Formation of Self-Assembled Monolayers by Chemisorption of Derivatives of Oligo(ethylene glycol) of Structure HS(CH$_2$)$_m$(OCH$_2$CH$_2$)$_n$OH on Gold

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Abstract: This paper describes the preparation of oligo(ethylene glycol)-terminated alkanethiols having structure HS(CH$_2$)$_m$(OCH$_2$CH$_2$)$_n$OH ($m = 3-7$) and their use in the formation of self-assembled monolayers (SAMs) on gold. A combination of experimental evidence derived from X-ray photoelectron spectroscopy (XPS), measurement of contact angles, and ellipsometry implies substantial disorder in the oligo(ethylene glycol)-containing segment. The order in the -(CH$_2$)$_n$- group is not defined by the available evidence. The SAMs are moderately hydrophilic: $\theta_\text{H}_2\text{O} = 34-38^\circ; \theta_\text{O}_2\text{N} = 22-25^\circ$. A study of monolayers containing mixtures of HS(CH$_2$)$_m$CH$_2$ and HS(CH$_2$)$_m$(OCH$_2$CH$_2$)$_n$OH suggests that the oligo(ethylene glycol) moieties are effective at preventing underlying methylene groups from influencing wetting by water. A limited study demonstrates that these oligo(ethylene glycol)-containing SAMs resist the adsorption of protein from solution and suggests that SAMs will be a useful model system for studying the adsorption of proteins onto organic surfaces.

Introduction

Oligomers of ethylene glycol are moderately hydrophilic groups: The Hansch $\pi$ parameter for ethylene glycol is $\sim$1.93.$^2$ These oligomers are commonly incorporated as components of materials when increased hydrophilicity is required$^1$ and have proved useful as constituents of biocompatible materials.$^4$ The structure of the oligo(ethylene glycol) units at a solid–water interface is relevant to the molecular level design of materials having desired degrees

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of hydrophilicity and adsorptivity toward biological (and other) molecules.

As part of a program to explore the physical organic chemistry of the interaction of biological molecules with surfaces, we have prepared materials incorporating oligomers of ethylene glycol into self-assembled monolayers (SAMs) of alkanethiols on gold.6,7 The objective of this work was to apply these SAMs—with whatever degree of structural order characterized them—to the study of the solid-water interfacial properties of materials having oligo(ethylene glycol) moieties as constituents. This paper describes the preparation of SAMs by chemisorption of compounds of structure HS(CH₂)ₙ(OCH₂CH₂)ₙOH (n = 0, 3–7) onto gold, the characterization of these SAMs, and preliminary measurements of their adsorptivity toward proteins in solution.

SAMs derived from unfunctionalized alkanethiols HS-(CH₂)ₙCH₃ are easily prepared by reaction of solutions or vapors of these compounds with gold.6,8 The polyethylene chains in these SAMs are predominantly trans-extended when n ≥ 10, although the terminal segments of the chains (those at the monolayer–vapor or liquid interface) contain some gauche bonds: when n = 10, the monolayer contain more gauche bonds than when n = 17.12-15 With terminally functionalized alkanethiols HS(CH₂)ₙR, the size and shape of the R group are important. When R is small, the (CH₂)ₙ-containing regions of the SAMs are still predominantly trans-extended.17 When R is large, we presume that the polyethylene regions of the SAMs contain a greater fraction of gauche bonds; i.e., they are more disordered.21

Our choice of the structure HS(CH₂)₁₁(OCH₂CH₂)ₙOH containing only 11 methylene groups as the basis for this work was a compromise between convenience of preparation and structural order in the SAMs. Monolayers containing the HS-(CH₂)₁₁⁻ moiety could be expected to have more gauche bonds in the polyethylene region than longer chain analogues (e.g., HS(CH₂)₁₅⁻), but the thiols are more easily synthesized and purified than these longer chain compounds. The compounds with structures HS(CH₂)₁₁(OCH₂CH₂)ₙOH are easily manipulated: They are soluble in ethanol and stable in air, and they form monolayers rapidly and reproducibly by chemisorption onto gold. The HS(CH₂)₁₁⁻ moiety provides a foundation for stable SAMs, and we expected the oligo(ethylene glycol) derivatives of this group also to be sufficiently stable for our studies.

