Cyclopolymerization of *N,N*-diglycidylaniline and polymer structure by ^{13}C nuclear magnetic resonance spectroscopy

P. Johncock*
Materials and Structures Department, DRA Aerospace Division, Farnborough, Hants GU14 6TD, UK

and A. V. Cunliffe
DRA Military Division, Fort Halstead, Sevenoaks, Kent TN14 7BP, UK
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Polymerization of *N,N*-diglycidylaniline with 10% (w/w) potassium t-butoxide gave soluble polymer with only a small amount of gel (2%), whereas 2% butoxide produced mainly gel (80%). Number-average molecular weights by ^{13}C nuclear magnetic resonance (n.m.r.) end-group analysis (supported by gel-phase chromatography) did not exceed about 20000. The structure of the polymers was established by ^{13}C n.m.r., and it was shown that the cyclopolymerization reaction produced a mixture of six- and seven-membered rings (each as a mixture of *cis* and *trans* isomers), with the ring distribution being probably random. A complete assignment of the n.m.r. spectra was made in terms of these structures. The formation of seven- over six-membered rings was favoured and contrary to Baldwin's rules. The data are relevant to the identification of cyclization reactions that occur in the amine cure of epoxy resins containing *N,N*-diglycidyl groups.

(Keywords: *N,N*-diglycidylaniline; cyclopolymerization; ether rings; potassium t-butoxide; gel permeation chromatography; ^{13}C nuclear magnetic resonance spectroscopy)

INTRODUCTION

Some years ago, Bauer reported[1] the cyclopolymerization of *N,N*-diglycidylaniline (DGA) with potassium t-butoxide in benzene, and favoured the formation of six- over seven-membered ether rings. N.m.r. spectroscopy was not sufficiently developed at that time to distinguish between these structures. Baldwin's rules[2] for ring closure, which are based on stereochemical considerations, predict that, in such a competitive situation, six-membered ring formation is, in fact, favoured. This contrasts with the non-cyclic situation when nucleophilic attack on epoxide occurs exclusively at the least hindered terminal carbon atom[3]. The validity of Baldwin's rules for the cyclization reactions between epoxide and hydroxyl groups have recently been tested, and the extent to which they hold very much depends on the system involved. Thus, although the formation of the morpholine ring is predominant in the base-catalysed reactions of (2,3-epoxypropyl)(2-hydroxyethyl)alkylamines[4], and is slightly favoured (60:40) in the reaction between the dipotassium salt of 1,2-dihydroxynaphthalene and epichlorohydrin[5], (2,3-epoxypropyl)(2-hydroxyethyl)dialkylammonium chlorides gave about equal amounts of the six- and seven-membered rings[4].

Three different cyclization reactions occur in the amine cure of epoxy resins containing *N,N*-diglycidyl groups to give perhydro-1,5-diazocine, morpholine and perhydro-1,4-oxazepine rings. The first ring system, derived from the reaction between epoxide and secondary amine groups, is now well characterized by ^{13}C n.m.r. and i.r. spectroscopy[6]. There is little detailed n.m.r. information available for the other two rings, which are formed in the intramolecular cyclization reactions between epoxide and hydroxide groups. It was concluded[7] from h.p.l.c. analysis and the ^{13}C n.m.r. spectra of the mixed products from the intramolecular cyclization of 3,7-diphenyl-5-hydroxy-9,10-epoxy-3,7-diazadecane that, in addition to the morpholine derivative, a sizeable proportion of the seven-membered ring product was formed. We have reported[8] the formation of ether rings in the reactions between DGA and aniline and substituted anilines, and that six- over seven-membered ring formation is favoured in accordance with Baldwin's rules, with the ratio being about 3:2. Such species were present as polymer end-groups and provided only limited ^{13}C n.m.r. spectral detail. It was considered that the cyclopolymerization product from DGA would be a good source of such data. Consequently, the reaction products have been examined in some detail by high-resolution ^{13}C n.m.r. in the aliphatic and aromatic regions, and the results are reported in this paper.

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* To whom correspondence should be addressed

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EXPERIMENTAL

Materials and instrumentation

DGA, b.p. 110–111°C (0.13 mmHg), was prepared by a literature procedure[9] and, by analysis[10], had an epoxy equivalent of 107 (theoretical, 103.5). Benzene (pure analytical grade, M&B) was dried over a molecular sieve (4 Å). Tetrahydrofuran (THF) (h.p.l.c. grade, Rathburn Chemicals), diethyl ether (AR grade, M&B) and potassium t-butoxide were used as received.

For analytical gel permeation chromatography (g.p.c.), a Waters 244 chromatograph was used with a 500 Å, 1000 Å, 10 000 Å Ultrastyragel column combination (each 30 cm × 0.78 cm): the eluant was THF at 1 ml min^{-1}, detection was by ultra-violet at 280 nm, and the data were recorded with a Spectra-Physics SP 4100 computing integrator. Poly(oxypropylene) glycol (POPG) and polystyrene (PS) $\bar{M}_n$ standards from Waters were used for molecular-weight calibrations.

