Self-Assembled Monolayers on Mica for Experiments Utilizing the Surface Forces Apparatus

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Strongly bound, closely packed self-assembled monolayers of condensed alkyltriethoxysilanes were formed on mica and other substrates with a packing density of about 20 Å^2/molecule. Techniques to exploit these monolayers in the surface forces apparatus (SFA) are described. The length of the alkyl chain of the amphiphiles was 18 carbons (methyl functionality at the terminus) or 20 and 22 carbons (vinyl functionality at the terminus). The thickness of both monolayers, determined independently by ellipsometry and by *in situ* SFA measurement, was consistent with models in which the alkyl chains were directed away from the surface in all-trans conformations. The average tilt angle of the alkyl chains, determined by Fourier transform infrared spectroscopy, was 13 ± 5° from the surface normal. The surface energies of the monolayers, determined by *in situ* SFA measurement of the pull-off forces and contact-area diameters, agreed with independent estimates from contact angle measurements. The monolayer surfaces were of a high degree of smoothness: when undecane ($C_{11}H_{24}$) fluid was confined between the surfaces, oscillatory force–distance profiles were measured over a range of liquid thickness similar to that over which oscillatory forces were measured between unmodified mica surfaces. The amount of water in the hydrolysis solutions greatly affected the ability to self-assemble as a tightly-bound monolayer, and the optimal water concentration was determined. All monolayers were resistant to attack by nonpolar solvents. The vinyl-terminated species could be chemically converted to the hydroxyl form, thereby creating a polar surface without apparent change in the organization of the monolayer.

Introduction

The behavior of liquids confined between solid surfaces to spaces of thickness on the order of a few molecular diameters can be studied using the surface forces apparatus (SFA).[1,2] Mica, a biaxial crystal with a large surface energy in air[3] of a few hundred mJ/m^2 depending on the atmosphere in which it is cleaved, is especially suited to these experiments and has been used as a solid substrate since the inception of this technique.[1] The reasons are essentially of expediency. Since mica is easily cleaved to prepare atomically smooth surfaces, this permits the easy formation of solid surfaces separated with a resolution of 1–2 Å. Since mica is transparent to visible light, the determination of film thickness is straightforward with the use of multiple beam interferometry.[1] Moreover, mica is relatively inert chemically, is physically robust, and is abundantly available at relatively low cost. Unfortunately, the interactions between liquids and mica surfaces present little fundamental interest. It is of evident interest to have available a variety of other solid surfaces, of lower surface energy and different chemical composition, while retaining the several advantages that are afforded by the use of mica. The approach that this research group has taken to create these new surfaces is to coat mica substrates with self-assembled organic monolayers.

Much is already known about how to coat solid surfaces with organic amphiphilic molecular films.[4,5] In the past, mica surfaces have been modified for SFA experiments by exposure to a gas plasma and subsequent chemical reaction,[6] by Langmuir–Blodgett (LB) deposition,[7,8] or by deposition of self-assembled monolayers of ionic surfactants[7] or trichlorosilanes.[9] However, each of these methods suffers from a limited range of application.

Gas plasma treatments present the advantage of simplicity; however, exposure of a surface to a gas plasma is known to roughen solids. The average roughness has been reported to be small,[10] but reflection shows that regions of large surface roughness should coexist with smoother regions; pits with cross sectional diameters of a nanometer or so would not be observable with standard AFM needles, whose radii of curvature may be 10–100 nm. The LB technique presents the possibility of preparing a wide variety of surfaces but suffers from the limitation that weak binding to the substrate[11] and between LB layers can result in destruction of the film structure[12] or intercalation of other species within the film[8] during the course of an experiment. Self-assembly of ionic surfactants—amphiphiles which electrostatically

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attach themselves to the mica substrate—also has the advantage of simplicity, but the resulting monolayers appear to suffer from structural rearrangement on the substrate, as evidenced by water contact angle behavior which degrades with time.[13] Finally, self-assembled monolayers of alkyltrichlorosilanes have already been formed successfully on mica.[9] These monolayers were closely-packed and strongly bound to the mica. But the technique to form the monolayers[9] was so complicated that it was deemed impractical.

Recently, we reported a new and simple method to modify the mica surface using self-assembled monolayers of hydrolyzed octadecyltriethoxysilane (OTE).[14] The OTE is hydrolyzed to the trisilanol before self-assembly, and the trisilanols are condensed after self-assembly by heating. One advantage of this technique over the use of chlorosilanes is the lower rate of condensation of the trisilanols in the self-assembly solution relative to trichlorosilane species. The lower rate of condensation allows the hydrolyzed OTE molecules time to self-assemble onto the mica surface without the intervention of gelation. The resulting monolayers have packing density comparable to that of an LB monolayer[14] but are robustly attached to the mica surface. These monolayers have already been employed in several studies of force–distance profiles and shear rheology of liquids confined between OTE surfaces.[15-18] In past work, however, our reported characterization of the OTE monolayers was not extensive, and methods to implement the use of OTE monolayers within the surface forces apparatus were not described.

Here we present much more complete characterization of OTE monolayers and describe in detail how to use the monolayers in surface forces experiments. We also characterize vinyl-terminated monolayers, showing that they give similar packing and organization as OTE but can be chemically modified to form a hydroxylated surface. Such functionalized surfaces are interesting in themselves and in the future can be substrates for polymer or protein absorption, or further chemical reaction.[19,20]

Preparation of OTE Monolayers

A detailed description of the experimental protocol that gave monolayers of optimal quality is given in the Experimental Section of this paper.

The mechanism of formation is believed to differ from that of monolayers at oxide surfaces that bear a high concentration of hydroxyl groups. At those surfaces, copious chemical reaction with the substrate may be expected.[4] The mica surface is almost entirely nonfunctional; there is no hydroxyl functionality to provide a handle for anchoring the silane monolayer. The likelihood is, however, good that an exchange reaction, which breaks mica surface Si–O–Si bonds and creates mica/monolayer Si–O–Si bonds, may result in occasional Si–O–Si linkages.[14] We expect that anchoring of the monolayer to the mica surface may be provided by this reaction, but at only occasional spots; formation of robust OTE monolayers is driven essentially by intramolecular condensation between Si–O–Si linkages of the self-assembled chains.

The formation of self-assembled monolayers using OTE is a three-step process:[14] (1) hydrolysis of the triethoxysilane headgroup to trisilanol form, (2) self-assembly from cyclohexane solution, and (3) condensation of the adsorbed silanols. With this simple procedure, autophobic monolayers are produced. As reported previously,[14] infrared measurements indicate that the hydrocarbon chains are closely-packed and with crystalline-like order. We also found that monolayers composed of the ω-terminated alkenyltriethoxysilane (discussed in detail below) can be prepared by the same method.

In this section, we describe the sensitivity of the quality of monolayer formation to variations in the concentrations of acid and water in the hydrolysis step. The hydrolysis solutions were mixtures of OTE, H_2O, and HCl in tetrahydrofuran (THF);[14] the standard concentrations were 0.02, 0.0066, and 0.28 M, respectively. Typically the hydrolysis solution was held at room temperature for a period of several hours to 1 week and then was diluted with cyclohexane to form a 1 mM OTE solution immediately before self-assembly.

To determine the most favorable conditions for self-assembly onto a mica substrate, the water and acid concentrations in the hydrolysis solution were varied systematically. The water and acid concentrations were expected not only to affect the kinetics of hydrolysis but also to affect the adsorption of OTE. Presence of acid during self-assembly might affect head group interactions with the mica surface. As suggested previously[14] chemical reaction between OTE and mica in the presence of acid may occur during the condensation/heating step. Finally, in principle, one can imagine that the proportion of water might also effect the degree of polymerization of hydrolyzed OTE in adsorption solution.

