RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 52, NUMBER 3 SEPTEMBER 1995

Spontaneous polarization parallel to the tilt plane in the antiferroelectric chiral smectic-C_A phase of liquid crystals as observed by polarized infrared spectroscopy

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(Received 19 June 1995)

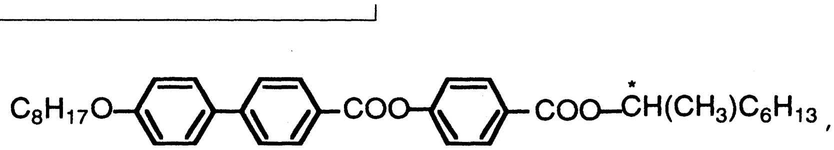
We have observed the absorbance vs polarizer rotation angle for the carbonyl and phenyl ring stretching peaks in an antiferroelectric liquid crystal, 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC), and found that the carbonyl group near the chiral center rather lies on the tilt plane in antiferroelectric Sm-C_A^* while it takes a considerably upright position in ferroelectric Sm-C^*. The spontaneous polarization exists at smectic layer boundaries and its importance to stabilize Sm-C_A^* has been discussed.

PACS number(s): 61.30.Gd, 77.80.−e, 78.30.−j

Meyer's initial speculations [1] about the classical ferroelectric chiral smectic-C (Sm-C^*) phase, based on symmetry arguments and some simple ideas about molecular structure, have been remarkably well confirmed by lots of experiments. Aside from the slight precession of at most a few degrees per layer resulting in its helicoidal structure, the director tilts uniformly relative to the smectic layer normal in the same direction and sense; spontaneous polarization emerges perpendicular to the tilt plane. However, only a few experiments have been aiming at quantitative, microscopic examination of the hindered rotational motion about the long molecular axis [2,3], which must play an important role for the emergence of the spontaneous polarization. Quite recently, Kim *et al.* [4] used the polarized infrared (ir) spectroscopy and gave the microscopic proof, at least in its static aspect, of the hindered rotational motion of carbonyl (C═O) groups about the long molecular axis in ferroelectric Sm-C^*. Some numerical analyses of the origin of ferroelectricity have also been made on the basis of the zigzag model by Photinos and Samulski [5] and by Glaser *et al.* [6].

In addition to the classical ferroelectric Sm-C^* phase, several antiferroelectric and ferrielectric phases have been so far observed in liquid crystals. Among them, the antiferroelectric chiral smectic-C_A (Sm-C_A^*) phase is another fundamental smectic C-like phase, having the so-called herringbone structure [7,8]. In any smectic layer, the director tilt is uniform relative to the layer normal; in adjacent layers, the tilt is equal in magnitude but opposite in sign. There are two kinds of twofold axes; one at the layer boundary is parallel to the X axis in the tilt plane (C_{2X}), and the other is located in the middle of the layer perpendicularly (C_{2Y}), as depicted in Fig. 1. The pairing of transverse dipole moments in adjacent layers has been considered to cause antiferroelectric Sm-C_A^*; the sign of the spontaneous polarization along the tilt plane normal, P_Y, alternates from layer to layer and the C_{2Y} axis is the only one so far taken into consideration explicitly [7–11]. However, Cladis and Brand [12,13] insisted on the importance of the C_{2X} axis in the tilt plane. Here we report a result obtained by the polarized ir spectroscopy that the hindered rotational motion of the C═O group near the chiral center (hereafter abbreviated as the chiral C═O group) in Sm-C_A^* produces spontaneous polarization parallel to the X axis, P_X, which is much larger than P_Y. It is worthwhile noting that the C═O group in question, although not in the core, is not at the end of the molecule either.

Materials were prepared by partially racemizing 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC),



a prototype antiferroelectric liquid crystal [7,8]. The partial racemization not only simplifies the phase sequence but also elongates the pitch of the helicoidal structure in Sm-C_A^* so that its unwinding occurs at a relatively low electric field. Still a high voltage power supply (NF, TK-21844) was needed to apply up to ±1500 V mm^{-1} at 800 Hz. A free-standing film of these materials formed in a frame depicted in Fig. 2 was mounted in an oven which had two SrF$_2$ windows for ir radiation and was temperature-controlled with an accuracy of ±10 mK. Note that the smectic layers are parallel to the interfaces. A JEOL 6000 system was improved so that polarized ir spectra were measured as a function of polarizer rotation angle conveniently; a wire-grid polarizer (Cambridge Physical Science, IGP 227) was rotated on an axis parallel to the propagation direction (the Z axis in Fig. 1). The measuring geometry is schematically illustrated in Fig. 2. The rotation angle is defined as zero when the polarization direction of incident ir radiation coincides with the tilt-plane normal. Three absorption peaks investigated are listed in Table I.

