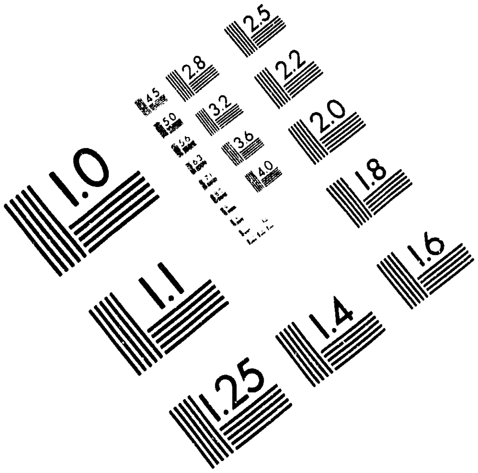
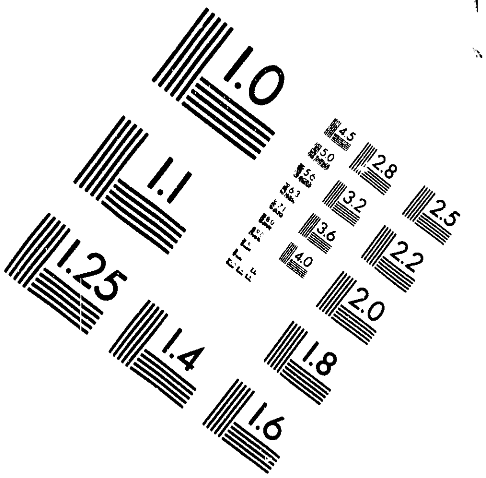
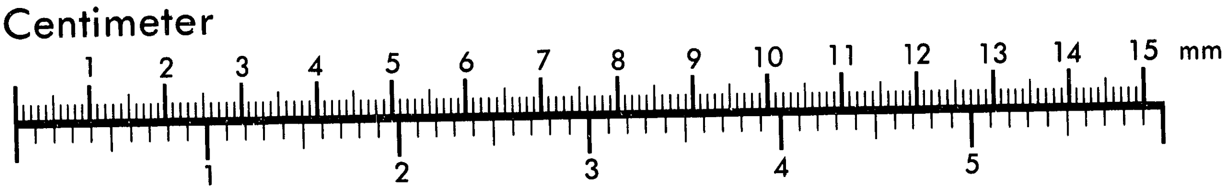


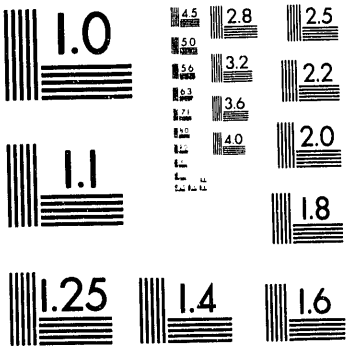
AIIM

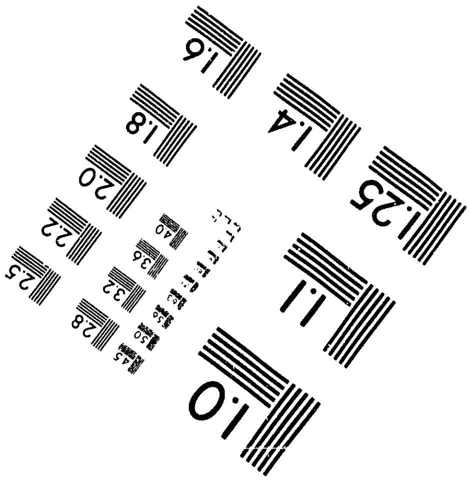
Association for Information and Image Management

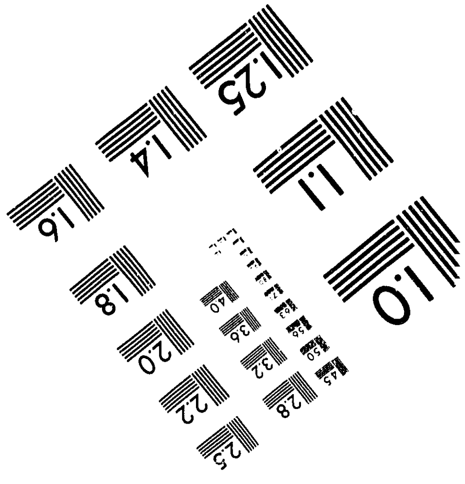
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202











MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

Progress Report:

DOE Grant Number: DE-FG02-90ER45438.

Computer Simulations for the Adsorption of Polymers onto Surfaces

Anna C. Balazs
Bicentennial Alumni Faculty Fellow
and Associate Professor

848 Benedum Hall
University of Pittsburgh
Pittsburgh, PA 15261

INTRODUCTION

The behavior of polymers at interfaces makes them a crucial ingredient in a broad range of contemporary manufacturing needs, including the production of food, pesticides, high-performance materials and the fuel to meet our energy requirements. In particular, polymer-modified surfaces facilitate every stage of oil and coal production. From drilling and mining, to transport and processing and finally to cleaning up undesirable by-products, polymer-surface interactions enhance the commercial viability of these processes (1). For example, by adsorbing at the fuel-water interface, polymers stabilize oil-water emulsions and prevent flocculation of coal particles in solution (2). This in turn allows the fuels to be processed and transported. Furthermore, polymer coatings prevent the corrosion of iron and steel that are used in oil and gas pipelines. In the cases of spills, macromolecular surfactants are used to disperse oil slicks.

