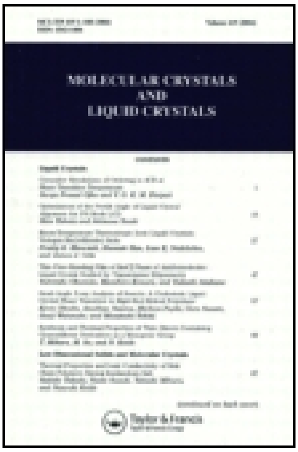

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Pretransitional Surface Phenomena in Ferroelectric Liquid Crystals

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Pretransitional Surface Phenomena in Ferroelectric Liquid Crystals

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Surface ordering in a ferroelectric liquid crystal was studied using ellipsometry. We observed a pretransitional divergence of the correlation length in the smectic A phase, as the smectic A-smectic C* transition was approached. In the isotropic phase, we measured the pretransitional growth of an ordered surface layer near the isotropic-smectic A transition. The observed surface phenomena support the model of a surface electroclinic effect at the smectic A-smectic C* transition in ferroelectric liquid crystals.

Keywords: ferroelectric liquid crystals, electroclinic effect, liquid crystal interface

INTRODUCTION

Liquid crystals (LCs) are known to exhibit a complex and varied set of surface ordering phenomena. The surface ordering in LCs is of interest from both the fundamental and applied standpoints. Several kinds of surface ordering and disordering behavior have been reported in isotropic and nematic LCs.[1-3] A particularly interesting surface phenomenon, the surface electroclinic effect (SEE), can occur in the smectic A (SmA) phase of ferroelectric liquid crystals (FLCs). According to the theory of the SEE[4], a local electric field at the FLC-substrate interface causes the FLC molecules in the interfacial region to tilt away from the smectic layer normal. The presence of a surface electric field may be expected since polar interactions between LC molecules and a substrate can result in an ordering of the LC dipole moments at the surface.[5,6] The field-induced molecular tilt in the SEE is thus analogous to the well-understood bulk electroclinic effect, except that the effect is localized near the interface.

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Nakagawa *et al.* first proposed the existence of a surface electroclinic effect in FLCs to explain a peculiar behavior in the alignment of FLC samples.[7] Monodomain FLC samples are typically prepared by sandwiching a thin layer of FLC between unidirectionally buffed, polymer-coated glass plates. The resulting bulk FLC structure forms with the smectic layer planes normal to the substrates and the smectic layer normal in the substrate plane, making an angle Θ with the rubbing direction. The existence of a nonzero angle Θ, called the layer deviation angle, is an effect peculiar to FLC samples and is not observed in the SmA phase of nonferroelectric LCs, where the bulk director lies along the rubbing direction. Noting that the sign of the layer deviation angle Θ correlated with the sign of the FLC dipole moment, Nakagawa *et al.*[7] proposed that the mechanism responsible for the deviation angle was electroclinic in origin. Recently, Patel *et al.*[8] have argued that the SEE cannot account for the magnitude of the layer deviation angle, proposing instead that the observed angle results from a disordered surface layer near an interface which imposes a reduced smectic ordering in the adjacent FLC. The two proposed models accounting for the layer deviation angle make different predictions for the temperature dependence of molecular ordering in the interfacial region near the SmA-SmC* transition temperature T_{AC}. Thus a study of the pretransitional ordering behavior in the interfacial region would distinguish between these models. We recently reported the results of our study of the interfacial region of an FLC sample using optical second harmonic generation, ellipsometry, and microscopy,[9] confirming that the SEE model alone is consistent with all the experimental observations.

In this paper, we report the details of our ellipsometric study of interfacial phenomena in FLCs. We have measured a divergence in the correlation length in the SmA phase, at the SmA-SmC* transition. This divergence corresponds to the pretransitional increase in the length-scale of the surface field-distorted region of the FLC. The effect is well explained using the Landau-deGennes theory for the SEE.[4] We have also measured the growth of an ordered surface region in the isotropic phase, approaching the I-SmA transition. This direct observation of pretransitional ordering at the interface argues against the notion of a disordered surface layer in the SmA phase. We begin with a brief outline of the theory of the SEE. Next, we discuss the result of our measurements in the SmA phase. Finally, we present our measurements of surface ordering in the isotropic phase.

