The nucleophilicity as the determining parameter in the curing of epoxy resins

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The reaction behaviour of epoxides was investigated using model reactions. For these, a monofunctional cresole epoxide was selected to be used and its reaction behaviour with compounds containing different functional groups was observed. The results of the investigations indicate that the nucleophilicity of the functional groups is the determining parameter in curing of epoxy resins. The most reactive were the aromatic mercapto groups. When using amines, the primary amino groups are the first to react followed by secondary amino groups of hardeners. The secondary amino groups of reaction products (β-aminoalcohols) formed are less reactive and the lowest reactivity in these systems is shown by hydroxy groups of these β-aminoalcohols. Thus it is concluded that in the first step of a reaction with primary diamines bifunctional epoxides always form linear polymers. It is also shown that cross-linking via secondary amino groups occurs more easily with increasing curing temperature. An additional cross-linking via additions of hydroxy groups only becomes possible with increasing cure temperature, but the amine additions are still preferred.

Key words: epoxides; amines; curing reactions; model reactions; nucleophilicity; order of reactivity

Polyamines and polyamidoamines are used as typical hardeners in cold-curing epoxy resins[1-5]. Their base material is derived from bisphenol-A epoxide (1) (Fig. 1) of different degrees of pre-polymerization[5,6]. The polymers are formed by polyaddition of the functional groups of the curing agents onto the epoxy groups of the resin[5,7-9]. Technical products are filled with epoxy novolak and nonreactive components[10] and in this combination, epoxy resins are widely used as adhesives or resins for laminates[5,11], for example.

From the chemical point of view, only the reactive components, bisphenol-A epoxide (1) and hardeners, have to be regarded. Their chemical behaviour rules mainly the properties of the resins. If amines are used as curing agents, different polymer systems (linear, thermoplastic or cross-linked, duroplastic) are possible.

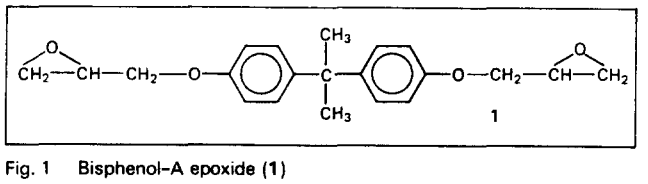

Fig. 1 Bisphenol-A epoxide (1)

The polymers can be formed by adding primary and secondary amino groups as well as hydroxy groups onto the epoxy rings. These functional groups differ in their chemical behaviour, which has been studied by model reactions. The results from these investigations allow some assumptions on curing conditions and properties of epoxy resins to be made.

Model epoxy resins

The difficulties in analysing cross-linked polymers are well known. Without chemical decomposition they are not analysable by most physical and chemical methods. Therefore, the model epoxy compound 1.2-epoxy-3-(4-methyl-phenoxy)-propane (2) (Fig. 2),

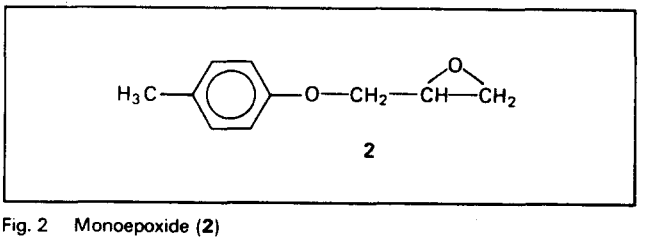

Fig. 2 Monoepoxide (2)

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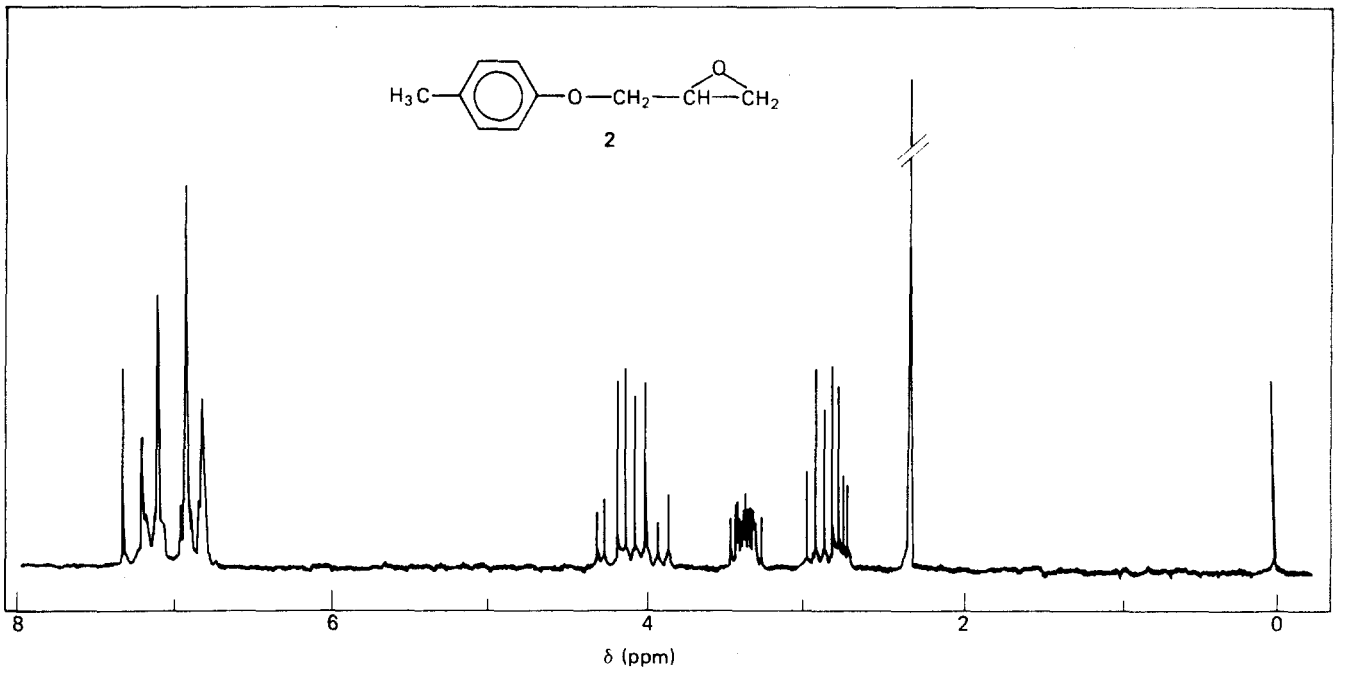

Fig. 3 80 MHz ^{1}H NMR spectrum of monoepoxide (2) ($CDCl_3$, TMS)

named 'monoepoxide', was chosen[12]. This compound (2) simulates the reactions which take place in an adhesive joint — without leading to polymeric products. Due to its monofunctionality the reactions occur at optimal conditions ie, the reaction products formed are monomeric and therefore can be stirred continuously. Compared with polymers, they are much more soluble. For this reason analytical and preparative separations as well as physical and chemical analyses are possible.

