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Surface ordering above the isotropic–smectic-*A* transition at a silane-treated substrate

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Surface ordering in a homologous series of alkyl cyanobiphenyl (nCB) liquid crystals having a direct isotropic–smectic-*A* (I-A) transition was investigated using evanescent-wave ellipsometry. The liquid crystal was bounded by a solid substrate treated with a silane surfactant which induced homeotropic (perpendicular) ordering of the liquid crystal molecules in the smectic-*A* phase. In the isotropic phase, one of the liquid crystals (10CB) partially wet the interface with an orientationally ordered, homeotropically aligned layer. The ordered interfacial layer grew without layering transitions but remained finite in thickness as the bulk *I-A* transition was approached. The interfacial layer has significantly lower orientational order than is observed in the smectic phase, indicating the possibility that the surface region of 10CB may be in a surface-induced, nonspontaneous nematic phase. The other liquid crystals (11 and 12CB) showed no surface ordering behavior whatsoever. Models describing the ordered surface layer of 10CB are presented. The results can be interpreted as a sharp transition in the surface ordering behavior as the chain length of the liquid crystal is varied, at the *I-A* transition of a liquid crystal.

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Molecular ordering of a liquid crystal (LC) near a free surface or boundary substrate is a problem of long-standing interest, since its prediction [1] and discovery [2] in the isotropic (*I*) phase of nematic (orientationally ordered) LCs. Recent studies of surface ordering have probed ordering on the nematic (*N*) side of the *I-N* transition, finding surface-induced ordering or disordering in various liquid crystal-substrate systems [3,4].

More recently, attention has shifted to the more complex problem of surface ordering in LCs having smectic (orientationally ordered and layered) phases. X-ray reflectivity and optical ellipsometry studies have demonstrated smectic ordering at the free surface of a variety of LCs [5–10]. Experiments have detected sharp layering transitions as successive molecular layers form at the interface [6,7,9,10] as well as growth of the smectic interfacial region without detectable layering transitions [8,9], and both partial wetting (formation of a finite-thickness layer) [6,7,9] and complete wetting (by an interfacial region of diverging thickness) [8–10] have been observed at the free surface as the temperature is cooled approaching the *I-A* transition.

So far there have been very few studies of interfacial ordering in a smectic LC near a solid substrate. Ocko has investigated smectic ordering of nCB on Si-100 substrates coated with alkylsilane using x-ray reflectivity, observing partial wetting by an interfacial smectic region with layering transitions for 11 and 12CB [11,12]. NMR and heat capacity measurements have been used to study interfacial ordering in porous glass, where both finite-size effects and interfacial ordering are present [13–15]. In this Rapid Communication, we report a study of interfacial ordering in 10–12CB above the *I-A* transition at a solid substrate, glass coated with the silane surfactant n,n-dimethyl-n-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP). Using evanescent-wave ellipsometry (EWE), we find an orientationally ordered interfacial layer in 10CB, but no molecular ordering whatsoever with 11 or 12CB. These results demonstrate a surface ordering transition in the interfacial region as alkyl chain length is varied. Even more surprisingly, our results indicate that the interfacial region of 10CB, above the *I-A* transition, has a significantly lower orientational ordering than its smectic bulk phase, suggesting the possibility that the interfacial region may be in a nonspontaneous nematic phase induced by the surface-LC interaction field.

We use EWE to investigate the surface ordering behavior in liquid crystalline samples. The EWE apparatus is briefly described below and elsewhere [4]. Linearly polarized light from a He-Ne laser is incident on the substrate-LC interface. The LC is confined in a thin film between a high-refractive-index glass prism ($n = 1.845$) and a glass plate, with the laser light incident from the prism side. The angle of incidence is chosen so that the light undergoes total internal reflection, with only an evanescent wave penetrating the interfacial region of the LC near the substrate. Initially equal *p*- and *s*-polarization components of the incident light acquire a phase shift upon reflection from the interface. As we show below, the phase shift $\Delta\phi_c$ at the critical angle for total internal reflection θ_c is proportional to the integrated surface order of the LC molecules in the interfacial region. The phase shift is measured using the null technique: An analyzer is positioned after the sample to cross the original light polarization, and a Pockels cell in the beam path is adjusted to induce an optical phase shift equal and opposite to the one induced by reflection from the sample cell, so that the light is restored to linear polarization before the analyzer and extinguished. To enhance sensitivity, an oscillating voltage (10 kHz) is applied to the Pockels cell and the optical detector (silicon photodiode) output is measured with a lock-in amplifier. System instability due to thermal drifts in the Pockels cell crystal or mount orientation is controlled by housing the Pockels cell and mount in a temperature-controlled enclosure ($\pm 0.02\,^\circ$C stability). The sample cell is enclosed in a two-stage oven with a temperature stability of ± 1 mK.

