

ROD-LIKE AGGREGATES FROM POLYSTYRENE-*b*-POLY(4-VINYLPYRIDINE)-*b*-POLYSTYRENE TRIBLOCK COPOLYMER IN AQUEOUS MEDIA

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Abstract The rod-like assembly from BAB block copolymer with hydrophilic middle block A in aqueous solution was described. The copolymer used is polystyrene (PS)₃₉-*b*-poly(4-vinylpyridine)(P4VP)₉₈-*b*-PS₃₉ (the subscripts are the average polymerization degree of corresponding blocks) triblock copolymer with $M_w/M_n = 1.15$. The aggregates were characterized by transmission electron microscopy and atomic force microscopy. The dependence of rod-like aggregate formation on solvents, pH, and polymer concentrations was investigated. The rod-like aggregates were formed when using dioxane as initial solvent, while spherical micelles were formed using DMF. Elevating pH values from 4 to 5 to 7 and decreasing initial copolymer concentrations from 1.5 wt% to 1.0 wt% to 0.5 wt% were favorable for the formation of well-defined rod-like aggregates. In addition, the bicontinuous rods and lamellae were observed when preparing colloid solutions in appropriate conditions.

Keywords Block copolymers, Self-assembly, Rod-like aggregates, Bicontinuous, Lamellae

INTRODUCTION

Recently, solution-state assembly of block copolymers has attracted much interest. On the one hand, the versatility of morphology control can be used for the preparation of unique nanostructured materials with various architectures^[1–8]. On the other hand, some self-assembled structures are biomimetic^[9, 10]. The balance between three major forces acting on the system affects block copolymer morphologies in solutions^[11, 12]. These three forces include the stretching of the core-forming blocks, the intercoronal interactions, and the interfacial energy between the solvent and the micellar core. For a given block copolymer composition, the changes in the solution pH^[13, 14], the solvent^[15], and the polymer concentration^[16, 17] have been found to effect the reorganization of block copolymer supramolecular assemblies.

Spherical assemblies were observed conventionally for the supramolecular assembly of amphiphilic block copolymers^[18]. However, it is very recent that multiple morphologies of block copolymers in solutions have been developed, including sphere, rod, lamellae, vesicle, tube, and so on^[19]. It is interesting to note that as focus has shifted from fullerenes to carbon nanotubes for carbon-based nanostructures, interest also has shifted from spherical nanoparticles to rod-like supramolecular assemblies. In the past years, the rod-like micelles have been obtained with AB^[2, 20–22], ABC^[4, 7, 23] block copolymers in solutions. However, to our best knowledge, the rod-like assemblies based on BAB block copolymer in A-selective solvent have been unprecedented. In this paper, the rod-like aggregates were demonstrated based on polystyrene (PS)₃₉-*b*-poly(4-vinylpyridine)(P4VP)₉₈-*b*-PS₃₉ (the subscripts are the polymerization degree of corresponding blocks) triblock copolymer in aqueous media. The

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dependence of rod-like aggregate formation on solvents, pH, and polymer concentrations were investigated.

EXPERIMENTAL

Polymer Synthesis

The polymers used were PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer with $M_w/M_n = 1.15$ synthesized by reversible addition fragmentation chain-transfer polymerization (RAFT)^[24]. Using dibenzyl trithiocarbonate (DBTTC) as the chain transfer agent (CTA), PS was firstly obtained. Then, PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ was prepared using the above obtained PS as macro-CTA. DBTTC was synthesized by reacting CS₂ and 33% aqueous NaOH solution with benzyl chloride under phase transfer catalysis condition (*n*-Bu₄NHSO₄, 3 mol% to the benzyl chloride used). For PS macro-CTA, 10 mL purified styrene and 0.0932 g DBTTC were added to a 100 mL flask equipped with a rubber septum and a magnetic stir bar under an argon atmosphere, and then sufficiently degassed. The polymerization was conducted at 110 °C for 24 h. For the preparation of PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer, 3.5 mL purified 4-vinylpyridine, 0.9980 g PS macro-CTA, 0.0045 g AIBN, and 1.5 mL DMF were used. The polymerization were conducted at 60 °C for 25 h. The chemical structures and composition of the polymers obtained were characterized with ¹H-NMR. ¹H-NMR spectra were obtained on a Varian XL-300 NMR instrument operated at 300 MHz using CDCl₃ as solvent. Molecular weights and molecular weight distributions were determined using GPC coupled with multi-angle laser light scattering (MALLS). The system includes a Styragel®HMW 6E GPC column (7.8 × 300 mm), a Wyatt Optilab RI detector, and a Wyatt multi-angle laser light scattering detector (DAWN E). The MALLS was operated at 18 angles, from 26° to 149°, and was equipped with a He-Ne laser (690 nm). The column and the RI detector were set at 40 °C. The mobile phase was DMF with added Bu₄NBr (0.1%, *W/V*) at a flow rate of 0.8 mL/min. The polymer sample solutions were filtered through a 0.2 μm syringe filter before injection.

