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Morphological Transition of Aggregates from ABA Amphiphilic Triblock Copolymer Induced by Hydrogen Bonding

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ABSTRACT: The hydrogen-bonding-induced aggregate morphological transition of the triblock copolymer poly(4-vinylpyridine)$_{43}$-*b*-polystyrene$_{366}$-*b*-poly(4-vinylpyridine)$_{43}$ (P4VP-*b*-PS-*b*-P4VP) in dilute solution was studied by introduction of a surfactant (pentadecylphenol, i.e., PDP) into the solution. The P4VP-*b*-PS-*b*-P4VP triblock copolymer exhibits spherical aggregates in 1 wt % of the surfactant (PDP)-free solution. However, the aggregate morphologies changed from short rods to networks and looped structures and then to vesicles and compound vesicles by increasing PDP content at the same copolymer concentrations to the PDP-free solutions. The striking feature is that a trace amount of PDP (molar ratio of 4VP/PDP = 1000) addition can change the aggregate morphologies to wormlike morphologies. The nature of the influence that PDP exercise over the copolymer aggregates was determined by comparing the results with those obtained for the addition of the *m*-cresol (without the long tail of linear alkyl) and pentadecylbenzene (without hydroxyl). The interactions of both the hydrophobic chain and the hydrogen bonding of the PDP headgroup with the block copolymer molecules affect the architecture of the copolymer aggregates. Hydrogen bonding weakens the interaction among the corona-building blocks, and hydrophobic chains of the PDP insert into the core of the aggregates, leading to the increases of the core dimension of the aggregates. The latter effect is more important on the morphological transition, which has been proved in experiment. Using the hydrogen bonds of block copolymers with small molecular amphiphiles opens up the possibility of reaching a certain fraction to produce a desired aggregate morphology, representing another tool for manipulation of these nanostructures.

1. Introduction

During the past decade, a large number of publications have appeared on the topic of synthesized block copolymer aggregate morphologies in solution.[1−9] Amphiphilic block copolymers can self-assemble into core−shell micelles with a variety of morphologies in dilute selective media.[1−10] These structures are of intrinsic interest, but they are also receiving attention because of their potential use in various fields, such as cosmetics, drug delivery, electronics, pollution control, advanced materials formation, separation, among others.[11−15]

"Crew-cut" aggregates represent a new type of block copolymer micelles.[10,16,17] The aggregates are formed through self-assembly of highly asymmetric amphiphilic block copolymers in which the insoluble core-forming blocks are much longer than the soluble corona-forming blocks.[16,17] It is found that crew-cut aggregates can give rise to several morphologies, as for example spheres, rods, vesicles, lamellae, large compound micelles, large compound vesicles, tubular, a hexagonally packed hollow hoop structure, onions, a bowl-shaped structure, and several others.[10,18−20]

It has been known that the equilibrium aggregate morphologies can be controlled by altering the influence exerted by a given parameter on the interplay of three major components of the free energy of the aggregates.[10,21] These components include the stretching of core-forming blocks, the interfacial free energy, and intercorona interactions. There are many factors that affect the above three terms, and by variation of one or more of these, the morphologies can then, in principle, be fine-tuned. Examples of such factors that have been studied previously include block length of the copolymer, initial copolymer concentration in solutions, common solvent used, precipitant, temperature, type and amount of the adding ions (salt, acid, or base), etc.[22]

Meanwhile, nanostructures' formation involving polymer−surfactant complexation has recently been studied extensively and offers many possibilities to vary the microstructures.[23] The attachment of the surfactant to the polymer backbone has been achieved by coordination bonding, ionic interactions in polyelectrolyte−surfactant complexes, and hydrogen bonding.[24−31] As for example, it has been reported that amphiphilic molecules can physically bond selectively to one block of a copolymer to form specific receptor−substrate supramolecules, and they self-assemble to form structure-within-structures.[32] These types of complexes system usually show a physical behavior quite different from that of the pure components, and they may have interesting applications in many fields such as medicine, pharmacology, biology, and environmental chemistry.[33] Hydrogen bonds play a fundamental role in the construction of supramolecular polymers by self-assembly processes due to their moderate bonding energy, which offers the flexibility for association and dissociation processes.[34,35] In nature, most biopolymers such as nucleic acids, proteins, and polysaccharides have hydrogen-bonding groups that participate in the structure formation and induce explicit functions. To the best of our knowledge, the study on hydrogen-bonded complexes is mainly focused on polymer blends and polymer thin films, as for example interpolymer complexes of poly(vinylpyridine), P4VP or P2VP, with polyacids, including poly(acrylic acid), pentadecylphenol (PDP),

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poly(vinylphenol), poly(carboxylic acid)s, 2-(4′-hydroxybenzeneazo)benzoic acid, and other Lewis acids.[36−38] Hydrogen-bonding complexes are rarely used to manipulate the aggregate morphologies of block copolymer in selective media.[29−31,39,40]

In this paper, we introduce a facile method to tune the amphiphilic aggregate morphologies in selective media by combining the self-assembly and hydrogen-bonding methods into the solution behavior of the amphiphilic block copolymer. Usually, the core−shell micelles have a core consisting of the insoluble PS block and a shell consisting of the soluble block such as poly(acrylic acid) (PAA), poly(ethylene oxide) (PEO), or PVP. It is thus reasonable that PDP can be adsorbed into the micelles self-assembled by P4VP-*b*-PS-*b*-P4VP due to hydrogen bonding between the P4VP chains and the PDP. This is the first example of the morphological change of P4VP-*b*-PS-*b*-P4VP aggregates that is brought about by the binding of hydrogen bonds to the pyridine unites. The formation of various morphologies by the block copolymer−surfactant complexes in this study demonstrates that the opportunities for the manipulation of morphology in these systems are much broader than has been previously considered. In addition, the specific aggregates morphologies can be easily tailored through using different amounts of PDP.