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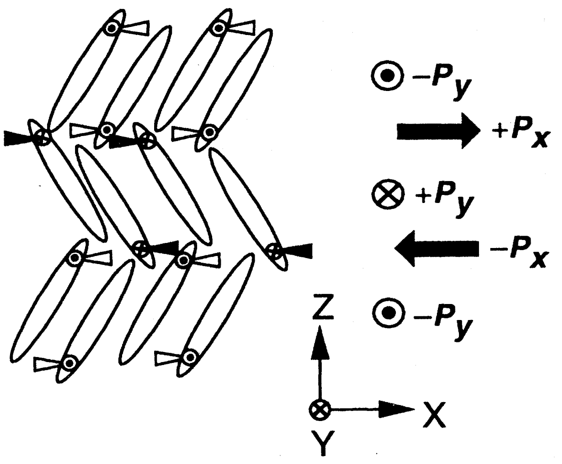

FIG. 1. Twofold symmetry axes and spontaneous polarizations along them together with the schematically illustrated most probable orientation of chiral carbonyl groups in Sm-C_A^*.

TABLE I. Five absorption peaks here investigated. Two carbonyl groups, the one in the chiral part (abbreviated as chiral C=O) and the other in the core part (abbreviated as core C=O) give well-separated absorption peaks, while three phenyl rings give absorption peaks at the same wave number.

Observed peaks (cm^{-1})	Assignments
1739	core C=O stretching
1720	chiral C=O stretching
1604	phenyl ring symmetric stretching

Figure 3 illustrates the absorbance vs polarizer rotation angle in unwound Sm-C_A^* of a partially racemized MHPOBC (the mixing ratio of R and S enantiomers, $R/S=84/16$). Similar results were obtained for other MHPOBCs with different enantiomeric purity, although it was not certain whether the helicoidal structure in Sm-C_A^* was unwound completely when the optical purity is high. Reference [4] discusses the corresponding data in Sm-C^* for enatiomeric MHPOBC. The angular dependence of the phenyl ring stretching peak in Sm-C_A^* is quite similar to that in Sm-C^* [4], indicating that the average stretching direction of phenyl rings is parallel to the long molecular axis and that its orientational order is fairly high. On the contrary, the angular dependence of the C=O stretching peaks in Sm-C_A^* is different from that in Sm-C^* [4]. The dependence in Sm-C_A^* is very characteristic and conspicuously in-phase with that of the phenyl ring stretching peak, while it is out-of-phase in Sm-C^* [4]. The hindered rotational motion of the C=O groups in Sm-C_A^* is substantially different from that in Sm-C^*.

To describe the hindered rotational motion, notice that there are four molecular configurations with the chiral C=O in the top or bottom and tilted to the right or left (see Fig. 1); ψ is defined as the angle between the tilt-plane normal (the Y axis) and the C=O group projection onto the plane perpendicular to the long molecular axis. Even in Sm-C^*, the most probable orientation is not $\psi=0$ but $\psi=\psi_0\neq 0$; there are two equivalent configurations [4]. In Sm-C_A^*, four equivalent configurations exist because the X and Y axes are the twofold symmetry axes; the C=O group rotational motion is biased not in a unique direction but in four directions. In the first approximation, the hindered rotational motion may be described by

$$f(\psi)=\left(\frac{1}{4}\right)\{f_{t+}(\psi)+f_{b+}(\psi)+f_{t-}(\psi)+f_{b-}(\psi)\}, \qquad (1)$$

