

Synthesis and Characterization of Side-Chain Liquid-Crystalline Ionomers Containing Quaternary Ammonium Salt Groups

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ABSTRACT: A series of thermotropic side-chain liquid-crystalline ionomers (LCIs) containing 4-(4-alkoxybenzyloxy)-4'-allyloxybiphenyl (M) as mesogenic units and allyl triethylammonium bromide (ATAB) as nonmesogenic units were synthesized by graft copolymerization upon polymethylhydrosiloxane. The chemical structures of the polymers were confirmed by IR spectroscopy. DSC was used to measure the thermal properties of these polymers. The mesogenic properties were characterized by polarizing optical microscopy, DSC, and X-ray diffraction. Homopolymers without ionic groups exhibit smectic and nematic mesophases. The nematic mesophases of the ionomers disap-

pear and the mesomorphic temperature ranges decrease with increasing concentration of ionic units. The influence of the alkoxy chain length on clearing temperature (T_c) values of ionomers clearly shows an odd-even effect, similar to that of other side-chain liquid-crystalline polymers. The mesomorphic temperature ranges increase with increasing alkoxy chain length when the number of alkoxy carbon is over 3. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2879–2886, 2003

Key words: liquid-crystalline ionomers; quaternary ammonium salt; polysiloxane; 4-(4-alkoxybenzyloxy)-4'-allyloxybiphenyl; phase behavior

INTRODUCTION

During recent years, increasing attention has focused on the study of side-chain liquid-crystalline polymers with ionic groups (SCLCIs). The existence of the ionic groups gives SCLCIs more exceptional properties and extends SCLCIs' applicational fields. One important applicational research is the SCLCIs' interpenetrating polymer networks.^{1,2} Ionic crosslinks can restrict the phase-separation process and can often result in microphases for the otherwise immiscible components. This means that different properties of two SCLCIs could be exhibited by a single system. It can be used to explore new liquid-crystalline materials. Side-chain liquid-crystalline ionomers also play an important role in the search for biocompatible materials as well as models for understanding of more complex biosystems.^{3–5} Barmatov et al.^{6,7} synthesized and investigated polymers containing metal ionic groups. These polymers, which possess both electric conductivity and magnetic activity, may find applications in the fields of nanotechnology and magnetic data recording.

SCLCIs also have other potential applications that await future exploration. Therefore it would be both necessary and useful to synthesize various kinds of side-chain liquid-crystalline ionomers.

In previous studies we reported the synthesis of two main-chain and two side-chain thermotropic LCIs containing sulfonate groups.^{8–11} One of the main-chain LCIs was blended with PA1010/polypropylene (PP). The results show that LCI, as a compatibilizer, could promote the crystallizability of the crystalline polymer PA1010 and PP. In this study, a series of novel side-chain thermotropic liquid-crystalline ionomers containing 4-(4-alkoxybenzyloxy)-4'-allyloxybiphenyl as mesogenic units and allyl triethylammonium bromide as nonmesogenic units were synthesized. Their mesomorphic properties were investigated by DSC, polarizing optical microscopy (POM), and X-ray diffraction. The effects of ionic aggregation on the mesomorphism, thermal stability, and textures are discussed.

