Macromolecules **1999,** *32,* 2239−2249

Thermodynamic vs Kinetic Aspects in the Formation and Morphological Transitions of Crew-Cut Aggregates Produced by Self-Assembly of Polystyrene-*b*-poly(acrylic acid) Block Copolymers in Dilute Solution

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Received July 1, 1998; Revised Manuscript Received January 12, 1999

ABSTRACT: Thermodynamic vs kinetic aspects of the formation of crew-cut aggregates of various structures prepared from polystyrene-*b*-poly(acrylic acid) diblock copolymers in DMF/water mixtures are explored. In particular, the reversibility of the transitions between the crew-cut aggregates of various morphologies is studied by “jumps” in the polymer or ion concentration at various water contents. The aggregates are prepared by two different methods: micellization is induced either by the addition of water to polymer/DMF solutions or by the direct dissolution of the polymer in DMF/water mixtures. It is shown that as the polymer concentration increases, the morphology of the aggregates changes from spheres to rodlike micelles, to interconnected rods, and then to bilayers. As the water content increases, the boundaries for the formation of the different morphologies move toward lower polymer concentrations. The thermodynamic vs kinetic control of the morphology depends largely on the water content and the method of aggregate formation. When water content is lower than 6.5 wt %, the formation of the aggregates is controlled by thermodynamics of micellization, and the morphological transitions are reversible. When the water content is between 7.5 and 9.5%, the morphology of the aggregates depends on the method of aggregate preparation. In this range of water contents, the morphological reversibility decreases significantly; for example, transitions from spheres to rods and then to bilayers are not achievable kinetically within a period of several days. The slow kinetics for the morphological transitions are mainly due to a low rate of polymer chain exchange and the strong repulsive interactions among the aggregates. The kinetics can be accelerated by decreasing the strength of the repulsive interactions and increasing the efficiency of adhesive collisions between the micelles through addition of ions or of polymer. Two different mechanisms for the morphological transitions as well as their kinetic aspects are discussed.

1. Introduction

It has been known for many years that block copolymers in a selective solvent for one of the blocks form micelles or aggregates as a result of the association of the insoluble blocks.[1] The micelles are stabilized in solution via the interactions of the soluble blocks with the solvent molecules. Depending on the composition of the block copolymers, two types of micelles can be distinguished: star and crew-cut. Although there is no sharp boundary between these two classes of aggregates, the former is usually made from block copolymers in which the corona-forming blocks are much longer than the core-forming blocks, while the latter is made from copolymers in which the core-forming blocks are much longer.

Different systems of star micelles have been studied extensively for about 3 decades.[1] The micelles are usually spherical, because the repulsive interactions among the corona chains are strong, due to the relatively high density of corona chains on the core surface. The dense packing of the corona chains can be judged from the fact that the expected coil dimensions of the corona chains in a good solvent are usually much larger than the actually occupied area per corona chain on a spherical surface drawn through the middle of the corona shell.[2] Because of the high packing density, any further decrease of the area per corona chain will increase the deformation energy of the corona chains and, correspondingly, the repulsive energy among the corona chains. Therefore, the structure of star micelles is mainly controlled by the minimization of the surface energy, which, in turn, is opposed by the increase of the intercorona chain repulsion.

Compared with star micelles, spherical crew-cut aggregates usually have much larger aggregation numbers.[3] This is due to the fact that the occupied area per corona chain, as well as the coil dimensions, decrease as the length of corona-forming blocks decreases. To decrease the interfacial energy attributed to each corona chain, the aggregation number and the core size increase. Because of the large aggregation number, the stretching of the PS chains in the cores becomes more important in restricting the growth of the core size. Therefore, the formation of crew-cut micelles is controlled by a force balance principally involving three factors, i.e., the stretching (deformation) of the core-forming blocks in the core, the surface tension between the micelle core and the solvent outside of the core, and the intercorona−chain interactions.[4−6] In particular, the minimization of the interfacial energy is balanced not only by an increase of the intercorona chain repulsion but also by an increase in the chain stretching of the core-forming blocks.

One of the noteworthy phenomena associated with crew-cut aggregates is the accessibility of a wide range of morphologies;[4,5,7−10] these include spheres, rods, vesicles, lamellae, large compound vesicles, a hexagonally packed hollow hoop structure, large compound

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10.1021/ma981039f CCC: $18.00

micelles, etc. The morphological continuity parallels to that known for block copolymer in bulk. The morphology of the aggregates is a function of several variables, such as block copolymer composition and concentration,[4,11] the type and concentration of added ions,[5] the concentration of added precipitant,[12] and the nature of the common solvent used in the preparation.[13] The morphogenic effects of the above parameters can, in general, be ascribed to their influence on the force balance during the formation of the aggregates.[14]

Because the fraction of insoluble blocks in the copolymers is large, crew-cut aggregates are conventionally prepared by first dissolving copolymers, such as polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA), in a common solvent for both PS and PAA blocks, e.g., dimethylformamide (DMF). Subsequently, deionized water is added slowly such that the quality of the mixed solvent for the long PS block gradually decreases. At a certain water content, the PS blocks start to associate to form the micelles.[4,5,15] In the early stages of micellization, the PS cores of the aggregates are usually highly swollen by the common solvent. The rate of polymer chain exchange among the aggregates can be very fast. As the water content increases, the concentration of unimers decreases, and the common solvent is gradually removed from the micelle core, which reduces the mobility of the chains. At some point in the water content range, the structures of the aggregates become kinetically locked over the experimental time scale.[15] This process is analogous to freezing the structures by decreasing the temperature in copolymers in bulk and in copolymer/homopolymer blends.

An important aspect of copolymer micelle studies involves the dynamics of the chain exchange between micelles. An equilibrated system must be in a dynamic equilibrium, with the micelles exchanging chains with one another. The chain exchange and hybridization of block copolymer micelles have been studied by several methods, including sedimentation velocity measurements,[16,17] fluorescence,[18,19] and theoretical calculations.[20,21] The rate of chain exchange was found to be influenced by many factors, such as the degree of incompatibility of the solvent and the insoluble block, the copolymer composition, and temperature. For example, the micelle structure may become totally frozen when the solvent is very poor with respect to the micelle core-forming blocks.

The dynamics of copolymer chain exchange among spherical crew-cut aggregates were also studied by mixing two solutions of micelles of different sizes (which had been prepared separately from different copolymers) at various water contents.[15] For the two solutions of micelles formed from PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33) copolymers, respectively, it has been found that when the water content is less than 6 wt %, the rate of chain exchange is still fast. However, when the water content is increased to 10 wt %, chain exchange over the time scale of 1 day becomes negligible, and the structures of the micelles are kinetically frozen.[15] The decreased rate of chain exchange or micelle hybridization at higher water contents are many caused by a decreased critical micellization concentration and a decreased degree of swelling of the PS cores.

