

Solvent Property Induced Morphological Changes of ABA Amphiphilic Triblock Copolymer Micelles in Dilute Solution: A Self-consistent Field Simulation Study*

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Abstract The morphological changes of ABA amphiphilic triblock copolymer micelles in dilute solution were systematically studied by tuning the solvent property using self-consistent field simulation. The solvent property was tuned by changing the Flory-Huggins interaction parameters between each type of blocks and solvent, respectively. The simulation results show that by changing the solvent properties, a series of micelle morphologies such as vesicle, cage-like, ring-shaped, rod-like and spherical micelle morphologies can be obtained. Variations of the free energy of the solution system and the surface area of micelles with the Flory-Huggins interaction parameters were calculated to better understand the effect of solvent property on micelle morphologies. In addition, a phase diagram showing the morphological changes of micelles with the Flory-Huggins interaction parameters is provided.

Keywords: Solvent property; Triblock copolymer; Self-consistent field; Simulation.

INTRODUCTION

Amphiphilic block copolymers have attracted large amounts of attention of many researchers for decades due to their fascinating self-assembly ability in selective solvents. As we know now, amphiphilic block copolymers can self-assemble into various ordered complex structures (*e.g.*, the spherical, the rod-like, the ring-shaped micelles, the large compound micelles and vesicles with various shapes, *etc.*^[1–4]) that are believed to have extensive industrial and biomedical potential applications such as microelectronics^[5, 6], bioreactor^[7], microcapsules^[8], materials^[9], drug delivery and targeting release^[10–12], and so forth. Zhang and Eisenberg have done a lot of work to study the aggregate morphologies of amphiphilic diblock copolymers in solution^[13, 14]. They put forward three key factors that affect the micelle morphology, they are: the chain stretch of the core-forming block; the interfacial energy between the core-forming block and the solvent molecule; the interaction between the corona-forming blocks. Any factors that affect any of the three terms will lead to the change in morphology.

In general, there are two kinds of mutual interactions in solutions formed by amphiphilic block copolymers and selective solvents: one is the intrinsic inner repulsive interactions between different blocks; the other is the interactions between the solvent molecules and different parts (*i.e.* blocks) of block copolymers. The former is the dominative driven force in phase separation in melt, while the latter governs the micellization in dilute

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solution. The effect of the intrinsic inner repulsive interactions on the phase behavior of polymer melt has already been investigated widely by theories and simulations, as well as experiments in polymer melt. One of the most famous examples is the phase diagram of AB diblock copolymer melt in bulk^[15]. This diagram has an important meaning of guidance for researchers to find various morphologies in experiments and has become the most important judging criterion for the correctness of the computer programs.

On the other hand, as for the case of solutions, researchers have done many comprehensive investigations in the field of amphiphilic block copolymers in selective solvent. However, most of researchers' interests were focused on the complex system, such as ABC triblock (both linear and star-like), ABC/AB mixture, AB/BC mixture, and the like^[16–27]. Very recently, Suo *et al.* studied the phase behavior of AB-type diblock copolymers in dilute solution by the self-consistent mean-field theory^[28]. All the possible thermodynamically stable ordered structures verified by experiments are considered and the phase diagrams, which are the most comprehensive up to now, are generated in their work. As for the ABA-type triblock copolymer solution, Jiang and Zhu *et al.* have done many investigations by experiments and simulations to study the self-assembly behavior of ABA amphiphilic triblock copolymers in solution^[29–32]. In addition, Kong *et al.* studied the self-assembly behavior of ABA triblock copolymers solution (in which the solvent is selective for middle block B) by Monte Carlo simulation and provide two phase diagrams showing how the interaction parameter and the copolymer concentration affect the micelle morphologies^[33]. We all know that the self-assembled structures of ABA triblock copolymers in selective solvent are very abundant. Therefore, systematic studies of phase behavior of ABA triblock copolymers in solution have great meaning of guidance for experimentalists to find novel morphologies.

In this paper, we systematically studied the morphological changes of ABA amphiphilic triblock copolymer micelles in dilute solution by computer simulation. The simulation method used is the real-space self-consistent field (SCF) method developed by Fredrickson's group^[34–36]. This method has been successfully used to study the self-assembly of amphiphilic block copolymers in dilute solution by He *et al.*^[37].

