Liquid crystalline twin epoxy monomers based on azomethine mesogen: synthesis and curing with aromatic diamines

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Abstract

Liquid crystalline (LC) epoxy monomers with twin mesogenic azomethines connected by different alkylene spacers ($x = 6, 7, 8,$ and 9) were synthesized to prepare LC thermosets. The epoxy monomers were characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC) and polarized microscopy. All four epoxy monomers were found to form nematic phase in the melt, and their melting (T_m) and isotropization temperatures (T_i) as well as corresponding thermodynamic values (ΔH_m, ΔH_i, ΔS_m and ΔS_i) decreased with increase of x in a zig-zag fashion, revealing the even–odd effect. Cure behavior of a stoichiometric mixture of an epoxy monomer with $x = 9$ and diaminodiphenlysulfone (DDS) was investigated by DSC for specimens cured under various cure conditions. Nematic LC texture for the cured specimen was identified by polarized microscopy and X-ray diffractometry. From the DSC results and microscopic observations, phase diagram of cure time vs. transition temperature was constructed for the epoxy ($x = 9$)/DDS system. This diagram shows the changes of T_m, T_i and glass transition temperatures (T_g) as cure proceeds. Regions for nematic LC phase are indicated in the diagram. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline thermosets; Twin epoxy monomers; Azomethine Mesogen

1. Introduction

During the past decade, there was renewal of interest in liquid crystalline (LC) thermosets because of their electrical, mechanical, and optical properties for advanced applications such as microelectrical packing, matrix for composites, and non-linear optics, respectively [1,2]. The excellent properties of LC thermosets stem from the preservation of molecular organization in the mesophase of LC precursors and monomers by means of crosslinking. The resulting highly crosslinked thermoset containing rigid rod molecules can offer improvement of rather poor properties in transverse direction to the chain orientation.

Of possible thermosetting polymers, epoxy resins are commercially important because of their superior adhesion, heat and corrosion resistance, and mechanical and electrical properties than other classical thermosets. Incorporating LC structure into epoxy network could enhance the properties [3]. Over last few years, several research groups have studied synthesis and curing of LC diepoxides with a flex-

ible spacer between epoxide moiety and mesogenic group [4–6], with two mesogens linked by a central flexible spacer [7,8], and with substituents in mesogenic units [9–11].

Aromatic poly(azomethines), also called polyimines or Schiff-base polymers, have been extensively studied, since the thermotropic LC poly(azomethines), which were readily spun into high-strength fibers, have been synthesized [12,13]. As in LC aromatic polyesters [14], many of the poly(azomethines) are insoluble in common organic solvents [15,16]. Even LC azomethine polymers with flexible spacers between mesogens have showed poor solubility but could maintain good thermal stability [17]. On the other hand, quite a few studies have been published on LC diepoxides containing azomethine mesogens. In an early paper published in the preparation of networks from oligomeric azomethines with epoxides groups [18], the mesogenic properties of the diepoxides did not appear. Synthesis of diepoxide monomers with diad or triad aromatic rings linked by azomethine groups have been recently published. However, in the paper the curing of the diepoxides was not described [11], and later the crosslinking anionic polymerization of the diepoxides has been reported [19].

In this work, we synthesized and characterized twin epoxy monomers having two mesogenic azomethines linked

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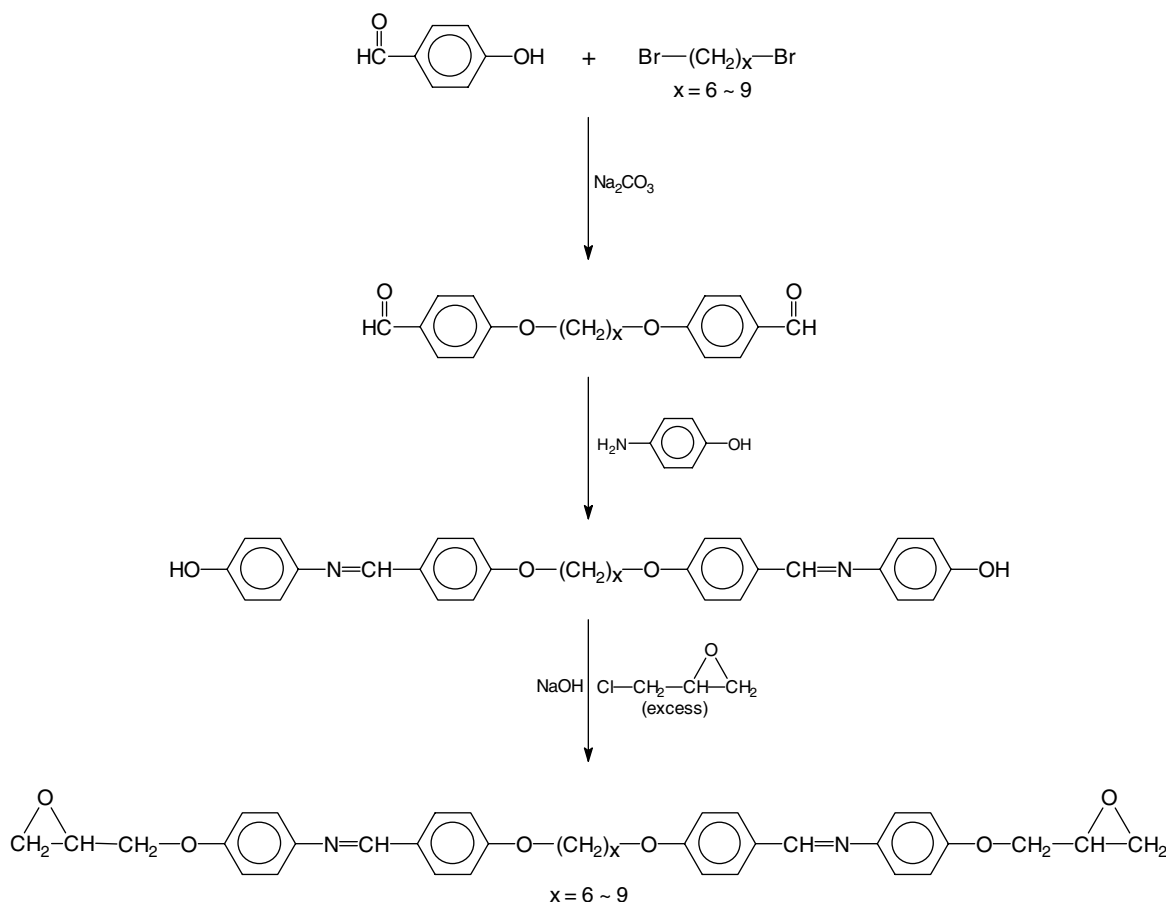
Scheme 1.

