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EXPERIMENTAL INDICATION OF MACROSCOPIC POLARIZATION PARALLEL TO THE TILT PLANE IN FREE-STANDING FILMS OF FERROELECTRIC LIQUID CRYSTALS 8SI* AND DOBAMBC

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Optical reflectivity and X-ray studies have been conducted on free-standing films and bulk samples of ferroelectric liquid crystals near the smectic-A–smectic-C^* transition. A tilt plane rotation with respect to the direction of an applied electric field is found in the ferroelectric films above the bulk transition temperature. Whereas the macroscopic polarization is perpendicular to the tilt plane at low temperature, it is parallel to the tilt plane at elevated temperature. The temperature dependence of the average tilt angle is measured.

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The smectic-C^* (SmC^*) phase in a free-standing film is a subject of much interest [1–8]. In this phase the direction of the long molecular axis is tilted with respect to the normal to the smectic layers. In the ferroelectric SmC^* phase, spontaneous polarization is perpendicular to the tilt plane and to the **c**-director (**c** is parallel to the tilt plane and the layer). Recently, the first observation of longitudinal (i.e., parallel to the tilt plane) polarization has been reported in free suspended films of an antiferroelectric smectic phase [9] and ferroelectric phase [10, 11].

In this paper we demonstrate an unusual behavior of the well-known ferroelectric compounds 8SI* and DOBAMBC: in SmC^* free-standing films the polarization can be parallel to the tilt plane, i.e., the molecular tilt plane is parallel to an electric field. The temperature dependence of the tilt angle is determined for structures with transverse and longitudinal polarization.

Our samples were the compounds (S)-4-(2′-methylbutyl) phenyl 4-(n-octyl)biphenyl-4-carboxylate (8SI*) and p-decyloxybenzylidene p-aminocinnamic acid 2-methylbutyl ester (DOBAMBC). In the bulk sample of 8SI* the following phase sequence was observed: SmI^*–(66°C)–SmC^*–(82°C)–SmA–(134°C)–Ch–(140°C)–I. DOBAMBC showed transition temperatures SmI*–(73°C)–SmC*–(90.5°C)–SmA–(115°C)–I.

Thick freely suspended films were prepared by drawing the liquid crystal in the smectic state over a 6-mm hole in a glass plate. Thin films were prepared by layer-by-layer thinning [12–14].

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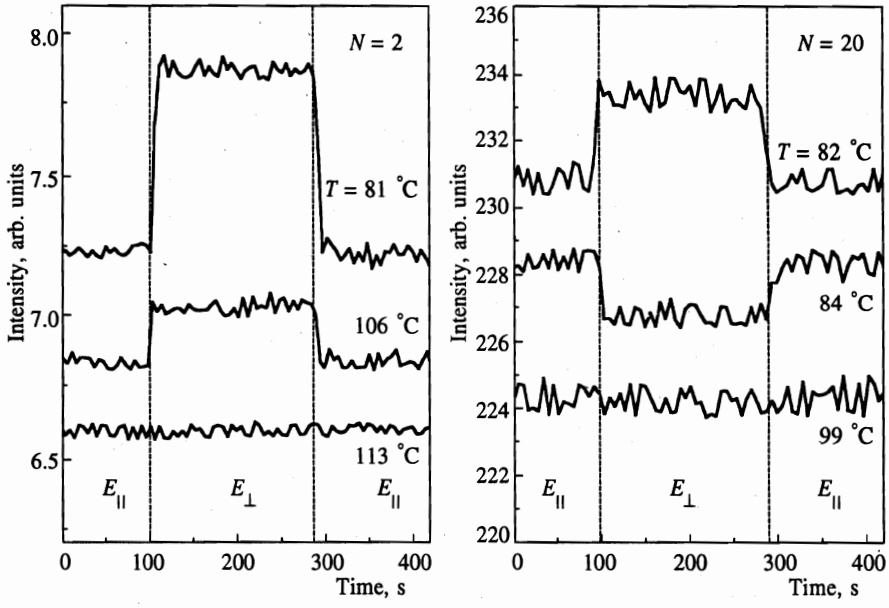


