Model studies on the cross-linking of epoxy resins with amines at room temperature

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The curing mechanisms of bisphenol-A epoxide with amines have been investigated using a cresol epoxide and mono- and diamines in model reactions which do not lead to polymers. With all amines the reaction begins with the formation of β-aminoalcohols, and the reaction product contains secondary amino groups of remarkably lower nucleophilicity. Thus it is concluded that the formation of a linear polymer is always the first step in the curing of epoxide resins with amines. Cross-linking by the addition of the secondary amines to the remaining epoxide will be hindered due to the immobility of the reaction partners of the first reaction. The whole curing reaction is governed by the nucleophilicity of the amines and steric effects.

Key words: epoxides; amines; curing mechanism; model reactions

The polymerization of cold-cured epoxy resins occurs via a polyaddition of amino groups of the hardener onto epoxy groups of the resin. Typical hardeners are polyamines and polyamidoamines[1,2]. Most resins used today are derived from bisphenol-A epoxide (1) of different degrees of prepolymerization. These are modified into technical products by the addition of reactive components such as epoxynovolak and non-reactive components such as fillers. Epoxy resins have found wide use as adhesives or resins for laminates. Nevertheless, only a limited number of publications[3-5] examine curing mechanisms and their influence upon the mechanical properties of the cured resins. Usually the general mechanism is described[5-7] (see Fig. 1).

The amino nitrogen atom with its lone pair of electrons is added to the sterically less hindered carbon atom of the epoxy group by opening the cyclic, three-membered ring. The reaction product thus obtained is a secondary β-aminoalcohol[8,9]. The second reaction, possible if primary amines are used as hardeners, is the addition of the β-aminoalcohols formed in the first step to further epoxide, and turns out to be responsible for the three-dimensional polymer structure of the cured resin. In this context it is remarkable that the basicity of secondary amino groups is higher than that of primary ones, whereas the nucleophilic character is smaller. For that reason, this reaction with its essential influence upon the mechanical properties of the cured resin represents the starting point of the present investigation.

Because it is difficult to analyse and characterize the structure of cross-linked polymers by physical or chemical methods, a model reaction system was chosen which shows similar chemical behaviour to real curing reactions without, however, leading to polymeric products.

Model reactions and the model systems

For a non-polymerizing and analysable epoxy system bisphenol-A epoxide (1) had to be notionally cut into two halves. It was therefore replaced by 1,2-epoxy-3-(4-methyl-phenoxy)-propane (7), which can be regarded as the monofunctional analogue of bisphenol-A epoxide (1), and is subsequently referred to as monoepoxide. Compound 7 is easily available from the sodium salt of p-cresol (5) and epichlorohydrin (6) as shown in Fig. 2.

The reaction products of this monoepoxide with amines can be investigated directly by thin layer chromatography (TLC), mass spectroscopy (MS)and proton nuclear magnetic resonance spectroscopy (^{1}H NMR).

Experimental details

Analytical techniques

Thin layer chromatography was carried out on TLC aluminium sheets coated with silica gel 60 F_{254} (layer thickness 0.2 mm, from Merck) with toluene/

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acetonitrile solvent at a ratio of 2:1. Data from the elemental analyses are expressed in percent of molecular weight. From each mass spectrum, obtained on a Varian MAT311A instrument, the molecular ion is given. ^{1}H NMR spectra were recorded on a Bruker WP 80 instrument at 80 MHz in deuterated trichloromethane ($CDCl_3$). All absorptions are given as chemical shifts (δ in parts per million, ppm) and the following notation is used: s — singlet, d — doublet, t — triplet, q — quartet and m — multiplet.

