

# Main-Chain Chiral Smectic Liquid-Crystalline Ionomers Containing Sulfonic Acid Groups

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**ABSTRACT:** Three series of main-chain liquid-crystalline polymers (P1, P2, and P3) were synthesized by an interfacial condensation reaction of sebacoyl dichloride with various amount of brilliant yellow, isosorbide, and 4,4'-biphenyldiol. P1 series are polyesters prepared from sebacoyl chloride and various amount of 4,4'-biphenyldiol and isosorbide. P2 series are polyesters prepared from sebacoyl chloride and various amount of 4,4'-biphenyldiol, brilliant yellow, and isosorbide. P3 series are polyesters prepared from sebacoyl chloride and various amount of 4,4'-biphenyldiol and brilliant yellow. P2 and P3 are main-chain liquid-crystalline ionomers. P1<sub>2</sub> and P3 series were prepared as model polymers for comparison with the liquid crystalline behavior of ionomers, P2 series. The structures of the polymers were characterized by IR and UV spectroscopy. Differential scanning calorimetry was used to measure the thermal properties of the polymers. The mesogenic properties were investigated

by polarized optical microscope, differential scanning calorimetry, and X-ray diffraction measurements. The results show that P2 series are chiral smectic C ( $S_mC^*$ ) and chiral smectic B ( $S_mB^*$ ) liquid crystalline ionomers exhibiting broken focal-conic texture and schlieren, as is the polymer P1<sub>2</sub>, which has the same amount of 4,4'-biphenyldiol and isosorbide. The introduction of ionic units in P2 series leads to an increase of clearing point, but has not affected the mesogenic type and texture, as compared with the corresponding polymer P1<sub>2</sub>. The introduction of chiral units in P2 series leads to a change of mesophase, as compared with P3 series, which exhibit smectic C mesogetic phase. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1254-1263, 2006

**Key words:** main-chain liquid-crystalline ionomers (LCIs); chiral; isosorbide; sulfonate group; smectic

## INTRODUCTION

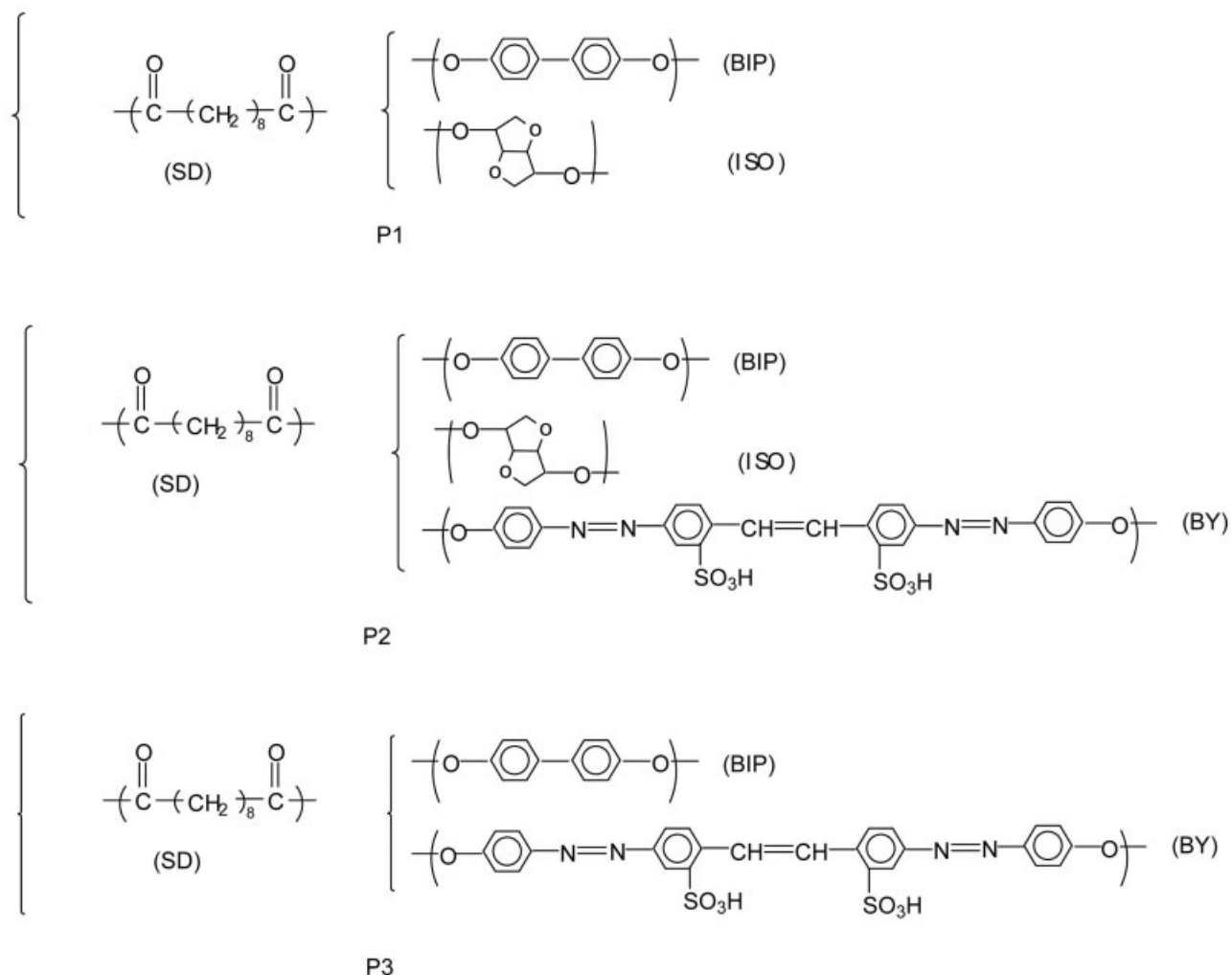
In 1975, Meyer<sup>1</sup> presented theoretically and then proved experimentally that the chiral smectic mesophase was ferroelectric. A small molecule called HOBACPC, which was bistable, fast-switching electro-optical device, was demonstrated a few years later by Clark and Lagerwall.<sup>2</sup> Although a number of studies concerning low molecular weight chiral smectic liquid crystalline materials were previously reported, there have been only a few reports on polymeric chiral smectic liquid crystalline materials, especially on main-chain.<sup>3</sup> Therefore, it would be both necessary and useful to synthesize various kinds of liquid crystalline polymers (LCPs) to explore their potential applications.

