

Comparative Atomic Force Microscopy Study of the Chain Length Dependence of Frictional Properties of Alkanethiols on Gold and Alkylsilanes on Mica

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A comparative study of the frictional properties of alkanethiols and alkylsilanes as a function of chain length is presented. The monolayers were produced by self-assembly on Au(111) and mica, respectively. The same tip was used for all the experiments, and freshly cleaved mica was used as a reference. For both types of films, the frictional forces depend strongly on the number of carbon atoms in the alkane chain ($\text{CH}_3-(\text{CH}_2)_{n-1}-\text{R}$). Thiols and silanes give rise to similar frictional force for the same n when $n > 11$, while for $n < 11$ the behavior is markedly different; the silanes exhibit higher friction, larger than that for the thiols by a factor of ~ 3 for $n = 6$. The increase in friction is attributed to the increased disorder that occurs when going from a thiol to a silane anchor or when decreasing n . It is proposed that disorder favors the increase of the number and type of low-energy modes (kinks, bending, distortions) that are available for excitation and energy dissipation.

Introduction

Ultrathin organic films have been of great interest in recent years due to their potential use as boundary lubricants in several technological applications, such as information storage devices and micromechanical systems.^{1–8} Requirements for effective boundary lubrication are strong adhesion of the molecules to the substrate, reduced friction, and high resistance to wear. Self-assembly and Langmuir–Blodgett (LB) techniques are the most common methods of forming monomolecular films on solid supports that can be used as model lubricants. However, in the case of LB films, the molecules interact with the substrate through weak van der Waals and ionic forces, and repeated shearing results in the molecules being worn away.⁹ On the contrary, self-assembled aliphatic molecules, such as alkanethiols $\text{R}-(\text{CH}_2)_{n-1}-\text{SH}$ and alkylsilanes $\text{R}-(\text{CH}_2)_{n-1}-\text{SiX}_3$ (R represents the molecular terminal group and X is either chloride or alkoxy), are covalently bonded to the substrate and therefore are better candidates as lubricants. Moreover, the possibility of changing the chain length, terminal group, and degree of cross-linking within the layer makes self-assembled monolayers attractive model systems to study the nature of frictional interactions at the molecular scale. Among the parameters that might have a strong effect on the frictional properties, the chemical nature of the end groups is very important, as shown by several authors.^{9–12}

Several studies in the past have already shown that the friction and wettability of aliphatic polar compounds are functions of the chain length (ref 13 and references therein). The shorter chain compounds ($n < 14$) were found to exhibit high friction and low contact angles. The authors interpreted their findings in terms of strong intermolecular attraction leading to solid monolayer formation for the longer chains and of a liquid-like monolayer structure for the shorter chains. In addition, they found a lower friction value for the fatty amine layers, relative to the acid and alcohol ones, which was explained by their stronger binding to the glass substrate. A recent study in our

laboratory using atomic force microscopy (AFM) to ensure single asperity contact has also shown¹⁴ that the chemical nature of the terminal group is not the only factor determining the frictional properties of self-assembled alkylsilane molecules on mica. In agreement with the previous studies, the frictional forces for molecules with the same methyl end group were found to depend strongly on the chain length, yielding higher values on shorter chains. This was explained as a result of decreased packing density and order for the shorter chains, which increases the number of energy modes such as kinks, defects, and chains distortions available for energy dissipation.

In order to further test these ideas and to elucidate the role of the molecular anchoring group, a comparative study of the frictional properties of methyl terminated ($\text{R} = \text{CH}_3$) self-assembled alkylsilanes on mica and alkanethiols on Au(111) was carried out. Molecules with $n = 18, 12, 8, 6$ (hereafter referred to as C_n) were investigated. The structural and wetting properties of such monolayers have been studied by a variety of techniques, including STM and AFM. Spectroscopic and contact angle studies have shown that many properties of the long-chain alkanethiols ($n > 8$) on Au(111) are independent of chain length, while a certain variation exists for the shorter chains.^{15,16} This has been explained by the fact that the short chains are less densely packed and/or increasingly disordered. Diffraction techniques all indicate that the alkyl chains of long-chain alkanethiols ($n > 8$) are closely packed and have a $\sqrt{3} \times \sqrt{3}$ R30° periodicity with respect to the 1×1 structure of Au(111).^{17–21} A $c(4 \times 2)$ superstructure has been observed by STM^{22,23} and diffraction studies.^{21,24,25} Recent STM studies performed in ultrahigh vacuum (UHV) have shown that, for $n < 6$, methyl-terminated alkanethiols on Au(111) single crystals are in a 2D liquid state when removed from solution. Through desorption of molecules, the layers evolve to an ordered phase, characterized by a lower density with respect to the longer chain case.²⁶ Low-energy electron diffraction (LEED) studies of vapor-deposited short-chain thiols ($n < 10$) on Au(111) single crystals found ordered structures, characterized by lower density of molecules with respect to the dense $\sqrt{3} \times \sqrt{3}$ R30° phase.²⁰ In other studies using He-diffraction studies, no diffraction peaks were found from layers with $n = 6$ on Au(111)/

