Formation and Characterization of a Highly Ordered and Well-Anchored Alkylsilane Monolayer on Mica by Self-Assembly

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A close-packed, well-ordered monolayer can be formed on a freshly cleaved muscovite mica surface by allowing hydrolyzed octadecyltriethoxysilane to self-assemble from a dilute hydrocarbon solution. The alkyl chains in the monolayer deposited by this method appear to be in a pseudocrystalline environment. Contact angle measurements and Fourier transform infrared spectroscopy indicate that the layer is in all respects equal to a Langmuir–Blodgett monolayer in packing density ($\approx$20 Å^2/molecule) and order, but the adhesion of the self-assembled monolayer to the mica surface is much better than that obtainable by any other method of monolayer formation. The self-assembling species, octadecylsilanetriol or low order oligomers, is shown to be surprisingly stable to condensation in dilute solution. The ability to form robust, well-ordered monolayers on mica should open up new possibilities for tailor-made surfaces to be studied in the surface forces apparatus.

Introduction

The development of the surface forces apparatus[1] has made it possible to measure the distance between two surfaces at separations in the range of angstroms while simultaneously recording the forces exerted between them. The ability to study microscopic interactions between surfaces[2,3] has had a significant impact on the understanding of the physical chemistry of surfaces and interfaces.

The requirement that the surfaces used in this technique be essentially atomically flat has restricted the choice of surfaces to be studied. While some recent progress has been made in using other surfaces,[4] surface forces measurements generally must be performed by using freshly cleaved mica sheets. Various techniques have been developed for modification of the mica surface, including surfactant adsorption,[5] Langmuir–Blodgett monolayer deposition,[6] self-assembly techniques,[7] and plasma treatment,[8] but all of these methods have weaknesses that

limit their utility for general construction of model surfaces, especially for use in the surface forces apparatus.

Our desire to study organic surfaces in the surface forces apparatus has led us to consider the best method for provision of well-characterized model surfaces using muscovite mica as a base substrate. The primary requirements for such a method would be (1) a simple experimental protocol requiring minimal manipulation of the mica surface resulting in a high success rate, (2) minimum disruption of the underlying atomically flat mica surface, (3) a resulting surface of maximum homogeneity that is robust enough to withstand further physical or chemical manipulation, and (4) a method that could be used to provide a range of organic functionality in the final surface to be studied.

At the outset of this work, we felt that none of the existing methods for mica surface modification approached these requirements closely enough. Many of the existing surface modification techniques referred to above satisfy one or more of the criteria, but none achieve a full realization of the potential that should exist for construction of model surfaces on mica.

The technique of monolayer self-assembly has been developed as an excellent method for formation of well-ordered and well-characterized monolayers on a variety of functional surfaces.[9–12] Self-assembled monolayers are most commonly prepared either by reaction of trichlorosilanes onto polar surfaces[10] or by adsorption of alkyl

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sulfur compounds onto gold surfaces.[11] The monolayers formed by this procedure are very homogeneous and regular,[10-12] and it has been demonstrated that significant chemical modification of the layer can be accomplished after deposition.[13]

The self-assembly of organosulfur compounds on gold depends on the high specific interaction between the sulfur head group and the gold surface,[14] but the self-assembly of trichlorosilanes can be accomplished on virtually any high-energy surface. Octadecyltrichlorosilane (OTS) forms a very robust monolayer on surfaces such as glass, oxidized silicon, or aluminum oxide, and it might be expected that such a self-assembled monolayer would be ideal for study in the surface forces apparatus. The exposed cleavage plane of mica is a high-energy surface, but it is almost entirely nonfunctional;[15] there is no hydroxyl functionality to provide a handle for anchoring the silane monolayer.
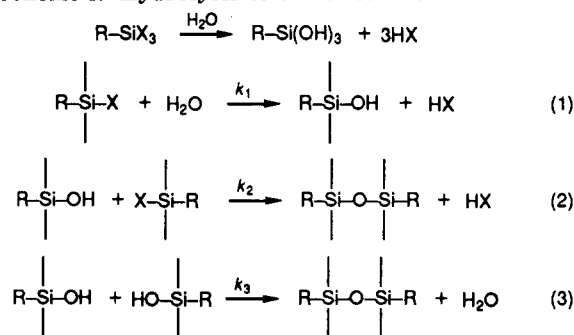
Some progress has recently been made in self-assembling OTS monolayers on mica by either plasma[8] or chemical[7] pretreatment of the cleaved surface. The chemical pretreatment studies, in particular, have shown that a silane monolayer can adhere well to the mica, presumably by formation of a densely cross-linked (in two dimensions) mat which anchors through any adventitious functionality available. This technique, however, requires that a complicated experimental protocol be followed in order to provide just the right amount of water and HCl (for hydrolysis of the chlorosilane) on the mica surface *prior* to treatment with the OTS.[7b]

Octadecyltrichlorosilane is extremely susceptible to hydrolysis and pre-cross-linking. If care is not taken to exclude water from the system until the appropriate time, then a three-dimensional network is deposited on the surface. The use of highly functional surfaces normally masks this problem, especially if the assembled layer is bonded to the surface sufficiently to allow any excess material to be buffed away.[13c,16]

The hydrolysis of trifunctional silanes is shown in Scheme I, and it can be seen that the ability to obtain non-cross-linked silanols will depend on the relative rates of eqs 1, 2, and 3. Thus, if k_2 and k_3 are very small relative to k_1, then it might be possible to obtain a solution of silanetriol that would have a finite, useful lifetime for use in self-assembly work.

