Controlling Adsorption of Polymers at Polymer-Modified Surfaces

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ABSTRACT: Monte Carlo simulation is used to study the adsorption of diblock copolymers and homopolymers on bare surfaces and surfaces modified by end-grafted polymers at densities well below the brush limit. Monomer distribution profiles for the adsorbed polymer are used to compute the surface excess (Γ_{exc}). The competitive adsorption of asymmetric diblock polymers on bare surfaces is studied first, in order to compare with experimental results and to test the validity of our method. Γ_{exc} values can be used to obtain the adsorption isotherm, which are fit to a Langmuir model in order to estimate the maximum surface excess, $\Gamma_{exc}{}^{max}$, as a function of end-grafted polymer coverage and molecular weight. Competitive adsorption of different molecular weight polymers is simulated and the relative adsorbed amounts correlate well with $\Gamma_{exc}{}^{max}$ for the individual polymer. We find that the adsorption of symmetric diblock polymers is very similar to that of homopolymers. Surfaces modified by end-grafting mixtures of two different lengths of polymers are also considered. Bimodal surface modification creates density profiles that differ strongly from monodisperse end-grafts, and in some cases this serves to enhance the effect of selective size adsorption.

1. Introduction

Polymers at interfaces are an important part of a number of technological applications and have been reviewed extensively from a variety of perspectives.[1−8] There have also been technological applications of end-grafted polymers at surfaces, mostly for biomedical[2] and chromatographic[9] uses. Much work has focused on the polymer brush structure of dense end-grafted chains at a surface.[8,10] Scaling theory has been used to analyze the effect of an adsorbed polymer on the depletion of solvated polymers near a solid−liquid interface[11] and the adsorption of block copolymers from a nonselective solvent.[12] Competitive adsorption of different length polymer chains has been studied by a self-consistent-field lattice theory.[3,13,14] Monte Carlo simulation of competitive adsorption or displacement of end-grafted polymers has been performed previously for very short chains.[15] Competitive adsorption of end-adsorbing polymers has also been studied theoretically.[16] The kinetics of chain desorption[17] and end adsorption have also been studied in detail by Monte Carlo simulation,[18] as have homopolymer adsorption and competitive chain displacement[19] and diblock adsorption.[20] The Monte Carlo calculations in these latter papers are largely concerned with the dynamics of adsorption although the equilibrated state is also studied. Experimental competitive adsorption studies have been performed on different length polymers,[21] polymers of different chemical nature,[22] and varying block lengths in diblock copolymers.[21−25]

Generally, it is found that on bare surfaces longer chains adsorb preferentially, either for homopolymers[3,19,21,22] or symmetric diblock copolymers.[3] For diblocks in which one block adsorbs and the other does not (and for end-adsorbing polymers), the polymers with shorter nonadsorbing blocks adsorb preferentially if the adsorbing blocks are of the same length.[15,16,23−26] Likewise, for diblock copolymers with equal lengths of nonadsorbing blocks, those with longer adsorbing blocks adsorb preferentially.[23] Monte Carlo simulations[27] and self-consistent-field lattice theory[28] have been used to study heterogeneous surfaces which have nonadsorbing and adsorbing sites. The arrangement of the sites has been shown to affect the adsorbed amount[28] and the segregation into domains.[27] Controlling competitive adsorption of diblock copolymers by altering the size of the colloidal particles has been examined with scaling analyses.[29] Although some of these experiments and simulations have included the effect of previously adsorbed polymers on a surface, none considers the explicit effect of designing a surface with end-grafted polymers toward the goal of controlling the result of competitive adsorption.

In a previous paper,[30] we considered the effect of modification of surfaces by end-grafting nonadsorbing polymer chains on the adsorption properties of homopolymers. This work demonstrated that by end-grafting polymers to a surface the amount of adsorbed polymer was reduced and this reduction depended on the length of the adsorbing chain such that selective size adsorption could be effected.

In this paper, we first consider competitive adsorption of diblock copolymers on a bare surface (note that most calculations consider the adsorption of one type of a polymer at a time). The qualitative agreement with experiment[23] is reasonable, which demonstrates that this pivot method can be satisfactorily applied as a "computer experiment" for competitive adsorption to test analytical theory or to compare with SCF calculations. We note that the overall density of polymers is not high, such that SCF theory may not be an accurate representation of the system.[31]

Next we examine the effect of modifying a surface by end-grafting on the adsorption of symmetric diblock polymers. These results are similar to homopolymer adsorption studied earlier.[30] A simulation of competitive adsorption of these copolymers indicates that those which adsorb in greater amounts independently also do so competitively, as expected. Adsorption of polymers on surfaces modified by end-grafting chains of more than one length is also studied. The combination of two end-grafted chains of differing lengths creates a mono-

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mer distribution profile which is distinct from that of a monodisperse end-grafted structure. We find that a bimodal grafted surface has adsorption properties that are not some simple average, and in fact, grafting short chains can enhance the effect of long grafted chains in repelling longer chains in the solution phase. Since longer chains would normally preferentially adsorb, we term this effect "selective size adsorption", roughly analogous to size exclusion chromatography, although with a quite different physical basis. The enhanced effect of a bimodal grafted surface is similar to phenomena observed for a bimodal brush,[32] although we are below the surface density required to form a brush.

