

Experimental characterization of layer thinning transitions

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The layer thinning transitions in free-standing films of several liquid-crystal compounds containing different combinations of flexible tails have been systematically investigated. The results clearly indicate that fluorination of liquid-crystal compounds plays an essential role in the layer-by-layer thinning transitions of free-standing films above the bulk smectic-A–isotropic transition temperature T_{AI} . The surface ordering effects of these fluorinated compounds above T_{AI} is contrasted with recent x-ray results that suggest surface disorder below T_{AI} in a fluorinated liquid-crystal compound. [S1063-651X(98)50809-4]

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For more than a decade, the role of the free surface in the nucleation of bulk melting or freezing has been an important subject of both theoretical [1] and experimental [2] interest. In virtually all solids studied, free surfaces have a disordering effect on the solid. Thus, the liquid phase may form at the surface as the bulk melting temperature is approached. Such phenomena, known as wetting, have been widely studied in solids. The empirical data is consistent with well-developed theories of wetting. In contrast with solids, the free surface of some complex fluids may have an ordering effect on the bulk phase. Surface freezing has been observed in liquid crystals [3] and alkanes [4]. Surface enhanced ordering in liquid crystals is also thought to be essential for compounds to exhibit the layer thinning transition, a rare melting phenomenon observed in some free-standing liquid-crystal films [5–9]. As the temperature is increased, single interior layers [10] of the free-standing film melt and slide out of the film to the meniscus. The layer thinning transition is related to wetting phenomena in that the thickness of the ordered phase diverges near the transition temperature, presumably due to the presence of the surface. Yet the unique geometry of the free-standing liquid-crystal film in which two free surfaces may be in microscopically close proximity fundamentally alters the nature of the thermodynamic problem. Unlike wetting phenomena, the details of the layer thinning transition remain mysterious. It is not at all clear, for example, what bulk and surface characteristics of the liquid-crystal compound are necessary in order for layer thinning to occur. In this series of experiments the effect of molecular structure on the layer thinning transition is examined systematically. We describe our investigations of four groups of liquid-crystal compounds with different degrees of fluorination. The results clearly indicate that fluorination plays an essential role in determining the behavior of the thinning transitions.

In 1994, our research group reported the existence of the layer-by-layer thinning transition above the bulk smectic-A (Sm-A)–isotropic transition temperature (T_{AI}) of one fluorinated compound [5]. Recently, such a transition was confirmed in another fluorinated compound [6]. Unlike free-standing films of most liquid-crystal compounds, a typical

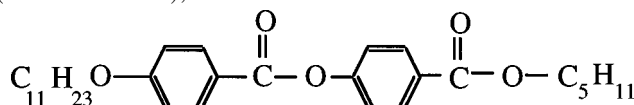
thick (>20 layers) film of one of these compounds [5,6] does not rupture when heated above the bulk T_{AI} . Instead, it undergoes a series of thinning transitions, in which the film thickness decreases in a stepwise fashion. For example, the thickness, measured in the number of smectic layers (N), might exhibit the following thinning series: $N=15, 11, 9, 8, 7, 6, 5, 4, 3$, and 2. The two-layer film ruptures at a temperature approximately 30 K above T_{AI} . Each layer thickness is about 30 Å. The thinning transition is thermally driven and irreversible. For example, a two-layer film does not rupture for more than 5 h at a temperature 20 K above T_{AI} and does not spontaneously thicken when cooled well into the Sm-A phase. Also, a film of N layers or less can be spread and will remain stable at temperatures below the thinning temperature [$T_c(N)$] for the N -layer film even though the film plate temperature is above T_{AI} . The thinning transitions for $N>10$ may occur in multilayer steps of variable size. For film thicknesses less than ten layers, both of these fluorinated compounds lose a single smectic layer per thinning transition, each transition occurring at a reproducible temperature. Such a series of thinning transitions can be characterized by the power law expression

$$h(t) = l_0 t^{-\zeta}. \quad (1)$$

Here h is the film thickness as a function of the reduced temperature t ($= [T_c(N) - T_0]/T_0$). Fitting to experimental data yields $\zeta = 0.70 \pm 0.04$ and $T_0 \approx T_{AI}$ [5,6]. Since our first report of the layer-by-layer thinning transition [5], considerable theoretical [11–13] and experimental [6–9] effort has been made toward understanding this unusual transition.

