Ellipsometric study of freely suspended smectic films of a partially fluorinated compound

D. Schlauf and Ch. Bahr

Fachbereich Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

C. C. Huang

School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455

High-resolution ellipsometric studies have been conducted on freely suspended films of a chiral, partially perfluorinated liquid-crystal compound near its smectic-A–smectic-C transition. The surface-enhanced transition is unusually close to the bulk transition temperature. Moreover, in the ferroelectric smectic-C phase an unexpected tilt direction inversion with respect to the direction of an applied electric field is found in films thinner than about 20 layers whereas it does not occur in thick films. [S1063-651X(97)51005-1]

PACS number(s): 61.30.Eb, 64.70.Md, 68.10.Cr

Thermotropic liquid crystals are prime examples of systems possessing enhanced surface order. Corresponding experimental studies are frequently carried out using freely suspended films which can be prepared from smectic (i.e., layered) liquid-crystal phases. Freely suspended films (for recent reviews see [1,2]) consist of an integral number (between several thousands and only two) of molecular smectic layers, the layer planes being parallel to the two free surfaces. The surface-enhanced order becomes apparent near the phase transitions between different smectic phases: approaching a phase transition from the high-temperature side, the surface layers of freely suspended films transform into the more ordered phase several degrees above the bulk transition temperature.

For most types of smectic transitions, the temperature difference between the surface transition and the corresponding bulk transition is within a range from 5 to 10 K (the values also vary, for a given type of transition, from compound to compound) [3]. The largest effect is observed for the smectic-A (Sm-A)–smectic-C (Sm-C) transition. These phases are the least ordered smectic phases: each layer can be regarded as a two-dimensional liquid, the mean direction of the long molecular axis being either parallel (Sm-A) or tilted (Sm-C) with respect to the layer normal. When a freely suspended film is cooled from the Sm-A to the Sm-C phase, the surface layers become tilted at a temperature usually 10 to 20 K above the bulk transition temperature [4,5].

A recent heat capacity study [6] of the partially fluorinated compound H10F5MOPP (5-n-decyl-2-[4-n-(perfluoropentylmethyleneoxy)phenyl]pyrimidine) yielded an indication of a surface Sm-A–Sm-C transition being situated unusually close to the bulk transition. The magnitude of the heat-capacity anomaly associated with the surface Sm-A–Sm-C transition may be so small that even with our high-resolution calorimetric system we might not be able to detect it. Consequently, it is essential to give an independent check of this important observation with another experimental probe. High-resolution ellipsometry which measures the optical tilt angle, the order parameter associated with this transition, is one of the powerful tools.

Ellipsometry enables us to directly measure changes of the direction of the optical axis resulting from the molecular tilt even in two-layer films [4]. In this paper, we report high-resolution ellipsometric measurements of freely suspended films of one perfluorinated compound [4-methyl-hexyloxybenzoate(4-n-perfluoropentyl)methyleneoxyphenyl, 4M6OBF5MOP] possessing a structure similar to H10F5MOPP. We had to choose the former compound because, as described below, our experiment requires a sample which exhibits a spontaneous polarization in the Sm-C phase. Thus the compound had to be chiral. Our data yield that the surface-enhanced transition temperature T_S of 4M6OBF5MOP is only about 2 K above the bulk transition temperature T_B. An explanation for the plausible relation between the magnitude of $\Delta T = T_S - T_B$ and the surface tension will be given. Furthermore, for a film thickness thinner than 20 layers, 4M6OBF5MOP films display an unusual reversal behavior: an unexpected tilt direction inversion with respect to the direction of an applied electric field is found. This feature is not observed in thick films.

The molecular structure of 4M6OBF5MOP is shown on top of Fig. 1. The bulk transition temperatures are: Sm-C 63 °C Sm-A 100 °C isotropic. Freely suspended films are drawn in the Sm-A phase using a rectangular variable-surface frame described in [1]. The area of the films is approximately 5×10 mm^2. Details about our ellipsometric set-up can be found in [7]. We determine the parameters Δ and Ψ which have the usual meaning [8] and describe the polarization of a laser beam ($\lambda = 633$ nm) which transmits the film at an angle of incidence of 45°.

