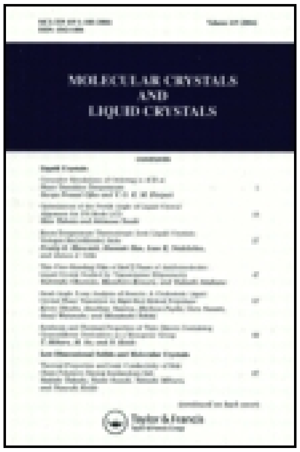

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Liquid Crystalline Epoxy Resins Consisting of Mesogenic Diepoxide and Mesogenic Hardner

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Two liquid crystalline (LC) epoxy resins consisting of LC diepoxide and LC hardner were synthesized, diglycidyloxyazoxybenzene (DGA), 4,4'-bis (ω-carboxy decanoxy) azoxybenzene (CAA10) and DGA with 4, 4'-bis (ω-hydroxy undecanoxy) azoxybenzene (HAA11), and their reaction mechanism, mesomorphic phase transition and thermal expansion were investigated by use of DSC, IR, polarized microscopy, X-ray diffractometry and capillary dilatometry. The fully gelated DGA-CAA10 formed a network structure in which one interchain crosslink was made per 5.6 repeating unit, and showed no mesophase. The DGA-HAA11 of linear typed polymer showed a smectic A phase when not fully cured, while a namatic phase when gelated. It was pointed out that the mesogenicity of epoxy resin is governed by the mesogenicity of monomers but is also correlated with the crosslinking density and degree of polymerization. In the fully gelated DGA-CAA10, thermal expansion coefficient (α) was about 2.2×10^{-4} ℃$^{-1}$ below Tg and 3.4×10^{-4} ℃$^{-1}$ above Tg, while about 2.3×10^{-4} ℃$^{-1}$ below Tg and above 6.5×10^{-4} ℃$^{-1}$

above Tg in the fully gelated DGA-HAA11. It is noted that the α value for DGA-CAA10 is low even above Tg.

Keyword: Epoxy Resin ; Liquid Crystals ; Low Thermal Expansion

INTRODUCTION

Liquid crystalline (LC) thermosetting resin is one of the attractive polymers, because it can bring forth new and characteristic properties functionalyzed with the existence of LC state. As well known[1], the epoxy resins have been widely used as important thermosetting engineering plastics, because of their characteristic properties such as strong bonding strength, high insulation, and good thermal, oil and chemical resistances. Recently, lower thermal expansion and smaller shrinkage in solidification have been desired for epoxy resins, for example, in order to improve the bonding strength with metal at high temperatures and produce laminating plate for precice electric parts. The LC epoxy resins should respond to these problems. On the other hand, it is, of course, scientifically important to study how the mesophase is formed in crosslinked polymeric systems such as epoxy resins having a network structure. Therefore, it is certainly of interest to get LC state for the epoxy resins. To date, the preparation and properties of LC epoxy resins have been studied by many researchers[2-12] and the characteristic LC epoxy resins have been designed. Most studies have been focused to LC epoxy resins obtained by reacting mesogenic diepoxides with commercial organic amine hardners (non-mesogenic). Very recently, we[11,12] reported two LC epoxy resins cured commercial diepoxides (non-mesogenic) with mesogenic hardners synthesized newly ; 4,4'-bis (2, 3-epoxypropoxy) bisphenol A (EPB) with 4,4'-bis (ω-carboxy decanoxy) azoxybenzene (CAA10) (EPB-CAA10) and 4,4-bis(2,3-epoxypropoxy) -3,3',5,5'-tetramethyl biphenol (EPTB) with CAA10(EPTB-CAA10) , whose chemical structures are illustrated in Fig.1. EPB-CAA10 showed a