by a central alkylene spacer with different lengths. Thermal and mesomorphic properties of the epoxy monomers and their mixtures with amine curing agents were investigated. Time–temperature phase diagram during isothermal curing for an epoxy/amine system was presented.

2. Experimental

2.1. Synthesis

Synthetic route to LC twin epoxy monomers with mesogenic azomethines varying the length of the central polymethylene spacers (x) from 6 to 9 is shown in Scheme 1. Since the synthetic procedures used to prepare the epoxy monomers were essentially same, a representative epoxy with $x = 9$ is given in the following.

Nonamethylene 1,9-bis(4-oxybenzaldehyde). In a typical synthesis, 4-hydroxybenzaldehyde (18 g, 0.15 mol) was dissolved in 60 ml of DMF at 80°C. To this solution were added 1,9-dibromononane (21 g, 0.073 mol) and Na_2CO_3 (32 g, 0.38 mol). The reaction mixture was stirred at 150°C for 4 h. After cooling to room temperature, the mixture was poured into 1 l of distilled water. The precipitate was collected by filtration and washed with 5% aqueous

NaHCO$_3$ solution and distilled water, sequentially. The crude product was recrystallized from ethanol. Yield was 14 g (52%). IR (KBr): 2850, 2730, 1686 (aldehyde), 1254, 1150, 1009 (ether) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.92 (2H, s, CHO), 7.83–7.90 (4H, d, aromatic), 7.01–7.05 (4H, d, aromatic), 4.01–4.11 (4H, t, C$_9$H$_{18}$), 1.87–1.97 (4H, m, C$_9$H$_{18}$), 1.57–1.64 (10H, m, C$_9$H$_{18}$).

Nonamethylene 1,9-bis[N-(4-oxybenzylidene)-4-hydroxyaniline]. Nonamethylene 1,9-bis(4-oxybenzaldehyde) (14 g, 0.38 mol), 4-aminophenol (8.3 g, 0.76 mol) and a catalytic amount of 4-tolueneslufonic acid were dissolved in 250 ml of dry ethanol. The reaction mixture was stirred at 80°C for 5 h. The mixture was then poured into 95% ethanol. The precipitate was collected by filtration and washed with 95% ethanol, thoroughly. The crude product was recrystallized from 130 ml of 1,4-dioxane. Yield was 15 g (72%). IR (KBr): 3384 (OH), 1607 (CH=N), 1253, 1169 (ether) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.52 (1H, s, CH=N), 9.41 (1H, s, OH), 7.83–7.90 (2H, d, aromatic), 7.14–7.18 (2H, d, aromatic), 7.03–7.07 (2H, d, aromatic), 6.78–6.82 (2H, d, aromatic), 4.00–4.15 (2H, t, C$_9$H$_{18}$), 1.76–1.79 (2H, m, C$_9$H$_{18}$), 1.50–1.58 (5H, m, C$_9$H$_{18}$).

