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Nonplanar structure of molecular tilt planes in the surface layers of smectic-*A* free-standing liquid crystal films

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We present ellipsometric results from thin free-standing films of one chiral liquid crystal compound. In the bulk Sm*A* range with surface-induced molecular tilt, a nonplanar arrangement of the molecular orientations of the tilted surface layers is found under a small applied electric field.

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For nearly three decades free-standing liquid crystal films have provided a unique context for studying the effects of surfaces and of reduced dimensionality on liquid crystal phase transitions. One such phenomenon is the surface-induced tilt of the molecules in the outer layers of a film at temperatures where the bulk is untilted, i.e., Sm*C*-like surface layers on interior Sm*A*-like layers. In thin films this leads to an increased Sm*C*-Sm*A* transition temperature with decreasing thicknesses. In early work it was assumed that in such a structure the tilts on the opposite surface layers were synclinic, i.e., had parallel molecular orientations [1]. However, recent experiments have revealed anticlinic ordering of the two tilted surfaces [2–4], as well as synclinic ordering. In extensive ellipsometric studies by Johnson *et al.* [5] on compounds showing the Sm*A*-SmC^* transition, it was found that the ordering of the tilted surface layers depended upon at least four physical parameters: temperature, in-plane applied electric field (E), film thickness and spontaneous polarization. However, there is no fundamental reason that the molecular arrangement of tilted surface layers has to be parallel or antiparallel if the long optical pitch for chiral compounds is neglected. In this paper we present the first experimental evidence of nonplanar orientations of tilted surface layers under a small applied E (between 0.081 and 0.6 V/cm).

Null transmission ellipsometry (NTE) was employed to study MDW1397 [6,7] enantiomer in the free-standing film geometry. In our NTE [see Figs. 1(a) and 1(b)] the parameter Δ measures the phase difference between $\hat{p}$ and $\hat{s}$ components of the incident light necessary to produce linearly polarized light after the film. The second parameter Ψ describes the polarization angle of this linearly polarized light. An in-plane smoothly rotatable E is created by eight electrodes uniformly spaced around the hole on the film plate. A 16-bit analog output board provides the voltages for the electrodes with a resolution of 0.002 V. Simulation of E shows that the direction of E in the hole is uniform except in the vicinity of the electrodes. Near the center of the opening, the accuracy of the strength of E is better than 5% [8]. For a film with a net in-plane polarization, the whole structure can be rotated smoothly about the layer normal by rotating E. The angle α [see Fig. 1(c)] denotes the angle between E and the incident plane of the laser light. Details of our NTE system are described in recent papers [8,9]. The molecular structure of MDW1397 is depicted on top of Fig. 2. From our optical microscopy studies the bulk sample exhibits the following phase sequence upon cooling: isotropic (81.9 °C) Sm*A* (71.3 °C) SmC^* (64.1 °C) SmC_A^*.

Films with thickness ranging from two to 14 layers have been investigated at various temperatures. Two typical experimental runs were conducted. (a) Temperature was decreased in the bulk Sm*A* range with steps of 1.0 K or 2.0 K. At each temperature, the strength of E was increased. For each value of E, the direction of E was rotated over 360° with steps of 22.5°. An opposite sense of rotation was also performed to check reproducibility. (b) Data were taken while temperature was ramped down through the bulk Sm*A* range with two opposite orientations of E perpendicular to the incident plane ($\alpha = 90°$ or $270°$).

In the bulk Sm*A* range, similar to the results of Johnson *et al.* [5], with $E > 0.6$ V/cm, the dependence of the anticlinic and synclinic arrangement upon film thickness, temperature, and strength of E was observed. However, with small E we have discovered a new state with a different arrangement of the tilted surface layers.

