Determination of network structure in butane-1,4-diol cured bisphenol A diglycidyl ether using ^{13}C CP–MAS n.m.r. and i.r. spectroscopy

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Solid state ^{13}C cross-polarization, magic angle spinning nuclear magnetic resonance and infra-red spectroscopy are utilized to characterize network systems based on bisphenol A diglycidyl ether cured with butane-1,4-diol in the presence of two different accelerators, magnesium perchlorate and *N,N*-dimethylbenzylamine. There are differences in the reaction courses and the fractions of primary and secondary alcohols, and also in the degree of etherification.

(Keywords: bisphenol A diglycidyl ether; butane-1,4-diol; etherification; nuclear magnetic resonance; infra-red)

INTRODUCTION

In recent years epoxy resins have been extensively studied as matrix materials for composite structures, and adhesives for numerous technical applications. Since most of the applied resins are based on bisphenol A diglycidyl ether (BADGE)[1], differences in the properties and applications of cured systems are achieved by the curing agent and accelerator used. Using aliphatic alcohols as the curing agent, flexible networks are produced. The flexibility depends on the chain length and the functionality of the alcohol[2–4].

In recent publications we reported the cure behaviour of BADGE/butane-1,4-diol (BD) systems[5–7]. ^{13}C nuclear magnetic resonance (n.m.r.) was a suitable means of studying the reaction courses in the pregel[5,6] and the network structure in the solid state[7].

The reaction of the BADGE oxirane rings with primary alcohols leads to secondary alcohols and ether linkages (linear growth). Ether branches and crosslinks result from reactions of secondary alcohols with further epoxies. The molar fractions of epoxies and their consumption of primary and secondary alcohols, and of ether branches or crosslinks, have been quantified by ^{13}C n.m.r.[5–7]. BADGE reacts with BD up to its complete consumption if magnesium perchlorate ($Mg(ClO_4)_2$) is used as accelerator[6]. Crosslink reactions occur first at high conversions. Ether branches are present in *N,N*-dimethylbenzylamine (DMBA)-accelerated systems even at low conversions[6]. (A residual fraction of primary alcohols was detected in the solid-state n.m.r. spectra[7].) It is not possible to distinguish between crosslinks and branches using n.m.r.. However, crosslinked samples are insoluble, and good solubility in $CDCl_3$ is dependent on composition, and indicates linear and short branch structures in the pregel. The aim of this study is to determine the network structures quantitatively and the dependence of the molar ratio of resin to curing agent, and the kind of accelerator used using infra-red (i.r.) and solid-state ^{13}C n.m.r. spectroscopy with cross-polarization (CP) and magic-angle spinning (MAS).

EXPERIMENTAL

Chemicals. BADGE, BD, $Mg(ClO_4)_2$ and *N,N*-dimethylbenzylamine (DMBA) are commercially available products. BADGE was recrystallized from acetone–methanol (m.p. = 42°C).

Preparation of crosslinked polymers. BADGE, BD and accelerator were mixed and stirred in a thermoregulated glass reactor in the molar ratio BADGE:BD:$Mg(ClO_4)_2$ = 1:0.25, 0.5, 0.75, 1:0.03 (samples 3.1–3.4) and BADGE:BD:DMBA = 1:0.25, 0.5, 0.75, 1:0.05 (samples 4.1–4.4). The reaction occurred at 100 and 60°C with $Mg(ClO_4)_2$ and DMBA as accelerators, respectively. If the reaction mixture became homogeneous the solution was poured into a preheated Teflon cylinder and then placed in an oven at the reaction temperature and allowed to cure for 24 h.

Analysis. ^{13}C CP–MAS n.m.r. spectra were obtained with a Bruker MSL 200 spectrometer operating at a frequency of 50.32 MHz. Dipolar decoupling, MAS and CP were used. Spinning side bands in the spectral regions of interest were avoided by using a spinning frequency of 5 kHz. To obtain quantitative spectra the contact time dependence of signal intensities was considered for sample 3.2 in the range 0.1–5 ms. The optimum contact

