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Ion Complex Type of Novel Chiral Smectic C* Liquid Crystal Having Chiral Hydrogentartrate Counterion

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A chirally ionic liquid crystal (ICLC) was prepared by the complexation of L(+)-tartaric acid and an achiral mesogenic group (NLC) with an amine unit, and its liquid crystalline behavior was examined by DSC, polarizing microscopy, and X-ray techniques. Ionic ICLC formed smectic A and chiral smectic C* phases. Due to an ionic aggregation, ionic ICLC exhibited a higher mesomorphic-isotropic phase transition temperature when compared to nonionic NLC.

The preparation of liquid crystals which possess ferroelectric properties is one of the main objectives in the study of liquid crystalline compounds. Various ferroelectric smectic C* liquid crystals have been synthesized and studied up to the present. The introduction of chirality into a smectic C liquid crystalline system can lead to the formation of a ferroelectric chiral smectic C* phase. It has been found that liquid crystalline mixtures of chiral and achiral compounds show the ferroelectric properties.[1-3] This resembles the behavior that a mixture of achirally nematic and chirally nonmesomorphic compounds forms an induced cholesteric phase.

We consider that the complexation of achirally smectic C and chirally nonmesomorphic compounds leads to the architecture of a ferroelectric smectic C* liquid crystal. Ion-ion interactions, which form a noncovalent bonding, can architect liquid crystalline molecules in producing smectic A, smectic C, or ordered smectic states, which have enhanced thermal stability.[4-9]

This paper describes the thermotropic phase behavior of a ferroelectric liquid crystalline ion complex which consists of chiral hydrogentartrate and a mesogenic group with an ammonium polar headgroup. In this work, we have synthesized a nonionic liquid crystal (NLC) with an amine unit, which exhibited smectic A and C phases (see Fig. 1 and Table 1).[10] Also,

we selected chiral tartaric acid as an acid group, which can form an ionic complex with nonionic NLC. Tartaric acid is a stable organic compound which produces complexes of tartrates or hydrogentartrates by reacting with amine compounds or metals. Many of the tartrate and hydrogentartrate complexes exhibit electroactive properties. For instance, it is well-known that potassium sodium tartrate tetrahydrate shows ferroelectric behavior. Also, tartaric acid has both chiral centers and dipole moments, which need for appearance of ferroelectricity in the smectic C liquid crystalline systems. The ion complex type of the ferroelectric liquid crystal to be discussed here is the ionic compound in which an azobenzene core links with an ammonium salt involving a chiral hydrogentartrate counterion through a hexamethylene chain (see Fig. 2).

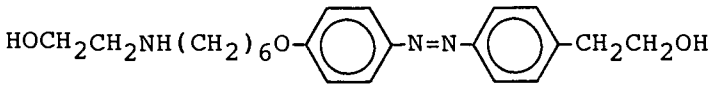

Fig. 1. Structure of nonionic liquid crystal (NLC).

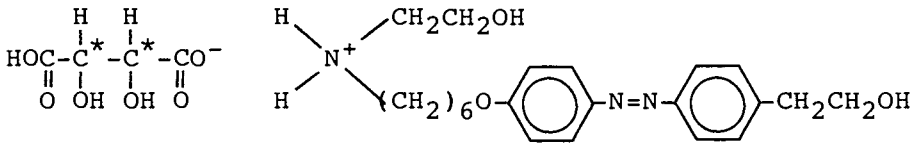

Fig. 2. Structure of ion complex type of liquid crystal with chiral hydrogentartrate counteranion (ICLC).

Nonionic NLC having the amine unit formed a homeotropic structure, in which a uniaxial conosopic figure was observed, on cooling into the smectic A phase from an isotropic phase. Also, a fan texture arised upon application of a shearing stress to the smectic homeotropic structure. When the smectic C phase formed on cooling from the smectic A phase with the homeotropic structure, a smectic C schlieren texture formed, due to the formation of a tilted layer structure.

The ion complex type of liquid crystal (ICLC), which is an amino-hydrogentartrate complex, was prepared by the complexation of NLC and L(+)-tartaric acid.[11] L(+)-Tartaric acid and NLC were dissolved in tetrahydrofuran (THF), respectively. The NLC-THF solution was added dropwise to the L(+)-tartaric acid-THF solution. The ion complex (ICLC) precipitated from the THF solution and was filtered off. In nonionic NLC, ^{1}H NMR spectra in two methylene groups which link to nitrogen atom were obtained at 2.63 ppm and 2.76 ppm. In ionic ICLC, however, those shifted at 3.02

ppm because of the ionization of the amine unit in NLC. Also, ICLC was characterized by FT-IR measurement.[12]

ICLC exhibited smectic A and chiral smectic C* phases. In the smectic A phase, ICLC formed the homeotropic structure in the same manner as NLC, in addition to the fan texture. On the other hand, ICLC exhibited a striped fan texture in the chiral smectic C* phase when cooled into the chiral smectic C* phase from the smectic A phase with the fan texture, as shown in Fig. 3. The striped fan texture indicates the formation of a helical structure in the chiral smectic C* phase.

