# Smectic-*O* Films

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(Received 15 November 1989)

An optical study of the smectic-*O* films which float on the free surface of droplets of racemate MHTAC [1(methyl)-heptyl-terephtalidene-bis-amino cinnamate] in the isotropic phase is presented. It allows us to elucidate the herringbone structure of the molecules in this original liquid-crystal phase, and to estimate the dipole moment ($\sim 5\times 10^{-3}$ D) that the molecules bear in the first smectic layer in contact with air.

PACS numbers: 61.30.Eb, 61.30.Gd, 64.70.Md

A few years ago, Levelut *et al.*[1] discovered a new liquid-crystal phase in 1-(methyl)-heptyl-terephthalidene-bis-amino cinnamate (MHTAC) that they called the smectic-*O* phase (Sm-*O*). Their preliminary observations with polarizing microscope and x-ray diffraction have shown that the smectic-*O* phase resembles very much the smectic-*C* phase. It has a layered structure with a spacing distance of 30 Å, and the molecules are tilted at an angle $\psi \simeq 50°$ with respect to the layer normal. The molecules, moreover, are positionally disordered inside the layers, which allows viscous flows in the smectic-*O* phase like in the smectic-*A* or -*C* phases. However, the smectic-*O* phase presents optical textures and x-ray-diffraction patterns which are very different from those obtained with the smectic-*C* phase, and this suggests that it may be considered as a new liquid-crystal phase.[1]

In this Letter, we report a detailed study of the Sm-*O* films which float on the free surface of droplets of racemate MHTAC (Ref. 2) heated in the isotropic phase (Iso). Using simple optical means, we elucidate the microscopic structure of the Sm-*O* phase, and therefore definitely prove the originality of this phase compared to the Sm-*C* one.

The smectic films, which are now currently observed at the free surface of the nematic or isotropic phases of liquid crystals,[3] are pretransitionally induced by the surface fields, i.e., by the interactions that the free surfaces, smooth at the angstrom scale, abruptly exert. Far enough above the bulk transition, the interface between the smectic film and the interior phase is also smooth, and when cooled down, the film begins to grow epitaxially in a layer-by-layer fashion. For most of the liquid crystals, however, the surface-induced film incompletely wets the interior phase of the droplet so that the layer-by-layer growth process is interrupted by the freezing of the whole sample. In the case of MHTAC, the film completely wets the isotropic droplet, and when cooled down, it grows indefinitely in the layer-by-layer manner. The film thickness then asymptotically diverges when approaching the isotropic to smectic-*O* transition temperature of the bulk ($T_c \simeq 158\,°\mathrm{C}$), the number of its smectic layers being given by the power law $N \propto (T-T_c)^{-1/3}$.[4] This behavior is quite similar to the one recently found by Swanson *et al.*[5] at the smectic-*B* to smectic-*I* phase transition of 90.4. It indicates that the dominant interactions in MHTAC are due to long-range van der Waals forces.

The experimental arrangement is shown in Fig. 1(a). A small quantity of racemate MHTAC, about 0.5 μm thick, is deposited on a clean and dried glass plate in the 2-mm interval between two gold electrodes. The sample is placed in a Mettler stage and heated up in the isotropic phase above $T_c$ ($\simeq 158\,°\mathrm{C}$). Careful interferential observations of this droplet with a polarizing microscope in transmitted light show that a thin Sm-*O* film covers its

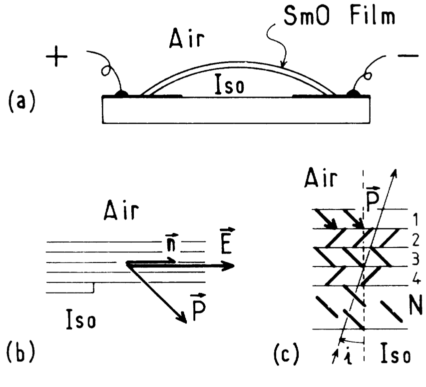

FIG. 1. (a) Vertical cut of the sample (not at scale). (b) Sm-*O* film oriented by the electric field **E**. A new layer is growing at the isotropic interface. (c) Herringbone structure of the Sm-*O* film. The last layer (*N*) in contact with the isotropic phase is most probably in the nematic phase. The polarization **P** ($\sim 5\times 10^{-3}$ D per molecule) of the Sm-*O* film is supported by the molecules of the first smectic layer (1), and oriented towards the interior of the film.

