Structural features in epoxy networks from *N,N*-diglycidyl epoxies and amines: 2. Ether ring formation and polymer structure in the reactions of *N,N*-diglycidylaniline with aniline and substituted anilines

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Intramolecular ether cyclization occurs much more readily than previously recognized in the cure of *N,N*-diglycidyl epoxies with aromatic amines. Even at a modest reaction temperature of 120°C, the polymer from *N,N*-diglycidylaniline (DGA) and aniline was shown by ^{13}C n.m.r. spectroscopy to contain morpholinyl and perhydro-1,4-oxazepinyl end groups which accounted for 6 and 4%, respectively, of consumed epoxy groups, whereas intramolecular amine cyclization to give the simple perhydro-1,5-diazocine isomers accounted for 19%. *ortho*-Methyl substituents in the amine had little steric influence on the extent of ether cyclization, but electronegative substituents had a very marked effect such that it was increased to 28% with 2,4,6-trichloroaniline and 26% with 3,5-bis(trifluoromethyl)aniline. The polymer from DGA and aniline was linear and had a completely random tacticity: variation of reaction temperature and reactant ratio led to only modest improvements in molecular weight (maximum value about 3000) because of the relative ease of chain termination by ether cylization. Two new thermal reactions of the polymer are proposed to explain n.m.r. spectral and g.p.c. data, a cleavage reaction to give secondary amine and tetrahydroquinolyl end groups, and water elimination from adjacent hydroxyl groups to form an in-chain morpholine ring. The reactions were surface- and temperature-dependent. Polymer degradation also occurred slowly in tetrahydrofuran solution at room temperature.

(Keywords: *N,N*-diglycidylaniline; aniline; substituted anilines; ether cyclization; polymer tacticity; polymer stability; g.p.c.; ^{13}C n.m.r. spectroscopy)

INTRODUCTION

As discussed in part 1[1], the structure of the polymer network obtained by the amine cure of *N,N*-diglycidyl epoxies is far from clear. The structure is much more complicated than that obtained from *O*-glycidyl epoxies because of competing intramolecular cyclization reactions with the possible formation of morpholine, perhydro-1,4-oxazepine, perhydro-1,5-diazocine, and tetrahydroquinoline rings. Factors affecting the formation of these rings in a competitive situation have not been reported. As previously stated[1], it was considered that the reactions of *N,N*-diglycidylaniline (DGA) with suitably substituted anilines would provide a useful model system for determining the extent to which the relative formation of these rings is influenced by steric and electronic effects. A further objective was to extend the ^{13}C n.m.r. spectroscopy data base of such structures as an aid to recognizing such features in a solid-state network structure. It was reported in part 1[1] that the predominant non-polymeric products in the reactions of DGA with aniline and substituted anilines were the *cis*- (equatorial/equitorial 3,7-dihydroxy) and *trans*- (axial/equitorial 3,7-dihydroxy) isomers of the 8-membered perhydro-1,5-diazocine ring, and that any other non-polymeric products were formed in very minor amounts. Steric effects were more important than polar effects in determining the extent of this cyclization reaction: the combined yield of these isomers increased from about 15% with aniline to about 35% with 2,6-dichloroaniline and to 45% with 2,6-dimethylaniline; electronegative *meta*-trifluoromethyl substituents, however, increased the yield only slightly. These results were somewhat surprising since it had been thought that such structural modifications might favour cyclization reactions between the hydroxyl and epoxy groups to give the 6-membered morpholine and 7-membered perhydro-1,4-oxazepine rings at the expense of the perhydro-1,5-diazocine ring, and that such simple products might be isolated and characterized. However, it was apparent by h.p.l.c. analysis that only traces of any other simple compounds were present, and that such structures, if formed, were incorporated into the polymer structure.

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In this paper, the use of ^{13}C n.m.r. spectroscopy to characterize the other cyclic structures and that of the polymer obtained in the aforementioned reactions is reported. Further, the extent to which the occurrence of these other cyclization reactions is effected by steric and electronic factors as well as by reaction temperature and reactant stoichiometry is discussed.

EXPERIMENTAL

Instrumentation

The instrumentation and procedures used were as described previously[1] except that for g.p.c. analysis, a 50 Å + 100 Å + 500 Å column combination was used. Molecular weight values (M_n) were based on poly(oxypropylene)glycol standards from Waters.

^{13}C n.m.r. spectra were measured in $CDCl_3$ or acetone-D_6 (about 20% concentration) with broadband proton decoupling at 75.47 MHz on a Bruker MSL-300 superconducting multinuclear n.m.r. spectrometer using a 5 mm $^{13}C/^{1}H$ dual or a 10 mm broadband multinuclear probe at ambient temperature (approximately 21°C). The number of scans varied from about 250 to 20000 depending upon the sample and the experiment. The INEPT pulse sequence was used to distinguish between methine and methylene carbons. Suitable precautions were taken to avoid errors in quantitative measurements. Chromium(III) acetylacetonate relaxation agent and long delay times were used to avoid errors from incomplete relaxation, and the standard gated decoupling technique was employed to eliminate nuclear Overhauser effects. Most of the spectra in this paper were recorded in acetone-D_6 solutions since this was a good solvent for the total reaction products. It was observed that solvent shifts of up to 2 ppm could occur between spectra in acetone-D_6 and $CDCl_3$. Some of the shifts quoted in part 1[1], particularly for the 8-membered ring compounds, refer to $CDCl_3$ solutions, and are significantly different from those observed in the acetone-D_6 solutions of this paper.

Reactions between DGA and aniline and substituted anilines

The products investigated in this paper were those obtained as described in part 1[1] from the sealed tube reactions between DGA and aniline, 2,6-dichloroaniline, 2,6-dimethylaniline and 2,4,6-trichloroaniline.

Sublimation treatment of the product from DGA and aniline

From soda glass. A small portion (0.55 g) of the product from the reaction at 176°C between equimolar amounts of DGA and aniline was heated in a soda glass sample tube at 180°C for 18 h at <0.005 mm to leave a polymeric residue (0.46 g).

From HF/HNO_3-washed Pyrex. A second portion (2.0 g) was heated at 160°C for 22 h at <0.1 mm in a Buchi GKR-50 sublimator which had previously been washed with an HF/HNO_3 cleaning solution, and gave a polymeric residue (1.65 g).

A third portion (0.59 g) was similarly treated at 160°C for 1 h, at 180°C for 1 h,at 200°C for 2 h, and then at 220°C for 18 h and gave polymeric residue (0.45 g).