^{13}C n.m.r. spectra were recorded on approximately 20% (w/v) solutions in benzene-d_6 at 300.13 MHz at ambient temperature (approximately 22°C) on a Bruker MSL-300 superconducting multinuclear n.m.r. spectrometer. A 5 mm ^{13}C probe was used, except for some of the quantitative runs, for which a 10 mm multinuclear probe, which gave better sensitivity because of the larger sample size, was used. Chemical shifts were measured with respect to tetramethylsilane (TMS) as internal reference. Samples were typically run overnight with the order of 5000 scans. Normal spectra were recorded with proton broad-band decoupling in the standard manner. Quantitative runs were measured using inverted gated coupling[11] to suppress the nuclear Overhauser effect, and with delays between pulses of 10 s to minimize errors due to different relaxation times between the various peaks. Assignment of the various types of carbon (quarternary, CH, CH_2, CH_3) was accomplished using the INEPT[12] (insensitive nuclei enhancement by polarization transfer) pulse sequence. The most successful measurement was that with a delay corresponding to $3/8J$, which was set at about 2.6 ms, and was used to distinguish between CH and CH_2 resonances in the aliphatic region. In all cases, standard pulse sequences supplied with the Bruker MSL software package were employed.

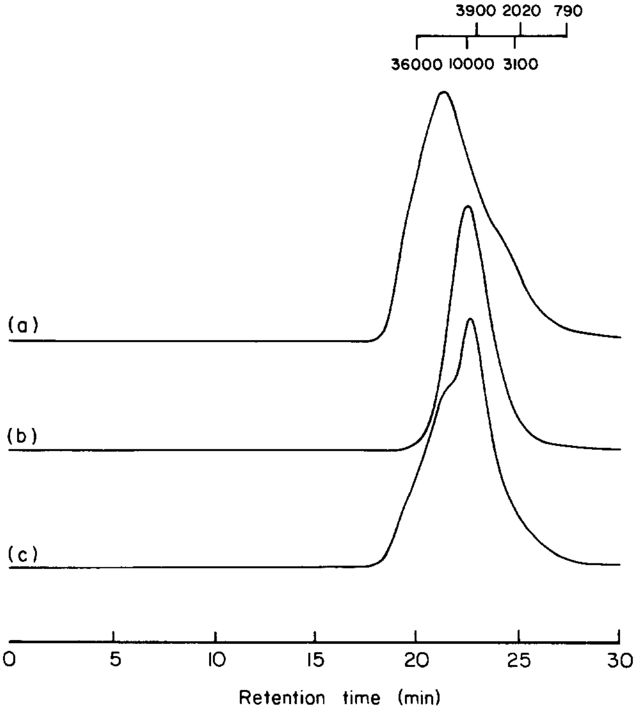


Figure 1 G.p.c. traces for soluble polymer obtained by the polymerization of DGA with potassium t-butoxide in benzene: (a) 10% t-butoxide, first fraction; (b) 10% t-butoxide, second fraction; (c) 2% t-butoxide, sol. $\bar{M}_n$ scales for POPG and PS are shown

Anionic polymerization of DGA

As described by Bauer[1], DGA (5.0 g) and potassium t-butoxide (0.50 g) in benzene (8.8 g), handled in the absence of moisture, were heated in a sealed tube (pre-degassed) at 50°C for 6 days. The resultant golden brown, highly viscous product, which contained a little insoluble solid, was treated with benzene (100 ml) and deionized water to remove any residual salt. The mixture would not de-emulsify, but addition of ether effected precipitation, and the filtered polymer was dried (65°C at 10^{-3} mmHg) and obtained as a pale cream friable solid (2.7 g). Addition of more ether to the filtrate gave a second polymer fraction (0.4 g). The main fraction contained a small amount of THF-insoluble gel, which prevented g.p.c. analysis; however, the gel (0.15 g) readily settled out from benzene and the sol solution was collected by decantation.

A similar reaction with a smaller amount of catalyst (2% by weight) gave a product with no tendency to flow. Treatment with benzene (250 ml) for 24 h and then filtration enabled gel (4.0 g) and sol (0.45 g) fractions to be separated.

The g.p.c. traces for the sol fractions are shown in *Figure 1*.

RESULTS AND DISCUSSION

Polymerization of DGA and g.p.c. analysis

Polymerization of DGA with 10% by weight of potassium t-butoxide as described by Bauer[1] gave, in addition to first and second fractions of soluble polymer (54% and 8%, respectively), a small amount of gel (3%). The g.p.c. traces of the soluble fractions are shown in *Figure 1*. Molecular weights as determined with PS standards were much higher than those based on POPG standards, and both values are given in the text, that with POPG in parentheses. The main fraction gave a very broad complex peak at M ~19 000 (~6000) with both lower- and higher-molecular-weight inflections, and the minor fraction showed a much sharper peak at ~10 000 (~4500). The amount of t-butoxide was reduced to 2% in an attempt to prepare higher-molecular-weight polymer, but this led mainly to the formation of gel (80%) with a small sol fraction (10%), which showed (see *Figure 1*) a broad complex peak at M ~9000 (~4300) with higher-molecular-weight inflections. The significance of these results in relation to the molecular-weight values based on quantitative n.m.r. data will be discussed later.

