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Self-Assembly and Adsorption of Diblock Copolymers from Selective Solvents. 2. Surface Adsorption

Yongjian Zhan and Wayne L. Mattice*

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

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ABSTRACT: The self-assembly and the adsorption of a diblock copolymer from a selective solvent have been simulated on a cubic lattice by a Monte Carlo method. We show that the self-assembly of the diblock copolymer greatly affects the adsorption. According to the adsorption behavior of the copolymer, the overall concentration can be divided into three regions. Below the cmc, the adsorption of the copolymer occurs from the free chains. The equilibrium mainly happens between the free chains and the adsorbed chains. Just above the cmc, the micelles have little contribution to the adsorption, and the adsorption of the copolymer also occurs from the free chains. There are two equilibria: one is the equilibrium between the free chains and the micelles, and the other, between the free chains and the adsorbed chains. The lower adsorbed amount just above the cmc is because the concentration of the free chains above the cmc is less than just below the cmc. At higher concentrations, the adsorption of the copolymer may occur from both the free chains and the micelles. There are three equilibria in the system, and the adsorbed amount is large because of the adsorption of the micelles. The simulation results of adsorption from a selective solvent are in good agreement with the experimental results. Below and just above the cmc the structures of the adsorbed layer in a selective solvent are similar to those in a nonselective solvent, and well above the cmc the segment density profiles have a different shape because of the self-assembly of the adsorbed chains.

I. Introduction

Block copolymers show an inherent interfacial activity that makes them useful as large surfactant molecules. One facet of their interfacial activity is the adsorption from solution onto an impenetrable substrate. From the point of view of the fundamental physics of selective adsorption in a selective solvent, the competition between the self-assembly and the adsorption of diblock copolymers cannot be manipulated independently. The copolymer chains can either compete for surface area on the substrate or aggregate with each other to form micelles in the solution. The formation of the aggregates may change the chemical potential of the free chains in solution, thereby affecting the adsorption. The question is how important are the relative influences of competition for the self-assembly and the adsorption in dictating the amount of polymer that becomes adsorbed.

The main motivation for this work arises from the fact that up to now, no theoretical model has been developed to describe the competition between the self-assembly and the adsorption of diblock copolymers in selective solvents. Most of the theoretical work discussed the micelle formation[1,2] and the surface adsorption[3,4] separately because of the complication of the system. In a problem involving the complex system, computer simulations provide a significant advantage over analytical models. Another motivation for focusing our attention on these systems arises from the observation that the final surface concentration is greater for adsorption from solutions just below the cmc than from solutions just above the cmc.[5]

A considerable effort has been devoted to the study of the adsorption of block copolymers in solutions as well as melts.[2-15] Marques et al.[3] studied the equilibrium adsorption of diblock copolymers in a highly selective solvent on a solid surface. They first presented a scaling theory of micelle formation, and then studied the geometry of the adsorbed film in equilibrium with the micellar phase. They showed that the structure of the adsorbed layer is governed by the chemical potential in the solution in contact with the surface, and the important issue is the role of the van der Waals interaction between the adsorbed layer and the surface. van Lent and Scheutjens[7] modified the self-consistent field theory of Scheutjens and Fleer to study the adsorption of block copolymers. They calculated the critical micelle concentration and showed the influence of the self-aggregation of block copolymer on their adsorption behavior. The adsorption of block copolymers on lyophobic surfaces increases sharply just below the cmc and is essentially constant at higher concentrations of polymer. Johner and Joanny[10] studied the adsorption kinetics of diblock copolymers onto a wall in a highly selective solvent. They suggested that the potential barrier for direct adsorption of chains belonging to micelles is so high that only free chains adsorb on the wall.

