

Control of Morphology through Polymer–Solvent Interactions in Crew-Cut Aggregates of Amphiphilic Block Copolymers

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Amphiphilic diblock copolymers in selective solvents generally yield colloidal aggregates or micelles.^{1–3} It has been shown recently that highly asymmetric diblocks of polystyrene and poly(acrylic acid) (PS-*b*-PAA) with very short PAA blocks in solution can form stable aggregates of various morphologies, i.e. spheres, cylinders, vesicles, and large compound micelles (LCMs) consisting of a spherical assembly of reverse micelles.^{4,5} To prepare these aggregates, PS-*b*-PAA diblock copolymers are first dissolved in a common solvent (*N,N*-dimethylformamide, DMF) for both blocks, and then a precipitant, water, is added to induce aggregation of the insoluble PS blocks. All these aggregates, which consist of a core or layer of the insoluble PS blocks surrounded by a thin shell of the soluble PAA blocks, are called crew-cut.^{6,7} More recently, crew-cut aggregates with various morphologies were also obtained from other ionizable or nonionic block copolymers.^{8–12} The morphologies assumed by the crew-cut aggregates are mainly controlled by a force balance involving three factors, i.e., the stretching of the PS blocks in the core, the repulsive interaction among the corona chains, and the surface tension at the core-corona interface at the onset of micellization.^{4,5} The morphogenic effect of changing the interaction among the corona chains on the aggregates has been evidenced by the addition of ions.¹³ Specifically, the presence of ionic species such as NaCl, HCl, and CaCl₂ changes the repulsion among the PAA corona chains due to electrostatic screening, protonation, and ion-binding, respectively; it thus changes the force balance and induces the formation of aggregates of different morphologies from the same block copolymer. The morphology of the aggregates is also a function of the initial polymer concentration in the solution.¹⁴

In this Communication, we show that solvent induced changes in the core dimensions can also induce morphological changes in aggregates of an identical block copolymer, due to changes in the dimension of the polystyrene coils and in the volume fraction of solvent in the core during self-assembly. It has been suggested by Nagarajan¹⁵ on theoretical grounds that changing

Table 1. Aggregate Morphologies of PS-*b*-PAA Diblock Copolymers in Different Solvents

PS- <i>b</i> -PAA ^a	PAA (mole %)	DMF $\epsilon = 38.2$ $\delta = 24.8$	THF $\epsilon = 7.5$ $\delta = 18.6$	dioxane $\epsilon = 2.2$ $\delta = 20.5$
168- <i>b</i> -59	26.0	sphere	sphere	sphere
490- <i>b</i> -87	15.1	sphere	sphere	cylinder
500- <i>b</i> -58	10.4	sphere	vesicle	vesicle
420- <i>b</i> -21	4.8	sphere	LCM	LCM

^a The initial copolymer concentrations in the solutions were 2 wt %: ϵ : dielectric constant;¹⁷ δ : solubility parameter ([MPa]^{1/2}).¹⁸

the solvent content of the core can change the aggregate morphology. We show that this is, indeed, the case.

Changing the solvent can change not only the core dimensions but also possibly the repulsion between corona chains, particularly when the corona chains are ionic and the dielectric constant of the solvent is allowed to change. Until now, it has been possible to prepare only spherical micelle-like aggregates or large compound micelles from diblocks of polystyrene and quaterized poly(4-vinylpyridine), even from blocks of widely different compositions. By changing the solvent out of which the aggregates are prepared, we have now succeeded in forming aggregates with other morphologies, i.e., cylinder and bilayer from that polymer also.

