PHYSICAL REVIEW E VOLUME 55, NUMBER 4 APRIL 1997

Layer thinning transition above the bulk smectic-*A*–isotropic transition in free-standing liquid-crystal films

P. M. Johnson,[1] P. Mach,[1] E. D. Wedell,[1] F. Lintgen,[1] M. Neubert,[2] and C. C. Huang[1,*]
[1]*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*
[2]*Liquid Crystal Institute, Kent State University, Kent, Ohio 44242*
(Received 26 December 1996)

Upon increasing temperature, high-resolution optical reflectivity data have revealed unusual melting transitions above the smectic-*A*–isotropic transition in free-standing films of one partially perfluorinated compound. For sufficiently thin films (fewer than nine layers), a sequence of regular layer-by-layer thinning transitions is found. The evolution of this unique thinning process can be well described by a simple power law with exponent $\zeta = 0.70$. [S1063-651X(97)07204-8]

PACS number(s): 64.70.Md, 61.30.Eb

Since the 1994 observation of a unique melting phenomenon in which a liquid-crystal film's innermost smectic layers melted one molecular layer at a time, we have been searching for a different liquid-crystal compound that shows the same behavior. One of our main goals has been to test whether the phenomenon can be described by a simple power law with a universally applicable exponent.

Many solids melt from the outside in [1]. Because the solid-vapor and solid-liquid interfaces have a disordering effect on the surface molecules, these surfaces melt at a lower temperature than the bulk. Thus as temperature increases, a solid's surface initiates the melting process after which melting penetrates the solid from the outermost surface inward. The bulk melting point is defined as the temperature at which the entire solid has melted. Given a smooth enough solid-liquid interface, the melting may occur one molecular layer at a time. Many of such melting processes can be described by a power law. The exponent has been shown to be a universal constant dependent on the dominant intermolecular force.

Certain liquid crystals defy this common behavior, essentially reversing the melting process seen in most solids. The liquid-crystal–vapor interface may have an ordering effect on smectic surface layers. This effect manifests itself in several forms. If this ordering penetrates into the liquid crystal, then at a given temperature the degree of order in the film's layers decreases from the surface layer in [2–4]. In a liquid-crystal film that is thin enough, the surface ordering may penetrate the entire film, raising the film's transition temperature above what one would expect of a bulk liquid-crystal sample. This model allows for the innermost layer to have a *lower* melting temperature than its outer neighbors.

In the past ten years, our research group has been conducting extensive heat capacity, optical reflectivity, and surface tension measurements on free-standing films of various liquid-crystal compounds. On many occasions, we have intentionally increased the film temperature beyond the bulk Sm-*A*–isotropic transition (T_{AI}) to check the existence of the surface-enhanced order. To our great surprise, in 1994 Stoebe, Mach, and Huang observed [5] a remarkable layer-by-layer thinning transition above T_{AI} ($=85\,^\circ\mathrm{C}$) of one partially perfluorinated liquid-crystal compound, H(10)F5MOPP [5-*n*-decyl-2-(4-*n*-(perfluoropentyl-methyleneoxy) phenyl) pyrimidine]. The films were spread across a 1 cm diameter opening. Upon heating above T_{AI}, instead of rupturing as is usual for most liquid-crystal films, the H(10)F5MOPP free-standing films exhibit multilayer thinning transitions for N (layer number) >9. Then above 88 °C, the film undergoes a sequence of regular layer-by-layer thinning transitions. Eventually, the two-layer film ruptures at 113 °C, which is more than 28 K above the T_{AI}. An example of thinning transition sequence is $N=25$, 15, 11, 9, 8, 7, 6, 5, 4, 3, and 2. This unusual thinning transition can be well characterized by a simple power law

