Synthesis and Thermal Properties of Combined Liquid Crystalline Epoxy Resins

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ABSTRACT: Liquid crystalline epoxy resins were prepared by the curing reaction of epoxy and amine compounds with a mesogenic group in the mesomorphic temperature range. Some epoxy resins exhibited a typical liquid crystalline phase. Curing reaction of a mesogenic epoxy compound with an aliphatic amine compound containing cyano biphenyl group was faster than that of another epoxy resins confirmed by thermally controlled Fourier transform infrared measurements. The glass transition temperature of the liquid crystalline epoxy resin containing cyano biphenyl group increased with increasing curing reaction time. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1979–1990, 1998

Key words: liquid crystalline polymer; epoxy resin; crosslinked polymer; thermoset

INTRODUCTION

Ordered and anisotropic network films have generated great interest due to their high potential usage as optical and mechanical materials. Amorphous thermosets are already widely used in electron packaging, owing to their good mechanical and thermal properties, and liquid crystals have a good orientational and optoelectric properties. Combining the properties of thermoset with the properties of liquid crystal, then new functional materials offer a great variety for the application of optical switches, nonlinear optical materials, and advanced composites. These liquid crystalline thermosets were obtained by *in situ* photopolymerization of diacrylate monomers with a mesogenic group in the mesomorphic temperature range.[1–7] The highly oriented state of these mesogenic monomers was maintained after photopolymerization. The film obtained by us can be applied to the orientational film, and the order parameter of a low molecular liquid crystal injected to the cell constructed by the orientational film was 0.35. Thus, we have concluded that the low molecular liquid crystal would be oriented spontaneously by the surface orientational anchoring of the films.[8]

We have also obtained the anisotropic film of poly(vinyl alcohol) derivatives containing the mesogenic cinnamoyl group in the side chain. The film can be easily elongated by a mechanical machine. Then, the photocrosslinking reaction of the polymer film was carried out under the elongated state in order to obtain a good orientational film. The elongated film showed an orientational behavior.[9]

Another attempt to obtain the anisotropic film has been performed by a curing reaction of epoxy compounds with amine compounds. Two reasons to use the epoxy resins as a based polymer are their good mechanical and chemical properties. Many researchers have investigated liquid crystalline epoxy resins for the preparation of the films with the anisotropic optical properties. Liquid crystalline epoxy resins were prepared by the curing reaction of a mesogenic diepoxy compound and a diamine compound. Stilbene, benzoate, and

biphenyl groups were employed for the cores of the mesogenic diepoxy compounds, while the non-mesogenic phenylenediamine derivatives were often used for the curing agents.[10-28]

We also tried to synthesize epoxy resins by curing reaction of mesogenic diepoxy compounds with nonmesogenic phenylenediamine (PDA), hexamethylenediamine (HMD), or 1,12-diaminododecane (DMDA); however, these mixed compounds were cured during evaporation of chloroform from the chloroform solution of the mixed compounds. The epoxy resins did not have a melting point due to the occurring the thermal decomposition before the molten state.[29]

Therefore, a mesogenic group was introduced to both a curing agent and a diepoxy compound. In previous literature, it was not necessary to employ the mesogenic amine compounds as a curing agent in order to obtain the liquid crystalline epoxy resins. It can be expected that the good orientation would arise from introducing mesogenic group into both reaction compounds compared with that of the mixture of the mesogenic epoxy compound with a nonmesogenic amine compound. Consequently, owing to an introduction of the mesogenic group into the epoxy and amine compounds, we would also anticipate the good mechanical strength for the epoxy resins prepared by curing reaction of mesogenic epoxy and amine compounds. Moreover, the orientation of the epoxy resins would be easily controlled by the external fields. The mixture of the mesogenic epoxy compound and curing agent was reacted at the mesomorphic temperature. Combined liquid crystalline epoxy resins were obtained from the mesogenic diepoxy compound and mono- or diamino compound containing a mesogenic group. In this article, the thermal and mechanical properties of the combined liquid crystalline epoxy resins were described.

EXPERIMENTAL

Characterization

[1]H nuclear magnetic resonance (^{1}H-NMR) was performed with a JEOL JNM-PMX60 spectrometer using $CDCl_3$ as the solvent. Infrared (IR) spectra were recorded on a JEOL JIR-7000 spectrometer. Spectra were collected at 2 cm^{-1} resolution. Differential scanning calorimetry (DSC) measurements were conducted with a Mettler 3000 series. Optical microscopy was performed on a Ni-
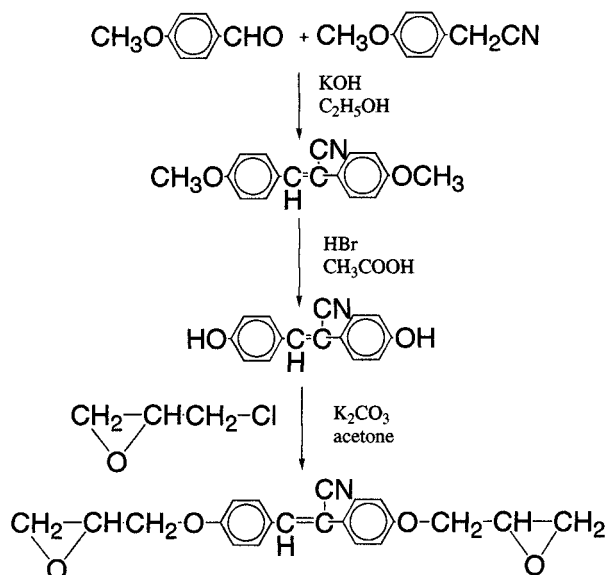
Scheme 1   Synthesis of diepoxy monomer.

kon polarizing optical microscopy equipped with a Mettler FP80 controller and a FP82 hot stage. Dynamic mechanical analysis (DMA) was carried out using a Rheology Co., LTD DVE-V4 Rheospectoler. The frequency was adjusted to 10 Hz and the heating rate was 2°C min^{-1}.

