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Effects of Competition on Selective Adsorption of Heteropolymers onto Heterogeneous Surfaces

Bhumin Patel, Jesse D. Ziebarth, and Yongmei Wang*

Department of Chemistry, The University of Memphis, Memphis, Tennessee 38152

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ABSTRACT: Lattice grand canonical Monte Carlo simulations of heteropolymers adsorbing on heterogeneous surfaces are performed to help understand molecular recognition. The heteropolymers are self-avoiding walks of AB copolymers, which interact with a single heterogeneous surface composed of two different types of surface sites, type 1 and type 2. Interactions of type A beads with type 1 sites and type B beads with type 2 sites are attractive, whereas other interactions are neutral. Two polymer chain types with different statistical sequences simultaneously interact with a surface with a defined statistical pattern, enabling the study of the effects of competition for the limited number of surface sites during adsorption. We find that competition results in a significant increase in selectivity. In some cases, for example, the adsorption of alternating sequences on an alternating surface completely suppresses the adsorption of other competing sequence types. The selection rules, however, remain the same as in the noncompetitive adsorption. Surfaces with extreme patterns (i.e., completely alternating or highly patchy) exhibit the highest selectivity toward the matching sequences (completely alternating or blocky, respectively). On moderately patchy or moderately alternating surfaces, sequences with extreme patterns (highly blocky or completely alternating), not the sequences with matching statistics, have the highest selectivity. Random surfaces have little or no selectivity toward different sequence types.

I. Introduction

The ubiquitousness and complexity of molecular recognition that takes place in biological organisms has attracted extensive research investigation. Molecular recognition plays a vital role in ligand−receptor interactions, antigen−antibody recognition, DNA−protein interactions, macromolecular assembly, and so on. Each specific system may achieve recognition through specific rules or interactions, and hence a great deal of effort has been put into elucidating specific interactions in each system. However, some generic questions regarding the molecular recognition could be asked. For example, what is the least number of interaction sites needed to achieve selective recognition of target molecule among many similar rival molecules? Are few but strong interaction sites better than weak but more interaction sites to achieve selective recognition? Will the flexibility of molecules (i.e., the entropy) add to or spoil selective recognition?[1] Answers to these generic questions can be pursued by studying model systems such as adsorption of simple, two-letter heteropolymers onto heterogeneous surfaces.

Adsorption of heteropolymers onto heterogeneous surfaces has been previously studied by Chakraborty and coworkers[2−6] and Muthukumar,[7] who both found that heterogeneous adsorption takes place in two stages: an initial weak adsorption, followed by a pattern matching adsorption where the heterpolymers adopt conformations that maximize attractive interactions with the surface. More recently, Kriksin et al.[8] and Sumithra and Straube[9] investigated the adsorption of block copolymers on stripe-patterned surfaces and found that block length and stripe width can significantly affect adsorption properties. Other groups have also attempted to design surfaces that are able to adsorb selectively a target, with Jayaraman et al.[10] focusing on surfaces that recognize block copolymer sequences and Behringer and Schmid[11] studying if a designed surface is able to select a target surface from a group of rival surfaces. Such study is not only relevant to the understanding of molecular recognition in biological systems but also may have other practical applications. Genzer[12,13] studied the ability of copolymers to transfer the pattern of a 2D into three dimensions. Selective adsorption is also relevant to the design of smart surfaces/sensors that are capable of discriminating different analytes and toxins and in the context of polymer separation is the analysis and separation of statistical copolymers according to composition and sequence distributions.

Recently, we reported a Monte Carlo simulation study that examined the selective adsorption of heteropolymers onto heterogeneous surfaces.[14] In the previous study, we focused on how statistical correlation between polymer sequences and surface patterns affects the critical adsorption point (CAP), the point that marks the transition of a polymer preferring the nonadsorbed to the adsorbed state. The motivation of our previous study is that if the two sequences have different CAP values, one may tune the surface interaction so that one type will be selectively adsorbed, hence reaching high selectivity. Our previous study confirmed that the correlation between polymer sequences and surface patterns affects the CAP. On patchy surfaces, blocky copolymers have the lowest CAP value (i.e., are more prone to adsorption). On alternating surfaces, alternating copolymers have the lowest CAP value and are most likely to be adsorbed. We also found that on moderate patchy (or moderate alternating) surfaces, the most blocky (or the most alternating) chains are preferentially adsorbed over moderating blocky (or moderate alternating) chains. Interestingly, random surfaces were shown to be unable to discriminate between different heteropolymer types. The previous study not only presented simulation results on the

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*Corresponding author. Tel: 901-678-2629. Fax: 901-678-3447. E-mail: ywang@memphis.edu.

CAP values but also presented grand canonical Monte Carlo (GCMC) simulations that examined selective adsorption of heteropolymers onto the heterogeneous surface. The selectivity, S, of a surface toward a given sequence against another sequence, defined by the ratio of the amount of each type adsorbed on the surface, was examined, and, in general, the selectivity results supported the conclusions drawn based on the CAP values.

