

# Synthesis and Curing of Liquid Crystalline Epoxy Resin Based on Asymmetric Mesogen

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**ABSTRACT:** A novel liquid crystalline epoxy resin (LCER) derived from asymmetric mesogen unit was synthesized. Its structure and liquid crystalline behavior were characterized by hydrogen nuclear magnetic resonance (H-NMR), differential scanning calorimetry (DSC), polarized optical microscopy (POM). The results indicated that the LCER converted to a nematic phase at 85°C during heating and finally became isotropic at 145°C. The curing behavior and phase behavior of the LCER with 4,4'-diaminodiphenyl methane and methyl hexahydrophthalic anhy-

dride were also studied by DSC and POM, respectively. Their apparent activation energy ( $E_a$ ) was evaluated according to the Ozawa's isoconversional method. The results suggested that autocatalytic reaction had occurred in these two systems. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** synthesis; liquid-crystalline polymers (LCP); asymmetric mesogen; curing of polymers; activation energy

## INTRODUCTION

Epoxy resins are widely used in the polymer industry as adhesives, surface coatings, high-voltage electrical insulation materials, electronic components, packaging materials, etc. Recently, liquid crystalline epoxy resin (LCER), which consists of a rigid backbone structure, has become attractive for their unique properties. At present, many investigators have reported the synthesis, characterization of texture, phase behavior, and the curing kinetics of LCER containing naphthyl,<sup>1–3</sup> stilbene,<sup>4,5</sup> aromatic ester,<sup>6</sup> azomethine,<sup>7–9</sup> biphenyl,<sup>10–13</sup> and other rigid-rod mesogenic unit.<sup>14,15</sup> Some unique and unusual properties were revealed in these studies, such as high thermal and orientational stability, low shrinkage upon curing, fracture resistance, low coefficients of thermal expansion, anisotropic optical properties, and high moduli.

Among these LCERs, most of them have high-melting point and high-phase transition temperature. When some curing agent having low-boiling point was used, low-melting point LCERs are generally required. As is known to all, the thermal properties of LCERs are dependent on the structure of the aromatic mesogenic group and the length of the flexible spacer. So the introducing of short mesogenic unit<sup>16</sup> and long flexible spacer<sup>17–19</sup> are effective methods

for decreasing the melting point. Existing of asymmetric mesogenic unit can lower the symmetry of molecule, which leads to the decrease of melting point. However, the LCER based on asymmetric mesogenic unit has been scarcely reported up to now.

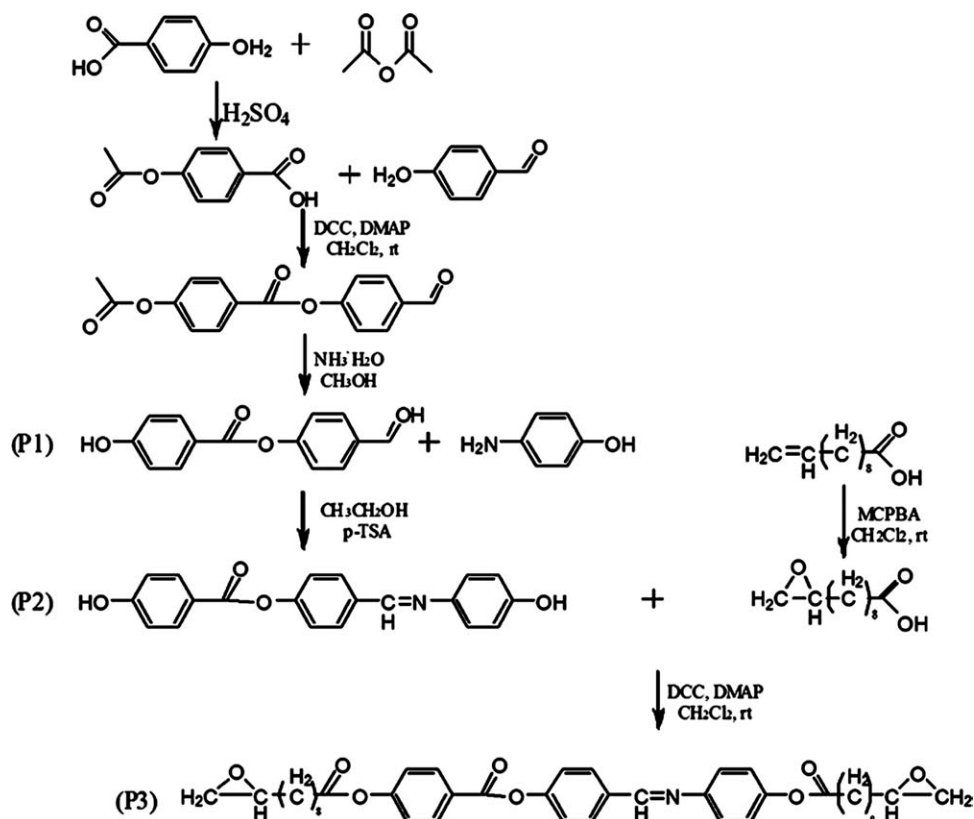
In this work, a novel LCER with low-transition temperature derived from asymmetric mesogen unit, 4-((4-(10,11-epoxy)undecanoatephenylimino)methyl)phenyl-4-(10,11-epoxy)undecanoate benzoate, was synthesized and characterized by hydrogen nuclear magnetic resonance (H-NMR), differential scanning calorimetry (DSC), and polarized optical microscopy (POM). To study intensively, DSC and POM were used to examine the curing behavior and phase behavior of the novel LCER with DDM and MHPA. Then kinetic analysis of them was performed by Ozawa's isoconversional method.

