

Morphology and Thermal Properties of Liquid Crystal *p*-PAEB/*n*-Propyl Methacrylate Copolymers

Jungang Gao,¹ Yong Wang,¹ Guixiang Hou,¹ Guodong Liu²

¹College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

²Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjing 300130, China

Received 15 December 2006; accepted 3 November 2007

DOI 10.1002/app.27674

Published online 23 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The copolymers of *p*-phenylene di[4-[2-(allyloxy) ethoxy]benzoate] (*p*-PAEB) with *n*-propyl methacrylate (PMA) were synthesized. The liquid crystalline behavior and thermal properties of copolymers were studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), X-ray diffractometer (XRD), and torsional braid analysis (TBA). The results of XRD, POM, and DSC demonstrate that the phase texture of copolymers is affected by the composition of liquid crystal units in copolymers. The POM and XRD reveal that liquid crystal monomer (*p*-PAEB) and copolymers of *p*-PAEB with PMA are all smectic phase texture. The dynamic mechanical properties of copolymers are investigated with

TBA. The results indicate that the phase transition temperatures and dynamic mechanical loss peak temperature T_p of copolymers are affected by the composition of copolymers and liquid crystal cross networks. The maximal mechanical loss T_p is 114°C and is decreased with added PMA. The behaviors of phase transition are affected by the crosslinking density, and it is revisable for lightly crosslinking LC polymer networks, but it is nonreversible for the densely crosslinking of LC polymer networks. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1223–1228, 2008

Key words: unsaturated liquid crystal monomer; methacrylate; copolymerization; morphology; thermal properties

INTRODUCTION

Liquid crystal (LC) materials have great potential for functional molecular systems because of their self-organized dynamic structure. Thermotropic LC compound is a sort of LC compounds that has become important in the field of advanced materials, such as electronic devices and high-strength fibers. Recently, many studies have been focused on LC polymer networks by polymerization of liquid crystal monomers.^{1–6} The macroscopically oriented polymer networks were found to exhibit anisotropic mechanical, optical properties, unique thermal properties, and can improve processability. In particular, densely crosslinked polymer network, which were prepared by bi- or polyfunctional LC monomers, showed excellent transparency and stable anisotropic molecular orientation. However, the densely crosslinking of LC polymer networks removed any phase transition due to extreme restriction of molecular motion of the mesogenic groups in the polymer networks. Therefore, the densely crosslinked LC 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 liquid crystal phase and an isotropic phase.⁷

LC monomers having polymerizable groups such as acrylate, methacrylate, vinyl ether, epoxide, and diene derivatives were used in the pursuit.^{7–16} Many studies on liquid crystal polymer networks have been reported with respect to LC epoxide/diamine and LC acrylate/LC vinyl ether.^{10,15,16} We have reported the copolymerization of *p*-PAEB with styrene.¹⁷ In this article, the copolymerization of *p*-PAEB with *n*-propyl methacrylate was investigated, and the morphological texture and thermal properties of these LC polymer networks were examined.

EXPERIMENTAL

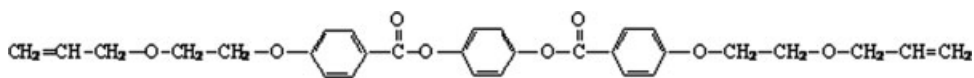
Materials

Allyl 2-hydroxyethyl ether, 4-hydroxy ethyl benzoate, hydroquinone, sulfoxide chloride, dimethylformamide (DMF), tetrahydrofuran (THF), and *n*-propyl methacrylate (PMA) were all analytically pure grades and were supplied by the Beijing Chemical Reagent Co. China.

Correspondence to: J. Gao (gaojg@mail.hbu.edu.cn).

Contract grant sponsor: Natural Science Foundation of Hebei Province; contract grant number: B2005000108.

Contract grant sponsor: Natural Science Foundation of Tianjin; contract grant number: 05YFJMJC05800.



Scheme 1 Molecular Structure of *p*-PAEB.

