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Wet Chemical Approaches to the Characterization of Organic Surfaces: Self-Assembled Monolayers, Wetting, and the Physical–Organic Chemistry of the Solid–Liquid Interface

George M. Whitesides* and Paul E. Laibinis

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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Physical–organic methods are useful in studying the surface chemistry of organic solids. These methods complement the usual spectroscopic approaches in characterizing the solid–liquid interface. This paper focuses on two topics drawn from physical–organic surface chemistry: preparations of ordered organic surfaces by self-assembly of organic molecules on inorganic supports and uses of wetting in characterizing these and other surfaces. Monolayer films prepared by chemisorption of alkanethiols and dialkyl disulfides on gold are the best characterized and most widely studied of the self-assembled systems. Wetting is uniquely valuable in characterizing surfaces for its combination of high surface sensitivity and applicability to disordered surfaces.

Introduction

The interfacial chemistry of organic materials is an important but underdeveloped subfield of surface science.[1] The relevance of this subject ranges from technology (adhesion to polymers,[2] biocompatible materials,[3] fiber–matrix interactions in composites[4]) to basic science (wetting of solids by liquids,[5–9] cell–surface biochemistry[10]). Organic surface science is less developed than corresponding subfields focused on inorganic surfaces (metals and metal oxides) for several reasons. First, organic surfaces are usually less ordered, less stable thermally, and less amenable to characterization by scattering and diffraction techniques than are crystalline inorganic surfaces. Second, many of the advances in surface science have relied on instrumental techniques derived from surface physics.[11] Because organic materials may be sensitive to radiation damage, and because they and their damage products are often volatile, techniques requiring high vacuum are often not applicable to them. Finally,

(1) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, I.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932–950.

(2) Zisman, W. A. In *Handbook of Adhesives*, 2nd ed.; Skeist, I., Ed.; Van Nostrand Reinhold: New York, 1977; Chapter 3. Schonhorn, H. In *Polymer Surfaces*; Clark, D. T., Feast, W. J., Eds.; Wiley: Chichester, 1978; Chapter 10. Leger, L. *Ann. Chim. (Paris)* **1987**, *12*, 175–184.

(3) Ratner, B. D. In *Biomaterials: Interfacial Phenomena and Applications*; Cooper, S. L., Peppas, N. A., Eds.; Advances in Chemistry 199; American Chemical Society: Washington, DC, 1982; Chapter 2, pp 9–23. *Surfaces and Interfacial Aspects of Biomedical Polymers*; Andrade, J. D., Ed.; Plenum: New York, 1985. Andrade, J. D.; Hlady, V. *Adv. Polym. Sci.* **1986**, *79*, 1–63. Durrani, A. A.; Chapman, D. In *Polymer Surfaces and Interfaces*; Feast, W. J., Munro, H. S., Eds.; Wiley: Chichester, 1987; Chapter 10. Lundstrom, I.; Ivarsson, B.; Jonsson, U.; Elwing, H. In *Polymer Surfaces and Interfaces*; Feast, W. J., Munro, H. S., Eds.; Wiley: Chichester, 1987; Chapter 11.

(4) Delannay, F.; Froyen, L.; Deruyttere, A. *J. Mater. Sci.* **1987**, *22*, 1–16. Schultz, J.; Lavielle, L. *ACS Symp. Ser.* **1989**, *391*, 185–202.

(5) Young, T. *Philos. Trans. R. Soc. (London)* **1805**, *95*, 65–87.

(6) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988–994. Wenzel, R. N. *J. Phys. Chem.* **1949**, *53*, 1466–1467. Bracke, M.; DeBisschop, F.; Joos, P. *Prog. Colloid Polym. Sci.* **1988**, *76*, 251–259.

(7) Neumann, A. W. *Adv. Colloid Interface Sci.* **1974**, *4*, 105–191. Adamson, A. W. In *Physical Chemistry of Surfaces*, 4th ed.; Wiley: New York; 1982. Joanny, J. F.; de Gennes, P.-G. *J. Chem. Phys.* **1984**, *81*, 552–562. de Gennes, P.-G. *Rev. Mod. Phys.* **1985**, *57*, 827–863. Schwartz, L. W.; Garoff, S. *Langmuir* **1985**, *1*, 219–230. Schwartz, L. W.; Garoff, S. *J. Colloid Interface Sci.* **1985**, *106*, 422–437. Pomeau, Y.; Vannimenus, J. *J. Colloid Interface Sci.* **1985**, *104*, 477–488.

(8) Neogi, P.; Miller, C. A. *J. Colloid Interface Sci.* **1983**, *92*, 338–49.

(9) Joanny, J. F. *J. Chem. Phys., Phys.-Chem. Biol.* **1987**, *84*, 197–8. Neogi, P.; Miller, C. A. *J. Colloid Interface Sci.* **1982**, *86*, 525–38. Lopez, J.; Miller, C. A.; Rudenstein, F. *J. Colloid Interface Sci.* **1976**, *56*, 460–8.

(10) Albersheim, P.; Anderson-Prouty, A. J. *Ann. Rev. Plant Physiol.* **1975**, *26*, 31–52. Denburg, J. L. *Adv. Comp. Physiol. Biochem.* **1978**, *7*, 105–226.

(11) Somorjai, G. A.; Bent, B. E. *Prog. Colloid Polym. Sci.* **1985**, *70*, 38–56. Feldman, L. C.; Mayer, J. W. In *Fundamentals of Surface and Thin Film Analysis*; Elsevier Science: New York, 1986.

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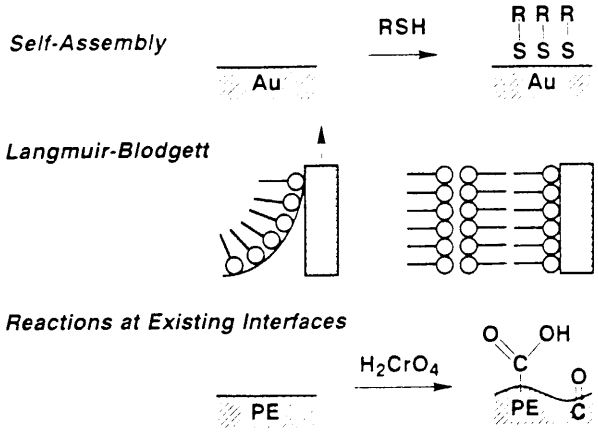
Scheme I. Methods for Preparing Functionalized Organic Surfaces: Self-Assembled Monolayers, Langmuir–Blodgett Films, and Surface-Functionalized Polymers



the questions of interest in organic surface chemistry—the type, distribution, and reactivity of functional groups in the interface and the character of solvent-swollen surface gel layers—are usually more qualitative than those that have been the focus of traditioinal surface physical chemistry. Accordingly, the community of scientists concerned with the surfaces of stable, well-ordered, inorganic solids has been less attracted to the area of unstable, disordered organic surfaces.

We have been developing physical–organic approaches to the study of organic surfaces.[12,13] Physical–organic chemistry is an area based on analogy rather than on absolute numerical measures. Thus, for example, comparisons of values of pK_a for acidic functional groups in solution and on surfaces can reveal the character of the surface. An absolute measure of a surface property can, of course, also be useful, but it is more often a comparison of that property with a related property of some other, better defined system, usually in solution, that is most efficient in yielding results.

A strategy for exploring organic surface chemistry based on the physical–organic approach inevitably involves two areas of research that have been relatively uncommon as primary foci in modern surface science. First, since much of physical–organic chemistry is based on studies in solution, the solid–liquid interface rather than the solid–vacuum interface is of primary importance. Second, reactivities (or, more precisely, *relative* reactivities) are invaluable in physical–organic chemistry as probes for characterizing structure and environment in solution; we believe that reactivity-based approaches also provide valuable information concerning interfaces.

