Phase Behavior of Side-Chain Liquid-Crystalline Elastomers and Their Precursors Containing *para*-Nitro Azobenzene

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Received 25 March 2002; accepted 12 August 2002

ABSTRACT: Side-chain liquid-crystalline copolymethacrylates (PMm's), containing *para*-nitro azobenzene as the mesogenic group and 2-hydroxylethyl methacrylate (HEMA) as a comonomer, were synthesized by radical polymerization, and their corresponding liquid-crystalline elastomers (LCEm's) were prepared through chemical crosslinking. All of the polymers (PMm's) and the elastomers studied showed enantiotropic smectic A phases; the clearing temperature (T_i) of the PMm polymers decreased with increasing amount of HEMA, and the T_i of the corresponding LCEm's decreased compared to that of their precursors. Small-angle X-ray scattering studies on the copolymers quenched from their liquid-crystalline phases indicated that the characteristic distance increased with increasing amorphous component content and thus, the amorphous components were in between the smectic layers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2275–2279, 2003

Key words: liquid-crystalline polymer; phase behavior

INTRODUCTION

Liquid-crystalline elastomers (LCEm's) have been highlighted as a new type of liquid-crystalline (LC) materials. They possess unique features originating from rubber elasticity, and the orientation of the mesogens can be controlled by mechanical forces-as-well as by electric and magnetic fields. As a result of these remarkable characteristics side-chain LCEm's are promising materials for optoelectrical applications, including polarization halography, optical memory, integrated optical circuitry, and nonlinear optical generators.[1,2]

Through chemical design, various mesogens can be introduced into the polymer networks for different application considerations. Until now, different kinds of side-chain LCEm's have been reported in the literature,[3–5] and their mechanisms of orientation under mechanical fields were studied. We prepared a series of side-chain LCEm's,[6] and this study focused on the synthesis and characterization of the crosslinkable side-chain LC polymers and the corresponding LCEm's prepared through chemical crosslinking. The effect of the amorphous component on the substructure of the LC polymers was also investigated by small angle X-ray scattering (SAXS).

EXPERIMENTAL

Synthesis of the polymers [copolymethacrylates (PMm's)] and the elastomers (LCEm's)

The polymers were prepared through the reaction given in Scheme I.

4-(4′-Nitrophenylazo)phenol was synthesized according to a method described elsewhere[6] (melting point = 219°C; yield = 85%).

10-[4-(4′-Nitrophenylazo)phenyloxy]decyl bromide (B10) was successfully synthesized by Williamson etherification.[7]

1-[4-Nitroazobenzene-4′-oxy]dodecyl methacrylate (MM10) was synthesized by a liquid–liquid phase-transfer catalysis reaction between B10 and potassium methylacrylate with tetrabutylammonium bromide as a phase-transfer catalyst. A mixture of B10 (0.01 mol), tetrabutylammonium bromide (0.001 mol) in 50 mL of chloroform, and 100 mL (0.1 mol) of potassium methacrylate solution was refluxed for 96 h. MM10 was extracted from the reaction mixture with chloroform, washed with water, and dried over sodium sulfate. The solvent was evaporated, and the solution was precipitated by the addition of a large excess of methanol; the precipitate was filtered off and dried under vacuum for 24 h at 50°C (yield = 91%).

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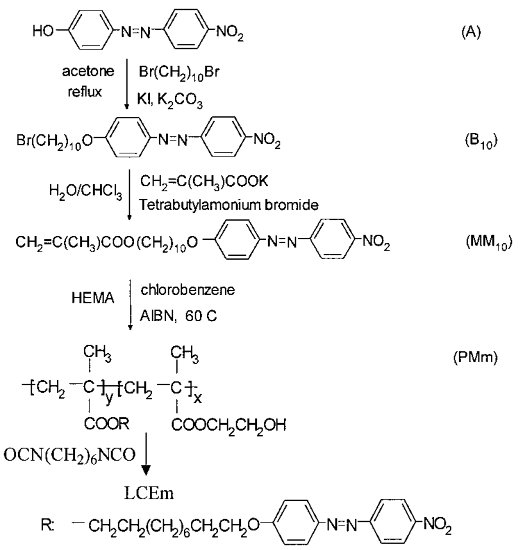
Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 29604002, 29974013.