## EXPERIMENTAL

### Materials

4-Hydroxybenzoic acid, acetic anhydride, 4-hydroxybenzaldehyde, 4-aminophenol, ammonia liquor, 10-undecylenic acid, 4-toluenesulfoic acid (p-TSA), *N,N'*-dicyclohexyl carbodiimide (DCC), 4-dimethylaminopyridine (DMAP), diaminodiphenyl methane (DDM), and methyl hexahydrophthalic anhydride (MHPA) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) in an analytical grade without further purification. 3-Chloroperoxybenzoic acid (m-CPBA) was purchased from Accela

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Scheme 1 The synthetic pathway of novel LCER.

ChemBio (ShangHai, China). All solvents were used as received.

### Instrument

Hydrogen nuclear magnetic resonance spectroscopy spectra was obtained on a 300 MHz Bruker NMR instrument using chloroform-D as solvent and tetramethyl silane as the internal standard. The textures of the mesophase were observed with Olympus BX51 equipped with a Linkam THMS 600 hotstage combined with a CI94 controller. Thermal properties of the polymer were examined in nitrogen using a NETZSCH STA 449C thermal analyzer at a heating rate of 10°C/min.

### Synthesis

The synthesis pathway for LCER is shown in Scheme 1. The 4-formylphenyl-4-acetoxybenzoate (FPAB) was synthesized according to the literature.<sup>20</sup> To protect the hydroxyl group of 4-hydroxybenzoic acid, acetic anhydride was used as an acetylating agent and ammonia liquor was used as a deacetylating agent.

P1: 4-Formylphenyl-4-hydroxybenzoate (FPHB)

To 30.0 g FPAB (0.106 mol) in 100 mL methanol, 24 mL AL was added dropwise over a period of 1 h

at ice bath. Then the temperature was raised to room temperature and the reaction was allowed to proceed at this temperature for additional 4 h. The reaction mixture was poured into ice water overnight. After filtration, the solid was dried under reduced pressure and a yellow solid product was obtained. Yield: 74% (18.9 g). <sup>1</sup>H-NMR: 10.08 (1H, s), 9.45 (1H, s), 8.10 (4H, m), 7.56 (2H, d), 7.05 (2H, d).

P2: 4-((4-Hydroxyphenylimino)methyl)phenyl-4-hydroxybenzoate

To a solution of 15.5 g FPHB (0.064 mol) and 6.93 g 4-aminophenol (0.064 mol) in 100 mL ethanol, a catalytic amount of 4-toluenesulfoic acid in 30 mL ethanol was added dropwise to the flask, and the mixture was stirred and refluxed for 6 h. The resulting mixture was filtered and washed thoroughly with diethylether to generate a yellow solid. Yield: 67% (14.32 g). <sup>1</sup>H-NMR: 9.43 (1H, s), 8.65 (1H, s), 8.47 (1H, s), 8.05 (4H, m), 7.40 (2H, d), 7.25 (2H, d), 7.03 (2H, d), 6.90 (2H, d).

P3: 4-((4-(10,11-Epoxy)undecanoatephenylimino)methyl)phenyl-4-(10,11-epoxy)undecanoate benzoate

10,11-Epoxyundecenoic acid: To a solution of 20 g (0.109 mol) of 10-undecylenic acid in 80 mL of dichloromethane, 25 g (0.145 mol, 75%) of MCPBA was added under continuous stirring. The mixture

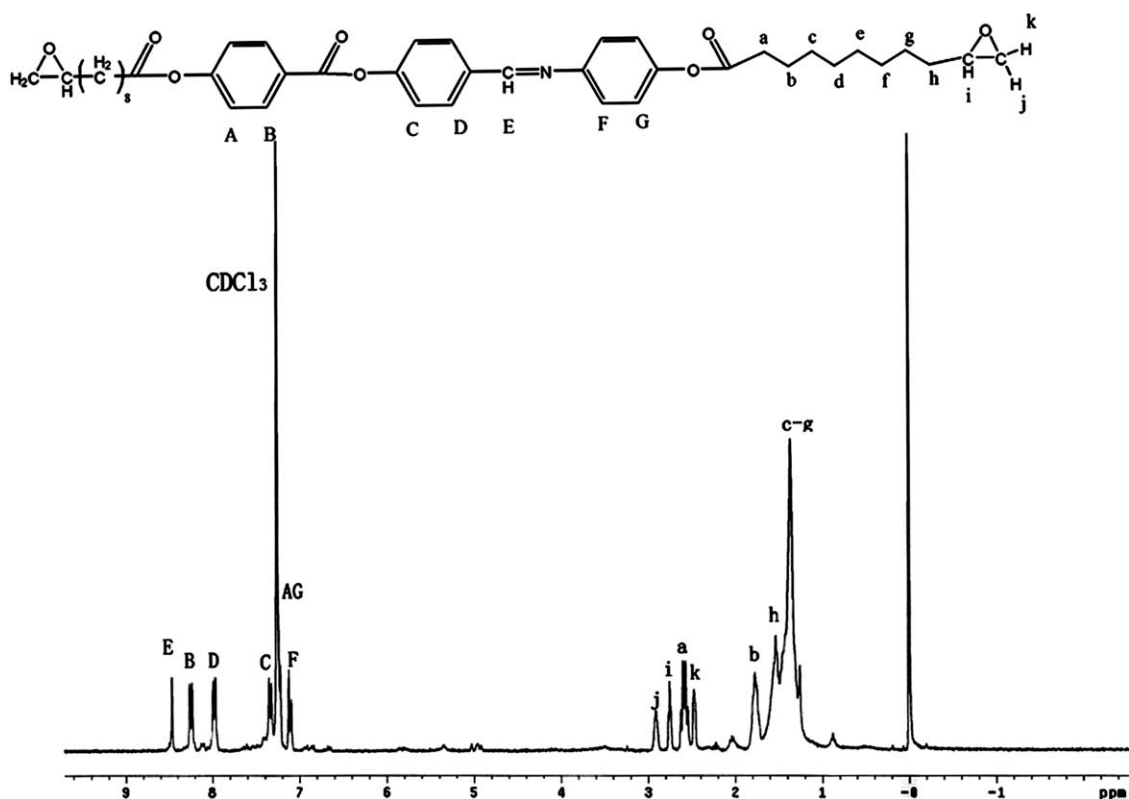


Figure 1  $^1\text{H-NMR}$  spectrum of LCER obtained in  $\text{CDCl}_3$ .

