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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Bao-Yan Zhang^a; Mei Tian^a; Fan-Bao Meng^a; Xiao-Zhi He^a

^a The Centre for Molecular Science and Engineering, Northeastern University, Shenyang 110004, P R China

To cite this Article Zhang, Bao-Yan , Tian, Mei , Meng, Fan-Bao and He, Xiao-Zhi(2005) 'Synthesis and characterization of main chain liquid crystalline ionomers containing sulphonate groups', *Liquid Crystals*, 32: 8, 997 – 1003

To link to this Article: DOI: 10.1080/02678290500036425

URL: <http://dx.doi.org/10.1080/02678290500036425>

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Synthesis and characterization of main chain liquid crystalline ionomers containing sulphonate groups

BAO-YAN ZHANG*, MEI TIAN, FAN-BAO MENG and XIAO-ZHI HE

The Centre for Molecular Science and Engineering, Northeastern University, Shenyang 110004, P R China

A series of main chain liquid crystalline ionomers containing sulphonate groups pendent to the polymer backbone were synthesized by an interfacial condensation reaction of 4,4'-bis(1,10-sebacoyloxy)benzoic acid, brilliant yellow (BY), and 4,4'-biphenyldiol. 4,4'-Bis(1,10-sebacoyloxy)benzoic acid exhibited nematic schlieren texture during heating and cooling. The ionomers are thermotropic liquid crystalline polymers and thermally stable to about 270°C. They exhibit broad mesophase regions over a range of 220°C and the same nematic mesomorph with a colourful thread texture as B₀-LCP, which implies that the introduction of an ionic group did not change the texture of the B₀-LCP. However, the thermotropic liquid crystalline properties were somewhat weakened when the concentration of BY was more than 5%. The inherent viscosity in *N,N*-dimethylformamide solution suggested that intermolecular associations of sulphonate groups occurred at low concentration, and intermolecular associations predominated at higher concentration.

1. Introduction

Liquid crystalline polymers (LCPs) show high strength and high stiffness properties. However, the major shortcoming limiting their application is the weakness transverse to the fibre axis [1]. 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; these should promote interchain interactions and improve the interfacial adhesion in the polymers [2], especially for main chain LCPs containing ionic groups [3–7]. For example, thermotropic LCPs with ionic groups would offer the possibility for promoting intermolecular interaction through hydrogen bonds or ion–dipole association, and the improvement of the interfacial adhesion between the phases in blends. We have been examining liquid crystalline ionomers (LCIs) containing sulphonate groups in recent years, and have reported the synthesis of three thermotropic main chain LCIs and two side chain LCIs with sulphonate groups in previous research [8–12]. In the present work a series of novel main chain LCIs containing sulphonate ionic monomer was synthesized. The effect of the ionic content on the mesomorphic properties, thermal stability and textures is discussed in the following.

2. Experimental

2.1. Characterization

IR spectra were recorded using a Nicolet 510P FTIR spectrometer with KBr pellet samples. The UV spectra of the polymer solutions in sulphuric acid (96%) were measured with a Shanghai 751 UV-visible spectrometer. ¹H NMR spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA).

Thermal transition temperatures were determined with a Netzsch Instruments DSC 204 equipped with a liquid nitrogen cooling system at a heating rate of 20°C min⁻¹ in a nitrogen atmosphere. The reported transition temperatures were collected during the second heating cycle. The textures of the liquid crystalline phase were observed with a Leica DMRX polarizing optical microscope (POM) equipped with a Linkam THMS-600 hot stage. The thermal stabilities of the polymers were measured with a thermogravimetric analyser using a nitrogen atmosphere and a 20°C min⁻¹ heating rate.

X-ray diffraction measurements were performed with nickel-filtered Cu-K_α radiation using a Rigaku powder diffractometer. Dilute solution viscosity measurements were carried out in *N,N*-dimethylformamide solution at 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.

