experiment, i.e., for N_2 or graphite, because the real N_2 molecule interacts with the solid with *two* Lenard-Jones centers, each according to its own potential to which eq 3.2 is a very good approximation. However, some tentative discussion is possible. Substituting $Q = 1.4$ esu ($\epsilon_{xc} = 62$ K), we find $T_c = 38.0$ K (as compared to $T_c = 38.9$ K from the calculation in ref 1); $Q = 1.17$ esu produces $T_c = 26.0$ K (as compared to 27.2 K).[1] Clearly the mean-field theory predicts the transition temperature in the right range of temperatures. Experimentally, $T_c = 22–29$ K, and from simulations $T_c = 33$ K, or $T_c = 25$ K for $Q = 1.4$ esu or $Q = 1.17$ esu, respectively.[2] Modifying the interaction with the solid by introducing two L-J centers (to model N_2) will certainly flatten the quadrupole phase as compared to the present model and the 3D rotator model[1] because now the interaction with the solid is independent of the orientation of the quadrupole. This effect will raise the transition temperature. There is another very important effect which will lower it again, i.e., allowing for displacement of quadrupoles in the x and y direction. Allowing for this displacement would introduce the translation–rotation coupling and the possibility of cooperative modes of the phonon and libron kind. Although $S(\mathbf{k},\omega)$ for model N_2 molecules on graphite was extracted[17] from simulations, and phonon and libron collective degrees of freedom were also studied, any soft mode(s) responsible for the orientational transition have not been identified so far, neither from theory nor from experiment.

5. Appendix

The matrix $C^{NM}(\hat{r}_{ij})$ is symmetric, $C^{NM} = C^{MN}$, and depends on the direction of the vector $\hat{r}_{ij}$ joining the centers of molecules i and j.

$$\hat{r}_{ij} = \left(\theta_{ij} = \arccos \frac{z_i - z_j}{r_{ij}} \phi_{ij}\right)$$

Introducing

$$S_n = \sin\,(n\phi_{ij}) \qquad n = 1–4$$

$$C_n = \cos\,(n\phi_{ij})$$

the matrix $C^{NM}(\hat{r}_{ij})$ is

$$C_{11} = 3P_{42}C_2 - 36P_{40}$$

$$C_{12} = 3P_{42}S_2$$

$$C_{13} = -9(3^{1/2})P_{41}C_1$$

$$C_{14} = -{}^3\!/_4P_{43}C_3 + {}^9\!/_2P_{41}C_1$$

$$C_{15} = {}^9\!/_2P_{41}S_1 - {}^3\!/_4P_{43}S_3$$

$$C_{22} = -3P_{42}C_2 - 36P_{40}$$

$$C_{23} = -9(3^{1/2})P_{41}S_1$$

$$C_{24} = -{}^3\!/_4P_{43}S_3 - {}^9\!/_2P_{41}S_1$$

$$C_{25} = {}^3\!/_4P_{43}C_3 + {}^9\!/_2P_{41}C_1$$

$$C_{33} = 54P_{40}$$

$$C_{34} = \frac{3(3^{1/2})}{2}P_{42}C_2$$

$$C_{35} = \frac{3(3^{1/2})}{2}P_{42}S_2$$

$$C_{44} = {}^3\!/_8P_{44}C_4 + 9P_{40}$$

$$C_{45} = {}^3\!/_8P_{44}S_4$$

$$C_{55} = 9P_{40} - {}^3\!/_8P_{44}C_4$$

Here P_{lm} are the associated Legendre polynomials. For centers of molecules confined to a plane, $\theta_{ij} = \pi/2$, and this matrix reduces to that given in ref 1.

We would like to note that in our previous paper[1] the matrix $\tilde{C}^{NM}(\hat{r}_{ij})$ was expressed in a different manner, i.e., in terms of the Clebsh–Gordon[10] coefficients and spherical harmonics.

Registry No. Graphite, 7782-42-5.

Structure and Reactivity of Alkylsiloxane Monolayers Formed by Reaction of Alkyltrichlorosilanes on Silicon Substrates

Stephen R. Wasserman, Yu-Tai Tao, and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received October 13, 1988. In Final Form: March 27, 1989

Long-chain alkyltrichlorosilanes, $Cl_3Si(CH_2)_nR$, adsorb from solution onto silicon–silicon dioxide (Si/SiO_2) substrates and form ordered alkylsiloxane monolayer films. These films were characterized by wettability, ellipsometry, and XPS. Except for very short chains ($n = 0, 1, 2$), the wetting of these monolayers was approximately independent of chain length. The presence of small amounts of water was necessary for the formation of these films. The alkylsiloxane monolayers were stable in common organic solvents, water, and acid but were destroyed by prolonged exposure to base. Simple reactions on vinyl-terminated monolayers generated alcohol-, carboxylic acid-, and bromine-terminated films whose contact angles were lower than the starting monolayers but whose lengths were largely unchanged. Measurements of the contact angle of acid-terminated interfaces as a function of pH indicated that ionization of the surface-immobilized acids required stronger base than does ionization of soluble carboxylic acids. Monolayers containing mixtures of methyl and carboxyl functionalities exhibited wetting properties that mirrored the composition of the interface.

Introduction

This paper describes the preparation of organic monolayer films by adsorption and reaction of alkyltrichlorosilanes on silicon–silicon dioxide (Si/SiO_2) substrates, the characterization of these films, and the correlation of the molecular structure of the organosilicon compounds with the macroscopic properties (e.g., wettability) of the monolayers derived from them. The formation of organic

0743-7463/89/2405-1074$01.50/0

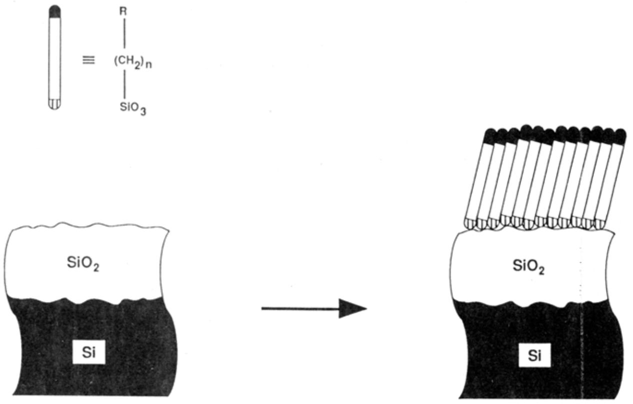
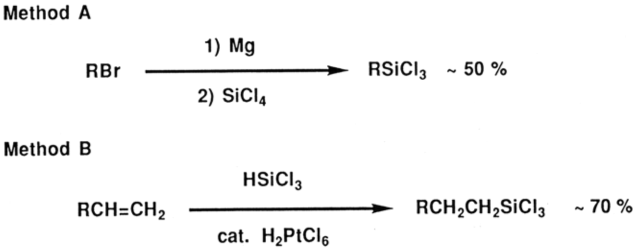


Figure 1. Schematic representation of the formation of alkylsiloxane monolayers by adsorption of alkyltrichlorosilanes ($R(CH_2)_nSiCl_3$, n = 0–17) from solution onto silicon–silicon dioxide (Si/SiO_2) substrates. The SiO_2 layer was 10–20 Å in thickness. The monolayers were 6–27 Å in thickness.

monolayers from organosilicon compounds on appropriate substrates (particularly on glass and on the native surface oxide layer of silicon)[1–7] is one of several methods for forming organic monolayers. Others include the adsorption of alkanethiols,[8–14] dialkyl disulfides,[15–17] and dialkyl sulfides[18,19] on gold; fatty acids on alumina;[20–22] and alcohols and amines on platinum.[23]

Because the organosilicon-derived monolayers are physically robust, they are widely used in technology,[24,25]

Scheme I. Methods for the Synthesis of Alkyltrichlorosilanes



The studies of Sagiv and co-workers have established that monolayers derived from long-chain n-alkyltrichlorosilanes are highly ordered.[1–6] Our examination of these systems had two objectives. First, we wished to compare the properties of these films with those of analogous monolayers formed by other methods. Second, we intended to examine simple organic reactions occurring in these monolayers and to use these reactions to characterize the chemical environment within the monolayer.

The alkyltrichlorosilanes used here had the structure $Cl_3Si(CH_2)_nR$ (Figure 1). The extent to which the group R is segregated at the solid–vapor (or solid–liquid) interface depends on the degree of order within the monolayer. We wished to compare monolayer films that differed primarily in the polarity of the group R. Many polar groups (i.e., R = CH_2OH, CO_2H) are, however, incompatible with the trichlorosilane group. We therefore generated such polar functional groups from nonpolar precursors (especially R = $CH{=}CH_2$) after formation of a monolayer film of the latter. Sagiv and co-workers have used similar strategies.[5,26–28]

This investigation relied heavily on comparisons of X-ray photoelectron spectroscopy (XPS), ellipsometry, and wettability. Our work and that of others have shown that wetting is one of the most surface-sensitive techniques currently available.[29–31] XPS and ellipsometry provide information averaged over the entire thickness of the monolayer (although XPS is certainly more sensitive to the organic groups close to the monolayer–air interface than to those near the silicon dioxide–monolayer interface).[32,33]

Results

Preparation of Alkyltrichlorosilanes. We synthesized alkyltrichlorosilanes using two procedures (Scheme I). Method A involved reaction of a Grignard reagent with tetrachlorosilane[34] and was used primarily for silanes containing a terminal vinyl group. Method B used the platinum-catalyzed addition of trichlorosilane ($HSiCl_3$) to a double bond[35] and provided a practical route to saturated

---

(1) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465–496.

(2) Gun, J.; Iscovici, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *101*, 201–213.

(3) Gun, J.; Sagiv, J. *J. Colloid Interface Sci.* **1986**, *112*, 457–472.

(4) Cohen, S. R.; Naaman, R.; Sagiv, J. *J. Phys. Chem.* **1986**, *90*, 3054–3056.

(5) Maoz, R.; Sagiv, J. *Langmuir* **1987**, *3*, 1034–1044.

(6) Maoz, R.; Sagiv, J. *Langmuir* **1987**, *3*, 1045–1051.

(7) Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050–8055.

(8) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.

(9) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3665–3666.

(10) Bain, C. D.; Whitesides, G. M. *Science* **1988**, *240*, 62–63.

(11) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.

(12) Diem, T.; Czajka, B.; Weber, B.; Regen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 6094–6095.

(13) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733–740.

(14) Strong, L.; Whitesides, G. M. *Langmuir* **1988**, *4*, 546–558.

(15) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.

(16) Nuzzo, R. G.; Fusco, R. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358–2368.

(17) Taniguchi, I.; Toyosawa, K.; Yamaguchi, H.; Yasukouchi, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1032–1033.

(18) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365–385.

(19) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107–6108.

(20) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45–52.

(21) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52–66.

(22) Ogawa, H.; Chihara, T.; Taya, K. *J. Am. Chem. Soc.* **1985**, *107*, 1365–1369.

(23) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513–538.

(24) Abel, E. W.; Pollard, F. H.; Uden, R. C.; Nickless, G. *J. Chromatogr.* **1966**, *22*, 23–28.

(25) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1982.

(26) Netzer, L.; Sagiv, J. *J. Am. Chem. Soc.* **1983**, *105*, 674–676.

(27) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *100*, 67–76.

(28) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *99*, 235–241.

(29) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725–740.

(30) Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1960**, *64*, 519–524.

(31) *Contact Angle, Wettability and Adhesion*; Fowkes, F. M., Ed.; Advances in Chemistry 43, American Chemical Society: Washington, D.C., 1964.

(32) Feldman, L. C.; Mayer, J. W. *Fundamentals of Surface and Thin Film Analysis*; North-Holland: New York, 1986; Chapter 6.

(33) Briggs, D.; Seah, M. P. In *Practical Surface Analysis*; Briggs, D.; Seah, M. P., Ed.; Wiley: Chichester, U.K., 1983; Chapter 1.

(34) Whitemore, F. C.; Sommer, L. H.; Di Giorgio, P. A.; Strong, W. A.; Van Strien, R. E.; Bailer, D. L.; Hall, H. K.; Pietrusza, E. W.; Kerr, G. T. *J. Am. Chem. Soc.* **1946**, *68*, 475–481.

trichlorosilanes and alkyltrichlorosilanes containing a terminal ester. NMR spectroscopy suggested that the purities of these compounds were greater than 97% and that the impurities which we could detect did not contain the $SiCl_3$ group.

Preparation of Monolayers. Monolayers were prepared on clean silicon wafers, whose surface is believed to be silicon dioxide,[36] with $\sim 5 \times 10^{14}$ SiOH groups/cm^2.[37] The substrate was immersed in an unstirred solution of the alkyltrichlorosilane in hexadecane or bicyclohexyl (1–25 mM) for 1–24 h. The wafer was then removed from the solution, rinsed with organic solvents, and dried. The substrate was typically exposed to the air for 10 min before immersion. During this period, the ellipsometric angles for the substrate were measured. The substrate was then transferred into a dry, nitrogen atmosphere.

