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# Synthesis and properties of side chain liquid crystalline ionomers containing quaternary ammonium salt groups

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New thermotropic side chain liquid crystalline ionomers (LCIs), containing 4-(4-allyloxybenzyloxy)-4′-alkoxybiphenyl (IM) as mesogenic unit and allyltriethylammonium bromide (ATAB) as non-mesogenic unit, were synthesized by graft copolymerization upon polymethylhydrosiloxane. The chemical structures of the polymers were confirmed by IR spectroscopy. Differential scanning calorimetry (DSC) was used to measure the thermal properties of these polymers; the mesogenic properties were characterized by polarizing optical micrography, DSC and X-ray diffraction. The influence of the alkoxy chain length on the clearing temperatures of the ionomers is clearly shown in an odd–even effect, similar to other side chain liquid crystal polymers. The mesomorphic behaviour of the ionomers is compared with that of isomeric ionomers synthesized in previous work. The results demonstrate that the phase behaviour of the two series of isomeric ionomers is similar, but with the difference that the melting temperature of ionomers with biphenyl located at the end of the mesogen is higher than for ionomers with biphenyl located at the middle of the mesogen. The latter are more useful for smectic orientational order than the former.

## 1. Introduction

Because liquid crystalline ionomers (LCIs) combine the characteristics of macromolecular liquid crystals (LCs) and those of ionomers, LCIs have shown promise in a wide variety of applications. In recent years increasing attention has been paid to scientific and technological research on LCIs.

In reviewing the literature on LCIs, the main research can be divided into three fields. The first concerns the synthesis and characterization of LCIs [1–13]. It explores synthetic routes for the introduction of ionic groups into liquid crystalline polymers (LCPs) and investigates the influence of ionic groups on the mesogenic properties of LCIs. The second field deals with the specific properties of LCIs containing different ionic groups [14–20]. For example, Barmatov *et al.* [19, 20] synthesized and investigated polymers containing metal ionic groups. These polymers possess electroconductibility and magnetism. The third research field concerns the applications of LCIs [21–25], including the use of LCI interpenetrating polymer networks [21, 22].

Allyltriethylammonium bromide (ATAB) to our knowledge, was first reported as an ionic monomer in our previous study [27]. ATAB contains quaternary ammonium salt groups and is a non-mesomorphic monomer. In our previous report, a series of thermotropic side chain LCIs, containing 4-(4-alkoxybenzyloxy)-4′-allyloxybiphenyl (M) as mesogenic unit and allyltriethylammonium bromide (ATAB) as non-mesogenic unit, were synthesized (PAMs). We investigated the influence of ionic units on the mesogenic properties of the polymers. The experimental results demonstrated that with the addition of ionic units the polymer melting temperature significantly increases, while the clearing temperature decreases slightly. These effects were the result of ionic crosslinking interactions in the ionomers. We also investigated the effect of the

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concentration of ionic units and alkoxy chain length on the phase transitions of the LCIs.

In the present study, a series of new side chain thermotropic LCIs, containing 4-(4-allyloxybenzyloxy)-4′-alkoxybiphenyl (IM) as mesogenic unit and allyltriethylammonium bromide (ATAB) as non-mesogenic unit, have been synthesized (PAIMs). Their characterization by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD) is presented. The comparison of the phase behaviour of ionomers PAIM with that of ionomers PAM could illustrate the influence of isomers on the mesogenic properties of the LCIs.

## 2. Experimental

### 2.1. *Materials*

Polymethylhydrosiloxane (PMHS) with $M_w$ 700–800 was obtained from Jilin Chemical Industry Co. Toluene was distilled and then dried with calcium hydride. Tetrahydrofuran (THF) was heated under reflux over cuprous chloride and distilled; it was then dried first with calcium chloride then with calcium hydride. All other solvents and reagents were used as received.

### 2.2. *Characterization*

Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer (Nicolet Instruments, Madison, WI) using KBr pellets. $^1$H NMR spectra (400 MHz) were recorded on a ARX 400NMR spectrometer (ZHB-HS Co.). Optical microscopy was performed on a Zeiss–Jena polarizing optical microscope equipped with a Mettler FP82 hot stage. XRD measurements of quenched samples were performed with a Rigaku DMAX-3A X-ray diffractometer at room temperature, using Cu K$_\alpha$ ($\lambda = 1.54$ Å) radiation. Thermal transitions and thermodynamic parameters were determined by a Perkin-Elmer DSC-7 under a nitrogen flow. The sample quantity was 10 mg with 10°C min$^{-1}$ heating and cooling rates.

### 2.3. *Synthesis of monomers*

The synthesis of monomers is outlined in the scheme.

#### 2.3.1. *Allyltriethylammonium 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), and the mixture was heated under reflux for 10 h. when the reaction was finished, diethyl ether (50 ml) was added to the mixture; the resulting precipitate was filtered, and then dried under vaccum to yield 76% white needle crystals. IR (KBr) cm$^{-1}$: 3050 (=CH$_2$), 2900–3000 (–CH$_3$, –CH$_2$–), 1650 (C=C), 1176(C–N$^+$). $^1$H NMR (CDCl$_3$) $\delta$ ppm: 1.42–1.46 (t, 9H, –CH$_3$), 3.48–3.53 (m, 6H, –CH$_2$–), 4.14–4.15 (d, 2H, –CH$_2$–), 5.71–5.85 (m, 2H, =CH$_2$), 5.94–6.04 (m, 1H, =CH–).

