Mesomorphic Phases of Main-Chain Liquid-Crystalline Polymers with Pendent Sulfonic Acid Groups

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ABSTRACT: Some main-chain liquid-crystalline polymers were synthesized with pendent sulfonic acid groups (0–6 wt %) on the polymer backbone. The solution viscosity behavior, the chemical structures, and the liquid-crystalline (LC) properties were characterized with Fourier transform infrared spectroscopy, elemental analysis, ^{1}H-NMR, differential scanning calorimetry, polarizing optical microscopy, and X-ray measurements. All the polymers displayed a smectic mesophase with a mesogenic range of 142–155°C and good thermal stability. With an increasing concentration of sulfonic acid groups in the polymer systems, some of the polymers exhibited two kinds of mesophases, including smectic and nematic phases. The glass-transition temperatures and isotropic-transition temperature were elevated slightly, whereas the temperature of the smectic–nematic phase transition changed a little. For polymers with a few sulfonated benzene groups, the regular mesogen/soft matrix structures led to a smectic structure because of microdomains between the mesogenic moieties and the soft main-chain matrix, whereas for polymers with an increased number of sulfonic groups, the ionic groups were distributed in both the soft matrix and the LC microphase. Although the increased ionic interactions between mesogens led to more crystalline phases, the strong electrostatic interactions in the ionic group/mesogen/soft matrix systems may have been tangled in domains. Therefore, they disturbed the regular mesogen/soft matrix smectic phase structure, leading to the appearance of a smectic–nematic transition. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 791–797, 2008

Key words: liquid-crystalline polymers (LCP); morphology; phase behavior

INTRODUCTION

Liquid-crystalline polymers (LCPs) show high strength and high stiffness properties, and many studies have been concerned with main-chain liquid-crystalline polymers (MLCPs) because of their technological potential and scientific challenges.[1–5] However, some problems have limited applications of MLCPs as high-performance polymers. A major shortcoming of MLCPs is the large anisotropy of the mechanical properties. Although oriented MLCPs generally have excellent properties in the direction of orientation, transverse properties tend to be poor. Besides, interfacial adhesion is weak when they are blended with other thermoplastic polymers. One approach to improving the transverse properties of MLCPs and their adhesion with other polymers is to introduce ionic groups.[6–9] Ionic groups should promote interchain interactions and improve the interfacial adhesion in the polymers.[10–12] For example, thermotropic MLCPs with ionic groups would offer the possibility of promoting intermolecular interactions through hydrogen bonds or ion–dipole association and improvement of the interfacial adhesion between the phases in blends.

We have been engaging in the study of LC ionomers containing sulfonate groups in recent years.[13–16] Because sulfonate groups show excellent ionic behavior, LCPs with a few sulfonate groups should exhibit ionic behavior and easily keep a liquid-crystalline (LC) mesophase. The incorporation of a small concentration of ions into organic polymers has been shown to lead to microphase-separated ionic domains that greatly influence the properties of the polymers.[17–20] One would like to know the fundamental link between sulfonic ionic aggregation found in the polymers and the behavior of the LC phases. Furthermore, it would be interesting to investigate how sulfonic ionic interactions modify the liquid crystallinity, LC structures, and overall morphology of such MLCPs.

In this study, we prepared a series of thermotropic MLCPs with sulfonic acid groups pendent to the
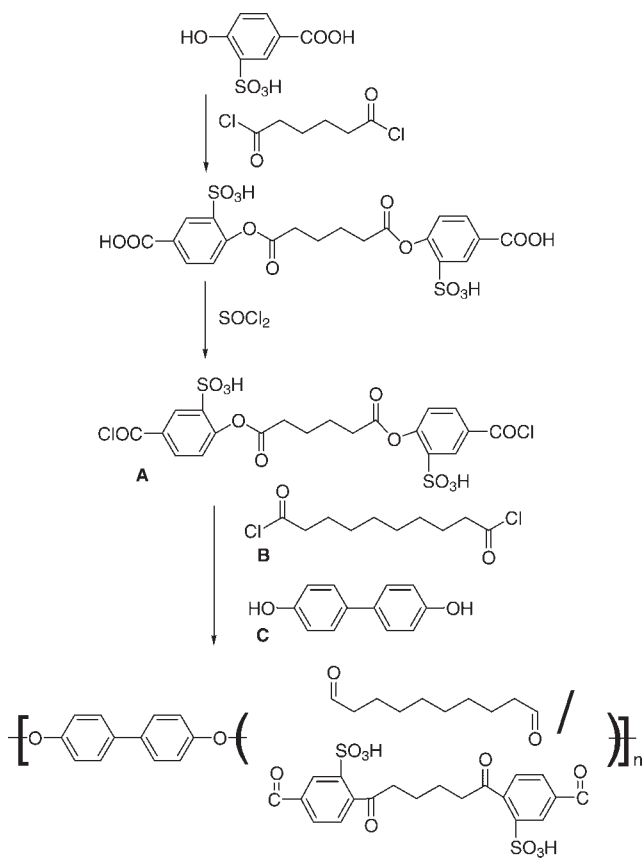
Scheme 1 Synthesis routes of the polymers with pendent sulfonic acid groups.