2. Experimental Section

2.1. Materials. The block copolymer used in this study was a triblock copolymer of $P4VP_{43}$-*b*-PS_{366}-*b*-$P4VP_{43}$ (the numbers in the subscripts indicate the number of repeat units of the blocks) ($M_n = 47\,000$ g/mol, PDI = 1.10), which was purchased from Polymer Source Inc., Canada.

3-*n*-Pentadecylphenol (PDP, purity 98%) and pentadecylbenzene (PDB, purity 97%) were purchased from Aldrich. *m*-Cresol was analytic grade.

All of the materials were used after receiving without further purifying.

2.2. Preparation of the PDP-Free P4VP-*b*-PS-*b*-P4VP Aggregates. The triblock copolymer was first dissolved in *N*,*N*-dimethylformamide (DMF) (which is a cosolvent for both P4VP and PS blocks) to make a different copolymer solution ranging from 0.5 to 4 wt %. The solutions were kept stirring overnight to make the copolymer dissolve into the cosolvent by single molecules forms. Then, a given volume of deionized water (7 wt % of the solution) was added slowly (ca. 0.2 wt %/30 s) into the copolymer/DMF solution with stirring. Micelles were taken place, which were indicated by appearance of blue tint, when the water content reached ca. 3.5 wt % in 1 wt % copolymer/DMF solution. Although the P4VP block is insoluble in pure water, it is soluble in DMF solutions containing up to 50 wt % water and is also soluble in water below a pH of 5.[41] After the water content reached 7 wt %, the solution were kept stirring for 3 days to make the aggregates reach equilibrium. Then, a large amount of water was added to the resulting solution to quench the aggregate morphologies. At this water content range, the microstructures of the aggregates become kinetically locked over the experimental time scale.[20,41] Subsequently, the resulting solution was placed in dialysis tubes and dialyzed against methanol (which is a nonsolvent for the PS blocks, but a solvent for both P4VP blocks and PDP) for a few days to remove all of the DMF and PDP from the solution. The morphology of the aggregates was stable during the dialysis process and after the dialysis. The length of the time between added water content reaching 7 wt % and subsequent large amount water addition is named the annealing time.

2.3. Preparation of the P4VP-*b*-PS-*b*-P4VP Aggregates by Adding PDP. $P4VP_{43}$-*b*-PS_{366}-*b*-$P4VP_{43}$ and PDP (*m*-cresol or pentadecylbenzene (PDB)) with different molar ratio *R* (the ratio of 4VP/PDP is named *R*), ranging from 1 to 1000, were dissolved separately in DMF. Then, the solutions were mixed and heated to 60 °C in an ultrasonic bath for 1 h. The resulting solution was kept stirring overnight to complete hydrogen bonding. The schematic illustration of hydrogen bonding between the poly(4-vinylpyridine) and 3-*n*-pentadecylphenol is given in Figure 1. The initial copolymer concentrations were all kept at 1 wt % for the PDP (and for *m*-cresol or PDB) adding samples. The following procedure for the aggregates preparation were all kept the same as the PDP free aggregates formations given above. The resulting aggregate solutions were dialyzed against methanol to remove the common solvent. Because methanol is also a good solvent for PDP, the hydrogen bonding between P4VP blocks of the copolymer and PDP were broken, and the PDP was moved from the aggregates solutions during the dialysis process.[42]

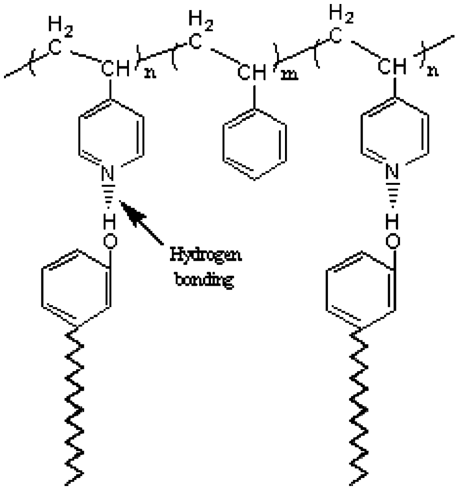

Figure 1. Schematic illustration of hydrogen bonding between poly(4-vinylpyridine) and 3-*n*-pentadecylphenol.

2.4. Transmission Electron Microscope (TEM) and Atomic Force Microscope (AFM). The aggregate morphologies were visualized with a regular TEM and AFM. TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV. The dialyzed colloidal solutions were diluted by a factor of 30−40 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 3 min, excess solution was blotted away using a strip of filter paper. The samples were allowed to dry in atmosphere and at room temperature for 1 day before observation. AFM was operated at SPA-300HV atomic force microscope with a SPI3800 controller (Seiko Instruments Industry Co. Ltd.) at the tapping mode. The contilever 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. 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

This section is organized in the following manner: in the first part, we present the results of characteristics of the aggregates from PDP-free block copolymer. Part 2 addresses the co-self-assembly of block copolymer and PDP in dilute solutions. Part 3 discusses the kinetics aspect of the aggregate morphology transition. Part 4 is devoted to the aggregate morphology transition mechanism of block copolymer by adding the desired amount of PDP and experimental argument.

3.1. Aggregate Morphologies of P4VP-*b*-PS-*b*-P4VP Triblock Copolymer in DMF/Water Mixtures. Figure 2 shows AFM height images of the

