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Effect of Selective Solvent Addition Rate on the Pathways for Spontaneous Vesicle Formation of ABA Amphiphilic Triblock Copolymers

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Abstract: In this study, the kinetics of vesicle formation of ABA amphiphilic triblock copolymers from an initially homogeneous state was theoretically and experimentally investigated by adding a selective solvent into the system. The pathway of spontaneous vesicle formation depended greatly on the selective solvent addition rate. At a slow addition rate, the pathway followed three stages: (1) the amphiphilic triblock copolymer combined into a large irregular aggregation; (2) the large irregular aggregation broke into big irregular spheres; and (3) some hydrophilic molecules in the big irregular spheres diffused toward the surface, and some hydrophilic molecules diffused toward the center, forming vesicles. However, at a fast addition rate, the pathway was as follows: (1) the amphiphilic triblock copolymer aggregated into many small spheres; (2) the small spheres merged to form rod-like micelles first and then oblate membranes; and (3) the oblate membranes closed up to form vesicles. This pathway difference for vesicle formation can be attributed to the existence of many metastable states in the system. This finding not only provides new insight into the origins of vesicles but also provides further understanding on the self-assembly kinetics of amphiphilic block copolymers in a selective solvent.

Introduction

Amphiphilic block copolymers can self-assemble into a vast variety of micelles in selective solvents.[1-3] Among these micelles, vesicles have become more attractive due to their special structures.[4-11] A vesicle is an enclosed structure of the molecular bilayer. It is assumed to play an important role in biological activity and has been used to mimic cells.[12,13] Moreover, vesicles may have special applications in many fields, including drug delivery, microreactors, and so on.[14-17] Therefore, great effort has been devoted to studying the formation of vesicles, both theoretically[18-23] and experimentally.[24-28] Previous studies indicate that bilayer membrane closing is an indispensable pathway for vesicle formation. However, recent simulation results by He and Schmid show that vesicles can be formed via nucleation of hydrophobic molecules in spherical micelles.[29,30] This indicates that bilayer membrane closing is not an exclusive pathway for vesicle formation. However, to the best of our knowledge, the pathway difference for vesicle formation remains unclear. In the work described in this paper,

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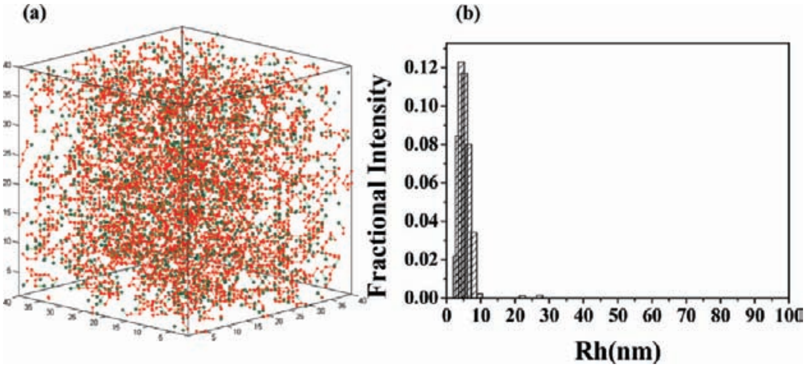

Figure 1. (a) Homogeneous ABA triblock copolymer solution (as initial state) obtained by simulation. (b) DLS histograms showing the hydrodynamic radius (R_h) distribution of the homogeneous ABA triblock copolymer/DMF solution.

