

Sign inversion of liquid-crystal-induced circular dichroism observed in the smectic-A and chiral smectic- C_α phases of binary mixture systems

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Liquid-crystal-induced circular dichroism (LCICD) measurements have been made to investigate the structure of smectic- C_α^* using liquid-crystal-mixture systems, in which zero spontaneous polarization $P_S=0$ or infinite pitch is realized. Two main observations are as follows: (1) LCICD shows a cusp but not a discontinuous change at the Sm-A–Sm- C_α^* phase transition; and (2) the sign of the LCICD in Sm-A and Sm- C_α^* is correlated with the sign of P_S , and LCICD is hardly observed near a mixing ratio of zero P_S . Based on these observations, we have concluded a dynamic helical structure with a very long average pitch in Sm- C_α^* and an important role played by the flexoelectric effect. [S1063-651X(97)51107-X]

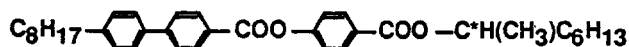
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Since the antiferroelectric liquid crystalline phase was discovered in 1989 [1], several subphases have been found and studied [2]. Almost all of them emerge between smectic- C_A^* and ordinary ferroelectric Sm- C^* , and are well explained by the axial next-nearest-neighbor Ising model with the third nearest-neighbor interaction [3]. A single exception is a subphase designated as Sm- C_α^* that emerges between Sm-A and Sm- C^* [4,5]. Although various investigations have been performed, it is still a mysterious phase. Its characteristic features are as follows: (1) Sm- C_α^* is a tilted smectic phase just below Sm-A and the tilt angle is small [6]. (2) The texture appears so uniform and uniaxial that it is not easy to optically distinguish Sm- C_α^* from Sm-A [5,7]. (3) The liquid-crystal-induced circular dichroism (LCICD) is very small [8]. (4) Sm- C_α^* exists at any mixing ratio of a binary system where the spontaneous polarization becomes zero, $P_S=0$ [9]. (5) The apparent tilt angle in homogeneous cells changes stepwise with the electric field [10], although the conoscopic figure in homeotropic cells varies continuously and looks ferrielectric [7]. (6) Dielectric measurements in homogeneous cells show thermal hysteresis in the lower temperature region of Sm- C_α^* [11]. (7) Ellipsometric measurements in free-standing films reveal stepwise structural changes with temperature [12]. (8) Electro-optic measurements in homogeneous cells reveal an antiferroelectric structure just below Sm-A, but the existence of a ferrielectric structure is also suggested with decreasing temperature [2,6].

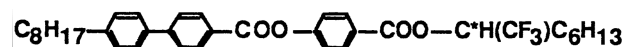
Features (5)–(8) suggest that Sm- C_α^* might be a devil's staircase caused by the frustration between antiferroelectricity and ferroelectricity [2,6,10]. However, feature (4) clearly indicates that the staircase is not essential for Sm- C_α^* . Another controversy is on the helical structure. The pitch was considered to be short because of features (1)–(3). Actually, Laux *et al.* [13] quite recently claimed to have measured the pitch as short as 100 nm by a sophisticated technique. The purpose of this Rapid Communication is to report a liquid-

crystal-mixture system which shows unambiguously that Sm- C_α^* has a dynamical helical structure with very long average pitch.

The antiferroelectric liquid crystals used in this experiment were the binary mixtures of (*R*)-4-(1-methylheptyloxycarbonyl)-phenyl 4'-octylbiphenyl-4-carboxylate [(*R*)-MHPBC]



and (*R*)- or (*S*)-4-(1-trifluoromethylheptyloxy carbonyl)phenyl 4'-octylbiphenyl-4-carboxylate [(*R*)- or (*S*)-TFMHPBC].



The phase diagrams of these binary mixtures have already been reported [9]. It must be noted that (*R*)-MHPBC and (*R*)-TFMHPBC have the opposite handednesses of the helices in the Sm- C_A^* phase, although they possess the same sign of the spontaneous polarization, so that there exists a mixture with an infinite pitch in the Sm- C_A^* phase at a certain mixing ratio. The experimental results will be reported mainly for the mixtures of (*R*)-MHPBC and (*S*)-TFMHPBC, in which the Sm- C_α^* phase exists in all the mixing ratios and the spontaneous polarization becomes zero at a certain mixing ratio [9].

