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Surface Electroclinic Effect on the Layer Structure of a Ferroelectric Liquid Crystal

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Optical second-harmonic generation and ellipsometry were used to study molecular alignment in an interfacial region and the deviation of the layer normal from the surface-rubbing axis in the smectic-*A* phase of a ferroelectric liquid crystal. The results can be well explained by the surface electroclinic effect.

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The problems of interfacial properties of liquid crystals (LCs) are not only of fundamental interest but also of practical importance to the design and construction of LC devices. It is well known that an LC film can be oriented by a rubbed polymer surface [1]. It has been recently shown that the rubbed polymer surface effectively aligns the first LC monolayer on the surface, and then via LC molecule-molecule interaction, the average molecular orientation (the director) in the bulk is aligned [2,3]. Recently, however, it has been found that in the smectic-*A* (Sm*A*) phase of chiral molecules the bulk LC director and hence the smectic layer normal deviate from the rubbing axis by an angle Θ, which can be as large as 18° [4,5]. Nakagawa *et al.* [4] observed that the sign of Θ correlates with the sign of spontaneous polarization in the smectic-C^* (SmC^*) phase. Based on this observation, they proposed that the deviation originated from the electroclinic (EC) effect [6] in the Sm*A* phase induced by a localized surface field. Using a different LC material, Patel, Lee, and Goodby [5] found a large Θ and suggested that it is too large to be described by the surface EC effect. They proposed an alternative mechanism based on molecular twist via chirality and reduction of smectic ordering at the surface. Both models qualitatively explain some aspects of the experimental observations but not others so that a complete understanding of the phenomenon is still lacking.

In this paper, we report results from a series of experiments that provide a better understanding of the above problem. Using optical second-harmonic generation (SHG), we could determine the average orientation of a monolayer of ferroelectric liquid-crystal (FLC) molecules at the LC/substrate interface, and found that it is parallel to the rubbing direction. We then used ellipsometry to study the molecular orientation in the interfacial region and found it has a pretransitional divergence at the Sm$A \rightarrow$ SmC^* transition. This result can be well explained by the surface EC effect and allows us to clearly distinguish it from the alternative model of Patel, Lee, and Goodby [5]. A simple formalism of the surface electroclinic effect will be presented and the dependence of the deviation angle on temperature and the rubbing strength will also be discussed.

The FLC material we used was 4′-(2*s*,3*s*)-2″-chloro-3″ methylpentanoloxy-phenyl-4-decyloxythiobenzoate (10·S·Cl Isoleucine), which has an isotropic (I) to Sm*A* transition at $T_{IA}=73.5\,°\mathrm{C}$ and a Sm*A*-to-SmC^* transition at $T_{AC}=66\,°\mathrm{C}$ [7]. It has a large spontaneous polarization of $P_s=-100$ nC/cm^2 ($T_{AC}-T=10\,°\mathrm{C}$) in the SmC^* phase. The observations of the LC alignment in the bulk were very similar to those described in Ref. [5]. Cells were made by sandwiching liquid crystal between two polyimide (JIB-1, Japan Synthetic Rubber Co.) coated glass substrates with 2-μm spacers. Only one of the substrate surfaces was rubbed. The cells were filled in the isotropic phase and cooled with a temperature gradient so that the Sm*A* phase grew from the rubbed substrate. The resulting homogeneous monodomain was observed under a polarizing microscope. The extinction direction was found to deviate from the rubbing direction by about 7°. The deviation angle Θ did not change with temperature within the Sm*A* phase. To see whether the deviation is unique to the polyimide we used, we also made a cell with Nylon 6,6–coated substrates. Similar behavior was observed except that Θ was about 10°.

It was not known whether the FLC molecules at the polyimide surface are aligned along the rubbing direction, or along the bulk alignment direction, or others. We thus used SHG to find the answer. The details of the SHG technique were described elsewhere [2,3]. Briefly, azimuthal dependence of SHG with different input-output polarizations was measured. The results then yielded information about the surface symmetry and orientation distribution of the FLC monolayer.

LC monolayers on rubbed, polyimide-coated glass substrates were prepared by the evaporation method [8]. SHG measurements were carried out with a frequency-doubled *Q*-switched mode-locked yttrium-aluminum garnet laser beam in reflection from the LC side. Four input-output polarization combinations were measured as in Ref. [2]. The result of *p*-in/*p*-out is presented in Fig. 1 as an example. All the signals exhibited a mirror symmetry about the rubbing axis. The magnitude of SHG from the FLC monolayer was comparable to that from a polar-oriented 8CB(4′-*n*-octyl-4-cyanobiphenyl) monolayer, indicating the existence of a polar ordering also in

