Modeling the Behavior of Random Copolymer Brushes

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Introduction

A polymer "brush" consists of a dense layer of chains that are anchored by one end onto a solid surface. The behavior of brushes has come under considerable scrutiny in the past several years.[1] Interest in these systems stems from the fact that the tethered chains can be used to control the properties of the underlying substrate. For example, tethering chains onto a nonreactive surface can facilitate the adsorption of a subsequent layer or coating. The brush, sandwiched between the solid surface and the outer coating, acts as a "primer" or glue between the two layers. Polymer brushes can also be used to prevent surface adsorption. Specifically, hydrophilic brushes can inhibit the deposition of biopolymers and thereby enhance the biocompatibility of artificial implants.[2] To take full advantage of these surface-modifying properties, we must enhance our understanding of how the composition of the chains, or the quality of the surrounding solvent, affects characteristics of the brush.

To date, there have only been a few studies relating the composition of the chains to the overall structure of the brush. Investigators have examined the behavior of a brush that contained a 50/50 mixture of incompatible homopolymers, A and B.[3,4] They predicted the formation of a "rippled" phase, where the polymers undergo a lateral phase separation into distinct A-rich and B-rich domains. In addition, Dong et al.[5] observed distinct patterns of phase separation in brushes composed of grafted diblocks. Unique structures have also been observed in polymer brushes where attractive functional groups are attached to the free ends of the chains.[6,7] In this case, a "layering" effect is observed: the functional groups are localized in a layer at the top of the brush. (Note that "rippling" refers to a lateral phase separation, while "layering" refers to a vertical segregation.)

In this paper, we probe the effects of chain composition by comparing brushes that are composed of different AB copolymers. Here, each chain contains both A and B monomers, where the A monomers are compatible with the surrounding solvent, while the B monomers are solvent incompatible. We alter the copolymer sequence distribution and determine how both the vertical and lateral morphologies of the brush are affected by these variations. We draw upon two different techniques to carry out our investigations: Monte Carlo simulations and numerical self-consistent field (SCF) lattice calculations. The advantage of the SCF method is that the results provide a description of the system at thermodynamic equilibrium. However, the one-dimensional calculations only yield information on the behavior of the brush in the direction perpendicular to the surface.[8] On the other hand, the Monte Carlo simulations allow us to determine the location and conformation of each individual chain and, therefore, allow us to probe both the perpendicular and lateral properties of the brush. Taken together, the methods form useful "design tools": through these techniques, we can vary the copolymer architecture and establish guidelines for fabricating brushes that yield the desired characteristics.

Models

In our Monte Carlo simulations, we consider systems of monodisperse, grafted copolymers. The chains are modeled as self-avoiding random walks on a three-dimensional, cubic lattice. Each chain is anchored at one end to the $Z = 1$ plane, which represents the surface of a solid substrate. (The anchoring bead is the first monomer in the chain.) We use the bond fluctuation model[6,9] to simulate the motion of the polymers. To model the solvophobic nature of the B sites, we introduced an attractive interaction, Δ, between these monomers. This parameter exerts an effect through the Metropolis algorithm:[10] moves that reduce the energy of the system are accepted with unit probability, and moves that increase the energy of the system are weighted by a Boltzmann factor. In the calculations presented here, the value of Δ was held fixed at $-0.7\ kT$.

The size of the lattice in our simulations was $64 \times 64 \times 156$ sites, the largest dimension being along the Z direction. Periodic boundary conditions were imposed in the X and Y directions, while the Z direction was bounded by impenetrable hard walls at $Z = 1$ (the grafting surface) and $Z = 156$. The system was equilibrated by running the simulation for at least 2×10^5 Monte Carlo steps, where each Monte Carlo step involved $N_{\text{chain}} \times (N_{\text{beads}})^3$ attempted moves. (The parameter N_{chain} refers to the number of chains in the system, and N_{beads} refers to the number of sites or beads on each chain.) The chain length was 36 segments for all the simulations, and the surface coverage was fixed at 15% (corresponding to $N_{\text{chain}} = 153$). Results were averaged over three to five independent runs for each system.

