Electron-Diffraction Study of Free-Standing Liquid-Crystal Films

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We have carried out the first electron-diffraction study of thin free-standing liquid-crystal films. Stable films were maintained in a finite atmosphere with use of a differentially pumped sample chamber. It is possible to observe the behavior of single domains even in thin hexatic films by limiting the sample area probed to several micrometers squared. Initial results on two systems exhibiting tilted hexatic behavior have provided novel information about the bond-orientational order parameters and their scaling relationship in films of a few molecular layers.

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Free-standing liquid-crystal films have been widely used to investigate novel hexatic phases of matter originally predicted by the theory of defect-mediated melting in two dimensions.[1-3] The structural technique most extensively applied to study these films is x-ray diffraction, often with the use of synchrotron sources.[4-8] X-ray studies offer very high resolution in **Q** space and therefore are well suited to provide detailed information on the extent of positional correlations. However, to obtain sufficient signal-to-noise ratio, it is in practice necessary to use an x-ray beam whose size ($\simeq 1$ mm^2) is larger than the typical size of domains in the films within which the direction of the bond-orientational (BO) order is uniform. Therefore, it is in general difficult to obtain reliable data on the extent of BO order in free-standing liquid-crystal films by the use of x rays. An exception to this limitation occurs in tilted hexatic phases, where domains larger than the beam size can be obtained with an aligning magnetic field. An elegant x-ray study of the BO order in thick films of a material exhibiting smectic-*I* (Sm-*I*) and smectic-*C* (Sm-*C*) phases has been reported recently.[8] Despite this advance, it is nevertheless highly desirable to have an alternative technique for measuring BO order that is particularly applicable for thin films and not limited to tilted phases. In this Letter, we report the first successful attempt to use electron diffraction to study thin free-standing liquid-crystal films that exhibit hexatic order. Although electron diffraction is a relatively low-resolution technique with respect to spatial correlations, it has the unique advantage in that useful data can be obtained with a beam size of the order of micrometers squared even in thin films, thus allowing the quantitative measurement of BO order within a single domain in films of a few molecular layers for both orthogonal and tilted phases.

A Siemens Elmiskop 1A electron microscope was used as a diffractometer. To prevent the destruction of the film in vacuum by evaporation, a special sample chamber at finite pressure was constructed, as shown schematically in Fig. 1(a). The inner sample compartment is connected to a nitrogen supply and separated from the main

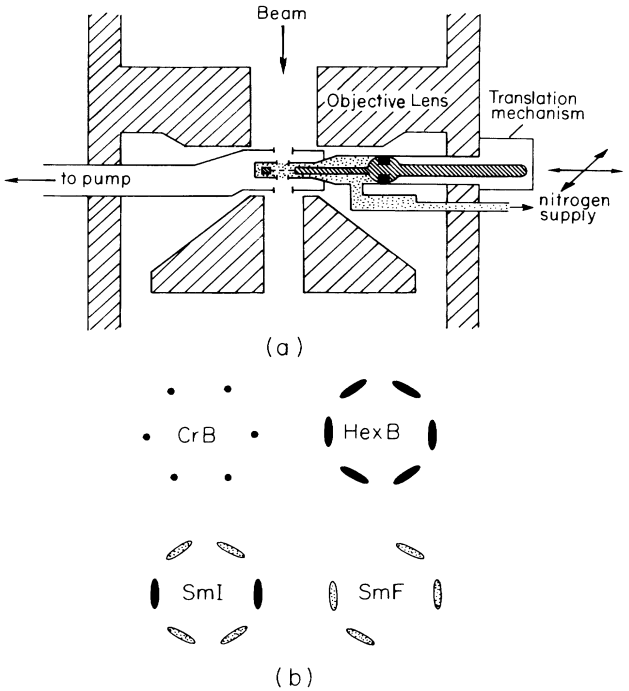
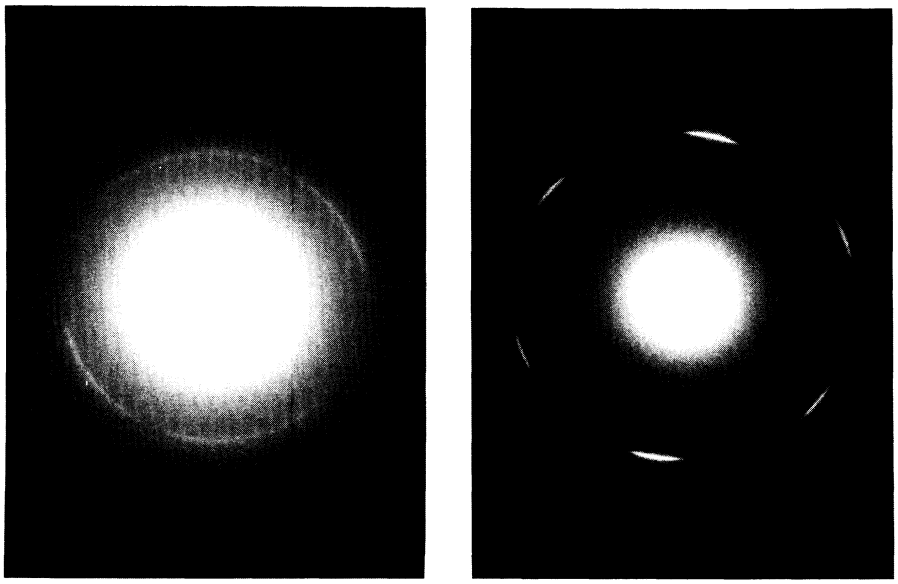


