Ionic Liquid Crystalline Systems Consisting of Polyammonium and Counter Carboxylate Ions

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Abstract: Novel ionic liquid crystals consisting of polyammonium and carboxylate ions were synthesized by ion complexation of polyethyleneimine and carboxylic acids (α,ω-dicarboxylic acids and hydroxyalkanoic acid). Their thermal properties and orientational behavior were examined by polarizing microscopic observation, differential scanning calorimetry, and variable temperature X-ray diffraction measurements. The ionic liquid crystals exhibited thermotropic liquid crystalline phases. The ionic liquid crystals (BP/ndA) bearing counter dicarboxylate ions formed a cubic phase upon heating and cooling. On the other hand, the ionic liquid crystal bearing the counter hydroxyalkanoate ion exhibited enantiotropic smectic A and smectic B phases with focal conic fan textures. These ionic liquid crystalline phases were formed by ionic and hydrophobic interactions because they did not have an aromatic mesogenic group.

Keywords: Ionic Liquid Crystal, Ionic Interaction, Polyammonium, Thermal Property, Orientational Behavior, Cubic, Smectic A, Smectic B

1. Introduction

In liquid crystalline systems, the noncovalent bond interaction, such as hydrogen bonding, donor-acceptor interaction, and ion interaction, plays an important role in the liquid crystal formation, thermal property, and orientation behavior. Introduction of ionic groups into liquid crystal molecules leads to the formation of thermotropic smectic phases with enhanced thermal stability [1-10]. Liquid crystal formation in ionic liquid crystalline systems strongly depends on ionic interactions. Furthermore, the ionic liquid crystalline system consists of both ionic and nonionic groups. The ionic groups aggregate and segregate from the nonionic groups. In such a case, a microphase separation occurs and induces liquid crystal formation. In ionic liquid crystalline systems, aromatic mesogenic groups are not necessarily required for liquid crystal formation [11-13]. A balance between ionic and hydrophobic interactions is important to form a liquid crystalline phase with enhanced thermal stability. For example, *N*-dodecylpyridinium chloride forms smectic A, columnar, and cubic phases. However, *N*-stearylpyridinium chloride

exhibits only a smectic A phase [14].

In ionic liquid crystalline systems, ionic groups such as ammonium, carboxylate, and sulfonate salts effectively form liquid crystals and enhance the thermal stability of the liquid crystalline alignment. Previously, ionic liquid crystalline systems without aromatic mesogenic groups were synthesized by ion complexation (a proton-transfer reaction) of polyethyleneimine and alkanoic acids [15, 16]. These ionic liquid crystalline systems exhibited a smectic A phase with an oily-streak texture and a homeotropic alignment upon heating and cooling. In the smectic A phase, which occurs due to a microphase separation through ionic interactions, a higher fluidity was observed. This result showed that the proton-transfer reaction was a useful method to obtain these liquid crystalline systems. The high fluidity of the smectic A phase is attributed to the fact that the ionic interaction becomes weaker with increasing temperature.

In this work, we synthesized novel ionic liquid crystalline systems through ion complexation of polyethyleneimine and carboxylic acids. Liquid crystal formation of these ionic liquid crystalline systems, their thermal properties, and orientational behavior are described herein.

2. Experimental

2.1. Materials

Liquid crystalline ion complexes (ionic liquid crystalline systems) were prepared by mixing a carboxylic acid (CA) (16-hydroxyhexadecanoic acid (16hA), dicarboxylic acid (*n*dA); where "*n*" refers to the number of carbon atoms: *n* = 11, 13, 15) and branched polyethyleneimine (BP; MW = 1,800) (Figure 1). The synthesis was carried out according to the literatures [15, 16]. Solutions of CAs and BP (the rate of "CA: amine unit of BP" was weighed 1:4 molecular ratio) were prepared in tetrahydrofuran (THF) and methanol, respectively. The *n*dA-THF solution was added dropwise to the BP-methanol solution under ultrasonic vibration at room temperature. The resulting mixture became cloudy. After the reaction, the solvent was allowed to evaporate at room temperature. The crude ion complex product was washed with THF, which was allowed to evaporate at room temperature. The ion complex (BP/*n*dA) was then dried under reduced

pressure. In IR measurements, BP/*n*dA exhibited a stretching vibration of the carboxylate ion (COO⁻). For example, the stretching vibration of carboxylate ion in BP/15dA was observed at 1639 cm⁻¹. However, the C=O stretching vibration of 15dA (dicarboxylic acid) appeared at 1699 cm⁻¹, which was not measured in BP/15dA. This result indicates that the carboxyl groups of 15dA completely changed to carboxylate ions through the proton-transfer reaction. BP/16hA was also obtained through the same method (the rate of "16hA: amine unit of BP" was weighed 1:2 molecular ratio).

