Reaction of glycidyl ethers with aliphatic alcohols in the presence of benzyl dimethylamine

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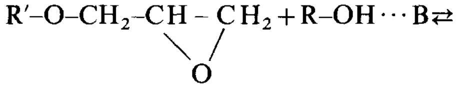
In the reaction of phenyl glycidyl ether with aliphatic alcohols in the presence of benzyl dimethylamine, four different oligomers are found at temperatures above 100°C. In the temperature range of 100–180°C, the length of oligomer chains decreases with increasing temperature. In bifunctional epoxide–alcohol systems the number of branched products increases simultaneously. These small branched oligomers are terminated by non-reactive end groups, preventing network formation above 140°C. At lower temperatures ($<60°C$), the proportion of the addition mechanism exceeds 90%, alternating with a combined mechanism including the homopolymerization of glycidyl ether at 100°C. This mechanism yields the fastest gel times in corresponding bifunctional epoxide–alcohol systems. Above 100°C, gel times decrease again owing to hindered crosslinking in an oligomeric system with short, branched and non-reactive products.

(Keywords: glycidyl ethers; alcohols; acceleration; model reaction; h.p.l.c.; oligomers; viscometry; network)

INTRODUCTION

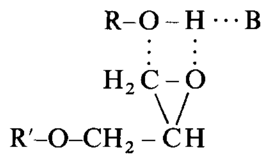
The reaction between epoxides and proton donors, e.g. water or alcohols, can be accelerated by tertiary amines. The reaction mechanism has been established by several authors and can be summarized by equations (1)–(4)[1–6]:

$$\mathrm{R{-}OH+B \rightleftarrows R{-}OH\cdots B} \tag{1}$$



$$\mathrm{R'{-}O{-}CH_2{-}\underbrace{CH{-}CH_2}_{O}+R{-}OH\cdots B \rightleftarrows}$$

1



$$\begin{array}{c}\mathrm{R{-}O{-}H\cdots B}\\ \vdots\quad\vdots\\ \mathrm{H_2C{-}O}\\ \diagdown\diagup\\ \mathrm{R'{-}O{-}CH_2{-}CH}\end{array} \tag{2}$$

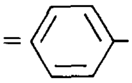
2

$$2\xrightarrow{k_1}\mathrm{R'{-}O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}OR+B} \tag{3}$$

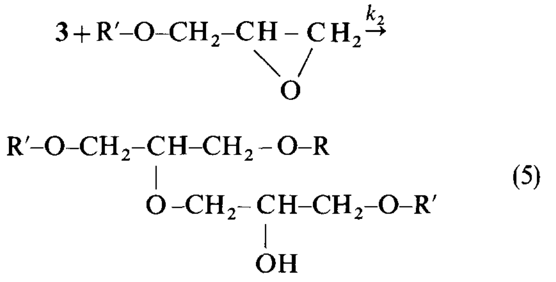
3

$$2\xrightarrow{k_1'}\mathrm{R'{-}O{-}CH_2{-}\underset{\displaystyle OR}{\underset{|}{CH}}{-}CH_2{-}OH+B} \tag{4}$$

4

$\mathrm{R=C}_n\mathrm{H}_{2n+1}$ R' =  B = base

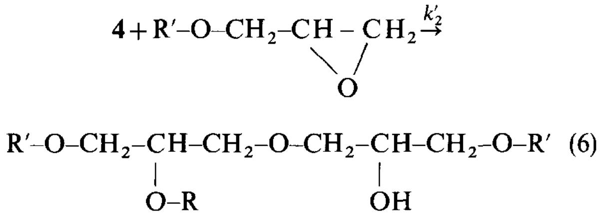
The ratio of **3** and **4** depends on the amount of accelerator, the ratio of epoxide to alcohol, the type and amount of the solvent and the reaction temperature[7,8]. 1-Phenoxy-2,3-epoxypropane (PGE) was used as epoxide model compound. The reaction of **3** and **4** with PGE leads to **6** and **7** according to equations (5) and (6):



$$3+\mathrm{R'{-}O{-}CH_2{-}\underbrace{CH{-}CH_2}_{O}}\xrightarrow{k_2}$$

$$\begin{array}{l}\mathrm{R'{-}O{-}CH_2{-}CH{-}CH_2{-}O{-}R}\\ \qquad\quad |\\ \qquad\quad \mathrm{O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}O{-}R'}\end{array} \tag{5}$$

6



$$4+\mathrm{R'{-}O{-}CH_2{-}\underbrace{CH{-}CH_2}_{O}}\xrightarrow{k_2'}$$

$$\mathrm{R'{-}O{-}CH_2{-}\underset{\displaystyle O{-}R}{\underset{|}{CH}}{-}CH_2{-}O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}O{-}R'} \tag{6}$$

7

For the reaction of **3** and **4** with PGE, the 'anomalous' ring-opening reactions at the least hindered carbon atom of the oxirane ring were not considered, because in most reactions of glycidyl ethers with aliphatic alcohols their concentration in the other reaction products is negligible.