Another area of significant technological importance is the production of new, more energy-efficient materials. Composite materials in which polymers are bound to ceramic, metal or other polymer substrates are seen as a key development in this area. These materials again highlight the commercial utility to be found in exploiting polymer-surface interactions.

A third and newly-emerging application of polymer-surface interactions is in the area of medicine. In particular, coating surfaces with polymers can enhance the biocompatibility of artificial implants (3). Recently, it has been observed that copolymers adsorbed onto the influenza virus are effective at inhibiting cell-virus binding (4) and consequently, the onset of disease. Understanding the role of the adsorbed copolymer can lead to the rational design of antiviral drugs.

In order to optimize the properties described above, it is important to isolate the factors that influence the interfacial activity of polymer chains. To accomplish this goal, we developed theoretical models and computer simulations to determine the effects of polymer architecture, solvent quality and surface morphology on the properties of chains at penetrable and impenetrable interfaces. Below, I briefly summarize the significant results that emerged from research that was supported by our prior DOE grant, DE-FG02-90ER45438. This work will form the framework on which we will build our new models.

Results From Prior DOE Support

Polymers at Penetrable Interfaces

The Behavior of Copolymers at a Liquid-Liquid Interface

We used both analytical arguments and molecular dynamics simulations to determine how the chemical sequence distribution affects the conformation of an AB copolymer at a penetrable interface, such as the boundary between two immiscible fluids or incompatible homopolymers (5-8). We defined a parameter f, which characterizes the sequence distribution along the chain. We determined L*, the length scale on which the copolymer weaves back and forth across the interface. We found that L*, as a function of f, has a well-defined minimum (see Fig. 1). The results have significant implications for tailoring chains to optimize the desired interfacial properties. First, consider the penetrable interface to represent the boundary between two immiscible low molecular weight fluids. In this case, the sequence distribution that corresponds to the minimum in the curves constitutes an optimal copolymer additive, or macromolecular surfactant. By forming small loops and frequently intersecting the boundary, this architecture will be most efficient at reducing the interfacial tension between the two fluids.

We can also consider the case where the penetrable boundary models the interface between two incompatible homopolymers. Recent studies by Kausch and Tirrell (9) and Kramer et al (10) indicate that in order for copolymers to act as adhesives, which effectively "stitch" phase-separated homopolymers together, the copolymers must make long excursions back and forth across the penetrable interface. Our results indicate that chains at both ends of the sequence distribution spectrum, namely multiblocks with long segments of A's and B's and alternating-like copolymers, will provide this optimal behavior. Thus, our predictions can also be used to design the optimal copolymer additive for improving the internal adhesion and mechanical integrity of immiscible polymer blends.

As an additional aspect of this study, we examined the behavior of an alternating AB copolymer at the fluid-fluid interface (11). 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.

Amphiphilic Comb Copolymers in Oil/Water Solutions

In addition to examining the properties of linear amphiphilic copolymers, we also investigated the solution behavior of comb amphiphiles. Comb copolymers are composed of a long, flexible backbone and side chains or "teeth" that branch off this main chain. In amphiphilic combs, the backbone and side chains can display different affinities toward a given solvent. As a consequence of this unique architecture, the chains will undergo unusual ordering in solution (12). In particular, these chains can form isolated micelles (13) or associate into extensive networks, which dramatically enhance the solvent viscosity (14). In order to optimize the utility of these copolymers in a broad range of technological applications, it is important to isolate the factors that control the microstructure of the comb clusters.

We used molecular dynamics simulations to determine how the location of hydrophobic segments within the comb affects its conformation in water and oil/water mixtures (15). We first investigated how single chains containing hydrophobic teeth versus a hydrophobic backbone behave in water. In agreement with florescence studies on water-soluble combs having

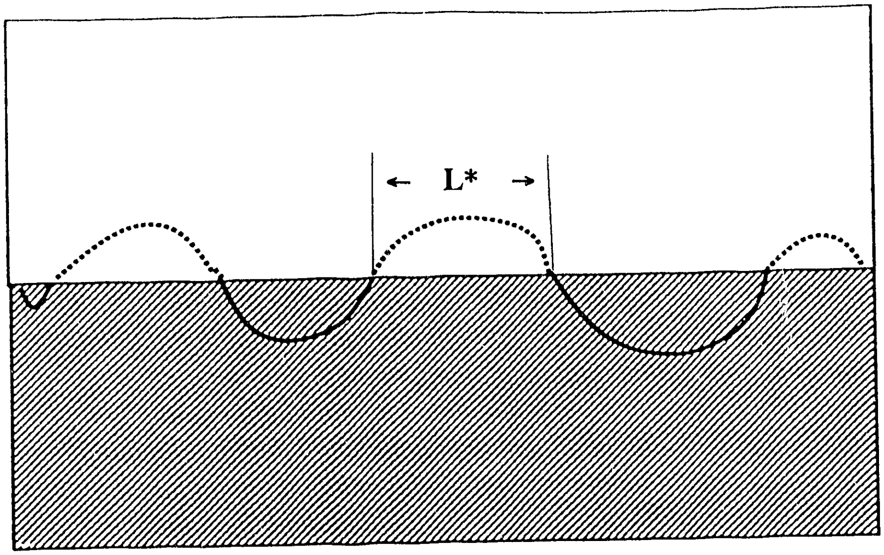


Figure 1(a). Schematic drawing of AB copolymer at the interface between two phase-separated homopolymers. The chain forms loops of length L* on either side of interface.

