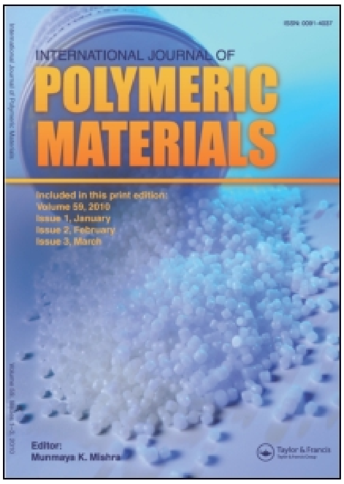

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Synthesis of LC p-Biphenyl di{4-[2-(2,3-epoxypropyl)ethoxy] benzoate} and Curing Kinetics with Succinic Anhydride

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A liquid crystalline (LC) diepoxide of p-biphenyl di{4-[2-(2,3-epoxypropyl)ethoxy] benzoate} (p-BPEPEB) was synthesized from allyl 2-hydroxyethyl ether, 4-hydroxy ethyl benzoate, 4,4-biphenol and m-chloroperoxybenzoic acid (MCPBA). Its structure was characterized by FTIR, ^{1}HNMR. The thermal properties and liquid crystalline behavior were investigated by using DSC, POM and XRD. The results show that the p-BPEPEB has a smectic liquid crystalline structure, and the melting point is 155°C. The curing kinetics of p-BPEPEB with succinic anhydride was investigated by nonisothermal DSC method. The results show that the cured system's initial temperature T_i is 90.8°C; peak temperature T_p is 128.4°C and finishing temperature T_f is 144.7°C. The apparent activation energy Ea is 213.69 KJ/mol, and with the increase of conversion rate the value reduces.

Keywords: cure kinetics, liquid crystalline epoxy resin, succinic anhydride, thermal analysis

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INTRODUCTION

Epoxy resins are commercially important as thermosets because of their superior adhesive strength, corrosion resistance, high-temperature resistance, dimensional stability, mechanical properties and electrical properties compared to other classical thermosets [1]. Therefore, the epoxy resins are applied to coatings, adhesives, electrical and optical equipments, mechanical and engineering technology, civil construction and other fields. However, they are limited in many high-performance applications because of their brittleness at low temperatures and thermal properties [2]. The factor that most influences the thermal and mechanical properties of epoxy resins is the structure of the molecular chain [3]. Thus, modified properties of epoxy resins have been frequently investigated [4–6].

The investigation of liquid crystalline epoxy resins began in the 1980s. As compared to ordinary epoxy resins, crosslinked LC epoxy resin exhibited higher fracture toughness and mechanical properties when oriented by magnetic fields and applied as advanced material in the optic and electric fields [7–10]. Recently, many researchers described the synthesis and LC properties of mesogenic diepoxide compounds [11,12]. In this work, an epoxy compound of p-biphenyl di{4-[2-(2,3-epoxypropyl)ethoxy]benzoate} (p-BPEPEB) was synthesized and the curing kinetics of p-BPEPEB with succinic anhydride was investigated using nonisothermal DSC method at different heating rates.

EXPERIMENTAL

Main Materials

Allyl 2-hydroxyethyl ether, 4,4-biphenol, thionyl chloride, dimethylformamide (DMF), m-chloroperoxybenzoic acid (MCPBA), succinic anhydride, tetrahydrofuran (THF), and N,N-dimethylbenzylamine were all analytically pure and were supplied by the Tianjin Chemical Reagent Co. (Tianjin, China).