main chain. Their chemical structure is shown in Scheme 1. The effects of the ions on the mesomorphic properties, thermal stability, and textures are discussed in this article.

EXPERIMENTAL

Materials

4,4′-Biphenyldiol (**C**), 2-hydroxy-5-carboxy-benzene-sulfonic acid, N,N-dimethylformamide, and sebacic acid were purchased from Beijing Chemical Co. (Beijing, China) and used without any further purification. Pyridine, adipoyl chloride, thionyl chloride, ethanol, chloroform, sulfuric acid, and tetrahydrofuran were purchased from Shenyang Chemical Co. (Shenyang, China). Pyridine was purified by distillation over KOH and NaH before being used.

Measurements

^{1}H-NMR (300 MHz) spectra were obtained with a Varian WH-90PFT NMR spectrometer (Varian Associates, Palo Alto, CA) with Fourier transform with dimethyl sulfoxide-d_6 or CDCl$_3$ as the solvent and tetramethylsilane as the internal standard. Fourier transform infrared (FTIR) spectra of the synthesized

polymers and monomers in the solid state were obtained by the KBr method with a Spectrum One spectrometer (PerkinElmer, Foster City, CA). The elemental analyses (EAs) were carried out with an Elementar Vario EL III (Elementar, Hanua, Germany). Thermal transition properties were characterized with a DSC 204 (Netzsch, Wittelsbacherstr, Selb, Germany) at a heating and cooling rate of 10°C/min under a nitrogen atmosphere. Visual observation of LC transitions and optical textures under cross-polarized light was made with a DMRX polarizing optical microscope (Leica, Wetzlar, Germany) equipped with a THMSE-600 hot stage (Linkam, Surrey, England). X-ray measurements of the samples were performed with monochromatic Cu Kα radiation (λ = 1.542 Å) with a DMAX-3A X-ray diffractometer (Rigaku, Tokyo, Japan). Dilute-solution viscosity measurements were carried out in an N,N-dimethylformamide solution at 30 ± 0.1°C with an Ubbelohde capillary viscometer. The flow times were kept sufficiently long, that is, greater than 100 s, so that kinetic energy corrections could be neglected.

Synthesis of bis(4-chlorocarbonyl-2-sulfophenyl) hexanedioate (A)

2-Hydroxy-5-carboxy-benzenesulfonic acid (27.6 g, 0.20 mol) and pyridine (25.0 mL, 0.30 mol) were dissolved in 120 mL of tetrahydrofuran to form a solution. Adipoyl chloride (18.3 g, 0.10 mol) was added to the solution and reacted at 80°C for 6 h, cooled, poured into 1000 mL of cold water, and acidified with 6N H$_2$SO$_4$. The precipitated crude product was filtered and recrystallized from ethanol and dried overnight at 85°C *in vacuo* to obtain a powder of bis(4-carboxy-2-sulfophenyl) hexanedioate in a yield of 70%. The melting point was 201°C.