Tassin et al.[6] used the surface plasmon technique to study the kinetics of adsorption of copolymer chains on a metal surface. The results showed that the kinetics of adsorption does not follow any Langmuir-type model. The first stages of the adsorption process correspond to the adsorption of micelles, whereas longer times involve adsorption of single chains. Munch and Gast[5] presented an experimental approach to investigate the adsorption of diblock copolymer on a dielectric surface. The adsorption kinetics demonstrates the drastic effect of the overall copolymer concentration. The initial rate of adsorption above the cmc is faster than that just below the cmc. In contrast, the final adsorbed amount is greater for adsorption from solutions just below the cmc than from solutions just above the cmc. They suggested two adsorption mechainsms: above the cmc, the rapid initial rate of adsorption indicates that micelles adsorb; below the cmc, the adsorption of single chains results in a more homogeneous coverage. Parsonage et al.[12] have reported isotherms for the adsorption of diblock copolymers of poly(2-vinylpyridine)–polystyrene from toluene solutions onto oxidized silicon and mica substrates. It was observed that over a range of dilute concentrations the surface density is fairly insensitive to the concentration of the incubation solution.

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Balazs and Lewandowski[8] described a Monte Carlo method for simulating the surface adsorption of triblock copolymers and showed the self-aggregation of the triblock copolymers affects the extent of the surface coverage, as well as the microstructure of the interfacial region. However, since they focused on the character and growth of the adsorbed layer, they did not allow free chains to associate among themselves. In other words, a free chain can bind to the surface or to a chain that is already adsorbed, but the free chains in solution cannot associate to form aggregates. There are only two kinds of chians in their system: the free chains and the adsorbed chains.

The goal of this work is to provide useful insight in the mechanism of the adsorption of a diblock copolymer in a selective solvent, a matter which is still controversial. We assume the A block is in a poor solvent and the B block is in a good solvent. Therefore, the former may adsorb on the surface, and the latter may extend into the solution and form an external layer. The diblock copolymer may also self-assemble to form aggregates if the concentration in solution exceeds the critical micelle concentration. When an equilibrium is reached, there are three types of chains in the system: the free chains, the adsorbed chains, and the chains self-assembled in the aggregates. In the previous paper[16] we described the micellization process of the diblock copolymer in the presence of the adsorption. One of the results of our work is that over a narrow concentration range the rate of change of the number of aggregates with overall concentrations is altered. We identify this regime with the critical micelle concentration. An important issue is that above the cmc, the concentration of the free chains decreases linearly as the concentration of copolymer increases, instead of keeping constant. Here we describe the adsorption process of the diblock copolymer in micellization. We present results demonstrating how the aggregation of diblock copolymers affects the adsorption.

II. Model

The model we used was described in the previous paper.[16] We study a solution of a selective solvent and a diblock copolymer $A_{10}B_{10}$ by Monte Carlo simulations. The dimension of the cubic lattice is $44 \times 44 \times 46$ with periodic boundary conditions in the X and Y directions. The top layer ($Z = 0$) and the bottom layer ($Z = 45$) are assumed to be impenetrable surfaces. The dimensionless interaction parameters E_{AB} and E_{AO}, which are applied whenever A has a nonbonded B or a solvent molecule as a nearest neighbor, are set to be 0.5. All remaining interaction parameters are set to be zero, including E_{AS} and $E_{AS'}$, which are the interaction parameters between A and the surfaces. The same thermodynamic factors driving the self-assembly cause the block copolymer to adsorb onto surfaces in a selective solvent.

The simulations are started by introducing a specified number of copolymer chains into the box, and the number of the chains is held constant throughout the simulation. The initial conformations for all simulations were generated from a set of parallel chains by conducting 10^6 iterations with all the interaction parameters being zero. The random configuration obtained was then run 10^8 iterations with $E_{AB} = E_{AO} = 0.5$. Three types of movements, Brownian motion, kink-jump (including end-flip and crank motion), and reptation were used to convert one replica into another. Trial moves were accepted or rejected according to the Metropolis rules.[17] The instantaneous conformations were recorded at intervals of 5×10^5 iterations for subsequent analysis. The equilibrium properties of the system are the average over the last 50 million iterations.