LCPs show high strength and high stiffness properties. However, the major shortcoming that limits their application is the weak properties transverse to the fibre axis.<sup>4</sup> Moreover, in blends with other thermoplastic polymers, interfacial adhesion is weak. One approach to improving the transverse properties of LCPs and their adhesion with other polymers is to introduce ionic groups. Ionic groups should promote interchain interactions and improve the interfacial adhesion in the polymers,<sup>5</sup> especially for main-chain LCP containing ionic groups.<sup>6-10</sup> For example, thermotropic LCPs with ionic groups would offer the possibility for promoting intermolecular interaction through hydrogen bonds or ion-dipole association and improvement of the interfacial adhesion between the phases in blends.

In previous studies, we reported the synthesis of four main-chain thermotropic LCIs containing sulfonate groups. They are all nematic ionomers.<sup>11-14</sup> In this study, a new series of main-chain chiral smectic ionomers, P2 series, was prepared to show the effect of ionic groups on chiral smectic LCP, P1<sub>2</sub>. In addition, a new series of main-chain smectic LCIs, P3 series, was prepared as model polymers for comparison with the liquid crystalline behavior of the ionomers, P2 series, to evaluate the effect of chiral building block on smectic LCIs, P3 series.

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Scheme 1 The synthesis of polymers

## EXPERIMENTAL

### Materials

Brilliant yellow (BY, 98%), sebacic acid (SD 99%), 4,4'-Biphenyldiol (BIP,  $\geq 99\%$ ) were obtained from Beijing Chemical Industry Company (China). Isosorbide (ISO,  $\geq 98\%$ ) was bought from Yangzhou Shenzhou new material Co. (China). Thionyl chloride (bp, 78.8°C) and pyridine were obtained from Shenyang Chemical Industry Company (China). Pyridine was purified by distillation over KOH, before using. All solvents and reagents were used as received.

### Characterization

IR spectra were measured using a Perkin–Elmer spectrum (Perkin–Elmer Instruments, Wellesley, MA), as KBr pellets. The UV spectra of solutions of the polymers P2 and P3 series in pyridine ( $c = 0.5$  g/L) were measured with a Perkin–Elmer model 3840 UV-vis spectrometer equipped with a model 7500 data station

(Perkin–Elmer Instruments, Wellesley, MA). Thermal transition temperatures were determined with a differential scanning calorimetry (DSC) 204 (Netzsch instruments) equipped with a liquid nitrogen cooling system at a heating and cooling rate of  $10^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. The reported thermal transition temperatures were collected during the second heating cycle. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) polarizing optical microscope (POM) equipped with a Mettler FP 82 hot stage and FP 80 central processor was used to observe phase transition temperature and analyze LC properties for the polymers through observation of optical textures. X-ray diffraction measurements were performed with nickel-filtered  $\text{Cu-K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation, using a Rigaku powder diffractometer. The optical rotations were determined with a Perkin–Elmer Model 341 Polarimeter. Solutions of 2 g/L in pyridine were measured in 2-mL cuvettes of 100 mm length, using light of a Na-lamp at  $\lambda = 589 \text{ nm}$ . Dilute solution viscosity measurements were carried out in pyridine solution at

TABLE 1  
Polymerization, Specific Rotation, and Intrinsic Viscosity

Polymer	Feed (mmol)				ISO <sup>a</sup> (mol %)	BY <sup>b</sup> (mol %)	[ $\alpha$ ] <sub>589</sub> <sup>30</sup>	[ $\eta$ ] <sup>c</sup>
	SD	BIP	ISO	BY				
P1 <sub>0</sub>	5.50	5.00	0	0	0	0	— <sup>d</sup>	0.560
P1 <sub>1</sub>	5.50	4.50	0.50	0	5	0	7.02	0.490
P1 <sub>2</sub>	5.50	4.00	1.00	0	10	0	28.6	0.451
P1 <sub>3</sub>	5.50	3.50	1.50	0	15	0	35.93	0.402
P1 <sub>4</sub>	5.50	3.00	2.00	0	20	0	38.18	0.371
P1 <sub>5</sub>	5.50	2.50	2.50	0	25	0	43.16	0.330
P1 <sub>6</sub>	5.50	2.00	3.00	0	30	0	57.29	0.305
P2 <sub>1</sub>	5.50	3.96	0.99	0.05	9.9	0.5	27.39	0.294
P2 <sub>2</sub>	5.50	3.92	0.98	0.10	9.8	1.0	26.54	0.287
P2 <sub>3</sub>	5.50	3.88	0.97	0.15	9.7	1.5	25.12	0.276
P2 <sub>4</sub>	5.50	3.84	0.96	0.20	9.6	2.0	25.80	0.275
P2 <sub>5</sub>	5.50	3.80	0.95	0.25	9.5	2.5	26.14	0.272
P2 <sub>6</sub>	5.50	3.76	0.94	0.30	9.4	3.0	26.26	0.263
P3 <sub>1</sub>	5.50	4.95	0	0.05	0	0.5	—	0.317
P3 <sub>2</sub>	5.50	4.90	0	0.10	0	1.0	—	0.208
P3 <sub>3</sub>	5.50	4.85	0	0.15	0	1.5	—	0.201
P3 <sub>4</sub>	5.50	4.80	0	0.20	0	2.0	—	0.192
P3 <sub>5</sub>	5.50	4.75	0	0.25	0	2.5	—	0.190
P3 <sub>6</sub>	5.50	4.70	0	0.30	0	3.0	—	0.184

<sup>a</sup> Mol % of ISO based on SD+BIP+ISO+BY.

<sup>b</sup> Mol % of B Y based on SD+BIP+ISO+BY.

<sup>c</sup> Intrinsic viscosity.

<sup>d</sup> No optical activity.

30 ± 0.2°C, using an Ubbelohde capillary viscometer. The flow times were kept sufficiently long, that is, >100 s, so that kinetic energy corrections could be neglected.

### Synthesis of sebacyl dichloride

Sebacic acid (0.1 mol) and thionyl chloride (0.3 mol) were placed in a 250-mL flask. The mixture was stirred for 2 h at room temperature, and then heated under reflux at 78°C for 4 h. The excess thionyl chloride was removed. The yield of SD is 85%. (bp, 168°C/12 mmHg).

### Synthesis of polymers

The polymer synthesis is outlined in the Scheme 1, and the material compositions used in polymerization are summarized in Table I. For the synthesis of polymers P2 series, interfacial polymerizations were carried out in a high-speed warring blender. SD (5.5 mmol each) in dichloromethane (30 mL) was rapidly added to a slowly stirred aqueous layer (30 mL) composed of BIP, ISO, BY, 0.66 g of sodium hydroxide, and 0.133 g of butyltriethylammonium chloride. The polymers were recovered by slowly adding the resulting slurry to methanol (100 mL), stirring, and filtering. The polymers were washed repeatedly with fresh methanol and methanol/water mixture till the filtrate

was clear and colorless, and finally dried in a vacuum oven at 50–60°C for at least 12 h.