This work describes the syntheses of oligo(ethylene glycol)- terminated alkanethiols and the characterization of one- and two-component SAMs on gold containing them. We examined these monolayers by X-ray photoelectron spectroscopy (XPS), ellipsometry, polarized infrared reflectance spectroscopy (PIERS), and measurement of contact angles; our results suggest that the oligo(ethylene glycol) groups in these SAMs are not highly ordered. The thickness of the portions of the films occupied by these groups, furthermore, appeared to be ~15% less than that expected if they occupied an ordered, trans-extended configuration. The thermal and mechanical stabilities of these SAMs were adequate for exploratory studies of protein adsorption. We did not, however, expect the oligo(ethylene glycol) derivatives of this group also to be sufficiently stable for our studies.

Results

Synthesis of Thiol. Thiols incorporating oligo(ethylene glycol) moieties were prepared via a three-step synthesis (Scheme I). The reaction of an 11-haloundec-1-ene with a slight excess of 50% sodium hydride and 3–10 equiv of oligo(ethylene glycol) pro-
The thickness of SAMs on gold is linear in the number of ethylene glycol units.

Characterization of SAMs. Ellipsometry. The thickness of SAMs on gold is linear in the number of ethylene glycol units. A plot of $d$ against $m$ is a straight line with a slope of 2.7 Å per OCH$_2$CH$_2$ unit and an intercept of 12 Å for $m = 0$ (Figure 1). The thickness was calculated with use of a parallel, homogeneous, three-layer (air, monolayer, substrate) model with an assumed refractive index of 1.45 for the monolayer. The refractive index for ethylene glycol is 1.43, that for hexadecylthiol is 1.46, and that for undecane is 1.42. Variations of this magnitude in the refractive index (1.45 ± 0.01) do not significantly affect the calculated values of thickness. The observed scatter in the data is ±2 Å for most thiol systems.

The linear plot suggests a consistent incremental increase in the thicknesses of the monolayers as a function of the number of ethylene glycol units. The value for the slope of the line (2.7 Å per OCH$_2$CH$_2$ group) is 15% lower than the value of 3.1 Å calculated for trans-extended chains of OCH$_2$CH$_2$ units tilted at an angle of 30° from the normal to the surface. The dotted line in Figure 1 shows the calculated thicknesses for these monolayers. The experimentally significant difference between the observed and calculated values of incremental thickness for OCH$_2$CH$_2$ units indicates that at least the oligo(ethylene glycol) portion of these SAMs deviates from the model of all-trans conformation and 30° tilt.

XPS. The high-resolution photoelectron spectrum of the carbon 1s region shows two peaks: one at 284.5 eV is characteristic of the internal units of the polymethylene chain (CH$_2$CH$_2$CH$_2$); the second at 286.5 eV corresponds to methylene groups adjacent to an oxygen (OCH$_2$) (Figure 2). The relative intensity of this latter peak increases with the number of glycol units ($m$). The attenuation of the Au(4f$_{7/2}$) signal (in arbitrary units) measured by XPS as a function of the number of oligo(ethylene glycol) units in Au-S-(EG)$_m$OH. The attenuation of the intensity as a function of $m$ is compatible with an exponential dependence and suggests a consistent incremental increase in the thickness of the monolayer as a function of the number of ethylene glycol units.

Preparation of SAMs. SAMs containing HS-(EG)$_m$OH were prepared from 1 mM solutions of the thiols dissolved in deoxygenated, absolute ethanol, by placing gold-coated wafers in the solutions for 24 h at room temperature. The contact angles measured for SAMs prepared by this method were indistinguishable from those of SAMs prepared by immersion for periods of up to 1 month.