The g.p.c. and ^{13}C n.m.r. data for the above residues are presented in the Results and Discussion section.

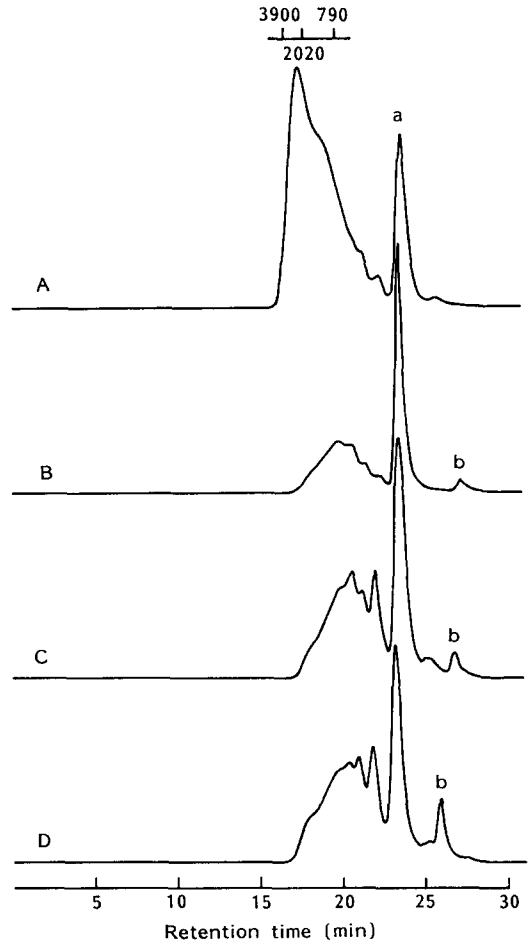


Figure 1 G.p.c. traces for the reaction products from DGA and: A, aniline at 180°C/18 h; B, 2,6-dimethylaniline at 160°C/18 h; C, 2,6-dichloroaniline at 200°C/12 h; D, 2,4,6-trichloroaniline at 200°C/24 h. The corresponding perhydro-1,5-diazocines (A) and unconsumed amines (B) are indicated, and an M_n scale for poly(oxypropylene)glycol standards is shown

Reactions between DGA and meta*-trifluoromethyl substituted anilines*

Mixtures of DGA (5.00 g) and an equimolar amount of the amine, 3-trifluoromethylaniline or 3,5-bis(trifluoromethyl)aniline, were stirred for a few minutes at 80°C. Each resultant solution was divided between two Pyrex tubes which were degassed and sealed. The first was heated at 150°C for 18 h and then at 180°C for 5 h; after this treatment, the second was then heated at 200°C for 4 h. The products were analysed by ^{13}C n.m.r. and g.p.c.

Effect of molar ratio on the product from DGA and aniline

Mixtures of freshly distilled aniline (about 0.7 g) and a 0, 2.5, 5.0 and 7.5% molar excess of DGA were stirred at 60°C for 10 min. Each resultant solution was subjected to different heat treatments by being roughly divided between three Pyrex tubes which were degassed and sealed: the first was heated at 120°C for 7 days, the second at 145°C for 7 days, and the third at 145°C for 7 days and then at 178°C for 17 h. The products were analysed by ^{13}C n.m.r. and g.p.c.

RESULTS AND DISCUSSION

Polymer structure

The g.p.c. traces of the crude products obtained from DGA and aniline, 2,6-dimethylaniline, 2,6-dichloroaniline and 2,4,6-trichloroaniline are shown in *Figure 1*.

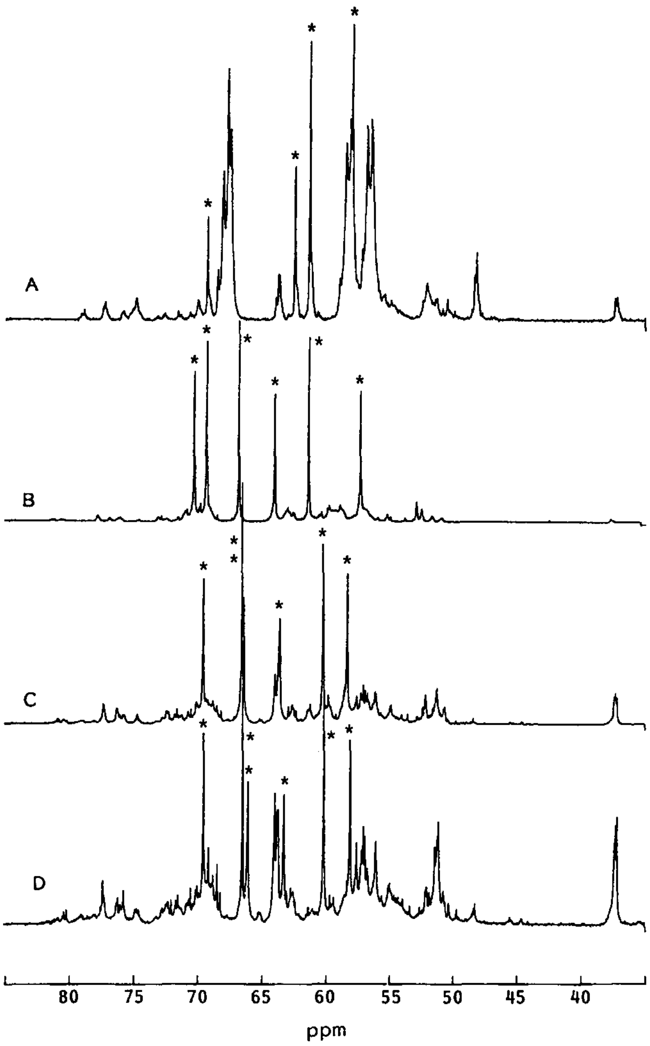


Figure 2 ^{13}C n.m.r. spectra (75.47 MHz) in acetone-D_6 of the reaction products from DGA and: A, aniline at 160°C/18 h; B, 2,6-dimethylaniline at 160°C/18 h; C, 2,6-dichloroaniline at 200°C/12 h; D, 2,4,6-trichloroaniline at 200°C/24 h

It can be seen that the perhydro-1,5-diazocine derivatives are well resolved from the polymeric and any oligomeric product. Aniline gave little oligomeric product, but the molecular weight of the polymer (about 2300) was only modest. The substituted anilines gave mainly oligomeric product. The corresponding ^{13}C n.m.r. spectra are shown in *Figure 2*. The high intensity sharp peaks associated with the *cis* and *trans* perhydro-1,5-diazocine isomers are marked with an asterisk and are fully discussed in part 1[1]. Only the polymer from the reaction with aniline gave a clearly defined ^{13}C n.m.r. spectrum, presumably because of its symmetrical features and low oligomeric content, and discussion of polymer structure will be confined to this system.