The conditions of curve-fitting of the region of NH and OH stretching vibration groups was carried out as follows. The region of NH and OH stretching vibration groups was resolved into four components according to the following conditions.

1. Four components were assigned to NH symmetric stretching, NH antisymmetric stretching, secondary NH stretching, and OH stretching vibration group.
2. The baseline was assumed to be from 3600 to 3220 cm^{-1} (left to right).
3. The range of curve-fitting agreed with that of the baseline.
4. The shape of each peak was assumed to be Gaussian.
5. The curve-fitting procedure involved an error of 1%.

Materials

The synthesis of liquid crystalline epoxy monomer and amine monomers is shown in Schemes 1, 2, and 3, respectively.

4,4′-Dimethoxycyanostilbene

Potassium hydroxide (10 g, 0.152 mol) was solved in ethanol (150 mL). 4-methoxybenzylaldehyde
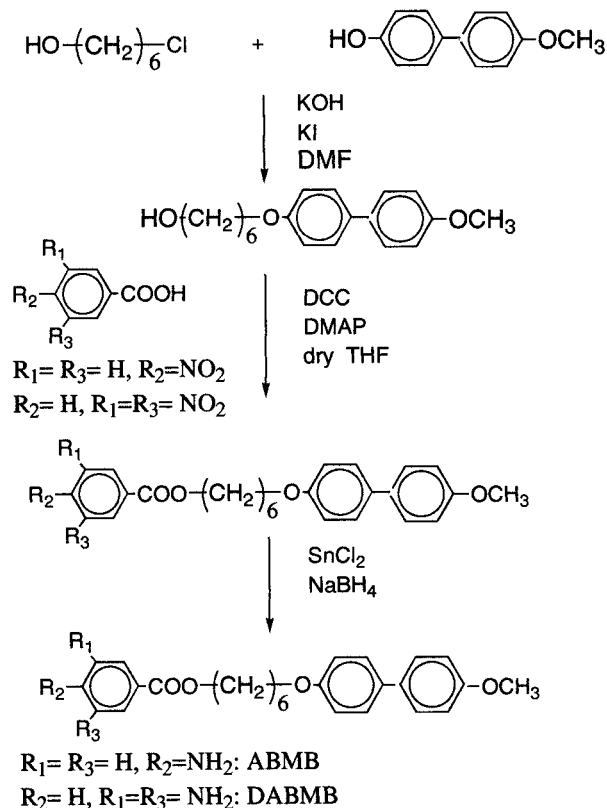
Scheme 2 Synthesis of aromatic amine compounds.

(12.8 mL, 0.102 mol) was added to the solution of ethanol containing potassium hydroxide. 4-methoxybenzylcyanide (13.3 mL, 0.102 mol) was added dropwise to the ethanol solution of 4-methoxybenzylaldehyde and potassium hydroxide. The reaction mixture was cooled at 0°C and stirred for 1 h. Precipitate was obtained. The reaction mixture containing the precipitate was cooled for 12 h at 0–5°C. The obtained solid was filtered and washed with ethanol. Further, the solid was washed with water. The solid was purified by recrystallization using mixture solvent of acetone and ethanol (2 : 5). The product was obtained in an 82% yield (mp, 108°C).

^{1}H-NMR(CDCl$_3$): δ 3.9 (s, —OCH$_3$), 7.0–8.0 (m, Ar and —CH=C(CN)—) IR(KBr): ν 2214 (CN), 1606, 1514 (Ar), 1034, 1253 (C—O—C), 1576 (—CH=C—)

### *4,4'-Dihydroxycyanostilbene*

Hydrobromide (47%, 37 mL) was added to 4,4'-dimethoxycyanostilbene in acetic acid. After the addition of hydrobromide, the reaction mixture was refluxed for 5 h. After cooling to room temperature, the precipitate was obtained. Then, the pre-

cipitate was poured into water and washed with water. The product was obtained in a 71.9% yield (mp, 243°C).

IR(KBr): ν 3354 (OH), 2220 (CN), 1606, 1514 (Ar), 1576 (—CH=C—)

4,4'-Diglycydyloxy-α-cyanostilbene

Epichlorohydrin (7.8 g, 0.084 mol), potassium carbonate (3.5 g, 0.025 mol), and a small amount of potassium iodide were added to a solution of acetone containing 4,4'-dihydroxycyanostilbene (2.0 g, 8.4×10^{-3} mol). The reaction mixture was refluxed for 24 h. The reaction mixture was concentrated and extracted with chloroform. The insoluble compound was removed by filtration. The filtrate was concentrated and added to large amount of methanol. The precipitate was obtained. The product was obtained in a 16.9% yield (mp, 47.8°C; clearing point, 83.2°C).
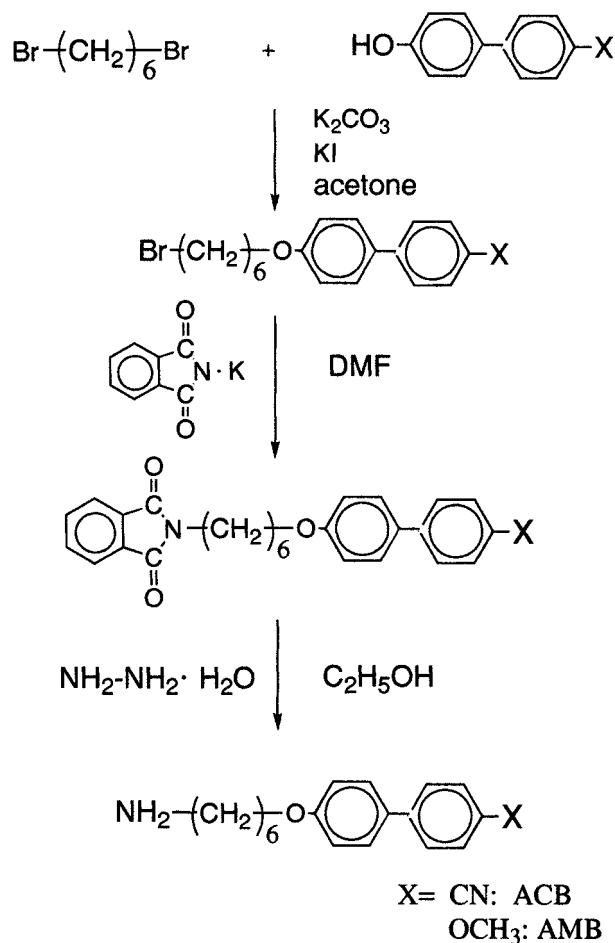
Scheme 3 Synthesis of aliphatic amine compounds.