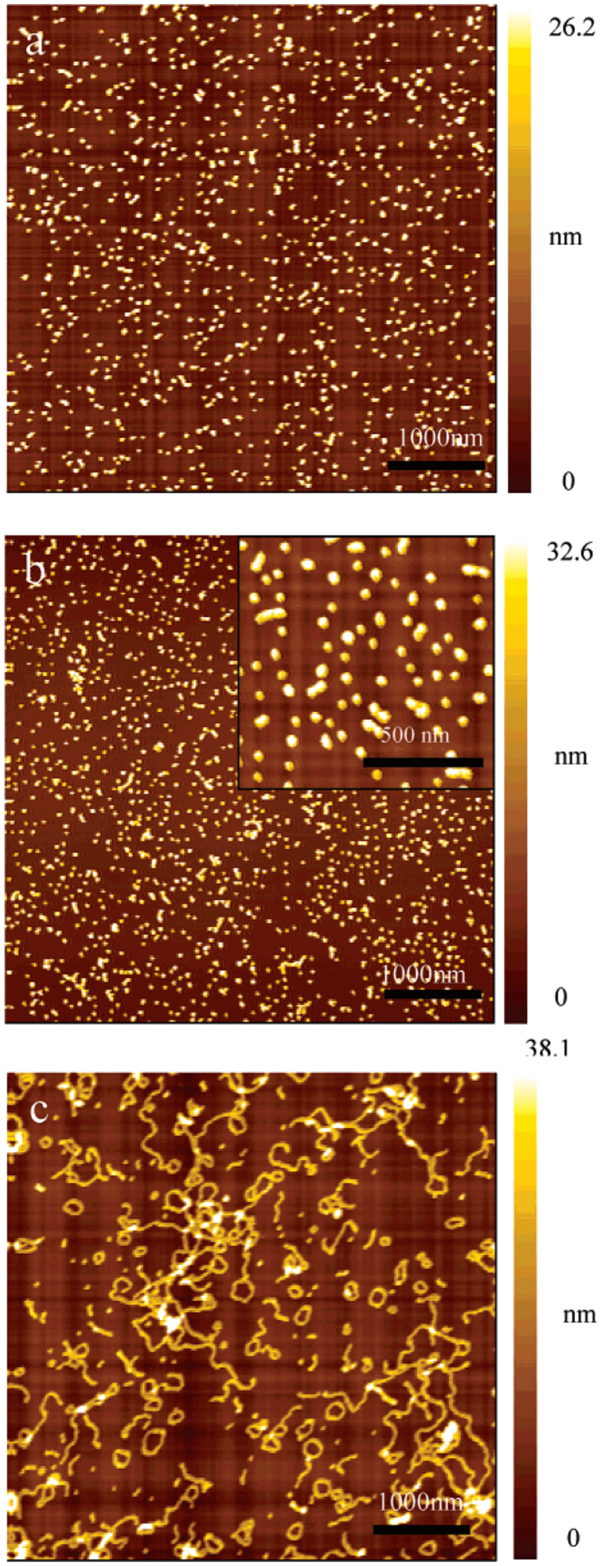

Figure 2. AFM height images of PDP free aggregates formed from $P4VP_{43}$-*b*-PS_{366}-*b*-$P4VP_{43}$ with different initial copolymer concentration: (a) 0.5, (b) 1, and (c) 4 wt %.

aggregate morphologies formed from self-assembly of the triblock copolymer $P4VP_{43}$-*b*-PS_{366}-*b*-$P4VP_{43}$ in DMF/water mixtures with different initial copolymer concentration. Spheres (Figure 2a), mixture of spheres and small fraction of very short rods (Figure 2b), and long wormlike (rods) and toroidal micelles (Figure 2c) are formed for 0.5, 1, and 4 wt % copolymer concentrations, respectively. It is worth noting that the initial (annealing time was 0) micellar morphology of 4 wt % copolymer in DMF/water mixture were long wormlike micelles. The micelle morphology changed from wormlike to toroidal when the annealing time was increased to 3 days. The result is similar to our previous report for the $P4VP_{43}$-*b*-PS_{260}-*b*-$P4VP_{43}$ assemblies in dioxane/water mixtures.[43] Although the lengths of the cylindrical micelles are quite polydisperse, their diameters are very uniform (Figure 2c). Clearly, the aggregate morphology depends strongly on the initial copolymer concentration. This result is similar to those observed by Eisenberg's group.[44] In our system, bilayer aggregate morphologies were hard to be formed even when the copolymer concentrations were increased to 6 wt %.

It is easy to be understood for the aggregate morphology transition by increasing the initial copolymer concentration. It has been reported that in thermodynamics the equilibrium structure of the aggregates is controlled mainly by the force balance of three parameters.[44] The effect of changing the copolymer concentration on the aggregates morphology can be understood by considering that the aggregate number (N_{agg}) is a function of the total copolymer concentration (C) and the critical micellization concentration of the copolymer (cmc).[45,46] The relationship can be written as

$$N_{agg} \sim (C/\mathrm{cmc})^{1/2} \qquad (1)$$

The critical micellization concentration is mainly a function of water content in the solution. Therefore, at constant water content, N_{agg} should increase with the copolymer concentration. Because the dimensions of the micellar cores are a function of the N_{agg}, as the copolymer concentration increases, the morphology transition can take place at some point when the degree of stretching of the PS blocks in the core has increased to some critical value of the extension.

3.2. Aggregate Morphology Transition of the Block Copolymer Induced by Adding PDP. Figure 3 contains a series of TEM micrographs of aggregates prepared in DMF/water (containing 7 wt % water) at fixed initial copolymer concentration of 1 wt %, but with varying concentration of PDP. In the absence of PDP, this system forms spherical micelles (with small fraction of very short rods, see Figure 2b). Thus, it is apparent that PDP can induce aggregate morphological transition in the P4VP-*b*-PS-*b*-P4VP assemblies. At a higher PDP concentration, i.e., lower R, the aggregate morphologies are vesicles and some compound vesicles. The compound vesicles (in Figure 3a) may result from the fusion of some small vesicles or trapping small vesicle in a bigger one. The vesicular nature (Figure 3a,b,d) was evidenced from the TEM micrograph demonstrating a higher transmission in the center of the aggregates than around their periphery, coupled with the AFM height image (Figure 4a) which shows the aggregates to be spherical.[21] When the R was increased to 20, networks and looped morphologies with small fraction of vesicles can be obtained (Figure 3c). The networks were composed of branched and looped microstructures. The branched and looped structures have recently been reported from amphiphilic block copolymer in aqueous solution.[2,43,47–49] The diameters of the wormlike micelles are uniform and slightly higher than that of the PDP free block copolymer micelles. When we further increased the R, the aggregate morphologies became mixtures of short rods and small vesicles, as can be seen

