Self-Assembly and Adsorption of Diblock Copolymers from Selective Solvents. 1. Self-Assembly

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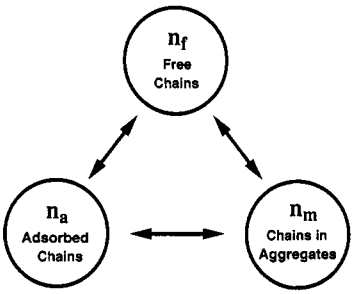
ABSTRACT: The self-assembly and the adsorption of a diblock copolymer, $A_{10}B_{10}$, from a selective solvent have been simulated on a cubic lattice by a Monte Carlo method. The simulation uses the periodic boundary conditions in the X and Y directions and places two surfaces at the edges of the box in the Z direction. The A block is in a poor solvent, and the B block, 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. This report describes the simulation results of the equilibrium properties between the free chains and the aggregates in the existence of the adsorption. We find that the rate of change of the number of aggregates with concentrations is altered in a narrow concentration range. We identify this regime with the critical micelle concentration. We also find that above the cmc, the concentration of the free chains decreases linearly as the overall concentration of copolymer decreases, instead of keeping constant. The average number of chains and the polydispersity are calculated. The effect of the adsorption on the self-assembly of the diblock copolymer in solution is discussed.

I. Introduction

Recently, a considerable effort has been devoted to the study of the self-assembly[1–8] and the adsorption[9–23] of block copolymers in solutions as well as in melts. A diblock copolymer in a selective solvent near a surface is a complicated system. The block interacting unfavorably with the solvent adsorbs onto the surface while the soluble block extends into the solution and forms a steric layer, which provides a means to stabilize colloidal particles. The diblock copolymer may also self-assemble to form aggregates if the concentration in the solution exceeds the critical micelle concentration (cmc). Since the cmc often occurs at very low concentration, an adsorption model of a diblock copolymer from a selective solvent must include a description of aggregation. When an equilibrium is reached, the system may contain copolymer chains in the three types of environments (Figure 1): (1) the free chains in solution; (2) the chains self-assembled to form aggregates in solution; (3) the chains adsorbed on the solid surface.

The motivation for this work arises from the fact that up to now, as we know, 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 theoretical work discussed the micelle formation[3] and the surface adsorption[10] separately because of the complication of the system. Using an analytical approach, one has to assume a particular geometry not only for the aggregates but also for the adsorbed layer. In this problem involving a complex system with many variables, computer simulations provide a significant advantage over analytical models. In simulations, few assumptions are made, and the polymer chains are allowed to adsorb or self-assemble in the way they prefer. In the previous report,[22,23] we have simulated the adsorption behavior of diblock copolymers in a nonselective solvent with the Monte Carlo method. Here, the method is extended to the study of the competition between the self-assembly and the adsorption of a diblock copolymer in a selective solvent. We will describe the self-assembly process in this paper, and then discuss the adsorption process in the following paper.[24]



$$n_{tot} = n_f + n_a + n_m$$

Figure 1. Three types of copolymer chains when an equilibrium is reached for the adsorption of a diblock copolymer from a selective solvent.

Leibler et al.[1] presented a simple microscopic model for micelle formation in mixtures of block copolymers and homopolymers. They calculated the fraction of chains aggregated in micelles, ζ, the volume fraction occupied by the micelles, $\xi\phi\zeta$, and the concentration of free chains outside the micelles, ϕ_1, as a function of the overall concentration, ϕ. The results suggested the average number of free chains and the size of a micelle are determined by the balance between the internal energy of micelles and the entropy of mixing of micelles, free polymer chains, and the homopolymer matrix. A critical micelle concentration behavior was found for low copolymer contents even for weak incompatibilities of species. Munch and Gast[3] applied the theory of Leibler et al.[1] to describe the micellization of diblock copolymers in solution. They found that the critical micelle concentration and aggregation number increase as the copolymer–solvent compatibility increases, as the insoluble block becomes smaller relative to the soluble block, and as the size of the solvent decreases. They also discussed some limiting cases and gave approximations for the model in the limit of small critical micelle concentration.