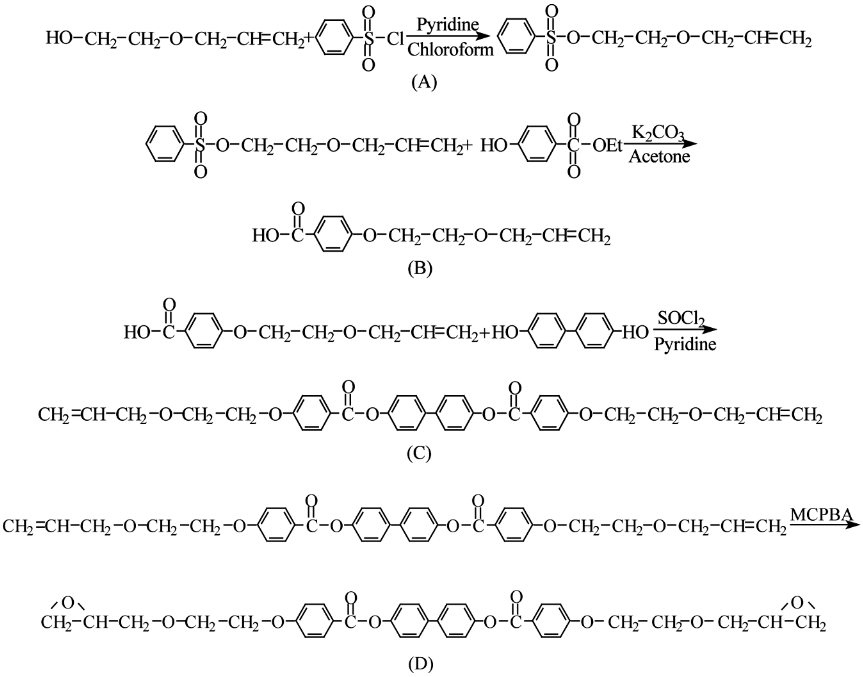
Instrument and Characterization

Fourier transform infrared (FTIR FTS-40, Bio-Rad, US) was used for the investigation of the structure of p-BPEPEB. The sample and KBr were mixed homogeneously and then pressed on potassium bromide plates. The nuclear magnetic resonance spectrometer (NMR, bruker 400k, Switzerland) was used for the ^{1}H NMR analysis of p-BPEPEB, using $CDCl_3$ as solvent. The texture of p-BPEPEB was examined by means of polarizing optical microscopy (POM, 59XA, Yong-Heng, Shanghai, China). The samples were heated to about 200°C and then immediately quenched to room temperature, the textures observed by polarizing optical microscopy. Thermal phase transition behavior was determined by means of differential scanning calorimetry (DSC, Diamond, Perkin-Elmer Co., US). DSC was calibrated with high-purity indium, and the peak temperatures obtained were taken as the phase transition temperatures.

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). The diffractometer was equipped with CuKa ($\lambda = 0.1542\,\text{nm}$) radiation, produced under conditions of 40 kV and 100 mA.

Synthesis of Epoxy Monomer

The synthetic process of p-BPEPEB was illustrated as follows in Scheme 1.



SCHEME 1 Synthetic scheme of p-BPEPEB.

2-(allyloxy)ethoxy p-toluenesulfonate (A), 4-[2-(allyloxy)ethoxy]-benzoic acid (B) and p-biphenyl di{4-[2-(allyloxy)ethoxy]benzoate} (C) were synthesized and characterized according to the literature [12,13]. The crude product was stirred for 1 h with Na_2CO_3 aqueous solution and then washed with water. Compound (C) was obtained and recrystallized with ethyl acetate. The yield is 55.3%.

Monomer (C) (5.94 g) and m-chloroperoxybenzoic acid (MCPBA) (5.0 g) was added into 80 mL of 1, 2-dichloroethane, then stirred for 48 h at 38°C. After filtration, the product was recrystallized with mixed solvent of ethyl acetate/isopropanol, the yield is 50.27%.

Curing of p-BPEPEB with Succinic Anhydride

The p-BPEPEB/succinic anhydride samples were prepared with a stoichiometric ratio of one epoxy group to a carboxy group and used N,N-dimethylbenzylamine as catalyst. Approximately 3.5 mg mixture of p-BPEPEB/succinic anhydride was used for DSC analysis. The dynamic DSC analysis was performed at a different heating rate: 5, 10, 15, 20 and 25°C/min respectively under a nitrogen flow 20 mL/min. The sample was heated from 25°C to around 300°C.

RESULT AND DISCUSSION

Structure Characterization of p-BPEPEB

The FTIR spectrum of p-BPEPEB shows that the epoxide group absorption peak is at 916 cm^{-1}; the carbonyl absorption peak is at 1726 cm^{-1}; the ether absorption peak is at 1265 cm^{-1}, 1131 cm^{-1}; the methylene absorption peak is at 762 cm^{-1}; and the phenyl absorption peak is at 849 cm^{-1}.

The ^1H NMR spectrum of p-BPEPEB shows: ^1H NMR ($CDCl_3$), δ (ppm) 2.65, 3.91 (2H, dd, C**H₂**, epoxy), 2.84 (2H, m, C**H**, epoxy), 3.23, 3.52 (2H, dd, C**H₂**, glycidyl), 3.91 (4H, m, C**H₂**, ethoxy), 4.23 (4H, t, C**H₂** of ethoxy), 7.01 (4H, d, aromatic), 8.16 (4H, d, aromatic), 7.26 (4H, s, aromatic), 7.62 (4H, d, aromatic). According to the result of FTIR and ^1H NMR as shown in Figure 1, the structure of the product conforms with the aim compound D.