Because of the susceptibility of the silicon–chloride bond to hydrolysis, it was necessary to limit the amount of water present in the system in order to obtain monolayers of good quality. Exceptional care (of the level used in handling organolithium reagents) was, however, not necessary. The surface of the silicon–silicon dioxide substrate was certainly not anhydrous,[38-40] and a thin film of surface-condensed water may be necessary for the formation of the monolayer. Although these monolayers were usually prepared while keeping the solution of alkyltrichlorosilane under a nitrogen atmosphere, they could also be formed under ambient laboratory conditions when the relative humidity was less than 40%. When stored under nitrogen, the solutions for the formation of the monolayers could be used for several weeks. When stored in the laboratory atmosphere, the solutions were used within 12 h; after 24 h a visible precipitate often formed.

Monolayers composed of methyl- and vinyl-terminated alkylsilanes were the easiest to form. These monlayers were autophobic to the hydrocarbon solution; that is, they emerged uniformly dry from the solution. Monolayers having terminal ester groups emerged wet from the solution used in their formation. Unfortunately, if the alkyltrichlorosilane in the solvent adhering to the substrate was exposed to water, a cloudy film deposited on the surface, presumably due to the formation of a gel of polymeric siloxane. Removal of this film by washing was impossible, although it could apparently be largely removed by actually wiping the surface with a tissue or swab.[41] We therefore prepared these films from dilute (0.1 mM) solutions in methylene chloride or carbon tetrachloride in order to minimize the amount of alkyltrichlorosilane that was left on the surface. These monolayers were rinsed with methylene chloride before exposure to the ambient atmosphere.

Contact Angles. The techniques used to measure contact angles have been described elsewhere.[29] These measurements were routinely made with deionized water (pH 5.6) and with hexadecane. The values reported are the usual quasi-equilibrium static advancing angles, θ_a.[29]

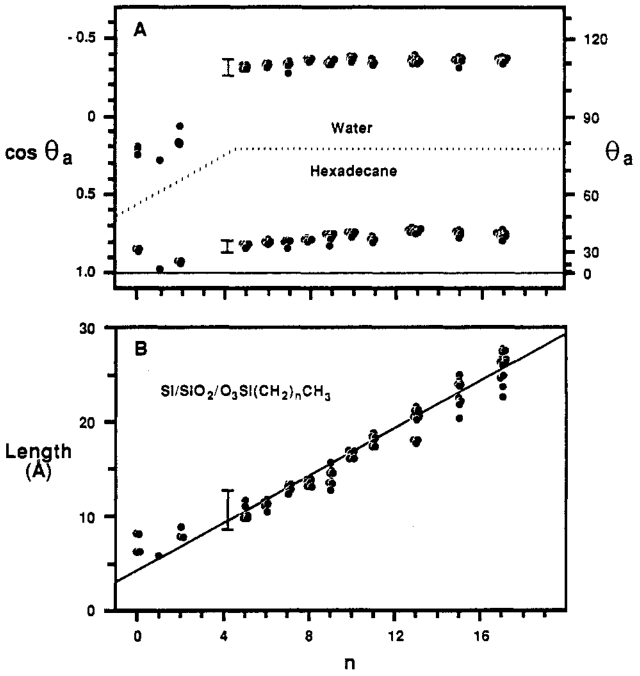


Figure 2. Methyl-terminated alkylsiloxane monolayers prepared by adsorption of *n*-alkyltrichlorosilanes, $CH_3(CH_2)_nSiCl_3$, onto Si/SiO_2 substrates. Each data point represents measurements on a different silicon substrate. Usually, monolayers containing a given chain length were prepared in at least two independently constituted solutions of the alkyltrichlorosilane in bicyclohexyl or hexadecane. (A) Advancing contact angles, θ_a. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses (Å). The solid line represents the best linear least-squares fit for n = 1–17.

Most discussions based on measured contact angles begin with Young's equation (eq 1).[29,42] Here the γ values

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \qquad (1)$$

represent the surface tensions (or energies) of the solid–vapor (sv), solid–liquid (sl), and liquid–vapor (lv) interfaces. The free energies of the interfaces are related to cos θ rather than to θ. We note that Young's law is an exact thermodynamic relationship only for systems at equilibrium.[42] All of the systems that we studied exhibited significant hysteresis[43] in the measured advancing, θ_a, and receding, θ_r, contact angles of water ($\theta_a^{H_2O} - \theta_r^{H_2O} \approx 10°$ (at $\theta_a^{H_2O} \approx 110°$), 12° (at $\theta_a^{H_2O} \approx 70°$), and 20° (at $\theta_a^{H_2O} \approx 34°$)) and are thus not at equilibrium. This hysteresis is approximately constant in terms of energy (that is, the value of $\cos \theta_a - \cos \theta_r \approx 0.2$ is constant).

Figure 2 presents θ_a for monolayers prepared from a homologous series of methyl-terminated alkyltrichlorosilanes. Our values of $\theta_a^{H_2O}$ agree with those reported by Sagiv.[1] Values of θ_a^{HD} are slightly lower than those of Sagiv but agree with the values of Ulman et al.[44] Values of $\theta_a^{H_2O}$ were consistently less (3–6°) than the corresponding values on self-assembled monolayers of *n*-alkanethiols on gold.[11] There was no alternation in θ_a^{HD} for alkylsilanes having odd and even numbers of carbon atoms. Such alternation has been reported for monolayers of *n*-alkylcarboxylic acids

---

(35) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. In *Journal of Organometallic Chemistry Library 5: Organometallic Chemistry Reviews*; Seyferth, D., Davies, A. G., Fischer, E. O., Normant, J. F., Reutov, O. A., Eds.; Elsevier: Amsterdam, 1977; pp 1–179 and the references cited therein.

(36) Carim, A. H.; Dovek, M. M.; Quate, C. F.; Sinclair, R.; Vorst, C. *Science* **1987**, *237*, 630–632.

(37) Zhuravlev, L. T. *Langmuir* **1987**, *3*, 316–318.

(38) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979; Chapter 6 and the references cited therein.

(39) van Roosmalen, A. J.; Mol, J. C. *J. Phys. Chem.* **1979**, *83*, 2485–2488.

(40) De Rooij, N. F.; Sieverdink, R. J. S.; Tromp, R. M. *Thin Solid Films* **1977**, *47*, 211–218.

(41) Sagiv initially observed that this procedure could be used to remove inorganic deposits left after oxidations with potassium permanganate. Whether this procedure causes any damage to the monolayer has not been established. See ref 5.

(42) Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; Wiley: New York, 1982; pp 338–341.

(43) Dettre, R. H.; Johnson, R. E., Jr. *J. Phys. Chem.* **1965**, *69*, 1506–1515.

(44) Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136–6144.

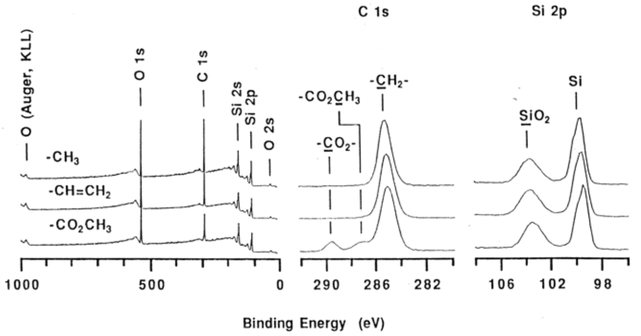


Figure 3. XPS spectra of alkyltrichlorosilane monolayers, $R(CH_2)_9SiCl_3$ ($R = CH_3CH_2$, $CH_2{=}CH$, CH_3OCOCH_2), on Si/SiO_2 substrates: survey spectra (left) and high-resolution spectra of the carbon 1s (center) and silicon 2p (right) regions. The C 1s and Si 2p spectra are each normalized to the same maximum peak height.

on alumina[20] and, to a smaller extent, for alkanethiols on gold.[11]

The contact angle of hexadecane on surfaces prepared from methyltrichlorosilane (CH_3SiCl_3) was anomalous. While these films were probably not monolayers (see below), the observed contact angle was higher than that on monolayers prepared from ethyl- and propyltrichlorosilane. Polysiloxane films prepared from $CH_3Si(OCH_3)_3$ have a lower critical surface tension (and thus a higher contact angle) than films prepared from the corresponding ethyl compound.[25]

Ellipsometry. Figure 2 presents the thicknesses estimated by ellipsometry[45,46] for a homologous series of methyl-terminated alkylsiloxane monolayers. We have compared these thicknesses with values estimated by low-angle X-ray reflection and found excellent agreement.[47,48] The X-ray measurements also demonstrated that these structures were actual monolayers rather than a mixture of uncovered and multilayer regions. We believe that these ellipsometric thicknesses have an uncertainty of ±2 Å.[49,50]

The data are remarkably consistent: for a given alkyl group, the thicknesses measured on different Si/SiO_2 substrates fall within a 5-Å range. These estimated thicknesses correspond well to a model for the monolayer having the *n*-alkyl chain in the all-trans conformation and oriented nearly perpendicular to the surface (Figure 1).[51]

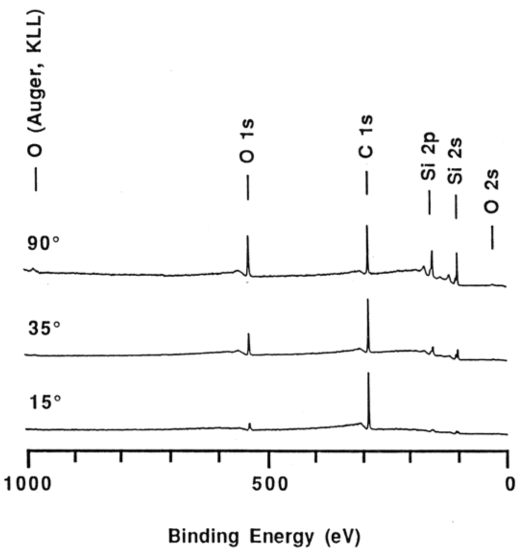


Figure 4. Angle-dependent XPS survey spectra of a monolayer prepared by adsorption of octadecyltrichlorosilane ($CH_3(CH_2)_{17}SiCl_3$, OTS), onto an Si/SiO_2 substrate. Spectra were obtained at takeoff angles of 90°, 35°, and 15°.

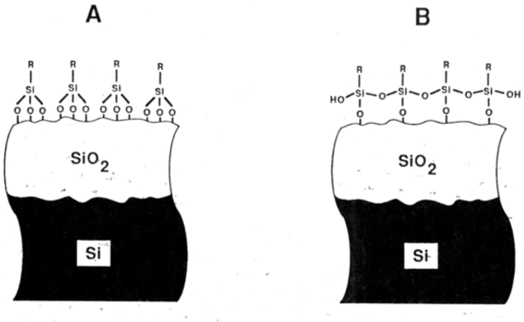


Figure 5. Models for the binding of alkylsiloxane monolayers to Si/SiO_2 substrates. (A) The silicon atom in the alkyltrichlorosilane, $RSiCl_3$, forms three bonds to hydroxyl groups at the surface of the substrate oxide layer. The formation of this structure does not require any adsorbed water. (B) The silicon atom in $RSiCl_3$ forms one or two bonds to surface hydroxyl groups. The remainder of the Si–Cl bonds are hydrolyzed, resulting in the formation of silanols (SiOH) and Si–O–Si linkages between adjacent alkylsilanes. The Si–O–Si links can also bind within the monolayer alkylsilanes whose silicon atom has not formed any bonds to the surface.

For a trans-extended chain, the projection of the carbon–carbon bond onto the surface normal (*z* axis) is 1.26 Å.[52] For the C–Si and Si–O bonds, the projections are 1.52 and 1.33 Å, respectively. Including an additional 1.92 Å for the terminal methyl group,[53] we expect a monolayer prepared from octadecyltrichlorosilane (OTS) to have a thickness of 26.2 Å. The observed range of 22.6–27.6 Å (Figure 2) brackets this value.

The length (*L*) of a methyl-terminated monolayer containing *n* methylene units should have the dependence given by eq 2. A best fit to the experimental data for *n*

$$L = 1.26n + 4.78 \tag{2}$$

= 1–17 has a slope of 1.26 Å per methylene unit and an

---

(45) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland: Amsterdam, 1977.

(46) McCrackin, F. L.; Passaglia, E.; Stromberg, R. R.; Steinberg, H. L. *J. Res. Natl. Bur. Stand., Sect. A.* **1963**, *67*, 363–377.

(47) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.*, in press.

(48) Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D.; Wasserman, S. R.; Whitesides, G. M. *Phys. Rev. B.*, submitted for publication.

(49) Ellipsometry is ultimately based upon Fresnel's equations for the reflection of light from an interface. These equations assume that the interfaces are perfectly smooth. While this assumption is, at best, only approximately true, theoretical and experimental studies indicate that roughnesses below 50 Å (peak to valley) should have little effect on the ellipsometric results. Fenstermaker, C. A.; McCrackin, F. L. *Surf. Sci.* **1969**, *16*, 85–96. Smith, T. *Surf. Sci.*, **1976**, *56*, 252–271.

(50) Ellipsometry can, in theory, determine both the length and refractive index of a thin film. This simultaneous determination relies on the precision of the measurement of the analyzer and polarizer angles. Our accuracy is such that, for films less than 100 Å in thickness, we cannot obtain values for both the length and the refractive index of the alkylsiloxane monolayers. See ref 46.

