Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Polymer 46 (2005) 11962–11968

polymer

www.elsevier.com/locate/polymer

Long-tailed spherical aggregates formed from ABA triblock copolymer by changing the properties of selective solvent

Jintao Zhu, Haizhou Yu, Wei Jiang *

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of the Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 11 May 2005; received in revised form 28 August 2005; accepted 3 October 2005
Available online 26 October 2005

Abstract

A convenient method of tuning aggregate morphologies from amphiphilic block copolymer by adding second selective solvent is introduced in this paper. Some novel aggregate morphologies, i.e. hierarchical vesicles (and compound spherical micelles) with one or more tails, were formed by introducing a second selective solvent for core-forming blocks into the poly(4-vinyl pyridine)-*b*-polystyrene-*b*-poly(4-vinyl pyridine) ABA amphiphilic block copolymer/co-solvent/water systems. Addition of selective solvent (toluene) for core-forming blocks (PS blocks) has significant effect on the aggregate morphologies from the amphiphilic triblock copolymer. The aggregate morphologies changed from spheres to rods, long tailed solid large compound spheres, and to long tailed hierarchical vesicles by adding 0.5, 10 and 30 wt% of toluene to the organic solvent, respectively. There exists an aggregate morphological transition of the long tailed hierarchical vesicles to long tailed solid spheres by decreasing the content of toluene in the organic solvent mixture. The tails disappeared, and irregular vesicular and spherical structures were formed when the toluene content was 20 wt%. The toluene addition is expected to increase the stretching of the core-forming blocks (PS), and to modify the interfacial tension of core–corona interface, which are the main reasons for the aggregate morphology transition. To the best of our knowledge, these tailed vesicles and spherical morphologies have not been found in block copolymer aggregates system up to now.

Keywords: Amphiphilic block copolymer; Micelles; Selective solvent

1. Introduction

It has been known for many years that block copolymers can self-assemble into large variety of aggregate morphologies in selective media [1–8]. These morphologies include spheres, rods, vesicles, lamellae, large compound micelles, large compound vesicles, tubular, a hexagonally packed hollow hoop structure (the 'HHH' structure), onions, a bowl-shaped, a ring-shaped structure and several others [1,4,9–21]. These structures are of intrinsic interest, and receiving much attention due to their potential application in cosmetics, drug delivery, electronics, pollution control and separation, among others [1,22–27].

The aggregate morphology assumed by an amphiphile results from a balance of three contributions to the free energy: chain stretching in the core, the interfacial energy, and the repulsion between coronal chains [13,28,29]. Thus, aggregate morphologies can be tuned by many factors, such as relative block length, ion type and content, common solvent properties, temperature, homopolymer addition etc. all of which influence one or more of the free energy contributions [1,28,30–34]. Previous studies have found many ways for the aggregate morphology controlling. For the highly asymmetric amphiphilic block copolymer, the insoluble core-forming blocks are much longer than the soluble corona-forming blocks. The aggregates of this type were called 'crew-cut' micelles [1,9,13]. Due to the fact that the insoluble blocks comprise a large fraction of the total chains, the aggregates are usually prepared by indirect method [1,13,35]. The procedures involve firstly dissolving copolymers in a common solvent, such as dimethylformamide (DMF), and then adding water, a non-solvent for polystyrene (PS) blocks, to the copolymer solution to induce the aggregation of the PS segments. Literatures have reported that aggregate morphologies can be tuned by changing the solvent properties [36–38]. However, most previous studies were focused on the variation of common solvent and precipitant properties, and little was known about changing the selective solvent properties by addition a selective solvent

---

* Corresponding author. Tel.: +86 431 5262151; fax: +86 431 5262126.
E-mail address: wjiang@ciac.jl.cn (W. Jiang).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.043

for core-forming blocks to copolymer/co-solvent/water system [39]. The core-forming blocks are expected to be stretched, and the free energy of the core–corona interface should be modified by adding a selective solvent for these blocks to the micellization medium. Therefore, aggregate morphological transition would occur accordingly.

In this paper, we select toluene as second selective solvent for the ABA amphiphilic block copolymer/co-solvent/water systems. The addition of the toluene to the micellization system is expected to increase the stretching of the core-forming blocks, and to modify the interfacial energy of the core–corona interface, which can induce the aggregate morphology transition. It has been found that the addition of selective solvent (toluene) for core-forming blocks (PS blocks) has significant effect on the aggregate morphologies of the amphiphilic triblock copolymer. The aggregate morphologies changed from spheres to rods, tailed solid large compound spherical micelles, and to tailed hierarchical vesicles with increasing the toluene content. To the best of our knowledge, these tailed vesicles and spherical morphologies have not been found in block copolymer aggregates system up to now.