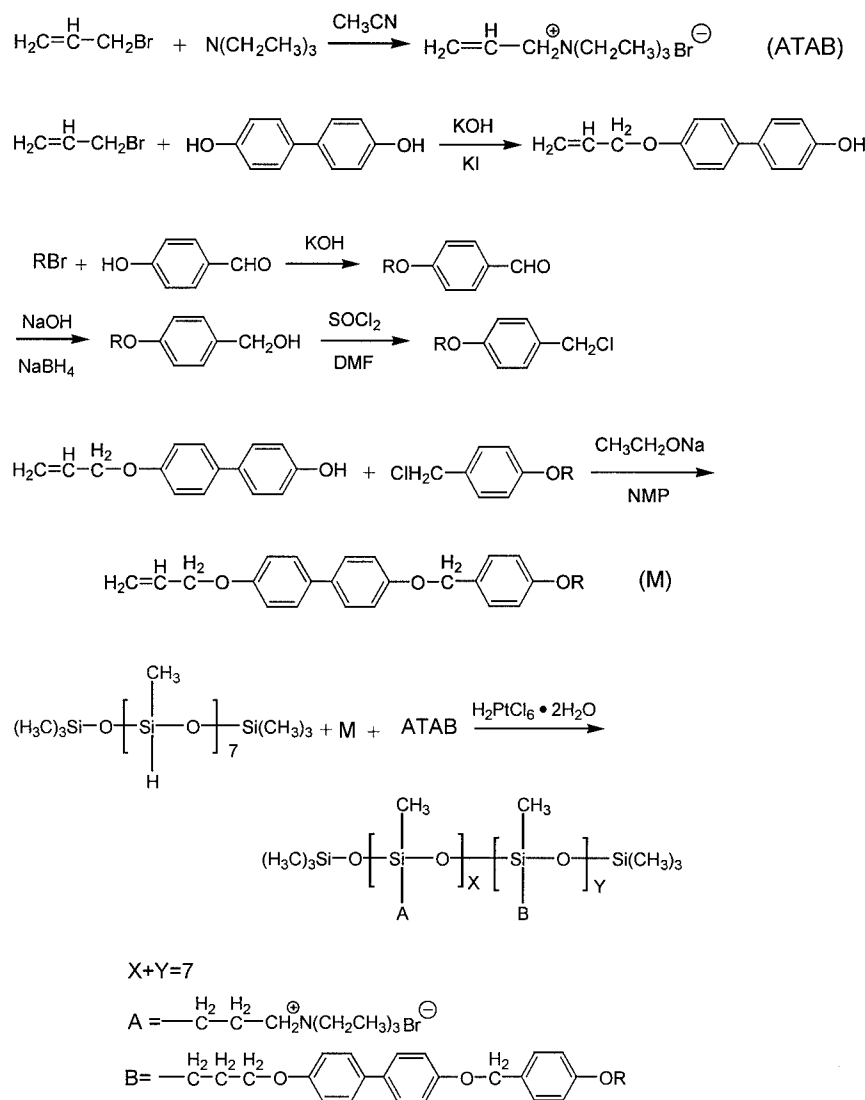
EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS) with MW 700–800 was obtained from Jilin Chemical Industry Company. Toluene was distilled and then dried with calcium hydride. Tetrahydrofuran (THF) was refluxed over cuprous chloride and distilled, then dried first with

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Monomers	M ₁	M ₂	M ₃	M ₄	M ₅
R	CH ₃	CH ₃ CH ₂	CH ₃ (CH ₂) ₂	CH ₃ (CH ₂) ₃	CH ₃ (CH ₂) ₄

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

calcium chloride then with calcium hydride. All other solvents and reagents were used as received.

Characterization techniques

Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI) on a KBr table. ¹H-NMR spectra (400 MHz) were recorded on a ARX 400NMR spectrometer (ZHB-HS Co.). Optical microscopy was performed on a Ziss-Jena polarizing optical microscope (POM) equipped with a Melter FP82 hot stage. X-ray diffraction measurements of quenched samples were performed with a Rigaku DMAX-3A X-ray diffractometer at room temperature, Cu target radiation. Thermal transitions and

thermodynamic parameters were determined by a Perkin-Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) under a nitrogen flow. The sample quantity was 10 mg with 10°C/min rate of heating and cooling.

Synthesis of monomers

The synthesis of monomers is outlined in Scheme 1.

Allyl triethylammonium bromide (ATAB)

Allyl bromide (3.0 g, 0.025 mol) was added to a solution of triethylamine (3.5 g, 0.035 mol) in acetonitrile (25 mL), after which the mixture was refluxed for 10 h.

After the reaction was finished, ethyl ether (50 mL) was added to the mixture. The precipitate was filtered and then dried under vacuum. Yield: 76% white needle crystals.

IR (KBr) cm^{-1} : 3050 ($=\text{CH}_2$), 2900–3000 ($-\text{CH}_3$, $-\text{CH}_2-$), 1650 ($\text{C}=\text{C}$), 1176 ($\text{C}-\text{N}^+$). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 1.42–1.46 (t, 9H, $-\text{CH}_3$), 3.48–3.53 (m, 6H, $-\text{CH}_2-$), 4.14–4.15 (d, 2H, $-\text{CH}_2-$), 5.71–5.85 (m, 2H, $=\text{CH}_2$), 5.94–6.04 (m, 1H, $=\text{CH}-$).

4-Allyloxy-4'-hydroxybiphenyl

4,4'-Dihydroxybiphenyl (10 g, 0.054 mol) and sodium hydroxide (2.5 g, 0.063 mol) were added to acetone (200 mL) under N_2 . The mixture was refluxed, after which ethyl bromide (8.5 mL, 0.11 mol) was added dropwise. The reaction was maintained for 8 h. After acetone was evaporated, water (50 mL) was added. The mixture was filtered and washed with water. The crude product was added to NaOH solution (50 mL, 10 wt %). The mixture was heated to 90°C, then cooled to room temperature, after which it was filtered and washed with NaOH solution (30 mL, 10 wt %) to remove the unreacted 4,4'-dihydroxybiphenyl. The solid was added to NaOH solution (200 mL, 2 wt %). The mixture was heated to 90°C, then filtered to remove the undissolved 4,4'-diallyloxybiphenyl. When the solution was cooled to 60°C, the pH value was adjusted to 5–6 using hydrochloric acid, then cooled to room temperature, filtered, and washed with water. The precipitate was recrystallized from methanol. White plate crystals were obtained. m.p.: 165–167°C; yield: 34.0%.

