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High-temperature n.m.r. techniques for studying cross-linked epoxy systems

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The network structures formed when the diglycidyl ether of bisphenol A is cured with two stoichiometries of diaminodiphenyl sulfone have been studied by solid-state ^{13}C n.m.r. at temperatures well above the glass transition temperature. High-resolution spectra have been obtained giving detailed information on the chemistry of these structures. Spectral editing and two-dimensional techniques more usually associated with solution-state n.m.r. have been used to confirm structural elements previously postulated. The value of high-temperature n.m.r. for amorphous and rigid systems such as epoxies is discussed.

(Keywords: diglycidyl ether of bisphenol A; carbon-13 nuclear magnetic resonance; high temperature)

INTRODUCTION

Epoxy resins have become increasingly important as matrices for composite materials. Numerous studies have been carried out on commercial networks based on the diglycidyl ether of bisphenol A (DGEBA) (I, $n = 0$) to investigate the curing mechanisms and the nature of the cross-linked structure. Solid-state ^{13}C n.m.r. at ambient probe temperature, using cross-polarization and magic-angle spinning (CP/MAS) coupled with high-power ^1H dipolar decoupling, has enabled correlation of individual peaks observed in the spectrum with chemical structural elements[1-3]. However, these investigations, at temperatures well below the glass transition temperature (T_g), are severely limited by the intrinsic linewidth of the signals that arise from inhomogeneous broadening. This broadening is mainly the result of a distribution of values of the isotropic chemical shift due to differing conformations and is not averaged by magic-angle spinning.

Such chemical shift dispersion can be reduced by molecular motion induced by raising the temperature. Additionally, the shielding anisotropy and proton–proton dipolar coupling may then become efficiently averaged. This molecular motion, coupled with magic-angle spinning, can give highly-resolved spectra comparable to those obtained by solution-state n.m.r.[4].

This paper considers the use, at temperatures well above T_g, of several n.m.r. techniques familiar to solution-state practice but applied with magic-angle spinning to insoluble network structures obtained by curing DGEBA (I) with 4,4′-diaminodiphenyl sulfone (DDS) (II). A detailed study of the reaction mechanism, kinetics and network structure of the DGEBA–DDS system has been reported by Grenier-Loustalot *et al.*[5], but without the benefit of temperatures for CP/MAS spectra as high as those achieved in the present work.

EXPERIMENTAL

Materials

The sample of DGEBA used was a commercial product, Shell Epon 825. In this case the predominant component is the monomer (I, $n = 0$), with only small contributions from oligomers (I, $n > 0$). Analysis by reverse-phase HPLC shows the material to contain 93% of the main component. The ^{13}C n.m.r. spectrum (see below) shows the sample to be even more highly monomeric. This simplifies the structural chemistry of the cured products. The diglycidyl ether of bisphenol A was cured with 100% and 66% stoichiometric amounts of diaminodiphenyl sulfone according to the regimes outlined in *Table 1*. The stoichiometries in question are based on the functionality of the two components (i.e. on the difunctional epoxy, I, and the tetrafunctional amine, II). The quoted glass transition temperatures (T_g) were obtained by monitoring the dynamic mechanical thermal analysis (d.m.t.a.) loss modulus peak at 10 Hz and 4° min^{-1}. The curing process and the d.m.t.a. measurements were carried out at the Defence Research Agency at Farnborough, whereas the n.m.r. work was done at Durham. Powdered samples of the cured material were obtained for the MAS n.m.r. studies by grinding in a cryogenic mill operating at liquid nitrogen temperatures. The castings for the T_g measurements and the powders for n.m.r. studies were dried before use.

