

Studies on diol modified epoxy resins by analytical pyrolysis

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Epoxy resins synthesized from diglycidyl ether of bisphenol A (DGEBA) and alkanediol cured with magnesium perchlorate or dimethylbenzylamine accelerator have been studied by direct inlet mass spectrometry (d.i.m.s.) and pyrolysis-gas chromatography-mass spectrometry (py-g.c.-m.s.). Both the evaporation of residual diol and oligomeric hydroxyethers of DGEBA and the thermal cleavage of terminal and side groups involving diolethers have been monitored by d.i.m.s. Phenols, bisphenol A and two benzofuranoic pyrolysis products identified by py-g.c.-m.s. have been found to reveal the network structure of the epoxy resins.

(Keywords: direct inlet mass spectrometry; pyrolysis-gas chromatography-mass spectrometry; epoxy resins; network structure)

INTRODUCTION

Epoxy resins have been successfully investigated by pyrolysis-gas chromatography-mass spectrometry (py-g.c.-m.s.)¹⁻⁴ and pyrolysis-field ionization mass spectrometry (py-f.i.m.s.)⁵. Diglycidyl ether of bisphenol was obtained from uncured resins by both methods. Characteristic pyrolysis products of the cured samples were the corresponding bisphenol and phenols in addition to some low boiling pyrolyzates such as propene, acetaldehyde, acrolein, acetone and allyl alcohol. The presence of volatile oligomers has been monitored by py-f.i.m.s., with the molecular ion intensities plotted *versus* the pyrolysis temperature.

The aim of our study was to clarify the modification caused by alkanediols in the structure of the macromolecule of epoxy resins cured with an accelerator of acidic or basic character.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA: EPILOX A 17-00, VEB Leuna-Werke) was recrystallized from a mixture of acetone and methanol (m.p. 42°C). DGEBA, aliphatic diol (VEB Leuna-Werke, technical grade vacuum distilled) and either Mg(ClO₄)₂·2H₂O (Merck, analytical grade) or N,N-dimethylbenzylamine (VEB Leuna-Werke) accelerator were mixed in a thermo-regulated glass reactor. The molar ratios of the reaction mixtures are given in *Table 1*. Temperatures of 60 and 100°C were held for the reactions accelerated by magnesium perchlorate and dimethylbenzylamine, respectively. The reaction was interrupted by cooling the mixture to room temperature at an epoxide consumption of ≈20%. The prepolymer was poured into a PTFE mould (100 × 10 × 1 mm³) and crosslinked at 100°C for 24 h and additionally at 130°C for 24 h.

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Pyrolytic methods

Fast pyrolysis was performed in a Pyroprobe 120 (Chemical Data System) interfaced either to a Hewlett-Packard 5985 B gas chromatograph-mass spectrometer or to a Hewlett-Packard 5880 A gas chromatograph equipped with flame ionization detector (f.i.d.) and thermal conductivity detector (t.c.d.). The sample mass was ≈0.1–0.4 mg. A helium carrier gas at a flow rate of 20 ml min⁻¹ purged the pyrolysis chamber held at 250°C. The gas chromatographic separation was carried out on a 20 m long (0.2 mm i.d.) fused silica capillary column coated with SE-52 siloxane phase for the analysis of organic pyrolysis products, or on a 3 m long (2 mm i.d.) column packed with Porapak S for the analysis of gases. In the mass spectrometer, either electron impact ionization (e.i.) at 70 eV or chemical ionization (c.i.) with methane reactant gas was applied.

Direct inlet mass spectrometry (d.i.m.s.) was carried out under vacuum (10⁻³ Pa) in the direct inlet probe of a Hewlett-Packard 5985 B GC/MS instrument. Samples of 0.05–0.1 mg mass were heated from 25 to 350°C at a rate of 30°C min⁻¹. A low ionization energy of 15 eV was applied to minimize mass fragmentation and obtain abundant molecular ions.

RESULTS AND DISCUSSION

Alkanediol residue

The first question to answer was: what has happened to the modifying diol during synthesis and under curing of the epoxy resins? A mechanism of epoxide ring opening by alcohols with the help of a catalyst resulting in hydroxyether was proposed^{6,7} and confirmed by i.r. spectroscopy^{8,9}. However, in our experience, when stoichiometric amounts of DGEBA and diol have been reacted, far from all the diol is consumed by this reaction. Temperature programmed d.i.m.s. monitors the evaporation of residual unreacted diols among other oligomeric

Table 1 Composition of samples

Modifier or accelerator	Amount (mol (mol DGEBA) ⁻¹)	Sample type
Diol ^a	1.0	A, B
Diol ^a	0.25	a, b
Magnesium perchlorate	0.03	a, A
Dimethylbenzylamine	0.05	b, B

^aNotation for nature of diol: 2 = 1,2-ethanediol; 4 = 1,4-butanediol; 6 = 1,6-hexanediol; 8 = 1,8-octanediol

compounds in the cured resins, and this is shown in *Figure 1* for sample **6A**. Diol peaks are also observed in the py-g.c.-m.s. chromatograms, for instance the 1,6-hexanediol peak in the pyrogram of sample **6A** (*Figure 2*). This peak also appears when the sample is held at 250°C for some minutes before running a chromatogram, proving that it is not a pyrolysis product but corresponds to the evaporation of a compound engaged in the macromolecule. The amounts of evaporated diols of different chain lengths are compared in *Figure 3*. In samples **a** almost all the (0.25 mol (mole DGEBA)⁻¹) diol is incorporated in the resin. In samples **b** the diol is only partly incorporated. In samples **A** and **B** a considerable amount of diol remained unreacted and became engaged in the resin network, except for ethanediol, which would probably evaporate under curing.

