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A Convenient Method of Tuning Amphiphilic Block Copolymer Micellar Morphology

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ABSTRACT: A strategy toward tuning amphiphilic block copolymer micellar morphology is proposed in this study. A binary solvent mixture of water and acetone with different acetone content instead of a unitary solvent of water is used as block-selective solvent to associate polystyrene-*b*-poly(acrylic acid-*co*-methyl acrylate) and polystyrene-*b*-poly(acrylic acid) chains into various morphological micelles. Following this method by adjusting the acetone content in the binary solvent mixture, various morphological micelle-like aggregates such as core−shell spheres, porous aggregates, core−shell cauliflower-like aggregates, and nanofibers are formed. The various morphological aggregates are observed by TEM and characterized by light scattering, and the possible reason for micellar morphology tuning is discussed.

Introduction

It has been known for many years that amphiphilic block copolymers in a selective solvent for one of the blocks can form colloidal size aggregates or core−shell micelles due to association of the insoluble blocks.[1] Depending on the composition of the block copolymers, two types of micelles can be distinguished: star and crew-cut micelles.[2] The star micelles have relatively large shells consisting of the long soluble block and relatively small cores consisting of the short insoluble block. Aggregates of another kind, namely crew-cuts, have cores whose dimension is relatively larger than that of shells. Generally, star micelles can be prepared directly by dissolving a highly asymmetric block copolymer, e.g., polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA), in a solvent selective for the long block or by adding water into polymer solution in a common solvent of *N*,*N*-dimethylformamide (DMF), while crew-cut micelles are usually prepared by the water addition method in most cases.[3−9] During micellization of amphiphilic block copolymer chains, core−shell micelles form quickly when water content is up to a given critical concentration, and the structure of the resulting core−shell micelles is frozen in a water-rich condition.[3−9] Usually, the structure of the resulting core−shell micelles can keep stable at temperatures below the glass temperature (T_g) of the core-forming block of PS even the micelle solution is much diluted with water.[10−12] One of the noteworthy phenomena associated with the resulting micelles is the accessibility of a wide range of morphologies such as spheres, rods, vesicles, lamellae, large compound micelles, nanofibers, and nanotubes.[13−19] The morphology of the aggregates is a function of several variables, such as block copolymer composition and concentration,[3] the type and concentration of added ions in block-selective solvent,[17,20] and the nature of the common solvent used in the preparation.[4,21] The morphological effects of the above parameters can, in general, be ascribed to their influence on the force balance during the formation of the aggregates.[3,4] To our best knowledge, a unitary solvent such as water was used in most cases as block-selective solvent to associate amphiphilic block copolymer chains into micelles. For examples, Zhang and Eisenberg used water as block-selective solvent to associate polystyrene-*b*-poly(acrylic acid) chains to micelles;[3,5] Yu and Eisenberg used water to associate polystyrene-*b*-poly(ethylene oxide) chains to micelles;[22,23] Shen and Eisenberg used water to associate polystyrene-*b*-poly(4-vinylpridine) chains to micelles;[24] Liu's group used hexane to associate polystyrene-*b*-poly(2-cinnamoylethyl methacrylate) chains into micelles;[25] Liang used water to associate polystyrene-*b*-poly[2-(β-D-glucopyranosyloxy)ethyl acrylate] chains into micelles,[26] etc. Does the nature of the block-selective solvent influence the morphology of resulting micelles? Here, we present such an easy and efficient method by using a binary solvent mixture of water and acetone with different acetone contents to associate amphiphilic block copolymer chains into various morphological aggregates.

