

Synthesis and Characterization of Chiral Smectic Side-Chain Liquid Crystalline Polysiloxanes and Ionomers Containing Sulfonic Acid Groups

JIAN SHE HU,¹ BAOYAN ZHANG,¹ ZHILIU FENG,² HONGGUANG WANG,¹ AIJUAN ZHOU¹

¹ Department of Chemistry, Northeastern University, Shenyang 110006, China

² Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Received 15 March 2000; accepted 3 July 2000

ABSTRACT: The synthesis of new chiral smectic A (S_A) side-chain liquid crystalline polysiloxanes (LCPs) and ionomers (LCIs) containing 4-allyloxy-benzoyl-4-(*S*-2-ethylhexanoyl) *p*-benzenediol bisate (ABB) as mesogenic units and 4-[[4-(2-propenyloxy)phenyl]azo]benzenesulfonic acid (AABS) as nonmesogenic units is presented. The chemical structures of the monomers and polymers are confirmed by FTIR spectroscopy or ¹H-NMR. Differential scanning calorimetry (DSC), optical polarizing microscopy, and X-ray diffraction measurements reveal that all the polymers P_I – P_{IV} and ionomers P_V – P_{VI} exhibit S_A texture. The results seem to demonstrate that the tendency toward the S_A -phase region increases with increasing sulfonic acid concentration, and the thermal stability of the S_A phase is determined by the flexibility of the polymer backbones and the interactions of sulfonic acid groups. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2335–2340, 2001

Key words: chiral; smectic; polysiloxane; liquid crystalline ionomer; sulfonic acid; 4-allyloxybenzoyl-4-(*S*-2-ethylhexanoyl) *p*-benzenediol bisate

INTRODUCTION

In 1975 Mayer¹ presented theoretically and then proved experimentally that the chiral smectic mesophase was probably ferroelectric. A bistable, fast switching electro-optical device, which used a chiral smectic liquid crystalline polymer, was demonstrated a few years later by Clark and Lagerwall.² Although a number of studies concerning low molecular weight chiral smectic liquid crystalline materials were previously reported, there have been only a few reports on polymeric

chiral smectic liquid crystalline materials. However, some successful investigations on the synthesis and characterization of chiral smectic side-chain liquid crystalline polysiloxanes were recently reported.^{3–7} Therefore it would be both necessary and useful to synthesize various kinds of liquid crystalline polysiloxanes to explore their potential applications.

For improving the transverse properties of liquid crystalline polymers (LCPs) and their adhesion with other polymers, ionic groups were introduced. Ionic interaction will promote interchain interactions and improve the interfacial adhesion between polymers. In previous studies, we reported the synthesis of two main-chain thermotropic LCPs containing sulfonate groups. The side-chain LCPs have recently attracted increased attention and interest, mainly because of

Correspondence to: B. Zhang (baoyanzhang@hotmail.com).
Contract grant sponsor: National Natural Science Fundamental Committee of China.

Contract grant sponsor: Science Committee of Liaoning Province.

Journal of Applied Polymer Science, Vol. 80, 2335–2340 (2001)
© 2001 John Wiley & Sons, Inc.

their special optical, mechanical, and ferroelectric properties.^{8–10}

In this study, the syntheses of some new chiral smectic liquid crystalline polysiloxanes and ionomers containing 4-allyloxybenzoyl-4-(*S*-2-ethylhexanoyl) *p*-benzenediol bisate (ABB) as mesogenic units and 4-[[4-(2-propenyloxy)phenyl]azo]benzenesulfonic acid (AABS) as nonmesogenic units are discussed. Their characterizations by differential scanning calorimetry, optical polarizing microscopy, and X-ray diffraction are presented. The effect of ionic aggregation on the mesomorphism, thermal stability, and textures are discussed.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS, $M_n = 700$ – 800) was obtained from Jilin Chemical Industry Company (China). (*s*)-2-Ethyl hexanoic acid, a commercial product, was obtained in Shenyang (China) and used as received. Toluene used in the hydroxylation reaction was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard methods.