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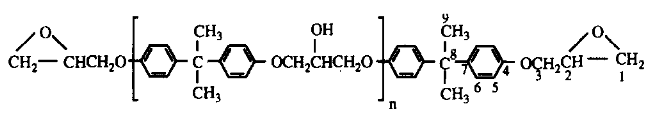
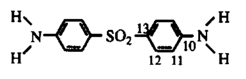


I: Diglycydyl ether of bisphenol A



II: 4,4′-diaminodiphenylsulphone

Table 1 Curing regimes of the two samples of diglycidyl ether of bisphenol A

Sample	Curing	T_g
100% stoichiometry DDS/ diglycidyl ether of bisphenol A	1 h @ 150°C 5 h @ 180°C 2 h @ 200°C *in vacuo*	220°C
66% stoichiometry DDS/ diglycidyl ether of bisphenol A	1 h @ 150°C 5 h @ 180°C	150°C

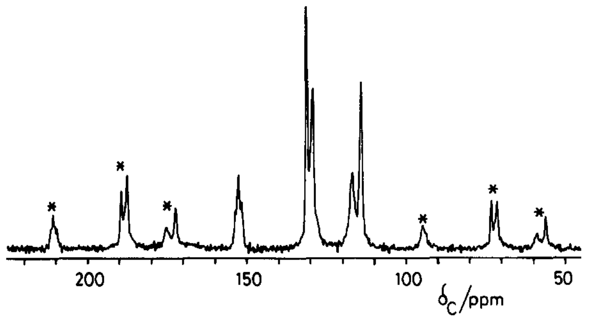


Figure 1 Carbon-13 CP/MAS spectrum of solid diaminodiphenyl sulfone (II) at ambient probe temperature. Spectrometer operating conditions: contact time 1 ms; recycle delay 60 s; spin rate 4.4 kHz; number of transients 54. Peaks marked with an asterisk are spinning sidebands

^{13}C *n.m.r. measurements*

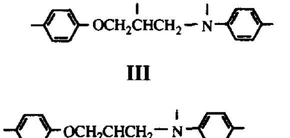
High-resolution solid-state ^{13}C and ^{1}H n.m.r. spectra were recorded at 75.4 MHz and 299.9 MHz, respectively, on a Varian VXR-300 spectrometer. A Doty Scientific high-speed MAS probe using 5 mm o.d. rotors was employed for experiments below 100°C. Carbon-13 cross-polarization with magic-angle spinning (CP/MAS) experiments were carried out for the cured materials at ambient probe temperature with typically ~3000 transients being acquired and a recycle delay of 1 s. The contact duration was 1 ms. Samples were spun at rates of 9–10 kHz. For the conditions used for the spectrum of DDS, see *Figure 1*. At temperatures above 100°C a Doty Scientific high-temperature probe was used. This probe has an operating temperature range of −100°C to +600°C and employs 7 mm o.d. zirconia rotor jackets with silicon nitride sample inserts. Carbon-13 and proton single-pulse with magic-angle spinning (SP/MAS) experiments were carried out at temperatures ranging from 150°C to 290°C. 90° pulse durations of 8 μs were used for both ^{13}C and ^{1}H. Typically 2000–3000 transients were acquired with a 0.5 s or 1 s recycle delay. Sample spinning rates were in the range of 3 kHz, although in the latter stages of the project spinning performance degraded so that rates of ca. 900 Hz were all that could be attained. The maximum temperatures reached for the 100% and 66% stoichiometry samples were 290°C and 260°C, respectively. All temperatures quoted are nominal, since calibration has not been carried out at high temperatures, the aim being to achieve the highest temperatures possible before degradation of the samples occurs. The temperatures represent $T_g + 70$°C for the 100% sample and $T_g + 110$°C for the 66% sample. At these temperatures further experiments, namely the attached proton test (APT), distortionless enhancement by polarization transfer[6] (DEPT) and two-dimensional heteronuclear shift correlation[7] (HETCOR), were also performed. The APT experiment was carried out with a 90° pulse duration of 19 μs, and the free induction decay (FID) was acquired using a spin echo. The modulation period τ was 7 ms which gives positive C, CH_2 signals and negative CH, CH_3 signals. In the DEPT and HETCOR experiments the ^{1}H 90° pulse duration was 9 μs and the ^{13}C 90° pulse duration was 5.5 μs. A value of 175 Hz was used as $^{1}J_{CH}$ for the 100% stoichiometry sample and 200 Hz for the 66% stoichiometry sample. Since difference coupling constants exist for the various carbons with differing multiplicities, these represent empirical average values.