Residual DGEBA hydroxyethers

Programmed d.i.m.s. experiments revealed that mono- and bis(hydroxyether)s of DGEBA and diol also remained unreacted, mainly in samples **A** and **B**. The ion curves of $m/z = 443$, 461 and 561 in *Figure 1* probably correspond to compounds **1**, **2** and **3** when $x = 6$ in *Scheme 1*. The given ions are the (M-15)⁺ parent ions of the mass spectra of these compounds at 15 eV. The relative amounts of these hydroxyethers evaporated from the samples are given in *Figure 4*. Compound **1** could originate from the hydroxyether formed in the reaction of diol and DGEBA, having lost its reactivity because of an intramolecular etherification or a rearrangement of the epoxide group. The large amount of this hydroxyether with long chain diols suggests that it has a cyclic ether structure. Compound **2** is the hydroxyether of a partially hydrolysed DGEBA. Compound **3**, a bis(hydroxyether), also persisted in the cured epoxy resins. Its amount is relatively high in samples **B**, in which a large amount of the residual diol was also found. The total mass of the diol and hydroxyethers evaporated from resins under vacuum was found in the range 4–20% of the sample mass.

Diolether terminal and side groups

Diols bound to the linear chain terminals must be the source of compounds **4** formed at $\approx 350^\circ\text{C}$ in d.i.m.s. experiments under the applied conditions through a cleavage demonstrated in *Scheme 2*. Under fast pyrolysis conditions different products are obtained from the same chain terminal through C–O cleavage followed either by H uptake or elimination as shown in *Scheme 2*. Chain-terminating diols are partly detached, resulting in both the corresponding alkenol and alkene (see hexenol and hexene in the pyrograms of sample **6A** in *Figure 2*). The e.i. and c.i. spectra of compounds **5** and **6** for

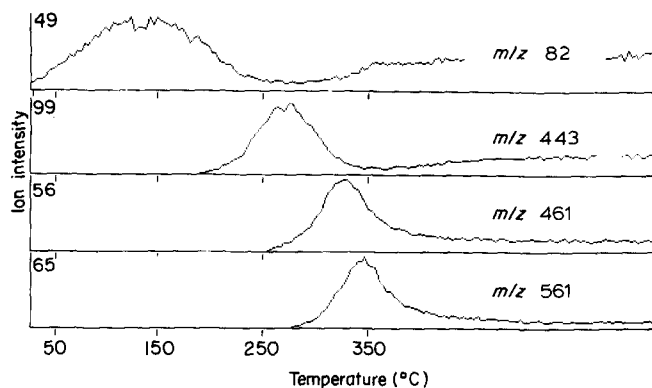


Figure 1 Evaporation of hexanediol ($m/z = 82$) and hydroxyethers ($m/z = 443$, 461, 561) during d.i.m.s. of sample **6A**

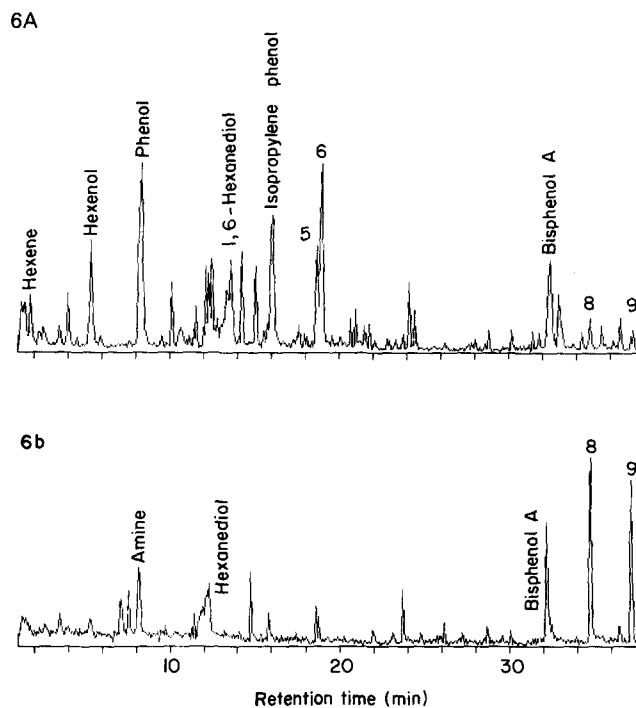


Figure 2 Pyrograms of hexanediol modified epoxy resins at 500°C (sample **6A** cured with magnesium perchlorate and sample **6b** with dimethylbenzylamine; notation is explained in *Table 1*)

