Plasticization and antiplasticization effects of photo- and heat-induced initiator fragments remaining in cured cycloaliphatic epoxy resins: solid-state ^{13}C n.m.r. study

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The molecular motions in cycloaliphatic epoxy resins cured by ultraviolet (u.v.) and heat-induced sulphonium salt initiators were found to depend on the type and concentration of the initiators. In the u.v. cured samples, the cyclohexyl ring motion is suppressed as the photoinitiator concentration increases in the range of 0.5–1 wt%, but is promoted with concentration values >1 wt%, indicating the antiplasticization and plasticization effects, respectively, of the initiator fragments remaining in the samples. In the heat cured samples, on the other hand, only slight suppression of the motion was observed below 5 wt% initiator concentration. The variable temperature $T_{1\rho}^{C}$ measurements revealed that the chair–chair inversion process of the cyclohexyl ring in the u.v. and heat cured samples studied was restricted and its correlation time was $>10^{-6}$ s even in the rubbery state. The T_1^C data clarified that the butyl chain moiety of these polymers undergoes much more rapid molecular motion compared with the cyclohexyl ring moiety at room temperature.

(Keywords: cycloaliphatic epoxy resin; latent curing agent; u.v. cure; solid-state ^{13}C n.m.r. spectroscopy; molecular motions; plasticization; antiplasticization)

INTRODUCTION

Aromatic sulphonium salts possessing a non-nucleophilic anion have been developed as photoinitiators for ultraviolet (u.v.)-induced cationic polymerization of epoxy resins[1–3]. Brønsted acids are produced from the photolysis of these sulphonium salts and then initiate the ring-opening polymerization of epoxy groups. Ultraviolet curable epoxy resin systems have been investigated for use as rapid curable coatings. Furthermore, aliphatic sulphonium salts have been recently developed as heat-induced initiators for epoxy cationic polymerization[4,5].

In our previous report[6], the dynamic mechanical properties of cycloaliphatic epoxy resins cured by u.v.- and heat-induced sulphonium salt initiators were found to depend on not only the type but also the concentration of the initiators. The glass transition temperatures, T_g, of both u.v. and heat cured samples decrease with an increase in initiator concentration due to the diluent effect of the initiator fragments remaining in the samples. Thus, our studies are aimed at obtaining more detailed dynamic structures of the cured epoxy resins as well as comparing the u.v. and heat cured epoxy resins with respect to molecular motion.

Various solid-state nuclear magnetic resonance (n.m.r.) relaxation parameters, such as ^{13}C spin-lattice relaxation time in the rotating frame $(T_{1\rho}^{C})$[7–9], ^{13}C spin-lattice relaxation time (T_1^C)[8,10] and ^1H spin diffusion[11,12], have been used for the characterization of molecular motions in glassy polymers with low molecular weight diluent. Sefcik *et al.*[7] reported from the $T_{1\rho}^{C}$ measurements that the cooperative main-chain motions of poly(vinyl chloride) are reduced when the diluent acts as an antiplasticizer and increase when the polymer is plasticized. Similar $T_{1\rho}^{C}$ data have also been reported for polycarbonate (PC)–diluent systems[8] and poly[oligoethylene glycol) dimethacrylates] – its residual monomer systems[9]. Belfiore *et al.*[8] reported that antiplasticization affects the mobility of PC in the megahertz region, while Edzes and Veeman[10] reported for poly(methyl methacrylate) (PMMA)-plasticizer systems that increased mobility of the polymer in the presence of plasticizer does not induce significant changes in T_1^C.

In this paper, molecular motions of the u.v. and heat cured cycloaliphatic epoxy resins are investigated in detail using both T_1^C and $T_{1\rho}^{C}$ measurements. At room temperature, Garroway *et al.*[13] have found that the $T_{1\rho}^{C}$ of cured epoxy resins is dominated by a spin-lattice relaxation process rather than a spin–spin relaxation process, thus reflecting the molecular motions in the mid kilohertz region. In the megahertz region, it is accepted that T_1^C is due to a spin-lattice process in the strict sense or is motional in origin. The T_1^C and $T_{1\rho}^{C}$ values are measured for the u.v. and heat cured epoxy resins in order to know the dependence on the concentration of initiators added. In other words, the plasticization or antiplasticization effect of the initiators is clarified in terms of their concentration. In addition, the mobility of the cyclohexyl rings and butyl chains in the epoxy polymers is discussed in some detail.

