Wettabilities of Self-Assembled Monolayers Generated from CF₃-Terminated Alkanethiols on Gold

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Received February 6, 1998

Self-assembled monolayers of terminally fluorinated alkanethiols, CF₃(CH₂)ₙ-SH with n = 9–15, and their nonfluorinated analogues, CH₃(CH₂)ₙ-SH with n = 9–15, were prepared by adsorption from solution onto evaporated gold. The monolayers were characterized by contact angle goniometry, ellipsometry, and X-ray photoelectron spectroscopy. The analyses indicate that the CF₃-terminated alkanethiols generate terminally fluorinated monolayers that are well-ordered, particularly when the chain lengths consist of 12 or more carbon atoms. Comparison of CF₃-terminated films to CH₃-terminated films of similar length reveals that terminal fluorination of the surface leads to an overall decrease in the surface tension of the films. This decrease arises from a relatively large decrease in the dispersive component of the surface tension upon the introduction of fluorine. Surprisingly, terminal fluorination also leads to a small but significant increase in the nondispersive component(s) of the surface tension. The origin of these opposing effects is discussed.

Introduction

Fluorinated organic materials have drawn considerable fundamental and technological interest because of their extremely low wettabilities and surface energies. In pioneering work more than 35 years ago, Zisman et al. examined the wettabilities of fluorinated organic thin films generated by the adsorption of fluorinated alkanoic acids and alkylamines on metal surfaces. Although these studies sought to provide a systematic exploration of the differences (with regard to molecular size and interfacial forces) between fluorinated films and those derived from hydrocarbons, the limited reproducibility and characterization of these early films hindered in many cases the establishment of firm conclusions.

More recently, the adsorption of alkanethiols onto gold has been shown to provide a convenient route to self-assembled monolayer (SAM) films that are highly ordered and well-defined. Alkanethiols that are predominantly fluorinated can also be used to generate high-quality films. The larger van der Waals radii of the fluorocarbon chains lead to a lower packing density than that observed for analogous hydrocarbon chains. For example, fluorinated SAMs generated from CF₃(CH₂)₉(CH₃)SH on Au(111) exhibit a p(2 × 2) structure at 95% bulk density, and films generated from CF₃(CH₂)₉(CH₃)SH (n = 5, 7, 11) on Au(111) exhibit a packing density of at most commensurate (7×7). The respective structures show packing densities that are 12% and 22% smaller than those of purely hydrocarbon-based SAMs.

In contrast to these earlier studies, our research explores the interfacial properties of a series of SAMs on gold generated from partially fluorinated alkanethiols, where the degree of fluorination is progressively increased from zero. In the present study, we compare the properties of SAMs derived from ω,ω,ω-trifluoromethylalkanethiols (CF₃(CH₂)ₙ-SH, where n = 9–15) to those of SAMs derived from the corresponding simple alkanethiols (CH₃(CH₂)ₙ-SH, where n = 9–15). Analysis of the new SAMs by contact angle goniometry, ellipsometry, and X-ray photoelectron spectroscopy indicates that all of the partially fluorinated alkanethiols generate analogous CF₃-terminated surfaces, which are supported by the well-organized chain structures characteristic of SAMs generated from the simple alkanethiols. An unexpected trend in the wettabilities was, however, observed: the CF₃-terminated SAMs were less wettable by hexadecane and methylene iodide, but surprisingly more wettable by water and glycerol than were the CH₃-terminated SAMs.

Experimental Section

Materials and Methods. The liquids used for the contact angle measurements (hexadecane, methylene iodide, glycerol, and water) were of the highest purity available from Aldrich Chemical Co. and were used without further purification. The simple alkanethiols used to generate the hydrocarbon SAMs were either commercially available or synthesized using unexceptional procedures. The ω,ω,ω-trifluoromethylalkanethiols were synthesized using an approach developed in our laboratories; the details of the synthesis and characterization are described elsewhere. The purity of all thiols was >99% as judged by integration of the corresponding nuclear magnetic resonance
spectra (H NMR, 300 MHz). Refractive indices of all thios were measured using a Bausch & Lomb refractometer operated at 24 °C (nD25).

**Preparation of SAMs.** The surfaces of gold were prepared by evaporation of ca. 2000 Å of gold onto silicon (100) wafers that were precoated with ca. 100 Å of chromium to promote adhesion. SAMs were prepared by immersing small pieces of the freshly prepared gold-coated wafers in deoxygenated ethanolic solutions containing the appropriate thios in 1 mM concentrations. The gold slides were allowed to remain in the ethanolic solution at ambient temperature for 24 h. After removal from solution, the slides were rinsed thoroughly with ethanol; the ethanol was then removed by passing a vigorous stream of nitrogen over the slide.