RESULTS AND DISCUSSION

In order to assist with the assignment of the ^{13}C spectra for cured DGEBA–DDS systems, discussed below, spectra were obtained at ambient probe temperature for liquid DGEBA and solid DDS (*Figure 1*). The spectrum of DGEBA shows no sign of impurity lines, suggesting a substantially higher content of the monomer (I, $n = 0$) than found by HPLC. *Table 2* lists the chemical shifts, with assignments taken from ref. 5. There is agreement between our results and those of ref. 5 to within ca. 0.2 ppm for DGEBA, but there are small consistent discrepancies for solid DDS. The shape of the signal for the C–N carbon of DDS arises from dipolar interactions with the quadrupolar ^{14}N nucleus, which are incompletely averaged by MAS.

When DGEBA and DDS are reacted together in stoichiometric amounts the principal reaction is between epoxy and primary/secondary amine. In the event of a deficiency of amine, reactions between epoxy groups and hydroxyls (from secondary alcohols produced from the initial reactions) play an increasing role. The reaction mechanism is shown in *Figure 2*. Model compound studies[8] between phenylglycidyl ether and aniline indicate that the order of reactivity of the three reactions is primary amine > secondary amine ≫ hydroxyl[8]. There is also the possibility of epoxy homopolymerization, catalysed (in the absence of added base catalyst) by tertiary amine groups formed in the other curing reactions. However, at the cure temperatures used, this reaction is almost certainly absent.

As a result of the reactions indicated in *Figure 2*, it is anticipated that the principal epoxy-derived network



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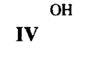


IV

Table 2 Carbon-13 chemical shifts and assignments for the high-temperature spectra of DGEBA/DDS

	δ_C (ppm)				
DGEBA/DDS[a]	100% cure[b]	66% cure[c]	Literature[d]	Assignment[e]	Theoretical intensity[f]
156.94	158.9 m	158.9 (158.8)	157.0	4	2
152.3[g]	155.0 w	154.6	(152.6)	10	1
143.86	146.3 m	146.0 (145.9)	143.5	7	2
131.0	133.4 w	132.9	129.9	13	1
129.0/131.0	130.5 s	[h]	128.9	12	2
127.99	129.6 vs	129.5 (129.4)	127.8	6	4
114.74	117.5 vs	117.4 (117.3)	114.8	5	4
116.6/113.9	115.9 s	115.5	112.2	11	2
	114.9 w			[i]	
		79.8[j]		16?	
69.46	74.0 s	73.7	70.3	3	2
		72.9		18/15	
		71.8 (71.6)		19[k]	
50.22	71.2 s	71.0	69.3/69.5	2/14?	2
44.22	57.6 s[j]	57.4[j]	56.7/57.9	1/17	2
–	–	51.9 (51.8)		[l]	
–	49.3 w			[i]	
–	–	46.1 (46.0)		[l]	
41.88	44.1 m	43.9 (43.8)	41.7	8	1
31.23	32.9 s	32.8 (32.8)	31.0	9	2

[a] Obtained (separately) for liquid DGEBA and solid DDS (see structures I and II for numbering)

[b] vs ≡ very strong; s ≡ strong; m ≡ medium; w ≡ weak (intensities)

[c] Values in brackets are from the APT spectrum and refer to uncured material present in the sample

[d] Ref. 5 (for fully cured material, except for the value in brackets)

[e] See structures VII and IX for numbering

[f] For the 100% cure

[g] Shoulder at 151.4, the complexity arising from interaction with ^{14}N (see text)

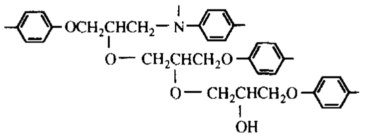
[h] Shoulder, frequency uncertain

[i] Uncertain

[j] Broad

[k] Includes C-3 of uncured epoxy end-groups

[l] Peaks of unreacted DGEBA (or end epoxide groups)