free surface even far above the melting temperature of the bulk, and that it keeps the same appearance for a wide temperature range, down to 164 °C. From birefringence and wall-width measurements (see below) the film is then estimated to contain only two layers. When slowly cooling down to temperatures lower than 164 °C, new smectic layers form one after the other, emitted from some germinal centers (Fig. 2). They begin with a one-layer step or a surface dislocation line [Fig. 1(b)], which is observed as a moving tiny line separating areas of different colors.[4] Counting these steps directly yields *N*, the number of the smectic layers in the film.

The surface-induced Sm-*O* film is stable, reproducible, and its thickness is directly controlled by means of temperature. It constitutes, in a simple manner, a Sm-*O* sample with spontaneously oriented layers, without the help, and the drawbacks, of solid contacts, similarly as in the free-standing-film technique.[6] This mechanically free Sm-*O* sample may be completely oriented by applying a weak electric field **E**. The director of the Sm-*O* film, **n**, which is defined by the projection of the molecules onto the 2D film[6] and which also, for symmetry reasons, bears the projection of the polarization **P**, is driven parallel to **E** [Fig. 1(b)]. Only two weak couplings are opposed to the aligning effects of **E**. They are the viscous torque exerted by the isotropic liquid in contact with the Sm-*O* film, and the elastic torque due to the distortion in the 2D Sm-*O* film itself. This elastic torque, which alone persists at equilibrium, is easily overwhelmed by weak electric fields in the 1-10-V/mm range, depending on the film thickness.

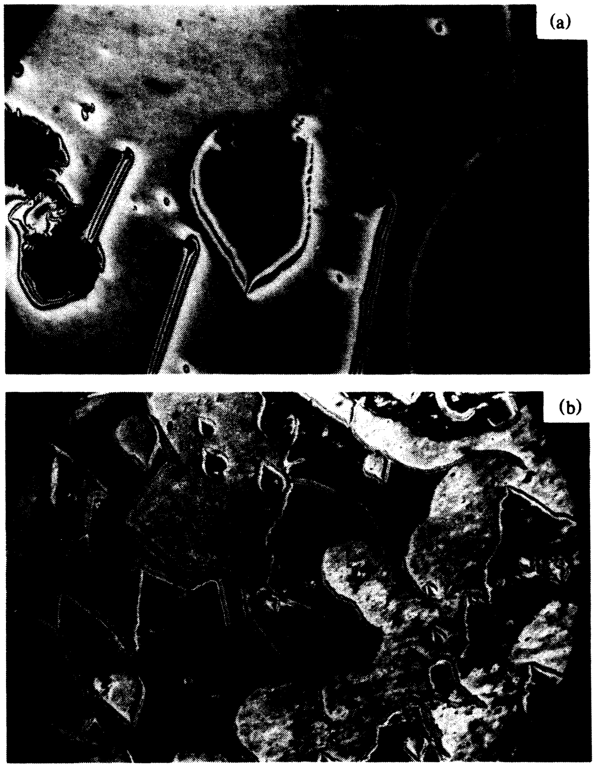

FIG. 2. Photographs of Sm-*O* films under the polarizing microscope. (a) A new layer growing at the isotropic-smectic-*O* interface of a film of uniform thickness. It has the typical arrowhead shape oriented in the electric field direction. (b) Film of nonuniform thickness (due to impurity gradients) showing several regions of odd and even numbers of layers. Their alternate grey colors and the correspondingly alternate directions of the arrow-shaped layers which grow on their isotropic interface demonstrate the parity properties characteristic of the Sm-*O* phase.