It is well-known in silicone chemistry that silanol end-capped silicone oligomers are stable for extended periods,

Scheme I. Hydrolysis of Trifunctional Silanes

$$R-SiX_3 \xrightarrow{H_2O} R-Si(OH)_3 + 3HX$$

$$R-\overset{|}{\underset{|}{Si}}-X + H_2O \xrightarrow{k_1} R-\overset{|}{\underset{|}{Si}}-OH + HX \qquad (1)$$

$$R-\overset{|}{\underset{|}{Si}}-OH + X-\overset{|}{\underset{|}{Si}}-R \xrightarrow{k_2} R-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-R + HX \qquad (2)$$

$$R-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}-R \xrightarrow{k_3} R-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-R + H_2O \qquad (3)$$

and condensation of even moderately sterically hindered organosilanols has been shown to be very slow.[17] This implies that, in nonpolar media in the absence of acid, k_3 in Scheme I can be very small, and the tendency for chlorosilanes (X = Cl) to form three-dimensional gels must be due to a relatively large k_2 or a dramatic increase in k_2 and/or k_3 in the presence of acid.

Alkoxysilanes (X = OR) are more stable to hydrolysis than chlorosilanes.[18] A major reason for this is that both steps 1 and 2 in Scheme I result in the production of acid when X = Cl, as in the hydrolysis of chlorosilanes. This acid catalyzes further reactions and quickly leads to gel formation. In addition, the fact that steps 1 and 2 for the hydrolysis of chlorosilanes are substantially more exothermic than for the hydrolysis of alkoxysilanes implies, via the Hammond postulate,[19] that the activation energy for steps 1 and 2 will be lower and the rate of hydrolysis of chlorosilanes may be faster. It is an empirical fact that moisture must be rigorously excluded from trichlorosilanes, but alkoxysilanes can be stored and used for extended periods with minimal protection from hydrolysis.

Following this logic, it seems reasonable that we might be able to generate solutions of hydrolyzed alkoxysilanes for use in self-assembly; such solutions of silanetriols would, in principle, be self-assembling and would require no other chemical species to be present on the surface. The final cross-linking of a self-assembled array of silanetriols would be accomplished via reaction 3 in Scheme I, and we would expect this to occur spontaneously at the high local surface concentration in the array.

The goal of the work described here is to provide a simple, efficient method for self-assembly of alkylsilane monolayers onto mica using *prehydrolyzed* silanes. The existing methods for assembling these layers on mica rely on modifying the mica surface in such a way as to provide the necessary chemistry on the mica surface; our intention is to attempt to move the critical chemistry away from the mica surface and into solution where it can be accomplished in a controlled fashion prior to handling the mica substrate. A substantial reduction in the handling of the mica will increase the probability of successful implementation into the surface forces experiment.

Results and Discussion

Deposition of Hydrolyzed Octadecyltriethoxysilane on Mica. Initial experiments showed that octadecyltriethoxysilane, OTE, cannot be used as a direct replacement for OTS in the previously developed proce-

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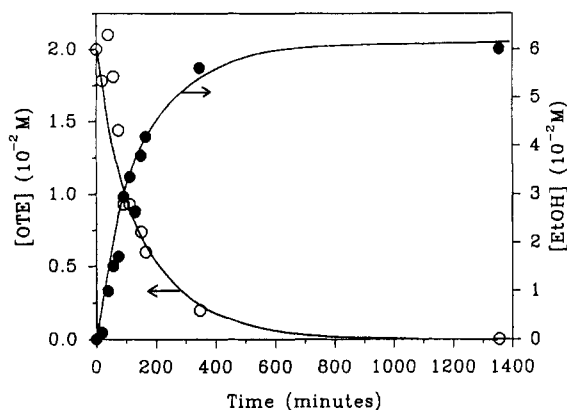
Figure 1. Concentration of OTE (O) and ethanol (●) as a function of time in THF. Initial concentrations were 0.02 M OTE, 0.28 M H_2O, and 0.007 M HCl. The reaction was run nonthermostated at room temperature (20–22 °C).

dure for forming a hydrocarbon monolayer on an acid-treated mica surface,[7] and we have concentrated our investigation on hydrolyzing OTE before attempting to form the monolayer. THF was chosen as the solvent for hydrolysis since this is an acceptable solvent for both OTE and small amounts of water.

