

# Morphology and Thermal Properties of Liquid Crystal *p*-PAEB/Styrene Copolymer

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**ABSTRACT:** The homopolymer of unsaturated liquid crystal (LC) monomer for *p*-phenylene di {4-[2-(allyloxy) ethoxy] benzoate} (*p*-PAEB), and copolymer poly (*p*-PAEB/St) of *p*-PAEB with styrene (St) have been synthesized. The LC behavior and thermal properties of *p*-PAEB and poly(*p*-PAEB/St) have been studied by Polarizing Optical Microscopic (POM), Differential Scanning Calorimetry, X-Ray Diffractometer (XRD), and Torsional Braid Analysis (TBA). The results demonstrate that LC phase texture and phase transition temperature of copolymers are affected by the composition of LC units in copolymers. The POM and XRD reveal that *p*-PAEB has a smectic phase structure; the copolymer of *p*-PAEB with styrene reveal deformed focal conics texture of

smectic phase. The phase transition temperature range of *p*-PAEB is 120.5–191.5°C, but the homopolymer of *p*-PAEB has a broad LC temperature range from 77 to 170°C. The LC temperature range of poly(*p*-PAEB/St) is broadened with increased content of *p*-PAEB. The dynamic mechanical properties of LC polymer networks were investigated with TBA. The results indicate that the peak temperature of maximal mechanical loss is 114°C and is decreased with the addition of styrene © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5731–5736, 2006

**Key words:** liquid crystal monomer; styrene; copolymerization; morphology; thermal properties

## INTRODUCTION

The effect of monomer organization on polymerization and the properties of polymers have been investigated from both scientific and industrial points of view. One of the typical monomer organization is based on the thermotropic liquid crystal (LC) order. LC materials have great potential for functional molecular systems because of their self-organized dynamic structure. Thermotropic LCs have become important in the field of advanced materials, such as electronic devices and high-strength fibers. Recently many studies have been focused on polymer networks with an anisotropic molecular orientation by polymerization of LC monomers in a unidirectional orientation.<sup>1–6</sup> The macroscopically oriented polymer networks were found to exhibit anisotropic mechanical and optical properties. In particular, densely crosslinked polymer network, which were prepared by bi- or polyfunctional LC monomers, showed excellent transparency and stable anisotropic molecular orientation.<sup>2</sup> Also, the dense crosslinking of the polymer networks removed any phase transition due to extreme restriction of molecular motion of the mesogenic groups in the polymer networks. There-

fore, the densely crosslinked polymer networks cannot respond to external stimuli such as electric field, magnetic field, temperature, and so on. Contrary to the densely crosslinked polymer networks, the lightly crosslinked polymer networks not only hold the stability of the macroscopic molecular orientation, but also show a reversible phase transition between a LC phase and an isotropic phase.<sup>7</sup>

LC monomers having polymerizable groups such as acrylate, methacrylate, vinyl ether, epoxide, and diene derivatives were used in the pursuit.<sup>7–15</sup> Many studies on LC polymer networks have been reported, such as LC epoxide/diamine, LC acrylate/LC vinyl ether.<sup>9,14,15</sup> These improved polymeric materials with thermotropic LC monomer exhibit unique thermal properties, and can improve processability and mechanical property, but studies based on copolymerization of unsaturated LC monomer indicates that with styrene it is not so. In this work, the divinyl LC monomer *p*-phenylene di {4-[2-(allyloxy) ethoxy] benzoate} (*p*-PAEB) was synthesized; the copolymerization and crosslinking of *p*-PAEB with styrene was investigated. The morphological texture and thermal properties of these LC polymer networks were examined.

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## EXPERIMENTAL

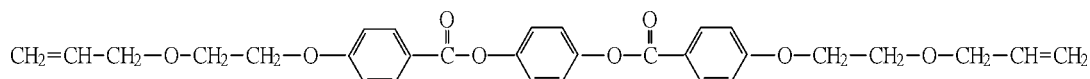
### Materials

Hydroquinone, sulfoxide chloride, allyl 2-hydroxyethyl ether, 4-hydroxy ethyl benzoate, dimethyl-

formamide, tetrahydrofuran (THF), and styrene (St) were all analytically pure grades and were supplied by the Beijing Chemical Reagent Co. China.