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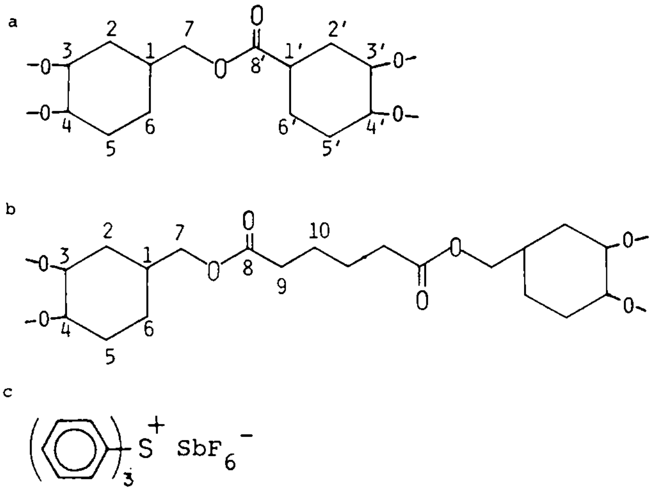

Figure 1 Structural formulae of the monomer units of ECC (a), EA (b) and TPSHA (c)

EXPERIMENTAL

Materials

The cycloaliphatic epoxy resins 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ECC) and 3,4-epoxycyclohexyl adipate (EA), were supplied from Union Carbide and were used without further purification. The photoinitiator, triphenylsulphonium hexafluoroantimonate (TPSHA), and the heat-induced initiator, aliphatic sulphonium (CP66), were supplied from 3M and Asahi Denka, respectively. The mixtures of the epoxy resin and the photo or heat initiator were prepared in various initiator concentrations between 0.5 wt% and 5 wt%. The samples were polymerized by the u.v. or heat curing procedure described elsewhere[6]. The structural formulae of each monomer unit of the ECC and EA polymers produced are shown in *Figure 1*.

High-resolution solid-state ^{13}C n.m.r. measurements

The ^{13}C cross-polarization[14,15] magic angle spinning[16,17] (CP/MAS) spectra were measured at the ^{13}C resonance frequency of 67.9 MHz on a JEOL GSX-270 spectrometer with a variable temperature CP/MAS accessory. Typical spectra were obtained using 27 kHz spectral width, 8 K data points, 1 ms contact time, 5 s pulse duration and 2000 accumulations at room temperature. The cured sample was packed in a cylindrical ceramic rotor. A spinning rate of 5.1–6.0 kHz was used for MAS. The typical 90° pulse width and spin-lock field were 4.1 μs and 60 kHz, respectively. Chemical shifts were calibrated through the methylene ^{13}C signal of adamantane (29.5 ppm) relative to tetramethylsilane.

The T_1^C measurements were performed using Torchia's pulse sequence[18]. Delay times between ^{13}C 90° pulses ranged from 0.1 to 15 s. The $T_{1\rho}^C$ values were obtained using standard procedures[19]. Delay times after the ^1H radiofrequency field was removed ranged from 1 to 10 ms.

Dynamic mechanical measurements

The complex Young's moduli, E^* $(=E'+iE'')$, of the cured samples were obtained with a Rheometrics RSA-2 solid analyser at 1 Hz at 5°C intervals in the temperature range from 50 to 250°C. The temperature was raised in 5°C steps every 30 s. The T_g value was defined as the temperature of maximum tan δ $(=E''/E')$.

RESULTS AND DISCUSSION

The CP/MAS spectra of the cured samples of ECC and EA are shown in *Figures 2* and *3*, respectively. In both figures, traces a and b show the spectra of the u.v. cured samples with photoinitiator concentrations of 2.0 and 4.8 wt%, respectively. On the other hand, traces c and d show the spectra of the heat cured samples with heat-induced initiator concentrations of 1.5 and 4.8 wt%, respectively. The signal assignments were made on the basis of the solution ^{13}C n.m.r. resonance assignments for the corresponding monomers[20], and are designated in the figures. The broad resonance at 110–150 ppm, which is absent in the solution spectra of the corresponding monomers and whose intensity becomes larger as the initiator concentration increases, should arise from the initiator fragments remaining in the samples. The resonance at 55 ppm, which appears in traces b and c in *Figure 2* (marked with arrows) was