$$h(t) = l_0 t^{-\zeta}, \tag{1}$$

where h is the film thickness (in units of layers), $t = [T_c(N) - T_0]/T_0$, and $T_c(N)$ is the maximum temperature at which the N-layer film exists. The fitting results yield $\zeta = 0.74 \pm 0.02$ and $T_0 = 84.84 \pm 0.04\,^\circ\mathrm{C}$, which is very close to the bulk $T_{AI}(=85\,^\circ\mathrm{C})$. Later, Demikhov, Dolganov, and Meletov [6] reported similar thinning behavior above the Sm-*A*–nematic (N) transition of 50.6 (4-*n*-pentyloxy-benzylidene-4-*n*-hexylaniline). This thinning transition was observed in a much smaller film hole ($0.1 \times 5\ \mathrm{mm}^2$). We have tried to reproduce the results with film diameters as small as 3 mm and failed. Thus we believe that such a small film is stabilized by the excess material in the meniscus along the small dimension, which may have a significant effect on the reported exponent ($\zeta = 0.82$).

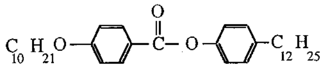
Among ordinary hydro-alkyl liquid-crystal compounds, Jin *et al.* [7] have recently found thinning transitions above the T_{AI} (70 °C) of 54COOBC (*n*-pentyl-4′-*n*-pentanoyloxy biphenyl-4-carboxylate). The film hole was also 1 cm in diameter. The sequence of thinning transitions is highly irregular. Both the temperatures at which each thinning occurs and the film thickness at which the film ruptures are not reproducible. Among 20 experimental runs, the one that came the closest to exhibiting regular layer-by-layer thinning shows the following sequence: $N=11$, 9, 8, 5, 4, 3, and 2. This

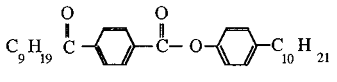
---

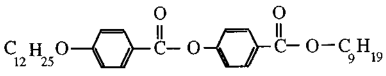
[*] Author to whom correspondence should be addressed. Electronic address: huang001@maroon.tc.umn.edu

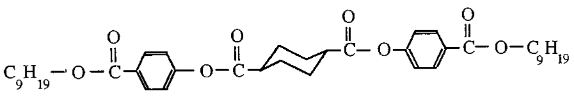
1063-651X/97/55(4)/4386(4)/$10.00

occurred only once. No such thinning transition was observed in *nm*OBC. Here *nm*OBC refers to *n-alkyl*-4′-*n-alkyl*oxy biphenyl-4-carboxylate. One hypothesis for why thinning transitions are seen in 54COOBC but not in *nm*OBC is that the former compound possesses a more symmetric molecular structure. We have specifically tested this hypothesis on the following four highly symmetric liquid-crystal compounds, in particular, the fourth compound, and failed to observe any thinning transition.



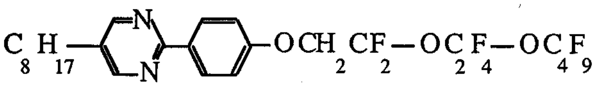






Currently, we are continuing our effort to identify regular layer-by-layer thinning transitions in the nonperfluorinated compounds. Meanwhile, among the perfluorinated compounds, it remains a very important task to experimentally identify and characterize the ‘‘regular’’ layer-by-layer thinning transition, find out the common features of such a transition, and see if the exponent ζ is the same in different liquid-crystal compounds.

Recently we have observed a regular layer-by-layer thinning transition in one of our newly acquired perfluorinated liquid-crystal compounds, 2-(4-(1,1-dihydro-2-(2-perfluorobutoxy-perfluoroethoxy) perfluoroethoxy)) phenyl-5-octyl pyrimidine [H8F(4,2,1)MOPP]. Its molecular structure is



The bulk transition sequence is isotropic (71 °C) Sm-*A* (48 °C) Sm-*C*.

Our surface tension (γ) measurement from free-standing films of this compound yields $\gamma = 12.8$ dyn/cm, which is similar to that of H(10)F5MOPP [8]. Following our argument for H(10)F5MOPP, this value of γ strongly suggests an antiparallel smectic layer structure, with a roughly equal population of CF_3 and CH_3 groups at the smectic layer surface.