The values of Δ and Ψ measured at zero tilt enable the determination of the film thickness N (number of smectic layers) as described in [7]. Further, the value of Δ is directly related to the amount and direction of a tilt of the optical axis of the film [7]. A weak dc electric field (8 V/cm) is applied along the film plane in order to predetermine the direction of the molecular tilt in the Sm-C phase [9]. In our experimental geometry, the molecules tilt within the plane of incidence, depending on the field polarity, either away from or towards the incident laser beam giving rise to Δ_+ and Δ_-, respectively. Usually, one finds for a given film $\Delta_+ < \Delta_A < \Delta_-$ with Δ_A being the value measured in the Sm-A phase [5,7].
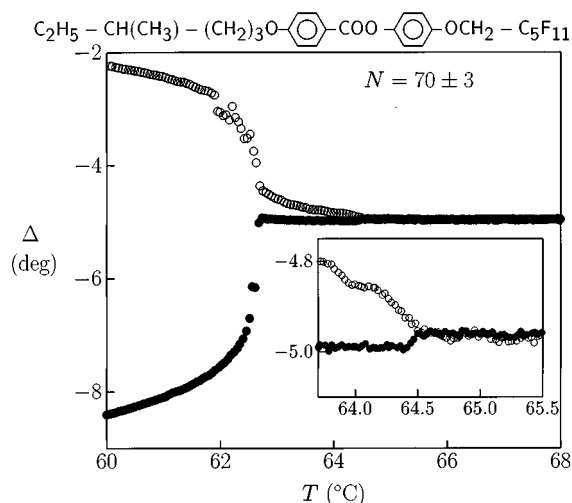
FIG. 1. Temperature dependence of Δ_+ ($\bullet$, tilt away from incident laser beam) and Δ_- ($\bigcirc$, tilt towards incident beam) for a 70-layer film of 4M6OBF5MOP (the molecular structure is shown on the top). The inset shows the behavior around the surface transition at 64.5 °C.

Figure 1 shows the temperature dependence of Δ_+ and Δ_- for a 70-layer 4M6OBF5MOP film. For $T > 64.5$ °C, we find $\Delta_+ = \Delta_-$, i.e., above this temperature the tilt angle is zero throughout the film. At 64.5 °C the surface transition takes place and $\Delta_+ \neq \Delta_-$, i.e., the direction of the optical axis of the film depends on the sign of the applied dc field. This indicates a finite tilt of the mean direction of the long axis of the molecules. Around the bulk transition temperature (62.5 °C), a large increase in the difference between Δ_+ and Δ_- takes place indicating that now all layers of the film become tilted. Similar results are obtained from a 55-layer film.

Qualitatively, the behavior described above for 4M6OBF5MOP is similar to other Sm-A–Sm-C compounds. The unusual feature is the small temperature difference between the surface and the bulk transition. For example, in thick films ($N \geq 10$) of the compound DOBAMBC, the surface Sm-A–Sm-C transition is enhanced by about 17 K [4]. However, for thick 4M6OBF5MOP films the enhancement is only 2 K. A plausible explanation for this significant difference will be given later.

Figure 2 shows some typical experimental results obtained from thin films ($N = 17$, 10, 4, and 3). For $N \geq 10$, similar to the thick film result, the surface enhanced transition occurs around 64.5 °C. Upon decreasing temperature, in contrast to the monotonic behavior of Δ_+ and Δ_- found in thick films, an unusual reversal behavior is found in the surface-enhanced Sm-C order of thin films. The applied dc electric field which produces a tilt direction away from the incident laser beam (Δ_+) for the 70-layer film (see Fig. 1), produces an opposite tilt direction for films with $N < 20$. Then in the vicinity of the bulk Sm-A–Sm-C transition temperature, a reversal between Δ_+ and Δ_- is found. Similar to other transitions between the smectic phases found in freely suspended films, further enhancement in the surface transition temperature is found in four- and three-layer films. Moreover, the crossing between Δ_+ and Δ_- occurs at lower temperatures. At a sufficiently low temperature, all films dis-
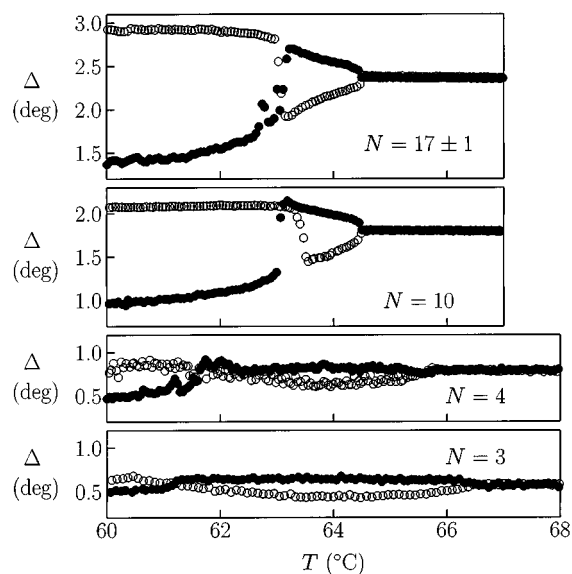