2. Experimental section

2.1. Materials and aggregate preparation method

The copolymers used in this study were two triblock copolymers of poly(4-vinyl pyridine)-*b*-polystyrene-*b*-poly(4-vinyl pyridine) (P4VP-*b*-PS-*b*-P4VP) which were purchased from Polymer Source Inc. Canada. The detailed information of the two triblock copolymers is listed in Table 1. The distinction of the two type of the ABA triblock copolymer is the difference of the middle block (PS) length.

To prepare the P4VP-*b*-PS-*b*-P4VP micelles, the triblock copolymers were firstly dissolved in DMF/toluene mixtures of various compositions, ranging from 30 to 0 wt% of toluene. When the toluene content was beyond 30 wt% in the organic solvent mixtures and the water content reached to that for micellization, macrophase separation between oil and water would occur. Under this condition, the aggregates cannot be isolated into water by dialysis. The initial copolymer concentrations were kept for 1 wt% in organic solvent for all of the samples. The solutions were kept stirring overnight to make the copolymer dissolve into the solvent to form a homogeneous solution. Then, a predetermined amount of deionized water (15 wt% of the solution) was added slowly (ca. 0.2 wt%/30 s) into the copolymer/DMF/toluene solution with stirring. The appearance of blue tint or turbidity in the solution indicated the initiation of micellization of the block copolymers. After the water content reached 15 wt%, the solution were kept stirring for 2 h. Then, a large amount of water (ca. 600 wt%) was added to the resulting solution in order to quench the aggregate morphologies. At this water content range, the structures of the aggregates become kinetically locked over the experimental time scale [13,37]. Subsequently, the resulting micellar solution was placed in a dialysis tube (DM27 EI9004, USA; cut off: 12,000–14,000) and dialyzed against deionized water for a few days to remove the organic solvent from the solution. During the dialysis process, the pH of the distilled water was adjusted to 4 by hydrochloric acid (HCl) to keep the colloid solutions from precipitating [14,40]. The aggregate morphologies were stable during the dialysis process and after the dialysis.

Table 1
Molecular characteristics of the triblock copolymer used in this study

Triblock copolymer	M_n	PDI	P4VP volume fraction	Micelle structure in pure DMF
P1: P4VP$_{43}$-*b*-PS$_{260}$-*b*-P4VP$_{43}$	4500–27,000–4500	1.09	25%	Spheres
P2: P4VP$_{43}$-*b*-PS$_{366}$-*b*-P4VP$_{43}$	4500–38,000–4500	1.10	19%	Spheres with some short rods

2.2. Transmission electron microscopy (TEM) and atomic force microscope (AFM)

The resulting aggregate morphologies were visualized with a regular TEM and AFM. TEM was performed on a JEOL JEM-1011transmission electron microscope operated at an acceleration voltage of 100 kV. The dialyzed colloidal solutions were diluted by a factor of 10–20 in order to prepare the TEM samples. A drop of the very dilute solution was placed onto TEM copper grid covered by a polymer support film precoated with carbon thin film. After 15 min, excess solution was blotted away using a strip of filter paper. The samples were allowed to dry in air and at room temperature for 1 day before observation. AFM measurement (SPA 300 atomic force microscopy) was operated with an SPI3800 controller (Seiko instruments Industry Co. Ltd) at the tapping mode. The cantilever used was fabricated from silicon with a spring constant of 2 N/m and a resonance frequency of 70 kHz. To prepare the samples for AFM, a few drops of the very dilute solution after dialysis were spin-coated onto the freshly cleaved mica substrates to prepare the AFM samples. All of the samples were dried in air and at room temperature for 1 day before observation. The experiments were all performed in air and at room temperature.

3. Results and discussion

From the AFM height images and corresponding TEM images of Fig. 1, we can see that the constituent of the two types of P4VP-*b*-PS-*b*-P4VP triblock copolymers individually tend to form spheres (Fig. 1(A) and (A$'$), diameter ca. 30 nm) and spheres with small fraction of short rods (Fig. 1(B) and (B$'$), diameter of spheres ca. 34 nm, short rods ca. 33 nm) in DMF/water mixtures. The aggregates possess core–shell structure and belong to the ‘crew-cut’ aggregate morphology type. For this block copolymer system, aggregates involve looping of the hydrophobic PS middle block into the core of the aggregates and tailing two hydrophilic P4VP end blocks to form the corona of aggregates (Fig. 2(A)) [11,14,41]. The copolymers in common solvent were in a single molecule form. After addition of water, the solubility of PS in solvent mixture