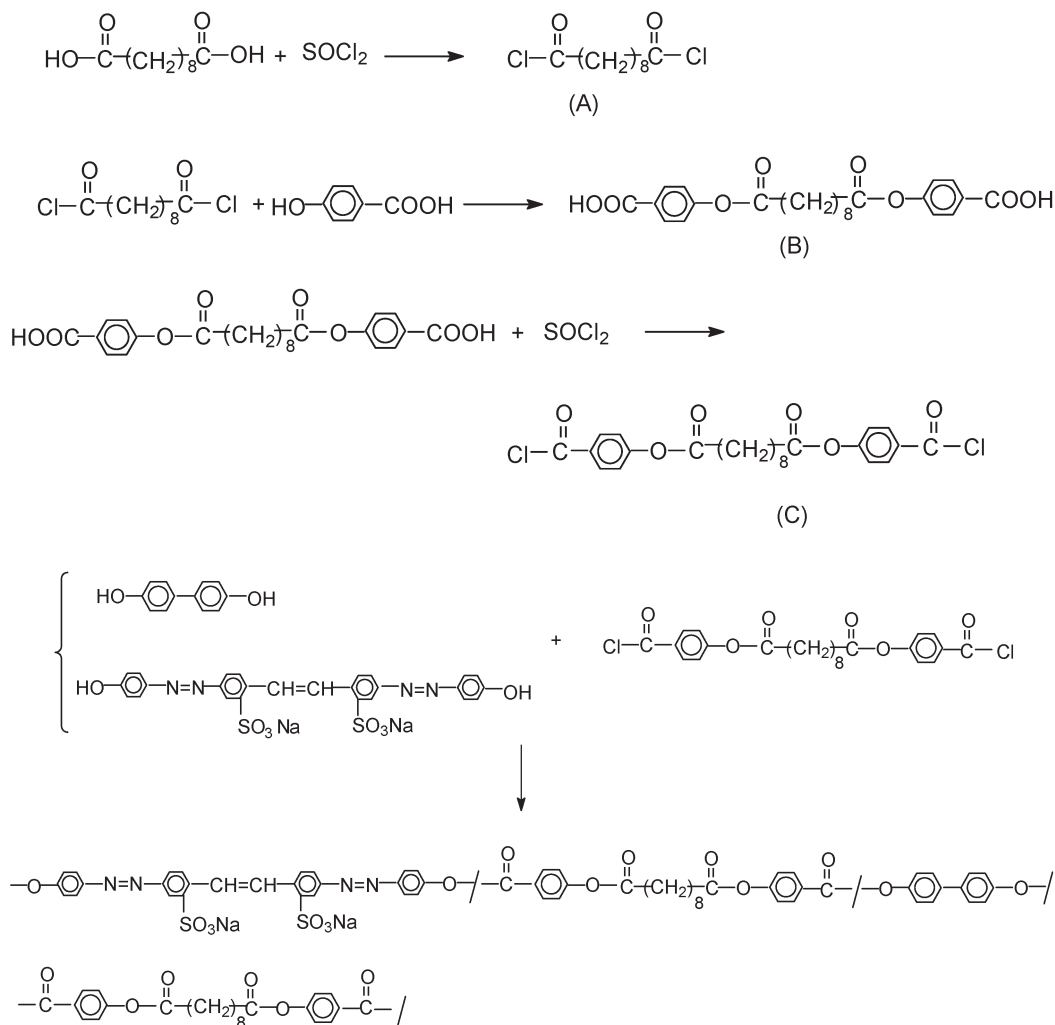
*Corresponding author. Email: baoyanzhang@hotmail.com

2.2. Synthesis

Brilliant yellow (98%), sebacic acid ($\geq 99\%$), *N,N*-dimethylformamide and 4,4'-biphenyldiol ($\geq 99\%$) were obtained from Beijing Chemical Industry Co. *p*-Hydroxybenzoic acid, thionyl chloride (b.p. 78.8°C) and pyridine were obtained from Shenyang Chemical Co. Pyridine was purified by distillation over KOH; all other solvents and reagents were used as received.

2.2.1. Synthesis of sebacoyl dichloride (A). Sebacic acid (0.099 mol) and thionyl chloride (0.294 mol) were stirred together for 2 h at room temperature, and then heated under reflux at 78°C for 4 h. The excess thionyl chloride was removed to give compound A in 85% yield (b.p. 168°C/12 mm Hg) (see the scheme).