FIG. 2. Temperature dependence of Δ for various thicknesses (N gives the number of layers) of 4M6OBF5MOP films; $\bullet$: same field polarity as the Δ_+ data in Fig. 1, $\bigcirc$: same field polarity as the Δ_- data in Fig. 1. Around 63 °C ($N=17,10$), 62 °C ($N=4$), and 61 °C ($N=3$) a spontaneous inversion of the tilt direction is observed.

play the same relation between tilt and field direction as the one for thick films. These experimental results strongly suggest that the reversal phenomena of Δ_+ and Δ_- in films with $N < 20$ is related to the surface effect. Further experimental work is necessary to get a better understanding of this novel reversal phenomenon.

Since the relation between directions of tilt and electric field is determined by the sign of the spontaneous polarization $\vec{P}_s$ [10], the inversion of the tilt direction at a given field direction may be described as a sign inversion of $\vec{P}_s$, a phenomenon, which is known [11] to occur in some unique bulk liquid-crystal compounds. A recent study [12] has shown that such a sign inversion also occurs in freely suspended films of one of the compounds regardless of the film thickness which ranged from 3 to nearly 100 layers. We believe that the origins of sign inversion of such compounds and 4M6OBF5MOP are different, because the latter compound only exhibits the inversion in thin films, but not in thick films.

We have found that in very thin films ($N < 10$) the occurrence of the inversion is sensitive to the experimental conditions. The inversion was only observed in freshly loaded samples and disappeared if the sample remained on the film plate for more than two days at elevated temperature. (The oven is not vacuum tight.) In the latter case, the relation between electric field and tilt direction is the same as that of the thick film over the whole temperature range. We have further observed that the $\vec{P}_s$ inversion temperature coincides sometimes only approximately in both runs (one for each field polarity) of a given film (see Fig. 2, $N=10$). This effect may be related to the thermal degradation of the sample but we do not have a conclusive explanation for it. For thicknesses between 20 and 40 layers we found it extremely difficult to achieve a homogeneous alignment of the tilt direc-
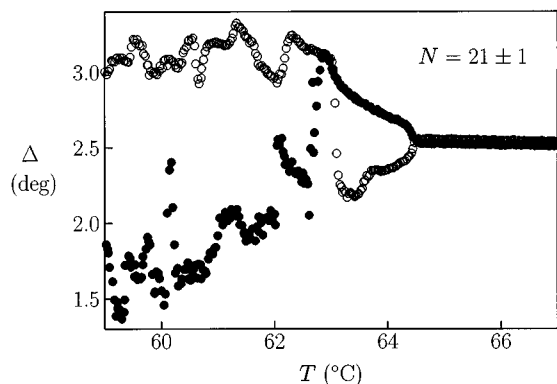
FIG. 3. Temperature dependence of Δ for a 21-layer film of 4M6OBF5MOP; the ● and ○ symbols designate the same field polarities as in the preceding figures.

tion by the external field. An example is given in Fig. 3 which shows the result from a 21-layer film. The inversion of $\vec{P}_s$ is discernible but the tilt alignment is rather poor. Direct optical inspection of such a film reveals the presence of a *schlieren* texture indicating that the magnitude of $\vec{P}_s$ is not sufficient to obtain a homogeneous alignment by a weak dc field. We varied the field strength ranging from 4 V/cm to 16 V/cm and failed to get good alignment. Larger fields cannot be used due to the onset of electroconvective flow in the film.

Table I gives the temperatures of the Sm-A–Sm-C bulk (T_B) and surface (T_S) transitions for various compounds studied in freely suspended films. The values of T_S are for films thicker than 10 layers for which T_S does not depend on the film thickness (whereas in thinner films T_S increases with decreasing thickness). It is obvious that the two fluorinated compounds show by far the smallest difference ($T_S - T_B$).

In liquid crystals, it has been demonstrated that a more ordered phase will usually establish at the free surface. A direct indication of this phenomenon is $T_S > T_B$ for many different types of smectic phase transitions. The physical origin of the surface stabilization is obviously not related to the detailed structures of the phases involved. Theoretical models [13,14] of freely suspended films use the surface tension γ in order to take the effect of the two free surfaces into account. For $\gamma > \sqrt{BK}$ (B and K being the elastic constants for compression and bending of the smectic layers) a damping of the fluctuations of the smectic layer displacements is expected near the surface which may result, near a phase transition, in the occurrence of a more ordered phase at the surface at temperatures above the bulk transition temperature [14].