#### 2.3.2. *4-Allyloxybenzyl chloride*

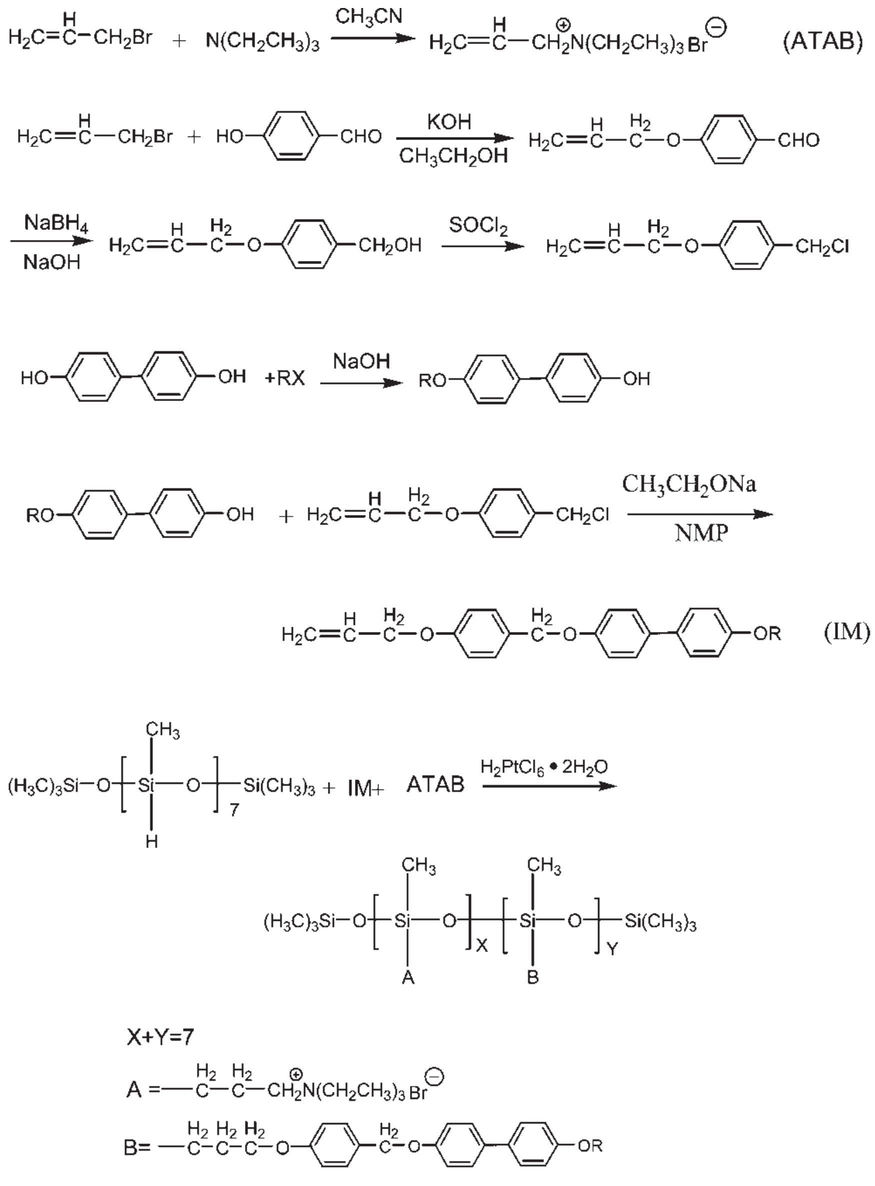
To a solution of 4-allyloxybenzyl alcohol (9.0 g, 0.055 mol) in methylene chloride (180 ml), thionyl chloride (10 ml, 0.137 mol) was added dropwise at room temperature. After 1 h the mixture was washed first with water, then with sodium dicarbonate solution (2 wt%) and again with water until it reached pH 7. The organic solution was dried over anhydrous sodium sulfate overnight, then passed through a silica gel column; the solvent was removed to yield 8.9 g of an oily product (90%). IR (KBr) cm$^{-1}$: 3082, 3025, 2921, 2865, 1648, 1610, 1584, 1512, 1245. $^1$H NMR (CDCl$_3$) $\delta$ ppm: 3.36 (s, 2H, –CH$_2$Cl), 4.43 (d, 2H, –CH$_2$O–), 5.40 (m, 2H, =CH$_2$), 5.80–6.30 (m, 1H, =CH), 6.80 (d, 2H, Ph), 7.23 (d, 2H, Ph).

#### 2.3.3. *4-(4-Allyloxybenzyloxy)-4′-alkoxybiphenyl (IM)*

The liquid crystal monomers were synthesized by etherification of the corresponding sodium phenolate with 4-allyoxybenzyl chloride. An example is presented as follows. 4-Methoxy-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 leave the sodium salt; water-free *N*-methyl-2-pyrrolidone (50 ml) was then added to dissolve the sodium ethanolate, followed by 4-allyloxybenzyl chloride (1.0 g, 0.0054 mol). The mixture was stirred for 5 h at 110°C, cooled to room temperature, and poured into water. The precipitate was filtered off, 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% of white crystals. Characterizations of the five monomers is shown as follows.

*4-(4-Allyloxybenzyloxy)-4′-methoxybiphenyl (IM$_1$)*: yield 83%. IR (KBr) cm$^{-1}$: 2930, 2850, 1650, 1610, 1590, 1520, 1500, 1270, 1240. $^1$H NMR (CDCl$_3$) $\delta$ ppm: 3.84 (s, 3H, –OCH$_3$), 4.54–4.56 (m, 2H, –OCH$_2$–), 5.01 (s, 2H, –OCH$_2$–), 5.27–5.31 (m, 1H, =CH), 5.39–5.44 (m, 1H, =CH), 6.01–6.11 (m, 1H, =CH), 6.93–6.97 (m, 4H, Ph), 6.99–7.03 (d, 2H, Ph), 7.35–7.38 (d, 2H, Ph), 7.45–7.49 (m, 4H, Ph).

