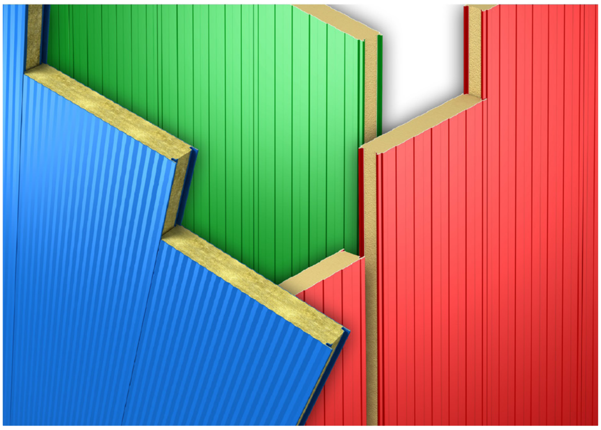
Chemistry and Technology of Polyols for Polyurethanes, 2nd Edition



Volume 2

Mihail Ionescu

SMITHERS RAPRA

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Dedication

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 in Rubber and Plastics Technology* has had great impact on the general worldwide development of polyurethane chemistry and polyurethane technology in the last five decades of the 20th 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.

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Acknowledgements

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

I am grateful to Professor Dr. Zoran S. Petrović, Research Director of Kansas Polymer Research Center (between 1994–2014), unanimously recognised as a world leader in the area of renewable polyols and polyurethanes (PU) based on natural compounds, for his continuous support and capability to open new valuable directions for scientific investigations.

I thank you very much to my colleagues from Kansas Polymer Research Center: Dr. Andy Myers, Dr. Ivan Javni, Xianmei Wan, Alisa Zlatanić, Dragana Radojčić, Nikola Bilić and others for helpful discussions, for synthesis and characterisation of new renewable polyols and of bio-based PU from these polyols.

I would like to thank Mrs. Helene Chavaroche, Commissioning Editor, and Mrs. Eleanor Garmson, Development Editor, from Smithers Rapra, for their effort, high competency and professionalism in producing the 2nd Edition of the book '*Chemistry and Technology of Polyols for Polyurethanes*' into two high quality volumes.

Preface

The decade 2005–2015 has seen impressive new developments in the synthesis of polyols for polyurethanes (PU). Due to the large amount of new information, the book *Chemistry and Technology of Polyols for Polyurethanes* (second edition) has been divided into two volumes. Volume 1 is dedicated to polyols for elastic PU and volume 2 is dedicated to polyols for rigid PU.

Polyols for rigid PU have two important characteristics: high functionality (3–8 hydroxyl groups/mol or more) and the chain derived from the 1-hydroxyl group is short (maximum 100–200 Da). As an immediate consequence of these two characteristics, reaction of these polyols with diisocyanates or polyiisocyanates leads to highly crosslinked rigid PU suitable for specific practical applications (e.g., rigid PU foams for thermal insulation of freezers, buildings, pipes and storage tanks for food and chemical industries; wood substitutes from rigid PU).

Main polyols for rigid PU are polyether polyols, polyester polyols, aminic polyols, polyols based on condensates of aromatic compounds with aldehydes (Mannich polyols, Novolac polyols), phosphorus polyols, and polyols by chemical recovery of PU foams wastes. A new group of polyols for rigid PU has been developed in the last decade: polyols synthesised by thiol-ene ‘click’ chemistry (described in detail in a special chapter of this monograph).

The most impressive research effort in 2005–2015 was dedicated to the synthesis of renewable polyols. That is, polyols based on natural compounds such as vegetable oils, fish oil, lignin, starch, castor oil, lactides, liquid from the shells of cashew nuts, terpenes, glycerol, polyglycerol, sucrose, sorbitol, xylitol, and isosorbide. Syntheses of polyols for PU-based renewable natural compounds are described in detail in a special chapter.

Use of natural compounds of infinite renewability as raw materials for synthesis of oligo-polyols (including polyols for rigid PU) is a real hope for the sustainable future of PU.

PU (including rigid polyurethanes) are polymers that burn completely. To protect human lives and materials used in everyday life (furniture, insulation of buildings, car seating), flame-retardant PU must be produced. Phosphorus polyols or bromine-containing polyols and reactive flame retardants have been produced for this purpose. These special polyols (which are described in a special chapter) enter into PU networks, thereby leading to the permanence of flame retardancy.

A special chapter is dedicated to the synthesis of polyols by chemical recovery of PU wastes. By various reactions (hydrolysis, alcoholysis, glycolysis, aminolysis, alkoxylation), PU wastes are transformed into useful new polyols. This strategy leads to substantial economy of energy and raw materials compared with classical routes of polyol synthesis.

The final chapter describes the relationship between the chemical structure of oligo-polyols and the characteristics of PU based on these polyols.

Covering all aspects and describing all the structures of oligo-polyols created during more than 75 years of PU is not possible. Nevertheless, the most important aspects of the synthesis and characteristics of polyols for rigid PU are detailed.

This monograph is addressed to all specialists working in the area of PU: students; researchers; scientists; engineers; professors; experts from industry, universities, research centers and research institutes.

I hope that this monograph will be the start of new and original developments in oligo-polyols for rigid PU, with new designs/architecture suitable for the manufacture of new rigid PU. Good luck in your endeavours!

Mihail Ionescu

February 2016

Contents

1

Polyols for Rigid Polyurethanes - General Considerations

In the previous chapters (**Volume 1**, **Chapters 4–11**) the chemistry and technology of oligo-polyols for elastic polyurethanes (PU) [flexible and semiflexible polyurethane foams (PUF), elastomers, adhesives, coatings, sealants, elastic fibres and microcellular elastomers] were presented. The elastic PU are the most important in commercial applications of PU, having around 72% of the global PU market. Rigid PU, especially in the form of rigid PUF, wood substitutes, flotation and packaging materials represent, at this moment, around 26% of the global PU market.

The oligo-polyols for rigid PU 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 (EW) 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] gives a highly crosslinked and very rigid PU structure. The high-density of urethane groups, as a consequence of their low EW, leads to strong and intensive interchain forces, by hydrogen bonds, and an increased rigidity. Thus, the oligo-polyols for rigid PU (mainly for rigid PUF), have a much higher hydroxyl number (OH#) than the oligo-polyols for flexible PU, for the majority of oligo-polyols in the average range of 300–600 mg potassium hydroxide (KOH)/g (some special polyols have a OH# 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 PU, 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 PU (**Volume 2**, **Chapter 11**). 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 PU structures [2] (**Volume 2**, **Chapters 4** and **5**).

The cellular structure of rigid PUF (the majority of rigid PU) is generated in two ways: in a reactive manner using water as a reactive blowing agent (the reaction of isocyanates with water generates gaseous carbon dioxide) or in an unreactive way with physical blowing agents which are low boiling point substances (such as pentanes, hydrofluorocarbons and so on), which are evaporated by the exothermic reaction between the hydroxyl groups of the oligo-polyols with isocyanate groups, with the simultaneous formation of a PU polymer, generating their cellular structure.

If the flexible foams have a predominantly open cell structure, the rigid PUF have a predominantly closed cell structure (more than 90% of the cells are closed), which confers to rigid PUF excellent thermoinsulation properties. As a consequence the main applications of rigid PUF 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 PUF 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 PUF leads to a considerable economy of energy e.g., 90% for storage tanks for 'crude' oil and 50% for thermoinsulation of buildings [5].

The most important oligo-polyols for rigid PU 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 (**Volume 2, Chapter 4**).

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 (**Volume 2, Chapter 3**).

By chemical recovery of polyester (polyethylene terephthalate) (**Volume 2, Chapter 5**) and PU wastes, by alcoholysis or by aminolysis (**Volume 2, Chapter 10**), new polyols are obtained that can be used in rigid PUF 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 (**Volume 2, Chapter 7**).

A special group of polyols for rigid PUF is the group of reactive flame retardant polyols containing phosphorus, chlorine or bromine, which confer fire resistance to the resulting PU (**Volume 2, Chapter 8**).

The nature of the oligo-polyol structure has a profound effect on the physico-mechanical, thermal and fire proofing properties of rigid PUF. 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 OH# (**Volume 2**, **Chapter 11**). Dimensional stability and friability vary in opposite directions, function of OH#, since higher OH# give better dimensional stability and higher friability (**Volume 2**, **Chapter 11**).

Generally, the polyether polyols for rigid PUF give softer foams and superior hydrolysis resistance than polyester polyols. At the same time, polyester polyols lead to more thermoresistant and fire resistant rigid PUF than the polyether polyols. Vegetable oil polyols confer onto the resulting rigid PUF hydrophobicity and an excellent compatibility with pentanes, used as blowing agents (**Volume 2**, **Chapter 7**).

Between 2005–2015, an impressive new development in the area of polyols for rigid PU from natural compounds has been carried out [e.g., natural oils (vegetable oils, fish oil, krill oil), lignin, starch, cellulose, limonene, lactides, proteins, terpenes, cashew nut shell liquid, betulinol and others (**Volume 2, Chapter 7**)].

After this general presentation of oligo-polyols for rigid PU, 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.

2. T.H. Ferrigno in *Rigid Plastic Foams,* 2nd Edition, Reinhold, New York, NY, USA, 1967.

3. M. Szycher in *Szycher's Handbook of Polyurethanes,* CRC Press, Boca Raton, FL, USA, 1999, 8, 1.

4. W. Green, G.M.F. Jeffs and D.J. Sparrow, *Plastics & Rubber International,* 1984, **9**, 5, 30.

5. M. Ionescu, Unpublished Work.

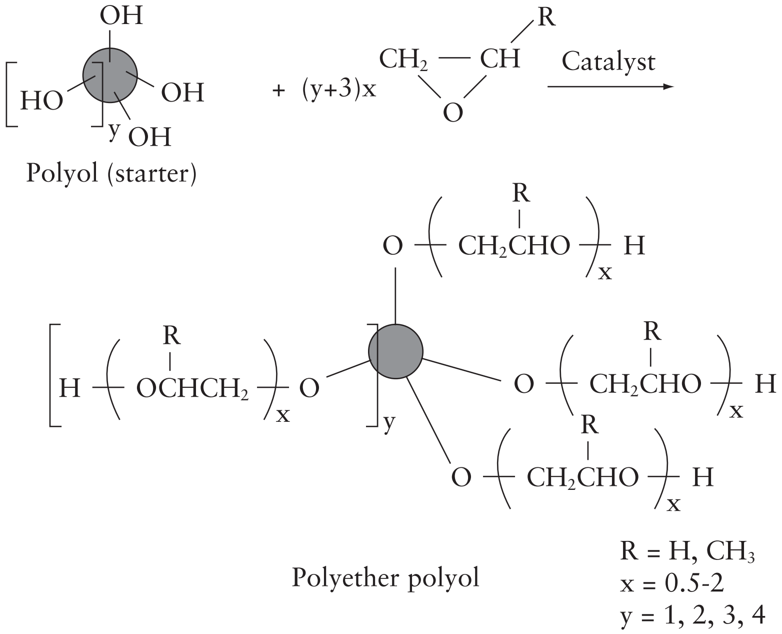
6. K.C. Frisch and J.E. Kresta in *Sucrochemistry*, Ed., J.L. Hickson, ACS Symposium Series No.41, American Chemical Society, Washington, DC, USA, 1976.

2

Polyether Polyols for Rigid Polyurethane Foams

Polyether polyols for rigid polyurethane foams (PUF) are low-molecular weight(s) (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 1 hydroxyl group being very short, approximately 0.5–2 alkylene oxide units. As mentioned previously, the hydroxyl number(s) (OH#) of these polyols is high, generally in the range 300–800 mg potassium hydroxide (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, approximately 60–200, as compared with polyether polyols for flexible PUF which have a much higher EW, of approximately 1,000–2,000.

The general synthesis reaction of polyether polyols for rigid PUF by polymerisation of alkylene oxides (PO, EO) initiated by polyolic starters is presented in **Reaction 2.1**.

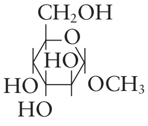
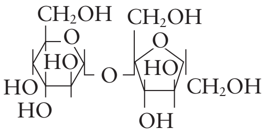


(2.1)

The most important low-MW polyols used as starters for polyether polyols destined for rigid PUF synthesis are: glycerol, trimethylolpropane (TMP), triethanolamine (TEOA), pentaerythritol (PER), dipentaerythritol, α-methyl glucoside, xylitol, sorbitol and sucrose [1–27]. The main properties of these starter polyols, which are of interest for polyurethane(s) (PU) chemistry, are presented in **Table 2.1**.

In **Table 2.1** one observes that some polyols used as starters have an aliphatic structure (glycerol, PER, 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 PUF with superior physico-mechanical, thermal and fire resistance properties compared to the polyether polyols having aliphatic structures, at the same functionalities and OH#.

Table 2.1 Some characteristics of polyols used frequently as starters for polyether polyols for rigid PUF

No.	Polyol used as starter	Formula	MW (daltons)	f	OH# (mg KOH/g)
1	Glycerol	$HOCH(CH_2OH)_2$	92.10	3	1,827.3
2	TMP	$CH_3CH_2C(CH_2OH)_3$	132.0	3	1,275.0
3	TEOA	$N(CH_2CH_2OH)_3$	149.19	3	1,128.0
4	PER	$C(CH_2OH)_4$	136.0	4	1,650.0
5	Dipentaerythritol	$(HOCH_2)_3CCH_2OCH_2C(CH_2OH)_3$	254.0	6	1,325.19
6	α-Methyl glucoside		194.19	4	1,155.56
7	Xylitol	$HOCH_2(CHOH)_3CH_2OH$	152.0	5	1,845.39
8	Sorbitol	$HOCH_2(CHOH)_4CH_2OH$	182.17	6	1,847.7
9	Sucrose		342.30	8	1,311.1

f: Functionality, hydroxyl groups/mol

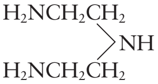
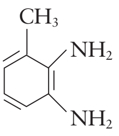
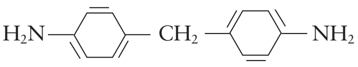
A second important group of starters used in the synthesis of polyether polyols for rigid PUF is the group of polyamines, aliphatic or aromatic, having 2–3 amino groups/mol (primary or secondary amino groups) such as: ethylenediamine (EDA), diethylenetriamine (DETA), *ortho*-toluene diamine (o-TDA) and 4,4′-methylenedianiline (MDA) [1, 2] (**Volume 2, Chapter 3**). The main properties of these polyamines which are of interest in PU chemistry are presented in **Table 2.2**.

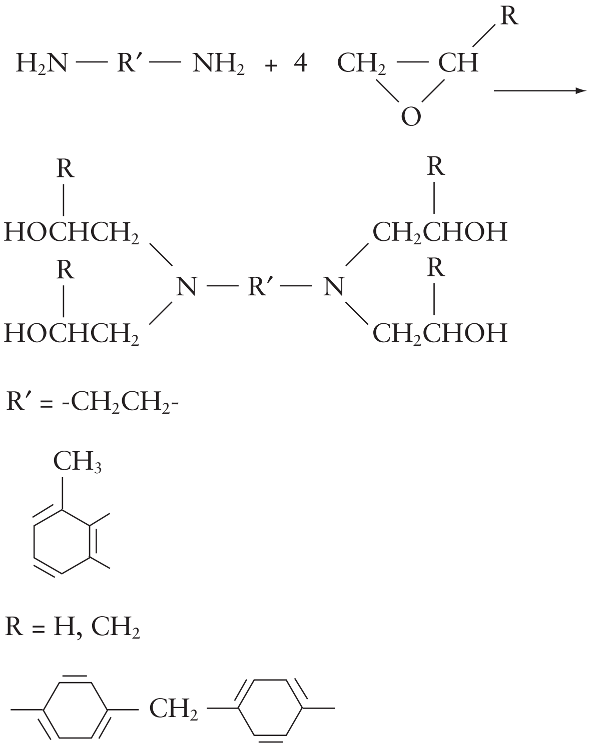
The amino groups (-NH_2) generate by the reaction with alkylene oxides (PO, EO) hydroxyalkyl groups, transforming the initial amine into an amino polyol (**Reaction 2.2**).

The resulting amino polyols (**Reaction 2.2**) 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 2.3**).

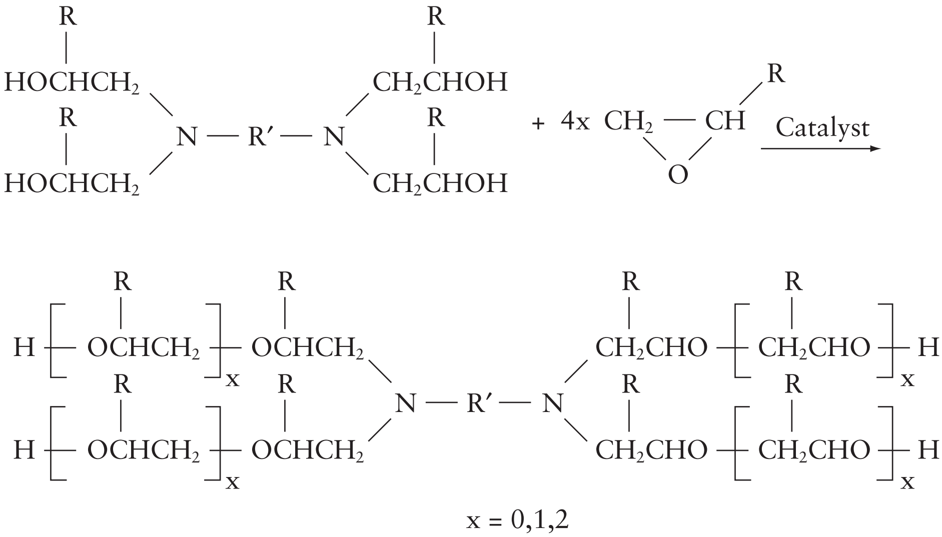
Of course the OH# presented in **Table 2.2** is a hypothetical one (the amines do not have hydroxyl groups), but it is very useful for the calculation of the final amino polyol OH#, after alkoxylation.

Table 2.2 Some characteristics of polyamines used frequently as starters for polyether polyols for rigid PUF

No.	Polyamine used as starter	Formula	MW	f	OH# (mg KOH/g)
1	EDA	$H_2NCH_2CH_2NH_2$	60.10	4	3,733.7
2	DETA	 $(H_2NCH_2CH_2)_2NH$	103.20	5	2,718.0
3	o-TDA (2,3 and 3,4 isomers)		122.16	4	1,836.9
4	MDA		198.27	4	1,131.78



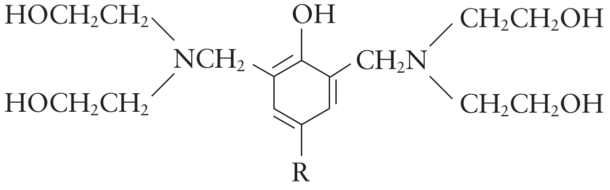
(2.2)



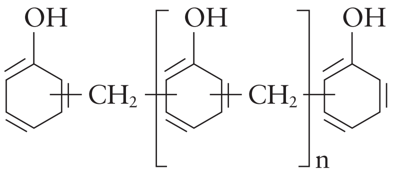
(2.3)

Both structures (**Reactions 2.2** and **2.3**) are used successfully in rigid PUF. **Reaction 2.2**, having a high OH#, is used more frequently as crosslinker in many PU applications (rigid PUF, coatings).

A third group of starters, used in the synthesis of polyether polyols for rigid PUF, is the group of condensates of aromatic compounds (e.g., phenols) with aldehydes (e.g., formaldehyde) such as Mannich bases or novolaks (**Figure 2.1**). This group of starters is very important because, by their reaction with alkylene oxides, they give aromatic polyols which confer to the resulting rigid PUF excellent physico-mechanical, thermal, and fire proofing properties as well as dimensional stability (**Volume 2, Chapter 4**).



Mannich base

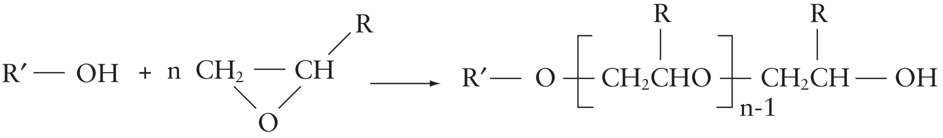


Novolak

Figure 2.1 Starters with aromatic structure (condensates of phenols with aldehydes)

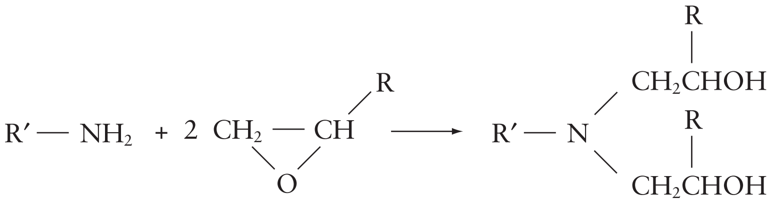
As a general observation, the main reactions involved in the synthesis of polyether polyols for rigid PUF are:

a) The polyaddition of alkylene oxides to hydroxyl groups (**Reaction 2.4**):



$$R'\text{—}OH + n\,\underbrace{CH_2\text{—}\overset{R}{CH}}_{O} \longrightarrow R'\text{—}O\left[CH_2\overset{R}{C}HO\right]_{n-1}CH_2\overset{R}{C}H\text{—}OH \tag{2.4}$$

b) The addition of alkylene oxides to amino groups (**Reaction 2.5**):



(2.5)

2.1 The Polyaddition of Alkylene Oxides to Hydroxyl Groups

The polyaddition of alkylene oxides to hydroxyl groups is catalysed by the alkali hydroxides [KOH and sodium hydroxide (NaOH)] or low hindered tertiary amines or, to a much lesser extent, by acid catalysts [Lewis acids and Bronstedt superacids in order to generate short polyetheric chains, (**Volume 1, Section 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-MW polyether chains (e.g., polyethers for flexible foams) but with short chain polyethers, having 1–3 alkylene oxide units, it is perfectly possible [31, 32].

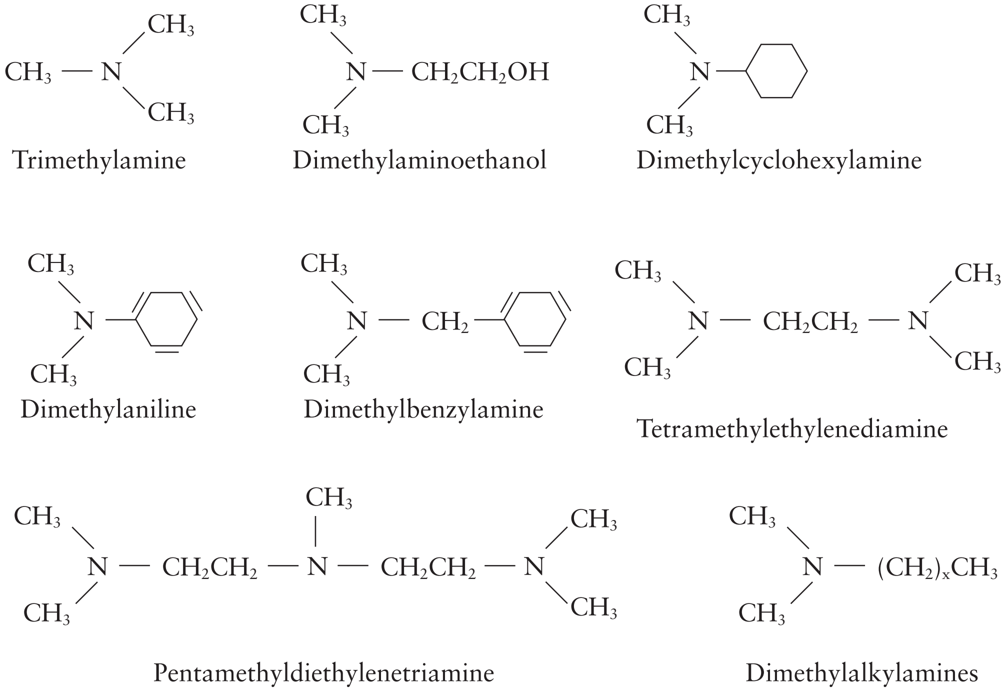
The mechanism of alkylene oxide anionic polyaddition to hydroxyl groups, catalysed by alkali hydroxides, is discussed in **Volume 1, Sections 4.1–4.1.5**, the real active centre being the alkaline alcoholate, and the propagation reaction being the repeated SN-2 attack of the alcoholate anion on the α-carbon 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, approximately 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 PUF.

2.1.1 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 2 methyl groups/aminic nitrogen (**Figure 2.2**) [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 2.3**). 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 TEOA, have a very poor catalytic activity [30, 31]. Triisopropanolamine has practically no catalytic activity [36]. *N*,*N*,*N*′,*N*′-tetrakis(hydroxypropyl)ethylenediamine has no catalytic activity in PO polyaddition to hydroxyl groups [37].



Trimethylamine

Dimethylaminoethanol

Dimethylcyclohexylamine

Dimethylaniline

Dimethylbenzylamine

Tetramethylethylenediamine

Pentamethyldiethylenetriamine

Dimethylalkylamines

Figure 2.2 Tertiary amines with high catalytic activity in alkoxylation reactions

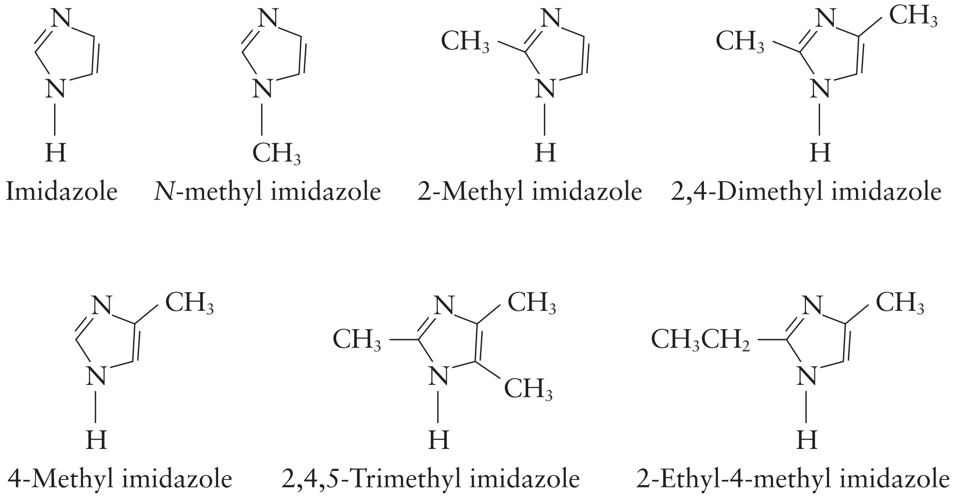
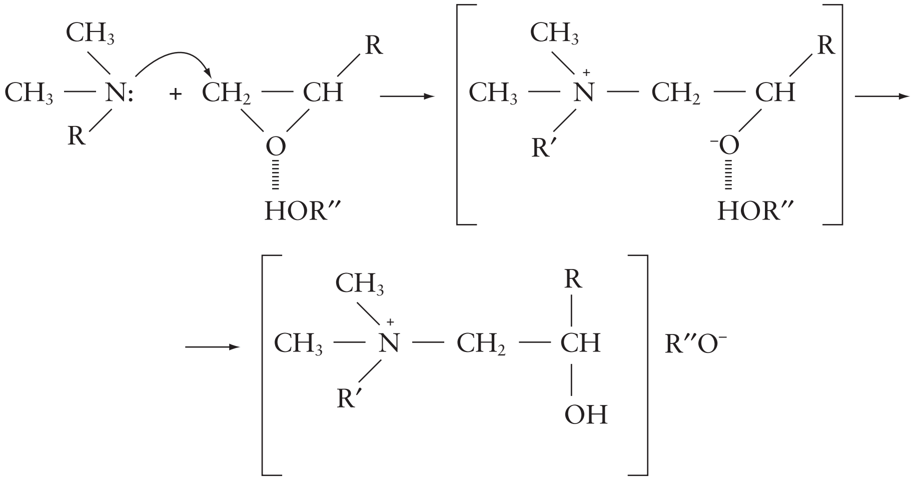

Imidazole
N-methyl imidazole
2-Methyl imidazole
2,4-Dimethyl imidazole
4-Methyl imidazole
2,4,5-Trimethyl imidazole
2-Ethyl-4-methyl imidazole

Figure 2.3 Imidazole and substituted imidazoles with high catalytic activity in alkoxylation reactions

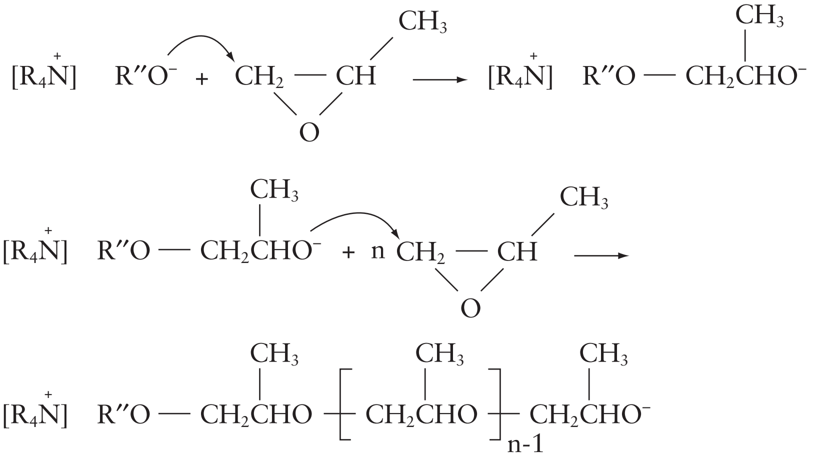
The first step of PO addition to hydroxyl groups is the SN-2 attack of the tertiary nitrogen atom to the α-carbon atom of the oxiranic ring, activated by a hydrogen bond between the oxiranic oxygen and hydrogen atom of hydroxyl groups (**Reaction 2.6**).


Quaternary ammonium alcoholate

(2.6)

In the absence of hydroxyl groups, **Reaction 2.6** does not take place. In the synthesis of polyether polyols for rigid PUF there is a large excess of hydroxyl groups which assist the ring-opening of PO. The weak hydrogen bond of approximately 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 (**Reaction 2.6**) 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 2.7**).

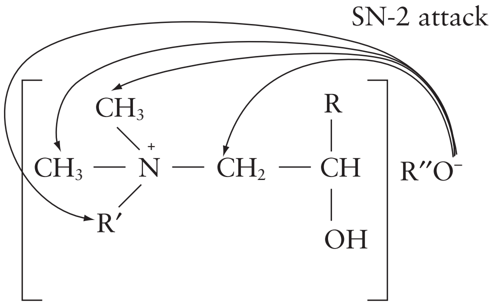


(2.7)

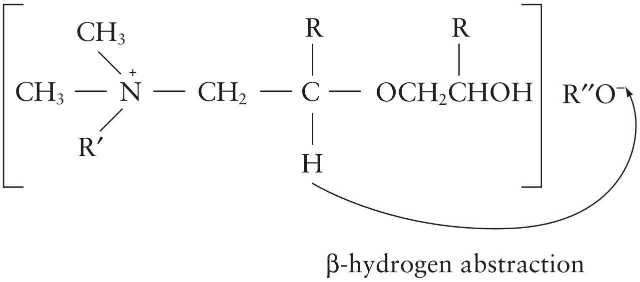
Unfortunately, the big difference between the potassium alcoholates and quaternary ammonium alcoholates is the fact that potassium alcoholate is perfectly stable at the polymerisation temperature, but the quaternary ammonium alcoholates are, on the contrary, not stable and are decomposed by two mechanisms (**Reactions 2.8** and **2.9**) [31, 32]:

a) Intramolecular SN-2 nucleophilic substitution (**Reaction 2.8**); and

b) Hofmann degradation (β-hydrogen abstraction, **Reaction 2.9**).

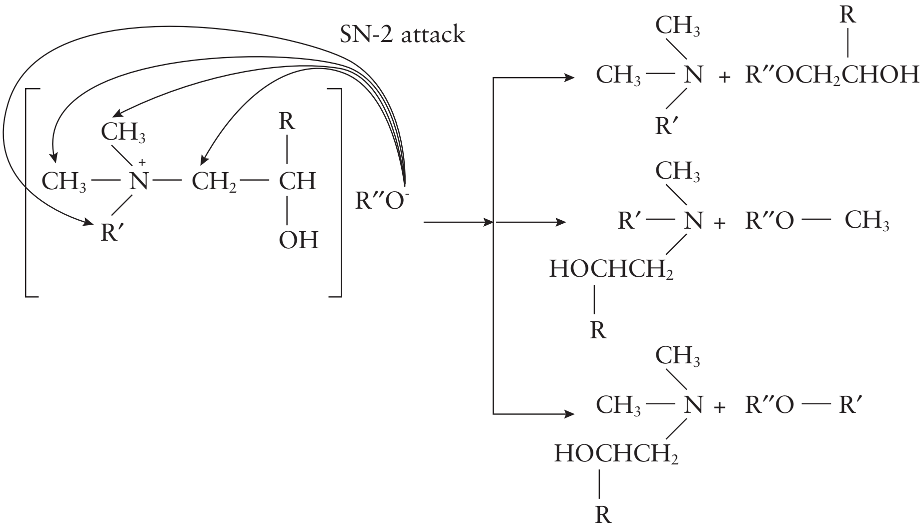


Quaternary ammonium alcoholate (2.8)



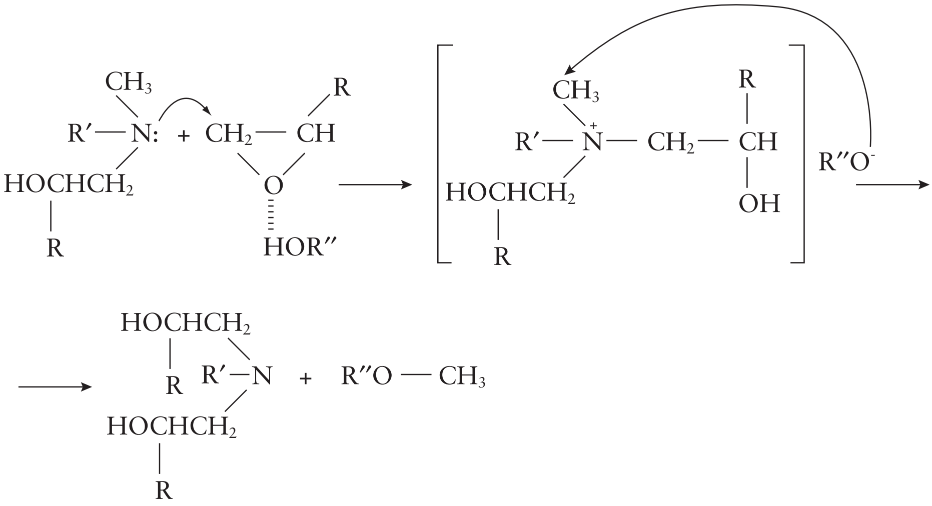
Quaternary ammonium alcoholate (2.9)

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 2.10**).

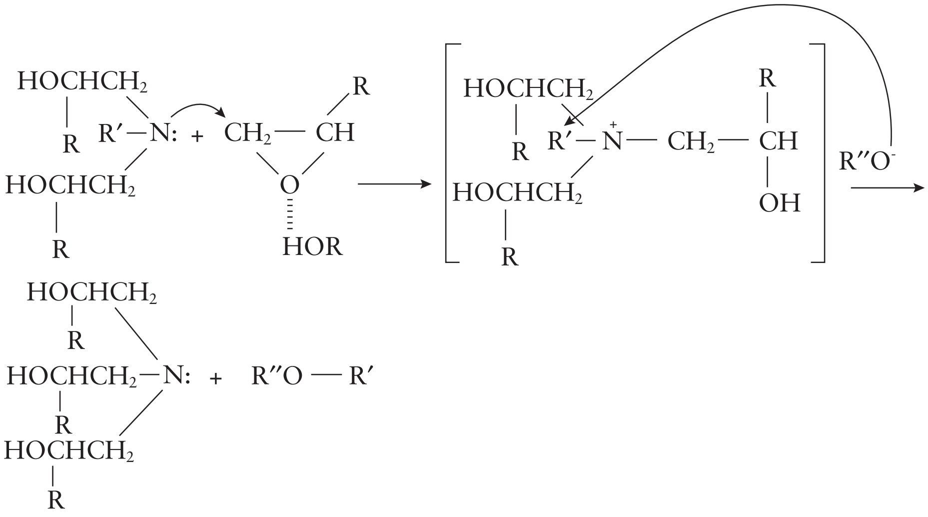


(2.10)

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 2.10**). 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 2.11** and **2.12**).



(2.11)



(2.12)

By these successive reactions, **Reactions 2.10–2.12**, 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 2.10–2.13**). This behaviour is clearly seen in **Figure 2.4**.

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 a OH# 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 2 PO units (**Reaction 2.13**).

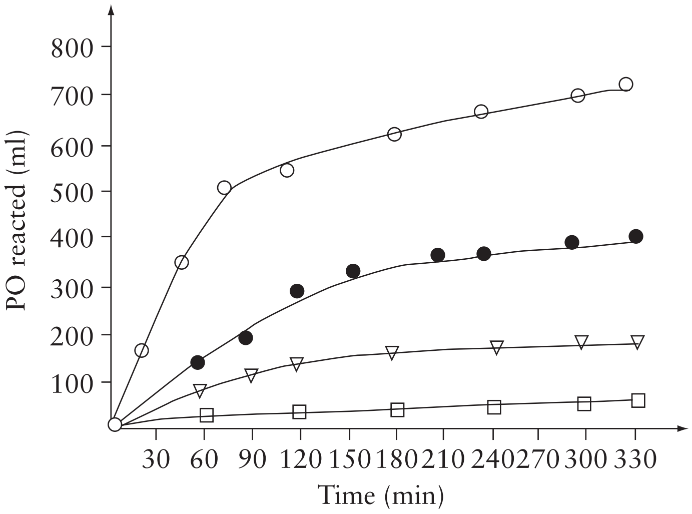
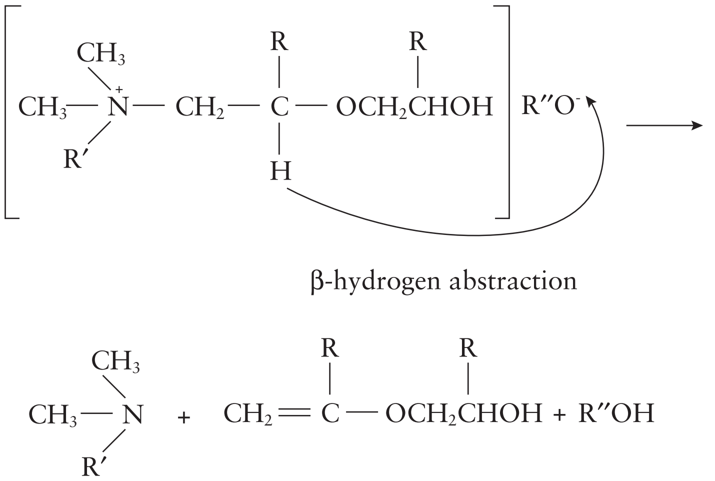


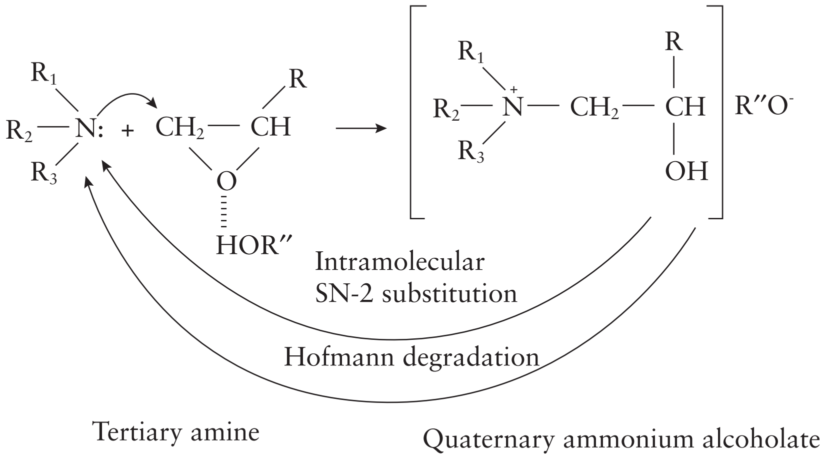
Figure 2.4 Volume of PO reacted *versus* time as function of the tertiary amine nature. Temperature: 120 °C; pressure: 0.35–0.4 MPa; catalyst: 0.0056 mol%; starter: sucrose:glycerol (3:1); dimethylaminoethanol (o); TEOA (•); tributylamine (∇); and triisopropanolamine (□)



(2.13)

The Hofmann degradation leads to a tertiary amine, an olefin and to the formation of a new hydroxyl group. **Reaction 2.13** 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).

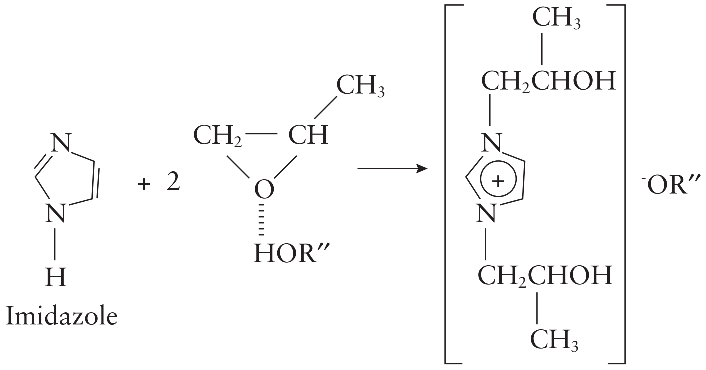
It was observed that, if the polymerisation in the presence of tertiary amines is developed at lower polymerisation temperatures, of approximately 80–90 °C, paradoxally higher reaction rates of PO polyaddition are obtained than at higher polymerisation temperatures, (e.g., 120 °C). The explanation of 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 (**Reaction 2.14**).



(2.14)

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] (**Reaction 2.15**).



(2.15)

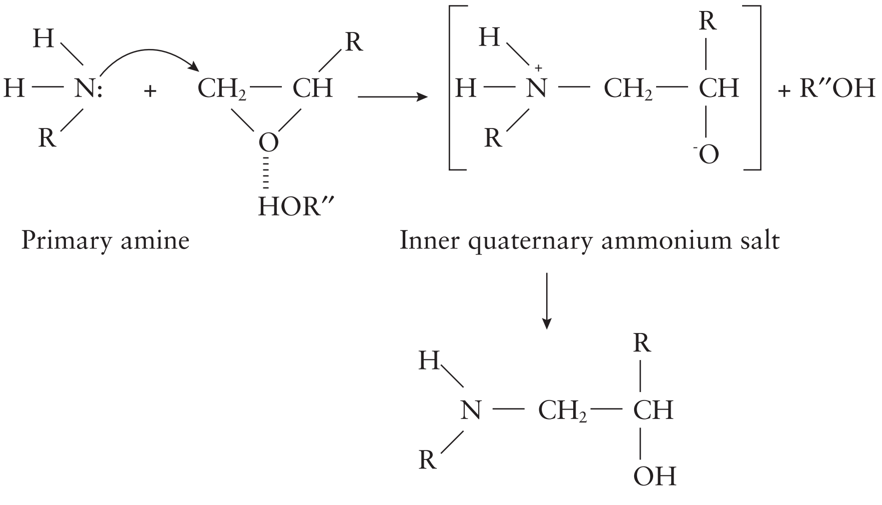
The dark colour of polyether polyols obtained in the presence of imidazoles as catalysts (Gardner colour > 18) can be improved substantially by the treatment with hydrogen peroxide (50% concentration) of approximately 0.1–0.3% against the polyol. The dark brown colour is the colour of the catalyst and 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 PUF 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 PUF 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-MW polyether polyols, with a 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 2.16**).



(2.16)

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 2.16**. 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/hydroxyl 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 2.16**). Thus, using EO as monomer it is possible to add to the hydroxyl groups until there are 8–9 EO units/hydroxyl group (for PO it is only possible to react 1–2 PO units/hydroxyl 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.

2.2 Polyether Polyol Technologies for Rigid Foam Fabrication

Polyether polyols for rigid PUF (called rigid polyether polyols) are obtained by a similar technology used for synthesis of high-MW polyether polyols and using the same installations. The difference is that polyether polyols for rigid foams having lower-MW than polyether polyols for elastic PU can be obtained in only one-step (no need to synthesise an intermediate prepolyether, of intermediate MW), 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 PU). 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 PUF are obtained in the same type of polymerisation reactors as those used for high-MW 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 (**Volume 1**, **Section 4.1.5**).

Reactors used for the synthesis of rigid polyether polyols need an internal stirrer, because frequently high melting point(s) (mp) polyols (such as PER 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; and

d) Alkoxylation time: 6–12 h (depending on the stirring efficiency in the reactor, the heat elimination speed).

For alkoxylation in the presence of tertiary amines, lower alkoxylation temperatures of approximately 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, approximately 0.0056 mol 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 PUF has the following steps:

a) Charge of starters and catalyst;

b) PO (or/and EO) polymerisation;

c) Digestion;

d) Degassing;

e) Purification; and

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 (e.g., 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 PER) is stirred for 1–2 h, 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.

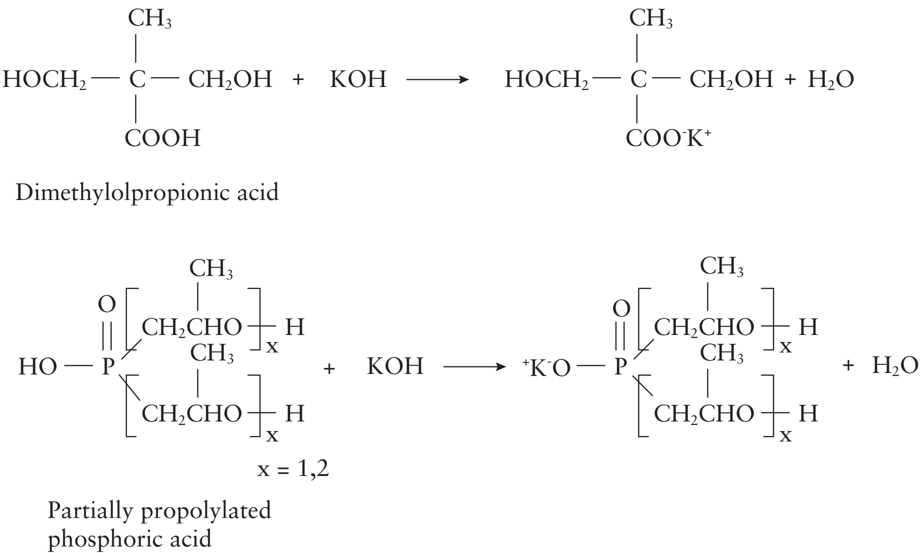
After the addition of all monomers (approximately 6–12 h), a digestion takes place, the reaction mass being maintained at the reaction temperature, under stirring for approximately 1–2 h. The unreacted PO is consumed and the pressure decreases from 0.35–0.45 MPa to less than 0.1 MPa. The last traces of unreacted PO are removed in two steps: first by nitrogen bubbling and finally by vacuum distillation. The degassing step of approximately 1–2 h 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 (hydrochloric acid, sulfuric acid, phosphoric acid, oxalic, tartaric or adipic acid) and the crystals of potassium salts formed in the polyether medium are filtered (**Volume 1**, **Section 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 PUF production the one-shot technique is used predominantly. The prepolymer technique is used to a small extent for one component rigid PUF, used as sealants or in coatings. In this case the polyol needs less than 2 ppm potassium ion (e.g., propoxylated glycerol), in order to avoid the gelification of the prepolymers, due to the trimerisation of -NCO groups catalysed by K^+ ions.

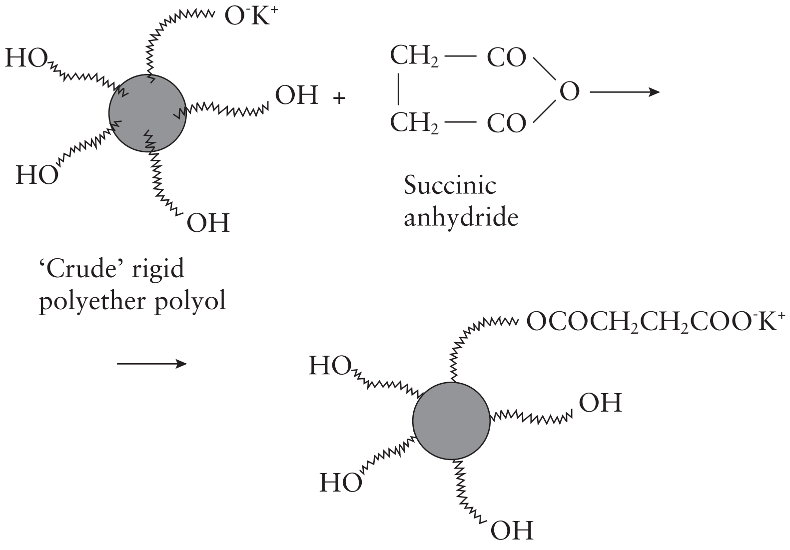
It is very interesting that it is possible to obtain rigid polyether polyols, with all potassium ions from the catalyst in the form of a soluble neutral potassium salt. The main condition is that the soluble potassium salt does not markedly catalyse the reaction between -NCO groups and hydroxyl groups. Thus, by using formic acid [43] or lactic acid [44] for neutralisation of the basic catalyst from crude polyethers, polyols are obtained with 2,000–3,000 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 PU 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 PU structure and the mobility of potassium ions decreases markedly as does the possibility of catalysis. Hydroxy acids, such as, lactic acid, dimethylolpropionic 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 (**Reaction 2.17**) and the hydroxyl groups of the resulting potassium salt, react with polyisocyanates and are chemically inserted in the PU structure [36].



(2.17)

A variant of the previously mentioned application is to make the neutralisation of the crude alkaline, rigid polyether polyol with a cyclic anhydride (e.g., with succinic or maleic anhydride). A structure is obtained in which the potassium salt is chemically linked to a rigid polyol structure (**Reaction 2.18**) and which enters the PU network during the foaming process. Unfortunately, phthalic anhydride, an easily available and cheap cyclic anhydride, leads to partially insoluble potassium salts [36].



(2.18)

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 2.5** and **2.6**, respectively.

Table 2.1 and **Table 2.2** 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 mp 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), and

b) Polyols which are solid at the PO polymerisation temperature, having higher mp (mp > 130 °C) such as: PER (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.

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 bp is 10.8 °C]. This problem was solved in various ways and is discussed in detail in this chapter, **Section 2.2.4**.

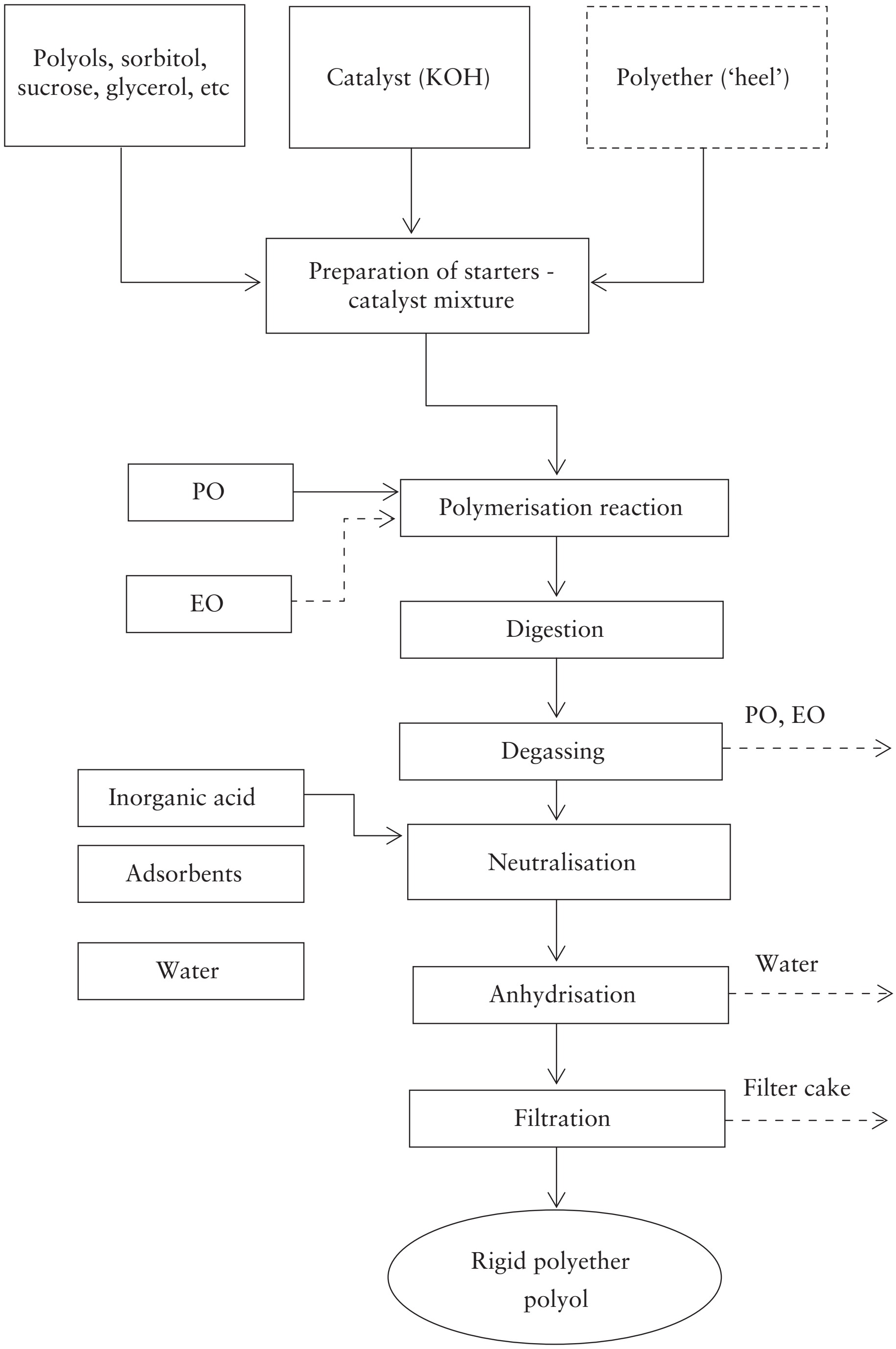


Figure 2.5 Flow diagram for rigid polyether polyol fabrication (catalyst: KOH)

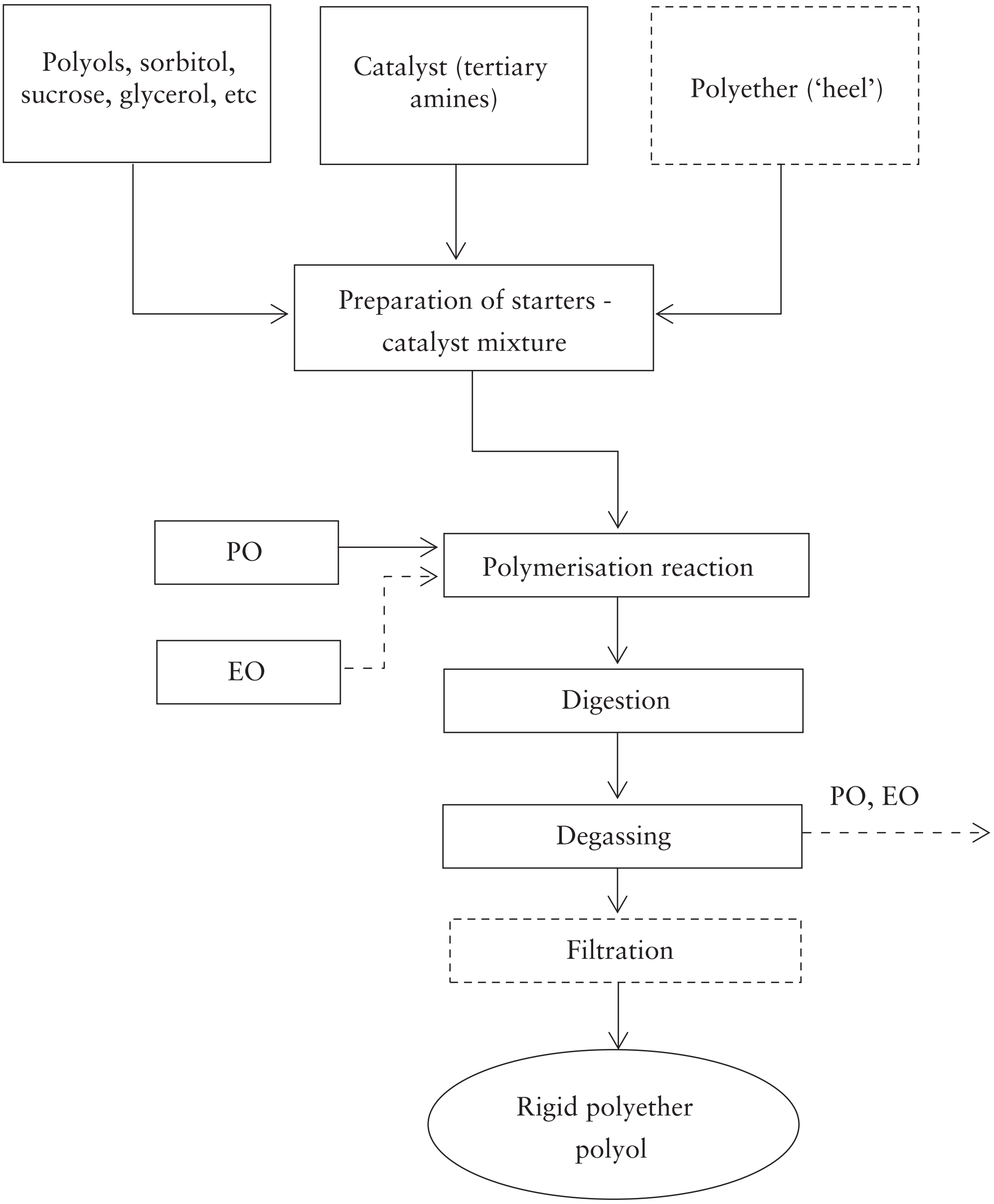


Figure 2.6 Flow diagram for rigid polyether polyol fabrication (catalyst: tertiary amines)

2.2.1 Anionic Polymerisation of Propylene Oxide (or/and Ethylene Oxide) 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 (**Volume 1, Sections 4.1.1** and **4.1.5**).

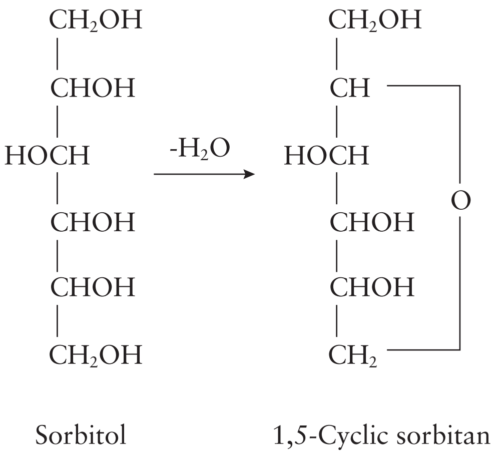
The polymerisation reactor is charged with a polyol-catalyst mixture and, under an inert atmosphere of nitrogen, PO (or EO) is added at the polymerisation temperature, preferable 105–125 °C for KOH or NaOH catalysts and 80–95 °C for tertiary amines.

The single polyol from this group that needs special attention is sorbitol, which is delivered in the form of an aqueous solution of approximately 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.

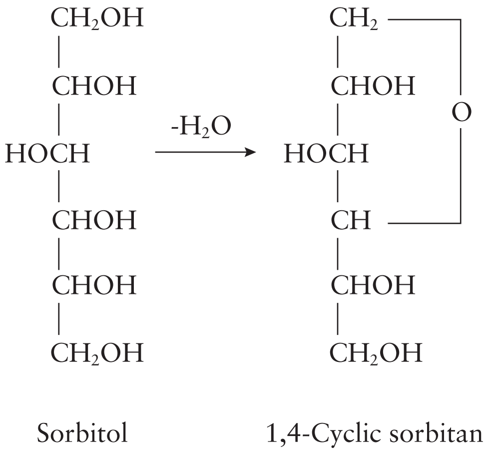
It is well-known that pure solid sorbitol gives polyether polyols with a very high viscosity, which are difficult to use in practice (higher than 50,000 mPa.s, at 25 °C). By using controlled quantities of water it is possible to decrease the functionality to a lower value, but this is perfectly acceptable. The equivalent functionality(ies) (f_e) of 4.5–5 hydroxyl groups/mol leads to much lower viscosities in the resulting polyether polyols (5,000–10,000 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 2.19** and **2.20**).

The most important polyether polyols from this first group of low mp starters are sorbitol-based polyether polyols, which are considered to be the universal polyols for rigid PUF. They can be used in all applications of rigid PUF, such as thermoinsulation, wood imitations, packaging, flotation materials and so on.



(2.19)



(2.20)

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-dipropylene glycol (DPG), sorbitol-water [19], or sorbitol-diethylene glycol (DEG).

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 OH# (I_f):

$$\begin{aligned}
&Q_1 \times I_1 + Q_2 \times I_2 = (Q_1 + Q_2 + Q_{PO}) \times I_f \\
&Q_1 \times I_1 + Q_2 \times I_2 = (Q_1 + Q_2) \times I_f + Q_{PO} \times I_f \\
&Q_{PO} = \frac{Q_1 \times I_1 + Q_2 \times I_2 - (Q_1 + Q_2) \times I_f}{I_f}
\end{aligned} \tag{2.21}$$

Where:

Q_1: Quantity of polyol 1;

Q_2: Quantity of polyol 2;

Q_{PO}: Quantity of PO;

I_1: OH# of polyol_1;

I_2: OH# of polyol_2; and

I_f: OH# of final polyether polyol.

Usually, in practice the sum is calculated first (**Reaction 2.22**) and the quantity of PO needed to obtain the desired final OH# is then easily calculated (**Reaction 2.23**).

$$Q_1 + Q_2 + Q_{PO} = \frac{Q_1 \times I_1 + Q_2 \times I_2}{I_f} \tag{2.22}$$

$$Q_{PO} = \frac{Q_1 \times I_1 + Q_2 \times I_2}{I_f} - (Q_1 + Q_2) \tag{2.23}$$

It is also important to calculate the f_e of the mixture of two polyols with different functionalities. The f_e, of a mixture of two polyols is calculated with the following general formula (**Relationship 2.24**):

$$f_e = x_1 \times f_1 + x_2 \times f_2 \tag{2.24}$$

Where:

f_1: Functionality of polyol 1;

f_2: Functionality of polyol 2;

x_1: Molar fraction of polyol 1; and

x_2: Molar fraction of polyol 2.

$$x_1 = \frac{n_1}{n_1 + n_2} \qquad x_2 = \frac{n_2}{n_1 + n_2}$$
$$n_1 = \frac{Q_1}{M_1} \qquad n_2 = \frac{Q_2}{M_2} \tag{2.25}$$

Where:

n_1: Number of mol of polyol$_1$;

n_2: Number of mol of polyol$_2$;

M_1: MW of polyol$_1$; and

M_2: MW of polyol$_2$.

$$f_e = \left[\frac{\frac{Q_1}{M_1}}{\frac{Q_1}{M_1} + \frac{Q_2}{M_2}}\right] \times f_1 + \left[\frac{\frac{Q_2}{M_2}}{\frac{Q_1}{M_1} + \frac{Q_2}{M_2}}\right] \times f_2 \tag{2.26}$$

The **Relationship 2.26**, is frequently used in practice, and after the rearrangement of terms, becomes **Relationship 2.27**:

$$f_e = \left[\frac{1}{\frac{Q_1}{M_1} + \frac{Q_2}{M_2}}\right] \times \left[\frac{Q_1}{M_1} \times f_1 + \frac{Q_2}{M_2} \times f_2\right]$$
$$f_e = \frac{Q_1 \times f_1 \times M_2 + Q_2 \times f_2 \times M_1}{Q_1 \times M_2 + Q_2 \times M_1} \tag{2.27}$$

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 f_e. Of course the problem is solved by using **Relationship 2.26**, but it is possible to use a more simplified relationship (**Relationship 2.26**) deduced from **Relationship 2.27**:

$$Q_1 \times M_2 \times f_e + Q_2 \times M_1 \times f_e = Q_1 \times f_1 \times M_2 + Q_2 \times f_2 \times M_1$$
$$Q_1 \times M_2 \times (f_e - f_1) = Q_2 \times M_1 \times (f_e - f_2) \tag{2.28}$$
$$Q_2 = \frac{Q_1 \times M_2 \times (f_e - f_1)}{M_1 \times (f_e - f_2)}$$

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 2.28** one obtains:

$$Q_2 = \frac{100 \times 182\,(5 - 6)}{92 \times (3 - 5)} = 25.2 \text{ parts of glycerol} \tag{2.29}$$

2.3 Kinetic Considerations Concerning the Alkoxylation of Polyols to Rigid Polyether Polyols

For glycerol propoxylation to high-MW 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-MW glycerol-based polyethers, where the molar ratio between PO/glycerol is approximately 80–140/1, the most important step is the propagation reaction because, after the addition of 5 mol 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 (NP), 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 NP, 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 (e.g., 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 3 primary hydroxyls and 5 secondary hydroxyls. In both polyols, the secondary hydroxyls have different substituents and they are not totally equivalent. TMP, PER 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:

$$Ro = -\frac{d[PO]}{dt} = K_i[catalyst]\times[PO] = K_{i1}[RX_1^-][PO] + K_{i2}[RX_2^-][PO] + \\ + \ldots\ldots\ldots\ldots K_{in}[RX_n^-][PO] \quad (2.30)$$

$$Ro = -\frac{d[PO]}{dt} = \sum_{n-1}^{n} K_{in}[RX_n^-][PO]$$

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:

$$Rp = -\frac{d[PO]}{dt} = Kp[RX_i(PO)^-][PO] \quad (2.31)$$

$RX_i(PO)$- = are the alcoholates derived from the formed hydroxypropyl groups:

$$\sum_{n=1}^{n}[RX_{n-}^-] + [RX_i(PO)^-] = [catalyst](\text{total catalyst concentration}) \quad (2.32)$$

The global reaction rate Rt of PO polyaddition to various polyols is the sum between the initiation reaction (Ro) and propagation reaction (Rp):

$$Rt = Ro + Rp = -\frac{d[PO]}{dt} = \sum_{n=1}^{n} K_{in}[RX_{n-}^-][PO] + Kp[RX_i(PO)^-][PO] \quad (2.33)$$

Of course, the repartition of the anionic active centres on various hydroxyl groups in the reaction system is based on the following equilibrium reactions:

$$\begin{gathered} RX_n^- + R_iOH \overset{Ke}{\rightleftharpoons} RX_nH + R_iO^- \\ Ke = \frac{[RX_nH][R_iO^-]}{[RX_n^-][R_iOH]} \end{gathered} \tag{2.34}$$

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 (**Volume 1, Section 4.1.5**). The PO (or EO) consumption rate, considering the mass transfer, is described by **Equation 2.35** [45–50]:

$$Rmt = -\frac{d[PO]}{dt} = K_L \times S \times ([PO_b] - [PO_t]) \tag{2.35}$$

In pseudo steady-state Rmt-Rt:

$$K_L \times S \times ([PO_b] - [PO_t]) = \sum_{n=1}^{n} K_{in}[RX_{n-}^-][PO] + Kp[RX_i(PO)^-][PO] \tag{2.36}$$

From the equation the $[PO_t]$ value is obtained:

$$[PO_t] = \frac{K_L \times S \times [PO_b]}{K_L \times S + \sum_{n=1}^{n} K_{in}[RX_n^-] + Kp[RX_i(PO)^-]} \tag{2.37}$$

Where:

K_L: Mass transfer constant;

S: Surface of the gas-liquid interface;

PO_b: Solubility of PO in liquid reaction conditions; and

PO_t: Concentration of PO in steady-state liquid.

Equation 2.37 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 **Volume 1**, **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 (e.g., 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 mol of PO/mol of sorbitol, the solubility of PO in the reaction mass increases substantially and the PO polymerisation reaction is strongly accelerated. **Figure 2.7** 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 min, 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 PUF based on polyols which are liquid under the conditions of alkylene oxides polymerisation are: glycerol and TMP polyether triols, of various MW, sorbitol-based polyols (based on a mixture of sorbitol-glycerol, sorbitol-DPG, sorbitol-DEG) and xylitol-based polyether pentaols.

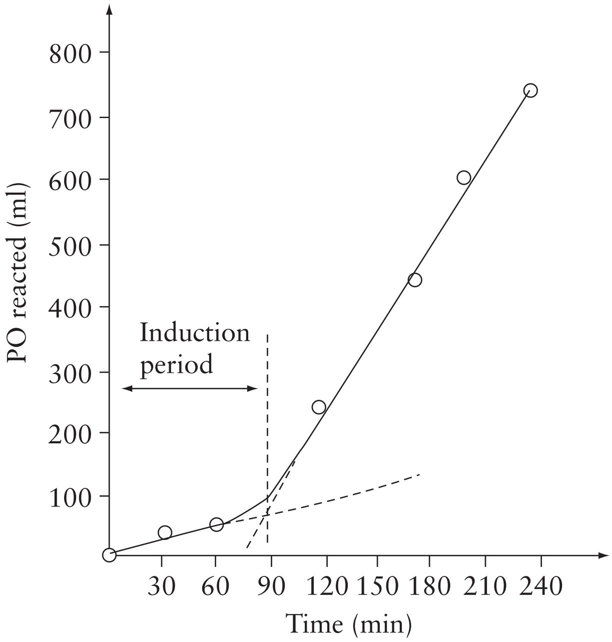
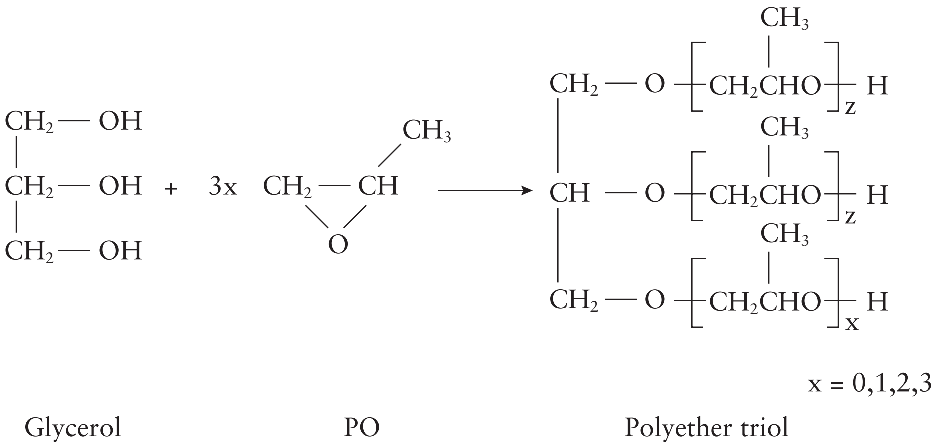


Figure 2.7 PO consumption *versus* time in sorbitol propoxylation. Temperature: 120 °C; pressure: 0.35–0.4 MPa; and catalyst [KOH] = 0.0056 mol%

Table 2.3 shows some polyether triols, based on glycerol, with various OH# between 250–600 mg KOH/g. Generally, these polyols are not used alone in foaming formulations, because they lead to rigid PUF 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:



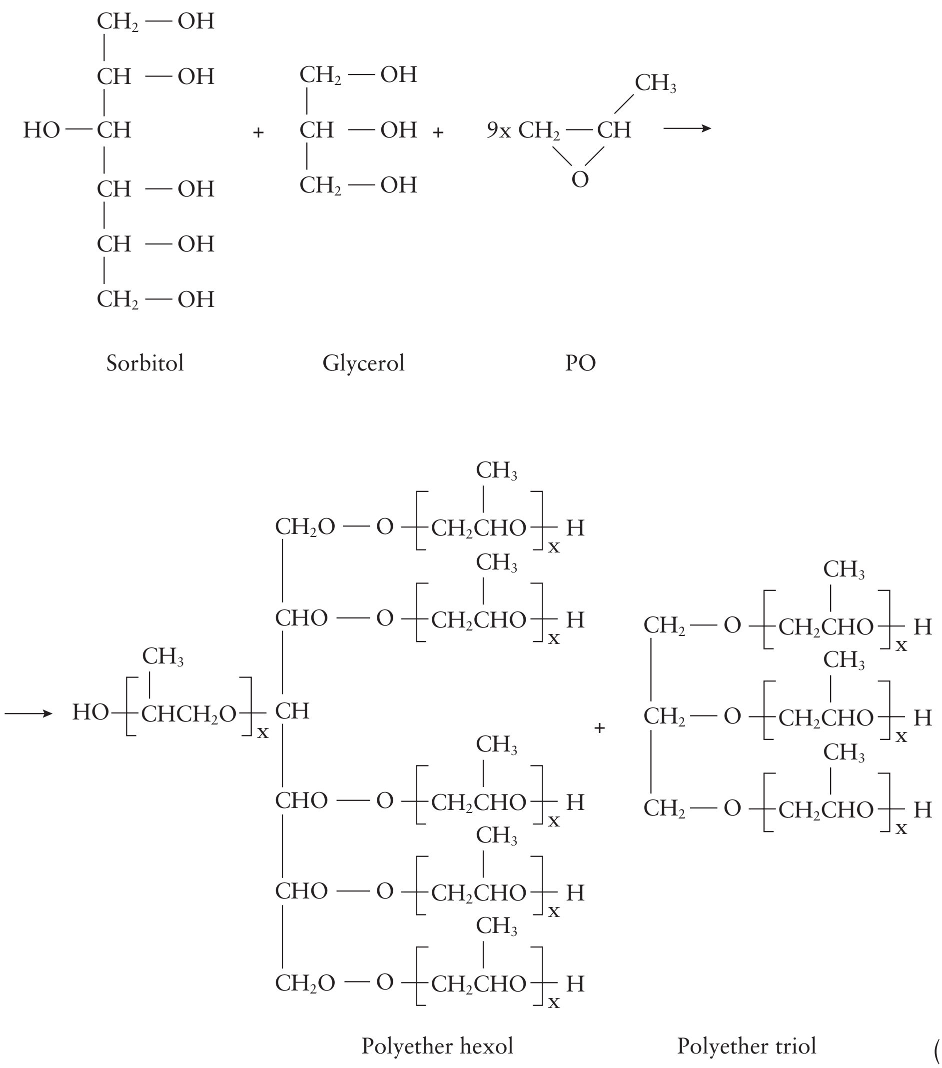
(2.38)

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-MW polyether triols, with double metal cyanide catalysts (**Volume 1, Chapter 5**). Some of these polyether triols are transformed into prepolymers, for example by the reaction with pure diphenylmethane diisocyanate and then used for monocomponent rigid PUF (the hardening is a consequence of the -NCO groups of prepolymers reaction with the atmospheric humidity).

Table 2.3 The characteristics of some glycerol-based triols for rigid PUF

Characteristic	Unit	MW = 1,000	MW = 550	MW = 400	MW = 300
Functionality	Hydroxyl groups/mol	3	3	3	3
MW	daltons	1,000–1,055	550	400	300
OH#	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	%	Maximum 0.05	Maximum 0.05	Maximum 0.05	Maximum 0.05

In **Table 2.4** 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:



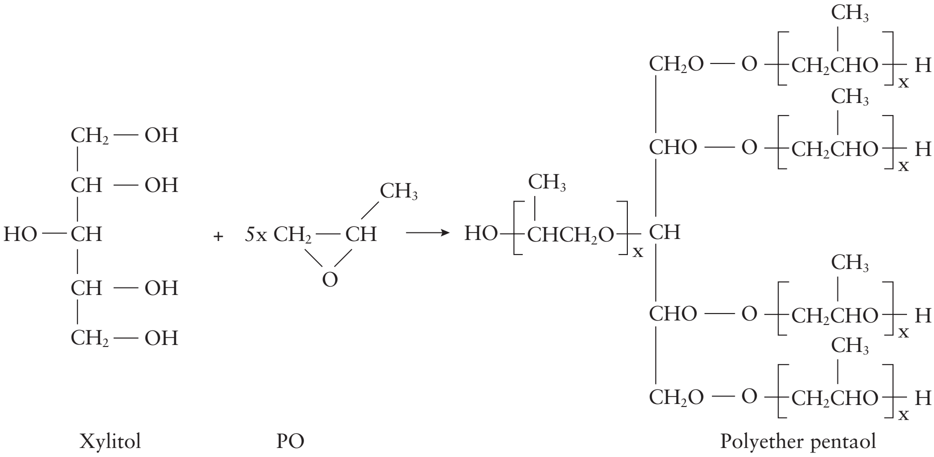
(2.39)

Of course similar sorbitol polyols are obtained by direct propoxylation of the mixtures sorbitol-DPG, sorbitol-DEG and sorbitol-water.

Table 2.4 The characteristics of some sorbitol-glycerol based rigid polyether polyols for rigid PUF

Characteristic	Unit	Type I MW = 570–620	Type II MW = 510–520
Functionality	Hydroxyl groups/mol	5	5
MW	daltons	570–620	510–520
OH#	mg KOH/g	450–490	500–550
Viscosity (25 °C)	mPa.s	4,500–8,000	20,000–30,000
Acid number	mg KOH/g	Maximum 0.1	Maximum 0.1
Water content	%	Maximum 0.1	Maximum 0.1
Density (25 °C)	g/ml	1.08–1.1	1.09–1.15
Na and K	ppm	Maximum 50	Maximum 50

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 PUF (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 (**Volume 1**, **Section 4.8**).



(2.40)

2.3.1 Anionic Polymerisation of Propylene Oxide (or/and Ethylene Oxide) 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 mp higher than 130 °C. Such polyols are: sucrose (mp = 179–180 °C), PER (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 mp polyol such as: sucrose-glycerol [12, 30], sucrose-TEOA [9, 10], sucrose-DEG [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 and so on.

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 PO or a mixture of PO–EO 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 mp solid polyol. Each variant for synthesis of rigid polyether polyols, based on high mp 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), PO (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 (**Volume 1, Chapter 4**). The reaction of PO with water causes diols (propyle glycol, DPG and so on) 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-MW 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 hydroxyl 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 (e.g., a filter press). In order to facilitate the filtration, a small quantity of filter aids (e.g., diatomites) is added. Sometimes, for improving the sucrose polyether polyol colour, a small quantity of hydrogen peroxide (approximately 50% concentration) is added after the neutralisation step. A flow chart for polyol-water mixture propoxylation technology is presented in **Figure 2.8**.

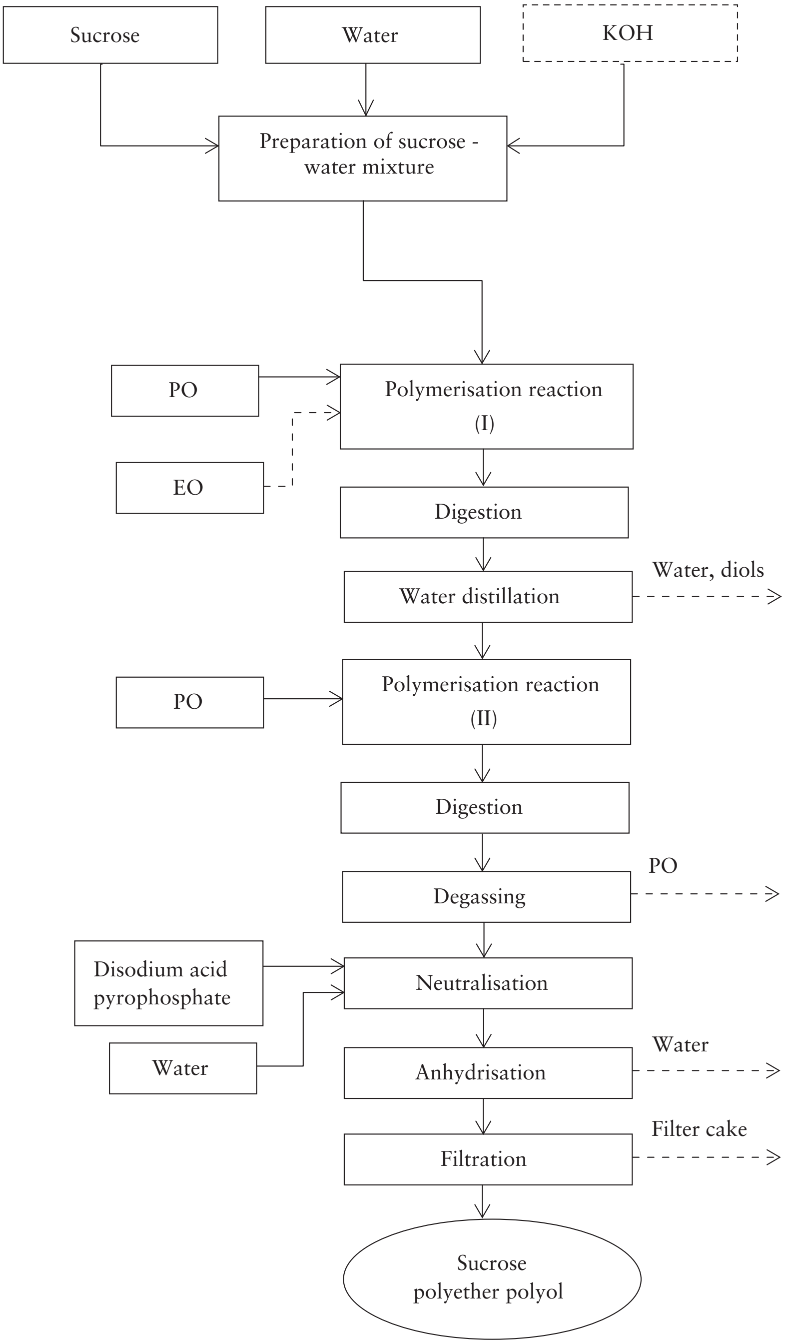


Figure 2.8 Flow chart for sucrose-water technology for polyether polyol fabrication

The resulting filter cakes contain approximately 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 and so on. 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 approximately 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 mp polyols – low mp polyols [9–19, 30]

The representative examples are the synthesis of sucrose-based polyether polyols with a low mp polyol. Sucrose is well solvated by low-MW polyols such as glycerol, DEG, DPG, TEOA and sorbitol. At the temperature of the propoxylation reaction part of sucrose is solubilised. For example, the solubility of sucrose in glycerol, at 120 °C is approximately 40–45% (40–45 parts of sucrose are solubility by 100 parts of glycerol). TEOA 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., $f = 7$ hydroxyl groups/mol). Generally, the polyols having EO units, have an exceptional solvating capacity for sucrose, superior to the propoxylated polyols. A very good co-polyol for sucrose from this category is DEG [51], which has a superior solvating capacity to DPG.

The f_e of the resulting rigid polyether polyols is situated between the functionality of sucrose ($f = 8$ hydroxyl groups/mol) and the functionality of the second polyol ($f = 2–3$ hydroxyl groups/mol for glycols, glycerol or TEOA and 6 hydroxyl groups/mol for sorbitol). The f_e is calculated easily by using the **Relationship 2.24**.

The advantage of these types of processes: direct propoxylation of a mixture of high mp polyol with a low mp 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 2.9 shows the f_e of different sucrose-polyol mixtures as a function of the gravimetric ratio of sucrose/second polyol. **Figure 2.9** shows that, except for the mixture sucrose-sorbitol, very high functionalities (f = 6.5–7 hydroxyl groups/mol) are obtained only at very high ratios of sucrose/second polyol.

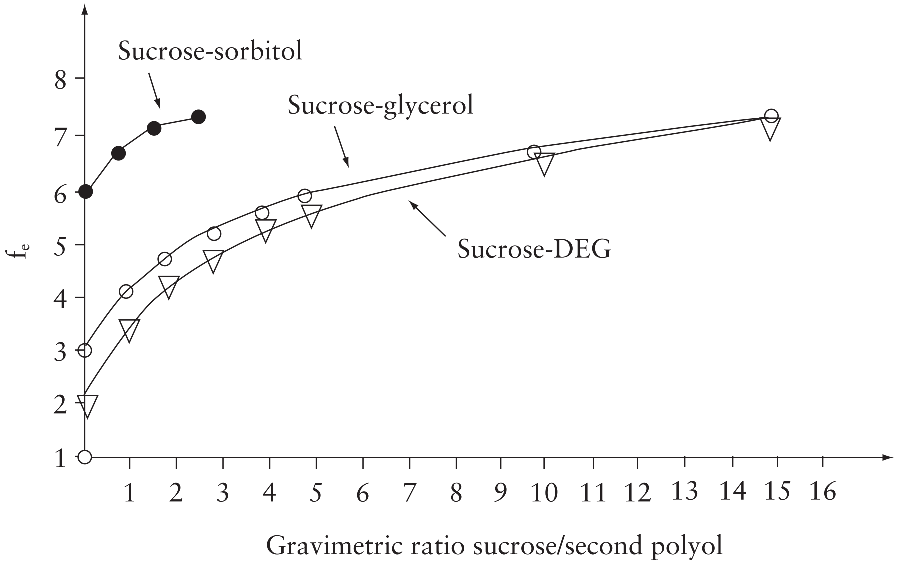


Figure 2.9 The f_e of mixtures of sucrose/second polyol as a function of the gravimetric ratio of sucrose:second polyol

One observes that an f_e of 7 needs a mixture of sucrose-glycerol, very rich in sucrose (ratio of sucrose/glycerol approximately 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 approximately 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-TEOA, usually of 1–1.5/1 (sucrose/TEOA) [9] are very stirrable mixtures, at the propoxylation temperature, and are frequently used in practice. TEOA 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-TEOA (**Table 2.6**) are frequently used to make rigid PUF 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 EO units, DEG-sucrose mixtures [51] show an excellent stirrability of the initial reaction mass, but only for medium functionalities of approximately 4–5 hydroxyl 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-TEOA and sucrose-DEG.

Table 2.5 shows the characteristics of some rigid polyether polyols, based on sucrose-glycerol and sucrose-TEOA.

Table 2.5 The characteristics of some sucrose-glycerol based rigid polyether polyols for rigid PUF (structures I, II and III)

Characteristic	Unit	I	II	III
Functionality	Hydroxyl groups/mol	4.3–4.5	5–5.5	6.5–7
MW	daltons	490–670	620–770	930–1,090
OH#	mg KOH/g	360–490	400–450	360-390
Viscosity (25 °C)	mPa.s	3,400–7,000	5,000–10,000	20,000–35,000
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 2.6 The characteristics of a representative sucrose-triethanolamine-based rigid polyether polyol for rigid PUF (structure I)

Characteristic	Unit	I
Functionality	Hydroxyl groups/mol	4.6–4.7
MW	daltons	510–550
OH#	mg KOH/g	480–500
Viscosity (25 °C)	mPa.s	6,000–8,000
Acid number	mg KOH/g	–
Water content	%	<0.1
Density	g/ml	1.076
pH	–	9.5–10.5

The reactions (**Reactions 2.43** and **2.44**), involved in the propoxylation of mixtures of sucrose –various polyols (glycerol, TEOA 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 mp polyols such as: dimethyl formamide, toluene, xylene [15, 16, 35, 52, 53] and so on. For example, DMF, 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 and so on., 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 PUF or intermediate polyether polyols (with a higher OH# 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.

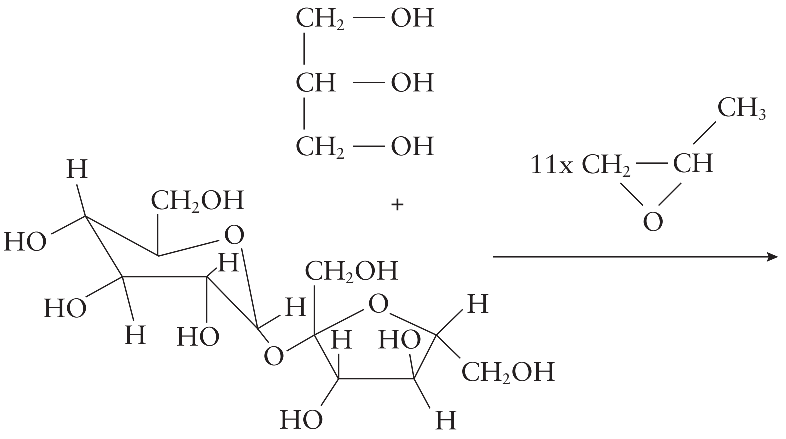
Thus, a mixture of a high concentration of sucrose, together with a small quantity of glycerol (sucrose/glycerol was approximately 15/1), suspended in a liquid polyether polyol is propoxylated totally in the presence of a tertiary amine, such as: dimethylaminoethanol, dimethylcyclohexylamine, or imidazoles. 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 OH# 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 EO 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-MW adducts of EO to sucrose was evident. By this technique it is possible to obtain low viscosity, very high functionality polyols (f = 6–7 hydroxyl 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 (e.g., 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 hydroxyl groups/mol. The viscosity of the resulting octol was very high, approximately 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 mp of polyols disappear but the problem of water elimination (the technology was described before) remains [14].



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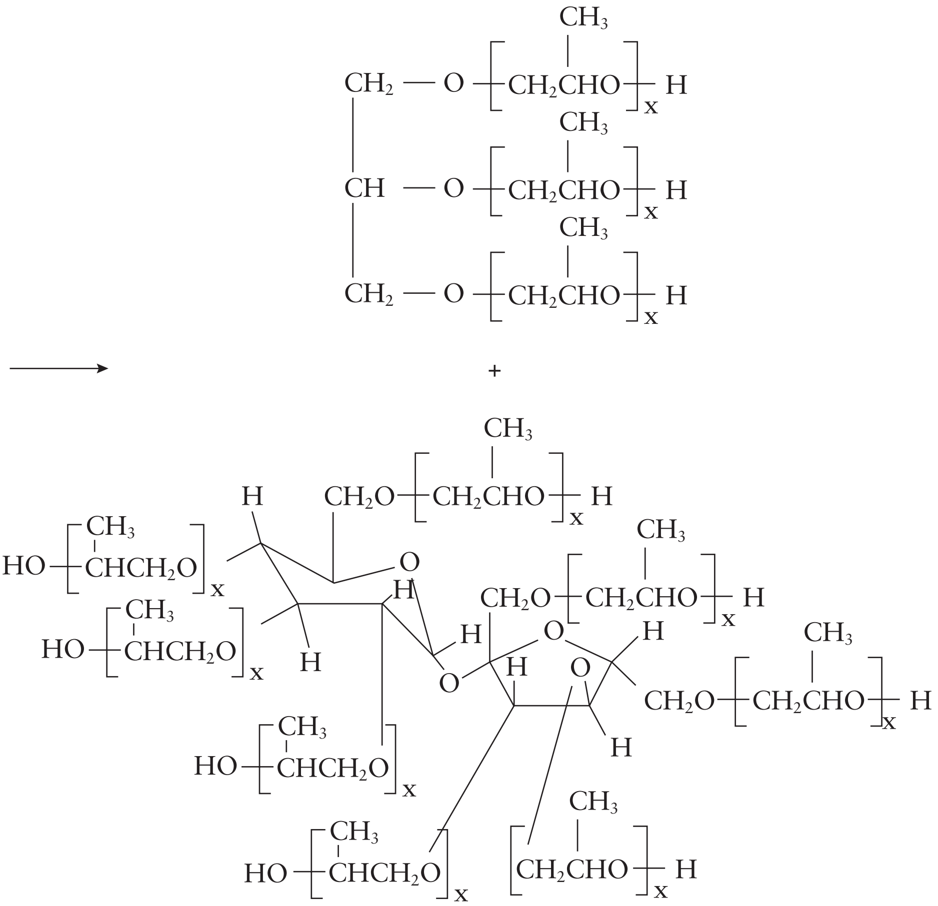
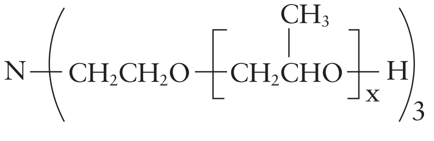


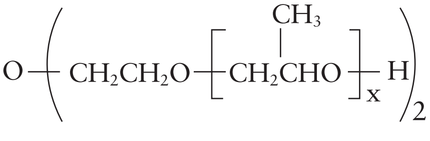
Polyether polyol based on sucrose-glycerol mixture (2.42)

One can easily imagine that if the glycerol is replaced by TEOA [9, 10] or by DEG [51], the resulting polyols are of course a mixture of propoxylated sucrose with propoxylated TEOA or propoxylated DEG (**Reaction 2.43**).



$$N\left(CH_2CH_2O\left[CH_2\overset{CH_3}{\overset{|}{C}}HO\right]_x H\right)_3$$

Propoxylated TEOA

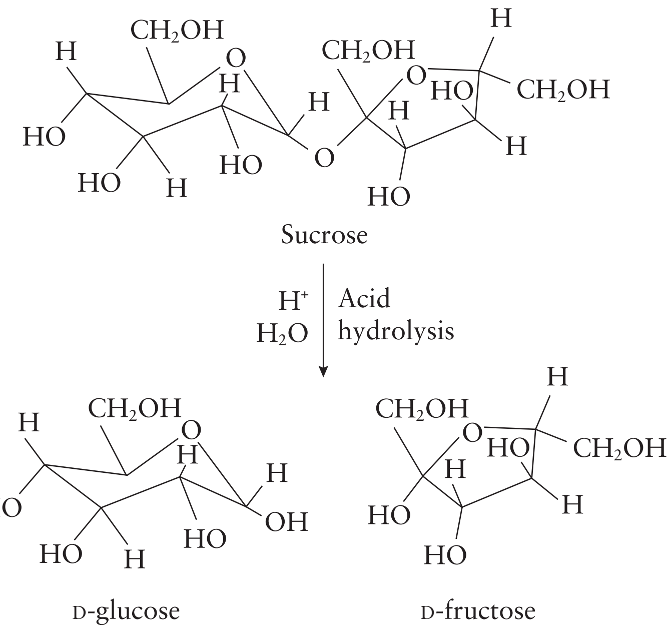


$$O\left(CH_2CH_2O\left[CH_2\overset{CH_3}{\overset{|}{C}}HO\right]_x H\right)_2$$

Propoxylated DEG (2.43)

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 1 unit of D-glucose linked to 1 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 2.44**) 1 mol of D-glucose (a reducing sugar) and 1 mol of D-fructose (a non-reducing sugar) is formed:



(2.44)

The presence of glucose, even in small quantities in sucrose leads to very unpleasant phenomena [59]:

a) The basic catalyst, KOH, decomposes glucose to acidic compounds (lactic acid, formic acid, saccharinic acids);

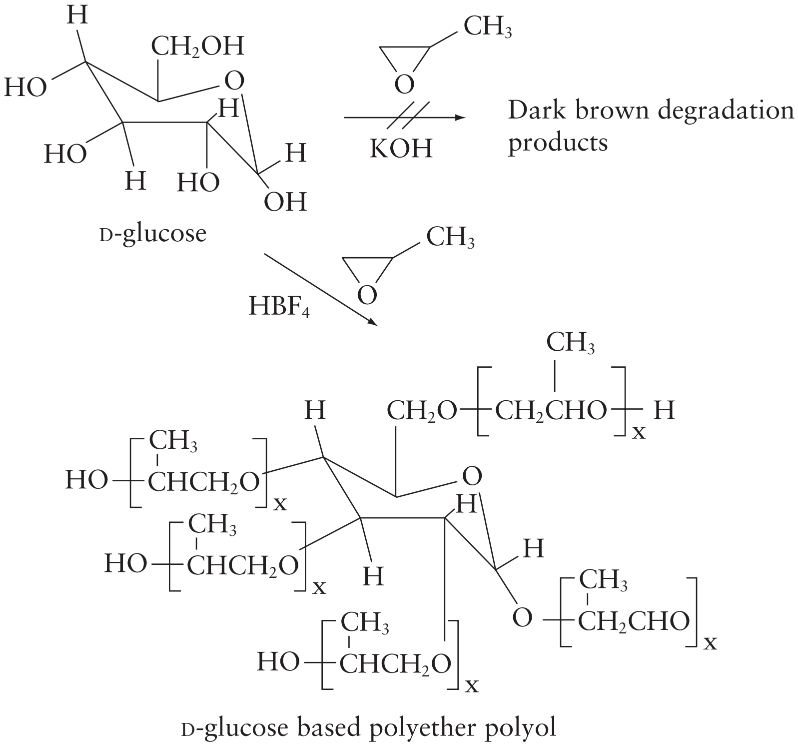
b) The alkaline catalyst is blocked by neutralisation with the acids of D-glucose degradation in the form of potassium salts of lactic, formic or saccharinic acids and the propoxylation rate decreases substantially and it is possible that it stops. A sucrose with a high content of reducing sugars is practically impossible to propoxylate; and

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 2.45**), in the presence of acidic catalysts (BF_3, HBF_4, HPF_6, $HSbF_6$) [21, 31].

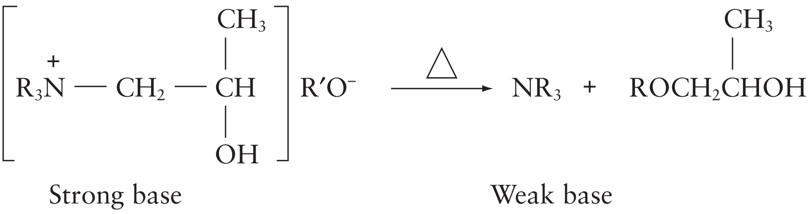


(2.45)

The removal of the remnant tertiary amines from rigid polyols synthesised in amine catalysis is not necessary [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 PU 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, approximately 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 2.46**):



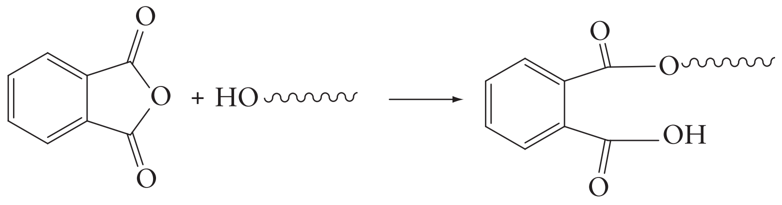
$$\left[R_3\overset{+}{N}-CH_2-\underset{\substack{|\\ OH}}{\overset{\substack{CH_3\\ |}}{CH}}\right]R'O^- \xrightarrow{\triangle} NR_3 + ROCH_2\overset{\substack{CH_3\\ |}}{C}HOH$$

Strong base Weak base

(2.46)

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 a half ester of phthalic acid. The formed acidic group neutralises the tertiary amine under the form of quaternary ammonium salt (**Reaction 2.47**).



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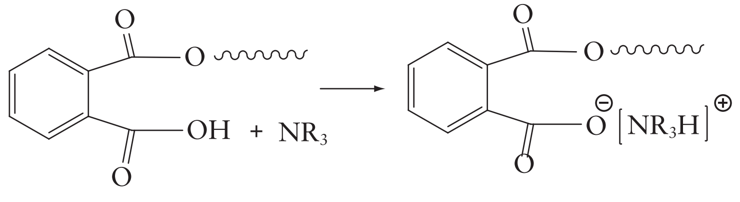
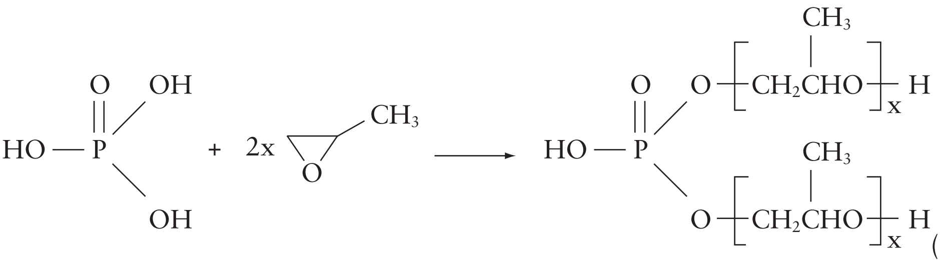


(2.48)

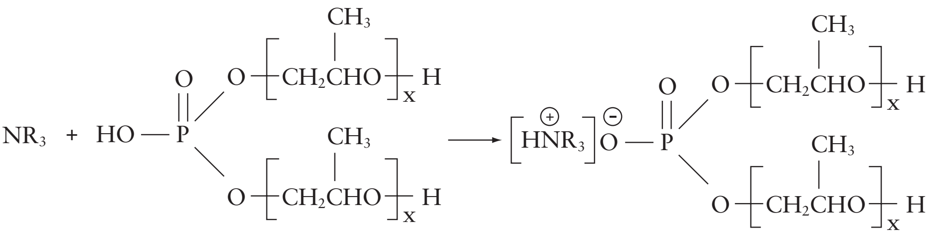
With formic acid, salts of formic acid are obtained, which have the structure of 'delayed catalysts' [61]:

$$HCOOH + NR_3 \rightarrow HCOO^-[\overset{+}{N}R_3H] \qquad (2.49)$$

The reaction with partially propoxylated phosphoric acid gives a very soluble amine salt in polyether polyol [36]:



(2.50)



(2.51)

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.

2. T.H. Ferrigno in *Rigid Plastic Foams*, 2nd Edition, Reinhold Publishing Corporation, New York, NY, USA, 1967.

3. M. Szycher in *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 Co., assignee; US3865806, 1975.

6. No inventor; Jefferson, assignee; GB1002272, 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 Co. and Eastman Chemical Co., assignees; CA821553, 1969.

   b) G.D. Edwards, R.L. Soulen and D.M. Riche, inventors; Jefferson Chemical Co. and Eastman Chemical Co., assignees; CA84402219, 1970.

9. No inventors; ICI, assignee; GB1154161, 1969.

10. No inventors; Allied Chemicals, assignee; GB1104733, 1968.

11. No inventors; ICI America, assignee; GB1434503, 1976.

12. No inventors, Dow, assignee; GB935424, 1963.

13. W.R. Fijal, inventor; BASF Wyandotte Corp., assignee; US3640997, 1972.

14. M. Wismer and J.F. Foote, inventors; Pittsburgh Plate Glass Co., assignee; US3085085, 1963.

15. No inventors; Union Carbide Corp.; GB1132004, 1968.

16. R.P. Gentles, inventor; ICI, assignee; GB864097, 1961.

17. No inventors; Shell International Research, assignee; GB2078764, 1982.

18. A.W. Anderson, inventor; The Dow Chemical Co., assignee; US2902478, 1959.

19. R.P. Gentles and A. Ibbotson, inventors; ICI, assignee; GB891776, 1962.

20. C. Granger, R. Gras and M. Buisson, inventors; Naphtachimie, assignee; US3505255, 1970.

21. No inventors; Olin Corp., assignee; GB1323184, 1973.

22. J.T. Patton, Jr., and W.F. Schulz, inventors; Wyandotte Chemical Corp., assignee; US3346557, 1967.

23. J.L. Haas, inventor; Mobay Chemical Corp., assignee; US4209609, 1980.

24. a) No inventor; Upjohn, assignee; GB1042220, 1966.

    b) No inventor; Upjohn, assignee; GB1147106, 1969.

25. A.J. Thomas, inventor; Huntsman ICI Chemicals LLC, assignee; WO0005289, 2000.

26. K. Wagner, inventor; Bayer AG, assignee; US4247654, 1981.

27. T. Richardson, D.M. Burrington and K.R. Viswanathan, inventors; Wisconsin Alumni Research Foundation, assignee; US4459397, 1984.

28. D.H. Champion and G.P. Speranza, inventors; Texaco Chemical Co., assignee; US5110991, 1992.

29. D.E Laycock, inventor; Dow Chemical Co., assignee; US4962237, 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; GB1082673, 1967.

34. T. Nakajima, K. Matsubara and K. Ueno, inventors; Mitsui Toatsu Chemicals, assignee; EP0395316A3, 1991

35. N.H. Nodelman, inventor; Mobay Chemical Corp., assignee; US4332936, 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 Co., assignee; WO9947581A1, 1999.

41. H.P. Klein and M.E. Brennan, inventors; Arco Chemical Technology, Inc., assignee; US4820810, 1989.

42. W. Hinz and E.M. Dexheimer, inventors; BASF Corp., assignee; US6410801, 2002.

43. J.D. Christen and H.B. Taylor III, inventors; Dow Chemical Co., assignee; US4521548, 1985.

44. W. Hinz and E.M. Dexheimer, inventors; BASF Corp., assignee; US6380367, 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, *Industrial & 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; US6563007, 2003.

52. D. Maassen, R. Nast, H. Bormann, H. Piechota and K-J. Kraft, inventors; Bayer AG, assignee; US3941769, 1976.

53. M. de Groote, inventor; Petrolite Corp., assignee; US2652394, 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; RO85851, 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; RO85853B1, 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; RO118433, 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; RO92858, 1987.

58. H.P. Klein, inventor; Texas Development Corp., assignee; US4166172, 1979.

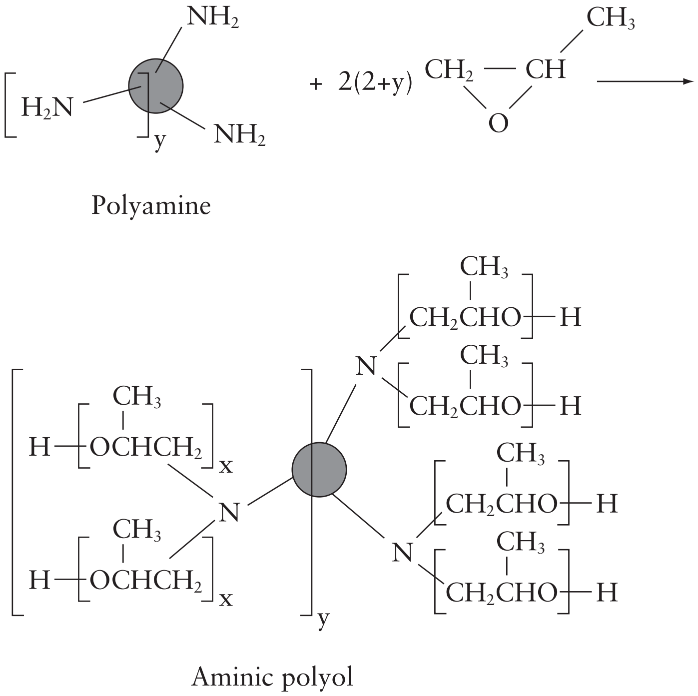
59. F. Stoenescu, M. Ionescu, V. Dumitriu and I. Mihalache, *Materiale Plastice*, 1979, **16**, 1, 4.

60. M.A.P. Gansow, inventor; Dow Chemical (Nederland) BV, assignee; US4877879, 1989.

3 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), diethylenetriamine (DETA) [1, 2], *ortho*-toluene diamine (o-TDA) [3, 4] or 4,4′-methylenedianiline (MDA) [2, 5, 6]. Because these starters are liquid at room temperature (RT) (EDA, DETA) or low melting point solids (o-TDA, MDA), they are alkoxylated in the absence of solvents.

The general reaction is:



(3.1)

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 foams

(PUF) 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 (**Volume 2, Reaction 2.15**).

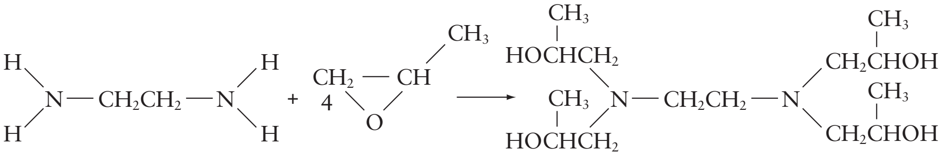
During the alkoxylation of the amino groups, as shown in **Reaction 3.1**, hydroxyl groups are formed, which have a strong catalytic effect on the reaction of alkylene oxides with the unreacted amino groups. As an immediate consequence, the reaction is strongly accelerated. Of course by the addition 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 potassium hydroxide (KOH), to an aminic polyol, having hydroxypropyl groups, the extension of the chains with PO units is possible.

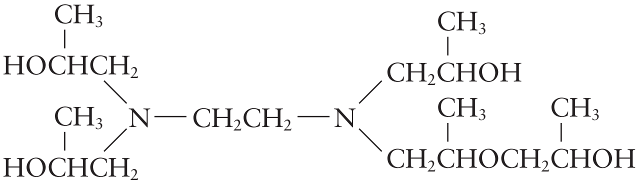
As a general rule, all the aminic polyols obtained by the propoxylation of the amines discussed have very high viscosities. By the introduction of EO units the aminic polyol viscosities decrease substantially [4].