Synthesis of 1,2-epoxy-3-(4-methyl-phenoxy)-propane (7)

One mole (108.1 g) of freshly distilled p-cresol was added slowly to 376 cm^3 water containing 37.6 g sodium

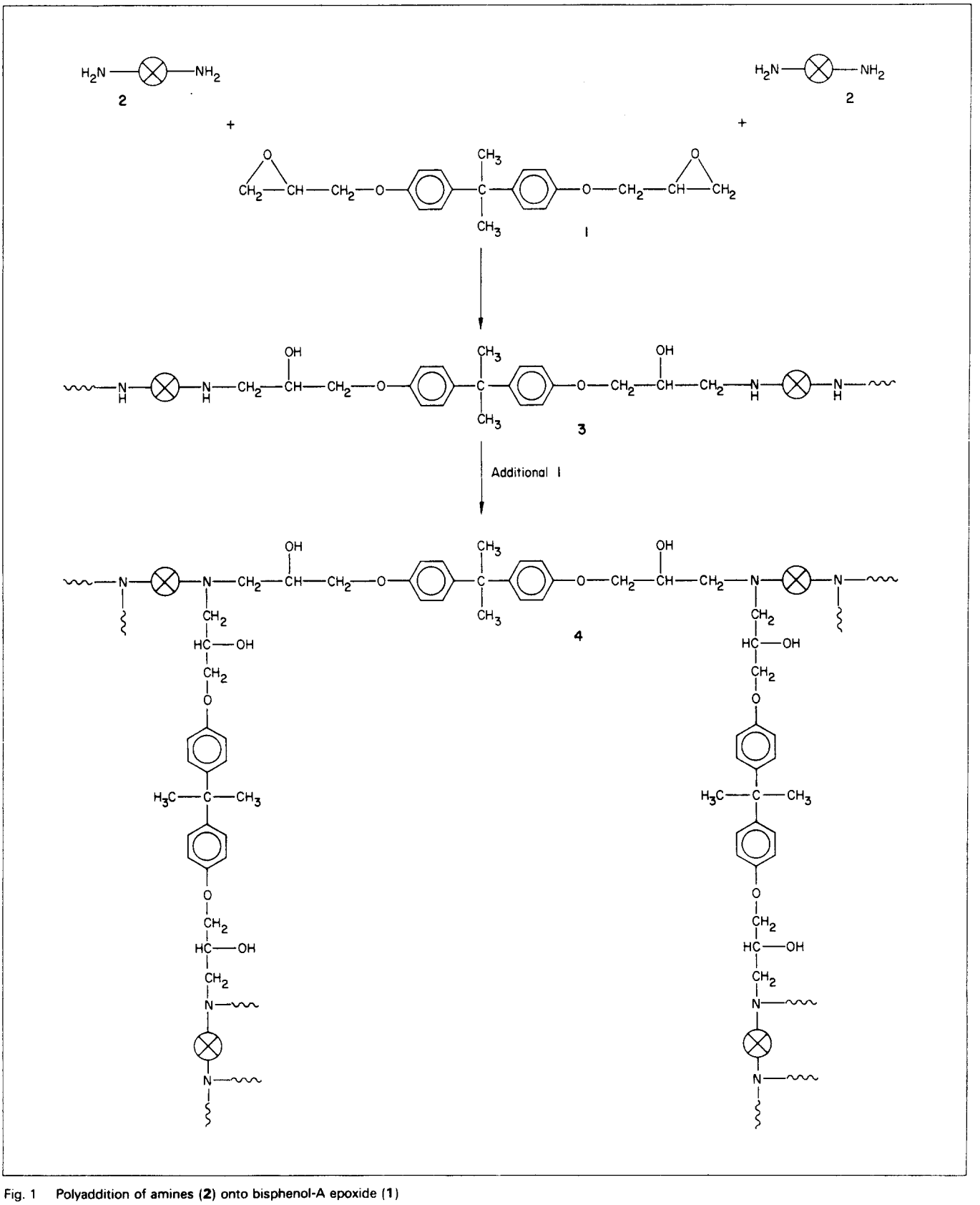


Fig. 1 Polyaddition of amines (**2**) onto bisphenol-A epoxide (**1**)

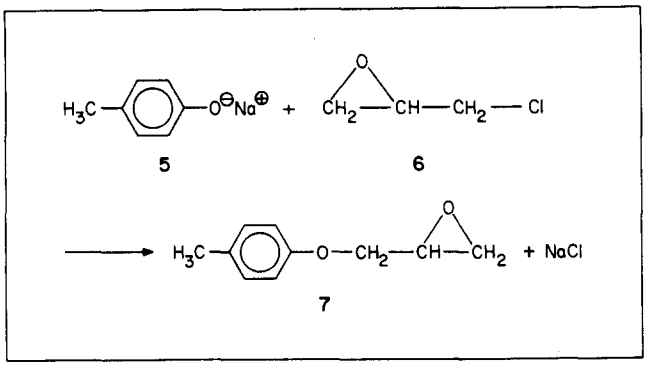


Fig. 2 Synthesis of monoepoxide (7)