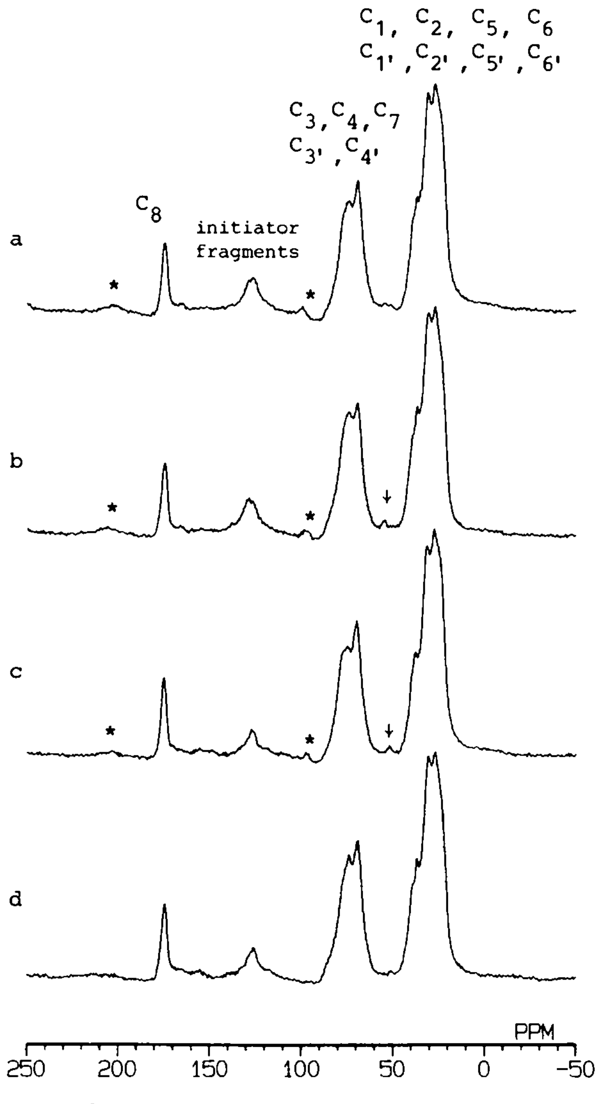

Figure 2 ^{13}C CP/MAS spectra of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate cured by u.v.- and heat-initiated cationic polymerizations: (a) ECC/TPSHA = 100/2; (b) ECC/TPSHA = 100/5; (c) ECC/CP66 = 100/1.5; (d) ECC/CP66 = 100/5. Spinning sidebands are marked with asterisks