The temperature-dependent micellization in aqueous block copolymer solutions was investigated experimentally and theoretically by Linse and Malmsten.[6] The experi-

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ments involved the determination of the temperature dependence of the critical micelle concentration and the fraction of polymer chains in micellar form. Comparison between theoretical and experimental findings shows qualitative agreement regarding the decrease in the cmc and the increase in the average aggregation number, the micellar size, and the fraction of polymer chains in micellar form, all with increasing temperature. Wang and Mattice[8] studied the self-assembly of diblock copolymers into micelles by computer simulation. The results showed that the cmc depends strongly on the length of the insoluble block and weakly on the length of the soluble block. The size of the micelle is close to that estimated by a simple hard-core shell model.

Recently, we have developed the simulations of the adsorption of diblock copolymers on a surface.[22,23] The emphasis in the previous papers was on the adsorption isotherms and adsorption kinetics of the diblock copolymers when the solvent is nonselective for both blocks and no micellization occurs. These simulations are extended here to the adsorption of diblock copolymers in a selective solvent, and our goal is to study the competition between self-assembly and adsorption. When the copolymer chains are added to the system, do they adsorb onto a surface or self-assemble into aggregates or remain isolated? In this paper, we provide some insight into the nature of micelle formation and the critical micelle concentration in the existence of surface adsorption. The simulation results are compared with the theoretical predictions and the experimental results.

II. Model

We study a solution of a selective solvent and a diblock copolymer A–B, containing N_A beads of type A and N_B beads of type B. For the sake of simplicity, here we consider a symmetric case $N_A = N_B = 10$. The A block is in a poor solvent, and the B block, in a good one. The simulations are performed on a cubic lattice of dimension $44 \times 44 \times 46$ with periodic boundary conditions in the X and Y directions, and there is no special interaction at the X and Y boundaries. The top layer ($Z = 0$) and the bottom layer ($Z = 45$) are assumed to be impenetrable and there are special energetics (E_{AS} and $E_{AS'}$) for these two layers. The dimensionless interaction parameters, reduced by kT, were introduced to describe the effective interactions among beads A, beads B, solvent molecules, and a surface site. All interactions were assumed to be short-range, i.e., nearest-neighbor interactions. The interaction energy between beads A and beads B or beads A and solvent molecules is positive, and this leads to incompatibility of beads A with beads B or solvent molecules and a tendency for self-assembly by the A blocks. The interaction energy between beads A and the surface is set to zero. It should be remembered that even if the interaction energy between beads A and the surface is zero, the same thermodynamic factors driving the self-assembly will cause the block copolymer to adsorb onto the surface.

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. No lattice site on a surface layer can be occupied by any bead, and no lattice site on the other layers can be occupied by more than one bead. The voids on the lattice are considered as the solvent molecules. Three types of movements, Brownian motion, kink-jump (including end-flip and crank motion), and reptation, as illustrated in ref 22, were used to convert one replica into another. Trial moves were accepted or rejected according to the Metropolis rules.[25] For convenience, we choose the same attempt for all movements. In each iteration, a chain is chosen randomly; then the Brownian motion and the reptation of the chain and the kink-jump of each bead are attempted once. A copolymer chain becomes adsorbed to the surface when a bead of A on this chain is a nearest neighbor of the surface layers or a bead of A on an adsorbed chain. A copolymer chain is considered to participate in an aggregate if a bead of A on the unadsorbed chain is a nearest neighbor of a bead of A on another unadsorbed chain.