Previous workers[2–4] have used model compound data to describe the chemical shifts expected for the >$NCH_2CH(OH)CH_2N$< unit in a linear situation but have not considered tacticity effects. Thus, just as the asymmetry of the epoxy group in DGA leads to cyclic isomers, it also leads to polymer tacticity as shown in *Figure 3*. Tacticity might be expected to cause small chemical shift differences, and such splittings are, in fact, observed. Three groups of peaks of about equal intensity are seen, and consist of an equal intensity doublet at 56.5 and 56.9 ppm, a similar doublet at 58.2 and 58.6 ppm, and a triplet at 68.2, 67.9 and 67.7 ppm of intensity ratio 1:2:1. The ratio of the combined doublets, clearly due to $-CH_2N$<, and the triplet, clearly due to $-CH(OH)-$, is 2:1. The spectrum is readily explained with reference to *Figure 3*. It is assumed that, because of ease of nitrogen inversion, the phenyl group occupies the lowest energy configuration and so tacticity does not arise directly from the arrangement of this ring. The asymmetry of the glycidyl group translates into *meso* (m) and *racemic* (r) arrangements of the derived adjacent hydroxyl groups. At first sight tacticity effects might be expected to be small since the asymmetrical centres are five atoms apart. However, the phenyl group has the effect of transmitting an interaction between adjacent hydroxyl groups: if the two hydroxyl groups are in a *meso* configuration, the phenyl group can take up the most favourable configuration and thus minimize the *γ-gauche* interaction, which is the prime cause of chemical shift differences due to tacticity effects in vinyl polymers[5,6]; however, for the *racemic* configuration, such steric adjustment cannot occur. The intervening phenyl groups should thus produce tacticity-dependent chemical shift differences similar to those observed in vinyl polymers, that is 2–5 ppm. In accordance with this argument, the $-CH_2-N$< carbon atom, designated 'a' in *Figure 3*, shows as a doublet because of the *meso* or *racemic* arrangement of the hydroxyl groups to its left and right, and the splitting of about 1.7 ppm between the bands centred at 56.7 and 58.4 ppm is assigned to this effect. However, this carbon atom also shows a similarly based smaller splitting of about 0.2 ppm due to the relative orientations of the two hydroxyl groups on its right. The $-CH_2-N$< carbons thus experience two unequal diad splittings. The four peaks are of approximately equal

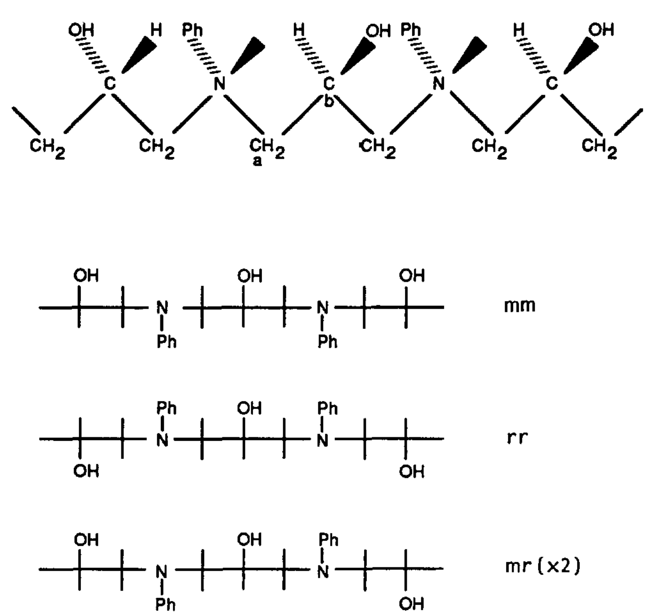


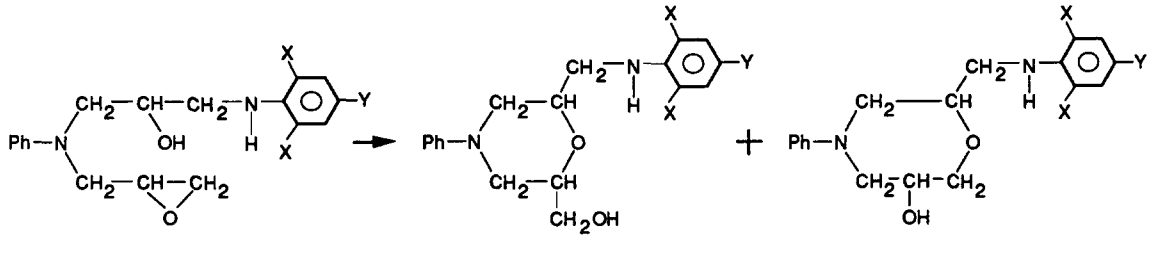
Figure 3 Tacticity in the polymer from DGA and aniline

areas indicating roughly equal amounts of *meso* and *racemic* units. A different symmetry holds for a –CH(OH)– carbon: this carbon, designated 'b' in *Figure 3*, is symmetrically placed relative to the two adjacent hydroxyl groups. Three peaks for the three possible triad configurations shown would be expected, and these are in fact observed in a ratio of 1:2:1 in accordance with a random arrangement of mm, mr and rr triads. The other region which shows measurable splitting is the quaternary carbon atom of the phenyl group at about 150 ppm: there are two peaks of approximately equal intensities at 148.6 and 149.3 ppm corresponding to the two possible arrangements of the adjacent hydroxyl groups. These peaks showed additional, much smaller splittings due to longer range effects.

The ^{13}C n.m.r. spectrum of the polymer is thus consistent with a linear structure having a completely random tacticity. It can thus be concluded that no intermolecular reaction between hydroxyl and epoxy groups, which would have caused chain branching, had occurred. This was as expected, since *N*-glycidyl compounds are essentially unreactive to ethanol in the presence of aromatic amines[7], and very recent model compound studies[8] have demonstrated the lack of reactivity between secondary alcohol and *N*-glycidyl groups.

