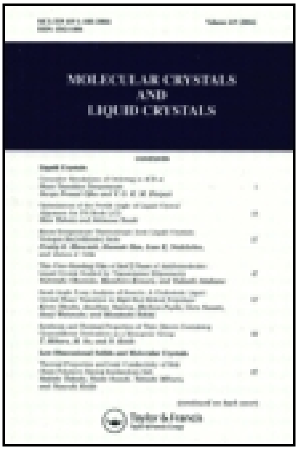

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Cubic Mesophase Formed by Thermotropic Liquid Crystalline Ionic Systems - Effects of Polymeric Counter Ion

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Cubic Mesophase Formed by Thermotropic Liquid Crystalline Ionic Systems – Effects of Polymeric Counter Ion

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Thermotropic ionic liquid crystals with a pyridinium skeleton were synthesized and the effects of counter ions for the liquid crystal formation were examined. The liquid crystal formation depended on the counter anions. The pyridinium liquid crystal, having chloride counter ion, showed columnar, cubic, and smectic A phases. The pyridinium liquid crystals with polymeric counter ions formed columnar and cubic phases. However, they did not show a smectic A phase. The polymeric counter ions enhanced the thermal stability of the cubic phase when compared to chloride counter ion.

Keywords: columnar; cubic; ionic liquid crystal; phase transition; polyion; thermotropic

INTRODUCTION

Various types of ionic liquid crystalline materials have been synthesized and their lyotropic and thermotropic liquid crystalline properties have been examined. The use of the ionic interactions is useful to design self-assembled liquid crystalline systems. Liquid crystalline polymer-ion systems, in which low-molecular-weight ionic molecules are binding to polyions, were reported [1–3]. The polymer-ion systems consisting of polyammonium and alkanoate formed smectic a and columnar mesophases [4–6]. Ammonium-terminated polyamidoamine dendrimers with alkanonate counter ions exhibited liquid crystalline

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phases [5,6]. The ionic dendrimers, which are a polyion with terminal ammonium groups, acted as a cationic component and formed a hydrophilic domain (sublayer). The increase in the molecular weight of the ionic dendrimers led to the formation of the columnar mesophase as well as the smectic a mesophase. The polyions can enhance the ability of the liquid crystal formation and the thermal stability of liquid crystalline phases. This paper describes the effects of polymeric counter ions for the liquid crystal formation of pyridinium systems.

EXPERIMENTAL METHODS

Ionic liquid crystalline materials with polyions were made from *N*-dodecylpyridinium chloride, which purchased as hydrate salts (Tokyo Kasei Kogyo), by ion exchange reaction. Phase transitions were examined by DSC (a Shimadzu DSC-60) and polarizing microscope observation (an Olympus polarizing microscope with equipped with a Mettler hot stage FP82). Since the ionic liquid crystalline materials used in this experiment are absorbent, the samples were perfectly reduced moisture for the measurement. The moisture content was checked with a Mettler Toledo HB43. The X-ray diffractions were obtained with a Rigaku Rint2000 using a Ni-filtered Cu-Kα radiation.

RESULTS AND DISCUSSION

Phase transitions of ionic liquid crystalline materials are summarized in Figure 1. In the literature [7], the formation of a smectic A phase was shown for the liquid crystalline *N*-dodecylpyridinium (Py12/Cl) with a chloride counter ion. However, this paper describes that Py12/Cl also forms columnar and cubic phases as well as the smectic A phase. In actual, Py12/Cl showed cubic and smectic A phases on a heating process, and columnar (16–46°C), cubic (46–66°C) and smectic A (46–143°C) phases on a cooling process (see Fig. 2). These phase transition temperatures were strongly influenced by a glass surface and on the thermal history. On the cooling process from the cubic phase, the columnar phase was not formed and the cubic phase changed to the solid state. A white powder of Py12/Cl changed to a transparent powder at the solid-cubic phase transition temperature on the first heating process. By heating from the cubic to smectic A phase, oily streak and fan textures were formed (see Fig. 3C). In the monotropic columnar phase, a fan texture was observed (see Fig. 3A, 3B). This fan texture clearly reveals the formation of the columnar phase [8].

