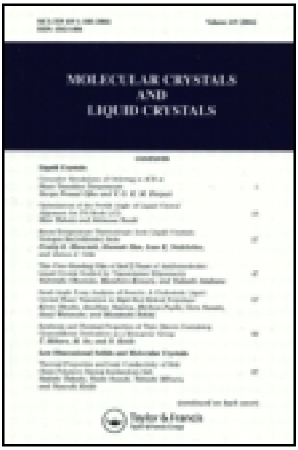

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Smectic Layering at the Free Surface of Isotropic Liquid Crystals in the Pre-Smectic Temperature Region Characterized by Ellipsometry

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Smectic Layering at the Free Surface of Isotropic Liquid Crystals in the Pre-Smectic Temperature Region Characterized by Ellipsometry

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We have recorded the angular dependence of the ellipsometric signal of bulkisotropic dodecylcyanobiphenyl (12CB) as a function of temperature in the pre-smectic temperature region. Using a simple model, the order parameter of the discontinuously growing smectic surface layer has been determined approaching the isotropic-smectic phase transition temperature. Also the pretransitional isotropic region of the isotropic-smectic transition of the liquid crystal compound 2-(4-(1,1 -dihydro-2-(2-perfluorobutoxy)perfluoroethoxy) phenyl-5-octyl pyrimidine (H8F(4,2,1)MOPP) has been investigated.

Keywords: pre-smectic layering; ellipsometry

INTRODUCTION

At the free surface of a liquid crystal, phase transitions between different thermotropic phases can be strongly influenced by the surface tension force, which results from the asymmetry of an air-liquid interface, and favors homeotropic alignment, and indirectly smectic order. Surface tension also acts as a non-zero field which keeps the phase transition away from the (zero field) critical point of the system. Resulting from this, while cooling down a thermotropic liquid crystal starting in the isotropic phase, the surface region undergoes a pre-transition from isotropic to an oriented state, already a couple of tenths of degrees before the inset of the bulk transition. As far as we know, it has always been observed that the pre-transitional surface order corresponds to the symmetry of the bulk oriented phase, which appears at the bulk critical temperature. We have investigated two compounds: dodecylcyanobiphenyl (12CB) and 2-(4-(1,1-dihydro-2-(2-perfluorobutoxy)perfluoroethoxy) phenyl-5-octyl pyrimidine (H8F(4,2,1)MOPP or 8422). Both liquid crystals exhibit an interesting isotropic to smectic phase transition behavior. For 12CB, which has already been thoroughly investigated by several groups[1-5] , we study the plausibility of ellipsometric depth profiling and present a quantitative evaluation of the pre-smectic layer thickness and nematic order parameter. The idea to investigate the pre-smectic behavior of H8F(4,2,1)MOPP was inspired by its very intriguing layer-by-layer thinning transition, which was recently reported by Johnson et al. [6] using high resolution optical reflectivity measurements.

DEPTH PROFILE OF THE ORIENTATION ORDER PARAMETER IN PRE-SMECTIC LAYERED 12CB

Pre-transitional smectic order in 12CB has already been thoroughly investigated by means of x-ray reflectivity[1,2] and ellipsometry[3-5]. A stepwise growth of several smectic surface layers was assessed. In x-ray experiments the depth dependence of the density modulations, which are related to smectic layer formation, is probed. Ellipsometric data yield information on the depth profile of the (anisotropic) refractive index, which is coupled to the

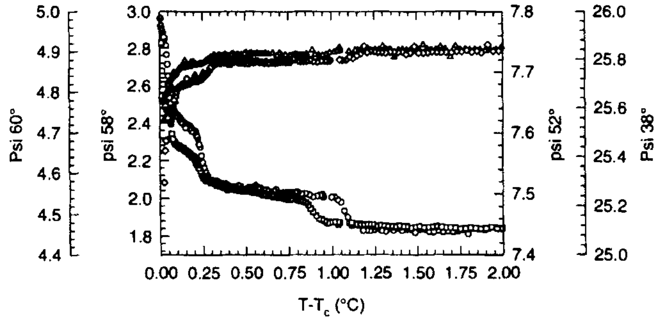

FIGURE 1 Temperature dependence of ψ for

θ= 38°(triangles), 52°(diamonds), 58°(squares), 60°(circles)

orientational order parameter. Both methods have led to the accurate determination of the temperature at which each smectic layer forms and of the thickness of these layers. During pre-smectic layer formation, along with the smectic order, the surface orientational order is enhanced by surface tension induced homeotropic aligning forces and decreased by the presence of isotropic orientational disorder in the bulk. The resulting orientational order parameter profile thus yields information about the strength and range of surface tension aligning forces relative to the disordering bulk influence. In this study we employ ellipsometry to obtain a depth profile, S(x), of the nematic order parameter.