In the previous study, however, the adsorption of heteropolymers for different sequence types was studied in two separate simulations, that is, the adsorbing surface is exposed to a solution containing heteropolymers with either sequence type I or sequence type II, but two sequence types are not present simultaneously in the solution phase. Therefore, the selectivity previously obtained did not contain the effect of two sequence types competing against the same surface. Such selectivity results would be useful when surface adsorption is undersaturated such that competition will not play a significant role. Polymer adsorption on solid surfaces is uniquely different from small molecule adsorption on surfaces. As soon as the surface interaction is above the CAP, polymer adsorption saturates the surface almost immediately, even when the polymer concentration in the bulk solution is very low. Therefore, competition of two sequence types over the same surface should be considered. In this study, we extend our previous GCMC simulation model to include two sequence types of heteropolymers present simultaneously over an adsorbing surface. We study the competitive adsorption of two sequence types onto a heterogeneous surface. The focus of this work is to investigate how competition affects the rules that govern the selective adsorption of heteropolymers onto heterogeneous surfaces.

II. Methods/Simulation Detail

II.1. Models for Surfaces and Chain Sequences. In our present study, we used methods very similar to those of our previous work[14] and deviate only slightly in our GCMC methods. The heteropolymer chains are modeled as self-avoiding walks on a simple cubic lattice. We mainly use a chain length, N, of 96 but also examine in a few cases $N = 50$ and 150. All of the chains used in our simulations are composed of two types of monomers, A and B, and all chains have equal numbers of A and B monomers. Chain sequence types used in the study include $(A_1B_1)_{N/2}$ alternating sequences, diblock sequences $(A_{N/2}B_{N/2})$, and many different statistical copolymers. The sequence type of the statistical copolymers is characterized by a statistical order parameter, λ, which can range in value from -1 to $+1$; $\lambda = P_{AA} + P_{BB} - 1$, where P_{XY} is the conditional probability of an X monomer immediately following a Y monomer.[6] According to this formula, a completely alternating chain would have a $\lambda = -1$ because both P_{AA} and P_{BB} would be zero. For random copolymers, the ith monomer is independent from the (i-1)th monomer, $P_{AA} = P_A$ and $P_{BB} = P_B$, where P_A and P_B are the fraction of A and B monomers on the sequence, respectively. Therefore, random copolymers have $\lambda = 0$, as $P_A + P_B = 1$. Here we limit our investigation to the situation where $P_A = P_B = 0.5$. If $P_{BB} > P_B$, then $\lambda > 0$, and the chain is statistically blocky with blocks of A and B monomers. However, if $\lambda < 0$, then the chain is statistically alternating. Sequences are generated via a Monte Carlo algorithm for a desired λ value and subsequently used in GCMC simulations. For reported results, only one sequence of a given λ is used in GCMC simulation. However, simulations with different sequences with a same λ have been performed, and usually, results are within the order of fluctuations.

The heterogeneous surfaces employed in the simulations also follow our previous study. The surfaces were composed of two types of sites with 50% of the sites of type 1 and 50% of the sites of type 2. The statistical pattern of each heterogeneous surface is characterized by the surface order parameter, OP, which is defined as $\mathrm{OP} = (\sum_{i=1}^{N} \sum_{j=1}^{v} s_i s_j)/vM$, where M is the total number of surface sites, $v = 4$ is the coordination number of a solid surface on a simple cubic lattice, i and j are the nearest neighboring sites, and s is defined based on the surface site identity, with $s(\text{type 2}) = -1$ and $s(\text{type1}) = +1$.[10] The OP describes the overall patchiness of the surface and has a range identical to the sequence order parameter λ from -1 to $+1$. If an OP for 1D system with $v = 2$ is used to describe the chain sequences, then it provides an identical value to λ. We generated statistically disordered surfaces with a given order parameter value by simulating an Ising model with nearest neighbor interaction. The generated surface was used in subsequent GCMC simulations. Both the sequence and surface patterns used in the GCMC simulations are quenched. Simulations results on different surfaces with the same order parameters are found to be within statistical errors.

II.2. Grand Canonical Monte Carlo Simulations. The GCMC simulations reported in this study were performed on a simple cubic lattice with dimensions $50 \times 50 \times 100$ along the x, y, and z directions. There are two solid surfaces located at $z = 1$ and 100 planes. Polymer beads may not occupy any sites on these two planes. Periodic boundary conditions are applied in the x and y directions. The bottom surface at the $z = 1$ plane is adsorptive. Whenever a polymer bead is adjacent to the $z = 1$ surface, a surface interaction energy, ε_w, is applied. Because there are two monomer types (A and B) and two surface site types (types 1 and 2), four combinations of interactions are possible: ε_{A1}, ε_{A2}, ε_{B1}, and ε_{B2}. We have chosen $\varepsilon_{A1} = \varepsilon_{B2} = -\varepsilon_w < 0$, representing an attractive/favorable interaction, whereas $\varepsilon_{A2} = \varepsilon_{B1} = 0$. The top surface at the $z = 100$ plane is nonadsorbing, and no surface interaction is applied between a polymer bead and surface sites on the $z = 100$ plane (i.e., $\varepsilon = 0$ at the $z = 100$ plane). For the chain lengths used in the study, the separation between the planes is sufficiently large so that the $z = 100$ plane does not affect adsorption on the attractive $z = 1$ plane. No other interactions were applied in our study, and the units of all of the interactions are reduced by kT.

