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Communications to the Editor

Block Copolymer "Crew-Cut" Micelles in Water

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Micelles formed by amphiphilic molecules in water are of great importance in biology, biochemistry, and pharmacology, as well as in many industrial processes.[1,2] We report here the preparation and characterization of self-assembling micelles with large hydrophobic cores (40−65 nm in diameter) and relatively thin hydrophilic coronas, the "crew-cut" micelles. These crew-cut micelles are in fact also a new family of microspheres since most microspheres currently used are polymer latexes made by emulsion polymerization. Microspheres stable in water have already found many applications in biology, colloid science, and controlled-release systems.[3,4]

The most important finding in the present study is that crew-cut micelles with very narrow size distribution, stable in water, can be prepared from amphiphilic monodisperse block ionomers (block copolymers with long nonionic blocks and short ionic blocks), synthesized by anionic polymerization. The size of the micelles is dependent on the method of preparation, indicating that minimum intermicellar exchange occurs in water. For crew-cut micelles prepared under identical conditions, it appears that the average core size is a linear function of the hydrophobic block length, N_B, and the average aggregation number is proportional to $N_B^{2/3}$, as predicted earlier by de Gennes.[5] However, more data are needed to prove these relationships. Some of the crew-cut micelles reported here are also stable in the presence of high concentrations of salts.

Microphase separation has been observed for many block copolymers in bulk and in solutions of selective solvents.[6−11] In bulk, for an asymmetric diblock copolymer (in which one block is longer than the other), a microphase consisting of short blocks is usually dispersed in the matrix of long blocks. When the block copolymer is dissolved in a good solvent selective for the long block, micelles are formed with short insoluble blocks in the cores and long soluble blocks in the coronas. On the other hand, if the block copolymer is dissolved in a good solvent selective for the short block, micelles with long insoluble blocks in the cores and short soluble blocks in the coronas, the so-called crew-cut micelles, should be obtained. However, block copolymers generaly cannot be directly dissolved in a good solvent selective for the short block, which makes the preparation of crew-cut micelles much more difficult. The term crew-cut micelle was proposed by Halperin,[6] and a theoretical study of this type of micelle was reported by de Gennes even earlier.[5] However, experimental data on stable crew-cut micelles are very limited.[12] The crew-cut micelles reported in this paper were prepared using block ionomer poly(styrene-*b*-4-vinylpyridinium methyl iodide) with a long styrene block and a short 4-vinylpyridinium methyl iodide block (Figure 1). The block ionomer crew-cut micelles have been found to be stable in aqueous solutions for more than 2 years by now, and are expected to be stable for much longer.

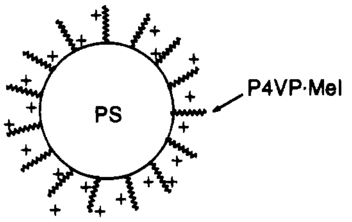

Figure 1. Schematic representation of a poly(styrene-*b*-4-vinylpyridinium methyl iodide) (PS-*b*-4VP·MeI) block ionomer "crew-cut" micelle in an aqueous solution.

It is well-known that, in ionomers, ionic interactions lead to strong association in the solid state and in solvents of low polarities.[13] In recent years, block ionomers were also found to form reverse micelles in low polarity solvents, with the short ionic blocks in the cores and the long nonionic blocks in the coronas.[14,15] The reverse micelles generally can be prepared by directly dissolving the asymmetric polymers. The micelles are mainly stabilized by steric repulsion between the long nonionic blocks. On the other hand, the preparation of block ionomer crew-cut micelles in water requires a very different procedure. We found that there are three key steps in the preparation of stable crew-cut micelles in water: (1) to dissolve the block copolymer in a nonselective solvent which is miscible with water and in which the block copolymer is in the single chain form, (2) to add a selective solvent and/or water slowly to the polymer solution of a nonselective solvent, and (3) to remove the nonselective solvent and the selective solvent if applicable and replace them with water.

