

Study on a Series of Main-Chain Liquid–Crystalline Ionomers Containing Sulfonate Groups

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ABSTRACT: A series of main-chain liquid–crystalline ionomers containing sulfonate groups pendant on the polymer backbone were synthesized by an interfacial condensation reaction of 4,4'-dihydroxy- α,α' -dimethyl benzalazine, a mesogenic monomer, with brilliant yellow (BY), a sulfonate-containing monomer, and a 1/9 mixture of terephthaloyl and sebacoyl dichloride. The structures of the polymers were characterized by IR and UV spectroscopies. DSC and thermogravimetric analysis were used to measure the thermal properties of those polymers, and the mesogenic properties were characterized by a polarized optical microscope, DSC, and wide-angle X-ray diffraction. The ionomers were thermally stable to about 310 °C. They were thermotropic liquid–crystalline polymers (LCPs) with high mesomorphic-phase transition temperatures and exhibited broad nematic mesogenic regions of 160–170 °C, and they were lyotropic LCPs with willowy leaf-shaped textures in sulfuric acid. However, the thermotropic liquid–crystalline properties were somewhat weakened because the concentration of BY was more than 8%. The inherent viscosity in *N*-methyl-2-pyrrolidone suggested that intramolecular associations of sulfonate groups occurred at low concentration, and intermolecular associations predominated at higher concentration. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2210–2218, 2001

Key words: main-chain liquid–crystalline ionomer; DDBA; sulfonate group; thermotropic; lyotropic

INTRODUCTION

Liquid–crystalline polymers (LCPs) have received great attention because of their high modulus, strength, and stiffness. However, a major shortcoming of LCPs is their poor intermolecular interaction that leads to weak transverse properties to the molecular axis, and blends of LCPs with other thermoplastic polymers also have

weak interfacial adhesion between the phases that limits the properties and application of the self-reinforcing LCP blends. One approach for improving the transverse properties of LCPs and their adhesion with other polymers is to introduce specific functional groups such as ionic groups that should promote specific interchain interactions. 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. We have been engaged in the study of

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liquid-crystalline ionomers containing sulfonate groups in recent years, and we reported the synthesis of two thermotropic main-chain liquid-crystalline ionomers (LCIs) and a side-chain LCI with sulfonate groups in previous research.¹⁻³ In the present article, a series of main-chain LCIs containing sulfonate ionic monomer [brilliant yellow (BY)], mesogenic monomer [4,4'-dihydroxy- α,α' -dimethyl benzalazine (DDBA)], and terephthaloyl/sebacoyl dichloride were synthesized. The thermotropic and lyotropic liquid-crystalline properties, the textures, the effect of ionic aggregation on the mesomorphic property, and the thermal stability are explored.

EXPERIMENTAL

Reagents and Intermediates

BY (98%, Eastman Kodak Co., Rochester, NY), terephthalic acid (>98%, Schuchardo, 8011 Hohenbrunn bei Munchen), hydrazinemonohydrate (71.5%), benzyltrimethylammonium (mp 273 °C), *N*-methyl-2-pyrrolidone, sodium hydroxide, dichloromethane, methanol, ethanol, and pyridine were used as received. 4'-Hydroxyacetophenone and sebacoyl dichloride were prepared in the laboratory.

Monomer Synthesis

4,4'-Dihydroxy- α,α' -dimethyl Benzalazine (DDBA)

Mesomorphic monomer DDBA was prepared according to the procedure of Blout et al.⁴ An ethanol solution of 0.45 M equivalents of hydrazine monohydrate was refluxed with 4-hydroxyacetophenone and a catalytic amount of concentrated hydrochloric acid for 6–8 h. DDBA (mp 226–228 °C, lit. value^{4,5} 225–226 °C) was separated out by cooling the solution overnight, filtered, and then recrystallized from aqueous ethanol.

IR(KBr) cm^{-1} : 3346.0 (OH); 2600.0 (N—N); 1367.7(CH_3); 1606.9, 1595.3, 1514.1 ($\text{C}=\text{N}$). ¹HNMR(CH_3OD , tetramethylsilane) δ ppm: 2.27 (CH_3), 7.79^a, 6.58^b (C—^a C —^b C —OH).

Terephthaloyl Dichloride

Terephthaloyl acid (3 mmol) was refluxed with thionyl chloride (30 mmol) for 10–12 h, and pyridine was used as a catalyst. The terephthaloyl dichloride (mp 82.5–84 °C, lit. value⁶ 82–84 °C) was separated by cooling the reactant overnight

and recrystallized from dichloromethane and hexane. The yield was 90%.