Our self-consistent field method is based on that developed by Scheutjens and Fleer,[11] which in turn is based on a Flory−Huggins approach, combining Markov chain statistics with a mean-field approximation. The equations in this model are solved numerically and self-consistently. The self-consistent potential is a function of the polymer segment density distribution and the Flory−Huggins interaction parameters. The effect of randomness on the properties of copolymers was first incorporated into the SCF model by van Lent and Scheutjens.[12] Here, each monomer has a finite probability of being either an A or B site. Thus, their model introduces an annealed randomness, where the ensemble of sequence distributions in the system is allowed to fluctuate. Consequently, it is difficult to isolate the effect of systematically varying the sequence distribution through this model.

We adopt a different approach to specifying the randomness of the chains. We consider each polymer as a separate molecule and fix its sequence distribution at the start of the calculation. This models a quenched or frozen randomness, where each chain retains its sequence distribution throughout the calculation. For all the SCF results presented in this paper, each system involved specifying the sequence distribution of 2500

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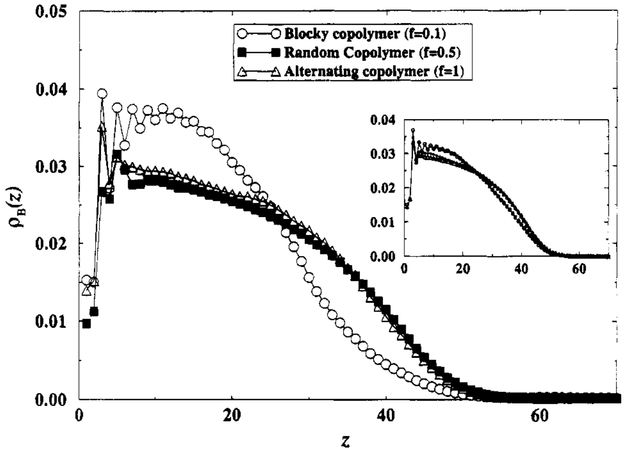

Figure 1. Normalized density profiles for the solvophobic component, $\varrho_B(z)$, in the Z direction for three values of the order parameter, f. The inset shows the normalized density profiles for the entire brush, $\varrho(z)$, for the corresponding values of f. These profiles were obtained from the Monte Carlo simulations.

individual chains and all the results were averaged over five different realizations of these systems. In addition, the Flory–Huggins χ parameter characterizing the A–B interaction was fixed at $\chi_{AB} = 1.0$. The B-solvent interaction was described by setting $\chi_{BS} = 1.0$, while the A-solvent interaction was given by $\chi_{AS} = 0.0$. The calculation was performed for a chain length of 100 units, keeping the grafting density fixed at 15%.

In both the Monte Carlo and SCF calculations, the sequence distribution of each chain is set as follows. We let the variables P_A and P_B denote the fraction of A and B monomers in the molecule, respectively. Given a site A on the chain, the conditional probability that the next site is a B monomer is given by the parameter $P_{A\rightarrow B}$. We define an order parameter, f, through the following equation:[13]

$$P_A P_{A\rightarrow B} = (P_A P_B)^{1/2} f \qquad (1)$$

where f lies between 0 and 1. For all the calculations in this paper, we chose $P_A = P_B = 0.5$. For these values, $f \rightarrow 0$ corresponds to a diblock copolymer, $f = 0.5$ represents a purely random chain, and $f = 1$ corresponds to an alternating chain.

Results and Discussion

In order to study the effect of sequence distribution on the properties of polymer brushes, we ran the simulations for three particular realizations of the order parameter f: $f = 0.1$, 0.5, and 1.0. The first case ($f = 0.1$) corresponds to a polymer brush composed of "blocky" copolymers, the second case ($f = 0.5$) corresponds to a brush consisting of purely random copolymers, and in the third case, the brush is made up of alternating copolymers.

