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Formation of flower-like aggregates from assembly of single polystyrene-*b*-poly(acrylic acid) micelles

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Amphiphilic block copolymer polystyrene-*block*-polyacrylic acid (PS-*b*-PAA) self-assembles into spherical core-shell micelles in the block-selective solvent water with the PS block as the core and the PAA block as the shell. When adding 1-propanol to the micellar solution and then casting the micellar solution at suitable temperatures, the spherical core-shell micelles are assembled into flower-like aggregates on substrates such as glass, formvar film or silicon. The size of the flower-like aggregates ranges from 2×2 μm^2 to 15×15 μm^2. Casting temperature, substrate type and character of the block copolymers and additive can all affect the assembly of PS-*b*-PAA micelles. The assembly of micelles is similar to the fractal aggregation of inorganic particles and a possible reason is discussed.

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Introduction

The spontaneous formation of patterns and shapes in nature has fascinated mankind for centuries. Many examples can be found in daily life and in all scientific areas, *e.g.*, the growth of snowflakes, the formation of coral reefs, the growth of bacterial colonies, crystal formation from pure melts or alloys, electrochemical deposition, fluid dynamics and epitaxial metal growth.[1] The existence of various morphologies of block copolymers in bulk has been known for many years. Originally, the three most common morphologies were spherical, cylindrical and lamellar, depending on the block copolymer composition. Later, the ordered bicontinuous double diamond or gyroid morphology was observed.[2,3] Recently, it is found that amphiphilic block copolymers and graft copolymers in block-selective solvents can self-assemble into various morphological micelles such as spheres, vesicles, cylinders, doughnuts, hollow spheres, nanotubes, nanofibres, *etc.*[4–13] Furthermore, Alexabdridis *et al.* reported a ternary system of poly(ethylene oxide)-*block*-poly(propylene oxide) (PEO-*b*-PPO)–water–*p*-xylene (where water is a selective solvent for PEO and *p*-xylene is a selective solvent for the PPO blocks), which exhibits nine different phases, all thermodynamically stable at the same temperature: normal micelle cubic, normal hexagonal, normal bicontinuous cubic, lamellar, reverse bicontinuous cubic, reverse hexagonal and reverse micelle cubic lyotropic liquid crystalline, as well as water-rich and water-lean micellar solutions.[14]

The collective properties of molecules or nanoparticles, which are critical for molecular devices such as molecular photoproducts, are dependent on the supramolecular structure and/or relative molecular alignments.[15] Several methods for revealing collective properties have been investigated.[16–18] Just as discussed above, self-assembly of molecules, such as block copolymers in bulk or in block-selective solvents, has been studied extensively. However, controlling the ordered aggregation of nanoparticles or micelles is still a great challenge to scientists. Here, we focus on the assembly of micelles. The micelles self-assembled by PS-*b*-PAA are chosen as the basic units, because PS-*b*-PAA is a typical amphiphilic block copolymer and its self-assembly in water into core-shell micelles has been studied extensively.[4–6] The spherical core-shell micelles consist of a core formed by the insoluble PS block and a shell of the soluble PAA block swollen in water. It is easily understood that the hydrophilic shell of the PAA block can be influenced by the addition of electrolytes, for example. Our strategy is to adjust the interaction between the micelles with organic additives in the micellar solution and then cast the micellar solution in order to achieve controlled assembly of the micelles on different substrates. In this article, we report the formation of flower-like aggregates on solid substrates by casting the PS-*b*-PAA micelles from mixtures of water and 1-propanol.