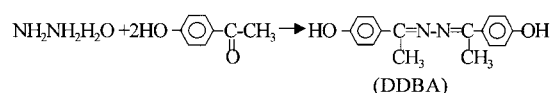
IR(KBr) cm^{-1} : 1744.6(C=O); 1576.0, 1498.0($\text{C}=\text{O}$); 637.8, 559.4(C—Cl), 852.7 (C—H).

Polymer Synthesis

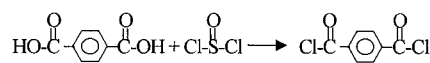
Interfacial polymerization was carried out in a high-speed warring blender. The terephthaloyl dichloride (0.26 mmol) and sebacoyl dichloride (2.34 mmol) in dichloromethane (25 mL) were rapidly added to a slowly stirred aqueous layer (40 mL) composed of 2.5 mmol (total) of DDBA and BY (Table I), 30 mg of sodium hydroxide, and 60 mg of butyltriethylammonium chloride. The mixture was stirred at high speed for 5–7 min, and then the resulting slurry was slowly added to methanol, stirred, and filtered. The products were washed with fresh methanol and methanol/water mixture repeatedly and then dried at 70–80 °C in a vacuum oven for at least 24 h.

The polymerization experiments are summarized in Table I. The sample nomenclature is S_n -LCP, where *n* corresponds to the BY molar concentration in the mixture of BY and DDBA. The polymer with no BY is referred to as S_0 -LCP. The color of the polymers darkened with an increasing BY concentration as shown in Table I.

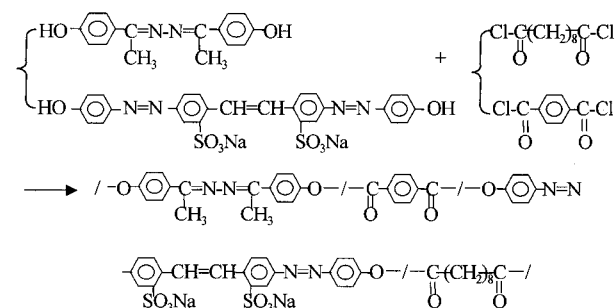
Preparation of 4,4'-dihydroxy- α,α' -dimethyl benzalazine(DDBA)



Preparation of terephthaloyl dichloride



Polymers(S_{0-12} -LCP) synthesis



Scheme 1

Table I Polymerizations

Polymers	Feed				Yield (%)	Color of Polymer
	DDBA (mmol)	BY (mmol)	(BY) ^a (%)	(A + B) ^b (mmol)		
S ₀ -LCP	2.500	0.000	0	2.5	85.3	Light yellow
S ₁ -LCP	2.475	0.025	1	2.5	83.3	Yellow
S ₂ -LCP	2.450	0.050	2	2.5	79.2	Light orange
S ₄ -LCP	2.400	0.100	4	2.5	79.2	Orange
S ₈ -LCP	2.300	0.200	8	2.5	87.5	Tangerine
S ₁₂ -LCP	2.200	0.300	12	2.5	87.5	Red

^a Molar percentage of BY based on DDBA + BY.

^b A: terephthaloyl dichloride, B: sebacoyl dichloride [A/B = 1/9 (molar ratio)].

IR Spectroscopy

The structures of the samples were determined with a Nicolet 510-PFT IR spectrometer, using all samples on KBr.

UV Spectroscopy

The UV spectra of the polymer solutions in *N*-methyl-2-pyrrolidone were measured with a Shanghai 751 UV-visible spectrometer.

Thermal Analysis

Thermal transitions were measured with a PerkinElmer DSC-7 equipped with a PE 7300

data station and a 20 °C/min heating rate; the thermal stabilities of the polymers were measured with a PerkinElmer TGA-7 thermogravimetric analyzer using nitrogen atmosphere and a 20 °C/min heating rate.

Polarized Optical Microscope (POM) Analysis

The polymer textures were observed with a Ziss-Jena polarizing optical microscope (POM) equipped with a Melter FP2 hot stage.

X-ray Diffraction Analysis

X-ray diffraction analysis of quenched samples was measured with a Rigaku DMAX-3A X-ray diffractometer at room temperature, Cu target radiation.

