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ORGANIC CHEMISTRY IN TWO DIMENSIONS:
SURFACE-FUNCTIONALIZED POLYMERS AND SELF-ASSEMBLED MONOLAYER FILMS

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Organic chemistry is largely derived from studies of the reactivity and properties of molecules in homogeneous solution, and much of the intuition of organic chemists is based on the behavior of molecules in solution. Surfaces and interfaces (that is, quasi two-dimensional assemblies of molecules or functional groups) provide environments that can be quite different from those of solutions, and chemical intuition derived from solution is often wrong when applied to processes occurring at surfaces. The central focus of our program in organic surface chemistry is on new science: that is, understanding and controlling the phenomena characteristic of surfaces, interfaces, and thin films. A charm of surface chemistry is, however, its ability to combine new science with relevance to a wide range of technological problems, and we hope to contribute to these applied areas as well.

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19. Abstract (cont'd)

Underlying our program in surface chemistry is a broad interest in the properties of organic surfaces as components of materials. In particular, we hope to develop the ability to rationalize and predict the macroscopic properties of surfaces -- wetting, adhesion, friction -- by knowing their microscopic, molecular-level structures. The issue of structure/property relationships in solids lies at the base of much of the current research in areas such as materials science, condensed matter and device physics, and polymer physical chemistry. Surface science spans these fields, and is currently a research area of particularly great activity. The appeal of surface chemistry as an avenue into detailed understanding of the relations between microscopic and macroscopic properties of matter is that interfaces are more accessible to analysis and more easily modified by synthesis than are the interiors of solids.

Organic chemistry has played a surprisingly small role in interfacial science. Although organic chemistry offers, in principal, the ability to introduce a wide range of functional and structural groups into surfaces, in practice it has been difficult to, much less design and synthesize, ordered two-dimensional arrays of organic moieties. We have taken a physical-organic approach to the study of organic interfacial chemistry: we formulate a hypothesis relating molecular-scale structure to macroscopic property, synthesize and characterize interfaces having structures appropriate to testing that hypothesis, measure the properties of interest, and interpret the information concerning structure and properties in terms of the original hypothesis. The physical-organic paradigm for the study of complex patterns of structure and reactivity is fundamentally a qualitative one, often relying more on analogy than on numerical calculations based on fundamental theory. It has, however, provided one of the most durable and useful methods of understanding complicated systems. Physical-organic chemistry counts among its many successes the correlation of organic structures with reactivities in solution, the rationalization of areas such as photochemistry and catalysis, and the inference of the properties and structures of reactive intermediates; we believe it will also be immensely valuable in understanding surfaces.

ORGANIC CHEMISTRY IN TWO DIMENSIONS: SURFACE-FUNCTIONALIZED POLYMERS AND SELF-ASSEMBLED MONOLAYER FILMS[1]

George M. Whitesides and Gregory S. Ferguson,[2] Harvard University

Organic chemistry is largely derived from studies of the reactivity and properties of molecules in homogeneous solution, and much of the intuition of organic chemists is based on the behavior of molecules in solution. Surfaces and interfaces[3] (that is, quasi two-dimensional assemblies of molecules or functional groups) provide environments that can be quite different from those of solutions, and chemical intuition derived from solution is often wrong when applied to processes occurring at surfaces. The central focus of our program in organic surface chemistry is on new science: that is, understanding and controlling the phenomena characteristic of surfaces, interfaces, and thin films. A charm of surface chemistry is, however, its ability to combine new science with relevance to a wide range of technological problems,[4,5] and we hope to contribute to these applied areas as well.[6]

Underlying our program in surface chemistry is a broad interest in the properties of organic surfaces as components of materials. In particular, we hope to develop the ability to rationalize and predict the *macroscopic* properties of surfaces—wetting, adhesion, friction—by knowing their *microscopic*, molecular-level structures. The issue of structure/property relationships in solids lies at the base of much of the current research in areas such as materials science, condensed matter and device physics, and polymer physical chemistry. Surface science spans these fields and is currently a research area of particularly great activity.[5,7-26] The appeal of surface chemistry as an avenue into detailed understanding of the relations between microscopic and macroscopic properties of matter is that interfaces are more accessible to analysis and more easily modified by synthesis than are the interiors of solids.
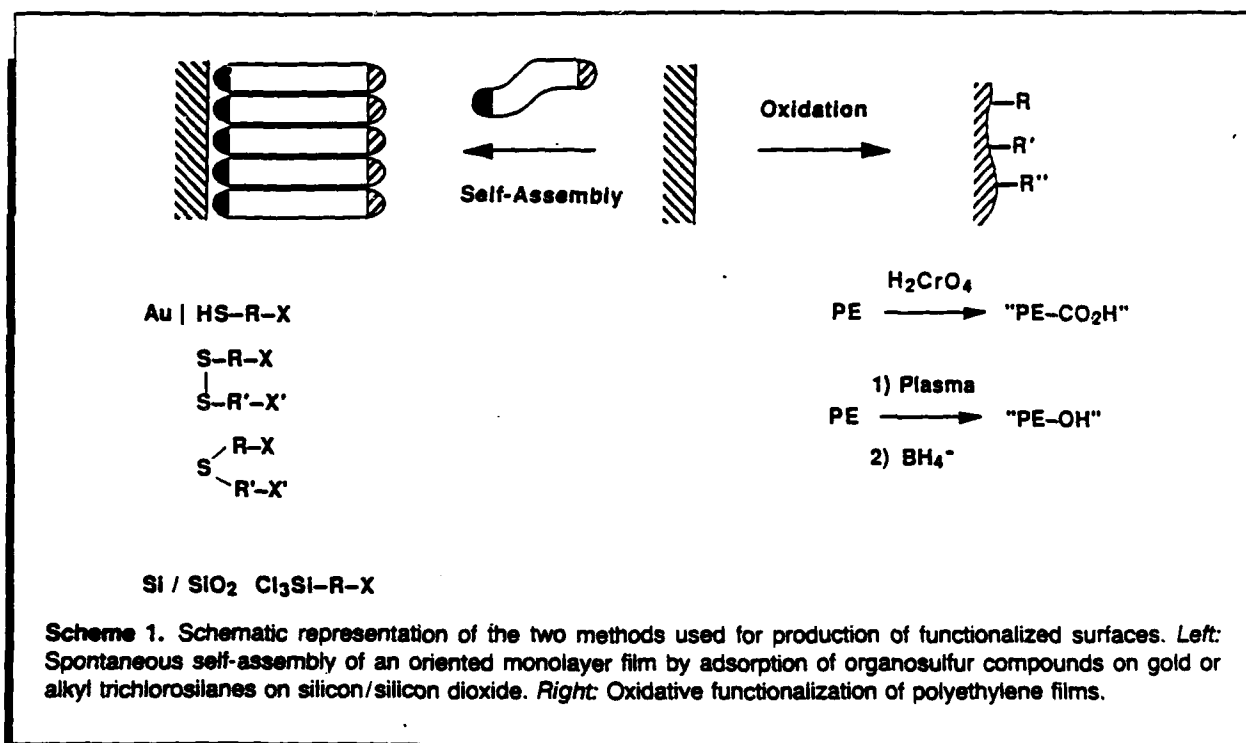
Organic chemistry has played a surprisingly small role in interfacial science.[27] Although organic chemistry offers, in principal, the ability to introduce a wide range of functional and structural groups into surfaces, in practice it has been difficult to rationalize, much less design and synthesize, ordered two-dimensional arrays of organic moieties.[28] We have taken a physical–organic approach to the study of organic interfacial chemistry: We *formulate a hypothesis* re-