The copolymers used in the present study were synthesized by anionic polymerization as described in detail elsewhere.^{5,6} For the preparation of the colloidal solutions, the precipitant, deionized water, was added at a rate of 0.3 wt % per 10 s with vigorous stirring to the copolymer solution in the common solvent. Self-assembly occurred at a water content of *ca.* 5 wt % in DMF, of *ca.* 11 wt % in 1,4-dioxane, and of *ca.* 18 wt % in tetrahydrofuran (THF). When a mixture of solvents was used, the critical water content (CWC) was related to the solvent composition. More water was added until the water content reached *ca.* 50 wt %. Stable aggregates in aqueous solution were obtained by dialyzing the colloidal solutions against distilled water for a few days to remove the common solvent. Transmission electron microscopy (TEM) was carried out on a Philips EM410 microscope operating at an acceleration voltage of 80 kV; the TEM samples were prepared as described elsewhere.^{4,5}

Table 1 illustrates the relationship between the morphology of PS-*b*-PAA aggregates and the nature of common solvent for several diblocks. At a concentration of 2 wt %, all the diblocks yield only spherical micelle-like aggregates in DMF. In contrast, vesicles and large compound micelles (LCMs) can be obtained in THF, while the aggregates prepared from dioxane show the entire range of morphologies. A study of the phase separation of homopolystyrene (homo-PS) from these different solvents by the addition of water shows that the degrees of swelling of homo-PS phase, which is defined as the volume ratio of the total PS-rich phase to that of the solid PS, are *ca.* 3.3 in THF, *ca.* 3.1 in dioxane, and *ca.* 1.6 in DMF.¹⁶ The higher degree of swelling of the homo-PS in THF and dioxane than in DMF reflects their solubility parameter values; the solubility parameters (δ) of THF ($\delta = 18.6$) and dioxane ($\delta = 20.5$) are closer to that of homo-PS ($\delta = 16.6$ – 20.2) than that of DMF ($\delta = 24.8$).¹⁸ Similar swelling ratios are likely to be found in the cores of the PS-*b*-PAA aggregates. Therefore, the dimensions of the aggregate cores, at the onset of micellization, must be much larger in THF and dioxane than in DMF. As a result, the degree of stretching of the PS chains has to increase

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correspondingly, which is entropically unfavorable. The high penalty for the larger stretching of PS chains in the core forces the aggregate to change morphology from a sphere (in DMF) to a cylinder or to a bilayer (in THF or dioxane) in order to decrease the free energy of micellization.⁵

The effect of changing the dimensions of the chains in the core on the morphologies of the aggregates becomes more versatile when a mixture of solvents is used. As a typical example, PS₂₀₀-b-PAA₁₈ (the numbers in the subscripts indicate the number of repeat units in the blocks) yields spherical micelle-like aggregates in DMF and large compound micelles (LCMs) in THF; however, aggregates of other morphologies can be obtained by using mixtures of DMF and THF in various ratios (the initial polymer concentration before the addition of water is 0.5 wt % for all experiments). For instance, the aggregates prepared in a mixture of 5 wt % THF and 95 wt % DMF are cylindrical. A mixture of rods, lamellae, and vesicles is obtained in a mixture of 10 wt % THF and 90 wt % DMF. When the THF contents are in the range of 25–67 wt %, the aggregate are vesicular. The sizes of the vesicles are found to depend on the solvent composition and to increase with increasing THF content. When the THF content is 67 wt %, the vesicles are still the dominant aggregates, but LCMs can be seen occasionally. With a further increase in the THF content, the fraction of vesicles decreases and that of LCMs increases. Finally LCMs are obtained in pure THF. The behavior described above can be explained by a progressive increase of the dimension of the core with increasing THF content. The repulsion among the corona chains is believed to change relatively little in mixtures of DMF and THF of different ratios because the PAA is, at best, only very slightly ionized in these solvents.

