Macromolecules **2005,** *38,* 9315−9323

Self-Assembly of ABC Triblock Copolymer into Giant Segmented Wormlike Micelles in Dilute Solution

Jintao Zhu and Wei Jiang*

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

Received June 15, 2005; Revised Manuscript Received August 19, 2005

ABSTRACT: We report the self-assembly of a linear ABC triblock copolymer into the previously unknown architecture of giant segmented wormlike micelles (SWMs). The lengths and diameters of these giant SWMs were as high as ca. 10 μm and 500 nm, respectively. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) analysis revealed that the SWMs comprised sequences of repeated elemental parts, i.e., disks having a thickness of ca. 65 nm. A most interesting feature is that disks having different diameters became connected through threads to form various giant segmented wormlike micelles. A kinetic study indicated that the process of SWM formation occurred basically through three stages: (1) the ABC triblock copolymer self-assembled into small spheres of ca. 38 nm diameter; (2) these small spheres joined together to form intermediate shuttlelike structures; (3) the spheres within the shuttlelike structures rearranged and underwent further adjustment to form the final SWMs.

1. Introduction

The self-assembly of amphiphiles into various supramolecular assemblies has been studied extensively within the past decade, because of not only scientific interest but also the continuing demands for their use in a range of nanotechnological applications, including drug delivery, microreactors, materials, and environmental toxin sequesters.[1−7] Self-assembly is an essential process in biological systems; it provides the diverse range of highly ordered structures observed in living organisms.[8] The behavior of small molecular amphiphiles of natural origin has inspired the engineering of higher-molecular-weight synthetic analogues, defined as superamphiphiles (because they resemble the traditional surfactants in shape but differ in size),[9] which include amphiphilic block copolymers composed of serial tandem hydrophobic and hydrophilic chains.[10−14] This class of block copolymers is now recognized as an excellent counterpart to conventional amphiphilic materials, such as lipids and surfactants.[15] A variety of self-assembled objects can be obtained from a single synthesized block copolymer by tuning the parameters of the systems that affect the balance of forces contributing to the free energy of the system.[16−21] Three basic structural micelles have been obtained previously using amphiphilic block copolymers: spheres, cylinders, bilayers.[22−24]

The micellar behavior of AB diblock and ABA triblock copolymers is relatively well understood, but the solution self-assembly of ABC triblocks or multiple-block copolymers are more complex.[23,25−35] Several recent reports on amphiphilic ABC systems have described the formation of multilayer (core/shell/corona) spherical micelles and oblate disks.[26,30,33,34,36] To date, only a limited amount of information is available regarding the formation of biomimetic micellar objects. Living cell membranes are the most common and significant type of vesicles. Prokaryotic systems, e.g., bacteria, have a single lipid bilayer dividing space, and thus, they are analogous to the vesicular assemblies in AB diblock copolymers.[37,38] Micelles comprising a flat bilayer and protruding cylindrical arms resemble living creatures, e.g., an octopus or jellyfish.[39]

In this paper, we present a new type of self-assembled object—giant segmented wormlike micelles (SWMs) obtained from a linear ABC triblock copolymer—that are composed of segmented parts, i.e., disks connected by threads. The thickness of the segment is nearly the same in each SWM. After quenching their solutions, we used transmission electron microscopy (TEM) to identify the formation process of these types of micelles. We found that the ABC triblock copolymer aggregates to form spherical micelles through primary self-assembly. The most important feature of these spherical micelles is that they can further self-assemble into more advanced structures, eventually leading to a large number of the giant segmented wormlike micelles.

2. Experimental Section

2.1. Materials. Figure 1 presents the molecular structure of the linear ABC triblock copolymer we used in this study: poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77}) ($M_n = 98\,000$ g/mol) which was purchased from Polymer Source Inc. Canada. Synthesis procedure, size exclusion chromatography (SEC), and nuclear magnetic resonance (NMR) spectroscopy characterization results for the ABC triblock copolymer are given in the Supporting Information (SI1−SI3). This triblock copolymer can be designed in the form $S_xP_yO_z$, where x, y, and z represent the number of repeat units of the S, P, and O blocks, respectively. The polydispersity index of this ABC triblock copolymer was 1.09.

2.2. Preparation of the Micelles. The triblock copolymer was first dissolved in tetrahydrofuran (THF), which was a cosolvent for all of three types of the blocks. The initial block copolymer concentration in cosolvent was 1.0 wt %. The triblock copolymer solution was kept stirring overnight to make the copolymers into the cosolvent by single molecules forms. Then, deionized water was added to the solution at the approximate rate of 0.2 wt %/30 s with stirring to induce the

---

* To whom all correspondences should be addressed. E-mail: wjiang@ciac.jl.cn.

10.1021/ma051258i CCC: $30.25

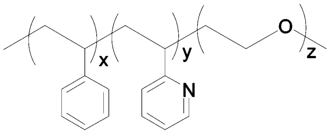

Figure 1. Chemical structure of the ABC PS-*b*-P2VP-*b*-PEO triblock copolymer.

self-assembly of the block copolymer. The appearance of cloudiness in the solution indicated that aggregation had taken place. Aggregation generally occurred at ca. 9 wt % water addition. A total of 15 wt % water was added to the block copolymer solution. The solution, at this water content, was kept stirring for 4 days (or for various time in the kinetic studies). Subsequently, a large amount of water (ca. 400 wt %) was added to the resulting solution to quench the micellar morphologies. At this water content range, the structures of the micelles became kinetically locked over the experimental time scale. Finally, the resulting solution was placed in dialysis tubes and dialyzed against distilled water for a few days to remove all of the organic solvent from the solution. Although the PVP block is not soluble in pure water, it is soluble in THF solutions containing up to 50 wt % water and is also soluble in water below a pH of 5.[19,40] Therefore, during the dialysis process, the pH of the distilled water was thus adjusted to 4 by hydrochloric acid (HCl) to keep the colloid solutions from precipitating. The morphology of the micelles was stable during the dialysis process and after the dialysis. When the THF molecules are forced out of the core of the micelles, the equilibrium is frozen because of the glassy nature of the PS chains.[14] The length of the time between the water content reached 15 wt % and the subsequent large amount water addition is named the annealing time.

