Hexatic and Crystal Phase Transitions in Thin Free-Standing Liquid-Crystal Films

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Thermal and structural studies have been performed on thin films of *n*-heptyl-4′-*n*-pentyloxylbiphenyl-4-carboxylate (75OBC). Similar to 65OBC, a surface hexatic phase is observed for films greater than four molecular layers in thickness. Four- and three-layer films display a single, two-dimensional liquid-hexatic transition. The four-layer heat-capacity anomaly is described well by a divergent power-law expression. The three-layer heat-capacity anomaly is qualitatively the same, although its size is greatly reduced. Also, a surface crystal-*E* phase is observed immediately below the liquid-hexatic transition(s).

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Hexatic liquid crystals have been the subject of substantial theoretical and experimental investigation since the first identification of such order nearly ten years ago.[1] Three-dimensional (3D) tilted and untilted hexatic liquid-crystal phases have demonstrated an exceedingly rich variety of novel phase transitions and critical phenomena.[2–5] Much of the progress in studying these liquid-crystal phases resulted from the ability to prepare free-standing films. The complications of substrates are avoided and the surface tension present at the vapor/film interface acts in some cases as an ordering field, an uncommon occurrence in condensed-matter physics. By varying the thickness of these films it is possible to study the three-dimensional to two-dimensional crossover as well as observe surface transitions in intermediate-thickness films. The thin- (2D) film results are of particular interest since they enable direct quantitative comparisons with the two-dimensional melting theories of Halperin and Nelson[6] and Young.[6]

In this work we report heat-capacity, x-ray-, and electron-diffraction studies performed on free-standing films of *n*-heptyl-4′-*n*-pentyloxylbiphenyl-4-carboxylate (75OBC). Heat-capacity studies reveal separate continuous surface and interior smectic-*A*–hexatic-*B* (Sm-*A*–Hex-*B*) transitions for layer number $N \geq 5$.[7,8] The three- and four-layer heat-capacity data possess a single anomaly indicating that the interlayer coupling drives the individual layers to order in unison. What is most striking is that both three- and four-layer anomalies are qualitatively the same although the magnitude of the three-layer peak is reduced much more than expected. The fact that they are qualitatively the same is a good indication that the 2D limit has been reached for this transition.

Heat-capacity data also reveal a precipitous drop immediately below the hexatic transition(s). For all film thicknesses studied this heat-capacity feature exhibits a large thermal hysteresis with no pretransitional fluctuations. For films of thickness $N \geq 5$, electron- and x-ray-diffraction studies unambiguously identify this heat-capacity feature as a surface crystal-*E* (Cry-*E*) phase transition. The interior layers crystallize at a lower temperature with a second heat-capacity feature. For three- and four-layer films there are indications that the Cry-*E* → Hex-*B* transition still occurs first in the surface layers, but the structural results are inconclusive at this time. More detailed structural studies of the thin films are in progress.

Details of the ac calorimetry used for thin, free-standing films have been reported elsewhere.[7,9] Bulk 75OBC possesses a Sm-*A*–Hex-*B* transition at 64.4 °C and a Hex-*B*–Cry-*E* transition at 59.5 °C (Ref. 10), in agreement with thick-film (~300 layers) heat-capacity data. Heat-capacity/area scans for five-, four-, and three-layer films of 75OBC are presented in Fig. 1. The temperature scale is referenced to the liquid-hexatic transition temperatures (T_p) for the four- and three-layer films, and to the liquid–surface-hexatic transition temperature for the five-layer data. These temperatures in degrees Celsius are 65.31, 65.57, and 66.31 for five-, four-, and three-layer films, respectively. The Sm-*A*–Hex-*B* transitions are marked by singular peaks while the Hex-*B*–Cry-*E* transitions appear as abrupt drops in heat capacity. In Fig. 1(a) the high- and low-temperature Sm-*A*–Hex-*B* peaks correspond to surface and interior transitions, respectively. For this film thickness the surface Sm-*A*–Hex-*B* transition dominates (greater entropy release) that of the interior. The four- and three-layer data show only one symmetric peak indicating a single Sm-*A*–Hex-*B* transition throughout the film. The peak positions and amplitudes of the Sm-*A*–Hex-*B* anomalies show no hysteresis to within our experimental resolution (7 mK and 0.015 $\mu J/cm^2K$, respectively). The lower-temperature Hex-*B*–Cry-*E* transitions are strongly first order with a thermal hysteresis of about 0.4 K. The jump amplitudes in units of specific heat are

