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### Ionic Liquid Crystalline Materials Exhibiting Smectic C Phase

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# Ionic Liquid Crystalline Materials Exhibiting Smectic C Phase

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*Ionic liquid crystalline compounds with a long terminal chain and their nonionic family were synthesized. The ionic liquid crystalline compound (I-7) with a heptyloxy terminal chain exhibited smectic A and C phases. On the other hand, a nonionic family of ionic I-7 showed a smectic A phase. In the case of the ionic liquid crystalline compound (I-4) with a butyloxy terminal chain, a smectic A phase was formed. A nonionic family of ionic I-4 did not show a liquid crystalline phase. The isotropization temperatures of the ionic liquid crystalline compounds were higher when compared to the nonionic family. These results exhibit that the ionic interactions act effectively in forming a liquid crystalline phase with enhanced thermal stability and enable the formation of the fluid smectic phases. In ionic I-7, the formation of the smectic C phase that the nonionic family of I-7 did not exhibit was led through the balance between an anisotropy formed by the mesogenic groups and the ionic interactions.*

**Keywords** Ionic liquid crystal; smectic c; terminal alkyl chain; phase transition; x-ray diffraction

## Introduction

Ionic liquid crystals are a key material in the field of self-organized materials. Low-molecular-weight and polymeric liquid crystals with ionic groups were already synthesized, and their thermal and orientational properties were examined [1–3]. In the ionic liquid crystalline compounds, ionic interactions also lead to the formation of liquid crystalline phases with enhanced thermal stability and induce a microphase separation consisting of hydrophilic and hydrophobic domains. The ionic liquid crystalline compounds that an ammonium ion attaches to a mesogenic group through a methylene chain have an ionic aggregation and an anisotropy through interactions between the mesogenic groups [4–6]. In this case, ionic liquid crystalline compounds have both characteristics of surfactants and calamitic liquid crystals. The liquid crystalline phases are formed by a balance of the ionic aggregation and the anisotropy produced by mesogenic groups.

In this study, we synthesized ionic liquid crystals with a long terminal chain and examined their thermal and orientational properties. The liquid crystalline properties of the ionic liquid crystals were compared with those of nonionic family. This paper describes the

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formation of a smectic C phase and an effect of the balance between ionic interactions and an anisotropy in the ionic liquid crystals.

## Experimental

### Synthesis

**Nonionic Compounds.** Iminodiethanol and 6-bromo-1-(4-(4-heptyloxy(phenylazo))phenoxy)hexane were dissolved in 100 mL of 2-propanol, and the solution was reacted at 120°C for 35 h. After the reaction, the mixture was cooled to room temperature, and the precipitated product (nonionic N-7, Fig. 1) was filtered off.  $^1\text{H NMR}(\text{CDCl}_3)$ ,  $\delta$ : 0.92 (3H,  $-\text{CH}_3$ ), 1.30–1.50 (14H,  $-\text{CH}_2-$ ), 1.60 (2H,  $\text{HO}-$ ), 1.81 (4H,  $-\text{CH}_2-$ ), 2.57 (2H,  $\text{N}-\text{CH}_2$ ), 2.65 (2H,  $\text{N}-\text{CH}_2$ ), 3.62 (4H,  $\text{HO}-\text{CH}_2$ ), 4.03 (4H, phenyl-O- $\text{CH}_2$ ), 6.99 (4H, phenyl), 7.86 (4H, phenyl).

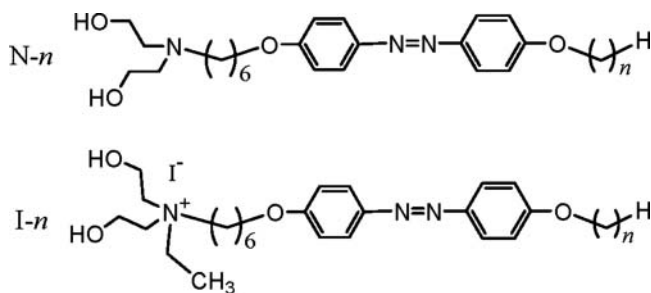
N-4 with a butyl terminal group was synthesized by the same method as the case of N-7.