TABLE I. Bulk (T_B) and surface (T_S) smectic-A–smectic-C transition temperatures

Compound	T_B (°C)	T_S (°C)	$T_S - T_B$ (K)
DOBAMBC [4]	95	112	17
MHPOBC [5]	120	135	15
MBOOBC [5]	41	51	10
H10F5MOPP [15]	75	76	1
4M6OBF5MOP	63	65	2

Experimental measurements of γ have shown that fluorinated compounds possess distinctly smaller values of γ ($\gamma = 14$ dyn/cm for H10F5MOPP [15]) compared to nonfluorinated compounds (which show γ values between 20 and 30 dyn/cm [16,17]). Furthermore, recent x-ray studies [18] of the fluctuations in freely suspended films of a fluorinated compound similar to H10F5MOPP have shown that the fluctuation profile across the film of such a compound is different from that of an nonfluorinated compound. For the nonfluorinated compound a considerable damping of the layer displacement fluctuations near the surface was found [19], whereas even a slight enhancement of the fluctuations near the surface was observed for the fluorinated compound [18]. The results of the present study, i.e., the small temperature difference between T_S and T_B, fit well to these observations and lead to the conclusion that the free surface of fluorinated liquid-crystal compounds has, compared to nonfluorinated compounds, only a small ordering effect because of the low surface tension.

The influence of γ on the surface transition temperature can be described by a simple Landau model if one adds a coupling between γ and the square of the tilt angle θ^2 to the Landau free energy g. A linear coupling term would not make sense since the surface does not prefer a certain direction of the molecular tilt. In its simplest form, g then reads

$$g = g_0 + \tfrac{1}{2}a(T - T_B)\theta^2 + \tfrac{1}{4}b\,\theta^4 - C\gamma\theta^2. \quad (1)$$

Here, T_B is the Sm-A–Sm-C bulk transition temperature, C describes the strength of the coupling between γ and θ, and a and b are positive constants. The introduction of the $\gamma\theta^2$ coupling shifts the transition temperature and one obtains a surface transition temperature T_S

$$T_S = T_B + \frac{2C\gamma}{a}. \quad (2)$$

The γ values of fluorinated compounds are typically about one half of those of nonfluorinated compounds and according to Eq. (2) one expects a corresponding reduction of the difference ($T_S - T_B$) by 1/2 (provided that there is only a minor variation of C and a). We are presently looking for a quantitative check of the prediction of Eq. (2).

The sign inversion of $\vec{P}_s$, which was observed in the present study in thin films, has been observed in bulk samples of several liquid crystals (see references in [12]). A recent study [12] of one of these compounds in freely suspended films has shown that the $\vec{P}_s$ inversion occurs also in thin films, the inversion temperature decreasing with decreasing film thickness. This shift of the inversion temperature is observed also in very thin films of the present study (see Fig. 2) and may result from the reduced dimensionality in very thin films as is discussed in [12].

The $\vec{P}_s$ inversion indicates a change (with temperature) of the average direction of the permanent molecular dipole moment and may result from molecular conformation changes [20] and/or changes of the potential of the molecular rotation around its long axis [21]. In any case, the magnitude of $\vec{P}_s$ (below and above the inversion temperature) in such a compound is small, indicating that the average direction of the molecular dipole is close to the tilt plane defined by the layer

normal and the molecular long axis. In the case that the dipole direction is exactly parallel to the tilt plane, one would find $P_s = 0$. Thus, small external distortions may be able to move the dipole direction to the other side of the tilt plane resulting in a sign inversion of $\vec{P}_s$. The results of the present study indicate that such a distortion may be produced near the film surfaces.

Since we do not observe the $\vec{P}_s$ inversion in thick films, the presence of one free surface alone is obviously not sufficient for a corresponding change of the mean dipole direction. According to our results, the influence of the second surface becomes relevant in the thickness range between 20 and 40 layers. The difficulty to achieve a tilt alignment by the external field in this thickness range indicates that the magnitude of $\vec{P}_s$ must be rather low, i.e., the mean dipole direction is almost within the tilt plane. These findings and the $\vec{P}_s$ inversion observed in thinner films show that the mo-lecular conformation and the resulting mean dipole direction of 4M6OBF5MOP is very sensitive to the spatial confinement of the sample. The chiral center, which is the molecular origin of $\vec{P}_s$, is situated in the flexible alkyl chain, far from the aromatic core. It is quite reasonable to assume that this fact alone sufficiently explains the sensitivity to spatial confinement. The role of the fluorinated alkyl chain in this reversal behavior is not clear. Further work is needed to find the origin of such behavior.