III. Results and Discussion

Munch and Gast[5] presented the results demonstrating that aggregation of block copolymers affects the kinetics and the final adsorbed amount. They suggested that below the cmc there are only single isolated chains in the solution and above the cmc there is a constant concentration of single chains in the solution. Therefore, below the cmc, the adsorption must only occur with the single chains. Above the cmc, if adsorption occurred from the single chains alone, the initial rate of adsorption and the final adsorbed amount would not change as the overall concentration increased; if adsorption occurred from both the single chains and the micelles, the final adsorbed amount would not be less than just below the cmc. So they suggested the adsorption mechanism is the adsorption of single chaines below the cmc and the adsorption of micelles above the cmc. Tassin et al.[6] also found that the presence of micelles at higher concentrations leads to a high initial rate of adsorption. The equilibrium coverage appears to be independent of concentrations above the cmc.

However, some questions arise from the above explanation of Munch and Gast. First, why do few of the single chains adsorb on the surface above the cmc? The diffusion coefficient of the single chain is larger than that of the micelle. A micelle has a steric layer and the adsorption of the micelle needs the rearrangement of its chains. The adsorption of a single chain should be much easier than that of a micelle. Therefore, the adsorbed amount of the free chains should be directly proportional to the concentration of the free chains in solutions. Second, why is the final adsorbed amount for the adsorption of micelles less than that of the single chains? We expect that the situation on the surface is similar to that in bulk solutions; i.e., there is the equilibrium between the free chains and micelles on the surface. At early times of the adsorption, the surface density is low, and the chains do not overlap. The adsorbed layer is formed by single chains or small aggregates. As more chains adsorb, they will begin to self-assemble to form micelles and be densely packed. So the final adsorbed amount when there are micelles on the surface should be larger than that where there are only single chains.

A. Adsorbed Amount. van Lent and Scheutjens[7] studied the influence of the association on the adsorption properties of block copolymers. They found the adsorbed amount of a diblock copolymer increases steadily until the cmc is reached. Then the adsorption hardly increases any further, because the concentration of free polymer in solution remains almost constant. Their results are different from those of experiments by Munch and Gast.[5]

Here we define the adsorbed amount Γ as the average number of beads (including A and B beads) per adsorption site on the surface. If n_a is the number of adsorbed chains, $N = N_A + N_B$ is the length of the chain, and S is the total number of adsorption sites available, then the adsorbed amount is

$$\Gamma = n_a N/S \qquad (1)$$

The adsorbed amount as a function of the overall copolymer concentration is depicted in Figures 1 and 2. The simulation results are similar to the experimental results of Munch and Gast.[5] Up to a certain concentration, the adsorbed amount increases as the overall concentration increases. Just above this concentration, the adsorbed amount is less than that seen just below the cmc (Figure

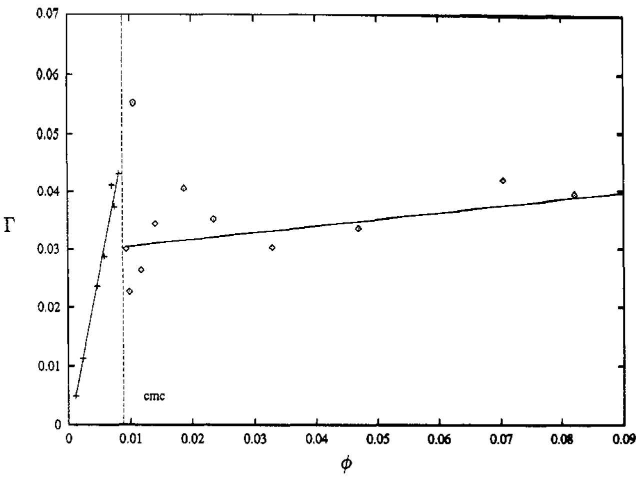

Figure 1. Adsorption amount Γ of copolymer chains as a function of the overall concentration ϕ below and slightly above the cmc.