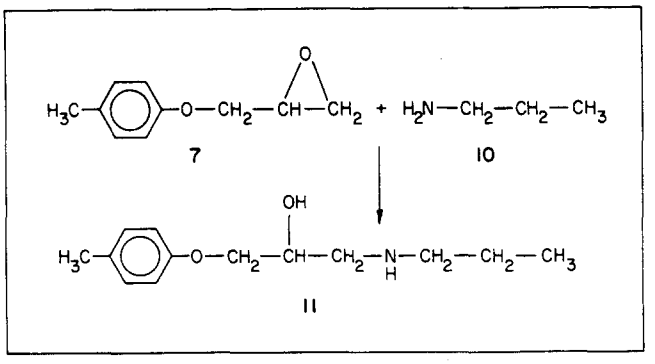


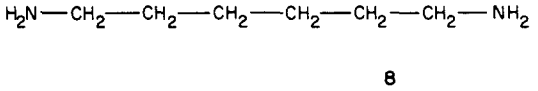
Fig. 3 Monoaddition of propyl amine (10) to monoepoxide (7)

hydroxide (0.94 moles). After stirring for 0.5 h at 25°C, 1.57 moles (145.3 g) of freshly distilled epichlorohydrin were added. The mixture was stirred for 1 h at 25°C and then refluxed for a further 1.5 h. After cooling to room temperature the mixture separated into two layers. The organic layer was isolated, dried with sodium sulphate and distilled in vacuo (yield — 114.8 g; boiling point — 72°C/0.3 torr).

Elemental analysis (164.2 g mol^{-1}): calculated — C, 73.15; H, 7.37. Found — C, 73.21; H, 7.29. MS: m/z = 164. ^{1}H NMR: H aromatic, 6.95 (AA'BB'); -O-C<u>H</u>$_2$, 4.05 (dq); -C<u>H</u>-, 3.42-3.23 (m); -C<u>H</u>$_2$, 2.81 (dq); C<u>H</u>$_3$ aromatic, 2.28 (s).

Synthesis of β-aminoalcohols

Monoepoxide (7) and amine in a variety of molar ratios were stirred at room temperature until no monoepoxide could be detected by TLC. As well as the amines shown in the figures, hexamethylene diamine (8) and aniline (9) were used.



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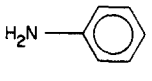

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The molar quantity of monoepoxide (7) used in these reactions was always 0.01 mole (1.64 g). The corresponding quantity of amine used follows from this.

N-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3]-propyl amine (propyl amine-monoadduct) (**11**)

Prepared from monoepoxide (7) and propyl amine (10) in ratio 1:1, see Fig. 3; reaction 1-1.5 days; R_f value 0.11. Elemental analysis (223.32 g mol^{-1}): calculated — C, 69.92; H, 9.48; N, 6.27. Found — C, 69.84; H, 9.41; N, 6.21. MS: m/z = 223. ^{1}H NMR: H aromatic, 7.26-6.75 (m); -C<u>H</u>(OH), 4.13-3.9 (m); -O-C<u>H</u>$_2$, 3.96 (d); N-C<u>H</u>$_2$, 2.84-2.53 (m); C<u>H</u>$_3$ aromatic, 2.28 (s); CH$_3$-C<u>H</u>$_2$, 1.67-1.3 (m); C<u>H</u>$_3$-CH$_2$, 0.92 (t).