lating molecular-scale structure to macroscopic property, *synthesize and characterize interfaces* having structures appropriate to testing that hypothesis, *measure the properties* of interest, and *interpret the information* concerning structure and properties in terms of the original hypothesis. The physical–organic paradigm for the study of complex patterns of structure and reactivity is fundamentally a qualitative one, often relying more on analogy than on numerical calculations based on fundamental theory. It has, however, provided one of the most durable and useful methods of understanding complicated systems. Physical–organic chemistry counts among its many successes the correlation of organic structures with reactivities in solution, the rationalization of areas such as photochemistry and catalysis, and the inference of the properties and structures of reactive intermediates;[29] we believe it will also be immensely valuable in understanding surfaces.

SYNTHESIS OF SURFACES AND INTERFACES

We have relied on two separate types of experimental systems in our studies (Scheme 1):
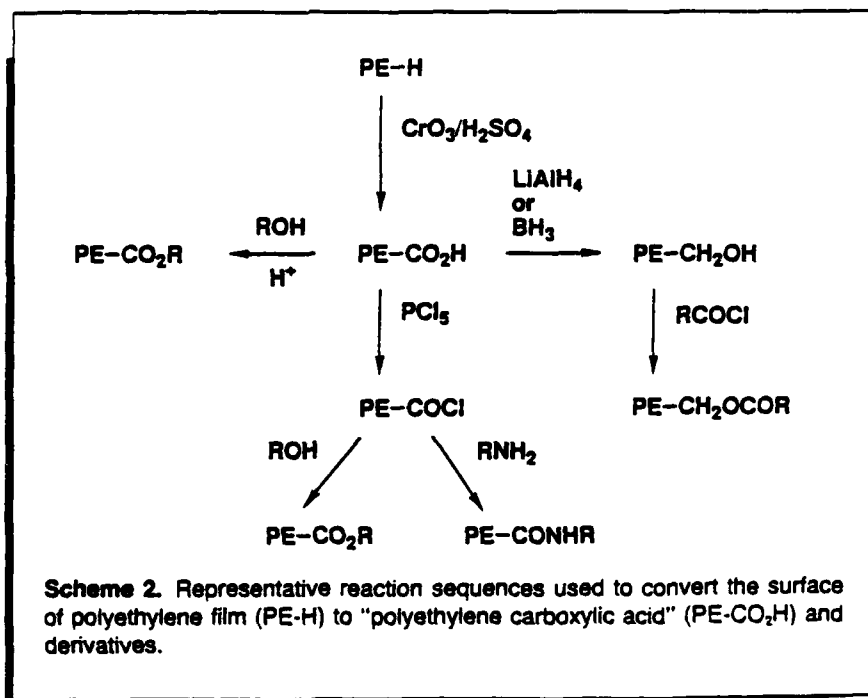

Scheme 1. Schematic representation of the two methods used for production of functionalized surfaces. *Left:* Spontaneous self-assembly of an oriented monolayer film by adsorption of organosulfur compounds on gold or alkyl trichlorosilanes on silicon/silicon dioxide. *Right:* Oxidative functionalization of polyethylene films.

1. **Surface-Functionalized Organic Polymers, Especially "Polyethylene Carboxylic Acid" (PE-CO$_2$H).** These systems are prepared by oxidizing polyethylene (PE) films with chromic acid and using the carboxylic acid groups introduced onto the surface as the starting point for more elaborate chemical modification (Scheme 1).[30-36] The chromic acid oxidation has the advantages of restraining the functionality to a very thin (less than 10 Å in depth) layer along the surface contour of the polymer and of generating a set of functionalities limited to carboxylic acids and ketones and/or aldehydes. PE-CO$_2$H is convenient to prepare and study and is an excellent material for exploratory studies. It also provides an entry into the examination of properties repre-

sentative of a "real" material. It is, however, a complex, microscopically heterogeneous and structurally ill-defined material.[37]

2. Self-Assembled Adsorbed Monolayer Films.[38,39]

We and others have focused on two classes of monolayers: organosulfur compounds (especially organic thiols) adsorbed on gold,[35,40–48] and alkyl siloxane monolayers prepared by reaction of alkyl trichlorosilanes with surfaces containing hydroxyl groups and/or adsorbed water.[49–52] Both of these systems, and others related to them, are excellent models for interpreting the characteristics of PE-CO_2H and its derivatives. Immersion of a silicon wafer coated with a thin film (~1000 Å) of evaporated gold in a solution of a fatty thiol for 1 hour at room temperature results in the formation of a highly ordered, quasicrystalline monolayer of fatty thiol attached to the gold surface by sulfur-gold coordination (Scheme 1). The essential processes occurring during the adsorption and organization of the thiol on the gold surface are still incompletely understood, but they are certainly related to the familiar, if complex, coordination chemistry of thiols and gold(0) or gold(I).[53,54]