2.2. Measurements

Thermal properties were examined by polarizing microscopic observation (Mettler-Toledo FP900-HP82 system) and differential scanning calorimetry (DSC; Shimadzu DSC60i). Variable temperature X-ray diffraction measurements were performed with a Shimadzu XRD6100/TTK-450 to examine the orientational structure of the liquid crystalline phases.
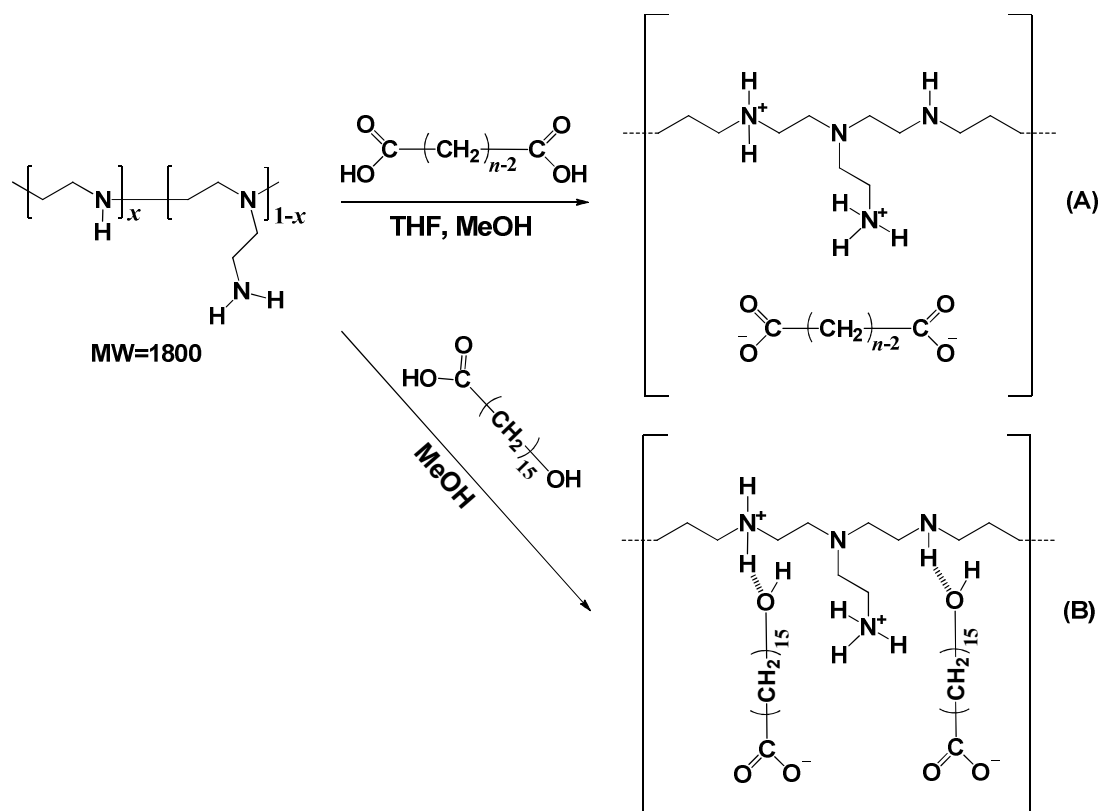

Figure 1. *Synthetic scheme of ion-complexes through the proton-transfer reaction of branched polyethyleneimine and carboxylic acids. (A): 50% of the amine residues remain, (B): 50% of amine residues remain. 16-Hydroxyhexadecanoate ions form hydrogen bond exhibiting a broken line as well as ionic interaction.*

3. Results and Discussion

3.1. Thermal and Optical Properties

The DSC curves for BP/*n*dA (*n* = 11, 13) indicated a secondary transition from a glass state to a liquid crystalline phase. However, a liquid crystalline-isotropic phase transition was not clearly found. The liquid crystalline-isotropic phase transitions of BP/*n*dA (*n* = 11, 13) cannot be determined by

polarizing microscopy, due to the optically isotropic liquid-crystalline phases. A dark field was observed under a crossed Nicol. An optical interference figure (isogyre) was not obtained for the dark field through conoscopic observation. This indicates that the dark field was not perpendicularly aligned [4].