2.3. Field Emission Scanning Electron Microscopy (SEM). SEM measurements were performed on a XL 30 E-SEM (FEG, Micrion FEI PHILIPS) operated at an acceleration voltage of 20 kV. The dialyzed colloidal solutions were diluted by a factor of 10−20 to prepare the SEM and the TEM samples. For preparing the samples for SEM, a drop of the very dilute micellar solution after dialysis was dropped onto the silicon (Si) wafers. Prior to coating, the silicon substrates were cleaned in a bath of 100 mL of 80% H_2SO_4, 35 mL of H_2O_2, and 15 mL of deionized water for 15 min at 80 °C and rinsed several times in deionized water. The silicon surface was then dried with compressed nitrogen gas. The coated substrates were then dried in air and at room temperature for 1 day to let the micelles set on the Si wafer. Then, the samples were coated with a thin layer of gold (Au). The Au layer coating time and density for all of the samples were under same condition to reduce the standard error of the measurement.

2.4. Transmission Electron Microscopy (TEM). A variety of experimental techniques can be used to characterize micellar morphologies of block copolymers formed in dilute solutions. However, it is suitable to adopt TEM to directly observe the morphologies of complicated, irregular, and polydisperse aggregates.[41] The resulting micellar morphologies were visualized with a regular TEM. TEM was performed on a JEOL JEM-1011 transmission electron microscopy operated at an acceleration voltage of 100 kV. A drop of the very dilute solution was placed onto TEM copper grid covered by a polymer support film precoated with carbon thin film. After 15 min, excess solution was blotted away using a strip of filter paper. The samples were allowed to dry in the atmosphere and at room temperature for 1 day before observation.

2.5. Microtomy and Stain Experiment. For observation of the internal structure of the SWMs, a powder sample of the SWMs was embedded in epoxy resin (Epon), and sections of about 70 nm thickness were obtained by microtoming the resin sample at room temperature using glass knives. The powder sample was obtained via filtration of the SWMs solution formed in section 2.2 by using poly(vinylidene fluoride) (PVDF) film (pore size: 200 nm) and then dried in air. Sections were picked up on 400-mesh copper grids and then stained in the vapor of I_2 crystals in order to increase the contrast between the P2VP and the PS (or PEO) microdomains. The P2VP domains which were selectively stained by I_2 vapor appeared dark in the TEM observations.

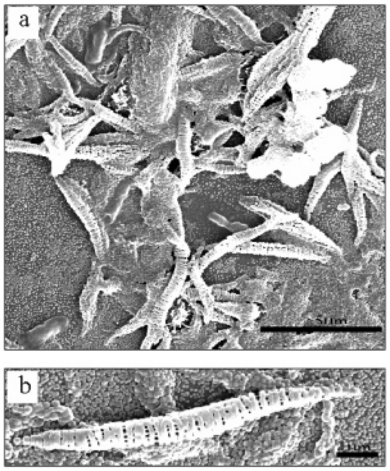

Figure 2. Typical SEM images of the segmented wormlike micelles formed from 1% of PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF/H_2O mixtures (water content: 15 wt %) annealing for 4 days.

The microstructures of the SWMs were also studied by selectively stained method directly. The sample-loaded TEM grid was exposed to the RuO_4 vapor, and the samples were contrast by the RuO_4. In addition, samples were stained by phosphotungstic acid ($H_3PO_4 \cdot 12WO_4$), by depositing a drop of 0.1 wt % $H_3PO_4 \cdot 12WO_4$ aqueous solution onto the surface of the sample-loaded grid. Three minutes later the solution was blotted with a filter paper, and the sample was then washed with deionized water and dried in air.

2.6. Ultraviolet−Visible (UV−vis) Measurement. The critical water content (CWC) of a block copolymer solution is defined as the water content at which micellization starts.[42] The CWC values are usually obtained by observation of the onset of turbidity of the block copolymer solutions or by light-scattering measurements. The CWC for the PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} was followed by monitoring the turbidity of the copolymer solution as a concentration. All turbidity measurements were performed on a Shimadzu UV-2450 ultraviolet−visible (UV−vis) spectrometer. The instrument was set at the absorbance (turbidity) mode, and measurements were recorded every 0.02 min at $\lambda = 650$ nm. At this wavelength the copolymer has minimal absorption, and any attenuation of light is due to scattering from the aggregates. THF was used as the referee for all the measurements. The solution of the block copolymer was placed in a quartz cuvette inside the UV−vis spectrometer and stirred using a magnetic stirrer. Water was added slowly (0.2 wt % each time), and the solution was stirred. The UV−vis measurements were taken about 10 min after the addition of each aliquot, and the experiments were performed at room temperature.

3. Results and Discussion

This section is presented in four parts. The results of characteristics of the SWMs from the ABC triblock copolymer are presented in the first part. Part two addresses kinetic study and possible mechanism for the SWMs formation. Part three discusses single-chain fraction of 1 wt % PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF/water mixtures. The factors which affect the self-assembled architectures are given in the fourth part.

3.1. Giant Segmented Wormlike Micelles. SEM images of a large number of the SWMs and individual SWM are given in parts a and b of Figure 2, respectively. Figure 3 displays typical TEM images (and Supporting Information Figures S3−S5 give the additional TEM, SEM, and atomic force microscopy (AFM)