Preparation of Colloid Solutions of Triblock Copolymers

The copolymer solution was prepared by first dissolving the copolymer in DMF, then stirring overnight at room temperature^[25]. To prepare the aggregate solution, twice-distilled water with a given pH, which was a precipitant for PS block, was added to the corresponding copolymer solution dropwise with stirring at a rate of 1 drop/10–15 s. When the water content reached *ca.* 90 wt%, the solution was placed in a dialysis bag and dialyzed against water with the same pH value for about 3 days to remove the solvent. Twice-distilled water for dialysis was changed twice a day.

Characterization of Aggregate

The aggregates were characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM) techniques. For TEM measurement, a drop of the prepared colloid solution was placed on a copper EM grid. Before sample deposition, the EM grid was precoated with a thin film of celloidin. After the drop has been in contact with the grid for a time, the remaining solution on the grid was blotted up using a strip of filter paper. The sample was dried in air for a few hours, and then was vacuum dried. The aggregates were observed on a H-7000 (Hitachi) transition electron microscope that was operated at an accelerating voltage of 60 kV. For AFM imaging, a drop of the colloid was placed on a clean mica substrate. The water was evaporated at ambient condition. The scanning was performed on an SII scanning probe microscope in a tapping mode.

RESULTS AND DISCUSSION

At a given chain length and composition, the aggregation of BAB block copolymer is generally more difficult than that of AB and ABA block copolymer in a good solvent for block A. The responsibility for the reduced aggregation ability of the BAB block copolymer has been attributed to the entropy loss associated with the looping of the middle block A when aggregation events occur^[26]. In past years, numerous works have focused on the aggregation of BAB block copolymers with relatively larger middle block A. The looser aggregates were formed by directly dissolving copolymers in the A-selective solvents. Moreover, aggregate clusters, even gel, have been claimed when increasing the concentration of copolymers^[27]. In contrast, the aggregates of PS₃₉-*b*-

P4VP₉₈-*b*-PS₃₉ triblock copolymer were prepared by first dissolving copolymer in the common solvents for both blocks, such as THF, DMF, and dioxane, then adding water of appropriate pH to the copolymer solutions with stirring in order to induce the self-assembly of copolymer. By a similar method, we have recently observed the vesicle morphology formed by PS₄₃-*b*-PEO₄₅-*b*-PS₄₃ block copolymer with relatively small middle block A^[28]. THF, dioxane, and DMF are good solvents for both blocks, while water with appropriate pH is a good solvent only for the middle block P4VP but is a precipitant for the end block PS. During the addition of water to the initial copolymer solutions, the solubilizing power of the solvent for the end block PS gradually decreases. The aggregation of PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ triblock copolymers used here is involved in looping of water-soluble middle block P4VP and tailing of hydrophobic end block PS. In the early stage of aggregation of the triblock copolymers, the relatively low water content in the system may facilitate the exchange of the copolymer chains between the unimers and aggregates to proceed at a significant rate. Thus a thermodynamic equilibrium would be operative for aggregation. As more water is added and more common solvent is extracted from the core of aggregates, the exchange rate of copolymer chain becomes low due to the decreased solubility of the copolymers. As a result, the aggregates become kinetically frozen with the further addition of water.

Effect of Solvents

Figure 1 shows the typical TEM images of aggregates of PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ triblock copolymer prepared from a 1 wt% triblock copolymer solution in DMF (Fig. 1a) and dioxane (Fig. 1b) at pH = 3. Clearly, the long rod/worm-like aggregates are formed when colloids are obtained from copolymer solutions of dioxane, while spherical micelles, cohesive spheres and even some short rod-like aggregates are observed in the case of using DMF as initial solvent. The aggregates of spheres and rod/worm-like micelles have a diameter of *ca.* 23 nm. The length of long rod/worm-like micelles can reach more than a micrometer. In addition, further aggregation occurs between the long rod/worm-like micelles. The secondary aggregates have a large number of rod/worm-like micelles. The formation of long rod/worm-like aggregates and spherical and short rod-like aggregates in different solvents is attributed to the interaction of polymer-solvent^[15]. PS block has better solubility in dioxane than in DMF. Therefore, the dimensions of aggregate cores, at the onset of micellization, must be much larger in dioxane than that in DMF. As a result, the degree of stretching of the PS chains has increased, correspondingly, which is entropically unfavorable. The high penalty for the larger stretching of PS chains in the core forces the aggregates to adopt vesicle morphology in order to decrease the free energy of micellization^[12].