*4-(4-Allyloxybenzyloxy)-4′-ethoxybiphenyl (IM$_2$)*: yield 81%. IR (KBr) cm$^{-1}$: 3050, 2980, 2900, 2850, 1650, 1600, 1580, 1520, 1500, 1270, 1240. $^1$H NMR (CDCl$_3$) $\delta$ ppm: 1.41–1.43 (t, 3H, –CH$_3$), 4.04–4.09 (m, 2H, –OCH$_2$–), 4.54–4.56 (m, 2H, –OCH$_2$–), 5.01 (s, 2H,



| Monomers | IM$_1$ | IM$_2$ | IM$_3$ | IM$_4$ | IM$_5$ |
|---|---|---|---|---|---|
| R | $CH_3$ | $CH_3CH_2$ | $CH_3(CH_2)_2$ | $CH_3(CH_2)_3$ | $CH_3(CH_2)_4$ |

Scheme. Synthetic routes of monomers and ionomers.

$–OCH_2–$), 5.27–5.30 (m, 1H, =CH), 5.39–5.44 (m, 1H, =CH), 6.01–6.11 (m, 1H, =CH), 6.92–6.96 (m, 4H, Ph), 7.00–7.03 (d, 2H, Ph), 7.35–7.37 (d, 2H, Ph), 7.44–7.48 (m, 4H, Ph).

*4-(4-Allyloxybenzyloxy)-4′-propoxybiphenyl (IM$_3$)*: yield 79%. IR (KBr) cm$^{-1}$: 3050, 2970, 2870, 2820, 1650, 1610, 1590, 1580, 1570, 1510, 1500, 1270, 1230. $^1$H NMR ($CDCl_3$) $\delta$ ppm: 1.03–1.07 (t, 3H, $–CH_3$), 1.80–1.85 (m, 2H, $–CH_2–$), 3.93–3.97 (t, 2H, $–OCH_2–$), 4.54–4.56 (m, 2H, $–OCH_2–$), 5.01 (s, 2H, $–OCH_2–$), 5.28–5.31 (m, 1H, =CH), 5.39–5.44 (m, 1H, =CH), 6.01–6.11 (m, 1H, =CH), 6.92–6.96 (m, 4H, Ph), 6.99–7.03 (d, 2H, Ph), 7.35–7.38 (d, 2H, Ph), 7.44–7.48 (m, 4H, Ph).

*4-(4-Allyloxybenzyloxy)-4′-butoxybiphenyl (IM$_4$)*: yield 81%. IR (KBr) cm$^{-1}$: 3050, 2950, 2870, 1650, 1610, 1600, 1580, 1510, 1500, 1270, 1230. $^1$H NMR ($CDCl_3$) $\delta$ ppm: 0.96–1.00 (t, 3H, $–CH_3$), 1.48–1.53 (m, 2H, $–CH_2–$), 1.76–1.80 (m, 2H, $–CH_2–$), 3.97–4.00 (t, 2H, $–OCH_2–$), 4.53–4.55 (m, 2H, $–OCH_2–$), 5.00 (s, 2H,

Table 1. Thermal analysis results of monomers IM$_1$–IM$_5$ on heating.

| | Transition temperature | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | $T_m$/°C | $T_{SN}$/°C | $T_c$/°C | $\Delta T^a$/°C | $\Delta H_m$/J g$^{-1}$ | $\Delta H_{SN}$/J g$^{-1}$ | $\Delta H_c$/J g$^{-1}$ |
| IM$_1$ | —$^b$ | | 182 | | | | 40.3 |
| IM$_2$ | 167 | 182 | 192 | 25 | 17.7 | 13.8 | 3.0 |
| IM$_3$ | 170 | 179 | 191 | 21 | 17.9 | 3.6 | 18.4 |
| IM$_4$ | 160 | 177 | 194 | 34 | 16.8 | 3.3 | 18.7 |
| IM$_5$ | 153 | 169 | 191 | 38 | 18.6 | 3.3 | 19.3 |

$^a$The mesomorphic temperature range (i.e. $T_c - T_m$).
$^b$It can be seen on the cooling curve.

–OCH$_2$–), 5.27–5.30 (m, 1H, =CH), 5.39–5.43 (m, 1H, =CH), 6.00–6.09 (m, 1H, =CH), 6.91–6.96 (m, 4H, Ph), 7.00–7.03 (d, 2H, Ph), 7.35–7.37 (d, 2H, Ph), 7.43–7.48 (m, 4H, Ph).

*4-(4-Allyloxybenzyloxy)-4′-pentoxybiphenyl (IM$_5$)*: yield 83%. IR (KBr) cm$^{-1}$: 3050, 2950, 2860, 1650, 1610, 1600, 1580, 1520, 1500, 1270, 1230. $^1$H NMR (CDCl$_3$) $\delta$ ppm: 0.92–0.96 (t, 3H, –CH$_3$), 1.38–1.46 (m, 4H, –CH$_2$CH$_2$–), 1.77–1.82 (m, 2H, –CH$_2$–), 3.97–4.00 (t, 2H, –OCH$_2$–), 4.54–4.56 (m, 2H, –OCH$_2$–), 5.01 (s, 2H, –OCH$_2$–), 5.28–5.31 (m, 1H, =CH), 5.40–5.44 (m, 1H, =CH), 6.01–6.11 (m, 1H, =CH), 6.92–6.96 (m, 4H, Ph), 6.99–7.03 (d, 2H, Ph), 7.35–7.38 (d, 2H, Ph), 7.44–7.48 (m, 4H, Ph).

Results of the thermal analyses of monomers IM are listed in table 1.

### 2.4. *Synthesis of ionomers*

The synthetic routes to the ionomers are outlined in the scheme. All the ionomers synthesized are listed in table 2. A general procedure is described below.

