

# Synthesis and Characterization of Liquid Crystalline Ionomers with Polymethylhydrosiloxane Main-Chain- and Side-Chain-Containing Sulfonic Acid Groups

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**ABSTRACT:** A novel thermotropic side-chain liquid crystalline ionomer (LCI) containing sulfonic acid groups on the side-chain was synthesized by graft copolymerization of mesogenic monomer 4-allyloxy-benzoxy-4'-methoxyphenyl (ABM) and nonemesogenic monomer 4-allyloxy-azobenzene sulfonic acid (AABS) upon polymethylhydrosiloxane (PMHS). The chemical structures of the polymers were confirmed by IR spectroscopy. DSC and TGA were used to measure the thermal properties of those polymers and the mesogenic properties were characterized by polarized optical micrography (POM), DSC, and WAXD. The clearing point temperature ( $T_c$ ) of these liquid crystalline ionomers was enhanced 50–60°C compared with the polymer without ionic groups. The LCIs exhibit a broad smectic mesogenic region of 80–90°C; the thermal stability below 200°C of the polymers decreases with increasing sulfonic acid concentration. The inherent viscosity of 0.5% solutions decreased with increasing sulfonic acid concentration in the polymer chains. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1555–1561, 1998

**Key words:** liquid crystalline ionomers; 4-allyloxyphenylazobenzene sulfonic acid; polymethylhydrosiloxane; smectic; nematic

## INTRODUCTION

Fibers from solution spinning of liquid crystalline polymers (LCPs) show high modulus, strength, and stiffness in the direction of the fiber axis. However, the major shortcoming limiting their application is the weak properties transverse to the fiber axis. Similarly, blends of LCPs with other thermoplastic polymers also have weak interfacial adhesion between the phases. One approach to improving the transverse properties of LCPs and their adhesion with other polymers is to introduce ionic groups. Ionic interaction should promote interchain interactions and improve the interfacial adhesion between the polymers, especially for main-chain LCP-containing ionic groups. In previous articles, we reported the syn-

thesis of two main-chain thermotropic LCIs that contained sulfonate groups.<sup>1,2</sup> The side-chain LCIs have received a lot of interest during recent years, mainly owing to their special optical, mechanical, piezoelectric, and ferroelectric properties. In this article, a novel side-chain thermotropic LCI was synthesized by graft copolymerization of a mesogenic monomer 4-allyloxybenzoxy-4'-methoxyphenyl (ABM), and a nonemesogenic monomer, 4-allyloxy-phenylazobenzene sulfonic acid (AABS), on to polymethylhydrosiloxane (PMHS). The effect of ionic aggregation on the mesomorphic property, thermal stability, and the textures are discussed in this article.

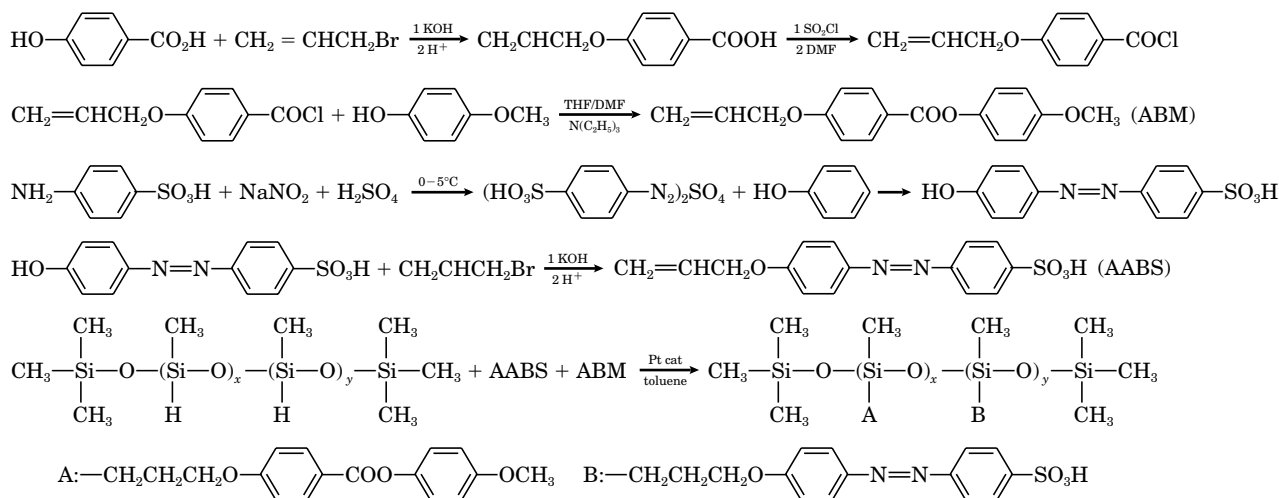
## EXPERIMENTAL

### Reagents and Intermediates

Polymethylhydrosiloxane (PMHS) with  $M_w$  700–800 was offered by Jilin Chemical Industry Com-