The GCMC simulation is performed at a specified chemical potential, μ, volume, V, and temperature, T. The total number of particles, or, in our case, the total number of polymer chains, is not fixed; instead, the simulation allows for the insertion/removal of the chain along with standard reptation moves for equilibration. We have used a configurational-biased insertion to facilitate the successful removal/insertion of the chain. In our previous study, only one sequence is used in a given GCMC run. The sequence is specified initially before the start of simulations. In the current study, two sequences are specified initially. During the insertion of a chain, one of the sequences is randomly chosen, and if insertion is successful, the sequence information is retained for this inserted chain until this chain is removed during a removal step. Additionally, we also included a trial move where an inserted chain is randomly picked and the sequence type is switched to the other sequence type. The sequence type switch is accepted or rejected according to the Metropolis rule by considering the change of energy accompanied with the switch.

We used the same chemical potential value for the two types of sequences. A fixed chemical potential of the chain, μ, would correspond to a fixed bulk concentration, ϕ_b. In our simulation, the box along the z axis is long enough such that there is a wide region resembling a bulk solution.

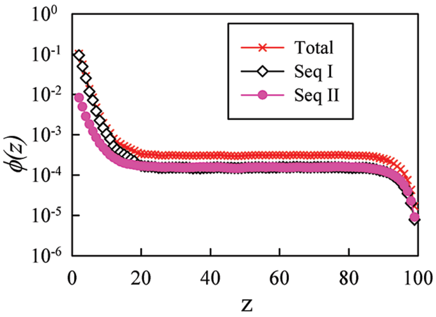

Figure 1. Density profiles along the z direction obtained in GCMC simulations of two sequences, Seq I ($\lambda = -0.3$) and Seq II ($\lambda = +0.9$) over a surface with OP $= -0.4$ located at $z = 1$ layer. Chain length $N = 96$, and chemical potential of the chains $\mu = 10kT$, bead/surface interaction $\varepsilon_w = 0.8$. Seq I is preferentially adsorbed on the surface, but the bulk concentrations of the two sequences are exactly same.

The corresponding bulk concentration, ϕ_b, is then determined by calculating the average volume fraction of polymers in that region (typically we used layers with z from 30 to 70). Alternatively, we can perform GCMC simulations in a simulation box with no walls at the same given μ and obtain the average volume fraction. We have confirmed that the ϕ_b determined through either method is the same. Because there are no sequence dependent interactions in bulk solution, the two types of heteropolymers behave exactly the same in the bulk solution. Therefore, the bulk concentrations, ϕ_b^{I} and ϕ_b^{II}, are equal and are half of the total bulk concentration ($\phi_b = \phi_b^{I} + \phi_b^{II}$). The two types of chains, however, may be adsorbed to different extents near the wall. We define a chain as being adsorbed if any segment of the chain is in direct contact with the $z = 1$ plane (i.e, a segment is located in the $z = 2$ plane). The statistical averages of the number of adsorbed chains for each sequence type, $<N_{ads}^{I}>$ and $<N_{ads}^{II}>$, are obtained. We define selectivity $S = <N_{ads}^{I}>/<N_{ads}^{II}>$ with the convention that sequence I is adsorbed more than sequence II. The selectivity obtained now contains the competition effect between the two sequence types. To obtain results for noncompetitive adsorption, we used the same simulation algorithm but with the two input sequences of the same type. We then repeated the simulations separately for different sequence types.

Simulations reported in this study used bead/surface interaction, ε_w, that varied from 0 to 2.0. We typically equilibrate the system for (1 to 2) $\times 10^7$ Monte Carlo steps, followed by 6.0×10^7 steps for obtaining statistical averages. For large values of ε_w, the simulation began with an output chain configuration achieved with a lower value of ε_w. As a proof of simulation method, we present in Figure 1 the typical average density profiles obtained from GCMC simulation for the two sequences individually and the combined total density profile.

III. Results

III.1. Effect of Competition on an Alternating Surface. We first examine the effects of competition on the selective adsorption of one heteropolymer type over another on an alternating surface. From previous studies, we expect that alternating chains will be most adsorbed on the alternating surface. Figure 2 shows competitive adsorption of an alternating ($\lambda = -1$) and a random ($\lambda = 0$) sequence on an alternating surface along with noncompetitive adsorption of the two sequences separately. Here the surface interaction, ε_w, has been incremented from 0 to 2.0, while keeping $\mu = 12$. The corresponding bulk concentration, ϕ_b, is 2.15×10^{-3}.