Synthesis of *p*-PAEB

The liquid-crystalline monomer *p*-PAEB was synthesized according to the literature.^{10,17} The molecular structure of *p*-PAEB is given in Scheme 1.

Copolymerization

The copolymers of poly (*p*-PAEB/PMA) were synthesized according Table I, for example P-5(A): *p*-PAEB (0.01 mol, 5.18 g), PMA (0.02 mol, 2.56 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 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; after filtration, the resulting solid was dried in vacuum overnight at 50°C.

Characterization of copolymers

FTIR spectra of LC copolymers 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., US), scanning rate of DSC measurements was 10°C min⁻¹, and the peak temperatures were taken as the phase transition temperatures. The textures of copolymers were observed by Polarizing optical microscopy (POM, 59XA, Yong-Heng Co. Shanghai, China). The samples for POM were made by melting a small quantity of the material between two thin glass cover slips to get uniform films with heating and holding 5 min at melting temperature, and then quenched them to room temperature quickly with ice water.

X-ray diffraction patterns were recorded by monitoring the diffraction angle 2θ from 1–30° using X-ray diffractometer (Rigaku-D/max-rB, Germany). The diffractometer was equipped with a Cu Kα (λ = 0.1542 nm) radiation, produced under conditions of 40 kV and 100 mA.

TABLE I
Recipes of Copolymerization

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

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 20–300°C.

RESULTS AND DISCUSSION

FTIR analysis

Figure 1 shows infrared spectra of the monomer *p*-PAEB and copolymer P-2(A). The IR spectra of *p*-PAEB and P-2(A) reveal the presence of characteristic absorptions of components. The absorption peaks at 3073 cm⁻¹ of *p*-PAEB can be associated with –C=C– stretching vibration absorption bands, on the other hand, at 3000–2800 cm⁻¹ (CH₂ stretching), 1750 cm⁻¹ (carbonyl group vibration) and 1620–1436 cm⁻¹ (aromatic C=C stretching) are consequences of the *p*-PAEB. Especially, an absorption peak of P-2(A) at 3073 cm⁻¹ becomes much lower than that of *p*-PAEB. Under the same condition and used same means, we can obtain the similar results for other copolymers of poly (*p*-PAEB/PMA) (those IR spectra are omitted, because of the content of *p*-PAEB is the most in P-2), these results show that the *p*-PAEB has polymerized with PMA.

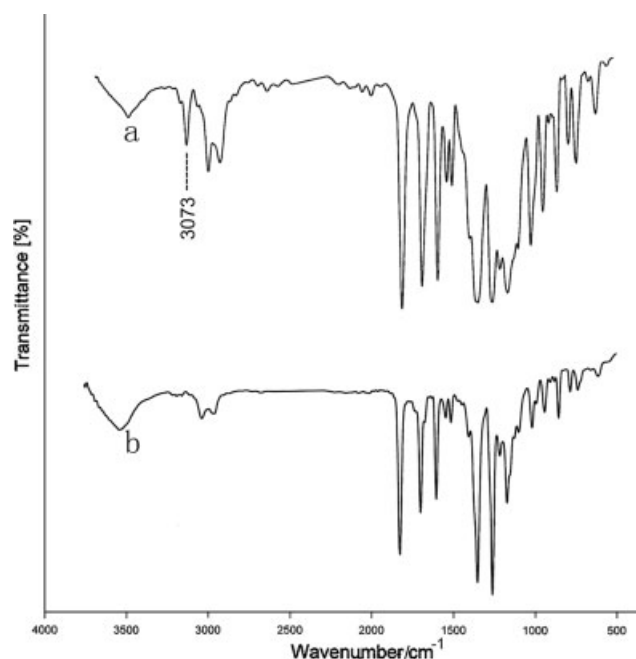


Figure 1 IR spectra of (a) monomer *p*-PAEB and (b) copolymer P-2(A).

