Polymer Adsorption on Laterally Heterogeneous Surfaces: A Monte Carlo Computer Model

Anna C. Balazs,* Kanglin Huang, and Pamela McElwain

Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

James E. Brady

Hercules Research Center, Hercules Incorporated, Wilmington, Delaware 19894

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ABSTRACT: We have developed an analytical model and Monte Carlo simulations to examine the adsorption of polymers onto laterally heterogeneous surfaces. The surface is composed of both S1 and S2 regions (stripes, checkerboards, random arrangements), and the chains have a higher binding affinity for the S1 sites. In the case where the number of S1 and S2 sites are held constant, decreasing the size of the respective regions will improve the segregation of the chains onto S1. Increasing the length of the polymer chain also affects the degree of segregation. These predictions are useful in improving the effectiveness of techniques aimed at controlling both the lateral and vertical properties of surfaces.

Introduction

Recently, Laibinis et al.[1] have developed a technique to control the characteristics of surfaces both parallel and perpendicular to the interface. Specificially, two distinct self-assembled monolayers are simultaneously formed by the adsorption of functionalized hydrocarbons (A1 and A2) from solution onto a laterally heterogeneous surface. This surface had been microlithographically prepared to contain defined regions of two different materials (S1 and S2). The constituents were chosen so that A1 displayed a high affinity for surface S1, while A2 possessed a high affinity for surface S2. The resulting system is highly ordered with A1's segregated onto the S1 domain and the A2's bound to the S2 region. This method permits the controlled generation and manipulation of surface structures on the micrometer scale. The technique can be exploited to create new interfacial materials with novel optical and electronic properties, as well as structures that will be useful in studying a wide range of issues in surface science.

The experimental results noted above clearly indicate the practicality and viability of this technique. However, systematic tests to determine the factors that control the degree of segregation of the absorbents onto the appropriate surface domains have yet to be undertaken. Here, we describe the first computer simulations to model the reversible adsorption of chainlike molecules or polymers onto laterally heterogeneous surfaces. In particular, we examine the adsorption of A1 chains from solution onto surfaces that are 50% S1 and 50% S2. With this 50/50 composition held constant, we alter the size and shape of the S1 and S2 domains on the surface and determine how these factors affect the degree of segregation of the A1 chains onto S1. It is critical to understand the behavior of this simpler system before investigating adsorption from multicomponent solutions.

Monte Carlo simulations provide distinct advantages in these investigations. They allow us to systematically and independently vary the size and shape of the surface domains, the length of the chains, and the adsorption and desorption rate constants. Such control and flexibility are difficult to achieve in laboratory experiments. Thus, simulations provide an optimal technique with which to predict how the above factors govern the behavior of this complex system. This model is also applicable to understanding the behavior of chain molecules near surfaces where the lateral heterogeneities are not intentionally introduced, but arise from corrosion or contamination of the interface. Thus, the results are also relevant to understanding the problem of creating a uniform film or coating over nonuniform surfaces.

The Model

We start by deriving an analytical expression for the degree of segregation of the chains onto the respective domains. We first consider the behavior of chemically identical chains near a laterally homogeneous surface. Each chain can bind to the surface through the reactive or "sticky" functional group located at one end of the chain. The total number of sites on the surface is given by N_t, and the number of surface sites occupied by the sticky ends ("stickers") is n_0. The other pertinent variables for the system are P_c, the probability, per unit time step, that a sticker on an unbound or free chain is one lattice site above a surface site; P_s, the sticking probability between a sticker and surface, or the probability that the sticker will actually bind to the surface when it collides with this interface; n_v, the number of unoccupied or vacant sites on the surface; P_r, the probability of the sticker desorbing from the surface; and, finally, P_v, which is comparable to an excluded volume parameter and which gives the probability that a chain can actually leave the surface when it desorbs, unhindered by steric effects from neighboring chains. This last parameter does not play a role when the adsorbents are solid particles, but is important in formulating the problem for chainlike molecules. (In other words, $P_v = 1.0$ in the case where the adsorbents are particles.) Using these parameters, we can write the following master equation for n_0:

$$dn_0/dt = P_c P_s n_v - P_r P_v n_0 \quad (1)$$

At steady state

$$dn_0/dt = 0 \quad (2)$$

Thus

$$P_c P_s n_v = P_r P_v n_0 \quad (3)$$

Now consider two surfaces of the same size, S1 and S2. The primed variables characterize the interactions on S2.