was refluxed for 48 h. After filtration, the mixture was washed with 60 mL of aqueous 5%  $\text{Na}_2\text{S}_2\text{O}_3$ , 60 mL of aqueous 5%  $\text{NaHCO}_3$ , and 45 mL of a saturated  $\text{NaCl}$  solution. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated. A light yellow liquid was obtained. Yield: 90% (19.6 g).

To 10.05 g (0.03 mol) of 4-((4-hydroxyphenylimino)methyl)phenyl-4-hydroxybenzoate and 13.35 g (0.062 mol) of 10,11-epoxyundecenoic acid in 180 mL of dichloromethane, 13.7 g (0.066 mol) of DCC and a catalytic amount of DMAP were added. The reaction mixture was stirred for 24 h, and then *N,N*-dicyclohexylurea was filtered off; after the removal of the solvent, the crude product was washed with methanol. A yellow liquid was obtained. Yield: 54% (11.40 g).  $^1\text{H-NMR}$ : 8.47 (1H, s), 8.25 (2H, d), 7.98 (2H, d), 7.34 (2H, d), 7.22 (4H, m), 7.15 (2H, d), 2.92 (2H, s), 2.76 (2H, m), 2.58 (4H, m), 2.48 (2H, s), 1.77 (4H, m), 1.53 (4H, d), 1.36 (20H, s).

### Curing of LCER

Stoichiometric amounts of LCER and DDM (or MHPA) were dissolved in chloroform, and the solvent was removed under reduced pressure at room temperature. The curing reaction of the samples was examined with DSC. Each sample was heated from

25 to 300°C at different heating rates of 3, 5, 8, 10, and 15°C/min under a nitrogen flow of 20 mL/min.