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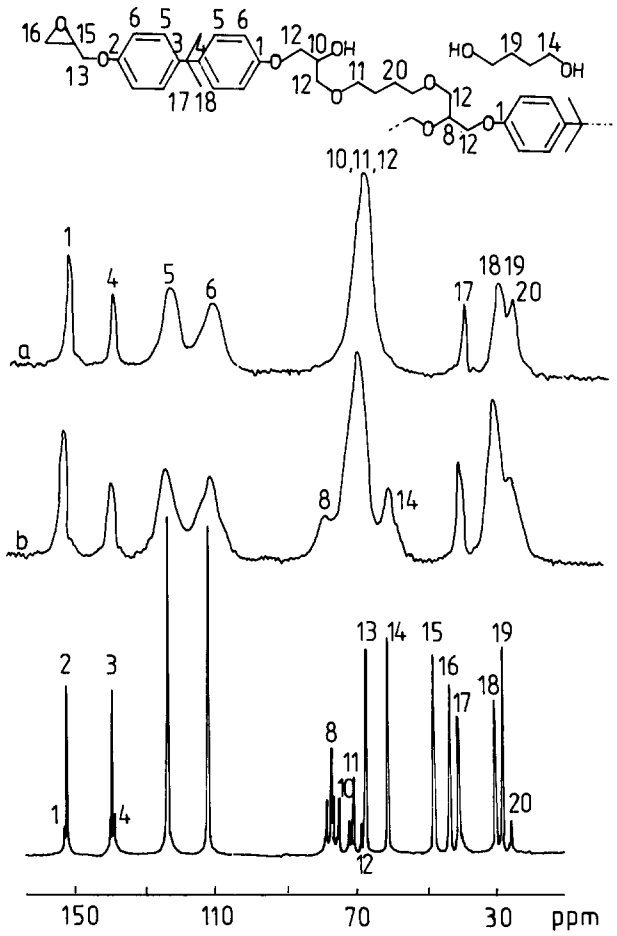

Figure 1 ^{13}C CP–MAS n.m.r. spectra of cured BADGE–BD systems: (a) sample 3.4 (accelerator $Mg(ClO_4)_2$); (b) sample 4.4 (accelerator DMBA). Also ^{13}C n.m.r. of low cured liquid-state sample 4.4. Solvent: $CDCl_3$ (77.0 ppm)

and delay times of the protonated carbons were found to be 0.7 ms and 3 s, respectively. At these values the standard deviation of the measured signal intensities to their maxima at different contact times is a minimum and intensity losses are negligible. Digitalization, separation of overlapped signals and integration of separated signals were carried out by computer simulations based on Lorentzian line shapes using a Tracor Northern TN 4000. Spectra were generally obtained after accumulating 2400 scans.

Infra-red analyses were performed using a Perkin Elmer 580B spectrometer in the range 4000–400 cm^{-1} with a resolution of 2.3 cm^{-1} at room temperature. Absorbance spectra were obtained with KBr pellets (350 mg) containing the sample (1.3 mg).

RESULTS

Nuclear magnetic resonance spectroscopy

The spectra of samples 3.4 and 4.4 (stoichiometric ratio BADGE:BD) are shown in *Figure 1*. For comparison and line assignments the solution ^{13}C n.m.r. spectrum of a low cured sample is included. Signals of the DMBA accelerator are not visible due to its low concentration. Epoxy signals 15 and 16 at 49.8 and 44.1 ppm (oxirane methine and methylene carbons) do not occur in the solid-state n.m.r. spectra of the cured samples. The opening of the epoxide groups shift them downfield to 71.4 (secondary alcohol) and 68.7 ppm (ether linkage), assigned 10 and 12. Etherification of carbon 10 occurs as signal 8 at 77.2 ppm. Signal 13 of the glycidyl ether carbons at 68.5 ppm occurs also as signal 12 if the ring-opening reaction takes place. The total intensities of the corresponding signals of monomeric BADGE and reacted groups, 15, 10 and 8, 16 and half of 12, 13 and half of 12, 2 and 1, 3 and 4, remain fairly constant with increasing epoxide consumption. Fractions of epoxy and hydroxy groups of low cured samples were determined by liquid-state ^{13}C n.m.r. as reported previously[6]. The signals of the aromatic methine carbons 5 and 6, the quaternary carbon 17 and the methyl carbon 18 were the same in the spectra of samples that differ in the cure state. We used signals 5 and 6 as internal intensity standards.

Unreacted BD methylene carbon signals 19 and 14 occur at 29.2 and 61.9 ppm (primary alcohols). Reaction with BADGE shifts them to 25.9 and 70.9 ppm (signals 20 and 11). Since epoxide consumption is complete in the cured samples, we assume that the largest signal at 70 ppm in the solid-state n.m.r. spectra is composed of signals 10, 11, 12 and a shoulder of signal 8. The contribution of reacted BD (signal 11) was separated by subtracting the intensity of signal 20, because its intensity corresponds to that of signal 11. The total intensity of reacted BADGE is given by the intensities of signals 8, 10 and 12.

The maximum percentage of residual epoxide groups in the cured samples was estimated to be 3% with reference to 100% initial epoxies by normalizing the noise magnitude in the chemical shift range between 50 ppm and 44 ppm on the intensity standard of signals 5 and 6.

