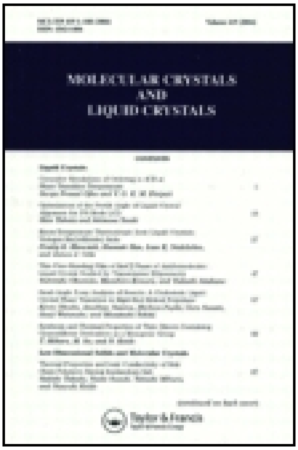

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Antiferroelectricity of a Chiral Smectic Liquid Crystal Having Three Isolated Phenyl Rings in the Core

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Phase sequence and helicoidal structure of a chiral smectic liquid crystal and its binary mixtures with a well-known antiferroelectric liquid crystal MHPOBC were studied by dielectric electro-optic and circular dichroism measurements. Structural difference between this material and MHPOBC is an ester group introduced into the biphenyl core. The fundamental phases of antiferroelectric liquid crystals, SmC*and SmC$_A{}^*$, do not appear in this pure material, but, by doping a small amount of MHPOBC, SmC$_A{}^*$ is stabilized in a wide temperature range. This material may be categorized as a potential antiferroelectric liquid crystal.

Keywords: antiferroelectric liquid crystal; potential antiferroelectric; three phenyl rings core; phase sequence; circular dichroism

INTRODUCTION

Since the discovery of antiferroelectricity in liquid crystals,[1] a large number of antiferroelectric liquid crystals (AFLCs) have been synthesized,[2] and various chiral smectic phases has been found in those compounds.[3,4] The possible stable phases observed in those AFLCs at zero electric field are as follows for decreasing temperature.[5,6]

$$\text{SmA-SmC}_\alpha\text{*-SmC*-FI-AF-FI}_\text{H}\text{-SmC}_\gamma\text{*-FI}_\text{L}\text{-SmC}_\text{A}\text{*-SmI}_\text{A}\text{*-SmI*}$$

In this phase sequence, paraelectric SmA, ferroelectric SmC* and antiferroelectric SmC_A* are the fundamental phases, and the subphases emerging between them, *i.e.*, ferrielectric FI, FI_H, FI_L and SmC_γ* and antiferroelectric AF, constitute a temperature induced devil's staircase of the competition between the molecular interactions stabilizing SmC_A* and SmC* structures, and are well explained by the ANNNI model taking account of the third-nearest-neighbor interaction.[7] The SmC_α* is not a single phase but forms as itself the temperature-induced staircase.[8] On the other hand, antiferroelectric SmI_A* and ferroelectric SmI* below SmC_A* are hexatic phases which have a short range in-plane-positional order and a long range bond-orientational order.[9] Some of these phases may not actually occur, but, when they exist, they exactly follow this order. For example, the well known AFLC, 4-(1-methylhepthyloxy-carbonyl) phenyl 4'-octyloxy-biphenyl-4-carboxylate (MHPOBC, Fig.1(a)), shows phase sequence as SmA - SmC_α*-SmC*-SmC_γ*-SmC_A*-SmI_A*. It depends on the chemical structure of the liquid crystal which phase will appear, and then introducing or substituting functional groups in the molecules may result a big change in the phase sequence and physical properties. In most AFLCs, the molecular core consists of a biphenyl group and a phenyl one connected by an ester bonding group. Several compounds of other type have been investigated; for example, Takenaka *et al.* succeeded to synthesized a few kinds of liquid crystals with three phenyl rings separated by ester groups,[10] and the physical properties of one of those materials was precisely investigated by O'Sullivan *et al.*[11]

In this study, the phase sequence and helicoidal structure of a liquid crystal, 4-(-methylheptyloxycarbonyl)phenyl 4-(4'-octyloxyphenylcarbonyloxy)benzoate (MHPOPB, Fig.1(b)), in which an ester group is introduced between the two phenyl rings of the biphenyl core of MHPOBC, and its binary mixing with MHPOBC were investigated by dielectric, electro-optic and circular dichroism (CD) measurements, and the stability of antiferroelectricity in these materials was discussed.