Block copolymers of styrene and 4-vinylpyridine (4VP) were prepared using anionic polymerization techniques in a flamed-glass reactor, under a nitrogen atmosphere.[16] THF was used as a solvent, and it was purified by refluxing over a fresh sodium−benzophenone complex (a deep purple is an indication that the solvent is free of oxygen and moisture). The 4VP monomer (Aldrich) was stirred over a sodium mirror until a light yellow color appeared and was then distilled under reduced pressure just before polymerization. The styrene monomer (Aldrich) was purified by mixing with calcium hydride for 24 h, distilled under vacuum, and stored under nitrogen at −20 °C. Before polymerization, it was further treated with fluorenyllithium for 15 min and distilled under vacuum. The initiator used was

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α-methylstyryllithium which was a reaction product of *sec*-butyllithium and a few units of α-methylstyrene. The solvent and initiator were transferred to the reactor using either a stainless steel capillary or a syringe. The solution was cooled to −78 °C by dry ice/acetone. The purified styrene and 4VP monomers were added sequentially. An aliquot of the reaction medium was withdrawn for size-exclusion chromatographic analysis (SEC) before 4VP was added to determine the molecular weight of the styrene block. The reaction was terminated by adding a small amount of methanol, and the styrene−4VP block copolymer was recovered by precipitation in hexanes and dried under vacuum at 80 °C for 48 h. The SEC analysis of the polymer was performed on a Waters CV 150 high-temperature SEC equipped with a reflective index detector, using *N*-methyl-2-pyrrolidinone as eluent.[16] The conversion of the 4-vinylpyridine block to 4-vinylpyridinium methyl iodide was achieved by refluxing in an ethanol/methyl iodide solution for a few days. The compositions of the styrene/4-vinylpyridinium methyl iodide block copolymers obtained were determined to be PS(575)-*b*-P4VP·MeI(85) ($M_w/M_n = 1.14$) and PS(933)-*b*-P4VP·MeI(82) ($M_w/M_n = 1.13$).

Two methods were used to prepare crew-cut micelles in the present study. The block copolymers (ca. 0.5 g) were first dissolved in dimethylformamide (DMF; reagent grade, BDH) (ca. 10 g), and the solutions were filtered (Waltman, size 41) to remove the insoluble particles.

Method 1. Water was added very slowly (20−30 s/drop) from a burette to the block copolymer solution until a total volume of ca. 100 mL was reached. The solution was then dialyzed against distilled water for 1 week to remove DMF.

Method 2. Methanol (reagent grade, ACP Chemicals) was added very slowly to the block copolymer solution. After the solution turned cloudy, methanol was continuously added until the total methanol content reached approximately twice of that at the cloud point. Water was then added slowly to the solution until a total volume of ca. 100 mL was reached. The crew-cut micellar solutions were then dialyzed against distilled water for 1 week to remove DMF and methanol.

Spectra/Por membranes (MWCO 8000 or 50 000) were used for dialysis. The amount of the block polymer in a certain quantity of dialyzed solution was determined by weight after the water was evaporated. The dialyzed solution were diluted with water to 8×10^{-5}–4×10^{-4} g of polymer/g of water and then transferred onto TEM copper grids precoated with Formvar and carbon. The grids were dried under a mild flow of air. The transmission electron micrographs were acquired using a Phillips ME410 operating at 80 kV.

In the preparation of crew-cut micelles, selective solvents (methanol or water) were added very slowly to a poly(styrene-*b*-4-vinylpyridinium methyl iodide) block copolymer in DMF to ensure a very gradual change in solvent property. As methanol or water was added, the styrene segments of the block copolymers associated to form the cores of crew-cut micelles, as indicated by a bluish turbidity. In this process, loose micelles with large aggregation numbers may form at the beginning, as shown in by Selb and Gallot in a block polyelectrolyte system (short nonionic block and long ionic block).[10] When more selective solvent is added, the solubility of the styrene block is further reduced and the micellar cores become more compact. In the present study, since the styrene blocks are very long, it is expected that the critical micelle concentrations of the block ionomers are very low in water, and, hence, the exchange between the single chains and the micelles is minimum. Thus, it is very likely that the structure of the crew-cut micelles is "locked in" before dialysis. It is of interest to compare the micelles initially formed in a water/DMF mixture (method 1) to those initially formed in a methanol/DMF mixture (method 2). In method 2, the use of methanol as a selective solvent should lead to a more gradual transition in solvent polarity.