where

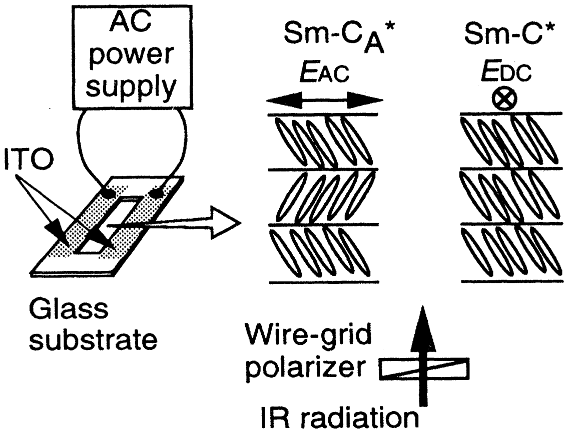

FIG. 2. Free-standing film prepared in a frame, where the smectic layer is formed parallel to the interfaces, and the measuring geometry with the incident ir radiation along the layer normal, where molecules are apparently configured equally both for Sm-C_A^* and Sm-C^*.

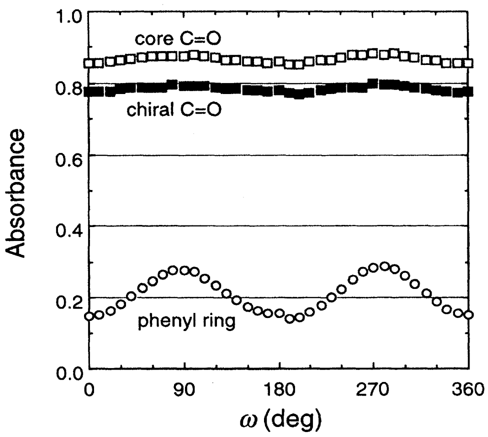

FIG. 3. Absorbance as a function of the polarizer rotation angle in Sm-C_A^* (85.0 °C) unwound by applying an 800 Hz, ±1400 V mm^{-1} electric field. A 10 μm thick, partially racemized (the mixing ratio of R and S enatiomers, $R/S=84/16$) MHPOBC cell was used. Measuring geometry is illustrated in Fig. 2.

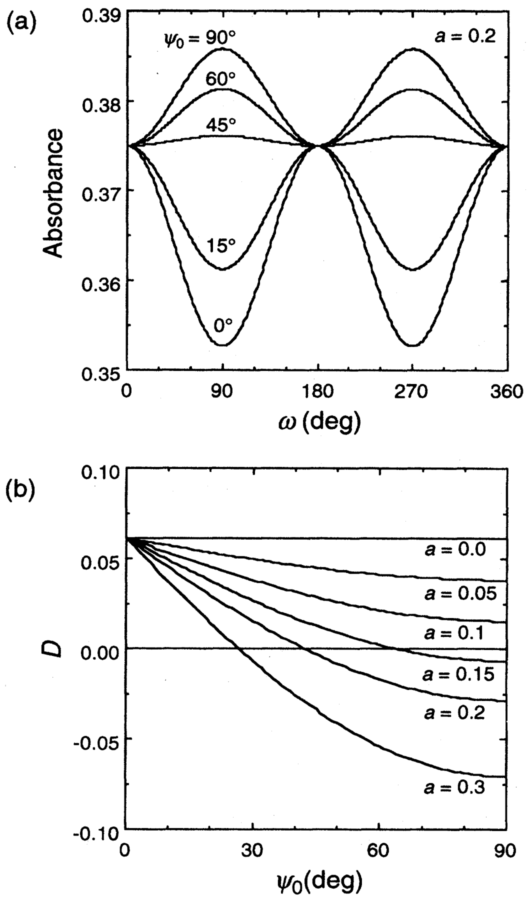

FIG. 4. (a) Normalized absorbance vs polarizer rotation angle, $A(\omega)$, calculated in Sm-C^* and Sm-C_A^* for the radiation incident along the smectic layer normal by using the distribution function given in Eq. (1). The molecular tilt angle and the degree of hindrance are assumed $\theta=25°$ and $a=0.2$, respectively, and $\omega=0$ is the tilt-plane normal. (b) Degree of polarization vs most probable orientation, $D(\psi_0)$, for several a's.

$$f_{t+}(\psi)=\left(\frac{1}{2\pi}\right)\{1+a\cos(\psi-\psi_0)\},$$

and the remaining three are the corresponding distribution functions with the other biased directions in the laboratory frame. Here a is the degree of hindrance, and t (b) and $+$ ($-$) refer to top (bottom) and left (right), respectively. By neglecting the fluctuation of the long molecular axis and by assuming the angle between the C=O stretching direction and the long molecular axis $\beta\approx60°$ and the molecular tilt angle $\theta\approx25°$ [4], we can simulate the absorbance vs polarizer rotation angle, $A(\omega)$.