The theoretical epoxy value of compound D should be 0.32 mol/100 g. But the computational value from the integral area of the characteristic hydrogen of p-BPEPEB is 0.29 mol/100 g and has an error of 0.03 mol/100 g between theoretical and actual value. The result shows that a few double bonds did not oxidize to change the epoxy group. The error between theoretical value and actual value is about 0.03 mol/100 g.

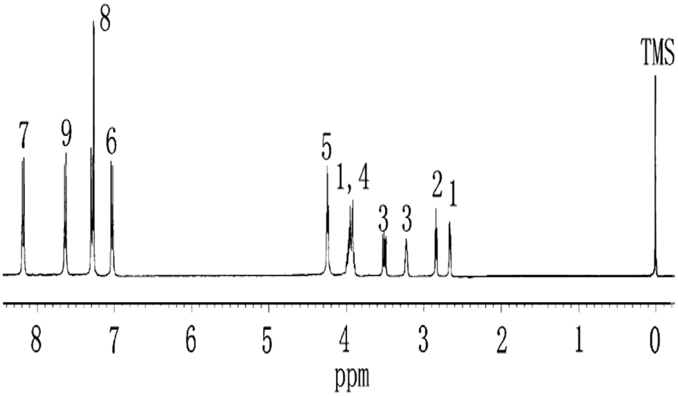


FIGURE 1 The ^1H NMR spectrum of p-BPEPEB.

Figure 2 shows the DSC spectra of compounds C and D. The compound C has two transition temperatures at 134 and 149°C respectively. 149°C is the melting point of LC compound C, and 134°C is the transition temperature of crystal morphology from one to another. The compound D has a melting point at 155°C, which is 6°C higher than C, because of the epoxy group. But the clearing points of C and D do not appear before 300°C, when it begins to decompose. This is because C and D have a larger liquid crystalline unit and a higher molecular weight, and the clearing point is higher than the decomposition temperature.

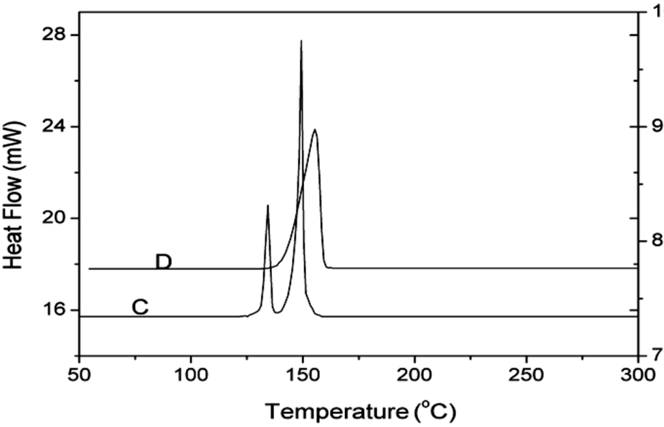


FIGURE 2 The DSC spectra of compound C and D.

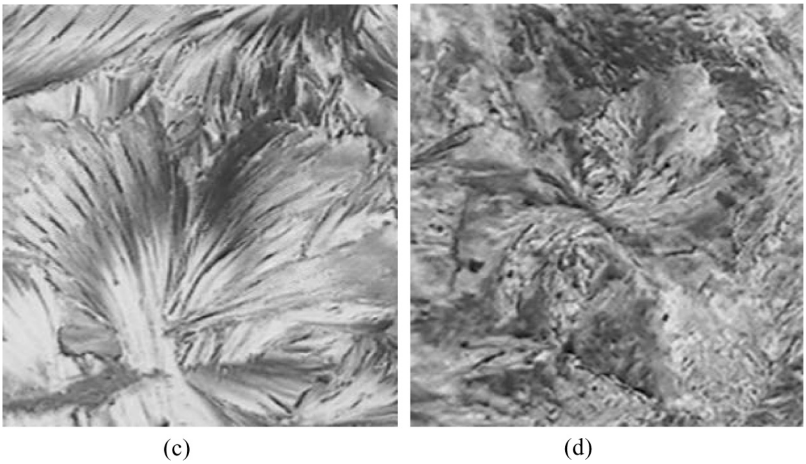


FIGURE 3 The POM photos of compound C and D.

