

Morphology and Ordering in Thin Liquid-Crystal Films on Flat Glass Substrates

Yushan Shi, Brian Cull, and Satyendra Kumar

Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242-0001

(Received 17 June 1993)

Results of a high-resolution x-ray reflectivity study of growth morphology and ordering of thin liquid-crystal films on flat glass substrate are reported. An adsorbed bilayer of crystalline order, under three dimensional clusters, was found to persist well beyond the nematic to isotropic transition. This adsorbed layer appears to be related to the surface memory effects in liquid-crystal devices. The morphology of these films can be described by the Stranski-Krastanov growth mode.

PACS numbers: 68.55.Jk, 61.30.Eb, 68.15.+e, 68.45.Da

Substrate effects, which principally refer to the interaction between molecules and solid surfaces, are of fundamental importance in liquid-crystal science and technology. Previous studies [1] of substrate effects on nematic liquid crystals found a transition region, of one to several molecular lengths, near the surface of the substrate. Clark [2] reported the *surface memory effect* (SME), of prime importance in liquid-crystal devices, which involves the memory of local directions of a broken symmetry even after the sample has been heated to the isotropic phase.

The growth of thin liquid-crystal films on solid surfaces is conceptually analogous to epitaxial growth. Principally governed by the relative strengths of the adsorbate-adsorbate and the adsorbate-substrate interactions, an epitaxial film can grow [3] via layer-by-layer (Frank-van der Merwe), layer plus clusters (Stranski-Krastanov), or simply cluster (Volmer-Weber) growth modes. Although the growth process of liquid-crystal films is complicated by the anisotropic shape of molecules, anisotropic interactions, and orientational and positional ordering, the knowledge of epitaxial growth can be extended to understand their morphology, ordering, and the mechanism of molecular anchoring.

In this Letter, we report results of high-resolution x-ray reflectivity studies of liquid-crystal films on flat soda-lime glass substrates. Thermally stable adsorbed bilayers of crystalline order were found to form on the substrate under three dimensional clusters and to persist beyond the nematic (*N*) to isotropic (*I*) transition. This bilayer appears to be related to the SME [2]. The morphology of liquid-crystal films can be described by the Stranski-Krastanov growth mode.

We studied samples prepared by spin coating 0.5, 5, and 50 wt.% solution of diheptylazoxybenzene [4] (D7AOB, shown in Fig. 1), to be referred to as samples 1, 2, and 3, in toluene at 5000 rpm for ~ 30 s at room temperature. We also studied films prepared by spin coating with acetone as solvent, by dipping, and by vacuum deposition. All techniques resulted in films with the basic features. D7AOB transforms from the crystalline to the smectic-*A* (*A*), *N*, and *I* phases at 34, 54.5, and 71 °C, respectively.

The surface of a clean substrate was examined by x-ray reflectivity before depositing a liquid-crystal film on it. The rms values of surface roughness σ_s , electron density ρ_s , and linear absorption coefficient μ_s for these surfaces were found to be $5.6 \pm 0.6 \text{ \AA}$, $0.78 \pm 0.05 \text{ \AA}^{-3}$, and