Nonamethylene 1,9-bis[N-(4-oxybenzylidene)-4-(2,3-epoxypropoxy)-aniline]. Nonamethylene 1,9-bis[N-(4-oxybenzylidene)-4-hydroxyanline] (15 g, 0.027 mol) was
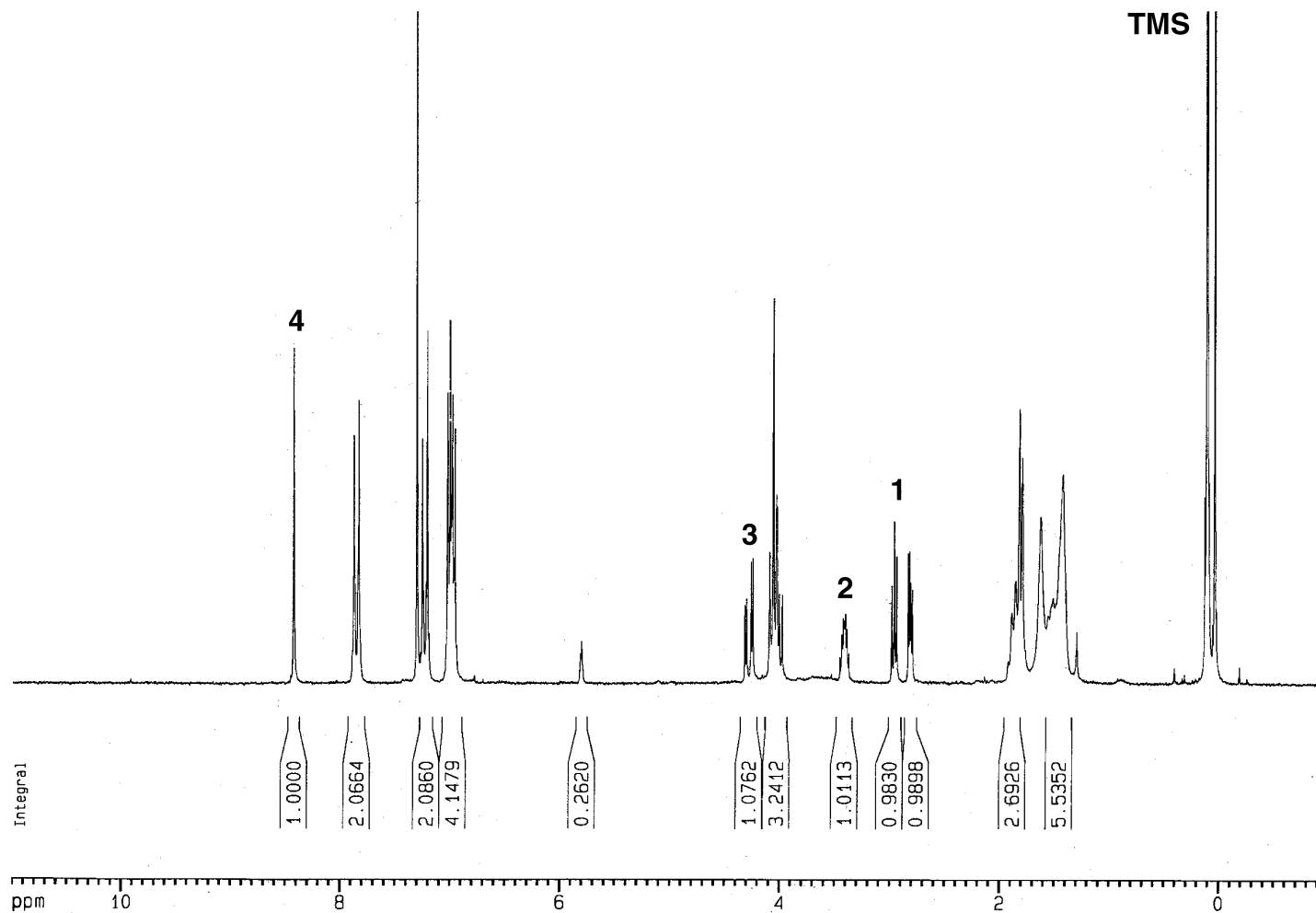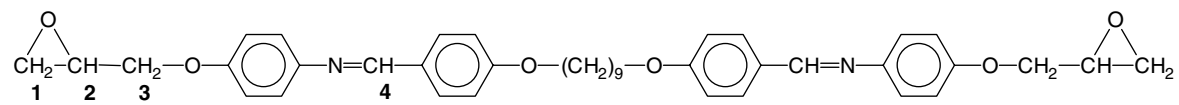
Fig. 1. A typical ^{1}H NMR spectrum for an epoxy monomer ($x = 9$) in CDCl$_3$. The chemical shift scale is relative to internal TMS:
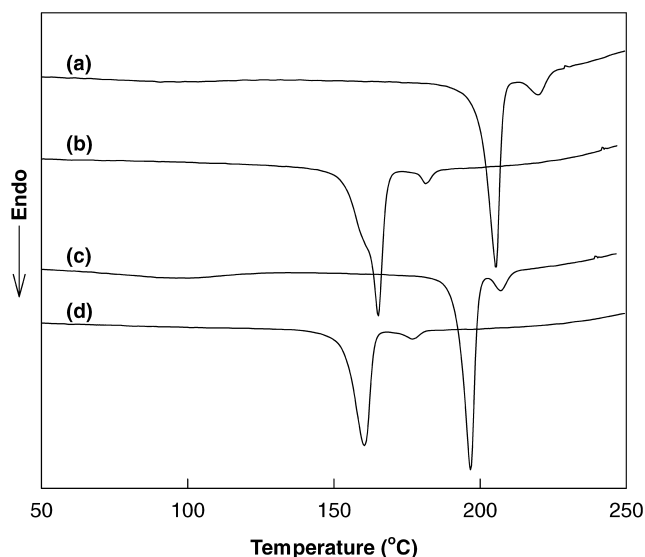
Fig. 2. DSC thermograms of epoxy monomers: (a) $x = 6$; (b) $x = 7$; (c) $x = 8$; (d) $x = 9$.