### Synthesis of *p*-PAEB

The LC monomer *p*-PAEB was synthesized according to the literature.<sup>9</sup> The molecular structure of *p*-PAEB is as follows:



### Copolymerization

The copolymers were synthesized according Table I, for example P-4: *p*-PAEB (0.01 mol, 5.18 g), St (0.01 mol, 1.04 g), and 50 mL THF were added into a 100-mL four-necked glass flask. The reaction was carried out under a nitrogen atmosphere, after 1%AIBN (mol of monomer) was added; the mixture was heated under reflux and stirred for 48 h. The formed polymers were isolated by precipitation into a large amount of methanol. The crude product obtained by filtration was dissolved with THF again, and then secondary sedimentation into methanol was done. After filtration, the resulting solid was dried in vacuum overnight at 50°C.

### Characterization of monomer and polymers

The structure of *p*-PAEB was examined by means of FTIR (FTS-40, Bio-Rad) and <sup>1</sup>H-NMR (bruker 400 MHz, Switzerland); FTIR spectra of LC monomer and polymers in the solid state were obtained by KBr method. Thermal phase transition behavior was examined by means of Differential Scanning Calorimetry (DSC, Diamond, Perkin-Elmer Co.) and Polarizing Optical Microscopic observation (POM, 59XA, Yong-Heng, Shanghai, China). Scanning rate of DSC measurements was 10°C min<sup>-1</sup>, 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 1 to 30° using an X-ray diffractometer (XRD) (Rigaku-D/max-rB, Germany). The diffractometer was equipped with a CuKα (λ = 0.1542 nm) radiation, produced under conditions of 40 kV and 100 mA.

TABLE I  
Recipes of Copolymerization

Polymers	<i>p</i> -PAEB/St (mol ratio)
P-1	1/0
P-2	3/1
P-3	2/1
P-4	1/1
P-5	1/2
P-6	1/3

Torsional braid analysis (TBA) were determined using GDP-4 Torsional Braid Analyzer (Jilin Univ. China) at the heating rate of 2°C min<sup>-1</sup> from 20 to 300°C.

## RESULTS AND DISCUSSION

### NMR and FTIR analysis

Monomer *p*-PAEB: <sup>1</sup>H-NMR (DMSO), δ (ppm) 3.76–4.26 (m, 12H, 2-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-); 5.16–5.31 (m, 4H, H<sub>2</sub>C=CH-); 5.8–5.9 (m, 2H, H<sub>2</sub>C=CH-); 7.36–8.11 (m, 12H, Ar-H). This assignment is in agreement with the structural compositions of the sample, like Figure 1.

Figure 2 shows infrared spectra of the monomer *p*-PAEB and polymer P-2. The IR spectra of *p*-PAEB and P-2 reveal the presence of characteristic absorptions of components. The absorption peaks at 3073 cm<sup>-1</sup> of *p*-PAEB associated with -C=C- stretching vibration absorption bands at 3000–2800 cm<sup>-1</sup> (CH<sub>2</sub> stretching), 1750 cm<sup>-1</sup> (carbonyl group vibration), 1620–1436 cm<sup>-1</sup> (aromatic C=C stretching) are consequences of the *p*-PAEB. Especially, a peak of P-2 at 3073 cm<sup>-1</sup> becomes much lower than that of *p*-PAEB. It is indicated that the *p*-PAEB has been polymerized.

### Optical texture and X-ray diffraction

The textures of *p*-PAEB at 130°C, poly(*p*-PAEB) at 90°C, and copolymers P-2 with P-4 at 120°C are shown in Figures 3 and 4. As seen from Figures 3 and 4, the *p*-PAEB under POM reveals fan optical texture of smectic phase or more completely focal-conics texture.<sup>16,17</sup> The texture of copolymer P-2 and P-4 reveals incomplete or deformed focal-conics texture. It is also entitled broken fanshaped texture, and the incomplete or deformed is more with increase of styrene content. This result is shown that the copolymers of unsaturated liquid monomer *p*-PAEB with styrene also have a smectic texture.