(51) Infrared spectroscopy using polarized radiation suggests that these monolayers are oriented nearly perpendicular to the surface (tilt angle $\phi = 14° \pm 18°$). This orientation would lower the lengths of alkylsiloxane monolayers by 3% compared to alignment with the normal to the plane of the monolayer. For a monolayer prepared from OTS, the change in length for $\phi = 14°$ compared to $\phi = 0°$ would be 0.8 Å. See ref 1 and 44.

(52) All distances are derived from standard bond lengths assuming that all bond angles in the trans chain are 109.5°.

(53) The contribution of the methyl group is estimated by summing the covalent radii of carbon (0.77 Å) and hydrogen (0.37 Å) and the van der Waals radius of hydrogen (1.2 Å) and projecting this sum onto the normal axis. *Lange's Handbook of Chemistry*, 11th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1973.

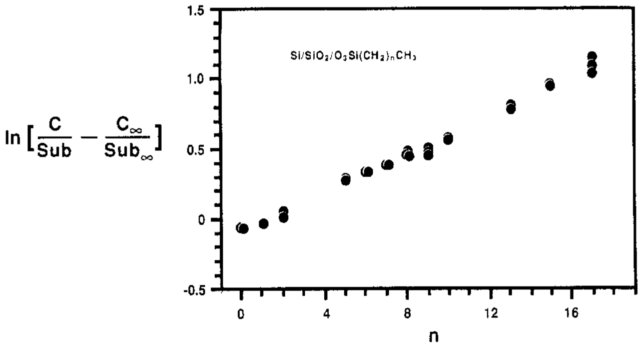


Figure 6. Ratio of the atomic intensities of the carbon 1s (C) and silicon substrate 2p (sub) peaks in XPS for alkylsiloxane monolayers prepared from $CH_3(CH_2)_nSiCl_3$. The intensity of the substrate is a mathematical construct from the intensities of the Si 2p, SiO_2 2p, and O 1s signals (see Appendix in supplementary material). The parameter C_∞/sub_∞ is the ratio of the volume atomic densities of crystalline silicon and of carbon within crystalline hydrocarbons. This parameter, C_∞/sub_∞, is theoretically 0.8. The function ln $(C/sub - C_\infty/sub_\infty)$ is approximately linear for $C_\infty/sub_\infty = 0.6$–1.5.

intercept of 4.02 Å.[54,55] We therefore concur with previous studies based on infrared spectroscopy[1,44] that the alkyl chains in these monolayers are trans-extended and that any tilting of the chains with respect to the normal axis is small.

X-ray Photoelectron Spectroscopy (XPS). The survey spectrum for a monolayer prepared from OTS (Figure 3) showed only three elements: silicon (2s, 150 eV; 2p, 99 eV),[56] carbon (1s, 285 eV),[57,58] and oxygen (1s, 532 eV; 2s, 23 eV; Auger-KLL, 977 eV).[56] The spectra distinguish between the bulk silicon (2s, 150 eV; 2p, 99 eV) signal and that due to the surface oxide (2s, 154 eV; 2p, 103 eV).[59] The peaks at 116, 133, 166, and 183 eV are subsidiary peaks of the silicon resulting from energy loss to the bulk plasmons of the substrate.[60,61] As the angle between the plane of the electron detector and the normal to the surface (takeoff angle) decreased (Figure 4), the intensity of the carbon signal increased relative to that of the signals of silicon and oxygen, the intensity of the oxygen signal increased relative to that of silicon, and the intensity of the silicon dioxide signal increased relative to that of bulk silicon. These observations are consistent with a model for the monolayer as a layer of hydrocarbon above a layer of silicon oxide, which in turn lies above bulk silicon.

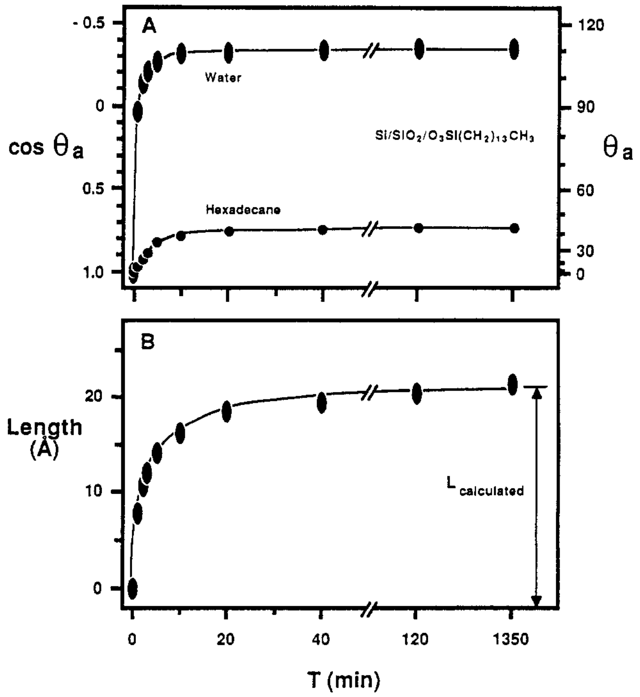


Figure 7. Rate of formation of an alkylsiloxane monolayer prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS) at 20 °C and 30% relative humidity. (A) Advancing contact angles of water and hexadecane. (B) Ellipsometric thicknesses. The calculated thickness for this monolayer, L_{calcd} = 21.1 Å, is based on the assumption of a trans-extended conformation for the alkyl groups, with the chain axis perpendicular to the surface.

XPS detected no chlorine in the monolayers, even for those derived from $Cl_3Si(CH_2)_nCH_3$ (n = 0, 1). Its absence was thus due to its absence on the surface, rather than to attenuation of the chlorine signal by the hydrocarbon layer. Since there was no chlorine in the monolayer, each silicon atom from the starting alkyltrichlorosilane must have formed three silicon–oxygen bonds of some type (Figure 5). Studies on silicas indicate that the density of hydroxyl groups in the oxide does not exceed one group every 20 Å^2 (approximately one for each exposed silicon atom).[37,38,62] This density is not sufficient to support attachment of a monolayer entirely by Si–O–Si bonds between the organosilane and the substrate. We have found, using the technique of X-ray reflection, that the area per RSi group in these monolayers is 21 ± 3 Å^2.[47] Attachment of the silicon atom of the starting silane entirely to surface hydroxyl groups would require one SiOH per 7 Å^2. We therefore conclude that water is involved in the creation of Si–O–Si bonds between the alkylsilane moieties of the monolayer and Si–OH bonds.[63-65] The rates of formation of these monolayers support this conclusion (vide infra).

---

(54) The best fit to the data for n = 5–17 has a slope of 1.31 Å per methylene unit and an intercept of 3.46 Å. The difference between these two fits is probably insignificant, since the intercepts differ by 0.56 Å and since, even for OTS, a change of 0.05 in the slope corresponds to a difference of less than 1 Å in thickness.

(55) The uncoated substrate has a higher surface energy than the monolayers. Contamination would therefore present a larger problem in the characterization of the substrate than of the monolayer and thus would lower the perceived length of the monolayer. Since the measured lengths were not systematically low relative to the model of a trans-extended chain and since the aqueous contact angle of the substrate was less than 10° after the measurement of its optical constants, we believe that contamination was negligible.

(56) Siegbahn, K.; Nordling, C.; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, G.; Bergmark, T.; Karlsson, S.; Lingbren, I.; Lindberg, B. *ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*; Almquist and Wiksells: Uppsala, Sweden, 1967.

(57) Gelius, U.; Hedén, P. F.; Hedmon, J.; Lindberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 70–80.

(58) High-resolution spectra of the carbon region contained only a single symmetrical peak even for thin monolayers (e.g., those from $Cl_3Si(CH_2)_5CH_3$). The implication that the carbon attached to silicon has the same core binding energy as the other carbon atoms in the alkyl tail was confirmed by comparison to monolayers prepared from $Cl_3Si(CH_2)_nCH_3$ (n = 0–2), all of which showed only one carbon signal.

(59) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perken-Elmer Corp.: Eden Prairie, MN, 1979; p 52.

(60) Kittel, C. *Introduction to Solid State Physics*, 6th ed.; Wiley: New York, 1986; p 262.

(61) Marton, L.; Leder, L. B. *Phys. Rev.* **1954**, *94*, 203–204.

(62) Madeley, J. D.; Richmond, R. C. *Z. Anorg. Allg. Chem.* **1972**, *389*, 92–96.

(63) Kallury, K. M. R.; Krull, U. J.; Thompson, M. *Anal. Chem.* **1988**, *60*, 169–172.

(64) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92–98.

(65) These types of structures are often assumed in discussions of solid supports for reversed-phase chromatography. Majors, R. E.; Hopper, M. J. *J. Chromatogr. Sci.* **1974**, *12*, 767–778. Melander, W. R.; Horvath, C. In *High Performance Liquid Chromatography*; Horvath, C., Ed.; Academic Press: New York, 1980; Vol. 2, pp 113–319.

Figure 6 presents the atomic ratio of carbon to the silicon substrate (C/Si_{sub}) as measured by XPS for monolayers prepared from saturated alkyltrichlorosilanes.[66] This ratio has approximately the expected exponential dependence on the thickness of the monolayer (see the supplementary material to this paper). This result demonstrates that the length of the monolayer as determined by ellipsometry correlates with the total number of carbon atoms in the monolayer.

The XPS spectra of monolayers prepared from CH_3SiCl_3 were, as in the contact angle measurements, atypical of alkylsiloxane monolayers. The intensity of the C 1s peak was 80–100% that from monolayers prepared from ethyltrichlorosilane ($CH_3CH_2SiCl_3$), instead of the expected 50%. This result suggests that these structures were probably disordered bilayers rather than monolayers.

Rate of Formation of Monolayers. Our objective in examining the rate of formation of these monolayers was primarily to determine conditions that yielded monolayers reproducibly. Figure 7 follows the formation of a monolayer prepared from tetradecyltrichlorosilane (TTS, $CH_3(CH_2)_{13}SiCl_3$). The length of the monolayer reached a plateau of 20 Å after ca. 40 min. This length was approximately that expected for a complete monolayer (21.1 Å).

Humidity influences the time needed to form a monolayer. When the monolayers were prepared by immersing the silicon wafer in a solution of alkyltrichlorosilane maintained under a dry atmosphere, a complete layer was obtained only after 5 h; when the same experiment was conducted under air at 30% relative humidity, formation of the monolayer was complete in approximately 1 h. We believe that this difference in rate was due primarily to different amounts of water adsorbed on the polar surface of the Si/SiO_2 substrate or otherwise available for the formation of Si–O–Si linkages.

Stability. After being washed with ethanol to remove contaminants adsorbed from the air, monolayers of methyl-terminated siloxanes that had been stored for 18 months in closed containers under air had contact angles and lengths indistinguishable from those determined immediately after preparation. More polar surfaces contaminated more rapidly than nonpolar ones, but even these could be cleaned by rinsing with ethanol. Rubbing the surface vigorously with a tissue or cotton swab did not change the thickness or wettability of the monolayer.

Monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS) were stable in contact with aqueous acid at room temperature and hexadecane at 75 °C (Figure 8). When exposed to aqueous base at room temperature, approximately 50% of the monolayer had been removed after 80 min. While the substrate appeared normal at 80 min, after 160 min its surface was visibly etched. The negative length observed at this point probably was due to attack on the native oxide. Since the silicon–oxygen bond hydrolyzes under basic conditions,[67] this destruction of the monolayer is not surprising.

The resistance of the alkylsiloxane monolayers to desorption in hot hexadecane contrasts with the rapid desorption observed for alkanethiols adsorbed on gold; hexadecanethiol has a half-life for desorption of 30 min at 83 °C in hexadecane.[11] Thus the formation of alkylsiloxane monolayers is not the result of a partitioning of the constituent molecules between substrate-bound and solution phases. We presume that the formation of these monolayers is driven by the formation of the covalent silicon–oxygen bond rather than by the maximization of van der Waals interactions between adjacent alkyl groups.

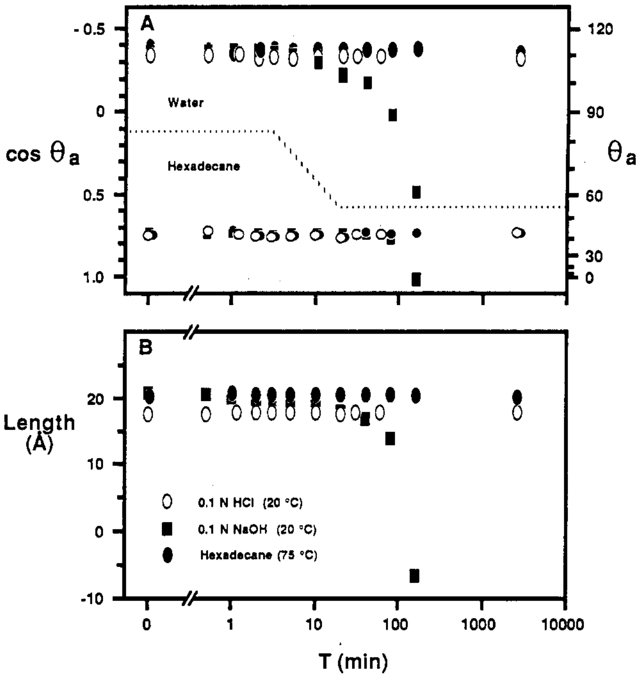


Figure 8. Stability of alkylsiloxane monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS) and exposed to 0.1 N HCl at 20 °C (○), 0.1 N NaOH at 20 °C (■), or hexadecane (●) at 75 °C. (A) Advancing contact angles. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses. The negative thickness after exposure to the 0.1 N NaOH probably indicates etching of the surface oxide after the monolayer had been removed.