Experimental

Polystyrene-*b*-polymethacrylate (PS-*b*-PMA) was synthesized by atom transfer radical polymerization (ATRP).[19] PS-*b*-PMA was hydrolyzed in NaOH aqueous solution (50 mL, 20 wt %) at 90 °C for 72 h or more. The hydrolysate of the block copolymer (PS-*b*-PAA) was precipitated by slowly dropping the solution into hydrochloric acid (40 mL, 33 vol %). The precipitate was centrifuged and washed with dilute hydrochloric acid (5 vol %) and deionized water, each for six times. The product (PS-*b*-PAA) was then dried at 50 °C in a vacuum oven for 24 h. In this study, three block copolymers, PS_{200}-*b*-PAA_{78}, PS_{115}-*b*-PAA_{63} and PS_{67}-*b*-PAA_{83}, were used, where the subscripts refer to the number of repeat units of monomers in the block copolymers. The structure and polydispersibility index (PDI) for the three block copolymers are listed in Table 1.

Table 1 Molecular structure and distribution for the PS-*b*-PAA copolymers

Polymer	PDI
PS_{67}-*b*-PAA_{83}	1.26
PS_{115}-*b*-PAA_{63}	1.28
PS_{200}-*b*-PAA_{78}	1.20

The block copolymer was first dissolved in *N*,*N*-dimethylformamide (DMF) to make a polymer solution (2.0 mg mL^{-1}) and then the polymer solution (0.50 mL) was added dropwise into water (4.50 mL) with stirring. The micellar solution was then dialyzed against water for 4 days to remove DMF; then a given volume of aqueous 1-propanol solution was added to the micellar solution. The resultant micellar solution, with the polymer concentration at 0.020 mg mL^{-1}, was shaken for 30 min. Subsequently, drops of about 0.05 mL of the mixed micellar solution were placed on the surface of a clean glass slide, a thin film of formvar covered on a copper EM grid and a silicon wafer, which were then subjected to different temperatures to vaporize the solvent quickly. Finally, the sample was put into a vacuum oven at 30 °C for 12 h before being observed by electron microscopy. In this study, all glass slides and silicon wafers were first treated with hydrochloric acid (about 33%) for 2 h, then washed with deionized water and finally preserved in acetone before use.

Scanning electron microscopy (SEM) was performed on a Hitachi S3500N or Philips XL30 microscope equipped with EDS (EDAX), at 20 or 25 kV. The samples for SEM observation were sputtered with a thin gold layer about 3 nm thickness with a Hitachi E-1010 ion sputtering machine. Transmission electron microscopy (TEM) observation was performed on a Philips EM400ST microscope operating at an acceleration voltage of 80 kV.

Results and discussion

Single micelles

Water is a block-selective solvent for the PAA block but a precipitant for the PS block. Therefore, when dropping PS-*b*-PAA solution into water, the insoluble PS chains will have a tendency to associate to form the core of the resulting micelles, while the soluble PAA chains form the shell of the micelles in water. Fig. 1 shows the morphology of single micellar units of PS_{115}-*b*-PAA_{63} that have self-assembled in water. The SEM and TEM images of single micelles shown in Fig. 1 were obtained by casting the micellar aqueous solution at 130 °C and at room temperature, respectively. The diameters of the spherical particles formed on glass or on a formvar film under the conditions discussed above are about 30 nm. For PS_{200}-*b*-PAA_{78} and PS_{67}-*b*-PAA_{83}, the resultant micelles (not shown) are spheres with diameters ranging from 30 to 80 nm.