To obtain more detailed information on the meso-phase structure of the polymers, XRD studies were carried out. It provided morphological information, especially on the structure of the LC polymers and layer spacing.<sup>18</sup> The samples of *p*-PAEB and poly(*p*-

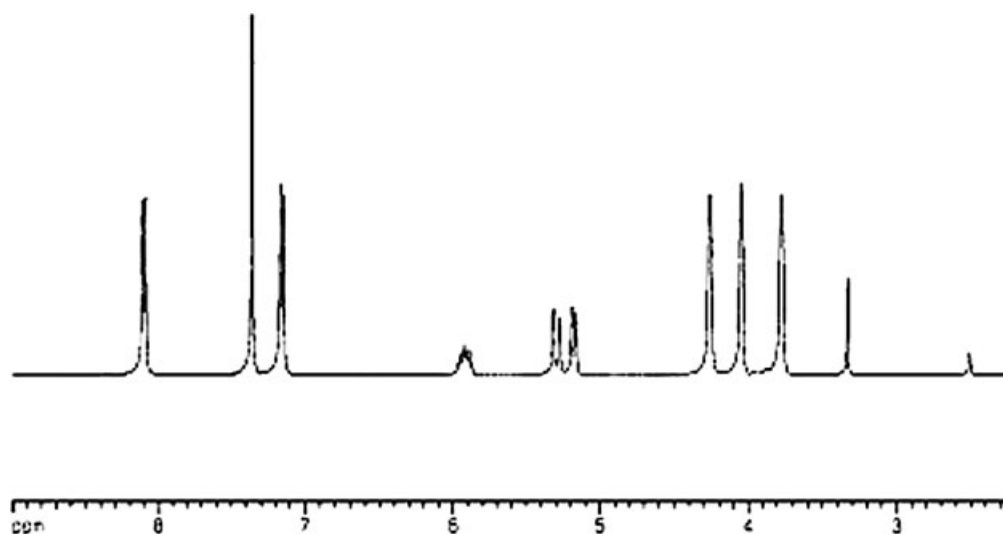


Figure 1 The  $^1\text{H-NMR}$  spectrum of the LC monomer *p*-PAEB.

PAEB/St) were heated to  $130^\circ\text{C}$ , held for 5 min at this temperature, and then cooled to room temperature quickly with liquid  $\text{N}_2$ .

XRD pattern of *p*-PAEB and copolymers of poly(*p*-PAEB/St) are shown in Figure 5. Thermotropic smectic LC character will be clearly identified in the X-ray analysis described. The diffraction pattern of *p*-PAEB exhibited high crystallinity and attributed to a smectic mesophase. It exhibited two narrow peaks in the wide-angle region ( $2\theta = 20^\circ$ ), in addition to one sharp peak in the small-angle region ( $2\theta = 5^\circ$ ). On the other hand, the X-ray patterns of poly(*p*-PAEB/St) showed smaller peak in the small-angle region and the same as two narrow peaks in the wide-angle region ( $2\theta = 20^\circ$ ); this is characteristic of smectic mesophase. But the crystallinity of poly(*p*-PAEB/St) is lower than that of *p*-PAEB, showing that copolymerization and St unit may inhibit crystallization of LC polymers.

The small-angle diffraction ( $2\theta = 5^\circ$ ) corresponds to the Bragg maximum of  $d = 17 \text{ \AA}$  for *p*-PAEB. The wide-angle diffraction ( $2\theta = 20^\circ$ ) corresponds to an intermolecular spacing (or the diffuse diffraction) of  $4.46 \text{ \AA}$  in the layer. The results suggest that the layer spacings correspond to a single-layer packing.