The etching of these monolayers in base was often heterogeneous. We sometimes observed etched surfaces containing patches in which the monolayer was apparently intact while in other areas the substrate had been visibly pitted. This result suggests that etching was initiated at defects in the film and proceeded through the creation of regions denuded of monolayer. This macroscopic heterogeneity demonstrates the presence of at least macroscopic islands, although it does not provide proof of the microscopic structure of the monolayer. In contrast, incomplete monolayers, prepared by removing the substrate from the solution of alkyltrichlorosilane before the monolayer has completely formed, have a uniform, liquidlike structure.[47,48,68]

Reactions Involving the Terminal Vinyl Group. We generated alcohols and carboxylic acid groups from vinyl-terminated monolayers, using procedures similar to those developed by Sagiv.[5,26] Figure 9 presents the contact angles and ellipsometric thicknesses for three vinyl-terminated monolayers. Although the contact angles were uniformly lower than those of the corresponding methyl-terminated monolayers, both the contact angles and thicknesses mirror the trends observed for the saturated alkylsiloxanes.

Figure 10 summarizes the oxidation of the vinyl group

---

[66] This ratio is used in order to eliminate variations resulting from changes in the X-ray flux impinging on each sample. The intensity of Si_{sub} is actually a mathematical construct which approximates the Si/SiO_2 substrate as an infinite layer of pure silicon. See Appendix in supplementary material.

[67] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1972; p 321.

[68] Previous characterizations of the structure of partial monolayers have relied on systems which had been prepared by etching of completely formed monolayers. Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *5*, 964–982. Tomar, M. S. *J. Phys. Chem.* **1974**, *78*, 947–950.

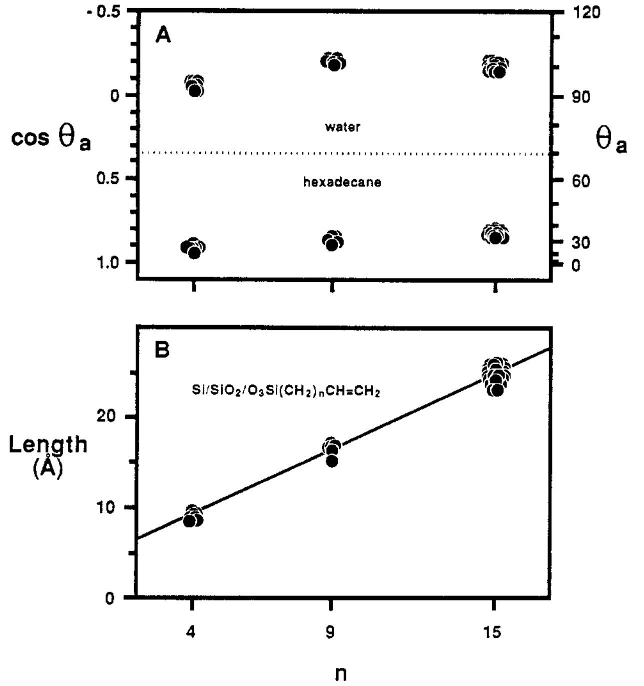


Figure 9. Vinyl-terminated alkylsiloxane monolayers prepared by adsorption of $CH_2{=}CH(CH_2)_nSiCl_3$ (n = 4, 9, 15) onto Si/SiO_2 substrates. Each data point represents measurements on a different silicon substrate. (A) Advancing contact angles. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses (Å). The solid line represents the best linear least-squares fit. The increment in thickness per methylene group is 1.44 Å.

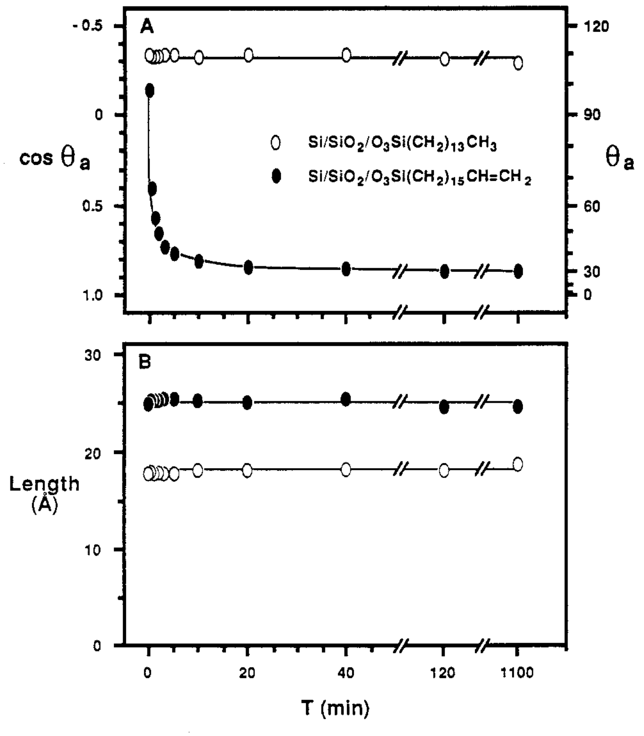


Figure 10. Oxidation of methyl- and vinyl-terminated alkylsiloxane monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ (○) and $CH_2{=}CH(CH_2)_{15}SiCl_3$ (●) by $KMnO_4$ (0.5 mM)/$NaIO_4$ (19.5 mM) at 20 °C. The advancing contact angles of water (A) and ellipsometric thicknesses (B, in Å) were measured as a function of the time, T, of oxidation.

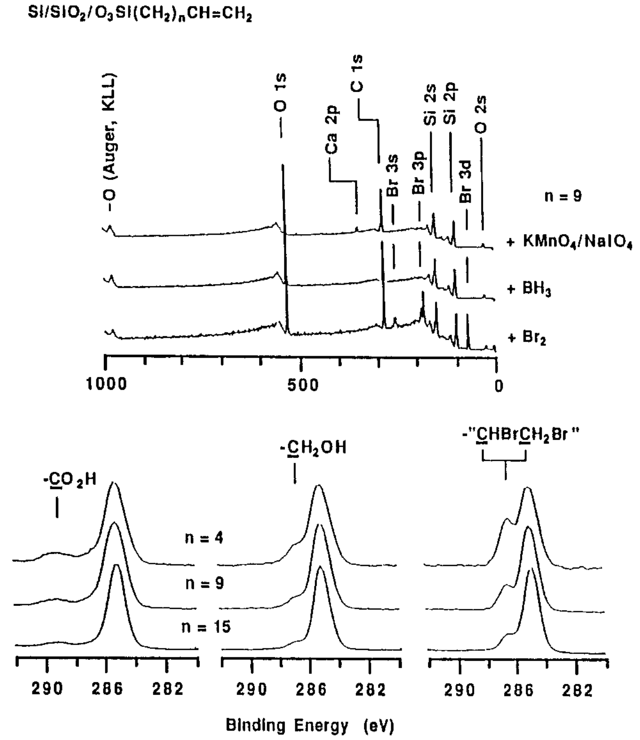


Figure 11. XPS spectra (survey and high resolution of the carbon 1s region) of reaction products from vinyl-terminated alkylsiloxane monolayers prepared from $CH_2{=}CH(CH_2)_nSiCl_3$ (n = 4, 9, 15): carboxylic acid from oxidation with $KMnO_4/NaIO_4$, alcohol from hydroboration (1, BH_3; 2, $H_2O_2/NaOH$), and 1,2-dibromide (and related brominated species) from reaction with elemental bromine (Br_2). The C 1s spectra are normalized to the same maximum peak height. As n increases, the signal from the functionalized carbon atom(s) decreases relative to the signal from the methylene groups in the monolayer.

of a monolayer prepared from 16-heptadecenyltrichlorosilane (HTS, $Cl_3Si(CH_2)_{15}CH{=}CH_2$) to a carboxylic acid by $KMnO_4$ and $NaIO_4$.[69,70] As expected, the surface became more hydrophilic as vinyl groups were converted to carboxylic acid moieties. The limiting value for the contact angle of water was $\theta_a^{H_2O} \approx 30°$. The wettability of a methyl-terminated monolayer was unchanged after exposure to the oxidant. Ellipsometry demonstrated that neither the vinyl- nor the methyl-terminated monolayer changed in thickness during the reaction.[71] The change in contact angle was thus due to oxidation of vinyl groups, rather than to etching of the monolayer. The conclusion that the thickness of the monolayer was unchanged upon oxidation is reasonable. The reaction replaces the $CH{=}CH_2$ group with a CO_2H group; the change in length resulting from this reaction is less than the precision of ellipsometry. Figure 11 shows XPS spectra for a monolayer prepared from 10-undecenyltrichlorosilane ($Cl_3Si(CH_2)_9CH{=}CH_2$) after oxidation. We were unable to de-

---

[69] Lemieux, R. U.; von Rudloff, E. *Can. J. Chem.* **1955**, *33*, 1701–1709.

[70] Sagiv has used $KMnO_4$ alone to oxidize olefins contained in a monolayer (ref 5). This reaction has two major products in solution, a vicinal diol and an α-hydroxy ketone (Wolfe, S.; Ingold, C. F. *J. Am. Chem. Soc.* **1981**, *103*, 938–939 and references cited therein). Although the $KMnO_4/NaIO_4$ reaction has a complex mechanism, it generates carboxylic acids quantitatively under similar conditions. In addition, Sagiv has used an oxidation procedure in which the oxidant is spread on the surface, while our oxidations were performed by completely immersing the sample in the oxidizing solution. Sagiv has reported that permanganate oxidation of a vinyl interface resulted in a surface which was completely wetted by water. These results were obtained for Langmuir–Blodgett films, which may lack the stability of the siloxane systems.

[71] We have continued to use an index of refraction of 1.45 for alkylsiloxane monolayers even after modification of the terminal vinyl group. This approach is clearly arbitrary, but, even for the bromination reactions discussed below, using the refractive index of elemental bromine (1.66) alters our estimate of the change in thickness by only ~0.4 Å.

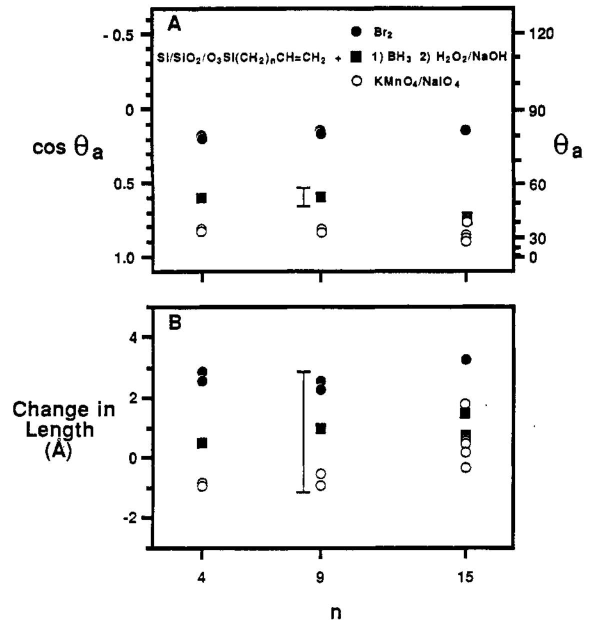


Figure 12. Reaction products from vinyl-terminated alkylsiloxane monolayers prepared from $CH_2{=}CH(CH_2)_nSiCl_3$ (n = 4, 9, 15): carboxylic acid from oxidation with $KMnO_4/NaIO_4$ (○), alcohol from hydroboration (1, BH_3; 2, $H_2O_2/NaOH$) (■), and 1,2-dibromide (and related brominated species) from reaction with elemental bromine (Br_2) (●). Each data point represents measurements on a different substrate. The markers represent typical errors in the measurements of contact angles and ellipsometric thicknesses. (A) Advancing contact angle of water. (B) Change in ellipsometric thickness (product minus reactant) of the monolayer as a result of the surface reaction.

tect the presence of manganese, iodine, potassium, or sulfur. Since the sensitivities of manganese and iodine are large in XPS (Mn $2p_{3/2} \simeq 7.2$ and I $3d_{5/2} \simeq 15.8$ relative to carbon),[72] we conclude that no residual oxidant remained on the surface. Although the sensitivities of S (2s $\simeq 1.48$) and K ($2p_{3/2}$) $\simeq 2.15$)[72] are lower, there were no signals from these elements in the XPS spectrum. We have occasionally found sodium (up to a monolayer) or calcium (up to 0.2 monolayer). The exact form or source of these contaminating elements is unclear, although sodium was present in the oxidizing solution.[73]

The high-resolution C 1s spectrum for the vinyl group after oxidation clearly showed the appearance of a broad, new peak centered at 289.2 eV ($\underline{C}O_2H$).[74] The main carbon peak also became asymmetric, presumably due to a small shift in binding energy for the carbon atom bound directly to the CO_2H group.[75] Although the oxygen atoms of the CO_2H group could not be distinguished from the SiO_2 background, the intensity of the oxygen signal had increased by 10%.