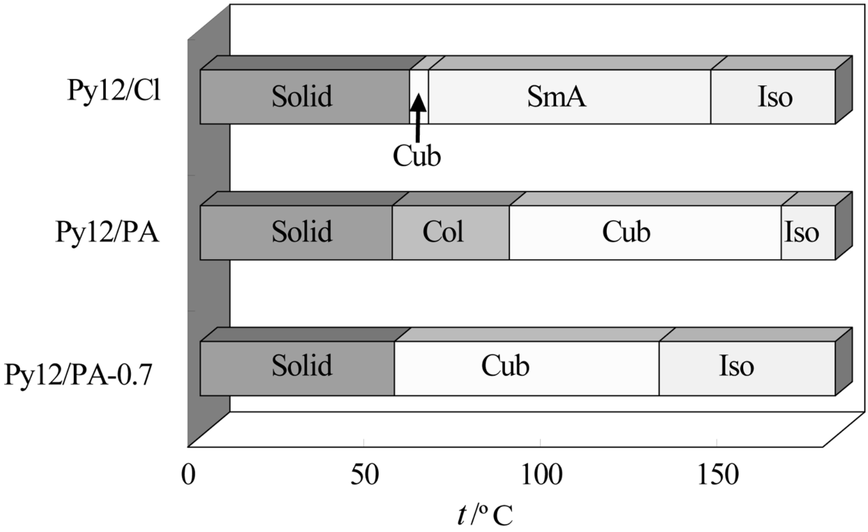

FIGURE 1 Phase transitions of ionic liquid crystalline systems. Cub: cubic, Col: columnar, SmA: smectic A, Iso: isotropic.

The X-ray diffraction patterns for Py12/Cl are shown in Figure 4. In the smectic A phase, a sharp inner reflection ($d = 2.80\,\text{nm}$) was measured (see Fig. 4A). This sharp reflection corresponds to the formation of the layer structure. In the case of the cubic phase (see Fig. 4B), several reflections at $d(110) = 5.88\,\text{nm}$, $d(220) = 2.94\,\text{nm}$, $d(222) = 2.44\,\text{nm}$, $d(321) = 2.29\,\text{nm}$, and $d(400) = 2.06\,\text{nm}$ [calculated d-spacings of small angle reflections: $d(110)\text{calc} = 5.88\,\text{nm}$, $d(220)\text{calc} = 2.96\,\text{nm}$, $d(222)\text{calc} = 2.41\,\text{nm}$, $d(321)\text{calc} = 2.24\,\text{nm}$, and $d(400)\text{calc} = 2.09\,\text{nm}$] at the X-ray small angles were obtained. These reflections match the space group of $Pn3m$ or $Im3m$ cubic structure [9–11]. Py12/Cl has the phase sequence of the smectic-cubic-columnar. In this case, the cubic

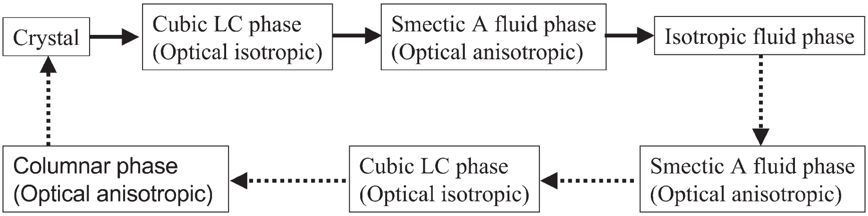

FIGURE 2 Phase transitions of *N*-dodecylpyridinium chloride (Py12/Cl). Solid arrow: heating process, Dotted arrow: cooling process.

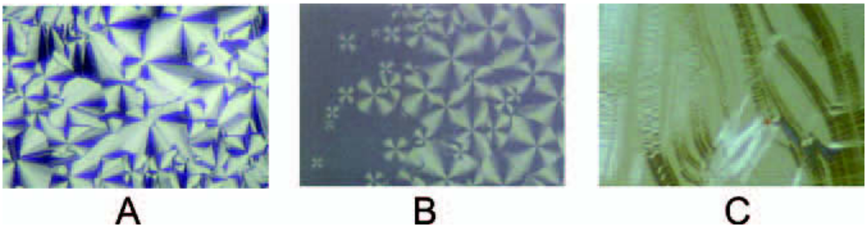

FIGURE 3 Optical textures of Py12/Cl on cooling. A: Fan texture of haxagonal columnar phase (20°C), B: Fan texture of hexagonal columnar phase observed at the cubic-columnar phase transition point (46°C). The dark region shows the cubic phase, C: Oily streak texture of smectic A phase (100°C).

phase of Py12/Cl is considered as an intermediate mesophase between layer and columnar structures [11]. The columnar phase showed a sharp peak at 2.94° ($d(100) = 3.01\,\text{nm}$) and a halo at 6.0°. It is considered that this halo at 6.0° is related to the existence in the reflections of $d(110)$ and $d(200)$.

