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Self-Assembled Monolayers Containing ω-Mercaptoalkylboronic Acids Adsorbed onto Gold Form a Highly Cross-Linked, Thermally Stable Borate Glass Surface[1]

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This paper describes the preparation and properties of self-assembled monolayers (SAMs) obtained by the adsorption of 11-mercaptoundecanyl-1-boronic acid, $HS(CH_2)_{11}B(OH)_2$, **1**, onto the surface of gold substrates. In solution in dry hydrocarbon solvents, 11-mercaptoundecanyl-1-boronic acid reversibly forms a tri-ω-mercaptoalkylboroxine that adsorbs onto gold and forms a hydrophobic boroxine bilayer: this bilayer is marginally stable in air; it can be completely hydrolyzed to a monolayer in aqueous ethanol, yielding a hydrophilic, 17-Å-thick SAM that presents boronic acid groups at its surface. Under water-saturated cyclooctane, SAMs exposing the boronic acid groups do not titrate appreciably over a pH range of 0 to 11—that is, the contact angle is independent of the pH of the contacting aqueous solution. At pH 13 to 14, there is a sharp increase in the hydrophilicity of the SAM, indicating an onset of ionization of the boronic acid groups. In dry hydrocarbon solvents or under vacuum, the boronic acid tail groups dehydrate rapidly and reversibly and form a cross-linked borate glass at the surface. At 147 °C in hexadecane, SAMs having this cross-linked borate glass as a surface are at least 5 times more stable to thermal desorption than SAMs of the structurally analogous 11-hydroxyundecane-1-thiol. The boronic acid/anhydride groups of SAMs of **1** can be derivatized with solutions of certain cis-diols (especially pinanediol), catechols, and alkyltrichlorosilanes to yield hydrophobic structures consisting of an inner monomer derived from **1** and an outer partial monolayer of the boronate ester or the alkylsiloxane.

Introduction

This paper describes studies of the preparation and characterization of self-assembled monolayers (SAMs) formed by the adsorption of an ω-mercaptoalkylboronic acid, 11-mercaptoundecanyl-1-boronic acid, **1**, onto a gold substrate. This work is part of a program to study the physicalorganic chemistry of organic interfaces.[2] SAMs of alkanethiolates on gold are particularly useful substrates for studying organic surface chemistry because the high affinity of sulfur for gold[3-6] allows the incorporation of a wide range of tail groups, X, into precursor alkanethiols of the general formula $HS(CH_2)_nX$.[7-15] SAMs of alkanethiolates on gold are useful model systems in fundamental studies of electrochemistry,[16] protein adsorption,[12] X-ray-induced damage to organic materials,[17] wetting,[2,5,7-10,12,18] and corrosion.[19]

Boronic acids are interesting groups to incorporate into the surface of SAMs. In solution, alkylboronic acids react with simple alcohols, diols, and polyols and form covalent esters reversibly under mild and easily controllable reaction conditions.[20-22] The ability of boronic acids to perform diol-specific molecular recognition in gels has formed the basis of affinity chromatography of carbohy-

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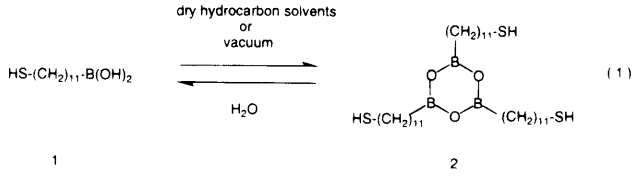
drates in a variety of boronate matrices,[23-27] and boronate esters have played a major role in enantioselective synthesis.[28-33] In bulk solution in dry hydrocarbon solvents, boronic acids dehydrate readily and form cyclic trimers (boroxines), eq 1. Dehydration of boronic acid tail groups constrained in position to the surface of a quasi two-dimensional, ordered SAM would form a surface comprising cross-linked boronic anhydrides (a "borate glass").

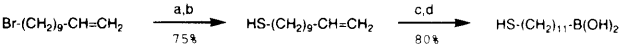


We have investigated the interfacial properties of SAMs presenting boronic acid groups at the surface of an ordered alkanethiolate monolayer on gold. The first goal in this study was to develop a convenient, gram-scale synthesis of the ω-mercaptoalkylboronic acid, **1**. The second goal was to prepare and to characterize SAMs obtained from **1** and to measure their wettability, stability, and reactivity. We particularly wished to determine how hydrophilic a surface of boronic acid groups would be and at what pH the boronic acid groups would begin to ionize. We also wished to establish conditions under which the boronic acid tail groups would dehydrate and give a surface layer of cross-linked, boronic anhydride groups and to determine if this cross-linked surface would be more stable to thermal desorption than a structurally analogous SAM that was not cross-linked. The last goal was to determine if boronic acid groups exposed on the surface of a SAM would react with cis-diols, catechols, simple alcohols, and alkyltrichlorosilanes in a manner similar to that of boronic acids in bulk solution.

Results and Discussion

Synthesis of $HS(CH_2)_{11}B(OH)_2$. We required a medium chain-length alkane substituted with a boronic acid at one end and a thiol at the other. The chemistry necessary for introducing the thiol group has been well studied[7] and many reagents for hydroboration are commerically available.[34-40] The synthesis in Scheme 1 yields multigram quantities of ω-mercaptoalkylboronic acids from ω-bromoalkenes.

Scheme 1. Synthesis of ω-Mercaptoalkylboronic acids



[a] Thiolacetic acid and NaOMe in methanol, 2 h. [b] Excess NaOMe in methanol, reflux, 1 h, N_2. [c] 2 equiv $HBBr_2 \cdot Me_2S$, CH_2Cl_2, N_2, 3 h. [d] Water, 10 min.