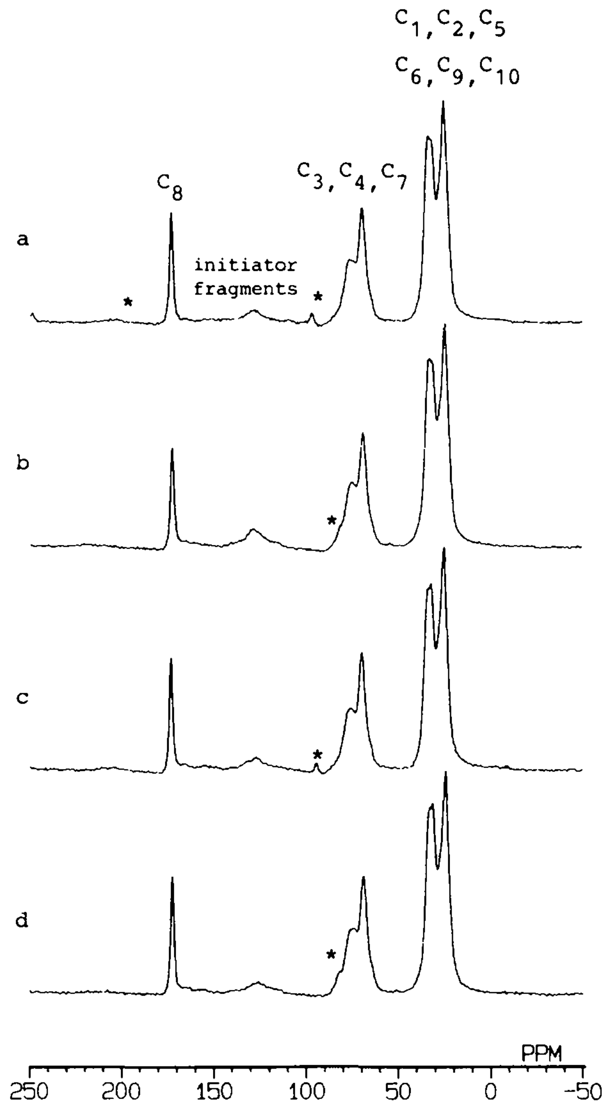

Figure 3 ^{13}C CP/MAS spectra of 3,4-epoxycyclohexyl adipate cured by u.v.- and heat-initiated cationic polymerizations: (a) EA/TPSHA = 100/2; (b) EA/TPSHA = 100/5; (c) EA/CP66 = 100/1.5; (d) EA/CP66 = 100/5. Spinning sidebands are marked with asterisks

assigned to unreacted epoxy carbons. The intensity ratio of the resonance at 55 ppm to that at 60–90 ppm in the CP/MAS spectrum was almost equal to that in its dipolar decoupling (DD)/MAS spectrum measured under the conditions sufficient for quantitative analysis (results not shown). In addition, no significant difference in the spectral pattern at 60–90 ppm was found between the DD/MAS and CP/MAS spectra. Therefore, the integrated signal intensities, X and Y, for the resonances at 60–90 and 55 ppm, respectively, in the CP/MAS spectra were used to calculate the conversion of the ECC samples, C, using the following equation:

$$C = 4X/(4X + 5Y)$$

The calculated conversion is >97% in all ECC samples. Since the sideband of the initiator fragments overlaps the unreacted epoxy resonance at around 55 ppm, the calculated value may be smaller than the 'real' value. In any case, the epoxy groups should be almost consumed during the polymerization. On the other hand, the resonance at 55 ppm completely disappears in the spectra of all EA samples, thus their conversion should be close to 100%. Since no significant difference in the spectral features was detected in the traces in *Figures 2* and *3*, except the resonance arising from the initiator fragments and the unreacted epoxy groups, there is no significant change in the chemical structures of the epoxy polymers produced due to initiator concentration and the type of curing process.

The T_g values of the cured samples of ECC and EA are plotted against initiator concentration in *Figure 4*. The T_g values decrease with increase in initiator concentration in all samples in spite of their identical CP/MAS spectra, indicating that the initiator fragments of TPSHA and CP66 remaining in the samples act as diluents in the epoxy resins[6].

The molecular dynamics of the u.v. and heat cured samples were investigated using T_1^C and $T_{1\rho}^C$. The insufficient resolution of the CP/MAS spectra, as shown in *Figures 2* and *3*, allows the calculation of only a mean relaxation time from the variation of integral intensity of the whole resonance at 10–50 or 60–90 ppm. Since the resonances at 10–50 and 60–90 ppm are mainly attributed to the methylene and ether carbons in the cyclohexyl rings, respectively, relaxation times obtained for both resonances should reflect the molecular motions of the cyclohexyl rings. We confirmed from $T_{1\rho}^C$ measurements using a variety of spin-lock field strengths that the $T_{1\rho}^C$ of the cured samples is dominated by spin-lattice relaxation under a spin-lock field of 60 kHz. In addition, variable temperature experiments indicate that molecular motions in the cured samples at room temperature are in the slow motion region relative to both T_1 and $T_{1\rho}$ minima in the curves of the Bloembergen-Purcell-Pound (BPP) theory[21]. Therefore, any increase in T_1^C and $T_{1\rho}^C$ indicates a decrease in mobility.

