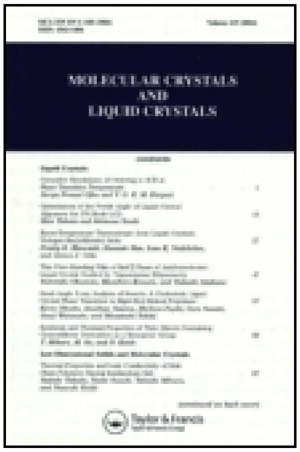

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SURFACE-INDUCED ORDERING IN A HOMOLOGOUS SERIES OF LIQUID CRYSTALS — ORIENTATIONAL WETTING

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Abstract We have studied the orientational wetting behavior of a liquid crystal homologous series. A change over from partial wetting to complete wetting has been observed as the length of the alkyl chain increases.

A properly treated solid surface can be used effectively to align liquid crystal (LC) molecules in their mesophases. Even when the bulk LC is in the isotropic phase, the anisotropic interactions between the LC molecules and the surface can induce an orientationally ordered LC layer next to the surface.[1-3] Such a phenomenon can be viewed as orientational wetting of the isotropic LC-solid interface by an ordered LC phase.[3] Depending on the relative strength of the molecule-surface interaction to the molecule-molecule interaction, wetting can either be partial or complete. A quantity that is often used to characterize the wetting behavior is the adsorption parameter Γ, defined as $\Gamma = \int_0^\infty [\, Q(z) - Q_b \,]\, dz$, where $Q(z)$ and Q_b are the order parameters in the surface layer and in the bulk, respectively. As the temperature approaches the bulk transition, Γ remains finite in the case of partial wetting, or diverges to infinity in complete wetting.

Orientational wetting and the transition from partial to complete wetting (orientational wetting transition) at the LC-solid interface have been studied theoretically by a number of authors using different models.[1-5] The possibility of such a transition was first suggested by Sheng[1] in the study of surface-induced pretransitional behavior of isotropic-nematic (I-N) phase transition. Using the Landau-de Gennes formalism and a short-ranged anisotropic interaction $V_s = - GQ_0\delta(z)$, where $Q_0 = Q(z = 0)$, he showed that as the temperature T approaches the I-N transition temperature T_c, the following behaviors are possible with increasing G: (a) Q_0 remains smaller than Q_c (the bulk order parameter in the nematic phase at T_c) as $T \rightarrow T_c$; Γ is finite; (b) A sudden increase of Γ results from a jump of Q_0 from a value smaller than Q_c to that larger than Q_c at a temperature higher than T_c; Γ diverges logarithmically as $T \rightarrow T_c$. (c) Q_0 increases continuously to some value larger than Q_c, and Γ diverges logarithmically as $T \rightarrow T_c$. The case (a) corresponds to partial wetting, and the other two cases to complete wetting. The sudden increase of Q_0 or Γ in (b) is now known as the prewetting transition, which is associated with first order wetting transition.

Since Sheng's pioneering work, several other models have been developed on the subject. Poniewierski and Sluckin[4] used the Maier-Saupe model for the bulk liquid crystal and a surface interaction of the form $V_s = (- GQ_0 - U_1Q_0^2 / 2)\ \delta(z = 0)$. With $U_1 = 0$, they were able to recover Sheng's results with only some quantitative difference. The presence of a nonvanishing U_1, however, could change the wetting transition from first order to second order. In this model, prewetting transition would only occur in a small parameter space of G and U_1.

Both models neglected the density difference between the nematic and the isotropic phases. Although it is quite small, Telo da Gama[5] found from her calculation that it could significantly affect the wetting behavior. However, this could be an artifact of the model as the mean-field theories often predict incorrectly the density difference by an order of magnitude. In the model, the qualitative behavior of change over from partial to complete wetting still prevails, but the profile Q(z) of the wetting layer does not necessarily decrease monotonically away from the interface. The wetting transition also strongly depends on the form of the anisotropic surface interaction. For example, it can change from second order to first order as the range of the interaction increases.

In short, all models predict an orientation wetting transition as LC molecule-surface interaction varies relative to the molecule-molecule interaction. However, the order of the transition may depend strongly on the details of the interactions. If complete wetting should occur, Γ will diverge logarithmically as $T \rightarrow T_c$ for a short-range interaction.

Despite the theoretical and practical interest, experimental progress in this area has been slow.[2-3] There is evidence[3] that both partial wetting and complete wetting could occur, but the systematic change over from one to the other has not yet been reported. Presumably this is due to the difficulty of varying the LC molecule-surface interaction in a systematic and controllable way. We report here an experimental study on the orientational wetting behavior of the homologous series of alkyl cycnobiphenyl liquid crystals (nCB, n = 5 to 9) on a glass substrate coated with silane surfactant n,n-dimethyl-n-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP), which induces a homeotropic alignment in the nematic phase. By changing the alkyl chain length (n = 5 to 9), but keeping the substrate unchanged, the LC-surface interaction is varied in a systematic way.

We have used the evanescent-wave ellipsometry[6] to measure the phase difference $\Delta\phi$ between the p- and s-polarized components of a laser beam reflected from the LC-glass interface as a function of the incident angle θ. Compared to the transmission ellipsometric techniques, it has a number of advantages. With the present technique, the signal from the interfacial region is enhanced by a factor of 8 or more because the evanescent wave preferentially probes only the interfacial region. In addition, the spurious birefringence in the bulk is suppressed, allowing us to do measurements even when the system is so close to the bulk I-N transition that the strong fluctuation of light lead to intense scattering of light in the bulk. Also, changing the incident angle of the incoming laser beam changes the effective penetration depth, making separate determination of Q_0 and the interfacial layer thickness possible. The phase retardation at the critical angle is closely proportional to the adsorption parameter Γ, and hence it gives us a direct indication of the wetting property. The value of the critical angle itself is an *in situ* monitor of the bulk LC, since it depends only on the refractive index of the bulk LC relative to that of the substrate. Our technique can also be used to study ordering or disordering at an LC/solid interface when the LC is in a mesophase. This is not possible with transmission ellipsometry, as the signal from the interface will be overwhelmed by the bulk contribution. The technique can also be applied to the study of density variation at an isotropic liquid-solid interface.