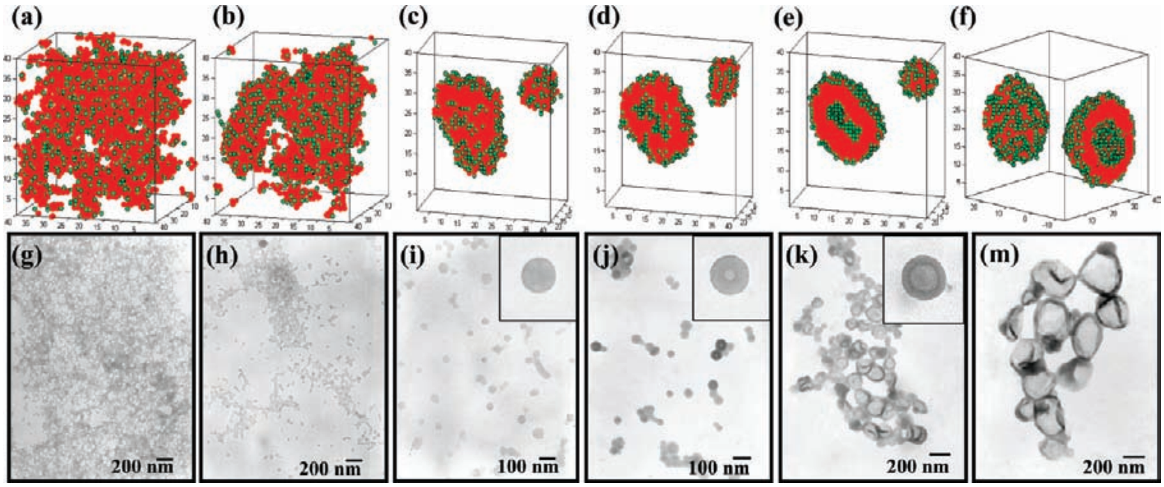

Figure 2. (a−f) Snapshots at different stages from simulation results showing the pathway of spontaneous vesicle formation of the amphiphilic triblock copolymer at a slow addition rate (green and red denote hydrophilic and hydrophobic molecules, respectively). Simulation time: (a) 8.3×10^4, (b) 9.0×10^4, (c) 1.1×10^5, (d) 1.2×10^5, (e) 2.0×10^5, and (f) 3.3×10^6 MCS. For the purpose of clarity, the cross sections of the micelles are given in panels c−f. Shown below are TEM images of the aggregates formed at different times when deionized water was added at the addition rate of 0.2 wt % per day for (g) 15, (h) 18, (i) 20, (j) 25, (k) 28, and (m) 30 days. Inset in panels i−k is the local magnification.

the kinetics of vesicle formation of ABA amphiphilic triblock copolymers from an initially homogeneous state was theoretically and experimentally studied by adding a selective solvent into the system. From the results, it was found that the selective solvent addition rate is the key factor that determines the pathway of spontaneous vesicle formation.

Theoretical Section

In simulations, the pathways of the spontaneous vesicle formation of an $A_1B_6A_1$ amphiphilic triblock copolymer in a selective solvent were studied via the Monte Carlo method ("A" refers to a hydrophilic molecule, whereas "B" refers to a hydrophobic molecule; the numbers 1 and 6 refer to the repeat units for corresponding molecules). Monte Carlo simulation of self-avoiding chains was carried out in a simple cubic lattice system. The length, width, and height of the cubic system were all 40. The periodic boundary condition was applied to all three directions. A Larson-type bond fluctuation model with a permitted bond length of either 1 or $\sqrt{2}$ was used.[31,32] Each lattice site was occupied by either a bead or a vacancy (a solvent molecule). Excluded volume interactions were enforced to ensure that only one bead existed per lattice site. No bond-crossing was allowed. If the attempted move violated the excluded volume condition or the no-bond-crossing or bond length restrictions, it was rejected. Attempted moves that satisfied the excluded volume condition and the no-bond-crossing and bond length restrictions were further accepted or rejected according to Metropolis rules.[33] The partial-reptation algorithm was applied in our simulation.[34,35] This algorithm enhances the efficiency of the simulation by introducing a cooperative motion of beads and has been proven suitable for studying the dynamic process. The microrelaxation modes are defined as follows.

A bead is randomly chosen to exchange with one of its 18 nearest neighbors. If the neighbor is a vacancy, exchange with the bead is attempted. If the exchange does not break the chain, it is allowed to do so. This process constitutes a single movement. If the exchange would break two chain connections, it is not allowed. If the exchange creates a single break in the chain, the vacancy will continue to exchange with subsequent beads along the chain until reconnection of the links occurs. This process constitutes a cooperative movement. The total number of beads in the entire simulated system is fixed at 6000, corresponding to a volume fraction of 9.375%. Only BB interactions are considered, and the strength of one pair of interactions is set as $\varepsilon_{BB} = \varepsilon'/\kappa_B T$ (where $\kappa_B$is the Boltzmann constant and ε' is the BB interaction energy). All other interaction energies are set to zero. The inverse temperature, $1/T$, is used and equals zero at the athermal state. In this

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study, time is measured in units of Monte Carlo step (MCS). One MCS means that, on the average, every bead has attempted one exchange.

