Available online at www.sciencedirect.com
ScienceDirect
Polymer 49 (2008) 1407–1413
polymer
www.elsevier.com/locate/polymer

Multicompartment micelles formed from star-dendritic triblock copolymers in selective solvents: A dissipative particle dynamics study

Dahuan Liu*, Chongli Zhong

Key Lab for Nanomaterials, Ministry of Education, Department of Chemical Engineering, Beijing University of Chemical Technology, 15 BeiSanhuan East Road, Beijing 100029, China

Received 26 October 2007; received in revised form 10 January 2008; accepted 10 January 2008
Available online 20 January 2008

Abstract

Dissipative particle dynamics method was used to study the multicompartment micelles formed from star-dendritic triblock copolymers in selective solvents, in which particular attention was paid to the effects of dendritic structure. The simulations show that the dendritic structure not only influences the morphology and the formation process of multicompartment micelles formed, but also the response of the micelle structure to solvent quality. The information obtained is useful for the future design of multicompartment micelles for practical applications, especially in the field of drug delivery.

Keywords: Dissipative particle dynamics simulation; Multicompartment micelle; Star-dendritic triblock copolymer

1. Introduction

Amphiphilic block copolymer can self-assemble into micelles and vesicles in selective solvent. For the past several decades, these materials with nanometer-scale microphase-separated structures have been applied to many fields, particularly to drug delivery [1,2]. Recently, multicompartment micelle has been introduced as a new class of micelles inspired originally by biological systems, showing great potential applications in biotechnology, multifunctional nanoreactors, medicine, etc. [3,4].

Multicompartment micelles have complex structures consisting of a hydrophilic shell and a hydrophobic core with multidomains, which may extend the applications of traditional micelles to a wide scope. Therefore, after the multicompartment micelles were synthesized successfully, special attentions have been paid to study their morphologies and structures [4]. As a result, several intriguing morphologies were observed, such as "worm" [5], "hamburger" [6], "sphere-on-sphere" [7], cylinder [8,9], polygonal bilayer sheets [10], and Y-junctions [11]. These works indicated that further investigations are needed to study the influence of the architecture of building block copolymers on the inner structure, as well as towards understanding multicompartment micelle thoroughly [12].

It is worth noting that to date almost all of the multicompartment micelles reported were formed from the linear block copolymers or miktoarm star triblock copolymer. At the same time, another kind of complex polymers, dendrimers [13–17] and hyperbranched copolymers [18], has received increasing attention due to their unique architecture and ability to form self-assembled fascinating structures. Recently, Yan and coworkers [19] have firstly investigated multicompartment micelles from amphiphilic hyperbranched star block copolymers. Unfortunately, the effects of the architecture of dendrimer on the morphology and formation process of the multicompartment micelles are not studied systematically as far as we know and the knowledge on the response to the

* Corresponding author. Fax: +86 10 64419862.
E-mail address: liudahuan2006@yahoo.com.cn (D. Liu).

0032-3861/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.01.034

change of circumstance is still quite lacking, which are pivotal to the practical applications of multicompartment micelles.

Considering that the synthesis of dendrimer as well as the control of architecture of block copolymers systematically are difficult and time-consuming in experiment, computer simulation is a suitable and powerful tool for investigating the behavior of micelles, as well as complementing experimental works in a wider parameter space [20,21]. Therefore, based on the results of star triblock copolymers got in our research group [22], the multicompartment micelles formed from star-dendritic triblock copolymers in selective solvent were studied in this work by a mesoscopic simulation technique, dissipative particle dynamics (DPD) method, which has been successfully used to study the self-assembly behavior of star or linear block copolymers in previous work [21–27]. The main purpose of this work is to try to provide preliminary numerical results and some useful information for further experimental study.

2. Method and simulation details

2.1. Dissipative particle dynamics method

Dissipative particle dynamics (DPD) method is a mesocopic simulation technique based on the fluctuation–dissipation theorem [28–30]. In this method, the force acting on a particle contains three pairwise additive parts:

$$\mathbf{f}_i = \sum_{j\neq i}(\mathbf{F}_{ij}^{\mathrm{C}} + \mathbf{F}_{ij}^{\mathrm{D}} + \mathbf{F}_{ij}^{\mathrm{R}}) \tag{1}$$

where $\boldsymbol{F}^{\mathrm{C}}$, $\boldsymbol{F}^{\mathrm{D}}$ and $\boldsymbol{F}^{\mathrm{R}}$ represent conservative, dissipative, and random forces, respectively, and the sum runs over all other particles within a certain cutoff radius r_{c}. As this is the only length-scale in the system, cutoff radius is always used as the unit of length, $r_{\mathrm{c}} = 1$.

