

Mechanical Measurements of the Melting Transition in Thin Liquid-Crystal Films

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Shear mechanical properties of the liquid crystal 4-*n*-pentylbenzenethio-4'-*n*-tetradecyloxybenzoate ($\overline{14S5}$) have been studied in films as thin as two molecular layers. Crystalline two-layer films were found to melt directly into a liquid phase by a large first-order transition. Crystalline films of three or more layers melted in two stages both by first-order transitions. Mechanical properties of the intermediate phase indicated crystalline surface layers with an anomalously soft response for a three-layer film.

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The nature of the melting transition in two dimensions and its evolution to three dimensions has been the subject of considerable theoretical and experimental effort. Freestanding smectic liquid-crystal films provide a unique experimental system to study such melting. First, their dimensionality can be varied since one can prepare films with thicknesses ranging from two to hundreds of molecular layers. Secondly, their properties can be studied without the influence of an orienting substrate. Unfortunately, enhanced surface crystallinity (described below) has made it difficult in practice to achieve detailed measurements on the thinnest films. In this Letter, we report the first such detailed measurements at the melting transition in freestanding films of the liquid crystal 4-*n*-pentylbenzenethio-4'-*n*-tetradecyloxybenzoate ($\overline{14S5}$) that were as thin as two molecular layers and clearly two dimensional. This paper reports the results of extensive in-plane shear mechanical measurements on these films. Extensive x-ray structural measurements are presented in the accompanying Letter of Moncton *et al.*¹

In the bulk $\overline{14S5}$ has a crystalline-*B* phase which melts at 66.5 °C into a smectic-*A* phase followed by a transition into an isotropic liquid at 86.6 °C. Our study of the thin-film properties of $\overline{14S5}$ has produced the following new results. (a) The crystalline-*B* phase of a two-layer film, which has the structural properties of a two-dimensional (2D) crystal, melts by a *single* large first-order transition into a liquidlike phase. The magnitude of the in-phase shear modulus in the crystalline phase is lower than the thermodynamic stability limit indicative of highly mobile de-

fect arrays within our films. (b) Films of three or more layers melt in two stages with both transitions showing hysteresis in their mechanical properties upon heating and cooling. Unlike the low-temperature phase, in the intermediate phase the shear response of the film does *not* scale with the number of layers, indicative of a surface effect. For films with thicknesses of five or more layers the magnitude of the shear response in the intermediate phase is consistent with each outer surface layer being crystalline. The magnitude of the shear response of a three-layer film in the intermediate phase is a factor of 3 softer. This soft mechanical response for a three-layer film is consistent with the structural characterization of its intermediate phase as having only bond-orientational order. (c) The low-frequency in-plane shear modulus of the crystalline-*B* phase for $\overline{14S5}$ is almost 2 orders of magnitude smaller than in the widely studied crystalline-*B* phase of N-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline (4O.8).²⁻⁴

Although a two-stage melting process had previously been observed in 4O.8,^{2,3} the detailed nature of the transitions could not be studied in films of fewer than four molecular layers. In *thicker* films, structural and mechanical evidence led to the conclusion that the interior layers melted first. The surface layers remained crystalline until a temperature approximately 10 °C higher. This enhancement in the surface melting temperature precluded detailed studies of the melting process in thin films of 4O.8 because before these films could melt the bulk material which wetted the film support frame underwent a transition into a phase without a layered structure

and the films ruptured. This did not occur in $\overline{14}S5$. The 20.1°C smectic- A range maintained a layered phase wetting the edge of the support frame, allowing detailed studies of the melting process in films as thin as two layers.

The dissipation and in-plane shear modulus of the freestanding films were measured with the high- Q BeCu torsional oscillator technique described elsewhere.² Several improvements have been made in constructing the present apparatus. First, the thermal uniformity was increased to better than 0.01°C by the addition of radiation shielding above and below the freestanding films. In addition the pressure in the cell was regulated to $\pm 0.2\%$ which allowed the period of the oscillator to be resolved to 1 part in 10^6 . Finally, a less massive oscillator was used which had greater sensitivity to the properties of the film. The resonant frequency was 720 Hz. The oscillator had a torsion rod 1.0 mm in diameter, 12.7 mm long, with a spring constant of 4.9×10^6 ergs. As before, an annular film (i.d. 0.64 cm, o.d. 0.74 cm) was introduced between the oscillator and a supporting ring. The amplitude and period decrease ΔA and ΔP of the oscillator-film system were measured as functions of temperature and film thickness. The period shift, ΔP , relative to the unloaded oscillator, is proportional to the sum of the shear elastic responses contributed by each layer of the film.