The EWE apparatus allows us to probe the integrated surface order in the interfacial region. The penetration depth of the evanescent wave is of the order of an optical wavelength

(633 nm), and the resulting optical phase shift is an average of the optical properties of interfacial region over its penetration depth. Hence, optical techniques cannot distinguish smectic layer order, with a distance scale of a molecular length (21 Å for 10CB [12]), from nematic or orientational order. However, layering transitions, or discrete jumps in the integrated surface ordering with temperature, have been detected in 12CB via ellipsometry, and our apparatus can easily resolve transitions involving the addition of a single ordered layer of molecules [8–10].

We prepared our samples as follows. A glass prism and plate were cleaned first in acetone and subsequently in chromic acid, then placed in a solution containing DMOAP (2% by weight in distilled water with 3% acetic acid). This procedure is believed to deposit a monolayer of DMOAP on the glass surfaces [16]. After baking for 1 h at 120 °C to remove water and promote adhesion of the DMOAP layer, a narrow gap between prism and plate is filled by capillary suction of the LC in the isotropic phase. The glass plate is separated from the prism at one end by a 130 μm mylar spacer, so that the LC film is wedge-shaped, facilitating the spatial discrimination of the beam reflected from the prism-LC interface from the one reflected from the glass plate. Samples were inspected visually and by polarized light microscopy; in all cases, the surface treatment induced uniform homeotropic alignment of the smectic phase.

We now describe our approach to analyzing the data obtained from the EWE apparatus. As mentioned previously, the phase shift $\Delta\phi_c$ that we measure is proportional to the integrated surface order. When the bulk medium is optically isotropic, the integrated birefringence Γ, also called the *coverage,* is defined by $\Gamma=\int_0^\infty dz[n_e(z)^2-n_o(z)^2]$, where z is the coordinate normal to the interface and n_e and n_o are the extraordinary and ordinary indices of refraction of the LC, which may vary with z in the interfacial region. The optical anisotropy $\Delta\varepsilon=n_e^2-n_o^2$ is related to the nematic orientational order parameter S by $S(z)=\Delta\varepsilon(z)/(\Delta\varepsilon)_{\mathrm{max}}$, where $(\Delta\varepsilon)_{\mathrm{max}}$ is the dielectric anisotropy of a perfectly aligned nematic. The integrated birefringence Γ is proportional to the well-known adsorption parameter Γ_{ads} given by $\Gamma_{\mathrm{ads}}=\int_0^\infty dz S(z)$. Hence, $\Delta\phi_c$, Γ, and Γ_{ads} are all proportional and the EWE apparatus directly measures Γ_{ads} as a function of sample temperature.

More specifically, from a detailed consideration of the reflectivity of the *p*- and *s*-polarized components of light reflected from an inhomogeneous, anisotropic interface, one can show that the phase shift $\Delta\phi_c$ at the critical angle for total reflection is given by the following approximate relation:

$$\Delta\phi_c=\frac{4\pi}{\lambda}(\varepsilon_g-\varepsilon_i)^{-1/2}\int_0^\infty dz(\varepsilon_g+\varepsilon_i-\varepsilon_g\varepsilon_i/\varepsilon_z-\varepsilon_x), \tag{1}$$