2.2.2. Synthesis of 4,4'-bis(1,10-sebacoyloxy)benzoic acid (B). *p*-Hydroxybenzoic acid (0.404 mol) was dissolved in 120 ml pyridine and compound A (0.2 mol) added to the mixture. The reaction mixture was heated under reflux for 8 h; it was then poured into 500 ml pH 3.5 hydrochloric acid solution. The precipitated crude product was separated, washed repeatedly with hot water, then washed with ethanol and dried overnight at 40°C in a vacuum oven, giving a 78% yield of compound B. Thermal properties are summarized in table 1. IR (KBr) cm^{-1} : 3450 (–OH), 2932, 2853 (–CH₂–), 1766 (C=O), 1603, 1507 (Ar), 1205 (C–O). ¹H NMR (CDCl₃) (ppm) δ =11.2, (s, 2H, H₂COO–C₆H₄–) 7.69(d, 4H, Ar C–H), 7.18(d, 4H, Ar C–H), 2.25(t, 4H, –OCO–CH₂–CH₂–), 1.31(m, 12H, –CH₂–(CH₂)₆–CH₂–).



Scheme. Synthesis of the ionomers.

Table 1. Thermal analysis results for compound B.

| Second heating | | | | | First cooling | | | | | Mesophase |
|----------------------|------------------------------|----------------------|------------------------------|-------------------------------|---------------------------|---------------------------------|------------------------|------------------------------|-------------------------------|-----------|
| $T_m/^\circ\text{C}$ | $\Delta H_m/\text{J g}^{-1}$ | $T_i/^\circ\text{C}$ | $\Delta H_i/\text{J g}^{-1}$ | $\Delta T_1^a/^\circ\text{C}$ | $T_{ai}^b/^\circ\text{C}$ | $\Delta H_{ai}/\text{J g}^{-1}$ | $T_c^c/^\circ\text{C}$ | $\Delta H_c/\text{J g}^{-1}$ | $\Delta T_2^d/^\circ\text{C}$ | |
| 112.3 | 0.76 | 231.2 | 0.40 | 118.9 | 210.5 | -0.18 | 91.1 | -0.43 | 119.4 | nematic |

^a The mesomorphic temperature range (T_i-T_m).

^b Transition temperature from isotropic to mesomorphic phase on cooling.

^c Transition temperature from mesomorphic phase to crystal phase on cooling.

^d The mesomorphic temperature range ($T_{ai}-T_c$).

2.2.3. Synthesis of 4,4'-bis(1,10-sebacoyloxy)benzoyl chloride (C). Compound B(0.138 mol) and thionyl chloride(0.6 mol) were mixed and stirred for 2 h at room temperature; the mixture was then heated under reflux for 4 h at 78°C and excess thionyl chloride distilled off. An 86% yield of compound C was obtained.

2.2.4. Synthesis of ionomers. Interfacial polymerizations (see table 2) were carried out in a high speed Warring blender. Compound C (2.5 mmol) in dichloromethane (30 ml) was rapidly added to a slowly stirred aqueous layer (30 ml) composed of 4,4'-biphenyldiol, and brilliant yellow (BY) and 36 mg of sodium hydroxide; 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 until the filtrate was clear and colourless; they were finally dried in a vacuum oven at 50–60°C for at last 12 h. IR (KBr) cm^{-1} : 3366 (–OH), 2920, 2850 (–CH₂–), 1737 (C=O), 1601, 1496 (Ar), 1200 (C–O–C).

3. Results and discussion

3.1. FTIR spectra

The characteristic absorption bands of the ionomers are indicated above. For organic sulphonate, the FTIR

absorption range of the O=S=O asymmetric and symmetric stretching modes lies in the range 1120–1230 cm^{-1} and 1010–1080 cm^{-1} , respectively; that of the S–O stretching mode lies in the range 600–700 cm^{-1} . Because of the overlap found for both asymmetric and symmetric stretching bands of SO₂ with C–O in the polymers, the S–O stretching mode is chosen for identification of sulphonate groups in the ionomers. Figure 1 compares the FTIR spectra in the range 400–1800 cm^{-1} for (a) non-ionic B₀-LCP and (b) B₃-LCP; while no S–O stretching mode is found in the non-ionic content B₀-LCP, such modes are found as weak absorption bands at 625 cm^{-1} for the ionomers. These results clearly indicate the successful incorporation of ionic groups.