An extensive set of experiments was conducted in which the concentrations of water, acid catalyst, and OTE were varied, along with the hydrolysis time, type of acid used, and immersion time of the mica in the hydrolysis solution. In no case was a durable monolayer formed on the mica surface. This is not an unexpected result; the driving force to form a low-energy surface in a polar solvent such as THF is undoubtedly lower than in the less polar solvents typically used in self-assembly, and the THF molecules themselves will also compete efficiently for coordination sites on the surface. While a polar solvent such as THF is necessary for compatibilization of the water and OTE in the hydrolysis stage, a less polar, noncoordinating system will be preferred for the actual deposition step, and we have investigated dilution of the THF hydrolysis solution into hydrocarbon solvent.

It was found that 1.25 mL of a hydrolysis solution which was initially 0.02 M OTE, 0.28 M water, and 0.007 M HCl in THF could be diluted to 25 mL with cyclohexane to give a solution that was only slightly hazy. A mica surface, immersed in this solution for even a fairly short time (15–20 min), emerged completely dry and exhibited an initial water contact angle of >100°. An autophobic coating could also be deposited on silicon by this method. These results suggested that hydrolyzed OTE could be used in self-assembly, and we turned our attention to a more complete characterization of the important aspects of this system.

Kinetics of OTE Hydrolysis. While it is outside the scope of this work to rigorously investigate the kinetics of the OTE hydrolysis reaction, we did need to have some understanding of the rate at which the reaction proceeds in our system. We found that both the OTE being hydrolyzed and the ethanol being produced in the reaction could be quantitatively analyzed by gas chromatography (GC) of the THF hydrolysis solution.[20] None of the silanol reaction products were detected in these experiments, presumably due to the reactivity of these species with the GC injector and column.

Figure 1 shows the concentrations of both OTE and ethanol as a function of time. Analysis of the reaction
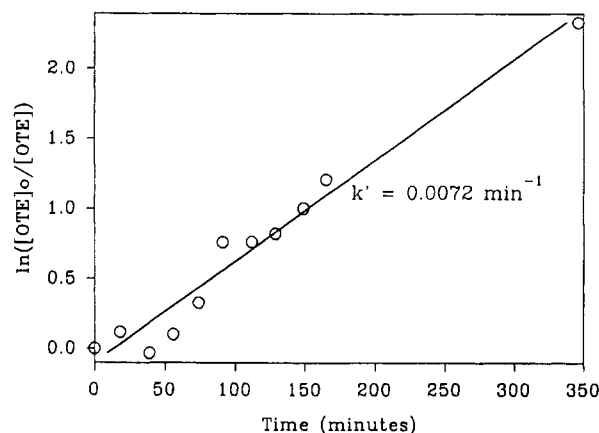
Figure 2. Pseudo-first-order plot of OTE disappearance as a function of time in the OTE hydrolysis reaction of Figure 1. $[OTE]_0$ is the initial concentration of OTE, and [OTE] is the instantaneous concentration of OTE in the reaction.
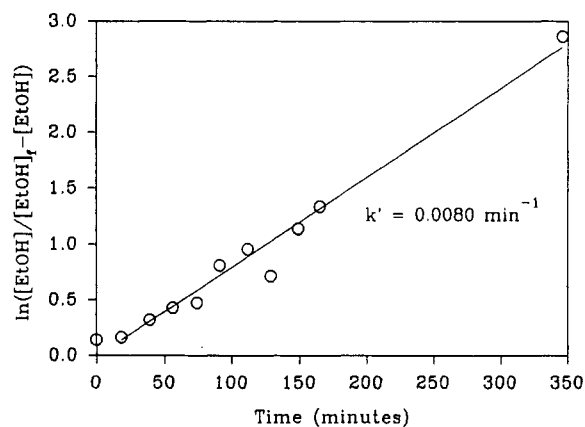
Figure 3. Pseudo-first-order plot of ethanol appearance as a function of time in the OTE hydrolysis reaction of Figure 1. $[EtOH]_f$ is the final concentration of ethanol in reaction after complete hydrolysis, and [EtOH] is the instantaneous concentration of ethanol in the reaction.

mixture after several days demonstrated that no additional ethanol was formed, and calibration experiments confirmed that the ethanol level seen in Figure 1 corresponds to 3 mol of alcohol generated per mole of OTE in the original reaction.

Figure 2 shows the concentration of OTE plotted as a pseudo-first-order reaction assuming the concentration of water to be high and constant. Figure 3 shows the equivalent treatment for the appearance of ethanol. Although there is modest scatter in both sets of data,[21] a straight line defining the apparent rate constant k' is evident for both. It is significant that k' is similar for both disappearance of OTE and appearance of ethanol. This, along with the observation that OTE is present throughout the course of ethanol generation, implies either that the hydrolysis reactions of all three alkoxy functionalities in a given OTE molecule proceed at comparable rates or that the *first* hydrolysis reaction is rate determining.

The kinetics of hydrolysis of alkoxysilanes are generally exceedingly complex due to the formation of intermediate condensed species at rates comparable to the rates of hydrolysis.[20,22-24] Pratt has reported that the rate-

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(21) In particular, the higher concentrations of OTE seemed to give the most scattered data, presumably due to the inherent reactivity of this molecule with syringes and GC hardware.