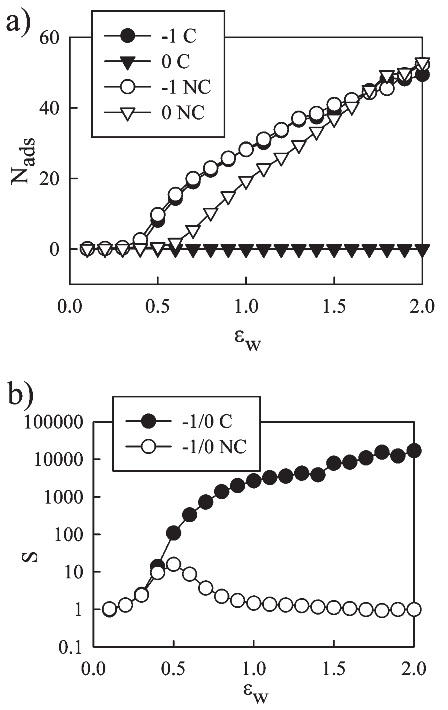

Figure 2. Competitive (C) and noncompetitive (NC) adsorption of two sequence types with $\lambda = -1$ and 0 on an alternating surface. Chain length $N = 96$ and $\mu = 12kT$ corresponding to $\phi_b = 2.15 \times 10^{-3}$. (a) Number of adsorbed chains of the two sequences as a function of ε_w. In the legend, the numbers -1 and 0 refer to the chain λ value. (b) Selectivity, S, defined by the ratio of adsorbed chains $S = N_{ads}^{I}/N_{ads}^{II}$ for the same simulations as those in part a.

The number of adsorbed chains, N_{ads}, for the alternating sequence ($\lambda = -1$) is nearly the same in competitive and noncompetitive adsorption modes. However, the numbers of adsorbed chains, N_{ads}, for the nonpreferred sequence are very different in two adsorption modes. In noncompetitive adsorption mode, the sequence with $\lambda = 0$ begins to accumulate on the surface when $\varepsilon_w > 0.5$, the CAP value of a random chain on an alternating surface. When both sequences are present, the preferred alternating sequence completely suppresses the adsorption of the nonpreferred random sequence ($\lambda = 0$). The N_{ads} for the random sequence remains nearly zero at high ε_w values. This complete suppression of adsorption of other sequence types on an alternating surface when alternating chains are present has been observed in previous simulations.[10] Figure 2b presents the selectivity obtained in the two adsorption modes. In noncompetitive adsorption mode, the selectivity is maximized at $\varepsilon_w = 0.5$. In competitive mode, the selectivity continues to increase with ε_w and did not level off within the range of ε_w examined here. The selectivity data, however, have to be taken with caution because $S = <N_{ads}^{I}>/<N_{ads}^{II}>$ when $<N_{ads}^{II}> \approx 0$, the value is not well-defined.

One factor that contributes to the high selectivity of the alternating surface for alternating chains is that adsorption in this case is very similar to adsorption of a homogeneous chain on an attractive homogeneous surface; once one attractive interaction pair forms between a bead on the chain with a site on the surface, all of the rest of beads will find matching sites on the surface, unless the first bead-surface site is a mismatch. The alternating sequence-alternating surface combination will always result in perfect pattern matching. The complete suppression of nonpreferred sequences by alternating chains can also be explained by the difference in average energy per adsorbed chain, $<E_{ads}>$,

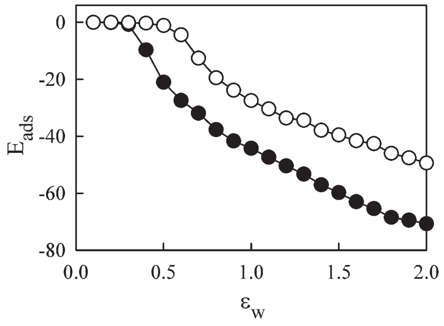

Figure 3. Average energy per adsorbed chain, $<E_{\mathrm{ads}}>$, for noncompetitive adsorption of chains with $\lambda = -1$ (●) and 0 (○) on an alternating surface.

for the two sequences in the noncompetitive adsorption mode. Figure 3 presents $<E_{\mathrm{ads}}>$ for the two sequences adsorbing on the alternating surface in noncompetitive adsorption mode. The energy for the random sequence ($\lambda = 0$) when adsorbed is about $+20kT$ higher than that of the alternating chain. Such a large enthalpic difference dictates that alternating chains will be preferentially adsorbed on the alternating surface. We did not present the $<E_{\mathrm{ads}}>$ for the two sequences in competitive adsorption mode because $<N_{\mathrm{ads}}>$ for the $\lambda = 0$ sequence is nearly zero; therefore, $<E_{\mathrm{ads}}>$ becomes undefined for the $\lambda = 0$ sequence. $<E_{\mathrm{ads}}>$ remains the same for alternating sequence in the competitive adsorption mode. For this combination of sequences, the selectivity correlates with $<E_{\mathrm{ads}}>$; the sequence that has a lower $<E_{\mathrm{ads}}>$ when adsorbed is selected in the competitive mode.