Table 1 shows the effect on the final monolayers of varying the water and acid concentrations in the hydrolysis solutions. The tenacity with which the head group was attached to the surface was assessed with contact angle measurements; those samples which displayed a decreasing contact angle with time are noted. The density of OTE adsorbed on the surface was determined by Fourier transform infrared spectroscopy (FTIR) in the transmission mode (as described in the Experimental Section). The age of the hydrolysis solutions was kept constant at 48 ± 2 h, and the adsorption solutions were prepared as described previously.[14] To assess the surface concentration of OTE, the integrated intensities of the FTIR absorbance spectrum of $\nu_a(CH_2)$ and $\nu_s(CH_2)$ between 2800 and 3000 cm^{-1} were compared to these features of an LB monolayer of barium stearate on mica, whose surface density was known to be 20 Å^2/molecule.[14]

Under some of these hydrolysis solution conditions, tightly-bound monolayer films did not form. For example, when the water concentration was doubled, white flakes precipitated visibly from the adsorption solution and FTIR analysis showed that significantly more than a single monolayer was deposited. For films prepared with acid and water concentrations at half of standard concentration, these surfaces were not autophobic. That is, liquid was left on the mica coupon as it was removed from the adsorption solution and spots were left behind as the liquid drained off it. In addition, films prepared with solutions at standard acid concentrations or higher, and half the standard water concentration, displayed decrease of the contact angle with elapsed time, indicating that the OTE chains were not strongly bound to the mica surface. For these coatings, FTIR spectra also showed surface coverages different—in some cases smaller, in some cases larger, as indicated in Table 1—than a single monolayer.

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Table 1. OTE Monolayer Quality as a Function of Hydrolysis Solution Composition[a]

hydrolysis conditions[b]	contact angle[c]	Γ/Γ_{max}
$[HCl] = 1/2X$ $[H_2O] = 1/2X$ $[OTE] = 1X$	d	
$[HCl] = 1/2X$ $[H_2O] = 1X$ $[OTE] = 1X$	111	1.0
$[HCl] = 1/2X$ $[H_2O] = 2X$ $[OTE] = 1X$	115	3.4
$[HCl] = 1X$ $[H_2O] = 1/2X$ $[OTE] = 1X$	112[e]	1.1
$[HCl] = 1X$ $[H_2O] = 1X$ $[OTE] = 1X$	111	1.0
$[HCl] = 1X$ $[H_2O] = 2X$ $[OTE] = 1X$	112	1.4
$[HCl] = 2X$ $[H_2O] = 1/2X$ $[OTE] = 1X$	111[e]	0.8
$[HCl] = 2X$ $[H_2O] = 1X$ $[OTE] = 1X$	111	1.0
$[HCl] = 2X$ $[H_2O] = 2X$ $[OTE] = 1X$	111	1.2
$[HCl] = 1X$ $[H_2O] = 1X$ $[OTE] = 1/3X$	111	1.0
$[HCl] = 1X$ $[H_2O] = 1X$ $[OTE] = 3X$	111	1.0

[a] The proportions of water, acid, and OTE were varied as described in text and specified in the table. The contact angle measurements refer to the advancing contact angle of water (in degrees). The relative surface coverage, Γ/Γ_{max}, is inferred from integrated infrared intensities of the symmetric and asymmetric C−H stretches, relative to that at single monolayer coverage, as described in text. [b] The symbol "*x*" denotes standard concentrations of 0.28, 0.0066, and 0.02 M, respectively, in THF. [c] In degrees. [d] Was not autophobic. [e] Contact angle decreased with time.

Table 2. Resistance of OTE to Attack by Various Liquids, under Conditions of Either Reflux or Soak[a]

solvent	θ_a (deg) on mica	θ_a (deg) on Si	Γ/Γ_{max} on mica
THF[b]	68[d]	109	0.38
CH_2Cl_2[b]	108	110	0.85
C_6H_{12}[b]	111	111	1.0
THF[c]	84[d]	111	
CH_2Cl_2[c]	110	109	1.0
C_6H_{12}[c]	111	111	1.0
H_2O	111	111	1.0

[a] Contact angle measurements refer to droplets of distilled water. The relative surface coverage, Γ/Γ_{max}, is inferred from infrared measurements as described in text. [b] Refluxed 8 h. [c] Soaked 8 h. [d] Contact angle decreased with time.

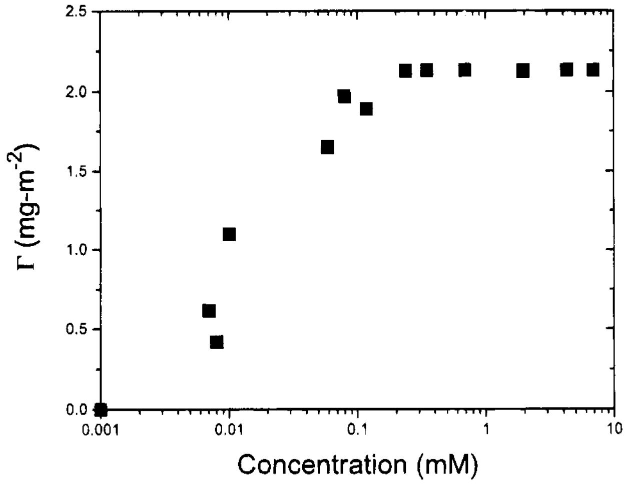

Figure 1. Adsorption isotherm of OTE from hydrolysis solutions of optimal acid and water composition. The mass coverage by alkyl chains (mass per area) is plotted against logarithmic OTE concentration in the adsorption solution. Mass coverage was quantified from transmission infrared measurements as described in the text.

On the other hand, the resulting monolayers were indistinguishable when the water concentration was kept at the standard concentration and the acid concentration was varied. The mass density was then that of a single monolayer; the contact angle was about 111° and did not decrease with elapsed time. These experiments showed that monolayer formation was affected by water concentration in the hydrolysis solution but not by acid concentration.

The other variable in the composition of hydrolysis solutions was the concentration of OTE. Two hydrolysis solutions were prepared, one with the OTE concentration higher than the standard level by a factor of 3, the other lower by the same factor. In both cases the acid and water concentrations were fixed at standard concentrations. Monolayers prepared using these hydrolysis solutions were indistinguishable from those made using standard hydrolysis conditions. This shows that the quality of the monolayer was not a strong function of the OTE concentration in the hydrolysis solution.

Table 2 shows the results of experiments in which the robustness of the monolayers to prolonged contact with organic liquids was explored. Sheets of OTE-coated mica were submerged and refluxed for 8 h in the liquid of interest. Stability to this procedure was assessed by changes of the water contact angle and also by changes in the mass coverage (determined by FTIR in transmission mode). In Table 2, one observes that THF had a deleterious effect in the cases of both reflux and submersion, that CH_2Cl_2 had a deleterious effect in the case of reflux only, and that monolayers exposed to cyclohexane were stable in both cases. The extent to which the deleterious effects of THF and CH_2Cl_2 may reflect the mode by which molecules within the monolayers were attached to the mica surface—those portions of the monolayer that could be removed were, presumably, anchored less strongly—remains an open question at present.

The excellent water stability of OTE monolayers was demonstrated previously;[14] neither the contact angle nor the mass coverage changed with immersion in water or with prolonged exposure to water droplets.

Characterization of OTE Monolayers Outside the Surface Forces Apparatus

Adsorption Isotherm. The OTE concentration in the adsorption solution was varied in order to determine the concentration of OTE at which a monolayer forms.