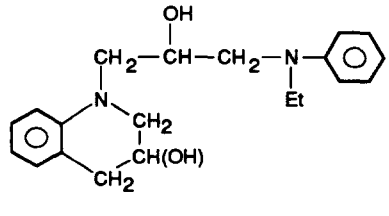
Other intramolecular cyclization reactions

The objective of this investigation was to try to encourage intramolecular reaction of the epoxy group with the secondary alcohol group at the expense of reaction with the secondary amine group by utilizing the steric and electronic effects of *X* and *Y* substituents in (*I*) to reduce the reactivity of the latter: It was pointed out[1] that Attias *et al.*[3] has reported the formation of such morpholine and perhydro-1,4-oxazepine derivatives from the reaction between DGA and *N*-ethylaniline, a system in which no competing reaction with secondary amine can occur. The carbons adjacent to ether oxygen in the



(I)

$\diagdown$
CH–O– element (present in both rings) and in the
$\diagup$
$-CH_2-O-$ element (present in the latter ring) were associated with shifts in the 70–80 ppm region, and the carbon of the primary alcohol, which is present as a morpholine ring substituent, with a shift of 64.1 ppm.



(II)

These authors[3] also recognized another cyclization reaction which yielded a tetrahydroquinoline product (*II*) for which peaks at about 38 ppm were assigned to the Ar–CH_2– carbon and at about 64 ppm to the

$\diagdown$
CH(OH) ring carbon. In a separate publication[9] on
$\diagup$

the base-catalysed cyclopolymerization of DGA, we shall report that the ether carbons present in the 6- and 7-membered ether rings formed, also provide complicated bands in the 70–80 ppm region. As can be seen in *Figure 2A*, the ^{13}C n.m.r. spectrum of the product from the reaction of DGA with aniline shows weak absorptions in the 70–80 ppm region and a peak at 64 ppm which can be attributed to 6- and 7-membered ether rings. Like Attias *et al.*[3], we also used a pulse sequence procedure to distinguish between methylene and methine carbon atoms in the complex 70–80 ppm region and, in good agreement with them, observed a split inverted shift at 76.0 and 75.1 ppm for the $-CH_2-O-$ element; this technique also supported the $-CH_2OH$ carbon assignment at 64.1 ppm. The spectrum also showed small peaks at 37.3 and 63.9 ppm consistent with the presence of the tetrahydroquinoline ring. The pulse sequence procedure allowed the $\diagdown$ CH(OH) $\diagup$ carbon of the tetrahydroquinoline ring and the carbon of the morpholine $-CH_2OH$ substituent to be clearly distinguished. As well as the split absorption for the $-CH_2-O-$ element of the perhydro-1,4-oxazepine ring mentioned above, the absorptions due to the $-CH_2OH$ (morpholine ring substituent) at 64.1 ppm and the tetrahydroquinoline ring at 37.3 (Ar–CH_2–) and 63.9 [$\diagdown$ CH(OH) $\diagup$] ppm were also split clearly showing that these rings, like the perhydro-1,5-diazocine ring[1], were present as pairs of isomers.

The ^{13}C n.m.r. spectra for the reactions of DGA with 2,6-dimethylaniline, 2,6-dichloroaniline and 2,4,6-trichloroaniline are also shown in *Figure 2B–D*. The amounts of cyclic species present in the crude products, derived from the ^{13}C n.m.r. spectra as a percentage of the original glycidyl content, are given in *Table 1*. Results for reactions with *meta*-trifluoromethyl substituted anilines, which enabled the effect of electronic deactivation alone to be examined, are also included in *Table 1*. The effect of substituents and, in particular, the powerful steric influence of *ortho*-methyl substituents in increasing the formation of the perhydro-1,5-diazocine ring was discussed in part 1[1]. In contrast, *ortho*-methyl substituents have little effect on the extent of ether ring formation, which can be seen to be much the same with both 2,6-dimethylaniline and aniline. Electronic deactivation,

Table 1 Relative amounts of cyclic species present in the reaction products from DGA and aniline and substituted anilines

	Species present by ^{13}C n.m.r.[a]				
	Perhydro-1,5-diazocine isomers				
Amine[b]	*cis*	*trans*	Morpholin-2-yl	Perhydro-1,4-oxazepin-2-yl	Tetrahydroquinol-1-yl
$C_6H_5NH_2$(1)	8.8	6.2	5.9	4.3	3.6
2,6-$(CH_3)_2C_6H_3NH_2$(2)	24.0	23.0	5.2	3.5	1.1
2,6-$Cl_2C_6H_3NH_2$(3)	18.4	16.8	12.9	8.1	9.7
2,4,6-$Cl_3C_6H_2NH_2$(4)	13.1	10.6	16.0	10.0	16.5
3-$CF_3C_6H_4NH_2$(5)	12.4	8.4	10.1	6.3	0.8
3-$CF_3C_6H_4NH_2$(6)	12.2	8.7	15.4	10.0	0.4
3,5-$(CF_3)_2C_6H_3NH_2$(7)	11.1	8.5	16.8	11.2	2.9
3,5-$(CF_3)_2C_6H_3NH_2$(8)	10.3	8.7	19.4	12.8	2.8

[a]Values represent the percentages of the original glycidyl groups present as each species
[b]Reaction conditions (maximum temperature/time): (1) 176°C/18 h; (2) 160°C/18 h; (3) 200°C/12 h; (4) 200°C/24 h; (5) 180°C/5 h; (6) 200°C/4 h; (7) 180°C/5 h; (8) 200°C/4 h

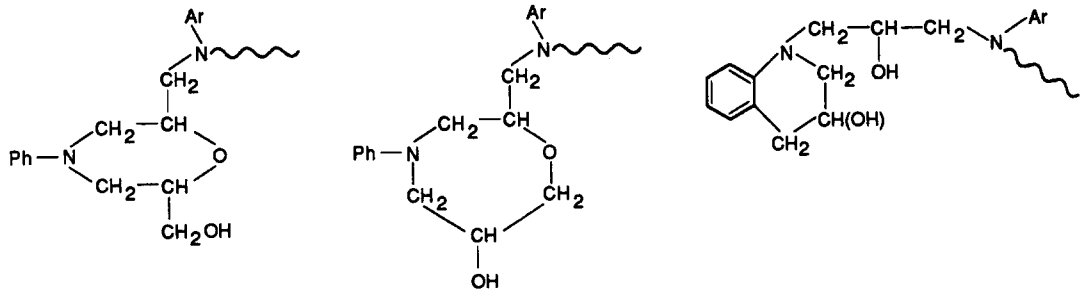


Figure 4 Morpholinyl, perhydro-1,4-oxazepinyl and tetrahydroquinolyl end groups produced in the reactions of DGA with aniline and substituted anilines