The conservative force is given by

$$\mathbf{F}_{ij}^{\mathrm{C}} = \begin{cases} a_{ij}\left(1 - r_{ij}/r_{\mathrm{c}}\right)\widehat{\mathbf{r}}_{ij} & \left(r_{ij} < r_{\mathrm{c}}\right) \\ 0 & \left(r_{ij} \geq r_{\mathrm{c}}\right) \end{cases} \tag{2}$$

where a_{ij} is the maximum repulsion between particles i and j, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, and $\widehat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$. This kind of force is soft repulsion acting along the line of centers between particles.

The dissipative force and the random force are given by

$$\mathbf{F}_{ij}^{\mathrm{D}} = -\gamma\omega^{\mathrm{D}}\left(r_{ij}\right)\left(\widehat{\mathbf{r}}_{ij}\cdot\mathbf{v}_{ij}\right)\widehat{\mathbf{r}}_{ij} \tag{3}$$

$$\mathbf{F}_{ij}^{\mathrm{R}} = \sigma\omega^{\mathrm{R}}\left(r_{ij}\right)\theta_{ij}\widehat{\mathbf{r}}_{ij} \tag{4}$$

where $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, ω^{D} and ω^{R} are weight functions vanishing for $r > r_{\mathrm{c}}$, γ is the friction coefficient, σ is the noise amplitude, and θ_{ij} is a randomly fluctuating variable with Gaussian statistics.

The two weight functions can be taken simply as

$$\omega^{\mathrm{D}}(r) = \left[\omega^{\mathrm{R}}(r)\right]^2 = \begin{cases} \left(1 - r_{ij}/r_{\mathrm{c}}\right)^2 & \left(r_{ij} < r_{\mathrm{c}}\right) \\ 0 & \left(r_{ij} \geq r_{\mathrm{c}}\right) \end{cases} \tag{5}$$

$$\sigma^2 = 2\gamma k_{\mathrm{B}}T \tag{6}$$

In this work, the relationship between a_{ij} and the Flory–Huggins χ-parameter proposed by Groot and Warren [30] is adopted to determine the repulsion parameter a_{ij} and then get the conservative force F^{C}:

$$a_{ij} = \begin{cases} a_{ii} + 3.27\chi_{ij} & \rho = 3 \\ a_{ii} + 1.45\chi_{ij} & \rho = 5 \end{cases} \tag{7}$$

where ρ is the density, a_{ii} is the repulsion parameter between particles of the same type, and its value is derived from the compressibility of pure component by

$$a_{ii} = 75k_{\mathrm{B}}/\rho \tag{8}$$

2.2. Simulation details

Multicompartment micelles from the self-assembly of ABC star triblock copolymer have been investigated both in experiment [5] and in simulation work [22,25], and this miktoarm star architecture is believed to be successful remarkably in promoting the formation of multicompartment cores [5]. Therefore, in this work we introduced the dendritic structure into ABC star triblock copolymer to perform preliminary numerical discussion on the multicompartment micelle formed from dendrimers. The numbers of DPD beads associated with A, B, and C blocks are set to 4, 10, and 2 respectively, to ensure the formation of segmented wormlike micelles [22] which have an intriguing structure for loading two or more kinds of agents simultaneously and may be a promising material for drug delivery. As depicted in Fig. 1, model I is in fact the star triblock copolymer to bring into comparison. For model II, the hydrophilic block B is dendritic, while the long hydrophobic block A is dendritic in model III for convenience.

In the previous work [22], we studied the self-assembly of ABC star triblock copolymers into multicompartment micelles in water, and the repulsive interaction parameter a_{ij} used for the four unlike species was determined by reproducing the experimental observations of Lodge and coworkers [5]:

$$a_{ij} = \begin{pmatrix} & \mathrm{A} & \mathrm{B} & \mathrm{C} & \mathrm{S} \\ \mathrm{A} & 25 & 45 & 75 & 50 \\ \mathrm{B} & 45 & 25 & 90 & 27 \\ \mathrm{C} & 75 & 90 & 25 & 120 \\ \mathrm{S} & 50 & 27 & 120 & 25 \end{pmatrix} \tag{9}$$

where A, B, C and S represent the weakly hydrophobic block, the hydrophilic block, the strongly hydrophobic block, and the solvent, respectively. In this work, DPD repulsion parameters were based on these values.