One of the most attractive features of organic chemistry is the wide variation in the structure of organic molecules that can be produced through synthesis. A challenge to our program in organic surface chemistry has been to bring these synthetic techniques to bear on two separate classes of problems in surface chemistry: first, the introduction of small fragments having desired functionality onto surfaces through chemical reaction; second, the preparation/assembly of these fragments in extended macroscopic arrays with control over position and orientation. The two approaches we have followed—one leading to PE-CO_2H and its derivatives, and the other to self-assembled organic monolayers—are quite different. The former introduces functional groups onto a preformed heterogeneous material (Scheme 2). This procedure is convenient and experimentally relevant to a broad range of polymer technologies, but it requires the study and analysis of materials that are intrinsically structurally ill-defined. The latter prepares well-defined, appropriately func-

Scheme 2. Representative reaction sequences used to convert the surface of polyethylene film (PE-H) to "polyethylene carboxylic acid" (PE-CO_2H) and derivatives.

tionalized molecules, which are then allowed to self-assemble on a reactive surface and form highly ordered two-dimensional structures. Self-assembly will, we believe, become a mainstay of ordered monolayer formation,[5,55] and will eventually prove invaluable in rational strategies for modification of the properties of interfaces. Preparing these systems is, however, experimentally more complex than generating functionalized polymer surfaces.

CHARACTERIZATION OF SURFACES

We have used the usual array of spectroscopic techniques to characterize surfaces: attenuated total reflectance-infrared (ATR-IR) and polarized infrared external reflective spectroscopy (PIERS), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), fluorescence, electron microscopy, and ellipsometry are all useful (Table). We have, however, also

**Table. Selected Methods for Analysis of Surfaces and Interfaces**

Technique	Application and Depth Sensed
Scanning tunneling microscopy (STM)	Individual atomic positions on surfaces
Low-angle X-ray scattering	Electron density map of the surface of very flat solids
Electron microscopy (SEM, TEM); electron diffraction	Surface morphology and degree of crystalline order
Contact angle (H_2O)	Polarity of top ~10 Å
X-ray photoelectron spectroscopy; (XPS); auger spectroscopy	Atomic and chemical composition of top ~50 Å
Ellipsometry	Determination of film thickness with a resolution of 2 Å
Attenuated total reflectance-infrared (ATR-IR) Polarized infrared external reflective spectroscopy (PIERS)	Vibrational analysis of top ~1000 Å
Rutherford backscattering (RBS)	Atomic composition as a function of depth with resolution of hundreds of Å
Fluorescence spectroscopy	Assay for density of functionality after covalent attachment of fluorescent probes
Electron spin resonance (ESR) spectroscopy	Location and mobility of paramagnetic centers (e.g., TMPO) in interfaces

been able to apply to problems in the physical-organic chemistry of surfaces two techniques for characterization that are less familiar to the spectroscopic community. The first is the measurement and interpretation of liquid–solid contact angles. This technique has proven to be the most surface-sensitive and most convenient (if not the most easily interpreted) method that we have available to characterize organic interfaces.[30-35,40,41] It is especially useful in characterizing the solid–water interface. The second technique involves studies of chemical reactivity at interfaces. This approach is especially useful when applied using simple, high-yield reactions that are well understood in homogeneous, liquid phase chemistry. Ionization and esterification of carboxylic acids and saponification of carboxylic acid esters are especially diagnostic.[34]

The combination of measurement of contact angle with studies of ionization of functional groups has resulted in a technique we call "contact angle titration": that is, study of the variation in the contact angle with the pH of the

aqueous drop (Scheme 3). This technique increases the information derived from the measurement of contact angles. Traditional approaches to studying contact angle generate only two numbers (the advancing contact angle θ_a and the receding contact angle θ_r).[56] Receding contact angles are presently very difficult to interpret. Efforts to characterize complex, heterogeneous interfaces using only advancing contact angles are unlikely to be very broadly useful. By measuring contact angle *as a function of pH*, however, one can often infer the existence, environment, and nature of ionizable groups present at the interface.