The liquid crystalline *N*-dodecylpyridinium system (Py12/PA) with a homopolyacrylate counter anion exhibited cubic and columnar

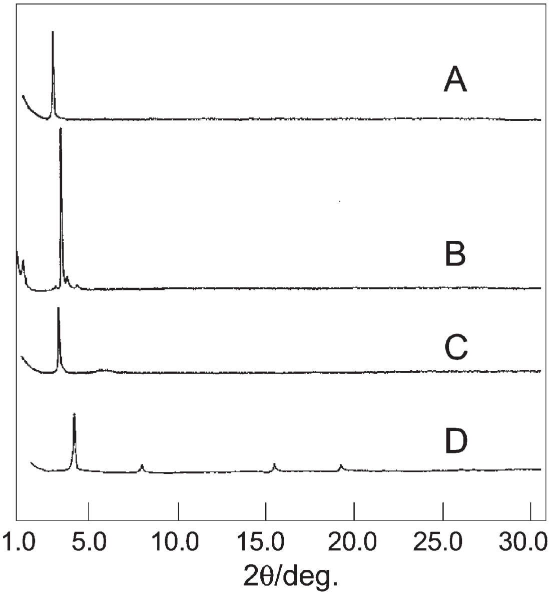

FIGURE 4 X-Ray diffraction patterns of Py12/Cl. A: 110°C (SmA), B: 65°C (Cub), C: 30°C (Col), D: 20°C (solid).

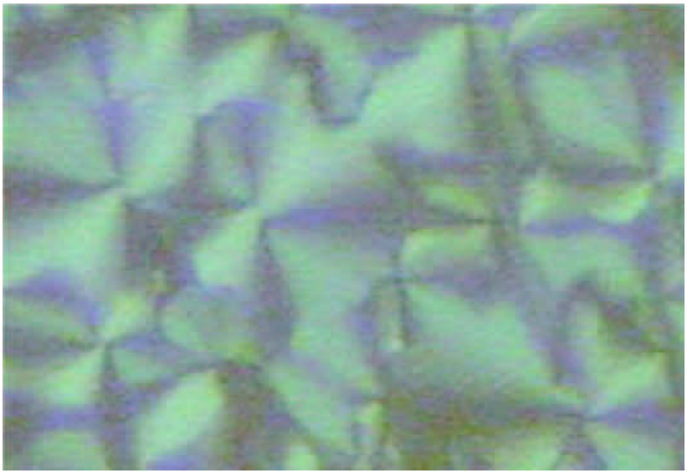

FIGURE 5 Optical texture for columnar phase of Py12/PA at 60°C.

phases on the heating and cooling processes. However, the smectic A phase was not observed on both the heating and cooling processes. This indicates that the homopolyacrylate counter anion effectively led to the formation of the enantiotropic cubic and columnar mesophases with the enhanced thermal stability. In the columnar phase of Py12/PA, a fan texture was observed (see Fig. 5). In the columnar phase of Py12/PA, a homogeneous alignment spontaneously developed from the optical isotropic structure. Extinction and diagonal

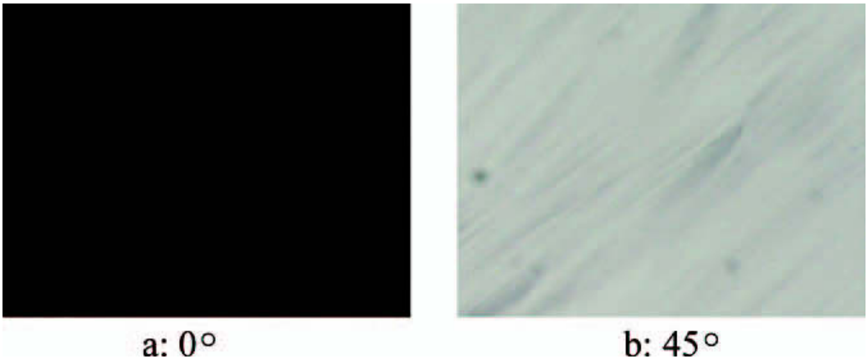

FIGURE 6 Extinction (a) and diagonal (b) positions observed for homogeneous alignment spontaneously formed in the columnar phase of Py12/PA.

positions were observed for the sample with the homogeneous alignment (see Fig. 6). The liquid crystalline *N*-dodecylpyridinium system (Py12/PA-0.7) with a copolyacrylate counter ion, in which a ratio of ionic carboxylate and carboxylic acid groups is 7:3, showed only a cubic phase. This cubic phase formation is related to the hydrogen bondings in the carboxyl groups of the copolyacrylate counter ion.