Three types of systems have been the principal subjects of research in organic surface chemistry (Scheme I): self-assembled monolayers (SAMs) derived from alkyltrichlorosilanes on silicon/silicon dioxide[14-16] and from organosulfur compounds chemisorbed on gold[17-35] and other metals;[36] Langmuir–Blodgett mono- and multilayers;[37] and functionalized polymer surfaces.[38-48]

Our work has been concerned primarily with self-assembled monolayers on gold[23-35] and with the functionalization of the surfaces of low-density polyethylene films.[40-48] "Wet chemical" methods are indispensable in preparing and characterizing these systems. A wet chemical method of analysis—wetting—has also proved remarkably useful and sensitive in characterizing surface

(12) Bain, C. D.; Whitesides, G. M. *Angew. Chem. Int. Ed. Engl.* **1989**, *101*, 522–528. Whitesides, G. M.; Biebuyck, H. A. In *Molecular Recognition: Chemical and Biochemical Problems*; Roberts, S. M., Ed.; Special Publication No. 78; Royal Society of Chemistry: Cambridge, 1989; pp 270–285.

(13) Whitesides, G. M.; Ferguson, G. S. *Chemtracts* **1988**, *1*, 171–187.

(14) Sagiv, J. *Isr. J. Chem.* **1979**, *78*, 339–345, 346–353. Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92–98.

(15) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074–1087.

(16) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5852–5861. Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Wasserman, S. R.; Whitesides, G. M.; Axe, J. D. *Phys. Rev. B*, in press.

(17) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483. Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358–2368.

(18) Li, T. T.-T.; Weaver, M. *J. Am. Chem. Soc.* **1984**, *106*, 6107–6108. Li, T. T.-T.; Weaver, M. *J. Am. Chem. Soc.* **1984**, *106*, 1233–1239. Finklea, H. O.; Avery, S.; Lynch, M.; Furtsch, T. *Langmuir* **1987**, *3*, 409–413.

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

(20) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.*, in press.

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

(22) Chidsey, C. E. D.; Liu, G.-Y.; Rowntree, P.; Scoles, G. *J. Chem. Phys.* **1989**, *91*, 4421–4423.

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

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

(25) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897–5898. Laibinis, P. E.; Bain, C. D.; Nuzzo, R. G.; Whitesides, G. M. Unpublished results.

(26) Laibinis, P. E.; Janes, L. E.; Prime, K. L.; Nuzzo, R. G.; Whitesides, G. M. Unpublished results. Prime, K. L.; Laibinis, P. E.; Burbaum, B. W.; Nuzzo, R. G.; Whitesides, G. M. Unpublished results.

(27) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 6560–6561. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155–7164.

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

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

(30) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164–7175.

(31) Laibinis, P. E.; Nuzzo, R. G.; Whitesides, G. M. Unpublished results.

(32) Bain, C. D.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1989**, *5*, 723–727.

(33) Bain, C. D.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1370–1378.

(34) Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 1670–1673.

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

(36) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Nuzzo, R. G. Unpublished results.

(37) Gaines, G. L., Jr. *Insoluble Monolayers*; Interscience: New York, 1966. Roberts, G. G. *Adv. Phys.* **1985**, *34*, 475–512. Peterson, I. R. *J. Mol. Electron.* **1987**, *3*, 103–111. Vandevyver, M.; Barraud, A. *J. Mol. Electron.* **1988**, *4*, 207–221. Vandevyver, M. *Thin Solid Films* **1988**, *159*, 243–251. Bubeck, C. *Thin Solid Films* **1988**, *160*, 1–14. Agarwal, V. K. *Phys. Today* **1988**, *41*, 40–46.

(38) Akelah, A.; Sherrington, D. C. *Polymer* **1983**, *24*, 1369–1386. Akelah, A. *J. Chem. Technol. Biotechnol., Chem. Technol.* **1984**, *34A*, 263–286. Akelah, A. *J. Mater. Sci.* **1986**, *21*, 2977–3001.

(39) Brewis, D. M. *J. Mater. Sci.* **1968**, *3*, 262–265. Blais, P.; Carlsson, J.; Csullog, G. W.; Wiles, D. M. *J. Colloid Interface Sci.* **1974**, *47*, 636–649. Kato, K. *J. Appl. Polym. Sci.* **1974**, *18*, 3087–3094. Kato, K. *J. Appl. Polym. Sci.* **1977**, *21*, 2735–2743.

(40) Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4736–4745.

(41) Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4746–4756.

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

(43) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1986**, *2*, 266–281.

(44) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1987**, *3*, 62–76.

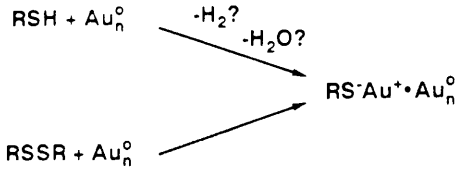
(45) Holmes-Farley, S. R.; Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* **1987**, *3*, 799–815.

(46) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921–937.

(47) Wilson, M. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 8718–8719.

(48) Wilson, M. D.; Ferguson, G. S.; Whitesides, G. M. *J. Am. Chem. Soc.*, in press. Wilson, M. D.; Ferguson, G. S.; Laibinis, P. E.; Whitesides, G. M. Unpublished results.

Scheme II. Gold(I) Alkyl Thiolates Are the Products of Reactions of both Alkanethiols and Dialkyl Disulfides with a Gold Surface



functionality[15,23-33,45-47] and structure[28-30,44,45] in these classes of materials. Traditional spectroscopic methods—especially XPS,[15,23-34,36,45] polarized infrared external reflectance spectroscopy (PIERS),[17,19,20,23,25-27,31,36] and optical ellipsometry[15-17,19,23-31]—are, of course, also highly useful.

An important motivation underlying these studies in organic surface science is to answer, for these materials, one of the fundamental questions of molecular-level structure of matter and its macroscopic physical properties. We have used organic materials in these studies for two reasons: organic materials are amenable to a wide range of variation in molecular-level structure; surfaces are accessible for characterization and study. We have used wettability as the physical property to be measured, because it is easily measured experimentally[49] and broadly relevant technologically.[1-4,50] One primary focus of our research can thus be reduced to a specific question: "How does the molecular-level structure of organic surfaces influence their wettability by water?"

We start this account with a brief description of methods used in preparation of self-assembled monolayers and surface-functionalized polymers. We continue with a qualitative discussion of the physical–organic chemistry of wetting and particularly of its use in measuring the depths of functional groups below the "surface" of an organic solid in contact with water. We close with an outline of experiments that extend these techniques for preparing homogeneous, self-assembled monolayers to systems combining self-assembly with microlithography to generate patterns *in* the plane of the monolayer.

