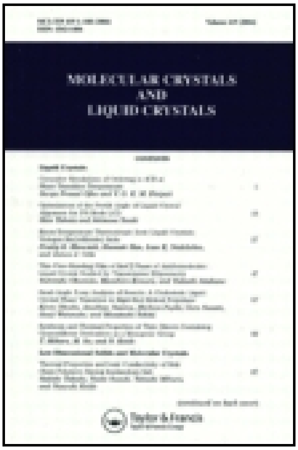

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Time Evolution of the Structure of Confined Sm-C* Films[†]

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The structural evolution of films of the liquid crystal mixture mx5112 in the Sm-A and Sm-C* phases has been studied using X-ray scattering techniques. Liquid crystal (LC) films spread on glass substrates with relief grating of 10 μm period are subjected to competing boundary conditions on opposite sides. On one side, the LC-air interface imposes a homeotropic boundary condition while on the other the glass substrate with grating generally imposes a homogeneous boundary condition. Near room temperature, the smectic layer normal is oriented parallel to the grating lines on the substrate. The measured smectic layer spacing reveals oscillations between a Sm-C* and a Sm-A like structures which depend on the film thickness as well as the distance from LC-air interface and is attributable to the difference in the molecular tilt imposed by a. the air-LC interface; b. the substrate; and c. the gratings' internal walls.

Keywords: Glancing angle X-rays; LC films; confined geometries

INTRODUCTION

All liquid crystals displays (LCD's) and devices require the confinement of liquid crystals to thin films between appropriately treated substrates. Consequently, the interaction of smectic liquid crystal films with solid substrates and the dependence of liquid crystal alignment direction of film's thickness, temperature, and depth is a subject of fundamental as well as technological interest [1 – 16].

In the past, a number of confined LC systems have been studied and modeled. These include free standing smectic films [13 – 15], nematic and smectic

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LC's contained in cavities of different sizes [6–12] as well as nematic [16, 17] and smectic [1–5, 13, 18–26] LC cells and in films of varying thickness. A number of papers on Sm-C* liquid crystals have reported the effects of film thickness phase transition temperatures, and on the existence of a helix unwinding transition line as a function of film thickness [26]. Previous studies on Sm-C* thin films indicate that the region between the induced homogeneous, in-plane alignment near the substrate, and the bulk of the thin films is mediated by disclination lines [27]. We have studied the orientational and structural evolution of hybrid films of a room temperature Sm-C* LC, using high resolution X-ray scattering. These films consist of a Sm-C* LC confined between air and a photolithographed grating on a glass substrate. The grating induces (homogeneous) alignment of the smectic planes perpendicular to both the surface of the film, and the long axis of the gratings; *i.e.*, the layer normal is parallel to the lines on the grating. The region of homogeneous alignment has a thickness comparable to the thickness of the films for the Sm-C* films studied [1–5, 28]. We have found previously that the value of the layer spacing varies as a function of depth within the films [28, 29], and that this variation increases with increasing film thickness.

In this paper, we present the results of an X-ray scattering study of the evolution of the Sm-C* layer spacing, *d*, in hybrid films of thickness ranging from 5 to 15 μm at constant temperature. We measure *d* as a function of time for the smectic layers with layer normal parallel to the grating lines. The time dependence of *d* varies as a function of depth (*i.e.*, distance from the LC-air interface). It is more pronounced far from the solid substrate. We relate the presence of oscillations in *d* to the competition among: a. the air LC interface; b. the surface of the substrate with grating; c. the internal vertical and horizontal surfaces of the grating. This type of time dependence at constant temperature has not previously been reported.

EXPERIMENTAL

The liquid crystal mixture mx5112 available from Displaytech was chosen for these measurements because it has a stable room temperature Sm-C* phase with the following phase sequence,

$$S_3 \xrightarrow[20.65^\circ\mathrm{C}]{} \text{Sm-C}^* \xrightarrow[49.5^\circ\mathrm{C}]{} \text{Sm-A} \xrightarrow[\sim 57^\circ\mathrm{C}]{} \text{I}.$$

MX5112 consists of a 1:1 mixture of 4-[(S)-(-)-2-Ethoxypropoxy]phenyl-4-(decyloxy)benzoate (W7) and 4-[(S)-(4-Methylhexyl)oxy]phenyl-4-(decyloxy) benzoate (W82). The Sm-A – Sm-C* and Sm-C* – S_3 transitions were measured in-house for our particular sample. The layer spacings for these smectic phases are 31.303 Å for the Sm-A at 49.5°C, 29.97 Å for the Sm-C* at 23°C and 31.639 Å for the S_3 phase at 20°C, respectively. At the Sm-C* – S_3 transition, the Sm-C* layer spacing is 30.076 Å. The latter transition is first order.