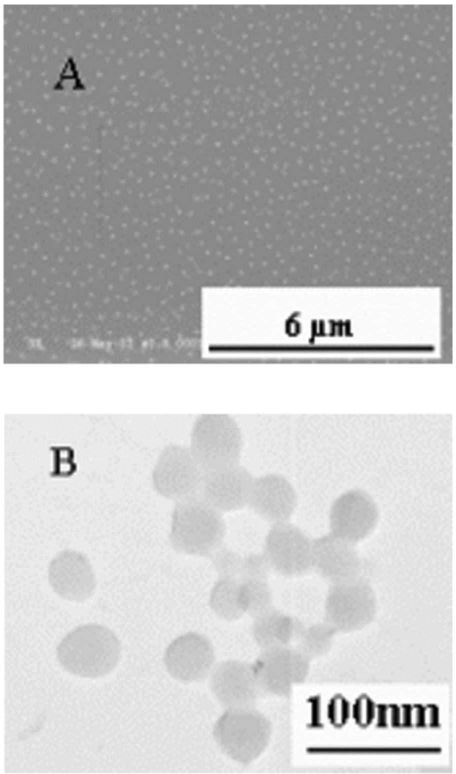

Fig. 1 (A) SEM and (B) TEM images of single PS_{115}-*b*-PAA_{63} micelles on a glass slide and a thin film of formvar formed by casting the aqueous micellar solution at 130 °C and at room temperature, respectively. The micellar solution was diluted with water and the polymer concentration was 5.0 μg mL^{-1}.

Aggregates from assembly of single micelles

The SEM images in Fig. 2 show the aggregates of PS_{67}-*b*-PAA_{83}, PS_{115}-*b*-PAA_{63} and PS_{200}-*b*-PAA_{78} micelles on a glass slide formed by casting aqueous micellar solutions with a 1-propanol content of 3 vol % at 130 °C. Clearly, the ordered, flower-like aggregates are much different from the single spherical micelles shown in Fig. 1. From the SEM images shown in Figs. 2(A) and 2(B), the coexistence of the micelles and the flower-like aggregates can clearly be seen, which further indicates that the flower-like aggregates result from the assembly of single micelles. The average sizes of the flower-like aggregates assembled from micelles of PS_{67}-*b*-PAA_{83}, PS_{115}-*b*-PAA_{63} and PS_{200}-*b*-PAA_{78} are about 8 × 8, 4 × 4 and 15 × 15 μm^2, respectively. Additionally, the shapes of the three kinds of flower-like aggregates are different from each other. The aggregates assembled from PS_{67}-*b*-PAA_{83} micelles are 'lotus-like', the PS_{115}-*b*-PAA_{63} aggregates are 'snowflake-like' and the PS_{200}-*b*-PAA_{78} aggregates are dendritic. To our knowledge, such phenomena have been observed mainly in crystal growth processes and fluid dynamics such as the growth of a snowflake.

Usually, nanoparticles such as colloids or micelles suspended in solvent tend to aggregate into random structures upon solvent removal, because of the high specific surface energy and irregular aggregation of micelles. Therefore, what are the possible reasons for the formation of flower-like aggregates in the present system? Our observations of the flower-like aggregates in this study were encountered just by chance. However, from the results, we can conclude that the addition of 1-propanol plays a key role in the formation of the flower-like structures. The formation of flower-like aggregates is possibly ascribed to the adjustment of the interaction between the micelles during casting of the micellar solution. 1-Propanol was chosen as an additive to adjust the interaction between the micelles on the basis of its physical and chemical properties. First, 1-propanol is easily dissolved in water, which provides the possibility to adjust the interaction between the PS-*b*-PAA micelles in water by changing their environment. Second, the boiling point of 1-propanol, which is 97 °C, is very close to that of water, which means that the evaporation characteristics should not change excessively when casting the micellar solution. Thirdly, the addition of 1-propanol would not chemically alter nor dissolve the micelles, but can affect the assembly through physical interactions such as hydrogen bonding between the additive and the PS-*b*-PAA micelles.

The structure of the flower-like aggregates is also confirmed by TEM. Fig. 3 shows the TEM images of the PS_{67}-*b*-PAA_{83} micellar aggregates formed by casting the micellar aqueous solution with a 1-propanol content of 3 vol % at 110 °C. It is clear that the morphology of the flower-like aggregates formed on the formvar film is similar to that shown in Fig. 2(A), although the size is a little smaller, at about 3 × 3 μm^2.