Preparations and Substrates

Self-assembled monolayers prepared by chemisorption of alkanethiols or dialkyl disulfides on gold are easily obtained by exposing a clean gold surface for a few minutes at room temperature to a 0.1 mM solution of the organosulfur compound.[17,19,24] These systems are the best understood of the organic surfaces now being studied.[17,19-22,24,34,35] Surprisingly, understanding of the reactions involved in interaction of the sulfur with the gold is still incomplete (Scheme II). The organosulfur species formed from both alkanethiols and dialkyl disulfides at the gold(0) surface is a gold(I) thiolate (RS^-Au^+) adsorbed epitaxially on the gold(0) substrate.[22,32,35] In the case of dialkyl disulfides, this surface gold thiolate is undoubtedly formed by oxidative addition of the sulfur–sulfur bond to gold(0). Formation of a gold thiolate from a thiol requires loss of hydrogen, but whether this hydrogen is lost as H_2 or lost as water by reaction with traces of oxidants in the system is not known. In both cases, adsorption is fast but not diffusion-limited. The half-time for adsorption of both octadecanethiol and dioctadecyl disulfide is $\tau_{1/2} \simeq 1$ h from a 1 μM solution in ethanol and faster for more concentrated solutions.[24] The energy of the bond between the organic thiolate and the gold surface is high (approximately 40–45 kcal/mol): desorption of these organosulfur species from the surface is slow. Exchange of alkyl thiolates on the gold surface with thiols or disulfides present in solution is relatively slow (requiring hours to days to proceed to significant conversion). Under vacuum, the species that desorbs on heating is a dialkyl disulfide.[21]

It is unclear how close these systems are to thermodynamic equilibrium. Certain observations—for example, the absence of large-scale "islanding" of the components in a monolayer comprising a mixture of different organosulfur compounds[29-31]—strongly argues against widespread lateral mobility of the alkyl thiolate moieties and thus against a system at equilibrium. The preference observed for long-chain alkanethiols over short-chain ones in competitive adsorptions at gold surfaces[28-31] is what one would expect on the basis of thermodynamic considerations. Thus, the system shows clear evidence of kinetic control, but may, nonetheless, produce results that correlate with those expected for a system at equilibrium.

The structure of the monolayers is better understood than the mechanisms by which they form. In brief, a number of studies now indicate that long-chain alkanethiolates adsorbed on gold constitute monolayers that are at least quasi-crystalline.[19-22,35] The alkyl chains are largely or exclusively trans extended, with the axis of the chain tilted ~30° from the normal to the surface (Figure 1).[19-21] The sulfur atoms rest in threefold hollows of the gold(111) surface.[35] Computer simulations[51] suggest that the outermost ends of the chains show greater mobility than the inner parts and may have occasional gauche conformations; the inner parts appear to be effectively crystalline.

Surface Chemistry of Surface-Oxidized Polyethylene. "Polyethylene carboxylic acid" (PE–CO_2H) has been reviewed thoroughly.[13,52] This material is formed by brief treatment of commercial, low-density polyethylene film with chromic acid solution.[39,40] The predominant reactive functional groups at the surface of PE–CO_2H are carboxylic acids, although other carbonyl-containing moieties are also present.[40] Alcohols are not present in the oxidized interface in significant concentrations. Oxidation is accompanied by extensive etching of the surfaces if it is prolonged, and the surfaces are probably microscopically rough, even when the exposure to the chromic acid solution is short. The polar functionalities are distributed over an interfacial region 2–3 nm thick.[42] There are undoubtedly differences in the density and distribution of functional groups in crystalline and amorphous regions of the polymer.

Despite (or perhaps because of) the disorder in the structure of the functionalized interface of PE–CO_2H, this material and its derivatives[41,45-48] (obtained by the familiar reactions of organic synthetic chemistry) are particu-

(49) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513–538. Johnson, R. E.; Dettre, R. H. *J. Colloid Sci.* **1965**, *20*, 173–176. Neumann, A. W.; Good, R. J. In *Surface and Colloid Science*, Good, R. J., Stromberg, R. R., Eds.; Plenum: New York, 1979; Vol. 11, pp 31–91.

(50) Markgraf, D. A. *Treatment Required for Printing with Water-based Inks*; TAPPI Proc., 1987; p 333. Armstrong, J. A.; Whitesides, G. M. *Chem. Eng. News* 1986, *64* (Aug 11), 22–25; *Research Briefings 1986*; National Academy: Washington, DC, 1986; *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 4665–4748.

(51) Harris, J.; Rice, S. A. *J. Chem. Phys.* **1988**, *88*, 1298–1308. Bareman, J. P.; Cardini, G.; Klein, M. L. *Mater. Res. Soc. Symp. Proc.* **1989**, *141*, 411–418; *Phys. Rev. Lett.* **1988**, *60*, 2152–5; *Chem. Phys. Lett.* **1988**, *145*, 483–8. Northrop, S. H.; Curvin, M. S. *J. Phys. Chem.* **1985**, *89*, 4707–13.

(52) Ferguson, G. S.; Whitesides, G. M. In *Modern Approaches to Wettability: Theory and Applications*; Schroder, M., Loeb, G., Eds., Plenum: New York, in press.

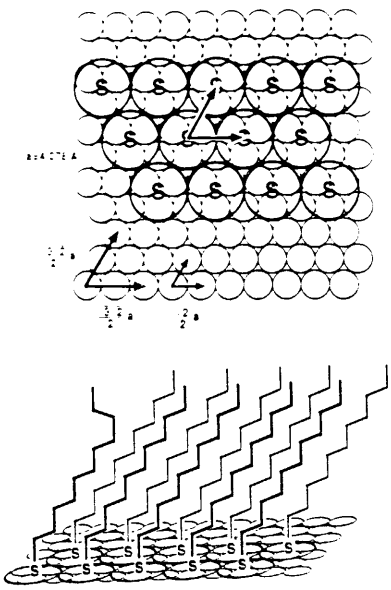


Figure 1. Schematic illustration of an alkyl thiolate monolayer on Au(111). The top figure, a top view, shows the inference from electron diffraction experiments (ref 35): the adsorbed thiolates are epitaxially located on the gold surface. The sulfur atoms are located in the threefold hollow sites. The circles surrounding the sulfur atoms are used to suggest the area parallel to the gold surface occupied by the alkyl chain. The bottom figure, a side view, shows the orientation of the alkyl chains inferred from polarized infrared external reflectance spectroscopy (PIERS) (ref 20). These alkyl chains exist largely in an ordered, trans, zigzag conformation canted at an angle of approximately 30° from the normal to the surface. The presence of gauche conformations in the alkyl chains cannot be ruled out.

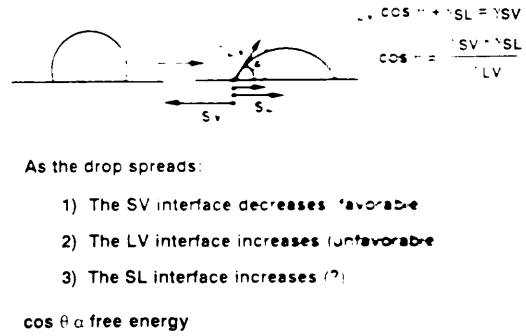


Figure 2. Schematic illustration of a spreading drop of liquid in contact with a solid surface, showing the relations between the relevant parameters: the contact angle, θ; the solid/vapor interfacial free energy, γ_{SV}; the liquid/vapor interfacial free energy, γ_{LV}; and the solid/liquid interfacial free energy, γ_{SL}. Young's equation describes the relationship between these parameters for a stationary drop at thermodynamic equilibrium.

larly useful substrates with which to explore property–structure relationships in organic surface chemistry. PE–CO_2H is readily available and easily manipulated. It shows complex phenomena such as surface reconstruction on heating[45,52] or mechanical deformation[53] that are not observed with SAMs on rigid substrates. Despite the obvious differences between PE–CO_2H (and its derivatives) and self-assembled monolayers of organic thiols on gold, results obtained with it correlate surprisingly closely with those obtained from the better defined but more difficulty obtainable SAMs.[26,48]

Physical-Organic Chemistry of Wetting

Wetting has been considered an archaic technique, capable of yielding little detailed information about surfaces. Measurement of a contact angle of a liquid on a solid surface typically yields a single number. The area of solid in contact with liquid ($\sim$1 mm^2) is large, and the contact angle averages contributions to solid–liquid and solid–vapor free energies from the smaller regions (10–100 Å^2) relevant to molecular-scale characterization of surfaces. The form of Young's equation[5] (Figure 2) is such that contact angles can be interpreted only in terms of differences and ratios of surface-free energies, rather than as a direct measure of γ_{SL} or γ_{SV}. Many features of the theoretical underpinnings of wetting remain unsatisfying, and the technique retains a strongly empirical character. For these reasons, the technique of contact angle measurement has been (correctly) considered to be an information-poor technique, at least relative to some of the surface spectroscopies (when they are applicable). In our hands, however, wetting has proved invaluable for probing the character of solid–liquid and solid–solid interfaces involving organic solids—an area of investigation in which surface spectroscopy has limited usefulness. The range of information obtained by contact angle measurements can be increased by measuring contact angles as a function of the pH of aqueous drops[15,23,33,42–46] ("contact angle titration"[42]), by using probe liquids other than water,[25,26,30,31] and by examining both advancing and retreating contact angles.[30,31] Like most techniques in physical–organic chemistry, measurement of contact angles relies heavily on comparisons of measurements in similar systems rather than on interpretation of absolute values obtained from only one system.