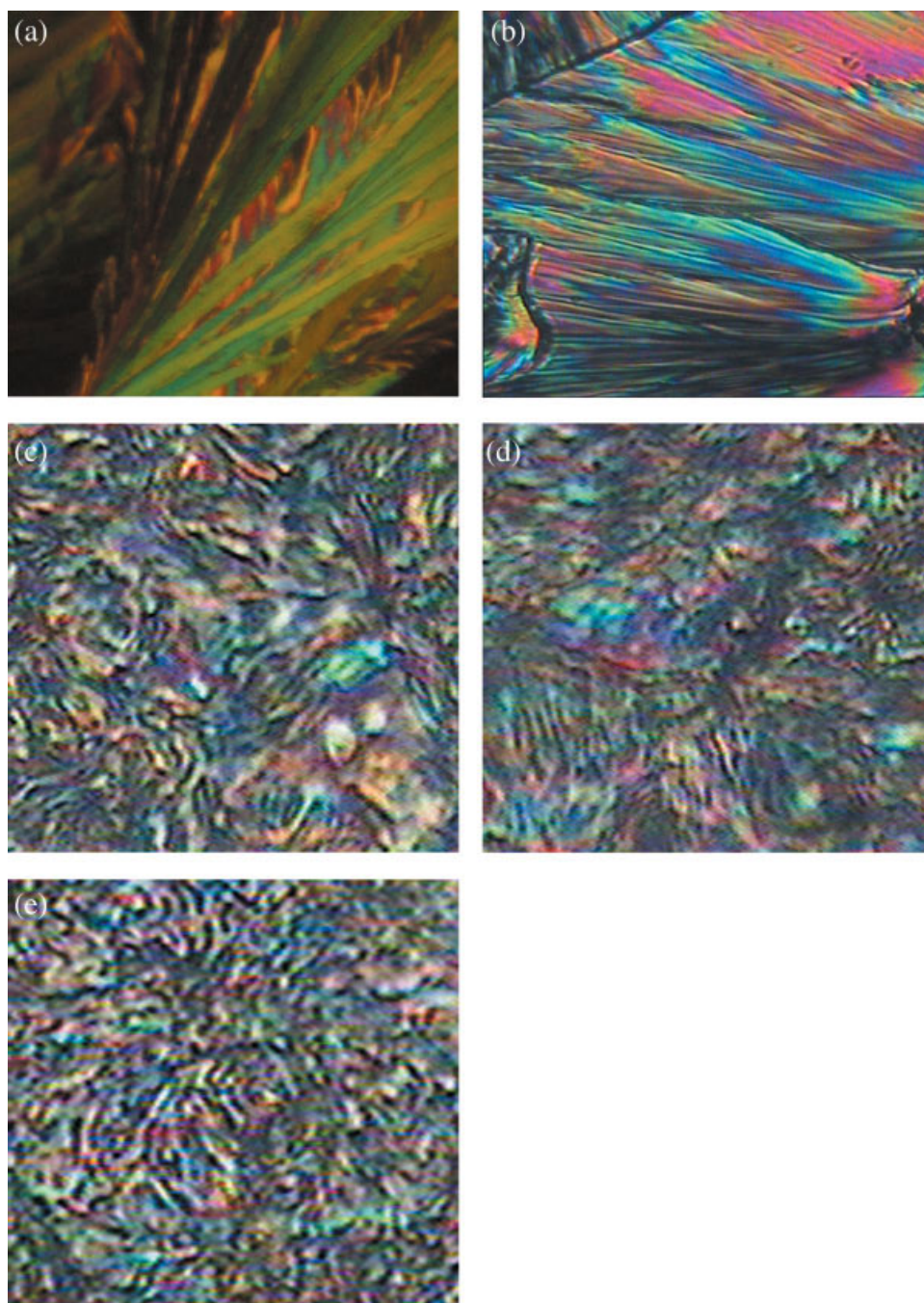


Figure 2 Textures of LC monomer and copolymers quenched at 130°C. (a) *p*-PAEB; (b) P-2(A); (c) P-3(A); (d) P-4(A); (e) P-5(A). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Optical texture and X-ray diffraction