3.2. UV spectroscopy

The UV absorption spectra of all the polymers in the region $\lambda=250$ –500 nm are shown in figure 2. The polymers containing BY exhibited two absorption, at $\lambda=285$ and 400–425 nm. The first absorption peak was due to the conjugated benzene, whereas the latter band was due to the BY of the LCIs ($\lambda=410$ nm). The absorbance intensity of the latter peak increased with increasing BY concentration in the reaction batch. The UV analysis showed that the amount of BY in the LCIs increased with the increasing amount of BY in the reaction batch. We are sure that the increase of the

Table 2. Polymerization conditions.

| Polymer | Feed | | | | | |
|---------------------|--------|----------------------|---------|----------------------|---------|------------|
| | C/mmol | D ^a /mmol | BY/mmol | (BY) ^b /% | Yield/% | $[\eta]^c$ |
| B ₀ -LCP | 2.500 | 2.500 | 0 | 0 | 83.5 | 0.731 |
| B ₁ -LCP | 2.500 | 2.475 | 0.025 | 1 | 82.4 | 0.702 |
| B ₂ -LCP | 2.500 | 2.450 | 0.050 | 2 | 83.2 | 0.651 |
| B ₃ -LCP | 2.500 | 2.425 | 0.075 | 3 | 80.1 | 0.594 |
| B ₄ -LCP | 2.500 | 2.400 | 0.100 | 4 | 82.5 | 0.453 |
| B ₅ -LCP | 2.500 | 2.375 | 0.125 | 5 | 82.0 | 0.312 |

^a 4,4'-Biphenyldiol.

^b Mol% of BY based on D+BY.

^c $[\eta]$: Inherent viscosity.

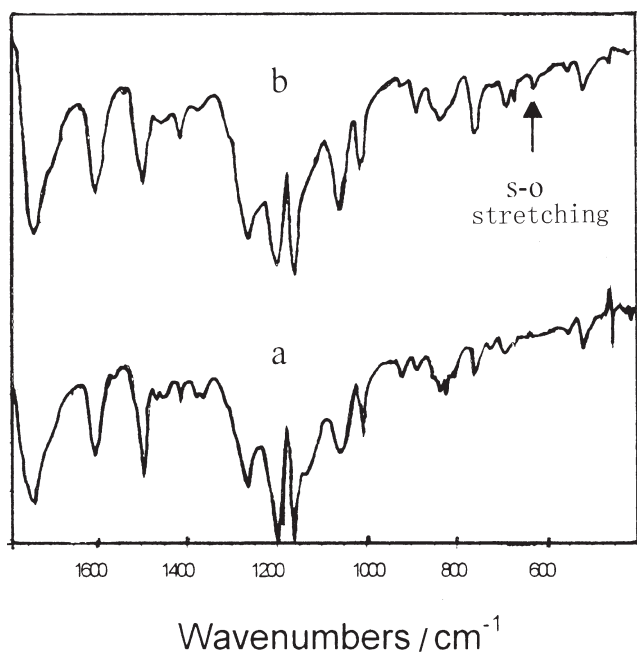


Figure 1. IR spectra in the range $400\text{--}1800\text{ cm}^{-1}$ for (a) B_0 -LCP, (b) B_3 -LCP.