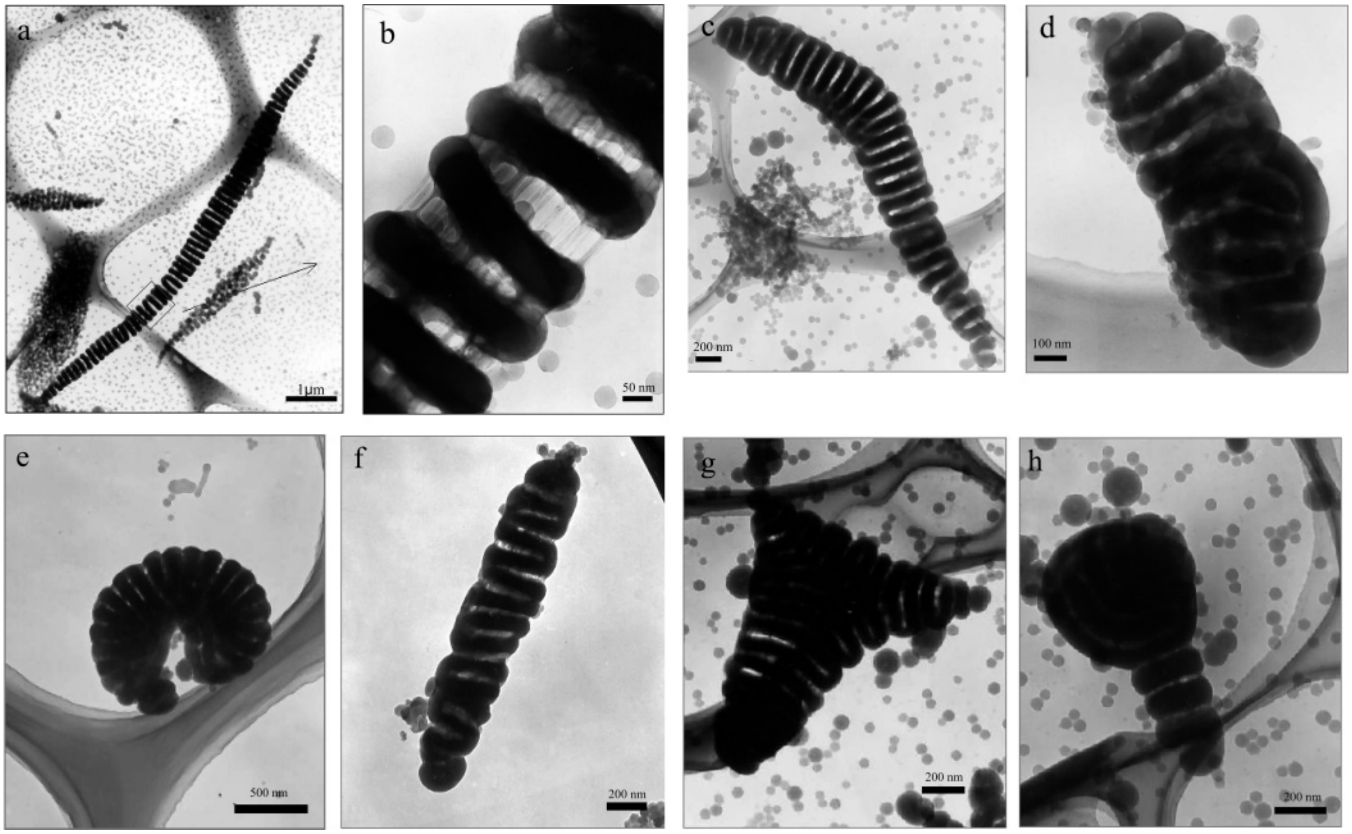

Figure 3. Representative TEM images of the segmented wormlike micelles formed from 1% of PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF/H_2O mixtures (water content 15 wt %) annealing for 4 days; (b) is the enlarged part boxed in (a), where the disks and threads can be seen most clearly. (g, h) are the "abnormal" structures.

images) that we recorded from samples of the giant segmented wormlike micelles obtained from a number of experiments. Besides the SWMs, only spherical micelles were observed in this system. Using the filtration method described in section 2.5, one can separate the SWMs from the spheres. It was found that at least ca. 25 wt % of the triblock copolymers formed the SWMs. It should be noted that a large number of SWMs were obtained in experiments. Only individual SWM was recorded and given here in order to exhibit the microstructures clearly. The "worms" are layered or segmented along their long axis. The most common structures of the SWM are shuttlelike (fusiform profile, i.e., the diameters were larger in the middle), and the direction of orientation of the segmented parts, i.e., disks, is perpendicular to the main axis (Figure 3a−f); we also observed some "abnormal" structures (Figure 3g,h). From the images of these complex micelles, we deduce that the SWMs are composed of the same elemental units, i.e., the disks (Figure 4a). A more interesting feature is that disks having different diameters are connected through threads to form the various giant segmented wormlike micelles. The thickness of each disk in each SWM is approximately the same (ca. 65 nm). The diameters of the disks are larger in the midaxis region than they are at the ends of the axes. The segmented wormlike micelles are gigantic, reaching sizes of several micrometers. Recently, Lodge's group reported that multicompartment wormlike micelles formed from an ABC star triblock copolymer in water;[41] these multicompartment wormlike micelles were cylindrically contoured and had segmented cores. In contrast, the SWMs we obtained in this study comprise separated disks connected by threads; we identified their external morphologies more clearly by recording SEM and AFM images (Figure 2 and Supporting Information Figures S3 and S5), which suggest that the lengths and diameters of the SWMs reached ca. 10 μm and 500 nm, respectively. In addition, the internal structures and mechanisms of formation of our and Lodge's systems are quite different (see below).

We used staining and microtome technology to study the internal structures of our SWMs. Figure 5a,b displays two TEM images of microtome section (thickness: ca. 70 nm) of the SWM, which we selectively stained using I_2 vapor. The dark and bright regions represent the P2VP and PS domains, respectively. The alternating parts correspond to the periodic disklike units. Meanwhile, PS core and P2VP shell in the disks of the SWMs shown in Figure 5c,d have been selectively stained by RuO_4 vapor (PS microdomains appeared dark in the center of the disks) and $H_3PO_4 \cdot 12WO_4$ (P2VP domains appeared dark at the periphery of the disks) in order to study the microstructures of the SWMs. From these studies, we can confirm that the interior of the segmented unit is packed with PS chains, while its outer parts comprise the PVP and PEO chains. Figure 4b provides a schematic image of the proposed chain packing in a SWM. In the disk, the hydrophobic PS units of polymer chains aggregate in the aqueous environment to form the core of the micelles, the hydrophilic P2VP units form a water-soluble shell that separates the core from its environment, and the hydrophilic PEO units form a corona. Figure 5c (the insert part) shows that the connected parts (the thin threads) between the disks appear dark (corresponding to the PS domains) because of the selectively staining by RuO_4. Thus, we consider that the threads also possess three-