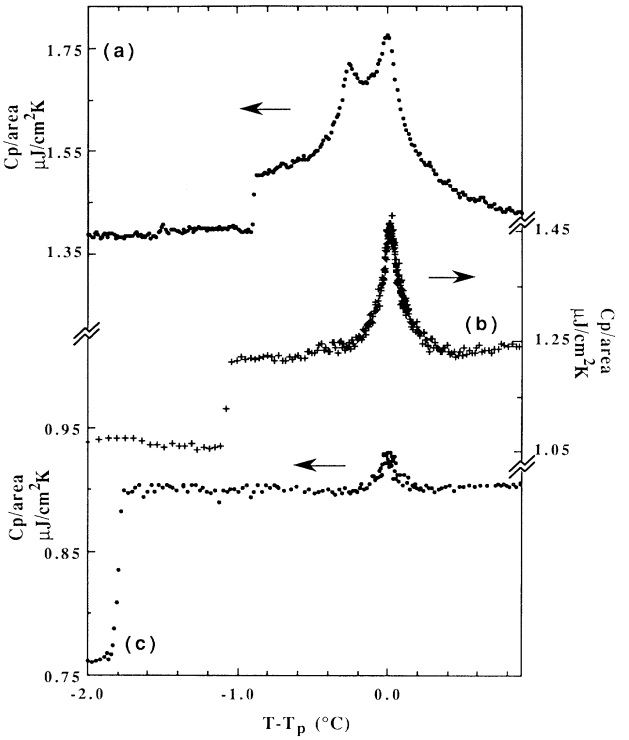

FIG. 1. Heat-capacity/area for (a) five-, (b) four-, and (c) three-layer 75OBC films. Absolute units for the data are inferred from thin-film (< 30 layers) signal (details discussed in Ref. 9). Transition temperatures are given in the text.

roughly equal for the three- and four-layer films but it decreases for the five-layer data. No pretransitional behavior was observed on cooling near the Hex-*B*-Cry-*E* transitions for scanning rates as low as 0.2 mK/min. Since we employ quasiadiabatic calorimetry, no latent-heat measurements could be made. A similar, hysteretic, surface crystalization transition had also been observed in mechanical measurements on 65OBC films[11] although, in that case, the surface crystalline phase was not structurally identified.

Previous work on the Sm-*A*-Hex-*B* transition in thin films of 65OBC pointed out the singular nature of the Sm-*A*-Hex-*B* heat-capacity anomaly.[7] Numerous improvements in the calorimetry system have increased the signal-to-noise ratio for the four-layer data by roughly a factor of 4. It is clear that the anomaly is symmetric and quite sharp (full width at half height =140 mK). For these reasons, a critical fitting was performed over one and a half decades in reduced temperature, yielding the heat-capacity critical exponent $\alpha = 0.30 \pm 0.05$ (Fig. 2). These fitting results were reproducible, and in contrast to the case of 65OBC (Ref. 7) there was no ambiguity in the sign of α. With the increased resolution of the calorimeter, α will be measured for thin films of other *nm*OBC compounds including 65OBC.

The three-layer 75OBC heat-capacity anomaly is surprisingly small. Its decreased size prevented any

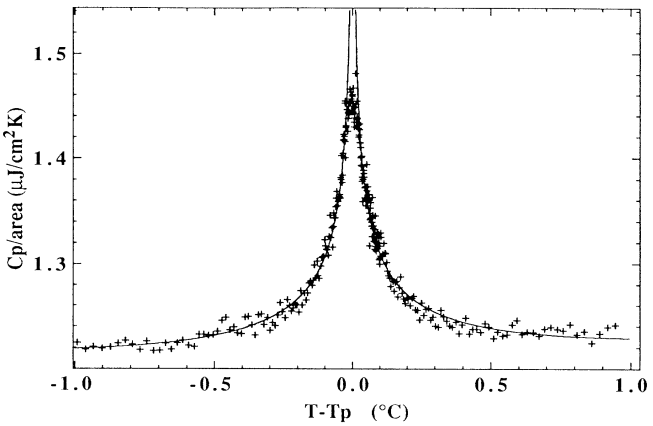

FIG. 2. Heat-capacity anomaly near the Sm-*A*-Hex-*B* transition of a 75OBC four-layer film. Power-law fit (shown as solid line) yields $\alpha = 0.30 \pm 0.05$.