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determining step for hydrolysis of phenyltrialkoxysilanes in aqueous media (where the rate of condensation is low) is the first hydrolysis,[25] and that result is consistent with the data presented here. While these experiments do not directly answer the question of whether a significant amount of silanol condensation occurs within the time frame of the hydrolysis, we might expect that condensation of partially hydrolyzed OTE molecules would result in more sterically hindered ethoxysilane sites and the hydrolysis of these sites would be slowed. The fact that we do not see any evidence for a reduction in the rate of ethanol formation implies (but does not prove) that silanol condensation may not be important in the first several hours of hydrolysis.

For the purposes of self-assembly, the GC data indicate that a solution containing substantial amounts of fully hydrolyzed OTE, $ODSi(OH)_3$, could be available within a short time after addition of water and acid. We have not determined whether the hydrolyzed OTE exists as the actual silanetriol monomer or as oligomers resulting from condensation reactions, but the extent of condensation cannot be high since three-dimensionality will occur at a fairly early stage in the oligomerization. Results presented below argue strongly for the absence of three-dimensional structures and show that condensations resulting in such structures must be very slow. This is consistent with Brown's observations on the condensation reactions of cyclohexylsilanetriol and phenylsilanetriol.[17]

Stability of $ODSi(OH)_3$ Monolayers. It has been previously noted that, particularly on mica, measurement of the contact angle of water as a function of time is an excellent test of the tenacity of a monolayer.[7] The hydrostatic pressures exerted at the water/monolayer contact line are considerable at the high contact angles (110°) characteristic of a well-organized hydrocarbon surface, and a monolayer that is not securely anchored or cross-linked will be quickly disrupted, with a corresponding decrease in water contact angle. We have found this experiment to be our most convenient test for monolayer stability and a rigorous one as well; any degradation in the water contact angle with time is taken to be an indication of a poorly formed or anchored layer. While we have generally restricted our contact angle stability test to 1 h duration, we have found that well-prepared OTE monolayers maintain their initial high water contact angle at least for several days (measured in a water-saturated enclosed environment to avoid evaporation of the water droplet).

In view of the kinetic data for OTE hydrolysis presented above, we would expect that the OTE hydrolysis solution would be ready for use within a fairly short time. Figure 4 shows contact angle stability for a series of monolayers in which the hydrolysis time was varied. A postbake, explaned below, is required, and all contact angle data presented here are after the postbake. It is somewhat surprising that a good monolayer can be formed after 30 min of hydrolysis since only a fraction of the OTE has been hydrolyzed at this point; either the small concentration of hydrolyzed OTE available at this time is sufficient for self-assembly or hydrolysis is promoted in the cyclohexane disperison or at the mica surface. The prehydrolysis solutions are not indefinitely stable as evidenced by the data for a 24 day old solution, but we routinely use solutions that are up to a week old to form good monolayers. We have noted no significant effect of hydrolysis solution age between 30 min and 1 week in

(25) McNeil, K. J.; DiCaprio, J. A.; Walsh, D. A.; Pratt, R. F. *J. Am. Chem. Soc.* 1980, *102*, 1859.
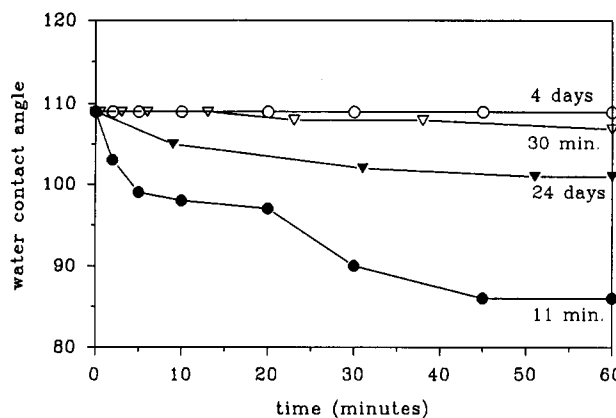
Figure 4. Effect of prehydrolysis time on $ODSi(OH)_3$ monolayer stability. The Y axis is the contact angle of a sessile water drop on the monolayer surface, and the X axis is the time since placement of the drop. Each data set represents an experiment in which the OTE was allowed to react in the THF/water solution for the indicated time before dilution into cyclohexane and self-assembly. All samples were baked at 120 °C for 2 h prior to testing.
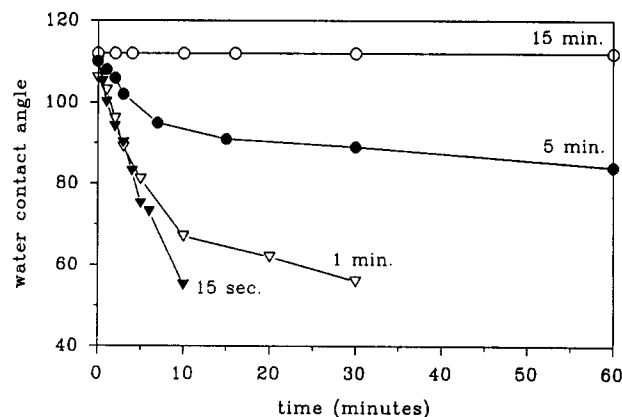
Figure 5. Effect of immersion time of the mica in the self-assembly solution on $ODSi(OH)_3$ monolayer stability. The X and Y axes are as in Figure 4. Each data set represents an experiment in which a mica coupon was immersed in a cyclohexane/$ODSi(OH)_3$ self-assembly solution for the indicated amount of time, removed, baked at 120 °C for 2 h, and tested.

forming robust monolayers, and this implies that self-condensation of the silanol groups in THF must be quite slow under these conditions.