Birefringence measurements with a 3λ Leitz compensator have been performed in normal incidence ($i = 0$) on perfectly oriented Sm-*O* films in order to corroborate the direct determination of *N*. They indicate linear variations of the phase shift with film thickness (Fig. 3) corresponding to a path difference $\delta(0) \simeq 0.5$ nm per smectic layer.[4] This unusually large value explains why the Sm-*O* films are so easily observable with an optical microscope in transmitted light. With a molecular tilt $\psi \simeq 50°$ and a layer thickness $D = 30$ Å,[1] we deduce the birefringence along the molecules to be $\Delta n = \delta(0)/D \sin^2\psi \simeq 0.3 \pm 10\%$. This birefringence is large, but of the same order of magnitude as the birefringence measured in liquid crystals of molecules resembling MHTAC (see for instance Ref. 7).

As visible in Fig. 2, the Sm-*O* films sometimes contain disclination walls, similar to those observed by Pindak *et al.*[8] in chiral Sm-*C* films. They correspond to $2\pi$ rotations of the director. When observed between crossed polarizers, they make three characteristic stripes which mark the places where **n** is parallel or perpendicular to the polarizers. Because of the presence of some impurities these walls can remain anchored for a long time; otherwise they slowly shrink and disappear. When the electric field is reversed, the walls are completely displaced. Because their central parts are now oriented in the good

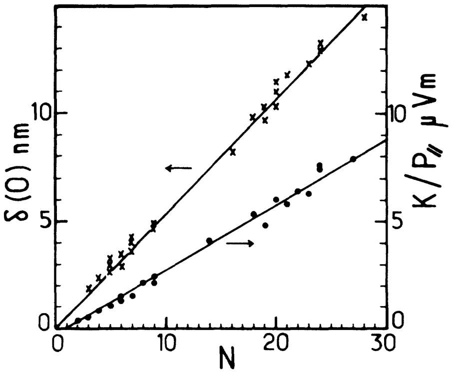

FIG. 3. Path-difference $\delta(O)$ between ordinary and extraordinary rays transversing the Sm-*O* film normally to it (crosses, left axis) vs the number of layers of the film, *N*. Right: Ratio $K/P_{\parallel}$ of the 2D elastic constant of the Sm-*O* film over its projected polarization (dots, right axis) vs *N*.

direction, they expand and push away two $\pi$ walls (equivalent to Bloch walls) until they meet other $\pi$ walls, combine, and reform $2\pi$ disclination walls elsewhere. This indicates that $\mathbf{E}$ interacts with a *permanent* polarization $\mathbf{P}$ attached to the Sm-$O$ film, more exactly with its projection $P_\parallel$ along $\mathbf{n}$. Neglecting the induced polarization and the space charges $\nabla \cdot \mathbf{P}$, and assuming one elastic constant $K$ for the 2D Sm-$O$ film, the free energy of a wall perpendicular to the $x$ axis simplifies to[8]

$$F=\int\left[\frac{K}{2}\left(\frac{\partial\phi}{\partial x}\right)^2-P_\parallel E\cos\phi\right]dS\,,$$

which is independent of the relative orientation of $\mathbf{E}$. The wall structure is the same as described by Pindak *et al.*,[8] and its width $w$, defined by the distance between the lines where $\mathbf{n}$ is perpendicular to $\mathbf{E}$, is given by

$$w=-2\left(\frac{K}{P_\parallel E}\right)^{1/2}\ln\left(\tan\frac{\pi}{8}\right).$$