The amphiphilic triblock copolymer used in the experimental studies is P4VP$_{43}$-*b*-PS$_{366}$-*b*-P4VP$_{43}$. Details about sample preparation and characterization are given in the Supporting Information.

Results and Discussion

In our simulation studies, ε_{BB} is set to 0.5 to ensure that the amphiphilic triblock copolymers can form a homogeneous solution (Figure 1a). This is necessary to ensure that the copolymer is dissolved in a common solvent, forming a homogeneous solution for the experiment. The homogeneous state was set as the initial state for all cases in this study. When ε_{BB} is changed from 0.5 to -0.7 (the other interaction energies remain zero), the system can evolve based on the Monte Carlo algorithm. Different addition rates, that is, changing ε_{BB} from 0.5 to -0.7 using different steps, were employed in this study. When the addition of a selective solvent is performed by changing ε_{BB} from 0.5 to -0.7 via a step of -0.05, the addition rate is considered slow. At each step, the simulation time was 5000 MCS. This process corresponds to the case in which a selective solvent such as water is slowly added to the homogeneous amphiphilic copolymer solution. Figure 2a−f shows the evolution of the system from the homogeneous state to the state where vesicles have formed. The process of spontaneous vesicle formation at this specific addition rate can be generally divided into three stages: (1) the amphiphilic triblock copolymer first combines into a large irregular aggregation (Figure 2a); (2) the large irregular aggregation breaks into large irregular spheres in which the hydrophilic molecules are randomly distributed (Figure 2b,c); and (3) some hydrophilic molecules in the large regular spheres diffuse toward the surface, and some hydrophilic molecules diffuse toward the center, forming small vesicles (Figure 2d−f).

In experimental studies, water is a widely accepted selective solvent for amphiphilic block copolymers. Adding water to the ABA copolymer solution can increase the repulsive interaction between the solvent and PS molecules, leading to the aggregation of PS blocks in the present study. Therefore, adding water is equivalent to decreasing ε_{BB} in the simulation. To study the effects of the addition rate on the pathways of spontaneous vesicle formation of ABA amphiphilic triblock copolymers, different water addition rates were employed in this research. Adding water to the solution at a rate of 0.2 wt % per day up to the predetermined amount (6 wt %) was considered as slow addition in this experiment. When the first drop of deionized water was added to the solution, the time was defined as zero. Figure 2g−m displays the morphologies of the micelles observed by transmission electron microscopy (TEM) at different stages during slow addition. Floccules first appeared (Figure 2g) 15 days after the initial addition of water, and then broke into irregular aggregates after 18 days (Figure 2h). The