**Ionic Compounds.** Nonionic N-7 and ethyl iodide was dissolved in 30 mL of 2-propanol, and the solution was reacted at 120°C for 50 h. Bis(2-hydroxyethyl)ethyl(6-(4-(4-heptyloxy(phenylazo))phenoxy)hexyl)ammonium iodide (ionic I-7, Fig. 1) precipitated from the solution, was filtered off, and was washed with cold 2-propanol.  $^1\text{H NMR}(\text{CDCl}_3)$ ,  $\delta$ : 0.88 (3H,  $-\text{CH}_3$ ), 1.10 (3H,  $-\text{CH}_3$ ), 1.20–1.60 (12H,  $-\text{CH}_2-$ ), 1.80 (4H,  $-\text{CH}_2-$ ), 2.60 (2H,  $-\text{CH}_2-$ ), 2.94 (2H,  $-\text{OH}$ ), 3.66 (8H,  $\text{N}^+-\text{CH}_2$ ), 4.05 (4H, phenyl-O- $\text{CH}_2$ ), 7.00 (4H, phenyl), 7.85 (4H, phenyl).

I-4 with a butyl terminal group was synthesized by the same method as the case of I-7.

### Measurements

Optical textures were observed with a polarizing microscope (Nikon Eclipse LV100POL) equipped with a hot stage (Mettler Toledo FP90-FP82HT). Phase transitions were measured by polarizing microscopic observation and DSC measurement (Shimadzu DSC60-EK90/SH). The orientational behavior was examined by the temperature-variable X-ray diffraction measurement (Shimadzu XRD-6100), and a possible packing model was proposed.



**Figure 1.** Structures of nonionic (N-*n*; *n* = 4, 7) and ionic (I-*n*; *n* = 4, 7) compounds.

**Table 1.** Phase transitions of nonionic and ionic compounds (N-4, N-7, I-4 and I-7)

Sample	Phase transition temperatures <sup>1)/°C</sup>
N-4	heating k 110.5 I cooling k 102.7 I
N-7	heating k 71.3 SmA 104.9 I cooling k 70.9 SmA 101.4 I
I-4	heating k 117.8 SmA 169.7 I cooling k 87.3 SmA 146.8 I
I-7	heating k <sub>1</sub> 46.7 k <sub>2</sub> 106.5 SmC 116.4 SmA 128.2 I cooling k <sub>1</sub> 41.1 k <sub>2</sub> 100.2 SmC 109.8 SmA 120.8 I

<sup>1)</sup> k, k<sub>1</sub>, k<sub>2</sub>:crystal, SmC:smectic C, SmA:smectic A, I:isotropic.

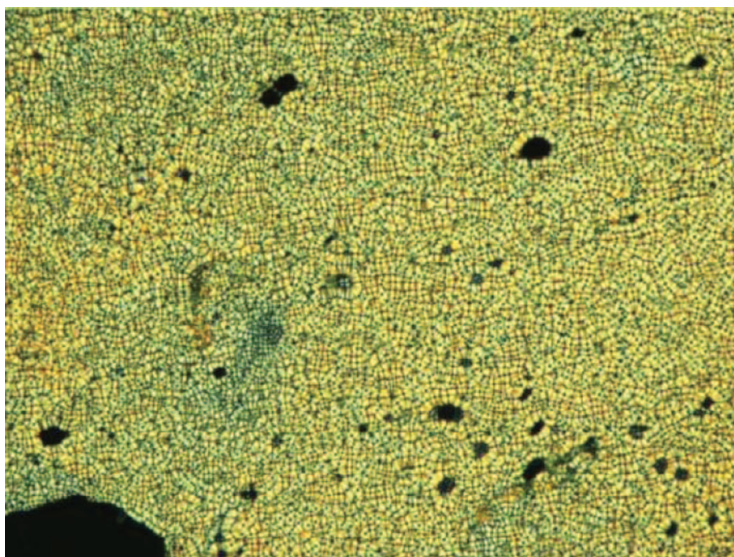
## Results and Discussion

### Phase Transitions

Phase transitions of ionic liquid crystalline compounds (I-4, I-7) and those nonionic family (N-4, N-7) are summarized in Table 1. Ionic I-4 that an ammonium group attaches to a butyloxyazobenzene mesogenic group through a hexamethylene chain showed a smectic A phase with a focal conic fan texture and a dark field exhibiting a perpendicular alignment, which is characterized by a conoscopic interference figure. Ionic I-7 with a heptyloxy terminal chain exhibited a smectic C phase characterizing by a schlieren texture as well as a smectic A phase. On the other hand, nonionic N-4 that the ammonium group of ionic I-4 is displaced to an amine group was crystalline and did not show a liquid crystalline phase. Nonionic N-7 exhibited a smectic A phase. This result for the liquid crystal formation of ionic and nonionic families indicates that the long terminal chain leads to the enhancement of a liquid crystal formation ability.