The films were deposited on photolithographed glass gratings, with an average grating period of 10 μm. The grating preparation method is discussed elsewhere [1 – 3]. The samples were cycled twice into the isotropic phase in a hot plate and were allowed to cool quickly into the smectic phase.

In-plane measurements using grazing incidence X-ray scattering (GIXS) [1 – 5] were performed at the National Synchrotron Light Source at Brookhaven National Laboratory, beamline X-22B, using 1.3776 Å (9.0 keV) X-rays and a resolution of 7×10^{-3} Å^{-1}. The beam sport size was 2 mm^2. Additional measurements were obtained using beamline X-18A, using 1.305 Å (9.5 keV) X-rays, a resolution of 3×10^{-3} Å^{-1} and a beam spot size of 1 mm^2. In all instances, the samples were mounted on a four-circle Huber goniometer. To perform the film depth studies, the incidence angle α was varied by tilting the sample into the X-ray beam in steps of 0.1°. Depth profiling was also achieved by varying the angle χ of the four circle configuration. In addition to Bragg diffraction scans, in-plane azimuthal ϕ scans were taken for all samples to ascertain the degree of layer ordering with respect to the direction of the gratings. The temperature at both beamlines was between 22.5°C and 24°C, which is in the Sm-C* range, where no significant variation in the value of the bulk Sm-C* layer spacing exists. The out-of-plane measurements were performed using a Rigaku 18 kW rotating anode source, using Cu K_α radiation, and a pair of single silicon (111) crystals as monochromator and analyzer, with a resolution of 4×10^{-4} Å^{-1}. The temperature was kept above 22°C with the use of an oven that could be adjusted to change temperature in 0.2°C steps.

RESULTS AND DISCUSSION

We show in Figure 1 the results of a series of $\theta - 2\theta$ in-plane scans taken at different times after deposition and temperature recycling [28] on a 15 μm thick film. The peak is asymmetric, and its position shifts with time. This shift is associated with a change in layer spacing, and a change in the molecular tilt. The relative intensity of the peak increases with time, indicating an increase in the degree of uniform alignment within the film. Figure 2a shows a plot of the value of the layer spacing as a function of time for this sample as well as for a 13 μm thick sample. The latter sample was monitored

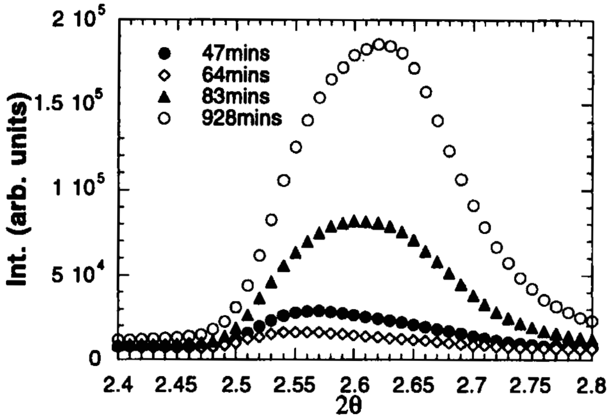

FIGURE 1 $\theta-2\theta$ scans on a 15 μm sample of mx5112, taken at different times after sample cycling. The smectic layer spacing oscillates between the Sm-C* and Sm-A phases.

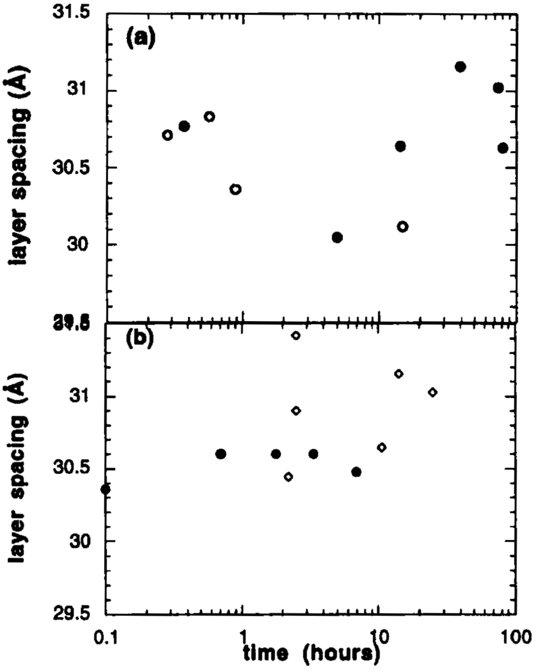

FIGURE 2 (a) Layer spacing as a function of time for a 13 μm (closed circles) and a 15 μm (open circles) film; (b) Layer spacing as a function of time for a 23 μm (diamonds) and a 5 μm (closed circles) film.

over a period of three days. Very clearly, the value of the layer spacing oscillates between values close to the Sm-A and the Sm-C* layer spacing. This oscillation is aperiodic, and slows down after the first few hours. For comparison, Figure 2b shows the layer spacing as a function of time for both a 5 μm thick film and a 23 μm thick film. The value of the layer spacing in the thinner film shows a smaller variation over time, while the variations in the layer spacing for the thicker film are more pronounced, and random.