The textures of liquid crystal C and D at 200°C quenched under POM are shown in Figure 3. As seen from Figure 3, the liquid crystal compounds C and D all reveal fan optical texture characteristic of the smectic phase [14], and the oxidation didn't change the liquid crystal texture but caused the fan-shaped texture to break.

Figure 4 shows the XRD diffraction curves of liquid crystalline compounds C and D. Compound C has diffraction peaks at 4.791°

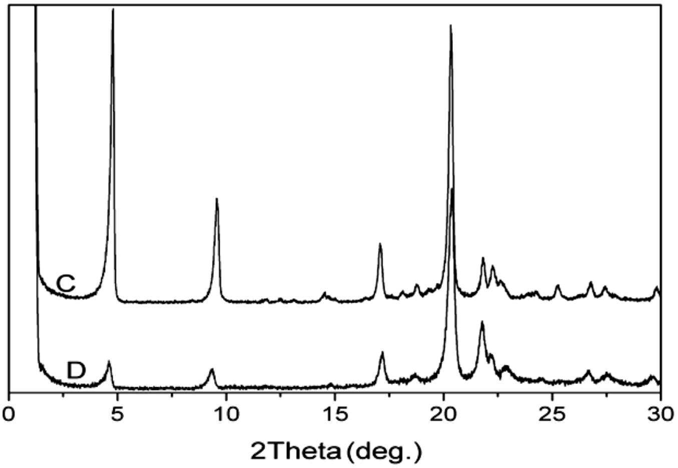


FIGURE 4 XRD patterns of compound C and D.

and 20.364° and the diffraction peak at 4.791° described the layer spacing. This is characteristic of smectic liquid crystal [14]. Compound D has diffraction peaks at 4.598° and 20.359°, but the diffraction peak at 4.598° is much smaller than compound C's. It indicates that the texture of compound D is irregular smectic phase compared with compound C. The reason is that the oxidation of double bond destroyed the order of the chain, and increased the polarity of terminal groups. It is also demonstrated by the blurry fan-shaped texture in Figure 3 (D).

Nonisothermal Curing Kinetics of p-BPEPEB/Succinic Anhydride System

Figure 5 shows the curing DSC spectra of p-BPEPEB/succinic anhydride at different heating rates. The system of p-BPEPEB/succinic anhydride shows eutectic points at about 130°C, and the p-BPEPEB became liquid crystalline state before curing in the mixed system. It ensures the fixation of the order of liquid crystal in the curing product. The exothermic peaks are attributed to the curing reaction of the p-BPEPEB/succinic anhydride system.

From Figure 5, the information about the curing reaction was obtained as follows: the initial temperature (T_i), the peak temperature

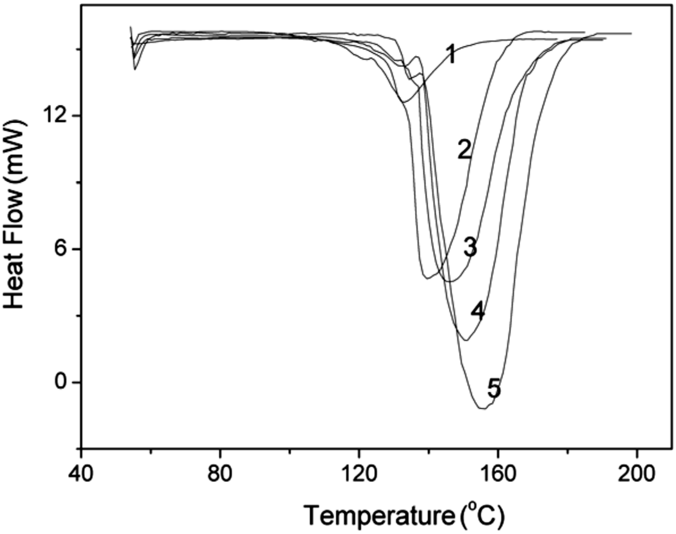


FIGURE 5 The DSC spectra of p-BPEPEB/succinic anhydride. Heating Rate: 1: 5°C/min; 2: 10°C/min; 3: 15°C/min; 4: 20°C/min; 5: 25°C/min.