Figure 1 summarizes the temperatures at which features are seen in ΔP and ΔA for films of $\overline{14}S5$ as a function of thickness. (In cases where

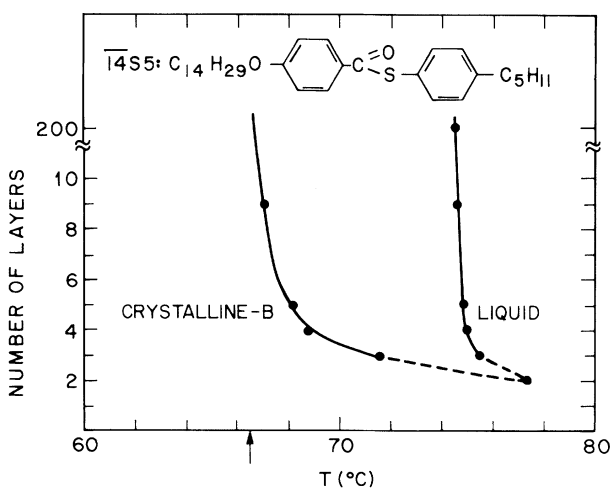


FIG. 1. The phase diagram obtained from our torsional oscillator measurements. The arrow indicates the bulk crystalline- B to smectic- A transition temperature.

the temperature at which jumps occurred differed on heating and cooling the average temperature has been plotted.) It was also noted that after the sample was pumped on for several weeks, the temperatures of the features increased by $\leq 0.4^\circ\text{C}$, but the overall temperature dependence described below remained unchanged. In Fig. 1 the arrow indicates the bulk crystalline- B to smectic- A transition temperature. As shown in the phase diagram in Fig. 1 our study indicates that, for films of three or more layers, there are three distinct regions of shear response. There is a crystalline- B , an intermediate, and a liquidlike region. In the liquidlike region both ΔP and ΔA vanish. This is the smectic- A phase which consists of fluid layers. A two-layer film melts directly from the crystalline- B phase into a liquidlike phase.

In Figs. 2(a) and 2(b) we show the shear response in the crystalline- B and intermediate regions. Figure 2(a) contains the temperature dependence of ΔP for films with thicknesses of two, three, five, and nine molecular layers. Figure 2(b) shows the change in amplitude ΔA for the same films. Films of five or more layers overdamped the oscillator at the transition from the liquid to the intermediate region and throughout most of the crystalline- B region; hence only limited temperature ranges could be probed for these thicker films, although enough data could be taken to determine the nature of each region.

In the crystalline- B region the shear response scaled with the number of molecular layers [compare the lower-temperature period decrease for the three- and nine-layer films in Fig. 2(a)]. From our measurements of the period shift we can obtain a value for the bulk in-plane shear modulus μ_B . Our result for $\overline{14}S5$ in the crystalline phase is $\mu_B = 2.0 \times 10^7$ ergs/cm³. The in-plane shear modulus in 4O.8 is $\mu_B = 1.5 \times 10^9$ ergs/cm³,² while the interlayer shear modulus is $\sim 10^6$ ergs/cm³.⁵ A four-layer film of 4O.8 was scanned in our present, more sensitive apparatus and was found to overdamp the system even in the intermediate region. To verify that our measurements in $\overline{14}S5$ are in the linear response regime we have varied the drive amplitude by a factor of 15 with no observed change in ΔP . Therefore we conclude that the low value for the in-plane shear modulus in $\overline{14}S5$ compared to 4O.8 is not the result of defect generation although a higher mobility of defect arrays already present may account for some of the difference.

