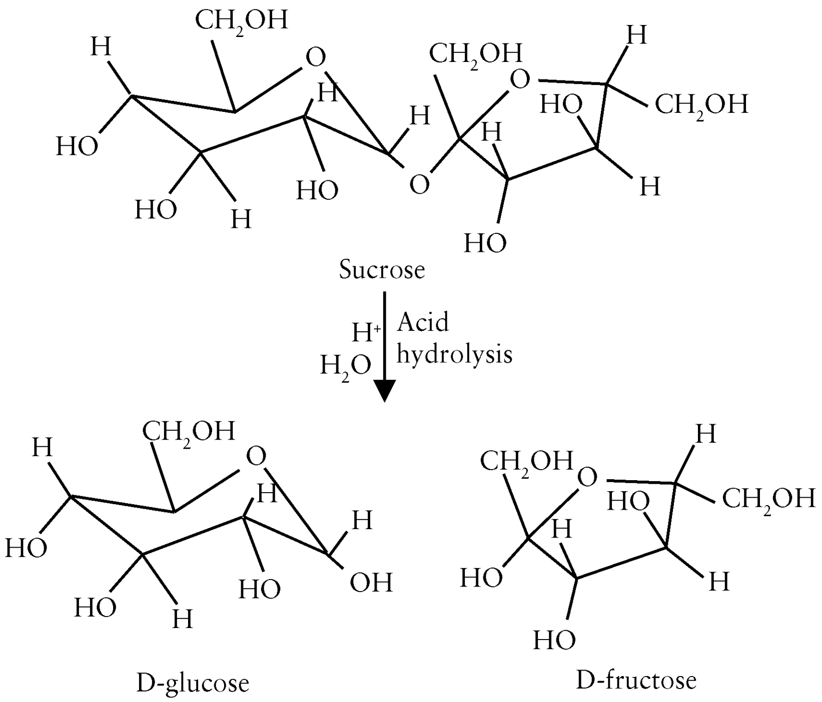
$$O\left(CH_2CH_2O-\left[CH_2\overset{CH_3}{\overset{|}{C}}HO\right]_x H\right)_2$$

Propoxylated DEG

(13.29)

Utilisation of sucrose as a starter polyol for rigid polyether polyols is extremely advantageous from the economic point of view. Sucrose is in fact a renewable raw material, commercialised on a large scale and available in a high purity form. The cycloaliphatic structure and the high functionality lead to high performance rigid polyether polyols.

Utilisation of sucrose as raw material leads to an important problem: the presence of reducing sugars in the composition of commercial sucrose. It is well known that sucrose is an oligosaccharide having one unit of D-glucose linked to one unit of D-fructose. This structure is resistant in basic media but is extremely labile in acidic media. For example, sucrose is hydrolysed by the atmospheric humidity in the catalysis of a very weak acidic compound: carbon dioxide from air. As a consequence of sucrose hydrolysis (reaction 13.30) one mol of D-glucose (a reducing sugar) and one mol of D-fructose (a non-reducing sugar) is formed:



(13.30)

The presence of glucose, even in small quantities in sucrose leads to very unpleasant phenomena [59]:

a) The basic catalyst, potassium hydroxide, decomposes glucose to acidic compounds (lactic acid, formic acid, saccharinic acids);

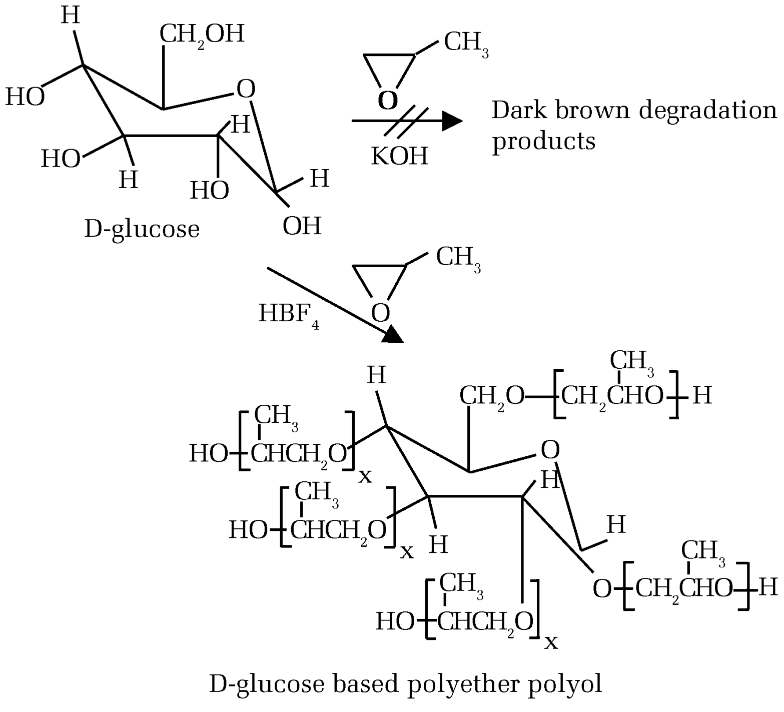
b) The alkaline catalyst is blocked by neutralisation with the acids of D-glucose degradation in the form of potassium salts of lactic, formic or saccharinic acids and the propoxylation rate decreases substantially and it is possible that it stops. A sucrose with a high content of reducing sugars is practically impossible to propoxylate;

c) The alkaline degradation of reducing sugars leads to dark-brown products, which strongly affects the colour of the final sucrose polyol.

Generally with a content of reducing sugars higher than 1%, very dark polyether polyols are obtained with a very low propoxylation rate (or impossibility to propoxylate). With a content of reducing sugars lower than 1% it is possible to develop the propoxylation reaction, at a convenient reaction rate. This decrease in reactivity in the presence of reducing sugars is explained by the neutralisation of the alkaline catalyst by the acids resulting from the thermal degradation of the reducing sugars. This explains why the alkalinity of sucrose polyols is always lower than the theoretical alkalinity. High quality and light coloured sucrose-based polyether polyols are obtained when the content of reducing sugars is lower than 0.05%.

In conclusion, to obtain high quality sucrose polyols it is recommended that a sucrose with a very low content of reducing sugars is used. The sucrose must be stored in dry conditions, with a minimum contact with atmospheric humidity.

Considering the reasons presented before, it is practically impossible to use D-glucose as a starter for rigid polyether polyols, with alkaline catalysis. Glucose can be used as starter only after etherification of glucosidic hydroxyl with alcohols in acidic media, glucose being transformed to an alkaline stable glucoside. Thus, α-methyl glucoside, hydroxyalkyl glucosides are excellent starters for propoxylation in alkaline media [20, 30]. Unfortunately, glucose is resistant to acidic media and excellent glucose-based polyether polyols are obtained by the direct propoxylation of glucose (reaction 13.31), in the presence of acidic catalysts (BF_3, HBF_4, HPF_6, $HSbF_6$) [21, 31].

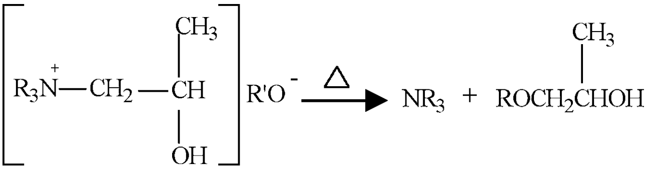


(13.31)

The removal of the catalytic effect of the remnant tertiary amines in the rigid polyether polyols synthesised in amine catalysis [36].

The remnant tertiary amines in the polyether polyols obtained in amine catalysis have a negligible effect in the reaction of -NCO groups with hydroxyl groups, in polyurethane fabrication. Generally, the formulations made with these polyols are corrected, by the decrease of the concentration of the amines used as catalysts in the foaming processes, in order to obtain similar reactivities as neutral polyols.

Immediately after synthesis, the pH of the polyether polyols obtained in aminic catalysis is very high, around is 11-11.5. It was observed experimentally that by heating a polyether polyol obtained by aminic catalysis at higher temperatures (120 -130 °C), the pH decreases to 9-10. The explanation of this behaviour is given by the presence of the remnant strongly basic quaternary ammonium alcoholates formed during propoxylation reaction. By heating the polyether at 120-130 °C, the strongly basic quaternary ammonium alcoholate is decomposed in weak basic tertiary amines, by intramolecular etherification or by Hofmann degradation (reaction 13.32):

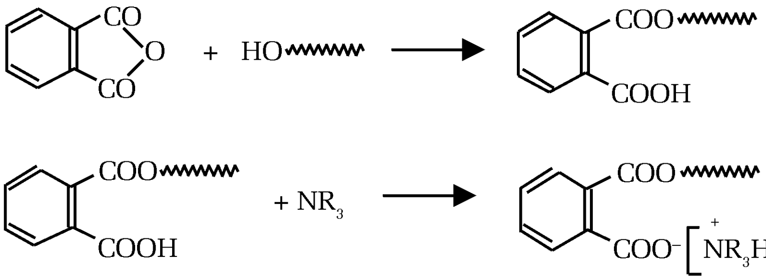


$$\left[R_3\overset{+}{N}-CH_2-\underset{OH}{\overset{CH_3}{CH}}\right]R'O^- \xrightarrow{\Delta} NR_3 + ROCH_2\overset{CH_3}{C}HOH$$

strong base weak base (13.32)

The commercial practice proved that many customers prefer a neutral polyol, in order not to change the formulations and to have the possibility of making a continuous production with polyether polyols from different polyether polyols producers, without major intervention in the composition of the polyols formulated. If neutral polyols are desired, the polyether polyols synthesised with tertiary amines as catalysts are neutralised with acidic substances, such as - phthalic anhydride, formic acid or propoxylated phosphoric acid.

Phthalic anhydride reacts *in situ* with the hydroxyl groups of polyether polyols forming an half ester of phthalic acid. The formed acidic group neutralises the tertiary amine under the form of quaternary ammonium salt (reaction 13.33).

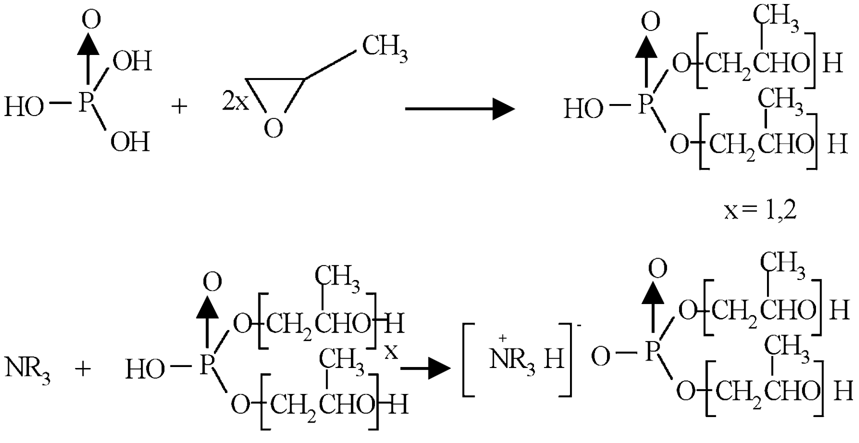


(13.33)

With formic acid, salts of formic acid are obtained, which have the structure of 'delayed catalysts' [61]:

$$HCOOH + NR_3 \rightarrow HCOO^- \left[\overset{+}{N}R_3H\right]$$

The reaction with partially propoxylated phosphoric acid gives a very soluble amine salt in polyether polyol [36]:



The quantity of the acidic substance is around the stoichiometric ratio or slightly higher than the stoichiometric ratio compared to the amine. A decrease in pH and in the polyether polyol reactivity is observed, which is similar to neutral polyether polyols.

References

1. D.J. Sparrow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.207-209.

2. T.H. Ferrigno, *Rigid Plastic Foams*, 2nd Edition, Reinhold Publishing Corporation, New York, NY, USA, 1967.

3. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, Chapter 8, p.1-18.

4. W. Green, G.M.F. Jeffs and D.J. Sparrow, *Plastics and Rubber International*, 1984, **9**, 5, 30.

5. L.R Knodel, inventor; The Dow Chemical Company, assignee; US 3,865,806, 1975.

6. No inventor; Jefferson. assignee; GB 1,002,272, 1965.

7. K.C.Frisch and J.E.Kresta in *Sucrochemistry*, Ed., J.L. Hickson, ACS Symposium Series No.41, American Chemical Society, Washington, DC, USA, 1976, p.41.

8. (a) G.D. Edwards, R.L. Soulen and D.M. Riche, inventors; Jefferson Chemical Company and Eastman Chemical Company, assignees; CA 821,553, 1969.
   (b) G.D. Edwards, R.L. Soulen and D.M. Riche, inventors; Jefferson Chemical Company and Eastman Chemical Company, assignees; CA 844,022,19, 1970.

9. No inventors; ICI, assignee; GB 1,154,161, 1969.

10. No inventors; Allied Chemicals, assignee; GB 1,104,733, 1968.

11. No inventors; ICI America, assignee; GB 1,434,503, 1976.

12. No inventors, Dow, assignee; GB 935,424, 1963.

13. W.R. Fijal, inventor; BASF Wyandotte Corp., assignee; US 3,640,997, 1972.

14. M. Wismer and J.F. Foote, inventors; Pittsburgh Plate Glass Company, assignee; US 3,085,085, 1963.

15. No inventors; Union Carbide Corporation; GB 1,132,004, 1968.

16. R.P. Gentles, inventor; ICI, assignee; GB 864,097, 1961.

17. No inventors; Shell International Research, assignee; GB 2,078,764, 1982.

18. A.W. Anderson, inventor; The Dow Chemical Company, assignee; US 2,902,478, 1959.

19. R.P. Gentles and A. Ibbotson, inventors; ICI, assignee; GB 891,776, 1962.

20. C. Granger, R. Gras and M. Buisson, inventors; Naphtachimie, assignee; US 3,505,255, 1970.

21. No inventors; Olin Corporation, assignee; GB 1,323,184, 1973.

22. J.T. Patton, Jr., and W.F. Schulz, inventors; Wyandotte Chemical Corporation, assignee; US 3,346,557, 1967.

23. J.L. Haas, inventor; Mobay Chemical Corporation, assignee; US 4,209,609, 1980.

24. (a) No inventor; Upjohn, assignee; GB 1,042,220, 1966.
    (b) No inventor; Upjohn, assignee; GB 1,147,106, 1969.

25. A.J. Thomas, inventor; Huntsman ICI Chemicals LLC, assignee; WO0005289, 2000.

26. K. Wagner, inventor; Bayer AG, assignee; US 4,247,654, 1981.

27. T. Richardson, D.M. Burrington and K.R. Viswanathan, inventors; Wisconsin Alumni Research Foundation, assignee; US 4,459,397, 1984.

28. D.H. Champion and G.P. Speranza, inventors; Texaco Chemical Company, assignee; US 5,110,991, 1992.

29. D.E Laycock, inventor; Dow Chemical Company, assignee; US 4,962,237, 1990.

30. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Proceedings of the Annual SPI Technical Conference*, *Polyurethanes 1994*, Boston, MA, USA, 1994, p.506.

31. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai, *Advances in Urethanes Science & Technology,* 1998, **14**, 151.

32. M. Ionescu, C. Roibu, V. Preoteasa and S. Mihai in *Proceedings of API Polyurethane Conference, Polyurethanes 2000*, Boston, MA, USA, 2000, p.311.

33. J.M. Ulyatt, inventor; Pfizer Ltd., assignee; GB 1,082,673, 1967.

34. T. Nakajima, K. Matsubara and K. Ueno, inventors; Mitsui Toatsu Chemicals, assignee; EP 0,395,316A3, 1991

35. N.H. Nodelman, inventor; Mobay Chemical Corporation, assignee; US 4,332,936, 1982.

36. M. Ionescu, unpublished work.

37. M. Ionescu, F. Stoenescu, V. Dumitriu and I. Mihalache in *Proceedings of 29th IUPAC Symposium on Macromolecular Chemistry*, Bucharest, Romania, 1983.

38. M.F. Sorokin, L.G. Shode, A.B. Sheinoress and L.N. Finiakin, *Kinetika i Kataliz,* 1968, **9**, 3, 548.

39. N.S. Enikolopiyan, *Pure & Applied Chemistry*, 1976, **48**, 3, 317.

40. R.K. Whitmire, R.A. Plepys, C.M. Keillor and V.L. Phillips, inventors; The Dow Chemical Company, assignee; WO 9947581A1, 1999.

41. H.P. Klein and M.E. Brennan, inventors; Arco Chemical Technology, Inc., assignee; US 4,820,810, 1989.

42. W. Hinz and E.M. Dexheimer, inventors; BASF Corporation, assignee; US 6,410,801, 2002.

43. J.D. Christen and H.B. Taylor III, inventors; Dow Chemical Company, assignee; US 4,521,548, 1985.

44. W. Hinz and E.M. Dexheimer, inventors; BASF Corporation, assignee; US 6,380,367, 2002.

45. E. Santacesaria, M.Di Serio and P. Iengo in *Reaction Kinetics and the Development of Catalytic Processes*, Eds., G.F. Froment and K.C. Waugh, Elsevier Science BV, Amsterdam, the Netherlands, 1999, p.267.

46. E. Santacesaria, M. Di Serio, L. Lisi and D. Gelosa, *Industrial & Engineering Chemistry Research*, 1990, **29**, 5, 719.

47. M. DI Serio, G. Vairo, P. Iengo, F. Felippone and E. Santacesaria, *Industrial & Engineering Chemistry Research,* 1996, **35**, 11, 3848.

48. E. Santacesaria, M. Di Serio, R. Garaffa and G. Addino, *Industrial & Engineering Chemistry Research*, 1992, **31**, 11, 2413.

49. M. Di Serio, R. Tesser, F. Felippone and E. Santacesaria, *Industrial & Engineering Chemistry Research,* 1995, **34**, 11, 4092.

50. E. Santacesaria, M. Di Serio, R. Garaffa, G. Addino, *Industral & Engineering Chemistry Research,* 1992, **31**, 11, 2419.

51. S. Dinsch, J. Winkler, G. Knorr, M. Reichelt, G. Hoppner and P. von Malotki, inventors; BASF AG, assignee; US 6,563,007, 2003.

52. D. Maassen, R. Nast, H. Bormann, H. Piechota and K-J. Kraft, inventors; Bayer AG, assignee; US 3,941,769, 1976.

53. M. de Groote, inventor; Petrolite Corporation, assignee; US 2,652,394, 1953.

54. M. Ionescu, V. Dumitriu, I. Mihalache, F. Stoenescu, M. Mateescu and M. Stanca, inventors; Institutul De Cercetari Chimice and Centrul de Cercetari Pentru Materiale Plastice, assignees; RO 85,851, 1982.

55. M. Ionescu, T.V. Dumitriu, I. Mihalache, F. Stoenescu, V.M. Mateescu and M. Stanca, inventors; Institutul De Cercetari Chimice, and Centrul De Cercetari Pentru Materiale Plastice, assignees; RO 85,853B1, 1985.

56. C. Roibu, V. Preoteasa, V. Zugravu, I. Mihalache, S. Mihai, I. Bejenariu and I. Puscasu, inventors; SC Oltchim SA, and Ramnicu Valcea, assignees; RO 118,433, 2003.

57. M. Ionescu, V. Dumitriu, I. Mihalache, F. Stoenescu, N. Chiroiu and M. Talpasanu, inventors; Institutul De Cercetari Chimice, and Centrul De Cercetari Pentru Materiale Plastice, assignees; RO 92,858, 1987.

58. H.P. Klein, inventor; Texas Development Corporation, assignee; US 4,166,172, 1979.

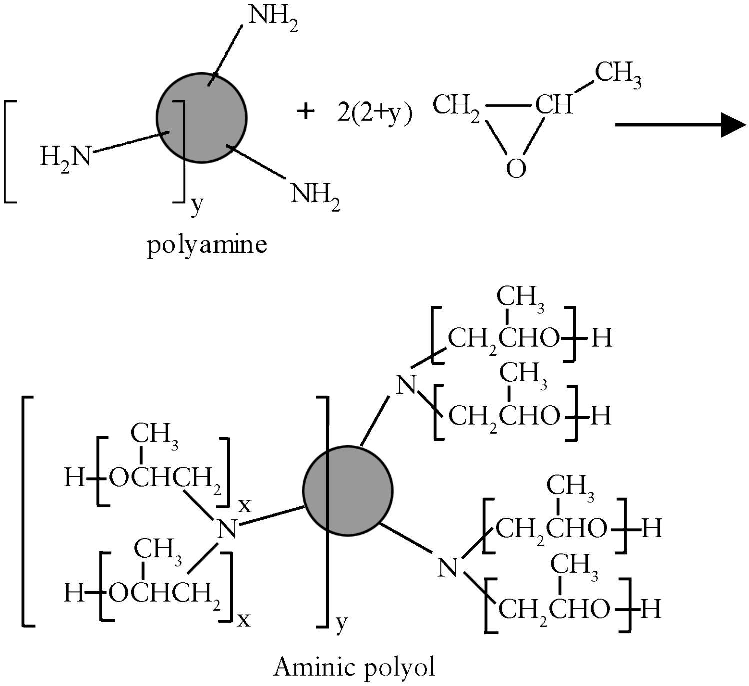
59. F. Stoenescu, M. Ionescu, V. Dumitriu and I. Mihalache, *Materiale Plastice,* 1979, **16,** 1, 4.

60. M.A.P. Gansow, inventor; Dow Chemical (Nederland) BV, assignee; US 4,877,879, 1989.

14 Aminic Polyols

Aminic polyols are low molecular weight adducts of propylene oxide (PO) [and/or ethylene oxide; (EO)] made from aliphatic or aromatic polyamines such as: ethylenediamine (EDA), diethylene triamine (DETA) [1, 2], *ortho*-toluene diamine (o-TDA) [3, 4] or diphenylmethanediamine (MDA) [2, 5, 6]. Because these starters are liquid at room temperature (EDA, DETA) or low melting point solids (o-TDA, MDA), they are alkoxylated in the absence of solvents.

The general reaction is:



(14.1)

As a general rule, all the aminic polyols are much more reactive in the reaction with the aromatic isocyanates than the polyether polyols for rigid polyurethane (PU) foams initiated by polyolic starters, due to the presence in their structure of the tertiary amino nitrogens with a strong catalytic effect in the reaction between -NCO groups and hydroxyl groups [7-9].

The reaction of primary or secondary amines with an alkylene oxide (PO or EO), does not take place in perfect anhydrous conditions. By the addition of small quantities of a compound having hydroxyl groups, such as: water, alcohols, phenols, organic acids and so on, the reaction is initiated immediately and takes place easily. As explained before, the weak hydrogen bonds formed between the hydrogen atoms of hydroxyl groups and the oxygen atom of the oxiranic cycle activate the epoxydic ring and the weak nucleophilic nitrogen atom of the amines attacks the carbon atom of the oxiranic cycle (see reaction 13.15).

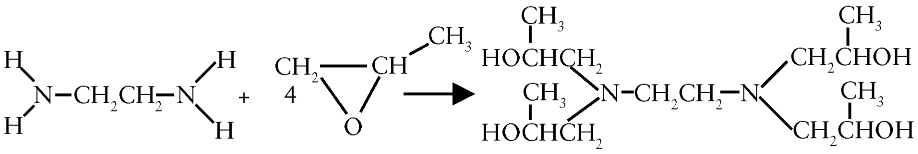
During the alkoxylation of the amino groups, as shown in reaction 14.1, hydroxyl groups are formed, which have a strong catalytic effect on the reaction of alkylene oxides with the unreacted amino groups. As an immediate consequence, the reaction is strongly accelerated. Of course by the addition of water as catalyst, during the alkoxylation reaction, diols are formed (propylene glycol, dipropylene glycol), which decrease the functionality of the amino polyol. A process which uses as a catalyst the final polyol (which has enough hydroxyl groups for catalysis) was developed [10], the structural purity and the functionality of the final aminic polyol are not affected.

After the transformation of all -NH groups in -N-hydroxyalkyl groups, the reaction becomes much slower or stops. PO does not react with the hydroxypropyl groups formed in the self catalysis of their own tertiary aminic nitrogen. The effect is explained by the fact that hydroxypropyl groups are a bulky substituent and for good catalysis of the PO addition to hydroxyl groups, the tertiary amine must have a low steric hindrance (minimum two methyl groups/nitrogen atom. Fortunately, EO reacts with the aminic polyols which have hydroxypropyl groups and it is possible to have an extension of the chains without any other catalyst. This is explained by the higher reactivity of EO, compared with PO in nucleophilic ring opening reactions and by the low steric hindrance of EO as compared with PO.

By the addition of a low steric hindrance amine (dimethylaminoethanol, dimethycyclohexylamine) or of KOH, to an aminic polyol, having hydroxypropyl groups, the extension of the chains with PO units is possible.

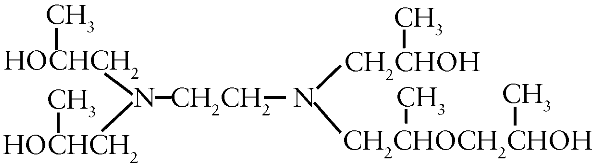
As a general rule, all the aminic polyols obtained by the propoxylation of the amines discussed have very high viscosities. By the introduction of EO units the aminic polyol viscosities decrease substantially [4].

For example EDA, with 4 mols of PO, is a well known crosslinking agent but has a high viscosity, around 50,000 mPa-s, at 25 °C (reaction 14.2).

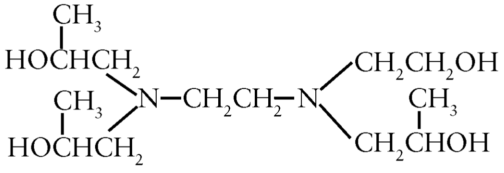


(14.2)

By the introduction of 5 mols of PO/mol of EDA (structure 14.3), the viscosity decreases to about 19,000-22,000 mPa-s, at 25 °C. By the reaction of EDA with 3 mols of PO and one mol of EO (structure 14.4), the viscosity decreases from 50,000 (for a product with 4 mols of PO/mol of EDA) to around 16,000-17,000 mPa-s, at 25 °C, the functionality being conserved (4 OH groups/mol) [7].



(14.3)



(14.4)

Propoxylated DETA with 5 mols of PO/mol of DETA has a very high viscosity, of around 150,000 mPa-s, at 25 °C, and it is very difficult to use it in the normal technologies for PU production.

Aromatic amines such as o-TDA and MDA, give useless aminic polyols because of the high viscosities resulting from the direct propoxylation.

Thus, aminic polyols of lower viscosities are obtained by the following three methods:

a) One increases the degree of polymerisation of the chain derived from one hydroxyl group (chain extension);

b) By the introduction of EO units (internal or terminal EO units);

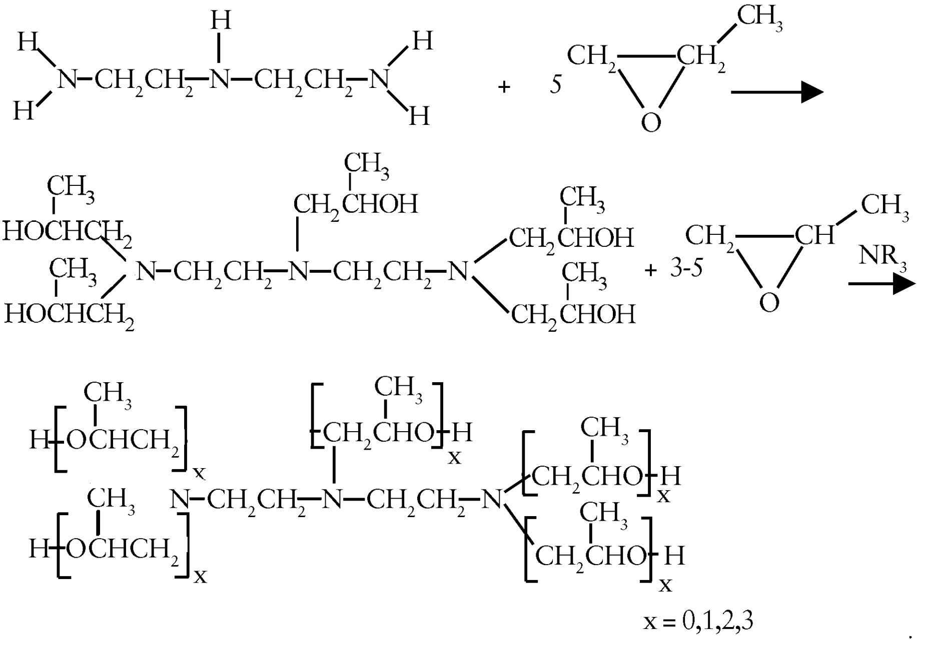
c) By the alkoxylation of a mixture between a polyamine and a low functionality amine (monoethanolamine or diethanolamine).

These three methods will now be considered in more detail.

a) Increase of polymerisation degree of a chain derived from one hydroxyl group

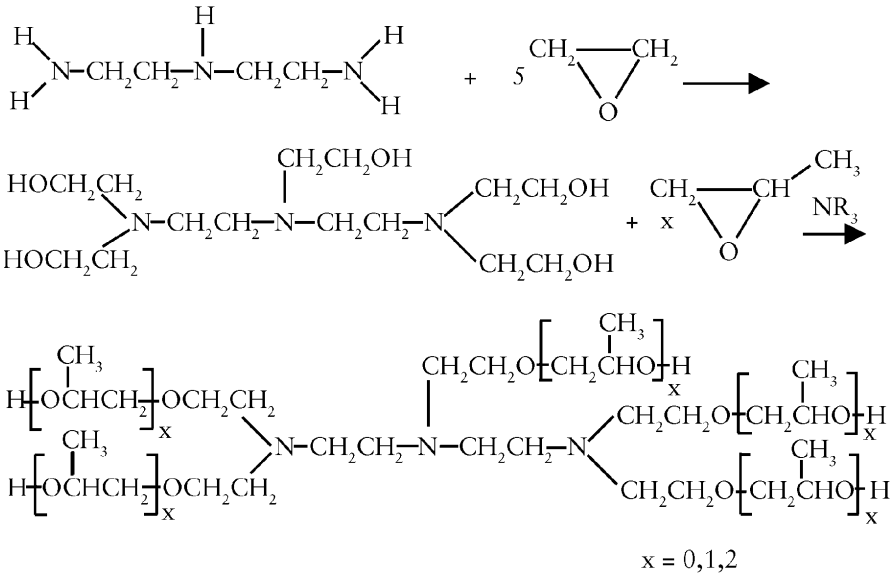
It was observed experimentally that by increasing the number of PO units per chain derived from one hydroxyl group there are obtained not only lower hydroxyl numbers but the viscosities of the resulting aminic polyols decrease significantly. The extension of the chains with PO is possible only after the addition of a catalyst, such as: KOH, NaOH, low hindered tertiary amines or imidazoles. Utilisation of KOH and NaOH as catalysts needs a purification step. Using a low hindered amine as catalyst (trimethylamine, dimethyethanolamine, dimethylcyclohexylamine) the resulting polyols do not need any purification.

Thus, by the propoxylation of DETA with around 8-10 mols of PO/mol of DETA, by using dimethylethanolamine as catalyst, aminic polyols of low hydroxyl number (390-420 mg KOH/g) are obtained, with low viscosity of around 6,000-9,000 mPa-s, at 25 °C [1, 10, 11]:



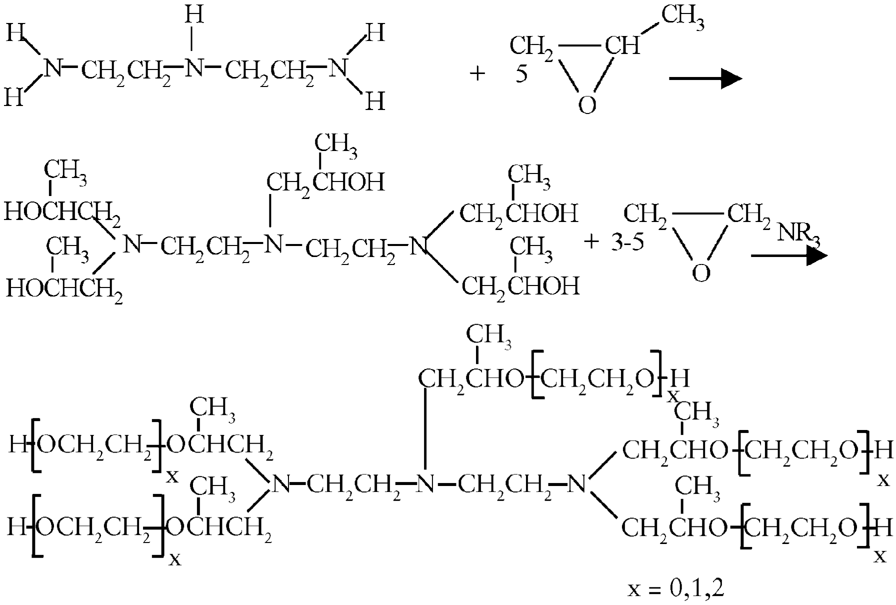
b) Introduction of EO units

By the reaction of 4-5 mols of EO with one mol of DETA, followed by a catalysed propoxylation step, it is possible to obtain aminic polyols with a functionality of 5 OH groups/mol with a high hydroxyl number and convenient low viscosities: (equation 14.5).



(14.5)

The DETA-based aminic polyols are synthesised by first adding 4 mols of PO and, in the second step, adding several units of EO without any other catalyst (self catalysis). The addition of EO to the hydroxyl groups formed, being catalysed by the tertiary aminic nitrogen from the aminic polyol structure resulting from propoxylation (reactions 14.6) [11, 12].

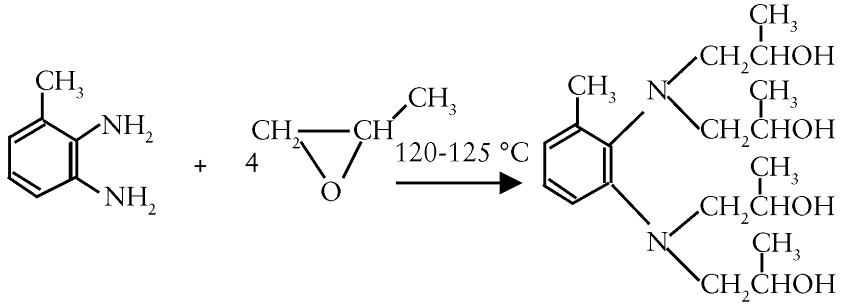


(14.6)

The effect on the viscosity decrease by the introduction of EO units in the polyetheric chains is more significant in the case of aromatic diamine alkoxylation, such as the alkoxylation of o-TDA [4].

o-TDA is a byproduct of toluene diisocyanate (TDI) technology (it appears together with 2,4 and 2,6 toluene diamine). The resulting o-TDA is in fact a mixture of 2,3-TDA (around 40%) and 3,4 TDA (around 60%).

By propoxylation of o-TDA with 4 PO mols, without any catalyst, an extremely viscous aminic polyol is obtained, of around 650,000 mPa-s at 25 °C (reaction 14.7).

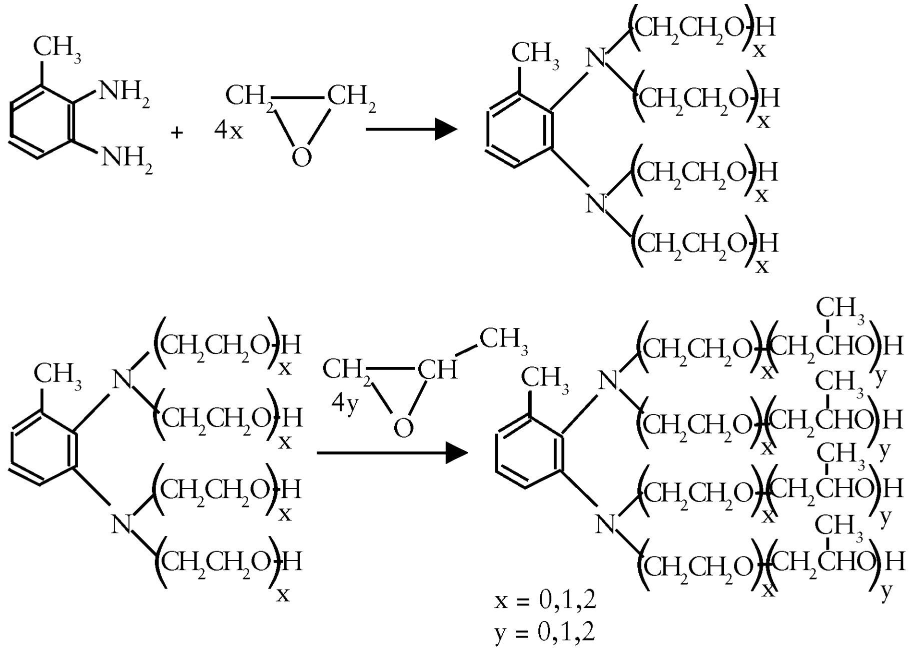


(14.7)

By increasing the degree of propoxylation (chain extension), by reacting the resulting amino polyol (14.7), with PO in the presence of a catalyst (for example KOH), until the hydroxyl number becomes 390-410 mg KOH/g, the resulting viscosity decreases, but remains very high, around 140,000-145,000 mPa-s, at 25 °C, which makes it difficult to use in practice [3, 4, 13].

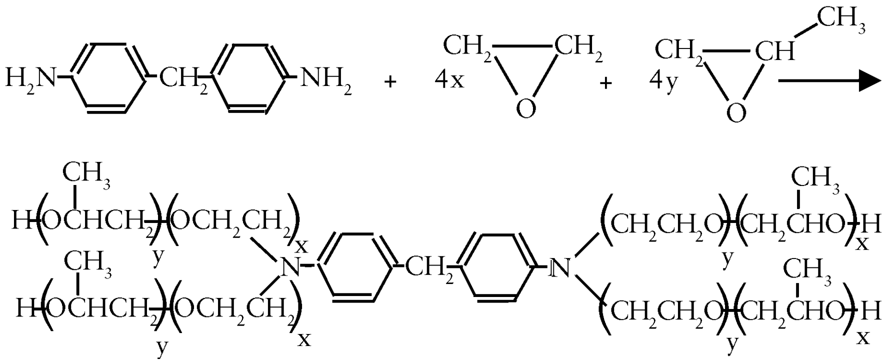
By the introduction of internal EO units (25-30% internal EO) it was possible to obtain an o-TDA-based aminic polyol with an acceptable viscosity, of around 10,000-15,000 mPa-s, at 25 °C (reaction 14.8.) [4].

o-TDA-based polyols are aromatic aminic polyols, which have excellent compatibility with blowing agents (pentanes, hydrofluorocarbons and so on) and which give rise to high performance physico-mechanical, thermal and flame proofing properties. The disadvantage of o-TDA-based polyols is the very dark colour. Better colour is obtained by using a freshly distilled o-TDA (maintained under nitrogen) or a stabilised o-TDA (by the addition of an organic acid, such as formic acid [14], a carbonyl compound [15] or ascorbic acid [16]) immediately in the alkoxylation reaction.

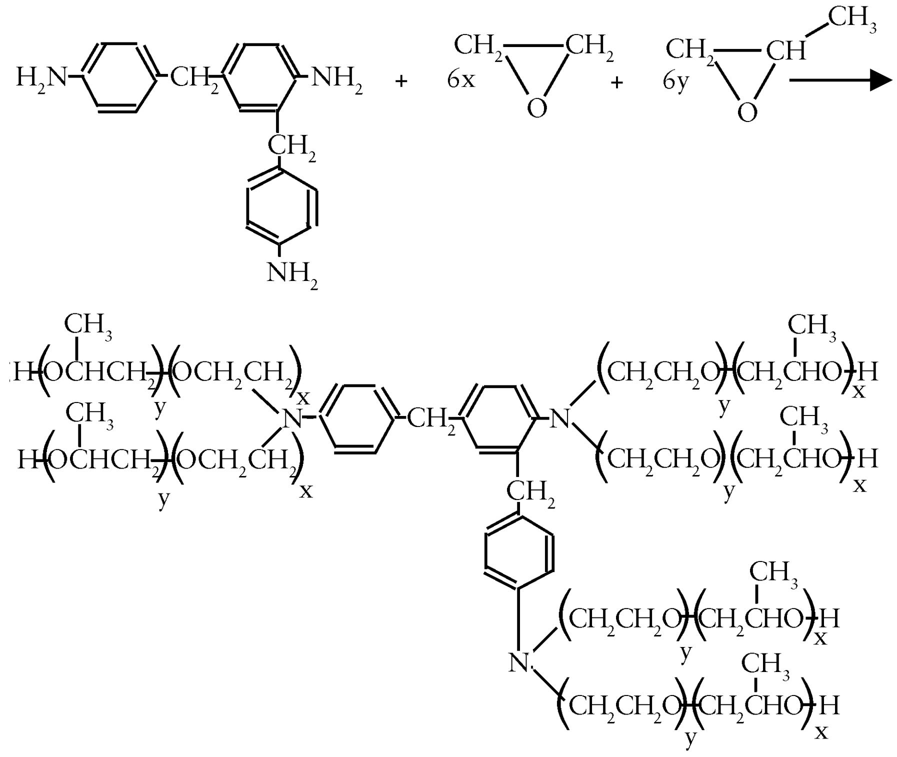


(14.8)

The same strong effect on the viscosity decrease was observed by the introduction of an internal poly [EO] block in the case of synthesis of aromatic aminic polyols derived from methylenedianiline (MDA), a precursor of diphenylmethane diisocyanate (MDI) [2, 5, 6]:



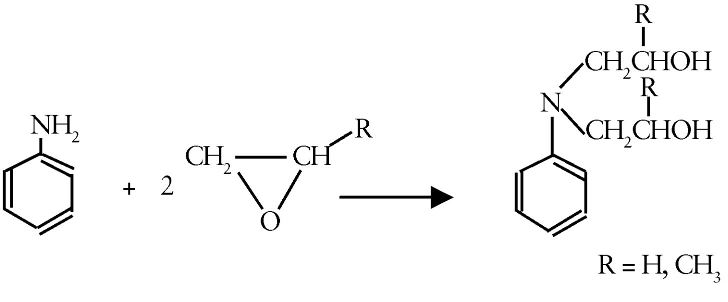
This method of viscosity decrease by introduction of internal EO units is very efficient for reusing wastes resulting from MDA fabrication, which have superior oligomers with 3, 4 or 5 aromatic nuclei (reaction 14.9). Propoxylation of these MDA wastes gives extremely viscous aminic polyols [2].



(14.9)

Highly aromatic and high functionality aminic polyols, of very convenient viscosities (15,000-25,000 mPa-s at 25 °C) are obtained. Similar effects of viscosity decrease were obtained by using as monomers a mixture of PO with EO (15-25% EO).

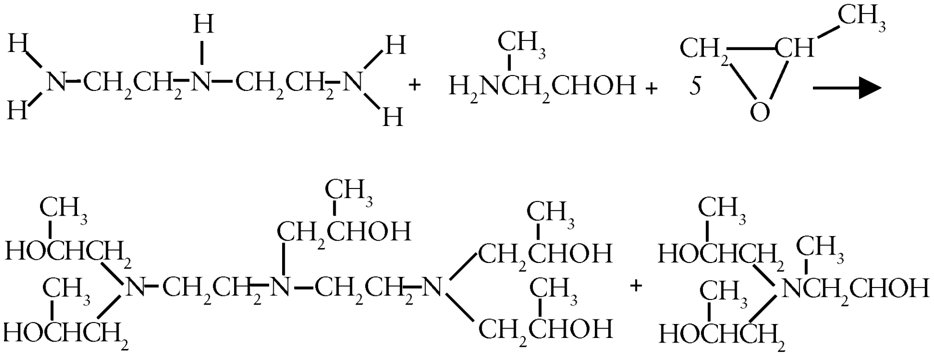
A special aromatic aminic polyol was obtained by propoxylation or ethoxylation of aniline [7]. These diols were used sometimes as chain extenders in elastomers and in coatings. The disadvantage of these aniline-based diols is the fact that at a ratio of 2 mols of alkylene oxide (PO, especially EO) they become solid at room temperature, by crystallisation:



c) *Alkoxylation of the mixture of polyamines with monoamines*

The third method to decrease the viscosity of aminic polyols is the alkoxylation of a mixture between a polyamine (which leads to very viscous polyols) with a monoamine, such as: monoethanolamine, diethanolamine, diisopropanolamine or monoisopropanolamine, (which lead to fluid polyols). The quantity of monoamine is calculated so as not to affect markedly the functionality of the final aminic polyol.

Thus, by propoxylation of a mixture of DETA and monoisopropanolamine, a very high hydroxyl number polyol (OH# = 700-800 mg KOH/g) is obtained, with a convenient viscosity (around 15,000–25,000 mPa-s, at 25 °C) and an intermediate functionality, between 3-5 or usually 3.5-4.5 OH groups/mol (reaction 14.10) [13].



(14.10)

The resulting mixtures of aminic polyols (4.10) are excellent crosslinkers for rigid PU foams and other PU products. The aminic polyols, due to their intrinsic high reactivity are used especially in rigid 'spray' PU foams.

References

1. M. Ionescu, F. Stoenescu, V. Dumitriu, I. Mihalache and M. Stanca, inventors, Institutul de Cercetari Chimice - Centrul de Cercetari Pntru Materiale Plastische, assignee; RO 85,851, 1982.

2. M. Ionescu, A.B. Mihis, I. Mihalache, V.T. Zugravu, S. Mihai, P. Botezatu, A.M. Miron, D. Stoica and D. Timpoc, inventors; Institutul de Cercetari Chimice - Centrul de Cercetari Pntru Materiale Plastische, assignee; RO 111,277, 1996.

3. No inventors; ICI, assignee; GB 1,154,161, 1969.

4. J.L. Haas, inventor; Mobay Chemical Corporation, assignee; US 4,209,609, 1980.

5. No inventor; Upjohn, assignee; GB 1,042,220, 1966.

6. No inventor; Upjohn, assignee; GB 1,147,106, 1969.

7. D.J. Sparrow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Inc., Boca Raton, FL, USA, 1989, p.207-209.

8. T.H. Ferrigno, *Rigid Plastic Foams*, 2nd Edition, Reinhold Publishing Corporation, New York, NY, USA, 1967.

9. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, Chapter 8, p.1-18.

10. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Advances in Urethane Science & Technology,* Volume 14, Eds., D Klempner and K.C. Frisch, ChemTec Publishing, Ontario, Canada, 1998, p.151.

11. F. Stoenescu, M. Ionescu, I. Mihalache, V.T. Dumitriu,M.V. Mateescu and S. Mihai, inventors; Institutul De Cercetari Chimice, and Centrul De Cercetari Pentru Materiale Plastice, assignees; RO 82,855, 1984.

12. M. Ionescu, F. Stoenescu, V. Dumitriu and I. Mihalache in *Proceedings of 29th IUPAC Symposium on Macromolecular Chemistry*, Bucharest, Romania, 1983.

13. M. Ionescu, unpublished work.

14. R.L. Adkins, inventor; Bayer Corporation, assignee; US 6,031,137, 2000.

15. R.L. Adkins, S.L. Schilling and K.J. Headley, inventors; BAYER Corporation, assignee; US 5,872,292, 1999.

16. G.A. Salensky, inventor; Union Carbide Corporation, assignee; US 3,595,918, 1971.

15 Rigid Polyols Based on the Alkoxylation of Aromatic Compound Condensates with Aldehydes

The polyols for rigid foams (referred to as rigid polyols) discussed before (Chapters 13 and 14), are based on the alkoxylation of different polyols or polyamines, commercialised in a relatively high purity form. Some important starters for rigid polyols are obtained by the synthesis of the starter *in situ*, before the alkoxylation reaction, by the condensation reaction of some aromatic compounds (phenols, melamine and so on) with aldehydes (mainly formaldehyde), followed by the reaction of the resulting condensate with alkylene oxides. Some important rigid polyols based on the condensates mentioned are:

a) Mannich polyols,

b) Novolak-based polyols,

c) Melamine-based polyols.

15.1 Mannich Polyols [1-21]

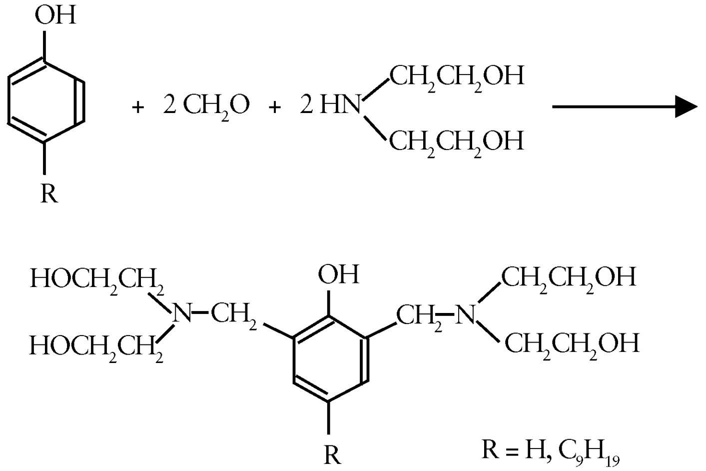
Mannich polyols is a very important group of aromatic polyols obtained by the alkoxylation with propylene oxide (PO) [(and/or ethylene oxide (EO)] of the Mannich bases obtained by classical Mannich reaction between phenols (for example phenol, *p*-nonylphenol), formaldehyde and alkanolamines (diethanolamine, diisopropanolamine, monoethanolamine, monoisopropanolamine and so on). Synthesis of Mannich polyols is divided into two important steps:

a) Synthesis of Mannich base (Mannich reaction), and

b) Alkoxylation with PO (or with PO and EO) of the synthesised Mannich base.

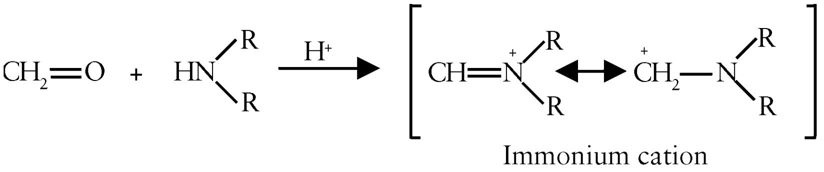
a) Synthesis of Mannich Base [2-16, 22, 23]

The Mannich bases are generally obtained by the stepwise addition of aqueous formaldehyde (25-37%) to a physical mixture of phenol - alkanolamine, at 50-70 °C. The reaction (reaction 15.1) is slightly exothermic and needs cooling in order to maintain the reaction temperature. After the addition of formaldehyde, the reaction mass is maintained for digestion, for about 60-120 minutes.



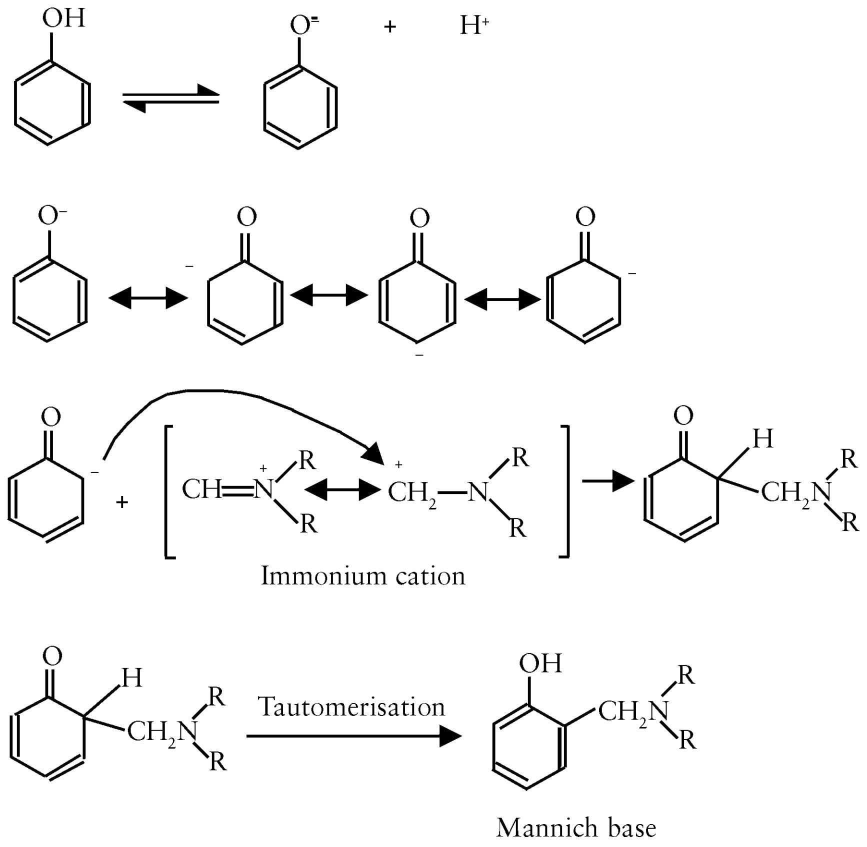
(15.1)

In the case of phenol, with the free *para* position, due to the interaction between the phenolic group (acidic) and the aminic nitrogen (basic) of the amino alcohol, the *ortho* position is occupied first [9]. After the synthesis of Mannich bases, the water resulting from the reaction and the water from the aqueous solution of formaldehyde is distilled under vacuum, at 90-125 °C (preferably in the range 90-100 °C). A low range of distillation temperatures is preferred in order to avoid the tendency of the Mannich base to condensate to superior oligomers (with 2-3 aromatic nuclei), which increase substantially the viscosity of Mannich base and, of course, of final Mannich polyol. The mechanism of the Mannich reaction is considered to be a two-step mechanism. In the first step the reaction between formaldehyde and the primary or secondary amine (reaction 15.2) takes place, with the formation of an immonium cation [7-9, 22, 23].



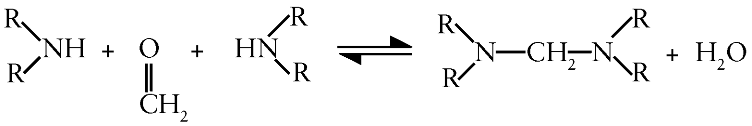
(15.2)

In the second step, the reactive immonium cation formed reacts with the tautomeric forms of the phenolate anions, having negative charges, in the *ortho* and *para* positions (reaction 15.3). Finally, by a tautomerisation reaction, the reformation of the aromatic phenolic structure of a substituted phenol with dihydroxyalkyl aminomethyl groups (reaction 15.3) takes place.



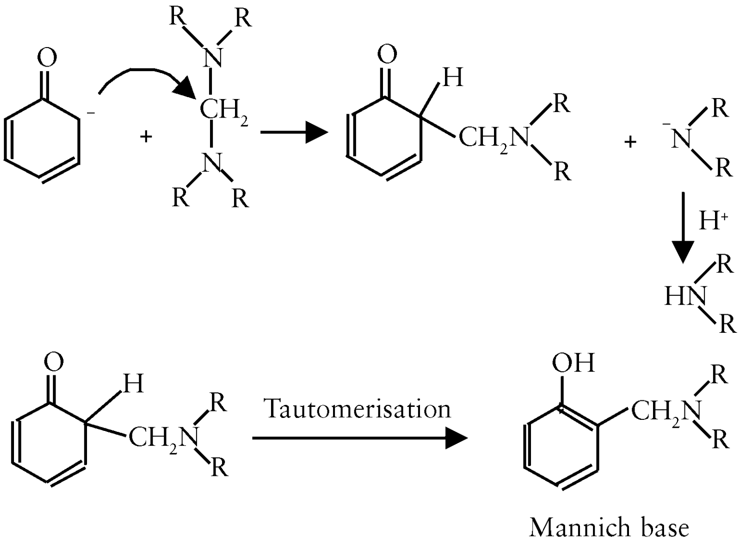
(15.3)

A second mechanism is based on an SN-2 nucleophilic substitution [7, 8]. In the first step, a reaction between formaldehyde and the primary or secondary amine takes place:



(15.4)

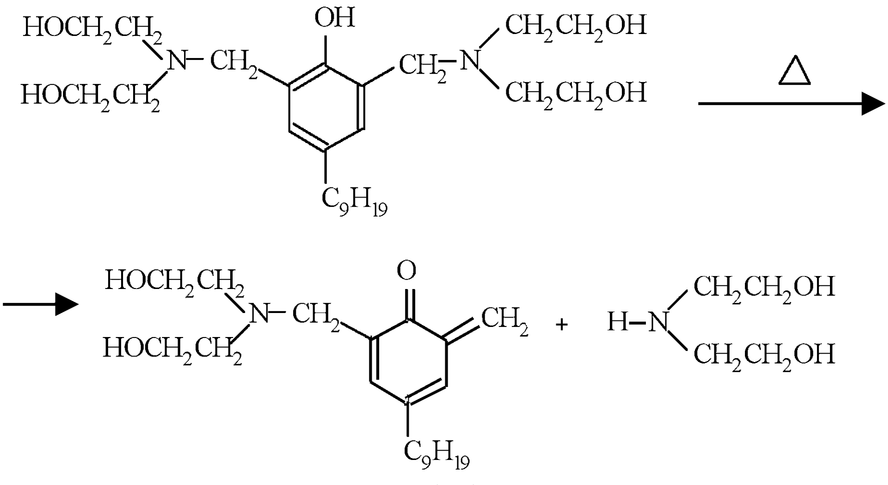
The anion of phenol, in tautomeric form with the negative charge in the nucleus, attacks the carbon atom of the methylene group in the labile methylene diamine formed in reaction 15.5.



(15.5)

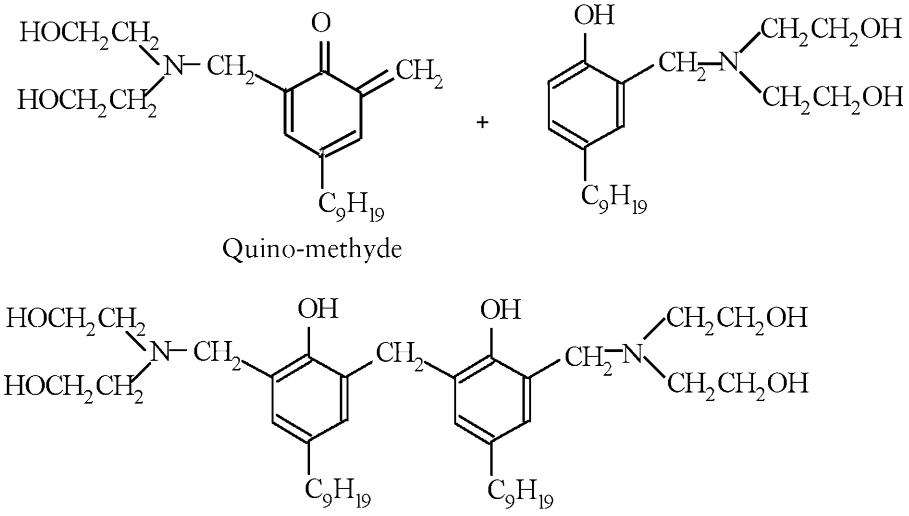
In acidic media, by using amine salts instead of free amines, the first mechanism is more probable. In neutral or basic media (for example the reaction of phenol with formaldehyde and alkanolamines), the second mechanism seems to be more probable [7, 8].

