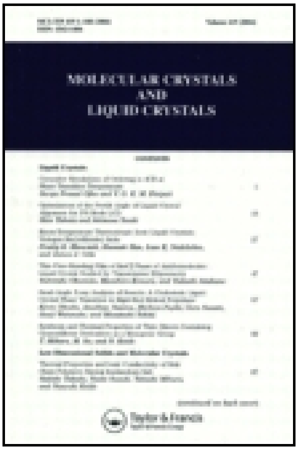

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Anomaly in Layer Ordering and Electro-Optic Properties of Smectic a Liquid Crystals

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To cite this article: Sin-Doo Lee, Jae-Hoon Kim, J. S. Patel & J. W. Goodby (1993): The Anomaly in Layer Ordering and Electro-Optic Properties of Smectic a Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 227:1, 39-48

To link to this article: http://dx.doi.org/10.1080/10587259308030959

Mol. Cryst. Liq. Cryst. 1993, Vol. 227, pp. 39–48
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Printed in the United States of America

THE ANOMALY IN LAYER ORDERING AND ELECTRO-OPTIC PROPERTIES OF SMECTIC A LIQUID CRYSTALS

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Abstract We have observed the deviation of the layer normal from an easy axis created by a unidirectional rubbing in the smectic A phase of a ferroelectric liquid crystal. The magnitude of the observed layer tilt is substantially larger than what has been previously reported. This larger tilt can be partially understood in terms of the surface electroclinic effect, but molecular chirality as well as the nature of surface smectic ordering should be taken into account in completely describing the layer tilt.

INTRODUCTION

It is widely known that rubbed-polymer films can be used to preferentially oriented liquid crystal (LC) molecules in a unique direction because of the anisotropy in the surface forces created by the rubbing process.[1] The surface interactions specific to an interface determine not only the nature of the surface induced ordering[2–4] but also the performance of LC-based devices. In a nematic LC which is characterized only by orientational order, the average molecular orientation in the bulk is aligned along the rubbing axis. However, in smectic LCs which are characterized by both positional and orientational order, it has been recently found that the layer normal often deviates from the rubbing axis.[5–7] Although the surface electroclinic (EC) effect[8–10] has been used to partially explain this deviation, a complete picture of the phenomenon is still lacking.

In this paper we report results for the unusual growth of the smectic layers, highly tilted away from the rubbing axis, in a class of chiral smectic materials. It was found that in the material being studied the tilt angle Ψ of the smectic layer with respect to the rubbing axis $\hat{b}$ is much larger ($\approx 20^\circ$) than what has been previously observed. We performed the EC measurements in the vicinity of a direct isotropic - smectic A (I-A) transition in order to see the strength of the EC coupling with the surface field. Moreover, the critical divergence of the EC effect at the smectic A - smectic C* (Sm A-Sm C*) transition was studied to deduce information about its temperature dependence and the nature of smectic ordering in the interfacial region. Based on the measured the layer tilt near the I-Sm A transition, it is suggested that in addition to the surface EC effect, molecular chirality as well as the nature of the surface smectic ordering should be taken into account for a better description of the observed phenomenon.

EXPERIMENTAL

We have measured the tilt angle Ψ of the smectic layer away from $\hat{b}$ near the I-Sm A transition in a chiral smectic compound, the R-enantiomers of 1-methylheptyl 4'-[(4"-dodecyloxyphenyl) propioloyl-oxy] biphenyl 4-carboxylate (C_{12}1M7). The critical temperatures for the I-Sm A and the Sm A-Sm C* transitions during heating are 94.2° C and 82.4° C, respectively. In higher homologues of this compound, a new helical smectic A* phase, which is a liquid crystal analog of the Abrikosov phase of type II superconductors, has been observed.[11] These materials are different from ordinary smectic LCs in that they are highly chiral and thus produce highly twisted structures, which is an important factor for explaining the large magnitude of Ψ in the compound studied.

