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Optical studies on free-standing films of an achiral smectic liquid crystal

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Employing null transmission ellipsometry and depolarized reflected light microscopy, we have studied two smectic phases, Sm-C_1 and Sm-C_2, of one achiral mesogen. Our results show that Sm-C_1 and Sm-C_2 are the synclinic Sm-C and anticlinic Sm-C_A phases, respectively. We find no evidence to support recent claims that the Sm-C_1 is chiral and ferroelectric [R. Stannarius *et al.*, Phys. Rev. Lett. **90**, 025502 (2003)].

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Rodlike liquid crystal molecules consist of a straight rigid core [1]. In the Sm-C and Sm-C_A phases formed by achiral rodlike molecules, there is a layered structure and the long axes of molecules on average tilt away from the layer normal. The tilt orientations of adjacent layers are the same (synclinic) and opposite (anticlinic), respectively, in the Sm-C and Sm-C_A phases. For a single Sm-C or Sm-C_A layer, due to its symmetry which consists of a two-fold rotational axis and a mirror plane perpendicular to the twofold axis, the spontaneous polarization P_{fe} does not exist. Recently, it has been shown by Link *et al.* [2] that the packing ordering of the polar axis of bent-core molecules [3,4] in the smectic layer can generate a P_{fe} although the forming molecules are achiral. Together with the tilt of the long axis of molecules, domains with different handedness or racemic domains with different properties can form in the B_2 phase [2]. In the past several years, these landmark discoveries have stimulated a lot of research (see, for instance, Refs. [5] and [6]). To date, the chemical structures of most of the achiral bent-core compounds, in whose smectic phases ferroelectricity or antiferroelectricity have been found, have a rigid bent core with at least five aromatic rings. Recently two research groups [7,8] have reported observations of ferroelectricity and chirality in achiral metasubstituted three-ring mesogens. Thick free-standing films were studied by Stannarius *et al.* They concluded that the symmetry of the smectic phases is similar to bent-core compounds rather than conventional rodlike ones [8].

In this paper, we report null transmission ellipsometry (NTE) [9] and depolarized reflected light microscopy (DRLM) [10] investigations on free-standing films of the compound studied in Ref. [8]. The chemical structure is shown on top of Fig. 1. The phase sequence of bulk samples is crystal 65 °C (Sm-C_2 57 °C) Sm-C_1 66.5 °C isotropic [11]. The Sm-C_2 phase is monotropic upon cooling. From NMR studies, the molecular orientation in the Sm-C_1 and Sm-C_2 phases has been found to be synclinic and anticlinic, respectively [11]. The structures of both phases are confirmed by our studies. Moreover, no mirror symmetry breaking has been observed in either phase. Upon cooling from the Sm-C_1 to the Sm-C_2 phase, a series of transitions characterized by a sudden inversion of the tilt direction of single layers [12,13] has been observed. In 7-layer films, a discrete layer-by-layer growth of the anticlinic interface from the surface to interior layers has been identified.

In our NTE, Δ measures the phase difference between the $\hat{p}$ and $\hat{s}$ components of the incident light with wavelength 633 nm to produce linearly polarized transmitted light. The polarization angle of this linearly polarized light is described by Ψ. The azimuthal angle of the rotatable electric field E in the film plane is denoted by α. The diameter of the opening over which films were prepared was 4.5 mm. Details of our NTE are described in Ref. [14]. DRLM is another optical probe that enables us to visualize the c-director of tilted smectic phases in thin free-standing films. The c-director is defined as the projection of the average long axes of molecules onto the layer plane. In our DRLM studies, most films were prepared over a 10×7 mm^2 rectangular or a 4.5-mm-diameter circular hole. In order to reach a large E ($E > 200$ V/cm), films were also pulled over a 2-mm-diameter circular hole. Films were illuminated with monochromatic or white light at nearly normal incidence. The thickness in number of layers (N) of thin films was determined by measuring the reflectivity of the film using a laser beam [15].