Figure 1 shows the mass coverage of alkyl chains on mica as a function of the logarithmic OTE concentration in the adsorption solution. The mass coverage (mass per area) was determined using FTIR as described below. Above the concentration of 0.1−0.2 mM of OTE in solution, the mass coverage was independent of OTE solution concentration over nearly 2 orders of magnitude. Higher OTE concentrations were not tested as the THF concentration was then too large to permit self-assembly. At the lowest concentrations the question of equilibration was explored, and in comparison between 15 and 60 min adsorption time (separate mica surfaces) no difference was noted.

Quantification of the Mass Coverage. In previous work,[14] the mass coverage of self-assembled monolayers (mass per area) was determined by transmission infrared spectroscopy,[9] by calibration with LB monolayers. In particular, the known surface coverage (20 Å^2/molecule) of an LB monolayer of stearic acid provided the calibrated infrared absorbance of this density of methylene groups. This method was used to determine the mass coverage shown in Figure 1. The measurement is believed to discriminate differences in mass coverage corresponding to approximately 5% of a full monolayer.

The calibration of mass coverage was verified in an independent way by using infrared spectroscopy in the mode of attenuated total reflection (ATR) with an infrared prism of cylindrical geometry,[21,22] as described in the Experimental Section.

Tilt Angle of Alkyl Chains. Monolayers were prepared on a trapezoidal Ge internal reflectance element, prepared as described in the Experimental Section, and FTIR spectra were taken in both the s and p polarizations.

The integrated intensities were determined and a dichroic ratio was calculated using the standard definitions for absorbance[23-25] and the electric field calculation of Haller and Rice.[23] The angle between the surface normal and the transition dipole moment was determined and tilt angles were calculated by using models in which the C−H groups are perpendicular to the chain axis.[26] Mean tilt angles of the alkyl chains were determined to be 13 ± 5° from the normal.

Ellipsometric Thickness. A Rudolph Research (Flanders, NJ) Model 43603-2001 null ellipsometer was employed. The measurements are carried out at 546 nm and 70° incidence. To obtain consistent results, it was critical to measure the optical constants of each substrate before adsorption. It was also critical to hold constant the time elapsed between substrate preparation and adsorption of OTE. The measurements were taken from zones 1 and 4 (identified by McCrakin et al.[27]). The ellipsometric thickness of OTE on Si was 24−26 Å, average value 25 Å.

Helium Scattering, AFM, X-ray Reflectivity. For He diffraction,[28] we are indebted to Professor G. Scoles and Dr. N. Camillone of Princeton University.[29] Helium diffraction probes the degree of order at the outermost point of the monolayers, i.e. at the methyl groups. In investigations at 45 K, no evidence of crystalline order was seen.

For specular X-ray reflectivity measurements of OTE on Si, we are indebted to Professor S. Barton of the University of Massachusetts.[30] The reflectivity curves were fit to give a thickness of 24 Å.

For atomic force microscopy (AFM) measurements, we are indebted to Professor M. Porter and Dr. C. McDermott of Iowa State University.[31] The measurements indicated surface roughness of roughly ±1 Å. No long-range order between the methyl groups was detected in measurements made at room temperature. It appears to remain an open question whether the AFM technique is sensitive to order among methyl groups.

It is more puzzling that no order was detected at the methyl groups by He scattering. This contrasts with measurements of alkanethiols on gold, for which correlations of the methyl groups up to 25−40 Å were identified.[28] On the other hand, infrared spectra of the present monolayers indicate a high degree of crystalline-like order in those regions of the alkyl chain below the methyl terminus (ref 14 and Table IV). In particular, the methylene vibrations indicate a crystalline-like state.[14] The difference in the degree of order at the methyl group is not understood at this time.

Surface Forces Characterization of OTE Monolayers

The goal of this endeavor was to produce self-assembled monolayers for use in surface forces experiments; accordingly, measurements within an SFA presented the decisive test of the usefulness of these monolayers. We note further that the monolayer thickness and adhesion measured in the SFA instrument are exceptionally sensitive to monolayer imperfections which serve to roughen the surface. For example, the presence of trace multilayers—over even a small portion of the contact zone—is sufficient to keep the two opposed surfaces separated at the thickness of these multilayers. This stands in contrast to characterization methods which measure a mean property (such as ellipsometry). Thickness and adhesion measurements in the surface forces apparatus, which characterize a large area of surface, contact diameter roughly 10 μm, present a test of the peak excursions from the mean value over this large area.

A technically challenging aspect was the need to work with mica sheets that were only 2−4 μm thick (necessary because of the optical technique that is used to determine surface separation in the SFA). The following method to handle these flexible sheets was convenient. First, in the customary manner,[1] mica sheets were cleaved to the desired thickness, deposited on a thick mica coupon so that they adhered by van der Waals attraction, and silvered. Just before self-assembly the mica sheets were removed using tweezers and deposited, silver-side down, on a freshly-cleaved new thick mica coupon. A droplet of water provided sufficient capillary attraction for secure adhesion during the ensuing manipulation.

Practical Aspects. The experiments described below were successful approximately 70% of the time. Unsuccessful experiments resulted from particles that kept OTE-coated mica surfaces at micrometer-sized separations when they were brought together in the surface forces apparatus. Evidence that these obstructions were particulate was obvious from deformations in the interferometric fringes[1] when the mica sheets were forced closer together. Because their abundance was low, it is not surprising that they did not show up in the IR measurements of the mean mass coverage (discussed above).

In seeking their origin there are three possibilities to consider: they may have resulted from intrinsic aspects of the hydrolysis chemistry in the protocols that we recommend here; they may have been already present in the OTE as purchased; they may have resulted from imperfect experimental conditions, especially imperfect cleaning of glassware. We are doubtful of the first possibility because the particles did not display a distri-

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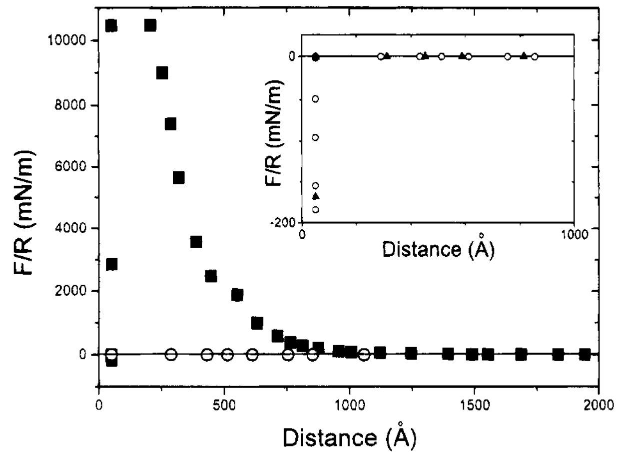

Figure 2. Force–distance profiles of OTE-coated mica surfaces in air. Force, normalized by the mean radius of surface curvature of the crossed cylinders, is plotted against surface separation as this was decreased: first approach, filled squares; second and later approaches, open circles. Inset shows adhesion measured upon separating the surfaces (circles) and subsequent approach back together and then apart (triangles). Adhesion forces were independent of the length of time the surfaces had remained in contact.