Another reason for choosing monoepoxide (2) as the model epoxy compound results from its ^{1}H NMR spectrum. The aromatic methyl group gives a significant singlet at 2.28 ppm. This absorption sign with its integral allows the additive rate in different addition products to be easily distinguished[13] (as can be seen from Fig. 3).

Analytical techniques

Thin layer chromatography (TLC) was carried out on TLC aluminium sheets coated with silica gel 60 F_{254} (layer thickness 0.2 mm, from Merck) with toluene/acetonitrile solvent at a ratio of 2:1. Data from elemental analyses, obtained on a Perkin-Elmer elemental analyser 240, were expressed in per cent of molecular weight. From each mass spectrum, obtained on a Varian MAT 331 A instrument, the molecular ion and important fragmentations with their relative intensity in per cent were given. ^{1}H NMR spectra were recorded on a Bruker WP 80DS instrument at 80 MHz and ^{13}C NMR spectra on a Bruker 300 MHz spectrometer AM 300 at 75.5 MHz. The samples were dissolved in deuterated trichloromethane ($CDCl_3$) containing 1% trimethyl silane (TMS). 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, m — multiplet, AX- and AA'BB'-spin systems.

The experimental details and analytical data are given.

Model reactions

Reactions with amino groups

The reaction behaviour of monoepoxide (2) with amines was investigated at room temperature. Each reaction course was directly controlled by TLC.

It has been shown in previous publications[12, 14] that primary and secondary amines show a different reactivity with respect to addition onto epoxides. After 15 min reaction time, aliphatic primary amino groups are the first to react with epoxides (as shown in Fig. 4). Then reactions of secondary amino groups of the hardener (compound DETA (6)) follow after 4 h (see Fig. 5). The final reaction step results from the secondary amino groups of the secondary β-aminoalcohols formed and can be first detected after 12 h (as can be seen from Figs 4, 5). In principle, aromatic amines show the same reaction behaviour as their aliphatic analogues, but react ten times more

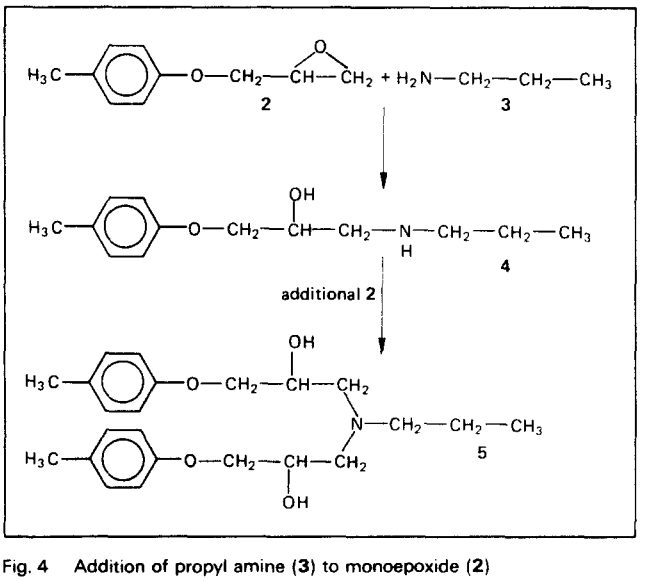

Fig. 4 Addition of propyl amine (3) to monoepoxide (2)

