Curing of glycidyl ethers with aromatic amines: model studies on the effects of tertiary amines as accelerators

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The effect of *N*,*N*-dimethylbenzylamine on the reaction of glycidyl ethers with primary aromatic amines has been investigated using diglycidyl ether of bisphenol A and 4,4′-diaminodiphenylmethane. With the help of model reactions of phenyl glycidyl ether and aniline, etherification and homopolymerization were found to interfere with the epoxy–amine reaction. Products arising from etherification were identified.

(**Keywords: glycidyl ether; aromatic amine; curing; accelerator; etherification; high-performance liquid chromatography; ^{13}C nuclear magnetic resonance**)

INTRODUCTION

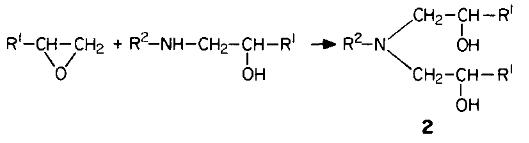
The crosslinking reaction of epoxy resins usually requires special accelerating or initiating agents. Many different types of accelerators are used, leading to highly developed techniques in epoxy resin crosslinking and processing. Tertiary amines, which accelerate the epoxy ring opening for polyaddition curing with carbon acid anhydrides and aromatic amines, are widely used. It is also well known that tertiary amines initiate the polymerization of oxiranes by an anionic mechanism. Nevertheless, there are still some questions to be answered concerning the chemical interpretation of the reactions and mechanisms that occur in the complex system consisting of epoxy/primary aromatic amine/tertiary amine, and their influence on the network structure and properties.

However, chemical analysis of the network structure is limited by the insolubility of the products that arise. For this reason we have investigated the reaction of phenyl glycidyl ether (PGE) with aniline in the absence and in the presence of *N*,*N*-dimethylbenzylamine (DMBA) as a model for the diepoxy/diamine system by high-performance liquid chromatography (h.p.l.c.), Fourier-transform infra-red (*FT*i.r.) spectroscopy and ^{13}C nuclear magnetic resonance (n.m.r.).

The reactions that occur during the curing of glycidyl ethers with primary aromatic amines have already been described by several authors[1–3]. Dušek *et al.*[4] have assumed that only the following reactions take place:


(1)

1


(2)

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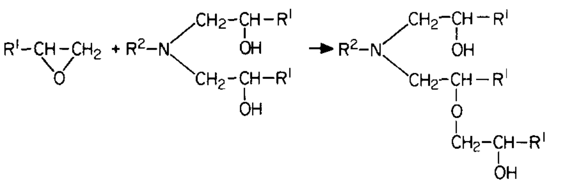
The further reaction between the secondary hydroxylic groups in the products according to equations (1) and (2) and the oxirane group must also be taken into account:


(3)

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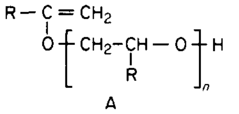
Reviews on this subject have been presented by Lee and Neville[5] and May and Tanaka[6], and the only conclusions that can be drawn are that the extent to which the etherification takes place depends on the particular systems under consideration, and that it cannot always be ignored.

Attention was also paid to the oligomerization reactions of the oxirane ring in the presence of tertiary amines such as DMBA[1,7,8]. There are three different types of oligomers[8]: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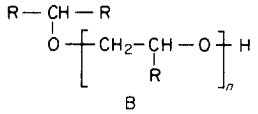
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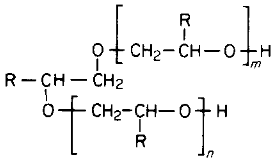
C

Rozenberg[1] and Mutin[9] have shown by kinetic investigations that the acceleration of the reaction observed in the systems of epoxides with primary and tertiary amines is connected with the acceleration of these