While the rate of chain exchange among spherical micelles has been studied, the thermodynamic vs kinetic aspects of the transitions between crew-cut aggregates of different morphologies still remain unexplored. In this paper, we report on a study which explores the influence of different preparation procedures, water content and polymer concentration on the formation of the crew-cut aggregates of polystyrene-*b*-poly(acrylic acid) diblock copolymers in DMF/water mixtures, and the reversibility of the morphologies of crew-cut aggregates. It is shown that although the morphology is mainly controlled by thermodynamics, the achievement of a morphological transition is largely influenced by kinetics under a wide range of conditions, especially of the water content. The kinetics mainly depend on the hydrodynamic interactions among the aggregates and the chain mobility in the core. Two different mechanisms for the morphological transitions as well as their kinetic aspects are discussed.

2. Experimental Section

The polymer used in this study is a polystyrene-*b*-poly(acrylic acid) diblock, PS(190)-*b*-PAA(20); the numbers indicate the degree of polymerization of the blocks. The polydispersity of both the polystyrene blocks and the diblocks is 1.05, measured by size exclusion chromatography. The copolymer was synthesized by sequential anionic polymerization. A description of detailed procedures can be found in our previous paper.[4]

The micelles or aggregates were prepared by two different methods, i.e., water addition (WA) and direct dissolution (DD). The first (WA) involves the dissolution of the block copolymer in DMF, a common solvent for both PS and PAA blocks, and subsequent addition of deionized water to the solution to induce aggregation of the PS blocks. After a predetermined water content between 5.5 and 9.5 wt % had been reached, the water addition was stopped for 5 days. In the second method (DD), the aggregates were formed by direct dissolution of the copolymers in DMF/water mixtures with water contents ranging from 5.5 to 9.5 wt %. In both methods, after the aggregate solutions had been stirred at a constant water content for a period of 5 days, more water was added dropwise to freeze the aggregate structures. Finally, aqueous solutions of the aggregates were obtained by dialyzing the resulting colloidal solution against water to remove DMF.

The selection of the water content range for this study is based on the following considerations: it was found that when the water content is relatively low, i.e., less than 5 wt %, the structure of the aggregates is very labile. In the course of further water addition after the dissolution step, the structure may still change somewhat initially, but then it becomes frozen. If the water content is too high, because of the lowered solubility and chain mobility, the kinetic process of polymer self-assembly and structural rearrangement of the aggregates can be so slow that an extremely long time is needed to dissolve the polymers and to establish a dynamic equilibrium between aggregates and polymer unimers. The range of water content from 5.5 to 9.5 wt % provides a satisfactory window. The kinetics of the morphological transitions are found to be very sensitive to the water content. For example, a morphological transition usually takes minutes to complete at 5.5% water content, but needs days at 8.5% water content. Therefore, the structures of the aggregates in the solvent mixture with a water content in the range used in the present study can very easily become kinetically locked when more water is added. Once the structure of the aggregates formed at some water content has been frozen, it becomes possible to study the structural transitions and boundaries of different morphologies as a function of different variables at a constant water content, i.e., a fixed Flory−Huggins χ parameter between the PS blocks and the solvent.

The morphologies of the aggregates were observed on a Phillips EM400 transmission microscope. A more detailed description of the sample preparation techniques for TEM can be found in our previous publications.[4,5]

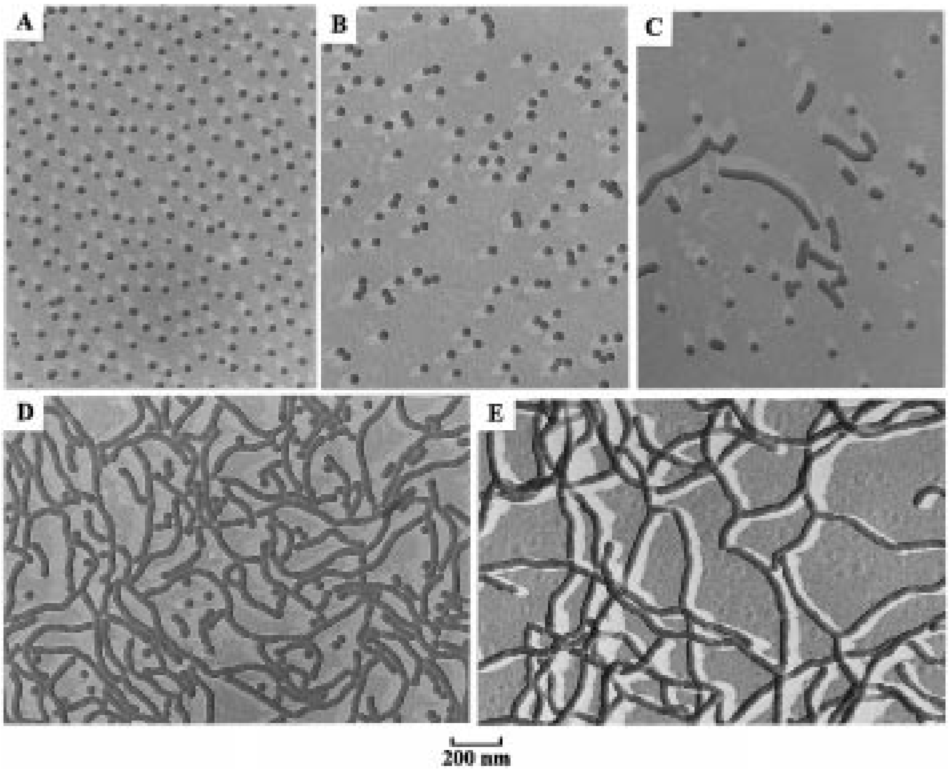

Figure 1. Aggregates made by dissolution of the diblocks in a 94.5/5.5 (w/w) DMF/water mixture to different final copolymer concentrations. Key: 1.0 (A), 2.0 (B), 2.5 (C), 3.0 (D), and 3.5 wt % (E).

3. Results and Discussion

3.1. Micellization of the Copolymers in Water/DMF Mixtures Containing 5.5 wt % Water. The addition of water to DMF decreases the solvent quality for the PS blocks. Therefore, the water content plays a very important role in the course of micellization. Several aspects of the micellization, such as the critical micellization concentration and the chain mobility,[15] are influenced by the water content. In this section, we describe the formation of the copolymer aggregates when the water content is relatively low.

Figure 1 shows the aggregates made by direct dissolution of the copolymer to different final concentrations in a DMF/water mixture containing 5.5% water. As expected, the aggregate morphology depends on the copolymer concentration. Specifically, as shown in Figure 1A, when the copolymer concentration is 1.0 wt %, spherical micelles with an average core diameter of 29 nm are formed. At 2.0% copolymer, spherical micelles are still formed (Figure 1B); however, the average size increased to 34 nm. As shown in Figure 1C, at a concentration of 2.5%, a mixture of spherical micelles and short rods is obtained. When the polymer concentration is 3%, rodlike micelles are formed, but some spheres are still seen (Figure 1D). At 3.5% copolymer, as shown in Figure 1E, very long wormlike micelles are seen. Branches are also frequently encountered, as has been discussed in our previous papers.[14] These morphological transitions can be ascribed to the fact that the aggregation number of the micelles and therefore the micelle core diameter increases as a function of the polymer concentration. At some point of the copolymer concentration, the micelles change morphology from spheres to rods to reduce the entropic penalty associated with the increase of the degree of stretching of the core-forming PS blocks.

