

Main-Chain Liquid-Crystalline Ionomers Bearing Potassium Sulfonate Groups

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ABSTRACT: A series of thermotropic main-chain liquid-crystalline (LC) ionomers were prepared, which contained potassium sulfonate groups pendent to the chains. The polymers were prepared in an esterifying reaction with potassium ion contents ranging between 0 and 3.9 wt %. The content of potassium ion was characterized by spectrophotometric analysis with sodium tetraphenylboron as the titrant. Chemical structures were determined by various experimental techniques including Fourier transform IR spectroscopy and $^1\text{H-NMR}$. LC properties were characterized by differential scanning calorimetry, polarizing optical microscopy, and X-rays. All of the polymers displayed nematic or

smectic mesophases. With increasing potassium sulfonate ionic concentration in the polymers, the melting temperatures and isotropic transition temperatures changed little, whereas the temperature of the smectic A–nematic phase transition increased. The ionic aggregation was tangled with the rigid mesogenic groups of LC segments to form multiple block domains, leading the soft main chains to fold and form a lamellar structure due to their electrostatic interactions.

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Key words: liquid-crystalline polymers (LCPs); ionomers; polyesters

INTRODUCTION

Many studies have been concerned with liquid-crystalline polymers (LCPs) because of their technological potential and scientific challenges.¹ Main-chain liquid-crystalline polymers (MLCPs) contain inherently rigid units, which thereby form a kind of high-strength and high-stiffness structure, resulting in remarkable mechanical properties and thermal stability. For example, some fibers made by these polymers compete with the best ceramic fibers and are far superior to metal fibers.² However, some problems have limited the application of MLCPs as high-performance polymers. A major shortcoming of MLCPs is the large anisotropy of their mechanical properties. Although oriented MLCPs generally have excellent properties in the direction of orientation, their transverse properties tend to be poor. A second shortcoming of MLCPs is their poor polymer miscibility and adhesion to other polymeric substrates. Both problems basically arise from weak intermolecular interactions either in the MLCP itself or in MLCP/polymer

blends. One approach to improving their transverse properties and their adhesion with other polymers is to introduce ionic groups.^{3–6} Strong ionic interactions between polymer molecules are known to significantly enhance mechanical properties, which include compressive strength,⁷ and are also known to dramatically improve the compatibility between different polymers in polymer blends.^{8,9} The incorporation of 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.¹⁰

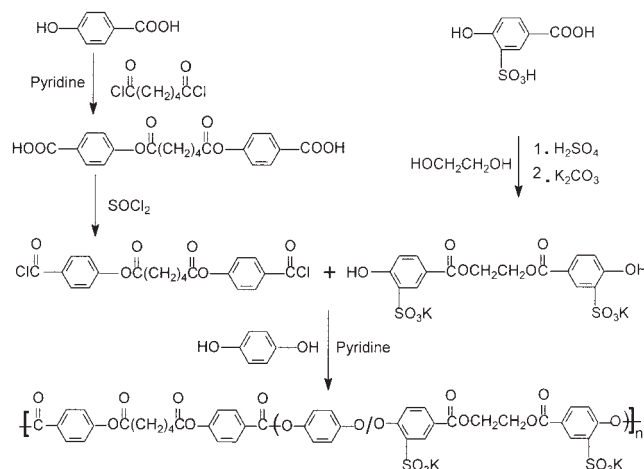
The initial investigations of main-chain liquid-crystalline (LC) ionomers occurred in the mid-1980s, which were studies of organic photoelectric materials containing 1,1'-dialkyl-4,4'-bipyridinium salts.¹¹ Recently, research on MLCP ionomers has focused on structural applications and adhesives for improving the intermolecular forces between the mesogen-containing chains. Zhang and Weiss^{12,13} used interfacial polymerization methods for the preparation of LC polyester ionomers with flexible spacers. Hara and coworkers¹⁴ incorporated an ionic monomer, sodium 5-sodiosulfoisophthalic acid, into an all-aromatic LC polyester. Zentel and coworkers¹⁵ studied several families of MLCP ionomers and concluded that ionic association stabilized the LC phase. However, MLCP ionomers have received less attention despite their technological potential.

We are currently developing MLCP ionomers by introducing sulfonate groups into MLCP chains to

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Scheme 1

obtain better mesogenic and ionic properties. We select sulfonate groups as ionic units because they show excellent ionic properties with a little component and preserve LC mesophase easily. We would like to know the fundamental link between ionic aggregation found in the polymers and the behavior of LC phases. Furthermore, it is of interest to investigate how the ionic interactions modify liquid crystallinity, LC structures, and the overall morphology of such kinds of MLCs.