meaningful fitting. However, Fig. 3 presents an overlay of three- and four-layer data (the three-layer heat-capacity scale has been expanded by a factor of 5.25). There is no increase in the width of the anomaly nor any detectable change in its symmetric nature. Along with the decreased height of the anomaly, the transition temperature increased by 0.75 K above the four-layer transition. This is roughly twice the increase seen between the four- and five-layer transitions. X-ray and optical studies have ruled out the appearance of tilted phases at three layers as a possible cause for the size decrease. Possible reasons for this behavior arise from the effects of free surfaces on the structure of the film. Recent x-ray investigations of free-standing liquid-crystal films by Tweet *et al.* point out the drastic reduction of molecular positional fluctuations (parallel to the layer normal) at free surfaces.[12] A quantitative measure of this effect is the width of the Gaussian molecular center-of-mass dis-

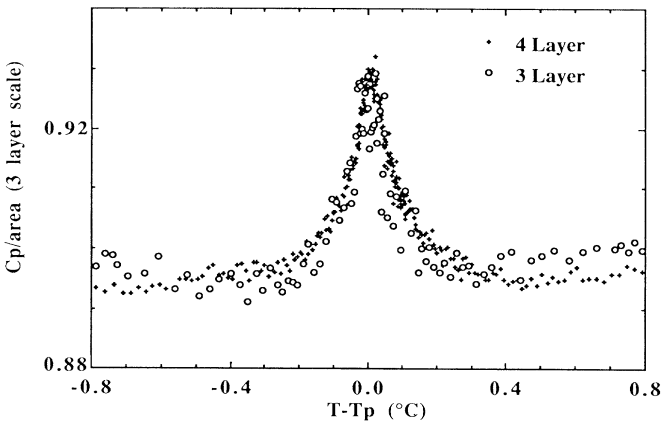

FIG. 3. Overlay of four- and three-layer heat-capacity anomalies. The three-layer scale has been expanded by a factor of 5.25. The anomalies are qualitatively the same to within experimental scatter.

tribution (essentially a mean-square fluctuation amplitude), which can be determined from low-angle x-ray scattering. From their measurements, the difference between surface and interior fluctuation amplitudes of a three-layer film is ≈ 0.23 Å. This difference nearly doubles for a five-layer film, and is increased by a factor of 5 for a 35-layer film. Although the fluctuation amplitude of the surface layers is relatively constant, it is clear that interior fluctuations decrease rapidly with film thickness. If the depression of molecular fluctuations (parallel to the layer normal) enhances local positional hexatic ordering,[13] the entropy change at a liquid-hexatic transition can be lessened. This occurs since the increase in short-range positional order is a major source of entropy release through the Sm-A–Hex-B transition.[14] A similar evolution occurring for 7OBC free-standing films could then drastically reduce the liquid-hexatic peak size between three and four layers without changing the critical nature of the transition.[15] Such effects should also increase the liquid-hexatic transition temperatures substantially.

To investigate the ordering which occurs at the heat-capacity jumps (the Cry-E ordering) we have performed synchrotron x-ray- and electron-diffraction studies on 7OBC free-standing films. This was necessary not only to identify the crystalline order present, but also to determine to what extent this order exists throughout the film thickness and how it is affected by the free surfaces. Details of the experimental techniques are presented in Refs. 1 and 16. Figure 4 shows an electron-beam diffraction pattern for a five-layer film at 64.2 °C. This beautifully illustrates the ordering present in the film. The sixfold symmetric diffuse hexatic scattering is evident along with sharp crystalline spots. The crystalline spots are what would be expected from two domains (rotated $\sim 4°$ with respect to each other) of the herringbone Cry-E structure (see inset Fig. 5). Since liquid-crystal films usually order from the surface inwards, due to the film's surface tension, the Cry-E spots correspond to two surface crystal domains with noncoincident axes, while the sixfold diffuse scattering results from the hexatic interior. The reproducibility of these results rules out the possibility that the crystal spots are due to separate Cry-E domains within one layer. Six-layer electron-scattering results are essentially the same with a stronger hexatic scattering. Four-layer diffraction shows a drastically reduced hexatic scattering, with the two crystal spots now nearly coincident. This suggests much stronger interlayer correlations for $N \leq 4$.

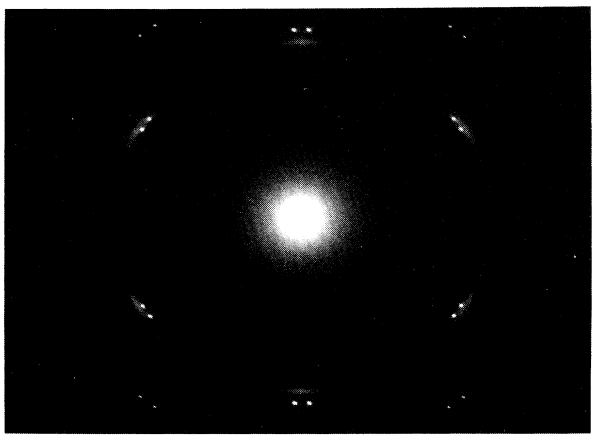

FIG. 4. Electron-diffraction pattern from a five-layer 7OBC film. The sixfold symmetric diffuse scattering identifies interior hexatic order, while the two sets of Cry-E spots reflect separate Cry-E surface domains.