Table 1. Contact Angles Measured on SAMs on Gold Obtained from HS(CH$_2$)$_n$R$^a$

<table>
<thead>
<tr>
<th>R$^a$</th>
<th>$\theta_a$</th>
<th>$\theta_d$</th>
<th>$\Delta \cos \theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>110</td>
<td>99</td>
<td>0.18</td>
</tr>
<tr>
<td>OH$^b$</td>
<td>10</td>
<td>&lt;10</td>
<td>$d$</td>
</tr>
<tr>
<td>OCH$_2$CH$_2$</td>
<td>85</td>
<td>71</td>
<td>0.24</td>
</tr>
<tr>
<td>(CH$_2$)$_2$OCH$_2$</td>
<td>85</td>
<td>75</td>
<td>0.17</td>
</tr>
<tr>
<td>(EG)$_1$OH</td>
<td>34</td>
<td>22</td>
<td>0.10</td>
</tr>
<tr>
<td>(EG)$_2$OH</td>
<td>38</td>
<td>24</td>
<td>0.12</td>
</tr>
<tr>
<td>(EG)$_3$OH</td>
<td>38</td>
<td>24</td>
<td>0.12</td>
</tr>
<tr>
<td>(EG)$_4$OH</td>
<td>38</td>
<td>25</td>
<td>0.12</td>
</tr>
</tbody>
</table>

$^a$Advancing ($\theta_a$) and receding ($\theta_d$) static contact angles of water.

Figure 2. XPS of monolayers prepared from HS(CH$_2$)$_n$R on gold: high-resolution spectra of the C(1s) region. Each spectrum is labeled by its $R$ group.

Figure 3. Intensity of the Au(4f$_{7/2}$) signal (in arbitrary units) measured by XPS as a function of the number of oligo(ethylene glycol) units in Au-S-(EG)$_m$OH. The attenuation of the intensity as a function of $m$ is compatible with an exponential dependence and suggests a consistent incremental increase in the thickness of the monolayer as a function of the number of ethylene glycol units.

Figure 4. Wettability of oligo(ethylene glycol)-modified gold and polyethylene (PE) surfaces as a function of the number of ethylene glycol units ($m$). The point at $m = 0$ for derivatives of polyethylene is for PE-CO-(OCH$_2$CH$_2$)$_0$OH. Values of $\theta$ for Au-(CH$_2$)$_n$-(OCH$_2$CH$_2$)$_m$OH are the advancing contact angles of water; those for PE-CO-(OCH$_2$CH$_2$)$_m$OH were measured by the sessile drop method. The roughness of the surface of PE causes the error in the measurement of contact angles on PE to be larger than those measured on Au.

Table 1. Contact Angles Measured on SAMs on Gold Obtained from HS(CH$_2$)$_n$R$^a$

- Advancing ($\theta_a$) and receding ($\theta_d$) static contact angles of water.
- $\Delta \cos \theta = \cos \theta_a - \cos \theta_d$.
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Figure 5. PIERs spectra of Au-S-(CH$_2$)$_{10}$(OCH$_2$CH$_2$)$_6$OH, Au-S-(CH$_2$)$_{11}$(OCH$_2$CH$_2$)$_3$OH, and Au-S-(CH$_2$)$_{16}$OH. The broad feature at ~2880 cm$^{-1}$ in the spectrum of Au-S-(CH$_2$)$_{10}$(OCH$_2$CH$_2$)$_6$OH is due to the perturbation of the C-H stretching modes in the CH$_2$ group adjacent to the OH group (for further discussion, see ref 17). The spectra are shown stacked. The same scale of absorbance applies to all.

Figure 6. Competitive adsorption of HS-(CH$_2$)$_{11}$OH and HS-(EG)$_6$OH onto gold from solution in ethanol: (top) ellipsometric thickness ($d$); (bottom) advancing (●) and receding (○) contact angles of water as a function of the relative concentration of the thiols in solution. The total concentration of thiol groups in deoxygenated, absolute ethanolic solution was 1 mM. SAMs were prepared by exposing the gold surface to the solution of thiols for 24 h at room temperature. The error in the contact angles is within the range of the points drawn. The caption to Figure 6 summarizes experimental parameters.

Figure 7. Competitive adsorption of HS-(CH$_2$)$_{11}$OH and HS-(EG)$_6$OH onto gold from solution in benzene: (top) ellipsometric thickness ($d$); (bottom) advancing (●) and receding (○) contact angles of water as a function of the relative concentration of the thiols in solution. The total concentration of thiol groups in deoxygenated, absolute benzanc solution was 1 mM. SAMs were prepared by exposing the gold surface to the solution of thiols for 24 h at room temperature. The error in the contact angles is within the range of the points drawn. The caption to Figure 6 summarizes experimental parameters.