dissolved in 300 ml of epichlorohydrin solution with 1 drop of water at 80°C. To this solution was added drop-wise with vigorously stirring 30 % aqueous NaOH solution (NaOH: 4.5 g, 0.11 mol) over 2 h to form the chlorohydrin. The reaction mixture was then heated to and maintained at 110°C for 12 h to promote ring closure to the epoxy. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected by filtration and washed with water and methanol, sequentially. The crude product was dissolved in chloroform, then filtered off and reprecipitated from methanol. Yield was 6.4 g (36%). IR (KBr): 1622, 1606 (CH=N), 1254, 1193 (ether), 920 (epoxy) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.42 (1H, s, CH=N), 7.83–7.87 (2H, d, aromatic), 7.19–7.22 (2H, d, aromatic), 7.02–7.95 (4H, m, aromatic), 3.97–4.31 (4H, m, CH$_2$ glycidyl, C$_9$H$_{18}$), 3.42 (1H, m, CH epoxy), 2.79–2.98 (2H, dd, CH$_2$ epoxy), 1.79–1.89 (2H, m, C$_9$H$_{18}$), 1.43–1.63 (5H, m, C$_9$H$_{18}$).

2.2. Characterization

The structures of epoxy monomers were determined using a Jasco 300E FT/IR and a Bruker AMX-200 NMR spectrometer. Thermal analyses were performed by a DSC (duPont DSC 910) at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. Optical texture was examined by a polarized microscope (Zeiss, Jenapol) equipped with a heating stage (Mettler FP82H). A Bruker AXS D5005 wide angle X-ray diffractometer was employed to examine diffraction pattern in a reflection mode using Co-Kα radiation ($\lambda = 1.790$ Å).

3. Results and discussion

3.1. Synthesis, thermal and mesomorphic properties of LC epoxy monomers

The molecular structures of the epoxy monomers shown in Scheme 1 were evaluated by means of FT/IR and NMR techniques. Fig. 1 shows the ^{1}H NMR spectrum of an epoxy monomer with $x = 9$, including the peak assignments corresponding to the structure. As shown in the figure, of methylene protons in epoxy ring, proton 1 displayed two doublets at 2.79–2.98 ppm, while proton 2 exhibited a multiplet centered at 3.42 ppm. Proton 3 in glycidyl ether group was expected to reveal two doublets: one was found at 4.24–4.31 ppm, but the other could not be defined due to overlapping in resonance with α-proton of 1,9-dioxynonamethylene unit. Proton 4 in azomethine moiety appeared as an intense singlet at 8.42 ppm. In its NMR spectrum, the ratio of the peak areas between two epoxy-protons and an azomethine-proton appears to be 3:1. This indicates that 1 mol of the epoxy monomer obtained consists of 2 mol of epichlorohydrin unit and 1 mol of diol unit as shown in Scheme 1.

Thermal and mesomorphic properties of epoxy monomers with different spacer lengths ($x = 6$, 7, 8 or 9) were examined using DSC as well as a polarized microscope. DSC thermograms of the epoxy monomers are displayed in Fig. 2. All the curves show two endothermic peaks: one at lower temperature is due to melting (T_m) and the other at higher temperature to isotropization (T_i). By a polarized microscope, a nematic mesophase showing Schlieren textures was observed for all the epoxy monomers in the melt between T_m and T_i (see Fig. 3). Table 1 contains transition temperatures, and changes of enthalpy (ΔH) and entropy (ΔS) for melting and isotropization obtained from DSC thermogram shown in Fig. 2. The table also shows the temperature interval between T_m and T_i ($\Delta T = T_i - T_m$), which stands for the extent of LC phase region. In Fig. 4, the transition temperatures are plotted against the chain length of the spacer (x). As shown in the figure, the values of T_m and T_i decreased in a zig-zag fashion with increasing x, revealing the even–odd effect. The values of ΔH and ΔS for melting and isotropization transitions in Table 1 also show the even–odd dependence on x. This result indicates that epoxy monomers with even numbers of methylene units in the spacer have a stronger chain interaction and a higher degree of order in their liquid crystalline phases than those with odd numbers [20,21]. Note that ΔT maintains almost constant with change of x. In this study, an epoxy monomer with the lowest T_m and T_i (i.e. $x = 9$) was used to examine curing with aromatic diamines.