N,N-di-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3]-propyl amine (propyl amine-diadduct) (**12**)

Prepared from 7 and propyl amine (10) in ratio 2:1, see Fig. 4; reaction time 4-5 days; R_f value 0.49. Elemental analysis (387.52 g mol^{-1}): calculated — C, 71.29; H, 8.58; N, 3.61. Found — C, 71.38; H, 8.72; N, 3.55. MS: m/z = 387. ^{1}H NMR: H aromatic, 7.26-6.75 (m); -C<u>H</u>(OH), 4.15-4 (m); -O-C<u>H</u>$_2$, 3.94 (d); N-C<u>H</u>$_2$, 2.97-2.49 (m); C<u>H</u>$_3$ aromatic, 2.28 (s); CH$_3$-C<u>H</u>$_2$, 1.76-1.3 (m); C<u>H</u>$_3$-CH$_2$, 0.89 (t).

N,N'-di-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3] -hexamethylene diamine (hexamethylene diamine-bis-monoadduct)

Prepared from 7 and hexamethylene diamine (8) in ratio 2:1; reaction time 1 day; R_f value 0.08. Elemental

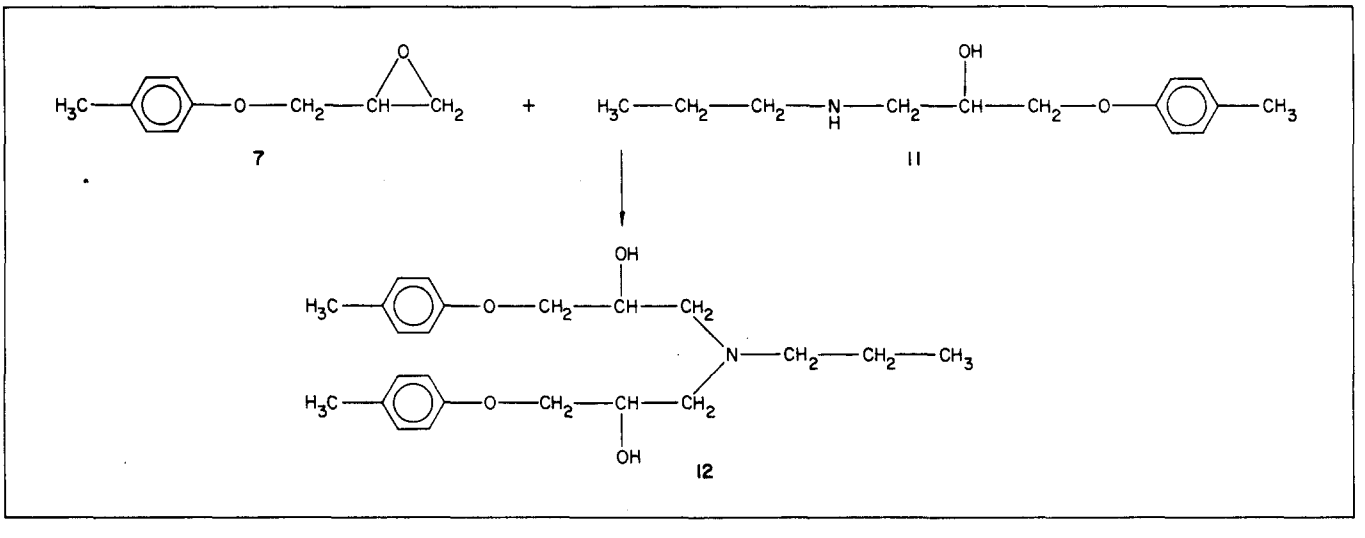


Fig. 4 Addition of a secondary β-aminoalcohol (11) to monoepoxide (7)

analysis (444.62 g mol^{-1}): calculated — C, 70.24; H, 9.07; N, 6.3. Found — C, 70.34; H, 8.96; N, 6.26. MS: *m/z* = 444. ^{1}H NMR: H aromatic, 7.26–6.75 (m); -C<u>H</u>(OH), 4.10–3.95 (m); -O-C<u>H</u>$_2$, 3.96 (d); N-C<u>H</u>$_2$, 2.83–2.51 (m); C<u>H</u>$_3$ aromatic, 2.28 (s); -C<u>H</u>$_2$-CH$_2$, 1.65–1.29 (m).

