

Phase Transitions and Orientational Structures of Ionic Liquid Crystalline Polymers and Their Nonionic Family

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Ionic liquid crystalline polymers and their nonionic family were synthesized. Their thermal and liquid crystalline properties were then measured. The ionic liquid crystalline polymers (ionic LCPs), having a poly(ethyleneiminium) backbone, showed a smectic A phase with a focal conic fan texture and a perpendicular structure. On the other hand, the nonionic liquid crystalline polymers (nonionic LCPs), which are a nonionic family of the ionic LCPs, formed only a nematic phase with a schlieren texture. The ionic LCPs have a higher isotropization temperature when compared to the nonionic LCPs due to the formation of an ionic sublayer composed of the poly(ammonium)s and halide counterions by ionic interactions in the ionic LCPs.

Key words: Liquid crystalline polymer, Ionic liquid crystal, Thermal property, X-Ray, Smectic

1. INTRODUCTION

Anhydrous amphiphilic materials such as alkali metal carboxylates and alkylammonium salts can show thermotropic liquid crystalline phases [1, 2]. In polymer systems, the introduction of the ionized units also leads to the formation of the thermotropic liquid crystalline phases with enhanced thermal stability [3]. We proposed a novel type of liquid crystalline polymer system incorporating ionic groups [4, 5]. Several ionic thermotropic liquid crystalline polymers were synthesized and their thermal and liquid crystalline properties were studied [6, 7]. In low-molecular-weight and polymeric liquid crystal systems with aromatic-mesogenic moieties, liquid crystalline phases are formed by ionic aggregation due to Coulomb's force as well as anisotropy through the interactions between the mesogenic moieties. We have synthesized ionic side chain liquid crystal polymers with a poly(ammonium) backbone and their nonionic family to clarify the effects of the ionic polymer backbone in the smectic liquid-crystal formation. It was found that the ionic polymer backbone functioned as a smectogenic species. Moreover, it is expected that the strong interactions between the ionic groups can control the orientational structures in the liquid crystalline systems.

This paper describes the effect of ionic groups

on the liquid crystal formation of ionic side chain liquid crystal polymers. The phase transitions and the orientational structures of the ionic and nonionic liquid crystalline polymer systems are compared.

2. EXPERIMENTALS

2.1. Materials

4-(4-(ETHYL)PHENYLAZO)PHENOL

4-Ethylaniline was dissolved in hydrochloric acid, and the solution was cooled below 5°C. For the diazotation, a small amount of sodium nitrite was added at a temperature below 5°C. To this cooled solution, a mixture of sodium hydroxide solution with phenol was then added. The reaction mixture was stirred for 1 h at about 5°C, and after the reaction, acidified with conc. hydrochloric acid. The precipitate was isolated by filtration and dried. Yield, 70%.

6-BROMO-1-(4-(4-ETHYLPHENYLAZO)PHENOXY) HEXANE (6-Et)

4-(4-(Ethyl)phenylazo)phenol and 1,6-dibromohexane were dissolved in acetone, and potassium carbonate was added. The mixture was refluxed for 72h. After the reaction, the mixture was filtered off, and the acetone was evaporated from

the filtrate. Chloroform was added to the crude product, and this chloroform solution was extracted with water and evaporated. The product was recrystallized from the ethanol solution. Yield, 80%. $^1\text{H NMR}(\text{CDCl}_3)$: 1.1(t, 3H, $-\text{CH}_3$), 1.5 (m, 8H, $-(\text{CH}_2)_4-$), 2.4(m, 2H, $-\text{CH}_2$ -phenyl-), 3.9(t, 2H, $-\text{O}-\text{CH}_2-$), 6.8(d, 2H, phenyl), 7.2(d, 2H, phenyl), 7.7(d, 4H, phenyl).