To probe the interlayer correlations, synchrotron x-ray studies were performed using beam line X16B at the National Synchrotron Light Source. With the free-standing films in a transmission geometry, scans were indexed as illustrated in the inset to Fig. 5. A Ge(111) crystal was used as a monochromator and a LiF(200) crystal as an analyzer providing an instrumental resolution of 9×10^{-4} Å (FWHM) in the scan direction. Figure 5 shows x-ray L scans along the layer normal ($\mathbf{c}^*$) direction through the (1,1,0) in-plane peak. The four-layer data were tak-

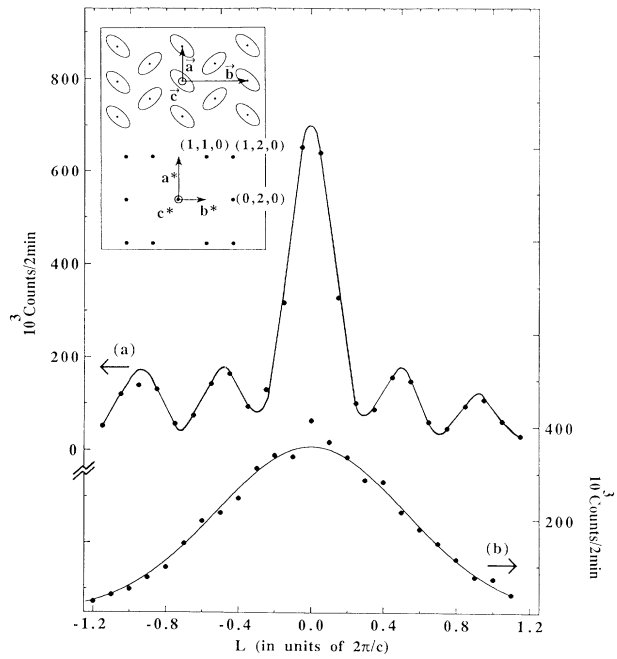

FIG. 5. X-ray L scans of four- and five-layer 7OBC films taken in a direction normal to the smectic layers through the (1,1,0) peak. (a) The four-layer data clearly show the modulation which results from the interlayer correlations of a four-layer crystal. (b) The five-layer data show no such structure indicating that the crystalline order is limited to the surface layers. The solid lines are a guide to the eye. Inset: the real-space structure of the Cry-E phase and the resultant peaks in the structure factor along with their indexing. From thick-film measurements $|\mathbf{a}| = 5.44$ Å, $|\mathbf{b}| = 8.27$ Å, and $|\mathbf{c}| = 29.1$ Å.

en at a temperature, $T=59.0\,^{\circ}C$, where the entire film was in the Cry-E phase. The L scan for this film clearly shows the modulation which results from the interlayer correlations of a four-layer crystalline film. In contrast, no such structure is observed for the five-layer film at 60.2 °C, only a gradual intensity decrease due to the molecular form factor. This is a strong confirmation that the heat-capacity feature in Fig. 1(a) results from a surface Cry-E phase transition.

Because of the appearance of liquid-hexatic and hexatic-crystal surface transitions in 75OBC it is a very unique system in which to study dimensional effects on these transitions. The single four-layer heat-capacity anomaly near the Sm-A-Hex-B transition implies the existence of saturated transverse correlations throughout the transition region. Its divergent character is inconsistent with the predictions of 2D XY melting theories.[17–19] In one sense this is surprising since those theories predicted the hexatic phase. However, there is, as yet, no consensus concerning the 3D Sm-A-Hex-B transition and the value of its critical exponent $\alpha=0.60$, which is certainly not the 3D XY value.[20] In light of this, it is not strange that the four-layer heat-capacity anomaly does not display the predicted 2D XY behavior.

