# Synthesis and Characterization of the Two Novel Liquid Crystalline Epoxy Resins Based on Bisphenol-S Mesogen

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**ABSTRACT:** Two novel liquid crystalline epoxy resins (LCER) based on bisphenol-S mesogen, 4,4'-Bis-(2,3-epoxy-propyloxy)-sulfonyl bis(1,4-phenylene) (*p*-BEPSBP) and sulfonyl bis(4,1-phenylene) bis[4-(2,3-epoxypropyloxy)benzoate] (*p*-SBPEPB), were synthesized. Their liquid crystalline behavior and structure were characterized by Fourier transmittance infrared ray (FTIR), differential scanning calorimetry (DSC), ^{1}HNMR, polarized optical microscopy (POM) and X-ray diffraction (XRD). The results show that *p*-BEPSBP is a kind of thermotropic liquid crystal and has a smectic mesophase with a melting point ($T_m$) at 165°C; the *p*-SBPEPB is a kind of nematic mesophase with the temperature range of 155–302°C from the $T_m$ to the clear-ing point $T_i$. The curing behaviors and texture of the liquid crystalline epoxy resins with 4,4'-diaminodiphenyl ether (DDE) were also studied by DSC and some kinetic parameters were evaluated according to the Ozawa's method. The dynamic mechanical properties of curing products were also investigated by torsional braid analysis (TBA), and the results suggest that the dynamic mechanical loss peak temperature ($T_p$) of *p*-BEPSBP/DDE and *p*-SBPEPB/DDE is 120 and 130°C, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3671–3677, 2008

**Key words:** liquid crystalline epoxy resins; bisphenol-S; 4,4-diaminodiphenyl ether; curing reaction; thermal analysis

## INTRODUCTION

Liquid crystalline (LC) thermosets have been extensively investigated in many research groups due to their excellent properties, such as high-strength, high modulus, a relatively low coefficient of thermal expansion and dimensional stability.[1–4] Liquid crystalline epoxy resin (LCER) is an important thermo-setting polymers, and have widely applied in numbers of scopes, such as electronics, advanced composites, nonlinear optics.[5–8] At present, many investigators have reported the synthesis, characterization of texture, phase behavior, and the curing kinetics of LCER containing hydroquinone or bisphenol, etc.[5–11] The synthesis and curing behavior of epoxy resins based on bisphenol-S had been investigated.[12,13] However, there are no reports about the LCER based on bisphenol-S mesogen until now. In this article, the two LCERs based on bisphenol-S were synthesized, and their texture and liquid crystalline behavior were characterized. Moreover, their nonisothermal curing behavior with 4,4-diaminodiphenyl ether (DDE) and thermal properties were investigated by DSC and torsional braid analysis (TBA).

## EXPERIMENTAL

### Materials and instrumentation

4,4'-Sulfonyldiphenol (bisphenol-S, BPS, $T_m$ = 240°C), C.P. grade, was recrystallization in toluene; 3-bromopropene (allyl bromide), supplied by Jiangsu fangqiao Chem, China; 4-hydroxy ethyl benzoate, thionyl chloride (SOCl$_2$), N,N'-dimethylformamide (DMF), m-chloroperbenzoic acid (MCPBA), pyridine, dichloromethane, cetyltrimethyl ammonium bromide (CTMAB) and 4,4-diaminodiphenyl ether (DDE) are all A.P. grade and supplied by the Beijing Chemical Reagent, China.

FTIR (Bio-Rad FTS-40 America) was used for infrared analysis. ^{1}H-NMR (Bruker 400 MHz, Switzerland) spectra were obtained with tetramethylsilane (TMS) as internal standard. The phase behavior of the target compounds were measured by polarizing optical microscope (POM, 59XA, Shanghai Yong-Heng, China). Differential scanning calorimeter (DSC, Diamond Perkin-Elmer, USA) was calibrated with high-purity indium. X-ray diffraction patterns were recorded by monitoring the diffraction angle 2θ from 0.6 to 30° using an X-ray diffractometer (XRD, Rigaku-D/max-2500, Germany) equipped
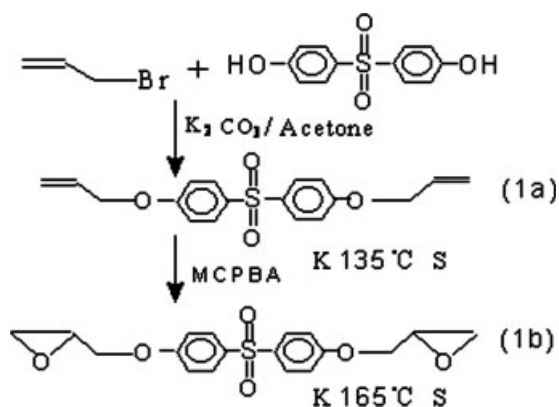
**Scheme 1** Synthetic scheme of *p*-BEPSBP.

with a CuKα (λ = 0.1542 nm) radiation under conditions of 40 kV and 100 mA. Torsional braid analysis (TBA) was determined using dynamic mechanical spectrometer (GDP-4, Jilin Univ., China) at the heating rate of 2°C min$^{-1}$ from 20 to 250°C.