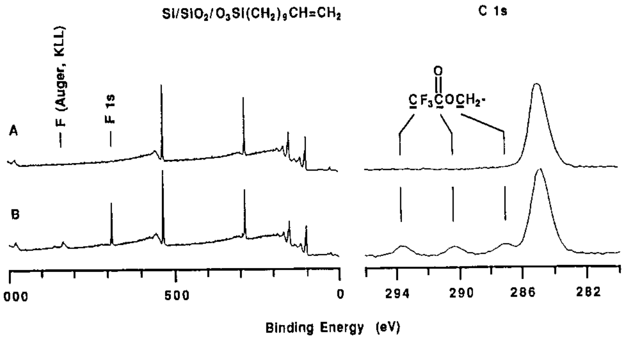


Figure 13. XPS spectra of alkylsiloxane monolayers prepared from $CH_2{=}CH(CH_2)_9SiCl_3$ and treated with trifluoroacetic anhydride (2% v:v in hexanes): survey (left) and high resolution of the carbon 1s region (right). The C 1s spectra are normalized to the same maximum peak height. (A) Vinyl-terminated monolayer. (B) Alcohol-terminated monolayer prepared from A by hydroboration (1, BH_3; 2, $H_2O_2/NaOH$).

Figure 12 compares aqueous contact angles for the monolayers obtained by oxidation of C_6, C_{11}, and C_{17} vinyl-terminated monolayers. The contact angles of the acid interfaces created by this process were approximately independent of the length of the silane.[76]

As a check on these results, we have used an alternative method for generating a monolayer having terminal carboxylic acids. We prepared a monolayer having terminal ester groups by adsorption of $Cl_3Si(CH_2)_{10}CO_2CH_3$ onto a silicon wafer. We then hydrolyzed the ester groups in this monolayer with concentrated aqueous HCl. The contact angle for the ester-containing interface was $\theta_a^{H_2O} = 73°$; that for the hydrolyzed, carboxylic acid-containing interface was $\theta_a^{H_2O} = 40°$. The corresponding contact angle for the interface prepared by oxidation of a monolayer of $Si(CH_2)_9CH{=}CH_2$ groups was $\theta_a^{H_2O} = 34°$.

Although we cannot prepare siloxane monolayers terminated with carboxylic acids directly since $RSiCl_3$ and RCO_2H react, structurally well-defined carboxylic acid terminated monolayers have been prepared by adsorbing alkanethiols with terminal CO_2H groups, $HS(CH_2)_{10-20}CO_2H$, onto gold.[11] The contact angle of water on these monolayers, $\theta_a^{H_2O} = 0°$, is significantly lower than that on the corresponding siloxane films. We can estimate the amount of acid at the solid–water interface of the oxidized siloxane monolayer by using Cassie's assumption that the interfacial free energy of a mixed surface is a linear combination of the energies of the functional groups at the interface.[77,78] This estimate suggests that approximately 80% of the exposed interface consists of carboxylic acid, with the remainder presumed to be hydrocarbon. Wetting alone, however, cannot distinguish between hydrocarbon remaining from incomplete oxidation of a highly ordered monolayer and hydrocarbon exposed in a disordered monolayer whose constituent vinyl groups have been completely oxidized.[79]

---

(72) These sensitivities are those supplied by Surface Science Laboratories in the ESCA 8.0B software. They are the photoionization cross sections calculated by Scofield, corrected for the dependence of the escape depth of an electron on its energy. Scofield, J. H. *J. Electon Spectrosc.* **1976**, *8*, 129–137.

(73) Polydentate acids such as EDTA complex strongly to calcium. Because of the high density of carboxylic acids at the monolayer–air interface, the interaction of calcium with chelating acids is a reasonable model for the interaction of calcium with the monolayer. Fenton, D. E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 3, pp 32–33.

(74) The carbon atom of a carboxyl group is expected to have a shift of 4.5 eV relative to the carbon atom of a methylene group. See ref 57.

(75) The asymmetry of the methylene signal could be modeled by an additional peak at +1.5 eV relative to the CH_2 signal. The energy observed here is 1.2 eV higher than that reported in the literature (ref 57) for a carbon atom α to a carboxylic acid. The intensity of this peak was equal to that of the carbon atom in the acid group.

(76) Although the range of contact angles ($\theta_a^{H_2O}$ = 25–38°) was larger than that of the initial vinyl-terminated interfaces, in terms of surface free energy this range corresponds to only ~15% of the total change induced by the oxidation. This range was calculated by comparing the difference in cos θ_a for the maximum and minimum contact angles of the acid-terminated monolayers to the difference in cos θ_a between the vinyl-terminated and the (average) acid-terminated monolayers.

(77) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *44*, 546–551.

(78) Cassie, A. B. D. *Discuss. Faraday Soc.* **1948**, *3*, 11–16.

We have examined two additional reactions involving the terminal vinyl group (Figures 11 and 12). The first is the introduction of an alcohol group via hydroboration. Sagiv has successfully used this reaction for the creation of multilayer assemblies.[26-28] We observed $\theta_a^{H_2O} = 45$–$55°$ for these ω-hydroxylated interfaces, in agreement with Sagiv. We conclude, by comparison with the analogous hydroxyl-terminated monolayers prepared by adsorption of ω-hydroxyl mercaptans on gold ($\theta_a^{H_2O} = 0°$),[11] that approximately 70% of the solid–water interface was hydroxyl groups. Ellipsometry indicated that the vinyl-terminated monolayers had thicknesses similar to those of the hydroxyl systems derived from them. XPS spectra of the oxidized monolayer (Figure 11) showed a new peak at 286.6 eV characteristic of a hydroxyl-substituted carbon atom. Survey spectra did not reveal surface contaminants, but the boron cross section is small (0.49 relative to carbon)[72] and occurs in the same region as the plasmons for Si 2s.

Additional evidence for interfacial hydroxyl groups was provided by trifluoroacetylation using trifluoroacetic anhydride. The contact angles of the resulting material ($\theta_a^{H_2O} = 88°$, $\theta_a^{HD} = 51°$) were similar to those observed for trifluoroacetate esters prepared from monolayers of $HS(CH_2)_{11}OH$ on gold ($\theta_a^{H_2O} = 96°$, $\theta_a^{HD} = 60°$)[80] but lower than those for monolayers prepared from $Cl_3Si(CH_2)_2(CF_2)_7CF_3$ ($\theta_a^{H_2O} = 109°$, $\theta_a^{HD} = 71°$). The XPS spectrum (Figure 13) showed the expected F 1s signal at 688.5 eV. The intensities of the acid and trifluoromethyl species in the high-resolution C 1s spectrum were equal to that of the alcohol, suggesting that this treatment had resulted in acylation of all the alcohol groups in the interface. Exposing the vinyl-terminated monolayers to the same reagent did not introduce fluorine into the monolayer (Figure 13).

We have also allowed the vinyl-terminated monolayers to react with Br_2 in a CH_2Cl_2 solution to generate terminal $CHBrCH_2Br$ and related brominated groups (Figures 11 and 12). This interface showed $\theta_a^{H_2O} = 80°$. Ellipsometry indicated that the apparent length of the monolayer had increased 2–3 Å. Since the reaction introduces two bromine atoms, each approximately the size of a methyl group, into the layer, the observed change in monolayer length is reasonable. XPS confirmed the presence of bromine in the surface (Figure 11). The bromine was labile on exposure to X-rays, and the initial intensity of the Br $3d_{5/2}$ and Br $3d_{3/2}$ peaks decreased by 10–15% in the time required to obtain reasonable spectra.

Comparisons of the C 1s peaks in high-resolution XPS for homologous monolayers terminated by CO_2H, CH_2OH, and $CHBrCH_2Br$ groups demonstrate that XPS can provide at least semiquantitative information concerning the relative quantities of functional groups in alkylsiloxane monolayers. For all three, as the number of methylene groups in the monolayer increased, the intensity of the peak due to the oxidized carbon atoms decreased relative to that of the unsubstituted polymethylene carbons (Figure 11). While the intensity of the carbon of the CO_2H group was difficult to quantify because of the breadth of the peak, the changes in intensity of the C 1s signals for the CH_2OH and $CHBrCH_2Br$ groups were approximately those expected.

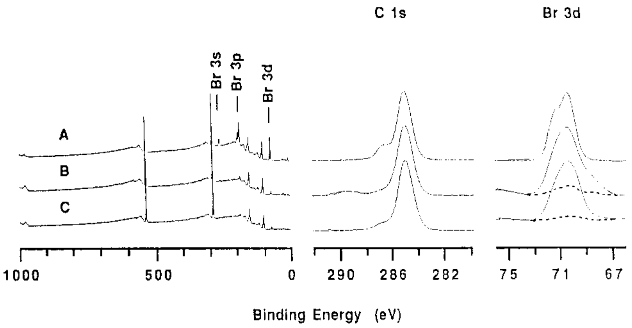


Figure 14. Extent of reaction within alkylsiloxane monolayers: XPS spectra (survey (left), high resolution of the carbon 1s (center) and bromine 3d regions (right)) of vinyl-, hydroxyl-, and carboxylic acid-terminated monolayers prepared from $CH_2{=}CH(CH_2)_{15}SiCl_3$ (HTS) and then functionalized with elemental bromine (Br_2, 1% in CH_2Cl_2). The C 1s and Br 3d spectra are each normalized to the same maximum peak height. The Br 3d spectra for B and C have been smoothed by using a nine-point algorithm with a symmetrical triangle convolution function (Savitsky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1627–1639). The dashed lines in the Br 3d spectra for B and C represent the amount of bromine remaining on these surfaces relative to A. (A) "$-CHBrCH_2Br$"-terminated monolayer prepared by bromination of the vinyl-terminated monolayer prepared from HTS. (B) Bromination product of the acid-terminated monolayer prepared by oxidation with $KMnO_4/NaIO_4$ of a monolayer prepared from HTS. This monolayer contained both CO_2H and "$-CHBrCH_2Br$" groups. (C) Bromination product of the alcohol-terminated monolayer prepared by hydroboration (1, BH_3; 2, H_2O_2/NaOH) of a monolayer prepared from HTS. This monolayer contained both CH_2OH and "$-CHBrCH_2Br$" groups. For A, B, and C, "$-CHBrCH_2Br$" represents the 1,2-dibromide and related brominated species.

We have used the bromination of vinyl groups in an attempt to assess the extent of reaction of the $KMnO_4/NaIO_4$ and hydroboration oxidations. The carboxyl- and hydroxyl-terminated monolayers that resulted from these reactions on monolayers prepared from HTS were placed in a 1% solution of Br_2 in CH_2Cl_2 for 2 h. The XPS spectra for these monolayers, as well as the $CHBrCH_2Br$-terminated interface prepared by reaction of the vinyl group with Br_2 alone, are shown in Figure 14. We note three features of these spectra. First, the brominated acid-terminated monolayer exhibited two bromine environments, one whose binding energy corresponds to $CHBrCH_2Br$ and another shifted by ~1.8 eV to lower binding energy. We have tentatively assigned this new environment to $\underline{C}HBrCO_2H$, although the only evidence for this assignment is the absence of this signal in the brominated hydroxyl-terminated monolayer. Second, the amount of bromine in the $CHBrCH_2Br$ environment for the acid was ~13% of that of the fully brominated interface; for the alcohol, the amount of bromine incorporated into the monolayer was ~7% of that of the fully brominated interface. On the basis of these spectra, we would conclude that the hydroboration reaction had proceeded to a greater extent than the permanganate–periodate oxidation. Although this conclusion is the opposite of that deduced from the contact angle data, these measurements may not be inconsistent. The assumption that the inherent wettabilities of alcohol- and acid-terminated monolayers are the same ($\theta_a^{H_2O} = 0°$) is not necessarily correct. Furthermore, the contact angle measurements indicate which groups are in contact with the liquid at the

---

(79) Angle-resolved XPS spectra for the CO_2H-terminated surfaces showed no change in the relative intensities of the C 1s (CH_2) and C 1s (CO_2H) peaks as the take-off angle was varied. If the acid group were located at the surface, we would expect to see the intensity of the carboxylic acid peak rise relative to that of the hydrocarbon signal as the takeoff angle decreases. While the effect of takeoff angle would be small for even a well-ordered monolayer (the relative intensity of the acid should approximately double as the takeoff angle changes from 90° to 15°), the absence of a detectable change in the ratio of the C 1s acid and hydrocarbon peaks suggests that the carboxyl-terminated monolayers were partially disordered. Some angle-resolved XPS spectra indicated that the location of OH and $CHBrCH_2Br$ groups in vinyl-terminated monolayers that had undergone hydroboration or addition of bromine was at or near the air–monolayer interface. Such spectra were not, however, reproducible.

(80) Bain, C. D., unpublished results.