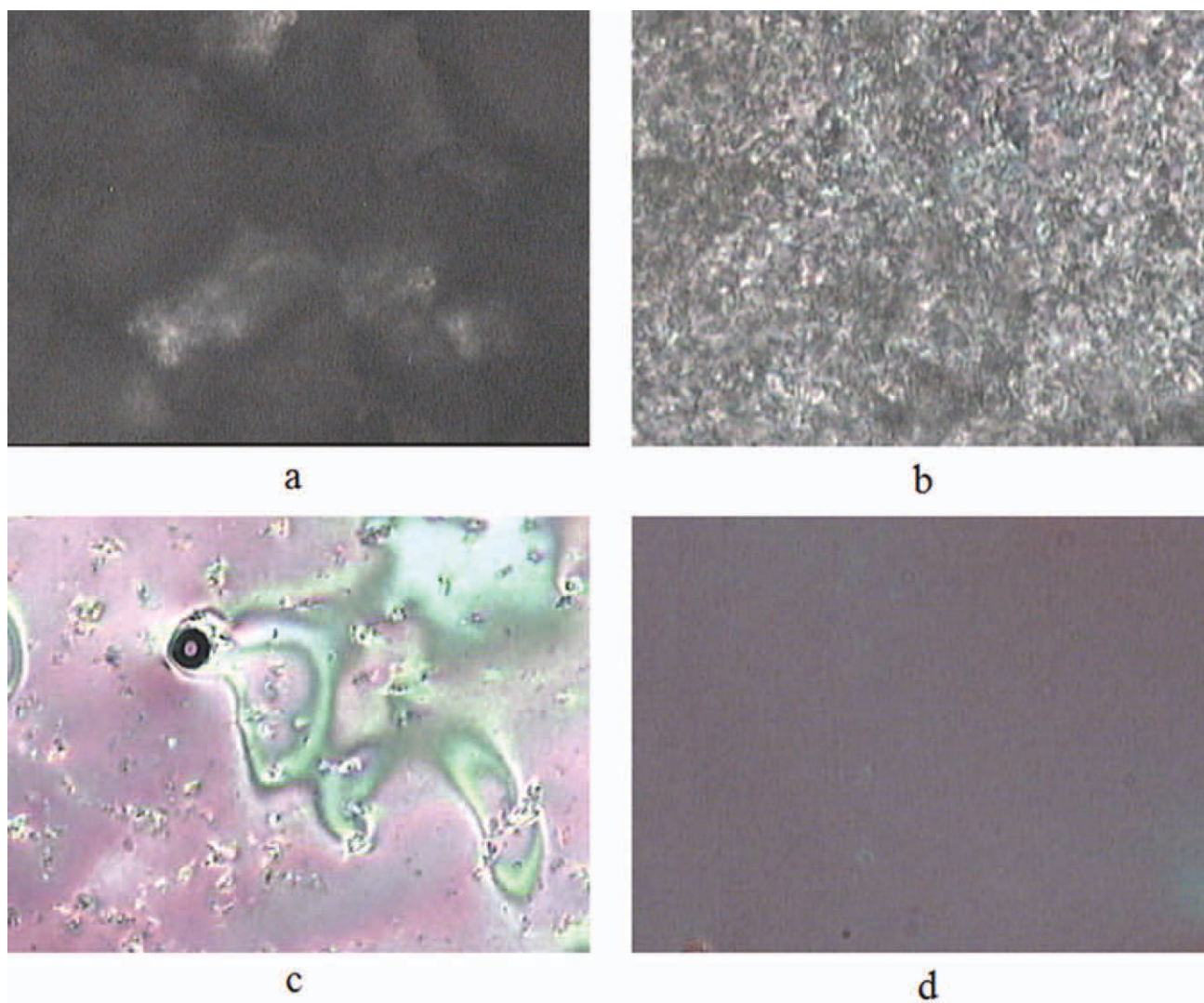
## RESULTS AND DISCUSSION

### Synthesis and characterization

The structure of LCER was obtained by NMR instrument using chloroform- $D$  as the solvent and tetramethyl silane as the internal standard, which is shown in Figure 1, in which all of the H protons in the molecule of LCER are corresponding to NMR peaks, 14 species of protons can be found according to the different chemical shifts. The protons of the azomethine and benzene ring (A-G) are in the low field (8.47, 8.25, 7.98, 7.34, 7.22, and 7.15, respectively). Those of aliphatic groups (a-k) are in the high field (2.92, 2.76, 2.58, 2.48, 1.77, 1.53, and 1.36, respectively).

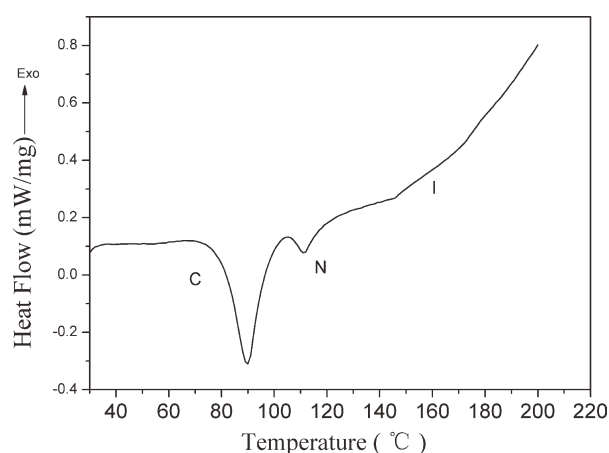
Liquid crystalline phase behavior of LCER was observed by an optical microscope. As LCER was heated up to 85°C, a nematic texture was observed. Having been consecutively heated to 145°C, the Birefringence disappeared. The polarized optical micrograph of the representative sample is displayed in Figure 2. Two obvious endothermic peaks at 90 and 113°C could be found in the graph from DSC measurement (Fig. 3). The former is due to the first transition endotherm from solid to nematic liquid



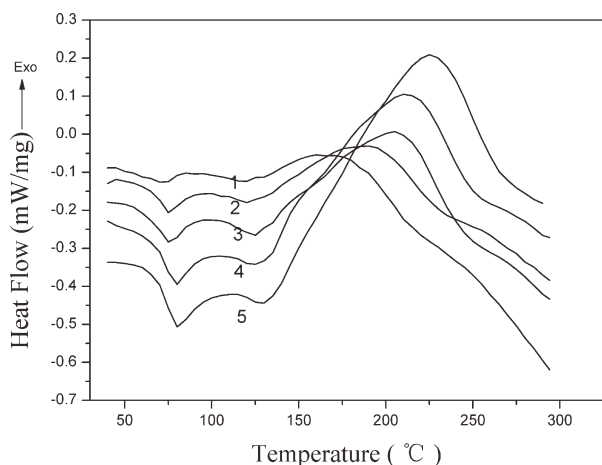


**Figure 2** Polarized optical micrographs of LCER ( $\times 200$ ). (a)  $85^{\circ}\text{C}$ ; (b)  $105^{\circ}\text{C}$ ; (c)  $140^{\circ}\text{C}$ ; (d)  $150^{\circ}\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

crystalline state. However, the crystal phase transition corresponding to the latter peak could not be found from the POM figure. And from the curve of curing (Figs. 4 and 5), only two endothermic peaks could be found at about  $85$  and  $135^{\circ}\text{C}$ , so we thought that the latter peak at  $113^{\circ}\text{C}$  was due to exist of impurity. When the LCER was heated individually, the impurity melted at  $113^{\circ}\text{C}$ . But when the mixture contained LCER and curing agent was heated, the impurity was dissolved in the melted curing agents (one is liquid, and the melting point of another is  $87^{\circ}\text{C}$ ). At  $145^{\circ}\text{C}$ , although no endothermic peak was observed, an obvious change of slope of curve was obtained in the figure, according to POM, which is due to the transition from nematic state to isotropic state. All of the transition temperature are lower than most of other LCERs, which have been reported. The result showed that introducing of asymmetric mesogenic unit was an



**Figure 3** The DSC curves of the novel LCER at a heating rate of  $10^{\circ}\text{C}/\text{min}$ .



**Figure 4** The nonisothermal cure curves of LCER/DDM system. 1–3°C/min; 2–5°C/min; 3–8°C/min; 4–10°C/min; 5–15°C/min.

effective way for decreasing the melting point and transition temperature.

### Studing of Curing

In this work, DSC was employed to study the nonisothermal curing behavior of LCER with DDM and MHHPA, and each sample was heated from 25 to 300°C at different heating rates of 3, 5, 8, 10, and 15°C/min under a nitrogen flow of 20 mL/min, respectively. As shown in Figures 4 and 5, there are two endothermic peaks in each DSC curve for all the samples of LCER/DDM and LCER/MHHPA curing systems. And the value of peaks increased with the increase of the heating rate. As shown in Figure 4, the first endothermic peak at about 85°C corresponds to the melting of DDM and the first transition of LCER from solid to nematic liquid crystalline state, and the second endothermic peak at about 130°C corresponds to the transition of LCER from nematic liquid crystalline phase to isotropic state. And in Figure 5, the first endothermic peak at about 81°C corresponds to the first transition of LCER from solid to nematic liquid crystalline state, and the second endothermic peak at about 135°C corresponds to the transition of LCER from nematic liquid crystalline phase to isotropic state. In these two figures, the exothermic peaks are corresponding to curing reaction of LCER and curing agent. Only one exothermic peak is found in the curing process of LCER/DDM system, but two exothermic peaks are found in the curing process of LCER/MHHPA system. This shows that there is more obvious autocatalytic phenomenon in LCER/MHHPA system than LCER/DDM system.