THEORY

I. Smectic A-Smectic C* Transition

The SEE can be understood in terms of a simple Landau-deGennes (LdG) theory.[4,10] The essential ingredients are a linear coupling between the tilt and polarization order parameters, θ and P, and an FLC-substrate interaction producing a nonzero polarization at the surface. The bulk free energy can be written as

$$F = F_A + \frac{1}{2}A'\theta^2 + \frac{1}{2\chi}P^2 - tP\theta + \frac{1}{2}K_2\left(\frac{d\theta}{dz}\right)^2$$

where F_A is the free energy of a uniform SmA phase, χ is a generalized dc electric susceptibility, t is the piezoelectric coupling constant, and K_2 is the twist elastic constant. The temperature dependence of the coefficient A' is given by $A' = a(T - T_{AC}) + t^2\chi$, where a is a constant depending on the FLC material. The surface free energy F_S contains a term proportional to the polarization P at the interface, $F_S = F_{SO} - \lambda P(z = 0)$, where the constant λ describes the strength of the polar interaction and F_{SO} is the polarization-independent contribution to the surface energy. Minimization of the total free energy and solution of the associated Euler-Lagrange equations give the following expression for the profile of the tilt order parameter:

$$\theta(z) = \theta_o e^{-z/\xi} \tag{1}$$

where the correlation length ξ is given by

$$\xi = \xi_o \left(\frac{T - T_{AC}}{T_{AC}}\right)^{-1/2} \tag{2}$$

with $\xi_o = \sqrt{K2/a}$. Thus the tilt angle θ between the FLC long molecular axis and the smectic layer normal decays exponentially from its contact value θ_o at the substrate. A critical divergence of the decay length ξ is predicted at the SmA-SmC* transition.

It is interesting to ask what temperture dependence the surface tilt angle θ_o exhibits. Minimization of the surface free energy yields the expression

$$\theta_o = \frac{\lambda t \chi}{\sqrt{aK_2}} \left(\frac{T - T_{AC}}{T_{AC}}\right)^{-1/2} \tag{3}$$

suggesting that θ_o also diverges at the transition. Since the molecules at the surface are azimuthally anchored along the rubbing direction,[9] we have $\theta_o = \Theta$, the layer deviation angle, and so we should observe a divergence of Θ at T_{AC}. However, in all our measurements Θ remained essentially constant with temperature over the entire SmA range. This can be explained if we realize that the smectic layer planes in the bulk, once formed at the isotropic (or nematic)-SmA transition, are not free to rotate but are instead pinned by boundary interactions at the edges of the sample; that is, $\theta_o = \Theta$ remains fixed and cannot diverge. A simple experiment verifying the existence of this pinning effect is described in Reference 9.

We thus expect the pretransitional behavior in the interfacial region to take the simple form predicted in Equations (1) and (2) with θ_o a constant. The correlation length ξ over which the FLC molecules in the interfacial region are twisted away from the smectic layer normal should diverge as $(T - T_{AC})^{-1/2}$. We note that the model of Patel *et al.*[8] for the layer deviation angle predicts no significant temperature dependence of ξ near the transition.

II. Isotropic-Smectic A Transition

Pretransitional ordering in the interfacial region of an isotropic LC near the isotropic (I)—SmA transition is a rather complicated problem in LC theory. In general, one expects that both nematic (orientational) and smectic (layering) ordering may occur in the interfacial region, and that the nematic and smectic order parameters decay with distance from the interface with different correlation lengths.[11,12,13] In our experimental geometry, the smectic layer normal and substrate normal are orthogonal, and one may then also expect biaxiality in the order parameters near the interface.

In order to greatly simplify the theoretical analysis while still preserving the qualitative features, we describe the ordering in the I phase of our FLC in terms of the LdG theory for pretransitional ordering near the I-nematic (N) transition.[1,2,14,15] Here we are ignoring the interfacial smectic order parameter and any biaxiality in the nematic ordering. Nevertheless, the LdG theory should still provide the correct qualitative picture of the surface ordering. Moreover, since careful experiments to determine the material constants of our high-polarization FLC have not yet been performed, we cannot expect to arrive at a quantitative confirmation of a particular theory.