### Synthesis of liquid crystalline epoxy resins

The synthetic routes of *p*-BEPSBP and *p*-SBPEPB are outlined in Schemes 1 and 2.

### Preparation of 4,4′-bis(2,3-epoxypropyloxy)-Sulfonyl bis(1,4-phenylene) (p-BEPSBP) (1b)

Bisphenol-S (10.0 g, 0.04 mol) was dissolved in 80 mL of acetone and was introduced in a 250 mL flask equipped with the stirrer, thermometer and a reflux condenser, then allyl bromide (8 mL, 0.1 mol), K$_2$CO$_3$ (13.8 g, 0.1 mol) and cetyltrimethyl ammonium bromide (CTMAB) (1.46 g, 0.004 mol) were added to the flask with stirring and refluxed for 24 h. Then the mixture was cooled to room temperature, filtered, and evaporated. Then the final white solid was recrystallized from ethanol and dried in vacuum. The yield of 1a is 88% (11.6 g) with melting point ($T_m$) at 135°C.

**1a:** IR (KBr. cm$^{-1}$), 840 cm$^{-1}$ (Ar), 1100 cm$^{-1}$ (Ar—O—C), 1150 cm$^{-1}$ (O=S=O), 1600 cm$^{-1}$ (—CH$_2$=CH—), 3060 cm$^{-1}$(C—H).
$^1$H-NMR (CDCl$_3$), δ(ppm), 5.3–5.5 (4H, t, CH$_2$=), 5.9–6.0 (2H, m, =CH—), 4.6 (4H, t, CH$_2$—O—), 7.0, 7.8 (8H, t, Ar—H).

Compound **1a** (4 g) was dissolved in 30 mL of CH$_2$Cl$_2$ in a 100 mL flask by stirring, and 5.4 g of *m*-chloroperbenzoic acid (MCPBA) was added in this flask, and the mixture was stirred and refluxed for 48 h, then was filtered off and the filtrate solution was washed successively with 5% NaHSO$_3$, 5% NaHCO$_3$, and saturated NaCl. After the solution was dried over 24 h with MgSO$_4$, and was concentrated under reduced pressure to obtain a white

solid. Then the white solid was purified by multiple recrystallizations from ethyl acetate and finally 2.1 g of white crystalline power was obtained (**1b**). The yield of 1b is 47% with $T_m$ at 165°C, and the epoxy value is 0.472 mol/100 g.

**1b:** IR (KBr. cm$^{-1}$), The IR spectrum of **1b** has a characteristic peak of epoxy group at 915 cm$^{-1}$ that is different to **1a**.
$^1$H-NMR (CDCl$_3$), δ(ppm), 5.3–5.5 (4H, d, O—CH$_2$—CH), 2.9–3.4 (2H, m, CH—CH$_2$), 4.0–4.6(4H, d, CH$_2$—O), 7.0,7.9(8H, t, Ar—H).

### Preparation of sulfonyl bis(4,1-phenylene) bis[4-(2,3-epoxypropyloxy) benzoate] (p-SBPEPB) (2b)

4-Hydroxy ethyl benzoate (24.94 g) and 100 mL of acetone were introduced in a 250 mL four-neck flask and heated to dissolve, and then 21.64 g of K$_2$CO$_3$, 1.91 g of CTMAB and 17 mL of allyl bromide were added under a nitrogen atmosphere. The mixture was heated and stirred under reflux for 20 h, then cooled to room temperature and filtered. The filtrates were poured into a 500 mL four-neck flask and the acetone solvent was removed by evaporation, then 280 mL of 13% KOH solution and 140 mL of ethanol was added into the flask. The mixture was heated to be a clear solution under reflux and continual stirring for 20 min. The solution was acidified with HCl to pH = 3 under ice bath. The raw product obtained by filtration was washed with water and recrystallized from ethanol, then dried in vacuum overnight at 50°C, then the final white powder of 4-(2-allyloxy)benzoic acid (**a**) was obtained, which has a yield of 24.7 g (92%) and with $T_m$ at 167°C.