where ε_g and ε_i are the dielectric constants of the incident medium (glass prism) and final medium (isotropic liquid) respectively, and ε_x and ε_z are the elements of the dielectric tensor of the liquid crystal in the inhomogeneous interfacial layer [17]. The above expression is appropriate to the case of a homeotropically oriented, uniaxial molecular ordering in the interfacial region, and it is valid when the length-scale L of the interfacial region is much smaller than the optical wavelength λ. We can express the dielectric constants ε_x and ε_z in terms of the anisotropy $\Delta\varepsilon=\varepsilon_z-\varepsilon_x$ and the isotropic phase dielectric constant ε_i using the relations

$$\varepsilon_z=\varepsilon_i+\frac{2}{3}\Delta\varepsilon \quad\text{and}\quad \varepsilon_x=\varepsilon_i-\frac{1}{3}\Delta\varepsilon. \tag{2}$$

Putting the above relations into Eq. (1) and using $S(z)=\Delta\varepsilon(z)/(\Delta\varepsilon)_{\mathrm{max}}$ we find the following expression relating the phase shift $\Delta\phi_c$ at the critical angle to the adsorption parameter Γ_{ads}:

$$\Delta\phi_c=\frac{4\pi}{\lambda}\,\frac{(2\varepsilon_g+\varepsilon_i)(\Delta\varepsilon)_m}{3\varepsilon_i(\varepsilon_g-\varepsilon_i)^{1/2}}\Gamma_{\mathrm{ads}}, \tag{3}$$

which shows that $\Delta\phi_c$ is proportional to Γ_{ads} as was indicated earlier. Equation (3) is valid when $\Delta\varepsilon\ll\varepsilon_i$ and $L\ll\lambda$, where L is the thickness of the interfacial region. For liquid crystals, the first condition, $\Delta\varepsilon\ll\varepsilon_i$, is satisfied only approximately due to the typically large value of the dielectric anisotropy, but Eq. (3) remains a helpful guide. For better accuracy in computations, Eq. (1) is preferred. For the most accurate calculation of $\Delta\phi_c$ for reflection from an anisotropic, inhomogeneous interfacial region of arbitrary length-scale, the numerical 4×4 matrix method of Berreman can be employed [18]. In this paper, all results described using Eqs. (1) or (3) were checked against a numerical calculation using the matrix method; Eq. (1) agreed within 2% of the accurate numerical matrix calculation, and the somewhat simpler Eq. (3) was valid within 10%.

Since ellipsometry cannot separately measure the thickness of the ordered region and the degree of ordering in the interfacial region, it is necessary to make some assumption about the order parameter profile $S(z)$ in order to deduce the thickness of the ordered layer. In the past work on interfacial ordering in nematics, Landau–de Gennes theories have been used to predict the functional form of $S(z)$ at different temperatures, so that the thickness of the ordered interfacial layer could be determined [2–4]. The theoretical picture of interfacial ordering in smectics is less clear, with several different frameworks competing. It seems clearest and most useful, at this point, to choose a simple form for $S(z)$, one that is not tied to a particular theoretical approach. Accordingly, in this paper, we analyze our results for two simple model profiles $S(z)$, either an interfacial layer of constant birefringence or a layer of exponentially-decaying birefringence. These models are described below.

For the case of an interfacial layer of thickness L and constant dielectric anisotropy $\Delta\varepsilon$, the coverage Γ is given simply by $\Gamma=\Delta\varepsilon L$ and the adsorption parameter Γ_{ads} is given by $\Gamma_{\mathrm{ads}}=\Delta\varepsilon L/(\Delta\varepsilon)_m$. Putting this expression into Eq. (3), we can find L, the thickness of the interfacial region, in terms of known optical constants and the experimentally measured value $\Delta\phi_c$, providing we know the value of $\Delta\varepsilon$; typically, one makes the reasonable assumption that $\Delta\varepsilon$ is equal to the dielectric anisotropy of the bulk smectic-*A*

TABLE I. Ordinary and extraordinary indices of refraction n_o and n_e in the Sm-*A* phase and refractive index n_i for the isotropic phase, determined within 0.1 °C of the *I*-*A* transition and measured at $\lambda = 632.8$ nm.