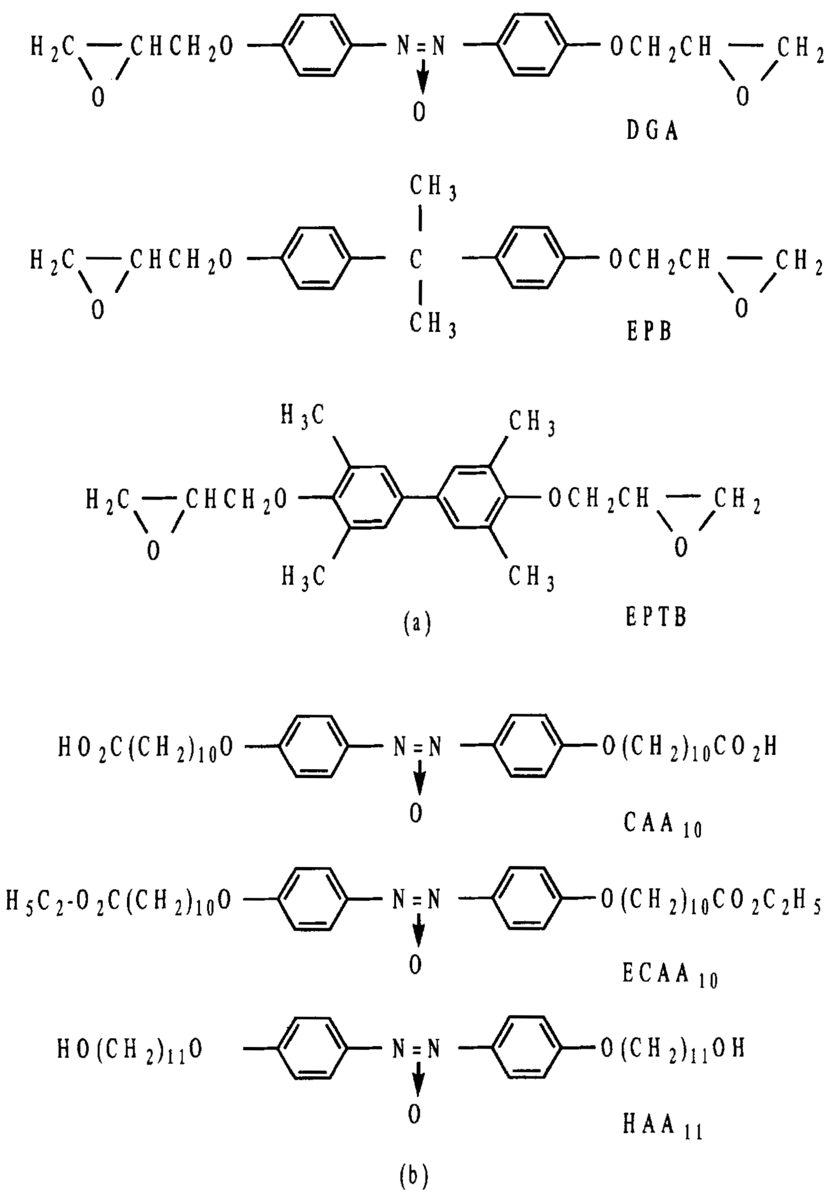

FIGURE 1 Chemical structures of diepoxides and monomers.

smectic-like mesophase between 70 and 90 ℃ when the polymer was not gelated, but no mesophase when fully gelated, while EPTB-CAA10 had a smectic-like mesophase between 60 and 87 ℃ when not gelated and a nematic phase between 50 and 80 ℃ when fully gelated. Both EPB-CAA10 and EPTB-CAA10 were found to have low thermal expansion coefficients among epoxy resins. These finding excites us to exploit new type of LC epoxy resins.

In the present work, we synthesize two LC epoxy resins cured diglycidyloxy azoxy benzene (DGA) with CAA10 (DGA-CAA10) and DGA with 4,4'-bis (ω-hydroxy undecanoxyoxy) azoxybenzene (HAA11) (DGA-HAA11), whose chemical structures are listed in Fig.1 and investigate their reacting mechanisms, mesomorphic phase transition and thermal expansion properties. Both DGA-CAA10 and DGA-HAA11 are a new type of LC epoxy resins cured LC diepoxide with LC hardner, and moreover, DGA-CAA10 have a network (crosslinked) structure, while DGA-HAA11 is a linear polymer. It is discussed how this difference in polymeric structure affects the mesogenicity.

EXPERIMENTAL

4,4'-dihydroxyazoxybenzene (HAB) was synthesized by mixing 175ml pyridine solution of p-nitrosophenol (25g, 0.20mol) and benzene sulfonyl chloride (26.6g, 0.15mol) for 12h at room temperature and further for 3h at 30 ℃.[13] The crude products were fully purified by several recrystallizations from ethanol-water solution (yellow needle crystals. yield=43.7 %).

(DGA) was obtained by dropwisely adding 50 % aq. NaOH (2.50g) to isopropyl alcohol (30ml) solution of HAB (3.00g, 0.013mol) and epichlorohydrin (9.73, 0.105mol) for 8h at 75 ℃.[14] The crude products were recrystallized from chloroform-ethanol solution (yellow needle crstals. yield=66 %). The crystals were judged to be fully purified by ^{1}H-NMR, E1-MS (70eV), FT-IR and TLC. ^{1}H-NMR (400MHz, $CDCl_3$) ; δ =2.79 (m,2H), 2.94 (m,2H), 3.39 (m,2H), 4.02 (m,2H), 4.32 (m,2H), 7.00 (dd,J_A=10.2Hz,J_B=3.2Hz,4H), 8.26 (t,J=8.5Hz,4H). E1-MS (70eV); m/z=378 (1.0), 342 (M^+;100), 286 (2.5), 229 (1.8), 93 (11.3). FT-IR

(KBr,cm^{-1});1503,1432,1300 ν (N=N),1264,1239,1029 ν (COC).

CAA10 was prepared by the same procedure as that reported previously.[12] HAA11 was obtained by dropwisely adding HAB (4.97g,21.59mol) and t-butoxy potassium(11.10g,100m mol)/methanol (200ml) solution to 11-bromoundecanol (25.12g,100mmol)/methanol (50ml) and then refluxing the mixture for 24h. The crude products were fully purified from ethanol after washing by 200ml water(yellow needle crystals. yield=56 %). ^{1}H-NMR(400MHz, DMSO-d6) : δ=1.37-1.78 (m,36H), 3.62(t,J=6.4Hz,4H), 4.06(m,4H), 4.36(m,2H), 7.08(m,4H), 8.19(m,4H).

DGA diepoxide and CAA10 hardening monomer(the equivalent ratio: 1/1) were mixed with trimethylamine of 4mol % to CAA10, and heated for 3min at 140 ℃, and then the mixture was qiuckly cooled to room temperature. The polymer obtained was used as DGA-CAA10 prepolymer in the subsequent experiments. DGA-HAA11 prepolymer was prepared by reacting DGA with HAA11 monomer(the ratio of mixing:1/1),for 3min at 160 ℃ using tetramethylammonium chloride of 4mol % to HAA11 as a catalyst and quickly cooling to room temperature.