The X-ray diffraction pattern of the cubic phase for Py12/PA-0.7 is shown in Figure 7. In the X-ray small angle region, the reflections corresponding to $d(111) = 5.88\,\mathrm{nm}$, $d(200) = 5.19\,\mathrm{nm}$, $d(310) = 3.31\,\mathrm{nm}$, $d(222) = 2.98\,\mathrm{nm}$, $d(420) = 2.32\,\mathrm{nm}$, and $d(444) = 1.50\,\mathrm{nm}$ [calculated d-spacings of small angle reflections: $d(111)\mathrm{calc} = 5.88\,\mathrm{nm}$, $d(200)\mathrm{calc} = 5.08\,\mathrm{nm}$, $d(310)\mathrm{calc} = 3.22\,\mathrm{nm}$, $d(222)\mathrm{calc} = 2.94\,\mathrm{nm}$, $d(420)\mathrm{calc} = 2.28\,\mathrm{nm}$, and $d(444)\mathrm{calc} = 1.47$] were observed. These reflections indicate

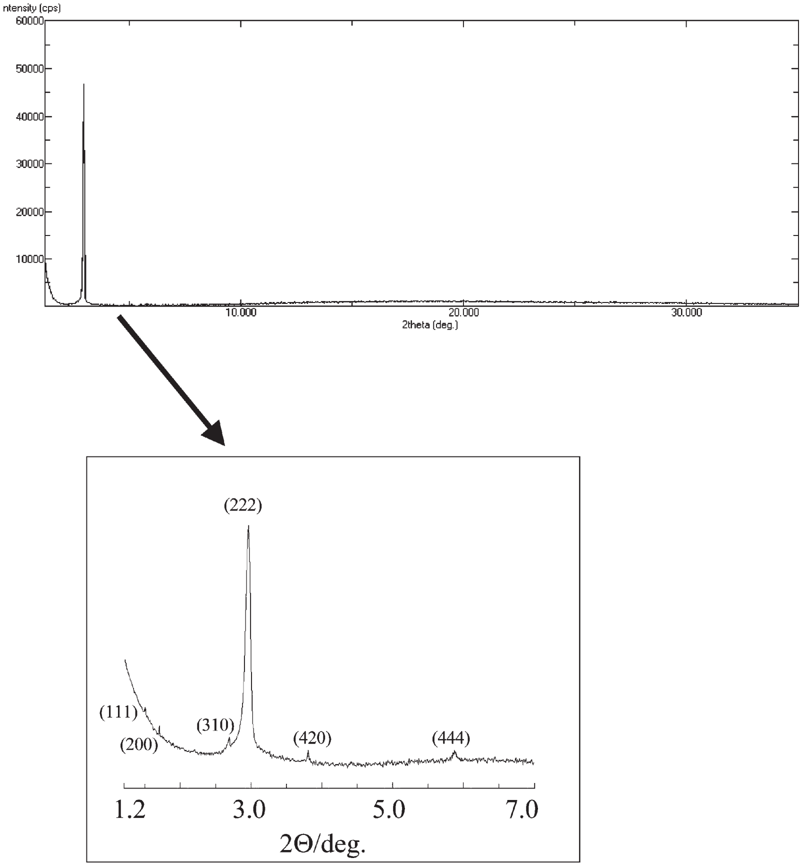

FIGURE 7 X-Ray diffraction pattern for cubic phase of PY12/PA-0.7 with copolyacrylate counter ion.

the formation of *Pn3m* cubic mesophase [9–11], which is 3D-columnar structure. On the other hand, unfortunately Py12/PA showed only a broad reflection at the X-ray small angle. Py12/PA and Py12/PA-0.7 showed the cubic phase with enhanced thermal stability when compared to Py12/Cl, and did not form a smectic A phase. In Py12/PA, the columnar phase was also stabilized. The polyacrylate and copolyacrylate counter ions act in forming columns and stabilizing a 3D-columnar structure (cubic structure).

CONCLUSIONS

The pyridinium liquid crystal with the chloride counter ion showed the cubic phase in the narrow temperature range and the smectic A phase in the wide temperature range. In the pyridinium liquid crystal with the polymeric counter ions, however, the smectic A phase was not formed and the cubic and columnar phases were shown in the wide temperature range. The polymeric counter ion was useful to stabilize the cubic and columnar phases.

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