Macromolecules **2007,** *40,* 8323−8328

Mixtures of Diblock Copolymer Micelles by Different Mixing Protocols

Seong Il Yoo,[†] Byeong-Hyeok Sohn,*,[†] Wang-Cheol Zin,[‡] Jin Chul Jung,[‡] and Cheolmin Park[§]

Department of Chemistry, NANO Systems Institute, Seoul National University, Seoul 151-747, Korea, Department of Materials Science and Engineering, Polymer Research Institute, Pohang University of Science and Technology, Pohang 790-784, Korea, and Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

Received July 11, 2007

ABSTRACT: A size distribution of a binary mixture of polystyrene-*block*-poly(4-vinylpyridine) (PS−P4VP) diblock copolymer micelles was investigated mainly by transmission electron microscopy. A single-layered film of PS−P4VP micelles fabricated by spin-coating enabled a precise measurement of the micellar size. Depending on the mixing protocols, a mixture of pristine small and large micelles or a mixture of pure small micelles and hybridized micelles were formed due to the difference in the kinetics of micelle formation between the copolymers having short and long insoluble P4VP blocks. In addition, the kinetically frozen micelles excluded further evolution of the micelles produced. We also demonstrated feasible creation of an ordered array of copolymer micelles with the mixing protocol which produced nonhybridizing micelles.

Introduction

In selective solvents that dissolve only one of the blocks, diblock copolymers self-associate into micelles with corona of the soluble block and cores of the insoluble block.[1] The size and structure of micelles are affected by the chemical affinity of each block to the solvent, the chemical miscibility between the blocks, the molecular weight of each block, and the ratio between the blocks.[1−3] Depending on the polarity of solvent, either normal micelles with the more polar block as soluble corona or inverse micelles with the less polar block as soluble corona can be formed.[1−3]

With respect to potential applications of diblock copolymer micelles, they can solubilize otherwise insoluble substances in the cores so that they can be suitable for colloidal stabilization, drug delivery, nanoreactors of particle synthesis, and so on.[4−11] For example, we recently demonstrated that arrays of functional nanoparticles were effectively fabricated by utilizing single-layered films of diblock copolymer micelles.[9−11]

In addition to practical applications of micelles consisting of a single kind of diblock copolymers, dependences of the aggregation number of copolymer molecules per micelle and the size of micelles on the chemical structure and molecular weight of each block have been relatively well characterized.[1−3] For a mixture of two dissimilar diblock copolymers in a selective solvent, however, fundamental studies on their micellization have been started in recent years. For example, in a binary mixture of diblock copolymers having different molecular weights and size ratios between the blocks but the same chemical structures, there have been reports on formation of only hybridized micelles of two dissimilar copolymer molecules or formation of pure micelles of identical copolymer molecules as well as hybridized micelles, depending on differences of the block size and its ratio between two dissimilar copolymers.[12−22] By hybridization, formation of interesting morphologies such as hamburger-like and octopus-like micelles was recently reported,[12,15] in which the importance of the kinetic aspects on the formation of micelles was explained.

In this article, we investigated size distributions of diblock copolymer micelles in mixtures by different mixing protocols. A single-layered film of diblock copolymer micelles in dry state was examined by transmission electron microscopy (TEM), which provided not only precise measurements of micellar sizes without overlapping of micelles but also practically applicable configuration for in situ synthesis of an array of nanoparticles on the substrate.[6,8−11] By the TEM analysis, the size distributions of diblock copolymer micelles in the mixtures showed either a simple mixture of pristine small and large micelles or a mixture of pure small micelles and additional hybridized micelles, which depended on the mixing procedure. The formation of pure micelles and hybridized micelle was explained by the difference in the kinetics of micelle formation between the copolymers having short and long insoluble core blocks. In addition, the kinetically frozen micelles excluded further evolution of micelles produced. We also demonstrated feasible creation of an ordered array of copolymer micelles with the mixing protocol which produced nonhybridizing micelles.

Experimental Section

Two dissimilar polystyrene-poly(4-vinylpyridine) diblock copolymers were purchased from Polymer Source Inc. The number-average molecular weights of PS and P4VP in the diblock copolymer denoted by PS(33)-P4VP(8) were 32 900 g/mol and 8000 g/mol, respectively. Its polydispersity index was 1.06. The other diblock copolymer denoted by PS(20)-P4VP(19) had the number-average molecular weight of 20 000 and 19 000 g/mol for each block with a polydispersity index of 1.09.

To make solutions of copolymer micelles, PS−P4VP diblock copolymers were added to toluene (typically 0.5 wt %), a strongly selective solvent for the PS block, and stirred for 2 h at room temperature and for additional 8 h at 80 °C, and then cooled down to room temperature. To prepare mixture solutions from two different PS−P4VP copolymers, we employed three different

---

* Corresponding author. Telephone: +82-2-883-2154. Fax: +82-2-889-1568. E-mail: bhsohn@snu.ac.kr.

