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**Annual Technical Progress Report
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**"Computer Simulations for the
Adsorption of Polymers onto Surfaces"**

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Statement of Progress

The objective of our current research is to develop theoretical models and computer simulations to examine the adsorption of polymers onto a variety of surfaces. Of particular interest is understanding how the architecture of the chain and conditions such as the nature of the surface or solvent affect the extent of adsorption and the morphology of the interfacial layers. By understanding the factors that affect adsorption, we can predict which chain geometries and conditions would yield the optimal interfacial structure for such applications as steric stabilization, adhesion and film growth. Below, we briefly summarize the results we have obtained in the last year.

The Behavior of Copolymers at a Liquid-Liquid Interface

We used both analytical arguments and molecular dynamics simulations to establish design criteria for interfacially active copolymers. Specifically, we have shown how the behavior of a linear AB copolymer at the interface between two immiscible fluids depends on: the chain's sequence distribution (arrangement of A's and B's along the backbone of a chain), solvent-polymer interaction energies and temperature (1,2). These predictions can be used in tailoring macromolecular surfactants that provide the optimal reduction in the surface tension between the two fluids.

Furthermore, we predicted the range of sequence distributions for which the copolymer will form large loops as it weaves back and forth across the interface. Thus, when we consider the fluids to be two phase-separated homopolymers, the predictions can be used to design the optimal copolymer additive for improving the internal adhesion and mechanical integrity of polymer blends.

As an additional aspect of this study, we examined the behavior of an alternating AB copolymer at the fluid-fluid interface (3). Here, we investigated the effect of varying the relative affinities between the monomers and the two different fluids. Through this study, we determined conditions under which the alternating chain becomes "delocalized," i.e., drifts away

from the interface and is preferentially located in one of the two fluids.

Through the above studies, we established molecular design criteria for fabricating polymers that will yield the desired interfacial behavior in both solutions and polymer blends.

Grafted Homopolymer Chains in a Poor Solvent

We determined the effect of solvent quality on a layer of end-grafted polymers using the random phase approximation combined with a numerical mean field analysis (4). For sufficiently poor solvents, the laterally homogeneous grafted layer is linearly unstable to fluctuations tangential to the grafting plane. In the unstable regime, the grafted layer forms a "dimpled" surface in which the depth of, and the distance between, the dimples depend on chain length, solvent quality and grafting density. Scaling relations are obtained for the length scale of the instability and for the phase boundary separating the linearly stable from the unstable regimes.

The general method we developed, numerical mean field analysis plus the random phase approximation, can be applied to a large class of systems to study both the equilibrium fluctuations and the structures formed when the mean field profile becomes unstable.

Amphiphilic Comb Copolymers in Oil/Water Solutions

We examined amphiphilic comb copolymers in which the backbone and side chains display different affinities toward water (5,6). Due to this unique architecture, the chains undergo unusual ordering in solution, from isolated micelles to extensive networks. To optimize the utility of these copolymers in a broad range of technological applications, it is important to isolate the factors that control structure formation in these complex macromolecules. We used molecular dynamics simulations to determine how the location of hydrophobic segments within the comb affects its conformation in water. We also examined the behavior of these chains in oil/water mixtures. From our conformational calculations, we determined the optimal comb architecture for adsorbing small concentrations of oil particles in aqueous solutions. We also investigated how the location of hydrophobic sites affects the interactions between two such

combs. The overall results from this study indicate how to tailor the comb architecture and solvent mixture in order to control the conformation and association of amphiphilic combs in solution. These predictions can be used to design emulsion stabilizers, detergents and micellar carriers for controlled release.

Modeling Polymer Adsorption Onto the Influenza Virus

Infection by influenza virus is initiated by the binding of virus to sialic acid (SA) groups located in glycoproteins and glycolipids on the surface of cells. Recent studies indicate that binding of influenza virus to erythrocytes is inhibited when polymers containing SA are adsorbed onto the viral surface (7). The extent of inhibition depends dramatically on the SA concentration in the polymer chains. We developed a Monte Carlo computer simulation to determine how the concentration of "stickers" (SA sites) in a polymer chain affects its conformation on a patterned, spherical surface (the virus) (8). For sticker concentrations between 25-75 %, the adsorbed chains form large loops that extend away from the viral surface. These loops act as steric stabilizers that effectively prevent virus-cell interactions. Our findings concerning the microstructure of the adsorbed polymers can rationalize the experimentally observed behavior.