A sample cell was made of two conductive indium-tin-oxide coated glasses, and the thickness of the liquid crystal was controlled by using 3 μm spacers. The homogeneous alignment was obtained by coating both surfaces of the cell with poly-1,4-butyleneterephthalate polymer, followed by a unidirectional rubbing. The sample was filled in the isotropic state and cooled into the mesophase. In order to examine the effect of various surface conditions on the alignment, parts of the polymer coating was purposely removed in some areas by plasma etching in a vacuum chamber. The cell surface has also a surfactant-treated region for obtaining the homeotropic alignment.

RESULTS AND DISCUSSION

The tilted layer growth in a Sm A sample of C_{12}1M7 on a substrate with treated surfaces is shown in Figures 1 and 2, which were photographs taken between crossed polarizers at 92.0° C and 88.0° C, respectively. The rubbing axis $\hat{b}$ is parallel to the long side of the striped pattern shown in Figure 1.

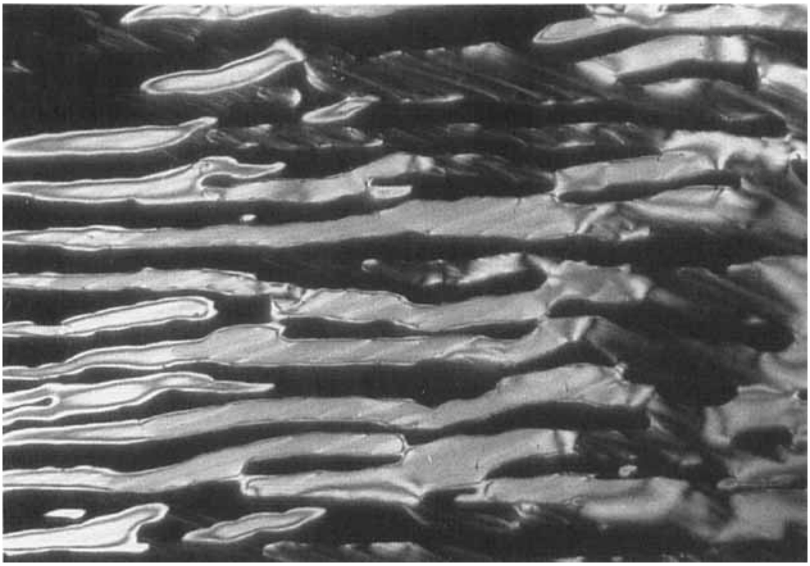

FIGURE 1 The tilted layer growth of the Sm A phase on a substrate with both aligning layers present.

As shown in Figure 1, two domains were observed in the region with both the top and the bottom surfaces rubbed. The growth of these two domains are probably due to two possible sites of nucleation which could be either at the top or the bottom surface. In a thicker cell (≈ 15 μm), it was observed that a relatively large difference in temperature between the top and the bottom surfaces caused a preferential growth of only one of the two domains from the cooler surface. By inverting the sample in the oven it was confirmed that nucleation always occurs on the top surface that is cooler one.

In Figure 2, the tilt angle Ψ of the optic axis from the rubbing axis $\hat{b}$ was found to be about 20^o. The optic axes in the two domains are symmetric with respect to the rubbing axis. The sample was rotated approximately 20^o so that the optic axis in the aligned region coincides with one of the polarizers and thus the maximum extinction was obtained.