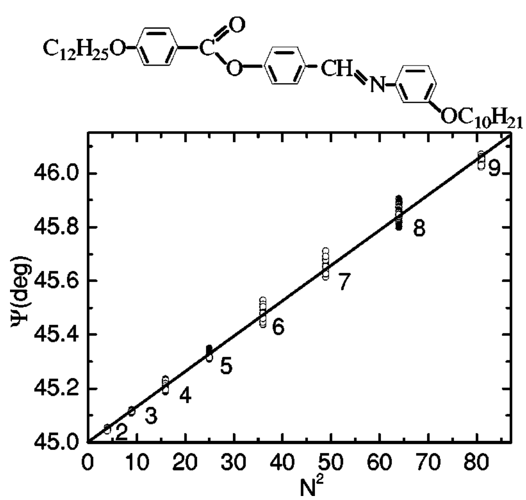

FIG. 1. Ψ vs N^2 for thin films. Open circles are data and the solid line is a fit. N is labeled beside the data. Data from 2-, 4-, 6-, 7-, and 9-layer films were obtained at 55.6 °C, 55.6 °C, 55.6 °C, 60.4 °C, and 62.6 °C, respectively, under rotations of E with $E = 22$ V/cm for the first four films and $E=9$ V/cm for the last one. Data from 3-, 5-, and 8-layer films were collected with $E=0$ at 55.6 °C, 55.6 °C, and 64.2 °C for 3, 3, and 6 h, respectively. On top of the figure is the chemical structure of the compound investigated.

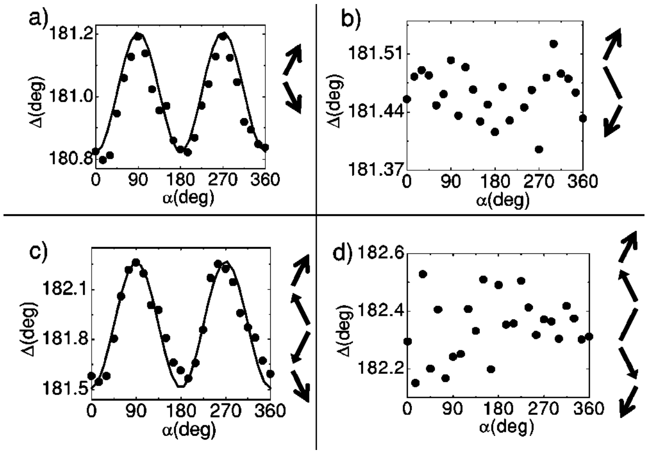

FIG. 2. Δ vs α at 55.6 °C in the Sm-C_2 phase under $E = 22$ V/cm. Data in (a), (b), (c), and (d) are from 2-, 3-, 4-, and 5-layer films, respectively. Symbols are data and the solid lines in (a) and (c) are simulation results. The cartoons depict the tilt structures with tilted bars and the directions of the longitudinal polarization are indicated with arrows.

To determine N of thin films in NTE, films can be approximately modeled as isotropic dielectric media [16]. It is straightforward to show that to the first-order approximation, Ψ is proportional to N^2 [17]. The results from a few thin films are presented in Fig. 1. Although Ψ obtained in the Sm-C_1 and Sm-C_2 phases depends on the orientation of the c-director, its discrete nature as a function of N still allows us to determine the thickness of thin films. In Fig. 1, the straight line is a linear fit to the average of Ψ of each film as a function of N^2. The fitting result is $\Psi = 44.996° + 0.0132° N^2$. Different assignments of N to the films cannot describe the data consistently.

To investigate the structure of the Sm-C_2 phase with DRLM, many films were pulled at 53.3 °C. Under an ac square wave of $E = 7$ V/cm and period of ≈ 20 s, in films with $2 \leqslant N \leqslant 9$, we have observed that even-layer films show ferroelectric response (polar) while odd-layer films do not respond to E (nonpolar). Similar to the observations made by Link *et al.* [18], the net polarization in even-layer films is found to be in the tilt plane. In addition, no evidence indicating that the Sm-C_2 phase is chiral has been observed.

The even-odd layering effect has been obtained in our NTE studies too. Data collected at 55.6 °C from four films are shown in Fig. 2 (we do not present Ψ to save space). For even-layer films, Δ versus α exhibits a 180° rotational symmetry with two peaks at $\alpha = 90°$ and $\alpha = 270°$ [19]. This indicates that the optical unit cell of the Sm-C_2 phase must have a 180° rotational symmetry. For odd-layer films, the absence of correlation between the data and α suggests that there is no detectable polarization. Our results from even- and odd-layer films indicate that the Sm-C_2 phase displays a Sm-C_A structure. The optical unit cell of the Sm-C_A structure consists of two layers. In free-standing films, due to the symmetry breaking at the surfaces, longitudinal polarization exists [18,20]. The direction of the longitudinal polarization is along the long axes of molecules. All the polarizations