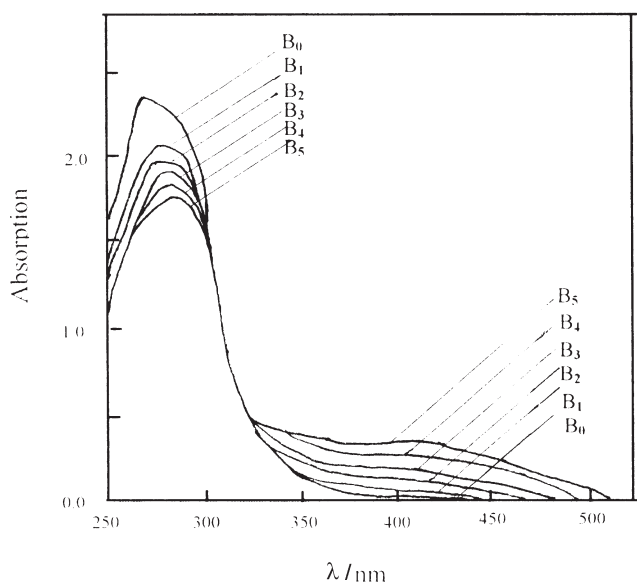


Figure 2. UV absorption spectra of polymers as a function of sulphonate concentration.

absorbance intensity of the peak ($\lambda=410\text{ nm}$) was not due to BY monomer because it is soluble in the water, and the polymers were washed repeatedly with fresh methanol and methanol/water mixture until the filtrate

was clear and colourless, showing that BY monomer had been washed away. This corresponds with the results of SPIT analysis.

3.3. Solution behaviour

The viscosity of the ionomers is summarized in table 2, indicating a decrease with increasing BY concentration. Figure 3 demonstrates the reduced viscosity of ionomers B_1 -LCP, B_3 -LCP and B_5 -LCP in N,N -dimethylformamide at $30 \pm 0.2^\circ\text{C}$. The solution viscosity behaviour of all the ionomers was similar. At concentrations lower than 1.6 g l^{-1} , the reduced viscosity of the ionomer solutions decreased markedly with increasing concentration of ionomer. At high polymer concentrations, the viscosity decreased very slowly with increasing solution concentration. The decrease of viscosity at low polymer concentration was due mainly to ionization of the ion pair [13,14]. As a consequence, the unshielded negative charges on the pendent sulphonate groups repelled each other, causing an expansion of the polymers and an increase in the hydrodynamic volume of the polymers; this is referred to as the polyelectrolyte effect. A polymer concentration above 1.6 g l^{-1} was high enough for intermolecular ionic interaction to reduce the effect of ionization of the ion pair; the viscosity then fell rather slowly. The solution viscosity behaviour in N,N -dimethylformamide was similar to the common ionomers [13,14].

3.4. Thermal analysis

The transition temperatures of the polymers were measured by DSC by first heating the samples to

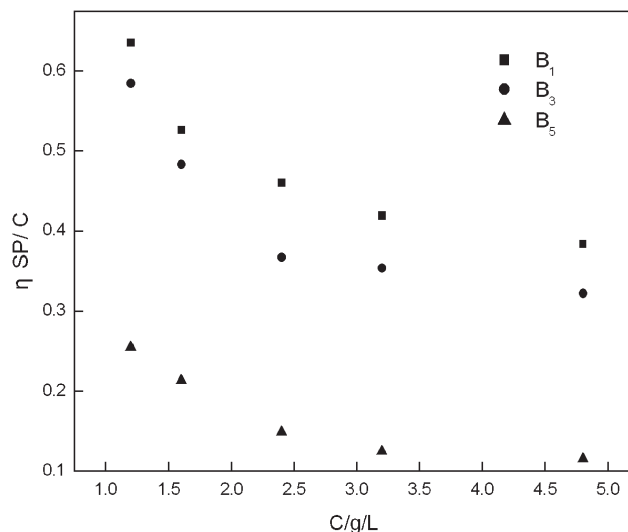


Figure 3. η_{sp}/C at $30 \pm 0.1^\circ\text{C}$ in N,N -dimethyl formamide versus concentration of ionomers.