The sum of the rate ratios k_1/k_2 and k_1'/k_2' (equation (7)) serves as a relative selectivity index for the extent of

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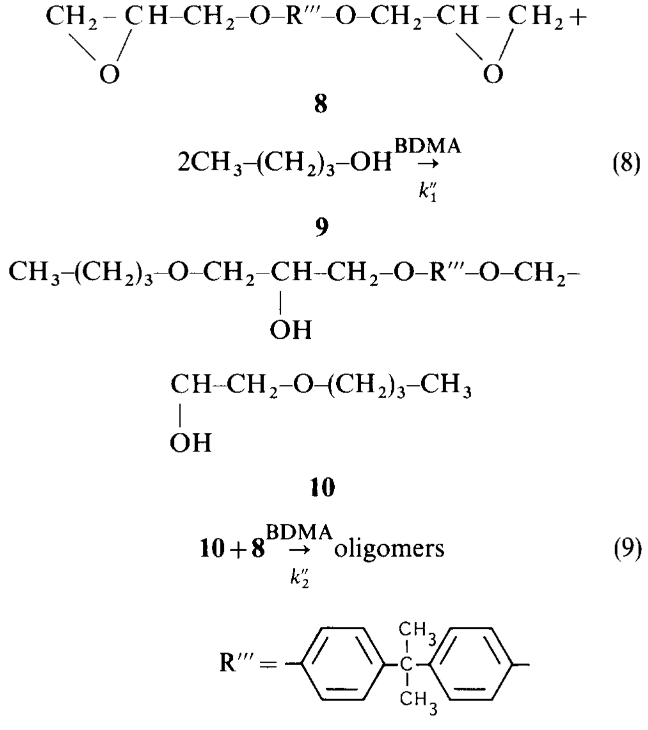
linear and branched step-growth reactions in bifunctional epoxide–alcohol systems.

$$S_i = k_1/k_2 + k_1'/k_2' \qquad (7)$$

where S_i = selectivity index. This is based on the assumption of equal reactivities of reactive groups in monofunctional model compounds and in multifunctional reactions in the pre-gel state at elevated temperatures. S_i may be used to compare the reactions of glycidyl ethers and aliphatic alcohols under various reaction conditions. The result should provide an idea of the behaviour in crosslinkable systems in which the measurement of single reactions is highly complicated. If k_1'/k_2' is negligible, the marginal cases are $k_1 \rightarrow 0$ (branching reaction of secondary hydroxyl groups) and $k_2 \rightarrow 0$ (linear products by reaction of primary hydroxyl groups).

Several workers[9-12] have investigated the branching reactions in epoxide systems. In most of these, phenols were used as hydroxyl compounds. Phenols possess higher acidity than aliphatic hydroxyl compounds, which leads to the formation of linear chains if bifunctional reactants (diglycidyl ether + bisphenols) are used.

Previous investigations of glycidyl ether–alcohol reactions in the presence of tertiary amines showed that only products of type **3** and **6** are formed[13]. It was found that the ratio S_i depends on the reaction temperature using a model system according to equations (8) and (9)[14]:



$$\underset{\diagdown O \diagup}{CH_2\text{-}CH}\text{-}CH_2\text{-}O\text{-}R'''\text{-}O\text{-}CH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} +$$

8

$$2CH_3\text{-}(CH_2)_3\text{-}OH \underset{k_1''}{\overset{BDMA}{\rightarrow}} \qquad (8)$$

9

$$CH_3\text{-}(CH_2)_3\text{-}O\text{-}CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_2\text{-}O\text{-}R'''\text{-}O\text{-}CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_2\text{-}O\text{-}(CH_2)_3\text{-}CH_3$$