Experimental Techniques

¹H-NMR spectra (300 MHz) and FTIR spectra were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA) and on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI), respectively. Polymer sample films used for measurements were obtained by casting on a KBr table. Thermal transitions and thermodynamic parameters were determined by using a Perkin-Elmer DSC (Perkin-Elmer, Foster City, CA) equipped with a liquid nitrogen cooling system. Heating and cooling rates were 10°C/min. Thermal transitions reported were collected during the second heating and cooling scans. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) optical polarized light microscope equipped with a Mettler FP82 hot stage and an FP 80 central processor were used to observe the thermal transitions and analyze the anisotropic textures. X-ray diffraction measurements were performed with a nickel-filtered Cu-K α radiation with a Rigaku powder diffractometer.

Synthesis of Monomers

The synthesis of olefin monomers is outlined in Scheme 1. AABS was synthesized according to procedures in the literature.^{10–12}

4-Allyloxybenzoyl-4-(*S*-2-ethylhexanoyl) *p*-benzenediol bisate (ABB)

In a flask, 1.6 g (0.011 mol) of 2-ethylhexanoyl chloride (laboratory-synthesized) was dissolved in 15 mL of tetrahydrofuran. This solution was added dropwise to a solution containing 1.5 g (0.0056 mol) of 4-hydroxyphenyl-4-allyloxybenzoate (laboratory-synthesized), and 20 mL of pyridine. This mixture was then stirred for 10 h at 25–30°C, and was neutralized with 6*M* hydrochloric acid. The resulting precipitate obtained by pouring the solution into water was recrystallized from ethanol. The white crystals obtained: mp = 45°C; yield = 57%.

IR (KBr) cm^{-1} : 3074 (=C—H), 2800–3000 (CH₃—, —CH₂—), 1735 (C=O), 1605, 1512 (Ar—), 1255 (C—O—C—); ¹H-NMR (CDCl₃, TMS) δ ppm: 0.93 [t, 3H, —(CH₂)₂CH₃], 1.01 (t, 3H, —CH₂—CH₃), 1.37 [m, 4H, —(CH₂)₂CH₃], 1.60 [m, 4H, —CH₂(CH₂)—], 2.27 [m, 1H, —CH(C₂H₅)—], 4.36 (d, 2H, —CH₂O—), 5.24–5.35 (m, 2H, CH₂—), 6.00 (m, 1H, =CH—), 6.92–8.05 (m, 8H, Ar—H).

Synthesis of Polymers and Ionomers

The synthetic routes of the polymers and ionomers are outlined in Scheme 1. All polymers and ionomers synthesized are listed in Table I. A general procedure is described below.

The monomers AABS, ABB, and PMHS were dissolved in dry, freshly distilled toluene. The reaction mixture was heated to 50–60°C under nitrogen, and then a proper amount of THF solution of hydrogen hexachloroplatinate(IV) hydrate catalyst was injected with a syringe. The reaction was kept for 72 h. The polymers were separated by precipitation into an excess amount of methanol, purified by repeated precipitation in toluene with excess methanol, and then dried under vacuum.