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**Scheme 1** Synthetic routes of monomers and polymers.

pany. Dimethylsulfoxide (DMSO) was dried with calcium hydride and has been distilled. Tetrahydrofuran (THF) was predried with molecular sieves, refluxed over lithium aluminum hydride, and then distilled; all other solvents and reagents were used as received.

### Monomer Synthesis

The synthetic routines of monomers are shown in Scheme 1. ABM was synthesized by the following procedure. 4-Allyloxy benzoic acid was prepared according to ref. 3. 4-Allyloxy benzoic acid (0.029 mol) and thionyl chloride ( $\text{SOCl}_2$ ) (10 mL) containing a drop of dimethyl formamide (DMF) were reacted overnight in a round flask equipped with an absorption instrument of hydrogen chloride at room temperature. The mixture was heated to  $60^\circ\text{C}$  and kept for 2 h in a water bath to ensure that the reaction finished. The excess thionyl chloride was removed under reduced pressure to ob-

tain 4-allyloxy benzoyl chloride. The 4-allyloxy benzoyl chloride was dissolved in 15 mL THF, slowly added to a solution containing 4-methoxyphenol (0.024 mol), triethylamine (4.5 mL), DMF (20 mL), and then was reacted for 4 h at room temperature. The mixture was heated to  $60^\circ\text{C}$  in a water bath for 1.5 h. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , then washed with water, concentrated, and precipitated. The crude product was recrystallized with ethanol. The ABM obtained: mp:  $98-100^\circ\text{C}$ ; yields: 59%.

4-Hydroxyazobenzenesulfonic acid was prepared according to the procedure of Hu<sup>4</sup> and AABS was prepared according to the procedure of Chien, Guo, and Chen.<sup>3</sup>

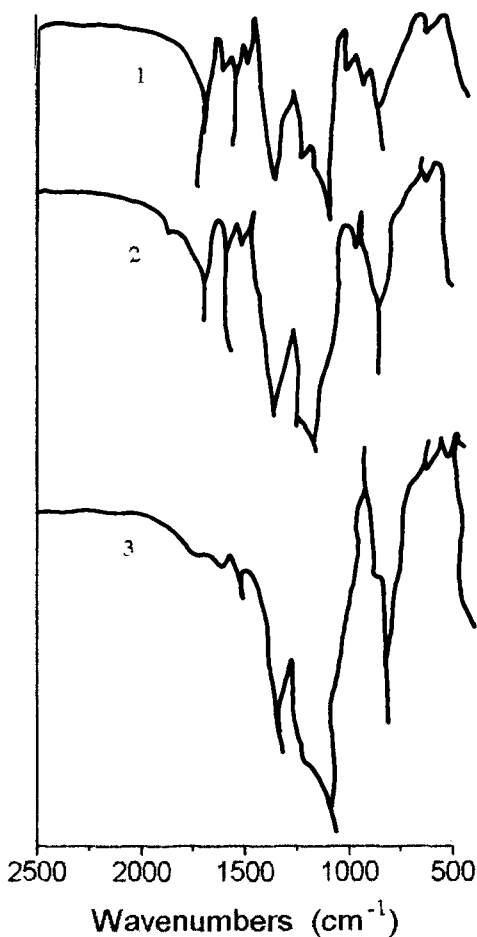
### Polymer Synthesis

The synthetic routines are shown in Scheme 1. All polymers synthesized are listed in Table I. The monomers AABS, ABM, and PMHS were dissolved