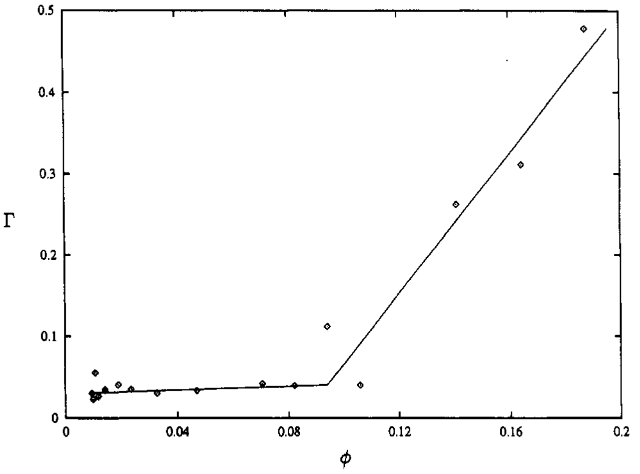

Figure 2. Adsorption amount Γ of copolymer chains as a function of the overall concentration ϕ above the cmc.

1). In both concentration regions, there is no adsorption of micelles because the number of adsorbed chains is less than 10. So the simulation results suggest that in these two concentration regions, below and just above the cmc, the adsorption occurs with single chains or the small aggregates.

In the previous paper,[16] we have shown that the concentration of the free chains in solution, ϕ_f, just above the cmc is lower than that just below the cmc, although the concentration of the free chains in the dilute phase, ϕ_1, may remain constant. If the adsorption occurred from free chains, the adsorbed amount just above the cmc should be lower than that just below the cmc. At higher concentrations (much larger than the cmc), the number of micelles in the solution is so large that some micelles are forced close to the surface. They may collide frequently with the surface and result in the adsorption of the micelles through a rearrangement of their chains. In this case, the adsorption may occur with the single chains and the micelles. There is a transition point from the adsorption without micelles to with micelles (Figure 2). Our simulation results can be directly compared with experimental results of diblock copolymer adsorption.[5]

B. Surface Coverage. Balazs and Lewandowski[8] investigated the effect of polymer concentration in the solution of the surface coverage. The concentration of free chains was held fixed throughout the course of a particular simulation but varied with the different simulations. Over the concentration range studied, surface coverage decreases with increased solution concentration.

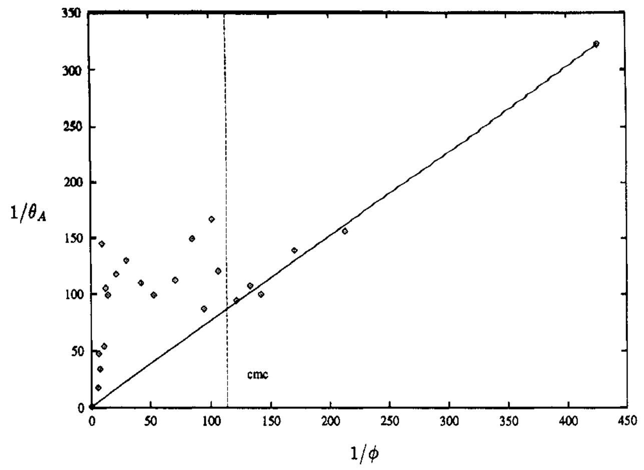

Figure 3. Inverse of the surface coverage $1/\theta_A$ as a function of the inverse of overall concentration $1/\phi$.

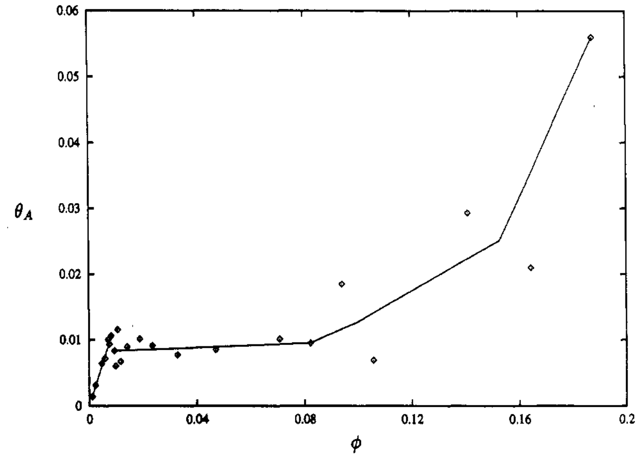

Figure 4. Surface coverage θ_A as a function of the overall concentration ϕ.