N,N,N', N'-tetra-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3] -hexamethylene diamine (hexamethylene diamine-bis-diadduct)

Prepared from 7 and hexamethylene diamine (**8**) in ratio 4:1; reaction time 2.5–3 days; R_f value 0.00. Elemental analysis (773.03 g mol^{-1}): calculated — C, 71.47; H, 8.35; N, 3.62. Found — C, 71.39; H, 8.44; N, 3.54. MS: *m/z* = 772. ^{1}H NMR: H aromatic, 7.28–6.74 (m); -C<u>H</u>(OH), 4.16–3.89 (m); -O-C<u>H</u>$_2$, 3.93 (d); N-C<u>H</u>$_2$, 2.83–2.51 (m); C<u>H</u>$_3$ aromatic, 2.28 (s); -C<u>H</u>$_2$-CH$_2$, 1.71–1.22 (m).

N-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3]-aniline (aniline-monoadduct)

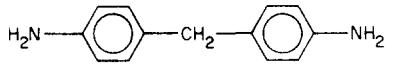
Prepared from 7 and aniline (**9**) in ratio 1:1; reaction time 5 days; R_f value 0.45. Elemental analysis (257.33 g mol^{-1}): calculated — C, 74.68; H, 7.44; N, 5.44. Found — C, 74.59; H, 7.52; N, 5.39. MS: *m/z* = 257. ^{1}H NMR: H aromatic, 7.33–6.71 (m); -C<u>H</u>(OH), 4.33–4.01 (m); -O-C<u>H</u>$_2$, 4.04 (d); N-C<u>H</u>$_2$, 3.41–3.36 (m); C<u>H</u>$_3$ aromatic, 2.29 (s).

N,N-di-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3]-aniline (aniline-diadduct)

Prepared from 7 and aniline (**9**) in ratio 2:1; reaction time 16 days; R_f value 0.40. Elemental analysis (421.54 g mol^{-1}): calculated — C, 74.08; H, 7.41; N, 3.32. Found — C, 74.02; H, 7.33; N, 3.11. MS: *m/z* = 421. ^{1}H NMR: H aromatic, 7.33–6.64 (m); -C<u>H</u>(OH), 4.34–3.92 (m); -O-C<u>H</u>$_2$, 3.99 (d); N-C<u>H</u>$_2$, 3.62–3.22 (m); C<u>H</u>$_3$ aromatic, 2.28 (s).

N,N'-di-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3] -4,4'-diamino-diphenylmethane (4,4'-diamino-diphenylmethane-bis-monoadduct)

Prepared from 7 and 4,4'-diamino-diphenylmethane (**13**, see below) in ratio 2:1; **13** not soluble in 7 at room temperature, reaction temperature 50°C; R_f value 0.45. Elemental analysis (526.68 g mol^{-1}): calculated — C, 75.26; H, 7.27; N, 5.32. Found — C, 75.07; H, 7.04; N, 5.41. MS: *m/z* = 526. ^{1}H NMR: H aromatic, 7.22–6.59 (m); -C<u>H</u>(OH), 4.41–3.75 (m); -O-C<u>H</u>$_2$, 3.94 (d); -C<u>H</u>$_2$ aromatic, 3.91 (s)[10]; N-C<u>H</u>$_2$, 3.61–3.32 (m); C<u>H</u>$_3$ aromatic, 2.28 (s).



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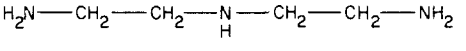
N,N,N,'N'-tetra-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3] -4,4'-diamino-diphenylmethane (4,4'-diamino-diphenylmethane-bis-diadduct)

Prepared from 7 and 4,4'-diamino-diphenylmethane (**13**) in ratio 4:1; **13** not soluble in 7 at room temperature, reaction temperature 50°C; R_f value 0.51. Elemental analysis (855.09 g mol^{-1}): calculated — C, 74.45; H, 7.31; N, 3.28. Found — C, 74.56; H, 7.39; N, 3.21. MS: *m/z* = 854. ^{1}H NMR: H aromatic, 7.25–6.63 (m); -CH(O<u>H</u>), 4.39–3.78 (m); -O-C<u>H</u>$_2$, 3.96 (d); -C<u>H</u>$_2$ aromatic, 3.91 (s)[10]; N-C<u>H</u>$_2$, 3.58–3.30 (m); C<u>H</u>$_3$ aromatic, 2.28 (s).