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} and $E_{AO} = 0.5$, where interaction parameters E_{AB} and E_{AO}, are applied whenever A has a nonbonded B or a solvent molecule as a nearest neighbor. All remaining interaction parameters, including E_{AS} and $E_{AS'}$, are set to be zero. 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

The copolymer chains in a selective solvent near a surface may exist as free chains, adsorbed chains, and chains self-assembled into aggregates (Figure 1). If n_i is the number of chains of type i (here i can be f, m, and a, representing the free chains, the chains in aggregates, and the adsorbed chains, respectively), N is the length of the chain, and V is the volume of the box, and concentration of chains of type i is

$$\phi_i = n_i N/V \tag{1}$$

The overall concentration, ϕ, equals the sum of concentrations of the three types of chains,

$$\phi = \phi_r + \phi_m + \phi_a \tag{2}$$

where ϕ_f, ϕ_m, and ϕ_a are the concentrations of the free chain, and chains self-assembled to form aggregates, and the adsorbed chains, respectively. The polymer concentration, the interaction parameters, the lengths of the blocks, and the symmetry of the copolymer chains have different effects on the equilibria among the three types of chains. Here we examine the effect of the overall concentration. It should be emphasized that there is a particular effect due to the size of the simulations. The systems have a large surface area per volume of solution compared to many experiments. The simulation results show the significant influence of adsorption on cmc and different chain concentrations. However, in most experimental systems, the amount of polymer on the surface is so small compared to the bulk that the influence of the adsorption will be negligible.

A. Critical Micelle Concentration. The ability of diblock copolymers to self-assemble into micelles, even in very dilute solution, has been established over 2 decades. At extremely low concentration only free chains are found in solution. When the concentration reaches the cmc, the micelles begin to occur. The IUPAC Manual and Symbols and Terminology makes the following statement about the cmc:[26] There is a relatively small range of concentrations separating the limit below which virtually no micelles are detected and the limit above which all additional surfactant forms micelles. Many properties of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By

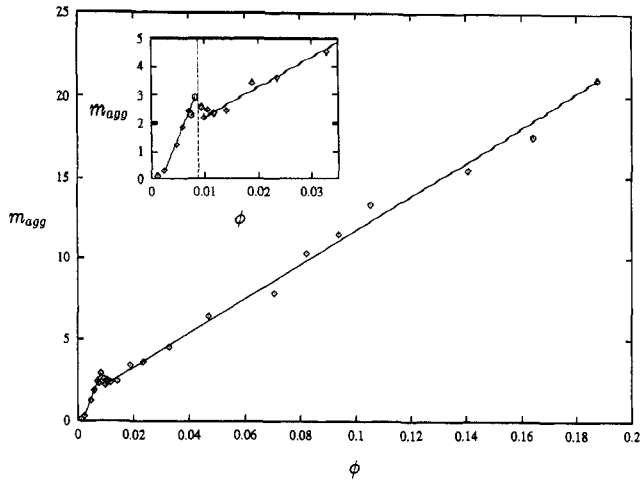

Figure 2. Number of aggregates m_{agg} as a function of the overall concentration ϕ.

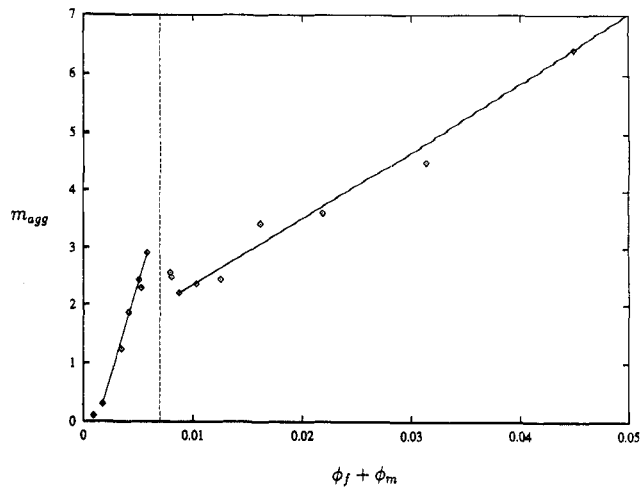

Figure 3. Number of aggregates m_{agg} as a function of the sum of the concentration of the free chains and the chains in the aggregates, $\phi_f + \phi_m$.

extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the *critical micellization concentration* (critical micelle concentration).