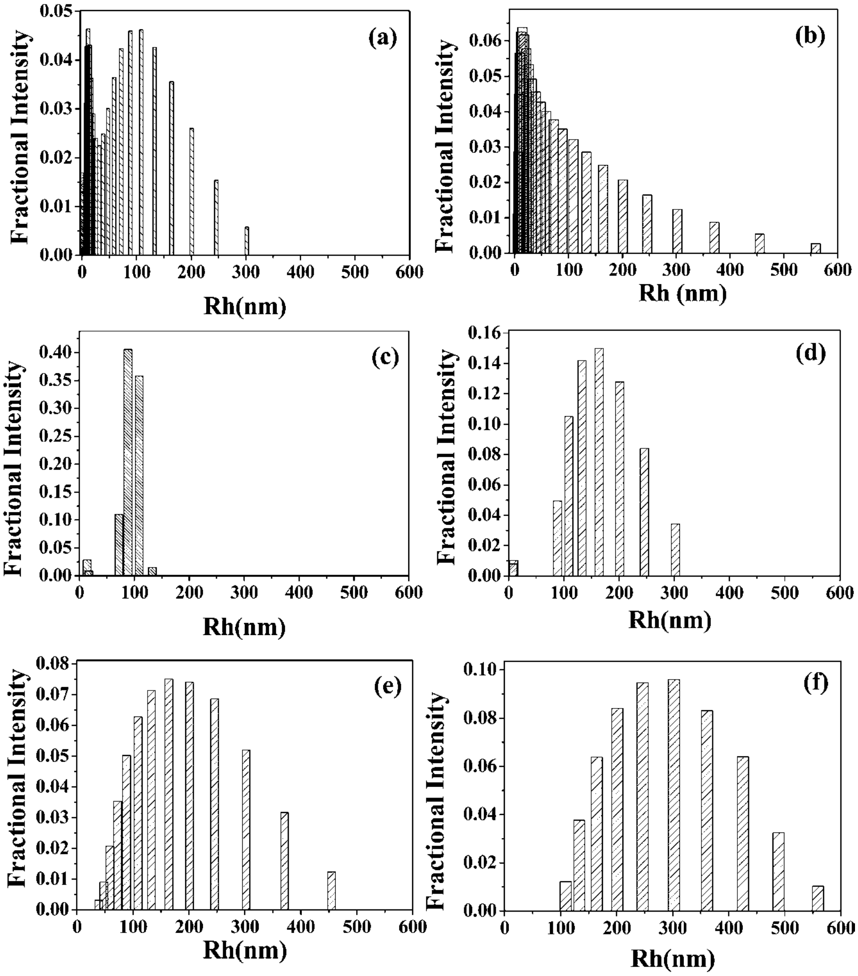

Figure 3. DLS histograms showing the hydrodynamic radius (R_h) distribution at different times when deionized water was added at the addition rate of 0.2 wt % per day for (a) 15, (b) 18, (c) 20, (d) 25, (e) 28, and (f) 30 days.

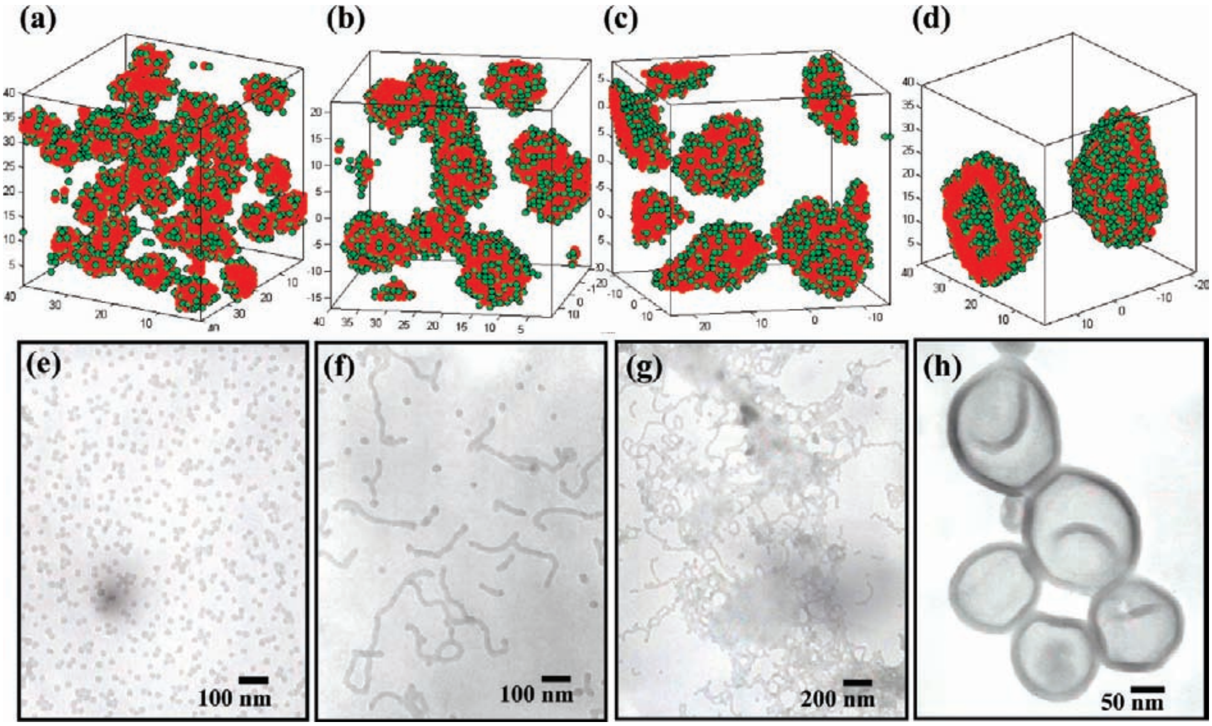

Figure 4. (a−d) Snapshots at different stages from simulation results showing the pathways of spontaneous vesicle formation of the amphiphilic triblock copolymer at a fast addition rate (green and red denote hydrophilic and hydrophobic molecules, respectively). Simulation time: (a) 5.0×10^3, (b) 1.0×10^5, (c) 1.8×10^5, and (d) 3.5×10^6 MCS. Shown below are TEM images of the aggregates formed after 6 wt % deionized water was added at one time (fast addition rate): (e) 8 s, (f) 10 h, (g) 29 h, and (h) 48 h.