Experimental Section

Materials. Amphiphilic block copolymers of polystyrene-*b*-poly(acrylic acid-*co*-methyl acrylate) [PS_{38}-*b*-P(AA_{190}-*co*-MA_{20})] and polystyrene-*b*-poly(acrylic acid) [PS_{200}-*b*-PAA_{78}] were prepared from partly hydrolysis of polystyrene-*block*-poly(methyl acrylate) (PS_{38}-*b*-PMA_{210}) and fully hydrolysis of PS_{200}-*b*-PMA_{78} in NaOH aqueous solution, respectively. PS_{38}-*b*-PMA_{210} and PS_{200}-*b*-PMA_{78} were synthesized by atom transfer radical polymerization (ATRP).[27] The detailed hydrolysis of PS-*b*-PMA in NaOH aqueous solution can be seen elsewhere.[28] The composition of block copolymer PS-*b*-PMA was determined from the ratio of the ^{1}H NMR intensities of the OCH_3 signal (at $\delta = 3.7$) and the aromatic signal (at $\delta = 6.6-7.3$) of the block copolymer. The polydispersity index (PDI) of PS_{38}-*b*-PMA_{210} and PS_{200}-*b*-PMA_{78} measured by gel permeation chromatography (GPC) was 1.28 and 1.20, respectively.

Preparation of the Micelles. The block copolymers PS_{38}-*b*-P(AA_{190}-*co*-MA_{20}) and PS_{200}-*b*-PAA_{78} were first dissolved in DMF to make a copolymer solution with the initial copolymer concentration at 0.20 and 2.0 mg/mL, respectively. Subsequently, a given volume of the binary solvent mixture of deionized water and acetone was added to 2.0 mL of the polymer solutions at a rate of 1 drop (1 drop is about 7 μL) every 10 s with stirring. As the addition of the binary solvent

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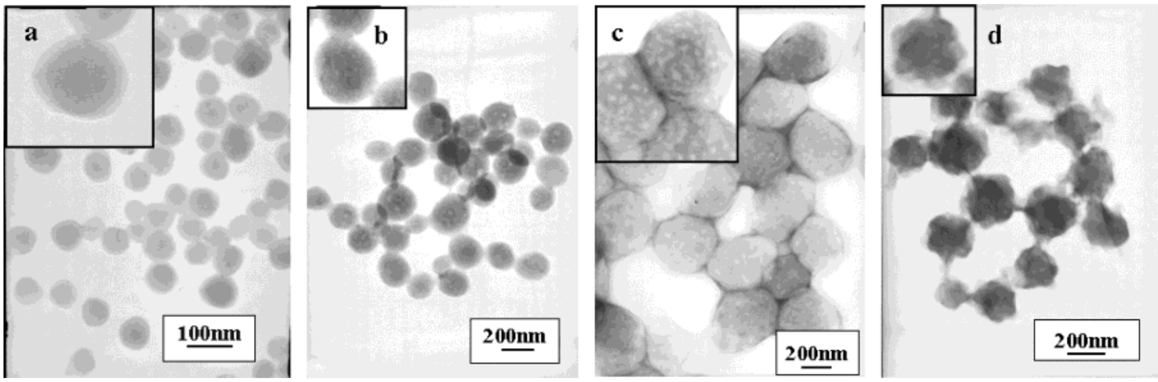

Figure 1. TEM images of the aggregates self-assembled by PS$_{38}$-*b*-P(AA$_{190}$-*co*-MA$_{20}$), where the block-selective solvent is water (a) and the binary solvent mixture of acetone and water with acetone fractions at 40 (b), 80 (c), and 90 vol % (d), respectively.

mixture progressed, the quality of the polymer solution decreased gradually. The formation of the aggregates, as indicated by the appearance of turbidity in the polymer solution, typically occurred when the content of the binary solvent mixture reached 5−20 vol %, depending on the water content in the binary solvent mixture. After 2 h, the addition of the binary solvent mixture was continued until 1.2 mL of the binary solvent mixture had been added. The solution series were kept overnight, and then 18.0 mL of water was further added. Then the solution series were dialyzed against water for 4 days to remove DMF and acetone in the micelle solution. Last, the micelle solution series were moved to a clean volumetric flask, and then a certain volume of deionized water was used to wash the dialysis bag and then added to the flask to make the final polymer volume at 20.0 mL, where the calculated polymer concentrations of the micelle solution series were 0.020 and 0.20 mg/mL, respectively.

Transmission Electron Microscopy (TEM). The structure of the resulting micelles was observed by a commercial transmission electron microscope (TEM) of Philips EM400ST at an acceleration voltage of 80 kV. For the observations of the size and distribution of the copolymer aggregates, a small drop of the micelle solution was directly deposited onto a copper EM grid, which had been precoated with a thin film of polyvinyl formal, then coated with carbon, and then dried at atmospheric pressure at room temperature.