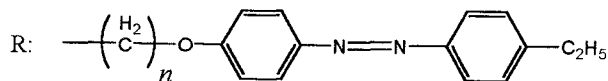
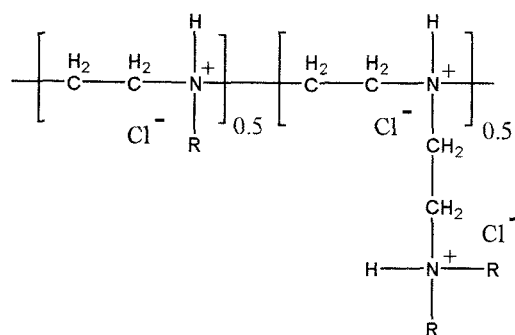
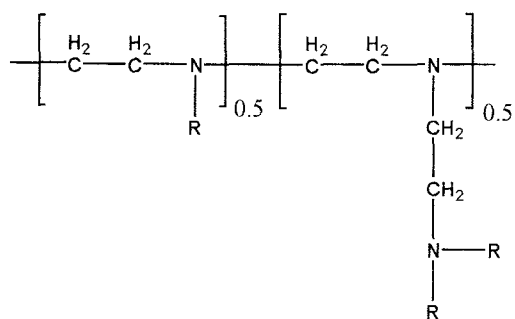


Fig. 1. Structures of nonionic (upper structure) and ionic (lower structure) liquid crystalline polymers with ethylazobenzene side-groups: $n=4,5,6$. The polymer backbone has equal amounts of primary, secondary, and tertiary amine groups.

4-Bromo-1-(4-(4-ethylphenylazo)phenoxy)butane (4-Et) with a tetramethylene chain and 5-bromo-1-(4-(4-ethylphenylazo)phenoxy)pentane (5-Et) with a pentamethylene chain were also obtained by the identical method as described above for 6-Et. The melting points of 4-Et and 6-Et were 85.6°C and 86.5°C , respectively. Both 4-Et and 6-Et did not form a liquid crystalline phase. However,

5-Et melted at 89.2°C and upon cooling, showed a monotropic nematic phase in the narrow temperature range from 65.4 to 64.9°C .

NONIONIC LIQUID CRYSTALLINE POLYMER (NP-6)

Poly[N-(6-(4-(4-ethylphenylazo)phenoxy)hexyl)ethyleneimine] was prepared by the reaction of polyethyleneimine with 6-Et.

Polyethyleneimine, having equal amounts of primary, secondary and tertiary amine groups, and 6-Et were dissolved in a mixed solution of tetrahydrofuran and ethanol, and then potassium carbonate was added. The reaction mixture was refluxed for 400h. After the reaction, the reaction mixture was evaporated. Chloroform was added to the crude product, and this chloroform solution was extracted with water and evaporated. The crude product was dissolved in tetrahydrofuran, and the polyamine was reprecipitated by adding hexane. The product was filtered off and dried under the reduced pressure. Yield, 70%. $^1\text{H NMR}(\text{CDCl}_3)$: 1.1 (t, 3H, $-\text{CH}_3$), 1.3-1.65 (m, 8H, $-(\text{CH}_2)_4-$), 2.5(m, 8H, $-\text{CH}_2$ -phenyl, $\text{N}-\text{CH}_2-$), 3.9(t, 2H, $\text{O}-\text{CH}_2-$), 6.8(d, 2H, phenyl), 7.2(d, 2H, phenyl), 7.7(d, 4H, phenyl).

NP-4 and NP-5 were also synthesized by the same method as described above for NP-6.

IONIC LIQUID CRYSTALLINE POLYMER (IP-6)

Poly[N-(6-(4-(4-ethylphenylazo)phenoxy)hexyl)ethyleneiminium chloride] (IP-6) was obtained by the reaction of NP-6 and hydrochloride.

NP-6 was dissolved in tetrahydrofuran, and into the solution, hydrochloride, which was obtained by reaction of calcium chloride and sulfuric acid, was introduced. After the reaction, the solution was added into hexane, and the ionized polymer was reprecipitated. The product was filtered off and dried under the reduced pressure. Yield, 95%. $^1\text{H NMR}(\text{CDCl}_3)$: 1.1 (t, 3H, $-\text{CH}_3$), 1.3-1.65 (m, 8H, $-(\text{CH}_2)_4-$), 2.4(m, 2H, $-\text{CH}_2$ -phenyl-), 3.2(m, 6H, N^+-CH_2-), 4.0(t, 2H, $\text{O}-\text{CH}_2-$), 6.8(d, 2H, phenyl), 7.2(d, 2H, phenyl), 7.7(d, 4H, phenyl).