**a:** $^1$H-NMR (CDCl$_3$), δ(ppm)5.2(2H, t, =CH$_2$), 6.0 (1H, m, =CH—), 4.6 (2H, t, —CH$_2$—O), 7.0–8.0 (4H, t, Ar—H), 11 (1H, m, —OH).
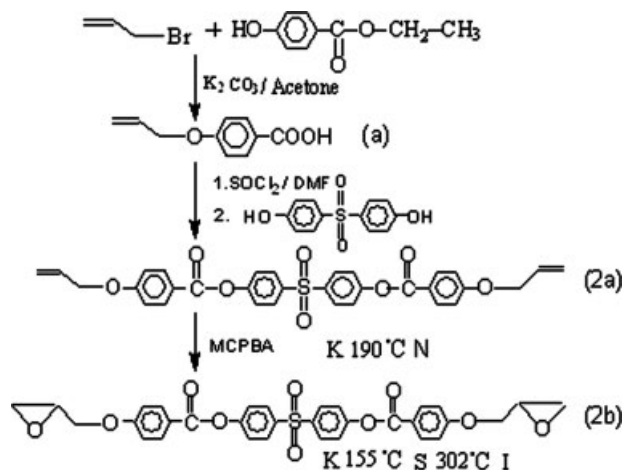


**Scheme 2** Synthetic scheme of *p*-SBPEPB.

Under continual stirring, 7.10 g of **a** (0.04 mol), 56 mL of $SOCl_2$ and 1.5 mL DMF were added into a 100 mL four-neck flask under a nitrogen atmosphere. The mixture was stirred to be a clear solution and continual reaction for another 2 h. Then the excess $SOCl_2$ was removed out under vacuum and a yellow liquid 4-allyloxybenzoyl chloride was obtained. Then 60 mL of pyridine followed by 5 g (0.02 mol) bisphenol-S were dripping into it and the solution was stirred for 1.5 h at 4–8°C, and stirred continually for another 20 h at room temperature. After that, the reaction mixture was poured into 1000 mL of acidified aqueous solution and the solid product was collected by filtration, and it was washed twice with distilled water. The product was purified by recrystallization from ethylacetate/ethanol (7/3) solvent and dried in vacuum. The 8.0 g of white powder (**2a**) was obtained with a yield of 70% and $T_m$ at 190°C.

**2a:** IR (KBr. $cm^{-1}$), 850 $cm^{-1}$ (Ar), 1075–1020 $cm^{-1}$ (Ar—O—C), 1750 $cm^{-1}$(—C=O), 1150 $cm^{-1}$ (O=S=O), 1640 $cm^{-1}$(—$CH_2$=CH—), 3030 $cm^{-1}$(C=H).
$^1$H-NMR (CDC1$_3$), δ(ppm), 5.3–5.5(4H, t, $CH_2$=), 6.0–6.2 (2H, m, =CH—), 4–4.6 (4H, t, $CH_2$—O—), 7.0–8.3 (8H, d, Ar—H).

The preparation of **2b** was analogous to that of **1b**; however, it was recrystallized from methanol to get about 1.3 g of the white powder (**2b**), which has a yield of 30% with $T_m$ at 155°C and $T_i$ at 302°C, and the epoxy value is 0.27 mol/100 g.

**2b:** IR (KBr. $cm^{-1}$), the IR spectra of **2b** has a characteristic peak of epoxy group at 915 $cm^{-1}$ that is different to **2a**.
$^1$H-NMR (CDC1$_3$), δ(ppm): 2.2 (4H, d, O—$CH_2$—CH), 2.8–3.0 (2H, m, CH—$CH_2$), 3.4–3.5(4H, d, $CH_2$—O), 7.0–8.2 (8H, d, Ar—H).

### Curing reaction of LCER with DDE

4,4-diaminodiphenyl ether (DDE) was used as a curing agent for the two LCERs. The **1b**/DDE samples (or **2b**/DDE) were mixed homogeneously with a stoichiometric ratio of one epoxy group to one N-hydrogen, and then grinded into fine powder. 4 mg sample was placed into an aluminum DSC sample cell and sealed with an aluminum lid. The entire operation was carried on in a dry chamber. The dynamic DSC analysis was performed at different heating rates under a nitrogen flow of 20 mL min$^{-1}$.