For example, EDA with 4 mol of PO, is a well-known crosslinking agent but has a high viscosity, approximately 50,000 mPa.s at 25 °C (**Reaction 3.2**):

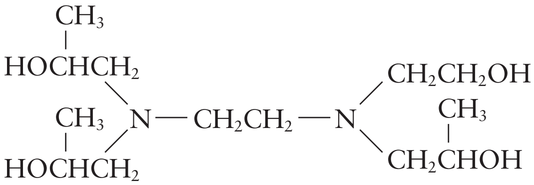


(3.2)

By the introduction of 5 mol of PO/mol of EDA (**Structure 3.3**), the viscosity decreases to approximately 19,000–22,000 mPa.s at 25 °C. By the reaction of EDA with 3 mol of PO and 1 mol of EO (**Structure 3.4**), the viscosity decreases from 50,000 (for a product with 4 mol of PO/mol of EDA) to approximately 16,000–17,000 mPa.s at 25 °C, the functionality being conserved (4 hydroxyl groups/mol) [7].



(3.3)



(3.4)

Propoxylated DETA with 5 mol of PO/mol of DETA has a very high viscosity, of approximately 150,000 mPa.s at 25 °C, and it is very difficult to use it in the normal technologies for polyurethane (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 1 hydroxyl group (chain extension);

b) By the introduction of EO units (internal or terminal EO units); and

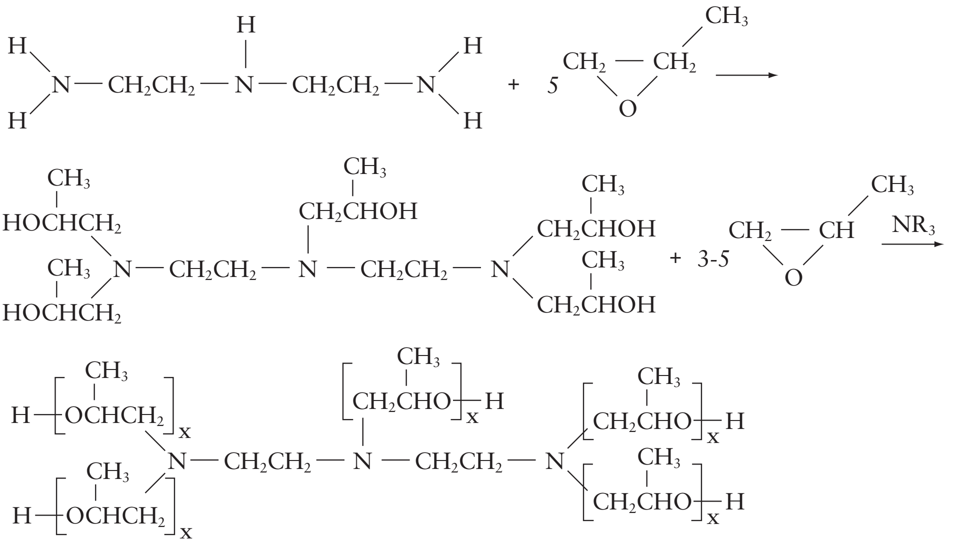
c) By the alkoxylation of a mixture between a polyamine and a low functionality amine (monoethanolamine or diethanolamine).

These three methods will now be considered in more detail:

a) Increase of polymerisation degree of a chain derived from 1 hydroxyl group

It was observed experimentally that by increasing the number of PO units per chain derived from 1 hydroxyl group there are obtained not only lower hydroxyl numbers (OH#) 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, sodium hydroxide (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, dimethylethanolamine, dimethylcyclohexylamine) the resulting polyols do not need any purification.

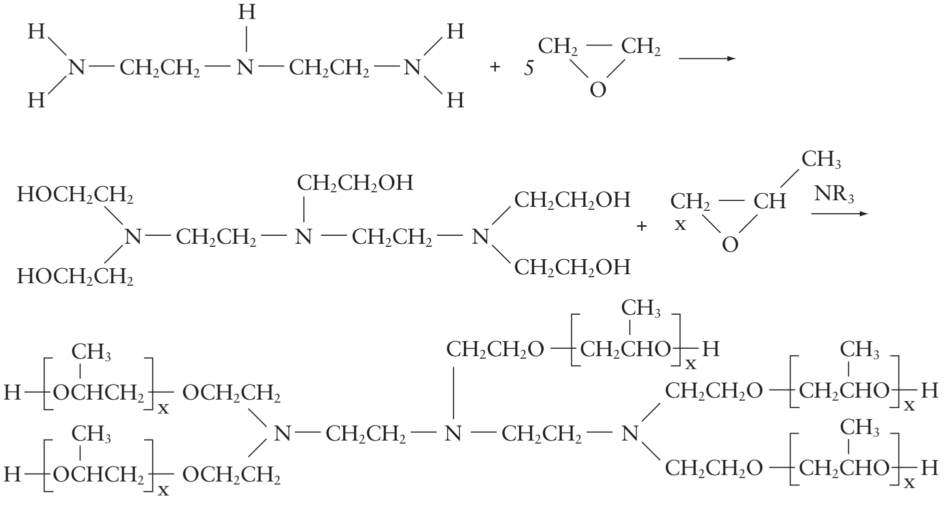
Thus, by the propoxylation of DETA with approximately 8–10 mol of PO/mol of DETA, by using dimethylethanolamine as catalyst, aminic polyols of low OH# (390–420 mg KOH/g) are obtained, with low viscosity of approximately 6,000–9,000 mPa.s at 25 °C [1, 10, 11]:



(3.5)

b) Introduction of EO units

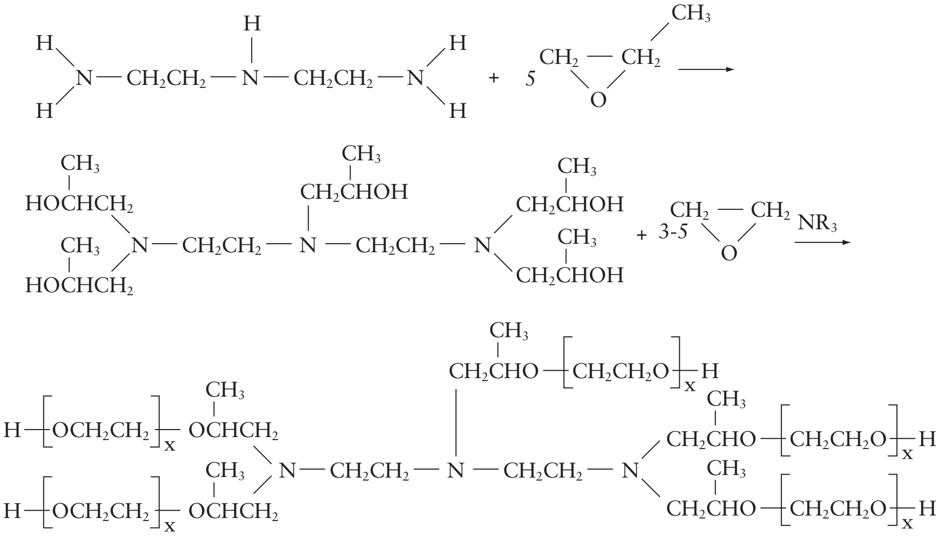
By the reaction of 4–5 mol of EO with 1 mol of DETA, followed by a catalysed propoxylation step, it is possible to obtain aminic polyols with a functionality of 5 hydroxyl groups/mol with a high OH# and convenient low viscosities (**Equation 3.6**):



x = 0,1,2

(3.6)

The DETA-based aminic polyols are synthesised by first adding 4 mol of PO and, in the second step, adding several units of EO without any other catalyst (self-catalysis). The addition of EO to the hydroxylpropyl groups formed is catalysed by the tertiary aminic nitrogen from the aminic polyol given in the propoxylation step (**Reaction 3.7**):



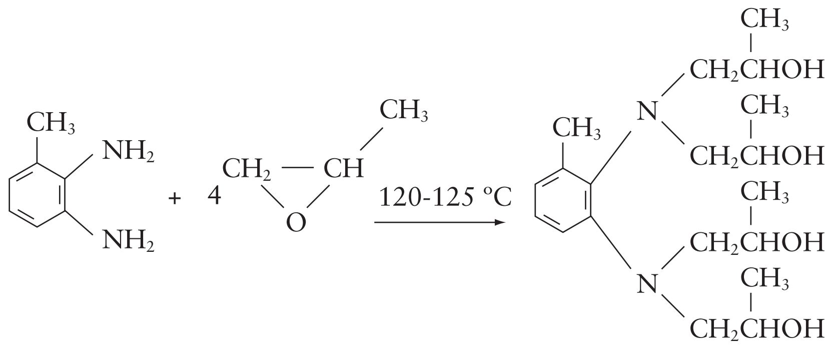
x = 0,1,2

(3.7)

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 by-product of toluene diisocyanate technology (it appears together with 2,4- and 2,6-toluene diamine). The resulting o-TDA is in fact a mixture of 2,3-toluene diamine (approximately 40%) and 3,4-toluene diamine (approximately 60%).

By propoxylation of o-TDA with 4 PO mol, without any catalyst, an extremely viscous aminic polyol is obtained, of approximately 650,000 mPa.s at 25 °C (**Reaction 3.8**):

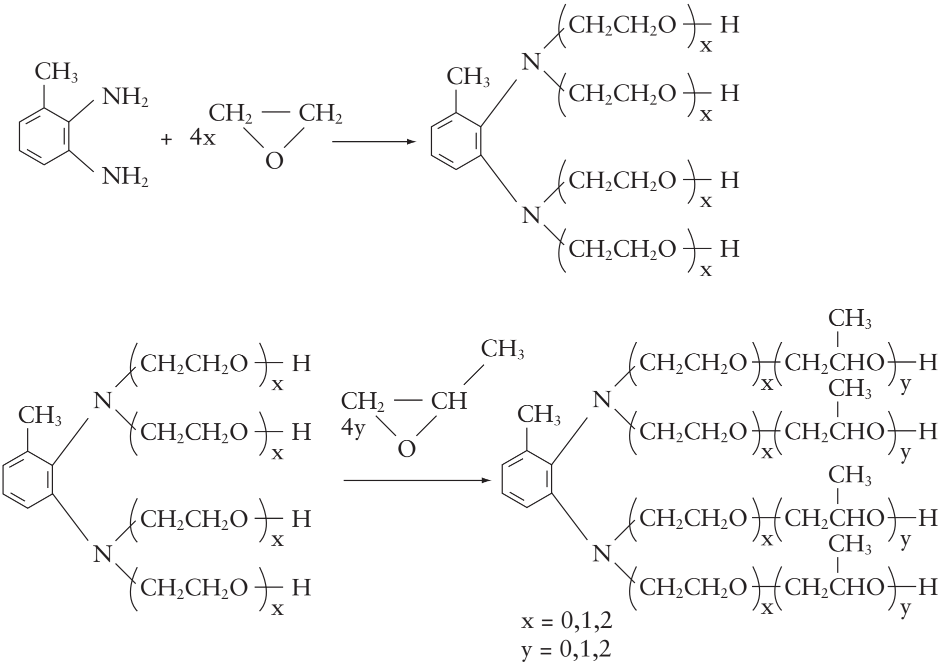


(3.8)

By increasing the degree of propoxylation (chain extension), by reacting the resulting amino polyol (**Reaction 3.8**), with PO in the presence of a catalyst (e.g., KOH), until the OH# becomes 390–410 mg KOH/g, the resulting viscosity decreases, but remains very high, approximately 140,000–145,000 mPa.s at 25 °C, which makes it difficult to use in practice [3, 4, 13].

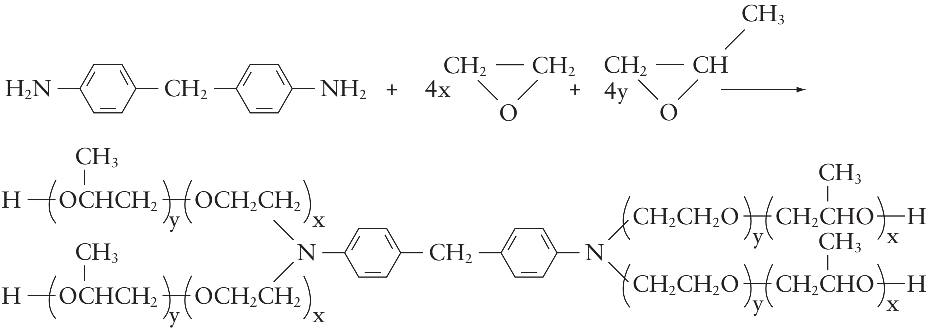
By the introduction of internal EO units (25–30% internal EO) it was possible to obtain an o-TDA-based aminic polyol with an acceptable viscosity, of approximately 10,000–15,000 mPa.s at 25 °C (**Reaction 3.9**) [4].

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.



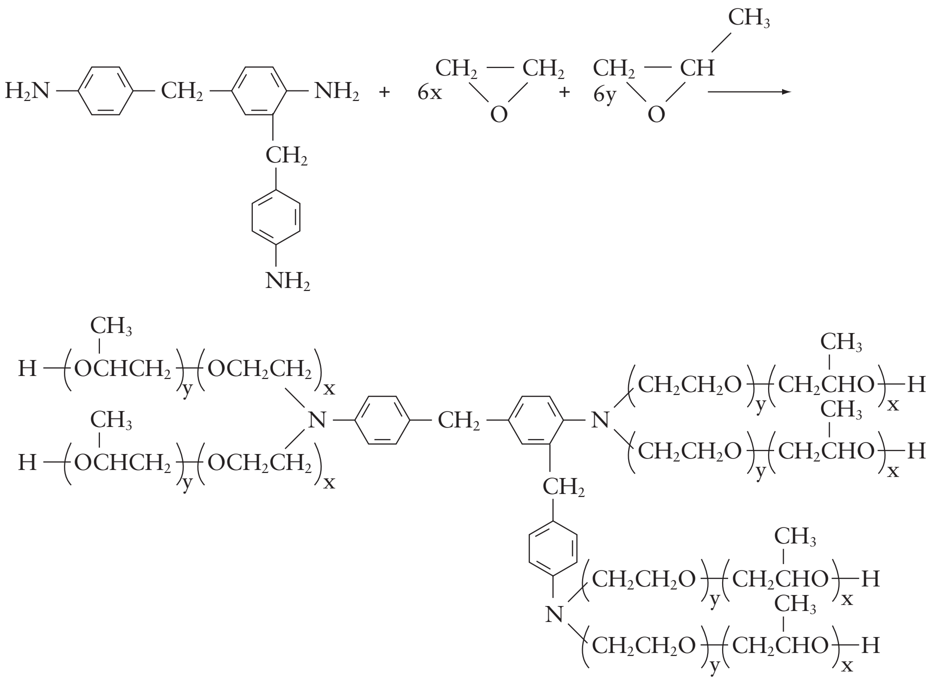
(3.9)

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 MDA, a precursor of diphenylmethane diisocyanate [2, 5, 6]:



(3.10)

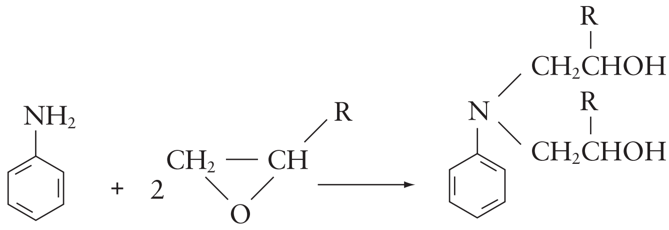
This method of viscosity decrease by introduction of internal EO units is very efficient for reusing wastes resulting from MDA fabrication, which have superior oligomers with 3, 4 or 5 aromatic nuclei (**Reaction 3.11**). Propoxylation of these MDA wastes gives extremely viscous aminic polyols [2].



(3.11)

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 mol of alkylene oxide (PO, especially EO) they become solid at RT, by crystallisation:



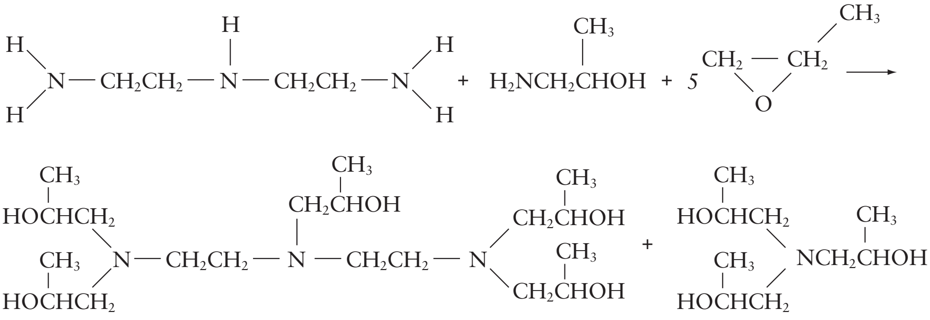
R = H, CH_3

(3.12)

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 OH# polyol = 700–800 mg KOH/g is obtained, with a convenient viscosity (approximately 15,000–25,000 mPa.s at 25 °C) and an intermediate functionality, between 3–5 or usually 3.5–4.5 hydroxyl groups/mol (**Reaction 3.13**) [13]:



(3.13)

The resulting mixtures of aminic polyols (**Reaction 3.13**) are excellent crosslinkers for rigid PUF and other PU products. The aminic polyols, due to their intrinsic high reactivity are used especially in rigid 'spray' PUF.

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; RO85851, 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; RO111277, 1996.

3. No inventors; ICI, assignee; GB1154161, 1969.

4. J.L. Haas, inventor; Mobay Chemical Corp., assignee; US4209609, 1980.

5. No inventor; Upjohn, assignee; GB1042220, 1966.

6. No inventor; Upjohn, assignee; GB1147106, 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.

8. T.H. Ferrigno in *Rigid Plastic Foams*, 2nd Edition, Reinhold Publishing Corp., New York, NY, USA, 1967.

9. M. Szycher in *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL, USA, 1999, Chapter 8, p.1.

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; RO82855, 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 Corp., assignee; US6031137, 2000.

15. R.L. Adkins, S.L. Schilling and K.J. Headley, inventors; BAYER Corp., assignee; US5872292, 1999.

16. G.A. Salensky, inventor; Union Carbide Corp., assignee; US3595918, 1971.

4 Rigid Polyols Based on the Alkoxylation of Aromatic Compound Condensates with Aldehydes

The polyols for rigid foams (referred to as rigid polyols) discussed before (**Volume 2, Chapters 2** and **3**), 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, and

c) Melamine-based polyols.

4.1 Mannich Polyols [1–21]

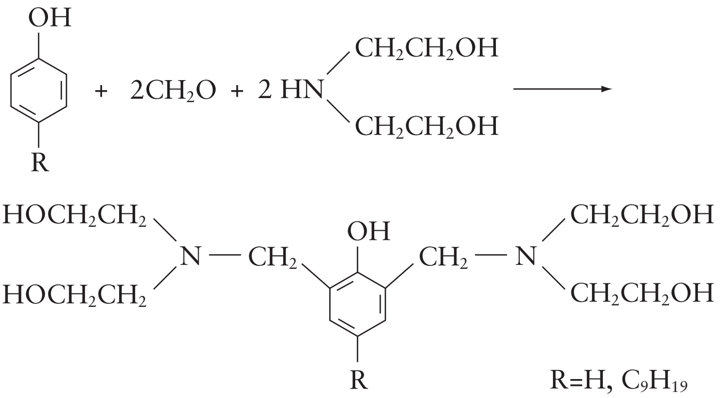
Mannich polyols is a very important group of aromatic polyols obtained by the alkoxylation with propylene oxide (PO) [and/or ethylene oxide (EO)] of the Mannich bases obtained by classical Mannich reaction between phenols [e.g., phenol, *p*-nonylphenol (NP)], formaldehyde and alkanolamines [diethanolamine (DEOA), 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.

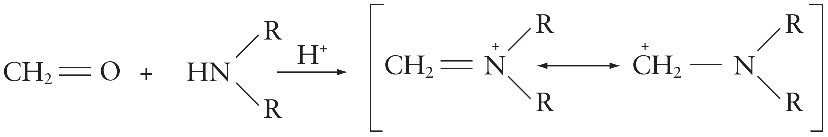
4.1.1 Synthesis of Mannich Base [2–16, 22, 23]

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 4.1**) 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 approximately 60–120 min.



(4.1)

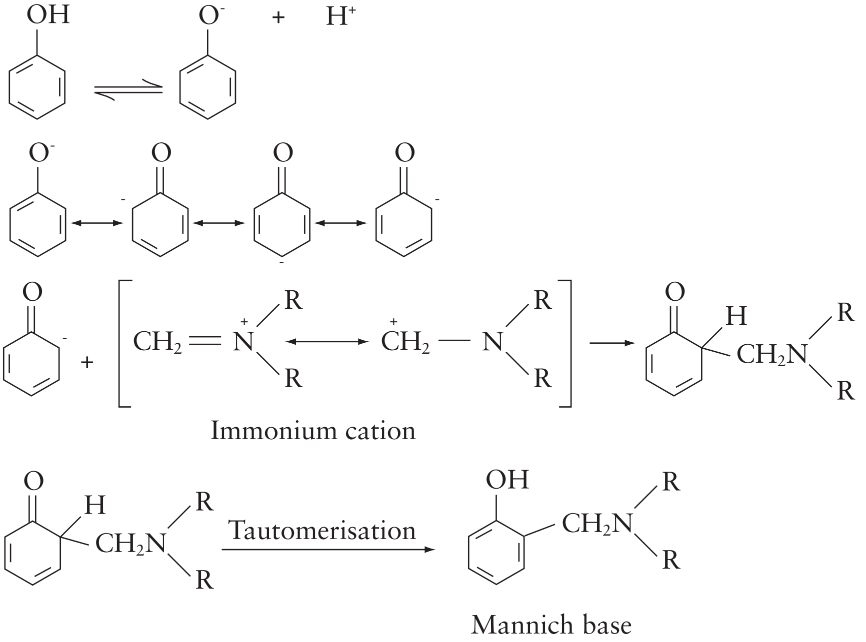
In the case of phenol, with the free *para* position, due to the interaction between the phenolic group (acidic) and the aminic nitrogen (basic) of the amino alcohol, the *ortho* position is occupied first [9]. After the synthesis of Mannich bases, the water resulting from the reaction and the water 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 4.2**) takes place, with the formation of an immonium cation [7–9, 22, 23].



Immonium cation

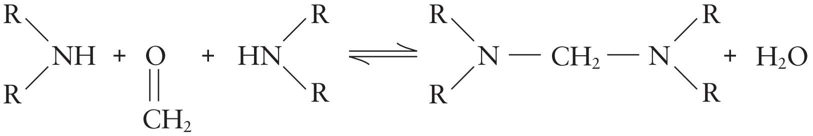
(4.2)

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 4.3**). Finally, by a tautomerisation reaction, the reformation of the aromatic phenolic structure of a substituted phenol with dihydroxyalkyl aminomethyl groups (**Reaction 4.3**) takes place.



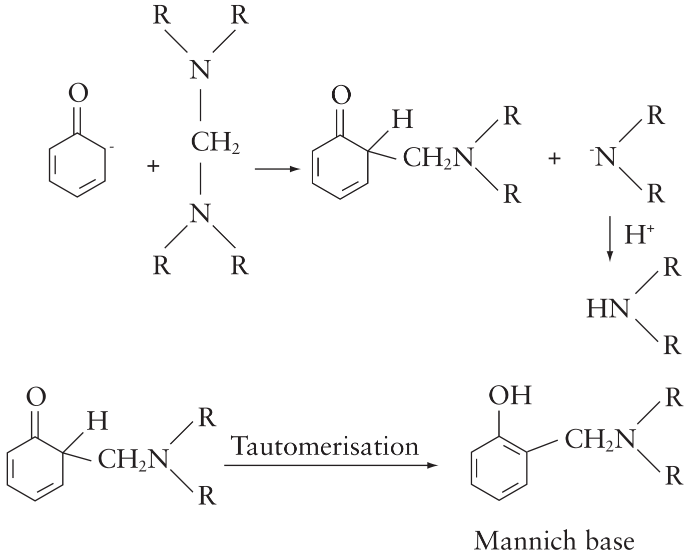
(4.3)

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:



(4.4)

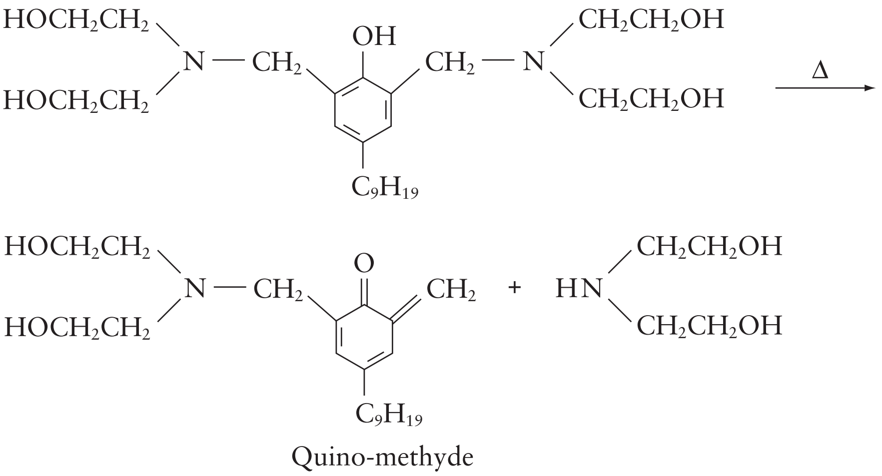
The anion of phenol, in tautomeric form with the negative charge in the nucleus, attacks the carbon atom of the methylene group in the labile methylene diamine formed in **Reaction 4.5**.



(4.5)

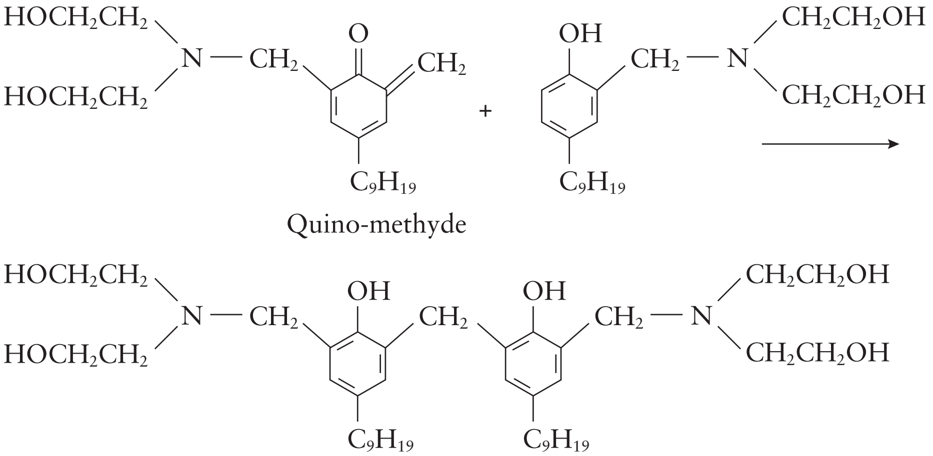
In acidic media, by using amine salts instead of free amines, the first mechanism is more probable. In neutral or basic media (e.g., the reaction of phenol with formaldehyde and alkanolamines), the second mechanism seems to be more probable [7, 8].

One possible side reaction of the synthesised Mannich base is its thermal decomposition to a very reactive quino-methyde (**Reaction 4.6**).

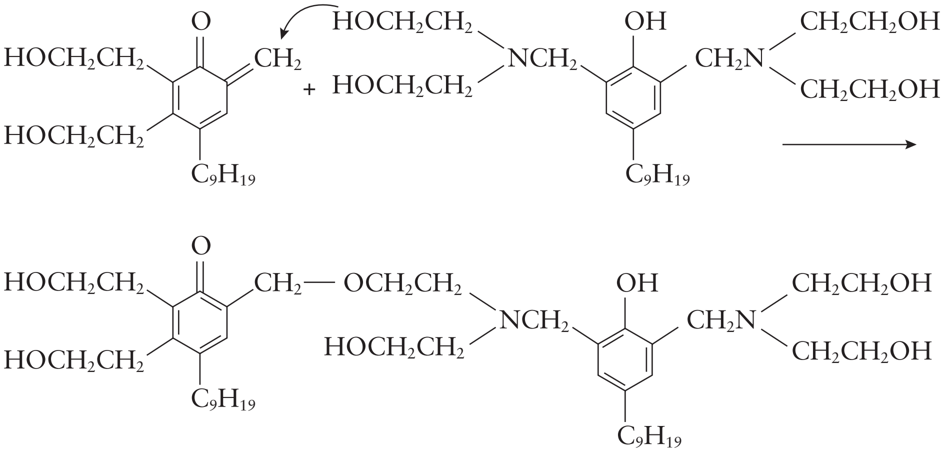


(4.6)

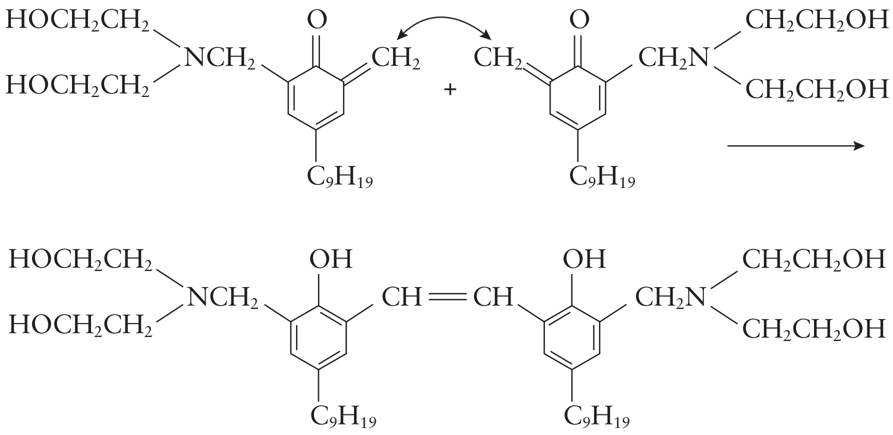
The quino-methyde reacts with *ortho*-free phenolic species from the reaction system giving superior oligomers (**Reaction 4.7**). Quino-methydes react with hydrogen active compounds, such as terminal hydroxyl groups (**Reaction 4.8**) and a specific reaction of quino-methydes is dimerisation (**Reaction 4.9**). All these reactions (**Reactions 4.6–4.9**) 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.



(4.7)



(4.8)



(4.9)

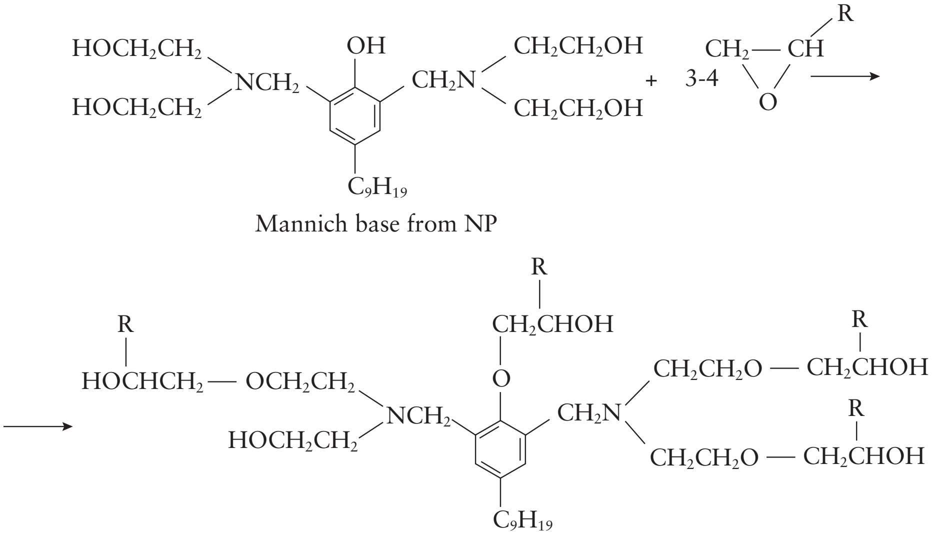
4.1.2 Alkoxylation of Mannich Base

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 h. 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 DEOA and diisopropanolamine (1:1 molar), Mannich polyols with lower viscosities than the Mannich polyols based exclusively on DEOA 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 (**Volume 2, Chapter 2**).

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 h).

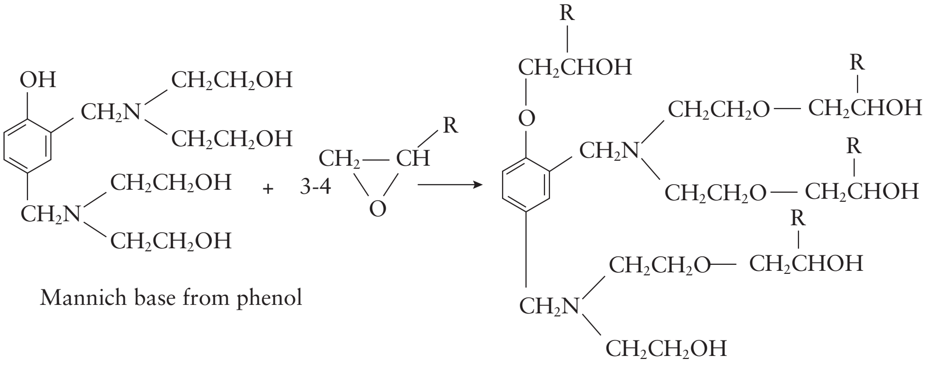
The last traces of alkylene oxides are removed by vacuum distillation at 100–110 °C. After the phenolic group alkoxylation, that is the first group which is alkoxylated, the resulting structure becomes much more stable and it is possible to develop degassing at higher temperature, without the risk of 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 4.10** [9].



Mannich polyol based on NP (4.10)

The general technological flow for the synthesis of Mannich polyols is shown in **Figure 4.1**.

For Mannich polyols from phenol, the alkoxylation reaction of the corresponding Mannich base is presented in **Reaction 4.11**. Of course, the Mannich base can have 1 or 2 aminomethyl groups or a mixture of these structures.



Mannich polyol based in phenol (4.11)

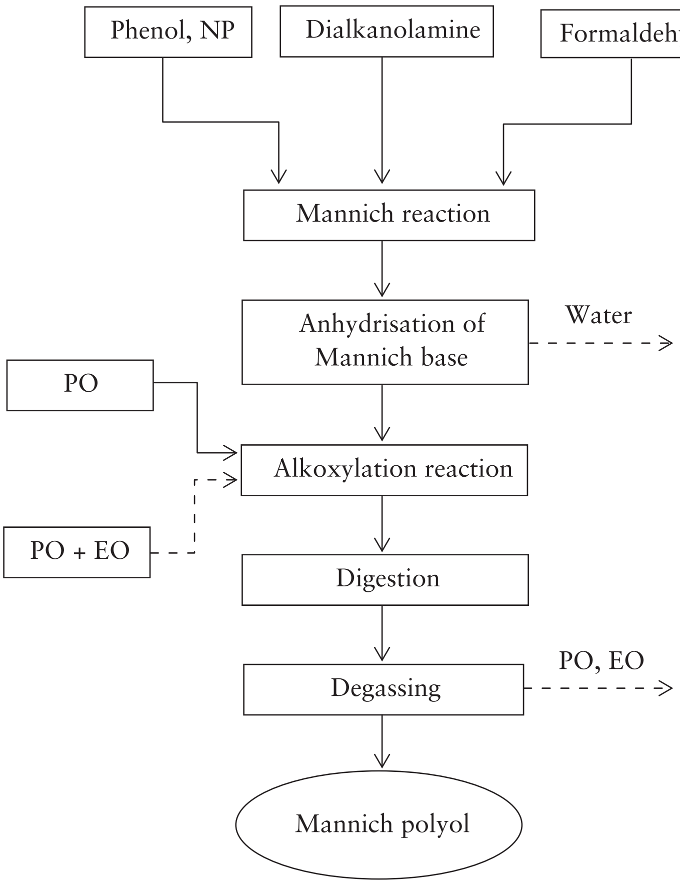


Figure 4.1 Flow chart for Mannich polyol synthesis

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*-NP]:[formaldehyde]:[DEOA]:[PO] = 1:2:2:2–3

Another important Mannich polyol is based on phenol and is characterised by the following molar ratios:

[phenol]:[formaldehyde]:[DEOA]:[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 4.2** 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 NP, 2 mol of formaldehyde and 2 mol of DEOA). One observes that after the addition of 1 PO mol/mol of Mannich base a maximum of viscosity is obtained and by the addition of 2–5 mol of PO the viscosity decreases continuously.

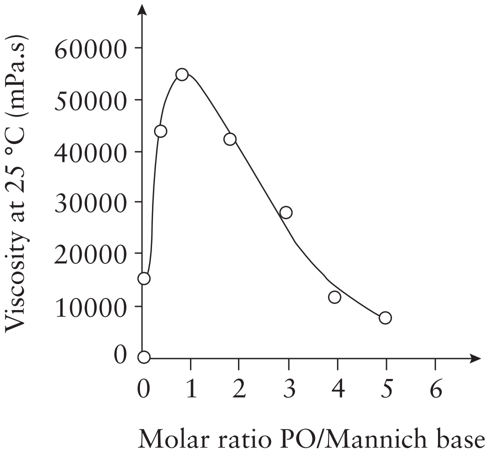


Figure 4.2 Variation of Mannich polyol's viscosity as function of molar ratio PO/ Mannich base, [NP]:[formaldehyde]:[DEOA] = 1:2:2

It is possible to add 2–3 mol of PO/mol of Mannich base in the self-catalysis of the tertiary amino nitrogen of the Mannich base, but 4–6 mol of PO/Mannich base needs a catalyst, such as a low hindered tertiary amine (e.g., dimethylaminoethanol, dimethylcyclohexylamine).

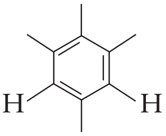
The Mannich polyols described are aromatic aminic polyols, the aromatic rings have a real contribution in improving the physico-mechanical, thermal and fire proofing properties of the resulting rigid polyurethane foams (PUF). The Mannich bases, for example the Mannich base resulting from 1 mol of NP, 2 mol of formaldehyde and 2 mol of DEOA, are viscous liquids, with a convenient viscosity of approximately 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 PUF, 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 NP 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:

$$\text{Aromaticity (\%)} = \frac{74}{\text{MW of Mannich polyol}} \times 100$$

74 = molar mass of a tetrasubstituted benzene nucleus



(4.12)

Where:

MW: Molecular weight

The approximate functionality of Mannich polyols is calculated with the following formula:

$$f = \frac{[\text{formaldehyde}]}{[\text{phenol}]} \times 2 + 1 \tag{4.13}$$

The MW of Mannich polyol can be calculated with **Formula 4.14** or with **Formula 4.15**.

$$M = \frac{f \times 56,100}{\text{OH\#}} = \frac{\left\{\frac{[\text{formaldehyde}]}{[\text{phenol}]} \times 2 + 1\right\} \times 56,100}{\text{OH\#}} \tag{4.14}$$

$$M = M_P + n(M_f + M_{am} - 18) + m \times 58 \qquad (4.15)$$

Where:

M: MW of Mannich polyol;

M_p: MW of phenol;

M_f: MW of aldehyde;

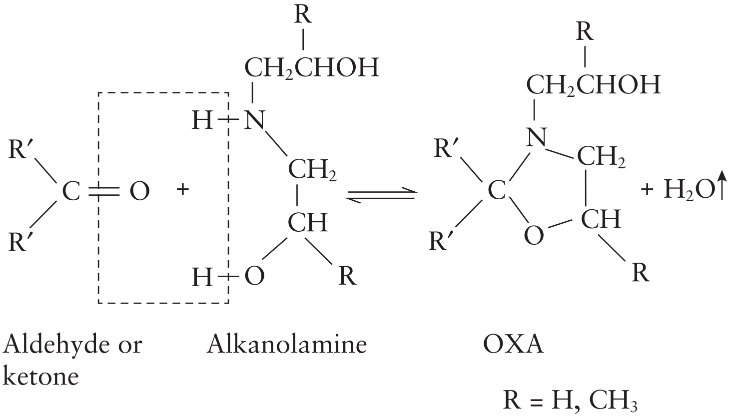
M_{am}: MW of alkanolamine;

n: Number of aldehyde mol/mol of phenol; and

18: MW of water (water eliminated from the reaction).

4.1.3 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(s) (OXA), a heterocyclic compound resulting from the reaction of an alkanolamine (primary or secondary, not tertiary) and an aldehyde or a ketone (**Reaction 4.16**).



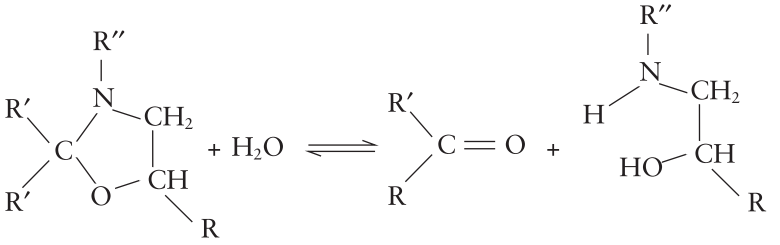
$R = H, CH_3$

$R' = H, CH_3$

(4.16)

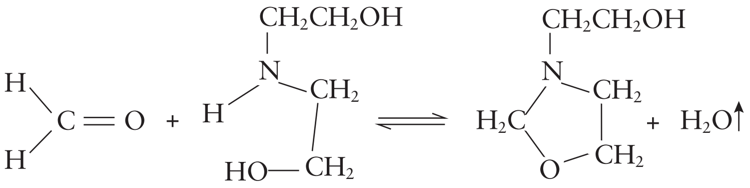
Reaction 4.16 is an equilibrium reaction and this equilibrium is pushed to the OXA formation by the water elimination from the reaction system under vacuum distillation. This reaction is used in practice to trap the traces of water in some polyurethane (PU) formulations which need a perfect anhydrous media e.g., in PU elastomers [26]. By the addition of OXA to these formulations reaction of these compounds with water takes place and the OXA 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 4.17**).

In the particular case of Mannich polyol synthesis, the main alkanolamine used is DEOA (and to a lesser extent, diisopropanolamine [11]) while the carbonyl compound is formaldehyde [5, 6, 9].



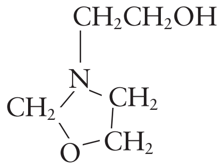
(4.17)

By the reaction of DEOA with formaldehyde (aqueous or paraformaldehyde), at 50–70 °C, the following OXA (**Reaction 4.18**) is formed with a high yield:



Formaldehyde DEOA OXA (4.18)

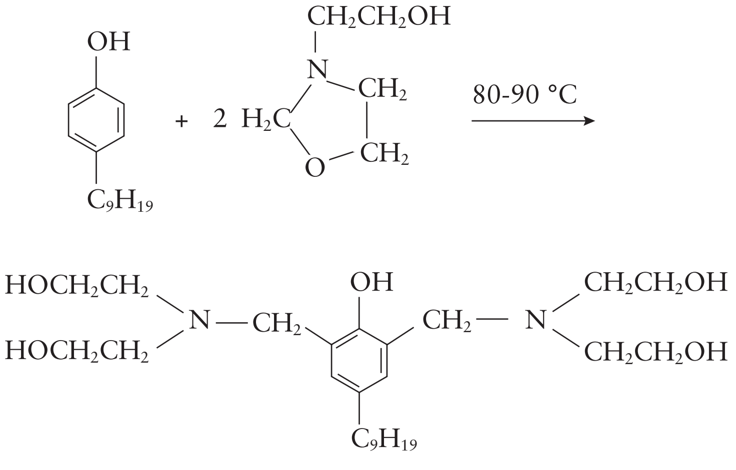
After the vacuum distillation of the resulting water (preferable at 90–100 °C and 1.35–26.65 Pa), a liquid substance of low viscosity is obtained, which is a distillable liquid, and very stable in anhydrous conditions. The characteristics of the OXA derived from DEOA and formaldehyde are shown in **Figure 4.3** [9].



1. Aspect: low viscosity, light yellow to light brown liquid (when freshly distilled it is a colourless transparent liquid)
2. MW: 117
3. OH#:800-1,000 mg KOH/g
4. Density at 25 °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 8,000 Pa
10. Strong infrared absorption at 1,650 cm^{-1} (C=N, imine group)

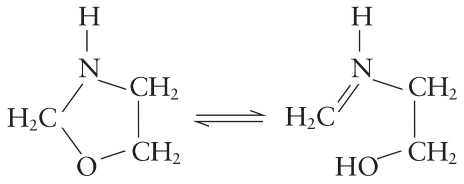
Figure 4.3 Structure and characteristics of 1,3-*N*-hydroxyethyl oxazolidine (HE-OXA)

The synthesised OXA react with phenols at 80–90 °C (**Reaction 4.19**) and give rise to the Mannich bases which have the same structure as those obtained by the direct classical Mannich reaction:



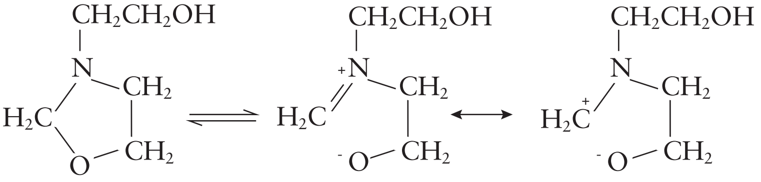
(4.19)

The mechanism of this unconventional reaction may be explained in two ways. OXA 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 OXA derived from formaldehyde and monoethanolamine, the equilibrium is presented in **Reaction 4.20**.



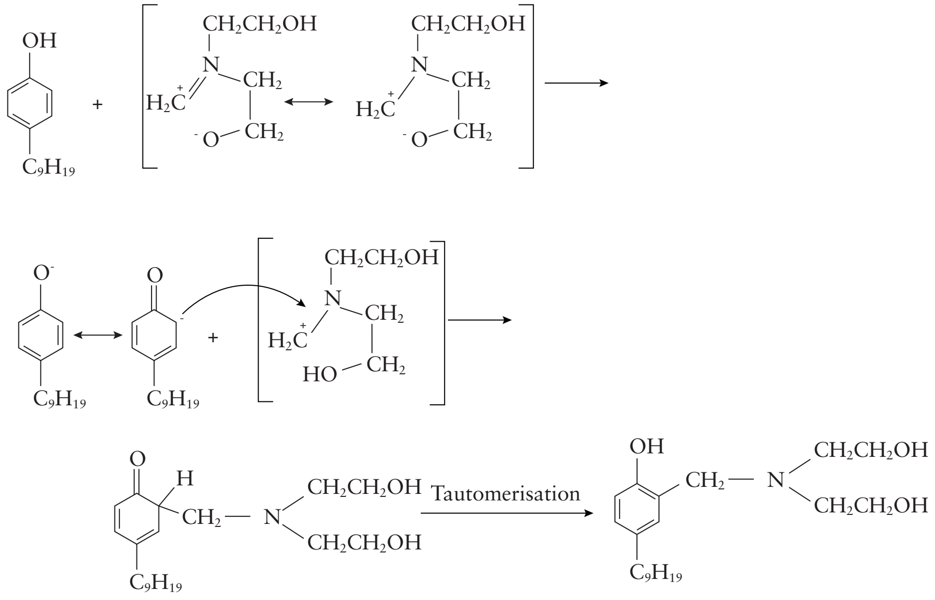
(4.20)

In the particular case of OXA derived from formaldehyde and DEOA, the equilibrium of the cyclic form with the open chain form is presented in **Reaction 4.21**.



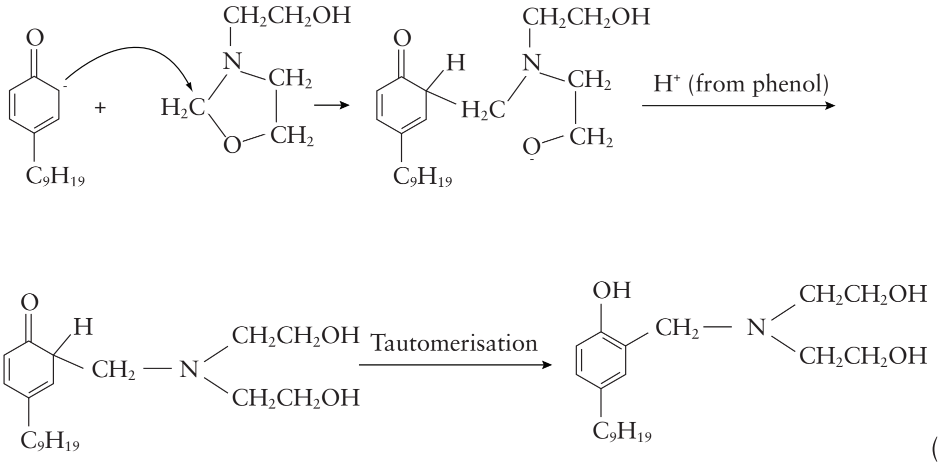
(4.21)

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 4.22**.



(4.22)

The second mechanism proposed to explain the reaction between an OXA 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 4.23**)



(4.23)

The synthesis of Mannich polyols based on OXA chemistry has the following three steps:

a) Synthesis of HE-OXA,

b) Synthesis of the Mannich base, and

c) Alkoxylation of the resulting Mannich base with PO (or PO–EO mixtures).

4.1.3.1 Synthesis of 1,3-N-hydroxyethyl oxazolidine

The synthesis of HE-OXA is based on a stepwise addition of aqueous formaldehyde (25–37%) or solid paraformaldehyde (85–97%) to DEOA, at 50–70 °C. The reaction leads to the rapid formation of a mixture of OXA-water, the reaction being only slightly exothermic. After the reaction (approximately 2 h 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 OXA. A short distillation time, at a high vacuum (0.6–2.7 MPa) and lower temperature, leads to a high quality OXA. A thin film water distillation is one of the best ways to obtain high quality anhydrous OXA.

4.1.3.2 Synthesis of the Mannich Base

The simple mixing of the anhydrous HE-OXA with a phenol, at 80–90 °C, for 2–3 h leads to the formation of Mannich bases. As a general observation, the Mannich bases made *via* the OXA route have lower viscosities than the Mannich bases obtained by the classical reaction of phenol with formaldehyde and DEOA. 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).

4.1.3.3 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 4.4** shows that the Mannich polyols obtained by the OXA 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 OXA route is well characterised by the following ratios:

$$[\text{phenol}]:[\text{OXA}]:[\text{PO}]$$

A Mannich polyol based on NP and OXA with a functionality of 5 hydroxyl groups/mol has the following molar ratios:

$$[\text{NP}]:[\text{OXA}]:[\text{PO}] = 1:2:2\text{–}3$$

A Mannich polyol based on NP and OXA with a functionality of 4 hydroxyl groups/mol is characterised by the following molar ratios:

$$[\text{NP}]:[\text{OXA}]:[\text{PO}] = 1:1.5:2\text{–}3$$

A Mannich polyol based on a phenol with a functionality of 3 is characterised by the following molar ratios:

$$[\text{phenol}]:[\text{OXA}]:[\text{PO}] = 1:1:2\text{–}2.5$$

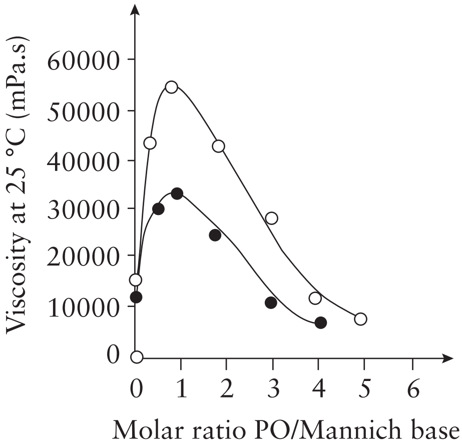


Figure 4.4 Variation of Mannich polyol's viscosity as function of the molar ratio of PO/Mannich base made by classic Mannich reaction (O) and by OXA route (•); [NP]:[formaldehyde]:[DEOA] = 1:2:2 (O); and [NP]:[OXA] = 1:2 (•)

The functionality of Mannich polyols obtained by OXA technology is given by the **Formula 4.24**:

$$f = \frac{[\text{OXA}]}{[\text{phenol}]} \times 2 + 1 \tag{4.24}$$

Where:

f: Functionality (hydroxyl groups/mol);

[OXA]: Number of OXA mol;

[phenol]: Number of phenol mol;

2: 1 mol of OXA generates 2 hydroxyl groups; and

1: 1 phenolic group generates 1 aliphatic hydroxyl group.

The theoretical hydroxyl number (OH#) for the Mannich base can be calculated with the **Formula 4.25**:

$$\text{OH\#} = \frac{f \times 56,100}{M} = \frac{\left(\frac{[\text{OXA}]}{[\text{phenol}]} \times 2 + 1\right) \times 56,100}{M_{ph} + \frac{[\text{OXA}]}{[\text{phenol}]} \times 117} \tag{4.25}$$

Where:

M_{ph}: MW of phenol, and

117: MW of OXA.

The quantity of PO (Q_{PO}) needed to be added to a quantity of Q_M of Mannich base in order to obtain the required final OH# (I_f) of Mannic polyol is given by the **Relationship 4.26**:

$$\begin{aligned} QM \times I_M &= (Q_M + Q_{PO}) \times I_f \\ Q_{PO} &= \frac{Q_M \times I_M}{I_f} - QM \end{aligned} \tag{4.26}$$

Where:

Q_M: Quantity of Mannich base;

Q_{PO}: Quantity of PO needed;

I_M: OH# of Mannich base; and

I_f: OH# 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 OXA technology is presented in **Figure 4.5**.

Mannich polyols are aromatic polyols, which confer excellent physico-mechanical, thermal and fire proofing properties to rigid PUF. Mannich polyols, especially those based on *p*-NP, have a very good compatibility with pentanes used as blowing agents (e.g., sucrose polyether polyols have a poor compatibility with pentanes, giving emulsions at normal concentrations for foaming, but not real solutions).

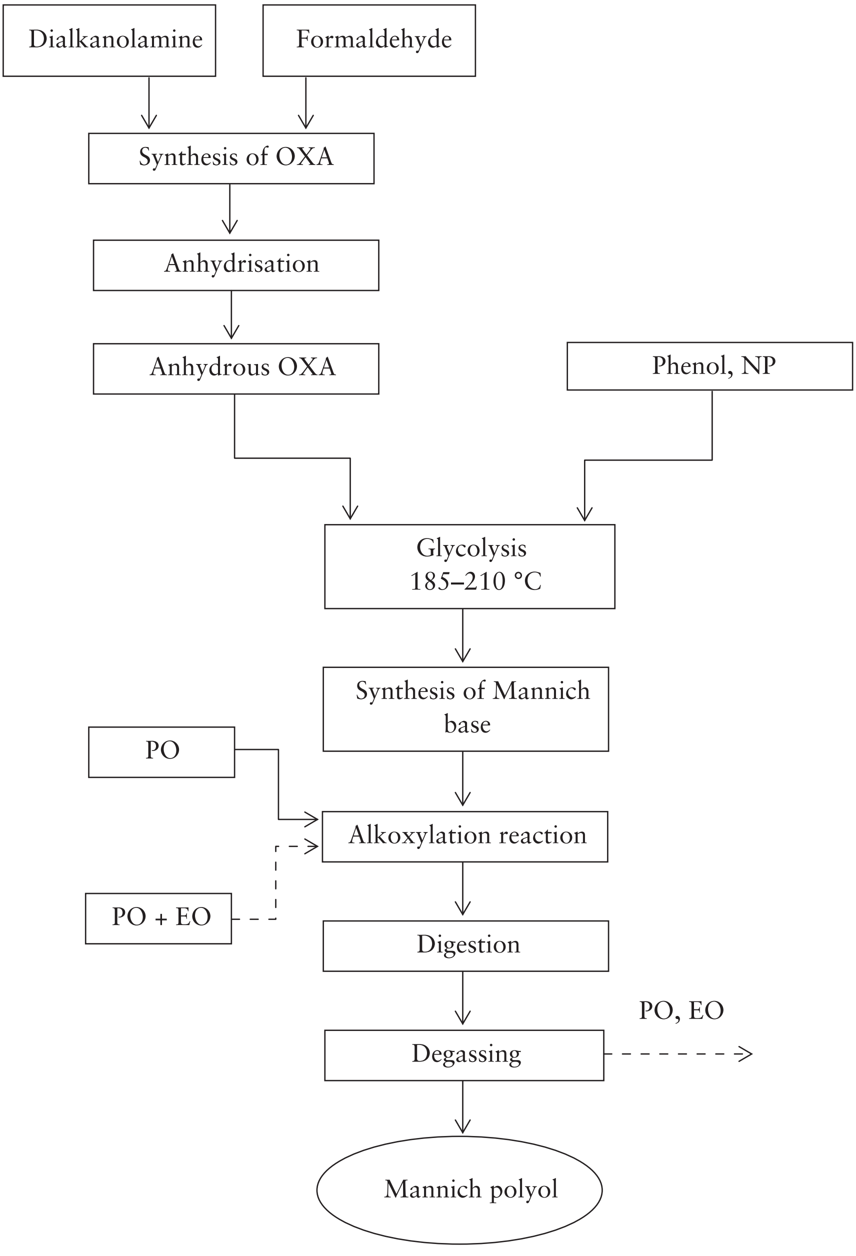


Figure 4.5 Synthesis of Mannich polyols by the OXA route

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 PUF are used successfully too [16–19]. By utilisation of Mannich polyols in pour-in-place, rigid PUF formulations – a reduction of catalysts for foaming of approximately 30–40% 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 hydroxyl groups/mol) and low OH# = 325 mg potassium hydroxide (KOH)/g], derived from NP was developed successfully for 'all water blown' rigid PUF [19].

Unpropoxylated Mannich bases were used successfully as polyols in combination with other polyols (e.g., with aromatic polyesters) or as crosslinkers in rigid PUF, 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 PUF. This high char yield confers to the rigid PUF an inherent fire resistance.

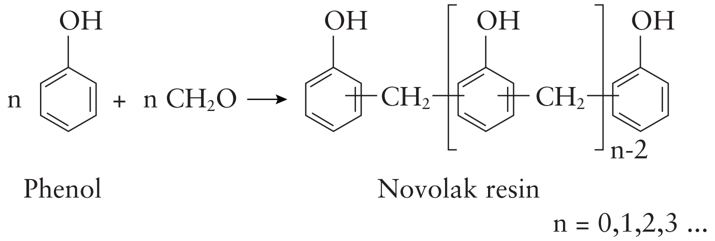
The fabrication of Mannich polyols by the OXA route has the following advantages:

1. The productivity of the reactor is higher because a large volume of water is replaced by a useful reaction product (an increase of productivity of approximately 40%). In classic Mannich technology, at a reaction mass of 5,000 kg, approximately 1,500 kg is water. In OXA technology (OXA made in a separate reactor), the reaction mass does not have any water and is in fact only a mixture of phenol with OXA.
2. The viscosity of Mannich polyols obtained by OXA 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 OXA route is shorter than the time needed for normal Mannich technology.
4. The quality of Mannich polyols obtained by the OXA 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 (OXA), it is possible to obtain a large range of Mannich polyols. Thus, by simple reaction of OXA 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 OXA technology, are presented in **Tables 4.1** and **4.2**. The characteristics of representative Mannich bases used as sole polyols are presented in **Table 4.3**.

4.2 Novolak-based Polyether Polyols

Novolaks are condensation products of formaldehyde with phenols, obtained by acidic catalysis (usually oxalic acid [27]):



(4.27)

Table 4.1 The characteristics of two representative Mannich polyols based on NP obtained by OXA technology

Characteristic	Unit	Type 1	Type 2
MW	daltons	584	510
Functionality	Hydroxyl groups/mol	5	4
OH#	mg KOH/g	480	440
Viscosity at 25 °C	mPa.s	25,000	7,800
Tertiary nitrogen	Equivalent %	0.34	0.29
Water content	%, maximum	0.1	0.1
Ratio [NP]:[OXA]:[PO]	[mol]:[mol]:[mol]	1:2:2–3	1:1.5:2–3

Table 4.2 The characteristics of two representative Mannich polyols based on phenol obtained by OXA technology [9]

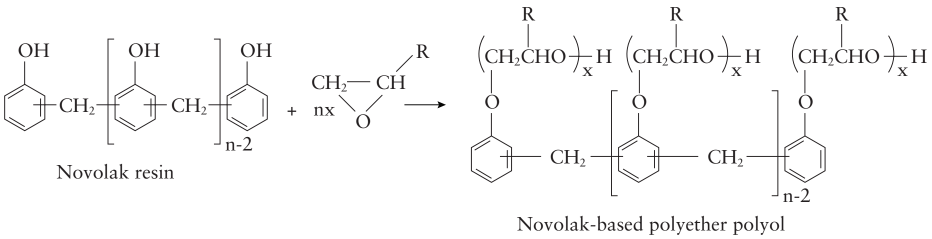
Characteristic	Unit	Type 1	Type 2
MW	daltons	330	578
Functionality	Hydroxyl groups/mol	3	5
OH#	mg KOH/g	510	485
Viscosity at 25 °C	mPa.s	9,000	16,000
Tertiary nitrogen	Equivalent %	0.30	0.34
Water content	%, maxmum	0.1	0.1
Ratio [NP]:[OXA]:[PO]	[mol]:[mol]:[mol]	1:1:2	1:2:4

Table 4.3 Some characteristics of representative Mannich bases obtained by OXA technology [9]

Characteristic	Unit	Mannich base from phenol	Mannich base from NP
OH#	mg KOH/g	839	645
Viscosity at 25 °C	mPa.s	27,700	9,800
Tertiary nitrogen	mequiv./g	6.28	4.61
pH (methanol/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, sodium hydroxide (NaOH)] or better, in the presence of a low hindered tertiary amine, aromatic polyether polyols of the following structure are obtained [27, 28] (**Reaction 4.28**):



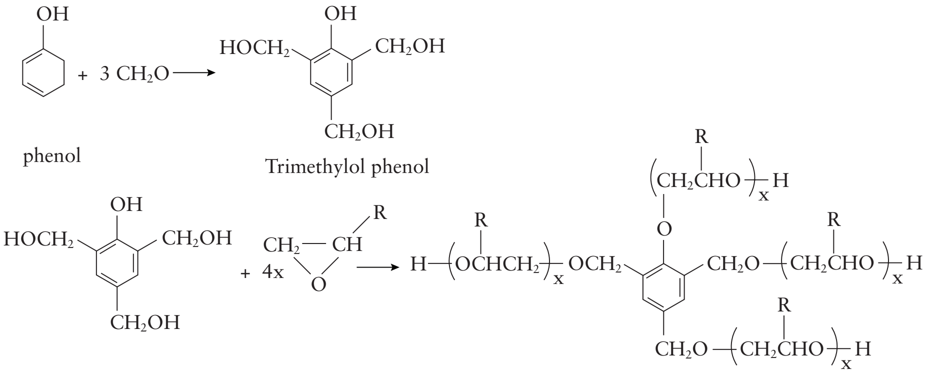
(4.28)

By the propoxylation of commercial novolaks, lower viscosities of approximately 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 OH# of novolak polyols obtained by the direct propoxylation of novolaks is low, approximately 230–250 mg KOH/g. The OH# is increased and the viscosity is decreased by propoxylation of a mixture of novolaks with high OH# 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 OH#, give rigid PUF 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 4.29**).



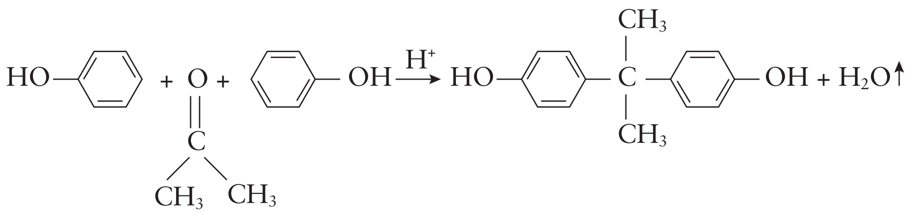
(4.29)

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.

4.3 Bisphenol A-based Polyols

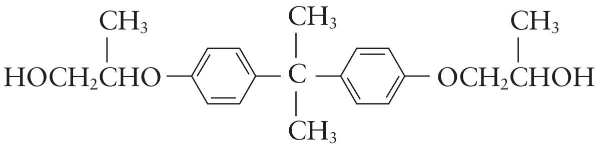
Bisphenol A (BPA) is a condensation product of 2 mol of phenol with 1 mol of acetone (**Reaction 4.30**):



(4.30)

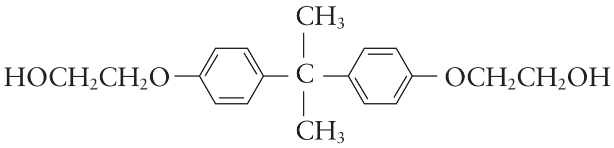
BPA is used in large quantities for fabrication of epoxy resins, polycarbonates and polyarylates.

Propoxylates of BPA with 2 mol of PO/mol of bisphenol (**Reaction 4.31**) and of the ethoxylated BPA (**Reaction 4.32**) with 2 mol 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

(4.31)



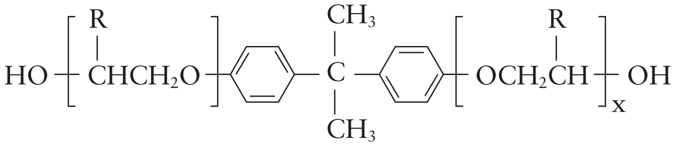
MW = 316.27
OH# = 354

(4.32)

Both aromatic diols are solid, at room temperature (RT), with convenient melting points (mp) and have high aromaticity. Thus, the propoxylated BPA has an aromatic content of 46.7% and ethoxylated BPA an aromatic content of approximately 48%.

By solubilisation of propoxylated BPA with the **Reaction 4.31**, 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 BPA. From these mixtures rigid PUF were obtained. Due to the aromaticity introduced by the propoxylated BPA, the physico-mechanical properties of the resulting rigid PUF were superior to the rigid PUF made with the sucrose-based polyether polyol alone [29].

BPA propoxylated or ethoxylated with 2–10 mol of alkylene oxides/mol of BPA are used as chain extenders for PU elastomers and as aromatic diols for isocyanuric and urethane isocyanuric foams [30] (**Reaction 4.33**).

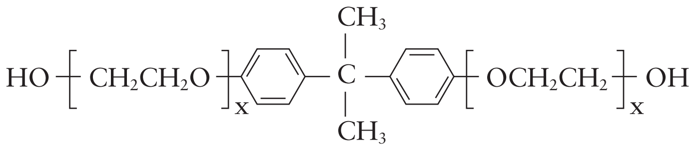


x = 1,2,3,4,5 ...
R = H, CH_3

(4.33)

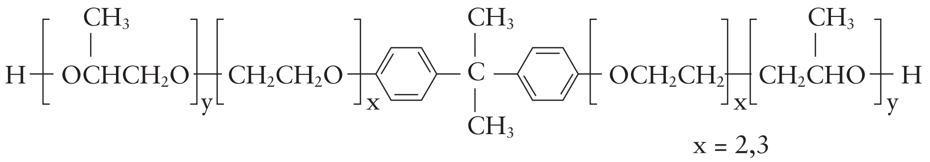
An excellent polyol for urethane isocyanuric foams is a diol-based on BPA, alkoxylated with 8–9 mol of EO or with 4 mol of PO and 4–5 mol of EO (**Reactions 4.34** and **4.35**).

BPA is a compound with a mp of approximately 157 °C, which is higher than the normal alkoxylation temperatures (90–120 °C). BPA 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

(4.34)



x = 2,3
y = 2

(4.35)

The catalysts for the alkoxylation of BPA 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 BPA.

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 BPA in liquid PO, in the presence of the tertiary amine used as catalyst (molar ratio 1 mol of bisphenol per 1.5–2 mol of PO). After 1.5–2 h of mixing at 90–100 °C, the alkoxylation is continued by adding 6–8 mol of EO. Finally, the resulting diol is degassed under vacuum and is used in PU fabrication without any purification step.

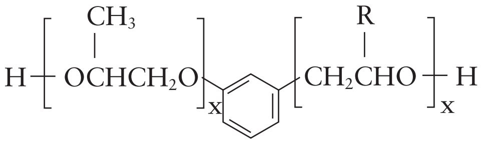
A third process of solid BPA alkoxylation is to use a suspension of solid BPA in final polyether polyol (40–60% BPA and 60–40% liquid polyether diol). This suspension, in the presence of a tertiary amine as catalyst, is ethoxylated at 80–95 °C, with 8–9 mol of EO/mol of BPA. At the end of the reaction, all the solid BPA 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 PUF are obtained by the simultaneous alkoxylation with PO (or EO) of a mixture from BPA and a costarter, such as: BPA–*ortho*-toluene diamine [32], BPA–diaminodiphenylmethane [32], BPA–polyethylene glycol of MW of 600 [11], or BPA–sorbitol-glycerol [11].

Simultaneous alkoxylation of BPA and an aromatic amine as second polyol is a variation used to obtain highly aromatic polyols.

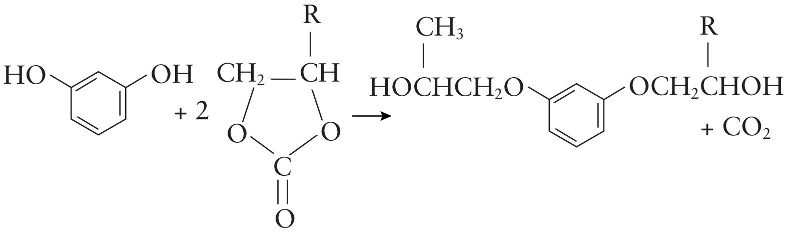
4.4 Resorcinol-based Diols [33, 34]

Resorcinol diols represent a new class of aromatic dihydroxylic compounds with the general formula (**Reaction 4.36**):



x = 0,1,2 R = H,CH$_3$ (4.36)

Resorcinol diols are obtained by the reaction of resorcinol with ethylene carbonate or propylene carbonate (**Reaction 4.37**), in the presence of basic catalysts (potassium carbonate, KOH, NaOH, tertiary amines), or even in the absence of catalysts, at higher temperatures (150–170 °C):

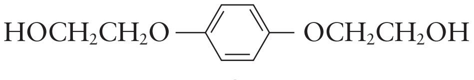


(4.37)

A resorcinol diol based on 1 mol of resorcinol and 2 EO units is a solid with a mp of 87–89 °C and a OH# of 555 mg KOH/g [34]. All the resorcinol diols having PO units or PO and EO units are liquids at RT, with a viscosity of between 3,900–20,000 mPa.s at 25 °C and OH# between 345–485 mg KOH/g [34]. The resorcinol diols based on resorcinol and more than 2 EO units are liquid at RT, with a viscosity of approximately 2,000 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 approximately 50% [33, 34].

Resorcinol diols are superior to the well-known hydroquinone di(β-hydroxyethyl) ether (HQEE), which is a solid with a mp of 100 °C:

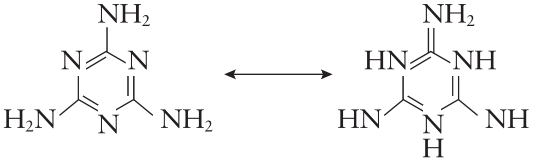


HQEE (4.38)

The resorcinol diols are used successfully in high durability and thermal stability PU adhesives, PU elastomers (cast and thermoplastic PU elastomers), sealants and coatings.

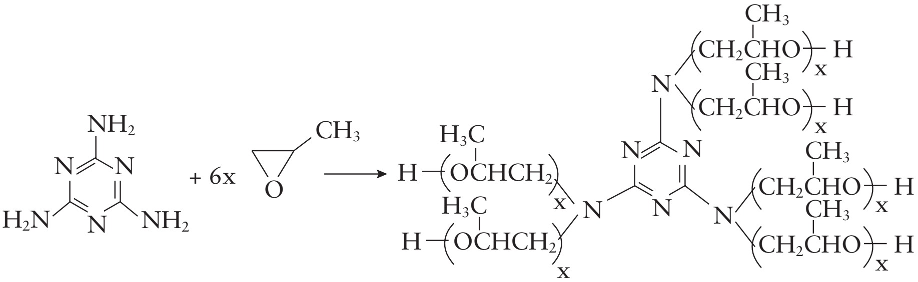
4.5 Melamine-based Polyols for Rigid Polyurethanes [14, 17, 19, 20, 24, 31, 35]

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]:



(4.39)

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 (EG) (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 (e.g., DMSO, dimethylformamide, *N*-methyl pyrrolidone and so on), in the presence of quaternary ammonium hydroxides as catalysts (e.g., tetrabutyl ammonium hydroxide), at a low reaction rate (**Reaction 4.40**), for a very long reaction time (40–50 h) [31, 37]. The resulting hexafunctional polyols give very thermostable rigid PU (up 200 °C).

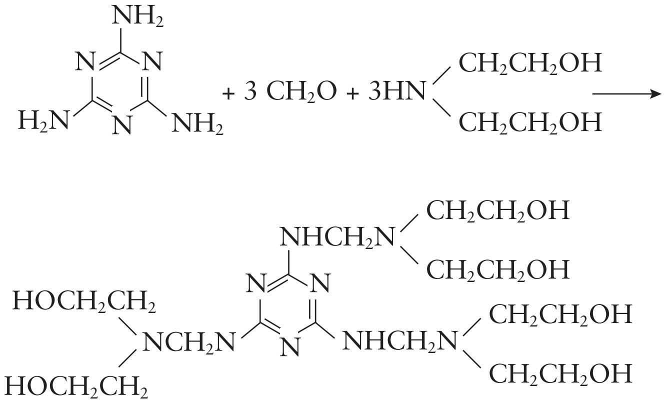


(4.40)

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 DEOA, a melamine-based Mannich base (**Reaction 4.41**), is obtained quantitatively in 1–2 h at 60–70 °C. The resulting Mannich base is a hexafunctional starter [10, 21, 31]:

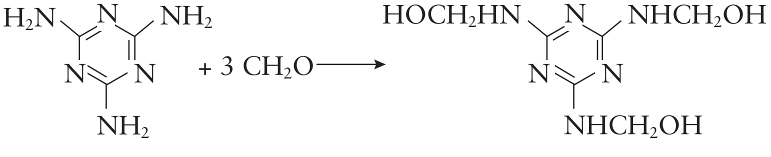


(4.41)

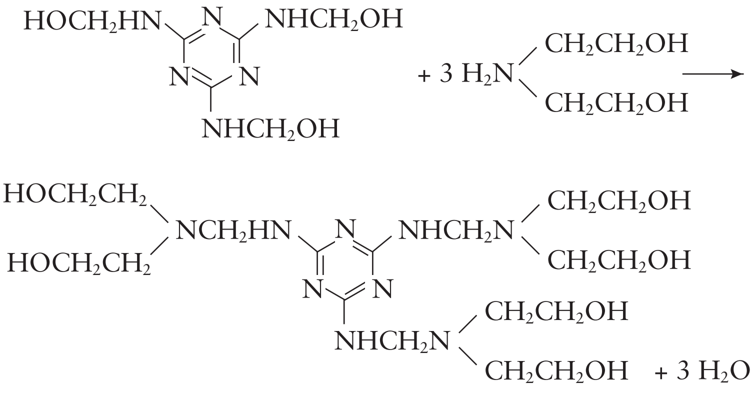
Practically, the reaction takes place by the addition of aqueous formaldehyde to a mixture of melamine suspended in DEOA, at a molar ratio of [melamine]:[formal dehyde]:[DEOA] = 1:3:3, followed by water distillation under vacuum, at a lower temperature of 65–75 °C, in order to avoid the viscosity increase produced by polycondensation. The maximum water accepted in the Mannich base can be high, approximately 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 DEOA [10] (**Reactions 4.42** and **4.43**).

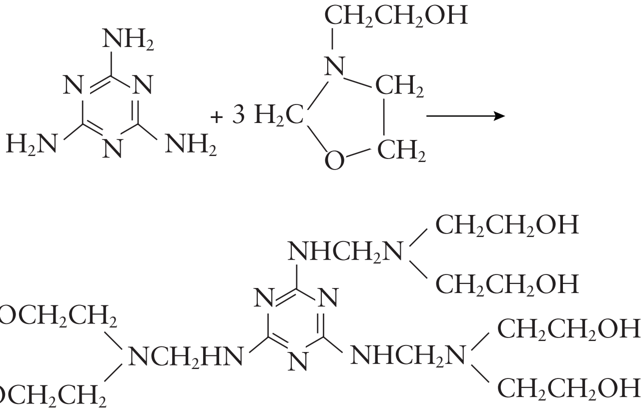


(4.42)



(4.43)

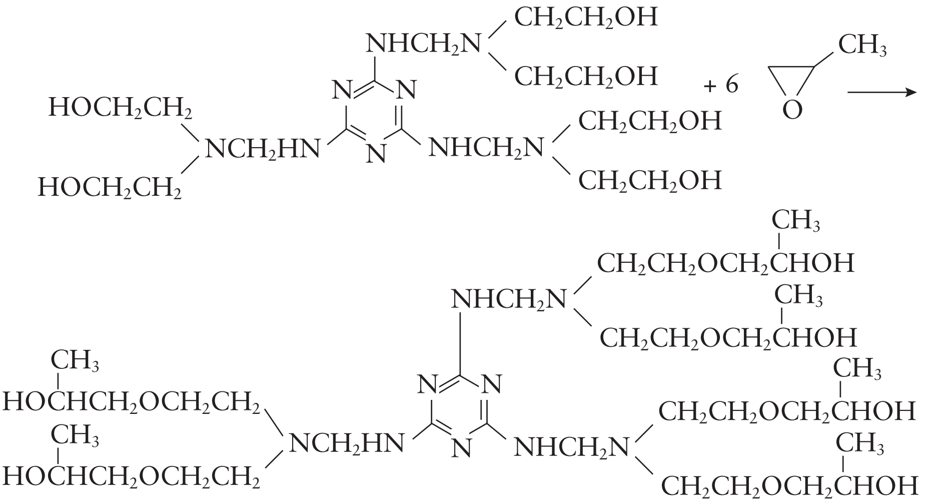
The second method consists of the reaction of melamine with OXA (**Reaction 4.44**) [31].



(4.44)

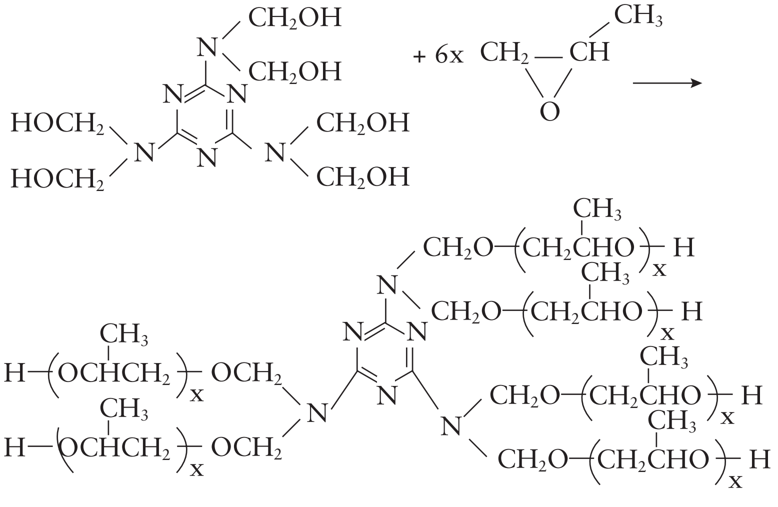
Unfortunately, due to the low solubility of melamine in OXA, **Reaction 4.44** takes place slowly, needs a long reaction time and unreacted melamine frequently remains. The best method for the synthesis of melamine Mannich base is the Mannich reaction in the presence of aqueous formaldehyde.

By the propoxylation of the synthesised melamine derived Mannich base, without catalyst, a hexafunctional polyether polyol is obtained (**Reaction 4.45**).



(4.45)

Very interesting polyols are obtained by hexamethylolmelamine alkoxylation with PO, in the presence of a low hindered tertiary amine (e.g., dimethylaminoethanol) as catalyst, at 80–95 °C (**Reaction 4.46**) [35, 38].

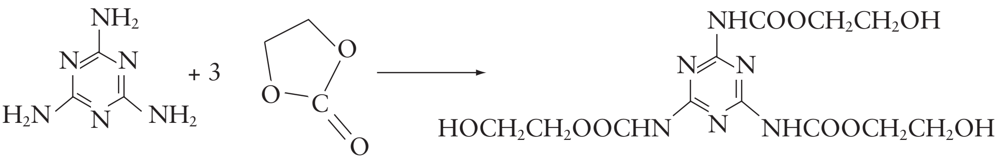


(4.46)

Other transformations of melamine in polyols are based on the reaction of melamine with ethylene carbonate and with alkanolamines.

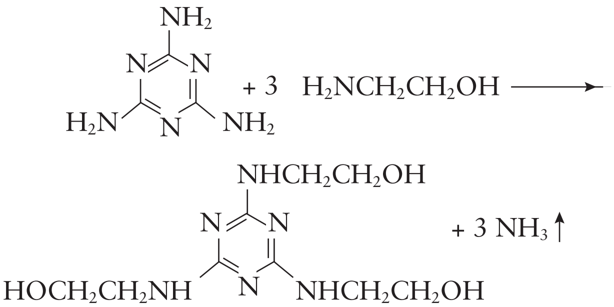
Reacting melamine with ethylene carbonate or propylene carbonate, at 150–200 °C, in liquid medium (e.g., a Mannich polyol derived from phenol), 2-hydroxyalkyl carbamates of melamine are obtained [4] (**Reaction 4.47**). The reaction developed in the absence of this liquid polyol takes place with difficulty 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 PUF 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].



(4.47)

The reaction of melamine with alkanolamines (monoethanolamine, 2-propanol amine, DEOA, and so on), in fact a transamidation reaction, leads to hydroxyalkyl derivatives of melamine and gaseous ammonia [39] see **Reaction 4.48**.



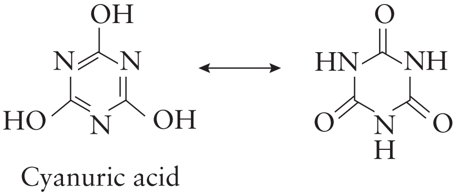
(4.48)

Reaction 4.48 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 mol of isopropanol amine in EG as solvent, in the presence of ammonium chloride as catalyst isopropanol melamine and 13% isomelamine [39] are obtained. EG was removed by vacuum distillation at 150 °C. If the same reaction was repeated with monoethanolamine, the formation of isomelamine was approximately 50% at 95%

conversion. Other catalysts for the reaction of melamine with amines are: hydrochloric acid, sulfuric acid, *p*-toluene sulfonic acid, phosphonic acids and so on.

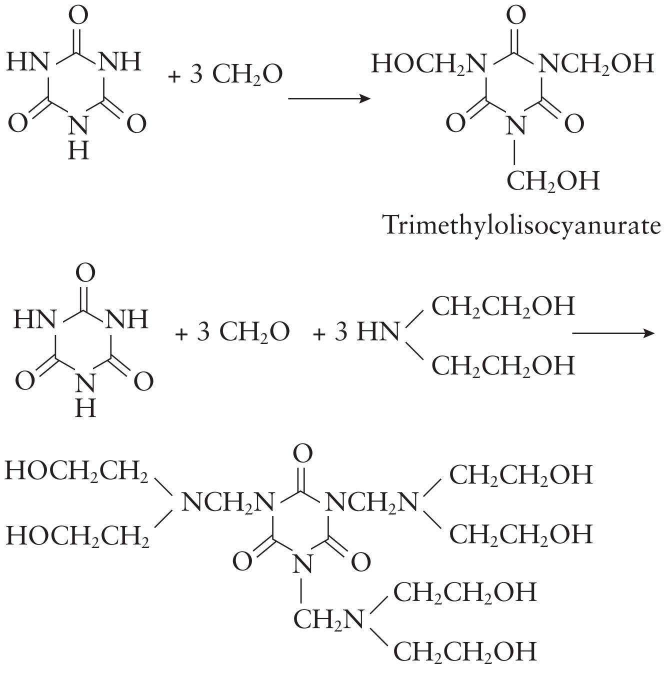
Similar polyols with triazinic structure are obtained by using cyanuric acid condensates. Cyanuric acid is a product of urea thermal decomposition or the product of hydrolysis of melamine or of cyanuryl chloride [40].

Similarly to melamine, cyanuric acid has two tautomeric forms [40]:



(4.49)

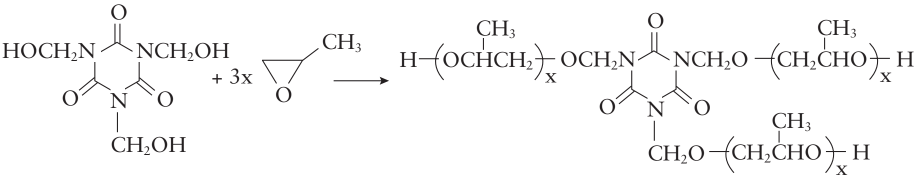
By the reaction of cyanuric acid with formaldehyde or by Mannich reaction with formaldehyde and DEOA interesting polyolic starters with heteroxyxlic triazinic structure are formed [31, 41]:



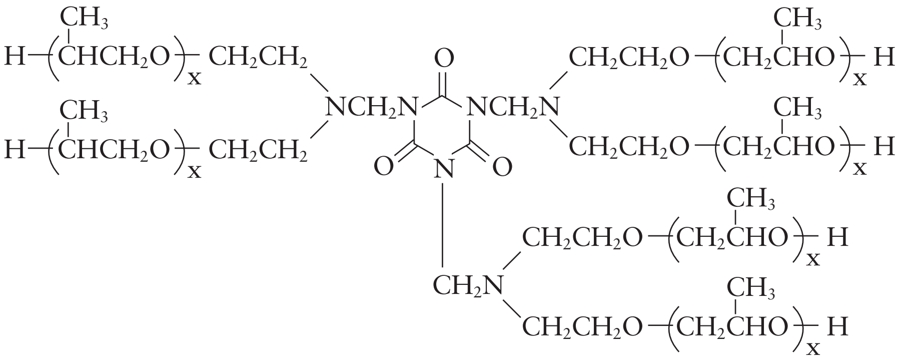
(4.50)

By propoxylation of the resulting polyols (trimethylol isocyanurate and the Mannich base (**Reaction 4.49**), in the presence of a tertiary amine as catalyst (e.g., dimethylaminoethanol) new heterocyclic polyols for rigid PUF with a triazinic structure are obtained (**Reactions 4.51** and **4.52**).

A well-known triol, *tris*(hydroxyethyl)isocyanurate (THEI) is produced industrially and currently used in PU manufacture, as a crosslinking agent (**Reaction 4.53**) [31, 41].



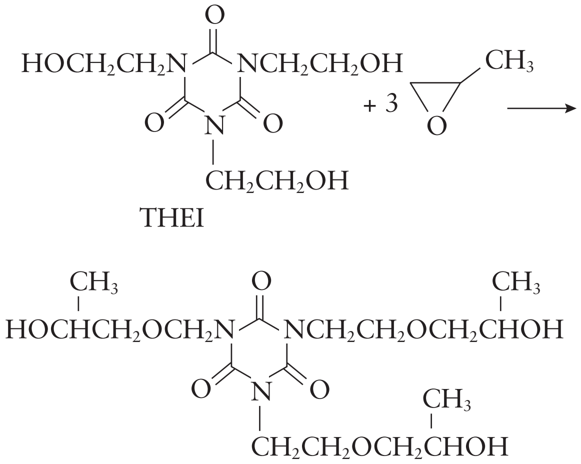
(4.51)



(4.52)

THEI, a solid substance, can be transformed into liquid polyol by reaction with 2–3 mol of PO/mol of THEI in the presence of a tertiary amine. The polyol with 3 mol of PO/mol of THEI has a OH# of approximately 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 PUF [24].



(4.53)

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 PUF.

At this moment, in spite of their high application potential, the triazinic polyols are only used to a very small extent for rigid PUF 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 in *Rigid Plastic Foams*, 2nd Edition, Reinhold, New York, NY, USA, 1967.

2. M.E. Brennan and G.P. Speranza, inventors; Texaco, Inc., assignee; US4485195, 1984.

3. J.E.Marugg, M.A.P. Gansow and J.A. Thoen, inventors; The Dow Chemical Co., assignee; EP0405557A3, 1991.

4. M.E. Brennan, inventor; Texaco, Inc., assignee; US4500655, 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; RO117695, 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, **2**, 893.

8. H. Heaney in *Comprehensive Organic Chemistry*, Eds., D. Barton and W.D. Ellis, Pergamon Press, Oxford, UK, 1991, **2**, 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 Co., assignee; US4939182, 1990.

11. J.E. Marugg, M.A.P. Gansow and J.A. Thoen, inventors; The Dow Chemical Co., assignee; US4883826, 1989.

12. M. Cuscurida and G.P. Speranza, inventors; Texaco, Inc., assignee; US4525488, 1985.

13. D. Thorpe, inventor; ICI, assignee; US4797429, 1989.

14. J. Jahme, inventor; BASF Corporation, assignee; US5254745, 1993.

15. G.P. Speranza, M.E. Brennan and R.A. Grigsby, Jr., inventors; Texaco, Inc., assignee; US4681965, 1987.

16. N.F. Molina and S.E. Moore, inventors; The Dow Chemical Co., assignee; US6281393, 2001.

17. M.E. Brennan, K.G. McDaniel and H.P. Klein, inventors; Texaco, Inc., assignee; US4654376, 1987.

18. M.E. Brennan and G.P. Speranza, inventors; Texaco, Inc., assignee; US4487852, 1984.

19. R.L. Zimmerman, M.P. Devine and P.L. Weaver, inventors; Huntsman Petrochemical Corp., assignee; US6495722, 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; RO114332B, 1999.

22. B. Reichert in *Die Mannich Reaktion*, Springer Verlag, Berlin, Germany, 1959.

23. H. Hellman and G. Optiz in *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 in *Polyurethane Sealants: Technology and Applications*, Technomic Publishing, Lancaster, PA, USA, 1993.

27. B.D. Davis and E.B. Jones, inventors; The Dow Chemical Co., assignee; US3686101, 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; RO79852, 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; RO103350, 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; US3773730, 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; RO103398, 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 Co., assignee; US4312988, 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.

5 Polyester Polyols for Rigid Polyurethane Foams

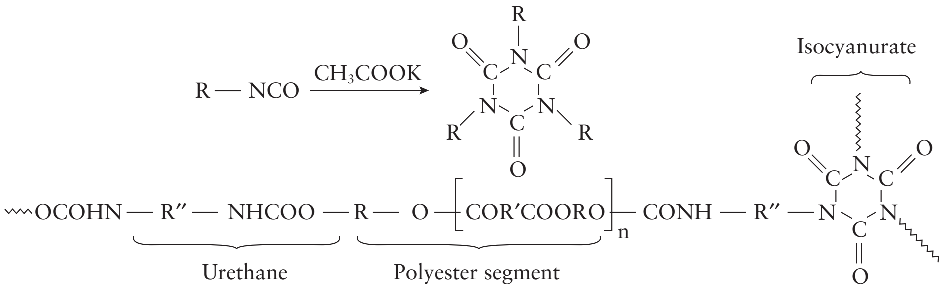
The first polyols used for rigid polyurethane foams (PUF) were low-molecular weight (MW) polyesters based on adipic acid (AA), phthalic anhydride and various glycols or polyols. One example of a polyester of this type is the polycondensation product between AA, phthalic anhydride and trimethylolpropane (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 polyurethane (PU), described in detail in the **Volume 1**, **Chapter 5**.

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 PUF and superior miscibility with fluorocarbon blowing agents. The polyether polyols proved to be superior in rigid PUF fabrication, when the isocyanate index was low, approximately 105–115. The characteristics of two representative polyester polyols for rigid PUF based on AA, phthalic anhydride and TMP are presented in **Table 5.1**.

The development of highly crosslinked rigid polyisocyanurate (PIR) 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 ethylene glycol (EG) or diethylene glycol (DEG) modified with phthalic anhydride or triols.

PIR foams 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:



(5.1)

Table 5.1 Characteristics of some polyester polyols for rigid PUF based on AA, phthalic anhydride and TMP

Characteristic	Unit	Polyester polyol based on AA, phthalic anhydride and TMP	Polyester polyol based on AA, phthalic anhydride, TMP and oleic acid
MW	daltons	900	1,030
OH#	mg KOH/g	350–390	350–390
Average functionality	Hydroxyl groups per mol	6.0	6.6
Viscosity, 70–75 °C	mPa.s	2,500–4,000	1,300–1,500
Pour point	°C	21	7
Acid number	mg KOH/g	<4	<1
Density, 25 °C	g/ml	1.12	1.1

KOH: Potassium hydroxide
OH#: Hydroxyl number(s)

The highly crosslinked structure is not derived from polyester polyol, which has a low functionality (f = 2–3 hydroxyl groups/mol), but is derived from the isocyanurate rings generated by the trimerisation of the excess of -NCO groups.

Urethane structures decompose at approximately 200 °C, giving approximately 20% char yield, but isocyanuric structures are much more thermostable and are decomposed at 325 °C, with a char yield of approximately 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 (DMT)] resulting in DMT fabrication;

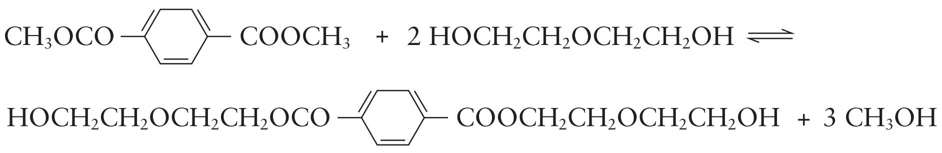
b) Polyethylene terephthalate (PET) wastes (bottles of soft drinks, fibres, X-ray films); and

c) Phthalic anhydride.

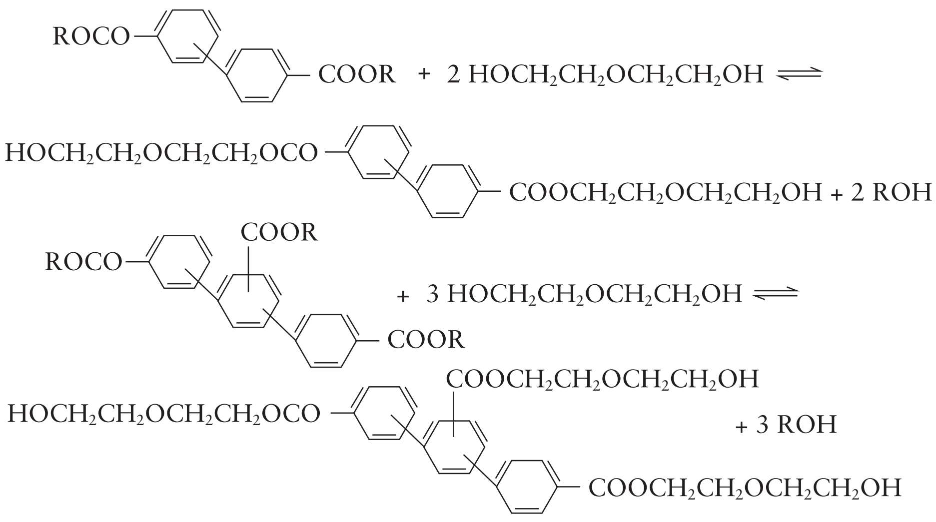
5.1 Aromatic Polyester Polyols from Bottom Residues Resulting in Dimethyl Terephthalate Fabrication [4, 6, 10, 11]

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 DEG, aromatic polyester polyols with a functionality in the range 2.2–2.3 hydroxyl groups/mol are obtained.

The product of transesterification with DEG has a complex structure (**Reactions 5.2** and **5.3**):



(5.2)

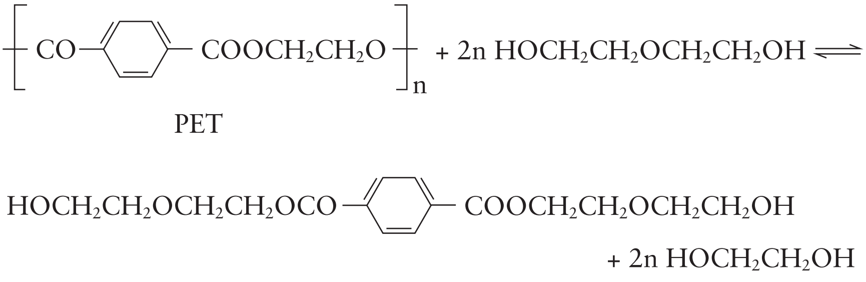


(5.3)

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 5.2**).

5.2 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 dipropylene glycol (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 5.4**) [4, 6–8, 12]:



(5.4)

Of course the product of the transesterification reaction is much more complex, being a mixture of superior oligomers and free DEG together with the main product and the mixed ester terephthalate of EG and DEG.

The reaction between PET and DEG takes place at higher temperatures, approximately 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 h [2, 4].

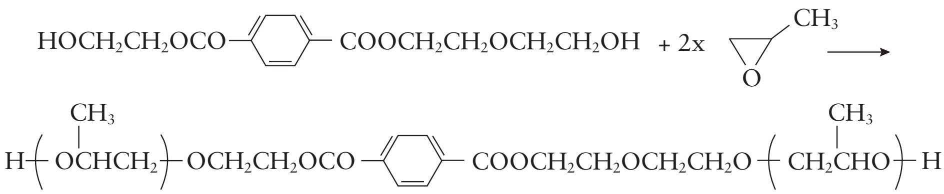
The process of PET glycolysis with DEG has several disadvantages: the reaction products are viscous liquids with a tendency to solidification or even to be solid at room temperature (RT), the reproducibility of the characteristics of the resulting polyester polyols are difficult to realise (poor consistency) 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 EG terephthalate has a tendency to crystallisation and a high melting point(s) (mp) (approximately 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: AA, 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 RT 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 (e.g., 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 OH# of approximately 375 mg KOH/g. By alkoxylation of this solid, at approximately 160 °C, with PO or with PO–ethylene oxide (EO) mixtures, in the presence of potassium acetate polyester polyols are obtained, with an OH# in the range 270–320 mg KOH/g and low viscosity of approximately 1,000–3,000 mPa.s at 25 °C, having the following idealised structure (**Structure 5.5**) [20–22]:



(5.5)

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 mp than the same esters of isophthalic or terephthalic acids. Thus the *ortho*-phthalic ester of DEG is a liquid with a mp of approximately 10–11 °C. At the same time the isophthalic ester of DEG has a mp of 55–60 °C and the terephthalic ester of DEG has a mp of 65–70 °C (the ester of EG with terephthalic acid has a mp of 256 °C and the ester of EG with *ortho*-phthalic acid has a mp 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 (EW) of 181, functionality of 2.3 hydroxyl groups/mol, OH# 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 PUF.

- Polyester polyols of with an EW of 238, functionality of 2 hydroxyl groups/mol, OH# 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.

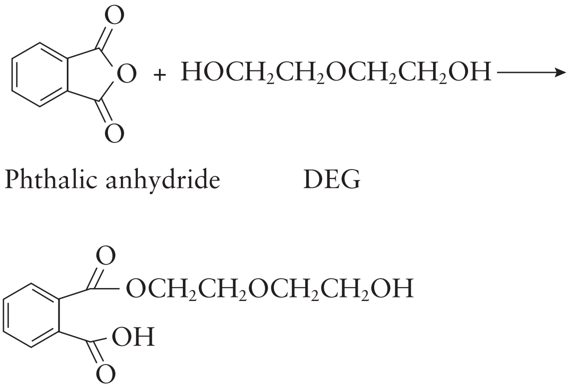
- Polyester polyols with EW of 167, functionality of 2 hydroxyl groups/mol, OH# of 310–350 mg KOH/g and viscosity of 1,300–3,000 mPa.s at 25 °C, are used in thermal insulation of appliances. The initial ratio between DEG and PET used in synthesis, followed by the utilisation of one of the previously mentioned procedures avoids solidification (**Section 5.2**, a–e), and means that a large range of aromatic polyester polyols, having various OH#, functionalities and aromaticity can be obtained.

5.3 Aromatic Polyester Polyols Based on Phthalic Anhydride [25, 26]

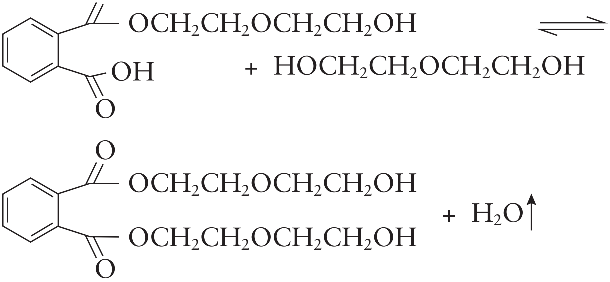
Phthalic anhydride is commercialised in large quantities (especially for use in plasticisers, such as dioctylphthalate and unsaturated polyesters), in high purity form. The aromatic polyester polyols based on phthalic anhydride, due to the purity of the raw materials, are colourless liquids and the process of fabrication, is very reproducible (good consistency). The polyester polyols based on phthalic anhydride and DEG are synthesised in two steps:

a) Synthesis of monoesters of phthalic acid by the reaction of phthalic anhydride with DEG (**Reaction 5.6**); and

b) The condensation of the carboxylic groups in the resulting half ester of phthalic acid with DEG (**Reaction 5.7**):

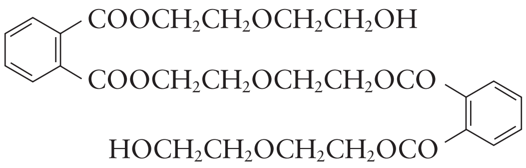


(5.6)



(5.7)

Of course during the polycondensation reaction superior oligomers are formed, such as the structure shown in **Reaction 5.8** and in the composition of the resulting polyester polyol, free DEG is present.



(5.8)

As a representative example, an aromatic polyester polyol derived from phthalic anhydride and DEG has an EW of 178–239, a functionality of 2 hydroxyl groups/mol, an OH# in the range of 230–390 mg KOH/g and the viscosities are lower, approximately 2,000–4,500 mPa.s at 25 °C.

All the aromatic polyester polyols have a high aromaticity, of approximately 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].

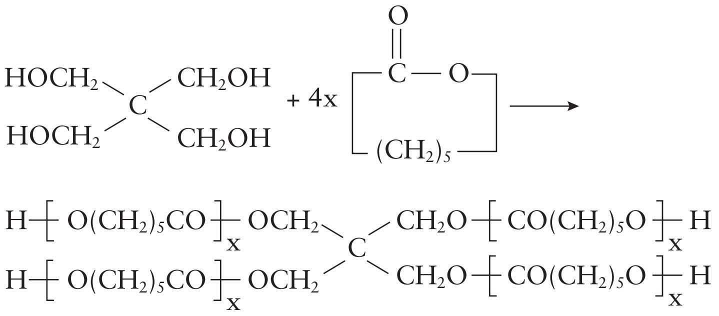
Due to the low cost, the excellent physico-mechanical properties of the resulting urethane-isocyanuric foams, thermal and fire resistance and low level of smoke generation, the most important applications of aromatic polyester polyols are for rigid PU/PIR foams in the boardstock market (continuous rigid foam lamination) and for building insulation.

The rigid PUF/PIR foam [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 PUF/PIR rigid foam based on aromatic polyesters has been limited, but the tendency is for a slow growth of aromatic polyester production.

5.4 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 PUF can be obtained by ring-opening polymerisation of ε-caprolactone (CPL), initiated by various polyols such as: α-methyl glucoside, sorbitol, pentaerythritol (PER) or TMP. A polyester polyol derived from PER has the following properties: functionality of 4 hydroxyl groups/mol, OH# of 600 mg KOH/g, acid number of approximately 2 mg KOH/g and a of viscosity 7,000 mPa.s at 25 °C (**Reaction 5.9**) [2, 33–35]:

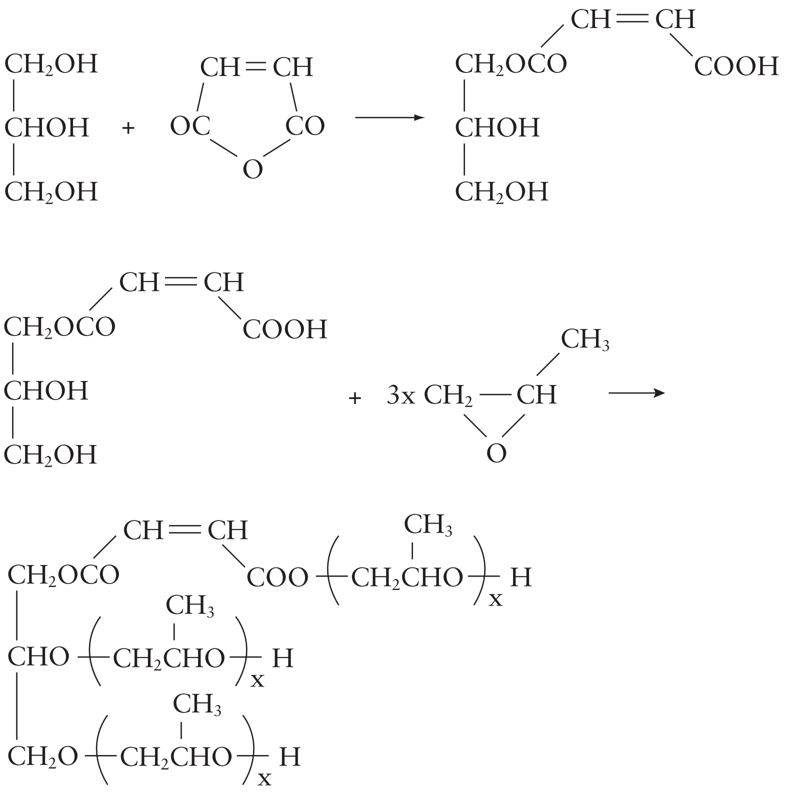


x = 0,1,2 (5.9)

α-Methyl glucoside and sorbitol give higher viscosity polyester polyols, of approximately 22,000–400,000 mPa.s at 25 °C [33]. Due to their high price these CPL-based polyester polyols have limited utilisation for rigid PUF. As explained before (**Volume 1, Section 8.4**), the high-MW poly(ε-caprolactone) polyols are used successfully in hydrolysis resistant PU elastomers.

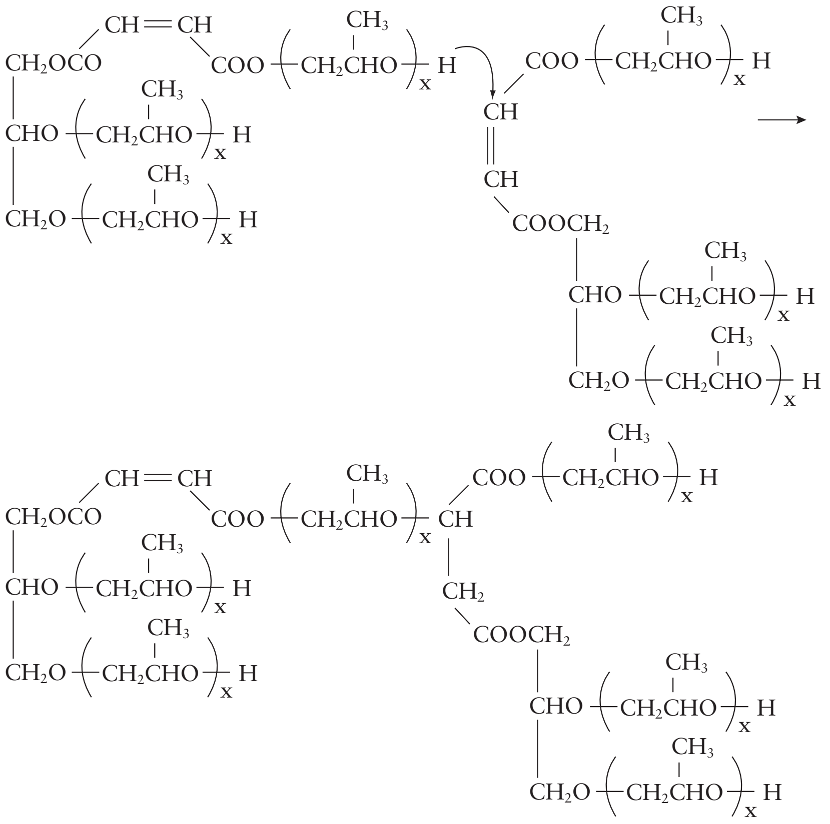
A synthetic method for rigid polyester polyols, by the propoxylation of compounds having both hydroxyl and carboxyl groups was developed [33, 34].

