



WETTABILITY AND FRICTION OF CF_3 -TERMINATED MONOLAYER FILMS ON GOLD

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ABSTRACT

Studies of the wettability and friction of self-assembled monolayers (SAMs) generated from the terminally fluorinated alkanethiols ($CF_3(CH_2)_nSH$, $n = 9-15$) on gold are reported. These data were compared to those of SAMs generated from the non-fluorinated analogs ($CH_3(CH_2)_nSH$, $n = 9-15$). The CF_3 -terminated SAMs were less wettable by hexadecane and methylene iodide, but surprisingly more wettable by water and glycerol than were the CH_3 -terminated SAMs. Measurements of friction by atomic force microscopy (AFM) revealed an approximate threefold increase in friction on the CF_3 -terminated films compared to the CH_3 -terminated films. A new model for the frictional response of fluorinated SAMs is proposed. © 1999 Elsevier Science Ltd

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INTRODUCTION

Fluorinated organic materials have found widespread use as coatings, lubricants, and sealants in a variety of interfacial applications [1]. Fluorocarbons are particularly useful because they

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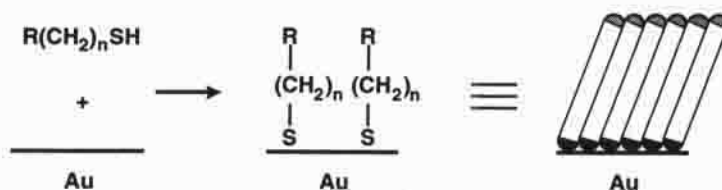


FIG. 1

Schematic depicting the formation of SAMs by exposing alkanethiols to the surface of gold.

are chemically and biologically inert, exhibit high thermal and mechanical stabilities, are resistant to oxidation and corrosion, and are water resistant and nonadhesive. Despite their widespread use, however, the relationships between the interfacial properties (e.g., wettability and friction) and the structure and composition of fluorinated surfaces remain poorly understood [2].

To further our understanding of fluorinated thin films, we chose to study self-assembled monolayers (SAMs) of fluorinated alkanethiols on gold as a model system [3]. In the technique of self-assembly, exposure of a gold surface to a solution of alkanethiol or dialkyldisulfide results in the formation of a well-defined and densely packed monolayer film with the sulfur atoms binding to the gold surface (Fig. 1). The alkyl chains in these films are tilted approximately 30° from the normal to the surface. One of the primary advantages of studying SAMs on gold is the convenience of using organic synthesis to provide atomic level control over the interfacial structure and composition of the films [4].

EXPERIMENTAL

SAMs were prepared by exposing ethanolic solutions of the fluorinated alkanethiols ($\text{CF}_3(\text{CH}_2)_n\text{SH}$, $n = 9-15$) and their non-fluorinated analogs ($\text{CH}_3(\text{CH}_2)_n\text{SH}$, $n = 9-15$) to either freshly evaporated gold (for the wettability studies) or crystalline gold (for the AFM studies) for 24 h. The 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 [5]. The wettabilities were determined by contact angle measurements using a Ramé-Hart model 100 contact angle goniometer. Atomic force microscopy (AFM) was used to explore both the molecular scale surface topographies and frictional properties of SAMs derived separately from $\text{CF}_3(\text{CH}_2)_{12}\text{SH}$ and $\text{CH}_3(\text{CH}_2)_{12}\text{SH}$. A detailed description of the procedures involved in these measurements is provided elsewhere [2].

RESULTS AND DISCUSSION

Wettability [6]. In studies of wettability [7], we employed three classes of contacting liquids: non-polar (hexadecane), polar without hydrogen bonding (methylene iodide) and polar with hydrogen bonding (water and glycerol). Figure 2 shows the observed advancing contact angles (θ_a) as a function of the number of carbon atoms in the alkyl chains. The values of θ_a for each test liquid are roughly constant over the entire range of chain lengths for each type of SAM. The data for the CH_3 -terminated SAMs agree with those published previously [8]. In contrasting the two types of SAMs, the differences in θ_a ($\Delta\theta_a = \theta_{\text{CF}(3)} -$

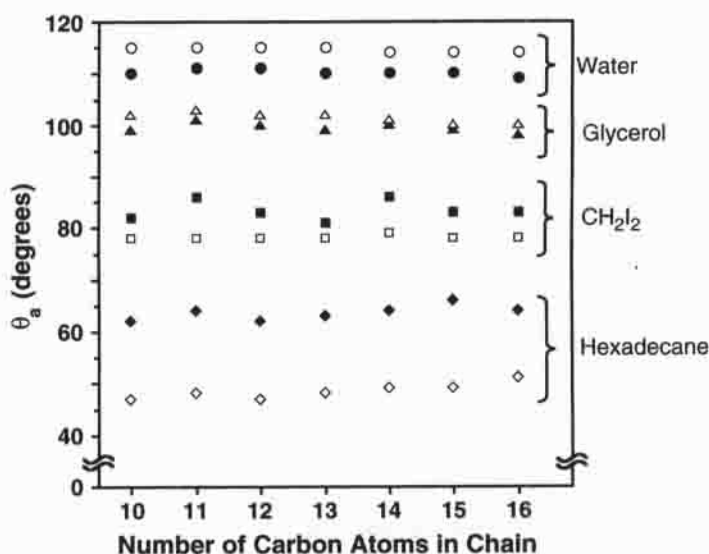


FIG. 2

Advancing contact angles of SAMs generated from $\text{CF}_3(\text{CH}_2)_n\text{SH}$ (filled symbols) and $\text{CH}_3(\text{CH}_2)_n\text{SH}$ (open symbols) as a function of the overall chain length of the thiol.