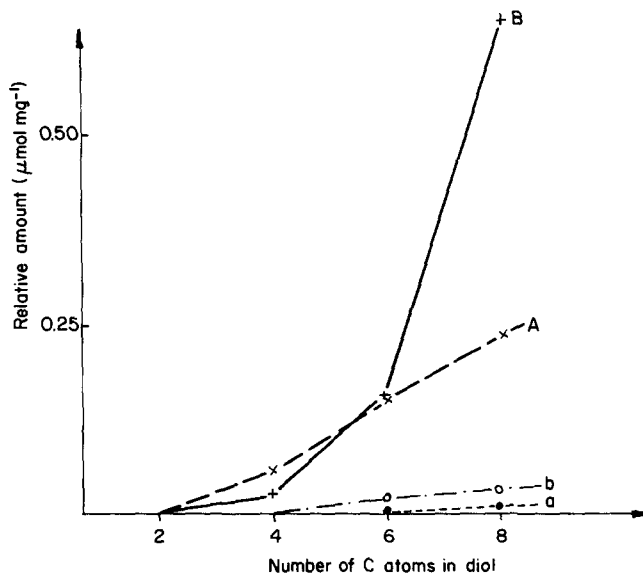
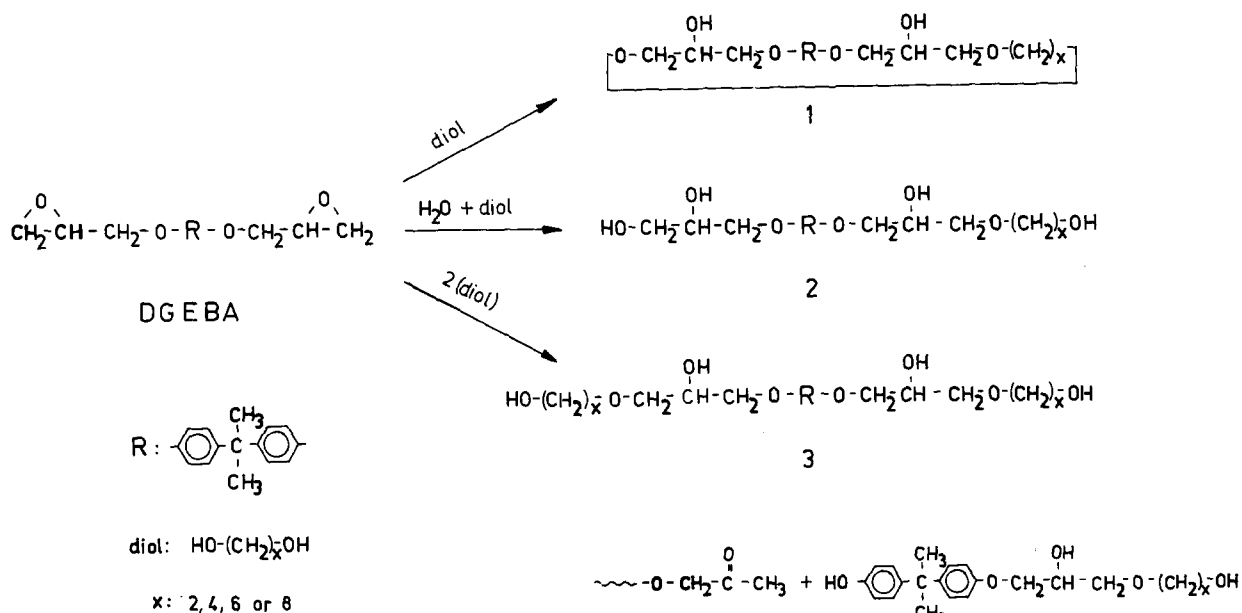


Figure 3 Relative amounts of residual diols evaporated from cured diol modified epoxy resins (notation is explained in *Table 1*)