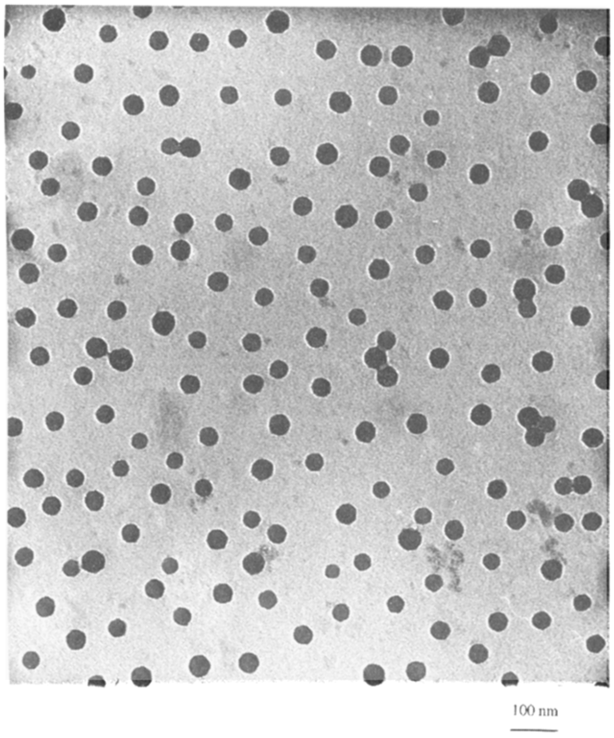

Figure 2. Transmission electron micrograph of the PS(933)-*b*-P4VP·MeI(82) micelles prepared using method 1.

Figure 2 shows the transmission electron micrograph of PS(933)-*b*-P4VP·MeI(82) crew-cut micelles, prepared by use of method 1. It is obvious that the micelles are basically spherical (this has also been confirmed by shadowing with Pt/Pd at an angle of 15−25°). The distribution of diameters of the PS(933)-*b*-P4VP·MeI(82) crew-cut micelles is shown in Figure 3a. On the basis of Figure 3a, the distribution of aggregation numbers of the micelles was also calculated (Figure 3b). It is of interest to note that the average aggregation number of the crew-cut micelles is relatively high (195). The mass distribution of the crew-cut micelles was also found to be very narrow, with a polydispersity index of 1.08.

In the cases where the crew-cut micelles were prepared using method 2, the average size of the micelles was found to be different from that prepared using method 1. The distribution of diameters of the PS(933)-*b*-P4VP·MeI(82) crew-cut micelles prepared using method 2 is shown in Figure 3c. The average diameter was found to be 62 nm, much higher than that of the crew-cut micelles prepared using method 1. In method 1, the crew-cut micelles were formed in a DMF/water mixture, while in method 2, methanol was used as a selective solvent to induce the crew-cut micelle formation. This clearly indicates that the process of adding selective solvent is critical in determining the sizes of the micelles, although at the end both DMF and methanol were removed by dialysis. It is expected that, for the