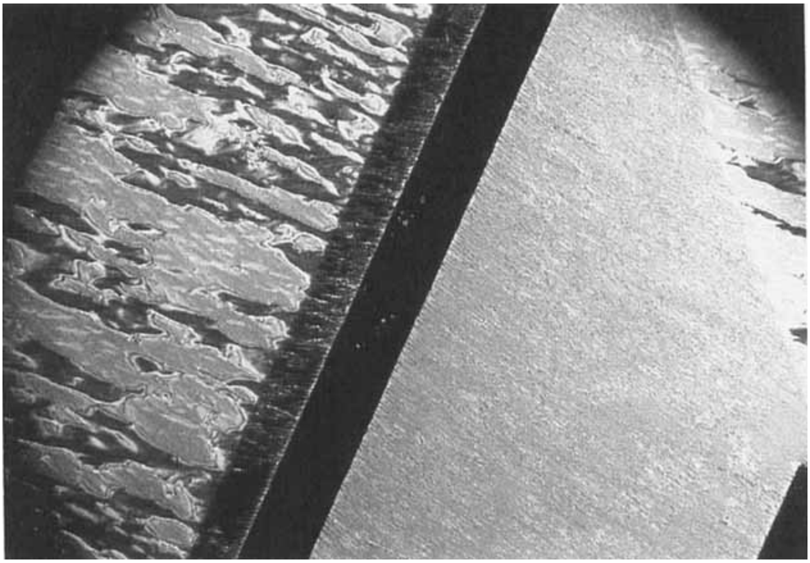

FIGURE 2 The angle of the tilted layer in the Sm A phase with respect to the rubbing axis. From left; both aligning layers present, only bottom aligning layer present, surfactant layers present, and only top aligning layer present.

In the region in which only the top or the bottom surface was rubbed, the direction of the layer tilt with respect to $\hat{b}$ was determined by the rubbed surface on which nucleation took place. Since the nucleation starts on the cooler rubbed surface, the quality of the alignment is much better in the regions where these conditions are satisfied as shown in Figure 2. The observed good extinction and the fact that optic axis does not line up with the rubbing axis indicate that the twist of the molecular director must be confined within a very thin boundary layer much less than the wavelength of the probing light.

We have studied the EC effect near the I-Sm A transition in a homogeneously aligned sample to estimate the magnitude of the layer tilt, resulting from the EC coupling with the surface field, with respect to the rubbing axis $\hat{b}$. In Figure 3 the data of the induced molecular tilt θ were shown as a function of the field strength E at several different temperatures.

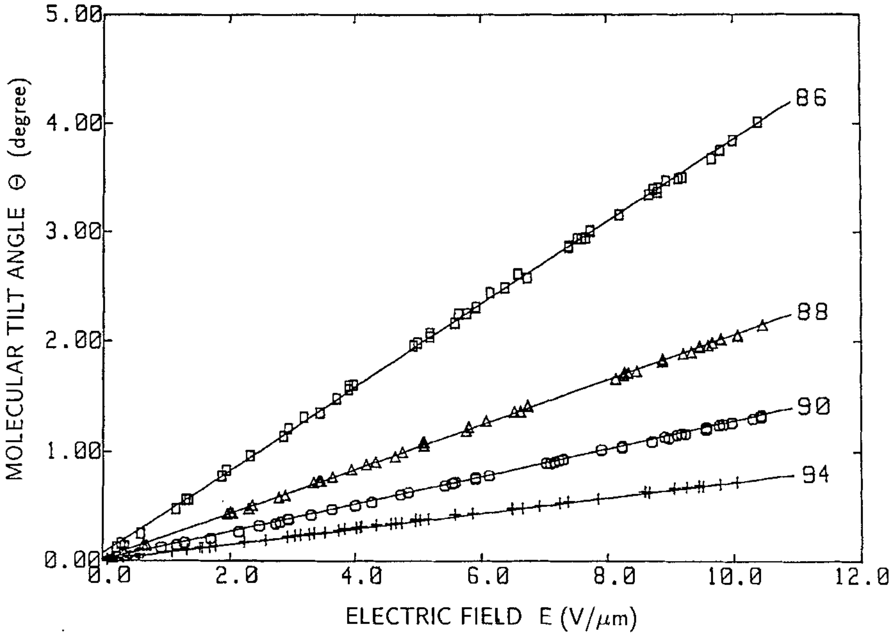

FIGURE 3 The molecular tilt θ as a function of an applied field E at various temperatures. The solid lines are the best linear fits.