The DPD simulations were performed in a cubic cell of size $30 \times 30 \times 30r_{\mathrm{c}}^3$ containing 81,000 DPD beads and periodic boundary conditions were applied. Bead density was taken

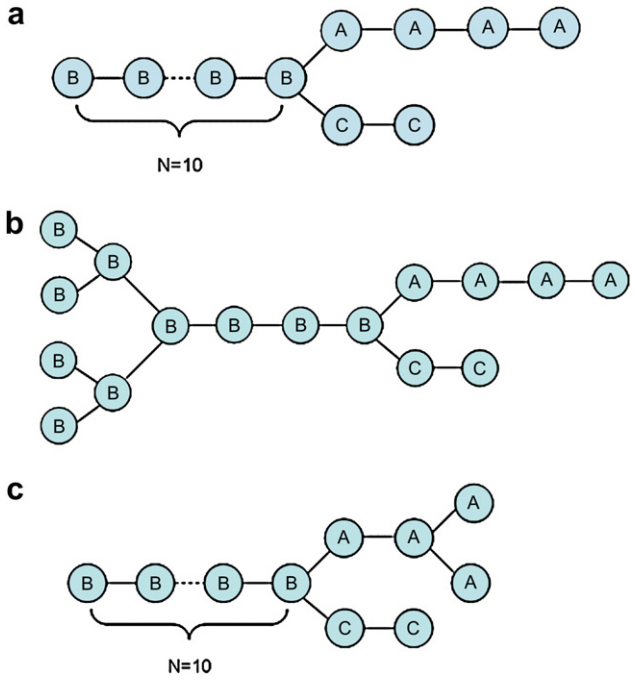

Fig. 1. Schematic structures of star-dendritic block copolymers: (a) model I, (b) model II, and (c) model III.

as 3.0 and the volume fraction of the copolymer was set to be 0.1 to ensure enough micelles can be formed in these systems. For convenience, the cutoff radius r_c, the particle mass m, and k_BT were all taken as unity. The time step Δt was taken as 0.05, and adjacent particles in the polymer chain interacted via a linear spring with a harmonic spring constant of 4.0, and a DPD thermostat with the friction/noise parameter $\gamma = 4.5$ was used. Depending on the stability of properties of the systems including the mean-square radius of gyration and conservative energy, a total of $3-5 \times 10^5$ DPD steps were carried out for each DPD simulation to ensure the equilibration.

3. Results and discussion

3.1. Effects of the dendritic structure on the formation of multicompartment micelles

First, the effects of dendritic structure on the formation of multicompartment micelles were studied by comparing the morphologies of micelles formed from models I–III on the same conditions, as given in Fig. 2.

The simulations show that these three kinds of star-dendritic triblock copolymers can all self-assemble into wormlike multicompartment micelles. Since the length of hydrophobic block A is not long enough, the number of branch points in dendritic part is small in model III, which induces that the difference between the micelles formed from models III and I is negligible. However, the copolymer with hydrophilic dendritic block (model II) trends to form longer wormlike micelle than the other models. Thus, we mainly focus on the cases of models I and II in the following section.

To further understand the effect of dendritic structure, the evolution processes of the corresponding micelle are investigated. Similar to the formation mechanism found in the previous works [22,26], these micelles are formed through fusion process and the general sequence is discrete "hamburger" micelle, short wormlike micelle, and long wormlike micelle. However, from the snapshots of evolution process given in Fig. 3, it can be seen that short wormlike structure and long wormlike structure first appear at 25,000 step (Fig. 3f) and at 87,000 step (Fig. 3h), respectively, in model II, while at 10,000 step (Fig. 3b) and at 35,000 step (Fig. 3d) in model I, that is, the dendritic hydrophilic block leads to the slower fusion process.

Interestingly, in spite of dendritic conformation forming a very protective layer and shielding the hydrophobic core to lead to a slow process, this structure also induces longer wormlike micelles in final formation as depicted in Fig. 2. In order to give a rough explanation of this behavior, we calculated the mean-square radius of gyration ($\langle R_g^2 \rangle$) of the hydrophilic block in star-dendritic triblock copolymer as well as time evolution of the number of clusters. The $\langle R_g^2 \rangle$ of the hydrophilic block is defined as

$$\left\langle R_g^2 \right\rangle_{\text{hydrophilic}} = \left\langle \frac{1}{N} \sum_{i=1}^{N} (r_i - r_{\text{cm}})^2 \right\rangle \tag{10}$$

where r_i and r_{cm} denote the position vector of each particle in the hydrophilic block and the center-of-mass for the whole hydrophilic block. Fig. 4 shows the calculated $\langle R_g^2 \rangle_{\text{hydrophilic}}$ as a function of simulation steps. It is clear that the sizes of hydrophilic domains increase rapidly to the equilibrium values at the beginning of simulation in both models. In addition, the $\langle R_g^2 \rangle_{\text{hydrophilic}}$ of model II is less than that of model I, which