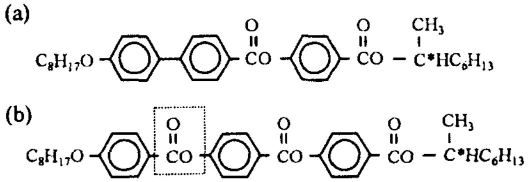
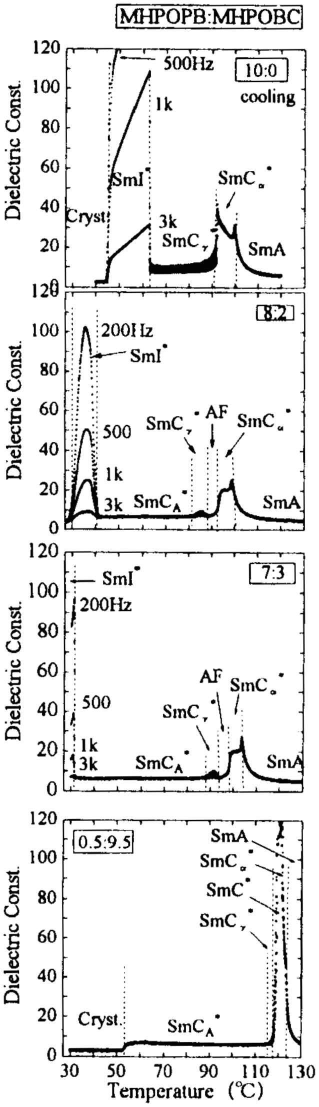


FIGURE 1 Chemical formulae of (a) MHPOBC and (b) MHPOPB.

EXPERIMENTALS

The liquid crystalline materials used in this study were *R*-MHPOPB and its binary mixtures with *R*-MHPOBC. For dielectric and electro-optic measurements, homogeneous (parallel alignment) cells were prepared by rubbing polyimide-coated surfaces of ITO glass plates which were separated by spacers of 10 μm in thickness. The electrode area was 16 mm^2. The dielectric measurements were performed by an impedance analyzer (YHP, 4194A and Solartron, SI-1260), where the applied AC field for the measurements was as low as 7 mV/μm to avoid nonlinear effects on dielectric constant. For the light transmittance hysteresis measurements, a triangular wave of electric field of 1 V/μm, 0.1 Hz was applied. The transmitted light intensity was detected by a photodiode (Advantest, TQ8210) attached to a polarization microscope. The axes of the crossed polarizers were set parallel and perpendicular to the smectic layer normal.

In the CD experiments, homeotropic (perpendicular alignment)



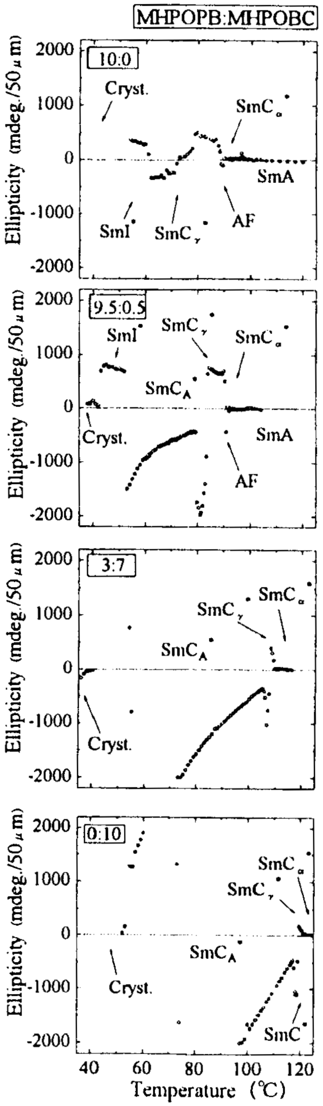


FIGURE 2 Temperature dependence of dielectric constant for various mixing ratio.

FIGURE 3 Temperature dependence of LCICD intensity for various mixing ratio.

cells were prepared using substrate glass plates with a surfactant (Shin-Etsu, Silicone). Pieces of PET film of 50 μ m thick were used as spacers. The CD measurements were performed by a spectro-polarimeter (JASCO, J-600), and the samples were set as the incident ray propagates along the helical axis. In chiral smectic liquid crystals of helicoidal structures, two absorption bands are usually observed: one corresponds to the selective reflection at a wavelength proportional to the pitch of the helix, and the other to the absorption due to the helical formation of transition moments of phenyl rings in the core. The latter is referred as liquid crystal induced circular dichroism (LCICD).[12] In the case the selective reflection bands of the materials used are out of the wavelength range of the present instrument (200-800 nm), LCICD was used for investigating the helical structure. The sign and the intensity of LCICD signals depend on the handedness and the pitch of the helix, respectively. The ellipticity of the transmitted elliptically polarized light was used as the measure of LCICD intensity. The sample cells were placed on a hot stage (Mettler, FP90) whose temperature was controlled with as accuracy of ±0.1℃.