2. Method

The method used in these calculations has been described previously.[30] A modified version of the pivot algorithm[33] is used to simulate chains end-grafted or adsorbing onto a surface. The pivot algorithm is a "dynamical" Monte Carlo algorithm which generates new polymer chain conformations from a prior conformation by the use of a Monte Carlo pivoting move. This method is effective at sampling conformations but provides no information about polymer dynamics *per se* because the pivot moves are not physically realistic. For computational convenience the conformations are usually constrained to lie on a lattice as is done here, but this is not a requirement. The polymer chain is modeled as N contiguously linked monomer units executing a self-avoiding walk on the lattice. The chains are set in an arbitrary starting configuration (a straight rod perpendicular to the solid−liquid interface in our case) and new ensembles are generated by randomly moving the chains and by changing the conformation of a randomly selected chain by the pivot algorithm procedure. Excluded volume, polymer contiguity, and chain length are preserved by this method. Metropolis biasing is applied in order to generate a thermally equilibrated ensemble.[34] No energetic parameters are employed with respect to the end-grafted polymers other than excluded volume. For the adsorbing polymers a short-range attractive monomer−surface interaction energy (χ_s, given in units of kT) is included along with the excluded volume constraint. The energy, E, of the system is the sum of all monomers of the adsorbing homopolymers or of the adsorbing blocks of the diblock polymers in contact with the surface, c_w, (monomers with coordinate $z = 0$) multiplied by χ_s as given by eq 1.

$$E = -c_w\chi_s \tag{1}$$

The chains are allowed to thermalize for a sufficient number of pivot moves before the chain conformations are sampled.

The solid−liquid interface is defined as a rectangular box with a square face in the xy plane having an impenetrable surface located at $z = 0$ in the lattice coordinate space. To simulate the modified surface, chains are randomly end-grafted to the square face at $z = 0$. The dimension of the square face can be varied to effect the variation in grafting density. Periodic boundary conditions are applied in the x and y directions. Bulk solution chains are randomly placed in the box and allowed to move. Again, periodic boundary conditions are applied in the x and y directions and there is a reflective boundary far from the adsorbing surface. A typical box size is 30 × 30 lattice units in the xy (surface) plane and 80 lattice units in the z direction. Depending on the bulk polymer concentration sought, 5−80 chains are placed in the box.

The surface excess, Γ_{exc}, is measured by summing the excess monomer concentration at the solid surface as shown in eq 2:

$$\Gamma_{exc} = \sum_i^M(\phi_i - \phi_b) \tag{2}$$

ϕ_i is the volume fraction of monomer units at the ith layer and $\phi_i > \phi_b$ for adsorbing polymers. The Mth layer is picked to be sufficiently far from the surface that ϕ_i converges to ϕ_b well before this layer. While it is easy to start a calculation with an arbitrary overall volume fraction of solution lattice sites occupied by polymer, the value of ϕ_b is taken to be the limiting value at large z and is determined by the final equilibration of the system. Therefore the final value of ϕ_b cannot be obtained *a priori*. ϕ_b and Γ_{exc} are then fit to the Langmuir isotherm (eq 3) and $\Gamma_{exc}{}^{max}$ is obtained from the slope of ϕ_b/Γ_{exc} vs ϕ_b:

$$\phi_b/\Gamma_{exc} = \phi_b/\Gamma_{exc}{}^{max} + 1/(K\Gamma_{exc}{}^{max}) \tag{3}$$

K is the equilibrium constant for adsorption and is found from the ratio of the slope and the intercept (see ref 30 for examples of this data analysis). In general, it is more difficult to obtain an accurate estimate of K in eq 3.[35] We have used the Langmuir isotherm in our earlier work on polymer adsorption, and the rationale for using this equation to fit our data empirically is given there.[30] This equation is most appropriate for adsorption from dilute solutions, which is the condition for all the calculations presented here ($\phi_b < 0.05$). The fit to this equation permits us to estimate the limiting surface excess when the surface is saturated ($\Gamma_{exc}{}^{max}$). It is this value which will serve to compare the relative strength of polymer chain adsorption on different surfaces. It is very common in polymer adsorption experiments to be working near this limit. However, in section 3.1 we calculate Γ_{exc} in order to qualitatively compare our calculations to experiment. The surfaces studied herein differ only in the preattachment of various densities and lengths of end-grafted nonadsorbing chains. In all cases presented here, the adsorbing polymers (or the adsorbing block of a copolymer) will have an energy of adsorption of $\chi_s = 1.0kT$ per segment and the interaction of all polymers with the solvent will be athermal ($\chi = 0$). We also take $\chi_s = 0$ for the end-grafted polymer and the nonadsorbing block of a copolymer.