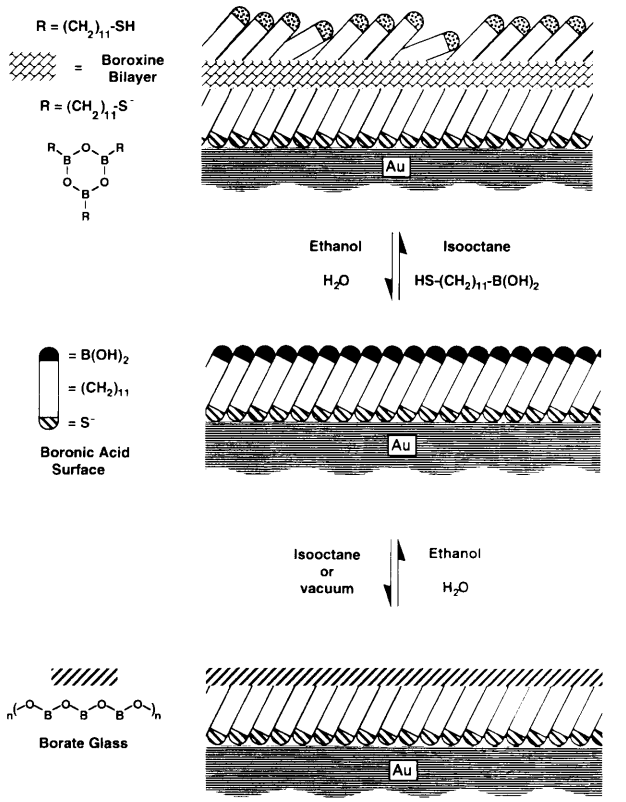


Figure 1. Stylized illustrations of monolayer structures. (top) Proposed structure of the boroxine bilayer that is obtained by the adsorption of **2** from isooctane solution onto gold substrates. This bilayer is hydrolytically unstable, exhibits high hysteresis in its contact angles, and is probably not well ordered. (middle) Proposed structure of the 17 Å monolayer of the boronic acid formed by exposure of the boroxine bilayer or the monolayer of the borate glass to washes with alcohol and water. (bottom) Proposed structure of the 17-Å borate glass surface formed by dehydration of the monolayer of the boronic acid under vacuum or in dry hydrocarbon solvents like hexadecane.

Preparation and Characterization of SAMs: Au/{$[S(CH_2)_{11}]_3(BO)_3$}, Au/$S(CH_2)_{11}B(OH)_2$, and Au/$[S(CH_2)_{11}BO]_n$. Figure 1 is a schematic illustration of the monolayer structures that are formed from **1**. Compound **1** exists in dry hydrocarbon solvents predominantly as the boroxine **2**. From solution in isooctane, the boroxine **2** adsorbed onto gold substrates and formed a boroxine bilayer that was marginally stable to hydrolysis and that had a thickness (as determined by both X-ray photoelectron spectroscopy (XPS) and ellipsometry) that varied with the conditions used in its preparation. XPS analysis showed a strong thiol signal, in addition to the thiolate signal that is normally observed in SAMs. The surface of this boroxine bilayer was hydrophobic, and high hysteresis in contact angles measured with drops of buffered water suggested that the bilayer was disordered or reactive with water. Treatment of this boroxine bilayer with ethanol and water yielded a hydrophilic monolayer composed of boronic acid tail groups that was consistently 17 Å thick as measured by ellipsometry. Dehydration of this monolayer under vacuum or by exposure to a dry

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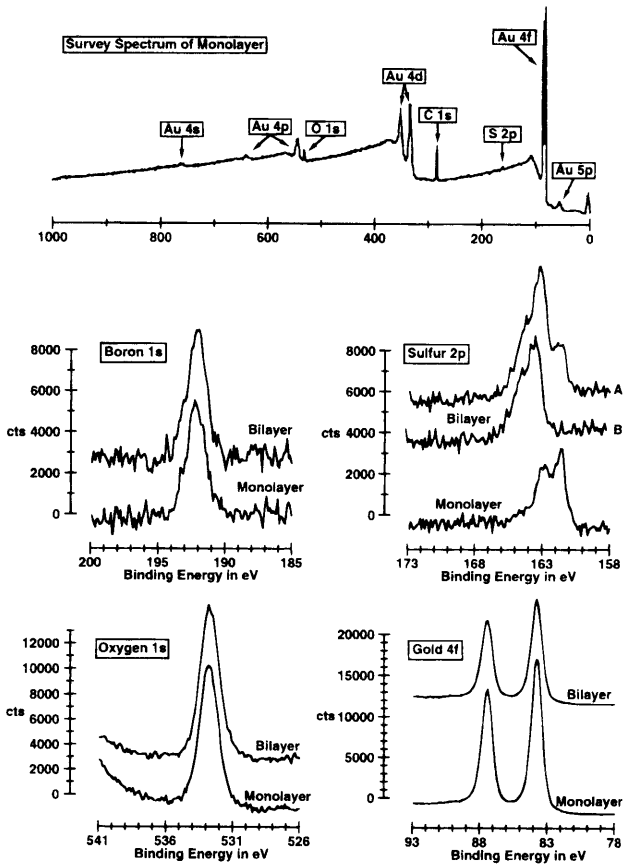

Figure 2. XPS spectra for a monolayer and a partial bilayer derived from the adsorption of $HS(CH_2)_{11}B(OH)_2$ onto gold. The top is a representative survey spectrum of the monolayer, including labels for the individual peaks. Note that the intensity of the B(1s) peak at 192 eV is too low to be seen in a survey spectrum. Below the survey spectrum are individual element scans for boron, sulfur, gold, and oxygen. For the sulfur spectrum of the bilayer, two spectra are shown. Spectrum A is the actual data. Spectrum B is a manipulation of the data in spectrum A to show the peaks due to thiol and disulfide. This manipulation was carried out by scaling the spectrum for the monolayer for attenuation through an extra 9 Å of hydrocarbon (the thickness determined from the ratio of the Au(4f) peaks) and subsequently subtracting these data from spectrum A.

hydrocarbon solvent left a boronic anhydride or "borate glass" monolayer; this SAM was 17 Å thick (by XPS) and had an atomic ratio of oxygen to boron that was 0.9 as determined by XPS. The XPS spectra for four separate samples of the monolayer had an average value of 1.0 ± 0.15 for the ratio of oxygen to boron. This value suggests that the species present on the surface under the ultrahigh vacuum (UHV) conditions of XPS was indeed the anhydride and not the boronic acid, for which one would expect a ratio of oxygen to boron of 2.0.

