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Communications to the Editor

Bowl-Shaped Aggregates from the Self-Assembly of an Amphiphilic Random Copolymer of Poly(styrene-*co*-methacrylic acid)

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During the past decade, most studies of self-assembly were focused on highly regular molecules such as amphiphilic block copolymers[1] or small molecule amphiphiles.[2] The structural regularity and compositional tunability of these molecules provides a high degree of control over the final morphologies in solution. Reported morphologies include spheres, rods, vesicles, and many others.[3]

Recently, Riegel et al. reported on the formation of aggregates with a bowl-shaped morphology from a triblock copolymer containing a long polystyrene (PS) mid block with short poly[5-(N,*N*,*N*-diethylmethylammonium)-isoprene] (PAI) blocks at both ends.[4] The bowl-shaped aggregates are members of a morphological family, which also includes large-compound micelles[5] (LCMs, spherical aggregates containing an assembly of inverse micelles) and porous spheres.[6] All the aggregates in this family consist of assemblies of inverse micelles in which the short hydrophilic blocks form the cores and the hydrophobic blocks, e.g., the PS in this case form the continuous matrix. The hydrophilic segments of the amphiphilic blocks also provide an exterior corona for the whole aggregate. LCMs were first observed in poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) diblocks, with aggregate sizes on the order of 1 μm.[3b,5] They were subsequently seen in other materials. Porous spheres consist of LCMs in which solvent bubbles are trapped during the course of formation. They were first formed from poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO).[6] The formation of bowls was explained as resulting from the presence of one additional step beyond the formation of porous spheres. When water is added to a solution of an amphiphilic diblock copolymer in some block length regions, aggregation occurs, leading to the formation of relatively large homogeneous polymer-rich spheres surrounded by a mixture of solvent and water and protected by a corona of hydrophilic chains. The further addition of water leads to a progressive extraction of the solvent, e.g., dimethylformamide (DMF), from the large sphere, which is accompanied by shrinkage of the sphere while maintaining the interior compositional homogeneity. If the hydrophobic chains are relatively short, the process will eventually lead to the formation of regular micelles with a hydrophobic core and a hydrophilic corona. If, however, the hydrophilic block is short, the aggregate sphere may contain both hydrophilic and hydrophobic segments. Below some critical interior water content, the hydrophilic segments will aggregate, leading to the formation of inverse micelles inside the aggregate. Further water addition leads to a progressive extraction of the solvent, leading eventually to the formation of LCMs. A variation of this process can lead to the formation of porous spheres. If, during the early stages of the course of water addition, liquid−liquid phase separation occurs inside the sphere, bubbles filled with the solvent-rich phase can form, and if the viscosity of the polymer is too high for extensive bubble coalescence,

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Table 1. Morphologies Obtained from Random Copolymers of P(S-*Co*-MAA) under Different Conditions

polymer	initial concentrated (wt %)	solvent	CWC[a] (wt %)	water content[b] (wt %)	morphologies	diameter (nm)
P(S-23MAA)−20K	1.0	dioxane	12	10	LCMs[c]	250 ± 90
P(S-23MAA)−20K	1.0	dioxane	12	15	bowls	395 ± 80
P(S-23MAA)−20K	0.5	dioxane	15	15	LCMs + bowls	270 ± 75
P(S-23MAA)−20K	1.0	THF	14	15	LCMs + porous spheres	285 ± 85
P(S-23MAA)−20K	0.5	THF	16	16	LCMs + porous spheres	245 ± 70
P(S-22MAA)−500K	1.0	dioxane	11	15	LCMs	275 ± 160
P(S-22MAA)−500K	0.5	dioxane	13	15	LCMs	205 ± 140

[a] Critical water content. [b] Before quenching with an excess of water. [c] Random copolymer analogues of LCMs.