[†] Department of Chemistry, NANO Systems Institute, Seoul National University.

[‡] Department of Materials Science and Engineering, Polymer Research Institute, Pohang University of Science and Technology.

[§] Department of Materials Science and Engineering, Yonsei University.

10.1021/ma071534o CCC: $37.00

mixing protocols. In the case of a mixture from a micellar state, independently prepared solutions of each micelle were mixed at room temperature and then stirred for 2 h at room temperature and for additional 8 h at 80 °C. For a mixture from a powdery state, two dissimilar diblock copolymers in a powdery form were first mixed and added together into toluene and then stirred for 2 h at room temperature and for additional 8 h at 80 °C. For a mixture from a blended state, a film of two copolymers were slowly cast from a dimethly formamide (DMF) solution, which is a good solvent for both PS and P4VP blocks. The solvent-cast film was annealed in a vacuum oven for 4 days at 210 °C. The blended film was added into toluene and stirred for 2 h at room temperature and for additional 8 h at 80 °C. Mixture solutions by different mixing protocols were cooled down to room temperature after stirring at 80 °C. The weight ratio between two diblock copolymers was kept at 1:1 for all mixture solutions, irrespective of the mixing method. From toluene solutions of micelles, thin films were spin-coated on freshly cleaved mica substrates. A single-layered film of PS−P4VP micelles was obtained typically at 3000 rpm.[9−11]

For plane-view images in transmission electron microscopy (TEM), a single-layered film of copolymer micelles was floated off from the mica substrate onto deionized water and collected on a carbon-coated TEM grid. For a cross-sectional TEM image of a blended film of two copolymers, the film was embedded in epoxy resin, and thin sections (ca. 80 nm thick) were obtained using a RMC MTX ultramicrotome with a diamond knife. All TEM samples were exposed to I_2 vapor in a sealed glass vessel for 2 h at room temperature to selectively stain the domains of P4VP blocks. TEM was performed on a Hitachi 7600 operating at 100 kV. An image analysis software was used to obtain an average size and distribution of stained cores from TEM images.

Small-angle X-ray scattering (SAXS) measurements were performed by the synchrotron X-ray radiation source at the 4C1 beamline of Pohang Accelerator Laboratory, Pohang, Korea.[23] The X-ray wavelength used was 1.608 Å.

Results and Discussion

In toluene, a selective solvent for the PS block, PS−P4VP diblock copolymers spontaneously associate into spherical inverse micelles consisting of a soluble PS corona and an insoluble P4VP core.[2,3] For the simplicity, micelles instead of inverse micelles will be used to describe PS−P4VP inverse micelles in toluene. The size of spherical micelles is related to the aggregation number (Z), the number of copolymer molecules per micelle, which depends on the degree of polymerization of each block. In general, the aggregation number for amphiphilic molecules can be expressed by[1−3]

$$Z = Z_o(N_A{}^{\alpha} N_B{}^{-\beta}) \tag{1}$$

where N_A and N_B are the degree of polymerization of the insoluble core and the soluble corona block, respectively. For all kinds of micellar systems, the exponents α and β are close to 2.0 and 0.8, respectively. Particularly for the PS−P4VP/tolune system, the experimental values of $\alpha = 1.93$ and $\beta = 0.79$ were reported.[2,3] The parameter Z_o is related to thermodynamic quantities such as an interaction parameter and a local packing parameter, and was reported as 1.66 for the PS−P4VP/toluene system.[3] The space filling condition for the core yields the simple relation between the aggregation number (Z) and the radius of the insoluble core (R_c).

$$\frac{4\pi}{3}R_c{}^3 = ZN_A\upsilon_A \tag{2}$$

where υ_A is the molar volume of core monomers. From eqs 1 and 2, the aggregation number and the radius of cores increase as the degree of polymerization of core blocks increases. Thus, we can expect that the core radius of PS(20)−P4VP(19) micelles is greater than that of PS(33)−P4VP(8) micelles because of a longer core-forming P4VP block of PS(20)−P4VP(19).

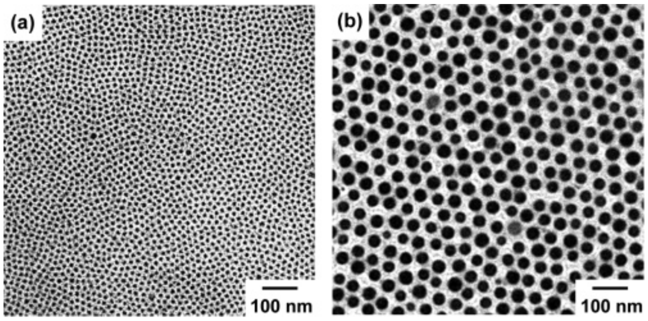


Figure 1. TEM images of single-layered films of PS−P4VP micelles: (a) small micelles of PS(33)−P4VP(8); (b) large micelles of PS(20)−P4VP(19). P4VP cores were stained with I_2.