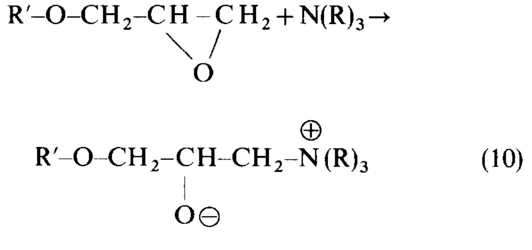
10

$$\mathbf{10} + \mathbf{8} \underset{k_2''}{\overset{BDMA}{\rightarrow}} \text{oligomers} \qquad (9)$$

$R''' =$

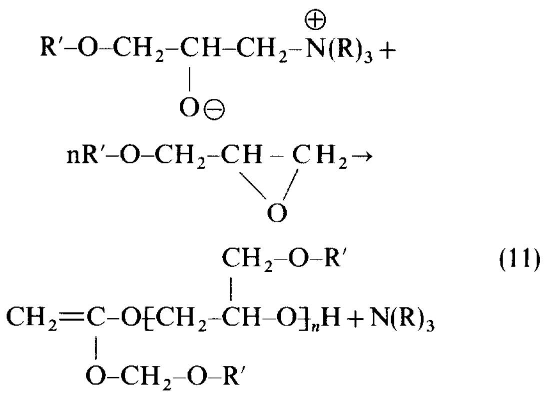
where BDMA = benzyl dimethylamine and $k_1''/k_2'' = 7.4$ (60°C) and 3.4 (100°C).

The homopolymerization induced by tertiary amines is a well known reaction[1-6]:



$$R'\text{-}O\text{-}CH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} + N(R)_3 \rightarrow$$

$$R'\text{-}O\text{-}CH_2\text{-}\underset{O^{\ominus}}{\underset{|}{CH}}\text{-}CH_2\text{-}\overset{\oplus}{N}(R)_3 \qquad (10)$$



$$R'\text{-}O\text{-}CH_2\text{-}\underset{O^{\ominus}}{\underset{|}{CH}}\text{-}CH_2\text{-}\overset{\oplus}{N}(R)_3 + nR'\text{-}O\text{-}CH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \rightarrow$$

$$CH_2{=}\underset{O\text{-}CH_2\text{-}O\text{-}R'}{\underset{|}{C}}\text{-}O[CH_2\text{-}\overset{CH_2\text{-}O\text{-}R'}{\overset{|}{CH}}\text{-}O]_nH + N(R)_3 \qquad (11)$$

The production of corresponding products can be expected in the same reaction systems.

The purpose of this work is to investigate the reaction behaviour of diglycidyl ether–aliphatic diol systems above 100°C as a function of reaction temperature. It can be assumed that highly branched systems are formed owing to the small difference in the acidity of aliphatic compounds with primary and secondary hydroxyl groups. The ratio of k_1''/k_2'' in model systems is < 10 and it decreases with increasing temperature.

RESULTS AND DISCUSSION

Reaction of PGE with 1-decanol in the presence of BDMA

The reaction of PGE with aliphatic alcohols proceeds via a pseudo-bimolecular mechanism at temperatures above 100°C[15]. Up to 180°C, the rate of epoxide consumption decreases with increasing temperature (*Figure 1*).

Investigations by high performance liquid chromatography (h.p.l.c.) showed that the product composition and the chain length of the oligomers change depending on the temperature (*Figure 2*, *Table 1*). Four different oligomers were found, among them the main products of the homo-oligomerization of PGE (type A) and the products of the oligo-addition reaction between PGE and 1-decanol (type B(De)). The molar ratio of type A to type B(De) oligomers increases with increase of the reaction temperature (*Figure 3*). The reason for this change can be assumed to be the decrease of the concentration of