Thus, by the propoxylation of the reaction product of 1 mol of maleic anhydride with 1 mol of glycerol, aliphatic polyester polyols having functionalities greater than 3, in the range of 3–4 hydroxyl groups/mol are obtained. The functionality of greater than 3 is created *in situ* by the addition of a hydroxyl group to the double-bond of the maleic esters formed (**Reactions 5.10**):

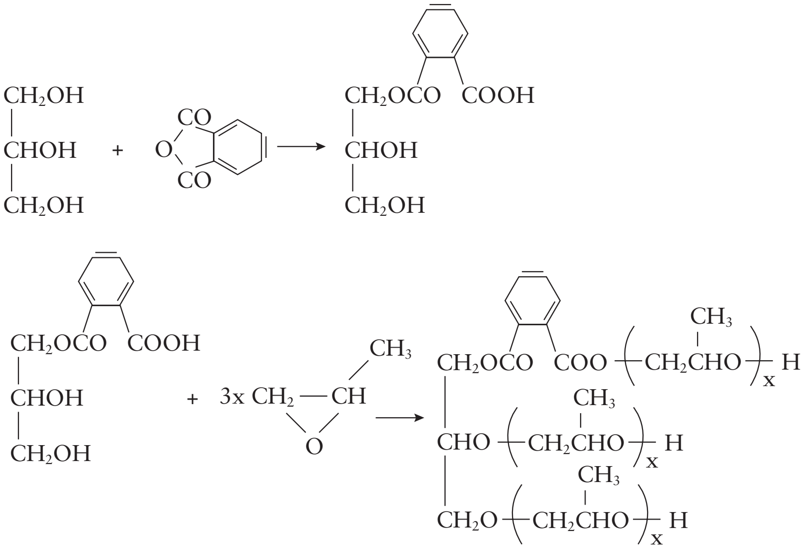


(5.10)

By using similar chemistry, aromatic polyester polyol structures are obtained by alkoxylation of the phthalic anhydride reaction product with glycerol (**Reaction 5.11**). By the propoxylation of the reaction product of pyromellitic anhydride with DEG, tetrafunctional, highly viscous aromatic polyester polyols (**Reaction 5.12**) are obtained:

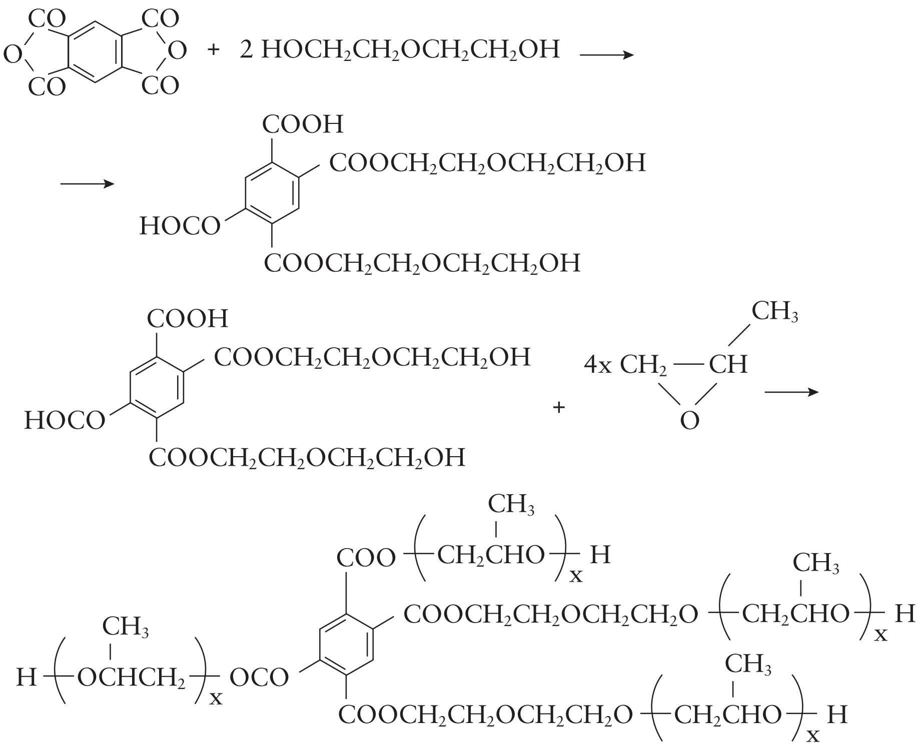


(5.11)

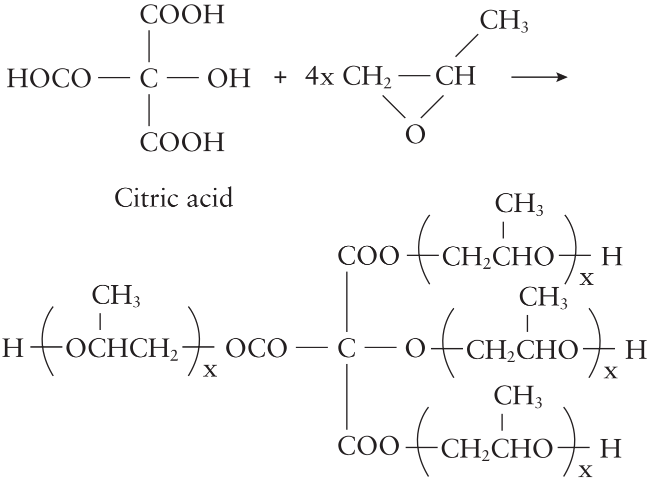


(5.12)

Propoxylation of organic hydroxy acids such as citric acid (**Reaction 5.13**) [34] or propoxylation of the mixture between polyols and polyacids (e.g., sorbitol and AA, **Reaction 5.14**) give rise to interesting rigid polyester polyols [34]:



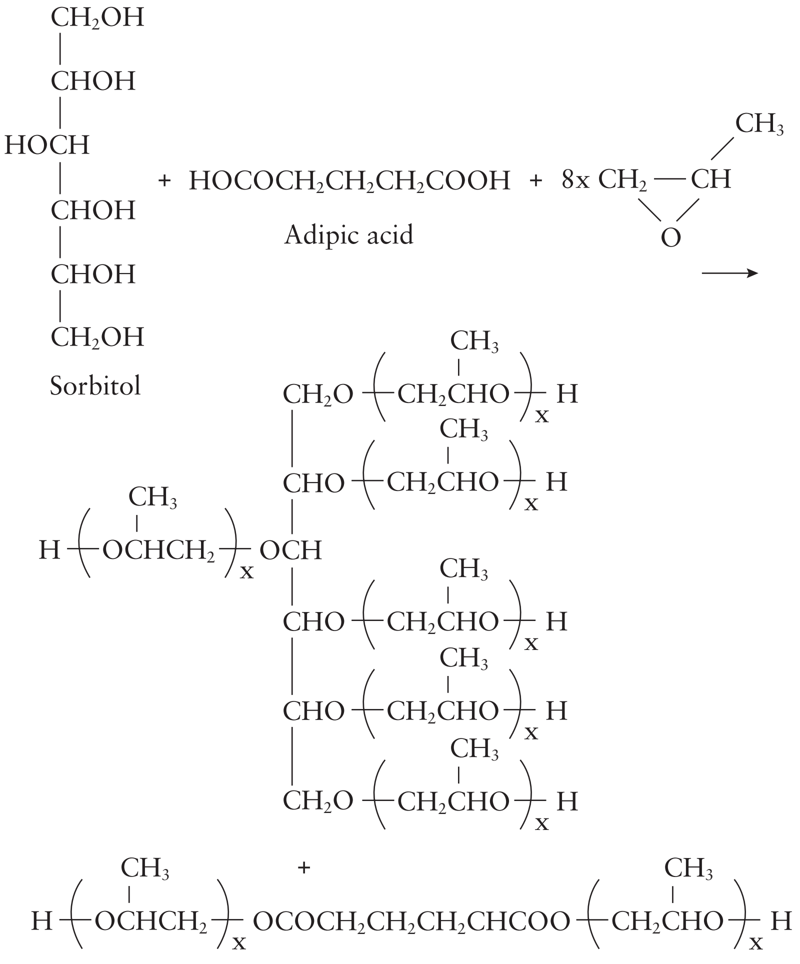
(5.13)



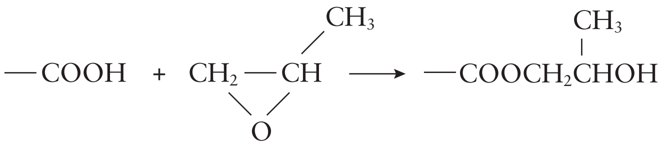
(5.14)

Instead of AA 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 5.15**) and the etherification of hydroxyl groups (**Reaction 5.16**) [34]:



(5.15)



(5.16)

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 (e.g., 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 are the low functionality aromatic polyester polyols with terephthalic or phthalic structures, used for PUR/PIR rigid foam.

References

1. R. Becker in *Polyuretane*, VEB, Leipzig, Germany, 1983, p.49.
2. F. Hostettler and D.M. Young, inventors; Union Carbide Corp., assignee; US3169945, 1965.
3. F. Hostettler and D.M. Young, inventors; Union Carbide Corp., assignee; US3186971, 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.
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.

10. J.F. Walker, inventor; Hercules, Inc., assignee; US3647759, 1972.

11. S.C. Snider and A. DeLeon, inventors; Celotex Corp., assignee; US4411949, 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, p.65.

14. W.L. Carlstrom, R.W. Reineck and G.R. Svoboda, inventors; Freeman Chemical Corp., assignee; US4223068, 1980.

15. G.R. Svoboda, W.L. Carlstrom and R.T. Stoehr, inventors; Freeman Chemical Corp., assignee; US4417001, 1983.

16. M.E. Brennan, inventor; Texaco, Inc., assignee; US4439550, 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; US4469824, 1984.

20. M.J. Altenberg and J. DeJong, inventors; Chardonol Corp., assignee; EP0134661A2, 1985.

21. G.P. Speranza, R.A. Grigsby, Jr., and M.E. Brennan, inventors; Texaco, Inc., assignee; US4485196, 1984.

22. M.J. Altenberg and J. DeJong, inventors; Chardonol, Division of Freeeman Corp., assignee; US4701477, 1987.

23. R.K. Hallmark, M.J. Skrowronski and W.D. Stephens, inventors; Jim Walter Resources, assignee; EP0152915A3, 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 Co., assignee; US4529744, 1985.

26. T.A. Barber, T.R. McClellan, inventors; E.I. DuPont de Nemours, assignee; CA2493024, 2004.

27. K.B. White, inventor; Akzo NV, assignee; EP0122648A1, 1984.

28. K.B. White and W.J. Largent, inventors; Akzo NV, assignee; EP0122649, 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; EP0161039, 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 Corp., assignee; US3051687, 1962.

35. C.H. Smith, *Industrial and Engineering Chemistry, Product Research & Development*, 1963, **2**, 1, 27.

6

Polyols by Thiol-ene ‘Click’ Chemistry

Thiols or mercaptans are organic sulfur compounds with the general structure shown in **Structure 6.1**:

$$R - SH \tag{6.1}$$

where R is an alkyl radical.

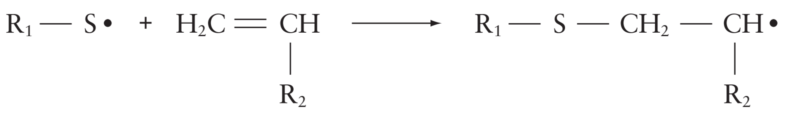
A thiol-ene reaction is the addition of thiols to the double-bonds of organic compounds. The thiol-ene reaction is part of the group of ‘click’ chemistry reactions characterised by high yield, high reaction rates, and absence of byproducts if run at an equimolecular ratio of thiol groups/double-bonds [1–10]. The general thiol-ene reaction with formation of thioethers is presented in **Reaction 6.2**:

$$R - SH + CH_2 = CH - CH_2 - R \xrightarrow[\text{Radical initiators}]{\text{UV light}} R - S - CH_2 - CH_2 - CH_2 - R \tag{6.2}$$

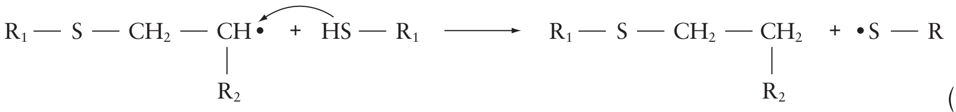
Addition of thiol groups to double-bonds is initiated by photochemical means using ultraviolet (UV) light (wavelength 200–400 nm) and photoinitiators, or by thermal splitting of radical initiators (azo derivatives, peroxides). The thiol-ene reaction is a chain reaction and proceeds through four steps (**Reactions 6.3–6.6**): thermal or photochemical generation of free radicals (**Reaction 6.3**); transfer reactions with thiol groups generating free radicals at the sulfur atom called thiyl radicals (**Reaction 6.4**); attack of sulfur radicals on double-bonds (anti-Markovnikov addition) forming new radicals (**Reaction 6.5**); new transfer reactions with thiol groups to obtain the final product and new thiyl radicals (**Reaction 6.6**):

$$\mathrm{R-R} \xrightarrow[\text{Photochemically}]{\text{Thermally}} \mathrm{R}\bullet \tag{6.3}$$

$$\mathrm{R_1-SH} + \mathrm{R}\bullet \longrightarrow \mathrm{R_1-S}\bullet + \mathrm{R-H} \tag{6.4}$$

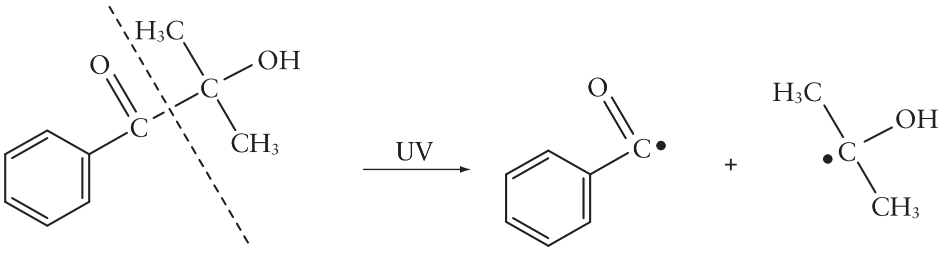


$$\mathrm{R_1-S}\bullet + \mathrm{H_2C{=}}\underset{\substack{|\\ \mathrm{R_2}}}{\mathrm{CH}} \longrightarrow \mathrm{R_1-S-CH_2-}\underset{\substack{|\\ \mathrm{R_2}}}{\mathrm{CH}}\bullet \tag{6.5}$$



$$\mathrm{R_1-S-CH_2-}\underset{\substack{|\\ \mathrm{R_2}}}{\mathrm{CH}}\bullet + \mathrm{HS-R_1} \longrightarrow \mathrm{R_1-S-CH_2-}\underset{\substack{|\\ \mathrm{R_2}}}{\mathrm{CH_2}} + \bullet\mathrm{S-R} \tag{6.6}$$

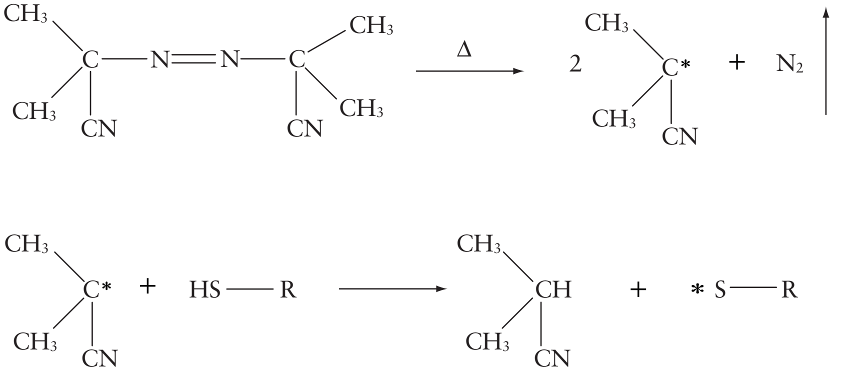
An example of a conventional photoinitiator is 2-hydroxy-2-methylpropiophenone (Irgacure 1173). This photoinitiator, by irradiation with UV light, generates two free radicals (**Reaction 6.7**), which initiate photochemical reactions conforming to the described mechanism (**Reactions 6.3–6.6**):



Irgacure 1173

(6.7)

Thermal thiol-ene reactions are initiated by thermal splitting of radical initiators. The most frequently used initiator is azobisisobutyronitrile (AIBN). AIBN is decomposed to two free radicals (**Reaction 6.8**):

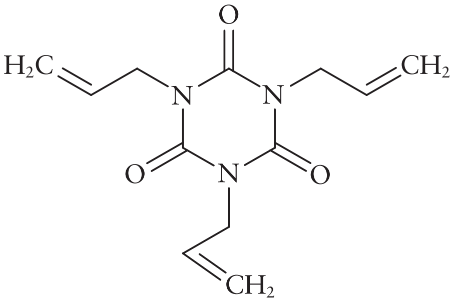

(6.8)

This chapter presents the syntheses of polyols for polyurethanes (PU) by a thiol-ene reaction using only petrochemical raw materials with multiple double-bonds. The synthesis of polyols for PU by thiol-ene reactions using natural compounds containing multiple double-bonds is described in the next chapter on renewable polyols.

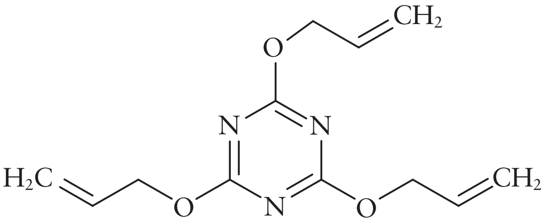
6.1 Synthesis of Polyols for Rigid Polyurethanes by Thiol-ene Reactions [13]

The best organic unsaturated compounds as partners for thiol-ene reactions are compounds with terminal double-bonds. Allyl groups are preferred because the tendency for radical polymerisation is very low, and the main reaction is addition of thiol groups to allyl groups. Compounds with internal double-bonds (e.g., vegetable oils) are less reactive in thiol-ene reactions (**Volume 2, Chapter 7**). **Structures 6.1–6.4** detail the structures of four petrochemical unsaturated compounds containing allyl groups that are very reactive in thiol-ene reactions: triallylisocyanurate, triallylcyanurate, triallylamine and diallylphthalate [13]. Other commercially available allyl and vinyl compounds are suitable for synthesis of polyols by thiol-ene reactions: allyltrimethylolpropane [8], allylpentaerythritol [8] 1-allyl glycerol, diallylmaleate, divinylbenzene, and divinylethers.

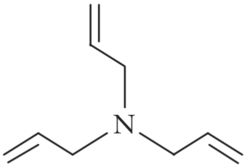
Structures 6.1–6.4 show organic compounds with multiple double-bonds used for synthesis of polyols by thiol-ene reactions.



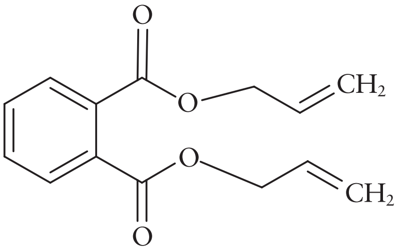
Structure 6.1 Triallylisocyanurate



Structure 6.2 Triallylcyanurate



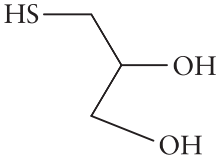
Structure 6.3 Triallylamine



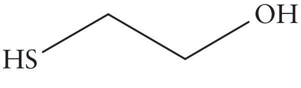
Structure 6.4 Diallylphthalate

Mercaptans used for synthesis of polyols by thiol-ene reaction are hydroxyalkyl mercaptans. Two representative hydroxyalkyl mercaptans available commercially and suitable for synthesis of polyols are 2-mercaptoethanol and 1-thio-glycerol (**Structures 6.5** and **6.6**).

Structures 6.5 and **6.6** show structures of hydroxyalkyl mercaptans suitable for thiol-ene reactions.

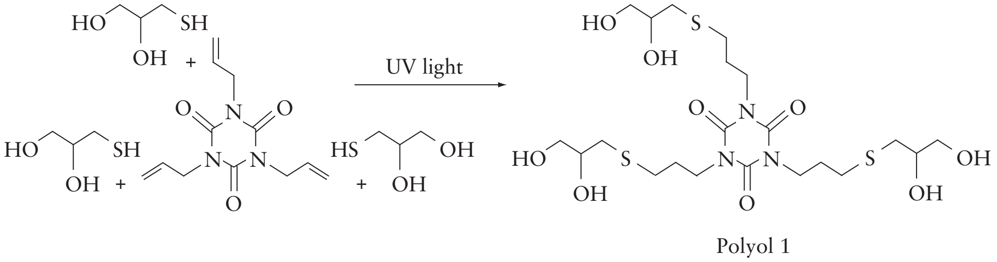


Structure 6.5 1-Thio-glycerol



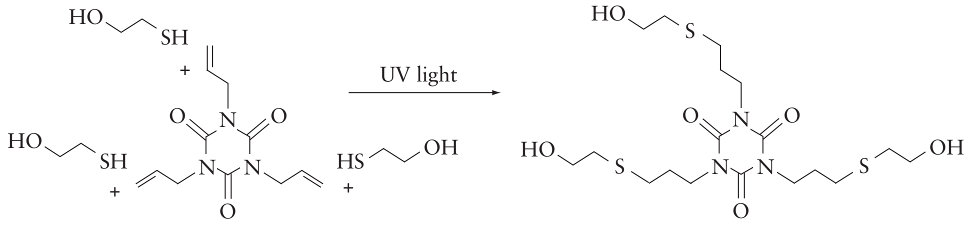
Structure 6.6 2-Mercaptoethanol

Isocyanuric foams obtained by trimerisation of –N=C=O groups of polyisocyanates have high physical-mechanical properties and inherent flame retardancy [11]. Another way to introduce highly thermostable isocyanuric rings in PU foams is to use polyols with an isocyanuric structure [12]. Thiol-ene reactions between triallylisocyanurate and hydroxyalkyl mercaptans are an efficient one-step pathway to prepare polyols with an isocyanuric structure with functionalities of 3–6 hydroxyl groups/mol and isocyanuric ring content of 22–26%. By using 1-thio-glycerol (3 mol) and triallylisocyanurate (1 mol) a polyol of functionality 6 hydroxyl groups/mol can be obtained (**Figure 6.1**). By using 2-mercaptoethanol (3 mol) and triallyll isocyanurate (1 mol) a polyol of functionality 3 hydroxyl groups/mol can be obtained (**Figure 6.2**). By using mixtures of 1-thio-glycerol with 2-mercaptoethanol polyols with functionalities between 3 and 6 hydroxyl groups/mol can be obtained (**Figures 6.3–6.4**). The reaction between triallylisocyanurate and hydroxyalkyl mercaptans is carried out by photochemical means using irradiation with UV light (200–400 nm) at room temperature (RT) or at 60–80 °C using AIBN as a radical initiator. All thiol-ene reactions between compounds with allyl groups and hydroxyalkyl mercaptans are strongly exothermal, with the reaction being practically complete after 1–3 h. Reactions between triallylisocyanurate and 1-thio-glycerol or 2-mercaptoethanol are typical examples of thiol-ene ‘click’ chemistry reactions, which carry a high reaction rate and very high yield.



Functionality f = 6
OH# = 587 mg KOH/g
Viscosity, 25 °C = 74.8 Pa.s
Isocyanuric rings = 21.9%

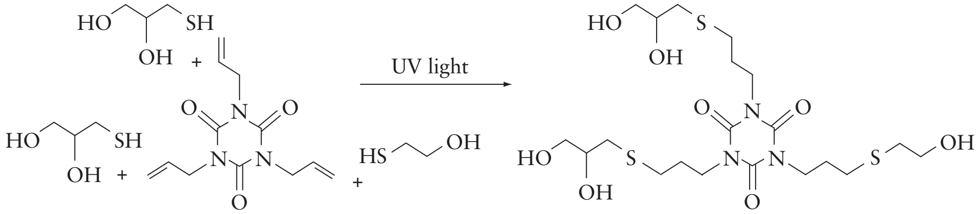
Figure 6.1 Synthesis and structure of an isocyanuric polyol based on triallyl isoyanurate (1 mol) and 1-thio-glycerol (3 mol)



Polyol 4

Functionality f = 3
OH# = 483 mg KOH/g
Viscosity, 25 °C = 13.16 Pa.s
Isocyanuric rings = 26%

Figure 6.2 Synthesis and structure of an isocyanuric polyol based on triallylisocyanurate (1 mol) and 2-mercaptoetthanol (3 mol)

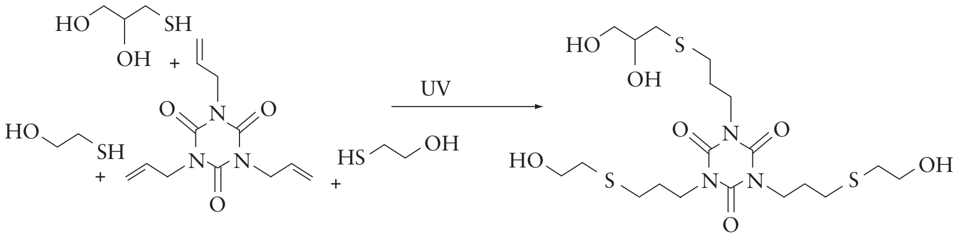


Polyol 2

Functionality f = 5
OH# = 447.06 mg KOH/g
Isocyanuric rings = 23.1%

Figure 6.3 Synthesis and structure of an isoyanuric polyol based on triallylisocyanurate (1 mol), 1-thio-glycerol (2 mol) and 2-mercaptoethanol (1 mol)

Isocyanuric polyols with 2–3 thio-glycerol units are very viscous, have higher functionalities and an isocyanuric content of 21–23%. These very viscous polyols can be used only in a mixture (30–50%) with polyether polyols of low or medium viscosity, and lead to rigid PU foams with high physical-mechanical properties. Polyols with high content in 2-mercaptoethanol have lower viscosities and functionalities (3–4 OH groups/mol) and higher isocyanuric ring content (24–26%). These polyols can be used as sole polyols for rigid PU foams, which leads to inherent self-extinguishing foams without the need for addition of flame retardants.

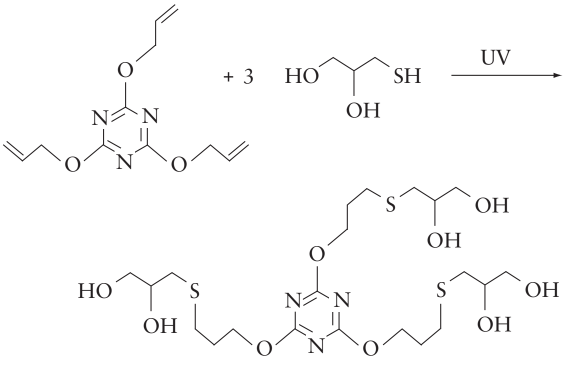


Polyol 3

Functionality f = 4
OH# = 408.5 mg KOH/g
Isocyanuric rings = 24.5%

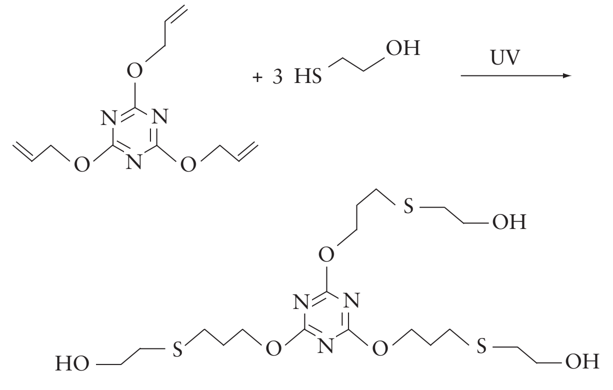
Figure 6.4 Synthesis and structure of an isocyanuric polyol based on triallylisocyanurate (1 mol), 1-thio-glycerol (1 mol) and 2-mercaptoethanol (2 mol)

Very similar polyols can be synthesised by a thiol-ene reaction of triallylcyanurate (isomer of triallylisocyanurate) [13] with 1-thio-glycerol (**Figure 6.5**) and 2-mercaptoethanol (**Figure 6.6**). Surprisingly, these polyols, despite their aromaticity, do not lead to inherently flame-retardant rigid PU foams. However, the physical-mechanical properties of foams based on these triazinic polyols as sole polyols or in a mixture with polyether polyols are high, similar with the properties of rigid foams based on isocyanuric polyols. The synthesis and structures of these triazinic polyols based on triallylcyanurate and hydroxyalkyl mercaptans are presented in **Figures 6.5–6.8**.



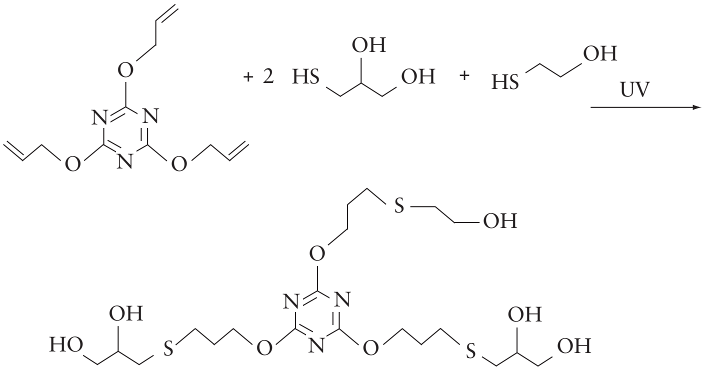
M = 573
OH# = 587 mg KOH/g
Aromatic triazinic rings = 13.7%

Figure 6.5 Synthesis and structure of a polyol by thiol-ene reaction of triallylcyanurate (1 mol) and 1-thio-glycerol (3 mol)



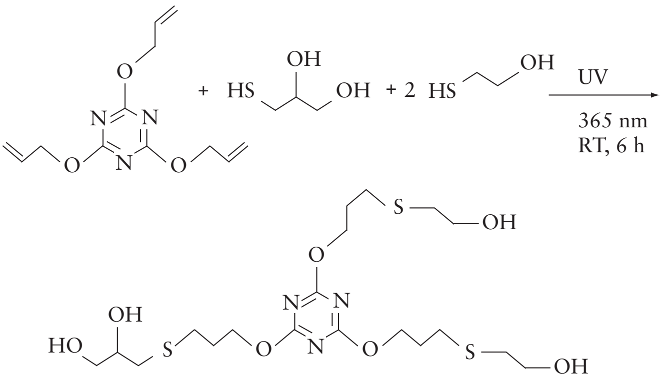
M = 483
OH# = 348.5 mg KOH/g
Aromatic triazinic rings = 16.14%

Figure 6.6 Synthesis and structure of a polyol by thiol-ene reaction of triallylcyanurate (1 mol) and 2-mercaptoethanol (3 mol)



M = 573
OH# = 516 mg KOH/g
Aromatic triazinic rings = 15.11%

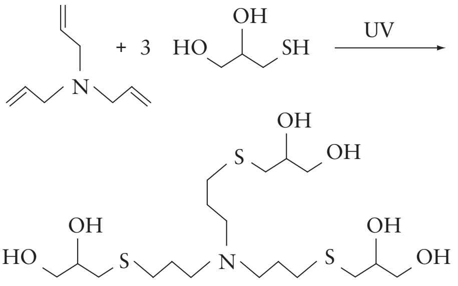
Figure 6.7 Synthesis and structure of a polyol by thiol-ene reaction of triallylcyanurate (1 mol), 1-thio-glycerol (2 mol) and 2-mercaptoethanol (1 mol)



M = 513
OH# = 437 mg KOH/g
Aromatic triazinic rings = 15.2%

Figure 6.8 Synthesis and structure of a polyol by thiol-ene reaction of triallylcyanurate (1 mol), 1-thio-glycerol (1 mol) and 2-mercaptoethanol (2 mol)

Triallylamine is a very interesting raw material for synthesis of very reactive amino polyols by thiol-ene reaction with 1-thio-glycerol and 2-mercaptoethanol [13]. The synthesis is very similar with those used for synthesis of polyols based on triallylisocyanurate and triallylcyanurate by irradiation with UV light (365 nm) at RT or by initiation with AIBN at 60–80 °C. **Figures 6.9–6.12** present the syntheses and structures of aminic polyols obtained by thiol-ene reactions of triallylamine with 1-thio-glycerol and 2-mercaptoethanol.



M = 461
OH# = 730 mg KOH/g

Figure 6.9 Synthesis and structure of an amino polyol based on triallylamine and 1-thio-glycerol

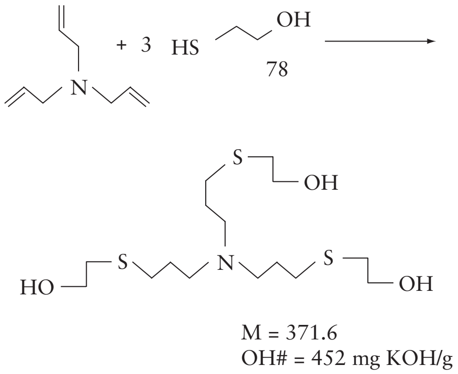


Figure 6.10 Synthesis and structure of an amino polyol based on triallylamine and 2-mercaptoethanol

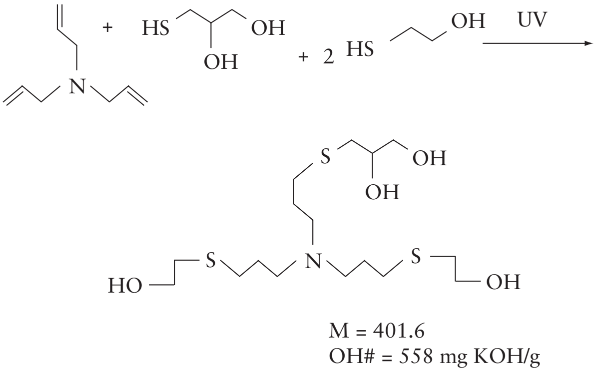
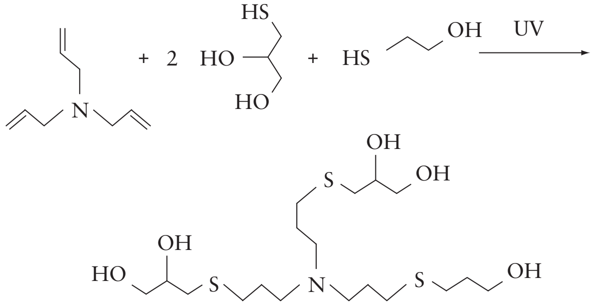


Figure 6.11 Synthesis and structure of an amino polyol based on triallylamine, 1-thio-glycerol (1 mol) and 2-mercaptoethanol (2 mol)

Amino polyols based on triallylamine and hydroxyalkyl mercaptans have hydroxyl numbers (OH#) of 450–610 mg potassium hydroxide (KOH)/g, functionalities of 3–6 OH groups/mol, low viscosities of 1,000–6,600 mPa.s at 25 °C, and are very reactive polyols suitable for rigid PU foams produced by a 'spray' process. The amine value of these amino polyols is ≈120–150 mg KOH/g.



M = 431.18
OH# = 650 mg KOH/g

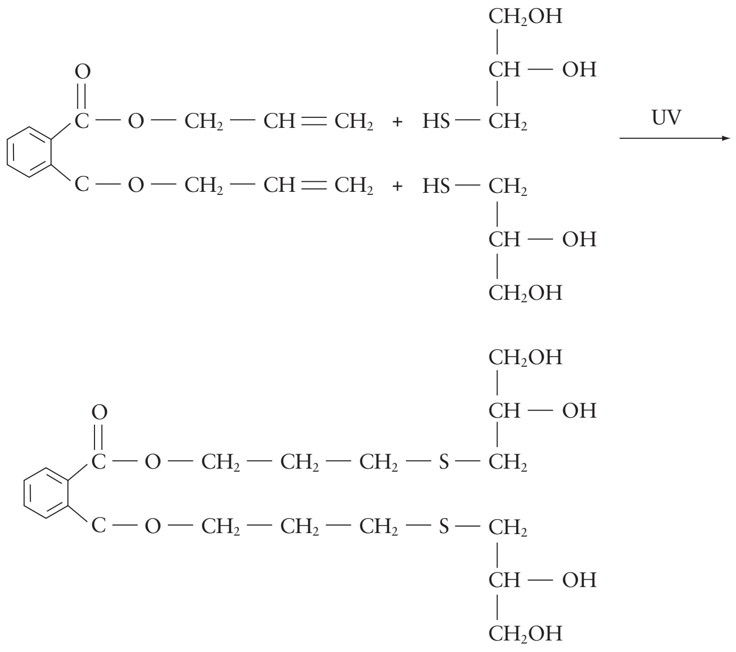
Figure 6.12 Synthesis and structure of an amino polyol based on triallylamine, 1-thio-glycerol (2 mol) and 2-mercaptoethanol (1 mol)

An aromatic unsaturated raw material suitable for thiol-ene ‘click’ chemistry reactions is diallylphthalate. By thiol-ene reaction of diallylphthalate (1 mol) with 1-thio-glycerol (2 mol) under UV irradiation (365 nm) at RT, an aromatic polyol is obtained in high yield in only 1.5 h (**Figure 6.13**) [13].

A polyol based on diallylphthalate (**Figure 6.13**) has an OH# = 445 mg KOH/g, a viscosity of 17,000 mPa.s at 25 °C, and an aromatic content of 16.45%. Due to its aromaticity, this polyol in mixture with sucrose polyether polyols (or even a single polyol) leads to rigid PU foams with high physical-mechanical properties.

6.2 Polyols for Elastic Polyurethanes by Thiol-ene Click Chemistry [14, 15]

Thiol-ene reactions of dimercaptans with divinyl or diallyl organic compounds lead to high-molecular weight (MW) linear dithiols or diols suitable for preparation of elastic PU (e.g., PU elastomers). Thiol-ene reactions of this type are initiated usually by UV light or radical initiators.



M = 462
OH# = 485 mg KOH/g
Aromatic content = 16.45%

Figure 6.13 Synthesis and structure of a polyol by thiol-ene reaction between diallylphthalate (1 mol) and 1-thio-glycerol (2 mol)

An example of synthesis of high-MW telechelic dithiol is the thiol-ene reaction between diallylether and a dimercaptan 2,2′-(ethylenedioxy)diethanethiol [15], which is a triethylene glycol with terminal thiol groups instead of hydroxyl groups (**Figure 6.14**). If an excess of dimercaptan is used, the terminal groups are –SH groups (thiol groups). Thiol groups react with isocyanates in the presence of tertiary amines with formation of thiourethane groups.

The MW is dependent upon the quantity of 2-mercaptoethanol used. Importantly, the molar ratio [SH]/[double-bonds] should be 1/1. Using this method, linear telechelic polymers (with terminal SH or OH groups) of MW = 1,000–2,000 are obtained.

Preparation of polyols for flexible foams involves using a trimercaptan (or a polymercaptan) as a starter together with diallylether and 2,2′-(ethylenedioxy) diethanethiol. The equivalent weight (EW) of these branched telechelic polymers is 1,000–2,000. Instead of using diallylether, divinylethers (e.g., triethylene glycol divinyl ether) or other divinyl compounds (e.g., diacrylates or dimethacrylates) can be employed.

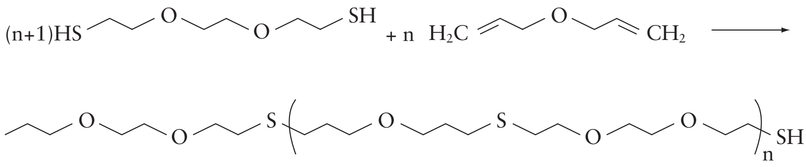


Figure 6.14 Synthesis and structure of a high-MW dithiol by thiol-ene reaction

If generation of terminal hydroxyl groups are desired, 2-mercaptoethanol can be used together with diallylether and dimercaptans (**Figure 6.15**).

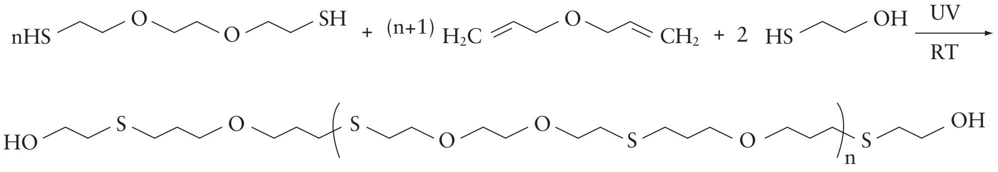


Figure 6.15 Synthesis and structure of a high-MW linear diol by thiol-ene reaction

Thiol-ene click chemistry reactions between unsaturated organic compounds and hydroxyalkyl mercaptans or polymercaptans have been shown to be very valuable to obtain, in a one-step process, polyols for rigid PU foams or for elastic PU (elastomers, foams). These polyols are synthesised without propylene oxide or ethylene oxide.

Syntheses of bio-based polyols by thiol-ene reactions of natural unsaturated compounds with hydroxyalkyl mercaptans are described in **Volume 2, Chapter 7.**

References

1. C.E. Hoyle and C.N. Bowman, *Angewandte Chemie International Edition*, 2010, **49**, 1540.

2. M.J. Kade, D.J. Burke and C.J. Hawker, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 2010, **48**, 743.

3. N.B. Cramer, S.K. Reddy, A.K. O'Brien and C.N. Bowman, *Macromolecules*, 2003, **36**, 7964.

4. A.B. Lowe and M.A. Harvison, *Australian Journal of Chemistry*, 2010, **63**, 1251.

5. 5. L.M. Campos, K.T. Killops, R. Sakai, J.M.J. Paulusse, D. Damiron, E. Drockenmuller, W. Messmore and C.J. Hawker, *Macromolecules*, 2008, **41**, 7063.

6. M. Uygun, M.A. Tasdelen and Y. Yagci, *Macromolecular Chemistry and Physics*, 2010, **211**, 103.

7. A.B. Lowe, *Polymer Chemistry*, 2010, **1**, 17.

8. I. Carlson, A. Harden, S. Lundmark, A. Manea, N. Rehnberg and L. Svensson, *ACS Symposium Series*, 2003, **847**, Chapter 6.

9. O. Turunc, M. Frdaus, G. Klein and M.A.R .Meier, *Green Chemistry*, 2012, **14**, 2577.

10. H. Mutlu, A.N. Parvulescu, P.C.A. Bruijnincs, B.M. Weckhuysen and M.A.R. Meier, *Macromolecules*, 2012, **41**, 1866.

11. M. Modesti and A. Lorenzetti, *Polymer Degradation and Stability*, 2002, **78**, 341.

12. M. Ionescu, I. Mihalache, V. Zugravu and S. Mihai, *Cellular Polymers*, 1994, **13**, 57.

13. M. Ionescu, Unpublished Work.

14. C.S. Marvel and P.H. Aldrich, *Journal of the American Chemical Society*, 1950, **72**, 1978-.

15. G. Cai and R.G. Gastinger, inventors; Arco Chemical Technology L.P., assignee; US5741884, 1978.

7 Polyols from Renewable Resources

Petrochemical resources (e.g., crude oil, natural gases) are used intensively in the chemical industry worldwide. They are limited resources and will be depleted in a certain period of time. The chemical industry is making considerable efforts to find alternatives to petrochemical raw materials.

One alternative is renewable resources (natural organic compounds and natural polymers), which already have an important role in development of the chemical industry. Renewable resources are relatively inexpensive, accessible, and can be produced in large quantities (with infinite renewability) [1–6].

Before providing detailed descriptions of the synthesis and structure of polyols from renewable resources, short explanations of important terms used in polyurethane (PU) chemistry and in connection with production of renewable polyols are necessary. These terms are ‘sustainability’, ‘renewability’, ‘global warming potential’ (GWP), ‘ozone depletion potential’ (ODP) and ‘bio-refinery’.

Sustainability [7, 8] is complex, economic, social and ecological concept. Sustainability has many definitions. In simple terms, sustainability means providing the best for people and the environment now and in the indefinite future. One of the most accepted definitions of sustainability is ‘meeting the needs of the present generation without compromising the ability of future generations to meet their needs’. Sustainability has three components: social sustainability, environmental sustainability and economic sustainability. Of the three components, the most important is environmental sustainability. The term ‘sustainable polymers’ is used in the case of polymers. A sustainable polymer is a plastic material that addresses the needs of consumers without damaging our environment, health, or economy. A sustainable polymer is produced in high yield, with low consumption of energy, without byproducts (or with non-toxic byproducts), without generation of greenhouse gases (GHG), and is synthesised from renewable resources (which are unlimited and of infinite renewability) that are biodegradable. All polyols synthesised from renewable resources [from vegetable oils, starch and cellulose, proteins, terpenes, and carbon dioxide (CO_2)] can be considered to be ‘sustainable polyols’.

Renewable content [9–13] – if a chemical compound is produced using known quantities of bio-based compounds (vegetable oils, starch, proteins) and quantities of petrochemical compounds are known, then the renewable content (Rc) can be determined readily (**Reaction 7.1**):

$$Rc = \frac{Q_1 \times 100}{(Q_1 + Q_2) - Q_R} \tag{7.1}$$

Where:

Q_1: Quantity of bio-based raw materials used;

Q_2: Quantity of petrochemical materials used; and

Q_R: Quantity of low-molecular-weight(s) (MW) compounds removed during synthesis (e.g., water, CO_2).

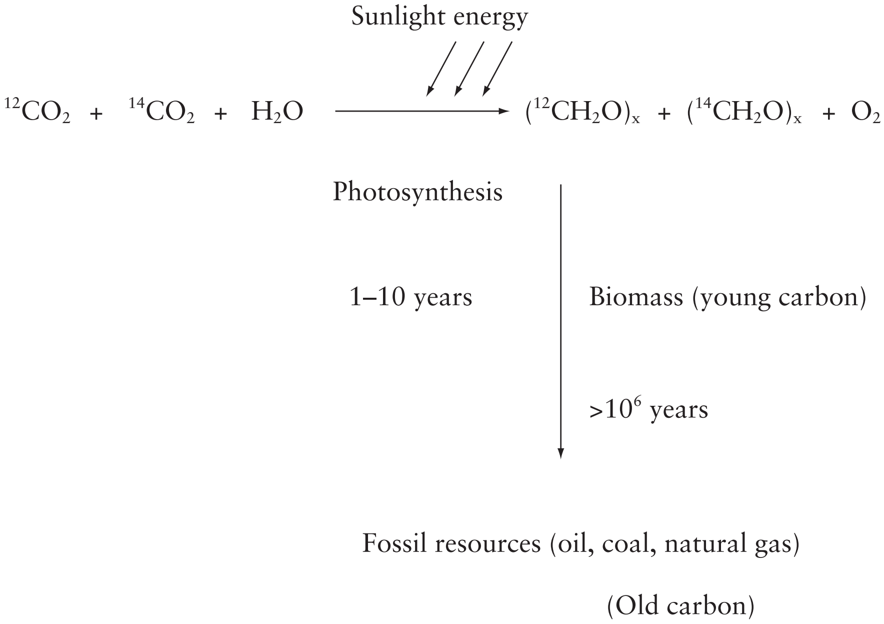
A problem arose for determination of the Rc of a compound when the content of bio-based compounds was not known. This problem was solved by determination of the content of the carbon-14 (^{14}C) isotope in the sample [American Society for Testing and Materials (ASTM), ASTM D6866]. This strategy was based on the observation that all bio-based compounds contain ^{14}C, but petrochemical compounds do not. The age of organic materials is estimated by determination of ^{14}C content in the sample. ^{14}C is a radioisotope and has a half-life of 5,730 years. After 50,000 years, organic compounds do not contain any ^{14}C. As an immediate consequence, petrochemical materials, with an age of millions of years, contain practically no ^{14}C. Why do bio-based materials contain ^{14}C?

Cosmic rays (mostly atoms without electrons) of high energy collide with the atmosphere at ≈9–10 km (troposphere) to generate neutrons. The latter collide with nitrogen atoms from the atmosphere to generate ^{14}C atoms (**Reaction 7.2**).

$${}^{1}_{0}n + {}^{14}_{7}N \rightarrow {}^{14}_{6}C + {}^{1}_{1}p \tag{7.2}$$

Upon oxidation, ^{14}C is transformed rapidly to $^{14}CO_2$. As a result, within the Earth's atmosphere, together with nitrogen and oxygen (O_2), a mixture of $^{14}CO_2$, and $^{12}CO_2$ from the respiration of plants, animals, and from human activities, is produced. $^{12}CO_2$

and $^{14}CO_2$ are used by plants in photosynthesis and by a photochemical reaction with water to generate glucose, and from glucose are formed starch and cellulose (**Reaction 7.3**).



(7.3)

When plants convert atmospheric CO_2 into organic compounds during photosynthesis, the resulting fraction of ^{14}C isotope in plant tissue matches the fraction of ^{14}C isotope in the atmosphere. This is why plants on the surface of the Earth contain ^{14}C. Animals eat these plants and have ^{14}C too.

^{14}C is a radioactive atom (radiocarbon) and is transformed by ^{14}N atoms (**Reaction 7.4**).

$$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}\beta + \text{antineutrino} \tag{7.4}$$

Recently-living materials (the bio-based component) have ^{14}C and fossil materials (derived from petroleum) have virtually no ^{14}C. The bio-based content of any organic compound can be determined as a result of ^{14}C content.

Bio-based content is the amount of carbon in the product derived from bio-based materials relative to the total amount of carbon in the entire product [13].

By determination of the ratio of ^{14}C to ^{12}C (conforming to ASTM D6866), the bio-based content of any organic compound can be determined. In spite of very low concentrations of ^{14}C in the atmosphere ($^{14}C/^{12}C$ = 1/1,000,000,000,000), the concentration of this isotope of carbon can be determined precisely by liquid scintillation counting, mass spectrometry, and ratio mass spectrometry [13].

GWP [14] – upon measurement of the Earth's temperature during the last century, it was observed that the atmosphere near the Earth surface is getting warmer, and that the temperature is increasing by ≈0.7 °C. This warming is related to GHG (e.g., water vapour, CO_2, methane, nitrous oxide, chlorofluorocarbons) in the atmosphere. The Earth absorbs energy from the sun, and some of this energy is reflected back into space. GHG absorb some of this energy and heat the lower parts of atmosphere, which emit some energy back to Earth. As a result, the Earth's surface is heated. GHG occur naturally in the Earth's atmosphere, but more are created by human activities. Many scientists have concluded that global warming can be explained by human-caused increases in the greenhouse effect. This is why technologies that consume CO_2, or technologies that do not emit CO_2, or use of blowing-agent compounds with low GWP or use of renewable compounds have a major contribution to reductions in global warming. Hence, technologies that do not emit greenhouse gases are considered to be 'sustainable technologies'. Earth plants (the main source of renewable compounds) insert in their structures CO_2 from the atmosphere during photosynthesis. Global warming has led to climate change with many negative effects: increases in sea levels (17 cm in the last century); increased temperatures in the globe and oceans; declining amounts of ice in the Arctic; glacier retreat; decrease of snow cover in the Northern Hemisphere.

The ODP [15] of a chemical compound is the relative amount of degradation of the ozone (O_3) layer of the atmosphere it can cause relative to that of trichlorofluoromethane ($CFCl_3$ or CFC-11), which has a ODP = 1. The highest ODP is found for compounds containing chlorine and bromine due to the weakness of C-Cl and C-Br bonds. Compounds containing only carbon, fluorine and hydrogen (HFC) have an ODP = 0. This characteristic is very important for practical use of blowing agents in preparation of polyurethane foams (PUF). For protection of the O_3 layer, blowing agents containing chlorine (CFC-11, CHFC-141b) have been eliminated from PU preparation. Now, blowing agents with an ODP = 0, such as pentanes (cyclopentane, iso-pentane, n-pentane) and hydrofluorocarbons (HFC-245fa, HFC-134a, HFC-365mfc) are used. A new, very promising blowing agent developed by Honeywell called Solstice® LBA (*trans*-1-chloro-3,3,3-trifluoropropene) has an ODP = 0, low GWP, and is non-flammable. The chlorine atom linked to a double-bond in Solstice® LBA is strong and stable. Preservation of the O_3 layer is very important for the protection of all life forms. O_3 absorbs most of the sun's dangerous ultraviolet (UV) radiation (200–315 nm), which could otherwise damage exposed life forms at the Earth's surface.

Bio-refinery [16] – a typical petrochemical refinery uses crude oil as the main raw material. Crude oil is transformed into various useful petrochemicals (fuels, monomers, solvents, polymers) using different technological processes.

The concept of bio-refinery (which is relatively new) is to prepare the same compounds produced in petrochemical refineries using natural compounds instead of crude oil, such as carbohydrates, vegetable/animal oils, lignin, cellulose, hemicellulose, starch, proteins, and terpenes. This is a provocation for chemists, and use of natural compounds as raw materials is a trend in the worldwide chemical industry. The first steps have been made. A good example is the production of polyethylene (PE) from ethylene, which involves dehydration of ethanol and results in fermentation processes (bio-ethanol). In Brazil, Braskem have an impressive industrial plant for production of PE [high-density polyethylene (HDPE)] from bio-ethanol. This results in fermentation of sugar cane, and 200,000 tonnes/year of bio-based or ‘green HDPE’ can be produced [17]. Braskem’s green PE is made from CO_2 sequestered from the atmosphere through sugarcane photosynthesis. This technology is one of the most competitive of all technologies for polymers made from renewable sources.

The synthesis of polyols from natural resources is another example of replacement of petrochemical polyols with compounds of natural origin that are renewable and practically unlimited. This chapter is dedicated to presenting the complex chemical pathways of transformation of natural compounds in bio-based polyols useful for preparation of PU as a consequence of the imagination and creativity of chemists worldwide.

In the PU industry, development of polyols based on renewable resources has always had an important role. One could say that the history of PU has been strongly linked to renewable resources [1–6].

7.1 Bio-based Monomers for Synthesis of Polyols

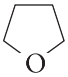
The monomers of natural origin useful for the synthesis of polyols for PU are bio-based compounds that react with hydroxyl groups of polyols to generate chains having hydroxyl groups at their end, or hydroxyl groups are generated by hydrolysis or alcoholysis of the active centres of terminal chains. The chain derived from one hydroxyl group can be short [maximum 100–300 daltons (Da)] or long (maximum 2,000–2,500 Da). This special group of bio-based monomers is divided in two main groups: monomers that generate new chains by ring-opening polymerisation (ROP) reactions and monomers that generate new chains by polycondensation reactions.

7.1.1 Bio-based Monomers that Generate New Chains by Ring-opening Polymerisation Reactions

In this group of bio-based monomers are cyclic ethers [e.g., tetrahydrofuran (THF), glycidol] and cyclic esters (e.g., lactides, glycerin carbonate).

7.1.1.1 Tetrahydrofuran [18–24]

THF is a five-membered cyclic ether (**Structure 7.1**)

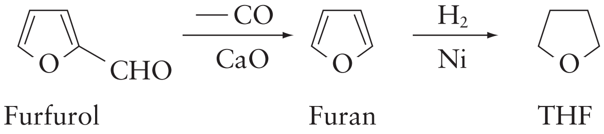


Structure 7.1 THF

THF is a colourless liquid compound of molecular weight (MW) = 72, boiling point (bp) of 66 °C, and density of 0.8892 g/ml at 20 °C.

THF, the cyclic monomer used for the synthesis of polytetramethylene glycols (PTMG) (**Volume 1, Chapter 7, Sections 7.1** and **7.3**) [19] by cationic ROP, was produced from furfurol in the earlier versions of this technology. Furfurol results from the acid hydrolysis of pentosanes present in many agricultural wastes (e.g., corn on the cob, straw).

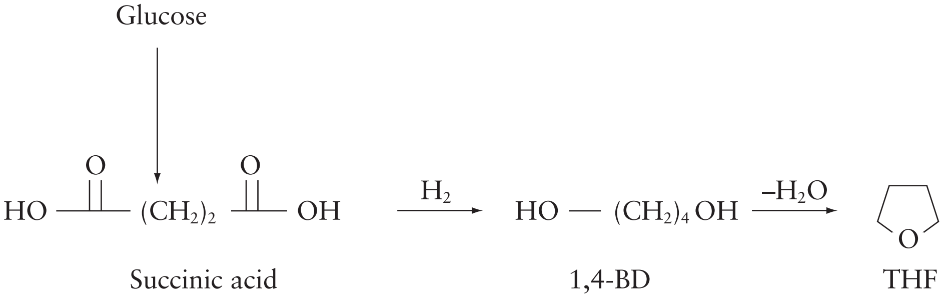
Furfurol is decarbonylated in the presence of special catalysts (calcium oxide) and the resulting furan is hydrogenated to THF in the presence of Raney–nickel catalysts [21] (**Reaction 7.5**).



(7.5)

This old technology based on furfurol may be reconsidered in the future because it uses a renewable resource as its raw material.

A new technology for the synthesis of bio-based THF from bio-succinic acid has been developed [22, 23]. Succinic acid resulting from by low-pH fermentation of glucose, called bio-succinic acid, is hydrogenated to 1,4-butanediol (1,4-BD). By catalytic dehydration of 1,4-BD yields THF (**Reaction 7.6**).

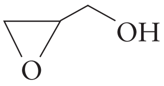


(7.6)

Today, THF is produced by selective hydrogenation of maleic anhydride (MA) [19, 21] or by dehydration of 1,4-BD (resulting from acetylene and formaldehyde, followed by hydrogenation of the resulting 2-butyne-1,4 diol [24]).

7.1.1.2 Glycidol [25–31]

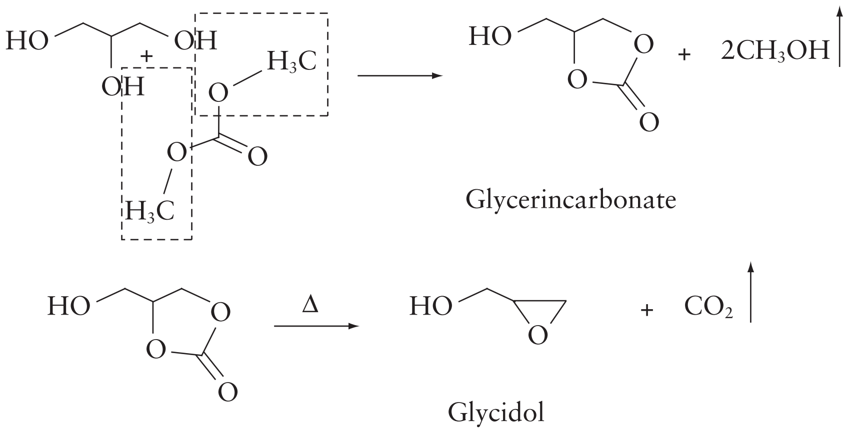
Glycidol is an epoxide having a methylol group as a substituent (**Structure 7.2**).



Structure 7.2 Glycidol

Glycidol is a colourless liquid of MW = 74, bp = 167 °C/760 mmHg (with decomposition) or 66 °C /2.5 mmHg and density of 1.148 g/ml at 25 °C.

Glycidol prepared from glycerol resulted in large quantities as a byproduct during the synthesis of methyl esters of fatty acids (biodiesel) by reaction of vegetable oils with methanol. Glycerol is converted first to glycerine carbonate by reaction with dimethylcarbonate or with urea. In the second step, glycerine carbonate is thermally decomposed to glycidol in the presence of catalysts [25] (**Reaction 7.7**).



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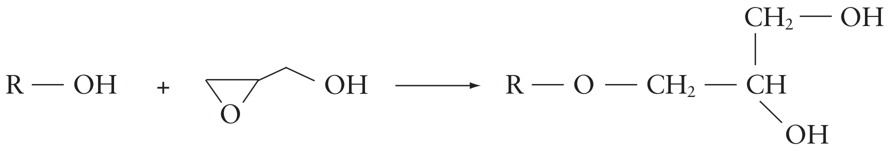
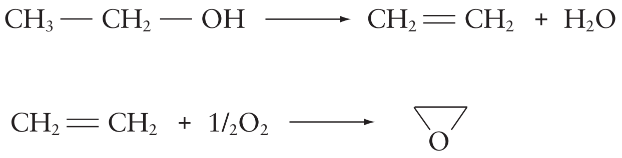
Interestingly, glycidol is an AB_2 monomer. By addition of glycidol to one hydroxyl group in the presence of acid or basic catalysts, a new compound with two hydroxyl groups is produced [26] (**Reaction 7.8**).



(7.8)

Glycidol is used for preparation of polyglycerol (PGL). The latter is an important starter for preparation of high-functionality polyols [27–30] or to increase the functionality of vegetable oil polyols [31]. An interesting bio-based cyclic monomer is epoxidised methyl oleate (EMO) (**Volume 2, Section 7.3.3.11**).

THF and glycidol are bio-based cyclic ethers. In the future, another important cyclic ether, ethylene oxide (EO), could be obtained starting from bio-based raw materials. Thus, by fermentation of glucose we can obtain ethanol and by dehydration of ethanol we can obtain ethylene [17]. By oxidation of ethylene from ethanol it is possible to prepare EO which, using this route, is a monomer from renewable resources (**Reaction 7.9**).

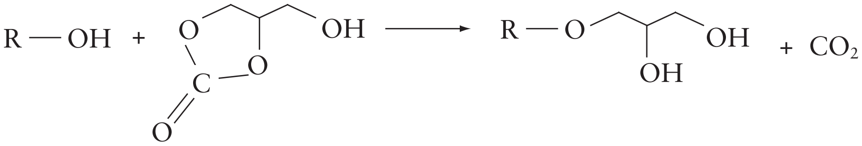


(7.9)

For preparation of polyols for PU, cyclic esters are also used (e.g., glycerine carbonate, lactides).

7.1.1.3 Glycerine Carbonate (4-Hydroxymethyl-1,3-Dioxolan-2-One) [31]

Glycerine carbonate prepared from glycerol (as described in **Volume 2, Section 7.1.1.2**) is a cyclic ester of carbonic acid and, similar to glycidol, is an AB_2 monomer. By reaction with one hydroxyl group it generates a compound with two hydroxyl groups with elimination of CO_2 (**Reaction 7.10**).



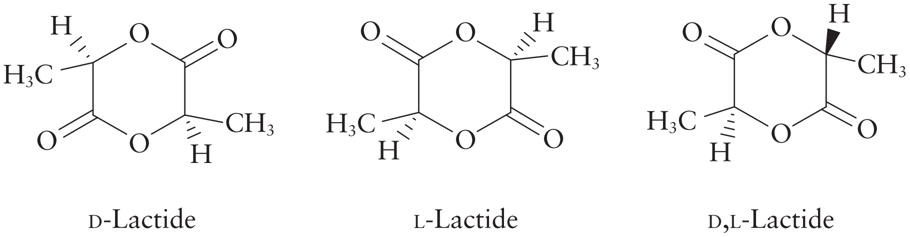
(7.10)

Glycerin carbonate is a clear liquid of MW = 118, bp of 110–115 °C/ 0.1 mmHg, density of 1.4 g/ml at 25 °C, and viscosity of 61 cSt at 25 °C.

Glycerine carbonate, similar to glycidol, can be used to increase the functionality of bio-based polyols and for preparation of PGL [31].

7.1.1.4 Lactides [32–37]

Lactic acid (2-hydroxypropionic acid) is a bio-based hydroxyacid obtained by fermentation of glucose with micro-organisms from *Lactobacillus* [32]. Polylactic acid is one of the most important biodegradable polymers [33]. Lactides are dilactones of lactic acid and, in fact, are bio-based cyclic esters [34] (**Structure 7.3**).



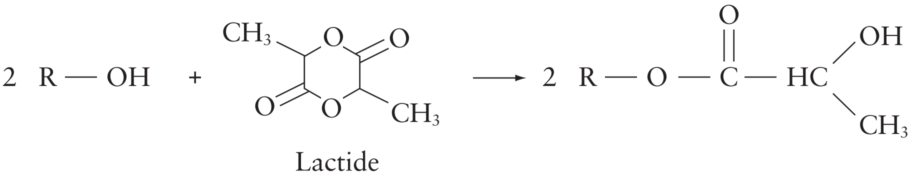
D-Lactide L-Lactide D,L-Lactide

Structure 7.3 D-Lactide, L-lactide and D,L-lactide

Lactides are white crystalline solids. D-lactide has a melting point (mp) of 116–119 °C and L-lactide has a mp of 92–94 °C.

The three types of lactide are: D-lactide, L-lactide and D,L-lactide (**Structure 7.1.3**). D-lactide is a dilactone from 2 units of D-lactic acid [(R,R)-3,6-dimethyl-1,4 dioxane-2,5 dione]. L-lactide is a dilactone containing two units of L-lactic acid [(S,S)-3,6-dimethyl-1,4 dioxane-2,5 dione]. D,L-lactide (or mezzo lactide) is a dilactone based on one D-lactic unit and one L-lactic unit [(R,S)-3,6-dimethyl-1,4 dioxane-2,5 dione]. All three lactides react in very high yield with hydroxyl groups in the presence of Ti(IV), Sn(II) or Sn(IV) catalysts at 120–140 °C, for 3–4 h. The best catalysts for this ring-opening reaction are $Ti(OiPr)_4$, $Ti(OiBu)_4$, stannous octoate and dibutyltin dilaurate, of 0.2–0.5% concentration.

Reaction of lactides with hydroxyl groups produces lactate esters [35, 36] (**Reaction 7.11**).



(7.11)

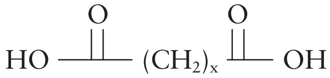
Reaction of soybean polyols with lactides produces bio-based polyols that lead to PU with an increased glass transition temperature (T_g) [37].

7.1.2 Bio-based Monomers that Generate New Chains by Polycondensation Reactions

The main polycondensation reactions used for polyol synthesis are: polyesterification reactions and polyetherification reactions. Polyesterification reactions between organic dicarboxylic acids and diols are important reaction for polyol preparation (**Volume 1, Chapter 8** and **Volume 2, Chapter 5**) [19]. Compounds having in the same structure carboxyl and hydroxyl groups ('hydroxyacids') are also excellent monomers for polyesterification. Several bio-based dicarboxylic acids, diols and hydroxyl acids can udergo polyesterification reactions to produce bio-based polyesters. If an excess of hydroxyl groups are used against carboxyl groups, then polyester polyols are produced (**Volume 1, Chapter 8**) [19].

7.1.2.1 Bio-based Diacids

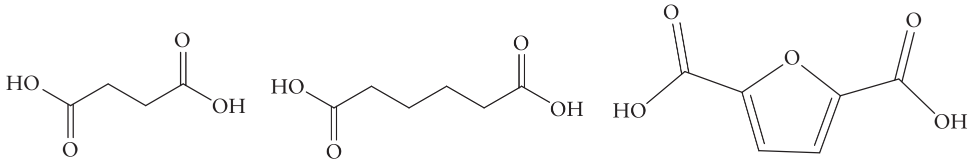
Bio-based dicarboxylic acids have the general shown in **Structure 7.4**.



$$HO-C(=O)-(CH_2)_x-C(=O)-OH$$

Structure 7.4 General structure of dicarboxylic acids

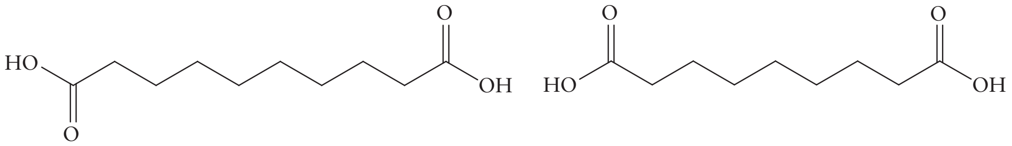
Several dicarboxylic acids can be obtained from natural compounds using various reactions, and are called ‘bio-based diacids’. The most important bio-based diacids used for preparation of polyols are succinic, adipic, sebacic, azelaic and dimeric acids (**Figure 7.1**).



Succinic acid

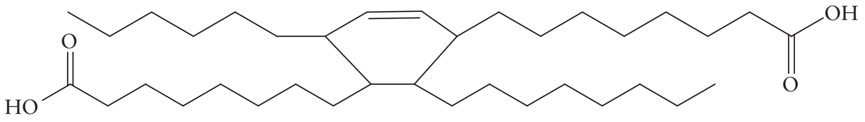
AA

2,5-Furandicarboxylic acid



Sebacic acid

Azelaic acid

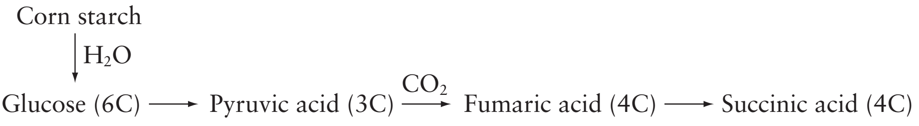


Dimer acid

Figure 7.1 Structures of main bio-based diacids

- Succinic acid (x = 2) [38–46]

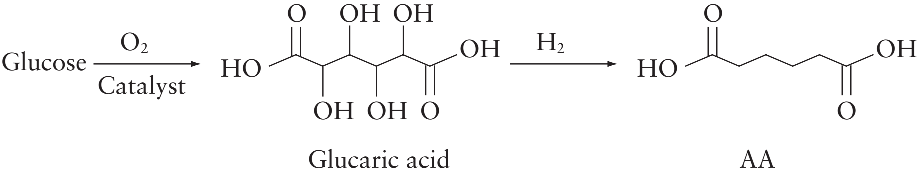
Myriant (MA, USA) [38–40] and BioAmber (Montreal, Canada) [41, 42] have developed a new bio-based route to succinic acid by fermentation of glucose with the bacteria *Escherichia coli* (**Reaction 7.12**). Also, bio-based succinic acid has been prepared by fermentation of glycerol [43] and sucrose [44–46].



$$\text{Corn starch} \xrightarrow{H_2O} \text{Glucose (6C)} \longrightarrow \text{Pyruvic acid (3C)} \xrightarrow{CO_2} \text{Fumaric acid (4C)} \longrightarrow \text{Succinic acid (4C)} \qquad (7.12)$$

- Adipic acid (AA) (x = 4) [47]

Recently, a new route to AA was developed starting from bio-based raw materials. Rennovia (CA, USA) developed a new route to AA by chemical modification of glucose [47]. The process comprises catalytic oxidation of glucose to glucaric acid, followed by catalytic hydrodeoxygenation of glucaric acid to AA (**Reaction 7.13**).



(7.13)

Oxidation of glucose to glucaric acid is carried out at 80–100 °C and 75 psi of O_2 (or 500 psi of air), in the presence of platinum catalysts (4% platinum supported on silica or carbon). Hydrodeoxygenation of glucaric acid is carried out at 140 °C and 710 psi in the presence of supported ruthenium/palladium or ruthenium/platinum on silica.

The process has not been industrialised on a large scale. However, it is hoped that a bio-based AA (the most important diacid for preparation of polyester polyols for PU) will be prepared in the future.

- Sebacic acid (x = 8) and azelaic acid (x = 9)

- Sebacic acid (x = 8) is obtained by caustic oxidation of castor oil (**Volume 2, Section 6.1**) [19]. Azelaic acid (x = 7) is obtained by ozonolysis of vegetable oils (**Volume 2, Section 6.1**) [19].

- Dimer acids are obtained by a Diels–Alder reaction of fatty acids resulting from hydrolysis of unsaturated vegetable oils (**Volume 2, Section 6.1.3.3**) [19].

The dialkylesters (especially dimethyl esters of the bio-based diacids mentioned above) are excellent monomers for preparation of polyester polyols by polycondensation reactions.

An interesting heterocyclic bio-based diacid is 2,5-furandicarboxylic acid (**Figure 7.1**). Carbohydrates with six carbon atoms (e.g., glucose, fructose) are converted to hydroxymethylfurfural, which is oxidised to 2,5-furandicarboxylic acid [48]. By a Diels–Alder reaction of 2,5-furandicarboxylic acid with ethylene followed by dehydration, an important monomer for polyester synthesis, bio-terephthalic acid, is obtained [49].

7.1.2.2 Bio-based Diols [50–57]

Figure 7.2 shows the structures of some bio-based diols (raw materials for the synthesis of bio-based polyester polyols by polyesterification with organic diacids).

One of the most important bio-based diols is 1,3-propanediol. 1,3-Propanediol (an isomer of 1,2-propanediol) was produced initially by petrochemical routes such as hydroformylation of ethylene oxide followed by hydrogenation [50], or by hydration of acrolein followed by hydrogenation [51]. A great biotechnology ‘success story’ was preparation of 1,3-propanediol by microbial fermentation of corn sugar, glucose or glycerol with various micro-organisms (e.g., *Citrobacter*, *Klebsiella*, *Lactobacillus*, *Enterobacter, Clostridium*). One of the best micro-organisms is *Klebsiella pneumoniae* [52, 53]. Susterra 1,3-propanediol is a 100% bio-based compound produced by DuPont (DE, USA) and Tate & Lyle (London, UK). Compared with petrochemical routes, the bio-based route to 1,3-propanediol uses 40% less energy with reductions of greenhouse gas emissions of 20%.

1,3-Propanediol is a colourless liquid of MW = 76.1, bp of 214 °C (at 760 mmHg), freezing point of –24 °C, density of 1.053 g/ml at 25 °C, with hydroxyl number(s) (OH#) of 1,475 mg potassium hydroxide (KOH)/g, and viscosity of 50 mPa.s at 25 °C [54].

Polyetherification of 1,3-propanediol in the presence of acidic catalysts produces polytrimethylene ether diols (Cerenol polyols of DuPont), very important polyethers for elastic PU (**Section 7.4.2**). 1,3-Propanediol is used frequently as a diol for polyester fabrication (e.g., Sorona® EP polytrimethylene terephthalate produced by DuPont) [55].

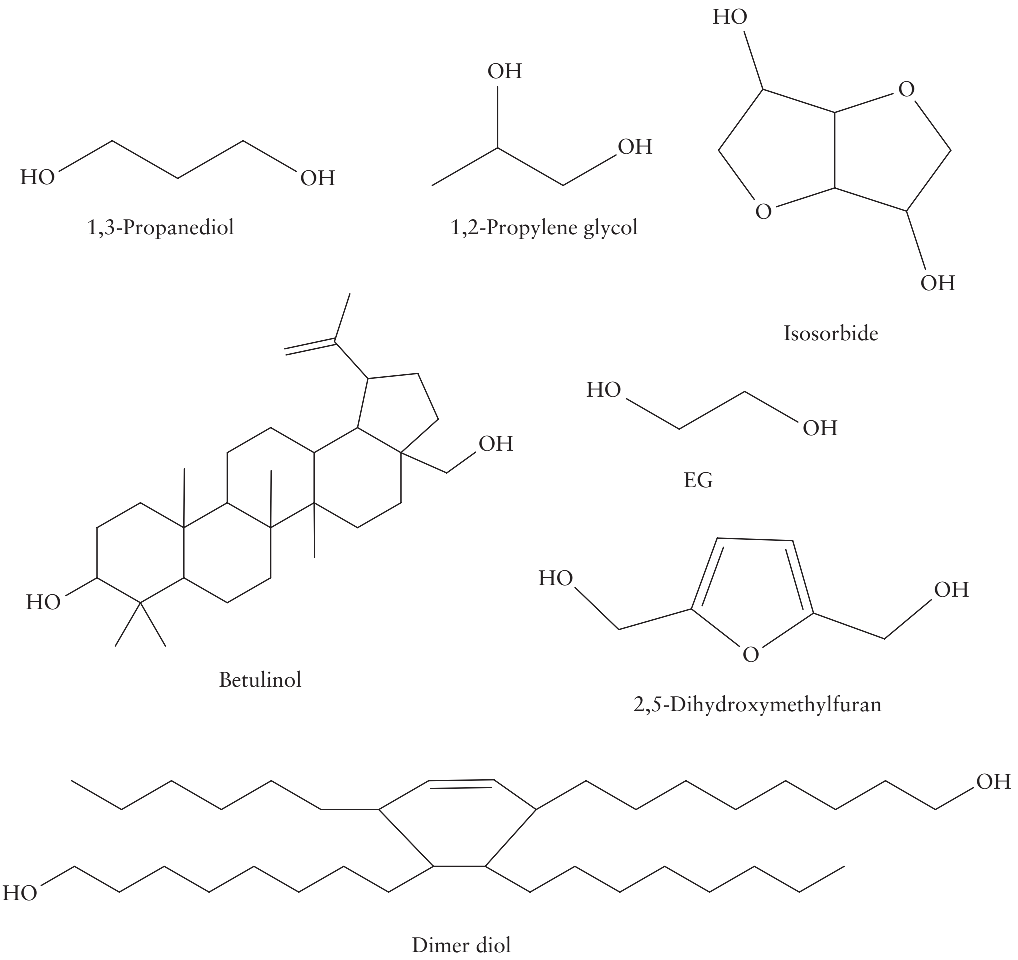


Figure 7.2 Structures of some bio-based diols

Production of dimer diols by polyesterification with dimer acids leads to extremely hydrophobic polyester polyols. PU based on these polyols are very resistant to hydrolysis [56].

D-isosorbide (1,4:3,6-dianhydro-D-glucitol) is obtained by double-dehydration of sorbitol (**Section 7.4.1**). Sorbitol is a bio-based compound obtained by hydrogenation of glucose.

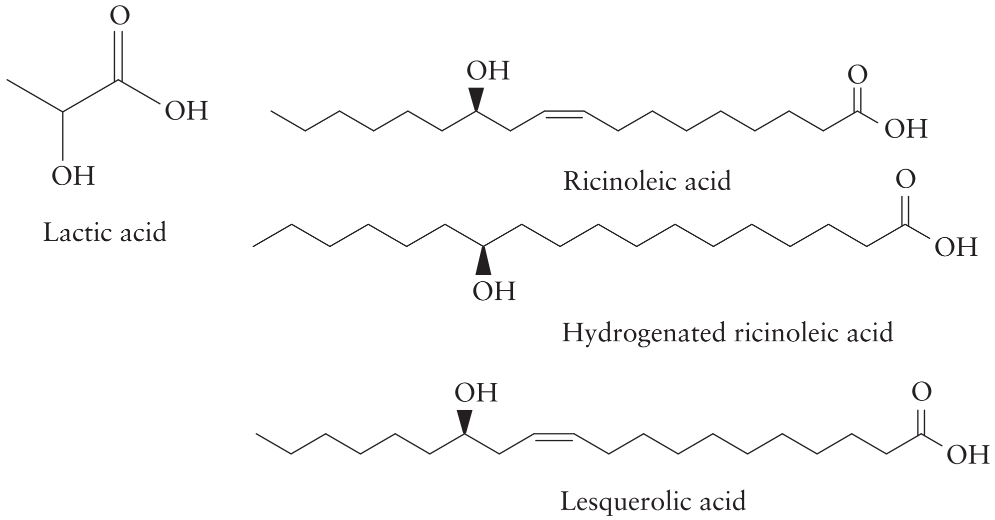
Isosorbide and betulinol are used as diols only for special applications in the synthesis of polyesters and PU.

2,5-Di(hydroxymethyl)furan (**Figure 7.2**) is obtained by hydrogenation of hydroxymethylfurfural (a product prepared from carbohydrates with six carbon atoms). Hydrogenation of the furan ring of 2,5-di(hydroxymethyl)furan yields a new diol: 2,5-di(hydroxymethyl)tetrahydrofuran [48].

Bio-based 1,2-propanediol (propylene glycol), a very important diol for preparation of polyesters (including polyester polyols), is prepared in high yield by hydrogenolysis of glycerol in the presence of specific catalysts (e.g., copper chromite, ruthenium supported on zirconium oxide) [57]. As a byproduct of glycerol hydrogenolysis, another diol in lower concentrations is obtained: bio-based ethylene glycol (EG) [58, 59].

7.1.2.3 Bio-based Hydroxyacids

Hydroxyacids are monomers used for preparation of polyesters having in the same structure the chemical groups involved in the synthesis of ester bonds, carboxyl groups and hydroxyl groups (**Volume 2**, **Section 6.1**) [19]. The most well-known bio-based hydroxyacids are lactic acid, ricinoleic acid, hydrogenated ricinoleic acid and lesquerolic acid (**Figure 7.3**).



Lactic acid

Ricinoleic acid

Hydrogenated ricinoleic acid

Lesquerolic acid

Figure 7.3 Structures of some bio-based hydroxyacids

Alkyl esters of hydroxyacids shown in **Figure 7.3** (especially ethyl and methyl esters) are bio-based monomers for polyol synthesis by polyesterification reactions.

7.2 Natural Compounds used as Starters for Polyol Synthesis

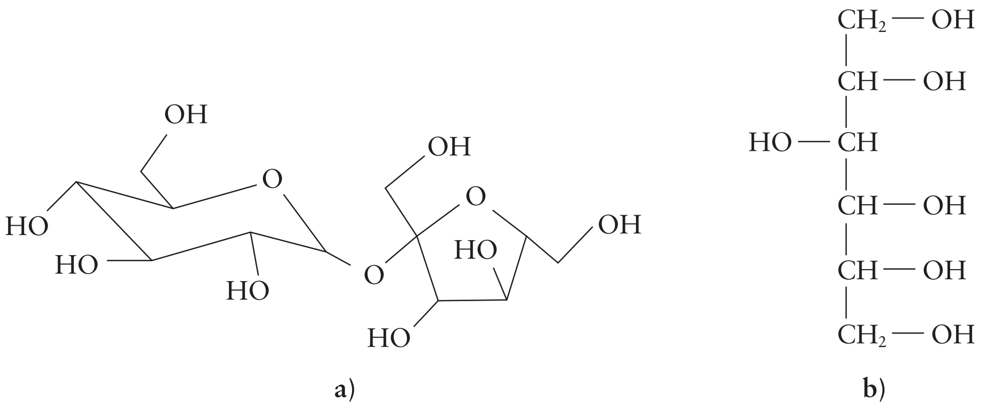
Many natural compounds containing hydroxyl groups are used as starters for polyol synthesis using alkoxylation or polyesterification reactions. These natural compounds are glycerol, sucrose, sorbitol, xylitol, starch, glucose, castor oil, isosorbide, lignin, and betulinol.

7.2.1 Glycerol, Sucrose, Sorbitol, and Xylitol [1, 18, 60]

Glycerol (the most important starter for the synthesis of polyether polyols for flexible PUF and for polyether for rigid foams) is produced by the hydrolysis of natural triglycerides (esters of glycerol with fatty acids with C6–C22 carbon atoms) from vegetable or animal resources (**Figure 7.4a**) [1]. Large quantities of glycerol appear in bio-diesel production by transesterification of natural oils with methanol (**Figure 7.4b**).

An interesting starter is PGL, which results from alkaline self-condensation of glycerol (**Volume 2, Section 7.4.6**).

Sucrose has high functionality (eight hydroxyl groups) and is the most important starter for rigid polyether polyols. Sucrose is produced exclusively by extraction from natural resources (**Structure 7.5a**) [1]. Sorbitol (another important bio-based starter for fabrication of rigid polyether polyols having six hydroxyl groups [19]) is produced by hydrogenation of D-glucose [60] (**Structure 7.5b**).



Structure 7.5 Structures of a) sucrose and b) sorbitol

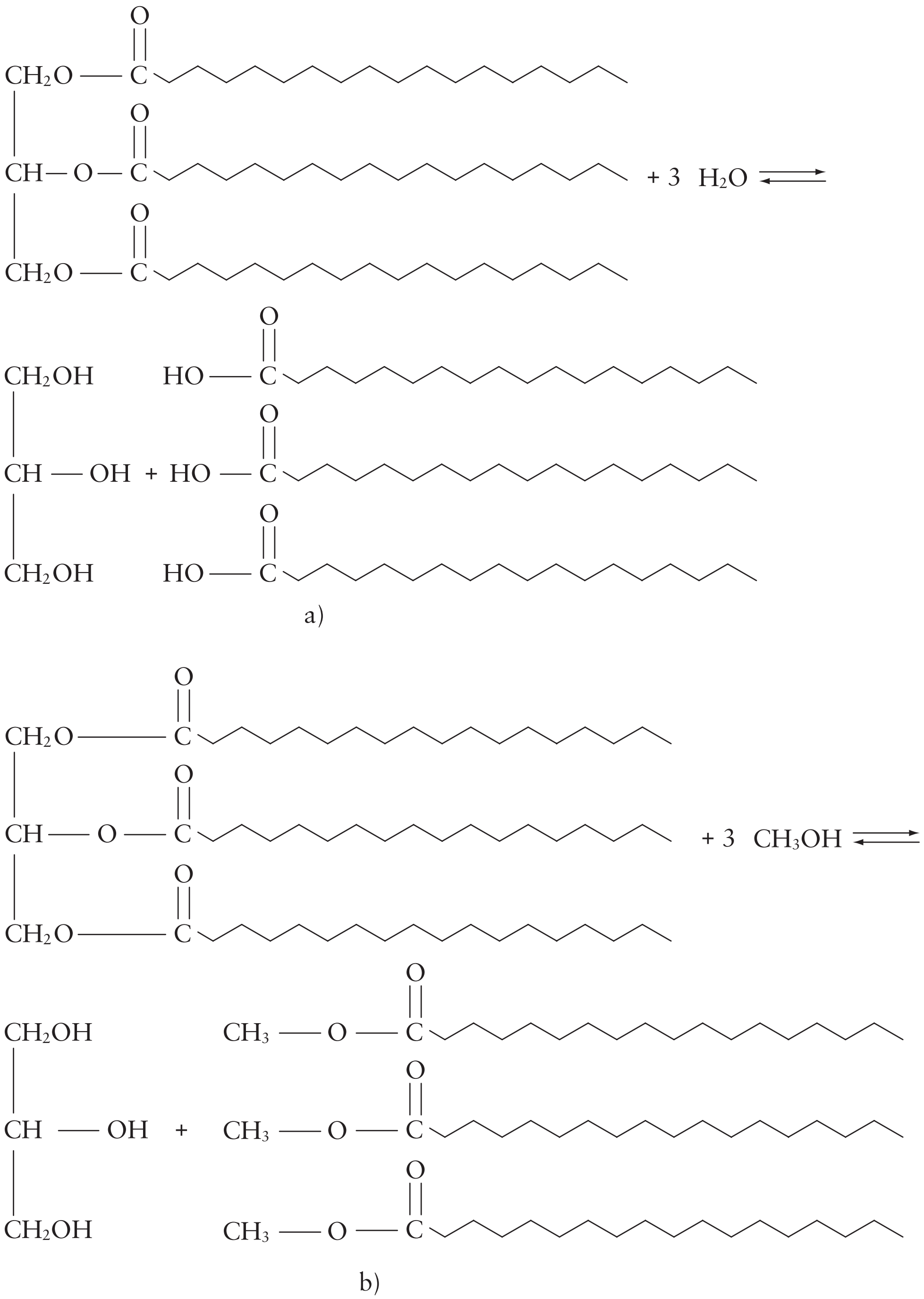
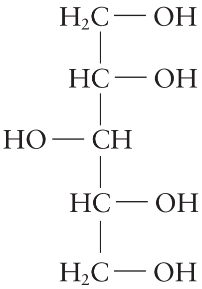


Figure 7.4 a) Hydrolysis and b) alcoholysis of vegetable oils

Xylitol (**Structure 7.6**) is a polyol starter for rigid polyether synthesis that has five hydroxyl groups). Xylitol is produced by the hydrogenation of the same pentosans used for THF synthesis [8]. By propoxylation of xylitol, excellent rigid polyether polyols (**Volume 2, Section 2.3.1**) [19] can be obtained.



Structure 7.6 Structure of xylitol

7.2.2 Starch, Glucose, and Glucosides [60–68]

Alkyl glucosides (α-methyl glucoside and hydroxyalkyl glucosides) [60–67] and glucose [68] are used as polyolic starters for synthesis of rigid polyether polyols. They are produced by alcoholysis or hydrolysis of starch from renewable resources (e.g., potatoes, corn). Starch is a polysaccharide having D-glucose units linked by α-glucosidic bonds.

Thus, D-glucose is obtained by the acid hydrolysis of starch. Upon acidic alcoholysis of starch with methanol or EG, α-methyl glucoside and hydroxyethyl glucoside, respectively, are obtained [60–68]. By the reaction of D-glucose with methanol in acidic media, α-methyl glucoside is obtained. By condensation of D-glucose with EG in the same acidic catalysis, hydroxyethyl glucoside is obtained. α-methyl glucoside and hydroxyethyl glucoside are excellent starters for the synthesis of polyether polyols [68]. The reactions from starch or D-glucose to alkyl glucosides are presented in **Figure 7.5** (**Volume 2, Chapter 6**) [19].

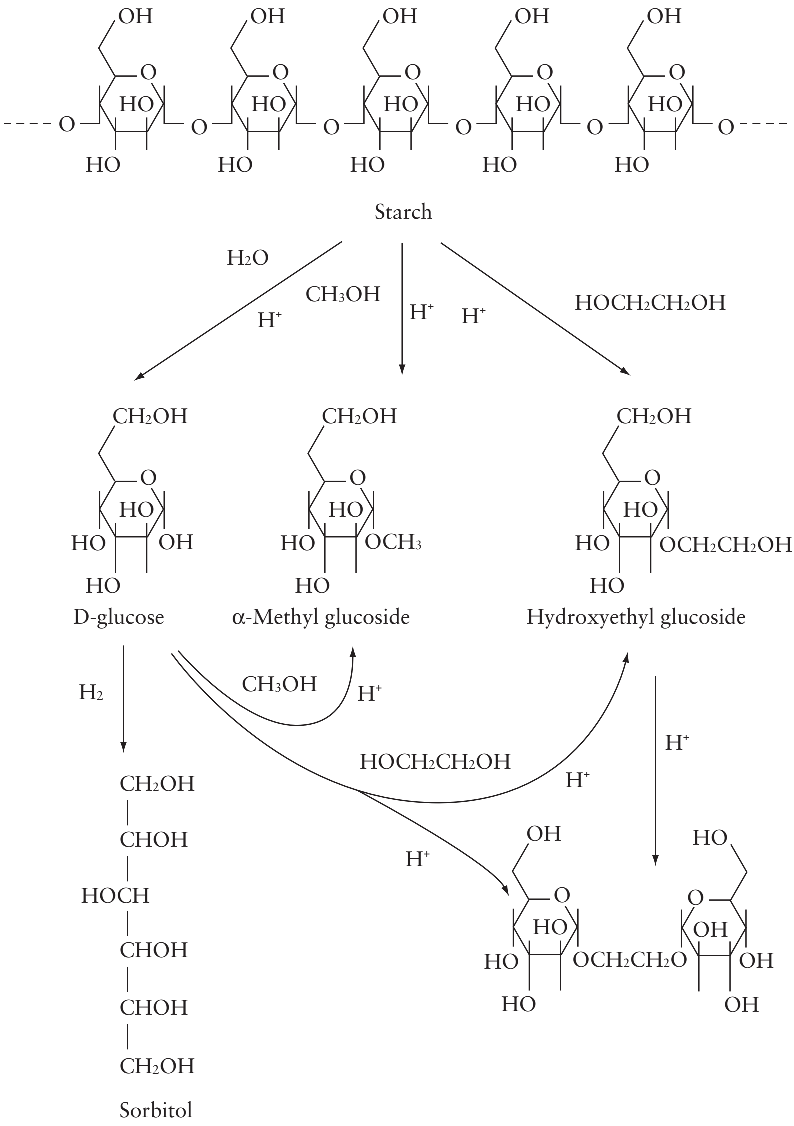
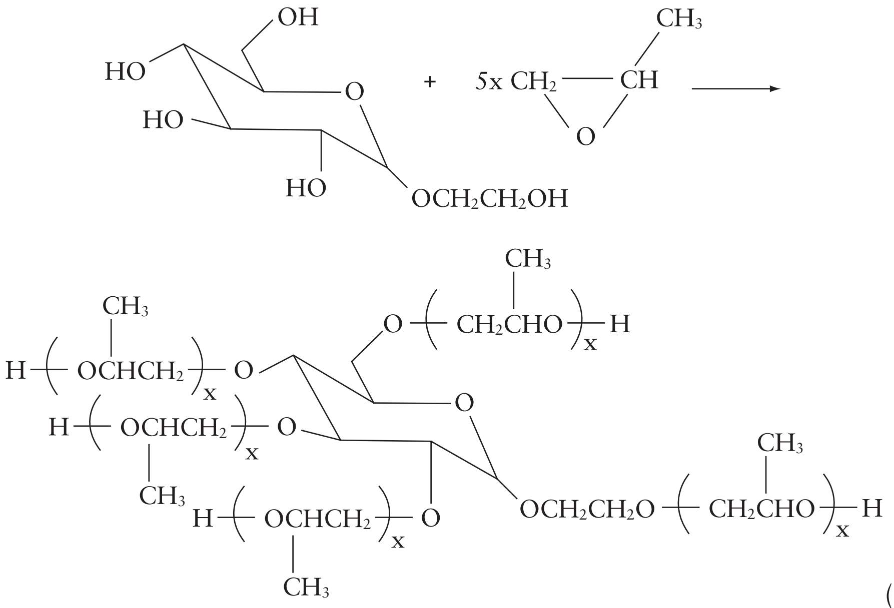


Figure 7.5 Chemical transformations of starch and D-glucose into polyols that can be used as polyfunctional starters for the synthesis of polyether polyols

Hydrogenation of D-glucose leads to the hexafunctional polyol sorbitol. The latter is one of the most important starters to initiate polymerisation of propylene oxide (PO) to hexafunctional rigid polyether polyols.

In general, all the reactions of acid catalysis shown in **Figure 7.5** occur in the presence of inexpensive acids such as sulfuric acid, water being removed by vacuum distillation. The acid is neutralised with calcium hydroxide, but $Ba(OH)_2$ is preferable. Then, KOH is added and normal anionic polymerisation of PO is developed, initiated by the synthesis of alkyl glucosides (**Reaction 7.14**). Content of reducing sugars (free D-glucose) in the resulting alkyl glucosides must be <1%. If the content of reducing sugars is >1%, the acids resulting from alkaline degradation of glucose (e.g., lactic acid, saccharinic acids) block the alkaline catalyst and make PO addition impossible [66].

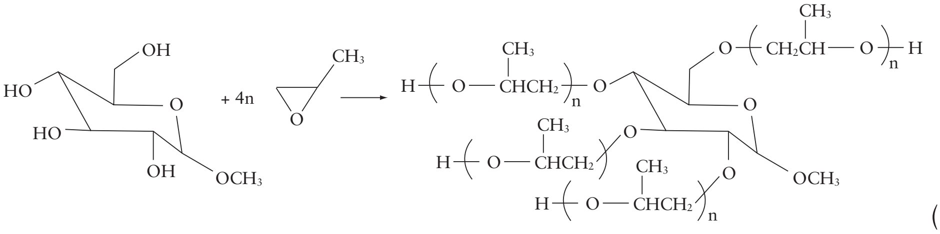


(7.14)

D-Glucose, in spite of its very attractive structure (five hydroxyl groups available for propoxylation) cannot be used as a starter for anionic polymerisation of PO because it is degraded in the presence of KOH.

Conversely, D-glucose is very stable in acidic media. Rigid polyether polyols are obtained directly from D-glucose by direct propoxylation in the presence of cationic catalysts (BF_3, BF_3 etherate, HBF_4, $HSbF_6$, HPF_6, CF_3SO_3H) [67].

α-Methyl glucoside is used as a tetrafunctional starter for fabrication of rigid polyether polyols, by propoxylation in alkaline catalysis, in the presence of KOH or tertiary amines (**Reaction 7.15**) [62].



(7.15)

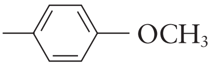
The carbohydrate content of polyether polyols derived from α-methyl glucoside is much higher than the carbohydrate content of sucrose-based polyether polyols at identical viscosities. Thus, at a viscosity of 10,000 mPa.s at 25 °C, sucrose polyols have a carbohydrate content of ≈20% and α-methyl glucoside-based 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% [62]. 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 PUF with physico-mechanical properties equivalent to rigid PUF derived from sucrose polyols with a functionality of 6 OH groups/mol [62]. A high carbohydrate content contributes to improving the fire resistance of the resulting rigid PUF because of the high char yield generated during burning.

7.2.3 Lignin [69–77]

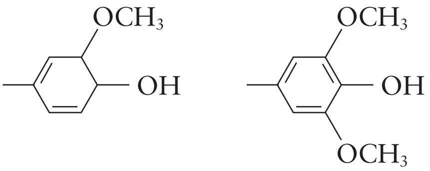
A very interesting natural starter for rigid polyols is lignin, which is available in large quantities from wood and cellulose industries [69]. Lignin is the second most important component of wood after cellulose. Lignin links the fibrillar cellulose, wood being a composite material. The content of lignin in wood varies (19–30%) according to the nature of the wood, the highest content being in coniferous wood (27–30%). Lignin is an aromatic macromolecular compound and a natural resin. It has a MW of ≈3,000–7,000 Da, ≈10–20 hydroxyl groups/mol, approximate OH# = 1,000–1,500 mg KOH/g, and a methoxy-group content of 13–14% [69, 77]. Lignin does not have a clear mp, and becomes a solid (‘sinterisation’) at 200 °C.

Lignin is soluble in alkaline aqueous solutions and in some organic solvents [dioxan, pyridine, aprotic dipolar solvents such as *N*-methyl pyrrolidone (NMP)] and has the following chemical groups [69]:

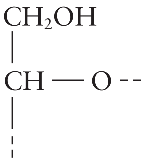
Methoxy groups, linked to aromatic nuclei:



Phenolic hydroxyl groups:

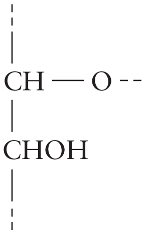


Primary hydroxyl groups:



$$\begin{array}{l} CH_2OH \\ | \\ CH - O\text{--} \\ | \\ \vdots \end{array}$$

Secondary hydroxyl groups:



$$\begin{array}{l} \vdots \\ | \\ CH - O\text{--} \\ | \\ CHOH \\ | \\ \vdots \end{array}$$

The idealised structure of lignin is presented in **Figure 7.6**.

Alkoxylation of lignin is possible in a solvent (dimethylformamide, NMP or in liquid PO [69]). A process using a lignin–glycerol mixture (3:1) in a polyether polyol based on lignin has been developed [69]. The catalyst of this reaction is KOH, but a tertiary amine, such as dimethylaminoethanol or tetramethylguanidine (TMG), is preferred. By alkoxylation with a PO–EO mixture (e.g., 18–25% EO) a totally liquid dark-brown lignin-based polyether polyol with a viscosity 4,700–8,000 mPa.s at 25 °C with an OH# of 400–450 mg KOH/g and a density of ≈1.14–1.16 g/ml at 25 °C was obtained [69].

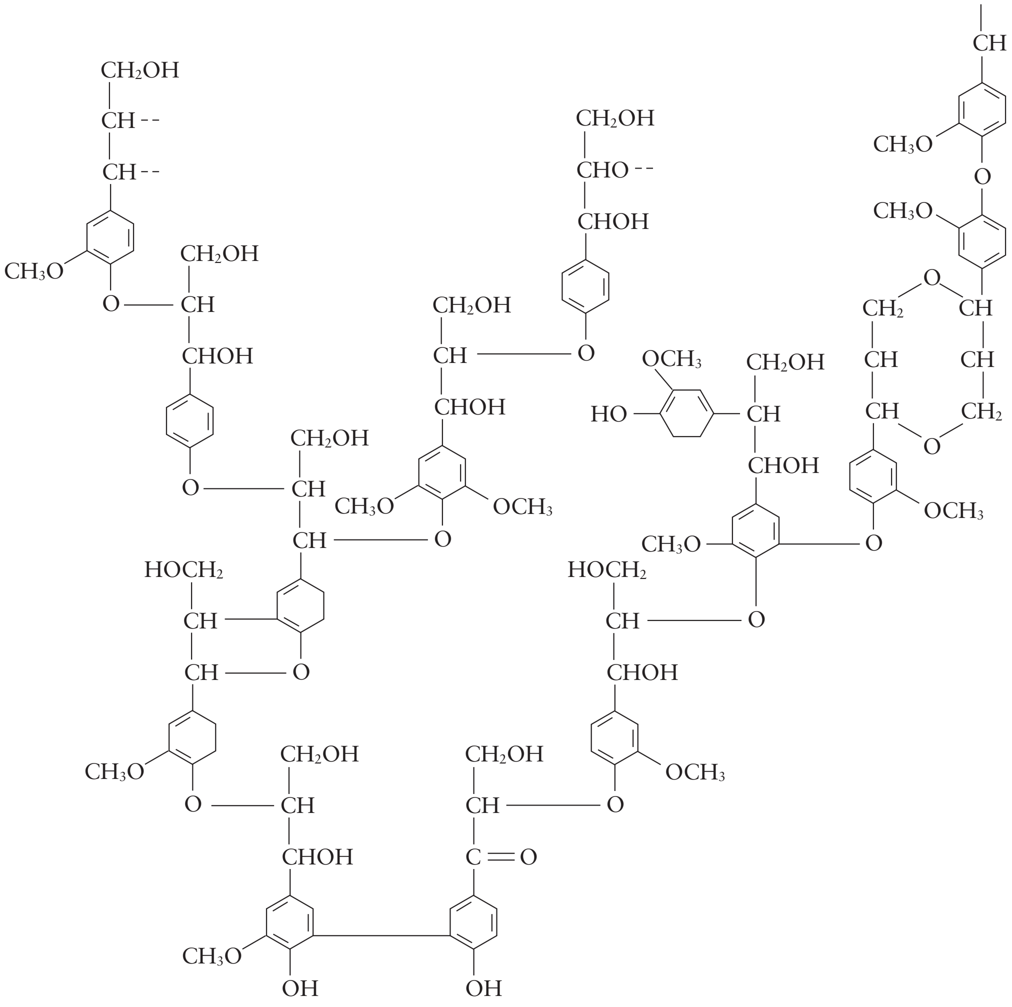


Figure 7.6 Structure of lignin

High-viscosity polyether polyols of ≈8,000–14,000 mPa.s at 25 °C are obtained by direct propoxylation of lignin [69]. The final lignin polyol is an excellent liquid medium (called ‘heel’) for propoxylation of solid lignin [69].

During alkoxylation, PO or EO are added to all hydroxyl groups from the reaction system (phenolic and aliphatic hydroxyl groups), but first to phenolic hydroxyl groups. Lignin-based polyester polyols formed by the reaction of lignin with ε-caprolactone (CPL) have been developed [63, 65, 70, 71].

The rigid PUF obtained with 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 ('kraft') lignin. This is why the best lignin for polyols for PU is 'organosolv' lignin, a lignin without sodium, which is obtained by extraction with organic solvents (e.g., ethanol/water solutions) [72].

Lignin can be used directly, without chemical modification, to obtain rigid PUF that can be employed as fillers or dissolved in polyether polyols. Thus, lignin was dissolved in polyether polyol PO–EO copolymer (it is not soluble in PO homopolymers). The resulting solution of lignin in polyether polyols was used to obtain various PU [73].

Utilisation of lignin in PU is limited. Lignin employed as raw material for PU manufacture represents good utilisation of a waste (lignin is a waste product of the wood and cellulose industries). Lignin has the advantage of low cost, aromaticity and is a renewable resource. However, it is a non-reproducible raw material, with impurities, very dark in colour, with a tendency to sinterisation.

7.2.4 Betulinol and Isosorbide [74–76]

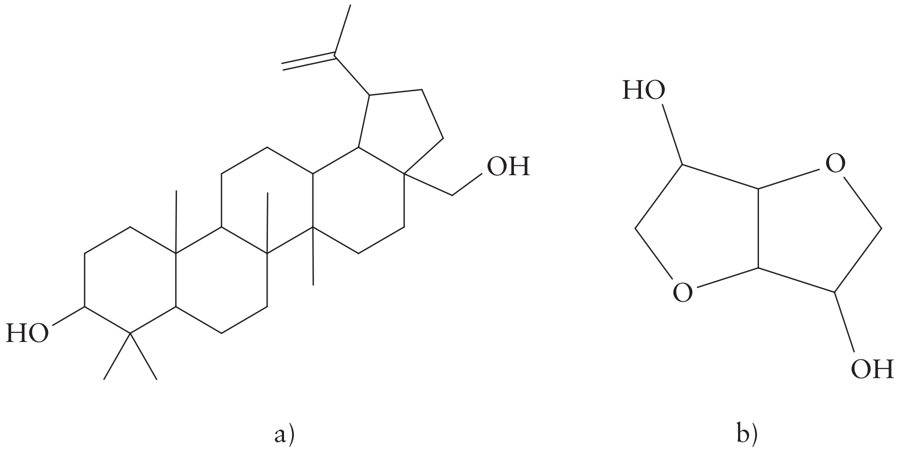
A very interesting natural diol with cycloaliphatic structure is betulinol. It is extracted from birch bark [74–76]. Betulinol is a triterpene diol, having 1 primary and 1 secondary hydroxyl group (**Structure 7.7a**).

PU can be prepared by reacting betulinol with diisocyanates [74–76]. Betulinol has also been used as a diol for polyester synthesis [74–76].

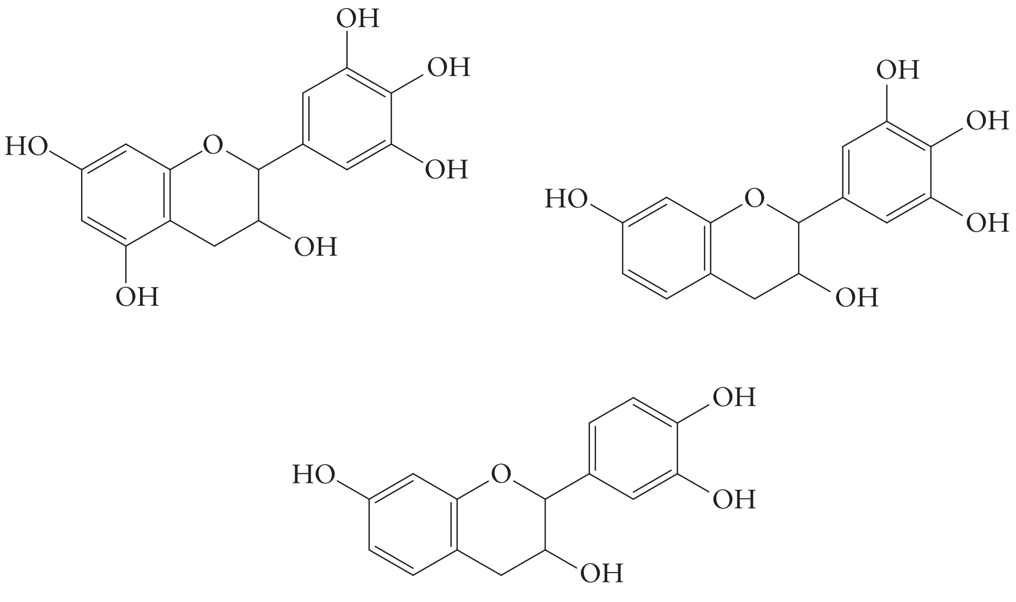
Isosorbide (**Structure 7.7b**) is a natural diol prepared by double-dehydration of sorbitol. Isosorbide is a very interesting bio-based starter for the synthesis of polyether diols, polyether polyols and of polyester polyols (**Volume 2**, **Section 7.4.1**).

7.2.5 Catechins and Tannins [78–80]

Catechins and tanins are natural compounds present in plants. They are highly aromatic compounds containing phenolic groups [78]. Catechins are part of a group of flavonoids (flavan-3-ols or simply 'flavanols') having 4–6 phenolic groups/mol (**Structure 7.8**). Catechin is a solid compound of mp = 175–177 °C. Catechins are found in cocoa, tea, green algae and barley grain. Catechins, due to the phenolic groups, are strong antioxidants.

