Communications to the Editor

Multiple Morphologies Formed from an Amphiphilic ABC Triblock Copolymer in Solution

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1. Introduction. The aggregation behavior of AB type block copolymers with highly asymmetric block lengths has received much attention recently. In these copolymers, the hydrophobic blocks are usually much longer than the hydrophilic blocks. Such copolymers form crew-cut aggregates[1−9] in aqueous solutions. They have bulky cores and small coronas, in contrast to star micelles[10] in which the relative sizes are reversed. The AB copolymers used for those studies include poly(styrene)-*b*-poly(acrylic acid),[1b,2−4,8−9] poly(styrene)-*b*-poly(oxyethylene)[5] and other copolymer systems.[6,7] The molecular weights of the copolymers range from 10^3 to 10^5. Because the hydrophobic blocks are long, the aggregates cannot be prepared by direct dissolution of the block copolymers in water. The usual method of preparation involves dissolution of the copolymers in a common solvent, followed by the addition of water to induce self-assembly of the copolymer, with the hydrophobic segments of the copolymer forming the cores. As the water content in the solution increases, the cores of the aggregates become kinetically frozen so that the morphologies are easily maintained. Dialysis against water removes residual solvent. Subsequently, TEM can be employed directly to investigate the morphologies in the dry state. Furthermore, because the hydrophilic block is short, aggregates with a wide range of morphologies can be prepared by changing parameters such as the block length ratios, ion concentration[3,4] or type of solvent.[9]

So far, crew-cut aggregates formed from ABC triblock copolymers have not been studied. In this paper, we report on our preliminary study of the morphologies formed from such an ABC type triblock copolymer, $PS_{180}PMMA_{67}PAA_{37}$, in dioxane, tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF), induced by addition of water. Static light scattering (SLS) was used to monitor the aggregation process in the course of addition of water to the copolymer. Transmission electron microscopy (TEM) was used to observe the resulting morphologies. In addition to a description of the different morphologies formed by the copolymer, we also discuss how the presence of the second hydrophobic block and changes of the solvent system affect the aggregation behavior.

Only very few studies have dealt with the solution properties of ABC type triblock copolymers, especially those containing two hydrophobic blocks.[11,12] Patrickios *et al.*[11] have studied a series of ABC triblock copolymers in water. The copolymers were composed of various block sequences of ethyl vinyl ether (water-insoluble unit), methyl vinyl ether (marginally water-soluble unit) and methyl tri(ethylene glycol) vinyl ether (water-soluble unit), which were prepared by sequential living cationic polymerization initiated by hydrogen chloride adduct of isobutyl vinyl ether (water-insoluble unit). Each block in the copolymers was 20 units long. At less than 1 wt %, the copolymers could not micellize in water but did micellize in aqueous salt solutions. The micelles were spherical. Kriz *et al.*[12] prepared an ABC triblock copolymer, poly(2-ethylhexyl acrylate)-*b*-poly(methyl methacrylate)-*b*-poly(acrylic acid), and studied its aqueous solution properties. A core−shell−shell structure in water was suggested for the spherical micelle of the copolymer. Other types of ABC triblock copolymers, related to polyampholytes[13,14] with a hydrophobic block, were also synthesized and investigated in aqueous solutions. For example,[13] Hatton's group investigated the solution properties of a series of ABC copolymers with different structures, which contained 2-(dimethylamino)ethyl methacrylate (A), methyl methacrylate (B), and methacrylic acid (C) blocks. The molecular weights of these copolymers were low ($<5 \times 10^3$). Copolymers with the structure ABC and ACB formed spherical micelles with B in the cores.

In contrast to the small number of studies on solution properties, the solid-state properties of linear ABC type block copolymers have received considerable attention. Many new morphologies have been described,[15] and a short review on the subject has recently been published.[16] Theoretical studies of the morphologies from ABC block copolymers have also appeared recently.[17,18]

2. Experimental Section. The block copolymer of poly(styrene)−poly(methyl methacrylate)−poly(*tert*-butyl acrylate), specifically $PS_{180}-PMMA_{67}-PtBuA_{37}$, was synthesized by sequential anionic polymerization of styrene (S), methyl methacrylate (MMA), and *tert*-butyl acrylate (tBuA). *sec*-Butyllithium in cyclohexane was used as the initiator. The procedure for the preparation of the triblock copolymer is similar to that for the preparation of PS−PtBuA diblock copolymers.[19]

The PtBuA block in the copolymer was hydrolyzed to poly(acrylic acid) by refluxing in toluene using *p*-toluenesulfonic acid as catalyst at 110 °C for 5 h. The final copolymer was dried in a vacuum oven at 60 °C for 3 days.