FIG. 1. (a) Schematic diagram of sample chamber. (b) Expected electron-diffraction pattern from thin liquid-crystal films in various smectic phases.

vacuum by an outer compartment. Four collinear apertures in the two compartments allow the electron beam to pass through. The outer compartment is differentially pumped to remove the small amount of gas leaking from the inner compartment through the apertures. Sample temperatures between $-10\,^{\circ}C$ and $55\,^{\circ}C$ were achieved with a thermoelectric module. Such a setup with the inner compartment containing saturated water vapor was used previously to study free-standing hydrated phospholipid bilayers.[9] In our experiments, the electron-beam diameter was between 5 and 10 μm and the pressure in the sample compartment was typically between 10 and 30 Torr. The diffraction data were recorded on photographic plates and analyzed with digital imaging techniques. It should be noted that the detection is limited to a single plane perpendicular to the incident beam and parallel to the sample plane. In Fig. 1(b) are sketched the diffraction patterns that are expected from thin films in crystal-*B* (Cr-*B*), hexatic-*B* (Hex-*B*), Sm-*I* and smectic-*F* (Sm-*F*) phases.

Two liquid-crystal systems were used in this initial study. The first is S-N-[4-(3,7-dimethyloctanoyloxy)-2-hydroxybenzylidene]-4-*n*-nonylaniline, which exhibits chiral Sm-C^*, Sm-I^*, and Sm-J^* phases upon cooling in the bulk. We have studied three- and four-layer films of this material. The identification of the phases in these films was made by means of polarized reflected-light microscopy.[10] Figure 2(a), taken with a four-layer film at $32\,^{\circ}C$, is an electron-diffraction pattern typical of these films in the hexatic phase. The presence of four weak arcs with twofold symmetry suggests that this material, in which Sm-I^* occurs in the bulk, exists as Sm-F^* in thin films. A similar switch from Sm-*I* to Sm-*F* when the thickness is reduced has been reported in 4-*n*-heptyloxybenzylidene-4-*n*-heptylaniline (7O.7), which does not exhibit hexatic phases in the bulk.[7] Since our data represent only a cut of the tilted $(\pm 1, \pm 1, 0)$ scattering cylinders in the detection plane, we are unable to apply the usual χ-scan analysis to yield absolute values of the BO order. However, assuming little temperature dependence of the tilt angle, we can nevertheless use the intensity modulation $\Delta I/I_0$ along the arcs in our detection plane, where I_0 is the average intensity and $\Delta I = I_0 - I_{\min}$, as a relative measure of the degree of BO order. Figure 3 shows a plot of $\Delta I/I_0$ and the radial linewidth $\Delta Q/Q_{\parallel}$ in the detection plane as a function of temperature for a three-layer film. The fact that distinct changes in $\Delta I/I_0$ and $\Delta Q/Q_{\parallel}$ can be seen to occur near the temperatures at which phase transitions were observed with polarized reflected-light microscopy indicates minimal sample degradation by the electron beam. Similar results were also obtained in a four-layer film with lower transition temperatures. The temperature dependence of the BO order in these thin films is qualitatively similar to that found in thick films of 4-(2-methylbutyl)phenyl-4′-(octyloxy)-(1,1′)-biphenyl-4-carboxylate (8OSI).[8] We note that the major change in the BO order occurs over a much larger temperature range in the thin films that we studied than in the thick 8OSI films. It is unclear whether this is an intrinsic effect of film thickness or is due to the difference in material or data analysis. The nonzero intensity modulation above the transition is indicative of the occurrence of hexatic order in the Sm-C^* phase, which has been predicted[11]