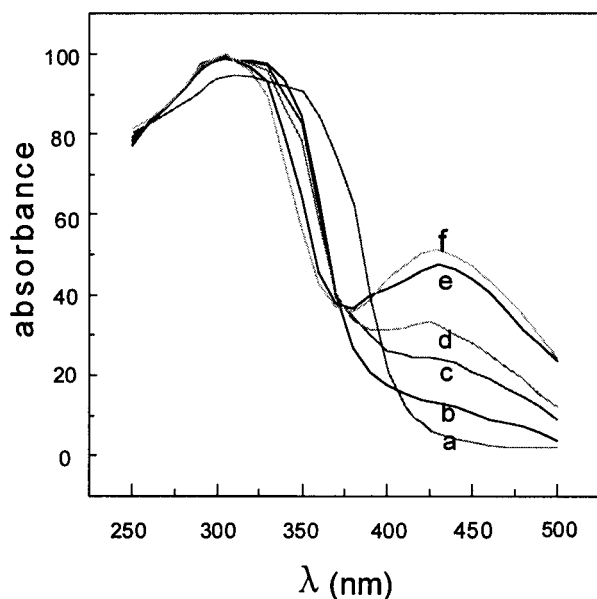


Figure 1 UV absorption spectra of polymers a: S₀-LCP, b: S₁-LCP, c: S₂-LCP, d: S₄-LCP, e: S₈-LCP, and f: S₁₂-LCP.

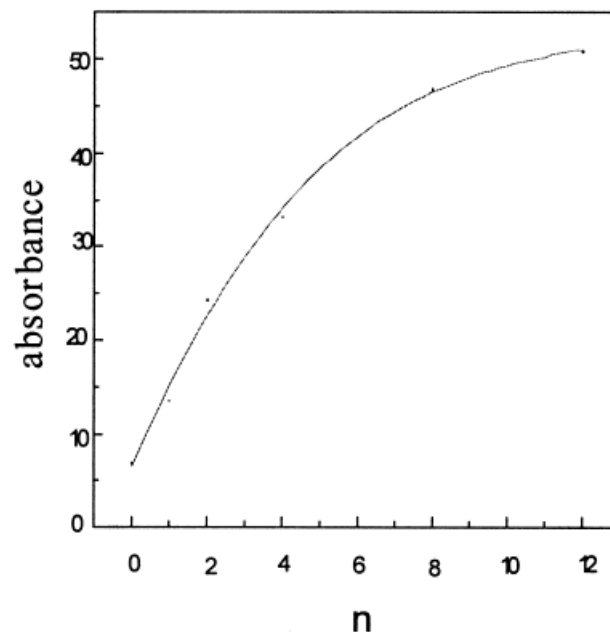


Figure 2 Absorption of polymers S_n-LCP at 425 nm.

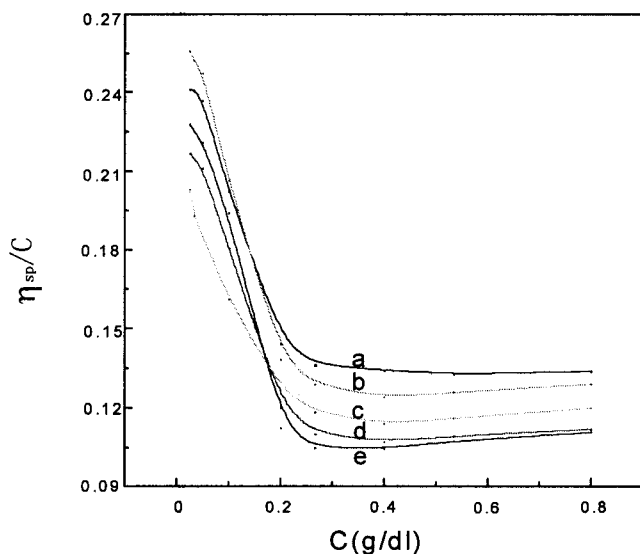


Figure 3 (η_{sp}/C at 80 °C in *N*-methyl-2-pyrrolidone versus concentration of ionomers a: S_1 -LCP, b: S_2 -LCP, c: S_4 -LCP, d: S_8 -LCP, and e: S_{12} -LCP.

Solution Viscosity

Dilute solution viscosity measurements were carried out in *N*-methyl-2-pyrrolidone solution at 80 ± 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.