The LdG theory of surface ordering at the I-N transition was developed by Sheng[14,15] and later elaborated by others.[1,2] Essentially, the nematic order parameter $Q(z)$ is predicted to decay monotonically with distance z from the interface from its value $Q_o = Q(z = 0)$ at the interface to its bulk value of zero. As the I-N transition temperature T_{NI} is approached, the correlation length ξ of the ordered region increases, and actually diverges if Q_o exceeds a threshold value Q_c, where Q_c is the value of the bulk nematic order parameter at T_c^-. For $Q_o < Q_c$, the correlation length ξ grows but does not diverge at T_{NI}. A quantity used to describe the ordering quantitatively is the adsorption parameter Γ defined by $\Gamma = \int_o^\infty Q(z)\, dz$. By minimizing the LdG free energy, the adsorption parameter may be found analytically[1]

$$\Gamma = \sqrt{\frac{2L}{c_I}} \ln P(T, Q_o) \tag{4}$$

where

$$P(T, Q_o) = \frac{\sqrt{F_1(Q_o)/Q_o^2} + \sqrt{\frac{1}{2} a_I (T - T^*)} + \frac{1}{2} Q_o \sqrt{c_I}}{\sqrt{F_1(Q_o)/Q_o^2} + \sqrt{\frac{1}{2} a_I (T - T^*)} - \frac{1}{2} Q_o \sqrt{c_I}}$$

and

$$F_1(Q) = \frac{1}{2} a_I (T - T^*) Q^2 - \frac{1}{3} b_I Q^3 + \frac{1}{4} c_I Q^4$$

and where a_I, b_I, c_I, L, and T^* are constants depending only on the LC material.[16] For $Q_o < Q_c$, corresponding to our experiment, Equation (4) predicts a nondivergent pretransitional increase in Γ. This phenomenon may be described as a partial wetting of the isotropic-substrate interface by a layer of FLC with nematic-like ordering.

Experiment

The FLC we used was the single-component, high spontaneous polarization compound 4′-(2s, 3s)-2″-chloro-3″ methylpentanoloxyphenyl-4-decycloxythiobenzoate (10·S·Cl·Isoleucine), which has an I-SmA transition at T_{IA} = 73.5°C and a SmA-SmC* transition at T_{AC} = 66°C.[17] The spontaneous polarization in the SmC* phase ($T_{AC} - T$ = 10°C) is 100 nC/cm^2. Samples were prepared by sandwiching a thin film (usually 2 μm) of FLC between a polyimide-coated (JIB-1, Japan Synthetic Rubber Co.) glass substrate and a bare glass substrate. The reason for using two differently treated substrates will be explained shortly. The polyimide-coated substrate was unidirectionally buffed. The cells were capillary-filled in air with FLC in the isotropic phase, and subsequently cooled to the SmA phase. The quality of the resulting monodomain was assured by microscope observation before the samples were loaded into an oven with ±20 mK stability. The layer deviation angle Θ was determined to be 7° ± 1° from our microscope observations.

I. Smectic A-Smectic C* Transition

We investigated the pretransitional behavior of the interfacial region using ellipsometry. The technique is sensitive to the optical birefringence caused by the twisting molecular director in the interfacial region. The SmA sample was inserted between a pair of crossed polarizers, and light from a 1 mW HeNe laser was propagated through it at normal incidence. The orientation of the sample was adjusted so that the bulk optic axis was aligned with the polarizer direction. In this geometry, the bulk medium induces no phase shift between the orthogonal components of the light polarized parallel and normal to the polarizer axis. However, the twisting molecular orientation in the interfacial region does induce a phase shift. In fact, one may think of the interfacial layer as, effectively, a very thin birefringent plate of thickness ξ inserted between the crossed polarizers, making an angle θ_o between its optic axis and the polarizer axis. The induced optical phase shift is compensated by adjusting the dc voltage on a Pockels cell in the beam path. A small, 10 kHz voltage modulation applied to the Pockels cell allows for ac detection of the signal using a lock-in amplifier. The sensitivity of the system is $\sim 1 \times 10^{-4}$ radian, corresponding to a minimum detectable θ_o of ~0.5 mrad for a 1000 Å layer. A diagram of the experimental geometry is shown in Figure 1.

A this point we comment on our choice of two differently treated glass substrates for the two sides of the sample cell. If the substrates had been identical, the phase shift induced by the back substrate of the cell would exactly cancel that induced by the front substrate. In fact, the phase shift measured in our experiment is really the difference between the phase shifts induced at each interface. We shall later

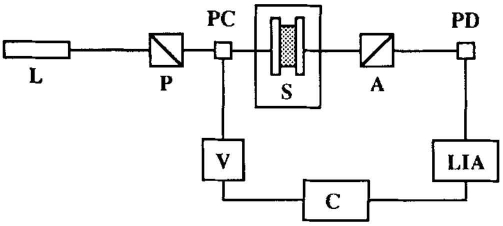

FIGURE 1 Ellipsometry apparatus. L = HeNe laser, P = polarizer, PC = Pockels' cell, S = FLC sample in temperature-controlled oven, A = analyzer, PD = photodiode, LIA = lock-in amplifier, V = voltage supply, C = computer.