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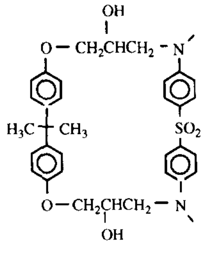
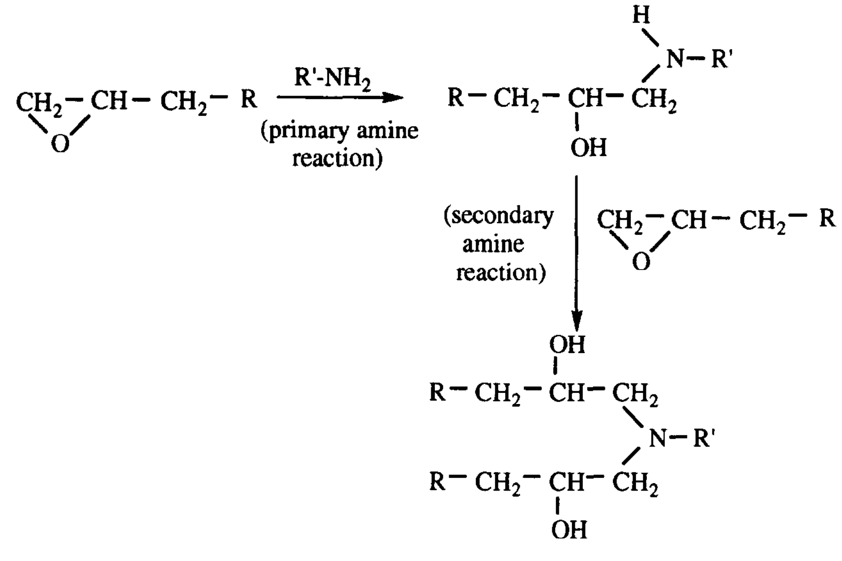


VI

linkage for the 100% material will be III, whereas the 66% system should show both III and IV, together with some V. Also, some intramolecular cyclization ('back-biting') might be expected to occur between epoxy units and amine groups (or, with a deficiency of hardener (II), hydroxyl groups) to give a distribution of ring sizes, of which VI is a simple example.

Carbon-13 CP/MAS spectra at 23°C of the two DGEBA–DDS stoichiometries are shown in *Figures 3a* and *4a*, with corresponding high-temperature SP/MAS spectra in *Figures 3b* and *4b*. Clearly there is substantial narrowing at the higher temperatures, although it is not certain in this case that all the sample is being detected since it was not feasible to use ideal experimental conditions. Note also the absence of spinning-sidebands in *Figures 3b* and *4b*, which indicates efficient motional averaging. Many motions will be present, including internal rotation of the aromatic rings about their *para* axes, which averages signals from relevant *ortho* carbon pairs, giving a single sharp line for all four C-5 carbons for a DGEBA unit in the polymer chain at high temperature, and also for all three C-6, C-11 and C-12 carbons. It may be noted that even in monomer systems related to DGEBA, rotation of the phenylene rings is sufficiently hindered at room temperature that multiple n.m.r. signals are seen for the relevant carbon atoms[9], although heating causes both polymorphic change and merging of lines because of the onset of rapid phenylene rotation. Solid DGEBA itself shows multiple signals for the aromatic CH carbons[5,10] at ambient probe temperature. Hindrance to phenylene rotation for solid DDS is also indicated by the number of lines seen (*Figure 1* and ref. 5). However, in spite of the averaging of signals caused by rapid phenylene internal rotation there is still sufficient rigidity in the DGEBA–DDS polymers at high temperature to allow CP spectra to be obtained

(a) Epoxy-amine reaction:



(b) Epoxy-hydroxyl reaction:

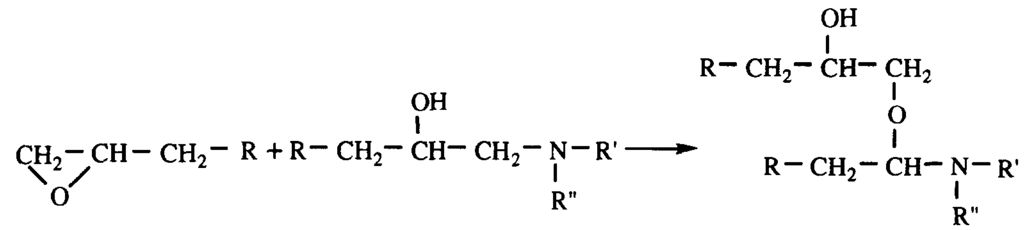
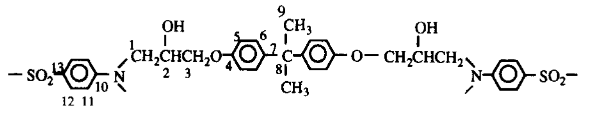
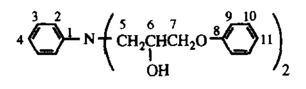


Figure 2 Curing reactions of the diglycidyl ether of bisphenol A with amine hardener



VII



VIII

successfully as an alternative to SPE operation. Such CP and SPE spectra are essentially identical, the resonances for the former being somewhat broader than for the latter.

The spectra of the two DGEBA-DDS stoichiometries show differences reflecting the different chemistry. *Table 2* lists the observed high-temperature chemical shifts. These in general appear to be ca. 1-3 ppm to higher frequency than those reported by Grenier-Loustalot *et al.*[5] at 100°C for the gelation point, but this is probably attributable largely to difficulties of comparison for the referencing as a function of temperature. The assignments of the peaks are made by comparison with the ^{13}C spectra of the uncured material, of the closely related model compound VIII[11], and with chemical shift values reported in the literature[2,3,12]. The 100% material is relatively simple to assign[5], in accordance with the major structure of VII. The asymmetric centres of VIII result[11] in a doubling of the peaks (in solution-state ^{13}C n.m.r.) for carbon nuclei 1, 2, 4, 5 and 6, with observed splittings up to 1.4 ppm in magnitude. The effect of asymmetry in complicating the ^{13}C n.m.r. of related polymer systems has been discussed[13]. Such splittings are in principal present for the systems studied here (see the structure resulting from the amine reaction in *Figure 2*). Although they are not in practice resolvable, they possibly contribute to linewidths for some signals. *Figure 3* can, in general, be entirely explained in terms of structure VII except that there are additional lines at $\delta_C = 114.9$ and 49.3 ppm which probably arise from C-2 and C-5 in unreacted DGEBA molecules or half-molecules (other carbons from such systems being hidden under the major peaks). Quantification is hindered by the short recycle delay (0.5 s), used because of the requirement to minimize total spectrometer time at the elevated temperature, but which may not be adequate for full relaxation (especially of quaternary carbons). The signal for C-1 ($\delta = 57.6$ ppm) is broad, probably because of second-order effects of dipolar coupling to the quadrupolar ^{14}N nucleus.

The situation is clearly more complex for the 66%-cured material, but some peaks additional to those for *Figure 3* can be tentatively assigned on the basis of structure IX and with the help of the SPECINFO

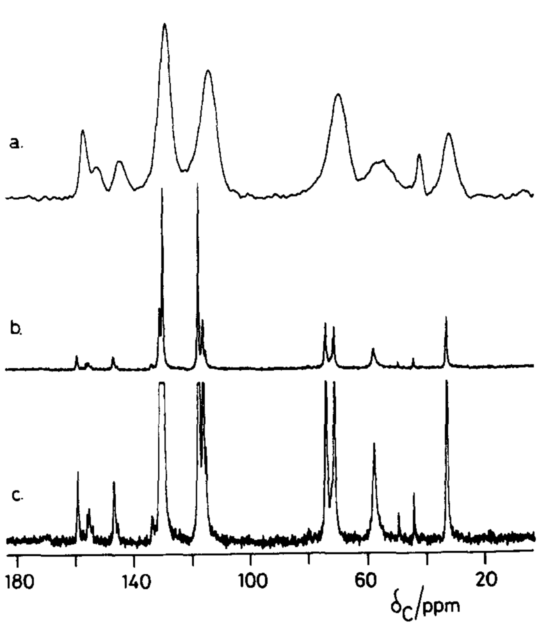


Figure 3 Carbon-13 MAS spectra of DGEBA–DDS with 100% stoichiometry at (a) 23°C with cross-polarization, (b) 290°C without CP, and (c) 290°C with vertical scale expansion