One possible side reaction of the synthesised Mannich base is its thermal decomposition to a very reactive quino-methyde (reaction 15.6).

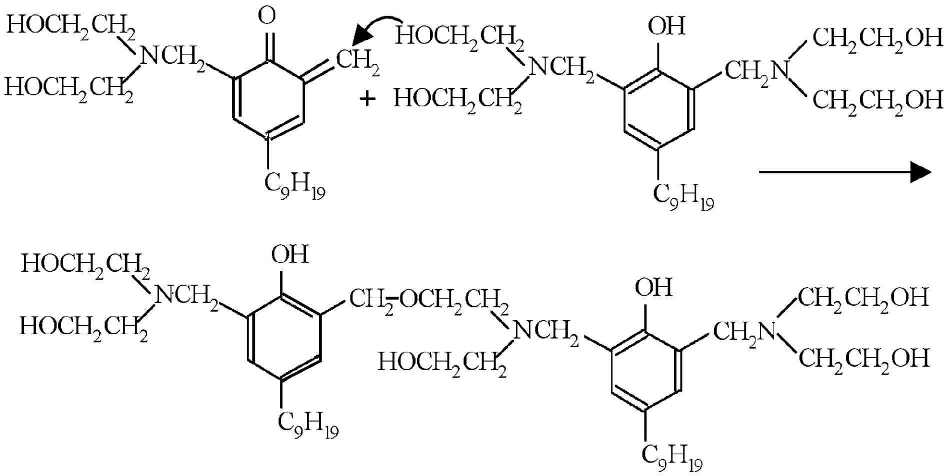


(15.6)

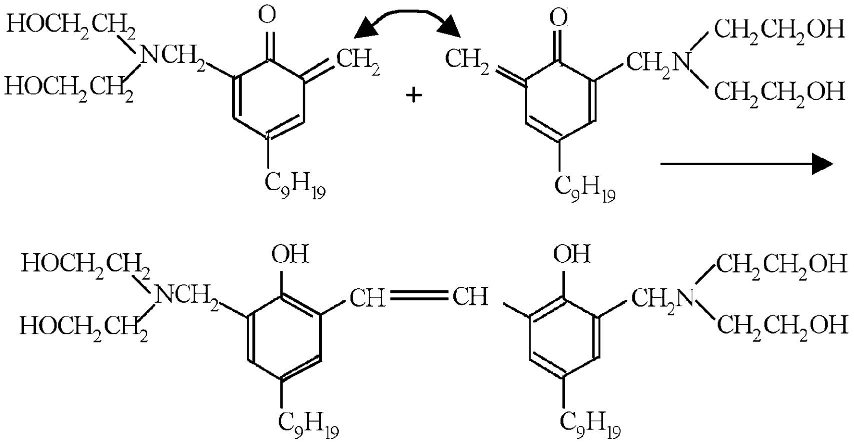
The quino-methyde reacts with *ortho*-free phenolic species from the reaction system giving superior oligomers (reaction 15.7). Quino-methydes react with hydrogen active compounds, such as terminal hydroxyl groups (reaction 15.8) and a specific reaction of quino-methydes is dimerisation (reaction 15.9). All these reactions (15.6 - 15.9) lead to polycondensation compounds having 2-3 aromatic nuclei which lead to a strong viscosity increase. Lower distillation temperatures lead to low viscosity Mannich bases and Mannich polyols.



(15.7)



(15.8)



(15.9)

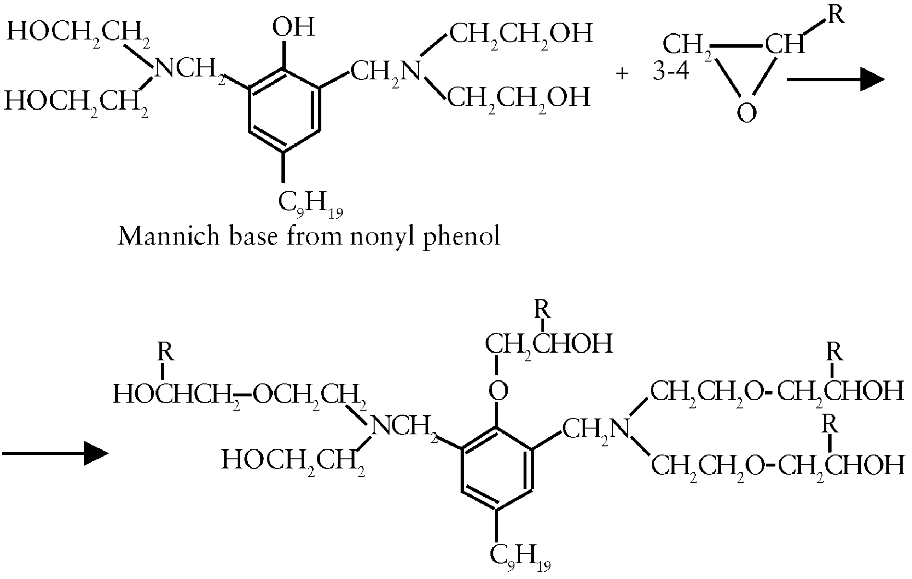
b) Alkoxylation of Mannich Base

The anhydrised Mannich base is heated under nitrogen at 80-125 °C (preferably at 80-90 °C to avoid viscosity increase) and PO (or a mixture of PO-EO or EO) is added stepwise within 4-6 hours. The reaction does not need a catalyst. The alkoxylation reaction is catalysed just by the tertiary amino nitrogen formed as a consequence of the Mannich reaction.

Addition of EO, together with PO (15-20% EO in the mixture with PO [16-18]), leads to Mannich polyols with lower viscosities than the polyols based exclusively on PO. By using a mixture of diethanolamine and diisopropanolamine (1:1 molar), Mannich polyols with lower viscosities than the Mannich polyols based exclusively on diethanolamine are obtained [11]. As mentioned previously, lower alkoxylation temperatures of 80-90 °C (maximum 95 °C), are preferred because polyols with lower final viscosities are obtained and the alkoxylation rate is higher at lower temperatures than at higher ones (see chapter 13).

After adding the necessary quantity of alkylene oxides, the reaction mass is maintained with stirring, at the same range of temperature, for digestion, for the consumption of unreacted monomer (1-2 hours).

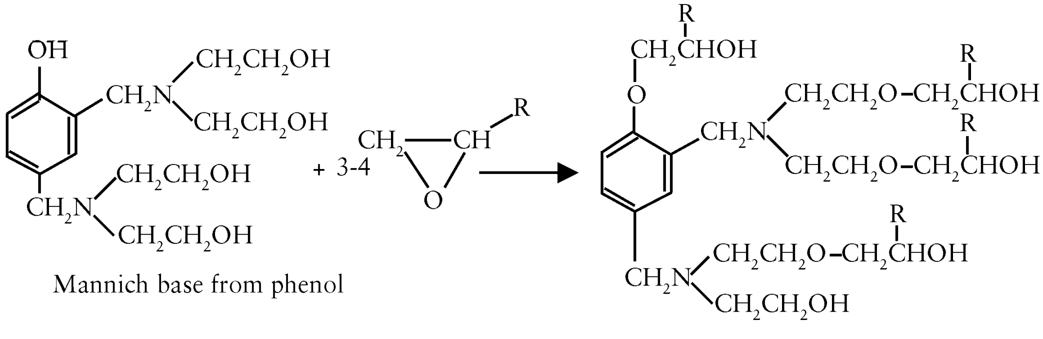
The last traces of alkylene oxides are removed by vacuum distillation at 100-110 °C. After the phenolic group alkoxylation, that is the first group which is alkoxylated, the resulting structure becomes much more stable and it is possible to develop degassing at higher temperature, without the risk of viscosity increase. The resulting Mannich polyols are used in polyurethane foam fabrication without any other supplementary purification. The reactions involved in the alkoxylation of Mannich bases to Mannich polyols are presented in reaction 15.10 [9].



(15.10)

The general technological flow for the synthesis of Mannich polyols is shown in **Figure 15.1**.

For Mannich polyols from phenol, the alkoxylation reaction of the corresponding Mannich base is presented in reaction 15.11. Of course, the Mannich base can have one or two aminomethyl groups or a mixture of these structures.



(15.11)

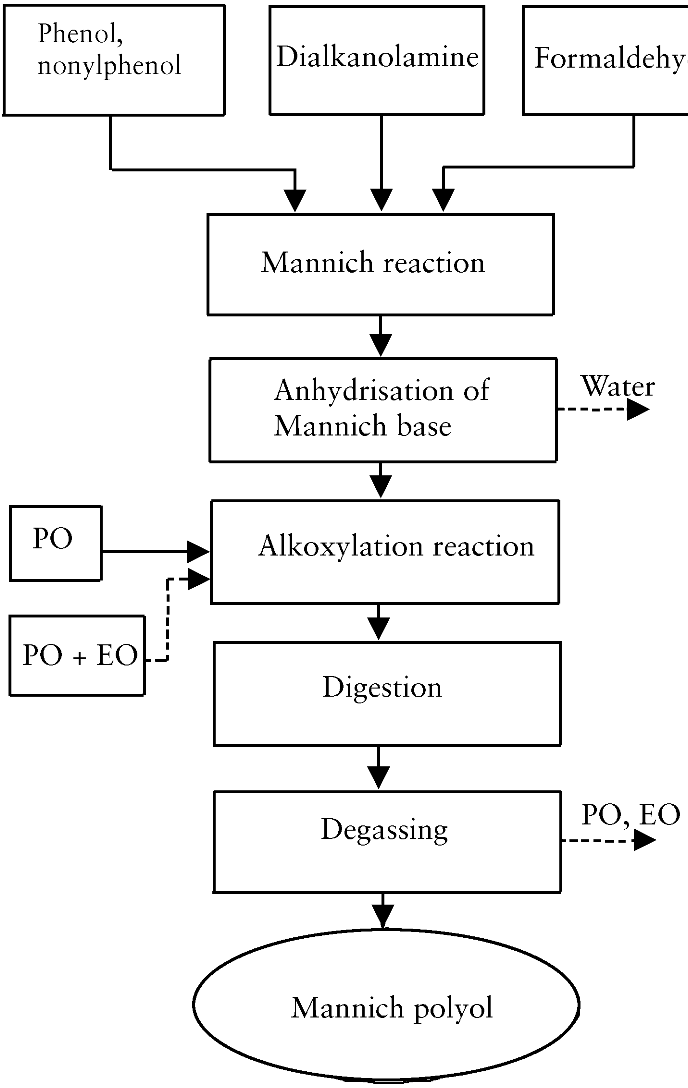


Figure 15.1 Flow chart for Mannich polyol synthesis

A Mannich polyol is well characterised by the molar ratio between reactants:

[phenol]:[formaldehyde]:[dialkanolamine]:[PO]

Thus, one of the most popular Mannich polyols is based on the following molar ratios:

[*p*-nonyl phenol]:[formaldehyde]:[diethanolamine]:[PO] = 1:2:2:2-3

Another important Mannich polyol is based on phenol and is characterised by the following molar ratios:

[phenol]:[formaldehyde]: [diethanolamine]:[PO] = 1:1:1:2-2.5

The viscosity of the final Mannich polyol depends on the functionalities of the resulting Mannich bases (lower functionalities lead to lower viscosities) and on the molar ratio between the reacted PO/mol of the Mannich base. **Figure 15.2** shows the variation of the Mannich polyol viscosities as a function of the molar ratio of the PO/Mannich base (Mannich base from 1 mol of nonyl-phenol, 2 mols of formaldehyde and 2 mols of diethanolamine). One observes that after the addition of one PO mol/mol of Mannich base a maximum of viscosity is obtained and by the addition of 2-5 mols of PO the viscosity decreases continuously.

It is possible to add 2-3 mols of PO/mol of Mannich base in the self catalysis of the tertiary amino nitrogen of the Mannich base, but 4-6 mols of PO/Mannich base needs a catalyst, such as a low hindered tertiary amine (for example dimethylaminoethanol, dimethylcyclohexylamine).

The Mannich polyols described are aromatic aminic polyols, the aromatic rings have a real contribution in improving the physico-mechanical, thermal and fire proofing properties of the resulting rigid polyurethane (PU) foams. The Mannich bases, for example the Mannich base resulting from one mol of nonyl-phenol, 2 mols of formaldehyde and 2 mols of

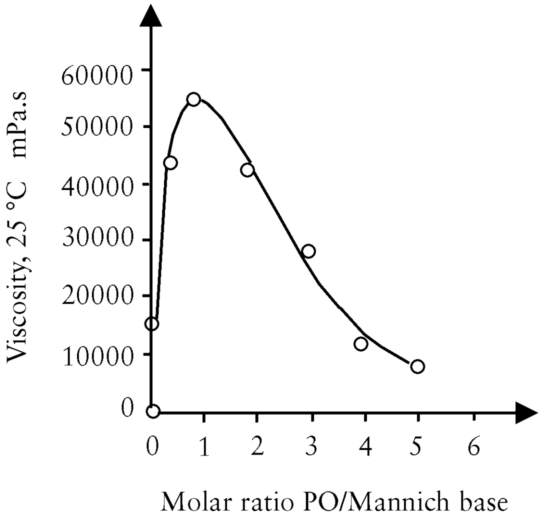


Figure 15.2 Variation of Mannich polyol's viscosity as function of molar ratio PO/Mannich base, [nonyl-phenol]:[formaldehyde]:[diethanolamine] = 1:2:2

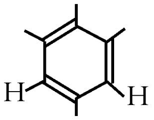
diethanolamine, are viscous liquids, with a convenient viscosity of around 16,000-20,000 mPa-s, at 25 °C and it is possible to use them as a sole polyol, without addition of PO [9]. The Mannich bases have a higher aromaticity than the propoxylated Mannich polyols. Formulations of these unpropoxylated Mannich bases and aromatic polyesters give high performance rigid PU foams, having an intrinsic fire resistance [1, 24, 25].

Unfortunately, due to the presence of free phenolic groups, the viscosity of Mannich bases increases slowly in time. For example in one year, the viscosity of a nonyl-phenol Mannich base increases from 16,000 mPa-s, at 25 °C, to 90,000-100,000 mPa-s, at 25 °C. Fortunately, in polyols, when an unpropoxylated Mannich base is used, the viscosity remains practically unchanged.

The aromaticity of a Mannich polyol is calculated with the following formula:

$$\text{Aromaticity}\,(\%) = \frac{74}{\text{Molecular weight of Mannich polyol}} * 100$$

74= molar mass of a tetrasubstituted benzene nucleus



The approximate functionality of Mannich polyols is calculated with the following formula:

$$f = \frac{[\text{formaldehyde}]}{[\text{phenol}]} * 2 + 1$$

The molecular weight of Mannich polyol can be calculated with formula 15.12 or with formula 15.13.

$$M = \frac{f * 56100}{OH\#} = \frac{\left\{\frac{[\text{formaldehyde}]}{[\text{phenol}]} * 2 + 1\right\} * 56100}{OH\#} \tag{15.12}$$

$$M = M_p + n * (M_f + M_{am} - 18) + \frac{[PO]}{[\text{phenol}]} \tag{15.13}$$

where:

M = molecular weight of Mannich polyol;

M_p = molecular weight of phenol;

M_f = molecular weight of aldehyde;

M_{am} = molecular weight of alkanolamine;

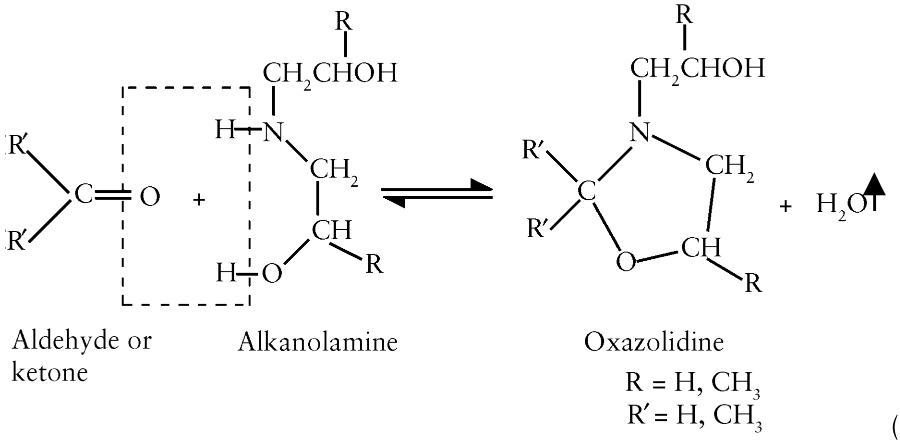
n = number of aldehyde mols/mol of phenol;

18 = molecular weight of water (water eliminated from the reaction); and

58 = PO molecular weight.

c) Synthesis of Mannich Polyols using Oxazolidine Chemistry [5, 9]

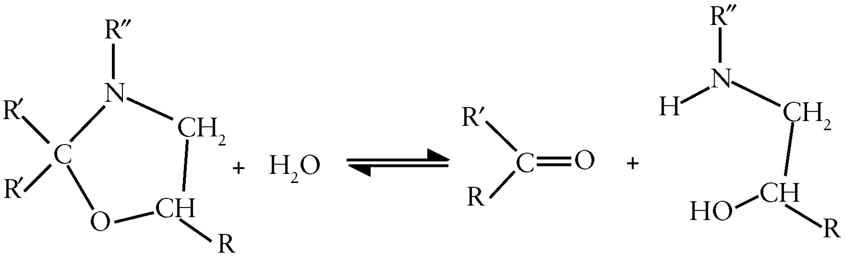
A variant of Mannich polyol synthesis is based on the reaction between phenols and an oxazolidine (OXA), a heterocyclic compound resulting from the reaction of an alkanolamine (primary or secondary, not tertiary) and an aldehyde or a ketone (reaction 15.14).



(15.14)

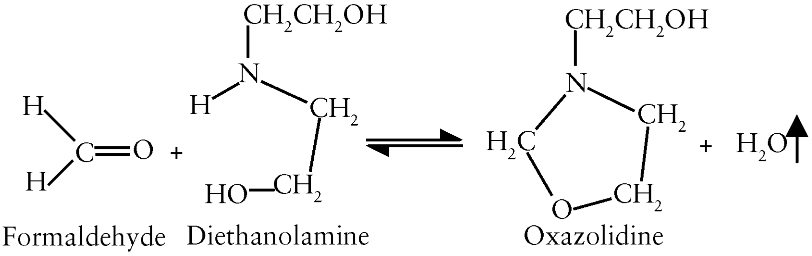
Reaction 15.14 is an equilibrium reaction and this equilibrium is pushed to the oxazolidine formation by the water elimination from the reaction system under vacuum distillation. This reaction is used in practice to trap the traces of water in some PU formulations which need a perfect anhydrous media, for example in PU elastomers [26]. By the addition of oxazolidines to these formulations reaction of these compounds with water takes place and the oxazolidine is transformed in an aminoalcohol which is in fact a 'chain extender' generated *in situ* and an aldehyde or a ketone practically inert in the reactions involved in PU chemistry (reaction 15.15).

In the particular case of Mannich polyol synthesis, the main alkanolamine used is diethanolamine (and to a lesser extent, diisopropanolamine [11]) while the carbonyl compound is formaldehyde [5, 6, 9].



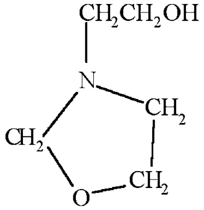
(15.15)

By the reaction of diethanolamine with formaldehyde (aqueous or paraformaldehyde), at 50-70 °C, the following oxazolidine (15.16) is formed with a high yield:



(15.16)

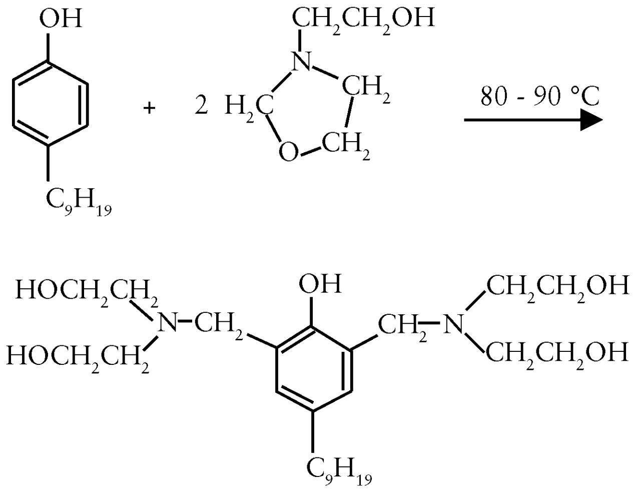
After the vacuum distillation of the resulting water (preferable at 90-100 °C and 1,35-26,65 Pa), a liquid substance of low viscosity is obtained, which is a distillable liquid, and very stable in anhydrous conditions. The characteristics of the oxazolidine derived from diethanolamine and formaldehyde are shown in **Figure 15.3** [9].



1. Aspect: low viscosity, light yellow to light brown liquid (when freshly distilled it is a colourless transparent liquid)
2. Molecular weight: 117
3. Hydroxyl number: 800-1000 mg KOH/g
4. Density, at 215 °C: 1.12-1.13 g/ml
5. Viscosity, at 25 °C: 25-35 mPa-s
6. pH (methanol/water: 10:1): 10.3
7. Refractive index (n_D) (25 °C): 1.4765
8. Water content: 0.06-0.5%
9. Boiling point: 125-130 °C at 8000 Pa
10. Strong IR absorption at 1650 cm^{-1} (C=N, imine group)

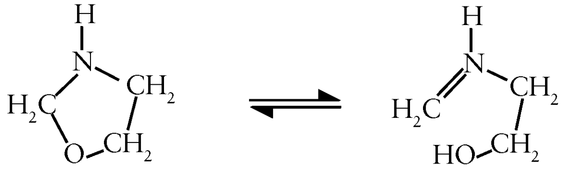
Figure 15.3

The synthesised oxazolidines react with phenols at 80-90 °C (reaction 15.17) and give rise to the Mannich bases which have the same structure as those obtained by the direct classical Mannich reaction:



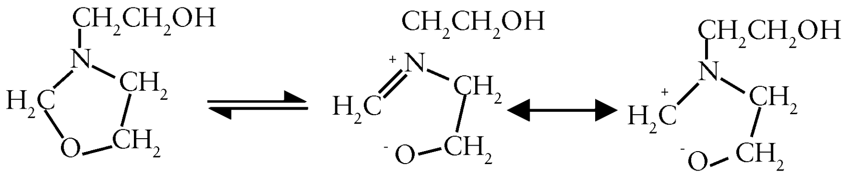
(15.17)

The mechanism of this unconventional reaction may be explained in two ways. Oxazolidines are substances which have a unique property: a cyclic form is in equilibrium with an open chain with the structure of a Schiff base. In the case of the oxazolidine derived from formaldehyde and monoethanolamine, the equilibrium is presented in reaction 15.18.



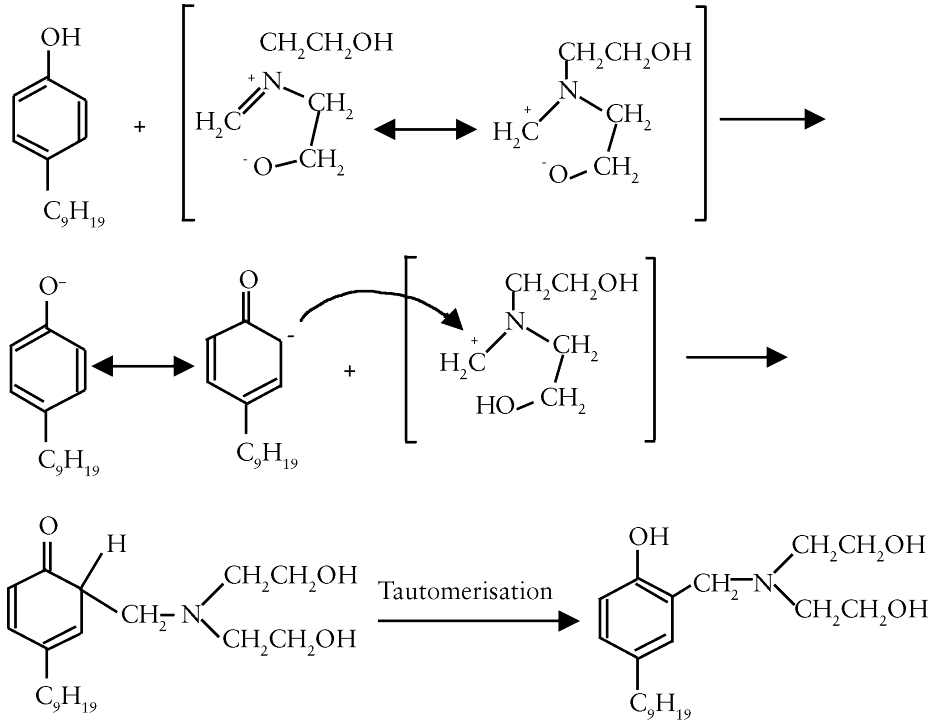
(15.18)

In the particular case of oxazolidine derived from formaldehyde and diethanolamine, the equilibrium of the cyclic form with the open chain form is presented in equation 15.19.



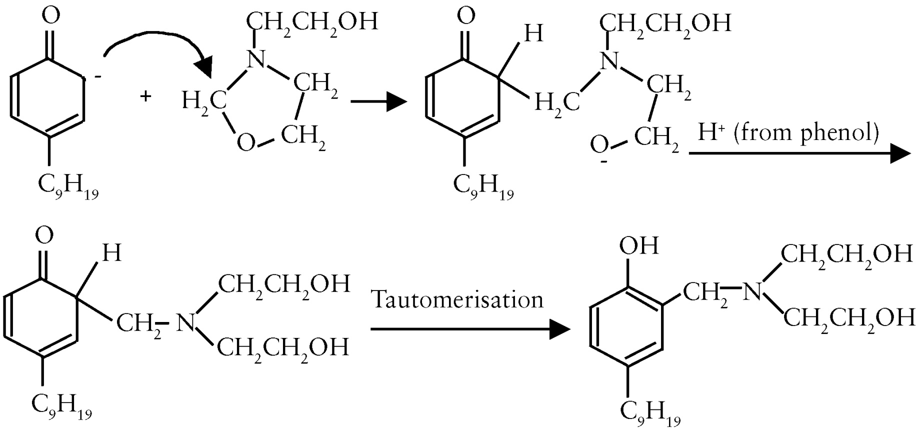
(15.19)

The open chain form has exactly the structure of the immonium cation, the classic intermediate of Mannich reaction. The mechanism of reaction with phenols is presented in reaction 15.20.



(15.20)

The second mechanism proposed to explain the reaction between an oxazolidine and a phenol is based on the nucleophilic attack of the phenolate anion (in its tautomeric form with negative charge at nucleus), to the carbon atom of the labile -N-CH_2-O- group (reaction 15.21).



(15.21)

The synthesis of Mannich polyols based on oxazolidine chemistry has the following three steps:

a) Synthesis of oxazolidine,

b) Synthesis of the Mannich base,

c) Alkoxylation of the resulting Mannich base with PO (or PO - EO mixtures).

a) Synthesis of Oxazolidine

The synthesis of oxazolidine is based on a stepwise addition of aqueous formaldehyde (25-37%) or solid paraformaldehyde (85-97%) to diethanolamine, at 50-70 °C. The reaction leads to the rapid formation of a mixture of oxazolidine - water, the reaction being only slightly exothermic. After the reaction (around 2 hours at 50-70 °C), the water is distilled at lower temperatures (80-100 °C) and under vacuum (1.3-26.6 MPa). In the last stage of distillation, the introduction of a slow flow of nitrogen to the reaction mass is a very efficient way to help water elimination. When the water content is 0.5-1%, the distillation is considered finished. Longer distillation times or higher distillation temperatures lead to the darkening of the labile oxazolidine. A short distillation time, at a high vacuum (0.6-2.7 MPa) and lower temperature, leads to a high quality oxazolidine. A thin film water distillation is one of the best ways to obtain high quality anhydrous oxazolidine.

b) Synthesis of the Mannich Base

The simple mixing of the anhydrous oxazolidine with a phenol, at 80-90 °C, for 2-3 hours leads to the formation of Mannich bases. As a general observation, the Mannich bases made via the oxazolidine route have lower viscosities than the Mannich bases obtained by the classical reaction of phenol with formaldehyde and diethanolamine. This effect is explained by the absence of vacuum distillation in the presence of phenolic compounds which leads to polycondensation of Mannich bases to form viscous oligomers (with 2-3 aromatic nuclei).

c) The Alkoxylation of the Synthesised Mannich Base

The alkoxylation of the Mannich base with PO (or PO-EO mixtures), takes place by the stepwise addition of the oxiranic monomers, at 80-95 °C, in an inert nitrogen atmosphere [5, 9]. **Figure 15.4** shows that the Mannich polyols obtained by the oxazolidine technology have lower viscosities than the corresponding Mannich polyols obtained by classical Mannich reactions. This effect is explained by the low viscosity of the intermediate Mannich bases used as starters.

A Mannich polyol obtained *via* the oxazolidine route is well characterised by the following ratios:

[phenol]:[oxazolidine]:[PO]

A Mannich polyol based on nonyl phenol and oxazolidine with a functionality of 5 OH groups/mol has the following molar ratios:

[nonyl phenol]:[oxazolidine]:[PO] = 1:2:2-3

A Mannich polyol based on nonylphenol and oxazolidine with a functionality of 4 OH groups/mol is characterised by the following molar ratios:

[nonyl phenol]:[oxazolidine]:[PO] = 1:1.5:2-3

A Mannich polyol based on a phenol with a functionality of 3 is characterised by the following molar ratios:

[phenol]:[oxazolidine]:[PO] = 1:1:2-2.5

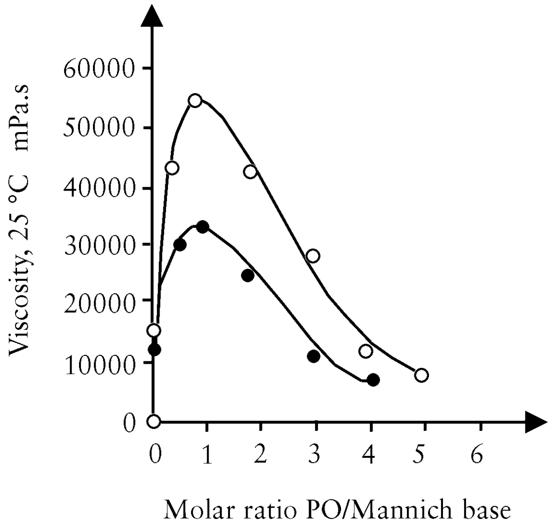


Figure 15.4 Variation of Mannich polyol's viscosity as function of the molar ratio of PO/Mannich base made by classic Mannich reaction (O) and by oxazolidine route (●); [nonyl-phenol]:[formaldehyde]:[diethanolamine] = 1:2:2 (O); [nonyl-phenol]:[oxazolidine] = 1:2 (●)

The functionality of Mannich polyols obtained by oxazolidine technology is given by the formula 15.22:

$$f = \frac{[\text{oxazolidine}]}{[\text{phenol}]} * 2 + 1 \tag{15.22}$$

where:

f = functionality (OH groups/mol);
[oxazolidine] = number of oxazolidine mols;
[phenol] = number of phenol mols;
2 = one mol of oxazolidine generates two hydroxyl groups;
1 = one phenolic group generates one aliphatic hydroxyl group.

The theoretical hydroxyl number for the Mannich base can be calculated with the formula 15.23:

$$\text{OH}\# = \frac{f * 56100}{M} = \frac{\left(\frac{[\text{oxazolidine}]}{[\text{phenol}]} * 2 + 1\right) * 56100}{M_{ph} + \frac{[\text{oxazolidine}]}{[\text{phenol}]} * 117} \tag{15.23}$$

where:

M_{ph} = molecular weight of phenol
117 = molecular weight of oxazolidine

The quantity of PO (Q_{PO}) needed to be added to a quantity Q_M of Mannich base in order to obtain the required final hydroxyl number (I_f) of Mannich polyol is given by the relationship 15.24:

$$Q_M * I_M = (Q_M + Q_{PO}) * I_f$$
$$Q_{PO} = \frac{Q_M * I_M}{I_f} - QM \tag{15.24}$$

where:

Q_M = quantity of Mannich base
Q_{PO} = quantity of PO needed
I_M = hydroxyl number of Mannich base
I_f = hydroxyl number of final Mannich polyol

Of course, the quantity of PO needed is slightly higher if the water content of Mannich base is considered.

A flow chart for the synthesis of Mannich polyols, by oxazolidine technology is presented in **Figure 15.5**.

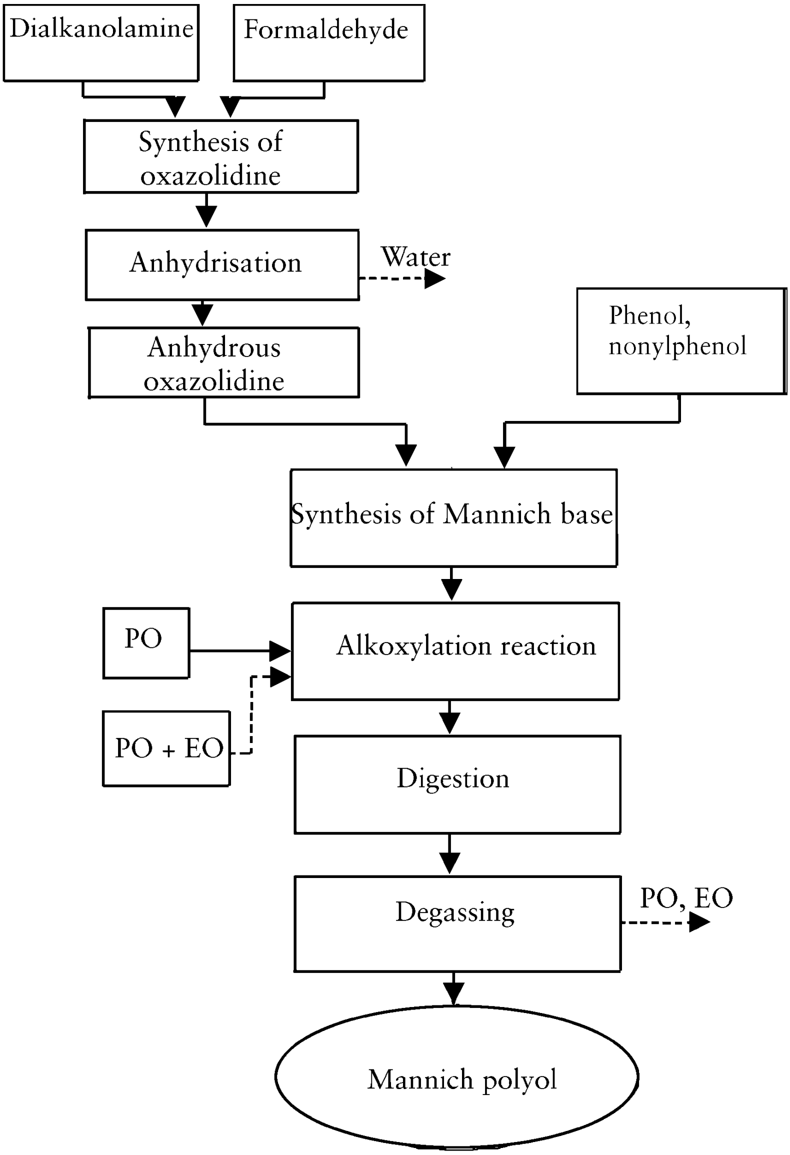


Figure 15.5 Synthesis of Mannich polyols by the oxazolidine route

Mannich polyols are aromatic polyols, which confer excellent physico-mechanical, thermal and fire proofing properties to rigid PU foams. Mannich polyols, especially those based on *p*-nonylphenol, have a very good compatibility with pentanes used as blowing agents (for example sucrose polyether polyols have a poor compatibility with pentanes, giving emulsions at normal concentrations for foaming, but not real solutions).

Due to the tertiary nitrogen content, the Mannich polyols are very reactive and are used especially in very reactive PU formulations such as for ‘spray’ rigid foams, but for pour-in-place, rigid PU foams are used successfully too [16-19]. By utilisation of Mannich polyols in pour-in-place, rigid PU foam formulations, a reduction of catalysts for foaming of around 30-40% it is possible, due to the intrinsic reactivity of Mannich polyols. Formulations using less catalyst produce a rising foam with very good flowability and the foam does not become solid too early and as a consequence flows and occupies all the volume and the details of the mould.

A very interesting Mannich polyol, of low functionality (f = 3.5 OH groups/mol) and low hydroxyl number (OH# = 325 mg KOH/g), derived from nonyl phenol was developed successfully for ‘all water blown’ rigid PU foams [19].

Unpropoxylated Mannich bases were used successfully as polyols in combination with other polyols (for example with aromatic polyesters) or as crosslinkers in rigid PU foams, including ‘ spray’ foams. The high aromaticity of unpropoxylated Mannich bases leads to a high yield of ‘char’ during the burning process of the resulting rigid PU foams. This high char yield confers to the rigid PU foam an inherent fire resistance.

The fabrication of Mannich polyols by the oxazolidine route has the following advantages:

1. The productivity of the reactor is higher because a large volume of water is replaced by an useful reaction product (an increase of productivity of around 40%). In classic Mannich technology, at a reaction mass of 5000 kg, around 1500 kg is water. In oxazolidine technology (oxazolidine made in a separate reactor), the reaction mass does not have any water and is in fact only a mixture of phenol with oxazolidine.

2. The viscosity of Mannich polyols obtained by oxazolidine technology is lower than the viscosities of polyols obtained by classical Mannich technology.

3. The total time needed for synthesis of a Mannich polyol via the oxazolidine route is shorter than the time needed for normal Mannich technology.

4. The quality of Mannich polyols obtained by the oxazolidine route is good, comparable with that of normal Mannich polyols.

One of the biggest advantages of Mannich technology is that by using only one substance (oxazolidine), it is possible to obtain a large range of Mannich polyols. Thus, by simple reaction of oxazolidine with various phenols and naphthols, dialkylphosphites, melamine, cyanuric acid, aniline and hydroxyalkyl anilines, a large range of new Mannich bases and of course new Mannich polyols are obtained. The characteristics of some representative Mannich polyols, obtained by oxazolidine technology, are presented in **Tables 15.1** and **15.2**. The characteristics of representative Mannich bases used as sole polyols are presented in **Table 15.3**.

15.2 Novolak-Based Polyether Polyols

Novolaks are condensation products of formaldehyde with phenols, obtained by acidic catalysis (usually oxalic acid [27]):

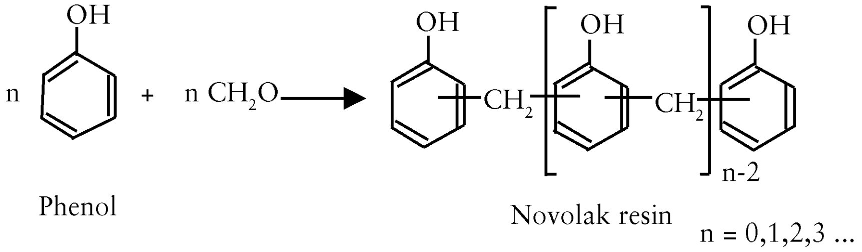


Table 15.1. The characteristics of two representative Mannich polyols based on nonyl-phenol (NP) obtained by oxazolidine technology

Characteristic	Unit	Type 1	Type 2
Molecular weight	daltons	584	510
Functionality	OH groups/mol	5	4
Hydroxyl number	mg KOH/g	480	440
Viscosity, at 25 °C	mPa-s	25000	7800
Tertiary nitrogen	equiv.%	0.34	0.29
Water content	%, max.	0.1	0.1
Ratio [NP]:[OXA]:[PO]	[mols]: [mols]: [mols]	1:2:2-3	1:1.5:2-3

Table 15.2. The characteristics of two representative Mannich polyols based on phenol obtained by oxazolidine technology [9]

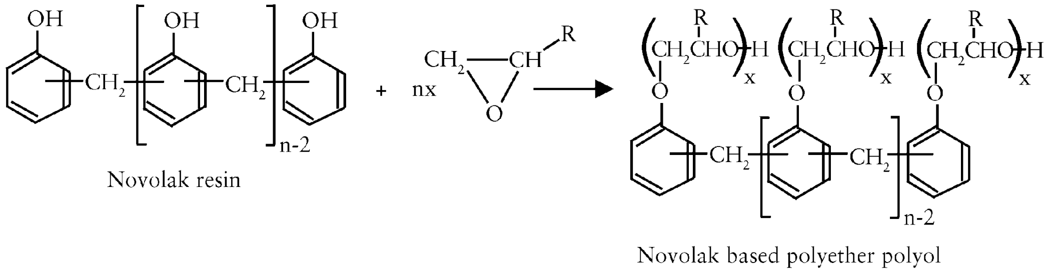
Characteristic	Unit	Type 1	Type 2
Molecular weight	daltons	330	578
Functionality	OH groups/mol	3	5
Hydroxyl number	mg KOH/g	510	485
Viscosity, at 25 °C	mPa-s	9000	16000
Tertiary nitrogen	equiv.%	0.30	0.34
Water content	%, max.	0.1	0.1
Ratio [P]:[OXA]:[PO]	[mols]:[mols]:[mols]	1:1:2	1:2:4

Table 15.3 Some characteristics of representative Mannich bases obtained by oxazolidine technology [9]

Characteristic	Unit	Mannich base from phenol	Mannich base from nonyl phenol
Hydroxyl number	mg KOH/g	839	645
Viscosity, at 25 °C	mPa-s	27700	9800
Tertiary nitrogen	mequiv./g	6.28	4.61
pH (MeOH/water)	-	10.0	10.1
Water content	%	0.12	0.06

The linkages between the aromatic nuclei are in the *ortho* and *para* positions. The novolak resins are amorphous solids which become liquid at 50-80 °C, depending on the value of n.

By the propoxylation of novolaks in the presence of alkaline catalysts (KOH, NaOH) or better, in the presence of a low hindered tertiary amine, aromatic polyether polyols of the following structure are obtained [27, 28] (15.25):



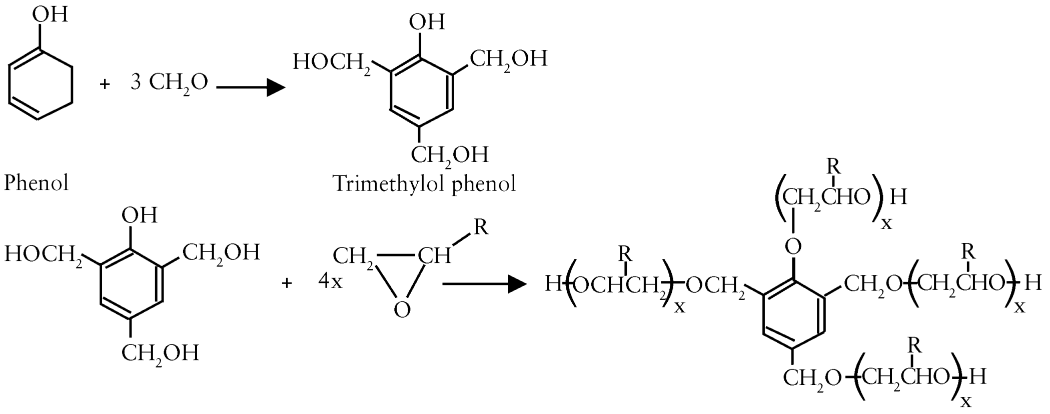
(15.25)

By the propoxylation of commercial novolaks, lower viscosities of around 3 phenolic units/mol are obtained. Novolaks with higher degrees of condensation (4-6 or more phenolic units/mol) have very high viscosities.

Usually the hydroxyl number of novolak polyols obtained by the direct propoxylation of novolaks is low, around 230-250 mg KOH/g. The hydroxyl number is increased and the viscosity is decreased by propoxylation of a mixture of novolaks with high hydroxyl number polyols of low functionality (e.g., glycerol or triethanolamine, maximum 20-25%) [28]. It is well known that by propoxylation of low functionality polyols, polyethers of very low viscosity result. By propoxylation of the mixtures of novolak – low functionality polyols, the low viscosity polyether polyols are formed *in situ* together with novolak polyols and the resulting viscosity is much lower than the viscosity of polyols derived exclusively from novolaks.

The resulting novolak polyols, in spite of their low functionalities and low hydroxyl numbers, give rigid PU foams with a very uniform cellular structure, with excellent physico-mechanical, thermal and fire proofing properties and good dimensional stability, characteristics which are associated with the high aromatic structure of novolak polyols.

Resol resins, having very reactive methylol groups (obtained by the condensation of phenol with formaldehyde in basic media), are rarely used as starters for rigid polyether polyols. One reason is the impossibility of melting these resins at the propoxylation temperature, because upon heating they rapidly polycondensate and crosslink. An interesting representative of this group of resin is trimethylol phenol (reaction 15.26).



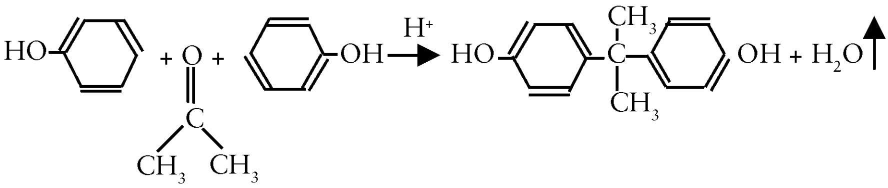
(15.26)

Synthesis of novolak polyols is possible by using some derivatives of formaldehyde instead of formaldehyde such as: trioxanes and dioxolanes.

In practice, novolak polyols are used to a lesser extent, because of the poor reproducibility of the polyether polyol characteristics, the resulting high viscosity and the presence of variable quantities of free monofunctional phenol, which decreases their functionality.

15.3 Bisphenol A Based Polyols

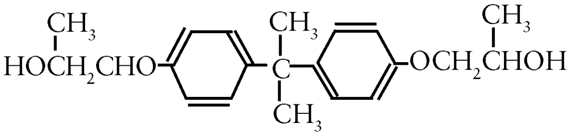
Bisphenol A is a condensation product of two mols of phenol with one mol of acetone (reaction 15.27):



(15.27)

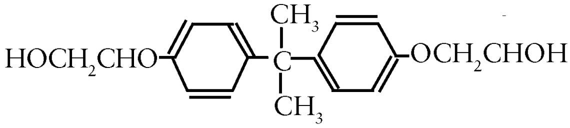
Bisphenol A is used in large quantities for fabrication of epoxy resins, polycarbonates and polyarylates.

Propoxylates of bisphenol A with 2 mols of PO/mol of bisphenol (15.28) and of the ethoxylated bisphenol A (15.29) with 2 mols of EO/mol of bisphenol have been used for many years as aromatic diols in the synthesis of unsaturated polyesters [29].



MW= 344.27
OH# = 325

(15.28)



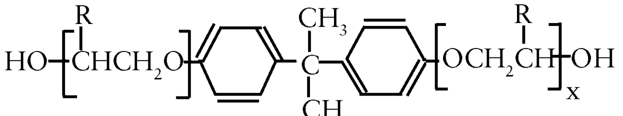
MW= 316.27
OH# = 354

(15.29)

Both aromatic diols are solid, at room temperature, with convenient melting points and have high aromaticity. Thus, the propoxylated bisphenol A has an aromatic content of 46.7% and ethoxylated bisphenol A an aromatic content of around 48%.

By solubilisation of propoxylated bisphenol A with the structure 15.28, in a sucrose-based polyether polyol for rigid foams, an homogeneous mixture is obtained [29]. The viscosities of these mixtures increase with the content of propoxylated bisphenol A. From these mixtures rigid PU foams were obtained. Due to the aromaticity introduced by the propoxylated bisphenol A, the physico-mechanical properties of the resulting rigid PU foams were superior to the rigid PU foams made with the sucrose-based polyether polyol alone [29].

Bisphenol A propoxylated or ethoxylated with 2-10 mols of alkylene oxides/mol of bisphenol A are used as chain extenders for PU elastomers and as aromatic diols for isocyanuric and urethane isocyanuric foams [30] (structure 15.30).

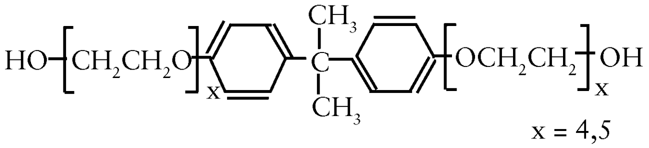


x = 1,2,3,4,5 ...
R = H, CH$_3$

(15.30)

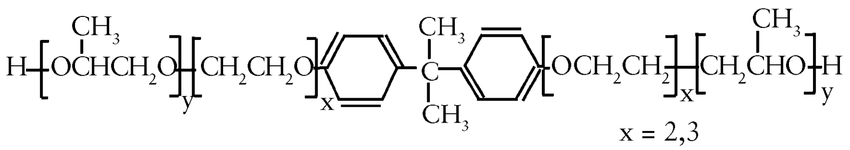
An excellent polyol for urethane isocyanuric foams is a diol based on bisphenol A, alkoxylated with 8-9 mols of EO or with 4 mols of PO and 4-5 mols of EO (structures 15.31 and 15.32).

Bisphenol A is a compound with a melting point of around 157 °C, which is higher than the normal alkoxylation temperatures (90-120 °C). Bisphenol A can be alkoxylated in a liquid reaction medium such as an inert solvent (toluene, xylene) or in a reactive liquid reaction medium such as PO or in the final polyether polyol [28, 30].



x = 4,5

(15.31)



x = 2,3
y = 2

(15.32)

The catalysts for the alkoxylation of bisphenol A are alkali hydroxides (KOH, NaOH) and tertiary amines (trimethylamine, dimethylaminoethanol, dimethylcyclohexylamine). Of course, the polyether diols obtained in KOH catalysis must be purified by removing the potassium ions, using conventional procedures.

It is well known that EO, a very reactive monomer in anionic polymerisation, can be added to the hydroxyl groups in the tertiary amine catalysis until 8-9 EO units/hydroxyl groups are added. One must remember that in the same type of catalyst reaction, PO can only be added until a maximum of 1-2 PO units/hydroxyl groups is reached [31].

There are some practical possibilities for alkoxylating the solid bisphenol A.

The first method is to suspend the bisphenol in an inert solvent, such as toluene, and to add PO or EO at 90-120 °C, in the presence of a basic catalyst, preferably a tertiary amine. Finally the solvent is distilled under vacuum and recycled to the process. This method has the disadvantage of needing solvent recycling.

A second method is to suspend the solid bisphenol A in liquid PO, in the presence of the tertiary amine used as catalyst (molar ratio 1 mol of bisphenol per 1.5-2 mols of PO). After 1.5-2 hours of mixing at 90-100 °C, the alkoxylation is continued by adding 6-8 mols of EO. Finally, the resulting diol is degassed under vacuum and is used in PU fabrication without any purification step.

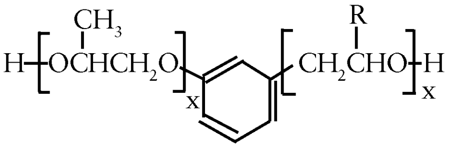
A third process of solid bisphenol A alkoxylation is to use a suspension of solid bisphenol A in final polyether polyol (40-60% bisphenol A and 60-40% liquid polyether diol). This suspension, in the presence of a tertiary amine as catalyst, is ethoxylated at 80-95 °C, with 8-9 mols of EO/mol of bisphenol A. At the end of the reaction, all the solid bisphenol A was totally transformed into liquid polyether diols [30]. The resulting polyether diols are used successfully for production of urethane-isocyanuric foams with very good physico-mechanical properties and intrinsic fire resistance.

Very interesting polyols for rigid PU foams are obtained by the simultaneous alkoxylation with PO (or EO) of a mixture from bisphenol A and a costarter, such as: bisphenol A - *ortho* toluene diamine [32], bisphenol A - diaminodiphenylmethane [32], bisphenol A - polyethylene glycol of MW of 600 [11], or bisphenol A - sorbitol-glycerol [11].

Simultaneous alkoxylation of bisphenol A and an aromatic amine as second polyol is a variation used to obtain highly aromatic polyols.

15.4 Resorcinol-Based Diols [33, 34]

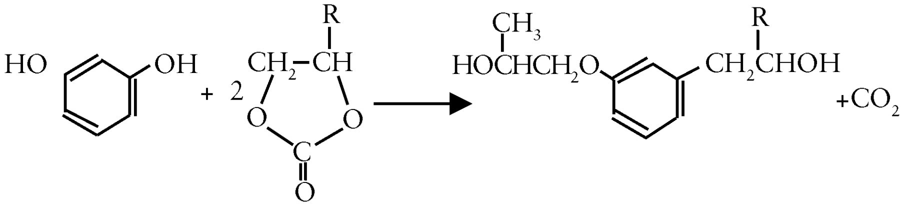
Resorcinol diols represent a new class of aromatic dihydroxylic compounds with the general formula (15.33):



(15.33)

x = 0,1, 2   R = H,CH_3

Resorcinol diols are obtained by the reaction of resorcinol with ethylene carbonate or propylene carbonate (reaction 15.34), in the presence of basic catalysts (K_2CO_3, KOH, NaOH, tertiary amines), or even in the absence of catalysts, at higher temperatures (150-170 °C):

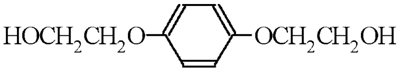


(15.34)

A resorcinol diol based on 1 mol of resorcinol and 2 EO units is a solid with a melting point of 87-89 °C and an hydroxyl number of 555 mg KOH/g [34]. All the resorcinol diols having PO units or PO and EO units are liquids at room temperature, with a viscosity of between 3,900 –20,000 mPa-s at 25 °C and hydroxyl numbers between 345-485 mg KOH/g [34]. The resorcinol diols based on resorcinol and more than 2 EO units are liquid at room temperature, with a viscosity of around 2000 mPa-s at 25 °C and 375-385 mg KOH/g [34].

It is very interesting that a resorcinol diol based on propylene carbonate has 85% secondary hydroxyl groups and 15% primary hydroxyl groups. In the resorcinol diols based on propylene carbonate and ethylene carbonate (terminal units), the terminal primary hydroxyl is around 50% [33, 34].

Resorcinol diols are superior to the well known hydroquinone di(beta-hydroxyethyl) ether (HQEE), which is a solid with a melting point of 100 °C:

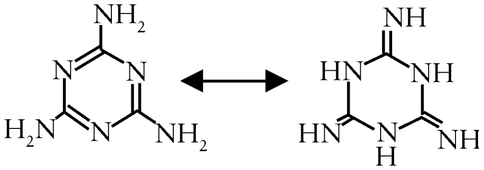


HQEE

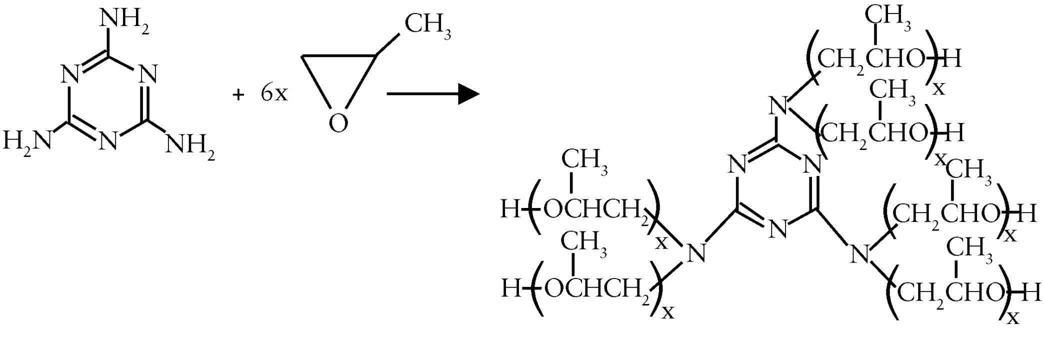
The resorcinol diols are used successfully in high durability and thermal stability PU adhesives, PU elastomers (cast and thermoplastic PU elastomers), sealants and coatings.

15.4 Melamine-Based Polyols for Rigid Polyurethanes [14, 17, 19, 20, 24, 31, 35]

Melamine is a very thermoresistant aromatic heterocyclic compound, with three -NH_2 groups, which makes it very attractive for use as a starter for polyol synthesis. Unfortunately, melamine is very difficult to directly alkoxylate with PO or EO. This difficulty is because of the amidic structure (melamine is the amide of cyanuric acid) and because of the tautomeric forms (characteristic to all amides) [31]:



Melamine is soluble only in water and has low solubility in dimethylsulfoxide (DMSO) and in other aprotic dipolar solvents (9% at 120 °C), in glycerol or ethylene glycol (10% at 140 °C). In the majority of other usual solvents it is insoluble. Kucharski and Lubczak discovered a new class of reactive solvents for melamine [36]: poly(hydroxymethyl) derivatives of cyclohexanone, acetone, nitromethane which are able to dissolve 50-60% melamine. Melamine can be totally propoxylated or ethoxylated at lower temperatures (70-90 °C), in aprotic dipolar solvents (for example DMSO, dimethylformamide, *N*-methyl pyrrolidone and so on), in the presence of quaternary ammonium hydroxides as catalysts [for example tetrabutyl ammonium hydroxide (TBAH)], at a low reaction rate (reaction 15.35), for a very long reaction time (40-50 hours) [31, 37]. The resulting hexafunctional polyols give very thermostable rigid PU (up 200 °C).

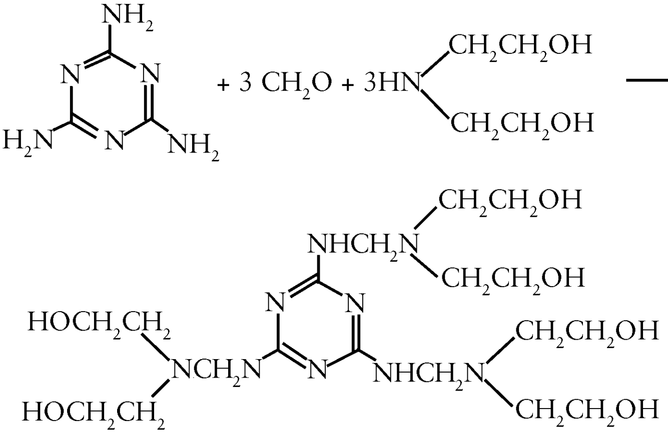


(15.35)

The very long reaction time, the necessity of recycling an expensive solvent, and the high cost of the catalyst, mean that this synthesis method is not applied in practice.

A useful synthetic variant to melamine-based polyols is to alkoxylate the condensates of melamine with carbonyl compounds.