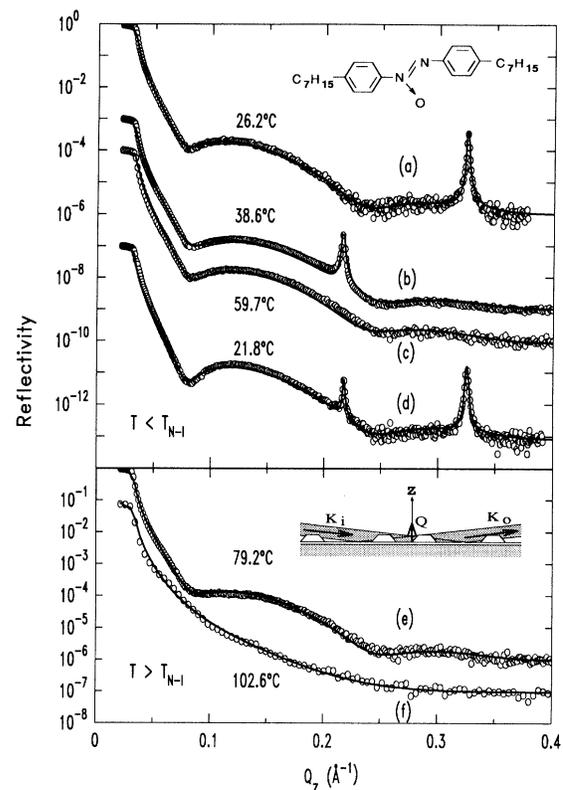


FIG. 1. Reflectivity profiles of sample 1 in the (a) crystalline, (b) *A*, and (c) *N* phases with fits discussed in the text. Curve (d), obtained after cooling, shows coexistence of the crystalline and *A* phases. The intensities below $Q_{zc} = 0.03 \text{ \AA}^{-1}$ are nearly unity; curves have been shifted down by an integer number of decades for clarity. The crystalline and smectic Bragg peaks were at $Q_z = 0.325 \text{ \AA}^{-1}$ and $Q_z = 0.216 \text{ \AA}^{-1}$, respectively. The adsorbed layer, 37.3 \AA , persisted beyond the *N*-*I* transition [(e)], and disappeared at 30 K above the *N*-*I* transition [(f)].

$(1.3 \times 0.3) \times 10^{-6} \text{ \AA}^{-1}$, respectively. These values were used in the analysis of the data taken on the liquid-crystal films.

Measurements were performed using the Cu-K α doublet of an 18 kW rotating anode x-ray source and a pair of Ge(111) single crystals as monochromator and analyzer. The details of the experimental setup can be found elsewhere [5]. For angles $\theta < \sin^{-1}(w_{\text{in}}/l)$, where l is the sample length and w_{in} the beam width, a footprint correction was applied by multiplying the intensity by $[w_{\text{in}}/\sin\theta]$. The coherence lengths in the directions parallel and perpendicular to the incident beam were $\sim 3000 \text{ \AA}$ and $\sim 100 \text{ \AA}$, respectively. The sample temperature stability was better than $\pm 0.01 \text{ K}$. The specular x-ray reflectivity profiles were normalized with respect to the incident beam intensity after the footprint correction, diffuse scattering, and background (1×10^{-6}) had been taken into account. We discuss in this paper two extreme cases of surface morphology in detail.

In *one extreme case*, an adsorbed layer under low coverage of D7AOB clusters (lower inset in Fig. 1) was obtained for sample 1. The reflectivity profiles of such films were approximated, as shown in Fig. 1, as an incoherent summation of the reflections from the adsorbed layer and Bragg scattering from molecular positional order in the clusters. Curve (a) shows the Kiessig fringes at room temperature from the adsorbed layer and the Bragg peak from crystalline clusters at $Q_z = 0.325 \text{ \AA}^{-1}$ with half width $\Delta Q_z = 0.0009 \text{ \AA}^{-1}$. The layer spacing in the crystalline phase and the average height of the clusters estimated from ΔQ_z were found to be $19.37 \pm 0.02 \text{ \AA}$ and $\sim 1400 \text{ \AA}$, respectively. A shift in the Bragg peak position [Fig. 1(b)] to $Q_z = 0.216 \text{ \AA}^{-1}$ was observed at 38.6°C , as the clusters transformed to the *A* phase. The smectic layers were perfectly parallel to the substrate with spacing of $29.40 \pm 0.02 \text{ \AA}$, in agreement with the length of D7AOB molecules. Above the *A-N* transition, the Bragg peak disappeared at 59.7°C [Fig. 1(c)]. Upon cooling to room temperature, the *A* and crystalline phases were found to coexist [Fig. 1(d)] for more than two days probably due to finite size effects.