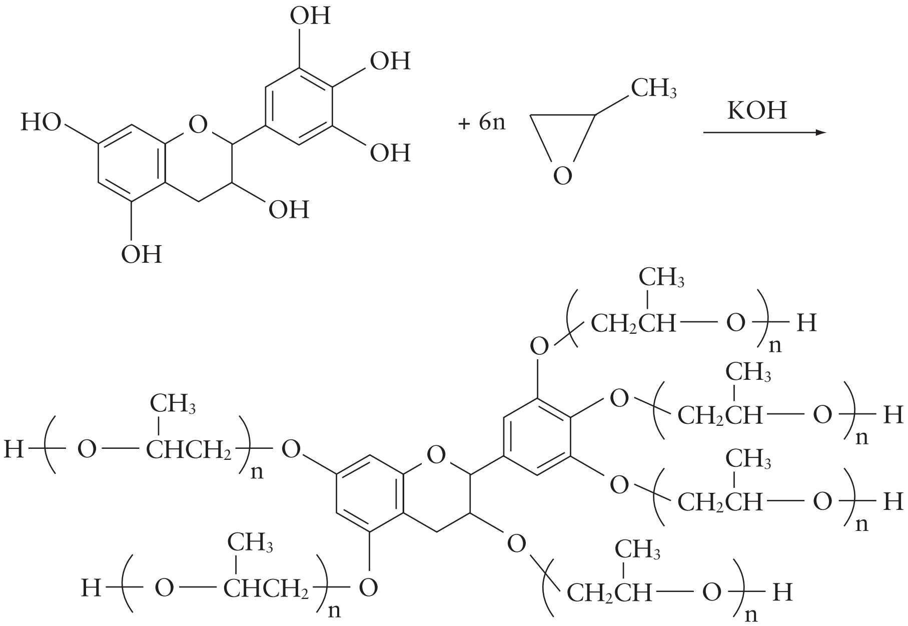


Structure 7.7 a) Betulinol and b) isosorbide



Structure 7.8 Natural catechins

Propoxylation of catechin in the presence of alkaline catalysts (KOH, tertiary amines) leads to aromatic polyether polyols (**Reaction 7.16**). **Reaction 7.16** is carried out only at the laboratory scale.



Tanins are natural polyphenols have aromatic structures close to those of catechins but, in general, with higher MW and higher content of penolic groups. They are present in oak bark, pine bark, nut shells and wood. Tannins are derivatives of gallic acid (**Figure 7.7**) and pyrogalol. Propoxylation of solid tannins leads to dark-brown aromatic polyols used for preparation of rigid PUF [79]. A possible structure of a polyether polyol based on tannins is presented in **Figure 7.7**.

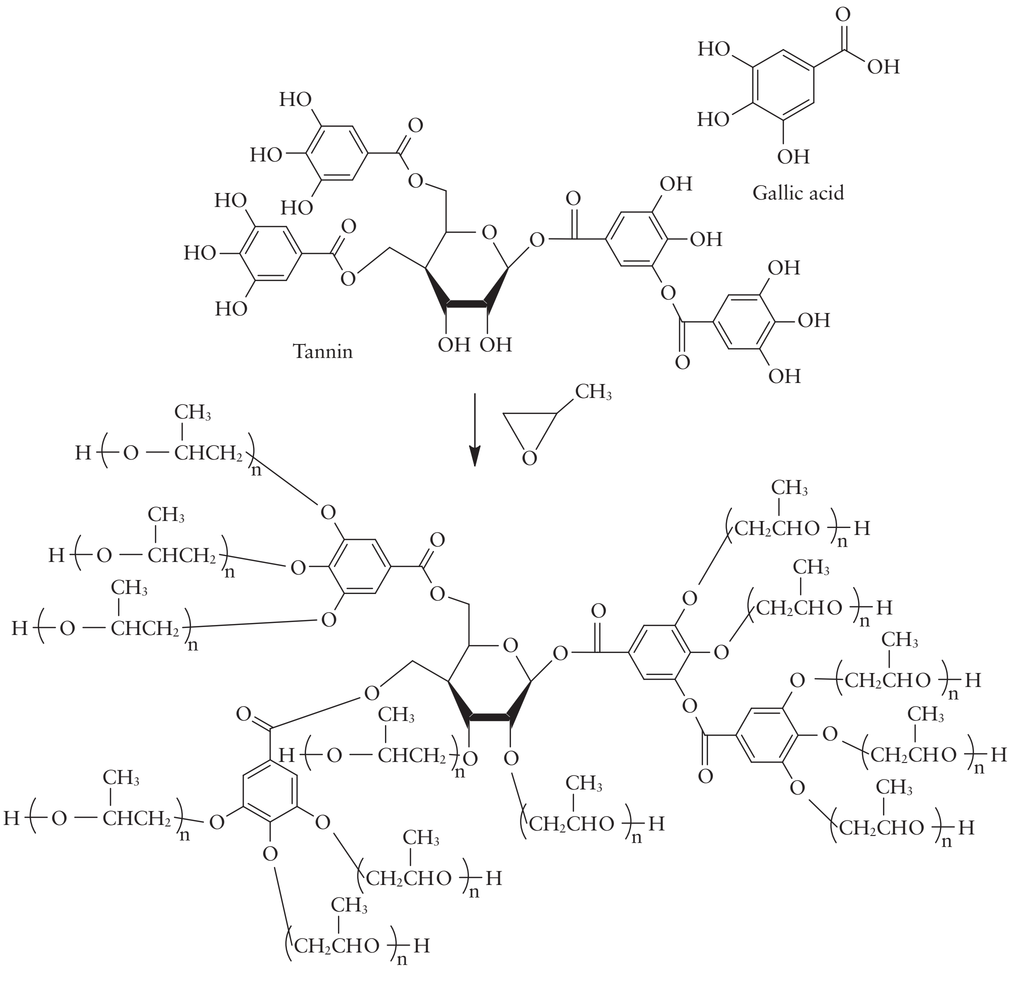


Figure 7.7 Structure of a tannin, gallic acid, and a polyol based on a tannin

Tannnins [79, 80] have been used in leather treatment for centuries. Tannins are divided into two groups: high-MW condensed tannins (90% of world production) and hydrolysable tannins (mixture of low-MW phenols (gallic acid, ellagic acid). **Figure 7.8** shows the general structure of a condensed tannin, a potential bio-based starter for high-functionality polyether polyols.

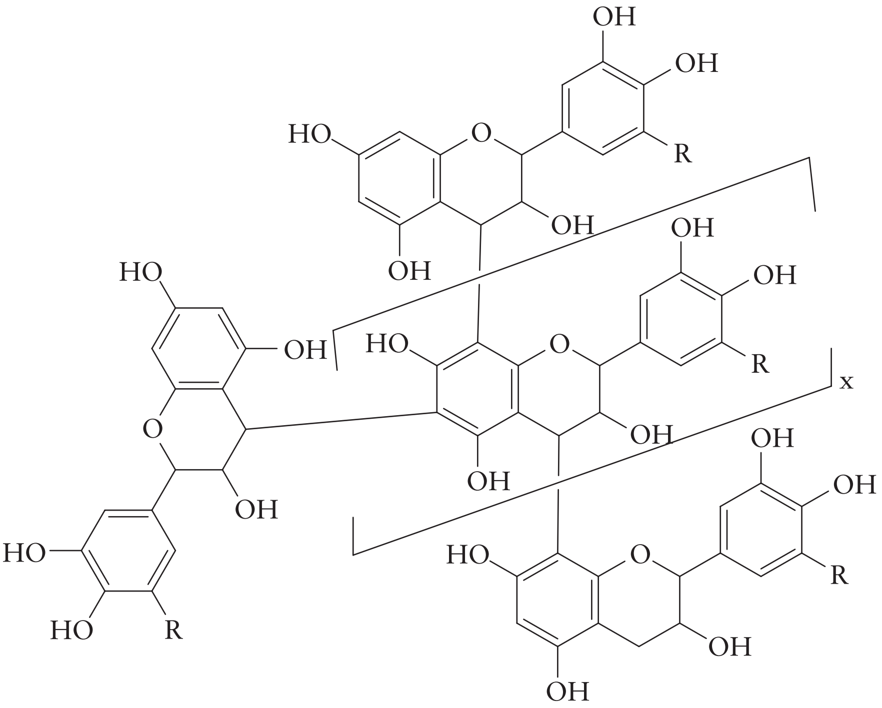


Figure 7.8 General structure of a condensed tannin

7.2.6 Castor Oil

Castor oil is an important natural starter used for the synthesis of hybrid high-MW bio-based-petrochemical polyether polyols. Polyaddition of PO and EO to the hydroxyl groups of castor oil, in the presence of double metal cyanide (DMC) as a catalyst, leads to polyols with long polyether chains, suitable for preparation of flexible PUF (**Volume 2, Section 7.3.4.4**).

7.3 Vegetable Oil Polyols (Oleochemical Polyols)

Vegetable oils and fats are very important resources for polyols. Soybean oil, castor oil, sunflower oil, palm oil, rapeseed oil, olive oil, and linseed oil had a worldwide production of ≈162.94 million tonnes in 2013. [81]. They are used mainly in human food applications (75–80%), and technical applications (biodiesel production, soaps, emulsifiers, cosmetics).

The vegetable oil produced in the largest quantity worldwide is palm oil (Indonesia and Malaysia produce the most palm oil), representing 35% of total oils and fats, the second place being occupied by soybean oil (≈26%) [81]. Palm oil, soybean oil, rapseed oil and sunflower oil are the four major vegetable oils produced worldwide, with (in million tonnes) 59.2, 45, 26.8 and 16.1, respectively, being produced in 2014.

For polyols for PU, the most important oils are highly unsaturated oils where, by using various chemical reactions, double-bonds are transformed into hydroxyl groups. In this category of highly unsaturated vegetable oils are soybean oil, sunflower oil, safflower oil, corn oil, linseed oil, olive oil, tung oil, castor oil, as well as oils of animal origin (e.g., fish oil, krill oil) [1–3, 5, 19, 82–101].

7.3.1 Castor Oil: a Natural Polyol

A unique vegetable oil is castor oil, which is extracted from the seeds of *Ricinus communis*. Castor oil is a triglyceride of ricinoleic acid. Ricinoleic acid has 18 carbon atoms, a '*cis*' double-bond (C9–C10) and a secondary hydroxyl group (C12) [96, 98, 101–104]. The idealised structure of castor oil is shown in **Figure 7.9**.

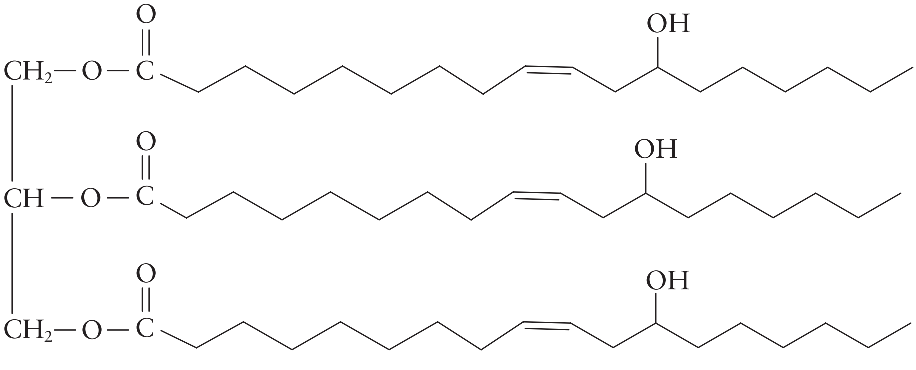


Figure 7.9 Structure of castor oil

Castor oil had a very important role in the early stages of the PU industry, even before synthetic polyols were available. Worldwide production of castor oil in 2012/2013 was ≈1,444,000 tonnes) [105]. The world leader in production of castor oil is India (1,080,000 tonnes [105]. India produces 75% of the world production of castor oil, followed by China (12.5%) and Brazil (5.5%).

Natural castor oil has an idealised structure very close to the one shown in **Figure 7.9**, which has a functionality of ≈2.7 OH groups/mol and OH# of 162–168 mg KOH/g. Castor oil has natural acidity of ≤2 mg KOH/g. Composition of the fatty acids in castor oil is given in **Table 7.1**.

Table 7.1 The fatty acids from castor oil [1, 84, 91, 96–98]

Fatty acid	Percentage 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
Eicosanoic acid	0.3

Castor oil is used in many PU applications: coatings, cast elastomers, thermoplastic elastomers, rigid foams, semi-rigid foams, sealants, adhesives, and flexible foams [84, 91, 96–98, 106, 107].

By reacting castor oil with 0.7 mol of phenylisocyanate or other monofunctional isocyanates, castor oil is transformed into a diol and used in elastomers, coatings and sealants [107].

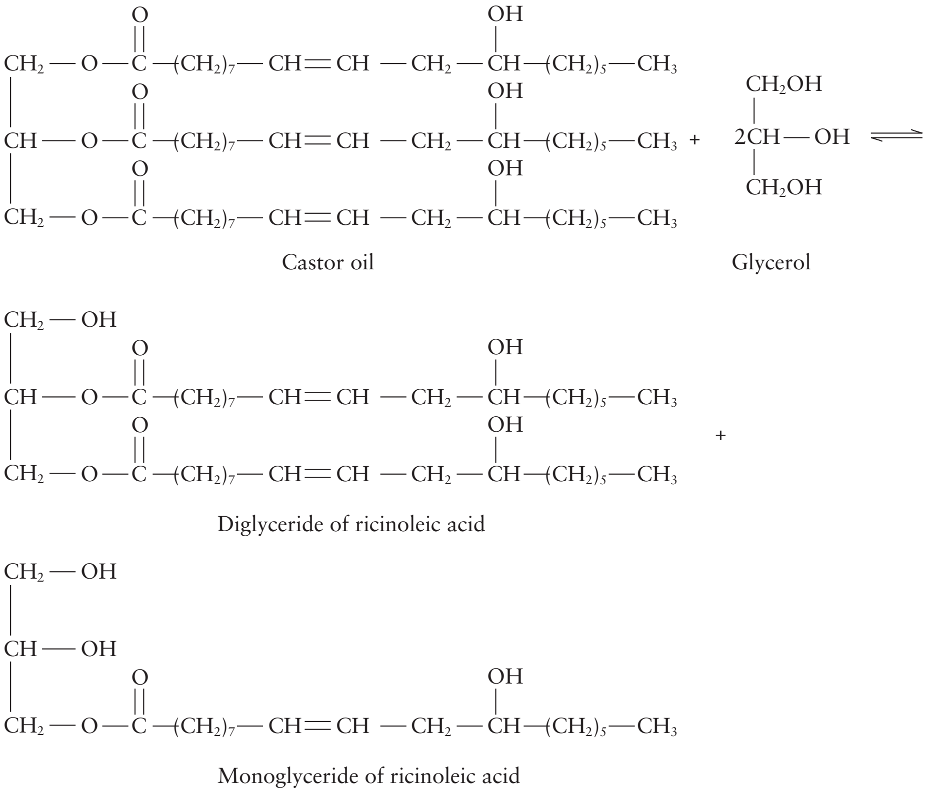
With repsect to direct utilisation in rigid PUF, castor oil has some major disadvantages: low functionality, and low OH# and secondary hydroxyl groups lead to low reactivity. Castor oil, as the sole polyol, leads to semiflexible/semi-rigid PUF.

By mixing castor oil with polyols such as glycerol (e.g., 75% castor oil and 25% glycerol) a higher OH# polyol mixture is obtained, which leads to rigid PUF with good physico-mechanical properties [106].

7.3.1.1 Bio-based Polyols by Chemical Reactions of Castor Oil.

By transesterification of castor oil with polyols with high functionality and high OH# [84], or by amidation with polyamines or alkanolamines [84], new polyols are obtained that are of real use in fabrication of rigid PUF with good physico-mechanical properties. These polyols are made without PO.

Polyols that can be used for transesterification with castor oil are glycerol, trimethylolpropane (TMP), pentaerythritol (PER), sorbitol, and sucrose. 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 1 mol of castor oil with 2 mols of glycerol, a mixture of mono, di and triglycerides of ricinoleic acid, having a much higher OH# than the initial castor oil, of ≈420–430 mg KOH/g (**Reaction 7.3.1**), are obtained.



(7.17)

By using PER instead of glycerol it is possible to obtain the structures shown in **Figure 7.10**, the composition of which depends on the molar ratio of castor oil/PER.

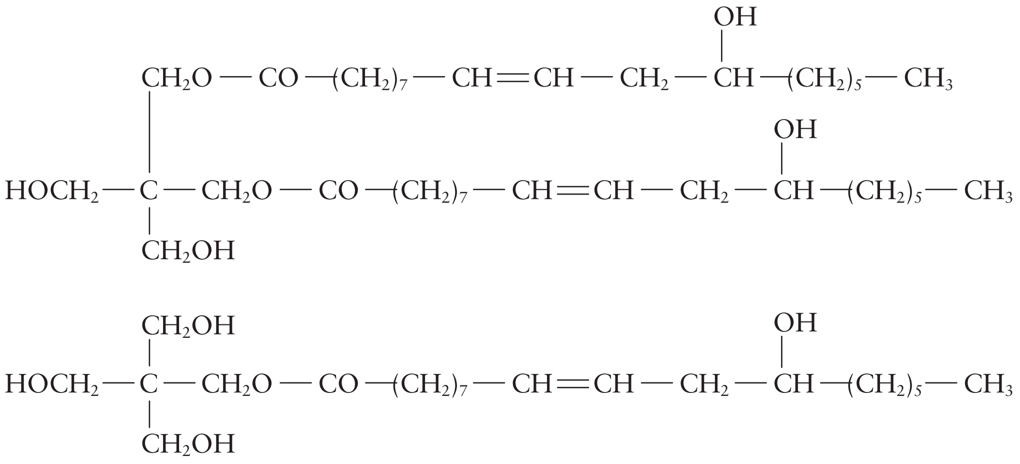
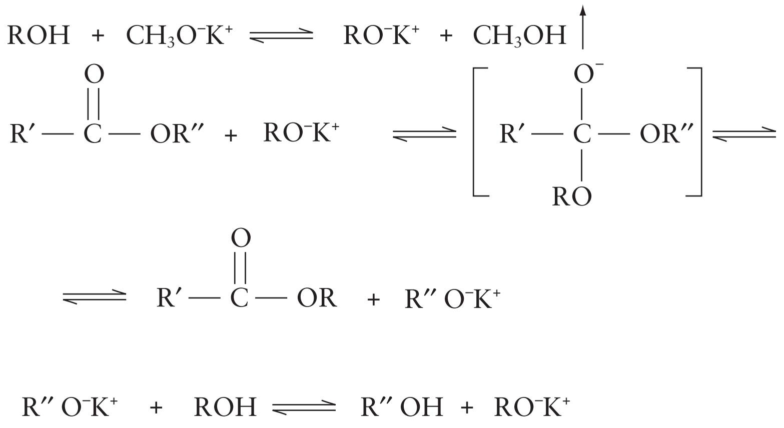


Figure 7.10 Structure of polyols resulting from transesterification of castor oil with PER

Transesterification between castor oil and various polyols is an equilibrium reaction of all the hydroxylgroup species from the reaction system with ester groups. A reaction component is not removed, so the reaction time is the time needed to establish the reaction equilibrium (≈1–2 h at 90–120 °C).

The mechanism of this equilibrium is typical for base-catalysed transesterification reactions: the alcoholate anion of the catalyst (e.g., sodium or potassium methoxide) attacks the carbonyl group of the ester bonds first (**Reaction 7.18**).



$$ROH + CH_3O^-K^+ \rightleftharpoons RO^-K^+ + CH_3OH\uparrow$$

$$R'-\overset{\overset{\displaystyle O}{\|}}{C}-OR'' + RO^-K^+ \rightleftharpoons \left[R'-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle RO}{|}}{C}}-OR''\right] \rightleftharpoons$$

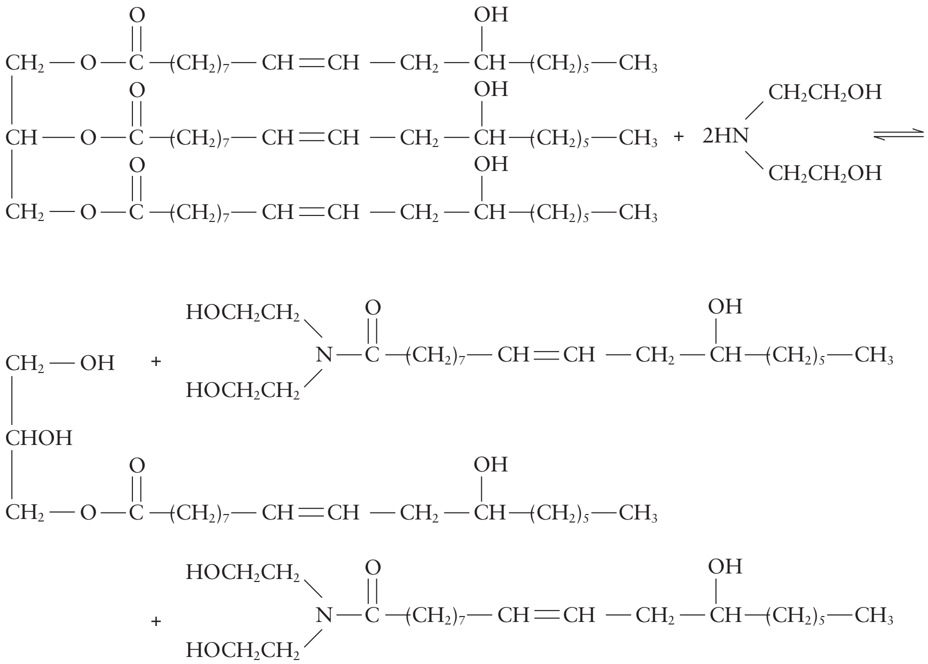
$$\rightleftharpoons R'-\overset{\overset{\displaystyle O}{\|}}{C}-OR + R''O^-K^+$$

$$R''O^-K^+ + ROH \rightleftharpoons R''OH + RO^-K^+ \qquad (7.18)$$

If catalysts Sn(II), Sn(IV) or Ti(IV) compounds are used, a transesterification equilibrium between castor oil and various polyols is established in 2–3 h at 200–220 °C.

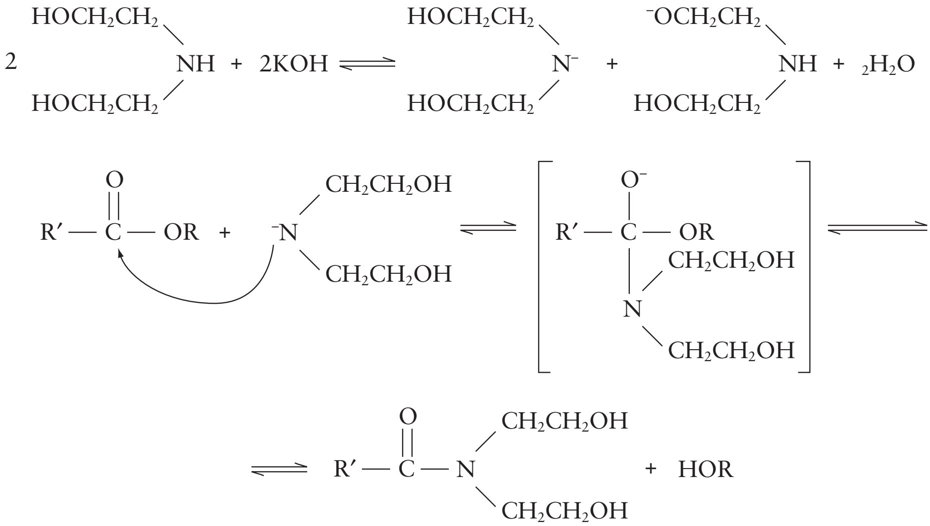
The amidation reaction is catalysed by alkaline catalysts (sodium or potassium methoxides or even NaOH or KOH). Thus, by the reaction of castor oil with diethanolamine (DEOA), in the presence of potassium methoxide at 90–120 °C, a mixture of polyols having ester and diethanolamide structures (**Reaction 7.19**) is obtained in a short reaction time [69].

The OH# of the resulting polyolic mixture is ≈410–420 mg KOH/g and the functionality is 3 OH groups/mol.



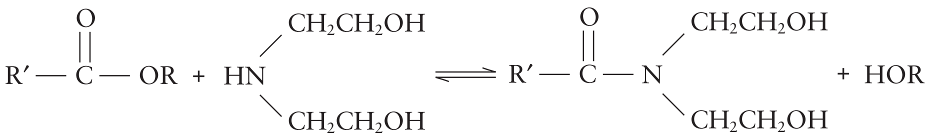
(7.19)

The mechanism of transamidation reaction involves attack of an amide anion to the carbonyl group of ester bonds (**Reaction 7.20**).



(7.20)

The ‘global’ reaction is between an ester and a primary or secondary amine, which gives an amide and an alcohol (**Reaction 7.21**).

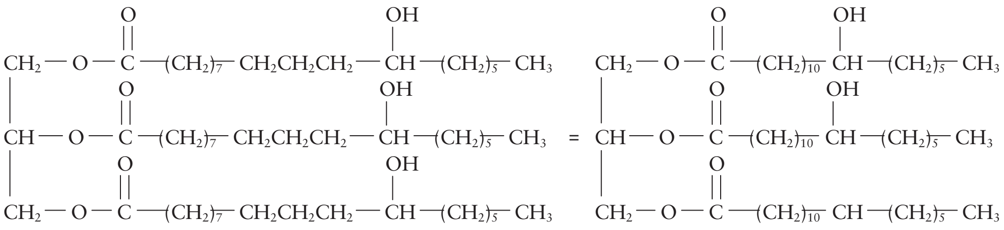


(7.21)

Instead of DEOA it is possible to use other amines such as ethylenediamine (EDA), diethylenetriamine [84], or diisopropanolamine.

The reaction between castor oil and amines can be developed without catalysts, but at longer reaction times (several hours) and higher temperatures (120–130 °C) [69, 108].

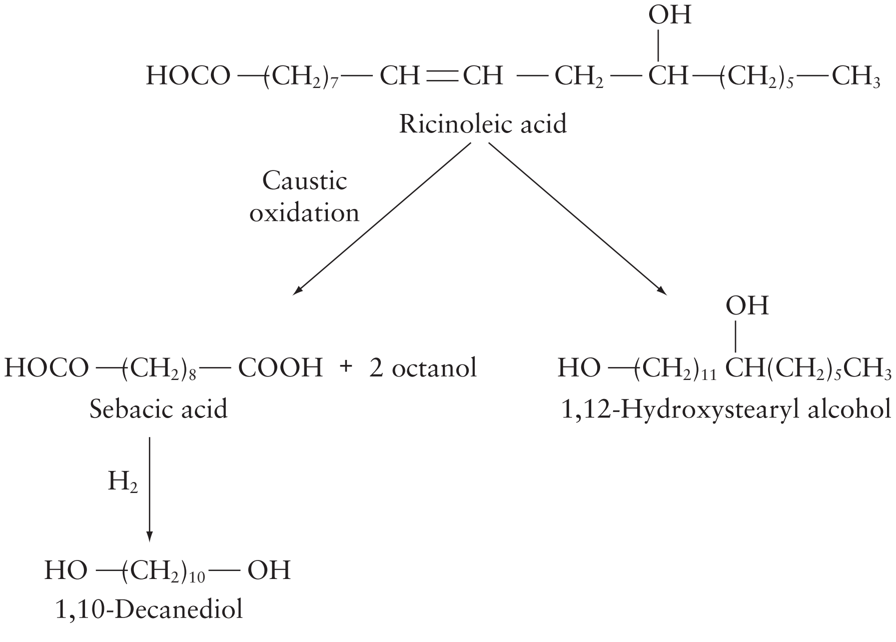
By hydrogenation of castor oil a solid polyol is obtained which is similar to castor oil, but without the double-bonds (**Structure 7.9**) [91, 92].



Structure 7.9 Hydrogenated castor oil

Hydrogenated castor oil is a solid with a mp of 82–86 °C, having a similar OH# to castor oil, of ≈160–162 mg KOH/g. Hydrogenated castor oil is used in coatings and gives adhesion, flexibility, water repellency and chemical resistance [91].

Castor oil and the hydrolysis product (ricinoleic acid) are sources of new valuable products. Thus, by caustic oxidation of ricinoleic acid, sebacic acid and 2-octanol are formed. By hydrogenation of sebacic acid (or even 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 7.22**).



(7.22)

All of 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, which is obtained on an industrial scale 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 hydrophobicity and water repellency on the resulting PU. These polyols have excellent compatibility with the pentanes used as blowing agents, and the resulting PUF have excellent resistance to humid ageing degradation.

Unsaturated vegetable oils (soybean oil, sunflower oil, linseed oil, corn oil, safflower oil, canola oil, palm oil), having multiple double-bonds but no hydroxyl groups, are transformed by various chemical reactions into polyols which, by reaction with isocyanates, are transformed into PU.

Reactions used for transformations of vegetable oils into polyols are divided into those involving: (a) ester bonds; and (b) double-bonds.

For better understanding of the transformation of vegetable oils and fats in polyols, some information about the structure of fatty acids and of natural oils must be presented.

General structure of a natural oil (vegetable oils or fats) is that of a triglyceride, the ester of glycerol and fatty acids (**Figure 7.11**).

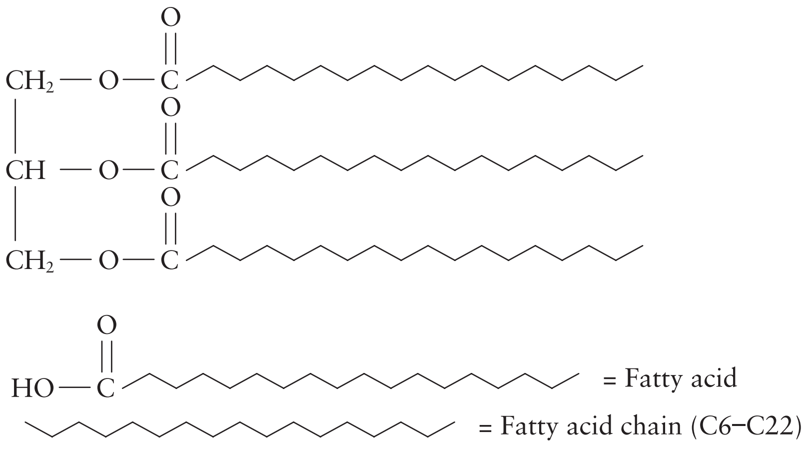
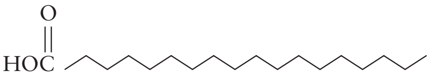
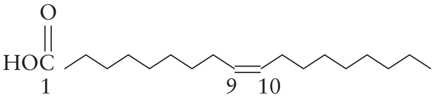
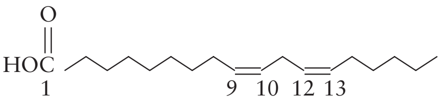
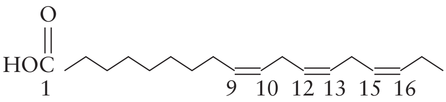
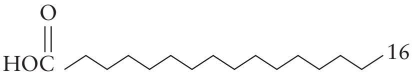
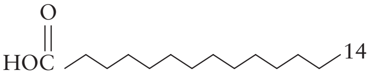
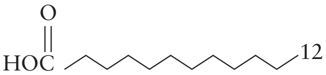
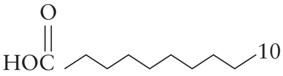
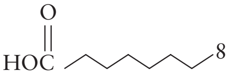
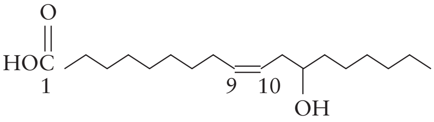


Figure 7.11 General structure of a natural oil

Most important natural fatty acids are presented in **Table 7.2**. Composition of three important vegetable oils is presented in **Tables 7.3–7.5**.

Table 7.2 The structure of most important natural fatty acids

Fatty acid	Carbon atoms	Number of double-bonds	Formula
Stearic acid	C18	0	
Oleic acid	C18:1	1 (C9–C10)	
Linoleic acid	C18:2	2 (C9–C10) (C12–C13)	
Linolenic acid	C18:3	3 (C9–C10) (C12–C13) (C15–C16)	
Palmitic acid	C16	0	
Myristic acid	C14	0	
Lauric acid	C12	0	
Capric acid	C10	0	
Caprylic acid	C8	0	
Ricinoleic acid	C18:1	1 (C9–C10) 1 OH group at C12	

C18:1 – with 1 double-bond;
C18:2 – with 2 double-bonds; and
C18:3 – with 3 double-bonds.

Table 7.3 Composition of soybean oil

Fatty acid	Number of carbon atoms: number of double-bonds	Approximate composition (%)
Linolenic acid	C18:3	9
Linoleic acid	C18:2	51
Oleic acid	C18:1	23.5–25
Stearic acid	C18	2-4
Palmitic acid	C16	11
Soybean oil has approximately 4.6 double-bonds/mol		

Table 7.4 Composition of sunflower oil

Fatty acid	Number of carbon atoms: number of double-bonds	Approximate composition (%)
Linolenic acid	C18:3	0.4
Linoleic acid	C18:2	61.5
Oleic acid	C18:1	26.4
Stearic acid	C18	4.7
Palmitic acid	C16	5.9

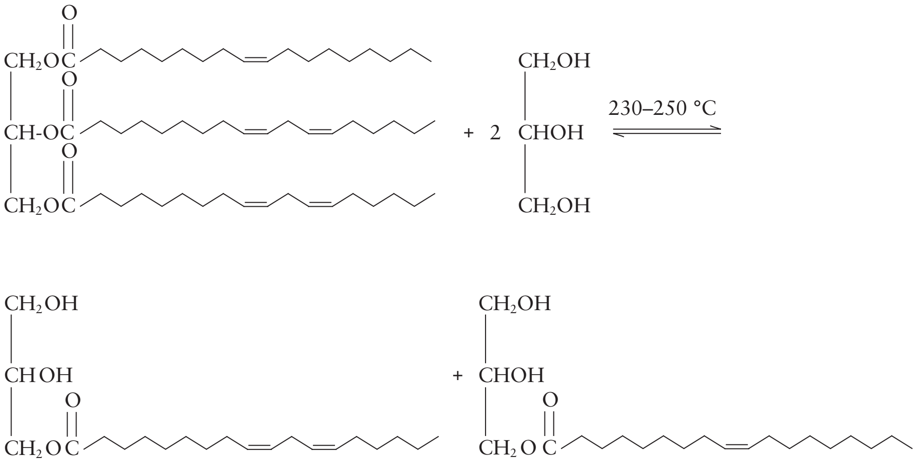
Table 7.5 Composition of linseed oil

Fatty acid	Number of carbon atoms: number of double-bonds	Approximate composition (%)
Linolenic acid	C18:3	52
Linoleic acid	C18:2	16
Oleic acid	C18:1	22
Stearic acid	C18	4
Palmitic acid	C16	6

7.3.2 Synthesis of Vegetable Oil Polyols using Reactions Involving Ester Bonds

Main ways to transform a vegetable oil into a polyol using reactions involving ester groups are transesterification and transamidation reactions.

By transesterification of an unsaturated triglyceride (e.g., soybean oil) with glycerol, a mixture of mono (majority), di and triglycerides of unsaturated fatty acids (**Reaction 7.23**) is obtained [109].

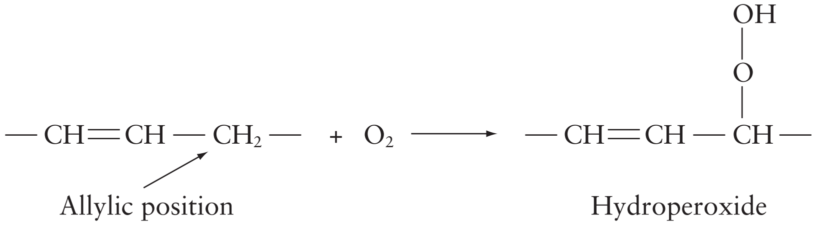


(7.23)

The resulting unsaturated diols [practically monoglycerides of fatty acids (**Reaction 7.23**)] react with diisocyanates [e.g., with toluene diisocyanate (TDI)] at ≈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 transformation of the multiple double-bond in a crosslinked network (**Figure 7.12**). This reaction is used for fabrication of urethane alkyd coatings. Other polyols may be used instead of glycerol: EG, neopentyl glycol, TMP, or PER.

Safflower oil, sunflower oil, linseed oil, cottonseed oil, tung oil, tall oil, fish oil, or castor oil are used as the vegetable oils [109].

The mechanism of curing urethane alkyd resins is based on oxidation (with molecular O_2) at the allylic position (**Reaction 7.24**).



$$-CH{=}CH-CH_2- + O_2 \longrightarrow -CH{=}CH-\overset{\overset{\displaystyle OH}{|}}{\underset{}{\overset{\displaystyle O}{\underset{}{\overset{|}{CH}}}}}-$$

(7.24)

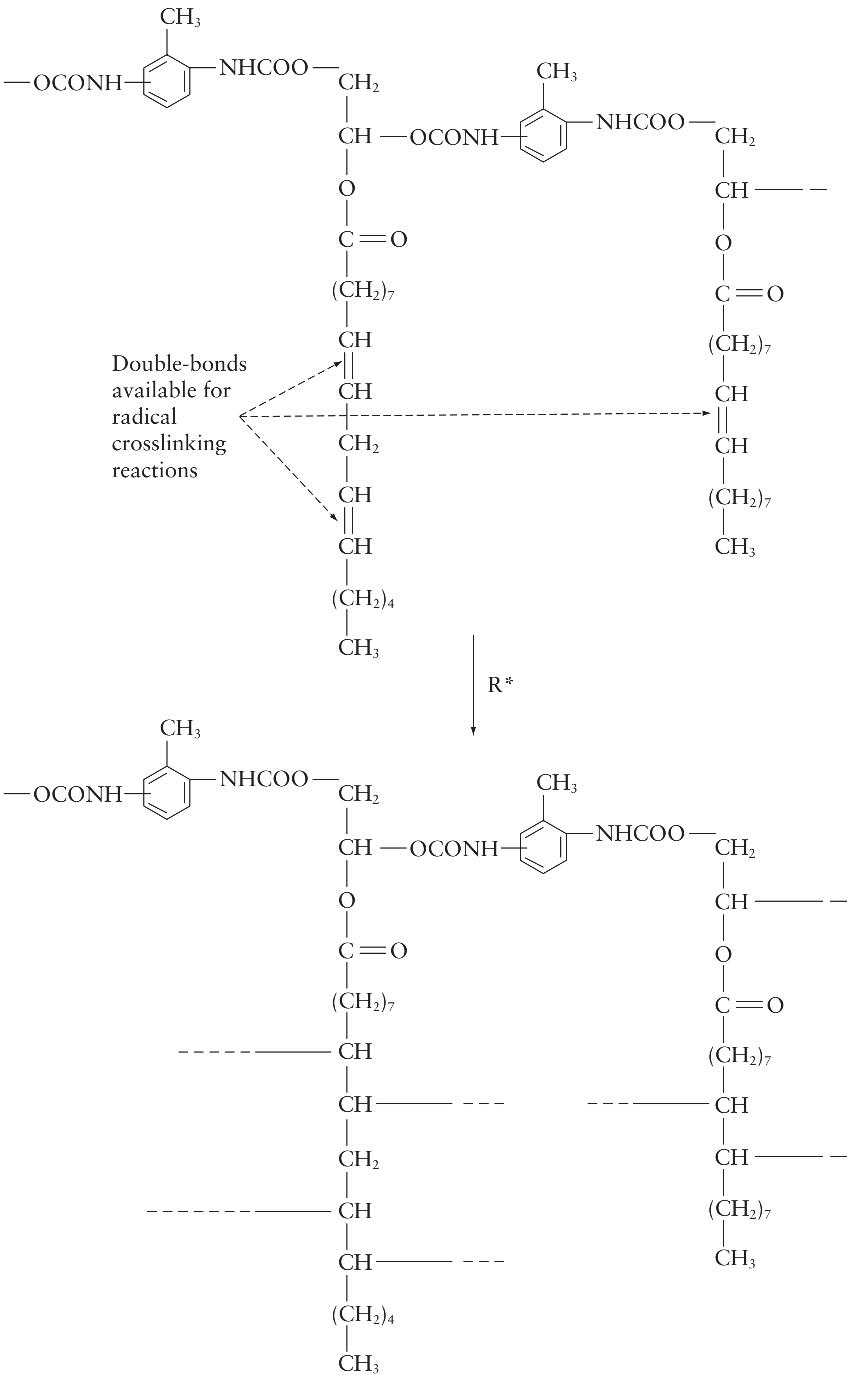
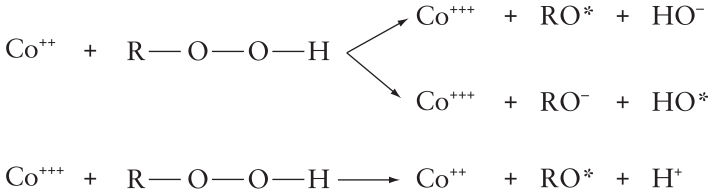


Figure 7.12 Crosslinking of unsaturated PU resulting from the reaction of diglycerides with TDI

The formed hydroperoxide initiates the radical crosslinking reaction. Metal salts are used frequently as catalysts to accelerate crosslinking reactions [e.g., with cobalt(II) compounds (**Reaction 7.25**)].

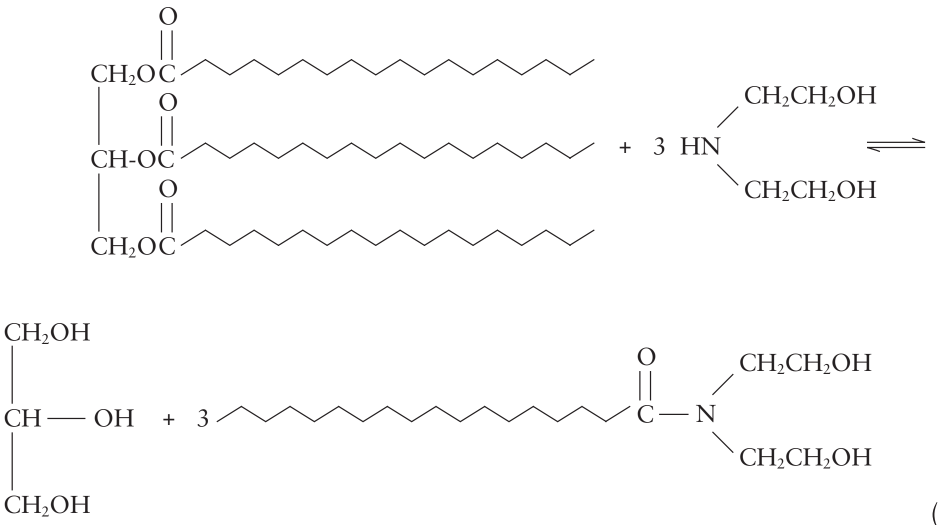


$$Co^{++} + R-O-O-H \rightarrow \begin{cases} Co^{+++} + RO^{*} + HO^{-} \\ Co^{+++} + RO^{-} + HO^{*} \end{cases}$$

$$Co^{+++} + R-O-O-H \longrightarrow Co^{++} + RO^{*} + H^{+} \qquad (7.25)$$

The radicals formed (RO* and HO*) initiate the crosslinking reaction. Soybean oil, sunflower oil and safflower oil give semi-drying urethane alkyds. However, highly unsaturated oils such as linseed oil give drying urethane alkyds.

Transamidation reactions, usually with DEOA, are used frequently to obtain diethanolamides of fatty acids (well-known as non-ionic surfactants [110–116]). Fatty acid diethanolamides are sometimes used together with other polyols to obtain rigid PUF. The fatty acid diethanolamides are bifunctional compounds and improve considerably the compatibility of various polyolic systems with pentanes used as blowing agents for rigid PUF (**Reaction 7.26**).



(7.26)

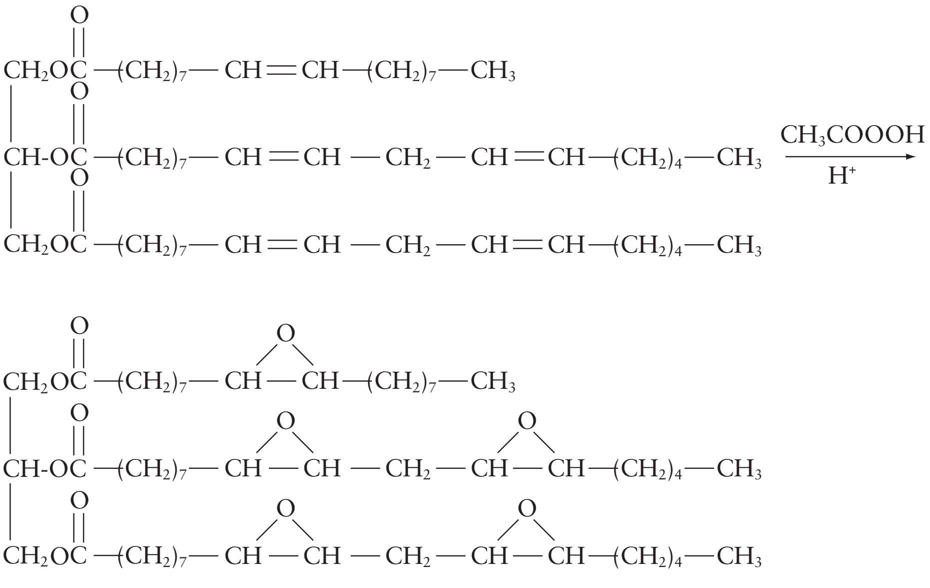
7.3.3 Synthesis of Vegetable oil Polyols by using Reactions Involving Double-Bonds

Transformation of an unsaturated triglyceride in a polyol occurs by generation of hydroxyl groups using various reactions of double-bonds. The most important way to transform an unsaturated vegetable oil into a polyol is epoxydation of double-bonds, followed by various types of opening of the resulting epoxidic rings with hydrogene-active compounds [1–3, 6, 82–87, 99–101].

7.3.3.1 Epoxidation Reactions followed by Ring-opening of Epoxy Groups with Hydrogene-active Compounds

Epoxidised soybean oil or epoxidised sunflower oil are commercial products obtained by epoxidation of vegetable oils with peroxyacetic acid or peroxiformic acid (generated *in situ* by the reaction of hydrogen peroxide with acetic or formic acid) in the presence of an acidic catalyst [82].

Epoxidation of soybean oil results in an oil with ≈4–4.2 epoxy groups/mol (**Reaction 7.27**).



(7.27)

Epoxidised vegetable oils are reacted with various reagents, with epoxidic groups being transformed into hydroxyl groups, resulting in vegetable oil polyols (frequently called 'oleochemical polyols'). The most important reactions for opening of the epoxidic ring to various structures containing hydroxyl groups are:

a) Reaction with acids (organic or inorganic),

b) Hydrolysis,

c) Alcoholysis,

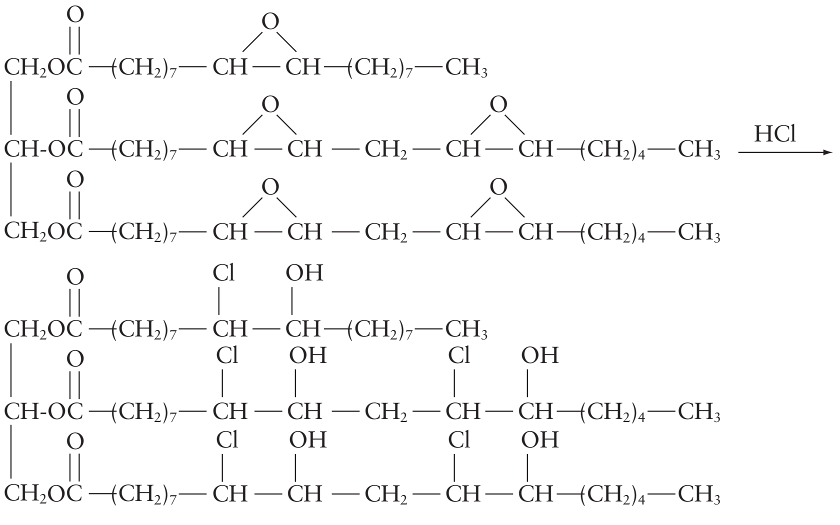
e) Hydrogenolysis, and

f) Aminolysis.

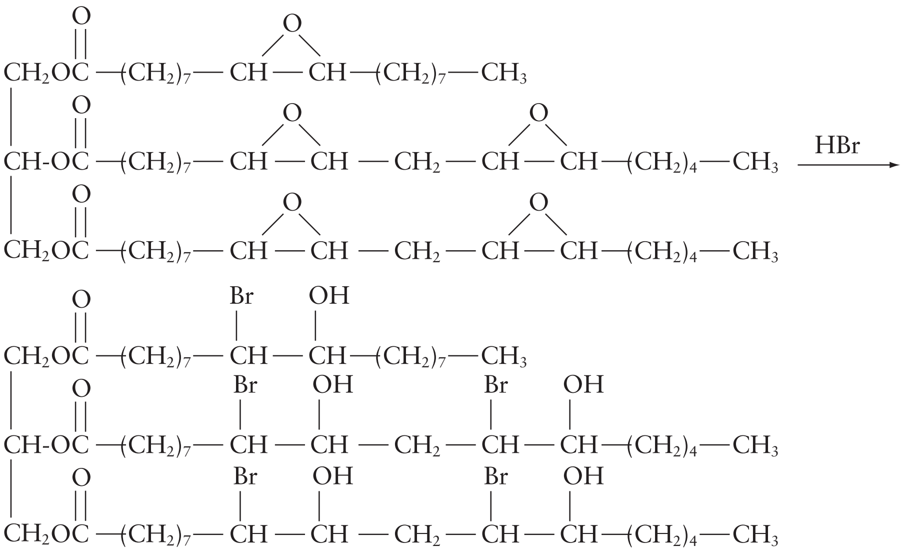
7.3.3.1.1 Reaction with Acids (Organic or Inorganic)

By the reaction of epoxidised vegetable oils with HCl, HBr or various organic acids (R-COOH), the epoxidic ring is opened with formation of polyols having chlorohydrin, bromohydrin or hydroxyalkyl ester structures (**Reactions 7.28–7.30**) [86–89].

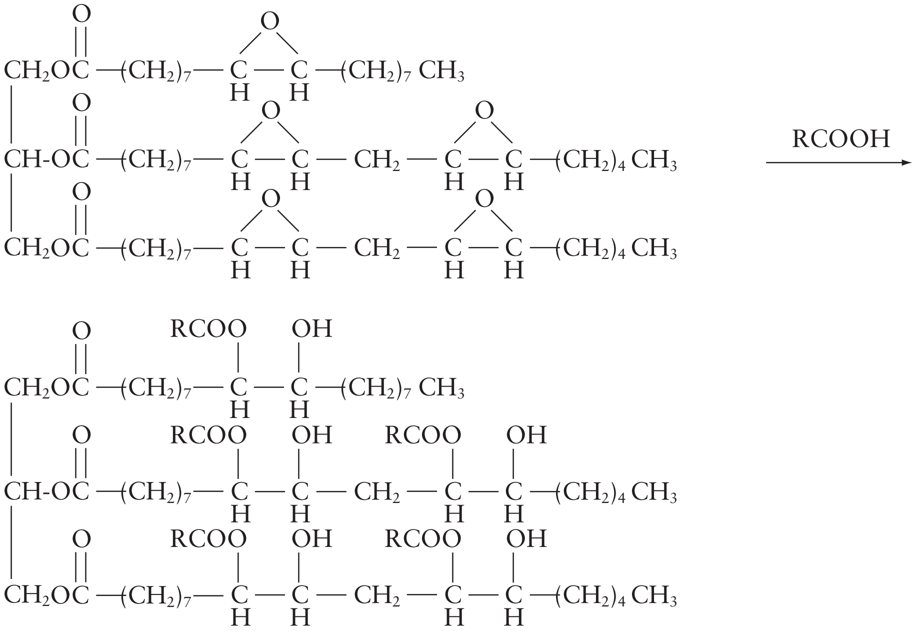
In general, the resulting vegetable oil polyols with inorganic acids are greases, with an OH# ≈180–200 mg KOH/g and a functionality of 3.8–4.1 OH groups/mol. Reactions take place at high yields (94–100%) and moderate temperatures (40–50 °C). The reaction with organic acids, due to low acidity, necessitates higher temperatures and a strong acid as a catalyst (e.g., sulfuric acid or *p*-toluene sulfonic acid). Basic compounds (e.g., benzimidazole) are good catalysts for the reaction of carboxyl groups with epoxy groups [69].



(7.28)



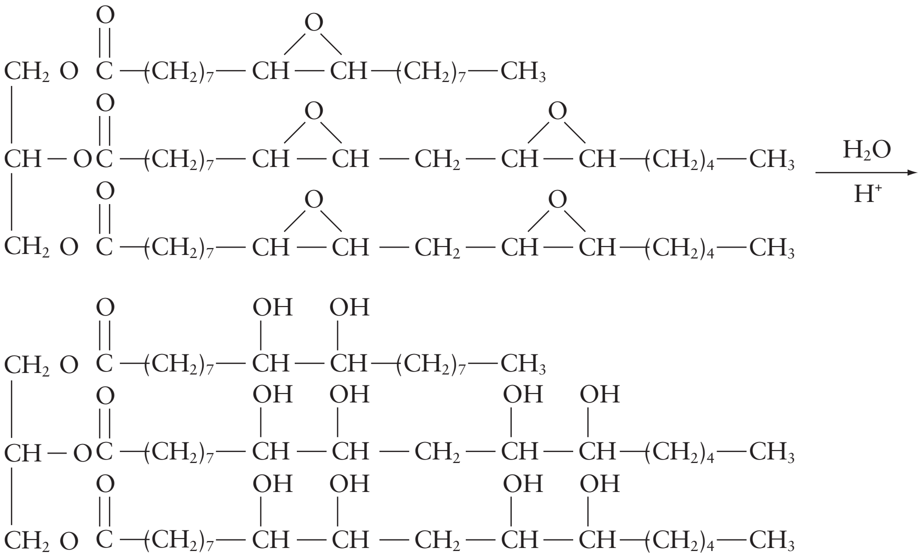
(7.29)



(7.30)

7.3.3.1.2 Hydrolysis [117]

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 OH# with a minimum hydrolysis of the ester bonds [117]. The idealised reaction for epoxidised soybean oil hydrolysis is presented in **Reaction 7.31**.

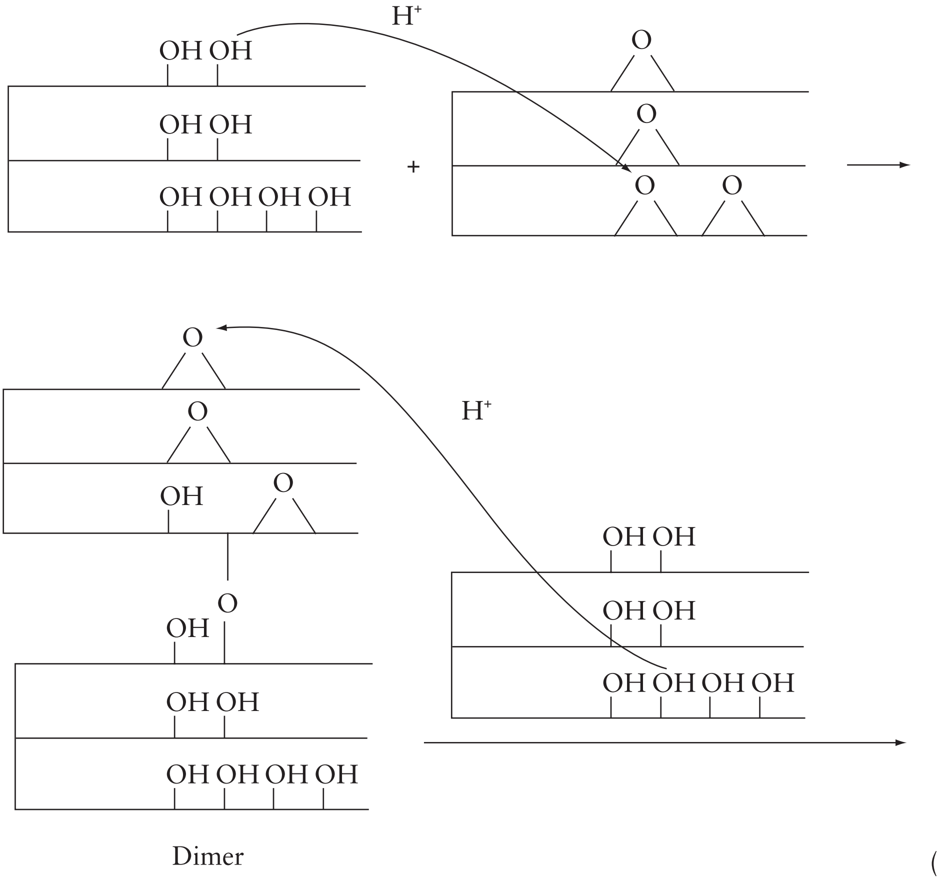


(7.31)

Theoretical OH# of the polyols resulting from epoxidised soybean oil hydrolysis are 440–450 mg KOH/g. If epoxidised soybean oil has 4 epoxy groups/mol, the resulting functionality of polyol obtained by hydrolysis is 8 hydroxyl groups/mol.

Unfortunately, the resulting OH# is much lower, ≈200–250 mg KOH/g, because of the reaction between the hydroxyl groups formed during hydrolysis with the epoxy groups of unreacted epoxidised soybean oil (**Reactions 7.32** and **7.33**). Intermolecular reactions form dimers, trimers and superior oligomers of higher functionality (f >8 OH groups/mol).

Upon intermolecular reactions between epoxy groups and the hydroxyl groups formed, new hydroxyl groups are not generated. However, the MW increases (dimers, trimers, oligomers) and the OH# decreases. In principle, intramolecular reactions of the same type are possible with formation of cyclic compounds and without generation of new hydroxyl groups.


H+
OH OH
OH OH
OH OH OH OH
+
O
O
O
O
H+
O
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O
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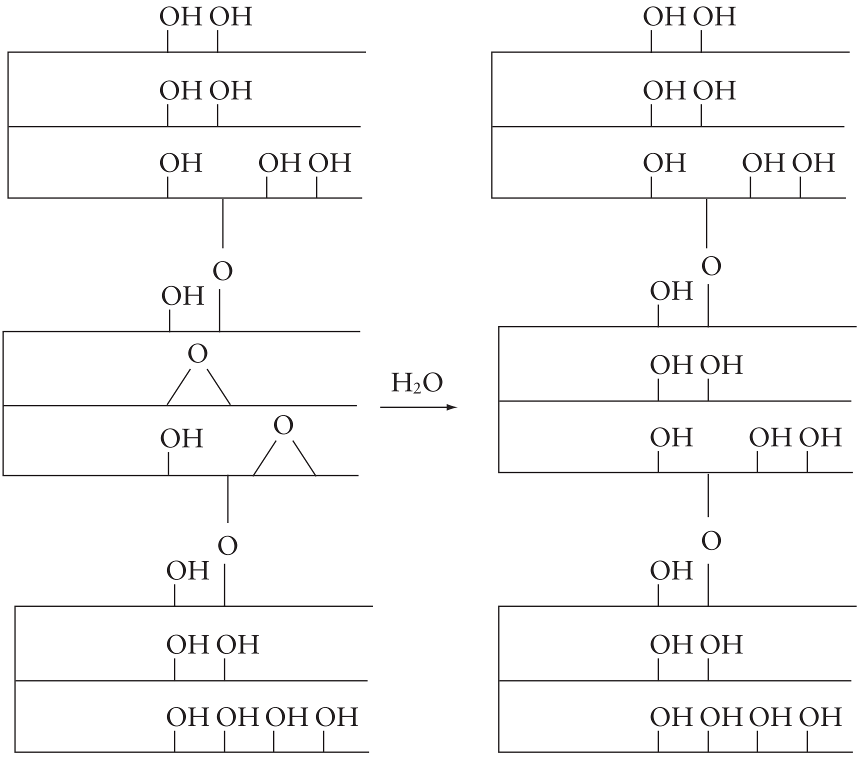
OH
OH OH
OH OH OH OH
OH OH
OH OH
OH OH OH OH
Dimer

(7.32)



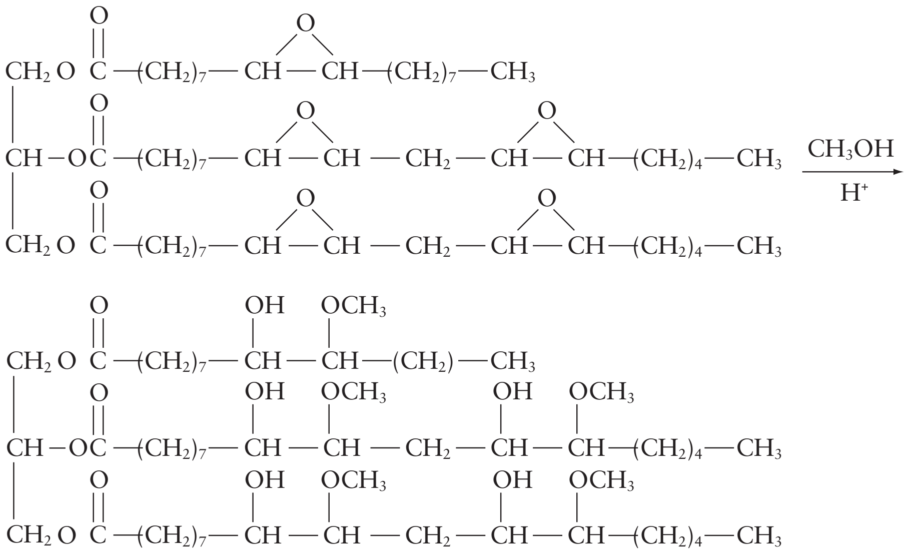
(7.33)

7.3.3.1.3 Alcoholysis [86–89, 99, 100, 118–121]

Liquid polyols are formed by the reaction of alcohols (in excess) with epoxidised vegetable oils in the presence of acids as catalysts (**Reaction 7.34**). For example, by alcoholysis of epoxidised soybean oil with methanol, at the reflux temperature of methanol (bp of methanol is 64.7 °C), in the presence of an acidic catalyst (sulfuric acid, *p*-toluene sulfonic acid, HBF_4 [86, 89, 99, 100], solid acidic clays [118], supported acidic catalysts), liquid soybean oil-based polyols are obtained, with an OH# ≈170–173 mg KOH/g, a functionality of ≈3–4 OH groups/mol and viscosity of ≈4,000–7,000 mPa.s at 25 °C. After neutralisation of the acidic catalyst or by filtration of solid acid catalysts, methanol is distilled under vacuum and recycled back into the process.

Other alcohols instead of methanol can be used: ethanol, 1-propanol and 2-propanol, butanol. Methanol is preferred due to its lower price, lower-MW, and lower bp.

As is the case with hydrolysis of epoxidised vegetable oils, upon alcoholysis the OH# obtained are always lower than expected theoretically. The explanation is the same: intermolecular and intramolecular reactions between the hydroxyl groups formed and 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 OH# and higher functionality are formed.

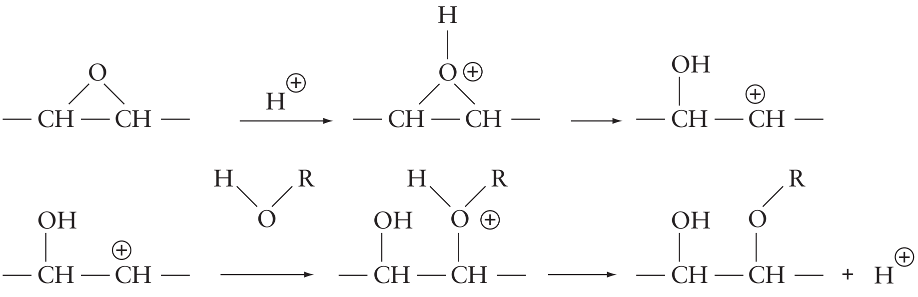


(7.34)

It is possible to increase the OH# 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 OH# of 200–210 mg KOH/g and a viscosity of 10,000–16,000 mPa.s at 25 °C [118, 120].

All reactions of epoxidic groups with alcohols or water (in excess) are S_N1 reactions (**Reaction 7.35**). These reactions have as intermediates organic cations such as oxonium ions and carbocations.



(7.35)

7.3.3.1.3.1 Bio-based Polyols from Palm Oil [122–127]

Palm oil has lower unsaturation levels [iodine value (IV) = 50–60 mgI_2/100 g] than soybean oil (125–132 mgI_2/100 g) or linseed oil (170–180 mgI_2/100 g), but can be transformed into polyols for flexible PU and foams [122–124]. Interestingly, polyols were developed in Malaysia, after derivation from palm oil for production of rigid PUF [122–124]. Composition of three representative oils from palm oil is presented in **Table 7.6** and is:

a) Palm oil (semi-solid oil derived from mesocarp of palm fruit).

b) Palm olein (the liquid fraction isolated by fractionation of palm oil after crystallisation at a controlled temperature).

c) Palm stearin (solid fraction after fractionation of palm oil by crystallisation).

Table 7.6 Fatty acid composition of palm oil, palm olein and palm stearin [125]

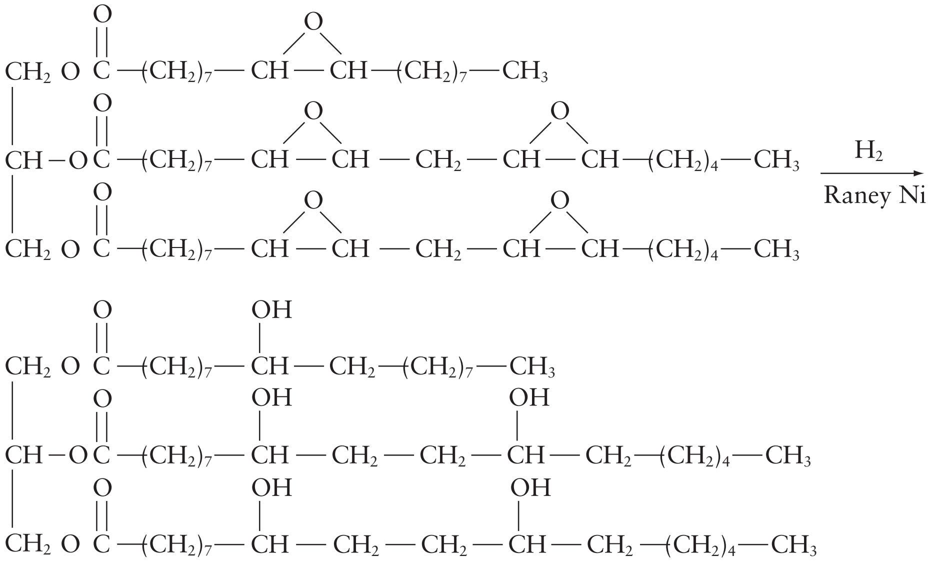
Fatty acid	Palm oil (wt%)	Palm olein (wt%)	Palm stearin (wt%)
C12:0	<1	<1	<1
C14:0	<2	<2	<2
C16:0	40–50	35–45	45–75
C16:1	<1	<1	<1
C18:0	3-6	3–5	4–6
C18:1	35–45	40–47	10–40
C18:2	8–12	10–15	2–10
C18:3	<1	<1	<1
C20:0	<1	<1	<1
IV	50–65	55–62	20–50

For preparation of palm oil polyols, a similar procedure described for that of soybean oil is used. In the first step, epoxidation of palm oil is carried out [epoxy O_2 content of 2.5–3.6%), followed by ring-opening of formed epoxy groups with alcohols or polyols with an acidic catalyst (Lewis acids (e.g., BF_3) or Brönsted acids (e.g., HBF_4)]. Unsaturation of palm oil is lower than that of soybean oil, so polyols such as glycerol [122–124] are used for ring-opening, but methanol can also be used successfully [125, 126]. Polyols of OH# of 170–200 mg KOH/g are obtained if glycerol is used, and 45–65 mg KOH/g if methanol is used [125, 126].

Flexible PUF prepared using 70–80% standard polyether polyol of MW = 3,000 and 20–30% palm oil polyol are excellent, and have properties similar to those obtained with petrochemical polyether polyol as the sole polyol. By increasing the concentration of palm oil polyol, the properties of flexible foams deteriorate. By using the reaction of glycerol with an epoxy group and with ester groups of epoxidised palm oil, polyols of high OH# suitable for rigid PUF are obtained [127]. Palm kernel oil is different from palm oil. It is a semi-solid oil having a high content of saturated fatty acids, predominantly lauric acid (C12: 0–48%), myristic acid (C14: 0–16%) and palmitic acid (C16: 0–8.4%), and a low content of unsaturated fatty acids (oleic, linoleic) of only 17–18%. In spite of low unsaturation, palm kernel oil has been used for preparation of polyols by a reaction at triglyceride ester bonds (e.g., amidation with DEOA) [128].

7.3.3.1.4 Hydrogenolysis [86, 87]

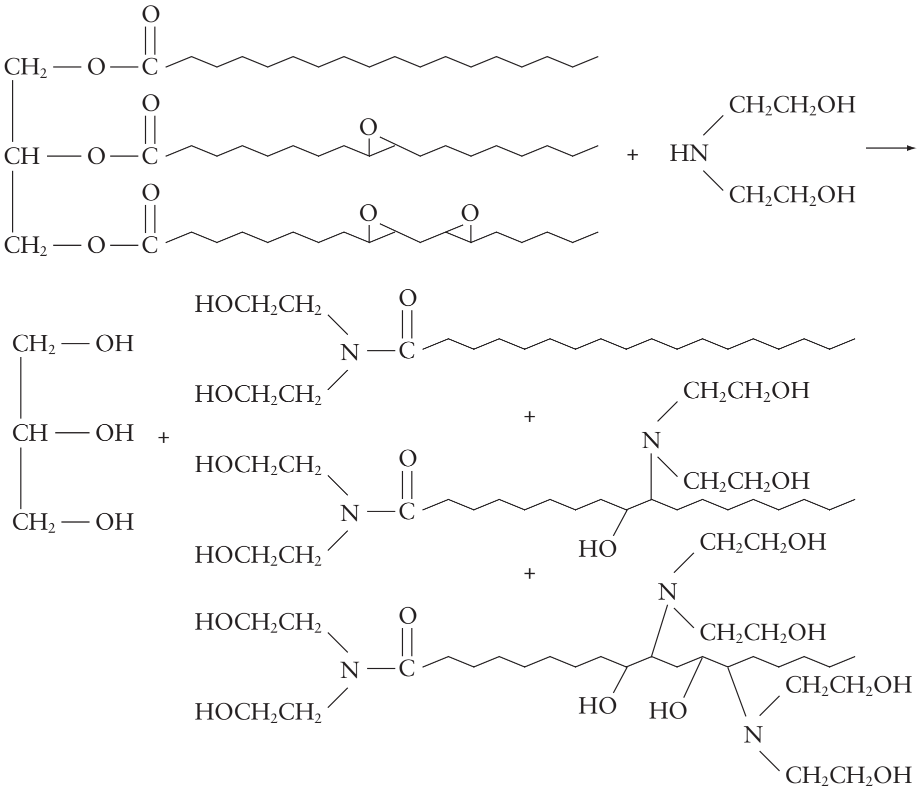
By hydrogenation of epoxidised vegetable oils with gaseous hydrogen under pressure (≈4.1–6.9 MPa), in the presence of a hydrogenation catalyst (e.g., Raney-nickel), solid polyols are obtained. They have the consistency of waxes, having a low mp of ≈25–50 °C, an OH# of ≈200–215 mg KOH/g, and functionality of ≈3.5 OH groups/mol [86, 87]. Hydrogenated epoxidised soybean oil has a melt viscosity at ≈38 °C of ≈2,000 mPa.s. One epoxidic ring generates one hydroxyl group (**Reaction 7.36**).



(7.36)

7.3.3.1.5 Aminolysis [129]

Upon reaction of epoxidised oils with amines, especially with hydroxyalkyl secondary amines (DEOA, methyl ethanolamine), high-OH# polyols with amido-amine structures are formed. Secondary amines react with ester bonds to generate amides and with epoxy groups to generate tertiary amines. Upon reaction of epoxidised soybean oil with a diethanol amine, a highly functional liquid polyol is obtained which has higher reactivity due to a tertiary nitrogen in its structure (**Reaction 7.37**).

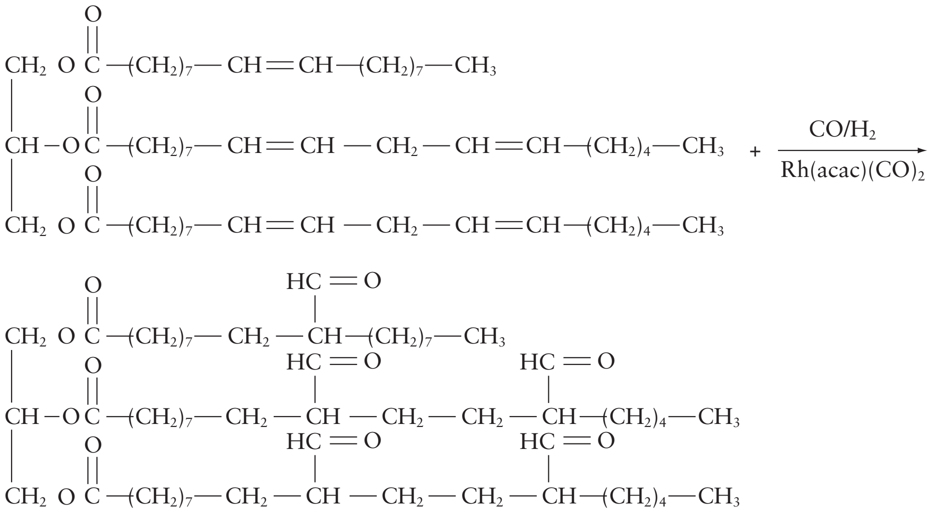


(7.37)

Reaction with DEOA is carried out in the presence of a catalyst (e.g., zinc chloride) at ≈170 °C [129]. Methyl ethanolamine is much more reactive than DEOA, and reacts with epoxidised soybean oil in the absence of catalysts at 120 °C [129]. Secondary amines lead to liquid polyols, and primary amines (monoethanolamine) lead to solid polyols [69]. Due to their high reactivity, these polyols obtained by reaction of epoxidised oils with secondary alkanolamines are suitable for 'spray' rigid PUF.

7.3.3.2 Hydroformylation Reactions [130, 131]

A very efficient method to transform directly an unsaturated triglyceride in polyols is to develop a hydroformylation reaction with a 'sin gas' (mixture of hydrogen/carbon monoxide), at 70–130 °C, in the presence of rhodium or cobalt catalysts [130, 131], at higher pressures (4,000–11,000 kPa). In the first step, the double-bonds are transformed in aldehyde groups, in high yield (**Reaction 7.38**).



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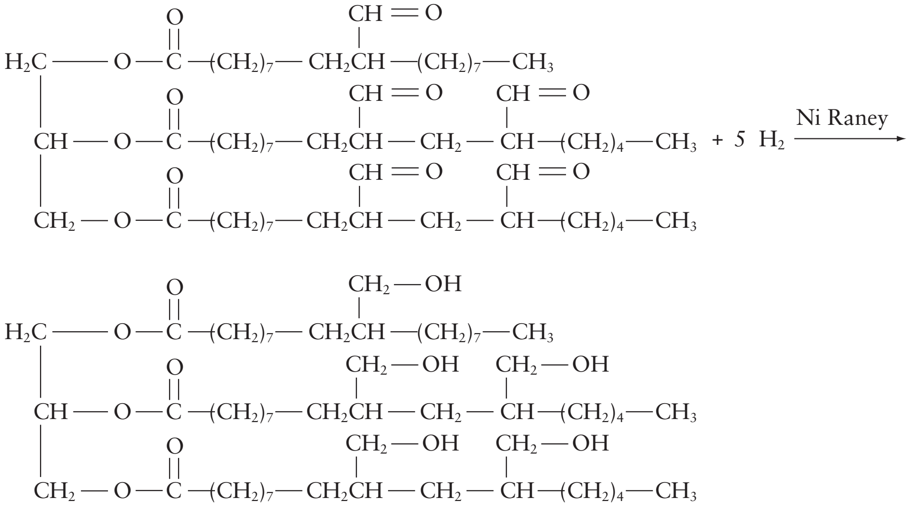
In the second step, the resulting aldehyde groups are hydrogenated to a polyol having 100% primary hydroxyl groups, very reactive in PU chemistry, with an OH# of 200–240 mg KOH/g [86, 87] (**Reaction 7.39**).



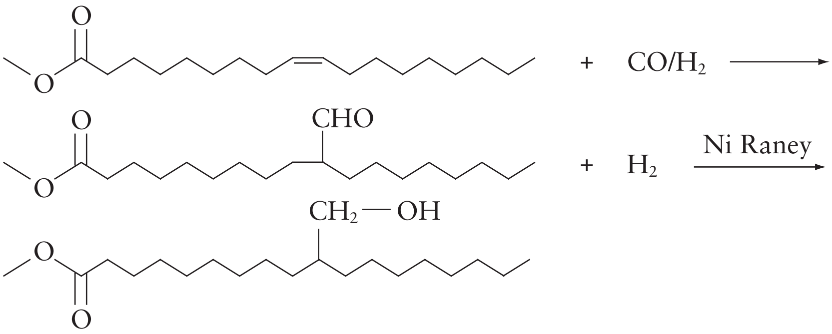
(7.39)

The resulting polyol, alone or in combination with classic rigid polyols, polyethers or polyesters, has good potential for fabrication of rigid PUF with excellent physical–mechanical and thermal insulation properties.

7.3.3.2.1 Bio-based Polyols for Flexible Polyurethane Foams by Hydroformylation Reactions [132–135]

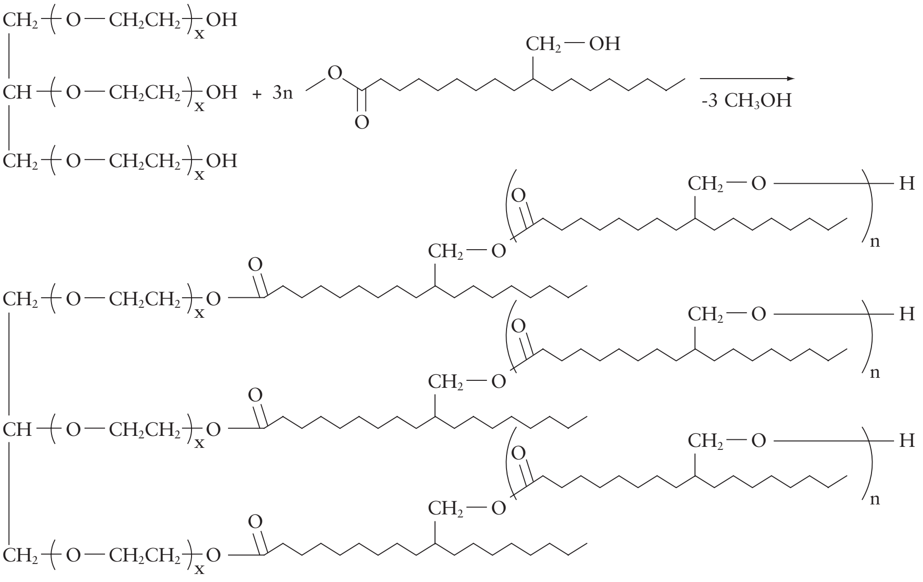
Dow Chemicals (MI, USA) have developed an important group of high-MW bio-based polyols with high renewable content that do not compromise PU performance (adhesives, sealants, coatings, foams).

The chemical pathway from vegetable oil to final polyol is based on several reactions. In the first step, triglyceride (e.g., soybean oil) is reacted with methanol in basic catalysis to fatty acid methyl esters and glycerol. In the second step, fatty acid methyl esters are hydroformylated selectively to a fatty acid aldehyde which, by hydrogenation, leads to a hydroxymethyl fatty acid methyl ester (**Reaction 7.40**). It has been found that the conditions to obtain hydroformylated methyl esters selectively require only one hydroxymethyl group per fatty acid chain and, in the hydrogenation step, the residual unreacted double-bonds are transformed into saturated single-bonds [132, 133].



(7.40)

The final polyol is obtained by polycondensation of hydroxymethyl fatty acid methyl esters initiated by a triol based on glycerol and EO of MW = 625 in the presence of 1,000 ppm stannous octoate as the catalyst (**Reaction 7.41**). A representative polyol with the structure of a polyether ester has 3.5–3.7 OH groups/mol, number average molecular weight (M_n) = 2,600–2,800, weight average molecular weight (Mw) = 3,900–4,400, polydispersity of 1.4–1.65, and an average viscosity of 3,500–3,900 mPa.s at 25 °C. Polyols prepared by this innovative technology are very reactive due to 100% primary hydroxyl content [132–135].



(7.41)

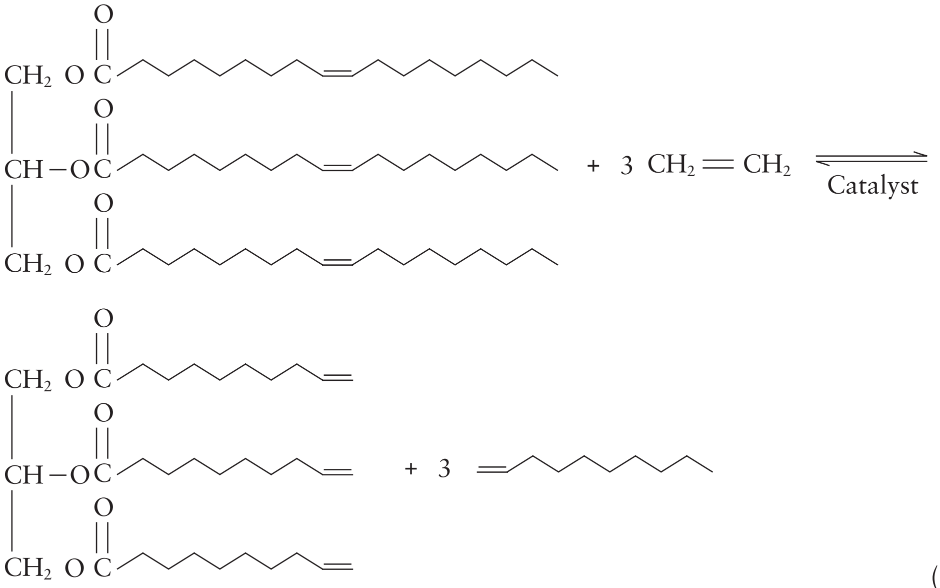
High-molecular-weight polyester diols are formed by polycondensation of hydroxymethylated methyl soyate using a diol as starter, and are suitable for coatings, adhesive, binders and PU elastomers.

Triols with the structure shown in **Reaction 7.41** are suitable for preparation of flexible PUF for furniture, car seating, viscoelastic foams, headlights and fascia for cars, and carpet backing. Properties of flexible PUF based on these polyols are excellent [132–135].

This remarkable technology created and engineered by Dow is one of the most important developments in bio-based polyols for elastic PU, especially for PUF.

7.3.3.3 Metathesis Reactions [136–138]

Metathesis of vegetable oils with ethylene is a very interesting way to obtain new unsaturated structures for transformation into new polyols *via* the epoxidation–alcoholysis route. Trioleine has been used as a model compound (triester of glycerol with oleic acid), with the metathesis reaction with ethylene being catalysed by a special ruthenium catalyst [136]. The resulting triglyceride, with terminal double-bonds, after removal of the 1-decene that is formed, is transformed into polyols by epoxidation, followed by alcoholysis with methanol (**Reactions 7.42** and **7.43**).



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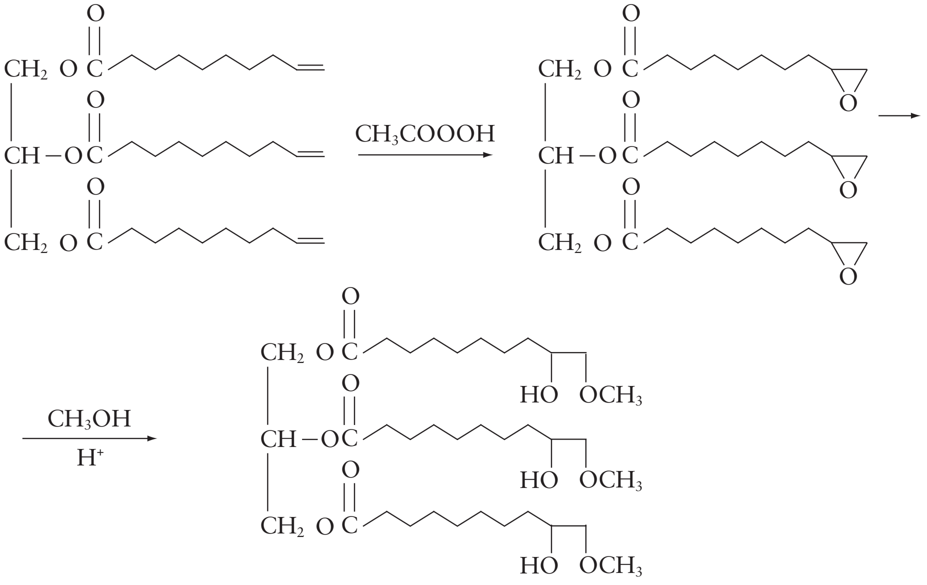
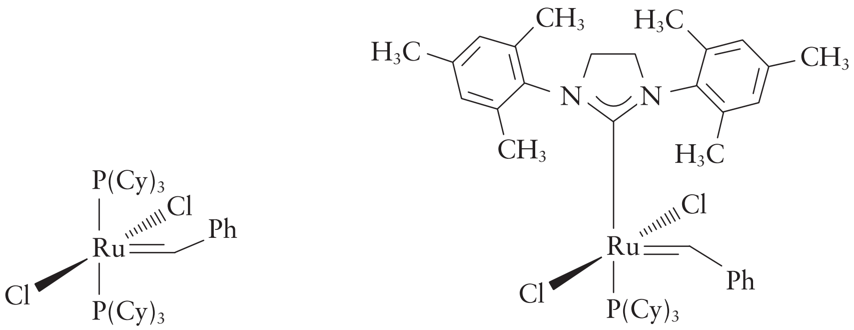


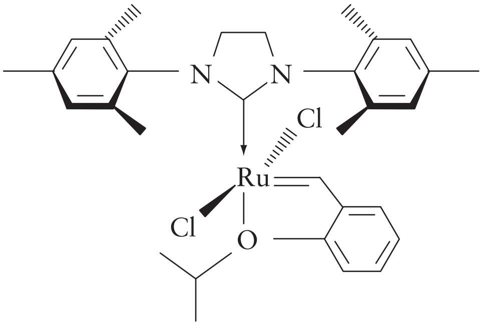
(7.43)

Resulting polyols have higher OH# than the product of methanolysis of epoxidised soybean oil, of ≈230–235 mg KOH/g, an equivalent weight (EW) of ≈240 Da and a MW of ≈756 Da (vapour-pressure osmometry), viscosity of ≈1,300 mPa.s at 25 °C, and functionality of 3.1–3.2 OH groups/mol [136]. The resulting polyol is similar to the product derived from epoxidised soybean oil [82], and contains dimers and trimers and, as an immediate consequence, the functionality is higher than 3 (f = 3.1–3.2 OH groups/mol) [136]. The best catalysts for metathesis of olefins (including metathesis of unsaturated vegetable oils) are Grubbs' catalysts, which are complex catalysts based on ruthenium (**Structure 7.10** of first-, second- and third-generation Grubbs' catalysts) [137].



1st Generation

2nd Generation



3rd Generation

Structure 7.10 First-, second- and third-generation Grubbs' catalysts

A very interesting bifunctional bio-based monomer for polycondensation reactions (dimethyl 9-octadecene-1,18-oate) is obtained by self-metathesis of methyl oleate [138] (**Figure 7.13**). This is a potential monomer for the synthesis of bio-based polyester polyols for PU (elastomers, adhesives).

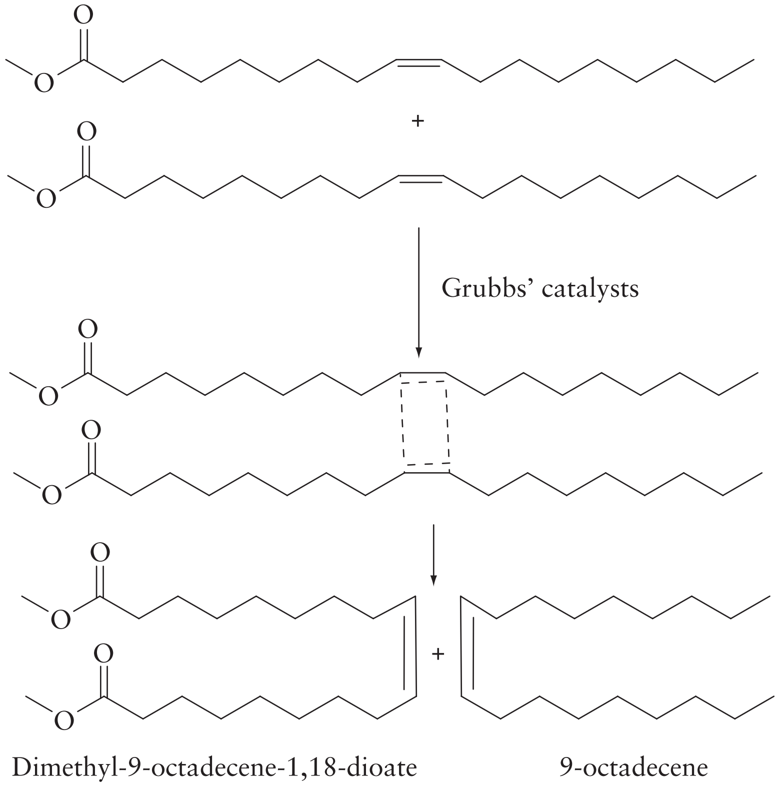


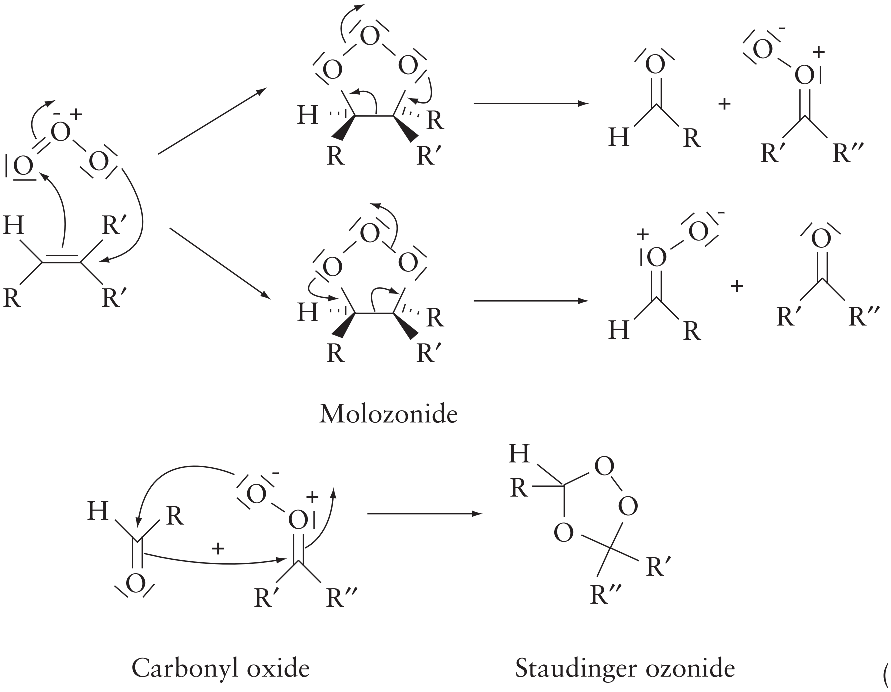
Figure 7.13 Self-metathesis reaction of methyl oleate

7.3.3.4 Polyols by Ozonolysis [139–149]

O_3 is an allotrope form of O_2.

Reaction of O_3 with the double-bonds of natural unsaturated compounds ('ozonolysis') is an old reaction. As a result of the products from ozonolysis, the exact positions and structures of double-bonds were established in fatty acids from vegetable oils and in natural rubber. Reaction of O_3 with the double-bonds of vegetable oils is rapid, and carried out in high yield at low temperatures of –78 to 20 °C in the absence/presence of solvents (e.g., methylene chloride, ethyl acetate).

The mechanism of ozonolysis was suggested by Criegee [139] (**Reaction 7.44**). The first step is a 1,3-dipolar cycloaddition of O_3 to the double-bonds with formation of cyclic molozonide (or 1,2,3-trioxolane). The molozonide decomposes to a carbonyl oxide and a carbonyl compound. Carbonyl oxide (a compound similar to O_3) undergoes 1,3-dipolar cycloaddition to the carbonyl compound with formation of a secondary ozonide (Staudinger ozonide or 1,2,4-trioxolanes). In the presence of reducing agents such as dimethyl thioether, ozonide decomposes into two carbonyl compounds which, by hydrogenation or reaction with sodium borohydride, lead to two alcohols (**Reaction 7.45**).



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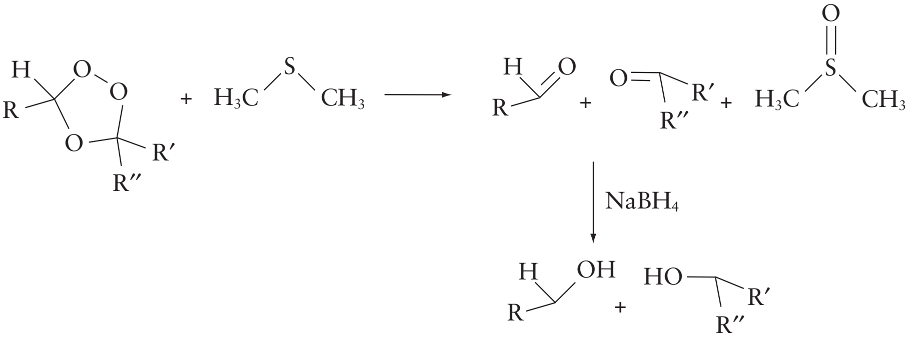
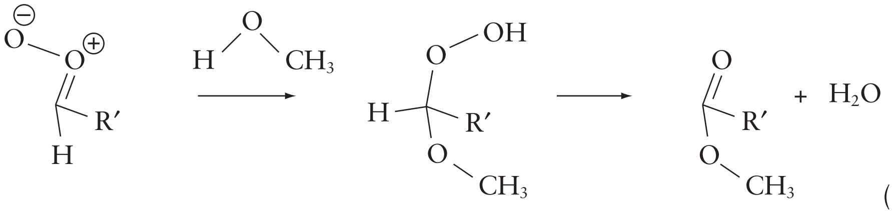


(7.45)

If ozonolysis is carried out in the presence of an alcohol, the carbonyl oxide reacts with the alcohol to form hydroperoxy hemiacetals which, in the presence of catalysts (basic or acidic) are thermally decomposed with ester formation (**Reaction 7.46**).



(7.46)

If a glycol or a polyol is used instead of methanol, new polyols with the structure of hydroxyalkyl esters are obtained. By ozonolysis of a vegetable oil in the presence of EG or glycerol with basic [140] or acidic catalysts [141], valuable bio-based polyols (**Figure 7.14**) are obtained, which are useful for PU preparation (foams, coatings, adhesives, sealants). In the presence of catalysts, simultaneously with ozonolysis of double-bonds, transesterification of triglyceride ester bonds with the polyols used (EG or glycerol) is carried out, leading to formation of partial fatty acid esters.

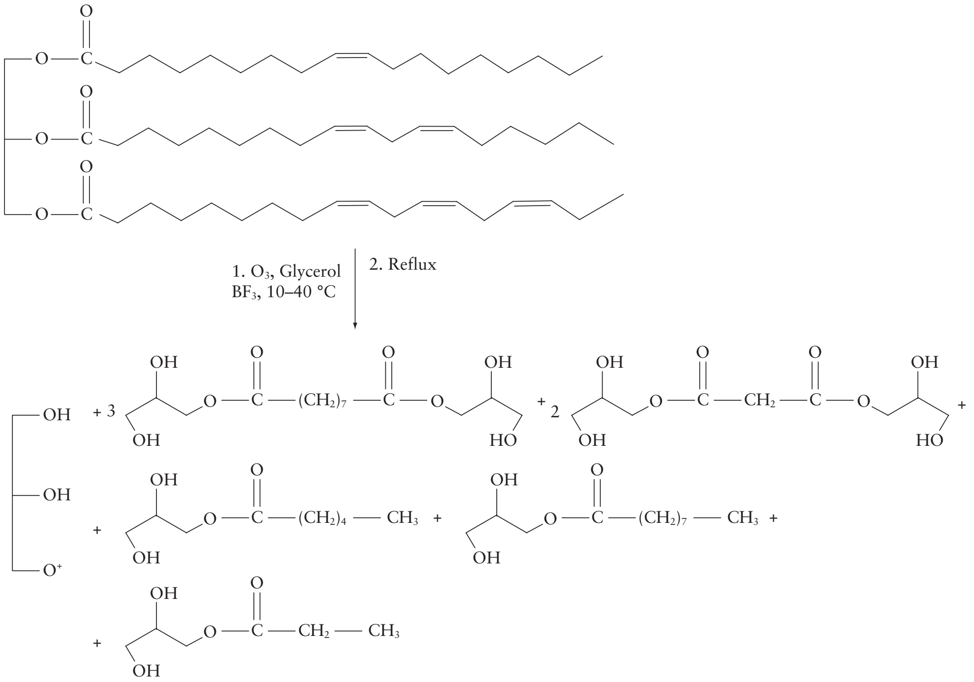
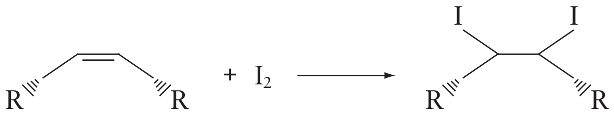


Figure 7.14 Synthesis and composition of a polyol by ozonolysis of soybean oil in the presence of glycerol. Catalyst: BF_3 [139]

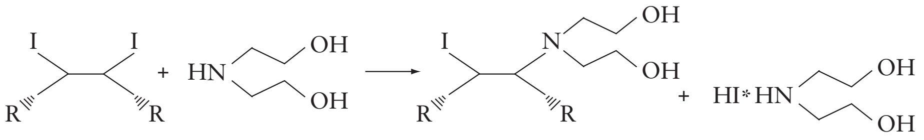
7.3.3.5 'Honey Bee' Polyols [150–153]

A very interesting and unconventional chemistry for hydroxyl functionalisation of vegetable oils was developed by MCPU Polymer Engineering (KS, USA). Upon reaction of DEOA with the double-bonds of vegetable oils (especially soybean oil) in the presence of elementary iodine as a catalyst, new structures with DEOA linked to the fatty acid chains are obtained. A possible mechanism of this unconventional reaction can be, in the first step, addition of iodine to double-bonds with formation of a diiodine derivative (**Reaction 7.47**).



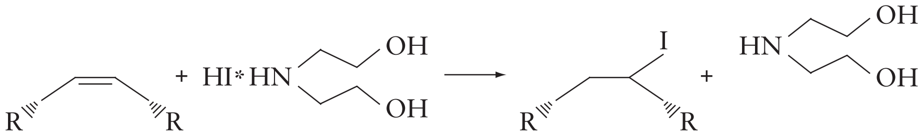
(7.47)

DEOA is a secondary amine and probably reacts with the iodine derivative through a bimolecular nucleophilic substitution, or S_N2 reaction, with formation of a tertiary amine and hydroiodic acid (HI) linked in the form of salt with the amine structures from the reaction system (**Reaction 7.48**).



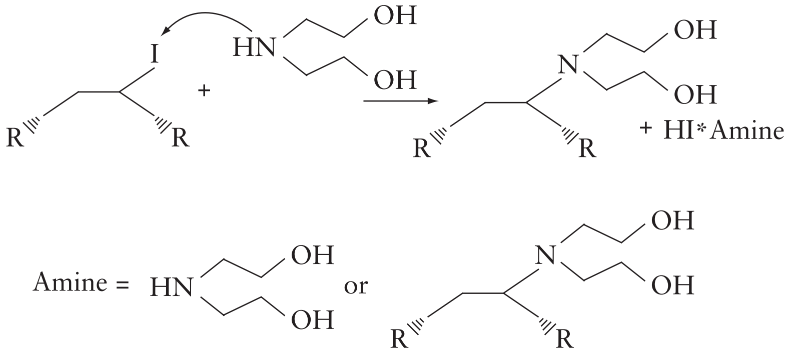
(7.48)

Hydrogen iodide reacts with another double-bond with formation of a mono-iodine derivative (**Reaction 7.49**).



(7.49)

This iodine derivative reacts again with DEOA, with formation of a tertiary amine and hydrogen iodide (linked to DEOA or a tertiary amine resulting from the reaction system). This chain reaction probably stops when the entire quantity of DEOA has reacted (**Reaction 7.50**).



(7.50)

Vegetable oil is mixed with DEOA and catalytic quantities of iodine for a relatively long time (e.g., 23–25 h) at 90–115 °C. Using this method, bio-based polyols have been prepared with average functionality of 2 OH groups/mol, OH# = 140–240 mg KOH/g, and low viscosities of 140–375 mPa.s at 25 °C [148, 149]. These polyols are especially suitable for CASE formulations and for some special flexible and rigid PUF.

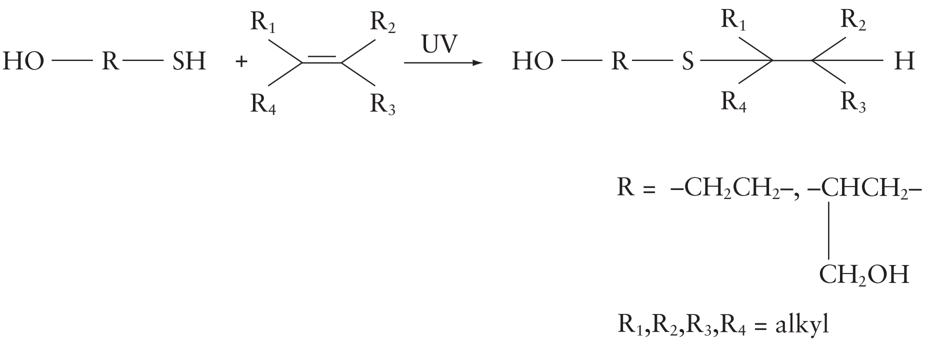
'Honey bee' polyols for flexible foams are prepared by chain extension of previously mentioned high-OH# polyols with MA in acidic catalysis (e.g., phosphoric acid, sulfuric acid, *p*-toluene sulfonic acid). This chain extension (**Volume 2, Section 7.3.4.1**) is a polyesterification reaction, and from the reaction water is formed, which is removed with a Dean–Stark trap. Sometimes, toluene is used for efficient removal of water which results from the polyesterification reaction as a toluene–water azeotrope. The chain-extended polyols have lower OH# (36–57 mg KOH/g) and are suitable for flexible PUF applications [150].

Polyols of higher functionality can be obtained using a polyfunctional polyol such as glycerol or sorbitol in the polyesterification step [153]. A typical honey bee polyol of functionality ≈6 OH groups/mol has OH# = 510–550 mg KOH/g and viscosity of 54,000 mPa.s at 25 °C. Such high-functionality polyols are suitable for rigid PUF.

Honey bee polyols have some advantages (e.g., 100% primary hydroxyl content, less colour, less steric hindrance) than other soy-based polyols. The chemistry used for preparation of honey bee polyols is unique and unconventional.

7.3.3.6 Bio-based Polyols by Thiol-ene Reactions [154–176]

As explained in the previous chapter (principles of thiol-ene reactions), radical addition of mercaptans to double-bonds of organic compounds is initiated by photochemical means with UV light and thermally by radical initiators. Many bio-based compounds are unsaturated with multiple double-bonds, such as vegetable oils, fish oils, as well as di and polyterpenes (e.g., limonene, mircene). Addition of hydroxyalkyl mercaptans to the double-bonds of natural compounds is a new and efficient pathway to obtain polyols suitable for preparation of bio-based PU [154, 160, 161] (**Reaction 7.51**).



$$R = -CH_2CH_2-,\ -\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCH_2-$$

R_1,R_2,R_3,R_4 = alkyl (7.51)

Addition of 2-mercaptoethanol to the double-bonds of vegetable oils (soybean oil, sunflower oil, safflower oil, linseed oil, canola oil, castor oil) is an one-step method to prepare bio-based polyols. In general, polyols are obtained from vegetable oils in two steps: epoxidation followed by ring-opening of the resulting epoxy groups with alcohols; hydroformylation with hydrogenation of the resulting polyaldehydes; ozonolysis followed by hydrogenation of the resulting polyaldehydes. The thiol-ene reaction is a direct way to obtain polyols from vegetable oils in a single step [158, 159]. **Figure 7.15** shows the synthesis of a bio-based polyol by thiol-ene addition of 2-mercaptoethanol to the double-bonds of soybean oil.

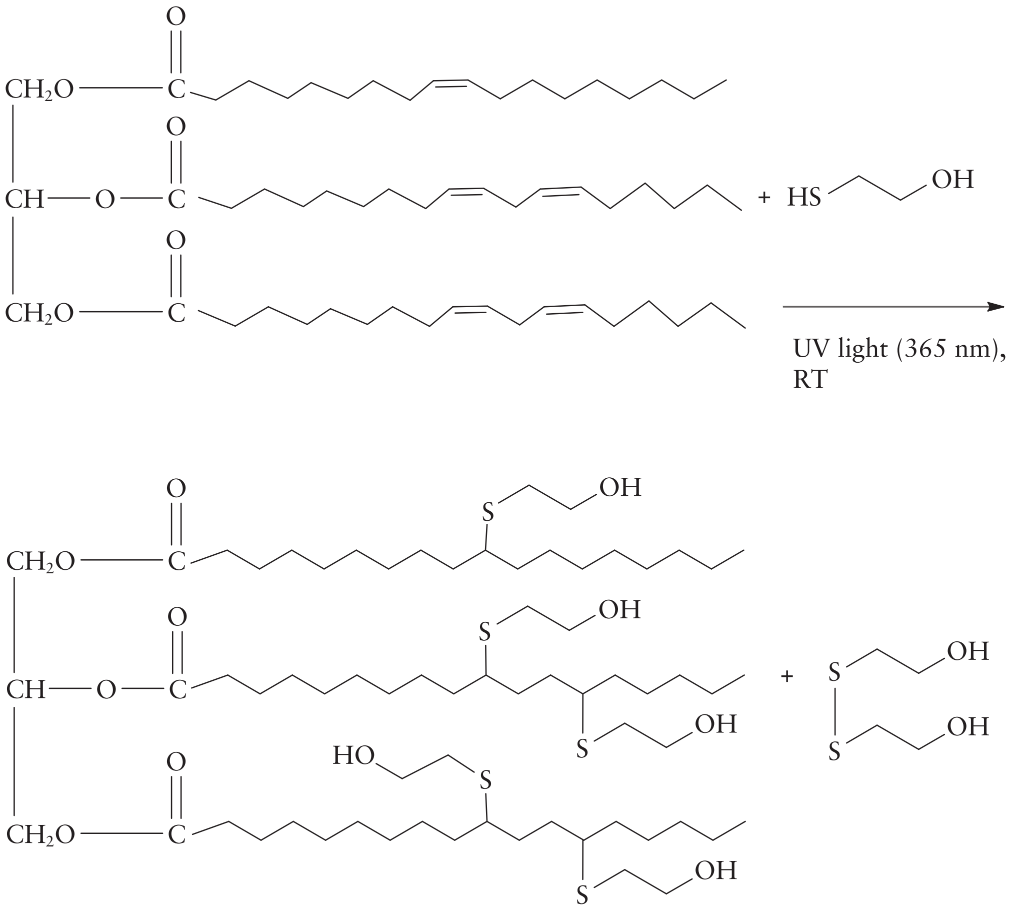
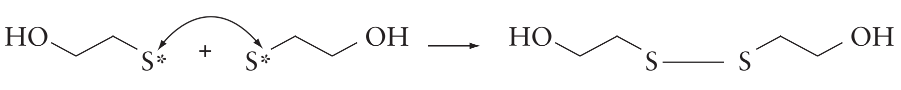


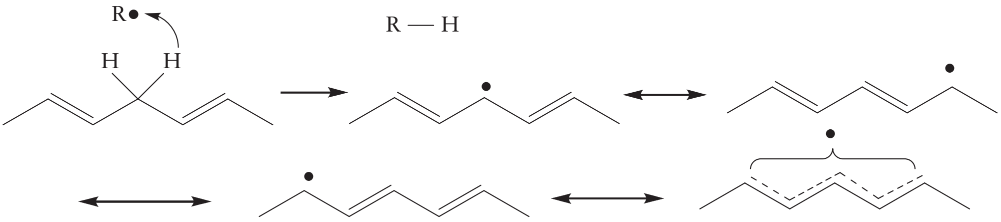
Figure 7.15 Synthesis and structure of a polyol by thiol-ene addition of 2-mercaptoethanol to soybean oil. RT: Room temperature

As a side reaction, to a small extent, is formation of *bis*(2-hydroxyethyl) disulfide by coupling of two thiyl radicals (**Reaction 7.52**).