The cmc data are determined by a variety of methods and are used in a wide range of areas and specialities.[5,6] Leibler et al.[1] found below the concentration ϕ_0, there are no micelles in the system. For $\phi > \phi_0$, the volume fraction occupied by micelles varies linearly with ϕ. They also found that the thermodynamic quantities such as the osmotic pressure of homopolymer chains change their behavior at the concentration ϕ_0. It is natural to identify the concentration ϕ_0 around which the volume occupied by micelles increases abruptly with the critical micelle concentration.

The simulation results are best illustrated in a plot of the number of aggregates m_{agg} as a function of the overall concentration ϕ (Figure 2). The value of m_{agg} must be an integer at any specified iteration, but it can be noninteger when averaged over multiple iterations. The existence of the cmc is reflected in the change in the concentration dependence of the number of aggregates over a narrow range. Below the cmc the chains form some small aggregates, and the number of aggregates increases linearly. However, the average number of chains in an aggregate is less than 5 in the low concentration region. After the overall concentration rises above the cmc, the number of aggregates increases linearly at a certain rate. If we assume all additional chains form micelles in this concentration region, we can estimate the size of the micelles from the slope of the straight line by the equation

$$p' = \frac{d\phi}{dm_{agg}} \frac{L_X L_Y L_Z}{N_A + N_B} \tag{3}$$

where L_X, L_Y, and L_Z are the box lengths. The average number of copolymer chains in a micelle, p', is about 40 and is independent of the overall concentration above the cmc. It should be mentioned that what we calculate here is the average number of copolymer chains in the micelles newly occurring above the cmc, and it is larger than the average number of copolymer chains in an aggregate p in the solution because the latter also counts the small aggregates that occurred below the cmc.

The intersection of the two straight lines defines the point with the overall concentration of 0.007. However, there is no large aggregate in the system until the overall concentration exceeds 0.009. In this region the values of ϕ_f are a little larger than that at the intersection point, which may be said to be *supersaturated*. Semenov[21] has shown that the system at the cmc has to overcome a high potential barrier in order to form a micelle. So the apparent (experimental) cmc might be controlled by the barrier (rather than the thermodynamic potential of a micelle) and might be several times larger than the equilibrium (infinite time) cmc.

The concentration range due to the supersaturation is a relatively small one, in which there is a maximum for the number of the aggregates at $\phi = 0.008$. We identify the point between the maximum and the concentration at which the first micelle is detected, $\phi \approx 0.0088$, as the cmc (Figure 2), instead of the intersection point because (1) only above this point are there large aggregates, in which the number of chains is larger than 20, (2) $d\phi_f/d\phi$ changes from positive to negative (see the next subsection), and (3) it is also the transition point for some other properties, such as the average size of the aggregates and the adsorbed amount, as described in the rest of this paper and in the following paper.

The existence of adsorption will affect the values of the cmc because the cmc is defined by the overall concentration which contains the concentration of the adsorbed chains. Apparently, the adsorption will shift the cmc to a higher concentration. If we plot the number of aggregates as a function of the sum of the concentrations of the free chains and chains in aggregates, and ignore the volume occupied by the adsorbed layer, we can estimate the real cmc in absence of the adsorption. The results are depicted in Figure 3. The value of the real cmc is about 0.007 when the chains are $A_{10}B_{10}$ and the interaction parameters $E_{AB} = E_{AO} = 0.50$. The stronger the surface adsorption, the higher the shift in the apparent cmc. However, there is little influence of adsorption in many experiments.