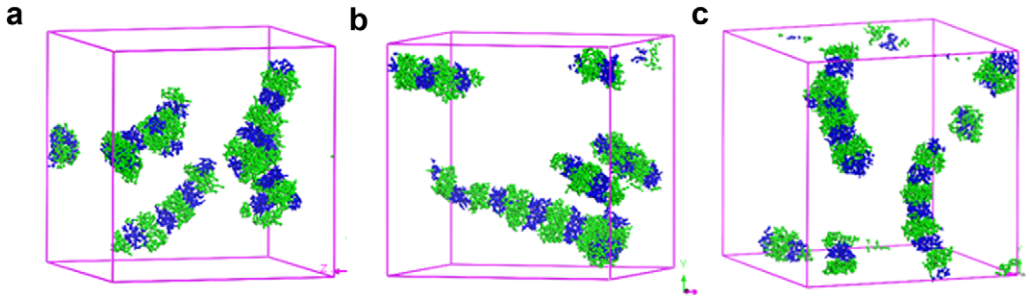

Fig. 2. Morphologies of multicompartment micelles formed from star-dendritic triblock copolymer: (a) model I, (b) model II, and (c) model III. B blocks and water were omitted for clarity; A, blue; C, green (for interpretation of colour in this figure, the reader is referred to the web version of this article).