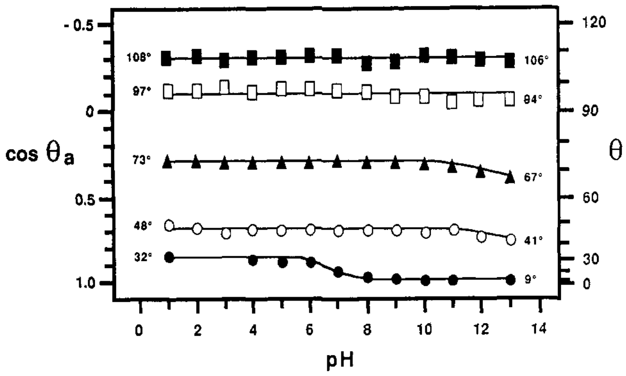


Figure 15. Dependence of the advancing contact angle of water, θ_a, on pH for alkylsiloxane monolayers: methyl-terminated monolayer prepared from $CH_3(CH_2)_{13}SiCl_3$ (■), vinyl-terminated monolayer prepared from $CH_2{=}CH(CH_2)_{15}SiCl_3$ (HTS) (□), methyl ester-terminated monolayer prepared from $CH_3OCO(CH_2)_{10}SiCl_3$ (▲), alcohol-terminated monolayer prepared by hydroboration of a monolayer prepared from HTS (○), and acid-terminated monolayer prepared by oxidation ($KMnO_4/NaIO_4$) of a monolayer prepared from HTS (●).

monolayer interface, while the bromination of these interfaces indicates the number of unreacted vinyl groups that are accessible to the bromine.[81]

Contact Angle Titrations. We have previously demonstrated the utility of contact angle titrations for the characterization of acids and bases that are localized at a solid–water interface.[18,29] These titrations involve the measurement of the advancing contact angle, θ_a, as a function of the pH of the aqueous solution in contact with the monolayer. In determining contact angle titration curves for the monolayers studied here, the values of θ_a for every pH were measured on a single substrate. After the contact angle for a solution of a given pH was measured, the substrate was washed and dried prior to measurements utilizing a solution of different pH. During this procedure, the substrates became visibly contaminated, even when the low-energy methyl- and vinyl-terminated monolayers were examined. In order to minimize any systematic error resulting from this contamination, we measured the contact angles for pH = 1–11 at random. Because of the instability of the siloxane monolayers in basic solution, the contact angles for pH 12 and 13 were measured last. The determination of each of these contact angles was rapid (<3 min), and within this time we did not observe any destruction of the monolayer as a result of exposure to the basic drops.

Figure 15 presents the contact angle titrations for methyl-, vinyl-, hydroxyl-, carboxyl-, and methyl ester-terminated alkylsiloxane monolayers. Neither the methyl- nor vinyl-terminated monolayers exhibited a significant change in contact angle as a function of pH. The apparent drift for the vinyl-terminated monolayer is probably an artifact of using cos θ to represent the energy of the surface: the full range of contact angles observed for this sample was only 4°. With the methyl ester terminated monolayer we observed a small (5–11°) decrease in θ_a at high pH. A similar decrease (6°) was found for the hydroxyl-terminated monolayer generated by hydroboration of a vinyl-terminated monolayer. We attribute this decrease to contamination of the surface and, in the case of the methyl ester, hydrolysis of the ester moiety since the contact angles at low pH for these two monolayers were reduced after the titrations had been completed. The acid-terminated monolayer, which was prepared by oxidation of a vinyl-terminated monolayer with $KMnO_4/NaIO_4$, also exhibited a pH dependence in its contact angle. Unlike the alcohol- and ester-terminated monolayers, however, the contact angle at low pH for these acid surfaces was unaffected by exposure of the monolayer to the basic solutions.

We define the $pH_{1/2}$ of a surface-localized carboxylic acid as the pH at which the value of cos θ_a is halfway between that of cos θ_a at pH 1 and 13 (ref 29) and the pH at which ionization of the carboxylic acid first appears (as reflected in a decrease in θ) as pK_i. The latter is probably more interpretable.[82] We note that, because of charge localized at the surface of the monolayer, the pH in the aqueous layer next to the monolayer may not be the same as the pH of the bulk solution.[83]

The fact that $pK_i \geq 6$ establishes that, to attain the same degree of ionization, the interfacial CO_2H groups require significantly higher values of solution pH than do the CO_2H groups in soluble carboxylic acids.[84] This decrease in acidity, which is also observed for carboxylic acid interfaces on polyethylene, probably reflects the fact that the interfacial carboxyl groups were in an environment of low dielectric constant.[29]

Interfaces Including Mixtures of Methyl and Carboxylic Acid Groups. We have investigated the effect of dilution of the carboxylic acid in the monolayer on the apparent acidity of that acid by creating interfaces that had mixtures of terminal carboxylic acid and methyl groups. The method for creating such interfaces had to be chosen carefully. There is evidence from other systems that, when the alkyl tails of the molecules used to create "mixed" monolayers are of different size or have different polarities, the composition of the monolayer may differ markedly from that of the solution from which it is formed.[9,10] Our method for preparing monolayers that contained mixtures of terminal functionalities probably minimized this problem. The monolayers studied here were prepared from solutions containing both HTS ($Cl_3Si(CH_2)_{15}CH{=}CH_2$) and $Cl_3Si(CH_2)_{15}CH_3$. Since the two silanes are similar in structure, polarity, and size, we believe that the ratio of vinyl and methyl groups in the resulting monolayer closely mirrored that in the solution from which they were prepared. Oxidation of the vinyl groups in these monolayers by $KMnO_4$ and $NaIO_4$ yielded the mixed methyl and acid monolayers of interest to us. We assume, in the absence of any supporting data, that the yield on conversion of vinyl to carboxylic acid groups was the same in all of these samples. Since the oxidation removed one carbon atom from the vinyl group, the numbers of carbon atoms (16) in the methyl- and acid-terminated molecules were the same.

Figure 16 presents contact angle titrations for carboxylic acid containing monolayers prepared by oxidation of monolayers that incorporated HTS in fractions from 0% to 100%. The fraction of carboxylic acids in these monolayers was probably ~80% that of the olefinic component. We note three important features of these mixed systems. First, as the concentration of acid groups within the monolayer increased, the monolayers became more

---

[81] The accessibility of bromine to unreacted vinyl groups in these two types of oxidized monolayers may be different. The $KMnO_4/NaIO_4$ oxidation, which does not increase the length of the monolayer, presumably leaves the unreacted vinyl groups at the air–monolayer interface. The hydroboration adds a monolayer of hydroxyl groups over the unreacted vinyl groups. The stoichiometry and products of reaction may also be different (for example, the extent of formation of bromo ethers or bromo lactones may differ).

(82) Bain, C. D.; Whitesides, G. M. *Langmuir*, in press.

(83) See the discussion on electrical phenomena at interfaces in ref 42, Chapter 5.

(84) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1981; p 253.

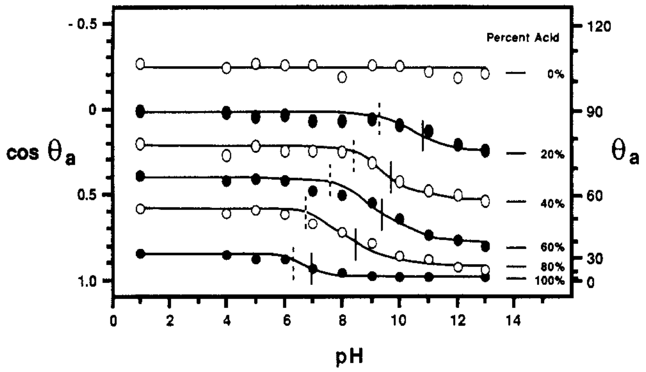


Figure 16. Dependence of the advancing contact angle of water, θ_a, on pH for alkylsiloxane monolayers that contained mixtures of terminal CH_3 and CO_2H groups. Monolayers were prepared by adsorption from solutions that contained $CH_2{=}CH(CH_2)_{15}SiCl_3$ and $CH_3(CH_2)_{15}SiCl_3$. The percentages of the vinyl-terminated alkylsilane in these solutions were 0%, 20%, 40%, 60%, 80%, and 100%. The vinyl groups in these monolayers were then oxidized to carboxylic acid moieties by using $KMnO_4/NaIO_4$. On the basis of the studies summarized in Figure 14, the yield of these oxidations was probably ~80%. The vertical lines represent values of $pH_{1/2}$: the value of pH at which cos θ_a is halfway between its high and low pH extremes.

hydrophilic. The contact angles of water ($\theta_a^{H_2O}$ = 30–108°) appeared to mirror the presumed composition of the outer interface. Second, the values of pK_i and $pH_{1/2}$ became larger as the concentration of the hydrophobic methyl tail group increased.[85] Third, the shape of the titration curve for 100% (and perhaps also for 80%) CO_2H groups probably contains a substantial element of artifact. The shapes of these curves almost certainly do not reflect solely a pH-dependent conversion of CO_2H to CO_2^- groups but rather the intersection of such a curve (for pH $\lesssim$7.5) with the axis θ_a = 0° (for pH $\gtrsim$7.5).[29,82] For a curve of this type, in which the value of $pH_{1/2}$ does not correspond in any simple way to the extent of ionization of the CO_2H groups, we cannot directly relate $pH_{1/2}$ to the acidity of these groups. The apparent decrease in the acidity of the carboxyl groups in the monolayer as the fraction of methyl groups increased probably results from the placement of the acid moiety in an increasingly hydrophobic environment.

Discussion

With the possible exception of CH_3SiCl_3, *n*-alkyltrichlorosilanes form stable, well-ordered alkylsiloxane monolayers on silicon–silicon dioxide substrates. Our results are in at least qualitative agreement with those of Sagiv[1-3,26-28] and others.[44] They also support our previous inference that wettability is a very surface-sensitive phenomenon.[86] Although covalent Si–O–Si linkages are clearly important in providing the exceptional stability of these monolayers, the degree that water is required to form these bonds is undefined. Ulman has used solutions of alkyltrichlorosilanes in a hydrocarbon/CCl_4 solvent to form this type of monolayer.[44] The solvent for these preparations had been equilibrated with water prior to use. This procedure resulted in methyl-terminated monolayers that had up to 20 Å of contaminating material on the surface. Our procedure, using an anhydrous solution under a dry atmosphere, appears to lead to cleaner monolayers.[87] When cleaning procedures similar to those used by Ulman (wiping the surface with a cotton swab that had been dipped in ethanol) were applied to the monolayers prepared using our process, the length of the monolayer, as monitored by ellipsometry, decreased by no more than 1 Å. We have also used immersion times of up to 3 days to prepare monolayers from HTS without any loss of oleophobicity.

The ellipsometric measurements imply that the alkylsiloxane monolayers are fairly well-packed systems. X-ray reflectivity measurements indicate that these monolayers have a density slightly less than that of crystalline hydrocarbons but higher than the density of liquid hydrocarbons.[47,48] Infrared spectroscopy also supports the idea that these monolayers are well-ordered. The estimated angle of tilt for monolayers prepared from OTS ($CH_3(CH_2)_{17}SiCl_3$), 14 ± 18°,[1,44] is only consistent with structures whose order approaches that of the crystalline state. These monolayers are therefore probably best described as liquid-crystalline or quasi-crystalline materials.

A limited study of reactions on terminal vinyl groups that were incorporated into alkylsiloxane monolayers indicated that synthetically useful transformations occurred readily but that the yields were not quantitative. The bromination of the residual vinyl groups in CO_2H- and CH_2OH-terminated monolayers implied that more vinyl groups remained in the former than in the latter.

Experimental Section

General. Chemicals: methyl-, ethyl, propyl-, hexyl-, 5-hexenyl-, heptyl-, octyl-, nonyl-, decyl-, undecyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecyltrichlorosilane were obtained from Petrarch and distilled prior to use. Silicon tetrachloride (Alfa, ultrapure), trichlorosilane (Petrarch), (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)trichlorosilane ($Cl_3Si(CH_2)_2(CF_2)_7CF_3$, Petrarch), undecenyl bromide (Pfaltz and Bauer), dihydrogenhexachloroplatinate (Alfa), trifluoroacetic anhydride (Aldrich), and 1,6-dibromohexane (Aldrich) were used as received. Tetrahydrofuran and ether were dried by distillation from sodium/benzophenone. Hexane was distilled from Na/K alloy. Materials for preparation of monolayers: silicon substrates were standard semiconductor grade silicon wafers (3-in. diameter) from Semiconductor Processing Corp. (Boston, MA) (n-type, laser grade) and Monsanto (p-type). Hydrogen peroxide (Mallinckrodt, 30%), and concentrated sulfuric acid (Baker) were used as received. Hexadecane (Aldrich) and bicyclohexyl (Aldrich) were purified by percolation twice through neutral, grade 1, alumina (Fisher). Solvents purified in this manner passed the Bigleow test.[23] Carbon tetrachloride was dried by distillation from P_2O_5. Methylene chloride was dried by distillation from CaH_2. All solvents for preparation of the monolayers were stored under nitrogen. Materials for surface reactions: potassium permanganate ($KMnO_4$, Mallinckrodt), sodium meta-periodate ($NaIO_4$, Mallinckrodt), K_2CO_3 (Mallinckrodt), $NaHSO_3$ (Fisher), BH_3–THF (Aldrich, 1 M), and bromine (Baker) were used as received.