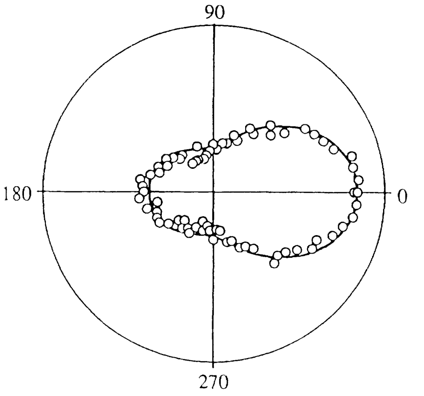

FIG. 1. Polar plots of the square root of the SHG signal as a function of the angle between the surface rubbing direction and the plane of incidence. Both the input and output beams are p polarized. The circles are experimental data; the solid line is the theoretical fit.

the FLC monolayer [9]. From a detailed analysis, we find that the long molecular axes of the LC molecules lie nearly flat on the surface and have an average orientation parallel to the rubbing axis with an order parameter $\langle\cos^2\phi\rangle = 0.64$, where ϕ is the azimuthal angle measured from the rubbing direction.

Detection of alignment of the LC molecules along the rubbing axis ascertains the existence of an interfacial region in which the LC director is twisted from the rubbing axis to the bulk alignment direction. The twist can be interpreted as resulting from either the surface EC effect [10] or the molecular chirality with reduced smectic ordering at the interface [5]. In the former case, the EC effect arises from interaction of the FLC molecules with a local electric field at the boundary. This local field can originate from the polar anchoring of the FLC monolayer on the rubbed surface. The surface EC effect then predicts that the interfacial layer thickness should diverge towards the Sm$A \rightarrow$ SmC^* transition following the divergence of the bulk correlation length [10]. In the latter case, the thickness of the interfacial layer is determined by the balance between the twisting power from molecular chirality and the reduced surface smectic ordering. As the temperature is lowered, the smectic order parameter increases and the thickness of the interfacial layer is expected to decrease, just the opposite to the previous case. Thus, studying the temperature dependence of the thickness of the interfacial layer will allow us to unambiguously distinguish between the two proposed models.

We studied the temperature dependence of the twisted interfacial layer by measuring the twist-induced optical birefringence using ellipsometry. The sample was composed of a FLC film sandwiched between a rubbed polyimide surface and a bare glass plate. It was then 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 optic axis was aligned with the polarizer direction. In this geometry, the bulk medium does not induce a 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 of the FLC does induce a phase shift between these orthogonal components of the light. The induced phase shift can be shown to be proportional to the integrated twist $\int_0^\infty \theta(z)dz$ in the interfacial region, where $\theta(z)$ is the angle between the molecular director and the layer normal at a distance z from the interface [11]. The result is shown in Fig. 2 as a function of temperature as the sample was cooled toward the Sm$A \rightarrow$ SmC^* transition. We observed a divergence of the phase shift as the transition is approached. Since $\theta(z)$ is bounded, the observed divergence implies that the length scale of the director-twisted interfacial region diverges at the transition. The contribution from the FLC/bare-glass interface is checked using a total internal reflection geometry [12] and found to be negligible.

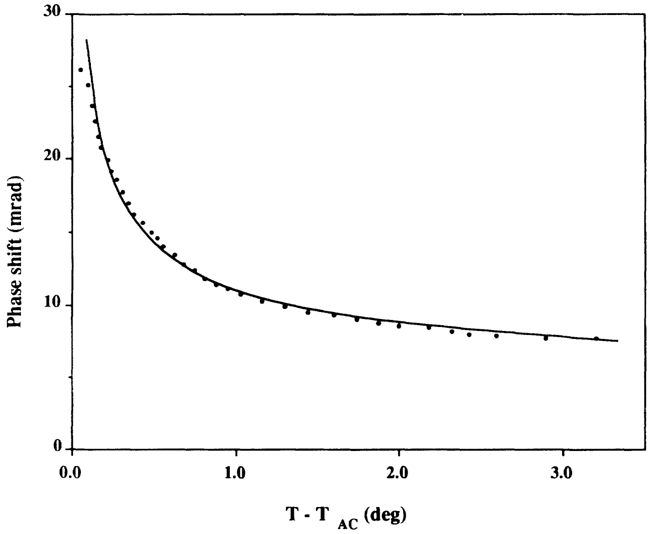

FIG. 2. The phase shift as a function of temperature. The circles are the experimental data; the solid line is a fit by the theory.

The strong temperature dependence measured by ellipsometry supports the surface EC effect model. To see how the results compare with theory, we follow the formalism of Xue and Clark [10]. The bulk free energy density of the system can be written in terms of the twist angle θ from the rubbing direction (which is also the molecular tilt angle from the smectic layer normal) and the spontaneous polarization P of the FLC:

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

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 surface free energy density is assumed to be proportional to the spontaneous polarization P at the surface [10], $F_s = -\lambda P(z=0)$, where λ measures the strength of the polar interaction. By minimizing the total free energy, we find

$$\theta(z) = \theta_0 \exp(-z/\xi)\,, \tag{2}$$

where

$$\xi = \xi_0 \left[\frac{T_{AC}}{T - T_{AC}} \right]^{1/2}, \tag{3}$$

$$\theta_0 = \frac{\lambda t \chi \xi}{K_2} = \lambda t \chi \left[\frac{T_{AC}}{a K_2 (T - T_{AC})} \right]^{1/2}, \tag{4}$$

with $\xi_0 = (K_2/a)^{1/2}$ and a is a constant depending on material parameters.