θ_{CH_3}) are roughly constant over the chain lengths examined here: $14\text{--}15^\circ$ for hexadecane, $6\text{--}7^\circ$ for methylene iodide, -2° for glycerol and -4° for water. These data suggest that the CF_3 -terminated surfaces, compared to the CH_3 -terminated surfaces, are wetted *less* by hexadecane and methylene iodide, but wetted *more* by glycerol and water. These trends in wettability are, to our knowledge, unprecedented for low free-energy surfaces. The hysteresis of the contact angles ($\theta_a - \theta_r$, where θ_r = receding contact angle) is similar for the two types of surfaces (data not shown), which suggests that the films have similar smoothness and homogeneity [9,10].

Surface Tensions [6]. We calculated the surface tensions of the films using the method of van Oss, Chaudhury, and Good [11]. This method yields the surface tension γ as a summation of the components γ^{LW} and γ^{AB} , based on Lifshitz-van der Waals (dispersive) interactions and acid-base (polar, hydrogen bonding) interactions, respectively. The γ^{AB} term further consists of the asymmetric components γ^+ for acid (electron acceptor) and γ^- for base (electron donor) interactions: $\gamma^{\text{AB}} = 2(\gamma^+\gamma^-)^{1/2}$. The contact angle θ and the components of the surface tension can be related by the modified Young-Dupré equation:

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

where γ_L represents the surface tension and γ_L^{LW} , γ_L^+ and γ_L^- the surface tension components of the test liquids [11]. For these calculations, we employed the measured values of θ_a together with literature values of surface tension for the contacting liquids [12]. We found the calculated values of γ to be consistent for all chain lengths for each type film [6]. For CH_3 -terminated films, for example, we obtained an average value for the surface tension of $\gamma = 19.0 \text{ mJ m}^{-2}$ with $\gamma^{\text{LW}} = 19.0 \text{ mJ m}^{-2}$ and γ^{AB} , γ^+ , and γ^- all equal to zero. For

CF₃-terminated films, we found $\gamma = 15.0 \text{ mJ m}^{-2}$ with $\gamma^{\text{LW}} = 14.3$, $\gamma^{\text{AB}} = 0.7$, $\gamma^+ = 0.2$, and $\gamma^- = 0.5 \text{ mJ m}^{-2}$.

Since the replacement of a CH₃ group by a CF₃ group will undoubtedly give rise to a strong dipole at the ω -terminus of an alkanethiol, the formation of a SAM from CF₃(CH₂)_nSH will generate an interface in which these strong dipoles are oriented near the contacting liquids. The interaction between the contacting liquids and these dipoles should give rise to a positive contribution to γ for the CF₃-terminated films. Hydrogen bonding between the CF₃ groups and the hydroxyl groups of glycerol and water [13] should also give rise to a positive contribution to γ for the CF₃-terminated films. Indeed, the presence of dipole interactions and/or hydrogen bonding can be used to rationalize the enhanced wettability of the CF₃-terminated films toward water and glycerol. Since, however, most perfluorinated surfaces exhibit little or no contribution from $\gamma_{\text{S}}^{\text{AB}}$ [12], we believe that dipole interactions are predominantly responsible for the enhanced wettabilities observed here.

The calculated value of the total surface tension γ for the CF₃-terminated films (15.0 mJ m^{-2}) is lower than that for the CH₃-terminated films (19.0 mJ m^{-2}). Consequently, any polar contribution to the surface tensions of the CF₃-terminated films appears to be more than compensated by weak dispersive interactions, which are characteristic of fluorinated interfaces [14].

Imaging of SAMs by AFM [2]. Atomic force microscopy is becoming increasingly used in the characterization of organic thin films [15]. A number of studies, for example, have used AFM to examine Langmuir-Blodgett films and SAMs, since they represent well-defined models of organic lubricant systems [16]. To systematically explore the effects of introducing fluorine into self-assembled monolayers, we prepared SAMs from CF₃(CH₂)₁₂SH and CH₃(CH₂)₁₂SH on atomically flat Au(111) surfaces, and characterized them using AFM [2]. The lateral force AFM images showed that the SAMs derived from both molecules were highly ordered (data not shown). Because a CF₃ group has an approximately 40% larger cross-sectional area than a CH₃ group [2], we were surprised to find the lattice spacings of the two films to be indistinguishable: $4.9 \pm 0.2 \text{ \AA}$ for the CH₃-terminated film and $4.8 \pm 0.2 \text{ \AA}$ for the CF₃-terminated film. We attribute the similar lattice spacings to the identical backbone structures of the SAMs, where the strong van der Waals interactions between the alkyl chains appear to more than compensate for repulsive interactions between terminal CF₃ groups. Indeed, reports from the literature [17,18] suggest that the CF₃ group can be substituted for the CH₃ group without disrupting the packing of alkyl chains in the solid state.