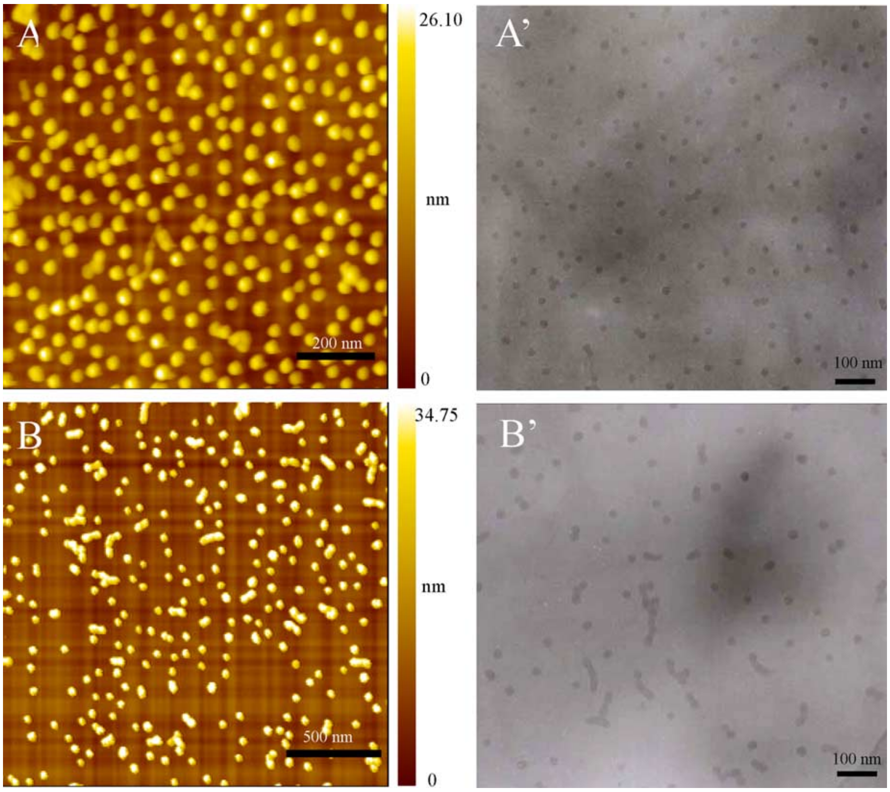

Fig. 1. AFM height images (A and B) and corresponding TEM images (A′ and B′) of aggregate morphologies formed from 1 wt% P4VP-*b*-PS-*b*-P4VP in pure DMF (A and A′). P1: $P4VP_{43}$-*b*-PS_{260}-*b*-$P4VP_{43}$; (B and B′) P2: $P4VP_{43}$-*b*-PS_{366}-*b*-$P4VP_{43}$. All solutions were at 15 wt% water content.

was decreased. Critical water content (CWC) was required for initiating the copolymer self-assembly [13,28]. Self-assembly of the triblock copolymer in solution occurred at a water content of ca. 5 wt% in DMF in this system. After the DMF was dialyzed from the solution, the aggregates were stable, being kinetically frozen in by the formation of a high T_g of the PS core, as previously reported [1,42] The micellar morphologies exhibited sphere-to-rod transition, as a result of the increased volume fraction of the core-forming blocks. Similar results have been observed in diblock copolymer system by Eisenberg's group [43]. In this study, we are interested in studying the aggregate morphology transition by adding a second selective solvent (i.e. toluene) to the triblock copolymer/co-solvent/water system.

Fig. 3 shows the TEM images of aggregate morphologies of P1 formed by adding different amount of toluene into the systems. From these images, we can clearly see that the aggregate morphology is in strong dependence on the toluene content in the organic solvent mixtures. The aggregate morphologies were irregular spheres and vesicles (Fig. 3(D)), irregular large spheres (Fig. 3(C)), vesicles and long rods (Fig. 3(B)), to vesicles in line and large compound rods (Fig. 3(A)) when the content of the toluene in organic solvent mixtures varied from 2 to 30 wt%. The vesicular nature was

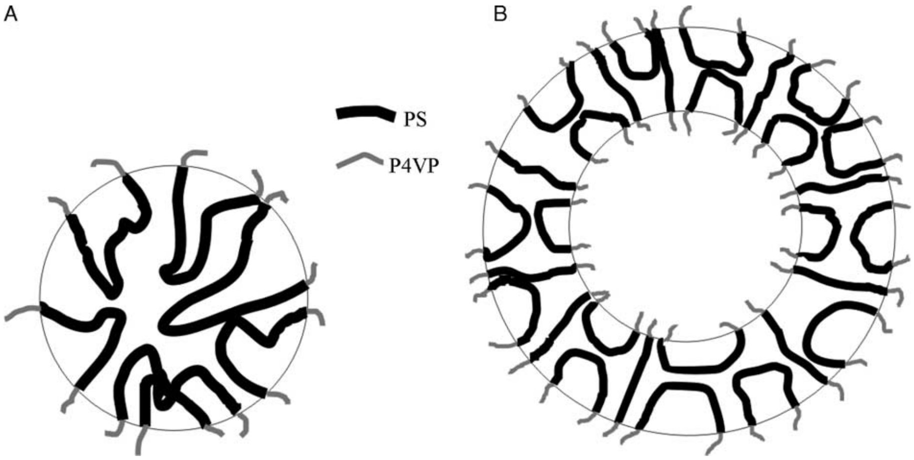

Fig. 2. Scheme representation of P4VP-*b*-PS-*b*-P4VP 'crew-cut' aggregates in aqueous solution (A, represent spheres or rods; B, represent vesicles or tubules).