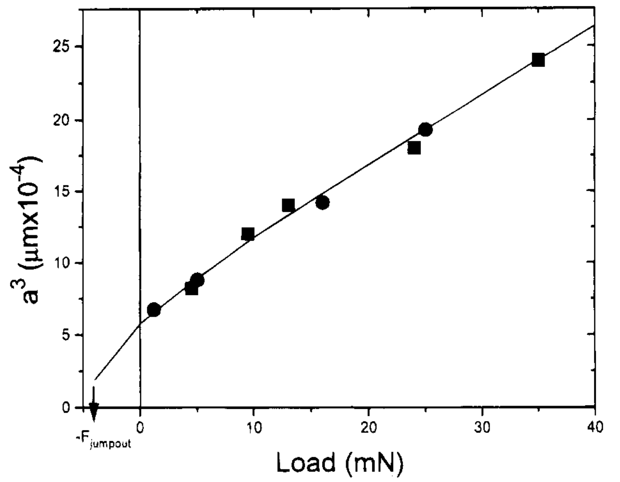

Figure 3. JKR analysis of adhesive contact between OTE monolayers in air. Mica sheets, coated with OTE monolayers, were glued to crossed cylinder quartz supports using *sym*-diphenylcarbazide (DPC) as glue. The cubed contact diameter is plotted against the applied load: filled squares, increasing load; filled circles, decreasing load. The line through the data corresponds to the parameters, in eq 1, γ = 22.1 mJ/m^2 and K = 2.52 × 10^9 N/m^2. The adhesive force, F_{jumpout}, is also indicated.

bution of size. This suggests that they were introduced to the surfaces at some point, not intrinsic to the procedure. This point was not pursued in detail. For present purposes we emphasize that the procedures described here did result in a consistently large proportion of successful experiments over a period of more than 3 years and successful implementation into the surface forces apparatus.[15-18]

Electrostatic Surface Charge in Air. OTE-coated mica sheets were mounted in the SFA and were brought together in air atmosphere. In Figure 2, surface force (force normalized by the mean radius of curvature of the crossed mica cylinders[1]) is plotted against surface separation.

A large difference was consistently observed between first and subsequent approaches in air. In Figure 2 is plotted an example of the repulsive force encountered at large separations on first approach, and the absence of this long-range force upon subsequent approaches at the same spot. In control experiments in which the surfaces were left separated for up to 5 days, the repulsive force did not return. Moving to a new contact spot resulted however in a new repulsive barrier, which was also quenched when the surfaces were touched together. These observations, together with the further observation that the long-range repulsion was always observed in air but never in liquid media, indicated that the repulsion did not reflect molecular contamination of the surfaces but had another origin.

Following the work of Horn and Smith,[32] it seems reasonable to expect that these repulsive forces were electrostatic in origin. The data in Figure 2 were fit to a model of two uniformly charged capacitor plates[32] and a surface charge of $\approx 1 \times 10^{-4}$ C/m^2 was calculated; this number varied slightly between different surface preparations at different levels of ambient humidity. This was a small surface charge and may be compared to $\approx 10^{-2}$ C/m^2 in the work of Horn and Smith,[32] which involved the interactions between chemically dissimilar surfaces. In future work it would be interesting to explore the mechanism of surface charging.

Thickness and Adhesion Measurements. The thickness of the OTE monolayers, in van der Waals adhesive contact in air, was measured in the conventional way by multiple beam interferometry.[1] First the thickness of the untreated mica sheets was measured, then the thickness of OTE-coated mica sheets from the same cleavage plane was measured. The OTE film thickness was determined by subtraction.

The mean thickness in repeated experiments was 26 Å per monolayer (standard deviation 2 Å). This small variability is believed to reflect in part some optical misalignment, in part some actual differences between the OTE surfaces formed. The mean thickness agrees well with the independent measurements (noted above), obtained by ellipsometry and X-ray specular reflectivity, of OTE on Si.

From the force required to pull the surfaces from adhesive contact, and the extent of flattening at contact, surface energy can be estimated. In the JKR theory[33]

$$a^3 = R/K[F + 6\pi R\gamma + (12\pi R\gamma F + (6\pi R\gamma)^2)^{1/2}] \quad (1)$$

where a is the contact diameter, R is the radius of curvature, K is the elastic constant, γ is the solid–vapor surface energy, and F is the normal load. In Figure 3, a^3 is plotted against the normal load, illustrating the good quality of the fit.

The parameters γ and K were fitted to the data in Figure 3 using a two-parameter fitting routine. The fitted parameters are 22.1 (±1.8) mJ/m^2 for the surface energy and 2.52 × 10^9 (±8.0 × 10^8) N/m^2 for the modulus of this *sym*-diphenylcarbazide glue. This surface energy agrees well with the calculated surface energy of 21.2 mJ/m^2 determined from our earlier contact angle correlations based upon Young's equation.[14]

The JKR theory can also be used to relate the force required to separate the surfaces, the pull-off force, to the surface energy by

$$F = 3\pi R\gamma \quad (2)$$

The results of pull-off measurements gave a surface energy of 22.5 mJ/m^2 (standard deviation 4.7 mJ/m^2) using sugar glue and 23.7 mJ/m^2 (standard deviation 2.4 mJ/m^2) using

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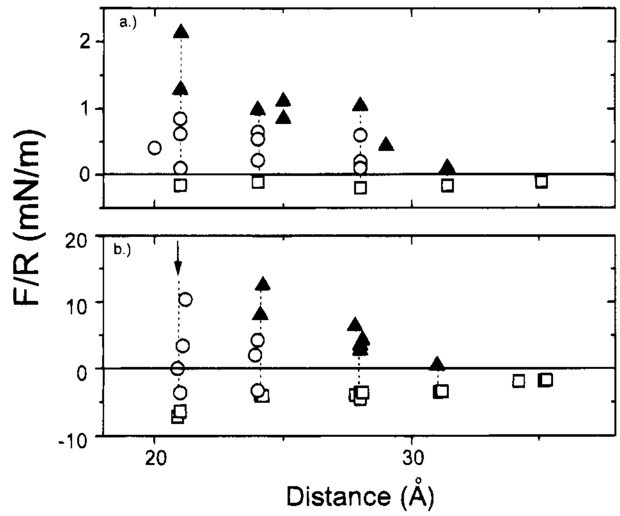


Figure 4. Force–distance profiles of undecane ($C_{11}H_{24}$) on (a) mica and (b) OTE. Force, normalized by the mean radius of surface curvature of the crossed cylinders, is plotted against undecane film thickness. The arrow in (b) indicates that forces larger than 20 mN/m were also measured. The filled triangles were measured on squeezing the surfaces together, the open symbols upon separation. Squares indicate the force at which plates jumped apart through loss of adhesive contact. Figure is replotted from ref 18.

sym-diphenylcarbizide glue. Here we refer to the glue used to attach the mica sheets to an underlying quartz lens.

Finally, we note that the pull-off forces did not depend on the time the surfaces were together; this indicated minimal interdigitation of the opposed monolayers and is consistent with the absence of hysteresis in the comparisons according to eq 1.

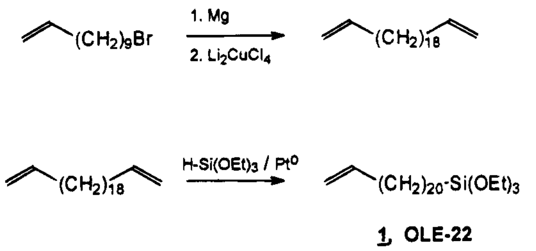
Oscillatory Forces Using OTE Surfaces. It is well established that the force–distance profiles of alkanes between mica are oscillatory in nature,[2] with period of a methylene diameter; the origin of the phenomenon is analogous to the radial distribution function that characterizes bulk liquids.[2] Theory also predicts an oscillatory force–distance profile when alkanes are confined between weakly attractive surfaces.[18] When a monolayer is imperfectly packed, this is not observed.[8]

Figure 4 shows force–distance profiles of undecane ($C_{11}H_{24}$) between mica and between OTE (note the smaller ordinate scale for the measurements with OTE). In both instances the adhesive minima increase with decreasing film thickness and oscillate with a period of $\approx$3–4 Å, the methylene segment diameter, indicating that the molecules were lying preferentially parallel to the surfaces in both cases. The observation that adhesive forces were an order of magnitude less between OTE than between mica is, from the integral equation theory of Schweizer,[18] consistent with the order of magnitude difference in surface energy. A detailed comparison with this theory was made in ref 18. For present purposes, the key observation is the observation of oscillatory surface forces in both cases. This gives clear indication (consistent with the AFM and specular reflectivity measurements referred to above) that the OTE monolayers were quite smooth.