Fig. 1. Optical reflection intensity for thin ($N = 2$) and thick ($N = 20$) ferroelectric films in an electric field applied parallel ($\mathbf{E}_{\|}$) and perpendicular ($\mathbf{E}_{\perp}$) to the direction of polarization of the light ($\lambda = 600$ nm). For thick film ($N = 20$), the change in reflection intensity when the direction of the electric field is changed is different at low ($T = 82°$C) and high ($T = 84°$C) temperatures (8SI*)

In a free-standing film the smectic layers are aligned parallel to the film surface. An electric field of 3 to 20 V/cm in the plane of the film was used to align the tilt direction in the SmC^* state. The incident beam was linearly polarized and was perpendicular to the film surface. An electric field could be applied in two mutually perpendicular directions (parallel ($E_{\|}$) and perpendicular ($E_{\perp}$) to the plane of polarization of the light). For thick films, the layer number N was determined from the spectral dependence of the optical reflection in the SmA phase [15]

$$I(\lambda) = \frac{(n^2-1)^2 \sin^2(2\pi n N d/\lambda)}{4n^2 + (n^2-1)^2 \sin^2(2\pi n N d/\lambda)}, \qquad (1)$$

were d is the interlayer spacing. In the SmA phase, $n = n_0$ (n_0 is the ordinary index of refraction). For thin films, the number of layers was determined from the relative intensity of reflections for films with a different number of layers:

$$I(\lambda) \simeq N^2\pi^2 d^2 (n^2-1)^2/\lambda^2. \qquad (2)$$

In the SmC^* phase, two values of the optical reflection (I_p and I_0) have been measured (for the plane of polarization of the light oriented parallel (I_p) and perpendicular (I_0) to the tilt plane). For our calculations of the average tilt angle θ we used the value of the birefringence in the SmA phase measured by Musevic et al. [16]. X-ray diffraction studies on bulk samples were made using a curved linear position-sensitive multidetector ($\lambda = 1.5406$ Å).

Figure 1 shows optical reflection intensities ($I_{\|}$, $I_{\perp}$) from 2- and 20-layer films: the electric field was applied parallel ($\mathbf{E}_{\|}$) and perpendicular ($\mathbf{E}_{\perp}$) to the direction of polarization of the

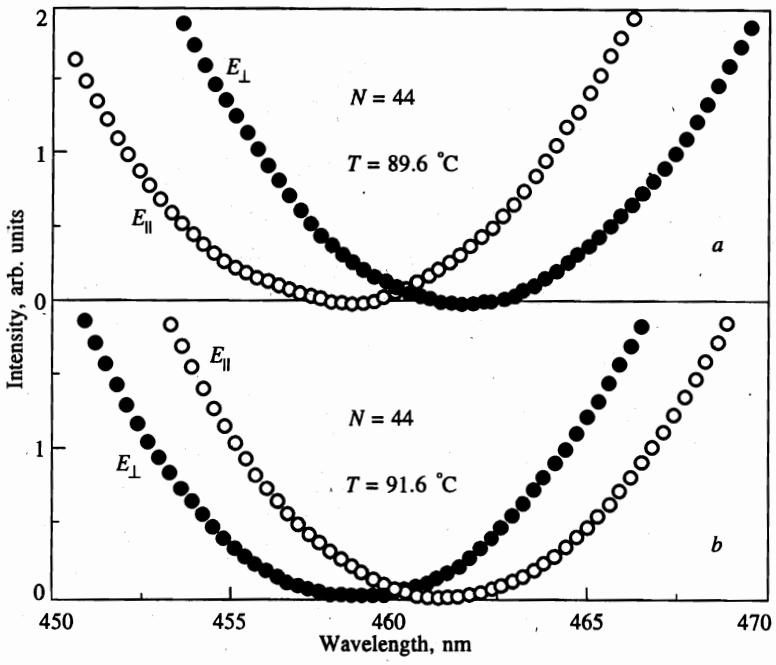
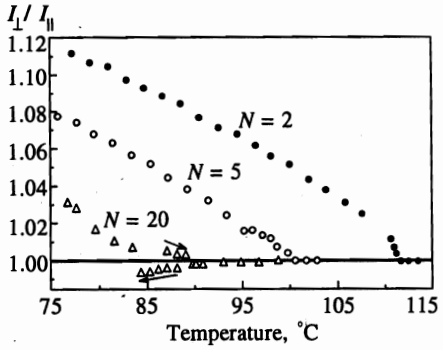