The monomers IM, ATAB and PMHS were dissolved in dry freshly distilled toluene (150 ml). The reaction mixture was heated to 50–60°C under nitrogen, and a solution of hydrogen hexchloroplatinate(IV) hydrate catalyst in THF (250 μl, 1.0 mg ml$^{-1}$) was injected with a syringe. The reaction was carried out until the disappearance of the Si–H IR band at 2160 cm$^{-1}$. The ionomers were isolated by precipitation in methanol; they were purified by reprecipitation from chloroform solutions with methanol, then dried under vacuum.

Table 2. Polymerization data.

| | Feed | | | | |
|---|---|---|---|---|---|
| Sample | PMHS/mmol | IM/mmol | ATAB/mmol | ATAB$^a$/mol % | Yield/% |
| PAIM$_4$-1 | 0.50 | 3.00 | 0.56 | 15.7 | 68 |
| PAIM$_4$-2 | 0.61 | 3.19 | 1.12 | 26.0 | 54 |
| PAIM$_4$-3 | 0.45 | 1.72 | 1.48 | 46.2 | 57 |
| PAIM$_4$-4 | 0.60 | 1.54 | 2.70 | 63.6 | 51 |
| PAIM$_1$-2 | 0.61 | 3.19 | 1.12 | 26.0 | 63 |
| PAIM$_2$-2 | 0.61 | 3.19 | 1.12 | 26.0 | 58 |
| PAIM$_3$-2 | 0.61 | 3.19 | 1.12 | 26.0 | 61 |
| PAIM$_5$-2 | 0.61 | 3.19 | 1.12 | 26.0 | 59 |
| PATAB | 0.32 | 0 | 2.25 | 100 | 58 |

$^a$Molar percentage of ATAB based on IM + ATAB.

Ionomers IR (KBr) cm$^{-1}$: 2800–3000 (–CH$_3$, –CH$_2$–), 1606, 1516, 1500 (Ar–, –Ar–Ar–), 1273, 1244 (C–O–C, Si–CH$_3$), 1178 (C–N$^+$) and 1000–1150 (Si–O–Si).

PATAB IR (KBr) cm$^{-1}$: 2800–3000 (–CH$_3$, –CH$_2$–), 1273 (Si–CH$_3$), 1178 (C–N$^+$) and 1000–1150 (Si–O–Si).

## 3. Results and discussion

### 3.1. *Thermal analysis*

Results of the thermal analyses of ionomers PAIM$_4$-1–PAIM$_4$-4 are listed in table 3. Figure 1 shows the DSC heating and cooling curves of ionomer PAIM$_4$-2. Figure 2 shows that the melting temperatures of ionomers PAIM$_4$-1–PAIM$_4$-4 increase with increasing concentration of ionic units. The clearing temperatures first quickly increase, then slightly decrease when the concentration of ionic units exceeds 26.0%. It can be seen that the mesormorphic temperature ranges have a tendency to decrease with increase of ionic units concentration in the ionomers. The four ionomers all display mesophases, smectic and nematic. An increase of the ionic content (15.7–63.6 mol %) has no influence on the type of mesophase exhibited by the ionomers. When the ionic unit concentration is 100%, the homopolymer PATAB displays no mesomorphism.

For ionomers (PAIM$_1$-2–PAIM$_5$-2) with a concentration of ionic units of 26.0 ionic mol %, we investigated the influence on phase transitions of the number of carbons in the alkoxy group located at the end of mesogen. The results are listed in table 4; DSC heating and cooling curves are presented in figure 3. In figure 4, the clearing temperatures of ionomers PAIM$_1$-2–PAIM$_5$-2 clearly follow an odd–even effect, the clearing temperatures of the ionomers

Table 3. Thermal analysis results of ionomers on heating.

| | | Temperature | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | Ionic/concn. mol% | $T_m$/°C | $T_{SN}$/°C | $T_c$/°C | $\Delta T^a$/°C | $\Delta H_m$/J g$^{-1}$ | $\Delta H_{SN}$/J g$^{-1}$ | $\Delta H_c$/J g$^{-1}$ |
| PAIM$_4$-1 | 15.7 | 147 | 165 | 174 | 27 | 1.0 | 5.0 | 6.1 |
| PAIM$_4$-2 | 26.0 | 157 | 178 | 188 | 31 | 36.0 | 6.9 | 36.0 |
| PAIM$_4$-3 | 46.2 | 163 | 178 | 187 | 24 | 32.7 | 7.3 | 28.9 |
| PAIM$_4$-4 | 63.6 | 165 | 178 | 186 | 21 | 30.4 | 8.0 | 31.2 |
| PAM$_4$-1 | 26.0 | 134 | 180 | 187 | 53 | 28.8 | 13.7 | 34.2 |
| PAM$_4$-5 | 63.6 | 148 | | 184 | 36 | 20.2 | | 23.0 |

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

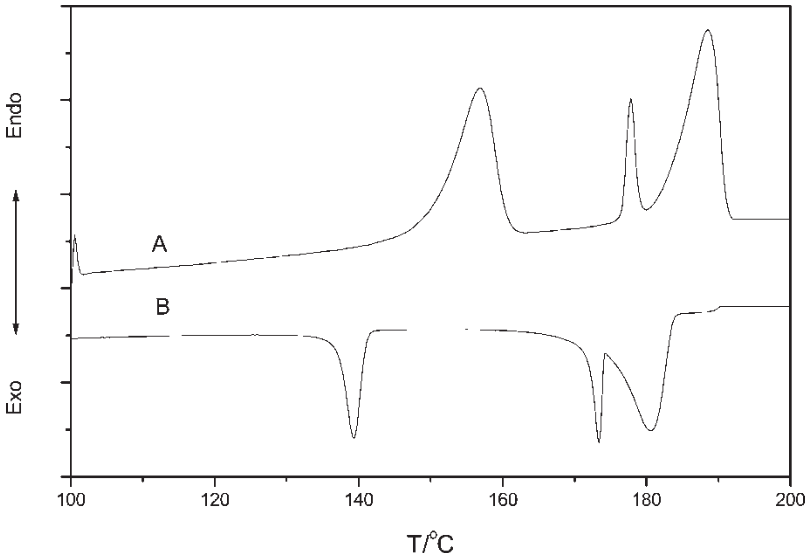


Figure 1. DSC scan of ionomer PAIM$_4$-2: A = heating scan; B = cooling scan.

