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Anticlinic structures at the surface of freely suspended smectic-*C* films

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Ellipsometric studies have been conducted on freely suspended films of chiral smectic liquid crystals. In the temperature range of the smectic-*C* phase, we observe sharp steplike changes of the ellipsometric quantity Δ indicating sudden inversions of the molecular tilt direction in single smectic layers near the surface. These tilt inversion transitions are strongly hysteretic with temperature differences up to 10 K between heating and cooling runs. Although the films possess two identical free surfaces, metastable states occur in which the tilt is inverted at only one surface. [S1063-651X(98)51302-5]

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Smectic liquid crystals can form freely suspended films which consist of an integral number (between several thousands and only two) of molecular smectic layers, the layer planes being parallel to the two free surfaces. Besides studies of phenomena related to reduced dimensionality and interfaces (for recent reviews, see [1,2]), freely suspended films enable structural studies [3] of the recently observed smectic-*C* (Sm-*C*) phases possessing antiferroelectric and ferrielectric properties.

In the Sm-*C* phase, in each layer the rodlike molecules are tilted with their long axis with respect to the layer normal. Most compounds show at higher temperatures the smectic-*A* (Sm-*A*) phase in which the molecules are not tilted. When the molecules are chiral, a spontaneous electric polarization $\vec{P}_s$ is present in the Sm-*C* phase in a direction along the layer planes and perpendicular to the tilt direction [4]. Whereas in the usual ferroelectric Sm-*C* phase the tilt direction, and thus the $\vec{P}_s$ direction, is essentially the same in neighboring layers [5], a number of new Sm-*C* phases possessing different tilt structures and antiferroelectric or ferrielectric properties was found in recent years [6]. Among these new phases, only the structure of the antiferroelectric Sm-C_A phase is clarified to date: in this phase the tilt and $\vec{P}_s$ direction alternates by $\pm 180°$ when going from layer to layer, thereby building up an anticlinic tilt structure. Anticlinic tilt structures of a different type have been recently observed for molecules possessing a strongly curved shape and in certain polymer-monomer mixtures [7].

In this paper, we report the occurrence of anticlinic tilt structures at the free surface of freely suspended ferroelectric Sm-*C* films. These structures develop with decreasing temperature by tilt inversions in single layers near the surface. The tilt inversion transitions possess a pronounced thermal hysteresis with heating-cooling differences of 10 K and more (at temperature rates of the order of 0.1 K/min) which is quite unusual for transitions between smectic phases. Another unusual observation is the occurrence of states in which the films have lost their structural symmetry with respect to their center plane. Although the films possess two identical free surfaces, we observed several times that a tilt inversion occurred at one surface at a temperature different from that at the second surface.

Most results of the present study concern the compound MHPOOCBC (Fig. 1), which shows the bulk phase sequence isotropic 104 °C Sm-*A* 87 °C Sm-*C*. This compound is reported [8] to show a transition to a ferrielectric phase (Sm-C_γ) at 42 °C; however, in our sample, crystallization occurs before this phase is reached.