This is because they simulated the irreversible adsorption of triblock copolymers. As the solution concentration increases, the free anchoring end of a bound chain is more likely to interact with an anchoring segment in solution. This interaction effectively traps incoming chains from ever reaching the surface. They suggested that if a trapped chain will break away and continue to diffuse toward the surface, the surface coverage will not decrease with an increase in polymer concentration.

Recently, we have shown that in a nonselective solvent the adsorption isotherms of a diblock copolymer have Langmuir character when the length of the anchoring block and the surface affinity are small,[18] *i.e.*

$$\frac{1}{\theta_A} = 1 + \frac{1}{b\phi_A} \tag{2}$$

where $b = k_a/k_d$, which is a measure of the intensity of adsorption. For the adsorption of a diblock copolymer in a selective solvent, the adsorption isotherms also have Langmuir character below the cmc. Figure 3 depicts $1/\theta_A$ as a function of the inverse of overall concentration. Below the cmc, the data fall on the straight line. However, above the cmc the adsorption isotherms deviate from the linear model. This is because the self-assembly of the diblock copolymer will limit the chemical potential of the solution and, hence, the adsorption.

Figure 4 shows the surface coverage, θ_A, as a function of the overall concentration ϕ. The situation is similar to the adsorbed amount. Below the cmc the surface coverage increases linearly as the overall concentration increases. Just above the cmc the surface coverage is less

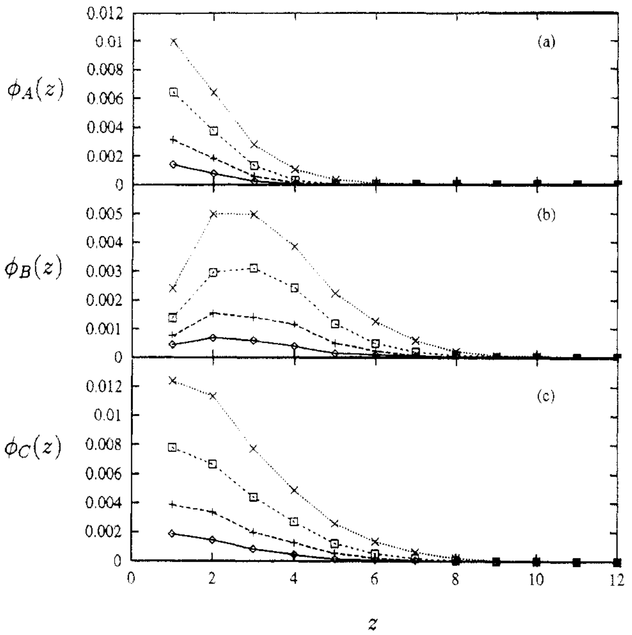

Figure 5. Density profiles for n_{tot} = 5 (◇), 10 (+), 20 (□), and 30 (×) below the cmc: (a) A block; (b) B block; (c) copolymer.

than that just below the cmc and is fairly insensitive to the overall concentration. The surface coverage increases again at higher concentrations because of the micelle adsorption.

C. Segment Density Profile of Adsorbed Layer. The segment density distributions of block A, block B, and the total chain for $A_{10}B_{10}$ below the cmc are depicted in Figure 5. In a nonselective solvent, the maximum of the adsorption for block A is at the first layer near the surface, and then the segment density of block A decreases monotonically away from the surface, like an exponential function.[19] In a selective solvent, the situation is a little different for the A block. The maximum of the adsorption for block A is at the first layer; however, the segment density of block A decreases linearly in the first three layers. The maxima of the density for block B are at the second or the third layer, which is similar to that in a nonselective solvent. An increase of the overall concentrations makes a corresponding increase of segment density near the surface for both blocks A and B and does not appreciably change the shape of the curve. The segment density distributions of copolymer at different overall concentrations are depicted in Figure 5c. The maximum of the adsorption of the copolymer is at the first layer.

