

Control on the Morphology of ABA Amphiphilic Triblock Copolymer Micelles in Dioxane/Water Mixture Solvent

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Electronic Supplementary Information

Abstract This work offers a typical understanding of the factors that govern the nanostructures of poly(4-vinyl pyridine)-*b*-polystyrene-*b*-poly(4-vinyl pyridine) (P4VP-*b*-PS-*b*-P4VP) block copolymers (BCs) in dioxane/water, in which water is a selective solvent for the P4VP block. It is achieved through an investigation of the amphiphilic triblock copolymer micelles by variation of three different factors, including water content (above CWC but under the immobile concentration), temperature (ranging from 20 °C to 80 °C), and copolymer composition (low and high PS block length). Transition of bead-like micelles to vesicles is observed with the increase of water content due to the increase of interfacial energy between the copolymer and the solvent. Effect of temperature superposed on that of water content results in various morphologies, such as beads, fibers, rods, capsules, toroids, lamellae, and vesicles. The interfacial tension between the BC and the solvent increases with the increase of water content but decreases with the increase of temperature, indicating that the micellar morphologies are resulted from the competitive interplay between the temperature and the water content and always change in a direction that decreases the interfacial energy. Based on the micellar structures obtained in this work and the effects of temperature superposed on water concentration, a diagram of phase evolution of different micellar morphologies is illustrated here, covering the temperature range from 20 °C to 80 °C and the water content changing from 20 vol% to 35 vol%. For the investigation of BC composition, morphological transition of vesicle-to-fiber, for high PS length, is observed as compared with bead-to-capsule for low PS length, as the temperature changes from 20 °C to 80 °C. Our research complements the protocols to control over the morphologies and the phase diagram describing P4VP-*b*-PS-*b*-P4VP micellar nanostructures in aqueous solution.

Keywords Micelles; Morphological control; Self-assembly; Block copolymer

Citation: Gan, Y.; Wang, Z. D.; Lu, Z. X.; Shi, Y.; Tan, H. Y.; Yan, C. F. Control on the Morphology of ABA Amphiphilic Triblock Copolymer Micelles in Dioxane/Water Mixture Solvent. *Chinese J. Polym. Sci.* 2018, 36(6), 728–735.

INTRODUCTION

In nature, self-assembly is a ubiquitous process by which an organized structure spontaneously forms as a result of specific interactions among individual components (“building blocks”)^[1–5]. It is one of the fundamental driving forces for life evolution and plays an important role in the conformation of a wide range of biological structures. Understanding the intricacies of self-assembly is of ultra-importance in the development of synthetic materials with the capabilities of mimicking nature-existing architectures^[6–9]. In the past decades, studies on nanomaterials have been increasingly focused on self-assemblies, with their structures well-defined in two or three-dimensional arrays otherwise inaccessible by lithographic procedures^[10–15].

In terms of applications of self-assembly, the right synthetic building block must be found since it underlies the

formation of nanoscale patterns. Amphiphilic block copolymer (amphiphilic BC), consisting of two or more chemically distinct segments (“building blocks”) covalently bonded as a complex macromolecule, stands out for years because it offers a great platform for material construction with a high level of precision and integrating order^[16–20]. It spontaneously segregates for the large incompatibility between hydrophilic and hydrophobic moieties to achieve various functions such as delivery, catalysis, sensor, adaptation, and stimuli-responsiveness^[21–23]. The micro-separated structures of block copolymers, as well as their facile fabrication, make them an excellent family of structural units for the bottom-up synthesis of complex materials^[24–26].

The different fragments in amphiphilic BC macromolecules contribute to both types of macromolecular interactions in an aqueous system. This factor makes amphiphilic BCs self-assemble into micelles in solution for one of the blocks forming core or aggregating as a result of association of the insoluble blocks. To target the desired stable structures, researchers have aspired to exploit

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Received September 6, 2017; Accepted October 17, 2017; Published online February 28, 2018

conditions of self-assembly to create hierarchical structures. The specific morphologies of the final micelles, such as spheres, rods, fibers, toroids, vesicles, lamellae, bicontinuous structures, large compound micelles (LCMs), and many others, are resulted from a balance between three contributions to the free energy, including core-chain stretching, corona-chain repulsion, and interfacial energy^[27–29].