Figure 2 presents Δ versus α data (symbols) and fits

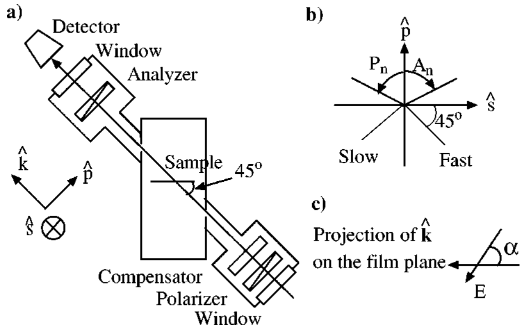

FIG. 1. (a) shows our NTE setup schematically. The directions of $\hat{p}$, $\hat{s}$ and propagation of the laser light $\hat{k}$ are also depicted. The compensator is a quarter-wave plate. The orientation of the compensator and the transmission axes of the polarizer and analyzer in the $\hat{p}$ and $\hat{s}$ plane are shown in (b). In our setup, the orientation of the compensator is fixed. At null, $\Psi = A_n$ and $\Delta = -2P_n + 90°$. The angle α of E is shown in (c).

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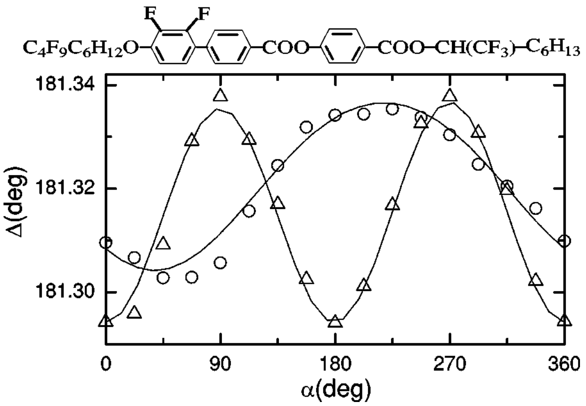

FIG. 2. α dependence of Δ from a four-layer film at 81.7 °C. Symbols are data and solid lines are fits. The strength of E is 0.14 and 5.4 V/cm for circles and triangles, respectively.

(solid lines) for a four-layer film [10]. For this film, rotations of E have been conducted using five values of E, 0.081, 0.14, 0.19, 0.24, and 5.4 V/cm at three temperatures, 81.7 °C, 80.7 °C, 79.7 °C. Δ versus α data with $E=0.14$ V/cm and 5.4 V/cm at 81.7 °C are shown in Fig. 2. The surface arrangement with $E=5.4$ V/cm is anticlinic, which is different from the state with $E=0.14$ V/cm. Similar data were obtained at all three temperatures for the four small fields and $E=5.4$ V/cm. The transition from the new state to the anticlinic state as E increased at different temperatures was also observed in all films being studied. The simulations are discussed below.

Shown in Fig. 3 is the α dependence of Δ from a 14-layer film at 76.4 °C. Rotations of E were performed using five values of E: 0.16, 0.24, 0.32, 2.7, and 24 V/cm. To conserve space, only rotations under $E=0.16$, 2.7, and 24 V/cm are shown in Figs. 3(a), 3(b) and 3(c), respectively. The surface arrangement is anticlinic and synclinic for $E=2.7$ V/cm and 24 V/cm, respectively. The state with $E\leqslant 0.32$ V/cm is different from the anticlinic and synclinic. The three states as E increased were also observed at 78.4 °C and 80.4 °C.