Mixed Monolayers. We prepared monolayers containing mixtures of two thiolates from ethanolic solutions containing mixtures of the two thiols. The mole fractions of the two adsorbates were varied while the total concentration of thiol in solution was kept constant at 1 mM (Figures 6–9). This strategy has been shown previously to be a useful method of identifying the ratio of components in solution ($R$) that leads to a mixture of these components in the SAMs derived from them.29,30

On plots of wettability ($cos \theta$) and thickness ($d$) as a function of $R$ (Figures 6–9), we indicate the midpoints for the changes in thickness and wettability from one extreme of the mixed monolayer to the other. We denote the value of $R$ for the midpoint of the change in thickness as $R_{1/2}(d)$ and the value of $R$ for the midpoint of the change in wettability as $R_{1/2}(cos \theta)$. These two parameters provide useful points of calibration for discussing mixed monolayers.

SAMs Containing HS-(CH$_2$)$_{11}$OH and HS-(EG)$_6$OH. The ellipsometric thicknesses of the monolayers formed by adsorption from ethanol decreased smoothly from 28 Å for pure HS-(CH$_2$)$_{11}$OH to 12 Å for pure HS-(EG)$_6$OH.
From the text:

- The series of monolayers formed from HS-11-(EG)6OH and HS-11-CH3 by adsorption from benzene does not show as large a difference between $R_{172}(d)$ and $R_{172}(\cos \theta)$ as that from ethanol.
- The fact that $\cos \theta$ is significantly different for monolayers formed by adsorption from these different solvents at the same values of $R$ suggests that hydrogen bonding of the oligo(ethylene glycol) chains to ethanol reduces their tendency to form SAMs.
changed relatively little over this region. There was little difference of proteins on three surfaces: Au-S-11-CH₃, Au-S-11-OH, and did not significantly affect the wettability of the surface. The observation suggests that microreconstruction did not occur, or heterogeneous monolayers was small for each system (Table I). This hysteresis of the surface, roughness of the surface, and the extent of microreconstruction of the surface under the drop. The hysteresis magnitude of the hysteresis was similar to that observed for pure HS-11-(EG)₆OH to 20 Å for pure HS-11-(EG)₆OH in the region centered at R = 0.4 (Figure 9). As expected, cos θ changed relatively little over this region. There was little difference in the values of R₁/₂(d) and R₁/₂(cos θ).

Hysteresis in Contact Angle. At least three factors contribute to hysteresis at nonreacting solid–liquid interfaces: heterogeneity of the surface, roughness of the surface, and the extent of microreconstruction of the surface under the drop. ¹³ The hysteresis (12–14°) in the measured values of the contact angle for homogeneous monolayers was small for each system (Table I). This observation suggests that microreconstruction did not occur, or did not significantly affect the wettability of the surface. The magnitude of the hysteresis was similar to that observed for well-ordered SAMs of alkanethiolates on gold. ¹⁵ In systems of mixed monolayers containing hydroxyl-terminated thiols (HS-11-OH) vs HS-11-(EG)₆OH and HS-11-(EG)₃OH vs HS-11-(EG)₆OH, the change in hysteresis from one extreme to another was smooth and nearly linear (Figure 11).

Adsorption of Proteins to SAMs. We examined the adsorption of proteins on three surfaces: Au-S-11-CH₃, Au-S-11-OH, and Au-S-11-(EG)₆OH. We exposed slides covered with SAMs to aqueous solutions of phosphate buffer (pH 7.5) containing a single protein (1 mg/mL) for 1 h at 25 °C. The apparent thickness of SAMs prepared from solutions of HS-11-CH₃ showed experimentally significant increases in thickness of >20 Å following exposure to avidin, hemoglobin, or pyruvate kinase. The apparent thickness of SAMs formed from HS-11-OH or HS-11-(EG)₆OH did not increase significantly following exposure to the same proteins, nor did the apparent thickness of SAMs formed from HS-11-(EG)₆OH increase after exposure to a 5% solution (pH 7.8) of adult chicken whole blood in Alsever solution. ¹² Table II gives representative data for the adsorption of avidin onto SAMs. There is more scatter in the data for SAMs of HS-11-OH than for HS-11-(EG)₆OH. This observation may reflect the different structures of the monolayers. SAMs formed from HS-11-OH expose only a single layer of hydroxyl groups to solution and, with regard to adsorption of proteins, may be more sensitive to defects that expose underlying methylene groups than are SAMs formed from HS-11-(EG)₆OH. The latter SAMs have a thicker outer hydrophilic layer than the former.