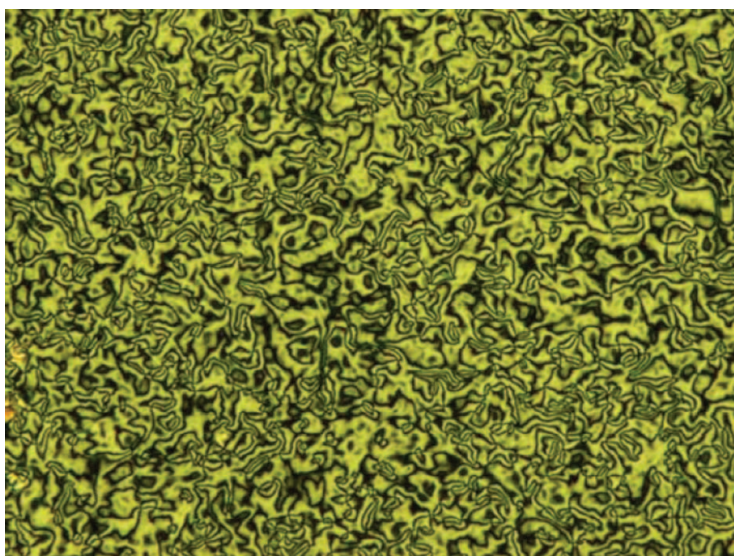
Optical textures of the smectic liquid crystalline phases were shown in Figs. 2–4. A focal conic fan texture was observed in the smectic A phases of N-7 and I-7 (Figs. 2 and 4). The smectic C phase of I-7 was characterized by a schlieren texture (Fig. 3). The smectic A-smectic C phase transition of I-7 was not clear by DSC measurement (Fig. 5). At the smectic C-smectic A phase transition temperature, however, the schlieren texture changed to the focal conic fan texture obviously. Moreover, the smectic A-isotropic phase transition was not observed by DSC measurement. However, N-7 clearly exhibited a smectic A-isotropic phase transition peak (Fig. 6). The smectic A phase of I-7 was formed in the isotropic temperature range of N-7, which the interactions between the mesogenic groups act in forming the smectic A phase. This indicates that the smectic A phase of I-7 was mainly formed by the ionic interactions between ammonium ions and counterions. Furthermore, in that temperature range, the interaction between the mesogenic groups is insufficient for maintaining the smectic A orientation in capability. It becomes impossible for the ionic interaction to maintain microphase separation with increasing temperature and the layer structure collapses gradually. Consequently, the smectic A-isotropic phase transition peak of I-7 is not observed.

**X-Ray Diffractions.** In general, the X-ray diffraction pattern for a fluid smectic phase such as smectic A and smectic C phases consists of the sharp inner reflections at the small-angles

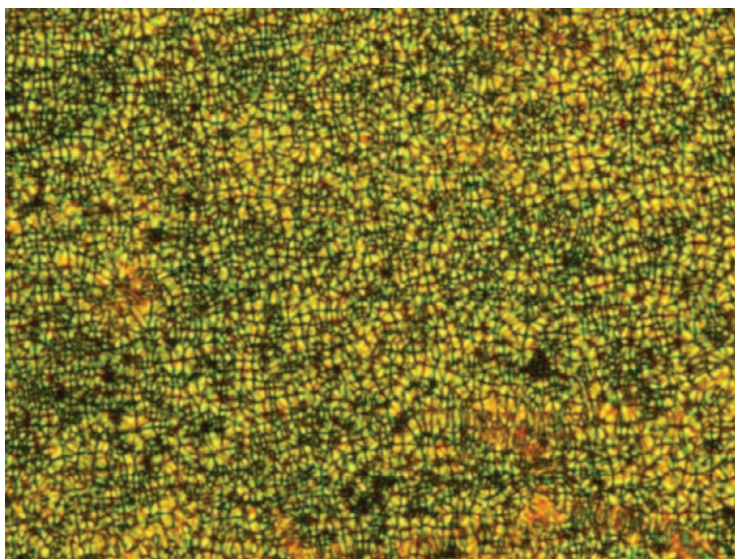


**Figure 2.** Focal conic texture of smectic A phase of N-7 at 85.4°C.

and the broad outer reflection in the wide-angle region. N-7, I-4 and I-7 exhibited the X-ray small-angle reflections and the X-ray wide-angle halo in the smectic A temperature range (Fig. 7). The same X-ray diffraction patterns were also observed in the smectic C temperature range (Fig. 7). The layer spacings and extended molecular lengths were summarized in Table 2. The extended molecular lengths were obtained by using both a space-filling model and chem3D. Since the formation of the fluid smectic phase is led by