## RESULTS AND DISCUSSION

### DSC analysis

DSC was employed to obtain the phase transition temperatures of the synthesized compounds **1a, 1b, 2a,** and **2b**. As seen from Figure 1, both **1a** and **1b**
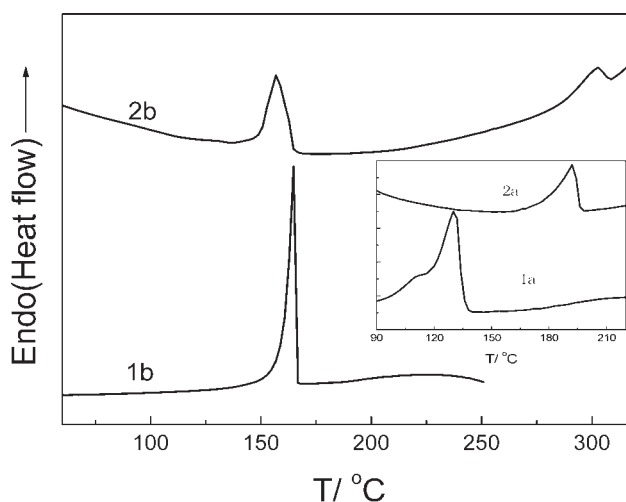


**Figure 1** The DSC curves of **1a**, **1b**, **2a**, and **2b**.

have only one endothermic peak in the DSC heating curves, $T_m$ of **1a** is 135°C and **1b** is 165°C with no clearing point $T_i$ (the transition temperature from LC phase to isotropy) before 300°C. However, **2a** has a higher $T_m$ at 190°C, and **2b** has a $T_m$ at 155°C and a $T_i$ at 302°C. When compared $T_m$ and $T_i$ of **2a** and **2b**, the difference should be attributed to the higher regularity of end group for **2a** than **2b**. In our previous work,[14] we found that if the 2,3-epoxypropyloxy end group of **2b** was substituted by 2,3-epoxypropyloxyethoxy, its $T_m$ will decrease to 102°C. This is because that $T_i$ is correlated with the whole molecular motion and the $T_m$ is correlated with the length of the end flexible chain, i.e., the longer of the end flexible chain, the lower the $T_m$ and the broader of liquid crystal temperature range is. For each compound of **1a**, **1b** and **2a**, only $T_m$ but no $T_i$ was shown in DSC before its decomposition because the $T_i$ was over the decomposed temperature $T_d$. The result shows that LC behaviors are associated with not only the main molecular chain but also the end groups, and the length and regularity of linear flexible end group influences markedly to the crystallization behavior, $T_m$, $T_i$, and thermostability of LC phase.

### Optical texture of LCERS

The texture morphology of samples **1a, 1b, 2a, 2b** was studied with a polarized optical microscopy equipped with a hot-stage and a digital camera system. The samples were prepared by sandwiching a tiny powder between two glass plates. At room temperature, some bright and color crystalline morphology were observed of all samples. When each sample was heated to the temperature a little higher than the $T_m$, the color pattern was still seen and stabile, suggesting that the compounds still keep
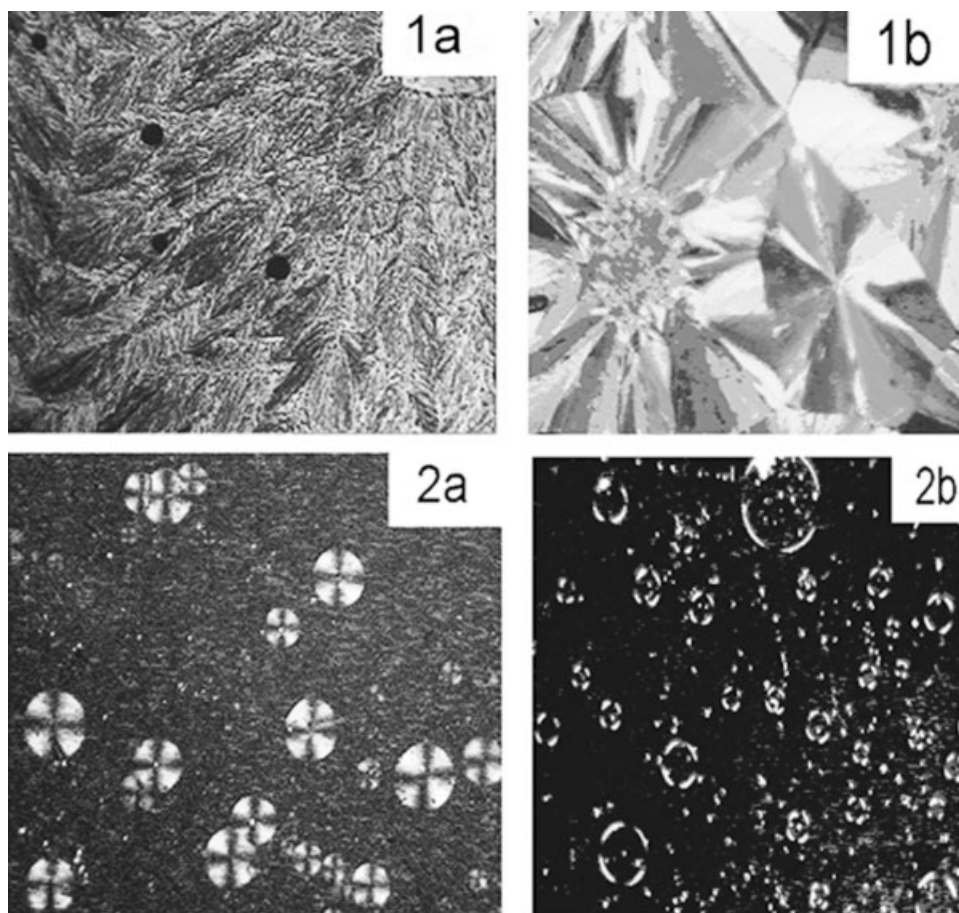
**Figure 2** The POM photographs of **1a**, **1b**, **2a**, **2b** Magnified POM textures (×100).