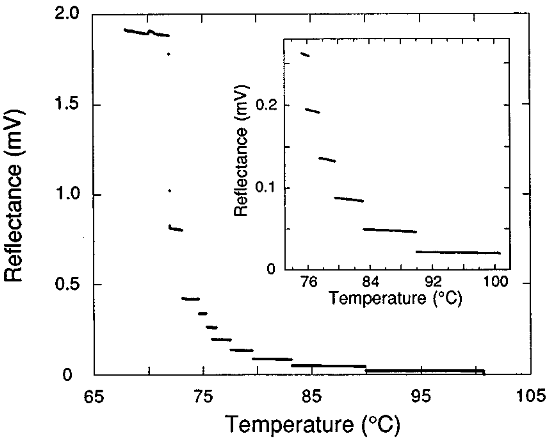


FIG. 1. Optical reflectance data showing thinning transitions in a free-standing film of H8F(4,2,1)MOPP. The original film thickness is about 25 layers. The inset highlights the negative slopes seen in all successive steps in the region of single-layer thinning ($N \leqslant 7$) before the two-layer film ultimately ruptured above 100 °C.

The free-standing films were prepared at 60 °C inside a temperature-regulated two-stage oven filled with 0.5 atm of argon gas. Optical reflectivity measurements were recorded for temperatures ramped upward from a starting temperature of about 68 °C at a rate of 75 mK/min. The temperature of the oven was computer controlled. To achieve a high signal-to-noise ratio, a He-Ne laser ($\lambda = 6328$ Å), amplitude stabilized through a proportional-integral-differential scheme, was used as the light source. The long term stability of laser output intensity is better than 0.1%/h. With a small incident angle, the optical reflectivity for an N-layer film of thickness $h = N\varepsilon$ can be written as [9]

$$R = [(n_0^2 - 1)\varepsilon k]^2 N^2/4 = cN^2, \tag{2}$$

where $c = [(n_0^2 - 1)\varepsilon k]^2/4$ is a constant. n_0 is the ordinary index of reflection, k the wave vector of the incident radiation. Equation (2) holds for $n_0 hk \ll 1$. For $\varepsilon \approx 30$ Å, this condition is satisfied for thin films with $N < 10$. Figure 1 shows the temperature variation of optical reflectivity as a function of temperature. Upon heating, a small hump near the T_{AI} ($=71$ °C) is discernible. The step-wise change in optical reflectivity signals the thinning transition. In comparison with the H(10)F5MOPP layer thinning data, Fig. 1 displays the following two new features: the existence of a small hump near T_{AI}, and a much larger slope for each step. The layer thicknesses determined through Eq. (2) are $N = 9$, 8, 7, 6, 5, 4, 3, and 2. This is the second compound exhibiting a regular layer-by-layer thinning transition for $N < 9$ in a large film hole (1 cm in diameter). Similar to H(10)F5MOPP, while the number of layers lost in each thinning in the thick-film region is highly irregular, for $N < 9$ a sequence of single-layer thinning transitions occurred reproducibly in six separate experimental runs of different initial film thicknesses. Ultimately, the two-layer film ruptures at above 100 °C, which is about 30 K above T_{AI}. Each thinning transition occurs in an extremely small temperature window (< a few mK). This thermally induced layer thinning transition is irreversible. For example, cooling down a two-layer film from 95 to 42 °C does not change the film's thickness. The inset shows the details of thinning transition for $N \leqslant 7$.

The data shown in Fig. 1 exhibit a noticeable negative slope for each step which indicates a significantly large negative thermal expansion coefficient in smectic layer spacing

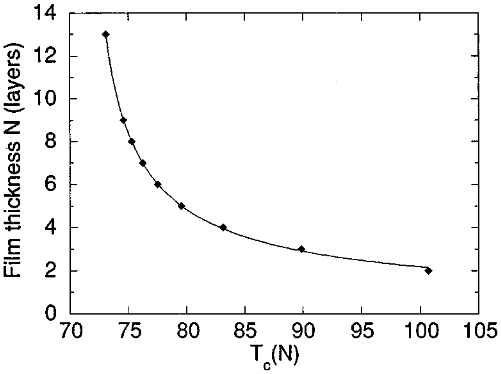


FIG. 2. N versus $T_c(N)$. The solid diamonds are the experimental data. The line is a fit to Eq. (1) discussed in the text.