*N,N''-di-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3]- diethylene triamine (DETA-bis-monoadduct, **15**, see Fig. 5)*

Prepared from 7 and diethylene triamine (DETA, **14**, see below) in ratio 2:1; reaction time 0.5 days; R_f value 0.00. Elemental analysis (431.58 g mol^{-1}): calculated — C, 66.79; H, 8.64; N, 9.74. Found — C, 66.71; H, 8.55; N, 9.81. MS: *m/z* = 431. ^{1}H NMR: H aromatic, 7.26–6.74 (m); -C<u>H</u>(OH), 4.2–3.82 (m); -O-C<u>H</u>$_2$, 3.94 (d); N-C<u>H</u>$_2$, 2.86–2.48 (m); C<u>H</u>$_3$ aromatic, 2.27 (s).



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*N,N',N''-tri-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3] -diethylene triamine (DETA-triadduct, **16**, see Fig. 6)*

Prepared from 7 and DETA (**14**) in ratio 3:1; reaction time 1 day; R_f value 0.07. Elemental analysis (595.78 g mol^{-1}): calculated — C, 68.54; H, 8.29; N, 7.05. Found — C, 68.65; H, 8.34; N, 6.95. MS: *m/z* = 595. ^{1}H NMR: H aromatic, 7.26–6.73 (m); -C<u>H</u>(OH), 4.25–3.8 (m); -O-C<u>H</u>$_2$, 3.92 (d); N-C<u>H</u>$_2$, 2.95–2.45 (m); C<u>H</u>$_3$ aromatic, 2.26 (s).

*N,N,N',N'',N''-penta-[1-(4-methyl-phenoxy) -2-hydroxy-propyl-3]-diethylene triamine (DETA-pentaadduct, **17**, see Fig. 6)*

Prepared from 7 and DETA (**14**) in ratio 5:1; reaction time 4.5–5 days; R_f value 0.18. Elemental analysis

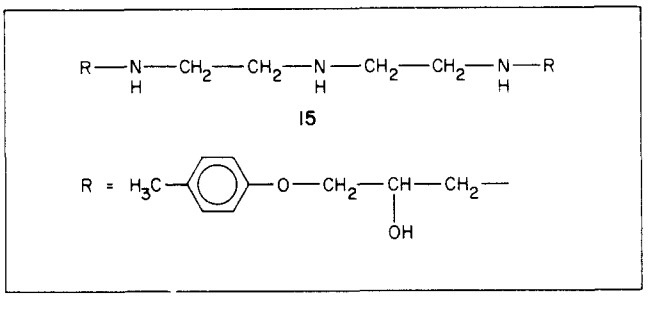

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Fig. 5 Bis-monoadduct (**15**) of DETA (**14**)

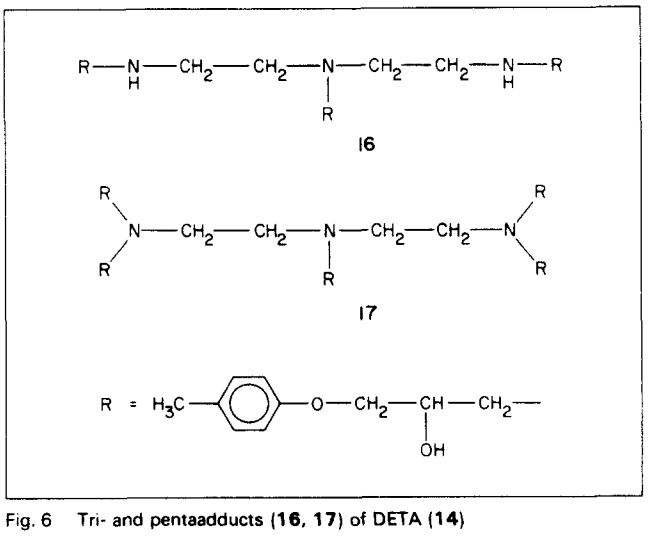

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Fig. 6 Tri- and pentaadducts (**16**, **17**) of DETA (**14**)