In addition to the additives such as 1-propanol discussed above, temperature and alcohol concentration in the solvent mixture can also affect the aggregation of PS-*b*-PAA micelles. The SEM images in Fig. 4 show the structure of the aggregates of the PS_{115}-*b*-PAA_{63} micelles on a glass slide obtained by casting the micellar solution with different 1-propanol contents at

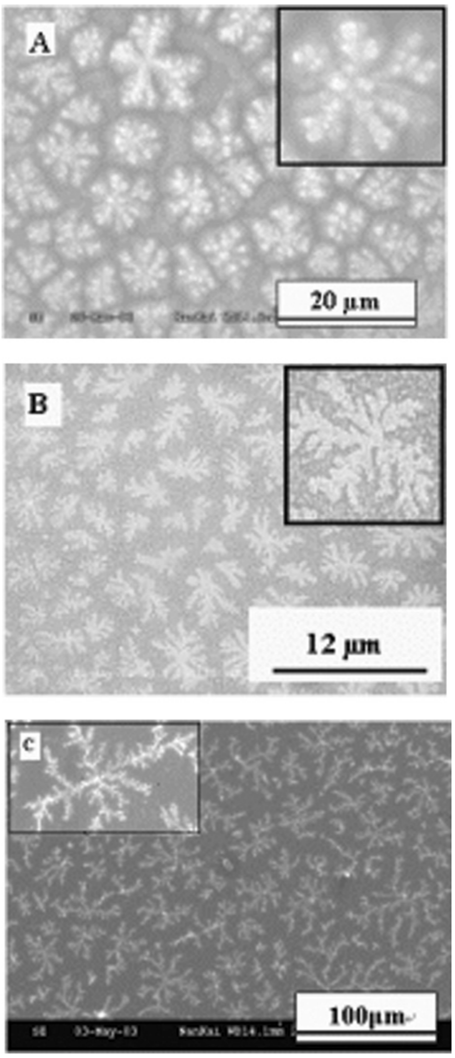

Fig. 2 SEM images of flower-like aggregates of (A) PS_{67}-*b*-PAA_{83}, (B) PS_{115}-*b*-PAA_{63} and (C) PS_{200}-*b*-PAA_{78} formed by casting the respective micellar aqueous solutions with 3 vol % 1-propanol on glass slides at 130 °C.

different temperatures. Fig. 4(A) shows a typical SEM image observed from a sample prepared by casting the micellar solution with a 1-propanol content of 3 vol % at 125 °C. We can clearly see that the average size of the flower-like aggregates is about 4 × 4 μm^2. From the SEM image, we can also see that the flower-like aggregates are not compact and comprise many single micelles, as shown in the magnification in Fig. 4(A). This result provides the most obvious proof that it is the single PS-*b*-PAA micelles that assemble into flower-like aggregates when casting the micellar solution with a 1-propanol content of 3 vol %. When the temperature is further increased to 130 and 135 °C, more compact flower-like aggregates are formed, as shown in Figs. 3(B) and 3(C), respectively. Of all the flower-like aggregates shown in Figs. 4(A)–(C), those formed at 135 °C are the most compact. Flower-like aggregates can also form when casting the micellar solution with a 1-propanol content of 6 vol % at 130 °C [Fig. 4(D)]. Compared with the three kinds of aggregates shown in Figs. 3(A)–(C), the flower-like aggregates formed by casting the micellar solutions with 1-propanol concentration at 6 vol % are a little larger, at about 5 × 5 μm^2.

Flower-like aggregates assembled from PS_{115}-*b*-PAA_{63} micelles can also be formed on a silicon wafer, as shown in Fig. 5, by casting the micellar solution with a 1-propanol content of 3 vol % at 80 °C. We show two SEM images taken in the same location but at different magnification.

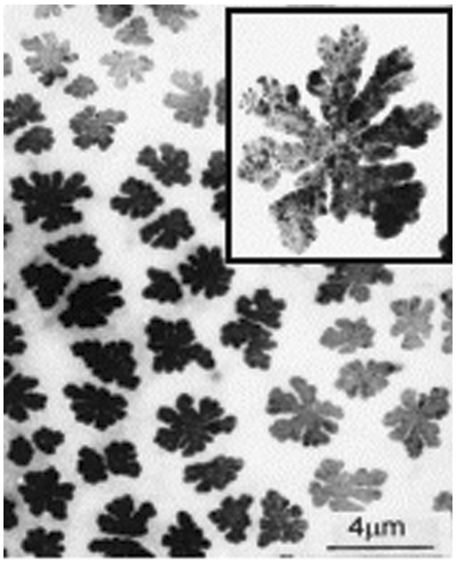

Fig. 3 TEM image of PS_{67}-*b*-PAA_{83} flower-like aggregates formed on a formvar film by casting the micellar aqueous solution with a 1-propanol content of 3 vol % at 110 °C.