Assuming the adsorbed layer to be a thin homogeneous film on an extended surface of the substrate, the best fit values of its thickness t , electron density ρ_a , and rms roughness calculated with Fresnel-Kiessig formalism [6] were found to be $37.3 \pm 0.6 \text{ \AA}$, $0.48 \pm 0.06 \text{ \AA}^{-3}$, and $5.0 \pm 0.5 \text{ \AA}$, respectively, for results represented by curves (a)-(d). The roughness of the air-adsorbed-layer interface was treated as an independent Gaussian roughness in data analysis and its rms value was approximately the same as that of the bare substrate surface [7]. The adsorbed layer was found to be $\sim 4\%$ thinner [8] than a crystalline bilayer in bulk samples. This difference suggested the presence of a deformed crystalline bilayer. The molecule-substrate interaction appears to be balanced by the strain in the adsorbed layer, allowing additional adsorbed layers or three dimensional clusters to

form freely over it. Using the relation between energy and the distance between the antiparallel coupled dipoles [9], $\Delta U/U = -3\Delta r/r$, we estimate the substrate-molecule interaction to be about 12% stronger than the competing intermolecular interaction.

Above the *N-I* transition, the adsorbed layer started to desorb and developed some porosity and voids which reduced the amplitude of the fringes as evident from Fig. 1(e). Analysis of this reflection profile required 8% stronger reflection from the substrate's surface. Finally, 30 K above the *N-I* transition, at 102.6°C , the adsorbed layer developed sufficient voids, nonuniformities, and local electron density fluctuations to completely wash out the Kiessig fringes. More than 90% reflection directly from the bare substrate was required to fit the reflectivity curve (f).

In the *second extreme case*, the adsorbed layer was nearly completely covered by D7AOB clusters in the crystalline phase of sample 2. This film was modeled as a stratified medium [7,8]. The reflectivity profiles of sample 2 in various phases depended on the rate of heating. The results obtained with fast temperature changes ($\sim 4 \text{ K/h}$) are shown in Fig. 2. The fit in Fig. 1(a) has also been replotted (dashed line) in Fig. 2(a) for comparison.

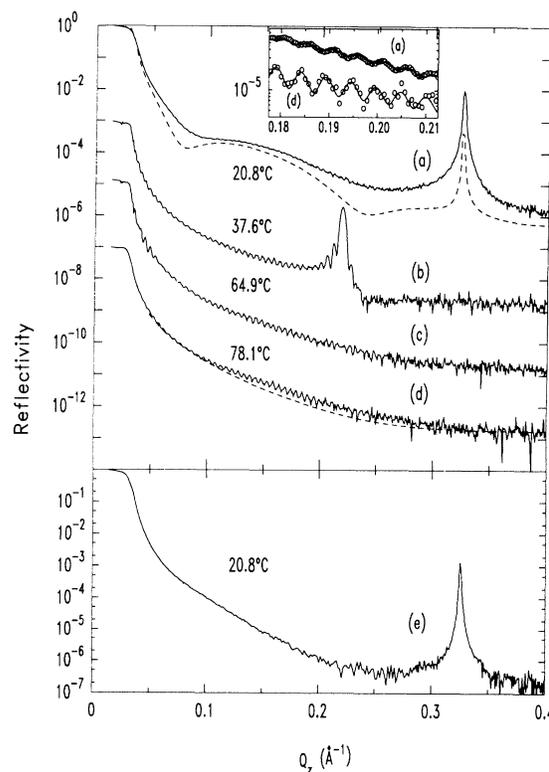


FIG. 2. The reflectivity profiles for sample 2 in (a) crystalline, (b) *A*, (c) *N*, and (d) *I* phases. Dashed line in (a) is the fit from Fig. 1(a). Inset shows the theoretical fit to curves (a) and (d). The adsorbed layer is barely visible in the crystalline phase of sample 3 [(e)].

It is evident that the thickness of the adsorbed layer was the same and that it was now buried under more D7AOB material. The maximum intensity of the Bragg peak for sample 2 was about 14 times higher than for sample 1. The structure in the clusters was highly ordered as evident from the presence of more than 7 higher order reflections. The average height of the clusters for both samples was approximately the same, i.e., 1400 Å, as estimated from the width of the Bragg peak. The surfaces of the clusters in this film were flat enough to generate the Kiessig fringes over a wide q range. The height of the clusters calculated from the period of these fine Kiessig fringes was ~ 1200 Å, in very good agreement with the value obtained from the width of the Bragg peak, suggesting a near complete coverage of D7AOB clusters.