We note that all alkylboronic acids readily interconvert between the acid (in air) and the boroxine when exposed to heat or vacuum.[20] SAMs of **1**, which concentrate and present boronic acid tail groups at a monolayer surface, can be expected to behave in a similar manner, interconverting between the anhydride form under vacuum and the hydrated boronic acid form upon exposure to humid air.

X-ray Photoelectron Spectroscopy (XPS). XPS was useful in the structural characterization of a boronic anhydride surface and a partial boroxine bilayer. XPS spectra were collected for boron (using the B(1s) peak), sulfur (S(2p) peaks), gold (Au(4f) peaks), and oxygen (O(1s) peak). Spectra for a monolayer and a partial bilayer are presented in Figure 2, along with a representative survey spectrum of the monolayer.

We used the relative intensities of the two sets of Au(4f) peaks to determine the difference in thickness between the monolayer and the partial bilayer. The attenuation of the signal was modeled as an exponential decay through the hydrocarbon overlayer using an attenuation length of 40 Å for the Au(4f) electrons.[41-43] For the layers whose data are presented in Figure 2, the partial bilayer was approximately 9 Å thicker than the monolayer. This difference in thickness corresponded approximately to an additional 50% of a monolayer.

For both of the layers, the binding energy of the B(1s) electrons was 192 eV, in good agreement with the published value for *p*-chlorobenzeneboronic acid of 191.5 eV.[44] The intensity of the B(1s) peak was compared to that of the corresponding O(1s) peak to obtain a ratio of the two elements in the samples. The oxygen signal could be attributed solely to the boronic acid groups of the layers, because gold does not form a native oxide and because spectra were taken on freshly prepared layers, thus limiting potential oxidation of the sulfur atoms.[45] The raw intensities for both samples were scaled by the Scofield cross sections of ionization (0.486 for B(1s); 2.93 for O(1s))[46] and by the efficiency of the detector (or "étendue"). The magnitude of the latter correction is dependent on the kinetic energies of the electrons; we used the reciprocal of the kinetic energy as an approximation of this dependence.[47]

In the case of the monolayer, we did not include the effect of attenuation of the intensities since we assumed that the boronic acid groups were at the monolayer–vacuum interface. Correcting the raw intensities for the cross sections of ionization and the étendue yielded a ratio of boron to oxygen of 1.1 in the monolayer. This result suggests that the surface of the monolayer is predominantly composed of a cross-linked borate glass, rather than of free boronic acids groups, for which we would have expected a ratio of boron to oxygen closer to 0.5.

To obtain a ratio of boron to oxygen for the partial bilayer, we needed to correct the data for attenuation of these signals through the 9 Å of additional hydrocarbon in the partial bilayer, in addition to the cross sections and the étendue. For this additional correction, we used attenuation lengths of 37.5 and 30 Å for the B(1s) and O(1s) electrons, respectively, which were estimated from an empirical equation that describes attenuation lengths through hydrocarbon as a function of the kinetic energy of the electrons.[42] Scaling the raw intensities by these factors yielded a boron to oxygen ratio of 1.1, suggesting formation of boroxine groups between the layers.

Figure 2 also summarizes XPS data for the S(2p) regions for both layers. The spectrum of the borate glass monolayer exhibited the expected two peaks in a 2:1 ratio due to spin–orbit coupling of the 2p electrons.[48] The binding

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energy of the peak at lower energy, the S(2p3/2) peak, was 161.6 eV, the expected value for thiolates.[5,6,15]

For the bilayer, there are two sets of peaks in the S(2p) region, whose overlap gives rise to the appearance of a triplet. Superimposed on the two peaks for the thiolate groups are two peaks at higher binding energy. Peak fitting the spectrum with four peaks yielded a binding energy of 163.2 eV for the S(2p3/2) of the second set of peaks.[49] The binding energy of this peak corresponds to thiol and possibly disulfide groups in the second layer of the partial bilayer.[6]

The XPS data present a picture of the layers consistent with the stylized illustrations drawn in Figure 1. For the monolayer, the sulfur atoms are adsorbed to the gold surface as thiolates, and the boronic acid groups are dehydrated, forming a cross-linked borate-glass-like network. The partial bilayer has all of characteristics of the monolayer plus the presence of sulfur atoms not bound to the gold surface. The partial second layer is stable in the ultrahigh vacuum conditions of the XPS (10^{-9} Torr) suggesting binding of the second layer to the monolayer presumably through boroxine groups as observed for boronic acids in solution.

Interfacial Properties: Wetting. Figure 3 shows that the 17-Å-thick SAM bearing the boronic acid tail groups had a hydrophilicity and hysteresis between the advancing and receding contact angles that is similar to the structurally analogous 11-hydroxyundecane-1-thiol (HUT). Contact angle titration under cyclooctane[50] suggested that the boronic acid groups of the SAM obtained from **1** began to ionize at pH 12; this ionization was reflected by a decrease in both advancing and receding contact angles. The SAM composed of HUT remained un-ionized over the titration range of pH 0 to pH 14 (as reflected in the independence of both advancing and receding contact angles to pH).

In air, the contact angles of buffered aqueous drops for the SAM having terminal boronic acid groups were constant over a range of pH 2 to pH 10 ($\theta_a^{H_2O} = 16-24°$). At pH 11 or above, the SAM of the boronic acid was wet completely by buffered aqueous drops. The receding contact angles in air for the SAM of the boronic acid were zero at all values of pH.