Material	n_o	n_e	n_i
10CB	1.499	1.646	1.546
11CB	1.493	1.639	1.537
12CB	1.490	1.631	1.536

(Sm-*A*) phase. The optical constants used for 10, 11, and 12CB are given in Table I. The refractive indices presented in Table I were determined from our measurements of the critical angle for total internal reflection on bulk Sm-*A* samples. For reference, from Eq. (1), we note that

$$\Delta\phi_c = c\Gamma, \quad \text{with} \quad c = 23.2 \quad \text{mrad/nm for } 10\text{–}12\text{CB}.$$

Next we consider the case of an exponentially-decaying anisotropy profile, given by $\Delta\varepsilon(z) = \Delta\varepsilon \exp(-z/L)$, where $\Delta\varepsilon$ is the dielectric anisotropy at the interface $(z=0)$ and L is the decay distance. For this profile, the coverage is $\Gamma = \Delta\varepsilon L$ just as before, and Eq. (3) results in the same expression for the characteristic decay length L that was obtained for the uniform interfacial layer. If the somewhat more accurate Eq. (1) is used, after a little algebra we can again find $\Delta\phi_c = c'\Gamma$, with c' a constant. For reference, we find $c' = 25.3$ mrad/nm for 10CB and $c' = 24.1$ mrad/nm for 11 and 12CB.

We measured the phase shift $\Delta\phi_c$ at the critical angle for total internal reflection as a function of temperature for three LC samples. Our results for 10, 11, and 12CB are shown in Fig. 1, where Γ (which is proportional to $\Delta\phi_c$) is plotted versus temperature. From the plot, we see that the integrated birefringence of 10CB grows but does not diverge as the temperature is cooled toward the *I*-*A* transition. Using the material parameters in Table I, we can find the maximum thickness of the ordered interfacial layer (just above the *I*-*A* transition) for our model birefringence profiles. For the step function profile with constant dielectric anisotropy equal to the Sm-*A*–phase bulk value, we find a maximum layer thickness of 13.6 Å. For the exponential profile with surface dielectric anisotropy equal to the Sm-*A*–phase bulk value, we find that the characteristic length of the interfacial layer is 12.4 Å. Noting that the thickness of a single layer (actually a bilayer [19]) of smectic 10CB is 35 Å and the length of one fully extended 10CB molecule is 21 Å [12], we calculate that the ordered interfacial region is less than one layer thick! An interfacial layer with a thickness smaller than a molecule is clearly impossible, so the assumption that the surface order parameter is equal to the order parameter in the Sm-*A* phase near the transition must be wrong: the magnitude of the surface ordering must be substantially less than the magnitude of the ordering in the Sm-*A* phase. Reducing our model parameters for the interfacial dielectric anisotropy $\Delta\epsilon$ would, of course, increase our estimate for the interfacial layer thickness, since $\Gamma = \Delta\epsilon L$. In particular, if the surface anisotropy were smaller by a factor *n*, the interfacial layer would be correspondingly *n* times thicker. To take a specific example, if the dielectric anisotropy were one-tenth the bulk Sm-*A* value, the interfacial layer thickness would be around 130 Å, or about six molecules thick, which is comparable to the thickness of the nematic interfacial layer observed in 5 and 8CB on DMOAP-coated glass substrates in previous work [3,4]. We also note that the measured integrated birefringence Γ increases smoothly, without discontinuities, as the *I*-*A* transition is approached. This continuous increase of Γ indicates an absence of layering transitions.

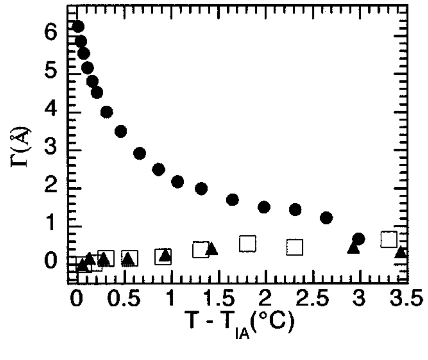

FIG. 1. Integrated birefringence Γ vs temperature T-T_{IA} for 10CB (circles), 11CB (squares), and 12CB (triangles). Typical uncertainty in Γ, based on different runs with identically prepared samples, is estimated to be ±0.6 mrad.