THEORETICAL MODEL

In this section, the SCF model for the linear ABA triblock copolymer dilute solution system is briefly described. The symmetric linear amphiphilic ABA triblock copolymer and solvent molecules S are involved in volume V . The length fractions of each type of block of the ABA triblock copolymers are l_A and l_B , respectively, and $l_A + l_B = 1$. The volume fraction of the ABA triblock copolymer in the dilute solution is f_p and the solvent volume fraction is $f_s = 1 - f_p$. As a result, the volume fraction of segment i ($i = A, B$) in the system is $f_i = f_p \cdot l_i$. Incompressibility is assumed in this mixture system. For such system, the free energy is given by:

$$F = F^{\text{entropy}} + F^{\text{enthalpy}} \quad (1)$$

F^{entropy} and F^{enthalpy} are the contributions of the entropy and the enthalpy to the total free energy, respectively, and they have the following forms:

$$\begin{aligned} F^{\text{entropy}} = & -f_p \ln(Q_p / f_p V) - N f_s \ln(Q_s / f_s V) - \\ & 1/V \int d\vec{r} [\omega_A \phi_A(\vec{r}) + \omega_B \phi_B(\vec{r}) + \omega_S \phi_S(\vec{r}) + P(\vec{r})(1 - \phi_A(\vec{r}) - \phi_B(\vec{r}) - \phi_S(\vec{r}))] \\ F^{\text{enthalpy}} = & 1/V \int d\vec{r} [\chi_{AB} N \phi_A(\vec{r}) \phi_B(\vec{r}) + \chi_{AS} N \phi_A(\vec{r}) \phi_S(\vec{r}) + \chi_{BS} N \phi_B(\vec{r}) \phi_S(\vec{r})] \end{aligned} \quad (2)$$

where N is the total length of the block copolymer chain, χ_{ij} is the Flory-Huggins interaction parameter between species i and j , and $\phi_A(\vec{r})$, $\phi_B(\vec{r})$, and $\phi_S(\vec{r})$ are the densities of blocks A, B, and solvent S, respectively. $P(\vec{r})$ is the known Lagrange multiplier which enforces the incompressibility. $Q_p = \int d\vec{r} \cdot q(\vec{r}, 1)$ is the partition function of a single polymer chain in an effective chemical potential field $\omega_A(\vec{r})$ and $\omega_B(\vec{r})$. $Q_s = \int d\vec{r} \cdot \exp(-\omega_S(\vec{r}) / N)$ is the partition function of the solvent in an effective chemical potential field $\omega_S(\vec{r})$. $q(\vec{r}, s)$ is the end-segment distribution function that gives the probability of finding segment s at position $\vec{r}$, and it satisfies the following

modified diffusion equation:

$$\partial q(\vec{r}, s) / \partial s = \nabla^2 q(\vec{r}, s) - \omega(\vec{r}, s) q(\vec{r}, s) \quad (3)$$

The second end-segment distribution function $q^+(\vec{r}, s)$ is not needed in this paper because $q^+(\vec{r}, s)$ is the same as $q(\vec{r}, s)$ for the reason that the triblock copolymer chosen in our work is symmetric. Thus the density of each component can be obtained by

$$\phi_A(\vec{r}) = \frac{f_p V}{Q_p} \left[\int_0^{\frac{l_A}{2}} ds \cdot q(\vec{r}, s) q(\vec{r}, 1-s) + \int_{\frac{l_A}{2}+l_B}^1 ds \cdot q(\vec{r}, s) q(\vec{r}, 1-s) \right] \quad (4)$$

$$\phi_B(\vec{r}) = \frac{f_p V}{Q_p} \int_{\frac{l_A}{2}}^{\frac{l_A}{2}+l_B} ds \cdot q(\vec{r}, s) q(\vec{r}, 1-s) \quad (5)$$

$$\phi_S(\vec{r}) = \frac{f_s V}{Q_s} \exp(-\omega_S(\vec{r}) / N) \quad (6)$$

From the equilibrium conditions (*i.e.*, the minimization of the free energy to the density, the potential field and the Lagrange multiplier), we have the following four equations:

