Dissipative Particle Dynamics Simulations of Toroidal Structure Formations of Amphiphilic Triblock Copolymers

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In this paper, the dynamic assembly of toroidal micelle structures of amphiphilic triblock copolymers in dilute solution has been investigated using dissipative particle dynamics simulations. The amphiphilic molecule is represented by a coarse-grained model, which contains hydrophilic and hydrophobic particles. Some microstructures of complex morphology having toroidal micelles have been observed in the simulations; the toroidal micelle formation is in accordance with the theoretical prediction of the toroidal structure in cylindrical micelle suspensions by Pochan et al. (*Science* **2004**, *306*, 94). These findings are very interesting, and these complex morphologies enrich our knowledge of the potential products obtained from the self-assembly of block copolymers.

1. Introduction

Block copolymers can self-assemble into a variety of ordered structures in solutions because of the repulsive interactions between the different blocks and the topological constraints caused by the subchains that are being linked permanently. Amphiphilic block copolymers, which contain hydrophilic groups and hydrophobic groups, represent an interesting class of polymeric materials that exhibit a rich variety of morphologies,[1,2] such as micelles, membranes, and vesicles, making them a subject of great interest for experiments, theories, and computer simulations. Among these complex microstructures, the branched and toroidal micelles have received increasing attention due to their great potential applications in the fields of drug delivery and nanotechnology. Jain and Bates[3,4] found that poly(1,2-butadiene-*b*-ethylene oxide) (PB-PEO) diblock copolymers formed Y-junctions and assembled into three-dimensional networks in water. The formation of toroidal micelles from the triblock copolymer of poly(acrylicacid-*b*-methyl acrylate-*b*-styrene) (PAA_{99}-PMA_{73}-PS_{66}) in dilute solution have been studied by Pochan et al.[5−7] Choi et al.[8] observed the controlled generation of micelle-templated organosilicate toroids and related structures from self-assembly of block copolymers. The toroidal morphologies have also been observed from the self-assembly of amphiphilic molecular dumbbells by Kim et al.[9] Recently, the self-assembly behavior of biohybrid triblock copolymers in aqueous solution has been studied by Reynhout et al.[10] A large variety of complex microstructures, including vesicles, toroids, and octopus structures, have been found in their study; however, the formation mechanism of these assemblies is not clear. In the theoretical and modeling research, Safran and co-workers[11−13] developed a generic model solved in the mean-field approximation that the polymer-like chains could branch and formed networks, and many possible cluster configurations except closed ring structures were found in their simulations. Kindt rederived the network of self-assembled chains connected by Y-junctions by using a complementary approach,[14,15] and his Monte Carlo simulation results[15] supported his qualitative theoretical predictions. In a very recent simulation, He and Schmid[16] observed the vesicular and toroidal micelles from amphiphilic block copolymers by using a mesoscopic field-based method. In our previous simulations,[17] we have observed some complex microstructures having toroidal structures by the real-space self-consistent field theory method. To our knowledge, little research has concerned the dynamic processes in the formation of toroidal micelles. In this paper, we study the self-assembled toroidal micelles of amphiphilic triblock copolymers in dilute solution. As an alternative choice, we employ the dissipative particle dynamics (DPD) method which is a continuum simulation technique in three dimensions and correctly represents the hydrodynamic interactions.[18] Groot and Madden have successfully applied this method to study the microphase separation of linear block copolymer melts.[19] Recently, the microphase separations of nonlinear block copolymers have been investigated by a similar method.[20−22] The phase behaviors of amphiphilic molecules in the presence of one or two solvents by this method have been studied by Huang et al.[23,24] Yamamoto and co-workers have employed this method to study the spontaneous vesicle formation of amphiphilic molecules in aqueous solution.[25] Then, the studies of membrane behaviors of vesicles from amphiphilic molecules by the DPD method have attracted considerable attention.[26−31] Thus, the particle-based DPD method may be applicable for studying the ring-forming processes and understanding the mechanism in the self-assembly process of these morphologies.

2. Simulation Details

Dissipative particle dynamics is a mesoscopic simulation method, introduced in 1992 by Hoogerbrugge and Koelman.[18] In a DPD simulation, a particle represents the center of mass of a cluster of atoms and the mass, length, and time scales are all unity. Particles i and j interact with each other via a pairwise additive force, consisting of three contributions: (i) a conservative force, F_{ij}^{C}; (ii) a dissipative force, F_{ij}^{D}; and (iii) a random force, F_{ij}^{R}. Hence, the total force on particle i is given by