The formation of gel in the reaction clearly demonstrated that linear cyclopolymerization was not exclusive as reported[1], but was accompanied by branching, presumably by the separate reaction of the two epoxide groups in a DGA molecule as shown in *Figure 2*. Gel formation requires, of course, the production of at least one such

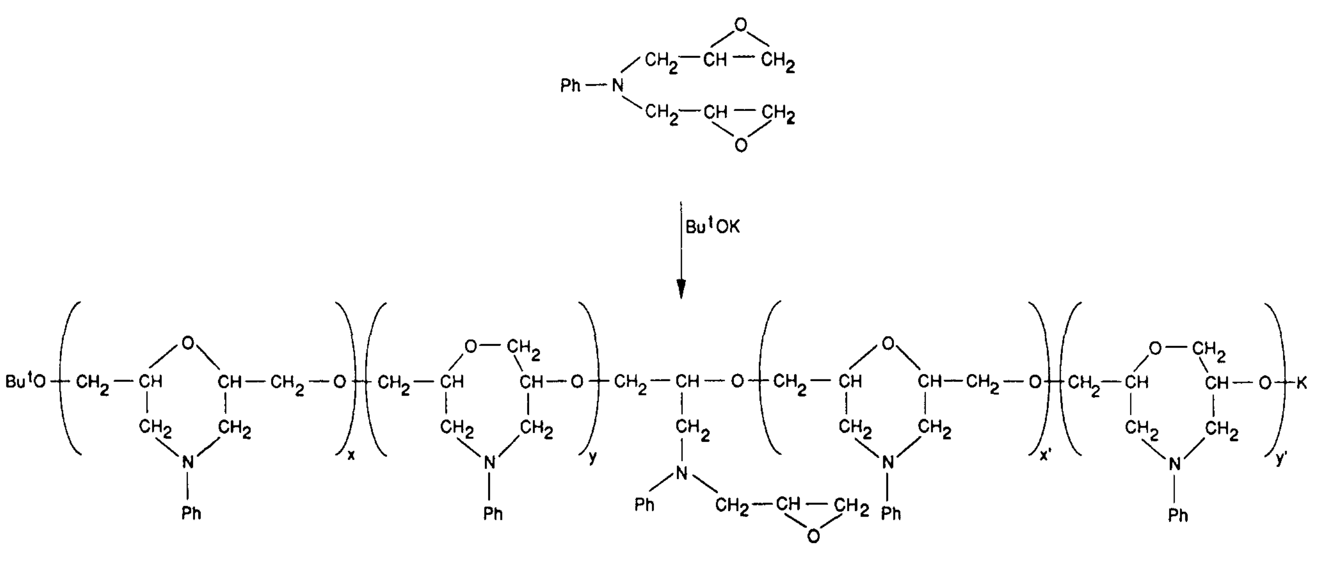


Figure 2 Polymerization of DGA with potassium t-butoxide

branch site per polymer chain and the incorporation of such chains into an infinite network. Sol would result if the epoxide branch sites were capped with t-butoxide or alkoxide-terminated polymer molecules not containing branch units. The dominant formation of gel with 2% t-butoxide and of sol with 10% t-butoxide is readily explained in these terms. It should be noted that, despite a high initiator concentration (i.e. molar ratio 1:5.4 for 10% w/w), relatively high-molecular-weight polymer was produced, showing that chain propagation was much faster than the initiation step.

General aspects of the ^{13}C n.m.r. analysis

The gel product could be readily swollen in benzene-d_6 and, with careful sample preparation, provided good-quality high-resolution n.m.r. spectra using normal high-resolution conditions appropriate to liquid or solution samples without the need of the high-power techniques necessary for high-resolution spectra in true solids. This indicated that the gel was relatively lightly crosslinked so that, on swelling, the polymer chains were in very mobile, almost liquid-like environments. The quality of the gel spectrum in comparison with a true solution spectrum is shown in *Figure 3*. Although the linewidths of the peaks are approximately twice those obtained for the soluble samples, the peaks are still very sharp. It is, in fact, possible to obtain from the gel spectrum almost all of the information obtainable from the true solution spectrum, so that the same analysis can be carried out for the gel and sol samples. This approach should be considered whenever insoluble samples with suitable properties are available. The standard cross-polarization/magic-angle sample spinning (c.p./m.a.s.s.) spectra of polymers are frequently disappointing in that the resolution is significantly inferior to that of solution spectra, and the subtle structural features that make solution n.m.r. so valuable often cannot be resolved. For example, in the c.p./m.a.s.s. spectra of the thermoset from bis[*N*,*N*-bis(2,3-epoxypropyl)-4-aminophenyl]methane and 4,4′-diaminodiphenylsulfone[13,14], the whole of the aliphatic region from 35 to 80 ppm gives a single broad resonance, with several shoulders resolved.

Degree of polymerization by ^{13}C n.m.r.