^{1}H-NMR(CDCl$_3$): δ 2.5–4.5 (m, epoxy ring and —CH$_2$O—), 7–8 (m, Ar and —CH=C(CN)—) IR(KBr): ν 1513, 1604 (Ar), 2212 (CN), 916 (epoxy ring)

4-(6-Hydroxyhexyloxy)-4′-methoxybiphenyl

The solution of dimethylformamide containing 4-hydroxy-4′-methoxybiphenyl (6.9 g, 0.0345 mol), 6-chloro-1-hexanol (5.7 g, 0.0414 mol), potassium hydroxide (2.7 g, 0.0414 mol), and potassium iodide was heated at 80°C for 24 h. Dichloromethane (500 mL) was added to the reaction mixture. The crude product was extracted with dichloromethane. Magnesium sulfate was added to the dichloromethane solution. The filtrate was evaporated to dryness. The residue was washed with methanol. The product was obtained in a 48.1% yield (mp, 149°C).

IR(Nujol): ν 3309 (OH), 1606, 1500 (Ar)

4-[6-(3,5-Diaminobenzoyloxy)hexyloxy]-4′-methoxybiphenyl

A solution of tetrahydrofuran containing dicyclohexylcarbodiimide (9.9 g, 0.048 mol) was added to a solution of tetrahydrofuran containing 4-(6-hydroxyhexyloxy)-4′-methoxybiphenyl (4.8 g, 0.016 mol), 3,5-dinitrobenzoic acid (5.0 g, 0.024 mol), and 4-dimethylaminopyridine (0.6 g, 5.0 × 10^{-3} mol). The reaction mixture was stirred at room temperature for 24 h. The filtrate was concentrated to dryness. The residue was washed with methanol. The crude product, 4-[6-(3,5-dinitrobenzoyloxy)hexyloxy]-4′-methoxybiphenyl, was obtained in 96% yield. The crude product was monitored with thin layer chromatography.

The ethanol and tetrahydrofuran (1 : 1) solution of stannous chloride (13.7 g, 0.0607 mol) and 4-[6-(3,5-dinitrobenzoyloxy)hexyloxy]-4′-methoxybiphenyl (3.0 g, 6.07 × 10^{-3} mol) was heated at 60°C. The NaBH$_4$ (0.23 g, 6.07 × 10^{-3} mol) was added to the solution over a period of 30 min. After heating for 30 min, the reaction mixture was cooled to 5–10°C. Chilled water was added to the cooled reaction mixture. The reaction mixture was neutralized with aqueous solution of sodium hydroxide. The reaction mixture was concentrated and extracted with diethyl ether. The solution of diethyl ether was dried with magnesium sulfate. The filtrate was concentrated to dryness. The product was obtained in a 90.9% yield.

^{1}H-NMR(CDCl$_3$): δ 1.4–2.3 (m, —(CH$_2$)$_4$—), 3.9 (s, —OCH$_3$), 4.15 (t, C$\underline{H}_2$OPh), 4.3 (t, COOC$\underline{H}_2$), 7.0–7.9 (m, Ar)
IR(KBr): ν 3345, 3369 (NH), 2937, 2863 (CH), 1709 (COO), 1606, 1500 (Ar), 1242 (—COC—)

4-(6-Aminohexyloxy)-4′-cyanobiphenyl

A dimethylformamide solution of 4-(6-bromohexyloxy)-4′-cyanobiphenyl (4.4 g, 0.01 mol) and phthalimide potassium salt (3.4 g, 0.018 mol) was heated to 90°C for 1.5 h. Then, the precipitate was removed by the filtration. The filtrate was concentrated under vacuum, and then the residue was extracted with ethyl acetate. The ethyl acetate solution was dried with magnesium sulfate. The ethyl acetate was evaporated to dryness, and then the residue was washed with methanol. The crude product was obtained in 82.3%. The crude product was employed in the next step. An ethanol suspension of the crude product was heated, and then hydrazine monohydrate was added to the ethanol suspension of the crude product. The reaction mixture was refluxed for 2.5 h. Ethanol was evaporated to dryness, and then the residue was extracted with chloroform. The chloroform solution was dried with magnesium sulfate. Chloroform was evaporated to dryness, and the residue was washed with methanol. The product was obtained in a 33.5% yield.

^{1}H-NMR(CDCl$_3$): δ 1.3–2.2 (m, 10 H, (C$\underline{H}_2$)$_4$, N$\underline{H}_2$), 2.7 (t, 2H, C$\underline{H}_2$NH$_2$), 4.1 (t, 2H, OC$\underline{H}_2$), 7.0 (d, 2H, Ar), 7.6 (m, 4H, Ar)
IR(KBr): ν 3305, 3377 (NH), 2854, 2931 (CH), 2224 (CN), 1494, 1605 (Ar), 1253 (C—O—C)

RESULTS AND DISCUSSION

In order to investigate the influence of the chemical structures for the diepoxy monomers on the thermal properties of the synthesized epoxy resins, three kinds of epoxy monomers (one mesogenic monomer and two nonmesogenic monomers), were prepared as shown in Figure 1. Cyanostilbene-type epoxy mesogenic monomer (DECS) shows a nematic phase between 47.8 and 83.2°C. The phase structures of the monomers were detected by using of optical microscopy and DSC measurements. Another nonmesogenic epoxy monomers were commercially available compounds, namely, bisphenol-type epoxy monomer (DEBPA) and ethylene glycol diglycidyl ether (DEEG).
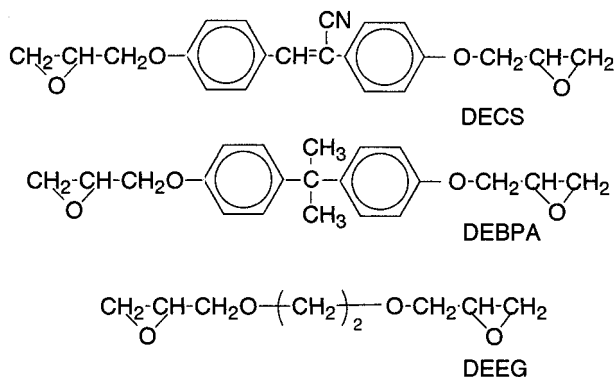
Figure 1 Structures of diepoxy monomers.