These titration results in air and under cyclooctane establish that SAMs of alkylboronic acids do not begin to ionize significantly until the aqueous drop is at least pH 11. Thus, in analogy to our previous findings for SAMs bearing carboxylic acid and phosphonic acid tail groups,[10,51] alkylboronic acids at the monolayer–water interface require contact with stronger base for ionization than alkaneboronic acids in bulk solution (ca. $pK_{a1} = 9.2$ and

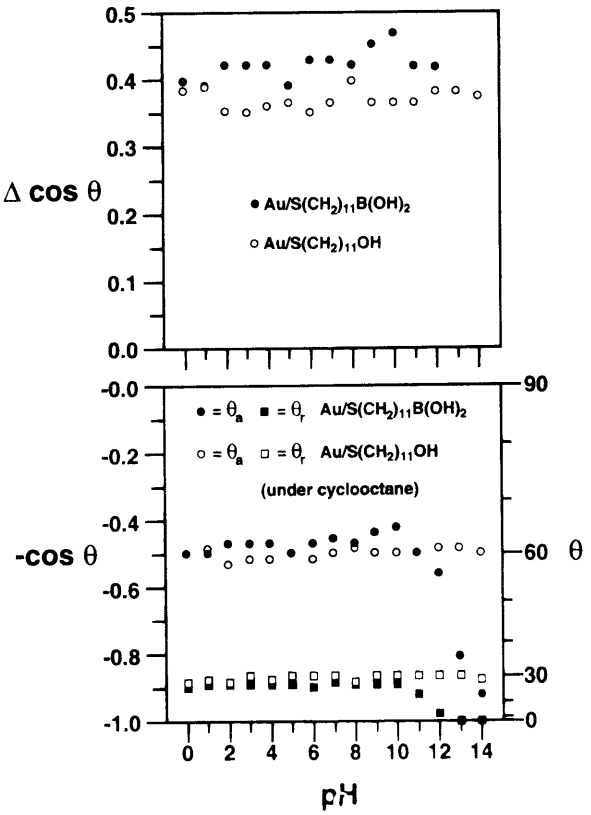

Figure 3. (top) Hysteresis in the contact angle of buffered aqueous solutions measured with drops under cyclooctane as a function of pH. Values of hysteresis cannot be determined when the receding angle of water is zero (which, in practical experimental terms, is any value of $\theta_r^{H_2O}$ less than or equal to 10°) and therefore there are no values of hysteresis for SAMs of **1** above pH = 11. (bottom) Advancing and receding contact angles of buffered aqueous solutions measured with drops under cyclooctane on monolayers of $HS-(CH_2)_{11}-B(OH)_2$ and $HS-(CH_2)_{11}-OH$. The size of the symbols gives our best estimate of the error of the measurement.

$pK_{a2} = 12.5$ in water). The origin of the apparent shift in the pK_a to higher values has not been completely established; the environment of the interface might influence both the properties of the functional groups and the partitioning of hydroxide ion into the interfacial region.[2,10]

Desorption of Au/[S(CH$_2$)$_{11}$BO]$_n$ in Contact with Hexadecane. Many technological applications of SAMs, particularly in microelectronic device fabrication, will require greater thermal stability than that displayed by SAMs of simple alkanethiolates on gold. Our prior studies of the thermal desorption of alkanethiolates from gold have used methyl-terminated SAMs that have low surface free energies; the SAMs of alkaneboronic acids have high surface energies and contaminate more easily than methyl-terminated SAMs.[2,10,51] Typically, thermal desorption is measured by exposing the SAM to a reservoir of hexadecane held at constant temperature and measuring the change in ellipsometric constants of the SAM (after removing and washing) as a function of time. We determined the thermal stability of the SAMs in this study in hexadecane at 147 °C: the choice of temperature allowed us reproducibly to observe complete desorption of the monolayer in a short time.[52]

Figure 4 is a plot of the rate of desorption vs time for SAMs of **1** and SAMs of HUT (used as a reference). HUT

(48) Briggs, D.; Rivière, J. C. In *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. P., Eds.; John Wiley and Sons: Chichester, 1983; Chapter 3. Although the ratio of the peaks is expected to be 2:1 due to spin–orbit coupling, the slight apparent increase in the intensity of the S($2p_{1/2}$) peak and the small shoulder on the high energy side of these peaks is due predominantly to sulfur–carbon bond cleavage during irradiation: the intensity of the higher energy peaks increased with the amount of irradiation.

(49) We fit the peaks by constraining the binding energy of S($2p_{1/2}$) peak for the thiolate to be 1.2 eV greater (or 162.8 eV) than the S($2p_{3/2}$) of the thiolate and also constraining its intensity to be half that of the S($2p_{3/2}$) peak. For information on the spin–orbit coupling of the S(2p) peak, see: Salaneck, W. R.; Lipari, N. O.; Paston, A.; Zallen, R.; Liang, K. S. *Phys. Rev. B* **1975**, *12*, 1493–1500.

(50) The contact angle titrations were performed under cyclooctane, C_8, in order to increase the contact angles and to reduce the rate of contamination of the surface of boronic acids. Under air as the ambient medium, a pure, clean surface of the boronic acid is wet (or very nearly wet) by water at all values of pH, but the high interfacial free energy causes the surface composed of boronic acids to become contaminated at a rate that is fast enough to interfere with the measurements. C_8 is relatively nonvolatile and can be obtained in high purity at low cost.

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(52) Although we observed thermal desorption of the monolayers at 80 to 90 °C, quantitative analysis of the data was hindered by a tendency of the monolayers to contaminate as a function of time. For this reason, we determined the thermal stability of the SAMs in this study at a higher temperature, 147 °C.

