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Molecular-Level Control over Surface Order in Self-Assembled Monolayer Films of Thiols on Gold

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Long-chain ω-hydroxyalkanethiols [$HS(CH_2)_nOH$] coordinate to gold surfaces through the sulfur atom and produce ordered, hydrophilic monolayers in which the hydroxyl groups are exposed at the outer surface. Coadsorption of two ω-hydroxyalkanethiols of different chain lengths *n* resulted in the formation of a monolayer having a disordered surface region that was markedly less hydrophilic than the homogeneous, hydroxylic surface formed from either pure compound. By controlling the composition of the monolayer, it was also possible to control simultaneously the degree of order in the surface and its hydrophilicity. In the monolayers containing a mixture of alkanethiol components, these components apparently did not phase-segregate into macroscopic islands, but were dispersed on a molecular scale.

LONG-CHAIN ALKANETHIOLS ADSORB spontaneously from solution onto clean gold surfaces and form monolayer films (*1, 2*). These films are densely packed and highly ordered both in the plane of the monolayer and perpendicular to it (*3, 4*); the thiol coordinates to the gold surface, and the polymethylene chains pack in an all-trans conformation tilted slightly from the normal to the surface. Although gold interacts strongly with sulfur, phosphorus, and other "soft" ligands, it is inert toward most "hard" organic functionalities containing only first-row elements (*5*). This selectivity for sulfur allows us to prepare oriented organic monolayer films containing many functional groups of chemical and biological interest and to exercise a high degree of control over the structure of these films. In particular, by using adsorbates having the structure $HS(CH_2)_nX$, we can prepare monolayers presenting a more or less well-ordered array of the group X at the monolayer–air interface. If the polymethylene chain of $HS(CH_2)_nX$ is at least ten carbon atoms long, the surface properties depend primarily on the tail group X, are independent of the chain length, and are influenced only indirectly by the sulfur–gold interface. These terminally functionalized films are versatile and convenient systems with which to study the physical-organic chemistry of interfaces. A central objective of our work with these monolayer films is to discover the relations between molecular-scale structure and macroscopic physical properties of interfaces—wettability, adhesion strength, coefficient of friction—that depend strongly on short-range intermolecular forces (*6*).

We have examined the wettability by water of monolayers composed of $HS(CH_2)_{11}OH$ (abbreviated as $HSC_{11}OH$), $HS(CH_2)_{19}OH$ ($HSC_{19}OH$), and mixtures of these two compounds. Figure 1 illustrates the theory on which this group of experiments rests. If the pure compounds form well-ordered monolayers (Fig. 1, A and C), these monolayers should present a dense, hydrophilic, wettable, two-dimensional array of hydroxyl groups at the monolayer–water interface; if the monolayers are disordered, a more hydrophobic, less wettable mixture of hydroxyl and methylene groups will be exposed (Fig. 1D). In the event that monolayers of the pure compounds are highly ordered, there are two plausible structures for monolayers containing mixtures of the two components. If the components are dispersed on a molecular scale (Fig. 1B), an interesting, two-layer structure

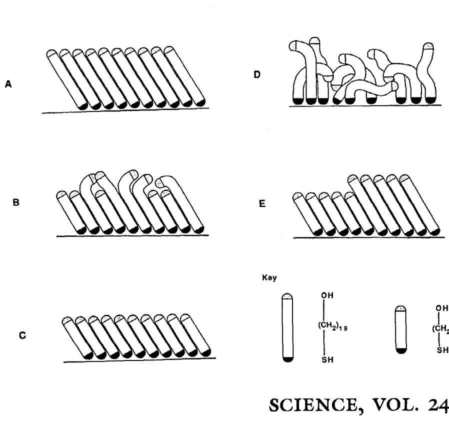

Fig. 1. Stylized illustrations of monolayer structures. Proposed structures of (**A**) pure monolayer of $HS(CH_2)_{19}OH$; (**B**) monolayer composed of 50% $HS(CH_2)_{19}OH$ and 50% $HS(CH_2)_{11}OH$; and (**C**) pure monolayer of $HS(CH_2)_{11}OH$. Structures we believe do not occur in the systems studied here are: (**D**) disordered monolayer and (**E**) monolayer containing a mixture of components and showing phase separation into islands.

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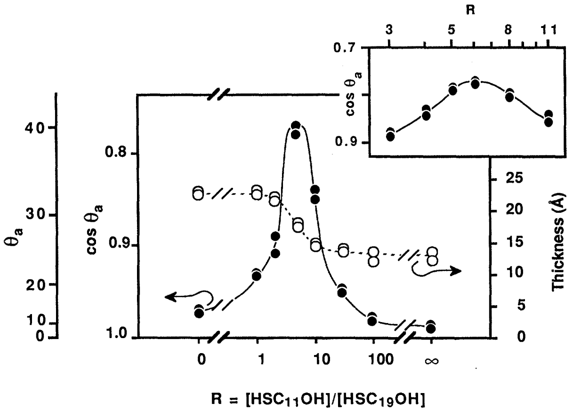