Figure 2 summarizes the essential features of a first-order analysis of contact angles. The thermodynamic analysis in this system is familiar: following application of a drop, the drop edge expands. This expansion increases the area of the liquid–vapor interface (always an energetically unfavorable process) and decreases the area of the solid–vapor interface (always a favorable process). The area of the solid–liquid interface also increases. In principle, the drop edge comes to rest when the changes in energies that accompany these changes in areas balance. The relationship describing this equilibrium situation is given by Young's equation.[5] This equation relates the cosine of the contact angle and a ratio of interfacial free energies. It assumes a system at thermodynamic equilibrium and a smooth, homogeneous, unreactive surface. We emphasize that, in using this approach, one should be aware of its limitations and approximations and note that for many systems in organic surface chemistry the hysteresis in contact angle—that is, the difference between the advancing and retreating contact angle—is far from zero. A large value in hysteresis is commonly taken to indicate a system not at equilibrium. Thus, we use contact angles because they are convenient, because they are very sensitive to details of interfacial structure at the angstrom scale (see below), and because they are applicable to the characterization of solid–liquid interfaces. We believe these measurements at least correlate with thermodynamically significant measures of surface and interfacial free energies.

In general, we follow Zisman and others in using cos θ_a, rather than θ_a, in our work, because cos θ is proportional to interfacial free energy; we use advancing rather than receding contact angles because the hysteresis in these systems is often very large, and θ_r may be zero even when θ_a is large.

Figure 3 summarizes data from measurements of con-

(53) Sung, N. H.; Lee, H. Y.; Yuan, P.; Sung, C. S. P. *Polym. Eng. Sci.* **1989**, *29*, 791–800.

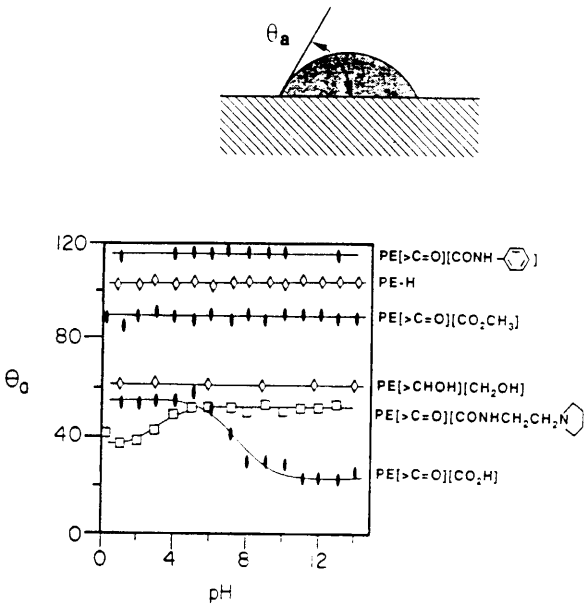


Figure 3. Change in the advancing contact angle of water on PE-CO_2H and derivatives as a function of the pH of the water. Data for unfunctionalized PE-H are included for reference.

tact angle on a number of derivatives of PE-CO_2H. These data[46] provide a useful introduction to the use of wetting in characterizing the interface between organic solids and water: they demonstrate several interesting phenomena and hint at the useful sensitivity of wetting to the depth of functional groups below the organic water interface. This figure plots the advancing contact angle of buffered water on a number of derivatives of PE-CO_2H as a function of the pH of this water. Unfunctionalized polyethylene is, as one would expect, hydrophobic (that is, the value of θ_a on it is large) and insensitive to the pH of the drop. In comparison, PE-CO_2H is less hydrophobic and shows a transition from a more hydrophobic state at low pH to a more hydrophilic state at high pH. It is clear that this transition reflects the conversion of PE-CO_2H groups to PE-CO_2^- groups as the drop becomes more basic. This system still defies detailed analysis because it exhibits large hysteresis and because it is unclear how to account for the reaction of carboxylic acid groups with hydroxide ion in analyzing the angle at which the spreading of the drop stops. The contact angle titration curves of tertiary amines also typically show inflections; those of many primary amines do not, for reasons that are complicated.[46] We note that the values of solution pH corresponding to the half-way points of these inflections are several pH units removed from the values of pK_a of the corresponding functional groups in homogeneous aqueous solution. A large part of this difference is probably attributable to the thermodynamic difficulty of creating a charged species in the relatively low dielectric constant region represented by a polyethylene-water interface,[43,46] but other factors may also contribute.

Perhaps the most interesting and unexpected observation in the data of Figure 3 is the high value of contact angle of PE-$CONHC_6H_5$.[47] This surface is very hydrophobic—even more hydrophobic than polyethylene itself. The amide group is itself very polar, and the presence of high densities of amide groups at the surface of PE-$CONHC_6H_5$ might have been expected to make the surface of this material hydrophilic. The fact that this surface is more *hydrophobic* than unfunctionalized polyethylene is probably a combination of two factors.

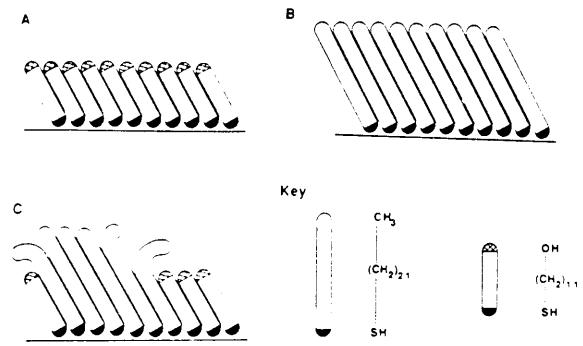


Figure 4. Schematic illustration of self-assembled monolayers on gold: (A) pure $HS(CH_2)_{11}OH$ yields a high-energy surface consisting of CH_2OH groups, (B) pure $HS(CH_2)_{21}CH_3$ yields a low-energy surface presenting CH_3 groups, and (C) mixture of the two thiols yields a complex, disordered interface.

First, the aromatic ring must effectively completely hide the underlying polar amide groups from contact with water. Second, the roughness of the surface[42] undoubtedly contributes to its apparent hydrophobicity.[6] The first observation—that a phenyl ring is sufficient to hide a polar amide group—suggests that a relatively small, nonpolar group can bury a polar one and that wettability must be sensitive to molecular-scale details of interfacial structure.

Although the thermodynamics and kinetics of spreading of water on chemically and morphologically heterogeneous organic surfaces are certainly still not understood,[7,8] it is clear that measurements of contact angle have a number of useful characteristics. First, contact angles are sensitive to the polarity of functional groups in the surface.[44-48] Second, they respond to the state of ionization of these groups and can thus be used to detect ionizable functionality.[44-47] Third, they are sensitive to local details of structure at the solid-liquid interface.[47,48] Characteristics of wetting that are now largely ignored—especially hysteresis and kinetics of spreading—have the potential to provide additional information, once their measurement is well controlled and their interpretation understood.