In this study, we used the aliphatic and aromatic amine compounds as a curing agent. Nine kinds of amine compounds were used as a curing agent, as shown in Figure 2. Four amine compounds (DABMB, ABMB, ACB, and AMB) had a mesogenic core. Another amine compound with no mesogenic groups was commercially available. Thermal properties of the amine compounds are summarized in Table I. No mesomorphic properties were observed for AMB and ABMB, which contained a methoxybiphenyl group as a mesogenic core; however, a mesophase was exhibited
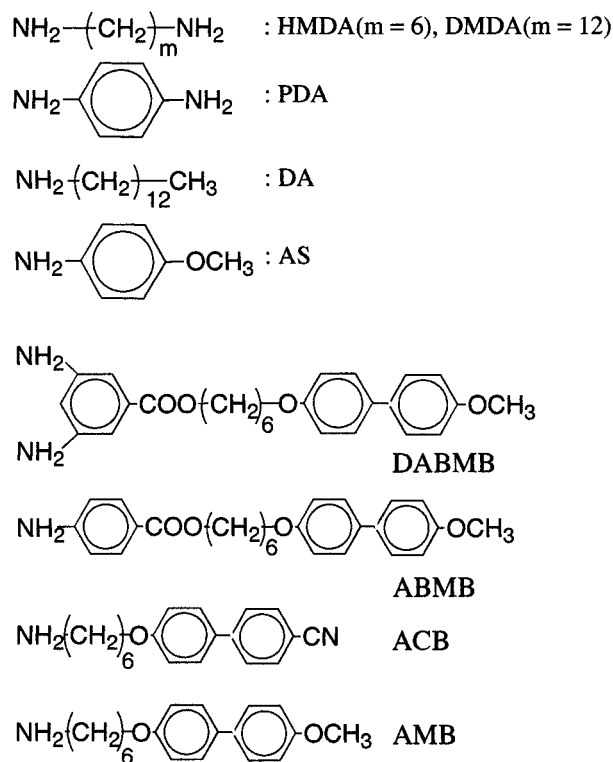

Figure 2 Structures of amine monomers.

Table I Phase Transition Temperatures of Amine Monomers

Abbreviation	Phase Transition Temperature (°C)[a]
ACB	$\overset{63.8}{K} \underset{?}{\rightleftharpoons} \overset{89.0}{N} \underset{88.6}{\rightleftharpoons} I$
AMB	$\overset{147.0}{K} \underset{127.8}{\rightleftharpoons} I$
ABMB	$\overset{107.4}{K} \underset{84.2}{\rightleftharpoons} I$
DABMB	$\overset{93.7}{K} \underset{90.6}{\rightleftharpoons} \overset{98.6}{M} \underset{93.1}{\rightleftharpoons} I$

[a] K indicates a solid; N, nematic; M, mesophase; I, isotropic.

for a diamine compound containing a methoxybiphenyl group (DABMB).

Reaction of Mesogenic Epoxy Compound with Nonmesogenic Amine Compound

The thermal properties of the homogeneous mixture, prepared by the evaporation of chloroform from the chloroform solution containing mesogenic epoxy compound (DECS) and nonmesogenic amine compound at room temperature, were evaluated. All homogeneous mixtures showed nonmesomorphic properties at the whole feed ratios. Furthermore, thermal decomposition for the mixtures of DECS with nonmesogenic diamines, HMDA, DMDA, and PDA, occurred before the molten state. These results showed that the curing reaction for the mixtures of DECS with nonmesogenic diamines proceeded during the preparation of the mixture at room temperature. However, we cannot explain the reason why the curing reaction started at room temperature. The curing reaction of these mixtures proceeded in a three-dimensional direction.

Reaction of Nonmesogenic Epoxy Compound with Mesogenic Amine Compound

The mixture of nonmesogenic epoxy compound (DEEG or DEBPA) with the mesogenic amine compound (ACB or DABMB) exhibited no mesophase while, after the mixture was annealed at 70 or 80°C for 1 or 6 h, the obtained epoxy resins exhibited a mesophase. A typical texture of the epoxy resins was not observed; however, birefringence was exhibited at the molten state range. So we assigned this state to the mesophase. Furthermore, in the case of the aromatic amine com-

Table II   Thermal Properties of Liquid Crystalline Epoxy Resins

Abbreviation (Molar Ratio = 1 : 1)	Phase Transition Temperature (°C)[b]	
	Cured for 1 h	Cured for 6 h
DECS−ACB (150)[a]	$S \overset{179.4}{\to} I$	$g \to S \overset{66.8 \quad 185}{\to} \text{Decom.}$
DECS−AMB (80)[a]	$K(M) \overset{125.9}{\to} I$	$K(M) \overset{123.3}{\to} I$
DECS−ABMB (80)[a]	$N \overset{83.5}{\to} I$	$N \overset{85.0}{\to} I$
DECS−DABMB (80)[a]	$N \overset{170}{\to} \text{Decom.}$	$g \to N \overset{85 \quad 170}{\to} \text{Decom.}$
DECS−DABMB : ACB (20 : 80) (95)[a]	$S \overset{162.0}{\to} I$	$g \to S \overset{56.7 \quad 195}{\to} \text{Decom.}$
DECS−DABMB : ABMB (50 : 50) (55)[a]	$M \overset{76.4}{\to} I$	$M \overset{90.6}{\to} I$

[a] Curing temperature (°C).
[b] g indicates glassy; K, solid; S, smectic; N, nematic; M, mesophase; I, isotropic.

pounds, mono- and diamine compounds were prepared for the investigation of the influence of the number of the amino group on the curing reaction. The amine group of the amine compounds with a mesogenic group was attached to the mesogenic group through the flexible spacer.