TEM images in Figure 1 clearly show that the core of PS(20)−P4VP(19) micelles was larger than that of PS(33)−P4VP(8) micelles. P4VP blocks were selectively stained with I_2 and appeared as dark cores. It should be noted that micellar films shown in Figure 1 were in dry state without solvent. But the aggregation number and the core size could not be different from those in solution state because the micellar film was in a kinetically frozen state by fast solvent evaporation during spin-coating and also the solubility of the P4VP block in toluene was negligible.

For the radius of micelle, the corona size should be added to the core radius. The corona dimension (D_h) for starlike molecules in good solvents scales as $D_h \sim Z^{0.2}N_B{}^{0.6}$.[2,3] The ratio of D_h between PS(33)−P4VP(8) and PS(20)−P4VP(19) is close to the unity. Thus, the radius of PS−P4VP micelles in this study can be directly proportional to the core radius. We are going to call PS(33)−P4VP(8) micelles as small micelles and PS(20)−P4VP(19) as large micelles. It should be noted that the corona size observed as the spacing between micelles in the TEM images of Figure 1 was much smaller than that in solution state because of absence of solvent molecules and overlapping of corona blocks.[3]

A single-layered film of PS−P4VP micelles fabricated by the spin-coating method enabled precise measurements of the core size because there was no overlapping of micelles. Accurate evaluation of micellar sizes is necessary to judge the formation of hybridized micelles in binary mixtures. Hybridized micelles of copolymers having two different molecular weights usually show an intermediate micellar size compared to small and large micelles of single-type copolymer molecules.[15,17−19,21,22] Distributions of the core size of PS−P4VP micelles from much larger areas than the images of Figure 1 are shown in Figure 2. The size distributions were not changed even after prolonged (longer than 1 week) storage. The average core diameters of small and large micelles were 9.2 and 33.9 nm, respectively.

First, we prepared a binary mixture of PS−P4VP micelles from a micellar state by mixing independently prepared solutions of small and large micelles. This mixing protocol was also called as "postmixing".[12,15] The size distribution of micelles was examined from their single-layered films to investigate whether hybridized micelles between two dissimilar diblock copolymers were formed or not. From the TEM image shown in Figure 3a, micelles having two different core sizes were clearly distinguishable. The size distribution of cores of the mixture of small and large micelles from much larger area than the image of Figure 3a is shown in Figure 4a. The size distribution clearly exhibited two maxima with the average core diameters of 9.1

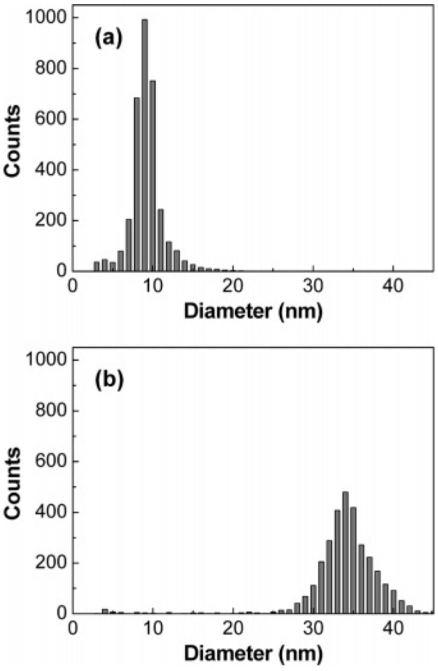


Figure 2. Size distributions of the cores of PS−P4VP micelles shown in Figure 1: (a) small micelles; (b) large micelles. The actual counts were obtained from larger areas than the images of Figure 1.

and 34.0 nm, which were not changed after prolonged stirring at room temperature. If hybridized micelles were formed by incorporation of two dissimilar diblock copolymers into a single micelle, population of micelles having an intermediate size between small and large micelles would be increased in the size distribution. However, the size distribution of cores of the mixture in Figure 4a was almost the same as a combined size distribution of pure PS(33)−P4VP(8) micelles and pure PS-(20)−P4VP(19) micelles shown in Figure 2, implying that hybridization of small and large micelles was not favored.

When two dissimilar diblock copolymer micelles having different molecular weights but the same chemical structures are mixed, hybridized micelles can be formed by mechanisms of the fusion−fission and/or the unimer (a single molecule not associated in micelles) transfer.[22,24] For fusion and fission of micelles, i.e., small micelles integrate into a large one and a large micelle disintegrates into small ones, redistribution of copolymer chains among micelles is necessary. For PS−P4VP micelles in toluene, however, insoluble glassy P4VP cores would not allow redistribution of PS−P4VP molecules among micelles. Thus, hybridization of small and large PS−P4VP micelles would not occur by the fusion−fission process. On the other hand, the unimer transfer mechanism that a molecule extricates from one micelle and reenters to other micelles can also result in hybridized micelles. However, in toluene solutions of PS−P4VP micelles having a reasonable length of P4VP blocks, an extremely small number of unimers or even no unimers could exist due to the negligible solubility of P4VP block in toluene.[3] Therefore, hybridized PS−P4VP micelles could not be formed by the unimer transfer. Thus, the hybridization did not occur in the mixture of two PS−P4VP copolymers prepared from a micellar state.