Spontaneous polarization (P_S) measurements were made in binary mixtures of (*R*)-MHPBC and (*S*)-TFMHPBC using the reversed current method, by applying rectangular wave with 5–10 Hz. We used 2–4 μm thick homogeneously aligned cells prepared by the temperature gradient method.

Thick free-standing films were made on a 240 μm thick aluminum plate with a small hole (3 mm in diameter) by stretching liquid crystals with a spatula across the small hole at the temperature region of Sm-A. The sample thickness determined by interference fringes using a Hitachi U3410 spectrophotometer was between 100 μm and 200 μm and was used to normalize the CD signal. CD due to the difference of the absorbance (but not a selective reflection) for right and

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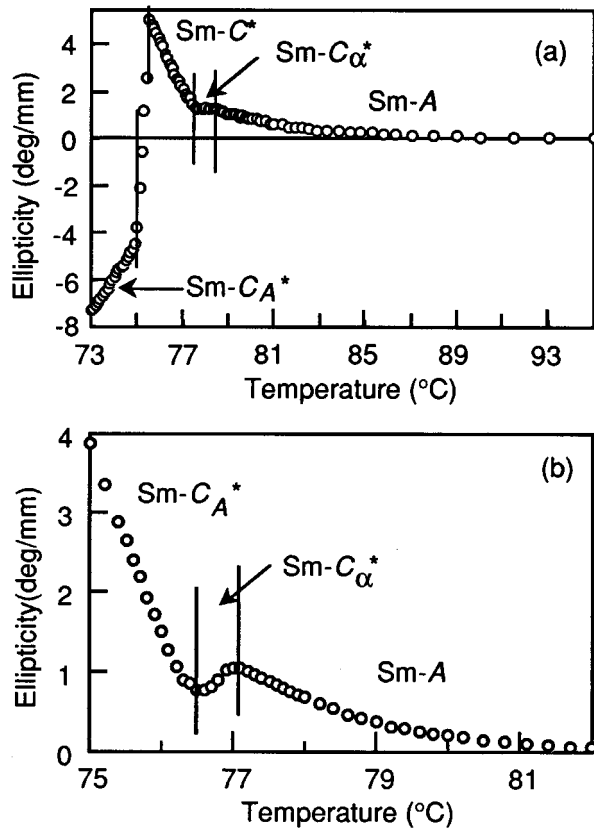


FIG. 1. Temperature dependence of LCICD at about 340 nm in the mixtures of (a) (R)-MHPBC:(R)-TFMHPBC=7:3 and (b) 2:8.

left circularly polarized light (LCICD) was measured using a spectropolarimeter (JASCO J-720WI). In thick free-standing films, the LCICD signal was detected only in the tail of the absorption band due to the large intrinsic absorption. The sample was always set so that the incident ray propagates along the helical axis; we rotated the sample around the beam axis and confirmed no change of the signal. This setting assures that the signal does not come from a liquid crystalline birefringence but is truly caused by LCICD due to the helical structure.

Figure 1 shows the temperature dependence of LCICD at about 340 nm in the binary mixture of (R)-MHPBC and (R)-TFMHPBC with (a) 30 wt % and (b) 80 wt % of (R)-TFMHPBC. The LCICD varies with a temperature and shows clear changes at the phase transition temperatures. A remarkable jump with a sign reversal appears at the $\text{Sm-C}^*-\text{Sm-C}_A^*$ phase transition, as shown in Fig. 1(a). It is consistent with the previous reports that the handednesses of helices in Sm-C_A^* and Sm-C^* are opposite [14,15]. Although the intensity of the LCICD signal in the Sm-C_A^* and Sm-A phases is much weaker than that in the Sm-C_α^* and Sm-C^* phases, the transition temperature is clearly distinguished. It is important to note that LCICD in Sm-C_A^* , which exists in all the mixtures, tends to diverge to negative and positive values in (R)-MHPBC and (R)-TFMHPBC sides, respectively, when approaching the mixture showing an infinite pitch, as suggested in Figs. 1(a) and 1(b).