(7.52)

Addition of mercaptans to the internal double-bonds of vegetable oils does not have the characteristics of thiol-ene 'click' reactions. Long reaction times and considerable excess of mercaptans (molar ratio [thiol groups]/[double-bonds] is 3–6/1) [156] are needed to obtain acceptable yields of bio-based polyols. Vegetable oils that perform better in thiol-ene reactions are those containing fatty acids with only one double-bond per fatty acid chain, such as high oleic soybean oil, high oleic safflower oil, olive oil and castor oil. This behaviour is because *bis*-allylic positions from fatty acids with two double-bonds (linoleic acid), or three double-bonds (linolenic acid) lead to strong radical-transfer reactions with formation of extremely stable allyl radicals of low reactivity (**Structure 7.11**).

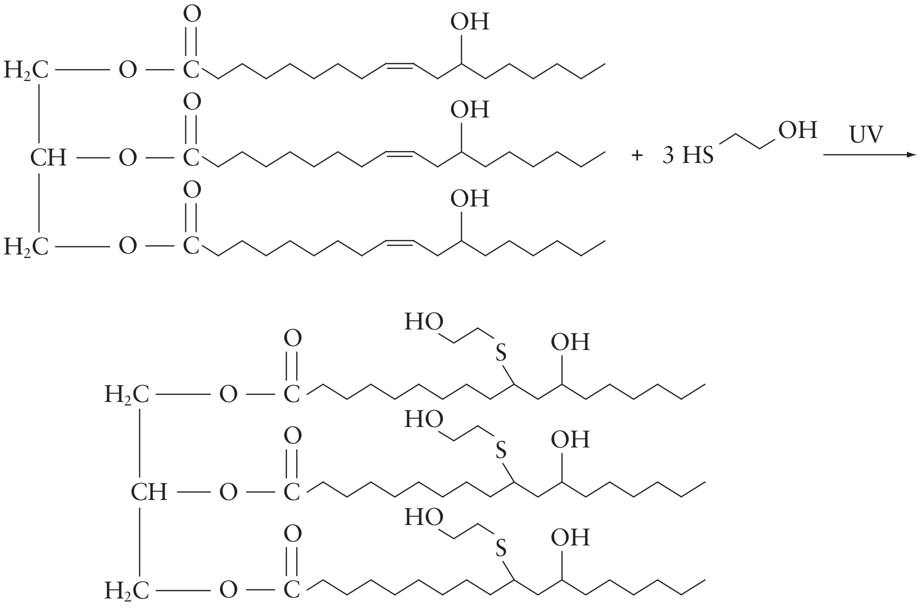


Structure 7.11 Formation of low-reactivity resonance hybrids by radical transfer with *bis*-allylic positions

Table 7.7 shows the characteristics of bio-based polyols by addition of 2-mercaptoethanol to various vegetable oils. In the case of oils containing linoleic and linolenic acids (canola oil, linseed oil), the resulting OH# are much lower than the theoretical OH#. In oils containing fatty acids with only one double-bond, the OH# of resulting bio-based polyols is very close to the theoretical OH#.

The acid value of polyols from **Table 7.7** is due to certain unreacted thiol groups that are acidic in nature. The excess of 2-mercaptoethanol is removed readily by high-vacuum distillation (bp of 2-mercaptoethanol is ≈155 °C) or by extractions with water (2-mercaptoethanol is soluble in water, whereas the resulting bio-based polyol is not).

The best polyol for rigid PUF is prepared by addition of 2-mercaptoethanol to castor oil (**Reaction 7.53**). The resulting polyol has a functionality of ≈5.4 OH groups /mol, an OH# = 260–275 mg KOH/g, and viscosity of 1,110–1,570 mPa.s at 25 °C. This polyol can be used as the sole polyol for rigid PUF with good physical–mechanical properties.



(7.53)

Table 7.7 Characteristics of bio-based polyols by thiol-ene addition of 2-mercaptoethanol to various vegetable oils [169]							
No.	Polyol	OH# (mg KOH/g)	Viscosity (mPa.s at 25 °C)	Acid value (mg KOH/g)	M_n	Mw	$\frac{M_n}{Mw}$
1	Soy oil polyol	181.2	1,160	1.23	1,420	1,570	1.10
2	Linseed oil polyol	201.0	1,470	1.65	1,490	1,670	1.12
3	Canola oil polyol	144.9	540	0.97	1,390	1,490	1.07
4	High oleic soy polyol	153,2	570	1.06	1,410	1,470	1.04
5	Tung oil polyol	163.9	3,720	4.50	1,560	2,590	1.65
6	Castor oil polyol (I)	275.5	1,570	2.50	1,440	1,470	1.02
7	Castor oil polyol (II)	262.7	1,100	2.30	1,420	1,460	1.02

Polyols based on soybean oil, sunflower oil, and canola oil (**Table 7.7**) can be used in a 30–50% mixture with polyether polyols based on sucrose or sorbitol, and lead to very good rigid PUF. **Figure 7.16** is a flow-sheet diagram for the synthesis of polyols by thiol-ene addition of 2-mercaptoethanol to vegetable oils.

The synthesis of polyols by direct addition of hydroxyalkyl mercaptans to the double-bonds of vegetable oils is possible by thermal initiation with radical initiators, but is less efficient than that by photochemical initiation [162]. Thus, to obtain acceptable yields in soybean polyols by thermal thiol-ene addition of 2-mercaptoethanol to soybean oil with *azobisisobutyronitrile* as the initiator, it is necessary to use a considerable excess of mercaptan ([2-mercaptoethanol]:[double-bonds] of ≈3–6:1), a long reaction time (6–10 h), and a considerable excess of initiator (0.1 mol of initiator per double-bond).

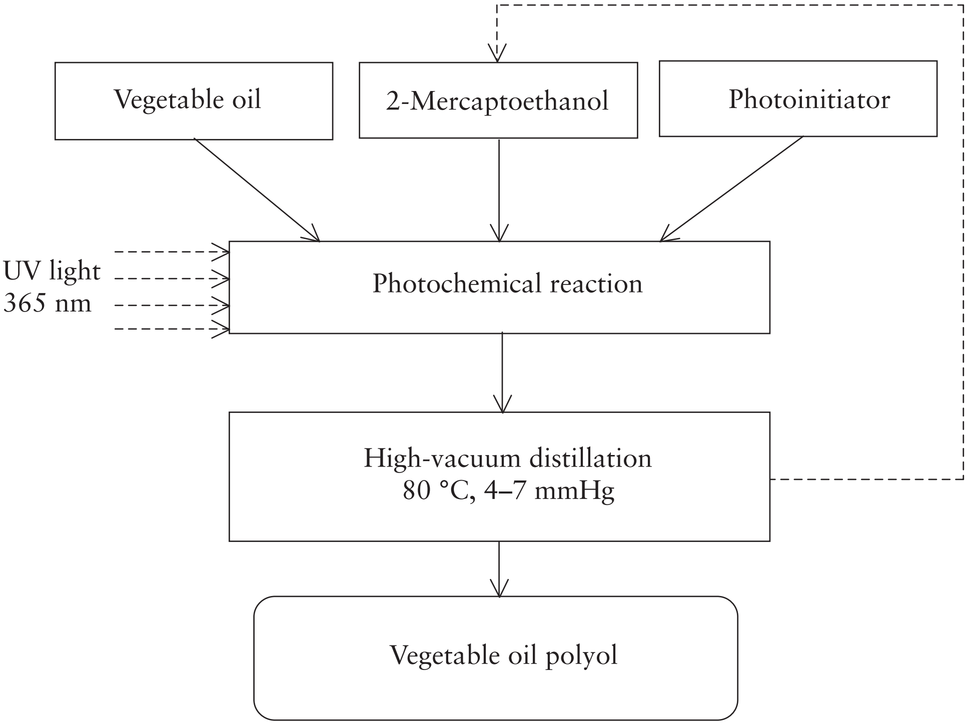
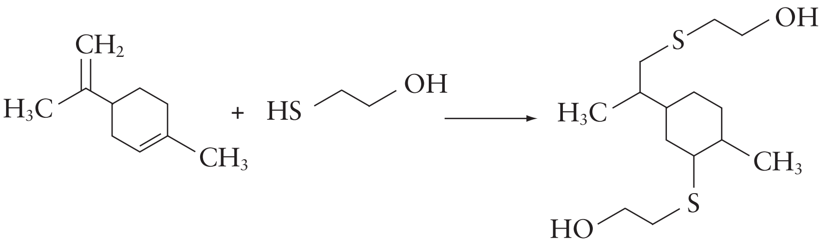


Figure 7.16 The synthesis of bio-based polyols by thiol-ene reaction of vegetable oils with 2-mercaptoethanol

Bio-based polyols prepared by addition of 2-mercaptoethanol to vegetable oils are suitable for PU coatings, adhesives, sealants and rigid PUF.

A very interesting natural unsaturated compound is D-limonene (a hydrocarbon present in large quantities in the peel of oranges, grapefruits and mandarins). Orange oil extracted from orange peel contains ≈90% limonene, which is a monoterpene. Thiol-ene reaction of limonene with hydroxyalkyl mercaptans initiated photochemically with UV light can produce bio-based diols (**Reaction 7.54**) and polyols (**Reaction 7.55**) [175, 176].



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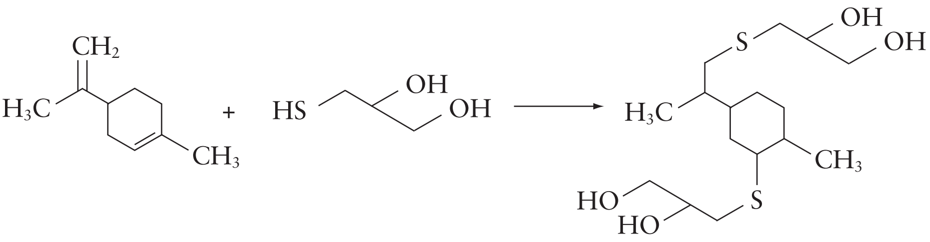
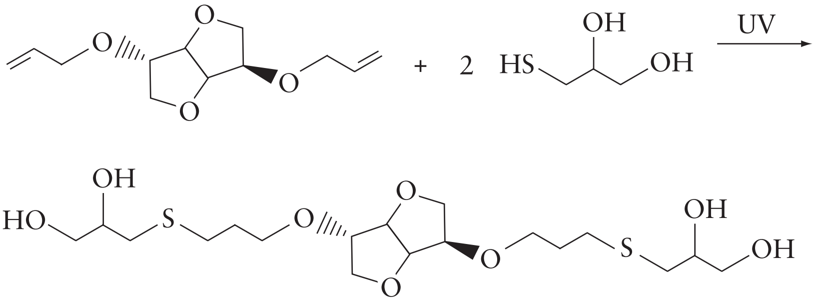


(7.55)

Limonene-based diol (**Reaction 7.54**) is suitable as a chain extender for PU elastomers or as a starter for polyether diols. Limonene-based tetraol (**Reaction 7.55**) is an excellent polyol for rigid PUF.

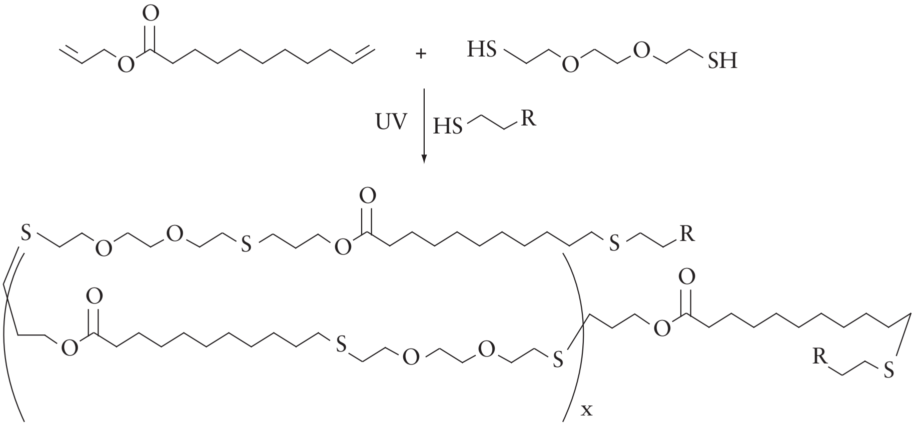
In a similar way, a tetrafunctional polyol can be prepared from isosorbide diallylether, which is an excellent reactant for radical thiol-ene reactions [171]. D-Isosorbide is a bio-based compound derived from corn, and is prepared by double-dehydration of D-sorbitol (**Volume 2**, **Section 7.4.1**). Isosorbide diallylether is prepared reaily by a Williamson reaction of isosorbide with allyl bromide in the presence of 50% sodium hydroxide or solid KOH [171]. By thiol-ene reaction of isosorbide diallylether with 2 mol of 1-thio-glycerol, an interesting bio-based polyol can be prepred for bio-based rigid PUF (**Reaction 7.56**).



(7.56)

7.3.3.6.1 High-Molecular-Weight Bio-based Telechelics by Thiol-ene Coupling

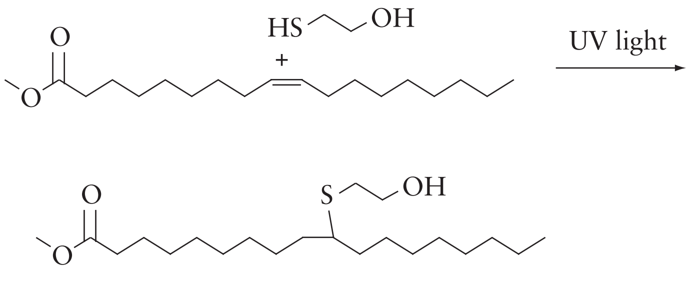
A very interesting bio-based compound with two terminal double-bonds is the allyl ester of undecylenic acid (allyl 10-undecenoate). By photochemical thiol-ene reaction of allyl 10-undecenoate in excess with a dimercaptan (e.g., 3,6-dioxa-1,8-octane-dithiol), and in the presence of 2,2-dimethoxy-2-phenylacetophenone as a photoinitiator, high-MW polymers with terminal double-bonds are produced. By thiol-ene additions of 2-mercaptoethanol, 3-mercaptopropionic acid and 3-mercaptopropyltrimethoxysilane to the aforementioned linear polymer with terminal double-bonds, high-MW telechelics have been prepared (**Reaction 7.57**) with hydroxyl, carboxyl, and trimethoxysilyl terminal groups, respectively [163, 164].



(7.57)

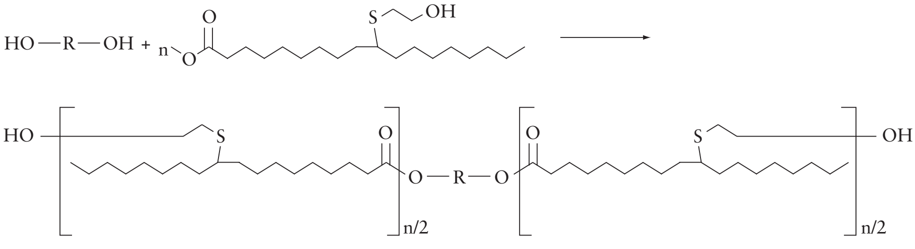
The linear telechelic polymers with the structure resulting from **Reaction 7.57** are suitable as building blocks for bio-based elastomers (R = OH, -COOH) and coatings [R = $-(CH_2)_3-Si(OCH_3)_3$].

A very interesting monomer for the synthesis of high-MW bio-based diols for PU elastomers is prepared by photochemical thiol-ene reaction of oleic acid or methyl oleate with 2-mercaptoethanol [171] (**Reaction 7.58**).



(7.58)

By polycondensation of these monomers, initiated by a diol such as diethylene glycol (DEG) or 1,6-hexanediol (HD), bio-based polyester diols of MW of 2,000–3,000 can be produced, which are suitable for preparation of PU elastomers [169] (**Reaction 7.59**).



(7.59)

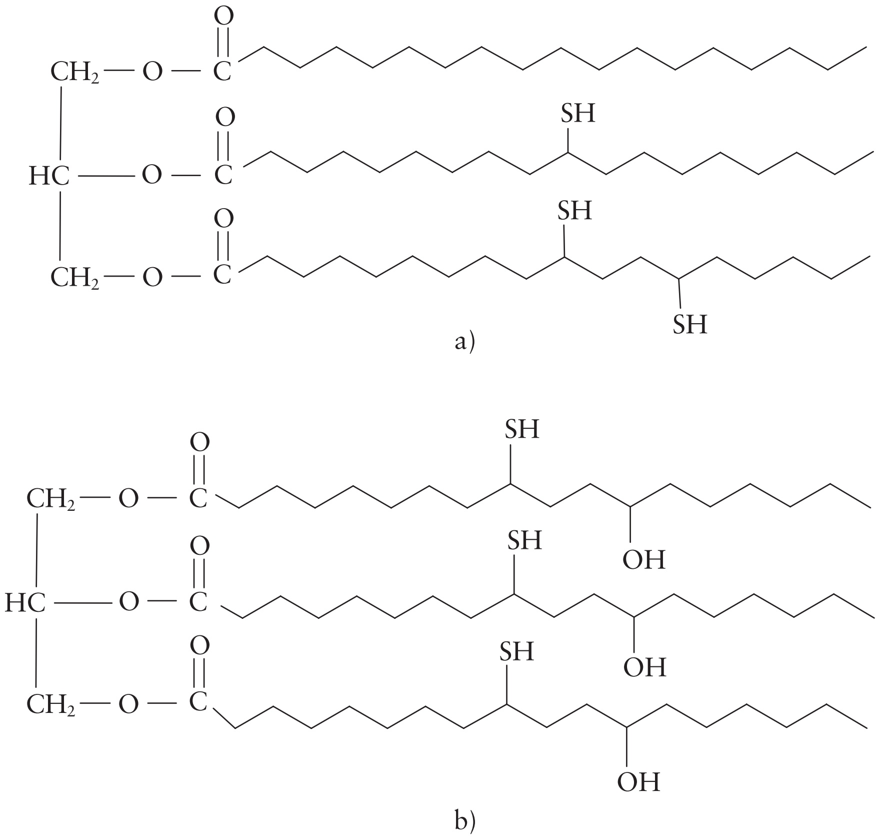
Very interesting bio-based polymercaptans derived from vegetable oils have been produced by Chevron Phillips (TX, USA) [172, 173].

Bio-based polymercaptans can be synthesised by two practical methods:

a) Addition of hydrogen sulfide to the double-bonds of unsaturated natural compounds (vegetable oils, limonene).

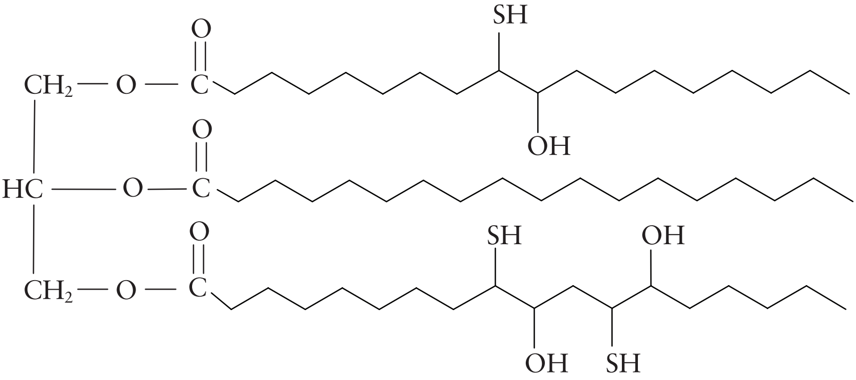
b) Ring-opening of epoxy groups of epoxidised oils with hydrogen sulfide.

Photochemical addition of hydrogen sulfide to the double-bonds of soybean oil leads to a polymercaptan ('mercaptanised soybean oil') with ≈2.9–3.1 thiol groups/triglyceride (**Structure 7.12a**). By addition of hydrogen sulfide to the double-bond of castor oil, a structure containing thiol groups and hydroxyl groups is obtained ('mercaptanised castor oil') (**Structure 7.12b**).



Structure 7.12 a) Mercaptanised soybean oil and b) mercaptanised castor oil

Ring-opening of epoxy groups of epoxidised soybean oil with hydrogen sulfide leads to a structure with thiol groups and hydroxyl groups (**Structure 7.13**), similar to mercaptanised castor oil. Thiol groups and hydroxyl groups in **Structure 7.13** derived from epoxidised soybean oil are at two neighbouring carbon atoms (C9–C10 or C12–C13) and, in the case of mercaptanised castor oil, thiol groups are at C9 or C10 and hydroxyl groups are at C12.



Structure 7.13 Polymercaptan production by ring-opening of epoxidised soybean oil with hydrogen sulfide

Interestingly, **Structures 7.14** and **7.15** can be used as intermediates for preparation of rigid PUF by reaction with diphenylmethane diisocyanate (MDI) (‘crude’ or ‘polymeric’). The thiol groups react with isocyanates in the catalysis of tertiary amines [e.g., 1,4-diazabicyclo[2,2,2]octane (DABCO) or dimethylcyclohexylamine] to generate thiourethane groups (**Reaction 7.60**). Hydroxyl groups react in a normal way by generating urethane groups.

$$\mathrm{R{-}SH + O{=}C{=}NR' \longrightarrow RS{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R'} \qquad (7.60)$$

Properties of rigid PUF based on polymercaptans with **Structures 7.13** and **7.14**, or mixtures of these polymercaptans with conventional polyether polyols are very good, similar to the properties of rigid PUF produced exclusively from petrochemical polyols.

A variant of the synthesis of bio-based polyols by thiol-ene reactions is carried out using mercaptanised vegetable oils and unsaturated alcohols or unsaturated polyols (allyl alcohol, 1-allyl glycerol, allyl TMP). **Figure 7.17** shows the synthesis and structure of a polyol obtained by thiol-ene reaction of mercaptanised soybean oil and allyl alcohol, initiated by photochemical means (UV light) or thermal (radical initiators) means.

A polyol of higher functionality is obtained by thiol-ene reaction of mercaptanised soybean oil with glycerol-1-allyl ether (**Figure 7.18**) [173]. A similar polyol is obtained by thiol-ene reaction of mercaptanised soybean oil with TMP allyl ether [173].

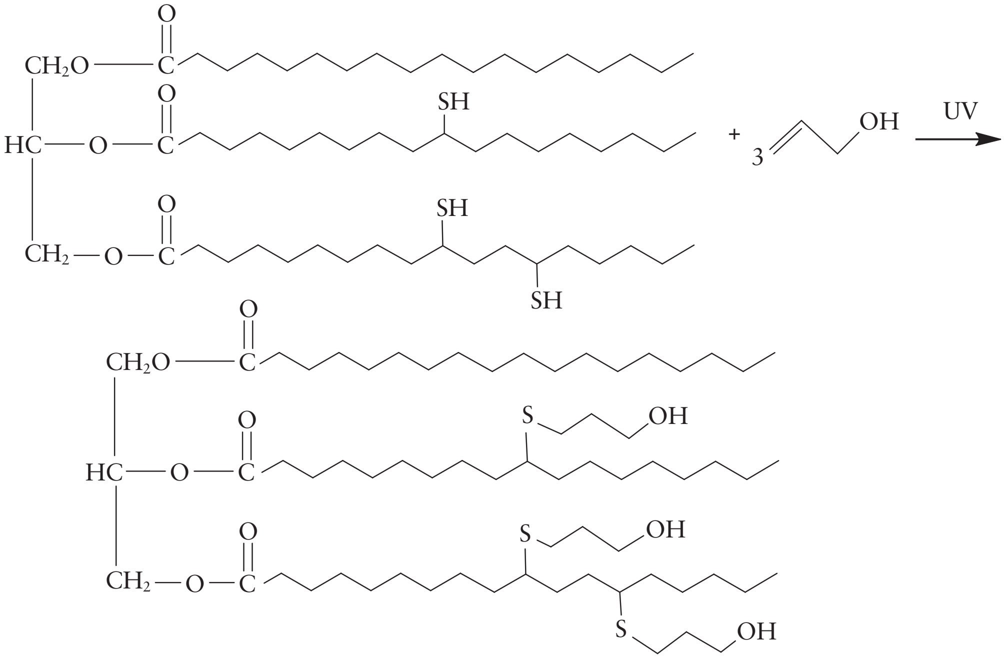


Figure 7.17 Synthesis and structure of a bio-based polyol by thiol-ene addition of mercaptanised soybean oil with allyl alcohol

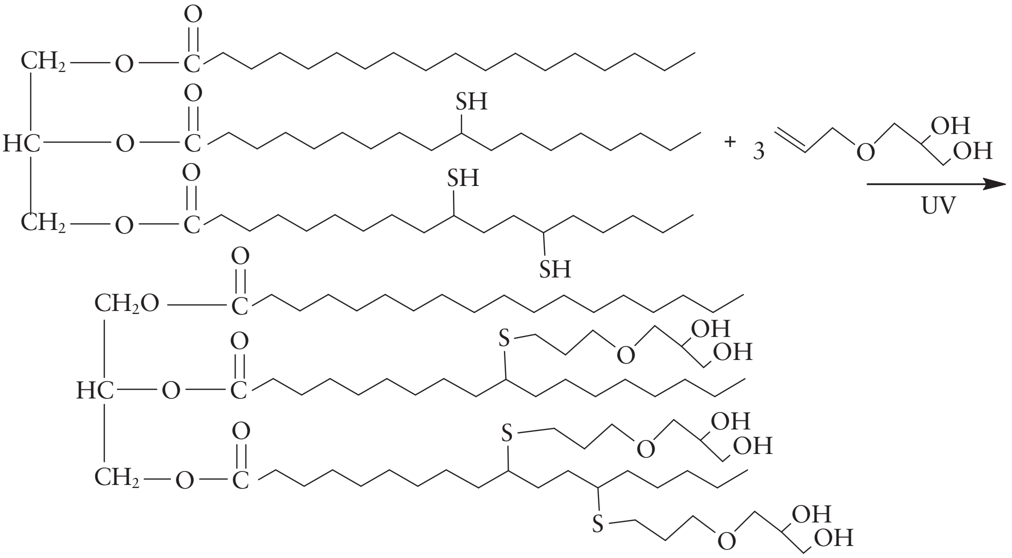
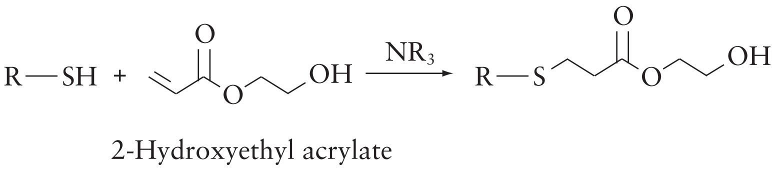


Figure 7.18 Synthesis and structure of a polyfunctional bio-based polyol by thiol-ene reaction of mercaptanised soybean oil with glycerol-1-allyl ether

7.3.3.6.2 Bio-based Polyols by Nucleophilic Michael Thiol-ene Reaction

A variant of a thiol-ene reaction is a nucleophilic Michael addition of thiol groups to activated double-bonds by electron-withdrawing substituents (>C=O, >S=O, >SO_2-, -CN), catalysed by tertiary amines, tertiary phosphines, and alkoxides [172]. To generate polyols, this type of Michael reaction is carried out efficiently between polymercaptans and hydroxyalkyl acrylates or hydroxyalkyl methacrylates (**Reaction 7.61**).



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The mechanism of nucleophilic thiol-ene addition of mercaptans to activated double-bonds of 2-hydroxyethylacrylate is presented in **Figure 7.19**.

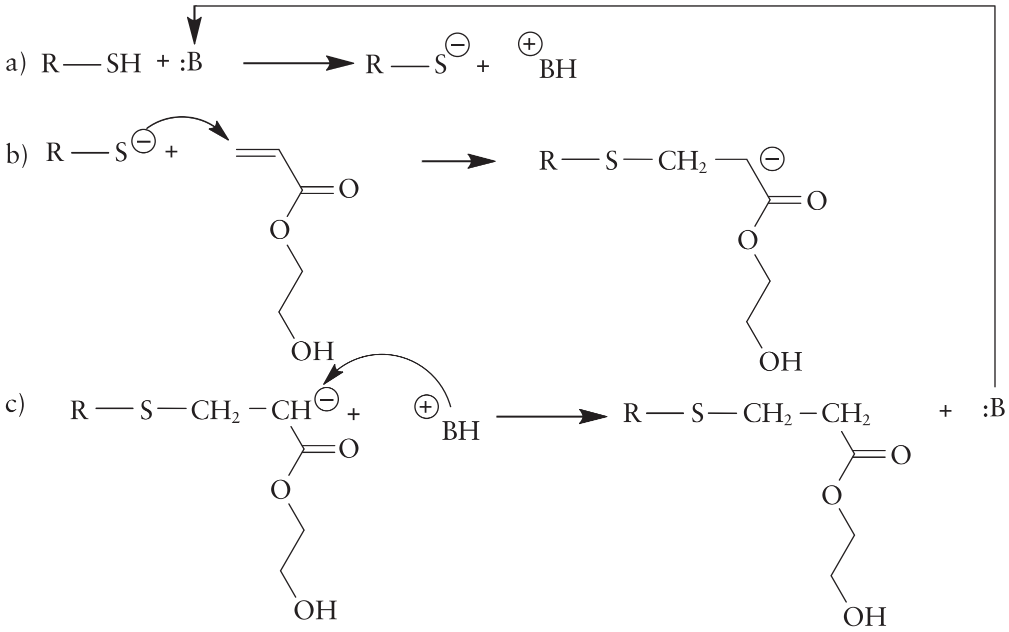


Figure 7.19 Mechanism of nucleophilic thiol-ene Michael reaction

Nucleophilic Michael thiol-ene reaction of mercaptanised soybean oil with 2-hydroxyethyl acrylate enables a polyol of functionality 2.9–3.1 OH groups/mol to be obtained (**Figure 7.20**). Some catalysts that can be used include triethylamine, tributylphosphine, diethyl phenyl phosphine, DABCO, and sodium methoxide. The reaction is very exothermic, and it is necessary to use efficient cooling to control the reaction temperature (50–80 °C).

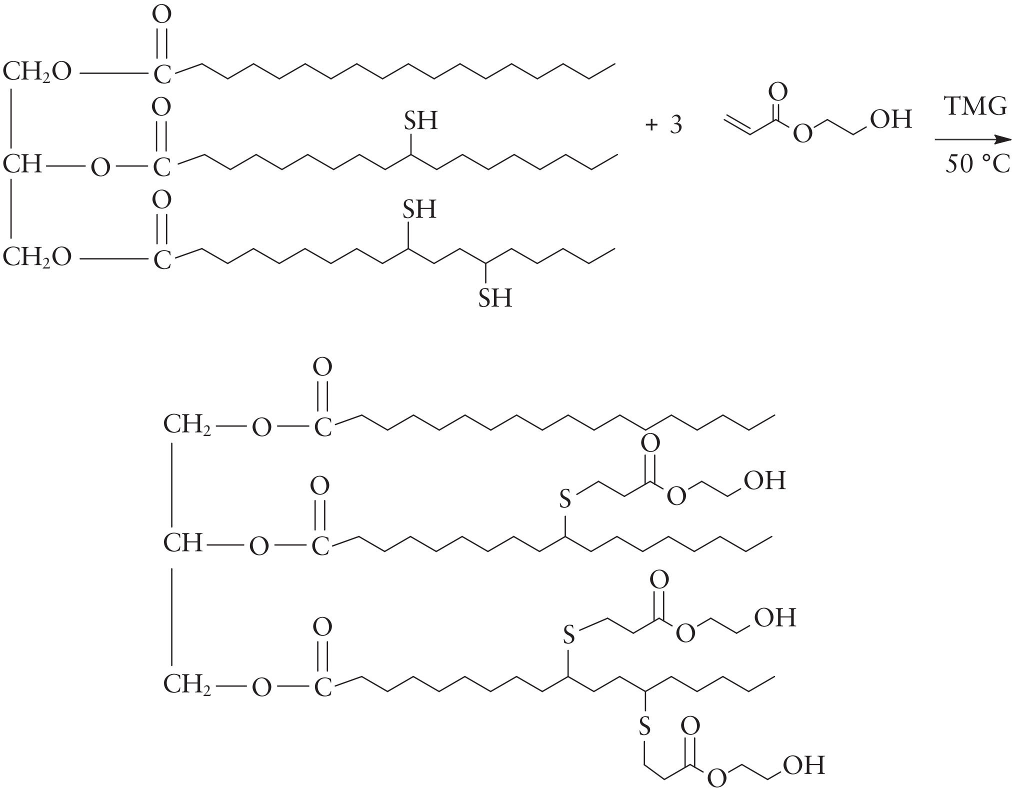


Figure 7.20 Synthesis of a bio-based polyol by nucleophilic Michael thiol-ene reaction of mercaptanised soybean oil with 2-hydroxyethyl acrylate

Nucleophilic Michael thiol-ene reaction of mercaptanised castor oil with 2-hydroxyethyl acrylate enables a polyol of higher functionality (≈5.4–5.7 OH groups/mol) to be synthesised (**Figure 7.21**).

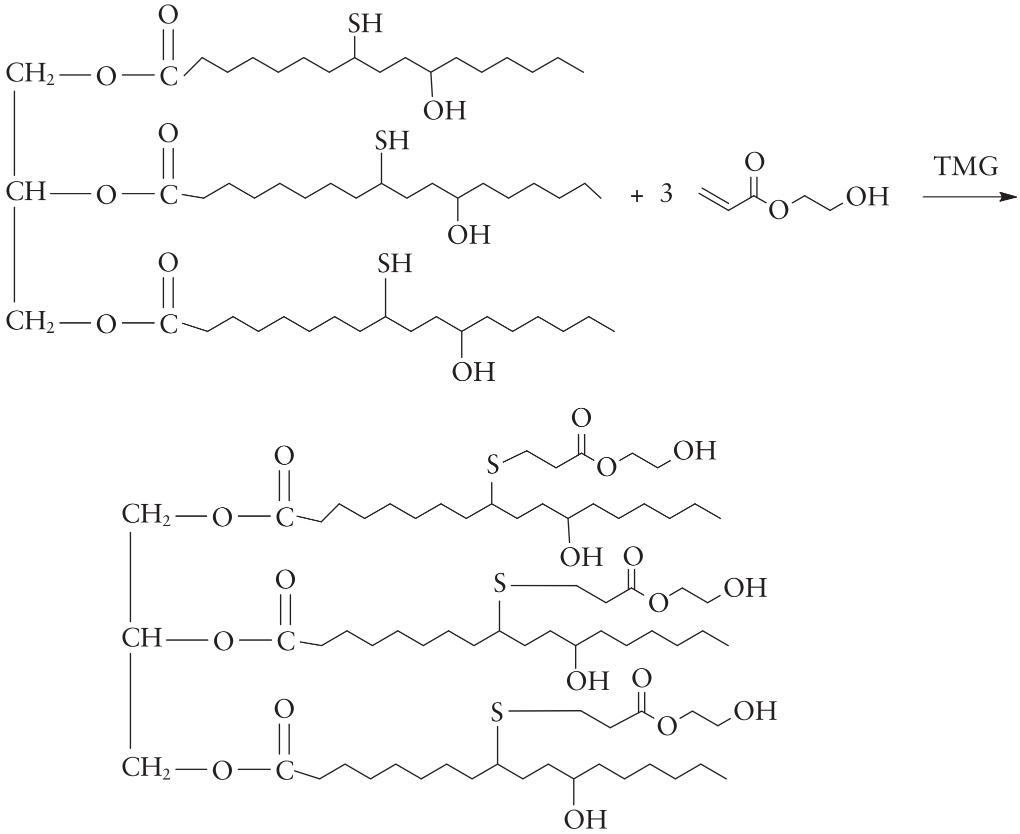


Figure 7.21 Synthesis and structure of a polyfunctional polyol by nucleophilic Michael thiol-ene reaction of mercaptanised castor oil with 2-hydroxyethyl acrylate

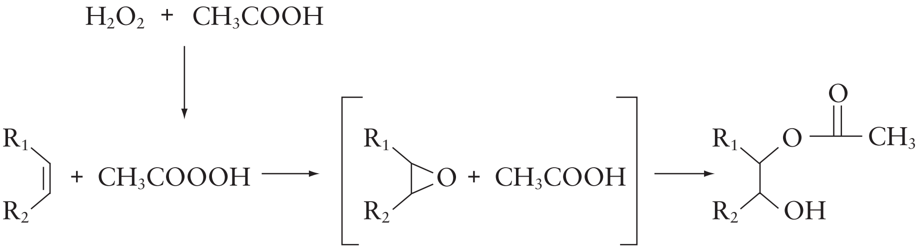
Bio-based polyols synthesised by nucleophilic Michael reaction from mercaptanised oils and hydroxyalkyl acrylates (or methacrylates) are suitable for rigid PUF, coatings, adhesives and sealants.

Presented in this section were a limited number of renewable polyols that can be prepared by thiol-ene reactions from natural unsaturated compounds and hydroxyalkyl mercaptans. Synthesis of many other bio-based polyols by thiol-ene reactions have been described [154–170]. Thiol-ene reaction is an old reaction, rediscovered in the last decade by scientists, and has great potential because it offers an efficient pathway for the synthesis of new bio-based polyols.

7.3.3.7 'One-Pot/One-Step' Synthesis of Polyols from Vegetable Oils [177–180]

Most polyols based on vegetable oils are synthesised in two steps: epoxidation followed by ring-opening with alcohols; hydroformylation followed by hydrogenation of resulting polyaldehydes; ozonolysis followed by hydrogenation (or reduction). In this section are described technologies that generate hydroxyl groups on the double-bonds of vegetable oil in only one reaction step.

'One-pot' synthesis of a vegetable oil polyol is based on the generation of hydroxyl groups in one, two or more steps in the same reactor. One-pot preparation of a vegetable oil polyol in only 'one-step' is a simple and economical synthetic pathway. One example of this type of technology is based on the reaction of vegetable oil with an excess of acetic acid (formic acid or a mixture of formic acid and acetic acid can also be used) and hydrogene peroxide [177–180]. By refluxing this mixture for 1–2 h, a polyol with a hydroxyalkyl acetate (or formate) structure is produced. Peroxyacetic acid is employed as an intermediate, which transforms the double-bonds of vegetable oil into epoxy groups. The epoxy groups react '*in situ*' with acetic acid to form hydroxyalkyl acetates (**Reaction 7.62**).



(7.62)

The reaction mass consists of two layers: the polyol is the upper layer and acetic acid and water form the bottom layer. The upper layer is washed with aqueous sodium bisulfite, aqueous sodium bicarbonate and a solution of sodium chloride in water. Finally, the upper layer is anhydrised by treatment with anhydrous sodium sulfate and vacuum distillation [177, 178].

As a function of the quantity of hydrogen peroxide used, polyols of functionality 1.99–4.2 OH groups/mol are obtained with OH# = 117–184 mg KOH/g [177–179]. The polyols has very high renewable content of 86–99%. The polyols are suitable for various PU applications, such as foams, coatings, adhesives, and cast PU.

Polyols with a higher OH# are obtained by reaction with the aforementioned polyols, obtained from one-pot/one-step synthesis, with DEOA or DEOA-glycerol mixtures, in the presence of Ti(IV) 2-ethylhexoxide at 140 °C [180]. DEOA reacts with the ester bonds from the reaction systems (triglyceride ester and acetate ester bonds) to form DEOA. Bio-based polyols of OH# = 239–500 mg KOH/g and viscosities of 2,200–5,530 mPa.s at 25 °C are obtained, which are suitable for rigid PUF [180].

Another example of polyol synthesis by one-pot/one-step is the tiol-ene addition of hydroxyalkyl mercaptans to the double-bonds of natural compounds (vegetable oils, limonene), by photochemical or thermal means. This method is described in detail in **Volume 2**, **Section 7.3.3.6**.

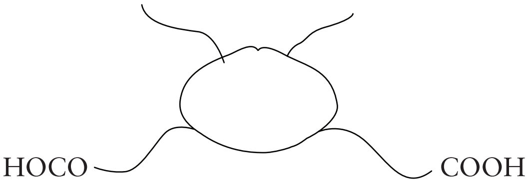
7.3.3.8 Dimerisation of Unsaturated Fatty Acid Polyols Based on Dimer Acids [56, 181]

An important development in the area of polyols from renewable resources was realised by transformation of dimeric or trimeric acids (or of corresponding methyl esters) by hydrogenation in C36 diols or C54 triols.

Thus, dimerisation of unsaturated fatty acids takes place at higher temperatures in the presence of catalysts (e.g., acidic clays, montmorillonite type). One molecule of oleic acid (which has one double-bond) reacts with 1 mol of linoleic acid (which has two double-bonds) to form 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 Diels–Alder reaction (**Figure 7.22**).

The structure of a dimeric acid is shown schematically in **Structure 7.14**.



Structure 7.14 Structure of a dimeric acid (schematic)

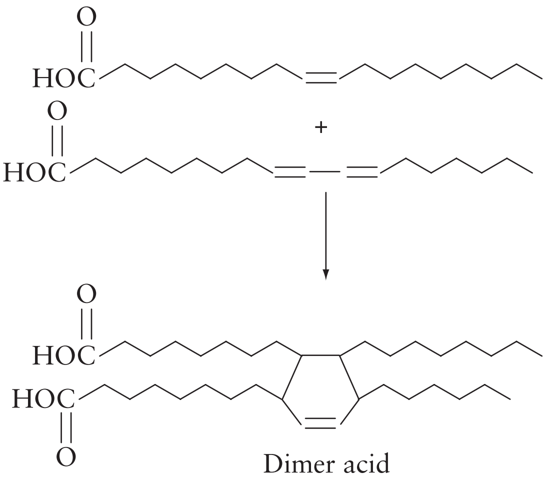
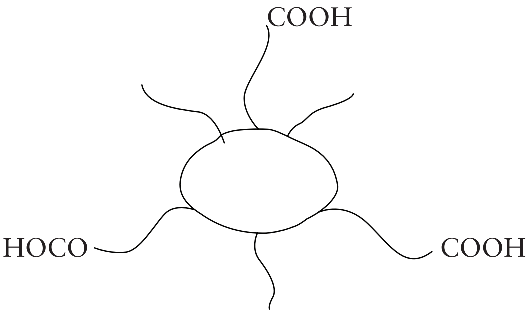


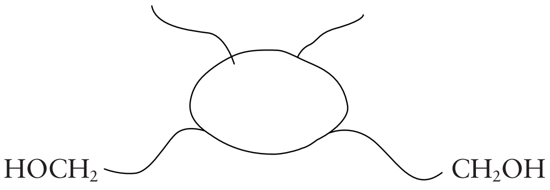
Figure 7.22 Diels–Alder reaction between oleic acid and isomerised linoleic acid

Acid trimers are formed by the reaction of the dimeric acid formed with another molecule of linoleic acid or by the reaction of 3 molecules of linoleic acid (**Structure 7.15**).

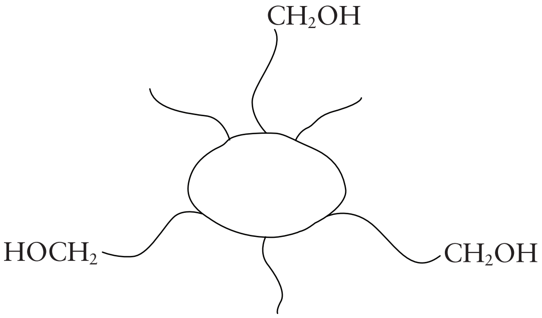


Structure 7.15 Structure of an acid trimer

By hydrogenation of these dimeric or trimeric acids, the corresponding diols or triols can be obtained. The dimer alcohol (**Structure 7.16**) has an OH# = 202–212 mg KOH/g, a MW of 565 Da, and a viscosity of ≈3,500 mPa.s at 25 °C [56, 181]. Trimer alcohols (**Structure 7.17**) have an OH# of ≈205 mg KOH/g and a viscosity of ≈9,500 mPa.s at 25 °C [181].



Structure 7.16 Structure of a dimer alcohol



Structure 7.17 Structure of a trimer alcohol

Dimer and trimer alcohols introduced into the structure of PU confer very high hydrophobicity, water repellency, flexibility and chemical stability onto them. Polyester urethanes based on dimeric diols and dimeric acids are the most hydrolysis-resistant polyester urethanes [56].

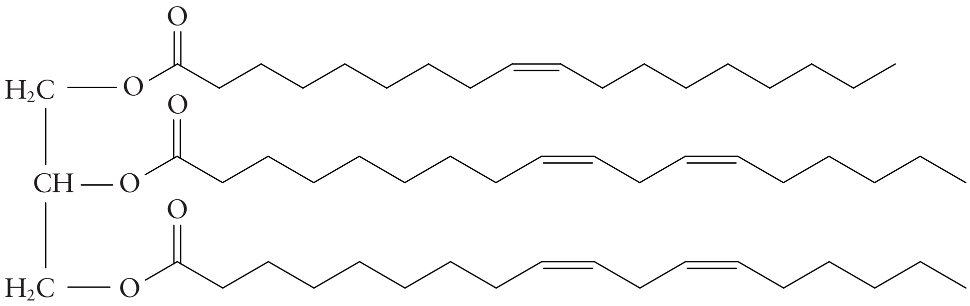
7.3.3.9 Bio-based Polyols from Polymerised Vegetable Oils [181–199]

Petrochemical polyols for flexible PUF, polyethers or polyesters have common characteristics: the chain derived from one hydroxyl group is long (≈1,000–2,000 Da) and the functionality is low (2–3 OH groups/mol). The T_g of polyols for flexible foams is between -70 to -20 °C, being in the elastic domain at RT. As an immediate consequence of the high-MW, low functionality, and low T_g of these polyols, reaction with aromatic isocyanates produces elastic PU.

Direct hydroxylation of vegetable oils leads to polyols of 3–6 hydroxyl groups/mol, which have a low-MW that is suitable for semi-rigid or rigid PU.

Creation of high-MW polyols from renewable raw materials used to be a difficult objective for chemists. In recent years, with imagination and creativity, scientists using innovative chemistries have developed several new synthetic pathways to high-MW renewable polyols that are suitable for flexible PUF starting from vegetable oils.

Vegetable oils are triesters of glycerol with fatty acids containing several double-bonds, such as oleic acid (one double-bond), linoleic acid (two double-bonds) and linolenic acid (three double-bonds), and can be considered to be polyfunctional monomers. Thus, soybean oil has ≈4.6 double-bonds/mol and linseed oil ≈6–8 double-bonds/mol (**Structure 7.18**).



Structure 7.18 Structure of a triglyceride containing unsaturated fatty acids

The double-bonds in vegetable oils are internal 1,2-disubstituted double-bonds of low reactivity and low polymerisability.

One hypothesis to prepare high-MW polyols for flexible PUF was to use polymerised vegetable oils as raw materials. In spite of the low reactivity of internal double-bonds, there are three methods to polymerise vegetable oils to high-MW structures:

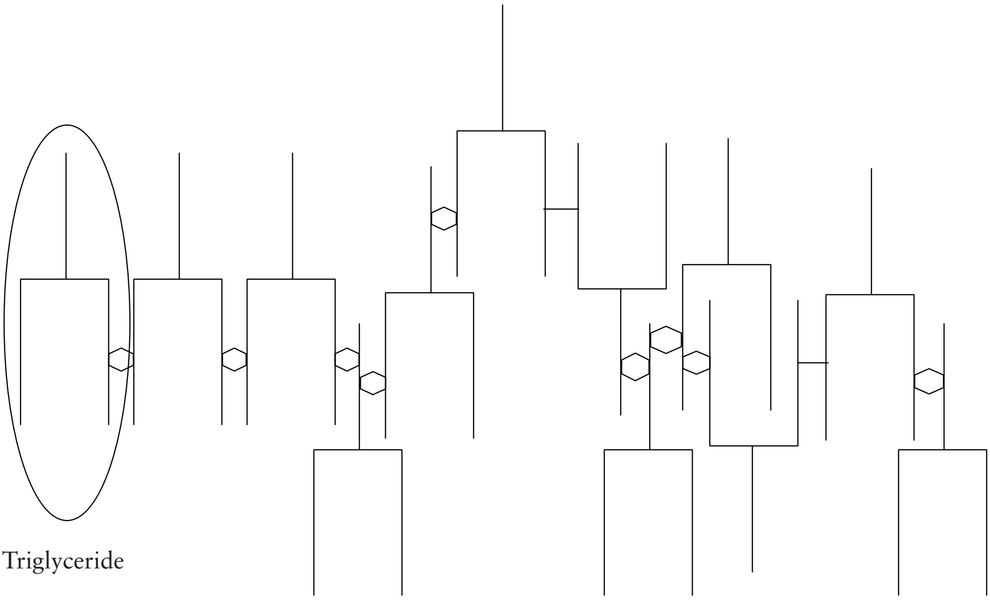
a) Thermal polymerisation of vegetable oils (‘bodied’ oils).

b) Air-blown polymerisation of vegetable oils.

c) Cationic polymerisation of vegetable oils.

7.3.3.9.1 Thermal Polymerisation of Vegetable Oils (Bodied Oils) [180–184]

By heating vegetable oils at 330–370 °C, viscosity increases considerably as a consequence of thermal polymerisation involving double-bonds. This thermal polymerisation of oils involves free radicals, but the mechanism is unconventional and totally different from the radical polymerisation of olefins. The free radicals generated by thermal means undergo strong transfer with *bis*-allylic positions from linoleic and linolenic structures to generate allyl radicals (which are resonance hybrids), which leads to formation of conjugated double-bonds. These conjugated double-bonds lead to a Diels–Alder reaction with various double-bonds from the reaction system, with formation of cyclics. This Diels–Alder reaction is the ‘key’ component of the unconventional polymerisation of oils, with the triglyceride structures of oils being linked by the cyclics formed (**Structure 7.19**). The thermally polymerised oils are called bodied oils. Unfortunately, as a consequence of thermal degradation, ≈20–25 wt% from the oils are lost in the form of volatile compounds.



Structure 7.19 Probable structure of thermally polymerised vegetable (‘bodied’) oils

Bis-allylic positions have an important role in the thermal polymerisation of oils. Hence, the best oils for this type of process are oils that contain linoleic and linolenic fatty acids. The best bodied oils are obtained by thermal polymerisation of linseed oil (which is ≈52–54% linolenic acid).

7.3.3.9.2 Air-Blown Polymerisation of Vegetable Oils [189–191]

By bubbling air through liquid vegetable oils heated at 80–100 °C, the viscosity of oils increases substantially. This process involves free radicals with formation of hydroxyl groups, and the product of the reaction is a polyol. Unfortunately, due to a combination of hydroxyl groups and a reaction of oils with O_2 from air, other functional groups such as hydroperoxides, peroxides, carboxyl groups, aldehydes, and ketones are formed. In spite of this functional heterogeneity, air-blown oils have been used for preparation of polyols suitable for flexible PUF [189–191]. The functionality of these air-blown polyols can be increased by transesterification with other polyols, such as glycerol and sorbitol.

7.3.3.9.3 Cationic Polymerisation of Vegetable Oils [194–199]

Vegetable oils such as soybean oil, linseed oil, and canola oil can be polymerised using Lewis acids (BF_3 or BF_3 diethylether complex) [195–198] and superacids (HBF_4, CF_3SO_3H, $HSbF_6$) [199]. Polymerisation is carried out in bulk at 90–140 °C [199] or in supercritical CO_2 [198]. By cationic polymerisation of soybean or linseed oil, highly viscous liquid polymerised oils can be prepared (or solid crosslinked polymers by advanced polymerisation). Liquid polymerised oils are preferred for preparation of polyols.

The mechanism of cationic polymerisation of vegetable oils is very similar to the mechanism of thermal polymerisation of oils: the difference is that the active species are carbocations instead of free radicals. Highly reactive carbocations are formed by the addition of protons of superacids used as catalysts to the double-bonds from fatty acid chains. These carbocations undergo transfer with *bis*-allylic positions to generate allyl cations (which are resonance hybrids), leading to the generation of conjugated double-bonds. The latter, by a Diels–Alder reaction with double-bonds, generate cyclics which link triglyceride structures into high-MW species.

Thus, by reaction of the ester bonds of polymerised oils, such as enzymatic hydrolysis [182–184], transesterification with glycols, glycerol or triethanolamine (TEOA) [179], or amidation with DEOA [181], polyols with an OH# = 25–100 mg KOH/g (preferably 28–60 mg KOH/g) can be obtained (the usual range for flexible PU foams). Addition of a hydroxylation agent, calculated to obtain a final low OH# in the aforementioned range, is recommended.

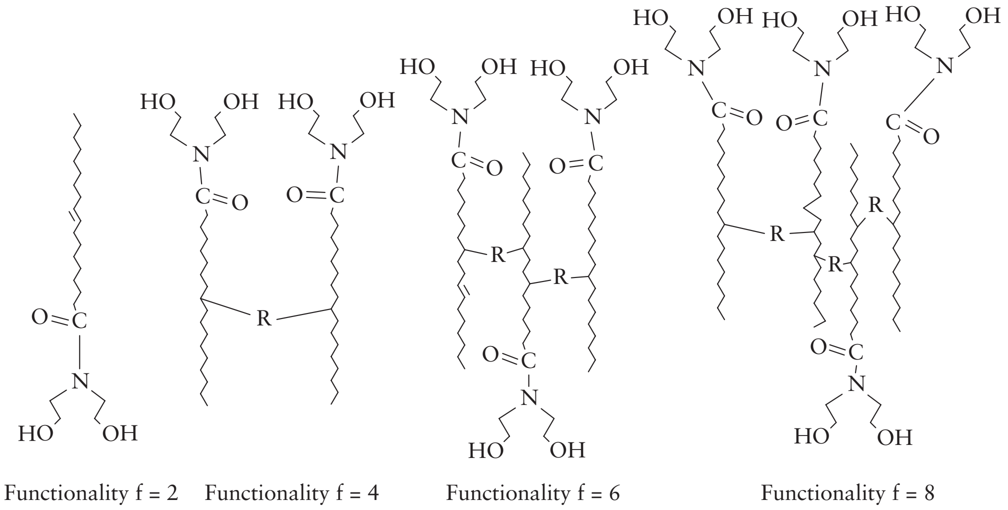
As a consequence of polymerisation of vegetable oils, the IV decreases. For example, in the case of soybean oil the IV decreases from initial values of 128–131 gI_2/100 g to 60–70 gI_2/100 g. The lower IV of polymerised oils is not problematic because the OH# of polyols suitable for flexible foams is low.

In general, because polymerised oils have ester bonds and residual double-bonds, all the methods used for hydroxylation of vegetable oils involving ester or double-bonds can be applied to polymerised oils. As an immediate consequence, higher-MW structures containing hydroxyl groups are obtained, which are suitable for preparation of flexible PUF.

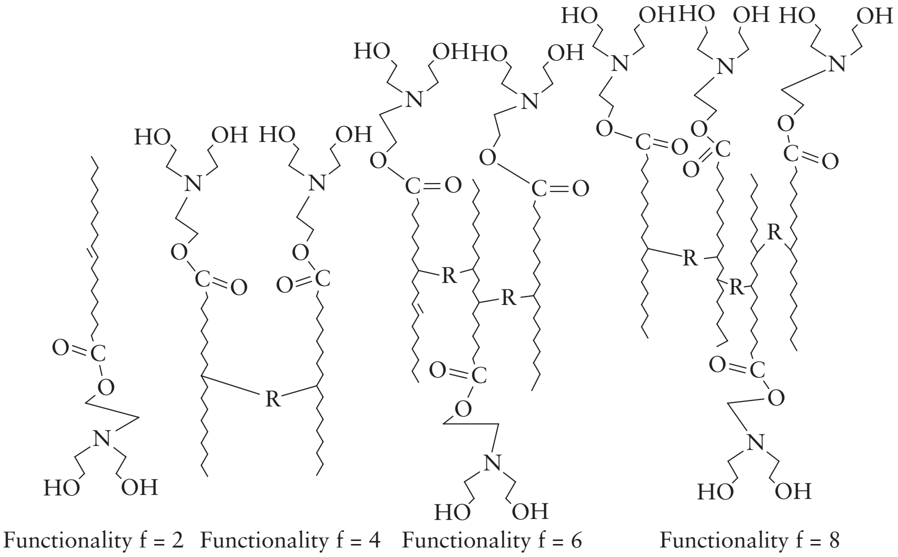
Thus, by epoxidation of thermal- or cationic-polymerised oils followed by ring-opening of epoxy groups with alcohols or with hydrogen, or by hydroformylation followed by hydrogenation of resulting polyaldehydes or by thiol-ene reaction with 2-mercaptoethanol, high-MW polyols suitable for flexible PUF with a convenient OH# of 28–60 mg KOH/g can be obtained.

Unfortunately, the polyols prepared from polymerised vegetable oils are very hydrophobic and sometimes, during foaming, they generate an undesired ‘boiling effect.’ The latter is due to the escape of CO_2 formed by the reaction of isocyanates with water incompatible with hydrophobic polyol; the liquid–gas in the system is stabilised poorly by a silicone surfactant and the foam collapses. Introduction of polar groups (epoxy, amide, tertiary amine, ether) into the structure of polyols from polymerised oils circumvents the boiling effect.

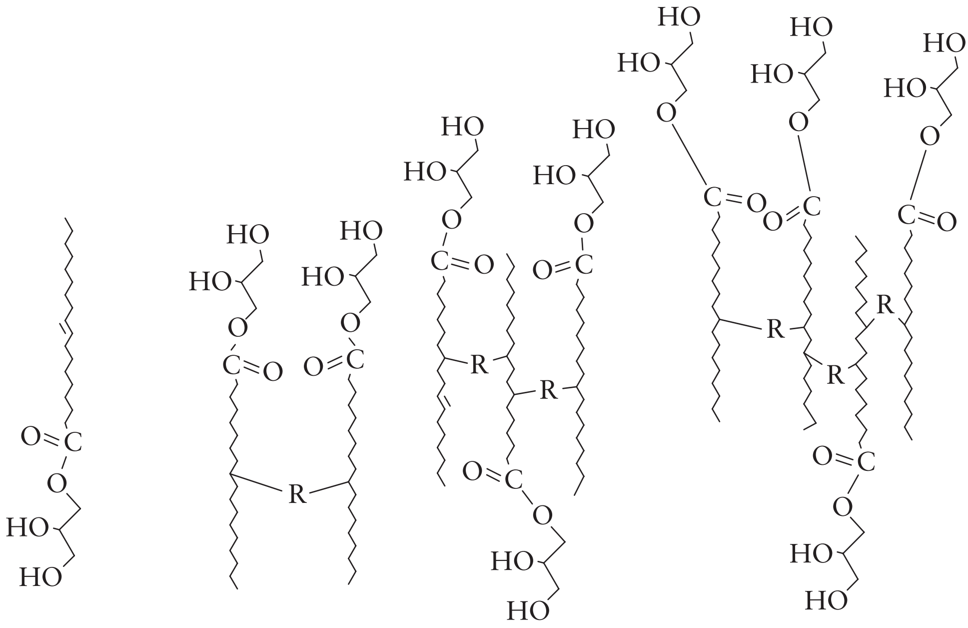
The possible structures of polyols resulting from the reaction of polymerised oils with DEOA, TEOA and glycerol are presented in **Structures 7.20**, **7.21** and **7.22**, respectively. The products of the polymerised oils amidation with DEOA or transesterification with TEOA or glycerol are a mixture of polyols of functionalities of 2–8 hydroxyl groups /mol and OH# of 270–320 mg KOH/g. Rigid PUF with good physical–mechanical properties can be prepared using polyols having the **Structures 7.20–7.22** by reaction with ‘crude’ MDI or polymeric MDI (PAPI).



Structure 7.20 Mixtures of amidic polyols resulting from amidation of polymerised soybean oil with DEOA



Structure 7.21 Mixtures of polyols resulting from transesterification of polymerised soybean oil with TEOA

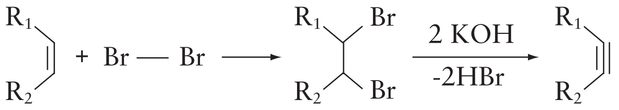


Structure 7.22 Mixtures of polyols resulting from transesterification of polymerised soybean oil with glycerol

7.3.3.10 Polyols from Fatty Acids with Triple-Bonds [200–202]

Most vegetable oils have fatty acids with double-bonds (e.g., oleic acid, linoleic acid, linolenic acid, ricinoleic acid). Interestingly, some plants produce fatty acids with triple-bonds, such as stearolic acid (9-octadecynoic acid, which is similar to oleic acid in having a triple-bond instead of a double-bond), which arises from the seed fat of *Santalaceae*. Also, tariric acid (6-octadecynoic acid) arises from the seed fat of *Simaroubiaceae,* and santalbic acid arises from the seed fat of *Santalum album*.

One way to prepare polyols is cyclotrimerisation of fatty acids with triple-bonds, followed by reduction of ester bonds to hydroxyl groups [200–202]. Natural fatty acids with triple-bonds are not readily available. Fortunately, fatty acids with triple-bonds can be prepared from fatty acids with double-bonds by bromination of a double-bond to a dibromo derivative (**Reaction 7.63**) and dehydrobromination of the dibromo derivative with aqueous alkali (**Reaction 7.64**) [201].



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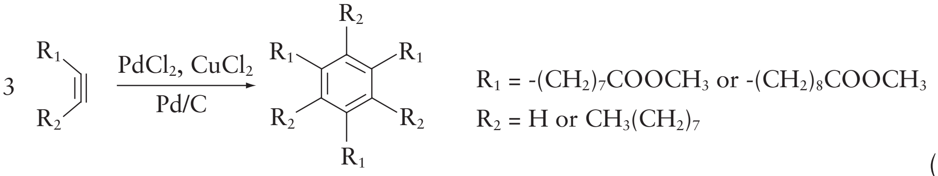
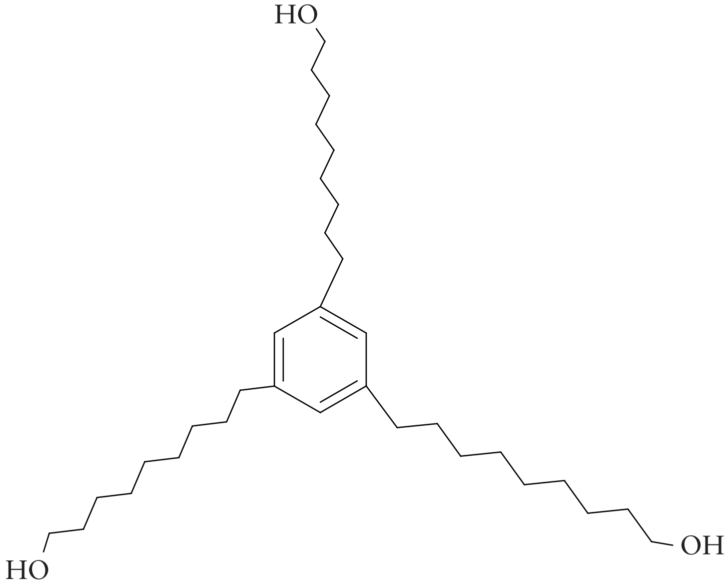


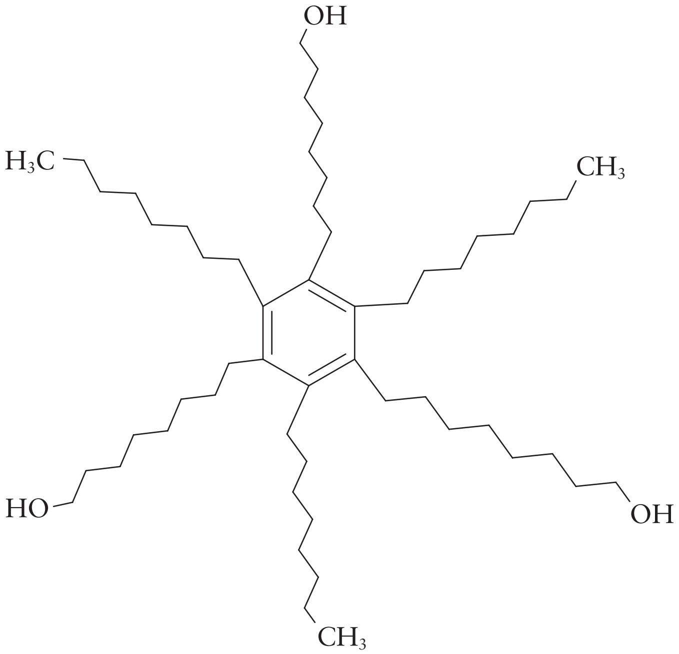
(7.64)

This reaction has been used to synthesise 10-undecylenic acid from 10-undecenoic acid and 9-octadecynoic acid from oleic acid. Both acids with triple-bonds were transformed in methyl esters by reaction with methanol and methyl ortoformate upon acid catalysis [201, 202]. Thus, methyl 10-undecynoate and methyl-9-octadecynoate were trimerised (general **Reaction 7.64**) by using $PdCl_2$-$CuCl_2$ and palladium/C-trimethylsililyl chloride as catalysts, respectively.

After trimerisation, the terminal methyl ester groups are reduced with $LiAlH_4$ in THF to terminal primary hydroxyl groups, resulting in bio-based polyols having aromatic and aliphatic structures. Thus, from methyl 10-undecynoate is formed 1,3,5-(9-hydroxynonyl) benzene (**Structure 7.23**) and from methyl 9-octadecynoate is formed 1,3,5-(8-hydroxyoctyl)-2,4,6-octyl benzene (**Structure 7.24**).



Structure 7.23 1,3,5-(9-Hydroxynonyl) benzene; OH# = 333 mg KOH/g



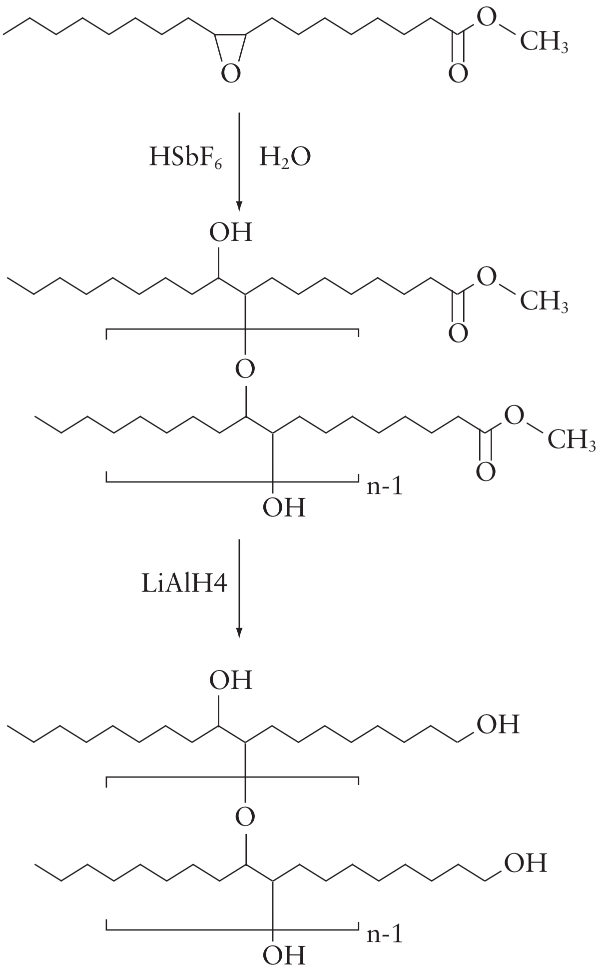
Structure 7.24 1,3,5-(8-Hydroxyoctyl)-2,4,6 octyl benzene; OH# = 210 mg KOH/g

From polyols with **Structures 7.23** and **7.24**, using 1,4-BD as a chain extender and MDI as coupling agent, cast PU have been obtained with ≈50% hard segments and a T_g = 58–61 °C.

Due to aromatic content, the polyols obtained by trimerisation of fatty acid esters with triple-bonds followed by reduction are potential polyols for high-performance rigid PUF.

7.3.3.11 Polyols from Polymerised Epoxidised Fatty Acids Esters [202–205]

EMO is an interesting bio-based monomer. By cationic ROP of EMO with $HSbF_6$ (0.5%) as catalyst, at RT, followed by reduction of ester bonds with $LiAlH_4$, bio-based polyols with linear and cyclic structures can be prepared [203] (**Reaction 7.65**).



(7.65)

The MW of these resulting polyols prepared with $HSbF_6$ catalyst is relatively low (≤1,200 Da).

By using ionic-coordinative catalysts, such as tetraisobutylaluminoxane or Vandenberg catalysts $[(CH_3CH_2)_3Al/H_2O]$, higher-MW polyols (≤9,000 Da) can be obtained.

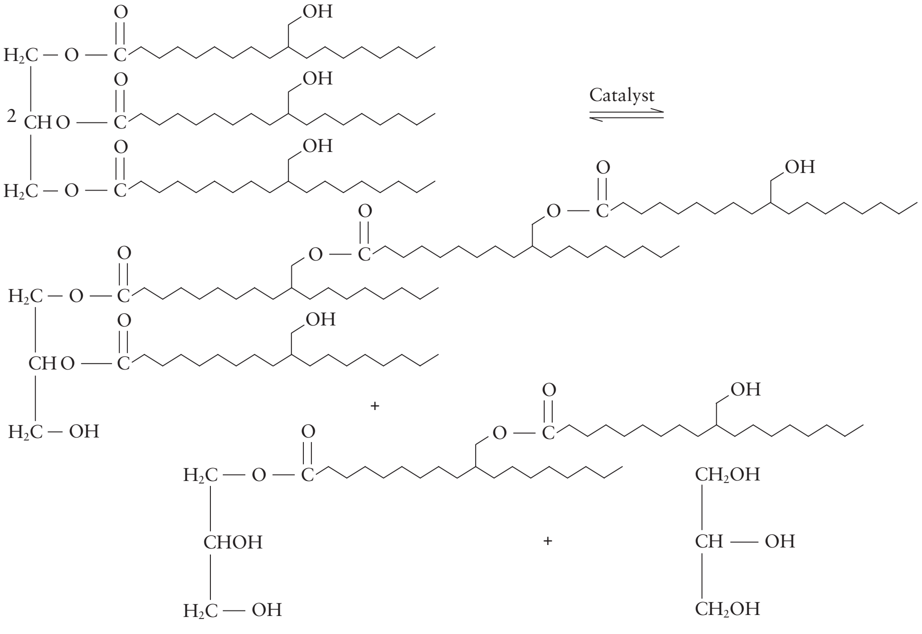
Segmented and non-segmented PU elastomers with good physical–mechanical properties have been prepared from the aforementioned polyols based on epoxy methyl oleate using MDI or L-lysine diisocyanate as coupling agents and 1,3-propanediol as a chain extender.

7.3.4 High-Molecular-Weight Bio-based Polyols from Low-Molecular-Weight Bio-based Polyols

7.3.4.1 Self-Condensed Polyols

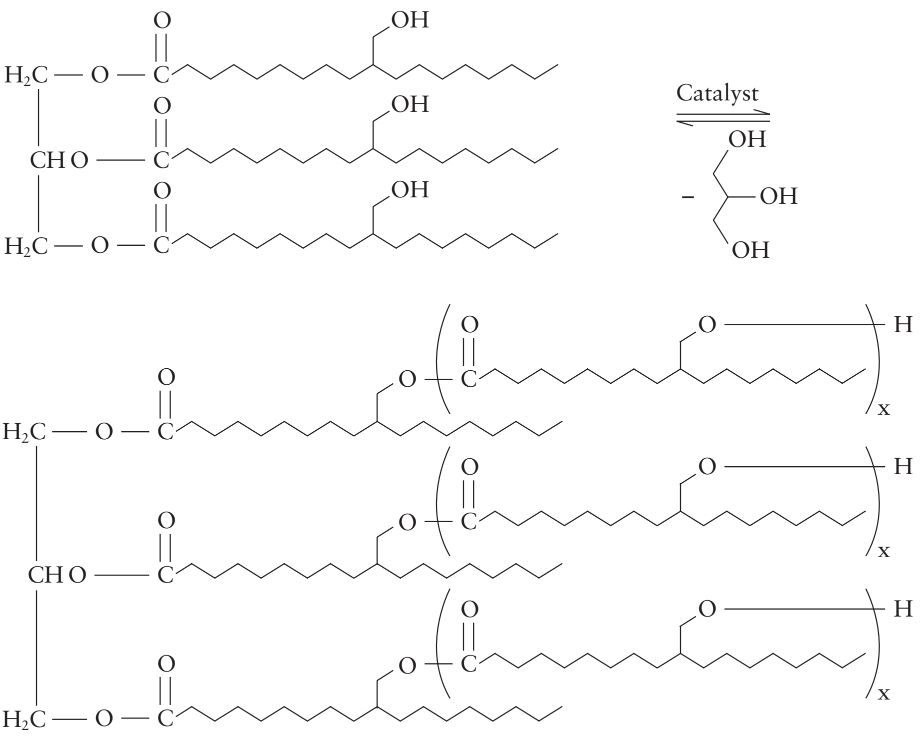
Castor oil and vegetable oil polyols prepared by ring-opening of epoxy groups of epoxidised oils with alcohols or by hydroformylation have ester bonds and hydroxyl groups in the same structure.

By heating such types of polyol at 190–220 °C in the presence of a transesterification catalyst, an equilibrium between triglycerides, diglycerides, monoglycerides and glycerol occurs through interaction of hydroxyl groups and ester groups (**Reaction 7.66**).



(7.66)

If the glycerol is removed by continuous distillation at 200–220 °C at 1–2 mmHg, the equilibrium is shifted to formation of a high-MW polyol (‘self-condensed polyol’). This reaction is analogous to formation of high-MW polyesters by polycondensation of methyl esters of hydroxyl fatty acids with removal of methanol, but instead with removal of glycerol (**Reaction 7.67**). Transesterification catalysts that can be used include potassium methoxide, stannous octoate, dibutyltin dilaurate, titanium isopropoxide, or titanium butoxide.



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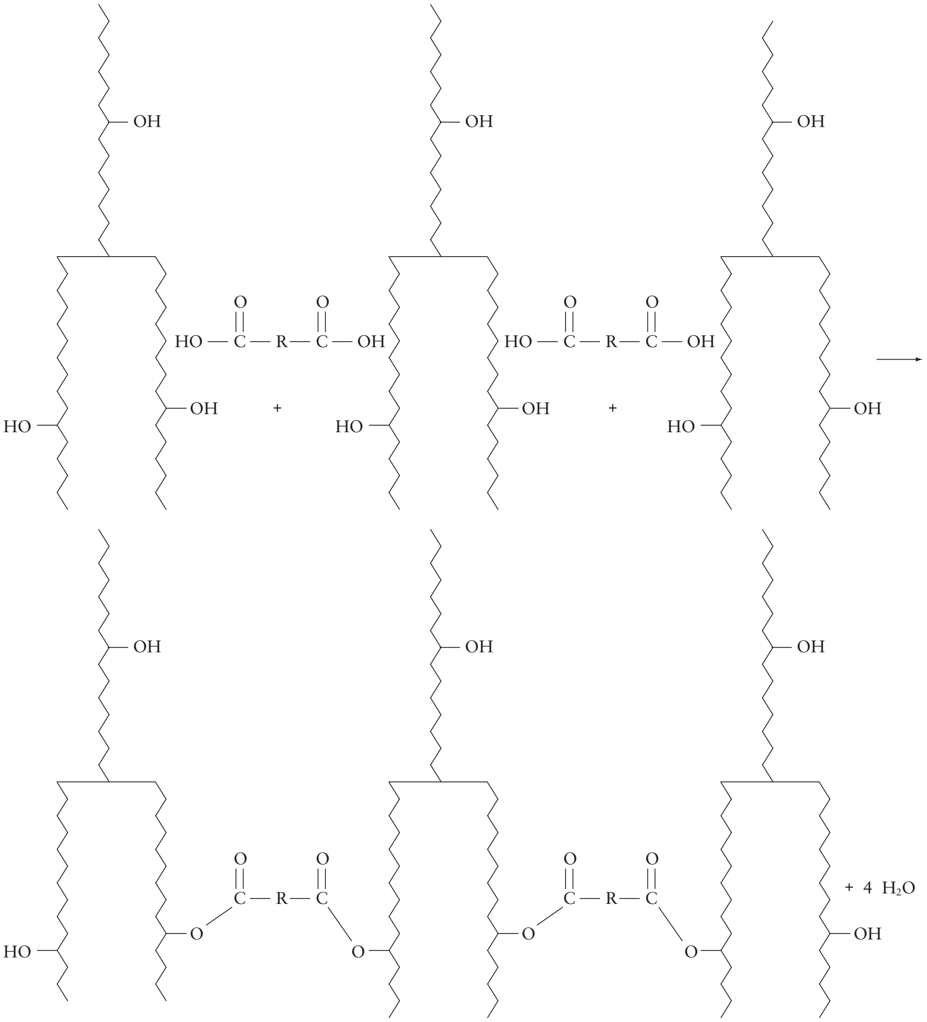
Hydroformylation polyols and polyols by ring-opening of epoxy groups of epoxidised oils with methanol lead to very-high-viscosity polyols in spite of a very convenient OH# (40–60 mg KOH/g). Only from castor oil or from copolymers of castor oil with other vegetable oil polyols can self-condensed polyols of low viscosity be obtained, which are useful for preparation of flexible PUF.

Self-condensed polyols can be used for preparation of cast PU elastomers, coatings, adhesives, and sealants.

7.3.4.2 Bio-based Polyols by Chain Extension [171]

Castor oil and bio-based polyols prepared by ring-opening of epoxy groups with alcohols, carboxylic acids or hydrogen, by hydroformylation, by ozonolysis, or by thiol-ene reactions have an OH# = 160–230 mg KOH/g corresponding to an EW of = 240–350. The OH# of these polyols is too high and, as a consequence, these polyols are suitable for semi-rigid or rigid PUF, but not for flexible PUF. A polyol is suitable for elastic PU (elastomers, flexible foams) if the OH# is ≈28–60 mg KOH/g and the average EW is ≈1,000–2,200.

A simple way to prepare a high-MW polyol starting from the previously mentioned bio-based polyols of OH# 160–230 mg KOH/g is by chain extension with diacids (succinic, adipic, phthalic, azelaic, and sebacic) or with dicarboxylic acid anhydrides (succinic anhydride, MA, phthalic anhydride). As a variant of dicarboxylic acids, their dimethylesters can be used. This type of chain extension is a polycondensation reaction between diacids (or dimethyl esters of diacids) with hydroxyl groups of bio-based polyols of OH# = 160–230 mg KOH/g. To avoid crosslinking reactions, the hydroxyl groups are always in excess. As a consequence of this type of condensation reaction between diacids and the previously mentioned bio-based polyols, the MW increases, the OH# decreases, and hydroxyl functionality increases (**Reaction 7.68**).



(7.68)

For example, if an initial bio-based polyol with three hydroxyl groups/mol (3 mol) and a diacid (2 mol) is used, a polyol of higher-MW and of average functionality of 5 OH groups/mol is obtained. Polyols with a functionality of ≈3 hydroxyl groups/mol are preferred for standard flexible PUF, so two hydroxyl groups from the new structure are blocked with monofunctional compounds (acetic anhydride, phenylisocyanate, methyl esters of monocarboxylic acids). The preferred compound is acetic anhydride.

Thus, starting from a bio-based polyol of MW = 1,100 (3 mol) and AA (2 mol), an extended polyol of MW ≈3,500 and OH# = 80 mg KOH/g is obtained. By blocking two hydroxyl groups with acetic anhydride, a trifunctional polyol of OH# ≈45–46 mg KOH/g is obtained, which is ideal for slabstock flexible PUF.

The lowest-viscosity and better-processable polyols are obtained by chain extension of castor oil with AA (or dimethyl adipate) or phthalic anhydride.

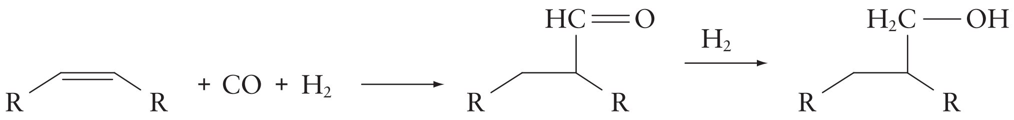
Chain-extended polyols can be used in mixtures with petrochemical polyether polyols or polyester polyols at 20–50% for production of slabstock flexible PUF while preserving most of their physical–mechanical properties: good compression strength, tensile strength, and tear strength. Sometimes, a poor-compression set is obtained and, in this situation, the polyols are suitable for non-foam PU applications (cast PU elastomers, elastic adhesives).

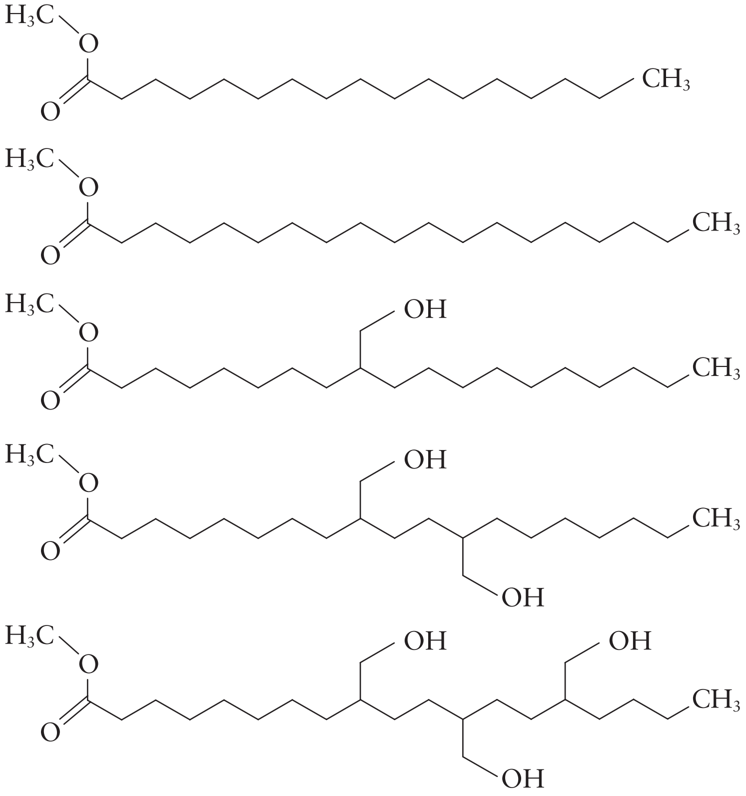
A variant of polyols by chain extension has been described for preparation of honey-bee polyols for flexible foams (**Volume 2**, **Section 7.3.3.5**). The chain extension was carried out with MA [150, 151].

7.3.4.3 Bio-based Hyperbranched Polyols for Flexible Polyurethane Foams [206, 207]

Soybean oil has ≈4.5–4.6 double-bonds per triglyceride unit. Methyl soyate is a mixture of methyl esters of fatty acids from the composition of soybean oil, such as methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate. If methyl soyate is hydroformylated followed by hydrogenation of the resulting polyaldehydes, a mixture of methyl esters of fatty acids with and without hydroxyl groups is obtained (**Structure 7.25**).

Methyl esters of palmitic acid and stearic acid are monofunctional monomers, and are chain stoppers in polycondensation reactions. Fortunately, the concentration of these monofunctional monomers in methyl soyate is low (≈15–18%).





Structure 7.25 Fatty acid methyl esters resulting from hydroformylation followed by hydrogenation of methyl soyate

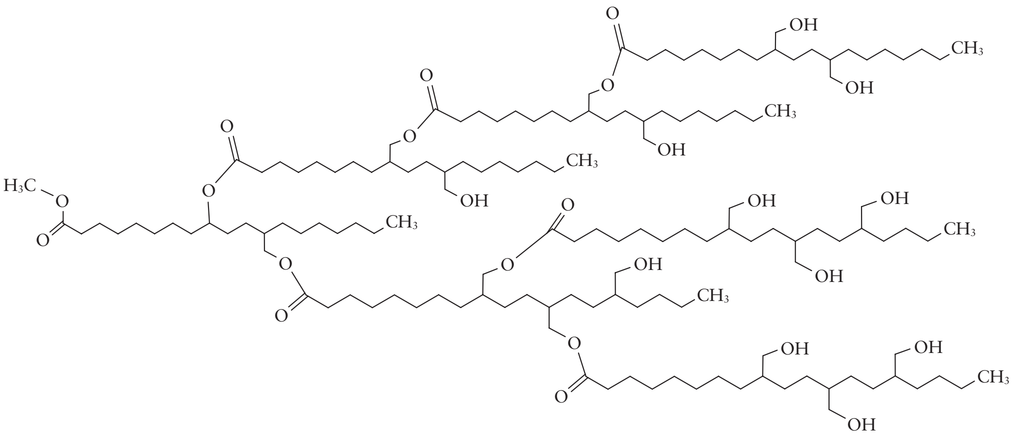
Hydroformylated methyl oleate is a bifunctional AB monomer in polycondensation reactions and acts as a chain extender. Hydroformylated methyl linoleate is a trifunctional AB_2 monomer and hydroformylated methyl linolenate is a tetrafunctional AB_3 monomer, and both act in polycondensation reactions as branching agents. As stated above, linoleic acid plus linolenic acid in soybean oil represent ≈60% from all fatty acids, and oleic acid ≈25%. As an immediate consequence, we expect the fatty acid methyl esters with one, two or three hydroxyl groups to have similar concentration to the corresponding non-formylated fatty acid methyl esters.

In hydroformylated methyl soyate we have methyl esters and hydroxyl groups in the presence of specific catalysts at 180–220 °C. Hence, a polycondensation reaction is carried out with the formation of a polyester, and methanol as a byproduct.

Due to the high concentration of trifunctional hydroformylated linoleic acid methyl ester and presence of tetrafunctional hydroformylated linolenic acid methyl ester, the resulting polyester is hyperbranched (**Structure 7.26**).

Thus, after 3.25 h of polycondensation, the OH# decreases from 230 mg KOH/g to 115 mg KOH/g, whereas the viscosity of the polyol is 1,700 mPa.s at 25 °C with an average functionality of 5.4 OH groups/mol [206].

After 4.5 h of polycondensation, the OH# decreases to 97 mg KOH/g, whereas the viscosity at 25 °C increases to 13,000 mPa.s and average functionality increases to 12.4 OH groups/mol. After 5.5 h, the OH# decreases to 86.6 mg KOH/g, viscosity at 25 °C increases to 32,000 mPa.s, and functionality increases to 23.2 OH groups/mol [206].



Structure 7.26 Idealised structure of a hyperbranched polyol from hydroformylated/hydrogenated methyl soyate of ≈11 OH groups/mol

These high-functionality hyperbranched polyols have been used as additives to petrochemical polyether polyols for increased hardness of flexible PUF. Flexible foams with acceptable properties have been obtained using ≤50–75% of these hyperbranched bio-based polyols in a mixture with 25–50% petrochemical polyether polyols. As expected, in spite of the improvement in hardness, some properties (e.g., elongation, tear strength) of flexible foams based on these hyperbranched polyols have deteriorated.

Most importantly, by using the natural distribution of double-bonds in polyunsaturated vegetable oils, it is possible to prepare high-functionality hyperbranched bio-based polyols that can be used for specific applications (e.g., replacement for graft polyols in high-indentation, load-deflection, flexible PUF).

7.3.4.4 Polyols by Alkoxylation of Low-Molecular Weight Bio-based Polyols [208–214]

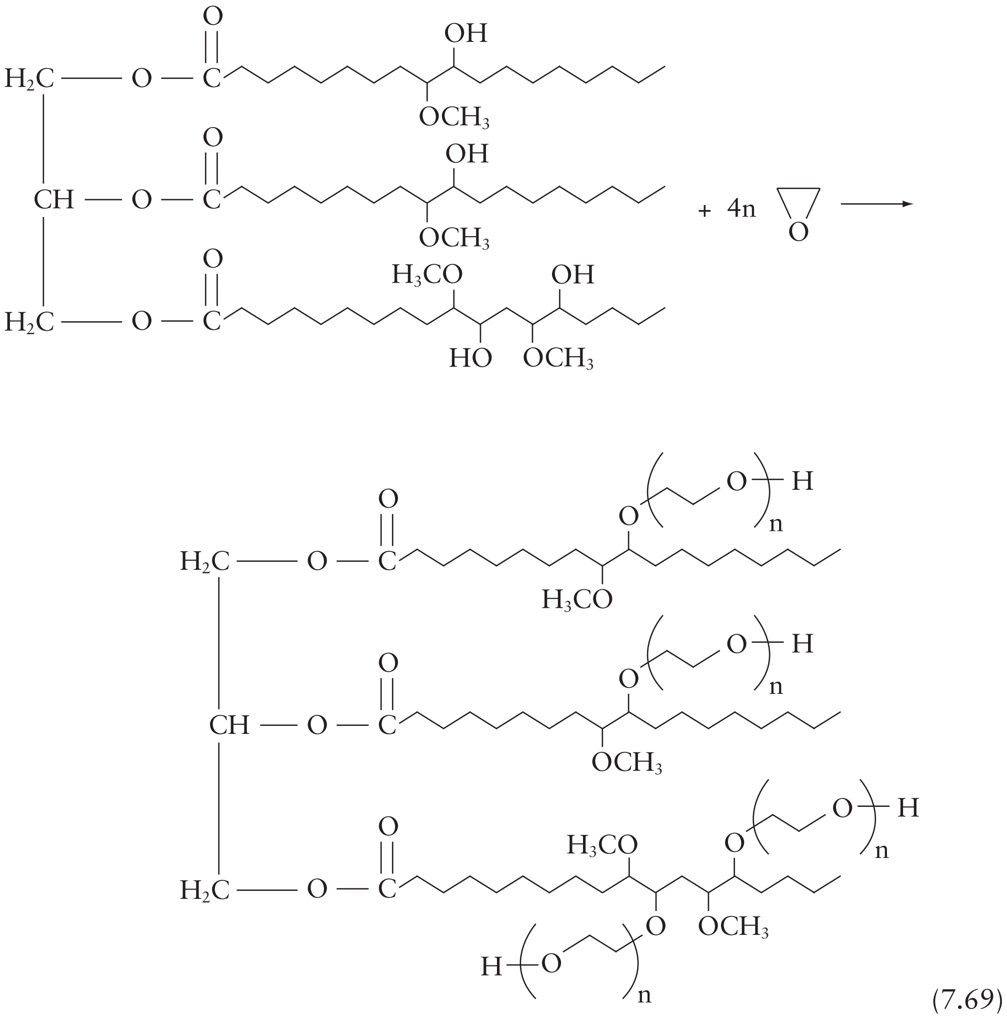
In **Volume 2**, **Section 7.3.3**, the synthesis of bio-based polyols starting from vegetable oils by several methods was presented, such as: epoxidation of oils followed by ring-opening with hydrogene active compounds; hydroformylation followed by hydrogenation of resulting polyaldehydes; hydrogenation of epoxidised oils; ozonolysis of oils in the presence of polyols. All of the bio-based polyols produced by the aforementioned synthetic pathways have an OH# = 170–230 mg KOH/g, which is too high for preparation of flexible PUF. Fortunately, these bio-based polyols have been used as starters for preparation of high-MW polyether polyols by polymerisation of PO, EO and THF initiated by the hydroxyl groups of these polyols. A similar structure to the previously mentioned bio-based starters is castor oil (a natural polyol with an OH# = 160–163 mg KOH/g).

In several industrial processes, polymerisation of PO or EO initiated by polyols, such as glycerol or TMP, are catalysed by alkali hydroxides (e.g., KOH). Unfortunately, in the presence of bio-based polyols with a triglyceride structure, the ester bonds react with KOH, thereby transforming into potassium salts of fatty acids with lower catalytic activity. Using alkali hydroxides as catalysts for alkoxylation of bio-based polyols enables the alkylene oxide (PO or EO) to be inserted in two positions: between glycerol and fatty acids, and by polyaddition to hydroxyl groups.

To preserve the favourable initial triglyceride structure for alkoxylation of bio-based polyols, catalysts that do not affect ester bonds have been used. These catalysts are cationic catalysts (BF_{3}.dethylether complex or HBF_4) working at low temperatures, and DMC catalysts.

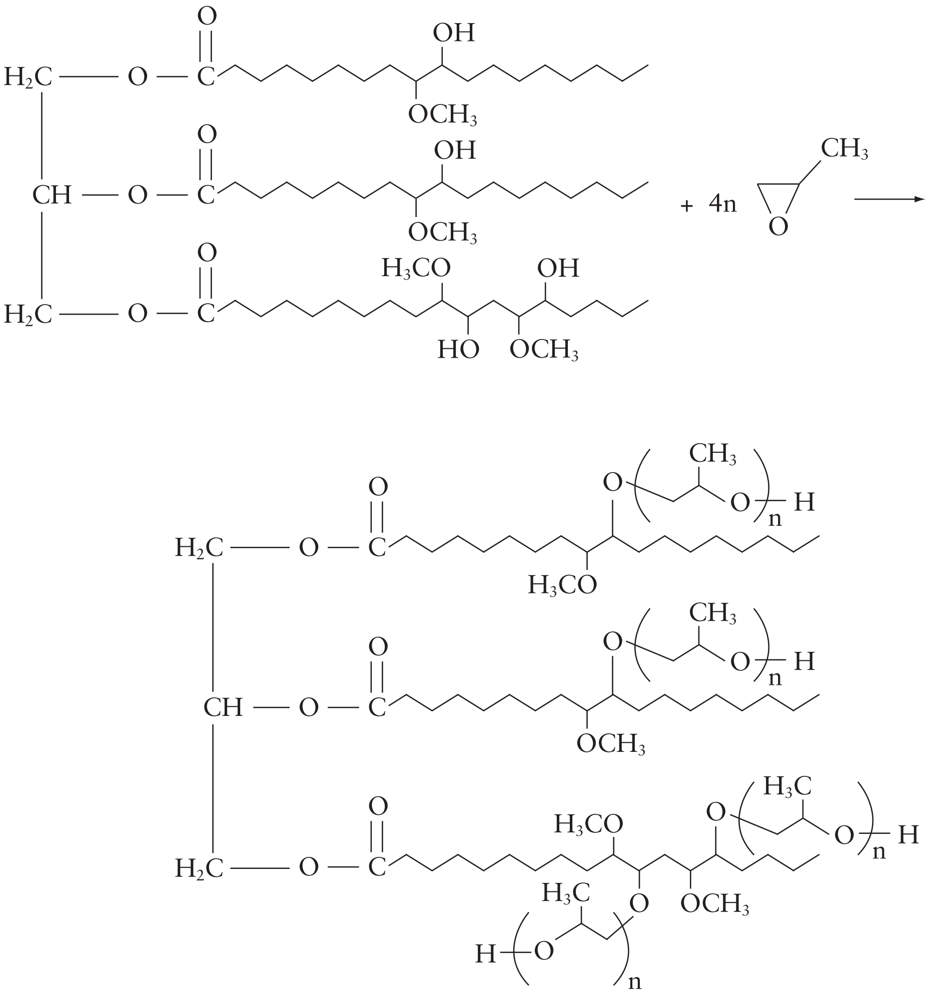
Upon ethoxylation of bio-based polyols containing secondary hydroxyl groups with low reactivity (including castor oil), in the presence of HBF_4 as a catalyst at 35–45 °C, highly reactive polyols with high primary hydroxyl content are obtained readily (**Reaction 7.69**) [208, 209]. The triglyceride ester bonds are preserved due to the low temperature used [208].

By ethoxylation of vegetable oil polyols using the method mentioned previously, polyols with 15–20% EO content and primary hydroxyls of 30–70% are prepared. These polyols have a relatively high OH# and can be used for coatings, adhesives, sealants, and cast PU, but not for flexible foams.



(7.69)

To prepare a polyol for flexible foams, it is necessary to add more alkylene oxides to decrease the OH# from 160–230 mg KOH/g to 28–60 mg KOH/g (which are the OH# suitable for flexible polyols). These types of polyols contain 67–80% alkylene oxides.



(7.70)

Two methods have been used in propoxylation of a soybean polyol (**Reaction 7.70**): cationic polymerisation of PO at lower temperatures (-20 to -5 °C) in methylene chloride as a solvent, and coordinative polymerisation catalysed by DMC catalysts [210].

Utilisation of lower negative temperatures and very slow addition of PO to a reaction mass comprising vegetable oil polyol, methylene chloride as solvent, and catalyst (0.2–0.3% HBF_4) permits preparation of high-MW hybrid bio-based-petrochemical polyether polyols practically without formation of cyclics. A solvent is used because at negative temperatures the viscosity of the polyol increases substantially, and solutions of polyol in methylene chloride have low viscosities. Methylene chloride is considered to be an excellent solvent for cationic polymerisation [210].

The catalysts used for cationic polymerisation (BF_3 or HBF_4) are removed from the polyether by treatment with anion exchangers, or with solid basic inorganic compounds such as calcium oxide or calcium hydroxide followed by filtration and solvent distillation.

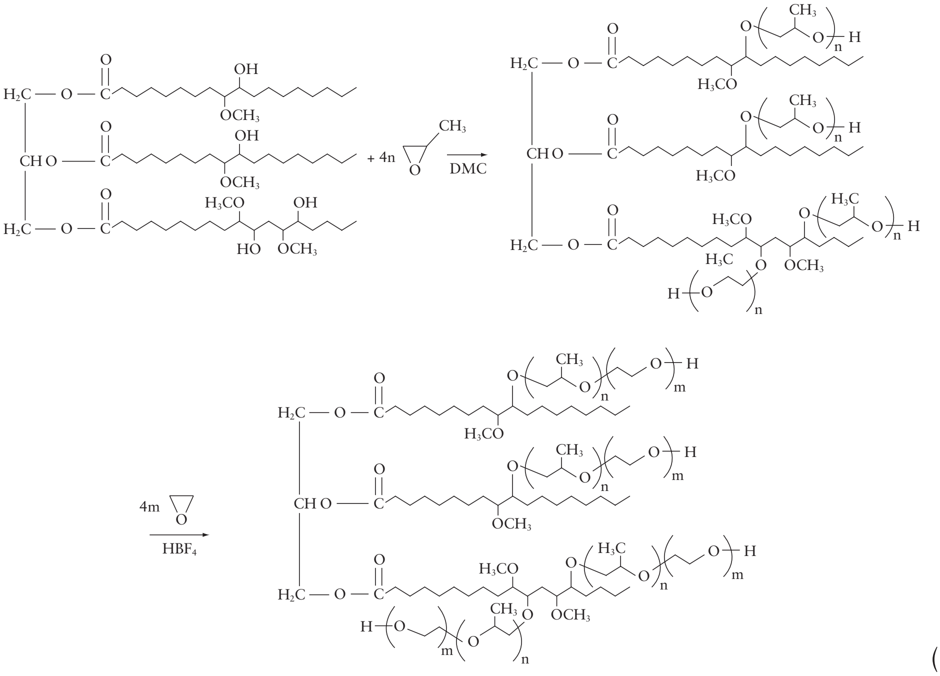
Cationic polymerisation of alkylene oxides initiated by soy polyols permits various polymers to be prepared: homopolymers of PO, random copolymers of PO–EO (by addition of a mixture of PO and EO), and block copolymers of PO–EO (by addition of PO followed by addition of EO) [210].

Cationic polymerisation of PO and EO initiated by soybean polyols permits polyether polyols of MW = 3,000–5,000 and bio-based content of 20–33% to be obtained, which are suitable for preparation of flexible PUF.

Vegetable oil polyols can be used as starters for preparation of high-MW polyethers by propoxylation in the presence of a DMC catalyst at 120–130 °C [210–214]. The ester bonds of triglyceride are preserved in the presence of a DMC catalyst. Due to the low concentration of DMC catalyst used (30–50 ppm), a purification step for the polyether is not necessary. Using this method, homopolymers of PO and random copolymers of PO–EO with MW of 3,000–6,000 can be prepared with high reaction rates and in short reaction times, but not block copolymers of PO–EO. Homopolymers of PO (**Reaction 7.70**) and random copolymers of PO–EO are suitable for slabstock flexible PUF.

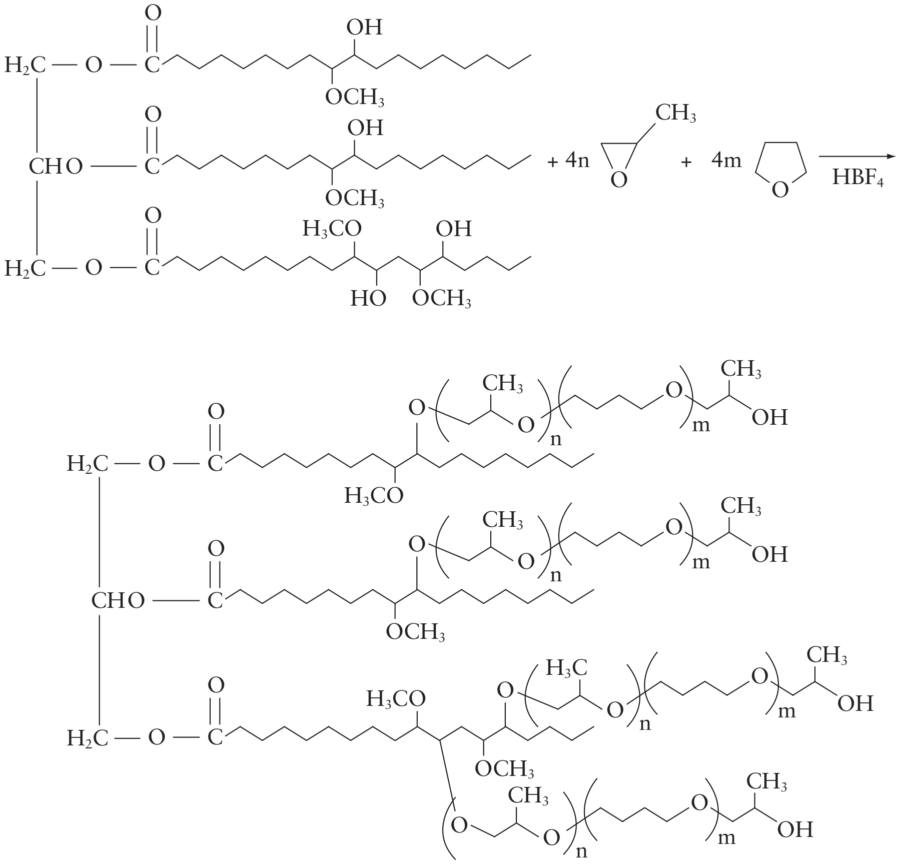
Block copolymers of PO–EO can be prepared in two steps. In the first step, a homopolymer of PO is prepared, initiated by vegetable oil polyol or castor oil. To the synthesised homopolymer of PO is added EO in the presence of a basic catalyst (KOH or potassium methoxide), followed by purification for removal of undesired potassium ions.

A novel variant of the synthesis for block copolymers of PO–EO has been carried out in acidic catalysis [209] (**Reaction 7.71**). Thus, after addition of PO, the homopolymer of PO synthesised with a DMC catalyst is cooled to 35–45 °C. HBF_4 is added as an acidic catalyst (0.2–0.3%), and EO is added slowly at 35–45 °C. The block copolymer PO–EO is suitable for fabrication of moulded flexible PUF, especially for car seating and furniture.



(7.71)

By cationic copolymerisation of PO or EO with THF in the presence of BF_3 or HBF_4 as a catalyst, initiated by vegetable oil polyols at RT, the liquid random copolymer PO–THF is obtained [210], which is suitable for flexible PUF (**Reaction 7.72**).



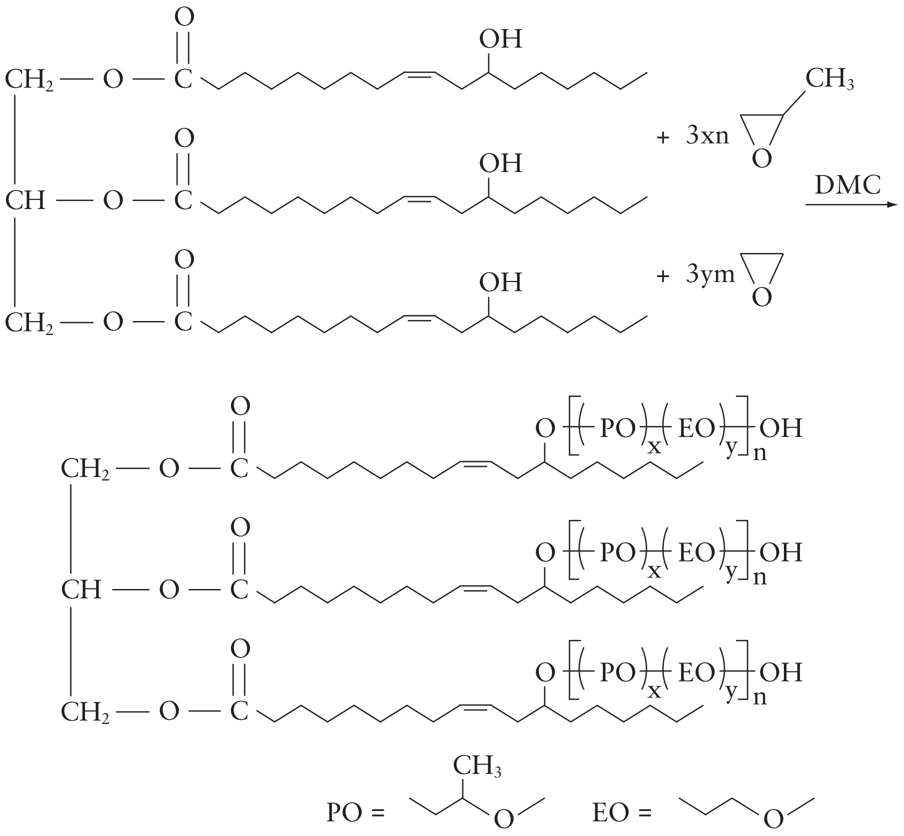
(7.72)

As a reminder, THF can be prepared from renewable raw materials: from furfural by decarbonylation followed by hydrogenation, or by hydrogenation of bio-succinic acid followed by dehydration of the resulting 1,4-BD (**Volume 2, Section 7.1.1.1**). The terminal groups in random copolymers THF-alkylene oxides are always from alkylene oxide and not from THF (**Volume 1, Chapter 7**) [19].

Petrochemical polyether polyols are prepared starting from glycerol of MW = 92. The described hybrid bio-based-petrochemical polyether polyols start from a vegetable oil polyol of MW = 1,000–1,200, and in that way, a substantial economy of materials, energy, and reaction time is enabled.

By alkoxylation of castor oil with PO (83–90%) and EO (10–17%) in the presence of DMC catalysts, polyols of MW 3,000–3,500, OH# = 50–56 mg KOH/g, and viscosity of 600–750 mPa.s are obtained at 25 °C [211, 212] (**Reaction 7.73**). A variant is to alkoxylate castor oil with a mixture of PO–ethylene and oxide-glycerol (1.5%), which leads to a mixture of a castor oil–glycerol-initiated polyol [212].

Polyols based on castor oil lead to excellent slabstock flexible PUF [210–212]. These castor oil polyols have terminal secondary hydroxyl groups. If the content of EO in the mixture of PO–EO is higher (e.g., 45–50%), polyols with slightly higher primary hydroxyl content (25–30%) are obtained [213].



(7.73)

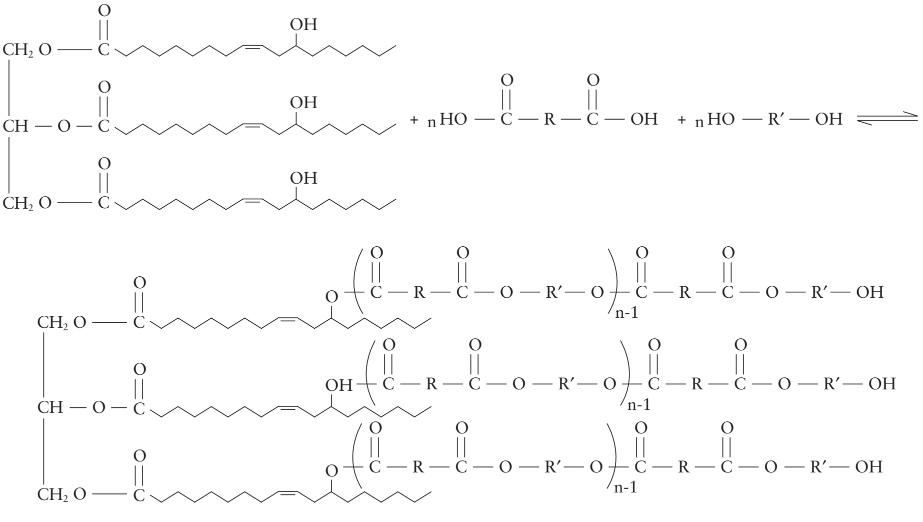
Alkoxylation of air-blown soybean polyols with PO or a PO–EO mixture in the presence of a DMC catalyst enables bio-based polyether polyols to be obtained [214], which are suitable for preparation of flexible PUF.