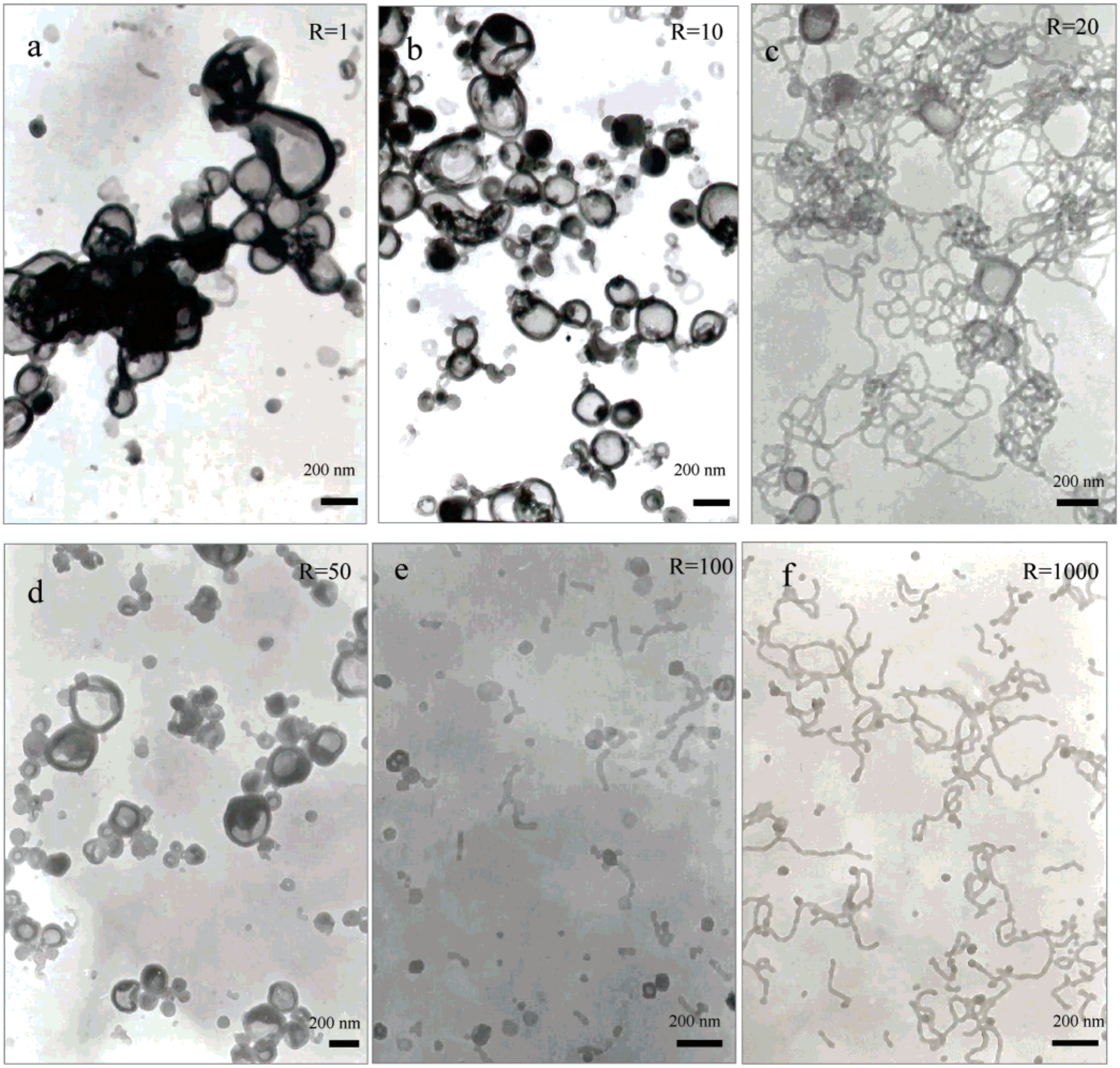

Figure 3. TEM images of aggregate morphologies formed from the block copolymer (1 wt %) in DMF/water mixtures by adding different amount of PDP.

from Figure 3e. The striking feature is that when *R* was increased to 1000, the aggregate morphology was cylinders (rods), as can be seen from TEM image (Figure 3f) and AFM height image (Figure 4b). At that concentration, the ratio of the 4VP units to PDP units was 1000 to 1, indicating that trace amount of PDP addition can change the aggregate morphology. The detailed information of the PDP effects on the aggregate morphologies of the triblock copolymer in DMF/water mixtures is listed in Table 1.

3.3. Kinetic Aspects of the Aggregate Morphology Transitions. In this study, two methods of sample preparation were employed to study the effect of PDP addition on the aggregate morphology of the block copolymer. The first method involved preadding PDP into the copolymer solution before water addition. As compared to the standard method described in the Experimental Section, in the second method, PDP was added after water content reached 7 wt %. The other sample preparation procedure was kept the same as the first method.

The purpose of using the two preparation methods is to test the equilibrium nature of the system. On the other hand, it can be learned from this of the interaction of the PDP and the P4VP chains. The final aggregate morphologies by TEM we obtained from the two methods were nearly the same, indicating that the solution preparation procedure has no effect on the final aggregate morphologies. In addition, this result indicated that the aggregate morphologies after 3 days' annealing were in equilibrium state.