B. Free Chains. There are two definitions of the concentration of the free chains in the references. One is the concentration of the free chains in the dilute phase or outside the micelles, ϕ_1, as defined by Leibler et al.[1] Another is defined by eq 1. In this report, we use ϕ_f to characterize the free chains in solution because it is proportional to the average number of free chains in solution, and determines the adsorbed amount of copolymer chains (see the following paper). The relation between ϕ_f and ϕ_1 is

$$\phi_f = \phi_1(1 - \xi\phi\zeta) \tag{4}$$

where $\xi\phi\zeta$ is the volume fraction of the micellar phase. The concentration of free chains may vary with the

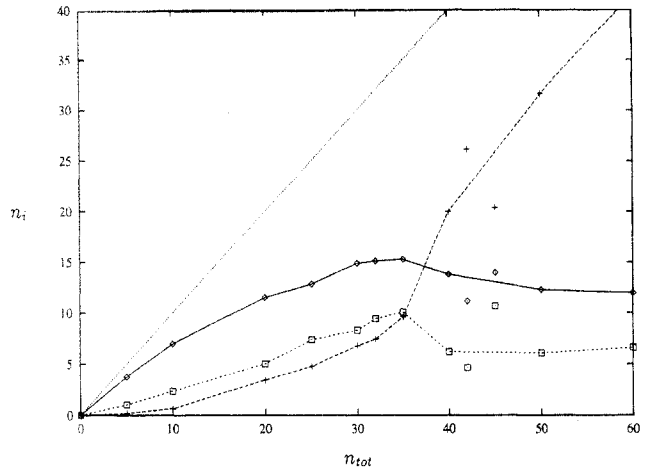

Figure 4. Numbers of the free chains (◇), the adsorbed chains (□), and the chains self-assembled in the aggregates (+) as a function of the number of the total chains. The straight line has a slope of one, and the other lines are to guide the eye.

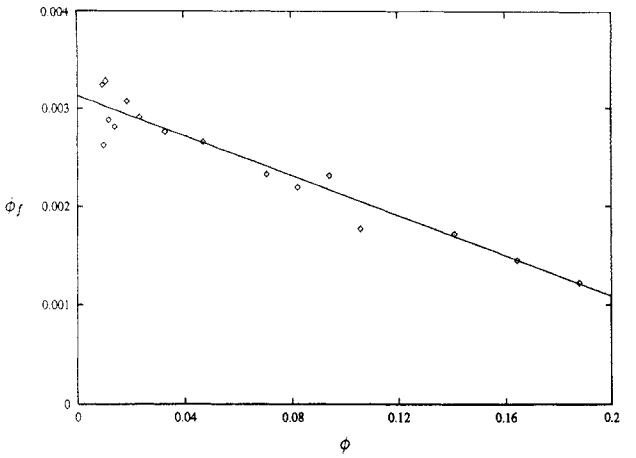

Figure 5. Concentration of the free chains as a function of the overall concentration.

different values of molecular parameters and interaction energies.

Sometimes it may be convenient to use the concentration of free chains outside of micelles, ϕ_1, to describe the characteristics of micellization. For example, Leibler et al.[1] found that below the cmc, ϕ_1 is equal to ϕ, and virtually no micelles exist. Above the cmc, little additional copolymer contributes to the free chain concentration, and ϕ_1 remains constant. The concentration of the solution where this sharp transition occurs is denoted as the critical micelle concentration. Here, ϕ_1 represents the background concentration of free chains in equilibrium with the micelles. Leibler et al.[1] also found that at the higher degree of incompatibility, ϕ_1 continues to increase slowly above the cmc due to a balance between the entropy of the free chain in solution and the stretching energy of the extended soluble blocks.

Below the cmc. Leibler et al.[1] found no micelles exist in the system below the cmc, and ϕ_1 is equal to ϕ. According to their theory, in the existence of the adsorption, there may be only two types of chains in the system, i.e. the free chains and the adsorbed chains. However, in our system, the molecules may collide with one another. When a bead of A on one chain is a nearest neighbor of a bead of A on another chain, there is an energy change with the assignments of the interaction parameters used here. So it is possible to form a small aggregate because of the collision, although this small aggregate is not as stable as a micelle.