With the orientation of the surface LC monolayer anchored along the rubbing axis as shown by the SHG measurement, the layer normal must deviate by an angle θ_0 from the rubbing direction, assuming that the layer normal remains unchanged throughout the LC film as it is energetically unfavorable to twist a smectic layer.

Equation (4) shows that θ_0 has a pretransitional temperature dependence. This is, however, not what we observed. The discrepancy can be explained by the fact that it is always difficult to rotate the overall smectic layer structure once it is formed because of constraints at boundaries. As a demonstration, we prepared a sample by cooling from the isotropic to Sm*A* phase in a 1.5-T magnetic field, oriented at about 10° to the rubbing axis in the surface plane. When the sample was removed from the field, we observed domains in which molecules were oriented along the field direction. These domains remained unchanged with time and temperature in the Sm*A* phase. We therefore conclude that the observed temperature independence of θ_0 is due to the pinning of the smectic layer structure, and the value of θ_0 is determined at the I-Sm*A* transition when the layer structure is initially formed.

Even though the layer structure is difficult to change once it is formed, the LC molecules within each layer can tilt away from the layer normal. Equation (2) describes the tilt angle $\theta(z)$ and its temperature dependence. Our ellipsometry data which are proportional to $\int_0^\infty \theta(z) dz$ can actually be fitted very well by Eq. (2) with ξ given by Eq. (3), $\theta_0 = 7°$, and $\xi_0 = 16 \pm 6$ Å, as shown in Fig. 2.

Equation (4) suggests that if θ_0 is fixed by the layer formation at $T = T_{IA}$, then we have $\theta_0 \propto \lambda/[K_2(T_{IA} - T_{AC})]^{1/2}$. FLC materials with narrower Sm*A* temperature ranges $(T_{IA} - T_{AC})$, larger polar interaction strengths with the surface (λ), and smaller twist elastic constants K_2 are expected to yield larger θ_0. Here K_2 refers to an average in the interfacial region. Since K_2 is proportional to the square of the nematic order parameter S [13], the value of which can be changed by the surface rubbing conditions, we expect that θ_0 depends on the rubbing strength. This was checked out experimentally. The rubbing strength was varied in our experiment in a manner described in Ref. [3]. Figure 3 shows the dependence of θ_0 as a function of the number of times the surface of the sample was rubbed. It is seen that θ_0 increases dramatically as the rubbing strength is decreased. Previous studies have found that a weaker rubbing strength yields a smaller surface anisotropy [3] as well as a weaker surface anchoring [14], and hence a small surface order parameter [15]. This results in a small K_2 at the interface and thus a larger θ_0 as expected from Eq. (4). Thus the strong dependence of θ_0 on the rubbing strength in Fig. 3 also agrees with the prediction of the surface EC effect.

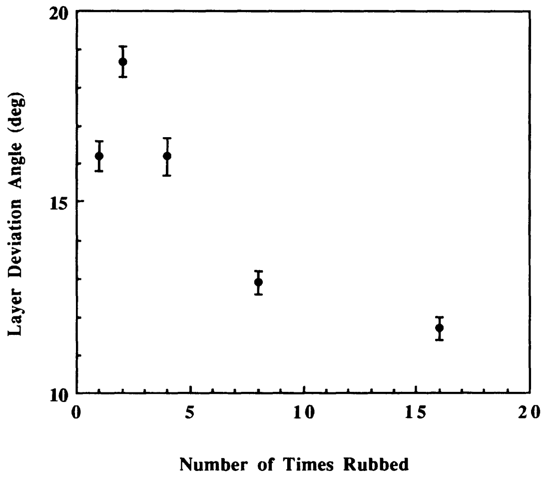

FIG. 3. The layer deviation angle as a function of the number of times the substrate was rubbed. The homogeneity of the sample alignment was rather poor for the substrate that was rubbed only once. Thus the trend of larger deviation angles for weaker rubbing is finally limited by a deterioration of the monodomain alignment for very weak rubbing.

Recently, Lee, Patel, and Goodby [16] have reported a surface electroclinic phenomenon in the isotropic phase of an FLC on a rubbed polymer surface. The result was explained in terms of *enhanced* smectic ordering near the surface. Using ellipsometry, we have measured the pretransitional growth of this ordered surface layer in the isotropic phase of our FLC sample as $T \rightarrow T_{IA}$ [11]. These experiments show that the rubbed polyimide surface actually promotes enhanced smectic ordering, which also contradicts the assumption of reduced surface smectic ordering used in Ref. [5] to explain the observed layer deviation angle θ_0.

In summary, we have studied the deviation of the smectic layer normal from the rubbing direction using SHG and ellipsometry. The experiments clearly distinguished between the two proposed models of the phenomenon. All our results can be well explained by the surface electroclinic effect.

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