### Curing kinetics

Cure kinetics of the obtained LCER was investigated by means of DSC technique. Through DSC tech-

nique, isoconversion methods are used to study active energy of curing process of obtained LCER and DDM, of which the advantage is that the activation energy can be measured over the entire course of the reaction.

The rate of the kinetic process can be described by eq. (1)<sup>21,22</sup>

$$\frac{d\alpha}{dx} = K(T)f(\alpha) \quad (1)$$

where  $K(T)$  is a temperature-dependent reaction rate constant, and  $f(\alpha)$  is a dependent kinetic model function.

There is an Arrhenius type dependence between  $K(T)$  and temperature according to eq. (2).

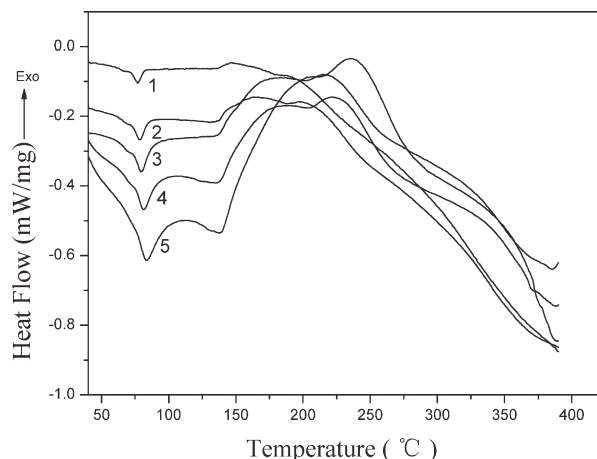
$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where  $A$  is the pre-exponential factor, and  $E_a$  is the apparent activation energy.

For nonisothermal curing process, the isoconversional method can be expressed in several ways. Equation (3) is known as the Ozawa's method,<sup>23–25</sup> which can be applied to different conversion  $\alpha$  of curing process. Thus, for a given  $\alpha$ , the  $E_a$  can be obtained from linear regression according to eq. (3).

$$\ln \beta = A' - 1.052 \frac{E_a}{RT} \quad (3)$$

where  $A'$  is the pre-exponential factor,  $T$  is the temperature (K),  $R$  is the gas constant (8.314 J mol/K),  $\beta$  is the heating rate, and  $E_a$  is the apparent activation energy.



**Figure 5** The nonisothermal cure curves of LCER/MHHPA system. 1–3°C/min; 2–5°C/min; 3–8°C/min; 4–10°C/min; 5–15°C/min.

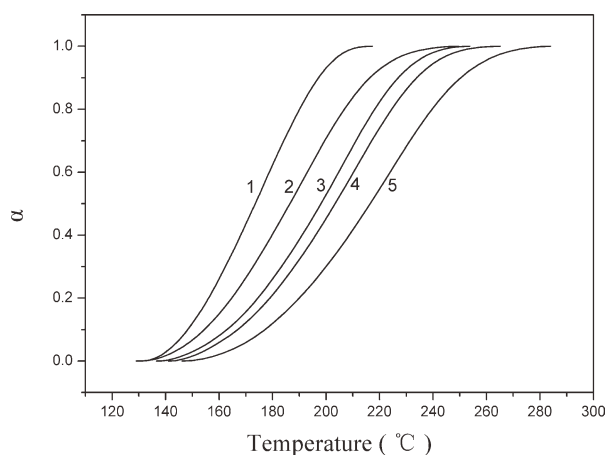
The conversion  $\alpha$  was calculated using:

$$\alpha = \frac{\Delta H_t}{\Delta H_{\max}} \quad (4)$$

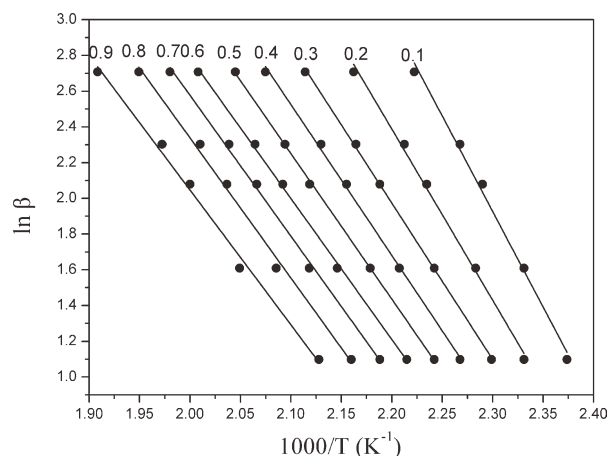
where  $\Delta H_t$  is the partial heat of reaction at time  $t$ , and  $\Delta H_{\max}$  is the maximum reaction heat.  $\Delta H_{\max}$  was obtained from the sum of the isothermal heat of the reaction and the residual heat obtained in a subsequent scan.