The molecular weight and molecular weight distribution of the PS block alone (prior to the addition of the second and third monomer) were analyzed against PS standards by a Waters GPC system with an HR1 and

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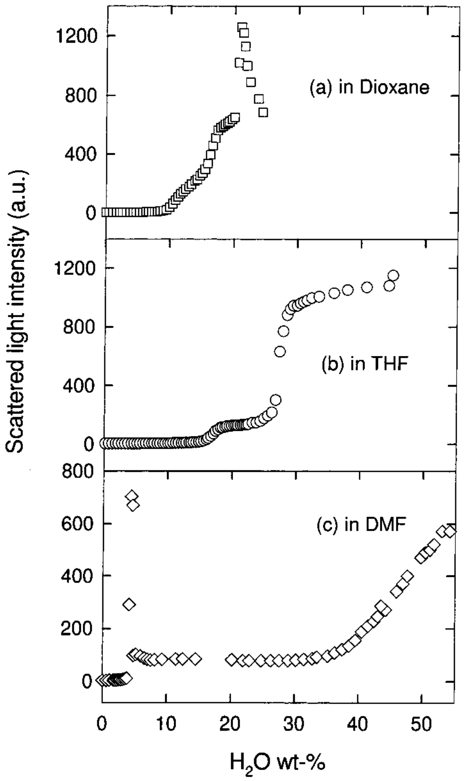

Figure 1. Plots of scattered light intensity against added water content in solutions with starting polymer concentration of 3 wt %: (a) in dioxane; (b) in THF; (c) in DMF.

an HR4 columns containing styragel, using THF as the eluent. The lengths of the second and the third blocks of the triblock copolymer were calculated from ^{1}H NMR spectra (Varian Gemini 200 for ^{1}H operating at 200 MHz) based on the knowledge of the PS block length. ^{1}H NMR spectra of the copolymers before and after hydrolysis showed that the ratios of MMA units to styrene units did not change within experimental error, which proved that the PMMA was not hydrolyzed under the conditions used for hydrolysis of poly(*tert*-butyl acrylate).

To monitor the changes of scattered light intensities in the course of addition of water to the copolymer solution in a solvent, a Brookhaven light scattering instrument with a BI9000 AT digital correlator was used. The instrument was equipped with an Uniphase μBlue laser with an output power of 125 mW which supplies vertically polarized light with wavelength $\lambda = 532$ nm. Measurements were made at 90° to the incident beam at 25 °C.

To obtain samples for the TEM studies, at several points during the light scattering experiments one or two drops of a solution were taken and quenched in about 5 cm^3 water to “freeze” the morphologies at the chosen stages. Residual solvent in the aggregates was removed by dialysis against water. The other procedures for preparing samples for TEM experiments were similar to those described elsewhere.[2b] TEM experiments were performed on a Phillips EM400 microscope operating at an acceleration voltage of 80 kV.

3. Results and Discussion. Static light scattering has been used to monitor the changes of scattered light intensity vs added water content in the copolymer solutions in dioxane, DMF and THF. Since the scattered light intensity (*I*) is proportional to the product of the polymer concentration (*c*) and the aggregate molecular weight (*M*), any change of *I* should reflect the change of *M* if *c* is nearly constant. It is therefore possible to monitor any change of the state of aggregation of the copolymer in a solution during the course of water addition. Figure 1 shows plots of scattered light intensity against the water content for the copolymer solutions, with a starting copolymer concentration of 3 wt %, in dioxane, THF and DMF. Changes in the scattered light intensity reflect changes in the molecular weights of the aggregates in the solutions. Two or three steps can be seen, depending on the solvent used. Typical morphologies observed by TEM for the solutions at various stages of water addition are shown in Figure 2.