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Clearly, eq 3 will apply to both surfaces; thus we can write for interactions on S2

$$P_c'P_s'n_v' = P_r'P_v'n_0' \tag{4}$$

Dividing eq 3 by eq 4 we obtain

$$D \equiv n_0/n_0' = \left(\frac{P_r'}{P_r}\frac{P_s}{P_s'}\right)\left(\frac{P_c}{P_c'}\right)\left(\frac{P_v'}{P_v}\right)\left(\frac{n_v}{n_v'}\right) \tag{5}$$

$$= K\left(\frac{P_c}{P_c'}\right)\left(\frac{P_v'}{P_v}\right)\left(\frac{n_v}{n_v'}\right) \tag{6}$$

This ratio represents the number of chains on S1 relative to the number on S2 and, thus, is a measure of the degree of segregation of the chains onto the appropriate domain. Equation 6 clearly pinpoints the factors that affect the degree of chain segregation. The first term on the right-hand side of the equation is just the equilibrium constant, K, for the process. As can be seen, D depends not only on K but also on the relevant probabilities that characterize this system.

D is expected to be particularly sensitive to the value of P_c/P_c'. First consider the limit in which the concentration of chains in solution is extremely dilute: the number of bound chains will be relatively small, or $n_v \gg n_0$. The bound chains will be sufficiently dispersed on the surface that they will not hinder each other's motions. Consequently, P_v and P_v' will both approach 1.0. Furthermore, $n_v \approx N_t$ and $n_v' \approx N_t'$, and if $N_t = N_t'$, we have

$$n_0/n_0' = \left(\frac{P_r'}{P_r}\frac{P_s}{P_s'}\right)\left(\frac{P_c}{P_c'}\right) = K\left(\frac{P_c}{P_c'}\right) \tag{7}$$

Since the A1 stickers have a higher affinity for the S1 surface, P_s, the sticking probability between these species, is greater than P_s' (the sticking probability between A1 and S2). At dilute chain concentrations, this difference in P_s values causes the A1 chains to have more nonbinding collisions with the S2 surface. Consequently, P_c' is greater then P_c and the ratio P_c/P_c' in eq 7 contributes significantly to the value of D.

This conclusion is equally valid when the adsorbing species are particles. Again, the difference in P_s and P_s' governs the value of P_c/P_c', which in turn affects the value of D.

At higher polymer concentrations (the regime we consider here), the value of P_c/P_c' will also contribute significantly to D. In this case, the S1 surface will eventually become saturated with the A1 chains. It becomes more and more difficult for a chain to penetrate the dense brush of chains already bound to the S1 domain. In effect, the bound chains sterically hinder new chains from absorbing to this domain and force the new polymers onto the S2 region. Thus, the probability that an A1 chain will be above the relatively empty S2 surface will increase with time. Consequently, at high surface coverage, P_c' will again be greater than P_c.

On the other hand, the above conclusions do not apply for high concentrations of adsorbing particles. Here, incoming particles are not sterically hindered from approaching the S1 plane, and, consequently, particles can continue to diffuse along and bind to this domain until the surface is completely saturated. Even at high particle concentrations, it is the difference in P_s and P_s' that controls the value of P_c relative to P_c'.

For polymer chains, the value of P_c/P_c' and, consequently, the degree of chain segregation will clearly depend on the size of the S1 and S2 domains. Here, we are interested in the case where S1 and S2 are the same size,