To study the kinetics process of the aggregate morphology transition, samples were extracted from the solution mixture at different time during the annealing process for final aggregates formation (vesicles, $R = 10$, for example). At present water content (7 wt %) in this study, the chain mobility is very low, so that intermediate micellar morphologies can be easily trapped. The

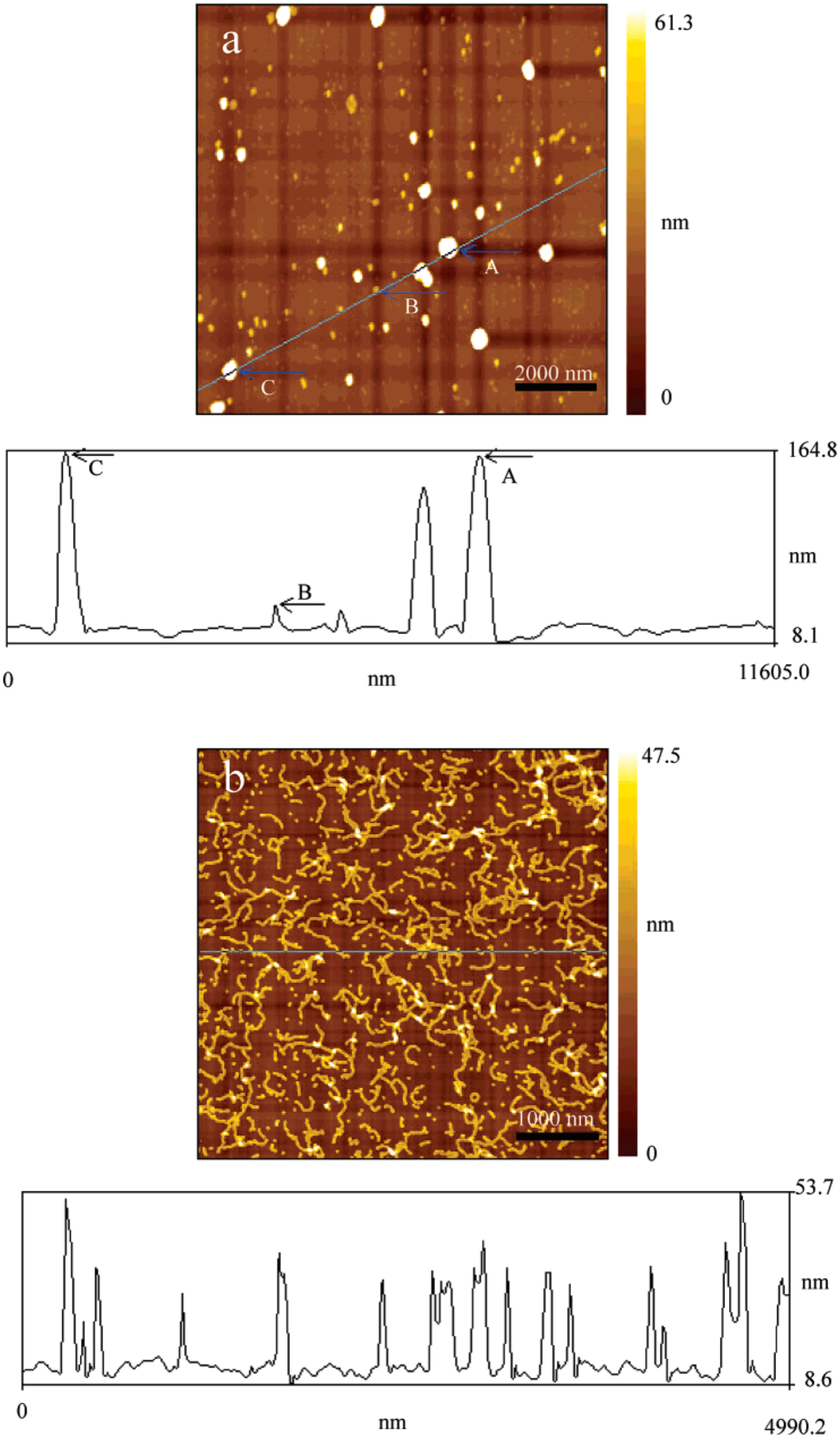

Figure 4. AFM height images of aggregate morphologies formed from 1 wt % P4VP$_{43}$-*b*-PS$_{366}$-*b*-P4VP$_{43}$ with adding different amount of PDP: (a) $R = 50$; (b) $R = 1000$.

morphologies of the extracted aggregates were quenched by quickly adding the extracted solutions to an excess of water. The intermediate structures can be trapped by using this method and then studied by TEM. It was found that the aggregate morphology transition undergoes a series of intermediate structures. Figure 5 shows TEM images of the aggregate morphologies at different annealing time of the morphological transition. At the beginning of water addition to 7 wt %, the aggregate morphologies were short rods (Figure 5a). The aggregates morphologies changed to long wormlike micelles (rods) (Figure 5b); wormlike micelles coexisted with lamellae structures and unclosed bilayers (see Figure 5c–e) and vesicles (Figure 5f) with increasing