The peak derived from the methyl groups of the t-butoxide initiator was clearly visible at 27.69 ppm in all samples, and its area and that of the in-chain units allowed a relative measure of the number of monomer units per butoxide end-group to be made. As a measure of the former, the CH_2N, CHO and CH_2O carbons in the range 50 to 85 ppm were used. The first and second fractions from the experiment with 10% initiator, and the soluble fraction from the experiment with 2% initiator, gave values of about 40, 35 and 25 monomer units per t-butoxide group, respectively. These values correspond to $\bar{M}_n$ values of about 8000, 7000 and 5000, respectively, which are up to a factor of 1.3 higher than the g.p.c. values based on POPG standards, but up to a factor of 2.4 lower than those based on PS standards. The PS values are at least in the right direction since, according to the scheme for sol formation discussed earlier, the actual $\bar{M}_n$ values must be higher than the n.m.r. values by a factor depending on the average number of branch sites per molecule. The number of DGA units to t-butoxide end-groups in the gel should be higher than that in the sol since only the longer chains containing at least one branch site are involved. A value of 110 was, in fact, obtained. The lower t-butoxide concentration presumably had the expected effect of increasing the polymer chain length and of thus increasing the average number of branch sites per polymer chain. Surplus epoxide groups within the network would then be consumed by intramolecular reaction with alkoxide and further raise the DGA-to-initiator ratio.

Whilst the exact molecular weights remain uncertain, the results do indicate that soluble polymers of appreciable molecular weight are formed in the polymerization process. In particular, it is clear that the intensities of the peaks associated with end-groups are negligible compared with those of the in-chain units, and thus, in the analysis, all major peaks in the spectrum must be assigned to in-chain units.

Polymer structure by ^{13}C n.m.r.

As pointed out in Bauer's paper[1], the formation of soluble polymer implies a cyclopolymerization process

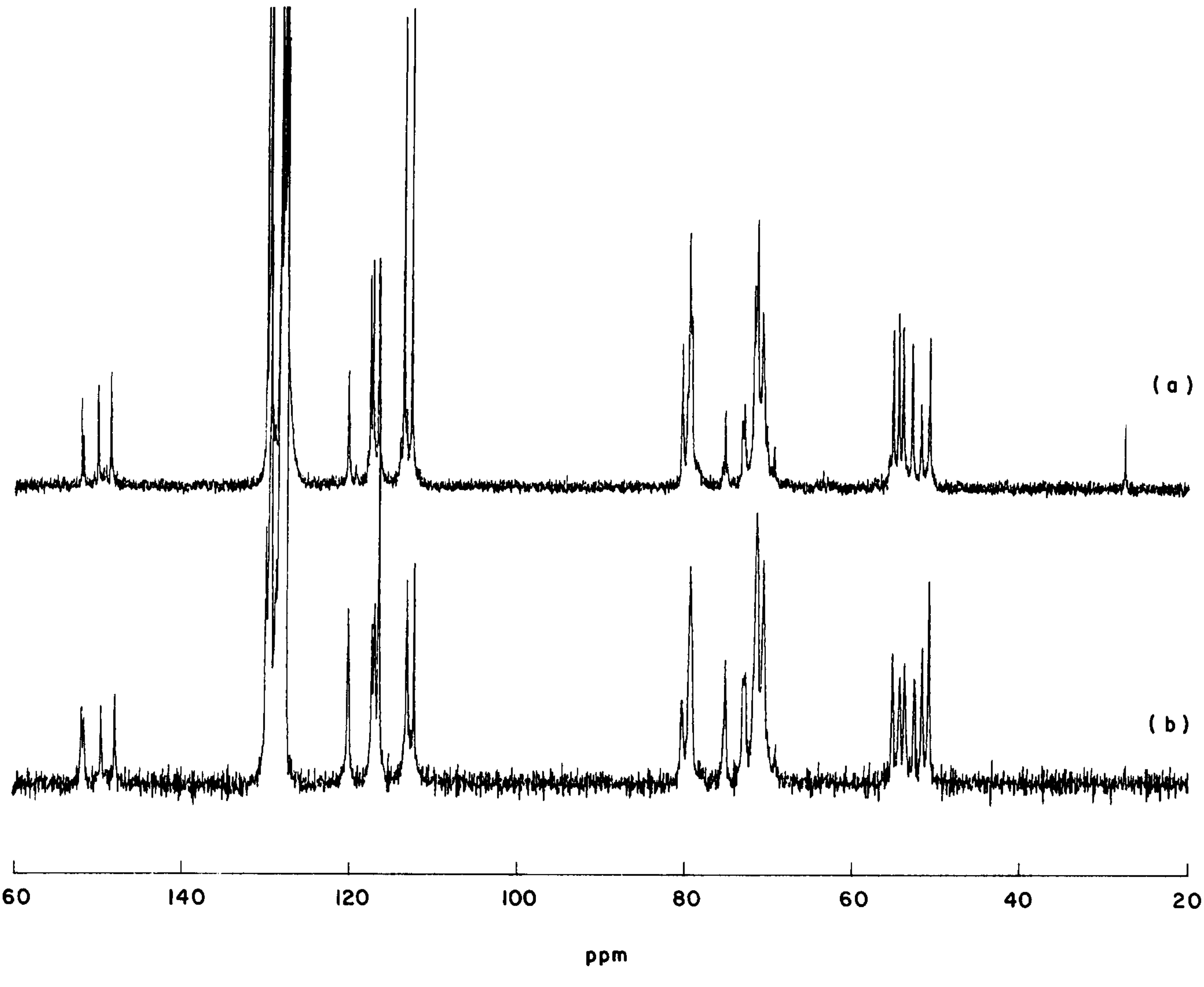


Figure 3 ^{13}C n.m.r. spectra in benzene-d_6 of the product from the polymerization of DGA with potassium t-butoxide: (a) 10% t-butoxide, first fraction; (b) 2% t-butoxide, gel fraction