IR (KBr) cm<sup>-1</sup>: 3,366 (—OH), 2,920, 2,850 (—CH<sub>2</sub>—), 1,737 (C=O), 1,601, 1,496 (Ar), 1,200 (C—O—C).

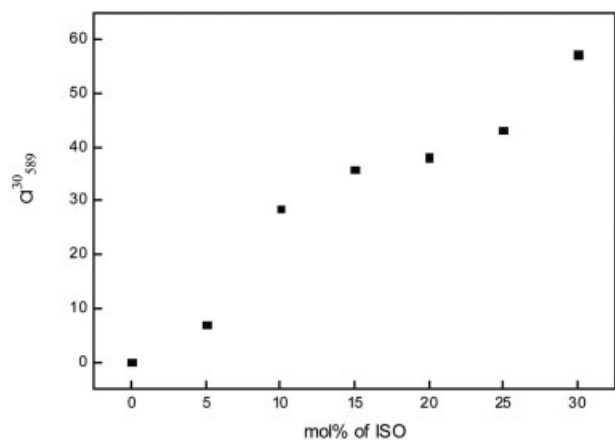
## RESULTS AND DISCUSSION

### Polymerizations

The polymerization experiments are summarized in Table I. The polymer molecular weight is represented by the intrinsic viscosity measured in pyridine at 30°C. The relationship between  $M_v$  and the intrinsic viscosity,  $[\eta] = kM_v^{\alpha}$ , was referred to as Mark-Houwink equation. It does provide estimates for the molecular weights achieved for these polymers.

The intrinsic viscosity of P1 series decreased with the increasing content of ISO in the feed. The main reason may be the increase of flexibility of the chains in the polymers with increasing content of ISO in them.

The intrinsic viscosity of P2 and P3 series decreased with the increasing content of BY in the feed. The reason may be that once the BY reacted, the chain ceased to grow, that is, the addition of the hydrophilic BY pulls the growing chain into the aqueous phase and by doing so, removes the reactive end from the interface. As a result, the reactive end of the chain cannot react further with the acid chloride monomers

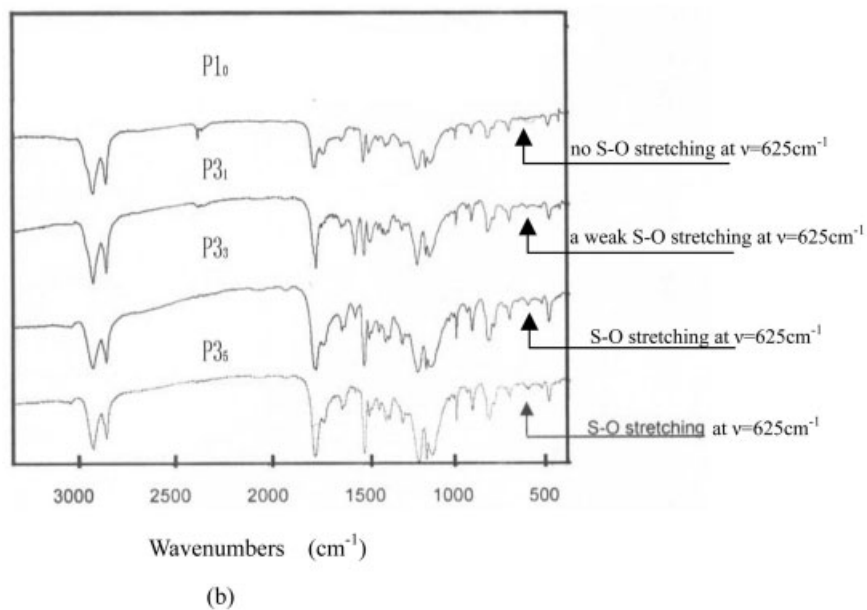
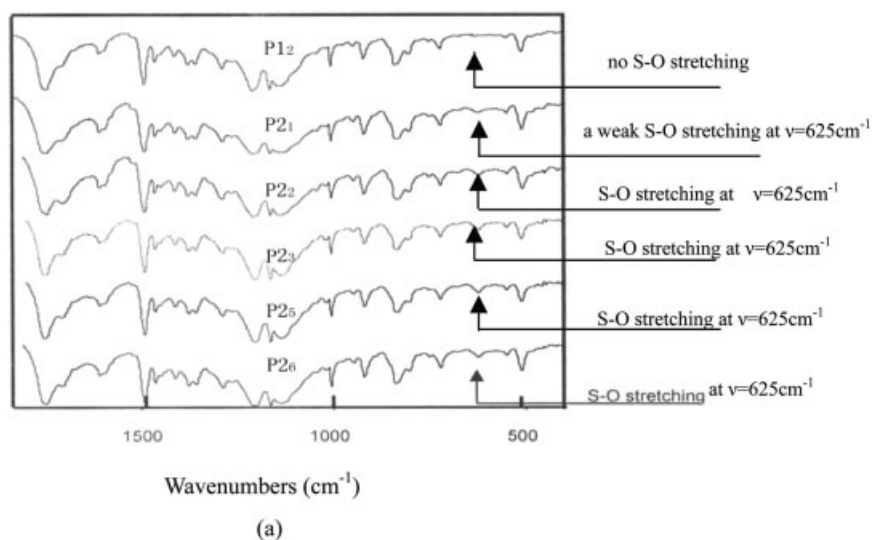


**Figure 1** Variation of SROT with concentration of ISO in the polymers P1 series.

in the oil phase. Thus, the molecular weight and the intrinsic viscosity of P2 and P3 series decrease with the increasing content of BY in the feed.

### Optical rotation

The isosorbide, the polymers P1<sub>1</sub>–P1<sub>6</sub> and P2 series in pyridine solution are optically active in the light of a Na-lamp at  $\lambda = 589$  nm. The specific rotation (SROT) of isosorbide is  $60.5^\circ$ , and the SROTs of the polymers P1<sub>1</sub>–P1<sub>6</sub> and P2 series show similar positive values to isosorbide, as shown in Table I. The isosorbide SROT value was higher than that of the polymers. The variation of SROT for P1 series with the isosorbide content is shown in Figure 1. Figure 1 shows that the SROTs of P1 series increase depending on the increasing isosor-