$$\omega_A(\vec{r}) = \chi_{AB} N (\phi_B(\vec{r}) - f_B) + \chi_{AS} N (\phi_S(\vec{r}) - f_S) + P(\vec{r}) \quad (7)$$

$$\omega_B(\vec{r}) = \chi_{AB} N (\phi_A(\vec{r}) - f_A) + \chi_{BS} N (\phi_S(\vec{r}) - f_S) + P(\vec{r}) \quad (8)$$

$$\omega_S(\vec{r}) = \chi_{AS} N (\phi_A(\vec{r}) - f_A) + \chi_{BS} N (\phi_B(\vec{r}) - f_B) + P(\vec{r}) \quad (9)$$

$$\phi_A(\vec{r}) + \phi_B(\vec{r}) + \phi_S(\vec{r}) = 1 \quad (10)$$

In simulations, the chemical potential field $\omega_i(\vec{r})$ can be updated by using the equation

$$\omega_i^{t+1}(\vec{r}) = \omega_i^t(\vec{r}) + \Delta t \left[\sum_{j \neq i} \chi_{ij} N (\phi_j(\vec{r}) - f_j) + P(\vec{r}) - \omega_i^t(\vec{r}) \right] \quad (11)$$

In this work, the numerical simulations were carried out in 3D cubic lattice with a volume of $V = 50^3$. Periodic boundary condition was imposed in all three directions and the grid size we chose was $\Delta x = 0.3636$ and the time step Δt was set to be 0.3. The simulation was carried out until the morphologies were stable. The same initial fluctuation amplitude in the order of 10^{-2} was used in our work. The volume fraction of the ABA triblock copolymer was fixed at $f_p = 0.1$.

RESULTS AND DISCUSSION

In this section, we focus on the effects of solvent property on the micelle morphologies formed by ABA triblock copolymers in selective solvent. In experiments, the solvent property can be tuned by using different common solvents^[38]. The change of solvent property will change the hydrophobicity of hydrophobic block and the hydrophilicity of hydrophilic block. Therefore, in this simulation work the change of solvent property was achieved by changing the hydrophobicity and hydrophilicity of corresponding blocks. According to large amounts of test works, we found that for the linear symmetric ABA triblock copolymers, rod-like and spherical micelles tend to be formed when the middle block B is relatively short (*i.e.*, l_B is small), while vesicles are easier to be obtained when the middle block B is relatively long (*i.e.*, l_B is large). In this work, we set the total chain length to be $N = 24$ and $l_B = 0.8333$, which means that the ABA triblock copolymer we chose can be denoted by $A_2B_{20}A_2$. In addition, the interaction parameter between blocks A and B is fixed at $\chi_{AB}N = 24$ in this paper. In what follows, $\chi_{AS}N$ and $\chi_{BS}N$ are the main subjects investigated in our simulation works.

Effect of Hydrophobicity of Block B

Firstly, we investigate the effect of the hydrophobicities of middle block B. The reason we study the middle block B first is that most of the experimental works have focused their attentions on the effect of the interaction between the hydrophobic block and selective solvent on the micelle morphologies formed by amphiphilic block copolymer in solution. In most experiments, one can change the mutual interactions between the hydrophobic blocks and the solvent molecules conveniently by changing the species of solvent molecules^[38].

Figure 1 shows the variation of the micelle morphologies formed by ABA triblock copolymer in selective solvent with the interaction parameter $\chi_{BS}N$ at $\chi_{AS}N = -7$. From Fig. 1 it can be clearly seen that the aggregated morphology changes from spherical vesicle (Fig. 1a) to rod-like micelle (Fig. 1f), and finally to spherical micelles (Fig. 1k) as the hydrophobicity of the middle block B increases. Besides these three kinds of morphologies, we also find some transitional morphologies. For instance, the ring-shaped micelles are considered to be found when the vesicles change toward the rods^[39]. From Fig. 1 we can see that between the vesicle (Fig. 1a) and the rod-like micelles (Fig. 1f), the ring-shaped micelles (Figs. 1d and 1e), as well as the cage-like micelles (Figs. 1b and 1c) were also obtained. The ring-shaped micelles have been widely investigated by many researchers in recent years and the mechanism for the formation of the ring-shaped micelle is still in debate up to now. In addition, it can be found that the geometrical characteristic of micelles changes from sphere to short rods then to long stick if we observe Fig. 1 from Fig. 1(k) to Fig. 1(e). In other words, the interaction parameter $\chi_{BS}N$ will affect the length-diameter ratio (LDR) of the rod-like structure. The small LDR corresponds to sphere or short rods, while the large LDR represents the long stick. The morphological changes shown in Fig. 1 with the increase of the hydrophobicity of middle block B is consistent with one of the previous experimental work^[38]. The experimental results showed that the micelle morphology formed by ABA-type