IR (KBr) cm^{-1} : 3350, 3080, 2850, 1650, 1610, 1600, 1500, 1250. $^1\text{H-NMR}$ (400 MHz, CD_3COCD_3) δ ppm: 3.67 (d, 2H, $-\text{O}-\text{CH}_2-$), 5.17–5.67 (m, 2H, $\text{CH}_2=$), 5.86–6.58 (m, 1H, $=\text{CH}-$), 6.90 (d, 2H, Ph-), 7.08 (d, 2H, Ph-), 7.47 (d, 2H, Ph), 7.63 (d, 2H, Ph), 8.40 (s, 1H, $-\text{OH}$).

4-Alkoxybenzyl chloride

An example is presented below. The other 4-alkoxybenzyl chlorides were synthesized using the same method. To a solution of 4-ethoxybenzalcohol (9.0 g, 0.055 mol) in methylene chloride (180 mL), sulfur oxychloride (10 mL, 0.137 mol) was added dropwise at room temperature. The reaction was maintained for 1 h. The mixture was transferred in a separation funnel, then washed first with water then with sodium dicarbonate solution (2 wt %) and with water until the pH value of the collected organic layers was 7. The organic layers were dried over anhydrous sodium sulfate overnight, filtered, and then evaporated under reduced pressure. A colorless oily liquid was obtained. Characterizations of the five 4-alkoxybenzyl chlorides are as follows.

TABLE I
Polymerization

Sample	Feed				Yield (%)
	PMHS (mmol)	M (mmol)	ATAB (mmol)	ATAB ^a (mmol)	
PAM ₄ -1	0.37	1.93	0.68	26.0	71
PAM ₄ -2	0.43	1.93	1.13	36.9	76
PAM ₄ -3	0.50	1.93	1.58	45.0	71
PAM ₄ -4	0.69	2.60	2.25	46.4	53
PAM ₄ -5	0.75	1.93	3.38	63.6	59
PAM ₄ -6	0.82	1.29	4.50	77.7	50
PAM ₁ -4	0.69	2.60	2.25	46.4	60
PAM ₂ -4	0.69	2.60	2.25	46.4	55
PAM ₃ -4	0.69	2.60	2.25	46.4	58
PAM ₅ -4	0.69	2.60	2.25	46.4	60
PM ₃	0.34	2.67	0	0	83
PM ₅	0.34	2.49	0	0	75
PATAB	0.32	0	2.25	100	58

^a Molar percentage of ATAB based on M + ATAB.

4-Methoxybenzyl chloride. b.p.: 72–74°C/170 Pa; yield: 90.5%.

IR (KBr) cm^{-1} : 3040, 2980, 2920, 2860, 1610, 1580, 1510, 1250. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 3.36 (s, 2H, $-\text{CH}_2\text{Cl}$), 3.83 (s, 3H, $-\text{OCH}_3$), 6.76 (d, 2H, Ph), 7.16 (d, 2H, Ph).

4-Ethoxybenzyl chloride. b.p.: 85–87°C/35 Pa; yield: 89.0%.

IR (KBr) cm^{-1} : 3040, 2980, 2920, 2860, 1610, 1580, 1510, 1260. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 1.46 (t, 3H, $-\text{CH}_3$), 3.36 (s, 2H, $-\text{CH}_2-$), 4.03 (m, 2H, $-\text{CH}_2\text{O}-$), 6.73 (d, 2H, Ph), 7.13 (d, 2H, Ph).

4-Propoxybenzyl chloride. b.p.: 94–96°C/45 Pa; yield: 87.0%.

IR (KBr) cm^{-1} : 3040, 2980, 2920, 2860, 1610, 1580, 1510, 1270. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 1.07 (t, 3H, $-\text{CH}_3$), 1.87 (m, 2H, $-\text{CH}_2-$), 3.36 (s, 2H, $-\text{CH}_2\text{Cl}$), 3.96 (t, 2H, $-\text{CH}_2\text{O}-$), 6.76 (d, 2H, Ph), 7.16 (d, 2H, Ph).

4-Butoxybenzyl chloride. b.p.: 102–104°C/20 Pa; yield: 88.0%.

IR (KBr) cm^{-1} : 3040, 2980, 2920, 2860, 1610, 1580, 1510, 1250. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 0.97–1.30 (t, 3H, $-\text{CH}_3$), 1.33–2.14 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 3.36 (s, 2H, $-\text{CH}_2\text{Cl}$), 3.98 (t, 2H, $-\text{CH}_2\text{O}-$), 6.80 (d, 2H, Ph), 7.19 (d, 2H, Ph).

4-Pentoxybenzyl chloride. b.p.: 112–114°C/70 Pa; yield: 86.0%.