Our simulation results are plotted in Figure 4. In extremely dilute solution, the sum of the number of the free chains and the adsorbed chains is equal approximately to the total number of chains. There are few chains in the form of aggregates. As the total number of chains increases, the number of the free chains increases while dn_f/dn_{tot} decreases. The sum of the numbers of the free chains and the adsorbed chains is less than the total number of chains because of the formation of small aggregates. It can be seen that $d\phi_f/d\phi$ ($=dn_f/dn_{tot}$) changes from positive to negative around the cmc (at $n_{tot} = 35$).

Above the cmc. Leibler et al.[1] showed that above the cmc, ϕ_1 remains constant or even increases. They also showed the volume fraction of the micellar phase, $\xi\phi\zeta$, varies linearly with ϕ. Here $\xi\phi\zeta$ is different from the volume fraction of chains in micelles because the former contains copolymer chains and the solvent molecules while the latter only contains copolymer chains. Assume that the adsorbed layer can be considered as a special aggregate, and the total volume fraction of the micellar phase (including the adsorbed layer), Φ, increases linearly with ϕ, i.e.

$$\Phi = a + b\phi \tag{5}$$

where a and b are constants, and $b > 0$ because Φ increases as ϕ increases. Insert eq 5 into eq 4 and assume ϕ_1 is constant above the cmc,

$$\phi_f = \phi_1[1 - (a + b\phi)] = a' - b'\phi \tag{6}$$

where $a' = \phi_1(1 - a)$ and $b' = b\phi_1 > 0$. Therefore, the concentration of the free chains in solution ϕ_f will decrease linearly as the overall concentration ϕ increases, and not remain constant.

The results of the Monte Carlo simulation prove the above prediction (Figure 5). All the data points above the cmc describe a straight line. The concentration of the free chains in solution does decrease as the overall concentration increases. Therefore, above the cmc not only may additional chains go into the micellar phase but also some free chains may go into the micellar phase because of the decrease of the dilute phase. Most of the previous references do not mention this effect. For example, Munch and Gast[14] thought that, above the cmc, there is a constant concentration of single chains in solution. Therefore, if adsorption occurred from single chains, the initial rate of adsorption would not change as the overall concentration rises past the cmc. However, the simulation results show that even though the concentration of free chains in the dilute phase, ϕ_1, keeps constant, the concentration of free chains in solution, ϕ_f, will decrease linearly as the overall concentration rises, because of the decrease of the volume of the dilute phase. In the following paper, we will show the adsorption is determined by the concentration of free chains in the solution instead of the concentration of free chains in the dilute phase.

From the data in Figure 5, we can estimate the concentration of free chains in the dilute phase, ϕ_1, and the slope, b, of eq 5. The intercept of the line is $a' = (1 - a)\phi_1$. When χN is large, $|a| \ll 1$ (see Figure 3 in ref 1). Therefore, $\phi_1 \approx a'$ and $b = b'/\phi_1$ where b' is the slope of the line in Figure 5. We find $\phi_1 \approx 0.003$, and $b = 3.24$ for $\chi N_A = 20$, $N = 20$, and $\alpha = 20$. Here $\chi = zE_{AS}$ is the dimensional Flory interaction parameter, z is the coordination number and is about 4 in our system,[8] N is the length of copolymer, and α is the ratio of length of copolymer over solvent or homopolymer. It is very interesting to compare these results with those of Leibler et al.[1] although the parameters and the method are different. For $\chi N = 20$, $N = 200$, and $\alpha = 5$, we find ϕ_1