The second mixing protocol was to prepare a mixture of diblock copolymer micelles from a powdery state. Two PS−P4VP copolymers in a powdery form were simply mixed and added together into toluene, and allowed to form micelles by stirring at room temperature and at the elevated temperature. Then the mixed solution was cooling down to room temperature. A typical TEM image of a single-layered film of this mixture is shown in Figure 3b, almost identical to that of the mixture from a micellar state shown in Figure 3a. Two different sizes of micelles were clearly discernible again and not changed after extended stirring at room temperature. The size distribution of cores of the mixture shown in Figure 4b revealed two maxima with the average core diameters of 8.6 and 33.4 nm, which are almost the same as those in the mixture from a micellar state in Figure 4a. The size distribution was again basically a combined size distribution of pure PS(33)−P4VP(8) micelles and pure PS(20)−P4VP(19) micelles in Figure 2. This result also implies unfavorable hybridization of PS−P4VP copolymers having two dissimilar molecular weights into the same micelle from a powdery state.

Although both mixtures from a micellar state and from a powdery state showed a bimodal size distribution, the kinetics of the micelle formation in toluene should be considered to explain the bimodal distribution in the mixture from a powdery state. When two copolymers are mixed in a powdery state, two copolymers cannot be mixed at the molecular level and simply exist separately. Thus, the micelle formation from the mixed powder of two copolymers can be mainly affected by the kinetics of the micelle formation of each diblock copolymer.

Since PS(33)−P4VP(8) copolymers have a relatively short P4VP block, they can form micelles in toluene at room temperature. The formation of micelles of PS(33)−P4VP(8) at room temperature was verified by the SAXS measurement (Figure 5a), in which the characteristic peak of micelles (marked by the arrow) was observed at room temperature. In contrast, PS(20)−P4VP(19) having a longer P4VP block remained as a powdery form in toluene at room-temperature even after prolonged stirring, and no discernible peak in the SAXS profile was observed at room temperature (Figure 5b). When PS(20)−P4VP(19) copolymers in toluene were stirred at the elevated temperature, the solution became clear, indicating the formation of micelles. After the micellar solution of PS(20)−P4VP(19) had cooled down to room temperature, the clear solution was maintained. The characteristic peak of PS(20)−P4VP(19) micelles were observed after heating the solution and also after cooling down to room temperature (Figure 5b). Thus, in the case that two copolymers of PS(33)−P4VP(8) and PS(20)−P4VP(19) were simply mixed from a powdery state, micelles of PS(33)−P4VP(8) were formed at room temperature, whereas the micellization of PS(20)−P4VP(19) did not proceed at room temperature.

Figure 6a shows a TEM image of the copolymer mixture from a powdery state only after stirring at room temperature without heating. Small micelles of PS(33)−P4VP(8) with dark P4VP cores were clearly discernible, whereas no large micelles of PS-(20)−P4VP(19) were observed. Instead, there were undefined aggregates that did not form micelles. When the mixture were heated, micelles of PS(20)−P4VP(19) were also formed. Thus, micelles of PS(33)−P4VP(8) were first formed at room temperature, and then PS(20)−P4VP(19) were micellized at the elevated temperature, resulting in the bimodal distribution of micelles shown in Figure 3b. The different temperature dependence of the micelle formation between PS(33)−P4VP(8) and PS(20)−P4VP(19) resulted in the bimodal size distribution of micelles without hybridization when they were simply mixed from a powdery state. Once the micelles of two different sizes were formed, they remained stable without further hybridization because of the lack of the fusion/fission of micelles and the unimer transfer as explained in the case for the mixture from a micellar state.

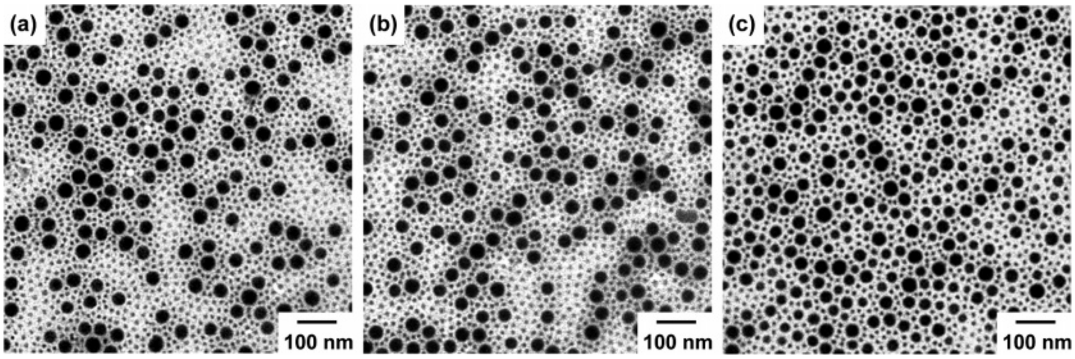


Figure 3. TEM images of single-layered films of micelle mixtures: (a) from a micellar state; (b) from a powdery state; (c) from a blended state. P4VP cores were stained with I_2.