At 37.6°C, the overall film thickness, determined from the period of fine Kiessig fringes [curve (b)], remained unchanged. However, the smectic layer spacing was approximately 50% higher than in the crystalline phase, suggesting that the clusters expanded laterally and coalesced to produce a uniform and well-oriented smectic- A film over the adsorbed layer as evident from increased amplitude of the fine Kiessig fringes. Consequently, the observed amplitude of the Kiessig fringes corresponding to the adsorbed layer diminished. The presence of the adsorbed layer in the I phase can be seen from the difference between the data and the dashed curve which was generated assuming no adsorbed layer. The interference between the Fresnel-Kiessig and the Bragg reflections, resulting in an enhancement (excitation) of intensity below (above) the Bragg peak [10], was clearly demonstrated. This film was stable with temperature as seen from curves (c) and (d) in the N and I phases. The reflectivity profiles of these liquid-crystal films were reproducible after more than 7 months, showing their remarkable stability with time.

The intensity of the Bragg peak in sample 3 [Fig. 2(e)] was an order of magnitude lower than for sample 2, and the amplitude of Kiessig fringes from the adsorbed layer was noticeably less, because a larger fraction of the sample was misaligned and the aligned part was buried under 10 times more material than in sample 2. It should be pointed out that the adsorbed layer developed fully only after the sample had been once heated to higher temperatures allowing the molecules to adjust to the substrate potential.

The behavior of the adsorbed layer (Fig. 3) was different and somewhat intriguing when the temperature was raised slowly, in 1 K steps, at an average heating rate of ~ 0.3 K/h. At 27.9°C, the thickness of the adsorbed layer doubled to 75 Å [curve (b)]. The smectic peak appeared at 32.2°C [curve (c)] and coexisted with the crystalline phase until ~ 34 °C. No changes in the adsorbed layer thickness were seen in the A and N phases [curves (d) and (e)]. The additional adsorbed bilayer melted at 71.6°C, just above the N - I transition as shown in (f). Adsorbed layers thicker than a bilayer were never found

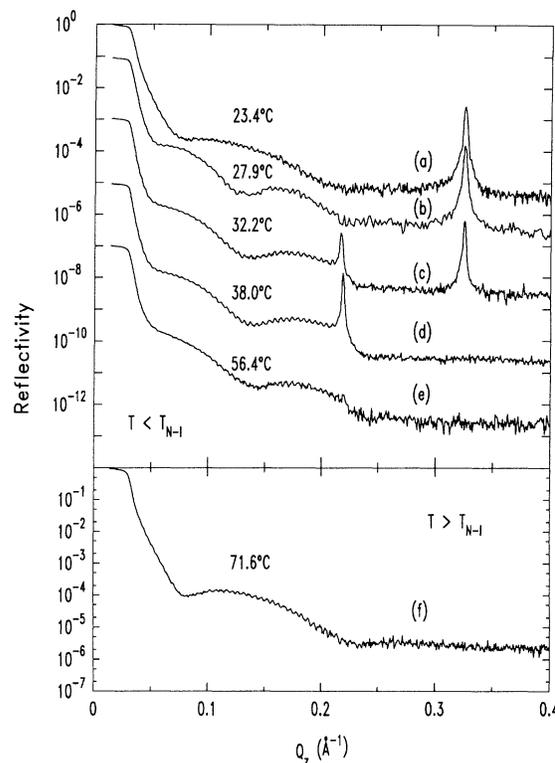


FIG. 3. The reflectivity profiles of sample 2 obtained with slow heating. Thickness of the adsorbed layer doubles in the crystal phase [(a) and (b)], and persists beyond the A - N transition [(e)] before changing back to a single bilayer above the N - I transition [(f)].

to be stable in the I phase. On cooling, the thickness of the adsorbed layer doubled in the A phase and halved again after long equilibration times at room temperature.