The liquid crystalline behavior of BP/15dA resembled that of BP/*n*dA (*n* = 11, 13). BP/15dA revealed the same optical isotropy as BP/*n*dA (*n* = 11, 13). On the other hand, the liquid

crystal (BP/16hA) with 16-hydroxyhexadecanoate ions exhibited smectic A and smectic B phases. In the smectic A and smectic B phases, focal conic fan textures were clearly observed.

Table 1. *Phase transitions and X-ray data of ionic liquid crystalline systems.*

Sample	Phase Transitions/°C[1]	X-ray data (spacing/nm)
BP/11dA	g - 8.0 Cub[2]	1.43
BP/13dA	g 4.1 Cub[2]	1.67
BP/15dA	g 4.5 Cub[2]	1.87, 1.12, 0.95
BP/16hA	g 64.3 SmB 83.1 SmA 110.8 I	SmB: 2.37, 0.43. SmA: 2.25

1) g: glass, Cub: cubic, SmB: smectic B, SmA: smectic A, I: isotropic.
2) We consider the formation of a cubic phase from three conditions of optical isotropy, lack of perpendicular alignment, and an ordered structure (the X-ray inner reflection).

BP/ndA (n = 11, 13) have a network structure in a solid phase. In the liquid crystalline phases, however, the ionic interaction decreased with increasing temperature, and the reorientation of the alkyl chain of the counter dicarboxylate ions occurs. In that case, BP/ndA (n = 11, 13, 15) form the fluid ordered structure such as the cubic or sponge mesophases with a microphase separation.

In the case of BP/16hA, the terminal hydroxyl groups of 16hA form hydrogen bonding with the amino groups of the polyethyleneimine chain. It is easy for the hydrophobic alkyl chains to form fluid liquid crystalline orientations because the hydrogen bonding is a weaker interaction when compared to the ionic interaction. Furthermore, the hydrogen bonding of the terminal groups leads to the formation of the smectic B phase with enhanced orientational order as well as the smectic A phase.

3.2. Structural Analysis

The X-ray diffraction patterns were measured for the BP/ndA series. In BP/ndA with n = 11, 13, the X-ray inner reflections were obtained in fluid phases. The layer distances obtained from the X-ray inner reflections corresponded to an extended molecular length (L) of ndA. BP/ndA with n = 11, 13 exhibited optical isotropy.
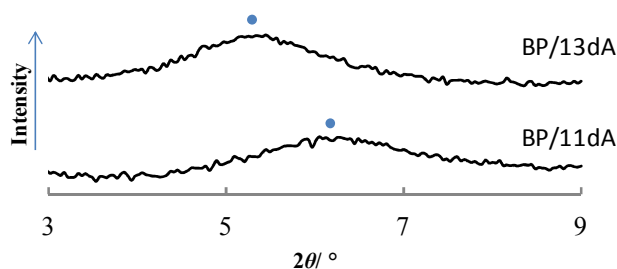

Figure 2. *X-ray diffraction patterns of BP/11dA and BP/13dA at 70°C. The scan rate is 0.1°/min.*

However, the existence of the X-ray inner reflections indicates that some ordered structure was formed in the fluid state. Three conditions, namely: optical isotropy, lack of perpendicular alignment, and an ordered structure (the X-ray inner reflection) indicated the formation of a liquid crystalline phase such as a cubic phase exhibiting optical isotropy. The X-ray inner reflections of BP/ndA with n = 11, 13 were not found above 150°C. This suggests that the liquid crystalline-isotropic phase transition temperatures were about 150°C.

BP/15dA revealed the X-ray reflections. We considered that the X-ray reflections corresponded to (220), (222) and (400) (Figure 3). In this case, it is expected that the fluid ordered phase of BP/15dA is a cubic phase such as *Pn3m* [14].
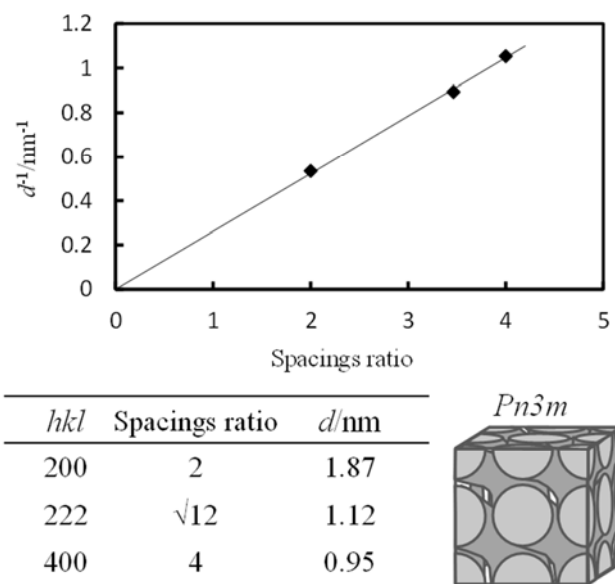