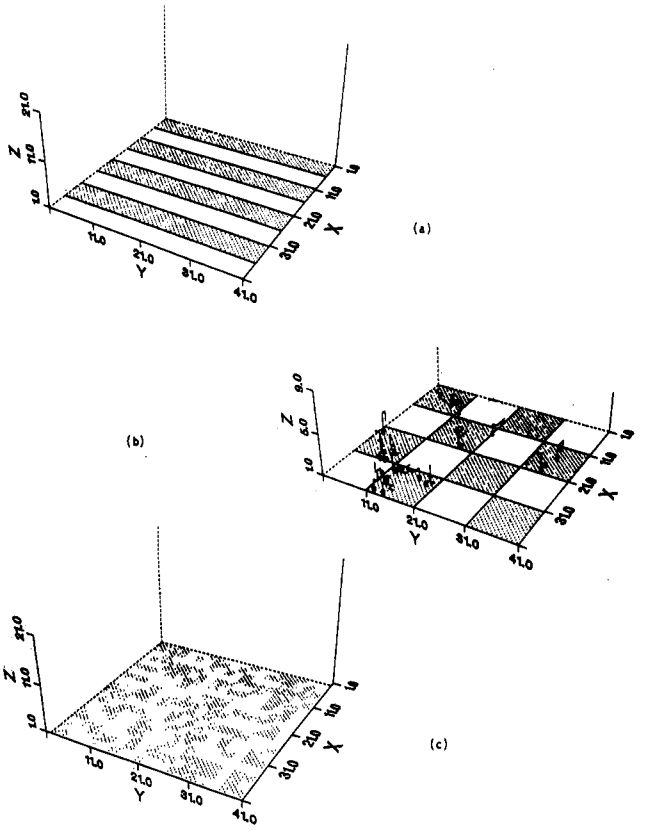


Figure 1. The various types of laterally heterogeneous surfaces that were investigated: (a) striped surfaces; (b) checkerboard surfaces; (c) random arrangements of S1 and S2 sites. The shaded region represents the S2 domain (or sites), while the white region represents the S1 domain. Each surface is composed of 50% S1 sites and 50% S2 sites.

and we first consider the domains to be arranged in a stripe pattern, with an S1 stripe adjacent to an S2 stripe (see Figure 1). The dependence of D on domain size is due to (1) kinetic effects and (2), more importantly, the increased importance of steric hindrance as the different domains are brought closer together.

To understand the origin of the kinetic effects, consider the scenario where each stripe is relatively wide: when an A1 chain is directly above the S2 domain, it must traverse a large area before it finds an energetically favorable S1 site. Here, the value of P_c' is large compared to P_c; thus, P_c/P_c' and D are small. However, when the size of the S2 domain is small, the A1 chain does not have to make such extensive excursions across this domain in order to locate the S1 region. Thus, the value of P_c' is relatively small and the values of P_c/P_c' and D are improved from the previous case.

Steric hindrance plays a significant role in improving the value of D as the domain size is decreased. The decrease in domain size brings the S1 and S2 sites into closer proximity. A chain that rapidly binds to the favorable S1 site can sterically hinder free chains from binding to neighboring S2 spots. This effect will be more pronounced as the domains are made smaller, since this change introduces more S1/S2 edges or interfaces. The effect will also be more pronounced for longer chains, where steric hindrance is more effective and, conversely, will diminish as the chain length is decreased to zero, i.e., in the case of particles.

Thus, for polymer chains, the degree of chain segregation can be manipulated by varying the size of the domain. This concept is tested below and examined for patterns of stripes, checkerboards, and random arrangements of

S1 and S2 sites. Furthermore, the behavior of polymers is contrasted with the properties of adsorbing particles.

In order to evaluate eq 6, we specify the values of P_s, P_s', P_r, and P_r'. The other terms on the right-hand side of the equation, P_c/P_c', P_v'/P_v, and n_v/n_v', can be obtained from the computer simulation of the system. The simulation will also yield a value for the degree of segregation. We will compare the results of eq 6 with the value obtained from the computer model.

The Computer Simulation

The simulation utilizes a three-dimensional cubic lattice that is $40 \times 40 \times 40$ lattice sites in size. Periodic boundary conditions are applied along the walls of the box. The $Z = 0$ plane represents the surface: half of the sites are designated S1 sites, while the other half are designated S2 sites. These sites are arranged in stripes or checkerboards of various sizes or in a random pattern (see Figure 1). Initially, 20 self-avoiding chains of uniform length are randomly placed in this volume. Here, each chain is 5 lattice sites in length, and the first bead of the chain is designated as the sticker, or associating site through which the chain binds to the surface. In this set of simulations, all the chains are type A1: they have a strong affinity for S1 and a much weaker attraction for S2. One of these chains is picked at random and is allowed to diffuse. The diffusive motion is accomplished by translating the entire chain one lattice site in one of six possible directions (to be chosen at random) and then "wiggling" the chain through the algorithm for chain dynamics developed by Verdier and Stockmayer[2] and Hilhorst and Deutch.[3] (One "wiggle" step is executed per every chain translation step.) All executed moves must obey the excluded volume criterion.

When a sticker is one lattice site above an S1 surface site, it can bind with a probability P_s. If the sticky end is above the S2 site, it can bind with a smaller sticking probability P_s'. Thus, in both cases, the chain may collide several times with the surface before it actually binds. The chain can also desorb from an S1 site with a probability P_r and from an S2 site with a probability P_r'. If a bound chain does not desorb, it can continue to wiggle about its point of attachment on the surface. (One "wiggling" motion is executed each time a particular bound chain is picked.)