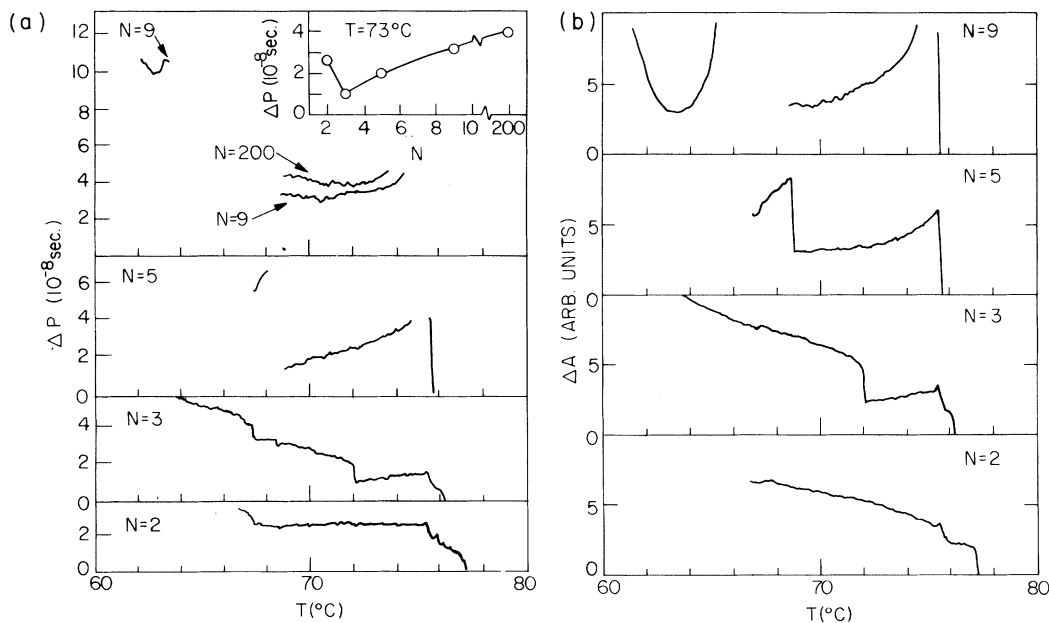


FIG. 2. The period shift ΔP and amplitude shift ΔA for films of two, three, five, and nine molecular layers. Inset: ΔP vs the film thickness at a temperature within the intermediate region.

In marked contrast to the crystalline region, in the intermediate region, for films of five or more layers, the shear response and period decrease are essentially independent of the number of layers, implying a surface effect. For example in Fig. 2(a) we show ΔP for a 9- and a 200-layer film. The magnitude of this surface shear response is measured to be 14 ergs/cm^2 which is comparable to the shear response from a two-layer film in the crystalline- B phase. From this fact we conclude that, in thicker films, each outer layer remains crystalline in the intermediate region. The thermodynamic stability limit⁶ for the shear modulus of a 2D crystal of $\overline{14}S5$ is $\mu = 4\pi k_B T_m / a_0^2 = 230 \text{ ergs/cm}^2$. Our measured value for the surface shear modulus is significantly lower. A detailed study⁷ of the stress relaxation in freestanding films of $4O.8$ demonstrated that the relaxation time decreased strongly as the film thickness was reduced, with a four-layer film exhibiting a shear relaxation time ~ 0.01 sec. Thermally activated glide of dislocations could provide the mechanism for this fast stress relaxation.⁸ The stress relaxation in the crystalline surface layers of $\overline{14}S5$ may be even faster than in the crystalline four-layer $4O.8$ films resulting in the small effective 720-Hz shear modulus which we measured.

In the inset of Fig. 2(a) we plot ΔP versus the film thickness at a temperature ($T=73^{\circ}\text{C}$) within the intermediate region. This plot again illu-

strates the thickness independence of ΔP for thicker films. It also illustrates an anomalously soft shear response for a three-layer film in the intermediate region. High-resolution x-ray studies presented in the accompanying paper demonstrate that, for films of five or more layers, the intermediate region consists of crystalline surface layers. For a three-layer film, however, although bond-orientational order (BOO) persists into the intermediate phase, positional correlations only extend $\sim 1000 \text{ \AA}$. The crystallinity at the outer surfaces of thicker films in the intermediate region is disrupted when the surfaces are only separated by one molecular layer. This highlights the importance of interlayer interactions in determining the in-plane structural and mechanical properties of the films. The positional correlations in the BOO phase of the three-layer $\overline{14}S5$ film are approximately an order of magnitude larger than the positional correlations in the bulk "stacked hexatic- B " phase of n -hexyl-4'- n -pentyloxybiphenyl-4-carboxylate (65 OBC).⁹ The larger extent of the positional correlations explains why a shear response is observed in the former but not the latter material.¹⁰ It also indicates the sensitivity of our present oscillator which can detect an in-plane shear modulus when the in-plane positional correlations become $\sim 1000 \text{ \AA}$.