The phase transition temperatures and their enthalpy changes were measured by use of a differential scanning calorimeter (Seiko Denshi Co. SSC-5000) operating at a heating / cooling rate of about 5K/min for DGA-CAA10 and DGA - HAA11 polymers. The textures of liquid crystalline state were examined by use of a polaized optical microscopy (Nikon XTP - 11) equipped with a hot stage (Mettler FP - 82) at a heating / cooling rate of 5K/min. The textures for the polymers were observed at different times during curing the prepolymer on the hot stage at 140 ℃ for DGA - CAA10 and 160 ℃ for DGA-HAA11.

IR spectral measurements were done with a KBr pellet method by use of a Perkin-Elmer 1640 FT - IR spectrometer. The DGA-CAA10 and DGA-HAA11 polymers with dfferent curing times were prepared in the same procedure as that described in the DSC mesurements ; the DGA-CAA10 and DGA-HAA11 were prepared by curing the prepolymer on the hot stage at 140 and 160 ℃, respectively.

X-ray diffraction measurements were performed with a Rigaku

Denshi 200 diffractometer, using monochromatic CuK α radiation (50kV, 200mA). The X-ray scattering intensities were detected by a scintillation counter incorporating a pulse-height analyser. Thermal expansion was measured at a heating rate of 0.3-0.6 K/min by use of a glass capillary dilatomerter (0.6mm i.d.). The sample was carefully immersed in liquid mercury in vacuo in order to avoid the formation of voids on the surface of the sample. The volume change of the sample with temperature was calculated from a reading of the height of mercury in the dilatometer capillary. The specific volume at 25 ℃ was obtained with a buoyancy method using n-hexane as the solvent.

RESULTS AND DISCUSSION

Mesogenicity of monomers

Table I shows phase transition parameters obtained by DSC measurements for DGA, HAA11 and CAA10. In DSC curves, DGA showed two peaks near 133 and 146 ℃ at the 2nd heating,which were also observed at the more than 2nd DSC heating prosesses. The phase between two peaks was identified a nematic from the appearance of

TABLE I Phase transition temperatures(℃) /entropy changes($J \cdot mol^{-1} \cdot K^{-1}$) in monomers[a)]

compound	K_1	:	K_2	:	Sc	:	N	:	I
DGA	•	133/57		-		-	•	146/12	•
HAA11	•	81/27	•	113/116	•	133/40		-	•
CAA10	•	142/59	•	158/173		-		-	•
ECAA10	•	-		65/174	•	88/36		-	•

a)Data were for the 2nd heating DSC curves.
K_1 and K_2:crystalline phases

nematic schlieren texture under crossed polarizers. HAA11 exhibited smectic C phase between 113 and 132 ℃ at the heating, which was identified by the appearance of Sc broken fan texture under crossed polarizers.

As we reported previously [11,12] ,CAA10 shows two peaks near 147 and 157 ℃ at the 1st heating DSC curves, corresponding to a phase transition in the crystalline state and melting point, respectively, but no mesophase. However, we regards CAA10 as mesogenic hardner for epoxy resins, because a Sc phase appears between 65 and 83 ℃ in 4,4'-bis (ω -ethylcarboxydecanoxy) azoxybensene (ECAA10) which is ethyl ester of CAA10. (see Table I)

Reaction mechanism

Figure 2 shows isothermal change in the prepolymer of DGA-CAA10 during curing at each temperature ; the curves are measured as a function of curing (t) after putting the prepolymer on the DSC pan at each

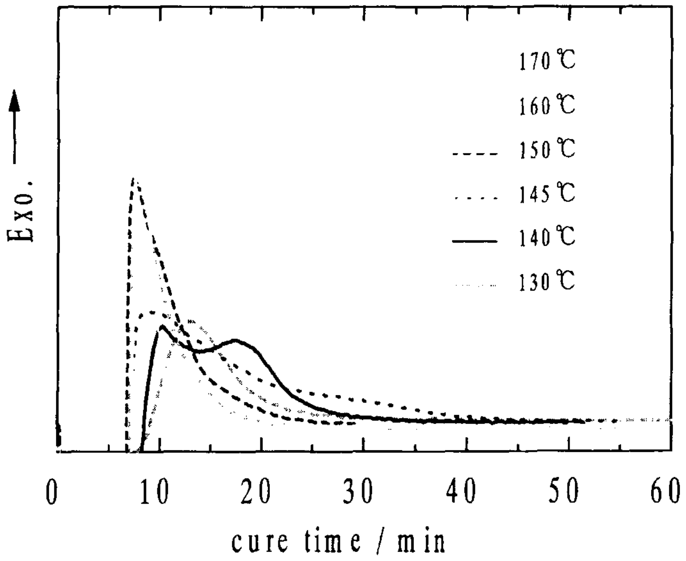

FIGURE 2 Isothermal DSC curves during curing at different temperatures for DGA-CAA10 prepolymer.