These results indicate that the mesogenic unit in the lightly crosslinked polymer networks can congregate as a smectic texture because the ability of self-congregation is higher than with styrene units.

#### Mesomorphic properties of LC monomer and polymer networks

It was found that the LC copolymers change to LC phase when heated to their melting temperatures  $T_m$ . The broken focal-conics texture can be observed in the range of  $T_m$  to isotropization temperatures  $T_i$  (Fig. 4).

Figures 6 and 7 show the DSC thermograms obtained for LC monomer (*p*-PAEB) and LC copolymers. In these figures, there is more than one peak that shows the glass-transition temperature  $T_g$ , melting point  $T_m$ , and anisotropic-isotropic transition  $T_i$  (clearing point).

As seen from Figure 6, in heating DSC scan of monomer (*p*-PAEB), two peaks are observed at  $T_m = 120.5^\circ\text{C}$  and  $T_i = 191.5^\circ\text{C}$ . The mesomorphic state of homopolymer (P-1) occurs in the range of  $77\text{--}170^\circ\text{C}$ ; but the  $T_m$  is decreased by  $43.5^\circ\text{C}$  and  $T_i$  is decreased by  $21.5^\circ\text{C}$ , the LC is bound to change to broad, and isotropic transition occurs lower than the monomer. This

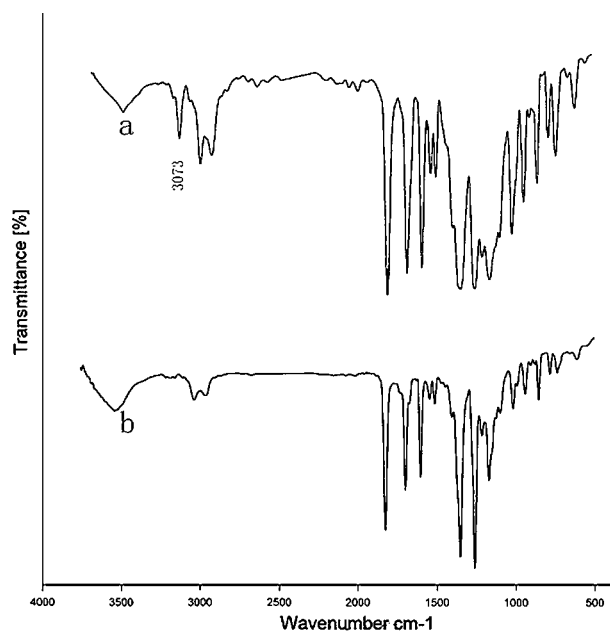
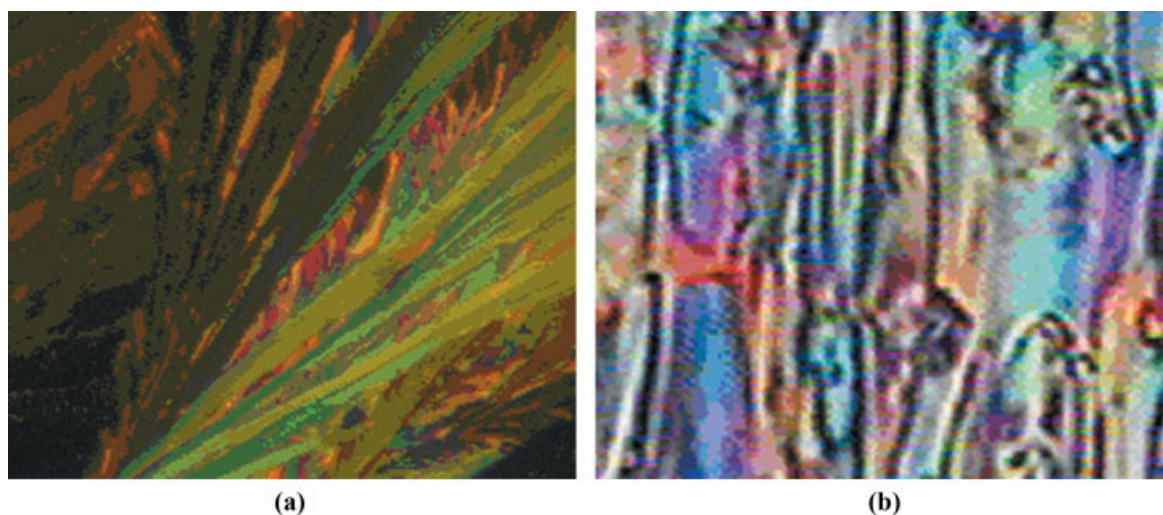