The Behavior of Polymers in Concentrated Surfactant Solutions

Using Monte Carlo simulations, we are currently examining the properties of polymers in dense surfactant systems. In the present system, we focus on a lamellar solution of amphiphilic chains in a low concentration of oil and water particles. To this mixture, we add a small concentration of either AB copolymers or A homopolymers. In the latter case, we varied the length of the homopolymer and discovered that at a finite length, the homopolymer forms a phase-separated region within the lamellar structures (9). This phenomena has recently been observed in a comparable experimental system (10).

Using this simulation, we will examine the behavior of AB copolymer chains in the oil/water/surfactant mixture. Both the architecture of the chains and the relative concentrations of the differing species will be varied.

Future Work

The focus of our future work will continue to be determining how molecular architecture affects the interfacial properties of polymers. We will continue to use both analytical modeling and computer simulations to examine the behavior of macromolecules at the liquid-liquid and liquid-solid interface. We will also examine the role of copolymers in modifying the interface between phase-separated homopolymers. Below, we give a brief description of the specific topics we will investigate .

Chains at Liquid-Liquid Interfaces

a) Linear Copolymers at the Boundary Between Two Immiscible Fluids

In our previous calculations (1-3), we focused on the properties of a single copolymer at the interface. Furthermore, we neglected intramolecular interactions between units in the chain. We will now introduce both excluded volume and energetic interactions between the monomer units. These additions will allow us to probe the conformation of proteins at a fluid-membrane interface. Specifically, we will determine how the arrangements of hydrophobic sites within the chain affects the protein's equilibrium structure. In addition, we will modify the model to include multiple chains at the interface. Of particular importance is understanding how the presence of other chains influences the self-assembly of the copolymers at the interface.

At present, we assume that the interface remains rigid with the introduction of the single copolymer. New calculations will be undertaken to determine how multiple copolymers affect the curvature elasticity of the interface. In particular, we will determine how the copolymer sequence distribution affects the three elastic coefficients: the spontaneous radius of curvature, the bending modulus, and the Gaussian bending modulus. These calculations will indicate how the characteristics of microemulsions (such as droplet size and shape) can be tailored through addition of the appropriate copolymer.

b) Combs and Surfactants in Oil/Water Mixtures

We developed molecular dynamics simulations to examine the behavior of amphiphilic comb copolymers in water and oil/water mixtures (5,6). Through the simulations, we will now

focus on the interactions of combs and surfactants in a variety of solvents. The results will indicate how to tailor the polymer/surfactant architectures and the solvent in order to control the viscosity or phase behavior of the mixture.

Chains at Fluid-Solid Interfaces

a) Self-Consistent Field Calculations for Adsorbed and Grafted Chains

Recently, we developed a two-dimensional self-consistent field (SCF) model for copolymer adsorption onto laterally heterogeneous surfaces (11). The model has been expanded to three dimensions, thus allowing us to obtain equilibrium adsorption profiles along all the relevant directions. Using this model, we will determine the polymer density profiles for chains adsorbed onto a variety of patterned and rough surfaces. Specifically, we will calculate how the surface morphology affects the adsorption properties not only perpendicular to a wall, but also parallel to the interface.

An area in which the above technique will be particularly useful is in the investigation of "pinned micelles." For a grafted layer in a sufficiently poor solvent, we observed that the grafted layers form a "dimpled" surface (4), displaying structural inhomogeneities both perpendicular and parallel to the grafting plane. By examining this problem with our 3D-SCF model, we can completely characterize the size and shape of these dimpled structures.

b) Monte Carlo Simulations of the Steric Stabilization of Colloidal Particles

We are currently developing a Monte Carlo computer simulation to model the interactions of polymer-coated spheres with penetrable and impenetrable surfaces. The specific problem we are investigating is how adsorbed copolymers inhibit the binding of influenza virus to cell surfaces (8), however, the model is also appropriate for examining the steric stabilization of other colloidal particles. In particular, we will determine how the conformation of the adsorbed chains affects the interactions between the particle and the wall.

Phase Separation in Polymer Blends

a) Blends of Linear and Comb Copolymers

A significant number of theoretical models have been developed to examine the phase behavior of mixtures of different linear chains. There has been very little work, however, on the thermodynamics of blends containing both linear and comb copolymers, or mixtures of different comb copolymers. Comb or branched macromolecules constitute a commercially important class of polymers. Thus, understanding how this architectural feature affects phase behavior is of significant scientific interest and technological importance. Our goal is to develop an expression for the free energy of mixing for linear and comb copolymers. Using this expression, we will determine how the presence of specific monomers in side chains versus along backbone sites affects miscibility. In previous work, we demonstrated that the sequence distribution in copolymers dramatically affects the phase behavior in copolymer/homopolymer or copolymer/copolymer blends (12-15). We showed that blends can be made miscible by altering the arrangement of the co-monomers in the backbone. Analogous to these studies, we will determine how to control phase behavior by varying the degree of branching in one of the polymer components.