Laser Scattering (LS). The structure of the resulting micelles is also characterized by a combination of static laser scattering (SLS) and dynamic laser scattering (DLS). Static laser scattering (SLS) and dynamic laser scattering (DLS) experiments were performed on a laser scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm. A given weight of water was first filtered with a 0.2 μm Millipore filter into a clean scintillation vial, and then a given weight of the micelle solution was further filtered with a 0.8 μm Millipore filter into the water in the clean scintillation vial. More than three concentrations were used to determine the weight-average molecular weight of micelles M_w, apparent radius of gyration R_g^0, radius of gyration R_g, and the second virial coefficient A_2 with the aid of a Debye plot. All LS measurements were performed at 25 °C. The detailed method of LS measurement can be seen in our recent works or Wu's study.[28−31]

Results and Discussion

The binary solvent mixture of water and acetone is a block-selective solvent for PAA block, while a precipitant for PS block of block copolymer PS-*b*-PAA. Thus, core−shell micelles with chains of PS block as core and chains of PAA blocks as shell are formed when water or the binary solvent mixture of water and acetone is added into the polymer solution. Figure 1 shows the TEM images of the resulting micelles self-assembled by PS$_{38}$-*b*-P(AA$_{190}$-*co*-MA$_{20}$) in water. The results reveals that when the block-selective solvent is the binary solvent mixture of water and acetone with acetone content at 0, 40, 80, and 90 vol %, core−shell spheres with diameter at about 60 nm, porous spheres with diameter at about 180 nm, elliptic porous aggregates with size about 280 nm, and core−shell cauliflower-like aggregates with size about 250 nm are formed as shown in Figure 1. The porosity of the aggregates in Figure 1b,c is evidenced by the contrast between the light dots and the surrounding part.

Clearly, the acetone content in the binary solvent mixture, or the nature of the binary solvent mixture, plays a key role in tuning the size and morphology of resulting micelles as demonstrated above. The tuning of the size and morphology of the resulting micelles is partly ascribed to the influence of the binary solvent mixture on the swell degree and dimension of the core-forming chains (PS chains) and repulsive interaction between shell-forming chains (PAA chains). In comparison with water, acetone is a solvent for PS block and PAA block [the solubility of polystyrene and poly(acrylic acid) in acetone is not very high, especially for block copolymers with high molecular weight], and its polarity is much lower than that of water; thus, the PS chains swell more, and the repulsion between the PAA chains in the binary solvent mixture with a higher acetone content is much weaker than in water. To our understanding, the weaker repulsion between the PAA chains in the binary solvent mixture of water and acetone will help to increase the PAA chains density in the shell of the resulting micelles or increase the number of aggregated polymer chains N_{agg} in the resulting micelles, which we will discuss subsequently. The PS block chains swell much more in the binary solvent mixture of water and acetone with acetone content ranging from 40 to 80 vol % than in the unitary solvent of water, while when much water (for example, 18 mL as discussed in the Experimental Section) is added at a relatively fast rate, the PS chains shrink quickly and the structure of resulting micelles are frozen, which results in cavities in the frozen micelles as shown in Figure 1b,c. While when the acetone content in the binary solvent mixture further increases to 90 vol %, the resulting micelles are core−shell cauliflower-like aggregates (Figure 1d), which is similar to some extent to the core−shell micelles shown in Figure 1a. We think the possible reason is that the acetone is a solvent for PS block with low molecular weight just as the block copolymer PS$_{38}$-*b*-P(AA$_{190}$-*co*-MA$_{20}$) used in this study. Thus, the micellization of the PS chains by addition of the mixture of 90 vol % acetone and 10 vol % water into a given polymer DMF solution is similar to that by addition of pure water into a little dilute polymer DMF solution. Furthermore, because the repulsion between the PAA chains is weaker in the binary solvent mixture with 90 vol % acetone than in unitary solvent of water, large-sized core−shell cauliflower-like aggregates are formed when the binary solvent mixture with 90 vol % acetone is added.