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mica but have recently confirmed the existence of lower density phases on layers deposited from a molecular beam onto Au(111) single crystals.¹⁹

In the case of alkylsilane SAMs, most studies have been performed on alkyltrichlorosilanes adsorbed at SiO_x surfaces.²⁷ Interestingly, monolayers can be formed both on surfaces that present a large number of hydroxyl groups (such as glass and SiO_x) and on mica, where the number of OH groups is expected to be very small. In the first case, covalent anchoring of the molecular Si—O— head groups to the surface and intermolecular cross-linking by Si—O—Si siloxane bonds is presumed to contribute to the film stability, in addition to the van der Waals interchain attraction. In the case of mica, little contribution from Si—O— bonds to the surface is expected. While the role of the preparation method and the nature of the substrate remain unclear to date, reports in general agree that there is an orientational order of the alkyl chains that is in *all-trans* conformation and slightly canted at <15°. He-diffraction did not reveal any crystalline order at the methyl termination of *n*-octadecyltriethoxysilane (OTE) layers on mica down to 45 K,²⁸ and X-ray grazing incidence diffraction studies of octadecyltrichlorosilanes (OTS) on SiO_x have indicated the existence of short-range liquid-like order.²⁹ Previous AFM studies of OTE layers on mica did not detect any long-range order of the molecules either.^{28,30} While few systematic studies of the chain dependent properties of silane monolayers have been reported, it is suggested that there is an increase of conformational disorder with decreasing chain length³¹ and that the contact angle remains constant for $n > 6$.³² It should, however, be pointed out that great caution has to be used in correlating wettability to molecular scale structural properties of the alkylsilane layers since, as shown in a previous report,³⁰ contact angle stability does not ensure the formation of high-quality, cluster-free layers.

Experimental Section

Materials. Alkanethiols were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) (C₁₈, C₁₂, C₈, C₆) and Pfaltz & Bauer Inc. (Waterbury, CT) (C₁₁). Alkylsilane monomers were purchased from United Chemical Technologies, Inc. (Bristol, PA) (C₁₈, C₈, C₆) and TCI America, Inc. (Portland, OR) (C₁₂). The C₁₈ silane was filtered through a 0.2 μm PTFE membrane prior to use. All other silanes and thiols were used as received. All alkylsilane materials were stored in a desiccator prior to use. House-distilled water was passed through a four-cartridge Millipore μQF purification train producing a resistivity of 18.2 M Ω cm. Tetrahydrofuran (THF) and cyclohexane were spectral quality. Glassware for preparation of prehydrolysis solution and for self-assembly was cleaned with chromic acid cleaning solution (Fisher Scientific). Mica chips were purchased from Asheville-Schoonmaker Company (Newport News, VA) and cleaved just prior to exposure to silane solution.

Monolayer Preparation. Gold films were prepared by resistive evaporation onto freshly cleaved mica. The mica substrates were heated in vacuum to 250 °C for 2–3 h. The Au was deposited at a rate of 2–3 Å/s. After evaporation, the substrates were allowed to cool radiatively to <60 °C in vacuum. Immediately after extraction, they were immersed in 1 mM ethanolic solutions of alkanethiols. The gold substrates were left in solution at room temperature for at least 36 h and then rinsed with ethanol and dried in a N₂ stream.

The preparation of alkylsilane monolayers on freshly cleaved mica was carried out as reported previously.³⁰ Briefly, prehydrolysis solutions were prepared by dissolving 0.2 g of the appropriate silane in 24 mL of THF containing 0.2 g of 1 N HCl. The solution was stirred at room temperature for 2–3

days. Just prior to self-assembly, the hydrolysis solution was filtered through a 0.2 μm Teflon membrane. Following this treatment, the solution was diluted 1:20 in cyclohexane and then added to a clean Petri dish containing the mica samples. Deposition was carried out at room temperature without stirring. Deposition time was varied depending on the chain length of the silane as follows: C₁₈, 5 min; C₁₂ and C₈, 10 min; C₆, 30 min. Samples were then rinsed with cyclohexane and sonicated (C₁₈) for half an hour or immediately stored in cyclohexane (C₁₂, C₈, C₆) until evaluation.

AFM Measurements. Experiments were carried out with a home-built system³³ operating under ambient conditions of 20 °C and 35–45% relative humidity. Commercially available gold-coated V-shaped Si₃N₄ cantilevers with a nominal force constant of 0.58 N/m (Digital Instruments, Santa Barbara, CA) were used.