**Characterization of SAMs.** The thicknesses of the films were measured with a Rudolph Auto EL III ellipsometer, which employs a He–Nel laser beam (632.8 nm) at an angle of incidence of 70°. For all films, a refractive index of n = 1.45 was assumed. To determine the precision, we performed at least 10 measurements of thickness for each type of film. For a given set of measurements, the values were typically reproducible to within ±1 Å. The atomic composition of the films was determined by X-ray photoelectron spectroscopy (XPS) using a Surface-Science SSX-100 spectrometer with a monochromatized Al Kα source. Advancing and receding contact angles were measured using a Ramé-Hart model 100 contact angle goniometer. Contacting liquids were applied (for advancing angles, θa) and withdrawn (for receding angles, θr) using a Matrix Technologies micro-Electrapette 25 operated at the slowest possible speed (ca. 1 μL/s). Two measurements of the contact angle at 293 K and ambient relative humidity were performed on opposite edges of at least three drops (ca. 3 mm diameter) with the pipet tip touching the drops. The contact angles were typically reproducible to within ±1°. Four types of pure test liquids were used: hexadecane (C18H36, HD), methylene iodide (CH2I2, MI), glycerol (C2H5OH, GL) and distilled water (H2O, W). The advancing contact angle θa was used for calculation of the surface tensions because of ready comparison with published data.

**Ellipsometric Thicknesses.** The surface tensions of the SAMs were estimated from the contact angle data utilizing a separation method proposed by van Oss, Chaudhury, and Good.12,13 This method yields the solid surface tension γs as a summation of the respective surface tension components γLW and γAB (i.e., γs = γLW + γAB), based on Lüscher–van der Waals (or dispersive interactions) and acid–base (or hydrogen bonding interactions), respectively. The term γAB is a combination of the asymmetric components γ+ (acid–electron acceptor interactions) and γ− (base or electron donor interactions): γAB = 2γ+γ−/γ++. The relationship between the equilibration contact angle θ and the solid surface component of liquids and solids is given by the modified Young–Dupré equation (eq 1)14

\[(1 + \cos \theta)\gamma_L = 2\left(\gamma_{LW} \gamma_L \cos \theta + 2\gamma_{LW} \gamma_L \cos \theta + 2\gamma_L \gamma_L \cos \theta\right)^{1/2}\]

The term γL is the surface tension of liquids against air or vapor; addition of the subscript “L” denotes the surface tension components of the test liquids. The geometric mean is assumed in the solid–liquid interfacial tensions. In our case, the calculations were performed using the θr data obtained with hexadecane (HD), methylene iodide (MI), glycerol (GL), and water (W). The respective values of the liquid surface tensions are shown in Table 1.

**Results and Discussion**

As a first step, it will be useful to establish an abbreviated nomenclature for the SAMs under consid-


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**Figure 1.** Ellipsometric thicknesses Ls of the CH3-terminated SAMs (circles) and the CF3-terminated SAMs (squares) as a function of the number of carbon atoms in the chain (n + 1). Straight lines are Ls (in Å) = 1.27 cos(30°)n + 2.8 (upper) or 0.3 (lower). The error bars assume an uncertainty of ±1 Å in the measured values of ellipsometric thickness.

**Table 1.** Values of Surface Tension for the Test Liquids at 293 K in mJ m⁻²

<table>
<thead>
<tr>
<th>Liquid</th>
<th>γL</th>
<th>γLW</th>
<th>γL+</th>
<th>γL−</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexadecane</td>
<td>27.5</td>
<td>27.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>methylene iodide</td>
<td>50.8</td>
<td>50.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>glycerol</td>
<td>64</td>
<td>34</td>
<td>5.3</td>
<td>42.5</td>
</tr>
<tr>
<td>water</td>
<td>72.8</td>
<td>21.8</td>
<td>34.2</td>
<td>19</td>
</tr>
</tbody>
</table>

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the ellipsometric data for the CH$_3$-terminated films, we obtain a value of $L_0 = 2.8 \pm 0.9 \text{ Å}$, which represents a reasonable value for the bond length and angle of the C–S/Au interaction. For the CF$_3$-terminated films, however, we obtain a value of $L_0 = 0.3 \pm 0.8 \text{ Å}$, which seems anomalously small.

