Macromolecules **1992,** *25,* 3174-3178

Thermal Properties and Orientational Behavior of a Liquid-Crystalline Ion Complex Polymer

Seiji Ujiie* and Kazuyoshi Iimura

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

Received August 28, 1991; Revised Manuscript Received January 21, 1992

ABSTRACT: The iodide (I/CA) and poly(vinylsulfonate) (PA/CA) of bis(2-hydroxyethyl)ethyl(6-((4-((4-nitrophenyl)azo)phenyl)oxy)hexyl)ammonium were prepared, and their liquid-crystalline behavior was compared. The orientational behavior was characterized by X-ray diffraction and conoscopic observation. I/CA and PA/CA exhibited enantiotropically smectic A phases. The ionic groups play an important role in forming the smectic layer structure and enhance the thermal stability of the smectic state. I/CA and PA/CA exhibit an oriented overgrowth on a glass plate by an orientational adsorption of ammonium ion groups. The homeotropic structures form spontaneously in the smectic phase of I/CA and PA/CA and remain unchanged on cooling in the solid phase.

Introduction

The liquid-crystalline behavior is known to be affected by molecular shape, conformation, and molecular interactions. Some amphiphilic compounds form a thermotropic smectic phase where an ionic group acts as a smectogen.[1-3] Alkylammonium amphiphiles also produce a surface alignment for thermotropic low-mass liquid crystals.[4] It is then expected that an ammonium ion group in a liquid-crystalline organic compound functions as the smectogen and organizes the uniform orientations. Furthermore, the introduction of various counterions of the ammonium cation leads to a variety of ionic liquid-crystalline polymers.

Recently, we synthesized thermotropic liquid-crystalline polymers with ammonium ion units and their low molecular weight model compounds and studied the relationship between the structures of the ammonium ions and thermotropic liquid-crystalline properties. Ammonium ions were very effective in producing a smectic layer structure and enhanced the thermal stability in the smectic phases. Furthermore, the smectic phases aligned spontaneously by an orientational effect caused by the ammonium ions.[5] Ion complexation led to liquid-crystalline composite materials.[6]

In this work we synthesized a complex (PA/CA) formed between the poly(vinylsulfonate) anion (PA) and a cationic low molecular weight liquid-crystalline group (CA). This paper describes the thermal properties and the orientational behavior of PA/CA and those of a low molecular weight liquid-crystalline complex of iodide ion and CA.

Experimental Section

Measurements. The phase transitions were measured with a Mettler DSC 20 system and an Olympus polarizing microscope BH-2 equipped with a Mettler FP52 hot stage apparatus with a Mettler FP5 temperature controller. X-ray diffraction was measured with a Regaku X-ray Rad 2B system.

Table I
Phase Transition Temperatures of I/CA and PA/CA

sample	phase transition temperatures,[a] °C
I/CA	K 40.5 Sm 170.2 I
PA/CA	G 50.0 Sm 235.0 I

[a] G, glassy state; K, solid phase; Sm, smectic phase; I, isotropic phase.

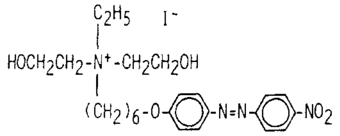

Figure 1. Structure of thermotropic liquid-crystalline ion complex (I/CA).

Synthesis. Diethanolamine (12 mmol) and 12 mmol of 6-bromo-1-((4-((4-nitrophenyl)azo)phenyl)oxy)hexane were dissolved in 100 mL of ethanol, and the mixed solution was reacted at 80 °C for 10 h. After the reaction, the mixture was cooled to room temperature, and the precipitated product was filtered off. The precipitated product (2.32 mmol) and 3.2 mmol of iodoethane were dissolved in 50 mL of ethanol, and the mixed solution was reacted at 30 °C for 20 h. Bis(2-hydroxyethyl)ethyl(6-((4-((4-nitrophenyl)azo)phenyl)oxy)hexyl)ammonium iodide (I/CA) precipitated from the mixture, was filtered off, and was washed with cold ethanol: yield 35%; ^{1}H NMR (tetrahydrofuran-d_8–$CDCl_3$) δ 1.4–2.4 (m, 8 H), 3.2–3.8 (m, 6 H), 3.8–4.5 (m, 6 H), 5–5.5 (bs, 2 H), 6.9–7.2 (d, 2 H), 7.8–8.2 (d, 4 H), 8.2–8.5 (d, 2 H).