However, the correlation between preferred sequences with their $<E_{\mathrm{ads}}>$ being lower when adsorbed does not always remain true. On this same alternating surface, we also examined competitive adsorption of two sequences with $\lambda = -0.33$ and 0 and compared against the noncompetitive adsorption results. In both competitive and noncompetitive adsorption modes, sequences with $\lambda = -0.33$ are adsorbed more than sequences with $\lambda = 0$. (See Figure 4a.) Competition again enhances the selectivity at higher ε_{w} values. The average energy per adsorbed chain, $<E_{\mathrm{ads}}>$ for $\lambda = -0.33$ however is slightly higher than $\lambda = 0$. (See Figure 4b.) In other words, the enthalpic gain for the sequence with $\lambda = -0.33$ during adsorption is less when compared with sequence with $\lambda = 0$, yet the sequence with $\lambda = -0.33$ is still the preferred one. An explanation of this behavior can be found through an examination of the average number of good and bad matches on the surface, where A beads bound to type 1 surface sites and B beads bound to type 2 surface sites are considered to be good matches. $<E_{\mathrm{ads}}>$ is simply calculated by multiplying the attractive interaction, $-\varepsilon_{\mathrm{w}}$, by the average number of good matches; therefore, the chain enthalpy is determined solely by the number of good matches. Figure 5 presents the number of good and bad matches for chains with $\lambda = 0$ and -0.33 as well as the ratio of good-to-bad matches. Adsorbed chains with sequence $\lambda = -0.33$ on average have fewer bound segments per chain, and, as a result, the enthalpic gain for adsorbed chains with $\lambda = -0.33$ is less than the sequence with $\lambda = 0$. However, the number of bad matches for the $\lambda = -0.33$ sequence is also less than that for the $\lambda = 0$ sequence. Bad matches on the surface reduce the entropy of the chain without providing any enthalpic benefit. When we determine the number of good matches and number of bad matches, we find that the good-to-bad match ratio is higher for the sequence with $\lambda = -0.33$ than for the sequence with $\lambda = 0$. Therefore, selective adsorption is determined by the ability of a sequence to maximize the ratio of good match over the bad match. In comparison, alternating chains adsorbed on the alternating surface typically have zero bad matches, and hence the good-to-bad match ratio is infinity, and high selectivity of the alternating chain on the alternating surface is achieved. Figure 5 also shows that the ratio of good-to-bad contacts gradually increases for both

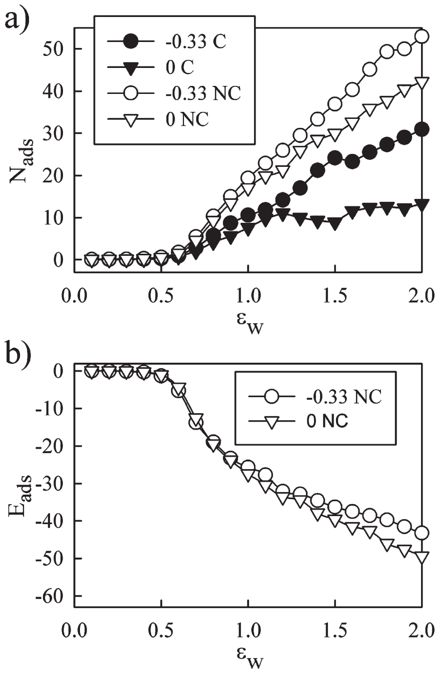

Figure 4. (a) Number of adsorbed chains for competitive (C) and noncompetitive (NC) adsorption of chains with $\lambda = -0.33$ and 0 on an alternating surface. (b) Average energy per adsorbed chain, $<E_{\mathrm{ads}}>$, for noncompetitive adsorption of chains with $\lambda = -0.33$ and 0 on an alternating surface.

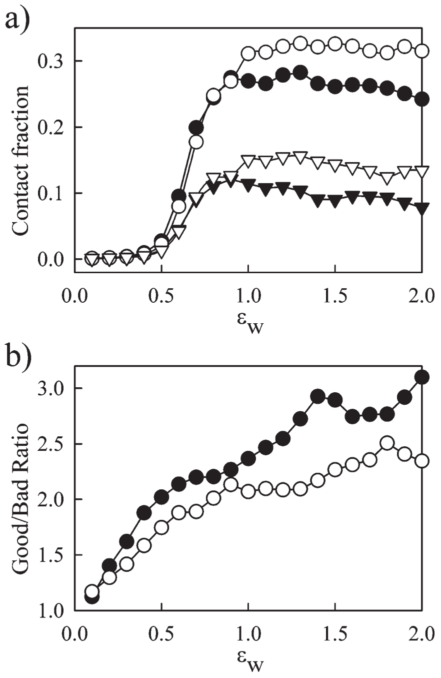

Figure 5. (a) Fraction of beads of adsorbed chains making good (circles) and bad (triangles) contacts chains for chains with $\lambda = -0.33$ (filled symbols) and 0 (open symbols) competitively adsorbing on an alternating surface. (b) Ratio of good-to-bad contacts for $\lambda = -0.33$ (●) and 0 (○).