IR (KBr) cm^{-1} : 3040, 2980, 2920, 2860, 1610, 1580, 1510, 1250. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 0.76–1.13 (t, 3H, $-\text{CH}_3$), 1.13–2.04 (m, 6H, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 3.36 (s, 2H, $-\text{CH}_2\text{Cl}$), 3.98 (t, 2H, $-\text{CH}_2\text{O}-$), 6.80 (d, 2H, Ph), 7.19 (d, 2H, Ph).

4-(4-Alkoxybenzyloxy)-4'-allyloxybiphenyl (M)

The liquid-crystalline monomers were synthesized by etherification of the corresponding sodium phenolate with 4-alkoxybenzyl chloride. An example is presented below. 4-Allyloxy-4'-hydroxybiphenyl (1.0 g, 0.005 mol) was added quickly to a solution of sodium (0.15 g, 0.0065 mol) in absolute alcohol (30 mL). The alcohol was evaporated to form sodium salt and wa-

TABLE II
Thermal Analysis Results of Heating Scan

Sample	Ionic (mol %)	Temperature			ΔH_m (J/g)	ΔH_{sn} (J/g)	ΔH_c (J/g)
		Phase transitions (°C)	ΔT^a (°C)				
M ₃	0	k162 s189 n 191i	29	18.4	8.8	13.0	
PM ₃	0	k129 s152 n190i	61	1.8	7.3	4.7	
PAM ₃ -4	46.4	k164 s181i	17	37.0	—	31.9	
M ₅	0	k139 s180 n190i	52	17.1	3.2	19.2	
PM ₅	0	k117 s137 n206i	89	2.1	6.2	2.6	
PAM ₅ -4	46.4	k144 s169 n185i	41	26.5	4.7	29.3	

^a The mesomorphic temperature range (i.e., $T_c - T_m$).

ter-free *N*-methyl-2-pyrrolidone(50 mL) was added to dissolve it; then 4-pentoxybenzyl chloride (1.0 g, 0.0054 mol) was added. The mixture was stirred for 5 h at 110°C, cooled to room temperature, and poured into water. The precipitate was filtered, washed with dilute NaOH aqueous solution and then water, and dried under vacuum. The product was purified by column chromatography (silica gel, dichloromethane) and recrystallized from methanol. Yield: 83.2% white crystals. The characterizations of monomers are listed in our previous publication.¹²

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 M, ATAB, and PMHS were dissolved in dry freshly distilled toluene. The reaction mixture was heated to 50–60°C under nitrogen, and a proper amount of THF solution of hydrogen hexachloroplatinate(IV) hydrate catalyst was injected with a syringe. The reaction was carried out until the disappearance of the Si—H IR band at 2160 cm⁻¹. The polymers were isolated by precipitation in methanol, purified by reprecipitation from chloroform solutions with methanol, and then dried under vacuum.

Ionomers IR (KBr) cm⁻¹: 2800–3000 (—CH₃, —CH₂—), 1606, 1516, 1500 (Ar—, —Ar—Ar—), 1273, 1244 (C—O—C, Si—CH₃), 1178 (C—N⁺), 1000–1150 (Si—O—Si).

PM₃ and PM₅ IR (KBr) cm⁻¹: 2800–3000 (—CH₃, —CH₂—), 1608, 1514, 1500 (Ar—, —Ar—Ar—), 1271, 1244 (C—O—C, Si—CH₃), 1000–1150 (Si—O—Si).

PATAB IR (KBr) cm⁻¹: 2800–3000 (—CH₃, —CH₂—), 1273 (Si—CH₃), 1178 (C—N⁺), 1000–1150 (Si—O—Si).

RESULTS AND DISCUSSION

Comparison of the mesogenic properties of the homopolymers with those of the ionomers

Results of the thermal analyses of monomers, homopolymers, and ionomers are listed in Table II. Comparing homopolymers (PM₃, PM₅) with corresponding ionomers (PAM₃-4, PAM₅-4), it is seen that with the addition of ionic units the melting temperature T_m significantly increases and the clearing temperature T_c decreases slightly, changes that result in the decrease of the mesomorphic temperature range ΔT . As we know, T_m involves the mobility of the whole chain in polymers, and increases with the decrease in the mobility of the whole chain. Ionic crosslink interactions in the ionomers restrict the mobility of the whole chain, thus causing the T_m to increase.