Let us consider the measuring geometry with free-standing films shown in Fig. 2. Molecules are apparently configured equally both for Sm-C^* and Sm-C_A^*, if we average the two possible Sm-C^* states, one tilted to the left and the other to the right; nevertheless, the results obtained experimentally offered a remarkable contrast as stated above. The normalized absorbance vs polarizer rotation angle, $A(\omega)$, is given by

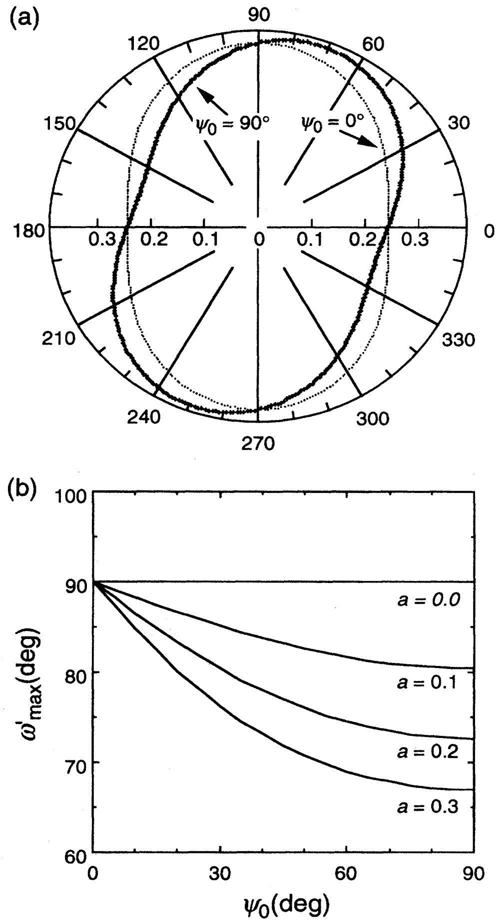

FIG. 5. (a) Normalized absorbance vs polarization rotation angle, $A(\omega')$, calculated in Sm-C^* for the ir radiation incident along the tilt-plane normal by using the distribution function given in Eq. (1). Here $a=0.2$, $\omega'=\omega-\theta$, and $\omega=0$ is the layer normal. (b) Maximum angle vs most probable orientation, $\omega'_{\max}(\psi_0)$, for several a's.

$$A(\omega)=\left(\frac{1}{4}\right)\int_0^{2\pi}f_{t+}(\psi)\{\sin\omega(-\cos\beta+\sin\beta\,\sin\psi)\cos\theta$$
$$+\cos\omega(\sin\beta\,\cos\psi)\}^2d\psi$$
$$+(\text{three corresponding terms}),\qquad(2)$$

where $\omega=0$ is the tilt-plane normal. Figure 4(a) illustrates some of the simulated results, which naturally depend on the degree of hindrance, a, and the most probable orientation, ψ_0. Figure 4(b) summarizes the degree of polarization vs the most probable orientation, $D(\psi_0)=2\ (A_{0°}-A_{90°})/(A_{0°}+A_{90°})$, for various a values. Note that positive and negative signs of $D(\psi_0)$ correspond to out-of-phase and in-phase with respect to the phenyl ring stretching peak, respectively. Since molecules are tilting from the smectic-layer normal along which the ir radiation is incident, the C=O group stretching peak does show the out-of-phase angular dependence even when the rotational motion is free. Nevertheless, the conspicuous in-phase angular dependence in Sm-C_A^* given in Fig. 3 clearly indicates that ψ_0 in Sm-C_A^* is different from ψ_0 in Sm-C^*; the angular dependence is out-of-phase in Sm-C^* as given in Fig. 9 of Ref. [4]. The changeover from in-phase to out-of-phase occurs at $\psi_0 \approx 45°$ when $a \approx 0.2$.