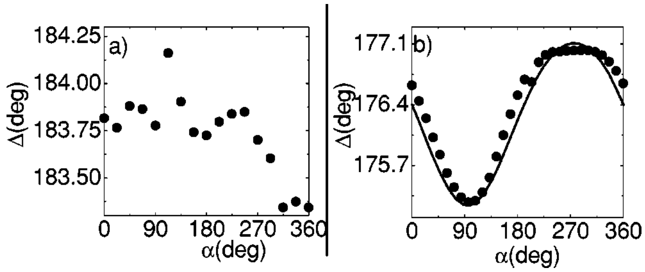

FIG. 3. Δ vs α. Symbols are data and the solid line in (b) is a fit. Data in (a) were taken from a 9-layer film under $E = 9$ V/cm at 61.6 °C in the Sm-C_1 phase of the compound shown at the top of Fig. 1. Data in (b) were collected from a 39-layer film of the compound DOBAMBC under $E = 4$ V/cm at 94.5 °C in the Sm-C^* phase.

point either toward or away from the closer surface. The magnitude of the longitudinal polarization decays from the surface to the interior layers. As the cartoons of Fig. 2 depict, even-layer Sm-C_A films have a net polarization in the tilt plane while odd-layer Sm-C_A films do not [21].

The ellipsometric parameters Δ and Ψ obtained under rotations of E are simulated with the 4×4 matrix method [22]. Each layer is modeled as a uniaxial slab with extraordinary index of refraction (n_e) along the long axes of molecules, and ordinary index of refraction (n_o) along the other two principal axes. In the simulation of Figs. 2(a) and 2(c), the layer spacing, tilt angle, n_e, and n_o are 3.7 nm, 28°, 1.6, and 1.45, respectively. The layer spacing and tilt angle are chosen to be consistent with the results in Ref. [11].

To study the Sm-C_1 phase with DRLM, films were pulled at 63.0 °C. Due to the enhanced surface ordering, 2-layer films were polar and 4-layer films were sometimes polar with the polarization in the tilt plane. The molecular arrangement of the 2-layer film is the anticlinic structure as the cartoon in Fig. 2(a) shows. Sometimes 4-layer films prepared at 63.0 °C were nonpolar. As temperature decreased by ≈ 0.2 K, they became polar with a net polarization in the tilt plane. We believe that 63.0 °C is close to the surface transition temperature window of 4-layer films. Except 2- and 4-layer films, no polarization has been observed from all other films studied. In addition, no evidence indicating that the mirror symmetry is broken in the Sm-C_1 phase has been observed.

No polarization in the Sm-C_1 phase has been detected in our NTE studies either. Typical data under rotation of E from a 9-layer film in the Sm-C_1 phase are shown in Fig. 3(a). The scattering nature of the data indicates that the molecules were not aligned by E. According to Ref. [8], P_{fe} is of the order of 0.5 nC/cm^2. To show our NTE's capability to detect such a small P_{fe}, data from the classical compound p-decyloxybenzylidene-p′-amino-2-methlybutylcinnamate (DOBAMBC) are shown in Fig. 3(b). The data were collected in the Sm-C^* phase close to the bulk Sm-A–Sm-C^* transition. The nature of the data as a function of α shows that the molecules were aligned by E. Note that the strength of E in Figs. 3(a) and 3(b) is of the same order. Assuming a uniform tilt structure with tilt angle of 4.5°, the fitting result in Fig. 3(b) is obtained [23]. From this tilt angle, the magnitude of P_{fe} at this temperature is ≈ 0.7 nC/cm^2 following

Ref. [24]. Thus if there is a P_{fe} of the order of 0.5 nC/cm^2, our NTE should be capable of detecting it. The facts that the longitudinal polarization has been identified to explain the observed polar response and no polarization has been observed from films with different thicknesses in the Sm-C_1 phase strongly suggest that the tilt orientations of adjacent layers of the Sm-C_1 phase are synclinic. Otherwise the longitudinal polarization will not cancel exactly and a polar response should have been observed.

Upon cooling from the Sm-C_1 to the Sm-C_2 phase, a series of transitions has been observed both in DRLM and NTE. In DRLM the transition is characterized by transition fronts which move across the film. In 7-layer films, a nonpolar-polar-nonpolar-polar-nonpolar sequence has been obtained in both NTE and DRLM.

Figure 4(a) shows the temperature dependence of Δ from a 7-layer film with two orientations of E, perpendicular to ($\alpha=90°$) and in ($\alpha=180°$) the incident plane. The two orientations, which are 90° apart, were chosen intentionally to see the transition sequence more clearly. From the data, four transitions can be identified. While the nonpolar response below T_4 and above T_1 is expected for the achiral Sm-C_A and Sm-C structures, the transitions can only be described by sudden inversions of the tilt direction of single layers. The transition on the two surfaces of the film can occur at different temperatures [12]. Although the sequence given in the cartoon is not unique due to the up and down symmetry of the film, among all the possible systematic tilt inversion scenarios this layer-by-layer growth of the Sm-C_A structure from the surface to the interior layers provides the most physically reasonable way to explain the observations. As the cartoons indicate, the longitudinal polarizations cancel exactly at temperatures above T_1, between T_2 and T_3 and below T_4, but not between T_1 and T_2 or between T_3 and T_4. In another study of a 7-layer film with NTE, the four transitions are reproduced. Due to the metastable nature of the intermediate states, the transition temperatures are slightly different from the four temperatures shown in Fig. 4(a).