**Figure 2** IR spectra for polymers.

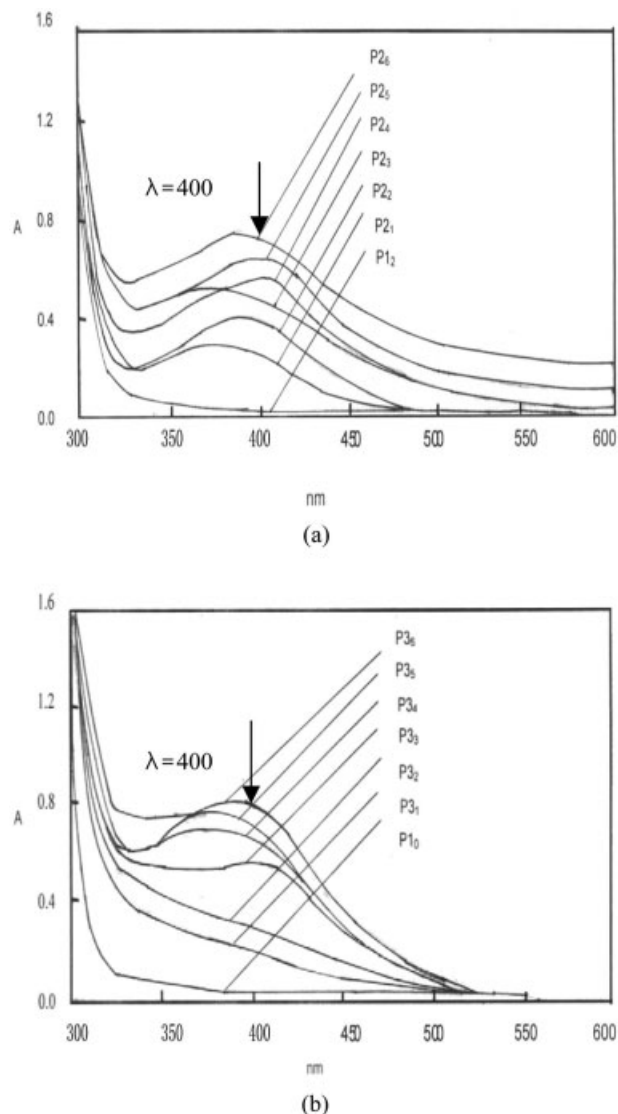
bide content. The higher SROT of isosorbide and the increase of SROT of P1 series with increasing isosorbide content may be explained by the Van't Hoff optical rotation addition theory.<sup>15</sup> The SROT of an optically active compound is the total contribution of every chiral molecule. The concentration of optically active center per mass of polymer sample is lower than that of isosorbide alone; thus, the SROT of isosorbide is higher. The increase of SROT of P1 series is attributed to the increase in density of optically active centers per mass of polymer sample as the isosorbide increased in the polymerization reactions.

### FTIR spectra

The characteristic absorption bands of the ionomers are mentioned above. For organic sulfonate, the FTIR absorption range of the O=S=O asymmetric and symmetric stretching modes lies in 1120–1230  $\text{cm}^{-1}$  and 1010–1080  $\text{cm}^{-1}$ , respectively, and that of the S—O stretching mode lies in 600–700  $\text{cm}^{-1}$ . Because of the overlap found for both asymmetric and symmetric stretching bands of  $\text{SO}_2$  with C—O in the polymers, the S—O stretching mode is chosen for identification of sulfonate groups in the ionomers. The difference between P1<sub>2</sub> and P2 series was that P1<sub>2</sub> did not contain BY groups, nevertheless P2 series contained them. Figure 2(a) compares the FTIR spectra in the range of 500–1500  $\text{cm}^{-1}$  of P1<sub>2</sub> and P2 series, while there is no S—O stretching mode found in that of P1<sub>2</sub>, and such modes as weak absorption bands are found at 625  $\text{cm}^{-1}$  for the P2 series. These results clearly indicate successful incorporation of ionic groups in P2. The difference between P1<sub>0</sub> and P3 series was similar to that between P1<sub>2</sub> and P2 series, namely P1<sub>0</sub> did not contain BY groups, nevertheless P3 series contained them. Figure 2(b) compares the FTIR spectra in the range of 500–3000  $\text{cm}^{-1}$  of P1<sub>0</sub> and P3 series, while there is no S—O stretching mode found in that of P1<sub>0</sub>, and such modes as weak absorption bands are found at 625  $\text{cm}^{-1}$  for the P3 series. These results clearly indicate successful incorporation of ionic groups in P3.

### UV spectroscopy

The UV absorption spectra of P1<sub>2</sub>, P2 series and P1<sub>0</sub>, P3 series in the region  $\lambda = 300\text{--}600$  nm are shown in Figures 3(a) and 3(b), respectively. The absorption peak at  $\lambda = 400$  nm was due to the BY in the LCIs. The absorbance intensity of the peak increased with an increasing BY concentration in the feed. The result of UV analysis showed that the amount of BY in the LCIs increased with the increasing amount of BY in the feed. We are sure that the increase of the absorbance intensity of the peak ( $\lambda = 400$  nm) was not due to the BY monomer because BY monomer is soluble in the



**Figure 3** Effect of the BY content on the UV absorption of polymers ( $C = 0.5$  g/L).

water, and the polymers were washed repeatedly with fresh methanol and methanol/water mixture until the filtrate was clear and colorless, which showed BY monomer was washed away. For the reason, we are sure that the increase of the absorbance intensity of the peak ( $\lambda = 400$  nm) was due to the increase of BY concentration in the polymers. The UV result indicated not only successful incorporation of BY groups, but also an increasing amount of BY in the polymers with increasing amount of BY in the feed.

### Thermal analysis

The phase-transition temperatures and corresponding enthalpy changes of P1, P2, and P3 series obtained on the second heating are summarized in Table II. Rep-