We explored the possibility that the small $L_0$ observed for the CF$_3$-terminated monolayers was due to the use of an inappropriately high value for the refractive index, which could give rise to an underestimate of the thicknesses of these films. We measured the refractive indices of the alkanethiols examined in this study and found the average value, $n_0^{24} = 1.458 \pm 0.004$; the average value obtained for the corresponding CF$_3$-terminated thiols was indeed lower: $n_0^{24} = 1.431 \pm 0.009$. The magnitude of the difference is, however, insufficient to completely account for the observed differences in the thicknesses of the two types of films.$^{17,18}$ Furthermore, analysis of the H13 and F13 SAMs by atomic force microscopy (AFM) revealed an indistinguishable difference in lattice spacing for the two films.$^{19}$ Consequently, it seems unlikely that differences in packing density are responsible for the differences in thicknesses of these films. A remaining possibility is that a difference in tilt angle for the two types of films is giving rise to the observed differences in thickness. We are currently examining these films by infrared reflection–absorption spectroscopy (IRRAS)$^{19,20}$ to evaluate this possibility.

Elemental Compositions of the Films. Analysis of the CF$_3$-terminated films by XPS revealed no detectable oxygen or other spurious elements (data not shown). The ratio of fluorine/gold was roughly constant over the range of chain lengths examined (F10–F13). Although we might have expected this ratio to increase with increasing chain length, the data are nevertheless consistent with a model in which all CF$_3$-terminated alkanethiols provide similar surface coverages, exposing fluorine atoms at the interface.

Wettability of the Films. Figure 3a shows the advancing contact angle $\theta_a$ (and $\cos \theta_a$) plotted against chain length for the CH$_3$-terminated monolayers H10–H16. The average values for $\theta_a$ (and $\cos \theta_a$) are 48° (0.67) for HD, 78° (0.21) for MI, 101.5° ($\pm 0.20$) for GL, and 114.5° ($\pm 0.41$) for W. For a given test liquid, the measured values are nearly constant for all chain lengths. To evaluate this possibility, published data for similar SAMs on gold with a wide range of chain lengths were available: $\theta_a$ values for H12–H15 are constant within $45^\circ - 48^\circ$ for HD and $111 - 114^\circ$ for W, while $\theta_a$ for shorter chain lengths are progressively lower.$^{21,22}$ Similar data have been observed for SAMs formed on other metals.$^{22}$ In addition, there are reports of a parity (or “odd–even”) effect in the contact angle versus chain length data observed for hexadecane wetting SAMs on gold.$^{16,23}$ The parity effect is generally interpreted to reflect the increased wettabilities of the methyl and hydroxyl groups exposed at the interface.$^{24,25}$ We routinely observe this effect;$^{26}$ in the data shown here, however, the effect is absent.$^{27}$ With regard to these results and the ellipsometry data above, we conclude that SAMs H10–H16 form similar well-ordered surfaces with oriented and densely packed chains.

Figure 3b shows the advancing contact angle $\theta_a$ (and $\cos \theta_a$) plotted against chain length for the CF$_3$-terminated monolayers F10–F16. The data for F10 slightly deviate toward lower contact angles (corresponding to higher wettabilities) for all test liquids employed. For a given test liquid, the measured values are nearly constant for chain lengths greater than F10, and no parity effect is observed. The average values for $\theta_a$ (and $\cos \theta_a$) for F11–F16 are $64^\circ$ (0.44) for HD, $84^\circ$ (0.10) for MI, $100^\circ$ (0.17) for GL, and $110^\circ$ (0.34) for W. In addition, the difference in contact angle between CH$_3$- and CF$_3$-terminated SAMs ($\Delta \theta_a = \theta_a^{\text{CH}_3} - \theta_a^{\text{CF}3}$) is roughly constant over all chain lengths: $15^\circ$ for HD, $6^\circ$ for MI, $-2^\circ$ for GL, and $-4^\circ$ for W. These data indicate that the dispersive liquids are repelled more at the CF$_3$-terminated surfaces, while the polar hydrogen-bonding liquids are repelled more at the CH$_3$-terminated surfaces.

Contact Angle Hysteresis. Figure 4 shows the contact angle hysteresis, $\Delta (\cos \theta) = |\cos \theta_2 - \cos \theta_1|$, as a function of chain length of both the CH$_3$- and the CF$_3$-terminated films.

![Figure 3](image-url)  
**Figure 3.** Advancing contact angles $\theta_a$ (and $\cos \theta_a$) for CH$_3$-terminated SAMs (a) and the CF$_3$-terminated SAMs (b) as a function of the number of carbon atoms in the chain $(n + 1)$. Hexadecane (HD), methylene iodide (MI), glycerol (GL), and water (W) were used as the test liquids. The contact angles were typically reproducible to within $\pm 1^\circ$.