The measurements of the wall width verify the behavior $w \propto E^{-1/2}$ within about 3% error bars.[4] This confirms the above approximations for calculating $w$, and therefore yields the measurement of the ratio $K/P_\parallel$. We thus find that $K/P_\parallel$ varies linearly versus $N$ (Fig. 3). With $K=ND\mathcal{K}\sin^2\psi$, where $\mathcal{K}$ is the average Franck elastic constant, and assuming only weak temperature variations for $\mathcal{K}$ (Ref. 9) ($\mathcal{K}\sim 5\times10^{-7}$ cgs), we deduce that the polarization per surface unit of the Sm-$O$ film is constant ($P_\parallel \sim 3\times10^{-7}$ nC/cm), independent of the number of smectic layers. It may therefore be considered attached to the film surfaces themselves. Let us also note that both the birefringence and wall-width measurements confirm the direct counting of the smectic layers with the microscope, with, however, a one-layer underestimate in the case of the wall-width measurements, probably arising from the nematic nature of the last layer (see below), which therefore would have a reduced elastic constant.

Indeed, the birefringence and wall-width measurements in the Sm-$O$ phase are not fundamentally different from those obtained in the Sm-$C$ phase.[4] What is really new in the Sm-$O$ phase is the dependence of the physical properties on the *parity* of $N$; i.e., the Sm-$O$ films behave differently depending on whether the number of their layers is odd or even. For instance, when looking at Sm-$O$ films with several regions of different numbers of layers separated by one-layer steps, we observe that the two kinds of regions with odd and even numbers of layers have two different grey colors,[10] and that the edges of the steps which separate them are heavier or thinner, depending, respectively, on whether $\mathbf{E}$ is oriented from the even region to the odd one, or vice versa. We also observe that when new smectic layers form, the heavy step edges can generate arrows which are oriented in their displacement direction (Fig. 2). They therefore appear to go alternatively up and down the electric field depending on the parity of their number of layers. All these parity effects indicate a parity in the layer structure itself, and therefore suggest a *herringbone* arrangement of the molecules in the Sm-$O$ phase, as sketched in Fig. 1(c).

In order to test such a possibility, birefringence measurements have been performed in the two symmetrically tilted directions $i=+0.265$ and $i=-0.265$ rad (by just reversing the electric field). The measurements yield about the same phase shift between the extraordinary and ordinary rays in both cases. This shows that the average molecular direction is along the normal to the layers (i.e., that the Sm-$O$ is optically a *biaxial smectic-A* phase), and therefore confirms the proposed herringbone structure. In fact, a small difference is observed between the two directions, again with a parity effect: $\Delta\delta=\delta(i)-\delta(-i)=0.8$ and $-0.3\pm0.2$ nm for the Sm-$O$ films of odd and even numbers of layers, respectively. These residual differences are due to the different nature of the smectic layers near the film surfaces, mainly the first (1) and the last ($N$) ones, respectively, in contact with air and with the isotropic phase. Taking the herringbone structure of the Sm-$O$ films into account, we deduce the optical path difference across the first and last layers to be $\Delta\delta_1=0.4\pm0.2$ nm and $\Delta\delta_N=0.7\pm0.2$ nm, respectively. A comparison to the expression of the path difference across one smectic layer,

$$\Delta\delta=D\sin i\sin(2\psi)\Big/\left(\frac{n_e^2}{n_e^2-n_o^2}-\sin^2\psi\right),$$

where $n_o \simeq 1.5$ and $n_e=n_o+\Delta n\simeq 1.8$ are the optical indices of the smetic layer, shows that the last layer is thicker ($\sim 7$ nm) than the others ($=3$ nm), while the first one seems very similar to the interior ones [Fig. 1(c)]. This result is obtained under the relatively unsensitive assumption that $\psi \simeq 50°$ for these particular layers too. It strongly suggests that the last layer is actually in the nematic phase ($N$), and that its thickness corresponds to $\xi$, the nematic correlation length.[11]