7.3.4.5 High-Molecular-Weight Polyesters from Low-Molecular-Weight Bio-based Polyols [215–217]

Branched polyesters for flexible foams are prepared by polycondensation of diols with diacids, initiated by glycerol or TMP. By polyesterification of diols with diacids initiated by vegetable oil polyols instead of glycerol, hybrid bio-based-petrochemical polyester polyols are obtained [215] (**Reaction 7.74**). By using renewable diols (e.g., 1,3-propanediol) and renewable diacids (succinic acid, azelaic acid, sebacic acid), and vegetable polyols as starters, 100% bio-based polyester polyols are obtained. Some starters that can be used include castor oil, polyols by ring-opening of epoxy groups of epoxidised oils with alcohols or hydrogen, polyols by hydroformylation, and polyols by ozonolysis. Polyester polyols based on castor oil with the aforementioned structure have the lowest viscosity [215].

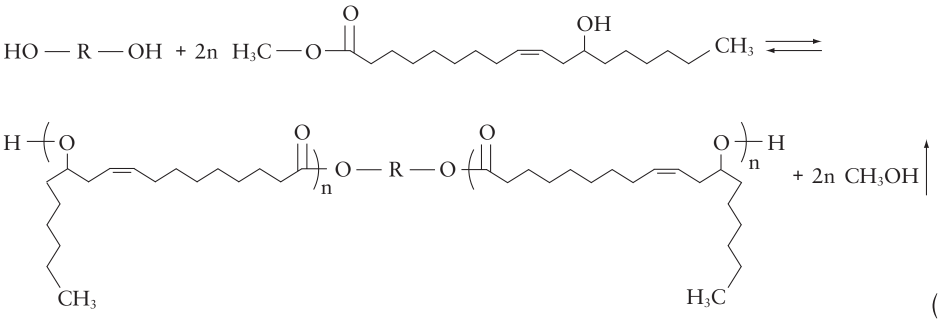
Diols commonly used include EG, DEG, polypropylene glycol (PPG), and 1,4-BD. Diacids include AA (used most often), succinic acid, and azelaic acid. Hydroxyacids, such as ricinoleic acid or lactic acid, can be used instead of diols and diacids.

The synthetic procedure is relatively simple. A vegetable oil polyol, diol, diacid and the catalyst (tin or titanium catalyst) are charged in a polyesterification reactor. The polyesterification reaction is carried out by slowly increasing the temperature from 160 °C to 200–220 °C, with continuous removal of water resulting from the reaction. A slow flow of nitrogen and moderate vacuum help the elimination of reaction water. Dimethyl esters of diacids can be used instead of diacids and, in this case, methanol is eliminated instead of water from polyesterification.



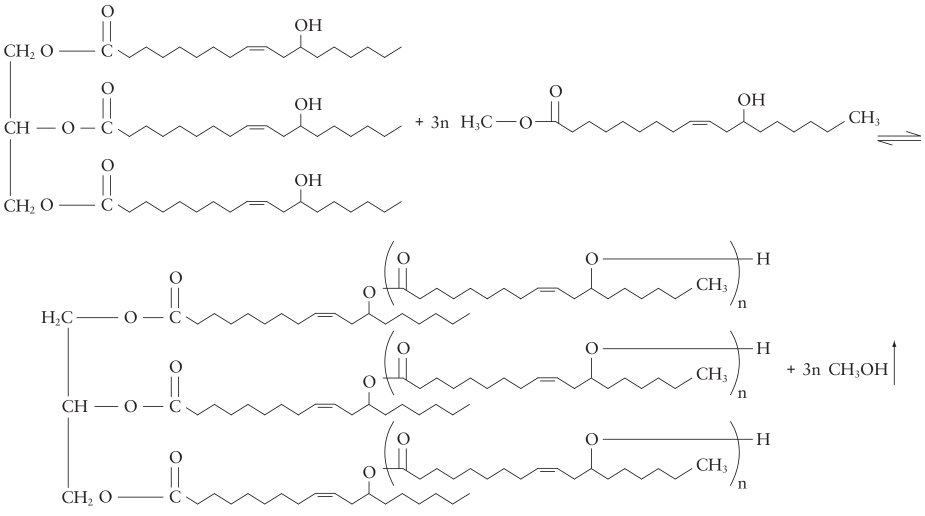
(7.74)

Bio-based polyester polyols for elastic PU (PU elastomers and flexible foams) can be prepared by polycondensation of methyl ricinoleate (or ricinoleic acid), initiated by diols (DEG, HD) [216] (**Reaction 7.75**) or polyols, such as glycerol, TMP or a vegetable oil polyol (e.g., castor oil). Catalysts typically used are Sn(II), Sn(IV) or Ti(IV) compounds (stannous octoate, dibutyltin dilaurate, titanium isopropoxide).



(7.75)

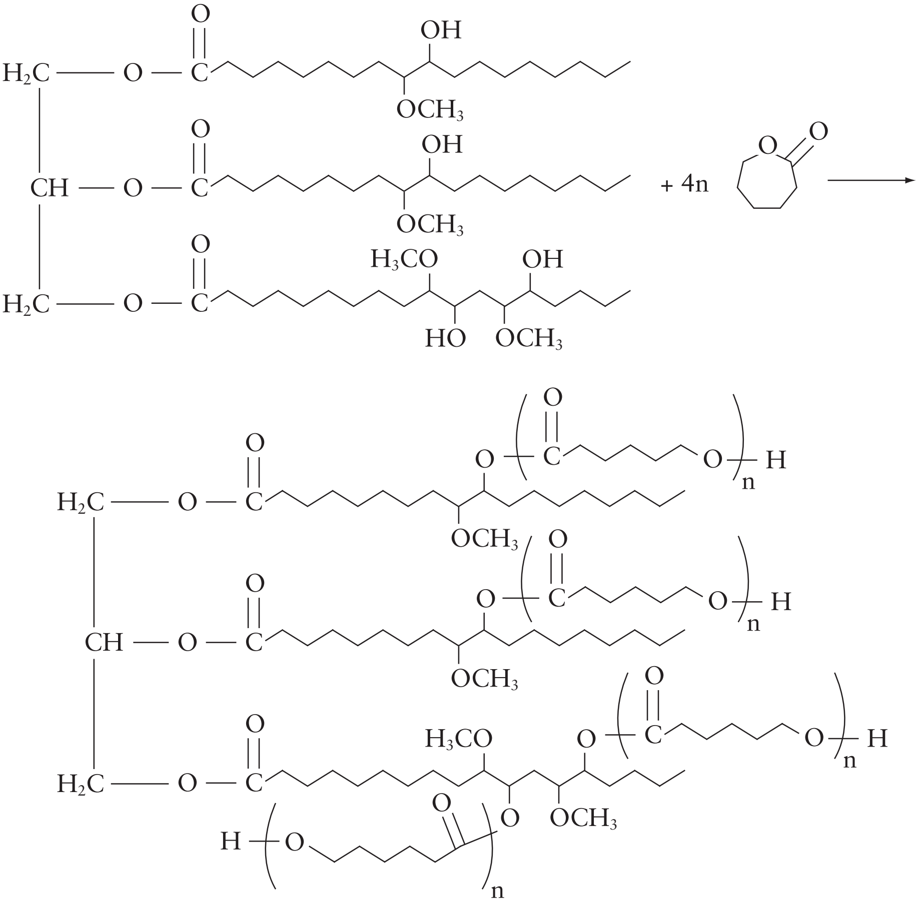
By polycondensation of ricinoleic acid (or methyl ricinoleate) initiated by castor oil (**Reaction 7.76**), a 100% bio-based polyol is obtained that is suitable for flexible PUF or cast PU elastomers. The resulting polyols are liquids with relatively low viscosity (1,000–3,000 mPa.s at 25 °C) with an OH# = 50–60 mg KOH/g [216–218].



(7.76)

Utilisation of ricinoleic acid or methyl ricinoleate as polycondensation catalysts leads to polyesters with much lower viscosity than those of polyesters from diols and saturated fatty acids (e.g., succinic acid, AA, sebacic acid, azelaic acid). A '*cis*' double-bond in ricinoleic acid is probably why low-viscosity polyester polyols are obtained. In contrast, hydrogenated ricinoleic acid (12-hydroxystearic acid) leads to high-viscosity polyester polyols.

Hybrid bio-based-petrochemical polyester polyols are obtained by ROP of CPL, initiated by vegetable oil polyols (**Reaction** 7.77), and catalysed by Sn(II), Sn(IV) or Ti(IV) compounds at 130–140 °C. Polyaddition of CPL to vegetable oil polyols with secondary hydroxyl groups (including castor oil) is a simple way to generate more reactive primary hydroxyl groups. As a function of the ratio between CPL and vegetable oil polyols, polyols with an OH# of 45–120 mg KOH/g can be obtained, which are suitable for preparation of PU coatings, adhesives, sealants, cast PU and PUF [171].

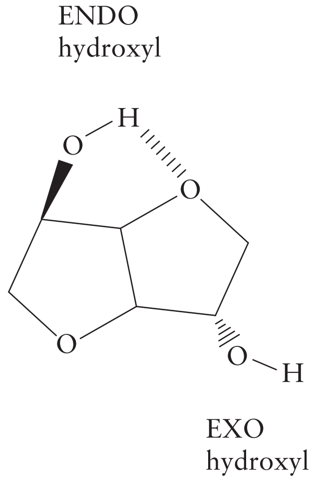


(7.77)

7.4 Bio-based Polyols Based on Other Natural Compounds

7.4.1 Bio-based Polyols from D-Isosorbide [219–225]

D-Isosorbide is a bio-based diol prepared by double-dehydration of sorbitol in the presence of acid catalysts [219–221, 223]. The source of D-isosorbide is corn starch, which is hydrolysed to glucose, followed by hydrogenation of glucose to sorbitol and finally by double-dehydration of sorbitol. D-Isosorbide has a special structure (**Structure** 7.27).



Structure 7.27 D-Isosorbide

D-isosorbide is a solid crystalline compound of MW = 146 and mp of 60–62 °C. The planes of THF rings are at 120° and one hydroxyl group is in the ENDO configuration (within the angle between THF rings) and the second is in the EXO configuration (outside of the angle between THF rings). The ENDO hydroxyl generates an intramolecular hydrogen bond with the O_2 atom of the neighbouring THF ring. As an immediate consequence, the ENDO hydroxyl is less reactive than the EXO hydroxyl in all the reactions of hydroxyl groups, including the reaction with isocyanates. D-Isosorbide is a rigid compound and, as an immediate consequence, increases the T_g of polymers containing D-isosorbide units.

D-isosorbide is a diol that can be used without transformation in some PU applications: as a chain extender for PU elastomers [224] and in a mixture (10–40%) with sucrose-based polyether polyols for preparation of rigid PUF with very good physical–mechanical properties [226]. D-isosorbide is perfectly soluble in polyether polyols based on sorbitol or sucrose.

The OH# of D-isosorbide is relatively high (768 mg KOH/g). By propoxylation or ethoxylation of D-isosorbide in the absence of any solvent, using as a catalyst tertiary amines (e.g., dimethylcyclohexylamine, TMG) or alkali alcoholates, at 110–115 °C, isosorbide-based liquid diols of low viscosity and lower OH# = 350–500 mg KOH/g can be prepared readily. The recommended molar ratio between PO (EO) per isosorbide is [PO]/[Isosorbide] = 2–3/1. These low-viscosity diols in mixture with high-functionality polyether polyols can be used for preparation of rigid PUF with good properties [226].

The synthesis and structures of isosorbide-based diols are presented in **Figure 7.23**.

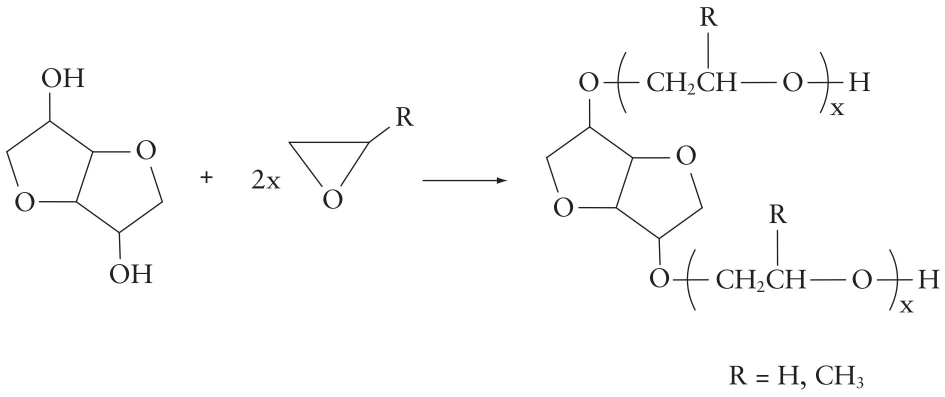


Figure 7.23 Synthesis and structure of polyether diols based on D-isosorbide

The best properties of rigid PU are obtained with polyols having higher functionalities (4–6 OH groups/mol). Isosorbide can be transformed in higher-functionality polyols by alkoxylation with glycidol (**Figure 7.24**) at 110–120 °C or with glycerine carbonate (**Figure 7.25**) at 170 °C, in the presence of a tertiary amine (TMG) or alkali alkoxides as a catalyst.

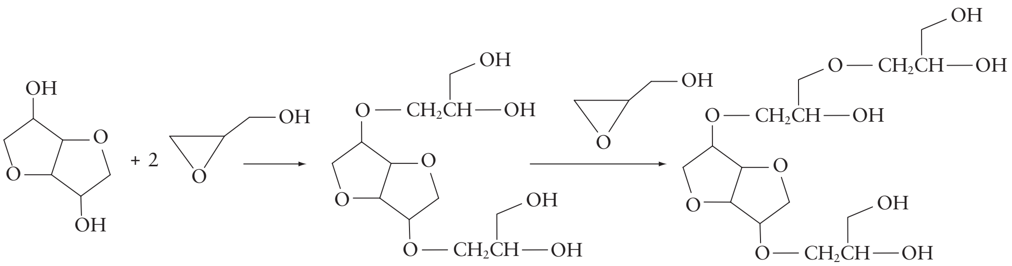


Figure 7.24 Synthesis of high-functionality polyols by the reaction of isosrbide with glycidol

Unfortunately, glycidol is an expensive compound and not readily available. Addition of glycerine carbonate to isosorbide leads to polyols with the same structure as those of polyols prepared addition of glycidol to isosorbide. The differences are that glycerin carbonate is less reactive than glycidol and needs higher reaction temperatures (170–180 °C) and the reaction results in liberation of CO_2 [225] (**Figure 7.25**). Glycerine carbonate is produced by Huntsman (UT, USA).

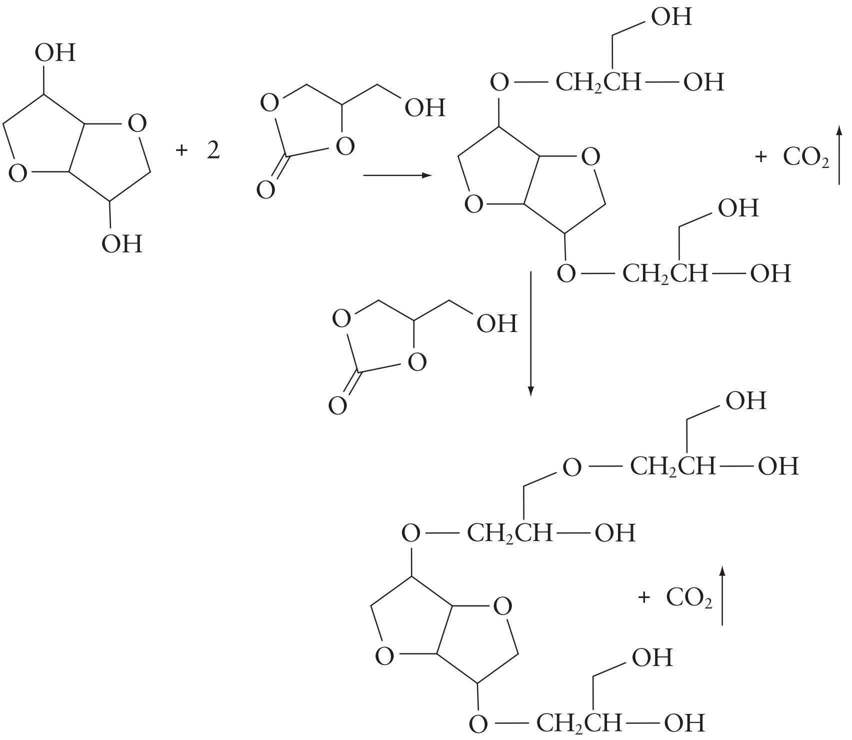


Figure 7.25 Synthesis of bio-based polyfunctional polyols by reaction of isosorbide with glycerine carbonate [225]

Polyols based on isosorbide and glycidol or glycerine carbonate, used as sole polyols or in mixture with sucrose or sorbitol polyether polyols, lead to rigid PUF with excellent properties, superior to those of rigid PUF based on isosorbide diols [225].

Isosorbide has proved to be a very valuable diol of natural origin for PU preparation. The intrinsic rigidity of isosorbide has made a real contribution to the increase in physical–mechanical properties of rigid PUF.

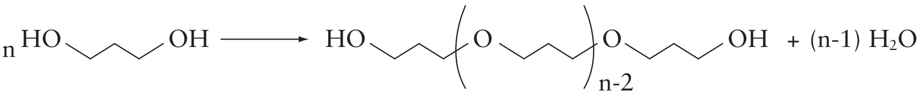
7.4.2 Polytrimethylene Ether Polyols [226–232]

1,3-Propanediol is an isomer of 1,2-propanediol, **Figure 7.28**:

Structure 7.28 a) 1,3-Propanediol and b) 1,2-propanediol

1,3-Propanediol obtained by fermentation of sugars (corn sugar, glucose, glycerol) is a bio-based monomer containing 100% renewable carbon (**Volume 2, Section 7.2.2**).

By polycondensation of 1,3-propanediol, in the presence of acidic catalysts (sulfuric acid, triflic acid, 1,1,1,2,3,3-hexafluoro propane sulfonic acid, 1,1,2,3-tetrafluoro ethane sulfonic acid [229]), at 160–190 °C (preferably at 175–185 °C), with continuous removal of water resulting from polyetherification reaction, enables polytrimethylene ether diol to be obtained (**Reaction 7.78**). A moderate vacuum (250–500 mmHg) helps the efficient removal of water.



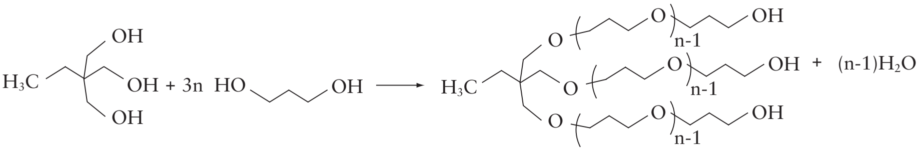
(7.78)

After polyetherification, the reaction mass is washed with water (water/polyol = 1/1 weight ratio) at 90 °C for several hours. In this step, the esters of sulfuric acid formed during the process are hydrolysed. At the end of washing, two layers are formed. The top layer is water with acidic catalysts and traces of unreacted monomer. The bottom layer is liquid polytrimethylene ether diol. After phase separation, the polyether phase is washed three times with hot distilled water. The residual acid in the bottom polyether phase is neutralised with basic compounds (e.g., calcium hydroxide, sodium bicarbonate solutions), weak anion exchangers [232] or solid bases (e.g., hydrated aluminium oxide or aluminium oxyhydroxides such as pseudobohemite) [227]. In the washing step, the sulfate esters formed during polycondensation of 1,3-propanediol and catalysed by sulfuric acid are hydrolised. Mixing of crude polyether with hot water in the presence of weak anion exchangers is a simple method for rapid hydrolysis of sulfate esters and efficient removal of the acidic catalyst [232]. The polyol is anhydrised under reduced pressure for 2–3 h and filtered. This method enables copolymers such as 1,3 propanediol and EG, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and neopenthylglycol to be obtained readily. EG is the preferred comonomer.

The polyetherification reaction of 1,3-propanediol enables practically colourless liquid polyether diols of MW = 500–3,000, with an OH# of 37–224 mg KOH/g, low unsaturation (<0.02 mequiv/g), mp of 10–22 °C, viscosity of 100–1,500 mPa.s at 25 °C, and colour APHA <70 to be obtained. The colour can be improved by catalytic hydrogenation [228] or using a very pure monomer.

Polytrimehylene ether diols are isomers with 1,2-PPG but, at an identical MW, the main chains of polytrimethylene ether diols are longer. The methyl groups of 1,2-PPG are not part of the main chain and, as an immediate consequence, the main chain is short.

If, as a starter, a triol such as TMP is used, then branched polyether polyols (**Reaction 7.79**) of MW = 3,000–5,000, with 100% primary hydroxyls are obtained. They are excellent polyether polyols used for high-quality flexible PUF (especially high-resilience moulded foams) [232] and high-quality coatings [230].



(7.79)

Polytrimethylene ether diols (trade name: Cerenol polyols) represent a new family of high-performance bio-based diols developed by DuPont. These polyols are suitable for preparation of thermoplastic PU elastomers, flexible PUF, PU coatings and adhesives, and as soft segments for thermoplastic polyesters.

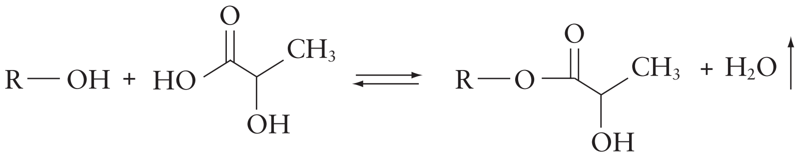
Compared with PTMG, Cerenol polyols offer a 40% saving on non-renewable energy and 42% reduction in greenhouse emissions.

Synthesis of polytrimethylene ether glycols (100% bio-based polyether diols) using as a monomer 1,3-propanediol obtained by fermentation, represents a great success of 'green chemistry' and is one of the most important developments in renewable intermediates for flexible PU.

7.4.3 Bio-based Polyols with Lactic Acid Units (Lactate Polyols) [32–36, 37, 233]

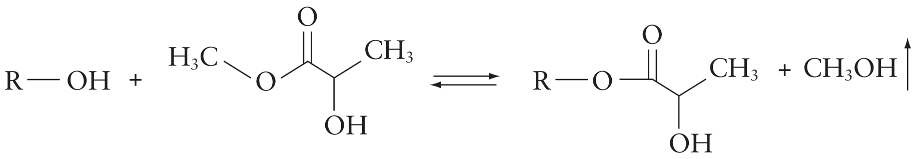
Lactic acid (2-hydroxypropionic acid) is a bio-based α-hydroxyacid obtained by fermentation of glucose with micro-organisms from *Lactobacillus* [32] (**Volume 2, Section 7.1.2.3**). Polyols with lactic acid units or esters of lactic acid ('lactate polyols') can be prepared in three ways [35, 36]:

a) Direct esterification of the hydroxyl groups of polyols with lactic acid (**Reaction 7.80**):



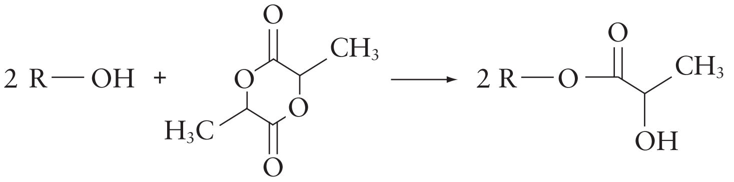
(7.80)

b) Transesterification of the hydroxyl groups of polyols with methyl lactate or ethyl lactate (**Reaction 7.81**):

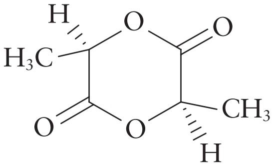


(7.81)

c) Ring-opening addition of lactides (cyclic dilactones of lactic acid) to the hydroxyl groups of various polyols (**Reaction 7.82**):


(7.82)

The best method by far is the reaction of lactides with different polyols. The most common lactide used is D-lactide [34] (**Structure 7.29**). D-lactide is a dilactone from D-lactic acid [(R,R)-3,6-dimethyl-1,4 dioxane-2,5 dione]. As mentioned in **Volume 2**, **Section 7.1.1.4**, D-lactide reacts in very high yield with hydroxyl groups in the presence of Ti(IV), Sn(II) or Sn(IV) catalysts at 120–140 °C, for 3–4 h. The well-known catalysts of this ring-opening reaction are $Ti(OiPr)_4$, $Ti(OiBu)_4$, stannous octoate and dibutyltin dilaurate, at 0.1–0.5% concentration.



Structure 7.29 Structure of D-lactide

D-Lactide is a white crystalline solid and has a mp of 116–119 °C.

Reaction of soybean polyols with lactide bio-based polyols lead to production of PU with increased T_g (**Figure 7.26**) [37]:

The polyols synthesised conform to the reaction shown in **Figure 7.26** and are relatively viscous (20,000–50,000 mPa.s at 25 °C). The viscosity increases with increasing content of lactic acid units [35, 36]. By using castor oil instead of soy polyol (**Figure 7.27**), lower-viscosity liquid lactate polyols of 5,000–15,000 mPa.s at 25 °C are obtained, even if the content of lactic acid units is high (45–50%) [35, 36]. As a general rule, all the derivatives of castor oil (esters or ethers) have much lower viscosity than the same derivatives of soybean polyols.

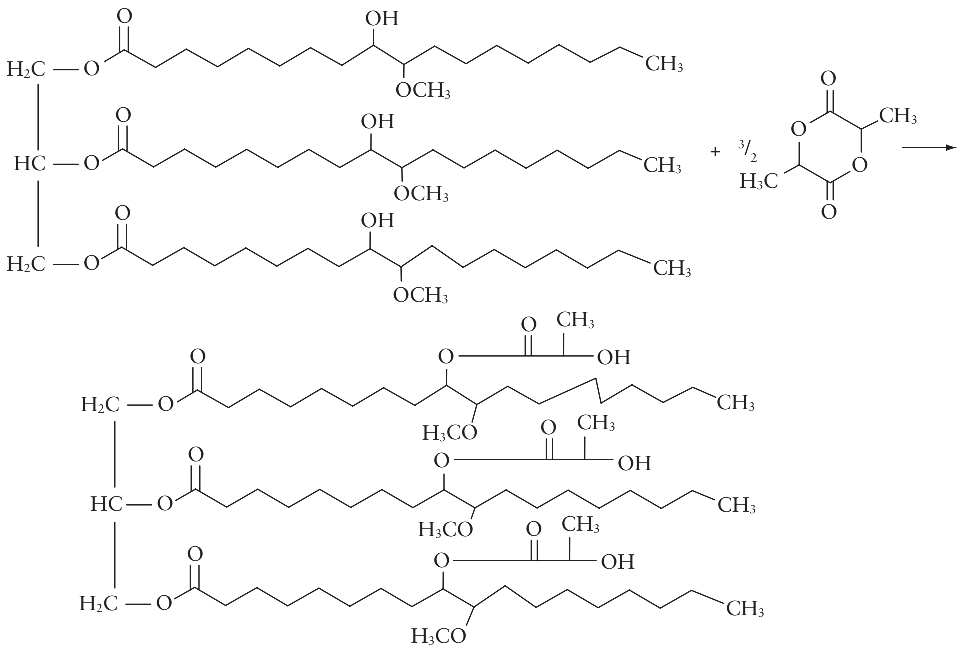


Figure 7.26 Synthesis of a lactate polyol by addition of lactides to a soybean polyol

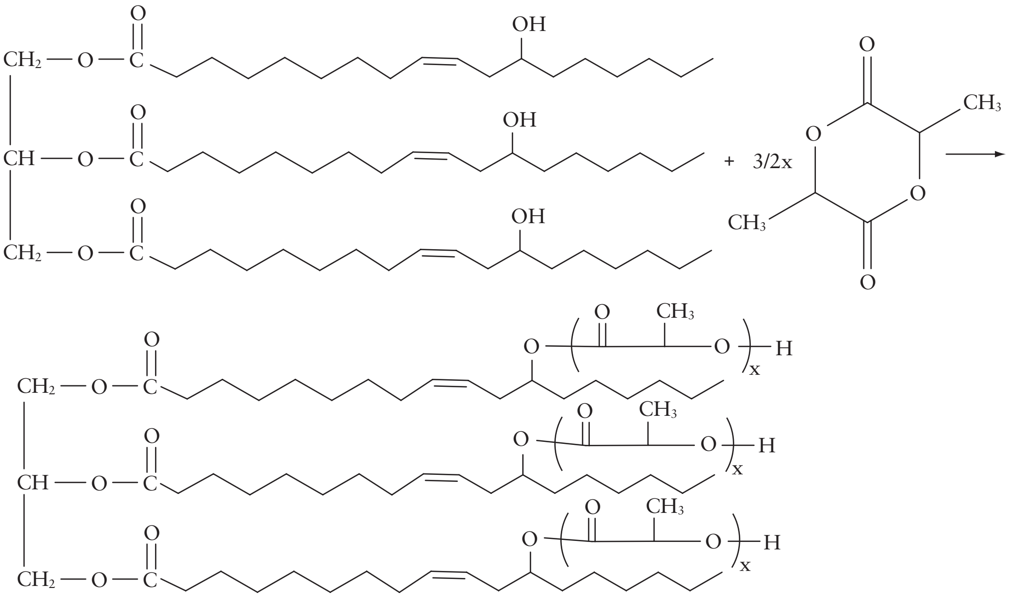


Figure 7.27 Synthesis of a lactate polyol by addition of lactides to castor oil

Addition of lactides to PGL is a simple way to prepare lactate polyols with 100% renewable content (**Figure 7.28**) [35, 36]. Unfortunately, lactate polyols based on PGL are incompatible with isocyanates due to the phase separation during the reaction between lactate polyol and isocyanates. Hence, PU with acceptable properties cannot be obtained. Fortunately, upon addition of lactides to partial fatty acid esters of PGL (**Figure 7.29**), lactate polyols that are perfectly compatible with isocyanates can be obtained, thereby enabling cast PU and rigid PUF with very good physical–mechanical properties to be obtained [35, 36]. Relatively rigid lactic units in lactate polyols leads to an increase in some of the properties of rigid PUF, such as compression strength and tensile strength.

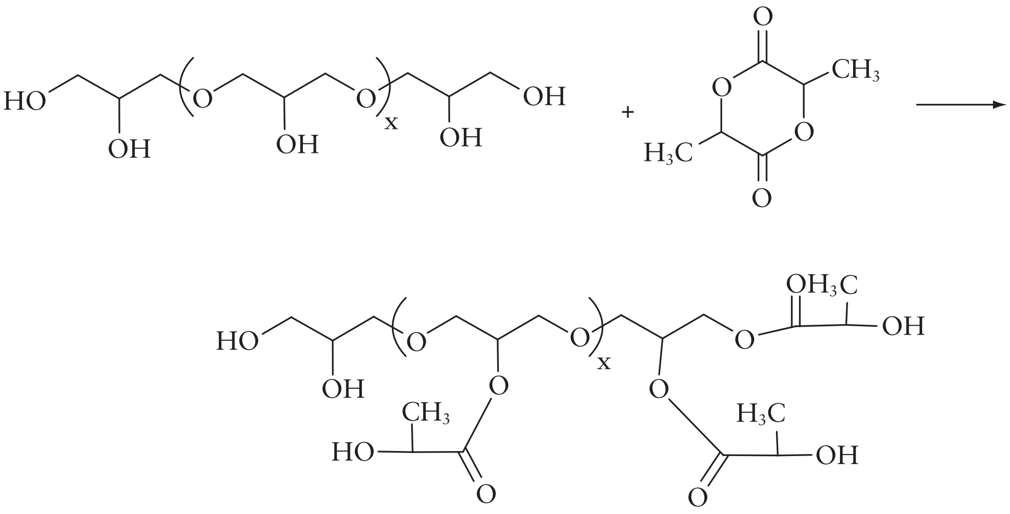


Figure 7.28 Synthesis of lactate polyols incompatible with isocyanates by addition of lactides to PGL

The synthesis of lactate polyols by addition of lactides to various polyols is a relatively simple way to prepare bio-based polyols. Unfortunately, lactides are expensive, and to prepare bio-based polyols by this method is less suitable.

Lactate polyols are readily biodegradable, so it is expected that the PU based on lactate polyols will also be biodegradable [233].

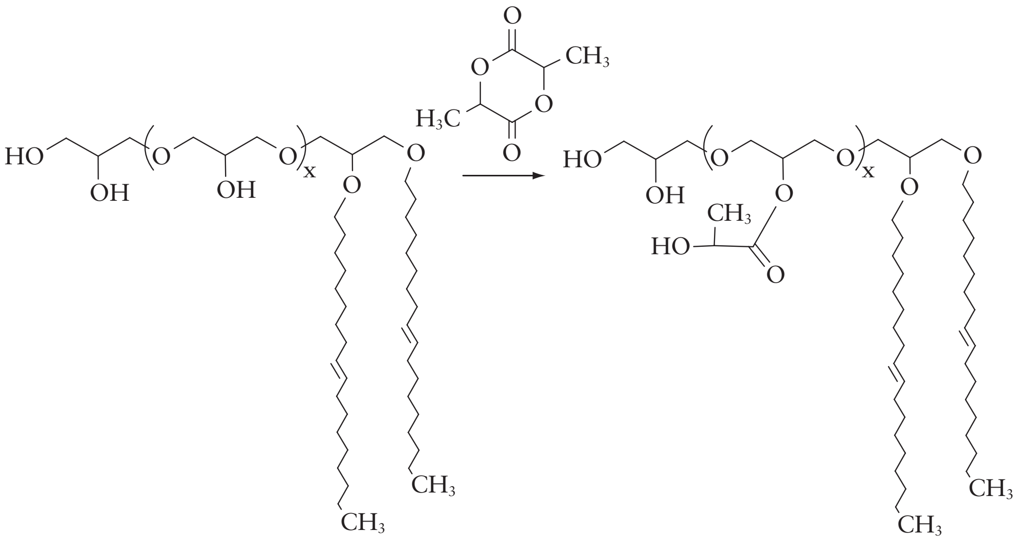


Figure 7.29 Synthesis of lactate polyols compatible with isocyanates by addition of lactides to partial fatty acid esters of PGL

7.4.4 Carbon Dioxide-based Polyols [234–245]

CO_2 is considered to be a bio-based compound. It is the product of respiration of plants and animals, or a byproduct of many biotechnological processes such as fermentation (e.g., fermentation of glucose to ethanol). Some CO_2 in the atmosphere is the result of human activities, such as burning of fossil fuels in automotives, and airplane engines.

CO_2 is considered to be a greenhouse gas. It is a very interesting bio-based monomer that is cheap and readily available. CO_2 is a waste product of many technologies (e.g., fermentation technologies). Using this compound to manufacture new bio-based chemical products is a worldwide effort. One valuable use of CO_2 is the synthesis of aliphatic polycarbonate(s) (PC) polyols by copolymerisation of CO_2 with alkylene oxides initiated by various polyols as starters [1–10].

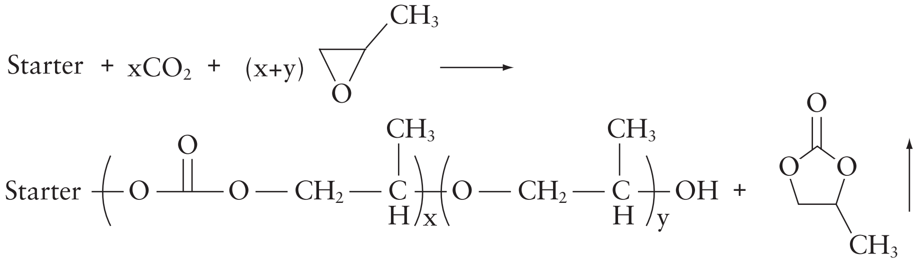
There are three groups of catalysts for copolymerisation of CO_2 with alkylene oxides: PO, EO, and cyclohexene oxide.

7.4.4.1 Copolymerisation of Carbon Dioxide with Alkylene Oxides in the Presence of Double Metal Cyanide Catalysts [234–237]

DMC catalysts are extremely efficient catalysts for homopolymerisation of PO and have been described in detail in **Volume 1, Chapter 5** [19]. These catalysts based on zinc hexacyanocobaltate have the general formula:

$$\mathrm{Zn_3[Co(CN)_6]_2 \quad {}_xZnCl_2 \quad {}_yLigand\ 1 \quad {}_zLigand\ 2 \quad {}_nWater} \tag{7.83}$$

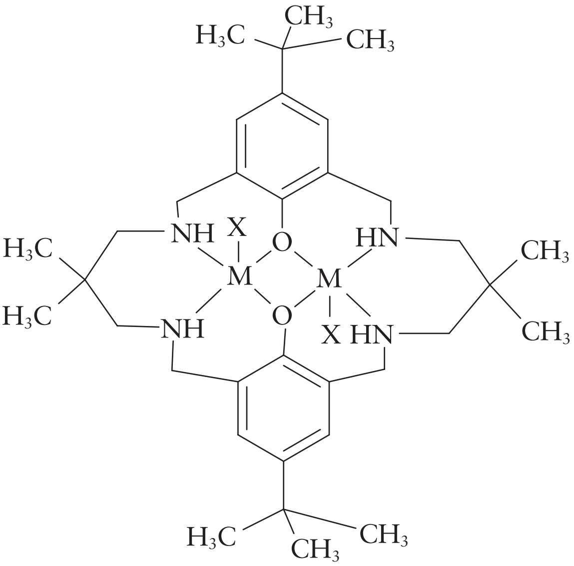
Interestingly, PO copolymerises with CO_2 in the presence of 50–100 ppm DMC catalysts at 130 °C and pressure of CO_2 of 5–10 bars. As a starter, short-chain polyethers (PPG or propoxylated glycerol of MW of 400–700) are used. The resulting polyols are liquid. The polyols have an OH# = 51–57 mg KOH/g, viscosity of 600–3,000 mPa.s at 25 °C, and a polydispersity index (PDI) of M_w/M_n=1.1–1.6. Unfortunately, the resulting polyols have polyether units and carbonate units, and result in 10–20% propylene carbonate as a byproduct (**Reaction 7.84**). The cyclic carbonate content decreases to 1–2% if the polymerisation temperature decreases to 90 °C [4]. Cyclic carbonate is removed by high-vacuum distillation.



(7.84)

7.4.4.2 Copolymerisation of Carbon Dioxide with Epoxides using Dinuclear Complex Catalysts [238–240]

A substantial effort has been made to increase the selectivity of catalysts for copolymerisation of CO_2 with alkylene oxides to avoid formation of cyclic carbonate and ether bonds. An efficient catalyst was discovered at Imperial College (London, UK) with the structure of a dinuclear complex of Zn(II), Co(II,III), Fe(III), or Mg(II) with macrocyclic ligands (**Structure 7.30**).



Structure 7.30 Highly active dinuclear complexes in copolymerisation of CO_2 with alkylene oxides. M = Zn(II), Co(II,III), Fe(III), Mg(II)

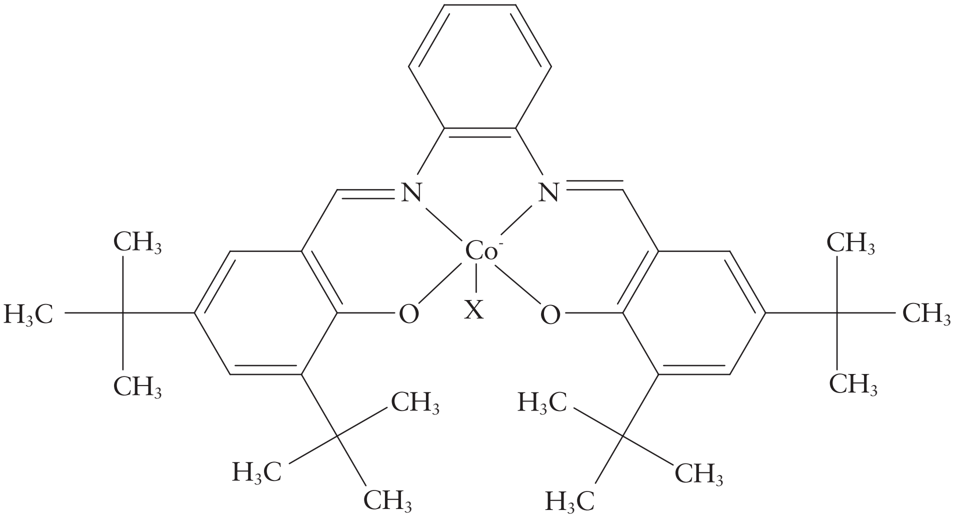
Catalysts with the **Structure 7.30** are very active and exhibit high selectivity for copolymerisation of CO_2 with alkylene oxides, even at a pressure of CO_2 of <1 bar. The Di-cobalt complex is the most active catalyst but, due to toxicity and expense, di-magnesium complex is preferred.

The Di-magnesium complex is very active at 80 °C and pressure of 1 bar of CO_2 at 1:1,000 catalyst loading. By increasing the temperature to 100 °C and CO_2 pressure to 12 bars, it is possible to decrease the catalyst concentration to 1:10,000 loading. In the absence of transfer agents, PC of 3,000–24,000 MW are obtained at very high yield (>99%) with a very narrow MW distribution (Mw/M_n=1.02–1.3). The resulting PC are solid at RT.

PC diols are obtained by using water as a transfer agent. DMC catalysts can lose catalytic activity in the presence of water, and binuclear Mg(II) or Zn(II) complexes with **Structure 7.30** are very active if water is used as a transfer agent. In the presence of 0.1–10 mol% water, CO_2 copolymerises with alkylene oxides, and leads to PC diols, practically no ether units, and a very low cyclic carbonate content (<1.2%).

7.4.4.3 Cobalt Chelates as Catalysts for Copolymerisation of Carbon Dioxide with Alkylene Oxides [241–243]

Novomer (NY, USA) have developed a new group of catalysts for preparation of PC polyols for PU applications by copolymerisation of CO_2 with PO or EO. These calaysts have the structure of cobalt salen complexes (**Structure 7.31**).



Structure 7.31 Very active cobalt chelate complex for copolymerisation of CO_2 with PO. X = Br, CF_3COO^-

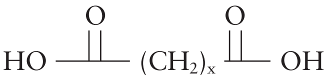
Copolymerisation of PO with CO_2 in the presence of a cobalt complex with a catalyst with **Structure 7.31** for several hours at 30 °C leads to polypropylene carbonate diols. These PC diols have MW of 500–10,000 as a function of the molar ratio of $[PO + CO_2]/[diol]$. PC based on CO_2 and PO are solid compounds at RT, with a T_g of approximately –17 °C and a low PDI of Mw/M_n = 1.03–1.35. The viscosity of a PC diol of MW = 624 (OH# = 182 mg KOH/g) at 50 °C is ≈3,200 mPa.s [10]. Polypropylene carbonate diols have perfectly alternating CO_2–epoxide backbones and perfect di-functionality.

PC obtained by copolymerisation of CO_2 with alkylene oxides can be used for a wide range of PU applications such as coatings, foams, adhesives, elastomers and thermoplastic PU. PC polyol-based PU have excellent strength, high hydrolytic stability, oxidative resistance and heat resistance.

7.4.5 Polyester Polyols from Bio-succinic Acid [245–264]

Dicarboxylic acids are very important intermediates for the synthesis of polyester polyols for PU by polyesterification with diols and polyols (**Volume 1, Chapter 8**) [19]. The most important diacid of petrochemical origin for preparation of polyesters for PU is AA.

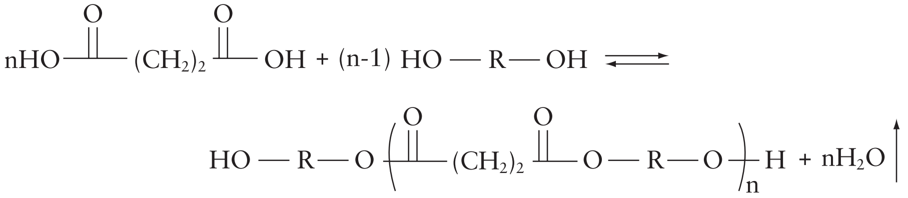
There are several bio-based dicarboxylic acids (**Structure 7.32**), such as oxalic acid (x = 0), azelaic acid (x = 7) and sebacic acid (x = 8). Two new routes to bio-based dicarboxylic acids have been developed for preparation of succinic acid ('bio-succinic acid', x = 2) and AA ('bio-AA', x = 4).



$$HO\overset{\overset{O}{\|}}{—}(CH_2)_x\overset{\overset{O}{\|}}{—}OH$$

Structure 7.32 General structure of bio-based diacids (x = 2, 4, 7 and 8)

Bio-succinic acid (**Volume 2, Section 7.1.2.1**) is a bio-based replacement of petrochemical AA for preparation of polyester polyols (**Reaction 7.85**).



$$nHO\overset{\overset{O}{\|}}{—}(CH_2)_2\overset{\overset{O}{\|}}{—}OH + (n\text{-}1)\ HO—R—OH \rightleftharpoons HO—R—O\left(\overset{\overset{O}{\|}}{—}(CH_2)_2\overset{\overset{O}{\|}}{—}O—R—O\right)_n H + nH_2O\uparrow \qquad (7.85)$$

Bio-succinic acid has low greenhouse emissions: 94% less than petrochemical succinic acid and 93% less than petrochemical AA.

Thus, by polycondensation of succinic acid with DEG and TMP, liquid branched polyols (functionality, f = 2.4–2.7 OH groups /mol) are obtained with OH# = 61–64 mg KOH/g and viscositity of 3,000–4,000 mPa.s at 25 °C, which are excellent replacements for similar branched polyester polyols based on petrochemical AA.

Polycondensation of succinic acid with EG, DEG and HD leads to linear polyester diols with OH# = 107–113 mg KOH/g. Polyesters based on succinic acid and EG are solid (mp = 60 °C), but polyesters based on succinic acid and DEG or HD are liquid at RT.

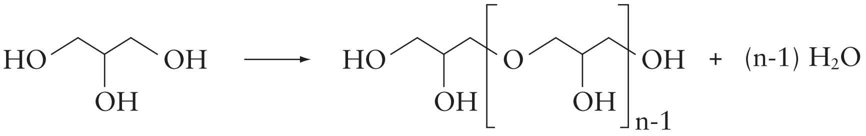
The bio-based carbon content of polyester polyols based on succinic acid is 40–66% as a function of the MW of diol used for polyesterification. Thus, by using EG (a diol of lower-MW), a higher bio-based carbon (66%) is obtained. By using HD (of higher-MW), a polyester diol of lower bio-based carbon content (40%) is obtained.

In general, PU based on succinic acid polyester polyols have a higher T_g (-6 to -17 °C) than PU based on AA polyester polyols (-28 to -30 °C). The slightly short of four carbon atoms that succinic acid has causes a small increase in the backbone rigidity of PU.

Polyester polyols based on bio-succinic acid can replace polyester polyols based on petrochemical AA for PU elastomers, paints and coatings, adhesive, sealants, artificial leaders, and thermoplastic PU.

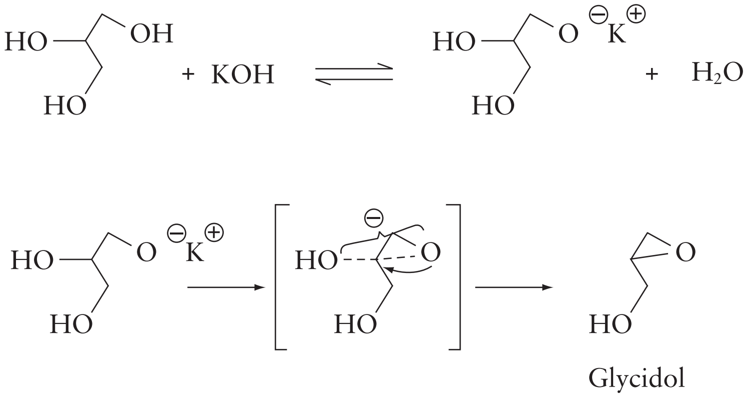
7.4.6 Polyglycerol-based Polyols [265–283]

PGL is a bio-based polyhydroxylic compound obtained by self-condensation of glycerol with basic or acidic catalysts (**Reaction 7.86**). The higher yield in PGL is obtained with basic catalysts such as sodium hydroxide, KOH, $NaOCH_3$, $KOCH_3$, calcium oxide, and calcium hydroxide. Acidic catalysts lead to side reactions, which diminishes the yield of PGL (e.g., formation of acrolein, of acetol and other compounds due to dehydration).



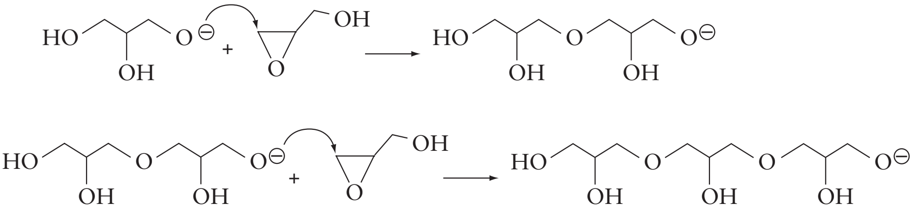
(7.86)

Self-condensation of glycerol to PGL with basic catalysts is carried out at high temperatures (230–270 °C) with continuous elimination of the water that results from the reaction. The mechanism of this reaction is based on transformation of glycerol into glycidol in the first step (**Reaction 7.87**), where the active centre of this reaction is the alkoholate anion formed by the reaction of glycerol with the basic catalyst.



(7.87)

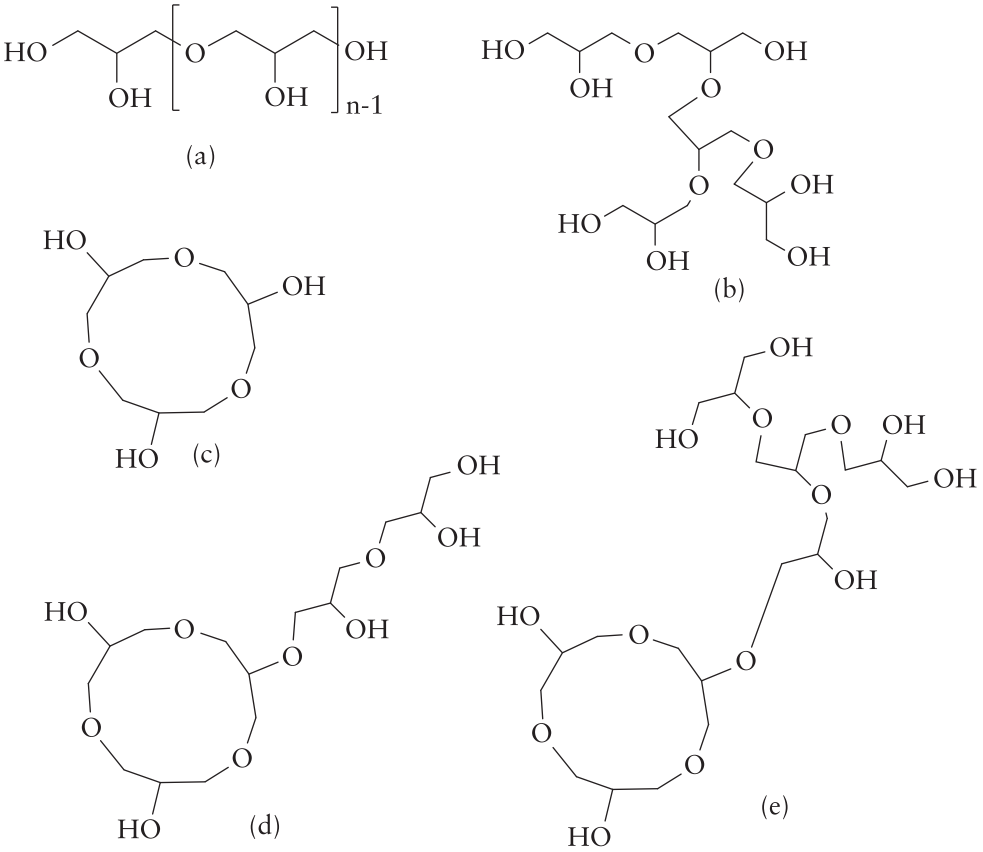
PGL is formed by ring-opening addition of glycidol to various hydroxyl groups from the reaction system (**Reaction 7.88**). This reaction is the ‘key’ for transformation of glycerol in PGL [275].



(7.88)

The composition of PGL obtained by self-condensation of glycerol in basic catalysts has been shown to be a mixture of several species, with the main species being linear PGL, branched PGL, cyclic PGL, hybrid linear–cyclic PGL, and hybrid branched–cyclic PGL [275–281] (**Structure 7.33**).

PGL is a highly valuable bio-based polyol. It is a viscous liquid that can be handled easily, and has very high functionality (4–20 hydroxyl groups/mol or more). Unfortunately, PGL is totally incompatible with isocyanates, and good PU cannot be obtained. Introduction of hydrophobic groups into the structure of PGL leads to polyfunctional polyols that are perfectly compatible with isocyanates and which are suitable for preparation of cast PU and PUF with good physical–mechanical properties.



Structure 7.33 Main structures present in PGL prepared with basic catalysts: a) linear PGL; b) branched PGL; c) cyclic PGL; d) hybrid cyclic–linear PGL; and e) hybrid cyclic–branched poyglycerol

Introduction of hydrophobic groups in the structure of PGL is carried out by:

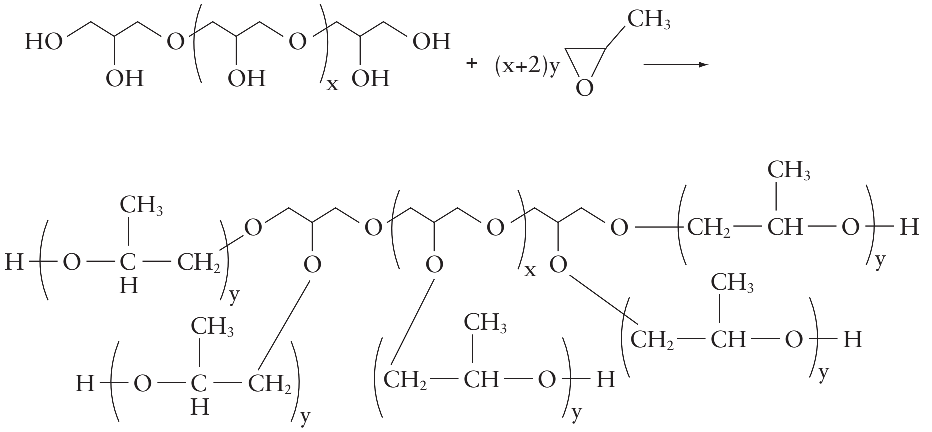
a) Propoxylation of PGL [273];

b) Reaction of PGL with CPL [274]; and

c) Formation of partial esters of PGL with fatty acids [35, 36].

7.4.6.1 Propoxylation of Polyglycerol [270]

Self-condensation of glycerol to PGL in the presence of KOH or $KOCH_3$ at ≈230–250 °C, followed by propoxylation in the presence of the same catalyst at 110–125 °C, is a practical way to obtain a polyol that is perfectly compatible with isocyanates. Upon propoxylation (**Reaction 7.89**) of PGL with an OH# = 1,100–1,200 mg, KOH/g decreases to OH# = 400–500 mg KOH/g and the resulting polyols have low viscosity (1,000–3,000 mPa.s at 25 °C), which is ideal for preparation of rigid PUF. Rigid PUF with excellent physical–mechanical properties and low friability (<5%) can be obtained from propoxylated PGL [273].

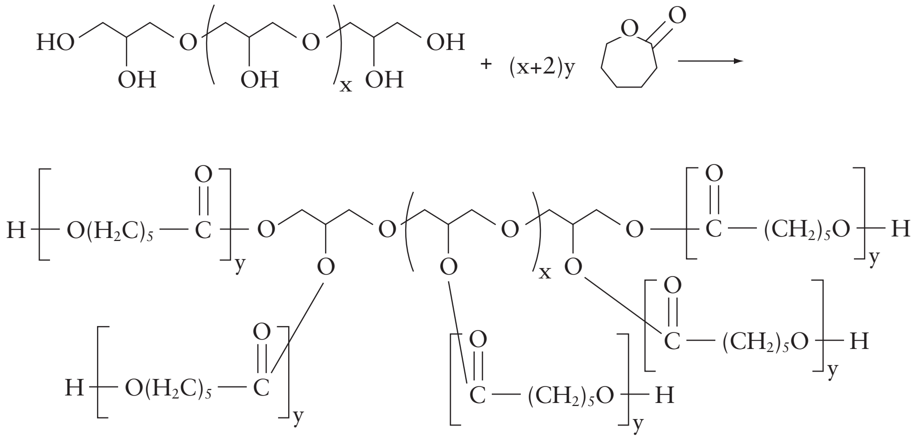


(7.89)

High-functionality polyols are obtained by propoxylation of a mixture of PGL with sucrose [284].

7.4.6.2 Reaction of Polyglycerol with ε-Caprolactone [274, 284]

A polyol that is perfectly compatible with isocyanates is produced by ring-opening addition of CPL to the hydroxyl groups of PGL (**Reaction 7.90**). The hydroxyl groups formed by addition of caprolactone to hydroxyl groups of PGL are primary hydroxyls with high reactivity. Adducts of CPL to PGL with an OH# of 350–500 mg KOH/g have a viscosity of 5,000–15,000 mPa.s at 25 °C.

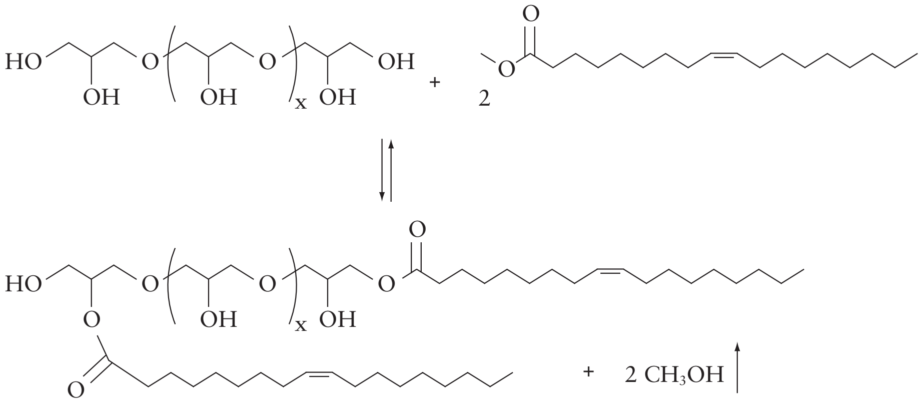


(7.90)

Rigid PUF based on adducts of CPL to PGL have high physical–mechanical properties, especially high compression strength of 200–300 MPa (at 10% strain).

7.4.6.3 Formation of Partial Esters of Polyglycerol with Fatty Acids [35, 36, 274]

Condensation of fatty acids or of fatty acid methyl esters with PGL leads to partial fatty acid esters of PGL (**Reaction 7.91**) that are compatible with isocyanates. Condensation of the methyl esters of fatty acids with PGL is catalysed by Ti(IV), Sn(II) and Sn(IV) compounds or by alkali akoxides at ≈120–140 °C with continuous removal of methanol resulting from the reaction (**Reaction 7.91**).



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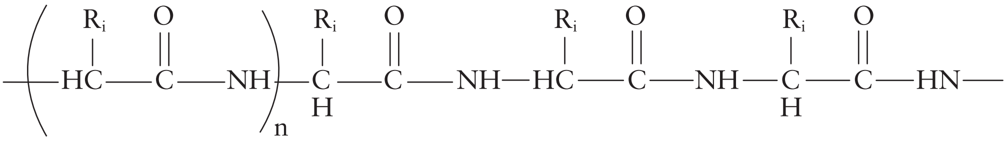
A very interesting way to prepare fatty acid esters of PGL is the condensation of glycerol to PGL in the presence of vegetable oils, at ≈250 °C, using sodium methoxide or potassium methoxide as a catalyst, with continuous removal of water. These polyols can be obtained in only one-step with OH# = 250–400 mg KOH/g and low viscosity of 2,000–3,000 mPa.s t 25 °C, and are perfectly compatible with isocyanates [271]. These polyols are suitable for preparation of cast PU, rigid PUF and urethane–isocyanuric foams with very good properties.

Fatty acid esters of PGL can be used in mixtures with petrochemical polyether polyols or even as sole polyols for preparation of rigid PUF and urethane–isocyanuric foams.

7.4.7 Polyols from Proteins [285–289]

Proteins have become a very interesting raw material for the synthesis of bio-based polyols for PU. Proteins are polymers from the condensation of natural α-amino acids, and are characterised by the general structure shown in **Structure 7.34**:

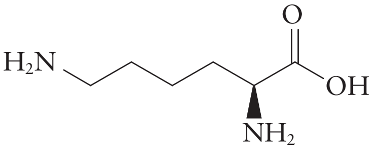


$$-\left(\overset{R_i}{\overset{|}{HC}}-\overset{O}{\overset{\|}{C}}-NH\right)_n-\underset{H}{\overset{R_i}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-NH-\overset{R_i}{\overset{|}{HC}}-\overset{O}{\overset{\|}{C}}-NH-\underset{H}{\overset{R_i}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-HN-$$

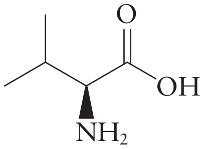
Structure 7.34 General structure of proteins

Essential amino acids differ accordin to the nature of the radical R_i. In fact, proteins are polyamides (PA) based on essential amino acids (**Structure 7.35**).

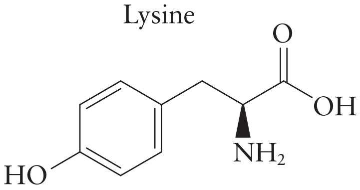
One interesting way to obtain PU without isocyanates is based on the acid hydrolysis of proteins to amino acids, and was developed at Michigan State University (MI, USA) [286]. This is followed by amidation of amino acids with EDA. In the third step, the amino groups are reacted with ethylene carbonate to form hydroxyethyl urethanes. Finally, by condensation of hydroxyethyl urethanes, PA urethanes are formed with elimination of EG. This succession of reactions is presented in **Figure 7.30**.



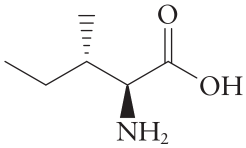
Lysine



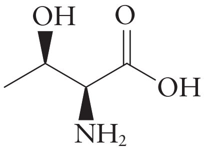
Valine



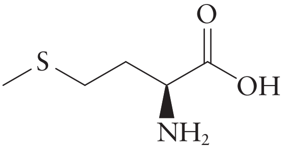
Tyrosine



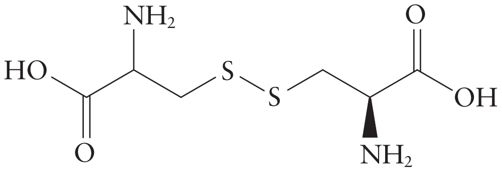
Isoleucine



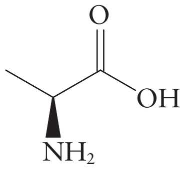
Threonine



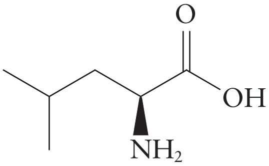
Methionine



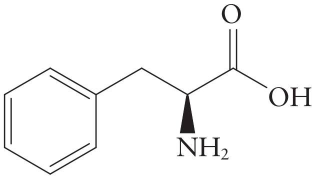
Cystine



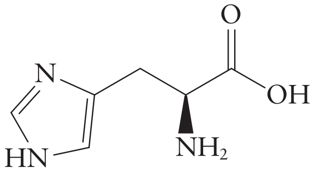
Alanine



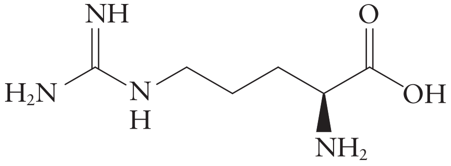
Leucine



Phenylalanine



Histidine



Arginine

Structure 7.35 Structures of some essential amino acids

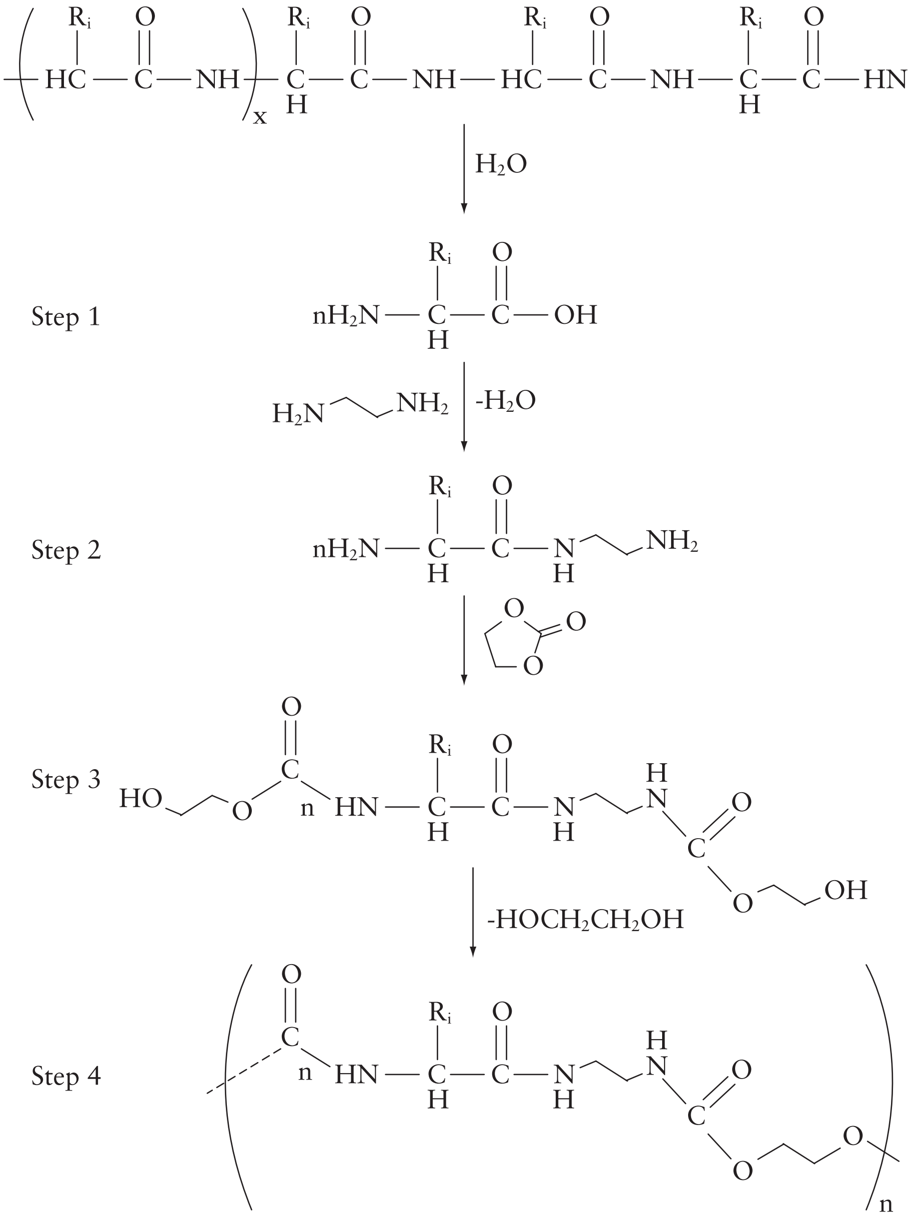


Figure 7.30 Synthesis of PA urethanes starting from proteins

Reaction between amino groups and cyclic carbonates is a very valuable way to prepare urethane groups without isocyanates.

Interestingly, addition of ethylene carbonate to the product of the reaction of amino acids with EDA leads to a urethane polyol.

Urethane-polyols starting from individual amino acids have been prepared using the same chemistry presented in **Figure 7.30** (steps 2 and 3) [287, 288]. Thus, urethane-polyols with the structure presented in **Figure 7.31** and **Figure 7.32**, respectively, can be prepared from L-arginine and L-glycine.

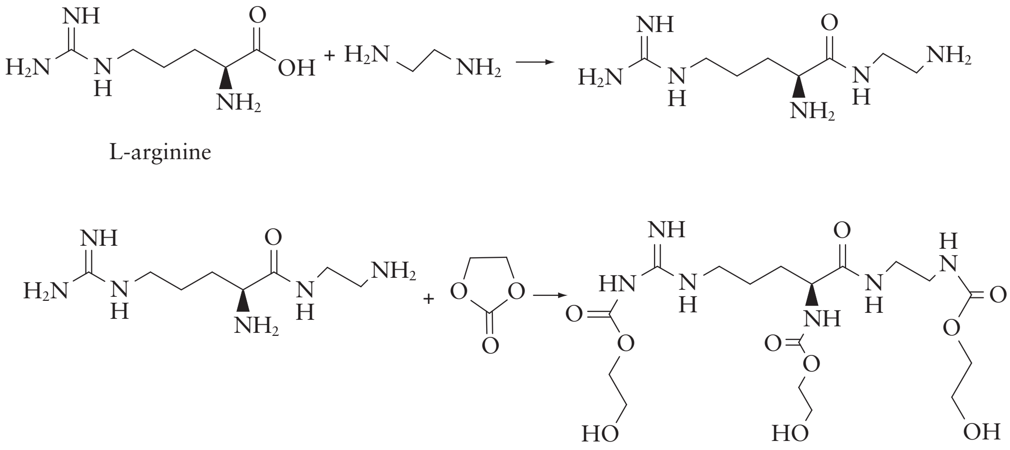


Figure 7.31 Synthesis of urethane-polyols from the amino acid L-arginine

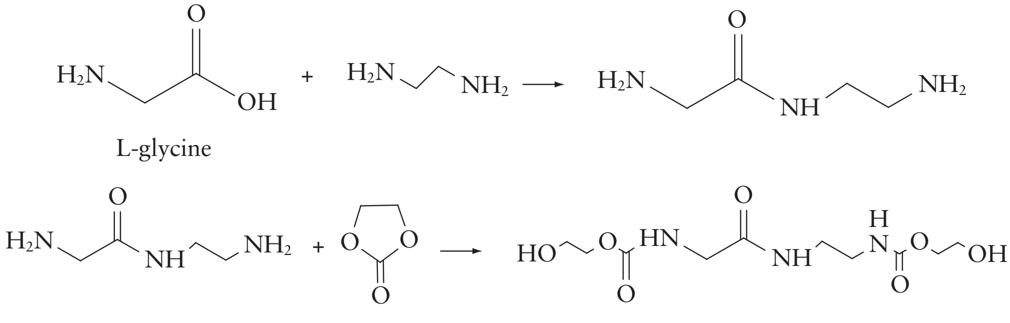


Figure 7.32 Synthesis of urethane polyol from the amino acid L-glycine

Some vegetable proteins, such as soybean meal or corn protein, contain not only proteins but also carbohydrates. The latter can be converted into multifunctional polyols by reaction with PO. This propoxylation step enables avoidance of the separation step of carbohydrates. By reaction with PO, some unreacted amino groups are also propoxylated. Presence of amino groups is sufficient to catalyse the propoxylation reaction. With these propoxylated polyols, rigid PUF with very good physical–mechanical properties can be prepared.

This methodology to prepare polyols can be applied to any protein, such as soy protein, corn protein, potato protein, algae and microalgae protein.

A variant of the synthesis of polyols from proteins, in two steps, was developed in Kansas Polymer Research Center (KS, USA) [289]. The process entails splitting proteins with dialkanolamines (e.g., DEOA) to amino-amides followed by propoxylation of the resulting amino-amides (**Figure 7.33**).

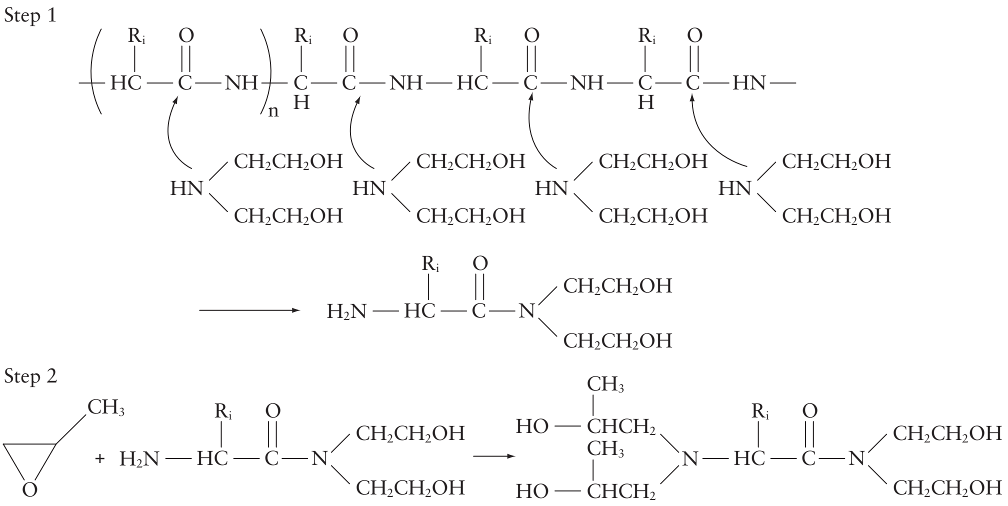


Figure 7.33 Synthesis of polyols from proteins by transamidation with DEOA (step 1) followed by propoxylation reactions (step 2)

The polyols contain tertiary amino groups, so these polyols obtained from proteins have high reactivity. These amino-amido polyols are suitable for rigid 'spray' PUF.

Polyols from any natural protein can be prepared by this two-step method, such as zein, soy protein, potato protein, and corn protein. This method can be applied for transformation of PA wastes into polyols, with the chemistry being identical with those presented in **Figure 7.33**.

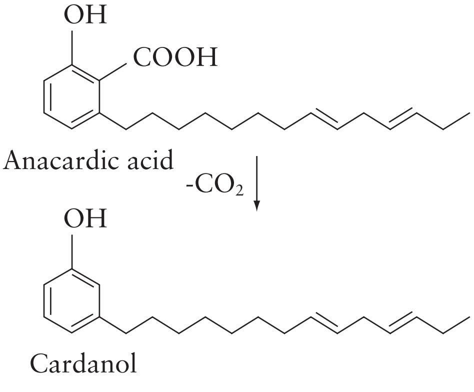
In general, the weight ratio of protein:DEOA is 1:1. In the case of zein (a protein from corn), as a function of the ratio of PO: amino-amide, polyols are obtained with an OH# = 420–600 mg KOH/g and viscosity of 18,000–22,000 mPa.s at 25 °C. Potato proteins lead to higher-viscosity polyols of 20,000–30,000 mPa.s at 25 °C and an OH# = 460–630 mg KOH/g. Viscosity of these amino-amido polyols from proteins can be decreased efficiently by replacing a part from PO with EO. A polyol with 15–20% EO has a viscosity of 2–3-fold lower than a similar polyol based exclusively on PO.

By using finely divided proteins as filler, suspended in a petrochemical polyether polyol at 10–20%, rigid PUF with good properties and good insulation properties can be obtained. By increasing the protein concentration to 30–40%, a dramatic decrease in compression strength is observed.

7.4.8 Polyols from the Liquid of Cashew Nut Shells [290–295]

The cashew tree (*Anacardium occidentale*) is originally from Brazil. Leading producers of the fruits of cashew nuts are Vietnam (32% of total world production), India (17%), Nigeria (16.5%), Côte d'Ivoire (10.3%) and Brazil (4.8%). Cashew fruit has a special structure: the nut is outside of the fruit (**Figure 7.34**). The nut kernel is covered by an inner shell and outer shell. A brown liquid called cashew nut shell liquid (CNSL) is located in a honeycomb structure, between the shells.

CNSL is a natural aromatic compound. The main component of CNSL is anacardic acid (90%) and Cardol (10%). Anacardic acid by decarboxylation during CNSL distillation leads to Cardanol (**Reaction 7.92**), a natural phenol substituted in the *meta*-position with a chain of 15 carbon atoms containing one double-bond (25–36%), two double-bonds (16–22%), three double-bonds (30–41%) or zero double-bonds (**Structure 7.36**) [290, 291, 295].



(7.92)

Main compounds in Cardanol are presented in **Structure 7.36**.

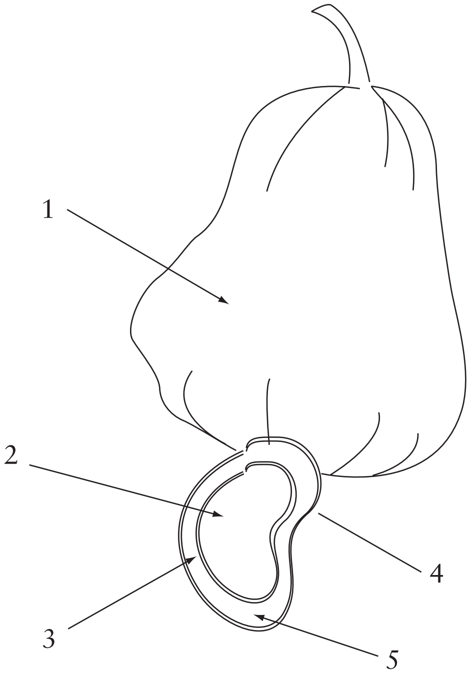
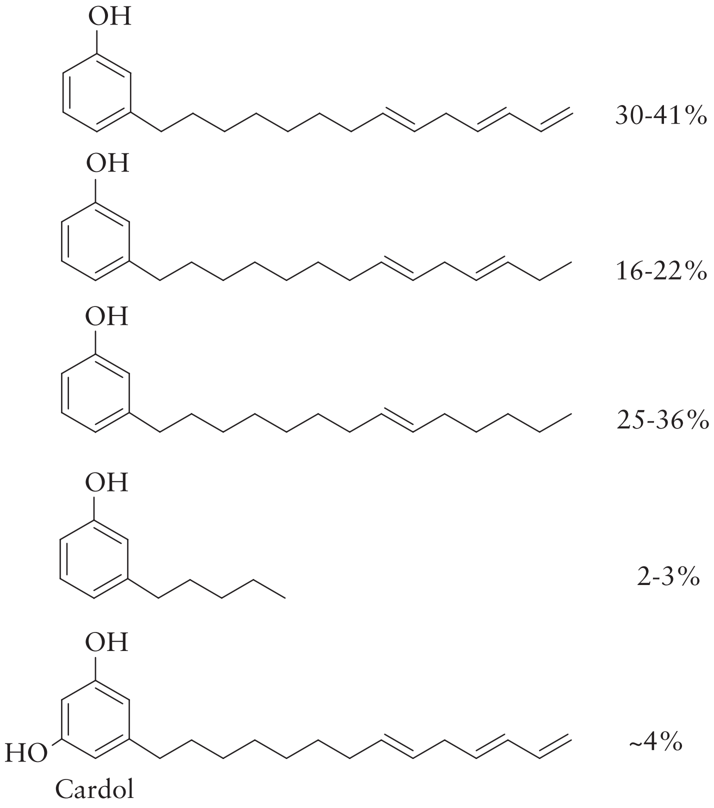


Figure 7.34 Section-view of the fruit of cashew nuts. 1) Apple, 2) kernel, 3) inner shell, 4) outer shell, and 5) CNSL

As observed in **Structure 7.36,** Cardanol has only phenolic hydroxyl groups, which react with isocyanates at a very low reaction rate and in very low yield. To transform this natural compound into a polyol suitable for PU, it is necessary to generate ≥2 aliphatic hydroxyl groups/mol of Cardanol using the reactions of phenolic hydroxyl groups and phenolic rings (alkoxylation, Mannich reactions, condensations with aldehydes) and reactions with the double-bonds of the C15 chain (epoxidation and ring-opening with alcohols, hydroformylation followed hydrogenation, and thiol-ene reactions with hydroxyalkyl mercaptans).



Structure 7.36 Composition of Cardanol (3-*n*-pentadecadienyl phenol)

7.4.8.1 Hydoxyl Functionalisation of Cashew Nut Shell Liquid by Mannich Reactions [291, 292, 296]

Cardanol is functionalised readily with hydroxyl groups by Mannich reactions with formaldehyde and DEOA [289]. However, the reaction with 1,3-*N*-hydroxyethyl oxazolidine (OXA), which is the cyclic product of the reaction of formaldehyde with DEOA, is much better, with the resultant product being Mannich bases [288, 293] (**Figure** 7.35).

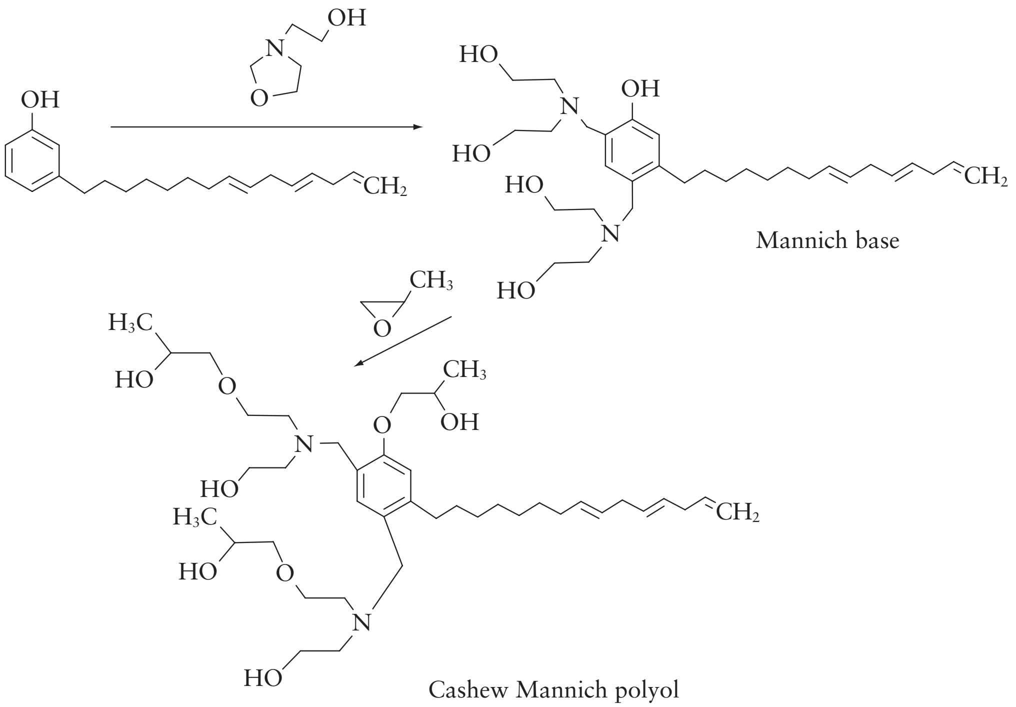


Figure 7.35 Synthesis of CNSL Mannich polyol

By propoxylation of CNSL Mannich bases, without catalysts, (molar ratio [Cardanol]/[OXA]/[PO] of 1/1–2/2–3), Mannich polyols are obtained with 3–5 hydroxyl groups/mol as a function of the molar ratio of DEOA/Cardanol [291, 296].

Interestingly, Mannich bases having higher aromatic content than propoxylated Mannich bases can be used as good polyols for rigid PUF but, unfortunately, they have lower functionality because phenolic groups react with isocyanates to a very small exstent.

Mannich polyols from Cardanol have much lower viscosity (4,000–5,000 mPa.s at 25 °C) than Mannich polyols from phenol and nonylphenol. Cardanol-based Mannich polyols with a functionality of 5 OH groups/mol (**Figure 7.35**) have an OH# = 340–420 mg KOH/g and a tertiary nitrogen content of 2.8–3.0 mg KOH/g [291, 297].

Due to the catalytic effect of tertiary nitrogen on the reaction between hydroxyl groups and isocyanate groups, Mannich polyols based on Cardanol are very reactive (autocatalytic polyols) suitable for preparation of rigid PUF by the spray process.

7.4.8.2 Synthesis of Polyols from Novolac Resins Derived from Cardanol [291, 296]

A condensation reaction of Cardanol with formaldehyde (or paraformaldehyde) catalysed by oxalic acid enables Novolacs with 3–6 phenolic rings to be obtained as a function of the ratio [formaldehyde]:[Cardanol]. Novolac resins have only phenolic hydroxyls of low reactivity. By propoxylation of Cardanol-based novolacs, in the presence of a tertiary amine as a catalyst, excellent bio-based aromatic polyols can be obtained with 3–6 secondary hydroxyl groups per mol of Cardanol (**Figure 7.36**).

Polyols with very high viscosity (e.g., 80,000 mPa.s at 25 °C) are obtained by propoxylation of Cardanol-based novolacs. However, if 15–20% EO is added after the propoxylation reaction, the viscosity decreases substantially to 15,000–20,000 mPa.s at 25 °C. The OH# of Cardanol-based novolac polyols is 150–180 mg KOH/g [296].

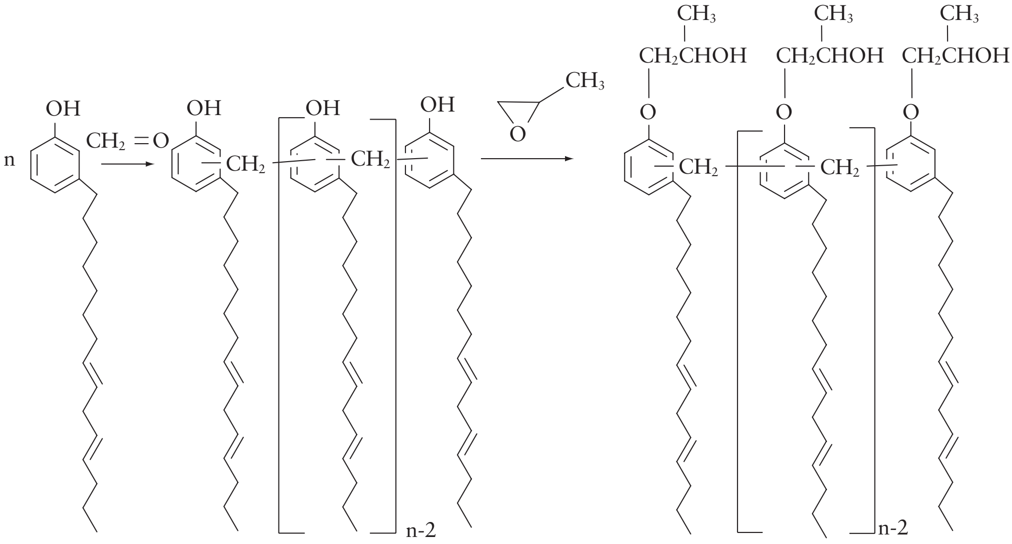


Figure 7.36 Synthesis and structure of a polyol based on novolac from Cardanol

Unfortunately, these polyols have non-functionalised ‘dangling chains’, with an IV of 100–126 gI_2/100 g. Despite dangling chains that do not participate in PU networks, the properties of rigid PUF based on Cardanol novolac polyols are very good, and are comparable with the properties of rigid foams from petrochemical polyols. The aromatic content of these polyols has a beneficial effect on foam characteristics.

7.4.8.3 Polyols from Cardanol by using Reactions Associated with the Double-bonds of C15 Chains [290, 294–296]

Hydroxyl groups can be generated from the double-bonds of Cardanol using the same chemistry employed to generate hydroxyl groups from the double-bonds of vegetable oils (e.g., epoxidation and ring-opening with alcohols; hydroformylation followed by hydrogenation; thiol-ene reaction with hydroxyalkyl mercaptans). Before carring out any reaction at the double-bonds of Cardanol, the phenolic hydroxyl is propoxylated in the presence of a tertiary amine at 100–110 °C to generate a hydroxypropyl group (an inert group against the reactions mentioned above involving the double-bonds). Preparation of polyols from propoxylated Cardanol using reactions associated with the double-bonds of C15 chains is presented in **Figure 7.37**.

Thus, the polyol obtained by hydroformylation of propoxylated Cardanol followed by hydrogenation has an OH# = 350 mg KOH/g and viscosity of 27,800 mPa.s at 25 °C. The polyol from propoxylated Cardanol obtained by epoxidation of double-bonds followed by ring-opening with methanol (HBF_4 as a catalyst) has an OH# = 305 mg KOH/g and viscosity of 28,000 mPa.s at 25 °C. The polyol obtained by thiol-ene addition of 2-mercaptoethanol to the double-bonds of propoxylated Cardanol has an OH# = 311 mg KOH/g and low viscosity of 800 mPa.s at 25 °C. The functionality of polyols shown in **Figure 7.37** is ≈3–4 hydroxyl groups/mol. The properties of rigid PUF obtained from all polyols shown in **Figure 7.37** are excellent. They have a density of 34–41 kg/m^3, compression strength (10% strain) of 311–380 kPa, and a closed cell content of 89–91% [296].

All the reactions shown in **Figure 7.37** can be applied to propoxylated Cardanol novolacs. Unfortunately, in the case of polyols obtained by epoxidation and ring-opening with methanol or hydroformylation-hydrogenation, the viscosities obtained are very high (100,000–150,000 mPa.s at 25 °C). Only by using the thiol-ene reaction of propoxylated Cardanol novolacs with 2-mercaptoethanol can polyols of acceptable viscosity (20,000–60,000 mPa.s at 25 °C) be obtained [296].

In conclusion, CNSL has been shown to be a very valuable raw material for the synthesis of bio-based polyols for PU. Due to the aromatic content of these polyols, the properties of rigid PUF prepared from these cashew-nut polyols are very good (especially compression strength, increased thermostability and flame resistance). Polyols based on CNSL for PU adhesives are produced by Cardolite (NJ, USA). Polyols from CNSL for rigid PUF (structural foams), adhesives and sealants are produced by Elmira (London, UK) [298].

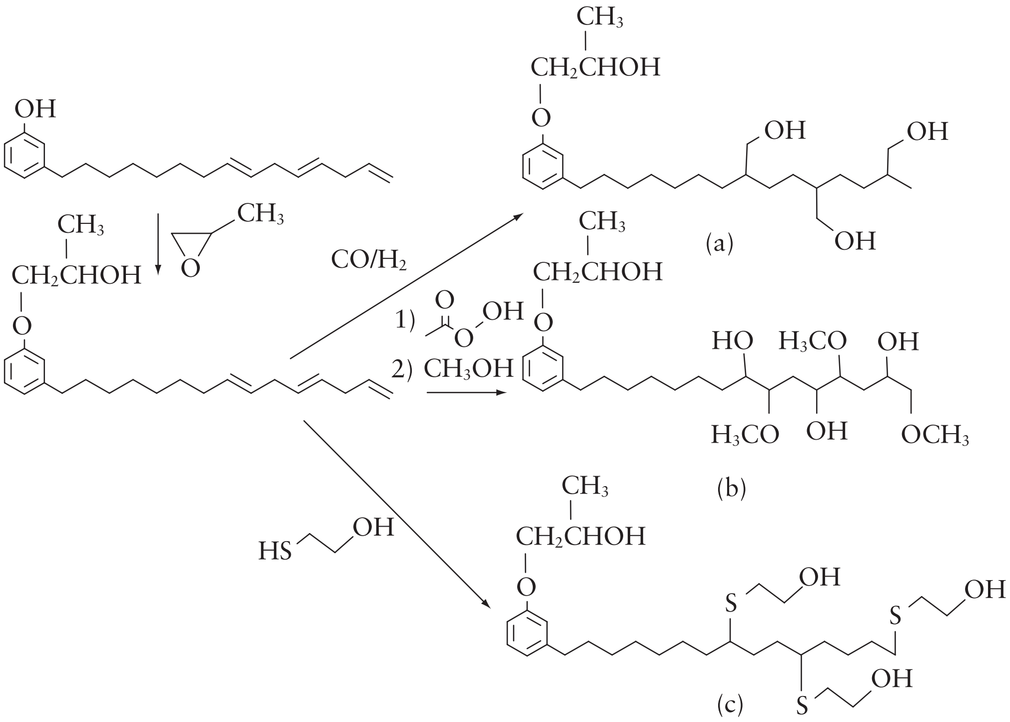
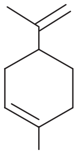


Figure 7.37 Synthesis of polyols from propoxylated Cardanol using reactions associated with the double-bonds a) hydroformylation; b) epoxidation and ring-opening with methanol; and c) thiol-ene reactions

7.4.9 Polyols for Polyurethanes Based on D-Limonene [298, 299]

D-limonene is a natural compound (monoterpene) present in appreciable quantities in the peel of oranges, lemons, mandarins and grapefruits. Orange oil extracted from orange peel contains 90% D-limonene. D-Limonene is a hydrocarbon with two double-bonds (**Structure** 7.37) and it is part of the group of mononoterpenes having 2 isoprene units.

D-Limonene in polyols can be transformed readily using the same reactions employed for transformation of vegetable oils in polyols: epoxidation and ring-opening of epoxy groups with hydrogene active compounds (alcohols, primary or secondary amines), hydroformylation followed by hydrogenation, and thiol-ene ‘click’ chemistry reactions.



Structure 7.37 Structure of D-limonene

By reaction of commercially available limonene diepoxide or limonene monoepoxide with polyols (e.g., glycerol), using an acid catalyst (BF_3 etherate, HBF_4), limonene-based polyols can be prepared which are suitable for rigid PUF [297] (**Figure 7.38**).

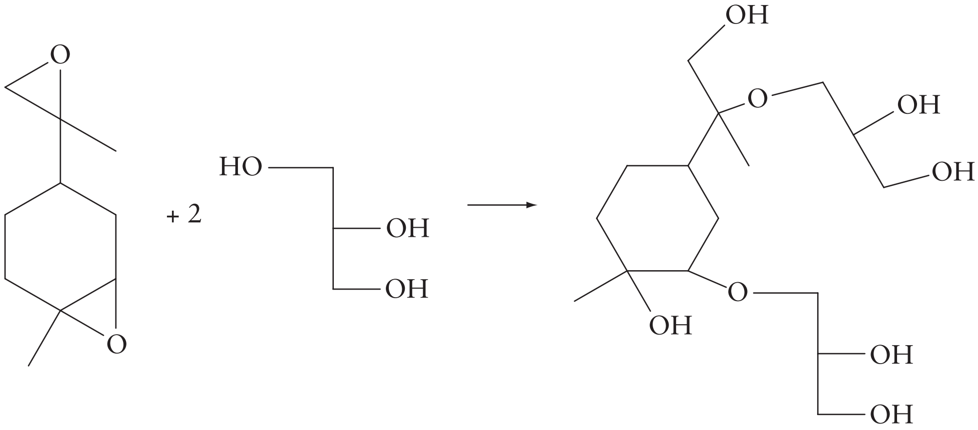


Figure 7.38 Synthesis of polyol from limonene diepoxide

The OH# of the adduct of glycerol to limonene diepoxide is too high (950 mg KOH/g). A polyol with lower OH#, in the range 500–600 mg KOH/g, and viscosity of 19,800 mPa.s at 25 °C, is prepared by propoxylation of the above-mentioned adduct of glycerol to limonene diepoxide (**Figure 7.39**) using a base as a catalyst (e.g., TMG) at 115–120 °C.

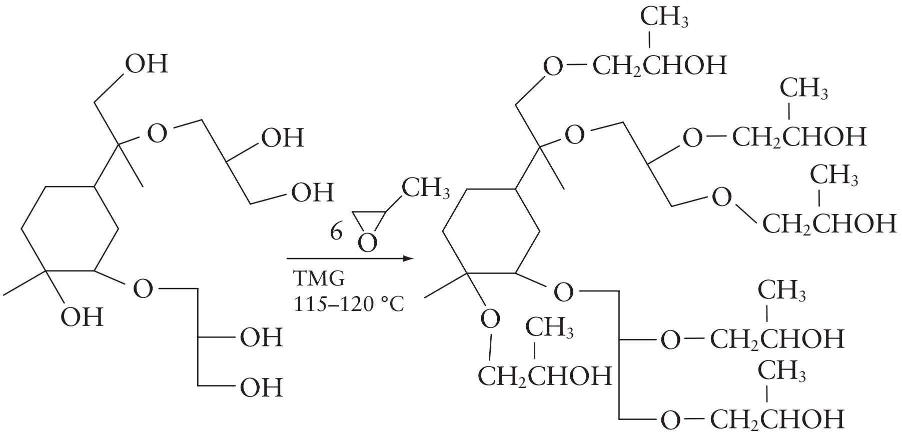
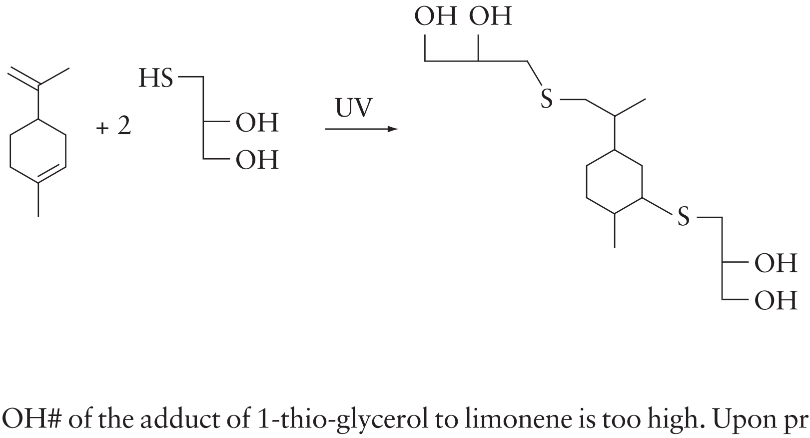


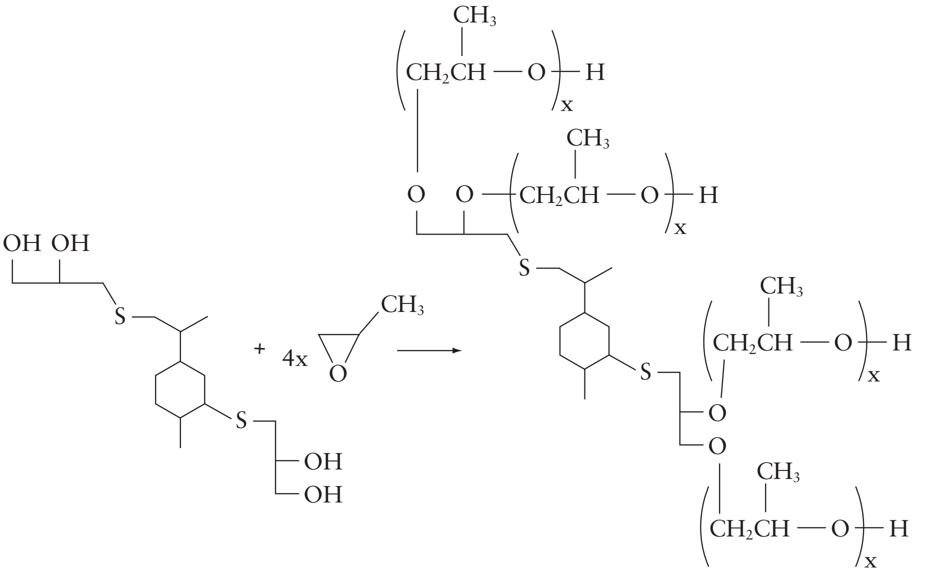
Figure 7.39 Synthesis of limonene polyol by propoxylation of the adduct of glycerol to limonene diepoxide [298]

Limonene-based polyols have been obtained by thiol-ene reactions of limonene with 1-thio-glycerol (**Reaction 7.93**) or of limonene dimercaptan with 1-allyl-glycerol or allyl TMP [298, 299].



(7.93)

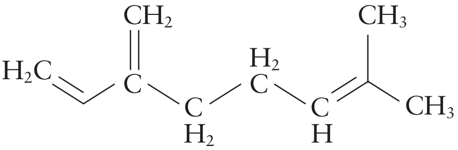
The OH# of the adduct of 1-thio-glycerol to limonene is too high. Upon propoxylation of this structure in the presence of a base (TMG), a limonene polyol, of OH# = 580 mg KOH/g and viscosity of 1,300 mPa.s at 25 °C, can be prepared (**Reaction 7.94**) [297].



(7.94)

Limonene polyols can be used in mixture with petrochemical polyether polyols based on sorbitol or sucrose (e.g., Voranol 490) or even as sole polyols for preparation of rigid PUF of good physical–mechanical properties such as: density of 33–41 kg/m^3; compression strength (at 10% strain) of 150–180 kPa; closed cell content of 88–91%; friability of <10%.

Another interesting renewable raw material is myrcene (a product of β-pinene pyrolysis), which has a high content of double-bonds (**Structure 7.38**).



Myrcene
MW = 136
bp = 165 °C

Structure 7.38 Myrcene

Myrcene-based polyols are obtained by classic reactions of double-bonds (epoxidation followed by ring-opening with methanol, thiol-ene reactions).

7.4.10 Polyols Derived from Fish Oil [300, 301]

Fish oil is a non-vegetable, highly unsaturated triglyceride. Fish oil is characterised by a high content of fatty acids containing four double-bonds and a chain of 20 carbon atoms (e.g., eicosapentaenoic acid) and five and six double-bonds and a chain of 22 carbon atoms (e.g., docosahexaenoic acid). 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 third carbon atom counting from the end of the fatty acid chain).

Composition of some fish oils is presented in **Table 7.8**.

Table 7.8 Composition of fish oils

Constituent	Percentage
Oleic acid	8–25
Linoleic acid	2–8
Linolenic acid	0–3
C20 (4 double-bonds)	15–30
C22 (5 or 6 double-bonds)	15–30

Fabrication of polyols for PU based on fish oil as mentioned in the literature is in operation at Newcastle (UK) using the classical transformation of double-bonds in hydroxyl groups [300].

7.4.11 Polyols by Phenolation of Unsaturated Natural Compounds [302, 303, 304]

Alkylation of phenols with alkenes by the Friedel–Crafts reaction catalysed by Lewis acids (e.g., BF_3) or Brönstedt acids (HBF_4, $HSbF_6$, triflic acid) leads to alkyl phenols. Alkyl groups enter the *para* or *ortho* positions of the aromatic ring of phenol. If the alkene is a natural unsaturated compound such as vegetable oils or terpenes, the product of the Friedel–Crafts reaction with phenols ('phenolation reaction') is a new compound: a bio-based alkylated phenol. **Figure 7.40** shows the hypothetical product possible that can be formed by Friedel–Crafts alkylation of phenol with soybean oil.

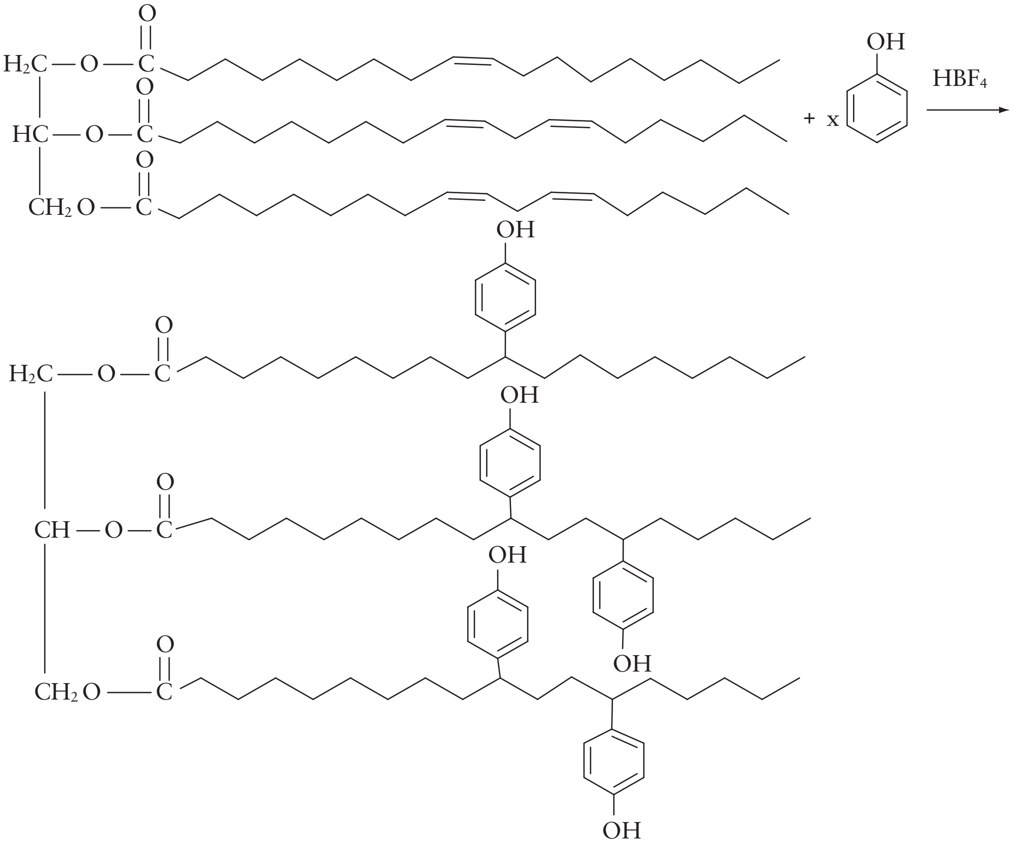
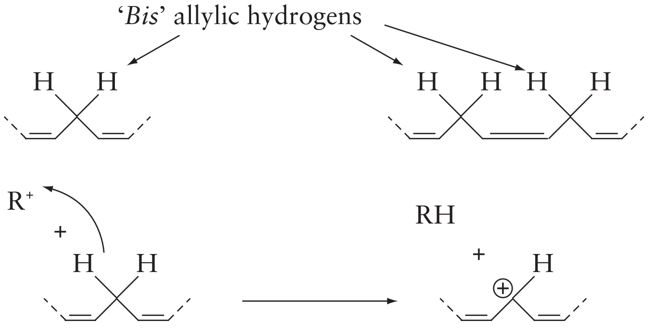


Figure 7.40 Phenolation of soybean oil

Alkylation of phenols with alkenes is carried out in three steps (**Figure 7.41**):

1) Formation of carbocations by reaction of double-bonds with the catalyst;
2) Formation of phenyl ethers by reaction of carbocations with a phenolic hydroxyl group; and
3) Rearrangement of phenyl ethers into *ortho* and *para* alkylated phenols.

Study of alkylation of vegetable oils with phenols has shown that the best oils for Friedel–Crafts alkylation are oils with a high content of fatty acids with only one double-bond (oleic acid) such as triolein, high-oleic soybean oil or high-oleic safflower oil. Oils such as soybean oil, sunflower oil, canola oil or linseed oil have fatty acids with multiple double-bonds (linoleic and linolenic acids) and are not good partners for Friedel–Crafts alkylation of phenols due to the presence of '*bis*' allylic positions, which elicit strong transfer reactions with carbocations involved in the alkylation reaction (**Reaction 7.95**).



(7.95)

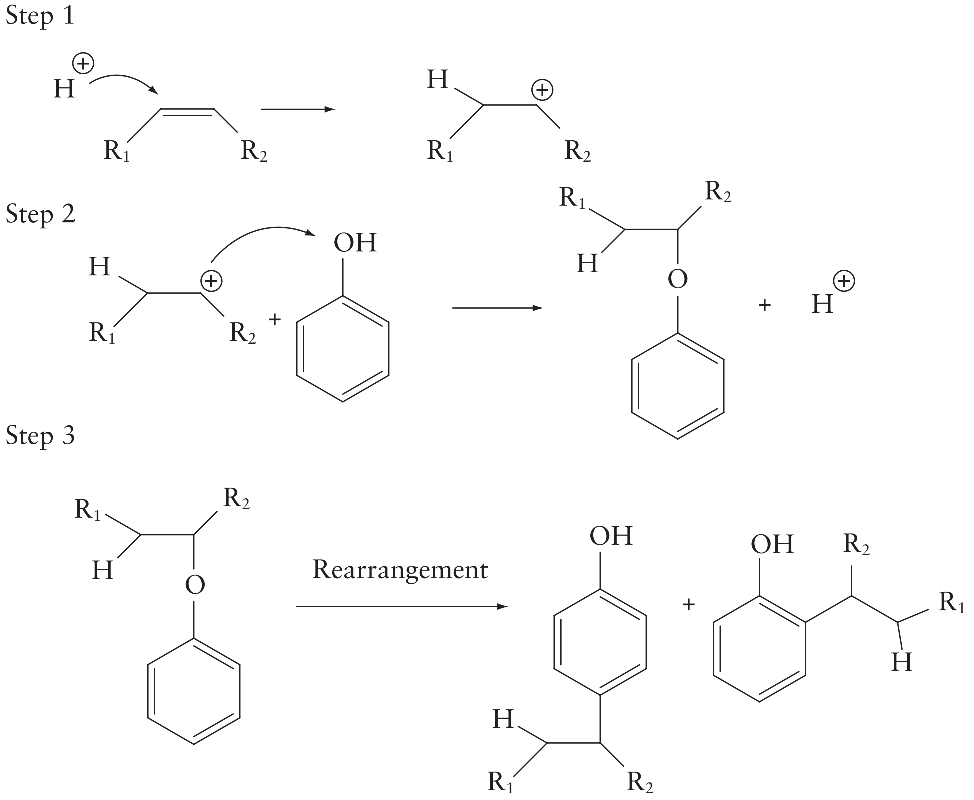
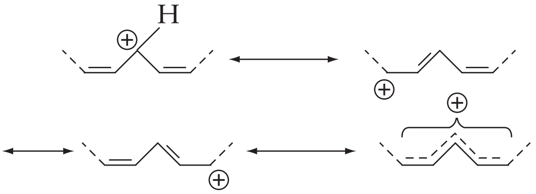


Figure 7.41 Mechanism of phenol alkylation with alkenes

As a consequence of this transfer reaction are formed very stable cations, of low reactivity, with positive charge distributed in resonance hybrids with five or seven carbon atoms (**Reaction 7.96**). The alkylation reaction of phenols with these stable cations is very slow and of low yield.