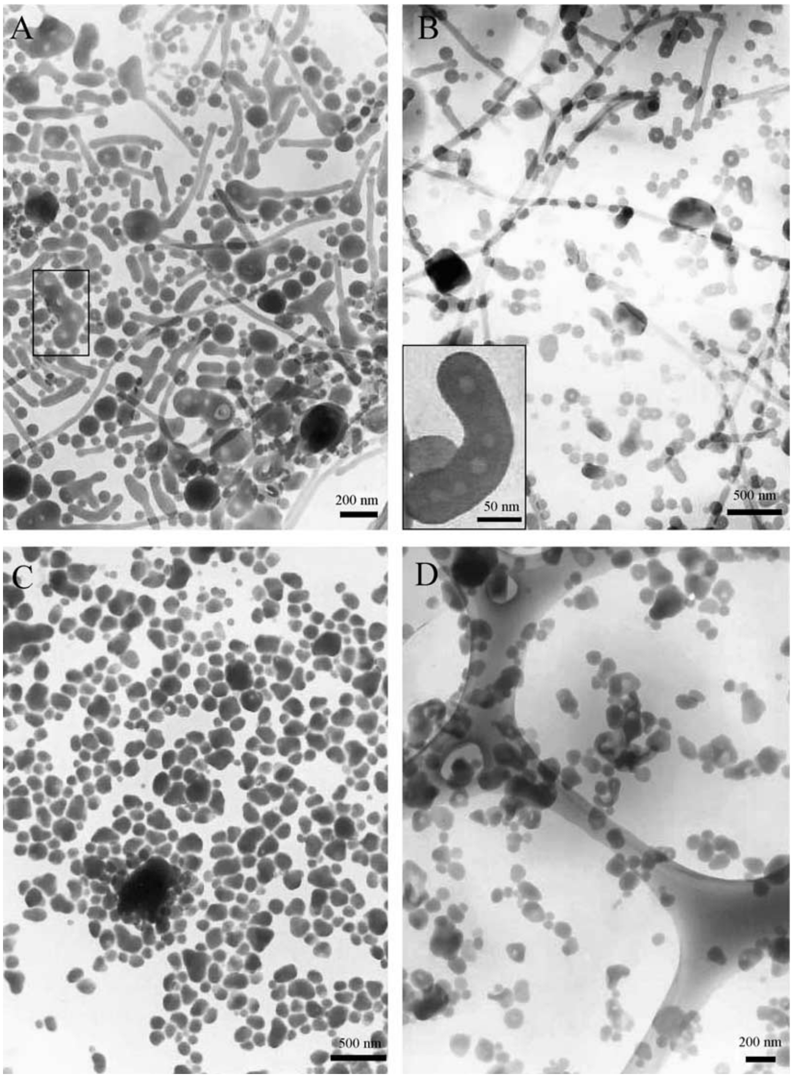

Fig. 3. TEM images of aggregate morphologies formed from 1 wt% $P4VP_{43}$-*b*-PS_{260}-*b*-$P4VP_{43}$ in DMF/toluene mixtures with the weight ratio of DMF/toluene: A, 70/30; B, 80/20; C, 95/5; D, 98/2. All solutions were at 15 wt% water content.

evidenced from a higher transmission in the center of the aggregates than around their periphery, coupled with the AFM height measurements which show the aggregates to be spherical [14,44]. In the vesicular structures, the insoluble blocks constituted the vesicle wall, while the chains of soluble block extended from the inner and outer surfaces into the solvent system (as can be seen in Fig. 2(B)) [14]. Therefore, the aggregates were very stable after dialysis because of the strong interactions between the P4VP blocks or the aqueous corona-forming P4VP blocks and the water (under the pH of 4.8) [14,40], as well as the glassy nature of the PS-cores at room temperature [1,42]. The striking thing was that the addition of a selective solvent (toluene) for the core-forming blocks had a dramatic impact on the micellar morphology, as shown in Fig. 3. The aggregate morphology changed to vesicle and large spheres by adding only 2% of toluene to the common solvent (Fig. 3(D)). The other interesting thing was that some vesicles array in-line, as could be seen from in Fig. 3(A) (in the box) and Fig. 3(B) (in the box). This structure might result from the fusion of small single vesicles.