Table 3. Thermal analysis results for the polymers.

| Polymer | $T_g/^\circ\text{C}$ | $T_m/^\circ\text{C}$ | $T_{5\%}^a/^\circ\text{C}$ | $\Delta T^b/^\circ\text{C}$ | $\Delta H_m^c/\text{J g}^{-1}$ |
|---------------------|----------------------|----------------------|----------------------------|-----------------------------|--------------------------------|
| B ₀ -LCP | 9.7 | 114.4 | 293.0 | 178.6 | 1.47 |
| B ₁ -LCP | -4.3 | 49.5 | 264.0 | 214.5 | 1.98 |
| B ₂ -LCP | -5.8 | 50.2 | 267.0 | 216.8 | 1.64 |
| B ₃ -LCP | -5.7 | 50.1 | 269.5 | 219.4 | 0.75 |
| B ₄ -LCP | -6.0 | 50.3 | 273.9 | 223.6 | 0.57 |
| B ₅ -LCP | -5.5 | 51.0 | 274.5 | 223.5 | 0.81 |

^a Temperature at which 5% weight loss occurred.

^b The mesomorphic temperature range ($T_{5\%}-T_m$).

150°C, then cooling to -50°C and reheating to 350°C at 20°C min⁻¹; the transition temperatures are summarized in table 3. The glass transition temperatures (T_g) of ionomers B₁₋₅-LCP decreased by about 15°C compared with that of the polymer B₀-LCP; the T_g also decreased somewhat with increasing BY concentration. This decrease was probably due to the decrease in molecular mass of the polymers as the BY content increased [11,15]. Table 2 illustrates that the inherent viscosities of polymers B₀₋₅-LCP decrease with increasing BY content; that is, the molecular mass of the polymers decreased with the increasing of BY content, which might be the reason for the decrease of T_g of the polymers. In addition, the polymer chains containing pendent sulphonate groups occupied a large volume and could not pack closely, and the single bond provided easy internal rotation. A common observation [16] in ionomers is that T_g increases with increasing salt group concentration, which is attributed to intermolecular ionic interactions. It has also been observed [9] that T_g decreases with increasing pendant concentration in polymers, due to the large free volume occupied by the polymer chains. In the present work, both of these effects may also have affected the T_g of the ionomers, but neither predominated; therefore the T_g decreased only slightly from B₁-LCP to B₅-LCP.

For all polymers B₀₋₅-LCP, T_m values were observed on DSC scans. The T_m of B₁-LCP was lower than that of B₀-LCP, which may be due in part to the decrease of molecular mass; the large free volume of the pendant concentration also had an effect. No T_i values were observed before all polymers were carbonised. Textures seen under POM did not disappear until the polymers were carbonised; therefore $T_{5\%}$ (the temperature at which 5% mass loss occurred in TGA) was adopted as the final temperature of the mesophase in the present study (because the mesogenic phase is meaningless after the polymers decompose). The mesogenic region $\Delta T=T_{5\%}-T_m$ of ionomers B₁₋₅-LCP were broadened by about 30–40°C compared with the polymer B₀-LCP.

TGA thermograms of the polymers measured under a nitrogen atmosphere are given in figure 4. The initial decomposition of the polymers was observed to start at about 250°C. The thermal stability of ionomers B₁₋₅-LCP increased with increasing BY concentration.

3.5. Texture analysis

The textures of compound B and the polymers observed by POM are shown in figure 5. During heating and cooling, B exhibited clear schlieren texture, as shown in figure 5(a); it also exhibited droplets below T_{ai} (transition temperature from isotropic to mesomorphic phase) on cooling, as shown in figure 5(b). These textures are typical for nematic phases. Polymer B₀-LCP exhibited the thread-like texture shown in figure 5(c), also typical for a nematic phase. The textures of ionomers B₁₋₄-LCP were similar to that of B₀-LCP; the typical nematic