since independent linear polymerization of the two epoxide groups on each monomer molecule would lead to heavily crosslinked, insoluble polymers. In fact, the rough estimates of the degree of polymerization just described indicate that the branching reaction only occurs for about one in 30 units. The ^{13}C n.m.r. spectra can be explained very well and all major peaks accounted for on the basis of a mixture of six- and seven-membered ether rings being formed. The approach adopted in assigning the spectral data was based upon comparison of chemical shifts with those of established structures, assignment of CH and CH_2 carbons in the aliphatic region from INEPT experiments, and comparison of relative areas of peaks. In particular, the changes in relative peak intensities between different samples were found to be the most useful way of assigning peaks in the aliphatic region. For this reason, care was taken to run spectra under reasonably quantitative conditions where necessary.

In previous publications, we showed that the six-, seven- and eight-membered rings produced in the reactions of DGA with aniline and substituted anilines each appeared as a pair of isomers in roughly equal proportions[6,8], and that the linear polymer obtained from DGA and aniline had a completely random tacticity[8]. This isomerism arises because of the two asymmetric centres, one for each epoxy group of the DGA, and is a general feature of the products from DGA. It should be noted that the chemical-shift difference between corresponding carbon atoms in the two isomers can be substantial (for example, for the eight-membered rings, differences of about 7 ppm and 3 ppm occur for the CHO and CH_2N carbons, respectively[6]). Attias and coworkers[7,14] have measured the ^{13}C n.m.r. spectra for six- and seven-membered ether rings formed in the reaction of DGA with *N*-ethylaniline and noted the formation of isomers. The skeletal ring structures are the same as ours and the spectra are very similar to those of our polymers.

We consider first the aromatic quaternary carbons in the region 148 to 152 ppm, which give, as can be seen in *Figure 4*, four resonances of comparable intensities. This indicates that the DGA units in the polymer are associated with four types of structure, and these are assigned to six- and seven-membered rings as shown in *Table 1*, with the ring-linking units having a *cis* or *trans* arrangement with respect to each ring. On this basis, the rest of the aromatic region can be assigned: a pair of

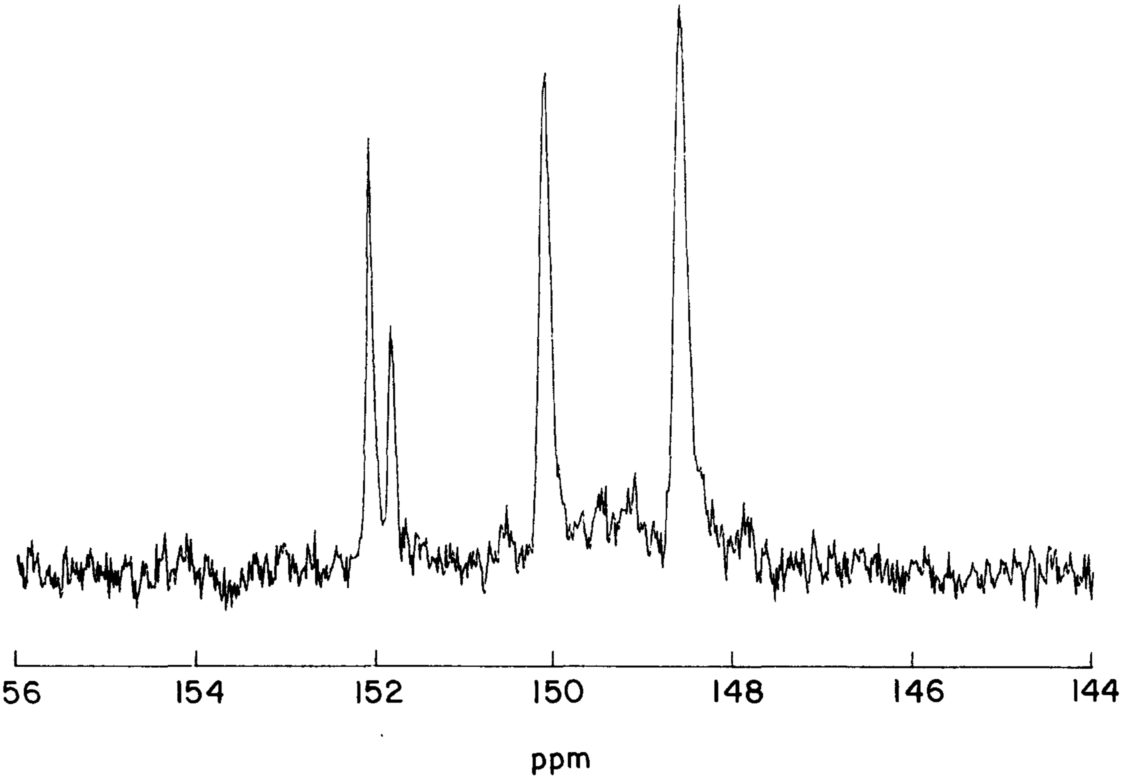


Figure 4 Quaternary aromatic resonances of the ^{13}C n.m.r. spectrum (in benzene-d_6) for the first fraction of the polymer obtained with 10% t-butoxide