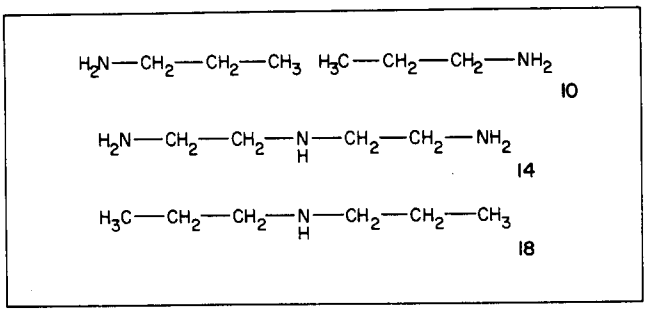

Fig. 7 Comparison of propyl amine (**10**) and di-propyl amine (**18**) with DETA (**14**)

(924.19 g mol^{-1}): calculated — C, 70.18; H, 7.96; N, 4.55. Found — C, 70.29; H, 8.21; N, 4.41. MS: molecular ion not observed. ^{1}H NMR: H aromatic, 7.26–6.72 (m); -CH(OH), 4.3–3.8 (m); -O-CH_2, 3.93 (d); N-CH_2, 2.98–2.45 (m); CH_3 aromatic, 2.26 (s).

N-[1-(4-methyl-phenoxy)-2-hydroxy-propyl-3]-di-propyl amine (di-propyl amine-adduct)

Prepared from 7 and di-propyl amine (**18**, see Fig. 7) in ratio 1:1; reaction time 4.5–5 days; R_f value 0.15. Elemental analysis (265.5 g mol^{-1}): calculated — C, 72.41; H, 10.25; N, 5.27. Found — C, 72.32; H, 10.3; N, 5.2. MS: m/z = 265. ^{1}H NMR: H aromatic, 7.26–6.76 (m); -CH(OH), 4.2–3.88 (m); -O-CH_2, 3.95 (d); N-CH_2, 2.6–2.38 (m); CH_3 aromatic, 2.28 (s); CH_3-CH_2, 1.75–1.2 (m); CH_3-CH_2, 0.95 (t).

Reactions of the model epoxide with different amines

Aliphatic amines

The reaction of the monofunctional epoxide with primary mono- and diamines at room temperature leads first to the formation of a monoadduct (**11**), see Fig. 3. This is exactly the first reaction depicted in Fig. 1. Thin layer chromatographic analysis of monoepoxide/primary amine mixtures show that monoadducts such as **11** can be detected after 15 min reaction time.

The further addition of the secondary β-aminoalcohol (**11**) formed in the first reaction to monoepoxide takes place more slowly in a following step (see Fig. 4). Bisadducts such as compound **12** are detected by thin layer chromatography only after 12 h, the monoepoxide (**7**) still being present.

The molar ratio of monoepoxide and amine governs the formation of diadducts such as **12**. Reaction of the monoepoxide with an aliphatic primary amine at a ratio of 1:1 leads to the almost quantitative formation of monoadducts such as **10** within 1 to 1.5 days. No monoepoxide is detectable after this time and only traces of the corresponding diadduct (**12**) can be found. The same reaction at a molar ratio of 2:1 also proceeds via the formation of monoadducts such as **10** in a first step (monoaddition). After almost 12 h, diaddition products such as **12** become detectable by thin layer chromatography; this second reaction is completed after 4 to 5 days at room temperature.

It is evident from these results that primary and secondary amines — and secondary β-aminoalcohols are secondary amines — do not show equal reactivities with respect to the addition to epoxides. Primary amino groups are added preferentially to epoxides to form monoaddition products, and the further possible addition of the secondary amino group of these reaction products to epoxides is clearly prejudiced. This results is supported by the fact that an asymmetric reaction product such as that depicted in Fig. 8 could not be detected using diamines.

Therefore the reasons for the preferential addition have to be the increased steric hindrance and simultaneous decreased nucleophilicity of the secondary amino group in the secondary β-aminoalcohol.

Aromatic amines

Aromatic amines are used mostly in hot-curing epoxy resins as hardeners[11, 12]. Because they are rather similar to the aliphatic primary amines, they have also been investigated. A typical aromatic diamine is 4,4'-diamino-diphenylmethane (**13**).