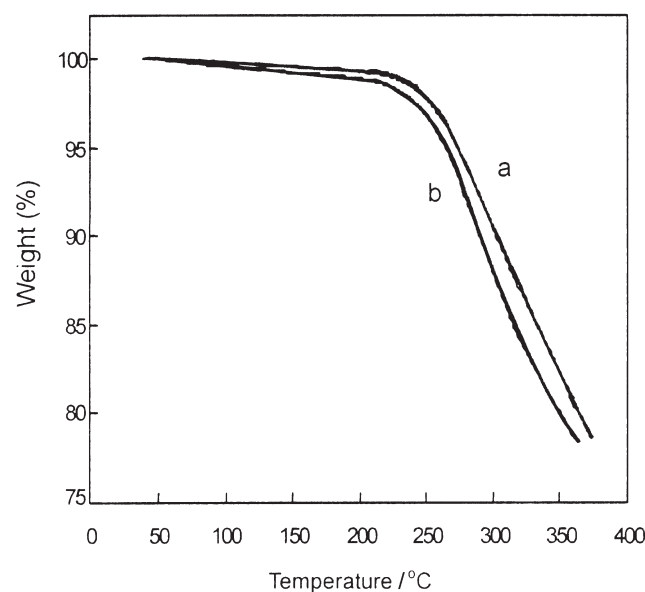


Figure 4. TGA thermograms of B_n-LCP; (a) B₀-LCP, (b) B₄-LCP.