3.2. Reactions between LC epoxy monomer and curing agents
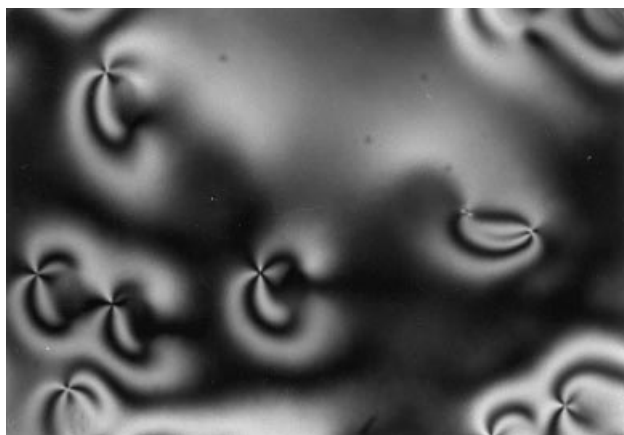
Reactivity of the epoxy monomer with $x = 9$ was

Fig. 3. Optical texture of an epoxy monomer ($x = 9$) taken at 170°C (magnification = 250 ×).

examined with four different aromatic diamines; 4,4′-diaminodiphenylmethane (DDM, mp = 93°C), 1,4-phenylenediamine (PDA, mp = 143°C), 4,4′-diaminodiphenylsulfone (DDS, mp = 180°C), and 4,4′-diaminodiphenylether (DDE, mp = 193°C). The melting points of the diamines were defined by DSC at a heating rate of 10°C min⁻¹. Mixtures for curing were obtained by dissolving stoichiometric amounts of the epoxy monomer and curing agent in chloroform, and removing the solvent under reduced pressure at room temperature. Fig. 5 displays DSC thermograms of the uncured mixtures during heating, including chemical formula of the aromatic diamines. DDE gave an exothermic peak due to cure reaction at the lowest temperature, meaning the highest reactivity with the epoxy monomer among the four diamines. Its high reactivity of the DDE is ascribed to the increase in electron density in the nitrogen atom of amino group by the oxygen atom in diphenylether unit. On the other hand, the electron withdrawing property of sulfone group in DDS produces the lowest reactivity with the epoxy monomer. Similarly, PDA and DDM are intermediate in the reactivity due to the polar effect.

In particular, DDS appears to form an eutectic mixture which shows the most distinguished melting transition, and cure reaction proceeds gradually after the melting compared to other curing agents as shown in Fig. 5. These characteristics of the DDS may provide advantages in study of transition behavior related to curing of the LC epoxy. Thus, we

selected an epoxy monomer ($x = 9$)/DDS system to examine the cure behavior, and detailed results are given in the following section.

3.3. Curing of LC epoxy monomer with DDS

A stoichiometric mixture of the epoxy monomer with $x = 9$ and DDS was cured under various isothermal cure conditions. The cure conditions are listed in Table 2 with transition temperatures (T_g, T_m or T_i) determined by DSC after the curing. As can be seen in the table, the cure condition includes two different ways; single step at an isothermal cure temperature and dual step at two successive cure temperatures for various cure times. Based on the transition temperatures of the epoxy monomer ($x = 9$) in Table 1, three different cure temperatures were used in this experiment; 160°C ($= T_m$), 170°C (between T_m and T_i), and 180°C (just above T_i) for each single step. For the dual step, unreacted mixture was cured at 160°C for 20 min first, and then at 115°C for various times up to 640 min. Note that the second temperature is lower than the first in the dual step. The cure temperature and time for the dual step were determined from the results obtained in the single step as explained below.

During the curing at 160°C in the single step, T_m and T_i appeared for 5–25 min, and T_g emerged after 60 min instead of T_m and T_i as shown in Table 2. The values of T_m and T_i decreased from 124 to 85°C and from 136 to 98°C between 5 and 25 min, respectively, whereas the T_g increased from 89 to 112°C between 60 and 180 min. At 160°C of cure, ΔT was 12°C after 5 min and then greatly and rapidly expanded to 41°C after 10 min. The expanded LC region maintained up to 20 min and finally decreased to 13°C after 25 min. However, expanded LC region appeared from the beginning of cure and maintained up to 10 and 5 min at 170 and 180°C, respectively. Thus, DSC analysis and microscopic observation for single step cure were mainly made at 160°C because LC phase lasted for longer period of cure time in the wide temperature range in this study. The microscopic observation for specimens uncured and cured by a single step at 160°C was made using a polarized microscope to confirm the results from DSC obtained during cure process. Although no mesomorphic evidence existed in the uncured mixture, the marble texture corresponding to nematic organization was observed after 5–25 min of cure (see Fig. 6).