Immersion time of the mica in the OTE/cyclohexane coating solution also has an effect on the quality of the monolayer formed. Figure 5 shows that, although high initial values can be obtained after very short immersion times, these values are not stable even for very short drop residence times. After immersion times of at least 15 min, however, a good quality monolayer can be formed. The reason for the high initial contact angles at even very short immersion times is not clear. We can speculate that the high-energy mica surface is quickly covered with enough hydrocarbon to give a fully covered but disordered surface which has silane units too widely dispersed to form surface cross-links on heating. Work on adsorption isotherms is currently underway.[26]

The water contact angle of the $ODSi(OH)_3$ monolayer is not stable immediately on removal from the coating

(26) The recipe for the self-assembly solution presented here is not optimized. We have not exhaustively studied the effects of water, acid, and OTE concentration, but we know that good monolayers can be prepared with at least a modest latitude in these variables. Further details on adsorption kinetics, concentration, and hydrolysis time effects are being investigated and will be published in a subsequent paper.
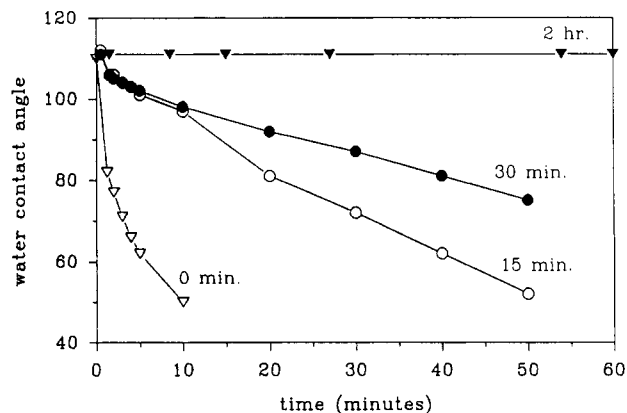
Figure 6. Effect of postbake on the stability of ODSi(OH)$_3$ monolayers on mica. The X and Y axes are as in Figures 4 and 5. The time indicated on each of the four data sets is the amount of time that the particular monolayer was baked at 120 °C after self-assembly and before testing.

Table I. Contact Angles and Surface Energy of OTE Monolayers on Mica and Silicon

	contact angles, deg				surface energy, mN/m	
	$\theta_{a(H_2O)}$	$\theta_{r(H_2O)}$	$\theta_{(CH_2I_2)}$	$\theta_{(HD)}$	γ^d	γ^P
mica	111	108	73	43	21.4	<0.1
silicon	111	105	71	42	22.6	<0.1

solution. Figure 6 shows that a postbake of 2 h at 120 °C is necessary to give a well-anchored layer. Heating at lower temperatures for longer times also results in stable monolayers, but heating at higher temperatures for longer times degrades the stability of the layer.[26]

The requirement for a postbake is probably due to the lack of available functionality on the mica surface. The hydrolyzed OTE can assemble onto the surface of the mica, but the only mechanisms to hold it in place are for the silanols to form a two-dimensionally cross-linked mat or for the silanols to react with the surface silicate network. Two-dimensional cross-linking will proceed via the condensation reaction 3 in Scheme I and may require some heat in order to proceed to a sufficient degree to give an adequate cross-link density to prevent disruption by the water droplet. We cannot rule out the formation of some monolayer/mica bonds which may form due to adventitious functionality on the mica surface, and it is also likely that silanols will bond to the surface by a degenerative exchange reaction which breaks mica surface Si–O–Si bonds and creates mica/monolayer Si–O–Si bonds. Such an exchange reaction would be even more likely in the presence of a catalyst, in this case the small amount of acid in the prehydrolysis solution.

Perhaps the most significant test of a monolayer's stability and tenacity is its resistance to solvent treatment. Immersion of the ODSi(OH)$_3$ monolayer on mica in refluxing cyclohexane overnight did not affect the monolayer. A sample treated in this fashion emerged dry from the cyclohexane and exhibited a water contact angle of 110°. The water contact angle did not decrease with time, indicating that the monolayer remained well anchored to the mica surface. Treatment of the ODSi(OH)$_3$ monolayer in refluxing tetrahydrofuran did cause some degradation, however. A monolayer on mica immersed in refluxing THF overnight gave a water contact angle of 62° after drying, and oven annealing did not improve this. Although this indicates that THF undercuts and/or dissolves the layer, the nonzero contact angle indicates that this treatment does not totally destroy the monolayer, and less vigorous treatment with THF may be possible.