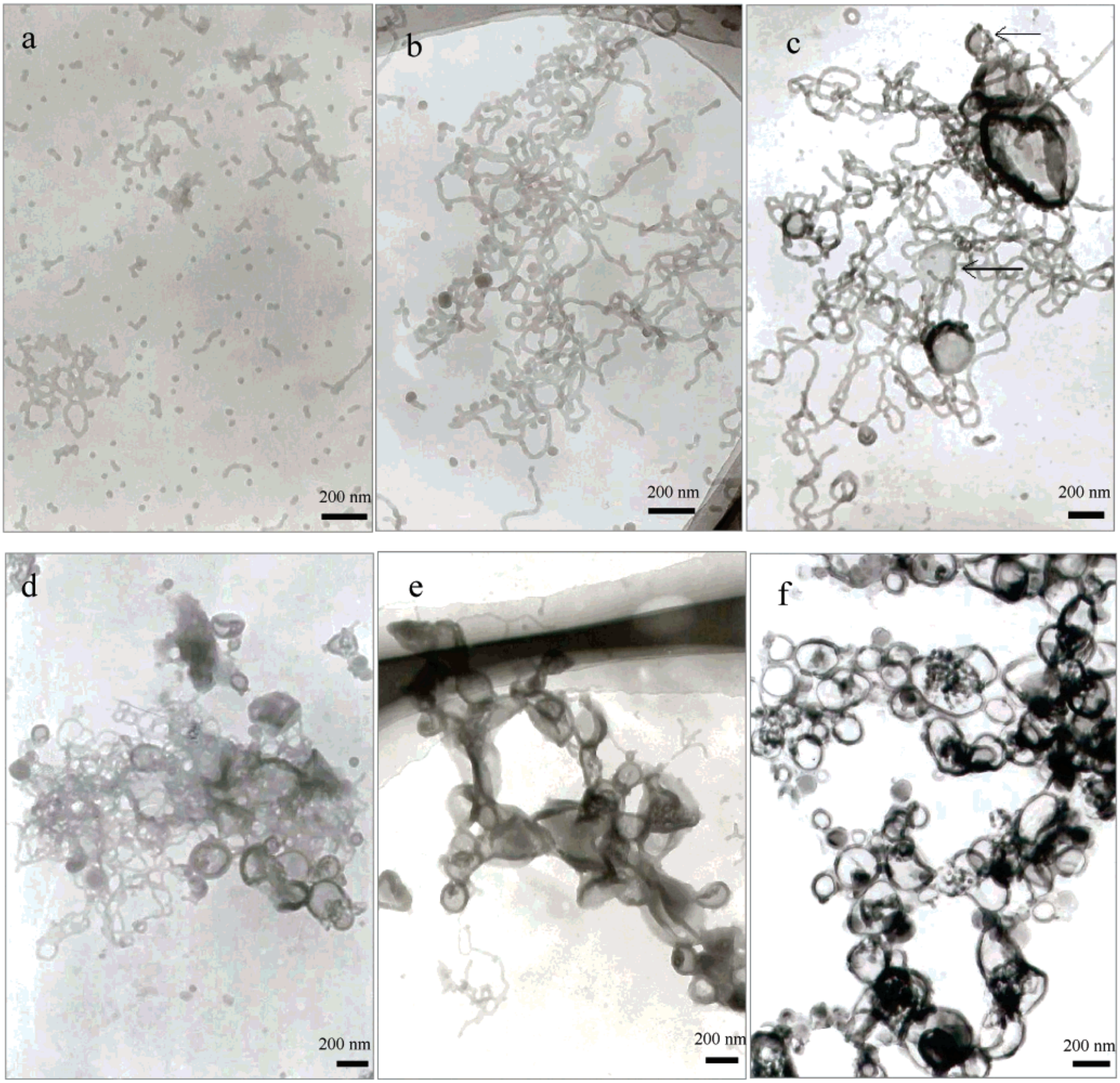

Figure 5. TEM images of 1 wt % block copolymer aggregate morphologies by adding PDP (R = 10) with different annealing time: (a) 0, (b) 8, (c) 25, (d) 48, (e) 57, and (f) 72 h.

Table 1. Aggregate Morphologies Formed from 1 wt % P4VP$_{43}$–PS$_{366}$–P4VP$_{43}$ by Adding Different Amounts of PDP, *m*-Cresol, and PDB[a]

ratio of 4VP/surfactant, R	PDP	m-cresol	PDB
1	V, CV	S, V, R	V, S, CV
10	V, R	S, R, V	R, L, N, V
20	V, N, L	S, R	R, L, V
50	V, LR, L, S	S	R, L, V
100	V, LR, S	S	R, L, S
200	R	S	R, S, L
500	R, S	S	S, R
1000	R, S	S	S, R

[a] Key: V, vesicles; CV, compound vesicles; L, loop; R, rods; S, spheres; LR, long rods, N, networks. If two or more morphologies are listed, the major one is given first.

the annealing time. The unclosed bilayer structures (Figure 5c, see arrows), which may be the precursor of the vesicles, appeared when the annealing time was 25 h. The lamellae and the unclosed bilayers may result from the fusion of the wormlike micelles. The amount of wormlike micelles and the unclosed bilayers became less and less, whereas the amount of vesicles became more and more with further increasing the annealing time. After 3 days, nearly all of the aggregates were vesicles (see Figure 5f), while the wormlike micelles and unclosed bilayers cannot be observed any more. Therefore, we can conclude that the vesicles were formed from initial wormlike micelles. The aggregate morphologies after the water addition were not in the stable state. The co-self-assembly of the block copolymer and the PDP formed cylindrical morphologies and then rearranged to form vesicles. The process of the aggregate morphological transition from cylindrical micelles to vesicles induced by PDP addition was slow, and the annealing (or stirring) can promote the aggregations toward equilibrium state.

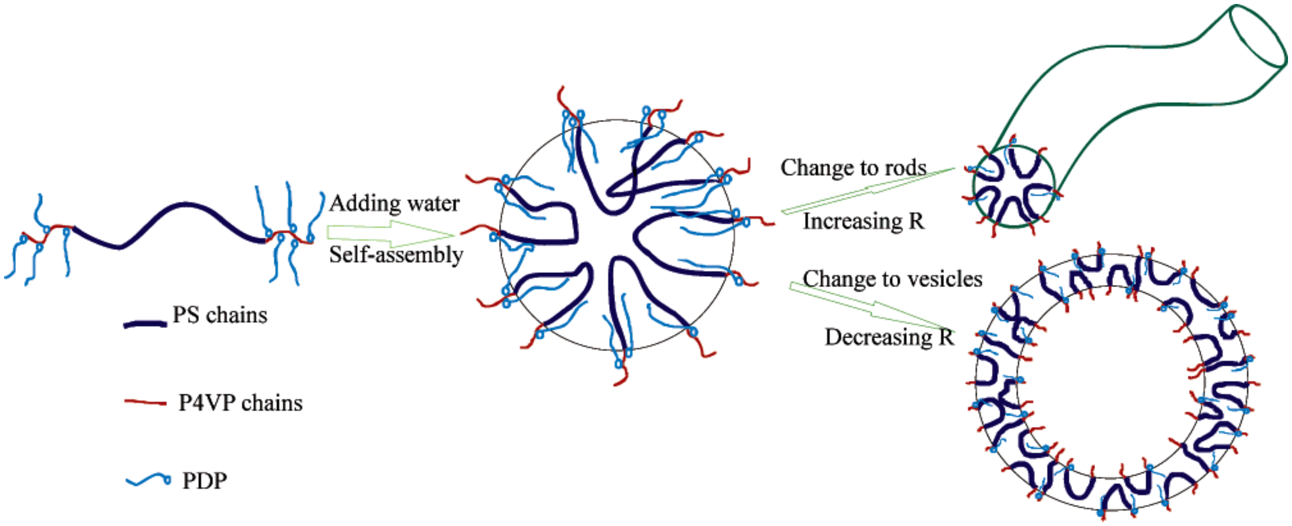

Figure 6. Schematic illustration of proposed morphological transition mechanism of the block copolymer aggregates by adding PDP.