Thus, by the reaction of melamine with formaldehyde and diethanolamine, a melamine-based Mannich base (reaction 15.36), is obtained quantitatively in 1-2 hours at 60-70 °C. The resulting Mannich base is a hexafunctional starter [10, 21, 31]:

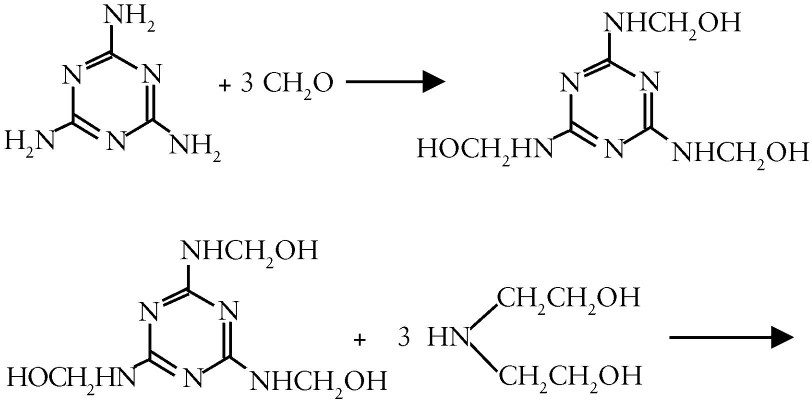


(15.36)

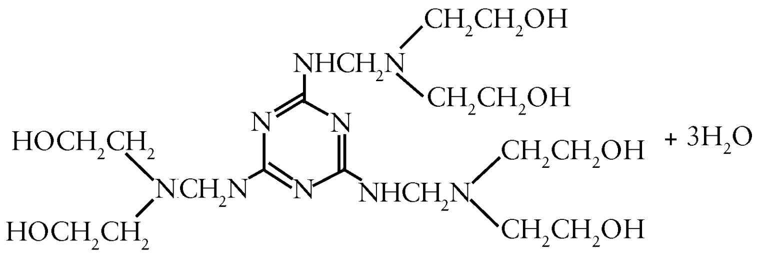
Practically, the reaction takes place by the addition of aqueous formaldehyde to a mixture of melamine suspended in diethanolamine, at a molar ratio of [melamine]:[formaldehyde]:[diethanolamine] = 1:3:3, followed by water distillation under vacuum, at a lower temperature of 65-75 °C, in order to avoid the viscosity increase produced by polycondensation. The maximum water accepted in the Mannich base can be high, around 5%.

The same Mannich base can be obtained by other two methods.

The first method is based on the melamine reaction with formaldehyde and the resulting trimethylol derivative is reacted with diethanolamine [10] (reactions 15.37 and 15.38).

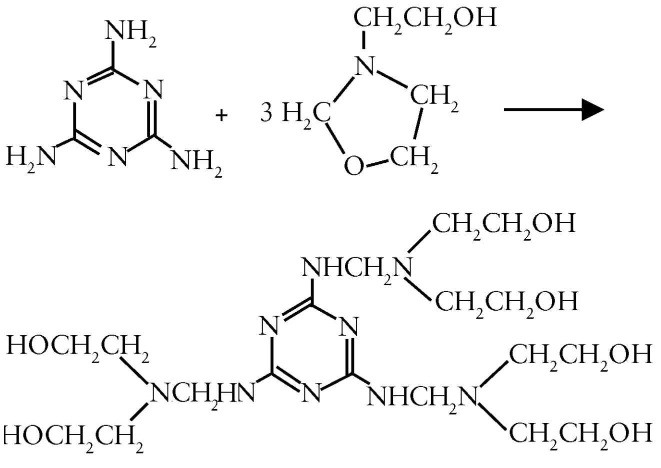


(15.37)



(15.38)

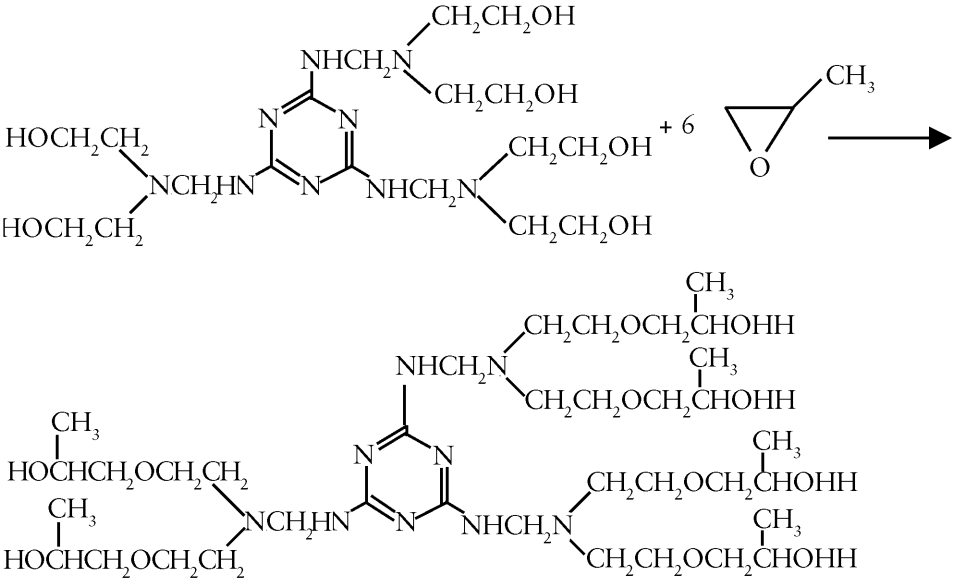
The second method consists of the reaction of melamine with oxazolidine (reaction 15.39) [31].



(15.39)

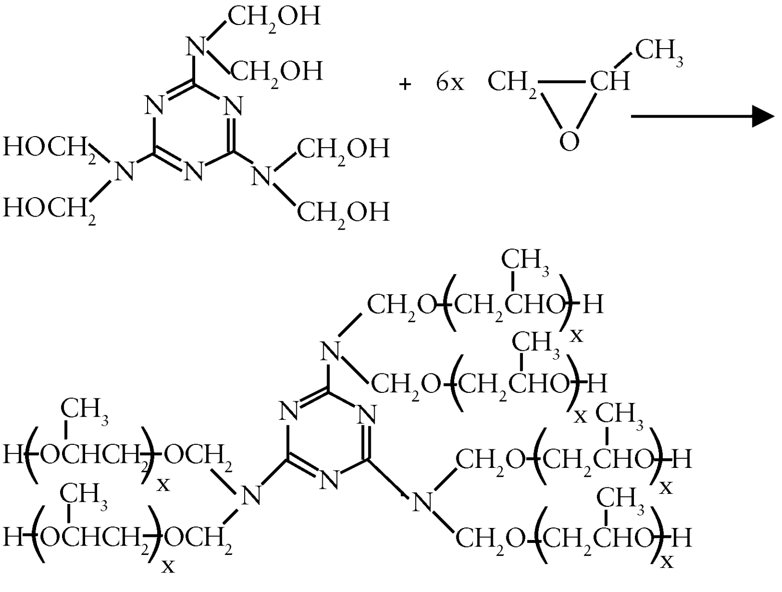
Unfortunately, due to the low solubility of melamine in oxazolidine, reaction 15.39 takes place slowly, needs a long reaction time and unreacted melamine frequently remains. The best method for the synthesis of melamine Mannich base is the Mannich reaction in the presence of aqueous formaldehyde.

By the propoxylation of the synthesised melamine derived Mannich base, without catalyst, a hexafunctional polyether polyol is obtained (reaction 15.40).



(15.40)

Very interesting polyols are obtained by hexamethylolmelamine alkoxylation with PO, in the presence of a low hindered tertiary amine (for example dimethylaminoethanol) as catalyst, at 80-95 °C (reaction 15.41) [35, 38].

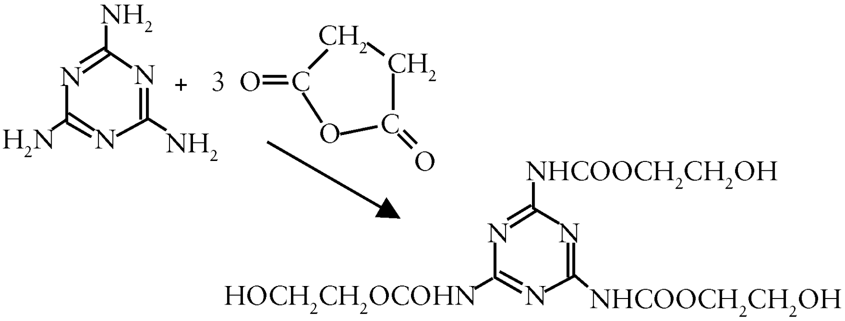


(15.41)

Other transformations of melamine in polyols are based on the reaction of melamine with ethylene carbonate and with alkanolamines.

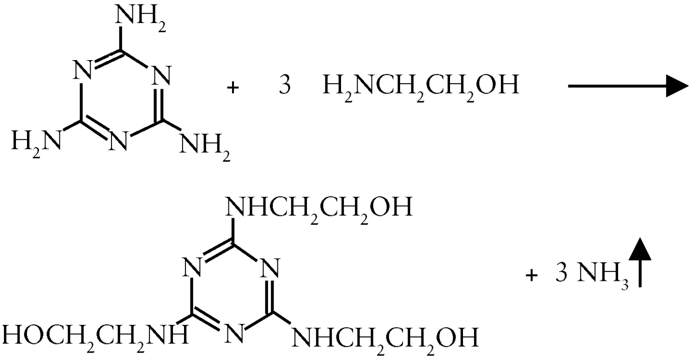
Reacting melamine with ethylene carbonate or propylene carbonate, at 150-200 °C, in liquid medium (for example a Mannich polyol derived from phenol), 2-hydroxyalkyl carbamates of melamine are obtained [4] (reaction 15.42). The reaction developed in the absence of this liquid polyol takes place with difficulty and with decomposition. Ethylene carbonate is reactive, but propylene carbonate has a much lower reactivity.

By using the synthesised hydroxyalkyl carbamates of melamine as polyols, rigid PU foams were obtained with good physico-mechanical properties, low friability and inherent self extinguishing properties. A highly aromatic polyol, based on the reaction of benzoguanamine with ethylene carbonate was successfully synthesised [4].



(15.42)

The reaction of melamine with alkanolamines (monoethanolamine, 2-propanol amine, diethanolamine, and so on), in fact a transamidation reaction, leads to hydroxyalkyl derivatives of melamine and gaseous ammonia [39] see reaction 15.43.

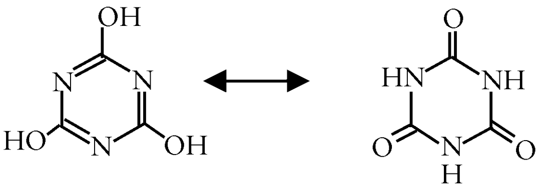


(15.43)

Reaction 15.43 is idealised because together with the normal product of the reaction there are formed a relatively high concentration of by products, i.e., isomelamine [39]. By substitution of monoethanolamine with 2-propanol amine, the isomelamine content was reduced drastically [39]. Thus, by the reaction of melamine with 3 mols of isopropanol amine in ethylene glycol as solvent, in the presence of ammonium chloride as catalyst isopropanol melamine and 13% isomelamine [39] are obtained. Ethylene glycol was removed by vacuum distillation at 150 °C. If the same reaction was repeated with monoethanolamine, the formation of isomelamine was around 50% at 95% conversion. Other catalysts for the reaction of melamine with amines are: HCl, H_2SO_4, *p*-toluene sulfonic acid, phosphonic acids and so on.

Similar polyols with triazinic structure are obtained by using cyanuric acid condensates. Cyanuric acid is a product of urea thermal decomposition or the product of hydrolysis of melamine or of cyanuryl chloride [40].

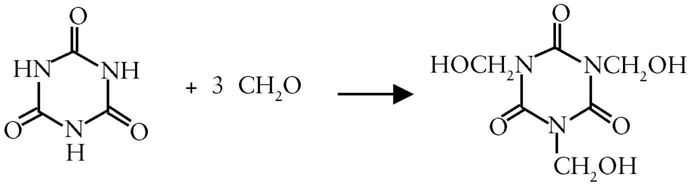
Similarly to melamine, cyanuric acid has two tautomeric forms [40]:



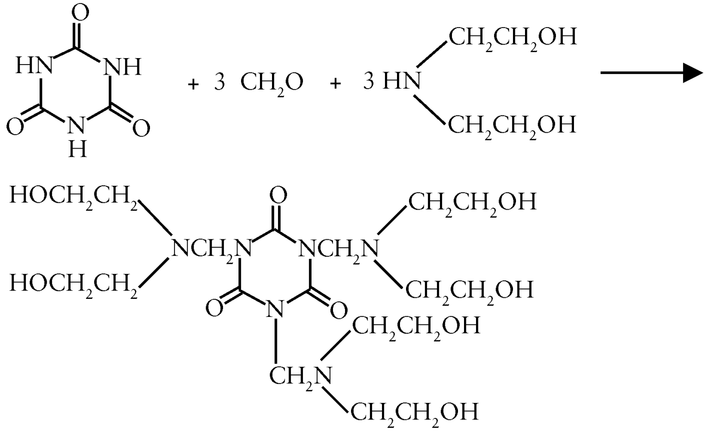
Cyanuric acid

(15.44)

By the reaction of cyanuric acid with formaldehyde or by Mannich reaction with formaldehyde and diethanolamine interesting polyolic starters with heteroxyxlic triazinic structure are formed [31, 41]:

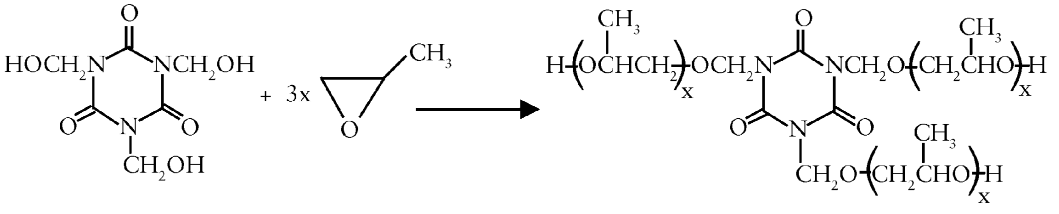


Trimethylol isocyanurate

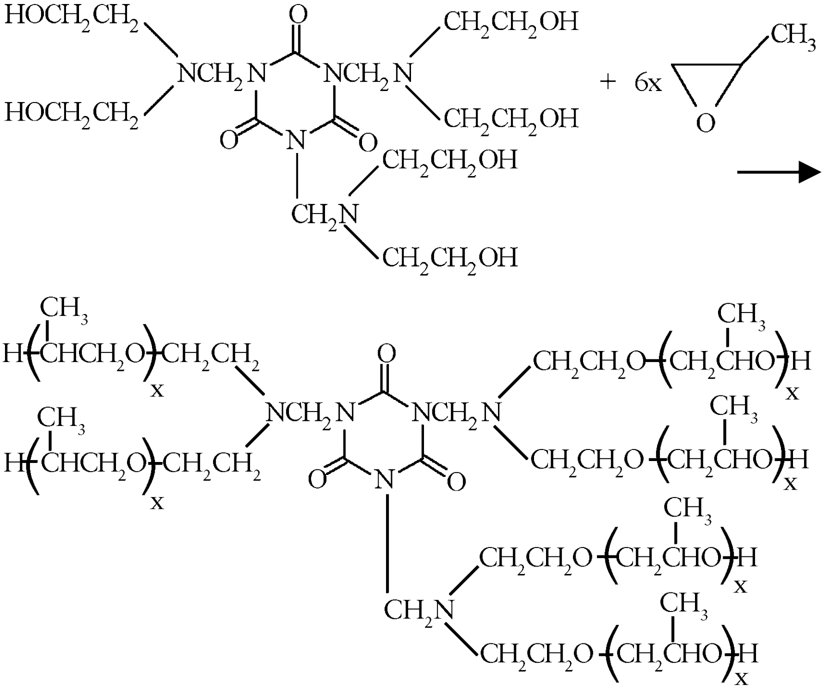


By propoxylation of the resulting polyols (trimethylolisocyanurate and the Mannich base (15.44), in the presence of a tertiary amine as catalyst (for example dimethylaminoethanol) new heterocyclic polyols for rigid PU foams with a triazinic structure are obtained (reactions 15.45 and 15.46).

A well known triol, tris (hydroxyethyl) isocyanurate (THEI) is produced industrially and currently used in PU manufacture, as a crosslinking agent (15.47) [31, 41].



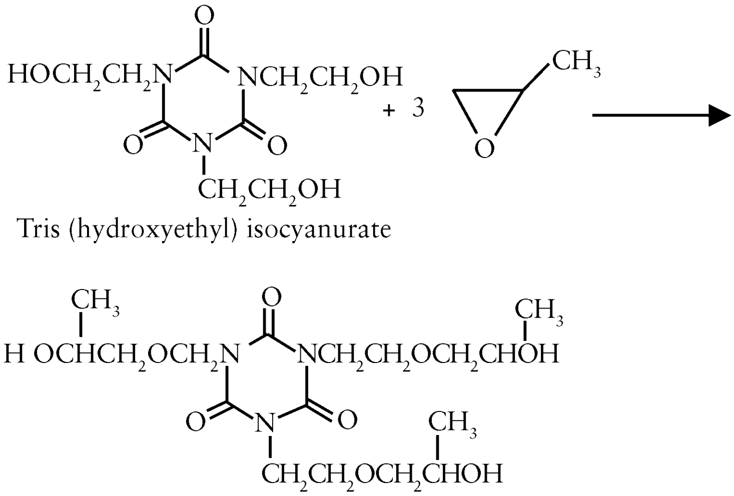
(15.45)



(15.46)

THEI, a solid substance, can be transformed into liquid polyol by reaction with 2-3 mols of PO/mol of THEI in the presence of a tertiary amine. The polyol with 3 mols of PO/mol of THEI has an hydroxyl number of around 375 mg KOH/g.

All the triazinic polyols discussed here, have a high thermostable triazinic structure and a high nitrogen content, which gives inherently flame retardant, rigid PU foams [24].


Tris (hydroxyethyl) isocyanurate

(15.47)

The explanation of this inherent flame retardancy is the high char yield generated by the thermal decomposition of organic structures containing triazinic rings. It is well known that melamine is used itself as a flame retardant additive in flexible PU foams.

At this moment, in spite of their high application potential, the triazinic polyols are only used to a very small extent for rigid PU foam production. The structure of these triazinic polyols has many similarities to the structure of urethane - isocyanuric foams, the difference being that the triazinic rings (isocyanuric rings) are introduced into the PU structure with the polyol and in urethane-isocyanuric foams they are generated *in situ* (by trimerisation of -NCO groups).

References

1. T.H. Ferrigno, *Rigid Plastic Foams*, 2nd Edition, Reinhold, New York, NY, USA, 1967.
2. M.E. Brennan and G.P. Speranza, inventors; Texaco, Inc., assignee; US 4,485,195, 1984.
3. J.E.Marugg, M.A.P. Gansow and J.A. Thoen, inventors; The Dow Chemical Company, assignee; EP 0405557A3, 1991.
4. M.E. Brennan, inventor; Texaco, Inc., assignee; US 4,500,655, 1985.

5. M. Ionescu, C. Roibu, V. Preoteasa, V. Zugavu, I. Mihalache, S. Mihai, E. Tataru and E. Benea, inventors; SC Oltchim and Ramnicu Valcea, assignees; RO 117,695, 2002.

6. M. Ionescu, S. Mihai, C. Roibu and V. Preoteasa in *Proceedings of the API Conference - Polyurethanes Expo 2003*, Orlando, FL, USA, 2003, p.641.

7. E.F. Kleinman in *Comprehensive Organic Chemistry*, Eds., D. Barton and W.D. Ellis, Volume 2, Part 2, Pergamon Press, Oxford, UK, 1991, Chapter 4.1, p.893.

8. H. Heaney in *Comprehensive Organic Chemistry*, Eds., D. Barton and W.D. Ellis, Volume 2, Pergamon Press, Oxford, UK, 1991, p.953.

9. M. Ionescu, L. Dumitrache, S. Mihai and E. Iolanda, *Chemical Bulletin of 'Polytechnica' University of Timisoara*, 2003, **46**, 60, 1.

10. J.E. Marugg, J.A. Thoen and M.A.P. Gansow, inventors; The Dow Chemical Company, assignee; US 4,939,182, 1990.

11. J.E. Marugg, M.A.P. Gansow and J.A. Thoen, inventors; The Dow Chemical Company, assignee; US 4,883,826, 1989.

12. M. Cuscurida and G.P. Speranza, inventors; Texaco, Inc., assignee; US 4,525,488, 1985.

13. D. Thorpe, inventor; ICI, assignee; US 4,797,429, 1989.

14. J. Jahme, inventor; BASF Corporation, assignee; US 5,254,745, 1993.

15. G.P. Speranza, M.E. Brennan and R.A. Grigsby, Jr., inventors; Texaco, Inc., assignee; US 4,681,965, 1987.

16. N.F. Molina and S.E. Moore, inventors; The Dow Chemical Company, assignee; US 6, 281,393, 2001.

17. M.E. Brennan, K.G. McDaniel and H.P. Klein, inventors; Texaco, Inc., assignee; US 4,654,376, 1987.

18. M.E. Brennan and G.P. Speranza, inventors; Texaco, Inc., assignee; US 4,487,852, 1984.

19. R.L. Zimmerman, M.P. Devine and P.L. Weaver, inventors; Huntsman Petrochemical Corporation, assignee; US 6,495,722, 2002.

20. R.D. Stewart and R.L. Zimmerman in *Proceedings of API Technical/Marketing Conference, Polyurethanes 2002*, Salt Lake City, UT, USA, 2002, p.601.

21. M. Ionescu, I. Mihalache, V.T. Zugravu, S. Mihai and F. Stoenescu, inventors; SC Oltchim and Ramnicu Valcea, assignees; RO 114,332B, 1999.

22. B. Reichert, *Die Mannich Reaktion*, Springer Verlag, Berlin, Germany, 1959.

23. H. Hellman and G. Optiz, *Alfa Amino Alkylierung*, Verlag Chemie, Weinheim, Germany, 1960.

24. M. Ionescu, I. Mihalache, V. Zugravu and S. Mihai, *Cellular Polymers*, 1994, **13**, 1, 57.

25. R. Brooks,*Urethanes Technology*, 1999, **16**, 1, 34.

26. R.M. Evans, *Polyurethane Sealants: Technology and Applications*, Technomic Publishing, Lancaster, PA, USA, 1993.

27. B.D. Davis and E.B. Jones, inventors; The Dow Chemical Company, assignee; US 3,686,101, 1972.

28. M. Ionescu, I. Mihalache and V. Zugravu, unpublished works.

29. M. Ionescu, V. Dumitriu, I. Mihalache, M.V.Mateescu and S. Mihai, inventors; Institutul de Cercetaria Chimice, assignee; RO 79,852, 1982.

30. S. Mihai, M. Ionescu, V.T. Zugravu, I. Mihalache, C. Dinu and F. Stoenescu, inventors; Combinatul Chimic, Rimnicu-Vilcea and Judetul Vilcea, assignees; RO 103,350, 1991.

31. M. Ionescu, V. Zugravu, I. Mihalache, S. Mihai in *Advances in Urethane Science & Technology,* Eds., D Klempner and K.C. Frisch, ChemTec Publishing, Ontario, Canada, 1998, p.151.

32. J. Hunsucker, inventor; Commercial Solvents Corporation, assignee; US 3,773,730, 1973.

33. R.B. Durairaj and J. de Almeida in *Proceedings of API Polyurethane Conference Polyurethanes 2000*, Boston, MA, USA, p.511.

34. R.B. Durairaj and J. de Almeida, *Adhesives Technology*, 1999, **16**, 1, 28.

35. M. Ionescu, I. Mihalache, V.T. Zugravu, S. Mihai, and F. Stoenescu, inventors; Combinatul Chimic, Rimnicu-Vilcea and Judetul Vilcea, assignees; RO 103,398, 1991.

36. Z. Wirpsza, M. Kucharski and J. Lubczak in *Proceedings of an International Symposium on Polycondensation, Polycondensation'96*, Paris, France, 1996.

37. M. Kucharski and J. Lubczak, *Acta Polimerica*, 1991, **42**, 4, 186.

38. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai, *Proceedings of the SPI 35th Annual Polyurethane Technical/Marketing Conference, Polyurethanes'94*, Boston, MA, USA, 1994, p.506.

39. W. Jacobs, III and J.C. Goebel, inventors; American Cyanamid Company, assignee; US 4,312,988, 1982.

40. M. Kucharski and J. Lubczak, *Polimery Tworzywa Wielkoczasteczkowe*, 1984, **29**, 7, 264.

41. M. Kucharski and J. Lubczak, *Polimery Tworzywa Wielkoczasteczkowe*, 1985, **30**, 9, 354.

16 Polyester Polyols for Rigid Polyurethane Foams

The first polyols used for rigid polyurethane (PU) foams were low molecular weight polyesters based on adipic acid, phthalic anhydride (PA) and various glycols or polyols. One example of a polyester of this type is the polycondensation product between adipic acid (AA), PA and trimethylolpropane (TMP) [1-3].

Sometimes, this polyester is modified with oleic acid in order to improve its compatibility with blowing agents. The chemistry for the synthesis of rigid polyester polyols is absolutely the same as the chemistry for the synthesis of polyester polyols used in elastic PU, described in detail in the Chapter 8.

These polyester polyols were of minor importance and during the period 1960-1970, they were replaced rapidly by low cost, low viscosity and high functionality polyether polyols, which lead to superior physico-mechanical properties of the resulting rigid PU foams and superior miscibility with fluorocarbon blowing agents. The polyether polyols proved to be superior in rigid PU foam fabrication, when the isocyanate index was low, around 105-115. The characteristics of two representative polyester polyols for rigid PU foams based on AA, PA and TMP are presented in **Table 16.1**.

The development of highly crosslinked rigid polyisocyanurate foams opens an excellent area of applications for polyester polyols [4-8]. The required polyols do not need high functionality and the plasticising effect of polyester structures is extremely beneficial for these highly crosslinked systems [6]. The first polyester polyols used for these applications were low viscosity polycondensation products of AA with ethyleneglycol (EG) or diethyleneglycol modified with phthalic anhydride or triols.

Polyisocyanurate foams (PIR) are in fact hybrid structures having both groups: urethane groups (resulting from the reaction of -NCO groups of isocyanates with hydroxyl groups of polyols) and isocyanurate rings, derived from the trimerisation of an excess of -NCO groups against the hydroxyl groups (isocyanate index of 200-300 or more). Trimerisation of -NCO groups is catalysed by special catalysts, such as tris(dimethylaminomethyl) phenol, potassium acetate and other catalysts:

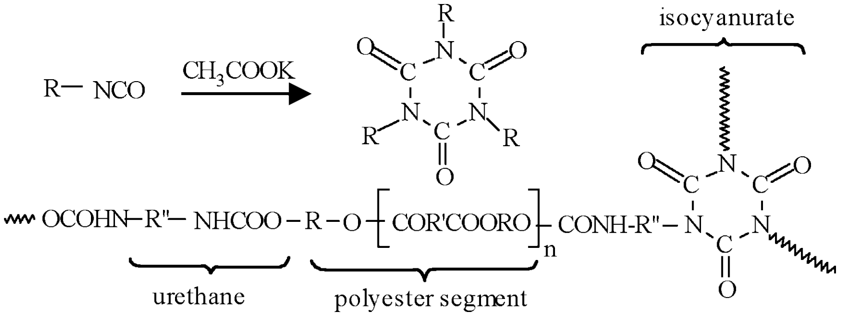


Table 16.1 Characteristics of some polyester polyols for rigid PU foams based on AA, PA and TMP			
Characteristic	**Unit**	**Polyester polyol based on AA, PA and TMP**	**Polyester polyol based on AA, PA, TMP and oleic acid**
Molecular weight	daltons	900	1030
Hydroxyl number	mg KOH/g	350-390	350-390
Average functionality	OH groups per mol	6.0	6.6
Viscosity, 70 °C 75 °C	mPa-s	- 2500-4000	1300-1500 -
Pour point	°C	21	7
Acid number	mg KOH/g	< 4	< 1
Density, 25 °C	g/ml	1.12	1.1

The highly crosslinked structure is not derived from polyester polyol, which has a low functionality (f = 2-3 OH groups/mol), but is derived from the isocyanurate rings generated by the trimerisation of the excess of -NCO groups.

Urethane structures decompose at around 200 °C, giving around 20% char yield, but isocyanuric structures are much more thermostable and are decomposed at 325 °C, with a char yield of around 50% [4, 5]. Due to this high char yield, polyisocyanuric foams have an intrinsic fire resistance [6-9].

Of course the thermal stability and char yield depend on the polyol structure too and the aromatic polyols are superior to aliphatic polyols from this point of view. This is the reason for the extremely rapid growth of aromatic polyester polyols, of low functionality, low viscosity and low cost.

The aromatic polyester polyols were developed based on the following cheap and accessible raw materials:

a) Bottom residue (substances remaining after distillation of pure dimethyl terephthalate) resulting in dimethylterephthalate (DMT) fabrication;

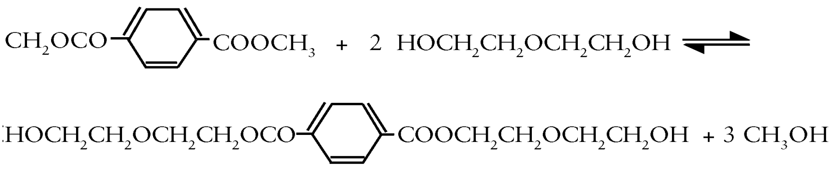
b) Poly(ethylene terephthalate) (PET) wastes (bottles of soft drinks, fibres, X-ray films);

c) PA.

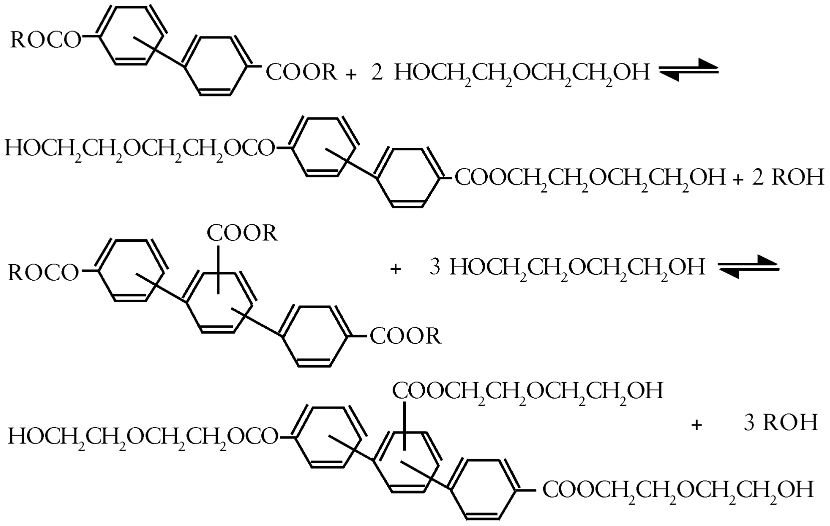
16.1 Aromatic Polyester Polyols from Bottom Residues Resulting in DMT Fabrication [4, 6, 10, 11]

The bottom residues from DMT fabrication are benzyl and methyl esters of dicarboxylic and tricarboxylic acids with biphenyl or triphenyl structures together with DMT [4, 6]. By the transesterification reactions of these complex ester residues with diethyleneglycol (DEG), aromatic polyester polyols with a functionality in the range 2.2-2.3 OH groups/mol are obtained.

The product of transesterification with DEG has a complex structure (reactions 16.1 and 16.2).



(16.1)

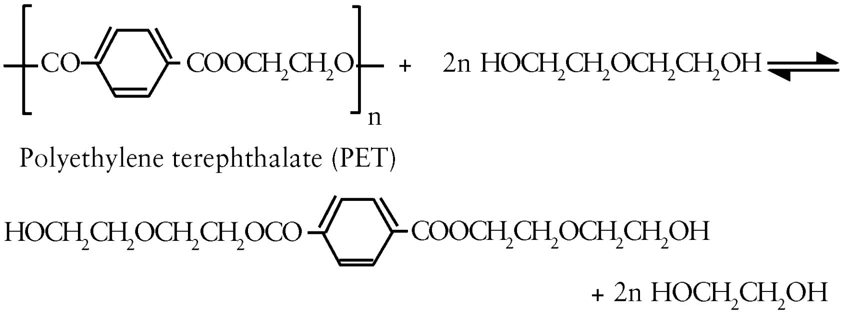


(16.2)

Generally, these residues from DMT fabrication are difficult to transport and are used on-site to be transformed into aromatic polyester polyols by transglycolysis [4]. Excellent rigid polyester polyols are obtained from pure DMT (reaction 16.1).

16.2 Aromatic Polyester Polyols from Polyethylene Terephthalate Wastes (Bottles, Films, Fibres) [12-24]

PET wastes, proved to be an excellent raw material for low cost aromatic polyester polyols. By transesterification with DEG and (or) propylene glycol or dipropyleneglycol (DPG), liquid, low viscosity and low functionality aromatic polyester polyols were obtained. Due to the low cost, DEG is the preferred glycol for transesterification (reaction 16.3) [4, 6-8, 12].



(16.3)

Of course the product of the transesterification reaction is much more complex, being a mixture of superior oligomers and free diethyleneglycol together with the main product and the mixed ester terephthalate of ethyleneglycol and DEG.

The reaction between PET and DEG takes place at higher temperatures, around 200-230 °C, without catalysts or better still in the presence of the usual catalysts for polyester synthesis (lead, manganese, tin, titanium or zinc compounds). In the situation of transesterification without catalyst, the catalyst existing in PET wastes acts as the catalyst for glycolysis, but the reaction needs longer times. The time for liquefaction of PET with DEG varies from 6-14 hours [2, 4].

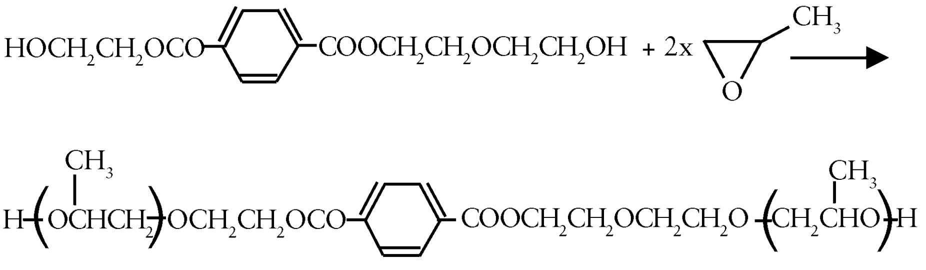
The process of PET glycolysis with DEG has several disadvantages: the reaction products are viscous liquids with a tendency to solidification or even to be solid at room temperature, the reproducibility of the characteristics of the resulting polyester polyols are difficult to realise (poor consistency) and the products of transesterification are not compatible with the blowing agents (pentanes or hydrofluorocarbons) [4, 6].

The main technical problem to be solved is to assure the liquid state of the PET glycolysis product. This problem was solved in various ways:

a) By distillation under vacuum of the resulting EG. It is well known that the ethyleneglycol terephthalate has a tendency to crystallisation and a high melting point (around 256 °C). By using an excess of DEG and by EG distillation, the terephthalic diester of DEG results, a liquid, without any tendency towards crystallisation [19].

b) Introduction of flexible aliphatic acids such as: adipic acid, sebacic acid, glutaric acid and so on, followed by the elimination of water resulted in the polycondensation reaction of these acids with the diols present in the reaction system. Low viscosity polyester polyols result, which remain liquid at room temperature, without any tendency to solidification [14-16].

c) Addition of PO to many solid polyols gives liquid adducts. Similarly, by alkoxylation, with propylene oxide (PO), of the reaction product of PET with DEG, in the presence of basic catalysts (for example KOH, potassium methoxide, potassium acetate) gives liquid polyesters without any tendency to crystallisation. Thus, by the reaction of one equivalent of PET with one equivalent of DEG, at 230 °C a solid product is obtained with an hydroxyl number of around 375 mg KOH/g. By alkoxylation of this solid, at around 160 °C, with PO or with PO-ethylene oxide mixtures, in the presence of potassium acetate polyester polyols are obtained, with an hydroxyl number in the range 270-320 mg KOH/g and low viscosity of around 1,000-3,000 mPa-s, at 25 °C, having the following idealised structure (16.4) [20-22]:



(16.4)

d) Replacement of DEG with DPG, in spite of the lower transesterification rate, leads to stable liquid aromatic polyester polyols, having better compatibility with blowing agents [12, 18].

e) Introduction of *ortho*-phthalic residues [23] is another synthetic variant to obtain liquid polyols by the transesterification of PET with DEG. It is well known that some alkylic esters of phthalic acid have much lower melting points than the same esters of isophthalic or terephthalic acids. Thus the *ortho*-phthalic ester of DEG is a liquid with a melting point of around 10-11 °C. At the same time the isophthalic ester of DEG has a melting point of 55-60 °C and the terephthalic ester of DEG has a melting point of 65-70 °C (the ester of EG with terephthalic acid has a melting point of 256 °C and the ester of EG with *ortho*-phthalic acid has a melting point of 63-65 °C) [4, 5]. These data explain the strongly favourable effect of the *ortho*-phthalic units introduction into the structure of polyester polyols synthesised from PET wastes.

The characteristics of some aromatic polyester polyols derived from the glycolysis of PET wastes are presented next:

Polyester polyols with an equivalent weight of 181, functionality of 2.3 OH groups/mol, hydroxyl numbers in the range of 295-335 mg KOH/g and viscosities of 8,000-22,000 mPa-s, at 25 °C, are used in rigid PU foams.

Polyester polyols of with an equivalent weight of 238, functionality of 2 OH groups/mol, hydroxyl number in the range of 230-250 mg KOH/g and viscosity of 2,700-5,500 mPa-s, at 25 °C, are used in PIR foams.

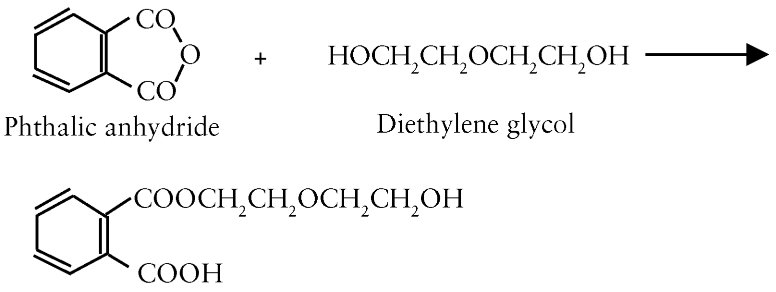
Polyester polyols with equivalent weight of 167, functionality of 2 OH groups/mol, hydroxyl number of 310-350 mg KOH/g and viscosity of 1,300-3,000 mPa-s at 25 °C, are used in thermal insulation of appliances. The initial ratio between DEG and PET used in synthesis, followed by the utilisation of one of the previously mentioned procedures avoids solidification (section 16.2, a-e), and means that a large range of aromatic polyester polyols, having various hydroxyl numbers, functionalities and aromaticity can be obtained.

16.3 Aromatic Polyester Polyols Based on Phthalic Anhydride (PA) [25, 26]

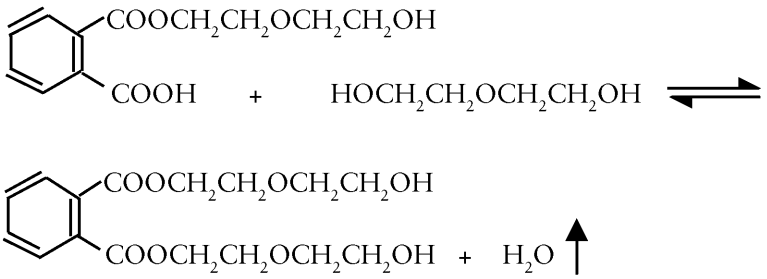
PA is commercialised in large quantities (especially for use in plasticisers, such as dioctylphthalate and unsaturated polyesters), in high purity form. The aromatic polyester polyols based on PA, due to the purity of the raw materials, are colourless liquids and the process of fabrication, is very reproducible (good consistency). The polyester polyols based on PA and DEG are synthesised in two steps:

a) Synthesis of monoesters of phthalic acid by the reaction of PA with DEG (reaction 16.5); and,

b) The condensation of the carboxylic groups in the resulting half ester of phthalic acid with DEG (reaction 16.6):

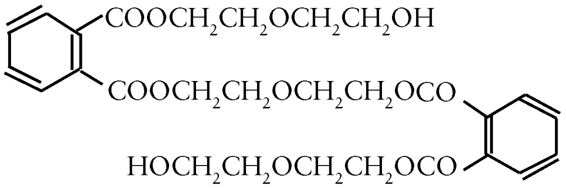


(16.5)



(16.6)

Of course during the polycondensation reaction superior oligomers are formed, such as the structure shown in reaction 16.7 and in the composition of the resulting polyester polyol, free DEG is present.



(16.7)

As a representative example, an aromatic polyester polyol derived from PA and DEG has an equivalent weight of 178-239, a functionality of 2 OH groups/mol, an hydroxyl number in the range of 230-390 mg KOH/g and the viscosities are lower, around 2,000-4,500 mPa-s at 25 °C.

All the aromatic polyester polyols have a high aromaticity, of around 20%.

All the aromatic polyesters based on DEG have poor compatibility with blowing agents (pentanes or fluorocarbons) and to improve this compatibility 'compatibilising polyols' such as: *ortho*-toluene diamine polyols, propoxylated α-methyl glucoside polyols, oxyethylated *p*-nonylphenol, amine and amide diols, PO-EO block copolymers, borate esters, silicone compounds and so on, are frequently used [27-30].

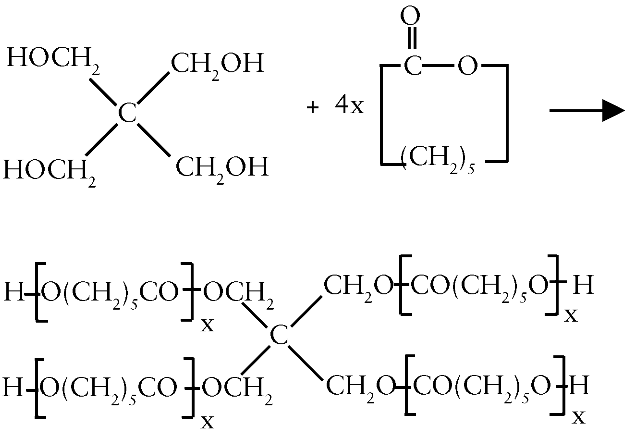
Due to the low cost, the excellent physico-mechanical properties of the resulting urethane - isocyanuric foams, thermal and fire resistance and low level of smoke generation, the most important applications of aromatic polyester polyols are for rigid PU/PIR foams in the boardstock market (continuous rigid foam lamination) and for building insulation.

The rigid PU/PIR foams [1, 4-32] enjoyed an enormous success in recent years, making the aromatic polyester polyols dominate the USA polyol for rigid foam business, bypassing the polyether polyol business [4, 6]. In Europe, the penetration of PU/PIR rigid foams based on aromatic polyesters has been limited, but the tendency is for a slow growth of aromatic polyester production.

16.4 Other Methods for the Synthesis of Polyester Polyols for Rigid Foams

In this section, several methods for rigid polyester polyols synthesis, of minor industrial importance at this moment, but which present a real potential for developing new polyol structures will be presented.

Polyester polyols for rigid PU foams can be obtained by ring opening polymerisation of ε-caprolactone, initiated by various polyols such as: α-methyl glucoside, sorbitol, pentaerythritol or trimethylolpropane. A polyester polyol derived from penteaerythritol has the following properties: functionality of 4 OH groups/mol, hydroxyl number of 600 mg KOH/g, acid number of around 2 mg KOH/g and a of viscosity 7,000 mPa-s, at 25 °C (reaction 16.8) [2, 33-35].



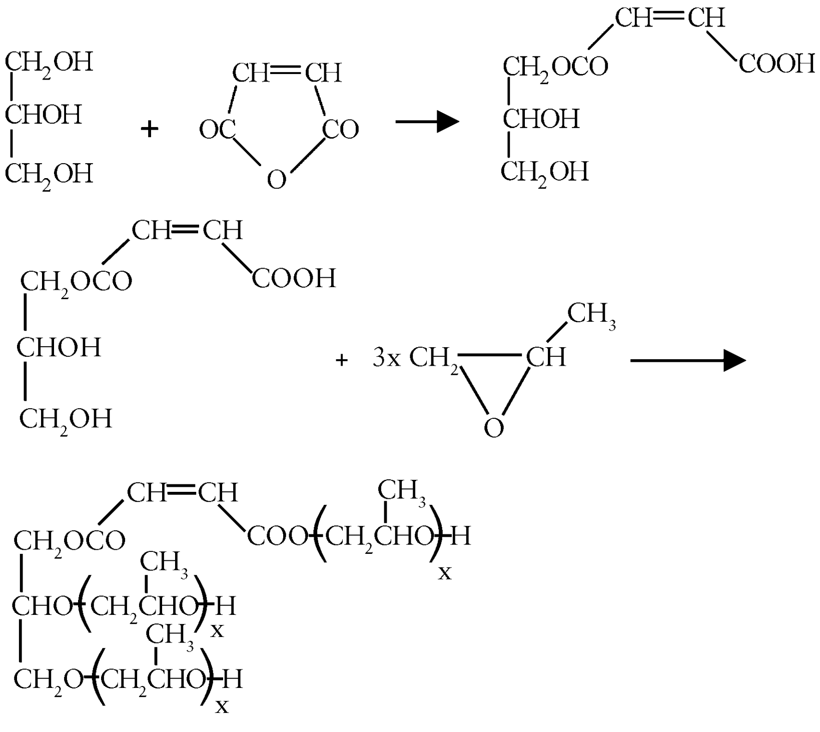
x = 0,1,2

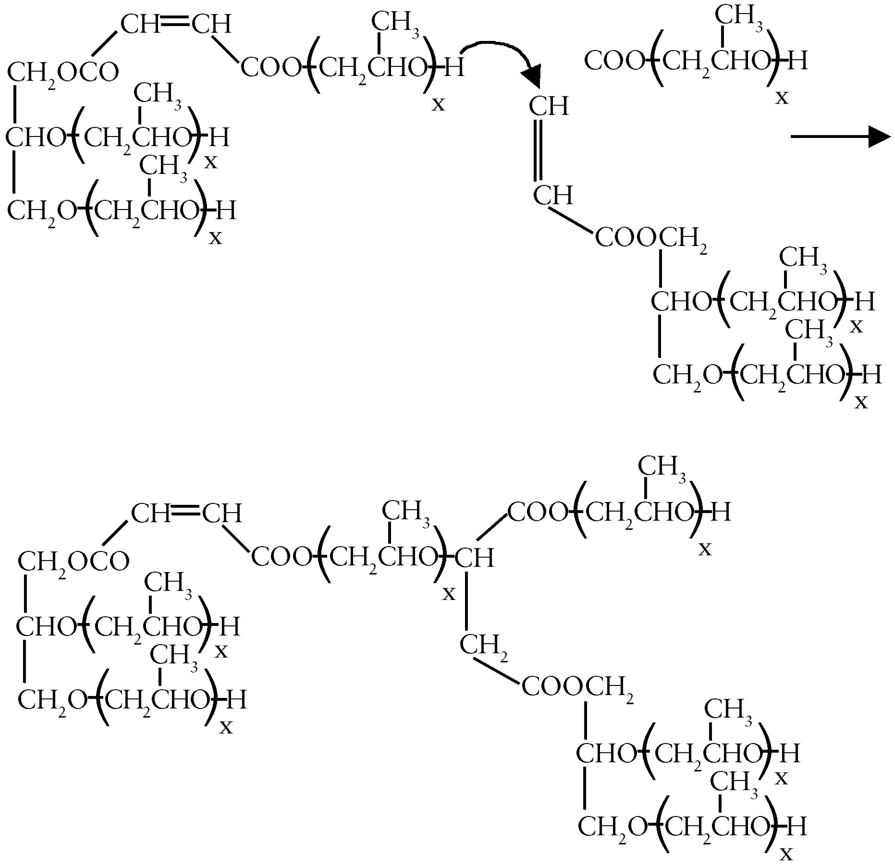
(16.8)

α-Methyl glucoside and sorbitol give higher viscosity polyester polyols, of around 22,000-400,000 mPa-s at 25 °C [33]. Due to their high price these ε-caprolactone-based polyester polyols have limited utilisation for rigid PU foams. As explained before (Section 8.4), the high molecular weight poly (ε-caprolactone) polyols are used successfully in hydrolysis resistant PU elastomers.

A synthetic method for rigid polyester polyols, by the propoxylation of compounds having both hydroxyl and carboxyl groups was developed [33, 34].

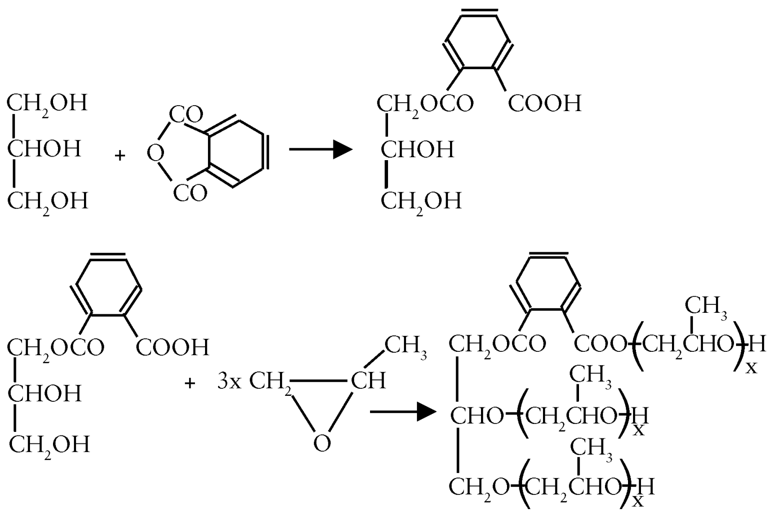
Thus, by the propoxylation of the reaction product of one mol of maleic anhydride with one mol of glycerol, aliphatic polyester polyols having functionalities greater than 3, in the range of 3-4 OH groups/mol are obtained. The functionality of greater than 3 is created *in situ* by the addition of an hydroxyl group to the double bond of the maleic esters formed (reactions 16.9).



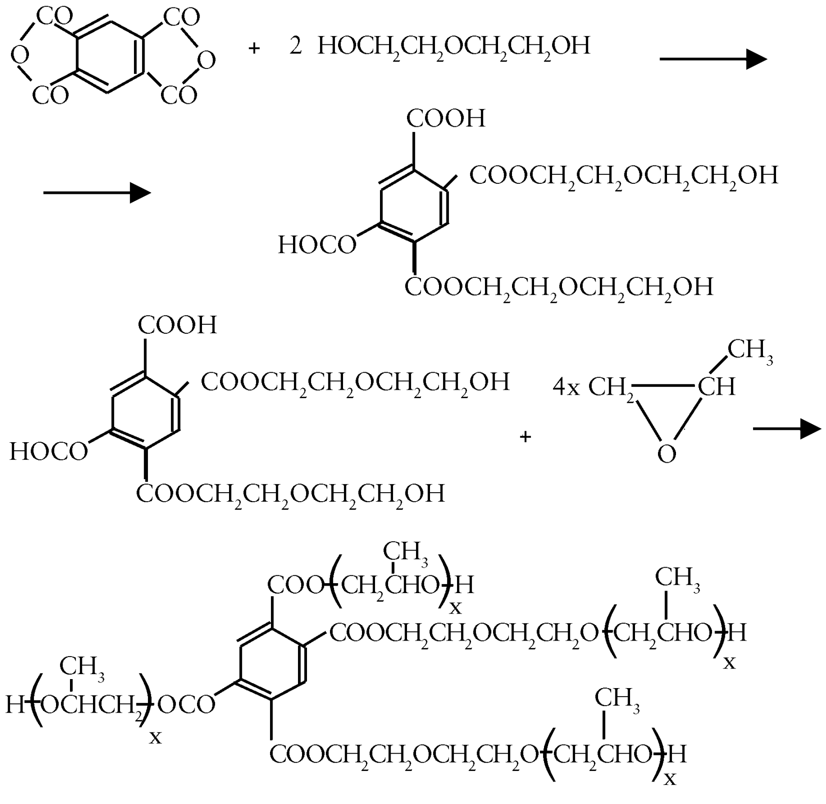


(16.9)

By using similar chemistry, aromatic polyester polyol structures are obtained by alkoxylation of the phthalic anhydride reaction product with glycerol (reaction 16.10). By the propoxylation of the reaction product of pyromellitic anhydride with DEG, tetrafunctional, highly viscous aromatic polyester polyols (16.11) are obtained.

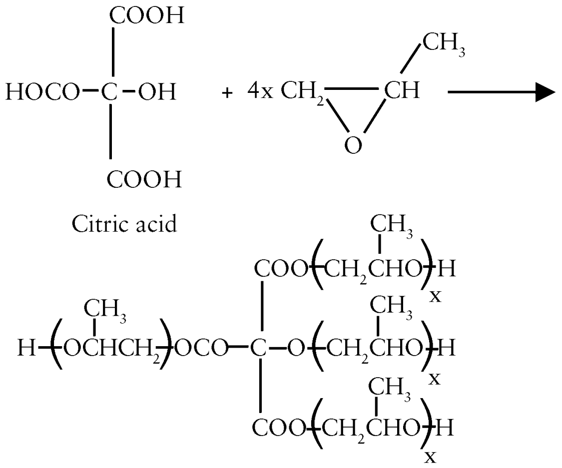


(16.10)

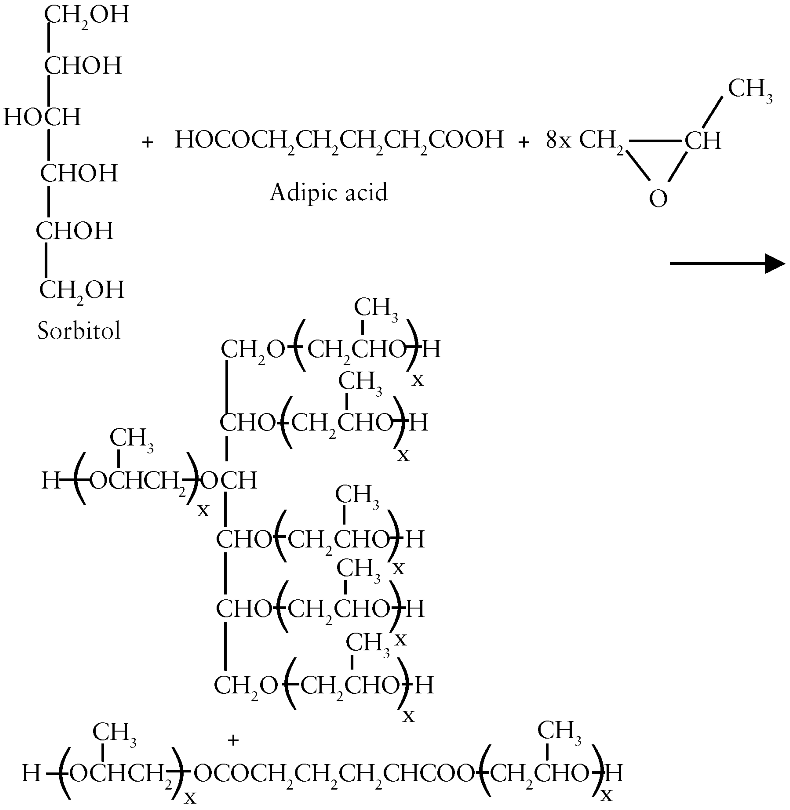


(16.11)

Propoxylation of organic hydroxy acids such as citric acid (16.12) [34] or propoxylation of the mixture between polyols and polyacids (for example sorbitol and adipic acid, reaction 16.13) give rise to interesting rigid polyester polyols [34].



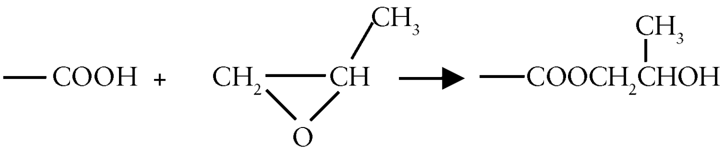
(16.12)



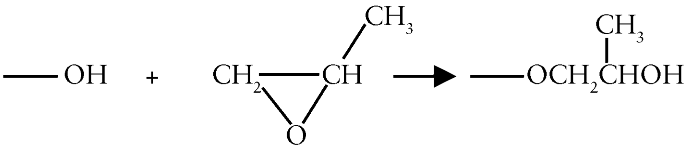
(16.13)

Instead of adipic acid it is possible to use succinic, glutaric, sebacic acids or even terephthalic acid.

The alkoxylation of these structures, having carboxyl groups and hydroxyl groups, is a self catalysis process, catalysed by the acidic -COOH groups. Two simultaneous reactions take place: the esterification of carboxyl groups with PO (reaction 16.14) and the etherification of hydroxyl groups (reaction 16.15) [34].



(16.14)



(16.15)

One disadvantage of this method is the very long time needed in the last part of the reaction to decrease the acidity number to less than 2 mg KOH/g (i.e., several hours). Sometimes, the esterification with PO of the last unreacted -COOH groups needs a catalyst such as: KOH [20-22], sodium or potassium acetate [20-22], DMC catalysts, tertiary amines and so on. Another disadvantage is the presence of a discrete and characteristic odour, due to the formation of some side products in very small quantities (for example cyclic compounds).

The synthesised polyester polyols obtained by propoxylation of different starter systems having hydroxyl and carboxyl groups, are in fact ether-ester polyols.

Practically all the polyester polyols based on DEG or DPG are in fact ether-ester polyols, because they have in the same structure ether and ester groups.

The most important structures of rigid polyester polyols presented in this chapter (Chapter 4.4) are the low functionality aromatic polyester polyols with terephthalic or phthalic structures, used for PU/PIR rigid foams.

References

1. R. Becker in *Polyuretane*, VEB, Leipzig, Germany, 1983, p.49.
2. F. Hostettler and D.M. Young, inventors; Union Carbide Corporation, assignee; US 3,169,945, 1965.

3. F. Hostettler and D.M. Young, inventors; Union Carbide Corporation, assignee; US 3,186,971, 1965.

4. R. Brooks, *Urethanes Technology*, 1999, **16**, 1, 34.

5. D. Reed, *Urethanes Technology*, 2000, **17**, 4, 41.

6. D.J. Sparrow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Boca Raton, FL, USA, 1989, p.217-218.

7. J.M. Hughes and J.L. Clinton, *Journal of Cellular Plastics*,1980, **16**, 3,152.

8. J.M. Hughes and J.L. Clinton in *Proceedings of the SPI 25th Annual Urethane Division Technical Conference, Polyurethanes – Looking Ahead to the Eighties*, Scottsdale, AZ, USA, 1979, p.6.