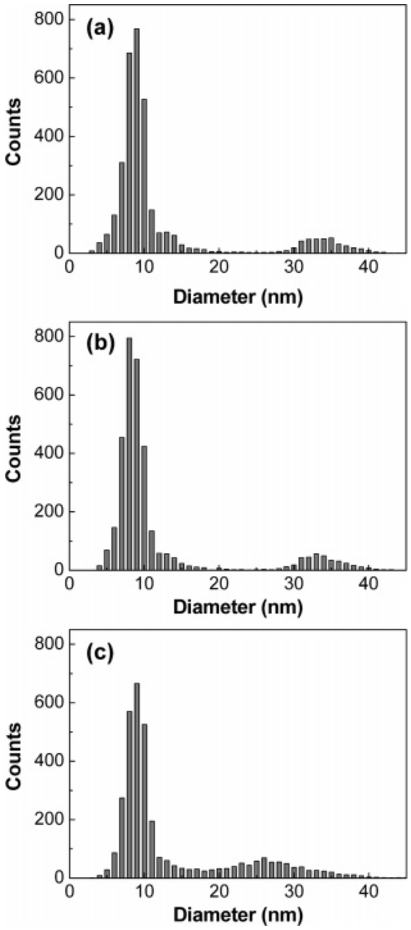


Figure 4. Bimodal size distributions of the cores of micelle mixtures shown in Figure 3: (a) from a micellar state; (b) from a powdery state; (c) from a blended state. The actual counts were obtained from larger areas than the images of Figure 3.

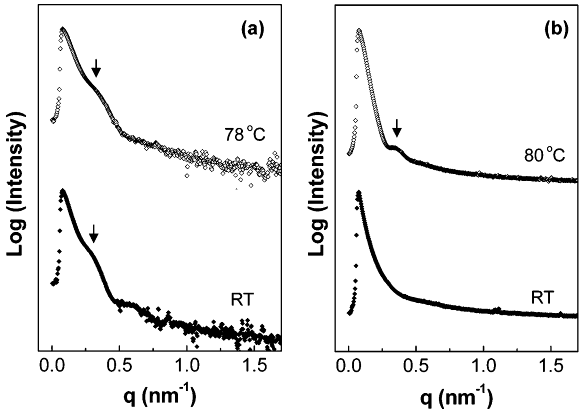


Figure 5. Temperature dependence of SAXS profiles for diblock copolymers in 0.5 wt % toluene solutions: (a) PS(33)−P4VP(8); (b) PS(20)−P4VP(19).

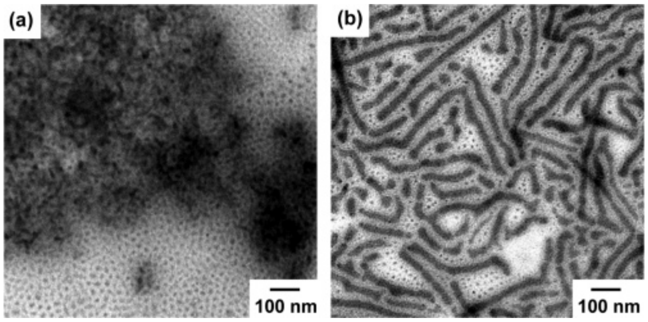


Figure 6. TEM images of micelle mixtures after stirring for 2 h at room temperature: (a) the mixture from a powdery state; (b) the mixture from a blended state. TEM samples were obtained by direct evaporation of the solutions on TEM grids. P4VP blocks were stained with I_2.

The third mixing protocol was preparing a mixture of diblock copolymer micelles from a blended state. This mixing protocol was also called as “premixing”.[12,15] Two copolymers were homogeneously dissolved in a good solvent for both PS and P4VP blocks. Then, a bulk film was cast from the solution. Since the molecular weight ratio of two copolymers is smaller than 5,[1,25] two copolymers can be miscible, i.e., mixed at the molecular level, and can form a single morphology without macrophase separation in a blended film, which was confirmed by SAXS and TEM results. In the SAXS profile of a blended film of PS(33)−P4VP(8) and PS(20)−P4VP(19) (Figure 7a), the multiple-order reflections indicated an ordered single morphology. The TEM image of Figure 7b also revealed a single morphology without a macrophase separated region of PS(33)−P4VP(8) and PS(20)−P4VP(19) copolymers. From the peak positions in SAXS and the image in TEM, the morphology can be neither cylindrical nor lamellar but can be considered as a distorted bicontinuous phase, which was often observed in a blend of diblock copolymers.[26]