To make a quantitative comparison between Figs. 3 and 4, let us check the appropriateness of the degree of hindrance assumed, $a \approx 0.2$. For this purpose, we try to simulate the absorbance vs polarizer rotation angle, $A(\omega)$, obtained by Kim *et al.* using a homogeneously aligned cell [4]. The normalized absorbance in this geometry is given by

$$A(\omega')=\left(\frac{1}{2}\right)\int_0^{2\pi} f_{t+}(\psi)(\sin\omega'\sin\beta\,\sin\psi+\cos\omega'\cos\beta)^2 d\varphi + \{\text{a corresponding term with } f_{b+}(\psi)\}, \qquad (3)$$

where $\omega' = \omega - \theta$ is used for convenience. Some of the calculated results are shown in Fig. 5. The absorbance takes the maxima at $\omega' = \omega'_{\max}$ and $\omega'_{\max} + 180°$, and its polarizer-rotation angle dependence is symmetrical with respect to the line connecting the maxima through the origin. When $\psi_0 = 0$, we obtain $\omega'_{\max} = 90°$ irrespective of the value of a, the degree of hindrance, so long as a is small. As ψ_0 increases, $\omega'_{\max}$ rotates clockwise as shown in Fig. 5. Since the C=O group in the core part (the core C=O group) is distantly separated from the chiral center, the mirror symmetry exists in the first approximation so that $\psi_0 = 90°$, i.e., the core C=O group appears to lie on the tilt plane. Hence we obtain from Fig. 8 of Ref. [4] $a \approx 0.3$ or slightly smaller and $\psi_0 \approx 165°$ (15°) for the S (R) enantiomer in Sm-C^*, confirming the appropriateness of the degree of hindrance assumed to calculate Fig. 4. Using the experimentally obtained degree of polarization, $D(\psi_0) \approx -0.03$, we obtain from Fig. 4 that $\psi_0 \approx 135°$ (45°) for the S (R) enantiomer in Sm-C_A^*. If $a \approx 0.2$, it gives $\psi_0 \approx 100°$ (80°).

In this way, we can conclude that the chiral C=O group has a tendency to lie on the tilt plane in Sm-C_A^* while it takes a considerably upright position in Sm-C^*; hence the in-layer spontaneous polarization parallel to the tilt plane exists at smectic-layer boundaries in Sm-C_A^*. The core C=O group does not produce the in-layer spontaneous polarization in the middle of the smectic layer because of the head-and-tail equivalence and the mirror symmetry with respect to the tilt plane.

We have considered in previous papers [8,10] that the pairing of the C=O permanent dipoles in adjacent layers is the cause of the antiferroelectric Sm-C_A^* phase. Although the C=O group in question is not at the end of the molecule, the unexpected bent shape of MHPOBC in its crystal phase just below Sm-C_A^* revealed by x-ray crystallographic studies [14] has been considered to support the pairing model. Since ψ_0 is larger than 45°, however, it is not reasonable to ascribe an essential role to the pairing alone; we have to look for other causes for the stabilization of Sm-C_A^*. In fact, the stabilization due to steric repulsive and dispersive attractive forces has been pointed out to play an essential role not only in Sm-C^* but also in Sm-C_A^* [15]. A possibility of the stabilization due to the Coulomb interaction among the C=O permanent dipoles resulting in the in-layer spontaneous polarization parallel to the tilt plane, P_X, is tempting, because P_X may interact through the fluctuation force [16,17]. In fact, Takanishi *et al.* [18] showed that the normalized distribution function of mass density along the layer normal has the standard deviation of 0.1 or more. Although, in the pairing model, we have to invoke rather *ad hoc* assumptions, the local spontaneous optical resolution and the conformational chirality [8,10], the present P_X model can naturally explain the existence of Sm-C_A; the spontaneous polarization in the tilt plane is independent of chirality [12,13,19] and emerges even in racemates and the nonchiral swallow-tail compounds with two terminal chains of equal length [15].

We thank Takaaki Manaka for his assistance in improving the JEOL 6000 system to perform the absorbance vs polarizer rotation angle measurement conveniently. We also thank Ed Samulski and Noel Clark for sending us their preprints. This work was supported by a Grant-in-Aid for Scientific Research (Specially Promoted Research No. 06102005) from the Ministry of Education, Science and Culture. K. Miyachi is grateful to the JSPS for financial support.

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