Water was passed through an ion exchanger (Cole-Parmer) and distilled in a Corning Model AG-1b glass distillation apparatus. The buffers used for the contact angle titrations were as follows (0.05 M except where stated):[29] pH 1, 0.1 N HCl; pH 2, sodium phosphate; pH 3, malonic acid; pH 4, sodium phosphate; pH 5, acetic acid; pH 6, sodium phosphate; pH 7, sodium phosphate; pH 8, sodium phosphate; pH 9, boric acid; pH 10, boric acid; pH 11, sodium phosphate; pH 12, sodium phosphate; pH 13, 0.1 N NaOH.

---

[85] The apparent trend in pK_i is complicated by two factors, both of which will exaggerate the shift in pK_i. First, as the concentration of acid within the monolayer decreases, a greater number of acid groups must ionize in order to have a given change in the free energy of the surface. For the data examined here, the shift caused by this dilution can only be on the order of a single pH unit. Second, since the energy of the interface is a function of cos θ, it is more difficult to determine the onset of ionization if the initial contact angle is near 90°.

[86] Holmes-Farley, S. R.; Reamey, R. H.; Nuzzo, R.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* **1987**, *3*, 799–815.

[87] We believe that it is presence of excess water that leads to the contamination observed by others. The removal of such contamination often requires the physical abrasion of the monolayer, which may affect the structure of the monolayer.

The purities of reagents and adsorbates were checked by gas chromatography (Perkin-Elmer 3920B) and ^{1}H and ^{13}C NMR spectroscopy (using Bruker AM-250 and AM-300 spectrometers).

Preparation of Silicon Substrates. The silicon wafers (0.015–0.2 in. thick) were cut into strips 4 cm × 1.5 cm. These strips were placed in glass weighing bottles and covered with a solution of concentrated H_2SO_4 and 30% H_2O_2 (70:30 v/v).[88] (*Caution: "piranha" solution reacts violently with many organic materials and should be handled with care.*) After the mixture had been heated for 30 min at 90 °C, it was cooled to room temperature and the liquid was poured off. The silicon was immediately rinsed by first completely covering the substrates with distilled water and then decanting the liquid. This process was repeated a minimum of 5 times. The substrates were stored under water until use. The silicon was used within 2 days of its cleaning. After longer times, sufficient organic species had accumulated at the air–water interface to recontaminate the samples. Clean substrates were completely wetted by water.

Formation of Self-Assembled Monolayers. The cleaned silicon strips were removed from water by using PTFE-coated forceps (Pelco). After all traces of water had been removed by exposing the sample to a stream of argon for 15–30 s, the silicon was placed in a scintillation vial that had been thoroughly rinsed with distilled water and acetone and dried in an oven at 150 °C. These vials contained approximately 20 mL of an unstirred 0.1–0.5% (by weight) solution of the alkyltrichlorosilane in bicyclohexyl or hexadecane. (For $Cl_3Si(CH_2)_{10}CO_2CH_3$ and $Cl_3Si(CH_2)_2(CF_2)_7CF_3$, 0.001% and 0.4% solutions in CCl_4 were used.) The containers were kept under a dry nitrogen atmosphere or in a desiccator containing P_2O_5 (Baker, "granusic"). After 1–48 h, the substrate was removed from the deposition solution and rinsed in 20 mL of CH_2Cl_2. After this wash, the substrates were removed from the dry atmosphere and rinsed in 20 mL of $CHCl_3$ and then 20 mL of ethanol to remove any residual organic contaminants. The sample was then rinsed with ethanol dispensed from a 2-mL disposable pipet. The monolayer was dried under a stream of argon, and contact angle and ellipsometric measurements were made immediately.

Contact Angle Measurements. Contact angles were determined on sessile drops by using a Ramé-Hart Model 100 contact angle goniometer equipped with a controlled environment chamber. The relative humidity in the chamber was maintained at greater than 80% by filling the wells of the chamber with water. The temperature was not controlled and varied from 20 to 25 °C. The volume of the drop used was 3 μL; the observed contact angle was, however, independent of the volume of the drop over the range 1–20 μL. The sessile drops were applied to the surface by first forming a 2-μL drop at the tip of a 50-mL syringe (Scientific Glass Engineering, Austin, TX) that was equipped with a PTFE-coated needle and a repeating dispenser (Hamilton). The syringe was lowered to the surface by turning the screw upon which the syringe platform rested. After the drop had come in contact with the monolayer, the needle was removed by rotating the screw in the opposite direction. While the needle was raised, another 1 μL of solvent was added to the drop. Contact angles were determined within 1 min of applying the drop to the monolayer. The tangent to the drop at its intersection with the surface was estimated visually. All reported values are the average of at least six measurements taken on both sides of at least three drops. Values obtained in this manner were typically 2–3° less than those from the maximum advancing angle technique described by Troughton et al.[18]

Ellipsometry Measurements. Ellipsometry measurements were made with a Rudolph Research Model 43603-200E thin-film ellipsometer. The light source was a He–Ne laser (λ = 6328 Å). The angle of incidence was 70.0°, and the compensator was set at −45.0°. The measurements necessary for the calculation of the film thickness consisted of the determination of two sets of polarizer and analyzer readings for the silicon substrate and of the corresponding values for the substrate coated with a monolayer film.

Each set of analyzer and polarizer angles, measured in zones 1 and 3,[46] was the average of at least four measurements taken at different locations (separated by at least 1 cm) on the sample. The angles that comprised this average had a maximum scatter of ±0.15°. These measurements were determined in air for the bare substrate within 3 min of its removal from water. The substrate was placed in solution immediately after these measurements. The ellipsometric angles for the substrate-monolayer systems were measured no more than 5 min after the samples had been washed with ethanol.

The refractive index of each substrate was determined directly from the analyzer and polarizer readings for the uncoated silicon. Refractive indices for the various substrates ranged from 3.84 to 3.88. This index reflects the combined contributions from the surface silica and the underlying bulk silicon. Using literature values for the refractive indices of silicon and silicon dioxide,[89] we have estimated that the oxide layer was 10–20 Å in thickness.[90] This thickness is consistent with those derived from scanning tunnelling electron microscopy,[36] high-resolution electron microscopy,[91] and other ellipsometric studies.[92]

The thicknesses of the monolayers were calculated by using the algorithm of McCrackin.[46] For this calculation, we assumed that the monolayer had a refractive index of 1.45 and was completely transparent to the laser beam. This index is approximately that of both liquid and solid straight-chain hydrocarbons (n = 1.42–1.44).[93] Altering this value by 0.05 resulted in less than a 1-Å change in the calculated thickness of the monolayer. The algorithm yielded two values for the length of the monolayer, both of which were complex. Since the length of the monolayer must be real, we chose the real part of the complex number with the smaller imaginary component as the thickness of the monolayer. The other choice was inherently unreasonable since it was greater than 1000 Å. Thicknesses determined in this fashion are accurate to ±2 Å.

X-ray Photoelectron Spectroscopy. The XPS spectra were obtained by using a Surface Science Laboratories Model SSX-100 spectrometer (monochromatized Al Kα X-ray source; 10^{-8}–10^{-9} Torr) referenced to Au 4f$_{7/2}$ at 84.0 (ref 94) according to ASTM STP 699. Samples were washed with ethanol and introduced into the spectrometer. A survey spectrum (resolution 1.1 eV, spot size 1000 μm, one scan) and high-resolution spectra of the C 1s, O 1s, and Si 2p regions (resolution 0.16 eV, spot size 300 μ, 5–30 scans) were taken for each sample. High-resolution spectra were also obtained for F 1s and Br 3d when these elements were present in the monolayer. Atomic compositions were determined by using standard multiplex fitting routines with the following sensitivity factors: C 1s, 1.00; Si 2p, 0.902; O 1s, 2.49; Br 3d, 3.188; F 1s, 3.33.[72]

16-Heptadecenyl Bromide. This compound was prepared by using the procedure of Friedman and Shani.[95] Undecenyl bromide (20.0 g, 86 mmol) and magnesium (3.3 g, 136 mg-atom) were sealed in a dry heavy-walled glass bottle. The bottle was evacuated, and the atmosphere was replaced with argon. Dry, degassed THF (50 mL) was added via cannula, and the bottle was placed in an ultrasonic bath for 24 h. The resulting solution of Grignard reagent was added slowly to a cooled, degassed solution containing 1,6-dibromohexane (21.0 g, 86 mmol), and Li_2CuCl_4 (10 mL of a 0.1 M THF solution, 1 mmol) in THF (55

---

[88] Pintchovski, F.; Price, J. B.; Tobin, P. J.; Peavey, J.; Kobold, K. *J. Electrochem. Soc.* **1979**, *26*, 1428–1430.

[89] The refractive indices of Si and SiO_2 are 4.086 and 1.4620, respectively. Taft, E. A. *J. Electrochem. Soc.* **1978**, *128*, 968–971.

[90] These estimates are crude. Ellipsometry actually yields a complex value for the thickness of the monolayer. For well-behaved systems, such as the monolayers described here, more than 95% of the absolute value of the length is real. For the estimates of the oxide thickness, the length was more than 60% imaginary. This result suggests that the silicon oxide on the substrate did not have a refractive index equal to the literature value. The ellipsometric measurements reported here relied on the direct determination of an "effective" index of refraction for the substrate, which included the contributions from the bulk silicon and the surface oxide of the substrate. The lack of a definitive index of refraction for the individual Si and SiO_2 layers of the substrate should, therefore, have had little effect on the measured thicknesses of the monolayers. A demonstration of the validity of the use of an effective refractive index for the substrate is found in ref 45, pp 332–340.

[91] Carim, A. H.; Sinclair, R. *Mater. Lett.* **1987**, *5*, 94–98.

[92] Archer, R. J. *J. Electrochem. Soc.* **1957**, *104*, 619–622.

[93] *CRC Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1975.

[94] Anthony, M. T. In *Practical Surface Analysis*; Briggs, D., Seah, M. P., Ed.; Wiley: Chichester, U.K., 1983; Appendix 1.

[95] Friedman, L.; Shani, A. *J. Am. Chem. Soc.* **1974**, *96*, 7101–7103.

mL). The solution was stirred for 2 h at 5 °C, after which the reaction was quenched with 200 mL of saturated aqueous ammonium chloride solution. Stirring overnight extracted the copper salts into the aqueous layer. The aqueous layer was extracted with ether (3 × 100 mL), and the combined organic layers were then extracted with saturated aqueous sodium chloride (2 × 100 mL). After the solution had been dried over magnesium sulfate, the solvent was evaporated and the remaining oil was dried under vacuum. The crude product was eluted in 3-g batches with hexane through a silica column (radius 2.5 cm, length 31 cm). All fractions containing the desired bromide, still impure, were collected. This process was continued until the material had been eluted 3 times. The enriched bromide was then purified in 2.2-g batches by MPLC through a Lobar (E. M. Merck) prepacked column (radius 3.7 cm, length 44 cm) containing silica-60 (63–125 μm) with hexane as the eluent. The solvent was delivered by a FMI RP-SY pump at a flow rate of 6 mL/min, and fractions were collected every 1.5 min. The fractions containing the pure bromide were combined, and the solvent was evaporated. The isolated yield was 8.1 g (25 mmol, 30%): ^{1}H NMR ($CDCl_3$) δ 5.8 (m, 1), 4.9 (m, 2), 2.0 (m, 2), 1.8 (m, 2), 1.5–1.1 (m, 24); ^{13}C NMR ($CDCl_3$) δ 139.0, 114.0, 33.85, 33.73, 32.94, 29.72, 29.67, 29.57, 29.49, 29.21, 29.04, 28.86, 28.27; mass spectrum, m/z (relative intensity): 318 (2), 316 (2), 164 (6), 162 (6), 41 (100).

Anal. Calcd for $C_{17}H_{33}Br$: C, 64.32; H, 10.50; Br, 25.17. Found: C, 64.51; H, 10.60; Br, 25.3.

16-Heptadecenyltrichlorosilane. This compound was prepared by using the procedure of Whitemore, et al.[34] Magnesium (2.02 g, 83 mg-atom), 16-heptadecenyl bromide (5.00 g, 16 mmol), and dry THF (75 mL) were placed in a dry heavy-walled glass bottle. The container was then sealed with a septum and metal cap. After the bottle had been cooled to −78 °C, the atmosphere was replaced by evacuating and purging with argon (three cycles). The bottle was then warmed to room temperature and placed in an ultrasonic bath (10 h). A 500-mL round-bottomed flask with a side arm was equipped with a magnetic stirring bar and flame-dried. Silicon tetrachloride (4.0 mL, 35 mmol) and dry ether (50 mL) were added to the flask while continually purging it with argon. A water-cooled condenser was attached to the flask, which was then sealed with a septum. The solution was degassed by using a procedure identical with that for the Grignard reagent. The flask was warmed to room temperature, and the Grignard solution was added through a cannula. The solution was heated at reflux (12 h) and then cooled to room temperature. The condenser was removed, and a liquid nitrogen cooled trap was connected. The solvent and residual tetrachlorosilane were removed by a trap-to-trap distillation. The remaining solid was triturated with dry hexane (2 × 125 mL). This solution was transferred via cannula through a sintered glass filter to a dry 500-mL round-bottomed flask. A cold trap was attached, and the hexane was removed under vacuum. After the remaining solid had been warmed to form an oil, the liquid was transferred by pipet to a dry Kugelrohr distillation apparatus. The crude product was distilled, and a fraction was collected from 91 (0.003 Torr) to 119 °C (0.008 Torr). This material was then redistilled in a short-path distillation apparatus. The product was collected as the fraction that boiled between 105 (0.005 Torr) and 115 °C (0.005 Torr). The product (2.87 g, 49%) was isolated as a clear oil: ^{1}H NMR ($CDCl_3$) δ 5.8 (m, 1), 4.9 (m, 2), 2.0 (m, 2), 1.7–1.1 (m, 28); ^{13}C NMR ($CDCl_3$) δ 139.2, 114.1, 33.8, 31.6, 29.66, 29.60, 29.52, 29.37, 29.17, 29.01, 24.4, 22.3.