(a) (b)

FIG. 2. Electron diffraction pattern obtained from four-layer films of (a) S-N-[4-(3,7-dimethyloctanoyloxy)-2-hydroxybenzylidene]-4-*n*-nonylaniline at $32\,^{\circ}C$ and (b) a mixture of 12 wt.% PP5CC in 6OBC at $41\,^{\circ}C$.

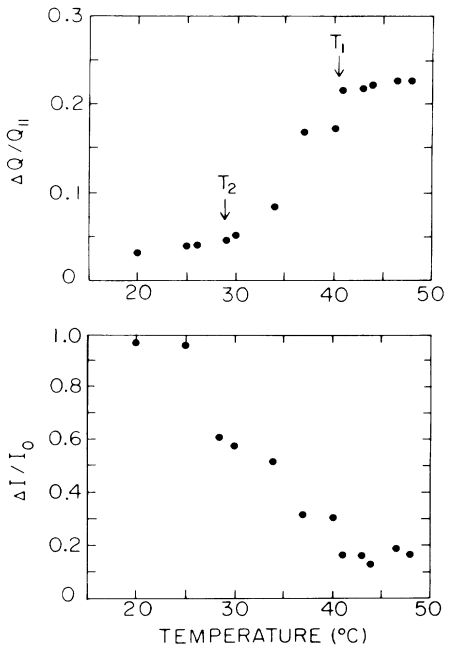


FIG. 3. Temperature dependence of the intensity modulation $\Delta I/I_0$ along the electron-diffraction arcs and the radial linewidth $\Delta Q/Q_{\parallel}$ in the detection plane in a three-layer film of S-N-[4-(3,7-dimethyloctanoyloxy)-2-hydroxybenzylidene]-4-*n*-nonylaniline. The arrows T_1 and T_2 indicate Sm-C^*–Sm-F^* and Sm-F^*–solid transition temperatures, respectively, observed by polarized reflected-light microscopy.

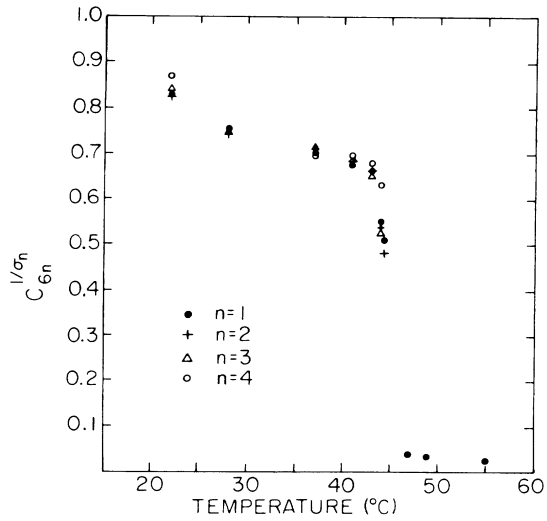


FIG. 4. Temperature dependence of scaled bond-orientational order parameters C_{6n}^{1/σ_n} for $n=1$ to 4 in a four-layer film of a mixture of 12 wt.% PP5CC in 65OBC, with use of Eq. (3) for σ_n with $\lambda=0.8$.

and experimentally verified.[8]

