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X-RAY SCATTERING STUDY OF A SMECTIC-A LIQUID CRYSTAL PARTIALLY CONFINED BETWEEN FREE SURFACE AND MICROGROOVED SUBSTRATES

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Abstract X-ray scattering is used to probe the smectic order in octyl-cyanobiphenyl partially confined between a free surface and a microgrooved glass substrate. It is found that the smectic order develops 6 K above the bulk nematic to smectic-A transition with layer spacing compressed up to 3% under a lateral confinement within the grooves. This lateral confinement is released as the thickness of the film above the grooves increases.

INTRODUCTION

Surface and confinement effects are fundamental issues in liquid crystal science and technology and have been extensively studied. The smectic orders induced at free liquid crystal-air interfaces or near planar solid boundaries^{1,2}, confined in freely suspended films^{3,4} and random media^{5,6} have been systematically investigated in recent years. The development of x-ray scattering technique allows us to explore more complex phenomena, such as the growth morphology of liquid crystal films⁷ and anisotropic surface roughnesses⁸. Studies of hybrid smectic octylcyanobiphenyl (8CB) films ranging between 5 and 40 μm in thickness, deposited between microgrooved substrates and air have revealed important effect of the competition between surface anchoring and elastic forces on the orientation⁹⁻¹¹ of smectic layers. In this paper, we report results of our study of smectic order in 8CB in such systems to understand the origin of smectic alignment.

EXPERIMENTAL

The well known liquid crystal 8CB has a phase sequence: isotropic- (40.5°C) -nematic- (33.5°C) -smectic- A_d - (21.5°C) -crystal in the bulk state. Microgrooved substrates were prepared using photolithographic techniques in the center of a microscope slide^{9,12}. As illustrated in Fig.1.a, 8CB was filled in the microgrooves with a dimen-

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sion $w=6\mu m$, $D=1.5\mu m$. The grooves of length $L_x=1cm$ cover a 1cm \times 1cm area. Naturally, no confinement effects are expected along the x-axis (perpendicular to the paper). The number of grooves filled with liquid crystal is $L_y/(w+m)\sim 1,100$,

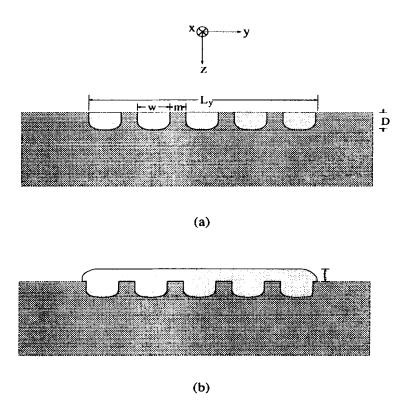


FIGURE 1: X-ray scattering from smectic liquid crystals confined within microgrooves (a), and confinement partially released by an additional liquid crystal film over the grooves (b).

where $m=3\mu m$ is the thickness of the wall seperating the grooves and L_v is the lateral dimension covered by grooves. The intensity of scattered x-rays is a summation of the signals from the liquid crystal contained inside all the grooves. The width of the incident x-ray beam defined by a pair of slits is 1.5mm, which uniformly covers a length of $1.5mm/\sin\theta_B\sim 6cm$ in the y-direction, where $\theta_B\sim 1.4^\circ$ is the first quasi-Bragg angle for smectic layers with Copper K_α radiation ($\lambda=1.540178 \text{\AA}$). The beam height is 1cm and is nearly uniformly distributed out of the scattering plane. Consequently, liquid crystal-filled grooves and the liquid crystal film covering them are uniformly illuminated with the incident x-ray beam (Fig.1.b).

The absorption of x-rays by liquid crystal is negligibly small for Cu-Ka radia-

tion. Liquid crystal deposited on the substrate, both inside and outside the grooves, contributes to scattering as the x-ray beam illuminates all parts of the sample when the scattering vector q lies in x-z plane. But when the x-ray beam is perpendicular to the grooves, i.e., q is in the y-z plane as shown in Fig.1.a, liquid crystal near the bottom of the grooves contribute less to the scattering than that near the surface due to the x-ray absorption by the solid glass walls in between the grooves. The depth sensitivity in x-ray scattering experiment can be controlled by changing sample orientation around the scattering vector which in turn changes the extent of absorption by the groove walls in this geometry. The development of this new surface and depth sensitive scattering technique will be reported in a separate paper 13.

RESULTS AND DISCUSSIONS

We present x-ray data collected from three samples. Sample S1 was prepared with capillary action to allow 8CB to fill only the grooves. Sample S2 was prepared combining a fast capillary action and spreading of a thin 8CB film over the grooves, which resulted an thin film of $t \sim 4000$ Å. Sample S3 was prepared by spreading 8CB over the grooves, and the additional film was approximately $4\mu m$ thick. The thickness of the films were determined from the integrated intensities of the quasi-Bragg smectic peaks⁷ which were in agreement with the values calculated from the amount of materials deposited.