In this study, we prepared a series of thermotropic MLCP ionomers containing potassium sulfonate groups pendent to the chains. Their chemical structures are shown in Scheme 1.

EXPERIMENTAL

Material and measurements

2-Hydroxy-5-carboxy-benzenesulfonic acid, 4-hydroxybenzoic acid, *p*-benzenediol (monomer **B**), and pyridine were purchased from Beijing Chemical Co. (Beijing, China). Adipic chloride, glycol, tetrahydrofuran (THF), benzene, and thionyl chloride were obtained from Shenyang Chemical Co. (Shenyang, China) and were used without any further purification. Pyridine was purified by distillation over KOH and NaH before use.

Fourier transform infrared (FTIR) spectroscopy of the synthesized polymers and monomers in the solid state were obtained by the KBr method performed on a Nicolet 510P FTIR spectrometer (Nicolet Instruments, Madison, WI). $^1\text{H-NMR}$ spectra (300 MHz) were recorded on a Varian WH-90 spectrometer (Varian Associates, Palo Alto, CA). Ultraviolet-visible spectrophotometry was measured by a PerkinElmer Lambda 900 instrument (PerkinElmer, Foster City, CA). Thermal transition properties were characterized by a TA Instruments V2.3C instrument (New Castle, DE) at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen

atmosphere. Visual observation of LC transitions under crosspolarized light was made by a Leitz Laborlux S polarizing optical microscope (Leitz, Wetzlar, Germany) equipped with a THMS-600 heating stage. X-ray measurements of the samples were performed with $\text{Cu K}\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation monochromatized with a Rigaku DMAX-3A X-ray diffractometer (The Woodlands, TX).

Syntheses

The syntheses of all the monomers and polymers are shown in Scheme 1.

Synthesis of bis(4-carboxyphenyl)hexanedioate

4-Hydroxybenzoic acid (27.6 g, 0.20 mol) and pyridine (25.0 mL, 0.30 mol) were dissolved in 120 mL of THF to form a solution. Adipic chloride (18.3 g, 0.10 mol) was added to the solution and reacted at 80°C for 6 h, cooled, poured in 500 mL of cold water, and acidified with $6N \text{ H}_2\text{SO}_4$. 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-carboxyphenyl)hexanedioate at a yield of 70% (mp = 284°C).

IR (KBr, cm^{-1}): 3060, 2949, 2852 ($-\text{CH}_2-$ and $=\text{C}-\text{H}$); 2672, 2554 ($-\text{OH}$ stretching); 1758, 1688 ($\text{C}=\text{O}$); 1603, 1508 (phenyl); 1427 ($\text{C}-\text{H}$ bending); 1318, 1292 ($\text{O}-\text{H}$ bending); 1258, 1206, 1166, 1117 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 10.98 (s, 2H, $-\text{COOH}$), 8.05–6.98 (m, 8H, Ar-H), 3.75–3.60 (m, 4H, $-\text{OOCCH}_2-$), 2.16–1.96 (m, 4H, $-\text{OOCCH}_2\text{CH}_2-$).

Synthesis of potassium bis(2-hydroxy-5-carboxybenzenesulfonate)

2-Hydroxy-5-carboxy-benzenesulfonic acid (15.0 g, 0.06 mol), glycol (31.0 g, 0.50 mol), H_2SO_4 (98%, 2.0 g, 0.02 mol), and 100 mL of benzene were added into a round flask equipped with a water separator. The mixture was refluxed for 6 h, and water was removed to ensure that the reaction finished. The mixture was cooled and neutralized with saturated potassium carbonate solution, and the organic layer was separated. The organic solution was distilled under reduced pressure to remove organic solvent. The residual was recrystallized from methanol and dried overnight at 80°C *in vacuo* to obtain a powder of monomer **C** at a yield of 50% (mp = 170°C).

IR (KBr, cm^{-1}): 3470 ($-\text{OH}$); 3201–2900 (Ar-H, $-\text{CH}_2-$); 1717 ($\text{C}=\text{O}$); 1608 (Ar-); 1418 ($\text{C}-\text{H}$ bending); 1280 ($\text{C}-\text{O}$); 1196, 1081 ($\text{S}=\text{O}$); 1025 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 8.46–6.90 (m, 6H, Ar-H), 5.67 (s, 2H, $-\text{OH}$), 5.36 (s, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$).