3. Results and Discussion

The results for various cases of modified and unmodified surfaces and adsorption of polymer chains onto them are considered. These calculations illustrate the effect that minor changes to the surface can make in the adsorption properties.

3.1. Competitive Adsorption of Asymmetric Diblock Polymers.

In order to compare our results with some experimental results,[23] several cases of competitive adsorption of asymmetric copolymers on bare surfaces were run. Note that in these experiments saturation behavior was not explicitly presented, so we compute only Γ_{exc}, not $\Gamma_{exc}{}^{max}$. ϕ_b was kept almost constant, in the range 0.0057−0.0064. In most Monte Carlo calculations the adsorption of a single molecular weight is considered as a function of molecular weight. An exception is the calculation of Zajac and Chakrabarti

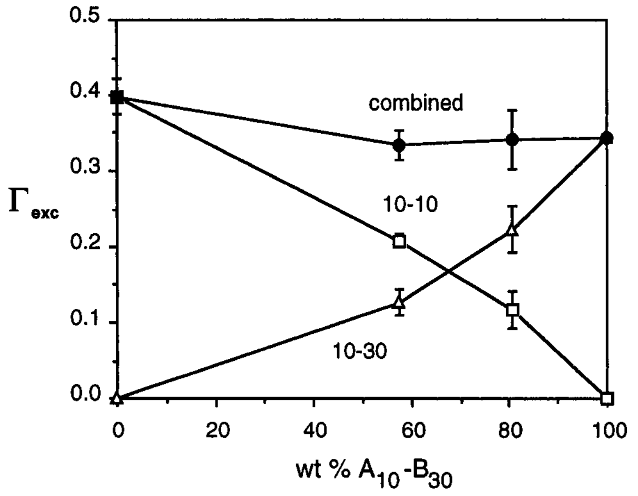

Figure 1. Plot of the surface excesses, Γ_{exc}, of two diblock copolymers and the combined surface excess of both in competitive adsorption. Both diblocks have the same adsorbing block length (10) but different nonadsorbing block lengths (10 and 30). The surface excesses, Γ_{exc}, are plotted as a function of the weight percent in solution of the 10–30 diblock copolymer. The total ϕ_b for both polymers taken together is in the range 0.0057–0.0064 for these calculations.

which explicitly considers the dynamics of displacement of one chain by another.[19] Figure 1 shows the results of two chains with the same length adsorbing block (10 monomer units) but with differing lengths of nonadsorbing block (10 and 30, respectively). We plot the data as in ref 23; *i.e.* the surface excess, Γ_{exc}, of each copolymer and the sum of both copolymers is plotted as a function of the weight percent in solution of the copolymer with the longer nonadsorbing or "buoy" length. This calculation is to be compared to 9–36 PVP–PS and 15–152 PVP–PS (Figure 2 of ref 23), in that the ratio between the sticker length (PVP) and the buoy (PS) is similar although we do not match the exact lengths. The copolymer with the longer buoy is preferentially excluded, as expected from prior theoretical considerations. The adsorbing block lowers the energy of the system upon adsorption, while the nonadsorbing block serves as a "buoy", which increases the chemical potential by entropic effects. Of course, our calculations only reflect the thermodynamics, while in experiments it is always possible that kinetics controls the results. We do not make any assumptions about interfacial surface tension or polymer elasticity except implicitly by the choice of parameters in the lattice model. These results demonstrate that our method seems to provide a reasonable approach to the simulation of competitive adsorption and agrees qualitatively with the experimental competitive adsorption data.[23] Next we consider the adsorption of diblock copolymers at modified surfaces.

3.2. Symmetric Diblock Copolymer Adsorption at End-Grafted Surfaces. A diblock copolymer with an adsorbing and a nonadsorbing block will form a structure upon adsorption in which the adsorbing block flattens out at the surface and the nonadsorbing block forms a tail (similar to an end-grafted polymer) which interacts entropically with other adsorbed copolymers and the end-grafted polymers.[3] It is reasonable to expect that this might lead to adsorption properties that are different from those of a homopolymer. We examine symmetric diblock copolymers (A_{NA}–B_{NB}, $N_A = N_B$) in an athermal solvent with one block energetically favored to adsorb at the surface ($(\chi_s)_A = 1.0kT$, $(\chi_s)_B = 0$). Adsorption on a bare surface increases with increasing polymer length, as expected from the results of self-consistent-field lattice theory.[3] In fact, the present results are quite similar to those for homopolymers,[30] although the nonadsorbing block does appear to be influenced more by the end-grafted chains on the modified surfaces. Three adsorbing copolymers are used in the simulation with a total length of 24, 50, and 100 lattice units (l.u.).