I/CA (0.345 mmol) was dissolved in 20 mL of ethanol. The I/CA–ethanol solution was added dropwise to a sodium poly(vinylsulfonate)–H_2O solution (0.1%, 30 mL) at 100 °C, and the mixed solution was refluxed for 2 h. After the reaction, the mixture was cooled and kept at room temperature. The liquid-crystalline ion complex polymer (PA/CA) was precipitated, and the precipitate was filtered off.

Results and Discussion

I/CA is a thermotropic liquid-crystalline ion complex as shown in Figure 1. The phase transition temperatures of I/CA are listed in Table I. I/CA exhibited solid–smectic (T_m) and smectic–isotropic (T_i) transitions and formed a smectic A phase in the temperature range of T_m–T_i. Figure 2 shows the optical textures of I/CA observed in the sandwich cell without an alignment treatment under crossed polarizers. The dark region found in Figure 2a indicates a homeotropic structure formed spontaneously in I/CA. The complete homeotropic structure was achieved by annealing in the smectic state as shown in Figure 2b. In this case, no fan texture was observed. As shown in Figure 2c, the fan texture appeared on application of a shearing stress to the sandwich cell. The defects were generated at the transition temperature of the smectic phase to the solid state on cooling as shown in Figure 2d. However, the observation of a conoscopic figure demonstrated that the homeotropic structure remains unaltered on cooling into the solid state. This feature, which is generally absent in nonionic low molecular weight liquid

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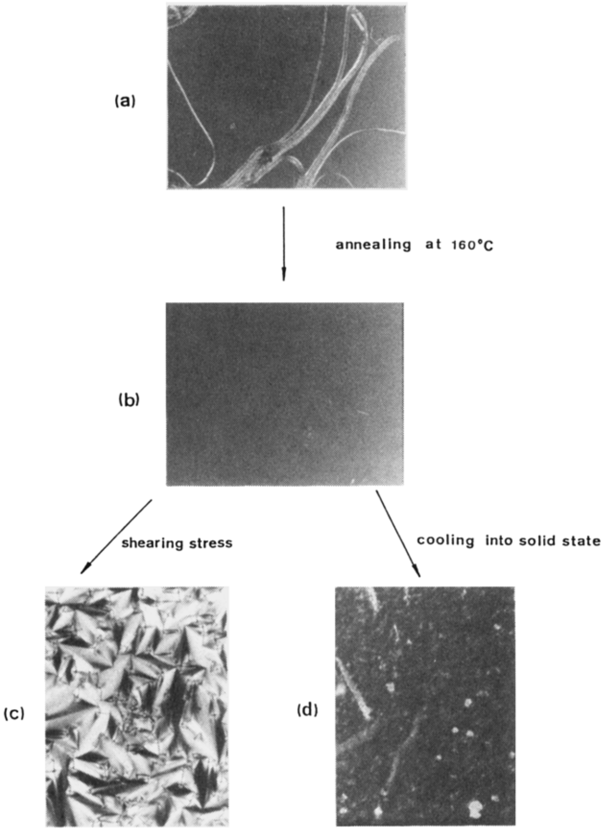

Figure 2. Optical textures observed for I/CA: (a) homeotropic alignment (dark region) and fan-like texture, (b) uniform homeotropic alignment formed by annealing, (c) fan texture obtained on application of shearing stress; (d) homeotropic alignment in solid state.