RESULTS AND DISCUSSION

UV Spectroscopy

The UV absorption spectra of all the polymers in the region $\lambda = 250$ – 500 nm are shown in Figure 1. The polymers containing BY exhibited two absorption peaks that were at 285 and 420–450 nm. The first absorption peak was due to the conjugated benzene, whereas the second peak was due to the ionic-unit BY of the LCIs. The lone pair electrons of $N=N$ in BY occurred in n - π transition and produced the R absorption band as they absorbed UV rays, and the R band shifted to a higher wavelength as a result of the conjugative effect of $N=N$ and C_6H_5 . The absorbance intensity of the second peak increased with an increasing BY concentration in the polymers, and the curves of absorbance with $n(S_n$ -LCP) at $\lambda = 425$ nm are illustrated in Figure 2.

Solution Behavior

Figure 3 demonstrates the reduced viscosity of ionomers S_{1-12} -LCP in *N*-methyl-2-pyrrolidone

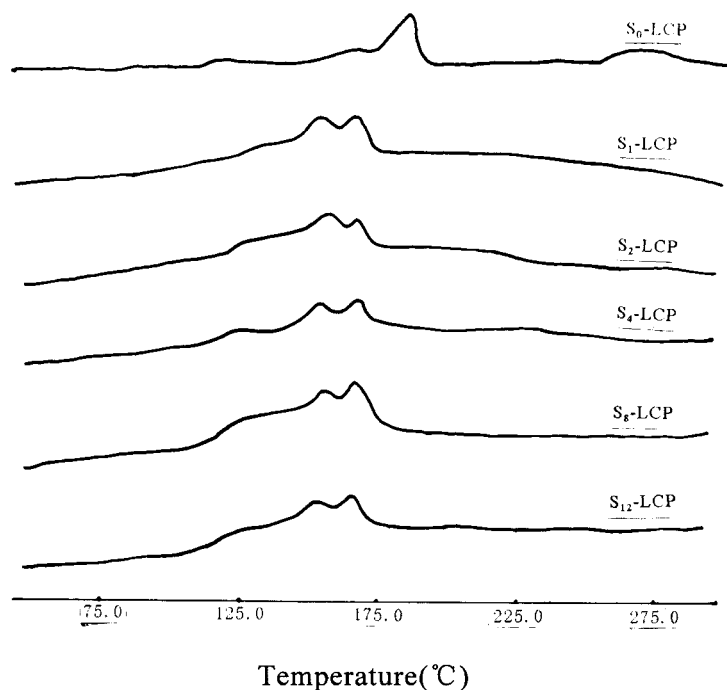


Figure 4 DSC thermograms (second heating) of S_n -LCP.

Table II DSC Results of S₀₋₁₂-LCP

Polymers	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	$T_{5\%}$ ^a (°C)	ΔT (°C)
S ₀ -LCP	122.6	164.2	185.5	269.2 ^b	105.0
S ₁ -LCP	119.9	148.6	171.9	318.6	170.0
S ₂ -LCP	119.7	151.9	170.6	318.1	166.2
S ₄ -LCP	119.5	158.3	169.3	318.5	160.2
S ₈ -LCP	119.2	158.7	168.5	325.1	166.5
S ₁₂ -LCP	118.8	153.8	165.3	324.7	170.9

^a $T_{5\%}$ of ionomers (S₁–S₁₂-LCP) come from Table III.

^b Clear point (T_c) of polymer S₀-LCP without ionic group.

at 80 ± 0.2 °C. The polymer S₀-LCP dissolved too little in *N*-methyl-2-pyrrolidone at 80 °C to be measured. The data of the polymers were normalized by the apparent intrinsic viscosity to minimize differences in molecular weight. The solution viscosity behavior of all the ionomers was similar. As the concentrations were lower than 0.25 g/dL, the reduced viscosity of these ionomer solutions decreased markedly in linearity with an increasing concentration of ionomers. However, at high polymer concentrations, the viscosity behavior increased rather

slowly with an increasing solution concentration. A similar viscosity behavior was previously reported^{7,8} for other ionomer solutions. The decrease of the reduced viscosity at low polymer concentration was mainly due to the ionization of the ion pair.⁷ As a consequence, the unshielded negative charges on the pendent sulfonate groups repelled each other and caused an expansion of the polymers that resulted in an increase in the hydrodynamic volume of the polymers, which is referred to as the “polyelectrolyte effect.”⁷ As the polymer concentration was above 0.25 g/dL, which was high enough for intermolecular ionic interaction dominating the solution behavior, intermolecular ionic interaction slightly reduced the hydrodynamic volume of the polymer coils; therefore, the viscosity tended to increase as the concentration was higher than 0.25 g/dL.