Scheme 1

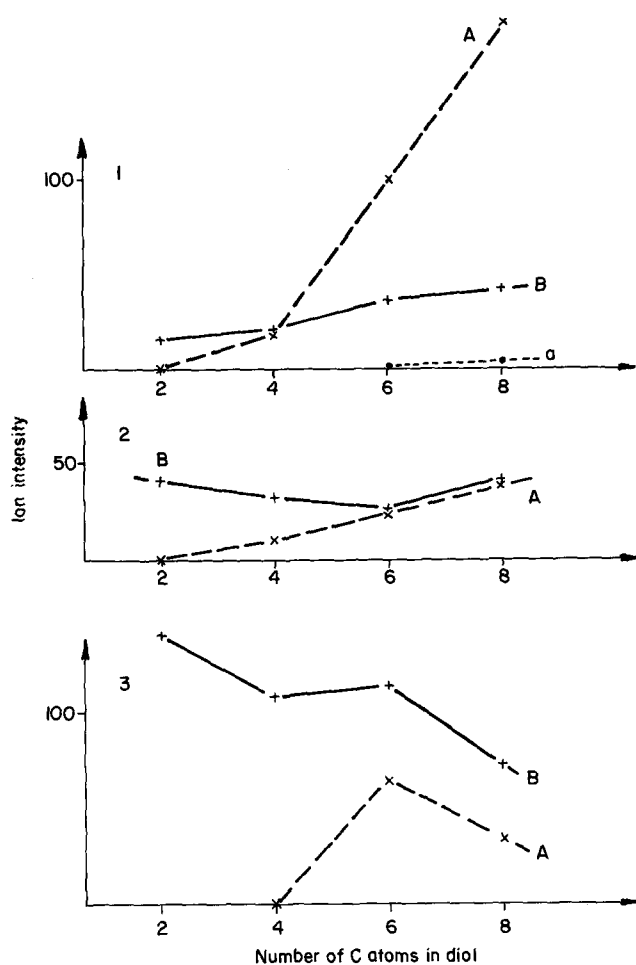


Figure 4 Relative amounts of hydroxyethers 1, 2 and 3 of hexanediol obtained by d.i.m.s. (notation is explained in Table 1 and Scheme 1)

hexanediol obtained by py-g.c.-m.s. are given in Figures 5 and 6. The relative amounts of these compounds in the pyrograms are shown in Figure 7. Considerably fewer pyrolysis products 4-6 are found in samples B than in samples A. However, a different product, again including a diol, is also formed from samples B under d.i.m.s. conditions. It could be derived from a side group of a

Scheme 2

crosslinked unit, according to Scheme 3. Figure 8 shows the parent and molecular ions of compounds 4 and 7 when $x = 6$ monitored at $m/z = 387, 402, 425$ and 440 , respectively, in d.i.m.s. of sample 6B. The relative amounts of the corresponding products from the investigated samples are given in Figure 9.

Diols incorporated in the resin

The diol molecules which have reacted with two epoxide groups to form dioldiether units incorporated in the epoxy resin are not fragmented into alkenol or alkene. No such pyrolysis products were obtained from samples a and b. Nevertheless, alkylether groups may result at least partially in carbon monoxide under pyrolysis. Thus the amount of carbon monoxide measured at 500°C (given in Table 2) is assumed to indicate the amount of diol built in the epoxy resin. Much more carbon monoxide was produced from samples a and A than from samples b and B.

Phenolic pyrolysis products

Phenol, isopropyl phenol, isopropylene phenol and bisphenol A predominate in the 500°C pyrograms of resins cured with magnesium perchlorate (samples a and A, see Figure 2). In contrast, very small amounts of phenols are obtained by pyrolysis at that temperature from resins cured with dimethylbenzylamine (samples