For assembly process of amphiphiles in solution, the micellar morphologies are frequently obtained by firstly dissolving BCs in a solvent soluble for both blocks, followed by the addition of a selective solvent good for one of the blocks but rather poor for the other (*e.g.*, water). Upon water addition to the solution, block segregation and microphase separation occur as a consequence of the BC self-assembly tendency^[30]. The physical and colloidal properties of the micellar aggregates can be tuned *via* variation of system compositions and external fields aiming at a much broader range of applications. Content of water, nature of solvent, presence of additives, and composition of the copolymer are system magnitudes, while temperature, shearing, microwave, and UV-light irradiation are external field factors^[31–35]. System magnitudes have been widely studied and reported in the literature. For example, a pH-induced micellization study of stimulus-responsive poly(glycerol monomethacrylate)-*b*-poly(2-(dimethylamino)ethyl methacrylate)-*b*-poly(2-(diethylamino)ethyl methacrylate) (GMA-DMA-DEA) triblock copolymer revealed that the “onionlike” micelles were formed, with DEA, DMA and GMA as cores, shells and coronas, respectively, upon addition of base^[36]. It was also of interest to control the composition of corona by use of hydrophilic chains such as poly(acrylic acid) (PAA) or poly(4-vinyl pyridine) (P4VP) to obtain acidic, basic, or mixed structures under appropriate pH environments^[37–39].

External fields (typically temperature and shear), presented for their easy manipulation and little interference, have been reported experimentally and computationally in previous studies by researchers^[40–44]. Typically, dynamic effects of changing water addition rate and temperature on the pathways of morphological transitions of P4VP-*b*-PS-*b*-P4VP BCs have also been proposed by Jiang's group^[45,46]. In the present work, the investigation is expanded to the effect of temperature superposed on that of water content, which is rarely reported previously, on the self-assembly of P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ block copolymer. A bead-to-vesicle transition is found with the increase of water content due to the increase of repulsion between the copolymer and solvent. However, the increase of temperature reduces the interfacial energy and has the negative interaction with the increase of water. As a result, morphologies formed at lower temperature and lower water content shift to the regime of higher temperature and higher water content. When the PS content is high, morphological transition of vesicle-to-fiber is found as compared with bead-to-capsule for BC with lower PS length. The structures of micelles were characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), and field emission scanning electron microscopy (SEM). The motivation of this work is to investigate different parameters affecting the design of BC self-assembly and to describe how

the parameters are executed in manipulating the self-assembly of BC micelles.

EXPERIMENTAL

Micelle Preparation

Triblock copolymers of poly(4-vinyl pyridine)-*b*-polystyrene-*b*-poly(4-vinyl pyridine) were purchased from Polymer Source Inc., Canada and used as received. The two BCs of P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ (PDI = 1.09) and P4VP₄₃-*b*-PS₃₆₆-*b*-P4VP₄₃ (PDI = 1.10), where the subscripts indicate the numbers of repeat units of the blocks, were selected here with the same hydrophilic P4VP but two different lengths of the hydrophobic PS units. First, 0.01 g of copolymer was dissolved in a mixed solvent (1 mL of dioxane and various contents of water depending on experimental requirement with pH values of ~7) in a 5 mL cone-like vial. The solution was kept stirring at 500 r/min for about 4 days to form the micelles (a cylindrical stirring bar was used in this study with a diameter of 5 mm and a length of 15 mm) and then quenched in a 4–5 fold excess of water to freeze the micellar morphology. Finally, the treated solution was placed in dialysis tubes and dialyzed against distilled water for a few days to remove the dioxane solvent from the solution. For the exploration of temperature effect, the micellar solution was heated in a water bath at different temperatures. The resulting solution was then quenched by a large amount of water and followed by the dialysis in deionized water.

Characterization

The turbidity was measured on a Shimadzu UV-2450 Ultraviolet-visible (UV-Vis) spectrometer in the absorbance (turbidity) mode and at $\lambda = 650$ nm, with dioxane as the reference. The solution was placed in a quartz cuvette inside UV-Vis spectrometer and stirred using a magnetic stirrer. All the experiments were performed at room temperature.