The implications of these experiments are clear; it should be possible to chemically manipulate ODSi(OH)$_3$ monolayers on mica. The ability to do chemistry on preformed monolayers has been demonstrated by several groups,[13] but the difficulty of adhering a monolayer to mica has, up to now, made this a technique that is restricted to high

functionality surfaces or those surfaces that have a high specific interaction with the adsorband. The focus of our continuing work in this area will be to demonstrate the feasibility of this approach on mica.

Contact Angles and Surface Energy of OTE Monolayers. Contact angle measurement is one of the most sensitive probes for the analysis of monolayer quality in self-assembled films.[10c,11f,27] It is generally accepted that a perfect hydrocarbon monolayer will exhibit a water contact angle of greater than 110° with minimum advancing/receding hysteresis. Table I gives the contact angle data for OTE monolayers on both mica and silicon. Also listed in Table I is the surface energy for each surface as calculated from the H$_2$O and CH$_2$I$_2$ data using the geometric mean method.[28] We note the very low surface energy (and total absence of a polar component) and the high receding contact angle on mica as evidence for a very ordered monolayer. These surface energies are comparable to critical surface tensions measured for OTS monolayers.[16] The contact angle differences between the silicon and the mica are close to the experimental error in the measurements, but the differences are consistent and may represent the more perfectly flat mica surface. The hexadecane contact angles, θ(HD), are several degrees lower than those seen by Sagiv in "perfectly" ordered monolayers[10c] but consistent with other work.[12d,13e]

Fourier Transform Infrared Measurement of OTE Monolayers. Transmission Fourier transform infrared (FTIR) spectra of OTE monolayers on mica can be obtained in the same manner as those previously reported for OTS monolayers.[29] FTIR spectra of self-assembled monolayers on silicon are also obtainable, although the thicker substrate leads to much more intense and closely spaced interference fringes. These fringes make quantitative analysis difficult, but the spectra on silicon are qualitatively the same as those on mica. Figure 7 shows a spectrum of the hydrolyzed OTE monolayer on mica along with that of a Langmuir–Blodgett monolayer of barium stearate[30] which was transferred onto a mica surface. Several factors are immediately apparent: the peak widths and positions are virtually identical for the two samples, and the total integrated intensities of the spectra are quite similar.

Table II gives the peak positions, widths at half-height, and integrations for the symmetric and asymmetric CH$_2$ stretches for both the self-assembled monolayer and the Langmuir–Blodgett monolayer. Also included are the peak position and width data for a thick layer (amorphous) IR spectrum of liquid OTE. Because these spectra are taken in transmission, we do not expect to see the orientational information that is typical of grazing angle spectra;[11d,31] however we can infer a high degree of order in the self-assembled system. The spectrum of the OTE monolayer

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Table II. Peak Positions and Integrations for CH$_2$ IR Bands

	CH$_2$(asymmetric)			CH$_2$(symmetric)		
sample	position, cm^{-1}	width, cm^{-1}	area	position, cm^{-1}	width, cm^{-1}	area
hydrolyzed OTE (self-assembly)	2917	14.1	1.09	2850	8.4	0.44
stearic acid (Langmuir–Blodgett)	2917	15.1	1.00	2850	8.8	0.44
amorphous (neat liquid)	2925	21.2	–	2855	14.0	–
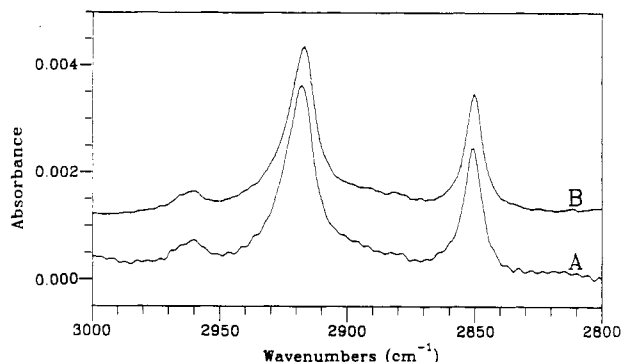
Figure 7. Transmission FTIR spectra of the alkyl stretching region of (A) an ODSi(OH)$_3$ self-assembled monolayer on mica and (B) a Langmuir–Blodgett monolayer of barium stearate transferred onto mica. Each spectrum is actually due to two monolayers, one on each face of the mica coupon. All other regions of the IR spectrum are obscured by strong signals due to the mica substrate.

is remarkably consistent, both in peak position and intensity, with the spectrum characteristic of isotropic crystalline alkyl groups,[31] and the decrease in stretching frequency and peak width relative to the liquid spectrum is also an indication of higher order in the monolayer.[12f] The correspondence, both in peak position and width, with the spectrum of the Langmuir–Blodgett monolayer also argues strongly for a high degree of order in the self-assembled layer.