Note that in the EC response to an external electric field E applied parallel to the smectic A* layers, the molecules tilt by θ in a direction perpendicular to E, and the magnitude of θ is directly proportional to E.[12] The change in the molecular tilt θ leads to the change in the transmitted light intensity through the sample cell when viewed between cross polarizers, which enables us to measure θ as a function of E. As shown in Figure 3, the linear response is clearly observed even at the I-Sm A transition. As the Sm A-Sm C* transition was approached, however, it was found that the EC response becomes increasingly non-linear, which is similar to what has been reported previously.[13]

The magnitude of θ reaches several degrees in the vicinity of the Sm A-Sm C* transition, although it is quite small at the I-Sm A transition. The magnitude of the molecular tilt θ at the strength of the surface polar field has been argued to give a qualitative explanation for the layer tilt Ψ away from the rubbing axis $\hat{b}$ in the Sm A phase. However, on approaching the I-A transition the discrepancy between Ψ and θ becomes profound.

The temperature dependence of the linear EC effect is in Figure 4. In the linear regime,[12] the molecular tilt angle θ is given by $(t\chi_p E/a')(T - T_c)^{-1}$ where $\chi_p{}^{-1}$ is the generalized susceptibility, a' is a temperature-independent constant, T_c is the critical temperature for the Sm A-Sm C* transition, and t is the EC constant.

Using this expression, we have $d\theta/dE = R(T - T_c)^{-1}$ where $R = t\chi_p/a'$, which gives a power-law divergence. The data were fitted to a form of $R/(T - T_c) + R_o$ with $R = t\chi_p/a'$ and $R_o \approx 0$. The least squares fit of the data was represented by the solid line in Figure 4. As expected, there is a critical slowing-down at the Sm A-Sm C*transition. The fitted value of T_c is given by 82.6° C which is in good agreement with the value determined by microscopic observation.

From the best fit of the data, we found R to be about $2.6 \times 10^{-8}\ mK/V$. The value of R for C_{12}1M7 is of the same order of magnitude for 764E aligned on the similar substrate.[13] Note that 764E material exhibits a strong nonlinear behavior of the induced molecular tilt. In this material, however, the tilt of the layer normal with respect to $\hat{b}$ was found to be essentially zero within experimental error. Thus, it is important to include molecular chirality and other possible factors for describing the observed layer tilt, which distinguishes at least qualitatively between these two cases.

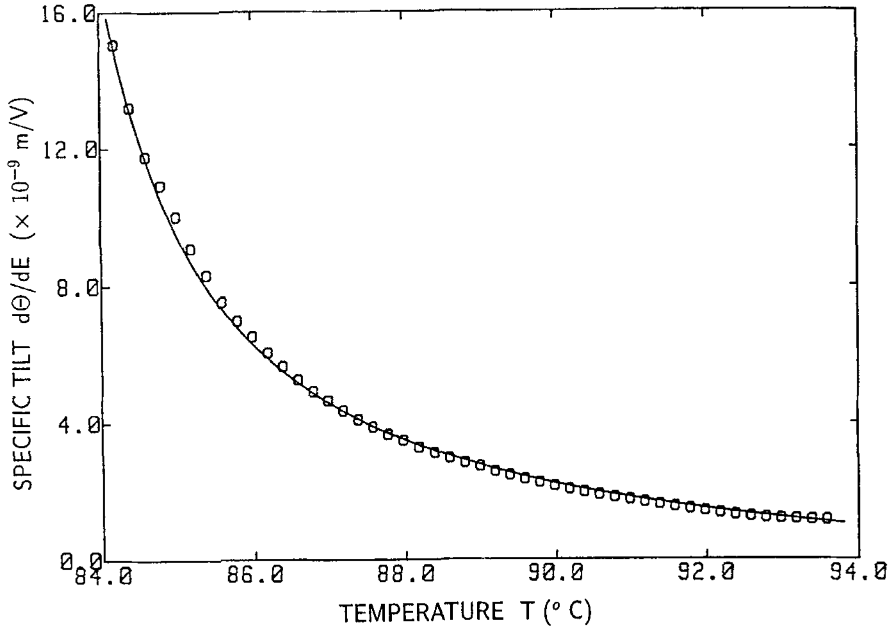

FIGURE 4 The specific tilt $d\theta/dE$ as a function of temperature T.