The microscope was operated in two different modes, as described in detail previously.³⁴ Briefly, in the imaging mode (topographic or friction), the tip is scanned while a feedback loop holds the externally applied load constant. Forward and backward scans are acquired simultaneously, so that a total of four images (two topographic and two lateral force) can be obtained. A $+x/-x$ pair of scan lines of the lateral force images gives a “friction loop”. Its average width is a measure of the frictional force.³⁵ Friction *vs* load curves were obtained as follows. The tip was scanned back and forth along the same horizontal line with the feedback loop disabled. The external load was changed at the end of the line by approaching or retracting the sample. In this way, the *y* axis of the images represents the normal load applied between tip and sample. To obtain friction data, the difference between the forward and backward scans is computed, the data along each *x* scan line is averaged together, and the average frictional force signal is plotted as a function of load. Calibration of the lever bending signal was obtained from approach–retract curves acquired simultaneously to the frictional force images. The normal force constant for the levers used in this study was estimated by using a continuum elasticity model, after measuring the levers’ critical dimensions by scanning electron microscopy (SEM).³⁶ In addition, the effect of the gold coating was taken into account according to a calculation reported previously.³⁷ Since an *in-situ* calibration for the lever twisting signal was not available at the time these measurements were made, the conversion of the lever twisting signal to frictional forces was made by using the estimated ratio between the bending and twisting of the lever.³⁶

Results

Film Morphology and Structure. Nanometer scale images of alkanethiol SAMs with $n = 18, 12, 11$, and 8 carbon atoms revealed hexagonal ordered structures with 5.0 Å periodicity, as shown in Figure 1a. This is a $\sqrt{3} \times \sqrt{3}$ R30° structure relative to the substrate, as shown by experiments at high loads that displaced the SAM and revealed the gold periodicity.^{34,38} However, in contrast to STM and diffraction studies, a disordered structure was observed for hexanethiol monolayers ($n = 6$).

For the alkylsilane on mica, formation of complete monolayers is increasingly difficult with decreasing chain length which required progressively longer incubation periods of time. For the shorter chains ($n = 8, 6$), several uncovered mica areas could be found. Furthermore, while sonication was necessary in the case of C₁₈ layers to remove 3D clusters present on top of the monolayer-covered surface, such process resulted in the disruption of the monolayers formed from shorter chain lengths.