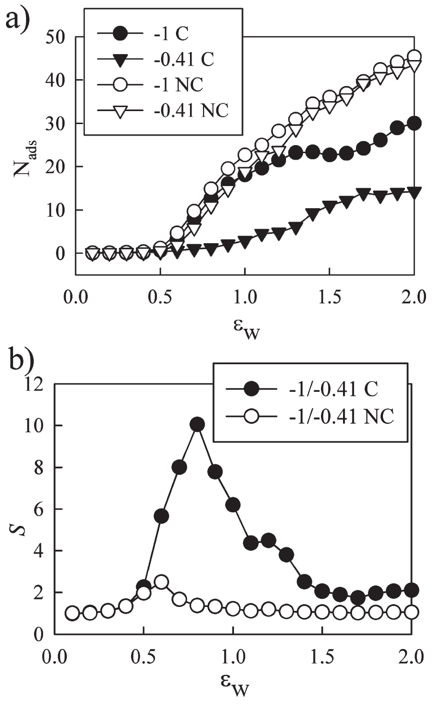

Figure 6. (a) Number of adsorbed chains for competitive (C) and noncompetitive (NC) adsorption of chains with $\lambda = -1.0$ and -0.41 on a surface with OP = -0.4. (b) Selectivity, *S*, defined as $N_{ads}(\lambda = -1)/N_{ads}(\lambda = -0.41)$ on an OP = -0.4 surface for competitive and noncompetitive adsorption.

the $\lambda = 0$ and -0.33 chains on the alternating surface for the interaction energies studied for this system. There is not an abrupt transition in the good-to-bad match ratio that would be consistent with a pattern matching adsorption transition; however, in this study, the bad matches are enthalpically neutral, not the repulsive enthalpic interactions that are often used when pattern matching has been found.

III.2. Effect of Competition on Moderately Alternating Surface. In our previous studies, we have shown that on a moderately alternating surface, sequences with more negative λ values (more alternating) are selectively adsorbed. Here we show results that confirm this conclusion even in the competitive adsorption mode. Figure 6 presents the number of adsorbed chains for an alternating sequence ($\lambda = -1$) and a sequence with $\lambda = -0.4$ on a surface with OP = -0.4 in competitive and noncompetitive adsorption modes. All other conditions are the same as those in Figure 2. Alternating chains are preferentially adsorbed in both competitive and noncompetitive adsorption modes, although the preference in the latter mode is very small. In competitive adsorption mode, the sequence with $\lambda = -0.4$ is suppressed but not completely. As a result, the number of adsorbed chains for $\lambda = -1$ in the competitive mode is less than that in noncompetitive mode; even the total number of adsorbed chains (counting both sequences) in the competitive mode is slightly below that of alternating sequence adsorption in the noncompetitive mode. Because the nonpreferred sequence is adsorbed at high ε_w, the selectivity in this case shows a peak at $\varepsilon_w \approx 1.0$. In this case, adsorbed chains with an alternating sequence have a lower $\langle E_{ads} \rangle$ and make more good contacts and less bad contacts than chains with $\lambda = -0.4$.

We have also examined many different combinations of sequences on this moderately alternating surface. In one set, we examined a sequence with $\lambda = -0.33$ in competition with sequences with $\lambda = -1$, -0.41, -0.5, -0.6, and -0.7, respectively. In all of these runs, the sequence with a more negative value tends to be adsorbed more. However, the selectivity remains small and is no more than 3.0 in most cases. In another set, we examined the alternating sequence in competition with sequences with $\lambda = -0.96, -0.92, -0.8, -0.7, -0.6$, and -0.4. In all of these runs, the alternating sequence is the most adsorbed. Moreover, the selectivity, *S*, is larger when $\Delta\lambda$, the difference in the two λ, is large. These data illustrate that best selectivity is not at the condition when λ = OP for moderately alternating or moderately patching surfaces.

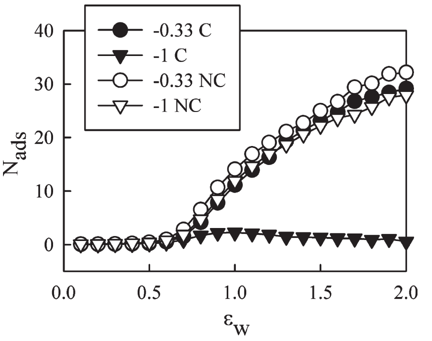

Figure 7. Number of adsorbed chains for competitive (C) and noncompetitive (NC) adsorption of chains with $\lambda = -0.33$ and -1.0 on a patchy surface with OP = $+0.9$.

III.3. Effect of Competition on Other Surfaces. On the highly patchy surface, blocky chains are preferentially adsorbed. We again observe results similar to those on alternating surface. The blocky chain ($\lambda = +0.9$) nearly completely suppresses the adsorption of an alternating sequence or a sequence with $\lambda = -0.33$ (data are not shown). Similar to the adsorption of an alternating chain on an alternating surface, the adsorption of a blocky chain on the patchy surface will often result in perfect pattern matching for adsorbed beads. If a bead of the A block of the chain adsorbs on a patch of 1 sites on the surface, the remainder of the A block can adsorb on that patch of the surface as a homopolymer. When a sequence with $\lambda = -0.33$ competes against $\lambda = -1$ (alternating) sequence, the sequence $\lambda = -0.33$ adsorbs more than alternating sequence. Figure 7 presents the $\langle N_{ads} \rangle$ for the two sequences on a surface with OP = $+0.9$ in the two adsorption modes. At high surface interaction, the alternating sequence is highly suppressed by sequence with $\lambda = -0.33$.