Self-Assembled Monolayers of Organic Thiols on Gold: Structure and Use in Studying the Depth Sensitivity of Wetting

Our most useful experiments[27-31] based on self-assembled monolayers have utilized so-called mixed monolayers: that is, monolayers prepared by exposing a gold substrate to a solution containing a mixture of two alkanethiols in concentrations chosen to give control over the relative concentrations of these species on the surface. Figures 4 and 5 illustrate the degree of control that can be exercised in building monolayers by using self-assembly. In this representative experiment,[28] we begin with two components: a long-chain alkanethiol terminating in a methyl group and a short-chain alkanethiol terminating in a hydroxyl group. We have prepared monolayers from solutions containing these two components over a range of values of the ratio $R = [HS(CH_2)_{10}CH_2OH]_{solution}/[HS(CH_2)_{21}CH_3]_{solution}$. Physical measurements of relevant properties of the resulting monolayers are summarized in Figure 5. Pure monolayers of the long-chain alkanethiol (Figure 4) form a thick, hydrophobic monolayer containing no oxygen by XPS spectroscopy; pure monolayers of the short, hydroxyl-terminated thiol form thinner monolayers, containing oxygen by XPS. The macroscopic property of the system—

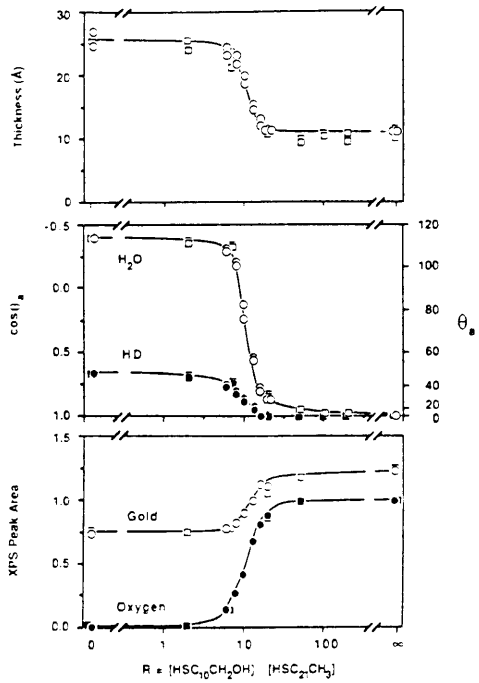


Figure 5. Properties of monolayers formed by the adsorption of mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$ onto gold from ethanolic solutions. R is the ratio of the concentrations of the two components in solution. Squares and circles represent data from two separate experiments. The lines are provided as guides to the eye. Upper figure: ellipsometric thickness. Middle figure: advancing contact angles of water (open symbols) and hexadecane (solid symbols) obtained by the sessile drop technique. Lower figure: areas of the Au($4f_{7/2}$) (open symbols) and O(1s) peaks (solid symbols) obtained by XPS. The vertical scale is arbitrary. Data were collected on a SSX-100 X-ray photoelectron spectrometer (Surface Science Instruments) with a monochromatized Al Kα source, 100-eV pass energy, 1-mm X-ray spot, and 35° takeoff angle. The peaks were fitted with a symmetrical 90% Gaussian/10% Lorentzian profile.

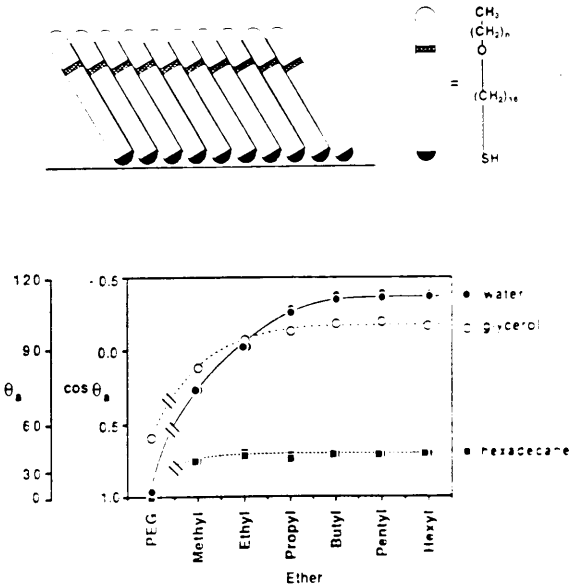


Figure 6. Monolayers formed by adsorption of alkanethiols terminated by alkyl ethers onto gold. Upper figure: Schematic illustration of a monolayer formed by adsorbing $HS(CH_2)_{16}O(CH_2)_nCH_3$ onto gold. Lower figure: Advancing contact angles of water (●), glycerol (○), and hexadecane (■) on monolayers formed by adsorbing $HS(CH_2)_{16}O(CH_2)_nCH_3$ onto gold as a function of the length of the terminal alkyl chain. PEG (poly(ethylene glycol)) is included for comparison as a surface in which the ether linkage is exposed to the contacting liquid. The value of the contact angle of water on PEG is approximate, since PEG rapidly dissolves in the drop of water.

wettability by water (and also by hexadecane, HD)—correlates well with the thickness and oxygen content of the film. Thus, by simply varying the value of R from ~1 to 100 it is possible to control the thickness of the monolayer (±1 Å) from ~25 to ~10 Å and to control its wettability by water from $\theta_a > 110°$ to $\theta_a < 10°$. This ability to control simultaneously the composition, structure, and macroscopic property of these mixed monolayer films makes them ideal for studying structure–property relations in this class of materials. The ability to control the film thickness to a few angstroms by simple organic synthetic techniques is particularly noteworthy. To achieve this level of control by using the techniques of classical surface science—vapor-phase epitaxy, sputtering, chemical vapor deposition, and others—requires sophisticated and often expensive experimental techniques.

The ability to prepare self-assembled monolayers incorporating a range of types of organic structures makes it possible to study the depth sensitivity of wetting in some detail. Figure 6 shows a representative experimental approach for the measurement of depth sensitivity. In this experiment,[25] we have positioned a polar functionality, an etheral oxygen atom, at various distances from the monolayer–water interface by varying the length of the n-alkyl chain, C_nH_{2n+1}, in a series of alkanethiols of structure $HS(CH_2)_{16}OC_nH_{2n+1}$. Wettability by water varies significantly as C_nH_{2n+1} ranges from methyl to butyl but is constant for alkyl groups larger than pentyl (at a value approximately that expected for molecules containing no ethereal oxygen). We infer from this experiment that the thickness of a hydrocarbon layer provided by a C_4 alkyl chain is sufficient to hide the polar oxygen functionality from contact with liquid water.

An obvious question in this type of experiment concerns the order in these functionalized monolayers, relative to the order in monolayers derived from unfunctionalized alkanethiols. A point of particular interest concerns the order in that part of the monolayer occupied by the group R (Figure 6). Is it necessary to have a high degree of order in this R group to achieve effective screening of the ethereal oxygens from water? We have begun to explore this question by examining a number of interfaces having polar functional groups separated from the solid–water interface by various means[26,48] (Figure 7). This figure summarizes results from several systems: monolayers on gold incorporating an ether or amide group as the "hidden" polar functionality,[26] and amide derivatives of PE–CO_2H.[48] The interest and surprise in these data are that all of these systems show similar behavior. Thus, a range of organic surfaces, varying in order from the quasi-crystalline alkanethiolates (RS^-Au) on gold to the disordered functionalized polymers PE–CONHR, all show similar response in their wettability by water to the length of the n-alkyl group R. We infer from these data that a high degree of order is not a prerequisite for burying the polar functional groups.