Using the experimental setup described in Ref.4, we have monitored the temperature dependence (Fig. 1) of $\psi = \mathrm{Arc}\tan(r_P / r_N)$ in the neighborhood of the smectic-isotropic transition. r_P and r_N are the reflection coefficients for in plane and out-of-plane polarized light, respectively. Combining temperature scans obtained for 17 incident angles θ between 30° and 80° using a HeNe laser beam on the free surface of a 12CB sample, we have determined angular spectra $\Delta\psi(\theta) = \psi(\theta) - \psi_{iso}(\theta)$. $\psi_{iso}(\theta)$ is the ellipsometric reference spectrum of the sample at $T-T_c=3°C$. The spectra $\Delta\psi(\theta)$ have a complex relationship to the orientational order parameter S(x) at temperature T. Analyzing $\Delta\psi$ rather than ψ allows us to reduce the influence of experimental offsets in the spectrum. Moreover, the differential quantity $\Delta\psi$ is more sensitive to S(x) features than ψ. Solving the inverse problem of ellipsometry, i.e. reconstructing S(x) from $\Delta\psi(\theta)$ without a priori knowledge is not a simple task. Straightforward methods are only available for the direct problem: determining $\Delta\psi(\theta)$ form S(x). By making use of known values[7] for the anisotropic refractive index of aligned samples (bulk dielectric permittivity $\varepsilon_{iso}=2.3716$ and anisotropy $\Delta\varepsilon=0.779$ for 12CB) and approximating the continuous profile by a stack of optically homogeneous layers, $\psi(\theta)$ can be calculated solving the Maxwell equations. In earlier work[5], we have proposed a neural network method for the solution for the inverse problem. However, in order to increase the accuracy, here we prefer to make use of the available a priori information about surface smectic layers. Given the stepped character of the order parameter profile of a smectic surface, we parametrize the orientational order parameter profile as a hyperbolic tangent function $S(x) = S_{-\infty} + (S_{+\infty} - S_{-\infty})(1 + \tanh((x - x_0)/x_1)/2$, with $S_{-\infty}$ and $S_{+\infty}$ the saturation values at $-\infty$ and $+\infty$, and x_0 the position and x_1 the width of the order-disorder interface. The inverse problem then reduces to a 4-parameter least-squares fit. The used parametrization allows sufficient freedom on the possible S(x) profile. However the limited signal-to-noise ratio of the experimental data excludes the possibility including a greater number of free parameters in the functional form of S(x). Fig. 2 shows the fitting results for experimental angular spectra obtained at different temperatures in the neighborhood of the isotropic-smectic transition

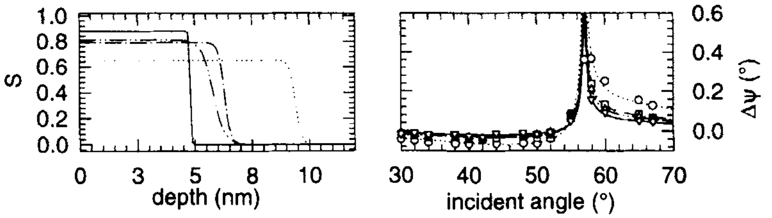

FIGURE 2 Best fitting hyperbolic tangent profiles and signals for T-T_c=0.2(dots),0.3(dash-dot),0.4(dash-dot-dot),0.7°C(full)

temperature T_c. The best fit corresponds well with the experimental data, confirming the plausibility of the proposed model. As expected, the order disappears completely in the bulk: $S_{+\infty}=0$. The area under S(x) increases approaching T_c. This reflects the globally increasing orientational (and smectic) order towards the smectic phase. At T-T_c=0.7°C, the thickness of the ordered layer is (4.8±0.4)nm. This result is somewhat different from Ref.2, where a thickness of 3.7nm was found. The difference is probably due to a not perfect coincidence between nematic and smectic order. We also did not observe steps at higher temperatures and assumed isotropy at T-T_c=3°C, the reference temperature to determine ψ_{iso}. The thickness of the ordered region increases upto (9.4±0.3)nm at T-T_c=0.2°C, indicating the growth of more and more smectic layers towards T_c. The magnitude of the order parameter in the surface smectic region decreases as the size of this region grows with decreasing temperature. The contour plots in Fig.3 show that, in spite of some uncertainty, the S_0 decrease from 0.88 at T-T_c=0.7°C down to 0.65 at T-T_c=0.2°C significantly exceeds the experimental uncertainty. It is somewhat surprising that the orientational order decreases as the smectic region thickness is growing. It is known that the orientational order in the first molecular layer at the air-liquid interface is very high due to the very large aligning force. It is very difficult in the nematic or smectic phase to tilt the