Figures 2(a)–2(c) show the temperature dependence of LCICD in the Sm-A and Sm-C_α^* phases of the three binary

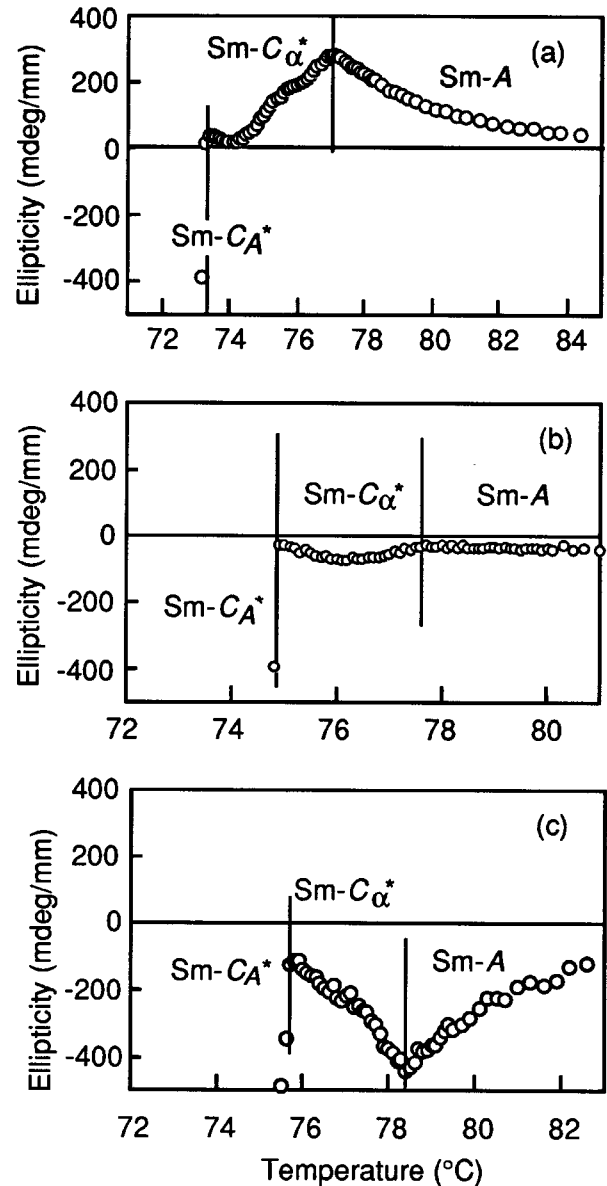


FIG. 2. Temperature dependence of LCICD at about 340 nm in the mixtures of (a) (R)-MHPBC:(S)-TFMHPBC=8:2, (b) 7:3, and (c) 6:4.

mixtures of 20 wt %, 30 wt %, and 40 wt % (S)-TFMHPBC in the mixture series of (R)-MHPBC and (S)-TFMHPBC. The following observations should be made in Fig. 2. (1) In 30 wt % (S)-TFMHPBC, the signal is vanishingly weak in both the Sm-C_α^* and Sm-A phases. (2) In 20 wt % and 40 wt %, the LCICD signals have positive and negative signs, respectively. Moreover, the sign of the LCICD signal in Sm-A is always the same as that in Sm-C_α^* . (3) If the signal appears, the $\text{Sm-A}-\text{Sm-C}_\alpha^*$ phase transition is clearly recognized by a cusp. (4) No discontinuity exists at the $\text{Sm-A}-\text{Sm-C}_\alpha^*$ phase transition. (5) The temperature dependence of LCICD exhibits some structure in Sm-C_α^* [see particularly Fig. 2(a)], while it shows only a monotonous change in Sm-A . (6) The phase transition between Sm-C_α^* and Sm-C_A^* is associated with a large discontinuous jump of the LCICD. The sign change is sometimes accompanied with this jump or transition [see Fig. 2(a)].

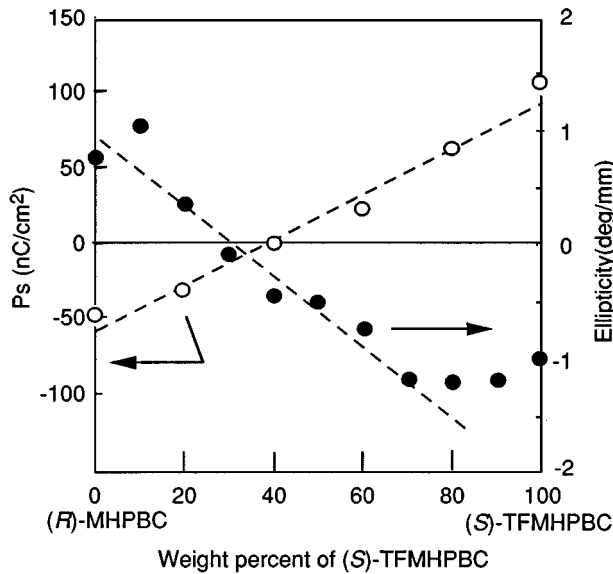


FIG. 3. LCICD at the Sm-A–Sm- C_{α}^* transition point and spontaneous polarization at 10 °C below the Sm-A–Sm- C_{α}^* transition point in a binary mixtures of (R)-MHPBC and (S)-TFMHPBC.