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$$F_i = \sum_{i \neq j} F_{ij}^{\mathrm{C}} + F_{ij}^{\mathrm{D}} + F_{ij}^{\mathrm{R}} \tag{1}$$

where the sum acts over all particles within a cutoff radius r_c. Specifically, in our simulation,

$$F_i = \sum_{i \neq j} a_{ij}\omega(r_{ij})\hat{r}_{ij} - \gamma\omega^2(r_{ij})(\hat{r}_{ij}\cdot v_{ij})\hat{r}_{ij} + \sigma\omega(r_{ij})\zeta_{ij}\Delta t^{-1/2}\hat{r}_{ij} \tag{2}$$

where a_{ij} is a maximum repulsion between particles i and j, r_{ij} is the distance between them, with the corresponding unit vector $\hat{r}_{ij}$, v_{ij} is the difference between the two velocities, ζ_{ij} is a random number with zero mean and unit variance, and γ and σ are parameters coupled by $\sigma^2 = 2\gamma kT$. The weighting function $\omega(r_{ij})$ is given by

$$\omega(r_{ij}) = \begin{cases} 1 - \dfrac{r_{ij}}{r_c} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \tag{3}$$

The standard values $\sigma = 3.0$ and $\gamma = 4.5$ are used in our study. By joining consecutively particles with spring force, one can construct coarse-grained (CG) models of polymers.[19,32] The harmonic spring force with a spring constant of $k_s = 4.0$ and an equilibrium bond length of $r_s = 0.86$ in our simulations has the form

$$F_{ij}^{\mathrm{S}} = k_s(1 - r_{ij}/r_s)\hat{r}_{ij} \tag{4}$$

Within the mesoscopic approach, an amphiphilic molecule is represented by a CG model with hydrophilic particles (denoted by A) and hydrophobic particles (denoted by B) in our study. Specifically, this model is built by one hydrophilic particle on each side and eight hydrophobic particles in the middle; i.e., an amphiphilic $A_1B_8A_1$ triblock copolymer molecule is modeled. Solvent particles (denoted by S) are included explicitly in the simulation; however, for clarity, only the hydrophobic particles are shown in the following figures. Moreover, to visualize the dynamic processes in the formation of the toroidal micelle structures more clearly, the density of the hydrophobic particles is measured on a three-dimensional grid. In the rich domains of hydrophobic particles, the density is high, and in the rich domains of hydrophilic particles, it is low. The dividing surface between these two domains is represented by the isosurface where the density is midway between these values. We use 9600 constituent particles of the amphiphilc molecules with a homogeneous distribution in a simulation box of 40 × 40 × 40 with a particle number density of 3. Therefore, the total number of particles in the system is 192 000 and the concentration of the amphiphilic molecules is 5.0 vol %. The simulations are performed using a modified version of the DPD code named MYDPD.[33,34] The time integration of motion equations is done using a modified velocity−Verlet algorithm with $\lambda = 0.65$ and time step $\Delta t = 0.04$.

3. Results and Discussion

Following Groot et al.,[32] the repulsive parameters between two alike particles are set to $a_{ii} = 25.0 (i = \mathrm{A, B, S})$. Whereas the value of the parameters between two particles of which one is hydrophilic (A) and the other hydrophobic (B), is chosen to be $a_{AB} = 50.0$, which implies that A and B components are incompatible. After these parameters are chosen, the microstructure of the $A_1B_8A_1$ triblock copolymers should be solely determined by the selectivity of solvents, i.e., the interactions between the solvent and the A/B particles. It has been demonstrated that the selectivity of solvent for each block on the triblock copolymers is a significant parameter for modulating the microstructures in experiments.[35,36] To model the amphiphilic nature of triblock copolymers, the repulsion parameter between hydrophilic (A) and solvent (S) particle is chosen to be smaller than the repulsion parameter between two alike particles. Likewise, the parameter related to the interaction between hydrophobic (B) and solvent (S) particle is chosen to be larger than the repulsion parameter between two similar particles, which ensures that the hydrophobic block of amphiphilie is sufficiently shielded from the solvents. These amphiphilic triblock copolymers can self-assemble into complex architectures having toroidal structures within these parameters. Some typical toroidal micelles obtained from the simulations are illustrated in Figure 1. These are toroidal structures with a single loop (Figure 1a), one loop with one end-cap (Figure 1b), and double loops (Figure 1c). We find several hundred polymer chains (it measures approximately from 80 to 100% of polymer chains in the system) are contained within a typical toroidal structure. More complex toroidal micelle structures have not been found in the simulations, which can be explained by the fact that there are only 960 polymer chains in the system. These structures tell us much about the self-assembly characteristics of the amphiphilic triblock copolymer, and they are in qualitative agreement with the results reported by Jiang and co-workers.[17]