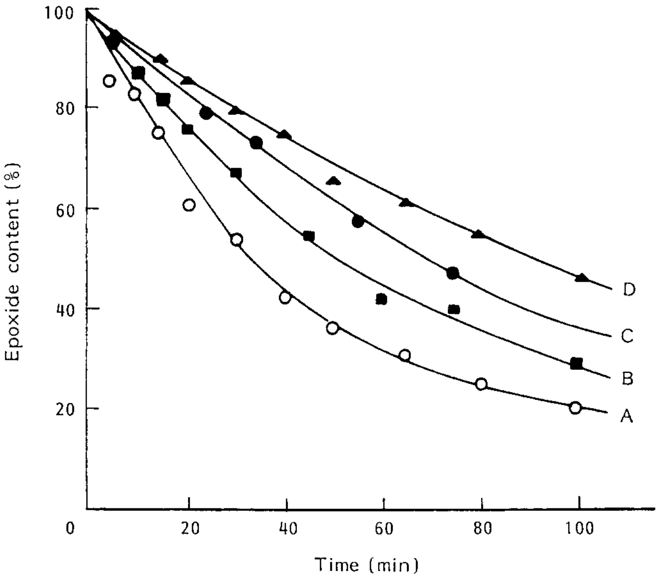


Figure 1 Epoxide conversion in the system PGE: 1-decanol: BDMA with molar ratio 1:1:0.05. A, 120°C; B, 140°C; C, 160°C; D, 180°C

final products according to equations (1) and (2) due to the hindrance of hydrogen bonding at higher temperatures. Hence, the slower homo-oligomerization of PGE proceeds and a negative activation energy is measured by following the epoxide consumption.

Table 1 Number of structural segments *n* for oligomers of different types, depending on reaction temperature

T (°C)	*n* for oligomers of type A	B(De)	B(Ph)	C
60	5	4	–	3
100	4	3	1	3
180	3	2	1	2

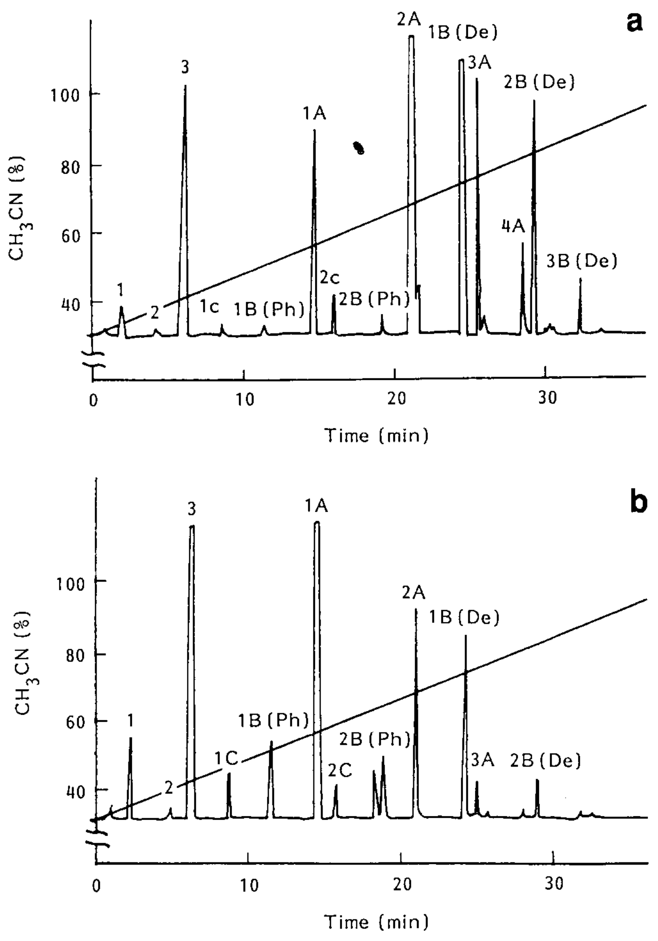
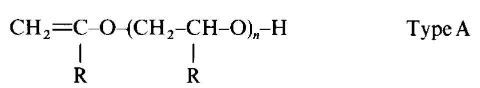
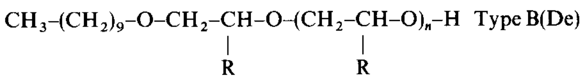


Figure 2 H.p.l.c. of reaction products in the system PGE: 1-decanol:BDMA with molar ratio 1:1:0.05. (a) 100°C; (b) 180°C. 1, 2, unknown; 3, PGE; 1A–4A, oligomers of the general formula **11**; 1B(De)–3B(De), oligomers of the general formula **12**; 1B(Ph)–2B(Ph), oligomers of the general formula **13**; 1C–3C, oligomers of the general formula **14**



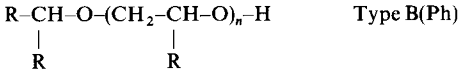
$$CH_2{=}\underset{R}{C}\text{-O-}(CH_2\text{-}\underset{R}{CH}\text{-O})_n\text{-H} \qquad \text{Type A}$$