It was found that the copolymers change to liquid crystal phase when heated to their T_m . The broken focal-conics texture or banded texture can be observed in the range of melting temperatures (T_m) to isotropization temperatures (T_i) under POM. The textures of liquid crystal *p*-PAEB and copolymers at 130°C quenched are shown in Figure 2. As seen from Figure 2, the liquid crystal monomer (*p*-PAEB) under POM reveals fan optical texture characteristic

of smectic phase.¹⁸ The texture of copolymer P-2(A) reveals a nonregular fan optical texture of smectic phase when they were cooled from melt, and the other copolymers (P-3 to P-5) reveal only some blurry and nonfan LC texture. The results shown the smectic phase texture was decreased or destroyed by the copolymerization and crosslink, which could be clearly identified in the X-ray analysis described.

XRD patterns of *p*-PAEB and poly(*p*-PAEB/PMA) are shown in Figure 3. The diffraction pattern of

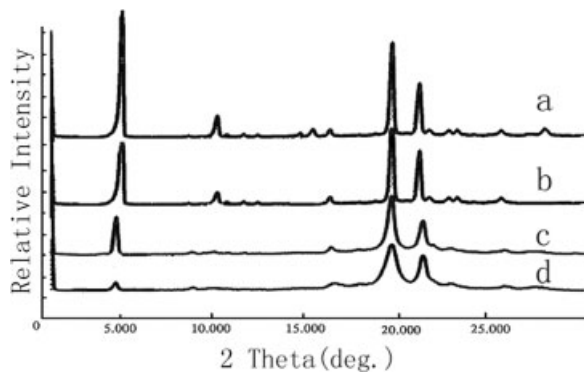


Figure 3 XRD curves of LC monomer and copolymers quenched at 130°C. (a) *p*-PAEB; (b) P-2(A); (c) P-3(A); (d) P-4(A).

p-PAEB exhibited two narrow peaks in the wide-angle region ($2\theta = 20^\circ$, associated to lateral packing), in addition to one sharp peak in the small-angle region ($2\theta = 5^\circ$, associated with smectic layer) which indicates the presence of smectic LC phase.^{18,19} The X-ray diffraction patterns of poly(*p*-PAEB/PMA) showed two higher diffuse peaks in the wide-angle region ($2\theta = 20^\circ$), but showed only a little peaks in the small-angle region ($2\theta = 5^\circ$), and the peak value decreased with decrease of LC *p*-PAEB content from P-2(A) to P-4(A). The result shows that the smectic texture is primary in the copolymers, which is same with the smectic texture of copolymers for *p*-PAEB/St.¹⁷ But the copolymers have a lower crystallinity than monomer and the copolymerization and crosslink can destroy or decrease the crystallinity. The small-angle diffraction ($2\theta = 5^\circ$) corresponds to layer spacing of smectic phase $d = 1.7$ nm for *p*-PAEB. The wide-angle diffraction ($2\theta = 20^\circ$) corresponds to an intermolecular spacing (or the diffuse diffraction) of 0.446 nm.

To obtain more structure information of meso-phase, the XRD data can be analyzed on the Scherrer equation.¹⁹

$$D_{hkl} = K\lambda/\beta \cos \theta$$

where D_{hkl} is grain size; K is a constant ($K = 0.9$); β is half bandwidth, ($\beta^2 = B^2 - \beta_0^2$), B is actual half bandwidth; β_0 is width factor (0.15°); θ is angle of diffraction (radian). Table II shows the main crystal data of poly (*p*-PAEB/PMA) from Figure 4. The

TABLE II
The Main Crystal Data of Poly(*p*-PAEB/PMA)

Sample	2θ ($^\circ$)	d_{hkl} (nm)	B	β	D_{hkl}
P-5(A)	20.005	0.4438	0.540	0.519	154.99
	21.664	0.4102	0.450	0.424	190.13
P-2(A)	19.987	0.4114	0.630	0.612	131.44
	21.600	0.4000	0.540	0.519	155.32