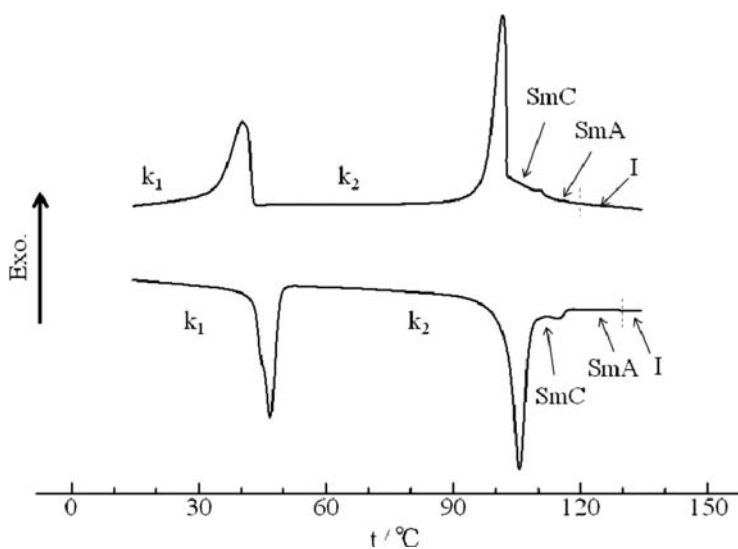


**Figure 3.** Schlieren texture of smectic C phase of I-7 at 107.0°C.



**Figure 4.** Focal conic texture of smectic A phase of I-7 at 120.0°C.

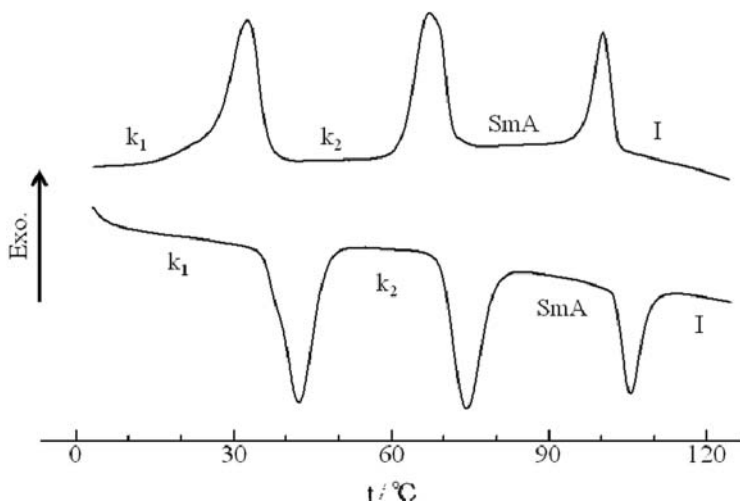
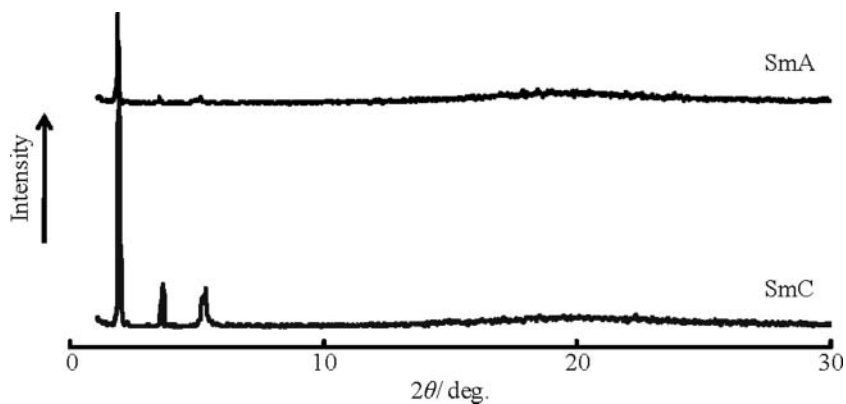
ionic aggregations, a hydrophilic sublayer is formed [1,4,5–7]. Moreover, the formation of the tilted phase occurs by an anisotropy through interactions between the mesogenic groups with the long alkyl chain. Consequently, the smectic layer is composed of the hydrophilic and hydrophobic sublayers, and those sublayers alternately pile in the smectic phase. Possible packing models are shown in Fig. 8. Hydroxyl, ammonium and iodide groups in the hydrophilic sublayer form hydrogen bonding and ionic interactions. These interactions enhanced the thermal stability of the hydrophilic sublayer.