11



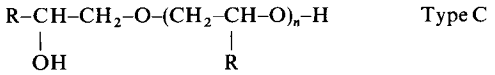
$$CH_3\text{-}(CH_2)_9\text{-O-}CH_2\text{-}\underset{R}{CH}\text{-O-}(CH_2\text{-}\underset{R}{CH}\text{-O})_n\text{-H} \qquad \text{Type B(De)}$$

12



$$R\text{-}\underset{R}{CH}\text{-O-}(CH_2\text{-}\underset{R}{CH}\text{-O})_n\text{-H} \qquad \text{Type B(Ph)}$$

13



$$R\text{-}\underset{OH}{CH}\text{-}CH_2\text{-O-}(CH_2\text{-}\underset{R}{CH}\text{-O})_n\text{-H} \qquad \text{Type C}$$

14

$R = \text{-}CH_2\text{-O-Ph}$

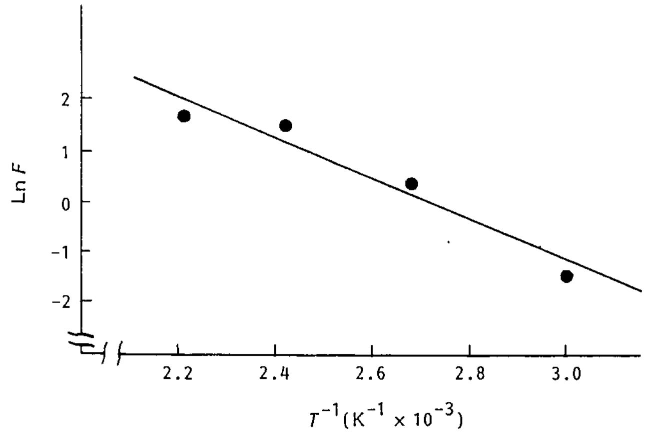
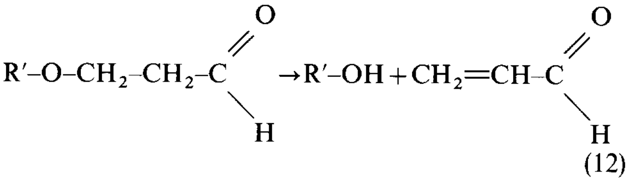
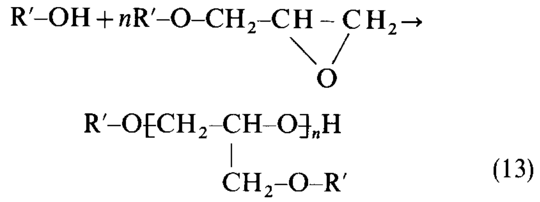


Figure 3 Ratio of type A to type B(De) oligomers (ln *F*) in dependence on the inverse reaction temperature. System PGE:1-decanol:BDMA with molar ratio 1:1:0.05

According to the Arrhenius law, the apparent activation energies are found to be $-25.6\,\text{kJ mol}^{-1}$ for the reaction of PGE with 1-hexanol and $-26.8\,\text{kJ mol}^{-1}$ with 1-decanol as hydroxyl compounds (accelerator: BDMA). Oligomers of type B result from the bond cleavage of the PGE isomerization product phenoxypropanal[16–18]:



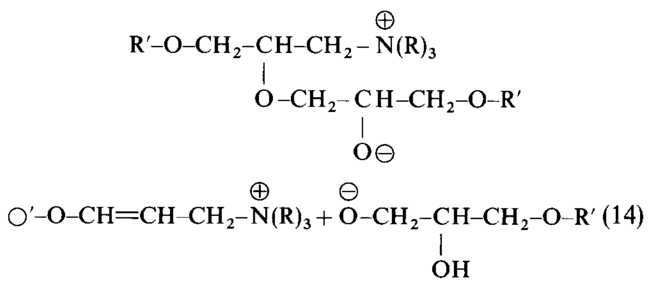
$$R'\text{-O-}CH_2\text{-}CH_2\text{-}C\overset{O}{\underset{H}{}} \rightarrow R'\text{-OH} + CH_2{=}CH\text{-}C\overset{O}{\underset{H}{}} \qquad (12)$$



$$R'\text{-OH} + nR'\text{-O-}CH_2\text{-}\underset{\diagdown O \diagup}{CH - CH_2} \rightarrow R'\text{-O}[CH_2\text{-}\underset{CH_2\text{-O-}R'}{CH}\text{-O}]_n\text{H} \qquad (13)$$