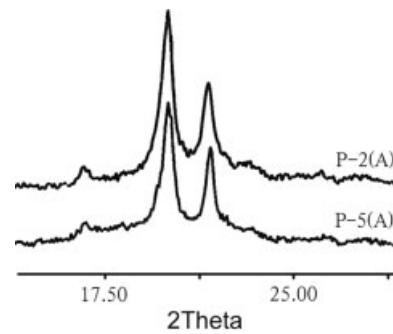


Figure 4 XRD curves of P-2(A) and P-5(A).

more content of PMA monomer favors longer intermolecular spacing, smaller crystalline density but higher crystalline size.

DSC studies of polymer networks

Figure 5 show the DSC thermograms obtained for LC monomer (*p*-PAEB) and LC copolymer P-3(A). As seen from Figure 5, in heating DSC scan of monomer (*p*-PAEB), two peaks are observed at $T_m = 120.5^\circ\text{C}$ and $T_i = 179.5^\circ\text{C}$, the enthalpy change ΔH_m is $30.51 \text{ kJ mol}^{-1}$ and ΔH_i is 0.89 kJ mol^{-1} , respectively. But the T_m of copolymer P-3(A) decreases about 6°C , it is 114.8°C and the isotropic transition temperature T_i (clearing point) of P-3(A) is so not clear because the effect of copolymerization and crosslinking. The crosslinking density in polymer networks is related to add amount of crosslinking agent. It is assumed that the amounts of *p*-PAEB fed in the monomer mixtures are roughly equal to the crosslinking density of the polymer networks, because the conversion of the monomer mixtures is higher than 90%. The effect of the crosslinking density is interpreted in terms of extreme depression in

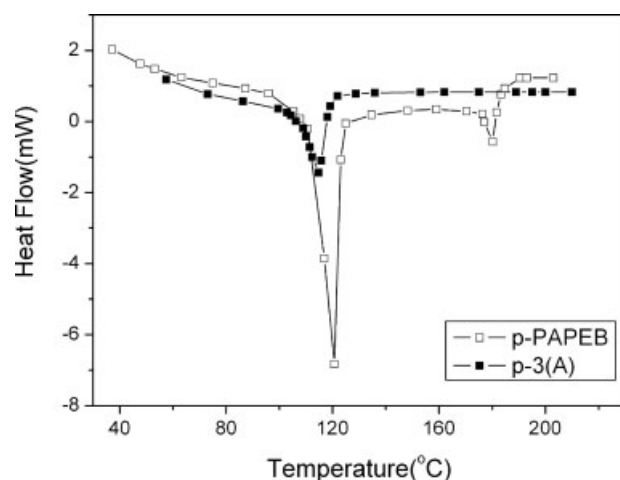


Figure 5 DSC thermograms of monomer *p*-PAEB and P-3(A).

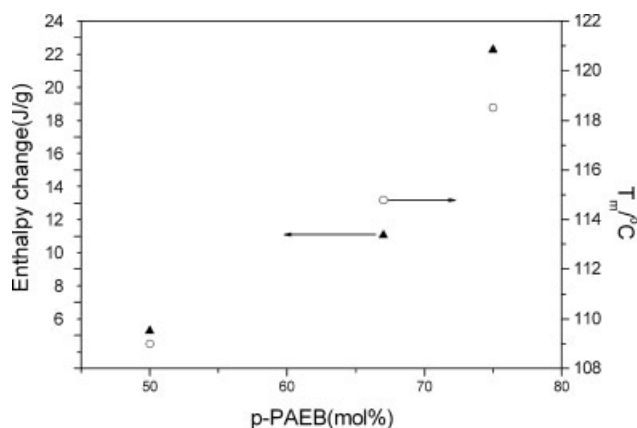


Figure 6 Effect of crosslinking density on enthalpy change and phase transition temperature (T_m) of poly (*p*-PAEB/PMA).

the molecular motion of the polymer segments in the polymer networks. The higher the crosslinking density, the lesser the molecular motion becomes. So, we can not see the T_i to the densely crosslinking of LC polymer networks.