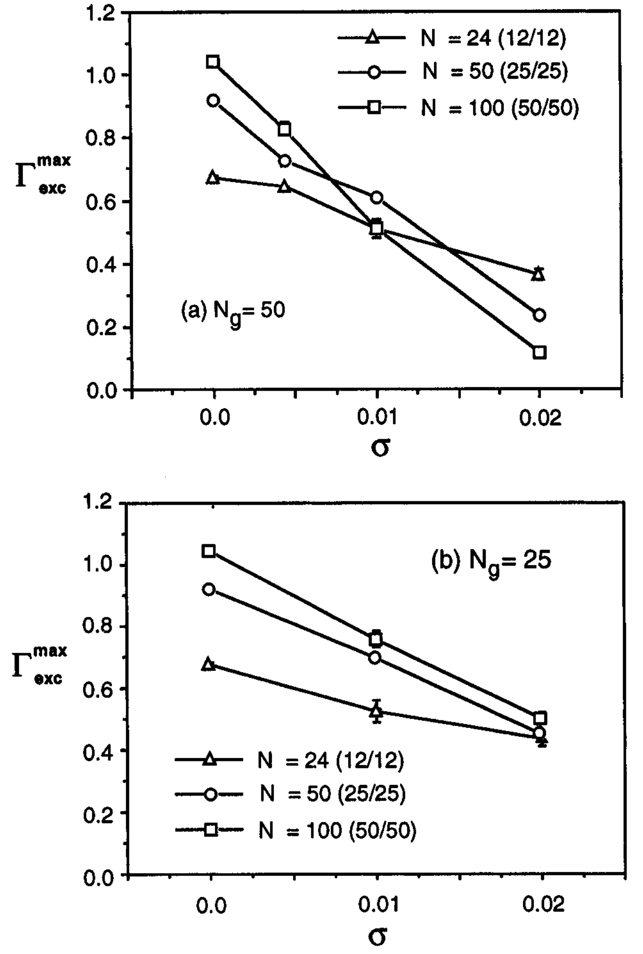

Figure 2. (a) Plot of the maximum surface excess, Γ_{exc}^{max}, of three symmetric diblock copolymers as a function of the grafting density, σ, of an end-grafted nonadsorbing polymer of length $N_g = 50$. (b) Same as (a) except an end-grafted nonadsorbing polymer of length $N_g = 25$.

Figure 2a shows the surface excess maximum, Γ_{exc}^{max}, for symmetric diblock copolymer chains as a function of the grafting density, σ, of end-grafted chains of length $N_g = 50$, attached to the surface. The error bars shown (which are often obscured by the plotting symbol) are the standard error values calculated from the least-squares fit to the Langmuir model.[36] The Γ_{exc}^{max} values for $\sigma = 0$ increase with N and are very similar to the homopolymer for length 100 and 50 but are slightly lower for the diblock with 24 units compared to the homopolymer with 25 units (*cf. ca.* 0.65 with *ca.* 0.8[30]). Diminishing the number of sticker groups has a small effect on Γ_{exc}^{max}, which is consistent with SCF calculations for symmetric diblock polymers.[37] As σ increases, Γ_{exc}^{max} decreases for all polymers, but they do not decrease by the same amount. At the highest grafting density ($\sigma = 0.02$), the order of Γ_{exc}^{max} with respect to N has inverted while at a medium grafting density ($\sigma = 0.01$), the Γ_{exc}^{max} are very similar. We note that from our previous study of grafted polymers, we estimated

Table 1. Competitive Adsorption Data for Symmetric Diblock Polymers

σ_g (N_g)[a]	N_1[b]	N_2[b]	$\phi_b(N_1)$	$\phi_b(N_2)$	$\Gamma_{exc}(N_1)$	$\Gamma_{exc}(N_2)$	$\Gamma_{exc}^{max}(N_1)$	$\Gamma_{exc}^{max}(N_2)$
0	24	50	0.00134 ± 0.00002	0.00082 ± 0.00001	0.11 ± 0.02	0.49 ± 0.02	0.675 ± 0.004	0.920 ± 0.009
0	50	100	0.00119 ± 0.00001	0.00092 ± 0.00001	0.29 ± 0.02	0.47 ± 0.03	0.920 ± 0.009	1.043 ± 0.006
0.01 (50)	24	50	0.0228 ± 0.0003	0.0216 ± 0.0003	0.24 ± 0.02	0.38 ± 0.04	0.51 ± 0.03	0.608 ± 0.007
0.01 (50)	50	100	0.0143 ± 0.0005	0.0155 ± 0.0006	0.46 ± 0.04	0.31 ± 0.05	0.608 ± 0.007	0.51 ± 0.02

[a] N_g is the length of end-grafted polymer at surface density σ_g. [b] N_1 and N_2 correspond to the two different molecular weights of the symmetric diblock polymers in bulk solution.