Table 1 Aromatic carbon chemical shifts (ppm from internal TMS in benzene-d_6) of the cyclopolymerization product from DGA

Associated ether ring[a]	Quaternary carbon	*Ortho* carbon	*Meta* carbon	*Para* carbon
Six-membered *cis*	151.9	116.8	129.6	120.3
Six-membered *trans*	152.2	116.7	129.7	120.3
Seven-membered *cis*	148.7	112.8	129.8	117.7
Seven-membered *trans*	150.2	113.4	130.0	118.1

[a] The assignments to *cis* and *trans* isomers are uncertain and it is possible that these are reversed for each type of ring

peaks at about 113 ppm and a pair at about 117 ppm (close to the *para* peaks) are assigned to the *ortho* aromatic carbons; pairs of peaks at 118 and 120 ppm to the *para* carbon; and four peaks near to 130 ppm to the *meta* carbons. The complete aromatic spectrum can be accounted for on the basis of four different aromatic rings, with the shifts shown in *Table 1*. The assignments given are based on an interpretation of the whole spectrum, as outlined below.

The assignment to six- and seven-membered rings, based on the interpretation of the aliphatic region given below is thought to be reasonably reliable, but the assignment to *cis* and *trans* isomers, based on comparisons with other ring systems[6], is somewhat speculative. The aliphatic resonances, as shown in *Figure 5*, fall into three main bands in the regions 50–56 ppm, 69–74 ppm and 78–81 ppm, with an additional isolated resonance at 75.4 ppm. Assignment of the resonances into CH or CH_2 groups was accomplished using the INEPT sequence, which indicated that all peaks in the 50–56 ppm region were CH_2 carbons, all those between 79 and 81 ppm were CH carbons, and that those between 69 and 75 ppm were predominantly CH_2 carbons but with some CH carbons. There was also an isolated CH peak at 75.4 ppm and a CH band at about 71.0 ppm. The chemical shifts for all of the major aliphatic peaks together with assignments are given in *Table 2*.

The clearest indication of the polymer structure was obtained from the peaks in the region 50–56 ppm, which, by comparison with shifts for similar compounds[6–8,14], arise from the CH_2N carbons. On examining the proposed structures for the six- and seven-membered rings, we see that the morpholine ring is symmetrical, so that the two CH_2N carbons are equivalent. It is appreciated that this symmetry is not strictly true, and that slight differences in their chemical shifts may arise when adjacent rings are taken into account. Each six-membered ring isomer should thus give a single CH_2N resonance, with a relative area of two carbons. In contrast, each seven-membered ring isomer has two different CH_2N carbon atoms, and should give two resonances each with relative areas of one carbon atom. A total of six peaks is thus expected, two from the six-membered rings and four from the seven-membered rings. In fact, all six resonances are clearly resolved. Specific assignments were made by considering the relative areas of the peaks from spectra run under quantitative conditions. From the aromatic quaternary carbons, it was possible to estimate the relative amounts of the four isomers. By examination of the spectrum of the first fraction from the experiment with 10% potassium t-butoxide, it was clear that two of the four rings were present in appreciably smaller amounts than the other two, and that one ring in particular represented only