Regular TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV. For preparation of TEM samples, a drop of the micellar solution was placed onto a TEM copper grid and then the excess solution was absorbed by using a stripe of filter paper. The samples were dried in atmosphere at room temperature for 1 day before observation.

For the measurement of hydrodynamic radius (R_h), dynamic light scattering (DLS) was conducted on a multi-angle light scattering (MALS) instrument with a digital correlator (QELS [690 nm]). The micelle solutions were filtered through a 450 nm Millipore filter before transferred into the clean scintillation vial. All the DLS measurements were carried out at 90° scattering angle and at room temperature.

SEM was performed on the XL 30 E-SEM (FEG, Micron FEI PHILIPS) operated at an acceleration voltage of 20 kV. Before micelle loading, the supports of silicon wafer were cleaned in a bath of 100 mL of 80% H₂SO₄, 35 mL of H₂O₂, and 15 mL of deionized water for 15 min at 80 °C and rinsed in deionized water, and then dried in compressed nitrogen gas flow. The micelles were then placed onto the wafer and dried in ambient condition for 1 day before SEM observation.

RESULTS AND DISCUSSION

Critical Water Content Determination by Turbidity

In the case of BC self-assembly, micelles are formed when water (if water is used as a selective solvent for one block) exceeds a critical concentration. This critical water content (CWC) is defined as the amount at which a sudden change of the turbidity occurs in the process of water addition^[37]. Figure 1 gives the turbidity measured from UV-Vis spectrometer for the copolymer in dioxane/water solution as a function of water content. With the increase of water content, the ability of solvent to dissolve PS block becomes poor and the single block chains start to aggregate. The approximate value of CWC can be obtained from the intercept of two line segments (horizontal section and steeply increasing section)^[47]. The evaluation of this quantity can guide the morphological control by variation of water content (to be discussed following), for which the addition of water may be higher than it to ensure that the micelles are formed in the aqueous solution. CWC is usually dependent on the BC composition and the nature of solvent^[48]. For the amphiphilic triblock copolymer of P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ in dioxane/water, the critical concentration is around 17 vol% as shown in Fig. 1.

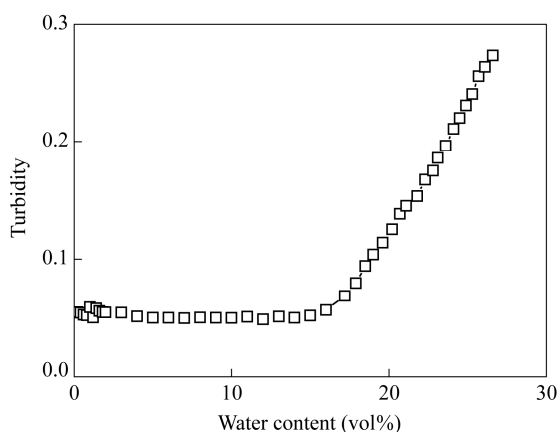


Fig. 1 Turbidity as a function of water content for P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ block copolymer in dioxane/water

Morphologies of the Micelles Formed at Different Water Contents

According to the measurement of turbidity discussed above, the water content (selective solvent) used for P4VP block in our study is above 17 vol% (CWC) but under 50 vol% (PS immobile water content, above which the segmental motion is frozen)^[49]. In parallel to the previous work of toroidal micelles from this P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ copolymer (where the water content was about 25 vol%)^[50], the initial water content was set as 20 vol% with an increment of 5 vol%. Figure 2 gives the TEM images of various morphologies of P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ micelles in water/dioxane. At first, the micelles show mainly bead-like morphology at 20 vol% water content (Fig. 2a). With the increase of water content to 25 vol%, large amounts of toroidal micelles are formed, which is consistent with the results in our previous work (Fig. 2b)^[50]. Then at 30 vol% of water, lamellae, which seem to be formed from association of toroids, become the