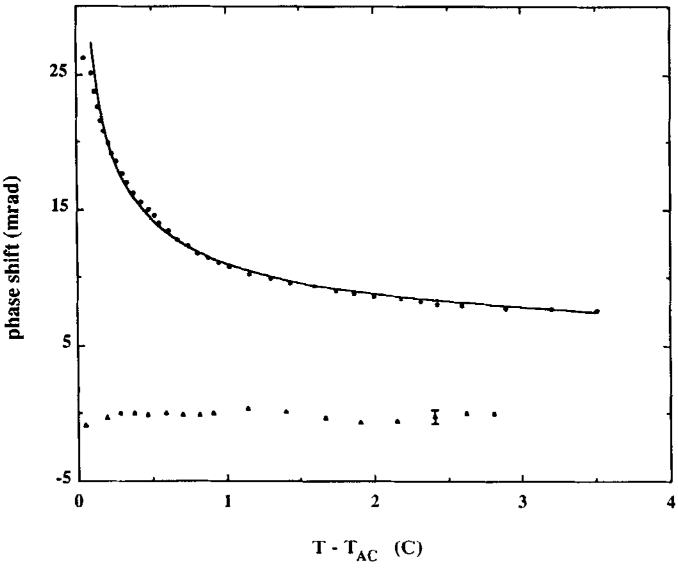

FIGURE 2 Pockels cell phase shift vs. sample temperature, above the SmA-SmC* transition. The Pockels cell phase shift is 2 × the phase shift $\Delta\phi$ induced by the sample. Circles are experimental data from the FLC-rubbed polyimide interface taken in the transmission geometry; the solid line is a fit to the LdG theory of the SEE. Triangles are experimental data from the FLC-bare glass interface, taken in the total reflection geometry.

describe an experiment in which we could directly measure the phase shift contribution from the bare glass interface and show that it was negligible. Thus the measured phase shift could be considered as coming solely from the FLC-polyimide interface.

The measured phase shift in our sample as a function of temperature is shown in Figure 2, for a series of temperatures approaching the SmA-SmC* transition temperature. The increase of the phase shift near T_{AC} can be attributed to a divergence in the correlation length ξ of the interfacial region, where the molecular orientation twists from its surface value along the rubbing direction to its bulk value along the smectic layer normal. From the Landau-deGennes theory of the SEE, we expect this length-scale ξ to diverge as $(T - T_{AC})^{-1/2}$ at the transition. Thus the LdG theory should be able to explain the observed pretransitional behavior.

To compare the experimental results more quantitatively with theoretical predictions, it is necessary to write an expression for the optical phase shift induced in the propagation of linearly polarized light through the interfacial region with a twisting optical axis. The procedure is straightforward using Jones matrices.[18] We begin by dividing up the interfacial region into thin slabs, each with its optic axis slightly rotated from the rubbing axis as described in Equation (1). Each thin slab is represented by a Jones matrix M_i, representing the medium in the interval from z to $z + dz$. For a surface twist angle $\theta_o << 1$, we have

$$M_i(z) = \begin{bmatrix} 1 & i\dfrac{2\pi\Delta n\, dz}{\lambda}\theta_o e^{-z/\xi} \\ i\dfrac{2\pi\Delta n\, dz}{\lambda}\theta_o e^{-z/\xi} & 1 + i\dfrac{2\pi\Delta n\, dz}{\lambda} \end{bmatrix} \tag{5}$$

where $2\pi\Delta n\, dz/\lambda$ is the phase shift of a slab of thickness dz, $\Delta n = n_e - n_o$ is the difference between the extraordinary and ordinary refractive indexes, ξ is the correlation length of the interfacial region, and λ is the laser wavelength. From Equation (5), we see that phase shift $\Delta\phi$ between components of the laser light polarized parallel and orthogonal to the bulk director is given by

$$\Delta\phi = \int_o^\infty dz \frac{2\pi\Delta n}{\lambda}\theta_o e^{-z/\xi} = \frac{2\pi\Delta n}{\lambda}\xi\theta_o \tag{6}$$

We measured Δn in the SmA phase by the critical angle method, obtaining $\Delta n = 0.11$. With $\theta_o = 7°$, $\Delta n = 0.11$, $\lambda = 633$ nm, and $\Delta\phi \approx 7.5$ mrad at $T_{AC} + 0.1°$, we estimate $\xi \approx 970$ Å at $T_{AC} + 0.10°$.