9. H.R. Friedly in *Reaction Polymers*, Ed., H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.80-86.

10. J.F. Walker, inventor; Hercules, Inc., assignee; US 3,647,759, 1972.

11. S.C. Snider and A. DeLeon, inventors; Celotex Corporation, assignee; US 4,411,949, 1983.

12. J.S. Canaday and M.J. Skowronski, *Journal of Cellular Plastics*, 1985, **21**, 5, 338.

13. W.L. Carlstrom, R.T. Stoehr and G.R. Svoboda in *Proceedings of the SPI 28th Annual Technical/Marketing Conference, Polyurethane Marketing and Technology – Partners in Progress*, San Antonio, TX, USA, 1984, 1972, p.65.

14. W.L. Carlstrom, R.W. Reineck and G.R. Svoboda, inventors; Freeman Chemical Corporation, assignee; US 4,223,068, 1980.

15. G.R. Svoboda, W.L. Carlstrom and R.T. Stoehr, inventors; Freeman Chemical Corporation, assignee; US 4,417,001, 1983.

16. M.E. Brennan, inventor; Texaco, Inc., assignee; US 4,439,550, 1984.

17. J.A. Murphy and B.C. Wilbur, *Journal of Cellular Plastics,* 1985, **21**, 2, 105.

18. J.M. Gaul, J.A. Murphy and B.C. Wilbur in *Proceedings of UTECH'86 Conference*, The Hague, The Netherlands, 1986, p.20.

19. R.A. Grigsby, Jr., G.P. Speranza and M.E. Brennan, inventors; Texaco, Inc., assignee; US 4,469,824, 1984.

20. M.J. Altenberg and J. DeJong, inventors; Chardonol Corporation, assignee; EP 0,134,661A2, 1985.

21. G.P. Speranza, R.A. Grigsby, Jr., and M.E. Brennan, inventors; Texaco, Inc., assignee; US 4,485,196, 1984.

22. M.J. Altenberg and J. DeJong, inventors; Chardonol, Division of Freeeman Corporation, assignee; US 4,701,477, 1987.

23. R.K. Hallmark, M.J. Skrowronski and W.D. Stephens, inventors; Jim Walter Resources, assignee; EP 0,152,915A3, 1987.

24. S.C. Cohen, M.J. Cartmell and R.K. Brown in *Proceedings of the SPI 6th International Technical/Marketing Conference*, *Polyurethane – New Paths to Progress*, San Diego, CA, USA, 1983, p.101.

25. R.J. Wood, inventor; Stepan Company, assignee; US 4,529,744, 1985.

26. T.A. Barber, T.R. McClellan, inventors; EI DuPont de Nemours, assignee; CA 2493024, 2004.

27. K.B. White, inventor; Akzo NV, assignee; EP 0,122,648A1, 1984.

28. K.B. White and W.J. Largent, inventors; Akzo NV, assignee; EP 0,122,649, 1984

29. K.B. White, B. Largent, L. Jirka and B. Bailey in *Proceedings of the SPI 29th Annual Technical/Marketing Conference*, *Magic of Polyurethanes*, Reno, NV, USA, 1985, p.72.

30. F. Guenther in *Proceedings of SPI 28th Annual Technical/Marketing Conference*, *Polyurethane Marketing and Technology – Partners in Progress*, San Antonio, TX, USA, 1984, p.44.

31. M.R. Cartmell, S.C. Cohen and A.T. Hurst, *Journal of Fire Sciences*, 1983, **1**, 6, 403

32. W.G. Carroll and I.D. Rosbotham, inventors; ICI plc, assignee; EP 0,161,039, 1985.

33. D.M. Young, F. Hostettler, L.K. Shriver and R.W. Laughlin in the *Proceedings of the 130th Meeting of the ACS Division of Paint, Plastics and Printing*, Atlantic City, NJ, USA, 1956.

34. D.M. Young and F. Hostettler, inventors; Union Carbide Corporation, assignee; US 3,051,687, 1962.

35. C.H. Smith, *Industrial and Engineering Chemistry, Product Research & Development,* 1963, **2**, 1, 27.

17

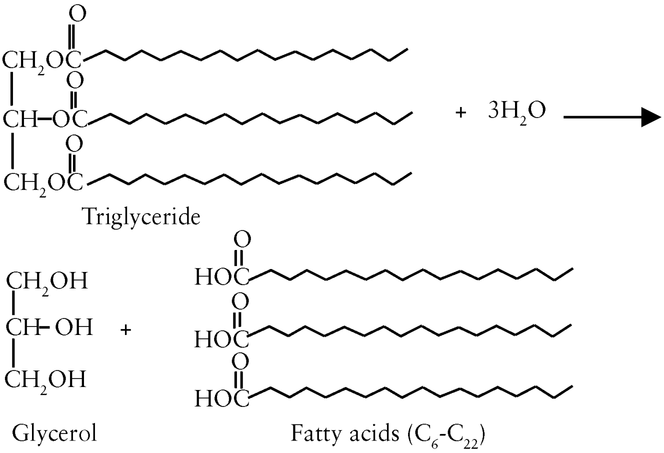
Polyols from Renewable Resources - Oleochemical Polyols

Petrochemical resources (crude oil, natural gases and so on), used intensively in the worldwide chemical industry, are in fact limited resources and in a certain period of time will be depleted. The chemical industry is making big efforts to find alternatives to the petrochemical raw materials.

One alternative represents the renewable resources which already play an important role in the development of the chemical industry. These renewable resources are relatively inexpensive, accessible, produced in large quantities (regeneratable every year and practically unlimited) [1-5].

In the polyurethane (PU) industry the development of polyols based on renewable resources always played an important role. One can say that all the history of PU was strongly linked to the renewable resources [1-5].

Thus, glycerol, the most important starter for the synthesis of polyether polyols for flexible PU foams and for polyether for rigid foams is produced by the hydrolysis of natural triglycerides (esters of glycerol with fatty acids with C_6 to C_{22} carbon atoms), from vegetable or animal resources (reaction 17.1) [1]. Large quantities of glycerol appear in bio-diesel production, by transesterification of natural oils with methanol.

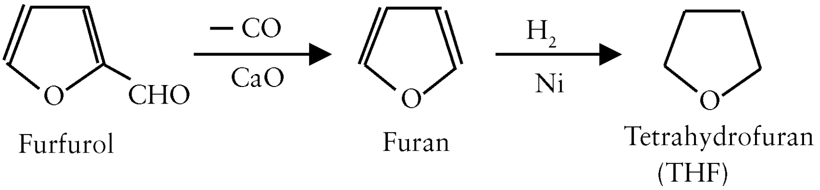


(17.1)

Sucrose, the most important starter for rigid polyether polyols is produced exclusively by extraction from naturally resources (**Figure 17.1**) [1].

Tetrahydrofuran (THF), the cyclic monomer used for the synthesis of polytetramethyleneglycols (see Chapters 7.1-7.3) by cationic ring opening polymerisation, was produced in the earlier stages of this technology from furfurol. Furfurol results from the acid hydrolysis of pentosanes existing in many agricultural wastes (corn on the cob, straw and so on).

Furfurol is firstly decarbonylated in the presence of special catalysts (CaO) and the resulting furan is hydrogenated to THF, by the classical manner in the presence of Raney-Ni catalysts (reaction 17.2).



(17.2)

Now, THF is produced by selective hydrogenation of maleic anhydride [6, 7] or by dehydration of 1,4 butanediol (resulting from acetylene and formaldehyde, followed by the hydrogenation of the resulting 2-butyne-1,4 diol [23]). The old technology based on furfurol may be reconsidered in the future, because it uses a renewable resource as its raw material.

Xylitol (**Figure 17.2**), a polyol starter for rigid polyether synthesis, having five hydroxyl groups, is produced by the hydrogenation of the same pentosans used for THF synthesis [8]. By propoxylation of xylitol excellent rigid polyether polyols (see Chapter 4.1) are obtained.

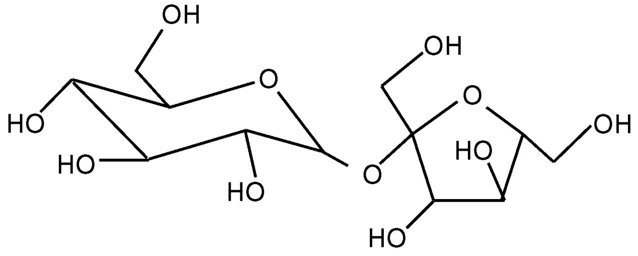


Figure 17.1 Structure of sucrose

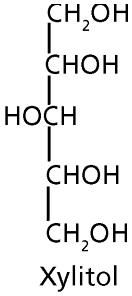


Figure 17.2 Structure of Xylitol

Alkyl glucosides (α-methyl glucoside and hydroxyalkyl glucosides) [8-13] and glucose [14], used as polyolic starters for rigid polyether polyols synthesis, were produced by alcoholysis or hydrolysis of starch from renewable resources (potatoes, corn and so on). Starch is a polysaccharide having D-glucose units linked by α-glucosidic bonds.

Thus, D-glucose is obtained by the acid hydrolysis of starch. By the acidic alcoholysis of starch with methanol or ethylene glycol, α-methyl glucoside and hydroxyethyl glucoside, respectively, are obtained [8-13]. By the reaction of D-glucose with methanol in acidic media, α-methyl glucoside is obtained too and by the condensation of D-glucose with ethylene glycol, in the same acidic catalysis, hydroxyethylglucoside is obtained. Both glucosides: α-methyl glucoside and hydroxyethyl glucoside are excellent starters for the synthesis of polyether polyols [15]. All the reactions mentioned, from starch or D-glucose to alkyl glucosides, are presented in **Figure 17.3**.

By the hydrogenation of D-glucose, a hexafunctional polyol, sorbitol is obtained, one of the most important starters to initiate the polymerisation of propylene oxide (PO) to hexafunctional rigid polyether polyols.

Generally, all the reactions in acid catalysis from **Figure 17.3** take place in the presence of cheap acids, such as H_2SO_4, water being removed by vacuum distillation. The acid is neutralised with $Ca(OH)_2$ but $Ba(OH)_2$ is better, KOH is then added and a normal anionic polymerisation of PO is developed, initiated by the alkyl glucosides synthesised in reaction 17.3. It is important that the content of reducing sugars (free D-glucose) in the resulting alkyl glucosides is lower than 1%. If the content of reducing sugars is higher than 1%, the acids resulting by the alkaline degradation of glucose (lactic acid, saccharinic acids and so on) block the alkaline catalyst and make the PO addition impossible [13].

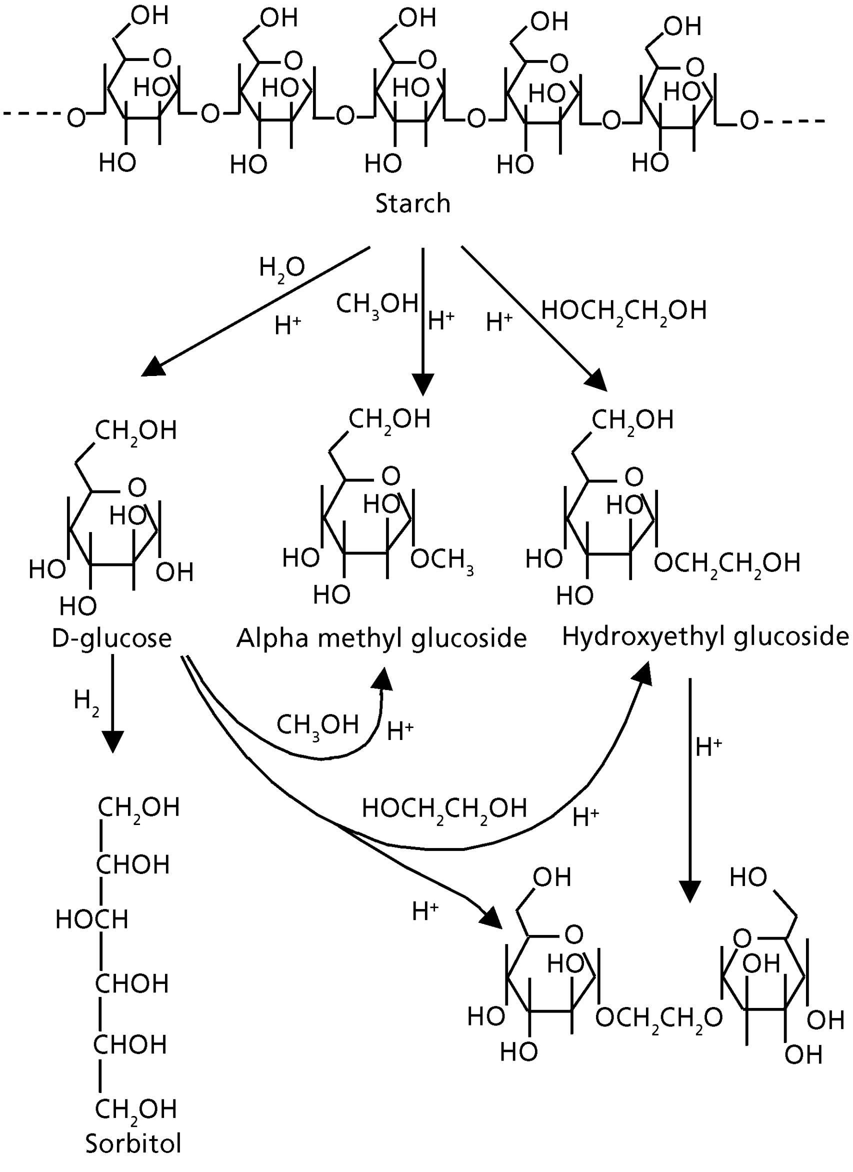
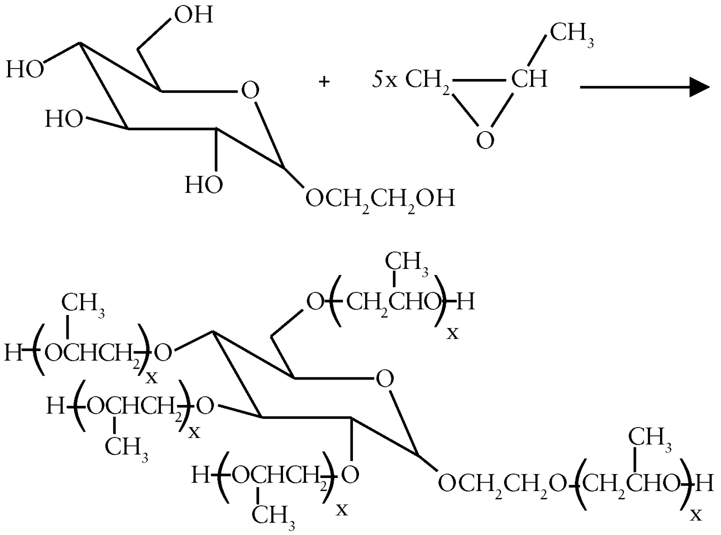


Figure 17.3 Chemical transformations of starch and D-glucose into polyols that can be used as polyfunctional starters for polyether polyols synthesis

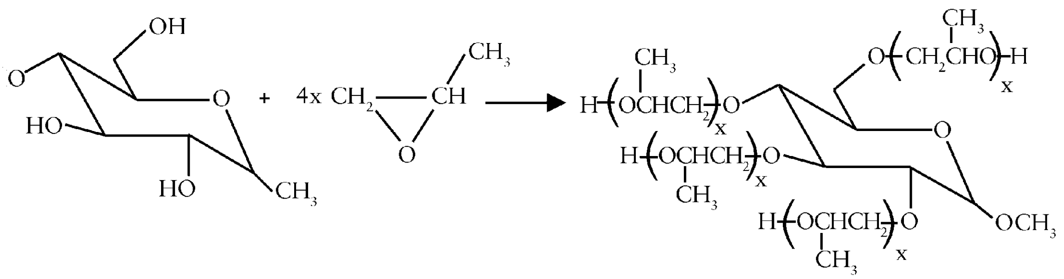


(17.3)

D-glucose, in spite of its very attractive structure (5 hydroxyl groups available for propoxylation) is impossible to use as a starter for anionic polymerisation of PO, because it is totally degraded in the presence of KOH.

On the other hand, D-glucose is very stable in acidic media. Rigid polyether polyols were obtained directly from D-glucose by direct propoxylation in the presence of cationic catalysts (BF_3, $BF_3{*}OEt_2$, HBF_4, $HSbF_6$, HPF_6, CF_3SO_3H) [14].

α-Methyl glucoside is currently used as a tetrafunctional starter for fabrication of rigid polyether polyols, by propoxylation in alkaline catalysis, in the presence of KOH or of tertiary amines (reaction 17.4) [9].



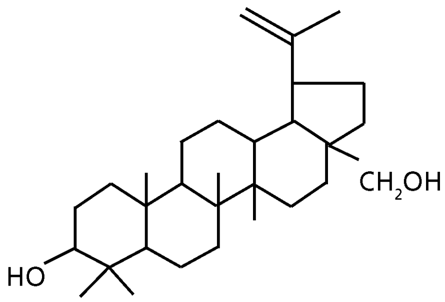
(17.4)

The carbohydrate content of polyether polyols derived from α-methyl glucoside is much higher than the carbohydrate content of sucrose-based polyether polyols at the same viscosities. Thus, at a viscosity of 10000 mPa-s at 25 °C, sucrose polyols have a carbohydrate content of around 20% and α-methyl glucoside based polyether polyols have a carbohydrate content of 30-32%. At a viscosity of 25,000 mPa-s at 25 °C, sucrose polyols have a carbohydrate content of 25% and α-methyl glucoside based polyether polyols, at the same viscosity have a carbohydrate content of 35% [9]. As a consequence of the higher carbohydrate content, α-methyl glucoside based polyether polyols have lower functionalities (3.5-4 OH groups/mol) and give rigid PU foams with physico-mechanical properties equivalent to the rigid PU foams derived from sucrose polyols with a functionality of 6 OH groups/mol [9]. A high carbohydrate content contributes to improving the fire resistance of the resulting rigid PU foams, because of the high char yield generated during the burning process.

A very interesting natural diol with cycloaliphatic structure is betulinol, extracted from birch bark [16-18], which is a triterpene diol, having one primary and one secondary hydroxyl group (**Figure 17.4**).

By reacting betulinol with diisocyanates, PU can be prepared [16-18]. Betulinol was used as a diol for polyester synthesis too [16-18].

A very interesting natural starter for rigid polyols is lignin, available in large quantities from the wood and cellulose industry [15]. Lignin is the second most important component of wood after cellulose. Lignin links the fibrillar cellulose, the wood being in fact a composite material. The content of lignin in wood varies according to the nature of the wood and is around 19-30%, the highest content being in coniferous wood (27-30%). Lignin is an aromatic macromolecular compound, a natural resin, having a molecular weight of around 3,000-7,000 daltons, around 10-20 hydroxyl groups/mol, an hydroxyl number of around 1,000-1,500 mg KOH/g and a methoxy group content of 13-14% [15, 19]. Lignin does not have a clear melting point, and at 200 °C becomes a solid (sinterisation).

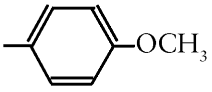


Betulinol
$C_{30}H_{45}O_2$
mp.=258-260 °C

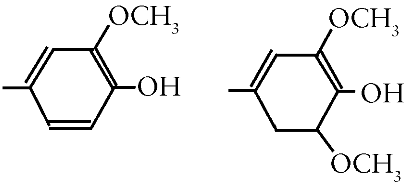
Figure 17.4 Structure of betulinol

Lignin is soluble in alkaline aqueous solutions and in some organic solvents (dioxan, pyridine, aprotic dipolar solvents such as *N*-methyl pyrrolidone). Lignin has the following chemical groups [15]:

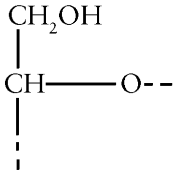
a) Methoxy groups, linked to aromatic nuclei:



b) Phenolic hydroxyl groups:

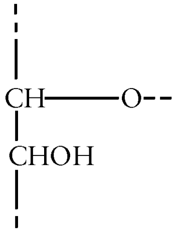


c) Primary hydroxyl groups:



$$\begin{array}{l} CH_2OH \\ | \\ CH\text{———}O\text{--} \\ | \\ \vdots \end{array}$$

d) Secondary hydroxyl groups:



$$\begin{array}{l} \vdots \\ | \\ CH\text{———}O\text{--} \\ | \\ CHOH \\ | \\ \vdots \end{array}$$

The idealised structure of lignin is presented in **Figure 17.5**.

The alkoxylation of lignin is possible in a solvent (dimethylformamide, *N*-methylpyrrolidone or in liquid PO [20]). A process using a lignin-glycerol mixture (3:1) in a polyether polyol based on lignin was developed [20]. The catalysts of this reaction are: KOH, but a tertiary amine, such as dimethylaminoethanol is preferred. By alkoxylation with a PO-EO mixture (e.g., 18-25% ethylene oxide; EO) a totally liquid dark-brown lignin-based polyether polyol with a viscosity in the range 4,700-8,000 mPa-s at 25 °C, with an hydroxyl number

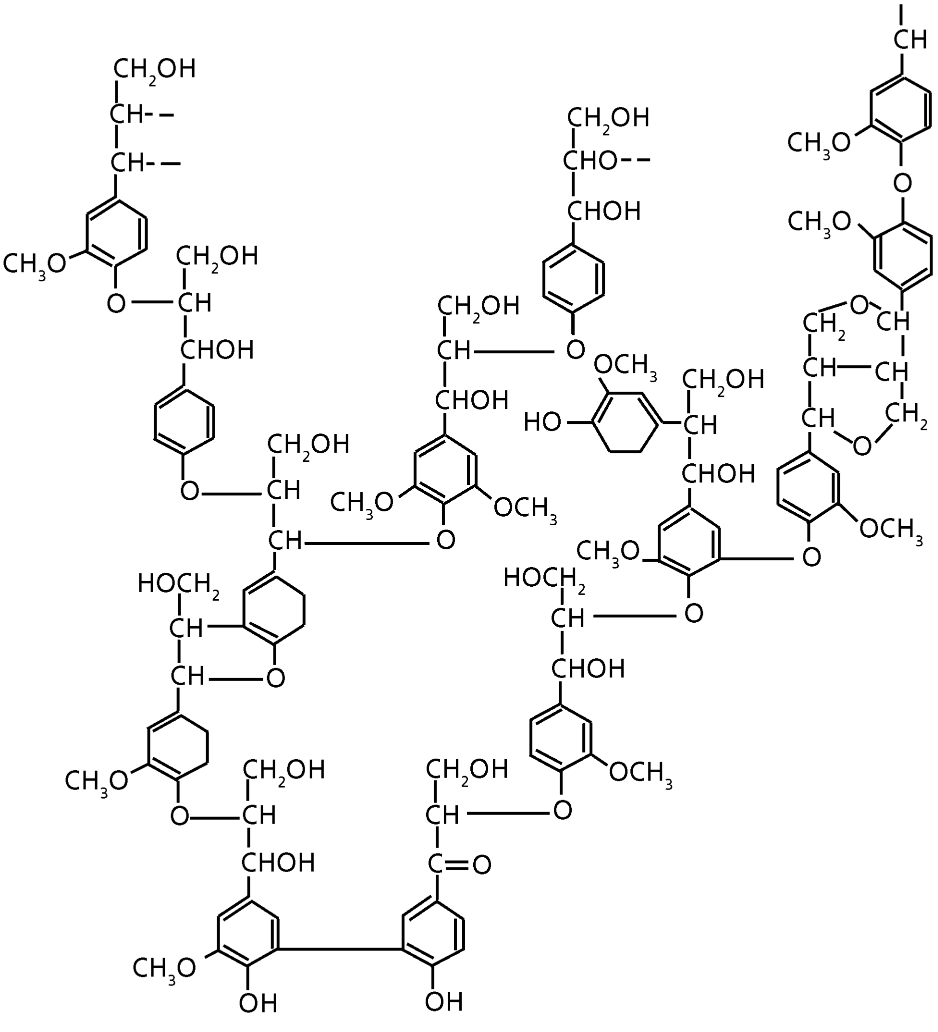


Figure 17.5 The structure of lignin

in the range 400-450 mg KOH/g and a density of around 1.14-1.16 g/ml at 25 °C was obtained [20]. High viscosity polyether polyols, of about 8,000-14,000 mPa-s at 25 °C are obtained by direct propoxylation of lignin [20].

During the alkoxylation reaction, PO or EO are added to all hydroxyl groups from the reaction system (phenolic and aliphatic hydroxyl groups), but firstly to the phenolic hydroxyl groups. Lignin-based polyester polyols formed by the reaction of lignin with ε-caprolactone were developed [10, 12, 21, 22].

The rigid PU foams obtained with the synthesised lignin-based polyols have acceptable physico-mechanical properties, but the reactivity in the foaming process is very high, probably due to the content of sodium in the initial lignin.

It is possible to use lignin directly, without any chemical modification, to obtain rigid PU foams that can be used as a filler or dissolved in polyether polyols. Thus, lignin was dissolved in polyether polyol PO-EO copolymer (in PO homopolymers it is not soluble). The resulting solution of lignin in polyether polyols was used to obtain various PU [23].

Utilisation of lignin in PU is limited. Lignin used as raw material for manufacture of PU represents a superior utilisation of a waste, because lignin is a waste product of the wood and cellulose industry. Lignin has the advantage of low cost, aromaticity and of course is a renewable resource, but its disadvantages are: it is a nonreproducible raw material, with impurities, very dark in colour, with tendency to sinterisation.

17.1 Vegetable Oil Polyols (Oleochemical Polyols)

Vegetable oils and fats are very important resources for polyols. The vegetable oils such as: soybean oil, castor oil, sunflower oil, palm oil, rapeseed oil, olive oil, linseed oil and so on, with a worldwide production of around 110 milions t/year (in 2000) [10, 12, 21, 22], are used mainly in human food applications (76%), in technical applications (19.5% only 7.5% is converted into soaps, and 10.5% is used in oleochemical industry) and 1.5% in other applications. Soybean oil is the most important vegetable oil produced worldwide, representing 25% from the total oils and fats, the second place being occupied by palm oil (18%) [10, 12, 21, 22, 24-26].

For polyols for PU, the most important oils are highly unsaturated oils, where, by using various chemical reactions, the double bonds are transformed into hydroxyl groups. In this category of highly unsaturated vegetable oils there are: soybean oil, sunflower oil, safflower oil, corn oil, linseed oil, olive oil, tung oil, castor oil and others as well as an oil of animal origin: fish oil [1-3, 5, 6, 27-46].

A unique vegetable oil is castor oil, extracted from the seeds of the plant *Ricinus communis,* which is a triglyceride of ricinoleic acid. Ricinoleic acid has 18 carbon atoms, a double bond (C_9-C_{10}) and a secondary hydroxyl group (C_{12}) [29, 38, 41-43, 46]. The idealised structure of castor oil is shown in **Figure 17.6.**

Castor oil plays a very important role, especially in the earlier stages of the PU industry, even before synthetic polyols were available. Worldwide production of castor oil is around 1,200,000-1,800,000 t/year [76], the world leader in castor oil production being India (750,000 t/year) [76] (India: 64%, China: 23%, and Brazil: 7%).

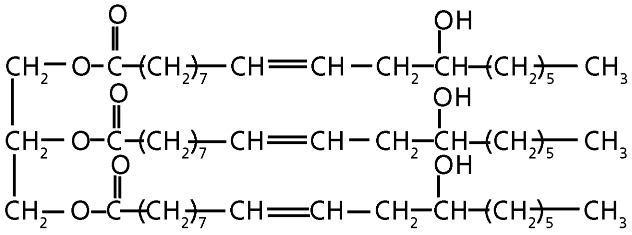


Figure 17.6 The structure of castor oil

Natural castor oil is very close to the idealised structure presented in **Figure 17.6**, which has a functionality of around 2.7 OH groups/mol and an hydroxyl number of around 160 mg KOH/g. Castor oil has a natural acidity of up to a maximum of 2 mg KOH/g.

The composition of the fatty acids from castor oil is given in **Table 17.1**.

Castor oil is used in many PU applications such as: coatings, cast elastomers, thermoplastic elastomers, rigid foams, semi-rigid foams, sealants, adhesives, flexible foams and so on [29, 36, 41-43, 47, 48].

By reacting castor oil with 0.7 mols of phenylisocyanate or other monofunctional isocyanates, castor oil is transformed into a diol and used in elastomers, coatings and sealants [48].

Table 17.1 The fatty acids from castor oil [1, 29, 36, 41-43]

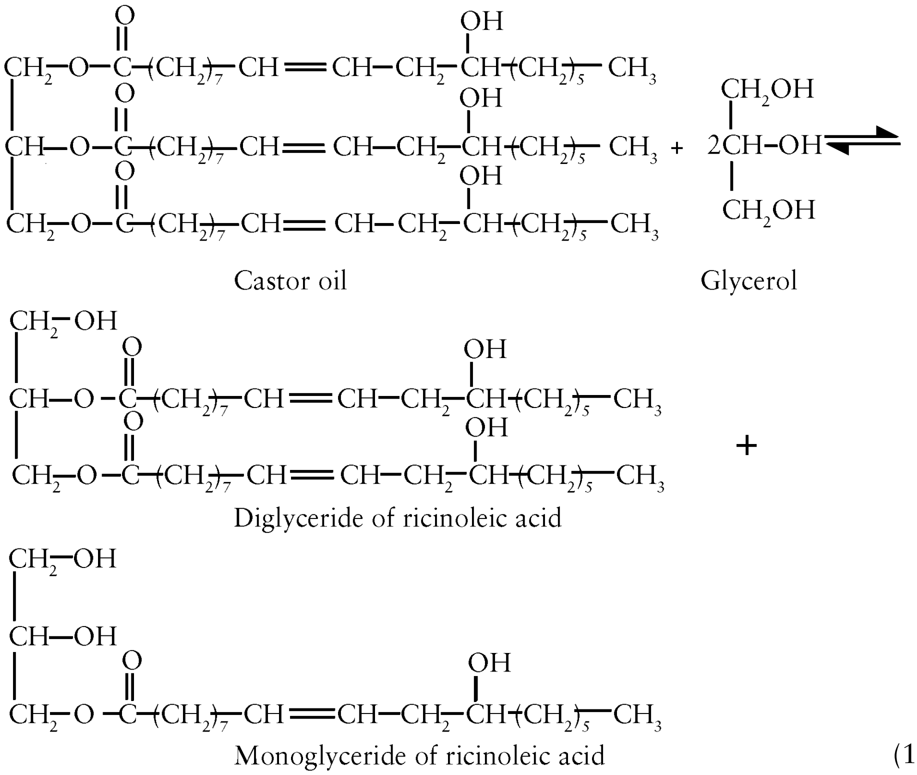
Fatty acid	**% from the total amount of fatty acids**
Ricinoleic acid	89.5
Linoleic acid	4.2
Oleic acid	3.0
Palmitic acid	1.0
Stearic acid	1.0
Dihydrostearic acid	0.7
Linolenic acid	0.3
Eicosanic acid	0.3

Concerning the direct utilisation in rigid PU foams, castor oil has some major disadvantages: low functionality, and low hydroxyl number and secondary hydroxyl groups lead to a low reactivity. Castor oil, as sole polyol, leads to semi-flexible to semi-rigid PU foams.

By mixing castor oil with polyols such as glycerol (for example 75% castor oil and 25% glycerol) a higher hydroxyl number polyol mixture is obtained, which leads to rigid PU foams with good physico-mechanical properties [47].

By the transesterification of castor oil with polyols with high functionality and high hydroxyl number [29], or by transamidation with polyamines or alkanolamines [29] new polyols are obtained which are of real use in the fabrication of rigid PU foams with good physico-mechanical properties. These polyols are made without PO.

The polyols that can be used for transesterification with castor oil are: glycerol, trimethylolpropane, pentaerythritol, sorbitol, and sucrose. The catalysts of the reaction between castor oil and various polyols are alkali alcoholates, such as: sodium methoxide or potassium methoxide. Thus, by the reaction of one mol of castor oil with two mols of glycerol, a mixture of mono, di and triglycerides of ricinoleic acid, having a much higher hydroxyl number than the initial castor oil, of around 420-430 mg KOH/g (reaction 17.5) is obtained.

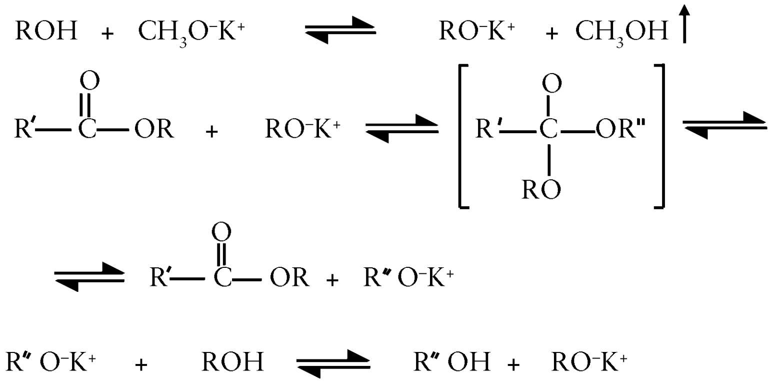


(17.5)

By using pentaerythritol instead of glycerol it is possible to obtain the structures shown in **Figure 17.7**, the composition depending on the molar ratio of castor oil/pentaerythritol.

The transesterification between castor oil and various polyols is an equilibrium reaction of all the hydroxyl group species from the reaction system with the ester groups. Because no reaction component is removed, the reaction time is in fact the time needed to establish the reaction equilibrium (around 1-2 hours at 90-120 °C).

The mechanism of this equilibrium is typical for base catalysed transesterification reactions, the alcoholate anion of the catalyst (for example sodium or potassium methoxide) attacks the carbonyl group of the ester bonds first (reactions 17.6).



$$ROH + CH_3O^-K^+ \rightleftharpoons RO^-K^+ + CH_3OH\uparrow$$

$$R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR + RO^-K^+ \rightleftharpoons \left[R'{-}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle RO}{|}}{C}}{-}OR'' \right] \rightleftharpoons$$

$$\rightleftharpoons R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR + R''O^-K^+$$

$$R''O^-K^+ + ROH \rightleftharpoons R''OH + RO^-K^+$$

(17.6)

The transamidation reaction is catalysed by the same catalysts (sodium or potassium methoxides or even sodium or potassium hydroxides). Thus, by the reaction of castor oil with

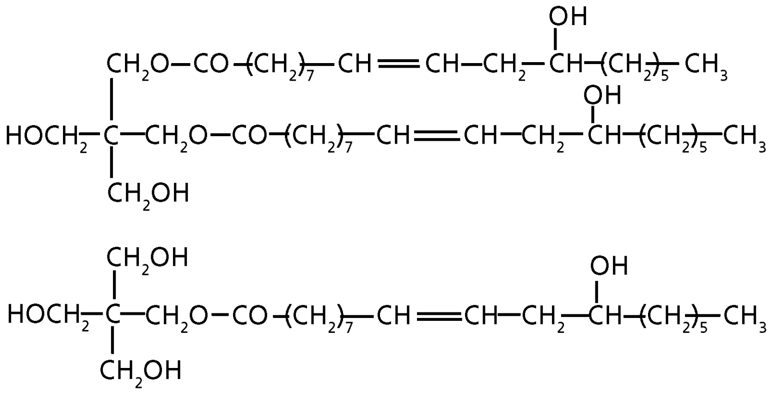
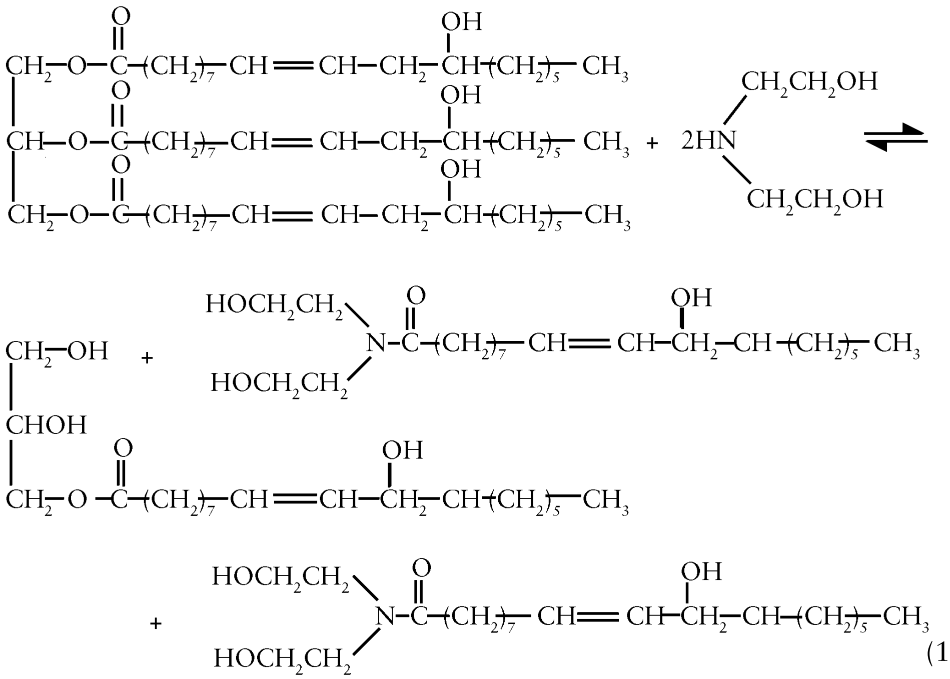


Figure 17.7 Structure of polyols resulting from transesterification of castor oil with pentaerythritol

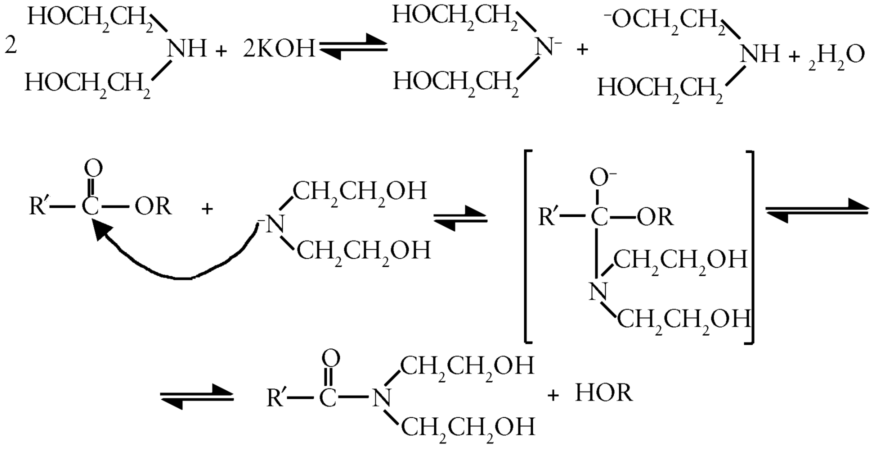
diethanolamine, in the presence of potassium methoxide at 90-120 °C, a mixture of polyols having ester and diethanolamide structures (reaction 17.7) is obtained in a short time [20].



(17.7)

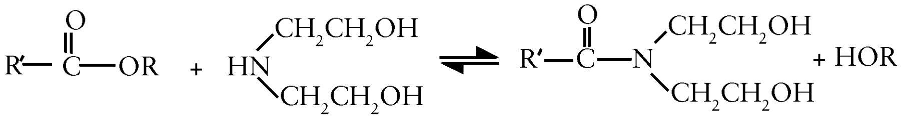
The hydroxyl number of the resulting polyolic mixture is around 410-420 mg KOH/g and the functionality is 3 OH groups/mol.

The mechanism of transamidation reaction involves the attack of an amide anion to the carbonyl group of ester bonds (reaction 17.8).



(17.8)

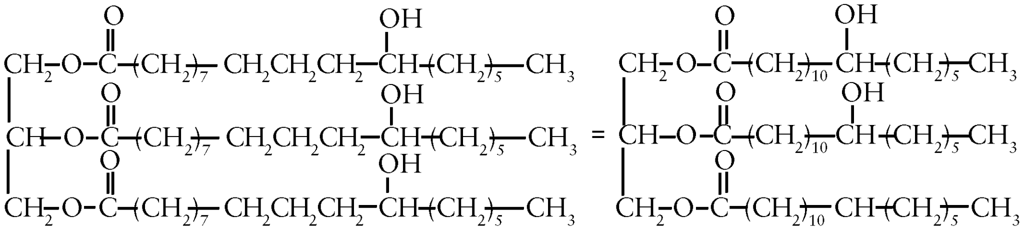
The global reaction is shown in reaction 17.9, and is in fact an ester with a primary or secondary amine which gives an amide and an alcohol:



(17.9)

Instead of diethanolamine it is possible to use other amines, such as: ethylene diamine, diethylene triamine [29], diisopropanolamine and so on.

The reaction between castor oil and amines can be developed without catalysts, but in longer reaction times (several hours) and at higher temperatures (120-130 °C) [20, 49]. By hydrogenation of castor oil a new polyol is obtained which is similar to castor oil, but without the double bonds (17.10) [36, 37].

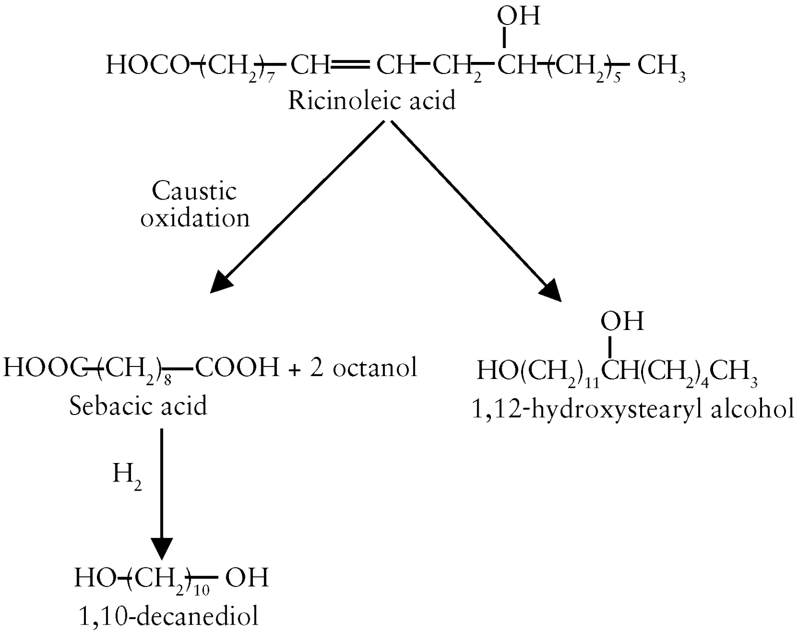


$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_7-CH_2CH_2CH_2-\overset{\overset{OH}{|}}{C}H-(CH_2)_5-CH_3 \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-(CH_2)_7-CH_2CH_2CH_2-\overset{\overset{OH}{|}}{C}H-(CH_2)_5-CH_3 \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_7-CH_2CH_2CH_2-\overset{\overset{OH}{|}}{C}H-(CH_2)_5-CH_3 \end{array} = \begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{10}-\overset{\overset{OH}{|}}{C}H-(CH_2)_5-CH_3 \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{10}-\overset{\overset{OH}{|}}{C}H-(CH_2)_5-CH_3 \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{10}-CH-(CH_2)_5-CH_3 \end{array}$$

(17.10)

Hydrogenated castor oil is a solid with a melting point of 82-86 °C, having similar hydroxyl number to castor oil, of around 160-162 mg KOH/g. Hydrogenated castor oil is used in coatings and gives adhesion, flexibility, water repellency and chemical resistance [36].

Castor oil and the hydrolysis product - ricinoleic acid are a source of new valuable products. Thus, by the caustic oxidation of ricinoleic acid, sebacic acid and 2-octanol are formed. By hydrogenation of sebacic acid (or better of dimethylsebacate), 12-decanediol is formed. By hydrogenation of ricinoleic acid an interesting diol is obtained: 1,12 hydroxystearyl alcohol having one primary and one secondary hydroxyl group (reaction 17.11).



(17.11)

All these products: sebacic acid, 1,10-decanediol and 1,12-hydroxystearyl alcohol are interesting raw materials for polyester polyol synthesis.

A very important acid is azelaic acid obtained industrially by the ozonolysis of vegetable oils ($HOOC[CH_2]_7COOH$). Azelaic acid is important as a raw material for polyester-based PU adhesives.

As a general rule, castor oil and its derivatives confer on the resulting PU hydrophobicity and water repellency. These polyols have an excellent compatibility with the pentanes that are used as blowing agents and the resulting PU foams have excellent resistance to humid ageing degradation.

The unsaturated vegetable oils, having double bonds but without hydroxyl groups, are transformed by various chemical reactions into polyols, which by reaction with isocyanates are transformed into PU.

The reactions of vegetable oil transformations in polyols are divided into two important groups:

a) Reactions involving esteric groups, and

b) Reactions involving double bonds.

Generation of hydroxyl groups by oxidation reactions is another variant of hydroxyl group generation, but in this chapter only the most important reactions involving ester groups and double bonds will be described.

For a better understanding, of the transformation of vegetable oils and fats in polyols, some information about the structure of fatty acids and of natural oils will be presented.

The general structure of a natural oil (vegetable oils or fats) is the structure of a triglyceride, the ester of glycerol and fatty acids (**Figure 17.8**).

The most important natural fatty acids are presented in **Table 17.2**. The composition of three important vegetable oils is presented in **Table 17.3**, **Table 17.4** and **Table 17.5**.

17.1.1 Synthesis of Vegetable Oil Polyols by using Reactions Involving Ester Groups

The main way to transform a vegetable oil into a polyol is by using reactions involving ester groups such as transesterification and transamidation reactions.

By the transesterification of an unsaturated triglyceride (for example soybean oil) with glycerol, a mixture of monoglycerides (majority), diglycerides and triglycerides of unsaturated fatty acids (reaction 17.12) is obtained [50].

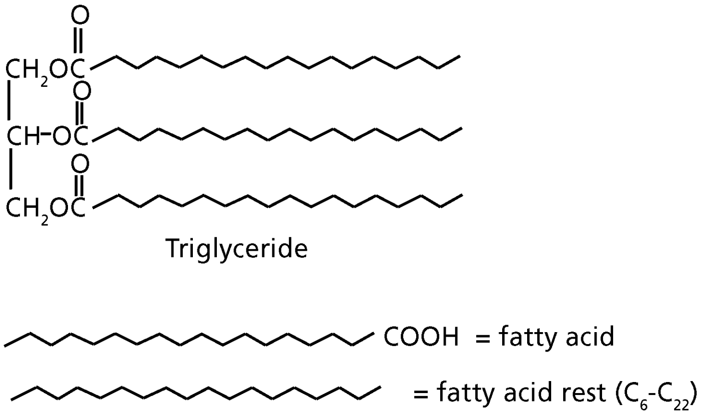
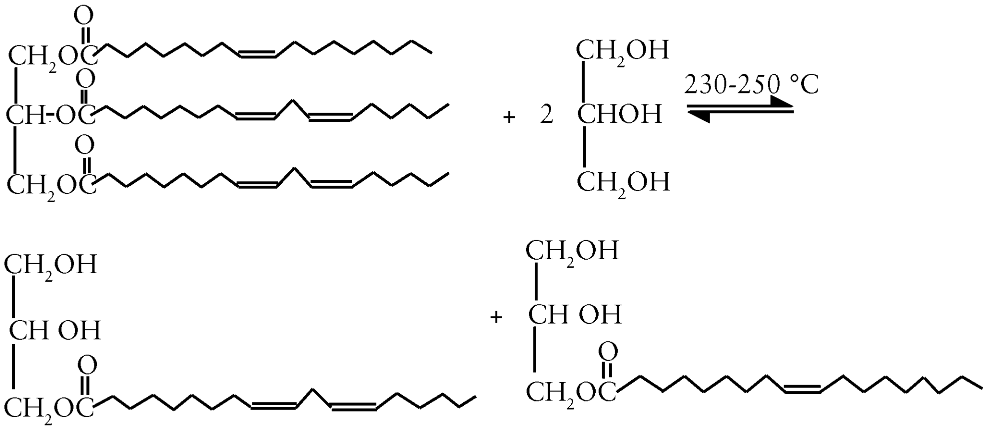


Figure 17.8 General structure of an oil



(17.12)

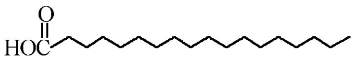
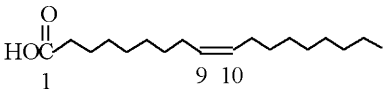
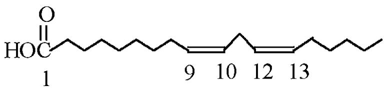
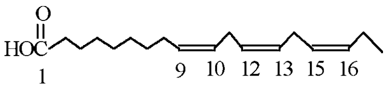
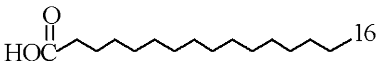
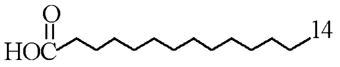
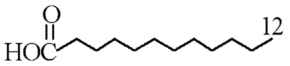
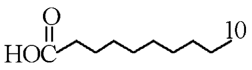
Table 17.2 The structure of most important natural fatty acids			
Fatty acid	**Carbon atoms**	**Number of double bonds**	**Formula**
Stearic acid	C_{18}	0	
Oleic acid	C_{18}: 1	1 ($C_9 - C_{10}$)	
Linoleic acid	C_{18}: 2	2 ($C_9 - C_{10}$) ($C_{12} - C_{13}$)	
Linolenic acid	C_{18}: 3	3 ($C_9 - C_{10}$) ($C_{12} - C_{13}$) ($C_{15} - C_{16}$)	
Palmitic acid	C_{16}	0	
Myrisic acid	C_{14}	0	
Lauric acid	C_{12}	0	
Capric acid	C_{10}	0	

Table 17.2 Continued ...

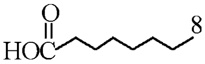
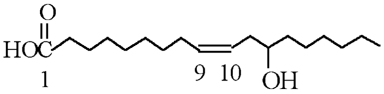
Fatty acid	Carbon atoms	Number of double bonds	Formula
Caprylic acid	C_8	0	
Ricinoleic acid	C_{18}: 1	1 ($C_9 - C_{10}$) 1 OH group at C_{12}	
C_{18}: 1 - with one double bond *C_{18}: 2 - with two double bonds* *C_{18}: 3 - with three double bonds*			

Table17.3 Composition of soybean oil

Fatty acid	Number of carbon atoms: number of double bonds	Approximate composition, %
Linolenic acid	C_{18}: 3	9
Linoleic acid	C_{18}: 2	51
Oleic acid	C_{18}: 1	23.5-25
Stearic acid	C_{18}	2-4
Palmitic acid	C_{16}	11
Soybean oil has around 4.6 double bonds/mol		

Table 17.4 Composition of sunflower oil

Fatty acid	Number of carbon atoms: number of double bonds	Approximate composition, %
Linolenic acid	C_{18}: 3	0.4
Linoleic acid	C_{18}: 2	61.5
Oleic acid	C_{18}: 1	26.4
Stearic acid	C_{18}	4.7
Palmitic acid	C_{16}	5.9

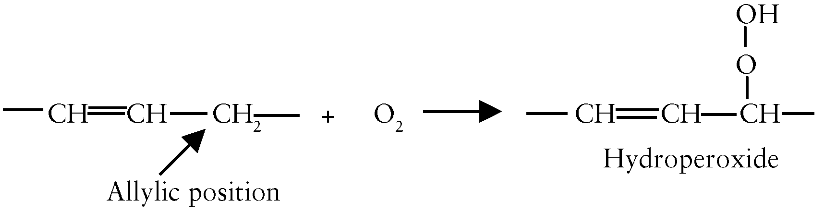
Table 17.5 Composition of linseed oil

Fatty acid	Number of carbon atoms: number of double bonds	Approximate composition, %
Linolenic acid	C_{18}: 3	52
Linoleic acid	C_{18}: 2	16
Oleic acid	C_{18}: 1	22
Stearic acid	C_{18}	4
Palmitic acid	C_{16}	6

The resulting unsaturated diols (practically monoglycerides of fatty acids, reaction 17.12) react with diisocyanates (for example with toluene diisocyanate) at around 80-90 °C, usually in a solvent such as toluene, xylene or naphtha. Unsaturated PU are obtained, which are crosslinked by a radical mechanism with the transformation of the multiple double bond in a crosslinked network (**Figure 17.9**). This reaction is used for the fabrication of urethane alkyd coatings. Other polyols may be used instead of glycerol: ethylene glycol, neopentylglycol, trimethylolpropane, pentaerythritol and others.

Safflower oil, sunflower oil, linseed oil, cottonseed oil, tung oil, tall oil, fish oil, castor oil, and so on are used as the vegetable oils [50].

The mechanism of curing urethane alkyd resins is based on the oxidation with molecular oxygen of the allylic position (reaction 17.13).



$$-CH{=}CH-CH_2- + O_2 \longrightarrow -CH{=}CH-\overset{\overset{\displaystyle OH}{|}}{\overset{\displaystyle O}{\overset{|}{CH}}}-$$

(17.13)

The formed hydroperoxide initiates the radical crosslinking reaction. Metal salts are used frequently as catalysts, to accelerate crosslinking reactions (for example with cobalt(II) compounds, reaction 17.14).

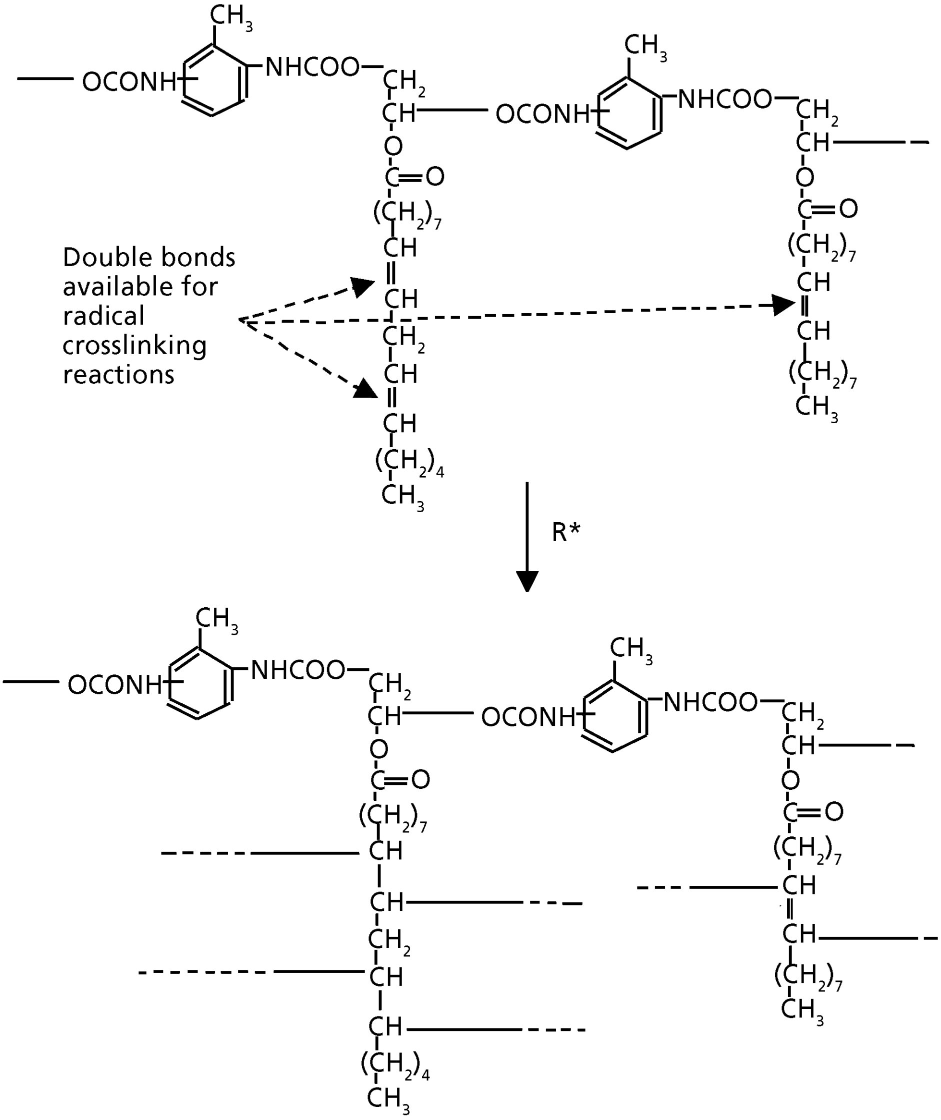
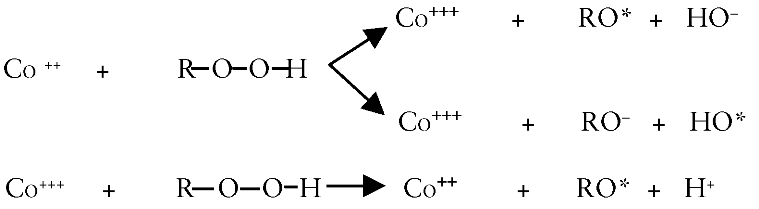


Figure 17.9 Radical crosslinking of urethane alkyd resins



$$Co^{++} + R{-}O{-}O{-}H \rightarrow Co^{+++} + RO^{*} + HO^{-}$$

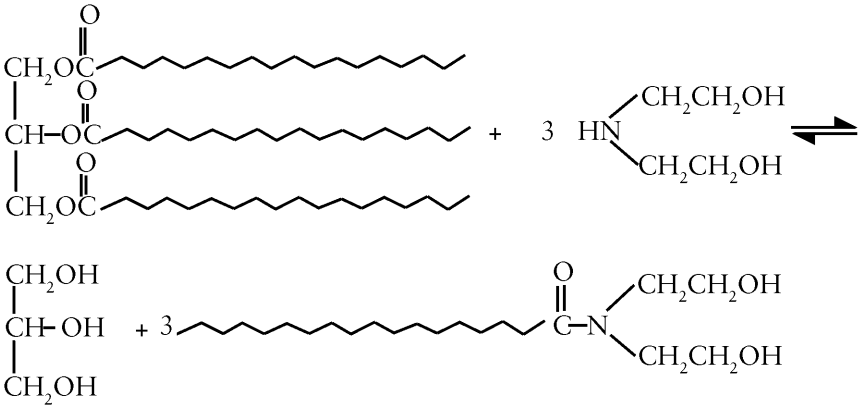
$$Co^{++} + R{-}O{-}O{-}H \rightarrow Co^{+++} + RO^{-} + HO^{*}$$

$$Co^{+++} + R{-}O{-}O{-}H \rightarrow Co^{++} + RO^{*} + H^{+}$$

(17.14)

The radicals formed: RO* and HO*, initiate the crosslinking reaction. Soybean oil, sunflower oil and safflower oil give semi-drying urethane alkyds but high unsaturated oils, such as linseed oil give drying urethane alkyds.