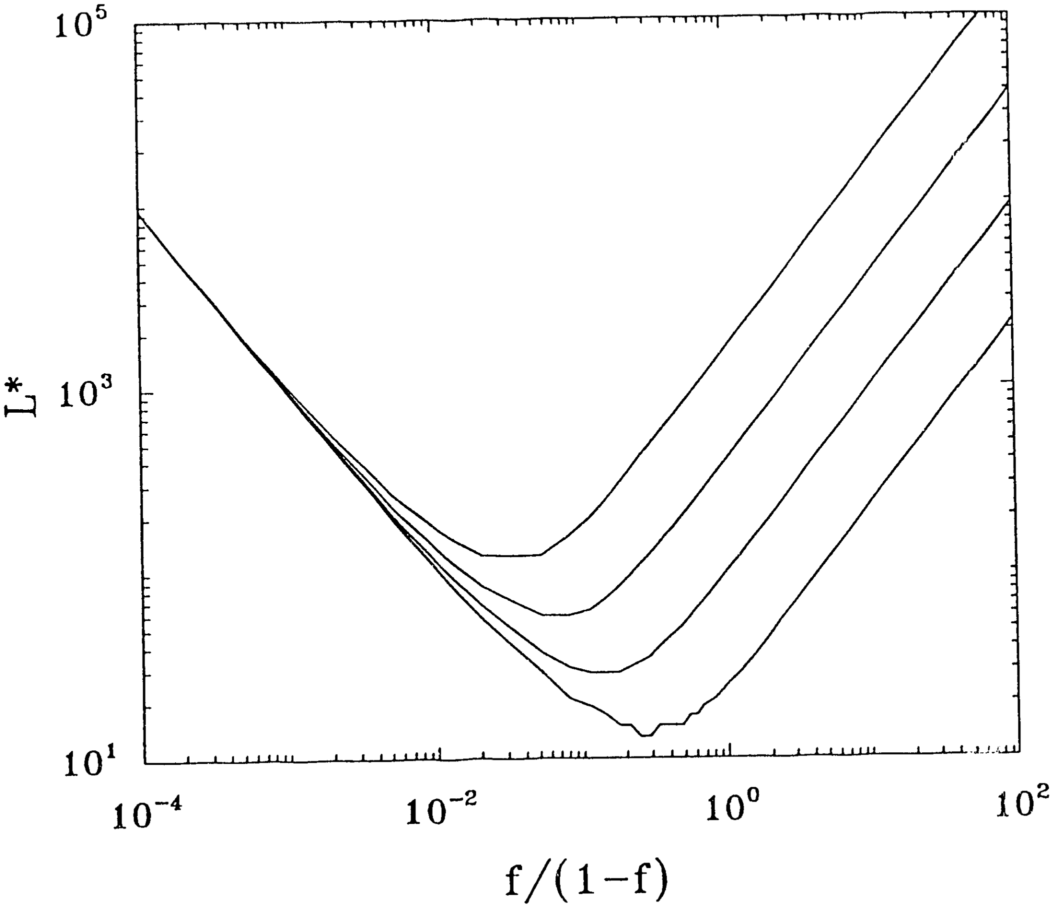


Figure 1(b). The plot of L* versus f. The parameter f describes the sequence distribution in the copolymer. For a copolymer that contains 50% A's and 50% B's, f=1 corresponds to an alternating chain, f=1/2 represents a purely random chain, and f → 0 corresponds to a blocky copolymer. The plot is shown for four values of Δ/T, where $\Delta \equiv \Delta_A = \Delta_B$ is the interaction energy between a monomer of A(B) and the homopolymer. Going from top to bottom, $\Delta/T = 0.05, 0.1, 0.2$ and 0.4.

hydrophobic teeth (16), we found that the oil-like teeth aggregate into a hydrophobic domain, causing the chain to form a micellar structure. In particular, the teeth form the core of the micelle and the hydrophilic backbone encircles this inner region. For the comb with the hydrophobic backbone, the chain also forms an intramolecular micelle. Here, the collapsed backbone forms the central core and the water-soluble teeth extend outward into the solution.

Of particular interest is determining how these combs behave when a small percentage of oil is introduced into the surrounding water. These studies can yield information on how the chains solubilize or incorporate small molecules into their micellar structures. We observed that the chain containing the long hydrophobic backbone is more effective at adsorbing and thus, removing oil particles from the aqueous environment (see Fig. 2).