TABLE III
Thermal Analysis Results of Heating Scan

Sample	Ionic (mol %)	Temperature (°C)				ΔH_m (J/g)	ΔH_{sn} (J/g)	ΔH_c (J/g)
		T_m	T_{sn}	T_c	ΔT^a			
PAM ₄ -1	26.0	134	180	187	53	28.8	13.7	34.2
PAM ₄ -2	36.9	142	184	186	44	35.8	19.1	23.5
PAM ₄ -3	45.0	145	183	187	42	27.6	13.5	20.2
PAM ₄ -4	46.4	148	183	187	39	16.6	6.4	11.4
PAM ₄ -5	63.6	148		184	36	20.2		23.0
PAM ₄ -6	77.7	144		174	30	20.2		18.5
PAM ₁ -4	46.4	178		183	5	40.4		32.4
PAM ₂ -4	46.4	164		187	23	26.1		31.8
PAM ₃ -4	46.4	164		181	17	37.0		31.9
PAM ₅ -4	46.4	144	169	185	41	26.5	4.7	29.3

^a The mesomorphic temperature range (i.e., $T_c - T_m$).

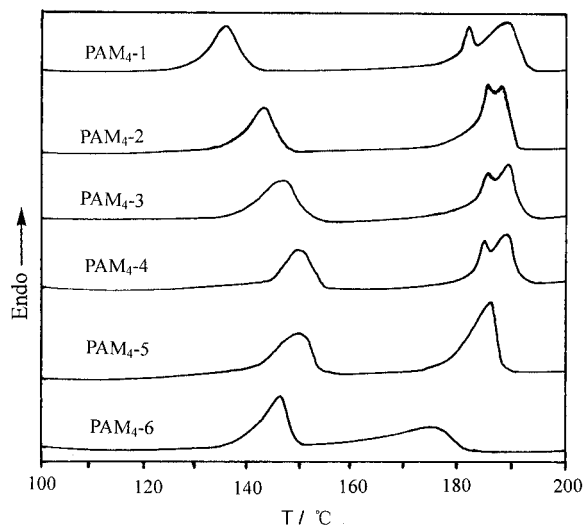


Figure 1 DSC scans of PAM₄-1, PAM₄-2, PAM₄-3, PAM₄-4, PAM₄-5, and PAM₄-6 (heating scan).

Homopolymer PM₃ exhibits two different kinds of mesophases, a smectic and a nematic mesophase, whereas the corresponding ionomer PAM₃-4 exhibits only a smectic mesophase. PM₅ and PAM₅-4 both exhibit two kinds of mesomorphism. By comparing the mesomorphic temperature range of PM₅ and PAM₅-4, it can be seen that with the addition of ionic units the smectic temperature range ΔT_s value increases, whereas the nematic temperature range ΔT_n value decreases. The above analyses, discussed further below, demonstrate that ionic units are useful for the formation of the smectic phase.

Influence of the concentration of ionic units on the phase transitions of ionomers

Table III summarizes the results of the DSC measurements of different ionomers. Figure 1 shows DSC heat-

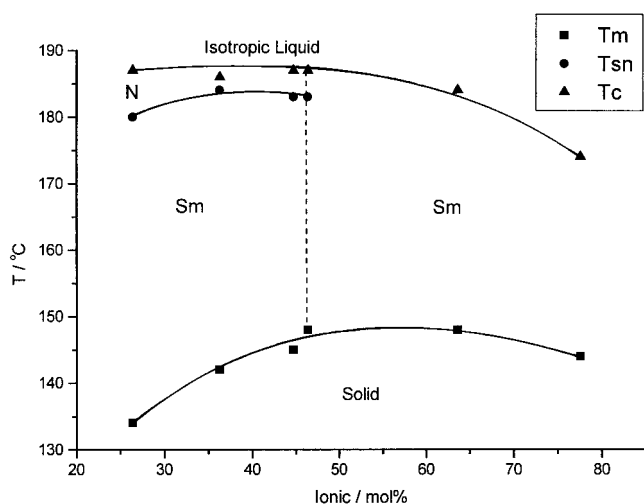


Figure 2 Phase diagrams of the polymers.

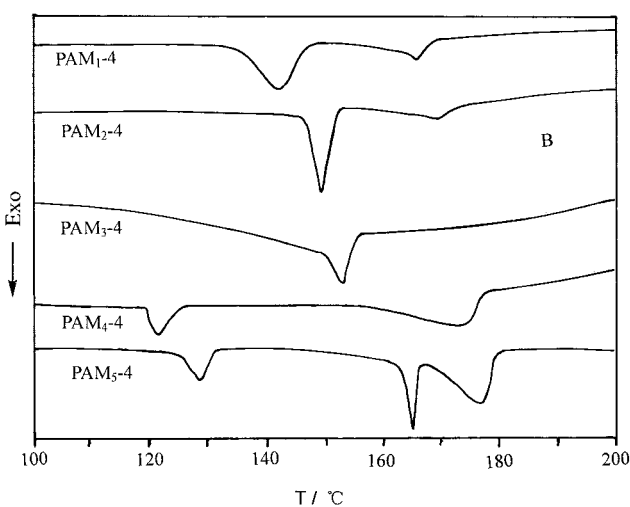
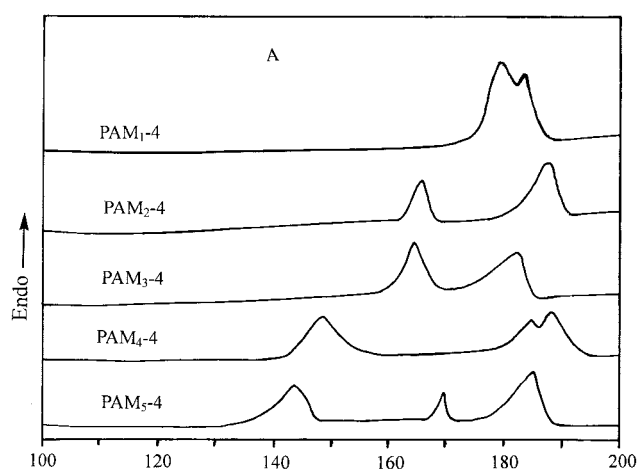