type B

It is difficult to determine the origin of type C-oligomers because they are formed even in the absence of water. One possible source is the hybrid ion from the reaction of glycidyl ethers with the tertiary amine:



$$\begin{array}{l} R'\text{-O-}CH_2\text{-}\underset{\substack{|\\ O\text{-}CH_2\text{-}\underset{O^\ominus}{CH}\text{-}CH_2\text{-O-}R'}}{CH}\text{-}CH_2\text{-}\overset{\oplus}{N}(R)_3 \\ O'\text{-O-}CH{=}CH\text{-}CH_2\text{-}\overset{\oplus}{N}(R)_3 + \overset{\ominus}{O}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-O-}R' \quad (14) \end{array}$$

15

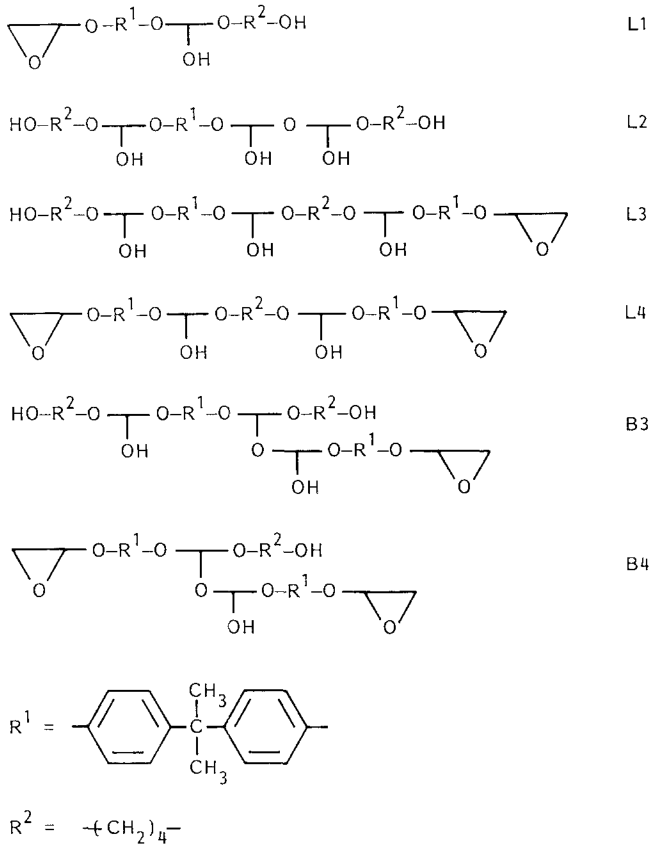
The source of the proton for chain termination is unknown and products according to structure **15** have not yet been detected.

Reaction of DGEBA with aliphatic diols in the presence of BDMA

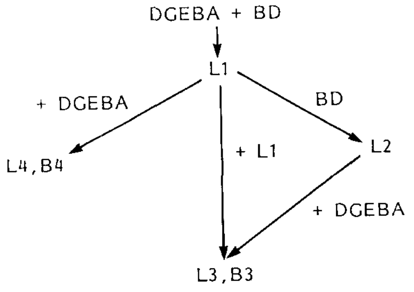
The reaction of PGE with 1-decanol was used as a model for the reaction of bifunctional compounds bisepoxide and diol. A comparable dependence of the reaction rate on time and temperature was measured using 2,2-bis[4-(2,3-epoxypropoxy)phenyl]propane (DGEBA) and 1,4-butanediol (BD) (*Figure 4*, compare with *Figure 1*). The activation energy was found to be $-29.4\,\mathrm{kJ\,mol^{-1}}$.

According to model reactions at 60°C, mainly oligomers of the addition reaction between DGEBA and diol are formed. The reason for the induction period up to 15% conversion of the epoxide is probably the formation of the active species (equations (1) and (2)).

Product distribution was determined by h.p.l.c. In all cases linear (L) and branched (B) oligomers of type B(Bu) are formed (L1–L4, B3, B4; see *Scheme 1*). A branched product with the molar mass of L2 was not observed. The concentration of branched oligomers increases in the temperature range of 100–180°C. The reactions at 60°C can be summarized as in *Scheme 2*. For epoxide conversions over 60%, the number of branched products increases considerably with conversion, and gelation occurs. In this region it is impossible to follow the change of product distribution by h.p.l.c.