TABLE 2  
DSC and POM Results of Polymers

Polymer	Cr <sub>1</sub> -Cr <sub>2</sub>		Cr-LC <sub>1</sub>		LC <sub>1</sub> -LC <sub>2</sub>		LC <sub>2</sub> -I		$\Delta T^f$ (°C)	LC Phase
	$T^a$ (°C)	$T_g^b$ (°C)	$T_m^c$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$T_1^d$ (°C)	$\Delta H_1$ (J g <sup>-1</sup> )	$T_i^e$ (°C)	$\Delta H_i$ (J g <sup>-1</sup> )		
P1 <sub>0</sub>	67.0	167.0	202.0	7.04	—	—	222.6	0.14	20.6	S <sub>m</sub> C
P1 <sub>1</sub>	64.8	123.9	159.6	9.14	195.0	3.10	213.0	0.40	53.4	S <sub>m</sub> B*, S <sub>m</sub> C*
P1 <sub>2</sub>	63.4	111.2	141.0	4.71	160.9	2.25	186.8	0.25	45.8	S <sub>m</sub> B*, S <sub>m</sub> C*
P1 <sub>3</sub>	61.0	110.0	140.2	3.14	151.8	0.80	175.1	0.66	34.9	S <sub>m</sub> B*, S <sub>m</sub> C*
P1 <sub>4</sub>	60.9	108.0	138.6	3.59	149.5	0.53	171.0	0.14	32.4	S <sub>m</sub> B*, S <sub>m</sub> C*
P1 <sub>5</sub>	60.6	105.0	137.4	3.37	145.1	0.37	163.8	0.58	26.4	S <sub>m</sub> B*, S <sub>m</sub> C*
P1 <sub>6</sub>	60.4	104.0	131.0	3.12	139.0	0.52	158.0	0.52	27.0	S <sub>m</sub> B*, S <sub>m</sub> C*
P2 <sub>1</sub>	66.0	130.9	159.9	1.53	179.7	0.51	216.1	0.61	56.2	S <sub>m</sub> B*, S <sub>m</sub> C*
P2 <sub>2</sub>	64.6	130.6	156.0	2.50	178.3	0.49	211.0	0.28	55.0	S <sub>m</sub> B*, S <sub>m</sub> C*
P2 <sub>3</sub>	65.0	130.2	155.6	1.65	176.6	0.33	207.0	0.33	51.4	S <sub>m</sub> B*, S <sub>m</sub> C*
P2 <sub>4</sub>	64.0	129.8	154.5	1.36	175.1	0.90	204.5	0.47	50.0	S <sub>m</sub> B*, S <sub>m</sub> C*
P2 <sub>5</sub>	63.5	129.2	154.0	1.05	174.0	0.98	203.5	0.98	49.5	S <sub>m</sub> B*, S <sub>m</sub> C*
P2 <sub>6</sub>	61.8	128.8	152.8	0.70	173.2	0.78	201.1	0.25	48.3	S <sub>m</sub> B*, S <sub>m</sub> C*
P3 <sub>1</sub>	68.4	136.1	164.5	3.62	—	—	242.0	0.60	77.5	S <sub>m</sub> C
P3 <sub>2</sub>	65.6	135.0	163.7	3.61	—	—	226.0	0.33	62.3	S <sub>m</sub> C
P3 <sub>3</sub>	60.3	134.6	162.6	5.25	—	—	211.0	0.32	48.4	S <sub>m</sub> C
P3 <sub>4</sub>	57.4	134.2	162.0	6.30	—	—	199.0	0.89	37.0	S <sub>m</sub> C
P3 <sub>5</sub>	56.7	133.4	159.0	3.76	—	—	190.0	0.41	31.0	S <sub>m</sub> C
P3 <sub>6</sub>	56.4	132.6	151.0	2.52	—	—	184.0	0.35	33.0	S <sub>m</sub> C

<sup>a</sup> Transition temperature from crystal 1 to crystal 2.

<sup>b</sup> The glass transition temperature.

<sup>c</sup> The melting temperature.

<sup>d</sup> Transition temperature from S<sub>m</sub>B\* to S<sub>m</sub>C\*.

<sup>e</sup> The clearing point.

<sup>f</sup> Mesophase temperature ranges ( $T_i$ - $T_m$ ).

representative DSC curves of the polymers are presented in Figure 4.

For P1, P2, and P3 series, an enthalpy change was observed at about 60°C. This is the transition temperature from crystal 1 to crystal 2.

The glass-transition temperature ( $T_g$ ) is an important parameter in connection with structures and properties of polymers. In general, the factors of chain

flexibility, molecular weight, and interchain interactions will affect the  $T_g$ . The results of the thermal analysis showed that  $T_g$  of the polymers P1 series decreased with an increase of the concentration of isosorbide in them. As we know,  $T_g$  decreases with an increase of the mobility of chain segments. For polymer P1 series, with an increase of the concentration of isosorbide, the concentration of 4,4'-biphenyldiol decreased, which made the chain flexibility increase, and thus the mobility of chain segments increased and the  $T_g$  decreased.

Table II shows that the  $T_g$  of P2 and P3 series decreased with an increase in BY concentration. A common observation in ionomers is that  $T_g$  increases with an increasing salt group concentration,<sup>16</sup> which attributes to intermolecular ionic interactions. The other observation is that  $T_g$  decreases with an increasing pendant concentration in the polymers, which is due to the large free-volume occupied by the polymer chains. In this study, both of the effects affected the  $T_g$  of P2 series, but neither of them predominated; therefore, the  $T_g$  decreased slightly from P2<sub>1</sub> to P2<sub>6</sub> and this is the same reason for the decrease of  $T_g$  of P3 series.

The melting temperature ( $T_m$ ) of P1 series decreases with an increasing isosorbide concentration, which may be due to the increase of the flexibility of the chains in them.

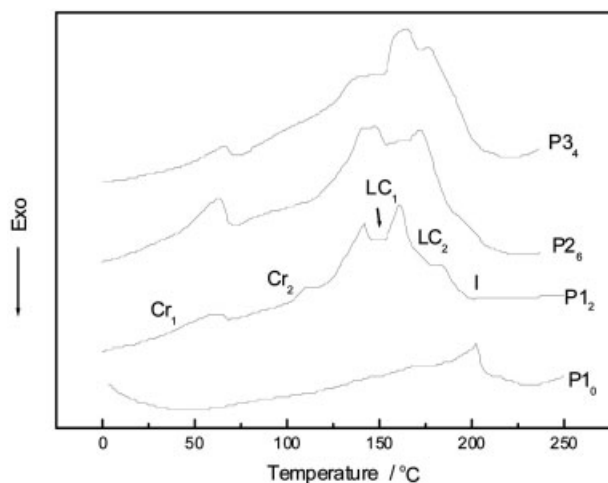
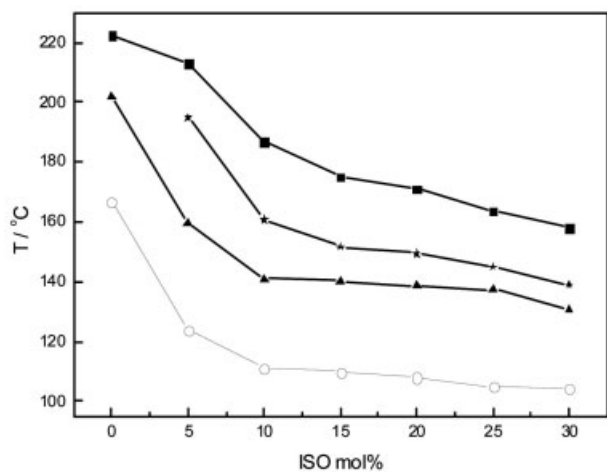
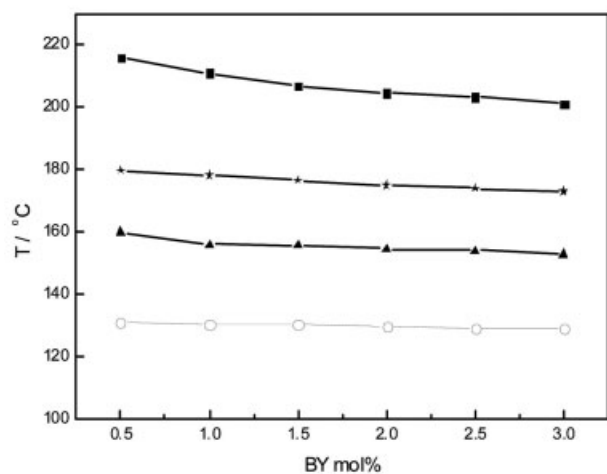