The percentage of primary alcohols at different cure states depends on the accelerator. Whereas in the $Mg(ClO_4)_2$-accelerated samples 3.1–3.4 the fraction of primary alcohols (signals 14 and 19) vanishes at epoxide consumptions corresponding to the mole fraction of BD in the initial mixture[6], that of the DMBA-accelerated samples 4.1–4.4 remains unreacted as residual primary alcohols ($\sim$50% of the initial fraction).

A further difference in the reaction course caused by the different accelerators is the degree of etherification. Ether branches or crosslinks (signal 8) were detected by liquid-state n.m.r. only in the DMBA-accelerated samples[6]. The degree of etherification increases with epoxy conversion depending on composition.

To determine the degree of etherification from cured sample solid-state n.m.r. spectra it is necessary to separate signals 8 and 10 from signal 12 and from each other. Since signals 8 and 10 correspond to 12 in the ratio 1:2, and 8 occurs as a shoulder their intensities have been detected separately as described in Experimental. The maximum degree of etherification reaches $\sim$43% of the initial epoxy groups in the DMBA-accelerated samples at BADGE:BD = 1:1 (sample 4.4). $Mg(ClO_4)_2$-accelerated samples reach a maximum degree of etherification of $\sim$37% of the initial epoxy groups at a molar ratio BADGE:BD of 2:1 (sample 3.2) (*Table 1*). The total

Table 1 Degree of etherification of cured samples

Sample	Degree of etherification	Sample	Degree of etherification
3.1	0.32	4.1	0.35
3.2	0.37	4.2	0.28
3.3	0.23	4.3	0.30
3.4	0.15	4.4	0.43

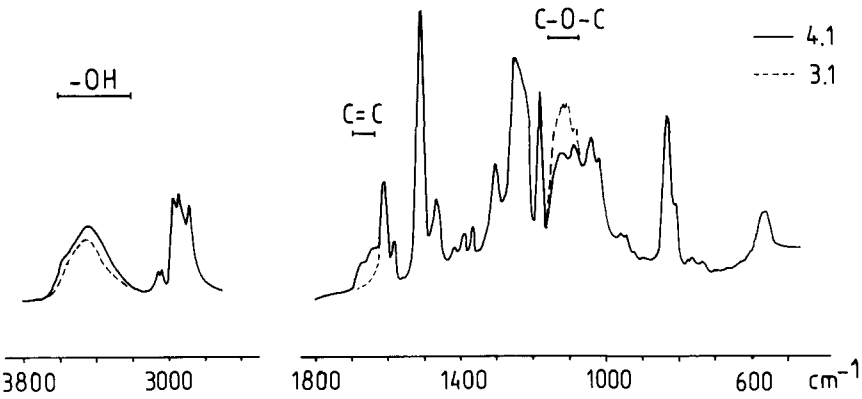

Figure 2 Infra-red spectra of cured samples 3.1 and 4.1

Table 2 Infra-red band assignments

Wavenumber (cm^{-1})	Assignment	Reference
3200–3650	ν(OH)	8
3057	$\nu(CH_2)$ epoxy as	1
3038	ν(Ph-H)	1
2929	ν(CH)	1
1650–1690	ν(C=C)[a]	8
1365–1395	$\delta(CH_3)$ sy	8
1185	δ(Ph-H) ip	1
1035–1170	ν(C—O—C)	8
1036	ν(Ph—O—C) sy	1
1012	δ(Ph-H) ip	1
916	Epoxy ring	8
831	δ(Ph-H)[b] oop	1

Abbreviations: ν, stretching; as, asymmetric; Ph, aromatic; δ, deformation; sy, symmetric; ip, in plane; oop, out of plane
[a] Only samples 4.1–4.4
[b] Reference band

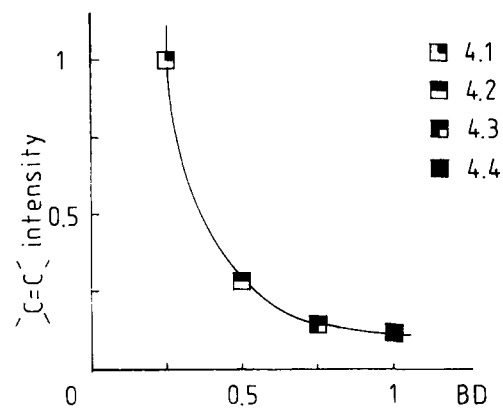

Figure 3 Plot of relative intensities of aliphatic double bonds *versus* BD mole fraction in DMBA-accelerated samples 4.1–4.4

fraction of hydroxy groups (primary and secondary) in the cured samples corresponds to the initial BD fraction only for samples 3.3, 3.4, 4.3 and 4.4. At lower BD content more secondary alcohols will be produced than BD consumed. Reactions other than between BADGE and BD could occur, such as BADGE homopolymerization and cyclization, and reactions with water. Evidence of BADGE dimers produced by gel permeation chromatography and Fourier transform infra-red spectroscopy[5] and the detection of double bonds by i.r. (this work) support this assumption.