Fig. 2 shows 2θ - θ and ω scans of first order quasi-Bragg peak for the three samples, measured at the same temperature $T=30^{\circ}C$. The open circles are the data measured with the incident x-ray beam parallel to the grooves. The filled circles are the data measured along the direction perpendicular to the grooves. The intensities of the peaks in 2θ - θ for all samples obtained in the perpendicular direction have been multiplied by 5 to clearly show the peak profiles. Two quasi-Bragg peaks at $2\theta = 2.874^{\circ}$ and $2\theta = 2.892^{\circ}$ were observed in S1. The smectic layer spacings were measured to be 30.71Å and 30.52Å, which were smaller by 2.5% and 3%, respectively than the bulk Sm-A layer spacing 31.5Å at the same temperature. The ω scans of the Bragg peaks show a sharp peak superimposed on a diffuse background. The main peak observed in the perpendicular incidence is at in $2\theta = 2.88^{\circ}$ with satellite peaks, suggesting a multilayer "domain" structure¹³. A detailed analysis of this scattering profile is in progress.

With the additional thin film of 4000Å in S2, which connected the liquid crystals in individual grooves to release partially the lateral confinement, the Bragg peak was at $2\theta = 2.819^{\circ}$. The smectic layer spacing in S2 was 31.31Å. The $4\mu m$ film in S3 brings the smectic layer spacing closer to that of the bulk, as observed

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previously in $5\mu m$ films⁹. The change in layer spacing can be attributed to the layer compression due to the surface tension³.

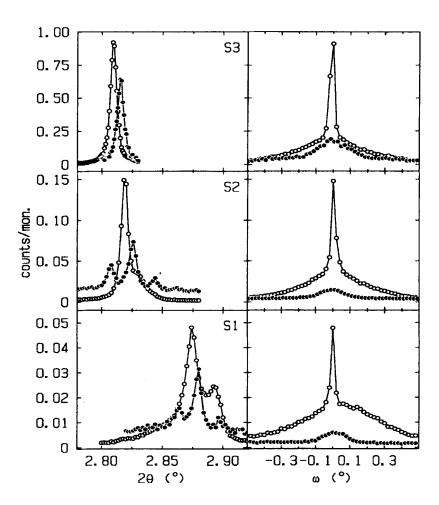


FIGURE 2: 2θ - θ and ω scans of quasi-Bragg smectic peaks of Samples S1, S2 and S3 at T=30°C. Beam is incident in parallel (open circles) and perpendicular (filled circles, intensity multiplied by 5 in 2θ - θ scans) direction to the microgrooves.

Fig. 3 shows the χ -scan of S1 at the Bragg peak which was achieved by rotating the sample around the x-axis⁹. The intensity at $\chi=0$ arises from the smectic layers parallel to the substrate. A peak that at $\chi=-90^\circ$ would be due to the layers perpendicular to the substrate and parallel to the wall of the grooves. The growth of intensity at $\chi=0$ with decreasing temperature indicates predominently homoetropic

alignment in the grooves due to surface tension rendering the smectic order laterally confined.

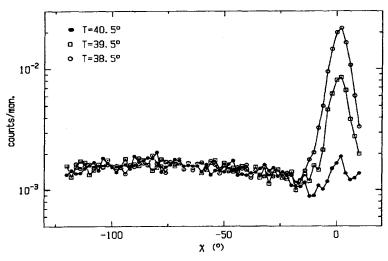


FIGURE 3: χ scan with rotation around x-axis at the Bragg peak of S1. The peak at $\chi = 0$ grows rapidly with decreasing temperature, indicating the domination of homeotropic alignment.

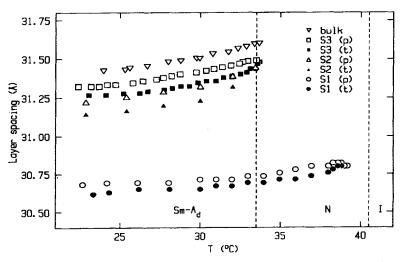


FIGURE 4: Smectic layer spacing of S1, S2, and S3 samples as a funcation of temperature. The letter p(t) indicates parallel (transverse) incidence.

As evident in Fig. 4, the smectic layers of 8CB in sample S1 develop 6 K above the nematic-smectic phase transition temperature of bulk, as it is laterally

confined within grooves. The over laying films in S2 and S3 partially release this lateral confinement by connecting the liquid crystals in the individual grooves and bring the smectic order closer to that of the bulk.

SUMMARY AND ACKNOWLEDGMENT

We have studied of smectic liquid crystal partially confined in between the free surface and microgrooved glass substrates. We found that the smectic layers forms at a significantly higher temperature and that they are strained under the lateral confinement. This compression may be accompanied with a molecular tilt along the length of the grooves, which can cause homogeneous alignment of the smectogen on grooved substrates¹⁰.

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