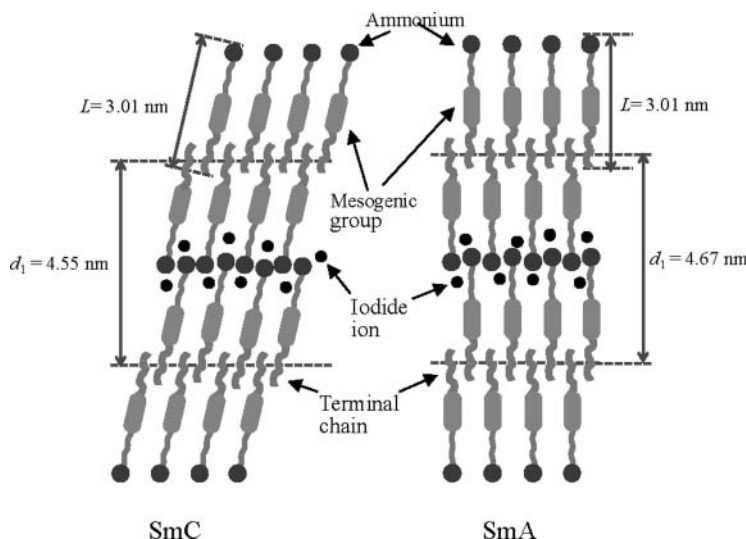


**Figure 5.** DSC curves of I-7 on heating and cooling processes.

**Table 2.** Layer spacings and extended molecular length

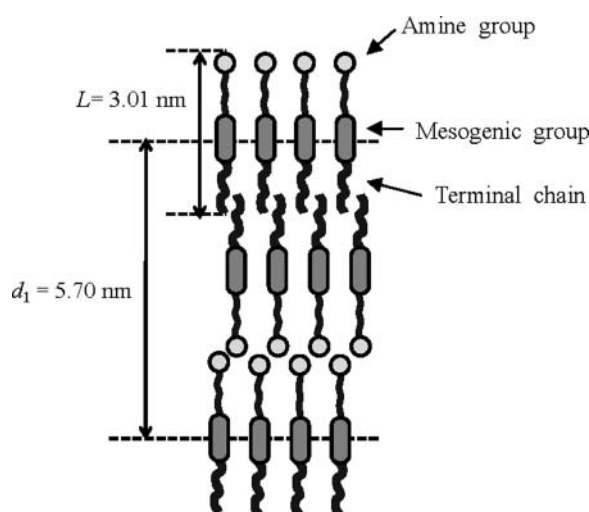
Sample	Layer spacing/nm		Extended molecular length/nm
	SmC	SmA	
N-7	—	5.70	3.01
I-4	—	4.39	2.68
I-7	4.55	4.97	3.01

**Figure 6.** DSC curves of N-7 on heating and cooling processes.**Figure 7.** X-ray diffraction patterns of smectic A (115.0°C) and smectic C (107.0°C) phases of I-7.



**Figure 8.** Possible packing models of smectic C and smectic A phases of I-7. Ammonium and iodide ions will be displaced above and below the plane of Fig. 8 to minimize repulsive force.

On the other hand, N-7 showed a smectic A layer spacing corresponding to twice extended molecular length. This indicates the formation of a bilayer structure in the smectic A phase as shown in Fig. 9. In this case, a part of the terminal group overlaps each other, and there is a microphase separation. The packing of N-7, which does not have an ionic group, is mainly determined by the anisotropy obtained by the interaction between the mesogenic groups. In the smectic A phases of I-7 and N-7, the molecular orientational structures are different. Also, the smectic C phase was shown for only I-7. These suggest that the liquid crystal formation strongly depends on the ionic interactions.



**Figure 9.** Possible packing model of smectic A phases of N-7.

## Conclusions

The use of ionic interactions led to the formation of the liquid crystalline phase with enhanced thermal stability. The ionic liquid crystal (I-7) formed the smectic C phase as well as the smectic A phase. However, the nonionic family (N-7) of I-7 exhibited only the smectic A phase. This shows that the presence of the ionic interactions enabled the generation of the smectic C phase. In the smectic C phase, the balance (IIAB) between the ionic interactions and an anisotropy formed by the mesogenic groups controlled the structure of the liquid crystalline state. In the smectic A phase, however, I-7 formed the smectic A phase through the segregation of the ionic and nonionic domains. It is sure that IIAB is an important factor for molecular designs of the ionic liquid crystals.

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