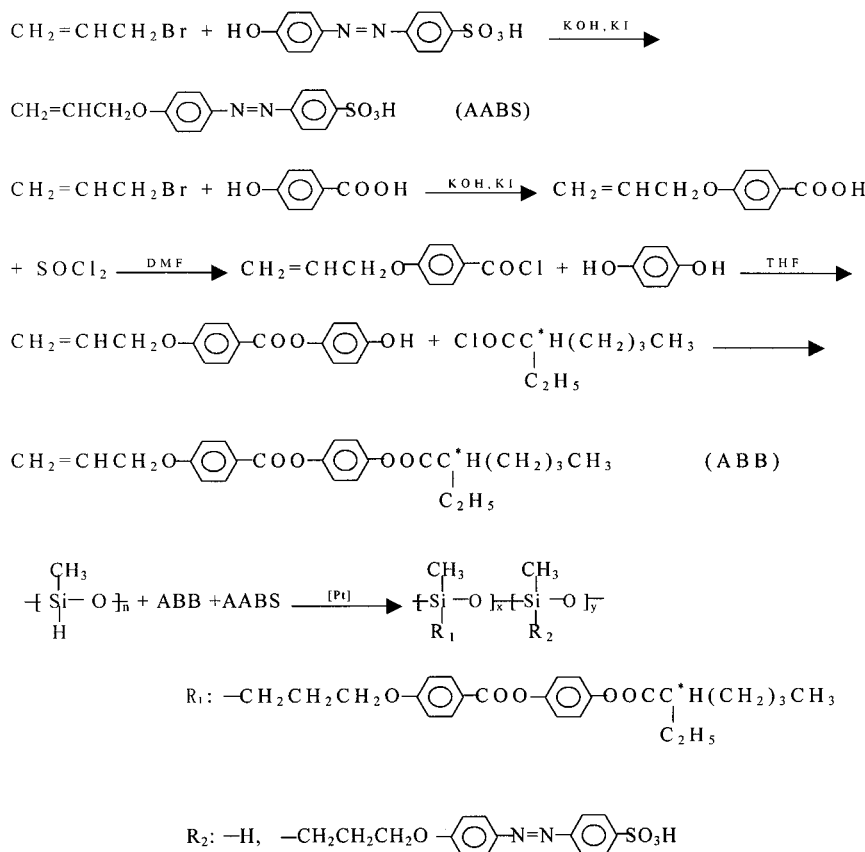
IR (KBr) cm^{-1} : 2800–3000 (—CH₃, —CH₂—), 1740 (C=O), 1606, 1508 (Ar—), 1265 (C—O—C, Si—CH₃), and 1000–1150 (Si—O—Si).

RESULTS AND DISCUSSION

Optical Micrograph Analysis

The textures of the monomers and polymers observed with optical polarizing microscope under nitrogen atmosphere are shown in Figure 1.

When the monomer ABB was heated to about 45°C, it exhibited mesophase as shown in Figure 1(a), which is an optical polarizing micrograph of



Scheme 1 Synthetic routes of monomers, polymers, and ionomers.

typical smectic mesomorphism. DSC thermographs and small-angle X-ray diffraction patterns are shown in Figure 2 and Figure 3(a), respectively. The monomer AABS did not show any melting point; when it was heated to higher temperature ($T > 300^\circ\text{C}$), it decomposed and no mesophase was observed. The polymers P_I–P_{IV} ex-

hibited mesomorphism of S_A textures. P_{III} is shown in Figure 1(b) as an example. The ionomers P_V–P_{VI} also exhibited S_A mesomorphism, as shown in Figure 1(c). The ionomer P_{VII} was not mesomorphic, as demonstrated by DSC and optical polarizing micrograph. The small amount of ionic units enhanced the thermal stability of the mesophases, broadening their temperature range. In the smectic layer of the polymers, sulfonate groups independently aggregated to form the sublayer. We think that the aggregation of sulfonate groups in the polymers is useful for forming the smectic layer structure, and the sulfonate groups are regarded as one of the smectogens, but when the amount of ionic units is large, it would destroy the mesomorphism of the polymers and make the mesomorphism of the polymers disappear.

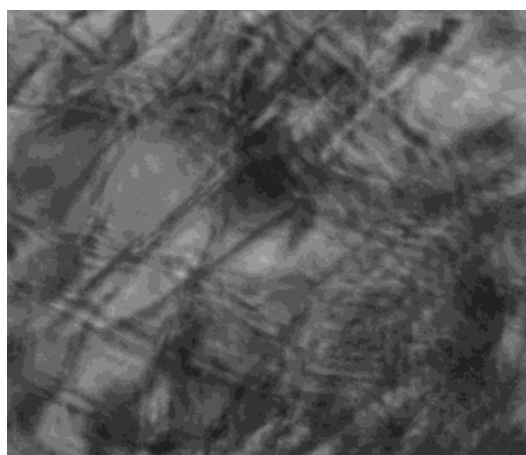
Thermal Analysis

Results of the thermal analyses of the samples are summarized in Table I. Representative DSC traces of the monomer ABB and the polymers are presented in Figure 2.