It is found that if the micelles are prepared by the WA method with the water addition halted at 5.5% for a period of 5 days, the aggregate morphology as a function of the copolymer concentration is identical with that shown in Figure 1. This suggests that under these circumstances (i.e., the water content and the experimental time period), the morphologies of the copolymer aggregates are controlled by the thermodynamics of micellization. Under thermodynamic control, the structures of the aggregates depend on the compositions of the system and are independent of the detailed procedures of aggregate preparation.

Reversibility between the different morphologies is an important aspect of the proof of thermodynamic control. It is demonstrated by diluting a more concentrated solution of the polymer aggregates to different polymer concentrations or by adding ions, while keeping the DMF/water ratio constant. It is found that aggregates prepared directly from a relatively dilute solution can also be obtained by dilution of a more concentrated solution with a different morphology. For example, as shown in Figure 1E, long rods are formed in a 3.5% polymer solution. When this solution is diluted with a DMF/water mixture to a copolymer concentration of less than 2%, the long rods change to small spheres. The morphological transition, which can be followed from the change in turbidity of the solution, is complete within a few minutes.

When the morphology of the aggregates is under thermodynamic control, it is expected that the change of spheres back to rodlike micelles can be controlled by adding an appropriate amount of NaCl ions. Due to the screening of the electrostatic field,[5] the addition of NaCl decreases the strength of the repulsion among the PAA corona chains and hence influences the force balance controlling the morphology. One example is the addition of NaCl in an amount equivalent to the concentration of the acrylic acid (AA) units of the copolymer in solution (the molar ratio of added NaCl to the AA units, R, is 1.0). It is found that although spherical micelles are still formed in 1.0% polymer solution after the addition of NaCl to a final concentration of 9 mM ($R = 1.0$), the average core diameter of the micelles is increased to 35 nm, compared to 29 nm in Figure 1A without added NaCl. After the addition of NaCl, rodlike micelles start to form in a 1.5% polymer solution at a NaCl concentration of 15 mM; while without the salt, the polymer concentration for the rodlike micelle formation needs to be 2.5%. Very long wormlike micelles are formed at 2.5% polymer with the addition of NaCl to a concentration of 23 mM, compared to those shown in Figure 1D obtained from 3.5% polymer without NaCl addition.

The reversibility between the different morphologies at 5.5% water content has also been examined by alternate additions of NaOH and HCl. Because the addition of NaOH or HCl changes the degree of ionization of the PAA, the electrostatic repulsions among the corona chains change, which, consequently, influences the thermodynamics (or the force balance) controlling the morphology.[5] Specifically, the addition of NaOH increases the degree of ionization and therefore the charge density, and the addition of HCl affects these in an opposite direction. It is found that when NaOH was added to a final concentration of 1.0 mM ($R = 0.03$) to a 3.5% polymer solution, the wormlike micelles (shown in Figure 1E) changed to spherical micelles. The morphological transition from rods to spheres induced by the addition of NaOH is a result of the increased repulsions among the PAA segments. When the added NaOH was neutralized by adding an equivalent amount of HCl, the spherical aggregates changed back to wormlike micelles. Each cycle of NaOH and HCl additions (at 1.0 mM) also produces an equivalent amount of NaCl. However, because the morphogenic effect of NaCl is much weaker than those of NaOH and HCl, it only becomes pronounced after several cycles of the NaOH and HCl additions. It also needs to be pointed out that each addition of an aqueous solution of NaOH or HCl also increases the water content slightly. Because the morphological boundaries of the aggregates are also a function of water content, the change of water content accompanying each addition of ions was kept as low as possible, e.g., less than 0.15%.

3.2. Micellization of Copolymers in DMF/Water Mixtures with Water Contents above 6.5%. In the previous section, it was shown that the micellization of the copolymer as well as the morphology of the aggregates are controlled by thermodynamics at a 5.5 % water content. Thermodynamic control should obviously also be operative when the water content is below 5.5%. However, as the water content increases, it is expected that the kinetics should become more and more important. Furthermore, because the Flory–Huggins χ parameter between the PS blocks and the solvent increases with increasing water content, thermodynamics of micellization also change as a function of water content. In this section, we discuss the formation of crew-cut aggregates in DMF/water mixtures with water contents ranging from 6.5 to 9.5%. We present the results for aggregates prepared by the method of direct dissolution first, and then those for aggregates prepared by the method of water addition.

3.2.1. Micelles Prepared by the Method of Direct Dissolution (DD). 3.2.1.1. DMF/Water Mixtures Containing 6.5% Water. For the aggregates prepared by the DD method to different final polymer concentrations, it is found that spherical micelles are formed in a solution of 1% block copolymer. When the polymer concentration is increased to 1.5%, short rods and small spheres coexist. At a 2.5% of polymer, very long wormlike micelles are formed. Finally, in a solution of 3.5% polymer, the major morphologies are interconnected (bicontinuous) rodlike aggregates and bilayers, as shown in Figure 2.

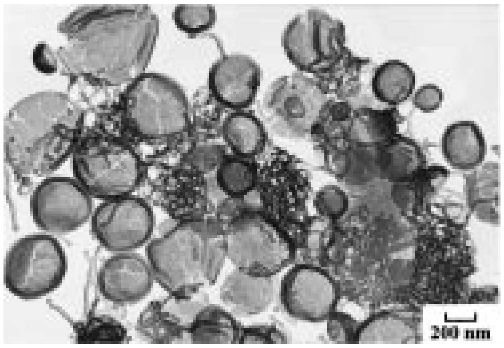

Figure 2. Aggregates made by dissolution of the diblocks in a 93.5/6.5 (w/w) DMF/water mixture to a final copolymer concentration of 3.5 wt %.

Compared with the aggregates formed in a mixed solvent containing 5.5% water, the boundaries for the morphological transitions in the 6.5% water system move to lower polymer concentrations. For example, at 5.5% water, the boundary for the transition from small spheres to rods is around 2.5% polymer. However, when the water content is 6.5%, this transition occurs between 1.0 and 1.5% polymer. The morphogenic effect of water content can be ascribed to an increase of the aggregation number with the water content, because the interfacial tension between the PS micelle core and the solvent increases and the critical micellization concentration decreases. As a result, the core dimension and the stretching of the core-forming blocks are increased.

To understand the reversibility of the morphologies of the aggregates formed at this water content, the morphological transitions between bilayer aggregates and rodlike micelles, and between rodlike micelles and small spheres, as induced by the addition of NaOH and HCl, were explored. It was found that, on addition of NaOH, the boundaries of the morphological transitions move to higher polymer concentrations. For example, the addition of NaOH to a concentration of 0.7 mM ($R = 0.03$) to an aggregate solution of 2.5% polymer changes long wormlike micelles to spherical micelles. In a solution of 3% polymer, bilayer aggregates and interconnected rods are formed without added NaOH; however, with added NaOH (0.8 mM or $R = 0.03$), short rods and spheres are the major morphologies. The original morphologies formed in the solution without added NaOH are reformed when the added NaOH is neutralized by an equivalent amount of HCl.