(17) In separate studies of the ellipsometric thicknesses of chelating SAMs on gold,$^{18}$ we varied the assumed refractive index from 1.40 to 1.60 and found the corresponding thicknesses to decrease by only 1 Å. Since the difference in average refractive index for the alkanethiols and the CF$_3$-terminated alkanethiols is at most 0.04, we believe that some other factor must be contributing to the observed differences in thickness ($\Delta L = 2.5 \pm 1.2$ Å) for these two types of films.


(27) We have yet to establish the origin of this inconsistency. Empirical observations suggest, however, a variance with the quality of the underlying gold; that is, SAMs grown on only the highest quality evaporated gold appear to exhibit the parity effect.
terminated films. These data provide a measure of the roughness or heterogeneity of the wetted surfaces. For the CH$_3$-terminated surfaces, average values of $\Delta (\cos \theta)$ for each test liquid are 0.15 for HD, 0.19 for MI, 0.23 for GL, and 0.20 for W. The observed values of hysteresis are comparable with those reported in the literature for SAMs of alkanethiols on gold. Our data also suggest that regardless of the chain length, the surfaces of the present CH$_3$-terminated SAMs are equally smooth and homogeneous (although a trend toward smoother, more homogeneous surfaces could be proposed for the thickest films, H15 and H16).

The CF$_3$-terminated SAMs having longer chain lengths (i.e., F12–F16) exhibit qualitatively similar behavior: the average values of $\Delta (\cos \theta)$ for all test liquids fall within the interval of 0.16–0.23. Furthermore, with the exception of W, the contact angle hystereses show a progressive decrease with increasing chain length. A deviation from this trend is, however, observed for the shorter CF$_3$-terminated SAMs, F10 and F11. This behavior might result from a transition to rougher, more heterogeneous surfaces for the shorter chain lengths, although a trend toward smoother, more homogeneous surfaces could be proposed for the thickest films, H15 and H16).

As shown in Figure 5b, the estimated surface tensions of the CF$_3$-terminated SAMs remain more or less constant for the chain lengths F11–F16. Deviations in the wettability of F10, perhaps due to disorder in the film, have been noted above. Overall, the estimated surface tensions for the terminally fluorinated SAMs consist of a large contribution from $\gamma^{SL}_{AB}$ and a small but significant contribution from $\gamma^{SL}_{CB}$ (see also Table 2). It is possible that the observed $\gamma^{SL}_{AB}$ component arises from hydrogen bonding between the CF$_3$ groups and the polar liquids. The energy of hydrogen bonds of the type C–F…H–O has been estimated to be as high as 2.4 kcal/mol. Furthermore, it seems plausible that optimal C–F…H–O bonds could exist in the CF$_3$-terminated SAMs when the chain lengths are not too long, because the CF$_3$ groups may be able to self-associate, thereby shielding the polar hydrogens.

van der Waals interactions between the CH$_3$ groups forming the backbones, which would afford stronger interchain packing and thus more highly ordered films.

For the model of surface heterogeneity proposed by Johnson and Dettre, the contact angle hysteresis is controlled by (1) the energies of two adjacent configurations where the drop is at a metastable equilibrium and (2) the energy barrier between those two configurations. It follows that a larger $\Delta (\cos \theta)$ should correlate with greater work required to move a drop from one position of a metastable equilibrium to a position of unstable equilibrium and ultimately again to a position of metastable equilibrium. If the SAMs generated by shorter chains are indeed less ordered than those with longer chains, this disorder might manifest itself in the formation of a large number of domains and the corresponding barriers between them. In the Johnson and Dettre model (based on work by Pease), the advancing angles are most closely associated with low-energy regions of the surface, while the receding angles are most closely associated with high-energy regions. If the boundaries and steps between domains can be characterized as higher energy regions compared to lower energy flat regions, the observed hystereses could indicate the existence of progressive disorder for decreasing chain lengths.

Since the handling and preparation (including the fabrication of the Au substrates) of all SAMs carried out under similar conditions, we assume that the hysteresis effects imposed by any adsorbed impurities or contaminants should be similar for all films. It is also known that the surfaces of low-energy SAMs are generally insensitive to contaminants. Additionally, the XPS analyses of the CF$_3$-terminated SAMs showed no detectable contamination.