Thermal Analysis

The thermal transitions of the polymers were measured by DSC by first heating the samples to 120 °C, then cooling to 20 °C after 5 min, and reheating the samples at 20 °C/min to 300 °C. The

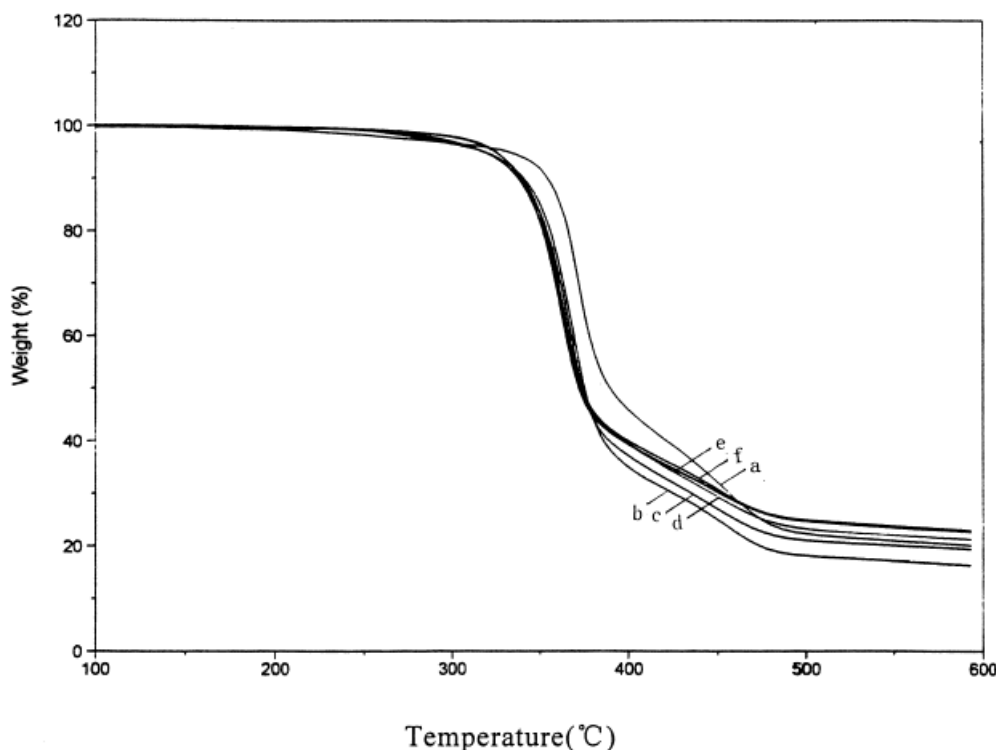


Figure 5 TGA thermograms of S_n-LCP a: S₀-LCP, b: S₁-LCP, c: S₂-LCP, d: S₄-LCP, e: S₈-LCP, and f: S₁₂-LCP.

second heating scans are shown in Figure 4, and the transition temperatures are summarized in Table II.

The glass-transition temperatures (T_g 's) of ionomers S_{1-12} -LCP decreased from 2.7 to 3.8 °C compared with the polymer S_0 -LCP, and the T_g also decreased as the BY concentration increased, which was due to the introduction of ionic group. The polymer chains containing pendant sulfonate groups occupied a larger volume and could not pack closely, and the single band provided easy internal rotation. A common observation⁹ in ionomers is that T_g increases with an increasing salt group concentration, 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 the present article, both of the effects affected the T_g 's of ionomers, but neither of them predominated; therefore, the T_g decreased slightly from S_1 -LCP to S_{12} -LCP. The mp (T_{m1}) of S_1 -LCP was lower than S_0 -LCP, which may be due in part to the decrease of molecular weight, and the large free volume of the pendant concentration also had an effect on it. The T_{m1} of S_{1-8} -LCP increased slightly with an increasing BY concentration, which attributes to the increase of intermolecular interactions in the ionomers. The mp T_{m2} of S_{1-12} -LCP was lower than S_0 -LCP for the same reason as T_{m1} . Two melting temperatures (T_{m1} and T_{m2}) were observed that may be due to the different T_m 's of the flexible region with sebacoyl and the rigid region with terephthaloyl in copolymers S_{0-12} -LCP, or the different mesogenic textures. The DSC thermogram of polymer S_0 -LCP shows the clearing point (T_i) at 269.2 °C, but for ionomers S_{1-12} -LCP, the T_i was not observed near 270

Table III TGA Results of S_{0-12} -LCP

Polymers	$T_{5\%}$ (°C) ^a	Weight Loss (%)			
		300 (°C)	350 (°C)	420 (°C)	600 (°C)
S_0 -LCP	332.5	3.4	8.0	54.6	80.0
S_1 -LCP	318.6	2.5	14.5	67.4	82.8
S_2 -LCP	318.1	2.6	17.5	64.8	80.7
S_4 -LCP	318.6	3.8	17.3	61.2	78.5
S_8 -LCP	325.2	3.2	17.3	61.1	76.8
S_{12} -LCP	324.7	3.7	17.8	59.5	76.5

^a Temperature of 5% mass loss of ionomers.

