Melting of Variable-Thickness Liquid-Crystal Thin Films: A Synchrotron X-Ray Study

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The results of a synchrotron x-ray study of the crystalline-B to smectic-A melting transition in 4-n-pentylbenzenethio-4'-n-tetradecyloxybenzoate ($\overline{1}4S5$) are presented. Samples of two, three, five, and twelve molecular layers were investigated with the free-standing thin-film technique. A single, abrupt, hysteretic transition is observed in two-layer films with temperature-independent positional correlations above the transition. All thicker films melt by two first-order phase transitions; the character of the intermediate phase depends strongly on film thickness.

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The planar melting behavior which occurs within the layers of smectic liquid crystals provides an opportunity to study the evolution of the melting transition from two to three dimensions with freestanding thin-film techniques.[1] The thinnest films consisting of only two layers are the only experimentally viable example of substrate-free two-dimensional (2D) melting known. The present study has been motivated by the expectations (1) that melting in two-dimensional systems might involve qualitatively new physical mechanisms and (2) that the behavior versus thickness would be relevant to our understanding of 3D melting transitions in smectics in particular and in solids in general. Additional interest in the problem has been stimulated by a detailed theory of second-order 2D melting via a dislocation mechanism,[2] by controversial molecular-dynamics calculations,[3] and by recent experimental studies demonstrating second-order melting in both incommensurate Xe and Ar monolayers adsorbed on a pyrolytic graphite substrate.[4]

Liquid-crystal thin films were prepared as previously described.[1] However, a new material, 4-n-pentylbenzenethio-4'-n-tetradecyloxybenzoate ($\overline{1}4S5$), was used, which has two distinct advantages over N-(4-n-butyloxybenzylidene)-4-n-octylaniline (4O.8) used in our previous studies of crystalline-B thin films: (1) $\overline{1}4S5$ is thermally stable and (2) it has a wide smectic-A range (66.5 to 86.6 °C). This last point is important because thin-film transitions occur some 10 °C above the respective bulk transition temperatures,[5] and films cannot be made when the bulk material is above the smectic regime. Our ex-

periments were carried out on the focused wiggler beam line VII-2 at the Stanford Synchrotron Radiation Laboratory. Two different resolution configurations were used. A high-resolution mode using two Si(111) crystals in the monochromator and one in the analyzer had a longitudinal resolution component $\Delta Q_{\parallel} = 7 \times 10^{-4}$ Å^{-1} [full width at half maximum (FWHM)] at $Q \approx 1.4$ Å^{-1}. For studying broad liquid scattering, we used pyrolytic graphite (002) monochromator and analyzer crystals, which relaxed the longitudinal resolution to $\Delta Q_{\parallel} \simeq 0.03$ Å^{-1} (FWHM).

The x-ray scattering work presented here is closely related to studies of the mechanical shear properties described in a Letter by Bishop *et al.*[6] We begin with results for the two-layer ($N = 2$) system. The mechanical measurements[1] found three distinguishable features, but x-ray scattering reveals that only the highest temperature feature at about 77 °C is associated with a phase transition in the thin film. Furthermore, the two other features at 67 and 75.5 °C in the mechanical data occur at the same respective temperature in each film thickness studied. Thus they indicate transitions in the material wetting the edges of the film's support frame. The nature of these transitions will become clear when we discuss the properties of thicker films. Focusing on the $N = 2$ behavior, Fig. 1 shows high-resolution longitudinal scans taken through the (10) Bragg rod of the 2D hexagonal crystal lattice at a temperature well below melting. Here we expect a 2D crystalline structure characterized by the power-law structure factor $S(Q) \propto (Q - 1)^{-2+\eta}$.[7] Indeed this is the case as seen by the solid line repre-
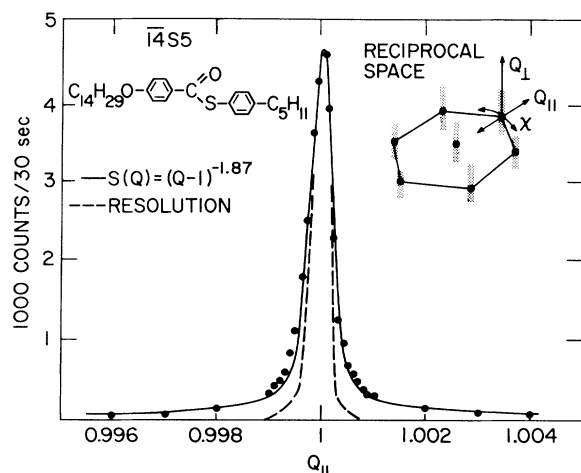
FIG. 1. High-resolution longitudinal scan taken at $65\,°C$ in an $N = 2$ film of $\overline{14}S5$ showing the fit to a two-dimensional power-law structure factor $S(Q) \approx (Q-1)^{-2+\eta}$ where $\eta = 0.13$. The resolution is shown by the dashed line. The in-plane momentum transfer $Q_\parallel$ is in units of $2\pi/a = 1.4177\ \text{Å}^{-1} - (6.6\times 10^{-4}\ \text{Å}^{-1}\ \text{deg}^{-1})(T - T_{AB})$ for $T > T_{AB} = 66.5\,°C$. Inset: the general scattering geometry.