anisotropic state at their liquid state and inner molecules arrange orderly and present LC behavior. When these samples for POM were heated to melt to form uniform films and holding 5 min at melting temperature, then quenched them quickly with ice water and take the photographs by the digital camera. As seen from Figure 2, **1a** shows the texture of leaves and **1b** shows fan shape optical texture or more completely focal-conics texture, so they are both belong to smectic phase according to the reference.[15] The texture of **2a** presents the obvious nematic droplet texture which is coincident with frame of reference 15. **2b** belong to single axis homeotropic alignment nematic droplet texture.[15] Because both **2a** and **2b** have longer rigid mesogen and a shorter end group, their textures are different to that of **1a** and **1b**.

## X-ray diffraction

XRD patterns of **1a**, **1b**, **2a**, and **2b** are all shown in Figure 3. According to Bragg diffractions formula ($2d\sin\theta = n\lambda$), in the XRD pattern of **1a**, the sharp diffraction peaks appear at about $2\theta = 6.6°$ ($d = 1.34$ nm) and $2\theta = 20.0°$ ($d = 0.443$ nm); For **1b**, it has a larger diffraction peak at $2\theta = 1.69°$ ($d = 5.22$ nm)

and a smaller diffraction peak at $2\theta = 6.8°$ ($d = 1.28$ nm) which is a character of smectic mesophase,[15] other diffraction peaks appear at $2\theta = 20.9°$ ($d = 0.425$ nm), $2\theta = 22.2°$ ($d = 0.340$ nm); For **2a**, two weak diffraction peaks appear only at $2\theta = 3.0°$, $2\theta = 6.0°$. These results indicate that when the molecular weight of rigid mesogen increases, the degree of
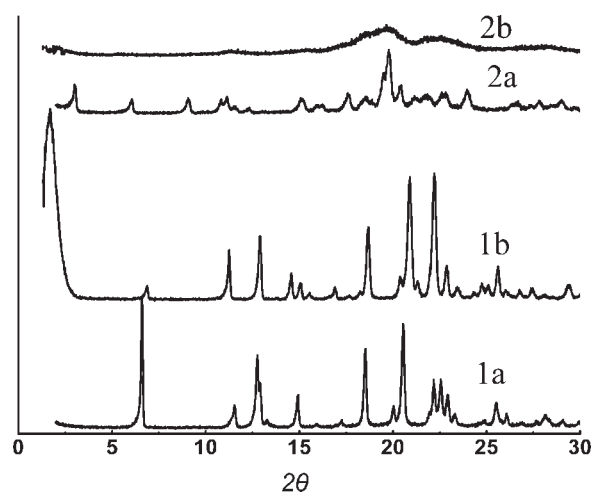


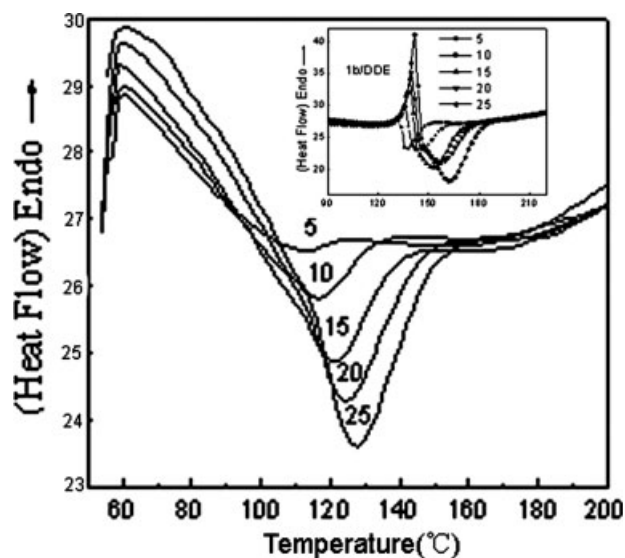**Figure 3** The XRD patterns of **1a**, **1b**, **2a**, and **2b**.

