Multiple Morphologies in Aqueous Solutions of Aggregates of Polystyrene-*block*-poly(ethylene oxide) Diblock Copolymers

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Aggregates of various morphologies have been observed in a number of self-assembled systems.[1−6] In solutions of block copolymers, spherical micelles have been observed frequently.[7] Only very rarely have nonspherical morphologies been reported, which are usually detected by indirect methods such as light scattering,[8,9] SAXS,[10] etc. Recently, it was shown that crew-cut aggregates of polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) diblocks in dilute aqueous solutions can yield micellelike aggregates of different morphologies,[11] i.e., spherical micelles, rodlike and vesicular aggregates, lamellae, and large compound micelles (LCMs). This is believed to be the first report of the observation in dilute solution of these multiple morphologies from an identical block copolymer family differing only in the relative block lengths. The appearance of multiple morphologies is a result of the interplay of a number of forces.[12] It is only for the amphiphilic systems, such as PS-*b*-PAA, with strong differential solubility of the components in water and organic solvents, that these various morphologies can be observed.

In the present paper, we wish to report the observation of multiple morphologies in aqueous solutions of a very different diblock copolymer family, i.e., polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO). These morphologies include normal spherical and rodlike aggregates, vesicles, and lamellae, as well as micrometer-size spheres. As the hydrophilic PEO content in the PS-*b*-PEO block copolymer decreases, the morphology of the aggregates changes from spheres to rods, to lamellae, and finally to vesicles. Coexisting multiple morphologies are seen frequently.

In the past, extensive aqueous solution studies have been performed on spherical micelles of PS-*b*-PEO diblock copolymers by a number of techniques.[13−17] In these systems, the lengths of soluble PEO blocks were much longer than those of the insoluble PS blocks. Turibity experiments by Riess and Rogez showed that the degree of association and the apparent molecular weight of the PS-*b*-PEO micelles in aqueous solutions increased with increasing copolymer molecular weight and decreasing PEO content.[14] Khan et al. showed an electron micrograph of PS-*b*-PEO aggregates prepared in water,[15] which demonstrated the presence of two spherical species. Light scattering experiments by Xu et al. showed that there were two narrowly distributed spherical populations in aqueous solutions of PS-*b*-PEO.[17] The smaller spheres were regular micelles, while the larger spheres were believed to consist of loose micellar clusters.

The above-mentioned studies represent only a small sampling of the rather extensive literature on amphiphilic PS-*b*-PEO block copolymers. It is well known that the PS-*b*-PEO block copolymers are potentially useful for encapsulation of hydrophobic materials in an aqueous suspension.[15] Because PEO is an inert synthetic polymer in vivo, the amphiphilic block copolymers containing PEO may have potential use as drug delivery systems.

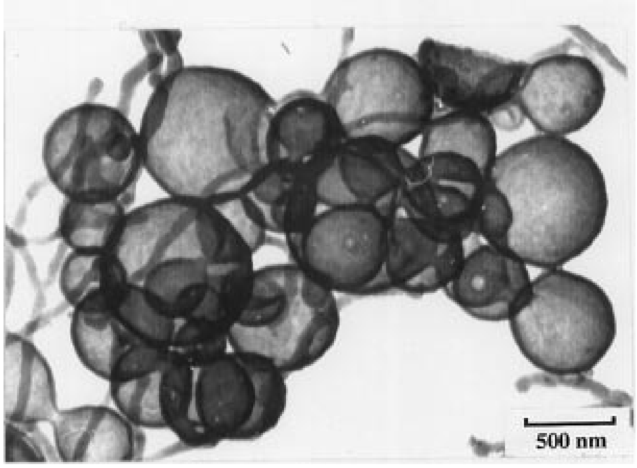

Figure 1. TEM picture of vesicles from an aqueous solution of the diblock copolymer PS(240)-*b*-PEO(15). The copolymer concentration in the initial DMF solution was 2.0%.

The styrene−ethylene oxide diblock copolymers used in this study were prepared by sequential anionic polymerization, generally following published procedures.[18,19] To prepare the colloidal aqueous solutions, the copolymers were first dissolved in DMF in several weight concentrations. Later, deionized water was slowly added to the stock solutions with stirring. After reaching the cloud point (at ca. 3−5 wt % of water), more water is added till the water content reaches ca. 25 wt %. The solutions were then placed in dialysis tubes and dialyzed against distilled water for a few days. The micellar solutions were then diluted by a factor of 10 or 20, depending on the copolymer concentration in the DMF. For transmission electron microscopy (TEM), a drop of the dilute solution was placed onto a copper grid and allowed to dry in air for a few hours. The grids were coated with a palladium/platinum alloy at a shadowing angle of ca. 30°. Transmission electron microscopy was performed on a Philips EM410 electron microscope.