irregular aggregates separated to form spheres with solid centers after 20 days (Figure 2i). Further along, spheres with small hollow centers (i.e., small vesicles) appeared clearly after 25 days (Figure 2j). These observations are consistent with the simulation results in Figure 2a−f. Moreover, small vesicles could further swell or merge into larger ones when the elapsed time continuously increased, as shown in Figure 2k (28 days) and Figure 2m (30 days).

Dynamic light scattering (DLS) conveniently demonstrates the presence of micelles.[36−39] In this experiment, DLS was used to detect changes in the size of the aggregates as the time lapse increased. Figure 1b shows the hydrodynamic radius (R_h) distribution of a homogeneous polymer/ *N*,*N*-dimethylformamide (DMF) solution, corresponding to the simulated initial state shown in Figure 1a. Typical unassociated copolymer molecules have apparent hydrodynamic radii in the range of 2−10 nm (Figure 1b). With the addition of water, R_h rose to higher values. A more detailed examination of the results at a slow addition rate is provided in Figure 3, which displays apparent particle size distributions obtained from DLS. Figure 3a,b shows that R_h rises to higher values early on. This indicates that an increasing number of unassociated copolymer molecules are incorporated into the aggregates, which in turn become larger with increasing time up to 18 days. When the time lapse increases to 20 days, however, R_h decreases to around 100 nm, as shown in Figure 3c. The TEM results (Figure 2i) show that small spheres form at this time. With further increases in elapsed time, R_h again increases (Figure 3d−f), corresponding to the swelling process of the spheres (Figure 2j−m). Thus, it can be concluded that DLS measurements are consistent with the experimental and simulated results. The values of R_h are a little higher than the sizes of the aggregates observed by TEM. The main reason for this observation may be that the samples for DLS measurements involved micelles in a water solution, whereas the samples for TEM observations were dried micelle aggregates.

When the addition of selective solvent is performed by directly changing ε_{BB} from 0.5 to −0.7, it is considered fast addition. This corresponds to the case in which a predetermined amount of selective solvent such as water is added only once to the solution in the experiment. Figure 4a−d shows the simulation results of the pathway for spontaneous vesicle formation. The amphiphilic triblock copolymer first aggregates into many small spheres covered by hydrophilic molecules (Figure 4a). This is different from the stages observed during slow addition. Interestingly, some spheres merge together to form rod-like micelles (Figure 4b) and then continue to fuse to form a big oblate membrane (Figure 4c). Afterward, the oblate membrane closed up to form small vesicles (Figure 4d). Similar simulation results have been obtained by Yamamoto et al.,[40,41] who used dissipative particle dynamics (DPD) simulations to study the vesicle formation of amphiphilic triblock copolymers. They found that spontaneous vesicle formation was due to the intermediate state of oblate micelles or a bilayer membrane. The membrane fluctuated and then closed to form a vesicle.

In this experiment, adding the 6 wt % deionized water only once was considered fast addition. Similar to the process involving slow addition, the time was set as zero when the deionized water was first added to the solution. Figure 4e−h shows the morphologies of the micelles observed by TEM

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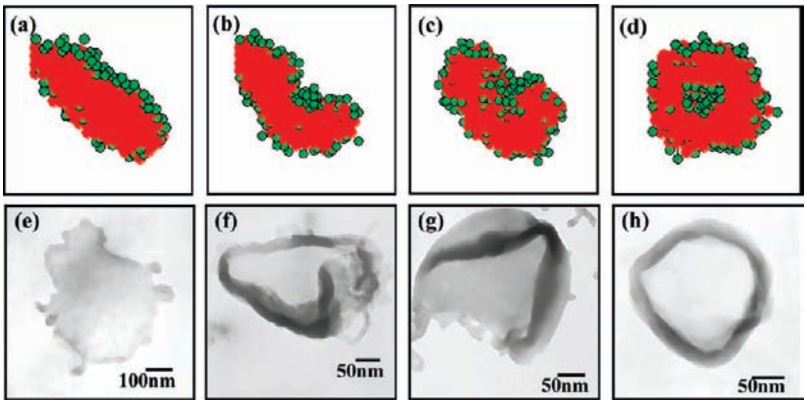

Figure 5. Detailed simulation (a−d) and experimental (e−h) results showing how a membrane bends and finally closes to form a vesicle at a fast addition rate. Simulation time: (a) 1.8 × 10^5, (b) 2.0 × 10^5, (c) 2.7 × 10^5, and (d) 3.0 × 10^5 MCS. Experimental time: (e) 29, (f) 32, (g) 35, and (h) 48 h.