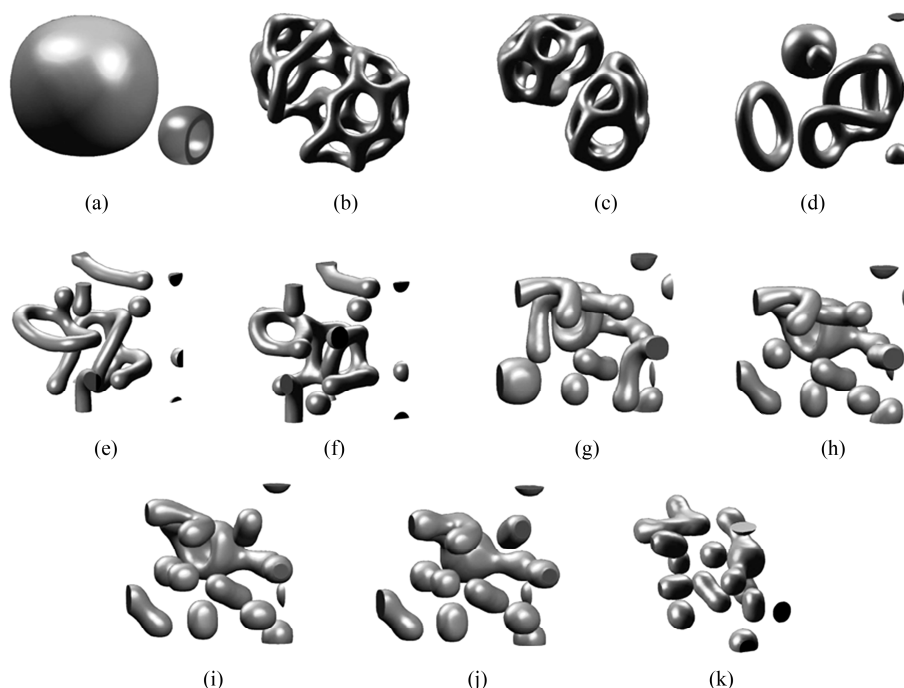


Fig. 1 Morphologies obtained at different $\chi_{BS}N$ in the case of $\chi_{AS}N = -7$: (a) $\chi_{BS}N = 27.5$, (b) $\chi_{BS}N = 27.7$, (c) $\chi_{BS}N = 28$, (d) $\chi_{BS}N = 29$, (e) $\chi_{BS}N = 30$, (f) $\chi_{BS}N = 31$, (g) $\chi_{BS}N = 32$, (h) $\chi_{BS}N = 33$, (i) $\chi_{BS}N = 34$, (j) $\chi_{BS}N = 35$, (k) $\chi_{BS}N = 36$

The iso-surface contours are only for the hydrophobic B domain. Corresponding cross-section view of the vesicle shown in (a) was also given.

triblock copolymer changed from spheres to rods and then to vesicles by changing the common solvent from *N,N*-dimethylformamide (DMF) to dioxane and then to tetrahydrofuran (THF). According to the polymer/solvent solubility parameter list provided in Ref. [38], it can be seen that when the interaction between the middle block and solvent molecules is weak, vesicles tend to be formed, and when the interaction is strong, spherical micelles will be obtained. While the interaction is moderate, one can obtain rod-like micelles in experiments.