The shape of the segment density distributions of the adsorbed layer for block A, block B, and the total chain just above the cmc (Figure 6) is similar to that below the cmc. It is interesting that just above the cmc, the segment density profiles are nearly independent of the overall concentration. At higher concentrations, the maximum of the adsorption for block A is also at the first layer; however, the segment density of block A drops from its maximum to practically zero along a sigmoidal profile, which spans a distance of more than 10 lattice sizes (Figure 7a). The maxima of the density for block B are similar to those below the cmc (Figure 7b). An increase of the overall concentrations makes a corresponding increase of segment density near the surface for both blocks A and B and may also change the shape of the curve. The shape of the segment density distributions for the total chain are different from those just below the cmc. The maximum of the adsorption of the copolymer moves from the first layer to the second layer (Figure 7c).

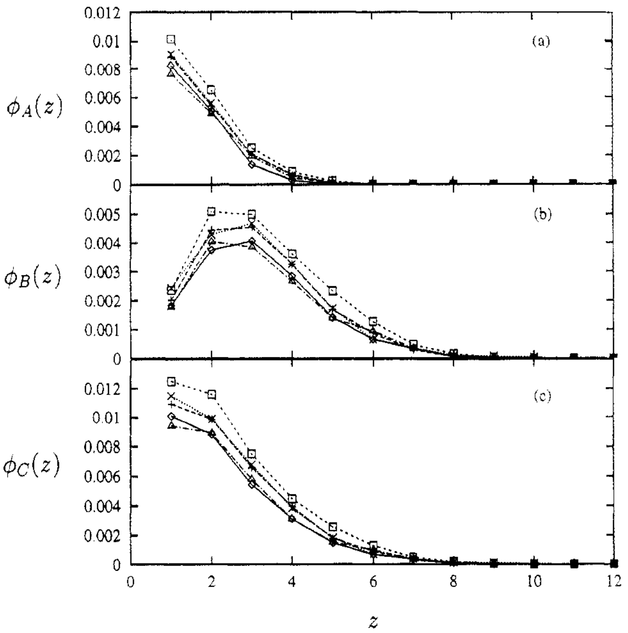

Figure 6. Density profiles for n_{tot} = 40 (◇), 60 (+), 80 (□), 100 (×), and 140 (△) just above the cmc: (a) A block; (b) B block; (c) copolymer.

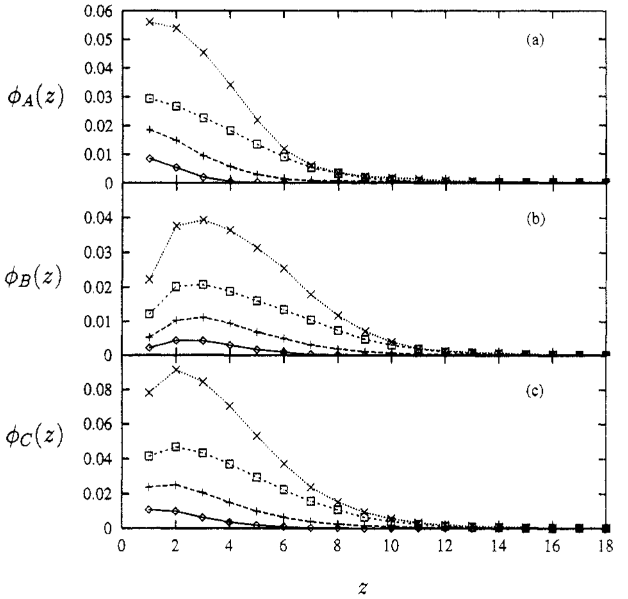

Figure 7. Density profiles for n_{tot} = 200 (◇), 400 (+), 600 (□), and 800 (×) well above the cmc: (a) A block; (b) B block; (c) copolymer.