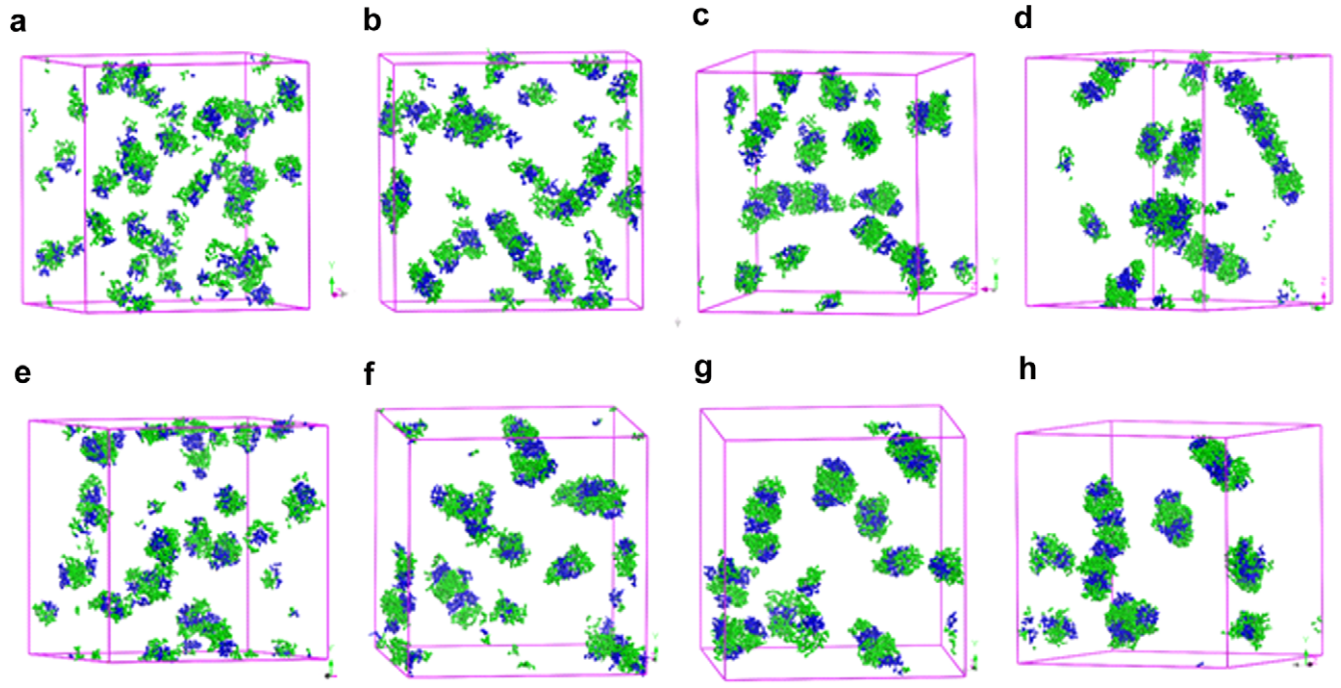

Fig. 3. Evolution of wormlike multicompartment micelle from different models obtained by DPD simulations: (a)–(d) for model I, (a) step = 5000, (b) step = 10,000, (c) step = 25,000, and (d) step = 35,000; (e)–(h) for model II, (e) step = 10,000, (f) step = 25,000, (g) step = 50,000, and (h) step = 87,000. B blocks and solvents were omitted for clarity; A, blue; C, green (for interpretation of colour in this figure, the reader is referred to the web version of this article).

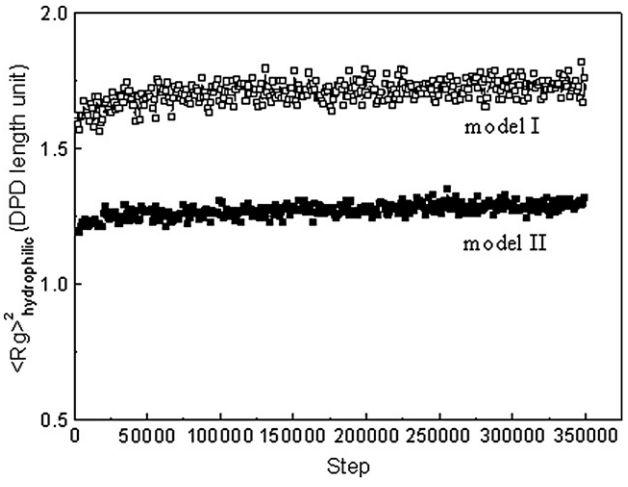

Fig. 4. The mean-square radius of gyration for the two models of star-dendritic triblock copolymers as a function of simulation step.

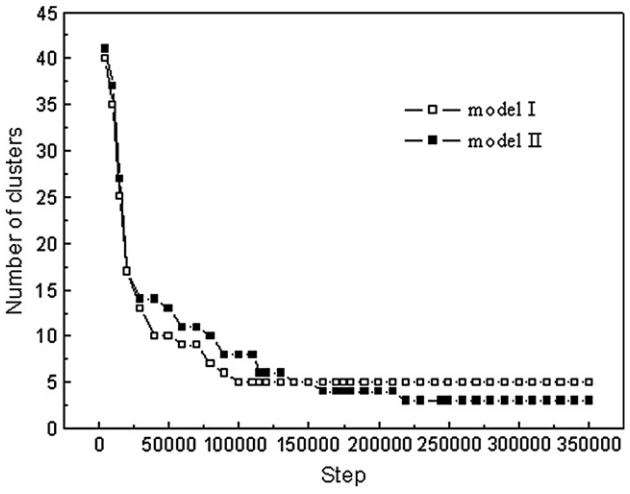

Fig. 5. The number of clusters for the two models of star-dendritic triblock copolymers as a function of simulation step.

means that dendritic hydrophilic blocks extend less fully than linear hydrophilic block with the same volume fraction in copolymer. Thus, since there are only a small number of hydrophobic blocks aggregating to form the core of micelle at the beginning of formation process, the compact structure of dendritic hydrophilic blocks is able to prevent the combination of hydrophobic cores and slows down the fusion process. This is corresponded to the fact that model II has larger number of clusters than model I during 1000–125,000 steps as shown in Fig. 5. On the other hand, the hydrophobic effect is commonly considered to be the main driving force in the formation of micelle. The solvents drive the hydrophobic blocks to get together to minimize the contact of hydrophobic blocks and solvents, inducing that the core of micelle grows longer. From the previous work, it is concluded that due to the starlike structure of copoylmer chains the discrete ‘‘hamburger’’ micelles tend to contact with each other from the top and bottom and they ‘‘superpose’’ one by one to form wormlike micelles with long layered cores [22]. In this case, dendritic hydrophilic block does not extend fully enough to shield the top and bottom of hydrophobic regions from the solvent completely with the core growing. Therefore, the interfacial tension of the micelles goes up and the fusion continues. As a result, the number of clusters in equilibrium state is low in star-dendritic triblock copolymer with dendritic hydrophilic block as shown in Fig. 5 and longer wormlike micelles are formed.