The high sensitivity of wetting to local details in structure can be used as the basis for synthesis of new types of materials showing unusual and potentially useful behavior. Figure 8 shows the wettability of a material, PE–$CONHC_6H_4$-o-CO_2H, obtained by converting the carboxylic acid groups of PE–CO_2H to amides by coupling with anthranilic acid (o-aminobenzoic acid).[47] At low pH, this material is extremely hydrophobic—more hydrophobic than unfunctionalized polyethylene itself. At high pH, it is as hydrophilic as any derivative of PE–CO_2H that

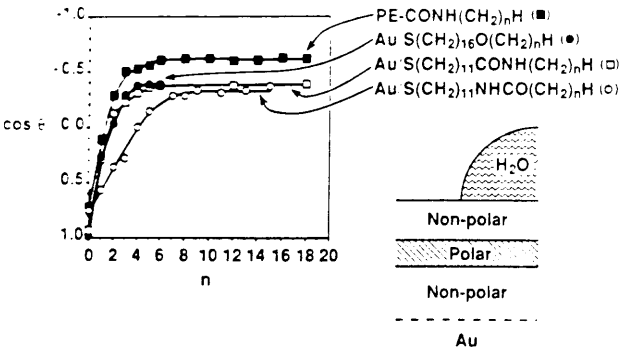


Figure 7. Depth sensitivity of wetting by water on various interfaces containing a submerged polar functionality: advancing contact angles of water as a function of the hydrocarbon chain length separating the polar functionality and the solid–liquid interface. The polyethylene derivatives (■) were prepared by reaction of PE–COCl with alkylamines (refs 46–48); the thiolate monolayers on Au were prepared by adsorption of authentic samples of $HS(CH_2)_{16}O(CH_2)_nH$ (●) and $HS(CH_2)_{11}CONH(CH_2)_nH$ (□) and by reaction of monolayers prepared by adsorption of $HS(CH_2)_{11}NH_2$ onto gold with alkanoyl chlorides (○) (refs 23 and 24). We believe the data represented by ○ were for monolayers that were less ordered than the other systems.

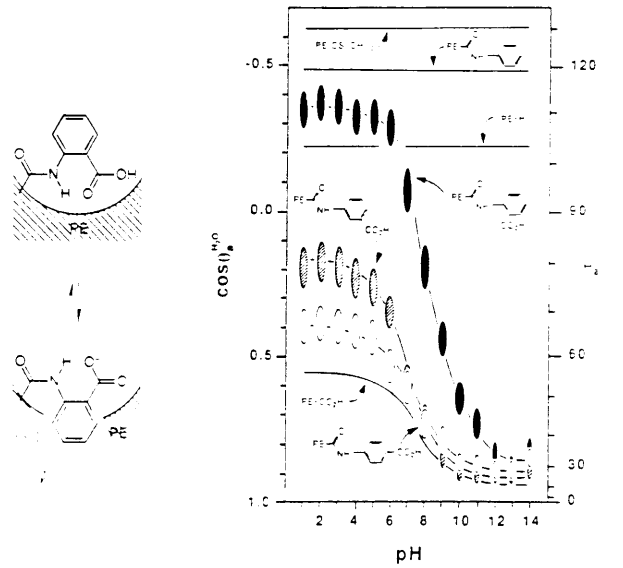


Figure 8. Right figure: advancing contact angle of water on $PE-CO_2H$ and anilide derivatives as a function of the pH of the liquid. Data for PE–H and $PE-CONH_2$ are included for reference. Left figure: proposed change in conformation for PE–anthranilate used in rationalizing the extraordinary change in wettability observed between low and high pH (upper and lower conformations, respectively).

we have observed. This extreme change in wettability with pH is remarkable, and will, we believe, form the basis for the design of pH-sensitive devices. Its detailed origin has not been established, although we believe it to be due to a change in conformation with pH. We hypothesize that at low pH the carboxylic acid group is protonated, and the interface adopts a local structure that exposes to water primarily the C–H bonds of the aromatic ring. In this low-pH conformation, the surface would thus resemble the surface of liquid benzene and would be hydrophobic. It is possible that intramolecular hydrogen bonding is responsible for the low-pH conformation, but we have no direct structural support for this hypothesis. At high pH, we hypothesize that the carboxylic acid groups ionize, the surface reconstructs by a rotation of the anthranilamide moieties that exposes the resulting carboxylate ions to water, and the interface becomes hydrophilic. In going from the low-pH to the high-pH forms, the elemental composition of the interface has not changed. Thus, the wettability of this surface-functionalized polymer must be due to relatively small changes in local conformation of the anthranilamide moieties—perhaps no more than a shift in the position of the aromatic ring by a few angstroms.

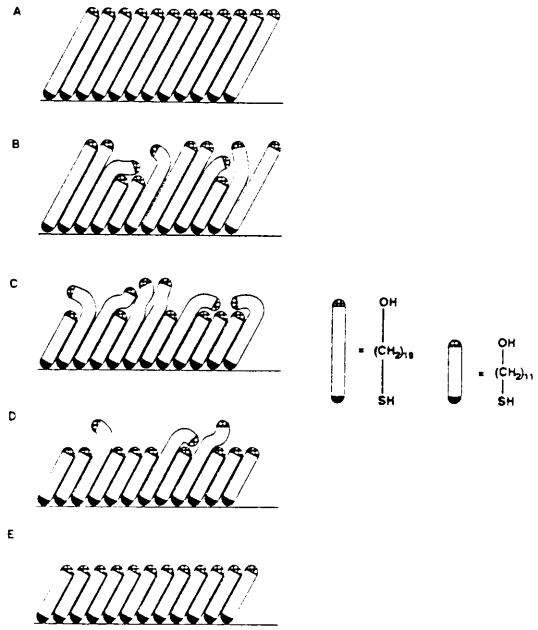


Figure 9. Schematic illustration of monolayers formed by adsorption of mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{19}OH$ onto gold: (A) pure monolayer of $HS(CH_2)_{19}OH$; (B–D) monolayers containing different mixtures of the two components; (E) pure monolayer of $HS(CH_2)_{11}OH$.

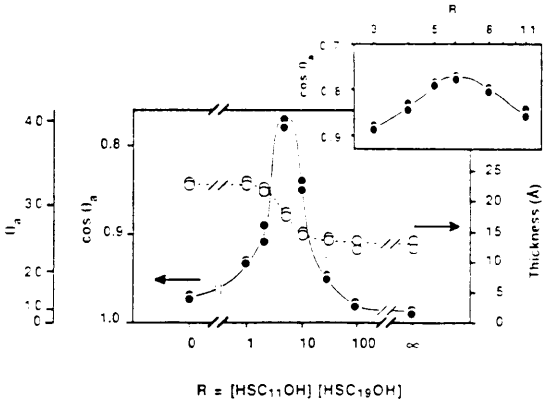


Figure 10. Properties of monolayers formed by the adsorption of mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{19}OH$ onto gold from ethanolic solutions as a function of solution composition R: ellipsometric thickness (○), cosine of the advancing contact angle of water (●). Inset: expanded plot of cos θ_a in the region of the maximum hydrophobicity.