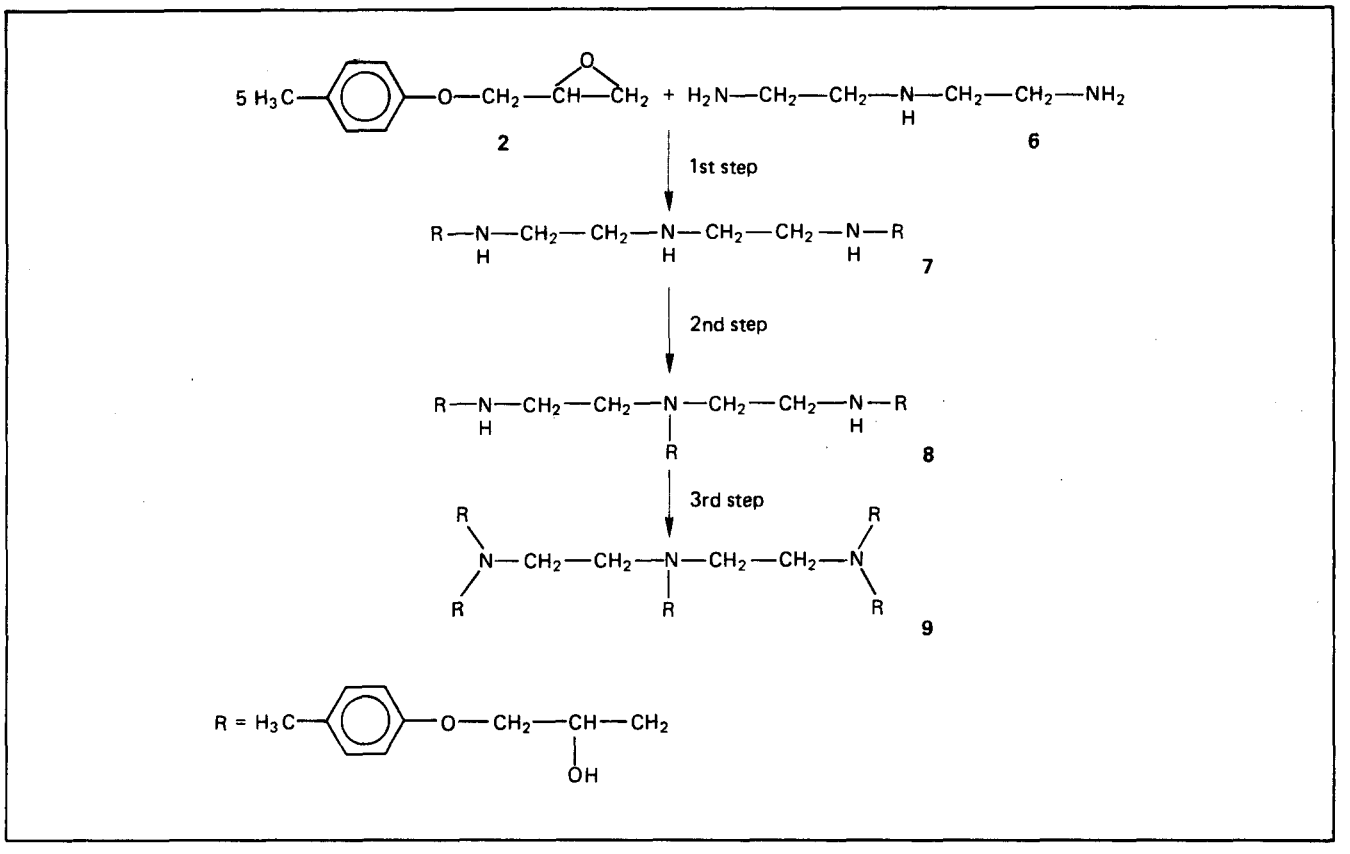

Fig. 5 Addition of DETA (**6**) to monoepoxide (**2**)

slowly. The reaction times are summarized in Figs 6 and 7.

Similar investigations[14] on a monoepoxide/^{tert}butyl amine system show that after comparable reaction times to those described for aliphatic amines, mono addition products are formed at first. The detection of the corresponding diadduct only becomes possible after 8 days. This second reaction is completed after 30 days.

It is evident from these results that the different reactivity of primary and secondary amino groups is directly ruled by their nucleophilicity. The reasons for this, therefore, have to be seen in terms of the increased steric hindrance of secondary amino groups,

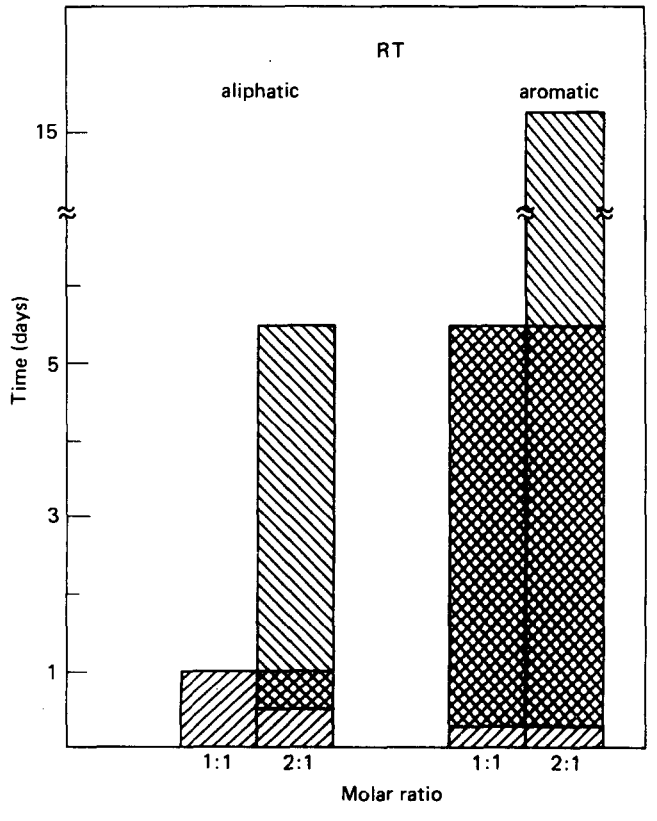

Fig. 6 Beginning and end of the mono- and diaddition of aliphatic and aromatic amines to monoepoxide (**2**); ▨ monoaddition, ▧ diaddition

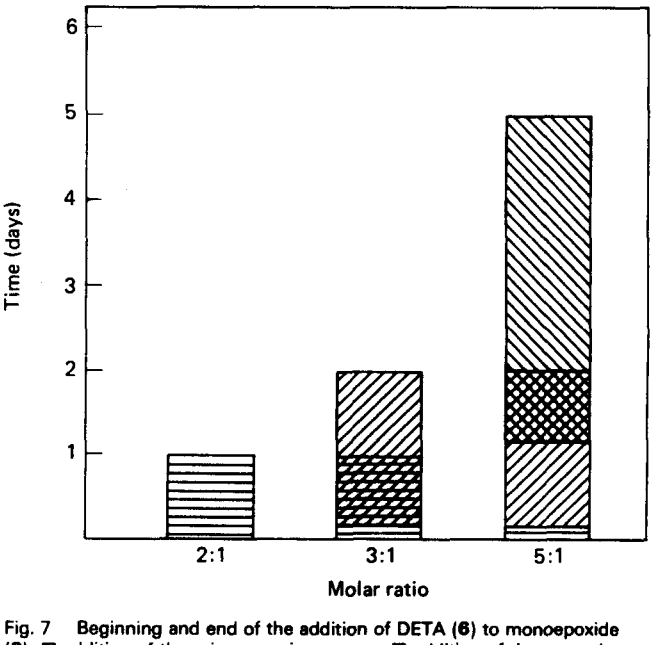

Fig. 7 Beginning and end of the addition of DETA (**6**) to monoepoxide (**2**); ■ addition of the primary amino groups, ▨ addition of the secondary amino group of 6, ▧ addition of the secondary amino group of 8