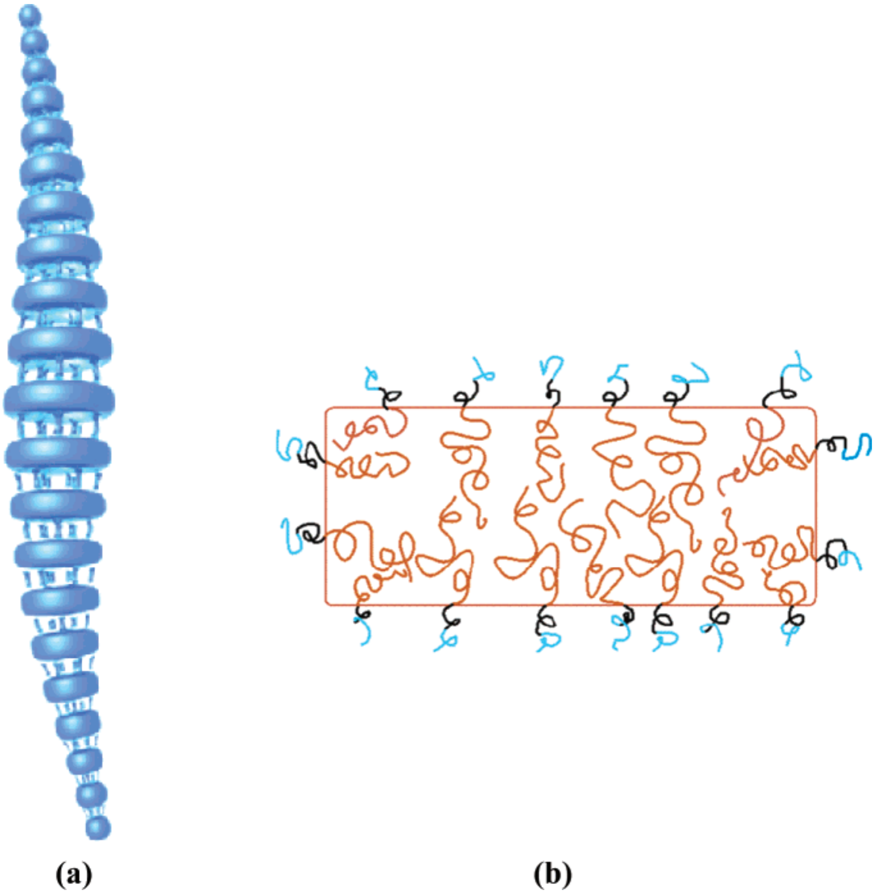

Figure 4. Schematic drawing of an individual SWM micelles and proposed chain packing in the disks. The cross section is parallel to the axes. The color of orange, black, and ice blue represent PS, P2VP, and PEO block in the cross section, respectively.

layer structures; i.e., PS blocks, P2VP blocks, and PEO blocks formed the core, shell, and corona domains in the threads, respectively. The difference is that the chains in the threads should be more elongated than in the disks.

3.2. Kinetics Study and Possible Mechanism for the SWMs Formation. To reveal the mechanism of the formation of the SWMs, samples were extracted from the solution mixture at different times during the annealing process for the SWMs formation.[19] The morphology of the extracted aggregates was quenched by quickly adding the extracted solutions to an excess of water. The intermediate structures can then be trapped by using this method and then studied by using TEM. We inferred a mechanism for the formation of the SWMs by observing intermediate structures obtained when quenching the micelles after various annealing time. Figure 6 displays the morphologies of the micelles observed by TEM at the different stages of their structural rearrangement; we froze the micelles kinetically through quenching of their solutions and subsequent dialysis. These images indicate that the process of SWM formation can be divided into three main stages. First, the ABC triblock copolymers self-assembled into small spheres of ca. 38 nm diameter (Figure 6a). It has been reported that these assembled spheres from SPO type of block copolymers possess core−shell−corona structures in which the PS, P2VP, and PEO blocks comprise the cores, shells, and coronas, respectively.[30,36] Next, these small spheres join together under stirring to form a shuttlelike contour (Figure 6b,c). It is clear that these spheres are packed very randomly in this arrangement (Figure 6f,g). Finally, these randomly packed spheres rearrange and undergo further adjustment to form the disks (Figure 6d,e,h,i). When a sphere attempts to enter into two nearby separate disks, it becomes drawn and elongated under the force of the stirring. Therefore, the threads that connect the disks in the SWMs might be highly elongated forms of the small spheres or their complexes. It is worth noting that the threads retain their relatively high strength: neither vigorous stirring nor the ultrasonic vibration damaged the structures of the SWMs. To test this, the SWMs solutions were placed into the ultrasonic bath (frequency 40 kHz, power 50 W) for about 2 h. The SWMs remained their original structures without damage, indicating that the strength of SWMs is enough to resist the ultrasonic. Thus, we consider that chains entanglement exists in the SWMs, particularly in the threadlike parts.

Our findings suggest that the attraction between spherical micelles occurs through a nonspecific interaction,[43] which is initially a surprising concept given the steric repulsion arising from the O corona and P shell. As the spheres approach one another, any fluctuation in the O and P concentration in the corona can expose the hydrophobic core components. During aggregation, water molecules and the hydrophilic units diffuse out of the aggregates, and the same components fuse upon increasing the annealing time. The fusion of the spheres is favored along the direction of perpendicular to the flow direction (i.e., the main axes of the shuttle-like structure) rather than along the axes themselves. Therefore, under the shearing (stirring) condition, the disklike structures grew in the direction perpendicular to the axes, leaving the threadlike structures in the