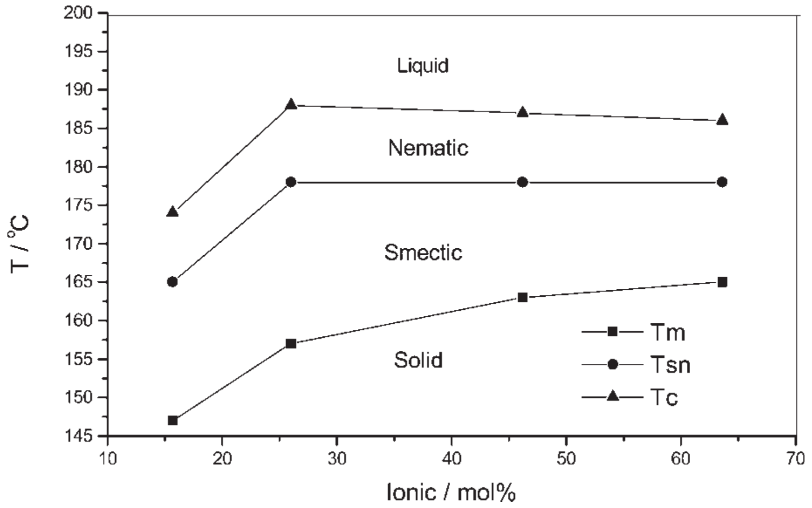


Figure 2. Phase diagrams of the ionomers PAIM$_4$-1–PAIM$_4$-4.

with an even number of carbons being higher than those with an odd number of carbons. The melting temperatures first increase, then decrease significantly with the increase of alkoxy chain length. The mesomorphic temperature ranges increase when the alkoxy carbon number is over 3.

Figure 3 (*a*) shows only one peak on the heating curve of ionomer PAIM$_1$-2, while figure 3 (*b*) shows two peaks

Table 4. Thermal analysis results of ionomers PAIM$_1$-2–PAIM$_5$-2 on heating. Cr = crystal, S = smectic, N = nematic, I = isotropic phase.

| Ionomer | Ionic/concn. mol% | Phase transition temperature/°C | $\Delta T^{a}$/°C | $\Delta H_m$/J g$^{-1}$ | $\Delta H_{SN}$/J g$^{-1}$ | $\Delta H_c$/J g$^{-1}$ |
|---|---|---|---|---|---|---|
| PAIM$_1$-2 | 26.0 | Cr181I | | | | 92.2 |
| PAIM$_2$-2 | 26.0 | Cr163S187I | 24 | 30.9 | | 32.2 |
| PAIM$_3$-2 | 26.0 | Cr170S181N186I | 16 | 26.7 | 8.7 | 25.3 |
| PAIM$_4$-2 | 26.0 | Cr157S178N188I | 31 | 36.0 | 6.9 | 36.0 |
| PAIM$_5$-2 | 26.0 | Cr131S183N186I | 55 | 8.7 | 2.6 | 11.5 |

[a] The mesomorphic temperature range (i.e. $T_c - T_m$).