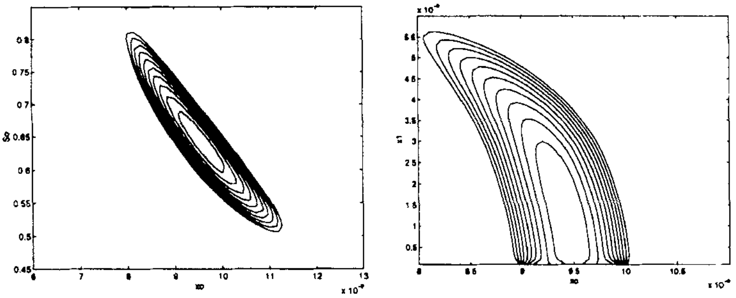

FIGURE 3 Contour plots of the χ^2-value around the best fit of 12CB data at $T\text{-}T_c = 0.2°$ in the (x_0, S_0) plane and in the (x_0, x_1) plane

spontaneously aligned molecules at the free surface by a magnetic field[8], explaining the large order parameter value in the initial smectic layer at $T\text{-}T_c = 0.7°C$. However, the surface anchoring force does not extend much deeper than the first molecular layer. If subsequent smectic layers are present, then their nematic alignment is a compromise between on one hand the elastic transmission of the surface anchoring order via the intermediate smectic layers and on the other hand the opposite influence of the isotropic bulk molecules, which favours disorder. In our hyperbolic tangent fit we have enforced a single uniform layer. Probably the apparent global decrease of order in this layer closer to T_c indicates that in reality a model in which S decreases stepwise away from the surface, would be more realistic. Indeed we have obtained good fits with such a model. Unfortunately, the confidence intervals on the fitting parameters were too large to be really conclusive.

PRE-SMECTIC LAYERING IN H8F(4,2,1)MOPP

The idea to investigate the pre-smectic behavior of H8F(4,2,1)MOPP was inspired by its very interesting thinning transition, which was recently studied by Johnson et al.[6] When a thin free-standing smectic film (FSF) of

H8F(4,2,1)MOPP is heated, it exhibits a reproducible stepwise decrease in the film thickness until the film finally pops at $T-T_{IS} = 30$ K. T_{IS} is the bulk isotropic-smectic transition temperature. Presumably, the observed phenomenon involves the melting and squeezing out to the meniscus of single smectic layers. In this work we try to reveal the structure of the meniscus region associated with such films where the material may be considered macroscopic. We have recorded the angular dependence of the ellipsometric signal of bulk-isotropic H8F(4,2,1)MOPP as a function of temperature in the pre-smectic temperature region. Some preliminary quick scans revealed only a noisy discontinuity in ψ at T_{IS}=75°C. The behavior was difficult to analyze quantitatively, because the quality of the signal in this temperature region deteriorated due to scattering. Surprisingly, steps in ψ, which are markers for the presence of smectic surface ordering, only showed up after several scans, several hours after filling the sample holder. Fig. 4 shows a scan of the ellipsometric parameter ψ at an incident angle of 51°, rather close to the isotropic Brewster angle (54.5°). Cooling down from 105°C, a pronounced step in ψ showed up at 93.4°C, revealing a sudden, considerable increase in surface order, far above T_{IS}. Between this temperature and T_{IS}, no further structure was detected. Heating from the smectic to the isotropic phase, the transition sets in a bit later and stepwise. However, while the clear step was easy to reproduce for different scans and incident angles, the small steps in some upward scans, if existing at all, were too smooth to be visible. Noth withstanding the problem of reproducibility, we were able to determine the angular dependence of the ψ-jump in the cooling scans in order to get an idea of the nature of the effect. By fitting with a step function and assuming that the sample is isotropic above the step temperature, we found a very strong correlation between x_0 and S_0, resulting an large ranges of possible values for these parameters. The evolution in our results over time, which most probably

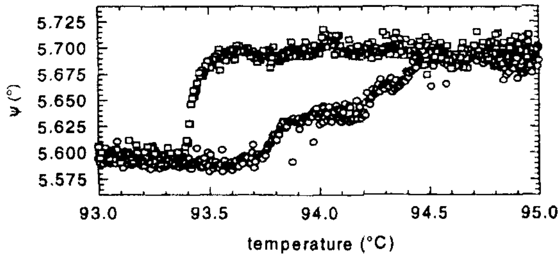

FIGURE 4 Upgoing (circles) and downgoing (squares) temperature scan of the ellipsometric angle ψ at an incident angle of 51°

is related to contamination with water in the ambient air, in addition introduces an important uncertainty. Nevertheless the results give a preliminary indication of the presence of a thick smectic surface region. Although more research in well controlled atmospheric circumstances will be necessary to obtain better control on the sample history, the presence of a thick smectic layer at the bulk isotropic-vapor interface along with the stability of FSF's of H8F(4,2,1)MOPP at temperatures well above T_{IS} points to a strong surface ordering effect relative to the bulk's disordering influence.

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