Reaction of Mesogenic Epoxy Compound with Mesogenic Amine Compound

As mentioned above, an exhibition of a typical liquid crystalline behavior for the mixture of diepoxy compounds with the amine compounds required the both compounds containing a mesogenic group. We synthesized the combined-type liquid crystalline epoxy resins by the use of the mesogenic amine compounds and mesogenic epoxy compound, DECS.

The combined liquid crystalline epoxy resins were prepared by the curing in the mesomorphic temperature range for the mixtures of DECS with the amine compounds. The thermal properties of the combined liquid crystalline epoxy resins are summarized in Table II. The four mesogenic amine compounds were used as a curing agent; furthermore, we employed the mixture of mesogenic amine compounds, DABMB with ACB, and DABMB with ABMB as a curing agent. The curing reaction by the use of the mesogenic amine mixtures would progress easily. The appropriate molar ratio of the amine mixture was adopted by the nearly equal transition temperature of DECS.

The combined liquid crystalline epoxy resin, DECS−ACB, was tried to prepare with the curing of the mixture of DECS with ACB in the mesomorphic temperature range. The mixture of DECS with ACB did not exhibit a typical mesomorphic texture until above 150°C; however, a focal conic texture appeared above 150°C, as shown in Figure 3. After the curing reaction was continued for 1 h, the mixture of DECS with ACB displayed a smectic phase even if each monomer exhibits a nematic phase, as shown in Table I. In the case of the curing reaction time for 1 h, the combined liquid crystalline epoxy resins, except DECS−DABMB, exhibited a clear transition temperature from the mesophase to the isotropic phase, while the thermal decomposition occurred for the DECS−DABMB system before the appearance of
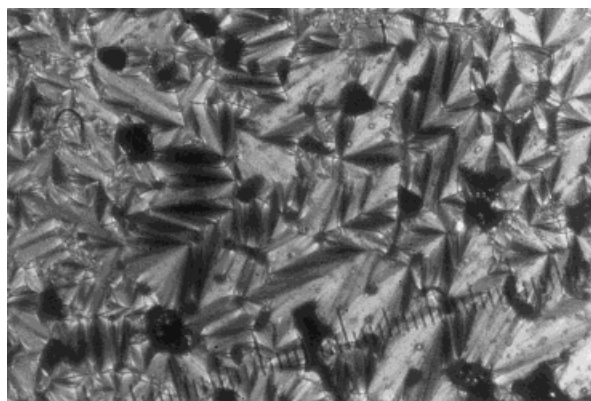

Figure 3   Optical texture of DECS−ACB.

Table III   Thermal Properties of Liquid Crystalline Epoxy Resins Cured for 1 h

| | Phase Transition Temperature (°C) (Cured for 1 h)[a] | | |
| | Functional Ratio (Epoxy−Amine) | | |
Abbreviation	2/1	1/1	1/2
DECS−ACB	143.9 $S \rightarrow I$ (80)	179.4 $S \rightarrow I$ (150)	158.3 $M \rightarrow I$ (115)
DECS−DABMB	100.0 $N \rightarrow I$ (55)	97.1 $N \rightarrow I$ (60)	170 $N \rightarrow$ Decom. (80)
DECS−DABMB : ACB (20 : 80)	148.1 $M \rightarrow I$ (60)	162.0 $S \rightarrow I$ (95)	178.4 $M \rightarrow I$ (80)

[a] S indicates smectic; N, nematic; M, mesophase; I, isotrotic. Curing temperatures (°C) are represented by the numbers in parentheses.

molten state. Curing reaction of the mixtures would be carried out in an isotropic phase, then the reaction proceeded rapidly. However the mesophase could not be preserved; that is to say, it could not produce the orientational polymer films. Therefore, one factor to obtain the good orientational film by the curing reaction procedure for the both mesogenic monomers to be considered is that the polymers can exhibit the thermal decomposition after transition from mesophase.

The influence of the ratio for the functional group (amine and epoxy group) on the thermal properties for the combined liquid crystalline epoxy resins was examined by the three mixtures, DECS−ACB, DECS−DABMB, and DECS−DABMB : ACB (20 : 80). The thermal properties for the combined liquid crystalline epoxy resins prepared by the curing reaction of the mixture of the amine and epoxy compounds with the different functional group ratio (amine : epoxy) are summarized in Table III. In the case of the combined liquid crystalline epoxy resins prepared by the 1-h curing reaction, combined liquid crystalline epoxy resins, except for DECS−DABMB, (epoxy-to-amine = 1 : 2) did not exhibit thermal decomposition. Further, in order to obtain the combined liquid crystalline epoxy resins that exhibited thermal decomposition, the curing reaction time was elongated by 6 h. The thermal properties of the combined liquid crystalline epoxy resins are shown in Table IV. Thermal decomposition for DECS−ACB (epoxy-to-amine = 2 : 1) was newly observed. This result indicates that the curing reaction time influenced the thermal properties for the

DECS−ACB (epoxy-to-amine = 2 : 1). In DECS−ACB (epoxy-to-amine = 2 : 1), the hydroxyl group generated by the curing reaction would attack unreacted excess epoxy groups. Thus, when the reaction time is elongated by 6 h, the crosslinking density in the liquid crystalline epoxy resins increased and then the thermal decomposition for DECS−ACB (epoxy-to-amine = 2 : 1, 6 h) occurred before the isotropic phase.