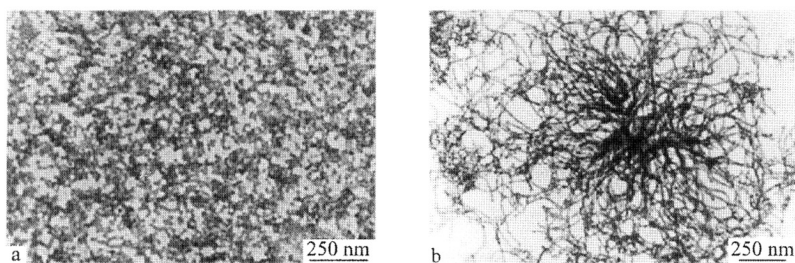
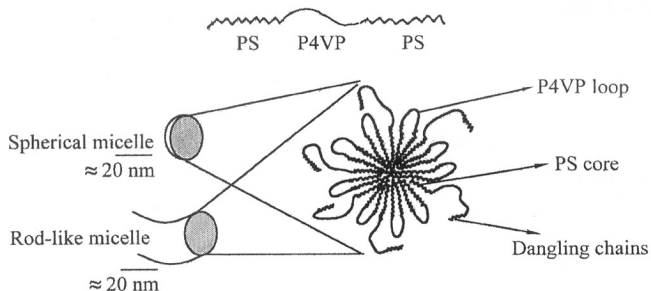


Fig. 1 The TEM pictures of aggregates of PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer in various initial solvents
(a) and (b) are made from 1 wt % copolymer in DMF and dioxane. The pH is 3.

Scheme 1 shows the conformation of PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer in the spherical and rod/worm-like micelles. The majority of PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer chains adopts the conformation of P4VP looping into the corona and PS tailing into the core of aggregates. But, for a given aggregate, it was difficult to accept that all PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ chains folded back to form a well-defined structure with a core of PS beads and corona of P4VP loops. It was more reasonable that PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ aggregated into some loose structure with PS core and P4VP corona comprised primarily of looped P4VP chains and a few dangling chains.



Scheme 1 The conformation of $\text{PS}_{39}\text{-}b\text{-P4VP}_{98}\text{-}b\text{-PS}_{39}$ triblock copolymer in the spherical and rod-like micelles

Effect of Concentration

Figure 2 demonstrates the typical TEM pictures of aggregates of $\text{PS}_{39}\text{-}b\text{-P4VP}_{98}\text{-}b\text{-PS}_{39}$ triblock copolymer prepared from dioxane solution at $\text{pH} = 4$. The concentrations of initial copolymer solutions were 0.5 wt% (Fig. 2a), 1.0 wt% (Fig. 2b), and 1.5 wt% (Fig. 2c). When the colloid was prepared from 0.5 wt% copolymer solution, the rod/worm-like aggregates with a diameter of *ca.* 23 nm and a length more than 500 nm were mostly observed. At the same time, a small quantity of spheres was also obtained. Furthermore, the secondary aggregation between the rod/worm-like aggregates was tenuous, and secondary aggregates assume an urchin-like shape. When the concentration of initial copolymer solutions increased to 1.0 wt% and 1.5 wt%, some complex structures consisting of spherical micelles and rod/worm-like aggregates were observed. It was possible that the increasing concentrations contributed to the kinetic entrapment of intermediate aggregates, which resulted in the more complex aggregation in the process of self-assembly.