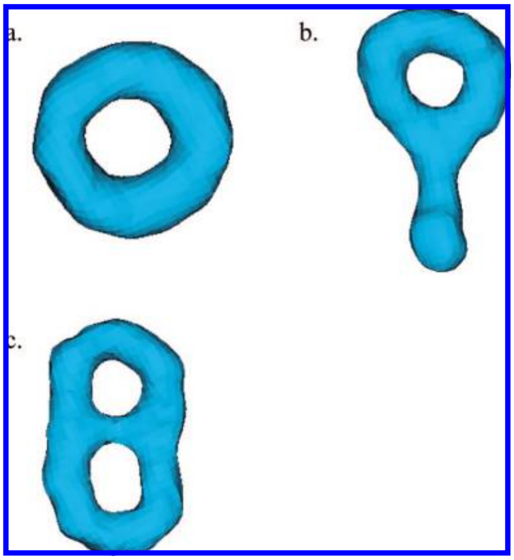

Figure 1. Toroidal structures of the $A_1B_8A_1$ amphiphilic triblock copolymer system in dilute solution obtained in DPD simulations. These toroids can be found with a single loop (Figure 1a), one loop with one end-cap (Figure 1b), and double loops (Figure 1c). For purposes of clarity, only the hydrophobic particles of each toroidal structure are displayed.

A direct observation of the dynamic process for the formation of complex microstructures is important for understanding their formation mechanism. However, this process is too fast to be captured via present experimental measurement. Hence, the simulation provides a good choice to understand this process. In Figure 2, a typical dynamic formation process of toroidal micelle structure is provided. The process of the toroidal micelle formation can be clearly understood from these figures. It reveals

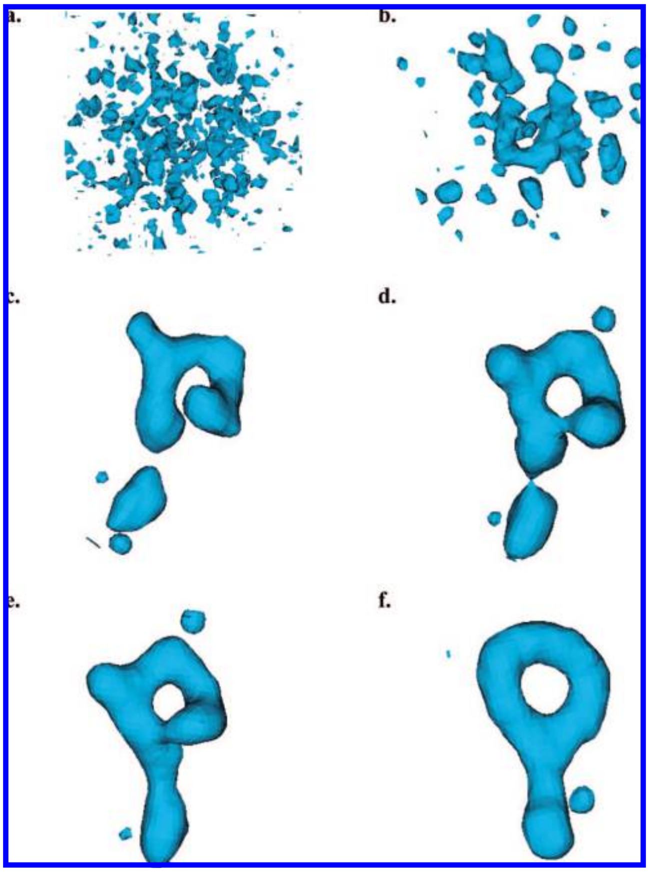

Figure 2. Sequential snapshots of the formation of a toroidal structure with a single loop from amphiphilic triblock copolymers in dilute solution at t = (a) 500, (b) 2500, (c) 18 000, (d) 19 000, (e) 20 000, and (f) 50 000.

that the amphiphilic molecules initially rapidly aggregate into spherical and cylindrical micelles. Then, the spherical micelles are subsequently attracted and merged into the neighboring cylindrical micelle and form a "U-like" junction. The "U-like" junction subsequently collapses and evolves into a toroidal structure through the end-to-end connection of two free end-caps of this junction. Then, the neighboring cylindrical or spherical micelles merge into the body of the toroidal micelle and forms a toroidal structure with one end-cap. Thus, most of the amphiphilic molecules (more than 80% of polymer chains in the system) are contained within a typical toroidal micelle at the final state.