The $T_{1\rho}^C$ values of the cured ECC samples are plotted

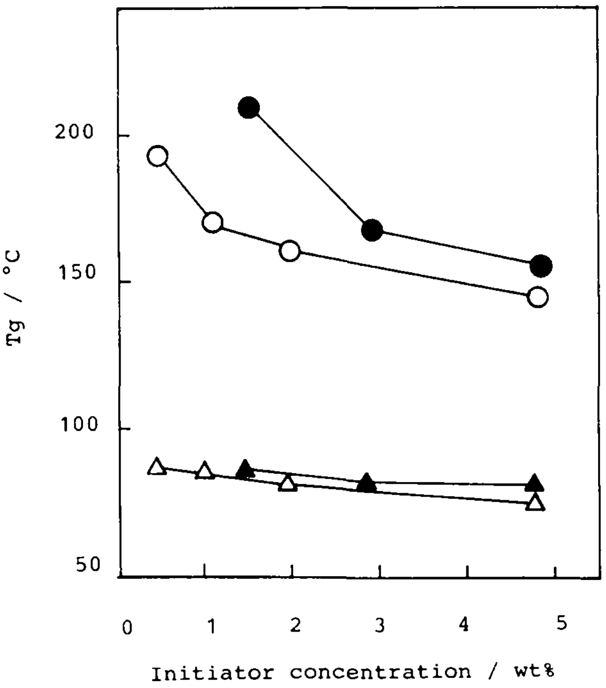

Figure 4 Initiator concentration dependence of the T_g for cycloaliphatic epoxy resins cured by u.v.- and heat-initiated cationic polymerizations: ECC/TPSHA (○); ECC/CP66 (●); EA/TPSHA (△); EA/CP66 (▲). The lack of data for the heat cured samples with <1 wt% CP66 concentration is due to incomplete curing

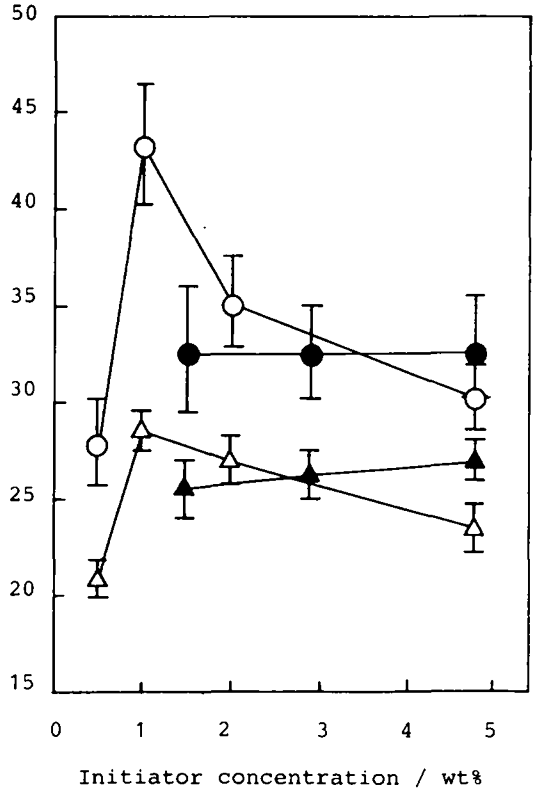

Figure 5 Initiator concentration dependence of the ^{13}C spin-lattice relaxation time in the rotating frame, $T_{1\rho}^C$, of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate cured by u.v.- and heat-initiated cationic polymerizations: ECC/TPSHA, 10–50 ppm (△); ECC/TPSHA, 60–90 ppm (○); ECC/CP66, 10–50 ppm (▲); ECC/CP66, 60–90 ppm (●)

against initiator concentration in *Figure 5*. As can be seen, the $T_{1\rho}^C$ of the u.v. cured ECC samples depends strongly on the TPSHA concentration. The increase in $T_{1\rho}^C$, i.e. decrease in the mobility of the cyclohexyl rings, was observed as the TPSHA concentration increased in the range of 0.5–1 wt%. In contrast, the $T_{1\rho}^C$ values decrease, i.e. the mobility increases, with increase in the TPSHA concentration above 1 wt%. This TPSHA concentration dependence of the $T_{1\rho}^C$ value accompanied by the monotonous decrease in the T_g clearly indicates the antiplasticization–plasticization effect of the TPSHA fragments remaining in the samples, i.e. they act as an antiplasticizer below 1 wt% but act as a plasticizer above 1 wt%. On the other hand, only a slight increase in $T_{1\rho}^C$ was observed in the heat cured ECC samples, thus the mid kilohertz motions in the heat cured epoxy polymers do not appear to depend significantly on the CP66 fragments remaining in the samples. These findings are consistent with the dynamic mechanical properties of the ECC samples previously reported[6]; the suppression of the β relaxation, observed in the samples around −80°C at 1 Hz and attributed to the molecular motions of the cyclohexyl rings, was found in ECC/TPSHA due to the antiplasticization of the TPSHA fragments, while no suppression was found in ECC/CP66.