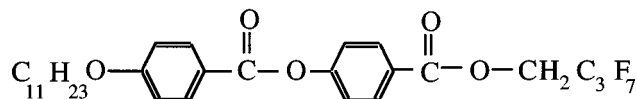
A series of fluorinated liquid-crystal compounds recently synthesized by Nguyen [14] has allowed us to systematically investigate the effect of fluorination on the thinning transition. The cores of these molecules are identical. The length of, the degree of fluorination in, and the location of the fluorine groups in one or both of the two flexible tails are varied. The compounds that we have studied may be divided into four different classes.

(A) Compounds with two hydro-alkyl tails, for example (H5OCPH11OB),

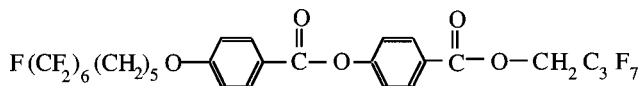


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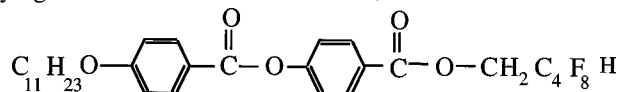
(B) Compounds with one hydro-alkyl and one fluoro-alkyl tail, for example (F3MOCPh11OB),



(C) A compound (F3MOCPh6H5OB) with two fluoro-alkyl tails,



(D) A special compound (F4hMOCPh11OB) similar to a group B compound but with a single hydrogen atom occupying the end of the fluorinated tail,



The bulk T_{AI} 's (in °C) are 52, 87, 105, and 58 for compounds shown in A, B, C, and D, respectively.

High-resolution optical reflectivity data were obtained from free-standing films in the bulk isotropic phase temperature range. The details of our optical reflectivity measuring system have been reported previously [15]. The reflectance of the film is a sensitive measure of film thickness. The dependence of reflectance on film thickness is the following for a sufficiently small incident and reflective angle ($\approx 3^\circ$):

$$R = (n_0^2 - 1)^2 \sin^2(n_0 h k) / \{4n_0^2 + (n_0^2 - 1)^2 \sin^2(n_0 h k)\}. \quad (2)$$

Here n_0 (≈ 1.5) is the ordinary index of refraction. $h = Nd$, where N is the number of layers and d (≈ 30 Å) is the layer thickness. k ($= 9.93 \times 10^{-4}$ Å $^{-1}$) denotes the wave vector of the probing beam from a He-Ne laser. Equation (2) is an oscillatory function. As film thickness increases, R reaches its first maximum near $N \approx 30$. In the thin film limit ($N < 12$), the reflectance is proportional to the square of the film thickness. The size of the free-standing film is approximately 1 cm 2 . The sample is typically heated at a rate of 75 mK/min. Variation of this rate from 20 to 100 mK/min yields the same experimental results. Operating at slower heating rates is impractical because the most interesting of these compounds requires an experimental window of approximately 30 K into the isotropic phase.

Two terms are used to describe the observed behavior in our liquid-crystal films. We describe as "regular" those thinning transitions that (1) reproducibly thin one layer at a time (layer-by-layer) below a certain film thickness; (2) show a systematic and reproducible trend in the thinning temperatures as a function of the film thickness. Those transitions that show irreproducible behavior are termed "irregular." We have achieved reproducible and analyzable results only for those films that show layer-by-layer thinning below a certain layer thickness (e.g., $N \leq 10$).