C12 thiol/gold

C18 silane/mica

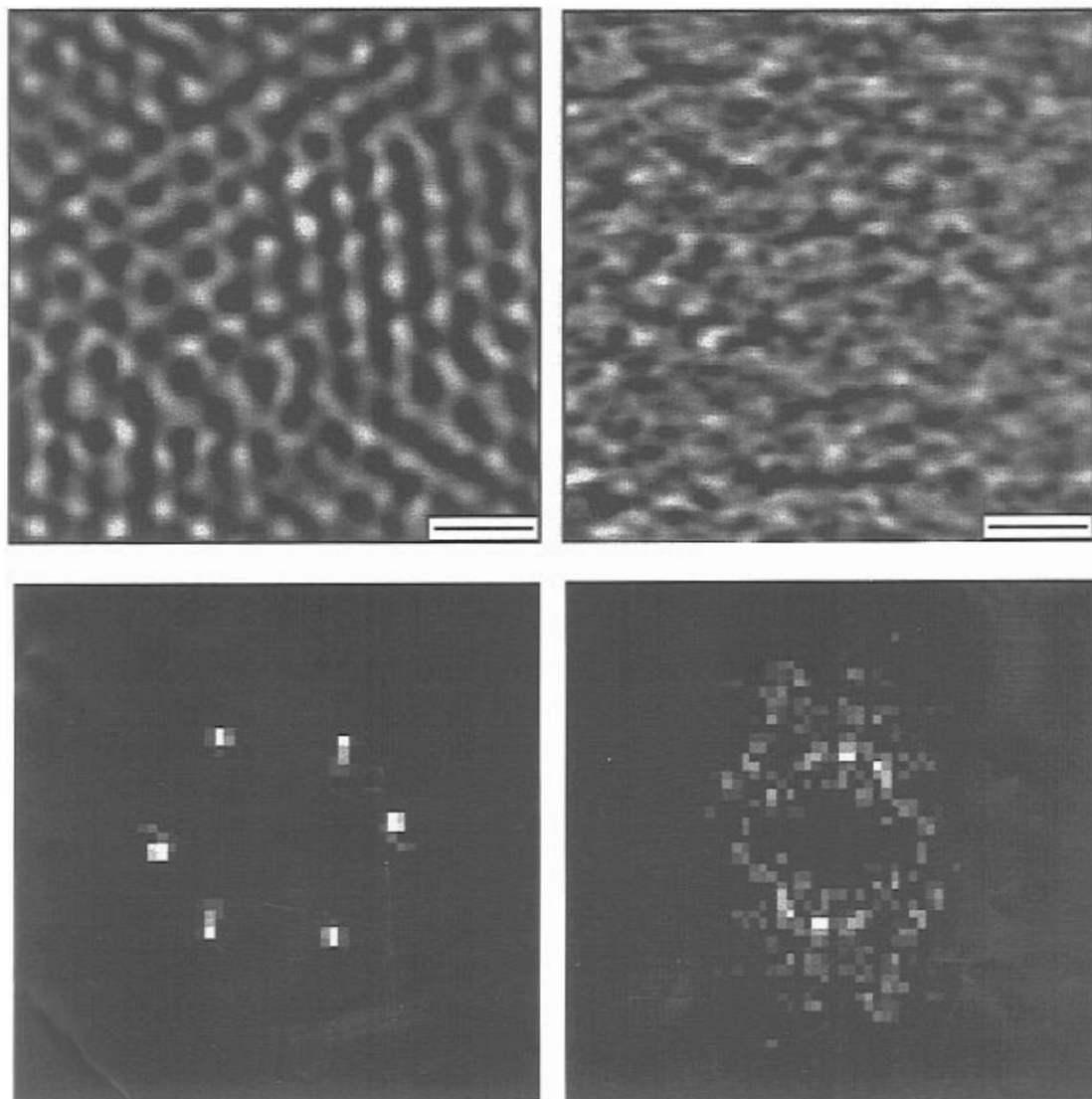


Figure 1. Frictional force images for dodecanethiol C_{12} on gold and octadecyltriethoxysilane C_{18} on mica. Scale bars = 10 Å. The corresponding 2D Fourier transform power spectra are also shown. The external load during imaging was 0.5 nN. Alkanethiol monolayers with $n = 18, 12, 11, 8$ all exhibit a hexagonal lattice (lattice constant = 5.0 ± 0.3 Å). No long-range order is observed for alkylsilane monolayers of all lengths, although residual short-range order is observed.

In all cases, no long-range order could be detected by AFM, although isolated areas showing some residual order could be observed, as shown in Figure 1b. Similar images showing a reduced degree of order were reported by Xiao et al.³⁰

Frictional Properties. Figure 2 shows friction *vs* load curves for alkanethiol monolayers ($CH_3-(CH_2)_{n-1}-S-Au$) with $n = 18, 12, 11, 8$, and 6. A curve taken on a freshly cleaved mica surface with the same tip is also shown as a reference. Each curve is composed of an approach and a retract branch corresponding to increasing and decreasing loads. There is a jump to contact in the approach branch that is used to define the zero of external load. For the lower chain lengths, there is a small amount of hysteresis, with the load branch being below the unload branch. This is most visible for the C_6 film. As can be seen, the friction curves for the C_{18} , C_{11} , and C_8 layers are essentially undistinguishable. The curve for the C_{12} layer lies below them, and the frictional forces on C_6 are roughly twice as large. Furthermore, all curves lie well below the mica curve. The applied load was limited to values that did not cause damage on any of the monolayers, as revealed by large scans

of the areas where the curves were acquired. It was shown previously that when high loads or sharper tips are used, the layers can be affected either reversibly^{34,38} or irreversibly¹⁴ and the frictional forces become unstable.

Adhesion energies can, in principle, be determined from the force *vs* distance curves as the tip moves toward and away from the surface. In most AFM experiments using soft levers, however, there is an instability that causes the tip to jump into contact with the surface during approach and to abruptly pull off during retraction. Therefore, the force curve cannot be determined and integrated in the important region of the surface proximity to obtain the adhesion energy. Instead the pull-off forces are used as a measure of adhesion, an approximation that implicitly assumes that all the potential curves have the same shape. Values of the pull-off forces found in our experiments are presented in Table 1. These values are averages of several measurements on different areas of the samples. The pull-off forces for the C_{18} , C_{12} , C_{11} , and C_8 thiol layers are identical within the uncertainty, while a 20% increase is observed for the C_6 layers.

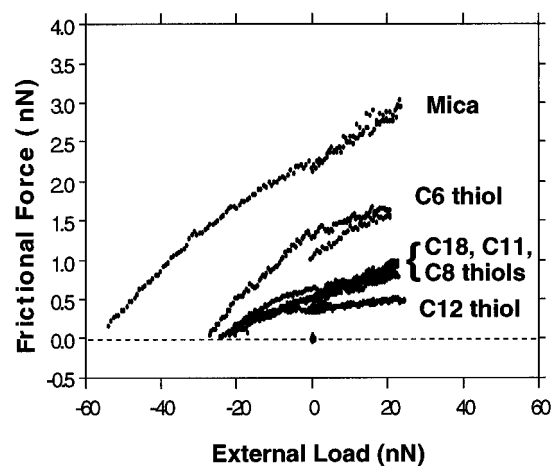


Figure 2. Friction *vs* load curves obtained for C₁₈, C₁₂, C₁₁, C₈ and C₆ alkanethiol monolayers on Au(111) and a Si₃N₄ tip. A curve for mica is also shown as a reference. The load was limited to values that did not cause any damage on the layers being probed. All curves were obtained with the same tip (with an estimated normal force constant of 0.34 N/m).⁴³ The calibration for the lateral force signal was derived from the estimate of the relative deflection due to bending and twisting of the cantilever.³⁶

TABLE 1: Pull-Off Force, F_{po} , Measured from Force *vs* Distance Curves

surface	pull-off force F_{po} (nN)	ΔF_{po}^a (nN)
alkanethiols		
C ₁₈	21.3	1.5
C ₁₂	22.0	1.7
C ₈	20.5	1.8
C ₆	24.5	3.1
alkylsilanes		
C ₁₈	20.7	1.6
C ₁₂	20.7	1.4
C ₈	23.1	1.3
C ₆	24.3	1.6
mica	54.2	1.8

^a ΔF_{po} is the statistical standard deviation.