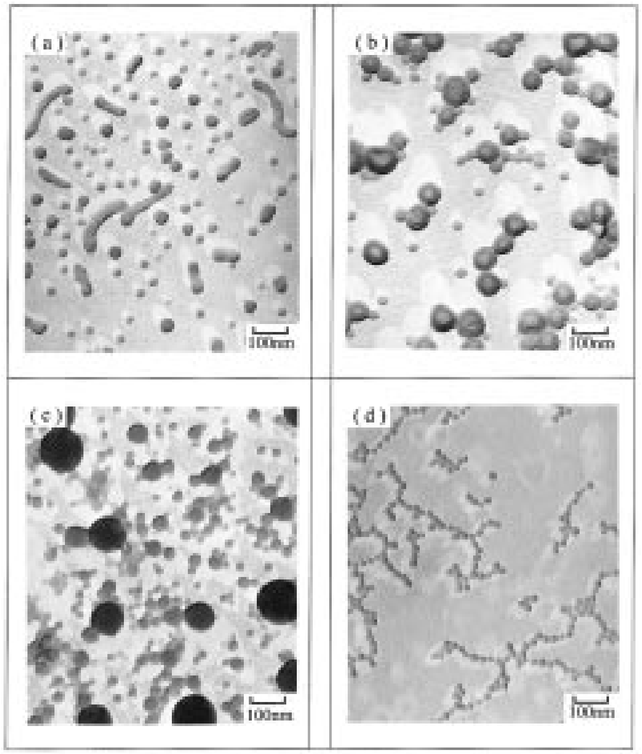

Figure 2. TEM pictures of aggregates from solutions with a starting polymer concentration of 3 wt % at different water contents: (a) from a dioxane solution at 18 wt % added water; (b) from a dioxane solution at 25 wt % added water; (c) from a THF solution at 40 wt % added water; (d) from DMF solution at 55 wt % added water.

Three regions can be distinguished in Figure 1a, which shows the scattered light intensity as a function of water content in dioxane. An increase in *I* is seen at about 9.5 wt % of water in the solution, which is caused by micellization of the copolymer; the water content at this point is defined as critical water content for micellization, or cwc. Above the cwc, the scattered light intensity generally increases further with increasing water content, with several additional identifiable regions of rapid increase in *I*. The second of these appears at a water content of ca. 17%. Next, the slope is found to decrease, followed by a final dramatic “jump”, or increase in the slope, at ca. 20% of added water. The slope change at 17% coincides with the start of a morphological change from spherical micelles to short rodlike micelles. Figure 2a shows short rods and spherical aggregates obtained at water content of 18%. The rapid increase in the scattered light intensity at 20% is due to the formation of vesicles, shown in Figure 2b. The vesicles were obtained from the solution at 25%

of added water. Once the vesicles are formed, internal scattering and interference decrease the measured scattered light intensity. In Figure 2b, vesicles and spherical aggregates are seen together. Spheres can be seen in both parts a and b of Figure 2, which implies that some spherical micelles may have been kinetically “frozen” during the addition of water, or that the spheres and vesicles coexist under the conditions of the experiment. This phenomenon is also seen in THF and DMF solutions.

In THF solution, there are two jumps in the scattered light intensity as the water content increases, as shown in Figure 1b. The first rise is seen at a water content of about 16 wt %. This is caused by the first micellization of the copolymer. The second jump is seen at a water content of ca. 25 wt %. The morphologies obtained at water content over 30% (see Figure 2c) contain large particles, possibly with a structure similar to that of an LCM.[2b] Some small spheres, which are primary micelles, are also seen in Figure 2c. The large particles have a very broad size distribution.

Figure 1c shows the plot of scattered light intensity vs water content for a solution of 3% copolymer in DMF. Just before micellization, a very intense narrow peak is seen in Figure 1c in the water content range between 4 and 5 wt %. In this region, the solution is cloudy. This cloudy region has been detected for all the DMF solutions with 0.1 to 5% copolymer. However, cloudiness could only be seen for the copolymer solutions in dioxane and THF at low polymer concentrations, i.e., lower than 2% for dioxane and lower than 1.5% for THF. It is believed that cloudiness is caused by the phase separation of the homo-PS, of the block copolymer (PS−PMMA) and possibly of some triblock copolymer with very short PAA block lengths which is present because of the PAA block length distribution in the copolymer. The concentration of these species must be small, because the homo-PS or diblock copolymer PS−PMMA were not detected by GPC. After the copolymer micellizes, the impurities are all solubilized by the micelles. Similar phenomena and explanations have also been reported in connection with other copolymer systems.[20]