A somewhat different situation is encountered in the study of ionic polystyrene-*b*-poly(4-vinylpyridinium methyl iodide) (PS-*b*-P4VPM₁) block polyelectrolytes to be described below. Preparation of aggregates with cylindrical or bilayer morphologies from these block polyelectrolytes in DMF has not been possible either by changing polymer composition or by adding various salts, most likely because of the strong repulsive interaction among corona chains in a solvent of such a high dielectric constant ($\epsilon = 38.2$), coupled with the small degree of swelling of the core (1.6). We now report the preparation of PS-*b*-P4VPM₁ aggregates with the entire range of morphologies from a single block copolymer (PS₁₉₅-*b*-P4VPM₁₈) induced by both increasing the core dimension and decreasing the repulsion among the corona chains. The morphologies are controlled in this case by using the solvents of THF and dioxane as well as their mixtures in various proportions. The core dimensions in both of these solvents are much larger than in DMF because of the higher swelling ratios. Meanwhile, the repulsive interaction between the corona chains decreases significantly because of low dielectric constant of THF ($\epsilon = 7.5$) and dioxane ($\epsilon = 2.2$). The interchain repulsion can be varied further by using various mixtures of THF and dioxane. Thus, as shown in Figure 1, small spheres are obtained in pure THF (strongest interchain repulsion), rod-like aggregates (with spheres) in a mixture of 60 wt % THF and 40 wt % dioxane, vesicles in a 50–50 THF/dioxane mixture, and finally LCMs in pure dioxane (weakest interchain repulsion).

It is worth noting that the control of morphologies by changing only the relative block length^{4,5} or the salt content¹³ or polymer concentration¹⁴ has some limitations. For example, of all the polymers listed in Table 1, only the 420-*b*-21 sample

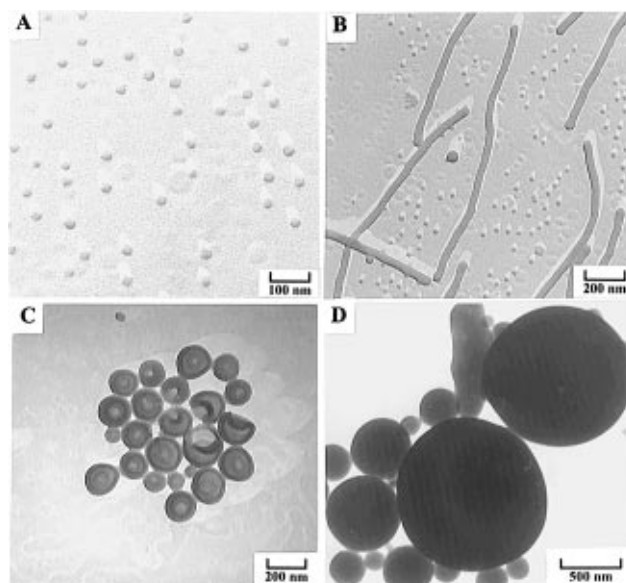


Figure 1. TEM pictures of PS₁₉₅-*b*-P4VPM₁₈ crew cut aggregates: (A) spheres from THF; (B) rods from a mixture of 60 wt % THF and 40 wt % dioxane; (C) vesicles from 50 wt % THF and 50 wt % dioxane; and (D) LCMs from dioxane. The initial copolymer concentration is 1 wt %.

yielded structures other than small spherical micelles when these various methods were employed in DMF as common solvent.^{13,14} The other three polymers yielded only small spheres under all the conditions we tried. Naturally, the present method also has its limitations, and for some polymers, notably those with very short soluble block lengths, DMF may be the better solvent for generating multiple morphologies.

In summary, it has been shown that the dimensions of the core chains during micellization have a major effect on the morphology of crew-cut aggregates. Furthermore, the control of repulsive interaction in corona chains composed of ionic segments, by varying the dielectric constant of the solvent at nearly constant core dimensions, allows further morphological fine-tuning such that various morphologies can now be obtained from block polyelectrolytes. These techniques now join the previously reported morphological control mechanisms based on block length, ion content, and polymer concentration to make the preparation of block copolymer aggregates of multiple morphologies very versatile. Now it may even be possible to predict the morphologies of the aggregates for new polymer systems by considering *a priori* the solubility parameters of the hydrophobic block and common solvent (which control the core dimension) and the dielectric constants of the common solvents (which control the interchain repulsion). If one wants to produce morphologies other than spherical micelle-like aggregates, a solvent which has a solubility parameter close to that of the core-forming block (to maximize the core dimension) and a low dielectric constant, particularly when the coronal block is ionic (to minimize the interchain repulsion), should be explored.

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