Figure 2 IR spectra of (a) monomer *p*-PAEB and (b) copolymer P-2.

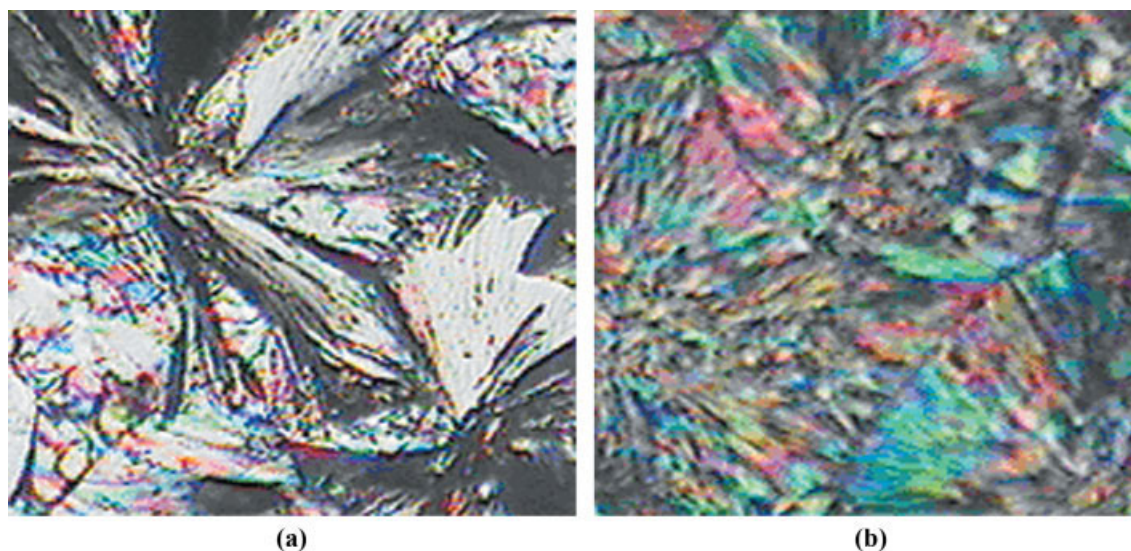


**Figure 3** Textures of (A) LC monomer (*p*-PAEB) and (B) homopolymer P-1. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

is probably due to the increased length of the flexible chain between the two LC units after homopolymerization and polydispersity of the copolymer.<sup>19</sup>

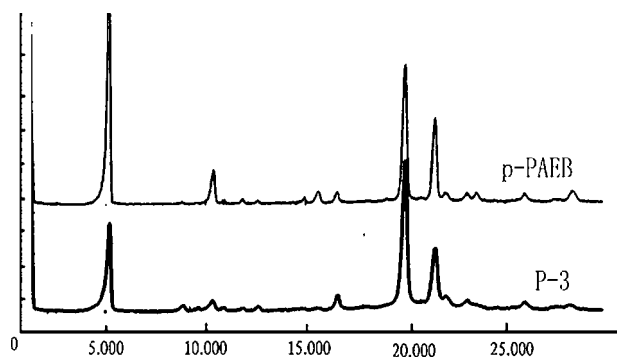
The crosslinking density in general polymer networks is related to the added amount of crosslinked agent. It is assumed that the amounts of crosslinked agent fed in the monomer mixtures are roughly equal to the crosslinking density of the polymer networks, when the conversion of the monomer mixtures is higher than 90%. Figure 7 indicates the effect of the crosslinking density on the phase transition behavior of the poly(*p*-PAEB/St). To clarify the effect of the crosslinking density on the phase transition behavior, the change in the phase transition temperature is shown in Table II. As seen from Figure 7 and Table II, the phase transition temperature