The morphologies are a function of both the hydrophilic PEO chain length and, to a lesser extent, the block copolymer concentration in DMF. The compositions of the block copolymers are indicated as *x*-*b*-*y*, where *x* and *y* are numbers of repeat units of the PS and PEO blocks, respectively. In most cases, aggregates of several different morphologies were seen in the same micrograph; only rarely were species of a single morphology observed. The various morphologies which were seen in this study are described below in order of increasing PEO content.

The sample 240-*b*-15 forms primarily vesicles, although on some of the micrographs, additional species, such as rods and (very rarely) small spheres are also seen. There is a substantial polydispersity in the sizes of the vesicles. The small spheres are clearly the normal "crew-cut" micelles[20,21] consisting of a polystyrene core and a poly(ethylene oxide) corona, with a total diameter in the dry state of ca. 40 nm. Figure 1 shows a typical example of the predominant vesicular structures ob-

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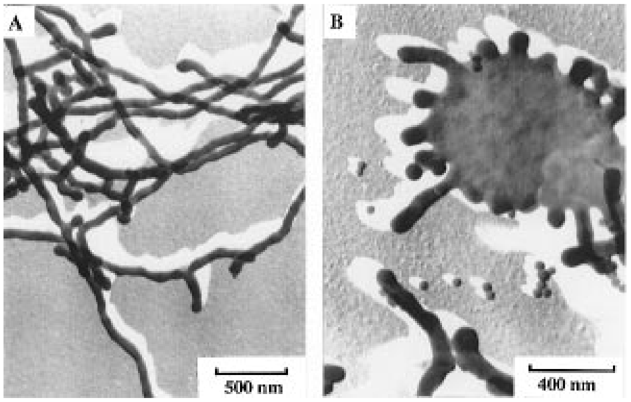

Figure 2. TEM pictures of rodlike aggregates (A) and lamellae (B) from aqueous solutions of the diblock copolymer PS(240)-*b*-PEO(45). The copolymer concentrations in the initial DMF solutions were 2.0% (A) and 1.5% (B).

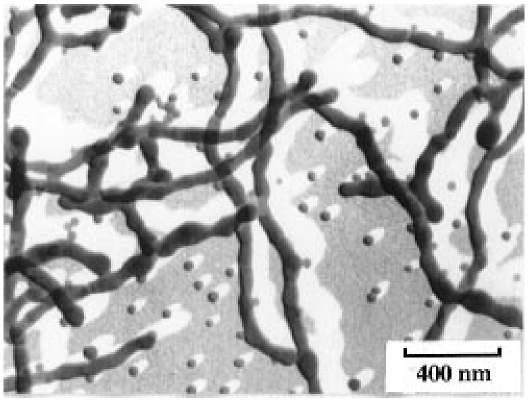

Figure 3. TEM picture of rodlike aggregates from an aqueous solution of the diblock copolymer PS(240)-*b*-PEO(80). The copolymer concentration in the initial DMF solution was 1.0%.

tained from this sample. The vesicles have a wall thickness of ca. 25 nm, while the rods are ca. 70 nm in diameter. Some of the vesicles are collapsed as a result of the readmission of air after shadowing.

The sample containing 45 units of EO forms primarily rodlike aggregates, with an admixture of vesicles and lamellae, including lamellae with protruding rods. Examples are shown in Figure 2. Several small vesicles and normal spheres are also encountered occasionally. This sample is possibly close to the composition at which one finds the transition from rods to bilayer aggregates at that polymer concentration. The small spheres have a diameter of ca. 40 nm, and the rods have a diameter of ca. 70 nm.

The sample containing 80 units of PEO also forms primarily rods. A larger number of small spheres is observed, but no lamellae are seen. The rods have a diameter of ca. 60 nm, and the small spheres have an average diameter of ca. 35 nm. A typical example is shown in Figure 3.