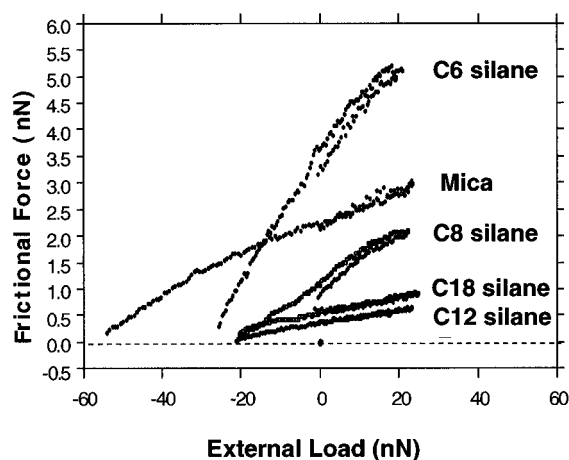


Figure 3. Friction *vs* load curves obtained for C₁₈, C₁₂, C₈ and C₆ alkylsilane monolayers on mica and a Si₃N₄ tip. A curve for mica is also shown as a reference. All curves were obtained with the same tip used for Figure 2.

Figure 3 shows friction *vs* load curves obtained on the alkylsilane monolayers self-assembled on mica. These results are similar to those of Xiao et al.,¹⁴ although the present study covers the lower (negative) load regime that was not measured in the previous work. The results show a trend similar to that of the thiols on gold presented in Figure 2, but there are also some important differences. As for the alkanethiol monolayers,

the lowest frictional forces are measured on the C₁₈ and C₁₂ layers. Higher frictional forces are measured on the C₈ and C₆ layers, with the C₆ layer yielding frictional forces that are 1 order of magnitude larger than those for the C₁₈ and C₁₂ layers. The frictional forces for the C₆ are larger than those on mica, except for very low loads corresponding to the tip being pulled from the surface (negative loads). Some hysteresis is visible for the curves taken on C₈ and C₆ layers.

As can be seen in Table 1, the pull-off forces measured on both types of monolayers are in the same range. As in the case of the thiols, the pull-off forces measured on C₆ silane layers are ~20% higher than those for the longer chains. The values measured on the organic layers are roughly half of the values measured on bare mica, which is a hydrophilic surface.

A more detailed comparison of the friction *vs* load curves obtained on alkanethiol and alkylsilane layers with the same chain length is shown in Figure 4. As the chain length decreases, the difference of frictional forces on silanes and thiol layers increases. For the longest chains examined, the C₁₈ layers (Figure 4a), the friction curves are indistinguishable from each other. Larger forces are measured on the C₁₂ silane with respect to the C₁₂ thiol (Figure 4b), although the two curves are indistinguishable in the lowest load region. Frictional forces on the C₈ silane layers are about three times higher than the values for corresponding thiols at all loads (Figure 4c). The C₆ silane layers continue this trend, yielding frictional forces at a ratio of ~3.5:1 to the thiol values (Figure 4d).

Discussion

The AFM lattice resolved images of the alkanethiol monolayers indicate, in agreement with other techniques, that layers with $n = 18, 12, 8$ are densely packed and well-ordered. For the first time to our knowledge, it is shown by AFM that the chains of C₁₁ layers are also hexagonally packed. However, no order was observed on the C₆ layers, in apparent disagreement with STM and some diffraction studies. This might be due to the fact that the samples used in these studies were analyzed within a few hours of their preparation to avoid possible contamination in air. STM and He-diffraction studies indicate that it takes a few days after the samples have been out of the solution for a complete ordering. Another possible explanation is that the layer may become disordered under the pressure applied by the AFM tip. Nonlinear optical experiments have shown that the chain terminations of similar molecules become disordered at pressures of 50–80 MPa.³⁹ During AFM imaging, a typical external load in the range of 1–5 nN was applied by tips with 400–600 Å radii. The corresponding pressure, calculated by the Hertz model,⁴⁰ is in the range of 200–300 MPa, which is four to five times larger than the pressures applied in the nonlinear optical experiments. This indicates that the chain terminations are disordered under the pressure of AFM tips (terminal gauche defects). In the case of long chains ($n > 10$), AFM images taken at these loads still reflect average long-range order of the main bodies of the alkyl chains.³⁴ However, in the case of short chains, the pressure-induced terminal defects may be sufficient to completely disorder the chains, an effect that will be magnified by the reduced stability and/or packing density of the shorter molecules.