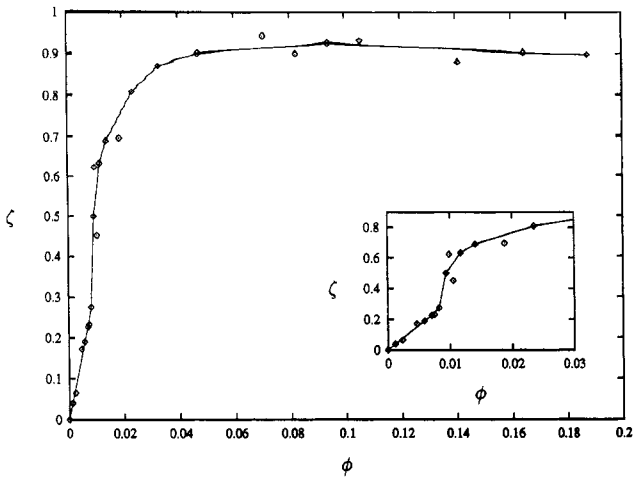

Figure 6. Fraction of the chains self-assembled in aggregates as a function of the overall concentration.

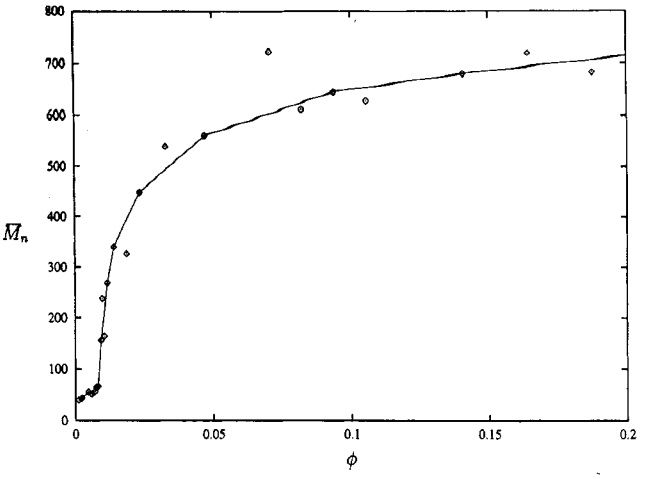

Figure 7. Number-average molecular weight of the aggregates as a function of the overall concentration. Each bead, whether A or B, contributes a weight of 1.

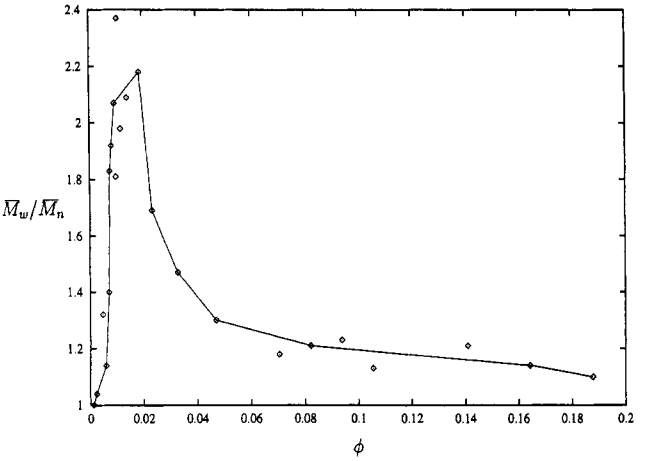

Figure 8. Polydispersity, $\bar{M}_w/\bar{M}_n$, of the aggregates in the system as a function of the overall concentration.

= 0.008 and b = 3.18 from Figures 3 and 4 in ref 1. Our simulation results are in good agreement with the theoretical calculation of Leibler et al.[1]

C. Aggregates in Solution. If there are one or more contacts of A beads among two or more unadsorbed chains, we define them as an aggregate. An aggregate may be a small aggregate or a micelle, the latter of which has a larger size and a more stable state. For any concentration of a diblock copolymer in a selective solvent, there is usually a certain fraction of chains in aggregates. The problem is to find when the aggregates become sizable. However, in the previous publications,[1,3] the small aggregates below the cmc were ignored, and only the micelles above the cmc were considered. Our simulations show that the small aggregates exist both below and above the cmc.