Contact angle titration is based on the observation of variations in contact angle with pH at surfaces containing ionizable groups.[35] This variation plau-
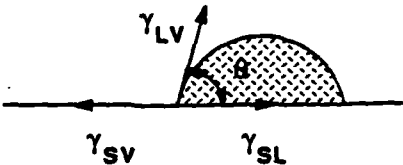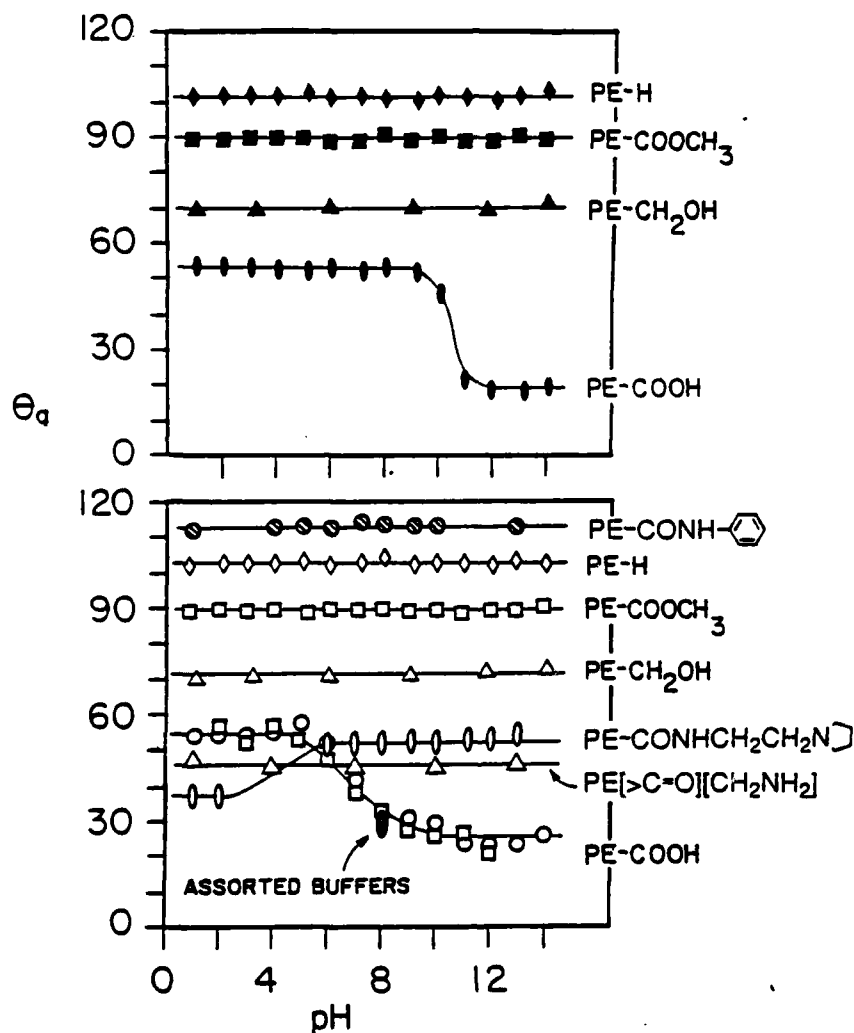

Scheme 3. Dependence of θ_a on pH for surface-functionalized polyethylene film. *Top:* Using unbuffered aqueous solutions. Buffers: (□) 0.1 M phosphate buffer; (○) all others (0.05 M), pH 1, 0.1 N HCl; pH 2, maleic acid; pH 3, tartaric acid; pH 4, succinic acid; pH 5, acetic acid; pH 6, maleic acid; pH 7 and 8, HEPES; pH 9 and 10, CHES, pH 11, triethylamine; pH 12, phosphate; pH 13, 0.1 N NaOH. The crosshatched and labeled "assorted buffers" at pH 8 include data for phosphates MOPS, HEPES, TAPS, TRIS, and triethanolamine.

sibly reflects ionization of the functional group: The charged form of an acid or base is more hydrophilic than the uncharged form, and the contact angle with water is lower. Although this simple explanation is fundamentally correct, and the technique is a very useful one in comparing acidities, its simplicity hides a number of complexities.[32,35]

One interesting aspect of contact angle titration concerns the intuitive concept of the "quantity" of a functional group present at an interface. Our initial intuition concerning surface functional group chemistry was that, in most systems likely to be studied experimentally, the number of functional groups present on a representative area of surface would be small compared with the quantity of a reagent present in the volume of solution used in experiments on that surface. This belief is largely incorrect for measurements of contact angles: The number of functional groups present at high density on a surface is comparable to that present in solutions used for contact angle titration in unbuffered systems. The difference between the titration curves obtained using buffered and unbuffered solutions (Scheme 3) exemplifies the phenomenon.[32]

Explanation of this observation helps to clarify the concept of "concentration" in a heterogeneous system consisting of a surface and a contacting liquid phase. We consider the spreading of an aqueous drop at an interface to be determined in part by the extent of ionization of the functionality present at that interface. Let us examine the "concentration" of this functionality in a system consisting of a 1-μl drop in contact with a derivatized polyethylene surface (a 1-μl drop typically covers an area of ~1 mm^2). The density of functional groups on the surface can be in the order of 6×10^{14}/cm^2 for a surface with typical roughness;[33] at this density, the concentration of reagent in solution in the contacting drop required to react stoichiometrically with that functionality is ~0.1 mM.[57] For an unbuffered aqueous solution and a monoprotic acid/base reaction, a concentration of acid or base > 0.1 mM (i.e., pH < 4 or pH > 10) is thus required to achieve a stoichiometric reaction. Clearly, the difference in contact angle titration curves obtained using buffered and unbuffered solutions is due to surface functionality that is itself sufficiently concentrated in the system comprising surface and drop to buffer the pH of the aqueous solution in the range pH 5–9. Thus, the qualitative idea that a monolayer of organic functionality is insignificantly small in quantity compared with the functionality present in solution is incorrect, if one is concerned with small volumes of solution.

A second interesting issue concerns the detailed interpretation of the contact angle titration curves. In particular, we ask how should the solid–liquid interfacial free energy γ_{SL} be related to the functional groups present on the surface? The fundamental relation connecting the contact angle to interfacial free energy terms is Young's equation (Eq. 1).[58]

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (1)$$

For aqueous solutions constituted with appropriate buffers, the liquid–vapor interfacial free energy γ_{LV} is the same as that for pure water. Variations in interfacial free energies are thus related to the observed value of θ primarily by the terms γ_{SV} and γ_{SL}. These terms, in turn, depend on a number of factors: the type, density, and distribution of functional groups present at the solid–vapor (liquid) interface; their extent of ionization; the roughness of the surface; the relative humidity of the vapor.