Since the common solvent content in the micelle core decreases as the water content increases, the mobility of the polymer chains in and out of the micelles is decreased at a water content of 6.5%, compared to that at 5.5%. Through the observation of the change in turbidity of the solution, it can be seen that the morphological transitions at 6.5% water content are completed within ca. 2 h of the addition of NaOH.

3.2.1.2. DMF/Water Mixtures Containing 8.5% Water or More. As the water content in the mixed

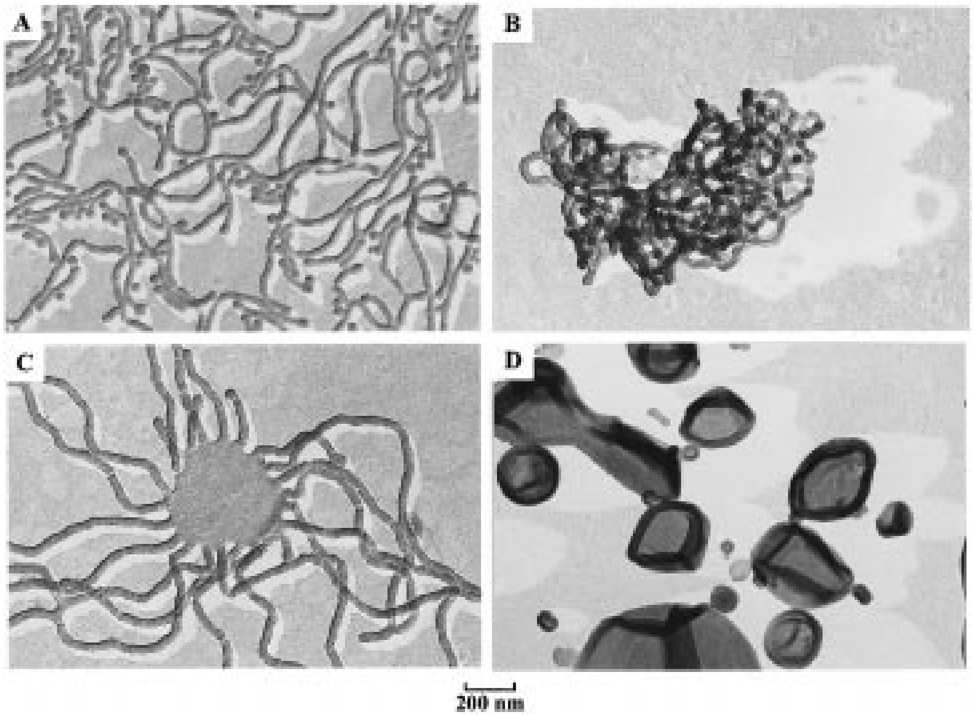

Figure 3. Aggregates made by dissolution of the diblocks in a 91.5/8.5 (w/w) DMF/water mixture to different final copolymer concentrations. Key: 0.5 (A), 1.0 (B and C), and 3.5 wt % (D).

solvent increases further, the boundaries of the formation of the aggregates of different morphologies move to even lower polymer concentrations. Figure 3 shows a set of TEM pictures of the aggregates made by direct dissolution of the copolymer to different concentrations in a mixed solvent containing 8.5% water. It is found that when the polymer concentration is 0.5%, rodlike micelles and spheres are formed, as shown in Figure 3A. Similar mixtures of rods and spheres are seen at 3% polymer in a solvent containing 5.5% water and at a 2% polymer in a solvent containing 6.5% water, respectively. When the copolymer concentration is 1%, very long wormlike micelles and interconnected rodlike aggregates are the major morphologies. One example of the interconnected rods is shown in Figure 3B. At this water content, because the chain mobility has become very slow, intermediate morphologies are easy to trap. Figure 3C shows one example of a trapped intermediate structure of the transition between rodlike micelles and the lamella, i.e., a lamella with rods extending from the edge. As the copolymer concentration increases further, bilayer aggregates are formed. Figure 3D shows an example of the aggregates formed in the solution of 3.5% polymer. Table 1 summaries the morphologies of the aggregates as a function of the water content and the polymer concentration. It is worth mentioning here briefly that, due to the hydrodynamic repulsions among the aggregates, the morphological transitions become only partially reversible at higher water contents. Details will be addressed in a later section of this paper.

3.2.2. Micelles Prepared by the Method of Water Addition (WA). 3.2.2.1. DMF/Water Mixtures Containing 6.5% Water. When the aggregates are prepared by adding 6.5% water to copolymer/DMF solutions, it is found that spherical micelles are formed when the polymer concentration is 1%. From an initial polymer concentration of 1.5%, a mixture of short rods and spherical micelles is formed. At a polymer concentration of 2.5%, as shown in Figure 4A, rodlike micelles are the major morphology, while spheres and vesicles are also seen. Compared to the rodlike micelles from 1.5 wt % copolymer solution, the average length of the rodlike micelles in this case is increased appreciably. At a copolymer concentration of 3.5%, a mixture of spheres, rods and vesicles is observed (Figure 4B), with the fraction of vesicles increased appreciably.

Table 1. Major Morphologies vs Water Content and Polymer Concentration for the Aggregates Prepared by the Direct Dissolution Method from PS(190)-*b*-PAA(20)

polymer concn (wt %)	water content in DMF (wt %)				
	5.5	6.5	7.5	8.5	9.5
0.5		S[a]	R, S	R, S	
1.0	S	S	LR	LR	B
1.5	S	S, R	LR, XR	XR, B	
2.0	S	R, S		B	
2.5	S, R	LR	B		
3.0	R, S				
3.5	LR	B, XR	B	B	

[a] Key: S, spheres; R, rods; LR, long rods; XR, interconnected rods; B, bilayer. If two morphologies are listed, the major one is given first.

It is noted that when the polymer concentration is lower than 2.0%, the morphological characteristics of the aggregates and the boundary of the morphological transition between spheres and rods are identical with the results for the aggregates prepared by the DD method in the solvent mixture containing 6.5% water. Therefore, the formation of the aggregates under these conditions, i.e., a polymer concentration below 2% and a water content of 6.5%, is under thermodynamic control. When the copolymer concentration is higher than 2.5%, one starts to see some differences in the morphologies for the aggregates prepared by the two different methods. For example, at a polymer concentration of 3.5%, flat bilayer aggregates are formed by the DD method, while the WA method yields closed spherical vesicles.

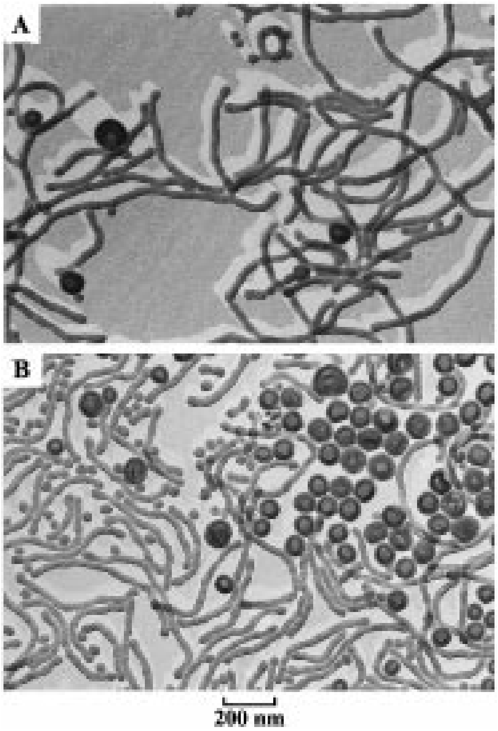

Figure 4. Aggregates prepared by adding 6.5% water to the diblock copolymer/DMF solution of different initial polymer concentrations: 2.5 (A) and 3.5 wt % (B).