The amount of material adsorbed on the mica surface can also be inferred by comparison with the Langmuir–Blodgett layer. The packing density of a barium stearate Langmuir–Blodgett monolayer is known to be approximately 20 Å^2/molecule,[30] and the monolayer is generally accepted to be well ordered. If we assume that the environment of the alkyl chains in the self-assembled monolayer is similar to the environment in the Langmuir–Blodgett film (i.e. both are packed into pseudocrystalline arrays), we can compare the total amount of material deposited by each method simply by comparing the integrated intensity of the two spectra.

The total integrated intensity of the high-frequency region (2800–3000 cm^{-1}) is not reproducible due to uncertainties in the baseline for these low intensity spectra; however we have found that curve fitting of the asymmetric and symmetric CH$_2$ stretches at 2917 and 2850 cm^{-1} does give reproducible results since a majority of the data points to be fit lie well above the baseline noise. The normalized integrated areas for these peaks are given in Table II, and it can be seen that the area for the self-assembled film is comparable to the area for the Langmuir–Blodgett monolayer. In fact, if we sum the two peak areas for each spectrum, we obtain an area ratio of 1.53/1.44 = 1.06 which is exactly the ratio expected for OTE (17 methylene units) and stearic acid (16 methylene units), 17/16 = 1.06. While we do not claim that the amounts deposited by the two methods are exactly equivalent, it is obvious that both techniques give substantially the same monolayer.

Conclusions

We have shown that octadecyltriethoxysilane can be used as a convenient precursor to well-ordered self-

assembled films that are tenaciously bound to the surface of mica. These self-assembled monolayers have essentially the same structure and packing density as found in Langmuir–Blodgett monolayers; the alkyl chains seem to be packed into a pseudocrystalline, close packed environment.

The large size of the alkyl group in OTE apparently protects the hydrolyzed silanetriol from self-condensation for a considerable period of time, and this result makes the self-assembly process extremely convenient and reliable. While we had initial hopes that the monomeric silanetriol would have sufficient lifetime for use in self-assembly, the fact that the hydrolysis solutions are usable for weeks is extraordinary. We are currently investigating this issue in greater detail.

We do not understand the exact mechanism for the anchorage of the self-assembled monolayer to the mica surface. It is tempting to argue that a two-dimensionally cross-linked silicate mat is formed by condensation of the trifunctional silanols after self-assembly; however at the apparent packing density of 20 Å^2/molecule, the silicon-silicon distance is on the order of 4.2 Å. This distance is much too long for silicon–oxygen bonds of 1.65 Å (3.30 Å maximum Si–O–Si distance) to span, so some reorganization of head groups must occur, and all silanol bonds cannot be resolved. The results on immersion time argue that close packing of the alkyl groups is critical for the ultimate stability of the layer, and this implies that head group–head group condensation must play at least a part in the anchorage mechanism. The extent to which head group–mica reactions participate in the final structure is not known.

The ability to form a "perfect" monolayer on mica under mild conditions will allow us to construct surfaces for use in the surface forces apparatus which have been unavailable until now. Functionalization of these surfaces should also be possible, and we hope to be able to construct and study a wide variety of idealized, well-characterized surfaces and interfaces using this technique.

Experimental Section

General Information. Octadecyltriethoxysilane was purchased from Petrarch and used as received. THF was used as received, and cyclohexane was distilled prior to use. Water used for hydrolysis mixtures, Langmuir–Blodgett experiments, and contact angle studies was purified by distillation followed by treatment through a Barnstead Nanopure II deionizing and filtering system. Mica was ASTM V-2 grade obtained from Asheville-Schoonmaker and was cleaved into stepfree samples immediately prior to use. Boron-doped p-type silicon was cleaned by ultrasound in CHCl$_3$/EtOH[10c] followed by argon plasma treatment immediately prior to self-assembly. Glassware used in self-assembly experiments was cleaned by soaking in a concentrated KOH/2-propanol bath for at least 24 h, exhaustively rinsing with water, rinsing with high-purity water, and oven or air-drying. Glassware treated in such a manner was shown to be free of surface-active impurities by Wilhelmy plate measurements.

OTE Deposition Method. A hydrolysis solution of OTE in THF was prepared by adding OTE (0.210 g, 0.50 mmol) to a clean dry 25.0-mL volumetric flask. The flask was almost filled with THF, and 1.31 N aqueous HCl (0.125 g, approximately 6.6 mmol of water, 0.16 mmol of HCl) was added. The solution was agitated and THF was added to give a final volume of 25.0 mL. This solution was sealed and stored at room temperature until

use. The amounts of water and OTE used in this recipe have not been fully optimized; a significant amount of leeway (at least 10%) is permissible with no deleterious effects on the quality of the monolayer formed.

The OTE solution for coating mica was prepared by measuring 1.25 mL of the above solution into a 25.0-mL volumetric flask and adding freshly distilled cyclohexane to give a 25.0 mL total volume. The slightly cloudy solution was agitated and poured immediately into the vessel containing the freshly cleaved mica sample to be coated. The cyclohexane coating solution was always used immediately after dilution.[26] The mica was immersed for the 15–30 min at room temperature and withdrawn, and the presence of a well-ordered monolayer film was indicated by the mica coupon emerging from the coating solution completely dry (autophobic). For experiments in which an exceptionally clean monolayer was required, the surface of the coating solution could be aspirated to remove any dust or mica chips prior to removal of the coated mica.

