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Monte Carlo simulation of morphologies of self-assembled amphiphilic diblock copolymers in solution

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The Monte Carlo method has been applied to simulate the process of the self-assembling of amphiphilic diblock copolymers in a selective solvent. The simulations illustrated that the aggregates morphologies of *A-b-B* diblock copolymers in solution strongly depend on the length of corona-forming segments, i.e., with the decrease of the corona-forming segments, the transition of spherical micelles to rodlike aggregates occurs, which are in accord with the experimental results of Eisenberg and co-workers [Science **268**, 1728 (1995); Macromolecules **32**, 2239 (1999); **31**, 3509 (1998); **29**, 6359 (1996); **31**, 9399 (1998)].

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I. INTRODUCTION

The self-assembly of block copolymers has been attracting much attention in recent years [1–3] because it has potential applications in many areas in addition to the fundamental interests [4]. In solutions of block copolymers, spherical micelles have been observed frequently [5]. Recently, Eisenberg's group reported that the crewcut aggregates of poly(styrene-*b*-acrylic acid) (PS-*b*-PAA), a charged polymer, and poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO), a neutral polymer, in a dilute selective solvent, a mixture of H_2O and dimethyl formamide (DMF), can yield micellelike aggregates with different morphologies [1,6–9], i.e., spherical micelles, rodlike and vesicular aggregates, lamellae, and large compound micelles (LCMs). The multiple morphologies are formed from an identical block copolymer family differing only in the relative block lengths. For example, as the length of hydrophilic PEO segments in PS-*b*-PEO decreased, the morphologies of aggregates changed from spheres to rods, to lamellae, and finally to vesicles. However, the mechanism of self-assembly of diblock copolymers in selective solvent is far from understanding. Seldom theoretical consideration on this problem was reported [10,11].

On the other hand, the computer simulation method has been proved to be a powerful tool in the studies of phase behaviors of polymers in melts or solutions [12–15]. With the Monte Carlo method, Larson *et al.* [16–18] and Ko and Mattice [19] studied the self-assembly of diblock copolymers in an oil-water system and a selective solvent in detail. These works studied the self-assembly of symmetrical diblock copolymers. The effects of diblock copolymers with asymmetrical structures on aggregates morphologies formed by self-assembly have not been reported. In this paper, the Monte Carlo method is applied to simulate the process of the self-assembly of amphiphilic diblock copolymers with asymmetrical structure, in a selective solvent similar to the condition the experiments of Eisenberg *et al.* [1,6–9]. Then the result obtained is compared with experimental data [6–9,20] for getting some insights on this interesting topic.

II. SIMULATION

A three-dimensional simulation was used to provide a direct inspection of the polymer configuration and the multiple morphologies of an amphiphilic diblock copolymer in selective solvent. Multiple-chain configurations were generated on a cube volume $50\times50\times50$ lattice. Diblock polymer (*A-b-B*) chains with ten *A* units in *A* segments and various amounts of *B* units in *B* segments are put in the cube. A standard periodic boundary condition was imposed on the lattice to mimic an infinite-size system [21]. The ''single-site bond fluctuation'' model proposed by Carmesin and Kramer [22] and Larson *et al.* [16,17] was used to implement the Monte Carlo simulations. Here, we briefly review the model and algorithm. In simulations, the evolution of the chain configuration was achieved by the random displacing of a single unit to its 18 nearest-neighboring sites. The distances between the single unit and the 18 nearest-neighboring sites are restricted to lengths of 1 and $\sqrt{2}$. Each attempted move may change the bond length, but the chain connectivity restricts the bond length to 1 and $\sqrt{2}$. The excluded volume interaction ensures no more than one bead per lattice site. If one attempted move violates either the excluded volume or the bond length restriction, it is rejected. The acceptance or rejection of one attempted move, which satisfies both the excluded volume and the bond length conditions, is further governed by the Metropolis rule [23]; namely, it is accepted if the energy change ΔE is negative; otherwise, it is accepted with a probability of p as the following equation:

$$p=\exp(-\Delta E/kT), \tag{1}$$

where $\Delta E=(\Delta N_{AA}\varepsilon_{AA}+\Delta N_{BB}\varepsilon_{BB}+\Delta N_{AB}\varepsilon_{AB}+\Delta N_{SS}\varepsilon_{SS}+\Delta N_{AS}\varepsilon_{AS}+\Delta N_{BS}\varepsilon_{BS})$ is the energy change of the movement; ΔN is the difference in the number of the nearest-neighboring pairs of the sites occupied by monomers or solvent after and before the movement; ε is the reduced interaction energy gained after the two neighboring sites are occupied by monomers or solvent; and the subscripts *A*, *B*, and *S* denote monomers *A*, *B*, and solvent, respectively.

In Eisenberg's experiments, the PS-*b*-PEO diblock copolymers were firstly dissolved into DMF, a good solvent to both PS and PEO segments, then the poor solvent of PS segment, such as water, was gradually added into the solution of the diblock copolymer. The mixed solvent was still good to the PEO segment; however, it gradually became

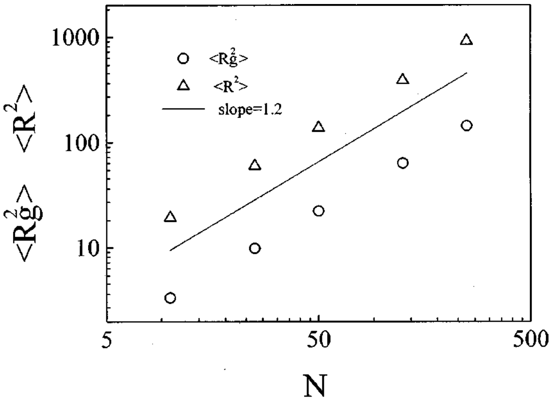

FIG. 1. Dependence of the radius of gyration $\langle R_g^2\rangle$ and the end-to-end distance $\langle R^2\rangle$ on chain length N, calculated on the basis of the one-site bond fluctuation model. The slope of the solid line is 1.2.

poor to the PS segment. Finally, the PS-*b*-PEO diblock copolymer aggregated to form the multiple morphologies as the addition of water. In our simulations, $1/kT = 0.3$ is invariable to simulate the constant temperature process in experiments [6–9]. Let $\varepsilon_{AB} = 1$, $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{SS} = 0$, $\varepsilon_{BS} = -1$, which ensures the immiscibility between the A and B segments, and the mixed solvent is good to the B segment all the time. We start our simulations from $\varepsilon_{AS} = -1$, which implies that the mixed solvent is good to the A segment. After the system reaches its equilibrium state, then the ε_{AS} is increased linearly from -1 to 1 in 160 000 Monte Carlo steps and remains unchanged after $\varepsilon_{AS} = 1$. This ensures the mixed solvent gradually becomes poor to the A segment.

III. RESULTS AND DISCUSSION

Figure 1 shows a verification of our algorithm and computer program in terms of the relationship of chain length with the radius of gyration $\langle R_g\rangle$ and the end-to-end distance $\langle R\rangle$. It is well known that for a polymer chain in the absence of interaction, $\langle R_g^2\rangle \propto N^{2\nu}$ and $\langle R^2\rangle \propto N^{2\nu}$ with ν of the Flory exponent. For a three-dimensional self-avoiding random walk $\nu = 0.6$ [24]. The simulation results in Fig. 1 show that the simulation algorithm and computational program we used are correct.

Figure 2 shows the aggregate morphologies of the *A*-*b*-*B* diblock copolymer with ten repeating units of A and B in A and B segments (10-*b*-10) in solution, respectively. It shows distinctly typical spherical micelles, which were usually observed for diblock copolymers in a selective solvent [5]. When the corona-forming segment (B segment in our simulation) contains ten repeating units, they stretch outside of the core with a high density, leading to strongly repulsive interactions between them (see Fig. 2). Any further decrease of the area per corona chain will increase the deformation energy of the corona chains, and correspondingly, the repulsive energy among the corona chain. Therefore, the structure of star micelles is mainly controlled by minimizing the surface energy. So the balance shape of micelles with a longer corona chain will be sphere.