As a first approximation, we have proposed that the interfacial free energy can be expressed as a linear combination of functional group contributions, multiplied by the normalized fraction β_i of these groups on the surface[32,34] (Eq. 2). The parameters $\gamma_{i,SL}$ and $\gamma_{i,SV}$ reflect intrinsic

$$\gamma_{SL} = \sum_i \beta_i \, \gamma_{i,SL} \qquad (2a)$$

$$\gamma_{SV} = \sum_i \beta_i \, \gamma_{i,SV} \qquad (2b)$$

hydrophilicity and group size or area. Comparisons of infrared spectroscopic data with contact angles indicate that this type of analysis is approximately
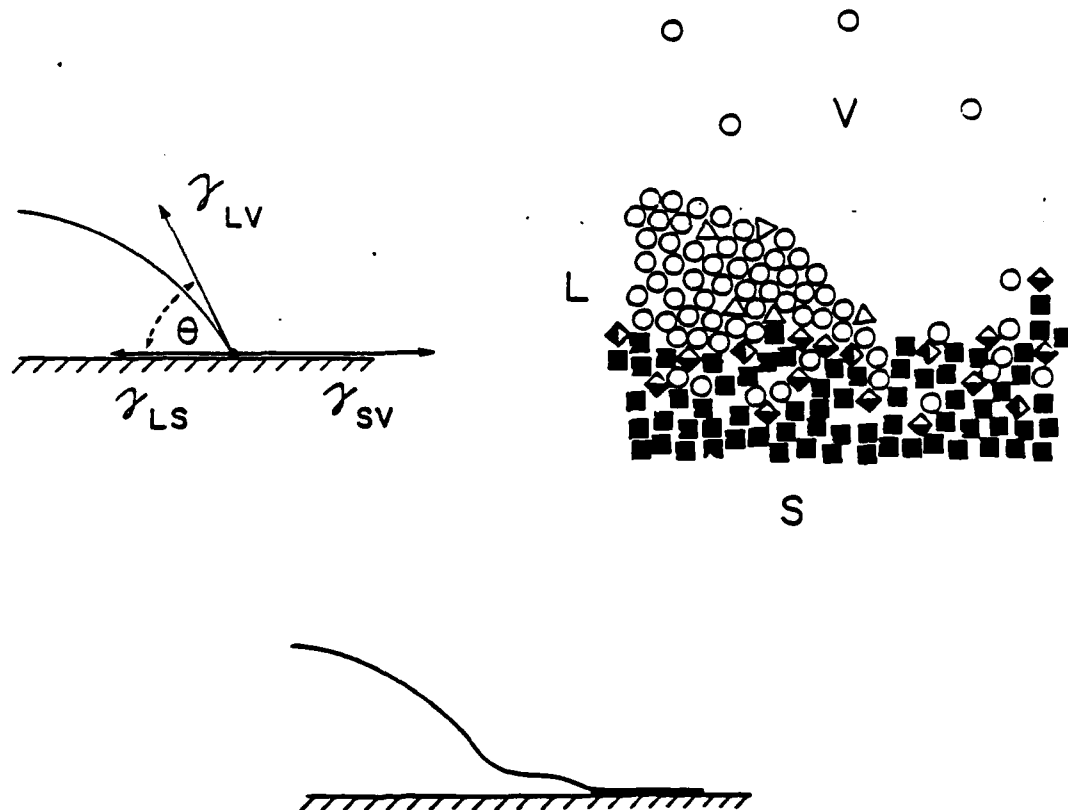

Figure. Schematic representation of an ideal (*top left*) and real (*top right, bottom*) drop of liquid (L) in contact with a solid (S) and vapor (V) with contact angle θ. The symbols in the upper right picture represent (O) water molecules, ($\triangle$) dissolved solutes (phosphate, buffer salts), ($\Diamond$, $\blacklozenge$) polar surface groups (CO_2H, CO_2^-, $C=O,...$), (■) nonpolar surface groups (CH_2, CH_3, ...). A lip of liquid (*bottom*; not drawn to scale), the "precursor film," extends microns beyond the edge of the drop in certain circumstances.

correct for PE-CO$_2$H and some of its acidic derivatives,[32] but that interactions between groups, and perhaps interfacial heterogeneity, make the problem more complex than can be described completely using this simple approach.[35] An understanding of these interactions and complexities remains to be established.

A third important issue is the meaning of hysteresis in the measurement of contact angles. For derivatives of PE-CO$_2$H, θ_a appears to provide a simple, semiquantitatively interpretable measure of interfacial group character and density. Contact angles are, however, a simple parameter derived from observations of a complex reality (Figure). Advancing and receding contact angles differ on many surfaces, and all the derivatives of PE-CO$_2$H (particularly polar derivatives) display very large hystereses in their contact angles: θ_r is frequently 0 even for systems having fairly large values of θ_a. Large hysteresis is usually interpreted to indicate a heterogeneous system far from thermodynamic equilibrium.[39] Yet analyses of θ_a based on Young's equation, an equation assuming thermodynamic equilibrium, seem to give interpretable and reasonable results. It is not clear how one should treat a system that is not at thermodynamic equilibrium, but for which physical measurements correlate with those expected based on physical-organic analogies to processes occurring at equilibrium in solution.
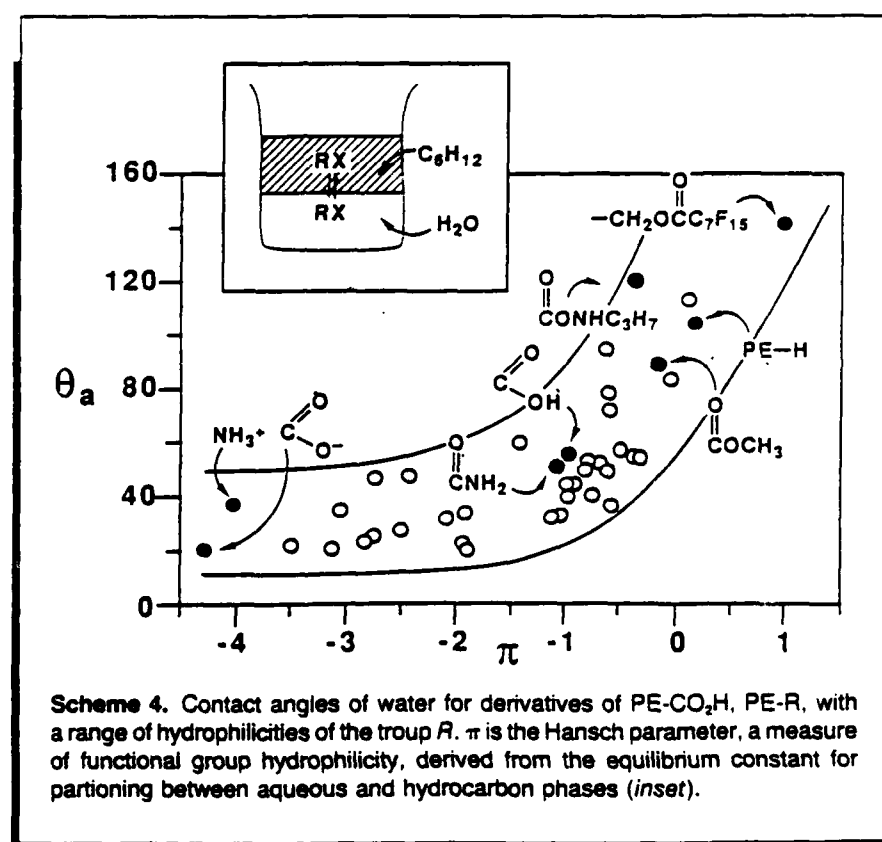
RESULTS