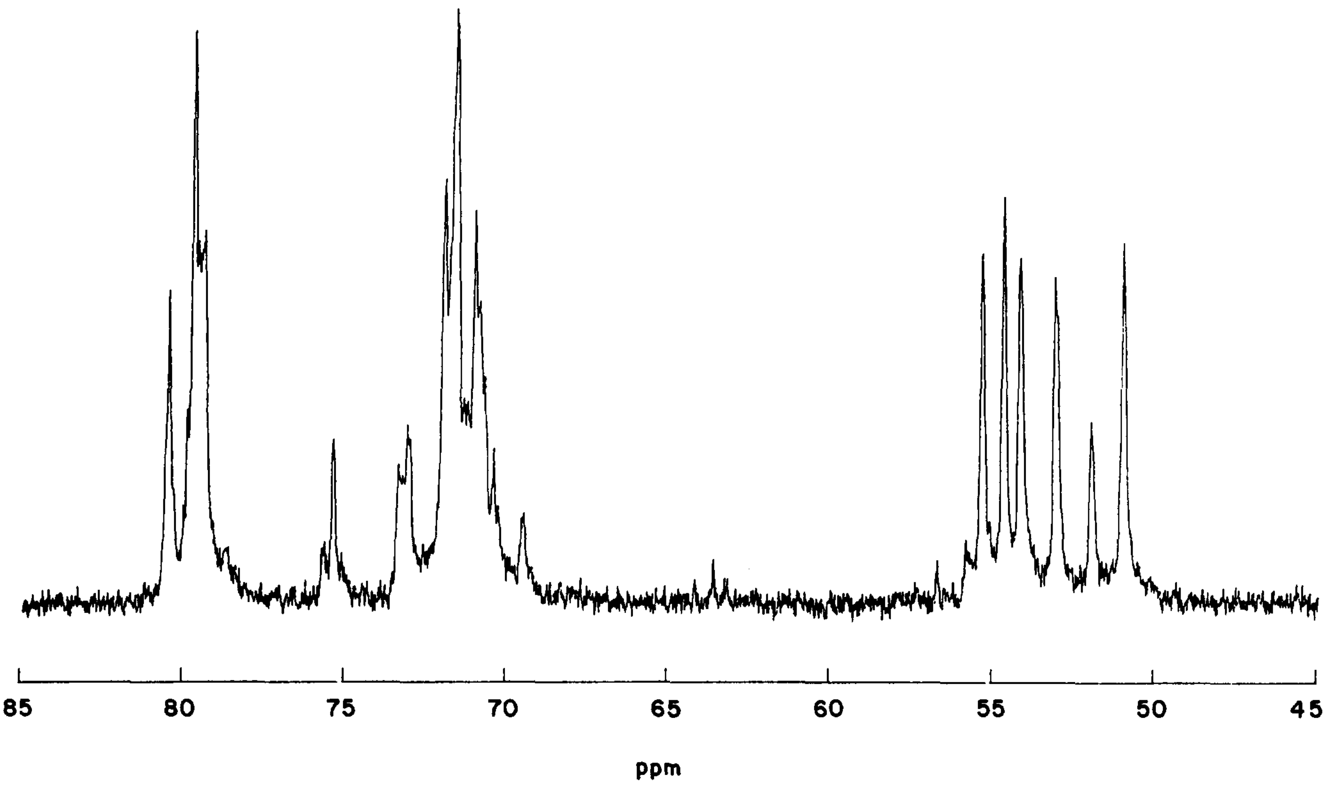
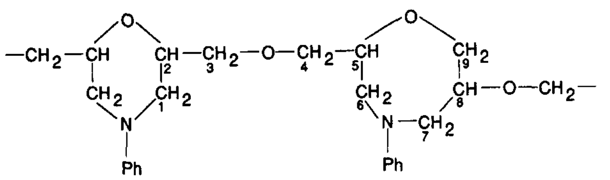


Figure 5 The aliphatic region of the ^{13}C n.m.r. spectrum (in benzene-d_6) for the second fraction of the polymer obtained with 10% t-butoxide

Table 2 Aliphatic carbon chemical shifts (ppm from internal TMS in benzene-d_6) of the cyclopolymerization product from DGA



Ether ring type[a]	Carbon atom Number	Type	Chemical-shift assignment, δ (ppm)
Six-membered *cis*	1	CH_2N	52.1
	2	CHO	75.4
	3	CH_2O	70–72
Six-membered *trans*	1	CH_2N	51.1
	2	CHO	71.0
	3	CH_2O	73.2
Seven-membered *cis*	4	CH_2O	70–72
	5	CHO	79–81
	6	CH_2N	55.4
	7	CH_2N	54.2
	8	CHO	79–81
	9	CH_2O	70–72
Seven-membered *trans*	4	CH_2O	70–72
	5	CHO	79–81
	6	CH_2N	54.8
	7	CH_2N	53.1
	8	CHO	79–81
	9	CH_2O	70–72

[a] See footnote to *Table 1*

about 15% of the total. The relative aromatic carbon areas were only consistent and in good agreement with those of the CH_2N carbons if it was assumed that the peaks at 51.1 and 52.1 ppm represented two carbons. They were thus assigned to the morpholine ring isomers. The remaining peaks at 53.1, 54.2, 54.8 and 55.4 ppm were assigned to the two seven-membered ring isomers. Confirmation of these assignments was obtained from the experiment with 2% t-butoxide: there was a substantial increase in the intensities of the peaks at 51.1 and 52.1 ppm, showing that the decrease in initiator concentration had led to an appreciably greater proportion of the six-membered ring being formed; again, the relative amounts of the different rings calculated from the aromatic and aliphatic regions were in good agreement.

The peaks in the CH_2O and CHO regions of the spectra were more difficult to assign because of considerable overlap of peaks, particularly for the CH and CH_2 resonances between 70 and 74 ppm. However, it was possible to make tentative assignments, and these are given in *Table 2*. The INEPT experiments indicated that the CH resonances occurred between 79 and 81 ppm, and at 75.4 and 71.0 ppm. Intensity considerations showed that the peak at 75.4 ppm was always about the same intensity as that at 52.1 ppm for the different samples, in particular showing the same increase for the experiment with 2% compared with that for 10% initiator, and was thus associated with a six-membered ring isomer. It was difficult to measure the area of the 71.0 ppm band directly because of overlap with CH_2 resonances; however, if the area expected for the CH_2 bands was subtracted from the total area between 69 and 74 ppm, the 71 ppm CH band had the correct intensity for the other six-membered ring isomer. In agreement with these assignments, the peaks between 79 and 81 ppm had the correct intensity for the CH carbons of the seven-membered ring isomers. The peaks in this region show a complicated multiplet, and further analysis was not attempted. Estimated chemical shifts of about 80 ppm for the CHO element associated with the seven-membered ring, and of about 71 ppm for the CH_2O substituent unit associated with the six-membered ring, were obtained by making additive corrections to the values given by Attias *et al.*[7,14] for the CHOH element and the CH_2OH substituent present in their analogous structures. In accordance with this, a CH_2O resonance at about 73.2 ppm, which had the same intensity as that for the CH_2N at 51.1 ppm irrespective of the sample, was assigned to the CH_2O resonance associated with the six-membered ring.