The tuning of the size and morphology of the resulting micelles is also partly ascribed to the dynamics of micellization. It is well-known that micellization of amphiphilic block copolymer chains is mainly due to microphase separation of the insoluble block, e.g., PS block, when block-selective solvent of water is added.[6] That means the dynamics or the mode of adding block-selective solvent into the polymer solution can possibly exert influence on the morphology of the resulting micelles. In this study, it is found micellar morphology tuning can be achieved only during the micellization. Once the PS_{38}-*b*-P(AA_{190}-*co*-MA_{20}) micelles shown in Figure 1A are formed and then frozen with water, addition of acetone into the micelle solution cannot change the morphology of the spherical micelles even when the acetone content in the micelle solution is as high as about 30 vol %. This suggests that the dynamics really plays a key role in controlling the morphology of the resulting micelles. Besides, as discussed in the Experimental Section, the various morphological micelles shown in Figure 1 keep suspending in the unitary solvent of water because DMF and acetone were removed from the micelle solution series by dialysis against water at the last stage of preparing the micelles as discussed in the Experimental Section, and all the final polymer concentrations of the four kinds of morphological micelle solution series are the same, which is 0.020 mg/mL. These further confirm the dynamics influence on morphology tuning during micellization of the amphiphilic block copolymer. Furthermore, Tannaka and Watanabe have studied the effect of viscoelasticity on the phase separation of block copolymer solutions and blends.[32−34] We suppose that the tuning of the size and morphology of the resulting micelles is also partly ascribed to the viscoelastic effect although it needs further careful study.

Eisenberg et al. observed various morphological micelles in dilute solutions formed by adding ions into block-selective solvent or by adjusting the nature of common solvent of PS-*b*-PAA.[4,13] In comparison with the methods proposed by Eisenberg et al., the present method has some merits. First, the methods proposed by Eisenberg et al. are used to affect the swell degree of the shell-forming block chains of PS and the interaction between the shell-forming block chains of PAA and then to tune the morphology of the resulting micelles, which can be easily achieved by changing the acetone content in the binary solvent mixture. Besides, the micellization of amphiphilic block copolymer chains can be controlled easily by adjusting acetone content in the binary solvent mixture or changing the volume of the binary solvent mixture added into the polymer DMF solution. It is found, because the polarity of the binary solvent mixture of water and acetone is lower than water, that for a given concentration of polymer DMF solution more volume of the binary solvent mixture is needed to associate PS_{38}-*b*-P(AA_{190}-*co*-MA_{20}) chains into micelles than water as demonstrated in the Experimental Section. This means the rate of micellization of the amphiphilic block copolymer can be more easily adjusted by using a binary solvent mixture of water and acetone than a unitary block-selective solvent of water. At last, many other mixed solvents such as a binary solvent mixture of aldehydes and water, ketones and water, acids and water, amines and water, or acylamides and water can possibly be used as the block-selective solvent to tune morphology of resulting micelles.

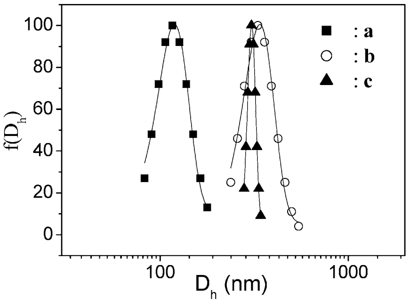

Figure 2. Hydrodynamic diameter distribution $f(D_h)$ of the core−shell spheres (a), the porous aggregates (b), and the core−shell cauliflower-like aggregates (c) in water at 25 °C, where the scattering angle is 90°, 60°, and 60°, respectively.

The structure of the core−shell spheres (Figure 1A), the elliptic porous aggregates (Figure 1C), and the core−shell cauliflower-like aggregates (Figure 1D) was further studied by a combination of SLS and DLS. Figure 2 shows the hydrodynamic diameter distribution $f(D_h)$ of the core−shell spheres (Figure 2a), the elliptic porous aggregates (Figure 2b), and the core−shell cauliflower-like aggregates (Figure 2c) in water. The result shows both the hydrodynamic radii of the core−shell spheres and the core−shell cauliflower-like aggregates are narrowly distributed with the diameter ranging from 83 to 178 nm and 280 to 342 nm, respectively, whereas the distribution of the porous aggregates is a little broader, which ranges from 238 to 544 nm. The D_h values of the micelles can be calculated from $f(D_h)$ by $\int_0^\infty f(D_h) D_h \, dD_h$, which are listed in Table 1. Herein, it must be noted that the hydrodynamic diameters of the core−shell spheres, porous aggregates, and the core−shell cauliflower-like aggregates measured by laser scattering are larger than those observed by TEM. This is because the core−shell spheres and the porous aggregates and the core−shell cauliflower-like aggregates are water swollen in water due to the soluble PAA block, while TEM observation shows the diameter of the dried aggregates.