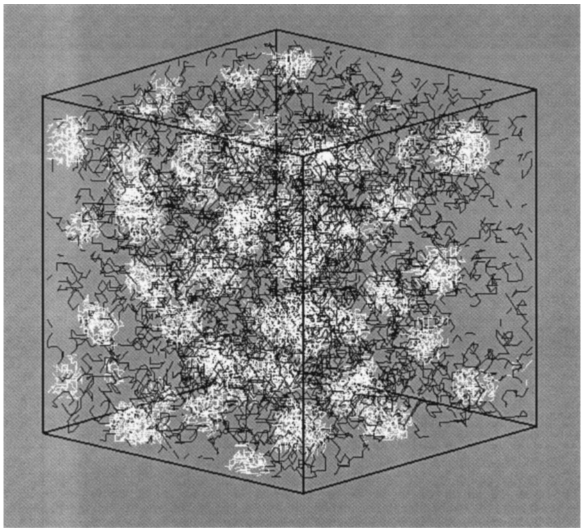

FIG. 2. Morphologies of *A*-*b*-*B* (10-*b*-10) diblock copolymers in a selective solvent; the concentration of the solution is 15%. The white and black lines are A and B segments.

Figure 3 shows the aggregate morphologies of the *A*-*b*-*B* (10-*b*-3) diblock copolymers in solution. With the length decrease of the corona-forming segments, the spherical micelles and rodlike aggregates exist together in the system, indicating that the transition of spherical micelles to rodlike aggregates occurs.

When the corona-forming segment contains less than two repeating units, the rodlike aggregates appear in the solution as shown in Figs. 4 and 5. After Eisenberg's group observed experimentally the similar aggregates with the diblock copolymers of PS-*b*-PAA [1], detailed studies on this interesting phenomenon have been performed by his group in recent years [6–9]. They reported that PS-*b*-PEO diblock copolymers formed multiple morphologies depending on the chain length of the corona-forming segment, and it was observed

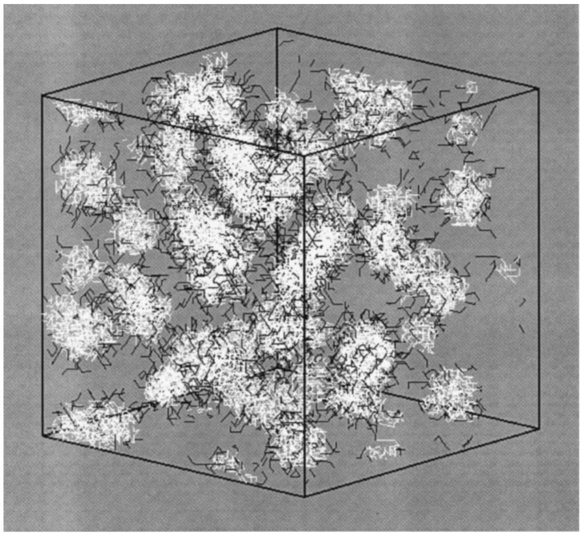

FIG. 3. Morphologies of *A*-*b*-*B* (10-*b*-3) diblock copolymers in a selective solvent; the concentration of the solution is 15%. The white and black lines are A and B segments.