The curve in Figure 1c shows that, after micellization, the scattered light intensities do not change very much for water contents up to about 35%. In this region, the aggregates are spherical micelles as seen by TEM. When the water content increases above 35%, the scattered light intensities increase. This is due to a gradual assembly of the spherical micelles in the solution to a irregular “necklace” structure, as shown in Figure 2d (obtained at 55% of water). It is believed that the aggregation of spheres to necklace chains is due to the decreasing solubility of the PMMA block. As the water content increases above ca. 35 wt % in the solution, the PMMA blocks stop acting as mobile chains in the corona and form a shell around the PS core with increasing water contents. At high water contents, the PAA chains are the only ones which act as corona chains. In the present case, due to the shortness of the PAA block, their repulsive interactions are not sufficient to protect the surface of the hydrophobic core so that the micelles join to reduce the surface energy when they approach to each other. The necklace chain structure is formed in preference to clumped aggregates because of the slightly charged PAA blocks of the aggregates in the solution lead to edge-on assembly. The slight charge of PAA at high water contents is due to the ionization of carboxylic groups of the PAA in dilute solution, as discussed in a previous paper.[4] The weakly basic property of the DMF solvent should also move the ionization equilibrium of the −COOH groups toward a higher degree of ionization, which would increase the charge on PAA blocks further. Obviously, the PS is frozen at high water content so that the basic spherical morphology of the micelles does not change. This rigidity prevents the formation of real rodlike micelles with smooth surface, and the necklace chain structure is retained for kinetic reasons.

It is of interest to compare the cwc in the different solvents. For a solution with a starting polymer concentration of 3%, the cwc is 4.5 wt % in DMF, 9.5 wt % in dioxane, and 16.0 wt % in THF, respectively. These cwc values are in the range of cwc values for diblock copolymers of PS−PAA,[8] indicating that the determining factor for the cwc value is the solubility of the PS block of the triblock copolymer. Spherical aggregates form first for the copolymer in all solutions in the course of addition of water; i.e., spherical aggregates are obtained up to 35% water in DMF, 15% of water in dioxane, and 23% of water in THF, respectively.

It is noteworthy that different final morphologies were obtained by dissolving the copolymer in different starting common solvents, as discussed above. It is known that by manipulation of the solvent or mixed solvents for the PS−PAA diblock systems, spherical, rodlike, vesicular, and even tubular morphologies can be obtained from an identical block copolymer.[9] Whether ABC triblock copolymers could offer advantages in the manipulation of the aggregation behavior of copolymers compared to the diblock systems is still not clear yet, and more studies on ABC triblock copolymers are needed in this connection. It is likely, however, that the presence of an additional hydrophobic polymer block might offer some advantages in the solvent-induced manipulation of morphologies since additional χ parameters come into play.

Dynamic light scattering (DLS) can also be used to detect changes of apparent sizes for the aggregates as the water content is increased. The apparent hydrodynamic radii, $r_{h,app}$, of the equivalent spherical micelles from one solution for each system at high water contents have been measured. Three aggregate populations were detected for these solutions. For example, particles with apparent hydrodynamic radii of 12, 30, and 200 nm were seen in a 3% polymer solution in dioxane at 23% H_2O; 5, 15, and 130 nm in a 3% polymer solution in THF at 31% H_2O and, 20, 65, and 400 nm in a 5% polymer solution in DMF at 41% H_2O, which corresponds to the situations as indicated in parts b−d of Figure 2. We should point out here that for these studies, TEM gives more information about the morphologies than DLS as can be seen from parts b−d of Figure 2.

A few points can be summarized from the above results.

The combined use of SLS and TEM enables us to study the detailed aggregation process, including morphological transitions, from a copolymer dissolved in a common solvent in which aggregation is induced by addition of a poor solvent for one block (in a diblock copolymer) or for two blocks (in an ABC block copolymer).

An ABC type triblock copolymer with two hydrophobic blocks with different hydrophobicity and relatively short hydrophilic block can form spherical, rodlike, and vesicular aggregates, depending on the solvents chosen and conditions used. The first micellization point is controlled by the most hydrophobic block. In this study, the PS controls the cwc.

Finally, the aggregate morphologies described here probably have a core(from PS)−shell(from PMMA)−shell(from PAA) structure for the spherical aggregates, and a CBABC lamellar structure for the vesicles. This suggestion is based on the fact that in solution, the PS block aggregates first, which is then followed by the aggregation of the PMMA during the micellization of the copolymer as described above, furthermore, PS and PMMA are likely to be phase separated ($\chi_{\mathrm{PS-PMMA}}$ values are about 0.008 to 0.024 depending on various parameters of the measurement.[21−23]). However, the sharpness of the boundary will depend on the values of χ and on the molecular weights of the blocks. In the present system, the block length of PS is 180 units and the block length of PMMA is 67, so that a sharp boundary between the PS core and the PMMA shell should not be expected. A core−shell−shell structure with sharp boundaries would be obtained for high molecular weight ABC block copolymers and for those with a higher values of χ.

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