The $T_{1\rho}^C$ values of the cured EA samples are plotted against initiator concentration in *Figure 6*. Although the $T_{1\rho}^C$ plot of the u.v. cured samples exhibits the antiplasticization–plasticization effect of the CP66 fragments remaining in the samples, this effect on the EA samples is much less than that on the ECC samples. The EA network is more flexible than the ECC network because there are mobile butyl moieties in the EA polymer and it has a lower crosslinking density than the ECC polymer[6]. The results in *Figures 4* and *6* indicate that the EA samples are so flexible in themselves at room temperature that the diluent effect of the initiator fragments is almost ineffective.

The mechanical relaxation of poly(cyclohexyl methacrylate) (PCHMA) observed around −80°C at 1 Hz has been attributed to the chair–chair conformational inversion of the side chain of the cyclohexyl ring[22–25]. The correlation time of this ring motion was reported to be 5×10^{-6} s at 20°C from the variable temperature CP/MAS experiments[26,27], thus the $T_{1\rho}^C$ minimum of this motion should be observed around room temperature. On the other hand, the molecular motion of the cyclohexyl rings in the cured ECC and EA samples at room temperature is in the slow motion region and the $T_{1\rho}^C$ values of this motion in these samples are one order of magnitude larger than those in PCHMA[26]. In addition, variable temperature experiments indicate that the temperatures at the $T_{1\rho}^C$ minimum in the EA samples should be higher than 100°C (the highest obtainable temperature for our n.m.r. instrument), which is ~15°C higher than their T_g values. Hence the correlation time for the molecular motion of the cyclohexyl ring even in the rubbery state (15°C above T_g) should be $>10^{-6}$ s. Such restriction of the cyclohexyl-ring motions was reported when the ring was introduced into the main chain of the polymers[28]. Because the cyclohexyl rings in the epoxy polymers are incorporated in the network, their motion should be much more restricted than in PCHMA.

The T_1^C values of the cured ECC samples are plotted against initiator concentration in *Figure 7*. The decrease of the molecular motions in the megahertz region reflected by the increase in the T_1^C was observed as the TPSHA concentration increased in the range of 0.5–2 wt%. Since antiplasticization of a polymer–diluent system has been attributed to the decrease in free volume

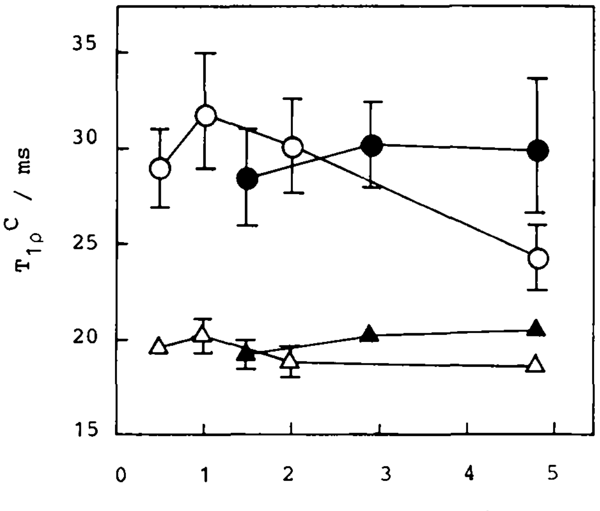

Figure 6 Initiator concentration dependence of the ^{13}C spin-lattice relaxation time in the rotating frame, $T_{1\rho}^C$, of 3,4-epoxycyclohexyl adipate cured by u.v.- and heat-initiated cationic polymerizations: EA/TPSHA, 10–50 ppm (△); EA/TPSHA, 60–90 ppm (○); EA/CP66, 10–50 ppm (▲); EA/CP66, 60–90 ppm (●)