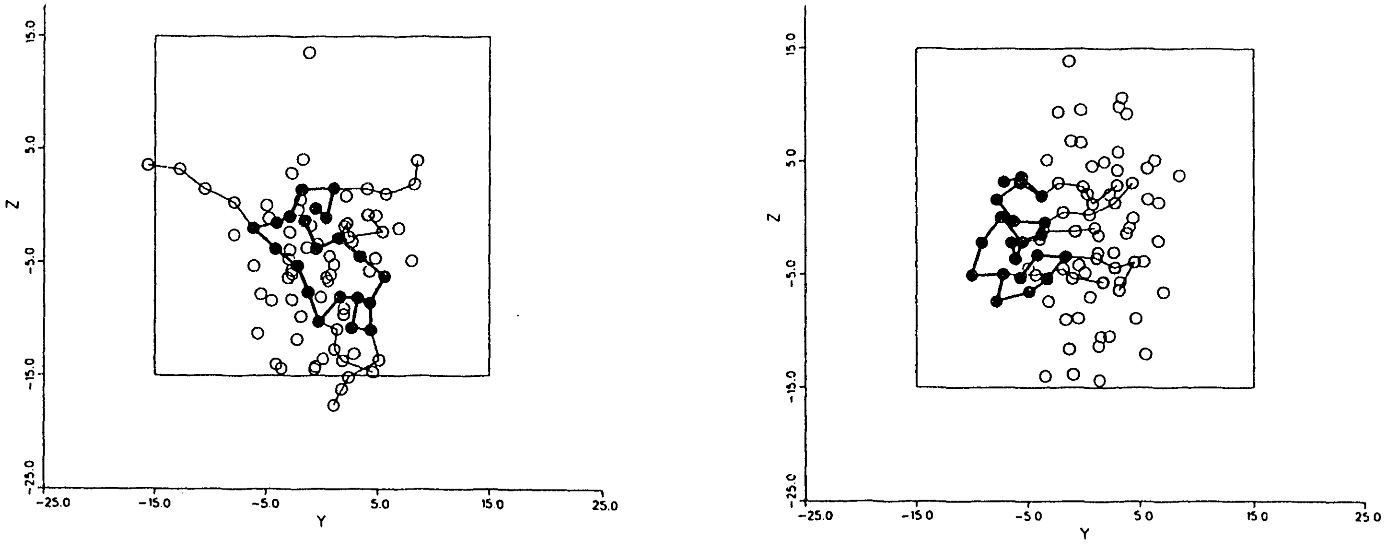


Figure 2. (a,left) Single chain with hydrophobic backbone (dark circles) and hydrophilic teeth (open circles) in 10% oil/90% water. (b,right) Single chain with hydrophilic backbone (dark circles) and hydrophobic teeth (open circles) in the same solution. The oil particles are drawn as open circles. 2D projection. (Reproduced from Balazs et al, Langmuir 8 (1992) 2295)

To gain insight into inter-comb association, we also investigated the interactions of two identical combs in solution. Figure 3(a) shows a typical view of the box containing combs with hydrophobic backbones and hydrophilic teeth. Here, the closely-spaced teeth sterically hinder the two chains from approaching each other. On the other hand, when these hydrophobic sites are located within the teeth, there is extensive intermolecular association. Now, the protruding hydrophobes can readily find the associated teeth on the neighboring chain. As can be seen in Figure 3(b), these chains form a single cluster. Consequently, such combs should prove to be more effective as viscosity modifiers than the reverse architecture.

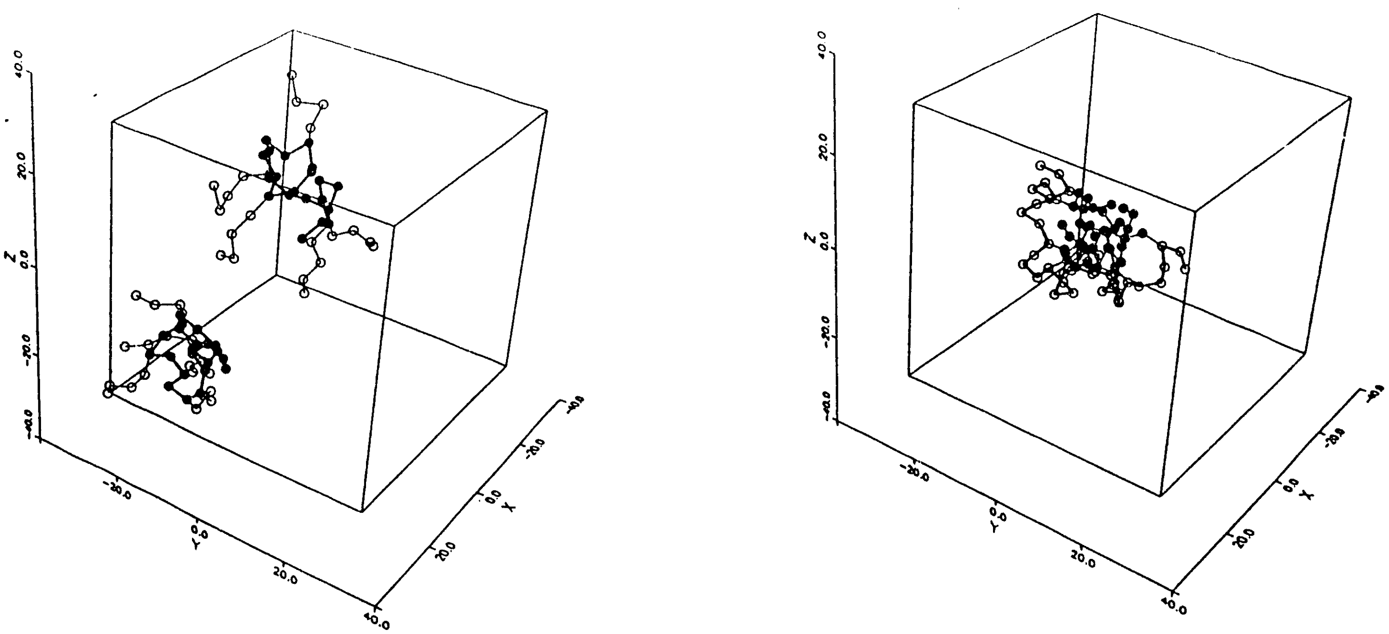


Figure 3. (a,left) Two chains in water. Both have hydrophobic backbones (dark circles) and hydrophilic teeth (open circles). 3D image. (b,right) Both chains now have hydrophilic backbones (open circles) and hydrophobic teeth (dark circles). 3D image. (Reproduced from Balazs et al, Langmuir 8 (1992) 2295)

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 "thickeners" for paints and coatings.