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oligomerization reactions. Grenier-Loustalot *et al.*[10] also determined by means of chemical data on ^{13}C n.m.r. and h.p.l.c. that oligomerization and the reaction of hydroxylic groups with the epoxy groups represent a significant part of the complex reaction system consisting of epoxy/primary aromatic amine/tertiary amine. We tried to explain these reactions and to determine the structures arising in the network.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA; Leuna AG) was purified by recrystallization from acetone/methanol (m.p. 42°C) and 4,4′-diaminodiphenylmethane (DDM; Merck-Schuchardt) by recrystallization from ethanol/water. Phenyl glycidyl ether (PGE) was prepared according to ref. 11 (b.p. 96–98°C/0.4 kPa). Aniline was distilled under reduced pressure. *N*,*N*-Dimethylbenzylamine (DMBA) was dried with KOH pellets, purified by the addition of small amounts of phenyl isocyanate and distilled under reduced pressure (b.p. 55–56°C/1.2 kPa). Imidazole was commercially available and was used without further purification.

Sample preparation

DGEBA and DDM were mixed in an equimolar epoxy/amine ratio at 80°C. The accelerator concentration was measured in terms of the epoxy group. The samples were cured for 5 h at 120°C in an oil bath.

The reactions between PGE and aniline were carried out in a thermostated three-necked flask equipped with a thermometer, a magnetic stirrer and a reflux condenser.

Separation of products

The monoadduct of the PGE/aniline reaction was obtained through the reaction of the system PGE/aniline = 1/10 mol for 2 h at 80°C. Aniline was redistilled under reduced pressure. The product was recrystallized from hexane/ether (needles, m.p. 58°C). Analysis: calculated for $C_{15}H_{17}O_2N$, N = 5.8; found, N = 6.2.

The diadduct of the PGE/aniline reaction was obtained from the system PGE/aniline = 4/1 mol, which was reacted at 120°C for 7.5 h. It was then recrystallized from methanol/water (amorphous, m.p. 72–77°C). Using preparative h.p.l.c., both stereoisomeric forms of the diadduct (**8**) were separated and precipitated in water. One form exists in needles (m.p. 83–84°C) and the other form exhibits plates (m.p. 92–93°C).

The etherification product from the diadduct (**9**) was also separated with preparative h.p.l.c. from the system consisting of PGE/aniline = 4/1 mol + 1 mol% imidazole per epoxy group, which was reacted at 140°C. It was recrystallized from acetone (needles, m.p. 119–120°C). Analysis: calculated for $C_{33}H_{37}O_6N$, N = 2.6; found, N = 2.4.

Analyses: calculated for (**5**) $C_{24}H_{27}O_4N$, N = 3.6, found, N = 3.7; for (**6**) $C_{33}H_{37}O_6N$, N = 2.6, found, N = 2.7; for (**7**) $C_{42}H_{47}O_8N$, N = 2.0, found, N = 2.3.

Techniques

H.p.l.c. was performed with a Knauer apparatus (Wissenschaftliche Geräte KG): column, 180 × 3.2 mm (anal.) or 180 × 16 mm (prep.) with LiChrosorb RP-18, 5 m; eluant, acetonitrile/water 30/70 to 100/0 linear; flow, 1.8 ml min^{-1}; detection, u.v. 254 nm; samples, 5% solution (anal.) or 50% solution (prep.) in acetonitrile.

^{13}C n.m.r. spectra were determined on a Bruker HX90R spectrometer operating at a frequency of 22.635 MHz using chloroform-d.

I.r. spectra were measured with a Nicolet FTIR spectrometer 205. Samples were prepared in chloroform (0.1 mm). The conversion was followed by an evaluation of the ratio of the i.r. absorption of epoxy groups at 917 cm^{-1} and of the aromatic structure at 1601 cm^{-1}.

Differential scanning calorimetry (d.s.c.) was carried out with a Perkin-Elmer DSC 7 apparatus. For measuring the uniaxial compression modulus, we used the apparatus described in refs 12 and 13.

RESULTS AND DISCUSSION

In order to examine the effect of tertiary amines on the network properties, we determined the glass transition temperature of networks of DGEBA and DDM prepared with an equimolar epoxy/amine ratio without an accelerator and in the presence of different amounts of DMBA. D.s.c. and uniaxial compression modulus measurements were used. *Figure 1* shows that, in the presence of the accelerator, the glass transition temperature T_g is smaller than without DMBA. In the investigated range of accelerator concentration, T_g decreases linearly.