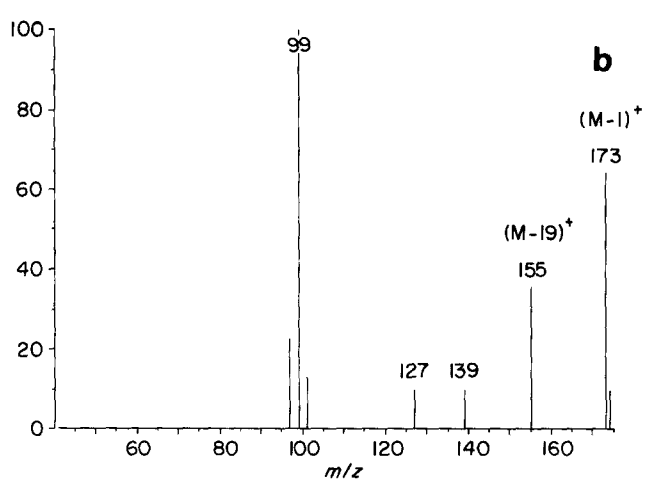
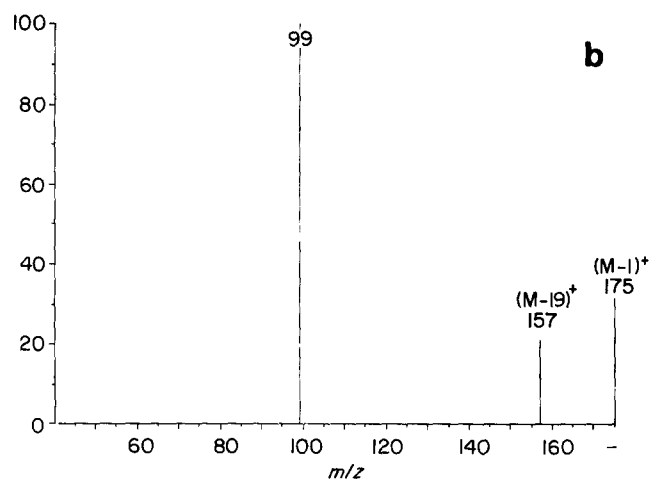
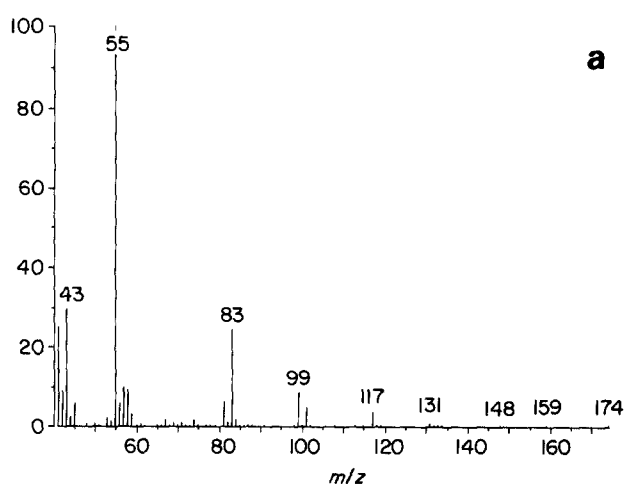
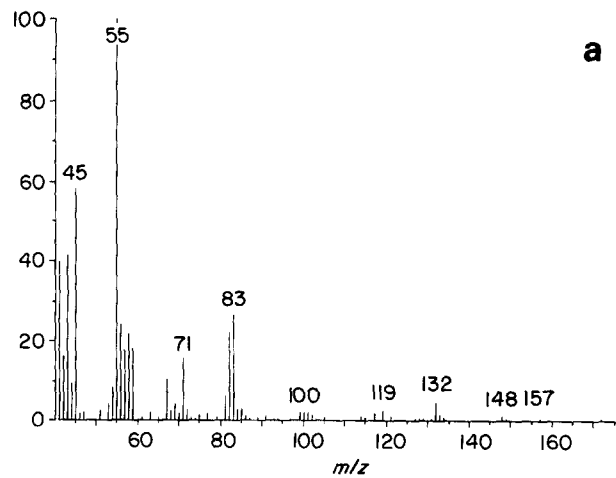
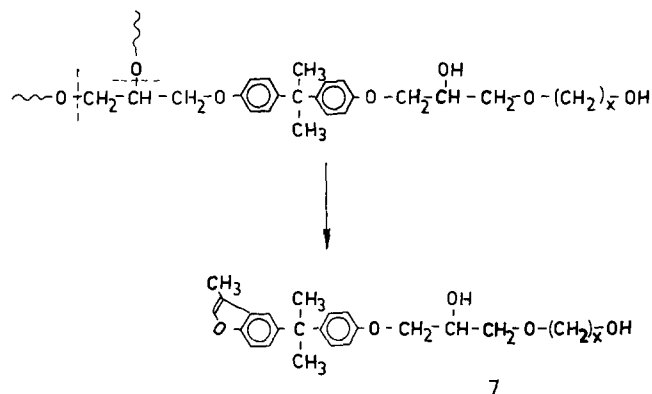


Figure 5 (a) E.i. and (b) c.i. mass spectra of compound **5** of hexanediol shown in Scheme 2 and Figure 2

Figure 6 (a) E.i. and (b) c.i. mass spectra of compound **6** of hexanediol shown in Scheme 2 and Figure 2



Scheme 3

type **b** and **B**, see Figure 2). The formation of large amounts of phenol must be the consequence of the catalytic effect of magnesium perchlorate, because phenol is produced instead of bisphenol A partly from sample **6b**, even at 500°C, when mixed with some magnesium perchlorate before pyrolysis. The same is observed at 600°C without catalyst. Phenolic hydroxyl groups are formed from aryl-alkyl ether bonds under pyrolysis, probably with the contribution of an available alcoholic hydroxyl group according to Scheme 4. The total amounts of phenolic products including bisphenol A are shown in Figure 10.

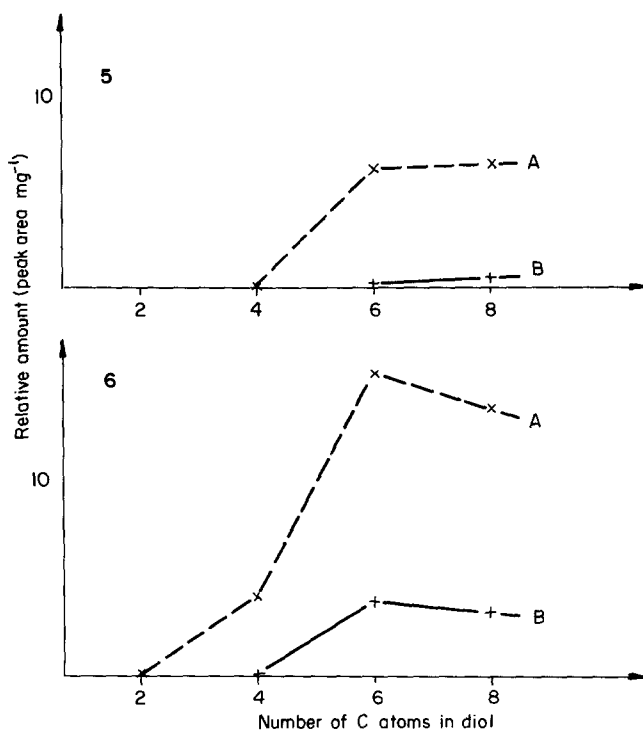


Figure 7 Relative amounts of compounds **5** and **6** formed at 500°C (notation is explained in Table 1 and Scheme 2)