As described in ref 5, the existence of complex microstructures having toroids, such as closed ring structures at the ends or in the middle of cylindrical micelles, cannot be placed exclusively in an end-to-end connection of cylindrical micelles. Indeed, we observed an additional ring-forming process in our amphiphilic triblock copolymer system, and the formation dynamics obtained during the self-assembly process are presented in Figure 3 and together with the video clip in the Supporting Information. In this case, once the "U-like" or "Y-like" junction forms, a toroidal structure with end-caps is first formed via the intra-association of the free end-cap of the junction with the midsection of itself. Subsequently, a toroidal structure with one end-cap is formed by burying more free end-caps and collapsing into the body of the toroidal micelle. Finally, a pure closed ring structure appears when all of the free end-caps merge into the toroidal micelle. The dynamic observation of the formation of a toroidal micelle is in accordance with the theoretical prediction reported by Pochan et al.[5]

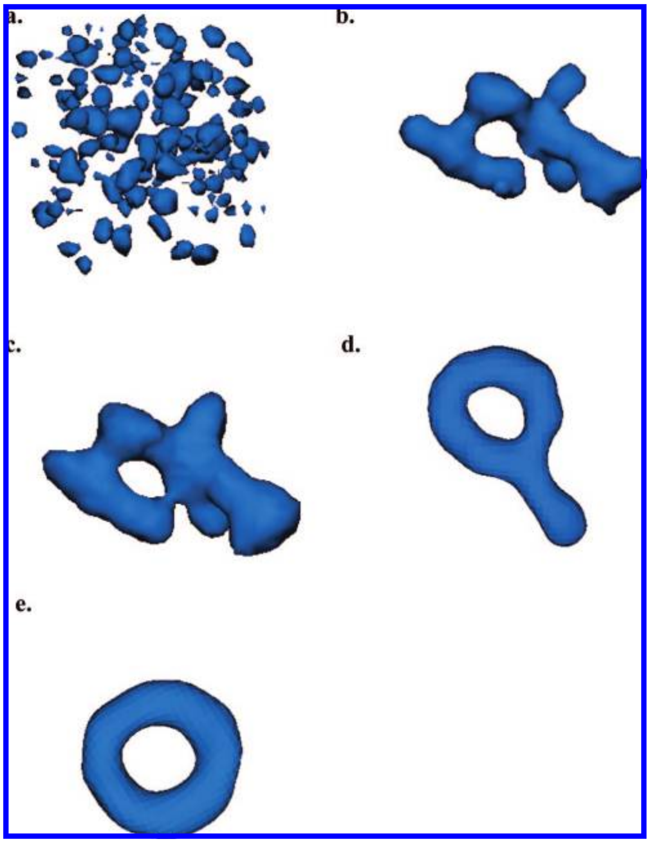

Figure 3. Sequential snapshots of the formation of toroidal structure with ternate loops from amphiphilic triblock copolymers in dilute solution at t = (a) 1000, (b) 5000, (c) 6000, (d) 17 000, and (e) 48 000.

At this point, it is necessary to find out the mechanism behind the formation of these toroidal micelle structures. Next, we turn to interpret the results above. It is recognized that an equilibrium system tends to adopt structures having lower energy. For illustrative purposes, we suppose that the total energies for a straight cylinder having an end-cap at each end are a contribution from two parts, one from the surface energy of the end-cap and another from the surface energy of the pure cylinder. Our results suggest that, due to the amphiphilic nature of block copolymers, the spherical and cylindrical micelles are spontaneously formed through the clustering of hydrophobic groups. On the other hand, the spherical and cylindrical micelles coalesce into toroidal structures to reduce the contact between hydrophobic sections and solvent particles. The enhanced stability of the toroidal micelles relative to the cylindrical micelles can be attributed to the strong hydrophobic association within the core consisting of the stiff rodlike units. The exposure of the surface of end-caps to solvents can induce a slight increase in the system energy in the amphiphilic system because of the strong hydrophobic interactions between the hydrophobic block and solvent particles. Then, the system adopts a strategy to reduce the system energy; that is, the spherical micelles (or cylindrical micelles) are attractive and coalesce into their neighboring cylinders and form "U-like" or "Y-like" junctions. The free end-caps of cylinders connect to the midsection of themselves and collapse into toroidal structures to reduce the surface area of end-caps. Then, the neighboring spherical and cylindrical micelles can fuse into the body of the toroidal micelle to bury free end-caps. On the other hand, the toroidal structures with end-caps can also bury more end-caps and collapse into pure closed ring structures to reduce the surface area of end-caps. This is why the amphiphilic molecules are attracted to toroidal micelle structures within the parameters in our DPD simulations.

4. Conclusions

We have studied the formation of toroidal micelles of amphiphilic triblock copolymer using the dissipative particle dynamics approach. We observed some complex morphology having toroidal micelles. The insight that we have obtained into the formation mechanism of these complex morphologies is useful in explaining how these aggregates are formed from this research. These findings are very interesting, and these complex morphologies enrich our knowledge of the potential products obtained from the self-assembly of block copolymers. In addition, it is confirmed that DPD simulation is an effective simulation technique for understanding the structure and dynamics of amphiphilic copolymers.

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Supporting Information Available: A video clip, which presents the dynamic process in the formation of the toroidal micelle structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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