Contract grant sponsor: Scientific and Technology Committee of Jilin Province.

Contract grant sponsor: Young Teachers Programs, Ministry of Education, People's Republic of China.

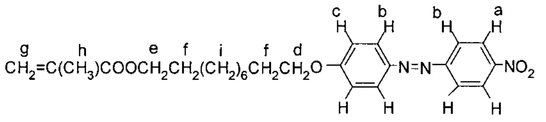
Journal of Applied Polymer Science, Vol. 88, 2275–2279 (2003)



Scheme 1

IR (KBr, γ, cm^{-1}): 2938, 2868 cm^{-1} (s, CH_2); 1726 (s,—C═O); 1640 cm^{-1} (s,—C═C); 1598, 1498, 1452 (aromatic ring stretch); 1520, 1342 (as, s, NO_2), 1252 (s,—C—O—); 859 (s,—C—N); 835 (s, Ar—H).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.35 (d, 2H, H^a); 7.95 (cross-doublets, 4H, H^b); 7.02 (d,2H,H^c); 5.54, 6.12 (2s, 2H, H^g); 4.10, 4.15 (2t, 2H, H^d, H^e); 2.01 (s, 3H, H^h); 1.87 (t, 4H, H^f); 1.4–1.5 (multi, 12H, H^i).

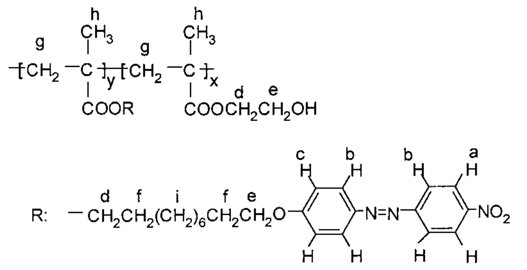


Polymerization

The polymerization of MM10 with different amounts of 2-hydroxyethyl methacrylate (HEMA) was conducted in chlorobenzene at 60°C under a nitrogen atmosphere for 48 h with AIBN as an initiator. The addition of a large amount of methanol precipitated the product.

IR (KBr, ν, cm^{-1}): 2938, 2868 (s, CH_2); 1726 (s,—C═O); 1598, 1498, 1452 (aromatic ring stretch); 1521, 1343 (as, s, NO_2); 1255, 1139 (s,—C—O—); 859 (s,—C—N); 835 (Ar—H); 752, 723.

^{1}H-NMR ($CDCl_3$, TMS δ): 8.35 (broad, 2H, H^a); 7.95 (broad, 4H, H^b), 7.02 (b, 2H, H^c), 4.02 (b, 4H, H^d, H^e), 1.2–2.0 (multi, 22H, H^g, H^h, H^f, H^i).



The composition of the polymers (PMm's) was determined from the integration areas of the peaks of the ^{1}H-NMR spectra. These results are given in Table I.

Crosslinking reaction

The elastomers were prepared by a chemical crosslinking reaction with 1,6-hexyl diisocynate (HDI) as a crosslinking agent and triethylamine as a catalyst. The amount of HDI in the crosslinking reaction was 20% in excess than that of hydroxyl group in the copolymers. Weighted copolymers, HDI, and a catalysis amount of triethylamine were dissolved in CH_2Cl_2, the solvent was evaporated under vacuum for 48 h at room temperature, and the resultant mixture was allowed to react at 80°C, which produced LCEm's. The degree of swelling of the elastomers was determined according to the following equation by the measurement of the weights of the elastomers before (W_1) and after (W_2) dissolution in chlorobenzene:

$$\text{Degree of swelling} = (W_1 - W_2)/W_1 \qquad (1)$$

The degrees of swelling of the elastomers are also listed in Table I

RESULTS AND DISCUSSION

Phase behavior of the polymers and the elastomers

Differential scanning calorimetry (DSC) curves of the polymers and the elastomers in the course of cooling are given in Figure 1. The two transitions for PMm corresponded to the isotropic–LC and LC–crystalline transitions, respectively, whereas that for the elastomers were isotropic–LC transition and glass transition. Wide-angle X-ray diffraction (WAXD) and polarized optical microscopy were used to further elucidate the types of their LC phases. The optical microscope observation indicated that on cooling from the isotropic phase, the batonnets first appeared, and then, the fan-like texture further developed from them; these results confirmed the existence of a smectic *A* phase. Figure 2 shows the WAXD spectra of sample PM1 at different temperatures. At room temperature, the

TABLE I
Structural Parameters of the Polymers (PMm's) and the Elastomers (LCEm's)

Polymer	*x* (%)	*y* (%)	Elastomer	Degree of swelling (%)
PM0	0	100		
PM1	4	96	LCE1	16
PM2	8	92	LCE2	8.0
PM3	12	88	LCE3	6.8
PM4	50	50		

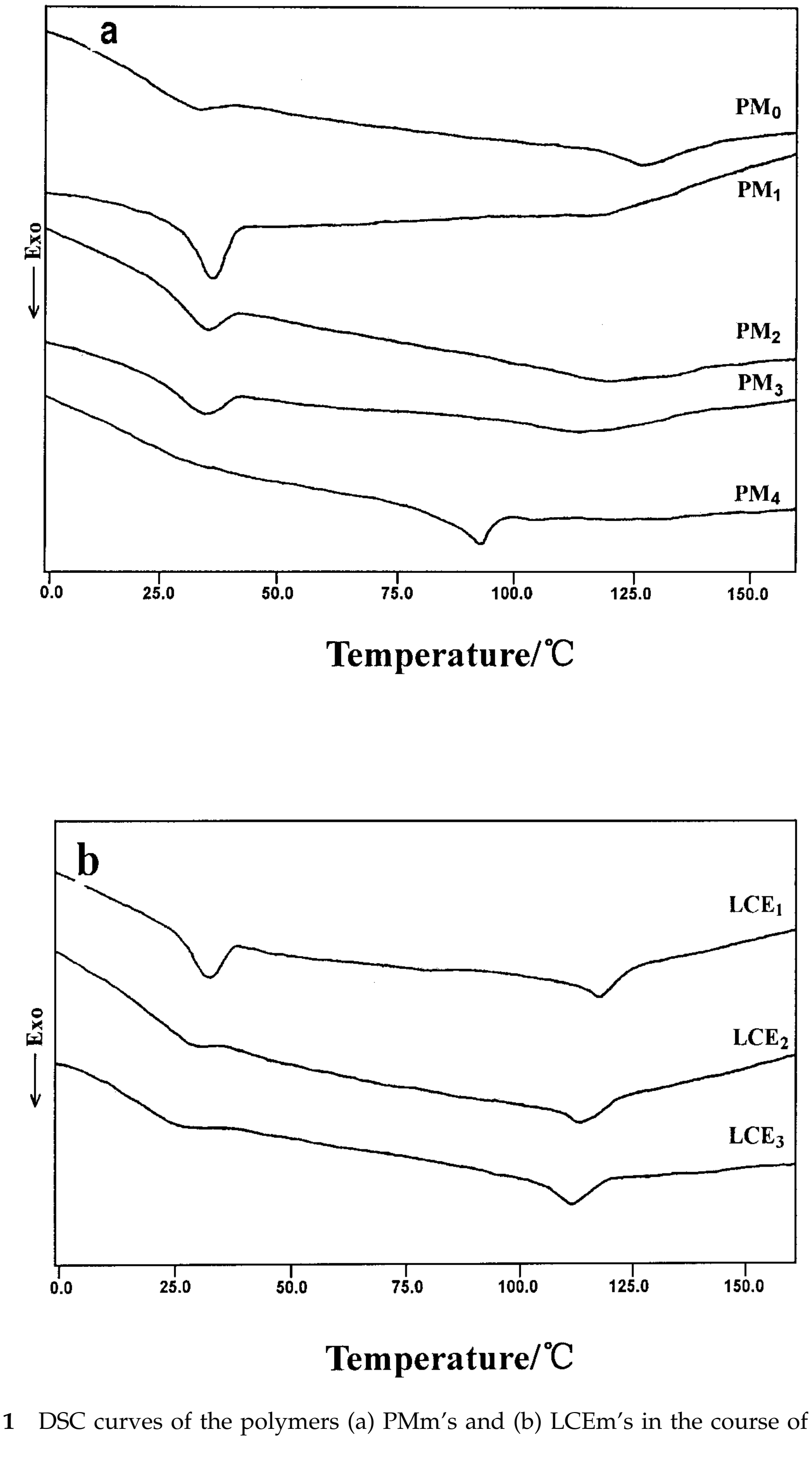


Figure 1 DSC curves of the polymers (a) PMm's and (b) LCEm's in the course of cooling.

spectra showed three diffraction peaks at low diffraction angles (*d*-spacings are given in Table II), corresponding to the two-dimensional arrangement of the mesogenic groups both in the LC phase and in the crystalline phases, and three diffraction peaks corresponding to *d*-spacings of 0.3, 0.35, and 0.52 nm, which were due to the crystallization of the mesogenic group according to our previous publications.[7–9] On increasing temperature to the LC state, the WAXD spectra showed characteristics of the LC phase, that is, a broad