The second liquid-crystal system studied is a mixture of 12 wt.% of 4-proprionylphenyl-*trans*-(4-*n*-pentyl) cyclohexane carboxylate (PP5CC) in *n*-hexyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC), which exhibits Hex-*B* and smectic-*A* phases in the bulk.[12] Figure 2(b) shows the electron-diffraction data for a four-layer film of this mixture at 41 °C. The excellent signal-to-noise ratio obtained by an exposure of a few seconds is apparent. The existence of a twofold symmetry with two strong arcs and four weaker ones in the diffraction pattern is indicative of a Sm-*I* phase, suggesting that the molecules, which are normal to the smectic layers in the bulk, have developed a tilt in the four-layer film. This phenomenon is probably related to the tendency of the molecules on the surface to tilt, which has also been observed in 7O.7.[13] Since the two intense arcs are due to $(0,\pm 2,0)$ scattering centered on the detection plane, we have fitted their intensity $I(\chi)$ over an angular range χ of 60° by the expression

$$I(\chi)=I_0\left[\frac{1}{2}+\sum_{n=1}^{\infty}C_{6n}\cos[6n(90°-\chi)]\right]+I_{\mathrm{BG}}, \tag{1}$$

where C_{6n} are the $6n$-fold BO order parameters and I_{BG} is the background intensity. Using reasonable assumptions about the width of the out-of-plane scattering structure factor,[14] we estimate that any distortion of the angular line shape due to molecular tilt is negligible. Our data, therefore, provide essentially a true χ scan. We find that Eq. (1) including terms up to $n=4$ represents an excellent description of our data. This constitutes the first measurement of C_{6n} in a thin-film system.

A recent theory[15] suggests the scaling relation

$$C_{6n}=C_6^{\sigma_n}. \tag{2}$$

By fitting our results by Eq. (2), we find that the values of σ_n can be closely approximated by the expression

$$\sigma_n=n+\lambda n(n-1), \tag{3}$$

with λ having a typical optimal value of 0.8 and only weakly dependent on temperature. Equation (3) with $\lambda\cong 0.3$ has been derived and experimentally verified in three dimensions.[15] Figure 4 shows that a reasonable universal curve is obtained from our data by plotting C_{6n}^{1/σ_n} versus temperature for $n=1$ to 4, if σ_n is assumed to follow Eq. (3) with $\lambda=0.8$. The scaling behavior in this four-layer film, including the apparent departure from a universal λ near the transition to Sm-*C*, is thus similar to that in thick films of 8OSI, apart from the difference in λ. Our result is consistent with the prediction that λ should increase as the dimension is reduced. However, our data are inconclusive on whether λ itself is dependent on *n*, as expected in reduced dimension.[15]

In summary, we have demonstrated the feasibility and power of electron diffraction as a tool to study free-

standing liquid-crystal films. Initial results on tilted hexatic phases have provided novel information on the BO order parameters and their scaling behavior in thin films.

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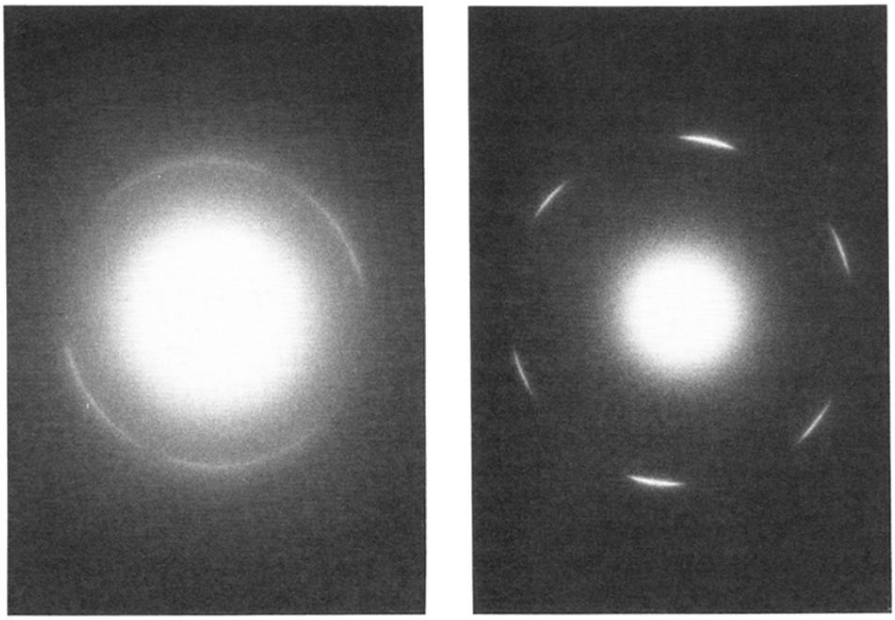

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