changed irregularly with the increase of the LC monomer in the polymer networks, but the range of mesomorphic state changed regularly. It is broadened with the increase of the LC monomer in the copolymeric networks. The result suggests that the irregularity in  $T_m$  and  $T_i$  may be due to liquid texture and entanglement by incorporation of mesogenic groups. As shown in Figures 3 and 4, the homopolymer is nematic in texture, but the copolymer is smectic in texture. The copolymer has a higher  $T_m$ , which is due to smectic texture of LC unit, and so the molecular motion becomes less. The melting point  $T_m$  becomes lower with increasing amounts of styrene; this is due to increased degree of incomplete focal-conics texture. The  $T_m$  and  $T_i$  have a maximum value for P-3; it may be due to the



**Figure 4** Textures of copolymer at 120°C (A) P-2 and (B) P-4. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



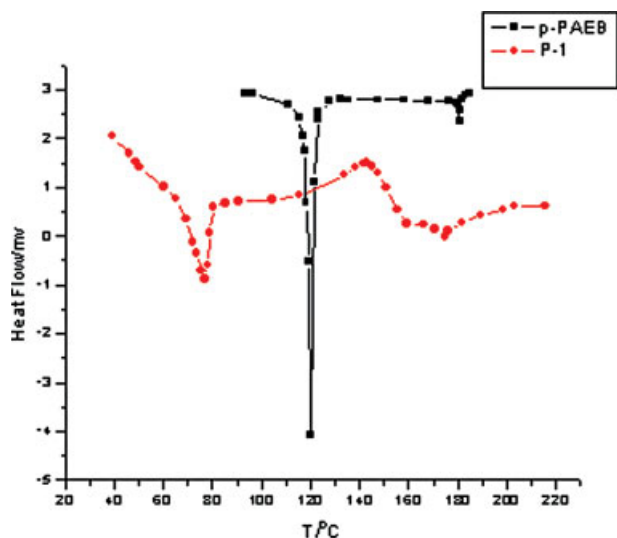


**Figure 5** WAXD curves of *p*-PAEB at 130°C annealed, P-3 at 135°C annealed.

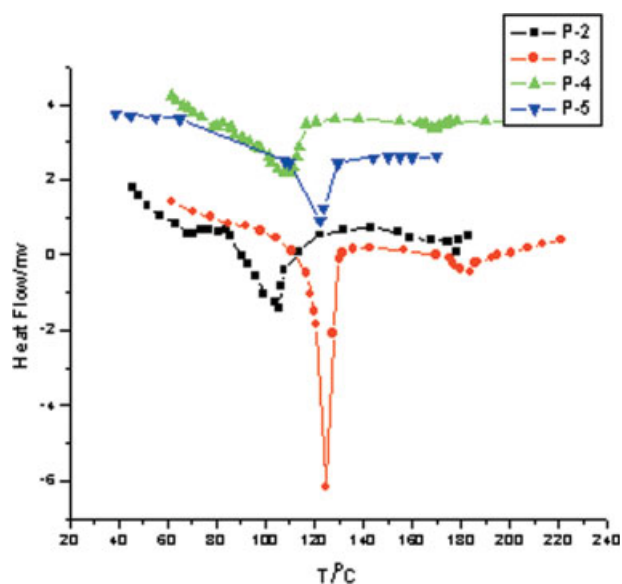
congregation of liquid texture and entanglement of mesogenic groups with styrene units, which is the most at this ratio.