on the other hand, has a greater effect on ether cyclization than it has on amine cyclization: the former is increased from 10 to 16% when 3-(trifluoromethyl)aniline and to 28% when 3,5-bis(trifluoromethyl)aniline are used instead of aniline, whereas both of these substituted anilines increase amine cyclization from 15 to about 20%. It is interesting to note in this respect that Attias *et al.*[10], using solid-state ^{13}C n.m.r. spectral analysis, report that replacement of 4,4'-methylenedianiline with the less reactive 4,4'-sulphonyldianiline to cure *N,N,N',N'*-tetraglycidyl-4,4'-methylenedianiline increases ether cyclization from 25 to 40% but decreases amine cyclization from 25 to 15%. A combination of steric and electronic factors deactivate the chloroanilines and it can be seen in *Table 1* that the extent of both ether cyclization and amine cyclization are considerably increased. It should be noted that complete decomposition of the perhydro-1,5-diazocine isomers occurred when the reaction between DGA and 2,4,6-trichloroaniline[1] was carried out at 220°C, and thus the yields quoted for this reacton at 200°C could be misleadingly low because of the time spent at this temperature. With 3-trifluoromethylaniline and 3,5-bis(trifluoromethyl)aniline, a short period at 200°C after reaction at 180°C had little effect on the total yield of the perhydro-1,5-diazocine derivatives but, in both cases, a very small decrease in the amount of the *cis* isomer was accompanied by an increase in that of the *trans* isomer. These differences are probably within the limits of accuracy of the analysis and so, whether in fact some racemization occurred must remain questionable. The reaction of primary aromatic amine with epoxide is commonly considered to be much faster than any ether forming process in the cure of *N,N*-diglycidyl compounds with deactivated aromatic amines such as 4,4'-sulphonyldianiline[8,11–15]. However, this behaviour clearly does not extend to highly deactivated chloroanilines since with 2,4,6-trichloroaniline, ether cyclization was observed to play a major role despite the large amount of unconsumed (37%) primary amine that we have previously reported to be present[1]. As will be seen later, it seems probable that ether cyclization plays a significant role during the early stages of cure even when more reactive diamines are used. As can be seen in *Table 1*, 6-membered ether ring formation was favoured over 7-membered ether rings, in accordance with Baldwin's rules[16], but only in a ratio of about 3:2. The marked increase in the formation of the tetrahydroquinoline ring observed with the chloroanilines is, as will be discussed later, probably partly due to some polymer chain cleavage under the more forcing reaction conditions used with these less reactive amines.

Returning to the reaction between DGA and aniline, it was confirmed, by removing the volatile components from the product by sublimation, that the 6- and 7-membered ether rings and the tetrahydroquinoline ring were present as polymer end groups, as shown in *Figure 4*. An unexpected consequence of this heat treatment was that the linear polymer underwent some degradation, the extent of this being surface-dependent as readily seen from the g.p.c. traces in *Figure 5*. Sublimation from a new soda glass sample tube had only a slight effect on the polymer profile, which showed a peak maximum at

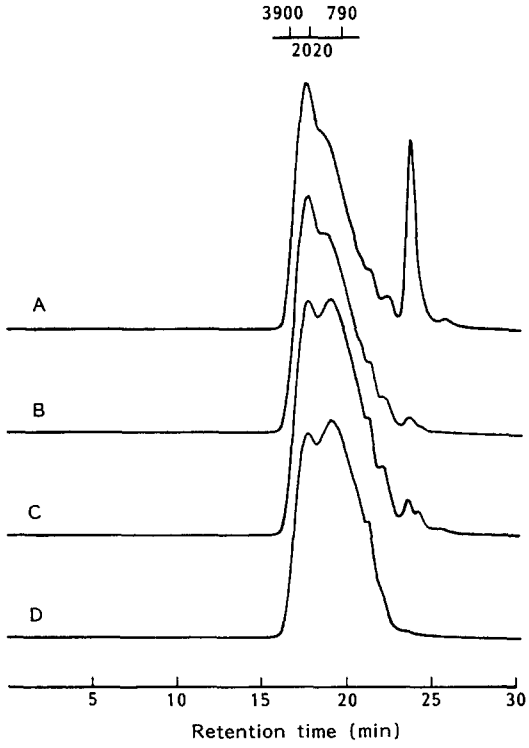


Figure 5 G.p.c. traces showing the effect of surface on the stability of the polymer from DGA and aniline after removal of the volatile fraction by sublimation: A, as prepared; B, unused soda glass, 180°C/18 h; C, HNO_3/HF-washed Pyrex, 160°C/22 h; D, HNO_3/HF-washed Pyrex, 220°C/18 h. An M_n scale for poly(oxypropylene)glycol standards is shown

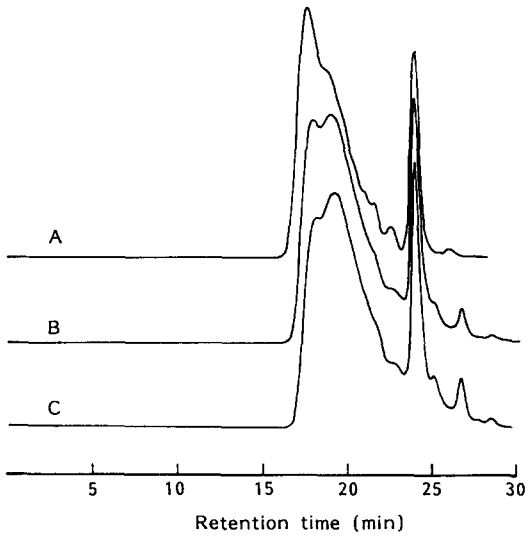


Figure 6 G.p.c. traces showing the effect of ageing in THF on the polymer from DGA and aniline: A, before ageing; B, after 32 days; C, after 54 days