Discussion

Spontaneous self-assembly of functionalized alkanethiols on gold provides a route to surfaces presenting oligo(ethylene glycol) moieties at the solid–water interface. How well-organized are these SAMs?

Three types of evidence combine to suggest that these structures are monolayers—probably with the same density of adsorbed thiolate groups on the gold surface as with SAMs of n-alkanethiols—without substantial disorder in the oligo(ethylene glycol) part of the monolayer. We have neither a direct measure of the


(32) Alsever's solution is a solution of sodium citrate (40 mM), NaCl (70 mM), and dextrose (110 mM) in distilled water.
order in the (CH₃)₄ portion of these SAMs nor a valid means of comparing them with SAMs derived from structurally simpler precursors. In fact, we cannot presently define “order” quantitatively: We have no well-defined metric for “order,” and relating the relevant observable physical and spectroscopic parameters—thickness, wettability, and IR spectra—to order is presently a qualitative process based on comparisons with better defined model systems.²⁹,³⁰

The ellipsometric thicknesses of the SAMs containing S-11-(EG)₆OH moieties are compatible with complete coverage of the gold surface by these thiolates. The measured thicknesses are systematically less than those expected if the conformations of the (EG)₆ moieties in the monolayers were strictly analogous to that of an n-alkyl moiety: all-trans with a cant angle of 30°. The densities of simple derivatives of ethylene glycol as liquids are higher than those of homologous alkanes by ~20% (presumably in part because the molar volume of an ether oxygen is less than that of a methylene group), and the (EG)₆OH derivatives may be able to condense into a smaller molar volume than corresponding derivatives of -(CH₂)₆OH.³³ This difference may be even more pronounced if hydrogen bonding between the terminal hydroxyl group and ether oxygen atoms is important. The differences in densities between derivatives of ethylene glycol and alkanes is compatible with the ~15% decrease in thickness of the OCH₂CH₂ portion of the SAM, relative to the thickness expected for a trans-extended structure.

In summary, the ellipsometric data are compatible with, but do not demand, a model for SAMs of S-11-(EG)₆OH in which the adsorbed sulfur atoms have the same surface density as those in homologous SAMs of composition S(CH₂)₁₁(CH₃)OH, but in which the lower molar volumes of the (EG)₆ groups, relative to those of the (CH₂)₆OH groups, permit ~15% condensation in volume of the oxygen-containing portion of the monolayer when it is dry and penetration of this part of the monolayer by water when it is wet.

PIERS has been extraordinarily useful in defining the conformations of (CH₂)₄ units in SAMs.³³⁻¹³ Its utility, is, unfortunately, limited for the SAMs of interest here because the CH₂ groups of the EG moieties provide broad, intense absorption. These latter absorptions are themselves not easily interpretable.³⁵

The wettability of the SAMs containing S-11-(EG)₆OH groups is interpretable qualitatively in terms of a disordered monolayer-water interface. These monolayers are substantially more hydrophobic than monolayers derived from molecules with composition HS(CH₂)₁₁OH. The most plausible explanation for this difference is that the latter SAMs are the more highly ordered and present a uniform array of CH₃OH groups at the solid-water interface, while the SAMs terminated with (EG)₆OH groups present a mixture of -CH₃OH and the more hydrophilic -CH₂OCH₂OH groups. We cannot justify more detailed interpretation of the wettability of SAMs derived from HS-11-(EG)₆OH beyond that attributing disorder to the (EG)₆OH group other than noting that the wettability is similar for m = 3⁻⁷ and that if the suggestion of disorder in these systems is correct, they are probably swollen when in contact with water.