Therefore, below the cmc the segment density profiles in a selective solvent are similar to those in a nonselective solvent, and above the cmc they are different in the two cases. In a nonselective solvent, the segment density profiles of the adsorbed layers are governed by a competition between adsorption and the entorpic effect.[19] The chains near the surface may decrease the energy by the interaction of the anchoring block with the surface and may experience a decrease in configurational entropy. In a selective solvent, the copolymer–solvent compatibility will further affect the structure of the adsorbed layer. First, the conformation of the A block will be more collapsed than that in a nonselective solvent. Second, the chains can adsorb not only on the surface but also on an adsorbed chain. The structure of the adsorbed layer can be characterized by the average bound fraction $\langle p_A \rangle$, which is defined as the fraction of segments attached directly to the surface per block A.[19] Figure 8 depicts the average bound fraction $\langle p_A \rangle$ as a function of the overall concen-

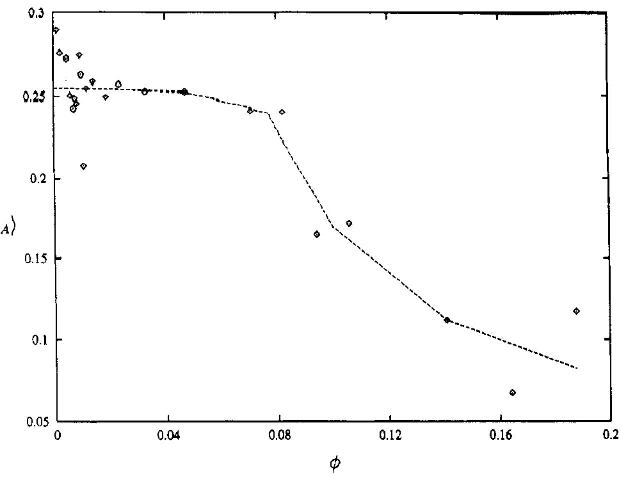

Figure 8. Average bound fraction $\langle p_A \rangle$ as a function of the overall concentration ϕ.

tration. Below and just above the cmc only the single chains adsorb directly on the surface, and $\langle p_A \rangle$ is fairly insensitive to the overall concentration. At higher concentrations, both the single chains and the micelles can adsorb, and $\langle p_A \rangle$ decreases dramatically because some adsorbed chains do not adsorb on the surface by direct means, but instead by association with other chains that have adsorbed directly onto the surface.

D. Adsorption Mechanism. Now we discuss the adsorption mechanism of a diblock copolymer in a selective solvent. At any concentration of copolymer, there may be three types of chains in the system: single chains, adsorbed chains, and the chains in aggregates. Accordingly, there are three equilibria among these chains. The adsorption mechanism obtained from our simulation results is different from that suggested by Munch and Gast.[5]

At very low concentrations, there are no micelles in the system, as shown in the previous paper.[16] The copolymer chains can exist as the free chains, the small aggregates, or the adsorbed chains. We did not observe a critical adsorption concentration, as suggested by Munch and Gast,[4] below which virtually no copolymers adsorb onto the surface and above which nearly all additional copolymer absorbs. Just like the collision of two chains will form a small aggregate, the collision between a chain and the surface also results in the adsorption of the chain. As the overall concentration increases, the adsorbed amount increases. Because both the concentration and the diffusion coefficient of the small aggregates are less than those of the single chains, the adsorption of the small aggregates in the lower concentration region can be ignored. The equilibrium mainly happens between the single chains and the adsorbed chains and is determined by the surface affinity and the copolymer–solvent compatibility. So we suggest the adsorption below the cmc occurs predominantly from the free chains.

As the overall concentration increases, the concentration of the small aggregates also increases. When ϕ reaches the cmc, the micelles begin to form. Above the cmc any additional chain will go into the micellar phase. However, an aggregate is not easy to adsorb on the surface because the diffusion rate of an aggregate is much smaller than that of a single chain and the aggregate has a steric layer. In order to bring its core in contact with the wall, the micelle has to overcome a potential barrier due to the B block corona. Johner and Joanny[10] suggested that the potential barrier for direct adsorption of micelles is so high that only free chains can adsorb on the surface. In the concentration region just above the cmc, the equilibrium between the micelles and the adsorbed chains can be ignored. The adsorbed chains are equilibrated with the concentration of the free chains in solution, ϕ_f, not the concentration in the dilute phase, ϕ_1. In this concentration regime, there are two equilibria: one is the equilibrium between the single chains and the micelles, and the other, that between the single chains and the adsorbed chains. So we suggest the adsorption just above the cmc also occurs predominantly from the free chains.

