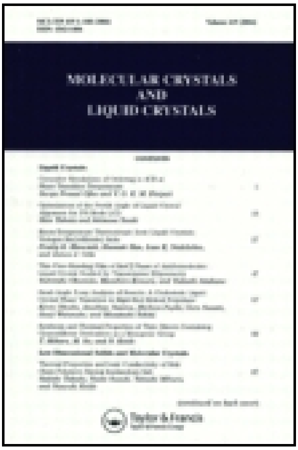

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Thickness Dependence of the Glass-Liquid Crystal Buried Interface Structure

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Version of record first published: 24 Sep 2006

To cite this article: L. J. Martínez-Miranda, Yufei Hu & Timir Misra (1999): Thickness Dependence of the Glass-Liquid Crystal Buried Interface Structure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 121-127

To link to this article: http://dx.doi.org/10.1080/10587259908025932

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 121-127
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Printed in Malaysia

Thickness Dependence of the Glass-Liquid Crystal Buried Interface Structure

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We have used Grazing Incidence X-ray Diffraction (GIXS) to study the structure of a smectic A liquid crystal (LC) at the buried LC-glass interface in liquid crystal films. This measurement is done in reflection mode through the glass substrate, which consists of a grating photolithographed onto a 0.2 mm thick slide. The observed in-plane alignment indicates the presence of tilted layers within 50Å of the glass interface, inside the grooves. These layers correspond to the tilted region observed previously in samples confined within the grating grooves. The tilted layer region is suppressed by the grating induced homogeneously aligned LC layers, which act as a new confining boundary that modifies the LC structure within the grooves. The interaction between the two observed in-plane regions depends on the thickness of the LC films as well as the depth of the gratings′ grooves.

Keywords: interface structure; confinement; grazing incidence X-ray scattering; competing interactions

INTRODUCTION

The study of confined liquid crystals (LC) is important both fundamentally and from a technological point of view. In recent years, a number of confined LC systems have been studied and modeled. These include free standing smectic films[13-15], nematic and smectic LC's contained in cavities of different sizes[6-12] as well as nematic[16,17] and smectic[1-5,13,18-27] LC cells and in films of varying thickness. When a smectic LC is confined between two competing aligning surfaces, the film can divide into regions or multilayers of varying smectic layer orientation[1-5, 28-29]. This is a result of the requirement that the ordered layers rotate to satisfy the boundary conditions at each surface[27-29]. The size and number of these regions depend on the type of liquid crystal, the film thickness, the film's thermal history and the type of aligning surfaces used[28].

In LC films, the competition between the substrate surface topography and the surface chemical and physical interaction forces affects the structure of both bulk nematic[30], and smectic films[1]. In buffed substrates, the depth of the resulting grooves in the surface modifies the molecular orientation in nematic films[30]. Both the depth and size of the grooves affect the molecular orientation in smectic LC films[1-4]. In this paper, we present the results of a depth dependent structural study of the region near the substrate-LC interface of smectic A octylcyanobiphenyl (8CB) films deposited on grated glass substrates. The glass substrates consist of gratings of varying depth and a period of approximately 9 μm. Our results show the presence of tilted layers 50Å above the interface, which are similar to those observed previously in samples confined within the grating grooves[27]. The structure evolves into a homogeneously aligned structure, where the molecules are aligned along the grooves' long axis. This second structure in turn acts as a new confining boundary that may suppress and modify the LC structure within the grooves. The presence and interaction between the two observed structures depends on the thickness and thermal history of the LC films as well as the depth of the gratings' grooves.

Experimental

We have prepared the substrates using conventional photolithography to prepare gratings on 0.22 mm thick glass of uniform period and depth. The procedure is described in references 1 - 4. By varying the cleaning and etching steps in this procedure, different groove depths can be obtained[31]. The resulting gratings had an average grating period of 9 μm, a surface area between 1.44 and 2.25 cm^2. We have studied films deposited into gratings with depths of 1.6 and 0.5 μm. The sample size is varied systematically with the use of a high precision 0.5μl resolution pipette set to dispense 10μl of material at a time. In this work, we deposited relatively thick films of 8CB, which have been previously found out to show homogeneous alignment in the bulk. These homogeneous layers align preferentially along the direction of the gratings[1-5].