TABLE I
Polymerization and Phase-Transition Temperatures of the Polymers

Sample	Feed			Yield (%)	Thermal transitions ^a			
	A (g)	B (g)	C (g)		T_g (°C)	T_m (°C)	T_{SN} (°C)	T_i (°C)
P1	4.23	1.10	0	91	20.05	60.23	—	224.79
P2	4.23	1.05	0.24	92	26.33	57.06	—	235.76
P3	4.23	1.00	0.47	90	31.78	64.10	108.28	232.06
P4	4.23	0.94	0.71	91	26.55	52.88	119.54	209.54
P5	4.23	0.88	0.95	92	20.63	58.60	125.32	229.05
P6	4.23	0.83	1.18	90	—	87.46	152.67	229.66

^a DSC data of the second heating curve: heating rate = 10°C/min.

Syntheses of the polymers

Bis(4-carboxyphenyl)hexanedioate (38.6 g, 0.10 mol) and thionyl chloride (75.0 g, 0.63 mol) were added into a round flask equipped with an absorption instrument of hydrogen chloride. The mixture was stirred at room temperature for 2 h, then heated to 60°C, and kept for 3 h in a water bath to ensure that the reaction finished. The mixture was distilled under reduced pressure to obtain 17.3 g of bis(4-chlorocarbonylphenyl)hexanedioate (monomer **A**) at 260–270°C/20 mmHg at a yield of 41%.

For synthesis of polymers **P1–P6**, the same method was adopted. The polymerization experiments are summarized in Table I. The synthesis of polymer **P4** is given here as an example. Monomer **A** (4.23 g, 0.010 mol) was dissolved in 30 mL of pyridine. To the stirred solution, monomer **B** (0.94 g, 0.0085 mol) and monomer **C** (0.71 g, 0.0015 mol) were added and heated under nitrogen and anhydrous conditions at 80°C for 36 h. The solution was cooled and poured into 100 mL of cold water. After filtration, the product was washed with ethanol and dried at 80°C for 2 h *in vacuo* to obtain 4.69 g of polymer at a yield of 91%.

IR (KBr, cm^{-1}): 2920–2850 (CH_3 — and — CH_2 —); 1760–1737 ($\text{C}=\text{O}$); 1603, 1506 (phenyl); 1413 ($\text{C}-\text{H}$ bending); 1265, 1211, 1181 ($\text{C}-\text{O}-\text{C}$); 1159, 1072 ($\text{S}=\text{O}$).

RESULTS AND DISCUSSION

FTIR spectra

Figure 1 shows the FTIR spectra of the monomer bis(4-carboxyphenyl)hexanedioate and the polymer **P4** at room temperature in KBr pellets. For the monomer bis(4-carboxyphenyl)hexanedioate, the characteristic absorption bands between 400 and 2000 cm^{-1} were as follows: 1758 ($\text{C}=\text{O}$ in aromatic ester mode); 1688 ($\text{C}=\text{O}$ in carboxylic acid mode); 1603 and 1508 ($\text{C}=\text{C}$ stretching in phenyl), 1427 ($\text{C}-\text{H}$ aliphatic bending); 1318 and 1292 ($\text{O}-\text{H}$ bending); 1258, 1206, 1166, and 1117 ($\text{C}-\text{O}$ stretching); and 1017 ($=\text{C}-\text{H}$ in plane bending). For the polymer **P4**, their characteris-

tic absorption bands were as follows: 1760–1737 ($\text{C}=\text{O}$ stretching); 1603 and 1506 ($\text{C}=\text{C}$ stretching in phenyl); 1413 ($\text{C}-\text{H}$ aliphatic bending); 1265, 1211, 1181, and 1121 ($\text{C}-\text{O}$ stretching); 1159 ($\text{S}=\text{O}$ asymmetric stretching); 1072 ($\text{S}=\text{O}$ symmetric stretching); and 1013 ($=\text{C}-\text{H}$ in plane bending). The FTIR absorption bands of the $\text{C}=\text{O}$ stretching vibration (1760–1737 cm^{-1} in **P4**) indicated different ester linkage.

