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Liquid Crystals

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Side chain type ionic liquid crystalline polymers having high Preliminary communication molecular weight

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Preliminary communication

Side chain type ionic liquid crystalline polymers having high molecular weight

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Side chain type ionic liquid crystalline polymers having a 4-(1,3-dioxan-2-yl)pyridinium structure in their mesogenic side chain were synthesized. These polymers exhibited the smectic A phase. The molecular weights of these ionic liquid crystalline polymers are very high, e.g. for compound **7-2** $M_w = 486\,000$.

There are few or no reports concerning side chain type ionic thermotropic liquid crystalline (LC) polymers synthesized by the polymerization of ionic LC monomers. In the few reported ionic thermotropic LC polymers, for example those with a mono-pyridinium ring in the side chain [1], or with an alkyl ammonium salt in the main chain [2], the polymers were synthesized initially in a non-ionic form. Thus in the first step of the syntheses of the former compounds, a non ionic polymer was synthesized, then *N*-alkylation was carried out to make the ionic polymer. These side chain type ionic LC polymers were not synthesized from ionic liquid crystal monomers mainly because ionic monomers and ionic polymers are difficult to dissolve in organic solvents. On the other hand, new pyridinium type ionic LC compounds having a 1,3-dioxan or 1,3-oxathian or 1,3-dithian ring have

been synthesized [3–5]. In this paper we report the syntheses and characterization of new pyridinium type ionic LC compounds having a 1,3-dioxan ring and polymerizable double bond, and the polymers of these compounds.

Side chain type ionic liquid crystalline polymers **7** were synthesized by the route shown in figure 1. In the syntheses of compounds **5**, both *trans*- and *cis*-isomers were produced. Repeated recrystallizations were required to obtain only the *trans*-isomers. On *N*-alkylation, ^1H NMR signals for the pyridinium proton were shifted downfield about 0.8 ppm. The purity of monomers **6** was confirmed by ^1H NMR spectroscopy and elemental analyses.

Ionic side chain polymers were synthesized by free radical polymerization of the monomers **6** (1 mmol) with AIBN (7 mg) as initiator, in *N,N*-dimethylformamide (2 ml) at 70°C for 72 h in de-aerated ampoules. The polymers **7** were purified by reprecipitation with acetone.

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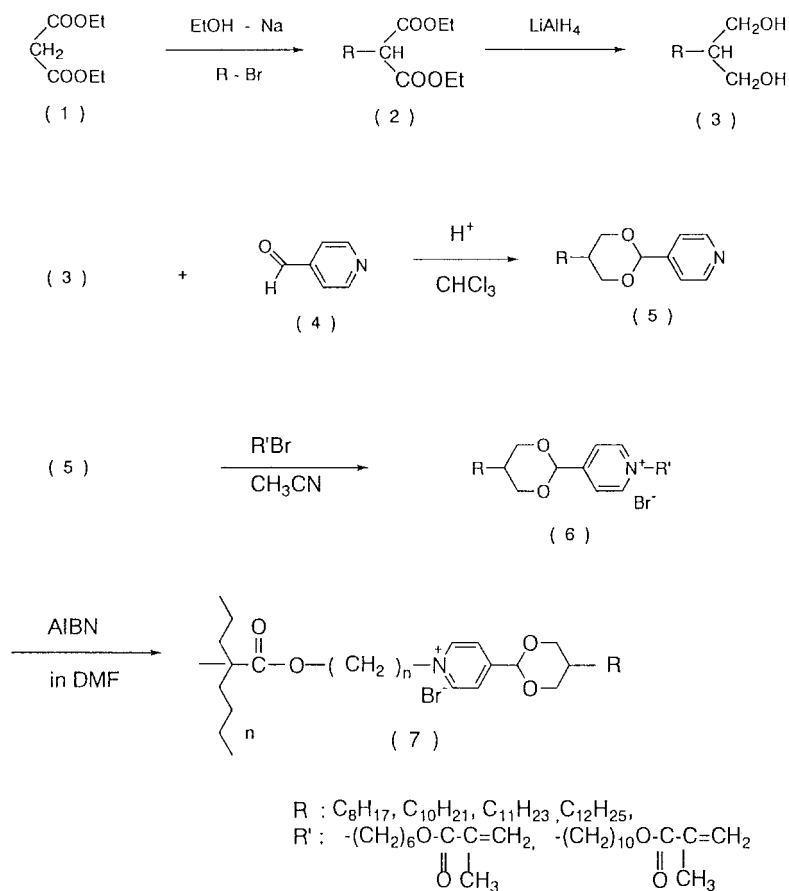


Figure 1. Synthetic pathway for ionic liquid crystal polymers 7.