We first consider the EC coupling of the surface field and determine the magnitude of the resultant molecular tilt. Since the strength of the surface field has been reported in the Sm A phase so far, we make its crude estimate from the available data in the Sm C* phase. Using the evanescent wave technique, it has been shown[8] that the molecules close to the surface are completely reoriented by applying an external electric field which overcomes the surface field. Furthermore, in the presence of polar surface interactions, the asymmetry in the switching characteristic was observed with changing the polarity of the applied field. The surface potential determined from this asymmetry was found to be about 15 V for 3 to 5 μm samples, giving about 3 to 5 $V/\mu m$ for the surface field strength E_s. Assuming that the value of this surface field E_s remains the same in the Sm A phase and is of the same order of magnitude in our case, we can determine the molecular tilt θ at E_s and compare that with the layer tilt Ψ observed. In the compound studied, $C_{12}1M7$, the molecular tilt θ at $E = E_s$ is at most 3° which is much less than the layer tilt ($\Psi \approx 20^\circ$) away from the rubbing axis. This clearly indicates that surface EC effect alone cannot account for the observed large layer tilt.

Besides the surface EC effect, we now consider another factor that may influence the magnitude of the layer tilt within a model based on molecular chirality and degree of the smectic ordering near the surface. In this model, the layer tilt is produced by the amount of twist due to molecular chirality, confined within a certain distance ξ away from the surface. The distance ξ is determined by the thickness of the surface layer in which the smectic order reaches at a limiting bulk value from a rather different value at the surface. This assertion that the smectic order parameter at the surface is different from the bulk may be supported by the fact[13] that in some materials such as a series of alkylcyanobipenyl, the packing structure of the molecules in a monolayer film is found to be quite different from that in the bulk. Note that in this model the rate of twist will depend on the spatial variations of the smectic order as well as the amount of the molecular chirality.

Consequently, the magnitude of the observed layer tilt in the bulk will be governed by the amount of twist at ξ with respect to the rubbing axis $\hat{b}$. This behavior is similar to the deviation of the tilt of the cholesteric helix from $\hat{b}$ in the plane of the substrate near the isotropic - cholesteric transition.[15]. In order to estimate the thickness ξ, we assume that the rate of twist within this layer remains constant and is on the order of the bulk value in the higher homologues of this compound. The pitch of the higher homologues in a bulk helical Sm A* phase was found to be about 0.5 μm.[16] From the measured value of $\Psi \approx 20^\circ$ together with the pitch $p \approx 0.5\ \mu m$ for the material studied, the thickness ξ is then given by $p/20 \approx 250\ \mathring{A}$, which is of the same order as a typical smectic correlation length at a few degrees from the second-order transition.[17] It should be noted that in contrast, the pitch of 764E mixture is compensated near the nematic - Sm A transition, hence no layer tilt is expected. Therefore, depending on the nature of surface interactions specific to a LC/substrate interface, the molecular chirality, and the range of the smectic correlation, the layer tilt will vary from zero to as much as 20° in the Sm A phase. It should be emphasized that in addition to the surface EC effect, the molecular chirality, the degree of the smectic order, and even the presence of a nematic phase play a significant role in the magnitude of the layer tilt with respect to the rubbing axis.

CONCLUDING REMARKS

We have observed a large tilt of smectic layers ($\approx 20^\circ$) away from the rubbing axis $\hat{b}$ in a class of chiral smectic materials, and discussed its physical mechanism in a simple model based on molecular chirality and the degree of smectic ordering in the interfacial region. The simple model contains the essential features of the experimental results. In addition, for $C_{12}1M7$, the thickness of the surface layer is estimated as about 250 Å which is of the order of the smectic correlation. It might be then concluded that molecular chirality as well as the nature of smectic ordering at an interface play a critical role in the growth of the tilted layer with respect to $\hat{b}$ near the I-Sm A transition.

ACKNOWLEDGEMENT

This work was supported in part by Ministry of Education of Korea through Project No. BSRI-92-222.

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