In Figure 1, we plot the normalized density profiles for the solvophobic component of the brush. The plot clearly shows an enhancement of the solvophobic component density, $\varrho_B(z)$, near the grafting surface. This indicates a "layering" transition, but the reason for this behavior is, at first glance, not entirely obvious. As the placement of the monomers along the chain length is random, there should be no preferential plane (in the Z direction) along which clustering occurs.

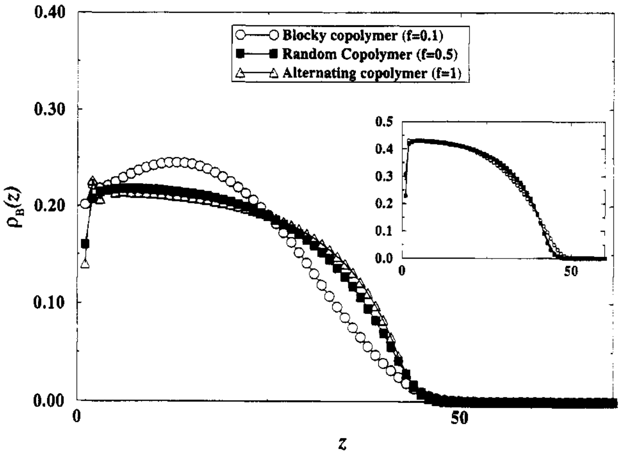

Figure 2. Normalized density profiles for the solvophobic component, $\varrho_B(z)$, in the Z direction for three values of the order parameter, f. The inset shows the normalized density profiles for the entire brush, $\varrho(z)$, for the corresponding values of f. These profiles were obtained from the self-consistent field calculations.

We believe that this "layering" is a result of chemical heterogeneities that stem from the statistical manner in which we add A and B monomers while growing the copolymers. As a result, the brush is composed of some A-rich polymers and some B-rich polymers, even though the overall composition of the brush is symmetric (equal numbers of A and B monomers). Consequently, when the system is exposed to a selective solvent, the B-rich copolymers contract to avoid the solvent. This results in an enhancement of the B monomers near the grafting surface. This effect is most pronounced in the blocky copolymer brush as finite size effects are strongest here. For the random and the alternating brush, the block length (which scales as $1/f$) is too small to cause any noticeable aggregation in the Z direction. We note that these compositional fluctuations are always present for finite length polymers and disappear only in the limit of infinitely long chains.[14]

The overall density profile of the brush, however, should be independent of f as the brush is compositionally symmetric. This is shown in the inset in Figure 1, where the total density profiles (for the A and the B monomers) are plotted for the three values of f. (The slight enhancement of density for the blocky copolymer brush arises from the statistical fluctuation described above.)

To check our Monte Carlo result, density profiles of the brush in the Z direction were calculated by the SCF method and are plotted in Figure 2. The overall density profiles for the three f values are now identical (see inset), reflecting the compositional symmetry in our system. The "layering" effect, however, is seen to persist in this calculation as the B monomers segregate to the surface (see Figure 2). This indicates that the "layering" transition is not an artifact of the Monte Carlo simulations.

To investigate the formation of lateral structures in the polymer brush, we define an order parameter following the treatment of Lai:[4]

$$\Psi(x,y) = \langle \varrho_B(x,y) - \varrho_A(x,y) \rangle \qquad (2)$$

where ϱ_A is the number of A sites in the Z direction for each point (x,y) and similarly, ϱ_B is the number of B sites in this direction. The angular brackets denote an ensemble average in the Monte Carlo simulation. The order parameter, $\Psi(x,y)$, for $f = 0.1$ and 0.5 is plotted in Figure 3. The darker regions in these plots denote