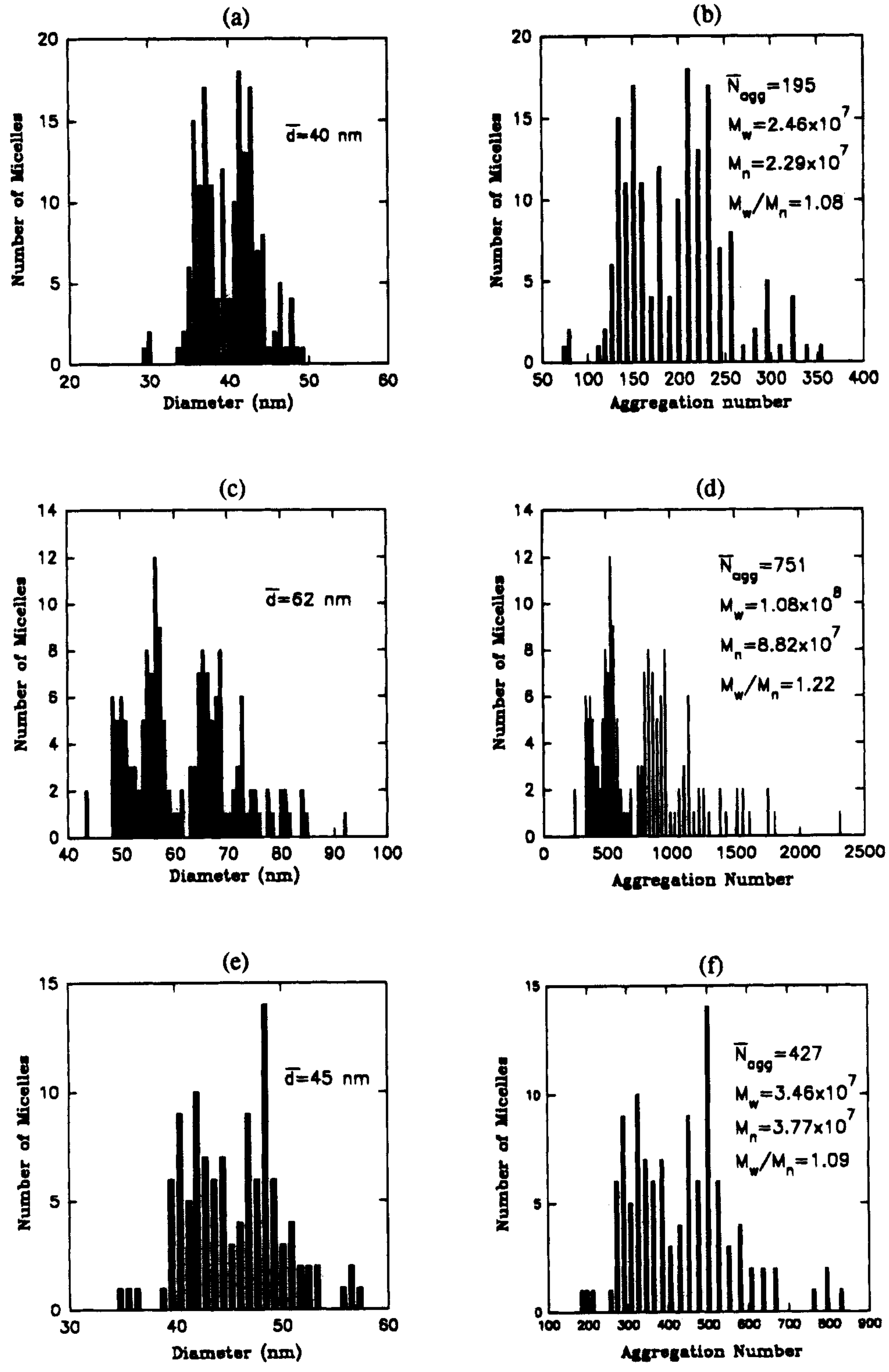

Figure 3. Distributions of diameters and aggregation numbers of crew-cut micelles: (a and b) PS(933)-*b*-P4VP·MeI(82), method 1; (c and d) PS(933)-*b*-P4VP·MeI(82), method 2; (e and f) PS(575)-*b*-P4VP·MeI(85), method 2. The densities of the styrene and the 4-vinylpyridinium methyl iodide blocks are 1.04 and 1.50, respectively.

crew-cut micelles in aqueous solution (after dialysis), the exchange of block copolymers is very slow. Thus, the sizes of the micelles are determined by the conditions under which the micelles are formed. The distribution of micellar aggregation numbers of the PS(933)-*b*-P4VP·MeI(82) crew-cut micelles prepared using method 2 is given in Figure 3d. The size distribution of these crew-cut micelles is also broader than that of the micelles prepared using method 1. The higher aggregation numbers and the broader distribution of the crew-cut micelles prepared using method 2 are probably due to the weaker incompatibility between the styrene segments and methanol.

For crew-cut micelles from block copolymers with shorter insoluble blocks but similar soluble blocks, the sizes of the micelles were found to be correspondingly smaller. The distributions of diameters and aggregation numbers of the PS(575)-*b*-P4VP·MeI(85) crew-cut micelles, prepared using method 2, are given in parts e and f of Figure 3, respectively. On the basis of scaling concepts, de Gennes[5] proposed that for micelles with thin coronas in the solution, the aggregation number,