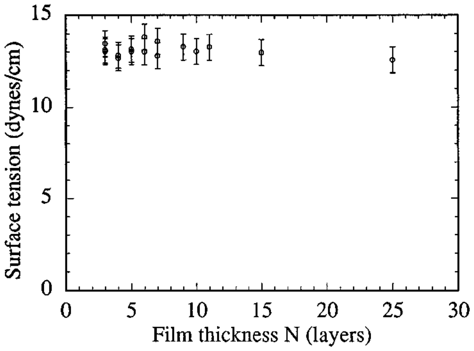


FIG. 3. Surface tension of H10F5MOPP as a function of film thickness which is essentially constant. The data were obtained during a thinning transition run.

($|\kappa_L|>0.12$ Å/K). Detailed data analyses [10] reveal an unusual large layer compression.

Figure 2 exhibits the experimental data (solid dots): the film thickness (N) versus the maximum temperature $T_c(N)$ at which N-layer films appear to be stable. The best fit to Eq. (1) is shown as a solid line with $l_0=0.37$, $\zeta=0.70\pm0.04$, and $T_0=70.7\pm0.3$°C. The exponent (ζ) is in good agreement with that of H(10)F5MOPP.

Since our work on the layer-by-layer thinning transition, two theoretical models [11,12] have been proposed. Both models employ the mean-field approach and impose a surface-enhanced ordering field. We believe that the surface-enhanced order is essential [13], but do not yet know if the observed thinning transition is mean-field-like. The model suggested by Mirantsev [11] yields an asymptotic variation of $T_c(N)$ in good agreement with our experimental results. The second one [12] requires the layer-by-layer thinning transition found above the Sm-A–isotropic transition to be close to a vapor–isotropic–nematic–Sm-A quadruple point and possess a continuous or a very weakly first-order nematic–Sm-A transition. Then the strong pretransitional effect associated with the nematic–Sm-A transition will promote a layer thinning transition instead of film rupture. Utilizing optical microscopic studies of binary mixtures, we have ruled out the possible existence of a hidden nematic phase in the H8F(4,2,1)MOPP compound. With a direct Sm-A–isotropic transition found in both perfluorinated compounds, the second model predicts the film rupture and no layer-by-layer thinning transition. Moreover, this model predicts a strong dependence of surface tension during the film thinning process. Figure 3 shows our surface tension data obtained during the layer thinning transition of an H(10)F5MOPP film. Within our resolution of 3%, the surface tension remains constant throughout the thinning transitions [14].

To obtain a better understanding of the nature of the layer-by-layer thinning transitions and to test their universal behavior, it remains an important research project to search for such transitions in any nonperfluorinated compound. Recent diffusive x-ray scattering measurements on partially perfluorinated compound display the existence of higher-order scattering peaks [15,16] and yield a significantly larger value for the smectic compressional elastic modulus ($B\approx10^9$ erg/cm) [15] than that ($B\approx10^8$ erg/cm) of purely alkyl-terminated compound. These experimental results indicate that the layer structure in the perfluorinated compound is much more well defined. Could this be why we have only seen regular layer-by-layer thinning transitions in perfluorinated compounds? Is the negative thermal expansion coefficient of the layer spacing found in both H10F5MOPP and H8F(4,2,1)MOPP a necessary condition for such a thinning transition? Further experimental investigations are in progress to obtain better insight into these intriguing questions.

We are grateful to Professor D. E. Sullivan for valuable discussions and to S. Pankratz for extensive help and numerous critical discussions and would like to thank Dr. K. A. Epstein and Dr. M. D. Radcliffe (3M Corporation, St. Paul, Minnesota) for providing the partially perfluorinated samples. This work was supported in part by the Donors of the Petroleum Research Fund, administered by the American Chemical Society and the National Science Foundation, Solid State Chemistry Program, Grant No. DMR-93-00781. One of us (P.M.) would like to acknowledge support from the National Science Foundation.