(empirically) that the crossover from the "mushroom" to "brush" regime occurs for $\sigma^* = 3.4(\pm 0.15)N_g^{-6/5}$, which is equal to 0.031 for $N_g = 50$. We also found that for $\sigma = 0.02$ that the density profile for $N_g = 50$ scaled according to the mushroom regime.[38] Therefore we conclude that formation of a brush is not required for selective size adsorption.

Figure 2b shows a similar plot for shorter ($N_g = 25$) end-grafted chains attached to the surface. In this case, the Γ_{exc}^{max} values decrease slightly more uniformly with σ and the relative ordering does not change. This indicates that the length of the grafted polymer on the modified surfaces as well as the grafting density affects the adsorption characteristics. This effect can be rationalized on the basis of the entropic barrier presented by the end-grafted polymer. In order for a higher molecular weight polymer to reach the surface, it must be deformed or stretched to avoid the grafted polymers. This entropic penalty offsets the situation for a bare surface; in this latter case the entropic loss upon adsorption is smaller for higher molecular weight polymers and adsorption is favored.

Next, we carry out a competitive adsorption calculation. It can generally be expected that at approximately equal weight percent concentrations in the solution a polymer with a larger value of Γ_{exc}^{max} will exhibit stronger adsorption (*i.e.* a greater Γ_{exc}) in competitive adsorption. As seen in Figure 2a, at medium grafting density ($N_g = 50$, $\sigma = 0.01$), Γ_{exc}^{max} is largest for the $N = 50$ diblock copolymer chain. Two competitive adsorption simulations were run with this surface: (1) $N = 24$ and $N = 50$ length chains and (2) $N = 50$ and $N = 100$ length chains. Parts a and b of Figure 3 show the monomer distribution profiles for the first and second cases, respectively. The two polymer chains have nearly the same bulk monomer concentration for each competitive adsorption calculation (see Table 1 for the values used). The surface excess for the $N = 50$ length chain is greater than that of the $N = 24$ or 100 length chain (Table 1). For comparison, competitive adsorption simulations were also run for these same pairs at a bare surface ($\sigma = 0$). As expected, the longer symmetric diblock copolymer adsorbs to a greater extent (Table 1). The precise choice of ϕ_b was arbitrarily chosen in these calculations (recall that the final values of ϕ_b are obtained after equilibration and are meant to be illustrative). Note that ϕ_b values are not the same for the two calculations and are lower for bare surfaces than for the modified surfaces. This is due in part to the stronger adsorption of a bare surface which depletes the bulk solution.

It is worth recalling the relationship between the partitioning of two different polymers on the surface and Γ_{exc}.[30] The amount of polymer adsorbed on the surface is given by