Figures 9 and 10 show another kind of behavior reflecting the high sensitivity of wetting to local structure at the solid–water interface. The system examined in these experiments[29,30] comprised mixed monolayers obtained by chemisorption of short-chain and long-chain hydroxyl-terminated alkanethiols on gold (Figure 9). Our hypothesis was that pure monolayers of either short- or long-chain components would have highly ordered structures presenting two-dimensional arrays of hydroxyl groups at the solid–liquid interface. Monolayers derived from either precursor would be polar and essentially indistinguishable by wettability. In monolayers containing a *mixture* of these components, wettability of the system should

be quite different provided that the mixture was an intimate one—that is, that there was no segregation of the two components into "islands." We expected, in these mixed monolayers, that the portions of the monolayer close to the gold would remain tightly packed and quasi-crystalline but that the outer portions of the monolayer would be disordered with methylene units exposed to the contacting water. In these intermediate regions of composition, when the monolayer contained a mixture of the long- and short-chain thiolates, it would thus be expected to be significantly hydrophobic. Figure 10 shows both contact angles and thicknesses of pure and mixed monolayers. The plot of R versus thickness establishes the range of concentrations of thiols in solution for which the composition of the monolayer is in transition ($R \simeq 6$–7). In this transition region—when the monolayer would be expected to be maximally disordered in its outer structure—the contact angle undergoes a significant excursion from hydrophilic toward hydrophobic.

This peak in hydrophobicity reconfirms the sensitivity of wettability to local structure of the solid–liquid interface. It also provides an important piece of evidence that mixed monolayers prepared by coadsorption of two alkanethiols from solution do *not*, in fact, form phase-segregated, "islanded" mixtures but rather monolayers in which the two alkanethiolates are mixed laterally on the gold surface. We do not know the minimum size of islands that would show the same behavior as pure monolayers of the components of which they were made, but it seems likely that mixtures of islands having radii greater than approximately 100 nm (for monolayers 2 nm thick) would be difficult to distinguish from extended sheets of pure components.

Extensions of Self-Assembly to Organic Surfaces Having Patterns in the Plane of the Surface

Our experiments with self-assembled monolayers on gold, and with organic polymers, have yielded systems in which composition and structure can be manipulated conveniently along the perpendicular to the plane of the interface. Clearly, the degree of control over composition and structure is greater for self-assembled monolayers than for functionalized organic polymers, but in both cases there are strong similarities between the systems. Neither, however, provides immediate opportunity to prepare systems in which structure can be controlled *in* the plane of the interface. We have recently developed (in collaboration with James Hickman and Mark Wrighton at MIT) a model system that combines microlithography with self-assembly.[54] We believe that this system demonstrates a widely applicable method for the preparation of organic surfaces having a useful degree of control over composition and structure *in* the plane of the surface.

The basis for this experimental technique is summarized in Figure 11. We pattern a substrate of interest (in these experiments, silicon nitride) by depositing thin gold and aluminum strips using conventional microlithographic techniques.[55] The aluminum oxidizes spontaneously in air and presents aluminum oxide at the solid–vapor interface; the gold remains clean (except for weakly adsorbed contaminants from the laboratory atmosphere). We select two adsorbates, L_1 and L_2, such that these two adsorbates adsorb strongly and selectively on

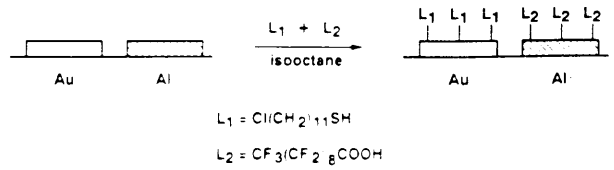


Figure 11. Schematic illustration of the simultaneous formation of two independent (orthogonal) self-assembled monolayers on gold and alumina surfaces by exposure to a solution containing both a thiol and a carboxylic acid.

gold and alumina. In the example given, L_1 is an alkanethiol and L_2 a fluorine-labeled alkanecarboxylic acid. Exposure of the substrate patterned with gold and aluminum/alumina to a solution containing L_1 and L_2 results in replicating the gold pattern with a self-assembled monolayer derived from the alkanethiol and the aluminum/alumina pattern with a self-assembled monolayer derived from the alkanecarboxylic acid.[56] Figure 12 suggests the selectivity that can be observed in this system by showing scanning Auger element maps for gold, aluminum, sulfur, and fluorine.

These systems are being extensively developed in our laboratory, and several combinations of substrates and adsorbates is now available giving "orthogonal" self-assembled monolayers.[57] It is experimentally straightforward, using existing technology, to obtain features by microlithography having dimensions in the range 0.5–1.0 μm. Techniques[58,59] presently being developed (especially shadow lithography[60]) promise to extend these techniques to features with dimensions of <100 Å. Thus, by combining microlithography and self-assembly, we hope eventually to be able to prepare interfaces in which we have control over both the in-plane and perpendicular-to-plane composition and structure on scales of dimensions ranging from 2 to 100 Å. We believe that these systems will be useful in studying a wide range of phenomena in surface science and technology.

The Future

Modern organic surface chemistry is at an early stage of development. Several systems are, however, now available for study.

Self-assembled monolayers on metals and metal oxides are the best characterized and most controllable.[12-36,56,61] They offer a range of materials that are flat and stable, and can be varied from highly ordered to disordered. Although preparation of most of these systems is straightforward, it is unlikely that they will be used in applications requiring large areas of functionalized interface.

(54) Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science (Washington, DC)* **1989**, *245*, 845–847.

(55) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389–7396.

(56) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45–52 and references cited therein.

(57) Laibinis, P. E.; Folkers, J. P.; Whitesides, G. M. Unpublished results.

(58) E-Beam and X-ray nanolithography: Wilkinson, C. D. W.; Beaumont, S. P. *Springer Proc. Phys.* **1986**, *13*, 36–50. Anderson, E. H.; Kern, D. P.; Smith, H. I. *Microelectron. Eng.* **1987**, *6*, 541–546. Newman, T. H.; Williams, K. E.; Pease, R. F. W. *J. Vac. Sci. Technol. B* **1987**, *5*, 88–91. Kuan, W.; Frank, C. W.; Fu, C. C.; Allee, D. R.; Maccagno, P.; Pease, R. F. W. *J. Vac Sci. Technol. B* **1988**, *6*, 2274–2279.

(59) Lithography by STM: Silver, R. M.; Ehrichs, E. E.; DeLozanne, A. L. *Appl. Phys. Lett.* **1987**, *51*, 247–249. Lin, C. W.; Fan, F. R. F.; Bard, A. J. *J. Electrochem. Soc.* **1987**, *134*, 1038–1039. Cranston, D. H.; Lin, C. W.; Bard, A. J. *J. Electrochem. Soc.* **1988**, *135*, 785–786. McCord, M. A.; Kern, D. P.; Chang, T. H. P. *J. Vac. Sci. Technol. B* **1988**, *6*, 1877–1880.

(60) Jones, E. T. T.; Chyan, O. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5226–5228.

(61) Hickman, J. J.; Zou, C.; Ofer, D.; Harvey, P. D.; Wrighton, M. S.; Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7271–7272.