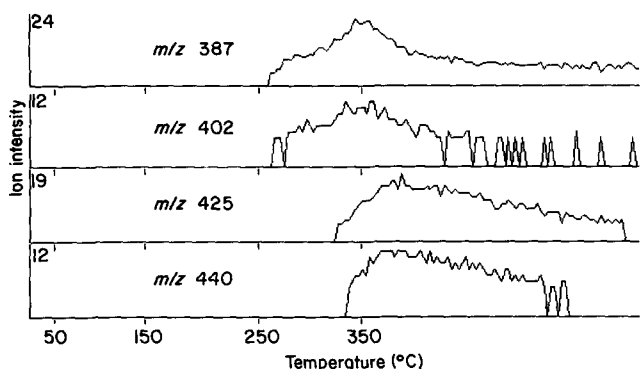


Figure 8 Formation of the pyrolysis products of chain terminating and side group hexanediol (compound **4**, $m/z = 387, 402$; compound **7**, $m/z = 425, 440$) during d.i.m.s. of compound **6B**

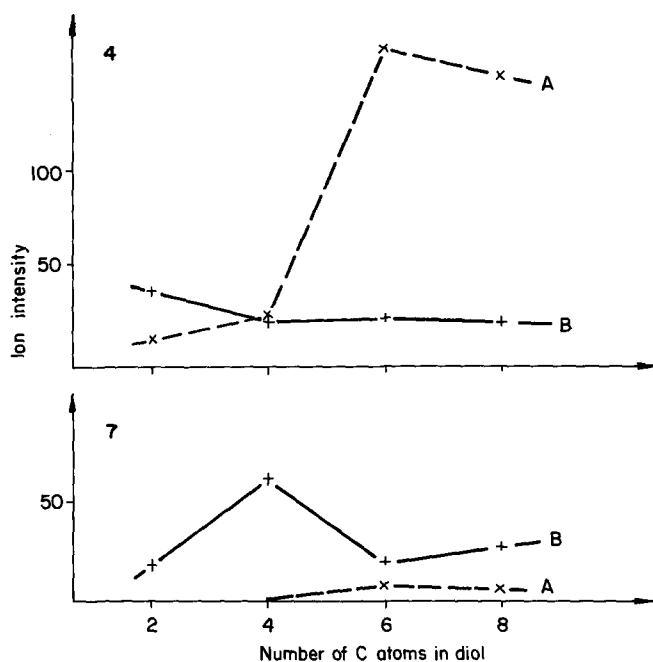


Figure 9 Relative amounts of chain terminating and side group diol pyrolysis products (compounds **4** and **7**) obtained by d.i.m.s. (notation is explained in Table 1 and Schemes 2 and 3)

Low boiling pyrolysis products

Propene, acetaldehyde, acetone, acrolein and allyl alcohol, the typical low boiling pyrolysis products of epoxy resins^{2,4}, have been found from the diol modified epoxy resins as well. Carbon monoxide and carbon dioxide were also measured by py-g.c.-t.c.d. as discussed earlier. The amounts of the low boiling pyrolysis products are summarized in Table 2. The amount of acrolein, acetone and allyl alcohol formed from samples A are considerably higher than from samples B. They could originate mainly from the hydroxy-propene section of the linear chain in the epoxy resin. Acetaldehyde may also be derived from dioldiether segments inserted in the polymer structure. The correlation between the amounts of acetaldehyde and carbon monoxide confirms this assumption. However, for samples 2 acetaldehyde is also the product of ethanol terminal group cleavage.

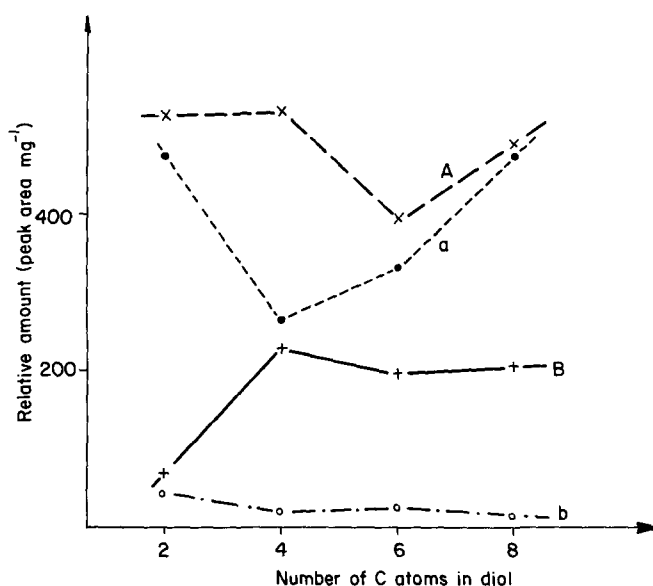
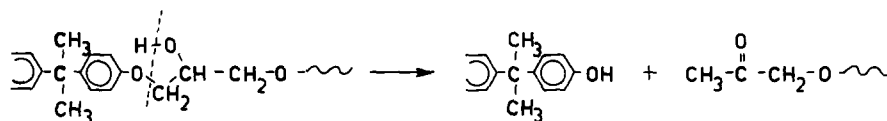