about 2300 with an inflection at about 1400; however, when a Buchi sublimator was used, which had been prewashed with an HF/HNO_3 cleaning solution, the polymer showed a bimodal molecular weight distribution with peaks at 2300 and 1100, and an increase in sublimation temperature from 160 to 220°C caused only a slight further increase in the relative amount of the later peak. A similar development of bimodal molecular weight distribution was observed for THF solutions which had been left standing for some time at room temperature, as can be seen in *Figure 6*. Thus, 2% g.p.c. analytical solutions showed even more degradation after 54 days than had been observed thermally. Analysis of the sublimation residues by ^{13}C n.m.r. spectroscopy gave an insight into the changes which had occurred; the spectra are shown in *Figure 7A–C*. Analysis of the residue in soda glass showed, apart from the loss of the perhydro-1,5-diazocine peaks, only a very slight enhancement of the other cyclic contributions. It should be noted that the peaks due to the linear polymer are now the dominant feature. In contrast, sublimation from acid-washed Pyrex had a very marked effect on the spectrum of the residue; there were significant increases in peak intensities due to the tetrahydroquinoline ring at 37.3 and 63.9 ppm (Ar–CH_2– and $\diagdown\!\!\diagup$CH(OH), respectively) and in the ether carbon region at about 75.3 ppm, together with an increase in intensity of the peak at about 52.3 ppm due to the –CH_2–N$\diagdown\!\!\diagup$ carbon present in these cyclics. In addition, the secondary amine carbon peak at 48.5 ppm was more intense and the polymer peaks were broader. The yields of cyclic species present after these sublimation treatments were determined by ^{13}C n.m.r. analysis and are given in *Table 2*. It was concluded that the two reactions shown in *Figure 8* were responsible for the observed spectral changes: the first involves chain cleavage and produces tetrahydroquinolyl and secondary amine end groups; the second reaction involves the elimination of water from adjacent hydroxyl groups to give an in-chain morpholine ring. Neither of these processes has previously been reported. The morpholine ring thus produced, presumably as a pair of isomers, is

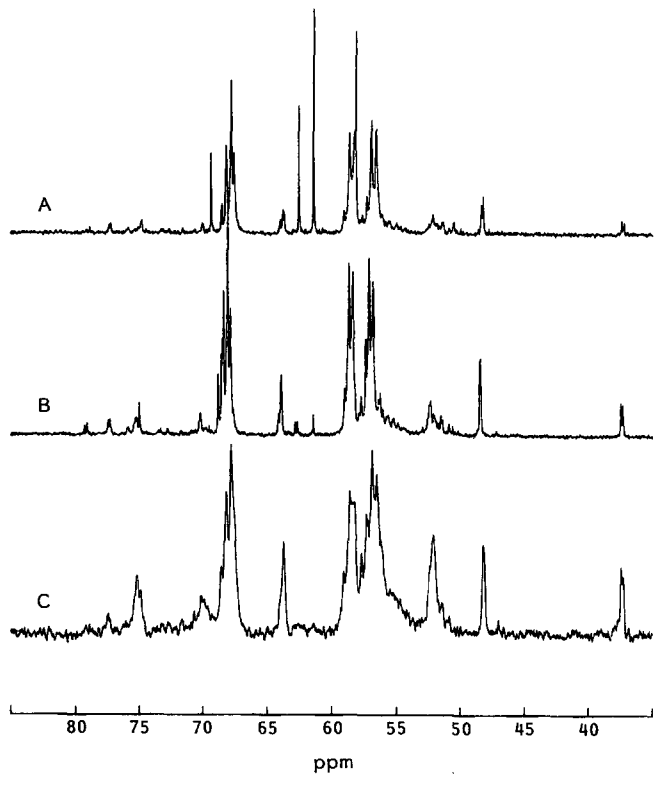


Figure 7 ^{13}C n.m.r. spectra (75.47 MHz) in acetone-D_6 showing the effect of surface on the stability of the polymer from DGA and aniline after removal of the volatile fraction by sublimation; A, as prepared; B, unused soda glass, 180°C/18 h; C, HNO_3/HF-washed Pyrex, 220°C/18 h

Table 2 Effect of surface on the formation of cyclic species and secondary amine during the separation of volatile product by sublimation from the polymer obtained in the reaction between DGA and aniline

	Species present by ^{13}C n.m.r.[a]					
	Perhydro-1,5-diazocine isomers					
Treatment[b]	*cis*	*trans*	Morpholin-2-yl	Perhydro-1,4-oxazepin-2-yl	Tetrahydro-quinol-1-yl	Secondary amine
(1)	8.8	6.2	5.9	4.3	3.6	10.6
(2)	1.1	0.7	11.0[c]		4.8	11.5
(3)	–	–	20.7[c]		7.6	14.3

[a]Values represent the percentages of the original glycidyl groups present as each species
[b](1) As prepared; (2) unused soda glass, 180°C/18 h; (3) HNO_3/HF-washed Pyrex, 220°C/18 h
[c]Total amount of 6- and 7-membered ether cyclic species including in-chain morpholine ring

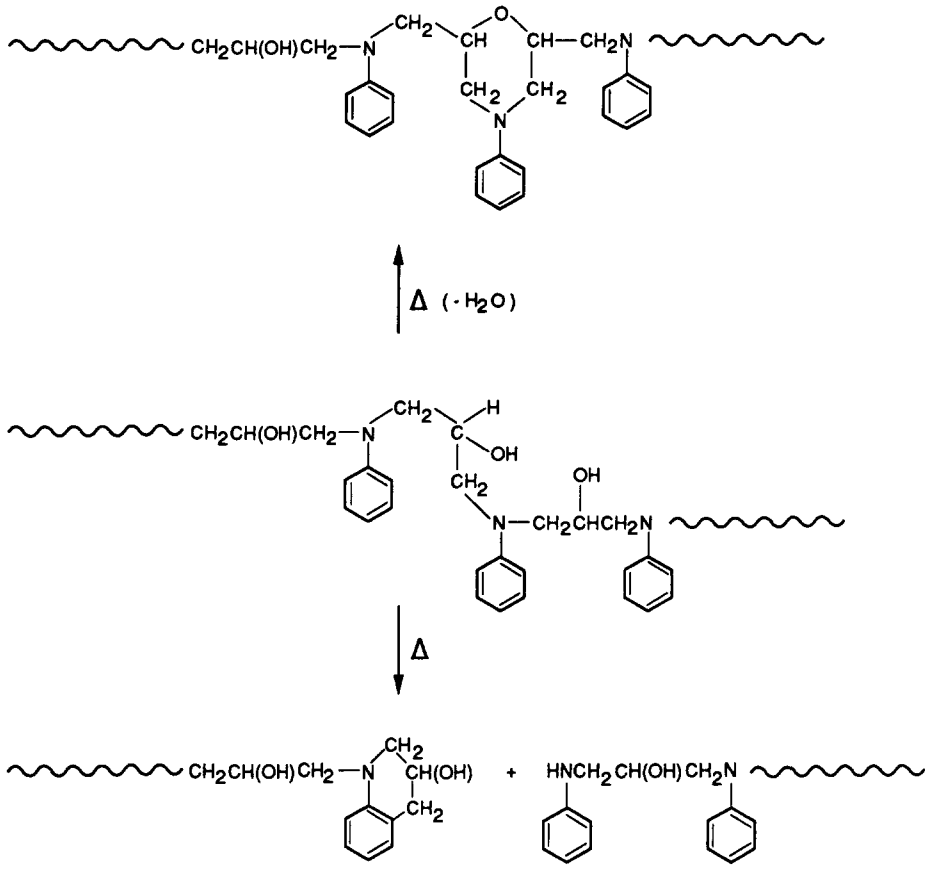


Figure 8 Thermal reactions undergone *in vacuo* by the polymer from DGA and aniline