In our experiment, strain birefringence in the glass substrates contributes a small, temperature-independent phase shift (<5 mrad). The transition temperature is determined from the onset of strong light scattering from the sample at the transition. Due to impurities in our sample, the transition region may be somewhat smeared out, resulting in a ±0.05°C uncertainty in $T_{AC}{}^+$. In our fits, we varied ξ_o, where $\xi = \xi_o (T - T_{AC}/T_{AC})^{-1/2}$, as well as allowing the background phase shift $\Delta\phi_o$ and the transition temperature T_{AC} to vary within their small allowed ranges. The result of the fits is shown in Figure 2. We find $\xi_o = 16 \pm 6$ Å. Clearly, the LdG theory of the SEE gives a good description of the pretransitional behavior of the interfacial region in an FLC.

In our experiment, both FLC-substrate interfaces could be expected to contribute to the phase shift of the transmitted laser light. The observed phase shift, as mentioned previously, is the difference between the phase shifts from the front and back interfacial regions. We expected the FLC-polyimide interface to contribute the dominant phase shift, due to a strong polar interaction between the FLC and polyimide. To check this assumption, we studied the phase shift from the FLC-bare glass interface in a total reflection geometry.[2]

In the total reflection experiment, the FLC sample was sandwiched between a high refractive index glass prism (Schott glass LaSF N9, $n = 1.845$) and a rubbed, polyimide-coated glass plate. The prism was cleaned in chromic acid, rinsed well with distilled water, and dried prior to filling the cell with FLC in the isotropic phase. The cell thickness was fixed by mylar spacers to be 130 μm. This large spacer thickness was necessary to spatially separate reflections from the prism-FLC and FLC-polyimide interfaces, although alignment of the thicker sample was more difficult. The sample was cooled from the isotropic phase in the presence of a 1.5 T magnetic field oriented along the bulk smectic director to aid in the alignment. Monodomain alignment in the probed region was verified by microscope observation. In the experiment, equal p- and s-polarized components of the laser light were incident on the sample at θ_c, the critical angle for total internal reflection, and the resulting phase shift between p and s components was measured. It can be shown that the phase shift $\Delta\phi_c$ at the critical angle is proportional to the integrated birefringence from the interfacial region.[2] The dependence of the phase shift $\Delta\phi_c$ on the sample temperature is shown in Figure 2. The small value of $\Delta\phi_c$ (< 2 mrad) indicates the absence of an interfacial region with twisting molecular director at the FLC-bare glass interface. In the transmission experiment, we are therefore justified in ignoring the FLC-bare glass interface and considering the measured phase shift to result wholly from the FLC-polyimide interface.

We repeated the transmission experiment using a sample cell consisting of FLC sandwiched between a rubbed, polyimide-coated plate and an unrubbed, polyimide-coated plate. The qualitative results were similar to those just discussed, but the magnitude of the phase shift was smaller by a factor of 2.6 at $T - T_C = 0.05°\text{C}$. This suggests that there was a phase shift induced at the unrubbed polyimide-FLC interface which cancelled some of the phase shift from the rubbed polyimide-FLC interface, resulting in the decreased signal from this sample. It is therefore likely that there is some dipole ordering at the FLC-unrubbed polyimide interface, leading to a weak SEE. Clearly, the rubbing process results in a greater alignment of the dipole moments at the FLC-rubbed polyimide interface compared to the FLC-unrubbed polyimide interface.

II. Isotropic-Smectic A Transition

We next studied the pretransitional surface behavior in the isotropic phase, near the I-SmA transition. The sample and experimental geometry were the same as in the transmission experiment. The sample orientation, however, was set so that the bulk SmA director made a 45° angle with the polarizer axis. The sample was then heated to the isotropic phase, and the phase shift measured as the sample temperature was reduced toward the transition to the SmA phase. In this geometry, a surface layer oriented along the rubbing axis would contribute nearly the maximum phase shift. The phase shift $\Delta\phi$ is again proportional to the integrated birefringence of the interfacial region. If we assume a SmA layer of birefringence Δn and thickness ξ', the phase shift is given by

$$\Delta\phi = \frac{2\pi}{\lambda}\Delta n\xi'.$$

Using $\Delta n = 0.11$, $\lambda = 633$ nm, and $\Delta\phi \approx 4.3$ mrad at $T - T_{IA} = 0.03°\text{C}$, we obtain $\xi' = 40$ Å at $T - T_{IA} = 0.03°\text{C}$. The phase shift as a function of the sample temperature is shown in Figure 3. The pretransitional increase of the phase shift indicates the growth of an ordered layer of FLC molecules near the FLC-polyimide interface.