According to eq. (4) and Figure 4, the relationship between the extent of conversion and dynamic curing temperature  $T$  for LCER/DDM system is shown in Figure 6. As seen from Figure 6, at the same  $\alpha$  value, the isoconversional temperature  $T$  increased with the heating rate. According to Ozawa eq. (3), for each degree of conversion, the logarithm of the heating rate was plotted against the inverse of the temperature (Fig. 7). The activation energy  $E_a$  at some conversion  $\alpha$  has been calculated, the linear coefficients are all between 0.99243 and 0.99955, and it shows that the curing systems well obey Ozawa's kinetics model. The calculated activation energies for LCER/DDM system in the interval of  $0 \leq \alpha \leq 1$  are plotted in Figure 8. Same method was applied in LCER/MHHPA system, the curve of  $E_a-\alpha$  for LCER/MHHPA system was shown in Figure 9.

For LCER/DDM curing system, during the early stage of the curing reaction, the value of  $E_a$  in the initial stage is higher. With the progress of the reaction, the  $E_a$  decreases from 84.5 kJ/mol to 59.6 kJ/mol, and it tends to decrease slightly. During the initial stage of curing, the primary amine addition was predominant, and the primary amine has a higher  $E_a$  in a noncatalyzed pathway. Etherification occurred only at elevated temperature until all the primary amine was exhausted. Therefore, a high  $E_a$  value at a lower conversion was attributed to the



**Figure 6** The relation of  $\alpha$  and  $T$  under different heating rates. 1–3°C/min; 2–5°C/min; 3–8°C/min; 4–10°C/min; 5–15°C/min.

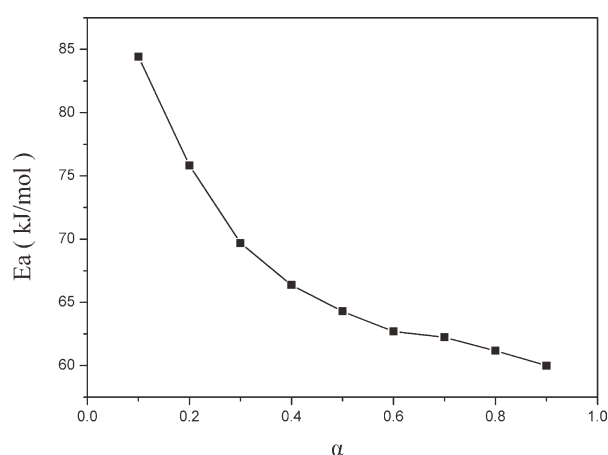


**Figure 7** The relation of  $\ln \beta$  and  $1/T$  under different degree of conversion.

primary amine addition. After the reaction started, the hydroxyl group was created first. Then the transition state of alcohol-catalyzed reaction occurred, having a lower  $E_a$  than nonalcohol-catalyzed reactions. Therefore, the tiny change of  $E_a$  in the middle stage was associated with the autocatalytic reaction. It started at a conversion of  $\sim 0.6$  and lasted until a high conversion. In the final stage, the value of  $E_a$  decreases gradually, which is associated with gelation and vitrification in the curing reaction process.

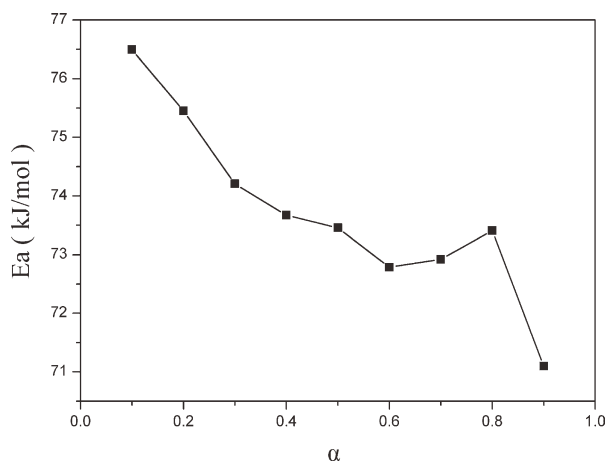
For LCER/MHHPA curing system, the  $E_a$  values decrease from 76 to 72.5 kJ/mol in the started stages of  $\alpha$  from 0 to 0.6, the  $E_a$  increases a little from 72.5 to 73.4 kJ/mol in the stages of  $\alpha$  from 0.6 to 0.8. This can be associated with the formation of LC phase (Fig. 11). After that, the  $E_a$  again decreases a little from 73.4 to 71.0 kJ/mol.

Comparing the two systems, from 0.6 to 0.8 for  $\alpha$ , the  $E_a$  increases a little from 72.5 to 73.4 kJ/mol for LCER/MHHPA curing system. But same phenomenon was not found in LCER/DDM curing



**Figure 8** The activation energy change ( $E_a$ ) calculated by the Ozawa method at various  $\alpha$  for LCER/DDM curing systems.



