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Organic Surface Chemistry: Polymers and Self-Assembled Monolayers

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Interfaces are a key to many properties of systems containing polymers. The general importance of interfaces in materials science is amplified by the current state of development of polymer science and technology. The pace of discovery and development of new polymers has slowed since the early days of the polymer revolution. The number of commercial large-volume polymers will certainly not increase rapidly in the future, if at all. The development of new polymer structures will be concentrated on low-volume, high-value functional systems (electrical conductors, piezoelectrics, polymers showing non-linear optical effects, polymers stable at very high temperatures). These polymers will be used as components of more complex systems, rather than as stand-alone materials. Maximizing the properties of materials composed of existing polymers, perhaps combined with new, functional polymeric components, will thus be increasingly important in producing new types of polymer-derived systems. The interfacial characteristics of bulk polymer systems (e.g. films and fibers) determine wettability and influence adhesion, among other properties. Interfaces are crucial in composites, alloys, and phase-separated systems. Fracture and corrosion create new interfaces, and controlling these phenomena requires control of interfaces. Even interactions between the molecules making up polymeric materials can be considered to be determined, in part, by interactions between their molecular surfaces. Thus, a broad range of important problems in polymer

science are focused on the properties of materials systems composed, in part, of important fractions of interface. Specific examples include: 1) controlling the performance of large-volume polymer systems (for example, the wettability, or suitability as a substrate for adhesives, of polyethylene film); 2) controlling characteristics of systems containing different components (for example, the fracture toughness of carbon-epoxy composites); 3) maximizing the efficiency of use of expensive components (fluorocarbon films for water repellancy); 4) minimizing size (and usually the ratio of surface to volume) of polymer components (polyimide thin films in microelectronic/optoelectronic devices); 5) promoting biocompatibility (by controlling the surface characteristics of high carbon thin films on devices intended for use as implants).

One of the classic – and still largely unsolved – problems in materials science is that of relating the microscopic (atomic and molecular level) structure of polymers to the macroscopic properties of components fabricated from them. A major difficulty hindering work in this area is that of specifying and controlling the microscopic structure. In general, in conducting research in this area, it is not sufficient simply to accept systems with whatever structures are generated by synthesis and processing. Rather, to test hypotheses connecting structure and properties adequately, one would like to specify, manipulate, and control the structure at the molecular level, and then to measure the properties of the resulting system. With full con-

trol over structure, one could compare the observed response of a property to a change in structure in a way that would allow interpretable tests of the relevant hypotheses.

How does one 'synthesize' macroscopic assemblies of atoms at surfaces? What properties are most amenable to measurement, and what measurements to interpretation? To take the second question first, we have focused on measuring the wettability of liquids by solids. Wetting is a fundamental macroscopic property of a solid material. It is also related to many important areas of technology. Wetting has many advantages as a subject for study. It is easily measured, and very sensitive to the structure of the solid at or close to the solid-liquid interface. The liquid in a wetting experiment comes into contact with the surface conformally: that is, there are no issues in assuring molecular-level contact between the contacting condensed phases. The theoretical underpinnings of wetting are firmer than those of other materials properties of broad interest (e.g., fracture and toughness), especially as these properties relate to three-dimensional solids. In addressing the first question, we have emphasized research involving organic surfaces (or thin films, or interfaces). Surfaces, as quasi-two-dimensional materials systems, are relatively easily prepared and characterized (or at least, *more* easily prepared and characterized than three-dimensional systems). We have concentrated on two materials and two associated synthetic strategies. The first, and simpler, is molecular self-assembly. Molecular self-assembly provides a broadly applicable strategy for preparing organic self-assembled monolayers (SAMs). The second involves treating a pre-existing polymer (in

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most of our work, low-density polyethylene film) with sequences of chemical reagents that introduce organic functionality onto its surface.

Self-assembled monolayers are becoming important model systems with which to study interfacial phenomena. In a typical experiment, a silicon wafer is coated, by evaporation, with a thin gold film. Exposure of this film to an organic thiol or disulfide, either in solution or in the vapor phase, results in chemisorption of the sulfur onto the gold surface (forming an organic gold(I) thiolate) and ordering of the organic residues. The strength of the attachment of the thiolate to the gold is high – these systems are quite stable under a variety of circumstances required for their use in experiments involving wetting, adhesion, and related studies. Characterization of these systems involves a variety of techniques. X-Ray photoelectron spectroscopy, reflectance polarized IR spectroscopy, and measurements of wettability have proved most broadly useful, although now a range of other techniques – low-energy helium scattering, scanning tunneling microscopy, computation, frequency sum spectroscopy, electrochemistry, and others – are being applied to characterizing SAMs. These systems have a number of advantages. They can be prepared with a wide variety of structures, and with controlled variation in the composition and properties of the solid-vapor (liquid) interface. The experimenter has good control over the order of the system. Their disadvantages have primarily to do with their stability: because they are relatively limited in their thermal and mechanical stability, their principal application in real technology is limited to areas such as microelectronics and biomedicine.