hkl	Spacings ratio	d/nm
200	2	1.87
222	√12	1.12
400	4	0.95

Figure 3. *Relationship between spacings ratio and 1/d in BP/15dA (70.0°C). It is expected that BP/15dA forms the cubic phase (Pn3m).*
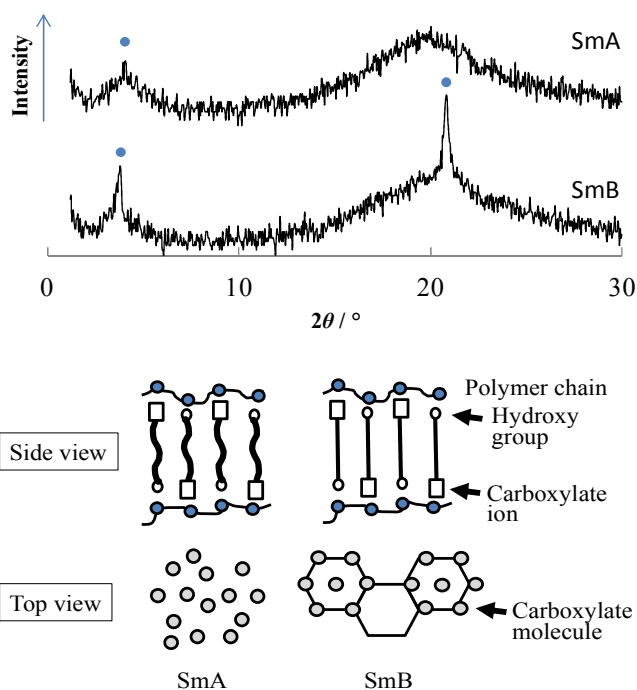

Figure 4. *X-ray diffraction patterns and possible packing models of smectic A (100°C) and smectic B (80°C) phases of BP/16hA.*

The X-ray diffraction patterns of BP/16hA consist of the

sharp inner reflections and the broad outer reflection in the smectic A phase (100°C) (Figure 4). In the smectic B phase (80°C), however, BP/16hA revealed the X-ray sharp inner and outer reflections (Figure 4). The X-ray sharp inner reflection exhibits the formation of layer structure. The X-ray sharp outer reflection indicates the existence of the ordered smectic phase such as the smectic B phase with a hexatic order within the layer. Possible packing models of the smectic A and smectic B phases are proposed as shown in Figure 4. The layer spacings (SmB: 2.37 nm, SmA: 2.25 nm) corresponded to the extended length (2.02 nm) of 16hA. This indicates the formation of a monolayer structure in the smectic B phase. The smectic A phase also has the monolayer structure. Furthermore, the alkyl chains of 16hA formed a hexatic structure within the smectic B layer. In the smectic A phase, however, the orientation with a short range order (without a positional order) is formed within the layer. In the smectic A and B phases, the layer structures consist of the hydrophilic and hydrophobic sublayers. The orientational structure of the smectic phases is stabilized by the hydrophilic sublayers consisting of polyammonium and counter dicarboxylate ions.

4. Conclusions

The novel ionic liquid crystalline systems were synthesized through the proton-transfer reaction of polyethyleneimine and carboxylic acids (α,ω-dicarboxylic acids and hydroxyalkanoic acid). The ionic interaction acted effectively to the formation of the fluid liquid crystalline phases. BP/*n*dA bearing the counter dicarboxylate ions formed the cubic phase. On the other hand, BP/16hA bearing the counter monocarboxylate ion exhibited the smectic A and smectic B phases. We consider that the balance between ionic and hydrophobic interactions is very important for liquid crystal formation. Since the ionic interaction is strong in the case of BP/*n*dA, the reorientation of the hydrophobic alkyl chains is inhibited. In BP/16hA, however, the hydrophobic alkyl chains possess the flexibility to allow a variety of orientations. The liquid crystalline behavior of BP/*n*dA and BP/16hA will be investigated still more. Thus, we can further clarify the

influence of noncovalent interactions such as ionic interaction and hydrogen bonding on the liquid crystal formation.

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