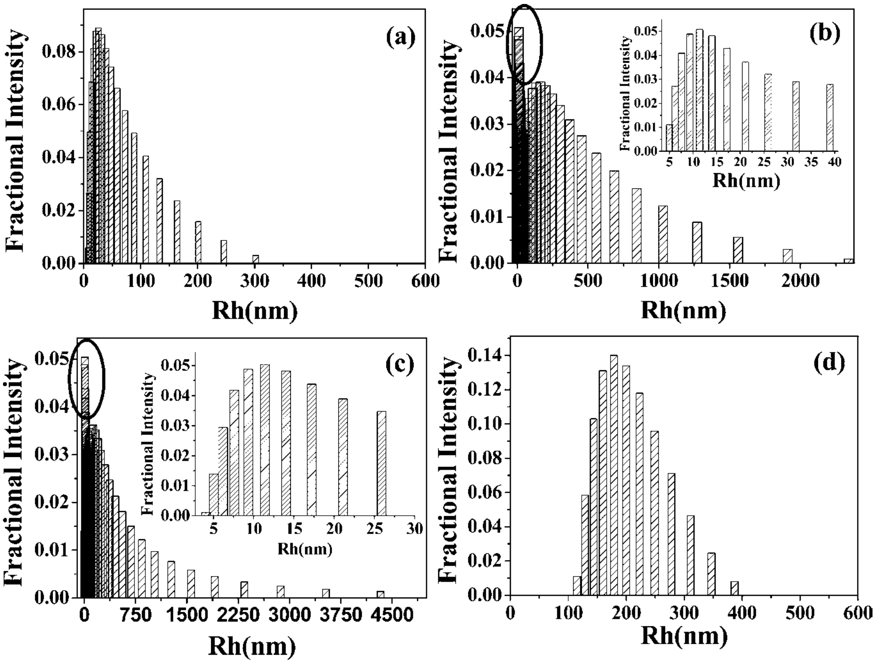

Figure 6. DLS histograms showing the hydrodynamic radius (R_h) distribution at different times under a fast addition rate (6 wt % deionized water added at one time): (a) 8 s, (b) 10 h, (c) 29 h, and (d) 48 h.

at different stages. These images indicate that the process of vesicle formation at fast addition can be divided into the following stages: (1) first, the copolymer self-assembles into small spheres (Figure 4e); (2) these spheres then merge together to form first rod-like micelles (Figure 4f) and then bilayer membranes (Figure 4g); and (3) the membranes bend and finally close to form small vesicles (Figure 4h). These observations agree with the simulation results (Figure 4a−d). For clarity, Figure 5 gives the detailed simulated and experimental results, showing how a membrane bends and finally closes to form a vesicle. It was easy to trace a micelle and study its kinetics in the simulation, as shown in Figure 5a−d. However, there appears to be no way to trace a micelle in the experiment. The images provided in Figure 5e−h were obtained from different micelles at different stages. Other images showing such intermediate structures are provided in Figures S2 and S3 of the Supporting Information.

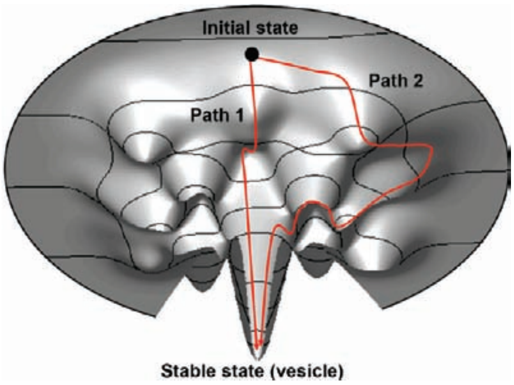

Figure 7. Schematic diagram showing the free energy landscape with a stable state and many metastable states (the valleys).

