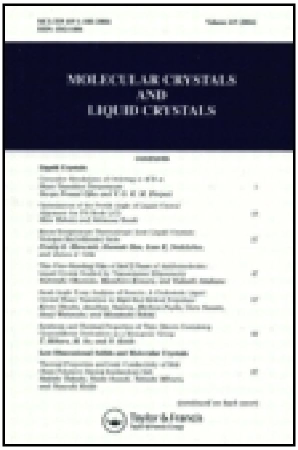

Molecular Crystals and Liquid Crystals

Thermal Properties of Ionic Liquid Crystalline Copolymers and their Nonionic Family

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Thermal Properties of Ionic Liquid Crystalline Copolymers and their Nonionic Family

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Ionic liquid crystalline copolymers and their nonionic family were synthesized. The thermal and orientational properties of these ionic and nonionic families were examined. Moreover, the effects of the ionic groups for the liquid crystal formation were investigated. The nonionic liquid crystalline copolymer formed only a nematic phase with a schlieren texture. The ionic liquid crystalline copolymers exhibited only a smectic A phase due to ionic interactions between ammonium cations and counter anions. A smectic A layer was composed of ionic and nonionic sublayers, which are formed by the hydrophilic ionic groups and the hydrophobic mesogenic side chains, respectively. The thermal stability of the smectic A phase was enhanced by an ionic aggregation.

Keywords: ionic interactions; ionic liquid crystalline polymer; phase transition; smectic

INTRODUCTION

Ionized materials such as alkali metal alkanoate and alkylammonium salts exhibit thermotropic liquid crystalline phases with enhanced thermal stability [1–3]. In general, nonionic liquid crystal systems with mesogenic groups form liquid crystalline phases through interactions between the mesogenic groups. The ionic liquid crystal systems form the liquid crystalline phases through ionic interactions as well

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as the anisotropy arising from the interactions between the mesogenic groups [4,5]. The ionic liquid crystal systems usually exhibit a smectic layered structure, due to the micro-segregation of ionic and nonionic groups. We have already reported various types of liquid crystalline polymers having ionic units and described the properties of the ionic liquid crystalline polymers incorporating ammonium ion groups [6–9].

In this work, ionic liquid crystalline copolymers and their nonionic family were synthesized and their liquid crystalline properties were examined. This article describes an effect of ionic interactions for the phase transitions and liquid crystal formation in the liquid crystalline copolymers.

EXPERIMENTAL

Materials

Nonionic liquid crystal copolymers (P-*n*) having an amphiphilic structure were synthesized by the reaction of polyethyleneimine (Mw = 1,200) with 6-bromo-1-(4-(4-(methyl)phenylazo)phenoxy)hexane (Br-6-N) (see Figure 1). Br-6-N was synthesized by the reaction of 1,6-dibromohexane

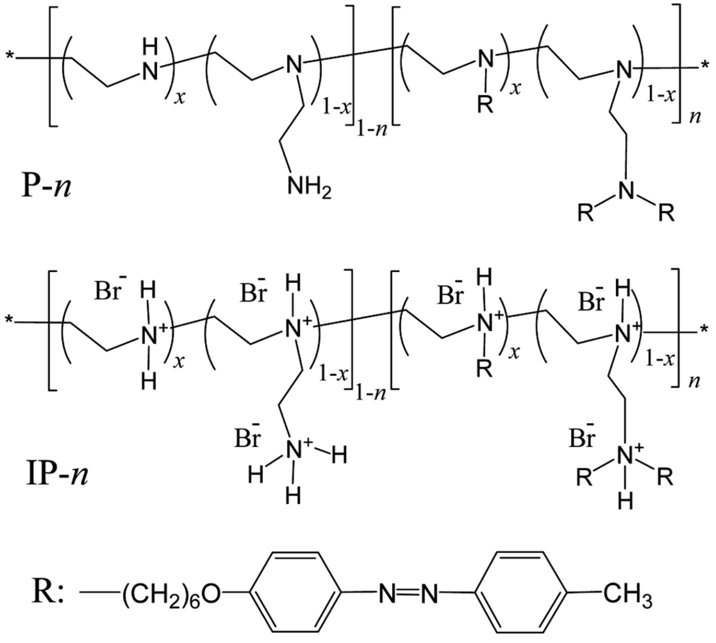

FIGURE 1 Structures of nonionic liquid crystalline copolymers (P-*n*) and ionic liquid crystalline copolymers (IP-*n*).

and 4-(4-(methyl)phenylazo)phenol. Polyethyleneimine and Br-6-N were dissolved in a solution of tetrahydrofuran and ethanol and potassium carbonate was added in the solution. The reaction mixture was refluxed for 400 h. The mixture was evaporated after the completion of the reaction. The crude product was dissolved in tetrahydrofuran and the polyamine was reprecipitated by adding hexane. Ionic liquid crystalline copolymers (IP-*n*) were synthesized by the reaction of P-*n* and hydrobromic acid (see Figure 1). The introduction proportion of the mesogenic side group was controlled by a feed amount of Br-6-N. Br-6-N reacted quantitatively because polyethyleneimine is a high reactive polymer. Thermal and orientational properties of P-1 and IP-1 have been already reported [9].

Measurements

The phase transitions were measured by a DSC measurement (Shimadzu DSC 60) and a polarizing microscopic observation (Olympus BH-2 equipped with a Mettler FP80 hot stage apparatus with a Mettler FP900).