The facts that the adsorbed layer was present in all samples, persisted beyond the clearing point, and melted at temperatures well above the N - I transition, just as the memory (effect) was lost, suggested that it may be responsible for the SME [2] observed for bare glass surfaces. Detailed x-ray reflectivity study of the structure and dynamics of adsorbed layers should provide better understanding of their role in SME.

The degree of alignment of the crystalline and smectic structures was measured by performing ω scans. The ω scans in the crystalline phase (top panel in Fig. 4), at $Q_z = 0.325$ Å $^{-1}$, were fitted to two Lorentzians: a narrow one centered at $\omega = 0^\circ$ to account for the layers aligned parallel to the substrate, and a broad peak arising from the misaligned scattering volumes. The FWHM of the narrow peak were $\Delta\omega = 0.022^\circ$, 0.015° , and 0.08° for samples 1, 2, and 3 [curves (a), (b), and (c)], respectively. The integrated intensities of Bragg reflections were 3.0×10^{-5} , 3.3×10^{-4} , and 5.7×10^{-4} , respectively, which monotonically increased with the amount of material deposited [11]. The average thickness of sample 1 was

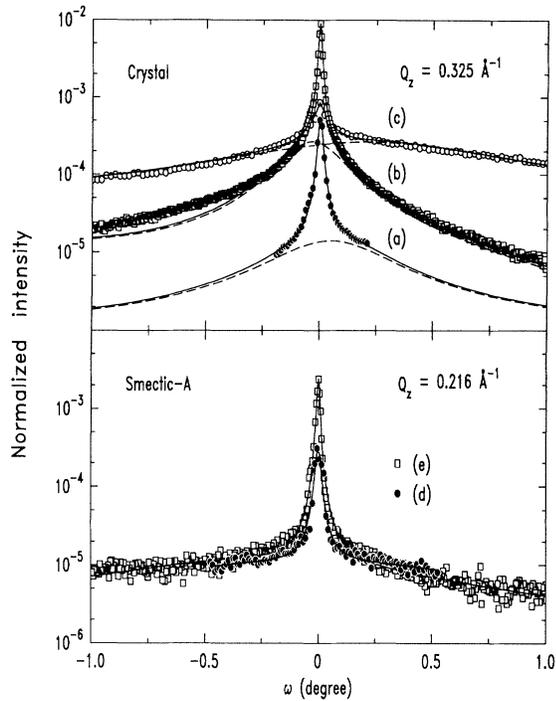


FIG. 4. Omega scans of crystalline peaks of (a) sample 1, (b) sample 2, and (c) sample 3. ω scans of the smectic peak of (d) sample 1 and (e) sample 2. The solid and dashed curves represent the fits.

about 12% of sample 2, i.e., 144 Å. Using the estimated height, 1400 Å, of the clusters in sample 1, we estimated approximately 8% lateral cluster coverage. The uniformity and alignment of D7AOB films were optimum at a thickness of approximately 1000 Å. The curves (d) and (e) show the ω scans in the A phase, at $Q_z = 0.261 \text{ \AA}^{-1}$, for samples 1 and 2, respectively. We obtained $\Delta\omega = 0.026^\circ$ for sample 1 and $\Delta\omega = 0.014^\circ$ for sample 2 with roughly the same ratio of the integrated intensities as in the crystalline phase.

To summarize, we have observed a strained adsorbed crystalline bilayer of D7AOB on flat soda-lime glass substrates which may be responsible for the surface memory effect. Three dimensional clusters formed on top of the adsorbed layer in conformity with the Stranski-Krastanov growth mode normally associated with growth of films on semiconductor and metal surfaces.

We wish to thank L. C. Chien, D. L. Johnson, S. K. Sinha, and J. West for helpful discussions, and S. Keast, A. Baldwin, P. Dunn, and M. Groom for technical assistance. This work was supported by NSF Science and Technology Center, ALCOM Grant No. DMR-89-20147.

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