The pull-off force values in Table 1 indicate that the surface energies of all the films studied, thiols and silanes with many different chain lengths, are very similar, as expected from their common CH₃ termination. A small increase in pull-off force could be expected for the shorter chains due to their higher compressibility, which gives rise to a higher contact area for the same applied load. This probably explains the higher pull-

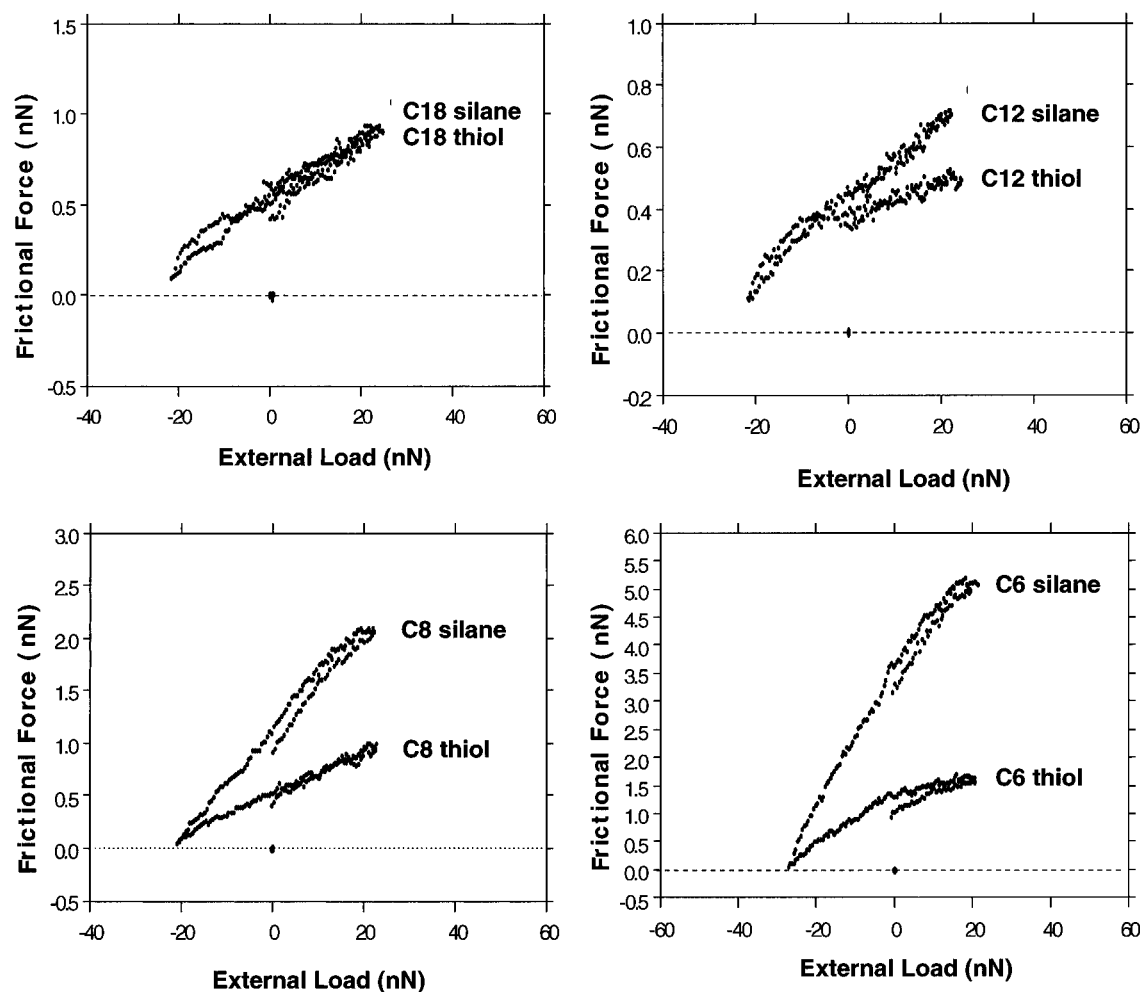


Figure 4. Comparison of the frictional behavior of alkanethiol and alkylsilane monolayers with the same chain length. (a) C₁₈ layers; (b) C₁₂ layers; (c) C₈ layers; (d) C₆ layers. A certain amount of hysteresis is observed for the C₈ silane layers and the C₆ thiol and silane layers. No hysteresis is observed for the C₁₈, C₁₂ layers and C₈ thiol.

off forces observed for the C₆ films. The effect of compressibility on pull-off force has been demonstrated in a recent study by Koleske et al.⁴¹ As can be seen in the table, the pull-off force for mica is roughly twice that of the thiol and silane covered surfaces, an effect that is likely due to the action of strong capillary forces because of the hydrophilic character of mica.

These observations indicate that the frictional properties of surfaces do not depend only on the chemical nature of the exposed groups, although these do determine the surface energy. Otherwise, all chain lengths should have yielded similar friction values. In order to understand the results in Figures 2–4, the molecular order and chemistry of the substrate have to be considered.