FIG. 2. Longitudinal scans in an $N = 2$ film taken as a function of $Q_\parallel$ (the in-plane momentum transfer) at temperatures approaching the melting transition (a) from below and (b) from above.

senting this fitted cross section with $\eta = 0.13$. Note that this shape differs significantly in the wings from the resolution function shown by the dashed curve, but the half-width is only a few percent broader. As the temperature is raised toward the melting transition the peak width remains essentially that of the instrumental resolution as shown in Fig. 2(a). The diminishing intensity at higher temperature is difficult to interpret quantitatively because the in-plane mosaic structure changes continuously at a fixed temperature in the vicinity of melting as noted in our earlier study of 4O.8.[1] It is nevertheless clear that the $N = 2$ system is in a 2D crystalline phase up to $77.7\,°C$ on heating. Immediately above this temperature the signal observed with the high-resolution configuration disappears. The high-intensity, low-resolution configuration is then required as shown in Fig. 2(b). We find a ring of uniform intensity in the plane with a longitudinal width $\Delta Q_\parallel \approx 0.16\ \text{Å}^{-1}$ (FWHM) implying correlation lengths of about 20 Å. We find no evidence for temperature dependence of the linewidths and, just as thermal hysteresis was observed in the mechanical measurements, the liquid scattering persists on cooling down to temperatures $\sim 1\,°C$ below the transition temperature measured on heating. We conclude that films consisting of two molecular layers melt via a strong first-order hysteretic phase transition at a tem-
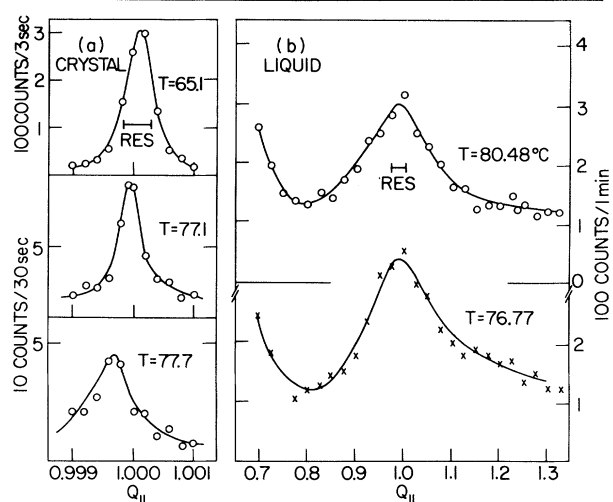
perature some $10\,°C$ above the bulk crystalline-B to smectic-A transition temperature.