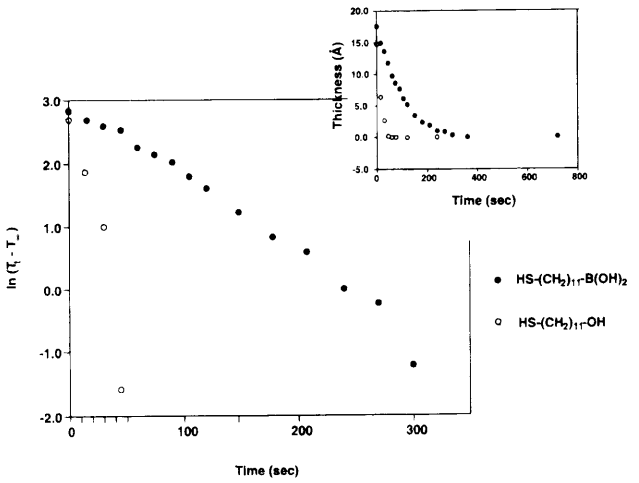
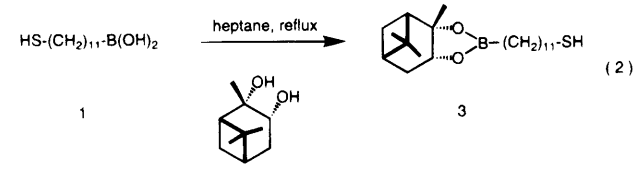


Figure 4. Thermal desorption of monolayers of thiols on gold in contact with hexadecane at 147 °C: (●) 11-mercaptoundecanyl-1-boronic acid; (○) 11-hydroxyundecane-1-thiol. In the first-order plot of the corrected thicknesses against time, $T_t - T_\infty$ represents the difference in ellipsometric thickness between time t and long times. The inset shows a plot of ellipsometric thickness vs time.

and **1** have the same C_{11} alkyl chain length and similar solubility in hexadecane. The primary difference in the chemical properties of the two SAMs is that the SAM of the boronic acid readily dehydrates to a cross-linked, borate glass surface that we expected to be more stable toward thermal desorption than the similar, but non-cross-linked surface of a SAM of HUT. The data in Figure 4 show that in hexadecane at 147 °C, a SAM of the boronic acid was approximately 5 times more stable to thermal desorption than a SAM of HUT. These data are consistent with the hypothesis that cross-linking the tail groups in SAMs enhances their stability to thermal desorption, but it may also reflect differences in solubilities.

Reactions: Formation and Stability of Boronate Esters on SAMs. Alkylboronic acids in solution can form strong covalent bonds reversibly under mild conditions with α-hydroxyacids, catechols, γ-hydroxyaldehydes, and cis-diols. In this section we describe the reactions of SAMs of **1** with pinanediol, catechol, simple alcohols and glycols, and alkyltrichlorosilanes (Table 1).

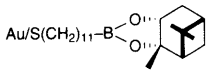
We compared the properties of SAMs prepared by the adsorption of **3** from solution in isooctane to SAMs prepared by the esterification in isooctane solution of a preexisting monolayer of **1** with pinanediol. We chose pinanediol as the diol constituent because the resulting boronate esters are very stable and easily manipulated without complications due to hydrolytic instability.[20,26,27,33] Compound **3** was prepared by refluxing equimolar amounts of **1** and (+)-pinanediol in heptane for 10 min (eq 2). Compound **3** was stable to an aqueous extractive workup and to elution through a column of silica gel.



1 3 (2)

SAMs formed from **3** and SAMs formed by reaction of pinanediol with a preexisting SAM of **1** are both hydrophobic, and each is stable toward water (pH = 7) for at least 24 h. The SAM formed in the surface reaction was actually slightly more hydrophobic and thicker than the SAM obtained from **3** (see Table 1).[53] The conclusion from the experiments with pinanediol is that SAMs presenting boronic acid tail groups react cleanly and rapidly (the derivatization requires only 5 min in a 5 mM solution of pinanediol in isooctane) if presented with the proper cis-diol.

Table 1. Wetting Properties and Thicknesses of SAMs Derived from 11-Mercaptoundecanylboronic Acid[a]

monolayer system	$\theta_a^{H_2O}$	$\theta_r^{H_2O}$	thickness, Å
$Au/S(CH_2)_{11}B(OH)_2$	15	0	17[b]
$Au/\{[S(CH_2)_{11}]_3(BO)_3\}$	97	50	28[b]
$Au/S(CH_2)_{11}B(OH)_2 + ZrOCl_2 + C_4H_9B(OH)_2$[c]	15	0	17[b]
$Au/S(CH_2)_{11}B(OH)_2 + ZrOCl_2 + H_2NCH_2CH_2PO_3H_2$[c]	15	0	17[b]
$Au/S(CH_2)_{11}B(OH)_2 + C_{18}H_{37}SiCl_3$[d]	102	65	37[e]
$Au/S(CH_2)_{11}B(OH)_2 + CF_3(CF_2)_5(CH_2)_2SiCl_3$[d]	110	74	25[e]
$Au/S(CH_2)_{11}B(OH)_2 + CF_3(CF_2)_7(CH_2)_2OH$[f]	58	30	
$Au/S(CH_2)_{11}B(OH)_2$ + catechol[f]	62	35	20[e]
$Au/S(CH_2)_{11}B(OH)_2$ + pinanediol	95	78	21[b,g]
	93	74	17[b,g]

[a] $\theta_a^{H_2O}$ and $\theta_r^{H_2O}$ refer to advancing and receding contact angles of water, respectively, using drops of water buffered at pH 7. [b] Thickness determined by XPS relative to a monolayer of undecanethiol at 15 Å. [c] These experiments attempted to build multilayers onto the surface of SAMs of **1** by the sequential deposition of $ZrOCl_2$ and either an alkylboronic acid or an alkylphosphonic acid. (See refs 52–54). By XPS, no zirconium was observed, and there was no increase in the thickness of the films. [d] SAMS of **1** were treated with an alkyl- or perfluoroalkyltrichlorosilane in dry CH_2Cl_2 or in the vapor phase. [e] Thickness determined by ellipsometry. [f] This boronate ester SAM and analogous SAMs derivatized with ethylene glycol, octanol, and dodecanol were not stable to high vacuum, excessive washes with aqueous ethanol, or prolonged exposure to air. [g] The 21 Å thick SAM of a pinanediol boronate ester was prepared by the esterification of a preexisting SAM of **1** with pinanediol in solution from isooctane. The 17 Å thick SAM of a pinanediol boronate ester was prepared by the adsorption of **3** onto a gold substrate. Both of these SAMs were stable to repeated washes with water and to vacuum.