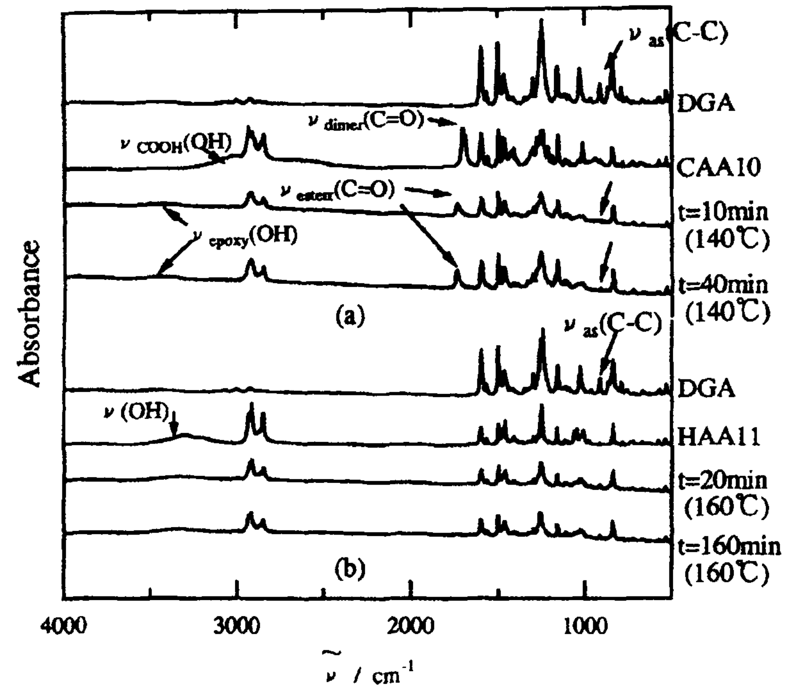

FIGURE 3 IR spectra for DGA-CAA10 (a) and DGA-HAA11 (b)

temperature. The curve shows only one peak at 170 ℃, but two distinct peaks at 140 ℃. The faster peak may be mainly related to a reaction of epoxide with COOH to grow main backbone chains, while the slower peak may be due to a side reaction of OH groups produced by the faster reaction with epoxide/COOH to construct a network structure. In the subsequent experiments, all hardening reactions for DGA-CAA10 were carried out at 140 ℃. The gelling time (tg), at which the isothermal curve reaches at a constant value, is larger, as the reaction temperature decreases, being about 30 min at 140 ℃.

Figure 3 (a) shows IR spectra DGA-CAA10. In DGA, there are observed three characteristic peaks near 910, 1700 and 3000cm^{-1} which are attributed, respectively, to anti-symmetric stretching vibration of epoxy group [ν_{as}(C-C)],C=O stretching vibration of dimeric COOH [ν_{dimer} (C=O)] and stretching vibration of OH of COOH[ν_{COOH} (OH)]. In DGA-CAA10, both ν_{as}(C-C) and ν_{dimer}(C=O) bands decrease in intensity and two new peaks appear near 1738 and 3400 cm^{-1} which are assigned to C=O stretching vibration of ester[ν_{ester}(C=O)] and stretching vibration of OH produced by the opening reaction of epoxy group[ν_{epoxy} (OH)].

The absorbances of all the IR peaks are normalized by division by height of the C=C stretching band of benzene at 1597 cm^{-1}. The IR spectra between 1650 and 1800cm^{-1} are shown in Figure 4(a) for DGA-CAA10 with diffrent curing time (t) at 140℃. The ν_{ester} (C=O) and ν_{dimer} (C=O) bands are seen around 1740 cm^{-1} and 1700cm^{-1} (a smal1 shoulder) , respectively, forming an isosbetic point around 1730 cm^{-1}. The existence of the isosbetic point indicates that the ν_{dimer} (C=O) peak is

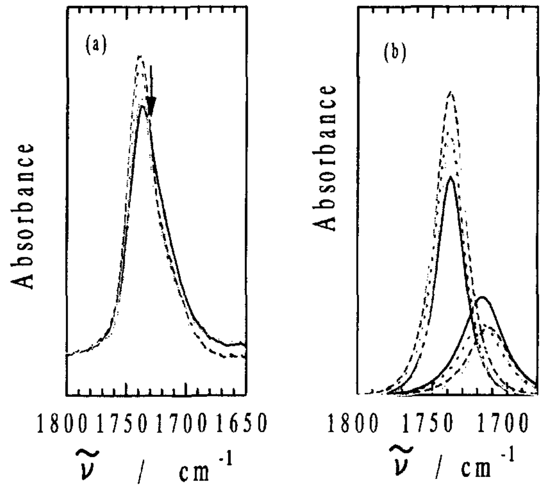

FIGURE 4 IR spectra between 1650 and 1800cm^{-1}, for DGA-CAA10(a) and the spectra splitted into ν_{dimer}(C=O) and ν_{ester}(C=O) (b).