Fourier Transform IR Measurements of Curing Reaction with the Mesogenic Monomers

In order to examine the progress of the curing reaction for the synthesis of the combined liquid crystalline epoxy resins, thermally controlled Fourier transform IR (FTIR) measurements were carried out. A decrease in the area of an epoxy peak at 917 cm^{-1} indicates the progress of the curing reaction of the combined liquid crystalline epoxy resins, as shown in Figure 4. The absorbance ratio of the epoxy ring to the unreacted antisymmetric stretching CH$_2$ indicated the progress of the curing reaction for DECS−ACB (epoxy-to-amine = 1 : 1) is shown in Figure 5. The absorbance ratio decreased remarkably at 150°C of a curing temperature for DECS−ACB (epoxy-to-amine = 1 : 1), as mentioned above. This result showed that a reaction of the epoxy group with the amine group proceeded as soon as the mixture of DECS with ACB was heated and that the reaction for DECS-to-ACB (epoxy-to-amine = 1 : 1) was almost finished at 130°C on a heating run.

Table IV   Thermal Properties of Liquid Crystalline Epoxy Resins Cured for 6 h

| | Phase Transition Temperature (°C) (Cured for 6 h) | | |
| | Functional Ratio (Epoxy−Amine) | | |
Abbreviation	2/1	1/1	1/2
DECS−ACB	$\overset{? \quad 180}{g \rightarrow S \rightarrow \text{Decom.}}$	$\overset{66.8 \quad 185}{g \rightarrow S \rightarrow \text{Decom.}}$	$\overset{160.1}{M \rightarrow I}$
	(80)	(150)	(115)
DECS−DABMB	$\overset{102.5}{N \rightarrow I}$	$\overset{135.0}{N \rightarrow I}$	$\overset{85 \quad 170}{g \rightarrow N \rightarrow \text{Decom.}}$
	(55)	(60)	(80)
DECS−DABMB : ACB (20 : 80)	$\overset{146.1}{M \rightarrow I}$	$\overset{56.7 \quad 195}{g \rightarrow S \rightarrow \text{Decom.}}$	$\overset{180.4}{M \rightarrow I}$
	(60)	(95)	(80)

g indicates glassy; S, smectic; N, nematic; M, mesophase; I, isotrotic. Curing temperatures (°C) are represented by the numbers in parentheses.

Further, a change in the absorbance ratio for DECS−DABMB was shown in Figure 6. The absorbance ratio of epoxy-to-cyano for DECS−DABMB changes slightly on the heating run. The curing reaction for DECS−DABMB proceeded gradually during annealing at 60°C as a curing temperature. After 10 h, the curing reaction for DECS−DABMB was almost finished.

The difference in the progress of the curing reaction between DECS−ACB and DECS−DABMB occurs at the curing temperature. In the case of DECS−ACB, both materials exhibited a nematic phase, and their transition temperature is nearly equal. Thus, the reaction of epoxy groups with amine groups started rapidly in the mesomorphic
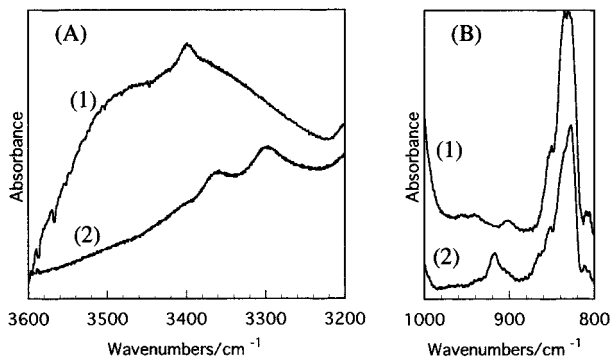
temperature range. On the contrary, in the case of DECS−DABMB, DECS exhibited a nematic phase at the curing temperature of 60°C; however, the DABMB did not exhibit a mesophase at 60°C. This is the reason why the curing reaction is slow below 60°C.

The curing reactions for DECS−AMB and for DECS−ABMB proceeded slowly compared with that of DECS−ACB. A decrease in the absorbance
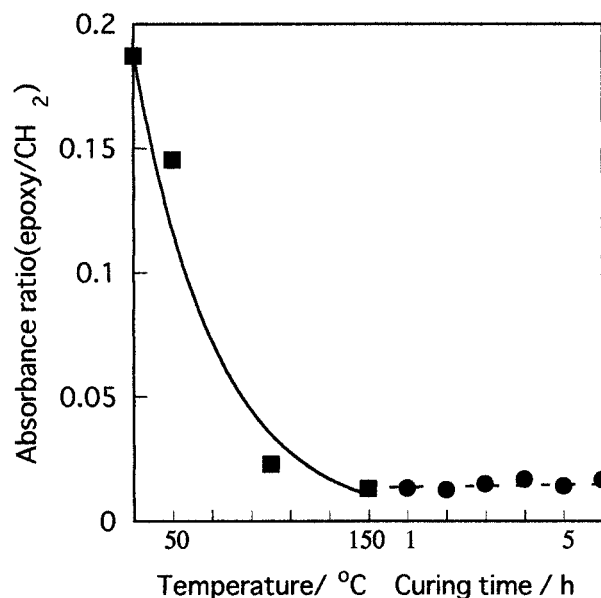

Figure 4 FTIR spectra of liquid crystalline epoxy resin (DECS−ACB) and mixture of DECS with ACB. (A) NH stretching region and (B) epoxy group region: (1) liquid crystalline epoxy resin (DECS−ACB) and (2) mixture of DECS with ACB.

Figure 5 Temperature and curing time dependence of absorbance ratio of epoxy group−CH$_2$ for liquid crystalline epoxy resin (DECS−ACB).
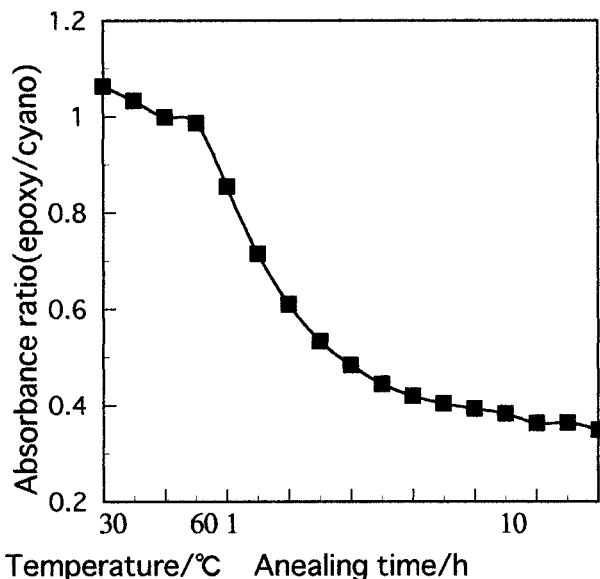
Figure 6 Temperature and curing time dependence of absorbance ratio of epoxy group–cyano group for liquid crystalline epoxy resin (DECS–DABMB).