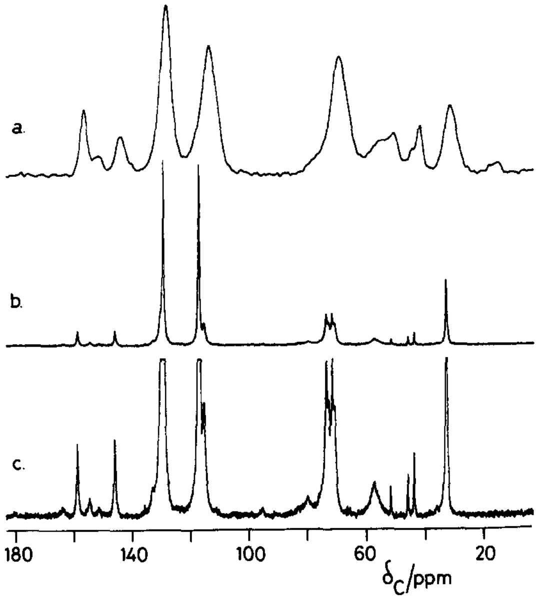
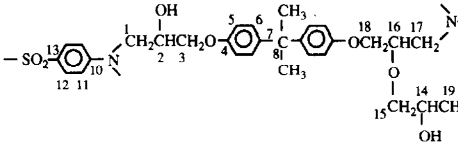


Figure 4 Carbon-13 MAS spectra of DGEBA–DDS with 66% stoichiometry at (a) 23°C with CP, (b) 260°C without CP, and (c) 260°C with vertical scale expansion



IX

database*. Thus, the shoulder to low frequency of that for C-3 may be accounted for by C-18 and C-15, the signal at δ 71.8 may arise in part from C-19, whilst the broad signal at $\delta \sim 80$ ppm can possibly be assigned to C-16 (although its broad nature is a puzzle), and C-14 may occur at the same position as C-2. The N–CH$_2$ resonance of C-17 is probably hidden by that of C-1 (and similarly broadened by the adjacent ^{14}N). As for the 100% material, some resonances in *Figure 4* are probably broadened by effects arising from the asymmetric centres. Although the minor peaks at $\delta = 114.9$ and 49.3 ppm shown by the 100% stoichiometry are absent for the 66% material, additional weak peaks are seen at $\delta = 51.9$ and 46.1 ppm. Since there is excess DGEBA in the latter sample and the final cure temperature did not exceed 180°C in this case, these peaks may well arise from the CH and CH$_2$ carbons (C-2 and C-1, respectively) in unreacted epoxy end groups. This suggestion was confirmed by the observation that after the sample was held at a nominal temperature of 260°C for several hours (i.e. in obtaining spectra) further curing apparently took place. It was then found to be necessary to raise the temperature to a nominal 280°C to get sharp n.m.r. lines (i.e. T_g increased), and the signals at δ 46.1 and δ 51.9 were no longer visible. It may be noted that apart from these two signals the only major difference between spectra of DGEBA itself and its cured product is expected to be for C-3: the shift for this carbon in DGEBA is close to the value for C-2 after curing. The behaviour of the 100%-cured material on being held at the elevated temperature (nominal 290°C) was entirely different. No peaks appeared to be lost but linewidths decreased so that resolution improved, which we assume arises from an annealing process which produces somewhat more uniform environments (or, less likely, an increase in mobility).

Neither *Figure 3* nor *Figure 4* shows any evidence of epoxy decomposition to give a ketone group. As mentioned earlier, the hydroxyl group produced in the ether reaction can react further to form structural element V. However, there are no distinctive structural differences between IV and V which can be identified by n.m.r. In principle, the proportions of III, IV and V present in the polymer network could be obtained from the assigned ArOCH$_2$– and –CH(OH)– peak areas. However, these cannot be estimated with any accuracy, especially since the recycle delay used in the experiment may not be adequate for full relaxation. Moreover, the detailed assignments in the region of 71–74 are by no means certain.