Figure 3 shows the variation of the layer spacing as a function of X-ray incidence angle, or depth within the film. The layer spacing varies through the thickness of the film, with the largest variation close to the air-LC interface, and a smaller variation near the grating's surface. The data taken after 14 and 48 hours clearly shows the time dependence of the layer spacing discussed above.

To understand these results, one can consider the hybrid films as comprising three different surfaces and interfaces: a. the LC-air interface near the top of the film; b. the LC-glass interface at the top surface of the substrate; and c. the vertical and horizontal surfaces inside the grooves of the grating. In region a, the air interface induces a homeotropic alignment in the region near the free surface of the film. The value of the layer spacing in this region remains constant over time, and corresponds to the bulk value of the layer spacing at each temperature respectively. In region b, the alignment is such that the layers are perpendicular to the surface of the

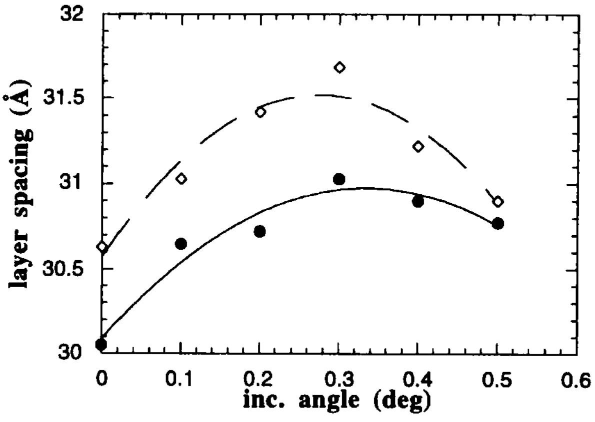

FIGURE 3 Depth dependence of the layer spacing in a 13 μm film over a 48 hour period. Closed circles: times *t*. Diamonds: time *t* + 48 hours; *t* = 14 hours. The higher incidence angles corresponds to measurements close to the glass-LC interface. The lines through the data are guides to the eye.

substrate and preferentially aligned along the direction of the gratings. In this region, the LC molecules are more free to tilt with respect to the smectic layer normal than at the air interface. The LC alignment in this region corresponds to the homogeneously aligned and unwound Sm-C* phase described in Refs. [26] and [27]. In region c, inside the gratings, the long axis of the LC molecules tends to align along the long axis of the grating's grooves due to the constraint imposed by the internal surface of the grooves. Within this region, the molecular ordering may resemble the Sm-A phase or the Sm-C* phase with a smaller tilt. The depth, size and uniformity of the gratings may play a role in determining the molecular order in this region. The smectic layers within the film experience a competition, and near balance, between the two molecular tilts imposed by surfaces in regions b and c. This may cause the layer spacing to oscillate about a value which is intermediate between the Sm-A and Sm-C* bulk values, as seen in Figures 1 and 2a. It explains also why this oscillation is observed along the in-plane direction only. Alternatively, a sharp boundary may exist between the Sm-A-like region on one side and Sm-C*-like region on the other side. This boundary may wander with time if the competing boundary conditions have comparable effect on the smectic layer orientation, thereby giving rise to changing value of layer spacing with time.

The variation in the value of the layer spacing becomes more pronounced as the distance from the glass substrate increases, as is clearly shown in Figure 3. This may be because (i) near the substrate, molecular motion is constrained, and (ii) at large distance from the substrate and close to the free surface, one is closer to the homeotropically aligned Sm-C* region, where the layer spacing is constant over time. Finally, Figure 2b suggest that the observed time oscillation in these film occurs within a range of thickness. This range may depend on the materials as well as on the substrate and substrate preparation method. More studies are needed to clarify this point.

The above result can have technological implications. Electro-optical devices based on ferroelectric LC's consist of closed cells with rubbed, *i.e.*, roughly grooved, substrates. Variations as a function of time of the smectic tilt angle or layer spacing can affect the reliability of these devices. This effect is similar to the effect of the presence of disclinations in the films [27].

CONCLUSIONS

We have observed, for the first time, a time dependent in-plane smectic layer spacing in Sm-C* films deposited on glass substrates with engraved gratings.

This time dependence appears to be a direct effect of the different and competing molecular tilts and smectic layer orientations dictated by the substrate and the interior secion of the gratings, and depends on the depth within the film as well as on the sample thickness. Further measurements and analysis of the behavior of these films are in progress.

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