crystals, is due to the ammonium structural units in I/CA. Figure 3 shows some conoscopic figures observed for the homeotropic structure in I/CA. The conoscopic observation was performed for homeotropically oriented samples with different thicknesses. The conoscopic figure clearly demonstrates that the complete homeotropic structure forms spontaneously even in the cell with a thickness of 250 μm. The X-ray diffraction pattern measured for the homeotropically oriented sample of I/CA is shown in Figure 4. The first-order diffraction peak corresponds to a spacing of 3.48 nm, while the molecular length of I/CA is 2.45 nm. The conoscopic figure also indicates that the homeotropic structure is optically uniaxial as shown in Figure 3. In this case, the neighboring mesogenic groups overlap each other and the ammonium ions aggregate to form a sublayer in the smectic layer. A schematic illustration of the orientational structure for I/CA is proposed in Figure 5. The organization of the ammonium ions contributes to the formation of the smectic layer structure. The thermal stability in the smectic state is therefore enhanced in comparison with nonionic liquid-crystalline compounds. This can be concluded from experimental results obtained for liquid-crystalline compounds (LM and LM–HBr) analogous to I/CA. As shown in Figure 6, structures of nonionic LM and ionic LM–HBr are similar to that of I/CA. Both LM and LM–HBr formed enantiotropically smectic phases and exhibited similar solid–smectic phase transition temperatures. However, the temperature of LM–HBr at which the isotropic phase forms is higher by 87.2 °C when compared to that of LM (see Table II).

We consider that the enhanced thermal stability of LM–HBr formed of ionic and nonionic structural parts is caused by the aggregation of the ionic structural part. Ethanolammonium chloride (mp 85 °C), which is made of ethanolamine and hydrogen chloride and resembles an ionic component of LM–HBr, exhibits a higher melting point than ethanolamine (mp 10.5 °C) which is a nonionic component of LM. This corresponds to the fact that nonmesomorphic ammonium salts generally exhibit higher melting points than their nonionic components because ammonium salts form the ionic aggregation by Coulomb's force which is absent between nonionic molecules. In LM–HBr, a segregation of ionic and nonionic structural parts leads to a smectic system with ionic and nonionic domains. Ammonium ions of LM–HBr in the ionic domain form the ionic aggregation in the similar manner as nonmesomorphic ammonium salts. Consequently, the thermal stability of LM–HBr also increases by the effect of the ionic aggregation, and LM–HBr exhibits higher phase transition temperatures than LM.[5,6]

Ionic LM–HBr formed spontaneously the homeotropic structure just as I/CA. On the other hand, nonionic LM did not exhibit the homeotropic structure. In I/CA and LM–HBr, the ammonium structural units adsorb to the glass plate. Since the adsorbed ionic molecules function as the perpendicular alignment agent, the homeotropic alignment formed spontaneously.

The cationic liquid-crystalline group in I/CA can have various types of mesogenic or nonmesogenic counteranions such as anionic low molecular weight compounds and polyanions. We selected, therefore, the nonmesomorphic poly(vinylsulfonate) anion as a counterion. The poly(vinylsulfonate) anion is expected to enhance the thermal stability of the smectic I/CA phase and to keep the smectic layer structure in the solid state. The liquid-crystalline complex (PA/CA) was prepared by ion-exchange reaction of sodium poly(vinylsulfonate) with I/CA. The structure of PA/CA is shown in Figure 7. In general, liquid-crystalline side-chain polymers are known to involve covalent bonds as shown in Figure 8a. However, as shown in Figure 8b, PA/CA is a liquid-crystalline complex in which the cationic liquid-crystalline unit is attached to the polyanion skeletal chain through an ionic bond.

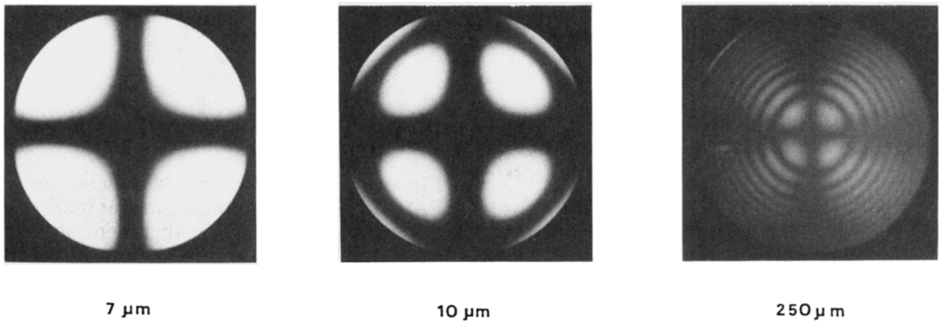

Figure 3. Conoscopic figures observed for the homeotropically oriented sample of I/CA with different thicknesses; the numbers indicated in the figure are the sample thicknesses.