From these results we assume that, by the use of the tertiary amine, new structures were formed that contain longer and more flexible chain segments leading to a decrease in T_g. The same effect was found using imidazole as an accelerator[14].

We contribute to this structure–property phenomenon by the determination of structures using the PGE/aniline/DMBA model system. The reaction was followed over a temperature range of 70 to 120°C.

Without an accelerator, only the monoadduct (**1**) and the diadduct (**2**) of the PGE/aniline reaction arise. In accordance with the results of Grenier-Loustalot *et al.*[15], the diadduct was found in two diastereoisomeric forms by h.p.l.c. We succeeded in separating these diastereoisomers by using preparative h.p.l.c. The characterization of these compounds was followed by ^{13}C n.m.r., elemental analysis and *FT*i.r.

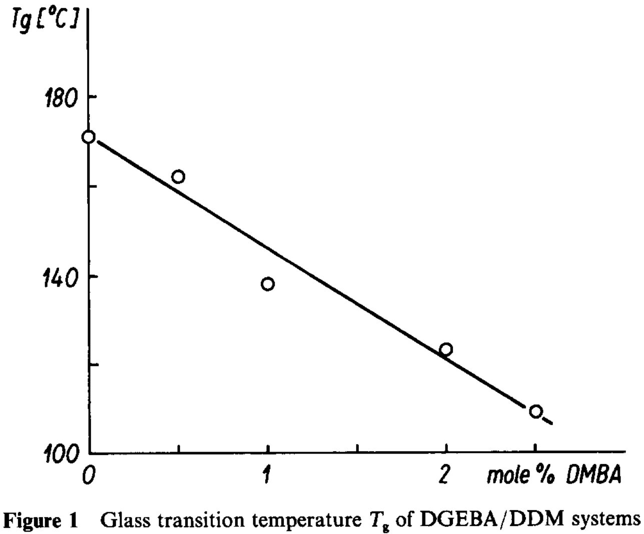


Figure 1 Glass transition temperature T_g of DGEBA/DDM systems as a function of the concentration of DMBA

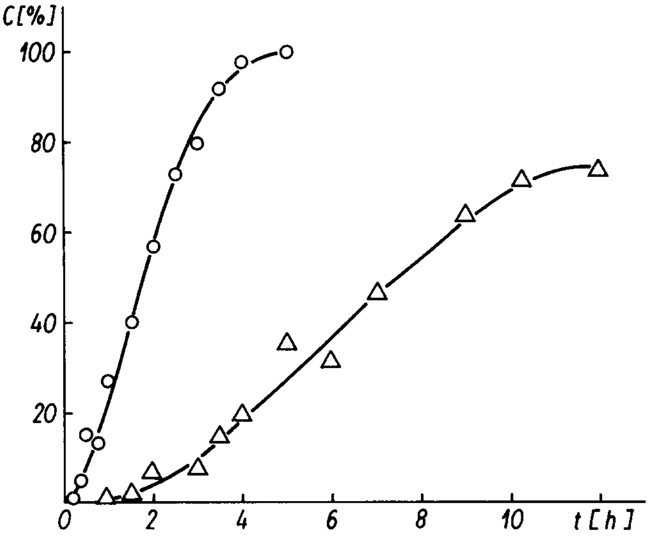


Figure 2 Kinetic curves of the conversion *C* of PGE in the reaction with aniline (epoxy/amine hydrogen = 1/1 mol) in the absence (△) and in the presence of 4 mol% DMBA per epoxy group (○), *T* = 70°C

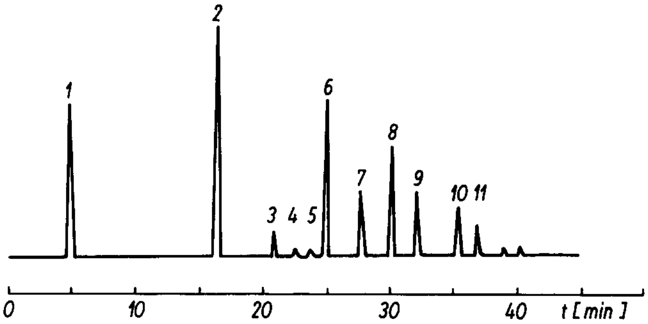


Figure 3 H.p.l.c. chromatogram of the PGE/aniline reaction (epoxy/amine hydrogen = 1/1 mol) in the presence of 4 mol% DMBA per epoxy group, *T* = 70°C, *t* = 600 min. Peaks: 1, aniline; 2, monoadduct **4**; 4, 5, diastereoisomeric forms of the diadduct **8**, **8'**; 3, 7, 9, 11, products of the oligomerization of PGE; 6, 8, 10, etherification products **5**, **6**, **7**