**Surface Tensions of the Films.**

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could form at the interface of CF3-terminated SAMs with polar test liquids such as glycerol and water.

Perfluorinated surfaces, however, typically exhibit little or no contribution from $\gamma_{AB}$. In addition, perfluorinated surfaces are typically wetter than hydrocarbon surfaces by all types of liquids, including those that are polar and exhibit hydrogen bonding. Consequently, it is likely that we are observing a different type of phenomenon. We propose that (at least in this system) the positive values $\gamma_{SA}$ instead represent attractive polar interactions between the contacting polar liquids and the surface CF3 dipoles. We are currently exploring this phenomenon in greater depth.

The fact that $\gamma_S$ for the CF3-terminated surfaces (ca. 15 mJ m$^{-2}$) is markedly smaller than that for the CH3-terminated surfaces (ca. 19 mJ m$^{-2}$) is due predominantly to the relatively large fluorinated CH2 dipoles present at the surface. The low surface energies of the CF3-terminated SAMs appear, however, to be predominantly influenced by the weakness of the dispersive interactions in these films.

**Table 2. Average Surface Tensions for CH3- and CF3-Terminated SAMs at 293 K in mJ m$^{-2}$**

<table>
<thead>
<tr>
<th>SAMs</th>
<th>$\gamma_S$</th>
<th>$\gamma_{SLW}$</th>
<th>$\gamma_{SA}$</th>
<th>$\gamma'-S_A$</th>
<th>$\gamma''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H10-H16a</td>
<td>19.1 ± 0.4</td>
<td>19.1 ± 0.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H10-H16b</td>
<td>18.5 ± 0.5</td>
<td>18.5 ± 0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F11-F16a</td>
<td>15.0 ± 0.4</td>
<td>14.3 ± 0.4</td>
<td>0.7 ± 0.2</td>
<td>0.2 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>F11-F16b</td>
<td>16.0 ± 0.8</td>
<td>15.8 ± 0.8</td>
<td>0.5 ± 0.2</td>
<td>0.1 ± 0.05</td>
<td>0.5 ± 0.1</td>
</tr>
</tbody>
</table>

$^a$ Calculated using HD as the dispersive test liquid. $^b$ Calculated using MI as the dispersive test liquid.

The uncertainties were estimated by propagating an uncertainty of $\pm 1$ mJ m$^{-2}$ in measurements of contact angle.

**Conclusions**

The composition, thickness, and wettability of terminally fluorinated SAMs prepared from CF3(CH2)$_n$SH (where $n = 9$–15) were examined and compared to their nonfluorinated analogues. While the terminally fluorinated SAMs appear to be highly oriented and densely packed like their hydrocarbon predecessors, several differences in the surface properties were observed. First, the ellipsometric thicknesses of the CF3-terminated SAMs were less than those of the corresponding CH3-terminated SAMs of identical chain length. This discrepancy arises at least in part from the use of an anomalously high value of the refractive index in the analysis of the CF3-terminated SAMs. Second, the contact angle hysteresis measured using a variety of test liquids was similar for all SAMs except those that were terminally fluorinated and of shorter chain length (i.e., F10 and F11), for these SAMs, the hysteresis was noticeably higher. We attribute this effect to greater disorder in the shorter terminally fluorinated SAMs, where the interchain van der Waals stabilization is apparently overcome by repulsion between the relatively large fluorinated end termini. Third, the CF3-terminated SAMs exhibited significantly lower surface energies than the CH3-terminated SAMs despite the presence of a significant positive contribution from $\gamma_{AB}$, which is zero for the CH3-terminated SAMs. Although $\gamma_{SA}$ is usually taken to represent Lewis acid–base (or hydrogen-bonding) interactions between contacting media, we propose that (at least in this system) the positive values $\gamma_{AB}$ instead represent attractive polar interactions between the contacting polar liquids and the surface CF3–CH2 dipoles of the terminally fluorinated SAMs. The low surface energies of the CF3-terminated SAMs appear, however, to be predominantly influenced by the weakness of the dispersive interactions in these films.

**Acknowledgment.** We thank the University of Houston Energy Laboratory for providing seed funding and the National Science Foundation (DMR-9700662) for current support of this research. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research (ACS-PRF 30614-G5). We thank Dr. Yuan Z. Lu for assistance with the XPS measurements, which were provided with support from the Harvard University MRSEC/NSF under Award Number DMR-9400396. We thank Mr. Lon Porter for assistance with the statistical analyses. We also thank Professors Manoj Chaudhury and Paul Laibinis for many helpful discussions.

LA980154G