Our research group has made many attempts to observe the layer-thinning transition in more than 25 different conventional liquid-crystal compounds with two hydro-alkyl tails (group A) as well as n CB and n OCB compounds, some of which display the partial bilayer smectic- A_d

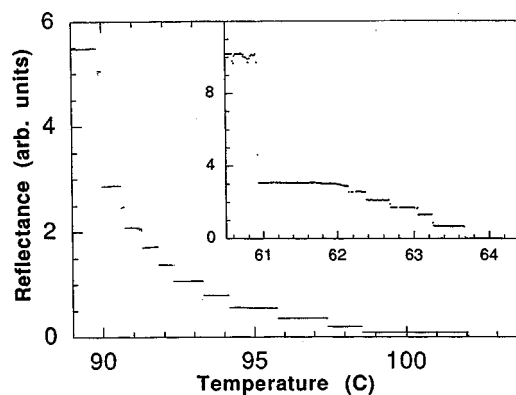


FIG. 1. The layer thinning sequence with a long sequence of thinning steps ($12 \leq N \leq 2$) obtained from the F3MOCPh11OB compound. The inset shows the largest number of thinning steps among four experimental runs obtained from the F4hMOCPh11OB compound. Six plateaus indicating layer thicknesses of 11, 10, 9, 8, 7, and 5 were observed in this experimental run.

(Sm- A_d) phase. Here, n CB and n OCB refer to cyano-alkyl-biphenyl and cyano-alkoxy-biphenyl, respectively. Free-standing films of a majority of these compounds rupture near the bulk Sm-A (or Sm- A_d)-nematic or Sm-A (or Sm- A_d)-isotropic transition. Only two of them display highly irregular layer-thinning transitions [16]. Other research groups have also reported irregular layer-thinning transitions in various compounds with two hydro-alkyl tails [7–9]. Similarly, among many experimental runs, only one or two thinning steps were detected upon heating the H5OCPh11OB free-standing films above its bulk T_{AI} ($= 52$ °C).

Regular layer thinning transitions have been previously reported [5,6] in two compounds from group B with one hydro-alkyl tail and one sufficiently long fluoro-alkyl tail. The F3MOCPh11OB compound, which has a shorter fluoro-alkyl tail ($-\text{C}_3\text{F}_7$), displays a somewhat irregular thinning transition. Among 14 experimental runs of F3MOCPh11OB, only one series of layer-by-layer thinning transitions from 12 to two layers (see Fig. 1). Of the rest of the runs, only another three exhibit irregular thinning to a two-layer film. Even in the run shown in Fig. 1, some irregularities are immediately obvious. For example, the temperature interval [$T_c(3) - T_c(4)$] is smaller than the intervals [$T_c(4) - T_c(5)$], [$T_c(5) - T_c(6)$], [$T_c(2) - T_c(3)$], etc. The other compound from group B has a longer fluoro-alkyl tail ($-\text{C}_4\text{F}_9$) and shows the layer-by-layer thinning transition over a slightly larger range of thicknesses ($N = 20, 17, 15, 14, 13, \dots, 5, 4$). Similar to Fig. 1, some irregularities in the temperature intervals between the thinning transition are observed. However, while the single layer thinnings occur in thicker films than in the $-\text{C}_3\text{F}_7$ compound, in five runs it never thinned below four layers. This compound also exhibits a smectic-C-isotropic (I) phase transition in the bulk, but we are unable to determine the smectic phase of the thin films in the bulk isotropic temperature window using the optical reflectivity. To summarize, all of the compounds studied from group B show a much higher degree of regularity in the layer thinning process than those from group A. A systematic investigation of the behavior of the thinning transition as a function of fluoro-alkyl tail length is an important next step.

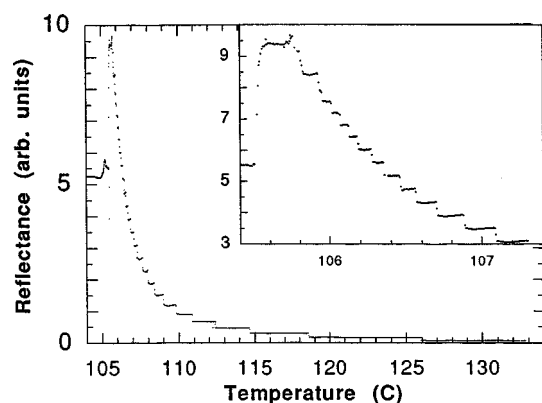


FIG. 2. The layer thinning transition sequence obtained from the bulk isotropic temperature range of the F3MOC PF6H5OB compound. The regular layer-by-layer thinning transitions begin at 25 layers and end at two layers. The two-layer film ruptures at about 25 K above the bulk Sm-A–isotropic transition temperature. The inset depicts the details of the layer thinning transitions for $N \geq 14$.