Figure 3 DSC scans of PAM₁-4, PAM₂-4, PAM₃-4, PAM₄-4, and PAM₅-4: (A) heating scan; (B) cooling scan.

ing curves of ionomers PAM₄-1 to PAM₄-6. Figure 2 shows that the T_m values of the ionomers PAM₄-1–PAM₄-6 increase with increasing concentration of ionic units in the ionomers. When the concentration of ionic units is $>46.4\%$, T_m 's decrease slowly, which is attributed to the results of two competing factors. On the one hand, ionic crosslink interaction caused T_m to increase; on the other hand, the formula weight of ionic units (ATAB) is lower than that of mesogenic units (M), so the formula weight of the ionomer decreases with increasing ionic concentration in the ionomer, thus causing T_m to decrease. The clearing temperatures decrease slightly with increasing ionic concentration. When the concentration of ionic units is 77.7% , the ionomer still displays mesomorphism. It can be seen that the mesomorphic temperature range decreases with the increase of concentration of ionic units in ionomers. When the concentration of ionic

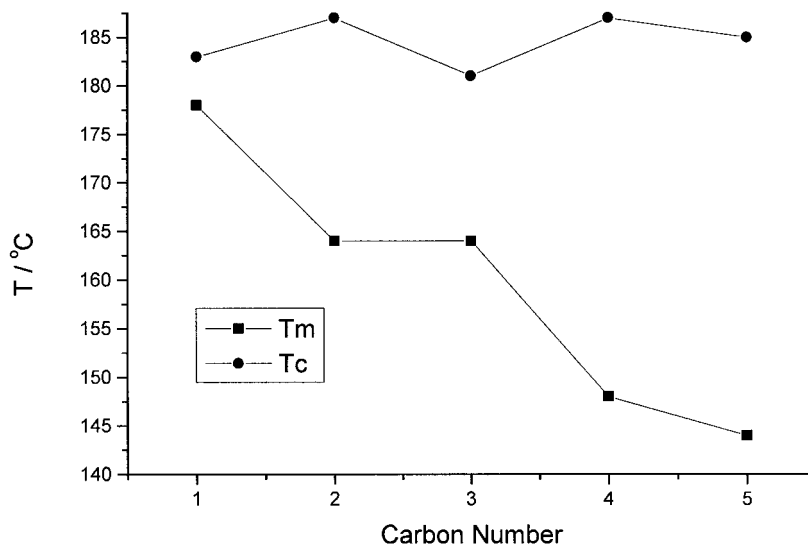
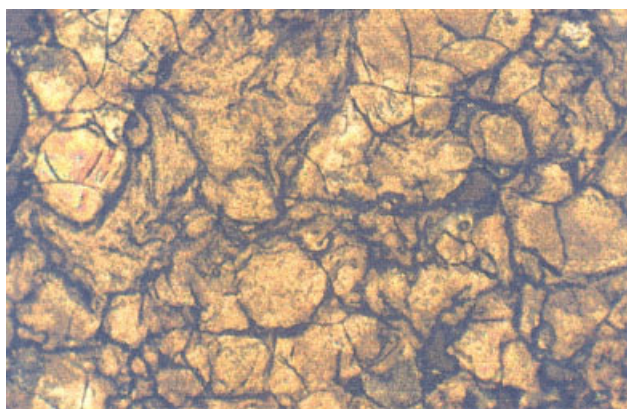
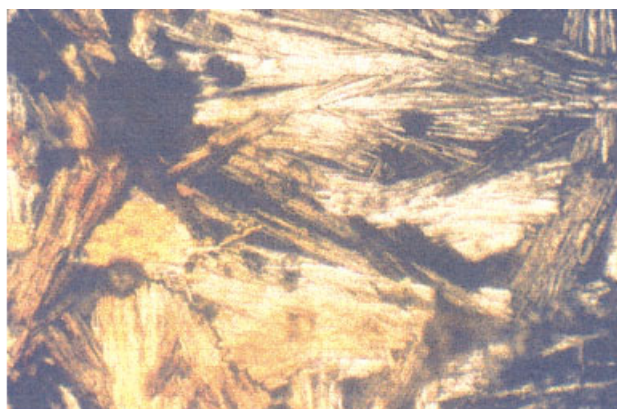