Whenever a chain sticks to a surface site, a new chain is introduced into the cubic box. (If a chain desorbs, the chain furthest from the surface is removed from the lattice; thus the polymer concentration in the solution is kept constant.) In this way, more chains are introduced into the simulation and the S1 surface can become saturated. The simulation is run until the number of chains on the respective domains has reached a constant value and, thus, the system has reached a steady state. (This can take 30–110 million time steps.)

The respective values of the P_c's are obtained after the steady-state condition has been reached by counting the number of collisions between the chain and surface per a fixed unit of time. This is done for a million time steps to obtain an average value. In a similar manner, we can obtain the P_v values (after the steady state has been reached) by counting the average number of chains that *successfully* desorb per a fixed unit of time. (In order to have a "successful" desorption, not only must the variable generated by the random number generator in the simulation be less than P_r but also the chain must be able to leave the surface sterically unhindered by neighboring chains.)

To obtain the degree of segregation from the simulations, we simply count the number of A1 chains on both S2 and S1 sites. This count is made after the system has reached steady state. We note that in the results reported here, the surface coverage of S1 provided by the A1 chains (including both the sticky and nonsticky segments) is approximately $51 \pm 5\%$ (or 218 ± 32 chains). Significantly higher surface coverages (70–80%) can be obtained by decreasing the value of P_r, the probability of a chain desorbing from the surface. (We predict that the degree of surface coverage can be further enhanced by making the chains less flexible or by introducing an attractive interaction between the nonadsorbing segments. These experiments will be attempted in future studies.)

The computer simulations for particles are performed in the identical manner; however, now there are no "wiggle" movements in the diffusion of these species.

Results

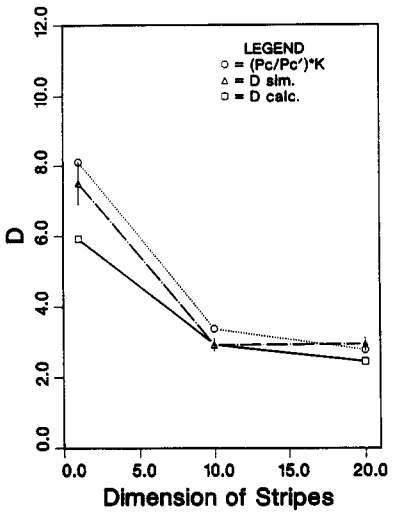
Figure 2a shows plots of D versus domain size for stripes of various sizes, and Figure 2b shows the same plot for the various sized checkerboards. Two different values of D are shown: D_{calc} represents the numbers obtained with eq 6, with the values for the relevant unknowns being obtained from the simulation, and D_{sim} represents the actual ratio of the amount of A1 on S1 to the amount on S2 observed in the computer model. Also shown are the corresponding values of $(P_c/P_c')K$, where K is the equilibrium constant and is equal to 10 in all the cases. These figures clearly indicate three important points. First, as predicted above, the degree of segregation of the A1 chains onto S1 is enhanced as the size of the domains is decreased. (Since P_c will be less than P_c', the optimum value of D will approach but be less than K, or in this case, 10.) Second, given the values of P_s, P_s', P_r, and P_r' chosen here, the value of P_c/P_c' dominates the behavior of D. This is clearly seen by noting the proximity of the $(P_c/P_c')K$ curves to the curves for D. Finally, the good agreement between D_{calc} and D_{sim} indicates the validity of eq 6.

It is interesting to note that there is no difference in the value of D for a stripe of 40×20 units and for two checks of 20×20 units each (which is comparable to cutting the stripe in half and shifting one square to the other side of the lattice). Though a given S2 site in the check is in greater proximity to a given S1 site, we see no difference in D values between the two cases since the domain size in both examples is so large compared to the size of the sticker site. Clearly, this suggests that there is a critical length scale that must be reached before the effects of domain size are felt.

In order to understand whether the shape of the domain is also critical, we compared the results for the case of the checkerboard pattern, where each check is 5×5 lattice sites, with the scenario where an equal number of S1 and S2 lattice sites are randomly arranged on the surface and the average dimensions of the resulting S1 (S2) batches are 4.6×4.6 lattice sites. Thus, while the average domain sizes are comparable, the shapes of the domains are different in these two cases. Table I contains a comparison of the values for D and P_c/P_c' for each of these systems. The proximity of the two sets of values indicates that the shape of the domain is less critical to the degree of chain segregation than the actual size of the domain.