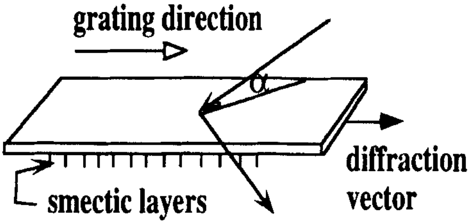

Figure 1. Sketch of the geometry of the X-ray diffraction experiment. The beam penetrates a 0.22 mm thick glass. A grating photolithographed on the side opposite X-ray incidence aligns the smectic layers as shown after the critical film thickness is achieved.

To measure the structure of the interface, we use the grazing incidence x-ray scattering technique (GIXS)[32]. The experiments were performed at the National Synchrotron Light Source in Brookhaven National Laboratories, beamlines X22B and X18A, using 1.3776Å, 1.3577Å and 1.308Å X-rays, and a resolution of 2×10^{-3} q_o ($q_o = 2\pi/\lambda$). The beam spot size was 2 mm^2. 8CB films were deposited as described above on grated glass substrates 0.2 mm thick. The penetration depth for this glass substrate at the above wavelengths is in the order of 280 μm, or 0.28 mm, approximately 1.5 times larger than using a conventional Cu K_α source. This ensures the ability to measure the glass-LC interfacial region with the glass substrates used. The samples were placed with the substrate facing the beam, and the grooves axis perpendicular to the beam on a four circle Huber diffractometer. This geometry is illustrated in Figure 1. The incidence angle was varied by tilting the angle α of Huber goniometer head or by changing the angle χ of the four circle diffractometer. The critical angle for 8CB at the wavelengths used is 0.13°. The angle at the air-LC interface is determined by the angle of refraction at the air-glass interface, which is related to the experimental incidence angle as $\cos\alpha_{glass} = \cos\alpha/n_{glass}$, for $\cos\alpha_{glass} <= 1$. The penetration depth depends on the absorption through both the glass and liquid crystal at the corresponding refraction angle at the glass-LC interface, and varies from approximately 40Å for $\alpha = 0°$ to about 800Å at $\alpha = 0.1°$ and 1500Å at $\alpha = 0.2°$[33].

Results and Discussion

Figure 2 shows the results of diffraction scans taken on 100 μm films of 8CB deposited on a 1.6 μm and a 0.5 μm deep grating respectively at incidence angles of 0°, 0.1° and 0.2°. The background signal from the glass substrate has been subtracted in these scans. At nominal grazing incidence ($\alpha = 0°$), which corresponds to the first 50Å below the glass - LC interface, the sample deposited on the deep grating has a diffraction signal consisting of a peak centered around $q = 0.23Å^{-1}$, as seen in Figure 2a. As the incidence angle increases, a second peak can be observed around $q = 0.198Å^{-1}$, which is close to the value of the bulk wavevector for 8CB of $0.199Å^{-1}$. This latter peak corresponds to smectic layers aligned homogeneously on the substrate.

The 100 μm thick film deposited on a 0.5 μm deep grating shown in Figure 2b shows a very strong homogeneous signal at all angles of incidence. The signal at higher q is at least ten times weaker and appears as a shoulder in all scans for this sample. For both samples, the relative intensity of the peak at higher q values remains fairly constant as a function of incidence angle. This may imply either that the coherent regions that give rise to this peak are located right at the glass - LC boundary, or that these regions become increasingly more disordered as the distance form the glass - LC boundary increases.

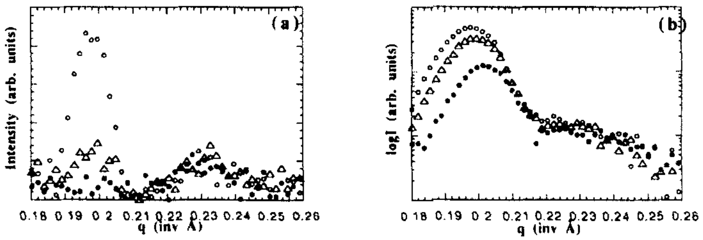

Figure 2. GIXS scans for a 100 μm thick 8CB film on: a) a 1.6 μm deep grating ; b) a 0.5 μm grating. Closed circles, $\alpha = 0°$; triangles, $\alpha = 0.1°$; open circles, $\alpha = 0.2°$.