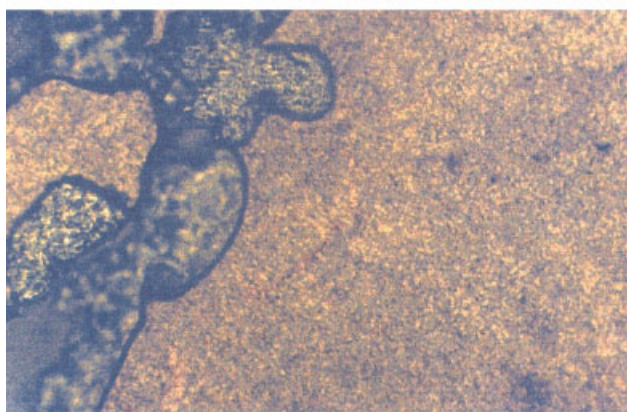
Figure 4 Phase-transition temperatures of polymers versus carbon number.



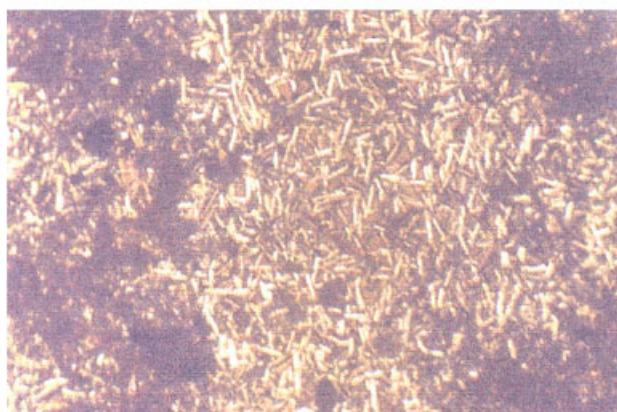
(a) Homopolymer PM₅ at 120°C



(c) Ionomer PAM₄₋₄ at 160°C



(b) Homopolymer PM₅ at 180°C



(d) Ionomer PAM₄₋₄ at 185°C

Figure 5 Textures of PM₅ and PAM₄₋₄ (×200). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

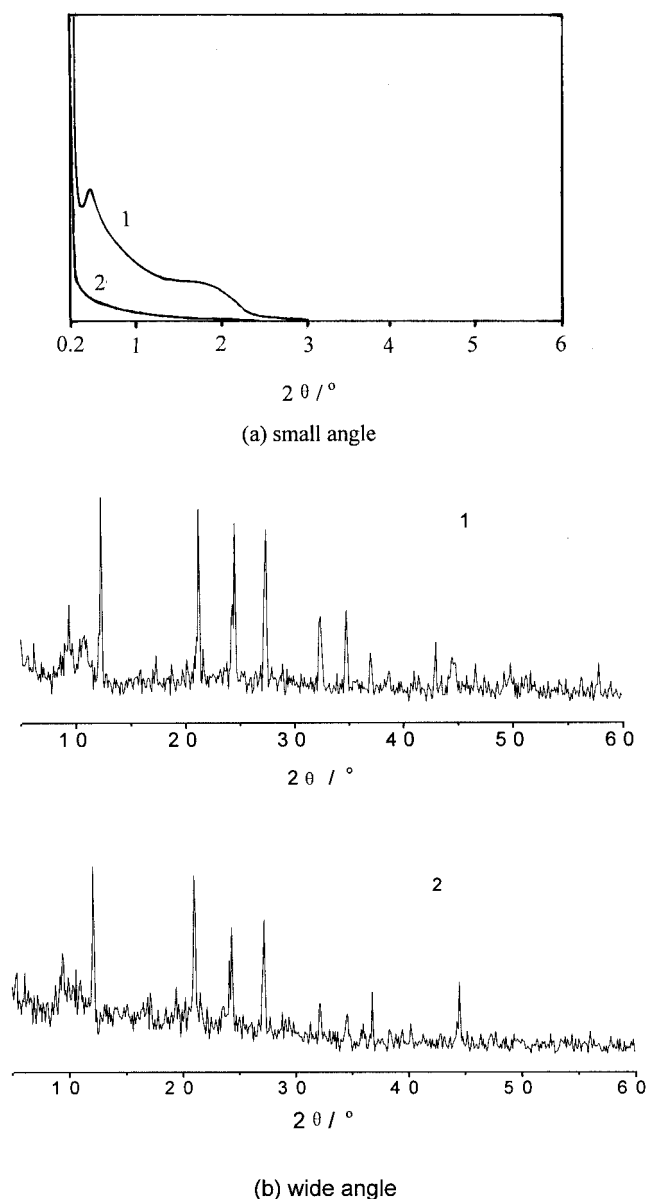


Figure 6 X-ray diffraction diagrams of the ionomer PAM₄-4: (1) at 160°C; (2) at 185°C.

units is 100%, the homopolymer PATAB does not display mesomorphism.