In conclusion, we have studied surface and interior Sm-A-Hex-B and Hex-B-Cry-E phase transitions in the liquid-crystal compound 75OCB using heat capacity, electron diffraction, and x-ray diffraction. Similar to other members of its homologous series there exists in 75OBC a surface hexatic phase which extends throughout the film thickness at four layers. In addition 75OBC possesses a surface Cry-E phase immediately below the liquid-hexatic transition(s). All Sm-A-Hex-B transitions are continuous to within experimental resolution while the Hex-B-Cry-E transitions are strongly first order even in the thinnest films studied. Furthermore, on the basis of the following two experimental facts, we believe that the four-layer-film heat-capacity anomaly near the liquid-hexatic transition displays two-dimensional behavior. First, both three- and four-layer films possess single heat-capacity peaks. Second, except for the difference in overall magnitude, the three-layer heat-capacity anomaly is the same as that of four layers, to within our resolution. To further support this statement, we propose to construct a calorimeter better able to measure heat capacity of three- and two-layer films.

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[1]R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981).

[2]J. D. Brock, D. Y. Noh, B. R. McClain, J. D. Litster, R. J. Birgeneau, A. Aharony, P. M. Horn, and J. C. Liang, Z. Phys. B **75**, 197–213 (1989).

[3]E. B. Sirota, P. S. Pershan, L. B. Sorenson, and J. Collett, Phys. Rev. A **36**, 2890 (1987).

[4]C. C. Huang, J. M. Viner, R. Pindak, and J. W. Goodby, Phys. Rev. Lett. **46**, 1289 (1981).

[5]G. Nounesis, C. C. Huang, and J. W. Goodby, Phys. Rev. Lett. **56**, 1712 (1986).

[6]B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979); A. P. Young, Phys. Rev. B **19**, 1855 (1979).

[7]R. Geer, C. C. Huang, R. Pindak, and J. W. Goodby, Phys. Rev. Lett. **63**, 540 (1989).

[8]R. Geer, T. Stoebe, C. C. Huang, R. Pindak, and J. W. Goodby, Mater. Res. Soc. Symp. Proc. **177**, 299 (1990).

[9]R. Geer, T. Stoebe, T. Pitchford, and C. C. Huang (to be published).

[10]T. Pitchford, G. Nounesis, S. Dumrongrattana, J. M. Viner, C. C. Huang, and J. W. Goodby, Phys. Rev. A **32**, 1938 (1985).

[11]R. Pindak, W. O. Springer, D. J. Bishop, D. D. Osheroff, and J. W. Goodby, Phys. Rev. Lett. **48**, 173 (1982).

[12]D. J. Tweet, R. Holyst, B. D. Swanson, H. Stragier, and L. B. Sorenson, Phys. Rev. Lett. **65**, 2157 (1990).

[13]J. V. Selinger, J. Phys. (Paris) **49**, 1387 (1988). It is demonstrated explicitly in this reference that layer undulations can frustrate hexatic order. Depression of layer fluctuations may relax this frustration for thin liquid-crystal films and increase local positional order.

[14]J. M. Viner, D. Lamey, C. C. Huang, R. Pindak, and J. W. Goodby, Phys. Rev. A **28**, 2433 (1983).

[15]It should be noted that the Cry-E surface transition present in 75OBC occurs much closer to the Sm-A-Hex-B transition than in any *nm*OBC compounds studied to date, implying the presence of very strong surface ordering effects in this compound.

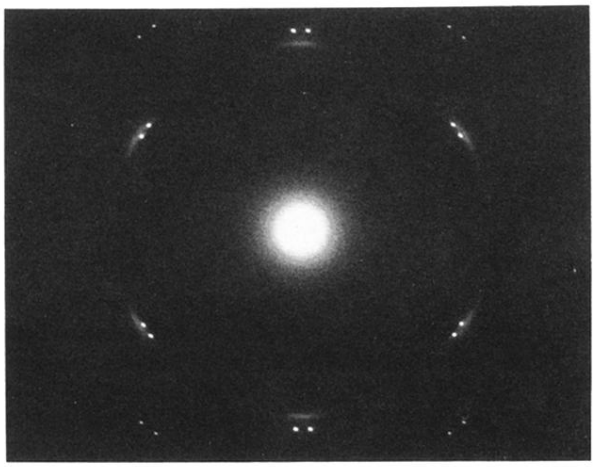
[16]M. Cheng, J. T. Ho, S. W. Hui, and R. Pindak, Phys. Rev. Lett. **59**, 1112 (1987).

[17]A. N. Berker and D. R. Nelson, Phys. Rev. B **19**, 2488 (1979).

[18]S. A. Solla and E. K. Reidel, Phys. Rev. B **23**, 6008 (1981).

[19]K. J. Strandburg, Rev. Mod. Phys. **59**, 1001 (1987).

[20]G. Nounesis, R. Geer, H. Y. Liu, C. C. Huang, and J. W. Goodby, Phys. Rev. A **40**, 5468 (1989).



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