The Behavior of Homopolymers at the Interface Between Microphase-Separated Diblocks Copolymers

The phase behavior and morphology of block copolymers can be controlled by blending these chains with homopolymers. Since the morphology greatly influences the behavior of the materials, the blend can be tailored to display a range of rheological, mechanical and optical properties. Previous researchers focused on mixtures where the length of the homopolymer is comparable to the length of the corresponding block in the diblock (17). We used Monte Carlo simulations to model mixtures of symmetric diblock copolymers with small quantities of homopolymer; however, we examined the behavior of the system as the homopolymer length is systematically increased (18, 19). We found that when the homopolymer molecular weight becomes greater than that of the corresponding copolymer block, the homopolymer forms aggregates. These aggregates are highly localized in space and form bridges between adjacent lamellar microdomains (see Fig. 4). The presence of these aggregates does not, however, perturb the underlying lamellar morphology. The results are shown to be in excellent agreement with transmission electron microscopy studies on thin films of homopolymer/diblock copolymer mixtures of similar, relative molecular weights (18, 20).

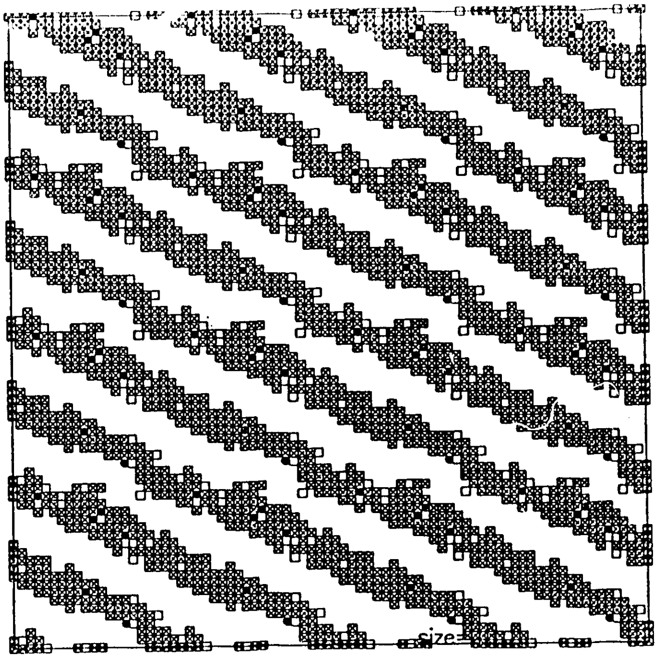


Figure 4a. One slice in a cubic lattice for a Monte Carlo simulation modeling an AB symmetric, diblock copolymer of 8 total units mixed with an A homopolymer of 20 units in length. Blank spaces are the B segments of the copolymer, ⊠ represent the A segments of the copolymer, • are the A homopolymer segments and □ are sites occupied by A solvent molecules. The simulation was for a 20 x 20 x 20 lattice. The 80 x 80 slice shown here was produced by periodic imaging.

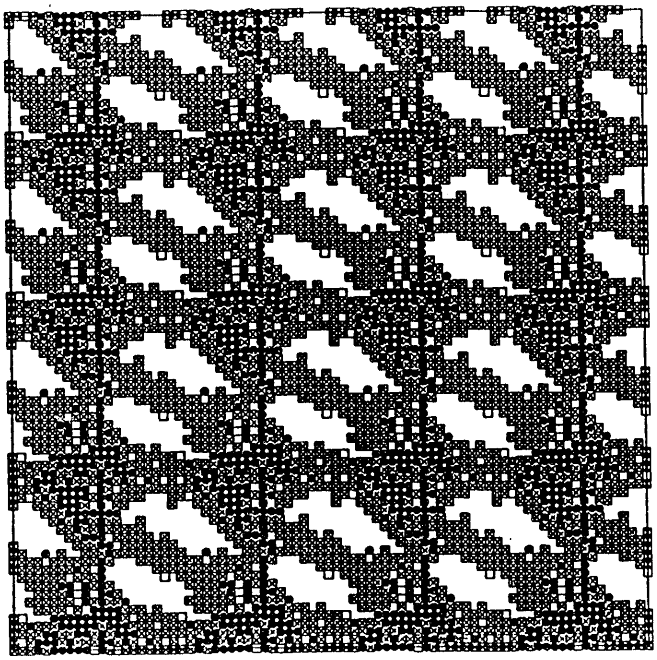


Figure 4b. Same as in Figure 4a, but showing a different slice in the cubic lattice.

Polymers at Impenetrable Interfaces

Grafted Homopolymer Chains in a Poor Solvent

We determined the effect of solvent quality on a layer of end-grafted polymers by using the random phase approximation (RPA) combined with a numerical self-consistent field analysis (21, 22). 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. In particular, for shorter chains, the depths of the dimples are approximately that of the layer height and the mean distance between dimples is proportional to the radius of gyration of the chain in a theta solvent (see Fig. 5(a)). As the chain length is increased, the instability is restricted to a region near the edge of the grafted layer. A dimpled structure is still formed, but the depth of the dimples is now given by the bulk correlation length, and the mean distance between the dimples is larger than the radius of gyration (see Fig. 5(b)). We also developed a two dimensional self-consistent field model for grafted chains (8). The results from this model confirm the predications we obtained from the RPA analysis, as can be seen in Figure 6. This figure represents the polymer density profile for the grafted layer. The density profile clearly shows the dimples predicted by our previous method. The figure illustrates the regime in which the dimples occur near the edge of the layer.