IR (KBr, cm^{-1}): 3460 (—OH stretching), 2950, 2851 (—CH$_2$—), 2672, 2554 (—OH stretching in —COOH), 1748, 1689 (C=O stretching in different linkages), 1605, 1509 (phenyl), 1427 (C—H bending), 1318, 1292, 1258, 1208, 1161, 1119. ANAL. Calcd for C$_{20}$H$_{18}$O$_{14}$S$_2$: C, 43.96%; H, 3.32%; S, 11.74%. Found: C, 43.45%; H, 3.26%; S, 11.84%. ^{1}H-NMR (δ, ppm): 1.53–2.24 [m, 8H, —OOC(CH$_2$)$_4$COO—], 7.55–8.78 (m, 6H, Ar—H), 10.21 (s, 2H, —COOH), 11.13 (s, 2H, —SO$_3$H).

The intermediate bis(4-carboxy-2-sulfophenyl) hexanedioate (18.0 g, 0.035 mol), 80 mL of thionyl chloride, and 1.0 mL of N,N-dimethylformamide were added to a round flask equipped with an absorption instrument of hydrogen chloride. The mixture was stirred at room temperature for 2 h and was then heated to 60°C and kept there for 24 h in a water bath to ensure that the reaction finished. The excess thionyl chloride was distilled under reduced pressure. Then, 100 mL of cold chloroform was added to

TABLE I
Polymerization and Intrinsic Viscosity ([η]) Values of the Polymers

Sample	Feed			Yield (%)	S from EA (%)	Sulfonic acid (%)[a]	[η]
	A (mmol)	B (mmol)	C (mmol)				
P1	0	2.00	2.0	90	0	0	0.835
P2	0.05	1.95	2.0	92	0.11	0.34	0.803
P3	0.10	1.90	2.0	90	0.29	0.73	0.735
P4	0.20	1.80	2.0	91	0.59	1.49	0.704
P5	0.40	1.60	2.0	92	1.19	3.02	0.571
P6	0.80	1.20	2.0	90	2.42	6.14	0.452

[a] Mass fraction of sulfonic acid groups in the polymer systems according to the EA results.

the residue at 20°C to obtain a chloroform solution of **A.**

Synthesis of sebacoyl dichloride (B)

Sebacic acid (0.099 mol) and thionyl chloride (0.294 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 **B** was 85% (bp = 168°C/12 mmHg).

Synthesis of the polymers

For the synthesis of polymers **P1–P6**, the same method was adopted. The polymerization experiments are summarized in Table I. The synthesis of polymer **P3** is given as an example.

Monomer **C** (0.37 g, 2.0 mmol) was dissolved in 30 mL of pyridine. To the stirred solution, a chloroform solution containing **A** (0.58 g, 0.10 mmol) and **B** (0.46 g, 1.9 mmol) was added, and it was heated under nitrogen and anhydrous conditions at 80°C for 36 h. The chloroform was distilled off. The residue solution was cooled, poured into 100 mL of cold water, and acidified with $6N$ H_2SO_4. After filtration, the product was washed with ethanol and dried at 80°C for 2 h *in vacuo* to obtain 1.20 g of the polymer in a yield of 90%.

IR (KBr): 3463 (—O—H), 2926, 2860 (—CH$_2$—), 1747, 1728 (C=O), 1605, 1497 (Ar), 1293, 1256, 1084. ANAL. Calcd for polymer **P3**. C, 73.85%; H, 7.43%; S, 0.32%. Found: C, 73.74%; H, 7.33%; S, 0.29%. ^{1}H-NMR (CDCl$_3$, δ, ppm): 1.29–2.28 (m, aliphatic hydrogen), 7.58–8.76 (m, Ar—H), 11.10 (s, —SO$_3$H).

RESULTS AND DISCUSSION

Syntheses

The synthetic routes for the target monomers and polymers are shown in Scheme 1. For the intermediate bis(4-carboxy-2-sulfophenyl) hexanedioate, the characteristic absorption bands in FTIR have been mentioned previously. For organic sulfonate, the characteristic FTIR absorption ranges of the O=S=O asymmetric and symmetric stretching modes are 1120–1230 and 1010–1080 cm^{-1}, respectively. Because of the overlap found for both asymmetric and symmetric stretching bands of SO$_2$ with C—O in the polymers, other test analysis technology was chosen for the identification of the sulfonate groups in the compound. The results of EAs and ^{1}H-NMR analysis for the compound clearly showed sulfonic acid groups in the compound. The structural characterizations of the monomers were in good agreement with the predictions.