In the reactions, which take place according to equations (1) and (2), secondary hydroxylic groups arise, which are able to catalyse the opening of the epoxide ring by a primary amine hydrogen[16]. This autocatalytic effect is the reason for the induction period visible in *Figure 2* for the non-catalytic reaction. In the presence of DMBA, the conversion of epoxide groups is much faster.

In the h.p.l.c. chromatogram of the reaction with DMBA at a relatively low temperature (70°C), it may be noted that not all the aniline has reacted (*Figure 3*). The diadduct from the addition of PGE and aniline only arises in a very small amount.

From the investigations of the PGE/DMBA system at this temperature, we can assume that peaks 3, 7, 9 and 11 are connected with structures formed by the oligomerization of PGE corresponding with types A, B and C. The three unknown compounds (peaks 6, 8 and 10) were separated by using preparative h.p.l.c., and they were identified as products of the etherification of the monoadduct of the PGE/aniline reaction by elemental analysis, ^{13}C n.m.r. and *FT*i.r. investigation.

In the *FT*i.r. spectra of these products, a new band appears at 1134 cm^{-1}, which can be attributed to the presence of the aliphatic ether structure (*Figure 4*).

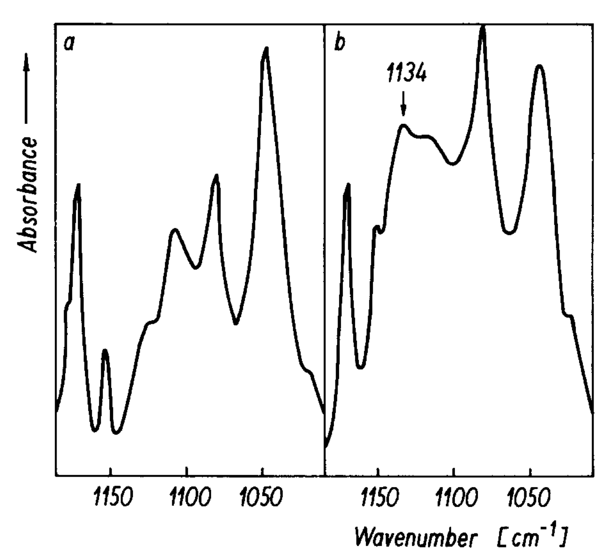


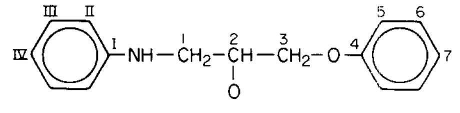
Figure 4 Sections from the *FT*i.r. spectra of (a) the monoadduct **4** and (b) the etherification product **7**

Table 1 ^{13}C chemical shifts observed of the monoadduct **4** and the etherification products **5**, **6** and **7**

	Compounds				
Carbons	**4**[15]	**4**	**5**	**6**	**7**
1	48.3	46.7	45.3	45.2	45.3
1'	–	–	71.7	67.7	67.8
1''	–	–	–	71.9	67.8
1'''	–	–	–	–	72.2
2	69.9	68.8	78.0	78.0	77.8
2'	–	–	68.7	70.4	70.5
2''	–	–	–	68.6	70.5
2'''	–	–	–	–	68.7
3	71.9	70.1	69.4	69.4	69.4
3'	–	–	69.4	69.4	69.4
3''	–	–	–	69.4	69.4
3'''	–	–	–	–	69.4
4, 4', 4'', 4'''	160.1	158.4	158.5	158.6	158.6
5, 5', 5'', 5'''	116.3	114.6	114.6	114.7	114.7
6, 6', 6'', 6'''	130.6	129.5	129.5	129.5	129.5
7, 7', 7'', 7'''	122.2	121.2	121.2	121.1	121.1
I	149.8	148.0	148.0	148.0	148.1
II	114.5	113.3	113.3	113.3	113.3
III	130.3	129.3	129.3	129.3	129.5
IV	118.5	118.0	118.0	117.9	117.7