The assignments of the SP/MAS spectra were partially confirmed by using spectral editing techniques such as APT and DEPT. *Figure 5* shows the APT spectrum of the 100% stoichiometry sample, with the C, CH$_2$ peaks clearly positive and the CH, CH$_3$ peaks negative. *Figures 6a* and *6b* show the CH$_2$ and CH DEPT subspectra for the 100% stoichiometry sample, with the CH$_3$ signal appearing in both. *Figure 6a* suggests that the peak at $\delta = 49.3$ ppm (see above) arises from a CH$_2$ carbon. APT experiments on the 66% stoichiometry material resulted, unexpectedly, in observation only of peaks associated with uncured DGEBA, presumably because of insufficient mobility for the cured groups. This effect had the merit of fully confirming the presence of uncured molecules, since all the peaks were clearly seen (including one at 71.2 ppm for the CH$_2$ at C-3).

Whilst the samples were at the higher temperatures, ^{1}H SP/MAS spectra were recorded and are shown in *Figure 7*. The spectra show a relatively high degree of

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* A multi-technique spectroscopic database package accessible via the Chemical Database Service, Daresbury Laboratory, UK

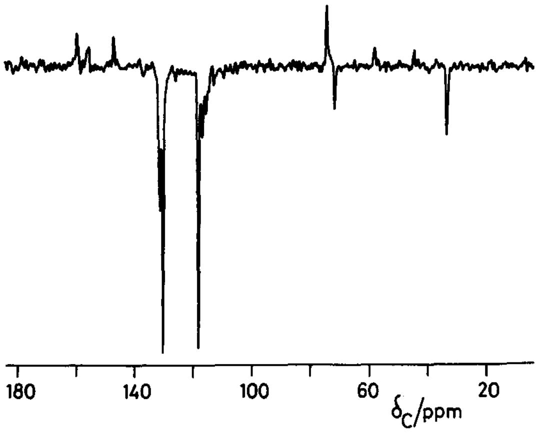

Figure 5 Carbon-13 APT spectrum (single-pulse operation) of DGEBA–DDS with 100% stoichiometry at 290°C

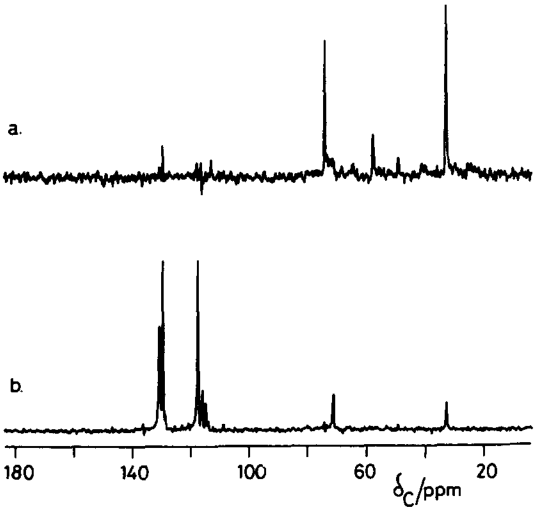

Figure 6 Carbon-13 DEPT spectra (single pulse operation) of DGEBA–DDS with 100% stoichiometry at 290°C: (a) CH_2 subspec-

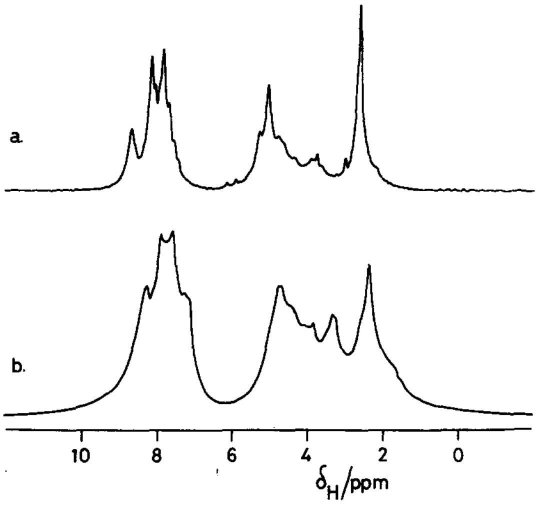

Figure 7 Proton SP/MAS spectra of DGEBA–DDS: (a) with 100% stoichiometry at 290°C, and (b) with 66% stoichiometry at 260°C