The blended film, in which two copolymers were molecularly mixed, was added to toluene and allowed to form micelles in the same condition as before, i.e., stirring at room temperature and at the elevated temperature, and then cooling down to room temperature. In the TEM image of a single-layered film of this mixture (Figure 3c), apparently small and large micelles were discernible again, but large micelles showed a broader size distribution than those in the previous cases, which can be clearly visualized in the size distribution of cores of micelles shown in Figure 4c. The size distribution of cores of small micelles in this mixture (the average core diameter = 9.3 nm) was not much different from that of pure PS(33)−P4VP(8)

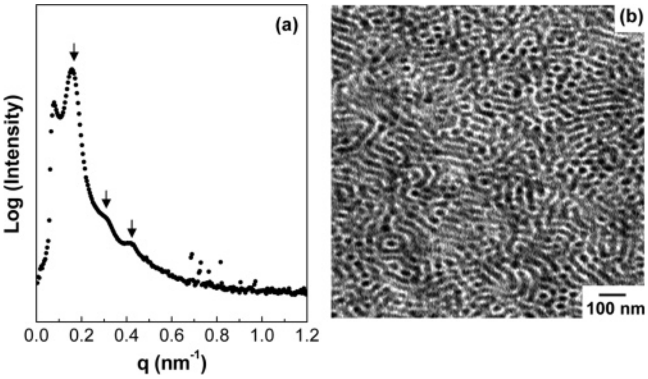
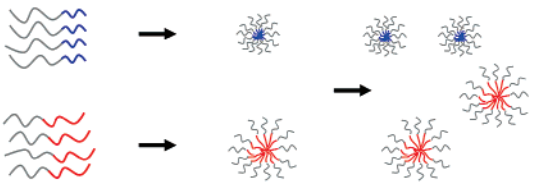


Figure 7. Blend of PS(33)−P4VP(8) and PS(20)−P4VP(19): (a) SAXS profile; (b) TEM image. In the TEM image, P4VP blocks were stained with I_2.

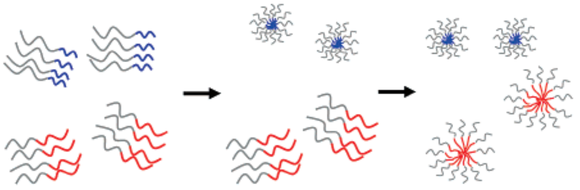
micelles. However, the size distribution of cores of large micelles was shifted to the lower values and became broader. In other words, the population of micelles having a size intermediate between small and large micelles was increased. The average core diameter in this intermediate population was 27.2 nm. The intermediate micelles between small and large micelles implies incorporation of two copolymers of PS(33)−P4VP(8) and PS(20)−P4VP(19) into the same micelle, i.e., the hybridization. Thus, in the micellar mixture induced from a blended state, there were pure small micelles of PS(33)−P4VP(8) and hybridized micelles of PS(33)−P4VP(8) and PS(20)−P4VP(19).

To explain the formation of pure micelles and hybridized micelles in the mixture of copolymers from a blended state,.i.e. from a molecularly mixed state, the kinetics of the micelle formation should be considered again. As the case of the micelle formation from a powdery state, micelles of PS(33)−P4VP(8) can be formed at room temperature but micelles of PS(20)−P4VP(19) can be formed only at the elevated temperature. Thus, by stirring the blended sample in toluene at room temperature, PS(33)−P4VP(8) formed micelles but micelles of PS(20)−P4VP(19) were not formed yet. In the TEM image of the copolymer mixture from a blended state obtained only after stirring at room temperature without heating (Figure 6b), small micelles without large micelles were observed as in the case of the mixture from a powdery state. However, the number of small micelles was smaller than that from a powdery state (Figure 6a), implying that disintegration of PS(33)−P4VP(8) copolymers from the molecularly mixed state with PS(20)−P4VP(19) copolymers could be limited due to the entanglement between two copolymers. In the TEM image (Figure 6b), there were large numbers of wormlike dark aggregates of stained P4VP domains, which could be formed by mixtures of two copolymers. When the mixture were heated at the elevated temperature where PS(20)−P4VP(19) can form micelles, both PS(20)−P4VP(19) and PS(33)−P4VP(8) copolymers were incorporated into the same micelle because they initially existed together in the molecularly mixed state. The incorporation of both copolymers into the same micelle resulted in the hybridized micelles with the intermediate micellar size. Once pure small micelles and hybridized micelles were formed, they remained stable because of the lack of the exchange mechanism of copolymers between micelles as explained in the previous cases.

(a) Mixture from a micellar state



(b) Mixture from a powdery state



(c) Mixture from a blended state

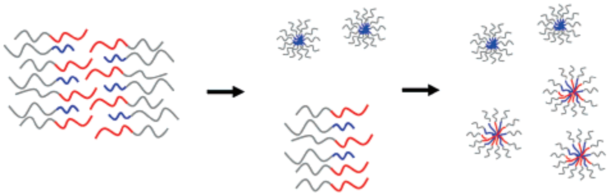


Figure 8. Schematics of the evolution of micelle mixtures: (a) from a micellar state; (b) from a powdery state; (c) from a blended state.