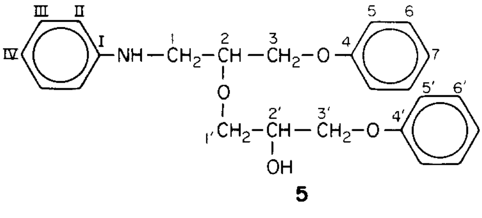
In evaluating the ^{13}C n.m.r. spectra obtained from these samples (*Table 1*), the following structures could be determined:

monoadduct of the PGE/aniline reaction



4

products of etherification



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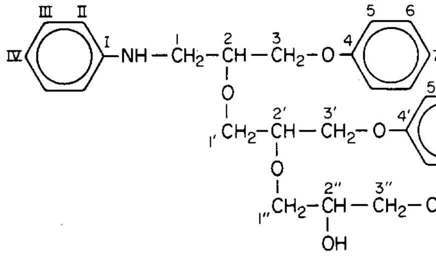

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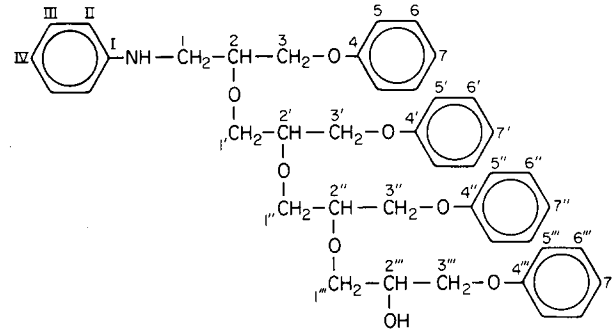


7

New signals are visible at 71.7–72.2 and 67.8 ppm comparing the spectra obtained with the monoadduct. They are due to the changed environments of the 1′, 1″ and 1‴ C atoms (*Table 1*). New signals for the 2, 2′ and 2″ C atoms at 70.5 and 78 ppm are also to be seen.

The diadduct from the PGE/aniline reaction only arises in very small amounts. We can assume that at a temperature of 70°C the reaction of the secondary hydroxylic group is preferred to the reaction of the secondary amine hydrogen.

The distribution of products of the same reaction system is very different at 120°C (*Figure 5*) compared with that at 70°C (*Figure 3*). At 120°C the diadduct of the PGE/aniline reaction (peaks 4 and 5) arises in higher amounts, but only the first product of etherification of the monoadduct (peak 6) and two peaks for the products of oligomerization (peaks 3 and 7) were found. Equal results were obtained with an accelerator concentration of 1 mol% DMBA. We can suppose that at this temperature more short chains were formed corresponding to more reactive centres[8]. But there is also another new peak 7. Because it was superimposed on a peak due to PGE oligomer of type A, we repeated this experiment by using imidazole as the accelerator. It is known that this accelerator catalyses the oligomerization of epoxides, forming only compounds from types B and C[17]. In this way the product corresponding to peak 7 was separated by using preparative h.p.l.c. and it could be isolated in its crystalline form. Identification was carried out by elemental analysis, *FT*i.r. and ^{13}C n.m.r. From analytical data we can conclude that peak 7 (*Figure 5*) contains an etherification product of both diastereoisomeric forms of the diadduct (**8**, **8′**):