We finally also examine the competitive adsorption on a random surface. Figure 8 presents $\langle N_{ads} \rangle$ in competitive adsorption mode for two sets of simulation, $\lambda = 0$ competes against $\lambda = -0.33$, and $\lambda = 0$ competes against $\lambda = +0.9$ sequences. The data are somewhat noisy. However, $\langle N_{ads} \rangle$ for these sequences do not differ more than the range of error bars for these sequences. When we examine the competitive adsorption of alternating sequence against a completely block chain, the $\langle N_{ads} \rangle$ value differs by more than error bars. For example, when a random sequence $\lambda = 0$ competes against an alternating sequence, the selectivity remained above one (the random sequence $\lambda = 0$ is the preferred sequence) but less than two at $\varepsilon_w > 1.0$. Because polymer adsorption at high surface interaction energy often has hysteresis, it is difficult to assess accurate values of selectivity at high surface interaction energy. In general, the random surface exhibits very little to no selectivity between any two sequences combinations. This corroborates our earlier finding: random surface cannot selectively adsorb a given sequence.

III.4. Effect of Concentration and Chain Length on the Selective Adsorption in Competitive Mode. To understand

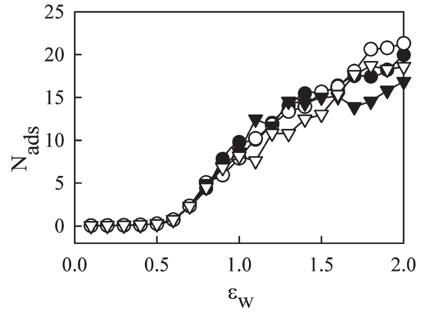

Figure 8. Number of adsorbed chains for two cases of competitive adsorption on a random surface with OP = 0. The circles show data for competition between chains with $\lambda = 0$ (●) and −0.33 (○), whereas the triangles show data for competition between chains with $\lambda = 0$ (▼) and +0.9 (▽).

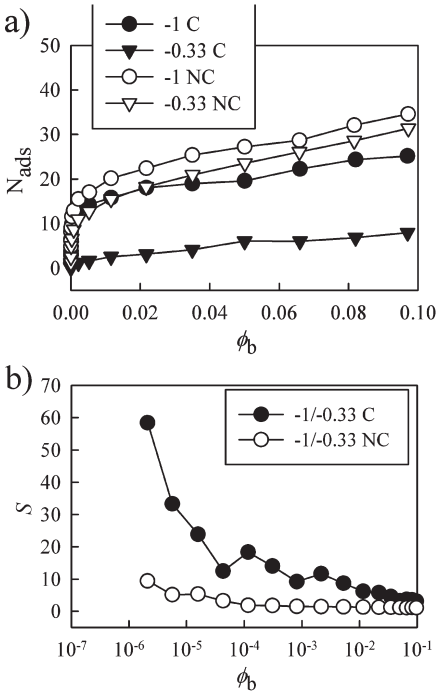

Figure 9. Effect of bulk concentration, ϕ_b, on (a) the number of adsorbed chains and (b) selectivity for competitive (C) and noncompetitive (NC) adsorption of chains with $\lambda = -1.0$ and -0.33 on a surface with OP = −0.4. Surface/bead interaction $\varepsilon_w = 0.8$.

how the change of bulk concentration ϕ_b may affect the selectivity of any two given sequences, we examined the competitive adsorption of $\lambda = -1$ (alternating) sequence with $\lambda = -0.33$ on a surface with OP = −0.4 when the bead/surface interaction kept constant at $\varepsilon_w = 0.8$, but the chemical potential of the chain μ (and thus ϕ_b) was varied. Figure 9 presents $<N_{ads}>$ for the two sequences as a function of ϕ_b in competitive and noncompetitive adsorption modes. The data exhibit typical strong adsorption behavior exhibited by polymer adsorption. The number of adsorbed chains quickly rises at very low ϕ_b and then rises more slowly at high ϕ_b. The simulation data always have better statistics when only one type of sequence is used (i.e., noncompetitive adsorption mode) and are noisier whenever in competitive adsorption mode. In the competitive mode, the $<N_{ads}>$ for nonpreferred sequence ($\lambda = -0.33$) is suppressed to a large degree but not completely suppressed. The selectivity S is higher at low ϕ_b values, as shown in Figure 9b. In general, lowering the bulk concentration enhances the selectivity, especially when in competitive adsorption mode.

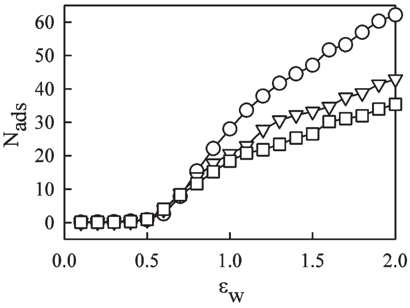

Figure 10. Effect of chain length on the number of chains adsorbed on a surface with OP = −0.41. N_{ads} is the total number of adsorbed chains for a system with $\lambda = 0$ and −1 and chain lengths 50 (○), 96 (▽), and 150 (□).