[1] P. Pieranski, L. Beliard, J.-Ph. Tournellec, X. Leoncini, C. Furtlehner, H. Dumoulin, E. Riou, B. Jouvin, J.-P. Fénerol, Ph. Palaric, J. Heuving, B. Cartier, and I. Kraus, Physica A **194**, 364 (1993).

[2] Ch. Bahr, Int. J. Mod. Phys. B **8**, 3051 (1994); T. Stoebe and C. C. Huang, *ibid.* **9**, 2285 (1995).

[3] B. D. Swanson, H. Stragier, D. J. Tweet, and L. B. Sorensen, Phys. Rev. Lett. **62**, 909 (1989); T. Stoebe, R. Geer, C. C. Huang, and J. W. Goodby, *ibid.* **69**, 2090 (1992); R. Geer, T. Stoebe, and C. C. Huang, Phys. Rev. E **48**, 408 (1993); T. Stoebe and C. C. Huang, *ibid.* **50**, R32 (1994); C. Y. Chao, C. F. Chou, J. T. Ho, S. W. Hui, A. J. Jin, and C. C. Huang, Phys. Rev. Lett. **77**, 2750 (1996).

[4] S. Heinekamp, R. A. Pelcovits, E. Fontes, E. Y. Chen, R. Pindak, and R. B. Meyer, Phys. Rev. Lett. **52**, 1017 (1984); S. M. Amador and P. S. Pershan, Phys. Rev. A **41**, 4326 (1990).

[5] Ch. Bahr and D. Fliegner, Ferroelectrics **147**, 1 (1993); Ch. Bahr, C. J. Booth, D. Fliegner, and J. W. Goodby, Phys. Rev. E **52**, R4612 (1995).

[6] T. Stoebe, L. Reed, M. Veum, and C. C. Huang, Phys. Rev. E **54**, 1584 (1996).

[7] Ch. Bahr and D. Fliegner, Phys. Rev. A **46**, 7657 (1992).

[8] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1989).

[9] In the case of 4M6OBF5MOP, a chiral molecule, its Sm-C phase possesses a spontaneous polarization $\vec{P}_s$ in each smectic layer [R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (France) Lett. **36**, L69 (1975)]. Because $\vec{P}_s$ is perpendicular to both the layer normal and molecular tilt direction, one can use an external electric field to fix the tilt direction.

[10] N. A. Clark and S. T. Lagerwall, Ferroelectrics **59**, 25 (1984).

[11] N. Mikami, R. Higuchi, T. Sakurai, M. Ozaki, and K. Yoshino, Jpn. J. Appl. Phys. Part 2 **25**, L833 (1986); J. W. Goodby, E. Chin, J. M. Geary, J. S. Patel, and P. L. Finn, J. Chem. Soc. Faraday Trans. **83**, 3429 (1987).

[12] Ch. Bahr, C. J. Booth, D. Fliegner, and J. W. Goodby, Europhys. Lett. **34**, 507 (1996).

[13] R. Hołyst, D. J. Tweet, and L. B. Sorensen, Phys. Rev. Lett. **65**, 2153 (1990); A. N. Shalaginov and V. P. Romanov, Phys. Rev. E **48**, 1073 (1993).

[14] R. Hołyst, Phys. Rev. A **44**, 3692 (1991).

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

[16] P. Mach, S. Grantz, D. A. Debe, T. Stoebe, and C. C. Huang, J. Phys. (France) II **5**, 217 (1995).

[17] M. Eberhardt and R. B. Meyer, Rev. Sci. Instrum. **67**, 2846 (1996).

[18] E. A. L. Mol, J. D. Shindler, A. Shalaginov, and W. H. de Jeu, Phys. Rev. E **54**, 536 (1996).

[19] D. J. Tweet, R. Hołyst, B. D. Swanson, H. Stragier, and L. B. Sorensen, Phys. Rev. Lett. **65**, 2157 (1990).

[20] J. S. Patel and J. W. Goodby, Philos. Mag. Lett. **55**, 283 (1987); A. M. Glass, J. W. Goodby, D. H. Olson, and J. S. Patel, Phys. Rev. A **38**, 1673 (1988).

[21] B. Urbanc and B. Žekš, Liq. Cryst. **5**, 1075 (1989); R. Meister and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. **97**, 1242 (1993).