Vinyl-Terminated Monolayers and Monolayer Chemistry

It was also desirable to produce other organic surfaces, of other terminal functionality than the simple methyl group presented by OTE. To this end, the self-assembly of vinyl-terminated ethoxysilanes, of similar alkyl chain length to that of OTE, was explored.

Scheme 1. Synthesis of OLE-22



Scheme 2. Synthesis of OLE-20

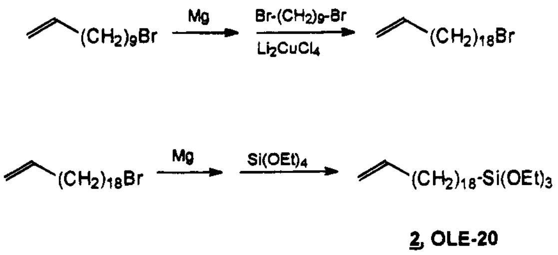


Figure 5. Schemes for synthesis of vinyl-terminated alkylethoxysilanes (OLE).

In this section we describe the synthesis, the characterization of the resulting self-assembled monolayers, and chemical reactions at the vinyl group to produce polar chemical functionality. Future elaboration of the monolayer functionality by well-known methods[4] is clearly possible.

Synthesis of ω-Olefin, OLE. Two ω-alkenyltriethoxysilanes were synthesized. The synthesis of the initially chosen silane, 21-docosenyltriethoxysilane, **1** (OLE-22), is outlined in Figure 5, Scheme 1. The ready availability of undecenyl bromide made this an attractive synthetic route in principle. However, it was found that the hydrosilation step invariably resulted in significant epimerization of the double bond into internal positions along the alkyl chain under a variety of conditions using either platinum or rhodium catalysts. All of the work with **1** reported in this paper utilized material which had approximately 15% internalized double bond. We have no compelling evidence for whether or not the internalized material was incorporated into monolayers formed from **1**. However, we have no evidence that the monolayer quality was significantly degraded by use of this material.

Several advantages were encountered in using the 19-eicosenyltriethoxysilane, **2** (OLE-20). The synthesis of OLE-20, outlined in Figure 5, Scheme 2, did not require a hydrosilation step with the potential of associated olefin internalization. This material could be synthesized with no increase in internalized olefin relative to that already present in starting material (less than 10%). In addition, the reagent used in excess in Scheme 2 was the cheaper, more easily-separated tetraethoxysilane, whereas Scheme 1 required the α,ω-diolefin to be used in excess. Finally, the shorter chain length of **2** resulted in a lower boiling point. This made the material significantly easier to purify by distillation (for the future, we note that the use of tetramethoxysilane rather than tetraethoxysilane would also be beneficial).

In the course of this work, we saw little difference in behavior between monolayers prepared from **1** and those prepared from **2**. One might speculate that there might be subtle differences in rates of self-assembly, and that there might be interesting differences in self-assembled

Table 3. The Contact Angles (θ_a, advancing; θ_r, receding) of Hexadecane and Water on Self-Assembled Monolayers of Various Chemical Composition at the Terminus

monolayer	water θ_a	water θ_r	hexadecane θ_a
OTE	111	105	44
OLE	101	96	35
50/50 OTE/OLE	104	98	37
75/25 OTE/OLE	106	98	33
hydroxylated OLE	42	31	0
carboxylated OLE	37		0
brominated OLE	81		0

layers comprised of mixtures with OTE. In the absence of compelling considerations, however, we anticipate that our future work on functionalized monolayers will be predominantly with the more conveniently prepared **2**.

Monolayer Formation of OLE. The technique to form monolayers of OLE on mica, Si, and Ge, was the same as for OTE. The OLE films were not quite as oleophobic, upon removal from the coating solution, as their OTE counterparts. The solutions clung slightly to the OLE as the substrates were removed from the adsorption solutions, though they did not actually wet the substrates. We also note that OTE substrates baked at 120 °C for 2 h after removal from the adsorption solution, and monolayers baked at 100 °C for 4 h, were indistinguishable in their properties. In independent studies of OLE on oxide surfaces, Sagiv[34] noted that the olefin shifted to internal positions along the alkyl chain at temperatures above 100 °C. However, we observed no functional difference between monolayers baked at 100 °C for 4 h and monolayers baked at 120 °C for 2 h. Films aged in sealed vials under ambient conditions for a few weeks were indistinguishable from those newly-made. In comparisons of films prepared from OLE-20 and OLE-22 (see Figure 5 and Experimental Section), no significant differences were noted.

Characterization Outside the Surface Forces Apparatus. In Table 3, contact angle measurements of distilled water and hexadecane against OLE and OTE monolayers are compared. Here θ_a and θ_r refer to advancing and receding contact angle, respectively, and OLE-20 and OLE-22 showed no difference in response. The contact angles were lower against OLE than OTE, as expected for this surface of slightly higher energy than the methyl surface. The numerical contact angles were similar to those found by other investigators on similar layers layers onto other surfaces.[34,35] The contact angles, measured over times of at least 1 h, showed no degradation with elapsed time. The surface energy, estimated as described previously from the contact angles of water and CH_2I_2 (from correlations based upon Young's equation[14]), was 29.0 mJ/m^2.

The transmission infrared spectrum of OLE on mica is shown in Figure 6. The integrated intensity in the C−H stretch region indicated the same surface packing density as for OTE. This was confirmed, with infrared measurements taken in the ATR mode,[21,22] to be the mass coverage, 2.55 mg/m^2, of alkyl chains.

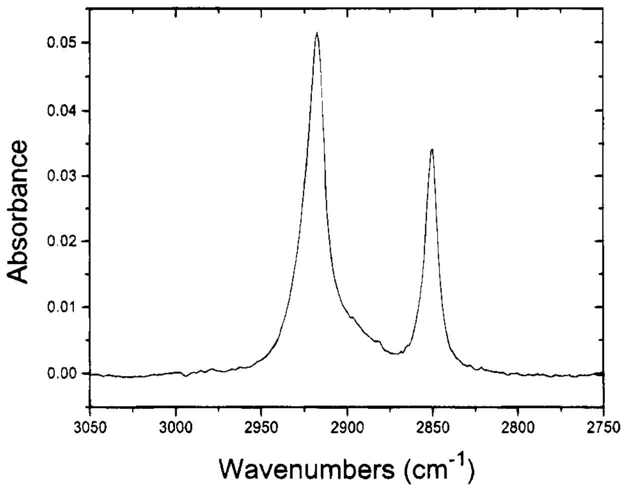


Figure 6. Transmission infrared spectrum, in the region of C−H vibration, of olefin-terminated self-assembled monolayers (OLE) on mica. The symmetric and asymmetric methylene stretches are apparent. The integrated intensity indicates the same surface packing density as for OTE.

In Figure 6, one observes the expected absence of methyl C−H stretches. Regarding the methylene group, the wavenumber at the band center is the same as for OTE, but the bandwidth is slightly narrower for OLE. As for OTE, the C−H scissors vibration of the OLE monolayer at 1465 cm^{-1} was weak and exhibited band splitting; as discussed extensively by Nuzzo and co-workers,[36,37] this constitutes further evidence (in addition to frequency shifts of the methylene bands) of crystalline-like packing. The C=C stretch at 1644 cm^{-1} was visible, but quantitative analysis was not possible because of uneven baseline in this area and low signal-to-noise. The quantitative results are summarized in Table 4.

Mixed Monolayers. Mixed monolayers of OLE and OTE could be prepared using the same protocol as for OLE or OTE individually if hydrolysis solutions containing the mixture of OLE and OTE were prepared. Contact angles of the resulting monolayers are given in Table 3. Here the indicated mixture composition refers to composition in the adsorption solution; the actual composition after self-assembly to a mixed monolayer was not determined. The contact angles showed no degradation with elapsed time. The hysteresis of the contact angle was no larger than for monolayers comprised on single OTE or OLE.

