

Surface tension of freestanding partially fluorinated liquid-crystal films

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The surface tension of freestanding liquid-crystal films has been measured as a function of film thickness and temperature. The data are independent of film thickness from over 100 down to only two molecular layers ($\approx 50 \text{ \AA}$) and no temperature dependence could be detected. The results obtained on recently synthesized partially fluorinated materials indicate that the film-vapor interfaces consist of roughly equal proportions of CF_3 and CH_3 terminal groups.

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Recently, primarily motivated by display applications, a novel class of liquid-crystalline materials has been synthesized. While these partially fluorinated compounds often exhibit properties highly desirable for the manufacture of displays, they are far from being fully characterized and some of their most interesting properties undoubtedly remain to be discovered. We have recently developed a simple technique capable of accurately determining the surface tension of freestanding liquid-crystal films [1]. This experiment has provided significant insight into the effects of fluorination on the film-vapor interface.

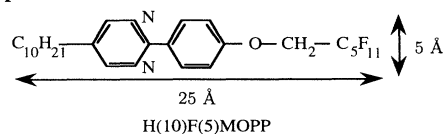
Many compounds that exhibit liquid-crystalline mesophases are comprised of highly anisotropic molecules that may be described as semirigid rods (typical molecular dimensions $\approx 25 \times 5 \times 3 \text{ \AA}^3$). These molecules generally possess a somewhat still aromatic core separating a pair of more flexible end chains. Often these end chains consist simply of a series of CH_2 groups terminated by a CH_3 group (alkyl chains). In some partially fluorinated compounds, most of the hydrogen atoms in one of the end chains are replaced by fluorine atoms. Fully fluorinated compounds often fail to exhibit liquid-crystalline phases and are therefore presently of more limited interest.

Unlike their fully fluorinated counterparts, partially fluorinated compounds have been shown to actually extend the temperature range over which certain liquid-crystalline states, particularly the smectic phases, are stable [2]. These smectic phases are important in a number of display applications [3] and they can be thought of as a stack of two-dimensional layers separated by roughly the dimension of the molecular long axis. In the simplest smectic phase, the smectic-*A* (*Sm-A*) phase, the long axes are aligned parallel to the layer normal and the center-of-mass ordering within each layer is liquidlike [4]. One of the most interesting aspects of smectic liquid crystals is that, under the appropriate conditions, they can be

spread across large openings ($> 1 \text{ cm}^2$) to form freestanding films [5]. In free-standing *Sm-A* films, the layer normals are all aligned parallel to the film normal, creating single smectic domain samples. Because of the smectic layer structure, film thickness is quantized in units of layers and uniform films from many hundreds down to only two molecular layers ($\approx 50 \text{ \AA}$) in thickness can be readily prepared and remain stable for weeks [6]. Since there is no substrate, these films represent excellent model systems for not only the study of bulk properties, but also the increased importance of surface effects as the film thickness is reduced.

The surface tension is clearly of fundamental importance to the stability of these films. Moreover, the presence of the surface tension is believed to be responsible for intriguing surface ordering phenomena exhibited by most liquid-crystal films. Unlike the preferential surface melting exhibited by ordinary systems, the liquid-crystal-vapor interface appears to enhance the order of the surface layers so that they become ordered at temperatures well above the bulk transition temperature [7].

Recent improvements to the imaging system of our surface tension apparatus have significantly reduced the estimated error (it is now less than $\pm 2.5\%$) [8]. A member of the partially fluorinated homologous series, 5-*n*-alkyl-2-(4-*n*-(perfluoroalkyl-metheleneoxy) phenyl) pyrimidine, denoted here as H(10)F(5)MOPP, was used in the present study. Here (10) and (5) denote the length of the alkyl (fluoro-alkyl) chain including the CH_3 (CF_3) terminal group.



Surface tension studies were performed as a function of film thickness throughout the *Sm-A* phase temperature range ($75\text{--}84^\circ\text{C}$) of H(10)F(5)MOPP. The film thickness (in units of layers) was determined by employing standard optical techniques [9]. The data presented in Fig. 1 were obtained at a fixed temperature ($T \approx 80^\circ\text{C}$) and demonstrate the surface tension data to be independent of film thickness to within our experimental resolution between

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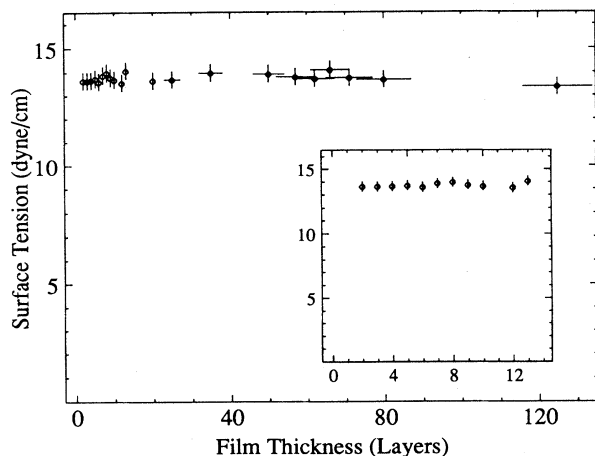


FIG. 1. Measured surface tension of freestanding H(10)F(5)MOPP films as a function of film thickness (given in terms of number of layers, N).