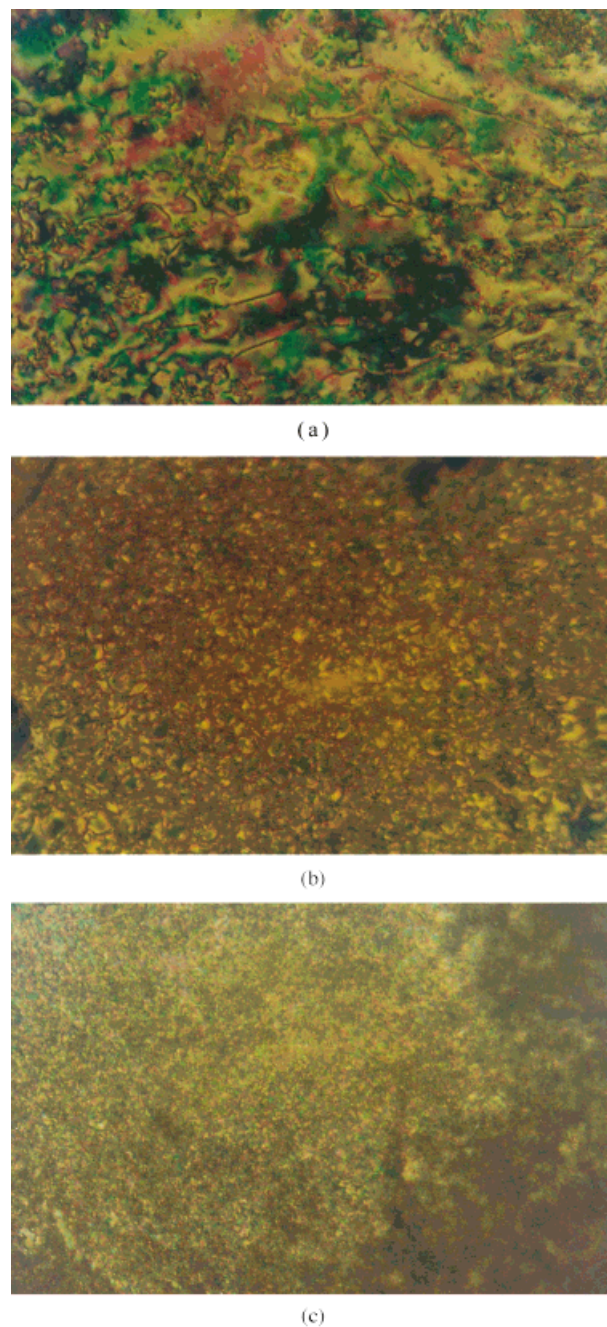


Figure 6 Polarized optical micrographs of S_n -LCP: (a) S_0 -LCP at 231.1 °C, (b) S_4 -LCP at 187.2 °C, and (c) S_8 -LCP at 197.3 °C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

°C, but they exhibited mesogenic textures above T_{m1} , and the textures did not disappear or weaken until they were carbonized by POM; thus, $T_{5\%}$ [temperature at which 5% mass loss occurred in thermogravimetric analysis (TGA)] was