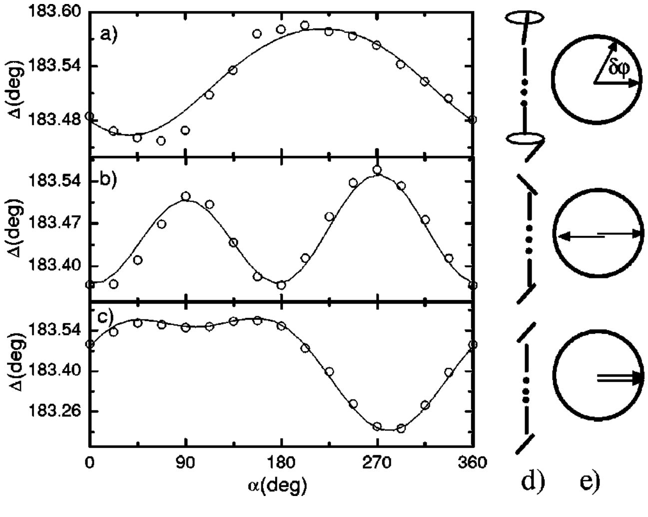

FIG. 3. (a)–(c) Δ versus α data (symbols) and fits (solid lines) from a 14-layer film at 76.4 °C. The strengths of E for (a), (b), and (c) are 0.16, 2.7, and 24 V/cm, respectively. (d) shows a cartoon of the corresponding tilt profiles used to model the data. The two ellipses in the cartoon for the nonplanar state depict the tilt cones. Cartoon (e) displays the corresponding arrangement of the c directors of the two tilted surface layers. The c director is defined in the text. In (d) and (e), only the two outermost surface layers are shown to be tilted. Extrapolation of the surface tilt into the interior layers is not drawn for clarity.

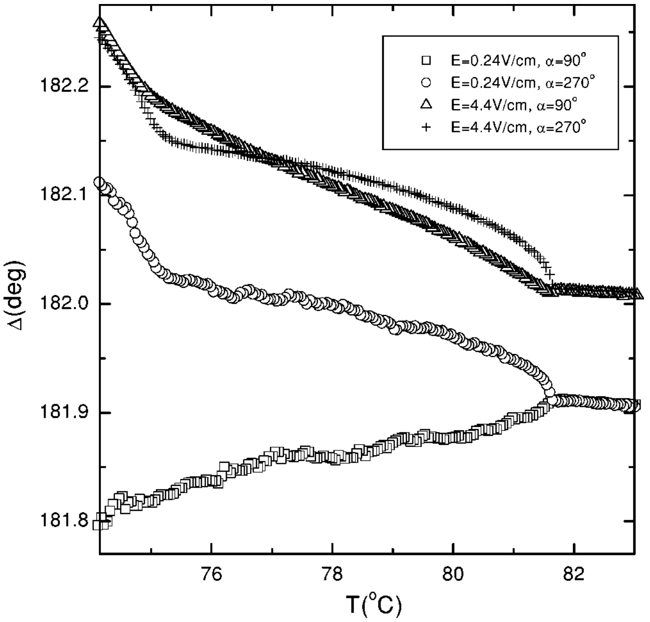

FIG. 4. Temperature dependence of Δ from a six-layer film with two values of E under opposite directions of E upon cooling. The cooling rate was 80 mK/min for all the data. For clarity data with $E=4.4$ are shifted up by 0.1°.

Both synclinic and anticlinic structures display distinct features in the Δ versus α curve. In films with an anticlinic arrangement, the net polarization is mainly due to the flexoelectric polarization (P_{fl}) which yields E in the tilt plane [5]. Because the average tilt angle of the optical axis is approximately zero for thin films Δ shows a 180° rotational symmetry as a function of α. The second distinct feature is that Δ shows two peaks at $\alpha=90°$ and $\alpha=270°$ [see the data in Fig. 2 with $E=5.4$ V/cm and Fig. 3(b)]. On the other hand, in films with a synclinic arrangement, spontaneous polarization (P_{fe}) (for chiral compounds) determines the normal of the tilt plane to be parallel to E [5], which yields a large difference of Δ between $\alpha=90°$ and $\alpha=270°$ [see Fig. 3(c)]. The data acquired using a low field do not have the right symmetry or peaks at the correct locations to support an anticlinic structure or a synclinic structure. Thus, the surface arrangement with low fields must be nonplanar.