(7.96)

Thus, if by phenolation of soybean oil only 20–22% of the double-bonds participate in the alkylation of the phenol ring (only 1 phenol/triglyceride unit), upon alkylation of high-oleic soybean oil ≈60–65% from the double-bonds are involved in the alkylation reaction. Thus, the phenol alkylated with high-oleic soybean oil has the probable structure shown in **Figure 7.42**.

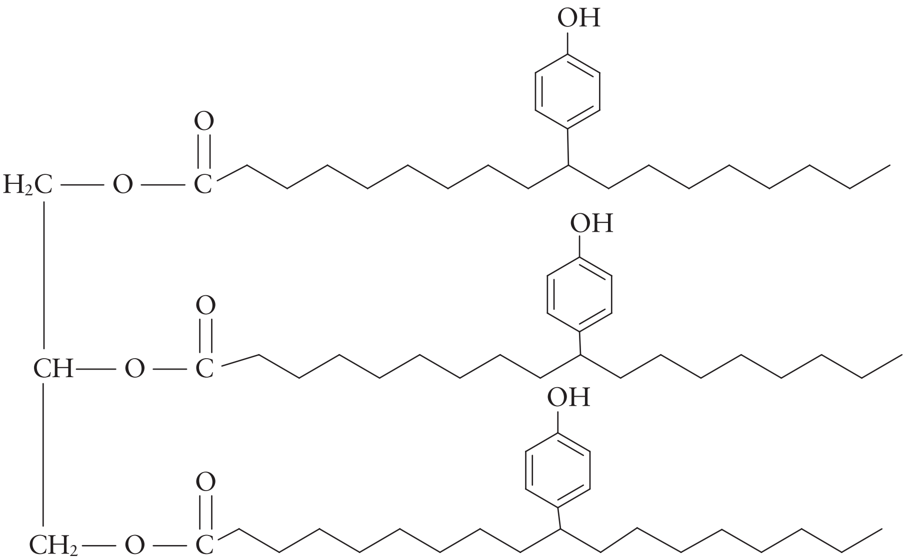


Figure 7.42 Probable structure of phenol alkylated with high-oleic soybean oil

Phenolic hydroxyl groups react with isocyanates only in very low yield. Hence, the phenolated oil shown in **Figure 7.42** can be transformed in a useful polyol for PU preparation by hydroxyalkylation of phenolic groups with alkylene oxides such as PO, EO, glycidol (**Figure 7.43**) or by the Mannich reaction (**Figure 7.44**).

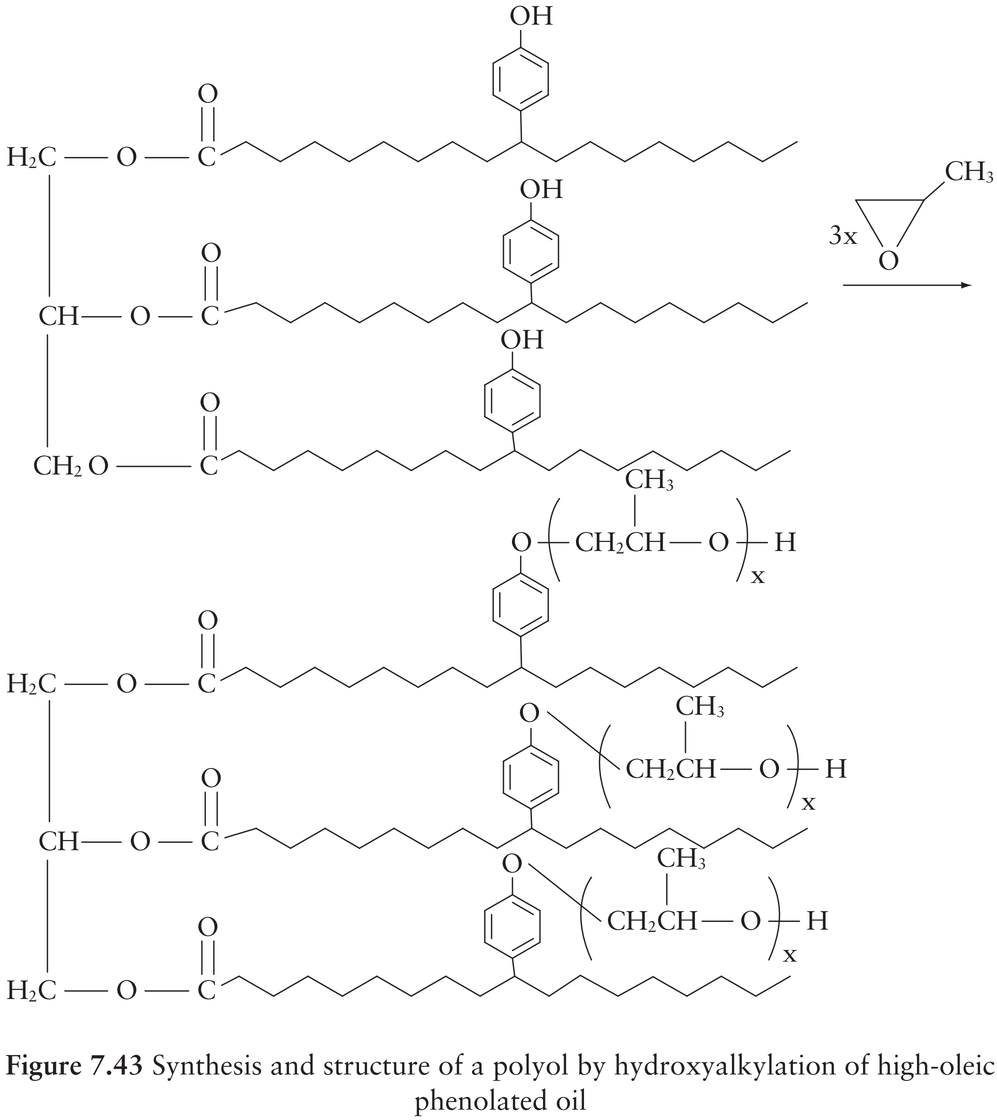


Figure 7.43 Synthesis and structure of a polyol by hydroxyalkylation of high-oleic phenolated oil

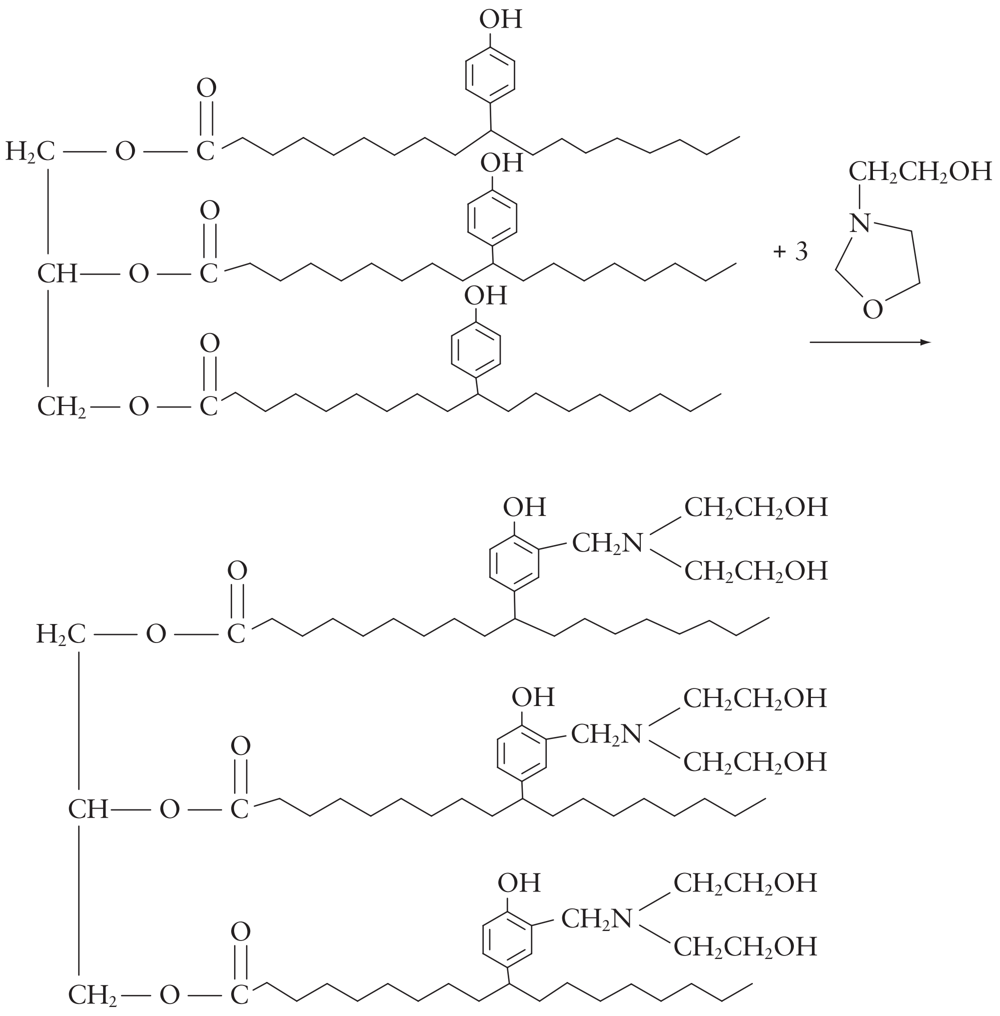


Figure 7.44 Synthesis and structure of a Mannich polyol by reaction of phenolated high-oleic soybean oil with 1,3-*N*-hydroxyethyl OXA

Fortunately, oils having fatty acids with multiple double-bonds such as soybean oil and linseed oil polymerise efficiently in the presence of the same catalysts used for the Friedel–Crafts reaction (HBF_4 or triflic acid) and, as an immediate consequence, the product of reaction is a polymerised oil having multiple phenol functionality.

Limonene is another natural unsaturated compound which, under the conditions of Friedel–Crafts reactions, alkylates the phenols efficiently with both double-bonds [302] (**Figure 7.45**). The phenols alkylated with limonene can be transformed into useful polyols for PU preparation by hydroxyalkylation with alkylene oxides (PO, glycidol) and by the Mannich reaction [302] (**Figure 7.46**).

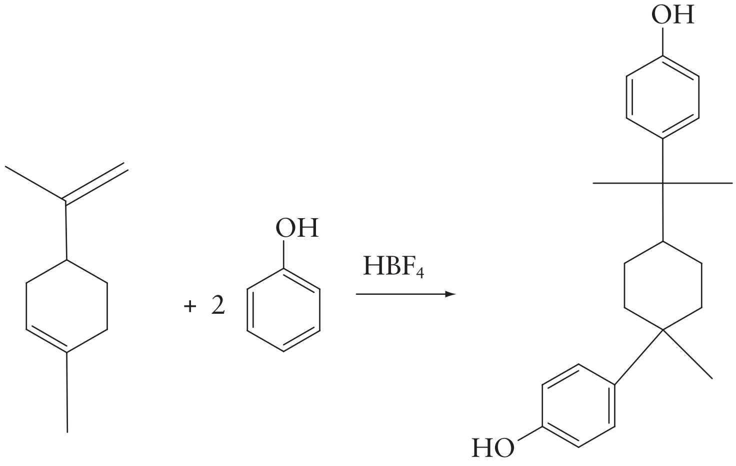


Figure 7.45 Friedel–Crafts alkylation of phenol with limonene

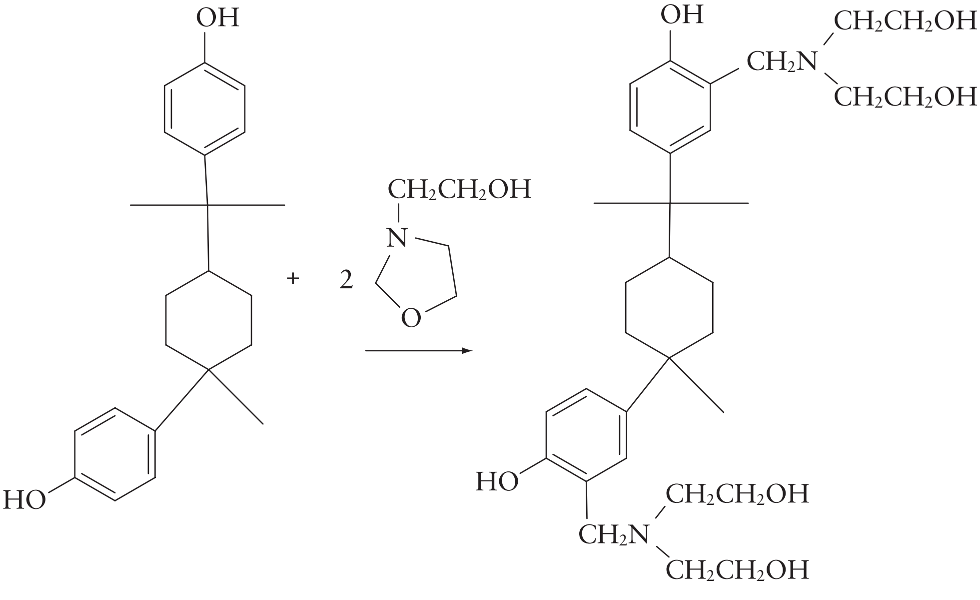
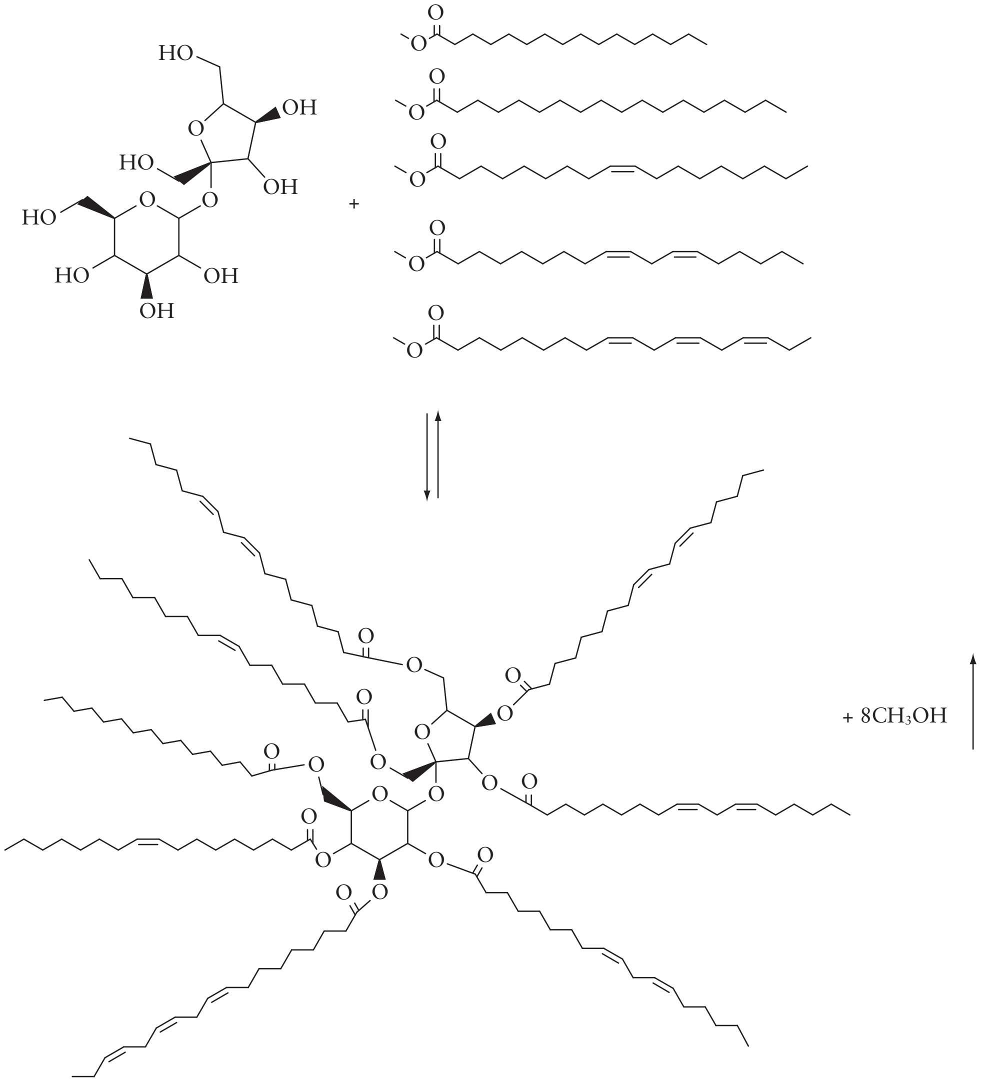


Figure 7.46 Synthesis of a Mannich polyol from phenol alkylated with limonene and 1,3-*N*-hydroxyethyl OXA

Polyols synthesised using phenolated oils or phenolated limonene (20–50% in the polyol mixture with petrochemical polyols) have been used for preparation of rigid PUF with good physical–mechanical properties [302, 303]. Very good rigid spray PUF have been prepared with Mannich polyols from phenolated soybean oil or phenolated limonene. The advantage of bio-based polyols prepared from phenolated oils and phenolated limonene is aromatic rings in their structure, which leads to the improved physical–mechanical, thermal and fireproofing properties of rigid PUF.

7.4.12 High Functionality Bio-based Polyols from Sucrose Soyate [305, 306]

A very interesting bio-based compound is sucrose: all the hydroxyl groups are esterified with unsaturated fatty acids. If the fatty acids are from soybean oil, the totally esterified sucrose is called ‘sucrose soyate’. Procter & Gamble Chemicals (CA, USA) developed a way of esterifying sucrose with unsaturated fatty acids to achieve a high degree of unsaturation [305]. The commercial name of this type of compound is Sefose, and it is prepared by transesterification of sucrose with methyl esters of fatty acids derived from soybean oil (methyl soyate or bio-diesel) in the presence of basic catalysts (e.g., potassium carbonate), at 135.5 °C, with continuous removal of methanol. Fully esterified sucrose with fatty acids has very low viscosity (300–400 mPa.s at 25 °C) due to its very compact molecular structure. The synthesis and structure of Sefose is presented in **Figure 7.47**.



Sefose

Figure 7.47 Synthesis and structure of fully esterified sucrose with methyl soyate

A high-functionality bio-based polyol from fully esterified sucrose with methyl soyate is prepared in two steps:

a) Classical epoxidation of fully esterified sucrose (**Figure 7.48**).

b) Ring-opening of epoxidised fully esterified sucrose with acetic acid or methanol (**Figure 7.49**).

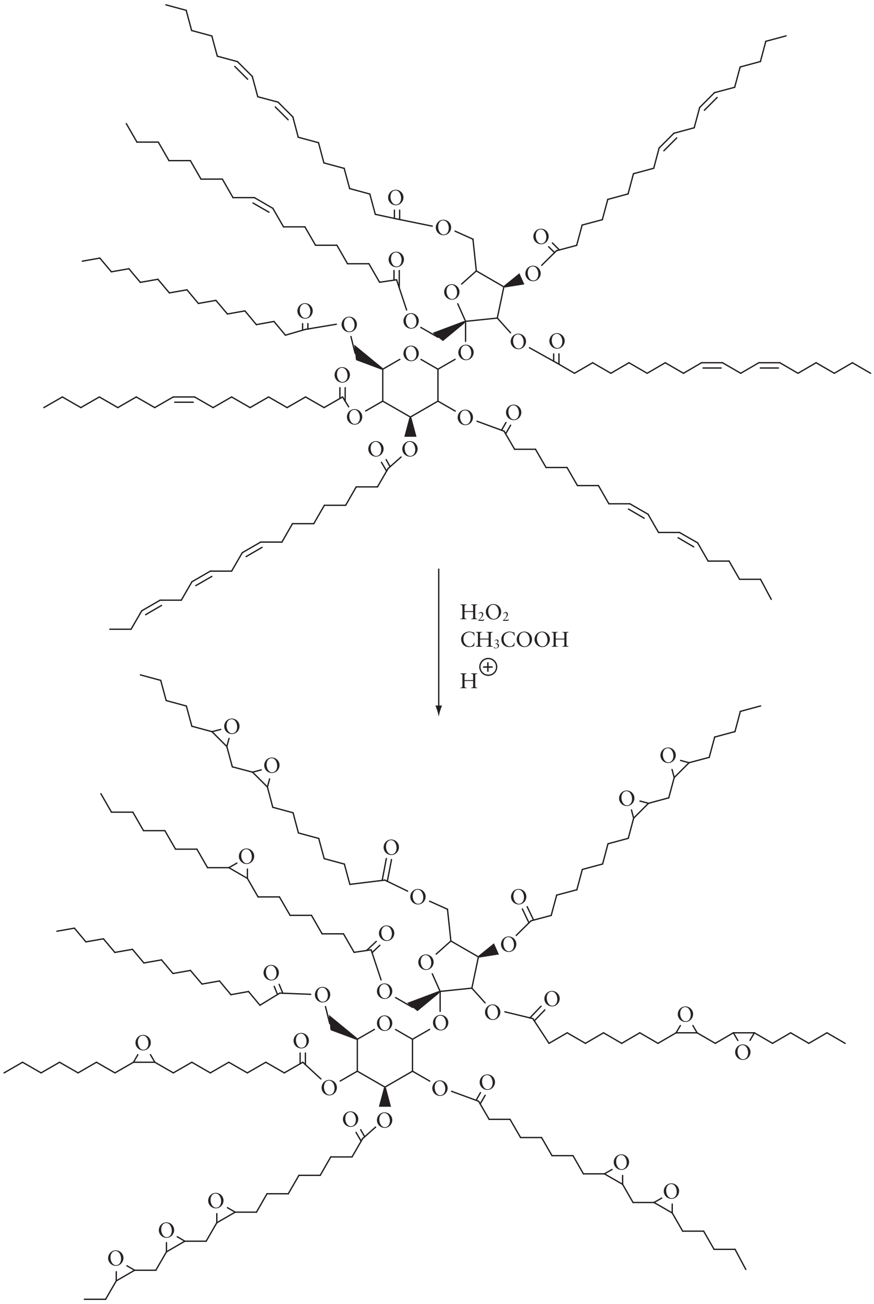


Figure 7.48 Synthesis and structure of epoxidised fully esterified sucrose

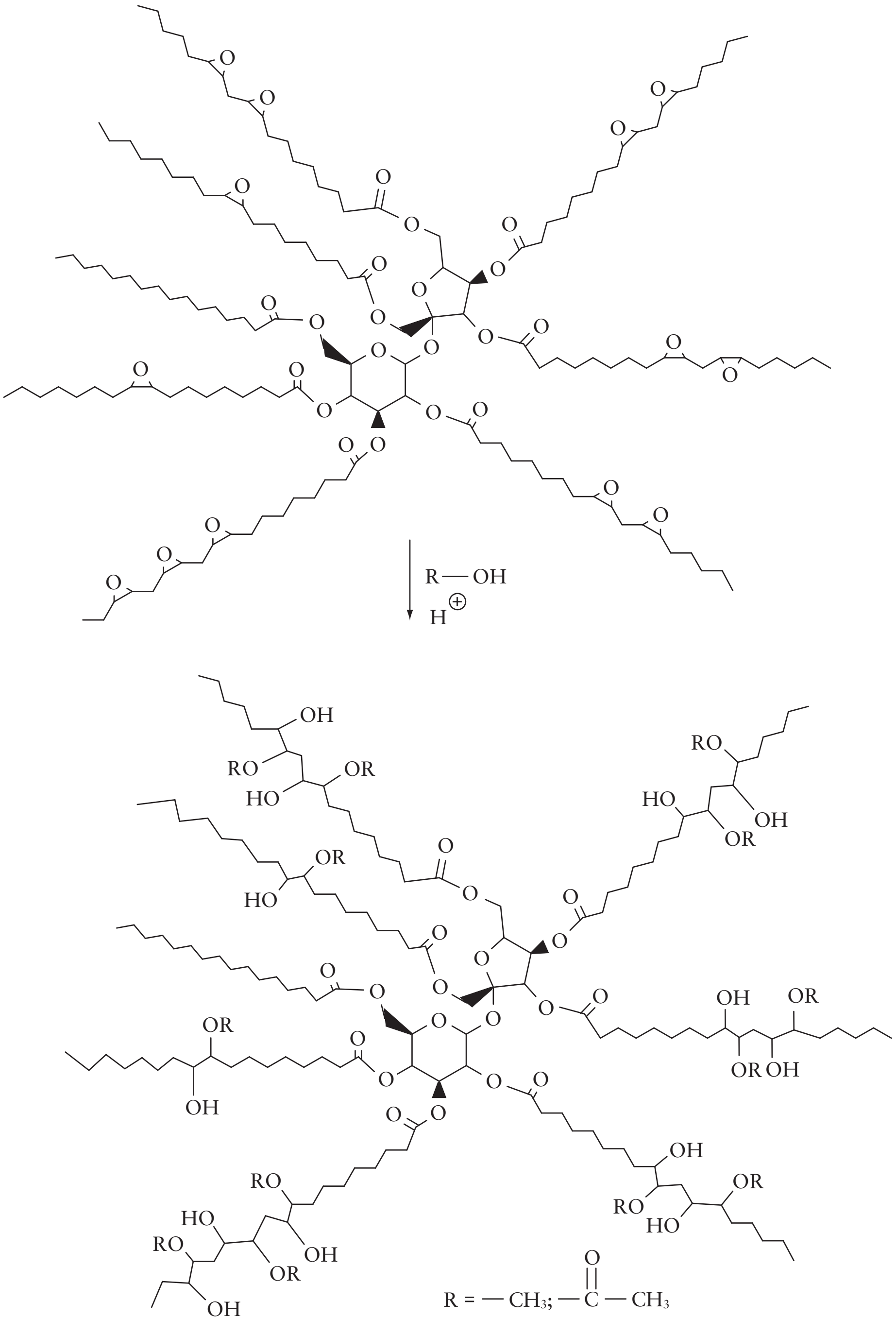


Figure 7.49 Synthesis and structure of a bio-based polyol from epoxidised fully esterified sucrose

Using the high-functionality polyol from **Figure 7.49** and aliphatic diisocyanates (e.g., isophorone diisocyanate), PU coatings with excellent hardness, solvent resistance, toughness and gloss have been prepared [306].

7.5 Looking to the Future of Polyols from Renewable Resources

Nature offers a generous range of compounds useful for preparation of bio-based polyols (vegetable oils, fish and krill oils, lignin, limonene, lactides, CNSL, proteins, starch, CO_2). Many compounds produced using petrochemicals can be synthesised by biotechnology routes or by using classical chemical routes from bio-based raw materials such as 1,3-propanediol, THF, succinic acid, 1,4-BD, AA, sebacic acid, azelaic acid, and isosorbide.

There are many chemical pathways for transformation of natural renewable materials into polyols for PU, and many of them have been presented in detail in this chapter.

Companies [e.g., Bayer, Leverkusen (Germany), Dow Chemicals (MI, USA), BASF (Ludwigshafen, Germany), Huntsman (UT, USA), Cargill (MN, USA), Henkel (Düsseldorf, Germany), Cognis (Monheim, Germany), Unichema (IL, USA), Biobased Technologies (AR, USA)], research institutes, and research centres within universities [e.g., Pittsburg State University, KS, USA), Michigan State University (MI, USA), Oldenburg University (Oldenburg, Germany), Karlsruhe University (Karlsruhe, Germany), Institut Charles Gerhardt (Montpellier, France), University of Guelph (Guelph, Canada), Trent University (Peterborough, Canada), Universitat Rovira I Virgili, (Tarragona, Spain)] have developed intensive research programmes focusing on the preparation of polyols starting from natural compounds.

Thus, some natural oil polyols are produced on the industrial scale by Cargill, Dow Chemicals, Urethane Soy Oil System (SD, USA), Biobased Technologies, BASF, Bayer, Vertellus (IN, USA), Mitsui Chemicals (Minato-Ku, Japan), Cognis, and Elmira (NY, USA).

Many renewable polyols produced worldwide from vegetable oils are used in PU industry (usually in combination with petrochemical polyols for slabstock flexible foams) for car sittings or different parts of cars, for rigid PUF, PU coatings, adhesives, sealants and elastomers.

The concentration of renewable polyols prepared from soybean oil or palm oil in a mixture with petrochemical polyols vary from 5% to 20–30% (rarely 50%) at a concentration that does not affect PU properties negatively. Vegetable oil polyols, due to certain structural imperfections (dangling chains that are non-participants to the

PU network; non-functionalised saturated fatty acids such as palmitic and stearic) cannot be used as the sole polyol because the properties of PU deteriorate.

Fortunately, there are many other polyols prepared from renewable raw materials that can be used as the sole polyol without the need for a petrochemical polyol.

Thus, some polyols [e.g., polyether polyols based on 1,3-propanediol (Cerenol Polyols of DuPont), RENUVA polyols (Dow), BALANCE polyols (BASF)] can be used as the sole polyol for high-performance PU flexible foams, elastomers and coatings. Polyols based on PGL and CNSL can be used as the sole polyol for high-performance rigid PUF without the need to use petrochemical polyols.

By increasing the functionality of castor oil by thiol-ene reaction with 2-mercaptoethanol or of mercaptanised soybean oil by thiol-ene reactions with 1-allyl glycerol or allyl TMP, it is possible to prepare rigid PUF with good physical–mechanical properties without the use of petrochemical copolyols.

A lot of research regarding renewable polyols was carried out in Malaysia (palm oil polyols), China, India and in Latin America (Peru, Venezuela, Brazil, Mexico), all of which are important producers of vegetable oils and natural products.

In contrast with petrochemical resources, the availability of renewable natural raw materials used for fabrication of polyols for PU is practically unlimited.

In the near future, new polyols starting from renewable resources that lead to PU with properties very close or better than the properties of PU from petrochemical polyols will be produced.

Fabrication of polyols from renewable resources is a very promising, sustainable and economic approach, and a real hope for the future of PU.

References

1. D. Reed, *Urethane Technology*, 1997, **14**, 2, 20.

2. A. Heidbreder, R. Höfer, R. Grützmacher, A. Westfechtel and C.W. Blewet, *European Journal of Lipid Science and Technology*, 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 in *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. A. Dotan in *Handbook of Thermosets Plastics*, Elsevier Inc., Amsterdam, The Netherlands, 2014, p.576.

7. National Non-Food Crops Center, Newsletter, York, UK, 2008, Issue 11. *http://www.renewableworld.org.UK/pdf.*

8. P.B. Smith and G.F. Payne, *Renewable and Sustainable Polymers – American Chemcal Society Symposium Series*, 2011, **1063**, 1, 1.

9. P.B. Smith, *Renewable and Sustainable Polymers – American Chemcal Society Symposium Series*, 2011, **1063**, 6, 966.

10. *Polymers from Renewable Resources*, Eds., S. Carlsson, Smithers Rapra Technology Ltd., Shawbury, Shropshire, UK, 2010.

11. *Monomers in Polymers and Composites from Renewable Resources*, Eds., M.N. Belgacem and A. Gandini, Elsevier, Amsterdam, The Netherlands, 2008.

12. A. Gandini, *Macromolecules*, 2008, **41**, 4, 949.

13. *ASTM D6866-12: Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis*, American Society for Testing and Materials, Washington, DC, USA, 2012.

14. T.M. Krieger, C. Johnas, S. Roy, and H.W. Terrinoni in *Proceedings of Polyurethanes Technical Conference*, 24–26th September, Atlanta, GA, USA, 2012, p.223.

15. A. Albouy, J.D. Roux, D. Mouton and J. Wu in *Proceedings of Blowing Agent Systems: Formulations and Processing*, 19th February, Smithers Rapra Technology Ltd, Shawbury, UK, 1998, Paper4/1–Paper4/9.

16. J.H. Clark, V. Budarin, F.E.I. Deswarte, J.J.E. Hardy, F.M. Kerton, A.J. Hunt, R. Luque, D.J. Macquarrie, K. Milkowski, A. Rodriguez, O.Samuel, S.J. Tavener, R.J. White and A.J. Wilson, *Green Chemistry*, 2006, **8**, 853.

17. A. Morschbacker, *Polymer Reviews*, 2009, **49**, 2, 79.

18. A. Morschbacker, C.E.S. Campos, L.C. Cassiano, L. Roza, F. Almada and R.W. do Carmo in *Handbook of Green Materials*, Eds., K. Osman, A.P. Mathew, A. Bismark, O. Rojas and M. Sain, World Scientific Publishing Company, Singapore, 2014, **4**, 89.

19. M. Ionescu in *Chemistry and Technology of Polyols for Polyurethanes*, Smithers Rapra Technology Ltd., Shawbury, Shropshire, UK, 2005, p.435.

20. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Eds., H.F. Mark, M. Grayson and D. Eckroth, Wiley, New York, NY, USA, 1979, **1**, 644.

21. K.C. Frisch and J.L. Reegen in *Ring Opening Polymerization*, Eds. K.J. Ivin and T. Saegusa, Marcel Dekker, New York, NY, USA, 1969.

22. P.M. Dreyfuss and M.P. Deyfuss in *Encyclopedia of Polymer Science and Technology*, Eds., H.F. Mark, N.G. Gaylord and N.M.B. Bikales, Interscience, New York, NY, USA, 1970, **13**, 670.

23. *http://www.bio-amber.com/bioamber/en/products.*

24. *http://www.Myriant.com/media/press-kit-files/Myriant-BioBD Brochure-0613.pdf.*

25. E.N. Frenkel and F.L. Thomas, *Journal of the American Oil Chemists Society*, 1972, **49**, 10.

26. L.H. Joo, A.B. Sung, L.S. Deuk and C.J. Sik, inventors; Korea Institute of Science and Technology, assignee; US2015239858, 2015.

27. P. Kubisa and S. Penczek, *Progress in Polymer Science*, 1999, **24**, 10, 1409.

28. A. Sunder, R. Hanselmann, H. Frey and R. Mülhaupt, *Macromolecules*, 1999, **32**, 13, 4240.

29. A. Sunder, R. Mülhaupt and H. Frey, *Macromolecules*, 2000, **33**, 2, 309.

30. J.F. Stumbé, A. Sunder and R. Haag in *Proceedings of American Chemical Society Polymeric Materials: Science and Engineering*, San Diego, CA, USA, 2001, **84**, 1023.

31. H. Kautz, A. Sunder and H. Frey, *Macromolecular Symposia*, 2001, **163**, 67.

32. M. Ionescu, Unpublished Work.

33. G.T. Peckham and E.M. Filachione in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Edition, John Wiley & Sons, Inc., New York, NY, USA, 1967, **12**, 170.

34. D. Garlota, *Journal of Polymers and the Environment*, 2002, **9**, 2, 63.

35. *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th Edition, John Wiley & Sons, Inc., New York, NY, USA, 2005, **14**, Hydroxycarbocylic Acids.

36. D. Radojčić in *Polyols Based on Lactic Acid for Polyurethanes*, Pittsburg State University, Pittsburg, KS, USA, 2010. [Masters' Thesis]

37. D. Radojčić, M. Ionescu and Z.S. Petrović, *Contemporary Materials*, 2013, **4**, 1, 9.

38. S. Miao, S. Zhang, Z. Su and P. Wang, *Journal o,f Polymer Science, Part A: Polymer Chemistry Edition*, 2010, **48**, 1, 243.

39. R.R. Yocum, S. Dole and J.G. Pero, inventors; Myriant Corp., assignee; WO2014043591, 2014.

40. W. Gong, S. Dole, T. Grabar, A.C. Collard, J.G. Pero and R.R. Yocum, inventors; Myriant Corp., assignee; US20090281481, 2009.

41. S. Dole, R.R. Yocum, T. Hermann and X. You, inventors; Myriant Corp., assignee; US2013337519, 2013.

42. D. Dunuwila and M. Cockrem, inventors; BioAmber International, assignee; WO2012138642, 2012.

43. O.S. Fruchey, B.T. Keen, B.A. Albin, N.A. Clinton, D. Dunuwila and B.D. Dombek, inventors; Bioamber SAS, assignee; CN102858731, 2011.

44. S.Y. Lee, J.W. Lee, H. Song, S. Choi and J.M. Kim, inventors; Korea Advanced Institute of Science and Technology, assignee; WO2009048202, 2009.

45. S. Dole, R.R. Yocum, T. Hermann and X. You, inventors; Myriant Corp., assignee; US2013337519, 2013.

46. S.Y. Lee, J.W. Lee, S. Shoi and J. Yi, inventors; Korrea Advanced Institute of Science and Teachnology, assignee; KR20100084327, 2010.

47. M. Jiang, W. Dai, Y. Xi, R. Xu, J. Zhang, K. Chen and M. Zhang, inventors; Nanjing University of Technology, assignee; CN20131144634, 2013.

48. T. Boussie, E. Dias, Z. Fresco, V. Murphy, J. Shoemaker, R. Archer and H. Jiang, inventors; Rennovia Inc, assignee; US20090268414, 2009.

49. M. Kröger, U. Prüsse and K.D. Vorlop, *Topics in Catalysis*, 2000, **13**, 3, 237.

50. W. Gong, inventor; BP Corp. North America Inc., assignee; WO2009064515, 2009.

51. J.P. Arhancet and L.H. Slaugh, inventors; Shell Oil Co., assignee; US5304691, 1994.

52. T. Haas and D. Amtz, inventors; Degussa Aktiengesellchaft, assignee; US5364987, 1994.

53. H. Biebe, K. Menzel, A.P. Zeng and W.D. Deckwer, *Applied Microbiology and Biotechnology*, 1999, **52**, 3, 289.

54. Z.L. Xiu and A.P. Zeng, *Applied Microbiology and Biotechnology*, 2008, **78**, 6, 917.

55. a) *IHS, Process Economics Program Report 227*, 1,3 Propanediol and Polytrimethylene Terephthalate (PTT), IHS, Englewood, CO, USA, December 1999.

    b) *http://www2.dupont.com/Bio-based_Propanediol/en_CN/products/susterra/index.html*

56. I.J. Desborough, I.H. Hall and J.Z. Neisser, *Polymer*, 1979, **20**, 5, 545.

57. *Dimerised Fatty Acids Technology for Use in Polyurethanes*, Unichema, Chicago, IL, USA, 2000.

58. R.L. Maglinao and B.B. He, *Biofuels*, 2012, **3**, 6, 675.

59. S. Wang, K. Yiu, Y. Zhang and H.Liu, *ACS Catalysis*, 2013, **3**, 9, 2112.

60. T. Jiana, M.X. Ren, S.S. Chen, Q. Huai, W.Y. Ying and F.H. Chao, *Advanced Materials Research*, 2014, **906**, 103.

61. 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.

62. J.J. Cimerol and S. Fuzesi, *Journal of Elastomers and Plastics*, 1981, **13**, 4, 224.

63. F.H. Otey, B.L. Zagoren and C.L. Mehltretter, *Industrial & Engineering Chemistry, Product Research and Development*, 1963, **2**, 4, 256.

64. F.H. Otey, B.L. Zagoren, F.L. Bennett and C.L. Mehltretter, *Industrial & Engineering Chemistry, Product Research and Development*, 1965, **4**, 4, 224.

65. R.H. Leitheiser, C.N. Impola, R.J. Reid and F.H. Otey, *Industrial & Engineering Chemistry, Product Research and Development*, 1966, **5**, 3, 276.

66. F. Stoenescu, M. Ionescu, V. Dumitriu and I. Mihalache, *Materiale Plastice*, 1979, **16**, 1, 4.

67. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Advances in Urethane Science & Technology*, Wiley, New York, NY, USA, 1998, **14**, 151.

68. *Oxidative Coupling of Phenols*, Eds., W.I. Taylor and A.R. Battersby, Marcel Dekker, New York, NY, USA, 1989.

69. M. Ionescu, Unpublished Work.

70. F.H. Otey, F.L. Bennett, B.L. Zagoren and C.L. Mehltretter, *Industrial & Engineering Chemistry, Product Research and Development*, 1965, **4**, 4, 228.

71. F.H. Otey, R.P. Westhoff and C.L. Mehltretter, *Journal of Cellular Plastics*, 1972, **8**, 3, 156.

72. J.H. Lara and R. Katzen, inventors; Repap Technology Inc., assignee; US4764596, 1988.

73. E.N. Frankel and F.L. Thomas, *Journal of the American Oil Chemists Society*, 1972, **49**, 10.

74. V. Erä, P. Jääskelainen and K. Ukkonen, *Angewandte Makromolekulare Chemie*, 1980, **88**, 79.

75. A. Lehtinen, V. Erä, T. Mustonen and E. Anttalainen, *Die Makromoleculare Chemie, Rapid Communications*, 1980, **1**, 8, 499.

76. V. Era and P. Jääskelainen, *Journal of the American Oil Chemists Society*, 1981, **57**, 1, 201.

77. I.A. Pearl in *Annual Review of Lignin Chemistry*, Institute of Paper Chemistry, Appleton, WA, USA, 1970.

78. *(+)– Catechin Hydrate*, Report: C1251 SIGMA, [225937-10-0], Sigma–Aldrich, St. Louis, MO, USA.

79. D.E. Garcia, A. Pizzi, W.G. Glosser, S. Pazkowski and P. Laborie, *European Polymer Journal*, 2015, **67**, 152.

80. A.E. Hagerman in *The Tannin Handbook*, Miami University, FL, USA, 2002. *http://chemistry.muohio.edu/hagerman.*

81. *http://www.slideshare.net/GreenPalmOil/2013-global-vegtable-oil-production.*

82. Z.S. Petrović, A. Zlatanić, C.C. Lava and S. Sinadinovic-Fiser, *European Journal of Lipid Science and Technology*, 2002, **104**, 5, 293.

83. M. Janković and Z.S. Petrović, *Journal of the American Oil Chemists Society*, 2001, **78**, 7, 725.

84. T. Heinemann, H.J. Scholl and R. Welte in *Proceedings of Polyurethanes EXPO '96 Conference*, Las Vegas, NV, USA, 1996, p.320.

85. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Eds., H.F. Mark, M. Grayson and D. Eckroth, John Wiley & Sons, New York, NY, USA, 1979, **5**, 1.

86. A. Guo, Y. Cho and Z.S. Petrović, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 2000, **38**, 21, 3900.

87. Z.S. Petrović, A. Guo, I. Javni and W. Zhang in *Proceedings of the Alliance for Polyurethane Industry Polyurethanes EXPO 2000*, Boston, MA, USA, 2000, p.323.

88. A. Guo, I. Javni and Z.S. Petrović, *Journal of Applied Polymer Science*, 2000, **77**, 2, 467.

89. Z.S. Petrović, A. Guo and I. Javni, inventors; Pittsburg State University, assignee; US6107433, 2000.

90. P. Daute, J. Klein, H. Kluth and R. Grützmacher, inventors; Henkel KGAA, P. Daute, J. Klein, H. Kluth and R. Grützmacher, assignees; WO9531493,1995.

91. V.D. Athawale and S.L. Kolekar, *Journal of Applied Polymer Science*, 2000, **75**, 6, 825.

92. V.D. Athawale, P.S. Pillay and S.L. Kolekar, *European Coatings Journal*, 2001, **1–2**, 18.

93. Z.S. Petrović and D.J. Fajnik, *Journal of Applied Polymer Science*, 1984, **29**, 4, 1031.

94. D. Chaser and M.J. Hughes, inventors; Noveon IP Holdings Corp., assignee; WO0329182, 2003.

95. G. Lakshminarayana. M.M. Paulose and B.N. Kumari, *Journal of the American Oil Chemists Society,* 1984, **61**, 12, 1871-2.

96. N.B. Tran, J. Vialle and Q.T. Pham, *Polymer*, 1997, **38**, 10, 2467.

97. K.R. Kunduru, A. Basu, M.H. Zada and A.J. Domb, *Biomacromolecules*, 2015, **16**, 2572–2587.

98. N.B. Tran and Q.T. Pham, *Polymer*, 1997, **38**, 13, 3307.

99. I. Javni and Z. Petrović in *Proceedings of Antec 1997*, Toronto, Canada, 1997, **1**, 791.

100. I. Javni, Z.S. Petrović, A. Guo and R. Fuller, *Journal of Applied Polymer Science*, 2000, 77, **8**, 1723.

101. R. Höfer, P. Daute, R. Grützmacher and A. Westfechtel, *Informations Chimie*, 1994, **362**, 95.

102. T. Heinemann, H.J. Scholl and R. Welte in *Proceedings of Polyurethanes EXPO '96 Conference*, Las Vegas, NV, USA, 1996, p.320.

103. Z.S. Petrović and D.J. Fajnik, *Journal of Applied Polymer Science*, 1984, **29**, 4, 1031.

104. G. Lakshminarayana, M.M. Paulose and B.N. Kumari, *Journal of the American Oil Chemists Society*, 1984, **61**, 12, 1871.

105. M. Pavaskar and A. Kishirsagar, *Financial Vision*, 2013, **1**, 5, 15.

106. S.A. Baser and D.V. Khakhar, *Cellular Polymers*, 1993, **12**, 5, 390.

107. J.Y. Jadhav, *International Journal of Polymeric Materials*, 1986, **11**, 3, 151.

108. M. Ionescu, S. Mihai, E. Stepan, C. Roibu and V. Preoteasa in *Proceedings of the Alliance for Polyurethane Industry Polyurethanes Conference*, Columbus, OH, USA, 2001, p.607.

109. R.T. Wojcik in *Polyurethane Coatings: From Raw Materials to End-Products*, Technomic Publishing Co., Inc., Lancaster, PA, USA, 2000, Chapter 2.

110. J.P. Boiteux, B. Brancq, N. Lecocu and F. Loussayre, inventors; Societe d'Exploitation de Produits pour les Industries Chimiques, assignee; US5108661, 1992.

111. No inventor; American Cyanamid Co., assignee; GB650940, 1951.

112. G.C. Tesora, inventor; Onix Oil & Chemical Co., assignee; US2844609, 1958.

113. V. Lamherti and G.J. McCrimlisk, inventors; Lever Brothers Co., assignee; US3107258, 1963.

114. H. Kroll and H. Nadeau, *Journal of the American Oil Chemists Society*, 1956, **34**, 323.

115. R.A. Reck, *Journal of the American Oil Chemists Society*, 1979, **56**, 796.

116. L.W. Brunette in *Nonionic Surfactants*, Volume 1, Ed., M.J. Schick, Marcel Dekker Inc., New York, NY, USA, 1967, p.395.

117. 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.

118. Z. Petrović, I. Javni, A. Guo and W. Zhang, inventors; Pittsburg State University, assignee; US6433121, 2002.

119. Z. Petrović, A. Guo and I. Javni, inventors; Pittsburg State University, assignee; US6573354, 2003.

120. Z. Petrović, I. Javni, A. Guo and W. Zhang, inventors; Pittsburg State University, assignee; US6686435, 2004.

121. D. Chaser and M.J. Hughes, inventors; Noveon IP Holdings Corp., assignee; WO0329182, 2003.

122. M.Z. Arniza, S.S. Hong, Z. Idris, S.K. Yeong, H.A. Hassan, A.K. Din and Y.M. Choo, *Journal of the American Oil Chemists Society,* 2015, **92**, 243.

123. K.S. Chian, L.H. Gan and K.M. Chow in *Proceedings of Antec* '97, Toronto, Canada, 1997, **2**, 1996.

124. K.S. Chian and L.H. Gan, *Journal of Applied Polymer Science*, 1998, **68**, 3, 509.

125. T.W. Abraham, J.A. Carter, J. Malsam and A. Zlatanic, inventors; Pittsburg State University, T.W. Abraham, J.A. Carter, J. Malsam and A. Zlatanic, assignees; WO2007123637, 2007.

126. R. DeGenova, J. Malsam, A. Zlatanic and Y. Wazirzada, *Journal of Oil Palm Research*, 2008, October, 53.

127. N.M. Saifuddin, C.O. Wen, L.W. Zhan and K.X. Ning in *Proceedings of International Conference on Advances in Renewable Energy Technologies, Palm Oil Polyols for Polyurethane Applications*, 6–7th July, Putrajaya, Malysia, 2010.

128. K.H. Badri, S.H. Ahmad and S. Zakaria, *Journal of Material Science Letters*, 2000, **19**, 1355.

129. H. Zhao, R. Herrington and F. Rodriguez, inventors; Huntsman Petrochemicals LLC, assignee; US20080081873, 2008.

130. P. Kandanarachchi, A. Guo and Z. Petrović, *Journal of Molecular Catalysis A: Chemical*, 2002, **184**, 1–2, 65.

131. P. Kandanarachchi, A. Guo, D. Demydov and Z. Petrović, *Journal of the American Oil Chemists Society*, 2002, **79**, 12, 1221.

132. E.P. Wiltz, Z. Lysenko, F. Aguire, A. Sanders, J. Tsavalas, D. Babb and A.K. Schrock, inventors; Dow Global Technologies, assignee; WO2004096883, 2004.

133. R. Jenkins, inventor; Dow Global Technologies, assignee; WO2006047432, 2006.

134. A. Larre and D. Babb in *Proceedings of United Soybean Board Conference*, 1st May, Detroit, MI, USA, 2007.

135. D. Babb, J. Moore and C. Keillor in *Proceedings of Aliance for Polyurethane Industry Conference 2006*, Salt Lake City, UT, USA, 2006.

136. A. Zlatanić, Z.S. Petrović and K. Dusek, *Biomacromolecules*, 2002, **3**, 5, 1048.

137. R.H. Grubbs in *Handbook of Metathesis*, 1st Edition, 2003, Wiley-VCH, Weinheim, Germany, 2003.

138. S.L. Scott, *HELIA*, 2007, 30, **46**, 133. [Journal of Serbian Academy of Science and Arts]

139. R. Criegee, *Angewandte Chemie International Edition*, 1975, **87**, 745.

140. P. Tran, D. Graiver and R. Narayan, *Journal of the American Oil Chemists Society*, 2005, **82**, 9, 653.

141. T.S. Osmonov, E. Kharaz and J.M. Curtis, *Journal of the American Oil Chemists Society*, 2011, **88**, 689.

142. D.B. Garbark and H.P. Benecke, inventors; Battelle Memorial Institute, assignee; US20110269978, 2011.

143. D. Gravier, M. Patel and R. Narayan, *Recent Patents on Material Science*, 2010, **3**, 3, 203.

144. I. Cvetković, J. Milić, M. Ionescu and Z.S. Petrović, *Hemijska Industrija*, 2008, 62, **6**, 319.

145. Z.S Petrović. W. Zhang and I. Javni, *Biomacromolecules*, 2005, **6**, 713.

146. P.E. Throckmorton and E.H. Pryde, *Journal of the American Oil Chemists Society*, 1972, **49**, 641.

147. S.S. Narine, J. Tue and X. Kong, *Journal of the American Oil Chemists Society*, 2007, **84**, 173.

148. X. Kong, and S.S. Narine, *Biomacromolecules*, 2007, **8**, 3584.

149. X. Kong, and S.S. Narine, *Biomacromolecules*, 2007, **8**, 2203.

150. T. Garett and X.X.Du, inventors; MCPU Polymer Engineering LLC, assignee; US20110166315, 2011.

151. T. Garett and X.X. Du, inventors; MCPU Polymer Engineering LLC, assignee; US2011060115, 2011.

152. T. Garett and X.X.Du, inventors; MCPU Polymer Engineering LLC, assignee; US20120116042, 2012.

153. T. Garett and X.X. Du, inventors; MCPU Polymer Engineering LLC, assignee; US2012116043, 2012.

154. C.E. Hoyle and C.N. Bowman, *Angewandte Chemie International Edition*, 2010, **49**, 1540.

155. M.J. Kade, D.J. Burke and C.J.Hawker, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 2010, **48**, 743.

156. N.B. Cramer, S.K. Reddy, A.K. O'Brien and C.N. Bowman, *Macromolecules*, 2003, **36**, 7964.

157. A.B. Lowe and M.A. Harvison, *Australian Journal of Chemistry*, 2010, **63**, 8, 1251.

158. G.B. Batchev, J.A. Kenar, G. Biresaw and M.G. Han, *Journal of Agricultural and Food Chemistry*, 2009, **57**, 1282.

159. L.M. Campos, K.T. Killops, R. Sakai, J.M.J. Paulusse, D. Damiron, E. Drockenmuller, W. Messmore and C.J. Hawker, *Macromolecules*, 2008, **41**, 7063.

160. M. Desroches, S. Caillol, V. Lapinte, R. Auvergne and B. Boutevin, *Macromolecules*, 2011, **44**, 8, 2489.

161. S. Caillol, B. Boutevin and M. Desroche, inventors; Centre Nationale De La Recherche Scientifique and Montpellier II University, assignees; WO2012001315, 2012.

162. M. Uygun, M.A. Tasdelen and Y. Yagci, *Macromolar Chemistry and Physics*, 2010, **211**, 103.

163. C. Lluch, J.C. Ronda, M. Galia, G. Lligadas and V. Cadiz, *Biomacromolecules*, 2010, **11**, 1646.

164. G. Lligadas, J.C. Ronda, M. Galia and V. Cadiz, *Polymers*, 2010, **2**, 440.

165. A.B. Lowe, *Polymer Chemistry*, 2010, **1**, 17.

166. M. Desroches, S. Caillol, R. Auvergne and B. Boutevin, *European of Lipd Science and Technology*, 2012, **114**, 1, 84.

167. I. Carlson, A. Harden, S. Lundmark, A. Manea, N. Rehnberg and L. Svensson in *American Chemical Society Symposium Series*, 2003, **847**, Chapter 6.

168. O. Turunc, M. Frdaus, G. Klein and M.A.R. Meier, *Green Chemistry*, 2012, **14**, 2577.

169. H. Mutlu, A.N. Parvulescu, P.C.A. Bruijnincs, B.M. Weckhuysen and M.A.R. Meier, *Macromolecules*, 2012, **41**, 1866.

170. A.B. Lowe and M.A. Harvison, *Australian Journal of Chemistry*, 2010, **63**, 8, 1251.

171. M. Ionescu, Unpublished Work.

172. M. Ionescu, D. Radojčić, X. Wan, Z.S. Petrović and T. Upshaw, *European Polymer Journal*, 2014, **67**, 439.

173. M. Ionescu, D. Radojčić, X. Wan, Z.S. Petrović and T. Upshaw in *Proceedings of the American Oil Chemists Society Annual Meeting and Industry Showcase*, 4–6th May, Industrial Oil sand Products Division, Phoenix, AZ, USA, 2015, p.3.

174. G.Z. Li, R.K. Randev, H. Soeriyadi, G. Rees, C. Boyer, T.P. Davis, C.R. Becer and D.M. Haddleton, *Polymer Chemistry*, 2010, **1**, 1196.

175. R.K. Gupta, M. Ionescu, D. Radojčić, X. Wan and Z.S. Petrović, *Journal of Polymers and the Environment*, 2014, **22**, 3, 304.

176. C. Diehel and M. Korell, inventors; Evonik Industries AG, assignee; DE102013208386, 2014.

177. D. Casper and T. Newbold, inventors; Biobased Technologies LLC, assignee; US20120172610, 2012.

178. D. Casper and T. Newbold, inventors; Biobased Technologies LLC, assignee; US2006041156, 2006.

179. A. Sorrel, T. Newbold, J. Qian, S. Yalamanchili and N. Nodelman, inventors; Biobased Technologies LLC, assignee; US2013217798, 2013.

180. N. Luo and T. Newbold, inventors; Biobased Technologies LLC, assignee, US2008262259, 2008.

181. P. Daute, R. Grutzmacher, R. Höfer and A. Wastfechtel, *Fat Science and Technology*, 1993, **3**, 91.

182. T. Abraham, J. Malsam, X.A. Guo, M. Ionescu, I. Javni and Z.S. Petrović, inventors; Cargill, assignee; US2010217022, 2010.

183. G. Suppes, F.H. Hsieh, Y.C. Tu and P. Kiatsimkul, inventors; University of Missouri, assignee; WO2008058097, 2008.

184. G. Suppes, F.H. Hsieh, Y.C. Tu and P. Kiatsimkul, inventors; University of Missouri, assignee; US2010197820, 2010.

185. G. Suppes, Z. Lozado and A. Lubguban, inventors; University of Missouri, assignee; US2013131302, 2013.

186. W.L. Taylor, *Journal of the American Oil Chemists Society*, 1950, **27**, 472.

187. J.C. Covan, *Industrial and Engineering Chemistry*, 1949, **41**, 294.

188. J.A. Kenar, J. McEligot, H.S. Hwang and S.Z. Erhan, *Journal of the American Oil Chemists Society*, 2002, **79**, 11, 1151.

189. T.M. Kurth, R.A. Kurth, R.B. Turner and L.P. Kraifels, inventors; Urethane Soy Oil Systems Co., assignee; US2004209971, 2004.

190. T.M. Kurth, R.A. Kurth, R.B. Turner and L.P. Kraifels, inventors; Urethane Soy Oil Systems Co., assignee; US7084230, 2004.

191. T.M. Kurth, R.A. Kurth, R.B. Turner and L.P. Kraifels, inventors; Urethane Soy Systems Co., assignee; US2003191274, 2003.

192. L. Mahlum, inventor; South Dakota Soybean Processors, assignee; US6476244, 2001.

193. Z. Lozan, G.J. Suppes, F.H. Siech and A. Lubguban, *Journal of Applied Polymer Science*, 2009, **112**, 4, 2127.

194. R. Uloth and M. Mueller-Conradi, inventors; Shell Dev, assignee; US2236919, 1944.

195. E. Egon, inventor; Shell Dev, assignee; US2160572, 1939.

196. R. Larock and M. Hanson, inventors; Iowa State University, assignee; US6211315, 2001.

197. R. Larock, M. Hanson and F. Li, inventors; R. Larock, M. Hanson and F. Li, assignees; US2002095007, 2002.

198. Z. Liu, B. Sharma and S. Erhan, *Biomacromolecules*, 2007, **8**, 233.

199. M. Ionescu and Z.S. Petrović, inventors; Pittsburg State University, assignee; US8013088, 2011.

200. D. Rubin, inventor and assignee; US4908162, 1990.

201. G. Lligadas, J.C. Ronda, M. Galià and V. Cadiz, *Biomacromolecules*, 2007, **8**, 1858.

202. G. Lligadas, J.C. Ronda, M. Galià and V. Cádiz, *Polymers*, 2010, **2**, 440.

203. G. Lligadas, J.C. Ronda, M. Galià, U. Biermann and J.O. Metzger, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 2006, **44**, 634.

204. E. del Rio, M. Galià, V. Cádiz, G. Lligadas and J.C. Ronda, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 2010, **48**, 22, 4995.

205. E del Rio, G. Lligadas, J.C. Ronda, M. Galià and V. Cádiz, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 2010, **48**, 22, 5009.

206. Z.S. Petrović, I. Cvetcović, J. Milić, D.P. Hong and I. Javni, *Journal of Applied Polymer Science*, 2012, **125**, 4, 2920.

207. A. Zlatanić, I. Javni, M. Ionescu, N. Bilić and Z.S. Petrović, *Journal of Cellular Plastics*, 2014, **51**, 289.

208. M. Ionescu, Z.S .Petrović and X. Wan, *Journal of Polymers and the Environment*, 2010, **18**, 1, 1.

209. M. Ionescu, Z.S. Petrović and X. Wan, *Journal of American Oil Chemists Society*, 2008, **85**, 5, 465.

210. M. Ionescu, Z.S. Petrovic and I. Javni, inventors; Pittsburg State University, assignee; US8692030, 2014.

211. S. Bauer, R. Ruppel, E. Baum, J. Winkler and E. Bohres, inventors; BASF AG, assignee; WO2004020497, 2004.

212. A. Kunst, B. Eling, A. Loeffler, H.D. Heinz, W. Han and J. Mueller, inventors; BASF SE, assignee; WO2011135027, 2011.

213. J.R. Reese, S. Hager and M. Moore, inventors; Bayer Material Science, assignee; US20140024733, 2014.

214. Y.L. Hsiao, R. Skorpenske, B. Kaushiva, K. McDaniel, J.F. Pazos, S.L. Hager and K.W. Haider, inventors; Bayer Material Science, assignee; US2013023599, 2013.

215. Z.S. Petrović, Y. Ji and M. Ionescu, *Polymer Preprints*, 2010, **51**, 1, 757.

216. Y. Xu, Z.S. Petrovic, S. Das and G.L. Wilkes, *Polymer*, 2008, **49**, 19, 4248.

217. Z.S. Petrović, Y. Xu and W. Zhang, *Polymer Preprints*, 2007, **48**, 2, 852.

218. Z.S. Petrović, I. Cvetković, D.P. Hong, X. Wan, W. Zhang and T Abraham, *Journal of Applied Polymer Science*, 2008, **108**, 2, 1184.

219. P. Stross and R. Hemmer, *Advances in Carbohydrate Chemistry and Biochemistry*, 1991, **49**, 93.

220. M.L. Wolfrom in *Advances in Carbohydrate Chemistry*, Academic Press, New York, NY, USA, 1955.

221. A.C. Cope and T.Y. Shen, *Journal of the American Chemical Society*, 1956, **78**, 3177.

222. F. Xianhong, M. Jaffe, W.B. Hammond and A.J. East in *Proceedings of the Bioengineering Conference (NEBEC), 2009 IEEE 35th Annual Northeast*, Boston, MA, USA, 2009, p.1.

223. F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup and J.P. Pascault, *Progress Polymer Science*, 2010, **35**, 578.

224. I. Javni, O. Bilić, N. Bilić, Z.S. Petrović, E. Eastwood, F. Zhang and J. Ilavský, *Journal of Applied Polymer Science*, 2015, **132**, 47.

225. M. Ionescu, Z.S. Petrović, M.D. Sandhu, I. Javni, N. Bilic and E. Eastwood in *Proceedings of Polyurethane Technical Conference*, 26–28th September, Nashville, TN, USA, 2011, p.144.

226. H.B. Sunkara, E.K.A. Markildon, C.H. Howard and L.E. Manzer, inventors; E.I. DuPont de Nemour and Co., assignee; US6720459, 2004.

227. E.B. Muliawan, R.H. Poladi and H.B. Sunkara, inventors; E.I. DuPont de Nemour and Co., assignee; US8884073, 2014.

228. H.B. Sunkara and H.Q. Do, inventors; E.I. DuPont de Nemour and Co., assignee; US7009082, 2006.

229. M.A. Harmer, D.C. Confer, C.K. Hoffman, S.C. Jackson, A.Y. Liauw, A.R. Minter, E.R. Murphy, R.E. Spence and H.B. Sunkara, *Green Chemistry*, 2010, **12**, 1410.

230. A. Yokoyama, R.G. Saliya and H.B. Sunkara, inventors; E.I. DuPont de Nemour and Co., assignee; WO2012177270, 2012.

231. J.A. Creazzo, G. Loh and H.B. Sunkara, inventors; E.I. DuPont de Nemour and Co., assignee; US20090124719, 2009.

232. M. Ionescu, X. Wan and Z.S. Petrovic in *Proceedings of the CPI Polyurethanes '2009, Technical Conference*, 5–7th October, National Harbor, MD, USA, 2009.

233. Z. Wang, L. Yu, M. Ding, H. Tan, J. Li and Q. Fu, *Polymer Chemistry*, 2011, **2–3**, 601.

234. D. Mijolovic, M. Kummeter, M. Stoesser, S. Bauer and S.Goetke, inventors; BASF SE, assignee; US20100048935, 2008.

235. K. Hnider, K. McDaniel, J.E. Hayes and J. Shen, inventors; BAYER, Material Science, assignee; US7977501, 2006.

236. C. Guertler, S. Grasser and A. Wolf, inventors; BAYER GmbH, assignee; US20130211042, 2010.

237. W. Hinz, E.M. Dexheimer, J. Borge, R. Neff and T.M. Sniecinski, inventors; BASF Corp., assignee; US20060223973, 2005.

238. K.C. Williams, M. Kember, A. Bouchard and F. Jutz, inventors; IMP Innovations Ltd., assignee; US20140249279, 2011.

239. C.K. Williams, M. Kember and P. Knight, inventors; IMP Innovations Ltd., assignee; WO2009130470, 2008.

240. M.R. Kember and C.K. Williams, *Journal of the American Chemical Society*, 2002, **124**, 15676.

241. C.T. Cohen, T. Chu and G.F. Coates, *Journal of the American Chemical Society*, 2005, **127**, 10869.

242. S. Allen, A.E. Cherian, C.A. Simoneau, J. Farmer, G.W. Coates, A. Gridnew and R.E. Lapointe, inventors, NOVOMER Inc., assignee; WO2010022388, 2008.

243. S. Allen, G.W. Coates, A.E. Cherian, C.A. Simoneau, A. Gridnew and J. Farmer, inventors; NOVOMER Inc., assignee; WO2010028362, 2008.

244. *Chemical Processing, Carbon Dioxide Gets A New Fizz Technologies Transform Greenhouse Gas into a Feedstock for Chemicals*, Ed., Seán Ottewell, Chemical Processing, Schaumburg, IL, USA, 2014. *http://www.chemicalprocessing.com/articles/2014/co2-a-new-fizz/*

245. G. Darsow, inventor; BAYER AG, assignee; US5770744, 1998.

246. R.R. Yocum, S. Dole and J.G. Pero, inventors; Myriant Corp., assignee; WO2014043591, 2014.

247. W. Gong, S. Dole, T. Grabar, A.C. Collard, J.G. Pero and R.R. Yocum, inventors; Myriant Corp., assignee; US20090281481, 2009.

248. D. Dunuwila and M. Cockrem, inventors; BioAmber International, assignee; WO2012138642, 2012.

249. O.S. Fruchey, B.T. Keen, B.A. Albin, N.A. Clinton, D. Dunuwila and B.D. Dombek, inventors; Bioamber SAS, assignee; CN102858731, 2011.

250. S. Dole, R.R. Yocum, T. Hermann and X. You, inventors; Myriant Corp., assignee; US2013337519, 2013.

251. S.Y. Lee, J.W. Lee, H. Song, S. Choi and J.M. Kim, inventors; Korea Advanced Institute of Science and Technology, assignee; WO2009048202, 2009.

252. S.Y. Lee, J.W. Lee, S. Shoi and J. Yi, inventors; Korea Advanced Institute of Science and Teachnology, assignee; KR20100084327, 2010.

253. M. Jiang, W. Dai, Y. Xi, R. Xu, J. Zhang, K. Chen and M. Zhang, inventors; Nanjing University of Technology, assignee; CN20131144634, 2013.

254. T. Boussie, E. Dias, Z Fresco, V. Murphy, J. Shoemaker, R. Archer and H. Jiang, inventors; Rennovia Inc, assignee; US20090268414, 2009.

255. G. Darsow, inventor; BAYER AG, assignee; US5770744, 1998.

256. R.R. Yocum, S. Dole and J.G. Pero, inventors; Myriant Corp., assignee; WO2014043591, 2014.

257. W. Gong, S. Dole, T. Grabar, A.C. Collard, J.G. Pero and R.R. Yocum, inventors; Myriant Corp., assignee; US20090281481, 2009.

258. D. Dunuwilaa and M. Cockrem, inventors; BioAmber International, assignee; WO2012138642, 2012.

259. O.S. Fruchey, B.T. Keen, B.A. Albin, N.A. Clinton, D. Dunuwila and B.D. Dombek, inventors; Bioamber SAS, assignee; CN102858731, 2011.

260. S. Dole, R.R. Yocum, T. Hermann and X. You, inventors; Myriant Corp., assignee; US2013337519, 2013.

261. S.Y. Lee, J.W. Lee, H. Song, S. Choi and J.M. Kim, inventors; Korea Advanced Institute of Science and Technology, assignee; WO2009048202, 2009.

262. S.Y. Lee, J.W. Lee, S.Shoi and J. Yi, inventors; Korrea Advanced Institute of Science and Teachnology, assignee; KR20100084327, 2010.

263. M. Jiang, W. Dai, Y. Xi, R. Xu, J. Zhang, K. Chen and M. Zhang, inventors; Nanjing University of Technology, assignee; CN20131144634, 2013.

264. T. Boussie, E. Dias, Z. Fresco, V. Murphy, J. Shoemaker, R. Archer and H. Jiang, inventors; Rennovia Inc., assignee; US20090268414, 2009.

265. S. Somaleh and M.A. Dubé, *Molecular Chemistry and Physics*, 2011, **212**, 12, 1284.

266. Y.Z. Xiaolong Chen and Y. Shen, *Chemical Reviews*, 2008, **108**, 5253.

267. D.W. Lemke, inventor; Lonza Inc., assignee; US20020058781, 2002.

268. G. Jakobson and W. Siemanowski, inventors; Deutsche Solvay Werke GmbH, assignee; US5041688, 1991.

269. J.W. Eshuis, J.A.M. Laan and G. Roberts, inventors; Unichema Chemice B.V., assignee; US5721305, 1998.

270. D.W. Lemke, inventor; Lonza AG, assignee; WO0236534, 2002.

271. P.M. Seiden and B. James, inventors; Procter & Gamble, assignee; US3968169, 1976.

272. H. Stuehler, inventor; Hoechst AG, assignee; US4551561, 1985.

273. M. Ionescu and Z.S. Petrović, *Journal of Cellular Plastics*, 2010, **46**, 223.

274. Z.S. Petrović, M. Ionescu and I. Javni, inventors and assignees; US20090082483, 2009.

275. A.M. Ruppert, J.D. Meeldijk, B.W.M. Kuipers, B.H. Ern and B.M. Weckhuysen, *Chemical European Journal*, 2008, **14**, 2016.

276. S. Cassel, C. Debaig, T. Benvegnu, P. Chaimbault, M. Lafosse, D. Plusquellec and P. Rollin, *European Journal of Organic Chemistry*, 2001, **5**, 875.

277. H. Dolhaine, W. Preuss and K. Wollmann, *Fette, Seifen, Anstrichmittel*, 1984, **86**, 9, 339.

278. W.R. Stenzel and C. Franzke, *Die Lebensmittel-Industrie*, 1977, **24**, 503

279. W.R. Stenzel and C. Franzke, *Die Nahrung*, 1977, **21**, 489.

280. A. Sunder, R. Mülhaupt and H. Frey, *Macromolecules*, 2000, **33**, 2, 309.

281. M.R. Nimlos, S. Blanksby, X. Quian, M. Himmel and D. Johnson, *The Journal of Physical Chemistry A*, 2006, **110**, 6145.

282. W. Sun, J. Liu, X. Chu, C. Zhang and C. Liu , *Journal of Molecular Structure*, 2010, **942**, 38.

283. T. Laino, C. Tuma, A. Curioni, E. Jochnowitz and S. Stolz, *The Journal of Physical Chemistry A*, 2011, **115**, 3592.

284. M. Ionescu, Unpublished Work.

285. G. Rokiki, P. Britt, D. Xie, E. Harth and J. Mays, *Chemical Communications*, 2005, **8**, 1046.

286. R. Narayan, D. Graiver, E. Heblot, V. Sendijarevic and R.K. Chalasani, inventors; BioPlastic Polymers and Composites LLC, assignee; US20140171535, 2014.

287. E. Hablot, D. Graiver and R. Narayan, *Polyurethane Magazine International*, 2012, **9**, 4, 255.

288. S. Kumar, E. Hablot, J.L.G. Macosco, W. Obeid, P.G. Hatcher, B.M. DuQuette, D. Graiver, R. Narayan and V. Balan, *Journal of Material Science*, 2014, **49**, 7824.

289. S. Bassi, M.D. Parker, M. Ionescu and Z. Petrovic, inventors; Pittsburg State University and M.G.P.I. Processing Inc., assignees; US20140200324, 2014.

290. P. Pandaram in *Synthesis of Polyols for Polyurethane Synthesis: Valuable Starting Materials for Polyurethane Synthesis*, Lap Lambert Academic Publisher, Saarbrücken, Germany, 2011.

291. M. Ionescu, X.Wan, N. Bilić and Z.S. Petrović, *Journal of Polymers and Environment*, 2012, **20**, 3, 647.

292. *Renewable Aromatic Polyol from By-Products*, Polycard XFN, Elmira Ltd., London, UK.
http://www.elmira.co.uk.

293. H.P. Bhunia, R.N. Jana, A. Basak, S. Lenka and G.B. Nando, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 1998, **36**, 3, 391.

294. K.I. Suresh and V.S. Kishanprasad, *Industrial and Engineering Chemistry Research*, 2005, **44**, 13, 4504.

295. K.I. Suresh and V.S. Kishanprasad, inventors; Council of Scientific and Industrial Research, assignee; US7249772, 2006.

296. M. Ionescu and Z.S. Petrović, *Inform*, 2013, **24**, 6, 393.

297. M. Ionescu, D. Hong, X. Wan, I. Javni, N. Bilić and Z.S. Petrović in *Proceedings of the 104th Americaan Oil Chemists Society Annual Meeting and Expo*, 28th April–1st May, Montreal, Canada, 2013.

298. M. Ionescu, R.K. Gupta, D. Radojčić, X. Wan and Z.S. Petrović in *Proceedings of the CPI Polyurethane Conference '2013*, 23–25th September, Pheonix, AZ, USA, 2013, Paper No.2.

299. R.K. Gupta, M. Ionescu, D. Radojčić, X. Wan and Z.S. Petrović, *Journal of Polymers and the Environment*, 2014, **22**, 3, 304.

300. G.O. Hustad, T. Richardson and C.H. Amundson, *Journal of the American Oil Chemists Society,* 1970, **47**, 9, 333.

301. H. Beneš, T. Vlček, R. Černá, J. Hromadková, Z. Walterová and R. Svitaková, *European Journal of Lipid Science and Technology*, 2012, **114**, 71.

302. R.K. Gupta, M. Ionescu, X. Wan, D. Radojčić and Z.S. Petrović, *Journal of Polymers and Environment*, 2015, **2**, 261.

303. Z.S. Petrović, K.H. Hong, W. Shirley and M. Ionescu, *Polymer Preprints*, 2005, **46**, 1, 294.

304. M. Ionescu and Z.S. Petrović, *Journal of the Serbian Chemical Society*, 2011, **76**, 4, 591.

305. J.K. Kenneally, A.G. Busch, J.P. Corrigan, P.E. Granbery, K.J. Hovie, G.R. Schafemeyer and E.J.Trout, inventors; Procter & Gamble Plaza, assignee; WO9938875, 1999.

306. X. Pan and D.C. Webster, *ChemSusChem*, 2012, **5**, 2, 419.

8 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 buildings 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 (Cl and Br) and phosphorous. Compounds of antimony or boron [1–13] are rarely used. Sometimes inorganic compounds are used as flame retardants for PU, such as, hydrated alumina ($Al_2O_3*nH_2O$), antimony oxide 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*:

$$HO* + HCl \rightarrow H_2O + Cl* \qquad (8.1)$$

The radical Cl* has a much lower energy and reacts with the organic substrate:

$$Cl * + RH \rightarrow HCl + R * \tag{8.2}$$

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 phosphorous 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].

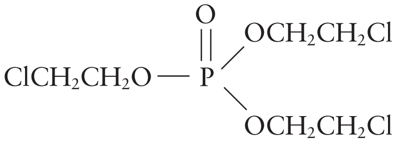
It is clear that halogens act in the flame and phosphorus compounds in the polymeric substrate. Having both groups of elements (halogens and phosphorus), in the same structure leads to a synergism. The significance of synergism is that a phosphorus-halogen combination has the same efficiency of fire 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].

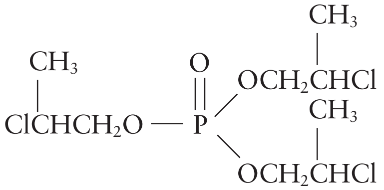
The additive type of flame retardants are compounds containing chlorine, bromine or phosphorus without reactive groups to get involved in PU chemistry (without -OH, -NH_2 or -NCO groups). These compounds are physically added to PU and are not part of the PU structure.

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 8.3**) [4]:



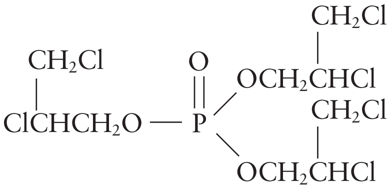
TCEP

MW = 283
P = 10.8%
Cl = 37.2%



TCPP

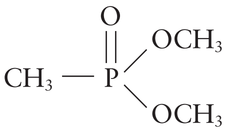
MW = 326
P = 9.5%
Cl = 32.5%



Tris(2,3-dichloripropyl)phosphate

MW = 430.9
P = 7.19%
Cl = 49.37% (8.3)

An important flame retardant additive is dimethyl methyl phosphonate (DMPP), a compound having a very high phosphorus content (**Figure 8.1**) [3, 17]:



P = 24.95%

Figure 8.1 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 polyurethane foam(s) (PUF) containing TCEP 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; and

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.

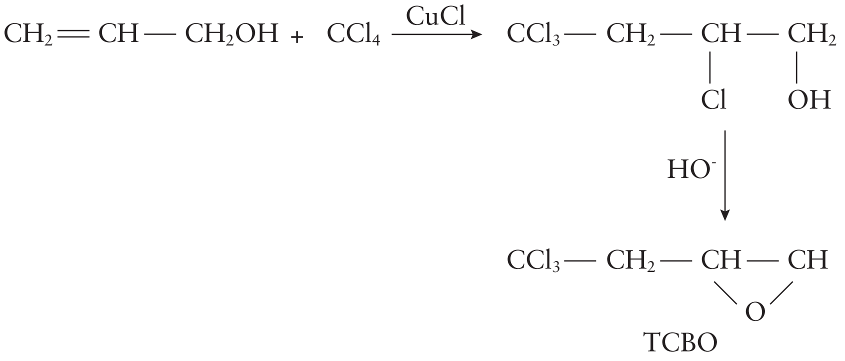
Chlorine is the less effective element for flame retardancy, the following relative order concerning the fireproofing efficiency being: $Cl < Br < P$.

A flame retarded rigid PUF needs approximately 20–25% chlorine (Cl) or 5–6% bromine (Br) 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.

8.1 Chlorine and Bromine Containing Polyols

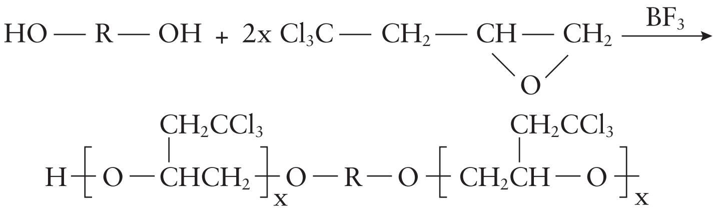
The representative raw materials to produce chlorine polyols are: epichlorohydrin, chlorendic anhydride and trichlorobutylene oxide (TCBO) (**Figure 8.2**).

TCBO, a monomer containing a high percentage of chlorine, is obtained from allyl alcohol and carbon tetrachloride (**Reaction 8.4**) [18–23]:



(8.4)

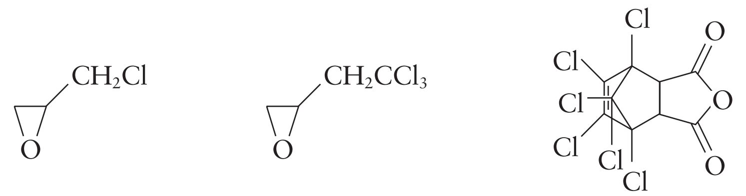
TCBO is reacted with various polyols (such as carbohydrates), in the presence of cationic catalysts (e.g., boron trifluoride), with the formation of very viscous and high chlorine content polyols (**Reaction 8.5**) [14, 22–24].



(8.5)

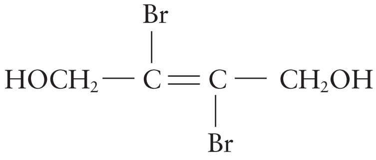
The extremely high viscosities of these polyols lead to difficulties if they are to be used on conventional foaming equipment. TCBO based polyols are not used and are not produced industrially at this moment [3].

Bromine containing polyols are very effective, reactive flame retardants. One of the most representative bromine polyols used in rigid and flexible flame retardant PUF is 2,3-dibromobutene diol (**Figure 8.3**) [25].



Epichlorohydrin Trichlorobutylene oxide Chlorendic anhydide

Figure 8.2 Structures of raw materials to make chlorine polyols

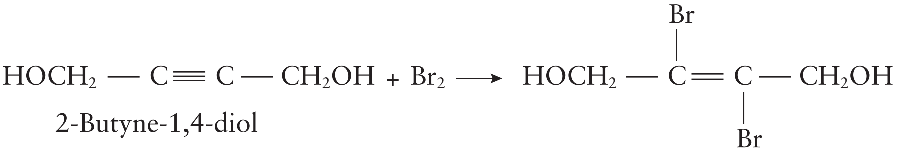


$$HOCH_2-\underset{\displaystyle Br}{\overset{\displaystyle Br}{C}}=\underset{\displaystyle Br}{C}-CH_2OH$$

MW = 245.9
OH# = 456 mg KOH/g
Br = 65%

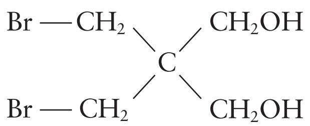
Figure 8.3 Structure of 2,3-dibromobutene diol. KOH: potassium hydroxide; MW: molecular weight; and OH#: hydroxyl number(s)

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 8.6.**



$$\underset{\text{2-Butyne-1,4-diol}}{HOCH_2-C\equiv C-CH_2OH} + Br_2 \longrightarrow HOCH_2-\overset{\displaystyle Br}{C}=\underset{\displaystyle Br}{C}-CH_2OH \qquad (8.6)$$

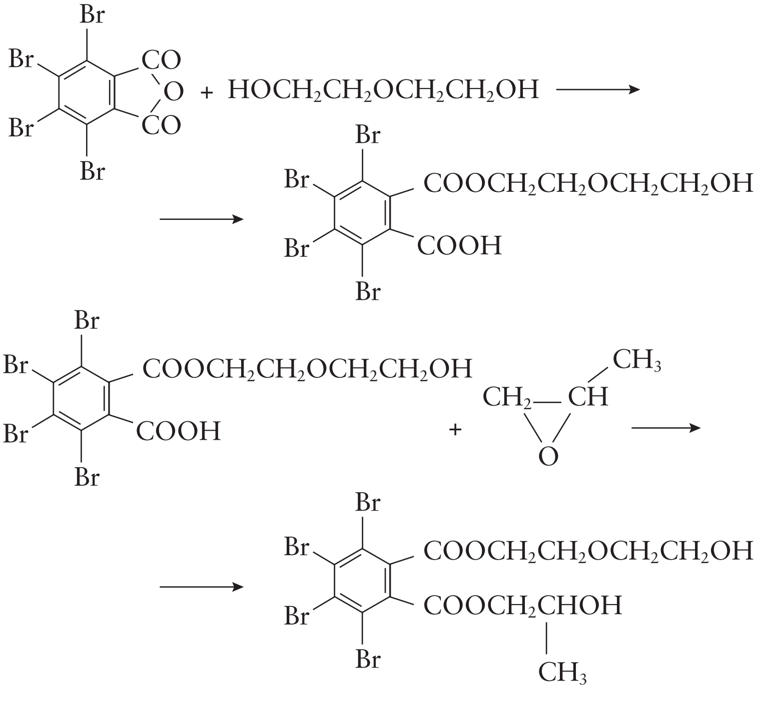
Dibromo neopentylglycol is another low-MW reactive flame retardant [26, 27], which unfortunately has labile aliphatic -C-Br bonds (**Figure 8.4**).



MW = 259.9
OH# = 431.7 mg KOH/g
Br = 61.1%

Figure 8.4 Structure of dibromo neopentylglycol

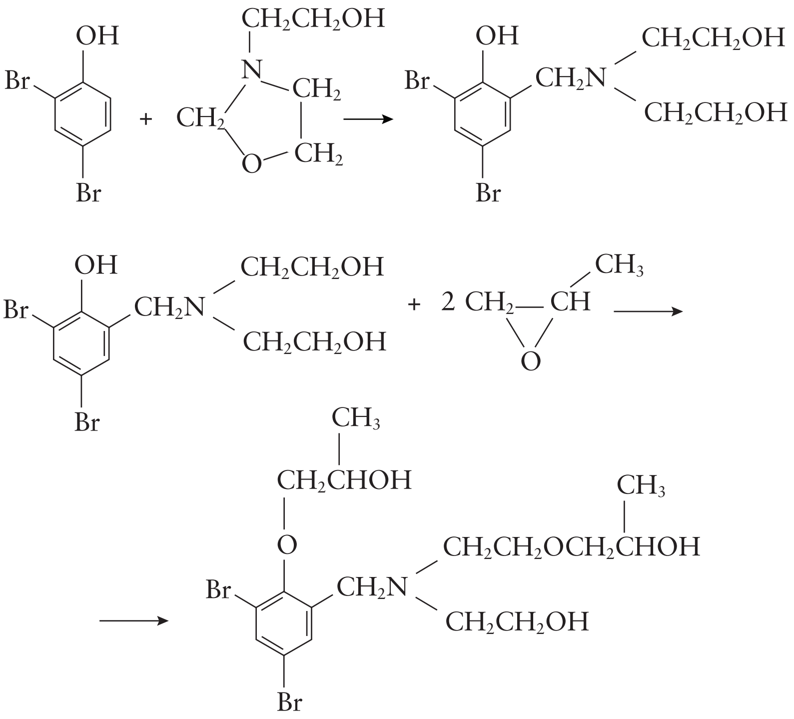
The bromine linked to a double-bond or linked to an aromatic nucleus are much more stable structures (not easily decomposed to HBr as dibromo neopentylglycol, a saturated aliphatic bromine compound). Thus, a very successful bromine containing diol, produced industrially [4, 24], is based on tetrabromophthalic anhydride. Tetrabromophthalic anhydride is reacted first with diethylene glycol and the resulting half ester is reacted with propylene oxide (PO) (**Reaction 8.7**) [3].



(8.7)

The bromine diol (**Reaction 8.7**), in combination with sucrose polyols gives rigid PUF with excellent fire retardancy properties [3, 24].

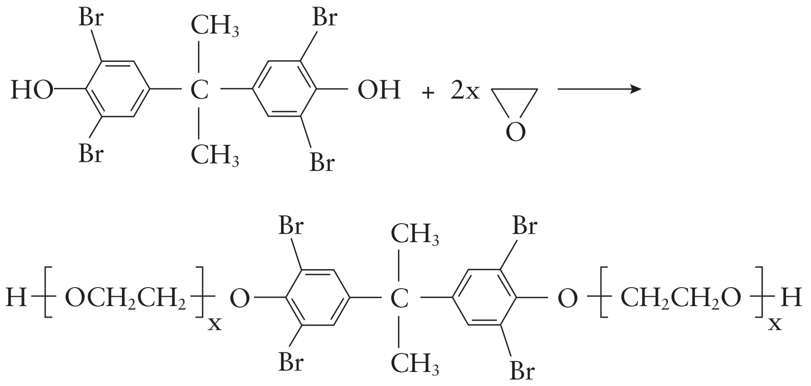
A very interesting bromine aromatic polyol is obtained by the Mannich type reaction between 2,4-dibromophenol (or 2,6-dibromophenol) with diethanolamine and formaldehyde [28] or better still with oxazolidine [29], followed by the propoxylation of the resulting Mannich base with 2–3 mol of PO [28, 29] (**Reactions 8.8**).



(8.8)

The resulting bromine polyol has a bromine content of approximately 33–38%, a OH# 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 mol of ethylene oxide, an interesting aromatic bromine diol is obtained which is useful as a reactive flame retardant for urethane-isocyanuric rigid foams (**Reaction 8.9**).



(8.9)

8.2 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;

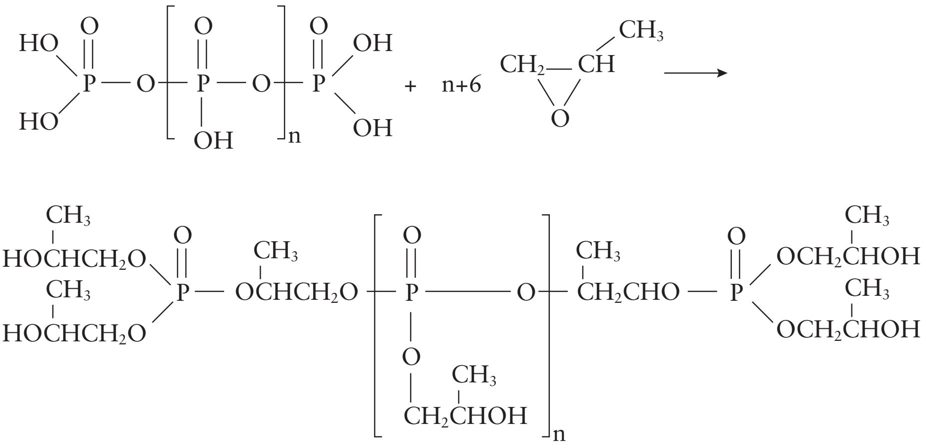
c) Phosphonate polyols;

d) Phosphine oxide polyols; and

e) Phosphoramidic polyols.

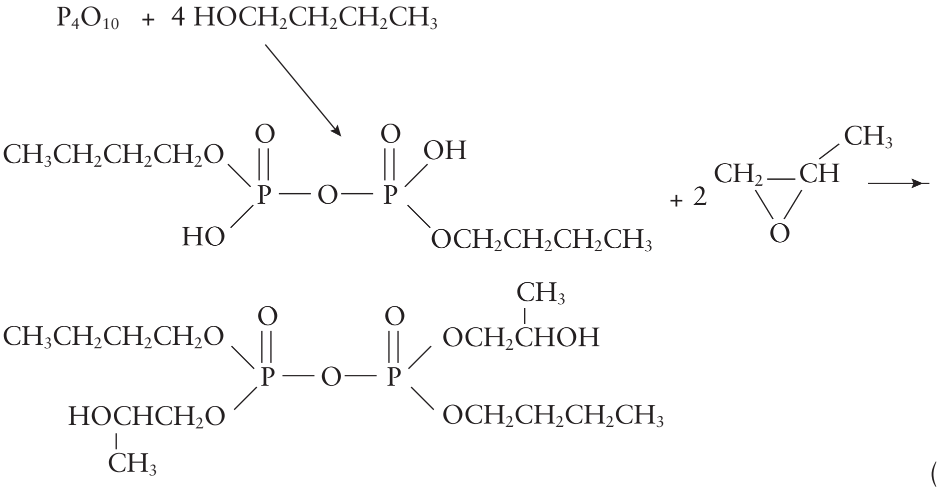
8.2.1 Esters of Ortho-Phosphoric Acid

Representative phosphorus polyols with *ortho*-phosphoric esteric structure are the products of a reaction of PO with polyphosphoric acids [4, 5, 30, 31] (**Reaction 8.10**) or the products of PO addition to the condensates of phosphorus pentoxide with *n*-butanol (or other alcohols) (**Reaction 8.11**) [5].



(8.10)

The phosphorus polyol (**Reaction 8.10**) has a OH# 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.



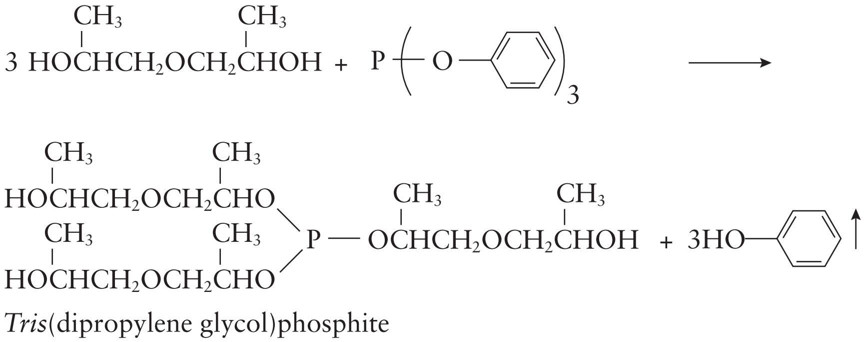
(8.11)

The resulting phosphorus diol has a OH# 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.

8.2.2 Esters of Phosphorus Acid

The esters of phosphorus acid are obtained by condensation of triphenyl phosphites or trialkyl phosphites with various polyols, such as dipropylene glycol (**Reaction 8.12**) [5, 32, 33].



(8.12)

The resulting *tris*(dipropylene glycol)phosphite has a OH# 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.

8.2.3 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 PUF. The phosphonate polyols are esters of phosphonic acids (**Figure 8.5**) [1, 4–6, 11, 30, 34].

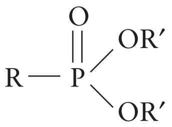
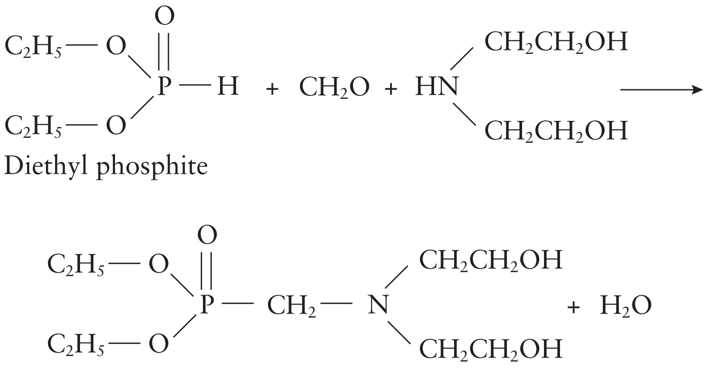


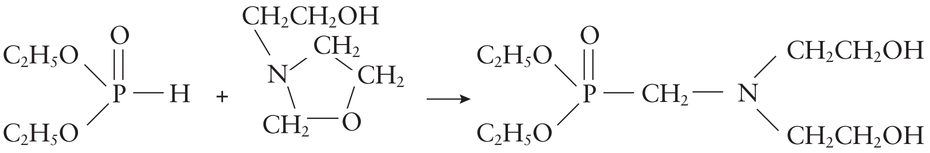
Figure 8.5 Structure of phosphonic acid esters

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 diethyl phosphite, formaldehyde and diethanolamine (**Reaction 8.13**) [5, 34]:



(8.13)

The same structure is easy to obtain by reacting diethyl phosphite with an oxazolidine [16, 35] (**Reaction 8.14**):



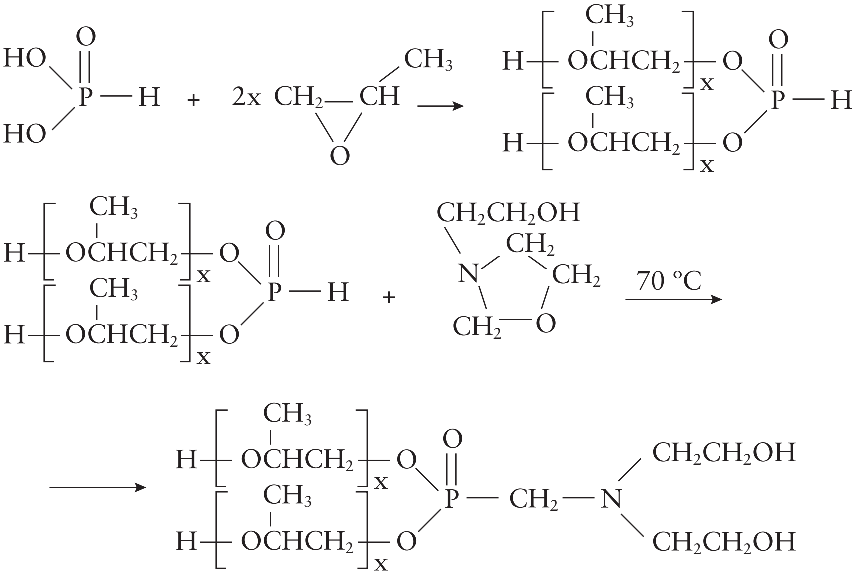
(8.14)

The characteristics of phosphonate polyol (**Reaction 8.12**) are shown in **Table 8.1** [5].

Table 8.1 Characteristics of phosphonate polyols	
MW	249–255 daltons
OH#	440–450 mg KOH/g
Functionality	2 Hydroxyl 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].

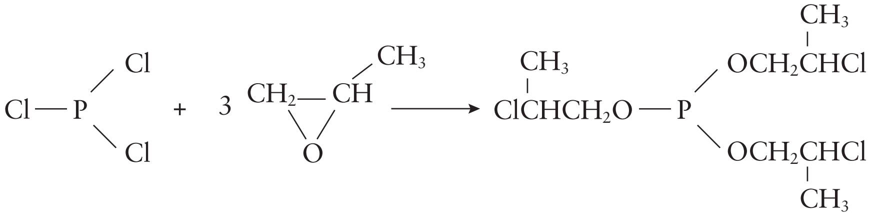
Phosphorous acid is used to generate, by direct alkoxylation with PO, a *bis*(hydroxypropyl)phosphite. The resulting *bis*(hydroxypropyl)phosphite is reacted with oxazolidine, under similar conditions to **Reaction 8.14** and a tetrafunctional phosphonate polyol is obtained (**Reaction 8.15**) [16]:



(8.15)

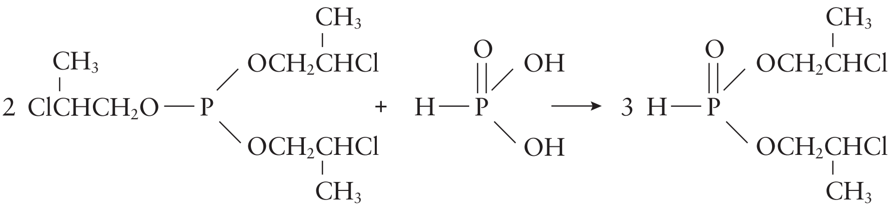
Unfortunately, the phosphorus content of phosphonate polyol in **Reaction 8.15** is lower (approximately 7–7.5%), but being a tetrafunctional polyol gives rigid PUF with excellent physico-mechanical properties.

A variant of the Mannich reaction using an equilibration between phosphorous 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 8.16**). By equilibration of phosphorus acid with *tris*(2-chloropropyl)phosphite, *bis*(2-chloropropyl)phosphite (**Reaction 8.17**) is formed which, by reaction with oxazolidine, gives an interesting phosphonate polyol containing phosphorus, chlorine and nitrogen (**Reaction 8.18**):

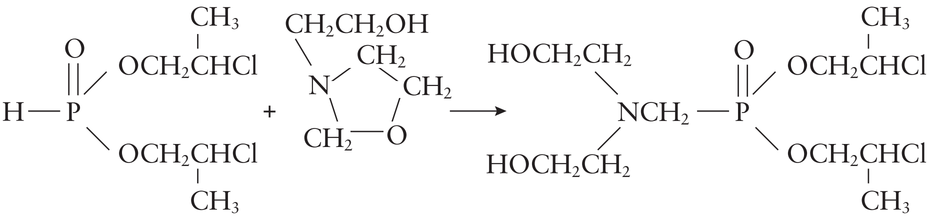


Phosphorus trichloride

Tris(2-chloropropyl)phosphite (8.16)



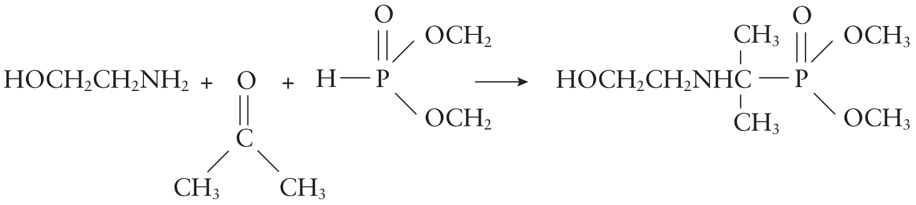
Bis(2-chloropropyl)phosphite (8.17)



(8.18)

The phosphonate polyol (**Reaction 8.18**) has a MW of 350–355 daltons, a OH# 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%.

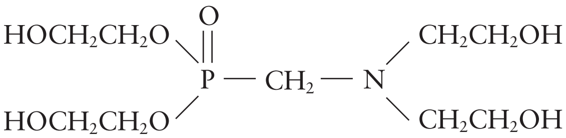
The scientific literature mentions some variants of the phosphonate polyols synthesis by Mannich reaction. For example, by reacting of dimethyl phosphite with acetone and monoethanolamine a higher phosphorus content (15%) phosphonate polyol is formed (**Reaction 8.19**) [37]:



(8.19)

The resulting phosphonate polyol (**Reaction 8.19**) is a bifunctional polyol having 1 hydroxyl group and 1 secondary amino group.

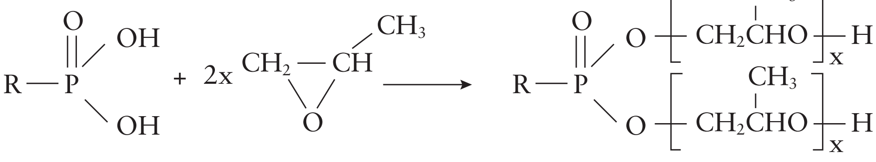
A very interesting phosphonate polyol (**Reaction 8.20**) was prepared by Mannich reaction using cyclic phosphites as raw materials [38]:



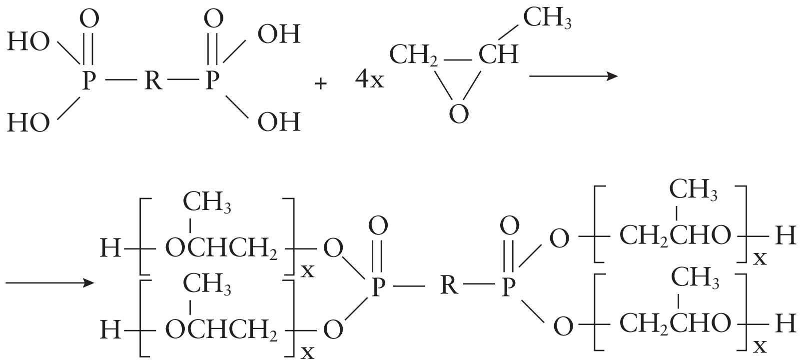
(8.20)

The resulting phosphonate polyol (**Reaction 8.20**) has a functionality of 4 hydroxyl groups per mol, a OH# of approximately 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 8.21** and **8.22**).

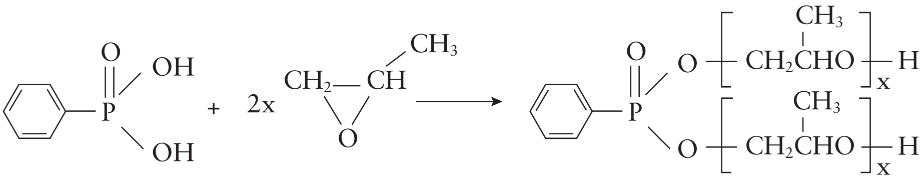


(8.21)



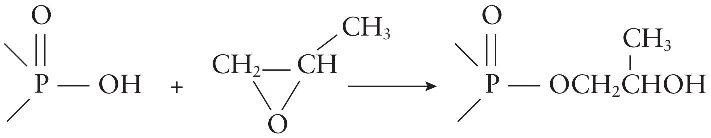
(8.22)

A representative phosphonate polyol is obtained by the propoxylation of phenylphosphonic acid (**Reaction 8.23**) [16]:

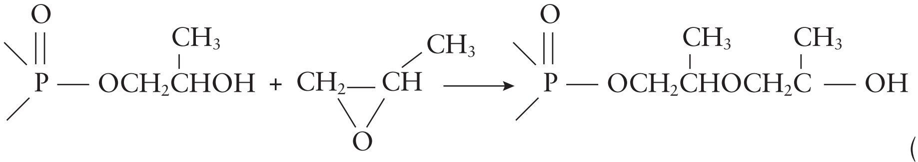


(8.23)

In all the reactions involving propoxylation of acidic groups such as -P-OH, two simultaneous reactions take place, i.e., esterification (**Reaction 8.23**) and etherification (**Reaction 8.24**) reactions:



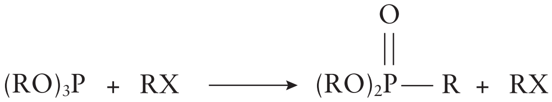
(8.24)



(8.25)

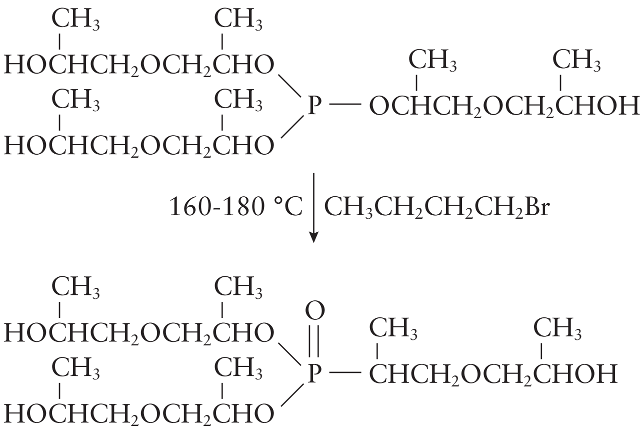
The etherification reaction (**Reaction 8.25**) shows that the number of PO units per hydroxyl group is higher than 1 (the value of x is in the range 1 < x < 2). This reaction leads to the decrease of the OH# and of the phosphorus content.

The Arbuzov reaction is an interesting way of transforming a trialkyl phosphite in a trialkylphosphonate by reaction with a halogenated compound (general **Reaction 8.26**) [4, 5, 39]:



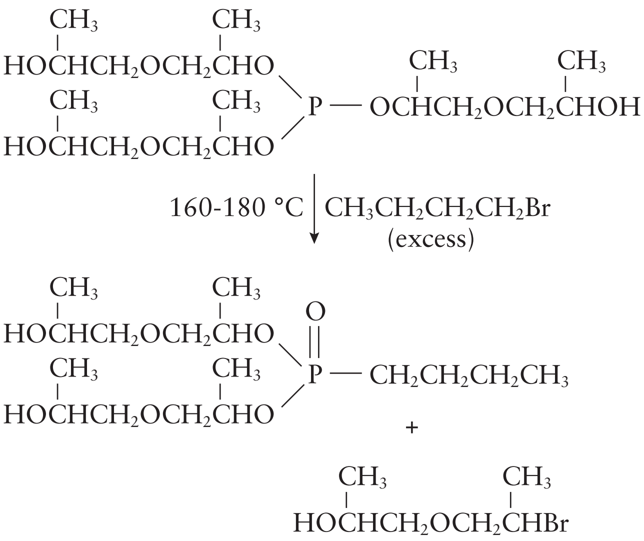
$$(RO)_3P + RX \longrightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}-R + RX \qquad (8.26)$$

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 8.27** with a catalytic quantity of butyl bromide).



(8.27)

By using an excess of butyl bromide, the product of the Arbuzov reaction is a phosphonate diol and a bromohydrin (**Reaction 8.28**):



(8.28)

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.

8.2.4 Phosphine Oxide Polyols

Phosphine oxide has three hydrolysis resistant -P-C- bonds. A phosphine oxide polyol, extremely resistant to hydrolysis (**Figure 8.6**), 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].