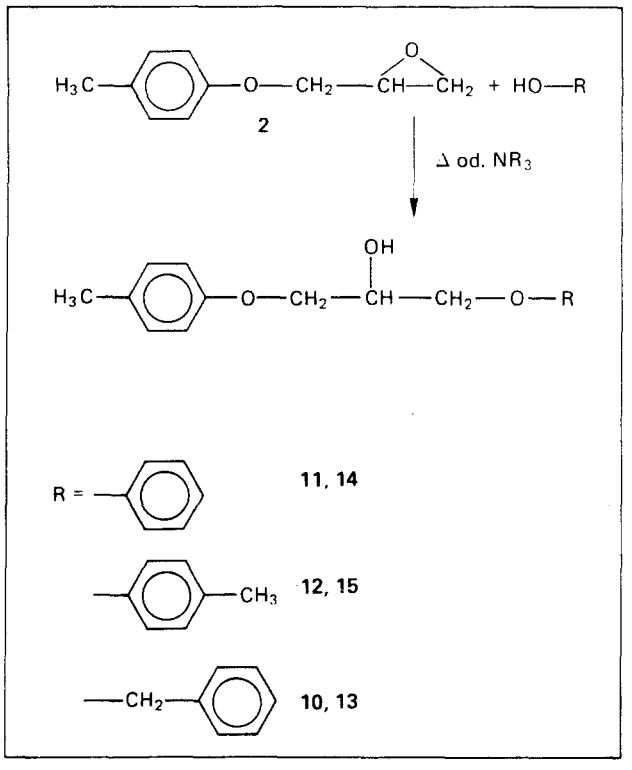

Fig. 8 Additions of alcohols (**10, 11, 12**) to monoepoxide (**2**)

which includes a decreased nucleophilic character. There is also another reason for this behaviour. In principle, the proton of the hydroxy group of the monoadduct is able to form an intramolecular hydrogen bridge bond with the nitrogen atom of the secondary amino group. The nucleophilicity is thereby reduced, as is the affinity to epoxy groups. In the case of the monoepoxide/^{tert}butyl amine monoadduct the chemical behaviour is mainly ruled by the steric crowding of the methyl groups at the N-combined tertiary carbon atom.

The β-aminoalcohols built up from monoepoxide (**2**) and amines have already been described[12, 13].

Reactions with hydroxy groups

In principle, hydroxy groups also are able to add on epoxy groups forming ether bonds. Therefore, their chemical behaviour was also studied[15].

First investigations were carried out with aliphatic alcohols (eg benzyl alcohol, **10**) and phenols (phenol, **11**, p-cresole, **12**) (Fig. 8). After 30 d at room temperature in no case did a reaction with monoepoxide (**2**) occur. Increasing the temperature to 80°C, the corresponding reaction products (**13, 14, 15**) could be detected by TLC after a reaction time of 4 d but these reactions had not been completed after 30 d.

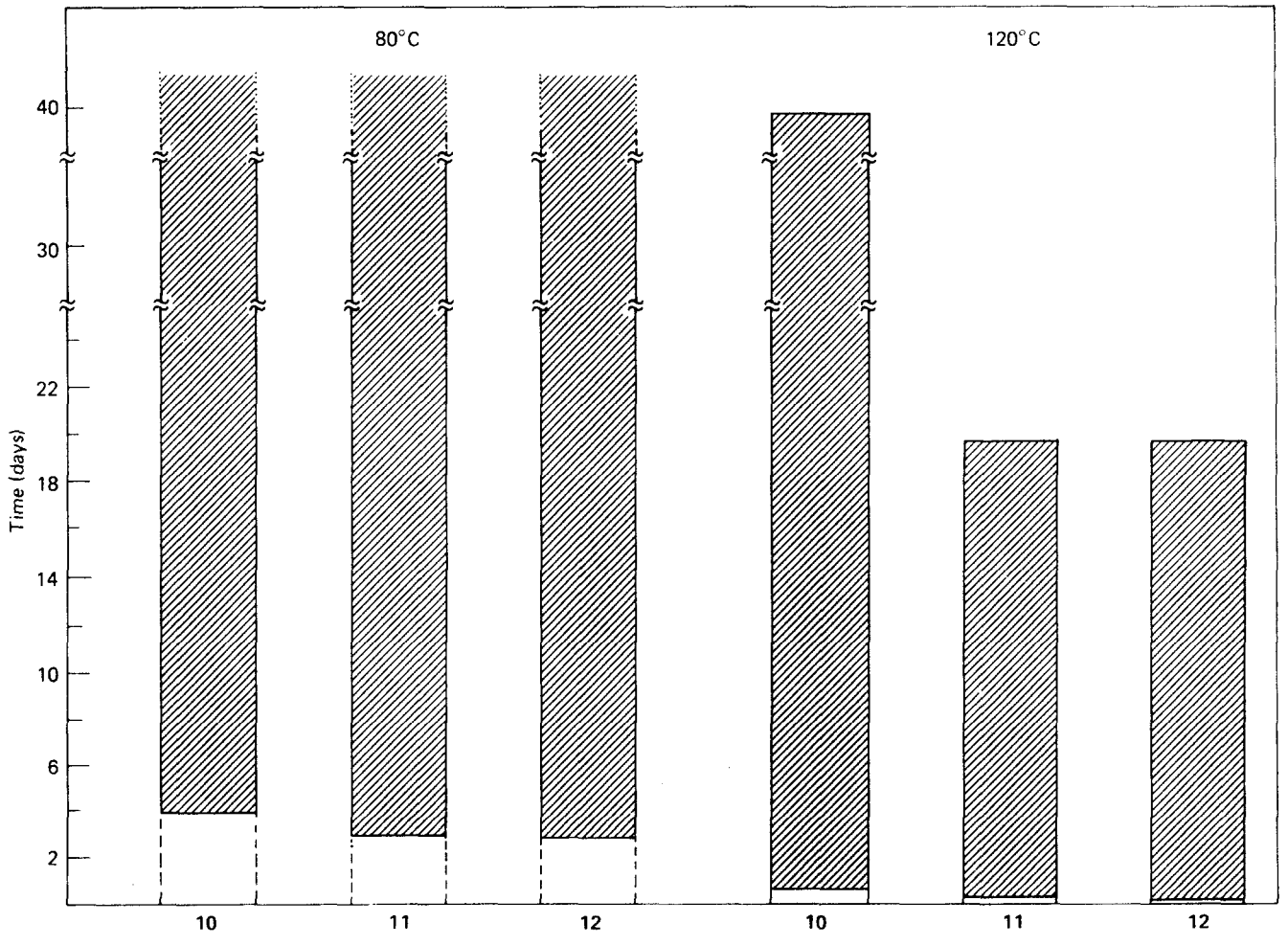

Fig. 9 Beginning and end of the uncatalysed addition of alcohols (**10, 11, 12**) to monoepoxide (**2**) at different temperatures; □ no addition product detectable, ▨ addition reaction