From the limited information available, it was not possible to be certain about specific isomer assignments. However, by comparison with the data for eight-membered rings[8], for which the *trans*-CH_2N shift occurs about 2 ppm lower than that for the *cis*-CH_2N, we tentatively assign the peaks at 51.1 and 52.1 ppm to the *trans* and *cis* isomers of the six-membered ring, respectively. On the same basis, the *trans* seven-membered ring may have peaks at 53.2 and 54.2 ppm, with the *cis* isomer having peaks at 54.8 and 55.4 ppm.

Some of the peaks show partly resolved extra splittings, particularly the peak at about 54.2 ppm. This peak is partly resolved into two peaks with an area ratio of about 65 to 35, which is approximately the ratio of seven- to six-membered rings in this sample. If this splitting reflects the relative amounts of these rings adjacent to that containing the observed carbon atom, then this indicates that the structures of adjacent rings is probably random; i.e. during cyclopolymerization, there is no particular preference for a given type of ring by the previous one in the chain.

Apart from the peaks described, the spectra showed only peaks with much lower intensity in the region between 50 and 85 ppm. However, peaks with intensities similar to that of the initiator fragment occurred at 63 to 65 ppm and at 70.3 ppm, which, from INEPT experiments, were recognized as CH_2 and CH peaks, respectively, and are assigned to CH_2OH and CHOH terminal end-groups. The values are in close agreement with values given[8] for these groups in analogous model compounds. Their peak aras were consistent with the molecular-weight values already discussed.

We thus see that the observed ^{13}C n.m.r. spectra are in full agreement with a polymer structure consisting of a mixture of six- and seven-membered rings, with each ring existing as a pair of isomers. However, the linear cyclopolymerization process producing these rings is interrupted by some chain branching, which occurs with about 30 to 40 cyclic units between junctions.

From the n.m.r. spectra, it was possible to estimate the relative amounts of the different rings. These are given in *Table 3*. It will be seen that the seven-membered ring isomers are formed in similar amounts, but that the yield of the tentatively assigned six-membered ring *cis* isomer is significantly greater than that of the corresponding *trans* isomer. It will also be noted that seven-membered ring formation is favoured, which is contrary to Baldwin's rules[2]. Quite unexpectedly, the extent of this preference was found to be significantly dependent on the amount of t-butoxide catalyst used: the ratio of seven- to six-membered rings was about 70:30 with 10% initiator and about 55:45 with 2% initiator. The reason for this variation in composition with catalyst concentration is not clear. In connection with our results, it is perhaps worth while noting that the liquid chromatographic traces of the six- and seven-membered ether ring products formed by the intramolecular cyclization of 3,7-diphenyl-5-hydroxy-9,10-epoxy-3,7-diazadecane, induced either thermally or catalytically with sodium butoxide (20 mol%) in butanol, show one of the four unassigned peaks at about half the concentration of the others and a modest difference in the product distribution for the two reactions[7].

Table 3 Relative amounts of six- and seven-membered ether rings formed in the cyclopolymerization of DGA from ^{13}C n.m.r. spectroscopy[a]

	Six-membered ring		Seven-membered ring	
Polymer sample	*cis*	*trans*	*cis*	*trans*
Fraction 1 (10% initiator)	0.19	0.11	0.40	0.30
Fraction 2 (10% initiator)	0.19	0.12	0.35	0.34
Sol fraction (2% initiator)	0.26	0.19	0.28	0.27
Gel fraction (2% initiator)	0.28	0.18	0.28	0.26

[a] See footnote to *Table 1*

CONCLUSIONS

It was possible to make a complete assignment of the ^{13}C n.m.r. spectra for the products obtained by the t-butoxide-catalysed polymerization of DGA. The linear cyclopolymerization process, which produced six- and seven-membered ether rings as isomeric pairs, was accompanied by a minor branching reaction. The polymer chains consisted of about 30–40 DGA units. The proportion of gel to soluble polymer depended on the concentration of t-butoxide used, since the base acted as both an initiator and a network-growth terminator. Contrary to Baldwin's rules, the formation of seven- over six-membered rings was favoured, and the extent of this depended, unexpectedly, on the concentration of t-butoxide used.

It was considered that the chemical-shift data for this cyclic polymer would be of importance in assigning peaks due to similar cyclic structures present in amine-cured *N*,*N*-diglycidyl epoxies. However, this study has illustrated once again the complexity of the ^{13}C n.m.r. spectra with these systems: different ring sizes, various non-equivalent carbons in the ring structures, and the occurrence of isomers mean that nominally similar fragments can have a wide range of chemical shifts. Moreover, the peaks associated with six- and seven-membered rings in the cyclic polymer are significantly different from those in simple compounds having similar rings prepared by reaction of DGA with *N*-ethylaniline[7,14]. We believe that this complexity underlies the difficulty in interpreting the solid-state c.p./m.a.s.s. ^{13}C n.m.r. spectra of cured epoxy resins, where the very poorly resolved resonances in the aliphatic region reflect the large number of different chemical shifts present.

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