**Table I** Polymerizations

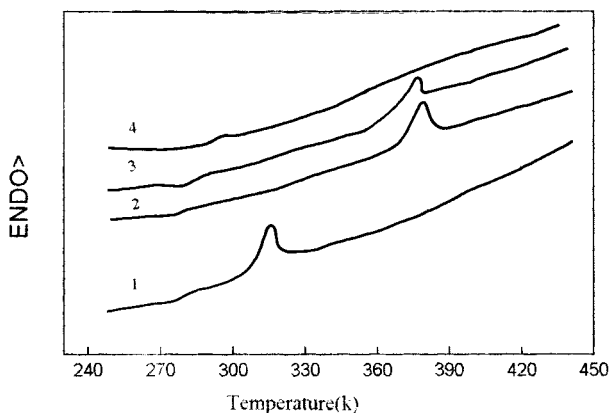
Samples	Feed				Polymers	
	PMHS (mmol)	ABM (mmol)	AABS (mmol)	AABS <sup>a</sup> (mol %)	Yields (%)	$\eta_{\text{inh}}$ (dL/g)
P <sub>I</sub>	1	7	0	0	87	0.021
P <sub>II</sub>	1	6	1	12.5	82	0.019
P <sub>III</sub>	1	3	4	50	80	0.013
P <sub>IV</sub>	1	0	7	87.5	72	0.012

<sup>a</sup> AABS (mol %) in aqueous phase (i.e., based on PMHS + ABM + AABS).

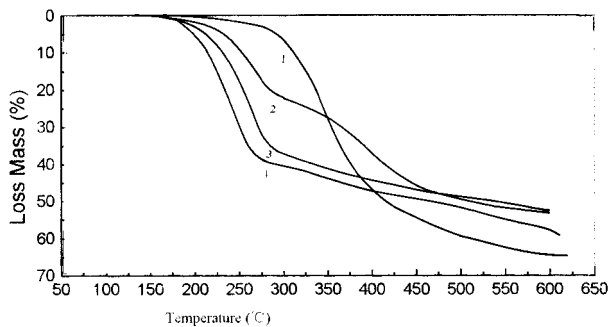


**Figure 1** IR spectra of (1) P<sub>I</sub>, (2) P<sub>II</sub>, and (3) P<sub>IV</sub>.

in toluene and were dried with sodium. A hydrogen hexachloroplatinate (IV) hydrate/THF solution was added to the above solution by means of a glass capillary tube; the mol ratio of Pt/alkene was 1 : 10<sup>3</sup>. The reaction temperature was 60–70°C, and



**Figure 2** DSC thermographs of (1) P<sub>I</sub>, (2) P<sub>II</sub>, (3) P<sub>III</sub>, and (4) P<sub>IV</sub>.



**Figure 3** TGA thermographs of (1) P<sub>I</sub>, (2) P<sub>II</sub>, (3) P<sub>III</sub>, and (4) P<sub>IV</sub>.

the reaction was carried out until the disappearance of the Si—H IR band at 2160 cm<sup>-1</sup>. The products were purified with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1 : 1) and dried in a vacuum oven at room temperature.

### IR Spectroscopy

The structure of polymers was determined with a Nicolet 510-PFI IR spectroscopy, using all polymer samples on KBr.

### Thermal Analysis

Thermal transitions were measured with a Perkin-Elmer DSC-2 using a nitrogen atmosphere and a 20°C/min heating rate; thermal stabilities were measured with a Perkin-Elmer TGA-2 thermogravimetric analyzer using a nitrogen atmosphere and a 10°C/min heating rate.