The surface energies, estimated from the contact angle measurements as described previously,[14] were 28.6 and 27.4 mJ/m^2 for 50/50 and 75/25 mixtures of OTE/OLE, respectively.

Surface Forces Characterization. The OLE monolayers were successfully exploited in surface forces experiments. In limited measurements of the monolayer thickness in the SFA, using the ω-eicosenyltriethoxysilane monolayers, the thickness was determined to be 29 Å. For comparison, ellipsometric measurements of the ω-docosenyltriethoxysilane monolayers on Si gave a thickness of 31 ± 2 Å.

In other SFA measurements, pull-off forces were measured, in the same way for OLE as for OTE, and were analyzed with use of eq 2. For the ω-eicosenyltriethoxysilane monolayers, the surface energy estimated in this way was 27 mJ/m^2.

Reactions on the OLE Monolayers

The desirability of chemical modification of these monolayers, to create surfaces of new chemical composition at the terminus, is evident. The chemical reactions necessary to functionalize self-assembled monolayers have been developed extensively by others;[4] in the present work, the new aspect was the capacity to create and utilize

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Table 4. Peak Wavenumber and Half-Width of Methylene Symmetric and Asymmetric Stretch Vibrations, for Self-Assembled OTE Monolayers on Mica[a]

	methylene asymmetric stretch			methylene symmetric stretch		
sample	position	width	Γ/Γ_{max}	position	width	Γ/Γ_{max}
OTE	2917	14.1	1.0	2850	8.4	1.0
OLE (before baking)	2917	13.4	1.03	2850	8.1	1.03
OLE (after baking)	2917	13.9	1.03	2850	8.5	1.03
OLE (hydroxylated)	2917	15.5	1.03	2850	8.8	1.03
OLE (carboxylated)	2917	14.4	0.72	2850	9.0	0.69
neat OLE[b]	2926	21.2		2855	14.2	

[a] The relative surface coverage, Γ/Γ_{max}, is also indicated. All data were taken at 2 cm^{-1} resolution. [b] The bulk liquid, not assembled to form a monolayer.

functionalized monolayers on mica, for use in future SFA experiments. Functionalized monolayers can be used for many purposes, among them to tether polymer chains and to immobilize proteins.[19,20,38]

The capacity to produce mixed monolayers will, in future work, further extend the range of interesting surface functionality. The concentration of olefin functionality can in principle be varied from undiluted OLE (20 Å^2/molecule) to a small number, depending upon the proportion of OLE and OTE in the adsorption solution.

Hydroxylation. Hydroxyl groups were formed using modifications of the hydroboration techniques described elsewhere.[34,35] No clear advantage was noted between the two methods of hydroxylation which were used (see Experimental Section). The IR spectra upon hydroxylation showed no fundamental associated changes in the C−H stretch absorbances. This is summarized in Table 4.

Since exposure of (inert) OTE to similar reaction conditions altered neither the contact angle nor the mass adsorbed of OTE, the higher wettability after chemical reaction can be attributed with confidence to chemical functionalization of the monolayers. Furthermore, after chemical reaction the IR spectra showed no decrease in intensity and no significant change in either bandwidth or center position. Unfortunately, the low signal-to-noise in the region of O−H vibrations precluded quantitative determination of the extent of reaction.

Contact angles of the functionalized monolayer are given in Table 3. These values are similar to those obtained by other investigators, and the inferred surface energy is about 50.2 mJ/m^2. The monolayers on Si gave the same results as those in mica.

Carboxylation. The carboxylation reaction, described in the Experimental Section, oxidizes the ω-olefin to carboxylic acid, while removing one carbon atom from the chain.[34,35] The reaction on ω-docosenyltriethoxy monolayers takes place in aqueous solution. This prohibits the monitoring of reaction using IR in the ATR mode as the broad water absorption bands are much larger than the peaks of interest. The samples emerged wet from the oxidizing and rinsing solutions and had to be blown dry with nitrogen. The advancing and receding contact angles of water and hexadecane, given in Table 3, agree with those previously reported by others.[35] The measured contact angles did not decrease with elapsed time.

However, the IR spectra of carboxylated monolayers showed that carboxylation resulted in diminished intensity of the C−H stretch bands, as summarized in Table 4. In this reaction, a major concern is the harsh conditions to which the monolayers were subjected. Loss of C−H stretches owing solely to chemical reaction should have resulted in a 7% loss in intensity; in fact, a 20−30% loss was found. However, on both mica and Ge substrates, only small changes occurred in band center position and width.

Bromination. Bromination of ω-olefin surfaces, as described in the Experimental Section, resulted in films that were wet upon removal from the reaction solution, even after rinsing. This reaction removed OLE from the mica substrates as evidenced by at least a 50% reduction the C−H stretch intensity of ω-olefin monolayers in all cases. Bromination of monolayers on Si or Ge also showed a reduction in C−H stretch intensity by about 30%. The water contact angles shown in Table 3 degraded with elapsed time. It is clear that bromination, using this reaction scheme, damaged the monolayers.

Conclusions

This study has shown that the mica surface can be easily and conveniently modified, by the self-assembly of hydrolyzed alkyltriethoxysilanes, to create surfaces of different chemical composition. This provides a method to tailor the chemical composition of the mica surface while retaining the advantages (high degree of smoothness, translucency, ease of preparation, low cost) that have made mica the surface of choice in surface forces experiments.[1,2] This study has described the characterization of these monolayers and their successful implementation for experiments in the SFA.[15−18]

As shown above, these monolayers approach the degree of perfection that has been achieved, by others,[4] for self-assembled monolayers on gold[37,39] and various oxide surfaces that are more chemically reactive.[25,35,40,41] In particular, the surface coverage is comparable to that of an LB film, the infrared spectra of the methylene groups indicate a high degree of crystalline-like order, and the expected monolayer thickness is measured by several independent methods. The absence of detectable order at the methyl terminus of OTE remains to be understood in future work, however.

Many possibilities for future SFA experiments are opened up by the availability of these new organic surfaces. As shown above, the self-assembled monolayers were quite robust. They did not degrade, or appear to swell, when immersed in water and many organic liquids, they displayed no adhesion hysteresis, and, as shown elsewhere, they presented a high degree of mechanical integrity under shear.[15−17] Secondly, the monolayers appeared to retain the atomic smoothness of mica to a large degree. The measured thickness was uniform over the large contact areas which typify SFA experiments, even to the point that oscillatory force−distance profiles of liquids could be measured. Independent estimates of the degree of smoothness, by X-ray specular reflectivity and by AFM, confirmed the conclusion as to molecular smoothness. The reactive end groups presented by films formed from olefin-terminated alkenyltriethoxysilanes

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will, in future studies, provide a means to elaborate new surface chemical functionalities.

Using the methods described in this paper, OTE monolayers have already been used to explore questions of friction,[15] stick–slip and adhesion,[16] polymer nanorheology,[17] and liquid structure near surfaces of low energy.[18]

Experimental Section

Experimental Protocol. Mica. We begin with the experimental protocol that gave monolayers of optimal quality. The chief concerns were the experimental protocol of self-assembly, and the technically challenging need (because of the optical technique that is used to determine surface separation in the SFA) to work with flexible mica sheets that were only 2–4 μm thick.