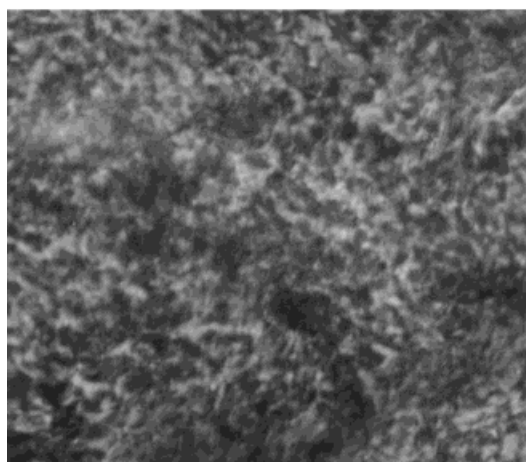
Table I Polymerization

Samples	Feed				Yields (%)
	PMHS (mmol)	ABB (mmol)	AABS (mmol)	AABS ^a (mol %)	
P _I	1	1	0	0	87
P _{II}	1	3	0	0	84
P _{III}	1	5	0	0	85
P _{IV}	1	7	0	0	89
P _V	1	5	0.5	7.7	71
P _{VI}	1	5	1.0	14.3	69
P _{VII}	1	5	1.5	20.0	66

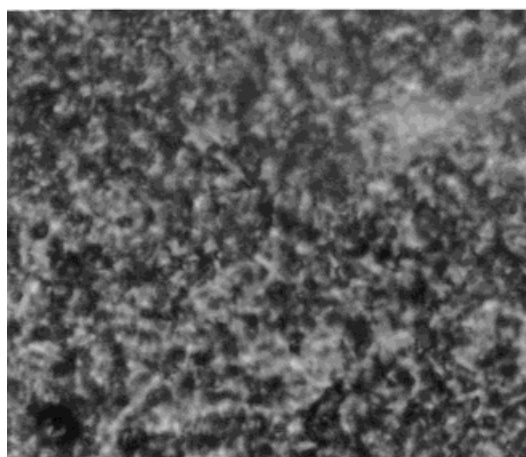
^a AABS (mol %) in aqueous phase (i.e., based on PMHS + ABB + AABS).



(a)



(b)



(c)

Figure 1 Optical polarizing micrographs of three samples ($\times 320$). (a) Monomer ABB at 48°C ; (b) polymer P_{III} at 80°C ; (c) polymer P_{V} at 100°C .

The glass-transition temperature (T_g) is an important parameter in connection with structures and properties of polymers. In general, the factors

of chain flexibility, molecular weight, and inter-chain interactions, for example, will affect the T_g . Figure 4 shows that the T_g 's of the polymers $\text{P}_{\text{I}}-\text{P}_{\text{IV}}$ increase with an increase in the concentration of mesogenic units (ABB) in the polymers $\text{P}_{\text{I}}-\text{P}_{\text{IV}}$. As we know, T_g involves the mobility of chain segments in polymers, increasing with the decrease in the mobility of chain segments. In polymers $\text{P}_{\text{I}}-\text{P}_{\text{IV}}$, with an increase in the concentration of mesogenic units, the space steric hindrance increases, which made the chain flexibility decrease; thus, the mobility of chain segments decreased and the T_g increases. Figure 5 shows that the T_g 's of polymers P_{III} and ionomers $\text{P}_{\text{V}}-\text{P}_{\text{VII}}$ increase with increasing concentration of sulfonate groups, which is most likely the result of the sulfonate ionic associations in the ionomers $\text{P}_{\text{V}}-\text{P}_{\text{VII}}$ that act as crosslinks in the polymer and, hence, restrict the mobility of the molecular backbone.