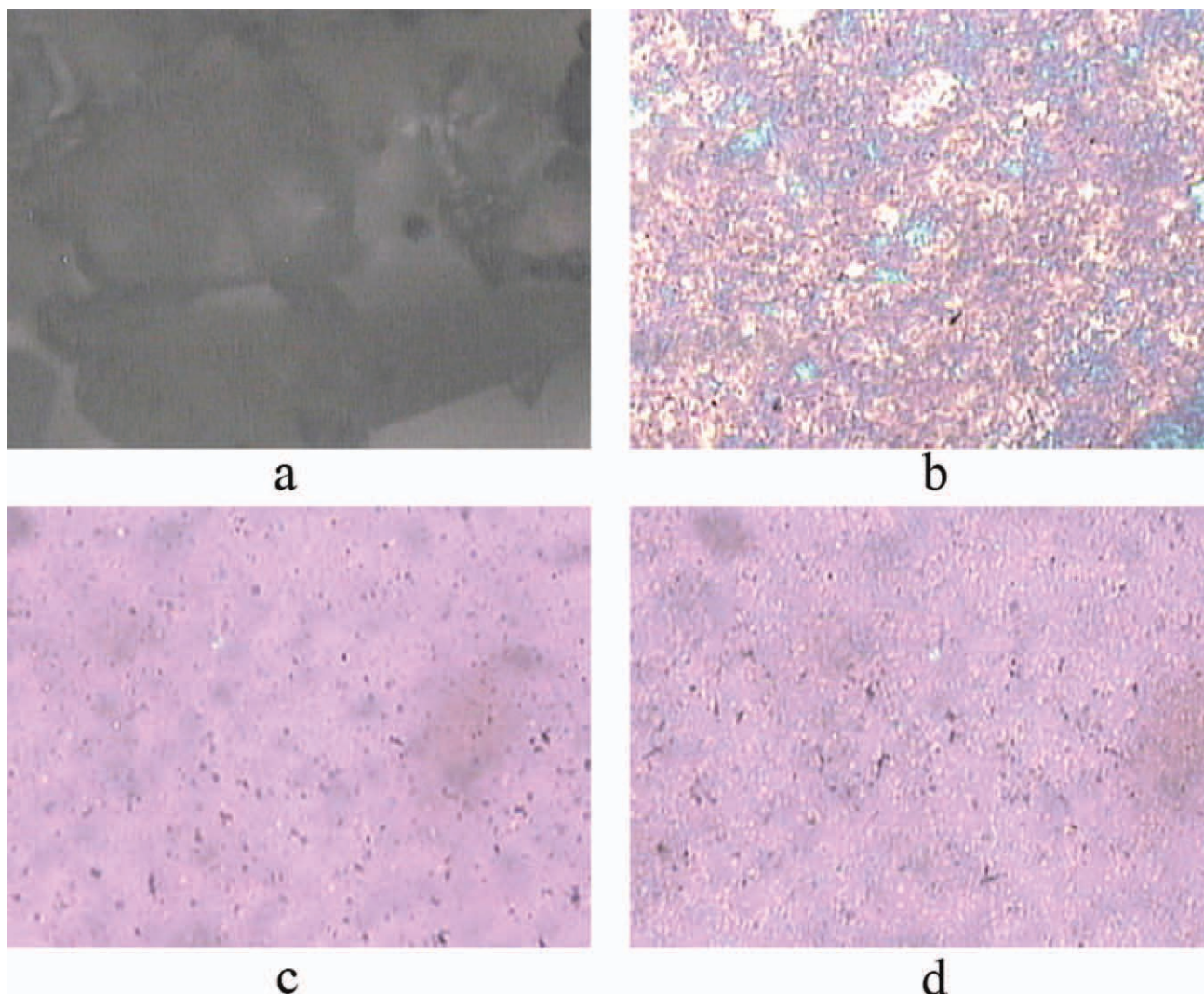


**Figure 9** The activation energy change ( $E_a$ ) calculated by the Ozawa method at various  $\alpha$  for LCER/MHHPA curing systems.

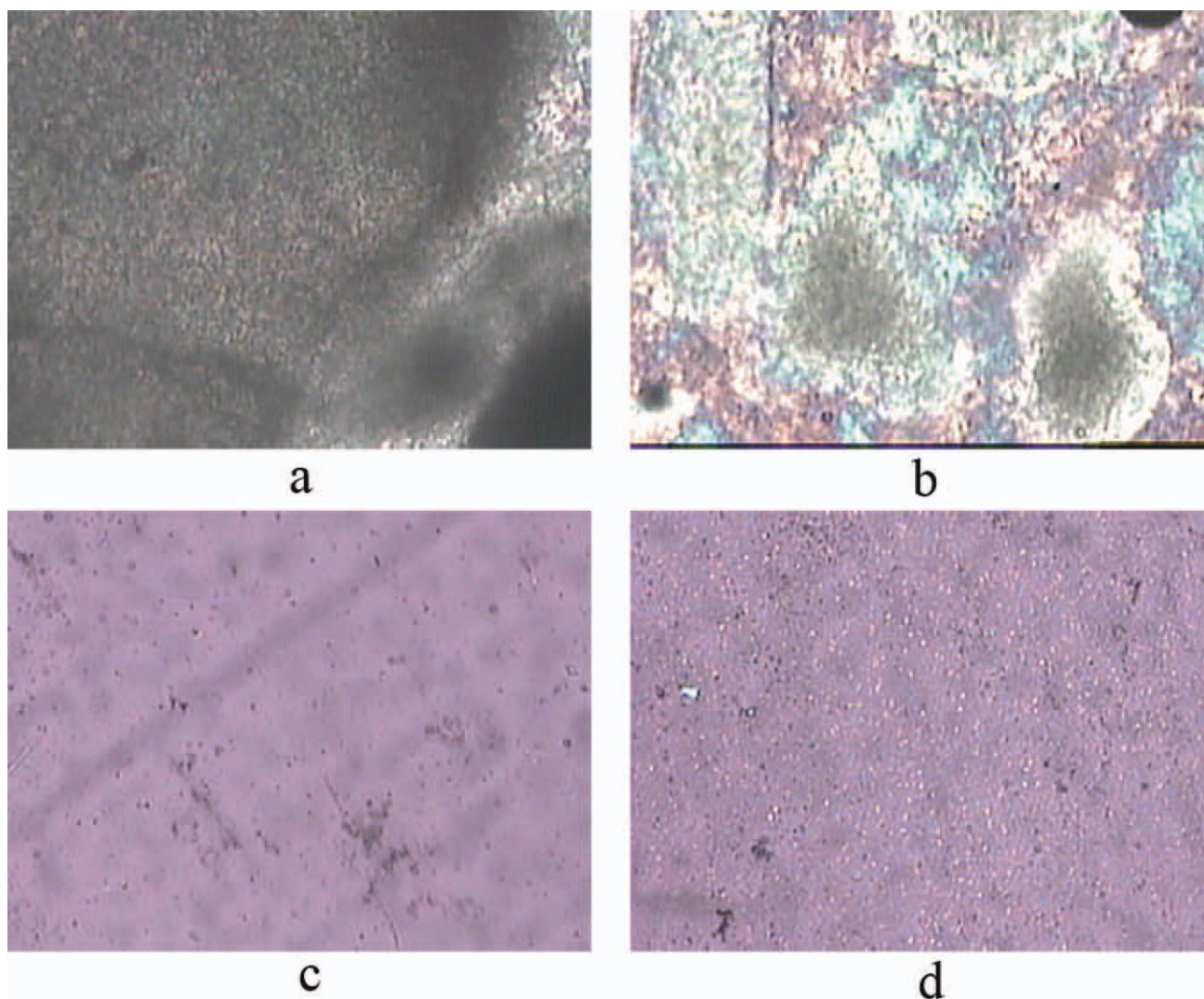
system. This can be associated with the amount of LC phase in the cured products, which significantly affects the kinetic parameters of the curing reaction. The POM of two curing systems at different temperature was displayed in Figures 10 and 11. As shown in these two figures, the LC phase in LCER/MHHPA curing system was clearer than that of in LCER/DDM curing system, which was due to the structure of curing agent. MHHPA has only one benzene ring, but DDM contains a methylene between two benzene rings.