IP-4 and IP-5 were prepared by the same method as for IP-6.

2.2. Measurements

The NMR spectra were measured using a JEOL JNM-EX270L. The phase transitions were measured

with a polarizing microscope equipped with a hot stage (Mettler FP900-FP82) and DSC (Mettler Thermosystem 2000). The X-ray diffractions were obtained using an X-ray diffractometer (Rigaku Rint2000). In the X-ray diffraction measurement, the samples were put on a hot stage (Linkam FHS 900).

Table I. Phase transitions of nonionic (NP-*n*) and ionic (IP-*n*) liquid crystalline polymers

Sample ¹⁾	Phase transition temp. ²⁾ /°C
NP-4	K 4.6 N 75.7 I
NP-5	K 14.0 N 70.1 I
NP-6	K 31.0 N 85.1 I
IP-4	g 52.5 M 109.5 SmA 210(Dec)
IP-5	g 40.3 M 98.0 SmA 202.2 I
IP-6	g 51.7 M 91.8 SmA 177.2 I

1)The number (4, 5, 6) denotes the length of the spacer chain.

2)I : isotropic, N : nematic, SmA : smectic A, M : mesomorphic, K : solid, g : glassy, Dec : thermal decomposition.

3. RESULTS AND DISCUSSION

The phase transition temperatures of the ionic and nonionic liquid crystalline polymers are listed in Table I. A nonionic liquid crystalline polymer (NP-6), having a hexamethylene spacer, exhibited a nematic phase with a schlieren texture during the heating and cooling processes. NP-4 and NP-5, which are the nonionic liquid crystalline polymers, also showed an enantiotropic nematic phase. On the other hand, the ionic liquid crystalline polymers (IP-4, IP-5 and IP-6), having an ionized skeletal main chain, formed an enantiotropic smectic A phase. A focal conic fan texture and a perpendicular structure were formed in the smectic A phase. The perpendicular structure with an optical-uniaxial property was characterized by conoscopic observation. The formation of the nematic phase in the nonionic NP-*n* mainly occurred by the interactions between the mesogenic side-groups. In the ionic IP-*n*, the formation of the smectic A phase is governed by the anisotropy formed through the ionic aggregation as well as the interactions between the mesogenic side-groups. In this case, the ionic polymer backbones effectively act, forming the smectic-layered structure, as a smectogenic species.

This corresponds to the fact that, in general, amphiphilic molecules such as ammonium salts with

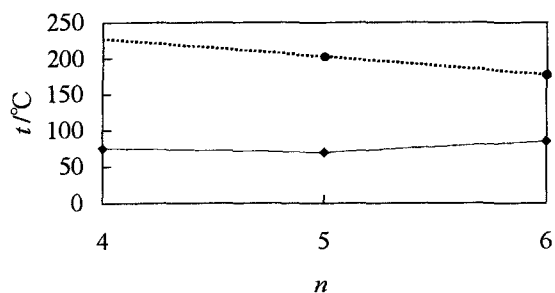


Fig. 2. Isotropization temperatures of nonionic (◆) and ionic (●) liquid crystalline polymers. *n* denotes the spacer chain length.

a long alkyl chain exhibit smectic phases through the Coulomb's force effect.

The isotropization temperature of the ionic liquid crystalline polymer is much higher than that of the nonionic liquid crystalline polymer. This enhanced thermal stability is led by the ionic aggregation through the ionic interactions between the ions in the ionic liquid crystalline polymer. Many alkylammonium salts exhibited higher melting points when compared to their nonionic components because ammonium salts form an ionic aggregation by Coulomb's force, which is absent between nonionic compounds. For example, ethylenediammonium chloride with an mp > 300°C, which is made of ethylenediamine and hydrochloride, shows a higher melting point than ethylenediamine with an mp of 8.5°C.

In the case of the nonionic liquid crystalline polymers, the isotropization temperatures slightly depended of the spacer length. However, the isotropization temperatures of the ionic liquid crystalline polymers increased with the decreasing spacer chain length. IP-4 with a shorter spacer chain underwent the thermal decomposition at 210°C. It is expected that the imaginary isotropization temperature of IP-4 is higher than 210°C (Fig. 2).