Figure 4(b) presents the second transition obtained with DRLM. During our observation, the front moved from the left to the right. The film changed from being polar to being nonpolar [25]. The polarization of the two polar states has been observed to be in the tilt plane [18], which is consistent with the tilt inversion transition.

So far, the layer-by-layer growth of the anticlinic interface has been clearly evidenced only in 7-layer films. Under the same experimental procedures with NTE, three and four transitions are identified in 8- and 9-layer films, respectively. Some polar states may be missed if the temperature window of such a state is too small.

In summary, DRLM and NTE have been performed on free-standing films of an achiral metasubstituted three-ring compound. No mirror symmetry breaking has been observed in the Sm-C_1 or Sm-C_2 phase. The Sm-C_1 and Sm-C_2 phases are found to have a Sm-C and Sm-C_A structures, respectively. Our results do not support recent conclusions that the mirror symmetry is broken in both phases and the Sm-C_1 is ferroelectric [26]. Transitions characterized by a sudden inversion of the tilt direction of single layers have been observed upon cooling from the Sm-C_1 to the Sm-C_2 phase. A layer-by-layer growth of the anticlinic interface from the surface to interior layers has been identified in 7-layer films.

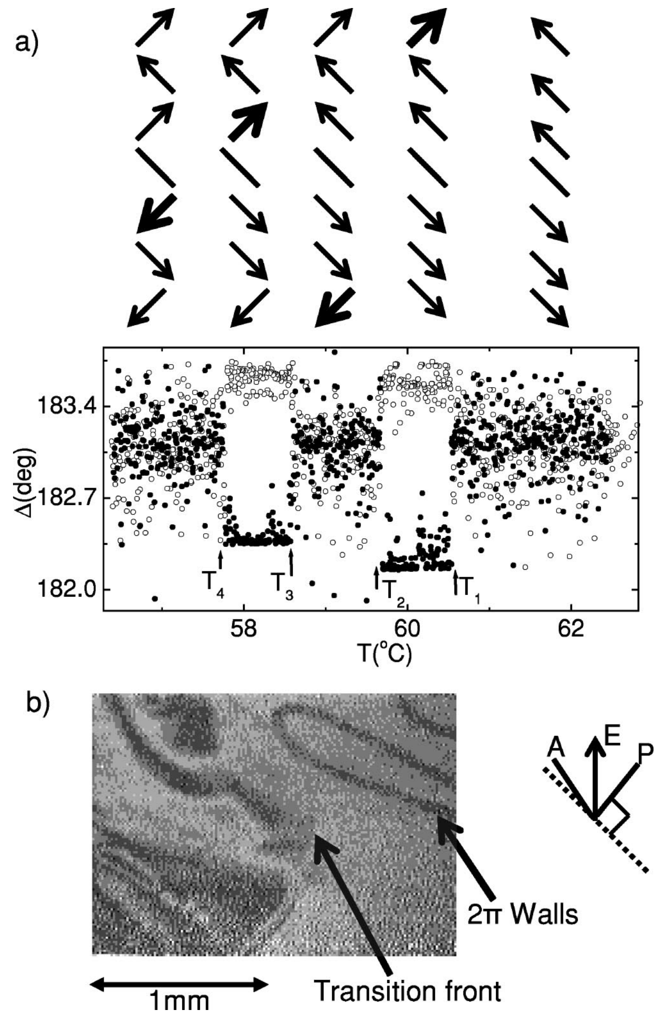

FIG. 4. (a) Δ vs temperature upon cooling at 5.5 mK/min from a 7-layer film with $E=22$ V/cm under two orientations of E. During cooling, the direction of E was switched between 90° (open circles) and 180° (solid circles) every 4 min. Four upward arrows indicate the four transition temperatures. On top of the figure, the cartoons show the tilt structures with tilted bars, the longitudinal polarizations with arrows in corresponding temperature windows. Heavier tilted bars indicate the layers which invert their tilt directions. (b) A DRLM image of a 7-layer film under $E=7$ V/cm during a transition. To the left of the transition front, there is no net polarization and the c-director is not aligned by E. To the right of the front, the c-director is aligned parallel to E and 2π walls can be seen. The direction of E and the transmission axes of the polarizer P and analyzer A are depicted beside the image.

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