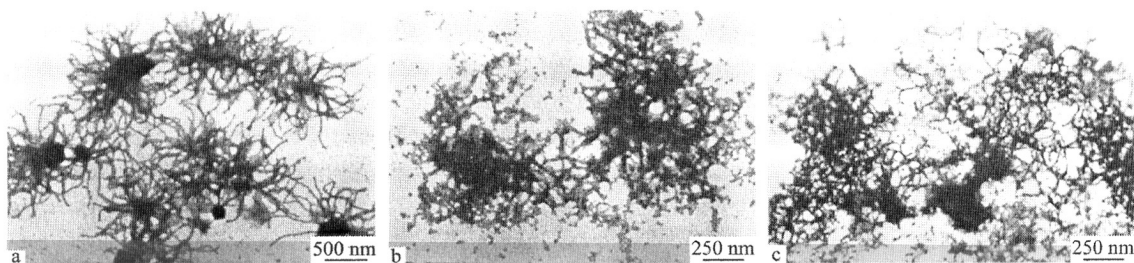


Fig. 2 The TEM images of aggregates made from $\text{PS}_{39}\text{-}b\text{-P4VP}_{98}\text{-}b\text{-PS}_{39}$ copolymer in dioxane at various initial concentrations, 0.5 wt % for (a), 1.0 wt % for (b), and 1.5 wt % for (c), respectively. The pH is 4.

Effect of pH

Figure 3 illustrates the TEM photographs of aggregates prepared from 1 wt% copolymer DMF solutions at different pH. The aggregates shown in Fig. 3(a), 3(b) and 3(c) were formed from $\text{pH} = 4, 5$, and 7 , respectively. It indicates that increasing pH values favor the formation of rod-like aggregates. In view of the solubility of the P4VP block in aqueous solutions at different pH values, this result is acceptable. When the pH value of the copolymer solution increases from 4 to 5 to 7, the solubility of P4VP block decreased, which results in a decrease of the repulsive interactions between coronal P4VP block chains, thus more chains can aggregate, leading to the formation of larger aggregates. As a result, the average degree of PS chain stretching in cores increases because PS chains tend to reach from the center of the core to the core-corona interface. The increased stretching of PS chains is associated with an entropic penalty. Therefore, the morphology with the lower energy is favorable, for example rod-like aggregates.

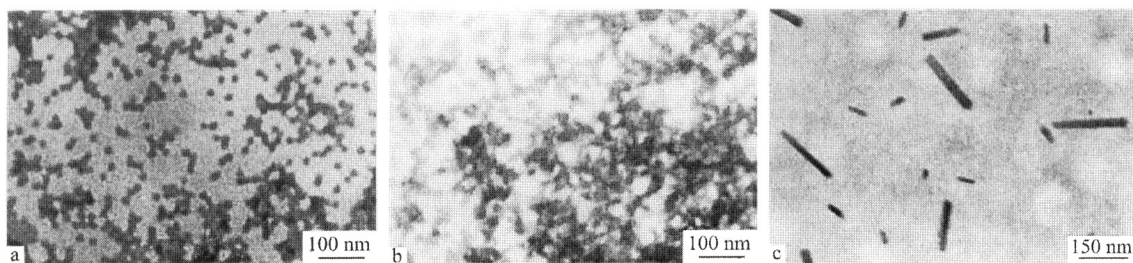


Fig. 3 The TEM images of aggregates of 1 wt % PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer in DMF at various pH, and (a), (b), and (c) are for pH = 4, pH = 5, and pH = 7, respectively