3.4. Possible Aggregate Morphological Transition Mechanism and Experimental Argument. PDP, like P4VP-*b*-PS-*b*-P4VP, is an amphiphile. Each PDP molecule has a headgroup composed of a hydroxyl, while the surfactant tail is a linear C_{15} alkyl chain. Although PDP is amphiphilic, it cannot self-assemble in the solvent (DMF/water) mixtures in this study. When PDP was added into the copolymer solution, the PDP molecules adsorbed onto the P4VP segments and formed hydrogen-bonded complexes (Figure 1). The hydrogen bonding between the PDP and P4VP chains is strong. The structures of the block copolymer complex were similar to comblike (see Figure 1). The comb copolymer-like molecules obtained by hydrogen bonding between flexible polymers and nonmesogenic amphiphiles represent a new class of supramolecular materials exhibiting a very rich phase behavior.[50] Recently, Jiang et al. studied the micellization of the complex of diblock copolymers with small molecules and reported the formation of solid spheres, cylinders, vesicles, etc., from the complexes in solutions.[29−31] In our study, hydrogen bonding not only takes place between pyridine units and PDP units but also may exist between pyridine units and water, pyridine units and DMF, PDP units and water, and PDP units and DMF. In this case, the final complex is the result of the balance of all these factors. Of the four components, the P4VP block chain is the strongest Lewis base while the PDP is the strongest Lewis acid. Thus, hydrogen bonding between P4VP-*b*-PS-*b*-P4VP and PDP units should be the most predominant. During the water addition into the initial copolymer solutions, the quality of the solvent for the middle PS blocks gradually decreases. The micellization of the hydrophobic segments (i.e., PS blocks) starts when the water content reaches a critical point, that is, a critical water content or CWC, usually given in wt % of water. As the water content increases, the concentration of unimers in the solution reduces, and the common solvent is gradually removed from the micelle core, which reduces the mobility of the chains. The resulting aggregates rearrange to form different morphologies with different amount of PDP addition during the annealing processes.

As has been given in the Introduction, there are three main factors that influence the aggregates morphologies of block copolymer. PDP molecules interact with the copolymer aggregates in two ways. The strong physical interaction of the hydrogen bonding between the P4VP units and PDP can lead to the change of the interaction among the shell building blocks (P4VP). This is one of the morphological transition reasons. Because of the hydrophobic character of the long tail of PDP, it is believed that they promote architectural changes by inserting their hydrophobic chains into the core of the aggregates. They act as spacers between the corona chains, leading to an increase in the size of the core of the aggregates. Meanwhile, the interfacial energy between the corona and the core is changed due to the increase of the amount of PDP. Bronstein et al. and Eisenberg et al. observed similar behavior in systems of PS-*b*-PEO and PS-*b*-PAA aggregates in the presence of sodium dodecyl sulfate (SDS), respectively.[51,52] The degree of PS stretching increases in response to the increase in the core diameter. This increased chain stretching is subject to an entropic penalty, and in the present system the aggregates undergo morphological change in order to relieve this entropy strain.[10] The aggregate morphology transition mechanism proposed is given in Figure 6.

It should be noticed that the two main factors, i.e., hydrogen bonding between the P4VP units and PDP, hydrophobic tails inserting into the micelles cores, for the morphological transition coexisted. The final morphologies are the results of the cooperation of the two factors. However, which one is more important for the morphological transition?

To make it clear, we used *m*-cresol to replace the PDP because the only difference between PDP and *m*-cresol is that PDP has long hydrophobic chains while *m*-cresol has not. The interaction between the copolymer and *m*-cresol is only the hydrogen bonding. A study of the effect of *m*-cresol on the P4VP-*b*-PS-*b*-P4VP aggregates was carried out in parallel to the study with PDP in order to analyze the nature of the interaction of the hydrogen bonding with P4VP chains and to determine how this interaction affects the block copolymer aggregate morphology from this specific copolymer under comparable conditions. In addition, *m*-cresol was added to the solutions containing the copolymer aggregates to evaluate the effect of the linear hydrocarbon chain on the aggregate behavior. Figure 7I shows the TEM images of the aggregate morphologies from the copoly-