Studies of Friction by AFM [2]. Lateral force measurements—performed by monitoring the twisting of the AFM cantilever as the surfaces were slid beneath the tip—were used to probe the frictional properties of the two films. It is well established that perfluorocarbon-based films exhibit higher frictional properties than simple hydrocarbon-based films [2]. Potential factors contributing to molecular-level frictional properties include packing energy, packing density, elasticity, local disorder, and chemical structure/composition. These factors are largely interrelated in thin film systems. We targeted the CF₃(CH₂)_nSH vs. CH₃(CH₂)_nSH system in an effort to deconvolute these factors: these two types of films should exhibit similar packing energy, packing density, elasticity, and disorder due to their identical backbone structures. Given the similar lattice spacings described above, the only difference lies in the chemical nature of the terminal methyl groups.

The results of our frictional measurements are shown in Figure 3 as a plot of friction versus

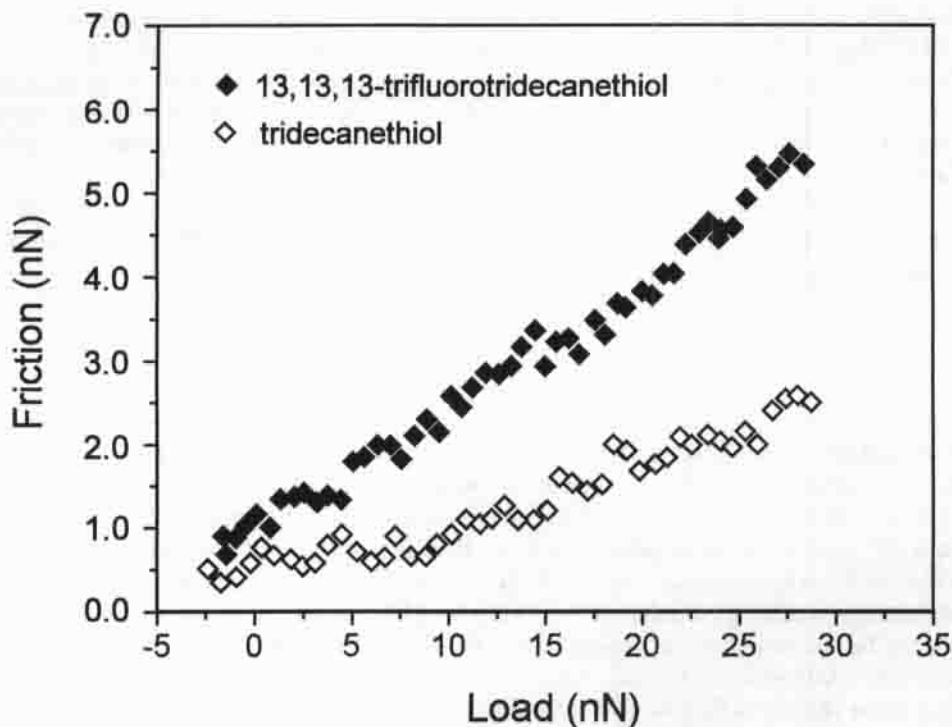


FIG. 3

Frictional force versus the applied load measured as a function of decreasing load for SAMs generated from $\text{CF}_3(\text{CH}_2)_{12}\text{SH}$ (filled symbols) and $\text{CH}_3(\text{CH}_2)_{12}\text{SH}$ (open symbols). Negative loads correspond to regimes where an attractive force arises due to adhesion between the tip and the sample.

applied load. We performed the studies at the low loads shown here to avoid substantial deformation of the monolayers. These data show that the frictional response (i.e., the friction observed at a specified load) of the CH_3 -terminated SAMs (1.6 nN at 20 nN applied load with a slope of $\mu = 0.08$) compares well with the data obtained by Porter and co-workers [19] for a monolayer of octadecanethiol on gold (1.4 nN at 20 nN applied load with a slope of $\alpha = 0.07$). The data also show that the frictional response of the CF_3 -terminated SAM is approximately three times that of the CH_3 -terminated SAM. There are at least two possible origins for this difference in frictional response. The first involves potential differences in adhesive forces between the AFM tip and the samples. It seems possible, for example, that the AFM tip would adhere most strongly to the CF_3 -terminated surface because of hydrogen bonding and/or dipole interactions at the interface, giving rise to the increased frictional response. The data from Figure 3 in the negative load regime (where an attractive normal force arises from adhesion between the tip and the sample) indicate, however, that the adhesive forces during sliding are similar for the two films. These data suggest that tip-sample adhesion is not responsible for the observed frictional difference [20].

Another possible origin of the observed differences in frictional response concerns the difference in size of the methyl and trifluoromethyl groups. This factor gives rise to two

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