Figure 7 Least-squares deconvolution of NH and OH stretching vibration region of liquid crystalline epoxy resin (DECS–ACB): (a) NH symmetric stretching, (b) NH antisymmetric stretching, (c) secondary NH stretching, and (d) OH stretching vibration groups.

ratio for DECS–AMB was about 0.15 until the temperature of the mixture of DECS with AMB was raised up to 80°C. No progress of the curing reaction for DECS–AMB was observed after 1 h. The progress of the curing reaction for DECS–ABMB was observed until the curing reaction time of 12 h was reached.

Furthermore, a change in NH stretching band of DECS–ACB in FTIR measurements was examined in order to investigate the progress of the curing reaction for DECS–ACB. As the curing reaction for an epoxy resin proceeded, a hydroxy group band was generated near the NH stretching band. An overlapping of NH and OH group bands was observed. The curve-fitting procedure was employed for the research on hydrogen bonding between amide I groups for polyurethanes or polyamides.[30,31] The procedure for the division of the NH and OH overlapping peak was employed for the study of the curing reaction for the liquid crystalline epoxy resin in this research. Therefore, the overlapping band of OH and NH group peaks was divided into four peaks, namely, NH symmetric stretching, NH antisymmetric stretching, secondary NH stretching, and OH stretching vibration groups, as shown in Figure 7.

Variation of four peak area ratios is shown in Figure 8. The peak area ratio in the NH symmetric and NH antisymmetric stretching vibration decreased remarkably on the heating run. After a secondary NH stretching vibration peak for a
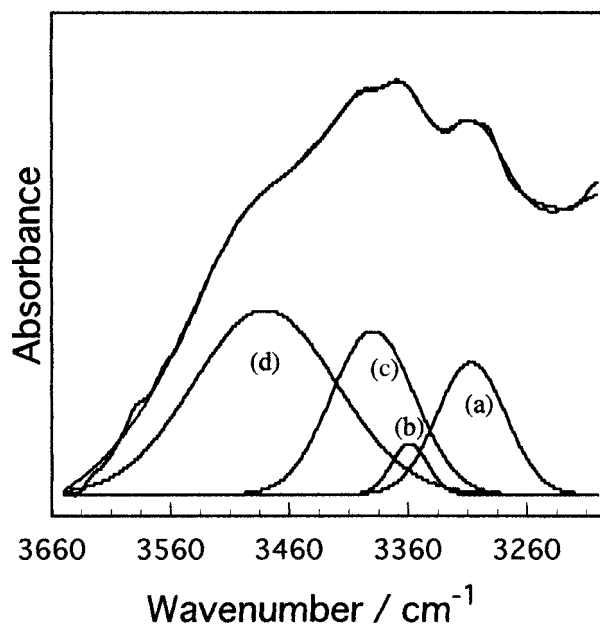
secondary amine was generated, the peak area ratio of the NH stretching vibration peak decreased with increasing temperature. Further-
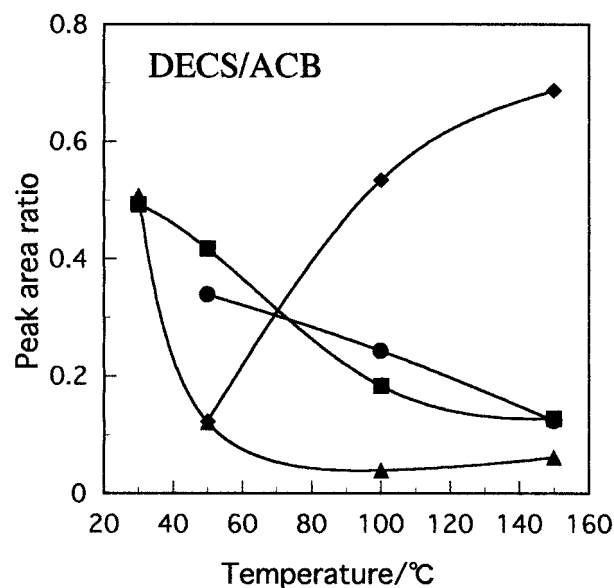

Figure 8 Variation of peak area ratio for (■) NH symmetric stretching, (▲) NH antisymmetric stretching, (●) secondary NH stretching, and (♦) OH stretching vibration group as a function of temperature.
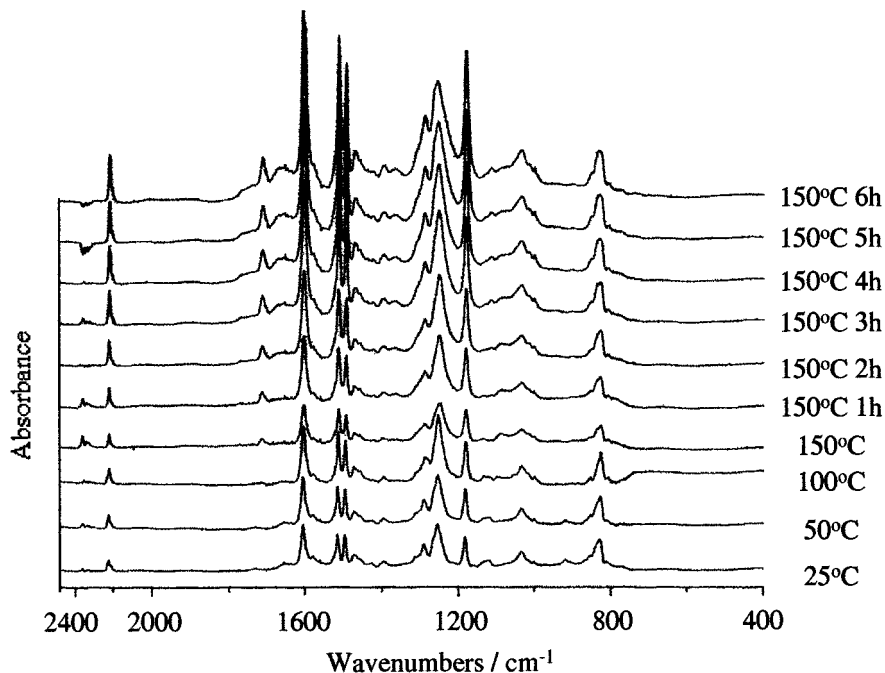
Figure 9   FTIR spectra of liquid crystalline epoxy resin (DECS–ACB).