From Table II and the DSC curves (Fig. 2), it is seen that the glass-transition temperatures of the polymers $\text{P}_{\text{I}}-\text{P}_{\text{IV}}$ are -6.8 to -3.6°C . The reason for such low glass-transition temperatures is the better flexibility of polysiloxanes' backbone and the terminal group of mesogenic units. T_g 's of the ionomers $\text{P}_{\text{V}}-\text{P}_{\text{VII}}$ are $19.2-63.8^\circ\text{C}$. Compared with the T_g 's of polymers $\text{P}_{\text{I}}-\text{P}_{\text{IV}}$, the T_g 's of the ionomers $\text{P}_{\text{V}}-\text{P}_{\text{VII}}$ are much higher, the possible reason for which is that a broad distribution of the sulfonic acid composition of the polymer chains and the existence of the ionic groups will

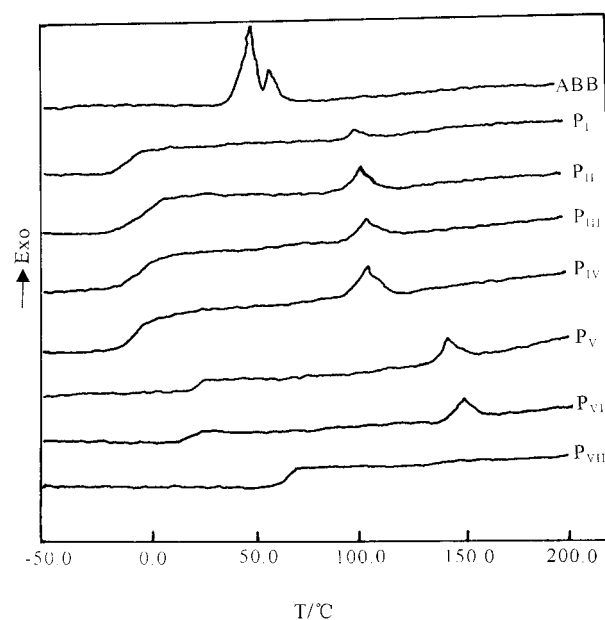


Figure 2 DSC thermographs ($10^\circ\text{C}/\text{min}$).

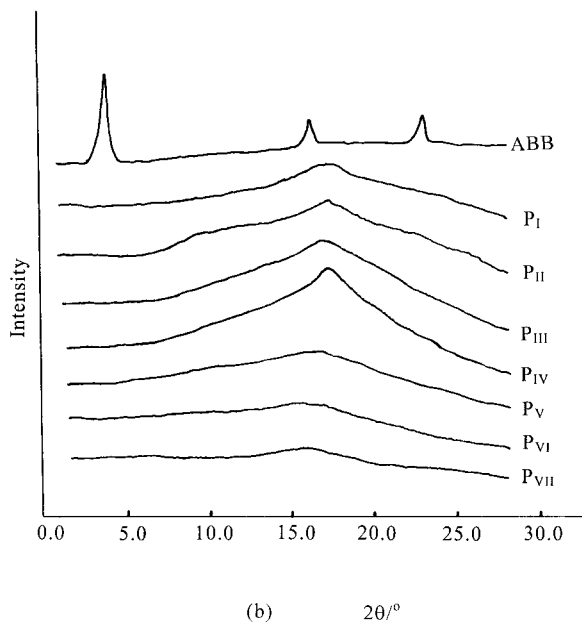
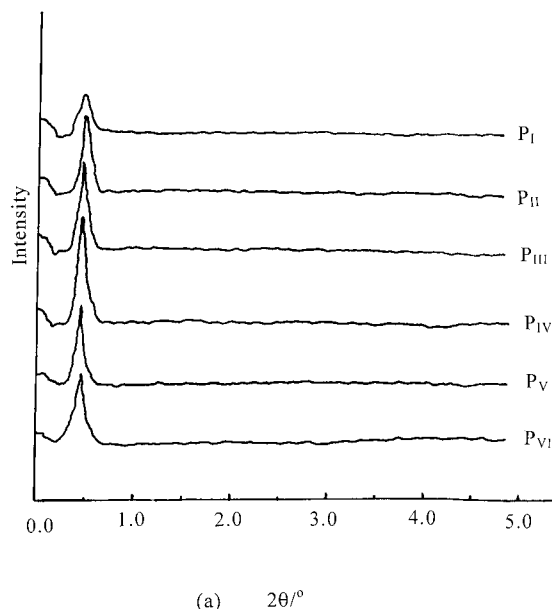