For the polymers, all the FTIR spectra were similar, except that for **P1**. The characteristic absorption bands of **P3** in the FTIR spectrum have been mentioned previously. It showed characteristic bands at 3463, 1747–1728, and 1605–1497 cm^{-1} attributable to hydroxyl group, ester C=O, and aromatic C=C stretching bands, respectively. The sulfonic acid groups in the polymer systems were also characterized with EA and ^{1}H-NMR, as shown previously. The concentration of sulfonic acid groups in the polymers was calculated according to the concentration of the element S, which was determined via EA, as listed in Table I.

Viscosity of the polymers

The intrinsic viscosity of the polymers is summarized in Table I. The results showed that the intrinsic viscosity of MLCPs with sulfonic acid groups decreased with an increasing concentration of the sulfonic acid groups.

The solution viscosity behavior of all the ionomers was similar. Figure 1 presents the reduced viscosity of polymers **P2**, **P4**, and **P6** in *N,N*-dimethylformamide at 30 ± 0.1°C. When the concentrations were lower than 1.8 g/L, the reduced viscosity of these
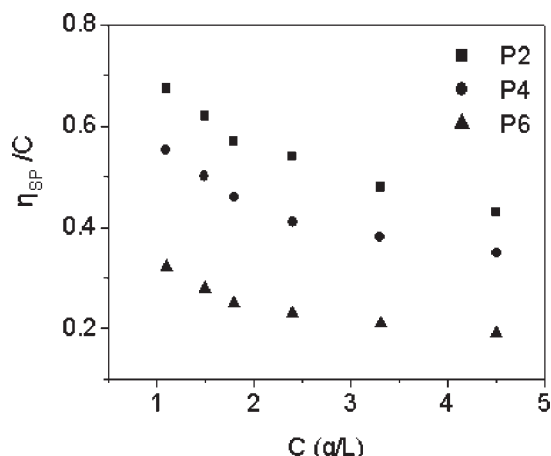
Figure 1 Viscosity (η_{sp})/concentration (C) at $30 \pm 0.1^{\circ}$C in N,N-dimethylformamide versus the concentration of the polymers.

polymer solutions decreased markedly with an increasing concentration of the polymers. However, at high polymer concentrations, the viscosity behavior decreased very slowly with an increasing solution concentration. The reduction of the viscosity at low polymer concentrations was mainly due to the ionization of the ion pair.[21,22] As a result, the unshielded negative charges on the pendent sulfonate groups repelled one another and caused an expansion of the polymers that resulted in an increase in the hydrodynamic volume of the polymers, which is called the polyelectrolyte effect. When the polymer concentration was above 1.8 g/L, which was high enough for intermolecular ionic interactions, reducing the effect of ionization of the ion pair, the viscosity decreased rather slowly.

Thermal analysis

The thermal transition temperatures of the polymers were measured with differential scanning calorimetry (DSC) on the second heating at a heating rate of 10°C/min, and the transition temperatures are summarized in Table II. Figure 2 shows the DSC thermo-

grams of representative synthesized polymers. In the DSC thermograms, polymers **P1** and **P2** revealed a glass transition at a low temperature [glass-transition temperature (T_g)] and a smectic–isotropic transition at a high temperature [isotropic-transition temperature (T_i)], but polymers **P3**–**P6** showed a smectic–nematic transition between T_g and T_i. With an increase in the concentration of sulfonic acid groups in polymers **P1**–**P6**, T_g and T_i increased slightly, whereas the temperature of the smectic–nematic transition (T_{S-N}) changed a little, as shown in Figure 2.

It is well-known that the incorporation of ionic groups leads to an elevation of T_g for ionomers based on amorphous, flexible polymers.[23] Besides, T_g will increase with an increase in the rigid composition of polymers. Therefore, two kinds of factors made T_g rise with an increase in the concentration of sulfonic acid groups in the polymers.

LCPs are most commonly composed of flexible and rigid moieties; self-assembly and microphase separation into specific microstructures frequently occur because of the geometric and chemical dissimilarity of the two moieties. On the other hand, ionic aggregates lead to microphase-separated morphologies.[24] For LC ionomers, it has been shown that ionic groups are compatible with the LC microphase,[25] with a consequent reduction in the mobility of neighboring nonpolar regions when they are in a mesomorphic state. These explain the reason for T_i increasing with an increase in the concentration of sulfonic acid groups in the MLCPs.