Another observation may be seen. The nematic mesophase weakens and then disappears with increasing ionic concentration. When the ionic concentration is over 46.4%, the ionomers exhibit only smectic mesophases. Together with results of the preceding analysis, we can draw a conclusion that quaternary ammonium salt is useful for smectic orientational order and has a tendency to stabilize the smectic layer structure. We think that in the smectic layer of the ionomers, the ionic aggregation caused by Coulomb's force of ammonium groups forms the sublayer, which is useful for forming the smectic layer structure.

Influence of alkoxy chain length on the phase transitions of the liquid-crystalline ionomers

For ionomers (PAM₁-4–PAM₅-4) with some concentration of ionic units (ionic mol % = 46.4) we investigated the influence of the length of the alkoxy group located at the end of mesogen on phase transitions. The results are listed in Table III. The DSC heating and cooling curves are presented in Figure 3. Figure 4 shows the clearing temperatures (T_c 's) of the ionomers PAM₁-4 to PAM₅-4, which clearly show an odd-even effect. T_c values of the ionomers with an even number of carbons are higher than those with an odd number of carbons. This property of ionomers is similar to that of other side-chain liquid-crystalline polymers.¹³ The melting temperatures first decrease significantly, then keep constant values, and then continue to decrease with the increase of alkoxy chain length. The mesomorphic temperature ranges increase when the alkoxy carbon number is over 3. With an increase of the alkoxy chain length in the ionomers, mesogenic groups occupy greater steric volume and enlarge the distance between macromolecules, thus leading to the decrease of the intermolecular interactions and causing the T_m values to decrease.

Optical microscopy analysis

The textures of homopolymer and ionomer observed by polarizing optical microscope under nitrogen atmosphere are shown in Figure 5.

Monomers M₁–M₅ all exhibit smectic and nematic mesophases.¹² The monomer ATAB decomposed when heated to 240°C and no mesophase was observed. Homopolymers PM₃ and PM₅ both showed a broken focal-conic texture in Figure 5(a), which is a typical smectic texture, and nematic droplets in Figure 5(b), which is a typical nematic texture. The smectic and nematic mesophases of all the ionomers, PAM₄-1–PAM₄-6 and PAM₁-4–PAM₅-4, respectively, all display similar textures. The textures of ionomer PAM₄-4 are shown in Figure 5(c,d) as an example. Figure 5(c) shows a fan-shaped texture that is a typical smectic texture. Figure 5(d) shows a threaded texture that is a typical nematic texture. These were confirmed by later X-ray diffraction results. For PATAB polymer no mesophase could be observed; it decomposed when heated to 270°C.

X-ray diffraction analysis

Figure 6(a,b) exhibits the small-angle and wide-angle X-ray diffraction diagrams of the quenched samples of ionomer PAM₄-4 at different temperatures.

For the small-angle X-ray diffraction [Fig. 6(a)], the ionomer PAM₄-4 exhibits one peak at $2\theta = 0.43^\circ$ at 160°C, derived from the corresponding d -spacing of

smectic orientations of mesogens, and no peak in the small-angle region at 185°C was observed. For the wide-angle X-ray diffraction [Fig. 6(b)], the ionomer PAM₄-4 exhibits a sharp peak at $2\theta = 21.24^\circ$ at 160°C and at $2\theta = 21.04^\circ$ at 185°C, respectively. These results indicate the ionomer PAM₄-4 exhibits a smectic mesophase at 160°C and a nematic mesophase at 185°C.¹⁴ The results of DSC, POM, and X-ray diffraction analyses of the ionomer PAM₄-4 are consistent.

It should be mentioned that patterns with many peaks in the wide-angle region are different from the patterns reported in our previous studies. Detailed structures await further investigation.

CONCLUSIONS

A series of liquid-crystalline ionomers containing quaternary ammonium salts on the side chain to the PMHS backbone were synthesized and characterized. The existence of ionic units is useful for the stabilization of the smectic mesophase. Although the mesomorphic temperature range decreases with increasing concentration of ionic units, the ionomer (ionic mol % = 77.7) still exhibits mesomorphic behavior. The influence of the alkoxy chain length on T_c values of ionomers clearly shows an odd-even effect, similar to that of other side-chain liquid-crystalline polymers. The mesomorphic tempera-

ture ranges of the investigated ionomers could be enlarged by increasing the alkoxy carbon number.

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