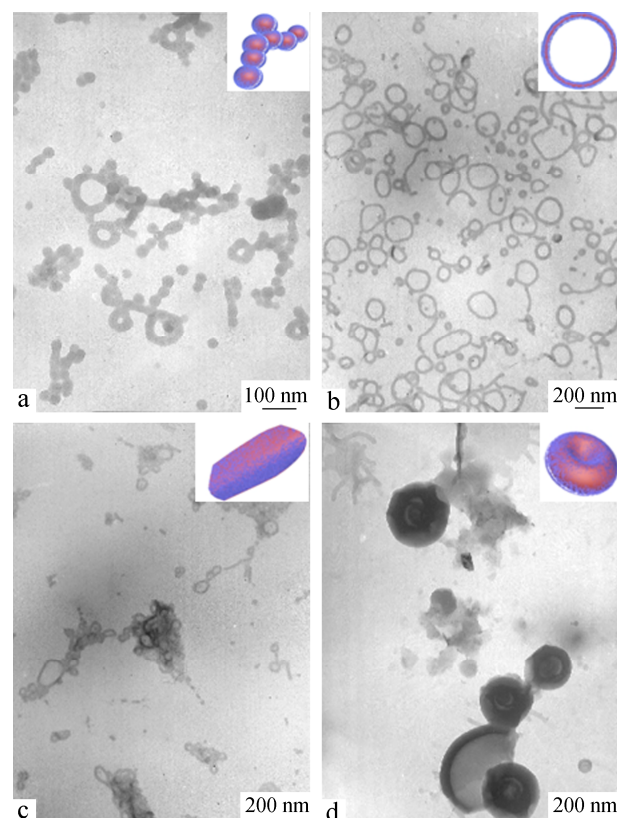


Fig. 2 TEM images of the micellar morphologies for the P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ system with 1 wt% copolymer concentration and various water contents: (a) beads at 20 vol%; (b) toroids at 25 vol%; (c) lamellae at 30 vol%; (d) vesicles at 35 vol% (The insets are the schematic images of the corresponding morphologies with red as PS core and blue as P4VP corona, respectively.)

dominant morphology (Fig. 2c). Finally, the micellar size increases significantly and the micelles change to vesicles at the water content of 35 vol%, as shown in Fig. 2(d). For clarity, four schematic images of bead, toroid, lamella, and vesicle are inserted on the right top of the corresponding TEM images.

The micellar sizes were characterized by dynamic light scattering (DLS), as shown in Fig. 3. At first, the hydrodynamic radius (R_h) is very narrow and distributes around 75 nm due to the formation of small-sized bead-like micelles (Fig. 3a). Then with the increase of water content, R_h distribution becomes broader and is mainly in a range of 50–400 nm with a peak value at 169 nm at 25 vol% water content (Fig. 3b), corresponding to the formation of toroidal micelles. At 30 vol% water content, the maximum R_h reaches 250 nm, indicating the transformation from toroids to lamellae (Fig. 3c). Finally, the peak value of R_h continually increases to 300 nm at 35 vol% water content and the distribution becomes broader than Fig. 3(c) when the lamellae are transformed into vesicles. A decrease of the peak is found in the region of < 20 nm, which is ascribed to the single molecules of block copolymer^[51], because block copolymer molecules precipitate into micelles with the increase of water content. Combined with the TEM observations in Fig. 2, the size distribution changes in DLS are attributed to the micelle evolution from beads to vesicles.