---

[1] A number of excellent review articles on wetting phenomena have been presented including work by M. Schick, in *Liquids at Interfaces*, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier, Amsterdam, 1990); and P. G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).

[2] B. M. Ocko, A. Braslau, P. S. Pershan, J. Als-Nielson, and M. Deutsch, Phys. Rev. Lett. **57**, 94 (1996).

[3] R. Pindak, D. J. Bishop, and W. O. Springer, Phys. Rev. Lett. **44**, 1461 (1980); S. Heinekamp, R. A. Pelcovits, E. Fontes, E. Y. Chen, R. Pindak, and R. B. Mayer, *ibid.* **52**, 1017 (1984); W. Chen, L. J. Martinez-Miranda, H. Hsiung, and Y. R. Shen, *ibid.* **62**, 1860 (1989); B. D. Swanson, H. Stragier, D. J. Tweet, and L. B. Sorensen, *ibid.* **62**, 909 (1989); B. M. Ocko, *ibid.* **64**, 2160 (1990); T. Stoebe, R. Geer, C. C. Huang, and J. W.

Goodby, *ibid.* **69**, 2090 (1992); Ch. Bahr, C. J. Booth, D. Fliegner, and J. W. Goodby, *ibid.* **77**, 1083 (1996); C. Y. Chao, C. F. Chou, J. T. Ho, S. W. Hui, A. Jin, and C. C. Huang, *ibid.* **77**, 2750 (1996); J. Als-Nielsen, Physica A **140**, 376 (1986); E. B. Sirota, P. S. Pershan, S. Amador, and L. B. Sorensen, Phys. Rev. A **35**, 2283 (1987).

[4] X. Z. Wu, B. M. Ocko, E. B. Sirota, S. K. Sinha, M. Deutsch, B. H. Cao, and M. W. Kim, Science **261**, 1018 (1993).

[5] T. Stoebe, P. Mach, and C. C. Huang, Phys. Rev. Lett. **73**, 1384 (1994).

[6] E. I. Demikhov, V. K. Dolganov, and K. P. Meletov, Phys. Rev. E **52**, R1285 (1995).

[7] A. J. Jin, M. Veum, T. Stoebe, C. F. Chou, J. T. Ho, S. W. Hui, V. Surendranath, and C. C. Huang, Phys. Rev. E **53**, 3639 (1996).

[8] T. Stoebe, P. Mach, S. Grantz, and C. C. Huang, Phys. Rev. E **53**, 1662 (1996).

[9] C. Rosenblatt and N. Amer, Appl. Phys. Lett. **36**, 432 (1980).

[10] P. Mach, P. Johnson, E. D. Wedell, F. Lintgen, and C. C. Huang (unpublished).

[11] L. V. Mirantsev, Phys. Lett. A **205**, 412 (1995).

[12] Y. Martinez-Raton, A. M. Somoza, L. Mederos, and D. E. Sullivan, Phys. Rev. E (to be published).

[13] E. A. L. Mol, J. D. Shindler, A. N. Shalaginov, and W. H. de Jeu, Phys. Rev. E **54**, 536 (1996). This paper reported the x-ray scattering results which revealed a larger thermal fluctuation profile near the film-vapor interfaces of the free-standing films of one perfluorinated compound.

[14] In our apparatus for surface tension measurements, the film has to be in the vertical orientation. Under this circumstance, the film usually failed to show the thinking transition from three- to two-layer films and it ruptured.

[15] J. D. Shindler, E. A. L. Mol, A. N. Shalaginov, and W. H. de Jeu, Phys. Rev. Lett. **74**, 722 (1995).

[16] B. I. Ostrovskii, F. G. Tournilhac, L. M. Blinov, and W. Haase, J. Phys. (France) II **5**, 979 (1995).