The transamidation reactions, usually with diethanolamine, are frequently used to obtain diethanolamides of fatty acids (well known as nonionic surfactants [51-57]). Fatty acid diethanolamides are sometimes used together with other polyols, to obtain rigid PU foams. The fatty acid diethanolamides are bifunctional compounds and improve the compatibility of various polyolic systems very much, with pentanes used as blowing agents for rigid PU foams (reaction 17.15).



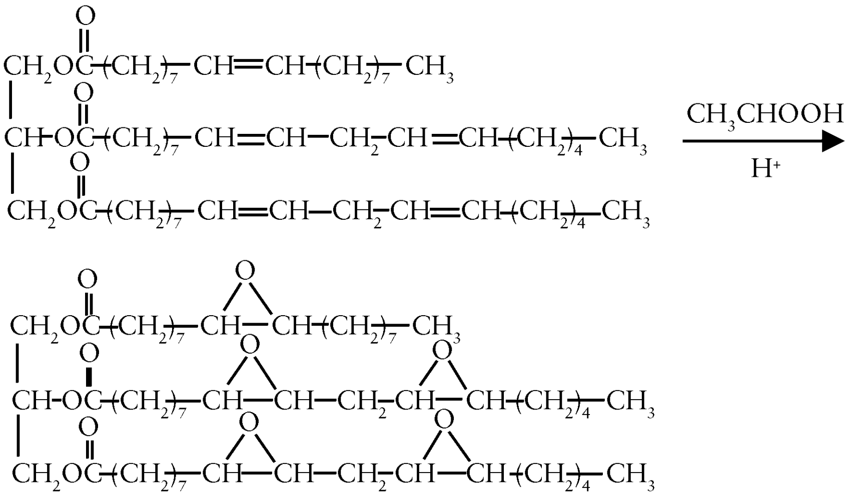
(17.15)

17.1.2 Synthesis of Vegetable Oil Polyols by Using Reactions Involving the Double Bonds

The transformation of an unsaturated triglyceride in a polyol was made by the generation of hydroxyl groups by using various reactions of double bonds. The most important way to transform an unsaturated vegetable oil into a polyol is the epoxydation of double bonds, followed by the various reactions of the resulting epoxidic ring which are transformed by hydroxyl groups [1-3, 6, 27-34, 44-46].

Epoxidised soybean oil or epoxidised sunflower oil are commercial products obtained by the epoxidation of vegetable oils with peroxyacetic or peroxiformic acid (generated *in situ* by the reaction of hydrogen peroxide with acetic or formic acid), in the presence of an acidic catalyst [27].

The epoxidation of soybean oil results in an oil with around 4-4.2 epoxidic groups/mol (reaction 17.16).



(17.16)

The epoxidised vegetable oils are reacted with various reagents, the epoxidic groups being transformed into hydroxyl groups, resulting in vegetable oil polyols (frequently called oleochemical polyols). The most important reactions for ring opening of the epoxidic ring to various structures containing hydroxyl groups are:

a) Reaction with acids (organic or inorganic),

b) Hydrolysis,

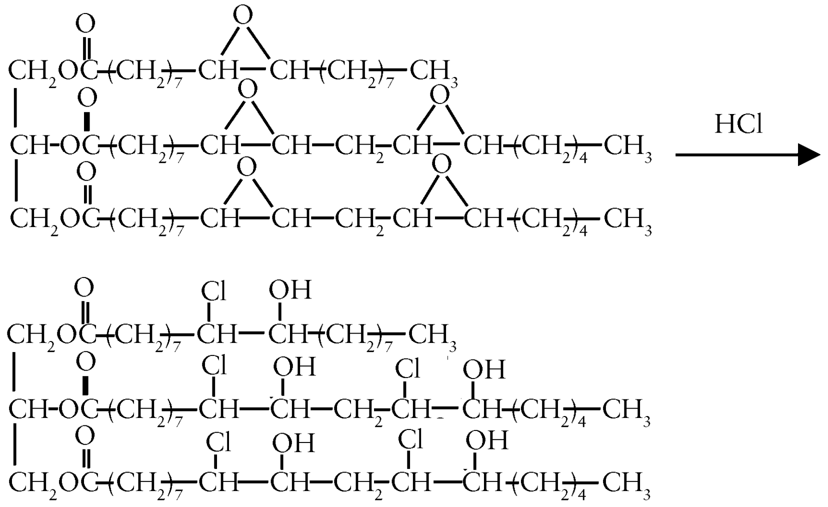
c) Alcoholysis, and

e) Hydrogenolysis.

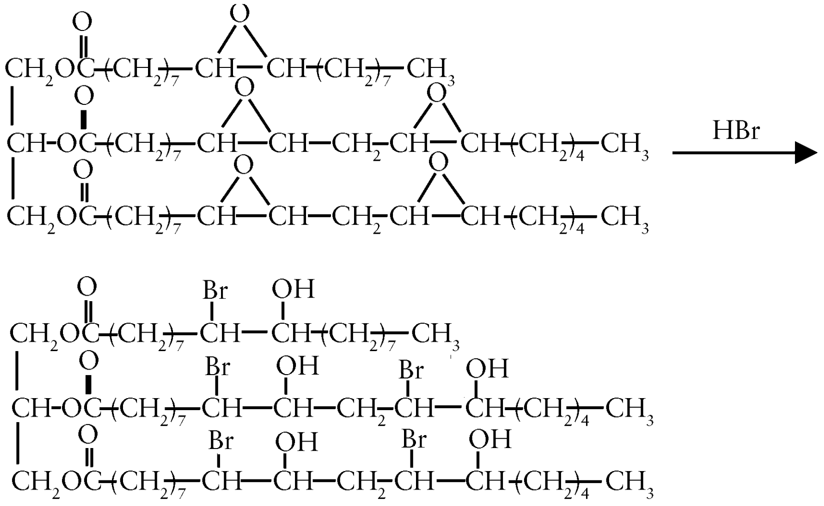
a) Reaction with Acids (Organic or Inorganic)

By the reaction of epoxidised vegetable oils with HCl, HBr or various organic acids (R-COOH), the epoxidic ring is opened with the formation of polyols having chlorohydrin, bromohydrin or hydroxyalkyl esters structures (reactions 17.17, 17.18 and 17.19) [31-34].

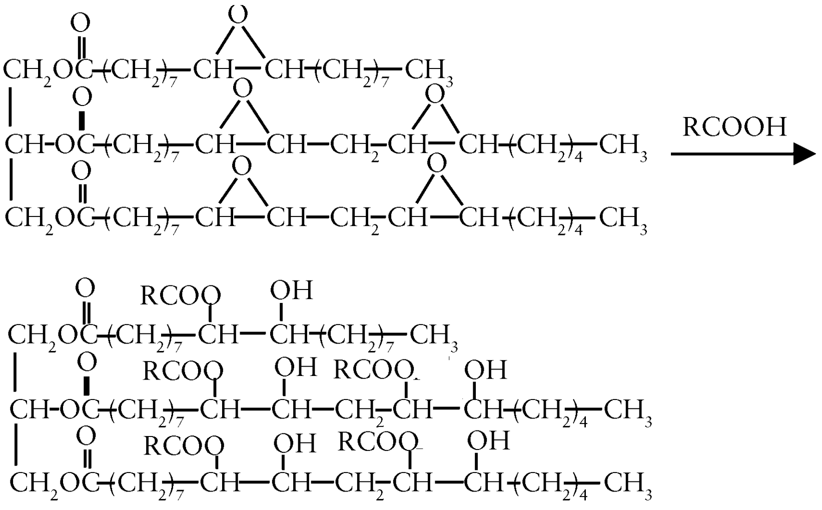
Generally the resulting vegetable oil polyols are greases, with an hydroxyl number of around 180-200 mg KOH/g and a functionality of 3.8-4.1 OH groups/mol. The reactions take place at high yields (94-100%) and moderate temperatures (40-50 °C). The reaction with organic acids, due to the low acidity, needs higher temperatures and a strong acid as catalyst (for example H_2SO_4 or *p*-toluene sulfonic acid).



(17.17)



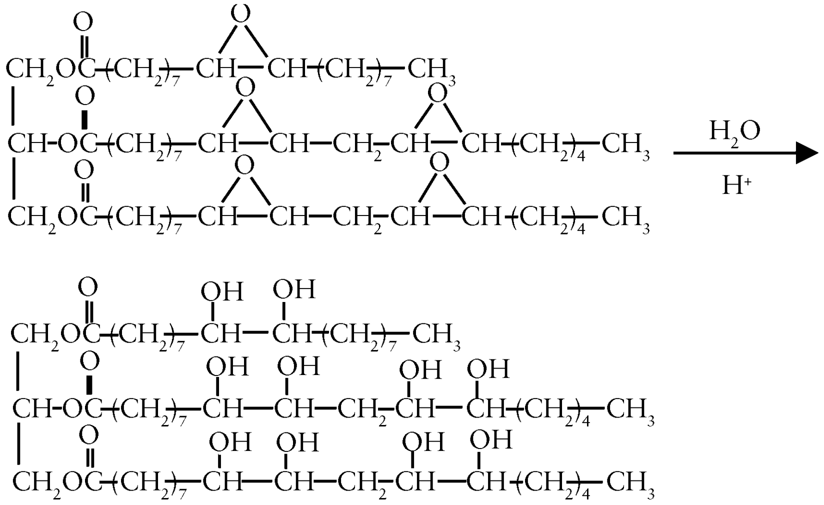
(17.18)



(17.19)

b) Hydrolysis [58]

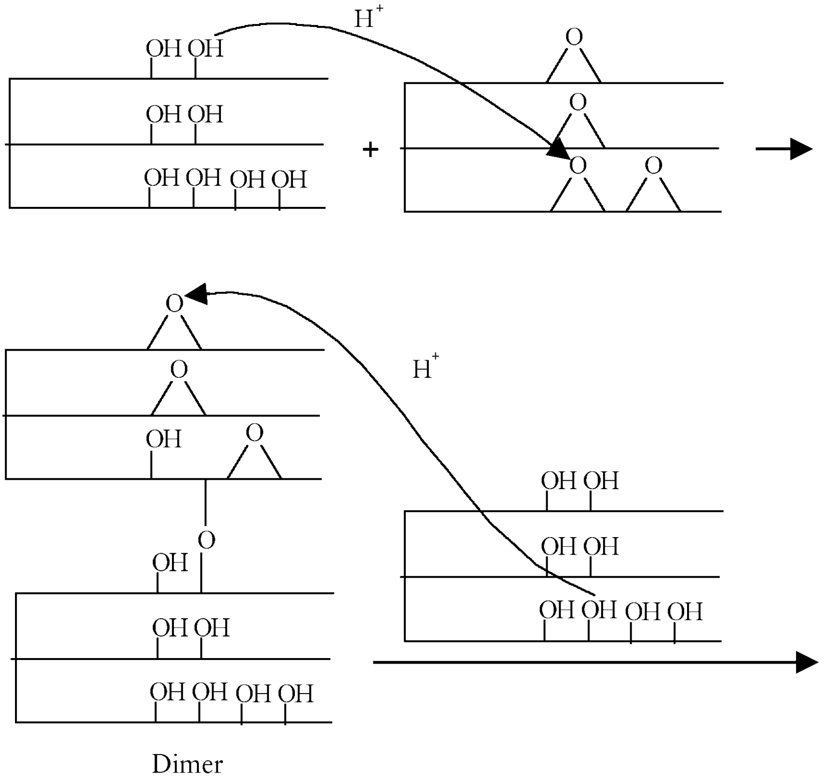
The hydrolysis of epoxidised soybean oil was investigated in the presence of acidic catalysts (sulfuric acid, *p*-toluene sulfonic acid, phosphoric acid). The objective was to obtain a maximum hydroxyl number with a minimum hydrolysis of the ester bonds [58]. The idealised reaction for epoxidised soybean oil hydrolysis is presented in reaction 17.20.



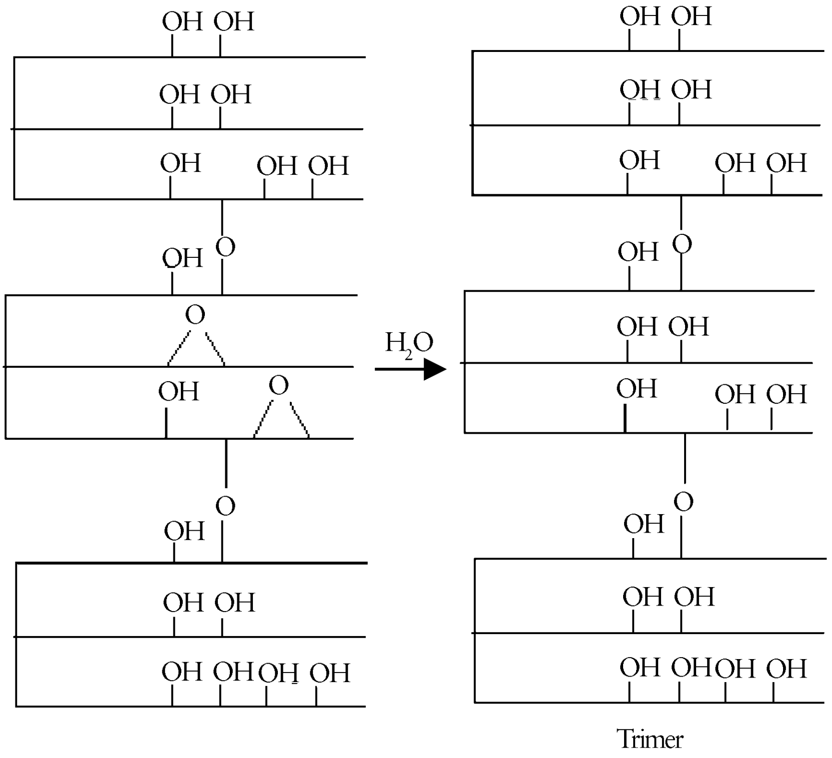
(17.20)

Theoretical hydroxyl numbers of the polyols resulting from epoxidised soybean oil hydrolysis are in the range 440-450 mg KOH/g. If the epoxidised soybean oil has 4 epoxy groups/mol, the resulting functionality of polyol obtained by hydrolysis is 8 hydroxyl groups/mol.

Unfortunately, the resulting hydroxyl number is much lower, around 200-250 mg KOH/g. The explanation of these lower hydroxyl numbers is the reaction between the hydroxyl groups formed during hydrolysis reaction with the epoxy groups of unreacted epoxidised soybean oil (reaction 17.21). The intermolecular reactions formed dimers, trimers and superior oligomers, of higher functionality (f > 8 OH groups/mol).



(17.21a)

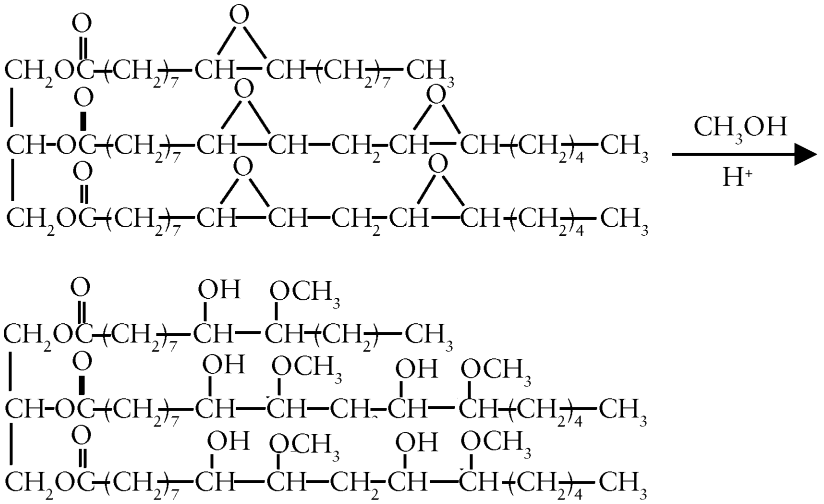


(17.21b)

By the intermolecular reactions between epoxy groups and the hydroxyl groups formed there are not generated new hydroxyl groups, but the molecular weight increases (dimers, trimers) and of course the hydroxyl number decreases. In principle, intramolecular reactions of the same type are possible with formation of cyclic compounds and of course, without generation of new hydroxyl groups.

c) Alcoholysis [31- 34, 44, 45, 59-61]

By the reaction of alcohols (in excess) with epoxidised vegetable oils in the presence of acids as catalysts - liquid polyols are formed (reaction 17.22). For example by the alcoholysis of epoxidised soybean oil with methanol, at the reflux temperature of methanol (the boiling point of methanol is 64.7 °C), in the presence of an acidic catalyst (H_2SO_4, *p*-toluene sulfonic acid, HBF_4 [31, 34, 44, 45], solid acidic clays [39], supported acidic catalysts), liquid soybean oil based polyols are obtained, with an hydroxyl number of around 170-173 mg KOH/g, a functionality of about 3 - 4 OH groups/mol and a viscosity of around 4,000-7,000 mPa-s at 25 °C. After the neutralisation of the acidic catalyst or by the filtration of solid acid catalysts, the methanol is distilled under vacuum and recycled back into the process.



(17.22)

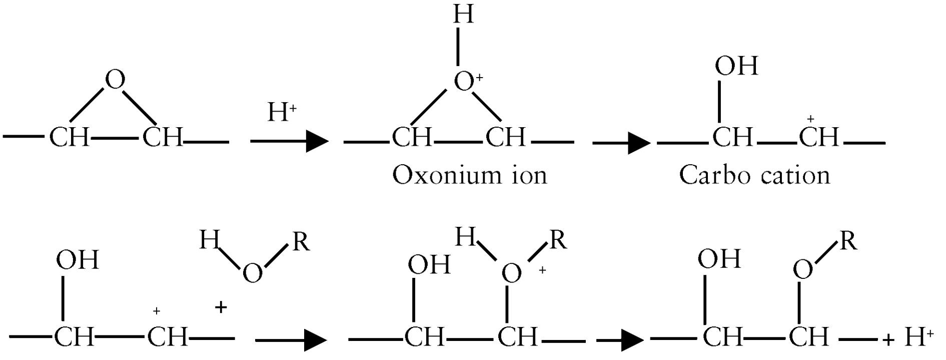
Of course it is possible to use other alcohols instead of methanol, such as: ethanol, 1-propanol and 2-propanol, butanol. Methanol is preferred due to its lower price, lower molecular weight and lower boiling point.

As is the case with hydrolysis of epoxidised vegetable oils, by alcoholysis the hydroxyl numbers obtained are always lower than theoretically expected. The explanation is the same: the intermolecular and intramolecular reactions between the formed hydroxyl groups and the unreacted epoxidic rings. These reactions conserve the number of hydroxyl groups and do not generate new hydroxyl groups. By intramolecular reactions dimers and trimers of lower hydroxyl number and higher functionality are formed.

It is possible to increase the hydroxyl number by developing an alcoholysis - hydrolysis reaction.

Thus, by reaction of epoxidised soybean oil with a mixture of methanol - water in the presence of an acidic catalyst, polyols are obtained, with an hydroxyl number in the range 200-210 mg KOH/g and a viscosity between 10,000-16,000 mPa-s at 25 °C [59, 61].

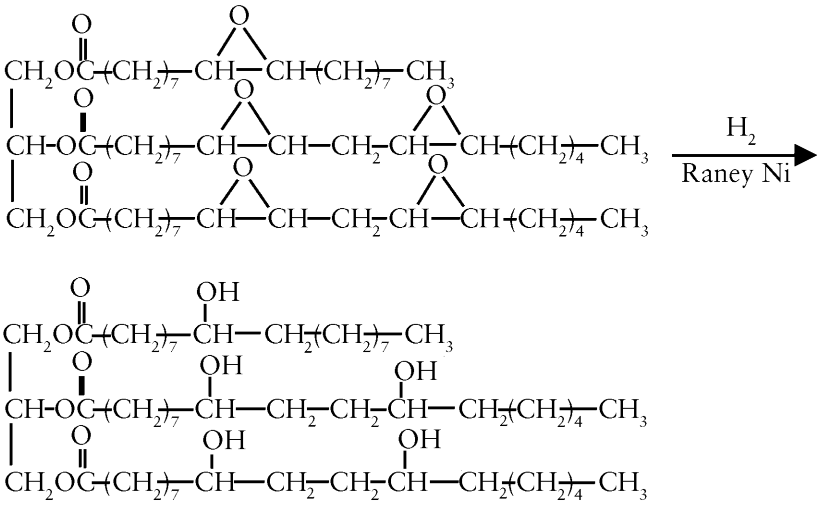
All the reactions of epoxidic groups with alcohols or water, in excess, are SN-1 reactions of the type shown in reaction 17.23, having as intermediates organic cations, such as oxonium ions and carbo cations.



(17.23)

d) Hydrogenolysis [31, 32]

By the hydrogenation of epoxidised vegetable oils with gaseous hydrogen under pressure (around 4.1-6.9 MPa), in the presence of an hydrogenation catalyst (for example Raney Ni) solid polyols are obtained, with the consistency of waxes, having a low melting point of around 25-50 °C, an hydroxyl number of about 200-215 °C and a functionality of around 3.5 OH groups/mol [31, 32]. The hydrogenated epoxidised soybean oil has a melt viscosity at around 38 °C of about 2000 mPa-s. One epoxidic ring generates one hydroxyl group:



(17.24)

In the last few years many other methods were developed for transformation of double bonds in hydroxyl groups, these are of minor importance at this moment, but have a real synthetic potential such as:

a) Reactions with aqueous potassium permanganate,

b) Hydroxylation in the presence of osmium oxide as catalyst [63-65],

c) Hydroxylation with hydrogen peroxide in the presence of heteropolyacids (for example phosphomolybdenic acid) [66],

d) Introduction of epoxide groups by oxidation of vegetable oils with molecular oxygen in the presence of nickel complexes (nickel acetylacetonate), in the presence of a reductant (butyraldehyde), at room temperature [67],

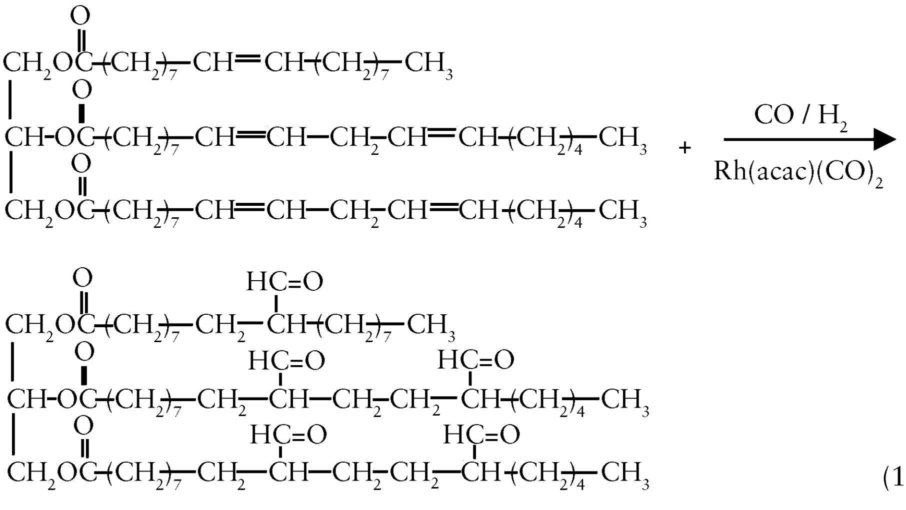
e) Hydroxylation with hydrogen peroxide in the presence of solid titanium silicalite catalysts [68, 69], and

f) Enzymic epoxydations and hydroxylations.

17.1.3 Other Reactions Involving Reactions of Double Bonds of Vegetable Oils

17.1.3.1 Hydroformylation Reactions

A very efficient method to transform directly an unsaturated triglyceride in polyols is to develop a hydroformylation reaction with 'sin gas' (mixture of hydrogen/carbon monoxide), at 70-130 °C, in the presence of rhodium or cobalt catalysts [70, 71], at higher pressures (4,000-11,000 kPa). In the first step the double bonds are transformed in aldehyde groups, in high yield (reaction 17.25).



$$\begin{array}{l} CH_2O\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_7\!-\!CH{=}CH\!-\!(CH_2)_7\!-\!CH_3 \\ |\\ CH\!-\!O\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_7\!-\!CH{=}CH\!-\!CH_2\!-\!CH{=}CH\!-\!(CH_2)_4\!-\!CH_3 \\ | \\ CH_2O\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_7\!-\!CH{=}CH\!-\!CH_2\!-\!CH{=}CH\!-\!(CH_2)_4\!-\!CH_3 \end{array} \quad + \quad \xrightarrow[Rh(acac)(CO)_2]{CO\,/\,H_2}$$

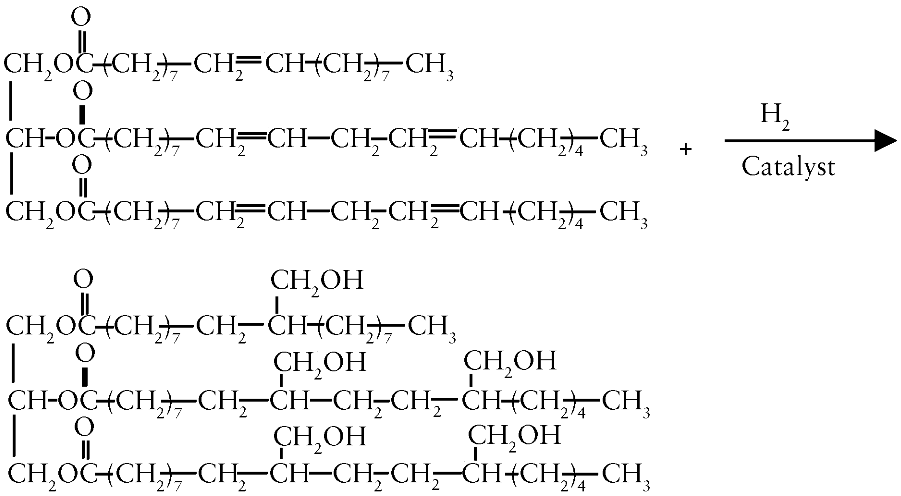
$$\begin{array}{l} CH_2O\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_7\!-\!CH_2\!-\!\overset{HC=O}{\overset{|}{CH}}\!-\!(CH_2)_7\!-\!CH_3 \\ | \\ CH\!-\!O\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_7\!-\!CH_2\!-\!\overset{HC=O}{\overset{|}{CH}}\!-\!CH_2\!-\!CH_2\!-\!\overset{HC=O}{\overset{|}{CH}}\!-\!(CH_2)_4\!-\!CH_3 \\ | \\ CH_2O\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_7\!-\!CH_2\!-\!\overset{HC=O}{\overset{|}{CH}}\!-\!CH_2\!-\!CH_2\!-\!\overset{HC=O}{\overset{|}{CH}}\!-\!(CH_2)_4\!-\!CH_3 \end{array}$$

(17.25)

In the second step, the resulting aldehyde groups are hydrogenated to a polyol having 100% primary hydroxyl groups, very reactive in PU chemistry, with hydroxyl numbers in the range of 200-240 mg KOH/g [31, 32] (reaction 17.26).

The resulting polyol, alone or in combination with classic rigid polyols, polyethers or polyesters, has a good potential use in fabricating rigid PU foams, especially in very reactive systems ('spray' foams).

Hydroformylation is one of the most important chemical transformations of vegetable oils in polyols. The raw material used is not the relatively expensive epoxydised vegetable oil, but the cheap natural vegetable oil.



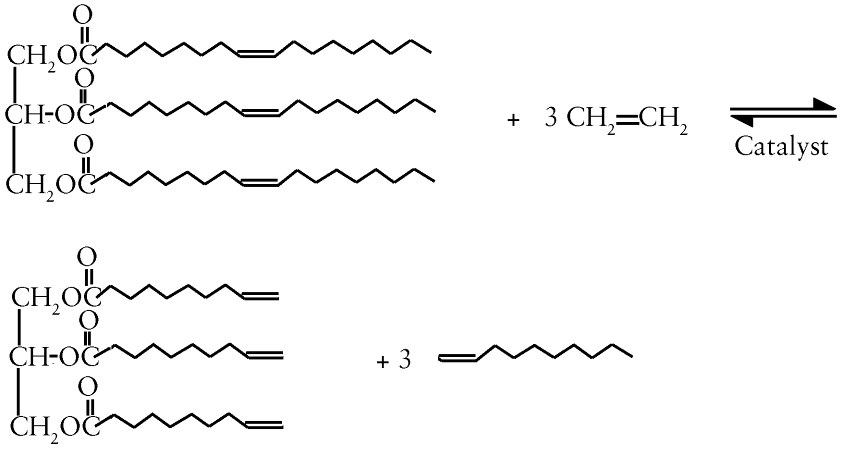
$$\begin{array}{l} CH_2O\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_3 \\ |\quad\; \overset{O}{\|} \\ CH\text{-}O\overset{}{C}\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3 \\ |\quad\; \overset{O}{\|} \\ CH_2O\overset{}{C}\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3 \end{array} + \xrightarrow[\text{Catalyst}]{H_2}$$

$$\begin{array}{l} CH_2O\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}CH_2\text{-}\overset{\overset{CH_2OH}{|}}{CH}\text{-}(CH_2)_7\text{-}CH_3 \\ |\quad\; \overset{O}{\|} \\ CH\text{-}O\overset{}{C}\text{-}(CH_2)_7\text{-}CH_2\text{-}\overset{\overset{CH_2OH}{|}}{CH}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{CH_2OH}{|}}{CH}\text{-}(CH_2)_4\text{-}CH_3 \\ |\quad\; \overset{O}{\|} \\ CH_2O\overset{}{C}\text{-}(CH_2)_7\text{-}CH_2\text{-}\overset{\overset{CH_2OH}{|}}{CH}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{CH_2OH}{|}}{CH}\text{-}(CH_2)_4\text{-}CH_3 \end{array}$$

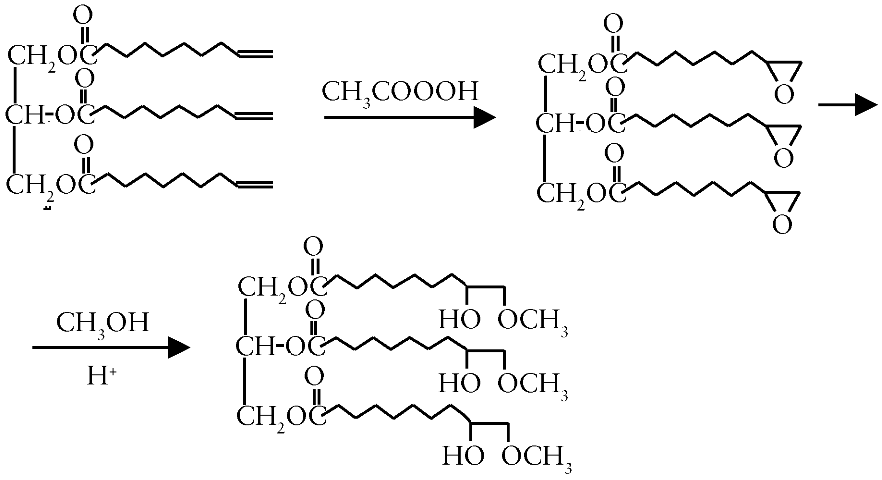
(17.26)

17.1.3.2 Methatesis Reactions

The methatesis of vegetable oils with ethylene is a very interesting way to obtain new unsaturated structures to be transformed into new polyols via the epoxidation - alcoholysis route. Trioleine was used as a model compound (the triester of glycerol with oleic acid), the methatesis reaction with ethylene being catalysed by a special ruthenium catalyst [72]. The resulting triglyceride, with terminal double bonds, after removal of the 1-decene formed, is transformed into polyols by epoxidation, followed by alcoholysis with methanol (reactions 17.27 and 17.28).



(17.27)



(17.28)

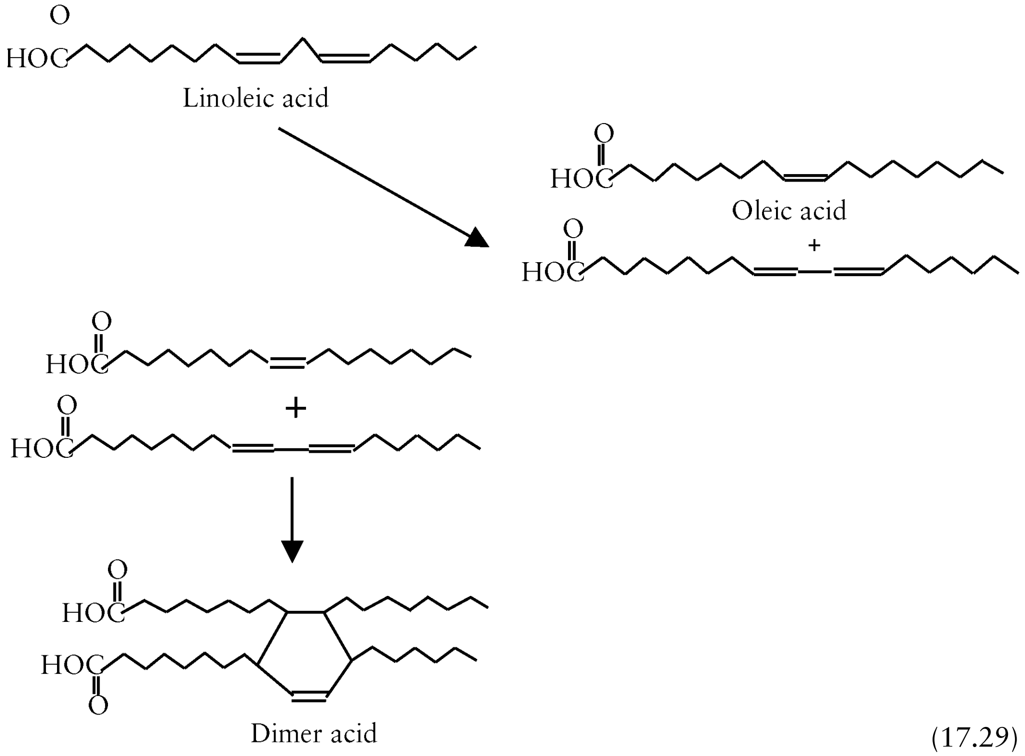
The resulting polyols have higher hydroxyl numbers than the product of methanolysis of epoxidised soybean oil, of around 230-235 mg KOH/g, an equivalent weight of about 240 daltons and a molecular weight of around 756 daltons (vapour pressure osmometry), a viscosity of around 1300 mPa-s at 25 °C and a functionality of 3.1-3.2 OH groups/mol [72]. The resulting polyol is similar to the product derived from epoxidised soybean oil (17.27), and contains dimers and trimers and, as an immediate consequence, the functionality is higher than 3 (f = 3.1-3.2 OH groups/mol) [72].

17.1.3.3 Dimerisation of Unsaturated Fatty Acids - Polyols Based on Dimeric Acids

An important development in the area of polyols from renewable resources was realised by transformation of the dimeric or trimeric acids (or of corresponding methyl esters) by hydrogenation in C_{36} diols or C_{54} triols.

Thus, the dimerisation of unsaturated fatty acids takes place at higher temperatures in the presence of catalysts (for example acidic clays, montmorillonite type). One molecule of oleic acid (having one double bond) reacts with one mol of linoleic acid (having two double bonds) and this forms a dimeric acid with a cycloaliphatic structure.

Probably, in the first step the double bonds of linoleic acid isomerise to a dienic structure which leads to dimeric acid by a formal Diels-Adler reaction (reaction 17.29).



(17.29)

Schematically the structure of a dimeric acid is shown in **Figure 17.10**.

By the reaction of the dimeric acid formed with another molecule of linoleic acid or by the reaction of three molecules of linoleic acid, acid trimers are formed, which, by analogy, are shown schematically in **Figure 17.11**.

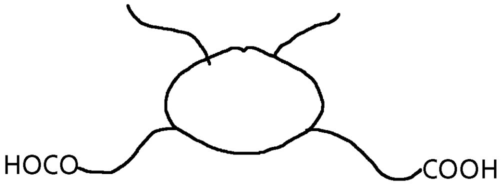


Figure 17.10 Structure of a dimeric acid

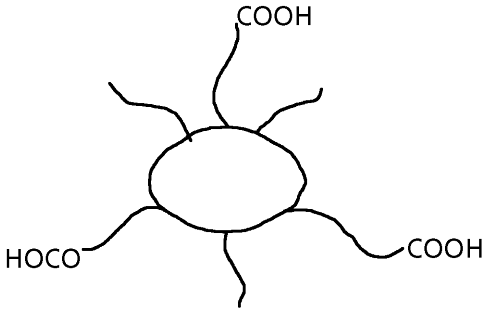


Figure 17.11 Structure of an acid trimer

By hydrogenation of these dimeric or trimeric acids the corresponding diols or triols are obtained. The dimer alcohol (**Figure 17.12**) has an hydroxyl number of 202-212 mg KOH/g and a molecular weight of 565 daltons and a viscosity of around 3,500 mPa-s at 25 °C [73, 74]. Trimer alcohols (**Figure 17.13**) have an hydroxyl number about 205 mg KOH/g and a viscosity of around 9,500 mPa-s at 25 °C [74].

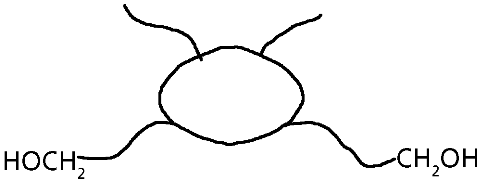


Figure 17.12 Structure of a dimer alcohol

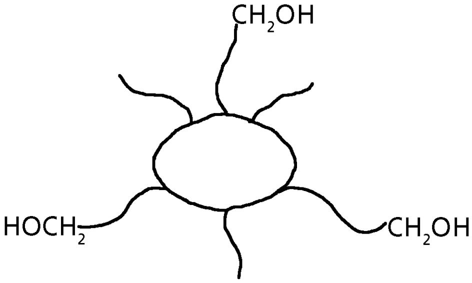


Figure 17.13 Structure of a trimer alcohol

Dimer and trimer alcohols introduced into the structure of PU confer on them: very high hydrophobicity, water repellency, flexibility and chemical stability. The polyester urethanes based on dimeric diols and dimeric acids are the most hydrolysis resistant polyester urethanes known so far [73].

17.1.3.4 Polyols Derived from Fish Oil

Fish oil is a non-vegetable, highly unsaturated triglyceride. Fish oil is characterised by a high content in fatty acids containing 4 double bonds (C_{20}) and 5 and 6 double bonds (C_{22}). These highly unsaturated fatty acids are called omega-3 fatty acids (the position of the first carbon atom of the first double bond is at the 3rd carbon atom counting from the fatty acid chain end).

The composition of some fish oils is presented in **Table 17.6** [1, 39, 40].

A fabrication of polyols for PU based on fish oil as mentioned in the literature is in operation at Newcastle (New Scotland), using the classical transformation of double bonds in hydroxyl groups [39, 40].

Table 17.6 Composition of fish oils

Constituent	Percentage
Oleic acid	8-25
Linoleic acid	2-8
Linolenic acid	0-3
C_{20} (4 double bonds)	15-30
C_{22} (5 or 6 double bonds)	15-30

17.1.4 Other Renewable Materials

Production of palm oil is the second largest worldwide (18% from the worldwide production of total oils and fats produced) after soybean oil. Palm oil has lower unsaturation levels (iodine value (IV) = 50-60 mgI_2/100g) than soybean oil (IV = 125-132 mgI_2/100g) or linseed oil (IV = 170-180 mgI_2/100g), but it was transformed successfully in polyols for rigid foams [24-26]. Very interesting polyols were developed in Malaysia, making derived from palm oil, for making rigid PU foams, [24-26].

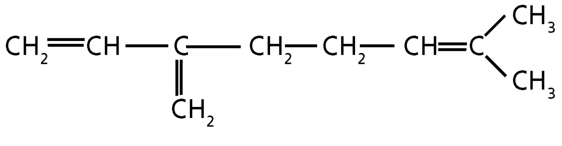
Another interesting renewable raw material is *myrcene* (a product of β-pinene pyrolysis), which has a high content of double bonds (**Figure 17.14**).

The myrcene-based polyols are obtained by classic reactions of double bonds.

Based on data from the literature, some important renewable resources used for polyols for polyurethane fabrication, without any attempt at an exhaustive presentation are presented. There are many ways of transforming natural renewable raw materials into polyols, as a consequence of the creativity and ingenuity of chemists. There are many possibilities for valorification of natural renewable materials in the area of polyols for PU.

The transformation of vegetable oils and other natural products in polyols has opened up and is a very promising area for new developments, such as: genetic engineering to create new triglycerides containing hydroxyl groups, synthesis of new polyols by selective oxidation of vegetable oils (for example microbial oxidation), new reactions for the transformation of double bonds in polyols such as ozonolysis-reduction, oxygenation reactions with molecular oxygen using special complex catalysts (nickel complexes such as nickel acetylacetonates), enzymic reactions, direct hydroxylation reactions with heterogeneous catalysts (titanium silicalite) and so on.

Many important developments are very confidential and in the literature there is not much available, very concrete information about many new processes for the transformation of natural



$CH_2{=}CH{-}C({=}CH_2){-}CH_2{-}CH_2{-}CH{=}C(CH_3)_2$

Myrcene
MW = 136
bp = 165 °C

Figure 17.14 Structure of myrcene

renewable resources into polyols. For example Envirofoam Chemicals developed an important process for the synthesis of polyols based on natural oils, by hydrolysis and breakdown of the natural oil to aliphatic hydrocarbon polyols and creation of short chain aromatic amines [1]. Other processes were developed by Polyol International Marketing Ltd., [1].

A lot of research and development in this area was made in Malaysia and in Latin America (Peru, Venezuela, Brazil, Mexico), both big producers of vegetable oils and natural products [75].

Soy Oil Systems successfully developed new polyols based on soybean oil oxidation (oxygen blown oils). Many other companies and research centres are involved in serious research on the valorification of natural renewable resources by transforming them into polyols and into PU. Very important research on unsaturated vegetable oil, chemical transformation into polyols for PU were developed in Pittsburg State University, Kansas (under Professor Zoran Petrović), Henkel and Cognis (Sovermol polyols), Unichema (dimer acids and dimer diols etc.), Bayer, Cargill and other companies.

Fabrication of polyols for PU from renewable resources is a very promising and economic way for the future. By contrast with the petrochemical resources, the availability of such kind of renewable natural raw materials is practically unlimited [1, 5].

References

1. D. Reed, *Urethanes Technology,* 1997, **14**, 2, 20.
2. A. Heidbreder, R. Höfer, R. Grützmacher, A. Westfechtel and C.W. Blewet, *Lipid-Fett*, 1999, **101**, 11, 418.
3. R. Höfer, P. Grützmacher and A. Westfechtel, *The Journal of Coatings Technology,* 1997, **69**, 869, 65.
4. G. Dieckelmann and H.J. Heinz, *The Basics of Industrial Oleochemistry*, Verlag Peter Pomp, Bottrop, Germany, 1988.
5. W. Hinz, P. Horn and H. Larbig in *Proceedings of the SPI Annual Technical/ Marketing Conference*, *Polyurethanes 95*, Chicago, IL, USA, 1995, p.230.
6. *Kirk-Othmer Encyclopedia of Chemical Technology*, Eds., H.F. Mark, M. Grayson and D. Eckroth, Third Edition, 1979, Volume 1, Wiley, New York, NY, USA, p.644-678.

7. P.M. Dreyfuss and M.P. Dreyfuss in *Encyclopedia of Polymer Science and Technology*, Ed., H.F. Mark, John Wiley & Sons, New York, NY, USA, 1970, Volume 13, p.670-691.

8. K.C. Frisch and J.E. Kresta in *Sucrochemistry*, Ed., J.L. Hickson, ACS Symposium Series No.41, American Chemical Society, Washington, DC, USA, 1976.

9. J.J. Cimerol and S. Fuzesi, *Journal of Elastomers and Plastics*, 1981, **13**, 4, 224.

10. F.H. Otey, B.L. Zagoren and C.L. Mehltretter, *Industrial & Engineering Chemistry, Product Research and Development*, 1963, **2**, 4, 256.

11. F.H. Otey, B.L. Zagoren, F.L. Bennett and C.L. Mehltretter, *Industrial & Engineering Chemistry, Product Research and Development*, 1965, **4**, 4, 224.

12. R.H. Leitheiser, C.N. Impola, R.J. Reid and F.H. Otey, *Industrial & Engineering Chemistry, Product Research and Development*, 1966, **5**, 3, 276.

13. F. Stoenescu, M. Ionescu, V. Dumitriu and I. Mihalache, *Materiale Plastice,* 1979, **16, 1,** 4.

14. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai, *Advances in Urethane Science & Technology,* Volume 14, Wiley, New York, NY, USA, 1998, p.151.

15. *Oxidative Coupling of Phenols*, Eds., W.I. Taylor and A.R. Battersby, Marcel Dekker, New York, NY, USA, 1989.

16. V. Erä, P. Jääskelainen and K. Ukkonen, *Angewandte Makromolekulare Chemie*, 1980, **88**, 79.

17. A. Lehtinen, V. Erä, T. Mustonen and E. Anttalainen, *Die Makromoleculare Chemie, Rapid Communications,* 1980, **1**, 8, 499.

18. V. Era and P. Jääskelainen, *Journal of American Oil Chemists Society*, 1981, **57**, 1, 201.

19. I.A. Pearl, *Annual Review of Lignin Chemistry*, Institute of Paper Chemistry, Appleton, WA, USA, 1970.

20. M. Ionescu, unpublished work.

21. F.H. Otey, F.L. Bennett, B.L. Zagoren and C.L. Mehltretter, *Industrial & Engineering Chemistry, Product Research and Development*, 1965, **4**, 4, 228.

22. F.H. Otey, R.P. Westhoff and C.L. Mehltretter, *Journal of Cellular Plastics*, 1972, 8, 3, 156.

23. E.N. Frankel and F.L. Thomas, *Journal of American Oil Chemists Society*, 1972, **49**, 10.

24. *Chemical Engineering*, 1995, **102**, 5, 21.

25. K.S. Chian, L.H. Gan and K.M. Chow in *Proceedings of Antec 97*, Toronto, Canada, 1997, Volume II, p.1996.

26. K.S. Chian and L.H. Gan, *Journal of Applied Polymer Science*, 1998, **68**, 3, 509.

27. Z.S. Petrović, A. Zlatanić, C.C. Lava and S. Sinadinovic-Fiser, *European Journal of Lipid Science and Technology,* 2002, **104**, 5, 293.

28. M. Janković and Z.S. Petrović, *Journal of the American Oil Chemists Society*, 2001, **78**, 7, 725.

29. T. Heinemann, H.J. Scholl and R. Welte, *Proceedings of Polyurethanes EXPO'96 Conference*, Las Vegas, NV, USA, 1996, p.320.

30. *Kirk-Othmer Encyclopedia of Chemical Technology*, Eds., H.F. Mark, M. Grayson and D. Eckroth, Third Edition, 1979, Volume 5, John Wiley & Sons, New York, NY, USA, p.1-15.

31. A. Guo, Y. Cho and Z.S. Petrović, *Journal of Polymer Science: Polymer Chemistry Edition*, 2000, **38**, 21, 3900.

32. Z.S. Petrović, A. Guo, I. Javni and W. Zhang, *Proceedings of the API Polyurethanes EXPO 2000*, Boston, MA, USA, 2000, p.323.

33. A. Guo, I. Javni and Z.S. Petrović, *Journal of Applied Polymer Science*, 2000, **77**, 2, 467.

34. Z.S. Petrović, A. Guo and I. Javni, inventors; Pittsburg State University, assignee; US 6,107,433, 2000.

35. P. Daute, J. Klein, H. Kluth and R. Grützmacher, inventors; Henkel KGAA, P. Daute, J. Klein, H. Kluth and R. Grützmacher, assignees; WO 9531493, 1995.

36. V.D. Athawale and S.L. Kolekar, *Journal of Applied Polymer Science*, 2000, **75**, 6, 825.

37. V.D. Athawale, P.S. Pillay and S.L. Kolekar, *European Coatings Journal*, 2001, **1-2**, 18.

38. Z.S. Petrović and D.J. Fajnik, *Journal of Applied Polymer Science*, 1984, **29**, 4, 1031.

39. D. Chaser and M.J. Hughes, inventors; Noveon IP Holdings Corporation (USA) assignee; WO 0329182, 2003.

40. *Urethanes Technology*, 1986, **3**, 4, 16.

41. N.B. Tran, J. Vialle and Q.T. Pham, *Polymer,* 1997, **38**, 10, 2467.

42. *Urethanes Technology*, 1997, **14**, 2, 21.

43. N.B. Tran and Q.T. Pham, *Polymer*, 1997, **38**, 13, 3307.

44. I. Javni and Z. Petrović in *Proceedings of Antec 97*, Toronto, Canada, 1997, Volume I, p.791.

45. I. Javni, Z.S. Petrović, A. Guo and R. Fuller, *Journal of Applied Polymer Science,* 2000, **77**, 8, 1723.

46. R. Höfer, P. Daute, R. Grützmacher and A. Westfechtel, *Informations Chimies,* 1994, **362**, 95.

47. S.A. Baser and D.V. Khakhar, *Cellular Polymers*, 1993, **12**, 5, 390.

48. J.Y. Jadhav*, International Journal of Polymeric Materials,* 1986, **11**, 3, 151.

49. M. Ionescu, S. Mihai, E. Stepan, C. Roibu and V. Preoteasa in *Proceedings of the APC Polyurethanes 2001 Conference*, Columbus, OH, USA, 2001, p.607.

50. R.T. Wojcik, *Polyurethane Coatings from Raw Materials to End Products*, Technomic Publishing Company Inc., Lancaster, PA, USA, Chapter 2.

51. J-P. Boiteux, B. Brancq, N. Lecocu and F. Loussayre, inventors; Societe d'Exploitation de Produits pour les Industries Chimiques, assignee; US 5,108,661, 1992.

52. No inventors, American Cyanamid Co., assignee; GB 650940, 1951.

53. G.C. Tesora, inventor; Onix Oil & Chemical Company, assignee; US 2,844,609, 1958.

54. V. Lambertl and G.J. McCrimlisk, inventors; Lever Brothers Company, assignee; US 3,107,258, 1963.

55. H. Kroll and H. Nadeau, *Journal of the American Oil Chemists Society*, 1956, **34,** 323.

56. R.A. Reck, *Journal of the American Oil Chemists Society*, 1979, **56**, 796.

57. L.W.Brunette in *Nonionic Surfactants*, Volume I, Ed., M.J. Schick, Marcel Dekker Inc., New York, NY, USA, 1967, p.395-403.

58. V. Mannari, Y. Guo, J. Hardeski and J. Maddingill, Jr., in *Proceedings of the 94th American Oil Chemists Society Annual Meeting*, Kansas City, MI, USA, 2003, p.76.

59. Z. Petrović, I. Javni, A. Guo and W. Zhang, inventors; Pittsburg State University, assignee; US 6,433,121, 2002.

60. Z. Petrović, A. Guo and I. Javni, inventors; Pittsburg State University, assignee; US 6,573,354, 2003.

61. Z. Petrović, I. Javni, A. Guo and W. Zhang, inventors; Pittsburg State University, assignee; US 6,686,435, 2004.

62. Z. Petrović, W. Zhang, I. Javni and X.A. Guo, inventors; No assignee; US 2003090016, 2003.

63. C. Döbler, G.M. Mehltretter, U. Sundermeier and M. Beller, *Journal of the American Chemical Society*, 2000, **122**, 42, 10289.

64. B.M. Choudary, N.S. Chowdari, M.L. Kantam and K.V. Raghavan, *Journal of the American Chemical Society*, 2001, **123,** 37, 9220.

65. S. Kobayashi, M. Endo and S. Nagayama, *Journal of the American Chemical Society,* 1999, **121,** 48, 11229.

66. S. Warwel, M.R. Klaas and M. Sojka, inventors; Solvay Interox GmbH, assignee; US 5,344,946, 1994.

67. T. Mukaiyama and T. Yamada, *Bulletin of the Chemical Society of Japan*, 1995, **68**, 1, 17-35.

68. M. Clerici and I. Patrisia in *Green Chemistry: Designing Chemistry for the Environment*, ACS Symposium Series, No.626, ACS, Washington, DC, USA, 1996, p.59-68.

69. A. Bhaumik and T. Tatsumi, *Journal of Catalysis*, 1998, **176**, 2, 305.

70. P. Kandanarachchi, A. Guo and Z. Petrović, *Journal of Molecular Catalysis A: Chemical*, 2002, **184**, 1-2, 65.

71. P. Kandanarachchi, A. Guo, D. Demydov and Z. Petrović, *Journal of the American Oil Chemists Society*, 2002, **79**, 12, 1221.

72. A. Zlatanić, Z.S. Petrović and K. Dusek, *Biomacromolecules*, 2002, **3**, 5, 1048.

73. *Dimerised Fatty Acids Technology for Use in Polyurethanes*, UNICHEMA, Chicago, IL, USA, 2000.

74. P. Daute, R. Grutzmacher, R. Höfer and A. Wastfechtel, *Fat Science and Technology,* 1993, **3**, 91.

75. N. Ramirez de Arellano-Abuto, A. Cohen-Barki and M.J. Cruz-Gomez, inventors; Resinas Y Materiales SA De CV, assignee, US 6,548,609, 2003.

76. *http://finance.indiamart.com/markets/commodity/castor-oil.html.*

18

Flame Retardant Polyols

Polyurethanes (PU) are polymers which, in a fire, burn totally. During the not very long history of PU, intensive research efforts were made to produce fire resistant PU.

Unfortunately, many human lives were lost and many valuable buildings, constructions and materials were totally destroyed due to the high combustibility of polymers, PU included.

The development of fire resistant polymers is dictated by the necessity for the safety, security and protection characteristic of modern life. The fire retardancy of polymers not only has a *scientific* implication, but also *social* (protection of human lives), *political* (obligation of utilisation of flame retardant polymers in specific fields which present danger for human lives in the accidental fire such as: construction, furniture, automotive, and so on), *economic* (protection of buldings and other valuable materials), *military* (protection of military equipment) and *ecological* implications (limitation of toxic and corrosive gases evolved during burning, limitation of the level of smoke generation during burning).

Fire resistant PU are obtained by the addition or by introduction into the PU structure of special compounds, called flame retardants. The flame retardants are organic compounds containing halogens (chlorine, bromine) and phosphorus. Compounds of antimony (Sb) or boron [1-13] are rarely used. Sometimes inorganic compounds are used as flame retardants for PU, such as, hydrated alumina ($Al_2O_{3*}nH_2O$), Sb_2O_3 or ammonium polyphosphate [1-3, 14].

Halogenated organic compounds act in the flame, by blocking the chain reactions which are characteristic for the flame [1, 6]. Thus, any organic compound containing chlorine or bromine is decomposed into the corresponding hydracids (HCl or HBr). These acids react with the most reactive radical existing in the flame, the hydroxyl radical, HO*:

$$HO* + HCl = H_2O + Cl*$$

The radical Cl* has a much lower energy and reacts with the organic substrate:

$$Cl* + RH = HCl + R*$$

The chain reactions from the flame are stopped and a phenomenon called self-extinguishing occurs which is characterised by the self-extinguishing time, a measure of flame retardant efficiency.

Organic phosphorus compounds, irrespective of their structure, decompose to polyphosphoric and methaphosphoric acids, which retain the acidity at higher temperatures and catalyse the rapid decomposition of the organic substrate to carbon. A carbonaceous layer containing phosphorus is formed, which is very difficult to burn, which is a true protective layer for the rest of material and the process of burning is stopped [1, 2, 6-8, 11, 15].

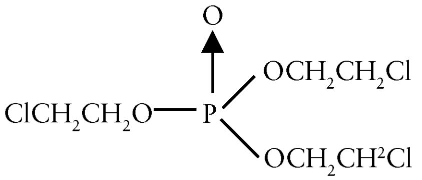
It is clear that halogens act in the flame and phosphorus compounds in the polymeric substrate. Having both groups of elements (halogens and phosphorus), in the same structure leads to a synergism. The significance of synergism is that a phosphorus - halogen combination has the same efficiency of fire retardancy at the lower concentration of each element, compared to the efficiency of a PU which is flame retarded independently with each element [1, 3, 11, 15].

The presence of nitrogen in the structure of a flame retardant is very beneficial because nitrogen is an element which burns with difficulty [4-6, 14, 16].

There are two types of flame retardant - additive flame retardants and reactive flame retardants [1, 4-6, 11].

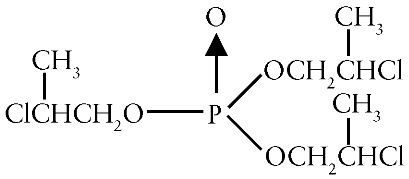
The additive type of flame retardants are compounds containing chlorine, bromine or phosphorus without reactive groups to get involved in PU chemistry (without -OH, -NH_2 or -NCO groups). These compounds are physically added to PU and are not part of the PU structure.

The most representative examples of additive flame retardants are: tris (2-chloroethyl) phosphate (TCEP) and tris (2-chloropropyl) phosphate (TCPP) and tris (2,3 dichloropropyl) phosphate (structures 18.1) [4]:



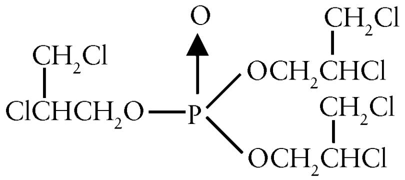
tris-(2-chloroethylphosphate)
TCEP

M = 283
P = 10.8%
Cl = 37.2%



tris-(2-chloroisopropylphosphate)
TCPP

M = 326
P = 9.5%
Cl = 32.5%

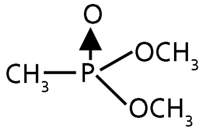


tris-(2,3 dichloropropylphosphate)

MW= 430.9
P = 7.19%
Cl = 49.37%

(18.1)

An important flame retardant additive is dimethyl methyl phosphonate (DMPP), a compound having a very high phosphorus content (**Figure 18.1**) [3, 17]:



P = 25%

Figure 18.1 Structure of DMPP

DMPP sometimes gives problems in PU formulations because it is not hydrolysis resistant and, as an immediate consequence, the acidity increases and the reactivity of the formulation decreases markedly. Unfortunately, the flame retardant additives mentioned previously, have a tendency to migrate and, in time, the flame retardancy is lost. For example, a rigid PU foam containing tris (2-chloroethyl) phosphate as an additive flame retardant, completely loses its flame retardancy after a year.

The reactive flame retardants are generally polyols containing halogens and/or phosphorus [1-11]. The presence of nitrogen in the structure of reactive flame retardants always improves the flame retardancy, as mentioned previously [1, 4, 14, 16].