To clarify the effect of the content of LC monomer in copolymers on the phase transition behavior, the change in the phase transition temperature T_m and enthalpy change were plotted as a function of the LC monomer in Figure 6. As seen from Figure 6, the T_m increased from 109 to 118.5°C when the amounts of *p*-PAEB increased from 50 to 75%. That is, the phase transition temperature and the enthalpy change increased with the increase of the LC monomer in the polymer networks. But when the mol rate of *p*-PAEB with PMA is lower than 1 : 1, the melting point T_m are changed so not clear. On the other hand, the phase transition temperatures of the liquid crystal polymers can be increased by the incorporation of a bulky rigid group, which increased the

rotational barrier. These all lead the result that the phase transition temperature and the enthalpy change increased with the increase of the LC monomer in the polymer networks. In the same time, the higher crosslink density leads higher stability of liquid crystal molecular orientation and the thermal nonreversibility of the macroscopically molecular orientation.

Mechanical loss and glass transition temperature T_g

Because the glass transition temperature (T_g) can be used effectively to monitor the molecular motion and curing reaction, the torsional braid analysis (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.²⁰ Generally, there is a one-to-one relationship between the T_g and mechanical loss peak temperature T_p . The higher T_p , the higher T_g , which depends upon the curing conditions, such as amount of crosslinked 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, which can be determined by TBA.^{20,21} Figure 7-1 is the TBA graphs of some copolymers. As seen from Figure 7-1, the mechanical loss peak temperature T_p reduced with the increasing content of PMA, and it is identical with T_m . The crosslinking degree will increase with the reaction time under the same amount of crosslinked agent. To know the effect of reaction time to T_p , the T_p s of P-2(A) and P-3(A) specimens cured isothermally at 130°C for various time periods are shown in Table III.

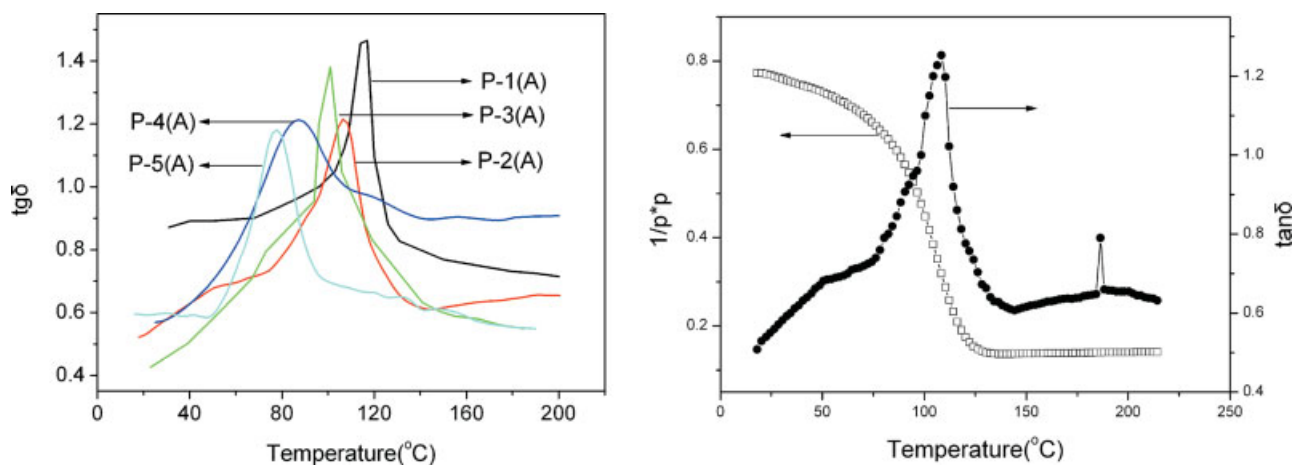


Figure 7 Dynamic mechanical graphs of the poly(*p*-PAEB/PMA). (1) Densely crosslinking copolymers. (2) Lightly crosslinking copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
 T_p of Copolymers for Crosslinking Different Times at the 130°C