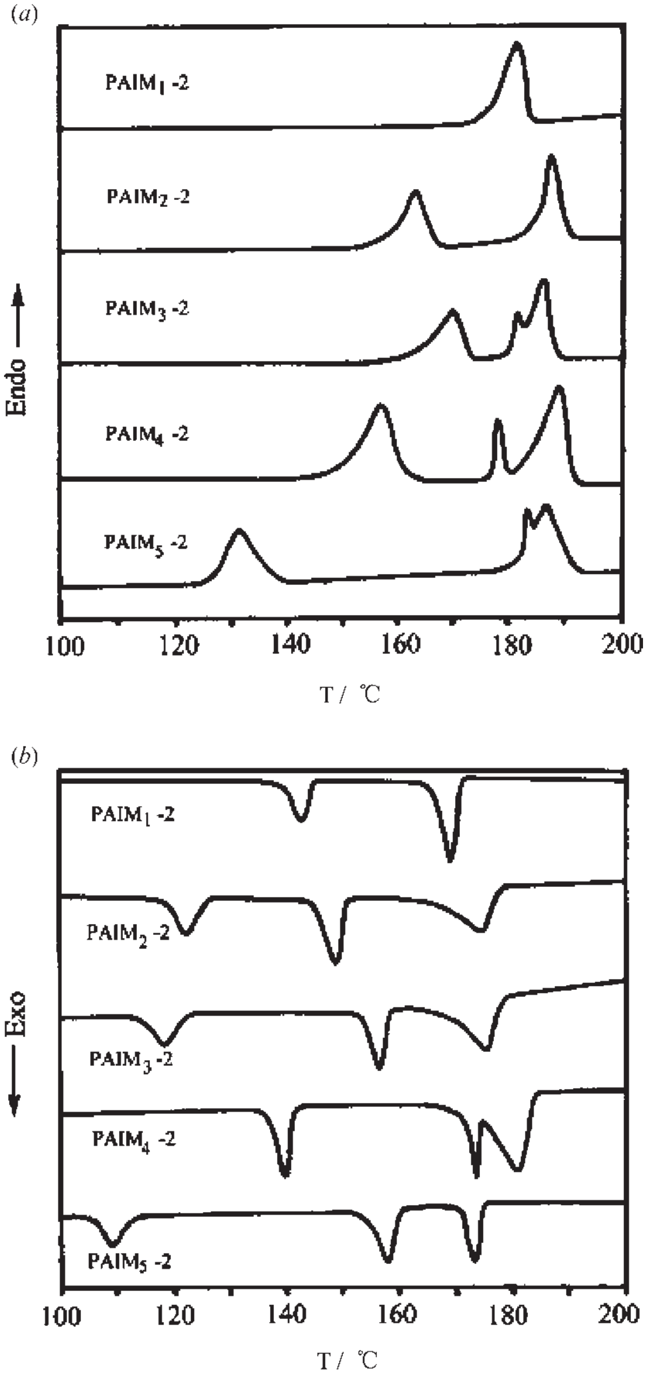


Figure 3. DSC curves of ionomers ($PAIM_1$-2–$PAIM_5$-2) (*a*) on heating, (*b*) on cooling.

on its cooling curve. POM observation of ionomer $PAIM_1$-2 displays a smectic texture in the range 160–181°C. This demonstrates that the smectic phase of the ionomer $PAIM_1$-2 is monotropic. Ionomer $PAIM_1$-2 is thus a monotropic smectic liquid crystalline polymer. Ionomer $PAIM_2$-2 exhits two peaks on the heating curve, and three peaks on the cooling curve. Under POM, ionomer $PAIM_2$-2 exhibits a smectic phase in the range 163–182°C and a nematic phase in the range 182–187°C. This demonstrates that the nematic phase of ionomer $PAIM_2$-2 is monotropic, and its smectic phase is enantiotropic. The ionomers $PAIM_3$-2–$PAIM_5$-2 all exhibit enantiotropic smectic and nematic phases.

### 3.2. *Optical micrograph analysis*

Monomer $IM_1$ exhibited only a smectic mesophase, while monomer $IM_2$–$IM_5$ all showed two types of mesophase. The smectic mesophases of monomers $IM_1$–$IM_5$ all have similar textures—broken focal-conic. The texture of monomer $IM_3$ is shown in figure 5 as an example. All the nematic mesophases of monomers $IM_2$–$IM_5$ exhibit schlieren textures. The monomer ATAB decomposed when heated to 240°C and no mesophase was observed.

All the ionomers $PAIM_4$-1–$PAIM_4$-4 showed two kinds of mesophase. The smectic and nematic phases of these ionomers exhibit similar textures, broken focal-conic and threaded textures, respectively. The ionomer $PAIM_1$-2 showed only a broken focal-conic smectic texture. The ionomers $PAIM_2$-2–$PAIM_5$-2 all exhibited two kinds of mesophase. Their smectic phases all show similar broken focal-conic textures. The nematic phases of ionomers $PAIM_2$-2 and $PAIM_3$-2 exhibit schlieren textures. The nematic phases of ionomers $PAIM_4$-2 and $PAIM_5$-2 exhibit threaded textures. Figure 6 shows the textures of ionomer $PAIM_3$-2. For ionomer PATAB, no mesophase could be observed, it decomposed when heated to 270°C.

### 3.3. *X-ray diffraction analysis*

Figures 7 (*a*) and 7 (*b*) show the small angle and wide angle XRD diagrams for quenched samples of ionomer $PAIM_4$-2 at different temperatures. For small angle XRD (*a*) ionomer $PAIM_4$-2 exhibits one peak at $2\theta = 0.43°$ at 165°C, derived from the corresponding *d*-spacing of smectic orientations of the mesogens; at 185°C no peak in the small angle region was observed. For wide angle XRD (*b*) ionomer $PAIM_4$-2 exhibits sharp peaks at $2\theta = 20.68°$ at 165°C, and at $2\theta = 20.52°$ at 185°C. These results indicate the presence of a smectic phase at 165°C and a nematic phase at 185°C [26]. The results of DSC, POM and XRD analyses of the ionomer $PAIM_4$-2 are consistent.

### 3.4. *Comparison of the mesogenic properties of two series of ionomers*

We synthesized another series of monomers and ionomers in previous work [27]. The monomers $M_1$–$M_5$

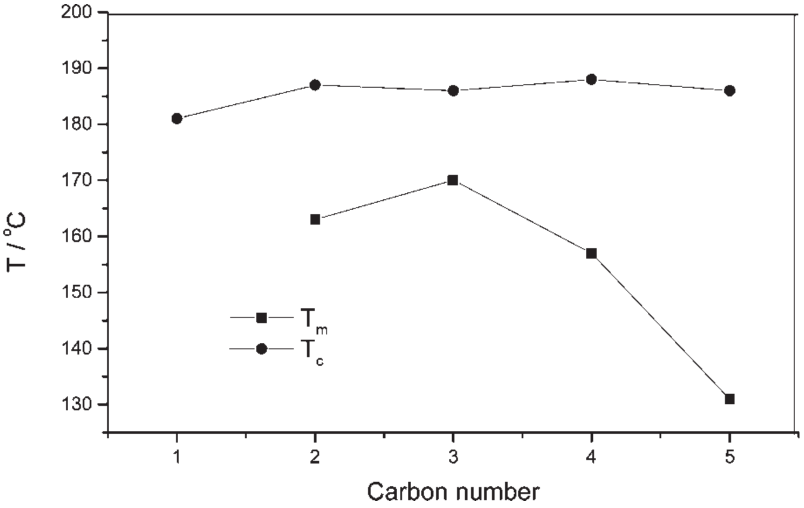


Figure 4. Phase transition temperatures of ionomers $PAIM_1$-2–$PAIM_5$-2 versus alkoxy carbon number.

are isomers, respectively, with monomers $IM_1$–$IM_5$ in this work. The ionic units in the two series of ionomers in both studies are the same, allyltriethylammonium bromide (ATAB). We now compare the mesogenic properties of the two series of ionomers, and further discuss the influence of the concentration of ionic units, the alkoxy chain length and the isomeric effect on the mesogenic properties.