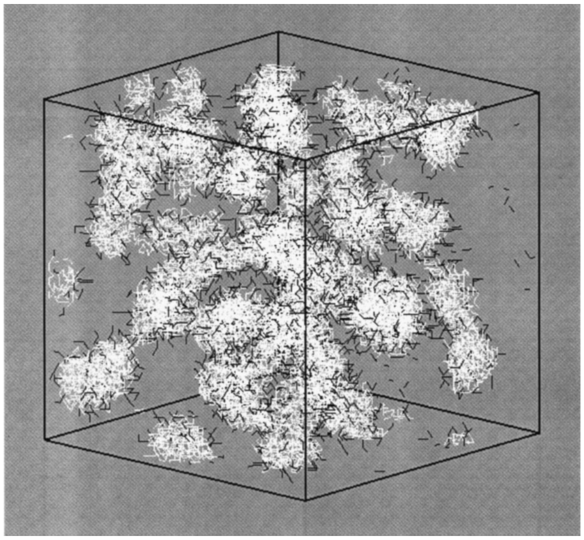

FIG. 4. Morphologies of A-b-B (10-b-2) diblock copolymers in a selective solvent; the concentration of the solution is 15%. The white and black lines are A and B segments.

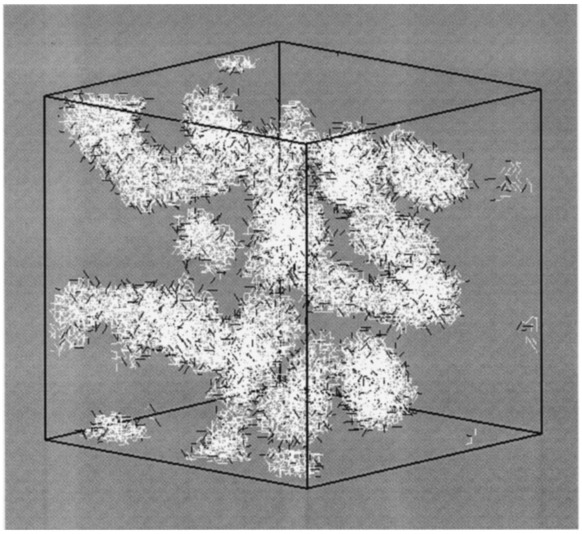

FIG. 5. Morphologies of A-b-B (10-b-1) diblock copolymers in a selective solvent; the concentration of the solution is 15%. The white and black lines are A and B segments.

by transmission electron microscopy (TEM) that the PS-*b*-PEO (240-*b*-80) formed primarily rods [8]. Nakano *et al.* [20] observed the transition from sphere to rod micelles using the small-angle neutron scattering (SANS) method when amphiphilic diblock copolymers of 2-hydroxyethyl vinyl ether and *n*-butyl vinyl ether was in an aqueous solution. They found that the micellar shape was strongly dependent on the hydrophobic chain length of the polymer; the copolymer with the shortest hydrophobic segment formed spherical micelles. With the increase of hydrophobic chain length, rodlike micelles were gradually formed. Our simulation results demonstrate the same phenomenon obtained by Yu and Eisenberg [8]. Although Nakano *et al.* [20] observed the transformation of micellar morphologies by changing the length of the hydrophobic segment, the results were the same. The transition behavior can be understood from the concept of the ‘‘critical packing parameter’’ introduced by Israelachvili [25] for low molecular weight surfactants. When the length of the hydrophobic chain keeps constant, the interface area of the core shell would not change. As the chain length of corona-forming segments decreases, the area occupied by each hydrophilic chain at the core-shell interface decreases. There is a limit area covered by a hydrophilic chain with a certain length, and below this area, spherical micelles become unstable, and are coagulated to form rodlike aggregates. Therefore, the transition of micelles from a sphere to rod shape would occur in order to reduce the area covered by the hydrophilic segment when the interfacial area per hydrophilic segment of diblock copolymers decreases below this limit.

IV. CONCLUSION

Our simulations lead to the insight of the self-assembling process of amphiphilic diblock copolymers in a selective solvent. Direct observation of the morphologies of the copolymers in solution reveals that the hydrophobic segments tend to aggregate into a condensed core while the hydrophilic segments tend to stretch outside the core. Further, with the decrease of the length of the hydrophilic segment, the aggregate morphologies of the diblock copolymer in solution will be transformed from sphere to rodlike micelles.

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