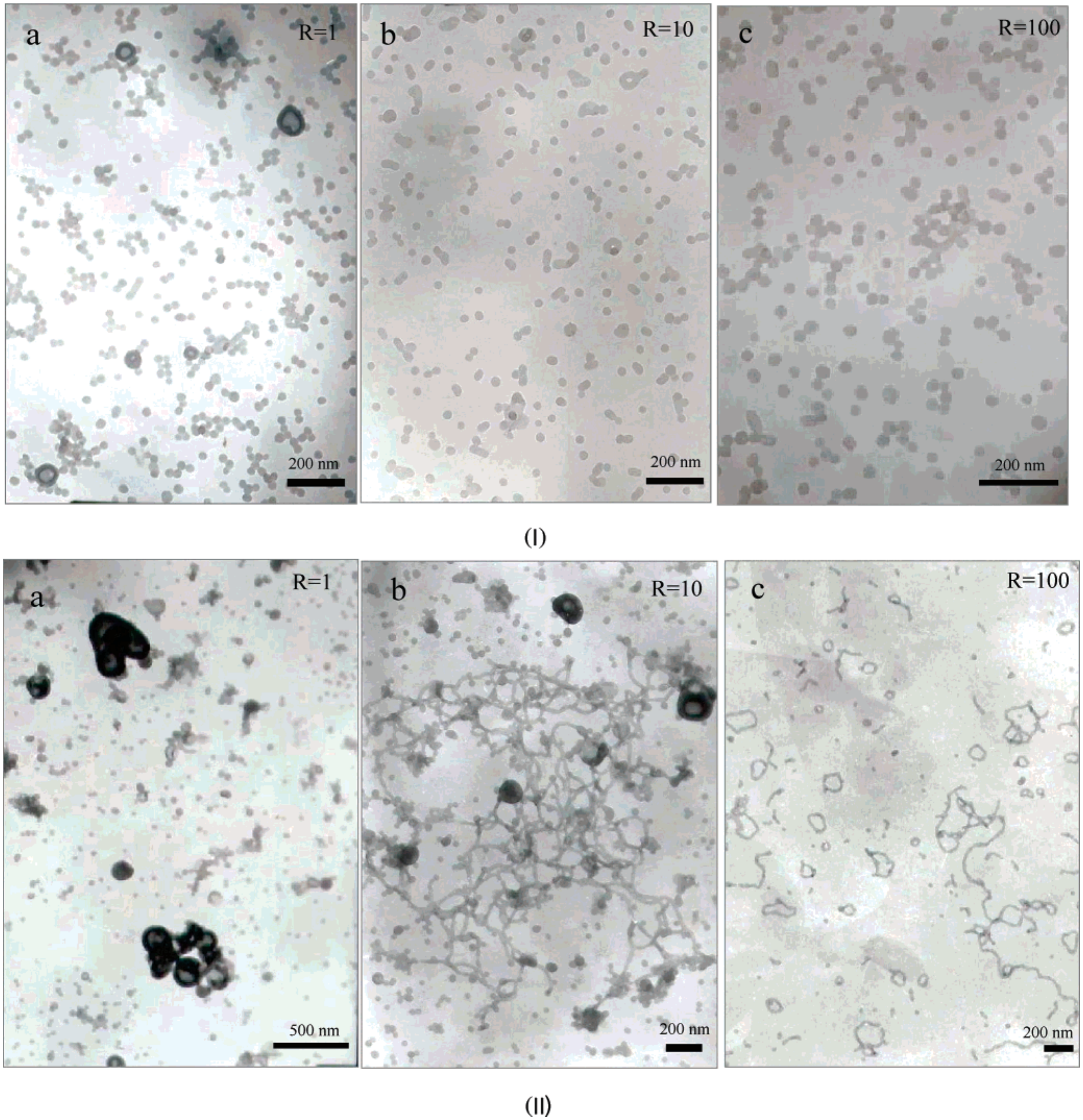

Figure 7. TEM images of 1 wt % block copolymer aggregate morphologies by adding different amount of *m*-cresol and PDB (for the purpose of comparison with those by adding PDP): (I) adding *m*-cresol; (II) adding PDB.

mer by adding desired amount of *m*-cresol. Compared Figure 7 with Figure 3, we can see clearly that the PDP have a more striking effect on the aggregate morphologies than *m*-cresol under the same adding amount (*R*). The detailed information is given in Table 1. The *m*-cresol can only change the aggregate morphology slightly.

For the purpose of comparison with *m*-cresol, pentadecylbenzene (PDB) was also used to replace the PDP to test the effect of PDP on the morphologies transition since the only difference is that PDB has no hydroxyl and cannot form hydrogen bonding with P4VP. The TEM images of the aggregates morphologies from the copolymer formed by adding desired amount of PDB is given in Figure 7II. By comparing Figure 3 with Figure 7 and the results in Table 1, we can see clearly that PDP and PDB have more striking effect on the aggregate morphologies than *m*-cresol, while PDP have a slightly more visible effect than PDB under the same *R*. This phenomenon possibly suggests that the inserting of the hydrophobic species into the core of the P4VP-*b*-PS-*b*-P4VP aggregates has a greater influence on the force balance governing the structure of the aggregates than the hydrogen bonding. The hydrogen bonding between the PDP and the P4VP and the inserting of the hydrophobic tail of PDP make it anchor the headgroup at the interface between the core and the corona of the micelles. Therefore, it would be seen from this argument that dual nature of the effect of PDP on the block copolymer aggregates makes it clear that PDP is a better morphologic transition agent than *m*-cresol and PDB. Meanwhile, this partitioning of the hydrophobic alkyl chain inserted into the core of the aggregates is similar to increasing the core dimension by increasing the copolymer concentration as has been described above. However, the change of initial copolymer concentration has less effect than the PDP addition on the morphological transition.

From the argument above, we can conclude that the main reason for the morphological transition by adding PDP is that the hydrophobic chains inserted into the core of the PS segments. However, the hydrogen bonding makes the PDP molecules interact with the corona blocks and makes comblike structures more stable, which can induce the aggregate morphology transition by co-self-assembly of the copolymer and PDP.

4. Conclusions

A facile method that can induce the aggregate morphological transition for block copolymer in selective media was successfully introduced in this study. The triblock copolymer exhibits spheres in 1 wt % of the surfactant (PDP)-free solution. However, the aggregates morphologies changed from short rods to networks and looped structures and then to vesicles and compound vesicles by increasing the PDP adding amount at the same copolymer concentrations to the PDP-free solutions. The striking feature is that trace amount of PDP ($R = 1000$) can change the aggregates to wormlike morphologies. The reason for the aggregate morphology transition had been discussed. The nature of the influence that PDP exercise over the copolymer aggregates was determined by comparing the results with those obtained for the addition of the *m*-cresol (without the long tail of linear alkyl) and PDB (without hydroxyl group). The interactions of both the hydrophobic chain and the hydrogen bonding of the PDP headgroup with the block copolymer molecules affect the architecture of the copolymer aggregates. There are two main reasons for the morphological transition, i.e., hydrogen bonding weakens the interaction among the corona-building blocks and hydrophobic chains of the PDP inserted into the core of the aggregates. The latter one is the more important reason for the morphological transition which had been proved in experiments. Using the hydrogen bonds of block copolymers with small molecular amphiphiles opens up the possibility of reaching a certain fraction to produce a desired aggregate morphology. Subsequently, with a selective solvent one can selectively extract the small molecular amphiphiles by rupture of the hydrogen bonds after quenching the aggregates. After removing the amphiphiles by dissolution, the resulting patterns can be stable. It provides a method over the aggregate architecture transition, which is important for any potential application of these systems.

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