——— 5min, ----- 10min, ▪▪▪▪▪ 20min,
----- 30min, 40min

gradually replaced by the ν_{ester} (C=O), during curing the prepolymer at 140 ℃. We attempted to split the two C=O peaks by using a Monte Carlo method proposed by Ivanov et al.[15] in almost the same procedure as that in the previous paper.[12] We assume a function for the C=O stretching (f_i) as

$$f_i = I_i[\exp\{-(\nu_i - \nu_{i0})^2/B_i^2\} / \{1.0+2.5(\nu_i - \nu_{i0})/B_i\}] \qquad (1)$$

where ν_i, ν_{i0}, B_i and I_i are the wave number, wave number at the peak

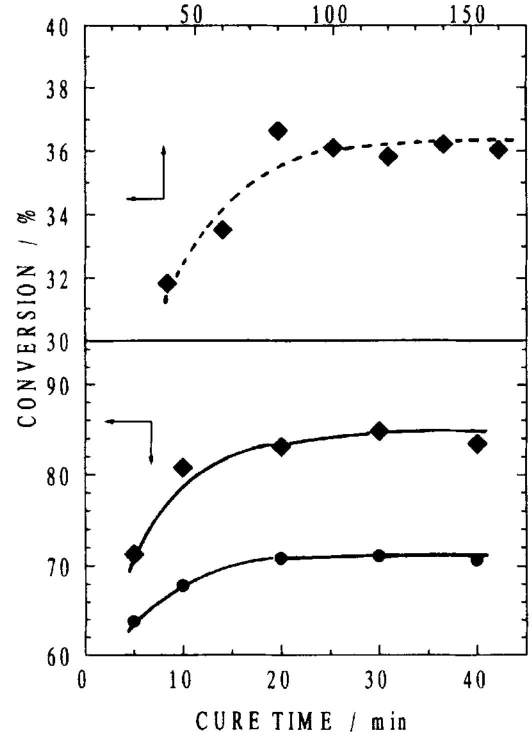

FIGURE 5
Reaction conversion (%) versus curing time (t) at 140 ℃ for DGA-CAA10 (——) and at 160 ℃ for DGA-HAA11 (------). (●) and (◆) are the data calculated from ν_{dimer}(C=O) and ν_{epoxy} (C-C), respectively.

top, band width and peak intensity for i-th component, respectively. We denoted i=1 and 2 for the ν_{ester} (C=O) and ν_{dimer} (C=O) peaks, respectively, and chose the parameters in order to minimize the difference between the experimental and calculated values during repeating of the calulations more than 2000 times. The IR spectra of the splitted ν_{ester} (C=O) and ν_{dimer} (C=O) are shown in Fig.4 (b). The caluculated spectra [the sum of ν_{ester} (C=O) and ν_{dimer} (C=O)] were fitted to the experimental ones within an error of ca. 1.6%. Apparently, ν_{dimer} (C=O) band decreases and ν_{ester} (C=O) increases, as the prepolymer is cured.

The ν_{epoxy} (C-C) and ν_{epoxy} (OH) band also reflected faithfully the degree of curing from the prepolymer, although the detailed data are not shown here. The ν_{epoxy} (C-C) band decreased with curing, while the ν_{epoxy} (OH) increased (roughly understood from Fig.3).

Figure 5 shows plots of reaction conversion versus curing time (t), where two reaction conversions were calculated for the ν_{epoxy} (C-C) and ν_{dimer} (C=O). The conversion was determined by deviding the normalized area of ν_{epoxy} (C-C) / ν_{dimer} (C=O) in DGA-CAA10 by that in an unreacted mixture. Here, the areas of ν_{epoxy} (C-C) and ν_{dimer} (C=O) peaks for the polymer were normalized by the area of C=C stretching vibration of benzene as before. The unreacted mixture was prepared in the following way ; DGA-CAA10 and trimethylammonium chloride (catalst) were dissolved in THF in the same ratio as that in the prepolymer. The THF solvent was fully evaporated from the solution and the remaining soil was fully dried in vacuo. The IR spectra were measured for the dry mixture by use of KBr method. The normalized area of ν_{epoxy} (C-C) and ν_{dimer} (C=O) obtained were used as those for the unreacted mixture, where we assume that the molar exitinction coefficients are scarcely changed by reacting to the DGA-CAA10 polymer. In Fig.5, the conversions obtained from ν_{epoxy} (C-C) and ν_{dimer} (C=O) increases with the increase of curing time (t) and are saturated around 30min which coresponds to the gelling time (tg), being well consistent with that obtained by DSC. Therefore, we concluded that the gelling time from the prepolymer is about 30 min at 140 ℃ for DGA-CAA10. The saturated conversions from ν_{epoxy} (C-C) and ν_{dimer} (C=O) were estimated to be about 83 and 71%, respectively. The value of the saturated conversion and its difference between ν_{epoxy} (C-C) and ν_{dimer} (C=O) may be closely connected with the existence of a side reaction of the epoxide with the OH group which produces interchain crosslinks. The interchain crosslinks would hinder the overall reaction. The degree of branching (side reaction) is represented by the relation :

degree of branching= (conversion of epoxide - conversion of COOH / (conversion of epoxide) (2)

When t=tg, the degree of branching was estimated to be about 15% for DGA-CAA10, which are larger than about 6% for EPTB-CAA10 obtained previously.[12] The calculated crosslink density was apparently calculated to be one interchain crosslink per 5.6 repeating unit in DGA-CAA10, being larger compared with 11 in EPB-CAA10 and 16 in EPTB-CAA10.