First, a hydrolysis solution of OTE in tetrahydrofuran (THF) was prepared. The hydrolysis solution concentrations were 0.02 M OTE, 0.0066 M HCl, and 0.28 M H_2O. The protocol began by filling a 25-mL volumetric flask about three-fourths full with THF. A small quantity of acid, 0.125 g of 1.31 N HCl, was then added and the solution was stirred. A small quantity of OTE, 0.21 g, was added and the solution was agitated. The clear solution was filled with THF to the mark of the volumetric flask. The flask was sealed, shaken once more, and stored until use. The kinetics of the hydrolysis reaction have been shown to follow pseudo-first-order kinetics with a time constant of about 2 h at room temperature.[14] We found that the hydrolysis solution could be up to 1 week old and still yield a monolayer which was indistinguishable from that formed from a solution only 3 or 4 time constants old.

The hydrolyzed OTE was allowed to self-assemble onto mica from a 1 mM solution in cyclohexane. This solution was prepared by adding 1.11 g of hydrolysis solution to 18.5 g of cyclohexane. This mixture was slightly cloudy even after extensive stirring. Within 5 min the solution was slowly and steadily poured into a glass vial, through a funnel whose spout was directed against the vial walls, until the liquid level rose above that of the top of the sample which was to be coated. The mica sample was freshly cleaved just before this procedure.

The self-assembly process was complete after 15 min. At this time the sample was slowly removed from the solution. The sample should emerge completely dry. Immediately after removal from the coating solution the sample was placed inside a clean glass vial with the sample face up, was covered with Al foil or a glass cover, and was heated in a clean oven. As discussed previously,[14] the required heating time depends on the temperature. Typically we use 2 h at 120 °C. The heating is believed[14] to drive the condensation of the adsorbed silanol and siloxane groups within the mica lattice.

Experimental Protocol. Si, Ge, Glass. The reaction at elevated temperature during a heating step was not required when we coated glass or oxidized Ge and Si. The presumed reason is that these surfaces (unlike mica) carry exposed hydroxyl moieties, which are sufficiently reactive at room temperature.

To prepare Si or Ge for subsequent monolayer self-assembly, the following procedure was used. First, the surfaces were degreased by immersion in an ultrasound with ethyl acetate for about 10 min. After being blown dry, the oxide was stripped by soaking the chip in a vial with 5% HF for 30 s and then rinsing out the vial with high-purity water. After repeating this last step a second time, a new oxide was grown by irradiating with a UV lamp in an O_2 atmosphere. The chips were placed on an aluminum or glass holder and brought to 1 mm or less from the lamp grid for 3 to 4 min. If both sides of the wafer were to be coated, the chip was then lowered, turned over, and then brought back close to the lamp for 2 more min. Glass substrates were prepared in like manner but did not require the HF soak.

The prepared substrates were immersed for 30 min in the adsorption solution and emerged completely dry upon removal from the solution.

General Information. OTE was purchased from Petrarch and was centrifuged for 1 h in an International Clinical Centrifuge (Model cl) to remove high molecular weight material; such material is present in much of the OTE as purchased. UV Spectrophotometric grade tetrahydrofuran, THF, carbon tetrachloride, CCl_4, and cyclohexane (Baxter Scientific) were used as received. Water for the hydrolysis mixtures and contact angle studies was purified by distillation followed by passage through a Barnstead/Nanopure II deionizing and filter system. Mica, ASTM V2 Grade 2, was obtained from Lawrence and Co., New Bedford, MA. It was cleaved in a laminar flow cabient into step-free samples immediately before use. Lightly p-doped (resistivity 1–10 Ω cm) (100) Si, cut from 3-in. wafers, was generously donated by Professor J. Abelson at the University of Illinois, Urbana-Champaign. The UV lamp was a low-pressure Hg grid lamp, purchased from BHK, Inc. (Model 88-9102-02), and was mounted in an aluminum box with 95% O_2 flowing at positive pressure through it. Glassware was cleaned by soaking in a saturated solution of KOH in 2-propanol for at least 12 h, typically more than 24 h. The glassware was then rinsed with high purity water, covered with Al foil or a crystallization dish to protect from dust, and dried in a mechanical convection oven (Precision 18-EM). Occasionally the glassware was cleaned by soaking in dilute HF for 30 s or so, followed by copious rinsing with pure water. The BH_3 complex in 1,4-oxathiane (7.8 M) or THF (1 M) was purchased from Aldrich. Reagent grade 30% H_2O_2, and solid NaOH were purchased from Fisher Chemical. Reagent grade $KMnO_4$, KIO_4, KCO_3, $NaHCO_3$, and HCl were used for the carboxylation reaction. Solutions of various pH ranging from 4 to 9 are purchased from Fisher Chemical. Undecane with a rated purity of greater than 99.5% is purchased from Fluka Chemika and used as received.

IR Measurements. Details of how to take a transmission spectrum of an organic monolayer on mica have been described previously.[14,41] For the ATR measurements two types of Si or Ge internal reflection elements (IRE) were used. One type is the Circle cell attachment to the IR with a cylindrical element, the other is a standard ATR attachment utilizing a trapezoidal prism; the latter presents the advantage that measurements can be made with polarized radiation. The entrance angle of the light beam was 45°. For the trapezoidal prism, the surface cleaning step was the same as for Si or Ge chips. For the cylindrical prism, the UV/ozone lamp exposure was carried out with a device acting like a rotisserie. The cylindrical IRE was placed in the rotisserie and exposed for about 18 min ($^1/_{12}$ turn every 1.5 min). The cleaned IRE was then mounted in the rinsed and dried stainless steel jackets of the ATR attachments, which themselves had been cleaned by soaking in concentrated HNO_3 for at least 12 h. The mounted IRE was then placed in the FTIR sample chamber and a background spectrum, typically 400–2000 averaged scans, was taken. The OTE adsorption solution was then introduced into the cell and removed, after 30 min of adsorption, by flushing out the system with CCl_4. Absorbance spectra of the self-assembled monolayers were taken at this point.

As noted above, the calibration of mass coverage was verified in an independent way by using infrared spectroscopy in the mode of attenuated total reflection (ATR) with an infrared prism of cylindrical geometry.[21,22] Measurements were made of the methylene vibrations of hexadecane solutions prepared in CCl_4 at concentrations from 1 to 8 mg/mL. The integrated intensity was directly proportional to solution concentration. The slope was corrected for the number of methylene stretches in hexadecane as against OTE. The product of this calibrated slope and the integrated intensity of the methylene group of OTE monolayers then gave the mass coverage of the OTE monolayer on mica.

SFA Measurements. The monolayer-coated mica sheets were mounted onto the quartz lenses using either sugar (50:50 mixture of dextrose and galactose) or *sym*-1,5-diphenylcarbazide as the "glue". The air within the SFA was desiccated using P_2O_5. Thickness measurements are accomplished by using two sets of mica of equal thickness: one for mica calibration and one for OTE monolayer formation. Bare mica calibrations were performed in water using the usual method.[42] Once calibrated these bare surfaces were discarded and the newly-made OTE surfaces were mounted into the SFA. Details of surface forces experiments in this laboratory have been described at length elsewhere.[43]

Synthesis of ω-Olefin Silanes. All reactions were performed under a slight positive pressure of nitrogen. Grignard reactions were run in glassware which was flame-dried immediately prior to use. THF was distilled from benzophenone ketyl immediately before use. Hexane was reagent grade and used as received.

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10-Undecenyl bromide was purchased form Pfalz & Bauer and was used as received. 1,9-Dibromononane was purchased from Aldrich. Triethoxysilane and tetraethoxysilane were purchased from Huels America and were used as received. NMR spectra were run in $CDCl_3$/TMS at 400 MHz for ^1H and at 101 MHz for ^{13}C.