	<i>p</i> -PAEB/MA (mol ratio)	T_p (°C) (cure at different times)			
		0.5 h	1 h	1.5 h	2 h
P-2(A)	3/1	110	108	98	97
P-3(A)	2/1	108	105	96	95

As seen from Table III, different glass transition behaviors occurred for the specimens with different curing degrees. T_p decreased with increased curing time. It is different from classical theory of thermosets which T_p increased with curing time. Table III might suggest that the macroscopically uniaxial orientation of LC monomer and LC order-distribution is playing a more important role for T_p or T_g in this system, the longer the reaction time, the lesser the organized property of LC segments, and the lower the T_p . On the other hand, it is pointed out that *n*-propyl methacrylate segments is random domain orientation and has a lower 35°C T_g ,²² the copolymerization of unsaturated LC monomer with methacrylate can raise T_g of polymer.

The second mechanical loss peak in Figure 7-2 is in the N-I transition range of the LC polymer networks. It owes to the lightly crosslinking effect on the thermal reversibility of the macroscopically molecular orientation of LC polymer networks. The intermolecular interaction between mesogenic units is an important factor influencing the phase transition behavior as well as the stability of macroscopically molecular orientation of the LC polymer networks.

CONCLUSIONS

1. The *p*-PAEB is a smectic LC compound, the copolymers of *p*-PAEB with methacrylate are smectic LC polymers, but smectic properties decrease with increase of copolymerized monomer PMA, and copolymerization and crosslinking destroy or decrease the LC regularity.

2. The liquid crystal properties, in particular, the phase transition temperatures (T_m , T_i) and enthalpies are affected by the content of *p*-PAEB, copolymeric monomer, and the crosslinking density.
3. The copolymerization of unsaturated LC monomer which has a higher T_m with methacrylate can raise T_g of polymer, but the crosslinking process of *p*-PAEB/PMA are different from classical systems, a long reaction time is not to achieve a higher T_g , it is affected by the orientation degree of LC monomer molecular.

References

1. Zhang, B.; Tang, G.; Shi, K.; You, Y.; Du, Z.; Huang, J. *J Appl Polym Sci* 1999, 71, 177.
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.; Klimes, M. *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. Jaromhi, S.; Kuipers, W. A. G.; Norder, B.; Ijs, W. J. M. *Macromolecules* 1995, 28, 2201.
10. Jahromi, S.; Lub, J.; Mol, G. N. *Polymer* 1994, 35, 622.
11. Giamberti, M.; Amendola, E.; Carafaga, C. *Macromol Chem Phys* 1997, 198, 3185.
12. Hoyt, A. E.; Benicewicz, B. C. *J Polym Sci Part A: Polym Chem* 1991, 28, 3417.
13. Liu, X. B.; Mi, J. *Polym Mater Sci Eng* 1995, 11, 112.
14. Mormann, W.; Zimmermann, J. *Liq Cryst* 1995, 19, 227.
15. Shiota, A.; Korner, H. *Macromol Chem Phys* 1997, 198, 2957.
16. Baner, J.; Hoper, L.; Bauer, M. *Macromol Chem Phys* 1998, 199, 2417.
17. Gao, J.; Wang, Y.; Hou, G. *J Appl Polym Sci* 2006, 102, 5732.
18. Zhou, Q. F.; Wang, X. J. *Liquid Crystal Polymers*; Science Press: Beijing, 1999; p 75.
19. Allock, H. R.; Kim, C. *Macromolecules* 1990, 23, 3881.
20. Wisanrakkit, G.; Gillham, J. K.; Enns, J. B. *J Appl Polym Sci* 1990, 41, 1895.
21. Venditti, R. A.; Gillham, J. K. *J Appl Polym Sci* 1997, 64, 3.
22. He, M. J.; Chen, W. X.; Dong, X. X. *Polymer Physics*; Fudan Univ. Press: Shanghai, 1990; p 250.