### CONCLUSION

By introducing asymmetric mesogen, a low-melting point and transition temperature LCER was synthesized. It revealed an effective way to product a low temperature LCER for some special curing



**Figure 10** Polarized optical micrographs of LCER/DDM curing system at a heating rate of  $10^\circ\text{C}/\text{min}$  ( $\times 200$ ). (a)  $75^\circ\text{C}$ ; (b)  $110^\circ\text{C}$ ; (c)  $160^\circ\text{C}$ ; (d)  $205^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11** Polarized optical micrographs of LCER/MHHPA curing system at a heating rate of 10°C/min ( $\times 200$ ). (a) 80°C; (b) 100°C; (c) 170°C; (d) 210°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

conditions. The curing behavior and phase behavior of the LCER with DDM and MHHPA were also studied by DSC and POM, respectively. The results showed that the formation of liquid crystal phase was more important for autocatalytic reaction. Furthermore, kinetic analysis of LCER/DDM and LCER/MHHPA curing system was performed and activation energies were calculated by the Ozawa's isoconversional method. The results showed that autocatalytic reaction had occurred in these two systems.

## References

- Carfagna, C.; Amendola, E.; Giamberini, M. *Macromol Chem Phys* 1994, 195, 2307.
- Castell, P.; Serraand, A.; Galia, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 1536.
- Mititelu-Mija, A.; Cascaval, C. N.; Navard, P. *Design Monom Polym* 2005, 8, 487.
- Cho, S.; Douglas, E. P.; Lee, J. Y. *Polym Eng Sci* 2006, 46, 623.
- Robinson, E. J.; Douglas, E. P.; Mecholsky, J. J. *Polym Eng Sci* 2002, 42, 269.
- Lee, J. Y. *J Appl Polym Sci* 2006, 102, 1712.
- Mija, A.; Navard, P.; Peiti, C.; Babor, D.; Guigo, N. *Eur Polym J* 2010, 46, 1380.
- Mititelu-Mija, A.; Cascaval, C. N. *High Perform Polym* 2007, 19, 135.
- Choi, E. J.; Ahn, H. K.; Lee, J. K.; Jin, J. I. *Polymer* 2000, 41, 7617.
- Yu, Y. F.; Gan, W. J.; Liu, X. Y.; Li, S. J. *J Appl Polym Sci* 2008, 109, 2964.
- Gao, Z. Y.; Yu, Y. F.; Xu, Y. Z.; Li, S. J. *J Appl Polym Sci* 2007, 105, 1861.
- Shen, M. M.; Lu, M. G.; Chen, Y. L.; Ha, C. Y. *J Appl Polym Sci* 2005, 96, 1329.
- Lee, J. Y.; Shim, M. J.; Kim, S. W. *J Appl Polym Sci* 2002, 83, 2419.



14. Balamurugan, R.; Kannan, P. *J Mater Sci* 2010, 45, 1321.
15. Murali, M.; Rao, V. S.; Samui, A. B. *J Polym Sci Part A: Polym Chem* 2007, 45, 3116.
16. Huo, L.; Gao, J. G.; Du, Y. G.; Chai, Z. H. *J Appl Polym Sci* 2008, 110, 3671.
17. Galina, H.; Mossety-Leszczak, B. *J Appl Polym Sci* 2007, 105, 224.
18. Mossety-Leszczak, B.; Wlodarska, M.; Galina, H.; Bak, G. W. *Mol Cryst Liquid Cryst* 2008, 490, 52.
19. Bialecka-Florjanczyk, E.; Sledzinska, I.; Stolarzewicz, I.; Makal, A.; Gorecka, E. *Liquid Cryst* 2009, 36, 67.
20. Su, C. X.; Mouscadet, J. F.; Chiang, C. C.; Tsai, H. J.; Hsu, L. Y. *Chem Pharm Bull* 2006, 54, 682.
21. Málek, J. *Thermochim Acta* 2000, 355, 239.
22. Montserrat, S. Málek, J. *Thermochim Acta* 1993, 228, 47.
23. Ozawa, T. *J Therm Anal* 1970, 2, 301.
24. Atarsia, A.; Boukhili, R. *Polym Eng Sci* 2000, 40, 607.
25. Rosu, D.; Mititelu, A.; Cascaval, C. N. *Polym Test* 2004, 23, 209.