In solution, boronate esters of catechols are much less stable toward hydrolysis than esters of pinanediol. Treatment of a boronic acid-terminated SAM with catechol from dilute solution in isooctane or from concentrated solution in THF yielded a derivatized monolayer surface that was 3 Å thicker than the underivatized boronic acid SAM and that had an advancing contact angle with water that varied from 62° to 65° depending on the sample. Although several washes with ethanol and water did not seem to change the wettability or thickness, a prolonged exposure (overnight) to aqueous ethanol reversed the esterification and yielded the surface exposing boronic acid groups again. When an analogous esterification was attempted with 3-fluorocatechol, very little change in thickness or wettability was observed, and after one wash with ethanol and water, no fluorine could be detected by XPS. We conclude that SAMs of **1** form only moderately stable boronate esters with catechols and that the greater the electron drawing constituent on the catechol, the lower the stability of the derivatized monolayer.[54]

(53) The reason for the observed difference in thickness and wettability of the two SAMs is probably that the tail group of **3** is so bulky that it prevents the formation of a complete monolayer. In the case of the SAM formed by the surface reaction, the underlying SAM of the boronic acid has already formed from **1** and is densely packed and highly ordered. Pinanediol can then react with these ordered boronic acids at the surface, filling up all of the sites and making a more ordered, more densely packed layer of pinanediol boronate terminal groups than the monolayer formed from **3**.

Although multilayers can be formed from SAMs of phosphonic acids by the sequential deposition of $ZrOCl_2$ and α,ω-alkylphosphonic acids,[55-57] attempts to build analogous multilayer systems from $ZrOCl_2$ and alkylboronic acids were unsuccessful due to the incomplete formation or the hydrolytic instability of the zirconium boronate compounds. XPS spectra contained no peaks for zirconium and showed no increase in the thickness of a SAM of 1 after it had been treated with $ZrOCl_2$ and $C_4H_9-B(OH)_2$ (see Table 1).

Formation of a Borosilicate Bilayer on SAMs: Reaction of Alkyltrichlorosilanes with Boronic Acid Tail Groups. Partial bilayers attached by borosilicate bonds have been formed by treatment of SAMs of **1** with either of two different alkyltrichlorosilanes: $C_{18}H_{37}-SiCl_3$ and $CF_3(CF_2)_7(CH_2)_2-SiCl_3$. These reactions were carried out both with the alkyltrichlorosilane in the vapor phase and in solution in dry CH_2Cl_2. The advancing contact angles of water and hexadecane on these bilayers were close to those of typical long-chain alkyl and perfluorinated alkyl-terminated SAMs ($\theta_a^{H_2O} = 115$ and $\theta_a^{HD} = 44$). The properties of these surfaces also compare well with bilayers formed in a similar fashion from the reaction of alcohol-terminated SAMs with alkyltrichlorosilanes,[58] although the hysteresis in the contact angles of drops of buffered water is slightly higher for the borosilicate bilayer than that observed for analogously derived siloxane bilayer from HUT.[59]

Conclusions

The ω-mercaptoalkylboronic acid, **1**, adsorbs onto gold from isooctane solution and forms a boroxine bilayer than can be hydrolytically cleaved by treatment with aqueous ethanol and yield a 17 Å thick monolayer bearing boronic acid tail groups. Under high vacuum or in dry organic solvents, the boronic acid monolayer reversibly dehydrates and forms a cross-linked boronic anhydride or "borate glass" surface. This cross-linking leads to a 5-fold decrease in the rate of thermal desorption in hexadecane at 147 °C relative to the rate of thermal desorption observed for a structurally analogous monolayer of hydroxyundecanethiol. Boronic acid or boronic anhydride groups on the surface of a SAM can be derivatized reversibly with cis-diols and form hydrophobic surfaces composed of boronate esters; boronate ester groups formed from pinanediol are stable to hydrolysis. Derivatization of boronic acid or boronic anhydride monolayers with alkyltrichlorosilanes yields hydrophobic surfaces that are held together by a borosilicate network.

Experimental Section

Materials. Absolute ethanol (Quantum Chemical Corp.) was deoxygenated with N_2 or Ar prior to use. Isooctane (Aldrich, 99%) and hexadecane (Aldrich, 99%) were percolated twice through activated, neutral alumina (EM Science). Water was deionized and distilled in a glass and Teflon apparatus. Undecanethiol (Pfalz & Bauer) was distilled prior to use. Undecylenic bromide (Pfalz & Bauer) and dibromoborane dimethyl sulfide complex (Aldrich) were purchased and used without further purification. Hydroxyundecanethiol was available from previous studies.[7]

Preparation of Substrates. Gold substrates were prepared by electron-beam evaporation of ~200 Å of gold (Materials Research Corp., Orangeburg, NY 99.999%) onto single crystal silicon(100) test wafers (Silicon Sense: Nashua, NH; 100 mm diameter, ~500 μm thick) that had been precoated with 50–100 Å of titanium to improve adhesion. The substrates were stored in Fluoroware wafer holders until used in experiments, generally as soon as possible after evaporation.