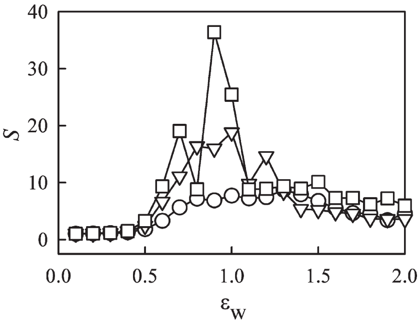

Figure 11. Selectivity of a surface with OP = −0.41 for chains with $\lambda = -1$ over chains with $\lambda = 0$ for systems with chain lengths 50 (○), 96 (▽), and 150 (□).

To understand how chain length may affect the competitive adsorption, we examined competitive adsorption with two sequences, $\lambda = -1$ (alternating) against $\lambda = 0$ (random) sequences on a surface with OP = −0.4, with chain length $N = 50$, 96, and 150. The simulations are all performed at nearly the same ϕ_b values. Figure 10 shows $<N_{ads}>$ for the three chain lengths studied; in this case, $<N_{ads}>$ is the total number of chains adsorbed on the surface with no differentiation between different sequence types. The $<N_{ads}>$ starts to increase at nearly the same interaction energy ($\varepsilon_w > 0.5$) for the three chain lengths because the CAP value is nearly independent of chain length. Once the surface interaction is above the CAP, the chains with $N = 50$ have the largest number of adsorbed chains on the surface. This is expected because shorter chains occupy a smaller adsorbing surface area than longer chains, and hence under the given condition, the surface should be able to adsorb more short chains. When $<N_{ads}>$ values for individual sequence are compared for different chain lengths, the same patterns are observed. The $<N_{ads}>$ values for the preferred sequence or nonpreferred sequence with a short chain length are always higher than those for the longer chain length (data not shown). Figure 11 presents the selectivity obtained for the three chain lengths. The data are somewhat noisy, but clearly, chain length $N = 150$ exhibits the highest selectivity in the region $0.5 < \varepsilon_w < 1.2$. At even higher surface interaction, the selectivity with different chain lengths is similar.

IV. Discussion and Conclusion

The physical picture emerged from the above results is the following. Most of our earlier conclusions about selectivity of heterogeneous surface toward heteropolymer sequences, derived on the basis of the study in noncompetitive adsorption, remain true in competitive adsorption mode. We saw that for surfaces with extreme patterns, either completely alternating surface or highly patchy, the highest selectivity is exhibited toward sequences with matching statistics (completely alternating or blocky, respectively). We also saw that on a moderately patchy surface, the more blocky chains will be adsorbed more. On a moderately alternating surface, more alternating sequences will be selectively adsorbed. The random surface shows little or no selectivity toward different heteropolymer sequences. The major difference between competitive adsorption and noncompetitive adsorption modes is that selectivity, S, is enhanced significantly during competitive adsorption mode. As a result, S is not always maximized near the CAP value. For some systems such as an alternating sequence competing against a sequence with $\lambda = -0.33$ on an alternating surface (data in Figure 2), S continually increases as the surface interaction ε_w increases up to 2.0. Because polymer adsorption at even higher surface interaction will have hysteresis, we did not extend the simulation to even higher surface interaction. For other systems such as data in Figure 6b, S is still maximized at intermediate surface interaction value. If surface interaction is somehow fixed, then the selectivity then depends on surface order parameter OP, and the two sequences order parameter, λ_1 and λ_2. The larger the absolute value of order parameter $|\mathrm{OP}|$, the higher the selectivity. Also the larger the difference in $|\lambda_1 - \lambda_2|$, the larger the selectivity will be.

Another important picture that emerges from the simulations is that the enthalpic energy of two adsorbed sequences on a given surface is not always the factor that determines which chain is selectively adsorbed on the surface. For example, although a random sequence has a lower enthalpic energy on an alternating surface than a sequence with $\lambda = -0.33$, the alternating surface selectively adsorbs the $\lambda = -0.33$ sequence. The chain with $\lambda = -0.33$ on average makes fewer total contacts than the random sequence does, and hence it has more entropy than the random sequence. A good indicator for selectivity is the ratio of good/bad contacts. The higher this ratio is, the higher the selectivity. We also ran simulations where the interaction between bad contacts (A-2 and B-1) are set to be repulsive, with an interaction energy equal to the opposite of good contacts, and the selectivity is significantly enhanced.

Recently Jhon et al.[15] reported a study on the effect of comonomer sequence distributions on the adsorption of statistical copolymers onto solid surface. Their experimental results showed that increasing the blockiness in copolymers enhances the adsorption of copolymers with the same chemical composition. This experimental result is in agreement with our earlier Monte Carlo simulations results[14,16] as well as observations made here. In ref 16, we examined the dependence of CAP of statistical copolymers above a homogeneous surface on the monomer compositions. There, we have shown that if the monomer sequence in the copolymer is not statistically random, then CAP of the copolymer chains will also depend on the sequence distribution in addition to the monomer compositions. Given the same monomer composition, the more blocky the chain, the lower the CAP, the easier it will be adsorbed on the surface. This fact is also reflected in the selectivity displayed by a patchy surface. Note a homogeneous surface can be thought of as a patchy surface with an extremely large patch. We have observed that on a patchy surface, the more blocky chains are more selectively adsorbed. This is in good agreement with experimental results reported by Jhon et al.

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