the bubbles can become trapped and thus yield porous spheres. Alternatively, if water addition occurs at a rate that results in the formation of a hardened "skin", then bubbles could form if a homogeneous shrinkage of the sphere cannot occur in response to extraction of the solvent from the sphere. This is an alternate mechanism, which could possibly lead to the formation of porous spheres. If, after the formation of bubbles, the interior viscosity is low enough or the storage time long enough to allow the bubbles to coalesce and to break through to the surface, but not so low as to allow the establishment of a spherical shape after break-through, then a bowl can be formed. For this process to occur, the internal viscosity must be within a very narrow range. It is very likely that that some additional viscosity-control mechanism needs to be present beyond that provided by the solvent content and the molecular weight of the polymer alone. In the case of Riegel et al., this added viscosity-control mechanism is provided by the ionic cross-links resulting from the aggregation of the terminal units of the triblock. The presence of the ionic cross-links in this case modifies the shape of the curve of the viscosity of PS as a function of the water content in the external solution in such a way as to bring it into the region for the phenomenon to occur. The details of the viscosity modification are not at the present understood, but it is clear that such a secondary mechanism is necessary for the phenomenon to occur.

Wang et al.[7] also observed bowl-shaped structures from a rigid polyimide homopolymer containing carboxyl end groups. In their case, the carboxyl end groups, together with the backbone rigidity, most likely provided the added viscosity-control mechanism.

In this communication, we report on the preparation of bowl-shaped structures through the self-assembly of still another polymeric system, i.e., a random copolymer of poly(styrene-*co*-methacrylic acid) [P(S-*co*-MAA)], in contrast to the block copolymers or functionally terminated homopolymers used before. The added viscosity control is probably provided by hydrogen bond interactions among carboxylate groups along the backbone, as is encountered in carboxylic acids in bulk or in organic solvents. It should be noted that this material is not an ionomer,[8] but a carboxylated random copolymer.

The amphiphilic random copolymers P(S-23MAA)-20K (MAA content ≈ 23 mol %, $M_n \approx 20$ kDa) and P(S-22MAA)-500K (MAA content ≈ 22 mol %, $M_n \approx 500$ kDa) were synthesized via free radical polymerization. The polydispersities are expected to be those typical of polymers produced by free radical methods. The details of the synthesis and characterization were reported previously.[9] The solutions of these aggregated polymers were prepared by first dissolving the random copolymer in dioxane or tetrahydrofuran (THF), followed by the addition of water (deionized to a resistivity of 18 MΩ/cm through a Millipore Milli-Q system after distillation) dropwise at a rate of ca. 0.2 wt % (one drop) per 5 min to the desired water contents (10 or 15 wt %). Self-assembly occurred during the water addition process. The aggregate solutions were quenched into excess water and dialyzed with a cellulose membrane bag (Spectrum Laboratories, molar mass cutoff: 50 000) against water to remove the organic solvent. The dialyzing water was changed once a day for three times. These dialyzed solutions, in which the polymer content was ca. 1.2×10^{-3} mg/mL, were deposited on to copper grids and were then freeze-dried.[5] The aggregates were examined by transmission electronic microscopy (TEM). The morphologies of aggregates from different polymers obtained under a variety of preparative conditions are summarized in Table 1, which also lists the critical water contents of the materials.

Figure 1 shows the TEM images of the aggregates formed by quenching from dioxane solutions of P(S-23MAA)-20K at different initial water contents. When the water content is 10 wt % (i.e., below the CWC), the random copolymer forms mainly a structure analogous to large-compound micelles (LCMs), in some of which we may be seeing the beginning of the phase separation process, which, at higher water content, leads to bowl formation (see Figure 1A). At a water content of 15 wt %, bowl-shaped aggregates are seen (see Figure 1B). The diameters of the bowls are in the range of 300−500 nm, the depths are in the range of 160−260 nm, and the diameters of the circular openings are between 70 and 150 nm. The bowl-shaped structure is maintained after quenching because of the presence of a large excess of water (or of pure water after dialysis), which extracts the organic solvent from the PS regions and raises their glass transition temperature to ca. 100 °C. Figure 1C is a TEM micrograph of the same sample of bowls as those shown in Figure 1B but after six months of storage in water at room temperature. The characteristics of the bowls remain essentially the same; the micrograph in Figure 1C looks somewhat sharper because of improved focus on the microscope.