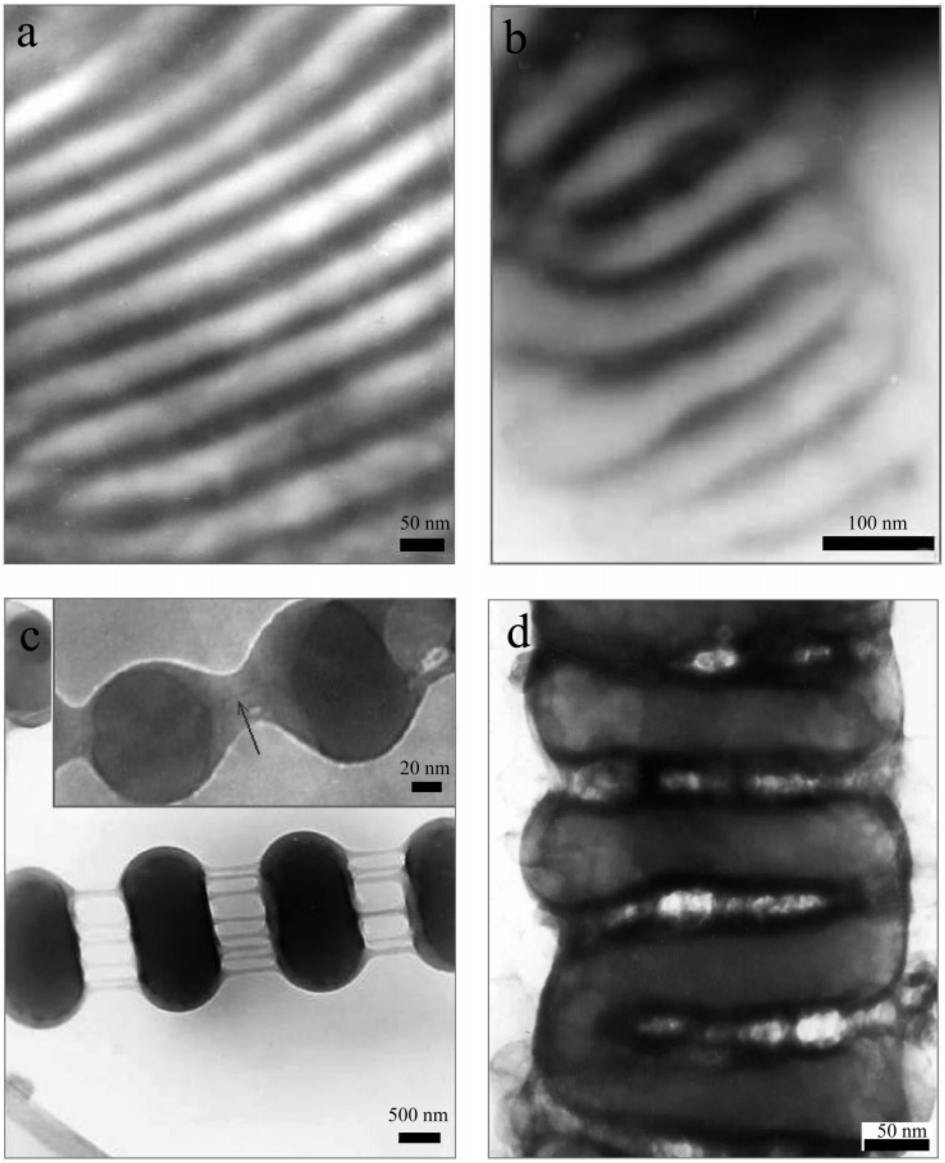

Figure 5. TEM images of microtome section (thickness 70 nm) of the SWMs which was stained by I_2 vapor (a, b). TEM images of the SWMs stained by RuO_4 vapor (c) and stained by $H_3PO_4 \cdot 12WO_4$ (d).

axial direction. Sufficient THF swelling of the PS micelle cores occurred under the shearing conditions to allow the formation of the SWMs through the fusion of spherical micelles. The need for THF molecules to be present during the supramolecular assembly transitions process has been observed also for vesicular fusion.[44] All of the spheres present initially in the direction of the disk share the common core, shell, and corona morphology within the SWM structures. The number of intermediate structures decreased while the sizes of the SWMs increased upon increasing the annealing time, which suggests that the intermediate structures rearrange into the SWMs (Figure 6d–i). From these observations, we conclude that the SWM forms as the result of secondary self-assembly of the spheres.

3.3. Single-Chain Fraction of PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF/Water Mixtures. It is necessary for us to study the possibility that single chains might be involved in the formation process of SWMs. When doing so, it is most useful to explore the concentration of single chains (critical micellization concentration, i.e., cmc) under the condition of SWMs formation (15 wt % water). Unfortunately, the cmc is too low to be measured directly at that water content. However, we can measure the critical water content as a function of the block copolymer concentration in THF.[42] It was found that when the water content is low, the turbidity intensity is nearly constant and zero. However, when the water content exceeds some critical value, the turbidity increases rapidly. The increase in the turbidity intensity indicates that micellization has taken place. An approximate value of the critical water content (CWC) is thus obtained from the intercept of two line segments (horizontal section and steeply increasing section) in the turbidity intensity curves.[23] The plot of the CWC as a function of the block copolymer concentration is thus obtained, as shown in Figure 7.

As more and more water is added to the block copolymer solution beyond the CWC, more and more copolymer chains associate to form micelles, and the concentration of the copolymers in single-chain form decreases. The micelle fraction is defined as the ratio of the associated polymer to the total polymer, $(C_0 - C_{cmc})/C_0$ (where C_0 and C_{cmc} are the initial polymer concentration and critical micellization concentration, respectively).[42] The micelle fraction can be obtained