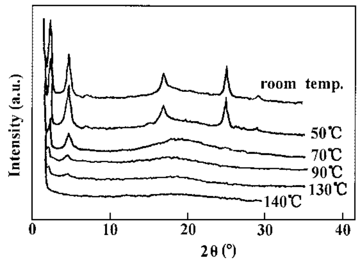


Figure 2 WAXD of PM1 at different temperatures.

TABLE II
d-Spacings, Calculated l's, and Crystallite Sizes (L's) of the Copolymers

Copolymer	d_1 (nm)	d_2 (nm)	d_3 (nm)	d/l	2θ (°)	Peak width (°)	L (nm)
PM0	3.54	1.82	1.23	1.19	2.495	0.3	52.4
PM1	3.80	1.90	1.26	1.28	2.325	0.3	52.4
PM2	3.76	1.95	1.29	1.27	2.350	0.3	52.4
PM4	3.75	2.04		1.26	2.330	0.4	31.4

l of the copolymers was 2.97 nm.

halo at $2\theta = 20°$, corresponding to the lateral arrangement of the mesogens and the two diffraction peaks at lower angles, which are characteristic of the smectic A (SmA) phase. The d-spacings obtained from the Bragger equation and the calculated length of the mesogenic groups, including the flexible spacer and the ester group when it was assumed that the —$(CH_2)_n$— groups were in all-*trans* configuration are listed in Table II. For all of the polymers (PMm's) studied, d/l (where l is the length of the side chains) was in the range of 1–2; thus, the LC phase of the polymers could be assigned to SmAd. No change in the type of LC phases for the elastomers was observed. With the results of DSC, polarized optical microscopy, and WAXD were combined, the thermal transitional properties of both polymers and elastomers are listed in Table III. Both the crystalline and melting temperatures changed little, whereas the smectic–isotropic transition temperatures decreased with increasing HEMA. The clearing temperature (T_i) of the elastomers decreased compared to that of their precursors.