Figure 2 shows that the layer spacing d corresponding to the lower q peak for both samples varies as a function of the incidence angle. The variation as a function of incidence angle is that expected of a chevron structure[11,22], and is less pronounced for the sample deposited on the 1.6 μm deep grating than the one deposited on the 0.5 μm deep grating. The higher q peaks correspond to an almost constant layer spacing of 27 ± 0.05Å, which corresponds to a molecular tilt of 30°. This compression is approximately

10% larger than that observed previously in 8CB samples contained within the grooves[27]. Further analysis of the chevron structure evolution and the variation of the layer tilt as a function of incident angle, reminiscent of the twist grain boundary phase[28], are in progress presently[31].

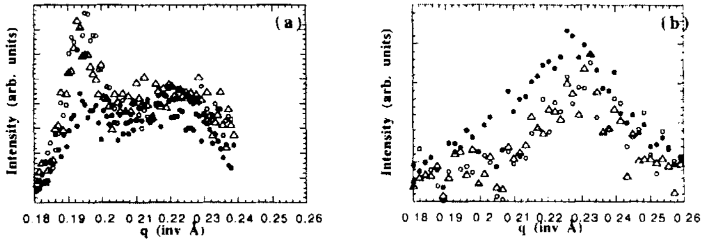

Figure 3. GIXS scans for 8CB deposited on a 1.6 μm deep grating. a) 25 μm film; b) 75 μm film. Closed circles, α = 0°; triangles, α = 0.1°; open circles, α = 0.2°.

The effects of sample size, and sample preparation method are shown in Figure 3. This Figure shows scans taken on 25 μm and 75 μm thick 8CB on a 1.6 μm deep grating. Both samples show a high q peak, which is 1.5 times broader than the high q peak for the 100 μm sample. The larger width of this peak in thinner films may be caused by a larger distribution of layer spacings for the tilted region near the glass - LC interface. The 25 μm sample scans show a low q peak at low incidence angles which correspond to a 3% dilation of the smectic A layer. A similar dilated layer is observed at incidence angles larger than 0.3° in the 75 μm thick film. One reason the lower q peak is not observed at low incidence in the 75 μm film is that this sample was prepared differently than either the 100 μm or 25 μm samples. The latter were prepared by depositing 8CB onto a clean substrate, and allowing the sample to cool slowly into the smectic A phase. The 75 μm sample was prepared by removing 8CB from a 100 μm sample. This may introduce a larger degree of disorder in the homogeneously aligned layer. Another factor that may contribute is the fact that the thermal cooling cycle sample in the 75 μm may have been faster than for the 100 or 25 μm samples, producing a more disordered homogenous layer[3].

The above results suggest the presence and competition of two aligning forces in the glass - LC interfacial region. The first is the one provided by the interior wall of each individual grating groove, which results in the formation of the tilted region, which has been observed independently before[27]. The layer arrangement and distribution within each groove depends on the thermal history of the sample. The in-plane structure of the sample is dominated by the individual grooves until the critical thickness[3,5] is reached. Beyond this thickness, the smectic layers rotate such that the molecules align along the axes of the grating grooves, which act cooperatively to align the sample. The formation of a homogeneously aligned layer over the entire grating area introduces a new aligning surface within the LC, which in turn can modify the orientation of the molecules near its interface. The amount of sample that rotates depends on the strength of this homogeneous "self-aligning" surface relative to the alignment imposed by the individual grooves. This is determined both by the thickness of the film as well as by the gratings' depth. Thus, for shallow gratings and thick films a strong homogeneous layer exists even within the gratings, as the GIXS measurements demonstrate. Similarly, thinner films exhibit a larger higher q (tilted) peak at low incidence angles.

Conclusion

We have performed a depth analysis of the structure of 8CB films deposited on grated glass substrates near the glass - LC interface. The results suggest that the LC alignment near this interface depends on the competition of two aligning forces: one provided by the walls of each individual grating channel or groove, and the other provided by the grating as a whole. This latter force produces the previously observed homogeneous layer which in turn becomes a third aligning surface, which propagates into the grating channels. This indicates the process of LC alignment near a grated substrate is a dynamic one.

Acknowledgments

This work was supported by the U. S. National Science Foundation, Grants No. ECS-95-30933 and ECS-96-96069. The measurements were performed at the National Synchrotron Light Source, which is supported by the U. S. Department of Energy (DOE).

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