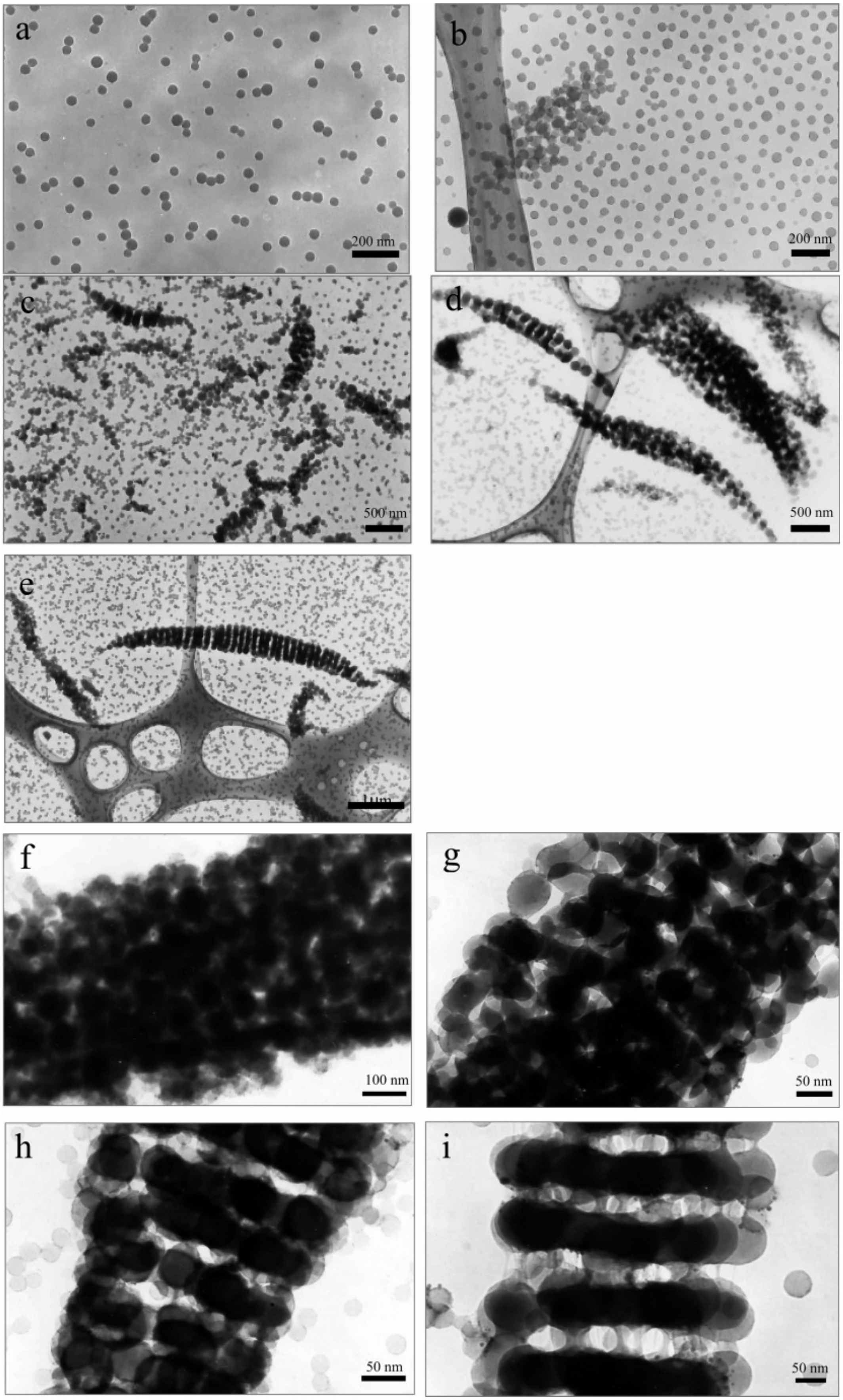

Figure 6. TEM images of the micelles morphologies at different stages of segmented wormlike micelles formation from 1% of PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF/H_2O mixtures (water content: 15 wt %). Annealing time varied at (a) 0 h, (b) 1 day, (c) 1.5 days, (d) 2 days, and (e) 3 days; (f−i) is the enlarged images of intermediate structures. These pictures were obtained by examining a large number of micrographs and then arranged in what appears to be a reasonable sequence.

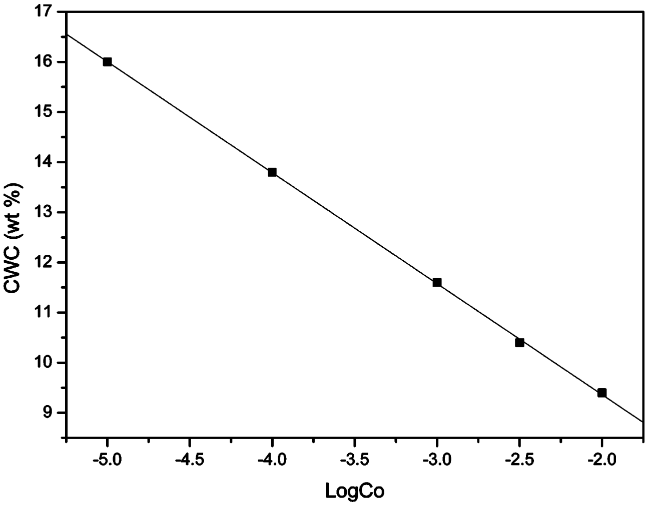

Figure 7. Critical water content vs logarithm of the block copolymer concentration for a solution of PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF.

using the following relationship:

$$(C_0 - C_{\mathrm{cmc}})/C_0 = 1 - \exp(-2.303\Delta \mathrm{H_2O}/A) \qquad (1)$$

where ΔH_2O is the increment of the water content above the CWC and the constant, A, can be obtained from the slop d[cwc]/d[log C_0] in Figure 7. When the ΔH_2O value is zero or less (i.e., for water contents below the CWC), the $(C_0 - C_{\mathrm{cmc}})/C_0$ is zero, and all the copolymer chains in the solution are unassociated.[23] Utilizing the above procedure, we can extrapolate the single-chain fraction (relative to total polymer content) at water content of 15 wt %, 10^{-3}. Therefore, the single-chain population in the triblock copolymer micelle systems is quit low and does not contribute significantly to the architectural changes.

3.4. Factors Which Affect the Self-Assembled Architectures. In addition to the molecular structure, the macroscopic self-assembly of the SPO copolymer is affected by other factors, such as the nature of the cosolvent, the ratio of the water to cosolvent, the copolymer concentration, the presence of ions, and the nature of self-assembly process. For instance, cosolvent used initially to dissolve the copolymer can be THF, dimethylformamide (DMF), and dioxane, but we observed SWMs only in THF/water mixtures and obtained them only when the copolymer concentration in THF ranged from 0.5 to 4 wt %. The micelles observed in DMF and dioxane systems were all spheres (see Figure 8), keeping other conditions the same as the THF/water system. No other micellar morphologies were observed in these systems. In addition, we observed SWM formation only when the water-to-THF ratio ranged between 12 and 20 wt %. At higher water content (27 wt %), we observed cylindrical and ringlike micelles (see Figure 9). At lower water content (10 wt %), nearly no SWM can be observed besides spheres.

Moreover, the self-assembly morphology was also influenced by the pH and ionic strength of the medium: vesicles and large compound micelles can be observed when operating at a suitable pH or ionic strength. To study the effect of ionic strength on the self-assemblies of SPO, HCl was added to the copolymer/THF/water system. Figure 10 shows the large compound micelles ($R = 10$, molar ratio of 2VP to HCl is named R) and vesicles ($R = 50$) by adding different amounts of HCl into the initial block copolymer solution, keeping other experimental conditions the same. No SWMs were observed when the value of R is below 500 in this

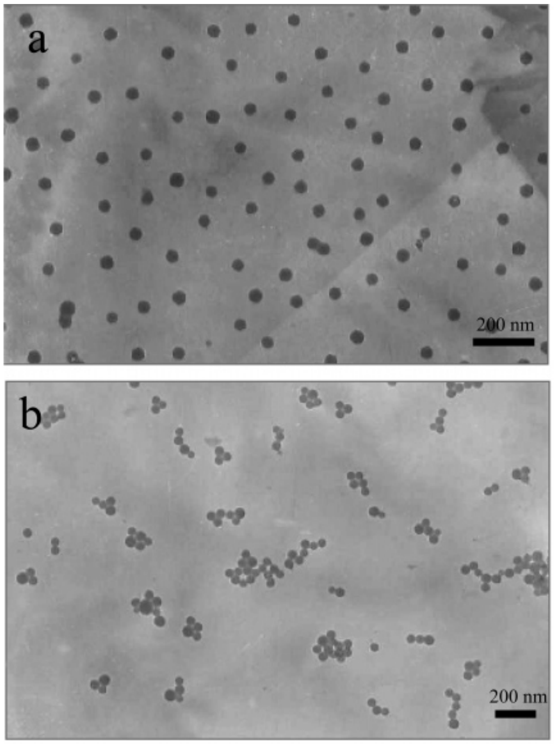

Figure 8. TEM images of the spherical micelles formed from 1 wt % of the PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in different cosolvent (water content: 15 wt %) annealing for 4 days: (a) in DMF and (b) in dioxane.