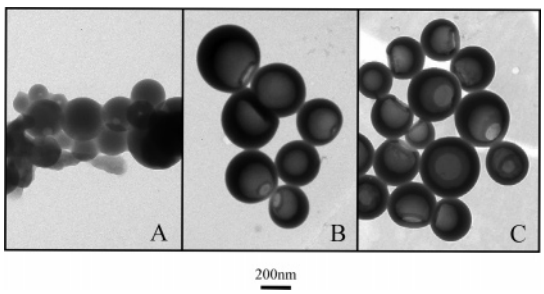

Figure 1. TEM images of aggregates formed from P(S-23MAA)-20K. A: quenched from a water content of 10 wt %. B: from a water content of 15 wt %. C: sample in B after storage at room temperature for six months; initial polymer concentration: 1.0 wt %; common solvent: dioxane.

We suggest that the formation of the bowl-shaped structure from the random copolymer P(S-23MAA)-20K involves a mechanism similar to that proposed by Riegel et al. When water is added to the solution of the random copolymer, the solvent becomes progressively less favorable for the hydrophobic segments of the P(S-*co*-MAA). At a critical water content [ca. 12 wt % of water for P(S-23MAA)-20K], the polymer chains lose their solubility and associate with each other to form spherical aggregates. Most of the MAA units are buried inside the aggregates and probably associate with other carboxylate units via hydrogen bonding. Some MAA units probably segregate to the interface between the aggregates and the external aqueous solution and serve to stabilize the aggregates. When the water content is low, the interiors of the aggregates have a relatively low viscosity, and the exterior of the spheres is soft. The low viscosity leads to a rapid solvent diffusion in and out of the soft "skin" and a homogeneous shrinkage of the whole aggregate, which, in turn, leads to the formation of large-compound micelles (Figure 1A). It should be stressed that the aggregates shown in Figure 1A were prepared by quenching from a solution containing 10 wt % water, i.e., below the critical water content of 12 wt %. The self-assembly thus occurred during the early stages of the quenching process at relatively low interior water contents.

For the other samples, as more water is added continuously to the medium, extraction of organic solvent from the aggregate core leads to an increase in the internal viscosity and possibly a hardened "skin". The confined droplets, formed inside the aggregate during water addition, coalesce to form a single large one. We speculate that the localization of this large droplet is random and placement at the center of the aggregate is rare. Upon further water addition to the system, the organic solvent in the interior diffuses out of cavities faster than the rate at which water diffuses in; thus, a difference in hydrostatic pressure is created with the lower pressure on the inside. Although the pressure difference is presumably equal all around the aggregate, the thinnest part of the wall is the weakest link for an inward break-through, which results in the formation of the opening of the bowl.

In Table 1, we list the morphologies of aggregates prepared under different conditions from two random P(S-*co*-MAA) copolymers. At an initial polymer concentration of 0.5 wt % in dioxane and at a water content of 15 wt %, after quenching in excess water, the random copolymer P(S-23MAA)-20K self-assembles into large-compound micelles (LCMs), coexisting with the bowl-shaped aggregates. The size of the particles is between 200 and 400 nm. The bowl-shaped structures from the same polymer are not seen when the common solvent is changed to THF. Attempts to obtain bowl-shaped aggregates from P(S-22MAA)-500K (with dioxane as the common solvent) were also unsuccessful. The absence of bowls for the THF solution or for the P(S-22MAA)-500K polymer is possibly due to the absence of liquid−liquid phase separation in the concentration regions investigated. It should be recalled that liquid−liquid phase separation is highly solvent-specific and strongly molecular weight dependent.[10]

In summary, a bowl-shaped structure was observed from a random copolymer of P(S-23MAA)-20K in dilute solution. We emphasize that the copolymer used here is a random copolymer P(S-*co*-MAA) instead of the previously employed block copolymers or functionally terminated polymers. In this random carboxylic acid-containing polymer, the supplemental viscosity control, which appears essential for the formation of bowls, is, most likely, provided by hydrogen bonding between the MAA units.

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