Freely suspended films are drawn in the Sm-*A* phase us-

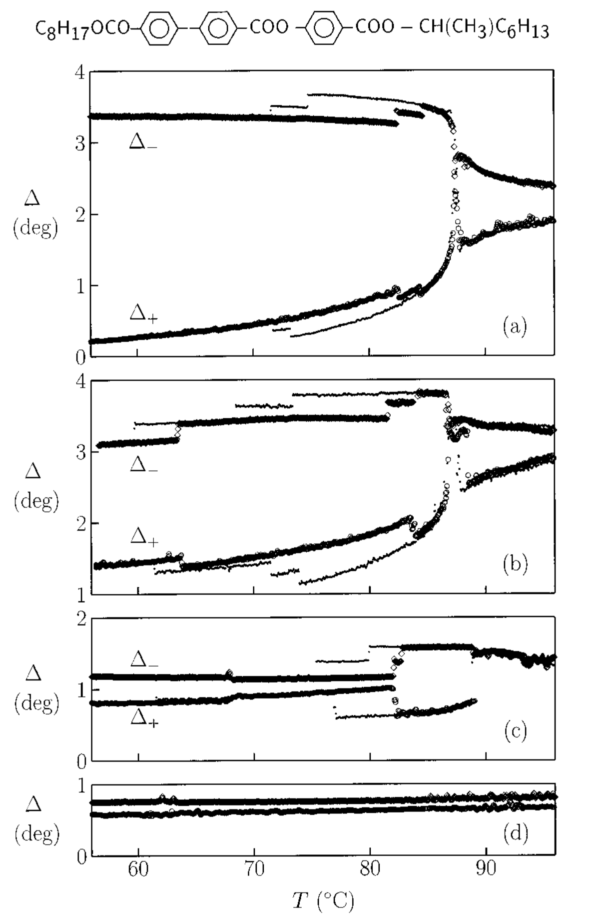

FIG. 1. Temperature dependence of Δ for freely suspended films of MHPOOCBC; ○: Δ_+, heating run, ◇: Δ_-, heating run, the corresponding cooling runs are given by the small dots. The film thicknesses are 22 (a), 15 (b), 5 (c), and three layers (d).

ing a rectangular variable-surface frame described in [1]. The area of the films is approximately 5×10 mm^2. Information about the molecular tilt in the films is obtained by ellipsometric measurements; details about our setup can be found in [9]. We determine the ellipsometric quantities Δ and Ψ [10] which describe the polarization of a laser beam ($\lambda=633$ nm) which transmits the film at an angle of incidence of 45°. The determination of the film thickness on the base of the measured Δ and Ψ values is described in [9].

Whereas Ψ is almost independent of a tilt of the optical axis, the value of Δ shows a specific relation to both the magnitude and the direction of the tilt of the optical axis of the film [9]. A weak dc electric field (8 V/cm) is applied along the film plane in order to predetermine the direction of the molecular tilt in the ferroelectric Sm-*C* phase. In our experimental geometry, the molecules tilt within the plane of incidence, depending on the field polarity, either away from or towards the incident laser beam giving rise to values Δ_+ and Δ_-, respectively. The difference $(\Delta_- - \Delta_+)$ is a measure of the average tilt angle of the optical axis of the film [9,11]. For each film at least four runs are successively conducted during which the temperature is changed at a constant rate typically between 0.05 and 0.1 K/min: after the constant dc field is applied we start with a cooling run, which is followed by a heating run. Then, the field polarity is inverted and again a cooling and a heating run is conducted.

Figure 1(a) shows results for a 22-layer film of MHPOOCBC. At high temperatures ($T>87$ °C), where in bulk the Sm-*A* phase exists, we observe nevertheless a difference between Δ_+ and Δ_- which results from tilted layers at the surfaces. The occurrence of tilted surface layers in the bulk Sm-*A* temperature range is a common behavior of compounds possessing a Sm-*A* – Sm-*C* transition [11,12]. In the case of MHPOOCBC the surface layers remain tilted up to the bulk transition to the isotropic phase. At the bulk Sm-*A* – Sm-*C* transition temperature (87 °C), there is a sudden change of the Δ values so that the difference $(\Delta_- - \Delta_+)$ becomes small for a narrow temperature interval before it shows a large increase immediately below 87 °C where obviously all layers of the film become tilted. A further decrease of temperature leads to a smooth increase of $(\Delta_- - \Delta_+)$ until, around 73 °C, the Δ curves show a sharp step leading to a decrease of $(\Delta_- - \Delta_+)$. A second step of same size occurs at 2 K (Δ_+ curve) or 3 K (Δ_- curve) below the first step. Then, $(\Delta_- - \Delta_+)$ increases smoothly down to 55 °C where we stopped the run (below 50 °C, crystallization occurs). The heating runs show the same sequence of two steps in the Δ curves but at a temperature about 10 K above that of the cooling runs.