For organic sulfonate groups, the FTIR absorption range of the $\text{O}=\text{S}=\text{O}$ asymmetric and symmetric stretching modes was in the ranges 1120–1230 and 1010–1080 cm^{-1} , respectively, and that of the $\text{S}-\text{O}$ stretching mode was in the range 600–700 cm^{-1} . In a previous study, the $\text{S}-\text{O}$ stretching mode was used to identify sulfonate groups in the ionic polymers.¹⁶ However, this is not suitable for distinguishing the nonionic monomer from the ionic polymer, which contained sulfonate groups, as shown in Figure 1. Although some overlapping was found between $\text{S}=\text{O}$ stretching bands and $\text{C}-\text{O}$ stretching bands in the polymers, the symmetric and asymmetric stretching frequency of SO_3^- is very sensitive to both counterions and physical state.¹⁷ As shown in Figure 1, the strong peaks at 1159 and 1072 cm^{-1} corresponding to $\text{S}=\text{O}$

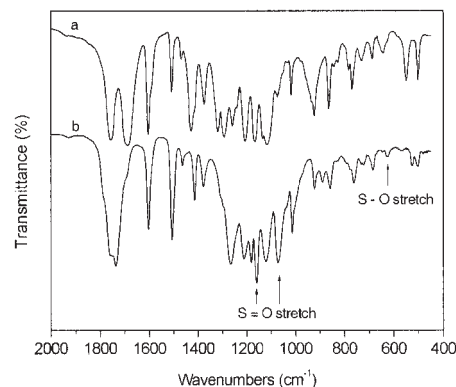


Figure 1 FTIR spectra for (a) the monomer bis(4-carboxyphenyl)hexanedioate and (b) the polymer **P4** in the range 2000–400 cm^{-1} .

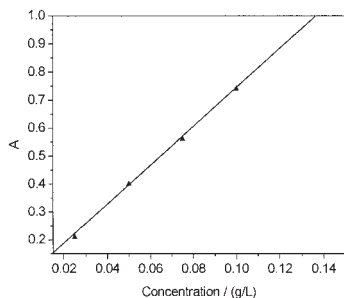


Figure 2 Standard curve of different potassium ion concentrations of the standard solution.

asymmetric and symmetric stretching mode, respectively, appeared in the FTIR spectrum of the ionic polymer **P4**, but they did not appear in the nonionic monomer. These results clearly indicate successful incorporation of sulfonate groups in the polymer systems.

Spectrophotometric analysis of the potassium ion

The content of metal ion the LC polymer systems influenced the LC properties greatly, but there was little report to assay the cation content. We studied the potassium ion in the synthetic polymers by spectrophotometric analysis.

For this method, sodium tetraphenylboron was used as the titrant. Therefore, potassium tetraphenylboron was formed and measured with the spectrophotometer on the basis of the fact that the sensitive absorption bands of potassium tetraphenylboron were 766.5 and 440.4 nm.

In this method, we first determined the maximum absorption for a constant concentration solution. With increasing titrant, the value of absorption increased at first and then decreased. Thus, the maximum absorption was acquired.

To assay the potassium ion, the standard curve was scaled with the maximum absorbance and the potassium ion concentration of the standard solution. The standard curve of the potassium ion is shown in Figure 2, and the data are list in Table II.

In the same way, the maximum absorbance of the sample solution was determined. For analysis of the potassium ion in polymers **P1–P6**, the same method was adopted. The polymer (2.500 g) was dissolved in

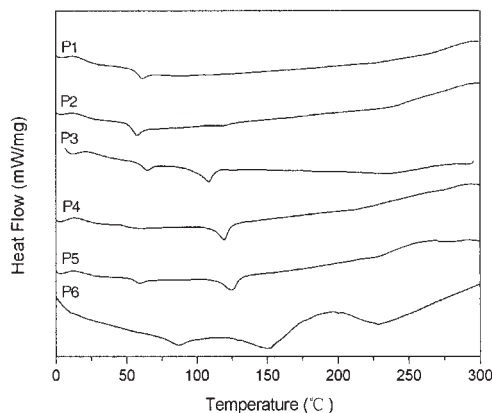


Figure 3 DSC thermograms of the polymers on the second heating (10°C/min).

1.0 L of THF to prepare concentrations of 2.500 g/L of the sample solutions. To obtain the maximum absorbance, 50 mL of this solution was also titrated with 5 g/L of sodium tetraphenylboron. Therefore, the K^+ concentration of the samples was acquired according to the standard curve, which is listed in Table II.

The mass percentage of the potassium ion was

$$K^+(\%) = C_0/C \times 100\% \quad (1)$$

where C_0 is the potassium ion concentration that was determined by consulting the standard curve and C is the polymer concentration, which was 2.500 g/L for the polymers. The resulting contents of potassium ion in the series of polymers are listed in Table II.