The bilayer aggregates formed by the DD method are usually much larger and more highly polydisperse in size than the closed vesicles formed by the WA method. As will be discussed in section 3.3, the formation of very large bilayers is probably related to a continuous addition of polymer chains to the aggregates in the course of the polymer dissolution. The formation of closed vesicles by the WA method is very probably due to the limited local polymer concentration, which limits the sizes of formed bilayer aggregates. When the size of a bilayer aggregate is not very big, the rim-capping energy due to the formation of a hemicylindrical structure is likely more important than the curvature energy when a sheetlike lamella closes into a vesicle. Therefore, a closed vesicle is expected to be more thermodynamically favorable than an open lamellar structure. Moreover, the typical stability of closed vesicles may also arise from their spherically symmetric structure and repulsive interactions which prevent their growth through adhesive collisions. A similar mechanism should be applicable to the formation of open rodlike micelles vs closed rodlike micelles (hoops). It has been shown in a recent study of the formation of mesosized aggregates, e.g., several hundreds of nanometers, that the end-capping energy of rodlike micelles is more important than the curvature energy, which leads to the formation of hoops.[10]

Similar to the aggregates prepared by the direct dissolution method (see section 3.2.1.1), the addition of NaOH at a water content of 6.5% also changes the morphology from bilayer aggregates to rodlike micelles, and then to small spheres. With the addition of NaOH, the boundaries of the morphological transitions move to higher polymer concentrations. Results are found to be consistent with those obtained by adding NaOH to aggregates prepared by the direct dissolution method. The addition of HCl at the water content of 6.5% changes the morphology from spheres to rods. For example, spherical micelles are formed in a 1% polymer solution. After HCl is added to a concentration of 0.5 mM ($R = 0.05$) to this solution, small spheres change to short rodlike micelles. The reversibility between the spherical and rodlike micelles also supports the suggestion that the formation of these micelles is mainly controlled by thermodynamics of micellization under the present experimental conditions.

Table 2. Major Morphologies vs Water Content and Polymer Concentration for the Aggregates Prepared by the Water Addition Method from PS(190)-*b*-PAA(20)

polymer concn (wt %)	water content in DMF (wt %)				
	5.5	6.5	7.5	8.5	9.5
1.0	S[a]	S	S		
1.5	S	S, R	S	S	S
2.0	S	R, S			
2.5	S, R	R, S, V	S	S	S
3.0	R, S	R, V, S			
3.5	LR	R, V, S	R, V, S	R, V, S	R, V, S

[a] Key: S, spheres; R, rods; LR, long rods; XR, interconnected rods; B, bilayer; V, vesicles. If two morphologies are listed, the major one is given first.

3.2.2.2. DMF/Water Mixtures Containing 7.5% Water or More. For the aggregates prepared by the WA method, the morphology depends on water content as long as it is below 6.5%; however, it becomes independent of the water content above a concentration of 7.5%. Table 2 summaries the predominant morphologies of the aggregates as a function of the water content and of the polymer concentration. As can be seen, when water content is at or below 6.5%, the boundaries between the different morphologies change with water content. For example, the sphere to rod boundary can be found between 2.0 and 2.5% polymer at 5.5% water but between 1.0 and 1.5% polymer at 6.5% water. For water contents of 7.5% or above, spherical micelles always form when the copolymer concentration is below 2.5%. For solutions of 3.5% copolymer, mixtures of spheres, rods, and vesicles are seen. The results for water contents at or above 7.5% are thus different from those for the aggregates prepared by direct dissolution of the polymer (see Table 1). Therefore, the formation of the aggregates by at least one of these two methods must be under kinetic control in this water content range. Because the Flory−Huggins χ parameter between the PS blocks and the solvent increases with the water content, the critical micellization concentration decreases. Furthermore, because the free energy change of micellization is a function of the critical micellization concentration, thermodynamics of the micellization should also change with water content. Specifically, at a constant polymer concentration, the aggregation number of the aggregates increases with the water content (χ parameter).[14] A morphological transition, for example from spheres to rods, may occur as the water content increases. Therefore, it seems that the direct dissolution method produces the aggregates for which the morphologies are closer to thermodynamic control since it has been shown that not only is the morphology a function of polymer concentration but also the morphological boundaries move to lower polymer concentration as the water content increases. In section 3.3, we will return to this point when discussing possible mechanisms underlying the morphological transitions.

Figure 5 shows a schematic drawing which attempts to explain why the formation of the aggregates by the method of water addition becomes independent of the

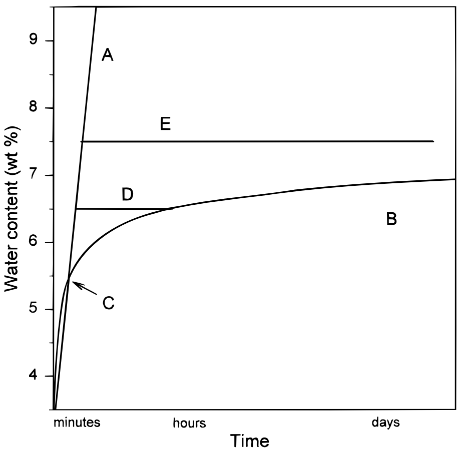

Figure 5. Schematic drawing of the kinetics of morphological transitions vs the water content.

water content above 7.5%. The straight line A represents the rate of water addition. In practice, the water content in the course of the micelle preparation increases stepwise, rather than continuously. The stepwise increment of water content is about 0.3% per 10 s. The water content in the plot starts from 3.5% because the micellization starts roughly at this water content for the copolymer concentration range used in this study. Therefore, once the copolymer starts to form micelles, it only takes about 1 min to increase the water content from 3.5 to 5.5% and 2 min from 3.5 to 7.5%.