### POM Analysis

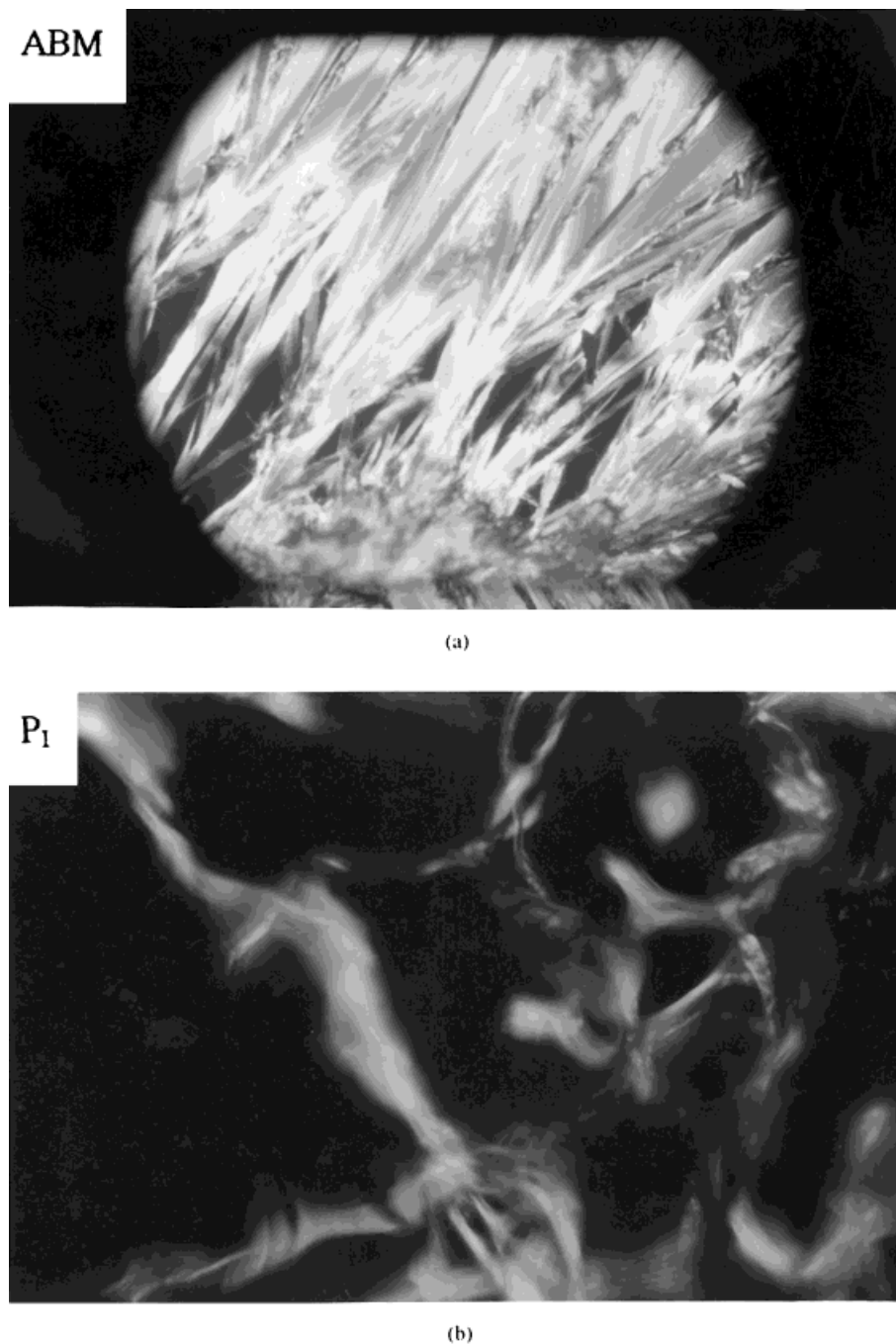
The polymer textures were observed with a Ziss-Jena polarizing optical microscope that was equipped with a Melter FP2 hot stage.

### X-ray Diffraction Analysis

The X-ray diffraction analysis was measured with a Rigaku DMAX X-ray instrument at room temperature.

### Solution Viscosity

Dilute solution viscosity measurements were carried out in acetone/dimethylsulfoxide (volume ratio 1 : 1) solution at 25 ± 0.1°C using a Ubbelohde capillary viscometer, No. 3-0.48. The flow times were sufficiently long, i.e., > 100 s, so that kinetic energy corrections were neglected.



**Figure 4** Polarized optical micrographs of ABM, P<sub>I</sub>, P<sub>II</sub>, and P<sub>III</sub>: (a) monomer ABM at 110°C; (b) polymer P<sub>I</sub> at 43.6°C; (c) polymer P<sub>II</sub> at 34.1°C; (d) polymer P<sub>III</sub> at 36°C.

## RESULTS AND DISCUSSION

### Polymerizations and Viscosities

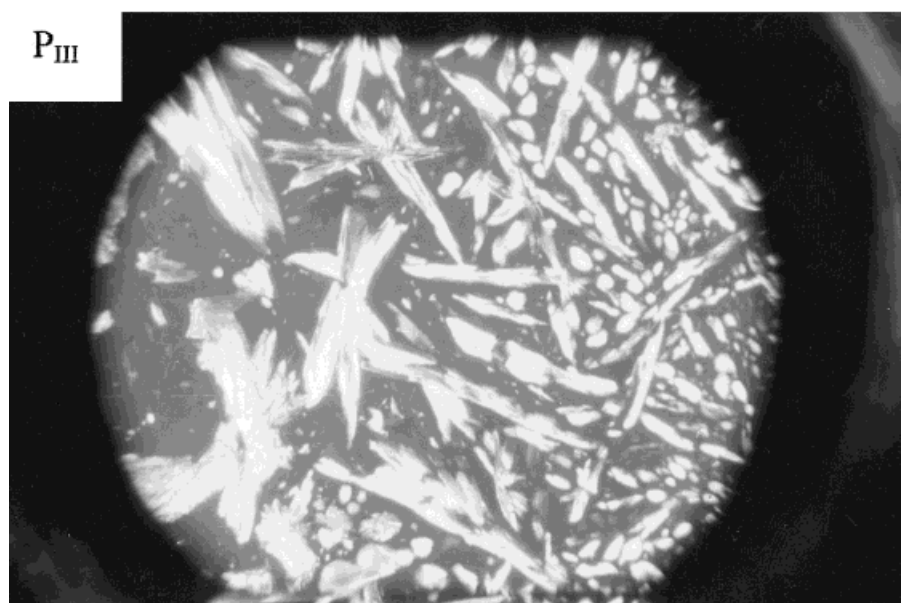
The polymerization experiments are summarized in Table I. The polymer yields decreased with increasing concentration of AABS in the feed. One probable reason is the ionization of the ionpair