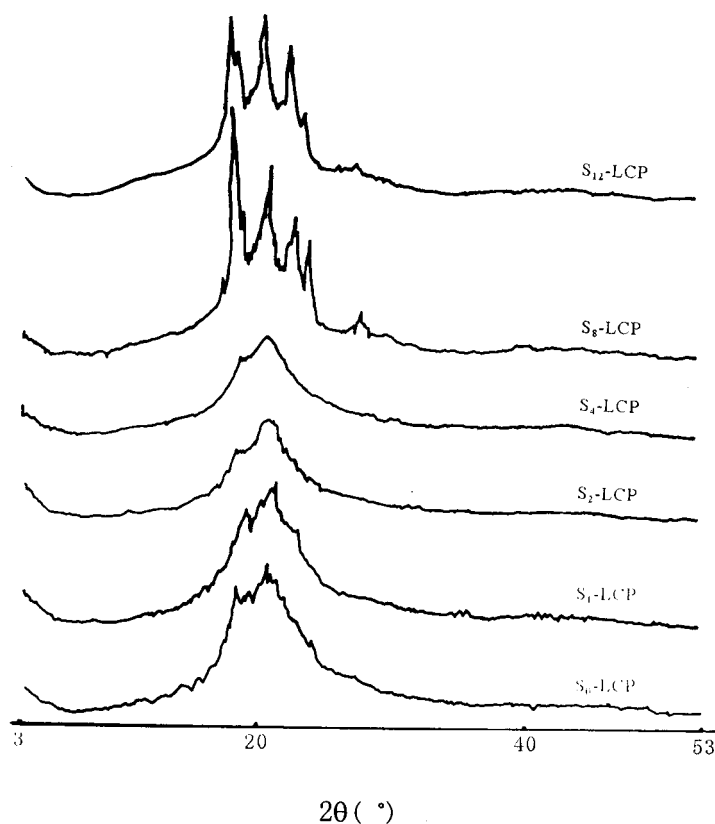


Figure 7 X-ray diffraction patterns of S_n -LCP.

adopted as the final temperature of the mesophase in the present article (because the mesogenic phase is meaningless after the polymers decompose). The mesogenic region $\Delta T = T_{5\%} - T_{m2}$ of ionomers S_{1-12} -LCP were broadened about 56–65 °C compared with the polymer S_0 -LCP.

TGA thermograms of the ionomers obtained under nitrogen atmosphere are given in Figure 5; the percent mass loss at various temperatures and temperature of 5% mass loss are listed in Table III. The initial decomposition temperatures of the polymers were observed at about 310 °C, and there are three distinct steps on the TGA curves. The mass loss of the polymers rapidly took place between 320 and 380 °C; the mass loss of all the polymers is nearly identical in this region. This is followed by a region of gradual mass loss between 380 and 475 °C. The mass loss of ionomers S_{1-12} -LCP decreased with an increasing BY concentration at 420 °C as shown in Table III. In the last region of 475–600 °C, the polymers nearly lost all their mass, the temperature at which 5% mass loss ($T_{5\%}$) decreased with an increasing BY concentration. The thermal stability

of the ionomers (S_{1-12} -LCP) increased with an increasing BY concentration but somewhat decreased compared with S_0 -LCP, which may be attributed to the decreased molecular weight for the introduction of the ionic groups.

Texture Analysis

The textures of polymers observed with POM under nitrogen atmosphere are shown in Figure 6. Polymer S_0 -LCP showed a threadlike texture in Figure 6(a), which is a typical nematic texture.¹⁰ Ionomers S_{1-8} -LCP were similar to S_0 -LCP and exhibited typical nematic threadlike textures as shown in Figures 6(b,c). Therefore, the introduction of an ionic group did not change the texture of the original polymer (S_0 -LCP). Threadlike texture was also observed for ionomer S_{12} -LCP by POM, but no clear photos could be taken; thus, the liquid-crystalline properties of the polymers were somewhat weakened as the concentration of ionic unit increased to higher than 8%.

Figure 7 shows typical wide-angle X-ray diffraction (WAXD) patterns of quenched samples of the polymers. Polymer S_0 -LCP was quenched at