Table 1
Thermal transitions of epoxy monomers

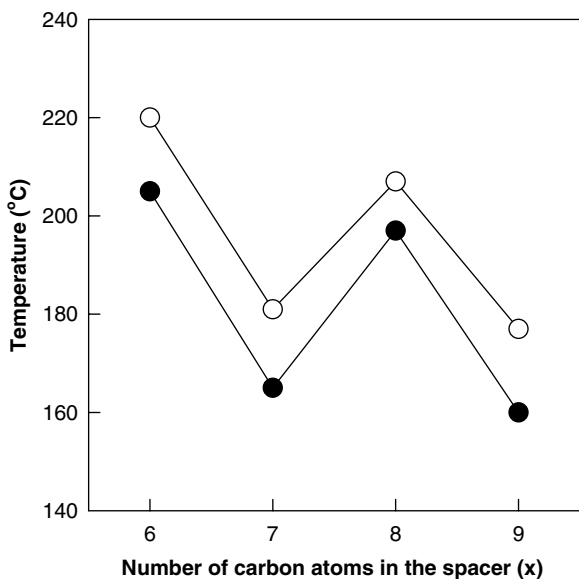| x	T_m (°C)	ΔH_m (kJ mol⁻¹)	ΔS_m (J mol⁻¹ Kmol⁻¹)	T_i (°C)	ΔH_i (kJ mol⁻¹)	ΔS_i (J mol⁻¹ Kmol⁻¹)	ΔT ($= T_i - T_m$)
6	205	60.1	126	220	6.2	13	15
7	165	40.6	92.7	181	1.6	3.5	16
8	197	55.1	117	207	3.2	6.7	10
9	160	43.7	101	177	2.4	5.3	17

Fig. 4. The dependence of transition temperatures of epoxy monomers on the length of the central alkylene spacer (x): ● = T_m; ○ = T_i.

However, the marble texture disappeared and no longer flow birefringence was observed after 60 min.

The results obtained above indicate that LC phase can not be retained when curing is continued in the isotropic state for longer period than 60 min at 160°C. In addition, the nematic LC region between T_m and T_i shifts to lower temperature as the reaction proceeds. Therefore, in order to obtain LC thermoset, it is necessary to catch up with the LC region. In this study, specimen was cured at 160°C for 20 min within the wide LC phase region, and the cure temperature was then lowered to 115°C to maintain the LC phase. The second cure temperature (i.e. 115°C) was
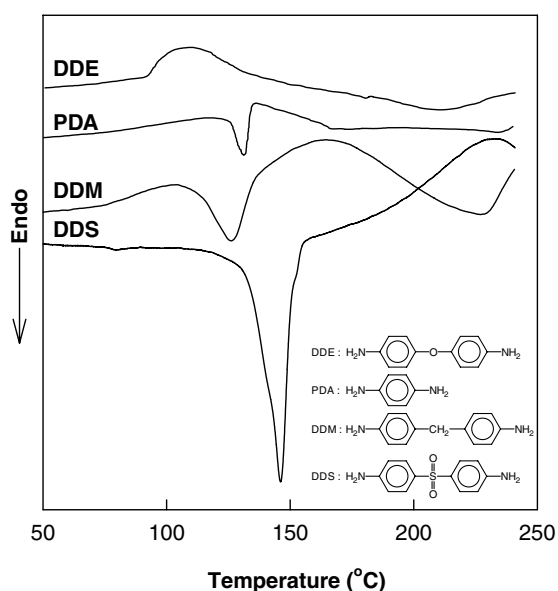
Table 2
Dependence of transition temperatures of an epoxy ($x = 9$)/DDS mixture on curing conditions

Curing condition	T_g (°C)	T_m (°C)	T_i (°C)	ΔT ($= T_i - T_m$)
Temperature (°C)/Time (min)				
Before curing	–	146	–	–
160/5	–	124	136	12
160/10	–	85	126	41
160/15	–	87	124	37
160/20	–	87	124	37
160/25	–	85	98	13
160/60	89	–	–	–
160/120	109	–	–	–
160/180	112	–	–	–
170/5	–	83	125	42
170/10	–	89	124	35
170/15	–	85	97	12
170/20	62	–	–	–
180/5	–	84	124	40
180/10	62	–	–	–
180/20	77	–	–	–
180/40	81	–	–	–
180/60	118	–	–	–
180/80	119	–	–	–
180/100	121	–	–	–
160/20 → 115/10	–	84	126	42
160/20 → 115/20	–	82	127	45
160/20 → 115/40	61	–	129	–
160/20 → 115/80	63	–	133	–
160/20 → 115/160	69	–	140	–
160/20 → 115/320	88	–	149	–
160/20 → 115/640	106	–	154	–

selected to be in the LC phase region between $T_m = 87$°C and $T_i = 124$°C of specimen pre-cured at 160°C for 20 min. As shown in Table 2, during cure at the second temperature of dual step, T_m was observed in the beginning at 84°C for 10 min and 82°C for 20 min, whereas T_g appeared at 61°C from 40 min and increased to 106°C after 640 min. The marble nematic texture was observed for all specimens cured for different times at the second temperature (picture
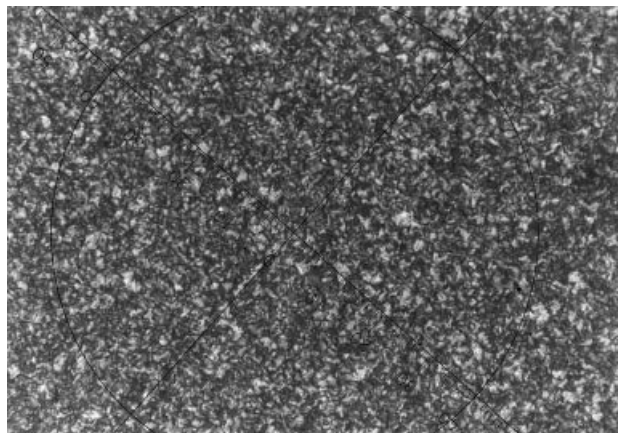

Fig. 5. DSC thermograms of an epoxy monomer ($x = 9$) mixed with different diamines.