**Figure 4** DSC curves of **1b**/DDE and **2b**/DDE cured system at different heating rate.

smectic mesophase decreases and the degree of nematic mesophase increases.[15] For **2b**, none diffraction peak appeared in small-angle region but only a weak widen peaks around $2\theta = 20°$, so **2b** belong to nematic phase. These results are conformed to the POM analysis.

## Curing behavior and mechanical loss

In this work, DSC was employed to study the nonisothermal curing behavior of these LC compounds, and each sample was heated from 25 to 250°C at five heating rates (β) of 5, 10, 15, 20, 25°C min$^{-1}$ under a nitrogen flow of 20 mL min$^{-1}$, respectively.

Figure 4 shows the curing curves of **1b**/DDE and **2b**/DDE system at five heating rates, respectively. Both of the two curing systems have general lower melting-point, and the melting peaks become stronger at higher heating rate. The curing reaction temperature range become broader and the initial curing temperature ($T_{ic}$), the peak temperature ($T_{pc}$) and the finishing temperature ($T_f$) are all increased as the heating rate increasing.

Because the different heating rates correspond to the different best curing temperature, when the heating rate β = 0, the curing technical temperature or information can be obtained from extrapolated plots of T-β curve as shown in Figure 5 (a,b). From Figure 5, we obtain: for **1b**/DDE, the gel point $T_{gel}$ is 129.9°C, the curing temperature $T_{cu}$ is 132.2°C, the finishing temperature $T_f$ is 146.9°C, respectively; for **2b**/DDE, the $T_{gel}$ is 71.8°C, the $T_{cu}$ is 105.0°C and the $T_f$ is 123.4°C, respectively.

The activation energy $E_a$ and the pre-exponential factor $A$ of the curing reactions can be calculated from the Ozawa's relationship.[7,16]
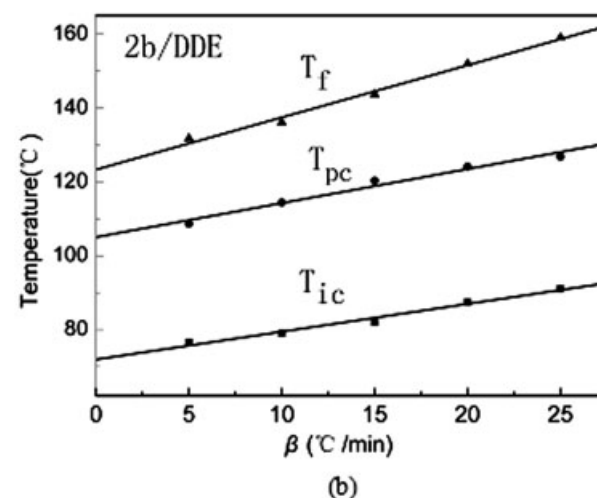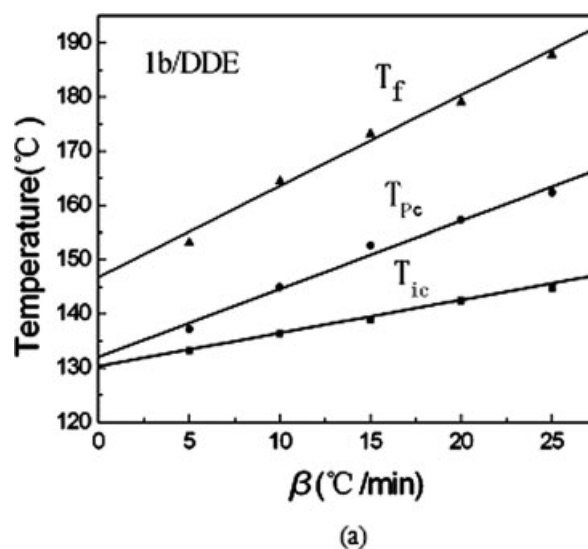