The above simulations show that the dendritic structure in star-dendritic triblock copolymer may affect the detail of final morphology of the multicompartment micelles, and at the same time the formation process of micelle has also been influenced.

3.2. Effects of the dendritic structure on the response to the solvent quality of multicompartment micelles

It is well known that one significant application of micelle is delivering drug molecules [1,2], in which the delivering method is a key aspect attracting more and more attention [31,32]. Recently a possible delivering way is proposed based on changing the solvent quality, such as pH value, to destabilize the loading compartment of micelle and then release the drug [33]. Therefore, in this section we attempt to investigate the effects of dendritic structure on the response to the solvent quality, which may provide useful information for the application of multicompartment micelle in the field of drug delivery.

We change the solvent quality by varying the interactions between solvent and hydrophobic block systematically, that is, decreasing the DPD repulsion parameters a_{AS} from 50 to 30 and a_{CS} from 120 to 30. It was found that with the decrease of a_{AS} or a_{CS} the multicompartment micelle has a morphological transition from compact wormlike structure to elongate wormlike structure, and finally to discrete spherical or "hamburger" micelles, as shown in Fig. 6. In fact, this transition is the gradual dissolution of the corresponding compartments in micelle with decreasing the degree of incompatibility between solvent and hydrophobic block. It is interesting that the morphological change is similar to the reverse course of the fusion process when wormlike multicompartment micelle was formed [22]. The morphologies with different a_{AS} or a_{CS} are listed in Table 1. Obviously, the transitions of micelle formed from model II take place at larger values of a_{AS} or a_{CS} than that of model I, which means the dendritic structure in hydrophilic block may enhance the stability of the multicompartment micelle when the solvent quality is changed. This is caused by the fact that dendritic structure can form more compact hydrophilic shell outside the multicompartment micelle.

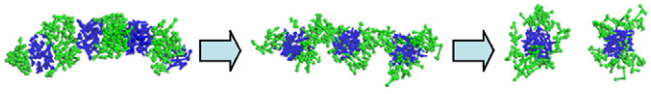

Fig. 6. The snapshots of morphological transition of multicompartment micelle with the change of a_{AS} or a_{CS}.

To quantitatively understand the difference in structural change of the micelles for models I and II with decreasing the value of a_{AS} or a_{CS}, the conservative energy between different parts of system was estimated from the conservative force as follows [34,35]:

$$U^{C}_{i<j} = \sum_{i<j} \frac{1}{2} a_{ij} \left(r_c - r_{ij}\right)^2 \tag{11}$$

Since a_{ij} is same in models I and II, the comparison of conservative energy may give a rough estimation of the difference in distance between particles in different models. We studied two parts of the conservative energy: one is that between block A (U^{C}_{AA}) when a_{AS} is changed, and the other is that between block C (U^{C}_{CC}) when a_{CS} is changed. Figs. 7 and 8 show the energy as a function of the value of a_{AS} or a_{CS}.

From Fig. 7, we can see that the conservative energy between block A was decreased with the decrease of a_{AS}. Considering that the conservative force in DPD is soft interaction and only validates within the cutoff radius r_c, the decrease of energy means that the distance between block A is increased correspondingly and the compartments formed from block A in micelle become elongate, as depicted in the morphological transition in Fig. 6. When a_{AS} is larger than 40 or less than 33, the conservative energy between block A in model I is similar to that in model II. However, the value of energy in model II is larger than that in model I by about 5% when a_{AS} is in the range of 33–40. These results indicate that dendritic structure in hydrophilic block has little effect on

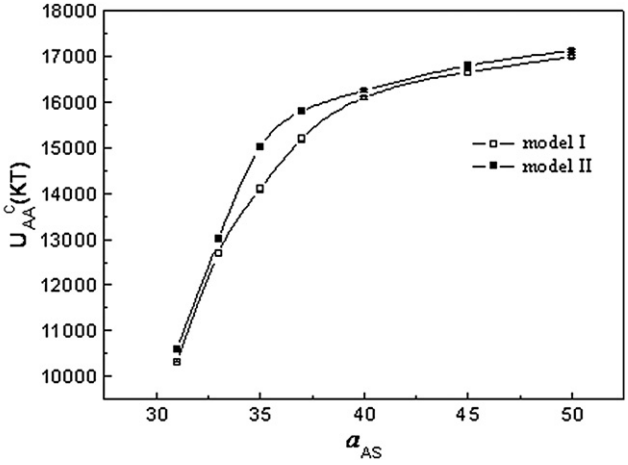

Fig. 7. The conservative energy between block A for the two models as a function of the interaction between block A and solvent.