These polyols called flame retardant polyols, have terminal hydroxyl groups, react with polyisocyanates in the process of PU synthesis and are chemically inserted in the PU structure. The reactive flame retardants being chemically linked in the PU chains assure a permanency of flame retardancy [5, 6, 11].

A good flame retardant must have some important characteristics [4, 5]:

a) To be economic;

b) Not to act as a plasticiser;

c) To assure a permanency of flame retardancy;

d) To have a low viscosity;

e) To be compatible with all the components used for PU fabrication;

f) To be hydrolytically resistant;

g) To produce when combusted a small amount of toxic gases and smoke;

h) Not to negatively affect the properties of PU.

In recent years there has been an effort to eliminate chlorine from all flame retardant compounds. Thus, there is a tendency to avoid the use of two of the most used additive flame retardants for fabrication of fire resistant PU: TCEP and TCPP. This ban is dictated by the toxic and corrosive gases formed during combustion and from ecological point of view.

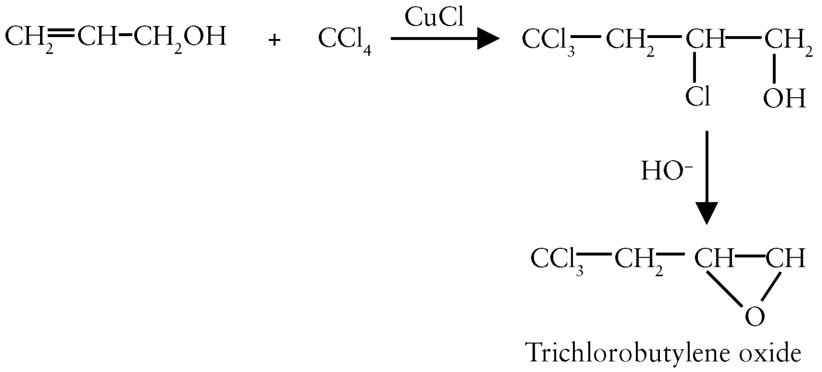
Chlorine is the less effective element for flame retardancy, the following relative order concerning the fireproofing efficiency being: Cl < Br < P.

A flame retarded rigid PU foam needs around 20-25% chlorine or 5-6% bromine or 1.5-2% phosphorus [1, 2, 4, 11]. During the history of PU many reactive flame retardants were developed, but only a few are used effectively in practice.

18.1 Chlorine and Bromine Containing Polyols

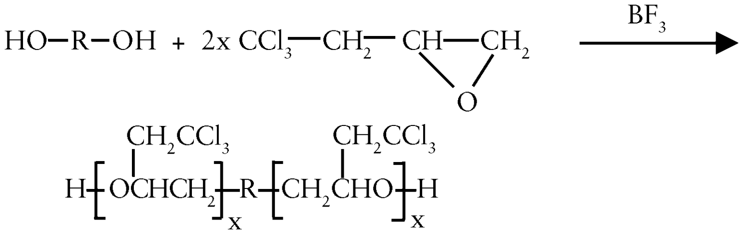
The representative raw materials to produce chlorine polyols are: epichlorohydrin, chlorendic anhydride and trichlorobutylene oxide (TCBO) (**Figure 18.2**).

(TCBO), a monomer containing a high percentage of chlorine, is obtained from allyl alcohol and carbon tetrachloride (reaction 18.2) [18-23]:

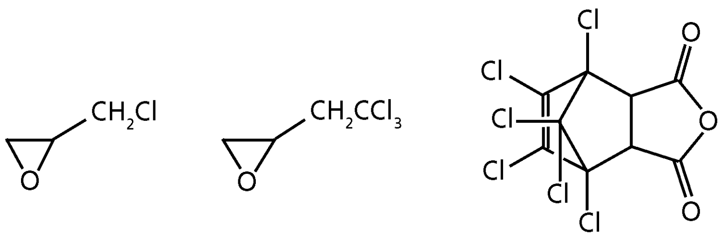


(18.2)

TCBO is reacted with various polyols (such as carbohydrates), in the presence of cationic catalysts (for example BF_3), with the formation of very viscous and high chlorine content polyols (18.3) [14, 22-24].



(18.3)

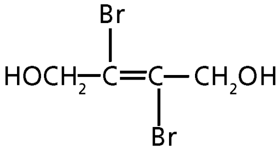


Epichlorohydrin Trichlorobutylene oxide Chlorendic anhydride

Figure 18.2 Structures of raw materials to make chlorine polyols

The extremely high viscosities of these polyols lead to difficulties if they are to be used on conventional foaming equipment. TCBO based polyols are not used and are not produced industrially at this moment [3].

Bromine containing polyols are very effective, reactive flame retardants. One of the most representative bromine polyols used in rigid and flexible flame retardant PU foams is 2,3 dibromobutene diol (**Figure 18.3**) [25]:

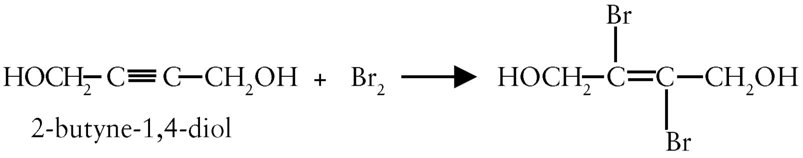


$HOCH_2-C(Br)=C(Br)-CH_2OH$

MW= 245.9
OH# = 456 mg KOH/g
Br = 65%

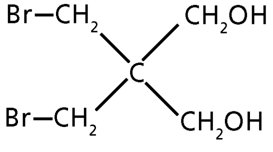
Figure 18.3 Structure of 2,3 dibromobutene diol

2,3 Dibromobutene diol is obtained by the addition of bromine to the triple bond of 2-butyne-1,4- diol (resulting from the addition of formaldehyde to acetylene), as shown in the reaction 18.4.



$$HOCH_2-C\equiv C-CH_2OH + Br_2 \longrightarrow HOCH_2-C(Br)=C(Br)-CH_2OH \quad (18.4)$$

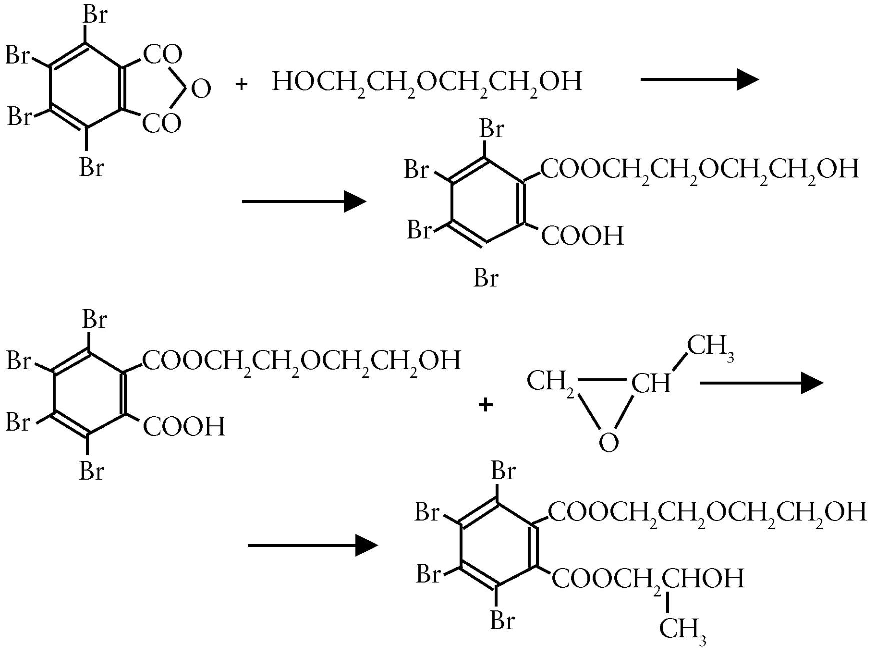
Dibromo neopentylglycol is another low molecular weight reactive flame retardant [26, 27], which unfortunately has labile aliphatic -C-Br bonds (**Figure 18.4**).



MW= 259.9
OH# = 431.7 mg KOH/g
Br = 61.1%

Figure 18.4 Structure of dibromo neopentylglycol

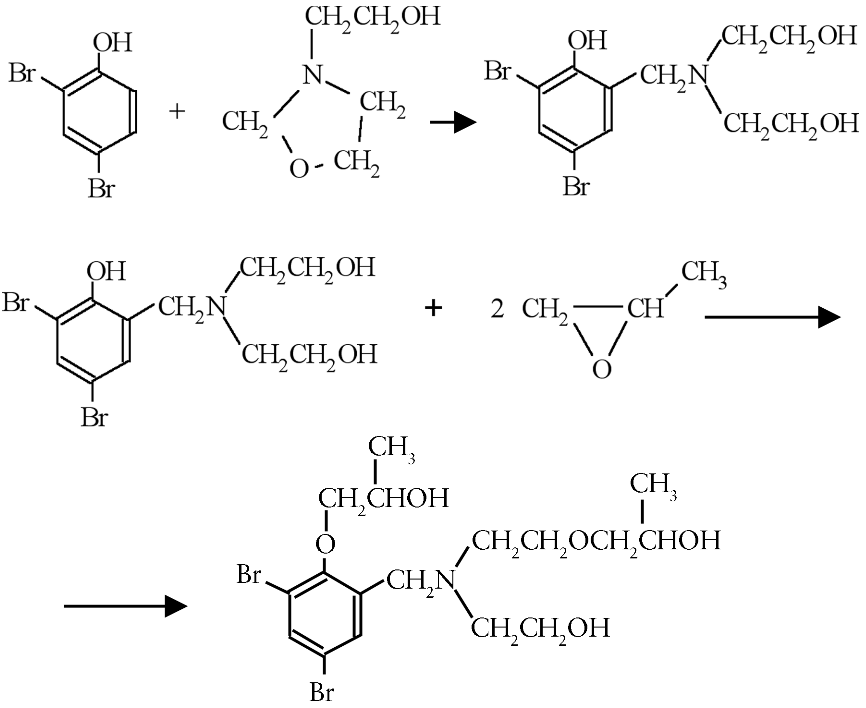
The bromine linked to a double bond or linked to an aromatic nucleus are much more stable structures (not easily decomposed to HBr as dibromo neopentylglycol, a saturated aliphatic bromine compound). Thus, a very successful bromine containing diol, produced industrially [4, 24], is based on tetrabromophthalic anhydride. Tetrabromophthalic anhydride is reacted first with diethylene glycol and the resulting half ester is reacted with propylene oxide (PO) (reaction 18.5) [3].



(18.5)

The bromine diol (18.5), in combination with sucrose polyols gives rigid PU foams with excellent fire retardancy properties [3, 24].

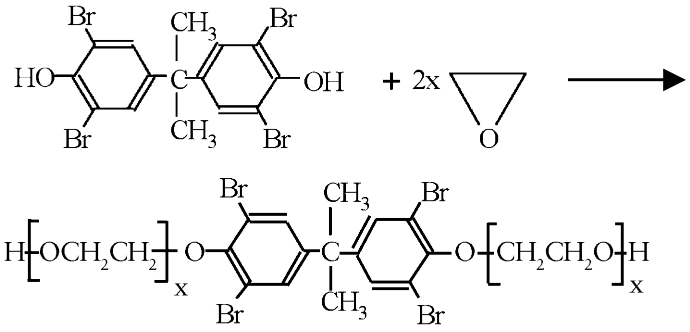
A very interesting bromine aromatic polyol is obtained by the Mannich type reaction between 2,4 dibromophenol (or 2,6 dibromophenol) with diethanolamine and formaldehyde [28] or better still with oxazolidine [29], followed by the propoxylation of the resulting Mannich base with 2-3 mols of PO [28, 29] (reactions 18.6).



(18.6)

The resulting bromine polyol has a bromine content of around 33-38%, an hydroxyl number of 360-390 mg KOH/g and a viscosity in the range 16,000-25,000 mPa-s at 25 °C.

Tetrabromobisphenol A is a very interesting bromine containing raw material produced industrially. By the ethoxylation of tetrabromobisphenol A with 8-9 mols of ethylene oxide (EO), an interesting aromatic bromine diol is obtained which is useful as a reactive flame retardant for urethane - isocyanuric rigid foams (18.7).



(18.7)

18.2 Phosphorus Polyols

Phosphorus polyols are the most important reactive flame retardants. A lot of research was done in the area of phosphorus polyols and after considering their structures, they were divided into the following groups:

a) Esters of *ortho*-phosphoric acid;

b) Esters of phosphorus acid;

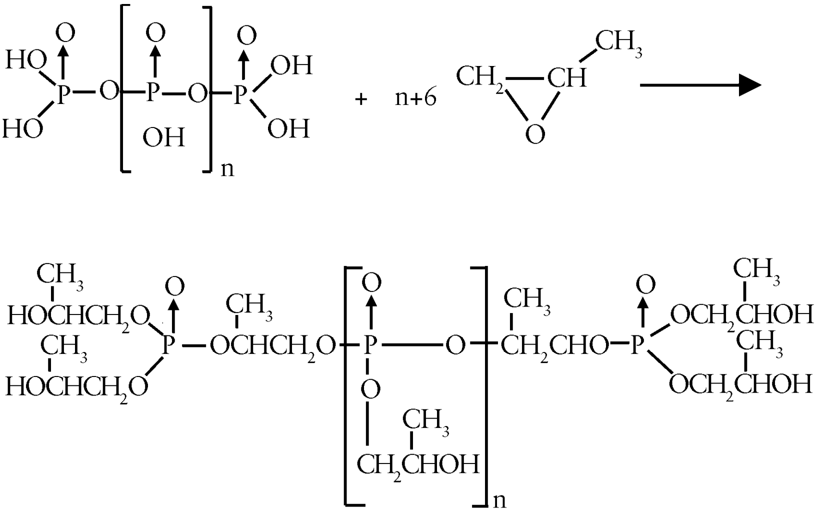
c) Phosphonate polyols;

d) Phosphine oxide polyols;

e) Phosphoramidic polyols.

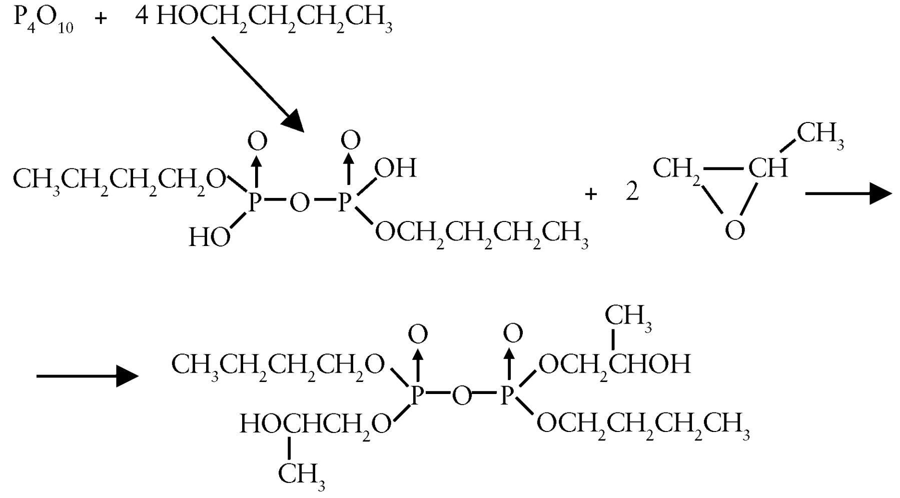
18.2.1 Esters of Ortho-Phosphoric Acid

Representative phosphorus polyols with *ortho*-phosphoric esteric structure are the products of a reaction of PO with polyphosphoric acids [4, 5, 30, 31] (reaction 18.8) or the products of PO addition to the condensates of phosphorus pentoxide with *n*-butanol (or other alcohols) (reaction 18.9) [5].



(18.8)

The phosphorus polyol (18.8) has an hydroxyl number of 300-310 mg KOH/g, a phosphorus content of 9.5-10% and a viscosity of 1,600-3,000 mPa-s at 5 °C. Of course due to some etherification reactions the number of PO units/hydroxyl group are higher than one, being in the range of 1-2 PO units.



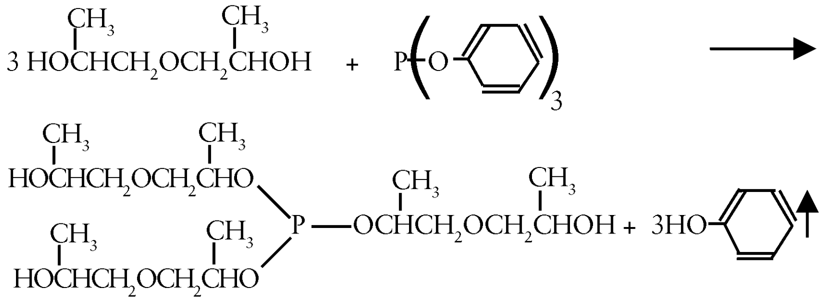
(18.9)

The resulting phosphorus diol has an hydroxyl number of 210-215 mg KOH/g and a phosphorus content of 11.2% [5].

These phosphorus polyols with *ortho*-phosphoric ester structure are not used at the moment because, the formulated polyols containing water as blowing agent are not resistant to hydrolysis. Due to hydrolysis, acidic groups appear which decrease markedly the reactivity of the formulated polyol. The resulting acidity inhibits the activity of the tertiary amine used as a catalyst in the foaming process.

18.2.2 Esters of Phosphorus Acid

The esters of phosphorus acid are obtained by condensation of triphenylphosphites or trialkylphosphites with various polyols, such as dipropylene glycol (reaction 18.10) [5, 32, 33].



tris(dipropylene glycol) phosphite

(18.10)

The resulting *tris*(dipropylene glycol) phosphite has an hydroxyl number of 395 mg KOH/g and a phosphorus content of 7.2% [5, 31, 33].

Unfortunately, trialkyl phosphites are extremely susceptible to hydrolysis, being more rapidly hydrolysed than the *ortho*-phosphoric esters. Due to their susceptibility to hydrolysis, the phosphorus polyols with phosphite ester structure are not used at the moment.

18.2.3 Phosphonate Polyols

The phosphonate polyols are characterised by the presence of -P-C- bonds which are very resistant to hydrolysis. The phosphonate polyols are one of the most important groups of reactive flame retardants - they are produced industrially and are used in many formulations, especially for rigid PU foams. The phosphonate polyols are esters of phosphonic acids (**Figure 18.5**) [1, 4-6, 11, 30, 34].

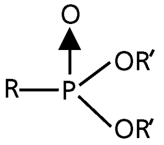
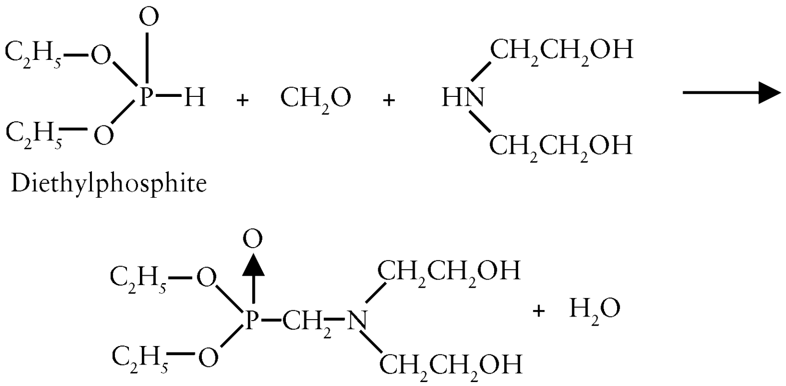


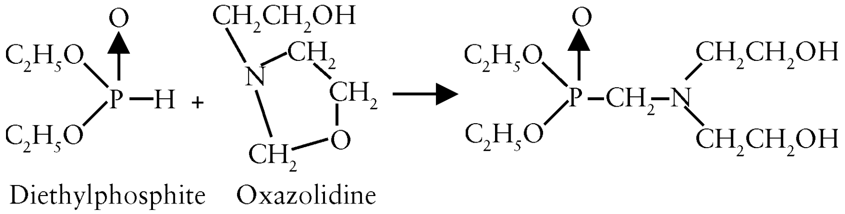
Figure 18.5 Structure of phosphonic acid esters

The best known phosphorus polyol of significant commercial importance is diethyl-*N*,*N*-bis (2-hydroxyethyl) aminomethyl phosphonate, which is obtained by a Mannich reaction between diethylphosphite, formaldehyde and diethanolamine (reaction 18.11) [5, 34]:



Diethyl-*N*,*N*-bis(2-hydroxyethyl) aminomethyl phosphonate (18.11)

The same structure is easy to obtain by reacting diethylphosphite with an oxazolidine [16, 35] (reaction 18.12):



(18.12)

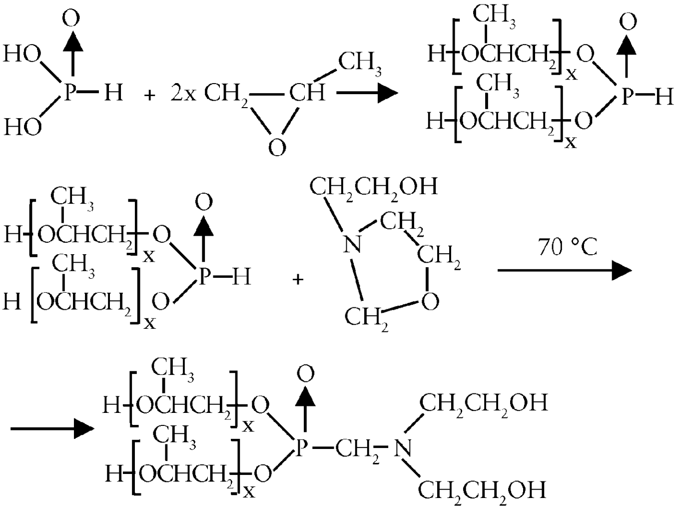
The characteristics of phosphonate polyol (18.12) are shown in **Table 18.1** [5].

Table 18.1 Characteristics of phosphonate polyols

Molecular weight	249-255 daltons
Hydroxyl number	440-450 mg KOH/g
Functionality	2 OH groups/mol
Phosphorus	12.2-12.6%
Nitrogen	5.2-5.8%
Density, at 25 °C	1.155-1.165 g/cm^3
Viscosity, at 25 °C	190-210 mPa-s
Acidity	Maximum 2 mg KOH/g

This phosphonate polyol is very resistant to hydrolysis and has in its structure both phosphorus and nitrogen. A synergism between phosphorus - nitrogen has previously been mentioned in this chapter [1, 4, 5, 11].

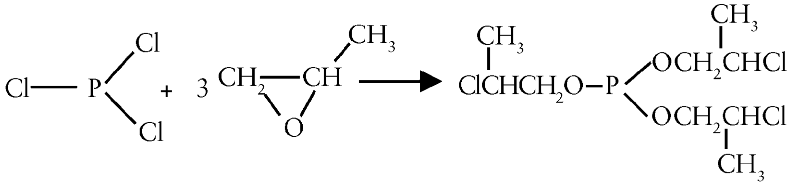
Phosphorus acid is used to generate, by direct alkoxylation with PO, a bis (hydroxypropyl) phosphite. The resulting bis (hydroxypropyl) phosphite is reacted with oxazolidine, under similar conditions to reaction 18.12 and a tetrafunctional phosphonate polyol is obtained (reaction 18.13) [16]:



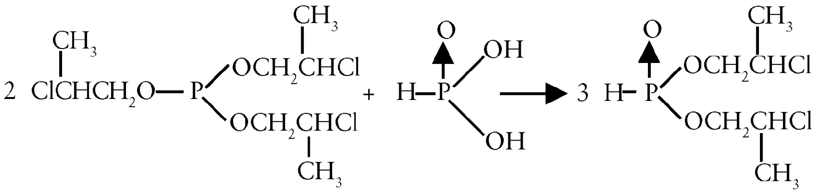
(18.13)

Unfortunately, the phosphorus content of phosphonate polyol in reaction 18.13 is lower (around 7-7.5%), but being a tetrafunctional polyol gives rigid PU foams with excellent physico-mechanical properties.

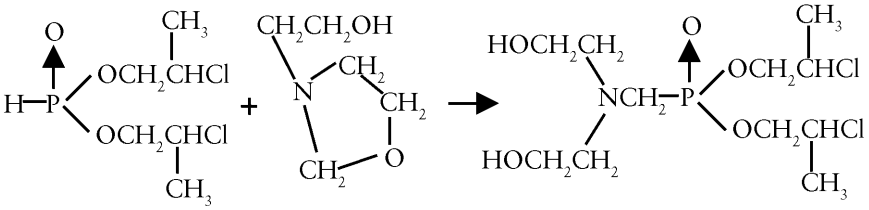
A variant of the Mannich reaction using an equilibration between phosphorus acid and a trialkyl phosphite was developed [36]. The trialkyl phosphite was synthesised *in situ* by the reaction of phosphorus trichloride with PO, with the formation of tris (2-chloropropyl) phosphite (reaction 18.14). By equilibration of phosphorus acid with tris (2-chloropropyl) phosphite, bis (2-chloropropyl) phosphite (reaction 18.15) is formed which, by reaction with oxazolidine, gives an interesting phosphonate polyol containing phosphorus, chlorine and nitrogen (reaction 18.16):



(18.14)



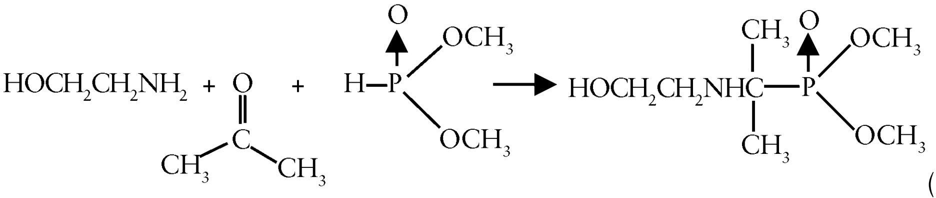
(18.15)



(18.16)

The phosphonate polyol (18.16) has a molecular weight of 350-355 daltons, an hydroxyl number of 310-320 mg KOH/g, a phosphorus content of 8.2-8.8%, a nitrogen content of 3.9-3.98% and a chlorine content of 20-20.1%.

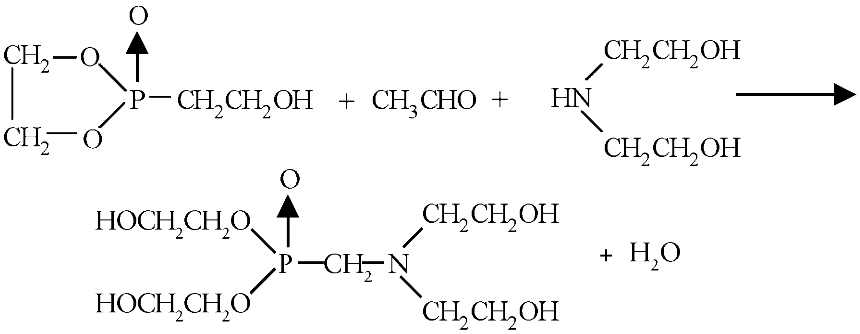
The scientific literature mentions some variants of the phosphonate polyols synthesis by Mannich reaction. For example, by reacting of dimethylphosphite with acetone and monoethanolamine a higher phosphorus content (15%) phosphonate polyol is formed (reaction 18.17) [37]:



(18.17)

The resulting phosphonate polyol (18.17) is a bifunctional polyol having one hydroxyl group and one secondary amino group.

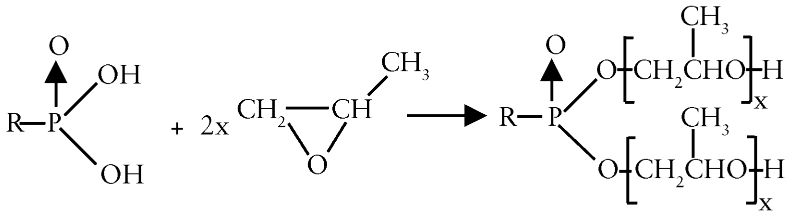
A very interesting variant of the Mannich reaction using reactive cyclic phosphites as raw materials was developed (reaction 18.18) [38]:



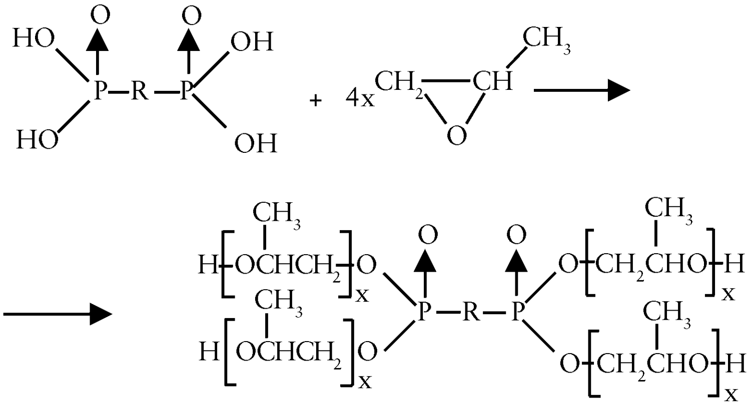
(18.18)

The resulting phosphonate polyol (18.18) has a functionality of 4 OH groups per mol, an hydroxyl number of around 690-695 mg KOH/g, a phosphorus content of 9.6% and a nitrogen content of 5.24% [38].

Phosphonate polyols are obtained by the direct alkoxylation of phosphonic acids with PO, at moderate temperatures (70-90 °C) [5, 16] (reactions 18.19 and 18.20).

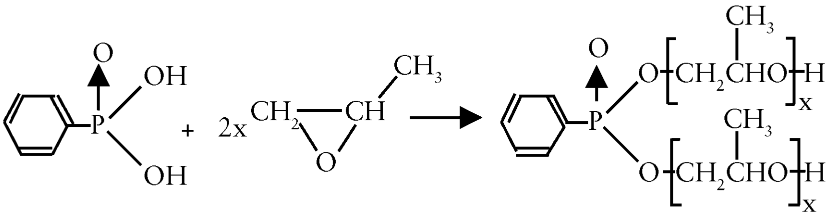


(18.19)



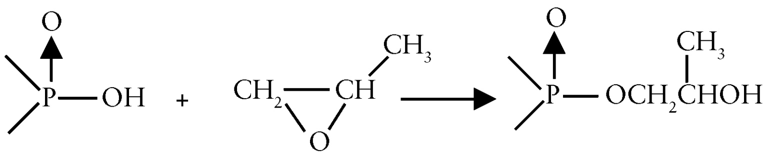
(18.20)

A representative phosphonate polyol is obtained by the propoxylation of phenylphosphonic acid (reaction 18.21) [16]:

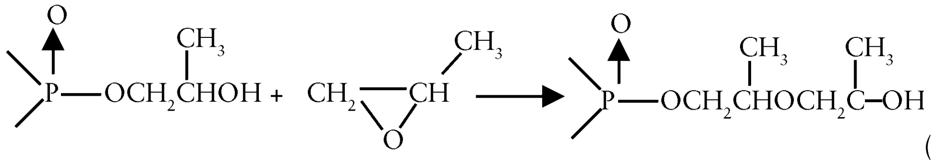


(18.21)

In all the reactions involving propoxylation of acidic groups such as -P-OH, two simultaneous reactions take place, i.e., esterification (reaction 18.21) and etherification (reaction 18.22) reactions:



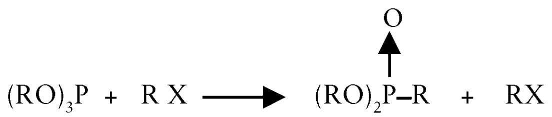
(18.22)



(18.23)

The etherification reaction (18.23) shows that the number of PO units per hydroxyl group is higher than one (the value of x is in the range 1 < x < 2). This reaction leads to the decrease of the hydroxyl number and of the phosphorus content.

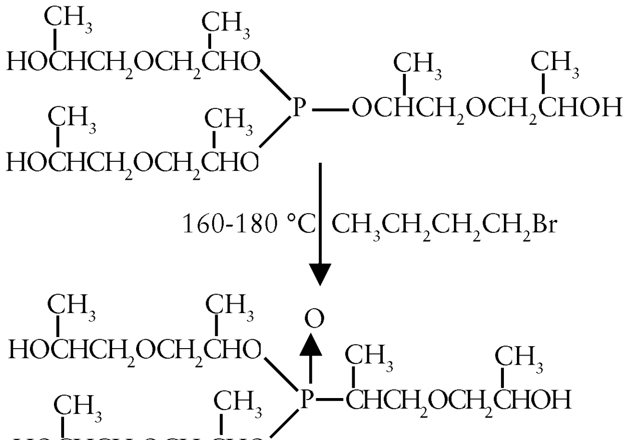
The Arbuzov reaction is an interesting way of transforming a trialkylphosphite in a trialkylphosphonate by reaction with a halogenated compound (general reaction 18.24) [4, 5, 39]:



$$(RO)_3P + RX \longrightarrow (RO)_2\overset{\overset{O}{\uparrow}}{P}\text{–}R + RX$$

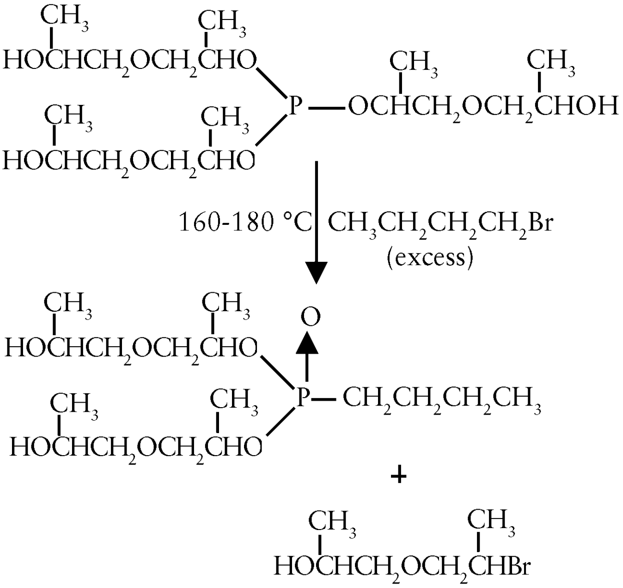
(18.24)

If the group R is a hydroxyalkyl group - phosphonate polyols are obtained. One example is the transformation of tris (dipropylene glycol) phosphite in phosphonate polyol, at 160-180 °C, by the following reactions with butyl bromide [5] (reaction 18.25 with a catalytic quantity of butylbromide).



(18.25)

By using an excess of butyl bromide, the product of the Arbuzov reaction is a phosphonate diol and a bromohydrin (reaction 18.26):



(18.26)

There are several possibilities for phosphonate polyol synthesis by Mannich reactions, Arbuzov reactions and by alkoxylation of phosphonic acids. Phosphonate polyols proved to be very efficient flame retardants in practice. An important quality of these phosphorus polyols is the stability over time of formulated polyols containing phosphonate and water as reactive blowing agent, without a significant loss of their reactivity.

18.2.4 Phosphine Oxide Polyols

Phosphine oxide has three hydrolysis resistant -P-C- bonds. A phosphine oxide polyol, extremely resistant to hydrolysis (**Figure 18.6**), was used for a short period of time but due to economic reasons the production was stopped [40-43].

Due to the high cost of the raw materials and of the final product, the manufacture of this phosphine oxide polyol was stopped [42].

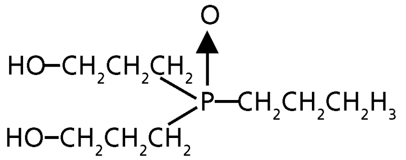


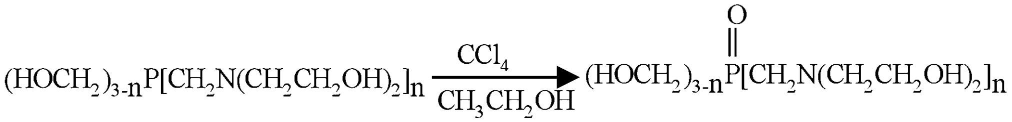
Figure 18.6 Structure of phosphine oxide polyol

Very interesting reactive flame retardants were used successfully in the fabrication of flame retardant rigid PU foams by Solvay under the name of Ixol polyols. These polyols are triols based on epichlorohydrin and brominated unsaturated diol. Ixol polyols have chlorine, bromine and phosphorus in each structure [3, 44, 45].

Very interesting new reactive flame retardants were developed by Borissov and Jedlinski [12, 43, 45-50]. A new phosphine oxide polyol is based on tetrakis (hydroxymethyl) phosphonium chloride as 80% aqueous solution. The reactions involved in the synthesis of this phosphine oxide polyol, bis(hydroxymethyl)-*N*,*N*-bis(2-hydroxyethyl) aminomethylphosphine oxide [45], are presented below:

$$(HOCH_2)_4PCl + NaOH \longrightarrow (HOCH_2)_3P + CH_2O + NaCl + H_2O$$

$$(HOCH_2)_2P + nHN(CH_2CH_2OH)_2 \longrightarrow (HOCH_2)_{3-n}P[CH_2N(CH_2CH_2OH)_2]_n + H_2O$$

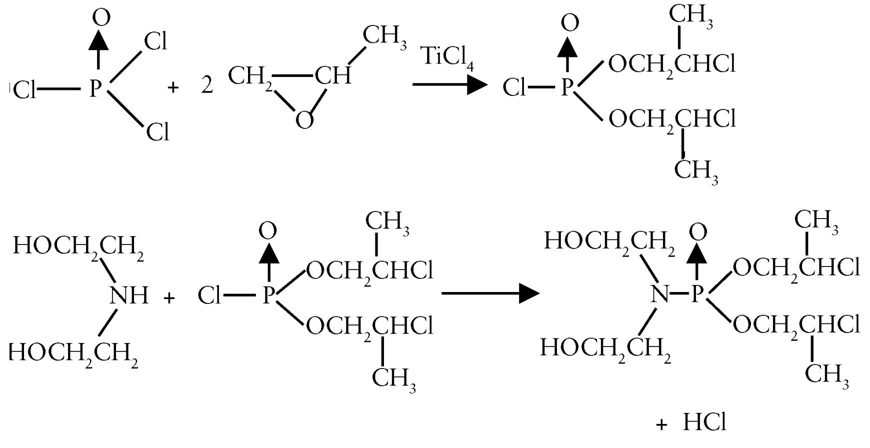


$$(HOCH_2)_{3-n}P[CH_2N(CH_2CH_2OH)_2]_n \xrightarrow[CH_3CH_2OH]{CCl_4} (HOCH_2)_{3-n}\overset{\overset{O}{\|}}{P}[CH_2N(CH_2CH_2OH)_2]_n$$

18.2.5 Phosphoramidic Polyols

An interesting structure of some phosphorus polyols used as reactive flame retardants is the phosphoramide.

An interesting polyol was produced by using phosphorus oxichloride, PO and diethanolamine as raw materials (reaction 18.27). First, one mol of phosphorus oxychloride is reacted with 2 mols of PO and the resulting product is reacted with diethanolamine, in the presence of an acid acceptor:

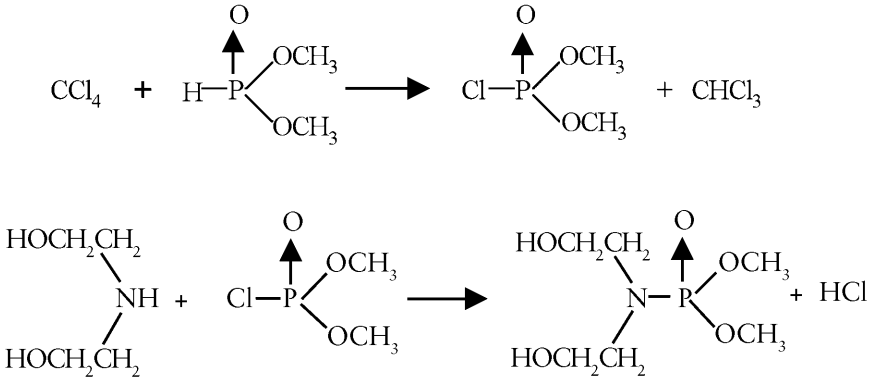


(18.27)

The polyol (18.27) has an hydroxyl number of 290-300 mg KOH/g, a phosphorus content of 8-8.1% and a nitrogen content of 3.65%.

Various substances are used as acid acceptors such as: PO (which is transformed in propylene chlorohydrin), Na_2CO_3, K_2CO_3, NaOH, KOH and so on [36].

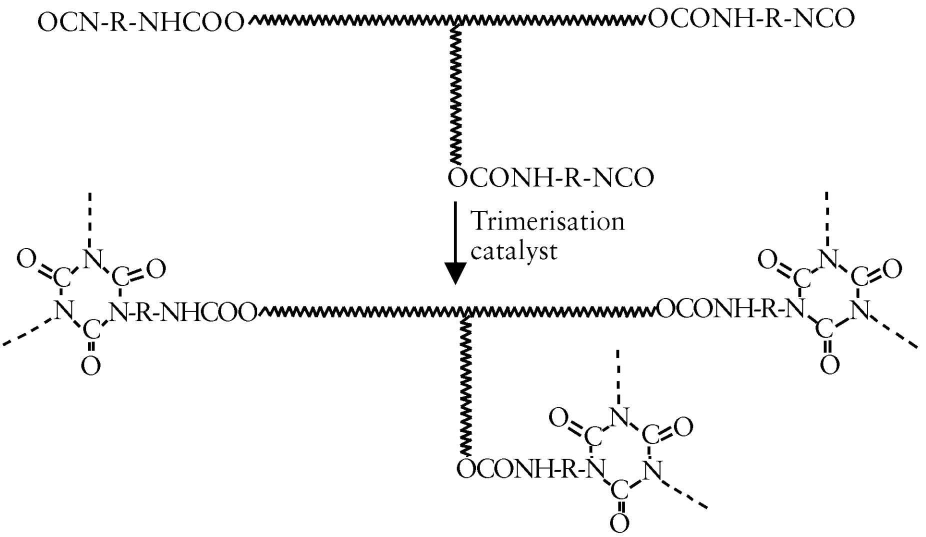
A variant for phosphoramide polyol synthesis by using dialkylphosphites and carbon tetrachloride as raw materials was developed (reaction 18.28).



(18.28)

The same substances mentioned before are used as acid acceptors. The phosphorus polyol shown in 18.28 has an hydroxyl number of 490-495 mg KOH/g, a phosphorus content of 13-13.6% and a nitrogen content of 6.1-6.2%. The acidity of all phosphorus polyols presented in Section 18.2 is a maximum of 2 mg KOH/g.

A method to improve the flame retardancy of rigid PU is to introduce into their structure highly thermostable structures (aromatic structures, thermostable heterocyclic rings such as isocyanuric, oxazolidone or imidic rings [1, 4, 5, 51, 52]). Aromatic polyester polyols and aromatic polyether polyols (Mannich polyols, novolak-based polyols, *ortho*-toluene diamine based polyols and so on) give a substantial improvement in the fire retardance of the resulting rigid PU foams. For some structures, the fire extinguishing properties are obtained in the absence of flame retardants, or the quantity of flame retardants needed is much lower than that needed for the rigid foams made with aliphatic polyols. This effect is due to the high char yield resulting from the burning process of the aromatic structures which is as a consequence of the very low ratio of H:C and to the presence of the rigid cyclic aromatic nuclei of the aromatic polyols [1, 4, 5, 11, 16, 51, 52]. A very high efficiency of flame retardancy is obtained by generation in the foaming process of very thermostable isocyanuric rings, by the trimerisation of an excess of -NCO groups. The resulting PU/polyisocyanuric foams (PIR) foams, having both urethane groups and isocyanuric rings, in combination with phosphorus compounds, and additive or reactive flame retardants, give a very high fireproofing efficiency (structure 18.29).



(18.29)

This chapter presents only general information concerning the synthesis of flame retardant polyols, polyols containing halogens and phosphorus. The scientific literature on this subject is very comprehensive [1-64], giving many possibilities for creating new compounds, but unfortunately, due the toxicity of some structures, their ecological problems, the toxicity of gases and the high smoke density resulting in the burning process, due to the very high prices of some reactive flame retardants, only a few of these structures will be produced industrially and then successfully commercialised.

References

1. W. Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, NY, USA, 1970.

2. C.J. Hilado, *Flammability Handbook for Plastics*, Technomic Publishers, Stamford, CT, USA, 1969.

3. D.J. Sparrow and D. Thorpe, in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals CRC Press, Boca Raton, FL, USA, 1989, p.219-221.

4. A.J. Papa, *Industrial & Engineering Chemistry, Product Research and Development,* 1970, **9**, 4, 478.

5. A.J. Papa, *Industrial & Engineering Chemistry, Product Research and Development,* 1972, **11**, 4, 379.

6. C.J. Hilado in *Polyurethane Technology*, Ed., P.F. Bruins, Interscience Publishers, New York, NY, USA, 1969, p.117.

7. J.H. Saunders and K.C. Frisch, *Polyurethanes: Chemistry and Technology*, Volume 1, Interscience, New York, NY, USA, 1962, p.106-121.

8. P. Thiery, *L'Ignifugation*, Dunod, Paris, France, 1967.

9. P. Thiery*, Plastiques Modernes et Elastomeres*, 1968, **20**, 8, 143.

10. C.P. Smith and H. Ulrich, inventors; The Upjohn Company, assignee; US 4,173,602, 1979.

11. J.K. Backus in *Urethane Science & Technology*, Volume 1, Eds., K.C. Frisch and S.I. Reegen, 1971, p.147.

12. K. Troev, K. Todorov and G. Borissov*, Journal of Applied Polymer Science,* 1984, **29**, 5, 1701.

13. K. Dorn, K. Frankenfeld, H-D. Nagerl, S. Schlarb and K. Sommer, inventors; Chemische Fabrik Budenheim Rudolph A Oetker Chemie, assignee; US 5,539,141, 1996.

14. W. Eberspach, inventor; Hoechst AG, assignee; US 5,096,961, 1992.

15. E.D.Weil in *Encyclopedia of Chemical Technology*, 3rd Edition,Volume 10, Eds., R.E. Kirk and D.E. Othmer, John Wily & Sons, New York, NY, USA, 1986, p.29.

16. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai, *Advances in Urethane Science & Technology,* Volume 14, Wiley, New York, NY, USA, 1998, p.151.

17. D.L. Buszard and R.J. Dellar, *Cellular Polymers*, 1985, **4**, 6, 431.

18. No inventors; Olin Mathieson Chemical Corporation, assignee; GB 1,211,109, 1970.

19. No inventors, Olin Mathieson Chemical Corporation, assignee; GB 1,341,903, 1973.

20. C.M.R. Davidson, inventor; Olin Mathieson Chemical Corporation, assignee; NL 6,413,843, 1965.

21. E. Smith, inventor; Olin Mathieson Chemical Corporation, assignee; US 3,399,241, 1968.

22. H.A. Bruson and J.S. Rose, inventors; Olin Mathieson Chemical Corporation, assignee; US 3,244,754, 1966.

23. H.A. Bruson and J.S. Rose, inventors; Olin Mathieson Chemical Corporation, assignee; US 3,269,961, 1966.

24. J.C. Jensen and R.S. Rose, *Journal of Fire Retardant Chemistry*, 1982, **9**, 4, 209.

25. *Plastic Foams*, Volume I, Eds., K.C. Frisch and J.H. Saunders, Marcel Dekker, New York, NY, 1972.

26. E.J. Termine and S.P. Ginter, inventors; The Dow Chemical Corporation, assignee; US 4,511,688, 1985.

27. J-C. Boulet, G. Bonnety, R. Walraevens, J. Lolivier and P. Trouillet, inventors; Solvay Cie, assignee; GB 1,371,488, 1974.

28. F.E. Paulik, inventor; Solutia Inc., assignee; US 5,844,028, 1998.

29. M. Modesti and F. Simioni, *Cellular Polymers*, 1994, **13**, 4, 277.

30. T.H. Ferrigno, *Rigid Plastic Foams*, 2nd Edition, Reinhold Publishing Corporation, New York, NY, USA, 1967, p.18, p.51, p.121.

31. M. Ionescu, V.T. Dumitriu, I. Mihalache, F. Stoenescu, M. Mateescu and S. Mihai, inventors; Institutul de Cercetari Chimice Centrul de Cercetari Materiale Plastiche, assignee; RO 85,852, 1985.

32. L. Friedman, inventor; Union Carbide Corporation, assignee; US 3,442,827, 1969.

33. G. Perot, *L'Industrie Chimique*, 1965, **52**, 203.

34. T.M. Beck and E.N. Walsh, inventors; Stauffer Chemical Corporation, assignee; US 3,076,010, 1963.

35. M. Ionescu, L. Dumitrache, I. Enache and S. Mihai, *Chemical Bulletin*, 2003, **46**, 60, 1.

36. M. Ionescu and I. Mihalache, unpublished work.

37. R.R. Hindersinn and M.I. Iliopulos, inventors; Hooker Chemical Corporation, assignee; US 3,501,421, 1970.

38. F. Salkowski and R. Wygleda, *Przemysl Chemiczny*, 1974, **53**, 1, 14.

39. C.F. Baranauckas and I. Gordon, inventors; Hooker Chemical Corporation, assignee; US 3,538,196, 1970.

40. F.H. Lee, J. Green and R.D. Gibilisco in *Proceedings of the SPI 6th International Technical/Marketing Conference, PU – New Paths to Progress*, San Diego, CA, USA, 1983, p.223.

41. D.L. Buszard, *Proceedings of the UTECH'86 Conference*, The Hague, The Netherlands, 1986, p.29.

42. D. Brownbill, *Modern Plastics International*, 1980, **10**, 11, 22.

43. C. Sivriev and L. Zabski, *European Polymer Journal*, 1994, **30**, 4, 509.

44. A. Hall, *Modern Plastics*, 1970, **47**, 10, 68.

45. H. Sivriev, G. Borissov, L. Zabski, W. Walczyk and Z. Jedlinski, *Journal of Applied Polymer Science*, 1982, **27**, 11, 4137.

46. I. Devedjiev, V. Ganev and G. Borissov, *European Polymer Journal*, 1989, **25**, 10, 1027.

47. E. Tashev, S. Shenkov, K. Troev, G. Borissov, L. Zabski and Z. Jedlinski, *European Polymer Journal*, 1988, **24**, 11, 1101.

48. G. Borissov, H. Sivriev, L. Zabski and Z. Jedlinski in *Proceedings of the SPI PU Division, PU'89 Technical/Marketing Conference*, San Francisco, CA, USA, 1989, p.388.

49. C. Sivriev, L. Zabski and G. Borissov, *European Polymer Journal,* 1992, **28**, 1, 9.

50. E. Tashev, L. Zabski, S. Shenkov and G. Borissov, *European Polymer Journal*, 1992, **28**, 6, 689.

51. J. Green, *Flammability and Flame Retardant in Plastics*, Rapra Review Report No.44, Rapra Technology, Shrewsbury, UK, 1990, 4, 8, 1-130.

52. M. Ionescu, I. Mihalache, V. Zugravu and S. Mihai, *Cellular Polymers*, 1994, **13**, 1, 57.

53. P.E. Burges, Jr., and C.J. Hilado in *Plastic Foams, Volume 2*, Eds., K.C. Frish and J.H. Saunders, Marcel Dekker, New York, NY, USA, 1972, p.855.

54. J.W.Crook and G.A.Haggis, *Journal of Cellular Plastics*, 1969, **5**, **2**, 119.

55. F-T.H. Lee and J. Green, inventors; FMC Corporation, assignee; US 4,555,562, 1985.

56. D.P. Miller, *Plastics Engineering*, 1980, **36**, 2, 29.

57. P. Walch, *Cellular Polymers*, 1986, **5**, 1, 33.

58. C.P. Smith and H. Ulrick, inventors; The Upjohn Company, assignee; US 4,173,602, 1979.

59. A.A. Oswald, *Canadian Journal of Chemistry*, 1959, **37**, 1498.

60. C.P. Smith and H. Ulrick, inventors; The Upjohn Company, assignee; US 4,202,946, 1980.

61. G.P. Speranza, M.E. Brennan and R.A. Grigsby, Jr., inventors; Texaco Inc., assignee; US 4,681,965, 1987.

62. D. Thorpe, inventor; ICI plc, assignee; US 4,797, 429, 1989.

63. No inventors; Stauffer Chemical Co., assignee; GB 1,500,756A, 1978.

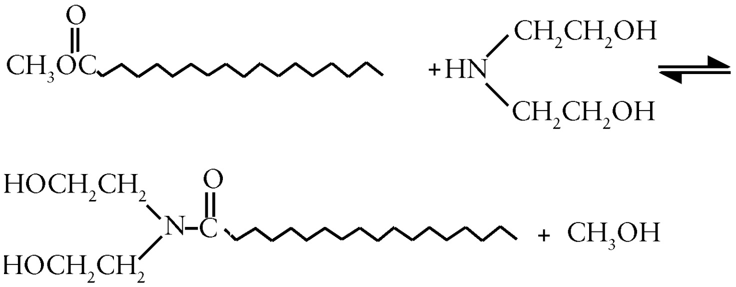
64. M. Ionescu, V.T. Dumitiu, I. Mihalache, F. Stoenescu and S. Mihai, inventors; Institutul de Cercetari Chimice Centrul de Cercetari Materiale Plastice, assignee; RO 92,989, 1985.

19

New Polyol Structures for Rigid Polyurethane Foams

19.1 Amidic Polyols

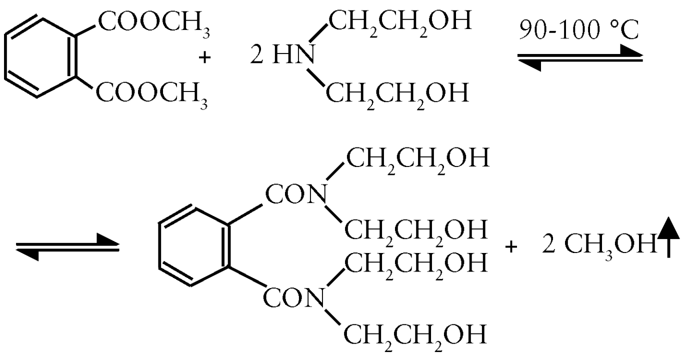
The reaction between dialkanolamines with organic acids or better still with their methyl esters gives the well known dialkanolamides. This reaction is used industrially for the synthesis of diethanolamides of fatty acids, which are well known nonionic surfactants (reaction 19.1) [1-10]:



(19.1)

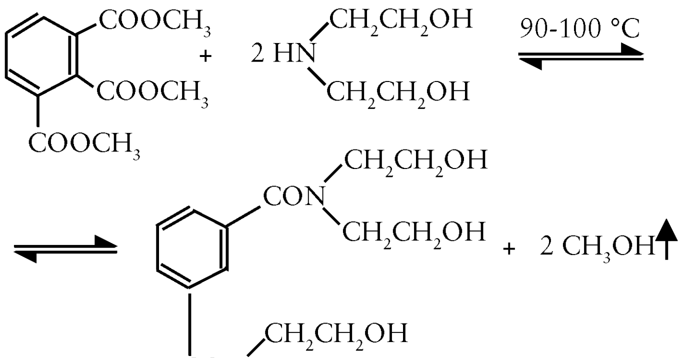
With methyl esters of fatty acids, the reaction takes place at a higher yield (around 90-92%) as compared to the free fatty acids (the yield is 60-70%) [2, 7-9]. The catalysts of this amidation reaction are: KOH, NaOH, CH_3ONa, CH_3OK, etc. (the most used catalyst is sodium methylate). The diethanolamides of fatty acids, as presented in Chapter 17, are used sometimes as copolyols in rigid polyurethane (PU) foams, to improve the compatibility of other rigid polyols with pentanes, used as blowing agents [4-8].

By using the principles of this classic reaction, new aromatic polyols were created, based on the reaction between dimethyl phthalate, dimethyl isophthalate and dimethylterephthalate with diethanolamine, using sodium or potassium methylate as catalyst (reactions 19.2, 19.3 and 19.4):



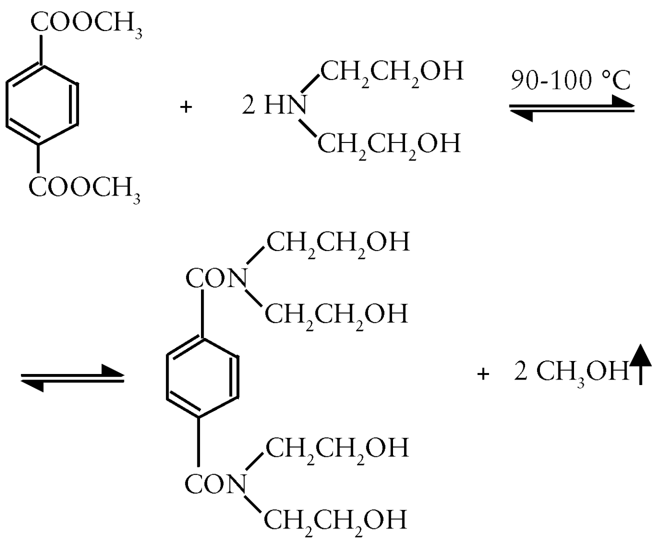
bis(diethanolamide)
of phthalic acid
(liquid polyol)

(19.2)



bis(diethanolamide)
of isophthalic acid
(melting point 40-42 °C)

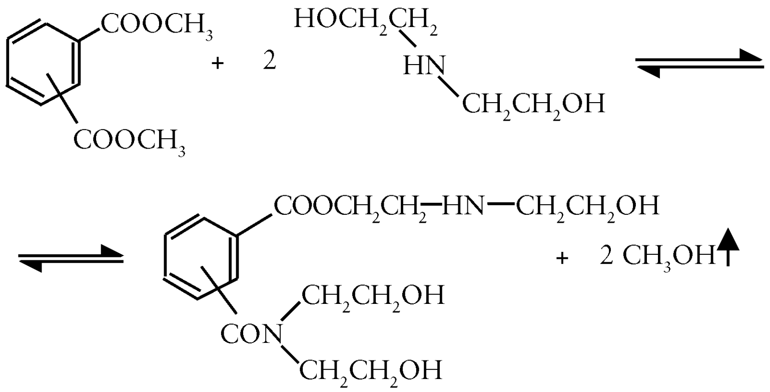
(19.3)



bis(diethanolamide)
of terephthalic acid
(melting point 120-125 °C)

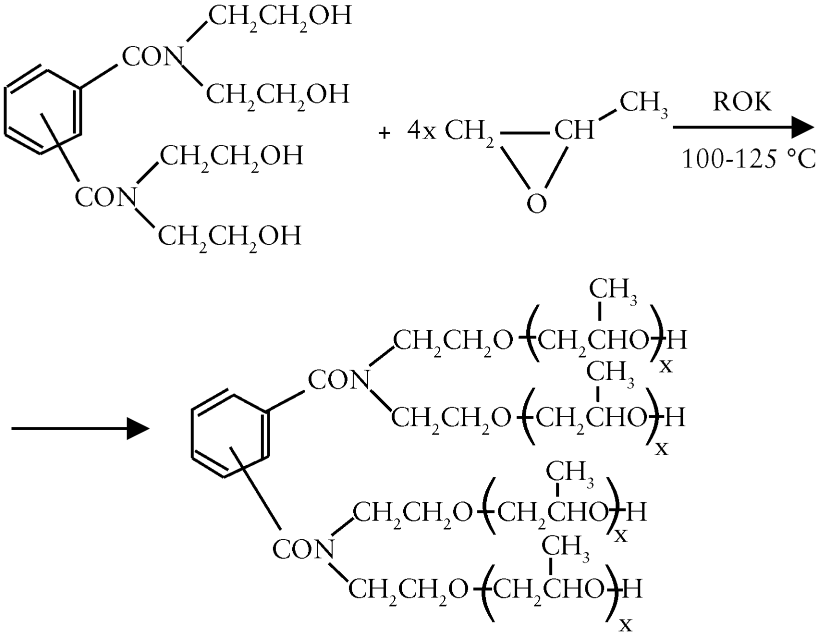
(19.4)

A partial esterification reaction takes places (19.5). This side reaction does not have a negative effect on rigid PU foam fabrication because it gives a very convenient tetrafunctional compound, which participates, together with the amidic polyol, to build the crosslinked structure of polyurethane. These compounds containing ester groups are present in low concentrations, maximum 5-7% [1, 2].