**Figure 5** β versus T curves of **1b**/DDE and **2b**/DDE cured systems (a) **1b**/DDE; (b) **2b**/DDE.

$$E_a = -R\Delta\ln\beta/1.052\Delta(1/T_{cp}). \quad (1)$$

$$A = \frac{\beta E_a \exp(E_a/RT_{cp})}{RT_P^2} \quad (2)$$

**TABLE I**
**$E_a$ and $A$ for LCERs and DDM Derived by the Ozawa's Method**

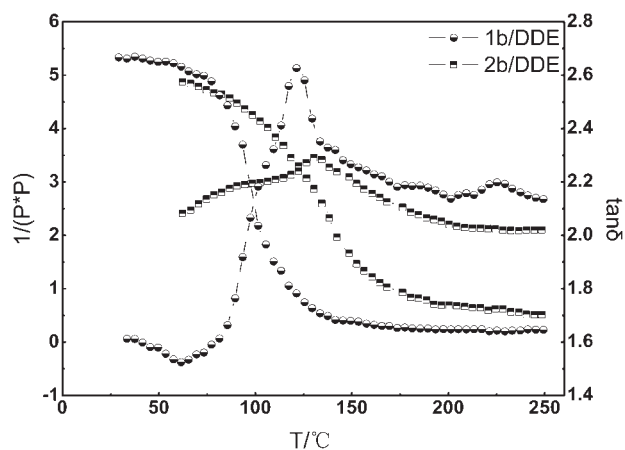| Samples | β(K/min) | $T_{cp}$ (°C) | $E_a$(kJ/mol) | $A$ (S$^{-1}$) | Mean |
|---|---|---|---|---|---|
| 1b/DDE | 5 | 137 | | $1.21 \times 10^9$ | |
| | 10 | 145 | | $1.42 \times 10^9$ | |
| | 15 | 153 | 89.16 | $1.26 \times 10^9$ | $1.28 \times 10^9$ |
| | 20 | 157 | | $1.31 \times 10^9$ | |
| | 25 | 162 | | $1.20 \times 10^9$ | |
| 2b/DDE | 5 | 109 | | $9.41 \times 10^{11}$ | |
| | 10 | 114 | | $1.20 \times 10^{12}$ | |
| | 15 | 120 | 103.28 | $1.07 \times 10^{12}$ | $1.04 \times 10^{12}$ |
| | 20 | 124 | | $1.02 \times 10^{12}$ | |
| | 25 | 127 | | $9.93 \times 10^{11}$ | |

**Figure 6** Dynamic mechanical graphs of the **1b**/DDE and **2b**/DDE.

where $\beta$ is the heating rate (K/min), $T_{cp}$ is the peak temperature (K) of cure reaction, $R$ is the gas constant, $E_a$ can be calculated from the plots of ln $\beta$ versus $1/T_{cp}$, and the basis on the principle of linear regression and the results were shown in Table I. The results indicate that when the curing temperature is the peak value, the average apparent activation energy $E_a$ of $p$-BEPSBP/DDE is 89.16 kJ/mol and $p$-SBPEPB/DDE is 103.28 kJ/mol. The $E_a$ increases with the increase length of mesogen; however, much greater increase of pre-exponential factor $A$ over $E_a$ indicates that the curing reaction occur more actively when LCER has a nematic phase.

Because the glass transition temperature ($T_g$) can be used effectively to monitor the curing reaction and thermal properties, the torsional braid analysis (TBA) was used to determine the $T_g$ of the thermosetting system. TBA is particularly useful at high conversion and after vitrification because of the non-
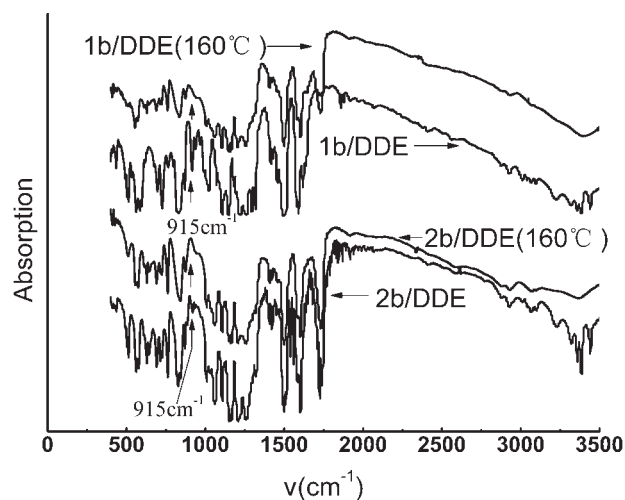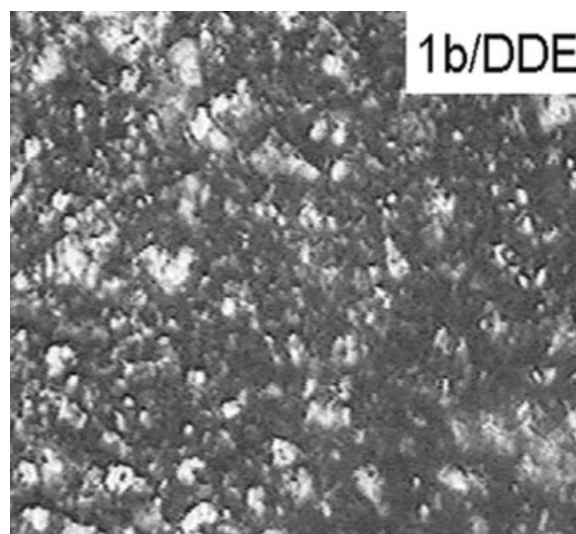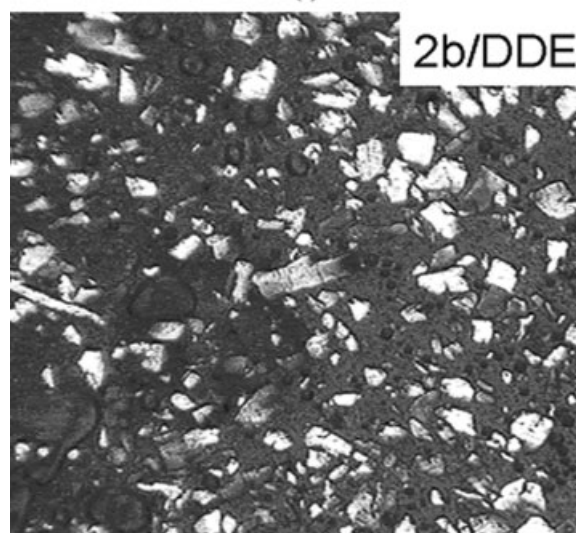