Figure 3 Temperature-dependent X-ray diffraction curves of the powder samples: (a) small angle (b) wide angle.

affect the movement of the soft segments for both the main chain and the side chain.

The monomer ABB exhibits a melting transition at 46.9°C and S_A-to-isotropic phase transition at 55.6°C. The polymers P_I–P_{IV} and ionomers P_V–P_{VI} have a clearing point (T_c) at 100.3–146.7°C, but have no melting point (T_m), which respectively show an enantiotropic S_A phase. The ionomer P_{VII} exhibits only T_g and does not have either T_c or T_m , considering that large amounts of

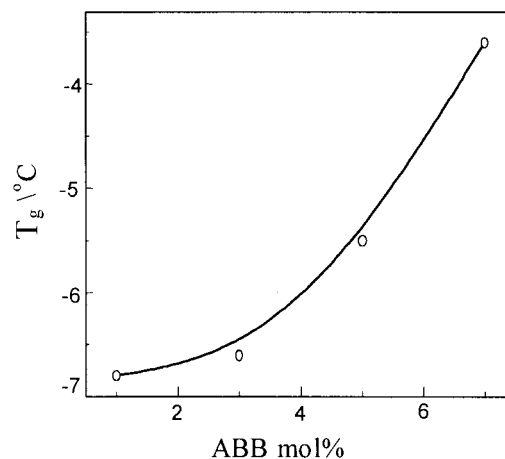


Figure 4 T_g versus ABB concentration of the polymers P_I–P_{IV}.

ionic units have destroyed the mesomorphism of P_{VII}.

Upon comparison of the thermal transitions and corresponding enthalpy change data of the polymers P_I–P_{IV} and ionomers P_V–P_{VI}, a flexible polymer backbone can be seen here to have a tendency toward having a lower glass transition, wider mesomorphic range, and enthalpy changes. The most important tendency is that the flexible polymer backbone also leads to a wide temperature range of the S_A phase.

X-ray Diffraction Analysis

X-ray diffraction studies were carried out to obtain more detailed information on both the mesophase structure and the crystalline structures of the polymers. Figure 3 reveals the X-ray dif-

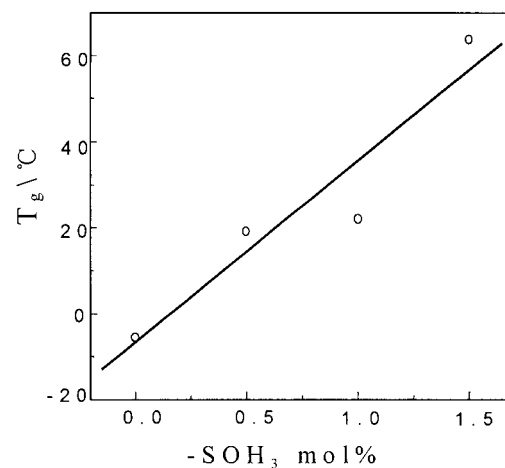


Figure 5 T_g versus $-\text{SO}_3\text{H}$ mol % of the polymers P_{III} and P_V–P_{VII}.

fraction diagrams of the quenched samples of the monomer and the polymers. A broad reflection at wide angle (associated with the lateral packing) and a sharp reflection at low angle (associated with the smectic layers), respectively, are shown by all the curves. The monomer ABB exhibits a sharp peak at 3.76° at 48°C . This is the evidence that ABB exhibits S_A mesophase. The polymers P_I – P_{IV} and ionomers P_V – P_{VI} give a sharp peak at low Bragg angle below 3° (Table III), derived from the corresponding d -spacing of smectic orientations of mesogens. The optical polarizing micrographs [Fig. 1(b) and (c)] reveal a fan texture at this temperature range. Both results are consistent with an S_A structure. The ionomer P_{VII} has no sharp peak in a lower or higher Bragg angle region, which implies that P_{VII} has no mesophase.