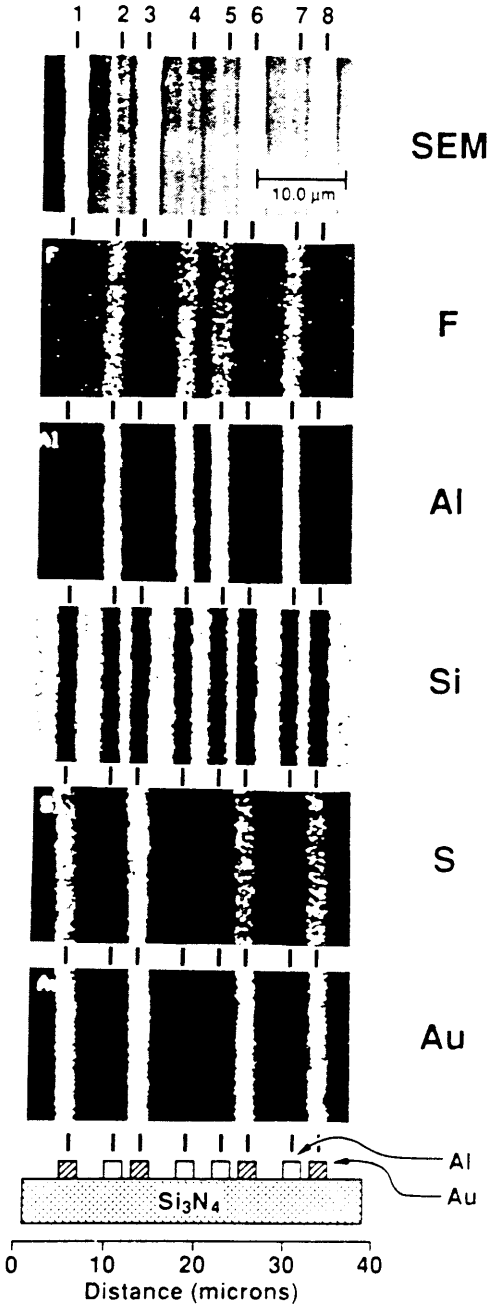


Figure 12. Scanning electron micrograph (SEM) and scanning Auger element maps for an array of four strips of gold (numbers 1, 3, 6, and 8) and four of aluminum/alumina (numbers 2, 4, 5, and 7) on a silicon nitride substrate that was exposed to a mixture of $HS(CH_2)_{11}Cl$ and $CF_3(CF_2)_6CO_2H$ in isooctane. The SEM and element maps are for the array viewed from above; the schematic of the device (the height of the strips is not drawn to scale) is a side view.

Langmuir–Blodgett films complement self-assembled monolayers. Although they are experimentally more difficult to work with than self-assembled monolayers (especially for highly ordered systems, in which transfer from the liquid–air interface to a solid support runs the risk of introducing cracks and other types of defects into the film), they are more easily applied to multilayer systems.

Functionalized polymer surfaces are, in general, disordered and complex. Large areas of these surfaces, are, however, readily available. Moreover, because the underlying polymer is permeable and deformable, these interfaces display a range of properties and phenomena on heating or mechanical deformation that cannot be observed with rigid silicon, glass, or metal substrates. The reconstruction of functionalized organic polymers is a fascinating and highly technologically relevant subject in its own right.[52] It may also lead to new classes of materials, by introducing functional groups at the solid–liquid interface and subsequently diffusing these functional groups a few angstroms below the surface by heating or by mechanical deformation.

Work to date has also established a range of techniques that seem immediately useful in studying organic interfacial chemistry. Of the classical surface spectroscopies, XPS is uniquely valuable in providing information about composition and about the location and character of functional groups. Polarized infrared external reflectance spectroscopy (PIERS) is exceptionally useful in the specialized task of characterizing the degree of order in self-assembled monolayers containing methylene chains. Optical ellipsometry and XPS provide complementary information about thickness in monolayers. The ultimate usefulness of instrumental techniques in studying organic surfaces remains circumscribed by the intrinsic characteristics of these materials. Organic interfaces are usually not sufficiently well-ordered to provide high-quality information by scattering techniques; organic materials damage readily on exposure to high-energy radiation or particles and may contaminate vacuum systems. Organic materials are often electrical insulators, and surface charging can make experiments difficult; the techniques of vacuum physics are usually not applicable to the condensed interphases (both solid–liquid and solid–solid) of primary interest in organic surface chemistry.

By contrast, contact angle measurements provide a convenient probe of the structure of the interface. The utility of this method is based on its high sensitivity to local surface structure and on its ability to detect certain types of reactions—especially those involving ionization of functional groups—that are well understood in physical–organic chemistry. Contact angle measurements thus constitute a first step in using reactivity as a probe of surface structure. Wetting has an additional advantage as a probe of surfaces that it is instrumentally straightforward and inexpensive:[49] it is, thus, accessible to scientists and technologists who might not have the financial or emotional resources to invest in the full panoply of high-vacuum surface spectrometry.

Although uncertainties remain concerning many aspects of the organic surfaces now available, they are sufficiently well defined that they can be used to discover and study new and complex phenomena. Adhesion and tribology are immediately accessible opportunities.[62] The condensation of thin liquid films on polar interfaces[63] is a subject of broad interest in a range of technologies[64] (especially when the condensing liquid is water) and is also relevant to the extensive body of information developing from applications of the surface force balance[65] and

(62) Hintermann, H. E. *J. Vac. Sci. Technol. B* **1984**, *2*, 816–822. Massignon, D. *J. Chim. Phys., Phys.-Chim. Biol.* **1987**, *84*, 135–140.

(63) Derjagin, B. V.; Churaev, N. V. in *Fluid Interfacial Phenomenon*; Croxton, C. A., Ed.; Wiley: Chichester, 1986; Chapter 15. Beysens, D.; Knobler, C. M. *Phys. Rev. Lett.* **1986**, *57*, 1433–1436. Kuroda, Y.; Kittaka, S.; Miura, K.; Morimoto, T. *Langmuir* **1988**, *4*, 210–215 and references therein.

(64) Sidemna, S.; Moalem Maron, D. In *Boiling Phenomena*; van Stralen, S., Cole, R., Eds.: Hemisphere: Washington, DC, 1979; Vol. 2, pp 903–922. Huang, P. H. *Sens. Actuators* **1988**, *13*, 329–337.

(65) Israelachvili, J. N.; Tabor, A. *Proc. R. Soc. London, A* **1982**, *331*, 19. Israelachvili, J. N. *J. Colloid Interface Sci.* **1986**, *100*, 263. Israelachvili, J. N.; Christenson, H. K. *Physica A* **1986**, *140*, 278.

atomic force microscope.[66] The application of the preparative techniques and design criteria already available to the preparation of new materials systems displaying new types of properties is just beginning.

These organic surface systems should also provide excellent substrates with which to study certain phenomena in basic science.[12,13] Wetting is providing an outstandingly useful probe with which to study the energetics of the solid–liquid interface and to explore the kinetics and thermodynamics of drop spreading.[7–9] The ability to control organic film thickness at the level of angstroms provides, for the first time, the capability of making very thin hydrocarbon barriers with very high dimensional control for use in studying electron transfer.[18] It should be possible to use these systems in electrochemistry to study the fundamentals of electron transport at interfaces and in the preparation of new types of microelectrochemical devices and electrochemically based sensors. With further development of synthetic techniques, it should be possible to attach macromolecules to SAMs and to begin to use them to model certain biological surfaces. In the more distant future, it may be practical to build cavities with defined dimension into self-assembled monolayers and perhaps to use them for shape-selective recognition and catalysis.

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(66) Martin, Y.; Williams, G. C.; Wickramasinghe, H. K. *J. Appl. Phys.* **1987**, *61*, 4723–4729. Marti, O.; Ribi, H. O.; Drake, B.; Albrecht, T. R.; Quate, C. F.; Hansma, P. K. *Science (Washington, DC)* **1988**, *239*, 50–52. Marti, O.; Drake, B.; Gould, S.; Hansma, P. K. *J. Vac. Sci. Technol., A* **1988**, *6*, 287–290. Schneir, J.; Marti, O.; Remmers, G.; Glaser, D.; Sonnenfeld, R.; Drake, B.; Hansma, P. K.; Ellngs, V. *J. Vac. Sci. Technol., A* **1988**, *6*, 283–286. Gould, S.; Marti, O.; Drake, B.; Hellemans, L.; Bracker, C. E.; Hansma, P. K.; Keder, N. L.; Eddy, M. M.; Stucky, G. D. *Nature* **1988**, *332*, 332–334. Burnham, N. A.; Colton, R. J. *J. Vac. Sci. Technol., A* **1989**, *7*, 2906–2913.