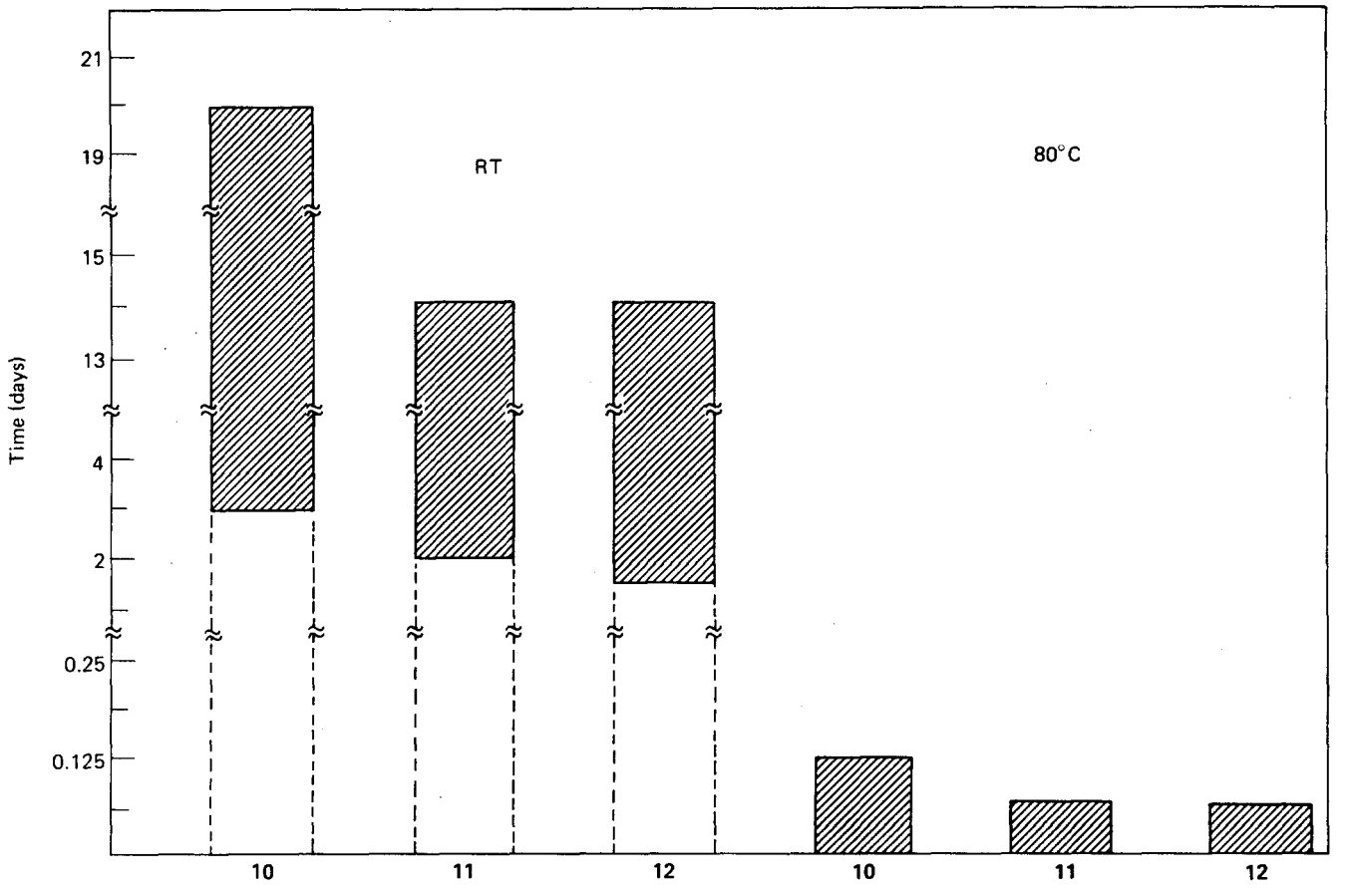

Fig. 10 Beginning and end of the catalysed addition of alcohols (**10, 11, 12**) to monoepoxide (**2**) at different temperatures; □ no addition product detectable, ▨ addition reaction

By increasing the temperature to 120°C the reaction times had been reduced. The adducts (**13, 14, 15**) became detectable after 6–8 h. After this, the reactions of the phenols (**11, 12**) were completed after 20 d, and of benzyl alcohol (**10**) after 40 d (Fig. 9).

The reaction times could be reduced remarkably if tertiary amines such as N,N-dimethylbenzyl amine were added in catalytic quantities (as can be seen from Fig. 10). At room temperature, the addition products became detectable after 2–3 d. The reactions of phenols (**11, 12**) were completed after 14 d, and of benzyl alcohol (**10**) after 20 d. Thus, in these systems, increasing the temperature to 120°C led to reaction times of 2–4 h.

Due to the catalysing effect of added tertiary amines, the intramolecular effect of the tertiary amino group formed in the monoepoxide/amine-adduct had also to be investigated.

Experimental details

The reactions with alcohol compounds were carried out as follows:

1.64 g (0.01 mole) monoepoxide (**2**) and the corresponding quantity of each alcohol respectively were stirred under different conditions. Benzyl alcohol (**10**), phenol (**11**) and p-cresole (**12**) were used initially. The reaction courses were controlled by TLC. In catalysed systems, 67 mg (0.0005 mole) N,N-dimethyl benzyl amine was added.

The reactions of the uncatalysed systems were carried out at room temperature, 80°C and 120°C, the reactions of the catalysed systems at room temperature and 80°C.