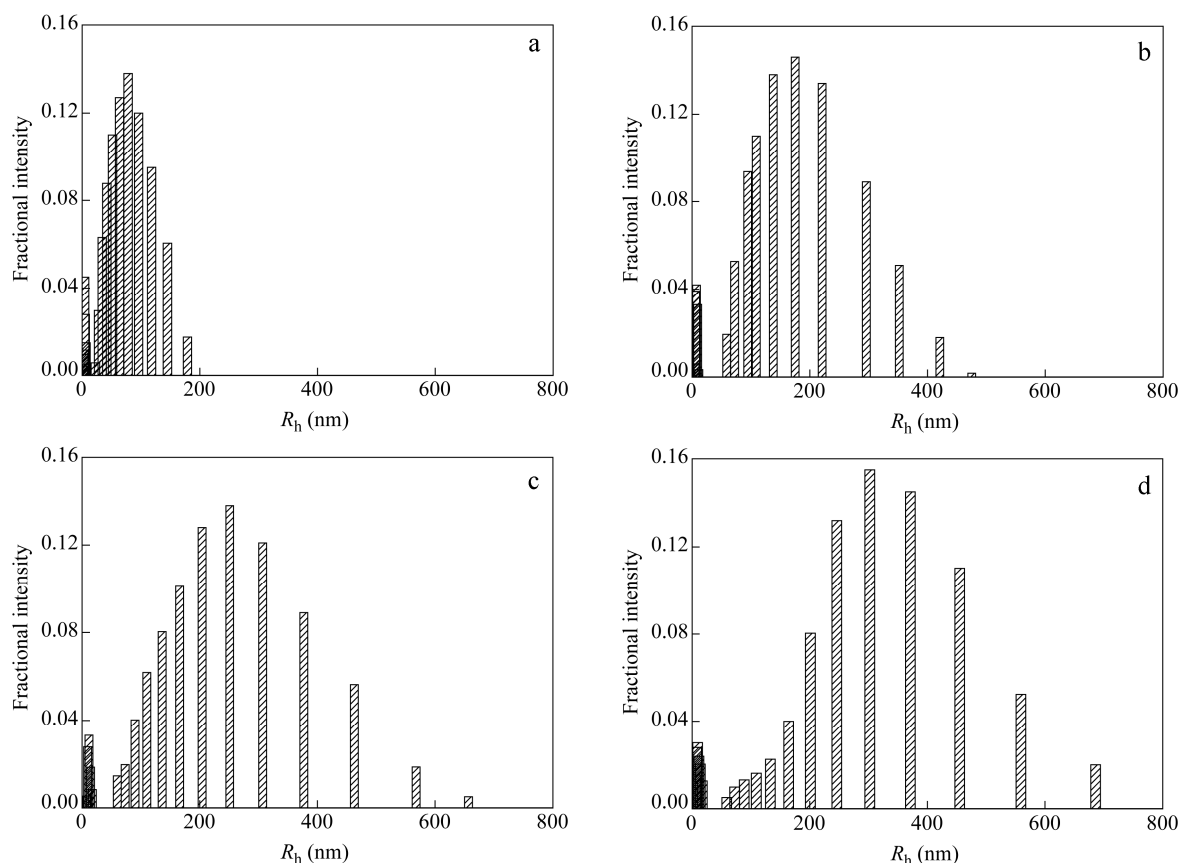


Fig. 3 Hydrodynamic radius (R_h) distribution from DLS experiments for the P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ micelles formed at different water contents: (a) 20 vol%, (b) 25 vol%, (c) 30 vol%, (d) 35 vol%

P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ micelles in dioxane/water consist of PS and P4VP as cores and coronas, respectively, due to the balance between polymer fragments' interactions with the solvent and interactions between the fragments themselves^[48, 52]. The morphological changes with variation of water content can be attributed to the change of the solvent quality toward hydrophilic and hydrophobic blocks of the triblock copolymer. Addition of more water makes the PS block less soluble, and the interfacial tension increases, while the corona repulsion may keep constant since water is a good solvent for P4VP block^[53]. Hence the micellar morphologies are mainly dominated by the interfacial repulsion between the solvent and the hydrophobic PS blocks. The spherical and bead-like micelles tend to aggregate and adapt to minimize the total interfacial energy. As a result, toroidal structures are formed (some embryo structures of rings can be seen in Fig. 2(a), indicating that they have the tendency to form toroids). When the water content continues to rise, the increased surface tension between PS and solvent makes water molecules and the hydrophilic units diffuse out of the clusters, and the hydrophobic components fuse to form large-sized micelles. The toroidal micelles begin to connect, their boundaries fuse, and lamellae are consequently formed. Finally, at the water content of 35 vol%, the large content of water gives rise to the repulsion between solvent and PS block, and the stretching of polymer chains in the core builds up again, which leads to a further adaption of the micellar geometry in order to reduce the interfacial energy of the

core-forming PS block. Thus, the micellar morphology undergoes further evolution and vesicle is formed as the final transition of the micellar structure. In summary, the morphological evolution results from the balance of interfacial tension, corona repulsion, and stretching. The micellar structure in the solution changes in a direction that decreases the overall free energy, which, in the present system, is from beads to toroids, then to lamellae, and finally to vesicles with the increase of water content.