Scheme 1



Scheme 2

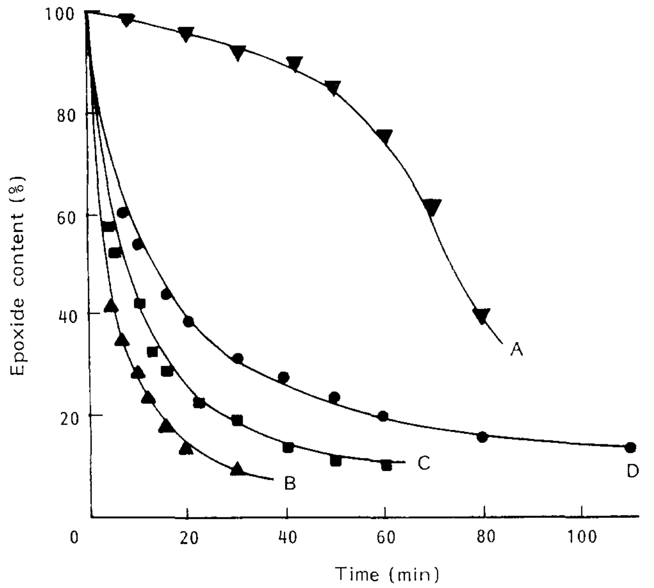


Figure 4 Epoxide conversion in the system DGEBA:BD:BDMA with molar ratio 1:1:0.03. A, 60°C; B, 100°C; C, 140°C; D, 180°C

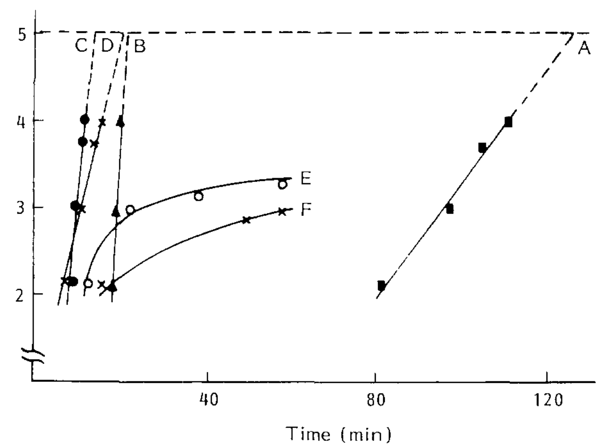


Figure 5 Plots of lg η against reaction time for the system DGEBA:BD:BDMA with molar ratio 1:1:0.05. A, 60°C; B, 80°C; C, 100°C; D, 120°C; E, 140°C; F, 160°C; ---, apparent gel time according to the literature[20,21]

Another approach to the extent of branching reactions near the gel point can be drawn from size exclusion chromatography (s.e.c.)[19]. The use of tetrahydrofuran as eluent allows the course of the reaction to be followed up to 66% epoxide conversion. At this point the polydispersity is 1.93. At 70% epoxide conversion a fraction of the reaction mixture becomes insoluble in acetone. This fraction gives the following s.e.c. data: $M_w = 9040\,\mathrm{g\,mol^{-1}}$, $M_n = 1336\,\mathrm{g\,mol^{-1}}$. The polydispersity is 6.77, indicating that the system is approaching gelation.

A correlation between the structure of compounds and the crosslinking behaviour was shown by viscometric methods.

Viscometry

The system DGEBA:BD:BDMA with molar ratio 1:1:0.05 exhibits a strong dependence of viscosity on temperature (*Figure 5*). The following conclusions can be

Table 2 Apparent gel times in the system DGEBA:BD:BDMA with different contents of BD, in relation to temperature

T	Apparent gel time (min) for DGEBA:BD:BDMA	
(°C)	1:0.25:0.05	1:1:0.05
60	63	129
80	23	22
100	22	14
120	29	20
140	57	–