$$A_{ad} = \Delta\phi_b(V/S) = \Gamma_{exc} \tag{4}$$

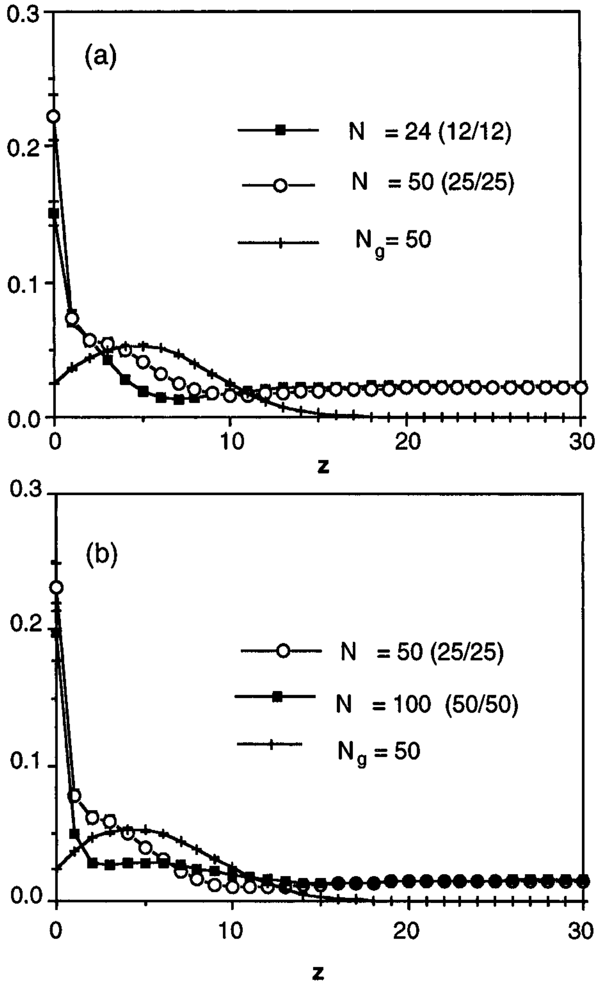

Figure 3. (a) Monomer distribution profile (ϕ) of two adsorbing symmetric diblock polymers ($N = 24$, $N = 50$) and the end-grafted polymer ($\sigma = 0.01$, $N_g = 50$). (b) Like (a) except $N = 50$, $N = 100$. See Table 1 for the ϕ_b values used and the derived Γ_{exc}.

Table 2. Ratio of Adsorbed Amount of Polymer for Bare and Modified Surfaces

$(\Gamma_{exc})_{24}/(\Gamma_{exc})_{50}$[a]		$(\Gamma_{exc})_{50}/(\Gamma_{exc})_{100}$[a]	
$\sigma = 0$	$\sigma = 0.01$	$\sigma = 0$	$\sigma = 0.01$
0.224 (0.138)	0.632 (0.596)	0.617 (0.477)	1.484 (1.608)

[a] Value in parentheses is the enrichment factor (see eq 5 of text). All data from Table 1.

where $\Delta\phi_b$ is the change in the bulk volume fraction after equilibration and V/S is the volume to surface area ratio, equal to L for a box of volume L^3. Using the Γ_{exc} data in Table 1, one can compare the ratio of the amount of adsorbed polymer of the two different molecular weights (Table 2). For the bare surface the lower molecular weight is always disfavored, but for the modified surface the relative amount of the adsorbed $N = 100$ polymer in competition with $N = 50$ is decreased by a factor of slightly more than 2. Note also that this is a larger factor than the comparison of Γ_{exc}^{max} values, which reflects the fact that Γ_{exc} for the longer

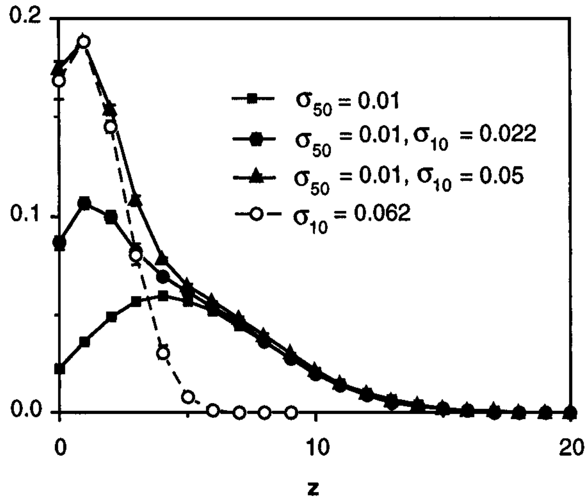

Figure 4. Monomer distribution profiles of end-grafted chains for four cases. Two are for end-grafted monodisperse chains ($N_g = 50$, $\sigma = 0.01$ and $N_g = 10$, $\sigma = 0.062$) and two are a bimodally modified surface (see figure for symbol identification).

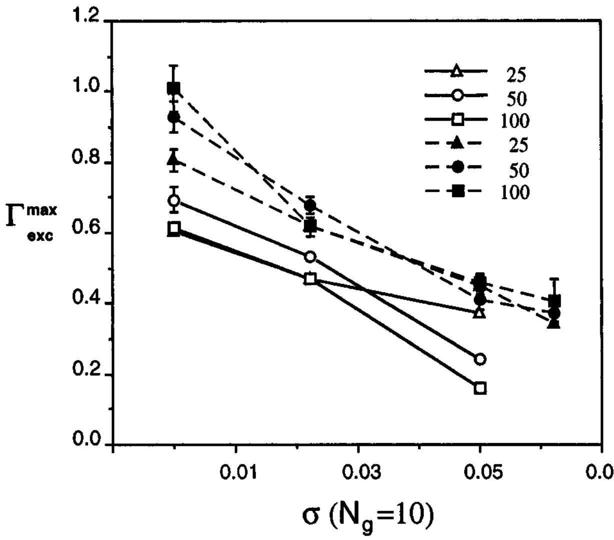

Figure 5. Plot of Γ_{exc}^{max} of three polymers at bimodally modified surfaces with $N_{g,a} = 50$ at density $\sigma_a = 0.01$ and $N_{g,b} = 10$ at variable σ_b (open symbols). For comparison, the Γ_{exc}^{max} values are shown for a surface with a monodisperse end-grafting with $N_g = 10$, σ variable (filled symbols, data from ref 30).