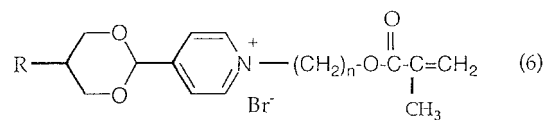
Measurement of transition temperatures and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Phase transition temperatures for monomers and the corresponding polymers are given in table 1. Observation indicated that these compounds exhibited the smectic A phase texture. To confirm this result, conoscopic figures and XRD measurements were obtained for this phase of compounds 6-4, and 7-2 (figure 2). The synthesized monomers 6 exhibited the smectic A phase over a very wide range including room temperature (table 1). Generally, the isotropic to smectic A phase transition temperatures of ionic LC monomers are higher than 100°C [6], therefore the I-SmA transition temperatures of compounds 6 are very low.

Molecular weights were measured by means of gel permeation chromatography (GPC). Generally, ionic monomers and polymers are difficult to dissolve in organic solvents, and it is difficult to measure high molecular weights. In the present case the solubilities of monomer and polymer are high enough to measure high molecular weights. For example the M_w of polymer 7-2 is about

486 000 (table 2). To confirm this result the molecular weight of polymer 7-3 was measured by means of the static light scattering method (using a Otuka Electronics SLS 6000 HL system). By this method the molecular weight (M_w) of polymer 7-3 was 270 000, close to the value obtained by GPC. Therefore, these ionic LC polymers have very high molecular weights.

The molecular weight distributions are extremely broad (figure 3); the part having large molecular weight seems to polymerize in the liquid crystalline state. In spite of these ionic polymers having extremely high molecular weights, their solubility in chloroform is very good. This seems to imply that they are perfectly linear. The layer spacings of monomers 6 are 26 ~ 28 Å and those of polymers 7 are 48 ~ 51 Å. These results indicate that the smectic A phases of monomers 6 are monolayer structures and those of polymers 7 are bilayer structures. Therefore, in the smectic phase of monomers 6, molecules must align, and double bonds seem to exist near to each other; this may facilitate the polymerization (figure 4). The effect of this arrangement leads to high molecular weight and good solubility of the ionic liquid crystalline polymers 7.

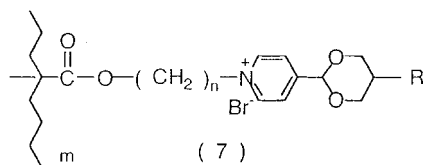
Table 1. Phase transition temperatures for compounds 6.



Compound	R	n	Phase transition temperatures/°C ^a
6-1	C ₈ H ₁₇	6	
6-2	C ₁₀ H ₂₁	6	
6-3	C ₁₂ H ₂₅	6	
6-4	C ₁₀ H ₂₁	10	

^a Cr: crystal, I: isotropic, SmA: smectic A.

Table 2. Phase transition temperatures for polymers 7.



Compound	R	n	Phase transition temperatures/°C ^a	M_n^b	M_w^b
7-1	C ₈ H ₁₇	6	Cr 211 SmA 225 I	21 000	315 000
7-2	C ₁₀ H ₂₁	6	Cr 200 SmA 243 dec	20 000	486 000
7-3	C ₁₂ H ₂₅	6	Cr 195 SmA 246 dec	17 000	250 000
7-4	C ₁₀ H ₂₁	10	Cr 203 Sma 215 I	16 000	459 000

^a Cr: Crystal, SmA: smectic A, I: isotropic, dec: decomposed

^b M_n : number average molecular weight; M_w : weight average molecular weight.