TABLE 1 DSC Data of Cured System at Different Heating Rate β

β (°C/min)	$-\Delta H$ (KJ/g)	T_i (°C)	T_p (°C)	T_f (°C)	t (min)
5	109.28	97.16	132.81	153.50	11.27
10	237.77	105.45	139.60	166.87	6.14
15	223.94	114.13	144.96	178.69	4.30
20	194.97	117.21	151.24	186.63	3.47
25	198.19	126.42	153.63	194.91	2.74

(T_p), the finishing temperature (T_f), the cure time (min), and the reaction enthalpy (ΔH). The data obtained are summarized in Table 1.

It can be seen from Table 1, that the ΔH have max-value 237.77 KJ/mol at the heating rate 10°C/min. On increasing the heating rate, the curing curves for the tested system are shifted to the higher temperatures and the ranges of reaction-temperature and reaction rate increased. Then the rate of molecular motion lagged and a number of molecules were fixed before reaction. Therefore, the increasing heating rate leads to decrease of the ΔH.

The plots of the initial temperature (T_i), the peak temperature (T_p) and the finishing temperature (T_f) vs. heating rate (β, °C/min) are represented in Figure 6. With the heating rate $\beta = 0$, it is seen that the initial temperature of this cured-system's (T_i) is 90.85°C, peak

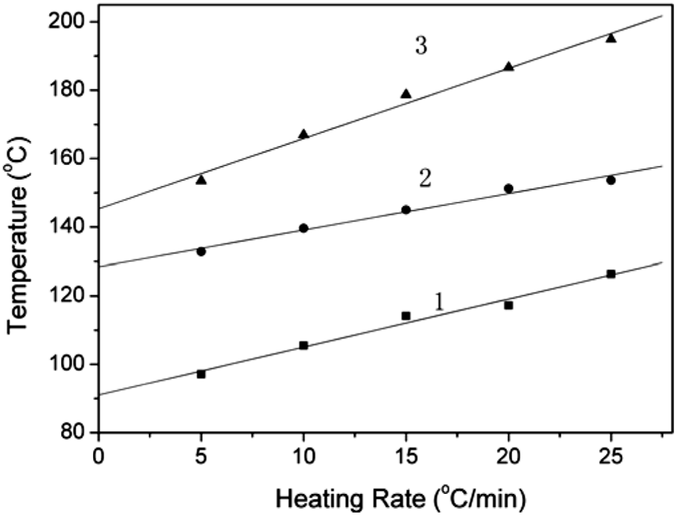


FIGURE 6 T-β curves of p-BPEPEB/succinic anhydride cured-system. 1: T_i-β; 2: T_p-β; 3: T_f-β.

temperature (T_P) is 128.44°C, and finishing temperature (T_f) is 144.68°C. The linear correlation coefficients R are between 0.9900 and 0.9929.

The apparent activation energy, Ea, of this curing reaction can be calculated from the Ozawa relationship [15]:

$$Ln\beta = A' - 0.4567 \cdot \frac{Ea}{RT} \tag{1}$$

where $A' = LogAEa/g(\alpha)R - 3.315$. This expression can be applied to different degrees of conversion. For each given conversion degree the logarithm of the heating rate is correlated with the inverse temperature. For a given heating rate, the temperature at different curing degrees is obtained from Figure 7, calculated by dynamic DSC curves. Table 2 shows the values obtained for the curing activation energy, Ea, and the constant, A', of p-BPEPEB/succinic anhydride system. It can be seen from Table 2 that on increasing the temperature, the value of A' and Ea decreases, but the Ea is between 250–180 KJ/mol, mol, and the A' between 35–25. This is because the molecule and reactive groups have higher moment energy and only need a lower energy for reaction at higher temperature, although the diffusion factors at higher conversion have some effect to the mobility of reactive groups. The linear correlation coefficient R is over 0.998 when the conversion degree is between 20–90%.

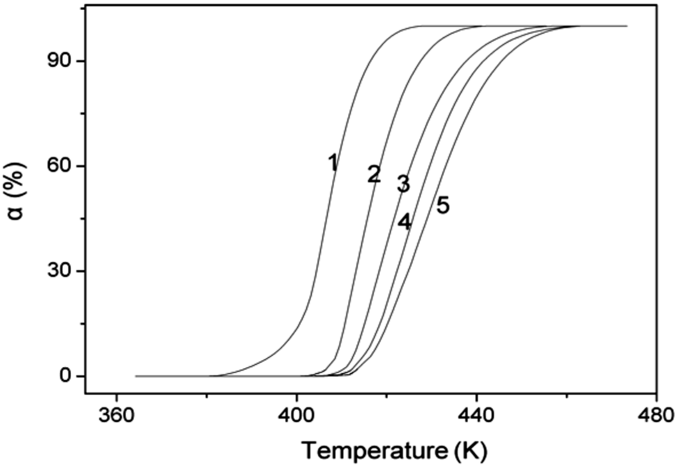


FIGURE 7 Relationship of curing degrees of p-BPEPEB/succinic anhydride vs. temperature. Heating rate: 1: 5°C/min; 2: 10°C/min; 3: 15°C/min; 4: 20°C/min; 5: 25°C/min.