Table 1
The morphologies of multicompartment micelle with the change of a_{AS} or a_{CS}

a_{AS}	50	40	37	35	33	31
Model I	Compact[a]	Compact	Elongate	Elongate	Discrete	Discrete
Model II	Compact	Compact	Compact	Compact	Elongate	Discrete
a_{CS}	120	50	43	40	37	33
Model I	Compact	Compact	Elongate	Elongate	Discrete	Discrete
Model II	Compact	Compact	Compact	Elongate	Elongate	Discrete

[a] Compact, elongate, and discrete represent compact wormlike micelle, elongate wormlike micelle, and discrete micelle, respectively.

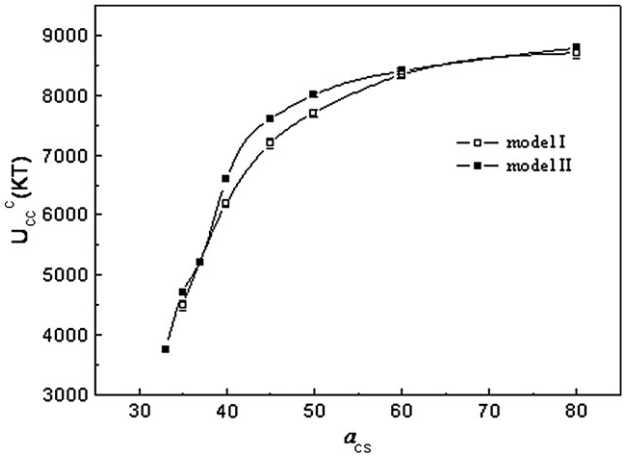

Fig. 8. The conservative energy between block C for the two models as a function of the interaction between block C and solvent.

the structure of hydrophobic core on the condition of compact wormlike micelle or discrete micelle, while this structure may induce more compact core than that of linear block when the corresponding compartment become loose with the change of solvent quality. Similar behavior is also observed when a_{CS} is varied as shown in Fig. 8.

Furthermore, the mean-square radius of gyration $\langle R_g^2 \rangle$ as a function of a_{AS} was calculated as an example to further understand the response to the solvent quality of two models. From the curves in Fig. 9, it can be seen that with the decrease of a_{AS} from 50 $\langle R_g^2 \rangle$ of the copolymer chains has a slight increase, corresponding to the appearance of the elongate wormlike micelles. When the discrete micelles were formed with further decreasing a_{AS}, the copolymer chains began to contract and $\langle R_g^2 \rangle$ was decreased. As expected, without shielded by the hydrophilic block with dendritic structure, the increment of $\langle R_g^2 \rangle$ in model I is larger than that in model II when the elongate wormlike micelles were formed, which is consistent with the difference in the conservative energy between block A as shown in Fig. 7.

The above simulations show that the dendritic structure influences the structural response of multicompartment micelle

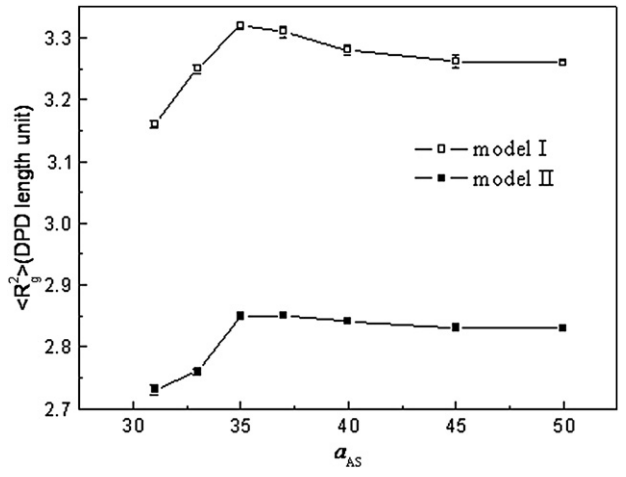

Fig. 9. The mean-square radius of gyration for the two models as a function of the interaction between block A and solvent.

to the change of solvent quality. When the dendritic part is in hydrophilic block, the micelle especially the hydrophobic core is more stable. Thus, the structure of building block copolymer may be chosen on the basis of the quality of target-circumstance where the micelle is used for drug release.