A 15-layer film of MHPOOCBC [Fig. 1(b)] shows essentially the same behavior with two differences: the temperature range near the bulk Sm-*A* – Sm-*C* transition, where the difference $(\Delta_- - \Delta_+)$ becomes small or even vanishes, is considerably larger (≈ 2 K), and around 60 °C an additional step occurs in the Δ curves. Concerning the behavior near the bulk Sm-*A* – Sm-*C* transition, we have presently no structural model that could explain the experimental observations; all we can say is that the temperature range, in which the difference $(\Delta_- - \Delta_+)$ is small or zero, considerably increases with decreasing film thickness. In films thinner than about ten layers, we do not observe above the Sm-*C* phase the Sm-*A* phase with tilted surface layers anymore but only this state of unknown structure [Fig. 1(c)]. Further studies are needed to clarify this behavior.

In a five-layer film of MHPOOCBC [Fig. 1(c)] the steps and the hysteresis are still present. Note that sometimes the sequence of two steps, separated by a few K, can appear as one single step possessing a height corresponding to the sum of the two subsequent steps [Fig. 1(c), cooling curve of Δ_+ at 76 °C]. A three-layer film [Fig. 1(d)] does not show any steps and its structure does not change with temperature, there is small difference between Δ_+ and Δ_- in the whole temperature range.

In summary, the observed steps in the Δ curves show the following properties: In subsequent runs (either heating or cooling) of a given film the steps appear approximately, but in most cases not exactly, at the same temperature. Between heating and cooling runs exists always a large thermal hysteresis. The steps occur frequently as a pair separated by a few K, sometimes, especially in heating runs, the pair is replaced by one single step possessing double height. In most cases, just two steps are observed in the experimentally studied temperature range; in some cases, however, one or at most two additional steps occur at low temperatures. Thermal hysteresis and the reduced reproducibility of the step temperatures indicate that these steps show the characteristics of strong first-order transitions which need some kind of nucleation to occur.

In the following we will argue that the mostly observed sequence of two steps corresponds to the inversion of the tilt direction in two single smectic layers which are located each at one surface. Probably because of nucleation effects, the tilt inversion can occur at each surface at a slightly different temperature. That we observe a phenomenon located at the surfaces can be concluded from the fact that the number of steps does not scale with the film thickness. In most films we observe just two steps and the few cases, where one or two additional steps occur at lower temperatures, do not show a discernable relation to the film thickness. Thus, the observed behavior cannot be a property of the interior layers of the films.

To support the hypothesis that the steps in the Δ curves result from tilt inversions in single layers, we calculate the Δ values which would result from corresponding model films. We make this model as simple as possible and assume that the magnitude of the tilt is the same in all layers of a given film and that its temperature dependence is described by a simple power law. We fit the parameters of this model to the experimental Δ values measured in the temperature range of the Sm-*C* phase (i.e., the range between the first step and ≈ 87 °C) assuming that the tilt direction is the same in all layers and perfectly aligned by the external d.c. field. We then invert at the temperature where a step occurs the tilt direction in one or two layers of our model film in order to simulate the Δ steps. Indeed we achieve a good agreement between the experimentally observed steps in the Δ curves and the calculated steps resulting from the simple model.

The details of the calculation of Δ_+ and Δ_- are described in [13]. Briefly, a given model N-layer film is described by $2N$ values θ_i and ϕ_i, which give magnitude and azimuthal direction of the tilt of the dielectric tensor in the ith layer.