For the $N = 3$ film, results are summarized in Fig. 3. In agreement with the features in the mechanical data, we find transitions in $N = 3$ films at $T \simeq 72$ and $75\,°C$. We emphasize that, unlike the single transition for $N = 2$ films, two transitions are seen in $N = 3$ films. At temperatures above $75\,°C$ on cooling, liquid scattering similar to Fig. 2(b) is seen with the low-resolution configuration. In the high-resolution data of Fig. 3 only background counts are observed as shown by the solid circles. Cooling below the upper transition, which is again strongly first order, leads to a very intriguing new state unique to films consisting of three layers. Three different temperatures in this regime are shown. The remarkable aspects of this scattering data are (1) that explicitly finite, albeit long (≈ 800 Å), correlations are present; (2) that these correlation lengths *decrease* (i.e., peak widths increase) with decreasing temperature; and (3) that the structure of the scattering has a broad temperature-independent sinusoidal shape in the in-plane angular variable χ as shown in the inset in Fig. 3. The qualitative features of these data are similar to expectations for the 2D "hexatic" phase proposed in conjunction with dislocation-mediated melting[8] as well as with observations in bulk liquid crystals in the "stacked hexatic" B phase.[9] In particular, the χ-scan structure is indicative of a phase characterized by bond-orientational
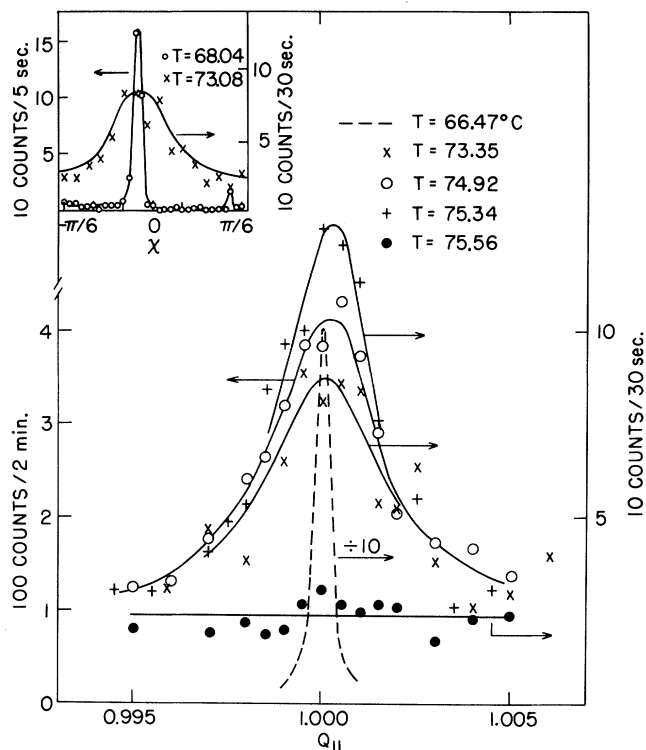
FIG. 3. High-resolution longitudinal scans for an
$N = 3$ film. At low temperatures (dashed line) the
scattering is resolution limited; at high temperature
(solid circles) liquid scattering similar to the $N = 2$
data of Fig. 2(b) is observed. The scattering at inter-
mediate temperatures has an observable width which
increases as the temperature decreases. Inset: χ
scans in the low-temperature phase (sharp profile) and
the intermediate phase (broad structure).

FIG. 4. Scattering profiles as a function of $Q_\perp$ (in
units of $2\pi/c = 0.1785$ Å^{-1}) at $Q_\parallel = 1.0$. The top panel
shows the crystalline phase of $N = 3$ films; the middle
panel shows the intermediate phase for an $N = 5$ film;
the bottom panel shows the evolution in interlayer cor-
relations as an $N = 12$ film is heated through the lower-
temperature transition.

order. Nevertheless, the conclusion that dislo-
cation-mediated melting is the physical mecha-
nism responsible for this bond-orientationally or-
dered phase *cannot* be reconciled with the long
correlation lengths observed, their contrary tem-
perature dependence, or the fact that strongly
first-order transitions into this phase are ob-
served on both heating and cooling. Returning to
Fig. 3, the crystallization is completed by a
transition at 72 °C which results in resolution-
limited scattering depicted by the dashed line. In
this phase, the χ structure is sharp (Fig. 3, in-
set), as expected for a 2D solid.