To better understand the effect of hydrophobicity of middle block B on the micelle morphologies, we calculated the following physical quantities. These quantities can be divided into two groups: group one includes total free energy, energy from entropy and energy from enthalpy (*i.e.* interaction energy); group two includes surface area and specific surface area (*i.e.* the ratio of the surface area with respect to the total volume of micelles). Firstly, based on Eqs. (1) and (2), we plotted the calculated total free energy, the energy from entropy and the interaction energy in Fig. 2. From Fig. 2(c), we can see that the total free energy increases with the increase of the interaction parameter $\chi_{BS}N$, while the interaction energy (Fig. 2b), as one of the two parts of the total free energy, decreases. This means that the other part of the total free energy, *i.e.* the entropic contribution to the total free energy (Fig. 2a), must increase and it must increase faster than the interaction energy decreases. Therefore, we may conclude that the entropy plays a major role during the transition from vesicle to spherical micelles.

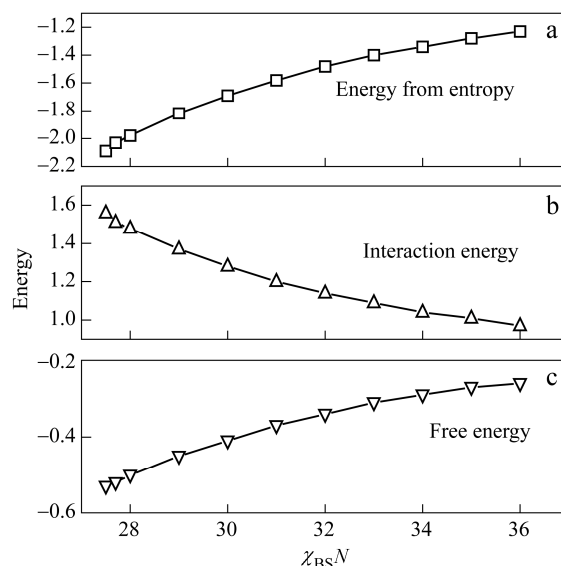


Fig. 2 Energy variations with the interaction parameter $\chi_{BS}N$ in the case of $\chi_{AS}N = -7$

Subsequently, we calculated the surface area and the specific surface area. We know that the hydrophobic block B has a high density distribution inside the aggregates. Outside the aggregates, it has a very low density distribution. In other words, the density of block B will gradually become lower from the inside to the outside of the micelles. Therefore, we can choose a certain density value to obtain an isodensity surface. This isodensity surface can be taken as the surface of the aggregates. The number of the lattice sites on the isodensity surface is proportional to the surface area and it is regarded as the surface area in this paper. After obtaining the isodensity surface (*i.e.* the surface of the aggregates), it is easy to calculate the total volume of the whole aggregates, *i.e.* the total number of the lattice sites within the isodensity surface. In this paper, the reference density value is chosen to be 0.1 (*i.e.* the average density of the block copolymer in solution). Figure 3 gives the variations of the surface area and the specific surface area with $\chi_{BS}N$, respectively. It can be seen from Fig. 3 that both of the two curves decrease with the increase of the interaction parameter $\chi_{BS}N$. Obviously, when $\chi_{BS}N$ is increased, the solubility of the hydrophobic block B in selective solvent becomes poor. The aggregates will shrink their volume to

decrease the contact area (*i.e.* surface area) between block B and solvent molecules so as to decrease the interaction energy of the whole system, as shown in Fig. 2(b). From Fig. 3 we can also see that the changes of the curves are not monotonic. This can be explained by the geometric difference in morphology between vesicle-type and other aggregates shown in Fig. 1. Vesicle wall has some kind of 2D continuity, which is similar to the case of 2D plane. As for the other aggregates close to vesicle-type structure shown in Fig. 1, most of them can be regarded as the combinations of many rods (which has only 1D continuity) with finite length. Namely, cage-like network (Fig. 1b) has more parts than vesicle has. As we all know that if two aggregates have the same or similar total volume, the one which is divided into more parts will have more surface area. This is why the surface area curve increases at the onset of the curves shown in Fig. 3.