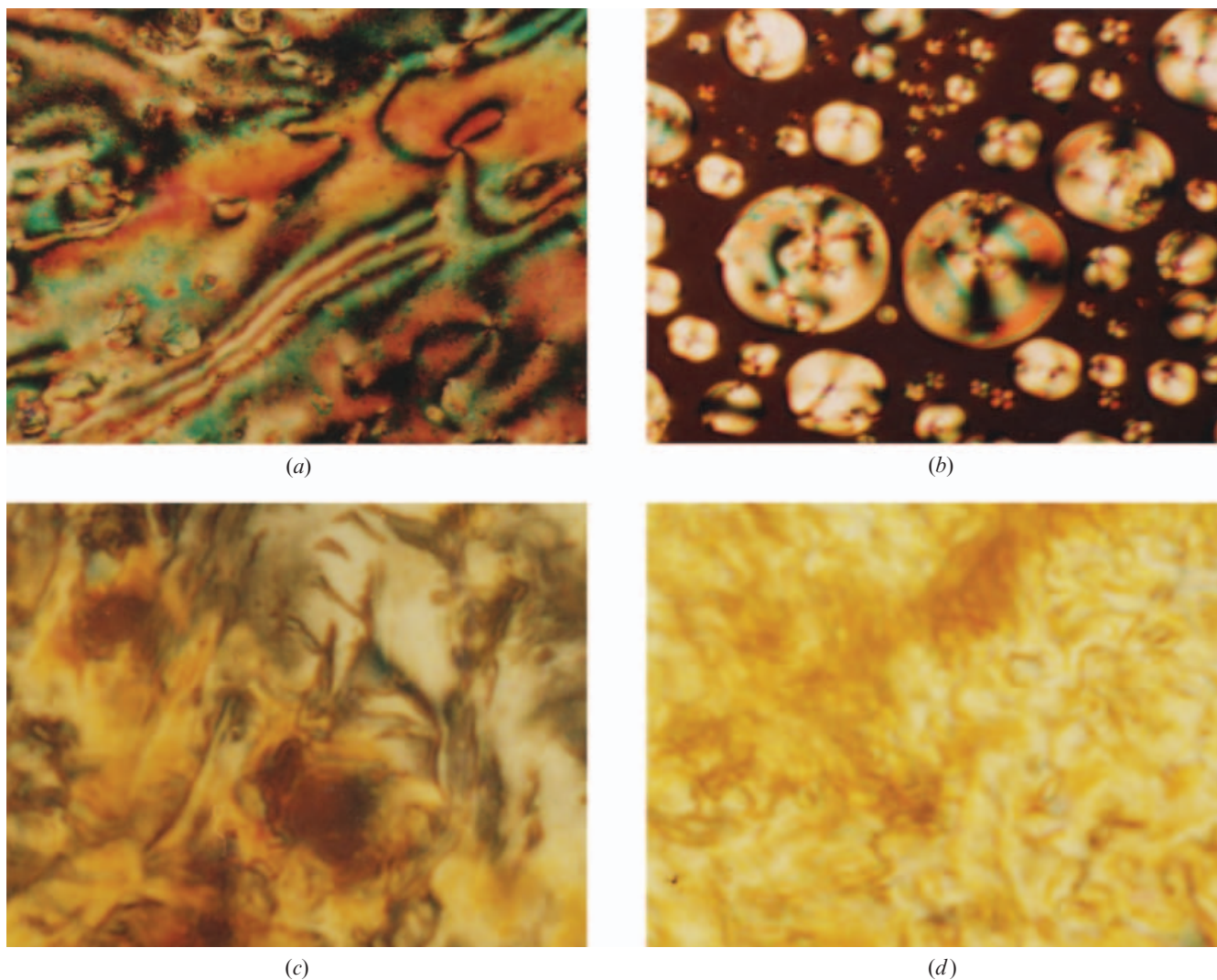


Figure 5. Polarizing optical micrographs ($200\times$) of B and polymers: (a) schlieren texture of B at 169.2°C on heating; (b) droplet texture of B at 197.2°C on cooling; (c) $\text{B}_0\text{-LCP}$ at 228.4°C on heating; (d) $\text{B}_2\text{-LCP}$ at 109.8°C on cooling.

threadlike texture of $\text{B}_2\text{-LCP}$ is shown in figure 5(d). Mesogenic behaviour for $\text{B}_5\text{-LCP}$ was also observed, but not clearly; the liquid crystalline properties of the polymers is somewhat weakened as the concentration of ionic unit exceeds 5%.

3.6. X-ray diffraction analysis

Figure 6 shows typical wide angle X-ray diffraction (WAXD) patterns of quenched samples of the polymers. Polymers $\text{B}_0\text{-LCP}$ and $\text{B}_1\text{-LCP}$ were quenched at 150°C , and were observed under WAXD and small angle X-ray scattering. Polymer $\text{B}_0\text{-LCP}$ and ionomer $\text{B}_1\text{-LCP}$ exhibited diffuse peaks between 20° and 22° in the higher angle region, and no sharp peak in the lower angle region. The results of texture observation and X-ray diffraction of the samples imply that they all exhibit

only nematic mesophases. The results also indicate that the introduction of ionic groups did not change the mesogenic texture of polymer $\text{B}_0\text{-LCP}$. The peak of $\text{B}_1\text{-LCP}$ is sharper than that of $\text{B}_0\text{-LCP}$, implying that $\text{B}_1\text{-LCP}$ is more highly crystalline.

4. Conclusions

Main chain liquid crystalline polymers containing sulphate groups pendent on the polymer backbone were synthesized and characterized. These polymers exhibited a broad mesogenic range of $180\text{--}220^\circ\text{C}$ and good thermal stability to about 270°C . They were all thermotropic liquid crystalline polymers and exhibited threadlike texture. The solution viscosity behaviour in N,N -dimethylformamide was similar to that of common ionomers.

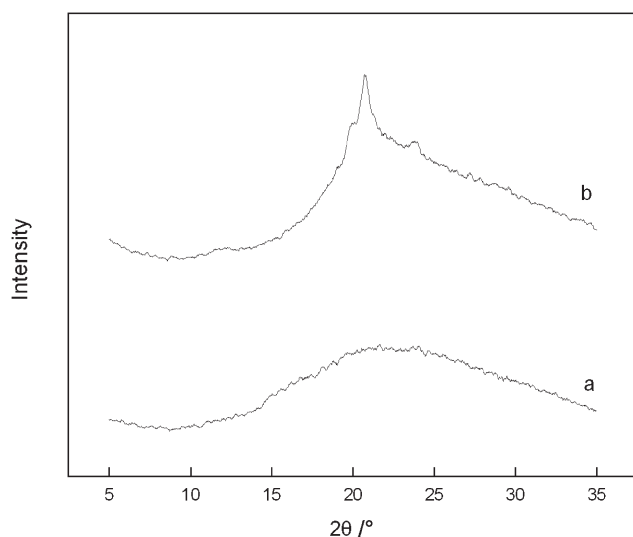


Figure 6. X-ray diffraction patterns of B_n -LCP; (a) B_0 -LCP, (b) B_1 -LCP.

Acknowledgments

The authors are grateful to the National Natural Scientific Fundamental Committee of China, and National Basic Research Priorities of China, for financial support of this work.

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