The sample containing 180 units of EO presents a very different morphology, in addition to small spheres with an average diameter of ca. 20 nm. An example of the large spheres is shown in Figure 4. The micrographs show large spheres with diameters varying from ca. 500 nm to 2 μm. Most of the samples of this composition show these two morphologies. The large spheres are probably the large compound micelles (LCMs) described before for the PS-*b*-PAA system.[11]

The presence of simultaneous multiple morphologies is characteristic of all the PS-*b*-PEO samples studied here. In addition to the normal small micelles which appear in each of the samples, vesicles and rods are seen in sample PS(240)-*b*-PEO(15), rods, lamellae, and a smaller number of vesicles are seen in sample PS(240)-*b*-PEO(45), and rods and the LCMs are seen in sample PS(240)-*b*-PEO(80) and PS(240)-*b*-PEO(180), respectively. Small spherical micelles also exist in almost all solutions in the PS-*b*-PAA block copolymer system.[11]

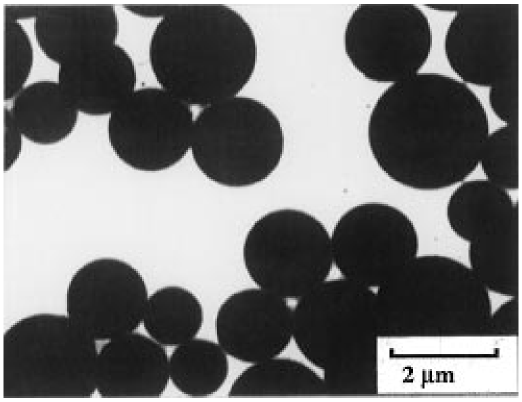

Figure 4. TEM picture of LCMs from an aqueous solution of the diblock copolymer PS(240)-*b*-PEO(180). The copolymer concentration in the initial DMF solution was 3.0%.

The morphological transition of spherical to nonspherical aggregates occurs in aqueous solutions of the PS-*b*-PEO block copolymer as the hydrophilic PEO block length decreases. The same trend has been observed in aqueous solutions of the PS-*b*-PAA block copolymer.[11] The driving forces involved in the transition from spherical to nonspherical aggregates in that system have been discussed; the same reasoning is believed to apply generally to the present PS-*b*-PEO block copolymer system. At a constant PS block length, it has been found that the radius of the spherical core increases with decreasing soluble block length.[12,22] Naturally, the degree of stretching of the PS chain is proportional to the radius of the micelle core.[11] The increase of the radius of spherical cores cannot go on indefinitely as the soluble block length decreases, because the stretching of the insoluble block (PS) results in a continuous decrease in the entropy. When the entropy of the micelle core decreases to some critical point, the system becomes unstable and a morphology change may occur. This might be a qualitative explanation why the morphology changes from spherical to nonspherical micelles as the soluble block length decreases.

The reason for the coexistence of the various morphologies is of interest. The morphology is a function of a number of factors, i.e., the lengths of both the hydrophobic PS and hydrophilic PEO blocks, the copolymer concentration, water concentration in the copolymer−DMF solution, and many other variables. For aqueous solutions of the PS-*b*-PAA block copolymer system, Zhang and Eisenberg have briefly discussed the reason for the coexistence of the multiple morphologies.[23] It is likely that the reason for the coexistence in the two systems is the same. One of the possibilities is that boundaries of various morphologies are being crossed in the process of water addition into the copolymer−DMF solution. As water is added, copolymer single chains form aggregates. The concentration of copolymer single chains thus decreases in the process of the addition of water to the solution, and a morphological boundary may be crossed. It is also possible that in some areas of the phase diagram, two morphologies coexist, and that the sample preparation procedure involves passing through such regions. Furthermore, the heterogeneity of chemical composition of block coplymers might be one possible reason. This aspect is now under study.

In conclusion, aggregates of various morphologies formed from PS-*b*-PEO diblock copolymers in dilute aqueous solutions were observed by transmission electron microscopy (TEM). The morphologies are a function of the soluble block (PEO) length, and, with decreasing PEO content, one obtains progressively, as the dominant morphologies, normal spherical micelle-like aggregates, rods, lamellae, and vesicles. The main reason for the morphological transitions is believed to be related to changes of the degree of stretching of the PS blocks in the core regions. The same phenomena have been observed in aqueous solutions in the PS-*b*-PAA diblock copolymers. It thus appears that the phenomenon of multiple morphologies in dilute solutions may be general for amphiphilic blocks. The spheres and vesicles might have potential use as drug delivery systems.

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