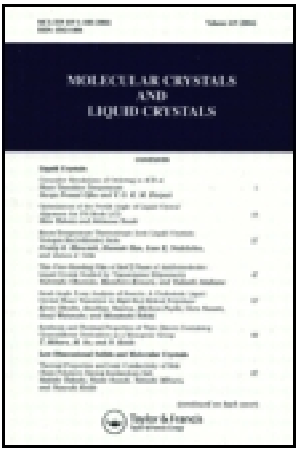

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Surface Induced Effects in Liquid Crystals: A Microscopic Study

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To cite this article: Marie-Pierre Valignat, Danilo Duca, Riccardo Barberi, Anne-Marie Cazabat & Roberto Bartolino (1997): Surface Induced Effects in Liquid Crystals: A Microscopic Study, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 151-156

To link to this article: http://dx.doi.org/10.1080/10587259708041760

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 151–156
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SURFACE INDUCED EFFECTS IN LIQUID CRYSTALS: A MICROSCOPIC STUDY

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Abstract We present a study of the wetting behavior of small drops of cyanobiphenyl on solid surfaces. Macroscopic and microscopic measurements are compared in order to understand the relationship between anchoring and wetting.

INTRODUCTION

In order to induce a suitable alignment in nematic liquid crystals (NLC), solid surfaces are treated. Several empirically known surface treatments are employed, one of them consists in an oblique deposition of SiO under vacuum. Varying the angle of incidence and the SiO film thickness, the NLC may be planar, tilted or bistable. The microscopic mechanism responsible for this behavior is not yet fully understood and it seemed to us necessary to go further in the studies of the microscopic properties of the LC-surface interaction: we performed microscopic studies by way of ellipsometry, the obtained measurements are compared to macroscopic optical observations in a standard liquid crystal cell.

EXPERIMENTAL METHOD

A very small drop of LC (V~ 10^{-7} mm^3) is deposited on a solid surface and its slow dynamical behavior is recorded. The thickness profile of the drop is measured by ellipsometry with the set-up already described elsewhere[1]. Due to the lateral resolution of the ellipsometer (30 × 130 μm^2), only complete wetting situation can be studied i.e. when the dynamic contact angle is close to zero and the shape of the drop is a quasi-flat film extending over a few millimeters. This condition is achieved in the present case. Most of our experiments were carried out with 5CB (4-cyano-4'-n-penthylbiphenyl) and 8CB (4-cyano-4'-n-octylbiphenyl) respectively in nematic and smectic phase at room temperature, their surface tension[2] is close to 40 dyne.cm^{-1}. The solid surfaces are silicon wafers cleaned by UV ozone[3] exposure or freshly coated with SiO under oblique evaporation in vacuum[4]. On the bare silicon wafer, the anchoring is planar and degenerated while on substrates coated under oblique incidence, molecules are planar or slightly tilted but homogeneously oriented normal to the plane of evaporation (the thickness of the evaporated layer are less than 100 Å).

EXPERIMENTAL OBSERVATIONS

Static observations

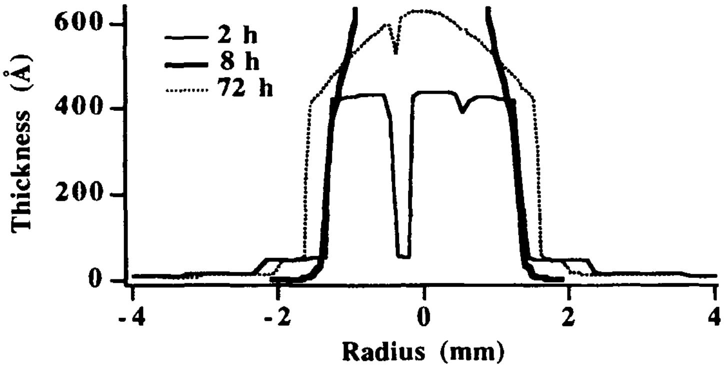

FIGURE 1 5CB spreading on a SiO evaporated surface (30°, 45 Å). Thickness profiles have been measured along a diameter of the drop at increasing time.