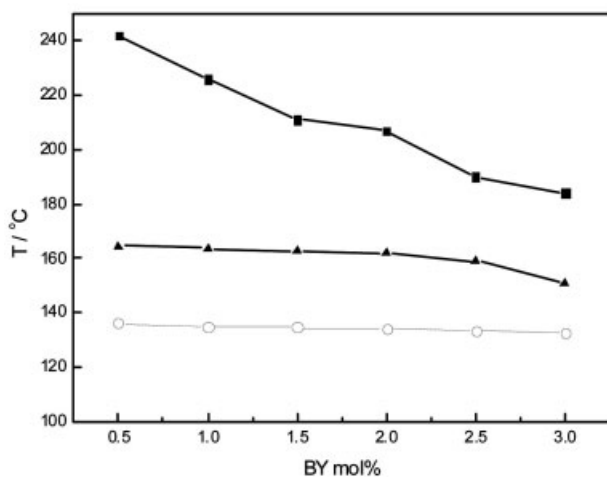
Figure 4 DSC thermograms (second heating) of polymers.



(a)



(b)



(c)

**Figure 5** Effect of ISO or BY content on phase transition temperatures of the polymers. (a) effect of ISO content on phase transition temperatures of P1 series. ■  $T_i$ , ★  $T_1$ , ▲  $T_m$ , ○  $T_g$ . (b) effect of BY content on phase transition temperatures of P2 series. ■  $T_i$ , ★  $T_1$ , ▲  $T_m$ , ○  $T_g$ . (c) effect of BY content on phase transition temperatures of P3 series. ■  $T_i$ , ▲  $T_m$ , ○  $T_g$ .

Table II shows that the  $T_m$  of P2<sub>1</sub> is higher than that of P1<sub>2</sub>. The reason may be due to P2<sub>1</sub> containing BY groups and the concentration of the BY is low, thus the effect of intermolecular ionic interaction dominated and made the  $T_m$  of P2<sub>1</sub> increase. With the increasing of the concentration of BY in P2 series, the effect of large free volume of the pendant groups increased gradually, which could make  $T_m$  decrease, and the both factors have affected the melting temperatures, but neither of them dominated. Thus the melting temperature of P2 series decreased slightly with the increase in the concentration of BY in them. On the other hand, the decrease of the melting temperature of P2 series may be due in part to the decrease in molecular weight. This is demonstrated by the decrease of the intrinsic viscosity of P2 series, shown in the Table I.

The melting temperature of P3 series decreased with the increase in the concentration of BY in them and this may be due to the same reason as that for P2 series.

P11–P16 and P2 series have a LC phase-transition temperature  $T_1$  (LC1–LC2), which has been identified by POM result and X-ray result.

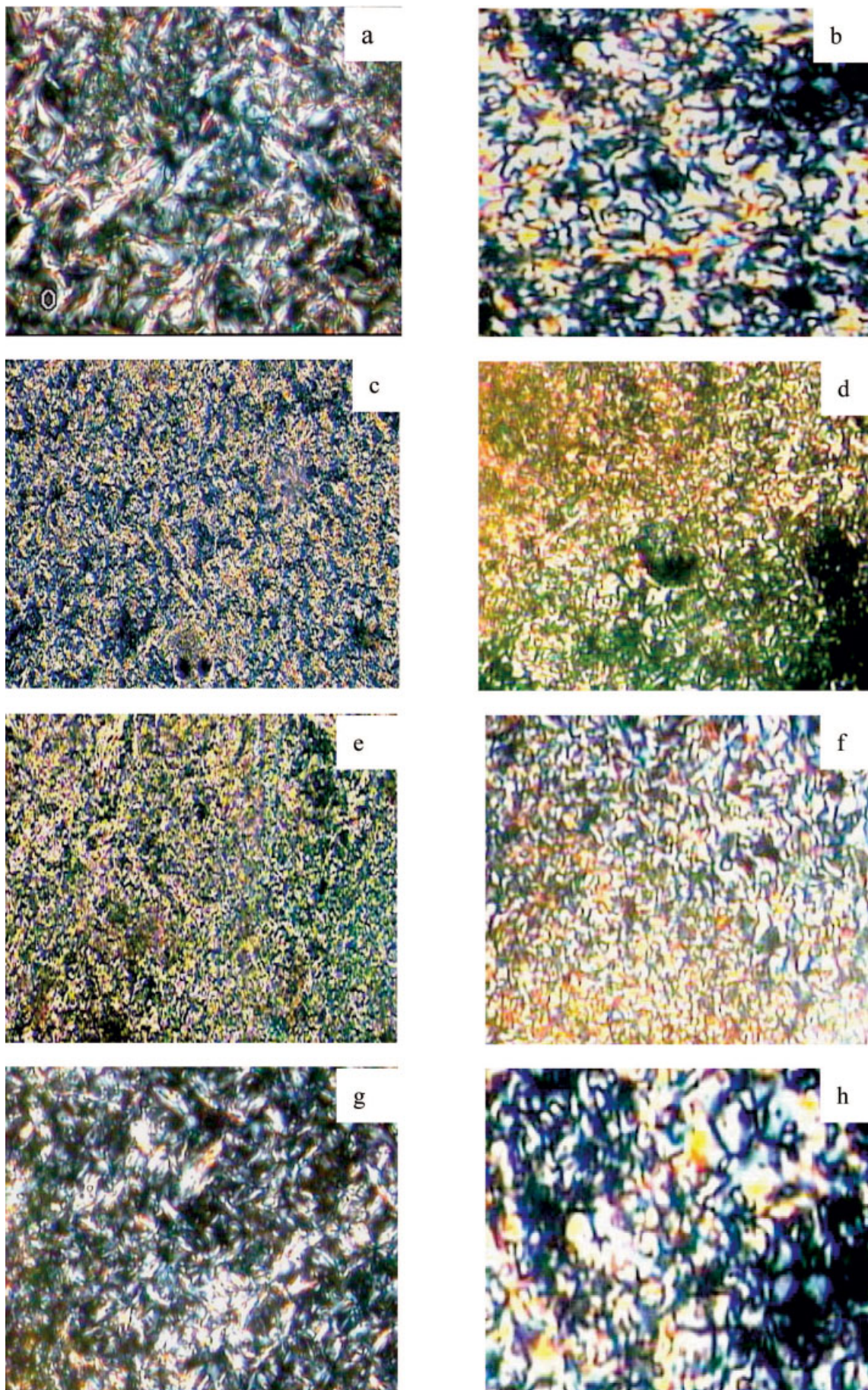
Clearing point ( $T_i$ ) is influenced by the flexibility of the chain, the regularity of polymer molecule, and the steric effect of large groups. The  $T_i$  of P1 series decreased with increasing the concentration of isosorbide. This may be due to the increase of flexibility of the chain in the polymers, which would reduce the energy of disorientation of polymer molecules in the LC phase.