Fraction of Aggregates. Leibler et al.[1] showed a variation of the fraction of copolymer chains aggregated in micelles, ζ, as a function of the overall concentration, ϕ. The most striking feature of the results is the abrupt onset of an increase of the fraction of chains involved in formation of micelles around the cmc. Figure 6 depicts the simulation results. Below the cmc, there are some small aggregates in the system and the fraction of the fraction of the chains in aggregates increases linearly as ϕ increases. Just above the cmc, the fraction of the chains in aggregates increases dramatically, which is in agreement with the theoretical prediction.[1] The transition point is around the cmc. The fraction of the chains in aggregates at higher concentration does not approach the limit value of 1.0 because of the adsorption at the surface.

Size of Aggregates. Leibler et al.[1] showed the size of the micelles is only weakly dependent on the overall concentration ϕ. For example, when $\chi N = 17.5$, $N = 200$, and $\alpha = 5$, for ϕ varying from 0.16 to 0.04, the average number of chains in a micelle p varies from 78.3 to 76.8. However, for concentrations close to the cmc, for instance $\phi = 0.022$, p drops to 70.4. Monte Carlo simulations obtain similar results (Figure 7). Below the cmc, the number-average molecular weight $\bar{M}_n$ is less than 100 or the average number of copolymer chains in an aggregate p is less than 5. Figure 7 suggests $\lim_{\phi \to 0} \bar{M}_n = 40$ because the smallest p is 2. Above the cmc, $\bar{M}_n$ increases dramatically, and then approaches a limit. Here the size of the aggregates also has a transition point at the cmc.

In the first subsection, we have estimated the average number of copolymer chains in a micelle newly occurring above the cmc. It equals 40 and is independent of the overall concentration. Here, the number-average molecular weight is the average weight of all aggregates in the solution, including the small aggregates occurring below the cmc. At higher concentrations, $\bar{M}_n$ is close to 800. As the overall concentration approaches the cmc from above, $\bar{M}_n$ decreases because the contribution of the small aggregates becomes larger and larger.

Polydispersity. Several authors have developed theories for the micelle formation by minimizing the free energy of the system.[1,2] All assume that the micelles are monodisperse, neglecting the possibility that the micelles could have a size distribution. In simulations, we can examine the change of the polydispersity of the aggregates with the concentration ϕ. Most of the properties, such as the concentration of the free chains and the average number of the aggregates, have their transition points at the cmc. However, the polydispersity of the aggregates increases as ϕ increases, even just above the cmc (Figure 8). Then it begins to decrease. As $\bar{M}_n$ approaches the limiting value, the polydispersity of the aggregates also approaches a limit. At higher concentrations, the aggregates are more uniform in size.

In fact, there are two types of aggregates in the system: the small aggregates and the micelles. Below the cmc, there are only the small aggregates in the system, and both $\bar{M}_n$ and the polydispersity are small. Just above the cmc, there are both the small aggregates and the micelles, and the concentration of micelles is small. Therefore, the polydispersity is large. As the overall concentration increases, the fraction of micelles increases in the aggregates, and $\bar{M}_n$ increases dramatically. At the higher overall concentration, the contribution of the micelles is much

larger than that of the small aggregates, so $\bar{M}_n$ approaches a limit and the polydispersity is small.

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 A block is in a poor solvent, and the B block, in a good solvent. 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. One of the main results of our work is that over a narrow concentration range the rate of change of the number of aggregates with overall concentration is altered. We identify this regime with the critical micelle concentration. We demonstrate that the surface adsorption has an influence on the critical micelle concentration. Below the cmc, the concentration of the free chains increases as the overall concentration of copolymer increases; while the important point is that above the cmc, the concentration of the free chains in solution decreases linearly as the concentration of copolymer increases, even though the concentration of free chains in the dilute phase remains constant. Around the cmc, there may be a *supersaturated* state in which the concentration of the free chains is a little larger than that just below the cmc. For any concentration of copolymer, there is usually a certain fraction of chains in aggregates, which increases as ϕ increases. Below the cmc, there are some small aggregates in the system; above the cmc, the size of the micelles is independent of the overall concentration. The polydispersity of the micelles reaches its maximum at a certain concentration sightly above the cmc.

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