Fig. 2. Reflection spectra at the temperature below (*a*) and above (*b*) the bulk transition temperature. The relative location of the reflectivity minima λ for $\mathbf{E}_\perp$- and $\mathbf{E}_\parallel$-field directions differs for temperatures below and above the bulk transition (DOBAMBC). In the figure, the intensities are shown with respect to the intensities in the minima of the curves

light. As a previously observed [1, 2], the SmC^*–SmA transition temperature is a function of film thickness ($T \approx 112$°C for $N = 2$; $T \approx 97$°C for $N = 20$). For two-layer film the observed change in intensity, when the direction of the electric field is switched ($\mathbf{E}_\parallel \leftrightarrow \mathbf{E}_\perp$), corresponds quantitatively to our conventional view of the SmC^* phase: the ferroelectric polarization is perpendicular to the tilt plane. Since the refractive index n_p (polarization of the light is parallel to the tilt plane) is greater than n_0, the larger value of the reflection intensity (Fig. 1, $N = 2$, $T = 81$°C and $T = 106$°C) corresponds to the direction perpendicular to the field (see Eqs. (1) and (2)). At low temperatures, all films show the same change in the reflected intensities (Fig. 1, $N = 20$, $T = 82$°C). Quantitatively different behavior is observed for thick SmC^* films at high temperature (Fig. 1, $N = 20$, $T = 84$°C). The reflection intensity $I_\perp$ is less than $I_\parallel$. This means that the tilt plane and **c**-director are oriented in the **E**-field direction.

Figure 2 provides additional evidence for anomalous field-induced orientation of the **c**-director. The wavelength λ_m of the reflectivity minimum for thick films depends on the index of refraction: the larger value of λ_m corresponds to the larger value of n ($\lambda_m = 2Nnd$; see Eq. (1)). At the temperatures below $T_i \approx 91$°C (Fig. 2*a*, DOBAMBC), the wavelength of reflectivity minimum λ_m for the field $\mathbf{E}_\perp$ is greater than λ_m for $\mathbf{E}_\parallel$ (**c**-director oriented perpendicular to the **E**-field). At $T_i \approx 91$°C, the reflection spectra belonging to $\mathbf{E}_\perp$- and $\mathbf{E}_\parallel$-field exchange position (Fig. 2*b*). This interchange of the spectra indicates that at temperatures above $T_i \approx 91$°C the **c**-director is parallel to the field.

We observed anomalous orientation in ferroelectric films with thickness between 12 and some hundreds of layers. For $N > 40$-layer films, T_i was nearly the same as the bulk transition



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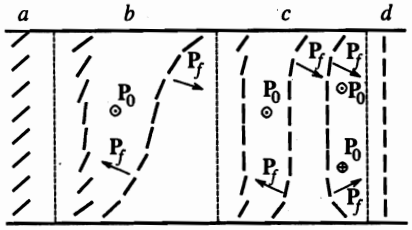