The coated mica was placed in a small clean vial, loosely covered with Al foil, and placed in a clean hot air oven at 120 °C for 2 h. Mica samples coated in this manner could be retained indefinitely in clean stoppered vials at room temperature.

Gas Chromatography. Gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph interfaced with a HP 3392A integrator. The GC was equipped with a 10 m × 530 μm wide bore capillary column and a thermal conductivity detector. Analysis of OTE hydrolysis was performed by direct injection of 0.4 μL of the hydrolysis solution which contained approximately 400 ppm undecane as an internal standard. The chromatograph oven was programmed for an initial temperature of 60 °C which was held for 1 min followed by a temperature ramp of 30 °C/min to a final temperature of 260 °C which was held for 10 min. Baseline separation of all components (including THF and EtOH) was achieved by using this protocol.

Infrared Measurements. Some details of the technique used in obtaining transmission infrared spectra of the monolayers on mica have been previously reported.[29] The critical factors involved in obtaining good quality spectra all involve techniques to minimize the interference fringes which result from internal reflections at the parallel faces of the mica sheet. The reflectivity of the mica is minimized by taking the spectra using p-polarized IR radiation at the Brewster angle of incidence (56.4°). Experimentally this is accomplished by using a commercial Brewster's angle attachment (Harrick Scientific). The optical axes of the mica are determined by using crossed polarizers, and spectra are taken with one of these axes aligned with the plane of polarization. A background spectrum is obtained on the mica coupon prior to coating, and the sample spectrum is obtained after coating, ensuring that the same orientation is maintained for both spectra. The reported spectrum is the result of ratioing the background and sample spectra. The spacing of the interference fringes can be increased, and their magnitude decreased, by using as thin a coupon as possible. We have found that mica coupons of >10 cm² can be cleaved to 15–25 μm thickness with no steps on either side. Samples of this thickness are difficult to handle without damage but give substantially better IR spectra than samples in the 50 μm range of thickness. A recent report has appeared in which the interference fringes from the mica were reduced by using sheets of 1 μm thickness.[32] We have found that our method gives spectra of comparable quality with the benefit of using thicker mica sheets which are easier to cleave, handle, and store.

The 2800–3000 cm⁻¹ region of each spectrum was integrated by separating the peak envelope into the constituent peaks using Spectra-Calc software (Galactic Industries) on an IBM personal computer. The total integrated intensity of the IR signal in this region is a sum of the four major absorbances (CH_2 symmetric and asymmetric vibrations at 2917 and 2850 cm⁻¹, respectively, and CH_3 symmetric and asymmetric vibrations at 2960 and 2875 cm⁻¹, respectively). The CH_3 vibrations are relatively weak, and the total area defined by these peaks is quite sensitive to variations in the baseline. For this reason, comparisons between spectra were made by curve fitting the envelope using all four peaks (Lorentzian line shapes) but comparing only the integrated intensity of the major CH_2 peaks at 2917 and 2850 cm⁻¹. These large peaks were well fit regardless of noise and uncertainties in the smaller peaks since a large portion of the curves lie above any of the other data.

Contact Angle Measurements. Contact angles were measured at 20× magnification using a Gaertner Scientific protractor microscope eyepiece. Advancing contact angles (θ_a) were measured by forcing a small droplet of test liquid from the end of a microliter syringe with an unbeveled tip. The size of the droplet used was adjusted for each liquid to give the largest droplet that would remain hanging from the needle tip. The test surface was then smoothly and evenly raised to the hanging droplet, and when the surface and the droplet came almost into contact, the droplet gently transferred from the needle tip to the surface. This method for depositing the droplet was found to give the most reproducible advancing contact angles. Receding contact angles (θ_r) were measured by gently reinserting the needle tip into the droplet and retracting the plunger to remove a portion of the liquid.

Single measurements of contact angles were performed in normal laboratory atmosphere, while those measurements requiring prolonged residence of the droplet on the surface were carried out in a small glass and Teflon chamber in an atmosphere saturated with the droplet vapor. No significant difference in contact angles was noted in these two environments.

Langmuir–Blodgett Monolayers. Langmuir–Blodgett monolayers of barium stearate were deposited on mica by using a KSV 2200 Langmuir–Blodgett system equipped with a 400 mm × 100 mm Teflon trough. Monolayers of stearic acid were spread from chloroform onto an aqueous subphase which was 3 × 10⁻⁵ M in $BaCl_2$ and 4 × 10⁻⁴ M in $KHCO_3$. The π–A isotherms for these monolayers were consistent with published results.[30] Transfer of the barium stearate monolayers was accomplished by immersing a freshly cleaved mica coupon in the clean subphase, spreading the monolayer, and compressing to a surface pressure of 17 mN/m. The mica was then automatically withdrawn from the subphase at a constant surface pressure. A transfer coefficient of 1 was calculated for this procedure.

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