Surface-functionalized polyethylene is prepared, typically, by exposure of polyethylene film to chromic-acid solution. The resulting interface is complicated both morphologically and in its functional-group chemistry, but has, as its principal functionalities, carboxylic acids and ketones aldehydes. It is possible selectively to functionalize the carboxylic acid groups, and the carbonyl-containing moieties are easily analyzed by internal reflectance IR spectroscopy. This material also has advantages: it is readily available in large quantities; it is relevant to real materials and technologies; it sometimes reveals phenomena that have no counterparts in the structurally simpler self-assembled monolayers, and directly exhibits properties characteristic of complex, heterogeneous materials. (The reconstruction of the functionalized polymer surface on heating or on mechanical deformation provides an example of a set of phenomena of this type.) Comparisons between functionalized polymers and self-assembled monolayers are particularly instructive. The disadvantages of polymer-derived surfaces are that they are, typically, not well ordered and often heterogeneous in both the

type and distribution of functional group.

Extensive studies of both systems have shown that it is, in fact, possible to correlate certain features of wetting with the behavior of functional groups on these organic surfaces. The translation of properties from solutions to surfaces is not, however, straightforward, although there are important parallels. Much of our effort has focused on studying the variation in wettability of surfaces containing acidic and basic groups by water as a function of the pH of the water. Our initial hypothesis in conducting these studies was very simple. For a surface containing carboxylic acids, for example, the transition from an acidic solution (for which surface carboxylic-acid groups would presumably be present in their protonated CO_2H form) to basic solutions (in which the carboxylic acid would be present as the more hydrophilic carboxylate CO_2^- form) should be accompanied by an increase in the wettability of the surface by water. The magnitude of this change would reveal the influence of hydrophilicity on wettability. It might also allow certain inferences to be drawn concerning the properties of carboxylic-acid groups at interfaces. Wettability, we hope, would also provide a technique for characterizing acidic and basic functional groups at interfaces.

In brief, these simple hypotheses were borne out, but the underlying physical phenomena are, perhaps, more complex than expected. Reactive spreading (driven by the heat of neutralization of carboxylic-acid groups by hydroxyl ions), adsorption of thin water films on the functionalized surfaces outside of the region of contact with the water drop; (quasi) reversible swelling and reconstruction of the solid surfaces on contact with water – all seem to be important. The apparent pK_a of the carboxylic-acid groups on the surface are also markedly different from those of similar groups in solution, for reasons that can be hypothesized but not yet unequivocally proved. The behavior of amine groups on surfaces is very poorly understood, and does not seem to follow any simple model.

Detailed examination of wetting on functionalized polymers and on SAMs is permitting the construction of a detailed physical-organic model of wetting, and leading to the preparation of new types of materials. This information is proving useful in a number of ways. It is valuable in understanding interactions of solid surfaces and contacting condensed phases, at a very basic level. It helps to rationalize and predict performance in technologies such as composite fabrication, adhesion, control of tribology, and inhibition of corrosion. It is generating and proving new analytical methods for surfaces and interfaces. It is leading to new materials, some with very complex structures. SAMs having surface-attached oligo (ethylene glycol) and oligosaccharide groups are of particular interest for their relevance to biotechnology and biocompatible materials.

These approaches to the relation of atomic-level structure and macroscopic properties are working very well, and promise to be of widespread utility in studies of a wide variety of systems involving organic surfaces. The relevance of these studies to polymer surfaces is clear. The next and more difficult phase of these research – making similar connections between structure and properties for three-dimensional solids containing or generating internal surfaces – is just beginning. Initial work suggests that solids containing extensive H-bond networks in the solid state – especially those derived from the cyanuric acid-melamine network – may be particularly valuable materials in making the transition from two-dimensional surfaces to three-dimensional solids. These H-bonded networks derived from CA·M are (or can be made to be) quasi-one- or two-dimensional, even in their three-dimensional form – that is, the three-dimensional solid can be considered in terms of ‘tapes’ or sheets. Thus, the architectural problems of designing and specifying solids based on molecular structure are relatively simple in these materials, and some of the lessons learned from studying solid-liquid interfaces may be carried over into studying solid-solid interfaces in these classes of materials.

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