HAA11 is divalent alcohol and is known as a hardner which predominantly produces a linear typed epoxy resins. Figure 3 (b) shows IR spectra for DGA, HAA11 and DGA-HAA11 of two curing times at 160 ℃. The ν_{as} (C-C) bands are seen near $910cm^{-1}$ and the streching vibration band of OH [ν (OH)] is observed near $3300cm^{-1}$. The ν_{epoxy} (C-C) band decreases with curing the prepolymer at 160 ℃. The ν_{alc} (OH) should be also decreased by curing but at the same time, the stretching vibration of OH [ν_{epoxy} (OH)] produced by the reaction of epoxide with OH group [ν_{epoxy} (OH)] is considered to superpose on the ν_{alc} (OH) . Actually, the OH stretching band near $3300cm^{-1}$ exists even at t=160min. Consequently, we were unable to eliminate the ν_{alc} (OH) band from the contribution of ν_{epoxy} (OH) . Figure 5 shows change of conversion with curing time (t) from the prepolymer in DGA-HAA11 at 160 ℃. Here the reaction conversion was estimated by almost the same procedure as that for DGA-CAA10 described already. The conversion is increased with curing and saturared to about 37% near 100min. This small saturation conversion suggests that the reactivity is considerably low.

Mesomorphic phase transition of polymer

In Fig. 6, DSC curves are shown for DGA-CAA10. The curves show one peak near 170 ℃ at the heating and two peaks near 163 and 112 ℃ at the cooling. The lower temperature peak near 112 ℃ was assigned to a phase transition in the crystalline phase on the polarized microscopic texture observation, and any mesophase was not observed for DGA-CAA10.

Figure 7 shows X-ray diffraction patterns for DGA-CAA10. In (a) of the figure, five sharp peaks are observed when t=5min, but when t ≧ 15min, only two peaks remain near 17.5 and 23.5 ° which correspond to about 5.1 and 3.8 A of spacings, respectively. Halo scatterings overlapping the sharp peaks are observed in the 2 θ range of 15 to 30 ° , and appear to be somewhat larger, as t increases. When t ≧ 60min, moreover, a small peaks is seen 4.5 ° (19.5 Å) (arrow in the figure) which is well consistent with the molecular length of DGA(19.64 Å). The (b) of Fig. 7 also shows temperature dependence of X-ray diffraction patterns for the fully gelated DGA-CAA10(t=70min at 140 ℃).The two peaks near 17.5 and 23.0 ° are unchanged during increasing temperature from room temperature to 100 ℃, showing no phase transition.

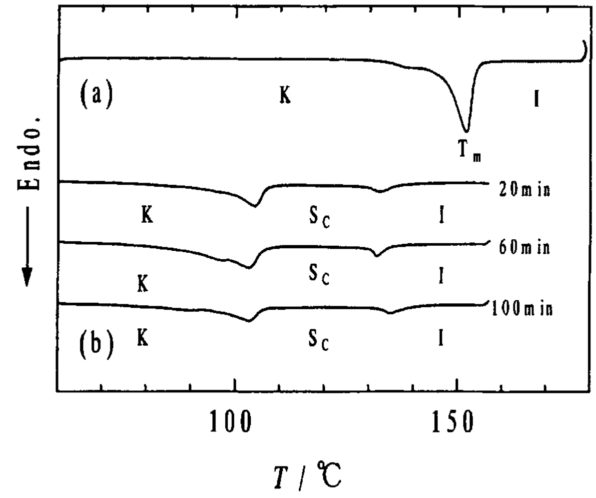

FIGURE 6 DSC heating curves for the fully gelated DGA-CAA10(a) and DGA-HAA11 with different curing time (t) at 160 ℃ from the prepolymer (b).

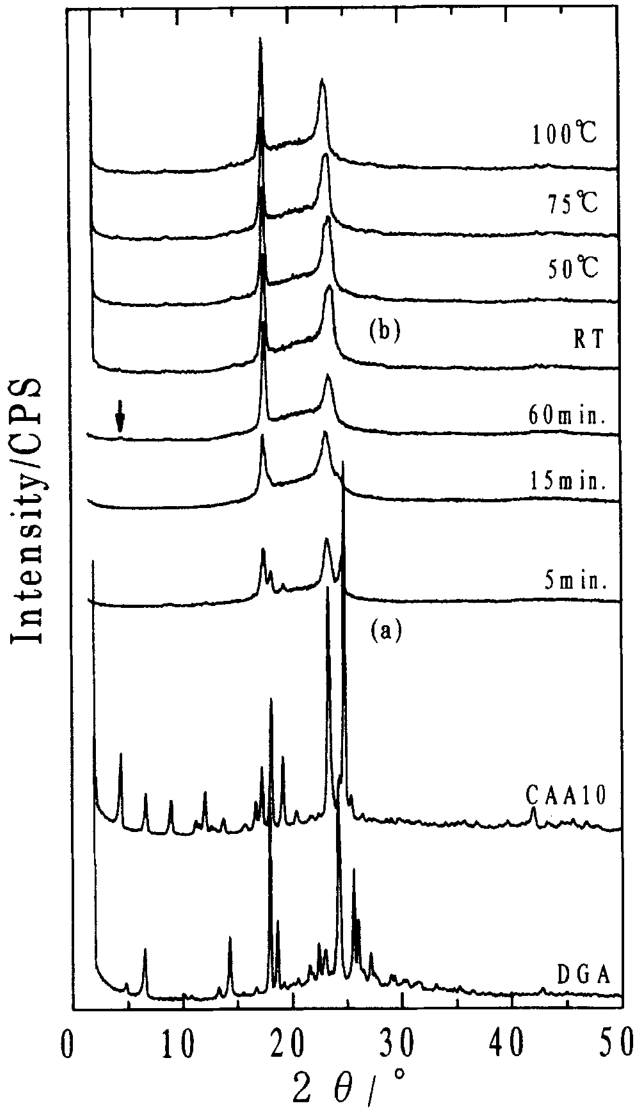

FIGURE 7 X-ray diffraction intensities-scattering angle (2 θ) curves for DGA-CAA10 system. (a) data at different curing times (t) at 140 ℃ from the prepolymer. (b) data at different temperatures for the sample of t=20min.