The existence of the nonplanar state with small fields is also supported by our data from temperature ramps. Figure 4 shows Δ from a six-layer film upon cooling from high temperature with no tilted surface layers ($T>81.7$ °C). The transition to the SmC^* phase occurred at 74.1 °C [11]. Data below this temperature are not shown for clarity. The anticlinic arrangement for $E=4.4$ V/cm is recognized from small difference of Δ with $\alpha=90°$ and 270°. Data with $E=0.24$ V/cm show the nonplanar state in the temperature window between the state where no surface layers are tilted and SmC^*. The nonplanar state was also observed from 3-, 11-, and 12-layer films with small fields using similar temperature ramps. For the 3-, 6-, and 11-layer films, the two states were also confirmed under rotations of E fields.

Two-layer films were studied in detail under rotations of E and temperature ramps. If a new state besides the synclinic and anticlinic is observed, it will give the most direct evidence for the nonplanar state. With small E fields (between 0.081 and 0.40 V/cm) the new state has been observed. However, data were irreproducible from different loadings of sample. Currently we do not have a good explanation for the observed irreproducible phenomenon in two-layer films.

While the behavior of the first order transition between the anticlinic and synclinic state as E increases or temperature changes has been characterized (see, for instance, [4,5]), the transition between the nonplanar state and the anticlinic is unclear. For three-, four-, and five-layer films, we have conducted E ramps with α being set to 90° and 180°, since with $\alpha = 90°$ Δ from the nonplanar state is smaller than Δ from the anticlinic state and the opposite occurs with $\alpha = 180°$. By doing so, we find that the critical E is around 0.6 V/cm at the temperatures we studied. From our E ramp data, we cannot tell if the transition is continuous or discontinuous. Further studies are under way to characterize the transition between the nonplanar and anticlinic state as well as the dependence of the critical E upon thickness and temperature.

Simulations of our ellipsometric data under rotations of E are done using the 4×4 matrix method [12]. Each tilted layer is modeled as a uniaxial slab with an extraordinary index of refraction (n_e) along the long axis of molecules, and ordinary index of refraction (n_o) along the other two principal axes. By pulling ~20 films of thickness varying from 20 to 200 layers at 77.4 °C without an applied E [13], we measured n_o, n_e, and layer spacing to be 1.450 ± 0.001, 1.544 ± 0.002, and 3.310 ± 0.005 nm, respectively [5,14]. The projection of the tilt direction onto the layer plane is called the c director. For synclinic and anticlinic arrangements, the c directors of the two outermost surface layers are parallel and antiparallel, respectively. For the nonplanar state, the c directors are neither parallel nor antiparallel. The tilt profile and the two c directors of the three structures are depicted in Figs. 3(d) and 3(e) schematically. For the simulation in Fig. 2, only the two outermost surface layers are assumed to be tilted. The tilt angle of surface layers (θ_s) is 12° for the data with $E = 5.4$ V/cm. θ_s and the azimuthal difference between the two c directors of the surface layers ($\delta\phi = \phi_{top}$-ϕ_{bottom}) are 3.5° and 64°, respectively, for the data with $E = 0.14$ V/cm. For the 14-layer film, the tilt angle is assumed to decay exponentially from the two outermost surface layers to the interior layers over an extrapolation length (λ) [2,15]. For the nonplanar state in Fig. 3(a), the progression of the azimuth of the layers is assumed to be linear. In the simulations of the data shown in Fig. 3 for the three states the following values of θ_s and λ (in number of layers) are used: (a) 9° and 1, (b) 24° and 1, (c) 24° and 1. $\delta\phi$ for the nonplanar state is 67°. The optical pitch is much larger than the film thickness studied and is neglected in all the simulations.

In the simulations, molecules were assumed to be perfectly aligned by E. This is a good approximation for the data from the anticlinic and synclinic state. For the nonplanar state, with small E fields, thermal fluctuation of the structure around E should be taken into account. However, this does not affect our conclusion that the molecular arrangement of the tilted surface layers is nonplanar with low fields because the fluctuation around E yields a reduction of the birefringence (n_e-n_o). It does not affect the symmetry or the location of the maximum or minimum of Δ in α space. However, this may explain our simulation result that θ_s in the nonplanar state appears to be smaller than θ_s in the anticlinic and synclinic state [16].