The schematics in Figure 8 summarize the evolution of micelle mixtures by three different mixing protocols. In the illustration, PS(33)−P4VP(8) and PS(20)−P4VP(19) are colored as gray−blue and gray−red copolymers, respectively. In the case of the mixture from a micellar state (Figure 8a), two copolymers first form small and large micelles in each solution. Then, mixing of two micelles yields a bimodal distribution of small and large micelles because of no mechanism for the hybridization due to the extremely poor solubility of the P4VP block to toluene and the glassy nature of the P4VP core at room temperature. Figure 8b shows the schematic evolution by the mixing protocol from a powdery state. Two copolymers mixed in a powdery state exist separately without mixing at the molecular level so that they can form micelles independently. Thus, small micelles of PS(33)−P4VP(8) having short P4VP blocks are first formed at room temperature, and then large micelles of PS(20)−P4VP(19) having long P4VP blocks are formed at the elevated temperature, resulting in the bimodal distribution of micelles. In the micellization from a blended state (Figure 8c), two copolymers initially form a single morphology mixed at the molecular level. At room temperature, small micelles of PS(33)−P4VP(8) are first formed as the case of mixing from a powdery state. But some of PS(33)−P4VP(8) still remain mixed with PS(20)−P4VP(19) due to the difficulty in disintegration from the molecularly mixed state. At the elevated temperature, both copolymers initially mixed at the molecular level are incorporated into the same micelle and form the hybridized micelles. Thus, there are pure small micelles and hybridized micelles of two copolymers.

The result in the mixture from a blended state was apparently different from the observation of only hybridized micelles or two pristine micelles without hybridization when micelles were prepared by the premixing protocol, i.e., mixing from a blended state.[12,15] In the report of only hybridized micelles formed, however, two copolymers were able to form micelles at the same temperature,[15] which can be a similar situation to the formation of hybridized micelles at the elevated temperature in the last stage of the micelle formation from a blended state if small micelles already formed were not considered (Figure 8c). In the report that two pure micelles were formed without hybrid-

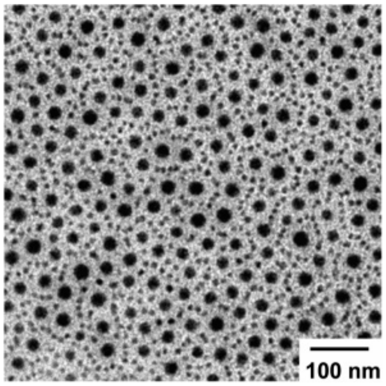


Figure 9. TEM image of an ordered array of small and large micelles from a single-layered film of the micelle mixture. P4VP cores were stained with I_2.

ization, two copolymers were not mixed molecularly at the beginning although they were mixed by a good solvent,[12] which was analogous to the mixture from a powdery state (Figure 8b). Thus, the results in this study were in agreement with the previous observations, even though the kinetics played an important role in the micelle formation from the mixture of copolymers.

Since the hybridization of two dissimilar PS−P4VP copolymers can be effectively excluded by using the nonhybridizing mixing protocol, the size ratio of small to large micelles can be controlled by adjusting molecular weights of copolymers. In addition, the number ratio of small to large micelles in a single-layered film of binary mixtures of micelles can be adjusted by changing the mixing ratio of small to large micelles. Thus, the full control over the size and number ratios can make it possible to fabricate an ordered array of small and large micelles in the film.[27,28] In Figure 3a, small and large micelles were distributed in the film without any particular pattern when the size ratio and the number ratio of small to large micelles were 0.27 and 7.4, respectively. However, with the size ratio of 0.51 and the number ratio of 3.7, for example, the single-layered film showed a mosaic pattern of small and large micelles, i.e., pseudo-hexagonally ordered large micelles surrounded by small micelles (Figure 9).

In a bimodal mixture of colloidal particles that were bigger than diblock copolymer micelles, it was reported that they showed a macroscopic separation, a random mixture, or an ordered assembly of small and large colloids, depending on the size ratio and the number ratio of small to large particles.[27−29] In addition, superlattice formation was recently reported in a binary mixture of block copolymer micelles.[30] We are currently investing two-dimensional phase behavior in a bimodal mixture of small and large micelles. In particular, if different types of nanoparticles or precursors of nanoparticles were incorporated in small and large micelles independently, an ordered assembly of bimodal mixtures of micelles can be applied to a nanostructured template to arrange two different types of nanoparticles in specific location. The work on this research topic is in progress.