At the M-smectic A phase transition, a peak was clearly found by DSC measurement. However, the optical texture and the X-ray diffraction pattern in the M phase resembled those in the smectic A phase. It is expected that the M phase with a very low fluidity is an ordered smectic phase such as the smectic G phase or the solid phase. This is related to the fact that a long time is required for realization of

polymorphic structural transformations in side chain liquid crystalline polymers [8].

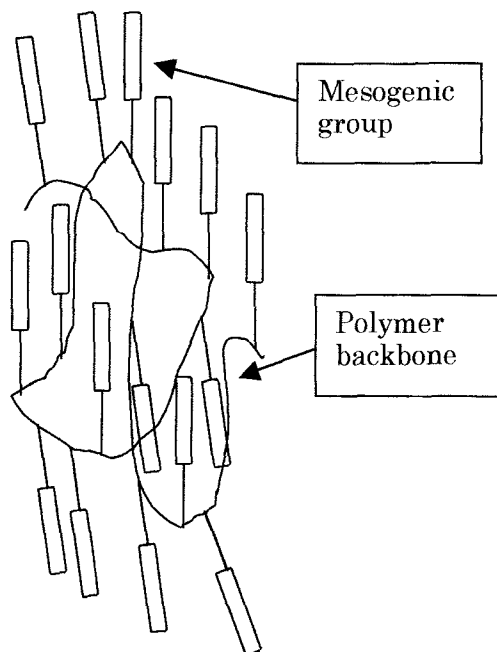


Fig. 3. Image of nematic orientation for nonionic liquid crystalline polymer. The polymer backbones disperse in the nematic orientation formed by the mesogenic groups.

The molecular orientation in the nematic phase of the nonionic liquid crystalline polymers is schematically illustrated as shown in Fig. 3. Both the polymer backbones and the mesogenic side-groups have no positional orientational order.

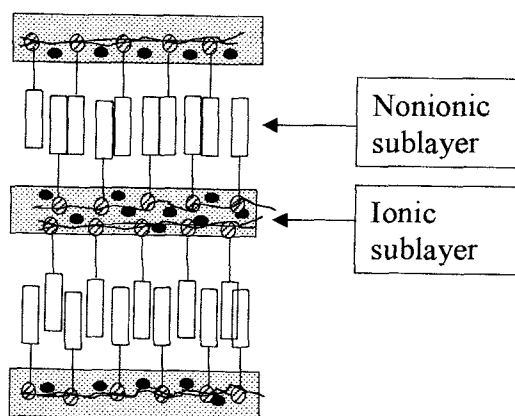


Fig. 4. Layer structure of ionic liquid crystalline polymer. The ionic liquid crystalline polymers form the smectic phase with the ionic and nonionic sublayers though the nonionic liquid crystalline polymers exhibit the nematic phase. The mesogenic cores partially overlap with each other.

In this system, the formation of the nematic order is governed by the anisotropy formed through the interactions between the mesogenic side-groups.

The X-ray diffraction measurement was performed for the smectic phase of IP-6. The X-ray diffraction pattern consisted of sharp inner reflections at the small-angles and a broad reflection in the wide-angle region. The smectic A layer spacing (d) was 4.3 nm, while the extended length (L) of the mesogenic side-group is 2.1 nm. The relationship between d and L is $d > 2L$. The fact that d is two times longer than L is related to the existence in an ionic sublayer. The smectic A layered structure of IP- n occurred due to the ionic aggregation between the polyammonium and chloride, due to Coulomb's force. The domains of the ionic groups segregate from the domains of the mesogenic side-chains. Consequently, the ionic aggregation leads to the formation of the smectic A layer consisting of ionic and nonionic sublayers. In the case of IP-6, the smectic A layered structure is schematically illustrated as shown in Fig. 4. The ionic sublayer acts by increasing the thermal stability of the smectic-layered structure.

4. CONCLUSIONS

The ionic interactions led to the formation of the smectic-layered structure and enhanced the thermal stability of the liquid crystalline phase. In the ionic liquid crystalline polymers, the phase transition temperatures decreased with the increasing spacer length.

5. REFERENCES

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