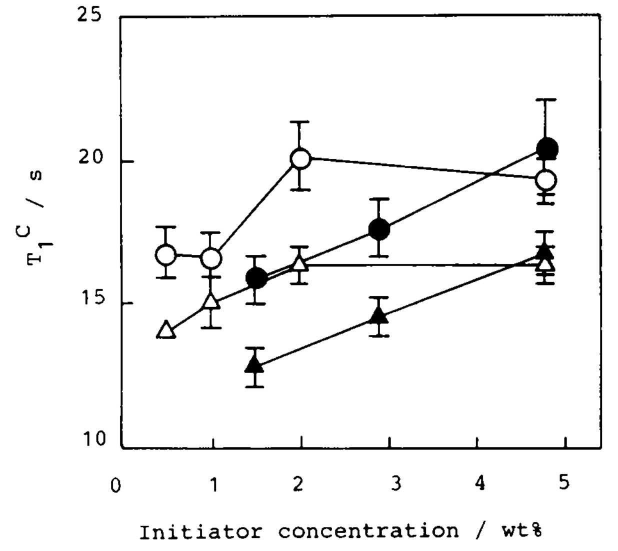

Figure 7 Initiator concentration dependence of the ^{13}C spin-lattice relaxation time, T_1^C, of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate cured by u.v.- and heat-initiated cationic polymerizations: ECC/TPSHA, 10–50 ppm (△); ECC/TPSHA, 60–90 ppm (○); ECC/CP66, 10–50 ppm (▲); ECC/CP66, 60–90 ppm (●)

due to the interaction between the diluent and the atomic groups in the polymer[22], the TPSHA fragments should suppress the localized motions in the epoxy polymer. To the contrary, the T_1^C trend above 2 wt% indicates that the TPSHA fragments negligibly affect the localized motions. A similar phenomenon has been reported for PMMA–plasticizer systems[10], in which increased mobility of the polymer in the presence of a plasticizer is not reflected in significant changes in T_1^C. This is the antiplasticization–plasticization effect of plasticizer, while our finding in this report is that of the initiator fragments.

The ECC/CP66 sample exhibits an increase in T_1^C as the CP66 concentration increases, thus the CP66 fragments suppress the localized motions in their epoxy polymers. This behaviour, accompanied by the T_g depression and the slight increase in $T_{1\rho}^C$, should originate from the antiplasticization effect of the CP66 fragments remaining in the samples. The antiplasticization effect of the CP66 fragments in the ECC samples is less than that of the TPSHA fragments, and therefore the physical properties of the heat cured polymer are not significantly altered by the CP66 concentration.

The T_1^C values of the cured EA samples are plotted against initiator concentration in *Figure 8*. The T_1^C values are almost constant irrespective of the initiator concentration in both EA/TPSHA and EA/CP66, thus the diluent effect of their fragments is nearly ineffective on the localized motions, its T_g and kilohertz motions in the epoxy polymer.

The partially relaxed spectra of the u.v. cured EA samples by Torchia's pulse sequence[18] are shown in *Figure 9*. Since the spectral pattern of the resonance at 60–90 ppm exhibits only slight distortion after the delay time of 6 s, the difference in the relaxation time should be negligible among the carbon nuclei resonating in this chemical shift region. In fact, the plot of the integrated signal intensity for the resonances at 60–90 ppm fits a single exponential curve. However, the spectral pattern at 10–50 ppm significantly depends on the delay time. The relaxation data for the resonances at 10–50 ppm were analysed using a bi-exponential curve and T_1^C values of 1.1 and 10.7 s were obtained for the rapid and slow relaxation components in EA/TPSHA = 100/2, respectively. Since the rapid relaxation component vanishes after the delay time of 6 s, only the slow relaxation component appears in trace c. Trace d shows the difference spectrum (a − b), and therefore only the spectrum of the rapid relaxation component is

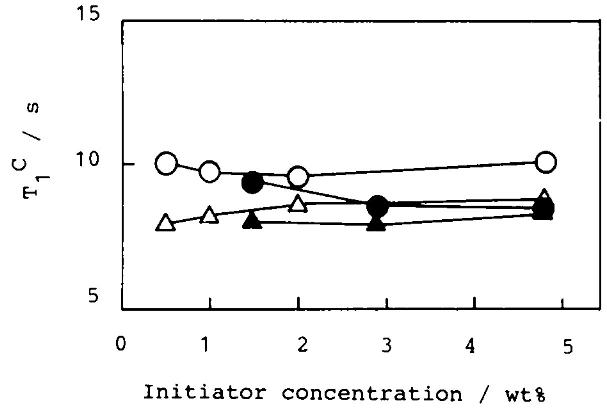

Figure 8 Initiator concentration dependence of the ^{13}C spin-lattice relaxation time, T_1^C, of 3,4-epoxycyclohexyl adipate cured by u.v.- and heat-initiated cationic polymerizations: EA/TPSHA, 10–50 ppm (△); EA/TPSHA, 60–90 ppm (○); EA/CP66, 10–50 ppm (▲); EA/CP66, 60–90 ppm (●)