Formation of Monolayers. Adsorptions were carried out in 10-mL glass weighing bottles that had been cleaned with "piranha solution" (7:3 concentrated H_2SO_4/30% H_2O_2) at 90 °C for 1 h, and rinsed first with distilled water and then with copious amounts of deionized water. **WARNING**: *"Piranha solution" should be handled with caution. It should not be allowed to contact significant quantities of oxidizable organic materials. In some circumstances (Most probably when mixed with significant quantities of an oxidizable organic material), it has detonated unexpectedly.*[60] The weighing bottles were stored in an oven at above 100 °C until use. Adsorptions were carried out in 10 mL of deoxygenated solvent (ethanol or isooctane) at a total thiol concentration of 1 mM.

Thermal Desorption Experiments. Desorptions were carried out in an unstirred solution of hexadecane in a 25-mL weighing bottle that was partially immersed in an oil bath thermostated at 153 ± 1 °C. The hexadecane was percolated twice through a column of activated alumina and was purged with N_2 immediately prior to use. The temperature of the hexadecane in the glass bottle was 147 ± 1 °C. Slides (~1 cm × 3 cm) with preformed monolayers were immersed in 20 mL of hot hexadecane, removed at the proper time intervals, rinsed with heptane, and blown dry with a stream of nitrogen. Ellipsometry was used to follow the desorption of the monolayers; ellipsometric constants were measured on the complete monolayer and then after each removal from solution. The thickness of the adsorbed organic layer was calculated using the optical constants for clean gold. Corrected thicknesses ($T_t - T_\infty$) were calculated by subtracting from the ellipsometric thickness at time t the mean of several readings obtained at long times after desorption was essentially complete.

Instrumentation. Ellipsometric measurements were performed on a Rudolf Research Type 43603-200E ellipsometer equipped with a He–Ne laser ($\lambda = 6328$ Å) at an incident angle of 70°. Samples were rinsed and blown dry in a stream of nitrogen prior to characterization. Values of thickness were calculated using a program written by Wasserman,[61] following an algorithm by McCrackin and co-workers;[62] in the calculation, we used a refractive index of 1.45 for the SAMs.[63]

Contact angles were measured on a Ramé-Hart Model 100 goniometer at room temperature and ambient humidity for both water and hexadecane. Advancing and receding contact angles were measured on both sides each of at least 3 drops of each liquid per slide; data in the figures represent the average of these

(54) Attempts to derivatize SAMs of the boronic acid, **1**, with simple alcohols or glycols such as ethylene glycol, octanol, or perfluorododecanol yielded derivatived monolayers that were at best transiently stable as judged by XPS, ellipsometry, and contact angles. After treatment of SAMs of **1** with simple alcohols and glycols in a dry hydrocarbon solvent, the contact angles with water and hexadecane increased and there were small changes in the ellipsometric constants. In all such cases, however, the derivatized SAMs were highly unstable in the presence of moisture, and extensive washing with ethanol and water always restored the underivatized surface of boronic acids. The reasons for this observation are that simple alcohols and glycols do not form boronate esters that are sufficiently stable to make a surface that is resistant to hydrolysis. Partial derivatization is typically not detected by XPS because if the alcohol is volatile, the small amount the alcohol adsorbed to the surface prior to an XPS experiment will be removed under the high vacuum conditions in the XPS chamber.

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(58) Ulman, A.; Tillman, N. *Langmuir* **1989**, *5*, 1418–1420. (b) Netzger, L.; Sagiv, J. *J. Am. Chem. Soc.* **1983**, *105*, 674. (c) Pomeranz, M.; Segmuller, A.; Netzer, L.; Sagiv, J. *Thin Solid Films* **1985**, *132*, 153.

(59) In our hands, treatment of monolayers of HUT with octadecyltrichlorosilane in dry CH_2Cl_2 yielded bilayers that had hysteresis in the contact angles with water consistently 10% lower than bilayers prepared in an analogous fashion from monolayers of **1** and octadecyltrichlorosilane.

(60) Several warnings have appeared concerning "piranha solution": Dobbs, D. A.; Bergman, R. G.; Theopold, K. H. *Chem. Eng. News* **1990**, *68* (17), 2. Wnuk, T. *Chem. Eng. News* **1990**, *68* (26), 2. Matlow, S. L. *Chem. Eng. News* **1990**, *68* (30), 2.

(61) Wasserman, S. R. Ph.D. Thesis, Harvard University, 1989.

(62) McCrackin, F. L.; Passaglia, E.; Stromberg, R. R.; Steinberg, H. L. *J. Res. Natl. Bur. Stand., Sect. A* **1963**, 467, 363–377.

measurements. A Micro-Electrapette syringe (Matrix Technologies, Lowell, MA) was used for dispensing/removing the liquids onto/from the SAMs (ca. 1 mL/s). The method used for measuring the advancing and receding angles has been described previously.[2,10]

XPS was carried out using a SSX-100 spectrometer (Surface Science Instruments) using monochromatic Al Kα X-rays (photon energy = 1487 eV; the peaks are referenced to Au($4f_{7/2}$) at 84.0 eV). For quantitation of the individual elements in the SAMs, we used the 4f doublet for gold ("Au(4f)" at 84 and 87 eV for Au($4f_{7/2}$) and Au($4f_{5/2}$), respectively), the 1s peaks for carbon, oxygen, and boron at 284, 532, and 192 eV, respectively, and the 2p peaks for sulfur between 161 and 164 eV. Data for gold, carbon, and sulfur were taken using a spot size of 600 μm and a pass energy of 50 eV. Data for oxygen and boron were taken using a spot size of 1000 μm and a pass energy of 100 eV because of the low intensity of the boron peak; both regions were checked at the lower pass energy to show that there was only one peak in each region. Two scans were taken for gold, three scans for carbon, eight scans for oxygen, thirty scans for boron, and fifty scans for sulfur. Each scan at the pass energy of 50 eV took approximately 1.5 min; each scan at the pass energy of 100 eV took approximately 2 min.