resolution with CH_3, CH_2 and aromatic CH peaks clearly defined. The spectrum of the 66% sample is noticeably the broader, presumably reflecting the additional complexity and lower mobility at the molecular level of this material. This helps to explain the anomalous APT results mentioned above. Due to the complicated network structures there are a variety of minor peaks associated with the major peaks. Clearly it is not feasible to assign the exact origin of these peaks from the ^1H spectra alone. However, an attempt was made to correlate the ^1H spectrum with that of the ^{13}C by heteronuclear shift correlation experiments. The result for the 100% stoichiometry sample is shown in *Figure 8*. The major peaks are clearly evident from the contour plot. Other peaks are not visible and are presumably lost in the noise. This experiment has limitations in that the number of transients acquired in a practicable time is relatively small, 64 in this case. Additionally, the number of points acquired in the second dimension is also limited by time and is restricted to 128.

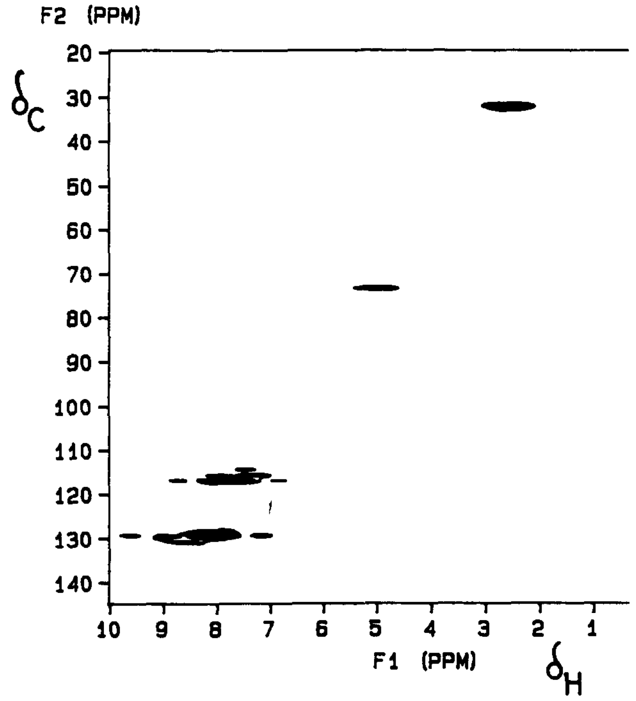

Figure 8 Two-dimensional $^1H/^{13}C$ HETCOR spectrum (single-pulse operation) of DGEBA–DDS with 100% stoichiometry at 290°C

CONCLUSION

Highly-resolved n.m.r. spectra can be obtained from very rigid amorphous materials such as cured epoxies, providing the temperature at which the measurement is made is sufficiently high to allow motional narrowing without sample degradation. At these temperatures features in the spectra reflect the chemistry of the curing process and confirm proposed structures. The details observable in the spectra are such that the completeness of the curing process and the degree of extra ether-link content are clearly visible. Motional narrowing at these temperatures reduces linewidths sufficiently to allow the use of spectral editing techniques to confirm assignments of the peaks. However, in order for these experiments to work the proton–proton dipolar interactions must be reduced sufficiently by molecular motion so that modulations contained in heteronuclear *J*-coupling can be converted into sign and intensity information as displayed in the APT spectrum. Similarly, in the absence of dipolar interactions, polarization transferred via *J*-coupling can suppress certain carbon signals whilst enhancing others as shown by the DEPT subspectra. Within these constraints, techniques hitherto strictly applicable only to the liquid state can be used to complement the information already available from solid-state spectra.

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