Two additional features of these monolayers provide information about their structure. The first observation is that comparison of the values of R₂θ(d) (Figures 6-9) establishes that it is favorable for the shorter alkanethiols to adsorb on the gold relative to HS-11-(EG)₆OH. In contrast, for unfunctionalized alkanethiols and for HS(CH₂)₁₁OH adsorption of the longer chain species is favored.³³ This result implies that it is relatively difficult to transfer the -(EG)₆OH moiety from the ethanol solution to the microenvironment of the SAM. The fact that it is more favorable to adsorb HS-11-(EG)₆OH onto gold from solutions of benzene rather than of ethanol suggests this difficulty reflects the loss of hydrogen bonding or conformational entropy in the SAM.

The second observation concerns the substantial difference in the values of R₂θ(cos θ) and R₂θ(d) of the mixed monolayer of S-11-CH₃ and S-11-(EG)₆OH prepared by adsorption from ethanol solution (Figure 6) (but not from benzene, Figure 7). A small extent of incorporation of the EG-containing component onto the monolayer (~10%) produces a large change (50%) in the wettability of the monolayer. Thus, a single (EG)₆OH moiety appears to be able to prevent several—perhaps 3—surface methyl (or CH₃OH, Figure 8) groups in its vicinity from interacting with water in a way that influences contact angle.³⁵,³⁶

The qualitative picture of the structure of these SAMs that emerges from this study is one in which the SAMs derived from pure derivatives of HS-11-(EG)₆OH probably consist of two-layer structures—a CH₃₁₁ layer and a -(EG)₆OH layer. Whether the -(CH₂)₁₁ is as ordered as corresponding layers in simpler derivatives is not defined by this work. The outer (EG)₆ layer is probably disordered when in contact with water.

In a preliminary survey, we found that proteins adsorbed to hydrophobic SAMs that were formed from HS-11-CH₃ but adsorbed significantly more weakly to relatively hydrophilic surfaces that were formed from HS-11-CH₃ or HS-11-(EG)₆OH. We emphasize that the term “protein adsorption” in the context of this paper is interpretable only with respect to the specific experimental protocol used; we detected only adsorption strong enough to survive the procedure for washing. Although these experiments of protein adsorption addressed an experimental system of minimal complexity, they achieved one goal of this work: to demonstrate the practicality of using SAMs prepared by adsorption of thiols on gold as model substrates for studying the adsorption of proteins onto organic surfaces. Since this class of SAMs provides the most ordered, best understood, and most easily controlled surfaces now available in organic chemistry, the success of these first experiments demonstrates the practicality of this approach and indicates a route toward more realistic studies with more complex systems.

**Experimental Section**

**Materials.** Absolute ethanol (U.S. Industrials Co.) was purified with either argon or nitrogen for 1 h before use as a solvent for the preparation of SAMs. Deionized water was distilled from glass in a Corning Ag₁b still.

1-Dodecanethiol (Aldrich, 98%), 11-bromo-1-undecene (Pfaltz and Bauer), tri(ethylene glycol) (Aldrich, 98%), tetra(ethylene glycol) (Fluka, >97%), penta(ethylene glycol) (Lancaster, 99%), hexa(ethylene glycol) (Aldrich, 98%), hept(ethylene glycol) (Aldrich, 97%), and trishydroxymethylaminomethane (Fluka, 97%) were used as received. 11-Mercapto-1-undecanol was available from previous studies.¹²

¹H NMR and ¹³C spectra were obtained at 300 or 250 MHz and were referenced to chloroform.

**Preparation and Handling of Gold Substrates.** Gold substrates were prepared by electron-beam evaporation of ~200 A of high-purity gold (99.999%) onto 100-mm single-crystal silicon wafers that had been precoated with chromium to improve adhesion (50-100 A of Cr followed by 2000 A of Au). The gold-coated wafers were stored in propylene oxide wafer holders (Fluoroware) and used as soon as possible after being exposed to the atmosphere. Before use, the gold-coated wafers were cut into pieces ~1 cm x 3 cm with a diamond-tipped stylus, rinsed with ethanol, and blown dry with a stream of nitrogen. Glassware was thoroughly cleaned, rinsed with copious amounts of distilled water, and dried.