**Figure 7** FTIR spectra of precuring and postcuring compound **1b**/DDE and **2b**/DDE showing removal of the epoxy stretch at 915 cm$^{-1}$.



**Figure 8** The morphology of curing of **1b**/DDE and **2b**/DDE (a) **1b**/DDE; (b) **2b**/DDE.

linearity of $T_g$ versus reaction conversion $\alpha$.[17] Generally, there is a one-to-one relationship between the $T_g$ and mechanical loss peak temperature $T_p$, and the higher $T_p$, the higher $T_g$ is; so that, $T_p$ has been used directly as a parameter in the analysis of reaction kinetic models.[18]

The specimens were prepared via the dipping of heat-cleaned glass fiber braid into $N,N'$-dimethylformamide solution of LC epoxy resins and DDE, then the solvent was completely evaporated in vacuum. The specimens were cured at 160°C in air oven, after that, they were taken out and cooled to room temperature, and the $T_p$ was determined with TBA spectra at a heating rate of 2°C min$^{-1}$. TBA spectra of $p$-BEPSBP/DDE and $p$-SBPEPB/DDE are shown in Figure 6. From Figure 6, we can obtain the $T_p$ of $p$-BEPSBP/DDE at 120 and 130°C for $p$-SBPEPB/DDE.

## Texture of curing materials

The curing resins had been determined by FTIR in Figure 7. The epoxy resins have a characteristic absorption peak of epoxy group at 915 cm$^{-1}$, however, the IR characteristic absorption peak of **1b**/DDE and **2b**/DDE systems at 915 cm$^{-1}$ had disappeared after curing.

POM was used at several stage of the curing reaction to monitor the texture of the samples. **1b**/DDE and **2b**/DDE system were heated to over the each corresponding melting points $T_m$ and curing at this temperature, and subsequently quenched rapidly to room temperature and observed by POM. In Figure 8, some brightness spots of anisotropy phase can be observed. This is because the liquid crystalline molecules have a tendency of self-conglomeration, and the liquid crystalline phase had been fixed in the system at cure process.

## CONCLUSIONS

1. Two liquid crystalline epoxy resins of *p*-BEPSBP and *p*-SBPEPB were synthesized using bisphenol-S. The *p*-BEPSBP has a smectic texture with melting point at 165°C, but without clearing point before 300°C; the *p*-SBPEPB has a nematic texture and the LC temperature range is 155–302°C.
2. The curing temperature condition: for *p*-BEPSBP/DDE, the gel point $T_{gel}$ is 129.9°C, the curing temperature $T_{cu}$ is 132.2°C, the finishing temperature $T_f$ is 146.9°C, respectively; for *p*-SBPEPB/DDE, the $T_{gel}$ is 71.8°C, the $T_{cu}$ is 105.0°C and the $T_f$ is 123.4°C, respectively.
3. Average apparent activation energy is 89.16 kJ/mol for *p*-BEPSBP/DDE and 103.28 kJ/mol for *p*-SBPEPB/DDE calculated by Ozawa's method. The dynamic mechanical loss peak $T_p$ is 120°C for *p*-BEPSBP/DDE and 130°C for *p*-SBPEPB/DDE.

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