These studies on grafted layers are important for preparing multilayer coatings, where the first or primer layer governs the degree of adhesion between the substrate and a subsequent polymer coating. Furthermore, 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.

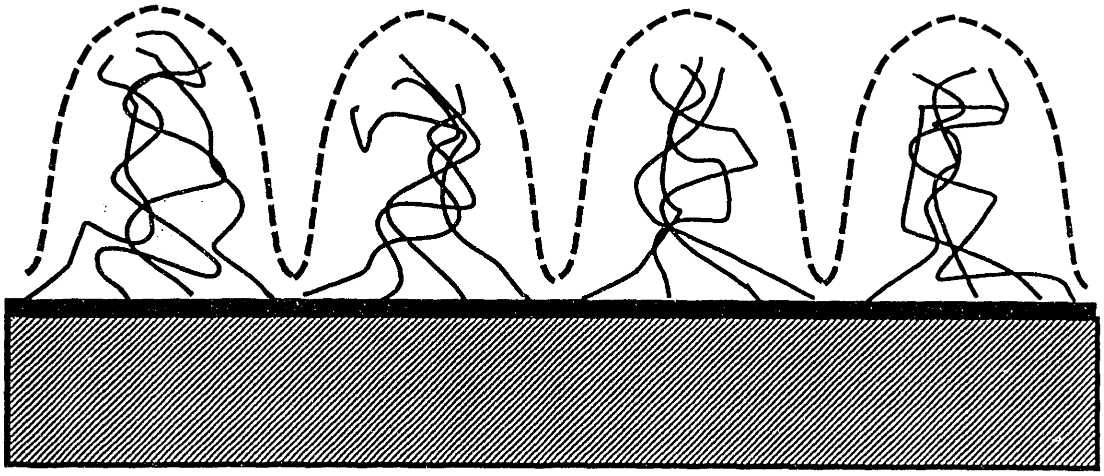


Figure 5a. A schematic showing the types of structures expected for short chains.

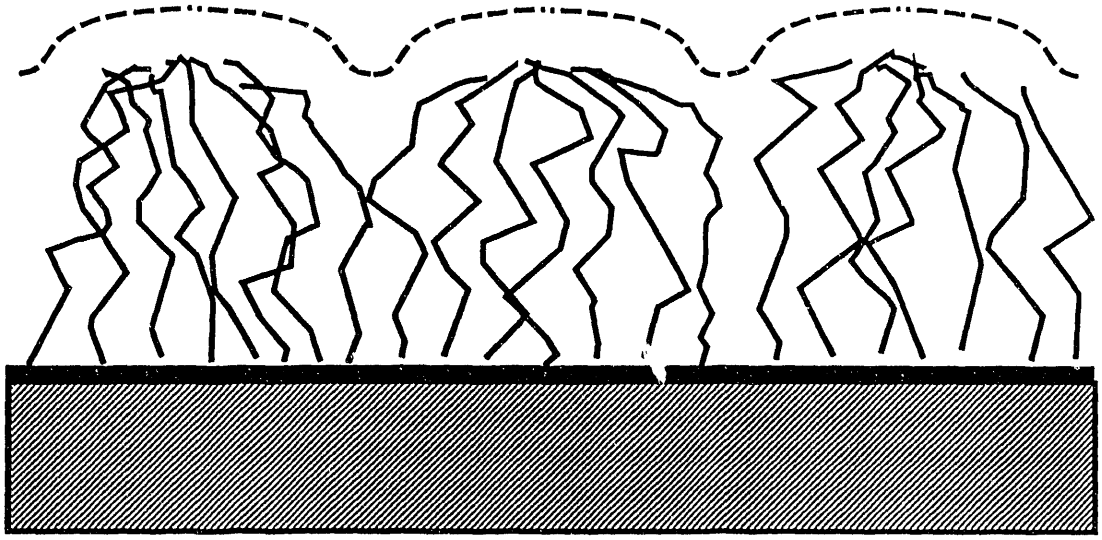


Figure 5b. A schematic showing the types of structures expected for longer chains.