suppressed the growth of the chain; another reason is a reduction of the activity of the catalyst by the presence of the sulfonic acid.

Due to the heterogeneous and associating nature of sulfonic acid of the polymers the determination of molecular weight is difficult. However, the molecular weights of polymers may be compared by using the inherent viscosity of a 0.5%



(c)



(d)

**Figure 4** (Continued from the previous page)

solution in dimethylsulfoxide/acetone (volume ratio 1 : 1) at  $25 \pm 0.1^\circ\text{C}$ . Viscosities are listed in Table I. The polymers were yellow in appearance, and the color became more intense as the AABS concentration increased. The good solvents were not found for all of the series polymers, the solubility of the polymers in dimethylsulfoxide/acetone became poor as the concentration of AABS in the polymers increased. The probable reason is

increasing intermolecular ionic associations with increasing AABS in the polymer chain. The inherent viscosity decreased from 0.021 dL/g to 0.012 dL/g with increasing AABS concentration. The inherent viscosities given indicated low molecular weight for the polymers, which is consistent with the low molecular weight of PMHS, only 700–800; The viscosities given are lower than the real viscosities for the polymers; the errors of the inher-

**Table II** The Thermal Analysis Results

Polymer	$n^a$	Temperature (°C)				Weight Loss (%)			
		$T_g$	$T_c$	$\Delta T^b$	$T^c$	200°C	250°C	350°C	610°C
P <sub>I</sub>	0	8.7	42.0	33.3	296	0.8	1.7	25	65
P <sub>II</sub>	12.5	10.0	91.6	81.6	236	1.0	8.5	26.8	49
P <sub>III</sub>	50	9.0	90.6	81.6	210	3.5	17.6	42.0	53.5
P <sub>IV</sub>	87.5	9.2	—	—	200	5.0	29.2	44	59.0

<sup>a</sup> The mole fraction of sulfonic acid.

<sup>b</sup> The mesomorphic temperature range (i.e.,  $T_c - T_g$ ).

<sup>c</sup> Temperature at which 5% loss occurred.

ent viscosities increases with ionic groups increasing in the polymer chain.

### IR Spectra Analysis

The IR spectra of the polymers are shown in Figure 1. The band from the Si—H bond at 2160  $\text{cm}^{-1}$  disappeared in the polymers; meanwhile, the band of sulfonic acid near 1100  $\text{cm}^{-1}$  increased and the band for the carbonyl group near 1730  $\text{cm}^{-1}$  disappeared as the AABS increased from P<sub>II</sub> to P<sub>IV</sub>.

### Thermal Analysis

The DSC heating thermograms in Figure 2 show the glass transition temperature at 8.7–10°C and a clearing point at 42.0–90.6°C have no melting point for the polymers P<sub>I</sub>, P<sub>II</sub>, and P<sub>III</sub>. The polymer P<sub>IV</sub> only exhibits glass transition temperature at 9.2°C. Compared with the polymer without sulfonic acid ions, the  $T_c$  of the LCIs was almost enhanced 50°C. The probable reason is that the low grafting ratio and a broad distribution of the sulfonic acid composition on the chain of the polymers and the existence of the ionic groups almost did not influence the movement of the soft segment for the main-chain and the side-chain; the  $T_g$  changed little because  $T_g$  involves movement of segments in the polymers. The  $T_c$  is the temperature involving whole-chain movement of the polymer, the effect of association or junction of the ionic groups may influence the chain movement, so the  $T_c$  of the LCIs was enhanced compared with polymer without ionic groups, and  $T_c$  increased with increasing of the sulfonic acid concentration.