Ionic ICLC showed a higher smectic A-isotropic phase transition temperature when compared to nonionic NLC. This is due to an aggregation of amphiphilic units in ICLC.[4-9] Also, this corresponds to the fact that, in general, amphiphilic molecules such as alkylammonium salts exhibit higher melting points than their nonionic components because the ammonium salts form an ionic aggregation through the effect of Coulomb's force which is absent between nonionic molecules. For instance, ethanolamine hydrochloride (mp 85°C), which corresponds to the component of ICLC, exhibits a higher melting point than ethanolamine (mp 10.5°C) which is the component of NLC.

Table 1. Phase transition temperatures of nonionic liquid crystal (NLC) and ion complex type of liquid crystal (ICLC)

Sample	Phase transition temperatures [a] / °C					
NLC	K	74.6	SmC	94.7	SmA	144.7 I
ICLC	K	50.5	SmC*	105.0	SmA	175.0 I

a) K, solid phase; SmC, smectic C phase; SmC*, chiral smectic C* phase; SmA, smectic A phase; I, isotropic phase.

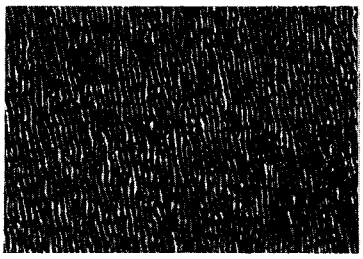

Fig. 3. Striped fan texture observed in chiral smectic C* phase of ICLC.

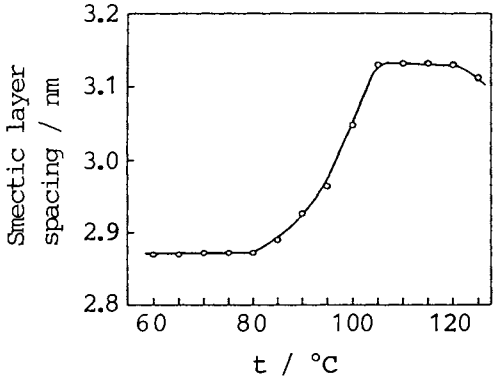

Fig. 4. Smectic layer spacing as a function of temperature in ICLC.

Figure 4 shows the temperature dependence of the smectic layer spacing in ICLC obtained by X-ray measurement. In this measurement, the measuring temperature was controlled with a Mettler FP80-FP82 system. The layer spacing in the smectic A phase was 3.13 nm, and in the chiral smectic C^* range from 80 to 105 °C, the layer spacing increased with temperature, due to the decrease in a tilt angle in the chiral smectic C^* phase.

References

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10) The nonionic liquid crystal (NLC) was prepared by a modification of a literature method.[4,6] ^{1}H NMR (CD_3OD-$CDCl_3$): δ =1.42 (9H, m), 2.63 (2H, t), 2.76 (2H, t), 2.89 (2H, t), 3.62 (2H, t), 3.92 (4H, m), 6.98 (2H, d), 7.32 (2H, d), 7.8 (2H, d), 7.88 (2H, d).
11) ^{1}H NMR (CD_3OD-$CDCl_3$): δ =1.62 (8H, m), 3.02 (8H, m), 3.8 (4H, m), 4.02 (2H, m), 4.42 (4H, hydrogentartrate -C*H(OH)-C*H(OH)-, s), 7.0 (2H, d), 7.35 (2H, d), 7.8 (4H, m).
The NMR data indicate that nonionic NLC and tartaric acid formed ionic ILC which is the amino-hydrogentartrate complex just as (2-hydroxyethyl)dimethylammonium hydrogentartrate and ammonium hydrogentartrate.
12) IR (KBr) 2800 (N^+-H stretching vibration), 1681 (nonionic carboxylic acid C=O stretching vibration), 1400 cm^{-1} (ionic carboxyl COO^- symmetric stretching vibration). The stretching vibrations of the both nonionic carboxylic acid C=O and ionic carboxyl COO^- groups indicate the existence in the hydrogentartrate counterion.

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