TABLE 2 Kinetic Parameters of Samples Curing at Different Conversion Degrees

A (%)	A'	Ea (KJ/mol)	R
10	34.19	236.695	0.9853
20	35.70	249.821	0.9986
30	35.10	246.708	0.9999
40	33.29	234.001	0.9999
50	31.92	224.753	0.9998
60	29.94	210.826	0.9997
70	29.25	206.639	0.9992
80	27.31	193.059	0.9994
90	25.63	182.009	0.9985

On the basis of the Crane method [16], the reaction order is obtained from the curves $\ln\beta - 1/\mathrm{T}_p$.

$$d(Ln\beta)/d(1/T_P) = -(Ea/nR + 2T_P) \tag{2}$$

The slope of rectilinear is $-Ea/nR$ on the term of $Ea/nR \gg 2T_p$. The value of the reaction order, n, is 2.0 and the linear correlation coefficient R is 0.9901.

CONCLUSION

(1) The smectic liquid crystalline epoxy compound p-biphenyl di{4-[2-(2,3-epoxypropyl)ethoxy]benzoate} (p-BPEPEB) was synthesized using allyl 2-hydroxyethyl ether, 4-hydroxy ethyl benzoate, 4,4-biphenol and m-chloroperoxybenzoic acid (MCPBA), yield: 50.27%. The epoxy value of p-BPEPEB is 0.29 mol/100 g. The melting point of p-BPEPEB is 155°C.

(2) The non-isothermal curing kinetics of p-BPEPEB with succinic anhydride was investigated by DSC. We obtained that the cured initial temperature T_i is 90.8°C; peak temperature T_p is 128.4°C and finishing temperature T_f is 144.7°C. The apparent curing activation energy Ea decrease with the temperature rise, the even Ea is 195.43 KJ/mol and the reaction order n is 2.0.

REFERENCES

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

[2] Bejoy, F., Ramaswamy, R., Lakshmana Rao, V., and Thomas, S., *Intert. J. Polym. Mater.* **55**, 681 (2006).

[3] Gao, J. G. and Zhao, M., *J. Appl. Polym. Sci.* **94**, 182 (2004).

[4] Yee, A. F. and Pearson, A. R., *J. Mater. Sci.* **21**, 2462 (1986).

[5] Kirshenbaum, S. L. (1984). In *Rubber-modified Thermoset Resins*. C. K. Riew, Ed., American Chemical Society, Washington, DC, pp. 163.

[6] Kunz, S. C., Sayre, J. A., and Assink, R. A., *Polymer* **23**, 1897 (1987).

[7] Muller, H. P., Gipp, R., Heine, H., US patent 4,764, 581 (1988).

[8] Giamberini, M., Amendola, E., Carfagna, C., *Mol. Cryst. Liq. Cryst.* **266**, 9 (1995).

[9] Weiss, R. and Ober, C. K. (1990). *Liquid Crystalline Polymers: Chemistry, Structure and Properties*, American Chemical Society, Washington, DC, pp. 198.

[10] Carfagna, C., Amendola, E., Giamberini, M., Hakemi, H., and Pane, S., *Polym. Int.* **44**, 465 (1997).

[11] Jahromi, S. and Mijs, W. J., *Mol. Cryst. Liq. Cryst.* **250**, 209 (1994).

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

[13] Gao, J. G., Hou, G. X., Wang, Y., Li, H., and Liu, Y., *Polymer-Plas. Tech. Eng.* **45**, 947 (2006).

[14] Zhou, Q. F. and Wang, X. J. (1999). *Liquid Crystal Polymers*, Science Press, Beijing, pp. 75.

[15] Ozawa, T., *J. Thermal Analysis* **2**, 301 (1970).

[16] Crane, L. W., *J. Polym. Sci.* **12**, 120 (1972).