Correspondingly, addition of a selective solvent for the core-forming blocks also had a significant effect on the micellar morphology for P2, as shown in Fig. 4. Fig. 4(A) and (C) show the long tailed spherical structures formed from the triblock copolymer (P2) in DMF/toluene/water mixtures. The structure is composed of spherical structures (solid spherical or ellipsoidal aggregates, see Fig. 4(C); or hollow spheres, i.e. hierarchical vesicles, see Fig. 4(A)) with one or more tails (rods). The tailed hollow spherical structures (Fig. 4(A)) are compound vesicles (hierarchical structures), which can be confirmed from AFM height image that the surface of the spherical structure is flat (not porous, as can be seen from Fig. 5, arrow B). The structure bears some resemblance to that of aggregated soap bubbles, and their outer and inner surfaces must be hydrophilic because of the presence of the short P4VP chains. Occasionally, regular vesicles can also be found in this system, which can be seen from the arrow in Fig. 4(A). The most striking feature is that the hollow structure size in the hierarchical vesicles is nearly the same (ca. 15 nm). When the volume fraction of toluene in

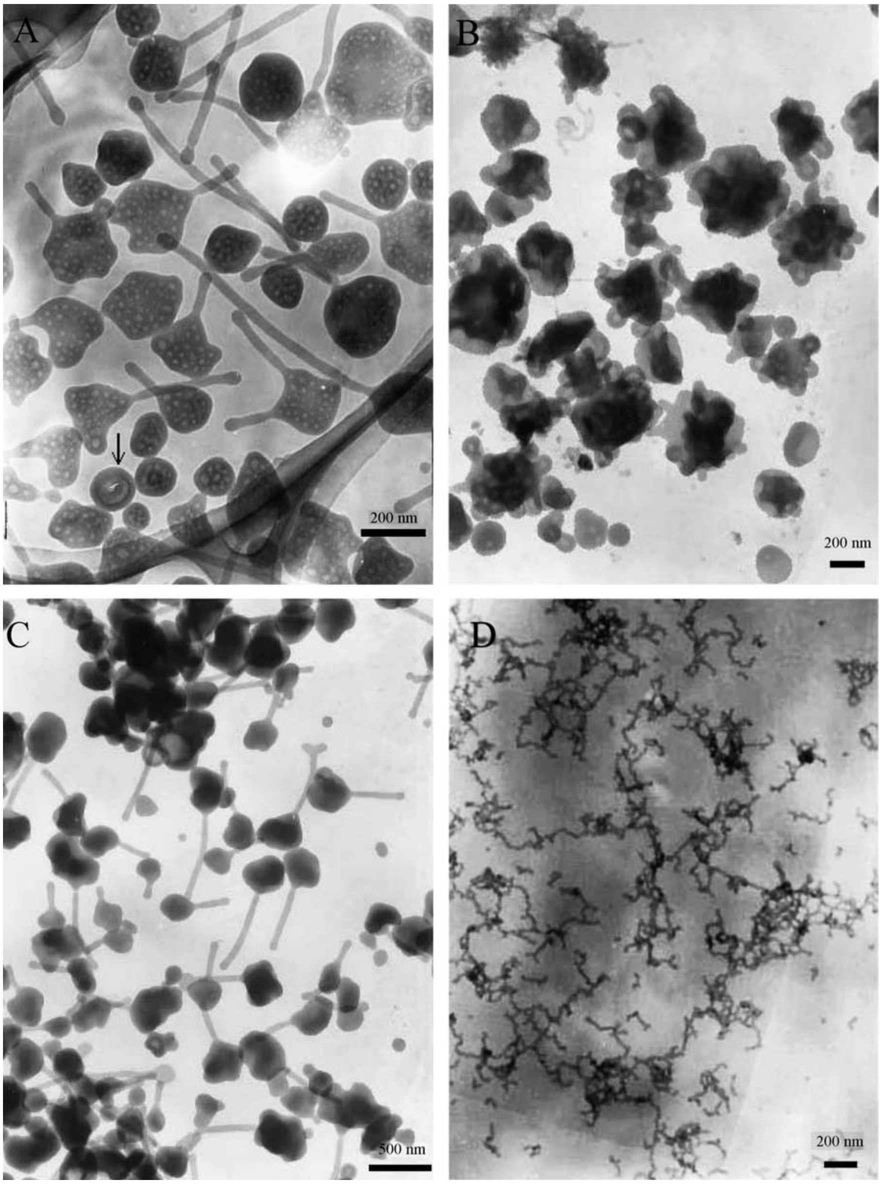

Fig. 4. TEM images of aggregate morphologies formed from 1 wt% P4VP$_{43}$-*b*-PS$_{366}$-*b*-P4VP$_{43}$ in DMF/toluene mixtures with the weight ratio of DMF/toluene: A, 70/30; B, 80/20; C, 90/10; D, 99.5/0.5. All solutions were at 15 wt% water content.