RESULTS AND DISCUSSION

Nonionic liquid crystalline copolymers (P-*n*) with $n = 0.2$–1 showed only a nematic phase with a schlieren texture (see Fig. 2). P-0.1 did not exhibit a liquid crystalline phase and was liquid at room temperature. A nematic temperature range and an isotropization temperature increased with increasing *n* (content of the mesogenic side chain).

Ionic liquid crystalline copolymers (IP-*n*) formed a smectic A phase with a focal conic fan texture and a perpendicular structure (see Fig. 2). Moreover, the ionic IP-*n* exhibited an ordered smectic phase (SmX) with a broken fan texture as well as the smectic A phase (SmA). This smectic liquid crystal formation is due to ionic interactions between the ammonium and counter ions. The SmA-SmX phase transition peak, which exhibits a first order transition, was obviously observed by DSC measurement. The optical texture and DSC data indicate that the SmX phase is an ordered smectic phase.

The X-ray diffractions of an ionic homopolymer IP-1 were already reported and a possible packing model of IP-1 was described [9]. A possible packing model of the ionic copolymers IP-*n* also resembles to that of the ionic homopolymer IP-1. The possible orientational structures of P-*n* (nematic) and IP-*n* (smectic A) are shown in Figure 3. P-*n* mainly forms the nematic phase by interactions between the mesogenic groups. In the nematic phase of P-*n*, the mesogenic side chains were aligned and the polymer backbones were distributed to the nematic orientational state. IP-*n* exhibits the smectic phase with ionic

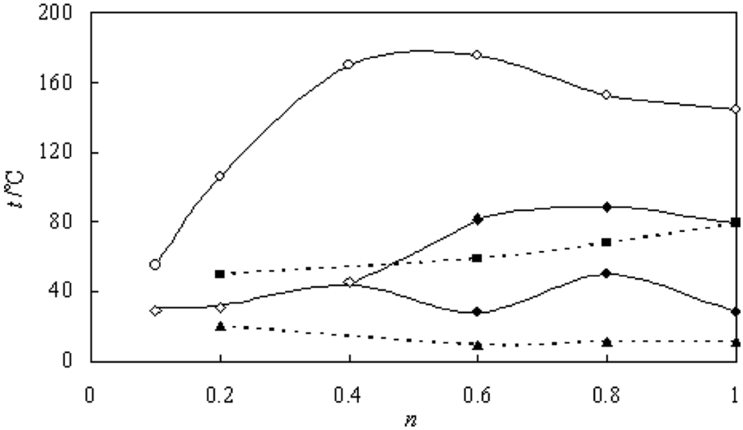

FIGURE 2 Phase transition temperatures of nonionic P-n and ionic IP-n. Filled triangle; a solid-nematic phase transition temperature of P-n: Filled square; a nematic-isotropic phase transition temperature of P-n: Filled circle; a glass-smectic X phase transition temperature of IP-n: Filled diamond; SmX-SmA phase transition temperature of IP-n: Open diamond; a solid-SmA phase transition temperature of IP-n: Open circle; a SmA-isotropic phase transition temperature of IP-n.

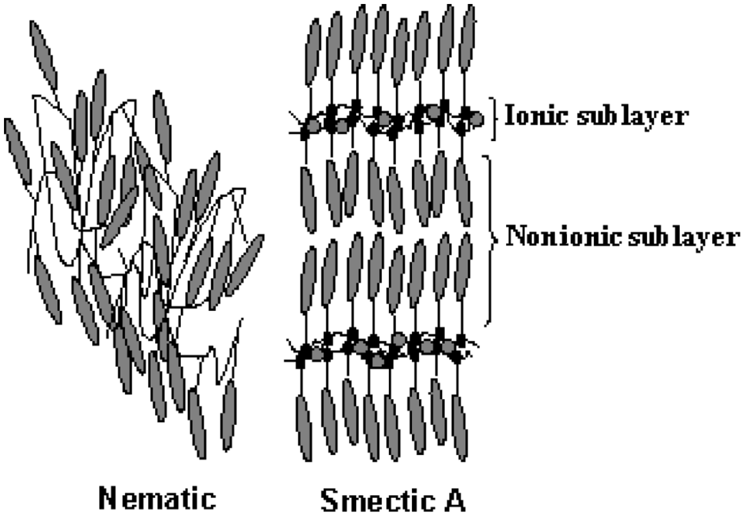

FIGURE 3 Schematic illustrations of nematic (P-n) and smectic A (IP-n) orientations. In the smectic A phase, the ionic sublayer is composed of polyammonium and counter ions.

and nonionic sublayers by the interactions between the mesogenic groups and anisotropy formed through a micro-segregation. In the ionic sublayer, the counter ions will be displaced above and below the plane of Figure 3 to minimize repulsive interactions. The existence in the ionic sublayers leads to the formation of enhanced thermal stability.

CONCLUSION

The nonionic liquid crystalline copolymers exhibited only a nematic phase. However, the ionizing liquid crystalline copolymers formed a smectic A phase. The nonionic liquid crystalline copolymers exhibited a lower isotropization temperature than the ionizing liquid crystalline copolymers. In the smectic A phase, the ionic liquid crystalline polymers formed a layered structure consisting of hydrophilic and hydrophobic sublayers. The hydrophilic sublayer segregates from the assembly of the hydrophobic mesogenic side chains. The hydrophilic sublayer was composed of ammonium cations and bromide anions, and led to enhanced thermal stability of the smectic A phase.

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