The reaction products 1-(4-methyl-phenoxy)-2-hydroxy-3-benzyloxy-propane (benzyl alcohol-adduct) (**13**), 1-(4-methyl-phenoxy)-2-hydroxy-3-phenoxy-propane (phenol-adduct) (**14**), and [1.3-di-(4-methyl-phenoxy)]-2-hydroxy-propane (p-cresole-adduct) (**15**) were obtained from monoepoxide and benzyl alcohol (**10**), monoepoxide and phenol (**11**) and monoepoxide and p-cresole (**12**) respectively, always in molar ratios of 1:1.

The reaction times are summarized in Table 1. Analytical data are given in Table 2 and spectroscopical data in Tables 3 and 4.

At room temperature, in the reaction of monoepoxide and propyl amine and also octyl amine at a molar ratio of 3:1, the amine-adducts (**5, 17**) were formed (as shown in Fig. 11). After six days, reaction products (**16, 19**) formed by addition of the hydroxy groups onto remaining epoxide (**2**) could be detected by TLC. The reaction was completed after 20 days, when no monoepoxide (**2**) remained. Increasing the temperature to 120°C led to shorter reaction times (Fig. 12). The monoepoxide/dimethylamine-adduct (**18**) showed that at these conditions an addition of the OH-group to monoepoxide (**2**) had occurred after 4 h. The reactions were completed after 4 d. The reaction times of monoepoxide and primary amine-diadducts (**5, 17**) were similar.

The same reaction with aromatic amines at room temperature and at 120°C was completed by forming

Table 1. Reaction times for compounds 10, 11, 12 with monoepoxide

Compound formed	Temperature (°C)	Reaction times (days)	
		uncatalysed	catalysed
13	RT	—	20
14		—	14
15		—	14
13	80	> 30	0.167
14		> 30	0.104
15		> 30	0.083
13	120	40	
14		20	
15		20	

diadducts. In this system the OH-groups do not react with epoxides.

The nucleophilicity of hydroxy groups rules their reaction behaviour in epoxy systems. Due to their lower nucleophilic character, alcohols and phenols need an increase in temperature for the addition to epoxides. Tertiary amines accelerate the reaction, but an increase in temperature is needed for shorter reaction times. Intramolecular tertiary amino groups accelerate the addition of β-aminoalcohols to epoxides. Due to the increased steric hindrance of these amino groups the acceleration is reducd. Aromatic tertiary amino groups are not able to catalyse the addition.

In this context it is remarkable that thiophenol (21) (Fig. 13) as a sulphur analogue to the aromatic alcohols (phenols) reacted extremely fast with monoepoxide (2). After 30 s reaction time the addition product (22) was detectable by TLC. The addition was completed after 2 d. This reaction occurred via an addition of the resonance-stabilized thiophenolate anion.

Monoepoxide (2) and β-aminoalcohols (5, 17, 18) were stirred in molar ratios of 1:1. The reaction was completed when no monoepoxide (2) could be detected by TLC (toluene/acetonitrile 2:1). The reaction products were not purified chromatographically. They were identified by mass spectroscopical methods. Details are given in Tables 5 and 6.

Thiophenol (21) and monoepoxide (2) at a molar ratio of 1:1 were stirred at room temperature. After 30 s reaction time the addition product (22): 1-thiophenyl-2-hydroxy-3-(4-methyl-phenoxy)-propane could be detected by TLC (solvent: dichloromethane). The reaction was completed after 2 days.

Table 2. Analytical data for compounds 13, 14, 15

	Compounds		
	13	**14**	**15**
R_f values	0.64	0.67	0.72
Molecular weights (g mol^{-1})	273.34	258.32	273.34
Elemental analyses (%MW)			
C (calculated)	74.97	74.40	74.97
C (measured)	74.88	74.31	75.06
H (calculated)	7.40	7.02	7.40
H (measured)	7.51	7.11	7.31

Conclusions

The results of the model studies indicate that the *nucleophilicity* of functional groups of the curing agents or reaction products formed is the determining parameter concerning the curing of epoxy resins. The functional group with the highest nucleophilic character is the most reactive. Thus, in this connection aromatic SH-groups show the highest reactivity due to their resonance-stabilization. The reactions with amines take place in several steps. Primary amino groups, due to their nucleophilic character, first add to epoxy groups, followed by secondary amino groups of

Table 3. Mass spectra$^+$ data for compounds 13, 14, 15

Compounds:	Relative intensities of ions, m/z (%)					
	13		**14**		**15**	
$M^+\cdot$	272	(18)	$M^+\cdot$	258 (50)	$M^+\cdot$	272 (45)
$(M-C_7H_7O)^+\cdot$	165	(4)	$(M-C_6H_5O)^+\cdot$	165 (2)	$(M-C_7H_7O)^+\cdot$	165 (14)
$(M-C_7H_8O)^+\cdot$	164	(1)	$(M-C_6H_6O)^+\cdot$	164 (8)	$(M-C_7H_8O)^+\cdot$	164 (56)
$(M-C_9H_{11}O_2)^+\cdot$	121	(7)	$(M-C_7H_8O)^+\cdot$	150 (23)	$(M-C_9H_{11}O_2)^+\cdot$	121 (73)
$(M-C_{10}H_{12}O_2)^+\cdot$	108	(48)	$(M-C_8H_9O_2)^+\cdot$	121 (27)	$(M-C_{10}H_{12}O_2)^+\cdot$	108 (100)
$(M-C_{10}H_{13}O_2)^+\cdot$	107	(13)	$(M-C_9H_{10}O_2)^+\cdot$	108 (100)	$(M-C_{10}H_{13}O_2)^+\cdot$	107 (46)
$(M-C_{10}H_{13}O_3)^+\cdot$	91	(100)	$(M-C_9H_{11}O_2)^+\cdot$	107 (52)	$(M-C_{10}H_{13}O_3)^+\cdot$	91 (64)
			$(M-C_{10}H_{12}O_2)^+\cdot$	94 (42)		
			$(M-C_9H_{11}O_3)^+\cdot$	91 (29)		