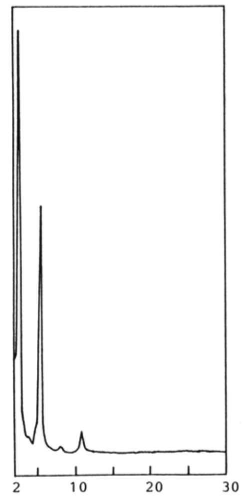

Figure 4. X-ray diffraction pattern measured for the homeotropically oriented sample of I/CA.

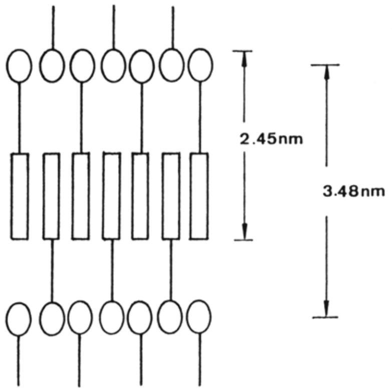

Figure 5. Possible packing model proposed for smectic phase of I/CA: (▭) mesogenic group, (○) ammonium structural unit.

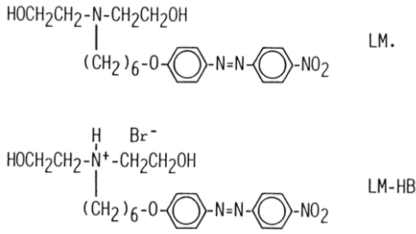

Figure 6. Structures of low-mass liquid crystals (LM and LM–HBr) analogous to I/CA.

Table II
Phase Transition Temperatures of LM and LM–HBr Analogous to I/CA

sample	phase transition temperatures,[a] °C
LM	K 61.2 Sm 119.8 I
LM–HBr	K 56.9 Sm 207.0 I

[a] K, solid phase; Sm, smectic phase; I, isotropic phase.

PA/CA formed an enantiotropically smectic A phase in a similar manner as I/CA. The phase transition temperatures of PA/CA are listed in Table I. The glass transition temperature (T_g), which could not be found for I/CA, appears in PA/CA at 50 °C to be governed by the thermal motion of the polyanion. The smectic–isotropic transition temperature of PA/CA was 64.8 °C higher than for I/CA. It is generally observed that mesomorphic–isotropic transition temperatures increase with increasing molecular weight.[7,8]

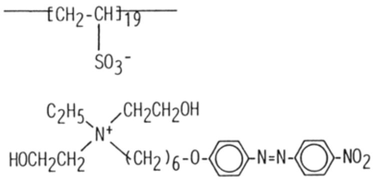

Figure 7. Structure of liquid-crystalline ion complex polymer (PA/CA).

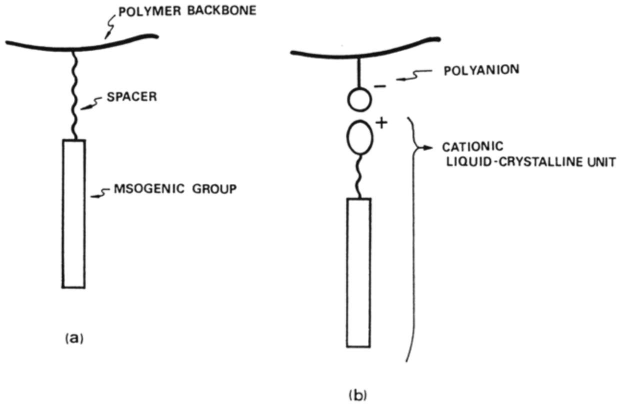

Figure 8. Schematic structures for general liquid-crystalline side-chain polymer (a) and liquid-crystalline ion complex polymer (b) studied in this work.