SAXS study on the polymers

SAXS curves of the copolymers at their LC states are given in Figure 3. SAXS curves showed two diffraction peaks, apparently, due to the existence of the periodicity structure, which was formed by the regular arrangement of the mesogenic groups. The characteristic distances calculated from the SAXS curves were 3.93, 4.00, and 4.76 nm for PM1, PM2, and PM4, respectively. Apparently, the characteristic distances changed little with increasing HEMA for the copolymers with lower amounts of HEMA, whereas it increased largely for copolymers with higher contents of HEMA (50%); thus, we inferred that the amorphous regions formed by the backbone were in between the smectic layers. The larger the amount of HEMA was, the longer was the characteristic distance. Like in the crystalline polymers, the characteristic distances were composed of two parts, the ordered region formed by the regular arrangement of the mesogenic groups and the amorphous region formed by the backbone and the amorphous comonomer units. Increasing the amount of amorphous component caused the decrease in the crystallite size. The crystallite sizes of the plane perpendicular to the first-order diffraction peak calculated form the Scherrer equation are also listed in Table II.

TABLE III
Thermal Transitional Properties of the Polymers (PMm's) and the Elastomers (LCEm's)

Sample	Heating	Cooling
PM0	K 54.8 SmA 137.5 I	I 126.8 SmA 31.8 K 25 T_g
PM1	K 55.9 SmA 128.1 I	I 119.7 SmA 37.1 K 25 T_g
PM2	K 55.7 SmA 127.0 I	I 121.1 SmA 35.4 K 25 T_g
PM3	K 54.4 SmA 124.4 I	I 117.8 SmA 35.1 K 25 T_g
PM4	K 54.0 SmA 98.0 I	I 95.0 SmA 34.9 K 25 T_g
LCE1	K 52.0 SmA 122.5 I	I 117.5 SmA 25 T_g
LCE2	K 51.6 SmA 118.5 I	I 112.5 SmA 25 T_g
LCE3	K 52.5.SmA 116.2 I	I 110.6 SmA 25 T_g

K = crystalline; I = isotropic; T_g = glass transition temperature (°C).

CONCLUSIONS

The effect of the amorphous component on the phase behavior and structure, such as the characteristic distance and crystallite sizes of the copolymers, was studied by WAXD, SAXS, and DSC. The results showed that the polymers exhibited smectic A LC behavior, and the amorphous backbones were in between the smectic layers; the characteristic distance and the crystallite size decreased due to the introduction of larger amounts of amorphous component. The melting temperatures of the elastomers changed little compared to that of their precursors, whereas their T_i's decreased

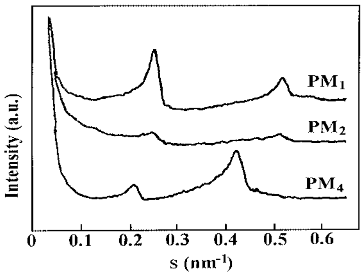


Figure 3 SAXS curves of the copolymers at their LC phases.

compared to that of their precursors due to the introduction of a crosslinking structure.

References

1. Kuzyk, M. G.; Singer, K. D.; Twieg, R. J. J Opt Soc Am B 1998, 15, 257.
2. Bowden, C. M.; Haus, J. J Opt Soc Am B 1989, 4, 685.
3. Davis, F. J.; Michell, G. R. Polymer 1996, 37, 1345.
4. Sommler, K.; Finkelmann, H. Macromol Chem Phys 1996, 196, 3197.
5. Nishikawa, E.; Finkelmann, H. Macromol Chem Phys 1997, 198, 2531.
6. Li, M.; Qiu, H.; Chen, X. Liq Cryst 2000, 27, 1641.
7. Li, M.; Zhou, E.; Xu, J.; Yang, C.; Tang, X. Polym Bull 1995, 35, 65.
8. Li, M.; Zhou, E.; Chen, X. J Appl Polym Sci 1996, 60, 2185.
9. Li, M.; Qiu, H.; Chen, X. Macromol Chem Phys 1999, 200, 834.