Replacing one of the fluorine atoms in the $-\text{CF}_3$ terminal group of the second compound in group B (F4MOC PH11OB) by a hydrogen atom yields the F4hMOC PH11OB compound which displays the Sm-A–I transition. Such a replacement both increases the thickness at which the film commonly ruptures and decreases the range of thicknesses over which thinnings occur. The experimental run that exhibits the largest number of thinning-transition steps among four runs is shown in the inset of Fig. 1 with the following thinning sequence: 11, 10, 9, 8, 7, and 5 layers. The five-layer film ruptured at about 3 K above the first detected thinning transitions. The thinnest film we have observed among these four experimental runs was five layers in thickness. By comparison, 10 out of 14 thinning runs of F3MOC PH11OB thinned down to $N \leq 5$ before rupture. Clearly, the substitution of a single hydrogen atom in the $-\text{CF}_3$ terminal group substantially reduces the regularity of the thinning behavior.

The doubly fluorinated F3MOC PF6H5OB compound exhibits by far the largest number of regular single-layer transitions of all the compounds studied to date. The layer-by-layer thinning transition starts at film thicknesses of up to 25 layers. Among six experimental runs, four of them displayed this long series of layer-by-layer thinning transitions. One of these runs is shown in Fig. 2. The details of the thinning sequence for $N \geq 14$ are depicted in the inset. The initial film thickness is more than 40 layers. The occurrence of the first maximum in optical reflectance for $N \approx 30$ is in good agreement with the calculated reflectivity [Eq. (2)] given an index of refraction $n_0 \approx 1.55$, a layer spacing $d \approx 30 \text{ \AA}$, and an incident angle of $\leq 3^\circ$. The other two runs exhibit several multilayer thinnings in the region $N > 10$.

Similar to previous results [5,6], the series of thinning transitions observed in F3MOC PF6H5OB can be characterized by Eq. (1). The least-squares fitting yields $l_0 = 0.52 \pm 0.04$, T_0 (in K) $= 378.43 \pm 0.05$, and $\zeta = 0.61 \pm 0.04$. Such a fitting result is shown in Fig. 3, where N is plotted versus $T_c(N)$. The value of T_0 is very close to the bulk T_{AI} . The exponent ζ is slightly lower than those obtained from two other fluorinated compounds [5,6]. To date, a theoretical ex-

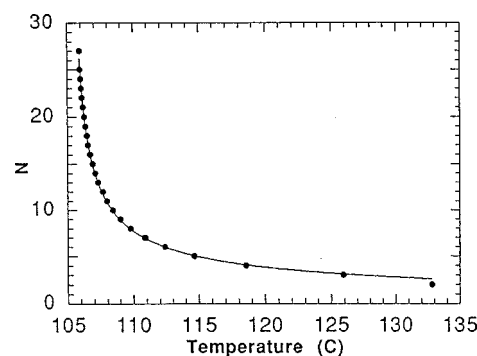


FIG. 3. N vs $T_c(N)$. The solid line is the fitted result [Eq. (1)] with exponent $\zeta = 0.61 \pm 0.04$.

planation of the exponent ζ remains unavailable.

We now summarize the salient results of this reflectivity study. Overall, the regularity of the thinning transition increases with the presence of fluorinated tails. With non-fluorinated tails, a compound does not exhibit any regular thinning transition. Fluorinating one of the two tails increases the degree of regularity substantially. Fluorinating both tails, as seen in the compound F3MOC PF6H5OB, results in the widest thickness range for a regular thinning transition. Our preliminary data also demonstrates that the degree of regularity increases with the length of the fluoro-alkyl tail. Furthermore, the molecular subgroup at the end of the tail plays a large role in determining the thinning behavior.