the organic solvent was decreased, the spherical structure became solid, leaving the long tails attached. End-caps existed at the bottom of the tails, as can be clearly seen from the TEM images (Fig. 4(A) and (C)). There exists a morphologies transition of the long tailed hierarchical vesicles to long tailed solid spheres by decreasing the volume fraction of toluene in organic solvent. The tails disappeared and irregular vesicular and spherical structures (as can be seen from Fig. 4(B)) were formed when the toluene content was 20 wt%. The aggregate morphologies became long rods when the toluene content in the organic solvent mixtures was only 0.5 wt% (Fig. 4(D)).

As mentioned above, the aggregate morphologies of the both two type triblock copolymer changed to vesicles, rods, large compound spheres, and tailed hierarchical vesicles and large spheres when we increased the volume fraction of the toluene in the organic solvent mixtures. It is clear that the aggregate morphology is very sensitive to the addition of selective solvent for the core-forming blocks. To understand the morphology transition mechanism for the addition of toluene, it must be reminded that the solubility parameter (δ) of toluene (18.2 MPa)$^{1/2}$ is much closer to that of PS (16.6–20.2 MPa)$^{1/2}$ and is lower than that of DMF (24.8 MPa)$^{1/2}$ (Table 2) [45,46]. Thus the PS chains interact more strongly with toluene than with DMF. The interactions between the amphiphilic copolymer chains and the solvent have been found to influence the dimensions of both the aggregates and the corona [29,44]. In the early stages of micellization by addition of water, the PS cores of the aggregates are usually swollen by the common solvent. As the water content increases, the concentration of the unimers reduces, and the common solvent is gradually removed from the micelle core, which reduces the mobility of the chains [1,9]. The lower degree of swelling of