For polymers **P1** and **P2**, because they had tiny sulfonated groups, their chemical structures were those of regular polymers, showing a smectic state, whereas for polymers **P3**–**P6**, they had more ionic groups that were compatible with the LC microphases. Because the electrostatic interactions among the ionic aggregates in domains became strong in **P3**–**P6**, they could disturb the regular smectic phase structure, leading to the appearance of a smectic–nematic transition.

TGA thermograms of the polymers were measured in a nitrogen atmosphere. Temperatures at

TABLE II
Thermal Analysis Results and Mesomorphic Properties of the Polymers

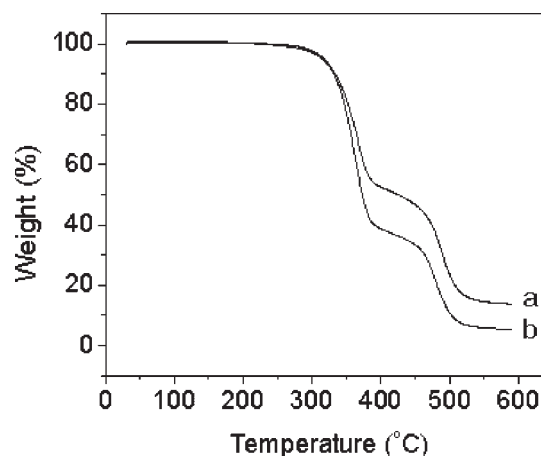| Sample	T_g (°C)	T_{S-N} (°C)	T_i (°C)	ΔT (°C)[a]	$T_{5\%}$ (°C)[b]	Mesomorphic phases
P1	38.7	—	181.2	142.5	285	Smectic
P2	39.8	—	183.7	143.9	285	Smectic
P3	41.3	147.1	187.3	146.0	286	Smectic, nematic
P4	45.6	146.7	196.8	151.2	287	Smectic, nematic
P5	47.5	148.9	201.4	153.9	289	Smectic, nematic
P6	52.4	149.6	208.2	155.8	293	Smectic, nematic

[a] Mesomorphic temperature range (T_i–T_g).
[b] Temperature at which 5% weight loss occurred.
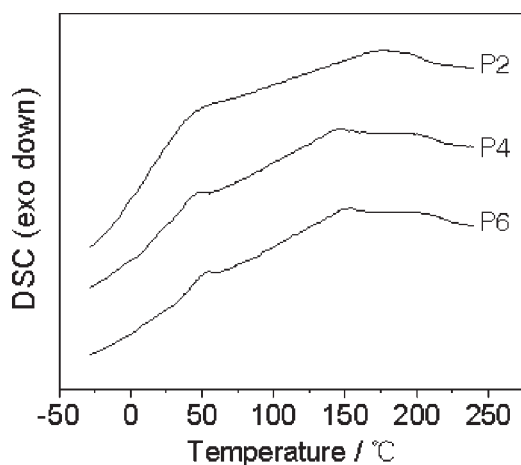
Figure 2 Representative DSC thermograms of polymers **P2, P4,** and **P6** on the second heating (10°C/min).

Figure 3 Representative TGA thermograms of the polymers (a) **P2** and (b) **P6.**

which 5% weight loss occurred are listed in Table II, and they showed a slight elevation with an increase in the concentration of sulfonic acid groups. The initial decomposition of the polymers was observed to start at about 270°C. The thermal stability of the polymers increased with the sulfonic acid concentra-