(19.5)

Except for the diamide derived from phthalic acid (19.2) which is a viscous liquid at room temperature, the diamides of isophthalic and terephthalic acids are solid, with convenient melting points. Because these diamides have a relatively high hydroxyl number of around 650 mg KOH/g, a propoxylation reaction (reaction 19.6) was developed. The addition of propylene oxide (PO) to the previously synthesised bis (diethanolamides) is catalysed by the same basic catalyst used for the amidation reaction [for example potassium methoxide, which is probably transformed with the potassium alcoholate of the bis (diethanolamides)].



(19.6)

After the propoxylation step, the resulting amidic polyols are purified by classical methods (for example by the treatment with solid disodium acid pyrophosphate). The liquid bis (diethanolamide) of phthalic acid, without any propoxylation step, can be used as a crosslinker or as a copolyol for rigid PU foams.

The amidic polyol obtained by the propoxylation of bis (diethanolamide) of phthalic acid, with an hydroxyl number in the range of 380-400 mg KOH/g, is an alternative for *ortho*-toluene diamine (o-TDA) based polyether polyols. The amidic polyols do not have the problems of a dark colour as the o-TDA polyols do and have lower viscosities than o-TDA polyols.

The amidic polyols derived from bis (diethanolamide) of phthalic acid (structure 19.6) have the same functionality as o-TDA based polyols and have internal ethylene oxide (EO), similar to commercial o-TDA polyether polyols. The difference is that: the labile amino groups are replaced with more stable amidic groups and the amidic polyol does not have a methyl group in the aromatic nucleus. The similarities between o-TDA based polyols and the amidic polyols derived from bis (diethanolamide) of phthalic acid are shown in the structures presented in **Figure 19.1**.

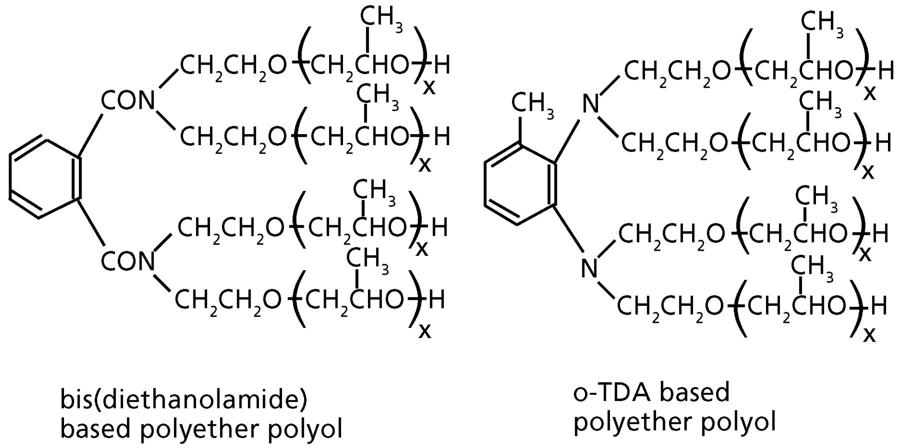


Figure 19.1 The structure of bis(diethanolamide) polyether polyol and of o-TDA polyether polyol

The synthesised amidic polyols have an hydroxyl number between 350-500 mg KOH/g and viscosities between 7000-25000 mPa-s at 25 °C, the lowest viscosity being in the polyols derived from the bis (diethanolamide) of phthalic acid. The pH of amidic polyols is slightly basic, in the range of 8-9.5.

Dimethyl phthalate, a very convenient liquid raw material, is a by-product in the fabrication of dimethylterephthalate. The amidic polyols can be used to replace the Mannich polyols. The self catalytic effect in PU formation is much less important in the case of amidic polyols, as compared with Mannich polyols. The rigid PU foams derived from amidic polyols are much more thermoresistant than the rigid PU foams derived from Mannich polyols [2].

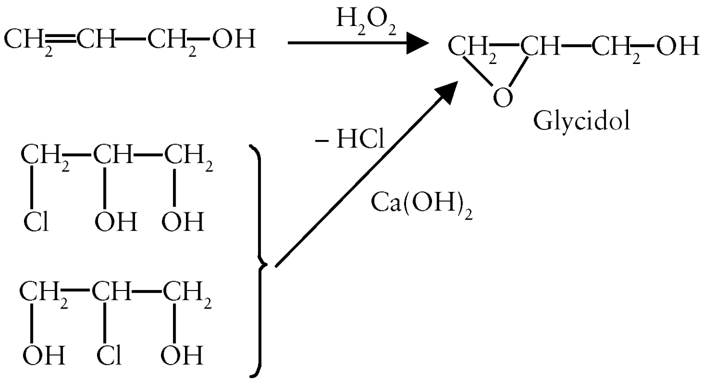
The amidic polyols represent a new generation of aromatic polyols for rigid PU foams, with an high application potential, all the raw materials used, dimethyl esters, dialkanolamines and PO being produced in large quantities industrially.

The reaction of poly(ethylene terephthalate) (PET) with diethanolamine, followed by propoxylation, gives liquid amidic polyols useful in rigid PU foam fabrication. This method is an efficient variant of PET waste chemical recovery (bottles, x-ray films, fibres and so on) [1].

19.2 Hyperbranched Polyols and Dendritic Polyols

Highly hyperbranched polyolic structures are obtained by the polyaddition of an hydroxy epoxidic compound, such as glycidol, to a polyol in cationic [1] or anionic catalysis [11-

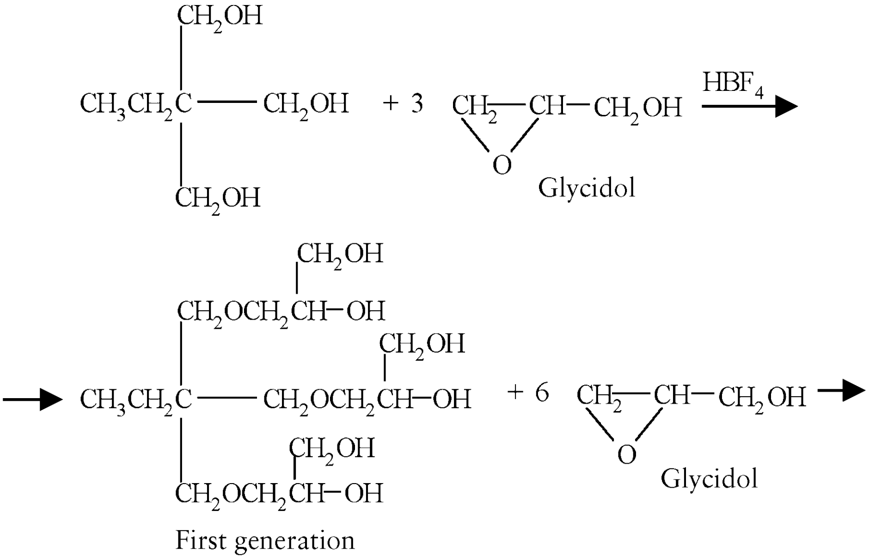
14]. Glycidol is obtained by epoxidation of allyl alcohol or by dehydrochlorination of the corresponding chlorohydrin, such as glycerin chlorohydrin (reaction 19.7).



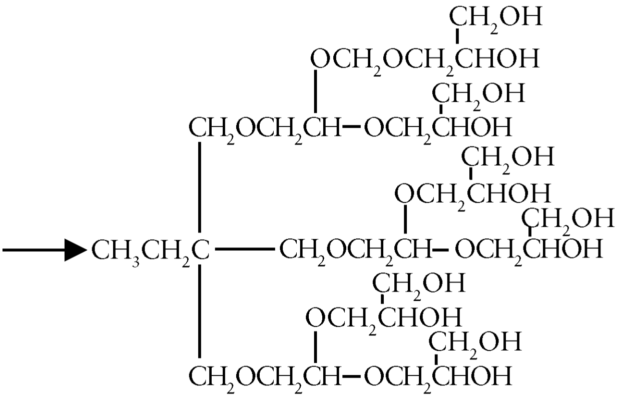
(19.7)

Polyaddition of glycidol to a symmetric triol such as trimethylolpropane (TMP), in the presence of a cationic catalyst (for example BF_3 or HBF_4) leads to highly branched structures, in fact a polyol of very high functionality. Each hydroxyl group by reaction with glycidol generates two hydroxyl groups [1].

Thus, by the reaction of TMP with 3 mols of glycidol a hexafunctional polyol is obtained (first generation) and by the reaction of this with 9 mols of PO, a polyol with 12 hydroxyl groups/mol is obtained (second generation) as shown in reaction 19.8.



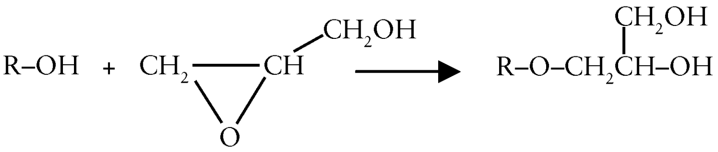
(19.8a)



Second generation (19.8b)

By the reaction of a highly branched polyol having 12 hydroxyl groups with 12 mols of glycidol a compound with 24 hydroxyl groups is obtained (third generation). The fourth generation (ratio of glycidol:TMP is around 35:1) is a polyol having 48 hydroxyl groups/mol (in fact it is a highly branched polyol with a functionality (f) of 48 OH groups/mol). **Figure 19.2** shows the idealised structure of a hyperbranched polyglycidol, (the fourth generation, having 48 hydroxyl groups/mol).

Unfortunately, by the ring opening of glycidol, one primary hydroxyl group and one secondary hydroxyl group are formed (reaction 19.9) which have different reactivities in the polyaddition reaction to hydroxyl groups (probably glycidol will be added preferentially to the primary hydroxyl groups) [15].



(19.9)

In reality, due to the previously mentioned difference in reactivities, the final product of glycidol polyaddition to TMP has not the symmetry of the idealised structure shown in **Figure 19.2**, but it is a highly branched polyol. It is very interesting that the introduction of these hyperbranched polyols in the formulations for rigid PU foams together with the usual polyols, give excellent rigid polyurethane foams, without the friability expected from polyols with very high functionalities. It is well known that such structures (for example dendrimers) have a special kind of internal flexibility which gives the resulting rigid PU foams very low friability.

This nonsymmetric addition of glycidol is very well illustrated by the slow addition to hydroxyl groups of glycerol, in the presence of alkaline catalysts [11-14]. Various highly

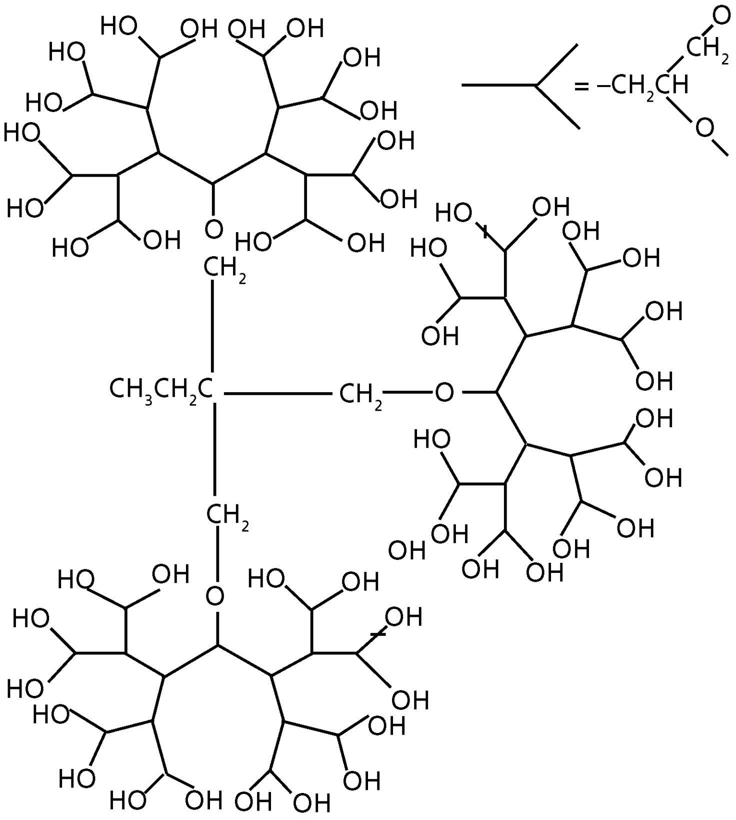
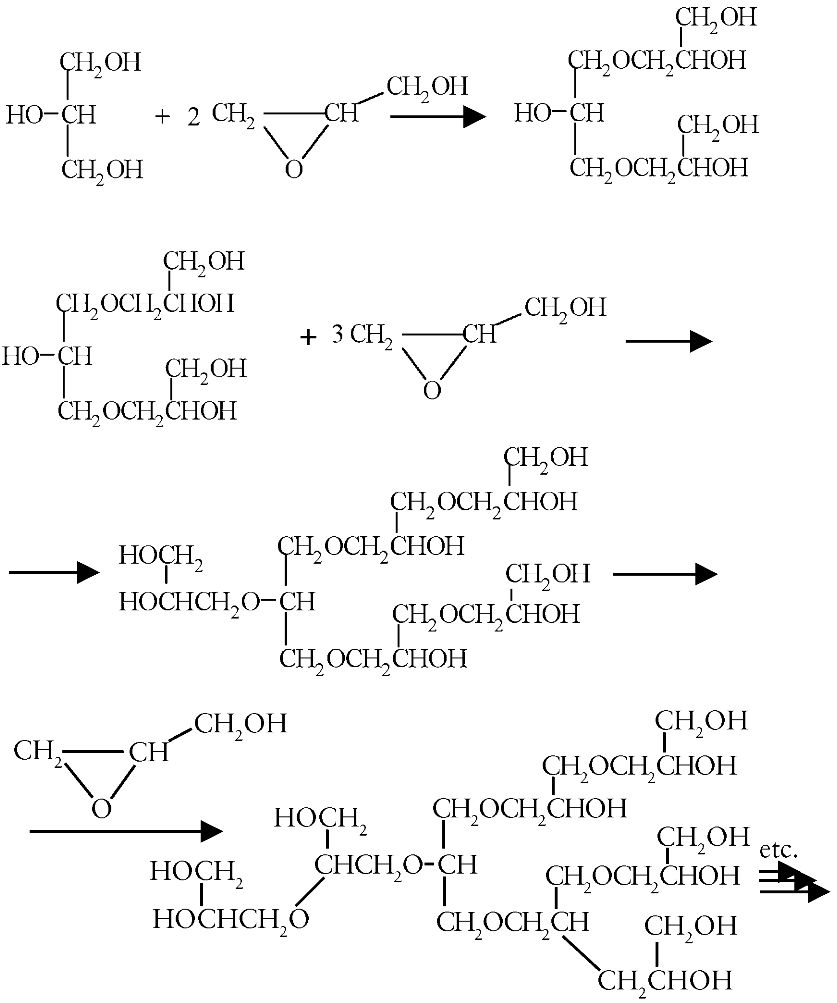


Figure 19.2 Hyperbranched polyglycidol (fourth generation)

branched polyglycerols, called 'pseudo-dendrimers' (**Figure 19.3**) are obtained (reaction 19.10), the degree of branching being around 0.5-0.66 (dendrimers have a degree of branching of 1 and linear polymers of course have a degree of branching of 0).

The hyperbranched polyglycerols were used successfully as copolyols for rigid PU foams and after the alkoxylation of polyglycerols with PO and EO. Higher molecular weight polyether polyols used for elastic PU were obtained [16].

A much more symmetric structure of hyperbranched polyols is obtained by using as monomer, an oxetane containing an hydroxyl group (produced industrially by Perstorp), 3-ethyl-3-methylol-oxetane, formally resulting from the intramolecular etherification of TMP (**Figure 19.4**).



Highly branched polyglycerol

(19.10)

By the addition of the oxetane monomer (**Figure 19.4**) to the hydroxyl groups a much more symmetrical structure is obtained [15] as compared to glycidol, because two primary hydroxyl groups, of equal reactivity are formed (reaction 19.11).

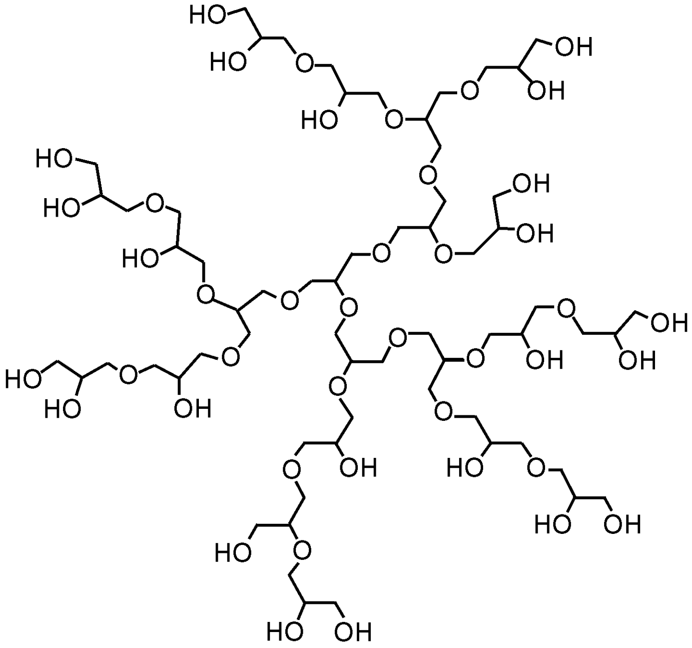


Figure 19.3 Hyperbranched polyglycerol with 20 glycidol units (pseudodendrimer) [11-14]

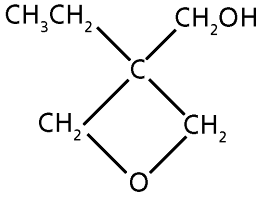
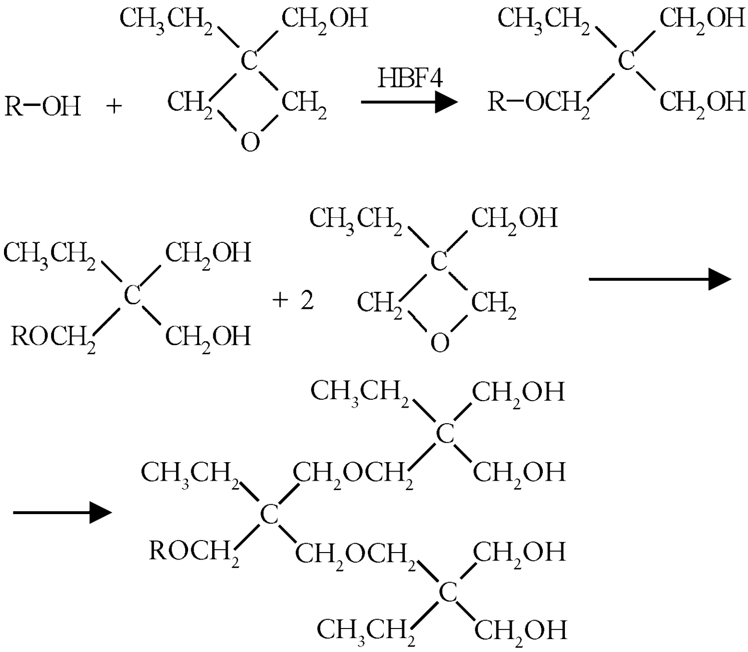


Figure 19.4 The structure of 3-ethyl-3-methylol oxetane



(19.11)

By polyaddition of 3-ethyl-3-methylol-oxetane to the hydroxyl group of TMP a dendritic polyol is obtained, with a hyperbranched and much more symmetrical structure compared to glycidol. In principle, the structure is very similar to the structure presented in the **Figure 20.2** with the difference that the repeating unit is different (**Figure 19.5**):

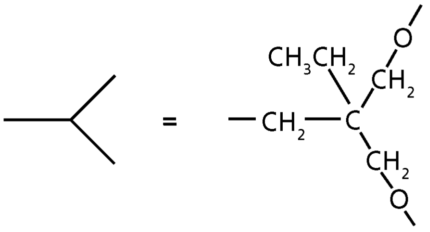
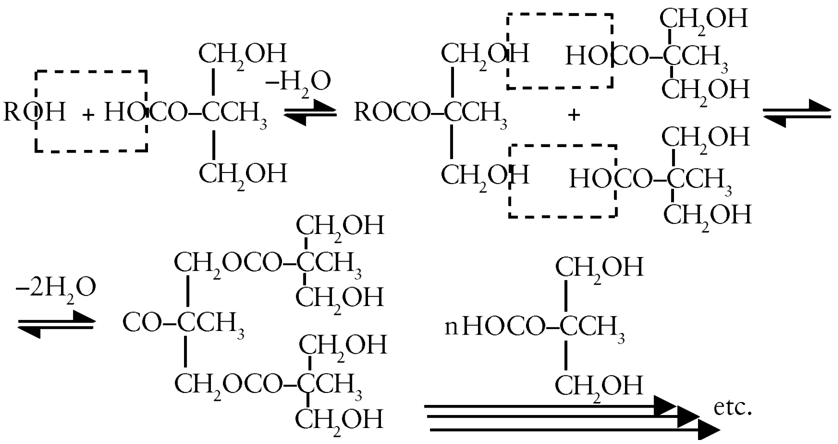


Figure 19.5 Repeating unit in the dendritic polyols based on 3-ethyl-3-methylol oxetane

A very interesting dendritic polyester polyol was developed by Perstorp (Sweden), by self-condensation of dimethylolpropionic acid, initiated by a polyol such as pentaerythritol [16]. Of course, the condensation of dimethylol propionic acid with one hydroxyl group generates two hydroxyl groups as shown in reaction 19.12.



(19.12)

Dendritic polyester polyols of 1st, 2nd, 3rd and 4th generation could be obtained by self-condensation of dimthylolpropionic acid initiated by pentaerythritol. The resulting dendritic polyols have 8, 16, 32 and 64 hydroxyl groups/mol, respectively.

Figure 19.6 shows the structure of a third generation of a dendritic polyester polyol, based on dimethylolpropionic acid, initiated by pentaerythritol.

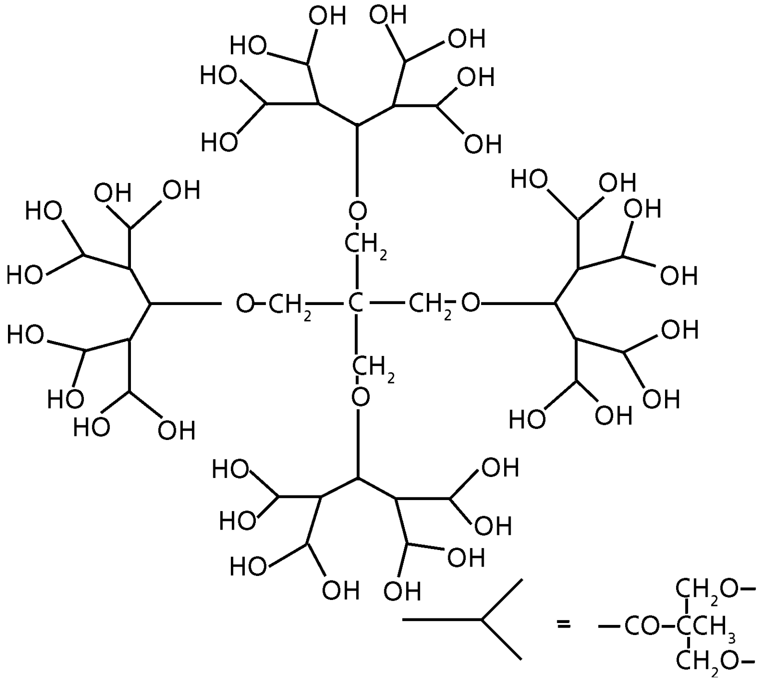


Figure 19.6 Dendritic polyester polyol based on dimethylolpropionic acid (3rd generation)

The dendritic polyester polyols based on dimethylolpropionic acid, are added to polyether polyols for flexible foams, in low concentration (for example around 8% dendritic polyol dissolved in the flexible polyether polyol), and give a remarkable increase in hardness of the resulting flexible PU foams, comparable or higher to that induced by the presence of polymer polyols (for example acrylonitrile-styrene graft polyether polyols) [16]. This is one of the most remarkable developments in the high functionality polyols area, used successfully for producing high load bearing flexible PU foams.

References

1. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai, *Advances in Urethane Science & Technology,* Volume 14, Wiley, New York, NY, USA, 1998, p.151-218.

2. M. Ionescu, S. Mihai, E. Stepan, C. Roibu and V. Preoteasa in *Proceedings of the APC Conference, Polyurethanes Expo 2001*, Columbus, OH, USA, 2001, p607.

3. J-P. Boiteaux, B. Brabq, N. Lecocu and F. Loussayne, inventors; Societe d'Exploitation de Produits pour les Industries Chimiques, assignee; US 5,108,661, 1992.

4. No inventors, American Cyanamid Company, assignee; GB 650940, 1951.

5. G.C. Tesoro, inventor; Onix Oil & Chemical Company, assignee; US 2,844,609, 1958.

6. V. Lamberti and G.J. McCrimilsk, inventors; Lever Brothers Company, assignee; US 3,107,258, 1963.

7. H. Kroll and H. Nadeau, *Journal of American Oil Chemists' Society*, 1956, **34**, 323.

8. R.A. Reck, *Journal of American Oil Chemists' Society*, 1979, **56**, 796.

9. L.W. Brunette in *Nonionic Surfactants*, Ed., M.J. Schick, Marcel Dekker, Inc., New York, NY, USA, 1966, p.395-403.

10. R.L. Zimmerman and G.P. Sperenza, inventors; Texaco, Inc., assignee; US 4,442,238, 1984.

11. A. Sunder, R. Hanselmann, H. Frey and R. Mülhaupt, *Macromolecules*, 1999, **32**, 13, 4240.

12. A. Sunder, R. Mülhaupt and H. Frey, *Macromolecules*, 2000, **33**, 2, 309.
13. J.F. Stumbé, A. Sunder and R. Haag in *Proceedings of ACS Polymeric Materials: Science and Engineering*, San Diego, CA, USA, 2001, **Volume 84**, p.1023.
14. H. Kautz, A. Sunder and H. Frey, *Macromolecular Symposia*, 2001, **163**, 67.
15. P. Kubisa and S. Penczek, *Progress in Polymer Science*, 1999, **24**, 10, 1409.
16. B. Midelf, A. Magnusson, B. Haggman, D. Thom, F. Valentin and A. Kee in *Proceedings of the APC Annual Conference, Polyurethanes Expo 2003*, Orlando, FL, USA, 2003, p.167.

20 Oligo-Polyols by Chemical Recovery of PU Wastes

Current methods of polyurethane (PU) fabrication result in up to 10% of wastes from the total production. These PU wastes are in the form of foaming 'heads' or 'tails' resulting from the foaming apparatus, excess material resulting from the cutting of PU foam buns (flexible or rigid), material resulting from the moulding processes (material rejected out from the moulds), noncorresponding foams and so on [1]. To this PU waste are added the PU resulting from dismantled objects such as: cars, furniture, refrigerators, buildings and constructions and so on.

What is it possible to do with these solid PU wastes?

From the ecological point of view it is forbidden to deposit the PU wastes in the surrounding medium, for example in the soil, because the products of natural degradation and biodegradation of PU are toxic, e.g., aromatic amines which are carcinogenic. The penetration of these biodegradation products into soil or in underground waters is extremely dangerous for human health.

On the other hand, the PU wastes represent a real value because in their composition there are extremely valuable petrochemical materials (e.g., oligo-polyols, isocyanates, silicon emulsifiers, flame retardants and so on) and for the formation of these petrochemical materials an appreciable quantity of energy was consumed. These ecological and economic reasons led to a very intensive research effort, to find a solution to render value to these valuable materials: PU wastes. The scope of the recycling technologies described is to recover as much as possible of the materials and energy resources invested in the PU material.

In the area of flexible foams the regrinding of foam wastes and their incorporation into new foams is the current way of recycling [2]. Rebounding process linking of cut PU foams wastes by an adhesive, to obtain new PU foam materials into high quality carpet underlay is another process without the chemical destruction of the PU polymer [3, 4, 5].

Other variants of PU recycling are the pyrolysis and the recovery of the organic products resulting from thermal destruction of PU and energy recovery by the combustion of the PU wastes [6-10].

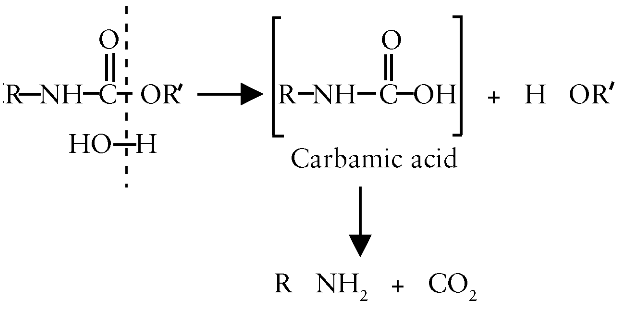
Chemical recovery processes by PU polymer breakdown through hydrolysis, glycolysis and aminolysis processes are extremely important because by using chemical reactions, the PU wastes are chemically transformed into new products which can possibly be used in the fabrication process of new PU. PU wastes are important raw materials for new polyols destined to become rigid and flexible foams.

The chemical splitting of ester bonds by hydrolysis, alcoholysis or aminolysis are specific reactions of all organic esters, including urethanes (or carbamates) which are in fact esters of carbamic acid.

For a better understanding of the PU foam wastes recovery by chemical processes. The model reactions for hydrolysis, glycolysis and aminolysis of urethane and urea groups will be presented in the next sections.

20.1 Hydrolysis of PU Polymers [11-24]

Hydrolysis of a urethane group leads to the formation of an amine, an alcohol and carbon dioxide (reaction 20.1).



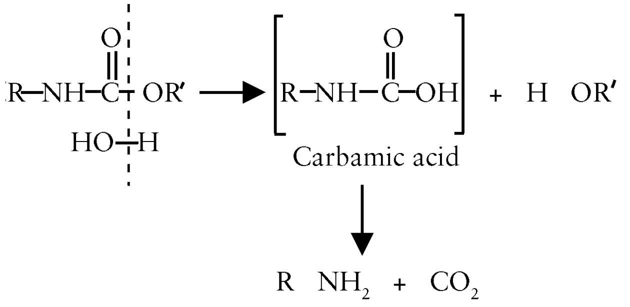
$$R{-}NH{-}\overset{\overset{\large O}{\|}}{C}{-}OR' + HO{-}H \longrightarrow \left[R{-}NH{-}\overset{\overset{\large O}{\|}}{C}{-}OH\right] + H\ OR'$$

Carbamic acid

$$\downarrow$$

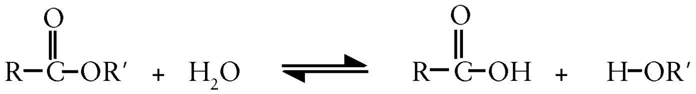
$$R\ NH_2 + CO_2 \qquad (20.1)$$

From the hydrolysis of a polyether-based PU a diamine (or a polyamine) such as toluene diamine or diphenylmethane diamine, a polyol and carbon dioxide are formed. The resulting diamines are the precursors used for the synthesis of isocyanates [11, 12, 16, 18]. The resulting polyol is the polyether polyol used for the initial synthesis of PU. Carbon dioxide results from the decomposition of the very unstable carbamic acid formed by the hydrolysis (20.2):



$$R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OR' + HO{-}H \longrightarrow \underset{\text{Carbamic acid}}{\left[R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OH\right]} + H\ OR' \longrightarrow R\ NH_2 + CO_2 \qquad (20.2)$$

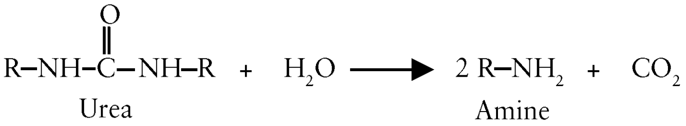
By hydrolysing a polyether PU, a polyether polyol is obtained with a similar structure to those of the initial virgin polyether polyol. For polyester PU the hydrolysis reaction is more complicated because the esteric groups of polyesters are hydrolysed back to monomers, such as diacids and glycols or polyols (reaction 20.3).



$$R{-}\overset{O}{\overset{\|}{C}}{-}OR' + H_2O \rightleftharpoons R{-}\overset{O}{\overset{\|}{C}}{-}OH + H{-}OR' \qquad (20.3)$$

Thus, by the hydrolysis of a PU based on a polyester derived from adipic acid and diethylene glycol (DEG) - adipic acid, DEG, diamine and carbon dioxide are obtained.

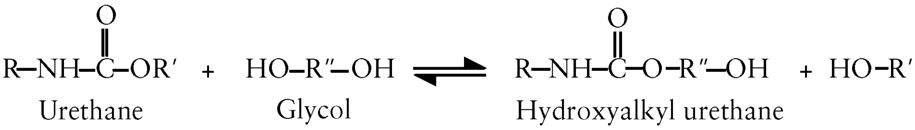
The real situation of PU hydrolysis is more complicated because together with the urethane groups, urea groups are also present [resulting from the reaction of isocyanates (with water as blowing agent), especially in flexible and rigid PU foams]. Urea groups are hydrolysed at a lower reaction rate than the urethane groups, being transformed into amines and carbon dioxide (reaction 20.4).



$$\underset{\text{Urea}}{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R} + H_2O \longrightarrow \underset{\text{Amine}}{2\,R{-}NH_2} + CO_2 \qquad (20.4)$$

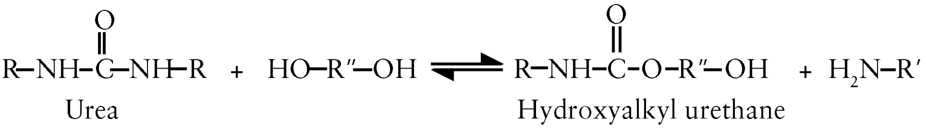
20.2 Glycolysis of PU Polymers [11, 12, 25-29]

Glycolysis of a PU polymer is similar to a transesterification reaction, in fact a reaction between a carbamic ester (urethane) and a glycol (reaction 20.5).



$$\underset{\text{Urethane}}{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OR'} + \underset{\text{Glycol}}{HO{-}R''{-}OH} \rightleftharpoons \underset{\text{Hydroxyalkyl urethane}}{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}R''{-}OH} + HO{-}R' \qquad (20.5)$$

By glycolysis of urea groups a hydroxyalkyl carbamate (or hydroxyalkyl urethane) and an amine are formed (reaction 20.6).

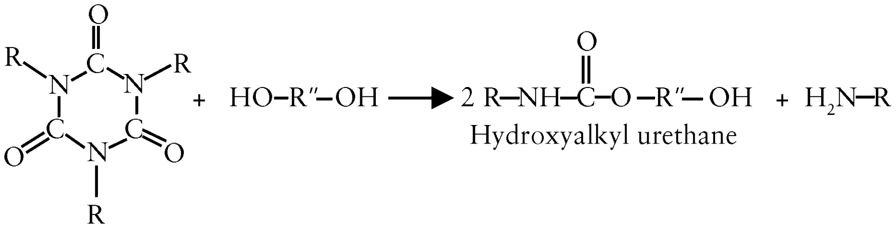


$$\underset{\text{Urea}}{R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R} + HO{-}R''{-}OH \rightleftharpoons \underset{\text{Hydroxyalkyl urethane}}{R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R''{-}OH} + H_2N{-}R'$$

(20.6)

The glycolysis of urea groups takes place at a lower reaction rate than the glycolysis of urethane groups. The catalysts for both reactions, glycolysis and hydrolysis are: alkali hydroxides (NaOH, KOH, LiOH) [11, 12, 25, 26, 30, 31], diethanolamine[11, 26] and some titanium or tin compounds. One of the best catalysts is LiOH [11].

Urethane - polyisocyanuric foams (PU/PIR) foams) contain isocyanuric rings. Isocyanuric rings are glycolysed at lower reaction rates than the urea or urethane groups, with the formation of hydroxyalkyl carbamates and an amine (reaction 20.7) [11]:

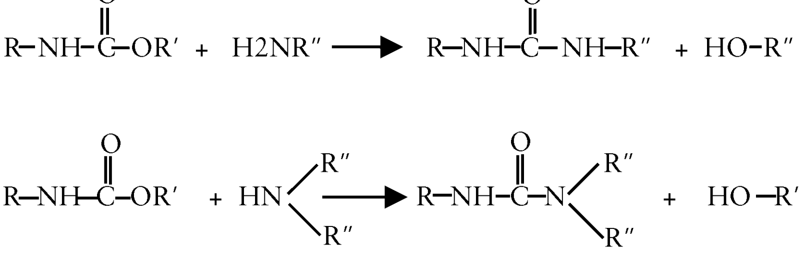


(20.7)

Of course allophanate and biuret groups are hydrolysed and glycolysed in a similar manner to urea groups, the first reaction takes place at the allophanate or biuret group. These reactions are presented in the **Figure 20.1**.

20.3 Aminolysis of PU Polymer [31-36]

Urethane groups react with primary and secondary amines leading to a disubstituted urea and an alcohol (reaction 20.8).



$$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}OR' + H2NR'' \longrightarrow R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R'' + HO{-}R''$$

$$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}OR' + HN\begin{matrix}R''\\R''\end{matrix} \longrightarrow R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}N\begin{matrix}R''\\R''\end{matrix} + HO{-}R'$$

(20.8)

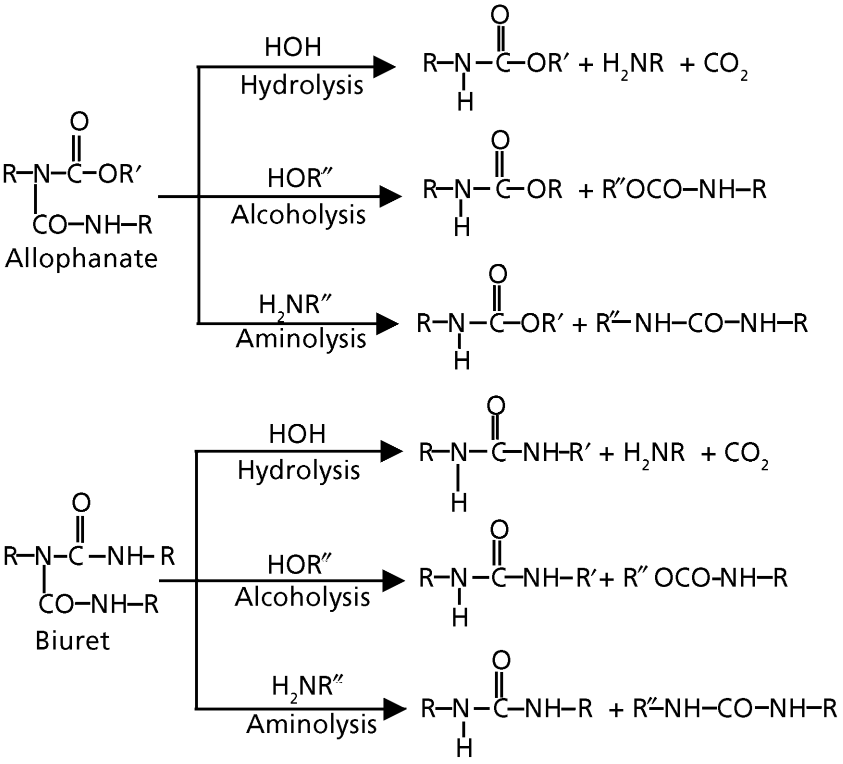
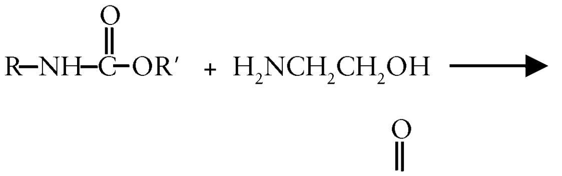


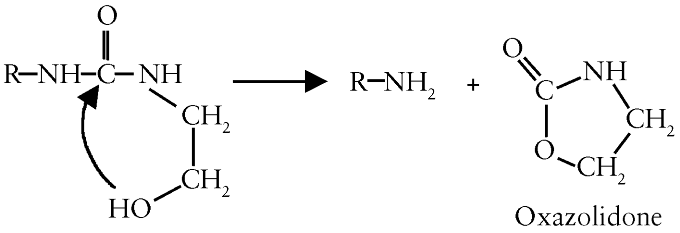
Figure 20.1 Chemical scission of allophanate and biuret bonds

In particular aminolysis with an alkanolamine such as monoethanolamine forms an hydroxyalkyl urea and an alcohol (reaction 20.9).



$$R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OR' + H_2NCH_2CH_2OH \longrightarrow R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2CH_2OH + HO{-}R' \qquad (20.9)$$

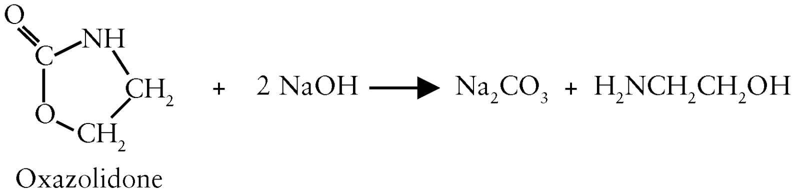
The disadvantage of hydroxyalkyl urea formation is an intramolecular reaction which leads to an oxazolidone, a cyclic urethane (reaction 20.10) [33].



(20.10)

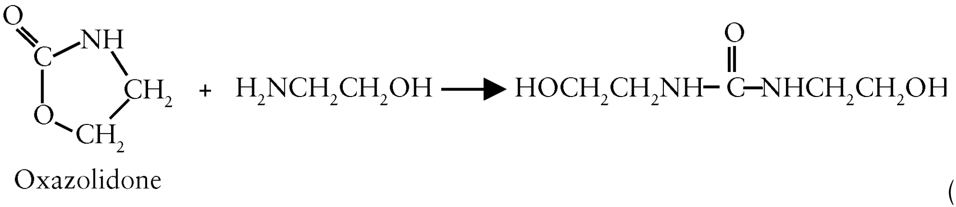
The oxazolidone formed is not an interesting component in PU chemistry because it does not have reactive groups such as hydroxyl or amino groups to enter into the PU structure (just the low reactivity -NH-COO- urethane group which leads to an allophanate).

By using sodium or potassium hydroxides as catalysts of aminolysis, it is possible to regenerate the initial monoethanolamine (a bifunctional compound in the conditions of PU chemistry and to destroy the oxazolidone formed (reaction 20.11) [33]:



$$\text{Oxazolidone} + 2\,\text{NaOH} \longrightarrow Na_2CO_3 + H_2NCH_2CH_2OH \quad (20.11)$$

The reaction between the oxazolidone and monoethanolamine (similar to the reaction of any urethane group with an amine) is very favourable, with the formation of a bis (hydroxyethyl) urea (a diol), which is an ideal chain extender in PU chemistry (reaction 20.12) [32, 33].



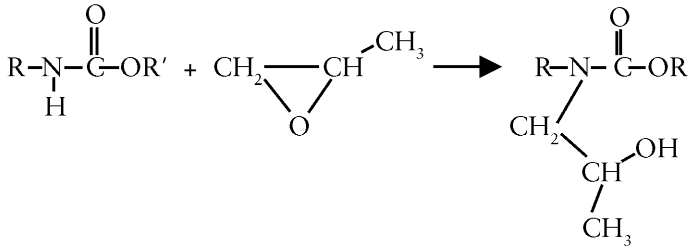
$$\text{Oxazolidone} + H_2NCH_2CH_2OH \longrightarrow HOCH_2CH_2NH-\overset{\overset{O}{\|}}{C}-NHCH_2CH_2OH \quad (20.12)$$

20.4 Alkoxylation of PU Polymer [37-39]

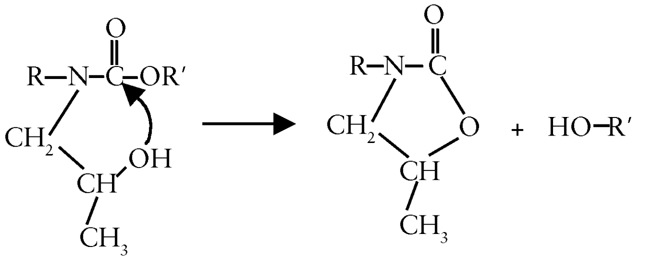
Urethane groups react with alkyleneoxides [(propylene oxide (PO), ethylene oxide (EO)], by the addition of epoxy compounds to the -NH- group containing active hydrogen, from the urethane groups.

It is very interesting that in the alkoxylation (with PO or EO) of a flexible or semiflexible PU foam, the PU crosslinked polymer is transformed into a liquid product.

The scission of urethane groups is explained by the following two consecutive reactions (20.13 and 20.14). The first reaction is the addition of alkylene oxide to the active hydrogen of urethane groups (20.13). The resulting hydroxyalkyl urethane, by an intramolecular transesterification, leads to the splitting of the urethane bonds of PU, the PU network is destroyed with the formation of an oxazolidone and a polyether polyol.

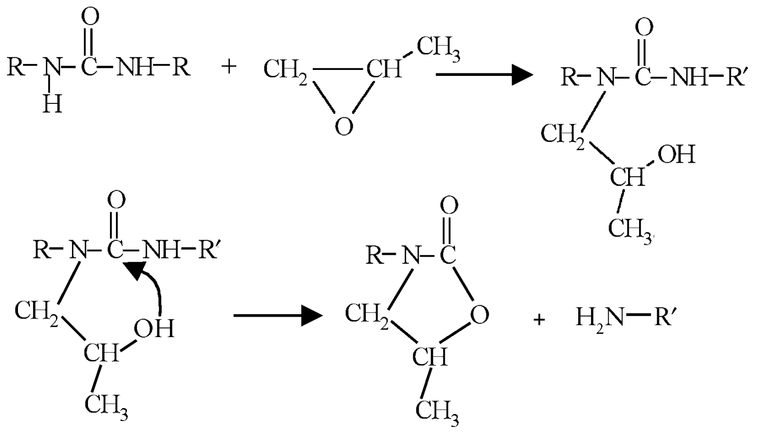


(20.13)



(20.14)

The alkoxylation process is easy to apply to PU foams having a low concentration of urethane and urea groups such as: flexible and semiflexible foams, integral skin foams, PU elastomers and so on. Urea groups react in a similar way with urethane groups, with the formation of oxazolidones and amines by an intramolecular alcoholysis of urea groups (reaction 20.15).

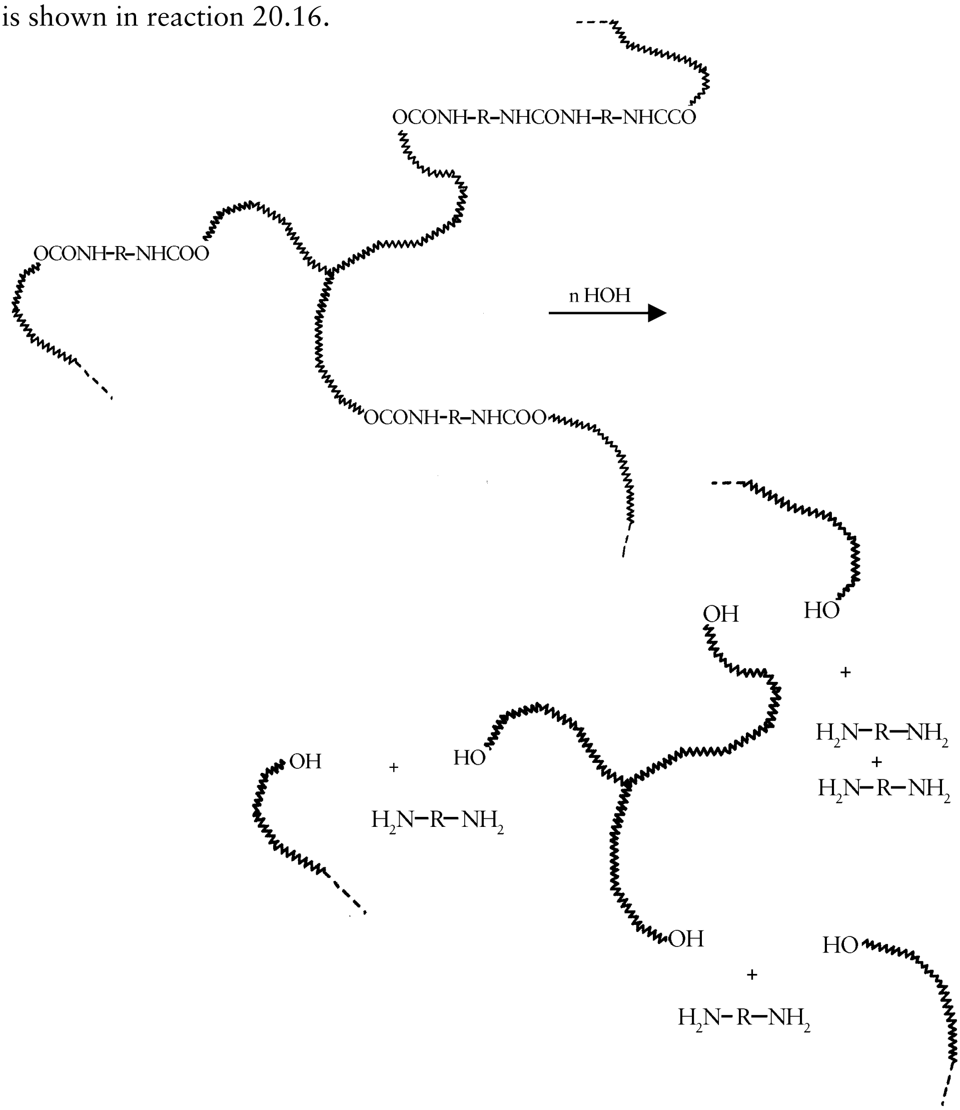


(20.15)

In Sections 20.1-20.4 the main reactions involved in the chemical recovery of PU wastes i.e., hydrolysis, glycolysis, aminolysis and alkoxylation reactions were presented. Several important processes for chemical recovery of PU polymers will be presented in the next chapters.

20.5 Chemical Recovery of Flexible PU Foam Wastes by Hydrolysis [12-24, 27]

The idealised reaction for the hydrolysis of the crosslinked structure of flexible PU foams is shown in reaction 20.16.



(20.16)

By the hydrolysis of a flexible foam based on toluene diisocyanate (TDI) one obtains toluene diamine (2,4 and 2,6 isomers), the polyether triol and, of course, carbon dioxide. The difficulty of the process is the separation of the amine. The amine may be used for TDI synthesis (after a previous purification), or be transformed into a valuable rigid polyol (aminic polyol) by alkoxylation with PO and EO.

The industrial process uses high pressure steam at 230-315 °C, which hydrolyses the flexible foam rapidly. The resulting diamines can be distilled and extracted from the steam stream. The polyols can be recovered from the residue and reused together with virgin polyol to make new flexible PU foams.

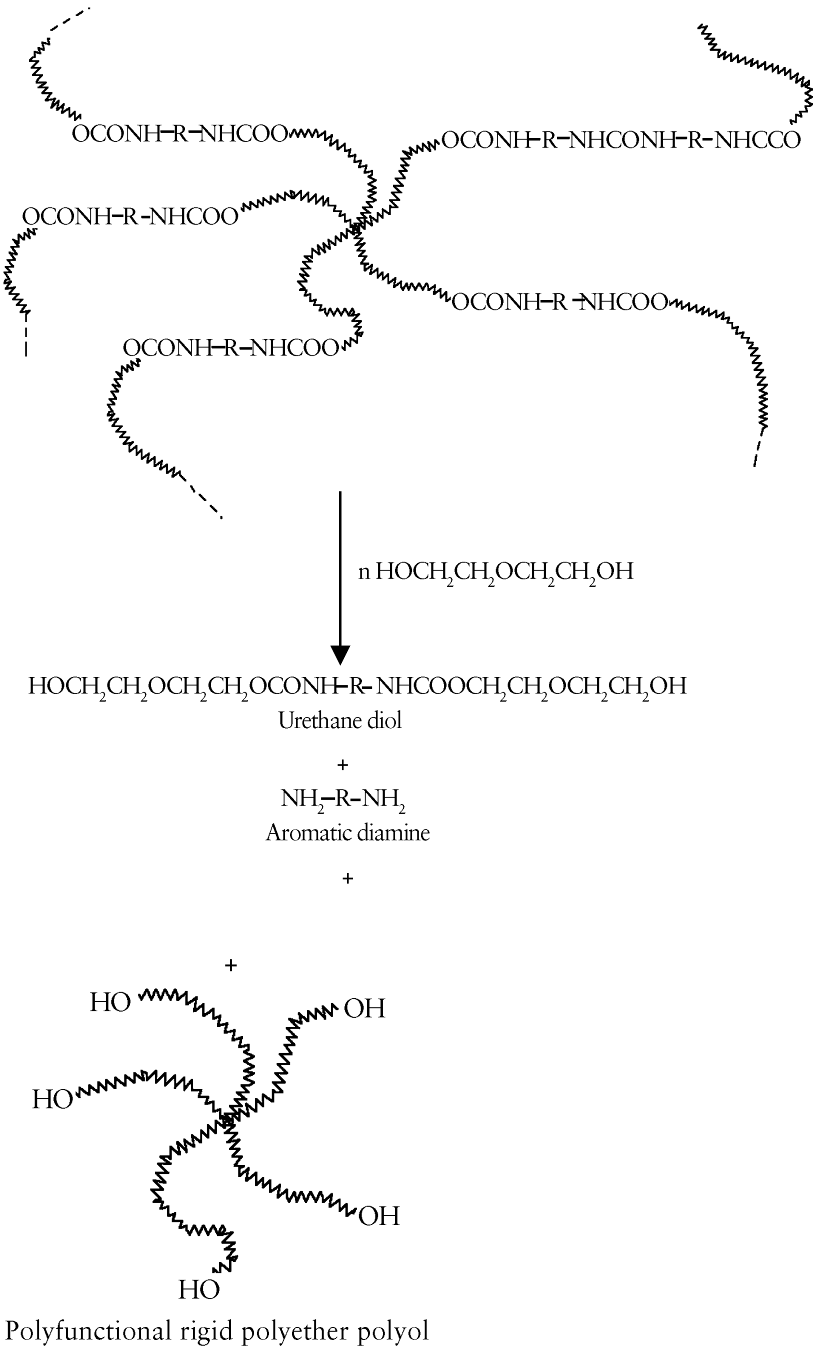
A variation of steam technology is a hydrolysis-glycolysis process at 190-200 °C. LiOH proved to be an excellent catalyst of these reactions and the degradation process is accelerated markedly to just a few minutes while the temperature may be decreased at 170-190 °C [12, 34].

The reaction product is the polyether polyol and the diamine, with DEG as solvent. The extraction of polyol with hexadecane and its evaporation lead to a high quality polyether polyol which could replace up to 50% virgin polyether polyol [12, 16, 34]. The polyol resulting from the hydrolysis of flexible foams is practically identical to the initial polyol which was used to make the original material of the PU foam waste. Because in the hydrolysis process new types of polyols do not appear, this type of technology is not described.

20.6 Rigid Polyols by Glycolysis of Rigid PU Foam Wastes [11, 12, 25, 26, 28-30]

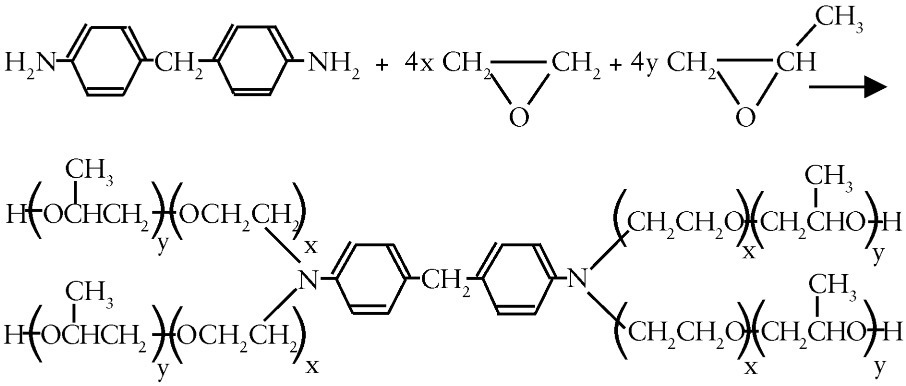
By reacting rigid PU foam wastes with glycols (ethylene glycol, DEG, dipropylene glycol and so on), a liquid mixture of polyols is obtained, which can be reused directly in rigid foam production. The process consists in the reaction of equal parts of ground PU scraps and DEG:diethanolamine mixture (9:1), at 190-210 °C, for several hours. The resulting polyols can be used as a substitute for up to 70% of the virgin polyols [28, 29, 34].

By reacting urea groups from rigid PU foam scraps with DEG, amines are formed. The amines are transformed into rigid polyols by alkoxylation of the resulting polyol mixture. The idealised reaction for glycolysis of a rigid PU foam is presented in reaction 20.17.



(20.17)

The diamine (for example diphenylmethane diamine) is transformed into a rigid polyether polyol by alkoxylation with PO and EO (reaction 20.18).



(20.18)

To conclude, the complex mixture of polyols resulting from glycolysis of rigid PU foam scraps probably has the following composition:

a) Urethane polyol;

b) High functionality polyether polyol;

c) The aminic polyol resulting from the alkoxylation of diphenylmethane diamine; and,

d) Excess of unreacted DEG.