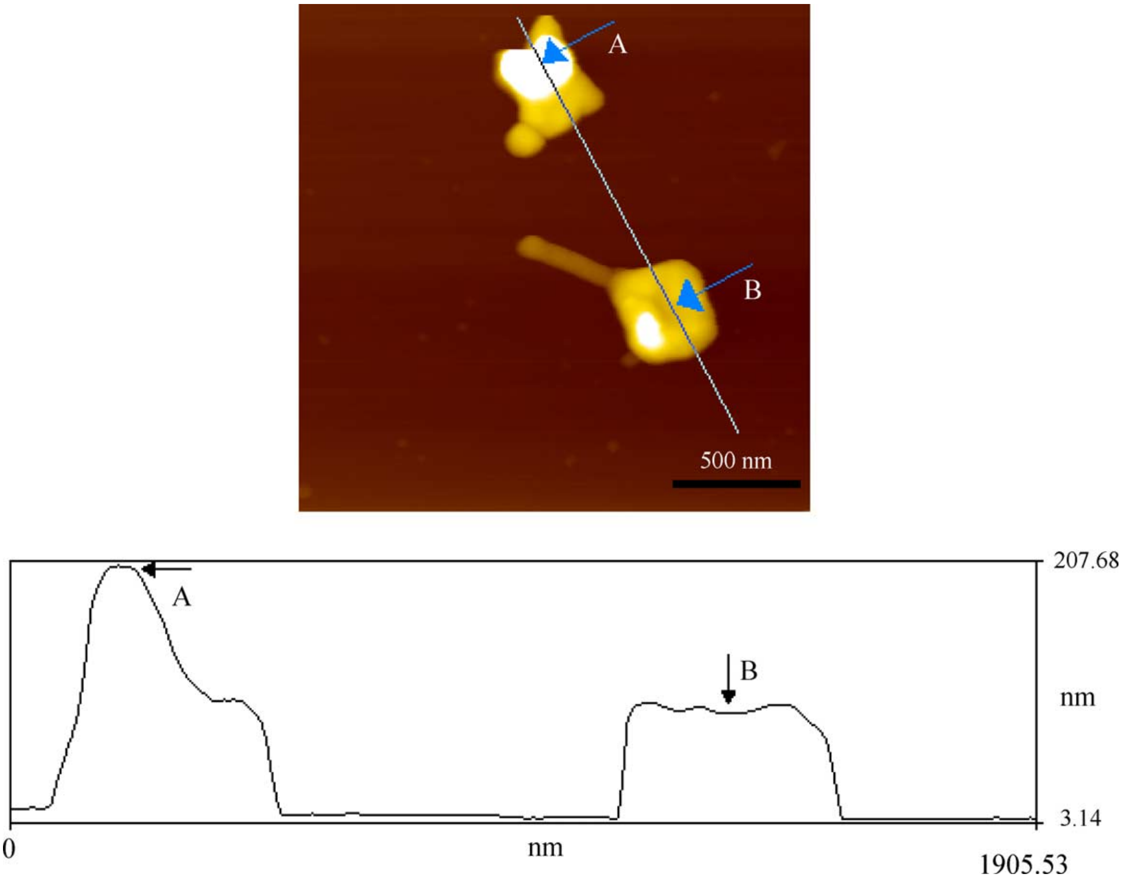

Fig. 5. AFM height images of the tailed hierarchical vesicular structures obtained from 1 wt% $P4VP_{43}$-*b*-PS_{366}-*b*-$P4VP_{43}$ in DMF/toluene mixtures (70/30, wt/wt), corresponding to Fig. 4(A) (at 15 wt% water content).

the PS in pure DMF than in DMF/toluene mixtures reflects their solubility parameter values. Macroscopically, the system is then similar to an emulsion. At the same time, the toluene-rich phase can accumulate within the PS core of the micelles, whose volume fraction is thus increased. Conformation and entropy of the PS blocks also change. Therefore, dimensions of the aggregates cores, at the onset of micellization, must be much larger in DMF/toluene mixtures and their mixtures with water than that in pure DMF and its mixture with water. As a result, the degree of stretching of PS chains has to increase correspondingly, which is entropically unfavorable. The penalty for the larger stretching of PS chains in the core forces the aggregates to adopt rods, large compound spheres and vesicle or other morphologies (in DMF/toluene mixtures) in order to decrease the free energy [28,29]. The situation is complicated further by the demixtion of the mixture of solvents. At some point, the mobility of the PS chains in the core is strongly decreased as water is substituted for the organic solvents, and the morphology of the micelles is kinetically frozen after the large amount water (ca. 600 wt%) addition and the dialysis process.

On the other hand, the interfacial tension of the core and corona solvent was modified when the pure DMF was changed to DMF/toluene mixtures, which was another reason for the morphological transition. Thus, the free energy changes via the core-forming chains stretching and interfacial tension modification was the main reason for the morphological transition by introducing a second selective solvent (toluene) to the copolymer/co-solvent system.

A remarkable aspect disclosed by TEM imaging of the polymeric aggregates is the coexistence of disparate morphologies for a single copolymer. For instance, there are vesicles and rods with different sizes and shapes, spheres, etc. in Fig. 3(A) and (B). This morphology coexisting phenomena is an indicative of nonergodic systems, as has been reported in diblock copolymer systems [4,28,47]. It has been proposed that the polydispersity inherent in macromolecular samples is one factor at least partially contribute to the coexistence behavior [28]. It is noteworthy that the individual objects formed in water by the block copolymer are practically isolated, and the coexistence most likely represents a nonequilibrium state (metastable state) [11], that is, the structure initially formed upon dissolution will likely be locked in. The crucial insight is

Table 2
Polymer/solvent solubility parameter (δ) [45,46]

Polymer/solvent	Solubility parameter $[MPa]^{1/2}$
PS	16.6–20.2
P4VP	9.9
Toluene	18.2
DMF	24.8
H_2O	46.7

that slow kinetics associated with the high molecular masses and prohibitively low chain exchange between the micelles may greatly hinder structural evolution toward global equilibrium after the genesis of the structures [17,47].

4. Summary and conclusion

Some novel aggregate morphologies, i.e. hierarchical vesicles (and compound spheres) with one or more tails, linear vesicles were formed by introducing a second selective solvent to the P4VP-*b*-PS-*b*-P4VP ABA amphiphilic block copolymer/co-solvent/water system. Addition of selective solvent for core-forming blocks has a significant impact on the aggregate morphologies. The addition of toluene to the micellization system is expected to increase the stretching of the core-forming blocks (PS) and to modify the interfacial tension of core–corona interface, which is the main reason for the aggregate morphology transition. To the best of our knowledge, these tailed vesicles and spherical morphologies have not been found in copolymer aggregates system. It is expected that the addition of selective solvent for core-forming blocks is also valuable in other similar micellar systems, such as copolymer/dioxane/water, copolymer/THF/water or copolymer/water systems.

Acknowledgements

This work was supported by the financial support of the General Program (20274047) and the Major Program (20490220) of National Natural Science Foundation of China (NSFC), the Project (KJCX2-SW-H07) of the Chinese Academy of Sciences, the Fund for distinguished youth of Jilin Province, and the 973 program of MOST (No.2003CB615600).