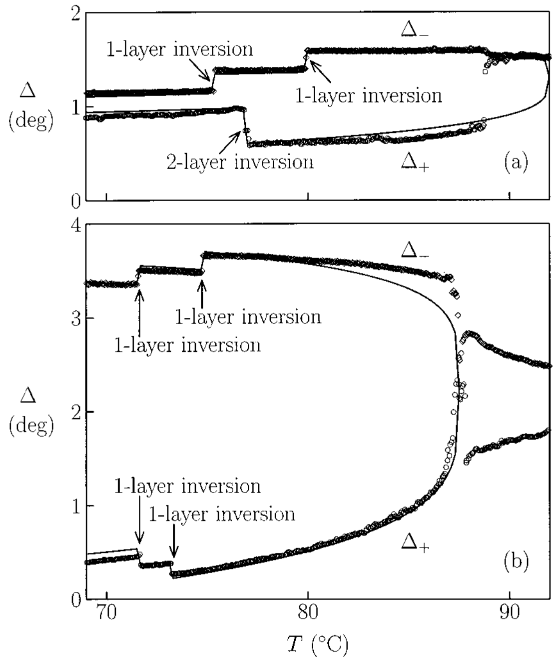

FIG. 2. Temperature dependence of calculated (solid lines) and measured (○/◇ symbols) Δ values for the five-layer (a) and 22-layer film (b) of MHPOOCBC (shown are the cooling runs).

The dielectric tensor of a single layer is considered as uniaxial (neglecting the weak biaxiality of the Sm-*C* structure) possessing eigenvalues $\epsilon_\perp$ (twofold) and $\epsilon_\parallel$. In our simple model, all θ_i are described by the same power law and the values of ϕ_i amount to either 0° or 180°. Then, an average dielectric tensor $\overline{\boldsymbol{\epsilon}}$ is calculated which is assumed to represent the optical properties of the whole film. The values of Δ_+ and Δ_- are then calculated using the three eigenvalues of $\overline{\boldsymbol{\epsilon}}$ and the angle between the principal axis of $\overline{\boldsymbol{\epsilon}}$ and the film normal as described in [13].

For MHPOOCBC, the dependence of Δ and Ψ on the film thickness leads to values $n_\perp = 1.44$, $n_\parallel = 1.625$, and $d = 3.2$ nm (thickness of a single untilted layer). These values are used for the calculation of Δ_+ and Δ_- resulting from a given set of θ_i and ϕ_i values.

In Fig. 2(a) measured and calculated Δ values are compared for the five-layer film of MHPOOCBC; all θ_i are assumed to vary with temperature as $\theta_i = 15° \ (T_c - T)^{1/4}$ with $T_c = 92$ °C [14], and all ϕ_i are set to zero for $T > 80$ °C (Δ_- curve) or $T > 76$ °C (Δ_+ curve). The two steps in the Δ_- curve are modeled by setting one ϕ_i value to 180° at 80 °C and a second ϕ_i to 180° at 75 °C. The step in the Δ_+ curve is modeled by setting two ϕ_i values to 180° at 76 °C. The agreement between calculated and measured step heights is almost quantitative which is a strong support that we are really observing tilt inversions in single layers.

In the same way we have modeled the Δ_+ and Δ_- curves of the 22-layer film [Fig. 2(b)]. The only change in the model parameters, apart from the film thickness, consists of a slight change of the temperature dependence of the tilt magnitude, we used for the 22-layer film $\theta_i = 12.5° \ (T_c - T)^{1/4}$ with $T_c = 87.5$ °C. There is still a fair agreement between calculated and measured step heights, the magnitude of the calculated steps is, however, somewhat larger than observed experimentally. Indeed, the measured step heights decrease with increasing film thickness, in a 100-layer film the steps in the Δ curves have almost completely vanished. This does not mean that the tilt inversions have dissappeared; rather, it is probably a result of the helical superstructure which is present in thick Sm-*C* films and strongly reduces the optical effect of a tilt inversion in a single layer: If in a 100-layer film the ϕ_i values vary with increasing *i* from $\phi_1 = 0°$ to, say, $\phi_{100} = 180°$, the average dielectric tensor is almost not affected if one ϕ_i is changed by 180° (contrary to the untwisted case where all ϕ_i have the same value). The difference between Δ_+ and Δ_- observed in the three-layer film [Fig. 1(d)] can be reproduced by the model if we assume for the whole temperature range a structure consisting of two layers tilted in a direction opposite to the third layer.