Peaks in the spectra were fitted using a 80% Gaussian/20% Lorentzian peak shapes, using a Shirley background subtraction.[64] For each oxidation state present, the sulfur peaks were fit using two peaks, corresponding to the $S(2p_{3/2})$ and $S(2p_{1/2})$ peaks due to spin–orbit coupling.[43,48] The ratio of these peaks is 2:1, and the splitting between them is 1.2 eV.[49] In the fitting program, these values were used as constraints to obtain realistic fits to the data. For both the monolayer and the bilayer, two sets of peaks were used in the fit. In the former, the set of peaks at higher energy was shown to be due to X-ray-induced damage[17] at the sulfur–carbon bond: the relative intensity of these peaks increased with time of irradiation from 25% to 43% after 4 h of irradiation. For each sample, spectra in the S(2p) region were taken first so as to minimize effects due to damage.

10-Undecene-1-thiol. To a clear solution of NaOMe (465 mg, 8.6 mmol) in degassed methanol (10 mL) was added thioacetic acid (0.70 mL, 1.15 equiv) and undecylenic bromide (2 g, 8.6 mmol). The reaction was refluxed under N_2 for 3 h. Additional NaOMe (930 mg, 17.2 mmol) was added, and the reaction was refluxed for another 1 h. Most of the CH_3OH was removed in vacuo, and the reaction was quenched by addition of degassed, half-saturated ammonium chloride solution. The aqueous layer was extracted with $CHCl_3$ (2×). The $CHCl_3$ extracts were combined, washed with H_2O (2×), dried over $MgSO_4$, and concentrated in vacuo to yield a crude oil (1.5 g, 94%) that was purified by flash chromatography using hexanes/ethyl acetate (95:5) as eluent to yield a clear colorless oil (1.2 g, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.8 (m, 1 H), 4.95 (m, 2 H), 2.52 (q, J = 8 Hz, 2 H), 2.04 (q, 2 H), 1.6 (m, 2 H), 1.2–1.4 (m, 13 H). MS EI (pos): 185 (M^+).

1-Mercapto-11-undecanylboronic Acid. To a solution of 10-undecene-1-thiol (1.1 g, 5.9 mmol) at 0 °C in freshly distilled CH_2Cl_2 was added via syringe dibromoborane dimethyl sulfide complex (12.0 mL, 1.0 M in CH_2Cl_2, 12 mmol). The reaction was allowed to warm to room temperature over 15 min and was refluxed for 3 h. Most of the CH_2Cl_2 was removed in vacuo, and the reaction was then transferred to a stirred mixture of water (10 mL) and ether (50 mL). The suspension was stirred for 10 min and transferred to a separatory funnel. The aqueous layer was extracted with ether (4×), and the ether layers were combined and extracted with brine (2×), dried over $MgSO_4$, and concentrated in vacuo to yield a white solid (1.31 g, 96%) that was purified by flash chromatography using hexanes/ethyl acetate (3:1) as eluent to yield a white solid (1.1 g, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (q, 8 Hz, 2 H), 1.55 (m, 8 Hz, 2 H), 1.2–1.4 (m, 17 H), 0.82 (t, 8 Hz, 2 H). FABMS (glycerol matrix): 289 [(M/glycerol ester)H^+], 576 [2(M/glycerol ester)H^+]. FABMS (nitrobenzyl alcohol matrix): 350 [(M/mononitrobenzyl ester − H_2O)H^+], 503 [(M/dinitrobenzyl ester)H^+], 1006 [2(M/dinitrobenzyl ester)H^+].

(+)-Pinanediol-1-mercapto-11-undecanylboronate. A solution of 1-mercapto-11-undecanylboronic acid (100 mg, 0.43 mmol) and (+)-pinanediol (73 mg, 0.43 mmol) in heptane was refluxed for 10 min and then left at ambient temperature for 1 h. The heptane was removed in vacuo, and the resulting oil was passed through a column of silica gel using hexanes/EtOAc (97:3) as eluent. The appropriate fractions were collected to yield a clear oil (130 mg, 80%). TLC: R_f = 0.8 (hexanes). ^1H NMR (300 MHz) δ 4.26–4.24 (1 H, dd, CHOB pinanyl); 2.54–2.47 (2 H, q, CH_2–S); 2.37–2.29 (1 H, m, pinanyl); 2.24–2.18 (1 H, m, pinanyl); 2.05–2.03 (1 h, t, pinanyl); 1.92–1.88 (1 H, septet, pinanyl); 1.85 and 1.81 (1 H, m, pinanyl); 1.64–1.52 (2 H, m, C_β–H_2); 1.41–1.39 (2 H, m, C_β–H_2); 1.38 (3 H, s, CH_3); 1.33 (1 H, t, SH); 1.29 (3 H, s, CH_3); 1.25 (14 H, s); 0.84 (3 H, s, CH_3); 0.82–0.78 (2 H, t, CH_2–B). High resolution FABMS: calcd for $C_{21}H_{38}BO_2S$, 366.2764; found, 366.2760.

Acknowledgment. XPS spectra were obtained by using instrumental facilities purchased under the DARPA/URI program and maintained by the Harvard University Research laboratory. NMR spectra were obtained in the Bruker NMR Facility at Harvard. R.I.C. was an NIH Postdoctoral Fellow (GM-13678).

(63) In the calculation of ellipsometric thickness, we assume an index of refraction of 1.45; the indices of refraction for various molecules similar to those used in this study vary from 1.42 to 1.46: undecane (liquid), 1.42; undecanol (liquid), 1.44; undecanethiol (liquid), 1.46; octadecanethiol (solid), 1.46; docosane (solid), 1.45. *CRC Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1984. This potential variation in the refractive index affects the thickness <±1.5 Å, which is less than the variation we normally observe for the SAMs of alkanethiolates on gold.

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