LC behavior

All of the polymers were observed by polarizing microscopy and studied by X-rays and differential scanning calorimetry (DSC), the data from which are included in Table I. Figure 3 shows the DSC thermograms of all of the synthesized polymers. In the DSC thermogram, the polymers **P1** and **P2** displayed three kinds of phase transition behavior corresponding to the glass transition, melting point, and clear point, whereas the others displayed four kinds of phase transitions. The additional phase transition was attributed to the smectic A (S_A)-nematic (N) phase transition. With increasing ionic groups in the polymers **P1–P6**,

TABLE II
Spectrophotometric Analyses of the Standard Potassium Ion Solutions and the Polymers

Sample	Standard K^+ solution				P1	P2	P3	P4	P5	P6
Concentration (g/L)	0.025	0.050	0.075	0.100	0	0.020	0.042	0.063	0.080	0.098
Maximum absorption	0.21	0.40	0.56	0.74	0	0.17	0.35	0.49	0.61	0.73
K^+ content (%)	—	—	—	—	0	0.8	1.7	2.5	3.2	3.9

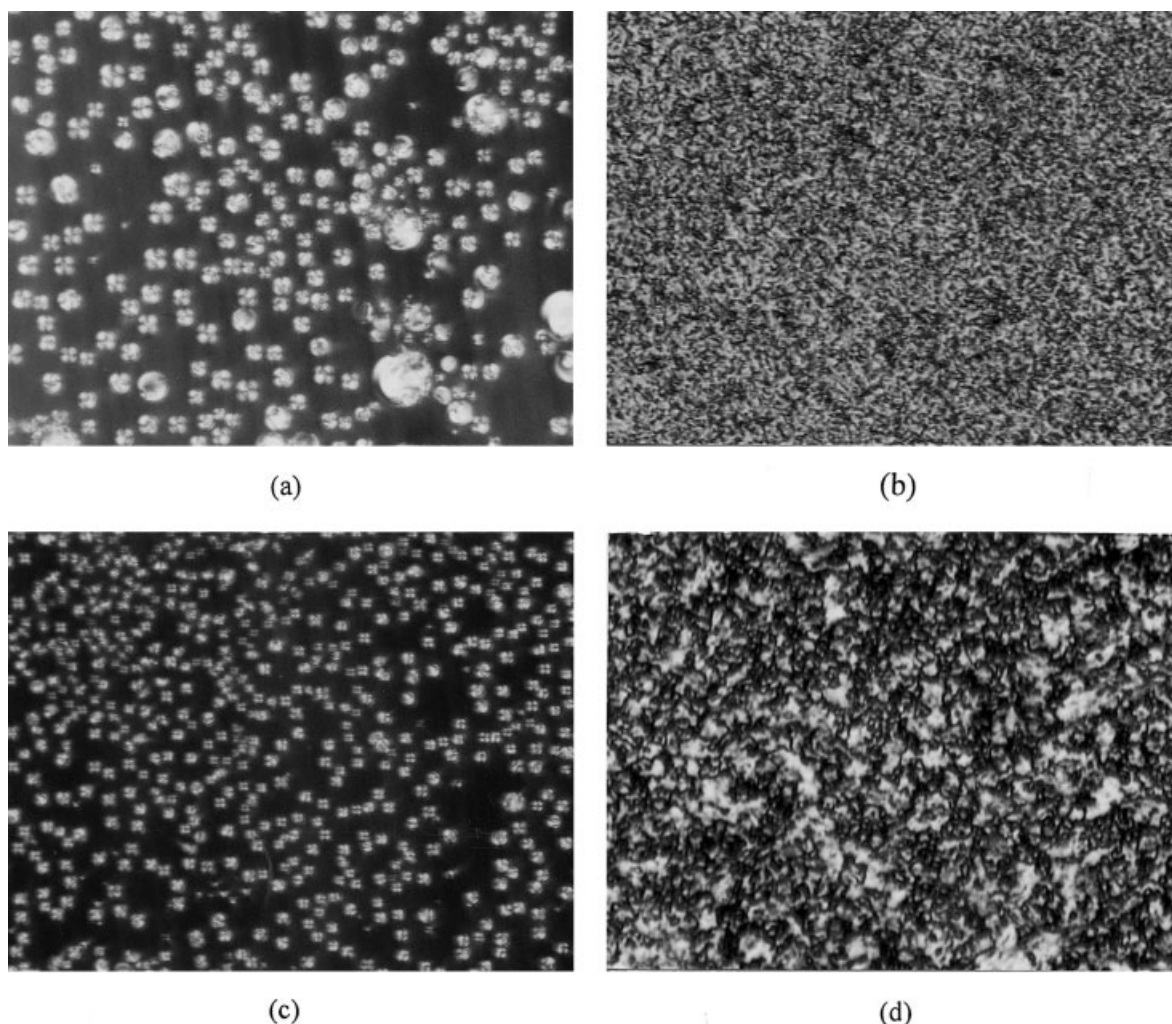


Figure 4 Optical polarizing micrographs for (a) **P1** at 178°C, (b) **P3** at 85°C, (c) **P3** at 115°C, and (d) **P5** at 88°C (200×).