Infra-red spectroscopy

Infra-red spectra of cured samples 3.1 and 4.1 are given in *Figure 2*. The band assignments listed in *Table 2* are quite well documented[1,8]. The major features in the cured samples spectra are: the intensity of the 916 cm^{-1} band is indicative of the content of unreacted epoxy groups; the intensity of the 1035–1170 cm^{-1} bands is a measure of ether linkages, mainly produced by BADGE–BD reactions; the intensity of bands at 1650 and 1690 cm^{-1} assigned to aliphatic double bonds decreases with increasing BD content; bands of hydroxy groups occur at 3200–3650 cm^{-1} (separation of primary and secondary alcohols is not possible).

For quantitative analysis all spectra were normalized on equal intensities of 831 cm^{-1} bands presumed to be associated with the benzene ring and therefore independent of the degree of cure.

The content of unreacted epoxy groups was determined to be < 2% in all samples according to n.m.r. estimations.

It is known, that aliphatic double bonds occur in the starting reaction if the concentration of aliphatic alcohols is low and DMBA is used as the accelerator[4]:

$$n\text{R—CH(O)CH}_2 \xrightarrow[100^\circ\text{C}]{\text{DMBA}} \text{CH}_2{=}\text{C(R)—O—(CH}_2\text{—CH(R)—O)}_{n-1}\text{H}$$

From normalized i.r. spectra, band intensities of double bonds were determined in DMBA-accelerated samples 4.1–4.4 relative to sample 3.1 (without double bonds, *Figure 2*). In *Figure 3* the relative intensities of double bonds are plotted *versus* diol mole fraction. A lowering of the number of double bonds with increasing BD indicates a change in the reaction mechanism.

The fraction of ether linkages differs in both sample series; higher values were detected in $Mg(ClO_4)_2$-accelerated samples. It was presumed that these bands are indicative of BADGE–BD reactions with higher values being associated with complete BD conversion. In DMBA-accelerated samples, half of the BD remains unreacted as determined from the n.m.r. studies. Quantitative i.r. measurements are not possible because the influence of etherification on the spectra is overlapped in this region.

Bands of hydroxy groups at 3400 cm^{-1} are not overlapped. Differences in both sample series occur as shown in *Figure 4*. The intensity maximum was found for sample 3.4. According to n.m.r. results with higher contents of hydroxy groups than primary alcohols in the

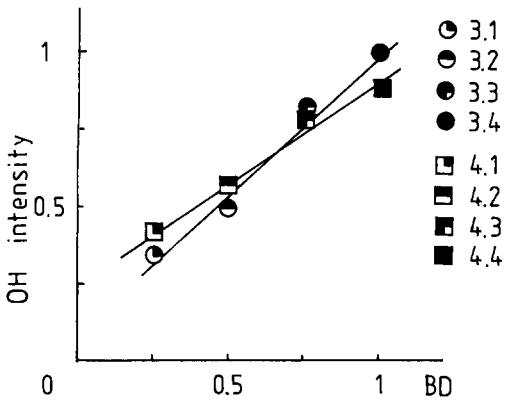

Figure 4 Plot of relative intensities of hydroxy group bands *versus* BD mole fraction

starting mixture in sample 3.1 and 4.1 differences in the sample series occur. These differences can be explained by different reaction courses.

CONCLUSIONS

The accelerators $Mg(ClO_4)_2$ and DMBA influence the reaction course and structure of BD-modified BADGE networks in a characteristic manner. Whereas in $Mg(ClO_4)_2$-accelerated systems BADGE–BD reactions are complete with respect to the consumption of primary alcohols, in DMBA-accelerated samples there are ~50% residual primary alcohols relative to the initial fraction. Also, reactions of epoxy groups and secondary alcohols producing ether branches and crosslinks dominate even in low cured liquid-state samples using $CDCl_3$ as solvent. Only in DMBA-accelerated systems do aliphatic double bonds occur as known from BADGE homopolymerization processes in the absence of BD. The number of double bonds decreases with increasing BD mole fraction. Furthermore, the maximum degree of etherification depends on the accelerator and the molar ratio of BADGE:BD.

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