Figure 3 shows the Berry plots of $[I^{-1}]^{0.5}$ of the core−shell spheres (Figure 3A), the porous aggregates (Figure 3B), and the core−shell cauliflower-like aggregates (Figure 3C) in water with the initial copolymer concentration at 0.20 mg/mL, where I is the scattering intensity of the sample at a scattering angle θ. From the fit lines in Figure 3, the values of R_g^0 of the three kinds of micelles in water at 25 °C are calculated as $R_g^0 = (6S/T)^{0.5}$, where S is the slope and T is the intercept of the fit line. The values of R_g^0 of core−shell spheres, the porous aggregates, and the core−shell cauliflower-like aggregates are 55, 290, and 227 nm, respectively. Thus, the R_g^0/R_h values of core−shell spheres, the porous aggregates, and the core−shell cauliflower-like aggregates in water at 25 °C are 0.83, 1.41, and 1.19, respectively. It is well-known that the R_g/R_h values can reveal the morphology of particles in solution.[35] The values of the R_g^0/R_h of the core−shell sphere micelles are larger than a typical crew-cut micelle,[29] a nondraining hard sphere,[36] but lower than that of a linear and

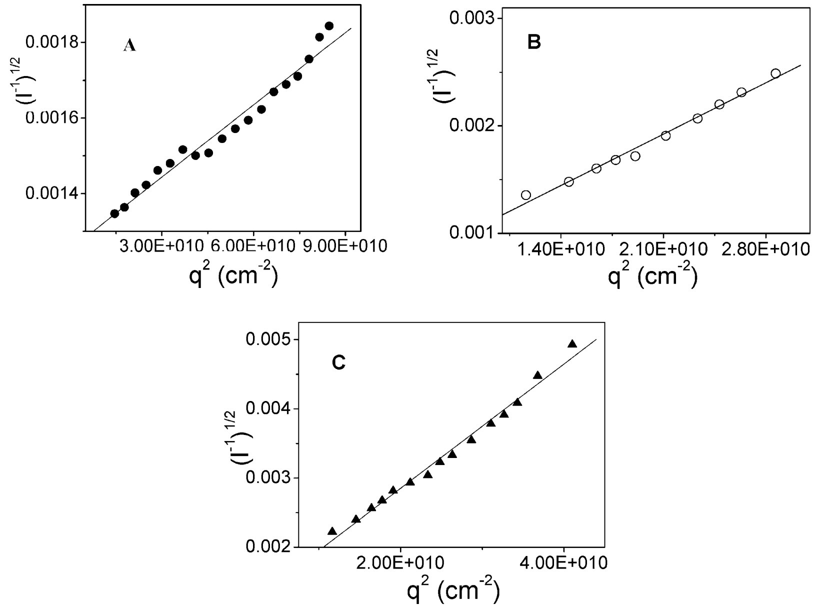

Figure 3. Berry plot of $[I^{-1}]^{0.5}$ of the core–shell spheres (A), the porous aggregates (B), and the core–shell cauliflower-like aggregates (C) in water vs q^2 with polymer concentration at 0.20 mg/mL.

Table 1. Summary of the DLS and SLS Results of the Core–Shell Spheres (a), the Porous Aggregates (b) and the Core–Shell Cauliflower-like Aggregates (c) in Water

micelles	D_0^0 (cm^2/s)	R_h (nm)	R_g^0 (nm)	R_g (nm)	R_g^0/R_h	M_w (g/mol)	A_2 (mol mL/g^2)	N_{agg}	ρ (g/cm^3)
a	3.738×10^8	66	55	60	0.83	1.19×10^8	6.12×10^{-5}	6 100	0.167
b	1.189×10^8	206	290	304	1.41	1.71×10^9	-1.24×10^{-5}	88 300	0.0773
c	1.289×10^8	190	227	242	1.19	2.69×10^9	9.38×10^{-6}	139 000	0.155

flexible polymer chain in a good solvent,[37,38] which suggests that the three kinds of aggregates are micellar clusters or compound micelles.[39] Subsequently, we further confirm that the three kinds of aggregates are compound micelles by the high number of aggregated polymer chains N_{agg}.