tion increasing. Representative TGA thermograms of polymers **P2** and **P6** displayed two-step weight-loss behaviors, as shown in Figure 3. The first step of the weight-loss behavior began at about 320°C, indicating the cracking of the main chains. The second step of the weight-loss behavior started around 320°C,
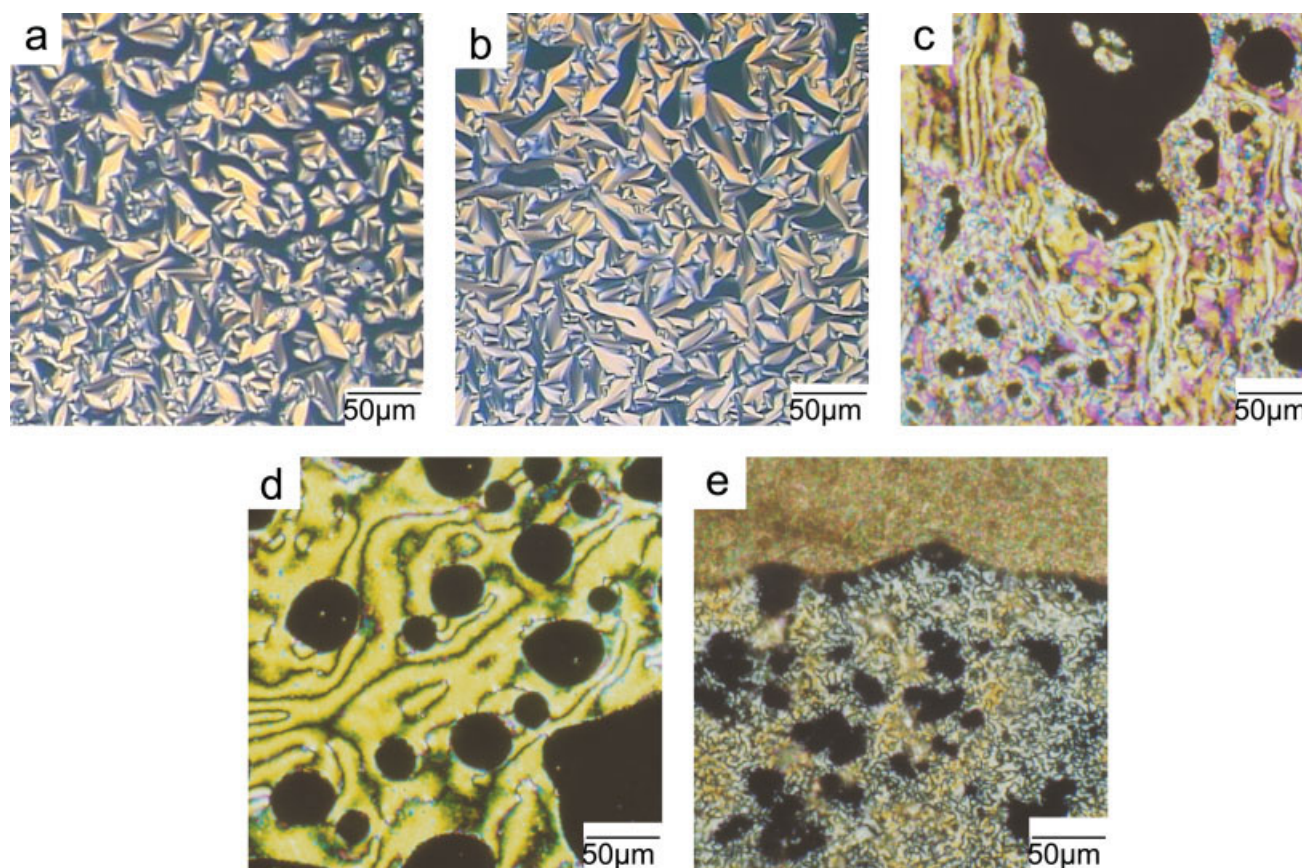
Figure 4 Optical texture of the polymers (200×): (a) deformed focal conic texture of polymer **P2** at cooling to 146°C, (b) deformed focal conic texture of polymer **P4** at cooling to 143°C, (c) schlieren texture of polymer **P4** at heating to 148°C, (d) schlieren texture of polymer **P6** at heating to 198°C, and (e) optical texture of polymer **P6** at cooling to 146°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
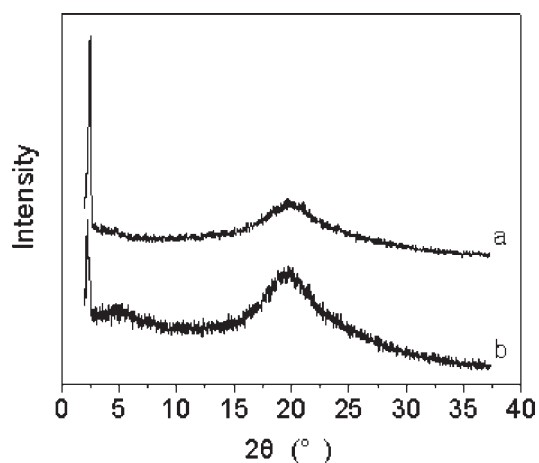
Figure 5 X-ray profiles of representative polymers for (a) **P2** and (b) **P6** at 80°C.

suggesting carbonization due to sulfonic acid in the polymers.