To understand thicker films, and perhaps the
above behavior, one must study the development
of interlayer order. We display a preliminary
selection of the results obtained so far in Fig. 4.
In the top panel a scan along the Bragg rod is
shown for an $N = 3$ film in the low-temperature
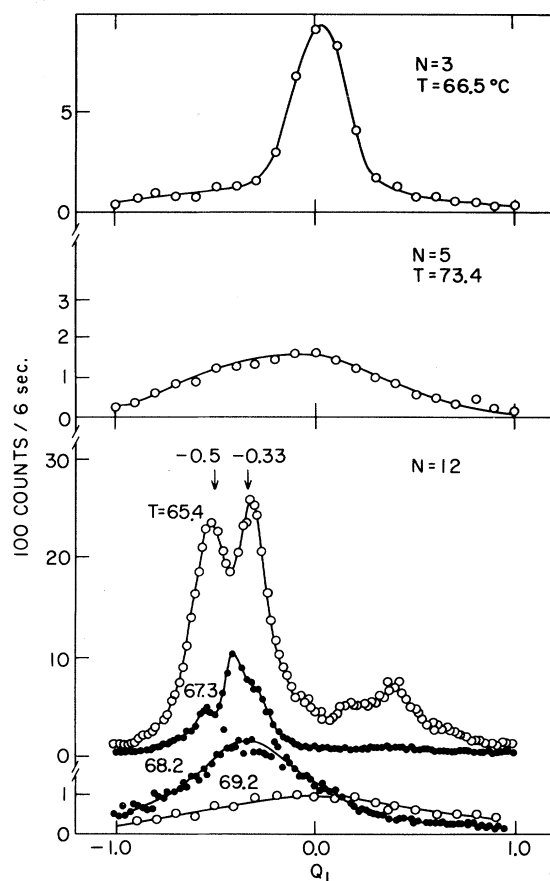crystalline phase. These data are at variance

with our expectations for three-layer diffraction.
The fundamental principle reflected in calculated
profiles is that, regardless of the stacking reg-
istry, $S(Q_\perp)$ is periodic in units of $2\pi/c$, where c
is the single-layer thickness. Although the mo-
lecular form factor decreases as $Q_\perp$ increases,
the (101) peak is clearly visible at a level of
about 30% of the (100) peak in the bulk crystalline-
B phase of 40.8.[1] Analogous behavior is clearly
not observed in the $N = 3$ data of Fig. 4. Rather a
single peak centered at $Q_\perp = 0$ is seen with no ad-
ditional peaks found at $Q_\perp = \pm 1$. The most direct
explanation is that the amplitude of the modula-
tion of the electron density which constitutes the
layering is unusually small. In spite of this weak
layering, the layers are clearly registered in
lateral position since the width of the scattering
is approximately the inverse three-layer thickness.

We now discuss briefly the behavior of thicker films. First consider $N = 5$. As for $N = 3$, there are two phase transitions. We find that the high-temperature phase is a liquid with scattering identical in shape to that for $N = 2$ [see Fig. 2(b)] and $N = 3$. The transition into the intermediate phase takes place at $T \simeq 75\,°C$ and results in scattering which is resolution limited along $Q_\parallel$ quite unlike the intermediate phase for $N = 3$. Although the scattering is sharp in $Q_\parallel$ it is broad in $Q_\perp$, as shown in the middle panel in Fig. 4. This broad scattering reveals that this phase consists of uncorrelated crystalline surface layers. Since the intensity is similar to that from an $N = 2$ film, the ordered surfaces must consist of essentially a single layer each. At a lower temperature ($T \simeq 68\,°C$) the $N = 5$ film develops interlayer order. Quite similar behavior is found in all thicker films. The nature of the transition from the intermediate to the lower-temperature phase is illustrated by data on an $N = 12$ film shown in the bottom panel of Fig. 4. These data indicate that this transition involves the rapid development of interlayer correlations. The shift of the peak away from $Q = 0$ and its structure are probably a result of a complicated phase-shift sequence occurring from layer to layer.

In conclusion we summarize the crystallization process versus film thickness. In thick films, typified by $N = 12$, surface layers crystallize abruptly at a temperature enhanced some $8\,°C$ over the bulk transition temperature of $66.5\,°C$. Cooling through the bulk transition temperature results in ordering of the interior layers apparently nucleated from the surface. As film thickness is decreased below $N = 5$, both transition temperatures increase. For $N = 3$, the nature of the intermediate phase is remarkably different, lacking long-range positional order, but having bond-orientational order. Finally, for $N = 2$ only one transition is observed. Contrary to theoretical predictions for continuous 2D melting, we find an abrupt hysteretic transition with no critical behavior. Of course the observation of such first-order behavior cannot be interpreted too generally; continuous transitions such as those observed in Xe monolayers on a graphite substrate may ultimately be discovered in substrate-free systems, although there is as yet no theoretical reason to expect them to prevail over first-order transitions.

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