In the formation of self-assembled monolayers, the molecule–substrate and molecule–molecule interactions both play important roles and determine the quality and character of the films. Interchain interactions are dominated by van der Waals forces. The cohesive energy for these systems can be approximately computed by summing the interactions of each CH₂ group with the CH₂ groups in the same chain and in the neighboring ones, under the approximation of an ideally close-packed monolayer.¹⁴ The stabilization energy provided by additional methylene groups saturates at $n = 8–10$, at which point the energy per methylene group is ~ 7 kJ/mol. Thus, the invariance of structure and properties for long chain alkanethiols and alkylsilanes as shown by different techniques is anticipated. It also explains the similarity of frictional behavior for all films, thiols and

silanes, with lengths $n > 12$, as shown in Figures 2, 3, and 4a, since these films are well packed. It is then reasonable to suggest that the increase in friction for the short chains ($n < 8$) is due to poor packing of the molecules, which makes possible the excitation of numerous defects and energy-dissipating modes, such as bending and rotation around kinks, that are sterically quenched in the densely packed films. The excitation of these modes is similar to viscoelastic behavior. The higher friction of short chain silanes relative to the corresponding thiols is thus an indication and a consequence of the additional disorder in these films.

Another conclusion can be drawn from the comparison of thiols and silanes with lengths corresponding to $n > 10$. There are two important differences between these two types of films. One is long-range order, which is present in the thiols and absent in the silanes. The other is the cross-linking of the head groups. In thiols, cross-linking is limited to dimer formation, as seen in the disulfide bonds forming between pairs of atoms in recent X-ray diffraction experiments.²⁶ This seems to have the effect of producing a superstructure with $c(4 \times 2)$ periodicity relative to the basic $\sqrt{3} \times \sqrt{3}$ R30° structure. In the case of the silanes, however, extensive covalent Si–O–Si networks form across the surface. The distance between Si atoms in adjacent molecules forming Si–O–Si bonds is 2.5 Å, while the chain diameter is ~ 4.5 Å. Therefore, there must be considerable chain distortions near the interface that is amplified along the network and must in turn cause a limitation in the size of the cross-linked cluster. This is probably at the origin of the lack of long-

range order in the silanes, which is observed both on amorphous glass substrates as well as on crystalline mica. In spite of these differences, the film properties are similar above $n = 10$. One must then conclude that the tight packing and short-range order provided by the main body of the alkane chains are the determinant characteristics and that long-range order does not necessarily lead to lower friction.

A surprising result of these studies is that both C_{12} thiol and silane layers yield lower frictional forces than their C_{18} counterparts. For thiols, the C_{18} , C_{11} , and C_8 monolayers exhibit frictional behavior that cannot be distinguished from one another. The anomalous behavior of the C_{12} 's could be related to the purity of the chemicals employed. In the case of silanes, the dodecyltriethoxysilane chemical is purer (97%) than octadecyltriethoxysilane (95%)⁴² with the Si in the longer chain being prone to α , β isomerization and branching. In the case of thiols, the difference between C_{12} and C_{18} is smaller (99.4% vs 99.2%). Although purity is an important consideration that might affect the ordering and packing of the film, the observed differences in friction are not yet understood at present.

Conclusion

AFM has been used to study the frictional behavior in the wearless regime of self-assembled alkanethiols and alkylsilanes on Au(111) and mica, respectively. We have shown that, with more than 8–11 carbons in the chain, the frictional behavior is very similar and independent of long-range order and head group linkage. A very strong dependence on chain length is observed for lengths below eight carbons. These differences exist in spite of the identical methyl terminal groups and similar surface energy of these films, as measured by the pull-off forces. The observed behavior has been ascribed to the increased formation of kinks, defects, and distortions in the alkyl chains that occur in the less densely packed short-chain films.