We note that in the above analysis, bulk values of refractive index of *n*CB have been used as estimates of the actual surface values of these parameters, which are probably slightly different. While this estimation renders the exact value of *c* (in expressions like $\Delta\phi_c = c\Gamma$) somewhat uncertain, the overall qualitative conclusion, that the interfacial region of the 10CB sample is substantially less ordered than bulk smectic 10CB, is unaffected.

For 11 and 12CB, there is no significant variation in the integrated birefringence Γ as the temperature approaches the bulk *I*-*A* transition. From this we can conclude that these LCs exhibit no measurable surface ordering behavior in the *I* phase near DMOAP-coated glass. This result is somewhat surprising in view of the fact that the Sm-*A* phase of these samples was a well-aligned homeotropic monodomain. We note that the above data were confirmed through measurements on multiple samples for each different LC.

Our measurements on surface ordering in the alkyl cyanobiphenyls are surprising in that we find surface ordering for 10CB but not for 11 or 12CB. As we noted, our results can be described as a surface ordering transition as the LC chain length is varied, an observation near the *I*-*A* transition. In a previous experiment on *n*CBs at a solid Si-100 substrate, quite different behavior was observed: all homologs exhibited ordering, with longer chains exhibiting the greatest ordering (three layering transitions for 12CB, two for 11CB, and the continuous growth of an ordered region without layering transitions for 10CB) [12]. Experiments studying molecular ordering at the free surface have also observed that 12CB exhibits a stronger surface ordering tendency than 10CB (around five layering transitions for 12CB [6,7,9], one indistinct layering transition for 10CB [7]).

Our samples differ from those used in the previous work in two important ways which may explain the different surface ordering behavior we observed. First, our surfactant (DMOAP) differed from ones used previously (alkylsilane, aliphatic acid, or free surface). Second, our glass substrates are probably rougher than the solid substrates used in previous experiments [12,14]. Our substrate surfaces, mechanically polished to $\lambda/10$ flatness for $\lambda = 633$ nm, are likely to be rough on the order of 10 nm, comparable to the LC molecular length. Mirantsev has modeled liquid crystals near a sinusoidally rough substrate, finding that the smectic order decreased as degree of corrugation increased, and that smectic order could be suppressed by a sufficiently wavy substrate [20]. It is not clear at this point whether surfactant selectivity or substrate roughness is responsible for the remarkable surface ordering transition we have observed. We note that while the sample surface is rough on the scale of a LC molecule, the laser beam illuminates an area very much larger; hence, the optical signal averages over a large region of the microscopically rough surface. Experimental results from different samples, prepared identically, were therefore expected and observed to be highly reproducible.

The most surprising feature of our observations reported here is that the nematiclike molecular order in the interfacial region of the 10CB sample is considerably less than the order parameter exhibited by its smectic bulk phase. One possibility, at this point speculative, that might explain both the different surface ordering behaviors of 10CB relative to 11 and 12CB and the small degree of molecular order in the 10CB interfacial layer, involves the formation of a nonspontaneous surface nematic phase. In a mixture of 8 and 10CB which normally undergoes a direct *I-A* transition, Lelidis and Durand have observed a nonspontaneous nematic phase induced by a strong electric field [21]. In our experiment, the substrate interaction orients adjacent LC molecules similarly to a localized external field and might be expected to induce a nonspontaneous nematic phase in the interfacial region if the interaction strength is sufficiently large and if smectic ordering is suppressed. The combination of a surfactant known to induce strong nematiclike ordering and a microscopically rough substrate, predicted to suppress smectic ordering [20], might be expected to induce a nonspontaneous nematic phase localized to the interfacial region. In the cyanobiphenyls, it is probable that 10CB would more readily form such a phase than 11 or 12CB, since 10CB is the shortest alkyl cyanobiphenyl to have a direct *I-A* transition (9CB has the phase sequence I-N-A). We will investigate this intriguing possibility, by examining mixtures of 9 and 10CB exhibiting a direct *I-A* transition, as well as smectic ordering of other mixtures and on differently treated substrates, in future work.

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