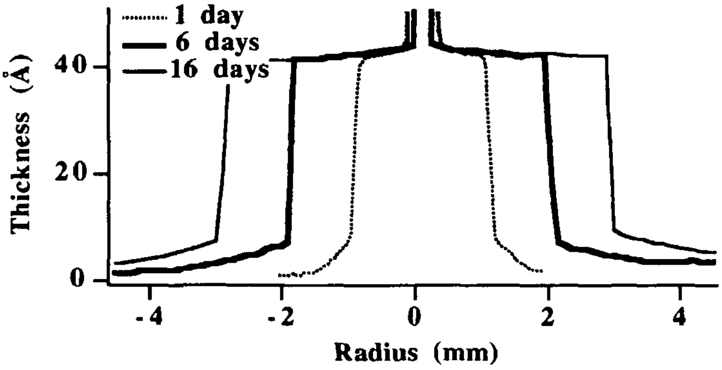

FIGURE 2 8CB spreading on a SiO evaporated surface (60°, 77 Å).

Typical experimental results are shown on figures 1 and 2. For small thickness, the same structure develops on the edge of the drop: a compact film of thickness L_1 ($L_1 \approx 33$ Å for 5CB and $L_1 \approx 40$ Å for 8CB) preceded by a thinner one with a thickness decreasing from 5 Å to 0. Both these films have macroscopic extension and spread over millimeters. A model for the structure of the L_1 film has already been proposed in the literature[5] which agrees with our results. The biphenyl head of the first molecule is against the polar surface and is covered by a layer formed of two intergitated molecules normal to the surface. This homeotropic arrangement of the molecules is confirmed by the increasing thickness of the layer as the length of the carbonyl chain also increases in the nCB series. The thinner film is a non compact monolayer of molecules. Let us remind that ellipsometry is an optical technique which leads to an optical path average over the size of the light spot. If the layer is non compact then the thickness may be less than the size of a molecule. Second harmonic generation measurements[6] have shown that the molecules in contact with the solid are slightly tilted and form with the surface normal an angle close to 60°.

The structure of the drop appears to be controlled by the details of molecular interaction[7]: at the interface solid/air the equilibrium state of a thin film is an homeotropic trilayer. One may ask if this structure is also preserved in the central part of the drop or if it is only a boundary condition achieved by very thin films. Let us first describe what happens in the thicker part of the 5CB: as the spreading goes on, the central part of the drop becomes flatter and its thickness decreases to a value L_2 close to 400 Å . Later on, the drops breaks down to the L_1 layer and holes appear connecting the L_1 and L_2 thickness. We interpret this thickness transition as the result of the competition between spreading and anchoring energies. In the following, we will remind the main results already developed in a previous paper[8].

"Macroscopic" surface tilt angle measurements in a liquid crystal cell have shown a quasi-planar anchoring of 5CB and 8CB on wafers ($\phi_1 = \pi/2$); with air, this anchoring is homeotropic ($\phi_2 = 0$, ϕ_1 and ϕ_2 being the easy axes respectively at the interface NLC/substrate (1) and NLC/air (2)); then in the drop volume, the nematic director is distorted to meet these conditions and the total energy per unit surface contains three terms :

(1) a spreading term S: $S = \sigma_{sa} - \sigma_{sn} - \sigma_{na} \approx \sigma_c - \sigma_{na} \geq 0$ where σ_{ij} are the interfacial surface tension (s: solid, a: air, n: nematic) and σ_c the solid critical surface tension.

(2) *a surface term due to the anchoring at both interfaces. This term may be seen as the* anisotropic part of the spreading coefficient. Assuming that the anchoring with air is stronger than the one with the solid surface[9], this term writes[10]:

$$F_a = w_1 \cos^2 \theta_1$$

$$\theta_2 = \phi_2 = 0$$

where θ_1 and θ_2 are the director angle at the interface 1 and 2 respectively.

(3) an elastic term which reads in the one elastic constant approximation:

$$F_e = \frac{K\theta_1^2}{2z}$$

K being the elastic constant and z the distance from the solid surface.

Minimizing the free energy per unit volume for a drop of constant volume leads to one or two energy minima depending on the ratio $\beta = S/w_1$.

If $\beta > 1.3$, then a cut-off has to be introduced to take into account short range specific interaction. The energy minimum corresponds to the cut-off value obtained for $z \sim L_1$ and $\theta_1 \sim 0$.

If β is in the range [0, 1.3] a second minimum exists and gives a typical film thickness L_2. For compounds with very strong anchoring energy, compared to the spreading parameter, the energy gets a second minimum for $\theta_1 = \phi_1 - \phi_2 = \pi/2$ at a thickness $L_2 = \frac{K}{S}\left(\frac{\pi}{2}\right)^2$. For intermediate values $\beta \sim 1$ the minimum θ_1 depends explicitly on S/w_1, but is still above $\pi/4$, and leads to a thickness L_2 of the same order. This length L_2 may be written in term of the extrapolation length as $L_2 = L_c \frac{\theta_1^2}{\frac{S}{w_1} - \cos^2\theta_1}$ where $L_c = \frac{K}{w_1}$. For a typical value of $L_c \sim 400$Å, $L_2 = 400$ Å for $\beta \sim 1$ and leads to reasonable values of $S \sim 0.3$ dyne/cm.