polymer approaches Γ_{exc}^{max} faster. The change in the ratio of $N = 24$ and $N = 50$ adsorbed is changed by a factor of *ca.* 3 by the surface modification. Another way to express the preferential adsorption is by the "enrichment factor"

$$F(N_1,N_2) = \frac{\Gamma_{exc}(N_1)/\phi_b(N_1)}{\Gamma_{exc}(N_2)/\phi_b(N_2)} \qquad (5)$$

3.3. Homo- and Copolymer Adsorption at Bimodal End-Grafted Surfaces. In this series of simulations a surface is modified by end-grafting chains of two lengths to the surface. The monomer distribution profile is more complex in such a case, arising from the polydispersity of the end-grafted chains. We find that such a surface tends to be more selective than those with monodisperse end-grafted chains. As in the previous cases, the solution is a good (athermal) solvent for all polymeric species present. The only energetic term is from the contact of an adsorbing section of the non-grafted polymer with the bare surface. We consider homopolymers for some of these calculations because our earlier calculations showed no significant difference between hompolymers and symmetric diblock copolymers (see later, Figure 7).

First, we consider a surface modified by end-grafting chains of length $N_{g,a} = 50$ at density $\sigma_a = 0.01$ and the surface is further modified by grafting a shorter chain $N_{g,b} = 10$ at several different grafting densities ($\sigma_b = 0.022, 0.05$). For comparison, the profiles for monodisperse $N_g = 10$ chains at $\sigma = 0.062$ and $N_g = 50$ and $\sigma = 0.01$ are shown. Figure 4 shows the monomer distribution profiles for these four surfaces. The density profile for the region primarily occupied by the $N_g = 50$ polymer chains ($z > 5$ l.u.) changes very little under the influence of the additional $N_g = 10$ chain. Our density profiles are qualitatively like those obtained by Dan and Tirrell using SCF methods at a much higher surface density ($\sigma = 0.1$) that is well into the brush regime.[32] The profile for the bimodal surfaces does not look very different from a simple sum of the two monodisperse profiles, but of course the total profile is quite different than either monodisperse case.

In Figure 5 we plot Γ_{exc}^{max} for these modified surfaces as a function of the grafting density of the shorter chain, σ_b for homopolymers of length 25, 50, and 100. As the grafting density of the shorter chain is increased, Γ_{exc}^{max} of the adsorbing polymers decreases, but not to the same extent. The different curves cross such that at the highest coverage there is selective size adsorption, as observed previously when increasing the density of the $N_g = 50$ end-grafted polymer.[30] For comparison the same plot is shown if only the $N_g = 10$ polymer is end-grafted. In this case the adsorption of all molecular weights decreases to nearly equivalent values of Γ_{exc}^{max}.[39] Thus the combination of these two end-grafted polymers has enhanced the efficiency of the modified surface in rejecting the higher molecular weight polymer. As mentioned earlier, the density profile for the mixed grafted polymers is close to the sum of the individual profiles. We suggest that this selective size adsorption is a combined effect of (1) a bimodal "near brush" structure and (2) adding the small polymer diminishes the ability of all molecular weight polymers to approach the bare surface while maintaining the steric effect of the $N_g = 50$ chains. So far as we know, this type of complex interplay has not been predicted using the analytical or SCF theories of polymers at surfaces.

A similar series of modified surfaces can be constructed by keeping the same fixed long end-grafted chain density ($N_{g,a} = 50$, $\sigma_a = 0.01$) and using an $N_{g,b} = 25$ chain at variable coverage. In Figure 6a, Γ_{exc}^{max} is plotted for $N = 25$, 50, and 100 as a function of the increasing grafting density, σ_b, of the $N_{g,b} = 25$ chain. Once again, there is curve crossing, but the effect of N is smaller than in Figure 5. While the use of chains of varying lengths grafted to the surface appears to allow for enhanced selectivity, there are situations in which this is not the case, as illustrated in Figure 6b. In this case, the modified surfaces have a short chain, $N_{g,a} = 10$, at a grafting density, $\sigma_a = 0.022$, with an additional longer chain, $N_{g,b} = 25$, grafted at several different densities. The decrease of Γ_{exc}^{max} as a function of σ_b for all the polymers is approximately equivalent.