Conclusions

A single-layered film of mixtures of PS−P4VP diblock copolymer micelles provided precise measurements of micellar sizes without overlapping of micelles and verified the size distribution of micelle mixtures from two dissimilar diblock copolymers. Depending on the mixing procedure, a mixture of pristine small and large micelles or a mixture of pure small micelles and hybridized micelles were formed because of the difference in the kinetics of micelle formation between the copolymers having short and long insoluble P4VP blocks. In addition, the kinetically frozen micelles excluded further evolution of the micelles produced. The different micelle formation by changing the mixing protocol implied that it was difficult to reach overall equilibrium in the micellar system investigated, mainly because of the lack of the copolymer exchange between micelles. With the nonhybridizing mixing protocol, feasible creation of an ordered array of small and large copolymer micelles in the single-layered film was introduced. The ordered array can be used for a nanostructured template to locate two different types of nanoparticles in a specific arrangement.

Acknowledgment. This work was supported by a Korea Research Foundation Grant (KRF-2004-042-D00062).

References and Notes

(1) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: New York, 1998.
(2) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.
(3) Förster, S.; Zisenis, M.; Wenz, E.; Antonietti, M. *J. Chem. Phys.* **1996**, *104*, 9956.
(4) Bronstein, L.; Antonietti, M.; Valetsky, P. In *Nanoparticles and Nanostructured Films*; Fendler, J. H., Ed.; Wiley-VCH: Weinheim, Germany, 1998.
(5) Förster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 688.
(6) Glass, R.; Möller, M.; Spatz, J. P. *Nanotechnology* **2003**, *14*, 1153.
(7) Hamley, I. W. *Nanotechnology* **2003**, *14*, R39.
(8) Boontongkong, Y.; Cohen, R. E. *Macromolecules* **2002**, *35*, 3647.
(9) Sohn, B. H.; Choi, J. M.; Yoo, S. I.; Yun, S. H.; Zin, W.-C.; Jung, J. C.; Kanehara, M.; Hirata, T.; Teranishi, T. *J. Am. Chem. Soc.* **2003**, *125*, 6368.
(10) Yoo, S. I.; Sohn, B. H.; Zin, W.-C.; An, S.-J.; Yi, G.-C. *Chem. Commun.* **2004**, 2850.
(11) Yun, S. H.; Sohn, B. H.; Jung, J. C.; Zin, W.-C.; Lee, J. K.; Song, O. *Langmuir* **2005**, *21*, 6548.
(12) Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Macromolecules* **2006**, *39*, 765.
(13) Kang, N.; Perron, M.-E.; Prud'homme, R. E.; Zhang, Y.; Gaucher, G.; Leroux, J.-C. *Nano Lett.* **2005**, *5*, 315.
(14) Cai, P.; Wang, C.; Ye, J.; Xie, Z.; Wu, C. *Macromolecules* **2004**, *37*, 3438.
(15) Jain, S.; Bates, F. S. *Macromolecules* **2004**, *37*, 1511.
(16) Won, Y.-Y.; Davis, H. T.; Bates, F. S. *Macromolecules* **2003**, *36*, 953.
(17) Koňák, Č.; Helmstedt, M. *Macromolecules* **2003**, *36*, 4603.
(18) Štěpánek, M.; Podhájecká, K.; Tesařová, E.; Procházka, K.; Tuzar, Z.; Brown, W. *Langmuir* **2001**, *17*, 4240.
(19) Esselink, F. J.; Dormidontova, E. E.; Hadziioannou, G. *Macromolecules* **1998**, *31*, 4873.
(20) Borovinskii, A. L.; Khokhlov, A. R. *Macromolecules* **1998**, *31*, 7636.
(21) Honda, C.; Yamamoto, K.; Nose, T. *Polymer* **1996**, *37*, 1975.
(22) Tian, M.; Qin, A.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z.; Procházka, K. *Langmuir* **1993**, *9*, 1741.
(23) Bolze, J.; Kim, J.; Huang, J.-Y.; Rah, S.; Youn, H. S.; Lee, B.; Shin, T. J.; Ree, M. *Macromol. Res.* **2002**, *10*, 2.
(24) Haliloğlu, T.; Bahar, I.; Erman, B.; Mattice, W. L. *Macromolecules* **1996**, *29*, 4764.
(25) Hashimoto, T.; Yamasaki, K.; Koizumi, S.; Hasegawa, H. *Macromolecules* **1993**, *26*, 2895.
(26) Court, F.; Yamaguchi, D.; Hashimoto, T. *Macromolecules* **2006**, *39*, 2596.
(27) Bartlett, P.; Ottewill, R. H.; Pusey, P. N. *Phys. Rev. Lett.* **1992**, *68*, 3801.
(28) Velikov, K. P.; Christova, C. G.; Dullens, R. P. A.; van Blaaderen, A. *Science* **2002**, *296*, 106.
(29) Yamaki, M.; Higo, J.; Nagayama, K. *Langmuir* **1995**, *11*, 2975.
(30) Abbas, S.; Lodge, T. P. *Phys. Rev. Lett.* **2006**, *97*, 097803.

MA071534O