Fig. 6. Optical texture of an epoxy ($x = 9$)/DDS mixture cured at 160°C/ 20 min, taken at 120°C (magnification = 250×).
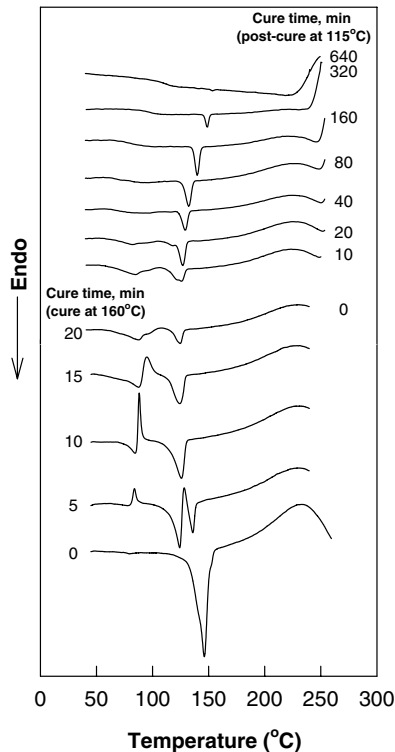
Fig. 7. DSC thermograms for an epoxy ($x = 9$)/DDS mixture uncured and cured at each condition shown on the curves.

of the texture is not shown in this paper since it looks same as in Fig. 6). This implies that LC phase formed in the single step can be persisted by post-curing at a lower temperature in the LC phase region.

DSC thermograms showing transitions for specimens uncured and cured by single step (160°C up to 20 min) and dual step (160°C/20 min → 115°C/various times) are
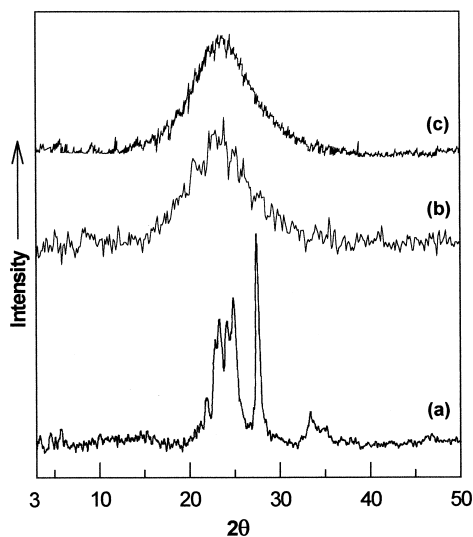

Fig. 8. Wide-angle X-ray diffractograms for an epoxy ($x = 9$)/DDS mixture: (a) uncured; (b) post-cured at 115°C/40 min after curing at 160°C/20 min; and (c) cured at 180°C/40 min.

given in Fig. 7. DSC scan of uncured mixture displayed a sharp melting transition at a temperature of 146°C with no indication of the LC phase. As cure proceeds, the non-LC mixture begins to show the melting and isotropization peak on the thermograms, indicating the formation of LC phase. During the second stage at 115°C in the dual step, peak area for melting decreased rapidly in the beginning and finally disappeared for 40 min, whereas peak areas for isotropization and residual exothermic cure reaction were retained for 160 min and then decreased largely after 320 min. After 640 min, isotropization endotherm and cure exotherm were hardly seen on the theromgram. According to polarized microscopic observations, the specimen after 640 min remained highly birefringent and showed no change in optical texture until decomposition. This means that the molecular organization of the LC phase was almost fastened in network by crosslinking.

Fig. 8 shows diffractograms obtained by a wide angle X-ray diffractometer for specimens: (a) uncured; (b) cured in dual step (160°C/20 min → 115°C/40 min); and (c) cured in single step (180°C/40 min). Uncured specimen exhibited sharp diffracted peaks, meaning that the mixture of the epoxy monomer and curing agent is crystallized. Specimen cured in the dual step has no specific peaks due to the nematic LC phase on a diffused halo from amorphous region in epoxy network as observed in other works [4,22]. The curing at 180°C produced only amorphous phase. These X-ray results coincide with DSC and microscopy data already described.