Finally, in Figure 3 we examine the effect of chain length on the degree of chain segregation by plotting the value of D_{sim} versus domain size for the checkered surfaces for two different chain lengths, 5 and 10, as well as for particles. As can be seen for the smaller domain sizes, the degree of

a $P_s = 1.0, P_s' = 0.1, P_r = P_r' = 1 \times 10^{-4}, K = 10$



b $P_s = 1.0, P_s' = 0.1, P_r = P_r' = 1 \times 10^{-4}, K = 10$

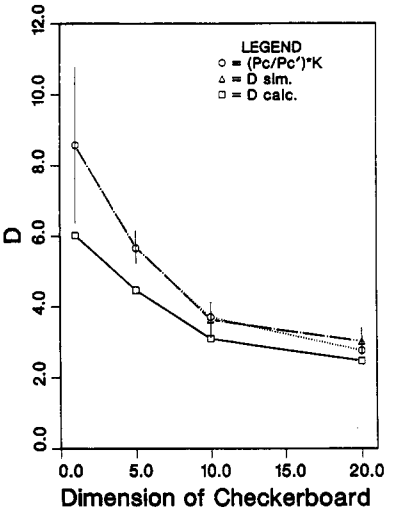


Figure 2. Plots of D_{calc}, D_{sim}, and $(P_c/P_c')K$ versus domain size for (a) the striped surfaces and (b) the checkerboard surfaces. In (a), the numbers along the horizontal axis represent the width of the stripe; the stripe length is held fixed at 40 lattice sites. In (b), the numbers along the horizontal axis represent the width and length of the check. The error bars refer to the measurements of D_{sim}. The chain length was held fixed at 5 lattice sites. The values of P_s, P_s', P_r, and P_r' used in the simulation are also given in the figure.

segregation is improved when the longer chain is used. However, in the case of the largest domains, there is no difference in the values of D_{sim} for the two cases. A decrease in domain size brings the S1 and S2 sites into closer proximity. As predicted above, the longer chains that rapidly bind to the favorable S1 sites can sterically hinder free chains from binding to neighboring S2 spots. As the domain size increases or the chain length decreases, this effect is suppressed. Consequently, for particles, the value of D is independent of domain size.

We note that the actual number of adsorbed species on S1 is reduced to approximately 132 ± 22 for the longer chains or a surface coverage of 39 ± 7%. Again, the overall steric hindrance from the nonadsorbing portion of the

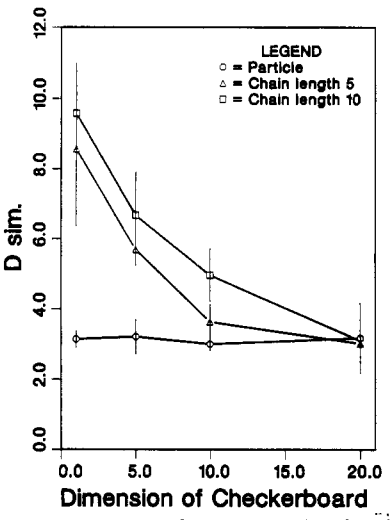


Figure 3. Plot of D_{sim} verus domain size for the checkerboard surface for chain lengths 5 and 10 and for particles. The values of P_s, P_s', P_r, and P_r' used in the simulation are given in Figure 2.

Table I

	P_c/P_c'	D_{sim}	D_{calc}
random (av cluster size = 4.6)	0.527	4.98 ± 0.59	4.09
checkerboard (5)	0.566	5.69 ± 0.45	4.47

chain prevents incoming chains from approaching the interface and subsequently binding to the surface.

Figure 3 highlights two other significant observations. First, the value of D is lowest for the particles. Here, the values of P_c/P_c' and D reflect the large disparity in P_s and P_s', and there are no nonadsorbing segments to improve the degree of segregation through the effects of steric hindrance. Finally, the value of D for all adsorbing species appears to reach this constant value when the domain size is large. On this length scale, the effects of steric hindrance are negligible, and the values of the specified parameters control the properties of the system.

In summary, we have shown that the degree of segregation of the chains onto the appropriate domain can be controlled by manipulating the morphology of the laterally heterogeneous surface. In particular, in the case where the number of S1 and S2 sites are held constant, decreasing the size of the respective domains will improve the segregation of the A1 chains onto S1. Altering the length of the polymer chain also affects the degree of segregation and thus provides another parameter through which to control the characteristics of the structure. These predictions are useful in enhancing the effectiveness of techniques aimed at providing both lateral and vertical control of surface properties.

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