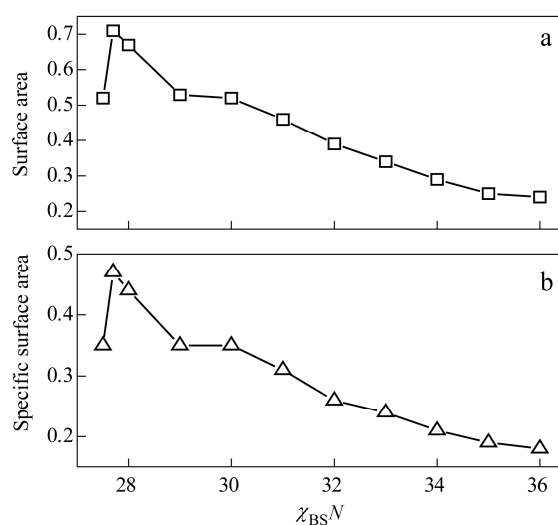


Fig. 3 Variations of surface area (a) and specific surface area (b) with the interaction parameter $\chi_{BS}N$ in the case of $\chi_{AS}N = -7$

Effect of Hydrophilicity of Block A

After the investigation of the effect of the hydrophobic properties of block B on the micelle morphologies, we studied the effect of the hydrophilic properties of block A on the micelle morphology. As far as we know, no experiments, theories and simulations have focused their attentions on the effect of hydrophilicity of hydrophilic blocks on the micelle morphology. Probably this is because the volume fraction of the hydrophilic block in amphiphilic block copolymer is small.

It is known that when the amphiphilic block copolymer aggregates into micelles or vesicles, the hydrophilic blocks (*i.e.* block A in this paper) will locate in between the solvent molecules (*i.e.* S) and the cores formed by the hydrophobic blocks (*i.e.* block B), playing the role of protected shells to prevent the hydrophobic blocks from aggregating into macroscopic phases and precipitating from the solution. Due to the fact that blocks A locate at the interface between blocks B and S, any change of the hydrophilic properties of block A will probably affect the ultimate morphologies of the system. Figure 4 shows the variation of micelle morphology formed by ABA triblock copolymer in selective solvent with the mutual interaction between block A and solvent S. The interaction parameter $\chi_{BS}N$ is set to be 28. From Fig. 4, we can see that the aggregated morphologies change from perfect vesicle to vesicle with disrepair on the surface and finally to cage-like networks with increasing the hydrophilicities of block A. Unlike the case shown in Fig. 1, the morphology does not change into small spherical micelles ultimately because the interaction parameter $\chi_{BS}N$ is not strong enough (relative to the case of $\chi_{BS}N = 36$ shown in Fig. 1) to compress the hydrophobic block B into spheres. In Fig. 4(i), the ring-shaped micelles are observed again. It can be speculated that the mechanism for the formation of the ring-shaped

micelles is not the same as the formation mechanism of the ring-shaped micelle shown in Fig. 1. From Fig. 4, one can find that the increase of the hydrophilicities of block A will destroy the integrity of vesicles. With the increase of the hydrophilicities of end block A, more and more solvent molecules will be attracted in the vesicle wall. Due to the repulsive interaction between block B and solvent molecules, the perfect vesicle wall will finally be broken by solvent molecules. Similar to the case shown in Fig. 1, the cage-like networks can be regarded as the combination of many linear elements which have only 1D tractility. More detailed discussion about the formation of ring-shaped micelles by the breaking of vesicles can be seen in Ref. [4] and Ref. [29].