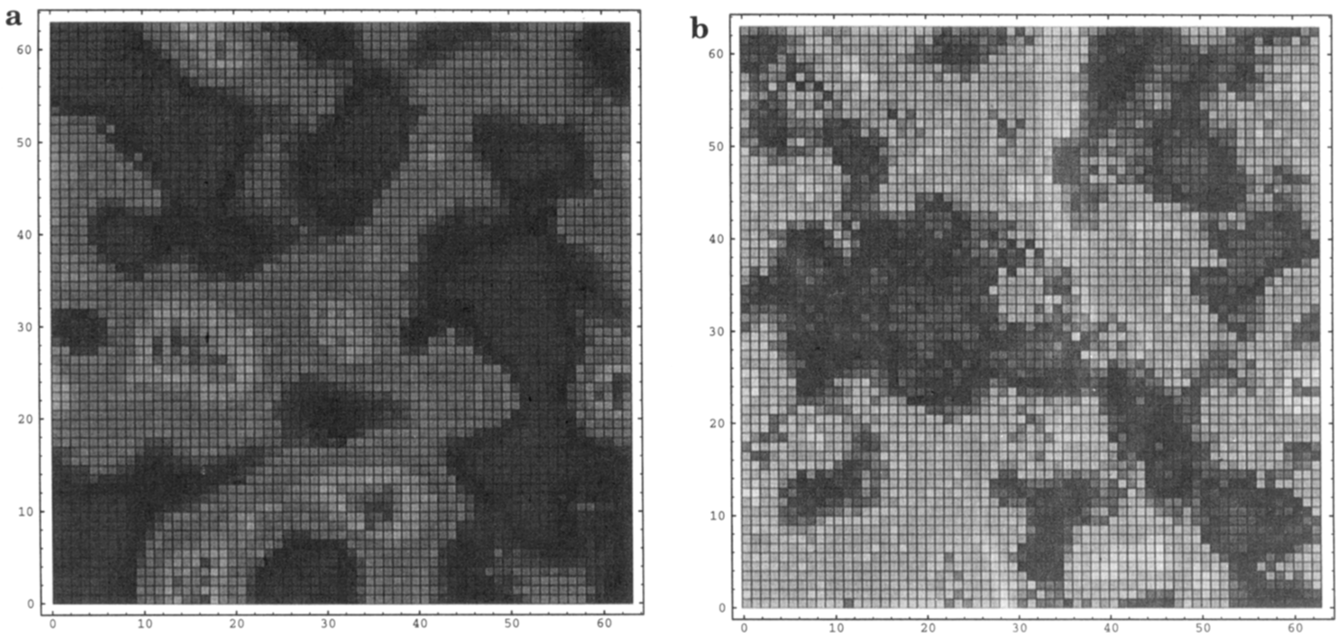

Figure 3. Plots of the two-dimensional order parameter, $\Psi(x,y)$. The darker regions represent the B-rich areas, while the lighter regions represent the A-rich areas. The plot in (a) is for the blocky copolymers. Note the well-defined domains of B's. The plot in (b) is for the random copolymers. The B domains are now smaller and not as clearly delineated. For the alternating copolymer brush, the order parameter is uniform over the *XY* plane, indicating that lateral phase separation does not occur in this system. These plots were generated from the Monte Carlo simulations.

the B-rich domains, while the lighter areas are the A-rich regions. The variations in the order parameter are clearly evident from these plots. The block copolymer brush shows the largest variations, with large, clearly defined domains of B monomers existing in the system. This behavior is reminiscent of the rippling phase seen in the grafted, incompatible homopolymers.[3,4] As seen in Figure 3b, the fluctuations in the order parameter are reduced for the random copolymer brush. These fluctuations disappear for the alternating copolymer brush.

In order to quantify these fluctuations, it is necessary to determine a characteristic length for the B domains. Unfortunately, finite size effects limit our ability to accurately extract these values from our simulations. In spite of this limitation, it can be clearly seen that the copolymer sequence distribution controls both the size and the distribution of these B-rich domains (Figure 3).

Conclusions

By combining SCF calculations and Monte Carlo simulations, we can visualize both the vertical and lateral structure of the brush. Our findings show that the overall morphology of the brush is dependent on the sequence distribution of the component copolymers. These results provide guidelines for controlling the size and shape of the B domains and, consequently, tailoring the brush for specific applications.

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