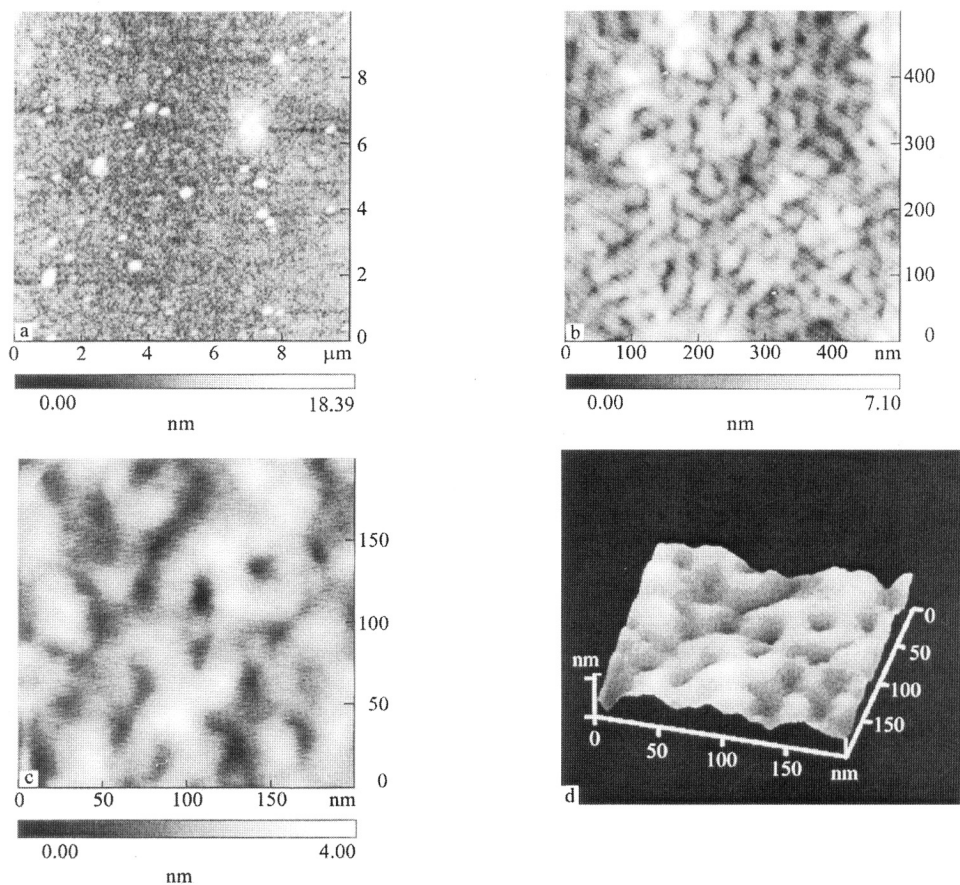


Fig. 4 The AFM images of bicontinuous rod aggregates made from 0.5 wt% PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer solution in DMF at pH = 7. The image of B is partially amplified from (a), and (c) from (b). (d) is the three-dimensional imaging of C.

Formation of Bicontinuous Rods

Figure 4 shows the AFM images of aggregates prepared from 0.5 wt% copolymer DMF solution at pH = 7. Clearly, the rods with bicontinuous structures are resolved. The diameter of the rods is *ca.* 29 nm. This size is larger than that obtained from TEM as shown in Figs. 1 and 2. The difference of imaging environment between TEM and AFM measurements accounts for such a discrepancy between sizes. The AFM work was performed under air and the hydrophilic surface of aggregates was saturated by atmospheric moisture. In contrast, TEM was conducted under vacuum and the surface of aggregates collapses to a greater extent. In addition, the AFM images

in Fig. 4 suggest that the bicontinuous rods are two-dimensional and partially bicontinuous. The bicontinuous rod structure has been observed in bulk^[29] or in copolymer/ homopolymer blends^[30], as well as in solutions of small molecule amphiphiles^[31]. Recently, the bicontinuous rods in dilute water-DMF solution of PS₁₉₀-*b*-PAA₂₀ block copolymers have been described by Yu *et al.*^[32].

Formation of Lamellae

When aggregates were formed from 1.5 wt% copolymer THF solution at pH = 4, the lamellae assembly was observed (as shown in Fig. 5). Interestingly, the small lamellae are irregular in shape, and are interconnected. It was suggested that these interconnected lamellae are transformed by the flattening of some short and branched rods. Further fusion of these network lamellae would form lamellae with regular shape. The specific chain conformation of block copolymer may be responsible to the formation of network lamellae. As depicted in Scheme 1, some PS end blocks dangle outward into the media when aggregation proceeds. The dangling PS chains may extend into another aggregate. In the case of rod-like aggregates, the extension of PS chains may result in the formation of network or branched rods.

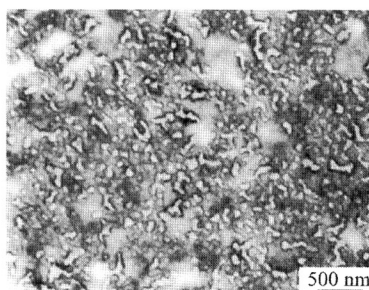


Fig. 5 The TEM picture of lamellae aggregates made from the 1.5 wt% PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ copolymer in THF at pH = 4

CONCLUSIONS

Rod-like assemblies can be formed from PS₃₉-*b*-P4VP₉₈-*b*-PS₃₉ triblock copolymer in aqueous solutions. Using dioxane as initial solvent rather than DMF, decreasing the initial copolymer concentration from 1.5 wt% to 1.0 wt% to 0.5 wt% and raising the pH from 4 to 5 to 7 favored the formation of well-defined rod/worm-like aggregates. In addition, further aggregation between rod-like aggregates tenuously takes place. Besides, bicontinuous rods and lamellae were obtained by preparing the colloid solutions in appropriate conditions.

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