In the early stages of micellization, spherical micelles always form because of the relatively low interfacial energy and the relatively small interaction parameter (χ) between the PS segments and the solvent molecules. As the water content gradually increases, the micelles change both their size (aggregation number) and their morphology. Curve B represents schematically the relationship between the water content and the time needed for the system to reach thermodynamic equilibrium. An equilibration time is considered to be related to the morphological reorganization time. Generally, curve B shows that the kinetics of the morphological transition decrease rapidly (longer time) as the water content increases. Specifically, when water content is below 5.5%, the kinetics are faster than the rate of water addition, and micellization will be under thermodynamic control. Around 5.5% water content, these two rates become very close (indicated by intersection C). If the water addition is stopped at this content, the system can establish a thermodynamic equilibrium rapidly. Once the water addition resumes, the aggregates with the morphologies which reflect the thermodynamics at a 5.5% water content can be easily frozen because the kinetics become slower than the rate of water addition. If the water addition is stopped at 6.5%, although the kinetics has slowed significantly, the thermodynamic equilibrium is still reachable after a certain waiting period (indicated by the intersection of the line segment D and the curve B). For the present system, it is found that this waiting period at a 6.5% water content is a few hours. Finally, if the water addition is stopped at a 7.5% or more, because the kinetics have become extremely slow, the thermodynamic state becomes unachievable, even over a time period of 1 week; as is shown in Figures, the horizontal line segment E does not intersect curve B over that time scale. As a result, the morphological characteristics of the aggregates will reflect the thermodynamics at much lower water contents, for example about 5.5%. As shown in Figure 5, around this water content, the rate of water addition becomes faster than the kinetics of the morphological transition. This phenomenon shows some similarity to the glass transition phenomenon in that the lengths of time needed to reach equilibrium increase at an exponential rate (or higher), while a constant cooling rate is employed. In the following section, we will discuss some aspects of the kinetics of different possible mechanisms as a function of water content.

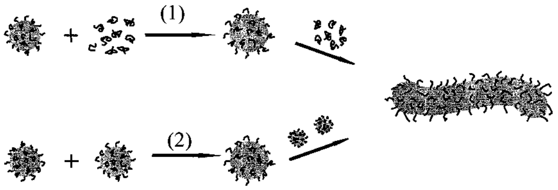

Figure 6. Schematic drawing of two possible mechanisms for the morphological transition from spheres to rod.

3.3. Possible Mechanisms for the Morphological Transitions. 3.3.1. Aggregates Prepared by the Method of Water Addition. As was discussed in the previous sections, both thermodynamics and kinetics of micellization are very important for the formation of the crew-cut aggregates. When the water content is relatively low, the morphology of the aggregates is mainly controlled by thermodynamics. As pointed out in the Introduction, the thermodynamics of the micellization reflects a force balance involving the repulsive interactions of the corona chains, the interfacial energy of the core/shell region, and the deformation of the PS blocks in the core. In the course of changing some of these parameters, for instance by increasing the water content, morphological transitions, for example from spheres to rods, 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.

With increasing water content, kinetic aspects become more and more important. Therefore, it is of interest to explore more extensively the kinetics of various possible mechanisms for the morphological transition as a function of water content. Similar to the mechanisms of chain insertion/expulsion and micellar merger/splitting suggested for the chain exchange of block copolymers between spherical micelles,[21] for aggregates prepared by the water addition method, two possible mechanisms can be postulated for the morphological transitions. Figure 6 shows a schematic drawing of these two mechanism for the transition from spheres to rods. The first involves a continuous insertion of single polymer chains into spherical micelles. The chain insertion increases the aggregation number and thus also the core dimension. Eventually the micelles change the structure from spherical to rodlike when the core diameter of the spherical micelles has reached some critical value. Another possible mechanism involves adhesive collisions of small spherical micelles which increase the aggregation number and form larger spherical micelles. Again, at some point, the morphology changes to rodlike. For both mechanisms, once the morphological transition occurs, further chain insertion or adhesive micelle collisions leads to an increase in the length of rodlike micelles.

Obviously, the kinetics of the morphological transition via mechanism 1 depend on the cmc (i.e., the polymer concentration in unimer form) as well as the mobility of the chains in and out of the micelles. The former is a function of the water content. The later is related to the solvent content in the core, which is also a function of water content. Specifically, both the cmc and the solvent content in the core decrease as the water content increases. For the PS(190)-*b*-PAA(20) block copolymer, the concentrations of the polymer in unimer form can be estimated to be of the order of 2×10^{-4} and 10^{-6} (w/w) at water contents of 5.5 and 7.5%, respectively.[15] The solvent content in the core also decreases rapidly. In a study of solvent content in separated PS phase for homopolystyrene/DMF solution as a function of water content, [13] it is noted that, at 5.5% water, the PS phase is highly swollen by DMF and is a very mobile liquid; however, the mobility of the PS phase decreases rapidly as the water content increases. In the region of 7.5−8.5% water, the separated PS phase becomes very solid or waxlike. This suggests that the mobility of polymer chains decreases drastically as the water content increases from 5.5% to 7.5%. Therefore, when the water content is relatively low, the kinetics via mechanism 1 can be very fast because of the relatively high cmc and the high mobility of the chains due to high solvent content in the core. At higher water contents, because of the decreased cmc and the lowered chain mobility (due to the decreased solvent content in the core), the kinetics of mechanism 1 can become very slow.

The kinetics via mechanism 2, the adhesive collision mechanism, depend on not only the mobility of chains for the structural rearrangement but also on the rate of adhesive collisions. Even if the chain mobility for the structural rearrangement of the micelles is reasonably high (as will be discussed in section 3.4), the kinetics via mechanism 2 could be still very slow if the efficiency of adhesive collisions of the micelles is low. The efficiency of adhesive collisions should depend on the repulsive interactions among the aggregates and the osmotic pressure between the gap of the micelles (due to the concentrated PAA phase in the micelle corona shell).

Obviously, the interactions between partially ionized PAA segments and the solvent molecules are strong, and their strength increases with increasing water content. Because of the existence of charges in the corona shell as well as the increase in the osmotic pressure between the gap as two micelles approach one another, the energy barrier for the adhesive collisions of micelles can be very high, and therefore the kinetics via the collision mechanism can be very slow when the water content is relatively high. Therefore, at a relatively low water content, because the kinetics of both mechanisms are fast, thermodynamic control of the morphology is readily achievable. However, when the water content is relatively high, the morphological transitions, for example from spheres to rods, become inaccessible kinetically within a reasonable time period.

Therefore, for the present system, when the aggregates are prepared by first dissolving the diblock copolymers in DMF and subsequently adding water to induce micelle formation, the maximum water content at which the thermodynamics of the micellization are still operative is around 5−5.5%. The aggregates which are finally isolated into aqueous solution are a manifestation of thermodynamics at that point. Certainly, the maximum water content at which the thermodynamics is still operative can vary with a number of parameters, such as copolymer composition and molecular weight and the rate and manner of the water addition. For example, if water is added very slowly, the maximum water content increases slightly, because the straight line A will intersect the curve B at a higher water content in Figure 5. In addition, for the present system, the maximum water content is also limited due to the low efficiency of adhesive collisions among micelles. The low efficiency is a result of the strong interactions between the PAA and the solvent molecules, the partial ionization of the PAA blocks, and the resulting strong repulsion among the particles. Therefore, it can be expected that the efficiency of the adhesive collisions could be improved by reducing the charge density and therefore the repulsion. Two potential examples are given below.

The first involves aggregates made from solutions of the PS-*b*-PAA or PS-*b*-P4VP·MeI copolymers in THF or in dioxane. Although the copolymers are ionizable, the dielectric constants of the common solvents THF ($\epsilon = 7.5$) and dioxane ($\epsilon = 2.2$) are much lower than that of DMF ($\epsilon = 38.2$). Therefore, the degree of ionization of the corona-forming blocks will be lowered, and the efficiency of adhesive collisions increased. The second case involves aggregates from PS-*b*-P4VP or PS-*b*-PEO copolymers in DMF. Although the common solvent, DMF, has a high dielectric constant, the copolymers are nonionic. Therefore, the efficiency of adhesive collision can be expected to be higher than that in the present system.