Anal. Calcd for $C_{17}H_{33}Cl_3Si$: C, 54.89; H, 8.96; Cl, 28.59. Found: C, 55.73; H, 9.17; Cl, 27.46.

By both NMR spectroscopy and elemental analysis, this material contained an approximately 3% impurity of 1-heptadecene. The presence of this compound has no effect on the formation of monolayers from the trichlorosilane.

10-Undecenyltrichlorosilane. This compound was prepared by a procedure similar to that for 16-heptadecenyltrichlorosilane: ^{1}H NMR ($CDCl_3$) δ 5.8 (m, 1), 5.0 (m, 2), 2.0 (m, 2), 1.7–1.2 (m, 16); ^{13}C NMR ($CDCl_3$) δ 139.0, 114.1, 33.88, 31.89, 29.52, 29.39, 29.16, 29.09, 29.04, 24.47, 22.38.

Anal. Calcd for $C_{11}H_{21}Cl_3Si$: C, 45.91; H, 7.37; Cl, 36.96. Found: C, 45.88; H, 7.36; Cl, 36.93.

Methyl 11-(Trichlorosilyl)undecanoate. Methyl 10-undecenoate (12.0 g, 61 mmol), dihydrogenhexachloroplatinate(II) (5.1 mL of a 0.01 M THF solution, 0.051 mmol), and trichlorosilane (7.9 mL, 78 mmol) were placed under argon in a dry heavy-walled glass tube (diameter 2.5 cm, length 21 cm) that was equipped with a side arm and a 0–10-mm PTFE stopcock. The solution was degassed (freeze–pump–thaw, three cycles), and the tube was sealed under vacuum at −195 °C. The tube was warmed to room temperature and heated in an oil bath (98 °C, 37 h). It was then cooled to −195 °C, and a liquid nitrogen cooled trap was attached. The reaction solution was warmed to room temperature, and the excess trichlorosilane was removed by a trap-to-trap distillation. The remaining liquid was transferred by pipet to a dry Kugelrohr distillation apparatus, and the residual THF was removed under vacuum. The liquid was distilled, and the product was collected from 98 (0.03 Torr) to 120 °C (0.03 Torr) (13.4 g, 40 mmol, 67%): ^{1}H NMR ($CDCl_3$) δ 3.7 (s, 3), 2.3 (t, 2), 1.8–1.1 (m, 18); ^{13}C NMR ($CDCl_3$) δ 175.1, 50.6, 34.0, 31.7, 29.26, 29.18, 29.11, 29.06, 28.89, 24.9, 24.3, 22.2.

Anal. Calcd for $C_{12}H_{23}Cl_3O_2Si$: C, 43.18; H, 6.96; Cl, 31.86. Found: C, 43.34; H, 7.01; Cl, 31.94.

Rate of Formation of Monolayers. Formation of the monolayer film was monitored by ellipsometry and contact angle measurements. The film was prepared by the procedures described above. Measurements of contact angles (both water and hexadecane) and thickness were made on a single substrate, which was immersed repeatedly in a solution of tetradecyltrichlorosilane ($Cl_3Si(CH_2)_{13}CH_3$) in bicyclohexyl (0.01 M). The sample was removed from the adsorption solution and washed with chloroform and ethanol. After determination of the thickness by ellipsometry, the sample was washed with ethanol, and the aqueous contact angle was measured. The ethanol wash was repeated before measurement of the contact angle for hexadecane. The sample was then washed with ethanol, dried under a stream of argon, and reimmersed in the adsorption solution.

Stability of Monolayers. The stability of the monolayers was monitored by a procedure similar to that for following the rate of formation. For both 0.1 N HCl and 0.1 N NaOH, the sample was repeatedly immersed in the solution for timed intervals. The monolayers were removed from the solution and washed with distilled water and ethanol. The thickness and the contact angles with water and hexadecane were measured as above. For the attempted hexadecane desorption, the solvent was kept in a glass vial in an oil bath at 75 °C. The monolayer was removed at timed intervals and washed with ethanol before the ellipsometry and contact angle measurements were taken.

Surface Reactions. Permanganate–Periodate Oxidation. Stock solutions of $KMnO_4$ (5 mM), $NaIO_4$ (195 mM), and K_2CO_3 (18 mM) in water were prepared. Immediately prior to the oxidation, 1 mL from each of these solutions was combined with 7 mL of distilled water to create the oxidizing solution ($KMnO_4$, 0.5 mM; $NaIO_4$, 19.5 mM; K_2CO_3, 1.8 mM, pH 7.5). The vinyl- and methyl-terminated monolayers were placed in this solution for periods of 24 h. (The kinetics of this reaction were monitored on a single sample by an identical procedure over shorter intervals.) The samples were removed from the oxidant and rinsed in 20 mL each of $NaHSO_3$ (0.3 M), water, 0.1 N HCl, water, and ethanol.

Hydroboration. The vinyl-terminated monolayers were placed in a glass vial which was then sealed with a rubber septum. The atmosphere was purged by passing argon gas through the container for 30 min. All solvent transfers were performed through cannula. Sufficient BH_3–THF complex (1 M) to completely cover the silicon (ca. 20 mL) was added. After 2 h, the borane solution was removed, and dry THF was added. The THF was removed, and approximately 15 mL of 30% H_2O_2/0.1 N NaOH was transferred into the vial. After 3 min, the vial was opened to the atmosphere. The monolayer was then rinsed thoroughly with water and ethanol.

Trifluoroacetylation of Hydroxyl-Terminated Monolayers. The hydroxyl-terminated monolayers generated by hydroboration were placed in a 2% (v:v) solution of trifluoroacetic anhydride in hexane. After 2 min, the substrate was removed from solution and rinsed with ethanol dispensed from a pipet. The aqueous contact angles of these surfaces were stable during the time necessary to measure these angles.

Bromination. The vinyl monolayers were placed for 2 h in a 2% (by volume) solution of elemental bromine in CH_2Cl_2. The wafers were then rinsed with CH_2Cl_2 (2 × 20 mL) and ethanol.

Mixed Acid and Methyl Surfaces. Stock solutions of hexadecyltrichlorosilane and 16-heptadecenyltrichlorosilane in hexadecane (25 mM) were prepared. These were then mixed in the appropriate ratios to generate solutions (25 mM total silane concentration) containing 0%, 20%, 40%, 60%, 80%, and 100% of the vinyl-terminated silane. Monolayers were prepared from these solutions according to the methods described above. Oxidation of the vinyl groups with $KMnO_4/NaIO_4$ according to the procedure described above yielded monolayers that contained terminal methyl and carboxyl groups.

Acknowledgment. This work was supported in part by the Defense Advanced Research Projects Agency and the Office of Naval Research. The XPS spectrometer was purchased under a DARPA/URI grant and maintained in the Cambridge Surface Facility in the Harvard University Materials Research Laboratory. A portion of the support for this facility is provided by the National Science Foundation, Grant DMR 86-14003. We would like to express our appreciation to Dr. Colin Bain for helpful discussions concerning the interpretation of XPS spectra and to Dr. Abraham Ulman of Eastman Kodak for supplying preprints of articles.

Registry No. Si, 7440-21-3; SiO_2, 7631-86-9; CH_3SiCl_3, 75-79-6; $CH_3CH_2SiCl_3$, 115-21-9; $CH_3(CH_2)_2SiCl_3$, 141-57-1; $CH_3(CH_2)_5SiCl_3$, 928-65-4; $CH_2{=}CH(CH_2)_4SiCl_3$, 18817-29-3; $CH_3(CH_2)_6SiCl_3$, 871-41-0; $CH_3(CH_2)_7SiCl_3$, 5283-66-9; $CH_3(CH_2)_8SiCl_3$, 5283-67-0; $CH_3(CH_2)_9SiCl_3$, 13829-21-5; $CH_3(CH_2)_{10}SiCl_3$, 18052-07-8; $CH_3(CH_2)_{11}SiCl_3$, 4484-72-4; $CH_3(CH_2)_{13}SiCl_3$, 18402-22-7; $CH_3(CH_2)_{15}SiCl_3$, 5894-60-0; $CH_3(CH_2)_{17}SiCl_3$, 112-04-9; $Cl_3Si(CH_2)_2(CF_2)_7CF_3$, 78560-44-8; $CH_2{=}CH(CH_2)_{15}SiCl_3$, 120905-09-1; $CH_2{=}CH(CH_2)_{15}Br$, 106110-87-6; $CH_2{=}CH(CH_2)_9SiCl_3$, 17963-29-0; $CH_3OCO(CH_2)_{10}SiCl_3$, 4211-29-4.

Supplementary Material Available: Text describing variation in ellipsometric angles, Appendix of text and equations describing the escape depth of an electron, and Figure 1 showing the range in ellipsometric polarizer angles for allylsiloxane monolayers on Si/SiO_2 substrates. Ordering information is given on any current masthead page.

Utilization of Pyridinium Salts as Microsensor Coatings

Alan R. Katritzky,* Rick J. Offerman, and Zouquan Wang

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received May 10, 1988. In Final Form: March 1, 1989

Numerous pyridine derivatives were synthesized and examined for their utility as coatings for microsensor devices (surface acoustic wave (SAW) and chemiresistor) in the detection of various vapors including dimethyl methylphosphonate (DMMP), chloroethyl ethyl sulfide (CEES), and water vapor. Classes of compounds synthesized include pyridines, pyridine 1-oxides, pyridinium salts, and pyridinium betaines. The most sensitive coatings for the detection of both DMMP and CEES vapors are pyridinium betaines and pyridine 1-oxides: each class showed utility as chemiresistor coatings with the former showing a large change in resistance upon exposure to DMMP. Methylated pyridinium sulfonates showed the greatest change in resistance of any of the compounds tested when exposed to CEES vapor, but their resistance change upon exposure to DMMP vapor was modest. None of the compounds showed large SAW frequency shifts with the exception of certain hygroscopic coatings upon exposure to water vapor.

Introduction

The development of miniature, specific, and sensitive microsensors offers great promise in the detection of hazardous chemicals at very low levels. Recent advances in microsensor technology have resulted in a new generation of microsensors based on planar microfabrication techniques. These include (i) metal oxide semiconductors (MOS), (ii) optical waveguides, (iii) chemically sensitive field effect transistors (CHEMFETs),[1,2] (iv) chemiresistors, and (v) surface acoustic wave devices (SAW).[2] Devices of type ii–v can also be termed chemical microsensors, as their selectivity relies on coatings which are applied to the surface of the device. These devices have found utility as sensors for gases, liquids, and solids and as environmental as well as biosensors.[1,2]

We are developing coatings for SAW and chemiresistor devices and will briefly review those technologies. Chemiresistors are chemically sensitive devices whose resistance changes when exposed to a vapor of interest. Recent chemiresistor devices have utilized a gold interdigital electrode lithographically fabricated onto the surface of a piezoelectric crystal.[3,4] The interdigital electrode is coated with a thin layer of an organic semiconductor film which is chosen to facilitate diffusion of species into the film.[3,4] At present, little is known about which types of compounds are best suited as selective and sensitive coatings for various vapors; however, certain phthalocyanine coatings have shown utility in the detection of iodine, ammonia, and nitrogen dioxide.[5,6]

Surface acoustic wave devices are mechanically resonant piezoelectric structures whose resonance frequency is perturbed by the mass or viscoelastic properties of a thin, selective coating layer on the surface.[7] A change in the

---

(1) *Solid State Chemical Sensors*; Janata, J.; Huber, R. J., Eds.; Academic: Orlando, FL 1985.

(2) *Fundamental and Applications of Chemical Sensors*; Schuetzle, D., Hammerle, R., Eds.; ACS Symposium Series 309; American Chemical Society: Washington, D.C., 1986.

(3) Barendsz, A. W.; Van Beest, C. A.; Wittgen, P. P. M. M. "Proceedings of the 1981 Scientific Conference on Chemical Defense Research"; *Spec. Publ.* ARCSL-SP-83026, June, 1983, p 35.

(4) Wohltjen, H.; Barger, W. R.; Snow, A. W.; Jarvis, N. L. *IEEE Trans. Elect. Dev. Ed-32*(7), **1985**, 1170.

(5) Snow, A. W.; Barger, W. R.; Klusty, M.; Wohltjen, H.; Jarvis, N. L. *Langmuir* **1986**, *2*, 513.

(6) Barger, W. R.; Wohltjen, H.; Snow, A. W.; Lint, J.; Jarvis, N. L. In *Fundamentals and Applications of Chemical Sensors*; Schuetzle, D., Hammerle, R., Eds.; ACS Symposium Series 309; American Chemical Society: Washington, D.C., 1986; pp 155-165.

(7) Wohltjen, H. *Sens. Actuators* **1984**, *5*, 307.