of course differently substituted to the morpholinyl end group and adds to the complexity of the spectrum in the ether carbon region. The extra peaks from the new species, together with the general broadening effect of the polymer degradation, in fact produced severe overlap of resonances in the ether region, as is evident in *Figure 7C*. This precluded accurate measurement of the individual cyclic ether species. However, it was possible to estimate the total amount of 6- and 7-membered ether rings and the amounts of the other species, and these are the values given in *Table 2*. An end group analysis of the crude, as-prepared polymer by ^{13}C n.m.r. gave a true M_n of about 1600 which was in reasonable agreement with that indicated by g.p.c. analysis. It should be pointed out that i.r. spectroscopy gave little indication that the polymer was undergoing such changes.

Effect of stoichiometry and reaction temperature on cyclization reactions

The molecular weight of the linear polymer from DGA and aniline is clearly controlled by the contribution of the chain terminating reactions which produce morpholinyl, perhydro-1,4-oxazepinyl and tetrahydroquinolyl end groups. As a possible means of increasing the molecular weight of the polymer, the effect of a lower reaction temperature and an increasing molar excess of epoxide on the reaction was examined. The temperatures used were 120, 145 and 145 with an additional heat treatment at 178°C, and the DGA was used in stoichiometric and 2.5, 5 and 7.5% molar excess amounts. G.p.c. showed that the increasing excess of DGA produced only a very slight increase in molecular weight and that the effect of a lower reaction temperature was only marginally better.

Thus the largest difference was seen between the reaction with 7.5% molar excess of DGA at 120°C and that with equimolar amounts of reactants at 145°C with a post-heat treatment at 178°C. The g.p.c. traces for these reactions and for the equimolar reaction at 120°C are shown in *Figure 9*; the use of a lower temperature for the equimolar reaction moved the polymer peak, based on poly(oxypropylene)glycol standards, from about 2300 to about 2600, and a 7.5% excess of DGA effected a further increase to about 3000. As discussed earlier, the inflection on the polymer peak is associated with polymer cleavage and results in broader, less well resolved ^{13}C n.m.r. spectra. As might be expected, the inflection is much less significant at the lower reaction temperature, and the spectrum of this product, shown in *Figure 10*, exhibits very sharp polymer peaks. These modest improvements in molecular weight indicated that the ether cyclization reactions were still significant even at 120°C, and analysis of the products by ^{13}C n.m.r. confirmed this. The amounts of the different cyclic species present as well as that of secondary amine are given in *Table 3*. G.p.c. values for the combined yield of the perhydro-1,5-diazocine isomers agree well with the ^{13}C n.m.r. values. The concentrations of this ring and the 6- and 7-membered ether rings are marginally higher than those recorded for the 'as prepared' material in *Table 2*; this was presumably due to difference both in reaction scale and the reaction conditions employed.

The most significant result of this particular series of experiments was that, even with a reactive amine such as aniline (present in equimolar amount) and a modest reaction temperature of 120°C, ether cyclization (11%) was fairly competitive with amine cyclization (19%) and polymer formation. At 145°C, the amounts of ether cyclization and amine cyclization products were 14 and 22%, respectively. At this higher reaction temperature, the epoxide groups were completely consumed, and the

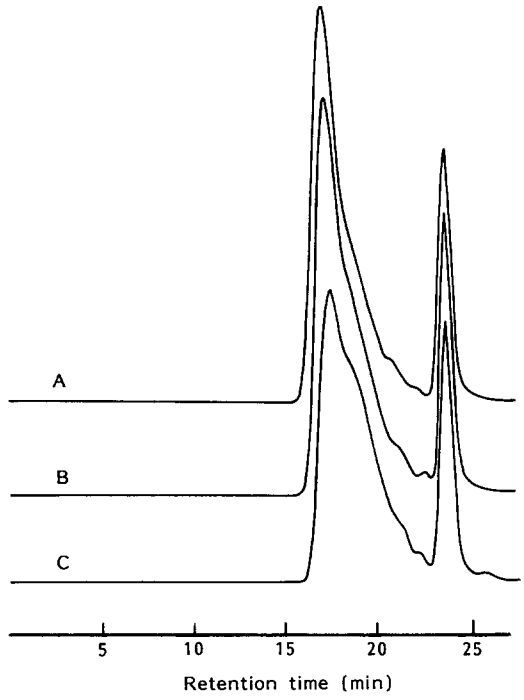


Figure 9 G.p.c. traces showing the effect of reaction temperature and reactant ratio on the molecular weight of polymer from DGA and aniline: A, 7.5% molar excess of DGA at 120°C/7 days; B, equimolar amounts at 120°C/7 days; C, equimolar amounts at 145°C/7 days + 178°C/17 h

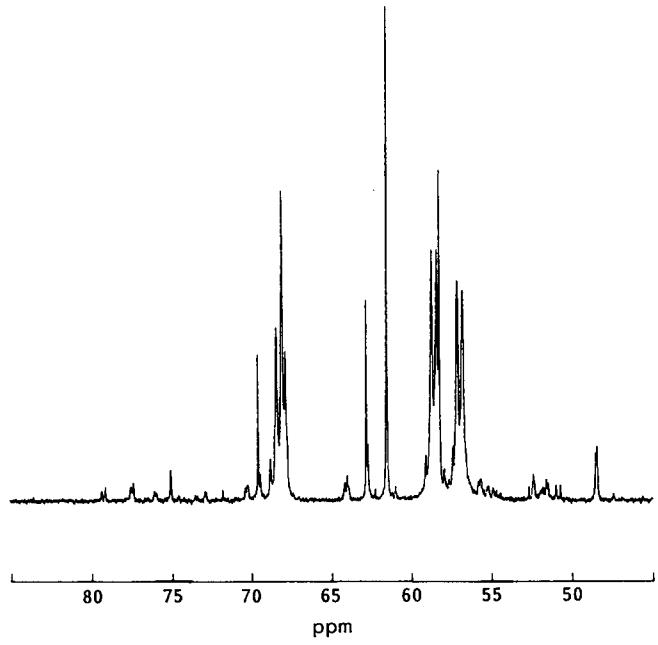


Figure 10 ^{13}C n.m.r. spectrum (75.47 MHz) in acetone-D_6 of product obtained from DGA and aniline at 120°C