### Mechanical loss and glass transition temperature

Because the glass-transition temperature ( $T_g$ ) can be used effectively to monitor the molecular motion and curing reaction, the TBA can be used to determine the  $T_g$  of the thermosetting system, and it is particularly useful at high conversion and after vitrification because of the nonlinearity of  $T_g$  versus conversion reaction.<sup>20</sup> Generally, there is a one-to-one relationship between the  $T_g$  and peak temperature  $T_p$  of mechanical loss factor. The higher the peak temperature  $T_p$  of mechanical loss factor, the higher the  $T_g$  and a densely crosslinking density, which depends upon the curing conditions, such as amount of cross-



**Figure 6** DSC thermograms of monomer (*p*-PAEB) and homopolymer poly(*p*-PAEB). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



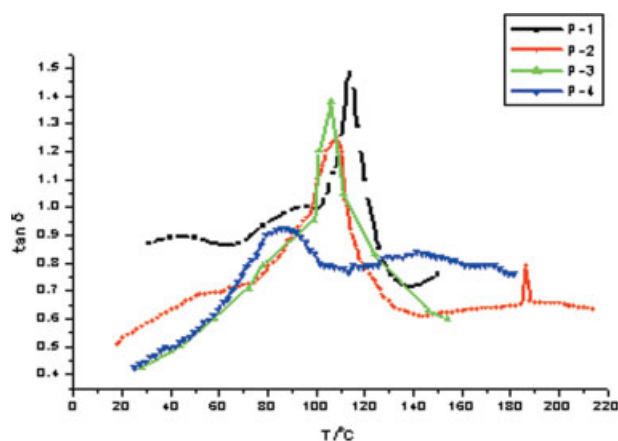
**Figure 7** DSC thermograms for copolymers poly(*p*-PAEB/St). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

linked agent, cure temperature, and time. With these curing conditions varying, the peak temperature  $T_p$  and  $T_g$  of the system will be changed, so that,  $T_g$  has been used directly as a parameter in the analysis of reaction kinetic models.<sup>20,21</sup> It is a convenient parameter because of the ease of measurement of  $T_g$  by TBA for the crosslinked polymer system.<sup>22</sup> In this work, the TBA was used to determine the mechanical loss of the LC polymer network systems. The peak temperature  $T_p$  of mechanical loss factor of poly(*p*-PAEB/St) specimens from TBA measurements are shown in Figure 8 and Table II.

As seen from Figure 8 and Table II, the dynamic mechanical spectrum for LC crosslinked copolymers and some difference in the  $T_p$ 's were observed in accordance with the ratio of the LC monomers. The low content of *p*-PAEB monomer favors lower  $T_p$ . These results also indicate that the macroscopically uniaxial molecular orientation of LC monomer and LC order-distribution is playing a more important role in the mechanical loss and glass transition.

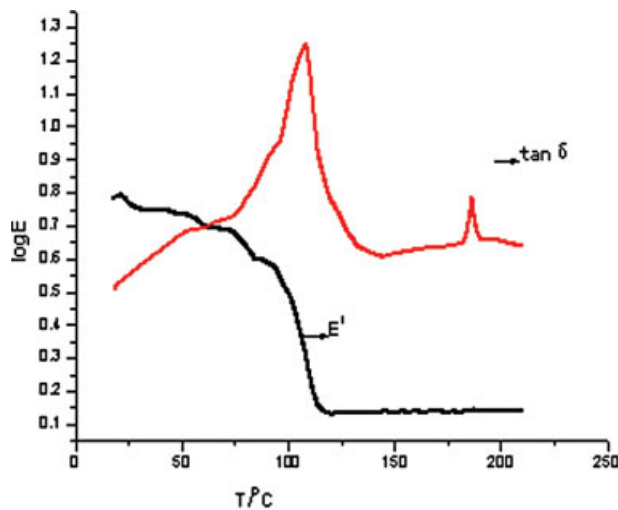
**TABLE II**  
Phase Transition Temperatures and  $T_p$  of LC Monomer and Copolymers

	Polymers					
	<i>p</i> -PAEB	P-1	P-2	P-3	P-4	P-5
<i>p</i> -PAEB/St (mol ratio)	—	1/0	3/1	2/1	1/1	1/2
Melting point (°C)	120.5	77	106	125	108	122.5
Clearing point (°C)	191.5	170	176	185	168	—
Range of LC state (°C)	71	93	70	60	60	—
$T_p$ (°C)	—	114	108	105	90	87



**Figure 8** Dynamic mechanical spectrums for crosslinking copolymers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The second mechanical loss peak  $T_{p2}$  for P-2 in Figure 9 is the transition temperature from LC phase to isotropic temperatures  $T_i$  of the LC polymer networks ( $N$ -I transition range). It is due to the lightly crosslinking effect on the thermal reversibility of the macroscopically molecular orientation of LC polymer networks.