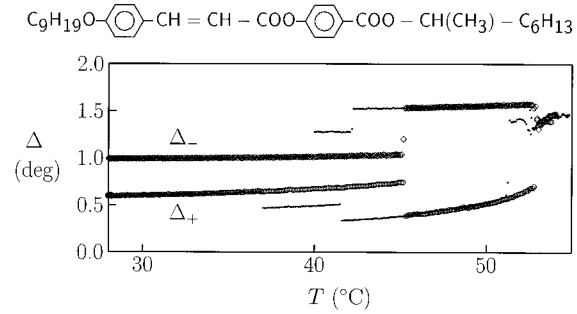

FIG. 3. Temperature dependence of Δ for a freely suspended six-layer film of DAF9; ○: Δ_+, heating run; ◇ : Δ_-, heating run. The corresponding cooling runs are given by the small dots.

We have observed the behavior found in MHPOOCBC in a second compound, abbreviated in the following as DAF9 (Fig. 3). The bulk phase sequence of DAF9 is isotropic 56 °C Sm-*A* 49 °C Sm-*C*. Below ≈30 °C a phase of unknown structure possessing antiferroelectric properties appears [15]; however, we observe tilt inversion steps in the Δ curves well within the temperature range of the ferroelectric Sm-*C* phase, as examplified for a six-layer film in Fig. 3. Although the molecular structure of DAF9 differs considerably from that of MHPOOCBC, the behavior concerning the tilt inversion steps is completely the same. On the other hand, the tilt inversion steps do not occur in the antiferroelectric compounds studied by us previously in freely suspended films [3]. Thus, at present we cannot decide if we observe a more general behavior or not.

The arguments presented above indicate that the observed steps in the Δ curves result from tilt inversions in single smectic layers but they do not give a hint concerning the physical origin of this behavior. Obviously, close to the surfaces interactions are enhanced which favor the formation of anticlinic layer-layer interfaces (antiparallel tilt directions in neighboring layers). Most probably, the tilt direction is inverted in the toplayer (first layer at the surface) creating one such anticlinic layer-layer interface. It might be that not the toplayer but the adjacent layer is inverted, because then not only one but two anticlinic interfaces are produced. It is, however, not possible to distinguish these two cases by ellipsometry: In the model used for the calculation of the step height it is completely arbitrary in which layer the tilt direction is inverted since we take the average across the film. If we treat the film as a multilayer system and calculate its optical properties by the matrix method [16] we can estimate the difference between different tilt patterns producing the same average tilt: For a five-layer film of MHPOOCBC with a tilt magnitude of 30° in each layer, the difference in Δ, between a layer-by-layer alternating structure and a structure with the three interior layers tilted in a direction opposite to the two toplayers, is of the order of 0.0005° and thus beyond the experimental resolution.

In conclusion, we have reported a kind of tilt inversion transition which occurs in single smectic layers near the surface of freely suspended ferroelectric Sm-*C* films. These transitions show a pronounced thermal hysteresis and can occur at different temperatures at each surface indicating the presence of a nucleation process. Our results could be seen as a partial wetting of the ferroelectric Sm-*C*–vapor interface by an antiferroelectric phase. Generally, it is observed at freely suspended film surfaces that near a phase transition the low-temperature phase appears in the surface layers already above the bulk transition temperature [12,17]. The behavior near a transition from the ferroelectic Sm-*C* phase to an antiferro- or ferrielectric phase is, however, not clear. In some cases, the free surface even seems to favor the high-temperature (ferroelectric Sm-*C*) phase [18]. Thus, the physical origin of the tilt inversion is still to clarify.

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