Figure 3 shows the mixing ratio dependence of P_S observed at 10 °C below the Sm-A–Sm- C_{α}^* phase transition in the mixture series of (R)-MHPBC and (S)-TFMHPBC. The LCICD at the Sm-A–Sm- C_{α}^* transition point is also shown. Note that both P_S and LCICD become zero between 30 wt % and 40 wt % (S)-TFMHPBC. Thus, there is a strong correlation between the LCICD signal in Sm- C_{α}^* and P_S including their signs.

Our final goal is to clarify the structure of the Sm- C_{α}^* phase. As the first step, let us consider the helical structure in Sm- C_{α}^* based on the present LCICD observation. The present LCICD observation clearly indicates the existence of some helical structures, not only in Sm-A but also in Sm- C_{α}^* . The LCICD signal in Sm-A is due to a helical structure dynamically formed as a result of soft mode fluctuations [8]. The fluctuation amplitude and, hence, the LCICD signal increases in Sm-A as the temperature approaches the phase transition to Sm- C_{α}^* . The dynamical helical structures have an average pitch l_0 or the corresponding wave number q_0 .

It is known that the LCICD tends to diverge when q_0 approaches to zero similar to the optical rotatory power [1], as schematically shown in Fig. 4 (regions A and C). Actually, in the real Sm- C_{α}^* phase in the mixture series of (R)-MHPBC and (R)-TFMHPBC, the LCICD signal grows to large negative and positive values when the mixing ratio approaches the critical value showing an infinite pitch, as already mentioned. From this point of view one may suggest that a very small LCICD in the Sm- C_{α}^* phase corresponds to a very short pitch (large q_0) as reported by Laux *et al.* [13]. We cannot agree with this conclusion, however. Indeed, LCICD formally vanishes when $q_0=0$ (i.e., when there is no helical structure) as shown in region B of Fig. 4; the LCICD linearly changes with q_0 at small q_0 , crossing the zero at the sense inversion point. We note that the mixing ratio corresponding to region B can be very small for Sm- C_{α}^* in our system. A much broader region of this kind is actually real-

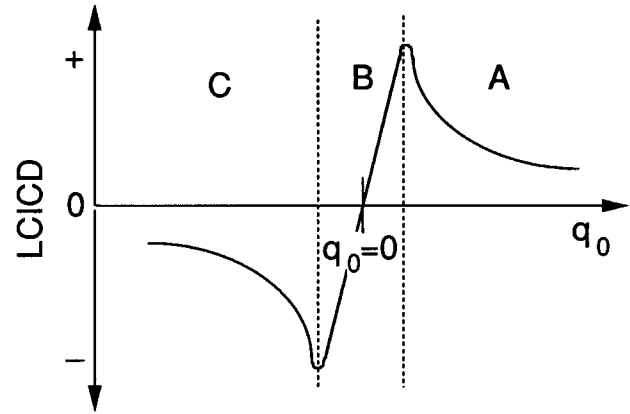


FIG. 4. Schematic illustration of LCICD as a function of q_0 .

ized in lyotropic systems where the pitch is always much larger than the wavelength of the light [16]. Thus, it is more reasonable to assume that the pitch in Sm- C_{α}^* is very long, i.e., $q_0 \approx 0$, existing in region B, irrespective of its helix character, fluctuating dynamic, or equilibrium static.

