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Self-assembled monolayers of CF₃-terminated alkanethiols on gold

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Abstract

The wettability and friction of self-assembled monolayers (SAMs) of terminally fluorinated alkanethiols, CF₃(CH₂)_nSH with $n = 9–15$, and their nonfluorinated analogs, CH₃(CH₂)_nSH with $n = 9–15$, were examined and compared. Surprisingly, the CF₃-terminated monolayers were wetted more by water, glycerol and *N,N*-dimethylformamide than were the CH₃-terminated SAMs. The terminally fluorinated films, however, exhibited significantly lower surface energies. The origin of these trends is discussed. The two types of monolayers were also studied by atomic force microscopy (AFM). Compared to the CH₃-terminated SAMs, the fluorinated films revealed an approximately 3-fold increase in friction. A new model for the frictional response, which is based on the difference in size between the methyl and trifluoromethyl groups, is proposed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Interfacial wetting, adhesion and friction play important roles in numerous technological, environmental and biological systems. Researchers have long sought to understand the microscopic and macroscopic issues related to these phenomena. Since wetting, adhesion and friction are the manifestation of intermolecular forces between

two interfaces, a detailed knowledge of the chemical structure and composition of these interfaces can give further insight into the nature and action of the forces involved.

An excellent technique for studying the effects of changes in molecular structure and composition upon interfacial properties involves the use of self assembled monolayers (SAMs) (for a recent review see [1]). Chemisorption of alkanethiols on bare gold generates densely packed and highly ordered monolayer films with the sulfur atoms binding tightly to the surface of gold (Fig. 1). Utilization of specific co-functionalized alkanethiols can be used to tailor the interfacial properties of the surfaces [2].

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Fluorinated organic materials enjoy widespread technological interest because of their low surface energies [3]. To further our understanding of fluorinated thin films and to facilitate the design and development of new and useful materials, we are undertaking a systematic exploration of the structure and interfacial properties of partially fluorinated organic thin films [4–7]. This paper describes studies of SAMs generated from $\text{CF}_3(\text{CH}_2)_n\text{SH}$ ($n = 9\text{--}15$). We compare their wettability and frictional response to those of SAMs generated from the corresponding non-fluorinated alkanethiols $\text{CH}_3(\text{CH}_2)_n\text{SH}$.

2. Experimental

2.1. Materials

Hexadecane, water, glycerol and *N,N*-dimethylformamide were obtained from Aldrich Chemical in the highest available purity, and were used as received. The ω,ω,ω -trifluoroalkanethiols were synthesized using an approach developed in our laboratories; the details of the syntheses and characterization are described elsewhere [8]. The normal alkanethiols were either commercially available or synthesized using unexceptional methods.

2.2. Preparation of SAMs

For the wettability studies, gold (2000 Å) was thermally evaporated onto silicon(100) wafers that had been precoated with chromium (100 Å) to promote adhesion. Pieces of the gold-coated

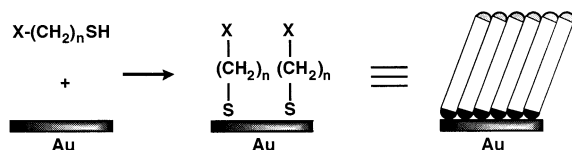


Fig. 1. Depiction of the formation of SAMs by chemisorption of alkanethiols on the surface of gold. The tail group X can be varied easily by organic synthetic methods to generate monolayers with tailored interfacial properties.

wafers were immersed in 1 mM ethanolic solutions of the thiols for 24 h. For the atomic force microscopy (AFM) studies, crystalline gold was prepared by annealing gold wire in an H_2/O_2 flame until a small ball containing several (111) facets formed at the end of the wire [9]. These balls were immersed in the thiol-containing solutions for 24 h before analysis by AFM.

2.3. Characterization of SAMs

The film thicknesses were measured with a Rudolph Auto EL III ellipsometer employing a HeNe laser beam (632.8 nm) at an angle of incidence of 70° . For all films, a refractive index of $n_D = 1.45$ was assumed. Advancing and receding contact angles were measured using a ramé-hart model 100 contact angle goniometer. Surface topographies and frictional properties were investigated by atomic force microscopy. In frictional measurements using AFM, the lateral deflection of the cantilever is monitored as the sample is scanned underneath the tip/cantilever assembly [4,7]. Detailed experimental procedures have been provided elsewhere [10].