Both functionalized polyethylene and its derivatives, and self-assembled monolayer films, provide systems with which to examine reactions occurring at interfaces and to test hypotheses concerning structure/reactivity and structure/property relationships. In so doing, we find that many of the results we obtain can be rationalized by analogy to phenomena in solution (often with characteristic differences that can be interpreted to compare and contrast the environments provided by homogeneous solutions and interfaces). We also frequently encounter unexpected phenomena, which suggest that any models of organic reactivity at interfaces, based exclusively on analogies with solution, are not complete. The studies that follow provide examples.

Surface Acidities. Scheme 3 indicates that carboxylic acids and many, but not all, amines show inflections in plots of θ_a vs the pH of the drop used in measuring the contact angle.[32-35] Assuming that the midpoint of the inflection corresponds to half-ionization of the functional group (an assumption supported by independent ATR-IR measurements on carboxylic acid surfaces),[32] we infer that acidities of functional groups at an interface and in solution are very different. For example, the value of pH for a solution in contact with a surface required to achieve half-ionization of the carboxylic acid groups at that surface can be as high as 12. What is the origin of this very large apparent decrease in acidity of carboxylic acids (and corresponding increase in the apparent acidity of ammonium ions)? We believe that the origin of these shifts can ultimately be attributed to the locally low dielectric constant at the polyethylene–water interface,[32-35,60] but rationalization of these anomalous values of pK_a is not yet complete.

Relations between Functional Group Hydrophilicity and Wettability of Interfaces. We assumed at the outset of our studies that more hydrophilic interfacial groups (as measured by some convenient parameter such as the Hansch π parameter[61]) would lead to more wettable surfaces. In fact, experimental observations relating wettability to functional group hydrophilicity

differ significantly from those expected (Scheme 4). As the value of π for the functional group on the surface decreases, θ_a also decreases, but only up to a point. Beyond that point, further increases in functional group hydrophilicity result in no further increase in wettability: that is, the hydrophilicity of the surface "saturates."[35] We postulate that the origin of this effect lies in condensation of water vapor at polar solid–vapor interfaces (Scheme 5). Nonpolar interfaces condense relatively little water. All of our experiments involving contact angles with water are carried out at 100% relative humidity in order to assure that the system is as close to thermodynamic equilibrium as possible. Polar functional groups at interfaces are undoubtedly associated with hydrating water adsorbed from the vapor phase. We postulate that, beyond a certain value of the Hansch π parameter, the polar surface functional groups become completely surrounded by condensed, hydrating water, producing a solid–vapor interface whose polarity is essentially independent of the underlying functional group. Under these circumstances, the wettability of the surface is determined primarily by the area fraction of the surface converted to polar functionality, and then hydrated by condensed water.

Scheme 4. Contact angles of water for derivatives of PE-CO$_2$H, PE-R, with a range of hydrophilicities of the troup R. π is the Hansch parameter, a measure of functional group hydrophilicity, derived from the equilibrium constant for partioning between aqueous and hydrocarbon phases (*inset*).

These observations and interpretations imply the existence of a thin, condensed water film on polar surfaces. The nature of this film, and especially the relation of its structure to that of bulk water, remains an important and complex problem.

The Range of Interactions Determining Wetting. Scheme 4 displays an astonishing observation: Although a surface incorporating amides (PE-CONH$_2$) is relatively hydrophilic, the analogous primary amide PE-CONHC$_3$H$_7$ is more hydrophobic than unfunctionalized polyethylene. Some of the apparent hy-
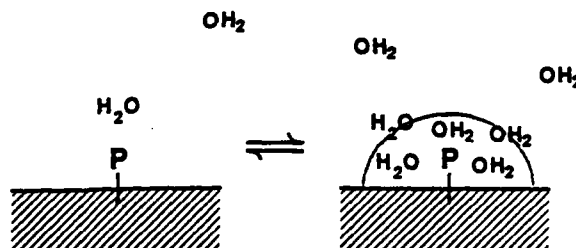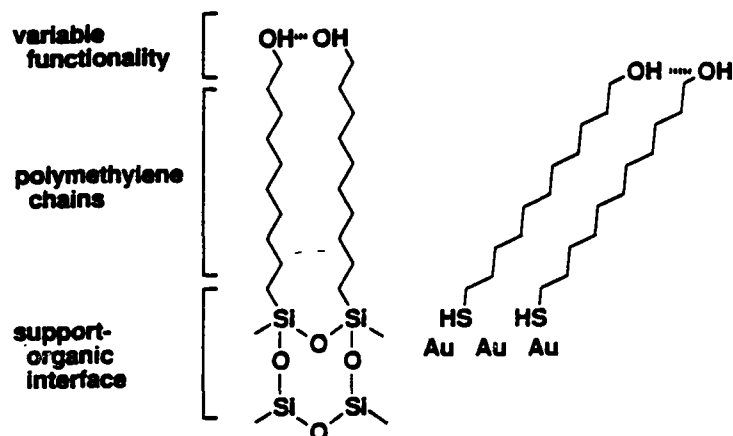
Scheme 5. Schematic illustration of the degree of hydration of a functional group P at the solid–vapor interface. When P is nonpolar, the equilibrium lies to the left; when P is polar, it lies to the right.