Рис. 4

Fig. 3. Temperature dependence of the optical reflection intensities $E_\perp/E_\parallel$ for films with 2, 5, and 20 smectic layers (λ = 600 nm). Arrows show the behavior of the intensity for a thick film (N = 20) in the temperature range of hysteresis (on heating and cooling), 8SI*

Fig. 4. Orientation of molecules in a smectic film: SmC^* phase (a), S-like orientation of the director near the bulk SmC^*–SmA transition temperature (b), S- and C-like orientation well above the bulk transition temperature (c), SmA phase (d)

temperature (SmC^*–SmA). In thinner films, T_i was shifted to higher temperatures, but could not be precisely determined because of temperature hysteresis. Figure 3 shows the temperature dependence of the relative optical reflection intensities $I_\perp/I_\parallel$ for films 2, 5, and 20 smectic layers thick. An anomalous orientation (c-director is parallel to the field) corresponds to $I_\perp/I_\parallel < 1$. The arrows show the behavior of the relative intensities $I_\perp/I_\parallel$ in the temperature range for hysteresis (on heating and cooling). At temperatures above 90°C, the anomalous orientation is observed in a very weak electric field (< 10 V/cm) without a transition between the two orientations. The temperature range of hysteresis can be reduced by turning an electric field on and off. At high enough fields, no perfectly oriented film is observed because of convection instability [16]. This precludes determining the E-field threshold of reorientation in the temperature range for hysteresis.

Our results can be interpreted with the aid of Fig. 4. Here we indicate the smectic layers in the SmC^* phase (a), SmA phase (d), and the layer structure above the bulk transition temperature (b, c; $T_c > T_b$). The possibility of spatial variation of the tilt angle across the film thickness (Figs. 4b, c) is related to the surface ordering of the smectic layers [1–8]. At high temperatures (Fig. 4c), only some surface layers are tilted. When a free-standing film is cooled, all layers become tilted (Fig. 4b) because of the diverging correlation length ξ of the SmC^* ordering.

The variation of the tilt angle across the film must play an important role for the analyses of the origin of the spontaneous polarization above the bulk transition temperature [10, 11]. The change in molecular tilt angle implies S-shaped bending of the liquid crystal director n (Fig. 4b). This should lead to macroscopic flexoelectric polarization. The polarization density in a nematic liquid crystal is given by [17]

$$\mathbf{P}_f = e_1(\mathbf{n}\,\mathrm{div}\,\mathbf{n}) + e_3[(\mathrm{rot}\,\mathbf{n})\mathbf{n}], \tag{3}$$

where e_1 and e_3 are the flexoelectric constants.

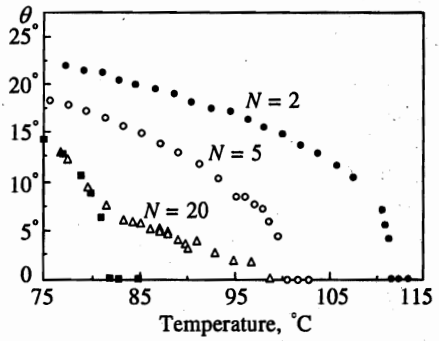

Fig. 5. Temperature dependence of the average tilt for the film thickness 2, 5, and 20 smectic layers. The filled-square symbols are X-ray data for bulk samples (8SI*)

In smectic liquid crystals, other kinds of deformations can cause flexoelectric polarization. However, for our estimate we use Eq. (3). For a bend deformation, the second term is dominant. Using $e_3 = 10^{-11}$ C/m [17] and a variation of the tilt angle from the surface layer to the center of the film $\Delta\theta \approx 0.3$ rad, we obtain from Eq. (3) that $P_f = 10^{-4}$ C/m^2 ($N = 20$). Our estimate shows that above the bulk transition temperature, the flexoelectric polarization in the tilt plane P_f and the bulk ferroelectric polarization in the SmC^* phase P_0 [18] are of the same order of magnitude.