Morphological Changes of the Micelles Induced by Temperature

Figure 4 gives the typical SEM images of the morphological changes induced by temperature for P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ micelles in dioxane/water with 1.0 wt% copolymer and 20 vol% water concentration. At 20 °C, the micellar morphology is mainly bead-like (Fig. 4a) and in agreement with the TEM image of Fig. 2(a). When the temperature increases to 40 °C, fibers are found (Fig. 4b). Then at 60 °C, short rod replaces the fiber-shaped structures (Fig. 4c) and becomes the dominated morphology. Finally at 80 °C, the micelle size decreases significantly and the micelles change to small capsules (Fig. 4d). Therefore, by changing the temperature, we can access bead-, fiber-, rod-, and capsule-like morphologies without changing compositions of the system. Similarly, the corresponding schematic images are also supplied here and are inserted on the right top of the corresponding SEM images for clarity.

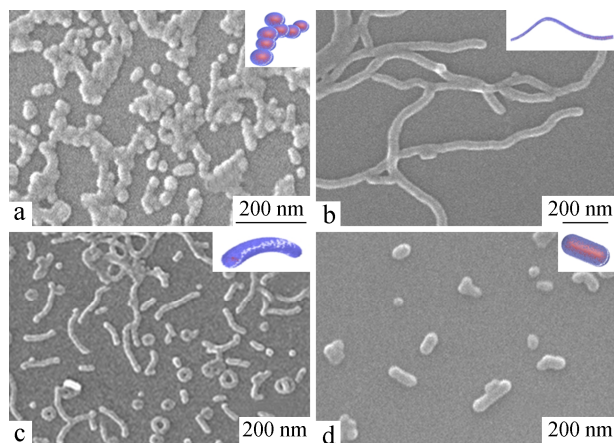


Fig. 4 Morphological changes characterized by SEM on heating a system with 1.0 wt% P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ copolymer and 20 vol% water concentration in dioxane/water: (a) bead-like micelles at 20 °C; (b) fibers at 40 °C; (c) rod-like micelles at 60 °C; (d) small capsules at 80 °C (The insets are the corresponding schematic image of the corresponding micellar morphologies.)

Generally, variation of temperature induces the change of interaction parameter between the solvent and the copolymer blocks, especially the hydrophobic PS blocks^[51]. With the increase of temperature, the solubility of solvent to the PS blocks is enhanced and the segmental movement is of little frictional resistance. Water molecules and the hydrophilic units can easily diffuse out of the clusters, and the hydrophobic components begin to fuse to form larger-size micelles due to the “orthokinetic” effect of temperature^[54]. Therefore, the small-sized beads aggregate and change to fibers. However, as the temperature continues to increase, the increased solubility makes the solvent molecules easily enter into the PS core of the fibers and destroys the PS chain entanglement. As a result, the micellar morphology changes to rods at 60 °C and then to small-sized capsules at 80 °C.

Effects of Temperature Superposed on Water Contents on the Morphological Changes

Specific trigger for a morphological transformation is impossible to identify among the many contributing factors, because micellar morphological changes are frequently induced by very small changes in the environment^[55]. Water content or temperature as a single protocol for controlling over self-assembled nanostructures was focused on in many researches^[56, 57]. However, few studies have been devoted to the interaction of the two factors affecting the nanostructure of BC self-assembly. Herein, effect of temperature superposed on water content is particularly investigated. The morphological changes of 20 vol% water system at different temperatures have been introduced in the above section. TEM images of the micellar structure of the other systems with different water contents (25 vol%–35 vol%) and at different temperatures (20–80 °C) are supplied in Figs. S1–S3 (in electronic supporting information, ESI). To provide an overview, the morphologies are summarized and a phase diagram is plotted in Fig. 5. The typically obtained morphologies in this study are bead, fiber, rod, capsule, toroid, lamella, and vesicle. For the system of 25 vol% water content,

<i>C</i> versus <i>T</i>	20 °C	40 °C	60 °C	80 °C
20 vol%	B	F	R	C
25 vol%	T	T + F	F	R + C
30 vol%	L	T + L	T	T + R
35 vol%	V	L	T + L	T + L