In summary, the 5CB drop has antagonist anchoring configuration and the director is distorted in volume. The volume $V = \Sigma h$ of the drop is constant and the elastic energy stored in bulk increases with the surface Σ until the thickness h reaches the value L_2. Then the drop develops with the constrain of constant height L_2 which implies the formation of holes connecting the thickness L_2 to the non distorted homeotropic thin film L_1.

Now, let us come back to the question about the structure in the central part of the drop. If we believe that the L_1 structure is preserved then we have to suppose specific interaction able to give a planar anchoring on a short distance. We can think about anisotropic van der Waals forces[11] but we also have to assume the presence of a specific phase (different from the nematic one) for the L_1 film in order to achieve the planar condition for $z > L_1$. In regard to these arguments, we reasonably expect an arrangement with a first molecule slightly tilted to the solid then a epitaxy-like growth leading to a quasi-planar anchoring of the molecules.

The structure of the L_1 film is also the one achieved by the smectic 8CB while the central part of the drop stays quasi-static. Up to now we have not followed the drop to the end of the spreading (the process being long) but we got results on the dynamics.

Dynamical observations

We have not found any scaling law for the nematic dynamics which seems to depend on the surface roughness in a complex way. Inversely, the precursor radius growth for the smectic phase is always proportional to the square root of the time: $\Delta R = \sqrt{Dt}$ with a "diffusion coefficient" D increasing with temperature. We although observed that when the temperature is below the solid/smectic transition temperature T_m, the L_1 film goes on spreading with a lower value of D while the bulk part remains in solid state. This effect is analyzed in terms of surface-induced premelting[12] assuming that van der Waals interaction are dominant. An adimensional interfacial potential f(z) of the form $f(z) = \frac{z^2}{z^2 + a^2}$ is introduced to take into account this interaction[13] (a is of the order of a molecular dimension). The interfacial free energy σ is then function of the thickness z and the equilibrium coordinates are shifted. The shift ΔT in temperature can be estimated as a function of the latent heat of melting per molecule (H) the density of the molten film ρ_M and $\Delta\sigma$ defined as the difference between the surface free energy of the infinite thick molten film and that of the bare substrate: $\Delta T = T_m\left(\frac{\Delta\sigma}{2\rho_M}\frac{1}{H}\right)a^{-1} \approx 10°K$. This means that a spreading film can be observed even 10 °K below the crystallization temperature. This numerical value is in good agreement with the temperatures at which we can observe the L_1 film.

Substrate and temperature effects

We tried to understand the role of the coated SiO layer on the microscopic wetting, changing its thickness (≤ 100 Å), the angle of evaporation and using substrates cleaned by UV ozone procedure. In any case, as long as the LC was wetting the substrate completely, we observed the L_1 layer extending out for the 5CB and the 8CB. The presence of both the air and the solid substrate is likely to induce a positional order of the molecules in the thin film. The wetting condition does not seem to have a link with the anisotropy of the surface. To confirm this assumption, we also observed the macroscopic wetting on substrates coated with polymers inducing planar anchoring. On PVA and polyimide coated wafers, the distribution of azimuthal orientation is isotropic. On the hydrophilic PVA coated substrate, the wetting is observed while it is not on the hydrophobic coated one. When those polymers are rubbed by translating the substrate in one direction on velvet, the isotropy is broken but no changes are observed in the wetting behavior.

A more striking dependence arises with temperature: an increase of temperature leads, for the 5CB on a bare substrate, to the reversible formation of a second layer of 25 Å which does not appear on a SiO coated substrate. This is the thickness of a homeotropic smectic layer formed of two associated molecules head-to-head with a partial overlap.

CONCLUSION

Wetting observation by ellipsometry gives information on microscopic mechanisms. The effect of a solid surface on a LC may lead to particular behavior as surface induced premelting or smectic-like ordering for a nematic. The formation of a second step on a bare substrate has not yet be interpreted and we are carrying on the study as a function of temperature. In this way, we hope to understand better the role of the SiO evaporated layer and the nematic/isotropic transition.

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