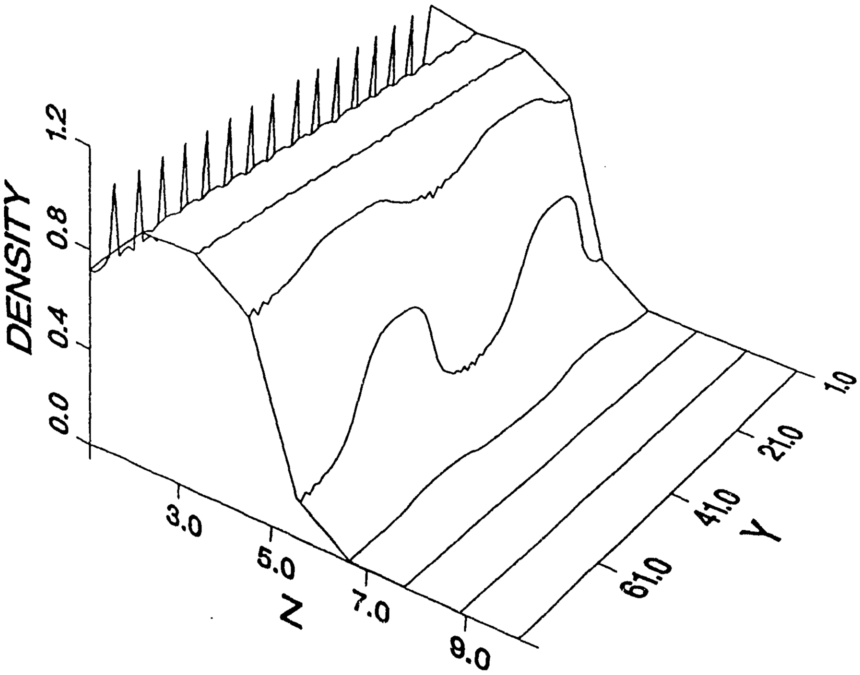


Figure 6. Three dimensional density profile for the grafted layer obtained from the SCF calculation. In this regime, the dimples occur near the edge of the layer, as in the schematic drawing above.

Contrasting the Surface Adsorption of Comb and Linear Polymers

Using Monte Carlo computer simulations, we contrasted the surface adsorption of comb and linear polymers that contain the same number of monomers (23). Both homopolymers and copolymer chains were examined. The homopolymers are composed of units that are strongly attracted to the surface ("stickers"), while the copolymers contain both stickers and sites that do not have a high affinity for the surface. Comb copolymers, which contain long "sticky" teeth, provide a higher or comparable surface coverage, thinner films and greater polymer-surface adhesion and wettability than the equivalent linear chains. For homopolymer and copolymer combs that contain sticky teeth, the behavior of the long teeth dominate the properties of the chains at the interface. Thus, differences between these two types of chains diminish as the tooth length is increased. Finally, combs that contain sticky backbones but non-sticky teeth provide a significant polymer density in the outer layers of the adsorbed film. Thus, the width of the adlayer can be tailored by varying the location of the stickers in the comb polymers.

Copolymer Adsorption onto Laterally Heterogeneous Surfaces

The aim of our investigations is to determine of the effects of molecular architecture on polymer-surface adsorption. By molecular architecture, we mean not only the geometry of the polymer chain, but also the structure of the adsorbing surface. Recently, we developed models for copolymer adsorption on laterally heterogeneous surfaces (24-26). Prior to these studies, work was focused on the adsorption of polymers onto chemically homogeneous surfaces. Real substrates, however, may be composed of more than one chemical species or can contain impurities that arise from contamination or corrosion. To determine how heterogeneities in the surface affect polymer adsorption, we developed a two-dimensional self-consistent field model (24) and Monte Carlo computer simulations (25, 26) to examine the adsorption of A homopolymers and various AB copolymers onto chemically heterogeneous substrates.

In the latter Monte Carlo simulation (26), the substrates contain random arrangements of two different molecules: S1 and S2. The A monomers are strongly attracted to the S1 sites, while the A-S2 and B surface interactions are weak in nature. The ratio of the S1/S2 surface sites was varied, and we determined how changing the fraction of S1 binding sites affects the properties of the adsorbed polymer films. To determine if the pattern of S1's and S2's affects polymer adsorption, we examined a random and ordered arrangement of surface sites. The results show that the arrangement of these sites influences the spatial distribution of the polymeric units on the surface. We also demonstrated that under certain circumstances AB copolymers are more effective at coating S1 surface domains than isolated A monomers. The results aid in tailoring polymers to yield films that display the desired characteristics on heterogeneous surfaces.

Another chemically heterogeneous interface that we examined is the surface of the influenza virus (27). 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 (4). 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). For sticker concentrations between 25-75%, the adsorbed chains form large loops that extend away from the viral surface (see Fig. 7). 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 (4).

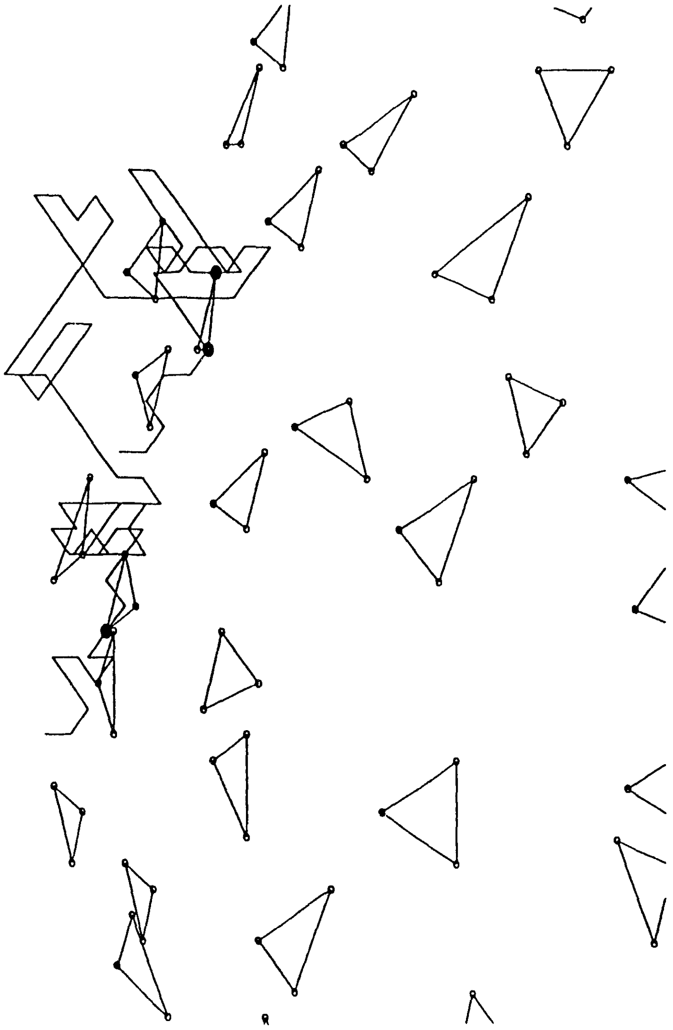


Figure 7. Copolymer adsorbed on the surface of the virus. The chain contains 50% stickers sites.