The flower-like aggregates are very regular and the average size is about 2 × 2 μm^2. Clearly, compared with those formed on glass slides, the flower-like aggregates are more perfect, but the size is much smaller. Additionally, we are almost unable to see any co-existing spherical nanoparticles with the flower-like aggregates. Furthermore, the flower-like aggregates are formed on a silicon wafer substrate at a much lower temperature than on a glass slide. The reason for needing to cast the solvent mixture at a higher temperature is possibly due to the greater hydrophilicity of a glass slide, which limits the mobility of the PS-*b*-PAA micelles on the surface of the glass slide. The results of X-ray diffraction and electron diffraction determinations indicate that the flower-like aggregates are amorphous, consistent with the assembly patterns of the PS-*b*-PAA micelles.

In summary, PS-*b*-PAA micelles can be assembled into ordered flower-like aggregates on suitable substrates when casting the micellar solution in the presence of 1-propanol at relatively high temperatures. The block composition of PS-*b*-PAA, temperature, alcohol concentration and substrate can all affect the morphology of the resultant aggregates.

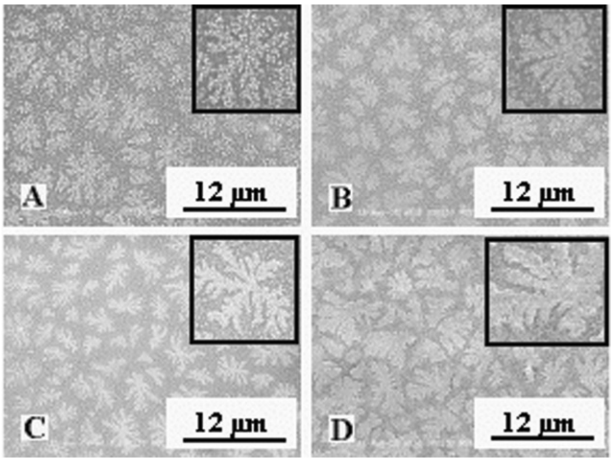

Fig. 4 SEM images of PS_{115}-*b*-PAA_{63} flower-like aggregates formed on a glass slide by casting the micellar aqueous solution with 1-propanol content of 3 vol % at (A) 125, (B) 130 and (C) 135 °C and with a 1-propanol content of 6 vol % (D) at 130 °C.

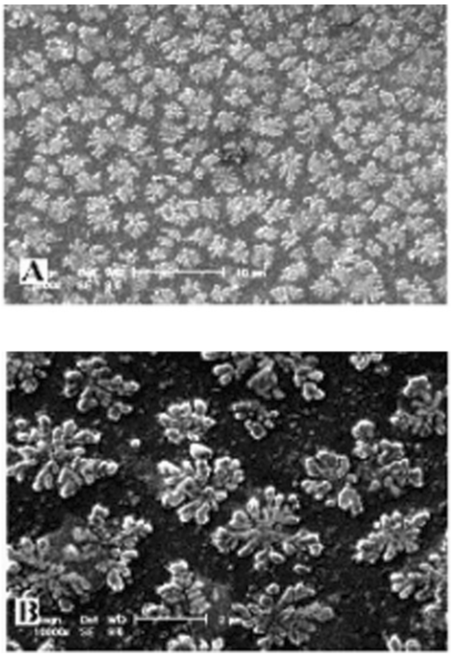

Fig. 5 SEM images of PS_{115}-*b*-PAA_{63} flower-like aggregates formed by casting the micellar solution with a 1-propanol content of 3 vol % on a silicon wafer at 80 °C. The scale bars are (A) 10 and (B) 2 μm.