4. Conclusions

In this work, the effect of dendritic structure on the formation as well as the response to the solvent quality of multicompartment micelles was studied in star-dendritic triblock copolymers by DPD method. The results indicate that the dendritic structure not only influences the detailed structure of the hydrophobic core of multicompartment micelles, but also the corresponding formation speed. In addition, dendritic structure in hydrophilic block can enhance the stability of micelle when the solvent quality was changed. Thus, choosing different dendritic block in building copolymers can generate various multicompartment micelles with different response to the solvent quality. This may provide information for the complete understanding of multicompartment micelles, as well as the design and application of this novel kind of micelles in the field of drug delivery.

Acknowledgements

The financial support of the NSFC (20676004, 20725622) and the Young Scholars Fund of Beijing University of Chemical Technology (QN0701) are greatly appreciated.

References

[1] Discher DE, Eisenberg A. Science 2002;297:967–73.
[2] Bucknall DG, Anderson HL. Science 2003;302:1904–5.
[3] Laschewsky A. Curr Opin Colloid Interface Sci 2003;8:274–81.
[4] Lutz J-F, Laschewsky A. Macromol Chem Phys 2005;206:813–7.
[5] Li Z, Kesselman E, Talmon Y, Hillmyer MA, Lodge TP. Science 2004; 306:98–101.
[6] Li Z, Hillmyer MA, Lodge TP. Macromolecules 2006;39:765–71.
[7] Kubowicz S, Baussard J-F, Lutz J-F, Thünemann AF, von Berlepsch H, Laschewsky A. Angew Chem Int Ed 2005;44:5262–5.
[8] Kubowicz S, Thünemann AF, Weberskirch R, Möhwald H. Langmuir 2005;21:7214–9.
[9] Thünemann AF, Kubowicz S, von Berlepsch H, Möhwald H. Langmuir 2006;22:2506–10.
[10] Li Z, Hillmyer MA, Lodge TP. Nano Lett 2006;6:1245–9.
[11] Li Z, Hillmyer MA, Lodge TP. Langmuir 2006;22:9409–17.
[12] Zhong C, Liu D. Macromol Theory Simul 2007;16:141–57.
[13] Tomalia DA, Majoros I. Polym Rev 2003;43:411–7.
[14] Tomalia DA. Dendrimeric supramolecular and supramacromolecular assemblies. 2nd ed. In: Ciferri A, editor. Supramolecular polymers. Boca Raton, FL: CRC Press Taylor & Francis; 2005 [chapter 7].
[15] Percec V, Glodde M, Bera TK, Miura Y, Shiyanovskaya I, Singer KD, et al. Nature 2002;419:384–7.
[16] Tomalia DA. Prog Polym Sci 2005;30:294–324.
[17] Liu D, Zhong C. Macromol Rapid Commun 2005;26:1960–4.
[18] Yan DY, Zhou YF, Hou J. Science 2004;303:65–7.
[19] Mao J, Ni P, Mai Y, Yan D. Langmuir 2007;23:5127–34.
[20] Pierleoni C, Addison C, Hansen J-P, Krakoviack V. Phys Rev Lett 2006; 96:128302.
[21] Arai N, Yasuoka K, Masubuchi Y. J Chem Phys 2007;126:244905.

[22] Xia J, Zhong C. Macromol Rapid Commun 2006;27:1110–4.
[23] Xu Y, Feng J, Liu H, Hu Y. Mol Simul 2006;32:375–83.
[24] Sheng Y-J, Nung C-H, Tsao H-K. J Phys Chem B 2006;110:21643–50.
[25] Chou S-H, Tsao H-K, Sheng Y-J. J Chem Phys 2006;125:194903.
[26] Liu D, Zhong C. Macromol Rapid Commun 2007;28:292–7.
[27] You L-Y, Chen L-J, Qian H-J, Lu Z-Y. Macromolecules 2007;40:5222–7.
[28] Hoogerbrugge PJ, Koelman JMVA. Europhys Lett 1992;19:155–60.
[29] Koelman JMVA, Hoogerbrugge PJ. Europhys Lett 1993;21:363–8.
[30] Groot RD, Warren PB. J Chem Phys 1997;107:4423–35.
[31] Chung JE, Yokoyama M, Okano T. J Controlled Release 2000;65:93–103.
[32] Rapoport N, Pitt WG, Sun H, Nelson JL. J Controlled Release 2003;91:85–95.
[33] Gillies ER, Jonsson TB, Fréchet JMJ. J Am Chem Soc 2004;126:11936–43.
[34] Yamamoto S, Maruyama Y, Hyodo S. J Chem Phys 2002;116:5842–9.
[35] Yamamoto S, Hyodo S. J Chem Phys 2005;122:204907.