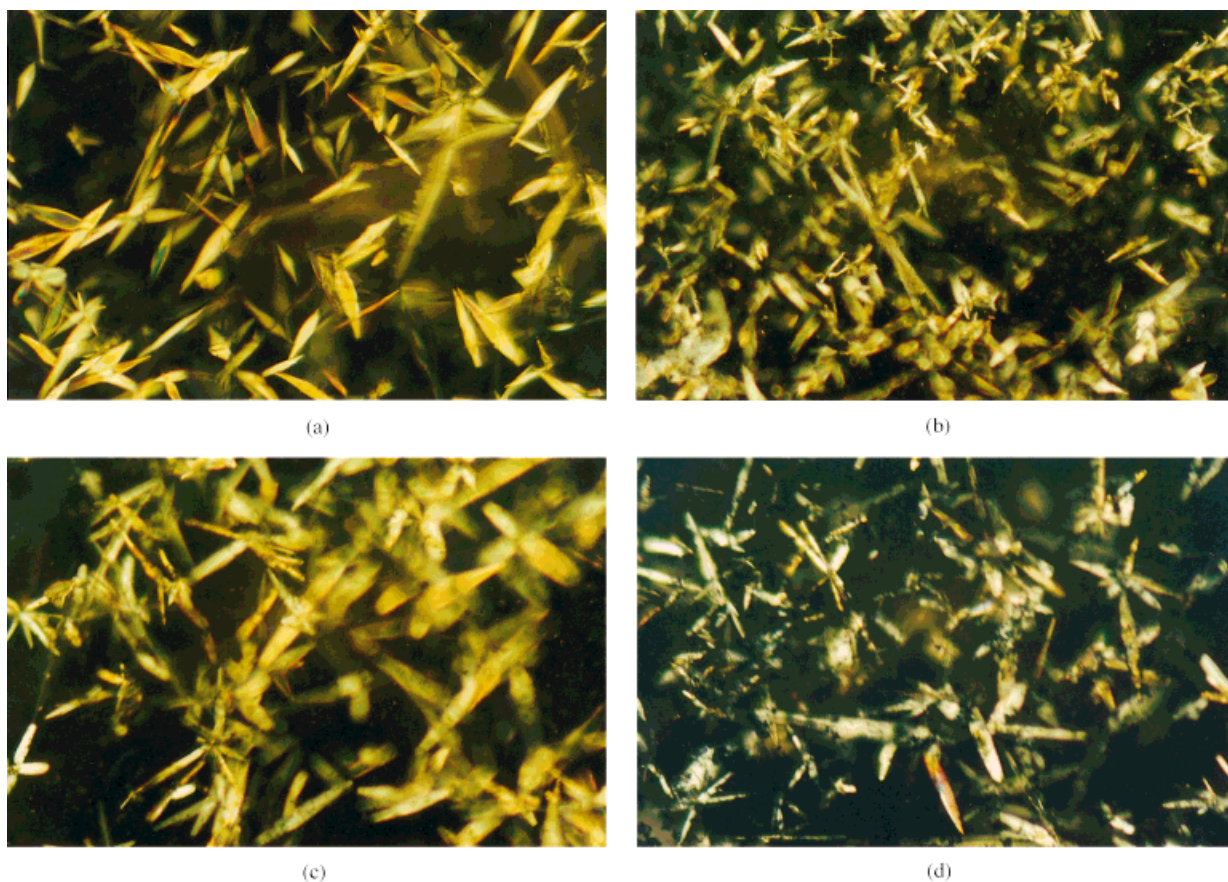


Figure 8 Polarized optical micrographs of S_n -LCP in H_2SO_4 : (a) S_0 -LCP, (b) S_4 -LCP, (c) S_8 -LCP, and (d) S_{12} -LCP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

200 °C. Ionomers S_{1-12} -LCP were quenched at 175 °C. The quenched samples were measured by WAXD and small-angle X-ray scattering. Polymer S_0 -LCP and ionomers S_{1-12} -LCP exhibited strong diffuse peaks between 18 and 23° in the higher angle region, and no sharp peak in the lower angle region was observed. This is evidence that they all exhibit only nematic mesophases.¹⁰ It also indicates that the introduction of an ionic group did not change the mesogenic texture of polymer S_0 -LCP. There are several sharper peaks in the diffuse peaks of S_8 -LCP and S_{12} -LCP that imply the two ionomers are higher crystalline.

Analysis of Lyotropic Liquid-Crystalline Property

Solution-casting thin samples of all the polymers were homogeneous as they were observed under a nonpolarizing optical system, but they exhibited multicolor textures as they were observed under a polarizing optical system by POM at ambient

temperature. Ionomers S_{1-12} -LCP in concentrated sulfuric acid exhibited multicolor willow leaf-shaped textures that are similar to polymer S_0 -LCP, as shown in Figure 8. It seems that the macromolecular chains of these ionomers oriented in solvent when the polymers dissolved in concentrated sulfuric acid, and the oriented macromolecular chains grouped together and formed many oriented microcrystals because of their continual motion in solution. Therefore, the polymers showed a willow leaf-shaped texture. The detailed lyotropic liquid-crystalline properties of the polymers are under further investigation.

CONCLUSIONS

Liquid-crystalline polymers containing sodium sulfonate groups pendant on the polymer backbone were synthesized and characterized. These polymers exhibited a broad mesogenic range of

160–170 °C and good thermal stability to 310 °C. They were all thermotropic liquid–crystalline polymers with clear nematic threadlike textures. The solution viscosity behavior in *N*-methyl-2-pyrrolidone was similar to the common ionomers. Further studies indicated that the polymers also exhibited lyotropic liquid–crystalline properties with willowy leaf-shaped textures.

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