As a general remark, the mixture of polyols resulting from the glycolysis of rigid PU foam wastes has in its composition aromatic polyols derived from a diphenylmethane diisocyanate (MDI) structure (component a and c), which lead to an improvement of physico-mechanical, thermal and fire proofing properties in the resulting rigid PU foams. The characteristics of a polyol mixture resulting by the glycolysis with DEG of a conventional rigid PU foam (density 30-50 kg/m^3) are presented in **Table 20.1**.

Table 20.1 Characteristics of recovered polyols obtained by the glycolysis with DEG of conventional rigid PU foams of density 30-50 kg/m^3

Characteristic	Unit	Value
Aspect	-	Dark-brown viscous liquid
Hydroxyl number	mg KOH/g	600 - 650
Acidity	mg KOH/g	max. 10
Viscosity, 25 °C	mPa-s	4,500-7,000
Water content	%	max. 0.2

The characteristics for a recycled polyol presented in **Table 20.1** have a large range of values due to the fact that the qualities of the rigid PU wastes used are not consistent (the rigid PU foam wastes are made in various densities, various formulations, some foams are degraded and so on).

By alkoxylation with PO and EO, after the glycolysis process, the polyols recovered have improved characteristics, as shown in **Table 20.2**.

The recovered polyols shown in **Table 20.2** have a lower acidity due to the alkoxylation of acidic groups, lower hydroxyl numbers and higher viscosities (due to the alkoxylation of diphenylmethane diamine, which leads to high viscosity polyols) compared to the polyols resulting directly from glycolysis (**Table 20.1**).

Glycolysis of flexible PU foams is also possible. At a ratio of PU waste:DEG of 1-1.5:1, two layers are formed (the superior layer being rich in polyether), but at a higher ratio of 2-4:1 a homogeneous polyol mixture results, with an hydroxyl number of 360-390 mg KOH/g, which was used successfully in rigid PU foam fabrication [35].

Table 20.2. Characteristics of polyols recovered by the glycolysis after alkoxylation with PO and EO

Characteristic	Unit	Value
Aspect	-	Dark-brown viscous liquid
Hydroxyl number	mg KOH/g	550-600
Acidity	mg KOH/g	max. 2
Viscosity, 25 °C	mPa-s	8,000-10,000
Water content	%	max. 0.1

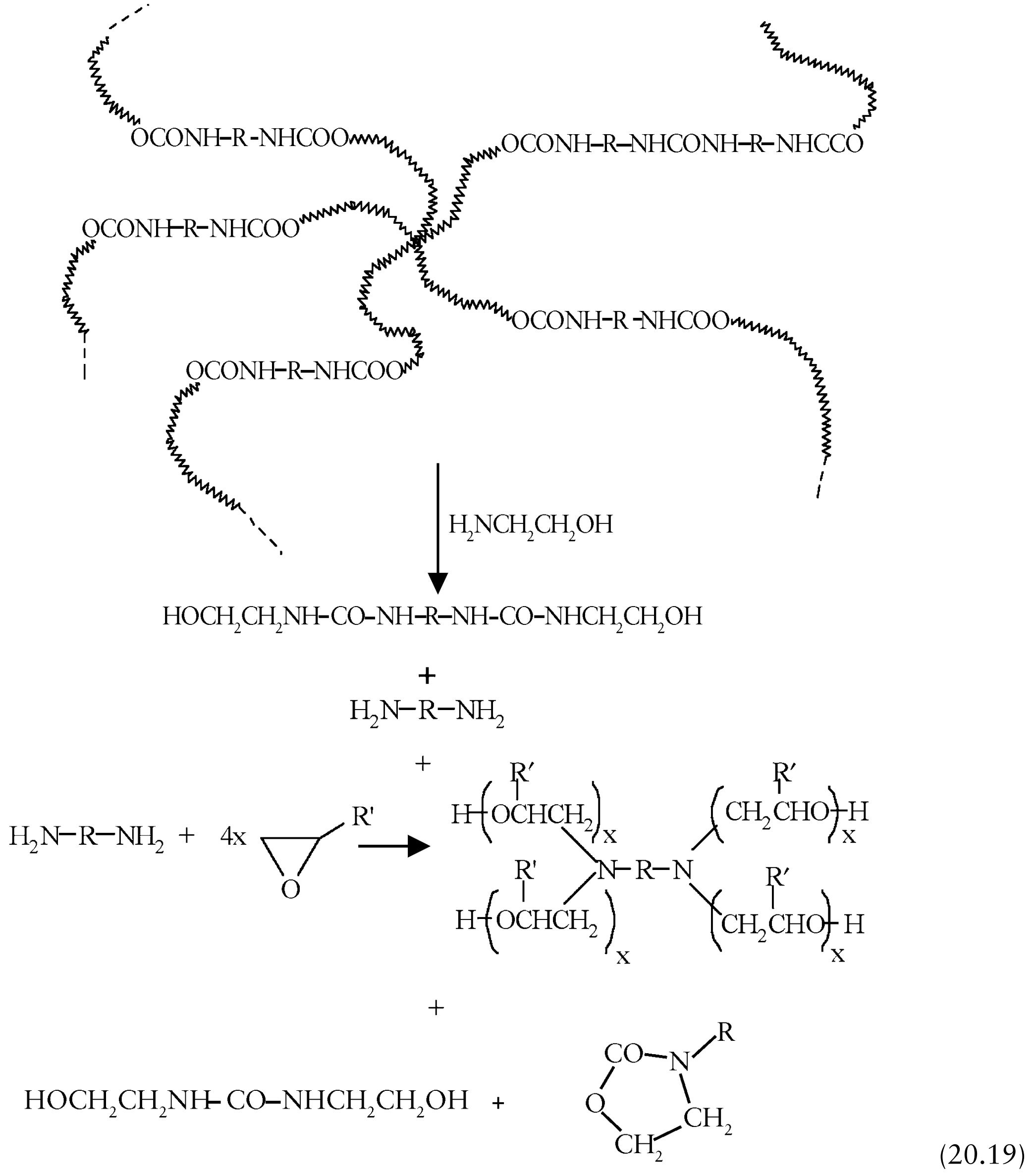
20.7 Rigid Polyols by Aminolysis of Rigid PU Foam Wastes [31-36, 40, 41]

Aminolysis of rigid PU foam wastes takes place at higher reaction rates than the glycolysis reaction and at lower temperatures (160-170 °C instead of 190-210 °C) [31-33].

An interesting aminolysis process based on the reaction of ground polyether-based rigid PU foam wastes with an alkanolamine, in the presence of an alkaly hydroxyde as catalyst was developed [36, 40, 41]. The ratio between PU waste and alkanolamine could be around 15:1 to 50:1 (one cubic meter of foam can be chemically destroyed by one litre of alkanolamine) [34, 41].

In the second step, the aromatic amines formed react with ethylene oxide or with propylene oxide. Two layers are formed. The top layer is the same polyol used in the original foam formulation (around 30% from the total volume). The bottom layer is a high functionality polyol, which it is possible to use successfully in various rigid foams formulations [34, 41].

The main reactions involved in the aminolysis of a rigid PU foam are presented in reaction 20.19.



(20.19)

A hybrid process: aminolysis - alkoxylation was developed [37-39]. The ground rigid PU foam waste was reacted simultaneously with an amine (ethylene diamine, monoethanolamine, ammonia) and with PO (or PO and EO), in a pressure reactor. The exothermal reaction between the amine and the PO (or EO) gives the high temperature needed for aminolysis (autothermal process). The temperature of around 180-200 °C is obtained rapidly (no cooling in the first stage of reaction) and in the reaction mass there is enough excess of amino groups to secure the chemical splitting of urethane and urea bonds).

A very rapid variant of chemical recovery by aminolysis is to add the ground PU rigid wastes to monoethanolamine or to diethanolamine at 160 °C, at a gravimetric ratio of rigid PU waste:monoethanolamine of 2-3:1. To avoid the formation of oxazolidone, an alkaline catalyst is added (NaOH or KOH). The product of aminolysis is alkoxylated with PO (or PO and EO) to transform the primary or secondary amino groups into hydroxyalkyl amines. If the primary and secondary amino groups are present in the polyol recovered, then during the foaming process urea groups are formed which lead to friable, rigid foams with very low adhesive properties. This effect is avoided by the use of the alkoxylation reaction. The polyols obtained by the aminolysis - alkoxylation process can be used together with up to 50-70% of virgin polyols, giving new rigid PU foams with good physico-mechanical properties.

20.8 Technology for Chemical Recovery of Rigid PU Foams (and Isocyanuric Foams) by the Glycolysis Processes

The technology for the chemical recovery of rigid PU foam and isocyanuric foam wastes (a variant) by glycolysis processes involves the following main steps:

a) The grinding of rigid PU foam waste;

b) Glycolysis reaction by the stepwise addition of ground PU waste to DEG in the presence of a catalyst;

c) Digestion;

d) Alkoxylation reaction with PO (or PO and EO);

e) Degassing; and

f) Filtration of the reaction mass.

A variant of an installation for the chemical recovery of rigid PU foam wastes by glycolysis is shown in **Figure 20.2**.

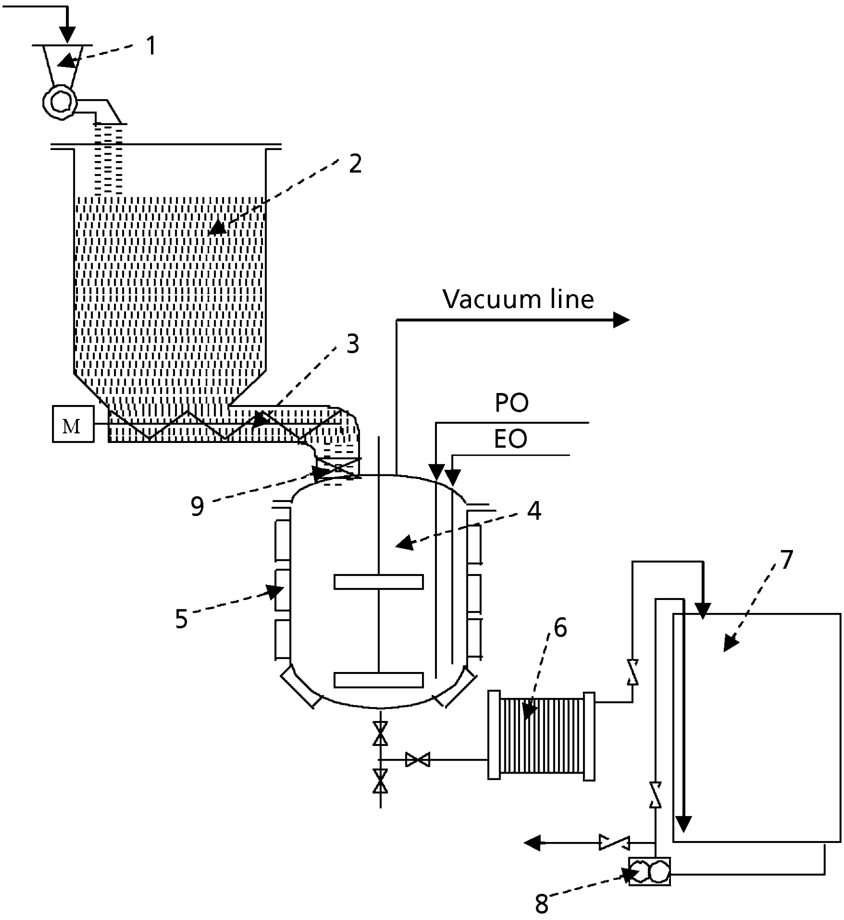


Figure 20.2 Technological scheme for recovery of rigid PU foam wastes by glycolysis process (variant) *1: Mills for PU scrap; 2: Storage of ground rigid PU foam; 3: Screw for powdered materials; 4: Glycolysis and alkoxylation reactor; 5: Electrical induction heaters; 6: Filter press; 7 Storage tank for the recovered polyol; 8: Gear or screw (or double screw) pump; 9: Valve*

The grinding of PU foam wastes is realised with: cryogenic mills, ball mills, two roll mills, solid state extrusion, pellet mills. A very efficient pulverisation process by using a two roll mill was commercialised by Henecke [34]. Fine to very fine particles of PU foam wastes are obtained.

The glycolysis reaction consists of the stepwise addition of finely ground rigid PU foam wastes, to DEG with a continuous screw feeder, in the presence of a catalyst (NaOH, KOH, LiOH), at atmospheric pressure, under an inert atmosphere of nitrogen, for several hours, at 185-210 °C. After the addition of all rigid PU waste, the reaction is digested with stirring for around 1-2 hours.

The resulting product of glycolysis, a dark brown liquid, which contains primary amino groups due to the reaction of DEG with urea groups, is reacted with an alkylene oxide (PO or EO or both), at 100-120 °C, to transform the amino groups to tertiary alkanolamines. After the alkylene oxides addition, the reaction mass is digested for 1-2 hours. The remaining alkylene oxides are removed by normal degassing procedures, by vacuum distillation.

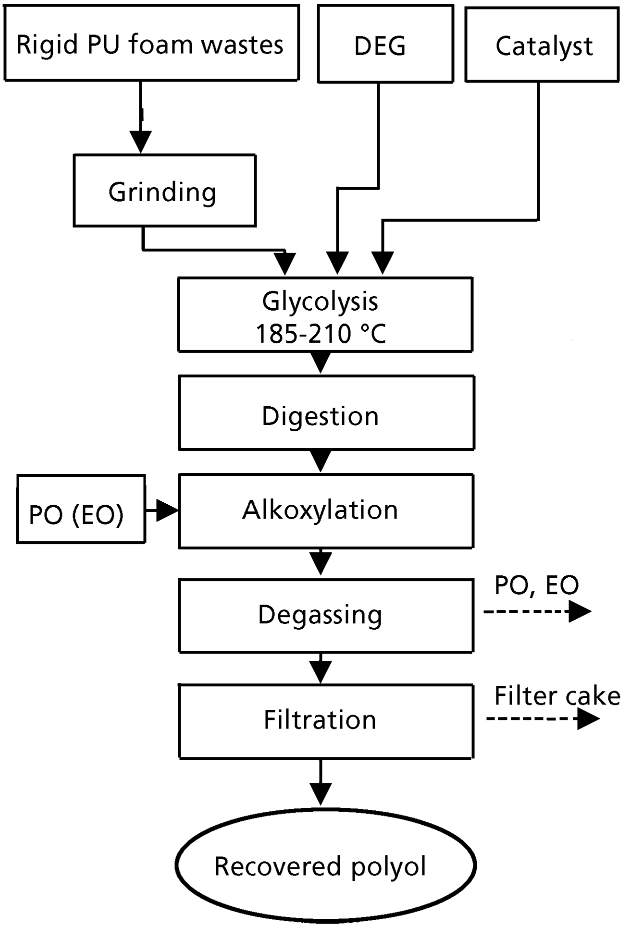


Figure 20.3 Schematic of the flow reaction for the chemical recovery of rigid PU foam wastes by glycolysis process

The recovered polyol is filtered on a convenient filter (for example a press filter) to remove the traces of solid materials, i.e, paper, unreacted ground rigid PU foams and so on. The resulting recovered polyol has the characteristics given in **Table 20.2**.

A schematic diagram of the chemical recovery of rigid PU foam wastes by glycolysis is presented in **Figure 20.3**. Similar technological flows would be used for aminolysis or aminolysis - alkoxylation processes.

References

1. T.M. Gritsenko, V.P. Matyushov and L.V. Stepanenko, *Plasticheskie Massy (USSR),* 1980, 7, 51

2. B.D. Bauman, P.E. Burdick, M.L. Bye and E.A. Galla in *Proceedings of the SPI 6th International Conference, PU – New Paths to Progress*, San Diego, CA, USA, 1983, p.139-141.

3. B-U. Kettemann, M. Melchiorre, T. Münzmay and W. Rasshofer, *Kunststoffe Plaste Europe*, 1995, **85**, 11, 33.

4. S.L. Madorsky and S. Straus, *Journal of Polymer Science,* 1959, **36**, 130, 183.

5. J. Ingham and N.S. Rapp, *Journal of Polymer Science: Part A,* 1964, **2**, 11, 4941.

6. J.N. Tilley, H.G. Nadeau, H.E. Reymore, P.H. Waszeciak and A.A.R. Sayigh, *Journal of Cellular Plastics*, 1968, **4**, 2, 56.

7. M. Paabo and B.C. Levin, *Fire and Materials*, 1987, **1**, 1, 1.

8. J. Chambers, J. Jiricny and C.B. Reese, *Fire and Materials*, 1981, **5**, 4, 133.

9. W.D. Woolley, *British Polymer Journal,* 1972, **4**, 1, 27.

10. J.I. Myers and W.J. Farrisey, *Energy Recovery Options for RIM PU*, SAE Technical Paper, SAE, Warrendale, PA, USA, 1991, Paper Number 910583.

11. H. Ulrich, A. Odinak, B. Tucker and A.A.R. Sayigh, *Polymer Engineering and Science,* 1978, **18**, 11, 844.

12. J. Gerlock, J. Braslaw and M. Zinbo, *Industrial and Engineering Chemistry, Product Design and Development,* 1984, **23**, 3, 545.

13. G.A. Campbell and W.C. Meluch, *Environmental Science and Technology,* 1976, **10**, 2, 182.

14. G.A. Campbell and W.C. Meluch, *Journal of Applied Polymer Science*, 1977, **21**, 2, 581.

15. L.R. Mahoney, S.A. Weiner and F.C. Ferris, *Environmental .Science and Technology,* 1974, **8**, 2, 135.

16. J. Braslaw and J.L. Gerlock, *Industrial and Engineering Chemistry, Product Design and Development,* 1984, **23**, 3, 552.

17. T.M. Chapman, *Journal of Polymer Science: Polymer Chemistry Edition,* 1989, **27**, 6, 1993.

18. J.L. Serlock, J. Braslaw, L.R. Mahoney and F.F. Ferris, *Journal of Polymer Science: Polymer Chemistry Edition,* 1980, **18**, 2, 541.

19. *Rubber Age*, 1975, **107**, 6, 52.

20. *Polymer Age*, 1975, 6, 8, 215.

21. M. Regent, *Kunststoffe*, 1976, **66**, 4, 242.

22. O.B. Johnson, inventor; Ford Motor Company, assignee; US 4,025,559, 1977.

23. E. Grigat, *Matériaux et Techniques*, 1978, **66**, 4, 141.

24. E. Grigat, *Kunststoffe*, 1978, **68**, 5, 281.

25. H. Ulrich in *Advances in Urethane Science & Technology, Volume 5*, Eds., K.C. Frisch and S.L. Reegen, Technomic, Lancaster, PA, USA, 1978, p.49-57.

26. J.Penfold and J.Kuypers, *Syspur Reporter*, 1976, **12**, 56.

27. No inventor; Bayer AG, assignee; FR 2,283,766B1, 1979.

28. F. Simioni, S. Bisello and M. Cambrini , 1983, *Macplas,* **8**, 47, 52.

29. F. Simioni, S. Bisello and M. Tavan, *Cellular Polymers,* 1983, **2**, 4, 281.

30. A. Sayigh, F. Frulla and A. Odinak, inventors; Upjohn Co.mpany, assignee; US 3,738,946, 1973.

31. M.B. Sheratte, inventor; McDonnell Douglas Corporation, assignee; US 4,110,266, 1978.

32. N. Matsudaira, S. Muto, Y. Kubota, T. Yoshimoto and S. Sato, inventors; Bridgestone Tire Co. Ltd., assignee; US 3,404,103, 1968

33. W.R. McElroy, inventor; Mobay Chemical Corporation, assignee; US 3,117,940, 1968

34. R. Herrington and K. Hock, *Flexible PU Foams*, Dow Chemical Company, USA, 1997, p.14.1-14.17.

35. M. Ionescu, unpublished work.

36. H.R. van der Wal in *Proceedings of UTECH 94*, The Hague, The Netherlands, 1994, Paper No.53.

37. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Proceedings of the SPI Annual Conference*, 1994, Boston, MA, USA, p.506.

38. M. Ionescu, V. Dumitriu, I. Mihalache, F. Stoenescu and S. Mihai, inventors; Institutul de Cercetari Chimice, assignee; RO 89,944, 1986.

39. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Advances in Urethane Science & Technology,* Eds., D. Klempner and K.C. Frisch, ChemTec Publishing, Ontario, Canada, 1998, p.151-218.

40. H.R. van der Wal, *Proceedings of the SPI 34th Annual PU Conference*, New Orleans, LA, USA, 1992, p.560-564.

41. S. Waddington and A.W. Duff in *Proceedings of the PU World Congress 1993*, Vancouver, BC, USA, 1993, p.558-563.

21 Relationships Between the Oligo-Polyol Structure and Polyurethane Properties

The structure - property relationships in polyurethanes (PU) have been excellently presented in the general monographs on PU [1-11]. As a consequence, this chapter will not be very long and it will present only the specific general effects of the oligo-polyol's structure on the resulting polyurethane properties.

Several general properties, characteristic to classical macromolecular chemistry, are strongly linked to the polyurethane structure, as a direct consequence of the oligo-polyol structure - these are [1, 2, 5, 9, 11]:

a) Molecular weight (MW),

b) Intermolecular forces,

c) Stiffness of chain,

d) Crystallinity, and

e) Crosslinking.

21.1 Molecular Weight

As a general rule, for linear polymers all the properties, such as tensile strength, elongation, elasticity, melting points, glass transition temperature (T_g), modulus and increase of the MW, increase up to a limited value, where all the properties remain practically constant. This behaviour is valuable for linear polymers, in our particular case in linear polyurethanes (PU elastomers, 'spandex' fibres, etc).

For crosslinked polymers (in this category they are the majority of polyurethanes, for example flexible, semiflexible and rigid PU foams, etc.), which have a MW that is practically infinite [12], the molecular weight between the branching points (M_c) is considered. The value of M_c depends strongly on the oligo-polyol structure.

21.1.1 The Effect of the Molecular Weight of Oligo-Polyols

The MW of oligo-polyols, is usually in the range of 400 to 6500 daltons, and it has an important effect on the polyurethane properties. Thus, if the polyol has a low MW, a hard polyurethane will result and if the polyol has a high MW, it creates elastic, flexible polyurethanes. Intermediate MW lead to semirigid or semiflexible structures [2].

It is clear that a short oligo-polyol chain (a short chain derived from one hydroxyl group or with a low equivalent weight) leads to higher concentrations of urethane and urea bonds. The high cohesive interaction between these bonds (mainly by secondary hydrogen bonds) leads to a rigid structure, i.e., to hard polyurethanes. This effect is combined with the high functionality that is characteristic of oligo-polyols for rigid PU foams.

On the contrary, in a long oligo-polyol chain (the chain derived from one hydroxyl group is long or the equivalent weight of the polyol is high), the concentration of urethane and urea bonds is lower, the cohesive interaction between these bonds decreases significantly and combined with the high mobility and elasticity and low T_g in the main chain of the polyol, results in a very elastic PU structure.

Thus, from high MW diols (MW = 1000-4000 daltons) polyethers (polyalkyleneoxides, polytetrahydrofuran (PTHF)), polyesters, polycarbonates (PC), polybutadienes, etc., by the reaction with diisocyanates [toluene diisocyanate (TDI), or ‘pure’ diphenyl methane diisocyanate (MDI)], high MW linear polyurethanes are obtained (no crosslinking), with high elasticity (polyurethane elastomers, spandex fibres, some adhesives and sealants, etc).

From high MW triols or low branched oligo-polyols (MW = 3000-6500 daltons): polyethers, polyesters, filled polyols (polymer polyols), are obtained elastic PU with a low degree of crosslinking (flexible and semiflexible foams, coatings etc).

From low MW oligo-polyols (400-1000 daltons; polyethers, polyesters, Mannich polyols, aromatic polyesters, oleochemical polyols, etc.), are obtained rigid, hard polyurethane structures (rigid PU foams, wood substitutes, etc).

An interesting remark for the thermoplastic polyurethane elastomers which are linear polyurethanes. These are polymers at room temperature which are hypothetically ‘crosslinked’ or ‘vulcanised’, by secondary forces between the polymeric chains, not by chemical bonds as in real crosslinked polymers. These secondary bonds are in fact strong hydrogen bonds between urethane and urea groups (hard segments - see Chapter 3). At higher temperatures, these secondary bonds are destroyed and the polyurethane elastomer becomes a melted polymer, that can be processed by injection or by extrusion processes, characteristic of thermoplastic polymers. After cooling, the hydrogen bonds between urea and urethane bonds are regenerated and the material again becomes an elastomer. This is the origin of the name 'thermoplastic elastomer', at higher temperatures it behaves like a thermoplastic material and at room temperature like an elastomeric material [8, 13-15]. The thermoplastic polyurethane elastomers are part of the group of thermoplastic elastomers together with styrene-butadiene rubber block copolymers (SBR), polyether-polyester block copolymers or polyamide-polyether block copolymers. Very important processes in polyurethane fabrication are reaction injection moulding (RIM) and reinforced reaction injection moulding (RRIM) processes, in which the thermoplastic polyurethane is obtained in a reactive manner, the reaction between two liquid components, i.e., liquid polyolic component and liquid isocyanate component (isocyanate, prepolymer or quasiprepolymer) [8, 13-15] is developed directly in the process of injecting.

The effect of the MW of some oligo-diols, such as polypropyleneglycols, polytetramethyleneglycols and poly(ethylene adipate) glycols upon the properties of the resulting polyurethane elastomers is significant. It was observed experimentally that some properties, such as the hardness and tensile strength, decrease with the oligo-diol MW increase. The strongest decrease was observed in polypropylene glycol based PU elastomers, but polytetramethylene glycols and poly (ethylene adipate) glycols based PU elastomers also show a slow decrease. The elastic properties, such as rebound resiliency and ultimate elongation, increase with the molecular weight of oligo diol, the best properties being obtained in PU elastomers based on polytetramethylene glycols and poly (ethylene adipate) glycols [2].

The abrasion loss of PU elastomers is markedly improved with the MW increase of the oligo-glycol. PU elastomers based on polytetramethylene glycols and on poly(ethylene adipate) glycols have the lowest abrasion loss. Polypropylene glycols (obtained in anionic catalysis) lead to PU elastomers with poorer abrasion resistance [2].

The independent effect of the molecular weight of oligo-polyols is possible only in linear polyurethanes (practically only in the case of oligo-diols). In crosslinked polyurethanes there is a cumulative effect of MW and functionality and the independent effect of the molecular weight of oligo-polyol is difficult to achieve. In order to have a better description and understanding of a crosslinked structure the notion of molecular weight between branching points (M_c) was introduced.

Generally by increasing the MW between the branching points some properties of crosslinked polyurethanes, such as: tensile strength, elongation, modulus and tear strength increase, while the hardness decreases [2].

In rigid polyurethane foams a strong dependence was observed between the hydroxyl number of oligo-polyol and the dimensional stability of the resulting rigid PU foams (hydroxyl number is a measure of the MW of an oligo-polyol, a high hydroxyl number represents low MW polyols and low hydroxyl numbers represent higher MW polyols).

Thus, high hydroxyl number polyols lead to better dimensional stability and higher compression strength in the resulting rigid PU foams than the lower hydroxyl number polyols [7]. Contrary to this effect, the increase of hydroxyl number of oligo-polyols leads to a marked increase in friability of the resulting rigid PU foams [7]. Lower hydroxyl numbers lead to lower friability rigid PU foams [7].

21.2 Intermolecular Forces [1, 2, 5, 9]

The secondary weak forces between polymeric chains (the attractive forces between the polymer molecules) have a very important role in solid polymer properties and confer the capability to resist mechanical, thermal, chemical, and electrical forces. These secondary forces are: Van der Waals forces (around 0.5-2 kcal/mol), hydrogen bonds (around 3-7 kcal/mol), London dispersion forces, permanent dipol interaction forces (1.5-3 kcal/mol), and ionic bond interactions (10-20 kcal/mol). All these forces give the cumulative cohesive energy. The nature of oligo-polyol chains has a profound effect on the physico-mechanical properties of the resulting PU, because the repeating units have various cohesive energies of functional groups.

A stronger cohesive energy, leads to higher physico-mechanical properties. Of course, in polyurethanes, the main contribution to the cohesive energy is due to the urethane and urea bond interactions and to the aromatic rings of the isocyanates which have a cumulative effect on the cohesive energy. As a general rule, lateral substituents and crosslinking decrease the intermolecular interactions.

21.2.1 The Effect of the Chemical Nature of Oligo-Polyol Chains

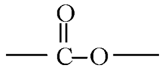
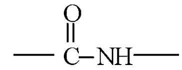
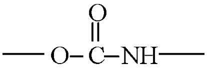
Table 21.1 shows the molar cohesive energies of functional groups in oligo-polyols and in PU.

Based on the data in **Table 21.1**, the relative cohesive energy of oligo-polyols:polyether polyols, polyester polyols and polyhydrocarbon polyols (for example polybutadiene or hydrogenated polybutadiene) occur in the following order:

polyester polyols > polyether polyols > polyhydrocarbon polyols

This relative order explains that numerous physico-mechanical properties of the polyurethanes based on polyester polyols are superior to the polyurethanes derived from polyether polyols or from polyhydrocarbon polyols (this relative order is valuable for PU elastomers, flexible and rigid PU foams).

Table 21.1. The molar cohesive energies of functional groups in oligo-polyols and in PU

Structure	Name of the group	Cohesive energy, kcal/mol
$-\mathrm{CH_2}-$	hydrocarbon	0.68
$-\mathrm{O}-$	ether	1.00
 $-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{O}-$	ester	2.90
$-\mathrm{C_6H_4}-$	aromatic	3.80
 $-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{NH}-$	amide	8.50
 $-\mathrm{O}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{NH}-$	urethane	8.74

In **Table 21.1** one can see that the cohesive energy of aromatic units is higher than that of ether or ester units. The presence of aromatic rings (especially in polyether and in polyester polyols) leads to a strong increase in some physico-mechanical properties, such as tensile strength and compression strength, with a decrease in elastic properties, such as ultimate elongation [7].

The effect of aromatic content, which confers rigidity to the resulting rigid PU foams is very evident in rigid oligo-polyols. Thus, an aromatic polyol of low functionality (for example a Mannich polyol of f = 3 OH groups/mol) gives higher physico-mechanical properties and better dimensional stability, compared to a similar rigid PU foam derived from an aliphatic polyol of the same functionality, (e.g., a rigid polyether polyol based on glycerol).

Table 21.2 shows the strength of the covalent bonds existing in oligo-polyols and in polyurethanes.

Thus, oligo-polyols having in the main chain covalent bonds with higher dissociation energy (C=O, C=C, C-F) lead to much more thermostable polyurethanes than the oligo-polyols having covalent bonds with lower dissociation energy (C-O, C-N or C-Cl bonds). As a general rule, polyether polyols having C-O bonds lead to polyurethanes with a lower thermostability than polyester polyols (having C=O bonds). Aminic polyols, lead to lower thermostable polyurethanes due to the low dissociation energy of C-N bond. Oligo polyols having in the main chain double bonds or aromatic content (conjugated double bonds) lead to much more thermostable polyurethanes than aliphatic saturated oligo-polyols.

Table 21.2 The strength of the covalent bonds existing in oligo-polyols and in polyurethanes

Covalent bond	Dissociation energy, kcal/mol
$C \equiv N$	213
$C = O$	174
$C = C$	146
C—F	103-123
O—H	111
C—H	99
N—H	93
C—O	86
C—C	83
C—Cl	81
C—N	73
C—S	62
O—O	35

As another general rule, more thermostable oligo-polyols give polyurethanes with improved fire resistance. Aromatic polyols sometimes give polyurethanes with intrinsic fire resistance, due to the very high char yield generated during the burning process [6].

21.3 Stiffness of the Chain

Flexible bonds (such as ether bonds) which permit a molecular flexibility due to the free rotation around the bonds (around C-O bonds) favour softness, elasticity, low melting points and low T_g [1, 2, 8]. Rigid chemical groups in polymer chains, which do not permit a molecular flexibility and free rotation, such as cycloaliphatic rings, aromatic rings, heterocyclic rings cause: hardness, high melting points, high T_g and decrease the elasticity.

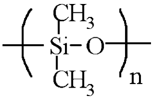
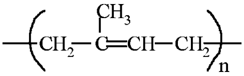
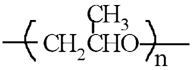
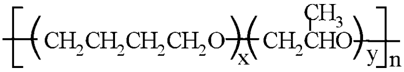
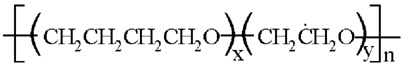
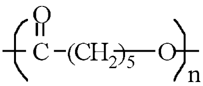
Molecular flexibility depends on the freedom of rotation around single bonds in the main chain of the polymer molecule, restrictions in this free rotation reduce the flexibility [2].

In linear aliphatic chains having C-C-C-C-C- bonds, free rotation around the C-C bonds is characteristic but this is restricted by the electropositive repulsion between adjacent H atoms. When a CH_2 group is replaced by oxygen (as in polyether chains), the rotation around the C-O bond (without hydrogen atoms) is easier and the molecule is more flexible. If a steric hindrance appears, it restricts the rotation around the main chain and the molecule becomes stiffer (for example cycloaliphatic groups). Aromatic rings in the main chain introduce large rigid units and strongly reduce the molecule flexibility.

The T_g is connected with the flexibility of polymeric chains. A low T_g of the oligo-polyol segment in polyurethanes is very important because it conserves the high elasticity at lower temperatures.

Table 21.3 shows the T_g of some important polymers for oligo-polyols structure.

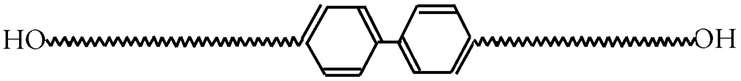
Table 21.3 The glass transition temperatures of some important polymers for oligo-polyols structure

Polymer	Repeat unit	Glass transition temperature, T_g (°C)
Polydimethylsiloxane	 $\left(-Si(CH_3)_2-O- \right)_n$	- 123
Polyisoprene (1,4 cis)	 $\left(-CH_2-C(CH_3)=CH-CH_2- \right)_n$	-73
Polybutadiene (1,4 cis)	$\left(-CH_2-CH=CH-CH_2- \right)_n$	-95
PTHF	$\left(-CH_2CH_2CH_2CH_2O- \right)_n$	-86
Polypropylene oxide (PO)	 $\left(-CH_2CH(CH_3)O- \right)_n$	-64
Copolymer THF - PO	 $\left[\left(CH_2CH_2CH_2CH_2O \right)_x \left(CH_2CH(CH_3)O \right)_y \right]_n$	-76.9
Copolymer THF - EO	 $\left[\left(CH_2CH_2CH_2CH_2O \right)_x \left(CH_2CH_2O \right)_y \right]_n$	-64.6
PCL	 $\left(-C(=O)-(CH_2)_5-O- \right)_n$	-60
THF: tetrahydrofuran		

21.4 Crystallinity

Crystallisation in polyurethanes is the organisation of different groups in a regular manner, in crystalline regions, which is another way to decrease the molecular flexibility and mobility of the polymeric chains [2]. As an immediate consequence of this mobility decrease in polyurethane polymers, hardness, tensile strength, melting point increase and the solubility, elongation and the flexibility generally decrease. Polyurethanes with crystalline regions are obtained from crystalline oligo-polyols. Generally, the majority of oligo-polyols are amorphous liquids. Some oligo-polyols show crystallinity such as: polytetramethylene glycols, poly (ε-caprolactone) polyols, poly (ethylene adipate) glycols and some other polyester polyols and polyethylene glycols .

Liquid crystalline polyurethanes are obtained by using oligo-polyols containing mesogenic units, such as biphenyl units:



21.5 Crosslinking

Crosslinking in polyurethanes leads to a decrease in the molecular mobility and flexibility and causes an increase of rigidity, softening points and modulus of elasticity and reduces elongation and swelling by solvents (only linear polymers are soluble, crosslinked polymers are only swelled by the organic solvents).

The degree of crosslinking depends firstly on the functionality of oligo-polyols and on the MW between the branch points (in fact on the MW of the oligo-polyol).

21.5.1 The Effect of Oligo-Polyol Functionality

The functionality of the oligo-polyol (the number of hydroxyl groups/mol), has a strong influence on the stiffness of the resulting polyurethanes. As mentioned before, high molecular weight oligo-polyols with low functionality (f = 2-3 OH groups/mol) lead to low crosslink density flexible, elastic polyurethanes and the reverse, low MW oligo-polyols, with high functionality (f = 3-8 OH groups/mol) lead to high crosslink density rigid polyurethanes.

This behaviour concerning the cumulative effect of functionality and molecular weight of oligo-polyols is observed in the case of PU foams (flexible, semiflexible and rigid) based on stress-strain relationship [2, 12].

Flexible foams have low load bearing properties and high recovery properties. Rigid polyurethane foams have high load bearing properties with a definite yield point and lack recovery. Semiflexible foams display higher load bearing properties as compared to flexible PU foam, but without definite yield point and good recovery properties.

These good recovery properties are the reason why the preferred term is semiflexible foams and not semirigid foams.

In the area of rigid polyurethane foams, the oligo-polyol functionality has a major influence on the compression strength and on the tensile strength. The compression strength increases if the functionality increases but the tensile strength decreases if the functionality increases. It is well known that if the oligo-polyol functionality increases, the crosslink density of the resulting rigid PU foams increases together with an increase in friability. The highly crosslinked rigid foams, such as isocyanuric foams or urethane-isocyanuric foams, have higher friability.

Dimensional stability of rigid PU foams (a very important characteristic in the thermoinsulation of refrigerators, especially at lower temperatures) is strongly improved by using high functionality oligo-polyols.

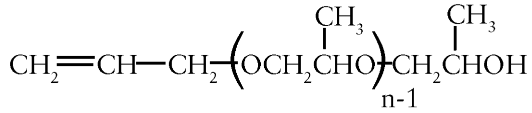
The conversion at gel point in polyurethane processes depends strongly on the medium functionality of the reaction system [5]. Thus, lower functionalities give high conversion at the gel point and high functionalities give low conversion at the gel point. This is the reason why sometimes the best properties of rigid PU foams are not obtained at very high functionalities of oligo-polyols (for example f = 7-8 OH groups/mol), but at medium functionalities (f = 4.5-5.5 OH groups/mol). **Table 21.4** shows the theoretical conversions at gel point, in rigid PU foams (by using a difunctional isocyanate).

Fortunately, after the gel point, the reaction between unreacted -NCO groups and unreacted OH groups continues slowly, over time, and the properties are improved, especially when very high functionality oligo-polyols are used which is when the best dimensional stabilities are obtained.

Table 21.4 Conversion at gel point as function of oligo-polyol functionality and isocyanate functionality

Oligo-polyol functionality	2	3	4	6	8
Functionality of isocyanate	Degree of reaction at gel point (%)				
2	-	72	58	45	38
3	72	50	33	20	14

A very subtle effect of the oligo-polyols functionality is seen in the case of propoxylated polyether polyols, due to the presence in oligo-polyol composition of a polyether monol as a consequence of the rearrangement of PO to allyl alcohol during anionic PO polymerisation (see section 4.1), with this structure:



$$CH_2{=}CH{-}CH_2{-}\left(OCH_2\overset{CH_3}{\overset{|}{C}}HO\right)_{n-1}CH_2\overset{CH_3}{\overset{|}{C}}HOH$$

Thus, a polyether triol is in reality a mixture between a polyether triol, a polyether diol and a polyether monol. The real functionality of a polyether triol derived from glycerol is not 3 OH groups/mol, but is lower, being situated in the range of 2-3 OH groups/mol [16]. The polyether diols are a mixture between a polyether diol and a polyether monol, the real functionality being lower than f = 2, situated in the range f = 1.5-2 OH groups/mol [17].

The functionality decrease in polyether polyols synthesised in anionic catalysis is more significant at higher MW polyethers.

Figure 21.1 shows the functionality decrease function of the polyether diols MW while **Figure 21.2** shows the variation of the functionality against the polyether triol MW.

The presence of the polyether monol leads to very modest properties of polyurethanes based on polypropylene glycols obtained by anionic catalysis. In polyaddition reactions involved in polyurethane synthesis a monofunctional polyether is a chain stopper and

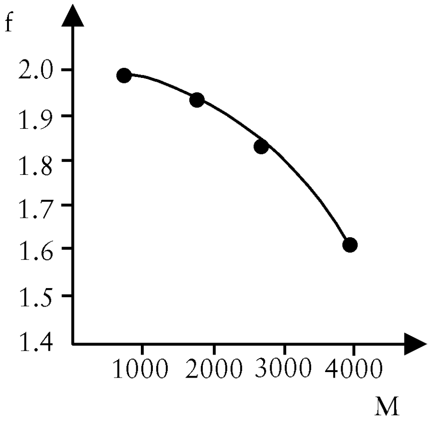


Figure 21.1 Functionality of polyether diols, PO homopolymers, obtained in anionic catalysis, as a function of the MW

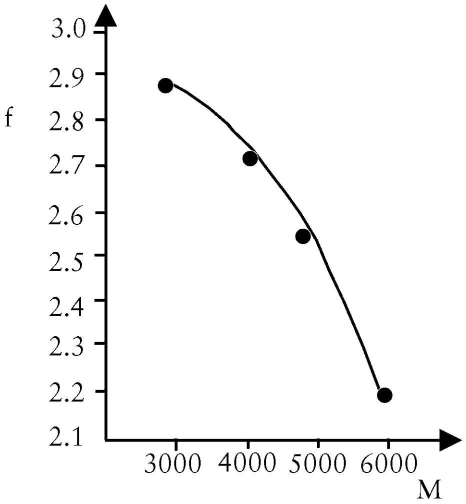


Figure 21.2 Functionality of polyether triols, PO homopolymers, obtained in anionic catalysis, as a function of the MW

decreases the molecular weight of final polyurethane. In flexible foams it was observed that a strong decrease in hardness, with higher MW polyether triols, is explained by the high content of polyether monols.

A spectacular increase in all properties was observed in elastic polyurethanes (especially in polyurethane elastomers, but in flexible foams too), by using polyethers obtained with dimetallic catalysts (DMC) instead of potassium hydroxide. There are obtained directly from synthesis, polyethers with a very low unsaturation, in essence polyethers with a very low content of polyether monols.

The polyether diols, PO homopolymers obtained with DMC catalysts (for example Bayer's Acclaim polyols) , having a functionality close to the theoretical functionality (f = 2 OH groups/mol), lead to polyurethane elastomers having a spectacular increase in all physico-mechanical properties such as: modulus, tensile strength, tear strength, elongation, hardness, etc. By using polyether diols, and PO homopolymers, with low monol content, linear polyurethanes of much higher molecular weight are obtained and as an immediate consequence all the properties of the resulting polyurethane elastomers increase (as mentioned in the section 21.1).

In flexible PU foams, obtained from polyether triols synthesised with DMC catalysts, an increase in many properties was observed, such as: hardness, resiliency, tear strength and an improvement in compression set [15].

Flexible polyether polyols based on high functionality starters (chain initiators) (for example a hexafunctional polyether polyol of equivalent weight 1000-2000, based on alkoxylation of sorbitol instead of glycerol), produces flexible PU foams with higher load bearing properties, but with a decrease in tensile strength and elongation. These polyols were used in carpet underlay [18].

21.5.2 The Effect of Oligo-Polyol Structure on the Polyurethane Behaviour in Contact with Organic Solvents and Water

The very polar urethane and urea groups and the very strong hydrogen bonding between these groups make polyurethanes very resistant to hydrocarbons and oils. This is one of the biggest advantages of PU elastomers over the conventional rubbers.

Linear polyurethanes dissolve in various solvents such as: ketones (methyl ethyl ketone, cyclohexanone, etc.), acetate alkyl esters (methyl acetate, butyl acetate), THF, dimethylformamide, methylene chloride, trichloroethane, etc.

The resulting solutions are frequently used for processing ‘spandex’ fibres, coatings, adhesives, synthetic leathers etc.

Crosslinked polyurethanes are not soluble and of course swell, the degree of swelling decreases with the increase in crosslink density. For example, for a flexible polyurethane foam in the presence of acetone, the degree of swelling is around 116% at a molecular weight between branch points (M_c) of 1650 and becomes 90% at a M_c of 1070 and 83% at a M_c of 690 [2].

The hydrolytic resistance of a polyurethane depends strongly on the nature of the oligo-polyol chain. As a general rule, very hydrophobic chains and water repellent polyols give polyurethanes with excellent hydrolytic stability. The relative order of the hydrolysis resistance of polyurethanes function of oligo-polyol nature is:

> oleochemical polyols, dimer acid based polyesters > polybutadiene polyols > PTHF > polyalkyleneoxide polyethers > PC-polyols > PCL-polyols > aliphatic polyesters based on diethylene glycol and adipic acid.

It is considered that the polyurethanes based on oleochemical polyols, dimer acids and dimer alcohols, PTHF and PC-polyols lead to polyurethanes with excellent hydrolytic stability. Polycaprolactone (PCL) polyols and poly (butylene adipate) lead to polyurethanes with good hydrolytic stability, but use of poly (diethylene glycol adipate) give polyurethanes with poor hydrolytic resistance.

Polyester urethanes are biodegradable by microbial attack (generally aliphatic polyesters are biodegradable). Polyurethanes based on oleochemical polyols are biodegradable too. This property, biodegradability, may be used for: controlled release for drugs, biodegradable packaging products, etc.

Biostability increases strongly by changing to polyether polyol based polyurethanes. Generally the polyethers are relatively non-toxic but nonbiodegradable products.

21.6 Thermal Stability and Flame Retardancy

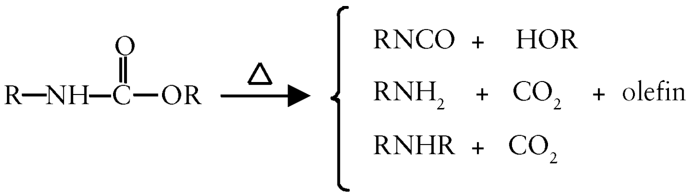
Based on the values of cohesive energies and dissociation energies of the bonds involved in the polyurethane structure, it may be possible to establish the following relative order regarding the thermal stability of polyurethanes function of the oligo-polyol structure:

polybutadiene polyols < polyether polyols < polyester polyols

aliphatic polyols < cycloaliphatic polyols < aromatic polyols

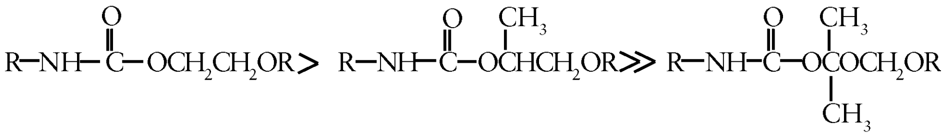
The thermostability of the urethane groups depends on the nature of isocyanate but at the same time on the nature of oligo-polyol terminal hydroxyl groups.

The general reaction of urethane groups decomposition is:



$$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}OR \xrightarrow{\Delta} \begin{cases} RNCO + HOR \\ RNH_2 + CO_2 + \text{olefin} \\ RNHR + CO_2 \end{cases}$$

Polyurethanes based on oligo-polyols with primary hydroxyl groups are more thermostable than the polyurethanes derived from polyols with secondary groups and much more thermostable than the polyurethanes derived from polyols with tertiary hydroxyl groups:



$$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}OCH_2CH_2OR > R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O\overset{\overset{CH_3}{|}}{C}HCH_2OR \gg R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}OCH_2OR$$

As a general rule the thermal stability of polyurethanes is directly linked with the mobility of polymeric chains. Low mobility, crosslinked polyurethane structures, based on high functionality polyols are more thermostable than the high mobility, low crosslinked polyurethanes (elastic polyurethanes). Generally cycloaliphatic structures and aromatic structures have low mobility and high rigidity. This is the explanation of the higher thermal resistance of polyurethanes based on cycloaliphatic and aromatic oligo polyols. Polyisocyanuric foams with a high degree of crosslinking have the highest thermostability in the area of rigid foams. Of course the thermal resistance of aromatic polyol based polyurethanes and of isocyanuric rigid foams is assured too by the high thermostability of the aromatic nucleus and of triazinic rings.

21.6.1 Flame Retardancy

The fire resistance of polyurethanes is based on the introduction of flame retardant compounds including polyols, containing chlorine, bromine or phosphorus in their structure. The polyols containing chlorine, bromine or phosphorus are linked chemically in the polyurethane structure and lead to self-extinguishing polyurethanes, with a permanent flame retardancy.

Generally, the polyurethanes without flame retardants burn completely, but some structural elements in the oligo-polyol architecture improve markedly, the fire resistance of the resulting polyurethanes.

Thus, the polyol nature has a marked effect on the fire resistance, which is in fact the order of thermostability. The most thermostable polyols lead to polyurethanes with improved fire resistance. Thus, polyesters are superior to polyethers in so far as the fire resistance of the resulting polyurethanes is concerned. Cycloaliphatic polyols (for example polyols based on carbohydrates, such as sucrose or alkyl glucosides) produce polyurethanes with superior fire resistance as compared to the simple aliphatic polyols (for example polyether based on glycerol or on pentaerythritol).

Aromatic polyols and triazinic polyols lead to polyurethanes with superior fire resistance due to the high char yield generated during the burning process. Sometimes, the rigid polyurethanes based on aromatic and triazinic polyols have an intrinsic flame retardancy (gives self-extinguishing foams without the addition of flame retardants).

Flame retardant flexible foams are very difficult to obtain due to the low crosslink density, low aromaticity, open cell structure and long polyolic aliphatic chains. Generally, flame retardants flexible foams are produced with additive flame retardants, for example with powdered melamine + tris (2-chloropropyl) phosphate [14].

Flame retardant rigid PU foams, due to their high aromaticity, and high crosslink density are easier to be obtain. An aromatic polyol has a supplementary contribution to improving the fire resistance (for example Mannich polyols, novolak polyols, triazinic polyols based on melamine, etc). For flame retardant rigid PU foams, reactive flame retardants are preferred (bromine polyols or phosphorus polyols, see Chapter 18).

References

1. G. Oertel, *Polyurethane Handbook*, Hanser Verlag, Munich, Germany, 1985.
2. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, Chapter 2, p.1-19 and Chapter 3, p.1-39.
3. H.R. Gillis in *Modern Plastic Encyclopedia Handbook*, Ed., Modern Plastics Magazine, McGraw-Hill, Inc., New York, NY, USA, 1994, p.82.
4. *Advances in Polyurethane Technology*, Eds., J.M. Buist and H.A. Gudgeon, McLaren and Sons, Ltd., London, UK, 1968.
5. J.H. Saunders and K.C. Frisch, *Polyurethanes: Chemistry and Technology*, Interscience Publishers, New York, NY, USA, 1962, Chapters 6, 9 and 12.
6. J.W. Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, NY, USA, 1970, Chapter 8.
7. T.H. Ferrigno, *Rigid Plastics Foams*, 2nd Edition, Reinhold, New York, NY, USA, 1967.
8. *Polyurethane Technology*, Ed., P.F. Bruins, Interscience Publishers, New York, NY, USA, 1969.
9. *The ICI Polyurethanes Book*, Second Edition, Ed., G. Woods John Wiley & Sons, Chichester, UK, 1990.
10. D.W. Baugh, Jr., in *Reaction Polymers*, Eds., W.F. Gum and W. Riese and H. Ulrich, Hanser Publishers, New York, NY, USA, 1992, p.259-357.
11. R. Becker, *Polyurethanes*, VEB, Leipzig, Germany, 1983.
12. D.W. Vilar, *Chemistry and Technology of Polyurethanes*, Third edition, Vilar Polyurethanes, Rio de Janeiro, Brazil, 2002.
13. D.J. Sparow and D. Thorpe in *Telechelic Polymers: Synthesis and Applications*, Ed., E.J. Goethals, CRC Press, Boca Raton, FL, USA, 1989, p.181.

14. O.M. Grace, R.E. Mericle and J.D. Taylor, *Journal of Cellular Plastics*, 1985, **21**, 5, 311.

15. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, USA, 1953.

16. N. Barksby, S.D. Seneker and G.L. Allen, *Urethanes Technology*, 2000, **13**, 1, 36.

17. J.L. Schuchardt and S.D. Harper, *Proceedings of the 32nd Annual Polyurethanes Technical/Marketing Conference*, *Polyurethanes '89*, San Francisco, CA, USA, 1989, p.360.

18. M. Yotsuzuka, A. Keshi, N. Hashimoto, K. Kodama and S. Nakahara, inventors; Takeda Chemical Industries, assignee; US 3,433,751, 1969.

Postface

This monograph 'Chemistry and Technology of Polyols for Polyurethanes' is in fact an introduction to the exciting world of polyols for polyurethanes.

This monograph has tried to give a flavour of the chemical subtleties of oligo-polyol manufacture based on a knowledge of classical organic and macromolecular chemistry. The objective was to explain, in a simple and accessible manner, the complex chemical and physico-chemical phenomena involved in oligo-polyol synthesis, which is extremely important in developing a fabrication technology.

The second objective of this monograph was to link together information about the large number of different oligo - polyols which are used to build the polyurethane architecture, which are totally different in chemical structure, but which have many things in common, such as:

- All oligo-polyols have terminal hydroxyl groups;
- All oligo-polyols have functionality (a definite number of hydroxyl grouyps/mol);
- All oligo-polyols have primary or secondary hydroxyl groups but not tertiary hydroxyl groups;
- All oligo-polyols are low molecular weight polymers, in the range of oligomer's molecular weight of 400-12000 daltons;
- All oligo-polyols are characterised by the same physico-chemical characteristics, determined by the same common analytical methods;
- The transformation of oligo-polyols in polyurethanes is based on a reactive process (the formation of high molecular weight polyurethane is a consequence of a chemical process);
- The majority of oligo-polyols are liquid or very low melting point solids and due to the low viscosities (much lower than those of melted polymers) are very easy and economical to process to form high molecular weight polyurethanes.

I hope that this way of approaching the use of oligo-polyols for making polyurethanes gives a better understanding of the profound aspects of oligo-polyol chemistry, to predict the relationships between the oligo-polyol structure and the properties of the resulting polyurethanes and to generate a model of thinking in this area, a starting point for creativity, to develop completly new, original oligo-polyol structures.

I hope that this monograph dedicated to oligo-polyols for polyurethanes, addressed to students, researchers, scientists, engineers, to all specialists in industry, universities, research centers and research institutes, will lead to the improvement of the existing technologies and to creating new fabrication processes.

I express my gratitude, the profound admiration and respect for the thousand and thousand of professors, specialists, experts, researchers, scientists from chemical companies, universities and research centres, who with their imagination, creativity and serious research played a decisive role in the development of the polyol field for polyurethanes.

The present monograph is an homage to all the chemical companies who invested considerable human and material resources in the development of polyols for polyurethanes, one of the most dynamic group of polymers, that have changed and improved considerably, the quality of modern human life.

Bucharest, August 2005

Abbreviations

PG	1,2 Propyleneglycol
BD	1,4 Butanediol
HD	1,6 Hexanediol
HMDI	4,4´ Dicyclohexyl diisocianate
AH	Acid catalyst
ACN	Acrylonitrile
ABS	Acrylonitrile-butadiene-styrene copolymer
ACE	Activated chain end mechanism
AM	Activated monomer mechanism
AA	Adipic acid
AIBN	Azoisobutyrodinitrile
bp	Boiling point
BVT	Brookfield Viscosity Test
BHT	Butylated hydroxytoluene
BO	Butylene oxide
CPL	ε-Caprolactone
T_c	Ceiling temperature
DEG	Diethyleneglycol
DETA	Diethylenetriamine
DSC	Differential scanning calorimetry
DGBA	Diglycidyl ether of bisphenol A
DMC	Dimetallic catalyst(s)

DMPP	Dimethyl methyl phosphonate
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DMT	Dimethylterephthalate
MDI	Diphenylmethane diisocyanate
MDA	Diphenylmethanediamine
DPG	Dipropyleneglycol(s)
EW	Equivalent weight
EG	Ethylene glycol
EO	Ethylene oxide
EDA	Ethylenediamine
f	Functionality
GPC	Gel permeation chromatography
T_g	Glass transition temperature
H-H	Head-to-head type
H-T	Head-to-tail type
HDI	Hexamethylene diisocyanate
HXR	Hydrogen active compounds
OH#	Hydroxyl number
IR	Infra red
IV	Iodine value
IPDI	Isophorone diisocyanate
IPA	Isophthalic acid
LiOH	Lithium hydroxide
MA	Maleic anhydride
mp	Melting point
MMA	Methyl methacrylate
M_c	Molecular weight between the branching points
MWD	Molecular weight distribution

MW	Molecular weight(s) in atomic mass units (Daltons)
NPG	Neopentyl glycol
NMP	*N*-Methyl pyrolidone
NAD	Nonaqueous dispersant(s)
NMR	Nuclear magnetic resonance
M_n	Number average molecular weight
o-TDA	*Ortho*-toluene diamine
OXA	Oxazolidine
OIT	Oxygen absorption induction time
ppm	Parts per million
%OH	Percentage of hydroxyl
PA	Phthalic anhydride
PHD	Poly Harnstoff Dispersion
PET	Poly(ethylene terephthalate)
PCL	Polycaprolactone
PC	Polycarbonate(s)
PDI	Polydispersity index
PIPA	Polyisocyanate polyaddition polyols
PIR	Polyisocyanuric/urate foams
PAPI	Polymeric MDI
PPG	Polypropylene glycol
PTHF	Polytetrahydrofuran(s)
PTMG	Polytetramethylene glycol(s)
PU	Polyurethane(s)
KOH	Potassium hydroxide
CH_3OK	Potassium methoxide
PO	Propylene oxide
RIM	Reaction injection moulding
RRIM	Reinforced reaction injection moulding

NaOH	Sodium hydroxide
CH_3ONa	Sodium methoxide
St	Styrene
St-ACN	Styrene-acrylonitrile copolymer
SBR	Styrene-butadiene rubber
TBAH	Tetrabutyl ammonium hydroxide
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TDI	Toluene diisocyanate
TEOA	Triethanolamine
TMP	Trimethylolpropane
TCEP	Tris(2-chloroethyl) phosphate
TCPP	Tris(2-chloropropyl) phosphate
THEI	Tris (hydroxyethyl) isocyanurate
VPO	Vapour pressure osmometry
VOC	Volatile organic compounds
M_w	Weight average molecular weight

Index

Page numbers in *italics* refer to figures and numbers in **bold** refer to tables.

Rapra Technology Limited

Rapra Technology is the leading independent international organisation with over 80 years of experience providing technology, information and consultancy on all aspects of rubbers and plastics.

The company has extensive processing, testing and analytical facilities. It provides testing to a range of national and international standards and offers UKAS accredited analytical services. Rapra also undertakes commercially focused innovative research projects through multi-client participation.

Rapra publishes books, technical journals, reports, technological and business surveys, conference proceedings and trade directories. These publishing activities are supported by an Information Centre which maintains and develops the world's most comprehensive database of commercial and technical information on rubbers and plastics.

rapra
TECHNOLOGY

Shawbury, Shrewsbury, Shropshire SY4 4NR, UK
Telephone: +44 (0)1939 250383
Fax: +44 (0)1939 251118
http://www.rapra.net