the melting temperatures (T_m 's) and isotropic transition temperature (T_i) changed little, whereas the temperature of the S_A -N phase transition (T_{SN}) increased. Moreover, the glass-transition temperature (T_g) changed little for **P1**–**P5**; whereas for **P6**, the T_g was not clearly displayed.

All of the polymers exhibited thermotropic LC properties during heating and cooling. Polymers **P1** and **P2** showed a N mesophase, whereas the other polymers displayed S_A and N mesophases. The samples were placed on glass plates, covered with a covering slide, and observed under the hot-stage optical polarizing microscope for their LC behavior and thermo-optical properties. The representative textures are shown in Figure 4. For polymer **P1**, the typical droplet texture of the N mesophase was observed at 178°C, as shown in Figure 4(a), on heating. For **P3**, when it was heated at 85°C, a broken focal-conic texture was displayed, as shown in Figure 4(b). This texture was destroyed at 108°C, and then a droplet texture appeared [see Fig. 4(c)], indicating the S_A -N

mesophase transition. For **P5**, when it was heated at 88°C, it showed a focal-conic fan-shaped texture, as shown in Figure 4(d). When it was heated continually, a droplet texture also appeared. The N or smectic nature of the LC phase was also characterized by X-ray analysis. **P1** did not show any intensive peak in the profile. Although for **P3** and **P5**, the presence of sharp reflections at small angles around $2\theta = 2.6^\circ$ (corresponding to a d spacing of 34 Å) in the X-ray profile, as shown in Figure 5, clearly revealed the S_A structure of the sample.

The potassium sulfonate groups in the polymer structures influenced the LC behavior of the polymers.

In the ionomer literature, cluster aggregation in which the ion clusters are completely surrounded by the organic material and actual microseparation of the ionic phase from the soft main chain matrix takes place. For LC ionomers, it has been shown that ionic clusters are compatible with the LC phase.¹⁸ Competition between the formation of ionic cluster phases and the LC phase depends on the chemical structure.

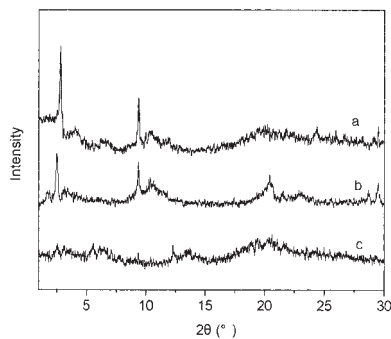


Figure 5 X-ray profiles for (a) P5, (b) P3, and (c) P1.

Because there were few ionic groups in the LCP systems, the ionic aggregation would have been tangled with the rigid mesogenic groups of LC segments to form multiple block domains. The ions aggregated in domains due to their electrostatic interactions, thus forcing the soft main chains to fold and form a lamellar structure. These illustrated the appearance of the S_A mesophase for polymers P3, P4, P5, and P6 with the increasing potassium sulfonate component in the LCP systems.

CONCLUSIONS

We prepared a series of thermotropic MLCP ionomers containing potassium sulfonate groups pendent to the chains. The polymers were prepared in an esterifying reaction with potassium ion contents ranging between 0 and 3.9 wt %. The content of potassium ion was characterized by spectrophotometric analysis with sodium tetraphenylboron as the titrant. Chemical structures were determined by various experimental techniques including FTIR and $^1\text{H-NMR}$. The LC properties were characterized by DSC, polarizing optical microscopy, and X-rays. All of the polymers displayed N or smectic mesophases.

With increasing potassium sulfonate ionic in the polymers, the T_m 's and T_i changed little, whereas T_{SN} increased.

The ionic aggregation would have been tangled with the rigid mesogenic groups of LC segments to form multiple block domains, leading the soft main chains to fold and form a lamellar structure due to their electrostatic interactions of the ion aggregates in the domains. These suggested the appearance of an S_A mesophase for polymers with increasing potassium sulfonate components in the LCP systems.

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