The  $T_i$  of P2 decrease with increasing the concentration of BY in them, which may be partly due to the decrease of molecular weight (which is identified by the decrease of the intrinsic viscosity of P2 series, shown in the Table I) and partly to the large free-volume occupied by the BY groups (which would destroy the regularity of the chains of polymer molecules and reduce the energy of disorientation of polymer molecules in the LC phase).

The  $T_i$  of P3 decrease with the increasing concentration of BY in them and this may be due to the same reason as that for P2.

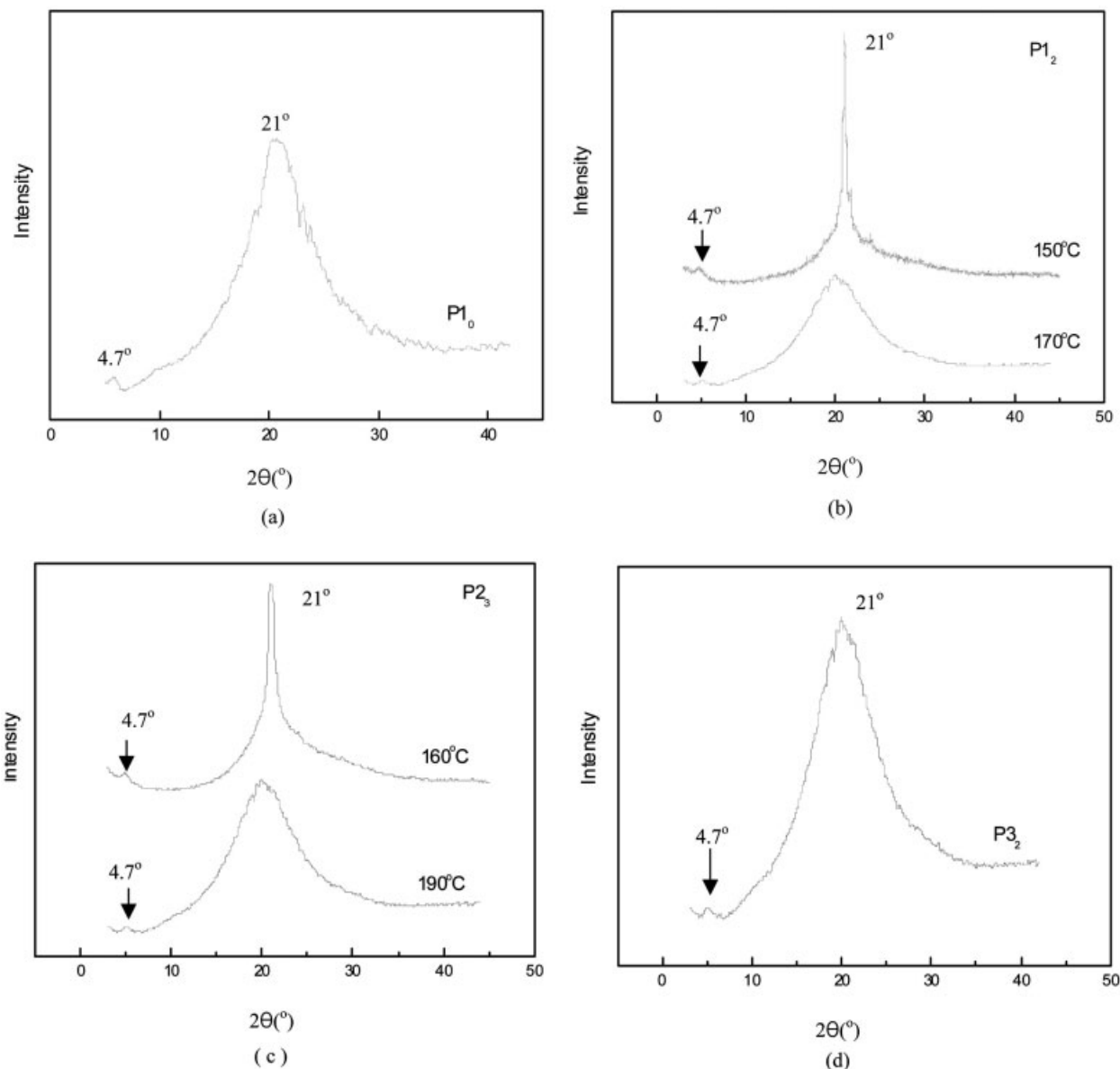
The  $T_i$  of P2<sub>1</sub> is higher than that of P1<sub>2</sub>. As we know, owing to the introduction of ionic groups, the intermolecular ionic interaction will increase the  $T_i$  of polymer, and the large free volume of BY will destroy the regularity resulting in the decrease of  $T_i$  of the polymer. In this condition, the former may be superior to the latter, due to P2<sub>1</sub> containing a low concentration of BY.

The effect of ISO content on phase transition temperatures of P1 series is shown in Figure 5(a), and the effect of BY content on phase transition temperatures of P2 series and P3 series is shown in Figures 5(b) and 5(c), respectively.



**Figure 6** Polarizing optical micrographs ( $\times 200$ ) of polymers: (a) Broken fan-shaped texture of the  $S_mC$  of  $P1_0$  on cooling to  $212^\circ\text{C}$ ; (b) Schlieren texture of the  $S_mC$  of  $P1_0$  on heating to  $206^\circ\text{C}$ ; (c) Broken fan-shaped texture of the  $S_mB^*$  of  $P1_4$  on heating to  $145^\circ\text{C}$ ; (d) Schlieren texture of the  $S_mC^*$  of  $P1_5$  on cooling to  $154^\circ\text{C}$ ; (e) Broken fan-shaped texture of the  $S_mB^*$  of  $P2_1$  on heating to  $175^\circ\text{C}$ ; (f) Schlieren texture of the  $S_mC^*$  of  $P2_1$  on heating to  $190^\circ\text{C}$ ; (g) Broken fan-shaped texture of the  $S_mC$  of  $P3_1$  on cooling to  $213.7^\circ\text{C}$ ; and (h) Schlieren texture of the  $S_mC$  of  $P3_1$  on heating to  $208^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]





**Figure 7** X-ray patterns of the quenched polymers.(a)  $P1_0$  was quenched at  $210^\circ\text{C}$ ;(b)  $P1_2$  was quenched at  $150$  and  $170^\circ\text{C}$ , respectively; (c)  $P2_3$  was quenched at  $160$  and  $190^\circ\text{C}$ , respectively; and (d)  $P3_2$  was quenched at  $190^\circ\text{C}$ .