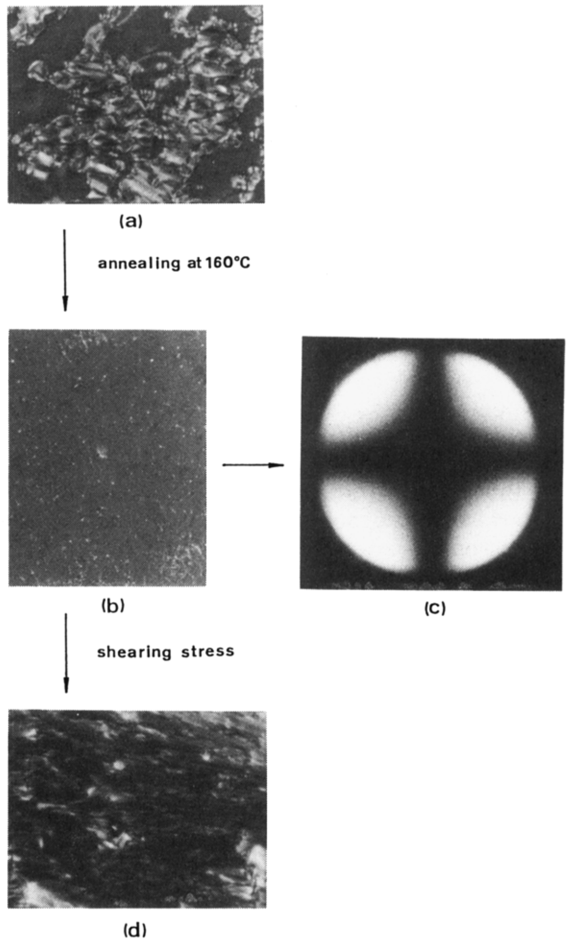

Figure 9. Orthoscopic and conoscopic figures observed for PA/CA: (a) homeotropic alignment (dark region) and fan texture, (b) uniform homeotropic alignment obtained by annealing, (c) conoscopic figure observed for homeotropically oriented sample, (d) fan texture obtained on application of shearing stress.

Figure 9 shows orthoscopic and conoscopic figures observed for PA/CA. Figure 9a shows the homeotropic

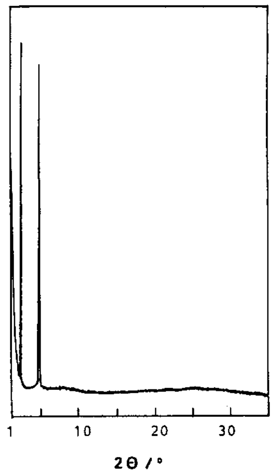

Figure 10. X-ray diffraction pattern measured for homeotropically oriented sample of PA/CA.

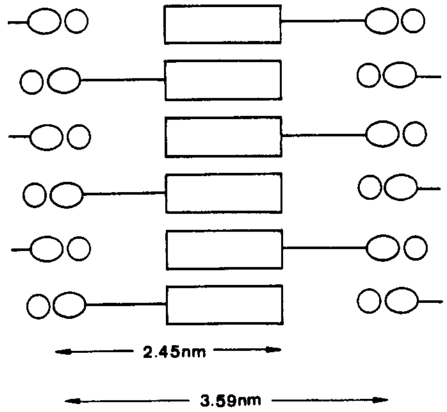

Figure 11. Schematic illustration for possible packing model for PA/CA: (▭) mesogenic group, (○) ammonium structural unit, (○) polyanion.

alignment in the dark region and a fan texture formed on cooling. A uniform homeotropic structure formed gradually on annealing as shown in Figure 9b. In addition, a fan texture was observed on applying a shearing stress to the homeotropic structure as shown in Figure 9d. Figure 9c shows the conoscopic figure characteristic of the optical-uniaxial state observed for the uniform homeotropic structure. The homeotropic structure formed in the smectic phase remained unaltered on cooling below T_g in the same way as nonionic liquid-crystalline side-chain polymers.

The X-ray diffraction pattern measured for the homeotropically oriented sample of PA/CA is shown in Figure 10. The smectic layer spacing calculated from the first-order diffraction angle is 3.59 nm, similar to the spacing in I/CA. Ammonium ion moieties and mesogenic groups form sublayers in the smectic layer as shown in Figure 5. PA/CA also exhibits a layer packing similar to that of I/CA because liquid-crystalline properties of PA/CA depend significantly on those of the cationic liquid-crystalline groups in I/CA. A possible packing model is illustrated in Figure 11. The smectic layer consists of the sublayers formed with mesogenic groups and ionic moieties. A similar layer packing is found in the liquid-crystalline ion complex polymer with poly(sulfopropylmethacrylate) as the polyanion.[6]

As shown in Figures 5 and 11, the aggregation of ammonium structural units plays a major role in organizing the smectic layer structure. Also, the ionic aggregation in the smectic phase is a strong stabilizing factor in comparison with the nonionic liquid-crystalline compounds.