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References and Notes

- (1) Bowden, F. P.; Tabor, D. *The Friction and Lubrication of Solids*; Clarendon Press: Oxford, 1986.
- (2) Suzuki, M.; Saotome, Y.; Yanagisawa, M. *Thin Solid Films* **1988**, *160*, 453.
- (3) Miyamoto, T.; Sato, I.; Ando, Y. In *Tribology and Mechanics of Magnetic Storage Devices*, 2nd ed.; Bhushan, B., Eiss, N. S., Eds.; Springer-Verlag: New York, 1990.
- (4) Ando, E.; Goto, Y.; Morimoto, K.; Ariga, K.; Okahata, Y. *Thin Solid Films* **1989**, *180*, 287.
- (5) Bhushan, B.; Gupta, B. K. *Handbook of Tribology: Materials, Coatings and Surface Treatments*; McGraw-Hill: New York, 1991.
- (6) Ruhe, J.; Novotny, V. J.; Kanazawa, K. K.; Clarke, T.; Street, G. B. *Langmuir* **1993**, *9*, 2383.
- (7) Zarrad, H.; Clechet, P.; Belin, M.; Martelet, C.; Jaffrezic-Renault, N. *J. Micromech. Microeng.* **1993**, *3*, 222.
- (8) Bhushan, B.; Koinkar, V. N. *J. Appl. Phys.* **1994**, *75*, 5741.
- (9) Bhushan, B.; Kulkarni, A. V.; Koinkar, V. N.; Boehm, M.; Odoni, L.; Martelet, C.; Belin, M. *Langmuir* **1995**, *11*, 3189.
- (10) Overney, R. M.; Meyer, E.; Frommer, J.; Güntherodt, H.-J. *Langmuir* **1994**, *10*, 1281.
- (11) Takano, H.; Fujihira, M. *J. Vac. Sci. Technol. B* **1996**, *14*, 1272.
- (12) Fujihira, M.; Morita, Y. *J. Vac. Sci. Technol. B* **1994**, *12*, 1609.
- (13) Levine, O.; Zisman, W. A. **1957**, *61*, 1068 and references therein.
- (14) Xiao, X.-d.; Hu, J.; Charych, D. H.; Salmeron, M. *Langmuir* **1996**, *12*, 235.
- (15) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.
- (16) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
- (17) Strong, L.; Whitesides, G. M. *Langmuir* **1988**, *4*, 546.
- (18) Chidsey, C. E. D.; Liu, G.-y.; Rowntree, P.; Scoles, G. J. *J. Chem. Phys.* **1989**, *91*, 4421.
- (19) Camillone, N.; Chidsey, C. E. D.; Liu, G.-y.; Putvinski, T. M.; Scoles, G. J. *J. Chem. Phys.* **1991**, *94*, 8493.
- (20) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Chem. Phys.* **1993**, *98*, 678.
- (21) Camillone, N.; Chidsey, C. E. D.; Liu, G.-y.; Scoles, G. J. *J. Chem. Phys.* **1993**, *98*, 3503.
- (22) Poirier, G. E.; Tarlov, M. *J. Langmuir* **1994**, *10*, 2853.
- (23) Anselmetti, D.; Baratoff, A.; Güntherodt, H.-J.; Delamarche, E.; Michel, B.; Gerber, C.; Kank, H.; Wolf, H.; Ringsdorf, H. *Europhys. Lett.* **1994**, *27*, 365.
- (24) Fenter, P.; Eisenberger, P.; Liang, K. S. *Phys. Rev. Lett.* **1993**, *70*, 2447.
- (25) Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216.
- (26) Poirier, G. E.; Tarlov, M. J.; Rushmeier, H. E. *Langmuir* **1994**, *10*, 3383.
- (27) Ulman, A. *Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press: San Diego, CA, 1991.
- (28) Peanasky, J.; Schneider, H. M.; Granick, S.; Kessel, C. R. *Langmuir* **1995**, *11*, 953.
- (29) Tidswell, I. M.; Rabedeau, T. A.; Pershan, P. S.; Kosowsky, S. D.; Folgers, J. P.; Whitesides, G. M. *J. Chem. Phys.* **1991**, *95*, 2854.
- (30) Xiao, X.-d.; Liu, G.-y.; Charych, D. H.; Salmeron, M. *Langmuir* **1995**, *11*, 1600.
- (31) Hoffman, H.; Mayer, U.; Krischanitz, A. *Langmuir* **1995**, *11*, 1304.
- (32) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.
- (33) Kolbe, W. F.; Ogletree, D. F.; Salmeron, M. *Ultramicroscopy* **1992**, *42–44*, 369.
- (34) Lio, A.; Morant, C.; Ogletree, D. F.; Salmeron, M. *J. Phys. Chem.* in press.
- (35) Mate, C. M.; McClelland, G. M.; Elandsson, R.; Chiang, S. *Phys. Rev. Lett.* **1987**, *59*, 1942.
- (36) Ogletree, D. F.; Carpick, R. W.; Salmeron, M. *Rev. Sci. Instrum.* **1996**, *67*, 3298.
- (37) Sader, J. E.; Larson, I.; Mulvaney, P.; White, L. R. *Rev. Sci. Instrum.* **1995**, *66*, 3789.
- (38) Liu, G.-y.; Salmeron, M. *Langmuir* **1994**, *10*, 367.
- (39) Du, Q.; Xiao, X.-d.; Charych, D. H.; Wolf, F.; Frantz, P.; Ogletree, D. F.; Shen, Y. R.; Salmeron, M. *Phys. Rev. B* **1995**, *51*, 7456.
- (40) Hertz, H. *J. Reine Angew. Math.* **1882**, *92*, 156.
- (41) Koleske, D. D.; Barger, W. R.; Lee, G. U.; Colton, R. *Thin Solid Films*, in press.
- (42) Thiol data from Aldrich Chemical Company.
- (43) The estimated value³⁶ significantly differs from the nominal value of 0.58 N/m provided by the manufacturer. However, the value reported in this paper is in agreement with the experimentally determined one for similar levers with resonance frequencies similar to the one observed in this study (52 kHz). See: Cleveland, J. P.; Manne, S.; Bocek, D.; Hansma, P. K. *Rev. Sci. Instrum.* **1993**, *64*, 403.