With increasing temperature, two effects take place: first, P_0 decreases and P_f can be greater than P_0; second, the tilt angle at the center of the film becomes zero (or small). The top and bottom parts of the film, from the point of view of the molecular tilt, are not (or weakly) coupled to each other and can be oriented independently. When $P_f > P_0$, a C-shaped orientation (Fig. 4*c*) is favored in an electric field. Reversal of the molecular tilt at the bottom of the film results in reversal of the ferroelectric (P_0) and flexoelectric (P_f) polarization (Fig. 4*c*). For $P_f \gg P_0$ the net polarization is parallel to the **c**-director, and, a $S \leftrightarrow C$ transition leads to a 90°C reorientation of the tilt planes with respect to the direction of the **E**-field.

Optical reflectivity is a convenient vehicle for determining of the average molecular tilt θ [11]. The value I_p/I_0 depends on the reflection n_p index in the tilt plane (Eqs. (1), (2)) and on the layer spacing in the SmC^* phase d_C (Eq. (1)). Considering the molecules to be rigid rods, d_C can be taken as

$$d_C = d_A \cos\theta, \tag{4}$$

where d_A is the layer spacing in the SmA phase. Near the temperature of the bulk phase transition, d_A was determined to be 3.0 nm (X-ray data, 8SI*, 83°C). Using results derived for uniaxial crystals [15], as in the case of ellipsometric studies [3], the relation between θ and n_p is taken to be

$$\cos^2\theta = \frac{n_0^2(n_e^2 - n_p^2)}{n_p^2(n_e^2 - n_0^2)} \quad . \tag{5}$$

When n_0, n_e, and d_A are known, I_p / I_0 alone is sufficient to determine the average tilt angle θ. It should be underscored that $I_p/I_0 = I_\perp/I_\parallel$ for the usual orientation and $I_p/I_0 = I_\parallel/I_\perp$ for anomalous orientation. Equations (1), (4), and (5) (or (2) and (5) for thin films) enable one to determine θ. The values of the average tilt angle θ resulting from the $I_\perp/I_\parallel$ values (Fig. 3) are shown in Fig. 5. Figure 5 also shows the temperature dependence of θ obtained from our X-ray measurements on a bulk sample. At low temperatures, the data for 20-layer film are in good agreement with measurements of the bulk sample. For the 20-layer film the change in the orientation of molecules is observed at an average angle of $\theta \simeq 5$°C. It is clear that the tilt angle is quite small at the center of the film. On the other hand, comparing the

data for films with 2 and 5 smectic layers (Fig. 5), it is obvious that the tilt angle is nonzero at the center of the 5-layer film at all temperatures. This is the reason why we do not observe anomalous orientation in thin films.

In an electric field, Galerne and Liebert [19] observed the orientation of SmO films floating on the free surface of droplets in the isotropic phase. Unlike the SmC^*, the SmO phase has a herringbone arrangement of molecules. In this case, the weak dipole moment results from the reduced polarizability of the aliphatic tips of the first-layer molecules in contact with air [19]. In SmC^* films the polarization P_f could originate from the flexoelectricity.

Adapting the conclusions of Ref. [1] about the SmC^* order to our model we can distinguish «low» and «high» temperatures. At «low» temperatures the tilt angle is nonzero throughout the film ($dN \ll 2\xi$, net polarization perpendicular to the tilt plane). At «high» temperatures the tilt angle is zero at the center of the film (net polarization parallel to the **c**-director). The crossover temperature T^* is defined by $2\xi(T^*) \sim dN$. We can speculate that T_i is defined by $T^*(T_i \sim T^*)$.

In summary, we report an observation of an anomalous orientation of ferroelectric films of 8SI* and DOBAMBC in an electric field. Above the bulk transition temperature the net ferroelectric polarization in thick films is parallel to **c** and the tilt plane. The applied field orients the tilt plane parallel to the electric field. A novel method for determining the tilt angle in ferroelectric films is described.

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