DLS measurements were also used to study this process. In the beginning, the single peak was at ca. 25 nm (Figure

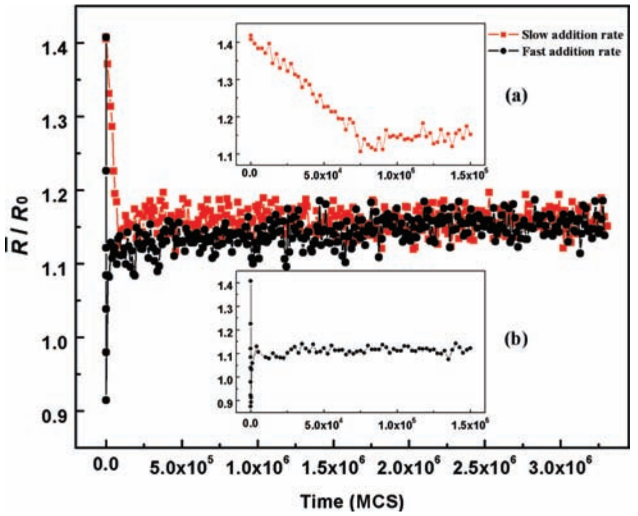

Figure 8. Simulation results showing the variation in average end-to-end distance of the B block with time at different addition rates. For the purpose of clarity, local enlarged graphs under slow (a) and fast (b) addition rates are also given.

6a), indicating that almost all unassociated copolymer molecules were incorporated into the aggregates. This result supports the TEM observation (Figure 4e) in which the aggregates were found to be small spheres and short rods. From Figure 6b, it is found that the distribution of R_h becomes wider when the time lapse is increased to 18 h, suggesting that sphere and rod morphologies coexist in the aggregates. When the time lapse increased to 29 h, large aggregate (R_h > 1000 nm) scattering signals could be detected, as shown in Figure 6c. These signals originate from the thin films, as observed via TEM in Figure 4g. Such scattering signals were not obtained at a slow addition rate. When the time lapse was further increased to 48 h, the distribution of R_h became narrower and formed a single peak (Figure 6d). The peak is located at 179 nm, which is close to the vesicle sizes as indicated in Figure 4h. Thus, the DLS results further confirm the TEM observation and simulation results; that is, the pathway of spontaneous vesicle formation depends on the selective solvent addition rate.

Why does the pathway of vesicle formation depend on the addition rate? It is generally known that many metastable states can exist in a block copolymer solution system.[5,42] These metastable states and the stable state correspond to the valleys and lowest valley, respectively, in the free energy landscape. Generally, the complete free energy landscape of a complicated system is difficult to obtain. In this case, a schematic diagram is provided (Figure 7) showing the free energy landscape of the system. In the present study, the presence of vesicles denotes the stable state, whereas the appearance of small spheres, short rods, and other formations is considered a metastable state of the system. Under different addition rates, the system evolves via different paths from the initial state to the final stable state, as indicated in Figure 7. The diagram shows that different valleys can be observed along different paths. Thus, the pathway of vesicle formation depends on the selective solvent addition rate.

To further reveal the mechanism for this phenomenon, the simulation result (Figure 8) showing the variation in average end-to-end distance ($\bar{R}$) of the B block copolymer chains with time under slow and fast addition rates is given. Figure 8 shows that the two curves exhibit obviously different behaviors at earlier stages and then tend to move closer to each other and finally overlap. The time that the $\varepsilon_{\mathrm{BB}}$ reached the same value (−0.7) for the two cases is 1.2×10^5 MCS. After this time, from Figure 8, the values of $\bar{R}$ are different for different addition rates up to 1.5×10^6 MCS. This indicates that the system evolves via different paths in the free energy landscape because the free energy is a function of $\bar{R}$. Further along, $\bar{R}/R_0 = 1.41$ (R_0 is the end-to-end distance at theta condition for the same chains) when the time is zero. This result indicates that the copolymer chains are stretched at the initial state. However, the value of $\bar{R}/R_0$ rapidly decreases from 1.41 to 0.91 with increasing time lapse at a fast addition rate. A value $\bar{R}/R_0 < 1$ means that the two ends of a hydrophobic block tend to be close