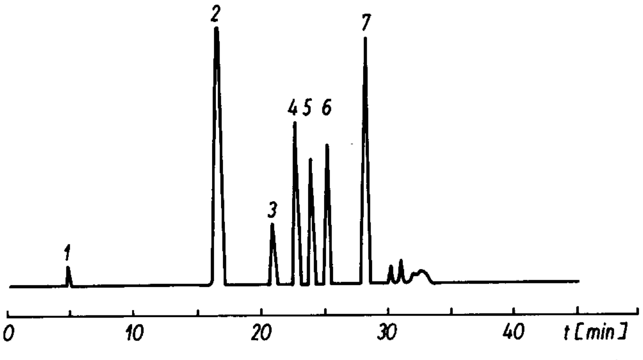
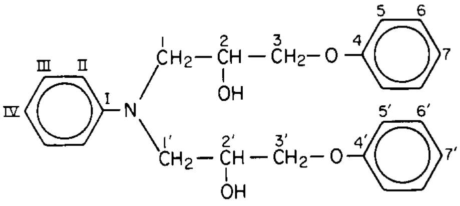


Figure 5 H.p.l.c. chromatogram of the PGE/aniline reaction (epoxy/amine hydrogen = 1/1 mol) in the presence of 4 mol% DMBA per epoxy group, $T = 120°C$, $t = 240$ min. Peaks: 1, aniline; 2, monoadduct **4**; 3, 7, products of the oligomerization of PGE; 4, 5, diastereoisomeric forms of the diadduct **8**, **8′**; 6, etherification product **5**; 7, etherification product **9**

Table 2 ^{13}C chemical shifts observed of the diastereoisomeric forms of the diadduct **8**, **8′** and the etherification product **9**

	Compounds				
Carbons	**8**[15]	**8′**[15]	**8**	**8′**	**9**
1	56.7	57.8	55.4	57.6	54,8,57.4
1′	56.7	57.8	55.4	57.6	54.8,57.4
1″	–	–	–	–	72.2
2	69.3	69.5	68.1	68.6	68.1,68.6
2′	69.3	69.5	68.1	68.6	67.8
2″	–	–	–	–	68.1,68.6
3		71.7		69.7	69.3
3′		71.7		69.7	69.3
3″		–		–	69.3
4, 4′, 4″		160.1		158.5	158.4
5, 5′, 5″		116.3		114.6	114.6
6, 6′, 6″		130.6		129.5	129.5
7, 7′, 7″		122.4		121.2	121.1
I	150.3	149.7	148.7	147.7	148.6
II	114.5	115.2	113.8	112.5	113.2
III		130.3		129.3	129.5
IV	118.5	118.2	117.8	117.2	117.9

diadduct of the PGE/aniline reaction

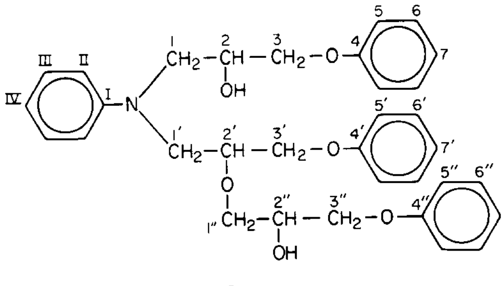


8,8′

The *FT*i.r. spectrum of the new product **9** and the spectra of the etherification products of the monoadduct (*Figure 4*) show a band for the structure of an aliphatic ether.

In the ^{13}C n.m.r. spectra, new signals appear at 72.2 and 67.8 ppm compared to the spectra of the diadduct (*Table 2*). This is a sign of the changed environment of the C atoms 1″ and 2′. Signal doubling on account of the diastereoisomeric forms of the diadduct is also visible in the etherification product **9**:

etherification product of the diadduct **8,8′**



9

From this result we can assume that at higher temperatures (120°C) the reaction of the secondary amine hydrogen takes part more competitively than the reaction of the secondary hydroxylic groups. With an excess of epoxy groups, only one product of etherification of the diadduct also arose in a greater amount. Further products were only formed in a small concentration, and we could not separate these compounds.

Overall, we can conclude that, in the presence of an accelerator such as DMBA, oligomerization of epoxide and etherification is significant. In contrast with the unaccelerated reaction, new structures were formed, leading to longer chain segments in the curing system. This also explains the lower glass transition temperature. There are still questions regarding the reactivity of the secondary amine hydrogen and of the secondary hydroxylic group, respectively, and their dependence on temperature. This problem will be discussed through kinetic investigations in a subsequent paper.

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