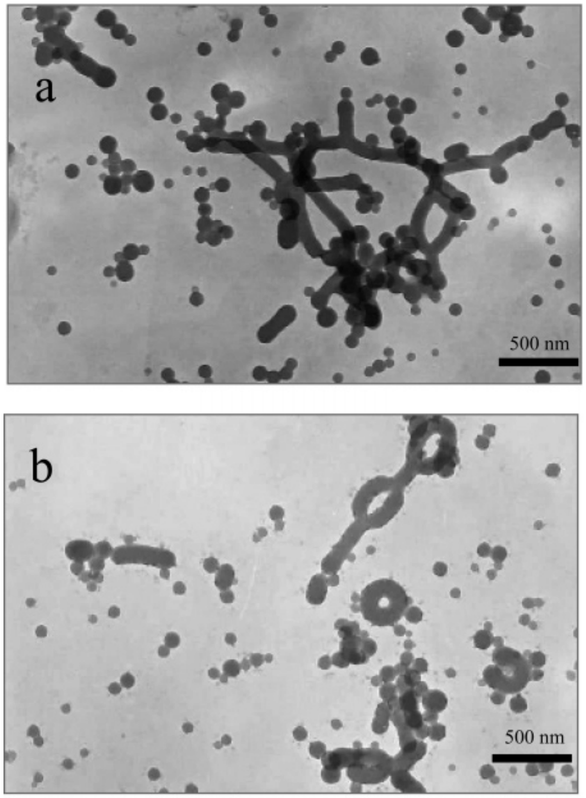

Figure 9. TEM images of the cylindrical (a) and ringlike (b) structures formed from 1 wt % PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF/water mixture (water content: 27 wt %) annealing for 4 days.

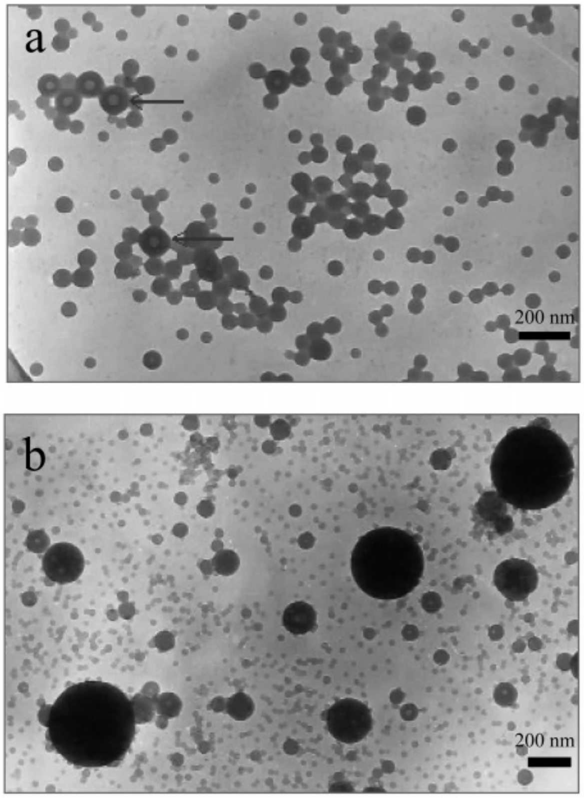

Figure 10. TEM images of the vesicles (a, see the arrows) and large compound micelles (b) formed from 1 wt % PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} in THF/water mixture (water content: 15 wt %) annealing for 4 days by adding different amount of HCl (molar ratio of 2VP to HCl is named R): (a) $R = 50$; (b) $R = 10$.

system. Meanwhile, shearing (or stirring) is one of the most important driving forces for the SWMs formation. It was found in experiment that it is difficult for the SWMs to be formed without (or with gentle) or with vigorous stirring, and only spherical micelles were observed in this case. The SWMs can easily be formed in this system at the stirring speed ranged approximately from 360 to1100 rpm/min in our experiment.

Generally, there are two methods to prepare the block copolymer micelles (in particular for the "crew-cut" micelles), i.e., direct and indirect preparation method.[45] To compare with the indirect method used above (section 2.2), the direct method was used to prepare the micelles. For the direct method, the block copolymer was dissolved in THF/water mixture (water content: 15 wt %). Then, the solution was kept stirring for the same time as for the indirect method. The resulting solutions were then quenched and dialyzed to obtain the stable micelles solution. It should be noted that using the direct method with the same of other conditions can also form the similar micellar morphologies, i.e., the SWMs. However, direct method tends to form more complex morphology (such as the "abnormal" SWMs) than those by the indirect method. In both methods, shearing or stirring is an important parameter that affected the formation of the SWMs. It is difficult for them to be formed under very gentle or vigorous stirring.

4. Summary and Conclusion

Our results suggest a strategy for the formation of new types of assemblies—giant segmented wormlike micelles. The segmented wormlike micelles are composed of segmented parts, i.e., disks connected by threads. The thickness of the segment is nearly the same in each SWM. The kinetic study indicated that the SWMs were formed from the secondary self-assembly of the initial spherical micelles. The nature of the cosolvent, the ratio of the water to cosolvent, the copolymer concentration, the presence of ions, and the nature of self-assembly process affected the macroscopic self-assembly of the PS_{755}-*b*-$P2VP_{130}$-*b*-PEO_{77} copolymer. These SWMs are stable once they have been frozen kinetically. It may be possible to enhance the robustness of these SWMs through posttreatment processing, such as surface cross-linking and functional group modification. These findings enrich our knowledge of the potential for the self-assembly of amphiphiles in selective media. We hope that our results provide motivation for related practical and theoretical studies that may aid our understanding of these phenomena.