Comparing the first series of ionomers $PAM_4$-1–$PAM_4$-6 with the second series $PAIM_4$-1–$PAIM_4$-4, it can be seen that in the same ionic unit concentration range (26.0–63.6 mol%), the influence of this concentration on the melting and clearing temperatures is similar in both series. The melting temperatures first increase significantly, then change slowly when the ionic unit concentration exceeds 46.4%. The clearing

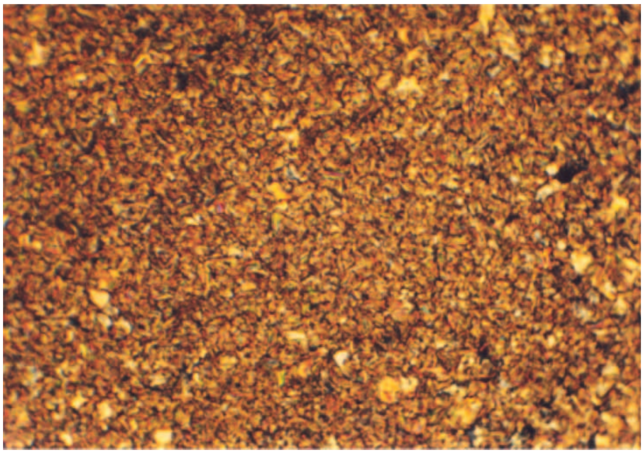
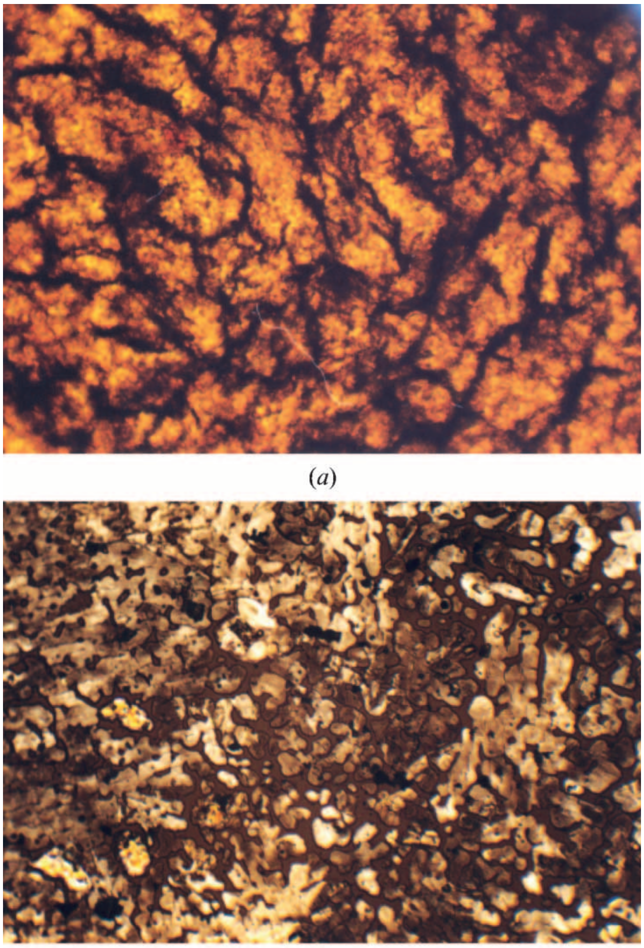


Figure 5. Texture of monomer $IM_3$ at 172°C (200X).



(a)

(b)

Figure 6. Textures of ionomer $PAIM_3$-2 (200X): (a) at 175°C, (b) at 183°C.