As the overall concentration further increases, the concentration of the aggregates becomes larger and larger. Upon reaching a certain concentration, the aggregates in solution are so crowded that micelles are forced close to the surface. These micelles collide frequently with the surface, which results in the adsorption of the micelles through a rearrangement of their chains. The third equilibrium between the adsorbed chains and the aggregates is established, and the adsorbed amount will increase again. There is a transition point from the adsorption without micelles to with micelles (Figure 2), which may be defined as the critical micelle adsorption concentration.

Therefore, we divide the overall concentration into three regions. Below the cmc, the adsorption of the copolymer occurs from the free chains. The only equilibrium happens between the free chains and the adsorbed chains. Just above the cmc, the adsorption of the copolymer also occurs from the free chains. There are two equilibria: one is the equilibrium between the free chains and the micelles, and the other is between the free chains and the adsorbed chains. The lower adsorbed amount just above the cmc is because the concentration of the free chains above the cmc is less than just below the cmc. At higher concentrations, the adsorption of the copolymer occurs from both the free chains and the micelles. There are three equilibria in the system, and the adsorbed amount is large because of the adsorption of the micelles.

If adsorption only occurred from the free chains below the cmc and just above the cmc, why is the initial rate of adsorption faster from solutions above the cmc than from the solutions just below the cmc, as observed by Munch and Gast?[5] We explain their results as follows. Above the cmc, there are free chains and micelles in the solution. If a fresh surface is exposed to the solution, both the free chains and the micelles can collide with the surface. Although adsorption of the micelles does not occur, it may contribute to the determination of the apparent initial rate of adsorption. On the other hand, Johner and Joanny[10] found the micelles never adsorb directly, and in a reasonable experimental time scale, only the free chains adsorb. However, this does not mean that the micelles play no role in the adsorption. The adsorption of free chains locally breaks the equilibrium between free chains and micelles. If the concentration is below the cmc there are no micelles, and the local equilibrium is restored by the diffusion of the free chains in the bulk. If the concentration is above the cmc, the local equilibrium can be restored by a relaxation of the micelles which release free chains. The presence of micelles thus accelerates strongly the formation of the adsorbed layer on the wall. This effect is particularly important in the early stages of the adsorption. So the initial rate of adsorption is faster from solutions above the cmc than from the solutions just below the cmc.

IV. Conclusions

The self-assembly and the adsorption of a diblock copolymer, $A_{10}B_{10}$, from a selective solvent have been simulated on a cubic lattice by the Monte Carlo method.

The results demonstrate the self-assembly of diblock copolymers has a dramatic influence on the adsorption. According to the adsorption behavior of the copolymer, the overall concentration can be divided into three regions: (1) Below the cmc, there are no micelles in the solution, and the adsorption of the copolymer occurs from the free chains. The only equilibrium is the one between the free chains and the adsorbed chains. As the overall concentration increases, the number of both the free chains and the adsorbed chains increases. (2) Just above the cmc, the concentration of the free chains in solution, ϕ_f, is lower than that just below the cmc. There are two equilibria in this concentration region: one is the equilibrium between the free chains and the adsorbed chains, and the other is between the free chains and the aggregates. The micelles have little contribution to the adsorption. The adsorption of the copolymer occurs mainly from the free chains, and the adsorbed amount is less than just below the cmc. (3) At very high concentrations, the adsorption may occur from both the free chains and the micelles. The adsorbed amount increases as the overall concentration increases because of the adsorption of the micelles. The simulation results of adsorption from a selective solvent are in good agreement with the experimental results.

Below the cmc the structures of the adsorbed layer in a selective solvent are similar to those in a nonselective solvent, and well above the cmc the segment density profiles have different curve shapes in the two cases. It is the copolymer–solvent compatibility that further affects the structure of the adsorbed layer in a selective solvent.

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