Figure 10 Relative amounts of phenolic compounds formed at 500°C (notation is explained in Table 1)



Scheme 4

Table 2 Low boiling pyrolysis products at 500°C ($\mu\text{mol (g sample)}^{-1}$)

Product	Sample a				Sample b				Sample A				Sample B			
	2	4	6	8	2	4	6	8	2	4	6	8	2	4	6	8
CO	225	288	283	329	46	214	128	144	413	436	323	356	29	141	107	92
CO ₂	126	126	114	166	47	35	23	31	123	220	120	135	10	26	15	18
CH ₄	29	35	35	44	14	50	33	37	53	60	31	43	8	35	25	27
C ₂ H ₄	8	7	6	9	6	6	4	5	34	29	12	14	4	7	4	4
C ₃ H ₆	52	92	78	115	13	99	63	48	111	114	62	65	8	42	38	25
CH ₃ CHO	130	115	198	146	94	110	135	84	354	292	166	188	99	104	83	63
Acrolein	67	77	80	82	5	19	16	13	100	103	33	76	—	21	12	4
Acetone	58	84	84	108	5	30	24	22	155	176	80	163	—	50	29	16
C ₃ H ₅ OH	35	47	41	45	12	42	44	40	76	86	38	33	—	40	25	—

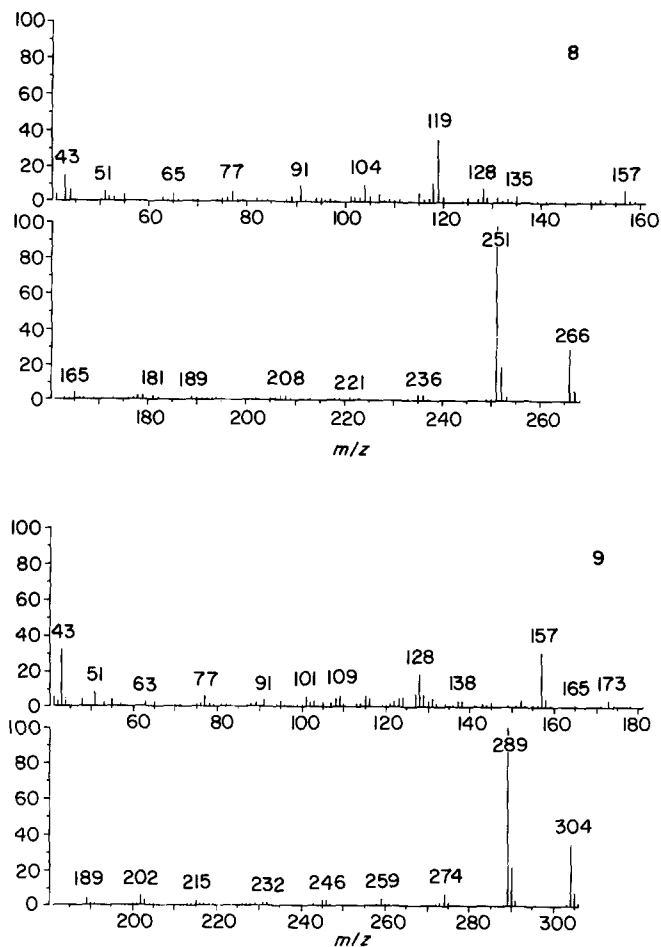


Figure 11 Mass spectra of compounds 8 and 9 in Scheme 5 and Figure 2

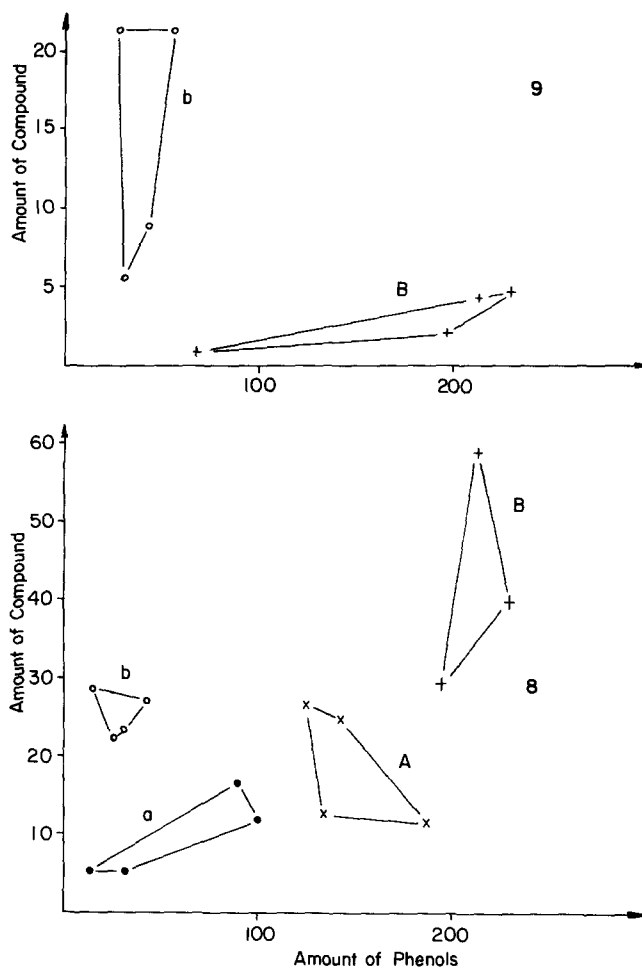
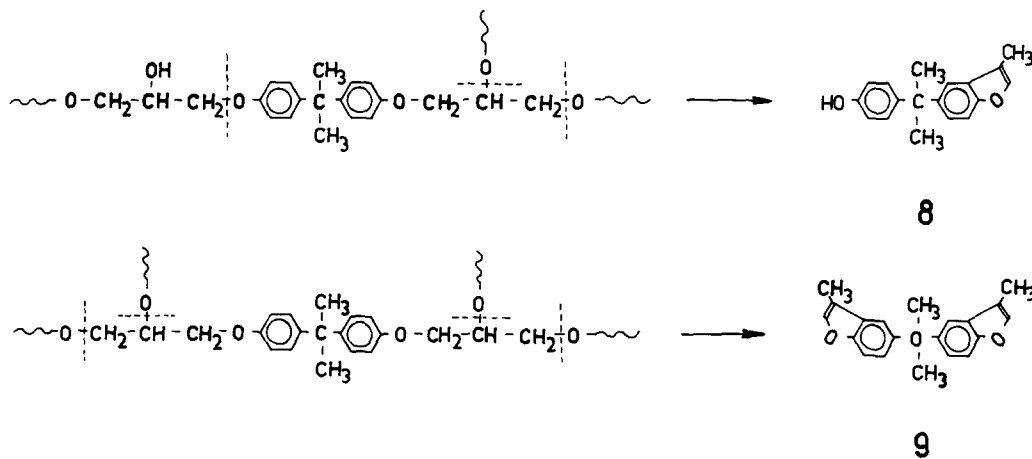


Figure 12 Amount of compounds 8 and 9 related to that of phenolic compounds formed at 500°C (notation is explained in Table 1 and Scheme 5)



Scheme 5

Benzofuranoic pyrolysis products

Some unknown pyrolysis products have been observed in the pyrograms of the diol modified epoxy resins eluted after bisphenol A. In some cases these peaks are fairly intensive, for example the peaks 8 and 9 in Figure 2. On the basis of their mass spectra given in Figure 11, these products are tentatively identified as the compounds

given in Scheme 5. We believe the crosslinked units in the resin to be the source of these pyrolysis products according to Scheme 5. Figure 12 gives the relative amounts of compounds 8 and 9 related to the amounts of phenolic products. The figure demonstrates that the ratio of crosslinked to linear units is roughly the same for samples a and A; it is higher for samples B and by far the highest for samples b.

CONCLUSION