3.3.2. Aggregates Prepared by the Method of Direct Dissolution. In general, the two mechanisms discussed above for morphological transitions in solutions are believed to be applicable also to the aggregates prepared by the method of direct dissolution. For the aggregates prepared by this method, the structures or morphologies can be controlled by the thermodynamics of micellization in a broader range of water contents, compared to the aggregates prepared by the water addition method. This is due to the fact that the dissolution of copolymers not only supplies single polymer chains which serve to increase the micelle size, but also decreases significantly the effective energy barrier for adhesive collisions of the micelles (as will be shown in section 3.5). As a result, the kinetics of the morphological transition via both mechanisms are accelerated. For the formation and morphological transition of the aggregates prepared by this method, a third mechanism is also possible, which involves a process of polymer swelling, rearrangement of the structure, and breaking up into primary aggregates.

3.4. Morphological Transition via a Fission Mechanism. It was shown that although the formation of the aggregates as well as their morphologies is driven by the thermodynamics of micellization, the achievement of a morphological transition is also determined by kinetics, especially at relatively high water contents. For example, the morphological transition from spheres to rods via mechanism 2, as shown in Figure 6, depends on the efficiency of adhesive collision of spherical micelles as well as the chain mobility in the core for the subsequent rearrangement of the structure. To estimate the relative importance of the two aspects influencing the kinetics, we study the morphological transitions, for example from rods to spheres, since these transitions depend mainly on the mobility of the chains to achieve a structural fission but do not involve the effective collision problem.

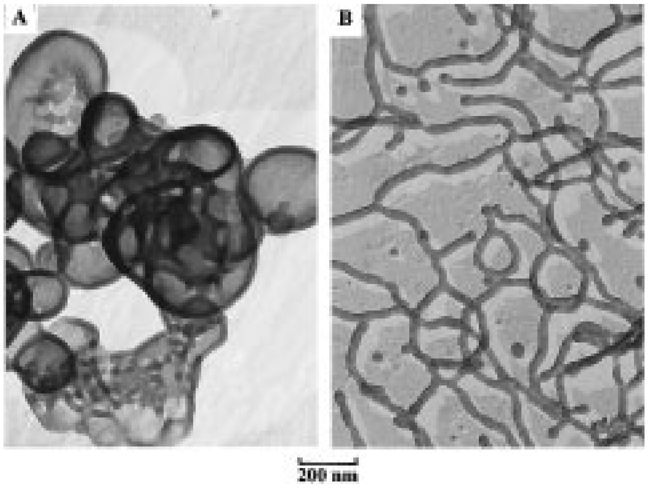

Figure 7. (A) Bilayer aggregates formed by direct dissolution of 1.0% copolymer in a 90.5/9.5 (w/w) DMF/water mixture. (B) Aggregates formed after adding NaOH to a final concentration of 0.5 mM ($R = 0.06$) to the solution of aggregates in (A).

Generally, it is found that the transitions from bilayers to rods and from rods to spheres are still achievable when water content is between 7.5 and 9.5%. The transitions can be induced by decreasing the polymer concentration and/or adding NaOH. Several examples are given below. At 7.5% water, bilayer aggregates are formed when the copolymer is directly dissolved to a concentration of 2.5%. When the solution is diluted to 1.5%, a mixture of bilayers, interconnected rods, and spheres is formed. If the solution is further diluted to 0.5%, rods and spheres are formed. Alternately, if NaOH were added to the 2.5% polymer solution of bilayer aggregates to a final concentration of 2.0 mM ($R = 0.08$), the bilayers would change within several hours to a mixture of short rodlike and spherical micelles. If the solution with added NaOH is further diluted to a polymer concentration of 1.5% with a DMF/water mixture containing 7.5% water, only spherical micelles are seen. Similarly, at 9.5% water content as shown in Figure 7, direct dissolution of 1% copolymer yields bilayer aggregates (Figure 7A). When NaOH is added to a final concentration of 0.5 mM ($R = 0.06$), the bilayers change to a mixture of long rodlike and spherical micelles (Figure 7B).

The above results prove that in the water content range of 7.5−9.5%, the mobility of polymer chains is still high enough for rearrangement of the structures to take place. Therefore, the slow kinetics of mechanism 2 for the morphological transitions of the aggregates prepared by the method of water addition should be due mainly to the low efficiency of the adhesive collision.

It is also found that the process of morphological transition from closed vesicles to spheres is slower than that from rods to spheres, As shown in Figure 4B, a mixture of spheres, rods, and vesicles is formed from 3.5% polymer solution by the method of water addition. Starting with this solution at 7.5% water and subsequently adding 2.8 mM NaOH ($R = 0.08$) and diluting the solution to different polymer concentrations (between 0.5 and 2.0%), it is found that while the rodlike micelles disappear due to the transition to spherical micelles, vesicles are still seen during TEM observation.

3.5. Morphological Transition through a Collision and Fusion Mechanism. In the range of 7.5−9.5% water, while the morphological transitions from bilayers to rods and then to spheres can still occur by simply decreasing the copolymer concentration or adding NaOH to increase the degree of the PAA block ionization, the morphological transitions are only partially reversible in the sense of that the addition of HCl usually does not change the morphology in the opposite direction. For example, direct dissolution of 1% polymer in a 7.5% water/DMF mixture yields long wormlike micelles (see Table 1). After addition of 0.5 mM NaOH ($R = 0.06$) to this solution, the wormlike micelles change to spheres. However, after an equivalent amount of HCl is added to the solution of the newly formed spherical micelles to neutralize the added NaOH, the aggregates do not change back to wormlike micelles within a period of 5 days. This is due to the metastability of the spherical micelles resulting from the repulsive interaction among the aggregates. Since the kinetics of the morphological transitions via mechanism 2 depend mainly on the efficiency of the adhesive collisions between micelles, they can be improved by decreasing the repulsion between the aggregates.

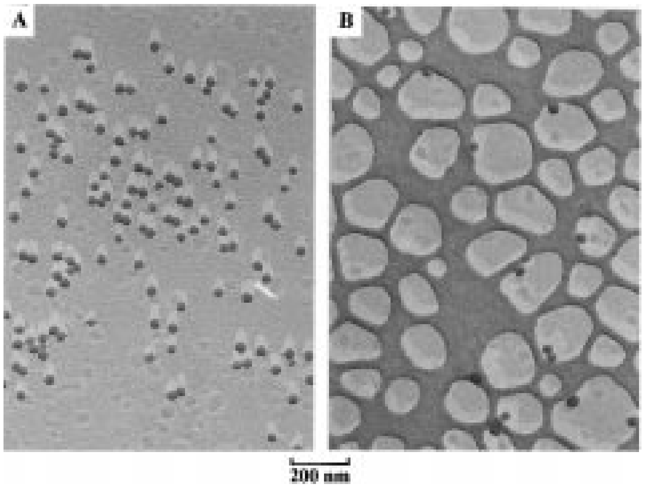

Figure 8. (A) Spherical micelles formed by adding 8.5% water to a 1.5% diblock copolymer/DMF solution. (B) Perforated bilayer structure formed after adding NaCl to a final concentration of 55 mM ($R = 4.0$) to the solution of aggregates from part A.