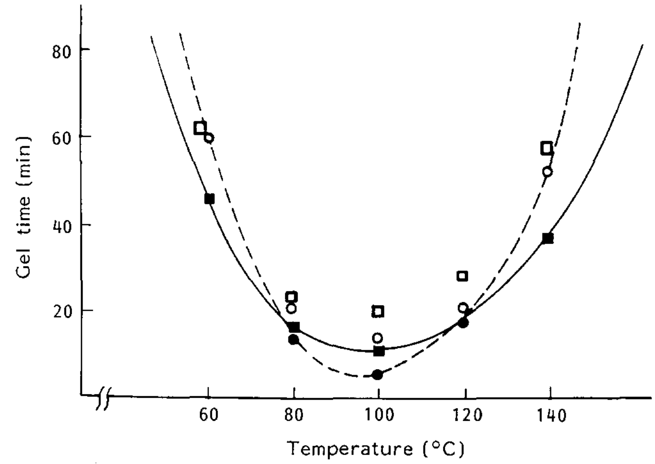


Figure 6 Dependence of gel time on the reaction temperature. Molar ratio of DGEBA:BD:BDMA: ■, 1:0.25:0.05 (experimental values); ●, 1:1:0.05 (experimental values); □, 1:0.25:0.05 (theoretical values); ○, 1:1:0.05 (theoretical values)

drawn from these measurements:

1. There is a considerable difference in the increase of the viscosities at 60, 80, 120 and 140°C.
2. At 140 and 160°C markedly non-linear plots were measured. A gel point cannot be observed, indicating the lack of network-forming products.

The linear extrapolation of log viscosity *versus* time to 10^5 mPa s gives apparent gel times according to the literature[20,21] (*Table 2*) in the case of the four linear plots. Experimental measurements of gel times give slightly lower values compared with the apparent gel times of *Table 2* (*Figure 6*). The differences are due to the method used (see Experimental section). Since the apparent gel times are too high, a real viscosity of 5×10^5 mPa s must be assumed just before the gel point is reached.

The course of the gel points over the reaction temperature confirms the reaction mechanism described above. The reason for the increase of gel time with increasing temperature has already been mentioned as being a decrease of the concentration of final products in equations (1) and (2), and a preferred slower homo-oligomerization reaction at higher temperatures (>100°C). Nevertheless, a network formation should be expected even from pure homopolymeric products. But the decrease of gel times above 100°C and the lack of gelation above 140°C indicates an increase in concentration of short and branched oligomers without network-forming properties. These compounds will be terminated by an excess of glycidyl groups before gelation occurs. The result is a mixture of branched oligomers with non-reactive chain ends.

CONCLUSIONS

Glycidyl ethers react with alcohols in the presence of BDMA to form different types of oligomers. At temperatures above 100°C the chain length of these oligomers decreases. They are terminated with –OH and $=CH_2$ groups before the gel point can be reached. Thus, a network formation of bisglycidyl monomers and aliphatic diols (25–100 mol%) in the presence of 5 mol% BDMA is impossible at temperatures above 140°C.

EXPERIMENTAL

Chemicals

2,2-Bis[4-(2,3-epoxypropoxy)phenyl]propane (DGEBA) was received as Epilox A 17-01 from Leuna-Werke AG and recrystallized from acetone–methanol (m.p. 42°C). 1-Phenoxy-2,3-epoxypropane (PGE) (Fluka), 1-decanol (Merck), benzyl dimethylamine (BDMA) (Leuna-Werke AG) and 1,4-butanediol (BD) (VEB Synthesewerk Schwarzheide) are commercially available products and were purified according to the literature[22].

Reactions

The reactants were mixed in a thermoregulated glass reactor equipped with mechanical stirrer and thermometer. At various time intervals aliquots were removed and stored at −70°C until analytical procedures could be performed. The composition of the reaction mixtures and the analysis temperatures are reported in the text.

Measurements

The epoxy content was determined by a direct method with perchloric acid in acetic acid/tetraethylammonium bromide; the indicator was crystal violet[23]. H.p.l.c. was carried out with an apparatus from Knauer Wissenschaftliche Geräte KG (Germany); column 250×4 mm, LiChrosorb RP-18, 5 μm; solvent gradient from 30 to 99% CH_3CN in water in 40 min; u.v. detection, $\lambda = 254$ nm. Identification of oligomeric products: separation by means of preparative h.p.l.c. and identification by mass spectrometry and spectroscopic methods[13,24].

Viscometry

A 12 V motor was equipped with a mechanical stirrer. The motor acts as part of a Wheatstone bridge giving an increase in current if the rotation of the stirrer is hindered. This increase was calibrated by standard samples with defined viscosities. The curves were drawn by a recorder. Aliquots of 2–5 g were poured into a glass beaker to measure the viscosity–time dependence.

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