Optical texture analysis

The optical textures of the MLCPs were observed via polarizing optical microscopy (POM) with a hot stage under a nitrogen atmosphere. POM observations showed that **P1** and **P2** exhibited an enantiotropic smectic phase, but **P3–P6** displayed an enantiotropic smectic phase and a nematic phase during heating and cooling cycles; this agrees with DSC thermograms.

Representative textures of the polymers are shown in Figure 4. When heated and cooled, all the polymers exhibited a deformed focal conic texture [see Fig. 4(a,b)]. The polymers, except for **P1** and **P2**, exhibited clear schlieren textures on heating [see Fig. 4(c,d)], which were typical nematic textures, indicating a nematic mesophase. For polymer **P6**, when it was cooled at 146°C, some irregularities could be seen in the mesophases, as shown in Figure 4(e).

X-ray diffraction analysis

The smectic nature of the LC phase and the effect of sulfonic acid on LC properties of the polymers were also characterized by X-ray analysis. X-ray diffraction studies were carried out to obtain more detailed information on the LC phase structure. In general, a sharp and strong peak at a low angle ($1° < 2\theta < 4°$) in small-angle X-ray scattering curves and a broad peak in wide-angle X-ray diffraction (WAXD) curves can be observed for a smectic structure. No peak appears in small-angle X-ray scattering, but a broad peak can be observed in WAXD for nematic and cholesteric structures. However, the angle of diffraction of the cholesteric structure is obviously lower than that of the smectic and nematic structures in WAXD.

For polymers **P1–P6**, the presence of a sharp and strong peak at a low angle around $2\theta \approx 2.6°$ (corresponding to a d-spacing of 34 Å) and a broad peak at a wide angle around $2\theta \approx 20°$ clearly revealed the smectic structures of the samples. Figure 5 shows representative X-ray diffraction curves of the polymers at 100°C.

However, there are some differences between the X-ray profiles of this series of polymers. The intensity of the reflections around $2\theta = 2.6°$, indicative of d stacking periods, is the strongest peak for **P1**. With an increase in the concentration of sulfonic acid groups in the polymer systems, it decreased greatly. Because the ionic groups were compatible with the LC microphase, the ion aggregates disturbed the LC orientation, leading to a reduction of the smectic order of the mesophases. Therefore, the X-ray diffraction studies of the polymers agreed with the DSC thermograms and POM results.

CONCLUSIONS

MLCPs were synthesized and characterized, and they contained pendent sulfonic acid groups on the polymer backbone with sulfonic acid contents ranging from 0 to 6 wt %. The solution viscosity behavior in N,N-dimethylformamide was similar to that of the common ionomers. Their chemical structures were determined with FTIR, EA, and ^{1}H-NMR. The LC properties were characterized with DSC, POM, and X-ray measurements.

All the polymers displayed a smectic mesophase. With an increasing concentration of sulfonic acid groups in the polymer systems, some polymers exhibited two kinds of mesophases, including smectic and nematic phases. With an increase in the concentration of sulfonic acid groups in the polymers, the T_g and T_i values rose slightly, whereas T_{S-N} changed a little. These polymers exhibited a broad mesogenic range of 142–155°C and good thermal stability.

For polymers with a few sulfonated benzene groups, the regular chemical structures lead to a smectic phase structure because of microdomains between the mesogenic moieties and the soft main-chain matrix, whereas for polymers with an increased number of ionic groups compatible with the LC microphase, because the electrostatic interactions of the ionic group/mesogen/soft matrix systems become tangled in domains, they disturb the regular smectic phase structure, leading to the appearance of a smectic–nematic transition.

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