

MOLECULAR LEVEL INTERPRETATIONS OF FRICTIONAL FORCE DATA COLLECTED WITH ATOMIC FORCE MICROSCOPY: CHAIN LENGTH EFFECTS IN SELF ASSEMBLED ORGANIC MONOLAYERS

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Introduction

Self-assembled monolayers (SAMs) have been adopted as models of organic surfaces within a number of research fields. Within the tribological community, these films have been studied as models of boundary layer lubricants as well as fundamental systems that allow insight into the origins of frictional events. Although atomic force microscopy (AFM) does not represent a molecularly specific probe of the surface, topographic and frictional data can be interpreted in terms of composition and structure for carefully designed systems.

Within the body of previous work, the dependence of friction on the molecular structure of thin organic films has been studied by a number of groups. A general trend emerging from these studies is well-ordered and closely-packed films exhibit lower interfacial friction than more disordered systems. A subset of this work has noted frictional variations with the specific orientation of film components. Studies such as these are yielding increasingly greater insight into the nature of interaction between the probe tip and the organic surface. The present study addresses the nature of tip-surface interactions giving rise to frictional forces for well-ordered SAMs. Specifically the frictional properties of methyl, trifluoromethyl, and phenyl terminated alkanethiol monolayers adsorbed on Au(111) have been measured as a function of chain length. These studies reveal that the contact area between the probe tip and film surface, on an atomic and molecular scale, contributes to systematic variations in the frictional properties of well-organized films.

Experimental

Materials. The SAMs used in this study were derived from a series of alkanethiols having chain lengths of 12 to 15 carbons and several different terminal groups. The thiols included $\text{CH}_3(\text{CH}_2)_n\text{SH}$, $\text{CF}_3(\text{CH}_2)_n\text{SH}$, and $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{SH}$ where $n = 12-15$ for each termination. These thiol adsorbates have been synthesized through procedures documented in previous reports.¹⁻³

Specifically, monolayers were generated by adsorption of thiols dissolved in ethanol (1 mM) onto gold substrates. These substrates were prepared by annealing a gold wire (~1 mm in diameter) in a H_2/O_2 flame to produce a number of atomically flat (111) terraces around the circumference of the 'micro-ball'. All AFM friction and topography data were measured on these (111) terraces. Wettability measurements were performed on polycrystalline gold substrates prepared by thermally evaporating gold on silicon wafers.

Water, hexadecane, and dimethylformamide (DMF) were used as received as contacting liquids for the wettability studies.

Instrumentation. The characterization of the frictional properties of the SAMs was performed using beam-deflection based AFM. In this approach, laser light is focused on the backside of microfabricated cantilever and the reflected beam is sensed by a position-sensitive photodiode. The SAM/Au sample is placed on top of a piezo scan tube and allowed to interact with a fixed AFM tip. The simultaneous measurements of normal bending and lateral twisting of a tip/cantilever assembly, arising from the interaction between the tip and the sample surface, are recorded and assigned as 'load' and 'friction'. Load forces are reported in nanonewtons using the manufacturer's supplied value for a normal force constant while frictional forces are reported in uncalibrated units of photodetector voltage. Preliminary experiments have been performed first with different tip/cantilever assemblies to investigate the frictional properties of each series of SAMs having identical terminal groups. Then, a single tip/cantilever assembly was employed to investigate the relative frictional properties of the SAM having three different terminal groups, CH_3 -, CF_3 -, and C_6H_5 -terminal groups. For wettability studies of these films, a rame-hart model 100 contact angle goniometer was used to measure the advancing contact angles.

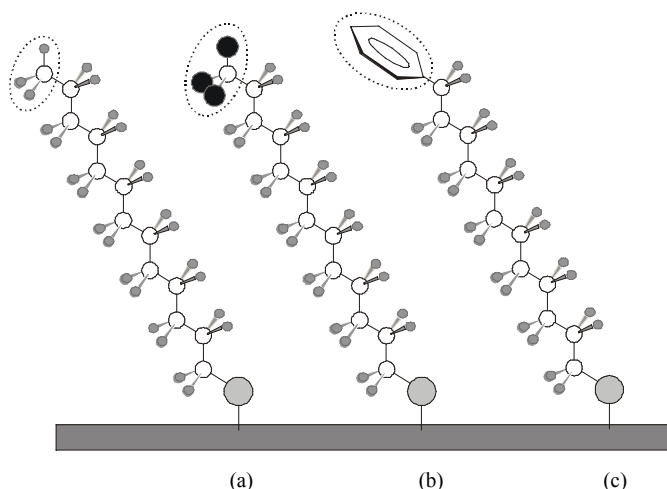


Figure 1. Schematic representation of the (a) methyl-terminated, (b) trifluoromethyl-terminated, and (c) phenyl-terminated SAMs studies as a function of chain length (12 to 15 total carbons).

Results and Discussion

The frictional responses, measured as a function of increasing load, for the methyl-terminated monolayers of four different chain lengths are shown in **Figure 2**. Similar data were obtained for decreasing loads as well. The films exhibit similar frictional properties at lower applied loads, however measurements at higher loads clearly distinguish among the films. The differences in the frictional properties are more clearly revealed by plotting the friction measured at a specified load versus chain length. Data plotted in this way are shown in **Figure 3** for the methyl-, trifluoromethyl-, and phenyl-terminated monolayers. The error bars shown in this plot represent the standard deviation of friction measurements made at different locations across the sample surface. All of the data presented in **Figure 3** were obtained with the same tip in order to allow the precise comparison between samples. The systematic variation in the frictional response of the methyl-terminated films as a function of chain length is apparent and has been previously reported by Porter and coworkers.⁴ In contrast, only a trend of decreasing frictional response with increasing chain length is observed for the trifluoromethyl- and phenyl-terminated SAMs.