1,21-Docosadiene. This material was prepared by Li_2CuCl_4 coupling[44] of the undecenyl Grignard reagent with undecenyl bromide. In a 1-L flask was placed THF (500 mL) and Mg turnings (8.37 g, 0.344 mol). In an addition funnel was placed undecenyl bromide (160.54 g, 0.689 mol), and approximately 30 g of this was added to the THF/Mg in one portion. Reaction was initiated by crushing several of the Mg turnings, and the remaining bromide was added at a rate sufficient to keep the reaction just below reflux (about 45 min). The reaction was allowed to stir for 1 h at which time the Mg was entirely consumed, and the reaction was then cooled in an ice bath to an internal $T < 5$ °C. A solution of LiCl (0.432 g, 10.19 mmol) and $CuCl_2$ (0.677 g, 5.04 mmol) in THF (50 mL) was prepared, and 10 mL of this was added dropwise to the Grignard solution over a 30-min period, keeping the internal $T < 10$ °C throughout. The reaction was allowed to warm to room temperature as it stirred overnight. The large amount of gray solid formed was removed by filtration and washed with petroleum ether, and the dark green filtrate was concentrated under reduced pressure. The concentrate was refiltered, and the filter cake was washed with 250 mL of petroleum ether to give a yellow filtrate. The yellow solution was washed with 400 mL of 15% NH_4OH. The aqueous layer was back-extracted with 150 mL of petroleum ether using brine to break the emulsion formed, and the combined organic layers were dried over $MgSO_4$. Solvent was removed under reduced pressure, and the product was fractionally distilled under high vacuum to give a low melting white crystalline solid (65.51 g, 0.214 mol, 62%), bp 120–140 °C (0.05 mmHg). ^1H NMR 1.20–1.35 (m, 28 H), 1.35–1.45 (m, 4 H), 2.00–2.10 (m, 4 H), 4.89–5.04 (m, 4 H), 5.75–5.87 (m 2 H). ^{13}C NMR 28.92, 29.13, 29.49, 29.66, 33.78, 114.00, 139.11.

21-Docosenyltriethoxysilane, 1. In a 1-L flask was placed 1,21-docosadiene (100.48 g, 0.328 mol) and hexane (139.0 g). An addition funnel containing triethoxysilane (32.50 g, 0.198 mol) was fitted, along with a syringe pump containing a solution of platinum/divinyl tetramethyldisiloxane complex[45] (15% Pt by weight, 0.025 g, 0.00375 g of Pt) in hexane (2.5 g). The solution was heated to 70 °C, and approximately one-third of the silane was added in one portion. Addition of the platinum solution was started at a rate of 2 mL/h, and the remainder of the silane was added over a 1.5-h period. After 4 h at 70 °C, the reaction was finished as evidenced by the disappearance of the strong Si–H band at 2130 cm^{-1} in the IR spectrum. Solvent was removed under reduced pressure followed by high vacuum to give a yellow oil which was fractionally distilled to give a clear liquid product (18.48 g, 0.0392 mol, 20%) bp 187–195 °C (0.05 mmHg). The ratio between terminal and internal olefin in the product can be calculated by ratioing the ^1H NMR signal due to the two protons in the internal olefin at 5.4 ppm with the protons in the terminal olefin at 4.9 ppm (2 protons) and 5.8 ppm (1 proton). ^1H NMR 0.60–0.68 (m, 2 H), 1.20–1.45 (m, 45 H), 2.00–2.10 (m, 2 H), 3.78–3.85 (q, 6 H), 4.88–5.04 (m, 1.7 H), 5.34–5.45 (m, 0.3 H), 5.75–5.84 (m, 0.85 H).

19-Eicosenyl Bromide. In a 1-L flask was placed 10-undecenyl bromide (96.88 g, 0.415 mol) and 300 mL of THF. Magnesium turnings (11.48 g, 0.472 mol) were added slowly over a 1-h period as the reaction proceeded, and the gray reaction mixture was allowed to stir for 1.25 h additional. The Grignard reagent thus formed was filtered into an addition funnel and added dropwise to a solution of 1,9-dibromononane (118.75 g, 0.415 mol) and Li_2CuCl_4[44] (15 mL of a solution of 0.215 g of LiCl and 0.340 g of $CuCl_2$ in 50 mL of THF) in THF (200 mL) which was cooled in an ice bath. The Grignard reagent was added to the THF solution over a 1.5-h period, and the temperature of the reaction was kept at <10 °C throughout. The reaction was stirred for 4 h additional, 300 mL of hexane was added, the solids were removed by filtration, and the filtrate was concentrated under reduced pressure. Hexane (500 mL) was added, and the solution was refiltered, washed with 2 × 300 mL 7% aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, and solvent was removed under reduced pressure. Fractional distillation gave a forecut of bp 45–145 °C (0.05 mmHg, 67.17 g), and a product cut of bp 145–160 °C (0.05 mmHg, 29.92 g, 0.0832 mol, 20%) as a clear liquid which slowly solidified to a low-melting solid. ^1H NMR 1.20–1.50 (m, 30 H), 1.80–1.90 (m, 2 H), 2.00–2.10 (m, 2 H), 3.38 (t, 2 H), 4.88–5.01 (m, 2 H), 5.75–5.83 (m, 1 H).

19-Eicosenyltriethoxysilane, 2. In a 500-mL flask was placed 19-eicosenyl bromide (28.20 g, 0.0785 mol), magnesium turnings (1.91 g, 0.0786 mol), and THF (200 mL). The reaction was initiated by crushing several of the turnings, and the Grignard reagent formed over a 2.5-h period as indicated by the consumption of the Mg. This solution was transferred by cannula to an addition funnel and added dropwise over a 1-h period to a solution of tetraethoxysilane (158 g, 0.758 mol) in THF (100 mL). The reaction was allowed to stir at room temperature for 5 h at which time hexane (500 mL) was added, and the white precipitate formed was filtered off. The filtrate was concentrated under reduced pressure, low boiling fractions were removed at 30–40 °C (0.2 mmHg), and the residue was fractionally distilled under high vacuum to give a clear liquid product, bp 175–185 °C (0.05 mmHg, 9.34 g, 0.0211 mol, 27%), which slowly solidified to a low melting solid on cooling. ^1H NMR 0.60–0.68 (m, 2 H), 1.20–1.35 (m, 39 H), 1.35–1.45 (m, 2 H), 2.00–2.10 (m, 2 H), 3.78–3.88 (q, 6 H), 4.90–5.01 (m, 2 H), 5.75–5.84 (m, 1 H).

Reactions on the ω-Olefin Surfaces. Hydroxylation of ω-olefin was performed using canula and septae. BH_3 complex in THF (diluted to 0.1 M BH_3 in cyclohexane because higher concentrations degraded the monolayers) or 1,4-oxathiane (diluted to 0.8 M with cyclohexane) was added to a vial containing a substrate with an ω-olefin monolayer in N_2 and a small stir bar. After 5 min the reaction was stopped by releasing the seals of the septum and removing the substrate from solution. The substrates were then immediately placed into a 0.1 M solution of NaOH in 10% H_2O_2 for 30 s. The mica and/or Si samples were removed from the H_2O_2/NaOH solution and immersed in THF for a few seconds and then in water for about 2 min. The newly-formed surface was dry and clear. No clear advantage was noted between the two methods of hydroxylation.

Carboxylation was carried out as previously reported by other investigators.[34,35] Aqueous stock solutions of 5 mM $KMnO_4$, 195 mM KIO_4, and 18 mM KCO_3 were prepared in advance. These are combined, 1 part each, with 7 parts water, and the substrate with w-olefin was introduced. After 1 h, the samples are removed and rinsed with 0.3 M $NaHSO_3$, H_2O, 0.1 N HCl, H_2O, and finally ethanol.

The bromination reaction was carried out by simply immersing a mica coupon or Si chip in a 0.2% or 2% Br_2 solution in cyclohexane or CH_2Cl_2. The sample was wet upon removal from the solution, so it was rinsed in ethanol or pure cyclohexane and dried with N_2.

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