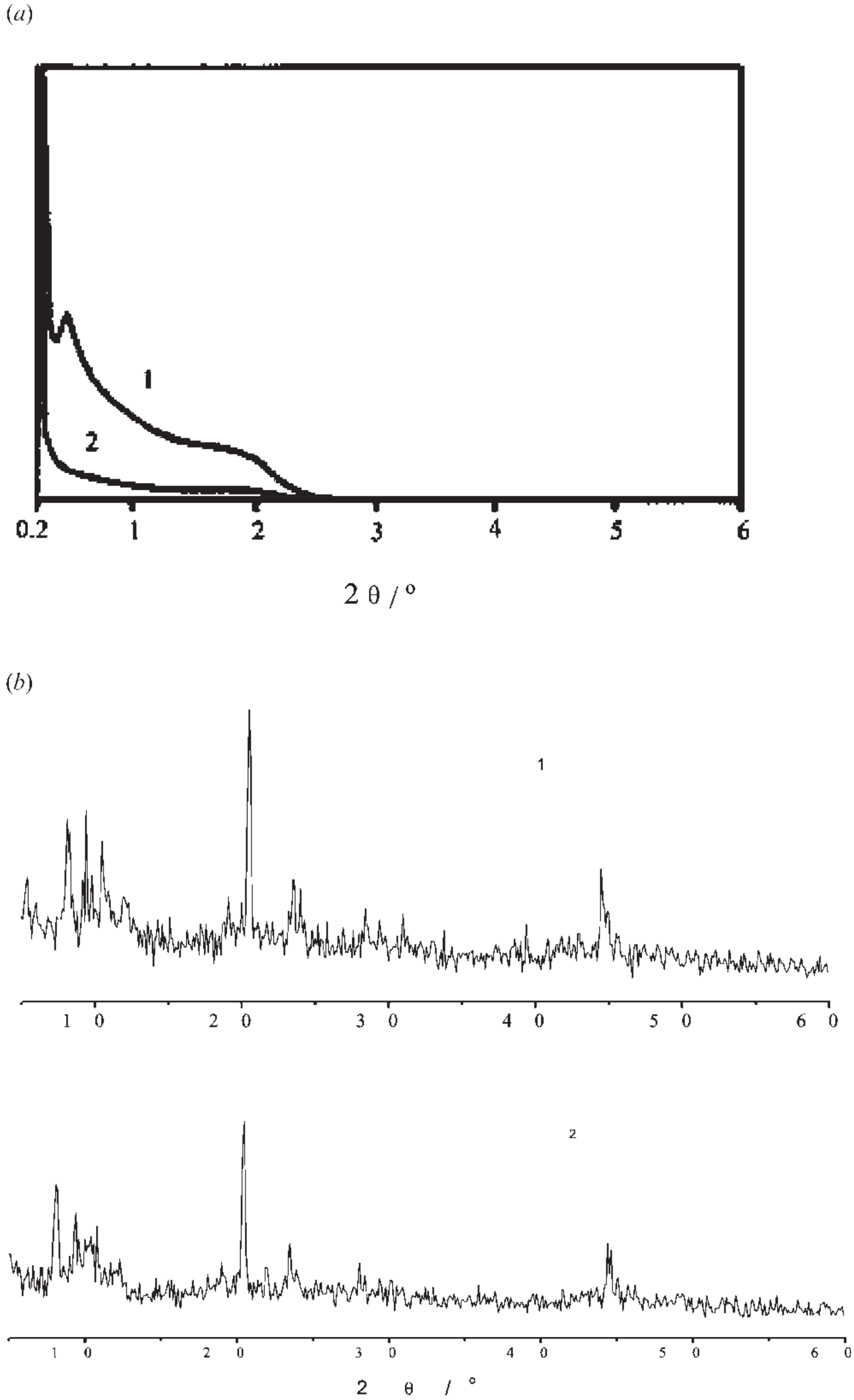


Figure 7. X-ray diffraction diagrams of the ionomer PAIM$_4$-2: (*a*) small angle, (*b*) wide angle. 1 = 165°C, 2 = 185°C.

temperatures show no obvious change when the ionic unit concentration is below 46.4%, then decrease slowly with further increase of the concentration. This experimental data may bring us to the conclusion that the interactive forces existing in all the investigated ionomers are same.

But a difference in the phase behaviour between the two series of ionomers has also been observed. In the first series of ionomers PAM$_4$-1–PAM$_4$-6, two types of mesophase are seen when the ionic unit concentration is below 46.4%, then the nematic phase disappears and only the smectic phase is seen with a further increase of ionic unit concentration. The second series of ionomers $PAIM_4$-1–$PAIM_4$-4 all exhibit two types of mesophase, which are unaffected by change in the ionic unit concentration. These experimental results indicate that the chemical structure with biphenyl located at the middle of the monomer is more useful in producing smectic orientational order, and tends to stabilize the smectic layer structure more than that with the biphenyl located at the end of the monomer.

By comparing ionomers $PAM_1$-4–$PAM_5$-4 (ionic mol% = 46.4) with ionomers $PAIM_1$-2–$PAIM_5$-2 (ionic mol% = 26.0), we investigate the influence of the alkoxy group chain length of the ionomers on phase behaviour. The clearing temperatures of both series of ionomers clearly show an odd–even effect with the increase of alkoxy chain length. This property of the ionomers is similar to that of other side chain LCPs [28]. The melting temperatures of the two types of ionomer decrease significantly and increase the mesomorphic temperature range when the number of alkoxy carbons exceeds 3. But when the carben number is below 3, the melting temperatures of ionomers $PAM_1$-4–$PAM_5$-4 first decrease, then remain constant; the melting temperatures of ionomers $PAIM_1$-2–$PAIM_5$-2 increase with increasing carbon numbers.

Ionomers $PAM_4$-1 and $PAIM_4$-2, having the same ionic unit concentration (26.0%), are isomers. Ionomers $PAM_4$-5 and $PAIM_4$-4, having the same ionic unit concentration (63.6%), are also isomers. Comparing the phase behaviours of $PAM_4$-1 with $PAIM_4$-2, and $PAM_4$-5 with $PAIM_4$-4 (listed in table 3), yields information on the effect of different monomers on mesogenic properties. The melting temperature of $PAIM_4$-2 is higher than that of $PAM_4$-1; the clearing temperature of $PAIM_4$-2 is a little higher than that of $PAM_4$-1. The mesomorphic temperature range of $PAIM_4$-2 is narrower than that of $PAM_4$-1; both isomers have two types of mesophase. The same results are seen when comparing $PAM_4$-5 with $PAIM_4$-4, except that $PAIM_4$-4 exhibits two types of mesophases, while $PAM_4$-5 exhibits only a smectic (no nematic). These experimental results show that the isomer with biphenyl located at the end of the monomer has a higher melting temperature and narrower mesomorphic temperature range than the isomer with biphenyl located at the middle of the monomer.

## 4. Conclusions

A series of liquid crystalline ionomers containing quaternary ammonium salts on the side chain to the PMHS backbone have been synthesized and characterized. The melting temperatures of the ionomers increase with increasing concentration of ionic units. When the ionic unit concentration is 63.6%, the ionomers still exhibit mesomorphic behaviour. The influence of the alkoxy chain length on the ionomer clearing temperatures clearly involves an odd–even effect, similar to other side chain LCPs. On comparing the mesomorphic behaviour of two series of isomeric ionomers with the same ionic unit concentration range, it is seen that the mesomorphic behaviours are similar. The significant difference is that the melting temperatures of the ionomers with biphenyl located at the end of the mesogen are higher than those of the ionomers with biphenyl located at the middle of the mesogen.

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