In principle, the orientation of the nonplanar state under E should be determined by the net in-plane polarization. However, the net polarization of a film in the nonplanar state consists of at least two competing contributions, namely, P_{fe} and P_{fl}. Currently, we do not have sufficient information to estimate the magnitude of P_{fe} and P_{fl} as well as the orientation of P_{fl}. Consequently, unlike the planar state, the α orientation for the nonplanar structure can only give relative but not absolute information concerning molecular tilt orientation. In the simulation, the choice of a positive $\delta\phi$ is arbitrary. Another set of solutions to the nonplanar structure is possible if $\delta\phi$ is chosen to be negative.

In recent depolarized reflected light microscopy (DRLM) [17] studies of MDW1397 in the free-standing film geometry, Chao *et al.* [6] reported that in the bulk SmA range, the ground state of the surface arrangement in films thinner than 17 layers was anticlinic. The anticlinic ground state was also reported by Link *et al.* from DRLM observations on TFMHPOBC enantiomer [4]. In their studies, the ground state was obtained by extrapolating observations with moderate E fields. However, oxbservations become intrinsically difficult for DRLM if E is small (less than 0.6 V/cm). For MDW1397, we have demonstrated that the nonplanar surface state is found under low E fields within the bulk SmA temperature window of various film thicknesses ranging from 2 to 14 layers. For TFMHPOBC, our NTE investigations yield similar results as from MDW1397 with low fields. Our work on TFMHPOBC is in progress. As shown in Fig. 3, for the 14-layer film, increasing E can drive the surface arrangement from the nonplanar state to the anticlinic, then to the synclinic state [18]. Our results suggest that the nonplanar state results from a strong chiral symmetry breaking. Upon increasing E, the stabilization of an anticlinic structure is most likely due to the coupling between the flexoelectric polarization and the E field [19].

So far more than 20 different liquid crystal compounds have been investigated by our NTE. We have not observed the nonplanar structure in other compounds except TFMHPOBC. The compound MDW1397 possesses two unique features: large spontaneous polarization and one partially fluorinated tail. This led us to carefully repeat low-field ellipsometric studies on four compounds. Two of them have large spontaneous polarizations in the tilted smectic phase. The other two are partially fluorinated. In addition, a common feature in the molecular structure of MDW1397 and TFMHPOBC is that there is a CF_3 group attached to the chiral center. We have studied another compound [20] which has the same feature and shows SmA-SmC^*-SmC_A^* transitions. However, for all these compounds, molecules could not be aligned well with small fields ($E<0.6$ V/cm), thus making it impossible to carry out rotations of E and temperature ramps. Further studies are ne eded to clarify the question of why these particular compounds, MDW1397 and TFMHPOBC, can be aligned well by small fields and exhibit the nonplanar state.

In conclusion, our detailed ellipsometric investigations on MDW1397 free-standing films of various thicknesses at different temperatures under small strengths of E have revealed a nonplanar arrangement of the tilted surface layers in the bulk SmA range. Our data differs from the previously reported anticlinic ground state obtained under moderate strengths of E.

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[10] Ψ is not presented in this paper. Usually changes in Ψ are much smaller than those in Δ. Moreover, the symmetry property of Ψ versus α curve is not as clearcut as that of Δ versus α curve.

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[16] Since measurements of θ_s and λ for the synclinic and anticlinic state are not the purpose of this paper, error bars for them are not given. For the nonplanar state, additional parameters are needed to take care of the fluctuation. Thus error bars are not given either.

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[18] The maximum strength of rotating E we applied was 40 V/cm. It was unable to induce the anticlinic-synclinic transition for very thin films. The transition was observed by Chao *et al.* with a larger strength of E [6].

[19] Andreeva *et al.* proposed that the coupling between E and the larger of P_{fl} and P_{fe} determines whether the structure is anticlinic or synclinic [2].

[20] The long alkyl tail ($C_5H_{10}OC_2H_5$) attached to the chiral center of this compound is different from that of MDW1397 and TFMHPOBC.