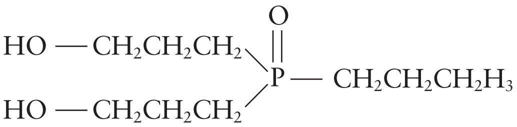


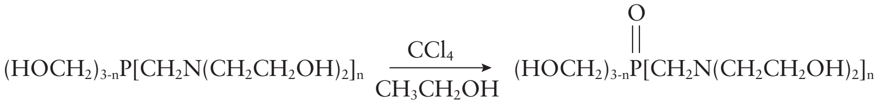
Figure 8.6 Structure of phosphine oxide polyol

Very interesting reactive flame retardants were used successfully in the fabrication of flame retardant rigid PUF 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) aminomethyl phosphine oxide [45], are presented below:

$$(HOCH_2)_4PCl + NaOH \longrightarrow (HOCH_2)_3P + CH_2O + NaCl + H_2O$$

$$(HOCH_2)_2P + nHN(CH_2CH_2OH)_2 \longrightarrow (HOCH_2)_{3\text{-}n}P[CH_2N(CH_2CH_2OH)_2]_n + H_2O$$



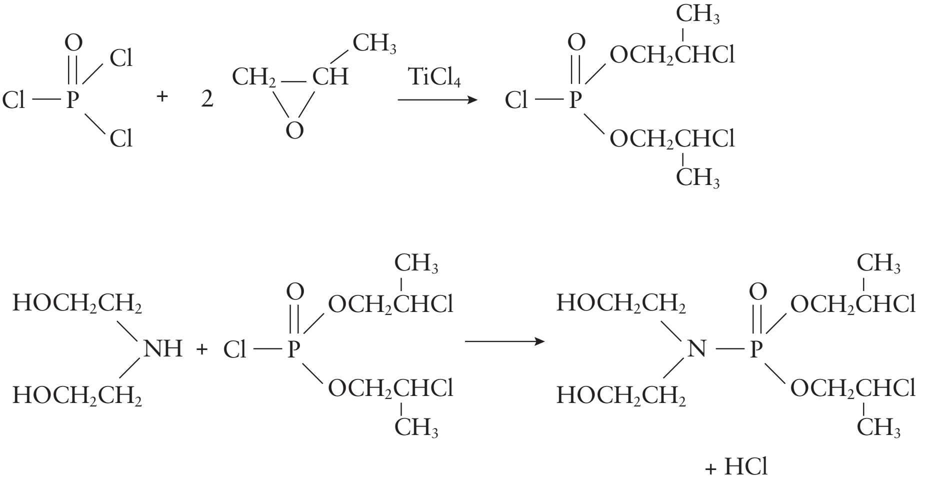
$$(HOCH_2)_{3\text{-}n}P[CH_2N(CH_2CH_2OH)_2]_n \xrightarrow[CH_3CH_2OH]{CCl_4} (HOCH_2)_{3\text{-}n}\overset{\overset{\displaystyle O}{\|}}{P}[CH_2N(CH_2CH_2OH)_2]_n$$

(8.29)

8.2.5 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 8.30**). First, 1 mol of phosphorus oxychloride is reacted with 2 mol of PO and the resulting product is reacted with diethanolamine, in the presence of an acid acceptor:

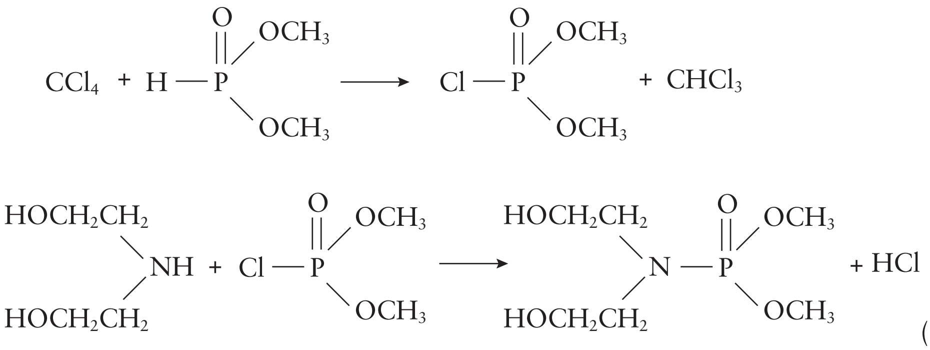


(8.30)

The polyol (**Reaction 8.30**) has a OH# 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), sodium carbonate, potassium carbonate, sodium hydroxide, KOH and so on [36].

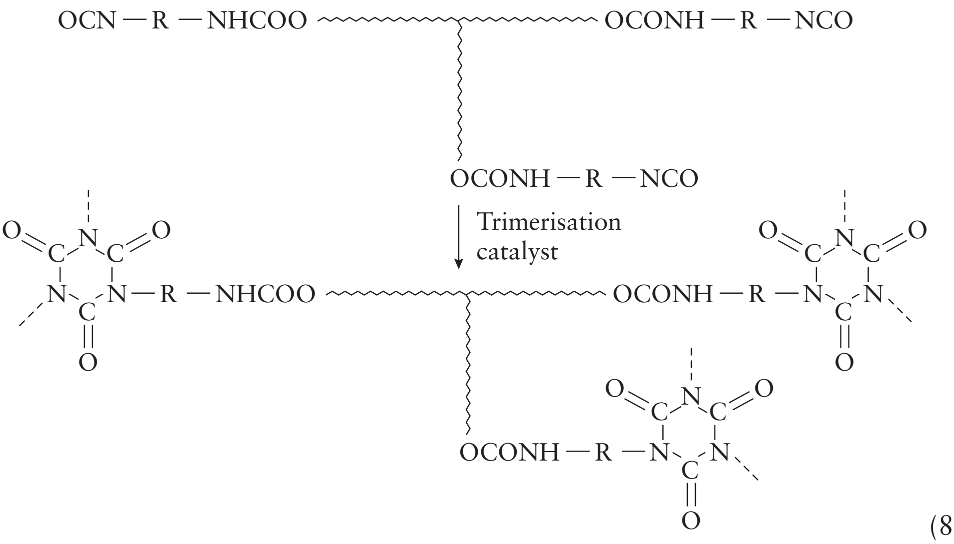
A variant for phosphoramide polyol synthesis by using dialkyl phosphites and carbon tetrachloride as raw materials was developed (**Reaction 8.31**).



(8.31)

The same substances mentioned before are used as acid acceptors. The phosphorus polyol shown in **Reaction 8.31** has a OH# 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 8.2** 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 PUF. 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 PUF/polyisocyanuric foam, 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 8.32**).



(8.32)

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 in *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, NY, USA, 1970.

2. C.J. Hilado in *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.

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 in *Polyurethanes: Chemistry and Technology*, Interscience, New York, NY, USA, 1962, **1**, 106.

8. P. Thiery in *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 Co., assignee; US4173602, 1979.

11. J.K. Backus, *Urethane Science & Technology*, 1971, **1**, 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; US5539141, 1996.

14. W. Eberspach, inventor; Hoechst AG, assignee; US5096961, 1992.

15. E.D. Weil in *Encyclopedia of Chemical Technology*, 3rd Edition, Eds., R.E. Kirk and D.E. Othmer, John Wily & Sons, New York, NY, USA, 1986, **10**, 29.

16. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Advances in Urethane Science & Technology*, Wiley, New York, NY, USA, 1998, **14**, 151.

17. D.L. Buszard and R.J. Dellar, *Cellular Polymers*, 1985, **4**, 6, 431.

18. No inventors; Olin Mathieson Chemical Corp., assignee; GB1211109, 1970.

19. No inventors, Olin Mathieson Chemical Corp., assignee; GB1341903, 1973.

20. C.M.R. Davidson, inventor; Olin Mathieson Chemical Corp., assignee; NL6413843, 1965.

21. E. Smith, inventor; Olin Mathieson Chemical Corp., assignee; US3399241, 1968.

22. H.A. Bruson and J.S. Rose, inventors; Olin Mathieson Chemical Corp., assignee; US3244754, 1966.

23. H.A. Bruson and J.S. Rose, inventors; Olin Mathieson Chemical Corp., assignee; US3269961, 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, USA, 1972.

26. E.J. Termine and S.P. Ginter, inventors; The Dow Chemical Corp., assignee; US4511688, 1985.

27. J-C. Boulet, G. Bonnety, R. Walraevens, J. Lolivier and P. Trouillet, inventors; Solvay Cie, assignee; GB1371488, 1974.

28. F.E. Paulik, inventor; Solutia Inc., assignee; US5844028, 1998.

29. M. Modesti and F. Simioni, *Cellular Polymers*, 1994, **13**, 4, 277.

30. T.H. Ferrigno in *Rigid Plastic Foams*, 2nd Edition, Reinhold Publishing Corp., New York, NY, USA, 1967, p.18, 51 and 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; RO85852, 1985.

32. L. Friedman, inventor; Union Carbide Corp., assignee; US3442827, 1969.

33. G. Perot, *L'Industrie Chimique*, 1965, **52**, 203.

34. T.M. Beck and E.N. Walsh, inventors; Stauffer Chemical Corp., assignee; US3076010, 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 Corp., assignee; US3501421, 1970.

38. F. Salkowski and R. Wygleda, *Przemysl Chemiczny*, 1974, **53**, 1, 14.

39. C.F. Baranauckas and I. Gordon, inventors; Hooker Chemical Corp., assignee; US3538196, 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 in *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 in *Flammability and Flame Retardant in Plastics*, Rapra Review Report No.44, Rapra Technology, Shrewsbury, UK, 1990, **4**, 8, p.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 Corp., assignee; US4555562, 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 Co., assignee; US4173602, 1979.

59. A.A. Oswald, *Canadian Journal of Chemistry*, 1959, **37**, 1498.

60. C.P. Smith and H. Ulrick, inventors; The Upjohn Co., assignee; US4202946, 1980.

61. G.P. Speranza, M.E. Brennan and R.A. Grigsby, Jr., inventors; Texaco Inc., assignee; US4681965, 1987.

62. D. Thorpe, inventor; ICI plc, assignee; US4797429, 1989.

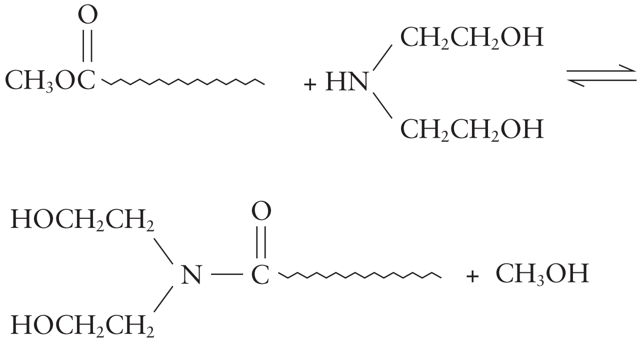
63. No inventors; Stauffer Chemical Co., assignee; GB1500756A, 1978.

64. M. Ionescu, V.T. Dumitiu, I. Mihalache, F. Stoenescu and S. Mihai, inventors; Institutul de Cercetari Chimice Centrul de Cercetari Materiale Plastice, assignee; RO92989, 1985.

9 Special Polyol Structures for Rigid Polyurethane Foams

9.1 Amidic Polyols

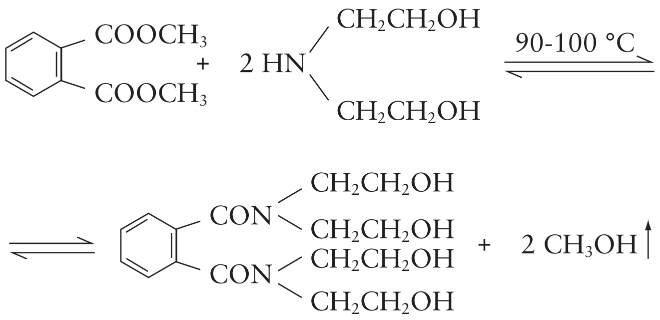
The reaction between dialkanolamines with organic acids or better still with their methyl esters gives the well-known dialkanolamides. This reaction is used industrially for the synthesis of diethanolamides of fatty acids, which are well-known non-ionic surfactants (**Reaction 9.1**) [1–10]:



(9.1)

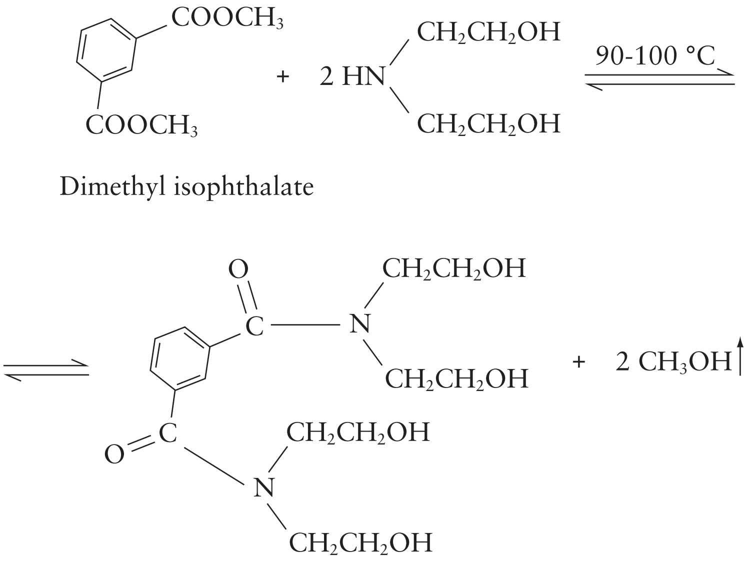
With methyl esters of fatty acids, the reaction takes place at a higher yield (around 90–92%) as compared to the free fatty acids (the yield is 60–70%) [2, 7–9]. The catalysts of this amidation reaction are: potassium hydroxide (KOH), sodium hydroxide, CH_3ONa, CH_3OK and so on (the most used catalyst is sodium methylate). The diethanolamides of fatty acids, as presented in **Volume 2**, **Chapter 7**, are used sometimes as copolyols in rigid polyurethane foams (PUF), 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 dimethyl terephthalate (DMT) with diethanolamine, using sodium or potassium methylate as catalyst (**Reactions 9.2–9.4**):



Bis(diethanolamide)
of phthalic acid
(liquid polyol)

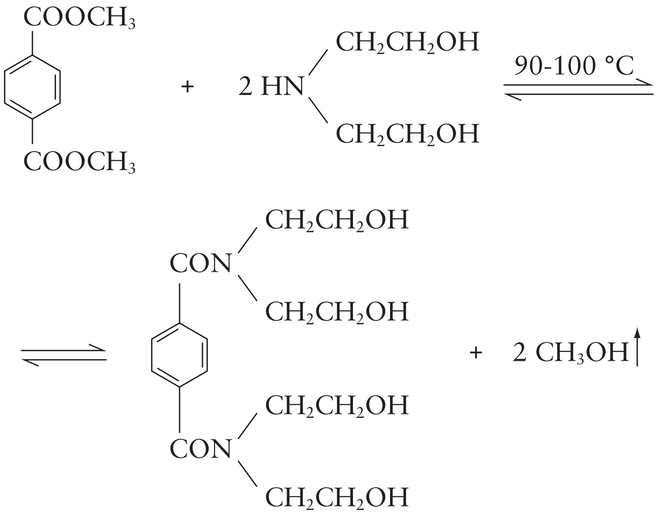
(9.2)



Dimethyl isophthalate

Bis(diethanolamide)
of isophthalic acid
(melting point 40-42 °C)

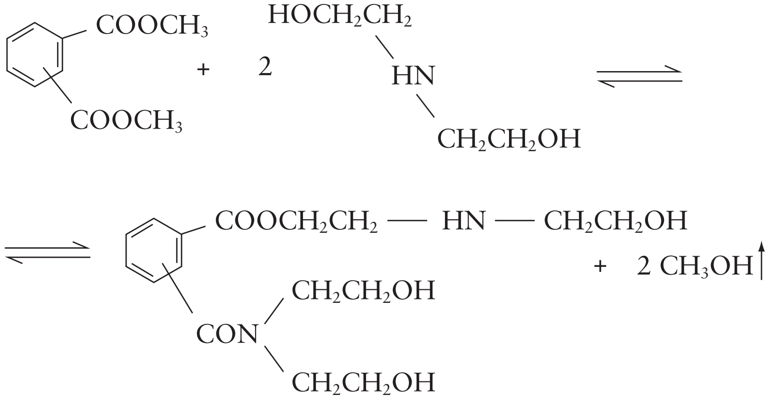
(9.3)



Bis(diethanolamide)
of terephthalic acid
(melting point 120-125 °C)

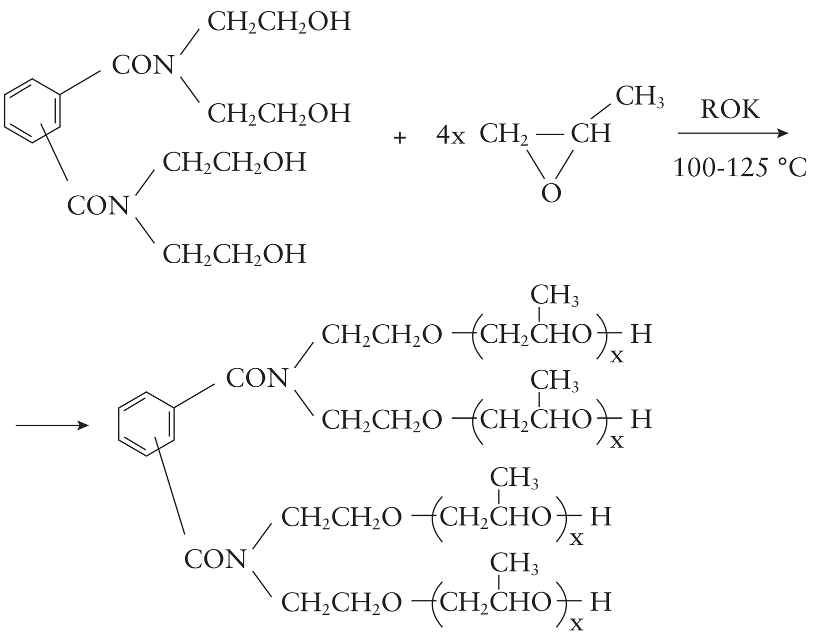
(9.4)

A partial esterification reaction takes places (**Reaction 9.5**). This side reaction does not have a negative effect on rigid PUF fabrication because it gives a very convenient tetrafunctional compound, which participates, together with the amidic polyol, to build the crosslinked structure of polyurethane (PU). These compounds containing ester groups are present in low concentrations, maximum 5–7% [1, 2].



(9.5)

Except for the diamide derived from phthalic acid (**Reaction 9.2**) 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 (OH#) of around 650 mg KOH/g, a propoxylation reaction (**Reaction 9.6**) 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 [e.g., potassium methoxide, which is probably transformed with the potassium alcoholate of the *bis*(diethanolamides)].



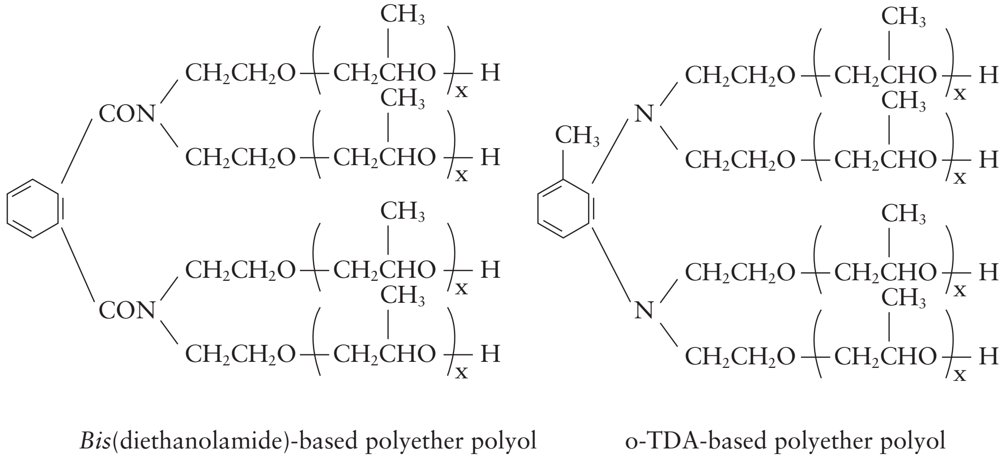
(9.6)

After the propoxylation step, the resulting amidic polyols are purified by classical methods (e.g., 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 PUF.

The amidic polyol obtained by the propoxylation of *bis*(diethanolamide) of phthalic acid, with an OH# 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 9.6**) 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 9.1**.


Bis(diethanolamide)-based polyether polyol

o-TDA-based polyether polyol

Figure 9.1 The structure of *bis*(diethanolamide) polyether polyol and of o-TDA polyether polyol

The synthesised amidic polyols have an OH# between 350–500 mg KOH/g and viscosities between 7,000–25,000 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.

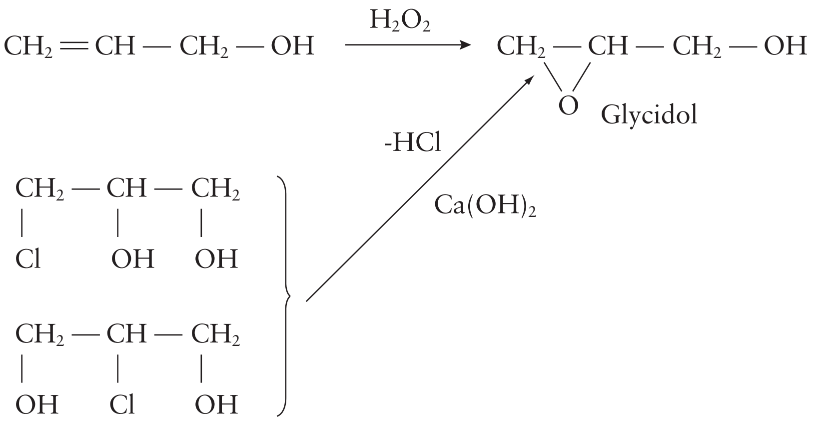
Dimethyl phthalate, a very convenient liquid raw material, is a byproduct in the fabrication of DMT. The amidic polyols can be used to replace the Mannich polyols. The self-catalytic effect in PU formation is much less important in the case of amidic polyols, as compared with Mannich polyols. The rigid PUF derived from amidic polyols are much more thermoresistant than the rigid PUF derived from Mannich polyols [2].

The amidic polyols represent a new generation of aromatic polyols for rigid PUF, with a high application potential, all the raw materials used, dimethyl esters, dialkanolamines and PO being produced in large quantities industrially.

The reaction of polyethylene terephthalate (PET) with diethanolamine, followed by propoxylation, gives liquid amidic polyols useful in rigid PUF fabrication. This method is an efficient variant of PET waste chemical recovery (bottles, X-ray films, fibres and so on) [1].

9.2 Hyperbranched Polyols and Dendritic Polyols

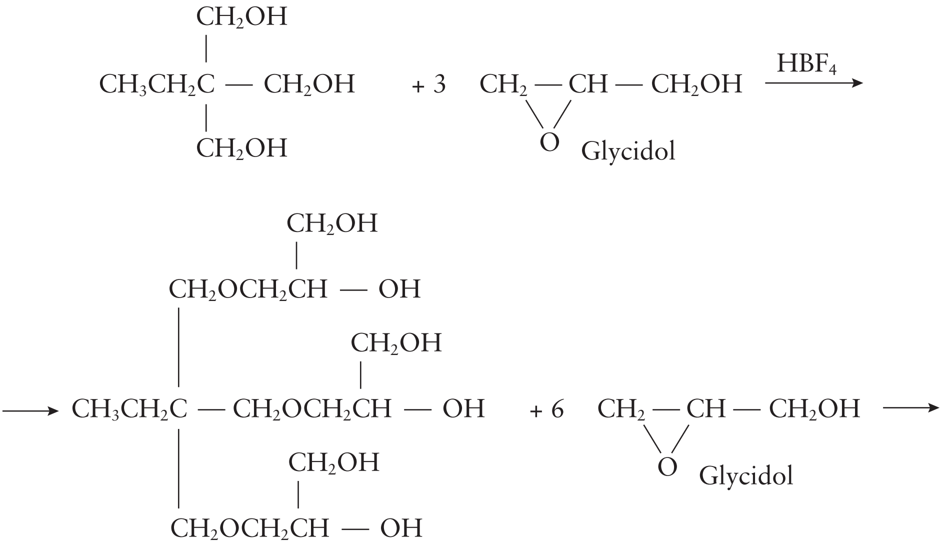
Highly hyperbranched polyolic structures are obtained by the polyaddition of a hydroxy epoxidic compound, such as glycidol, to a polyol in cationic [1] or anionic catalysis [11–14]. Glycidol is obtained by epoxidation of allyl alcohol or by dehydrochlorination of the corresponding chlorohydrin, such as glycerin chlorohydrin (**Reaction 9.7**).



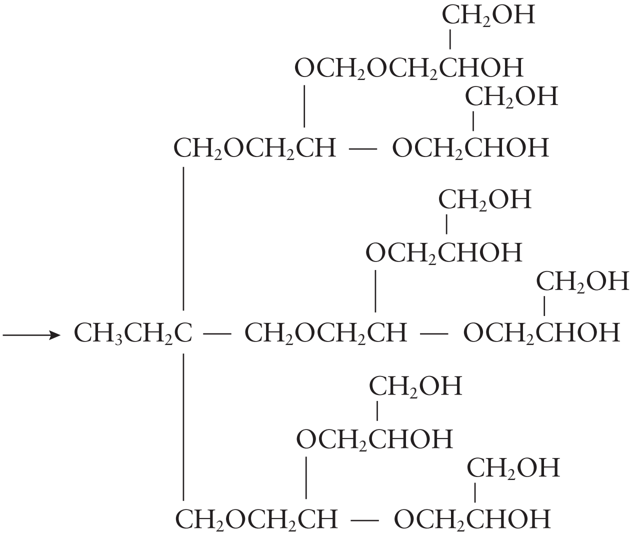
(9.7)

Polyaddition of glycidol to a symmetric triol such as trimethylolpropane (TMP), in the presence of a cationic catalyst (e.g., 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 2 hydroxyl groups [1].

Thus, by the reaction of TMP with 3 mol of glycidol a hexafunctional polyol is obtained (1^{st} generation) and by the reaction of this polyol with 6 mol of glycidol a polyol with 12 hydroxyl groups/mol is obtained (2^{nd} generation) as shown in **Reaction 9.8–9.9**.



First generation (9.8)

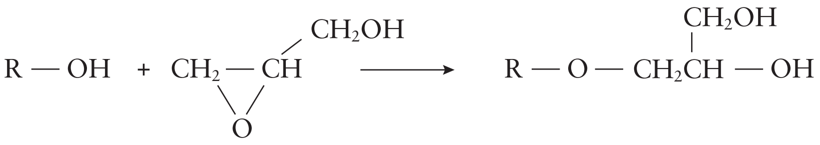


Second generation (9.9)

By the reaction of a highly branched polyol having 12 hydroxyl groups with 12 mol of glycidol a compound with 24 hydroxyl groups is obtained (3rd generation). The 4th 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 hydroxyl groups/mol). **Figure 9.2** shows the idealised structure of a hyperbranched polyglycidol, (the 4th generation, having 48 hydroxyl groups/mol).

Unfortunately, by the ring-opening of glycidol, 1 primary hydroxyl group and 1 secondary hydroxyl group are formed (**Reaction 9.10**) which have different reactivities in the polyaddition reaction to hydroxyl groups (probably glycidol will be added preferentially to the primary hydroxyl groups) [15].



(9.10)

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 9.2**, but it is a highly branched polyol. It is very interesting that the introduction of these hyperbranched polyols in the formulations for rigid PUF together with the usual polyols, give excellent rigid PUF, without the friability expected from polyols with very high functionalities. It is well-known that such structures (e.g., dendrimers) have a special kind of internal flexibility which gives the resulting rigid PUF very low friability.

This non-symmetric 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 branched polyglycerols, called 'pseudo-dendrimers' (**Figure 9.3**) are obtained (**Reaction 9.11**), 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 PUF 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 a hydroxyl group (produced industrially by Perstorp), 3-ethyl-3-methylol-oxetane, formally resulting from the intramolecular etherification of TMP (**Figure 9.4**).

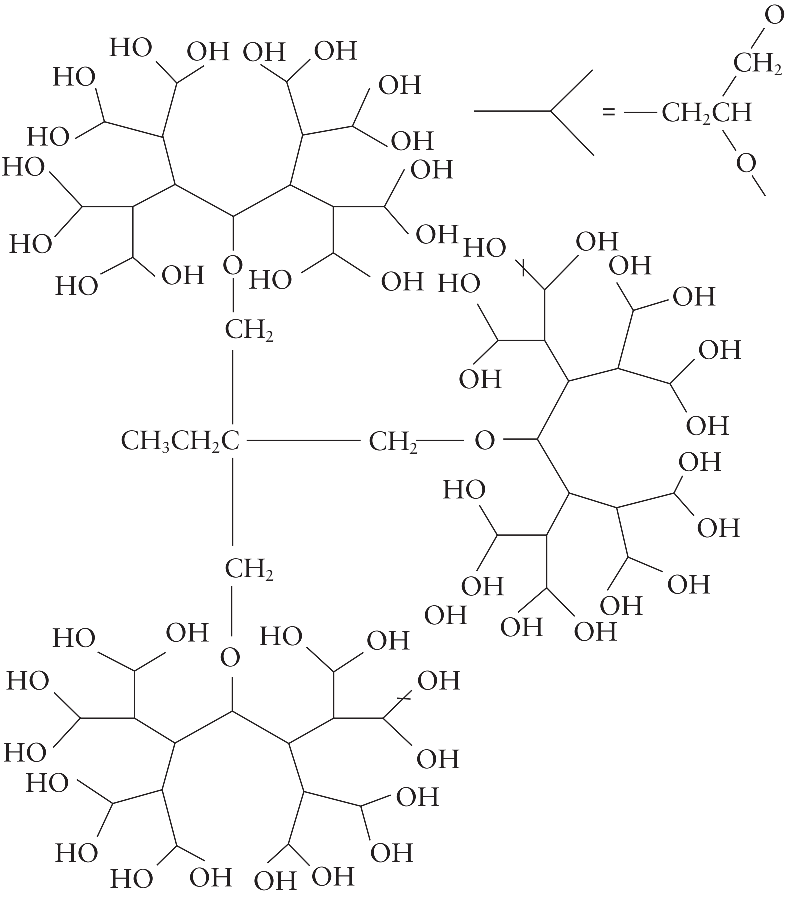
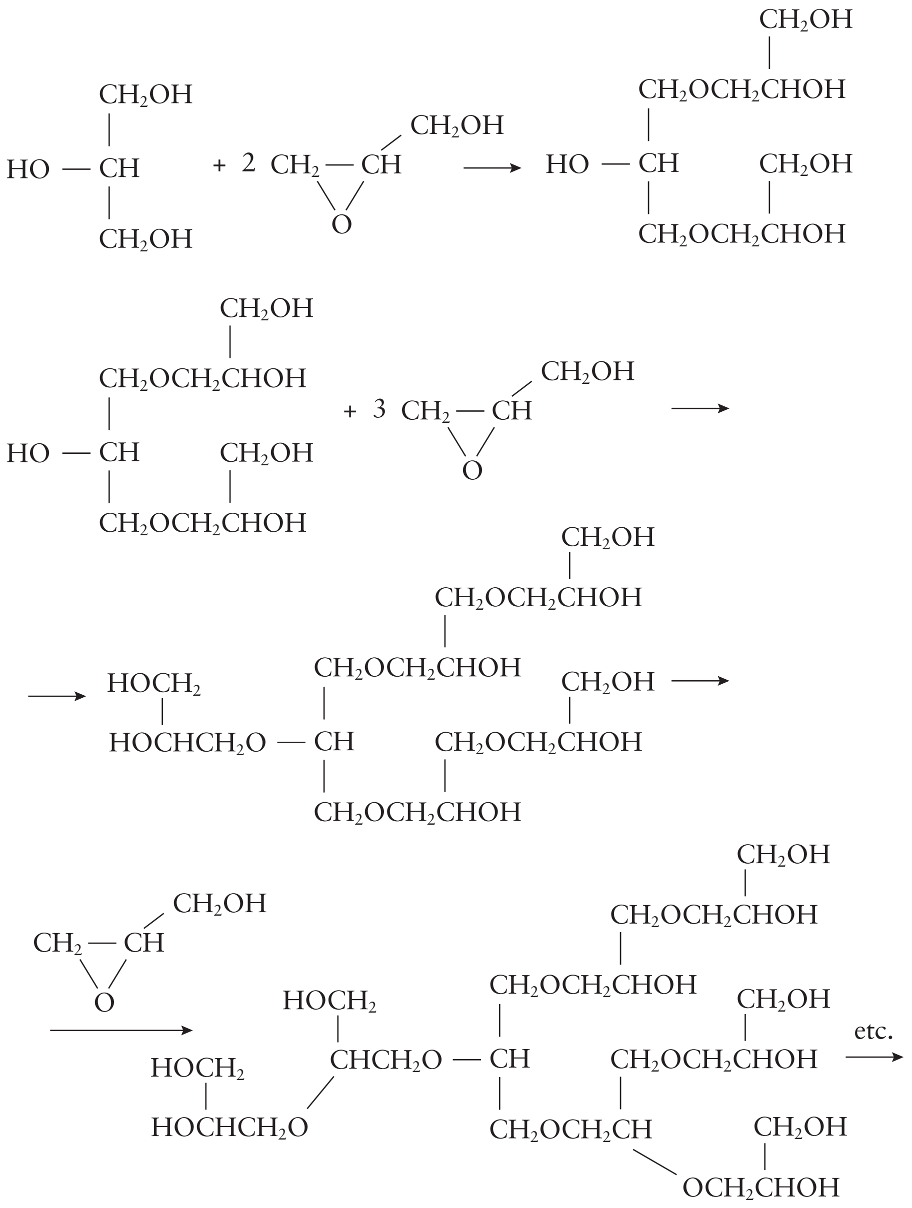


Figure 9.2 Hyperbranched polyglycidol (4th generation)

By the addition of the oxetane monomer (**Figure 9.4**) to the hydroxyl groups a much more symmetrical structure is obtained [15] as compared to glycidol, because 2 primary hydroxyl groups, of equal reactivity are formed (**Reaction 9.12**).



Highly branched polyglycerol (9.11)

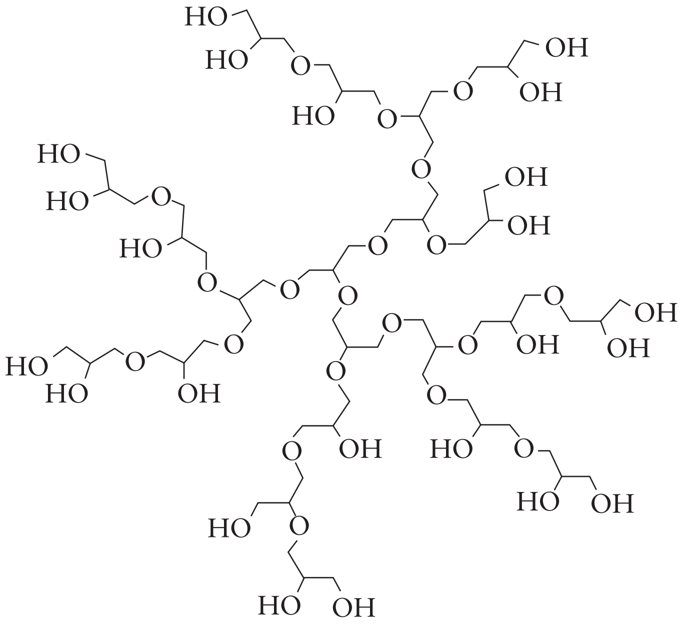


Figure 9.3 Hyperbranched polyglycerol with 20 glycidol units (pseudo-dendrimer) [11–14]

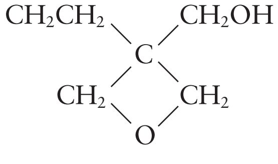
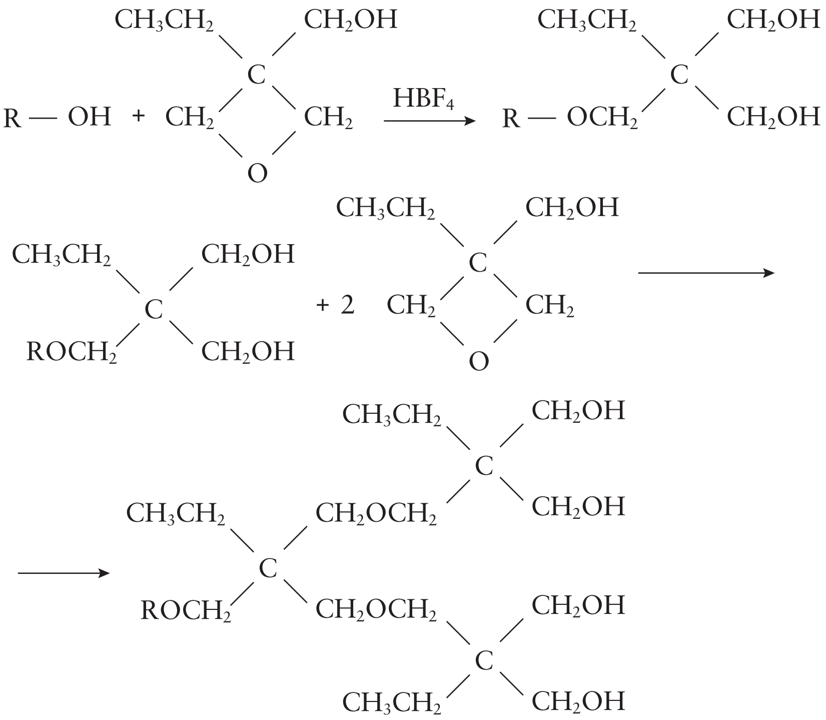


Figure 9.4 The structure of 3-ethyl-3-methylol-oxetane

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 9.2** with the difference that the repeating unit is different (**Figure 9.5**):



(9.12)

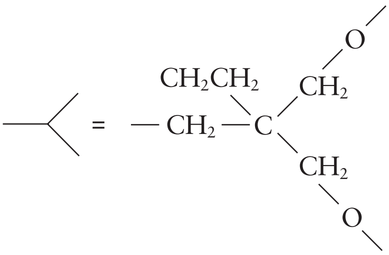
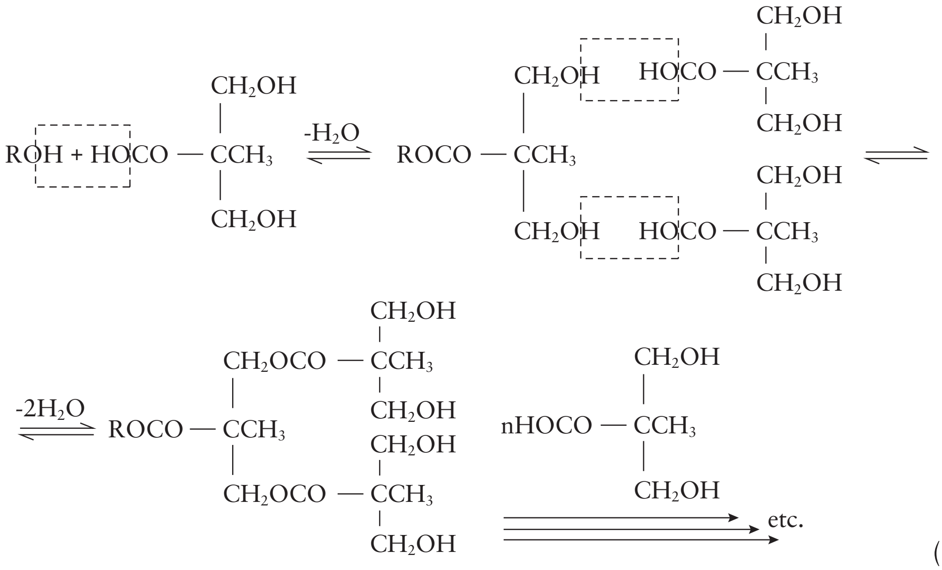


Figure 9.5 Repeating unit in the dendritic polyols based on 3-ethyl-3-methylol-oxetane

A very interesting dendritic polyester polyol was developed by Perstorp (Sweden), by self-condensation of dimethylolpropionic acid, initiated by a polyol such as pentaerythritol (PER) [16]. Of course, the condensation of dimethylol propionic acid with 1 hydroxyl group generates 2 hydroxyl groups as shown in **Reaction 9.13**.



(9.13)

Dendritic polyester polyols of 1st, 2nd, 3rd and 4th generation could be obtained by self-condensation of dimethylolpropionic acid initiated by PER. The resulting dendritic polyols have 8, 16, 32 and 64 hydroxyl groups/mol, respectively.

Figure 9.6 shows the structure of a 3rd generation of a dendritic polyester polyol, based on dimethylolpropionic acid, initiated by PER.

The dendritic polyester polyols based on dimethylolpropionic acid, are added to polyether polyols for flexible foams, in low concentration (e.g., approximately 8% dendritic polyol dissolved in the flexible polyether polyol), and give a remarkable increase in hardness of the resulting flexible PUF, comparable or higher to that induced by the presence of polymer polyols (e.g., 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 PUF.

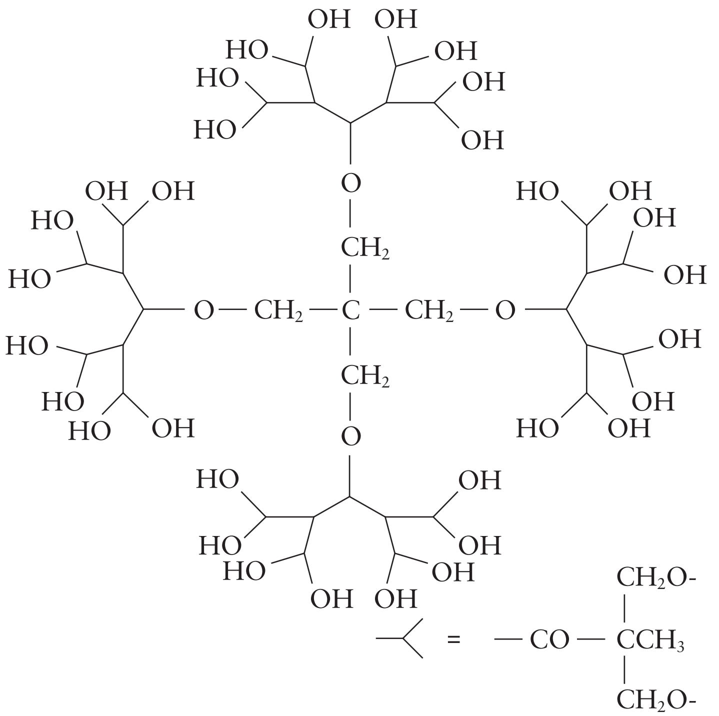


Figure 9.6 Dendritic polyester polyol based on dimethylolpropionic acid (3rd generation)

References

1. M. Ionescu, V. Zugravu, I. Mihalache and S. Mihai in *Advances in Urethane Science & Technology*, Wiley, New York, NY, USA, 1998, **14**, 151.

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, p.607.

3. J-P. Boiteaux, B. Brabq, N. Lecocu and F. Loussayne, inventors; Societe d'Exploitation de Produits pour les Industries Chimiques, assignee; US5108661, 1992.

4. No inventors, American Cyanamid Co., assignee; GB650940, 1951.

5. G.C. Tesoro, inventor; Onix Oil & Chemical Co., assignee; US2844609, 1958.
6. V. Lamberti and G.J. McCrimilsk, inventors; Lever Brothers Co., assignee; US3107258, 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.
10. R.L. Zimmerman and G.P. Sperenza, inventors; Texaco, Inc., assignee; US4442238, 1984.
11. A. Sunder, R. Hanselmann, H. Frey and R. Mulhaupt, *Macromolecules*, 1999, **32**, 13, 4240.
12. A. Sunder, R. Mulhaupt 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, **84**, 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.

10

Oligo-Polyols by Chemical Recovery of Polyurethane 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 polyurethane foam(s) (PUF) buns (flexible or rigid), material resulting from the moulding processes (material rejected out from the moulds), non-corresponding 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 PUF wastes by an adhesive, to obtain new PUF 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].

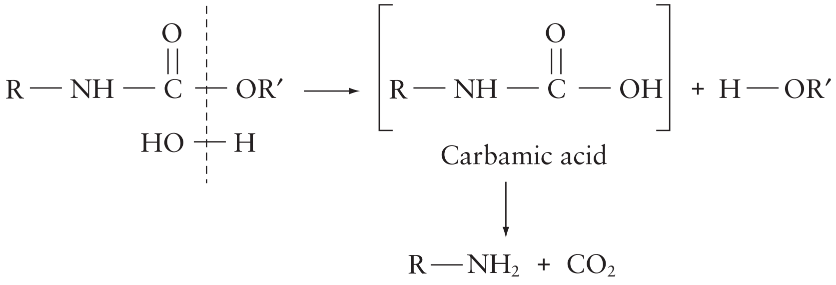
Chemical recovery processes by PU polymer breakdown through hydrolysis, glycolysis and aminolysis processes are extremely important because by using chemical reactions, the PU wastes are chemically transformed into new products which can possibly be used in the fabrication process of new PU. PU wastes 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 PUF 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.

10.1 Hydrolysis of Polyurethane Polymers [11–24]

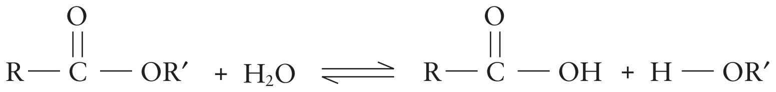
Hydrolysis of a urethane group leads to the formation of an amine, an alcohol and carbon dioxide (CO_2) (**Reaction 10.1**):



(10.1)

From the hydrolysis of a polyether-based PU a diamine (or a polyamine) such as toluene diamine or diphenylmethane diamine, a polyol and CO_2 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. CO_2 results from the decomposition of the very unstable carbamic acid formed by the hydrolysis (**Reaction 10.1**):

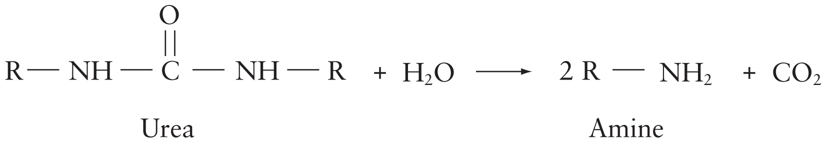
By hydrolysing a polyether PU, a polyether polyol is obtained with a similar structure to those of the initial virgin polyether polyol. For polyester PU the hydrolysis reaction is more complicated because the esteric groups of polyesters are hydrolysed back to monomers, such as diacids and glycols or polyols (**Reaction 10.2**):



$$R-\overset{\overset{O}{||}}{C}-OR' + H_2O \rightleftharpoons R-\overset{\overset{O}{||}}{C}-OH + H-OR' \qquad (10.2)$$

Thus, by the hydrolysis of a PU based on a polyester derived from adipic acid and diethylene glycol (DEG) adipic acid, DEG, diamine and CO_2 are obtained.

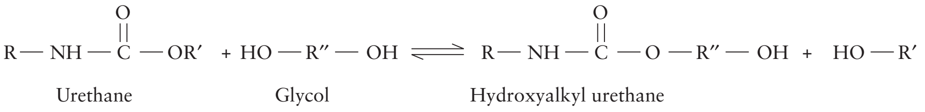
The real situation of PU hydrolysis is more complicated because together with the urethane groups, urea groups are also present resulting from the reaction of isocyanates (with water as the blowing agent), especially in flexible and rigid PUF. Urea groups are hydrolysed at a lower reaction rate than the urethane groups, being transformed into amines and CO_2 (**Reaction 10.3**).



$$\underset{\text{Urea}}{R-NH-\overset{\overset{O}{||}}{C}-NH-R} + H_2O \longrightarrow \underset{\text{Amine}}{2\,R-NH_2} + CO_2 \qquad (10.3)$$

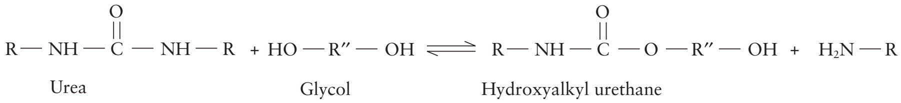
10.2 Glycolysis of Polyurethane Polymers [11, 12, 25–29]

Glycolysis of a PU polymer is similar to a transesterification reaction, in fact a reaction between a carbamic ester (urethane) and a glycol (**Reaction 10.4**):



$$\underset{\text{Urethane}}{R-NH-\overset{\overset{O}{||}}{C}-OR'} + \underset{\text{Glycol}}{HO-R''-OH} \rightleftharpoons \underset{\text{Hydroxyalkyl urethane}}{R-NH-\overset{\overset{O}{||}}{C}-O-R''-OH} + HO-R' \qquad (10.4)$$

By glycolysis of urea groups a hydroxyalkyl carbamate (or hydroxyalkyl urethane) and an amine are formed (**Reaction 10.5**):

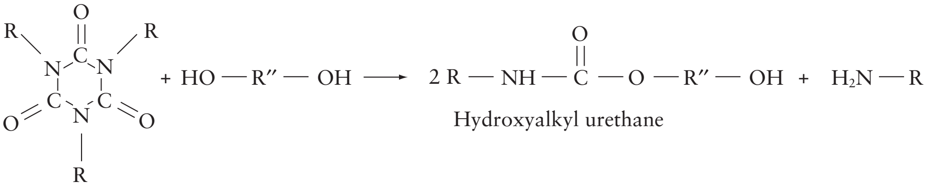


$$\underset{\text{Urea}}{R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R} + \underset{\text{Glycol}}{HO-R''-OH} \rightleftharpoons \underset{\text{Hydroxyalkyl urethane}}{R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O-R''-OH} + H_2N-R$$

(10.5)

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 [sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (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 (PIR) 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 10.6**) [11]:



(10.6)

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 **Figure 10.1**.

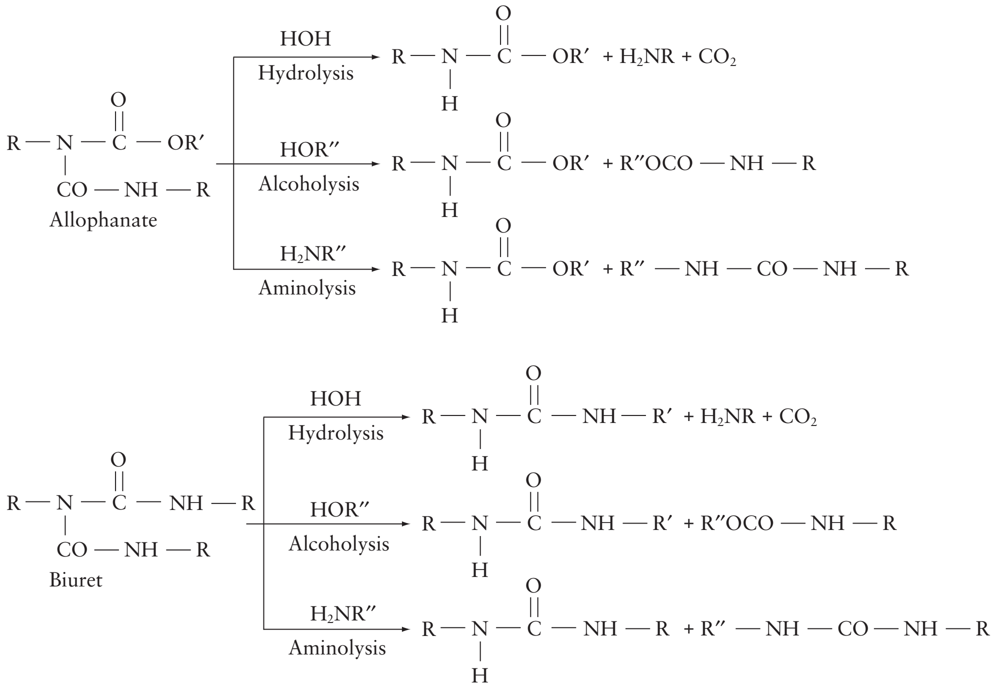
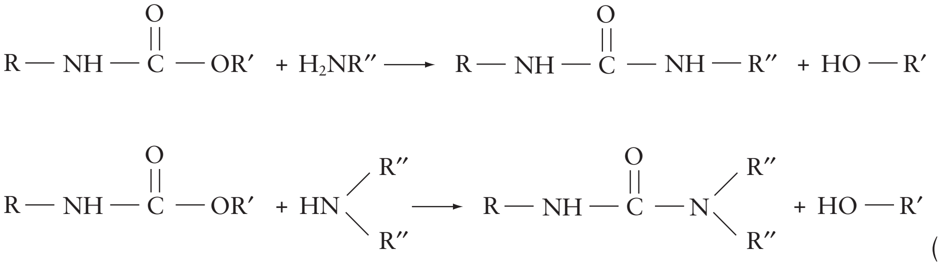


Figure 10.1 Chemical scission of allophanate and biuret bonds

10.3 Aminolysis of Polyurethane Polymer [31–36]

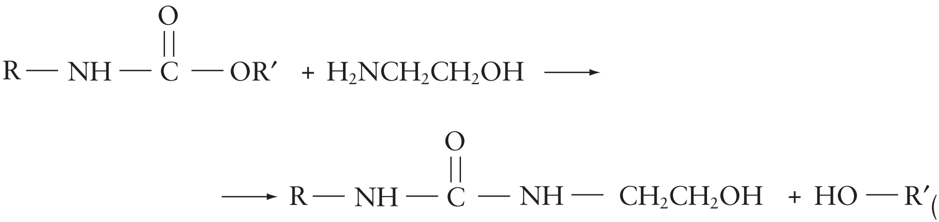
Urethane groups react with primary and secondary amines leading to a disubstituted urea and an alcohol (**Reaction 10.7**):



$$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}OR' + H_2NR'' \longrightarrow R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R'' + HO{-}R'$$

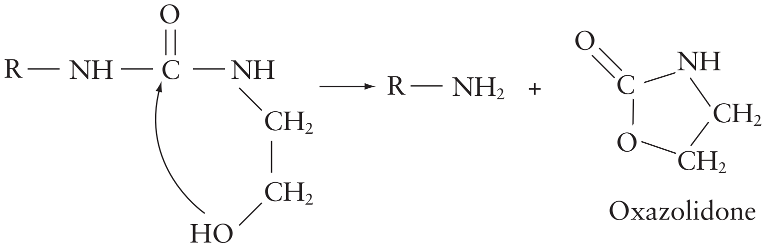
$$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}OR' + HN\begin{matrix}\diagup R'' \\ \diagdown R''\end{matrix} \longrightarrow R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}N\begin{matrix}\diagup R'' \\ \diagdown R''\end{matrix} + HO{-}R' \qquad (10.7)$$

In particular aminolysis with an alkanolamine such as monoethanolamine forms a hydroxyalkyl urea and an alcohol (**Reaction 10.8**):



$$R-NH-\overset{O}{\overset{\|}{C}}-OR' + H_2NCH_2CH_2OH \longrightarrow R-NH-\overset{O}{\overset{\|}{C}}-NH-CH_2CH_2OH + HO-R' \qquad (10.8)$$

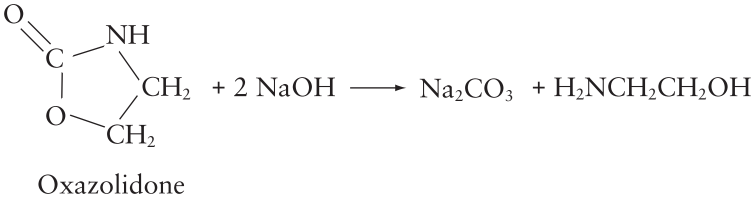
The disadvantage of hydroxyalkyl urea formation is an intramolecular reaction which leads to an oxazolidone, a cyclic urethane (**Reaction 10.9**) [33]:



(10.9)

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 NaOH or KOH 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 10.10**) [33]:



(10.10)

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 10.11**) [32, 33]:


Oxazolidone

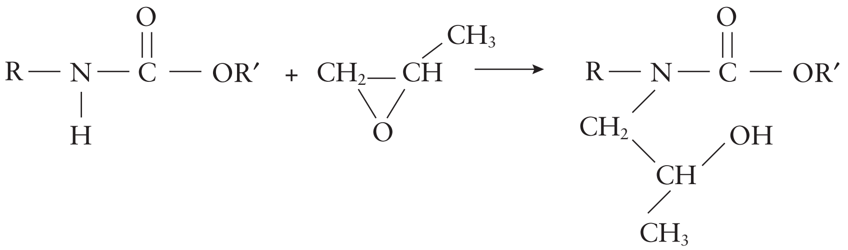
(10.11)

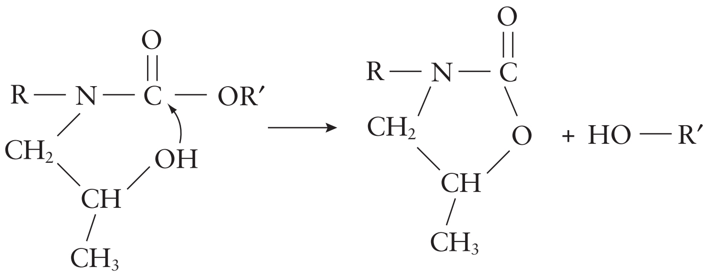
10.4 Alkoxylation of Polyurethane Polymer [37–39]

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 PUF, the PU crosslinked polymer is transformed into a liquid product.

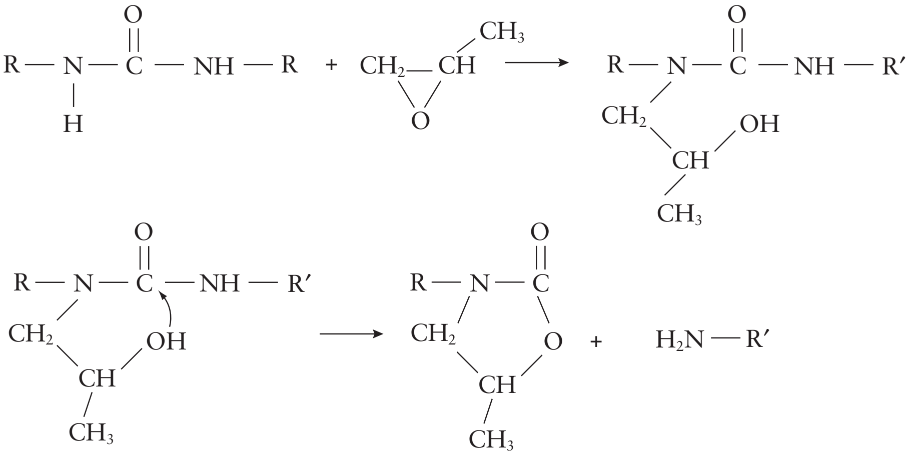
The scission of urethane groups is explained by the following two consecutive reactions (**Reactions 10.12** and **10.13**). The first reaction is the addition of alkylene oxide to the active hydrogen of urethane groups (**Reaction 10.12**). The resulting hydroxyalkyl urethane, by an intramolecular transesterification, 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.


(10.12)



(10.13)

The alkoxylation process is easy to apply to PUF 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 10.14**):

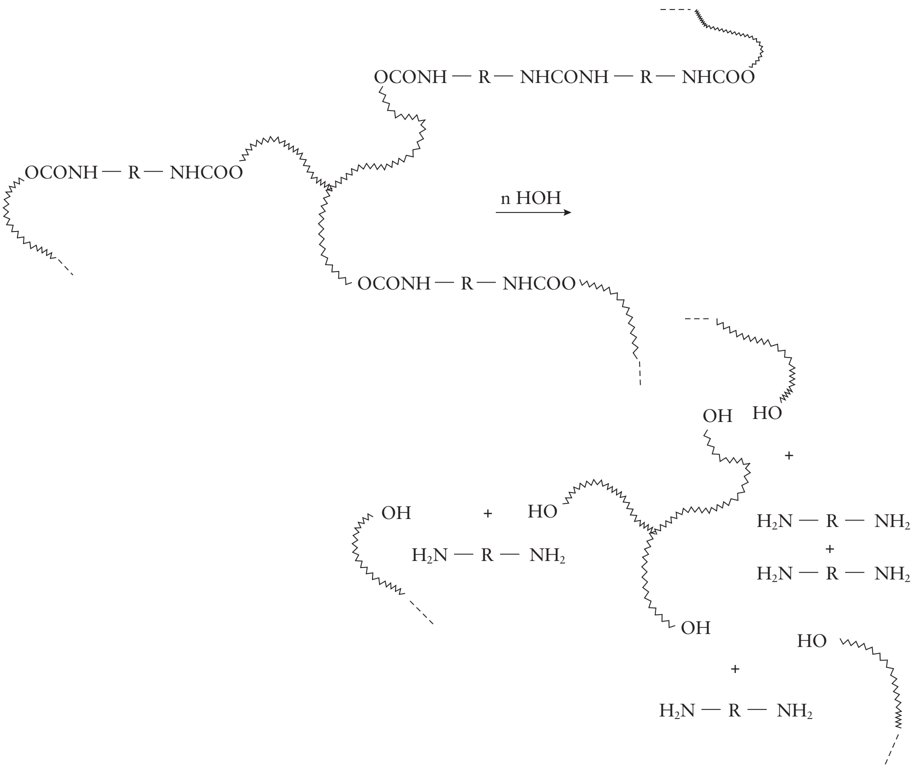


(10.14)

In **Sections 10.1–10.4** 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.

10.5 Chemical Recovery of Flexible Polyurethane Foam Wastes by Hydrolysis [12–24, 27]

The idealised reaction for the hydrolysis of the crosslinked structure of flexible PUF is shown in **Reaction 10.15**:



(10.15)

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, CO_2. 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 PUF.

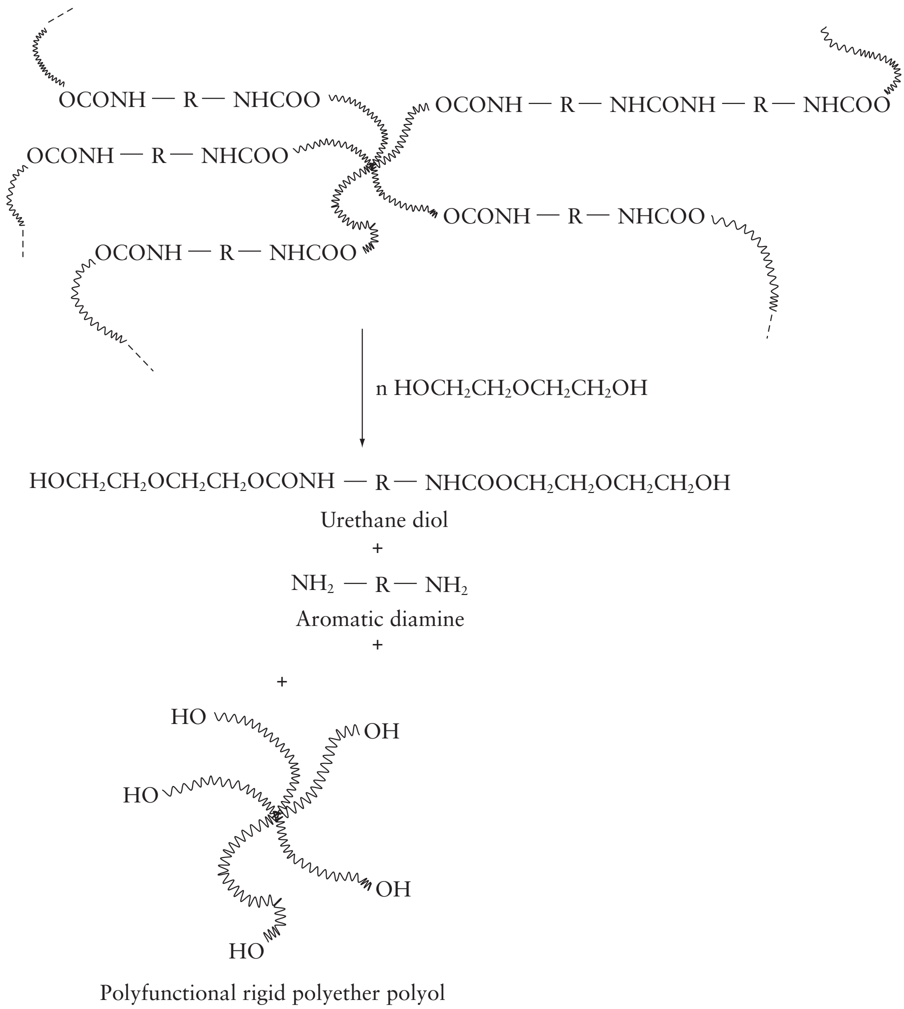
A variation of steam technology is a hydrolysis-glycolysis process at 190–200 °C. LiOH proved to be an excellent catalyst of these reactions and the degradation process is accelerated markedly to just a few minutes while the temperature may be decreased at 170–190 °C [12, 34].

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 PUF waste. Because in the hydrolysis process new types of polyols do not appear, this type of technology is not described.

10.6 Rigid Polyols by Glycolysis of Rigid Polyurethane Foam Wastes [11, 12, 25, 26, 28–30]

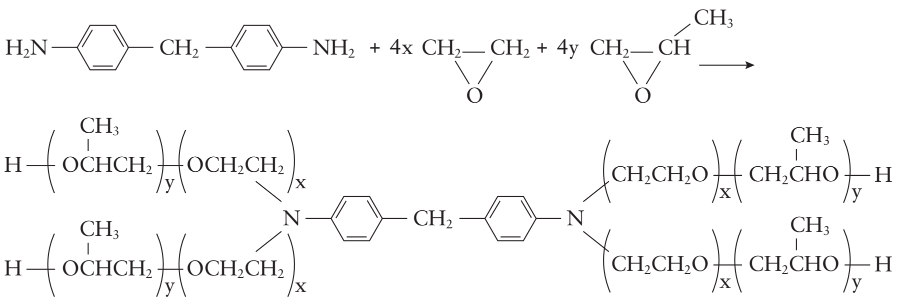
By reacting rigid PUF wastes with glycols (ethylene glycol, DEG, dipropylene glycol and so on), a liquid mixture of polyols is obtained, which can be reused directly in rigid foam production. The process consists in the reaction of equal parts of ground PU scraps and DEG:diethanolamine mixture (9:1), 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 PUF 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 PUF is presented in **Reaction 10.16**:



(10.16)

The diamine (e.g., diphenylmethane diamine) is transformed into a rigid polyether polyol by alkoxylation with PO and EO (**Reaction 10.17**):



(10.17)

To conclude, the complex mixture of polyols resulting from glycolysis of rigid PUF 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 PUF wastes has in its composition aromatic polyols derived from a diphenylmethane diisocyanate structure (component a and c), which lead to an improvement of physico-mechanical, thermal and fire proofing properties in the resulting rigid PUF. The characteristics of a polyol mixture resulting by the glycolysis with DEG of a conventional rigid PUF (density 30–50 kg/m^3) are presented in **Table 10.1**.

Table 10.1 Characteristics of recovered polyols obtained by the glycolysis with DEG of conventional rigid PUF of density 30-50 kg/m^3

Characteristic	Unit	Value
Aspect	–	Dark-brown viscous liquid
OH#	mg KOH/g	600–650
Acidity	mg KOH/g	Maximum 10
Viscosity (25 °C)	mPa.s	4,500–7,000
Water content	%	Maximum 0.2

OH#: Hydroxyl number(s)

The characteristics for a recycled polyol presented in **Table 10.1** have a large range of values due to the fact that the qualities of the rigid PU wastes used are not consistent (the rigid PUF 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 10.2**.

Table 10.2 Characteristics of polyols recovered by the glycolysis after alkoxylation with PO and EO

Characteristic	Unit	Value
Aspect	–	Dark-brown viscous liquid
OH#	mg KOH/g	550–600
Acidity	mg KOH/g	Maximum 2
Viscosity (25 °C)	mPa.s	8,000–10,000
Water content	%	Maximum 0.1

The recovered polyols shown in **Table 10.2** have a lower acidity due to the alkoxylation of acidic groups, lower OH# 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 10.1**).

Glycolysis of flexible PUF 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 OH# of 360–390 mg KOH/g, which was used successfully in rigid PUF fabrication [35].

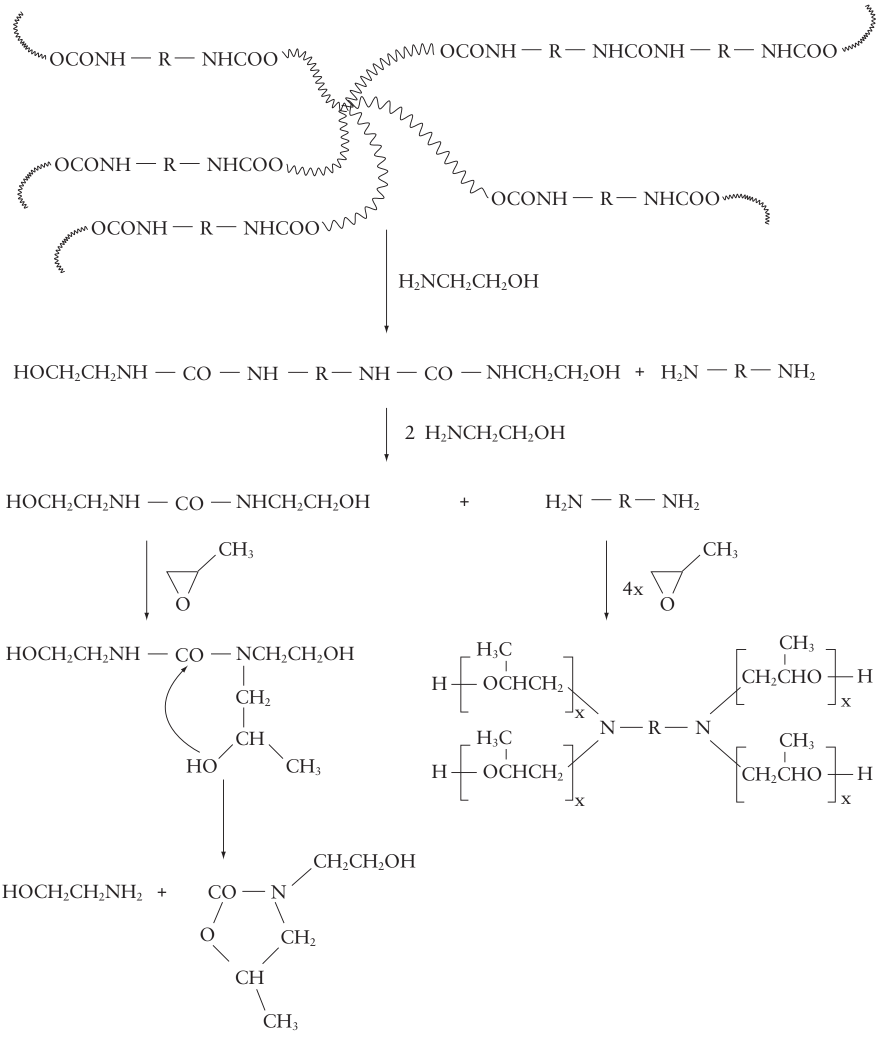
10.7 Rigid Polyols by Aminolysis of Rigid Polyurethane Foam Wastes [31–36, 40, 41]

Aminolysis of rigid PUF wastes takes place at higher reaction rates than the glycolysis reaction and at lower temperatures (160–170 instead of 190–210 °C) [31–33].

An interesting aminolysis process based on the reaction of ground polyether-based rigid PUF 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 1 litre of alkanolamine) [34, 41].

In the second step, the aromatic amines formed react with EO or with PO. 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 PUF are presented in **Reaction 10.18:**



(10.18)

A hybrid process: aminolysis-alkoxylation was developed [37–39]. The ground rigid PUF 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 PUF with good physico-mechanical properties.

10.8 Technology for Chemical Recovery of Rigid Polyurethane Foams (and Isocyanuric Foams) by the Glycolysis Processes

The technology for the chemical recovery of rigid PUF and isocyanuric foam wastes (a variant) by glycolysis processes involves the following main steps:

a) The grinding of rigid PUF 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 PUF wastes by glycolysis is shown in **Figure 10.2**.

The grinding of PUF 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 PUF wastes are obtained.

The glycolysis reaction consists of the stepwise addition of finely ground rigid PUF 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 h.

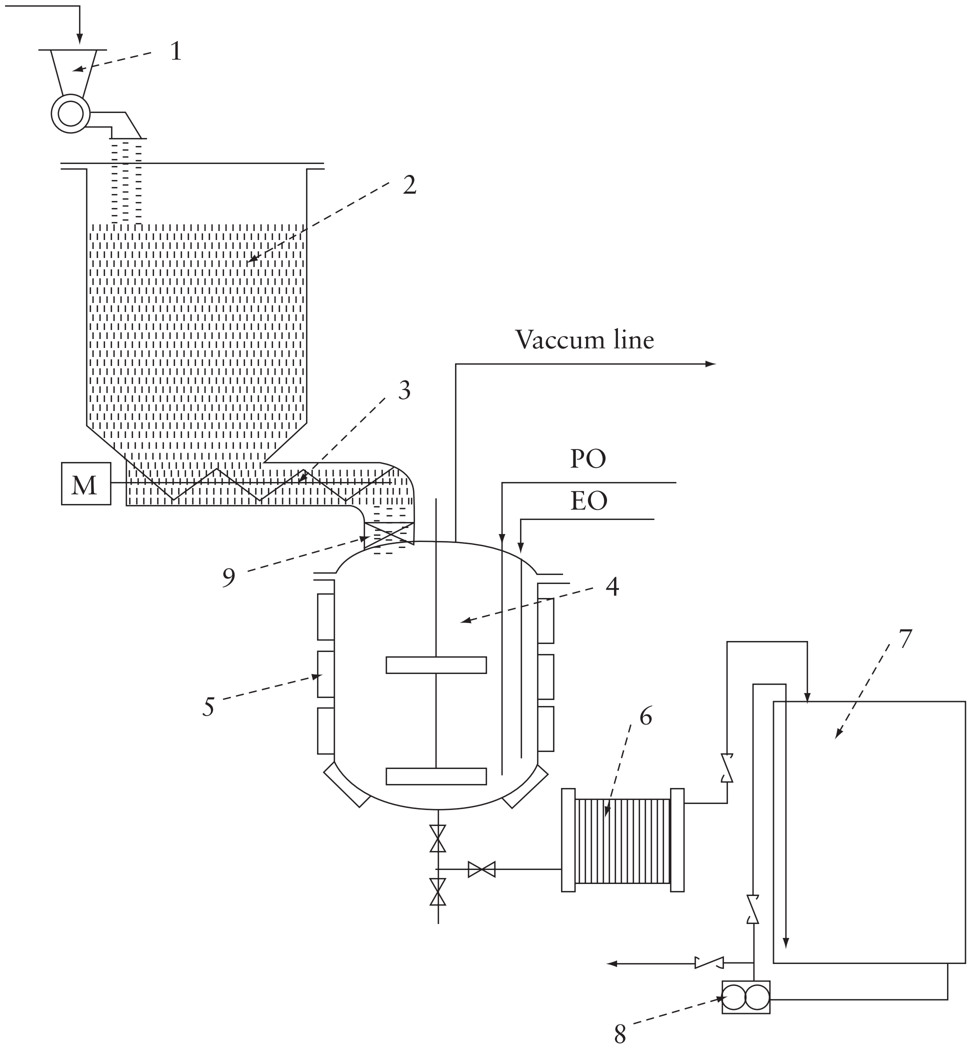


Figure 10.2 Technological scheme for recovery of rigid PUF wastes by glycolysis process (variant). 1) Mills for PU scrap; 2) storage of ground rigid PUF; 3) screw for powdered materials; 4) glycolysis and alkoxylation reactor; 5) electrical induction heaters; 6) filter press; 7) storage tank for the recovered polyol; 8) gear or screw-screw (or double-screw) pump; and 9) valve

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 h. The remaining alkylene oxides are removed by normal degassing procedures, by vacuum distillation.

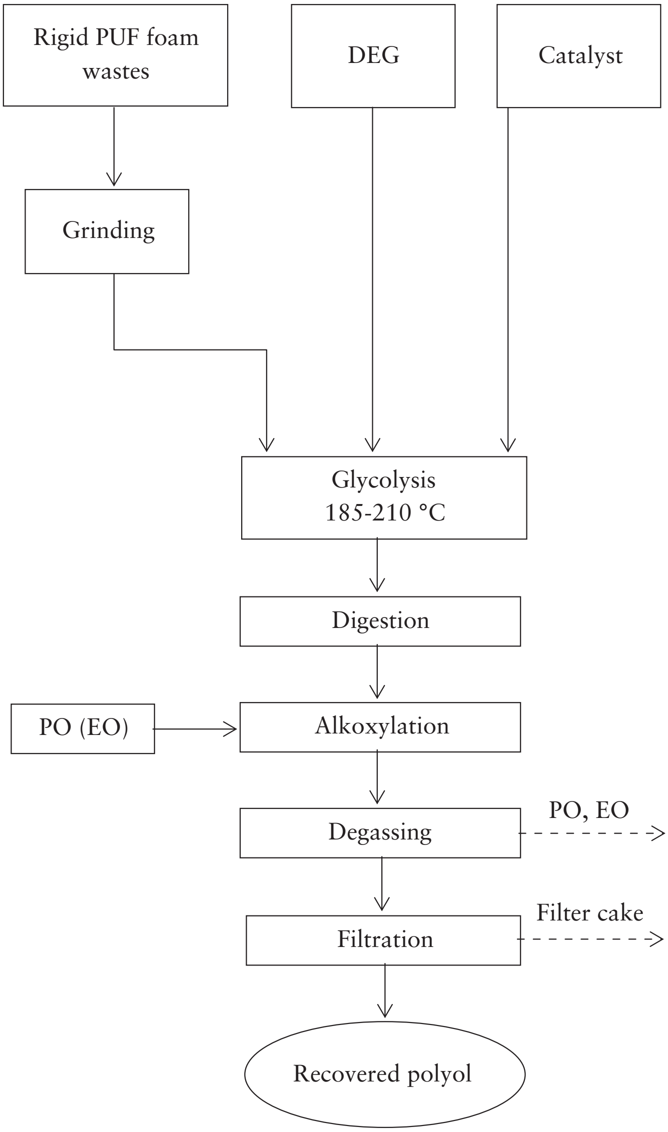


Figure 10.3 Schematic of the flow reaction for the chemical recovery of rigid PUF wastes by glycolysis process

The recovered polyol is filtered on a convenient filter (e.g., a press filter) to remove the traces of solid materials, i.e., paper, unreacted ground rigid PUF and so on. The resulting recovered polyol has the characteristics given in **Table 10.2**.

A schematic diagram of the chemical recovery of rigid PUF wastes by glycolysis is presented in **Figure 10.3**. 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.

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: Polymer Chemistry Edition,* 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 in *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, Part A: Polymer Chemistry Edition,* 1989, **27**, 6, 1993.

18. J.L. Serlock, J. Braslaw, L.R. Mahoney and F.F. Ferris, *Journal of Polymer Science, Part A: 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 Co., assignee; US4025559, 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.

26. J. Penfold and J. Kuypers, *Syspur Reporter*, 1976, **12**, 56.

27. No inventor; Bayer AG, assignee; FR2283766B1, 1979.

28. F. Simioni, S. Bisello and M. Cambrini, *Macplas*, 1983, 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., assignee; US3738946, 1973.

31. M.B. Sheratte, inventor; McDonnell Douglas Corp., assignee; US4110266, 1978.

32. N. Matsudaira, S. Muto, Y. Kubota, T. Yoshimoto and S. Sato, inventors; Bridgestone Tire Co. Ltd., assignee; US3404103, 1968

33. W.R. McElroy, inventor; Mobay Chemical Corp., assignee; US3117940, 1968

34. R. Herrington and K. Hock in *Flexible PU Foams*, Dow Chemical Co., 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*, Boston, MA, USA, 1994, p.506.

38. M. Ionescu, V. Dumitriu, I. Mihalache, F. Stoenescu and S. Mihai, inventors; Institutul de Cercetari Chimice, assignee; RO89944, 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.

40. H.R. van der Wal, *Proceedings of the SPI 34th Annual PU Conference*, New Orleans, LA, USA, 1992, p.560.

41. S. Waddington and A.W. Duff in *Proceedings of the PU World Congress 1993*, Vancouver, BC, USA, 1993, p.558.

11 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 PU properties.

Several general properties, characteristic to classical macromolecular chemistry, are strongly linked to the PU 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.

11.1 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 PU (PU elastomers, 'spandex' fibres and so on).

For crosslinked polymers (in this category they are the majority of PU, e.g., flexible, semiflexible and rigid PUF and so on), which have a MW that is practically infinite [12], the MW between the branching points (M_c) is considered. The value of M_c depends strongly on the oligo-polyol structure.

11.1.1 The Effect of the Molecular Weight of Oligo-Polyols

The MW of oligo-polyols, is usually in the range of 400 to 6,500 daltons, and it has an important effect on the PU properties. Thus, if the polyol has a low-MW, a hard PU will result and if the polyol has a high-MW, it creates elastic, flexible PU. Intermediate MW lead to semirigid or semiflexible structures [2].

It is clear that a short oligo-polyol chain [a short chain derived from 1 hydroxyl group or with a low equivalent weight (EW)] leads to higher concentrations of urethane bonds. The high cohesive interaction between these bonds (mainly by secondary hydrogen bonds) leads to a rigid structure, i.e., to hard PU. This effect is combined with the high functionality that is characteristic of oligo-polyols for rigid PUF.

On the contrary, in a long oligo-polyol chain (the chain derived from 1 hydroxyl group is long or the EW of the polyol is high), the concentration of urethane 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 = 1,000–4,000 daltons) polyethers [polyalkyleneoxides, polytetrahydrofuran (PTHF)], polyesters, polycarbonates (PC), polybutadienes and so on., by the reaction with diisocyanates (toluene diisocyanate or ‘pure’ diphenylmethane diisocyanate), high-MW linear PU are obtained (no crosslinking), with high elasticity (PU elastomers, spandex fibres, some adhesives and sealants and so on).

From high-MW triols or low branched oligo-polyols (MW = 3,000–6,500 daltons): polyethers, polyesters, filled polyols (polymer polyols), are obtained elastic PU with a low degree of crosslinking (flexible and semiflexible foams, coatings and so on).

From low-MW oligo-polyols (400–1,000 daltons; polyethers, polyesters, Mannich polyols, aromatic polyesters, oleochemical polyols and so on.), are obtained rigid, hard PU structures (rigid PUF, wood substitutes and so on).

An interesting remark for the thermoplastic PU elastomers which are linear PU. These are polymers at room temperature (RT) 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, **Volume 1, Chapter 3**). At higher temperatures, these secondary bonds are destroyed and the PU 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 RT like an elastomeric material [8, 13–15]. The thermoplastic PU elastomers are part of the group of thermoplastic elastomers together with styrene-butadiene rubber block copolymers, polyether-polyester block copolymers or polyamide-polyether block copolymers. Very important processes in PU fabrication are reaction injection moulding (RIM) and reinforced RIM processes, in which the thermoplastic PU is obtained in a reactive manner, the reaction between two liquid components, i.e., liquid polyolic component and liquid isocyanate component (isocyanate, prepolymer or quasi-prepolymer) [8, 13–15] is developed directly in the process of injecting.

The effect of the MW of some oligo-diols, such as polypropylene glycols (PPG), polytetramethylene glycols and polyethylene adipate glycols upon the properties of the resulting PU 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 PPG based PU elastomers, but polytetramethylene glycols and polyethylene adipate glycols based PU elastomers also show a slow decrease. The elastic properties, such as rebound resiliency and ultimate elongation, increase with the MW of oligo diol, the best properties being obtained in PU elastomers based on polytetramethylene glycols and polyethylene 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 polyethylene adipate glycols have the lowest abrasion loss. PPG (obtained in anionic catalysis) lead to PU elastomers with poorer abrasion resistance [2].

The independent effect of the MW of oligo-polyols is possible only in linear PU (practically only in the case of oligo-diols). In crosslinked PU there is a cumulative effect of MW and functionality and the independent effect of the MW of oligo-polyol is difficult to achieve. In order to have a better description and understanding of a crosslinked structure the notion of MW between branching points (M_c) was introduced.

Generally by increasing the MW between branching points (M_c) some properties of crosslinked PU, such as: tensile strength, elongation, modulus and tear strength increase, while the hardness decreases [2].

In rigid polyurethane foams (PUF) a strong dependence was observed between the hydroxyl number (s) OH# of oligo-polyol and the dimensional stability of the resulting rigid PUF (OH# is a measure of the MW of an oligo-polyol, a high OH# represents low-MW polyols and low OH# represent higher-MW polyols).

Thus, high OH# polyols lead to better dimensional stability and higher compression strength in the resulting rigid PUF than the lower OH# polyols [7]. Contrary to this effect, the increase of OH# of oligo-polyols leads to a marked increase in friability of the resulting rigid PUF [7]. Lower OH# lead to lower friability rigid PUF [7].

11.2 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 (approximately 0.5–2 kcal/mol), hydrogen bonds (approximately 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 PU, 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.

11.2.1 The Effect of the Chemical Nature of Oligo-Polyol Chains

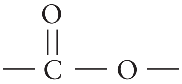
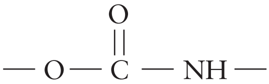
Table 11.1 shows the molar cohesive energies of functional groups in oligo-polyols and in PU.

Based on the data in **Table 11.1**, the relative cohesive energy of oligo-polyols:polyether polyols, polyester polyols and polyhydrocarbon polyols (e.g., 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 PU based on polyester polyols are superior to the PU derived from polyether polyols or from polyhydrocarbon polyols (this relative order is valuable for PU elastomers, flexible and rigid PUF).

Table 11.1 The molar cohesive energies of functional groups in oligo-polyols and in PU

Structure	Name of the group	Cohesive energy (kcal/mol)
$-CH_2-$	Hydrocarbon	0.68
$-O-$	Ether	1.00
 $-\overset{\overset{O}{\|}}{C}-O-$	Ester	2.90
$-C_6H_4-$	Aromatic	3.80
 $-\overset{\overset{O}{\|}}{C}-NH-$	Amide	8.50
 $-O-\overset{\overset{O}{\|}}{C}-NH-$	Urethane	8.74

In **Table 11.1** 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 PUF is very evident in rigid oligo-polyols. Thus, an aromatic polyol of low functionality (e.g., a Mannich polyol of f = 3 hydroxyl groups/mol) gives higher physico-mechanical properties and better dimensional stability, compared to a similar rigid PUF derived from an aliphatic polyol of the same functionality, (e.g., a rigid polyether polyol based on glycerol).

Table 11.2 shows the strength of the covalent bonds existing in oligo-polyols and in PU.

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 PU 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 PU with a lower thermostability than polyester polyols (having C=O bonds). Aminic polyols, lead to lower thermostable PU 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 PU than aliphatic saturated oligo-polyols.

Table 11.2 The strength of the covalent bonds existing in oligo-polyols and in PU

Covalent bond	Dissociation energy (kcal/mol)
C≡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 PU with improved fire resistance. Aromatic polyols sometimes give PU with intrinsic fire resistance, due to the very high char yield generated during the burning process [6].

11.3 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 (mp) 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 mp, high T_g and decrease the elasticity.

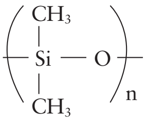
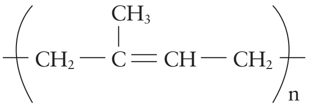
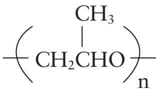
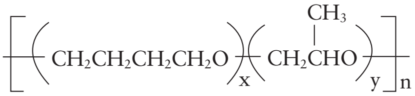
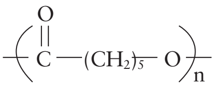
Molecular flexibility depends on the freedom of rotation around single-bonds in the main chain of the polymer molecule, restrictions in this free rotation reduce the flexibility [2].

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 (e.g., 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 PU is very important because it conserves the high elasticity at lower temperatures.

Table 11.3 shows the T_g of some important polymers for oligo-polyols structure.

Table 11.3 The T_g of some important polymers for oligo-polyols structure

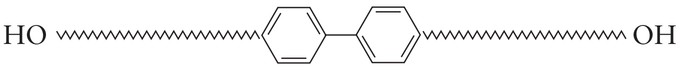
Polymer	Repeat unit	T_g (°C)
Polydimethylsiloxane	 $\left(\mathrm{Si(CH_3)_2-O}\right)_n$	-123
Polyisoprene (1,4-*cis*)	 $\left(\mathrm{CH_2-C(CH_3)=CH-CH_2}\right)_n$	-73
Polybutadiene (1,4-*cis*)	$\left(\mathrm{CH_2-CH=CH-CH_2}\right)_n$	-95
PTHF	$\left(\mathrm{CH_2CH_2CH_2CH_2O}\right)_n$	-86
Polypropylene oxide	 $\left(\mathrm{CH_2CH(CH_3)O}\right)_n$	-64
Copolymer THF–PO	 $\left[\left(\mathrm{CH_2CH_2CH_2CH_2O}\right)_x\left(\mathrm{CH_2CH(CH_3)O}\right)_y\right]_n$	-76.9
Copolymer THF–EO	$\left[\left(\mathrm{CH_2CH_2CH_2CH_2O}\right)_x\left(\mathrm{CH_2CHO}\right)_y\right]_n$	-64.6
PCL	 $\left(\mathrm{C(=O)-(CH_2)_5-O}\right)_n$	-60

PCL: Polycaprolactone
PO: Propylene oxide
THF: Tetrahydrofuran

11.4 Crystallinity

Crystallisation in PU 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 PU polymers, hardness, tensile strength, mp increase and the solubility, elongation and the flexibility generally decrease. PU 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, polyethylene adipate glycols and some other polyester polyols and polyethylene glycols.

Liquid crystalline PU are obtained by using oligo-polyols containing mesogenic units, such as biphenyl units:



(11.1)

11.5 Crosslinking

Crosslinking in PU 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 branching points (M_c) (in fact on the MW of the oligo-polyol).

11.5.1 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 PU. As mentioned before, high-MW oligo-polyols with low functionality (f = 2–3 hydroxyl groups/mol) lead to low crosslink density flexible, elastic PU and the reverse, low-MW oligo-polyols, with high functionality (f = 3–8 hydroxyl groups/mol) lead to high crosslink density rigid PU.

This behaviour concerning the cumulative effect of functionality and MW of oligo-polyols is observed in the case of PUF (flexible, semiflexible and rigid) based on stress-strain relationship [2, 12].

Flexible foams have low load bearing properties and high recovery properties. Rigid PUF have high load bearing properties with a definite yield point and lack recovery. Semiflexible foams display higher load bearing properties as compared to flexible PUF, 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 PUF, 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 PUF 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 PUF (a very important characteristic in the thermoinsulation of refrigerators, especially at lower temperatures) is strongly improved by using high functionality oligo-polyols.

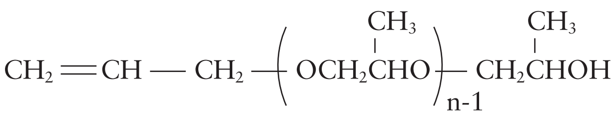
The conversion at gel point in PU processes depends strongly on the medium functionality of the reaction system [5]. Thus, lower functionalities give high conversion at the gel point and high functionalities give low conversion at the gel point. This is the reason why sometimes the best properties of rigid PUF are not obtained at very high functionalities of oligo-polyols (e.g., $f = 7–8$ hydroxyl groups/mol), but at medium functionalities ($f = 4.5–5.5$ hydroxyl groups/mol). **Table 11.4** shows the theoretical conversions at gel point, in rigid PUF (by using a difunctional isocyanate).

Fortunately, after the gel point, the reaction between unreacted -NCO groups and unreacted hydroxyl 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 11.4 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 (**Volume 1, Section 4.1**), with this structure:



$$CH_2{=}CH-CH_2-\left(OCH_2\overset{CH_3}{\overset{|}{C}}HO\right)_{n-1}-CH_2\overset{CH_3}{\overset{|}{C}}HOH$$

(11.2)

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 hydroxyl groups/mol, but is lower, being situated in the range of 2–3 hydroxyl 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 hydroxyl groups/mol [17].

The functionality decrease in polyether polyols synthesised in anionic catalysis is more significant at higher-MW polyethers.

Figure 11.1 shows the functionality decrease function of the polyether diols MW while **Figure 11.2** shows the variation of the functionality against the polyether triol MW.

The presence of the polyether monol leads to very modest properties of PU based on PPG obtained by anionic catalysis. In polyaddition reactions involved in PU synthesis a monofunctional polyether is a chain stopper and decreases the MW of final PU. 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.

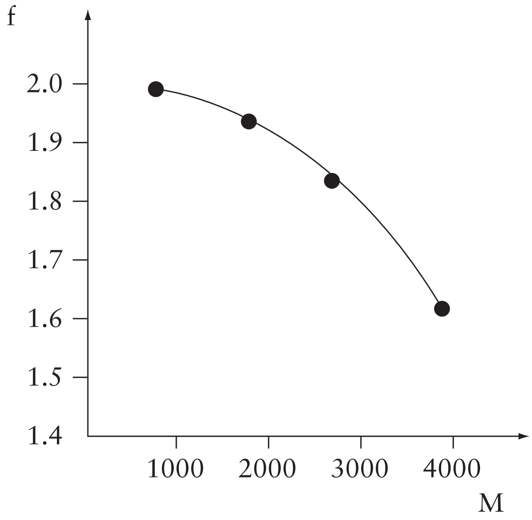


Figure 11.1 Functionality of polyether diols, PO homopolymers, obtained in anionic catalysis, as a function of the MW

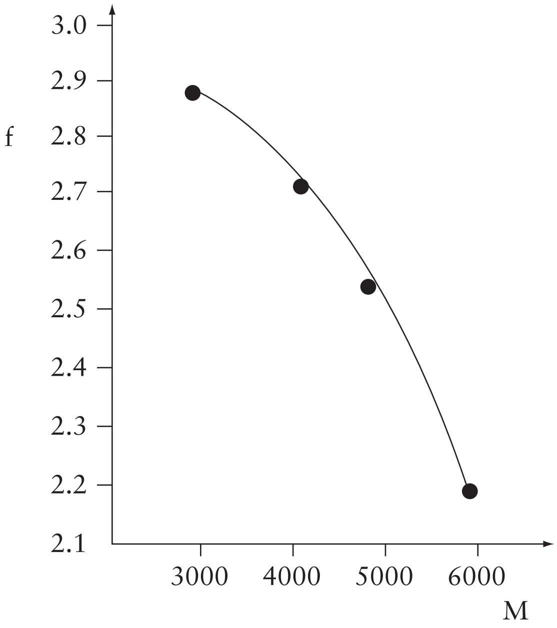


Figure 11.2 Functionality of polyether triols, PO homopolymers, obtained in anionic catalysis, as a function of the MW

A spectacular increase in all properties was observed in elastic PU (especially in PU elastomers, but in flexible foams too), by using polyethers obtained with double metal cyanide (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 (e.g., Bayer's Acclaim polyols), having a functionality close to the theoretical functionality (f = 2 hydroxyl groups/mol), lead to PU elastomers having a spectacular increase in all physico-mechanical properties such as: modulus, tensile strength, tear strength, elongation, hardness and so on. By using polyether diols, and PO homopolymers, with low monol content, linear PU of much higher-MW are obtained and as an immediate consequence all the properties of the resulting PU elastomers increase (as mentioned in the **Section 11.1**).

In flexible PUF, 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) (e.g., a hexafunctional polyether polyol of EW 1,000–2,000, based on alkoxylation of sorbitol instead of glycerol), produces flexible PUF with higher load bearing properties, but with a decrease in tensile strength and elongation. These polyols were used in carpet underlay [18].

11.5.2 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 PU very resistant to hydrocarbons and oils. This is one of the biggest advantages of PU elastomers over the conventional rubbers.

Linear PU dissolve in various solvents such as: ketones (methyl ethyl ketone, cyclohexanone and so on), acetate alkyl esters (methyl acetate, butyl acetate), THF, dimethylformamide, methylene chloride, trichloroethane and so on.

The resulting solutions are frequently used for processing 'spandex' fibres, coatings, adhesives, synthetic leathers and so on.

Crosslinked PU are not soluble and of course swell, the degree of swelling decreases with the increase in crosslink density. For example, for a flexible PUF in the presence of acetone, the degree of swelling is approximately 116% at a M_c of 1,650 and becomes 90% at a M_c of 1,070 and 83% at a M_c of 690 [2].

The hydrolytic resistance of a PU depends strongly on the nature of the oligo-polyol chain. As a general rule, very hydrophobic chains and water repellent polyols give PU with excellent hydrolytic stability. The relative order of the hydrolysis resistance of PU 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 PU based on oleochemical polyols, dimer acids and dimer alcohols, PTHF and PC-polyols lead to PU with excellent hydrolytic stability. PCL polyols and polybutylene adipate lead to PU with good hydrolytic stability, but use of polydiethylene glycol adipate give PU with poor hydrolytic resistance.

Polyester urethanes are biodegradable by microbial attack (generally aliphatic polyesters are biodegradable). PU based on oleochemical polyols are biodegradable too. This property, biodegradability, may be used for: controlled release for drugs, biodegradable packaging products and so on.

Biostability increases strongly by changing to polyether polyol based PU. Generally the polyethers are relatively non-toxic but non-biodegradable products.

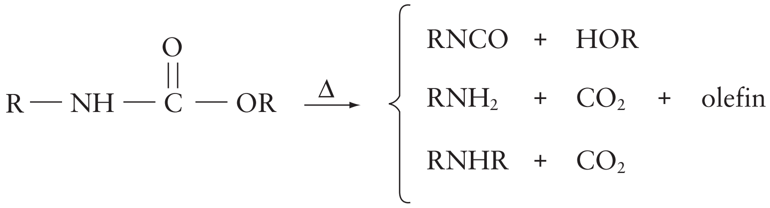
11.6 Thermal Stability and Flame Retardancy

Based on the values of cohesive energies and dissociation energies of the bonds involved in the PU structure, it may be possible to establish the following relative order regarding the thermal stability of PU 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.

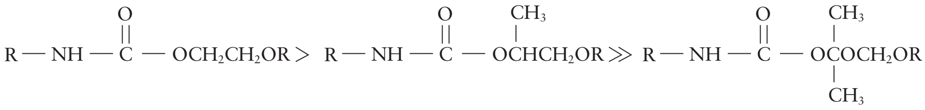
The general reaction of urethane groups decomposition is:



$$R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-OR \xrightarrow{\Delta} \begin{cases} RNCO + HOR \\ RNH_2 + CO_2 + \text{olefin} \\ RNHR + CO_2 \end{cases}$$

(11.3)

PU based on oligo-polyols with primary hydroxyl groups are more thermostable than the PU derived from polyols with secondary groups and much more thermostable than the PU derived from polyols with tertiary hydroxyl groups:



$$R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_2OR > R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OR \gg R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}OCH_2OR$$

(11.4)

As a general rule the thermal stability of PU is directly linked with the mobility of polymeric chains. Low mobility, crosslinked PU structures, based on high functionality polyols are more thermostable than the high mobility, low crosslinked PU (elastic PU). Generally cycloaliphatic structures and aromatic structures have low mobility and high rigidity. This is the explanation of the higher thermal resistance of PU 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 PU and of isocyanuric rigid foams is assured too by the high thermostability of the aromatic nucleus and of triazinic rings.

11.6.1 Flame Retardancy

The fire resistance of PU 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 PU structure and lead to self-extinguishing PU, with a permanent flame retardancy.

Generally, the PU without flame retardants burn completely, but some structural elements in the oligo-polyol architecture improve markedly, the fire resistance of the resulting PU.

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 PU with improved fire resistance. Thus, polyesters are superior to polyethers in so far as the fire resistance of the resulting PU is concerned. Cycloaliphatic polyols (e.g., polyols based on carbohydrates, such as sucrose or alkyl glucosides) produce PU with superior fire resistance as compared to the simple aliphatic polyols (e.g., polyether based on glycerol or on pentaerythritol).

Aromatic polyols and triazinic polyols lead to PU with superior fire resistance due to the high char yield generated during the burning process. Sometimes, the rigid PU 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 e.g., with powdered melamine + *tris*(2-chloropropyl) phosphate [14].

Flame retardant rigid PUF, 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 (e.g., Mannich polyols, novolak polyols, triazinic polyols based on melamine and so on). For flame retardant rigid PUF, reactive flame retardants are preferred (bromine polyols or phosphorus polyols, **Volume 2**, **Chapter 8**).

References

1. G. Oertel in *Polyurethane Handbook*, Hanser Verlag, Munich, Germany, 1985.

2. M. Szycher in *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 in *Polyurethanes: Chemistry and Technology*, Interscience Publishers, New York, NY, USA, 1962, Chapters 6, 9 and 12.

6. J.W. Lyons in *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, NY, USA, 1970, Chapter 8.

7. T.H. Ferrigno in *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*, 2nd 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.

11. R. Becker in *Polyurethanes*, VEB, Leipzig, Germany, 1983.

12. D.W. Vilar in *Chemistry and Technology of Polyurethanes*, 3rd 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 in *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 in *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; US3433751, 1969

Postface

Volume 2 of *Chemistry and Technology of Polyols for Polyurethanes* is dedicated to polyols for rigid polyurethanes (PU). Rigid PU foams can be used for thermal insulation of buildings, freezers, pipes and storage tanks for food and chemical industries, as well as for packaging, wood substitutes, and flotation materials.

Polyols for rigid PU, irrespective of their structure, have two important specific characteristics: high hydroxyl functionality (3–8 or more hydroxyl groups/mol) and the chain derived from the 1-hydroxyl group is short [maximum 100–200 daltons (Da)]. As a consequence of this special structure, hard, rigid PU can be produced.

PU for rigid PU are polyether polyols, polyester polyols, aminic polyols, polyols from condensates of aldehydes with phenols, polyols by thiol-ene reactions, and polyols from renewable resources (vegetable oils, fish oil, lignin, starch, lactides, limonene, glycerol, polyglycerol, liquid from the shells of cashew nuts, sucrose, sorbitol, xylitol). Special polyols for rigid PU are flame-retardant polyols (phosphorus and bromine-containing polyols) and polyols by chemical recovery of rigid PU wastes.

PU remain one of the most dynamic group of polymers. In 2004, 10.6 million tonnes of PU were produced worldwide. In 2014, worldwide production was ≈20 million tonnes. In 2005–2015 has seen important new developments in the polyols for PU, especially polyols from renewable resources (which are described in detail this volume).

In a similar manner to polyols for elastic PU, irrespective of their structure, polyols for rigid PU have common characteristics:

- All oligo-polyols have terminal hydroxyl groups;
- All oligo-polyols have functionality (definite number of hydroxyl groups/mol);
- All oligo-polyols have primary or secondary hydroxyl groups but not tertiary hydroxyl groups;
- All oligo-polyols are low-molecular weight (MW) polymers (molecular weight of in oligomers = 400–1,000 Da);

- All oligo-polyols are characterised by identical physico-chemical characteristics determined by identical analytical methods;
- Transformation of oligo-polyols in PU is based on a reactive process (formation of high-MW PU is a consequence of a chemical process);
- Most oligo-polyols are liquid or very-low-melting-point solids and, due to their low viscosities (much lower than those of melted polymers), are very easy and economical to process to form high-MW PU; and
- A common characteristic of oligo polyols for PU is renewable content (content of natural raw materials used to build their chemical architecture).

The synthesis of polyols from renewable resources is a real hope for a sustainable future of PU.

I hope that this method of approaching use of oligo-polyols for making PU provides good understanding of the profound aspects of oligo-polyol chemistry, and to predict the relationships between the oligo-polyol structure and properties of the resulting PU. I also hope that this book fosters a starting point for creativity and to develop completely new, original oligo-polyol structures.

This book is addressed to students, researchers, scientists, engineers, as well as to all specialists in industry, universities, research centers and research institutes. I hope that this book will lead to improvements in existing technologies and to creation of new fabrication processes.

I express my gratitude, profound admiration and respect for the thousands and thousands of professors, specialists, experts, researchers, scientists from chemical companies, universities and research centers who, with their imagination, creativity and in-depth research, have played a decisive part in the development of polyol for PU.

The book is a *homage* to all the chemical companies who invested considerable human and material resources in the development of polyols for PU. This dynamic group of polymers has improved considerably the quality of human life.

Abbreviations

1,4-BD	1,4-Butanediol
AA	Adipic acid
AIBN	Azobisisobutyronitrile
ASTM	American Society for Testing and Materials
bp	Boiling point(s)
BPA	Bisphenol A
CNSL	Cashew nut shell liquid
CO_2	Carbon dioxide
CPL	ε-Caprolactone
DABCO	1,4-Diazabicyclo[2,2,2]octane
DEG	Diethylene glycol
DEOA	Diethanolamine
DETA	Diethylenetriamine
DMC	Double metal cyanide
DMF	Dimethylformamide
DMPP	Dimethyl methyl phosphonate
DMSO	Dimethylsulfoxide
DMT	Dimethyl terephthalate

DPG	Dipropylene glycol
EDA	Ethylenediamine
EG	Ethylene glycol
EMO	Epoxidised methyl oleate
EO	Ethylene oxide
EW	Equivalent weight
f_e	Equivalent functionality(ies)
GHG	Greenhouse gas(es)
GWP	Global warming potential
HD	1,6-Hexanediol
HDPE	High-density polyethylene
HE-OXA	1,3-*N*-hydroxyethyl oxazolidine
HI	Hydroiodic acid
HQEE	Hydroquinone di(β-hydroxyethyl) ether
IV	Iodine value
KOH	Potassium hydroxide
LiOH	Lithium hydroxide
MA	Maleic anhydride
M_c	Branching point(s)
MDA	4,4′-Methylenedianiline
MDI	Diphenylmethane diisocyanate
M_n	Number average molecular weight
mp	Melting point(s)

MW	Molecular weight(s)
Mw	Weight average molecular weight
NaOH	Sodium hydroxide
NMP	*N*-methyl pyrrolidone
NP	Nonylphenol
O_2	Oxygen
O_3	Ozone
ODP	Ozone depletion potential
OH#	Hydroxyl number(s)
o-TDA	*Ortho*-toluene diamine
OXA	Oxazolidine
PA	Polyamide(s)
PC	Polycarbonate(s)
PCL	Polycaprolactone
PDI	Polydispersity index
PE	Polyethylene
PER	Pentaerythritol
PET	Polyethylene terephthalate
PGL	Polyglycerol
PIR	Polyisocyanurate
PO	Propylene oxide(s)
PPG	Polypropylene glycol(s)
PTHF	Polytetrahydrofuran

PTMG	Polytetramethylene glycol(s)
PU	Polyurethane(s)
PUF	Polyurethane foam(s)
RIM	Reaction injection moulding
ROP	Ring-opening polymerisation
RT	Room temperature
TCBO	Trichlorobutylene oxide
TCEP	*Tris*(2-chloroethyl)phosphate
TCPP	*Tris*(2-chloropropyl)phosphate
TDI	Toluene diisocyanate
TEOA	Triethanolamine
T_g	Glass transition temperature
THEI	*Tris*(hydroxyethyl)isocyanurate
THF	Tetrahydrofuran
TMG	Tetramethylguanidine
TMP	Trimethylolpropane
UV	Ultraviolet

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Polyurethanes (PU) have become one of the most dynamic groups of polymers. They find use in nearly every aspect of daily life in applications such as: furniture; bedding, seating and instrument panels for cars, shoe soles, thermoinsulation, carpet backings, packaging, adhesives, sealants, binders, and as coatings.

Main raw materials used for PU production are polyols and isocyanates. The former are the subject of this handbook in two volumes:

- **Volume 1** is dedicated to polyols for elastic PU (flexible foams, elastomers)
- **Volume 2** is dedicated to polyols for rigid PU (rigid foams, wood substitute, packaging, flotation materials)

This book considers the raw materials used to build the architecture of PU polymers. It covers the: chemistry and technology of oligo-polyol fabrication; characteristics of the various oligo-polyol families; effects of oligo-polyol structure on the properties of the resulting PU. It presents the details of oligo-polyol synthesis, and explains the chemical and physico-chemical subtleties of oligo-polyol fabrication.

This book in two volumes attempts to link data and information concerning the chemistry and technology of oligo-polyols for PU to provide a comprehensive overview of:

- Basic PU chemistry
- Key characteristics of oligo-polyols
- Synthesis of the main oligo-polyol families (polyether polyols, filled polyether polyols, polyester polyols, polybutadiene polyols, acrylic polyols, polysiloxane polyols, aminic polyols)
- Polyols from renewable resources
- Flame-retardant polyols
- Chemical recovery of polyols
- Relationships between the structure and properties of PU

This book will be of interest to all specialists working with polyols for PU manufacture, and to all researchers wishing to know more about polyol chemistry.

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