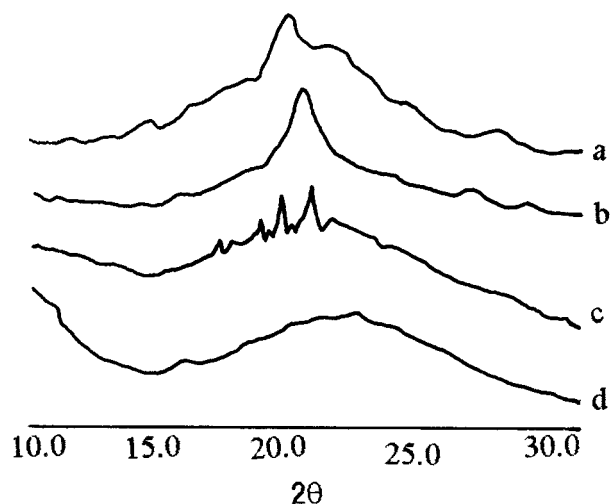
TGA thermograms of the polymers measured using a nitrogen atmosphere are given in Figure

3, and the temperature at which 5% mass loss occurred and the percent mass loss at various temperatures are listed in Table II. The temperature at which 5% mass loss occurred decreased with increasing of the sulfonic acid concentration, which was consistent with other reported articles,<sup>1,2</sup> but the mass loss decreased with increasing sulfonic acid concentrations between 370 and 600°C. The probable cause was that the ionic association retarded the decomposition at higher temperature.

### Textures Analysis

The textures of monomers and polymers observed with polarized optical micrographs under nitrogen atmosphere are shown in Figure 4. The monomer ABM showed a fan-shaped mesophase in Figure 4(a), which is a typical smectic texture. AABS did not melt below 300°C; when it was heated to higher temperature, it decomposed and no mesophase was observed, thus illustrating that AABS was not a mesogenic monomer. In this article, the polymer P<sub>I</sub> showed a schlieren texture as shown in Figure 4(b), which is a typical nematic texture, Figure 4(c,d) show smectic textures of P<sub>II</sub> and P<sub>III</sub>, respectively. Polymer P<sub>IV</sub> was not mesomorphic as demonstrated by DSC and polarized optical micrographs.

Figure 5 shows typical wide angle X-ray diffraction patterns of polymers P<sub>I</sub>, P<sub>II</sub>, P<sub>III</sub>, and P<sub>IV</sub>. Polymer P<sub>I</sub> indicated a sharp peak in the higher angle region around 20° at 25°C, and no sharp peak in a lower Bragg angle region was observed [Fig. 5(a)]. This is the evidence that P<sub>I</sub> exhibits only a nematic mesophase. The polymers P<sub>II</sub> and P<sub>III</sub> indicated one peak at low Bragg angle below 10°, as shown in Figure 5(b,c), derived from the corresponding  $d$ -spacing of smectic orientations



**Figure 5** X-ray diffraction patterns of the polymers at 25°C: (a) polymer P<sub>I</sub>, (b) polymer P<sub>II</sub>, (c) polymer P<sub>III</sub>, (d) polymer P<sub>IV</sub>.

of mesogens. A sharp peak was observed in the higher angle region around 20° at 25°C. Therefore, P<sub>II</sub> and P<sub>III</sub> represent a highly ordered smectic phase in the low temperature range. The polymer P<sub>IV</sub> has no sharp peak in a lower nor higher Bragg angle region. This implies that P<sub>IV</sub> exhibits no mesophase [Fig. 5(d)].

## CONCLUSIONS

Liquid crystalline ionomers containing sulfonic acid groups on the side-chain to the PMHS backbone were synthesized by graft copolymerization and were characterized. These LCIs exhibited mesomorphic behavior over a broad temperature range of 80°C, the  $T_g$  of the LCIs were around 9°C and had good thermal stabilities.

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## REFERENCES

1. B. Y. Zhang and R. A. Weiss, *J. Polym. Sci. Polym. Chem.*, **30**, 91 (1992).
2. B. Y. Zhang and R. A. Weiss, *J. Polym. Sci. Polym. Chem.*, **30**, 989 (1992).
3. G. C. Chien, J. F. Kuo, and C. Chen, *J. Polym. Sci. Polym. Chem.*, **31**, 2423 (1993).
4. H. W. Hu, *Organic Chemistry*, Higher Education Press, 1991, p. 574.