In principle the aromatic amines show the same reaction behaviour as the aliphatic analogues: first monoadducts are formed, followed by diadducts in a second step. However, because of their lower nucleophilicity, these amines react 10 times more slowly than the aliphatic amines. Another difference between the reaction behaviour is that, after a short reaction time (eg, 4–5 h using aniline (**9**)), the monoaddition of aromatic amines to monoepoxide (**7**) is accompanied by diaddition, the difference in the reactivities of primary and secondary amino groups in aromatic systems being less distinct than in aliphatic systems. Again, the reason for this behaviour is the smaller nucleophilic character of primary aromatic amines compared with primary aliphatic ones.

Aliphatic polyfunctional amines containing primary and secondary amino groups

An other typical group of hardeners is represented by polyalklylene polyamines such as diethylene triamine (DETA, **14**). This compound, which contains two equivalent primary amino groups at both ends and a secondary amino group in the centre of the molecule, was chosen for testing the reactivities of the non-equivalent amino groups. Experiments were performed with molar ratios of monoepoxide/DETA of 2:1, 3:1 and 5:1 at room temperature. The progress of the reactions was tested from time to time by thin layer chromatography.

Again, each of the primary amino groups first added to one monoepoxide to give a bis-monoadduct (**15**) (see Fig. 5). When the reactants were present in a ratio of 2:1 the reaction stopped at this point. After a reaction

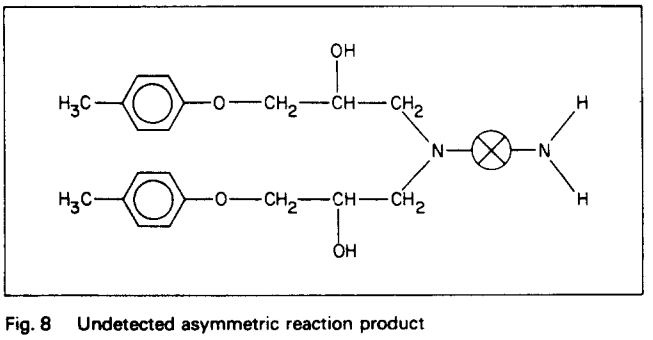

Fig. 8 Undetected asymmetric reaction product

time of 4 h at molar ratios of 3:1 and 5:1 a triadduct (**16**), in which the secondary amino group had reacted, became detectable for the first time. The corresponding pentaadduct (**17**) was finally formed quantitatively after 4 days at a ratio of 5:1 (see Fig. 6).

These experiments are in agreement with the following observation of the reaction behaviour of different amines. The monoadduct of primary propyl amine (**10**) with monoepoxide becomes detectable after reaction times of 15 min; for the secondary amine di-propyl amine (**18**) the monoadduct is detected after 1 h.

Conclusions

The present investigation indicates that *nucleophilicity* is the determining parameter concerning the reactivity of a particular amino group: the amino group with the highest nucleophilic character is the most reactive one. In this context primary amines are more reactive than secondary ones, and the lowest reactivity is shown by the secondary amino groups of secondary β-aminoalcohols, which in principle add to epoxides last. Thence the reaction behaviour is ruled by steric properties. The smaller nucleophilicity of aromatic amines arises from their electronic properties: the lone pair of electrons on the nitrogen atom of the amino group is conjugated with the aromatic ring. The reduced reactivity of such monoadducts is then ruled by electronic and steric properties.

Only the fundamental reaction of amine-curing epoxy systems can be simulated by this model. Application of these results to similar polymerizing systems needed for mechanical tests leads merely to simply formulated resin systems built up from bisphenol-A epoxide (**1**) and diamines (**2**). The results of these investigations will be published in a separate communication.

From the results of this investigation a few first assumptions on the curing mechanism of cold-curing amine/epoxide systems can be made. The curing reaction begins with the formation of a linear polymer. This causes an increase in the viscosity of the resin, connected with reduced mobility of the unreacted monomers. Thus the rate of chain growth in the resin decreases and the addition of the secondary amino groups of the β-aminoalcohols onto remaining epoxide can start. This latter reaction leads to cross-linking of the polymer, the rate of which will be slow at room temperature in all cases.

Acknowledgement

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