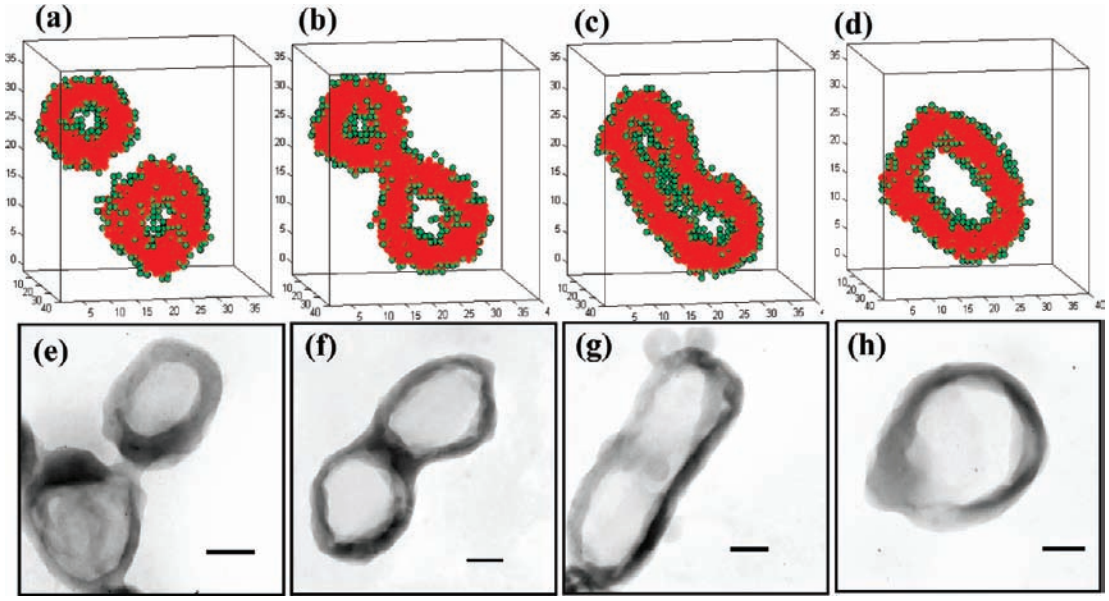

Figure 9. Simulated (a−d) and experimental (e−h) results showing how two small vesicles merge into a bigger one. Simulation time at a fast addition rate: (a) 2.8×10^6, (b) 2.9×10^6, (c) 3.0×10^6, and (d) 3.5×10^6 MCS. Experimental time at a slow addition rate: (e) 25, (f) 26, (g) 28, and (h) 30 days. The scale bars in panels e−h represent 100 nm.

to each other, forming a folding conformation. The folding conformation is unstable due to the repulsive interaction between the hydrophobic block and the solvent molecule. Thus, the folding copolymer chains are more likely to form small spheres or short rods with hydrophobic cores and hydrophilic shells.[43] In contrast, the end-to-end distance decreases slowly with increasing time lapse and remains >1 at all times under slow addition. A value $\bar{R}/R_0 > 1$ means that the copolymer chains are relatively stretched in the solvent. Compared with folded copolymer chains, stretched chains have more difficulty forming small spheres or short rods with hydrophobic cores. This is the main reason ABA triblock copolymers first form small spheres covered by hydrophilic blocks at a fast addition rate, whereas they initially form large aggregates at a slow addition rate.

Small vesicles can merge into larger vesicles under both fast and slow addition rates. Figure 9a−d shows a typical process of two small vesicles merging into a bigger one. Similar results are also obtained in our experiment. The entrapment of intermediate aggregates is shown in Figure 9e−h. Thus far, the pathways taken by ABA amphiphilic molecules in a selective solvent via self-assembly, from an initially homogeneous state to a state in which perfect vesicles are formed at slow and fast addition rates, have been determined in both simulations and experiments. This combination study involving experiments and simulations not only provides new insight into the origins of vesicles but also helps us further understand the self-assembly kinetics of amphiphilic block copolymer in selective solvents.

Conclusion

In summary, our theoretical and experimental studies revealed that the pathways for spontaneous vesicle formation of ABA amphiphilic triblock copolymers in selective solvents rely on the selective solvent addition rate. At a slow addition rate, vesicles are formed via hydrophobic molecules' diffusion into the center of spherical micelles, whereas they are formed via oblate membrane closing at a fast addition rate. This pathway difference for vesicle formation can be attributed to the existence of many metastable states in the system.

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Supporting Information Available: Experimental details and additional TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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