Finally, several apparent jumps occur in the thin-film data of Fig. 2 which were not included

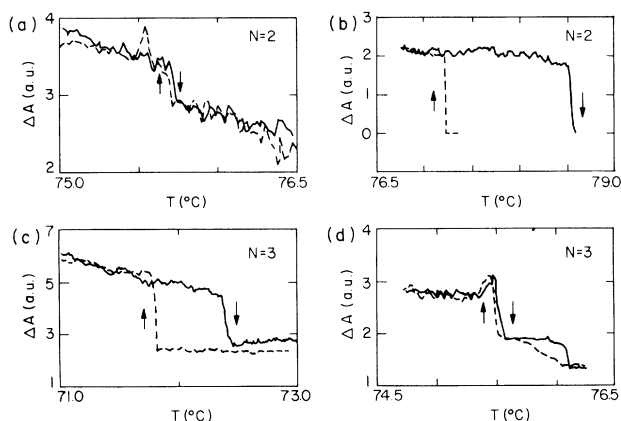


FIG. 3. The thermal hysteresis for a two- and a three-layer film. The solid curves were taken while heating and the dashed while cooling.

in Fig. 1. These features were not found to correlate with any structural change as determined by x rays.¹ For example, in the data for two- and three-layer films in Fig. 2(b) a second jump occurs at $T = 75.5^\circ\text{C}$. We suspect that this feature is an artifact due to the bulk material which wets the edge of the oscillator and couples the film to the apparatus. The bulk material is undergoing a phase transition in which the surface layers are crystallizing and enhancing the coupling of the film to the oscillator and support ring. This produces an apparent increase in the shear modulus. For this feature we found negligible hysteresis in its mechanical properties [shown for a two-layer film in Fig. 3(a) and for a three-layer film in Fig. 3(d)]. Although we cannot study the surface melting transition directly in thick films because of overdamping of the oscillator, its effect on the thin-film response provides indirect evidence that the thermal hysteresis at the thick-film surface melting transition is small. For a two-layer film there is also a feature at $\Delta T \sim 0.6^\circ$. The intermediate BOO-phase to liquid transition in a three-layer film appears as the higher-temperature feature in Fig. 3(d) with $\Delta T \sim 0.2^\circ$.

The thermal hysteresis found for actual transitions within the thin films is shown in Fig. 3. Figure 3(b) shows the crystalline-*B* to liquid

transition in a two-layer film with $\Delta T \sim 1.3^\circ$. Figure 3(c) is the crystalline-*B* to intermediate BOO-phase transition in a three-layer film with $T \sim 66.5^\circ\text{C}$ [Fig. 2(a)]. This feature is another artifact due, this time, to the *interior* layers of the bulk material crystallizing.

In conclusion, extensive mechanical measurements have shown that freestanding films of 14S5 exhibit several distinct regions of shear response as a function of temperature and film thickness. The mechanical properties of the films in each region have been detailed in this paper while their structural properties are described in an accompanying paper by Moncton *et al.*¹ The structural and mechanical properties of the films are consistent and demonstrate that two-layer films melt by a single, strongly first-order transition. They also demonstrate the occurrence of a bond-orientationally ordered phase in an unexpected region of the temperature-thickness phase diagram. Measurements on different materials are in progress to determine the universality of the observed behavior.

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¹D. E. Moncton, R. Pindak, S. C. Davey, and G. S. Brown, following Letter [Phys. Rev. Lett. **49**, 1865 (1982)].

²R. Pindak, D. J. Bishop, and W. O. Sprenger, Phys. Rev. Lett. **44**, 1461 (1980).

³J. C. Tarczon and K. Miyano, Phys. Rev. Lett. **46**, 119 (1981).

⁴D. E. Moncton and R. Pindak, Phys. Rev. Lett. **43**, 7016 (1979).

⁵M. Cagnon and G. Durand, Phys. Rev. Lett. **45**, 1418 (1980).

⁶J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).

⁷W. O. Sprenger, R. Pindak, and D. D. Osheroff, to be published.

⁸R. Bruinsma, B. I. Halperin, and A. Zippelius, Phys. Rev. B **25**, 579 (1982).

⁹R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981).

¹⁰R. Pindak, W. O. Sprenger, D. J. Bishop, D. D. Osheroff, and J. W. Goodby, Phys. Rev. Lett. **48**, 173 (1982).