Figure 6 shows DSC curves at the 2nd heating for DGA-HAA11 obtained by curing the prepolymer at 160 ℃. When t=20min, DGA-HAA11 shows two peaks near 105 and 129 ℃. At temperatures between 105 and 129 ℃, the texture was uniformly dark under crossed polarizers on the polarized microscopy observations, but showed a S_A fan texture between two glass plates treated with repellent detergent (Daikin Kogyo CoMS77). The two peaks appear near 104 and 122 ℃ when t=60min. and near 104 and 135 ℃ when t=100min, where a nematic schlieren texture was observed at temperatures between the two peaks.

Figure 8 shows X-ray diffraction patterns for DGA-HAA11 cured at 160 ℃. At t=10min , many peaks were observed in a wide angle range for DGA and HAA11 monomers but at 160min, the peaks are observed near 19.54, 20.58 and 23.62 ° and are broad, accompanying the increase of halo scatterings. Consequently, DGA-HAA11 shows S_A phase when not fully cured ($t < 90min(tg)$) and nematic phase when fully cured ($t > tg$). As already described, DGA and HAA11 monomers had nematic phase between 133 and 146 ℃ at the heating and S_C phase between 133 and 132 ℃, respectively. DGA-HAA11 polymer showed S_A phase with

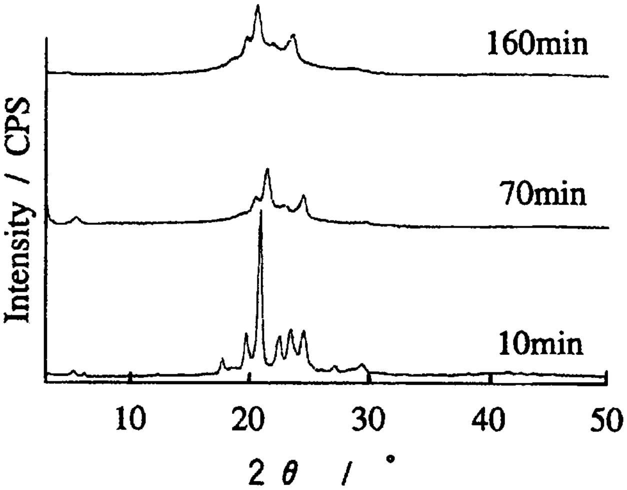

FIGURE 8 X-ray diffraction patterns for DGA-HAA11 with different curing times (t) at 160 ℃ from the prepolymer.

layered structure when not fully cured, which may be caused by the mesogenicity of the monomers, while when fully cured, the longer rigid main backbone chains would disturb the formation of the layered structure, resulting in forming the nematic phase. The similar mesomorphic behavior has been found for EPB-CAA10 system. EPB-CAA10 exhibits smectic-like mesophase when $t < tg$ but nematic-like mesophase when $t > tg$ [12], as shown in Table. II

The crosslinking may hinder the formation of layered structure, and so the fully gelated epoxy resins may prefer nematic phase to smectic phase. In general, the mesogenicity in epoxy resins may be mainly drived from the mesogenic repeating units (monomers). As the epoxy resins are cured, the increase of polymerization degree and the formation of

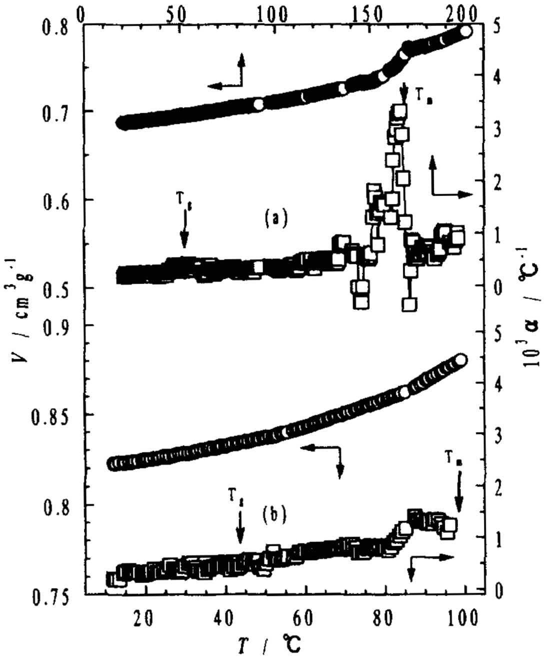

FIGURE 9 Temperature dependence of specific volume (V) and volume thermal expansion coefficient (α) for the fully gelated DGA-CAA10 (a) and DGA-HAA11 (b)

crosslinks would perturb the ordering of the mesogenic chains to construct a mesophase, resulting in changing smectic phase to nematic phase. When the crosslinking density is large, the chain mobility may be too low to form a mesophase and then the epoxy resins may show only crystalline phase as seen in DGA-CAA10. It is of interest how the crosslinking density, structure of mesogenic component and polymerization degree affect the appearance and orderness of mesophase.