Alkanediols are incorporated into the chain of epoxy resins by their addition to epoxide groups in the presence of magnesium perchlorate. The extent of diol addition is influenced by the concentration of the diol in the reaction mixture. However, significant amount of the diol remained unreacted when the reaction started with stoichiometric amounts of diol and DGEBA. In addition, large amounts of chain terminating diols could be detected, mainly in resins modified with longer chain diols, and hydroxyethers of DGEBA and diol(s) were also present in this case.

In the presence of dimethylbenzylamine a smaller amount of diol is incorporated in the epoxy resin structure, depending little on the diol concentration in the range $0.25\text{--}1\text{ mol (mol DGEBA)}^{-1}$. Similarly, a smaller amount of chain terminating or side group diol was found in cured resins, even if they contained considerable amounts of unreacted diol. In contrast, many DGEBA hydroxyethers were present, mainly those which were the product of the addition of two diol molecules to one DGEBA (compound **3** in *Scheme 1*). This observation, together with the above, indicates that diol addition to epoxies is less favoured in the presence of dimethylbenzylamine than in the presence of magnesium perchlorate.

Comparison of the amounts of pyrolysis products, which can be related to the epoxy resin structure (compounds **8** and **9**), indicates that the frequency of the branching points must be considerably higher in the

samples cured with dimethylbenzylamine than those cured with magnesium perchlorate. When diol was present in high concentration fewer crosslinks could form in the presence of dimethylbenzylamine, because some of the epoxide groups reacted with diol to form terminal or side groups instead of crosslinks. However, the relatively low frequency of the branching points is not much affected by the diol concentration in the samples cured with magnesium perchlorate.

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