### Textures analysis

All the polymers displayed a thermotropic mesophase and exhibited different colorful textures when observed under POM. The  $P1_0$  exhibited clear schlieren texture and broken fan-shaped texture on heating and cooling cycles. When  $P1_0$  was heated to  $202^\circ\text{C}$ , the sample began to melt, the typical schlieren texture gradually appeared, and the texture disappeared at  $223^\circ\text{C}$ . When the isotropic state was cooled to  $218^\circ\text{C}$ , the broken fan-shaped texture appeared, and then transformed into schlieren texture, which did not disappear till room temperature. Photomicrographs of  $P1_0$  are shown in Figure 6(a,b).

$P1_1$ – $P1_6$  exhibited the broken fan-shaped and schlieren texture on heating and cooling cycles, as

shown in Figure 6(c,d).  $P2$  series displayed the broken fan-shaped texture and schlieren texture on heating and cooling cycles, as shown in Figure 6(e,f).  $P3$  series exhibited clear schlieren texture and broken fan-shaped texture on heating and cooling cycles, as shown in Figure 6(g,h).

### X-ray diffraction analysis

XRD studies were carried out to obtain more detailed information on the LC phase structure and type. Representative XRD curves of quenched samples are shown in Figure 7. A diffuse peak at about  $2\theta = 21^\circ$  in WAXD curves and a weak small-angle reflection at about  $2\theta = 4.7^\circ$ , which correspond to a  $d$ -spacing of  $d$

= 18.8 and 4.2 Å, were observed for P1<sub>0</sub>, which is shown in Figure 7(a). This was in correspondence with the result of the textures of P1<sub>0</sub>, which indicated P1<sub>0</sub> is S<sub>m</sub>C phase. For P1<sub>1</sub>–P1<sub>6</sub> and P2 series quenched between the  $T_m$  and the  $T_1$  (the transition temperature from LC<sub>1</sub> to LC<sub>2</sub>), a weak small-angle reflection associated with the smectic layers and a strong sharp peak associated with lateral packing were observed at about  $2\theta = 4.7$  and  $21^\circ$ , as shown in Figure 7(b,c). However, when quenched between the  $T_1$  and the  $T_i$ , a diffuse peak at about  $2\theta = 21^\circ$  and a weak small-angle reflection at about  $2\theta = 4.7^\circ$  were observed, as shown in Figure 7(b,c). Generally, in LC main-chain polymers sharp reflections at small angles and reflections at wide angles arising from the ordered smectic phase are observed in the solid state (solid mesophase).<sup>17</sup> The sharp peak at about  $2\theta = 21^\circ$  reflected that the polymers had highly ordered smectic phase. The result of X-ray diffraction analysis, POM, and optical rotation of the P1<sub>1</sub>–P1<sub>6</sub> and P2 series indicated that they can exhibit S<sub>m</sub>B\* and S<sub>m</sub>C\* mesophase at different temperature. The results also indicated that the introduction of ionic groups in P2 did not affect the mesogenic type and texture of P1<sub>2</sub>. For P3 series, a diffuse peak at about  $2\theta = 21^\circ$  and a weak small-angle reflection at about  $2\theta = 4.7^\circ$  were observed, as shown in Figure 7(d). The result of X-ray diffraction analysis, POM, and optical rotation of the P3 indicated that P3 series is S<sub>m</sub>C mesophase.

### CONCLUSIONS

Three series of new main-chain LCPs P1, P2, and P3 series were prepared from sebacoyl chloride and various amount of 4,4'-biphenyldiol, isosorbide, and brilliant yellow. P1<sub>1</sub>–P1<sub>6</sub> are S<sub>m</sub>B\* and S<sub>m</sub>C\* LCPs, which

exhibited broken focal-conics texture and schlieren texture. P1<sub>0</sub>, which does not contain isosorbide and BY, exhibited a typical smectic C texture. P3 series, which contained BY groups, are smectic C LCs. P2 series are S<sub>m</sub>B\* and S<sub>m</sub>C\* LCs containing both isosorbide and BY groups, which exhibited the broken focal-conics texture and schlieren texture. The introduction of ionic units in P2 will increase the thermal stability of the mesophase, but has not affected the mesogenic type and textures of LCP. Nevertheless, the introduction of chiral units in P2 leads to a change of mesophase, as compared with P3 series, which exhibited S<sub>m</sub>C mesogetic phases.

### References

1. Meyer, R. B. *Mol Cryst Liq Cryst Sci Technol* 1977, 40, 33.
2. Clark, N. A.; Lagerwall, S. T. *Appl Phys Lett* 1980, 36, 899.
3. Hans, R. K.; Nicolas, P.; Mihai, G.; Matthias, B. *Macromolecules* 1995, 28, 6565.
4. Aharoni, S. M. *Macromolecules* 1989, 22, 686.
5. Walba, D. M.; Keller, P.; Parmar, D. S.; Clark, N. A.; Wand, D. M. *J Am Chem Soc* 1989, 111, 8273.
6. Yuan, G.; Zhao, Y. *Polymer* 1995, 36, 2725.
7. Wiemesann, A.; Zentel, R. *Polymer* 1992, 33, 5315.
8. Zhao, Y.; Lei, H. *Macromolecules* 1994, 27, 4525.
9. Cochlin, D.; Passmann, M. *Macromolecules* 1997, 30, 4775.
10. Wilbert, G.; Traud, S.; Zentel, R. *Macromol Chem Phys* 1997, 198, 3769.
11. Zhang, B. Y.; Weiss, R. A. *J Polym Sci Part A: Polym Chem* 1992, 30, 91.
12. Zhang, B. Y.; Weiss, R. A. *J Polym Sci Part A: Polym Chem* 1992, 30, 989.
13. Zhang, B. Y.; Guo, S. M.; Shao, B. *J Appl Polym Sci* 1998, 68, 1555.
14. Zhi, J. G.; Zhang, B. Y. *J Appl Polym Sci* 2001, 81, 2210.
15. Van't Hoff, J. H. *Dielagerung der Atome im Raum*, 2nd ed.; Vieweg & Sohn: Braunschweig, 1894; p 119.
16. Fitzgerald, J. J.; Weiss, R. A. *J Macromol Sci Rev Macromol Chem Phys* 1988, 28, 99.
17. Sato, M.; Kitani, Y. *Liq Cryst* 2003, 30, 9.