RESULTS AND DISCUSSION

In Fig.2, temperature dependences of dielectric constant of the mixtures including the pure materials are shown for various frequencies on cooling process under zero electric bias fields. The phase on the low temperature side of SmA was recognized as SmC_α^* because of its polarization reversal current behavior. On the high temperature side of the crystal phase, a ferroelectric phase with high value of dielectric constant due to Goldstone mode appears. This phase was assigned as not SmC* but SmI* from the order of phase appearance in cooling process. The wide temperature phase between this ferroelectric SmI* and SmC_α^* was concluded as the ferrielectric SmC_γ^* because of the shape of light transmittance hysteresis loop and of the bias field

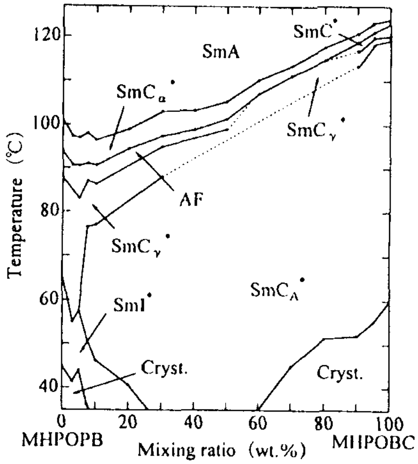


FIGURE 4 Phase diagram of the binary system of *R*-MHPOPB and *R*-MHPOBC.

treatment effect on the dielectric constant.[4] The antiferroelectric SmC$_A$* appears in a wide temperature range by doping a small amount of MHPOBC into MHPOPB. In Fig.3, temperature dependence of LCICD intensity of the mixtures of various mixing ratio is shown. Existence of a narrow temperature phase was confirmed between SmC$_\alpha$* and SmC$_\gamma$* in the mixtures of small amount of MHPOBC. This phase was assigned as the antiferroelectric AF phase by the light transmittance hysteresis loop measurement.

The resultant phase diagram of this binary system is shown in Fig.4. The phase transition temperatures were determined by the dielectric measurements. The SmC$_A$* phase comes in and is stabilized by a small amount of MHPOBC. According to these experimental results, the phase sequence in the cooling process of pure MHPOPB at zero electric field is concluded as SmA-SmC$_\alpha$*-SmC*-AF-SmC$_\gamma$*-SmC$_A$*-SmI*. This sequence obeys the empirical rule of the order of phase appearance in usual AFLCs. It can, therefore, be said MHPOPB is categorized as AFLC, but may be a *potential* one, because the fundamentals phases, SmC_A* and SmC*, are not included in this sequence.

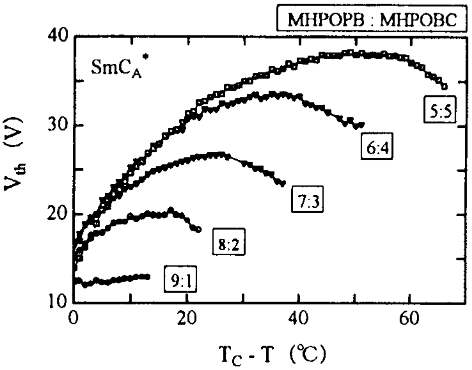


FIGURE 5 Temperature dependence of the threshold voltage of field induce phase transition.

In Fig. 5, temperature dependence of the threshold voltage V_{th} of the field induce phase transition from SmC_A* to SmC* is shown for various mixing ratio. The V_{th} increases with the amount of MHPOBC; that is, doping the MHPOBC molecule exposes the *latent* SmC_A* phase in the *potential* AFLC, MHPOPB, and stabilizes its antiferroelectricity. Conversely, it can be said that introducing an ester bond into the biphenyl group in the core weakens the antiferroelectric interaction between the molecules.

As shown in Fig.3, the LCICD intensity curve crosses the horizontal axis at a temperature in $SmC_\gamma*$ of pure MHPOPB and its mixtures with small amount of MHPOBC, and also in SmC_A* of pure MHPOBC[1] and its mixtures with small amount of MHPOPB. This phenomenon corresponds to the divergence of helical pitch followed by the reversal of helical handedness at this temperature. The helical pitch is determined by the thickness of smectic layer and the twisting angle between the neighboring layers. As the twisting direction between the layers of antiferroelectric ordering is opposite in sign to that of ferroelectric one, the resultant pitch of the helix in SmC$_\gamma$* is determined by the competition between the twisting angles of different sign, and, therefore, the apparent twisting angle is much smaller than those in SmC$_A$* and SmC*. Both the twisting angles and the layer thickness must be temperature dependent in general, then the divergence of the pitch may take place at the temperature where the apparent twisting angle reaches zero.

Acknowledgments

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