3. Results and discussion

3.1. Film thicknesses

As shown in Fig. 2, the observed ellipsometric thicknesses for the CH_3 -terminated films increase successively from 12.5 to 19.5 Å with increasing chain length. The CF_3 -terminated films showed slightly lower thicknesses for the same chain lengths—due in part to the use of an inappropriate value of refractive index for these films [5]. Since, however, we observe the same increase of about 1.25 Å per methylene group for both types of films, the ellipsometric data suggest that the CF_3 -terminated alkanethiols form densely packed and highly ordered SAMs.

3.2. Wettabilities

Contact angle measurements can provide useful insight into the structure and order of organic

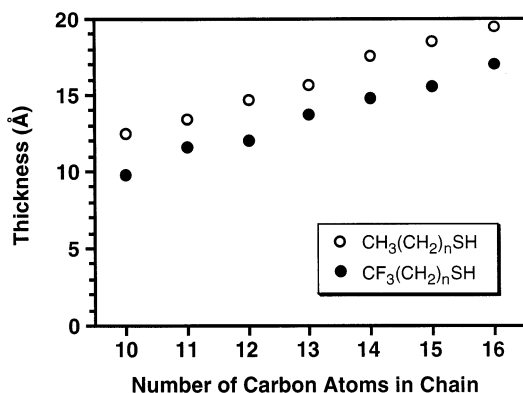


Fig. 2. Ellipsometric thicknesses of CH₃- and CF₃-terminated monolayers versus the number of carbon atoms in the chain. Filled circles (●), CF₃(CH₂)_nSH; open circles (○), CH₃(CH₂)_nSH.

thin films [11,12]. We measured the contact angles of the CF₃- and CH₃-terminated SAMs using four different test liquids: hexadecane (HD), water (W), glycerol (GL) and *N,N*-dimethylformamide (DMF). Hexadecane interacts with the surface only through dispersive forces, whereas water and glycerol are capable of hydrogen bonding and dipole–dipole interactions. We chose to employ DMF as a contacting liquid because of its large dipole moment and its inability to hydrogen bond.

Figure 3 shows the advancing contact angles (θ_a) of the test liquids on both the hydrocarbon and the fluorocarbon surfaces as a function of the chain length of the alkanethiols. The contact angles of hexadecane, water and glycerol on the hydrocarbon SAMs agree with those reported in the literature [13]. The contact angles of hexadecane on the fluorinated SAMs were about 17° higher than those on the hydrocarbon SAMs, indicating weaker dispersive interactions between the liquid and the fluorocarbon surfaces. Surprisingly, the contact angles of water, glycerol and DMF were measurably lower on the fluorinated surfaces. While hydrogen bonding might account for the enhanced wettability of the CF₃-terminated SAMs by water and glycerol [14], DMF is incapable of hydrogen bonding; consequently, some other effect must be responsible for the

enhanced wettability of the CF₃-terminated surfaces by DMF.

Zisman proposed that switching from a CH₃ to a CF₃ group at the surface of oriented films would create a strong dipole that could interact with contacting liquids [15]. Based on this model, it seems plausible that the wettabilities of the polar liquids could be influenced by surface dipoles. Insight into this issue was provided by examining the relationship between the contact angles and the chain lengths of the thiols used to generate the SAMs. Hexadecane, for example, exhibits a parity (or ‘odd–even’) effect on the hydrocarbon surfaces: as illustrated in Fig. 3, this liquid appears to sense the orientation of the terminal CH₃ group as a function of the odd or even number of methylenes in the alkyl chains [16,17]. We observed a similar effect with DMF as the contacting liquid, but not with water or glycerol. On the fluorocarbon surfaces, however, only DMF exhibits a strong ‘odd–even’ effect. Interestingly, the relationship between odd/even chain lengths and the magnitude of the contact angles are reversed for DMF on the two types of surfaces. Since the orientation of the surface dipoles are