$^+$ at 70 eV

Table 4. NMR spectra† data for compounds 13, 14, 15

Compounds:		Chemical shifts, δ (ppm) 13	14	15
^1H NMR spectra (80 MHz):				
H-aromatic	m	7.33	7.20	
H-aromatic	AA'BB'	6.93	6.95	6.95
$\underline{CH}_2$-aromatic	AX	4.63		
-$\underline{CH}$(OH)	m	4.02	4.35	4.33
Ph-O-$\underline{CH}_2$	d		4.14	
-O-$\underline{CH}_2$	d	4.00	4.12	4.11
-CH_2-O-$\underline{CH}_2$	d	3.65		
$\underline{CH}_3$-aromatic	s	2.28	2.28	2.28
^{13}C NMR spectra (75.5 MHz)				
C-aromatic				
C-O*	s	158.44		
C-O	s	156.34	156.34	156.38
$\underline{C}$-CH_2	s	137.70		
$\underline{C}$-CH_3	s	130.06	130.48	130.40
C-3, C-5	d	129.70	130.00	129.93
C-3, C-5*	d	128.22	129.52	
C-2, C-6	d	127.55	114.56	
C-4*	d	126.75		
C-2, C-6	d	114.27	114.43	114.44
$\underline{CH}_2$	t	70.98		
$\underline{CH}_3$	q	20.25	20.46	20.43
C-aliphatic				
-CH_2-O-$\underline{CH}_2$	t	73.22		
-O-$\underline{CH}_2$	t	68.94	68.89	68.93
-$\underline{CH}$(OH)	d	68.80	68.79	68.72
Ph-O-$\underline{CH}_2$	t	68.71		

*mono-substituted rings
†samples dissolved in $CDCl_3$ containing 1% trimethyl silane
s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; AX, AA'BB', spin systems

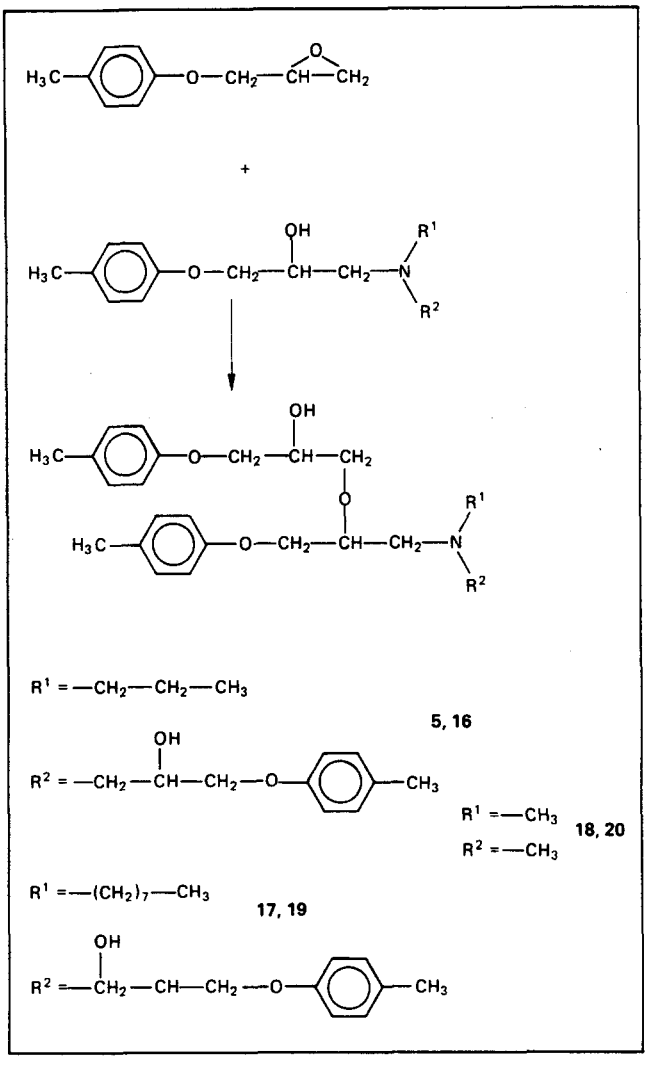

Fig. 11 Addition of β-aminoalcohols (**5, 17, 18**) to monoepoxide (**2**)

Table 5. Data for compounds 16, 19, 20

	Compounds 16	19	20
Reaction time (days) (for compounds to be formed)			
at RT	20	—	20
at 120°C	4	2	4
R_f values	0.51	0.37	0.57

the hardener, then by secondary amino groups formed in addition products (β-aminoalcohols), and finally hydroxy groups of the β-aminoalcohols formed react with epoxides. In a first approximation the following order of reactivity results:

$$-SH_{arom} \gg -NH_2 > = NH > -NH^* \gg -OH^* > -OH$$

where * indicates belonging to β-aminoalcohols.

In this context it is remarkable that in the case of amines containing roomy groups at the N-combined tertiary carbon atom the difference in the reactivity between amine and corresponding monoadduct is very distinct. The reason, therefore, has to be seen in the greatly increased steric hindrance in these mono-addition products.

Table 6. Mass spectra† data for compounds 16, 19, 20

Compounds:	16		19		20	
	Relative intensities of ions, m/z (%)					
$M^+\cdot$	551	(2)	$M^+\cdot$	373 (2)	$M^+\cdot$	621 (1)
$(M-C_2H_5)^+\cdot$	522	(3)	$(M-C_8H_9O)^+\cdot$	252 (4)	$(M-C_7H_{15})^+\cdot$	522 (3)
$(M-C_8H_9O)^+\cdot$	430	(3)	$(M-C_{19}H_{23}O_4)^+\cdot$	58 (100)	$(M-C_8H_9O)^+\cdot$	500 (5)
$(M-C_{19}H_{23}O_4)^+\cdot$	236	(100)			$(M-C_{19}H_{23}O_4)^+\cdot$	306 (100)