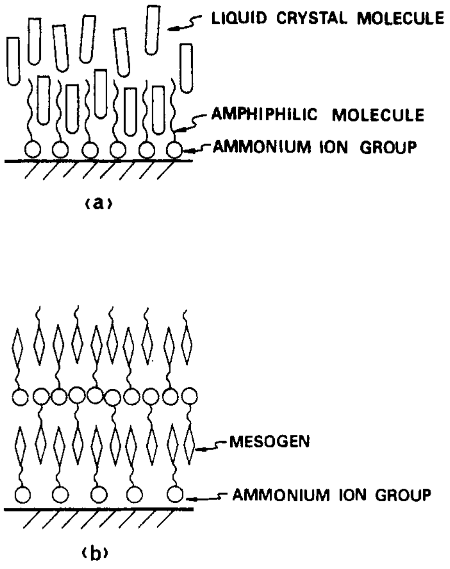

Figure 12. Molecular orientation model on glass plate: (a) in the case of orientational adsorption of alkylammonium amphiphile, (b) oriented overgrowth in I/CA.

The high orientational order in the smectic phases of I/CA and PA/CA is indicated by the clear conoscopic figures and the sharp X-ray scattering peaks measured for the homeotropically oriented samples. The polyanion in PA/CA enhances the stability of orientational structure. The results indicate that various types of liquid-crystalline composite materials can be prepared by the ion complex method.

As mentioned above, liquid-crystalline ion complexes I/CA and PA/CA formed spontaneously homeotropic alignment in the sandwich cell without surface treatment. Also, the homeotropic alignment formed spontaneously when the upper glass plate of the sandwich cell was removed. This demonstrates that the spontaneous organization of homeotropic alignment is an oriented overgrowth such as in epitaxy. The surface-active agent such as an alkylammonium halide is known to be effective as a perpendicular alignment–treatment agent. In the case of a mixture of small amounts of surface-active agent with the liquid-crystalline compound, the orientational adsorption of the surface-active agent is known to enable liquid crystal molecules to form some orientational states. Uchida et al. studied the influence of amphiphilic materials for a molecular orientation of a liquid crystal.[9,10] They showed that the perpendicular alignment of liquid-crystalline compounds on inorganic surfaces is caused from the perpendicular adsorption of the amphiphilic materials. A model for the homeotropic structure formed by the effect of surface-active agent is shown in Figure 12a. The liquid-crystalline molecules are aligned along the axis of the long alkyl chains of surface-active agents. In the case of I/CA studied in our work, ammonium ion units adsorbed on the glass plate contribute to the formation of a homeotropic structure. The orientational adsorption on the glass plate in I/CA is schematically illustrated in Figure 12b. The nitroazobenzene mesogenic group in the adsorbed I/CA molecule forms an overlapping arrangement by a strong interaction of the nitro terminal group as shown in Figure 12b. Thus, the perpendicular orientation on the glass plate is stabilized more effectively in I/CA than in the alkylammonium surface-active agent. Also, the aggregation moiety in ammonium ion groups and the arrangement in mesogenic groups are alternately repeated as shown in Figure 12b, producing the oriented overgrowth in I/CA and PA/CA. The homeotropic alignment of PA/CA is induced by the orientational effect of ammonium ion units just as in I/CA. The poly(vinylsulfonate) anion stabilizes the aggregation of ammonium ion groups. The orientational effect of SO_3^- groups in the poly(vinylsulfonate) may also be related to the formation of the homeotropic alignment.[10]

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Registry No. PA/CA (homopolymer salt), 140659-71-8; I/CA, 129577-55-5; LM, 129577-53-3; LM–HBr, 129577-54-4; NH$(CH_2CH_2OH)_2$, 111-42-2; ICH_2CH_3, 75-03-6; (*E*)-6-bromo-1-[4-(4-nitrophenylazo)phenoxy]hexane, 125769-27-9.