Selective size adsorption behavior can also be obtained for the adsorption of symmetric diblock copolymers on a bimodally modified surface. This set of

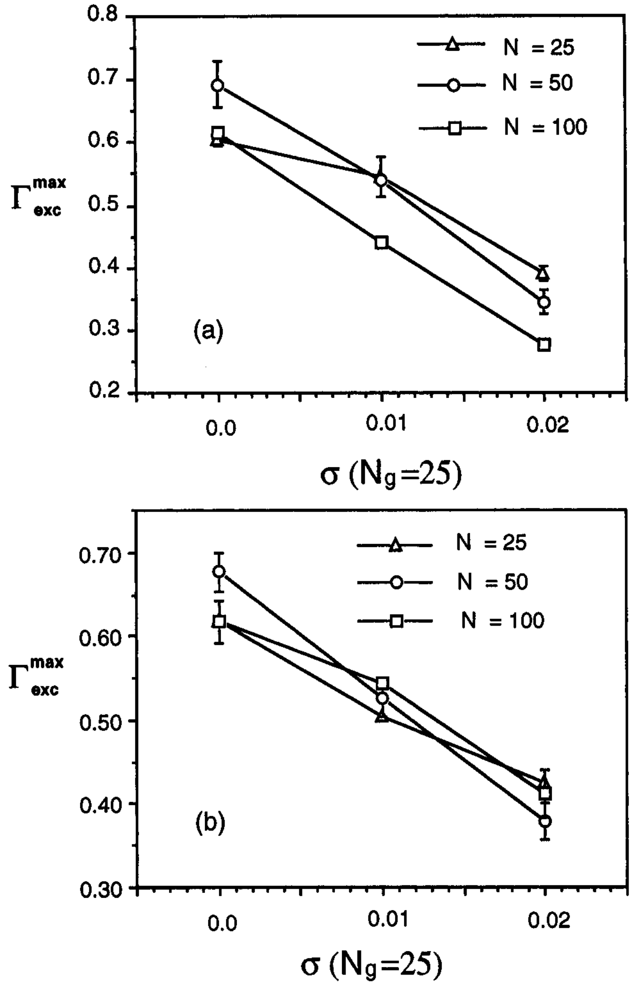

Figure 6. (a) Plot of Γ_{exc}^{max} for bimodally modified surfaces ($N_{g,a} = 50$, $\sigma_a = 0.01$ and $N_{g,b} = 25$, variable σ_b). (b) Like (a) except $N_{g,a} = 10$ and $\sigma_a = 0.022$ and $N_{g,b} = 25$ with variable σ_b.

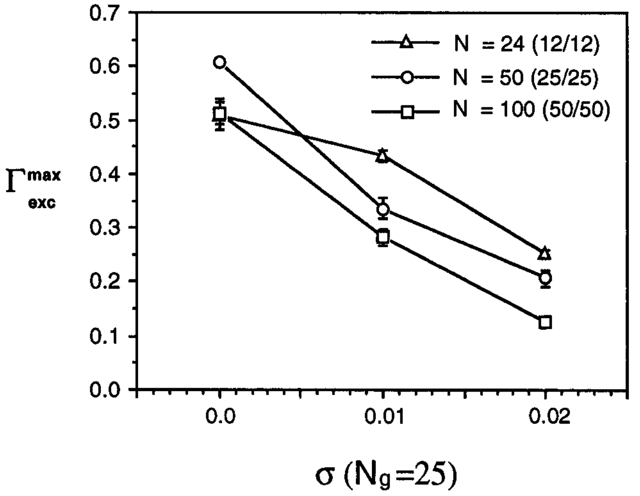

Figure 7. Plot of the maximum surfaces, Γ_{exc}^{max}, of three symmetric diblock copolymers at bimodally modified surfaces ($N_{g,a} = 50$, $\sigma_a = 0.01$ and $N_{g,b} = 25$, variable σ_b.

modified surfaces is constructed like Figure 6a ($N_{g,a} = 50$, $\sigma_a = 0.01$ and $N_{g,b} = 25$, σ_b variable). Figure 7 shows a plot of Γ_{exc}^{max} vs σ_b for $N = 24$, 50, and 100. The result is very similar to that shown in Figure 6a for the corresponding homopolymers of the same lengths, except the Γ_{exc}^{max} values are lower and the resolution is slightly better. Thus, as discussed in section 3.2, the symmetric diblock copolymers behave in much the same way as the corresponding homopolymers.

4. Summary

The simulations presented herein demonstrate that a surface can be tailored to control the relative amounts of adsorption of different length adsorbing polymers by modifying the structure of the surface with different lengths and mixtures of end-grafted polymers. We are not aware of any previous analytical theory, SCF calculation, or Monte Carlo simulations that illustrate the effects we report. It would be interesting to know if SCF calculations would predict a similar synergistic effect for a bimodally modified surface as found here. While our method provides for a computer experiment to help guide a rational strategy for preparing tailored surfaces, it does not provide a general theoretical structure to permit optimization of selective adsorption at surfaces. So far as we can see, the optimization of an adsorptive surface will depend on the polymer architecture (*e.g.* homopolymer or diblock, symmetric or not) and, of course, the molecular weight range. We presume that the energetics (χ_s) would have a strong effect on the behavior of Γ_{exc}, but we have not systematically examined this in our studies.

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