**Figure 9** Dynamic mechanical spectrum of the fully cured P-2 system. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

## CONCLUSIONS

1. The  $p$ -PAEB is a smectic LC compound, the homopolymer of  $p$ -PAEB has a nematic texture and copolymers with styrene are smectic LC polymers.
2. The LC properties, in particular the phase transition temperatures ( $T_m$ ,  $T_i$ ) of the monomer  $p$ -PAEB has a temperature range of 120.5–191.5°C, but the homopolymer of  $p$ -PAEB has a broader LC temperature range from 77 to 170°C. The LC temperature range of poly( $p$ -PAEB/St) was broadened with increased content of  $p$ -PAEB.
3. The temperature  $T_p$  of mechanical loss peak and  $T_g$  of poly( $p$ -PAEB/St) varied with content of LC monomer, the more the content, the higher  $T_p$  or  $T_g$ , but  $T_g$  is not higher than  $T_m$  of LC monomer in the copolymer.

## References

1. Broer, D. J.; Hynderickx, I. *Macromolecules* 1990, 23, 2774.
2. Hikmet, R. A.; Lub, J. *Prog Polym Sci* 1996, 21, 1165.
3. Hoyle, C. E.; Watanab, T.; Whitehead, J. *Macromolecules* 1994, 27, 6581.
4. Kurihara, S.; Ohta, H.; Nonaka, T. *Polymer* 1995, 36, 849.
5. Kurihara, S.; Iwamoto, K.; Nonaka, T. *Polymer* 1998, 39, 3565.
6. Braun, D.; Frick, G.; Grell, M.; Klimes, M.; Wendorff, J. H. *Liq Cryst* 1992, 11, 929.
7. Kurihara, S.; Sakamoto, A.; Nonaka, T. *Macromolecules* 1999, 32, 3150.
8. Broer, D. J.; Finkelmann, H.; Koudo, K. *Makromol Chem* 1988, 189, 185.
9. Jahromi, S.; Lub, J.; Mol, G. N. *Polymer* 1994, 35, 622.
10. Giamberti, M.; Amendola, E.; Carafagna, C. *Macromol Chem Phys* 1997, 198, 3185.
11. Hoyt, A. E.; Benicewicz, B. C. *J Polym Sci Part A: Polym Chem* 1990, 28, 3417.
12. Liu, X. B.; Mi, J.; Gu, Y. *Polym Mater Sci Eng* 1995, 11, 112.
13. Mormann, W.; Zimmermann, J. *Liq Cryst* 1995, 19, 227.
14. Shiota, A.; Korner, H.; Ober, C. K. *Macromol Chem Phys* 1997, 198, 2957.
15. Baner, J.; Hoper, L.; Bauer, M. *Macromol Chem Phys* 1998, 199, 2417.
16. Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals*; Leonard Hill: London, 1984.
17. Zhou, Q. F.; Wang, X. J. *Liquid Crystal Polymers*; Science Press: Beijing, 1999; p 75.
18. Hsiue, G. H.; Wen, J. S.; Hsu, C. S. *Polym Bull* 1993, 30, 141.
19. Allock, H. R.; Kim, C. *Macromolecules* 1990, 23, 3881.
20. Simon, S. L.; Gillham, J. K. *J Appl Polym Sci* 1993, 47, 461.
21. Gillham, J. K. *Polym Int* 1997, 44, 262.
22. Venditti, R. A.; Gillham, J. K. *J Appl Polym Sci* 1997, 64, 3.