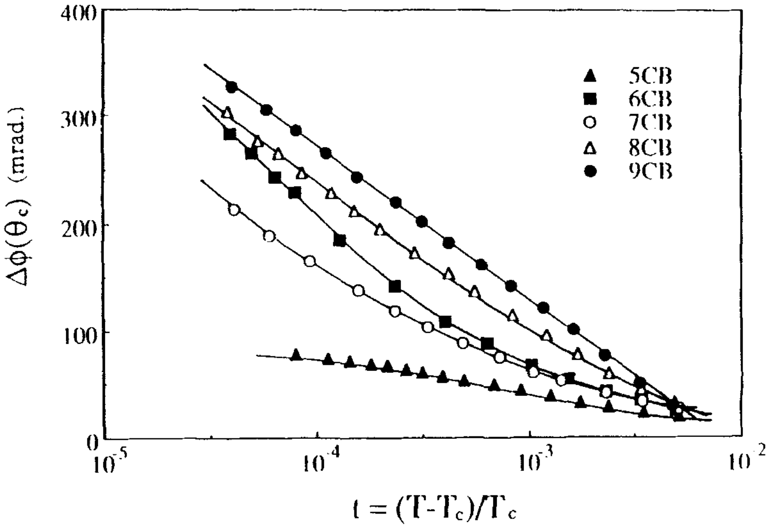

FIGURE 1 Phase difference at critical angle, $\Delta\phi(\theta_C)$, as a function of reduced temperature $t = (T - T_C) / T_C$.

For each LC sample, $\Delta\phi(\theta)$ was measured at a series of temperatures at $T > T_C$, decreasing towards T_C. In Fig. 1, we presented the measured $\Delta\phi(\theta_C)$, which is proportional to Γ, as a function of the reduced temperature $t = (T - T_C) / T_C$ for nCB, (n = 5 to 9). It is seen that for 5CB, $\Delta\phi(\theta_c)$ approaches a finite value as $T \rightarrow T_C$, which is characteristic of partial wetting, where as for 6CB to 9CB, $\Delta\phi(\theta_c)$ diverges logarithmically as $T \rightarrow T_C$, characteristic of complete wetting. The logarithmic divergence fits over a wider temperature range with large n, indicating that the complete wetting character becomes more pronounced with increase of n. Prewetting was not observed in the experiment.

The angular scan $\Delta\phi(\theta)$ at various temperatures can be used to further check the theoretical models, as $\Delta\phi(\theta)$ can be calculated if the profile of the order parameter Q(z) is known. In Sheng's model,[1] assuming a δ-function surface anchoring potential and using the Landau-de Gennes formalism, one finds[2]

$$Q(z) = \frac{2a(T - T^*)\, R(Q_0)\, e^{z/\xi}}{(\, R(Q_0)\, e^{z/\xi} + b/3\,)^2 - ac(T - T^*)/2} \qquad (1)$$

with

$$R(Q_0) = \frac{1}{Q_0}\,[2a(T - T^*)]^{1/2}\,[\,\frac{1}{2}a(T - T^*) - \frac{1}{3}bQ_0 + \frac{1}{4}cQ_0^2\,)^{1/2} + \frac{a}{Q_0}(T - T^*)$$

and

$$\xi = \xi_0\,(\,T/T^* - 1\,)^{-1/2},$$

where a, b, c, ξ_0, and T^* are constants of the LC medium independent of temperature, and $Q_0 = Q\,(z = 0)$ is generally temperature dependent. We can use in Eq. (1) the values of a, b, c given in Ref. 7, $\xi_0 = 5Å$, $T^* = T_c - 2b^2/9ac$, with T_c determined experimentally, and $Q_0(T)$ as an adjustable parameter to calculate $\Delta\phi(\theta)$ and compare with the experimental $\Delta\phi(\theta)$ at each temperature. The results show that for 5CB, Q_0 is always less than the bulk order parameter in the nematic phase Q_c, and is only weakly dependent on temperature. For 8CB and 9CB, the temperature dependence is definitely stronger and Q_0 is clearly larger than Q_c as T approaches T_c. According to the Landau-de Gennes model[1] or some other mean-field theory,[4] the above two cases should lead to partial and complete wetting behavior respectively, as was observed in our experiment.

However, the theoretical fit to the experimental data on $\Delta\phi$ vs. θ using Q(z) of Eq. (1) sometimes had deviations exceeding the experimental uncertainty of 1×10^{-4} rad. This is not surprising since if $Q(z) \approx Q_c$, the approximation using a truncated power series of Q(z) to describe the free energy density in the Landau-de Gennes formalism becomes questionable. Also the assumption of a δ-function surface anchoring potential may not be realistic, and the order-parameter fluctuations can be quite significant near the phase transition. All these can affect the wetting behavior quantitatively.

In conclusion, our results here show clearly a partial orientational wetting behavior for 5CB and complete wetting for 6CB to 9CB. The complete wetting character becomes more pronounced with increase of n. The very significant change in the wetting characteristics of the LC in response to a change in the alkyl chain length suggests that the chain-chain interaction between DMOAP and LC molecules must play an important role in the homeotropic alignment of LC.

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