In summary, the results from the previous research allowed us to establish design criteria for fabricating macromolecular surfactants that are effective at:

- reducing the interfacial tension between immiscible liquids,
- extracting oil from aqueous solutions,
- forming viscosity-enhancing networks.

We also developed guidelines for creating coatings that:

- display a prescribed layer thickness and surface coverage,
- cover chemically heterogeneous surfaces,
- promote the adhesion of a subsequent polymer coating,
- provide optimal steric stabilization.

Our investigations of polymer/polymer composites yielded:

- a novel phase behavior in copolymer/homopolymer blends,
- copolymer architectures that enhance the strength of the interface between phase-separated homopolymers.

Overall, these results highlight the utility of using theoretical models and computer simulations to design interfacially active copolymers for specific applications.

REFERENCES

(An * indicates publications resulting from previous DOE award .)

1. Hancock, R.I. In "Surfactants"; Tadros, Th., F., Ed.; Academic Press: London, 1984; p. 287.

2. Napper, D.H. "Polymeric Stabilization of Colloidal Dispersions"; Academic Press: London, 1983.

3. Ward, R.S. IEEE Eng. Med. Biol. Mag. 1989, 6, 22.

4. Spaltenstein, A; Whitesides, G.M. J. Amer. Chem. Soc. 1991, 113, 686.

*5. Yeung, C.; Balzs, A.C.; Jasnow, D. Macromolecules 1992, 25, 1357.

*6. Yeung, C.; Balazs, A.C.; Jasnow, D. Polymer Preprints, 1992, 33, 558.

*7. Yeung, C.; Balazs, A.C.; Jasnow, D. In "Complex Fluids"; Sirota, E.B.; Weitz, D.; Witten, T.; Israelachvili, J. Eds.; Materials Research Society: Pittsburgh, 1992; p. 413.

*8. Balazs, A.C., Acc. Chem. Res., in press.

9. Kausch, H.H.; Tirrell, M. Annu. Rev. Mater. Sci. 1989, 19, 341.

10. Creton, C.; Kramer, E.J.; Hui, C.-Y.; Brown, H.R. Macromolecules 1992, 25, 3075.

11. Li, W.; Yeung, C.; Jasnow, D.; Balazs, A.C. Macromolecules 1992, 25, 3685.

12. Plate, N.A.; Shibaev, V.P. "Comb-Shaped Polymers and Liquid Crystals"; Plenum Press: New York, 1987.

13. Chu, D.Y.; Thomas, J.K. Macromolecules 1987, 20, 2133.

14. Bock, J.; Valint, P.L.; Pace, S.J.; Siano, D.B.; Schultz, D.N.; Turner, S.R. In "Water-Soluble Polymers for Petroleum Recovery"; Stahl, G.E.; Schultz, D.N., Eds.; Plenum Press: New York, 1986; p. 147.

*15. Balazs, A.C.; Zhou, Z.; Yeung, C. Langmuir 1992, 8, 2295.

16. (a) Ringsdorf, H.; Venzmer, J.; Winnik, F.M. Macromolecules 1991, 24, 1678.
(b) Winnik, F.M.; Ringdorf, H.; Venzmer, J. Langmuir 1991, 7, 905, 912.

17. (a) Shull, K.R.; Winey, K.I. Macromolecules 1992, 25, 2637, and references therein.
(b) Banaszak, M.; Whitmore, M.D.; Macromolecules 1992, 25, 2757.
(c) Winey, K.I.; Thomas, E.L.; Fetters, L.J. Macromolecules 1991, 24, 6182.

*18. Pan, T.; Huang, K.; Balazs, A.C.; Kunz, M.S.; Mayes, A.M.; Russell, T.P., submitted, Macromolecules.

*19. Balazs, A.C., Colloids and Surfaces, in press.

20. Mayes, A.M.; Russell, T.P.; Satija, S.K.; Majkrzak, C.F. Macromolecules 1992, 25, 6523.

*21. Yeung, C.; Balazs, A.C.; Jasnow, D. Macromolecules, in press.

*22. Yeung, C.; Jasnow, D.; Balazs, A.C., submitted, Colloids and Surfaces.

*23. Balazs, A.C.; Siemasko, C.P. J. Chem. Phys. 1991, 95, 3798.

24. Huang, K.; Balazs, A.C. Phys. Rev. Letts. 1991, 66, 620.

25. Balazs, A.C.; Huang, K.; McElwain, P.; Brady, J.E. Macromolecules 1991, 24, 714.

*26. Balazs, A.C.; Gempe, M.; Zhou, Z. Macromolecules 1991, 24, 4918.

*27. Zagst, K.J.; Balazs, A.C.; Whitesides, G.M. In "Proceedings, Sixth National Conference on Undergraduate Research"; Yearout, R.D.; Ed. University of North Carolina: Asheville, N.C., 1992; Vol. II, p. 1201.

8/5/93

END