Thermal expansion

Figure 9 shows plots of specific volume (V) and thermal expansion coefficient (α) versus temperature for the fully gelated DGA-CAA10 and DGA-HAA11. Here, the values of V were measured at the interval of about 0.8 ℃ during increasing temperature. The value of α was

TABLE II Thermal volume expansion coefficient and phase transition temperature for the fully gelated epoxy resins.[a)]

	Phase transition temperature (K)			Thermal expansion coefficient ($\times 10^{-4}\,°C^{-1}$)			
Sample	T_g	T_m	T_{N-I}	α_1	α_2	α_N	α_I
DGA-CAA10	52	170	–	2.2	3.4	–	10.0
DGA-HAA11	43	103	135	2.3	6.5	10.3	–
EPB-CAA10[b)]	45	81	–	3.4	6.9	–	7.0
EPTB-CAA10[b)]	42	–	82	2.1	–	6.0	10.0

a) T_g, T_m and T_{N-I} are glass transition, melting and nematic-isotropic liquid phase transition temperatures respectively. α_1, α_2, α_N, and α_I are thermal volume expansion coefficients below T_g, above T_g, at nematic phase and at isotropic liquid phase, respectively.

b) Data in the preceding paper.[12]

calculated by using the least squares method for V values at five temperatures including two spots before and after one temperature. In DGA-CAA10, the V value gradually increases with increasing temperature, making a small bend near 52 ℃ and a skip near 170 ℃ which correspond to Tg and Tm, respectively. On the other hand, DGA-HAA11 shows a bend near 43 ℃ and a very small skip near 95 ℃, which are assigned to Tg and $T_{N\text{-}I}$, respectively. The α values are listed in Table Ⅱ, where α_1, α_2, α_N and α_I are expansion coefficients below Tg, above Tg, at the nematic phase and at the isotropic liquid phase, respectively. The values of α_1 below Tg are 2.1 ~ 3.4 × 10^{-4} ℃$^{-1}$ for all the polymers, but the value of α_2 is 3.4 × 10^{-4} ℃$^{-1}$ for DGA-CAA10, smaller than about 7 × 10^{-4} ℃$^{-1}$for DGA-HAA11 and EPB-CAA10. DGA-CAA10 is the LC diepoxide-LC harder type of epoxy resin and highly crystalline as already described. This high crystallinity may be responsible for the low thermal expansion above Tg in DGA-CAA10.

CONCLUSION

In this work, we synthesized two new LC epoxy resins cured mesogenic diepoxide with mesogenic hardening compound, DGA-CAA10 and DGA-HAA11, and investigated their mesomorphic phase transitions and thermal expansion properties. In DGA-CAA10, the saturated reaction conversion was 71 ~ 83 % in the presence of trimethyl ammonium as catalyst 140 ℃ and the degree of branching was about 15 % when fully gelated. The fully gelated DGA-CAA10 was highly crystalline but showed no mesophase. On the other hand, DGA-HAA11 is linear typed polymer. The saturated reaction conversion was estimated 37 % at 160 ℃ in the presence of tetramethylammonium chloride as catalst. It is noticed that DGA-CAA10 showed low expansion coefficient value of about 3.4 × 10^{-4} ℃$^{-1}$ even above Tg. It is important to clarify relationship of mesomorphic and thermal expansion properties with the structure and mesogenicity of diepoxide and hardening monomers. The present work newly gives one possible way to design functional and mesomorphic epoxy resins.

References

[1] for example, H. Lee and K. Neville, *Handbook of Epoxy Resins* (McGraw Hill, NewYork,1967)

[2] S. Kirchmeyer, A. Karbach, H. Muller, H. Merer, R. Dheir, *Angew. Makromol. Chem.,* **185/186**, 33 (1991)

[3] A. A. Robinson, S. G. McNamee, Y. S. Freidzon and C. K. Ober, *Am. Chem. Soc. Div. Polym. Prepr.,* **34**, 743 (1991)

[4] D. J. Broer, J. Lub and G. N. Mol, *Macromolecules*, **26**, 1224 (1993)

[5] C. Carfaagna, E. Amendola and M. Giamberini, *Liq. Crystals,* **13**, 571 (1993)

[6] O. Lim, A. F. Yee and H. Sue, *Polymer*, **35**, 2679 (1994)

[7] S. Jahromi, *Macromolecules*, **27**, 2804 (1994)

[8] S. Jahromi, J. Lub and G.W. Mol, *Polymer*, **35**, 622 (1994)

[9] S. Jahromi, W. A. G. Kuipers, B. Norder and W. J. Mijs, *Macromolecules,* **28**, 2201 (1995)

[10] B. Szcepaniak, K. C. Frisch, P. Perzek, I. Leszczynska, and E. Rundnik, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 1275 (1995)

[11] S. Osada, K. Tsunashima, T. Inoue and S. Yano, *Polym. Bull.,* **35**, 1275 (1995)

[12] S. Osada, S. Yano, K. Tsunashima and T. Inoue, *Polmer,* **37**, 1925 (1996)

[13] N. J. Leonard and J.W. Curry, *J. Org. Chem.*, **17**, 1071 (1952)

[14] D. S. Sadafule, R. N. Raghuraman, N. G. Navele and C. G. Kumbhar, *J. Macromol. Sci. Chem.*, **A25**, 121 (1988)

[15] Y. O. Ivanov, S. G. Makarov and V. Y. Iharov, *Vibrational Spectrosc.*, **5**, 175 (1993)