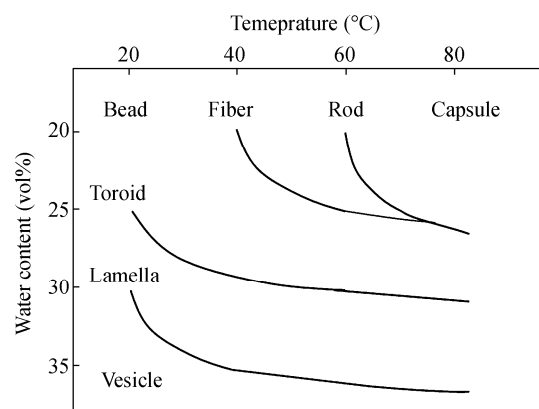


Fig. 5 Morphologies of the systems with different water contents at different temperatures (Symbols: *C* versus *T* as content of water versus temperature, B-beads, F-fiber, R-rod, C-capsule, T-toroid, L-lamella, V-vesicle.)

the polymer firstly self-assembles to toroids, then to the mixture of toroids and fibers, to fibers, and finally to rods mixed with capsules by the increase of temperature, as shown in Fig. S1 (in ESI). Then for the system with water content of 30 vol%, the morphologies evolve from initial lamellae to a final mixture of toroids and rods (Fig. S2, in ESI). Further, for the system containing 35 vol% of water, a transition from vesicle to a mixture of toroid and lamella is found (Fig. S3, in ESI).

As discussed above, the increase of water content is to increase the interfacial tension between the PS-core and the solvent, whereas the increase of temperature is to decrease the interfacial energy. The solubility of solvent to the PS blocks is enhanced and the segmental movement of PS chains is of little frictional resistance at higher temperature, which leads to a minimization of the micellar size. The interfacial tension between the copolymer and the solvent decreases with the increase of temperature, but it increases with the increase of water content. Therefore, vesicles with the highest interfacial energy appear at the temperature of 20 °C with the water content of 35 vol%. On the contrary, small capsules with the lowest energy are observed at 80 °C for the system with 20 vol% water content. Meanwhile, in relevance to the interplay of the two factors, micellar morphology formed for the system at lower temperature and lower water content shifts to the regime with higher temperature and higher water content. For examples, fibers are found at 40 °C for the system with 20 vol% water content, and then found at 60 °C for the 25 vol% water content system; toroids are formed at 20 °C for the solution with 25 vol% water, and also formed at 60 °C for 30 vol% water solution. Fibers, rods, toroids, capsules, lamellae, and vesicles are considered as the equilibrium structures^[38]. Mixture is found at the intermediate temperature region between two different equilibrium morphologies. For examples, fibers mixed with toroids are

observed at 40 °C for the system with 25 vol% water content, and toroids with lamellae are seen at 40 °C for the 30 vol% water content system.

Effect of the Block Copolymer Composition

For comparison, another triblock copolymer was selected with the same P4VP of 43 but different PS of 366 repeat units, *i.e.* P4VP₄₃-*b*-PS₃₆₆-*b*-P4VP₄₃. The micelles were prepared with 1.0 wt% copolymer and 20 vol% water concentration in dioxane/water (the measurement of turbidity of this copolymer was shown in Fig. S4, in ESI). Figure 6 shows the TEM images of micellar morphologies of P4VP₄₃-*b*-PS₃₆₆-*b*-P4VP₄₃ copolymer with different temperatures. At first, vesicles are formed at 20 °C (Fig. 6a), instead of the bead-like micelles for P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃. Then lamellae combined with vesicles are found at 40 °C (Fig. 6b). As the temperature continues to increase, lamella becomes the dominant morphology at 60 °C (Fig. 6c), but finally changes to fibers at 80 °C (Fig. 6d).

Increasing the fraction of hydrophobic block is to increase the surface tension between the copolymer and the solvent. It reduces the molecular curvature, and is sufficient to drive the formation of vesicles^[58]. As a result, vesicles are easily formed from P4VP₄₃-*b*-PS₃₆₆-*b*-P4VP₄₃ having lower water content of 20 vol%, as compared with P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ containing 35 vol% of water. Then as the temperature increases, solvent is more likely to enter into and swell the

core-forming PS blocks and prompts the dissociation of micelles, which leads to the morphological transition from vesicles to fibers.