Figure 8A shows spherical micelles prepared by adding 8.5% water to a 1.5% polymer/DMF solution. Because the kinetics of the morphological transition are very slow, the spherical micelles are solvated and are very stable even if the thermodynamically stable structures under these conditions are bilayers (see Table 1). It is found that even after 1.4 mM HCl ($R = 0.10$) is added to this solution, there is no appreciable change in terms of the aggregate morphology after a 5-day waiting period. Only a few short rods are seen occasionally during the TEM observation. When 14 mM NaCl ($R = 1.0$) is added to the solution, a result similar to the case of adding HCl is obtained. However, when the NaCl is added to a final concentration of 55 mM ($R = 4.0$), changes occur immediately, which can be seen from the increase in the turbidity of the solution. As shown in Figure 8B, the morphology consists mainly of perforated bilayers. The formation of the perforated bilayers should involve fast adhesive micelle collisions induced by the addition of NaCl and subsequently a fusion and structural rearrangement of the contacting micelles. The perforated structures may very well be a manifestation of the thermodynamics of micellization for some entropic reasons, especially in view of the fact that their sizes

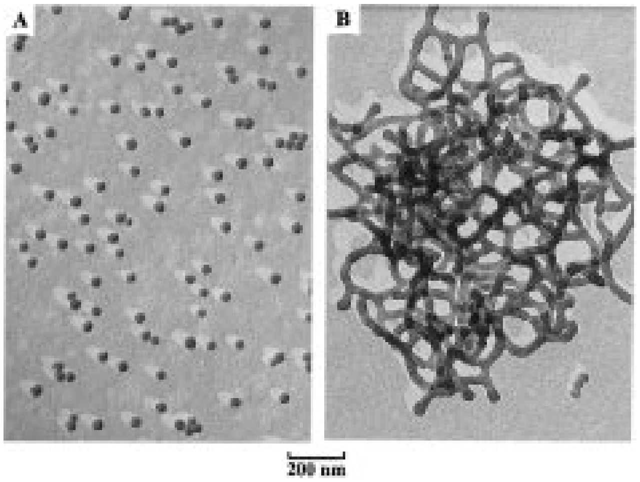

Figure 9. (A) Spherical micelles formed by adding 7.5% water to a 1.0% diblock copolymer/DMF solution. (B) Aggregates formed after directly dissolving an additional 0.5% polymer to the solution of the spherical micelles from part A at a water content of 7.5%.

can be several tens of square micrometers. Furthermore, a hexagonally perforated layered phase has been seen recently in block copolymers in bulk,[22,23] and a randomly perforated lamellar phase has been observed in lyotropics.[24] We believe that our perforated bilayer structure in solution is morphologically similar to those formed in other systems.

It is found that the efficiency of the adhesive micelle collisions also increases during the process of polymer dissolution. One example is given in Figure 9. As can be seen, adding 7.5% water to a 1% polymer/DMF solution yields spherical micelles with an average core diameter of 29 nm (Figure 9A). Although a thermodynamic structure under these conditions is a long rodlike micelle (see Table 1), spherical micelles are obtained because the strong repulsive interactions among the micelles result in slow kinetics for the morphological transition. At a 7.5% water content, an additional 0.5% polymer is directly dissolved in this spherical micelle solution to increase the polymer concentration to 1.5%. It is found that the formed aggregates are very similar to those obtained by direct dissolution of 1.5% polymer in a 7.5% water/DMF mixture. As shown in Figure 9B, the major morphologies are the long and interconnected rods. Although spherical micelles are still frequently seen, their average diameter is increased to 35 nm. Because the original spherical micelles formed from 1% polymer from a major fraction of the total polymer, the formation of interconnected and long rods cannot be only due to a continuous chain insertion into the original spherical micelles during the dissolution of the additional 0.5% polymer. Their formation must be mainly a result of adhesive collisions and fusion of the micelles. Therefore, the dissolution of copolymers not only supplies single polymer chains which serve to increase the micelle size, but also, and perhaps even more importantly, increases significantly the efficiency of adhesive collisions of the micelles. The detailed mechanism for the increased efficiency is not very clear. One possibility can be an interaction of the micelles and the dissolving polymer interface. As a result, the effective energy for the micelles to achieve adhesive collision is decreased, a pathway that is analogous to a process of surface catalysis.

4. Conclusions

The formation of crew-cut aggregates of various structures from polystyrene-*b*-poly(acrylic acid), PS(190)-*b*-PAA(20), diblock copolymers in solvent mixtures of DMF and water were studied by varying the polymer concentration and water content and by adding ions. Two different methods are used for the aggregate preparation, i.e., adding water to polymer/DMF solution and directly dissolving the polymer in DMF/water mixtures. Generally, it is found that as the polymer concentration increases, the morphology of the aggregates changes in the direction from spheres to rodlike micelles, to interconnected rods, and then to bilayers. As the water content increases, the boundaries of the formation of the aggregates of different morphologies shift to lower polymer concentrations.

The thermodynamic vs kinetic aspects for the formation of crew-cut aggregates of different morphologies were explored as a function of water content. In particular, the reversibility of the transitions between the crew-cut aggregates of various morphologies was studied by changing the polymer concentration and adding ions, such as NaCl, HCl, and NaOH. When water content is relatively low (less than 6.5%), the kinetics are fast on the experimental time scale and the formation of the aggregates is controlled by thermodynamics of micellization; the morphological transitions are reversible. The morphological reversibility decreases significantly and the kinetics become more important as the water content is increased to the range 7.5−9.5%. In particular, when the aggregates are prepared by the water addition method, morphological transitions from spheres to rods, and then to bilayers are not achievable kinetically within several days due to the low rate of the polymer chain exchange and the strong repulsive interactions among the aggregates. However, the transitions in the opposite direction are possible because the mobility of the chains is still high enough to achieve structural fission and rearrangement.

When the aggregates are prepared by the direct dissolution method, the structures or morphologies are still appreciably controlled by the thermodynamics of micellization in the water range 7.5−9.5%, due to the fact that the dissolution of copolymers not only supplies single polymer chains for micelle growth but also decreases significantly the effective energy barrier for micelles to achieve adhesive collisions and fusion. As a result, the kinetics of the morphological transition are accelerated.

Acknowledgment. We thank the Donors of Petroleum Research Fund, administrated by the American Chemical Society, and the NSERC, Canada, for support of this research.

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(2) For star micelles, the curvature of the micelle core surface is very large and the dimension of the corona shell is usually larger than the core. When the curvature is taken into consideration, the actually occupied area per corona chain on a spherical surface drawn through the middle of the corona

shell (or a distance from the core surface equivalent to the radius of gyration of the corona-forming blocks) is considered to be at least more reasonable than the area on the surface of micelle core for the comparison.

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MA981039F