Fig. 2. Properties of mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{19}OH$ as a function of solution composition: ellipsometric thickness (○) and cosine of the advancing contact angle of water (●). Inset: expanded plot of contact angles in the region of the peak maximum.

could result in which a disordered surface region is isolated from the gold by a deeper layer of densely packed, ordered polymethylene chains. Since this disorder would expose methylene groups at the monolayer–water interface, the mixed monolayers would be more hydrophobic than monolayers of the pure compounds. Alternatively, the two components could separate into discrete, macroscopic islands (Fig. 1E), each of which would present a hydrophilic array of hydroxyl groups at the surface. We expect the wettability of an "island" monolayer containing two components to be only marginally different from that of an ordered, homogeneous monolayer containing only one pure component, so long as the island size is relatively large ($\geq$10 nm). An "island" structure would present only a small fraction of the area of the monolayer–water interface as methylene groups, and would thus be similar in its hydrophilicity to a single-component monolayer. Thus examination of the wettability of monolayers of $HSC_{11}OH$, $HSC_{19}OH$, and mixtures of the two compounds addresses a number of questions about the structure of these monolayer films: (i) the order in monolayers of pure compounds; (ii) the relative order in pure and mixed monolayers; and (iii) the extent of phase separation in the mixed monolayers.

We prepared monolayers by immersing freshly evaporated, gold films in solutions of the thiols in degassed ethanol for 12 hours at room temperature (*7*). The total concentration of thiol was 1 m*M*. We measured the ellipsometric constants of the gold films before and after adsorption of the monolayer, computed the thickness of the monolayer by standard procedures (*8*), and determined advancing contact angles θ_a with water by the sessile drop technique (*2*). Ellipsometric thicknesses and contact angles are shown in Fig. 2, plotted against the ratio *R* of $HSC_{11}OH$ to $HSC_{19}OH$ in solution (*9*).

The ellipsometric thickness of the monolayers decreased in a smooth step from 23 Å for pure $HSC_{19}OH$ to 13 Å for pure $HSC_{11}OH$ in the region between $R = 1$ and $R = 30$. The change in thickness by 10 Å is consistent with a difference in chain length of eight methylene units, if we assume a model in which the chains are fully trans-extended and tilted 20° to 30° from the normal to the gold surface, as inferred from infrared spectra (*3*). Both of the pure component surfaces showed contact angles with water near 0° (<15° for $HSC_{19}OH$, <10° for $HSC_{11}OH$)—observations that are consistent with our model of well-ordered monolayers exposing only the polar hydroxyl group at the film–water interface (*10*). Polarized external reflectance infrared spectra of a long-chain, alcohol-terminated thiol $[HS(CH_2)_{16}OH]$ adsorbed on gold showed narrow (12 cm^{-1} full width at half-maximum) CH_2 symmetric and asymmetric vibrations at 2851 cm^{-1} and 2919 cm^{-1}, frequencies that are indicative of crystalline packing of polymethylene chains (*11*).

The compositions of the monolayers and the solutions from which they were adsorbed were not the same. We presume that the midpoint in the thickness of the monolayers corresponds to a film containing equal concentrations of $HSC_{11}OH$ and $HSC_{19}OH$; this point occurs at $R = 6$, that is, when $[HSC_{11}OH]_{soln} = 6[HSC_{19}OH]_{soln}$. The observation that the concentration of $HSC_{11}OH$ in solution is higher than in the monolayer is not surprising; the longer chain compound forms a monolayer that is intrinsically more stable than the monolayer formed from the shorter chain, since it has a larger molecular surface to participate in energetically favorable van der Waals interactions with adjacent chains. We have observed substantial differences in composition between solutions and their derived monolayers for many two-component systems (*2*).

The point of central interest in Fig. 2 is the pronounced maximum in the hydrophobicity of the monolayer films at a value of *R* corresponding to a monolayer with the greatest degree of mixing and, we believe, the greatest extent of disorder at the monolayer–water interface (Fig. 1B) (*12*). This maximum is important because it provides a clear example of the successful correlation of molecular-scale structure with a macroscopic physical property, because it supports the inference of high order in the pure single-component monolayer systems, and because it argues against phase separation (*13*).

Self-assembled monolayers on gold of compounds of the structure $HS(CH_2)_{n>10}X$ are exceptionally useful systems with which to explore the physical-organic chemistry and materials science of monolayers and thin films; they are easily prepared and have high structural order. A wide variety of groups X are compatible with the system, which allows design of the solid–liquid interface on an angstrom scale. These results illustrate the degree of control that can be achieved over wettability, a representative macroscopic materials property, by rational variation in the structures and proportions of the components of these self-assembled monolayers, and emphasizes the importance of short-range (<5 Å) structure in determining wettability.

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13. The distribution of molecules in the monolayers containing a mixture of the two alkanethiols, near $R = 6$, is not necessarily entirely random, but any clusters of molecules of one component must be small.
14. Supported in part by the Office of Naval Research and the Defense Advanced Research Projects Agency, and by the National Science Foundation (CHE-85-08702). Infrared spectra were taken by R. Nuzzo (AT&T Bell Laboratories), whom we thank for assistance and many useful discussions.

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