drophobicity of PE-CONHC$_3$H$_7$ and its analogs undoubtedly reflects the microscopic roughness of the surface of these materials (generated during the oxidative surface functionalization). Nonetheless, we find that it takes only a small hydrophilic or hydrophobic group to determine the wettability of a surface. Furthermore, a small hydrophobic group is capable of completely masking an underlying, intrinsically hydrophilic core functionality. Thus, for example, replacement of a terminal CH$_3$ group in one of the well-defined, self-assembled monolayer systems by a CH$_2$OH group changes the monolayer from being very hydrophobic to very hydrophilic,[41] and reacylation of the terminal hydroxyl (CH$_2$OCOR) once again makes it very hydrophobic. The interactions that determine macroscopic wettability are, apparently, very short in range.[10] We believe, in fact, that measurement of contact angle is the most surface-sensitive technique presently available for examining the solid–liquid interface. The great advantages of wetting as a probe of surface structure (relative, for example, to XPS) are that its measurement is very simple, convenient, and inexpensive, and that it is intrinsically applicable to the solid–liquid interface and to heterogeneous, noncrystalline surfaces. Its disadvantages are that contact angle measurements are information poor, that they *require* a liquid–solid interface, and that their physical basis is complex and still incompletely understood.

Designed Interfaces. The materials PE-CO-X are convenient but heterogeneous. The best characterized and structurally best defined organic interfaces now available are those formed by adsorbing long-chain alkyl thiols on gold, or by allowing long-chain alkyl trichlorosilanes to react with surface hydroxyl groups and adsorbed water present on the surface of glass or silica. Both of these systems have the alkyl groups in completely *trans*-extended conformations, provided that the terminal functional group is relatively small. For organic thiols on gold, the chains are tilted ~30° from the normal to the metal surface;[42,45] for alkyl siloxanes on silicon/silicon dioxide, they are approximately perpendicular to the substrate surface (Scheme 6).[50] Transmission electron microscopy indicates that the thiol/gold system has at least microcrystalline order in the plane of the monolayer.[42]

These ordered monolayer systems permit an exquisite degree of control over structure and dimensionality at the interface. As one example, consider a monolayer formed by adsorption of HS(CH$_2$)$_{19}$OH on gold. Formation of such a monolayer is experimentally very straightforward: one simply dips the gold-coated substrate into a solution of the α,ω-thioalcohol in a solvent such as acetonitrile for 1 hour at room temperature, withdraws it, and washes it briefly. At the conclusion of this procedure, the entire accessible surface of

Scheme 6. Schematic illustration of conformation and packing order in monolayers of organic thiols on gold and alkyl siloxanes on silicon/silicon dioxide. The monolayer is composed of three important regions: the head groups (portion binding to solid substrate), the polymethylene chains (for formation of van der Waals surface), and the tail groups (terminal functionality that determines the character of the solid–liquid and solid–vapor interfaces).
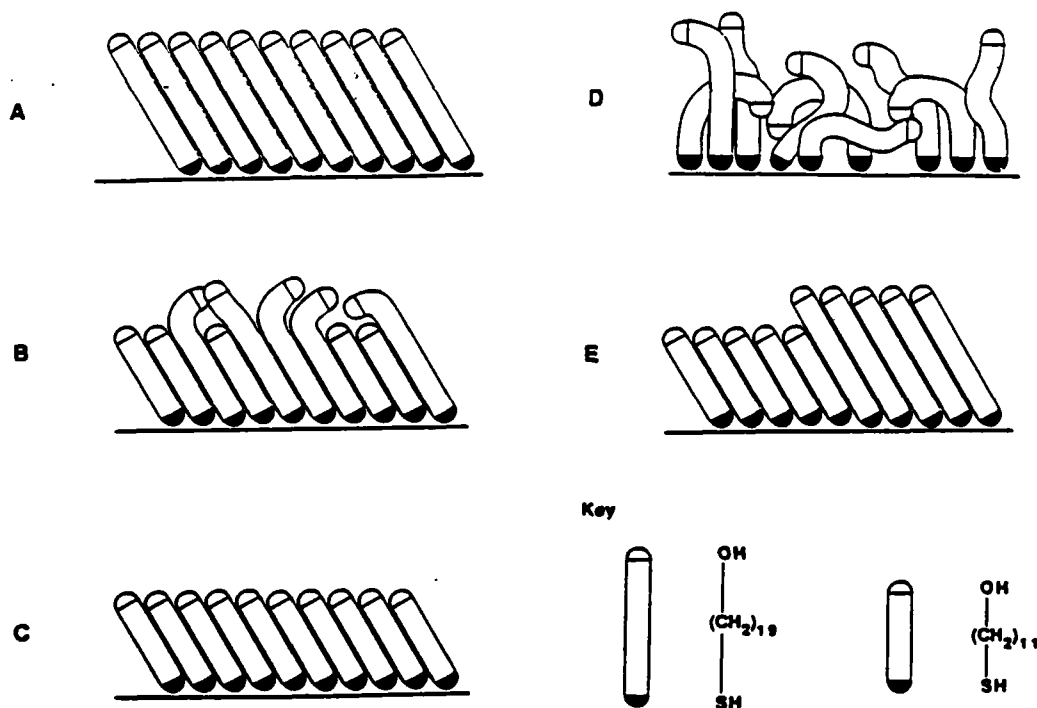
Scheme 7. Stylized illustrations of monolayer structures.[41] Proposed structures of (A) pure monolayer of $HS(CH_2)_{19}OH$; (B) monolayer composed of 50% $HS(CH_2)_{19}OH$ and 50% $HS(CH_2)_{11}OH$; (C) pure monolayer of $HS(CH_2)_{11}OH$. Structures we believe do not occur in the systems studied here: (D) disordered monolayer and (E) monolayer containing a mixture of components and showing phase separation into islands.

the gold is covered with a uniform monolayer 23 Å thick, and the exposed surface is a densely packed monolayer of hydroxyl groups. The thickness of the monolayer is easily controlled at the scale of angstroms by varying the number of methylene groups in the thiol chain; the surface properties are independently controllable through variations in the terminal functional group. If mixtures of two different terminally functionalized thiols are used, monolayers can be made having the two mixed on the surface (Scheme 7).