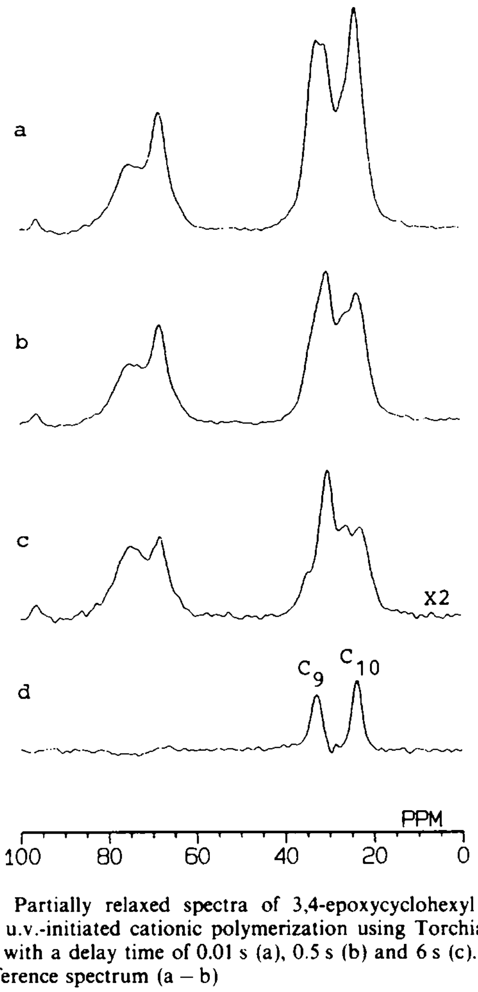

Figure 9 Partially relaxed spectra of 3,4-epoxycyclohexyl adipate cured by u.v.-initiated cationic polymerization using Torchia's pulse sequence with a delay time of 0.01 s (a), 0.5 s (b) and 6 s (c). Trace d is the difference spectrum (a − b)

emphasized. Compared with the solution ^{13}C n.m.r. assignments of EA[20], two peaks observed in trace d are assigned to the methylene carbons in the butyl moiety of the EA polymer (C_9 and C_{10}). Four peaks (one is a shoulder) observed in trace c are, hence, assigned to the methylene and methine carbons in the cyclohexyl rings (C_1, C_2, C_5 and C_6). This result indicates that the localized molecular motions of the butyl moiety are more effective on the spin-lattice relaxation process than those of the cyclohexyl ring. Therefore, the correlation time of the former is smaller than that of the latter at room temperature. This interpretation is supported by the dynamic mechanical properties of the EA samples[6], where the mechanical relaxations observed around −140 and −80°C are attributed to the molecular motions of the butyl chain and the cyclohexyl ring, respectively. The former motion may be *trans-gauche* conformational transitions occurring in the polymer without concomitant large-scale reorientation of the ends of the butyl chain[29].

CONCLUSIONS

The cycloaliphatic epoxy resins cured by u.v.- and heat-induced initiators for cationic polymerization were investigated by high-resolution solid-state ^{13}C n.m.r. spectroscopy. The CP/MAS spectra of the cured samples indicate that their chemical structures are identical irrespective of the initiator concentration and the type of curing process used. However, the T_g values of the polymers decrease with an increase in initiator concentration and these results are interpreted in terms of the diluent effect of the initiator fragments remaining in the samples.

Molecular dynamics of the u.v. and heat cured samples were investigated using T_1^C and $T_{1\rho}^C$. In the u.v. cured ECC samples, a decrease in the cooperative molecular motions of the cyclohexyl rings was observed as the TPSHA concentration increased in the range of 0.5–1 wt%, while these motions increase with an increase in the TPSHA concentration above 1 wt%, clearly indicating the antiplasticization–plasticization effect of the TPSHA fragments remaining in the samples. In contrast, monotonous increases in $T_{1\rho}^C$ and T_1^C were observed for the heat cured ECC samples. The EA samples are flexible in themselves at room temperature and the diluent effect of the initiator fragments should be almost ineffective.

Variable temperature experiments indicate that the correlation time of the cyclohexyl ring motions in the EA polymer even in the rubbery state (15°C above T_g) is $>10^{-6}$ s. The molecular motions of the butyl moiety were found to be more effective on the spin-lattice relaxation than those of the cyclohexyl ring, thus the correlation time of the former is smaller than that of the latter at room temperature.

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