The static laser scattering results of the core–shell spheres and the porous aggregates and the core–shell cauliflower-like aggregates are summarized in Table 1. The values of the second virial coefficient A_2 of the core–shell spheres, the porous aggregates, and the core–shell cauliflower-like aggregates are close to 0, which suggests the solubility of the core–shell spheres and the porous aggregates and the core–shell cauliflower-like aggregates is poor. Clearly, the weight-average molecular weight M_w and number of aggregated polymer chains N_{agg} of the core–shell spheres are much larger than those of common micelles,[22] which shows the core–shell micelles are compound micelles. It is possibly due to the residual methyl acrylate units in the PAA chains, which decreases the repulsive interaction between PAA chains. In comparison with the core–shell spheres, the M_w and N_{agg} values of the porous aggregates and the core–shell cauliflower-like aggregates are even bigger, which is possibly due to the repulsive interaction decreasing further in the binary solvent mixture of acetone than in the unitary solvent of water. The value of the density of polymer chains ρ in the porous aggregates is much lower than those of the core–shell spheres and core–shell cauliflower-like aggregates, which further confirms the structure of the porous aggregates.

For block copolymer of PS$_{200}$-*b*-PAA$_{78}$, which has a relatively shorter shell-forming block of PAA compared with PS$_{38}$-*b*-P(AA$_{190}$-*co*-MA$_{20}$), micellar morphology tuning can also be achieved when the binary solvent mixture of water and acetone is used as block-selective solvent. The structure of the resulting micelles changes from core–shell spheres with average diameter about 80 nm to nanofibers with size about 50 nm × 600 nm as shown in Figure 4 when the acetone content in the water and acetone mixture ranges from 0 to 10 vol %.

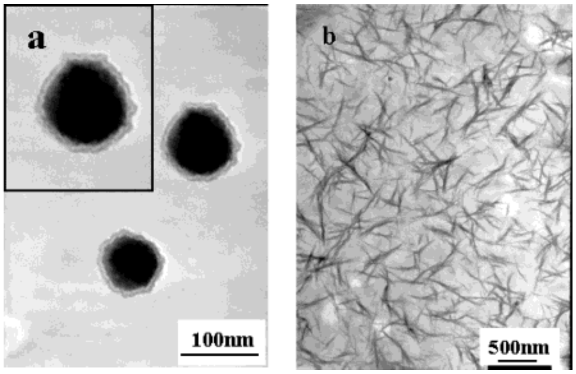

Figure 4. TEM images of the aggregates self-assembled by PS$_{200}$-*b*-PAA$_{78}$, where the block-selective solvent is water (a) and the binary solvent mixture of acetone and water with acetone content at 10 vol % (b).

Conclusion

The micellization of PS$_{38}$-*b*-P(AA$_{190}$-*co*-MA$_{20}$) by addition of a binary solvent mixture of water and acetone with different acetone content was studied. The nature of the binary solvent mixture exerts remarkable influence on the morphology of the resulting micelles. When the block-selective solvent is a binary solvent mixture of acetone and water and with acetone content ranging from 0 to 90 vol %, core–shell spheres with diameter about 60 nm, porous spheres with diameter at about 180 nm, elliptic porous aggregates with size about 280 nm, and core–shell cauliflower-like aggregates with size about 250 nm are formed. The influence of the binary solvent mixture on the morphology of the resulting micelles self-assembled by PS_{200}-*b*-PAA_{78} is also studied. By tuning the nature of the binary solvent mixture, core−shell spheres and nanofibers are self-assembled in water. The reason that morphology changes with the acetone content in the binary solvent mixture of acetone and water is discussed, which is partly ascribed to the variation of the repulsive interaction between PAA chains in very dilute polymer concentrations, partly ascribed to the dynamics of micellization.

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