2 and over 100 layers. (Based on our estimated error, any thickness dependence is less than 5×10^{-3} dyn/cm layer.) These results indicate that the mechanism responsible for the creation of the surface tension is localized, it does not extend beyond a single molecular layer. This observation supports Langmuir's conclusion (in 1916) and the adsorptive properties of surfaces are principally determined by the composition and packing of the atoms or groups of atoms nearest the interface, his "principle of independent surface action" [10]. Interestingly, in seeming violation of Langmuir's principle, Pieranski *et al.* [11] report using a different technique to measure a small positive thickness dependence of the surface tension for much thicker freestanding films of the commercial liquid-crystal mixture, S2. This observation provides a potential explanation for the commonly observed expansion of the thinner regions of mixed thickness films until a film of uniform thickness is achieved. However, spontaneous thinning is not universal and films created using some compounds accrete material from the surrounding reservoir of sample and thicken with time. It would be interesting to determine the sign of any surface tension thickness dependence of these compounds. Unfortunately, such a small thickness dependence could not be independently confirmed using our technique [12]. Studies were also performed on a series of four-layer-thick H(10)F(5)MOPP films as a function of temperature. The data shown in Fig. 2 demonstrate any surface tension dependence on temperature to be fairly weak (< 0.1 dyn/cm K), suggesting that neither the packing nor the surface conformation is appreciably altered through this temperature regime.

The average value for the surface tension, $\gamma = 13.75 \pm 0.35$ dyn/cm is informative. Recalling that H(10)F(5)MOPP possesses both CH_3 and CF_3 terminal groups, three general surface configurations are possible (see Fig. 3) [13]. In his pioneering critical contact angle measurements, Zisman estimated the critical surface energy (surface tension) of close-packed CF_3 groups to be

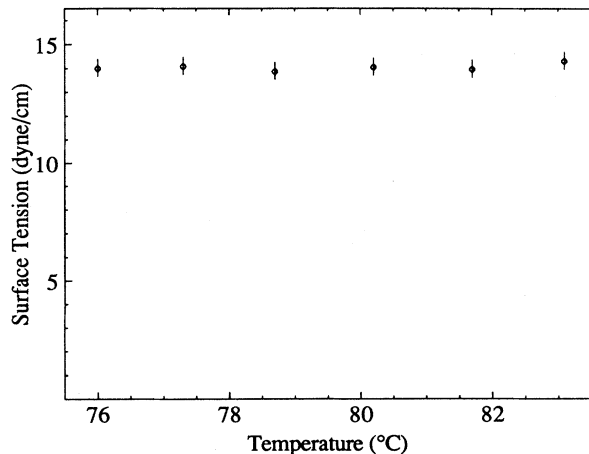


FIG. 2. Surface tension of four-layer freestanding H(10)F(5)MOPP films as a function of temperature.

quite small, ≈ 6 dyn/cm [14]. It is interesting to note, therefore, that scheme (a) of Fig. 3, although it possesses a lower surface energy, clearly does not represent the surface of these films. Furthermore, Zisman found the critical surface energy of close-packed CH_3 groups to be ≈ 23 dyn/cm and scheme (b) is also inconsistent with our data. The surface therefore appears to be comprised of *both* CH_3 and CF_3 terminal groups.

Based on the principle of independent surface action, the surface tension is expected to be directly related to the strength of the intermolecular interaction nearest the surface. The groups in question, alkyl and fluoro-alkyl, are nonpolar and should interact primarily via van der Waals dispersion forces. To a first approximation, the van der Waals interaction between two species (i) and (j) depends strongly on the corresponding dielectric polarizabilities α_i and α_j , so that the coupling is simply proportional to their product, $V_{ij} = k\alpha_i\alpha_j$ and k is roughly independent of (i) and (j) [15]. The (i)-(j) interaction

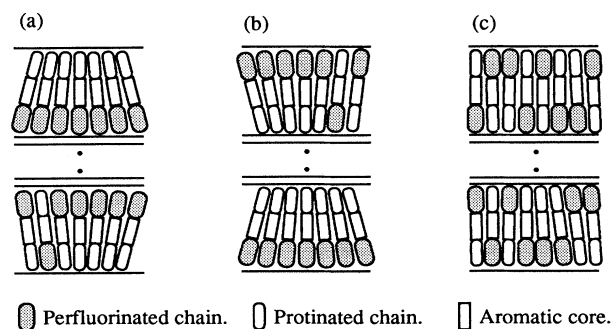


FIG. 3. General configurations possible at the film-vapor interface. (a) Predominantly fluorinated terminal groups. (b) Predominantly alkyl terminal groups. (c) Average antiparallel layer structure.