Based on the results from DSC and microscopic observation, a time–temperature phase diagram for the epoxy monomer ($x = 9$)/DDS system was constructed and shown in Fig. 9. Same type of phase diagram was previously presented by other workers [4,8] to explain the thermal cure behavior of LC epoxies with amines. Fig. 9(a) represents phase changes during the initial stage of isothermal cure at 160°C for 20 min. This figure shows that T_m and T_i shift to lower temperature and the temperature range forming LC nematic phase is rapidly expanding up to 10 min and remained almost constant thereafter. This means that LC phase, which is not observed for uncured mixture, starts to form as cure begins and fully develops within 10 min of cure. Shiota and Ober [8] have observed a similar trend for an LC epoxy monomer/sulphanilamide (SAA) system. The authors have suggested that, in the initial stage of the reaction, linear chain oligomers are created by the reaction of the epoxy monomer and SAA, which play an important role in constructing macroscopic LC order. In Fig. 9(b), phase changes are shown during isothermal cure at 115°C for the specimen pre-cured at 160°C for 20 min. Melting transition disappeared after 20 min of cure, and glass transition appeared from 40 min as already explained in Table 2. Both values of T_g and T_i are continuously raised with cure time, while temperature range in rubbery nematic phase maintained almost constant during the curing. The increase of the T_g and T_i may be due to the restriction of molecular
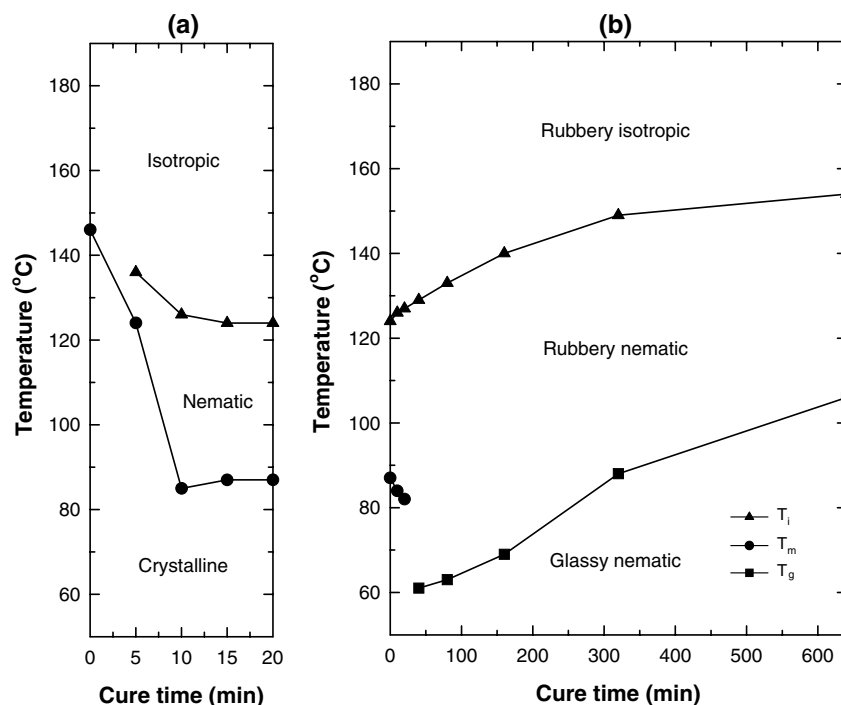
Fig. 9. Time–temperature phase diagram for an epoxy ($x = 9$)/DDS mixture system: (a) cured at 160°C for different times; (b) post-cured at 115°C for different times after curing at 160°C/20 min.

movement by the increase of molecular weight and formation of network.

4. Conclusion

Twin epoxy monomers based on the azomethine mesogen having different alkylene spacers ($x = 6, 7, 8,$ and 9) were synthesized, and cure behavior of the epoxy monomers with amine curing agents was investigated in this study. From the FT/IR and NMR spectroscopic analysis, molecular structures of the epoxy monomer were identified. A polarized microscope was used to observe mesomorphic optical texture. From the thermal behavior of epoxy monomers and mixtures of epoxy/amine investigated by DSC, an epoxy monomer ($x = 9$) and DDS curing agent system are eventually selected as the most suitable to examine cure behavior.

For the epoxy monomers, the values of melting (T_m) and isotropization (T_i) temperatures as well as their changes of enthalpy and entropy revealed even–odd dependence on x. All the epoxy monomers formed a nematogenic liquid crystal. From the DSC study of the epoxy monomer ($x = 9$)/ DDS system, T_m and T_i decreased and the temperature range forming nematic phase expands greatly in the very beginning of cure. The great change in the DSC scan is attributed to formation of network with the low crosslinking density that may be considered to behave as highly viscous liquid in the mesophase. Since the region showing nematic LC phase shifts to lower temperature, uncured specimen

was reacted by dual step at two successive temperatures (high → low). During the curing at the second low temperature, the values of T_g and T_i increased with cure time. Region between T_g and T_i corresponds to a rubbery nematic phase. The increase of the T_g and T_i is due to growth of molecular weight and higher crosslinking density. Ultimately, the highly crosslinked LC elastomer with the highest T_g of 106°C could be obtained by the curing of 160°C/ 20 min → 115°C/640 min. In this study, LC thermoset could be prepared successfully through the dual cure step. A time–temperature phase diagram is constructed based on the DSC results, which can provide the proper cure conditions for processing of LC thermosets.

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