Figure 2 indicates that the Sm-A–Sm- C_{α}^* transition is one of the higher order [17] and, hence, the temperature change of the LCICD signal looks continuous; the helical structures of Sm-A and Sm- C_{α}^* have the same (average) wave number q_0 at the phase transition temperature. Suppose there exists an ordinary static helix of such a long pitch, a characteristic disordered texture is expected to appear. Actually, however, the Sm- C_{α}^* texture is always so uniform that it is not easy to distinguish between Sm-A and Sm- C_{α}^* . Therefore, we have to consider that the dynamical helical structure plays an important role not only in Sm-A but also in Sm- C_{α}^* . As a possible cause for the dynamical helical structure of the tilted Sm- C_{α}^* phase, we speculate thermally excited C-director disclinations. Since Sm- C_{α}^* always appears just below Sm-A and hence the tilt angle is very small, a large number of C-director disclinations may easily be excited thermally; the average distance between disclinations must be much shorter than the visible light wavelength so that Sm- C_{α}^* appears to be uniform and uniaxial when observed with an optical microscope. Even if the disclination formation requires a little energy, their creation and annihilation do not always freely occur; this fact may explain stepwise changes in the field-induced apparent tilt angle [10], and some hysteresis in heating and cooling processes observed during dielectric measurements [11].

The next question is related to the formation of the fluctuating helical structure. Let us first consider the ferroelectric Sm- C^* type soft mode fluctuations. The microscopic origin of the helical structure in the Sm- C^* phase is known to be twofold. First, there exists a direct contribution from chiral intermolecular interactions that are also responsible for the helical twisting in cholesteric liquid crystals. Second, there is an additional contribution from the flexoelectric effect. According to the phenomenological theory by Pikin and Indenbom [18], the helical pitch wave number q^C and the spontaneous polarization P_S in Sm- C^* are given by

$$q^C = -\frac{\lambda + \chi_e \mu_p \mu_f}{K - \chi_e \mu_f^2}, \quad (1)$$

$$P_S = \chi_e(\mu_p - \mu_f q^C) \theta, \quad (2)$$

where λ is a quantity related to molecular chirality and is a measure of a twisting power, θ , χ_e , and K are a tilt angle, an electric susceptibility, and an elastic constant, respectively. μ_p and μ_f are piezoelectric and flexoelectric constants, respectively. Using Eqs. (1) and (2), we obtain q^C as

$$q^C = -\frac{\lambda}{K} - \frac{P_S}{K\theta} \mu_f. \quad (3)$$

At present it is impossible to develop a consistent theory of the Sm-C_α^* phase because too little is known about its particular structure. Nevertheless, we are going to present a sequence of relevant arguments which will be used to justify our conclusions about the helical structure and the role of the flexoelectric effect. In a dynamical helical structure, the fluctuations of the tilt angle, the polarization, and the helical wave number possess different relaxation times. We assume that the relaxation time of the polarization is smaller than that of the tilt angle because it is related to the rotation of short molecular axes about the long one. In this case the fluctuations of polarization are peaked around the value given by Eq. (2), when the system is far from the resonance condition (pitch \gg light wavelength). In a similar way the most probable value of the pitch is given by Eq. (1). We note that this expression does not depend on the tilt angle and thus the fluctuations of the pitch are independent of the tilt angle fluctuations in the first approximation.

We also note that the sign of helix does not change in the Sm-C_α^* phase of the mixture series of (*R*)-MHPBC and (*S*)-TFMHPBC but the sign of P_S does. Since Eqs. (1)–(3)

are valid even in Sm-C_α^* , the first term in Eq. (3) is predominant for the pitch in this phase. However, by some reason, the first and the second terms in Eq. (3) nearly cancel each other in the Sm-A and Sm-C_α^* phases resulting in the very long pitch. The strong correlation between the LCICD signal and P_S indicates that the flexoelectric effect plays an important role to form a helix in Sm-A and Sm-C_α^* . The small but nonzero λ may be the reason why the mixing ratio which shows zero LCICD is slightly different from that which shows zero P_S , as shown in Fig. 3.

It is also possible that the antiferroelectric Sm-C_α^* type soft mode fluctuations are responsible for the dynamical helical structures in Sm-A and Sm-C_α^* . Nevertheless, we still can conclude that the flexoelectric effect plays an important role in this case. One can readily see from simple symmetry reasons that even in the Sm-C_α^* phase the helix wave number q^{CA} and the spontaneous polarization P_S^{CA} (measured in the field induced Sm-C state) satisfy the same linear relation as in Eq. (3).

In conclusion, the Sm-C_α^* phase has a dynamic helical structure with a very long pitch contrary to the observation by Laux *et al.* [13]. We also found that the sign of the LCICD in Sm-A and Sm-C_α^* is strongly correlated with the sign of P_S , suggesting the importance of the contribution from the flexoelectric effect to the dynamic helix.

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