Possible mechanism

Up to the present time, only a few reports on formation of inorganic flower-like aggregates have been reported.[1,20] To the best of our knowledge, this is the first time that flower-like aggregates formed by casting amphiphilic block copolymer aqueous micellar solutions have been observed directly. It is found that flower-like aggregates as mentioned above cannot be formed on substrates when casting the micellar solution at room temperature. This means that conditions far from an equilibrium state favour formation of the PS-*b*-PAA flower-like aggregates. From the thermodynamic point of view, the spherical morphology of a particle is possibly the most stable. However, it has been recognized that the spherical morphology of a growing particle may become unstable at a critical value of parameters such as temperature and pressure, and the final morphology is then given by a more complex space- and time-dependent configuration.[21] This means, from the dynamics point of view, that dissipative structures with larger surfaces, such as flower-like aggregates, may be formed at a state far from equilibrium.

The PS-*b*-PAA flower-like aggregates are very similar to fractal aggregates resulting from crystal growth, which is described and explained by models of diffusion-limited aggregation (DLA).[22] During DLA, a particle moves randomly until it contacts other particles, which then stick together to form a free-moving cluster of particles. In comparison with the DLA situation, the aggregation of PS-*b*-PAA micelles may be much more complex. First, strong interactions exist between PS-*b*-PAA micelles and the mixed solvent, which will greatly affect the movement of micelles. The size of PS-*b*-PAA micelles is much larger than that of particles undergoing DLA. However, a possible aggregation process is shown schematically in Fig. 6. First, one drop (about 0.05 mL) of PS-*b*-PAA micellar solution spreads on a glass slide or a silicon wafer to form a liquid thin film. When the temperature increases to a given point and part of the water–1-propanol mixed solvent has been vaporized, the micelles start to deposit onto the substrate directionally; this also means the thin film splits up into tiny droplets. The directional deposition of the micelles is possibly due to the presence of 1-propanol. Finally, flower-like aggregates form on the substrate through ordered aggregation of the micelles, as the mixed solvent is continuously vaporized. It must be noted, however, that Fig. 6 simply describes the basic aggregation process; further details, such as how and why 1-propanol plays such an important role in the ordered aggregation, *etc.*, will need further study.

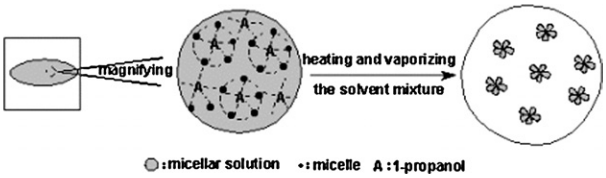

Fig. 6 A schematic representation of the possible process for the aggregation of PS-*b*-PAA micelles into flower-like aggregates on a substrate.

Conclusion

Block copolymers of the type PS-*b*-PAA have been shown to self-assemble into spherical micelles in a water–1-propanol mixture. When casting the micellar aqueous solution with 1-propanol contents ranging from 3 to 6 vol % at a suitable temperature, flower-like aggregates are formed on a glass slide. The flower-like aggregates apparently only form under conditions far from thermodynamic equilibrium and exhibit sizes ranging from 3×3 μm^2 to 15×15 μm^2. The casting temperature, the block composition of the copolymer, the additive and the substrate can all affect the aggregation of PS-*b*-PAA micelles and the morphology of the resultant structures. For PS_{115}-*b*-PAA_{63} micelles, when the temperature increases from 125 to 135 °C, the structure of the resultant flower-like aggregates becomes more regular and compact. Flower-like aggregates with sizes about 2×2 μm^2 can also form on silicon wafers when casting the micellar solution with a 1-propanol content of 3 vol % at 80 °C. Compared with those formed on glass slides, the flower-like aggregates formed on silicon are a little smaller but more perfect and regular.

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