References

[1] Zhang LF, Eisenberg A. Science 1995;268:1728.
[2] Booth C, Attwood D. Macromol Rapid Commun 2000;21:501.
[3] Kukula H, Schlaad H, Antonietti M, Föerster S. J Am Chem Soc 2002;124:1658.
[4] Jain S, Bates FS. Science 2003;300:460.
[5] Zhang W, Shi L, An Y, Gao L, Wu K, Ma R. Macromolecules 2004;37:2551.
[6] Raez J, Manners I, Winnik MA. J Am Chem Soc 2002;124:10381.
[7] Riess G. Prog Polym Sci 2003;28:1107.
[8] Nuopponen M, Ojala J, Tenhu H. Polymer 2004;45:3643.
[9] Cameron NS, Corbierre MK, Eisenberg A. Can J Chem 1999;77:1311.
[10] Ravi P, Dai S, Hong KM, Tam KC, Gan LH. Polymer 2005;46:4714.
[11] Zhu JT, Jiang Y, Liang HJ, Jiang W. J Phys Chem B 2005;109:8619.
[12] Zhang LF, Bartele C, Yu Y, Shen HW, Eiserberg A. Phys Rev Lett 1997;79:503.
[13] Burke SE, Eisenberg A. Polymer 2001;42:9111.
[14] Zhu JT, Liao YG, Jiang W. Langmuir 2004;20:3809.
[15] Liu GJ, Li Z, Yan XH. Polymer 2003;44:7721.
[16] Liu Y, Wang LX, Pan CY. Polymer 2002;43:7063.
[17] Li Z, Kesselman E, Talmon Y, Hillmyer MA, Lodge TP. Science 2004;306:98.
[18] Yu K, Zhang LF, Eisenberg A. Langmuir 1996;12:5980.
[19] Du JZ, Chen YM, Zhang YH, Han CC, Fischer K, Schmidt M. J Am Chem Soc 2003;125:14710.
[20] Pochan DJ, Chen Z, Cui H, Hales K, Qi K, Wooley KL. Science 2004;306:94.
[21] Zhou Z, Li Z, Ren Y, Hillmyer MA, Lodge TP. J Am Chem Soc 2003;125:10182.
[22] Qiu XP, Liu GJ. Polymer 2004;45:7203.
[23] Massey J, Power KN, Manners I, Winnik MA. J Am Chem Soc 1998;120:9533.
[24] Savic R, Luo LB, Eisenberg A. Science 2003;300:615.
[25] Rosler A, Vandermeuler GWM, Klok HA. Adv Drug Deliv Rev 2001;53:95.
[26] Liu T, Kim K, Hsiao RS, Chu B. Polymer 2004;45:7989.
[27] Chan YN, Lu XL, Chen EQ, Mi YL. Polymer 2004;45:3465.
[28] Zhang LF, Eisenberg A. Polym Adv Technol 1999;9:677.
[29] Zhang LF, Eisenberg A. Macromolecules 1999;32:2239.
[30] Yu G, Eisenberg A. Macromolecules 1998;31:5546.
[31] Xu JT, Jin W, Liang GD, Fan ZQ. Polymer 2005;46:1709.
[32] Zhang LF, Shen HW, Eisenberg A. Macromolecules 1997;30:1001.
[33] Lei L, Gohy J-F, Willet N, Zhang JX, Varshney S, Jérôme R. Polymer 2004;45:4375.
[34] Pinteala M, Budtova T, Epure V, Belnikevich N, Harabagiu V, Simionescu BC. Polymer 2005;46:7047.
[35] Yu K, Eisenberg A. Macromolecules 1996;29:6359.
[36] Riegel CIC, Samios D, Petzhold CL, Eisenberg A. Polymer 2003;44:2117.
[37] Yu Y, Eisenberg A. J Am Chem Soc 1997;119:8383.
[38] Yu Y, Zhang LF, Eisenberg A. Macromolecules 1998;31:1144.
[39] Lei L, Gohy J-F, Willet N, Zhang JX, Varshney S, Jérôme R. Macromolecules 2004;37:1089.
[40] Shen HW, Zhang LF, Eisenberg A. J Am Chem Soc 1999;121:2728.
[41] Yuan JJ, Ma R, Gao D, Wang YF, Cheng SY, Feng LX, et al. J Appl Polym Sci 2003;89:1017.
[42] Zhang LF, Yu K, Eisenberg A. Science 1996;272:1777.
[43] Shen HW, Eisenberg A. Macromolecules 2000;33:2561.
[44] Burke SE, Eisenberg A. Langmuir 2001;17:6705.
[45] Lide DR. CRC handbook of chemistry and physics. 77th ed. New York: CRC Press; 1996 p. 6–151.
[46] Brandrup J, Immergut EH.. 3rd ed Polymer handbook. vol. VII. New York: Wiley-Interscience; 1989 p. 526.
[47] Won YY, Brannan AK, Davis HT, Bates FS. J Phys Chem B 2002;106:3354.