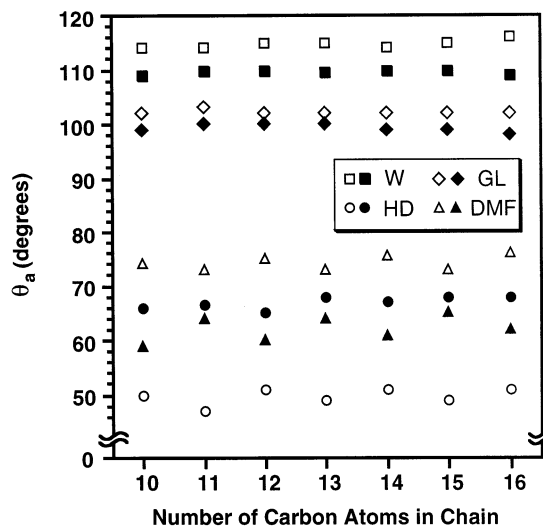


Fig. 3. Advancing contact angles θ_a of SAMs as a function of the chain length of the thiols. Filled symbols, CF₃(CH₂)_nSH; open symbols, CH₃(CH₂)_nSH.

likely to change with odd or even chain lengths, these results strongly suggest that dipole–dipole interactions influence the wettabilities of the CF₃-terminated surfaces.

From the contact angles of hexadecane, water, and glycerol, we calculated the surface tensions of the films using the method of van Oss et al. [18], which gives the surface tension γ as the summation of a Lifshitz–van der Waals component γ^{LW} and an acid–base component γ^{AB} . The term γ^{AB} further consists of the components γ^+ for acid (electron acceptor) and γ^- for base (electron donor) interactions: $\gamma^{\text{AB}} = 2(\gamma^+ \gamma^-)^{1/2}$. To calculate the surface tension components from our contact angle data, we used the modified Young–Dupré equation:

$$(1 + \cos \theta)\gamma_{\text{L}} \\ = 2(\gamma^{\text{LW}}\gamma_{\text{L}}^{\text{LW}})^{1/2} + 2(\gamma^+ \gamma_{\text{L}}^-)^{1/2} + 2(\gamma^- \gamma_{\text{L}}^+)^{1/2}$$

In this equation, γ_{L} represents the surface tension, and $\gamma_{\text{L}}^{\text{LW}}$, γ_{L}^+ , γ_{L}^- represent the surface tension components of the test liquids, which were obtained from the literature [19]. The γ values we calculated varied little with changes in the chain lengths of the alkanethiols. For the CH₃-terminated films, we obtained an average value of $\gamma = 19.0 \text{ mJ/m}^2$ with γ^{AB} , γ^+ and γ^- equal to zero. For the CF₃-terminated films, we obtained an average value of $\gamma = 15.0 \text{ mJ/m}^2$ with $\gamma^{\text{LW}} = 14.3$, $\gamma^{\text{AB}} = 0.7$, $\gamma^+ = 0.2$ and $\gamma^- = 0.5 \text{ mJ/m}^2$. Accordingly, the positive value of γ^{AB} can be interpreted to indicate that hydrogen bonding between water or glycerol and the CF₃ groups on the surface gives rise to the enhanced wettability observed for these liquids on the CF₃-terminated surfaces [14]. The wettability data obtained using DMF, however, suggest that dipole–dipole interactions might also give rise to an enhanced wettability (vice supra). Nevertheless, since the calculated surface tension is lower for the CF₃-terminated films than for the CH₃-terminated films, the dispersive components of the surface tension appear to dominate these polar (or hydrogen bonding) contributions.

3.3. AFM studies

Atomic force microscopy has become increasingly useful in the characterization of organic materials such as self-assembled monolayer (SAM) and Langmuir–Blodgett (LB) films, which can serve as well-defined models of organic thin film lubricants (for a review, see [20,21]). In measurements of friction using AFM, fluorinated SAMs and LB films have been observed to exhibit higher frictional properties than similar hydrogenated ones (for an overview, see references [4] and [7] and references therein). Possible factors influencing this phenomenon include differences in packing energy, packing density, elasticity, local disorder and chemical structure/composition; all of which can be largely interrelated. In this report, we describe the frictional differences that arise solely from small differences in the chemical makeup of the terminal group of SAMs on gold.