Acknowledgment. We thank Prof. Haojun Liang for fruitful discussions. We are grateful for the financial support of the Major Program (20490220 and 50390090) and the General Program (20274047) of National Natural Science Foundation of China (NSFC), the Project (KJCX2-SW-H07) of the Chinese Academy of Sciences, the 973 program of MOST (No. 2003CB615600), and the Fund for the excellent youth of Jilin Province, P. R. China.

Supporting Information Available: Synthesis and characterization information on the ABC triblock copolymer used; additional SEM, TEM, and AFM figures (SI1−SI8). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Alexandridis, P., Lindman, B., Eds.; *Amphiphilic Block Copolymer Copolymers: Self-Assembly and Applications*; Elsevier: Amsterdam, 2000.
(2) Walker, S. A.; Kennedy, M. T.; Zasadzinski, J. A. *Nature (London)* **1997**, *387*, 61.
(3) Savic, R.; Luo, L.; Eisenberg, A.; Maysinger, D. *Science* **2003**, *300*, 615.
(4) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903.
(5) Hu, Z. J.; Jonas, A. M.; Varshney, S. K.; Gohy, J.-F. *J. Am. Chem. Soc.* **2005**, *127*, 6526.
(6) Kukula, H.; Schlaad, H.; Antonietti, M.; Förster, S. *J. Am. Chem. Soc.* **2002**, *124*, 1658.
(7) Vinogradov, S. V.; Bronich, T. K.; Kabanov, A. V. *Adv. Drug. Delivery Rev.* **2002**, *54*, 135.
(8) Ilhan, F.; Galow, T. H.; Gray, M.; Clavier, G.; Rotello, V. M. *J. Am. Chem. Soc.* **2000** *122*, 5895.
(9) Cornelissen, J. J. L. M.; Fischer, M.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Science* **1998**, *280*, 1427.
(10) Wang, X. S.; Winnik, M. A.; Manners, I. *Macromol. Rapid Commun.* **2002**, *23*, 210.
(11) Won, Y. Y.; Davis, H. T.; Bates, F. S. *Science* **1999**, *283*, 960.
(12) Jungmann, N.; Schmidt, M.; Maskos, M. *Macromolecules* **2001**, *34*, 8347.
(13) Du, J. Z.; Chen, Y. M.; Zhang, Y. H.; Han, C. C.; Fischer, K.; Schmidt, M. *J. Am. Chem. Soc.* **2003**, *125*, 14710.
(14) Zhang, L. F.; Eisenberg, A. *Science* **1995**, *268*, 1728.
(15) Won, Y. Y.; Brannan, A. K.; Davis, H. T.; Bates, F. S. *J. Phys. Chem. B* **2002**, *106*, 3354.
(16) Disher, B. M.; Won, Y. Y.; Ege, D. S.; Lee, J. C.-M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. *Science* **1999**, *284*, 1143.
(17) Yu, Y.; Eisenberg, A. *J. Am. Chem. Soc.* **1997**, *119*, 8383.
(18) Zhang, L. F.; Yu, K.; Eisenberg, A. *Science* **1996**, *272*, 1777.
(19) Zhu, J. T.; Liao, Y. G.; Jiang, W. *Langmuir* **2004**, *20*, 3809.
(20) Pochan, D. J.; Chen, Z.; Cui, H.; Hales, K.; Qi, K.; Wooley, K. L. *Science* **2004**, *306*, 94.
(21) Loos, K.; Müller, A. H. E. *Biomacromolecules* **2002**, *3*, 368.
(22) Jain, S.; Bates, F. S. *Science* **2003**, *300*, 460.
(23) Liu, F.; Eisenberg, A. *J. Am. Chem. Soc.* **2003**, *125*, 15059.

(24) Cameron, N. S.; Corbierre, M. K.; Eisenberg, A. *Can. J. Chem.* **1999**, *77*, 1311.
(25) Riess, G. *Prog. Polym. Sci.* **2003**, *28*, 1107.
(26) Zhou, Z.; Li, Z.; Ren, Y.; Hillmyer, M. A.; Lodge, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 10182.
(27) Stewart, S.; Liu, G. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 340.
(28) Discher, D. E.; Kamien, R. D. *Nature (London)* **2004**, *430*, 519.
(29) Brannan, A. K.; Bates, F. S. *Macromolecules* **2004**, *37*, 8816.
(30) Lei, L.; Gohy, J.-F.; Willet, N.; Zhang, J.-X.; Varshney, S.; Jérôme, R. *Macromolecules* **2004**, *37*, 1089.
(31) Sfika, V.; Tsitsilianis, C. *Macromolecules* **2004**, *37*, 9551.
(32) Cai, Y.; Armes, S. P. *Macromolecules* **2004**, *37*, 7116.
(33) Lodge, T. P.; Hillmyer, M. A.; Zhou, Z. *Macromolecules* **2004**, *37*, 6680.
(34) Fustin, C.-A.; Abeta, V.; Gohy, J.-F. *Eur. Phys. J. E* **2005**, *16*, 291.
(35) Kríž, J.; Masar, B.; Pleštil, J.; Tuzar, Z.; Pospíšil, H.; Doskocilová, D. *Macromolecules* **1998**, *31*, 41.
(36) Gohy, J.-F.; Willet, N.; Varshney, S.; Zhang, J.-X.; Jéróme, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 3214.
(37) Discher, D. E.; Eisenberg, A. *Science* **2002**, *297*, 967.
(38) Vriezema, D. M.; Hoogboom, J.; Velonia, K.; Takazawa, K.; Christianen, P. C. M.; Maan, J. C.; Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 772.
(39) Jain, S.; Bates, F. S. *Macromolecules* **2004**, *37*, 1511.
(40) Shen, H. W.; Zhang, L. F.; Eisenberg, A. *J. Am. Chem. Soc.* **1999**, *121*, 2728.
(41) Li, Z.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. *Science* **2004**, *306*, 98.
(42) Yu, Y.; Zhang, L. F.; Eisenberg, A. *Macromolecules* **1998**, *31*, 1144.
(43) Chiruvolu, S.; Walker, S.; Israelachvihi, J.; Schnitt, F.-J.; Leckband, D.; Zasadzinski, J. A. *Science* **1994**, *264*, 1753.
(44) Vriezema, D. M.; Kros, A.; de Gelder, R.; Cornelissen, J. J. L. M.; Rowan, A. F.; Nolte, R. J. M. *Macromolecules* **2004**, *37*, 4736.
(45) Zhang, L. F.; Eisenberg, A. *Macromolecules* **1999**, *32*, 2239.

MA051258I