b) Copolymer Compatibilizers

Understanding the role of molecular architecture is important not only for producing miscible, homogeneous blends but also in controlling the interfacial tension at the boundary between two immiscible polymers. Copolymers that are effective at lowering this surface tension are referred to as "compatibilizers." Such chains are crucial in maintaining the structural integrity and improving the mechanical properties of materials containing domains of phase-separated polymers. We are currently developing models to contrast the compatibilizing activity of linear versus branched copolymers at the interface between two phase-separated homopolymers. While linear, diblock chains are hypothesized to be the most effective compatibilizers, graft and branch compatibilizers are commonly used in actual industrial applications (16). An important goal of our calculations will be to quantify the effect of molecular architecture on reducing interfacial tension.

c) Effect of Temperature on the Interface Between Two Immiscible Homopolymers

In addition to investigating the effect copolymers exert on the properties of the interface between immiscible homopolymers, we will also examine the effect of varying temperature on the phase behavior at the interface. This interface becomes unstable when temperature is elevated. In order to examine this instability, we generalized the mean field theory developed by Hong and Noolandi (17) to the case where there is no solvent. We obtain numerical solutions for this new mean field model and then apply the recently developed random phase approximation (4) to study the instability of the mean field solution.

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(Papers Acknowledging DOE support are indicated by an *)

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Recent Presentations

Acknowledging DOE Support

Gordon Conference on Polymers, Wolfsboro, New Hampshire, June 29-July 3, 1992.
"Theoretical Models for Polymer Blends." *invited talk*

American Chemical Society, San Francisco, CA, April 5-10, 1992.

- "Adsorption of Copolymer Chains at the Liquid-Liquid Interface." *invited talk*
- "Molecular Models for Film Formation Between Solid-Solid and at Liquid-Liquid Interfaces." *invited talk*
- "Modeling the Interactions Between Polymer-Coated Viruses and a Cell Surface." *invited talk*

American Physical Society, Indianapolis, IN, March 15-20, 1992. "Localization of Copolymer Chains at Penetrable Interfaces."

Case Western Reserve University, Cleveland, OH, March 6, 1992. "Theoretical Models for the Behavior of Polymers at Interfaces." *invited talk*

Massachusetts Institute of Technology, Cambridge, MA, December 9, 1991. "Theoretical Models for the Interfacial Behavior of Copolymers." *invited talk*

Dow Chemical Company, Midland, MI, November 1991. "Interfacial Properties of Comb and Linear Copolymers." *invited talk*

Akron Polymer Science Lecture Group, Akron, OH, November 1, 1991. "Modeling Polymer Behavior at Interfaces." *invited talk*

University of Connecticut, Institute of Materials Science, Storrs, CT, October 25, 1991.
"Theoretical Modeling of the Interfacial Properties of Copolymers." *invited talk*

American Institute of Chemical Engineers, Pittsburgh, PA, August, 1991.

- "The Behavior of Associating Polymers Between Two Parallel Surfaces." *invited talk*
- "Effect of Polymer Geometry on Surface Adsorption." *invited talk*

IBM Almaden Research Center, San Jose, CA, May, 1991. "Effect of Molecular Architecture on Copolymer Surface Adsorption." *invited talk*

University of California, Davis, Chemical Engineering Department, Davis, CA, May 1991.
"Effect of Molecular Architecture on Copolymer Surface Adsorption." *invited talk*

Naval Research Laboratories, Washington, D.C., May 1991. "Polymer Adsorption on Laterally Heterogeneous Surfaces." *invited talk*

American Chemical Society, Atlanta, GA, April 1991.

"The Effect of Copolymer Sequence Distribution on the Miscibility of Ternary Blends." *invited talk*

"Modeling Copolymer Adsorption on Chemically Heterogeneous Surfaces." *invited talk*

"Modeling the Behavior of Comb Polymers in Solution." *invited talk*

Kodak Corporation, Rochester, NY, March 1991. "Modeling Copolymer Adsorption on Chemically Heterogeneous Surfaces." *invited talk*

American Physical Society, Cincinnati, OH, March 1991. "Modeling Copolymers Adsorption on Laterally Heterogeneous Surfaces."

Dartmouth College, Chemistry Department, Hanover, NH, February 1991. "Computer Models for Polymer Adsorption on Chemically Heterogeneous Substrates." *invited talk*

Indiana University - Purdue University at Indianapolis (IUPUI), Chemistry Department, January 1991. "Modeling Polymer Adsorption on Chemically Heterogeneous Substrates." *invited talk*

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