CONCLUSIONS

A series of new chiral side-chain liquid crystalline polysiloxanes and ionomers containing ABB and AABS were prepared. The polymers P_I – P_{IV} exhibit chiral smectic A texture. Flexible polymer backbones enhance the coupling of the motions of the side chains and the main chains; therefore, they tend to give rise to a higher thermal stability of the mesophases, including the smectic phase. The ionomers P_V – P_{VI} also exhibit S_A texture, although ionomer P_{VII} does not. The small amount of ionic units will increase the thermal stability of

Table II Thermal Analysis Results

Samples	n^a	Temperature			ΔH_c (J/g)
		T_g ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	ΔT^b ($^\circ\text{C}$)	
P_I	0	–6.8	101.3	108.1	9.9
P_{II}	0	–6.6	101.6	108.2	5.2
P_{III}	0	–5.5	100.5	106.0	4.9
P_{IV}	0	–3.6	100.3	103.9	8.7
P_V	0.5	19.2	141.4	122.2	8.3
P_{VI}	1.0	22.1	146.7	124.6	10.5
P_{VII}	1.5	63.8	—	—	—

^a The mole fraction of sulfonic acid.

^b The mesomorphic temperature range (i.e., $T_c - T_g$).

Table III Small-Angle X-ray Diffraction Analysis of the Samples

Samples	Temperature ($^\circ\text{C}$)	$2\theta/^\circ$	d (nm)
ABB	48	3.760	23.5
P_I	80	0.370	238.6
P_{II}	80	0.470	187.8
P_{III}	80	0.430	205.3
P_{IV}	80	0.610	144.7
P_V	110	0.470	187.8
P_{VI}	110	0.410	210.6

the mesophases and a wider temperature range of the S_A phase, but a large amount of ionic units will completely destroy the mesomorphism of the polymers.

The authors are grateful to the National Natural Science Fundamental Committee of China and the Science Committee of Liaoning Province for financial support of this work.

REFERENCES

- Mayer, R. B. *Mol Cryst Liq Cryst Sci Technol* 1977, 40, 33.
- Clark, N. A.; Lagerwall, S. T. *Appl Phys Lett* 1980, 36, 899.
- Hamn, B.; Percec, V. *Macromolecules* 1987, 20, 2961.
- Scherowsky, G.; Schliwa, A.; Springer, J.; Kuhn-past, K.; Trapp, W. *Liq Cryst* 1989, 5, 1281.
- Walba, D. M.; Keller, P.; Parmar, D. S.; Clark, N. A.; Wand, D. M. *J Am Chem Soc* 1989, 111, 8273.
- Dumon, M.; Nguygn, H. T.; Mauzac, M.; Destrade, C.; Achard, M. F.; Gasparoux, H. *Macromolecules* 1990, 23, 357.
- Hsu, C. H.; Lin, J. H.; Chou, L. R.; Hsiue, G. H. *Macromolecules* 1992, 25, 7126.
- Zhang, B. Y.; Weiss, R. A. *J Polym Sci Part A Polym Chem* 1992, 30, 91.
- Zhang, B. Y.; Weiss, R. A. *J Polym Sci Part A Polym Chem* 1992, 30, 989.
- Zhang, B. Y.; Guo, S. M. *J Appl Polym Sci* 1998, 68, 1555.
- Chien, G. C.; Kuo, J. F.; Chen, C. *J Polym Sci Part A Polym Chem* 1993, 31, 2423.
- Hu, H. W. *Organic Chemistry*; Higher Education Press: City, 1991, p. 574.