In order to address the effect of fluorination on the nature of layer-by-layer thinning transitions, the unique features of fluorinated liquid-crystal compounds should be considered. Our studies show that such compounds display dramatically lower surface tensions (γ) [17–19] than the conventional liquid-crystal compounds. In the series of compounds considered in this paper, γ decreases with an increased degree of fluorination [18,19]. For example, the compounds H5OC PH11OB (group A), F3MOC PH11OB and F4MOC PH11OB (group B), and F3MOC F6H5OB (group C), listed here in order of increased degree of fluorination, show the surface tensions 21.5, 14.6, 14.0, and 11.5 dyn/cm, respectively. Replacing a single fluorine atom in the $-\text{CF}_3$ terminal group of F4MOC PH11OB increases γ to 18.4 dyn/cm [19]. Experimental results indicate that the regularity of the thinning transition increases with decreasing surface tension.

Fluorinated liquid crystals also show a high T_{AI} that increases with the degree of fluorination, higher order x-ray diffraction peaks (up to third order) produced by the smectic layer structure [20], and a high compressional elastic constant [21]. These three properties suggest that fluorination heightens the tendency of a liquid-crystal compound toward smectic ordering. The rigidity of the fluorinated tails may cause the high compressional constant [21]. de Jeu and co-workers [21] have drawn further conclusions about the smectic ordering in free-standing films of one fluorinated compound of type B. From detailed x-ray studies they construct thermal fluctuation profiles for 4, 20, and 34 layer films at temperatures within the bulk Sm-A range. The average degree of thermal fluctuations is seen to increase with decreasing film thickness. Also, the magnitude of thermally induced layer fluctuations is greater near the surface-vapor interface

of the film than in the center of the film.

Our observations of the thinning transition suggest just the opposite behavior at temperatures above T_{AI} . We posit that the survival of a film to temperatures well above T_{AI} implies the presence of surface enhanced ordering. Therefore, the magnitude of fluctuations for a film above T_{AI} should be *less* near the film surface than in the center of the film. Since the thinner films survive to higher temperatures, we also conclude that the average fluctuation amplitude at a given temperature above T_{AI} *decreases* with decreasing film thickness. Such assumptions about the fluctuation profile for films that exhibit the thinning transition are consistent with x-ray studies of free-standing films of 4,4'-diheptylazoxybenzene [9]. This compound exhibits irregular layer thinning above the bulk Sm-A to nematic transition temperature.

The crossover from surface disordering to surface ordering is addressed in a recently formulated continuum model of Sm-A films [22]. The layer fluctuation profile is shown to be sensitive to the ratio $\nu = \gamma/(KB)^{1/2}$, in which B and K refer to the bulk compressional and undulation elastic constants, respectively [23]. For $\nu > 1$, one expects damping of the fluctuations at the surface and surface enhanced ordering, while for $\nu < 1$ the fluctuation amplitudes will be enhanced at the surface. Since our thinning results suggest surface enhanced ordering, we expect $\nu > 1$. We may contrast this with the experiments of de Jeu and co-workers [21], in which fitting of the x-ray data at temperatures below T_{AI} yields $\nu \approx 0.15$

($\gamma = 13$ dyn/cm, $K = 10^{-6}$ dyn, and $B = 7.5 \times 10^9$ dyn/cm) for the fluorinated compound FPP. Since our recent surface tension studies have yielded a small value of γ for F3MOC PF6H5OB and show no measurable change in γ throughout the thinning transition [17] for another fluorinated compound, we expect that at least one of the bulk elastic constants is lower than might be expected, at least at temperatures above T_{AI} . It seems possible that the value of the bulk compressional constant in these free-standing films is much lower at temperatures above T_{AI} than below. Such behavior would suggest a crossing over from $\nu > 1$ to $\nu < 1$ near T_{AI} . Studies of the fluctuation profile of these fluorinated films at different temperatures during the thinning transition as well as in the bulk Sm-A temperature would be intriguing.

No regular layer-by-layer thinning transitions have been observed in nonfluorinated liquid-crystal compounds. Although we are continuing our effort to identify regular layer-by-layer thinning transitions in the nonfluorinated compounds, this study demonstrates that a successful theoretical model of this transition should include some of the unique features of fluorinated compounds.

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