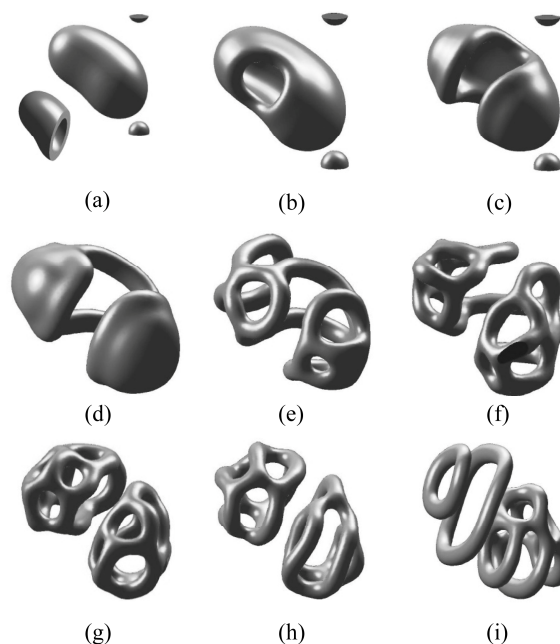


Fig. 4 Morphologies obtained at different $\chi_{AS}N$ in the case of $\chi_{BS}N = 28$: (a) $\chi_{AS}N = -1$, (b) $\chi_{AS}N = -2$, (c) $\chi_{AS}N = -3$, (d) $\chi_{AS}N = -4$, (e) $\chi_{AS}N = -5$, (f) $\chi_{AS}N = -6$, (g) $\chi_{AS}N = -7$, (h) $\chi_{AS}N = -8$ and (i) $\chi_{AS}N = -9$. The iso-surface contours are only for the hydrophobic B domain. Corresponding cross-section view of the vesicle shown in (a) was also given.

Figure 5 shows the variations of energies with the increase of $\chi_{AS}N$ at $\chi_{BS}N = 28$. From Fig. 5(b), we can see that the interaction energy almost unchanged when $\chi_{AS}N$ is increased, meaning that the change in the total free energy is caused almost completely by the change of entropy, *i.e.*, the morphology of the system is determined by the entropy of the system. On the other hand, we know that the more hydrophilic the block A is, the more stretched the hydrophobic block B is. Therefore, the entropy of the system will decrease with the increase of the stretch degree of block B.

Subsequently, we calculated the surface area and the specific surface area of the system, respectively. With the increase of $\chi_{AS}N$, more and more hydrophobic block B will be ‘pulled’ into the solvent by the hydrophilic block A. Therefore, it is obvious that the surface area of the aggregates will increase correspondingly, which is shown in Fig. 6. From Fig. 6, it can be found that not only the surface area, but also the specific surface area increases with the increase of $\chi_{AS}N$.

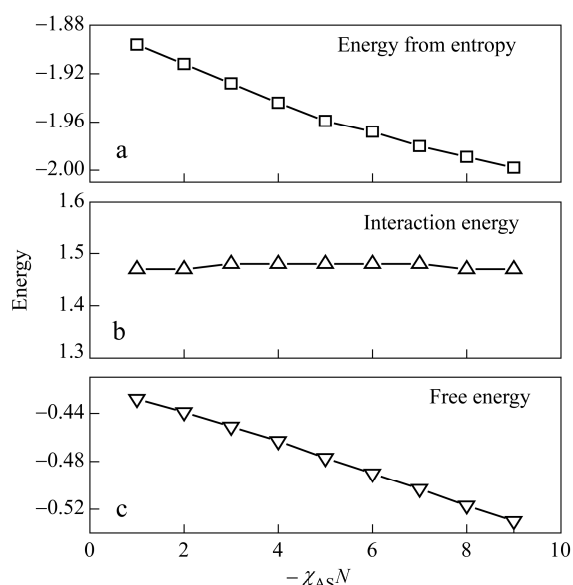


Fig. 5 Energy variations with the interaction parameter $\chi_{AS}N$ in the case of $\chi_{BS}N = 28$

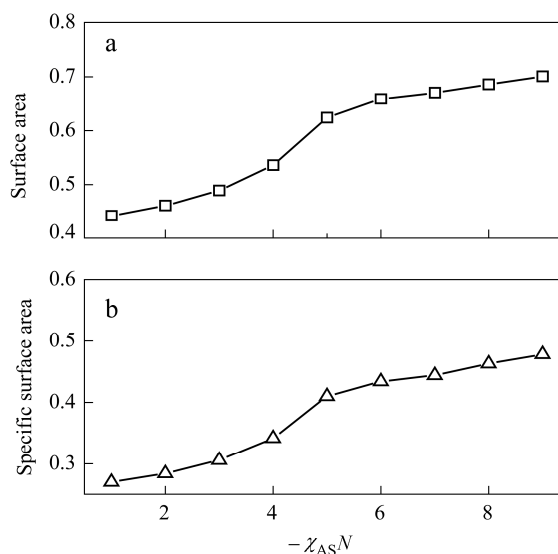


Fig. 6 Variations of surface area and specific surface area with the interaction parameter $\chi_{AS}N$ in the case of $\chi_{BS}N = 28$