Let us finally notice that the alternate structure of Sm-$O$ does not produce observable parity effects in the $P_\parallel(N)$ measurements (Fig. 3). This indicates that the polarization $P_\parallel$ (shown above to be attached to the surface layers of the Sm-$O$ film) is located on only one surface, and more precisely, on the *first* one in contact with the air since the surface-dislocation lines at the isotropic–Sm-$O$ interface are not observed to reverse $\mathbf{n}$, i.e., to push $\pi$ walls[12] (while the polarization remains oriented along $\mathbf{E}$). The birefringence measurements in tilted incidence moreover allow the determination of the orientation of the molecules of the first smectic layer referred to $\mathbf{E}$, i.e., referred to $P_\parallel$, or to the total polarization $\mathbf{P}$ of the molecules in the first layer (assumed roughly parallel to them). $\mathbf{P}$ is thus found to be oriented towards the bulk of the Sm-$O$ phase [Fig. 1(c)]. Its very weak amplitude ($\sim 5\times 10^{-3}$ D per molecule) and its orientation indicate that it could originate from the reduced polarizability[13] of the aliphatic tips of the first-layer molecules which experience a reduced dielectric constant in contact with air.

In conclusion, using simple macroscopic means, we have elucidated the herringbone structure of the molecules in the Sm-*O* phase, and estimated the dipole moment ($\sim 5\times 10^{-3}$ D) that is supported by the molecules of the first smectic layer in contact with air. It remains now to find the physical mechanism responsible for such an unusual piling of the molecules, and in the same way, to understand why the MHTAC molecule is so unique.

We wish to thank A. M. Levelut, G. Durand, and P. Martinot-Lagarde for many fruitful discussions. We are indebted to P. Keller and C. Germain for providing the MHTAC.

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[2] The MHTAC molecule has two chiral centers. The racemate studied here is the mixture of 25%++, 25%−−, and 50%+−.

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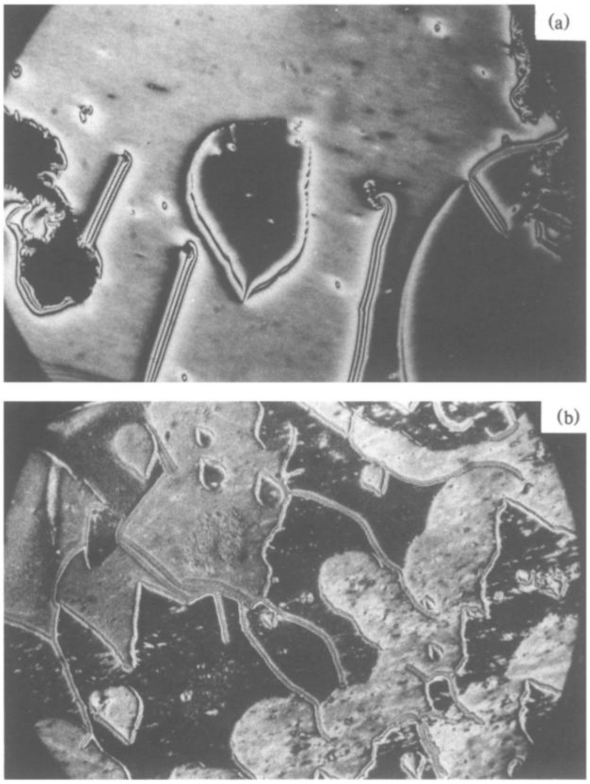
[9] The Franck elastic constants of the smectic phases present only weak temperature variations because they are essentially related to the orientational (or nematic) order parameter which is then almost saturated.

[10] This observation indeed indicates residual chirality in our samples (see Ref. 4).

[11] Such a short correlation length ($\xi \sim 7$ nm) is consistent with the existence of a virtual nematic phase with a nematic-isotropic transition temperature $T_{NI} \sim 110\text{–}150$ K depending on the actual value of the bare correlation length $\xi_0$. The correlation length $\xi = \xi_0[(T/T_{NI})-1]^{-1/2}$ should therefore have negligible temperature dependence in our temperature range of a few degrees.

[12] However, small distortions sometimes exist near surface dislocation lines (Fig. 2), which indicates a preferred orientation of the director in their vicinity (Ref. 4).

[13] The ordoelectric polarization averages to zero over the whole Sm-*O* film. It is therefore not considered here.



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