A theoretical fit to the data using Equation (4) is shown in Figure 3. In order to avoid using an excessive number of fitting parameters and thereby rendering the fit meaningless, we assumed the LdG constants a, b, c and L of our FLC were identical to those of another, well-characterized LC, 4'n-octyl-4-cyanobiphenyl (8CB). A small adjustable phase shift (<5 mrad) was included to account for background birefringence. The theory curve was shifted to make the transition temperatures for 8CB and our FLC coincide. Thus the theory curve is the result of a two-parameter fit for the value of the surface order parameter Q_o, which was assumed to be temperature-independent. The best fit was obtained with $Q_o = 0.185 \pm 0.005$, corresponding to the partial wetting behavior since $Q_o < Q_c = 0.30$.[16] Due to the number of approximations made, one should not expect a good quantitative agreement between our experimental results at the I-SmA transition and the LdG theory for surface ordering at the I-N transition. Nevertheless, the theory describes the experimentally observed surface ordering surprisingly well.

Finally, we note that our optical experiment cannot distinguish a smectic from a nematic-like surface ordering, since the optical wavelength is very much greater than the smectic density wavelength. Smectic surface ordering in the homeotropic geometry at an LC-solid interface has been observed by Ocko[19] using x-ray reflectivity. Therefore it is possible that there is some pretransitional smectic ordering in our FLC system.

Random-planar surface ordering has been observed in certain nematics at the LC/bare glass or LC/unrubbed surfactant interface above the isotropic-nematic transition.[1-3] We checked for such surface ordering at the isotropic FLC-bare glass

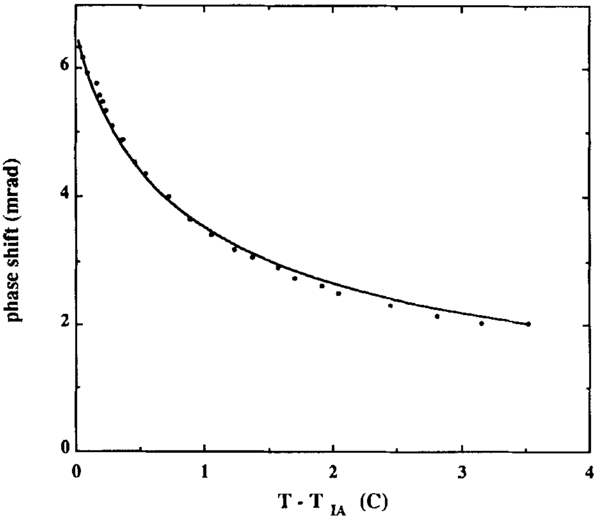

FIGURE 3 Phase shift Δϕ vs. sample temperature in the transmission geometry, above the I-SmA transmission. Circles are experimental data; the solid line is a fit to the LdG theory for surface ordering near the I-N transition.

interface in the total reflection geometry, near the transition to the SmA phase. The sample and experimental geometry were the same as used previously to study the FLC-bare glass interface near the SmA-SmC* transition. No pretransitional behavior was observed. This implies that the interaction between the FLC molecules and the bare glass substrate is rather weak.

DISCUSSION AND CONCLUSIONS

The observed pretransitional behavior of the interfacial region near the SmA-SmC* transition is well explained by the LdG theory for the SEE. The predicted $(T - T_{AC})^{-1/2}$ divergence of the correlation length ξ of the interfacial layer was verified experimentally. The pretransitional surface ordering above the I-SmA transition is also in accord with the model for the SEE. This pretransitional ordering suggests that the rubbed polyimide substrate enhances the ordering of the adjacent FLC, which is consistent with the aligned-dipole structure necessary for a SEE. The surface ordering in the isotropic phase is also consistent with the observation by Lee *et al.*[20] of an electroclinic response in the isotropic phase of an FLC, which they ascribe to a SEE in a pretransitional ordered smectic surface layer. Together with the bulk layer deviation studies[7,9] and the isotropic phase electroclinic experiments[20], our work here using ellipsometry gives a consistent picture of the SEE at the interface between a FLC and a rubbed polymer.

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