CURRENT PROBLEMS

The physical–organic chemistry of surfaces promises to provide new materials based on rational synthetic modification of surfaces and interfaces, new analytical methods with which to characterize surfaces, and deeper levels of understanding of familiar processes such as dissolution, wetting, adsorption, and adhesion occurring at interfaces and in solutions. The phenomena being observed are, however, usually more complex than those occurring in homogeneous solution, and are, consequently, still incompletely understood at even the simplest levels. The field presents a number of fascinating fundamental problems in interfacial chemistry, among which we place the following:

1. **Molecular-Level Order.** How should the order in these systems be defined and measured? One advantage of a two-dimensional system is that it is, in principle, less complex structurally than a three-dimensional system: The components of a two-dimensional system are by definition restricted to a plane rather than free to translate and rotate in three dimensions. In practice, however, the problem of defining order in surface-functionalized polymers and self-assembled monolayers remains very complex. All of these systems are, in reality, only quasi two-dimensional. Materials such as functionalized polyethylene are obviously microscopically rough and heterogeneous and have functionality distributed nonuniformly in a thin interfacial layer. Contact of these systems with a liquid phase may result in interfacial swelling and reconstruction. Self-assembled monolayers are better defined structurally, but even with these systems, subtle issues of order in the plane of the monolayer, at the gold–monolayer and monolayer–liquid interfaces and between adjacent organic molecules require the development of new analytical techniques and new criteria for order.

2. **Kinetics vs Thermodynamics.** The extent to which any of the systems currently studied are at thermodynamic equilibrium, and the influence of departures from equilibrium on their behavior, is almost completely uncertain at present.

3. **Wetting.** Despite interesting and provocative theoretical contributions to the theory of wetting in certain idealized systems,[9,62-78] there is no usefully detailed theory of wetting relevant to real, microscopically heterogeneous surfaces. The current rationalization of hysteresis in the measurement of contact angles is especially unsatisfactory. Detailed examination of hysteresis, both theoretically and experimentally would be particularly useful, because hysteresis appears to be very sensitive to order; an understanding of the relation between interfacial structure and hysteresis might provide a new avenue of approach to this important subject.

4. **Molecular Design of Monolayers.** Essentially all work so far carried out with self-assembled monolayers has focused on derivatives of fatty

acids. These systems have the two virtues that they are easy to manipulate synthetically and that they do, for whatever reason, form well-ordered monolayers. They are, however, not stable at even modestly elevated temperatures and have no strong intermolecular interactions contributing to order in the plane of the monolayer or to thermal or oxidative stability. It is important to develop molecular structures other than fatty acids that form ordered, stable two-dimensional sheet structures.

CONCLUSIONS

Organic chemistry at interfaces is a field offering major opportunities for both the conduct of basic science and the development of new technology. It also provides, through the synthesis of extended functionalized interfaces, a bridge between the science of isolated molecules and the science and technology of materials. Since chemical reactivity and wettability provide what we believe will prove to be invaluable probes of interfacial structure for organic systems. these systems are particularly attractive for studies aimed at understanding the characteristics of solid–liquid interfaces.

Surface-functionalized polymers (of which the best developed is PE-CO$_2$H) are proving to be convenient systems with which to conduct exploratory work. They are easily prepared and manipulated. and because they present solid–vapor interfaces that have low surface free energies. they are relatively resistant to contamination by atmospheric contaminants. Further. since they are physically robust. surface-modified polymers can be used to examine complex materials problems such as biocompatibility,[79,80] adhesion.[31] gas permeation.[32] friction.[33] and the influence of bending, stretching,[34] and surface reconstruction[35] on interfacial properties.

Self-assembled monolayers will, we believe. prove to be the ultimate cornerstone of the basic science in organic surface chemistry. They will certainly also find technological application in areas such as promotion of adhesion. inhibition of corrosion, and control of friction. and they may prove important in the production of sensors and microelectronic devices. The remarkable ease with which very complex monolayer structures can be assembled from molecules of very modest complexity will be invaluable in studying the properties of organized molecular assemblies. The best defined of these systems is presently obtained by adsorption of ω-functionalized fatty thiols on gold, although organosilicon compounds on silicon dioxide and glass may ultimately prove equally ordered. Alkyl thiols on gold have as their major advantage the compatibility of the thiol moiety with a wide range of organic functional groups, and the fact that these systems lead to highly ordered monolayers. Silanes on silica are more economical. better adapted to the formation of multilayer structures, and more robust structurally. .

Given the astonishing sensitivity of wettability to local surface structure. its study should provide a range of important new types of information about interfaces, especially solid–liquid interfaces. Designing and interpreting these experiments will require a physical–organic approach—the systems being studied are too complex to be defined using conventional, spectroscopy-based physical chemistry. Because wetting is directly relevant to a broad range of technological problems, these studies should be exceptionally valuable in applications. The experimental techniques required to study wetting are very simple. Surface science based on studies of wettability should thus be accessible even to those without routine access to the instrumentation of high-

vacuum physics. A more realistic theoretical basis for wetting is desperately needed. Current treatments do not deal adequately with subjects such as molecular-scale heterogeneity, hysteresis, deviations from thermodynamic equilibrium, and the nature of the interactions between solids and liquids.

REFERENCES AND NOTES

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2. NIH Postdoctoral Fellow, 1988–1989.

3. The words "surface" and "interface" have clearly defined meanings only in the context of an ideal system, a liquid and vapor in contact with a smooth. homogeneous solid. In the real systems discussed here (especially functionalized polyethylene films), these words should be understood as indicating the more complicated notion of an "interphase region." which incorporates the complexities (roughness, inhomogeneity, surface reconstruction and swelling, etc.) inevitably encountered.

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