more, a remarkable increase in the peak area ratio of OH group was observed. These changes in the peak area ratios indicated that polymer chains of the DECS–ACB grew at the initial stage of the curing reaction. At first, epoxy groups reacted with primary amino groups based on the peak area ratio for primary amino groups decreased on the heating run. Furthermore, secondary amine groups were generated. Next, these secondary amine groups reacted with other epoxy
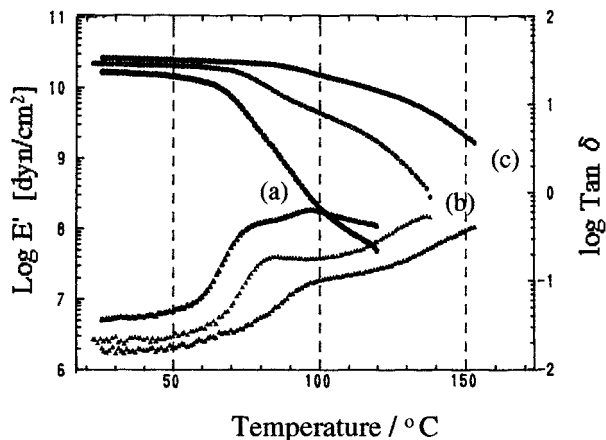
groups. Therefore, polymer chains of DECS–ACB would grow linearly. As the curing reaction time increased, the glass transition temperature of the product for the DECS–ACB system was increased. This increase in the glass transition temperature for DECS–ACB would occur from a formation of a network by the curing reaction of DECS–ACB, as mentioned below.

In contrast, the changes in the peak absorbance ratio for the four components of DECS–AMB were about 0.1. The curing reaction of DECS–AMB did not proceed very well. The curing reaction of DECS–ACB was faster than that of DECS–AMB. AMB did not exhibit a mesophase and showed a solid phase at the curing temperature; however, ACB exhibited a nematic phase. Thus, a difference in the phases for the epoxy compound and amine compounds influenced the curing reaction progress. Further, with respect to a mesophase for the liquid crystalline epoxy resins, a typical smectic texture was observed for DECS–ACB prepared by the DECS and ACB, which contained mesogenic groups respectively. No typical mesophase was observed for DECS–AMB. These results indicated that the ability of an exhibition of liquid crystalline epoxy resins was deeply influenced by the appearance of the mesophase for starting epoxy and amine compounds.

Figure 9 showed FTIR spectra in the range of

Figure 10   (●) Tensile modulus and (▲) tan δ as a function of temperature at 10 Hz for liquid crystalline epoxy resin (DECS–ACB) cured for (a) 6, (b) 12, and (c) 24 h.

$400-2400$ cm^{-1} for DECS–ACB. A new peak near 1700 cm^{-1} was observed with curing reaction time. This peak was attributed to the amide I band. The amide I band was generated by the reaction of cyano groups with hydroxyl groups.[32] Further, a new peak and shoulder near 1100 cm^{-1} was observed as the curing proceeded. A small peak in the higher wave number (near 1115 cm^{-1}) was attributed to aliphatic ether group. An appearance of aliphatic ether peak near 1115 cm^{-1} indicated that the secondary OH groups reacted with epoxy groups. The reaction resulted in the formation of networks between the polymer chains. The new peak attributed to the amide I peak was observed as the curing at 150°C proceeded. Thus, two types of networks for this epoxy resin (DECS–ACB) were formed.

Mechanical Properties of the Curing Polymers

The stress modulus and tan δ against temperature for DECS–ACB are shown in Figure 10. A maximum of tan δ for DECS–ACB shifted to the higher temperature with increasing curing time. The increase in the glass transition temperature would occur from increasing crosslinking density. As mentioned above, FTIR results indicate that epoxy groups reacted with amine groups rapidly. Furthermore, generated OH groups reacted with the remained epoxy groups and cyano groups in the end of the rigid core. Whereas, in the case of the two-component amine system, DECS–DABMB : ACB, the mechanical properties of the polymer did not change significantly compared with that of the polymer for DECS–ACB. The curing temperature for DECS–DABMB : ACB was lower than that of DECS–ACB. Therefore, the crosslinking reaction of OH groups with cyano groups did not proceeded quickly in this system.

The curing reaction of DECS–ACB would consist of two steps. The first step was a reaction of epoxy groups with amine groups. This step showed that a polymer chain would extend linearly. The second step exhibited a crosslinking process. This supported the fact that the progress of the crosslinking reaction for DECS–ACB depended on the curing time.

CONCLUSIONS

Liquid crystalline epoxy resins were prepared by the curing reaction of diepoxy mesogenic monomer with amine compounds containing mesogenic groups. In the case of DECS–ACB, a typical smectic phase was frozen. The curing reaction for DECS–ACB was faster than that of the other epoxy resins. With regard to thermal stability for liquid crystalline epoxy resins, DECS–ACB was superior to the other liquid crystalline epoxy resins. The glass transition temperature for DECS–ACB increased with increasing curing time.

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