A Phase Diagram

In the above two sections, we have investigated the effects of the interaction parameters ($\chi_{AS}N$ and $\chi_{BS}N$, respectively) on the micelle morphologies in detail. In order to give a comprehensive survey of the morphology variations with the interaction parameters, we provide a phase diagram as a function of the two parameters $\chi_{AS}N$ and $\chi_{BS}N$. Figure 7 gives the phase diagram in which $\chi_{AS}N$ and $\chi_{BS}N$ are horizontal axis and vertical axis, respectively. Through this diagram, it can be clearly seen how the interaction parameters affect the micelle morphologies formed by the ABA triblock copolymer chosen in this work. Besides the micelle morphologies we have mentioned above (such as the spheres, rods and vesicles), there are also some other types of morphologies. From Fig. 7, the lamellar region can be easily found in the phase diagram. When $\chi_{BS}N \approx 32$ and $\chi_{AS}N \approx -9$, the so called Y-junction structures are also obtained. Bates and co-workers have pointed out that the Y-junction structure can be regarded as the structure elements prior to the formation of network structures.

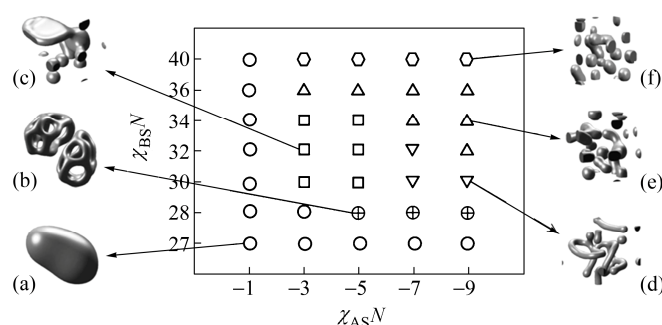


Fig. 7 Phase diagram of A2B20A2 triblock copolymer in selective solvent as a function of the interaction parameters $\chi_{AS}N$ and $\chi_{BS}N$ with typical morphologies listed around the phase diagram: (a) vesicle, (b) cage, (c) lamellar, (d) long stick, (e) sphere and short rod, (f) sphere

Though the sample Bates *et al.* chose is a diblock copolymer (PB-PEO)^[40], our simulation results support, to some extent, the mechanism they proposed for the formation of 3D networks. In the above section, we have pointed out that the variation of $\chi_{AS}N$ does not lead to the change of the interaction energy of the whole system if $\chi_{BS}N$ is fixed at $\chi_{BS}N = 28$. We also selected some other values of $\chi_{BS}N$, such as $\chi_{BS}N = 32$ and $\chi_{BS}N = 36$, to test whether the total interaction energy of the whole system varies with $\chi_{AS}N$. The result is that when $\chi_{BS}N$ is increased, the total interaction energy of the whole system will decrease with the increase of $\chi_{AS}N$. This is because when $\chi_{BS}N$ is increased, the ability of the whole system to adjust the total interaction energy by changing morphologies become weak. Especially when $\chi_{BS}N \geq 36$, $\chi_{AS}N$ will almost have no effect on the micelle morphologies of the system.

CONCLUSIONS

Using 3D real-space self-consistent field method, we systematically investigated the effects of the solvent properties on the micelle morphologies formed by ABA amphiphilic triblock copolymer in selective solvent by varying the mutual interaction between each block and the solvent molecules. We find a possible reason why different researchers observed different mechanism for the formation of the ring-shaped morphologies. This is because the same morphologies can be obtained by tuning either the hydrophilicity of the hydrophilic block or the hydrophobicity of the hydrophobic block. Moreover, a phase diagram is provided to give a survey of the morphology changes with the interaction parameters. Through this phase diagram, we can see how the morphology changes with the change of the interaction parameters, which can help researchers to analyze the mechanism for the formation of various micelle morphologies.

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