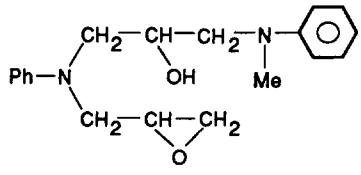
Table 3 Effect of temperature and reactant ratio on the extent of cyclization in the reaction between DGA and aniline

Reaction conditions[b]	Species present by ^{13}C n.m.r.[a]					
	Perhydro-1,5-diazocine isomers					
	cis	*trans*	Morpholin-2-yl	Perhydro-1,4-oxazepin-2-yl	Tetrahydro-quinol-1-yl	Secondary amine
(1)	11.1	7.6 (19)	6.2	4.4	1.0	9.8
(2)	12.9	8.2 (19)	7.6	5.1	1.1	2.2
(3)	14.5	7.7 (22)	8.5	5.0	1.4	7.3
(4)	14.6	7.5 (22)	8.4	5.2	1.2	3.6
(5)	12.7	8.2 (20)	8.9	5.4	2.9	7.0

[a] Values represent the percentages of the original glycidyl groups present as each species. Values in parentheses obtained by g.p.c. are for the combined isomer yield

[b] (1) Equimolar quantities of reactants at 120°C for 7 days; (2) with 7.5% molar excess of DGA at 120°C for 7 days; (3) equimolar quantities of reactants at 145°C for 7 days; (4) with 7.5% molar excess of DGA at 145°C for 7 days; (5) equimolar quantities of reactants at 145°C for 7 days and then at 178°C for 17 h

percentage of original glycidyl groups associated with unconsumed secondary amine (7%) agreed well with the percentage associated with non-epoxide/amine cyclization products (8%). (Each ether cyclic product is, of course, associated with two original glycidyl groups.) The comparative ease of ether cyclization which we observe for this system contrasts with conclusions reached by Matejka and Dusek who report[17] that the rate constant for the reaction of the model compound (*III*) with



(III)

N-methylaniline is about an order of magnitude faster than that for the intramolecular ether cyclization reaction. They conclude[18] that ether cyclization is only possible in the later stages of the reaction between DGA and aniline after the amine has been consumed. The implication of our results is that ether cyclization should be significant during the earlier stages of the cure of commercial resins based on *N,N,N',N'*-tetraglycidyl-4,4'-methylenedianiline even when a reactive diamine such as 4,4'-methylenedianiline is used, and that it should be enhanced when deactivated amines are employed since, as discussed above, such deactivation encourages ether cyclization. This is not supported by recent conclusions based on solid-state ^{13}C n.m.r.[13,14] and i.r.[15] spectroscopic analysis that ether formation only occurs in the later stages of the cure of this epoxy compound with 4,4'-sulphonyldianiline. It should be appreciated, however, that the difficulty of quantitative ether group analysis, particularly by the latter technique, is fully recognized by the authors.

It is interesting to note that whereas the polymer from DGA and aniline has a completely random tacticity, the formation of the *cis* perhydro-1,5-diazocine isomer is markedly favoured. Presumably the transition state leading to the formation of the *trans* cyclic isomer is subject to more steric hindrance than for the other isomers. It is further interesting to note that DGA and the *ortho*-substituted amines produce the *cis* and *trans* perhydro-1,5-diazocine isomers in very similar yields, but that these derivatives, unlike those from DGA and aniline, have distorted crown conformations[1].

The formation of the tetrahydroquinoline ring was much less significant, and was only about 3% at the highest reaction temperature employed. It probably arose partly by polymer cleavage as discussed above. It was confirmed by ^{13}C n.m.r. that the DGA used in these reactions contained no tetrahydroquinoline derivative.

CONCLUSIONS

Investigations into the reactions of DGA with aniline and substituted anilines revealed that the intramolecular cyclization reactions between epoxide and hydroxyl groups occur much more readily than hitherto recognized and, as chain terminating processes, limited the molecular weight of the resultant polymers. Even with a fairly reactive amine such as aniline at a moderate temperature of 120°C, ether cyclization accounted for about 11% of epoxide consumption compared with about 19% for amine cyclization. Only the polymer from aniline had a reasonably high molecular weight (about 3000), and its ^{13}C n.m.r. spectrum showed no branching (which would have resulted from any intermolecular reaction between epoxide and hydroxyl groups) and a completely random tacticity. Somewhat unexpectedly, the steric effect of the methyl groups in 2,6-dimethylaniline considerably enhanced the amine cyclization reaction but had little effect on the ether cyclization reaction. In contrast, electronegative chlorine and trifluoromethyl substituents in the amine had the expected effect of reducing the reactivity of the amine group and markedly enhancing ether cyclization. The extent of this cyclization was also marginally increased at higher reaction temperatures. In accordance with Baldwin's rules[16], the formation of 6-membered ether rings was favoured over 7-membered rings but only by a factor of about 3:2.

The polymer from DGA and aniline showed some instability at higher temperatures and two new thermal reactions are proposed to explain observed changes in the ^{13}C n.m.r. spectra and g.p.c. traces, chain cleavage to give tetrahydroquinolyl and secondary amine end groups, and elimination of water from adjacent hydroxyl groups to produce in-chain morpholine rings. A solution of the polymer in THF showed similar unstable behaviour. The formation of the tetrahydroquinoline structure, which was observed in the reactions between DGA and aniline and substituted anilines, was more significant at higher reaction temperatures, and probably arose partly by the polymer degradation route.

The implication of these model system studies for the cure of *N,N,N',N'*-tetraglycidyl epoxies with aromatic diamines is that ether cyclization, like amine cyclization, plays an important part in the earlier stages of cure, even with fairly reactive diamines. It is also clear that deactivating steric and electronic effects due to substituents present in the aromatic diamines can have very different effects on the relative contributions of these cyclization processes. The thermal reactions observed with the linear polymer may not, of course, extend to a highly crosslinked situation in which the necessary molecular alignments for the reaction transition states may be precluded.

The differences between solution and solid-state spectra for model compounds and polymers used in this investigation, together with an assessment of the application of such data for analysing network structures in the solid state, will be addressed in another paper.

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