(33) The densities (g cm⁻³) of simple oligo(ethylene glycol) compounds are higher than those of alkanes: CH₃OH, CH₁₂OH, 0.965; HOCH₂CH₂OH, 0.930; CH₂OCH₂OCH₂CH₂OH, 0.937; HOCH₂CH₂OCH₂OCH₂CH₂OH, 0.999; CH₃CH₂OCH₂OCH₂OCH₂OCH₂CH₃, 0.909; CH₃C₂H₄OCH₂OCH₂OCH₂OCH₂OCH₂OCH₂CH₃, 0.855; n-C₆H₆O, 0.659; n-C₂H₄O, 0.727.

(34) Preparation and analysis of deuterated compounds (e.g., HS-11-OCD₂CD₂O) could simplify the interpretation of the IR spectra.


(36) We are examining this same phenomenon with pendant oligosaccharide chains. These chains are more hydrophobic, but also larger and more rigid than the oligo(ethylene glycol) chains. A comparison of oligo-saccharide- and oligo(ethylene glycol)-containing systems should help to disentangle contributions to the shielding of surfaces of SAMs on gold.
then soaked in freshly prepared "piranha" solution (7:3 v/v mixture of concentrated H2SO4 and 30% aqueous H2O2) for 1 h, followed by exhausative rinsing with distilled water, a final rinsing with absolute ethanol, and drying in an oven. (Caution: "piranha" solution reacts violently with many organic materials and should be handled with extreme care.) Solutions used in the preparation of SAMs containing two thiols were prepared in glass weighing bottles by diluting 5 mM stock solutions. The accuracy of the concentrations of the stock solutions (±3%) was limited by the analytical balance used. An Eppendorf micropipet was used to transfer solutions (concluding an error of ±5% in the final concentra-
tion). The total concentration of thiol in the solution was 1 mM. Gold slides were washed with ethanol, blown dry with a stream of nitrogen, and immersed in freshly prepared solutions overnight at room tempera-
ture.

Contact Angles. Contact angles were determined at ambient labora-
tory temperatures (17-22 °C) with a Ramé-Hart Model 100 contact angle goniometer. Probe liquids were dispensed from a Matrix Tech-
ologies Micro-electrapipette. Measurement of contact angles is de-
scribed elsewhere.24 Reported values are the average of at least five measurements, taken at different locations on the surface.

Ellipsometry. Ellipsometric measurements were made with a Rudolf Research Type 43603-2000 thin-film ellipsometer with a wavelength of 6328 Å (He-Ne laser) and an incident angle of 70°. All spectra were referenced to Au(4f7/2) at 84.00 eV. The diam-
eter of the spot size for all spectra was 1000 pm. Spectra were fitted with

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X-ray Photoelectron Spectroscopy (XPS). XPS spectra were obtained on an SSX-100 spectrometer (Surface Science Instruments) equipped with an Al Kα source, quartz monochromator, concentric hemispherical analyzer in transmission mode, and a microchannel plate detector. The take-off angle was 35°, and the operating pressure was approximately 5 × 10−10 Torr. All spectra were referenced to Au(4f7/2) at 84.00 eV. The diam-
eter of the spot size for all spectra was 1000 pm. Spectra were fitted with an 80% Gaussian/20% Lorentzian function with the Surface Science Instruments software.

Syntheses of HS-(CH2)n-OH, Oligo(ethylene glycol). Undec-1-11-
yl(ethylene glycol) (1). A mixture of 0.34 mL of 50% aqueous sodium
hydroxide (4.3 mmol) and 3.2 g of tri(ethylene glycol) (21 mmol) was

1-Mercaptoundec-11-yltetra(ethylene glycol) (1). Reaction of 10 equiv of tris(ethylene glycol) (21 mmol) was

1-Mercaptoundec-1-1-yl-hexa(ethylene glycol) (9). General Syntheses of (1-Mercaptoundec-11-yl) oligo-

1-Mercaptoundec-11-yl-hepta(ethylene glycol) (10). 1-Mercaptoundec-11-yl-hepta(ethylene glycol) (10).
phosphate buffer (pH 7.5) for 1 h at 25 °C. Slides then were removed, washed with 10 mL of water, mounted on the ellipsometer, and allowed to dry before their thickness was measured. At least three measurements were taken on each slide and averaged; the data reported in Table II represent the average increase in thickness of five slides.

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