Polymer Surfaces and Interfaces –
Key to High Performance Materials

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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 unresolved – 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 control 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. Wettability is a fundamental macroscopic property of a solid material. It is also related to many important areas of technology. Wettability 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 on Gold', C. Pale-Grosdemange, E. S. Simon, G. M. Whitesides, J. Am. Chem. Soc. 1998, 120, 10245. 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.

These approaches to the relation of atomic-level structure and macroscopic properties are working very well, and promise to be of interest 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 interfaces 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.