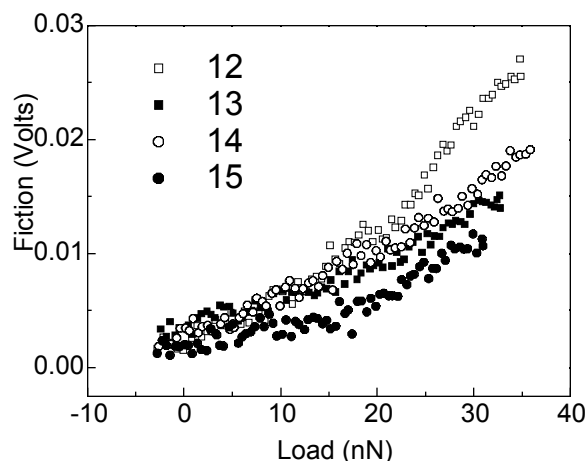


Figure 2. Frictional responses of the methyl-terminated n -alkanethiols of four different carbon chain lengths (12 to 15) measured with AFM.

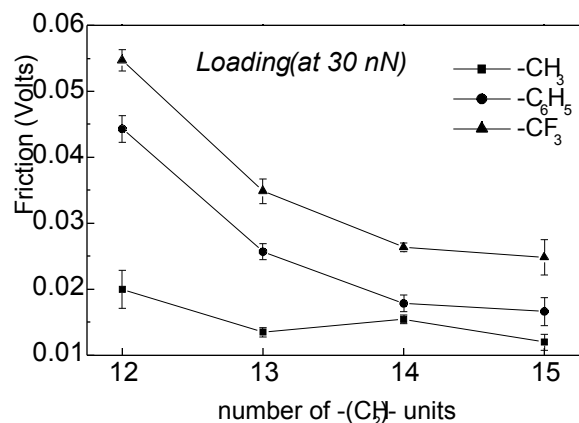


Figure 3. Frictional forces measured at an applied load of 30 nN for methyl-, trifluoromethyl-, and phenyl-terminated alkanethiols ranging in chain length from 12 to 15 methylene units.

The influence of molecular structure on interfacial properties was further investigated for these films by measuring the advancing contact angle of water, hexadecane, and dimethylformamide on each of the SAM surfaces. The results of these measurements have been previously reported in detail elsewhere.^{5,6} Briefly, a systematic variation in contact angle was observed on the methyl-terminated monolayers for hexadecane and DMF contacting liquids with the chains containing an even number of methylene units exhibiting lower contact angles. For the trifluoromethyl- and phenyl-terminated films, only the results of contact angles formed with DMF showed a dependence on chain length. (Note that hexadecane fully wet the surfaces of the phenyl-terminated films.)

The variation in contact angle as a function of contacting liquid is commonly understood in terms of interfacial free energies. The variation in contact angle as a function of chain length can be understood in terms of variations in the specific molecular structure of the exposed surface. A similar explanation (dipole orientation) was offered in the previous discussion of the variation in friction for methyl-terminated monolayers.⁴ The results measured for a series of functional terminations and presented here suggest an alternative mechanism may be responsible for the frictional variation. As the presence of both the trifluoromethyl and phenyl groups lead to the greater surface dipoles, a greater frictional variation would be expected with changes in chain length if this were the dominating interaction.

We propose that the frictional differences observed with varying chain length for the methyl-terminated films arises as a result of an increased effective area of contact between the tip and the molecular structure of the film. This concept is different from the traditional idea of contact area in that it involves the density of atomic species within the interacting region. Each of these alkanethiols forms an ordered ($\sqrt{3} \times \sqrt{3}$)R30° structure, with respect to the underlying gold surface, with a lattice spacing of ~ 5 Å. This represents an average spacing between the methyl carbons of the terminal groups at the film surface. For films containing an odd number of methylene units, the terminal group is oriented approximately 30° from surface normal (measured with respect to the final C-C bond). For films containing an even number of methylene units, the terminal group is oriented approximately 60° from surface normal. This more canted orientation effectively exposes the methylene unit lying beneath the terminal methyl group to contact with the probe tip. This increases the number of atomic contacts per unit area and as a result leads to higher friction. In the case of films containing an odd number of methylene units, this interaction is shielded in the absence of substantial film deformation. Both the trifluoromethyl and phenyl terminal groups are substantially larger than the methyl group. We believe that these groups shield the underlying methylene units, regardless of head group orientation, and thus do not exhibit frictional variations as a function of chain length. The overall higher magnitude of frictional forces measured at the surfaces of trifluoromethyl and phenyl terminated films results from additional steric interactions, which arise from the presence of the bulkier terminal groups.^{7,8}

Conclusions

This work demonstrates the sensitivity of frictional measurements performed with atomic-scale areas of contact to details of molecular structure and orientation. The frictional properties of methyl-terminated SAMs exhibit a variation with chain length that is ascribed in this work to an increased contact between the probe tip and the molecular components of the film surface. This increased interaction arises as a result of the orientation of the chain structure at the film surface and the effective exposure of underlying methylene units. The presence of bulkier trifluoromethyl and phenyl terminal groups precludes such an interaction and frictional variations are therefore absent for these surfaces.

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