†at 70 eV

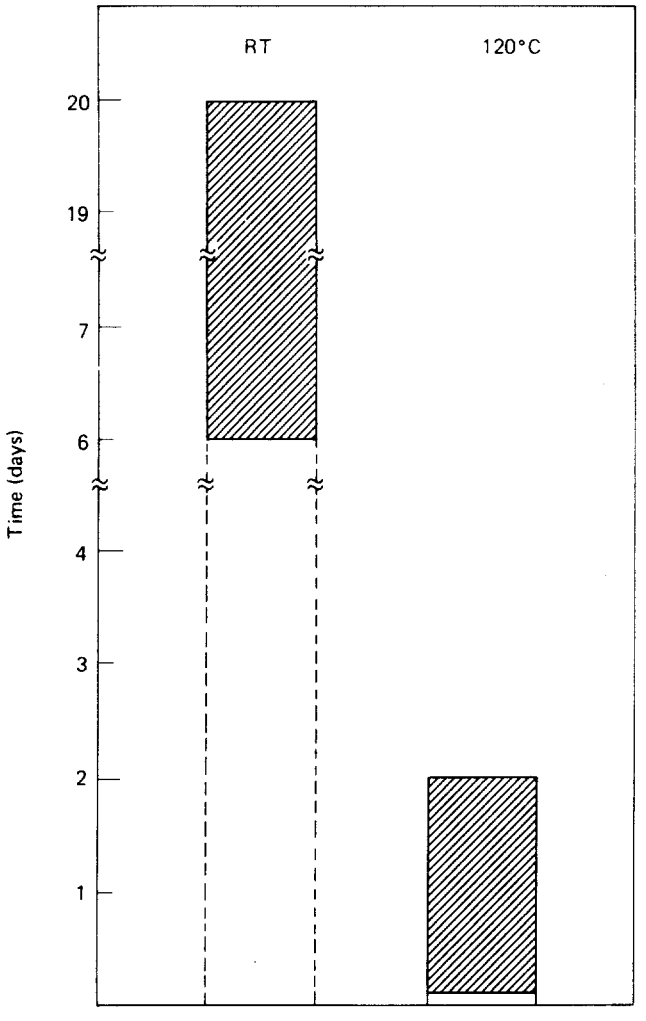

Fig. 12 Beginning and end of the addition of β-aminoalcohols (**5**, **17**, **18**) to monoepoxide (**2**) at different temperatures; □ no addition product detectable, ▨ addition reaction

Due to their lower nucleophilic character the reactivity of hydroxy groups is rather low. Their reactions with epoxy groups only become possible with an increase in reaction temperature or addition of tertiary amines as accelerators. The catalytic effect of an intramolecular tertiary amino group in reaction products (β-aminoalcohols) is less distinct due to their rather high steric hindrance. Therefore, reactions with epoxides via additions of hydroxy groups of epoxide/amine reaction products only take place after completing the amine additions.

The transfer onto technical, bifunctional epoxy

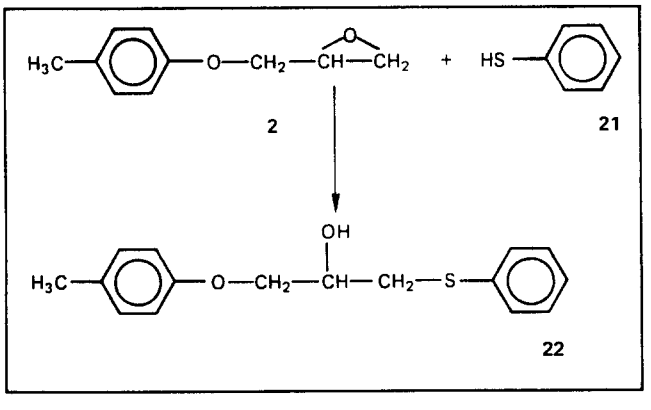

Fig. 13 Addition of thiophenol (**21**) to monoepoxide (**2**)

Table 7. Data for compound 22

R_f value	0.53
Molecular weight (g mol^{-1})	274.38
Elemental analysis:	
C (calculated)	70.04
C (measured)	70.13
H (calculated)	6.61
H (measured)	6.43
S (calculated)	11.69
S (measured)	11.78

Mass spectrum (70 eV)
m/z, relative intensity (%)

$M^+ \cdot$	274	(43)
$(M-C_7H_7O)^+ \cdot$	167	(100)
$(M-C_8H_9O)^+ \cdot$	153	(2)
$(M-C_7H_7S)^+ \cdot$	151	(2)
$(M-C_7H_8S)^+ \cdot$	150	(4)
$(M-C_9H_{11}O_2)^+ \cdot$	123	(65)
$(M-C_9H_{10}SO)^+ \cdot$	108	(29)
$(M-C_9H_{11}SO)^+ \cdot$	107	(14)
$(M-C_9H_{11}SO_2)^+ \cdot$	91	(28)

Table 8. NMR spectrum† data for compound 22

	Chemical shifts, δ (ppm)	
^1H NMR spectrum (80 MHz):		
H-aromatic*	m	7.31
H-aromatic	AA'BB'	6.93
-CH(OH)	m	4.01
-O-CH_2	d	4.02
-S-CH_2	dd	3.19
CH_3-aromatic	s	2.28
^{13}C NMR spectrum (75.5 MHz):		
C-aromatic		
C-O	s	156.30
C-S	s	135.20
C-CH_3	s	130.52
C-3, C-5	d	129.96
C-3, C-5*	d	129.11
C-2, C-6*	d	126.61
C-4*	d	123.96
C-2, C-6	d	114.45
CH_3	q	20.46
C-aliphatic		
-O-CH_2	t	70.32
-CH(OH)	d	68.65
-S-CH_2	t	29.71

*mono-substituted ring
†sample dissolved in $CDCl_3$ containing 1% trimethyl silane
s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet; AA'BB', spin system

systems allows the conclusion that with primary diamines the curing reactions always start with formation of linear polymers with thermoplastic properties. This reaction behaviour leads to an increasing viscosity of the resin. A reduced mobility of the unreacted monomers results from this and, in a resin, the growth of chains will decrease. The addition of the secondary amino groups of β-aminoalcohols

formed onto the remaining epoxide is hindered for two reasons: the lower reactivity of these reaction products which results from the decreased nucleophilic character of the functional groups; and the immobility of reaction partners in the polymer system. For these reasons in all cases the rate of cross-linking at room temperature will be small. Increasing the curing temperature leads to higher rates of cross-linking but, generally, the formation of linear polymer chains is preferred.

An additional cross-linking via additions of hydroxy groups formed only becomes possible if all amino groups have reacted and the curing temperature is increased. Nevertheless, the possible etherification in epoxy resins becomes interesting when considering the storage stability of epoxy monomers. If ageing stability in adhesive joints is to be observed, the hydrophobic character of ether bonds should promise interesting properties of resins. This is the subject of further investigations, the results of which will be published in a separate communication.

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