can therefore be estimated as the geometric mean of the (i) - (i) and (j) - (j) interactions [16]. Assuming that the surface of the H(10)F(5)MOPP freestanding films are comprised of equal proportions of CH_3 and CF_3 terminal groups yields a predicted surface tension of $\approx(6 \times 23)^{1/2} = 12$ dyn/cm [17]. Considering the lack of sophistication in this analysis, this result is in good agreement with our measured value (≈ 14 dyn/cm), indicating that the surfaces of these films are comprised of large proportions of both types of terminal groups [scheme (c)].

This hypothesis is strongly supported by recent x-ray diffraction experiments by Shindler *et al.*, on freestanding Sm-*A* films of a partially fluorinated compound very similar to H(10)F(5)MOPP [18]. The diffraction data were found to be well described by a model assuming a *symmetric* molecular form factor and the surface tension was obtained as a fitting parameter and reported as 13 dyn/cm. Because the fluoro-alkyl group is more electron dense, preferential head-tail ordering at the surfaces would modify the diffraction data. The effects would become more apparent with decreasing film thickness. The diffraction data from 34-, 20-, and 4-layer films are all well described using the model assuming a *symmetric* molecular form factor. This success suggests that any preferential head-tail ordering is weak and that the *symmetric* form factor is an effective average of roughly equal numbers of molecules in the two possible orientations both at the surfaces and within interior layers [19].

Because the surface does not adopt what initially appears to be the lowest-energy state available to it (close-packed CF_3 terminal groups), other effects must be considered. The fluorinated tail has been estimated to occupy more ($\approx 25\%$) volume than a simple alkyl tail of equal length [20]. Macroscopic regions of schemes (a) or (b) would therefore result in substantial curvature. Because the films are constrained to be planar, this suggests that steric (excluded volume) effects promote an average antiparallel structure to achieve the most efficient packing while minimizing the overall bend of the film. It is important to recall that the Sm-*A* phase is characterized by a lack of translational order within the layers so this antiparallel structure is not expected to be perfect. In fact, the assumed local triangular packing would result in a highly frustrated system unless large numbers of head-tail orientational defects are allowed. Furthermore, in view of the absence of translational order, the fixed head-tail orientation states of schemes (a) and (b) are certainly

more ordered (and hence less favored by entropy) than the mixed state of scheme (c). In this case steric and entropic effects dominate surface energetics. Moreover, the above considerations also hold for the interior layers, suggesting that they may also share the average antiparallel structure of the surface layers, consistent with our interpretation of the x-ray results.

The introduction of the low α fluorocarbon groups has a dramatic effect on other important structural and elastic properties of these compounds. Since the van der Waals interaction between the smectic layers is also proportional to the polarizability of the end groups in closest contact, the ratio of interlayer to intralayer coupling of the partially fluorinated compounds should be reduced relative to purely alkyl-terminated compounds. In this argument, we assume that a significant portion of the intralayer interaction is due to the core, which is not affected by the fluorination. The layers of the partially fluorinated smectic phases are therefore expected to be more rigid and stable than their protonated counterparts. Such an argument most likely explains the observed enhancement of the smectic temperature regions upon increasing fluorination.

Although additional characterization is clearly necessary, these surface tension results provide significant insight into novel partially fluorinated liquid-crystal compounds. The independence of the surface tension of film thickness to within our resolution supports the concept of highly localized surface activity introduced by Langmuir. The lack of an observed change in surface tension as a function of temperature indicates that the conformation of the film-vapor interface does not change appreciably through the Sm-*A* phase. The intermediate value obtained for γ demonstrates the relative importance of steric and van der Waals forces and entropy as it suggests an average antiparallel smectic layer structure. Furthermore, our measurements corroborate recent x-ray diffraction experiments in which the surface tension was obtained as an important fitting exponent and support the use of an analysis based on a *symmetric* molecular form factor.

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- [12] Our thickness dependence resolution was limited primarily by our inability to create and characterize uniform, thick (> 500 layers) films of sufficient size (≈ 1 cm²). Stresses associated with line energies induced by discontinuous variations in thickness of nonuniform films could alter the effective film tension. Therefore, only results obtained on films of uniform thickness are presented here. However, nonuniform thicker (but still much less than 6000 layers) films exhibited surface tension values consistent with those reported on uniform films to within our estimated error, suggesting a smaller lower limit for the surface tension dependence on film thickness.
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