We prepared SAMs from CF₃(CH₂)₁₂SH and CH₃(CH₂)₁₂SH on atomically flat Au(111) surfaces. We observed indistinguishable lattice spacings for both films: $4.9 \pm 0.2 \text{ \AA}$ for the CH₃-terminated film and $4.8 \pm 0.2 \text{ \AA}$ for the CF₃-terminated film [4,7]. This result is somewhat surprising considering that a CF₃ group has an approximately 40% larger cross sectional area than a CH₃ group. Reports from the literature, however, suggest that the CF₃ group can be substituted for the CH₃ group without disrupting the packing of alkyl chains in the solid state [22,23]. Furthermore, due to the identical backbone structures of the two types of films, we would expect them to exhibit similar order, elasticity, packing energy, and packing density. The only clear difference between these two types of films is the chemical makeup of the terminal methyl groups.

A plot of friction versus applied load (Fig. 4) shows that the frictional response for the CF₃-terminated film is approximately three times that for the CH₃-terminated film at identical loads (despite potential differences in device design and calibration techniques, the frictional data for the hydrocarbon surface are consistent with those

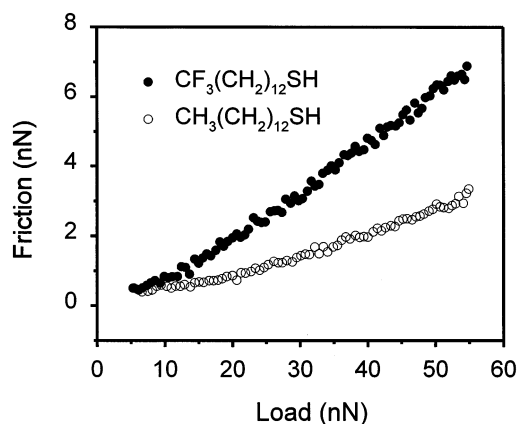


Fig. 4. From friction-load maps acquired on the two films, the average kinetic friction is plotted versus the external applied load: CF₃-terminated (●) and CH₃-terminated (○). The frictional response of the film is defined as the force of friction at a specified load.

reported previously [24]). One possible origin for the frictional difference could be the difference in adhesive forces between the AFM tip and the two types of films, perhaps arising from dipole–dipole interactions and/or hydrogen bonding at the interface. However, normal pull-off forces and the adhesive forces during sliding were indistinguishable for the two types of films [4,7].

Another possible origin of the frictional difference revolves around the difference in size of the methyl and trifluoromethyl groups. One effect of the difference in size is that the CF₃–CH₂ bond possesses a higher rotational barrier than the CH₃–CH₂ bond [4,7], which might contribute to an increase in friction [25]. Additionally, since the lattice spacings of both SAMs are indistinguishable, the larger size of the trifluoromethyl groups suggests a more densely packed arrangement at the outermost portion of these films. As a consequence, lateral (and perhaps rotational) motions within the plane of the CF₃ groups are likely to be highly cooperative over relatively long distances, leading to long range multimolecular interactions. These additional interactions can be used to rationalize the higher frictional response observed for the CF₃-terminated films [4,7].

4. Conclusions

We prepared SAMs from CF₃-terminated alkanethiols and compared their wettabilities, surface structures, and frictional responses with those of their nonfluorinated analogs. We observed the surprising effect that polar solvents like water, glycerol, and DMF wet the CF₃-terminated films more than the CH₃-terminated films. Wettability by hexadecane exhibited the opposite trend. Calculation of the acid–base contribution γ^{AB} to the surface tension γ according to the approach of van Oss, Chaudhury and Good indicated the possibility of hydrogen bonding between water or glycerol and the CF₃ groups on the surface. Since, however, the aprotic liquid DMF showed similar trends in wettability, we propose that oriented strong dipoles in the outermost portion of the CF₃-terminated films contributes partially (if not solely) to the increase in wettability toward the polar liquids. Studies by AFM showed that the CF₃-terminated alkanethiols formed densely packed and well ordered SAMs with lattice spacings that are indistinguishable from their nonfluorinated analogs. An approximate 3-fold greater frictional response was observed for the CF₃-terminated films. We propose that the higher friction results from additional modes of energy dissipation through long range lateral (and perhaps rotational) interactions in the outermost portion of the CF₃-terminated films.

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