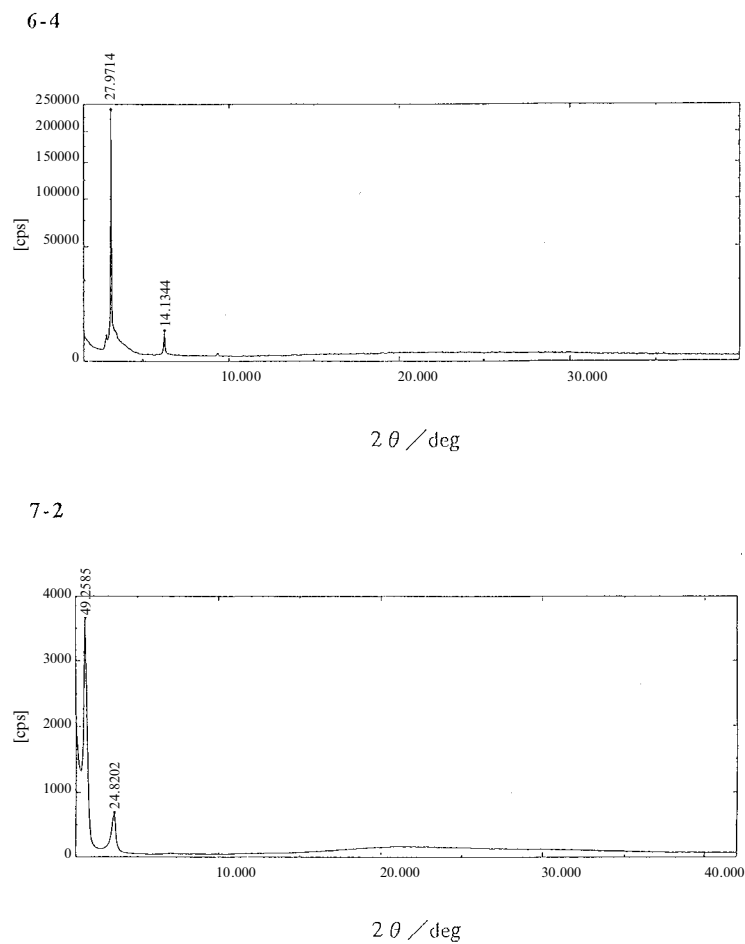


Figure 2. X-ray diffraction pattern of the smectic phase of compounds **6-4** and **7-2**.

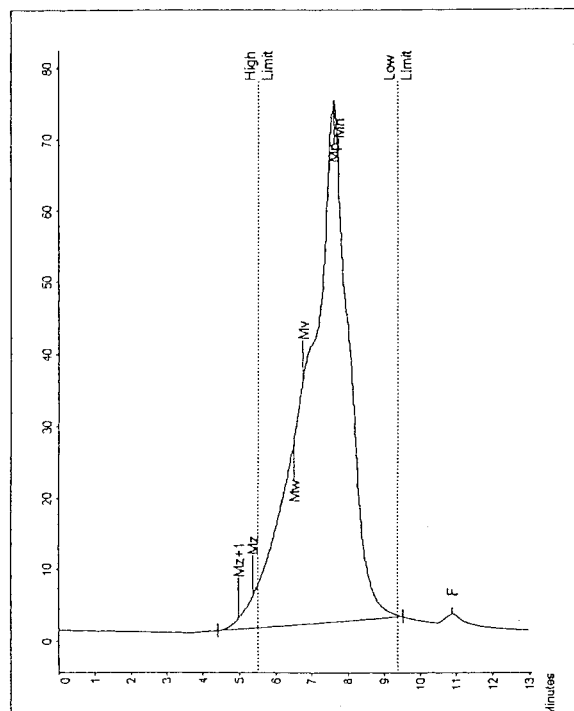


Figure 3. Molecular weight distribution of the ionic polymer **7-3**.

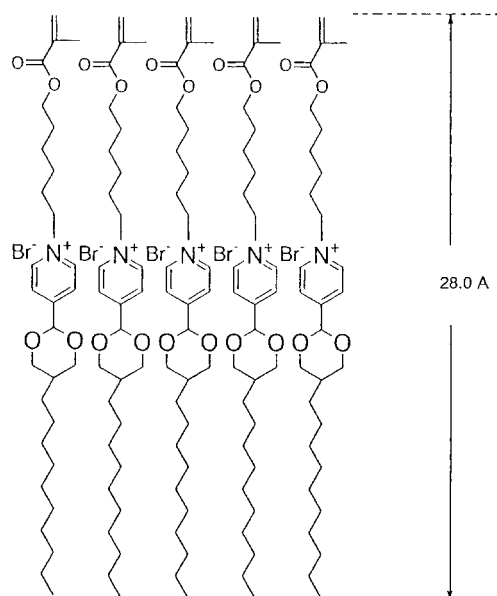


Figure 4. Molecular arrangement of the ionic liquid crystal monomer **6**.

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