CONCLUSIONS

Morphological changes of P4VP₄₃-*b*-PS₂₆₀-*b*-P4VP₄₃ block copolymers in dioxane/water, in which water is a selective solvent for P4VP block, were studied by variation of water content and temperature. The bead-like micelles gradually evolve to vesicles as the water content increases from 20 vol% to 35 vol%. The results are further confirmed by dynamic light scattering, with which the distribution of hydrodynamic radius (R_h) changes from around 75 nm to 300 nm. Effect of temperature on the micellar morphology has also been studied. For the system containing 20 vol% water, the micellar morphology changes from beads to fibers, then to rods and finally to capsules as the temperature increases from 20 °C to 80 °C. However, the structures of the micelles are quite different for the systems with different water contents. The copolymer firstly assembles to toroids, then to the mixture of toroids and fibers, to fibers, and finally to rods and capsules with the increase of temperature for the system of 25 vol% water content. For 30 vol% water content, a morphological transition from initial lamellae to a final mixture of toroids and rods is observed. Then for the system containing 35 vol% of water, the micellar morphology changes from vesicle to a mixture of toroids and lamellae. The interfacial tension between the PS-core blocks and the solvent increases with the increase of water content but decreases with the increase of temperature. As a result, the block copolymer in solution intends to form vesicles as water content increases but to form small-sized micelles, such as capsules or rods, with the increase of temperature. The morphologies of micelles are resulted from the interplay of the temperature and water content, and always change in a direction that decreases the overall free energy. Based on these results, the morphological phase diagram of temperature dependence is described in details, covering the range of water content from 20 vol% to 35 vol% and the phase transitions for five main micellar morphologies termed toroids, fibers, rods, lamellae, and vesicles.

Electronic Supplementary Information

Electronic supplementary information (ESI) including additional TEM images of the micellar structure of the systems with different water contents (25 vol%–35 vol%) at different temperatures (20–80 °C) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2066-2>.

ACKNOWLEDGMENTS

This work was financially supported by Key Lab of Renewable Energy Foundation of Chinese Academy of Sciences (No. Y609JK1001), the National Natural Science Foundation of China for Major Program (Nos. 51433009 and 51576201), Natural Science Foundation of Guangdong (No. 2015A030313716), Natural Science Foundation of Guangdong for Research Team (No. 2015A030312007), and Guangdong Science and Technology Project (Nos. 2013B050800007 and 2013J4500027).

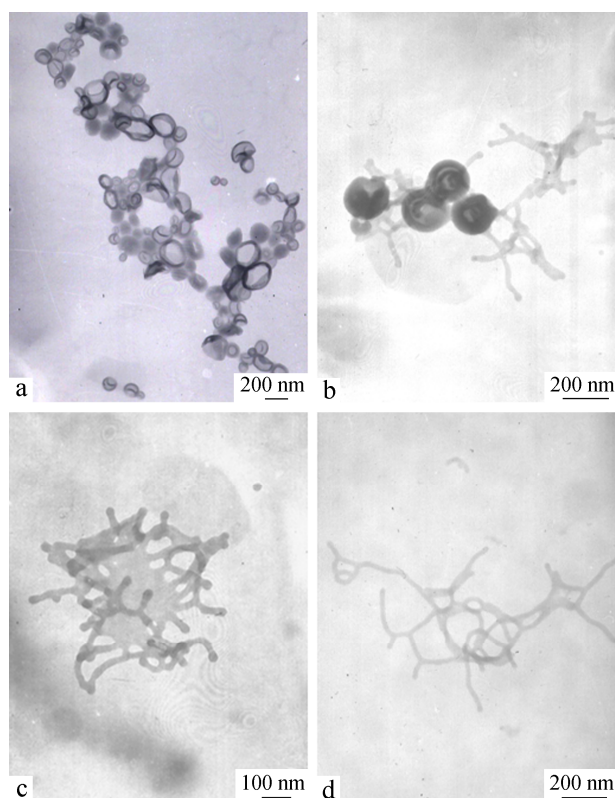


Fig. 6 TEM images of the micellar structures of P4VP₄₃-*b*-PS₃₆₆-*b*-P4VP₄₃ block copolymer with 1.0 wt% copolymer and 20 vol% water concentration at different temperatures in dioxane/water: (a) vesicles at 20 °C; (b) lamellae and vesicles at 40 °C; (c) lamellae at 60 °C; (d) fibers at 80 °C

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