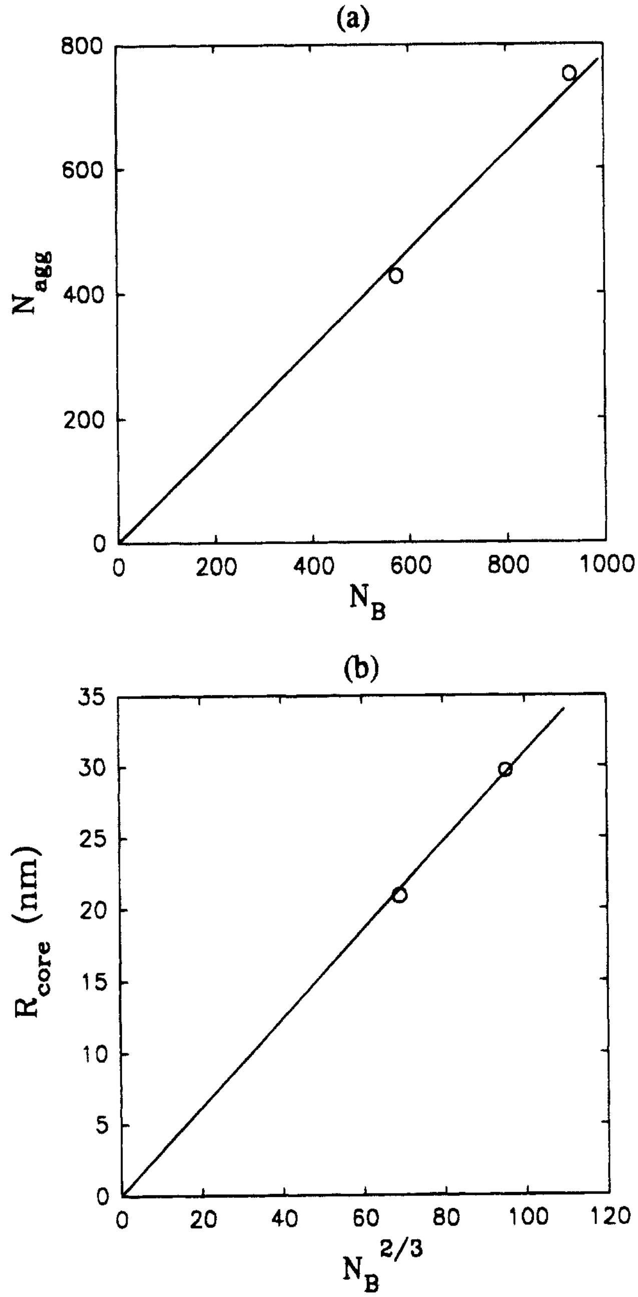

Figure 4. Plots of the number-average aggregation number of crew-cut micelles vs number of repeat units in the styrene block, N_B (a), and the number-average core radius vs $N_B^{2/3}$ (b).

N_{agg}, and the radius of the micellar core, R_{core}, are dependent on the number of repeat units of the insoluble block, N_B

$$N_{agg} \sim N_B \tag{1}$$

$$R_{core} \sim N_B^{2/3}a \tag{2}$$

where a is the length of the repeat unit in the insoluble block. The plots of the number average aggregation number vs the number of repeat units of the insoluble block, N_B, and the average size of the micellar core vs $N_B^{2/3}$ are shown in parts a and b of Figure 4, respectively. When $N_B = 0$, both the aggregation number and the size of the micellar cores must equal zero; therefore, the plots should pass through the origins. Although there are only two data points, linear relationships are observed between the aggregation number and N_B as well as between the size of the micellar core and $N_B^{2/3}$; this supports the earlier prediction by de Gennes.[5] Clearly, more experimental data are needed to demonstrate the validity of the power law.

The dependence of micellar size on the method of preparation indicates that the micelles are not in equilibrium in water. The minimum exchange between micelles in water can be attributed to the long styrene block and the large surface tension between the ionic corona and the neutral core.[17] The micelles might retain an equilibrium structure attained in a mixed solvent during the preparation process, so that the de Gennes model, which is based on equilibrium condition, is still applicable. One should also note that the scaling laws for the equilibrium structure of micelles with nonionic cores and polyelectrolyte coronas are quite different from those in the de Gennes model, as indicated by Marko and Rabin[18] and by Wittmer and Joanny.[19] The good agreement between the de Gennes model and the data presented here might be an indication that when the micelles attained the equilibrium structure during the preparation process, the polyelectrolyte effect is not that pronounced in a mixed solvent.

The crew-cut micellar solutions at concentrations between 0.2 and 0.4 wt % were found to be very stable in distilled water. The high stability could be attributed to the strong electrostatic repulsion between the micelles, as a result of the presence of the soluble ionic blocks. Similar to other colloidal systems, the stability of the crew-cut micelles is mainly determined by the balance of the electrostatic interaction energy and the London–van der Waals energy, as described by the classic Deryagin–Landau[20] and Verwey–Overbeek[21] (DLVO) theory. Thus, the steric effect may not be important in the present case since the soluble blocks are relatively short. It is well-known that the electrostatic repulsion can be suppressed by addition of inner electrolytes and the electrolyte concentration adequate to induce coagulation is called the critical coagulation concentration (ccc). For the PS(933)-*b*-P4VP·MeI(82) crew-cut micelles prepared using method 1, the ccc of NaCl was found to be around 1.8 M, while for the same block ionomer crew-cut micelles prepared using method 2, no coagulation was observed at a NaCl concentration as high as 4.0 M. This is very likely due to the fact that the aggregation numbers of the crew-cut micelles prepared using method 1 are much lower than those of the crew-cut micelles prepared using method 2. The average surface area per chain[22] in the former (26 nm^2) is much larger than that in the latter (16 nm^2). Higher charge density near the surface is expected for crew-cut micelles with smaller surface area per chain. This argument is supported by the fact that no coagulation was found in 4.0 M NaCl solution for the PS(575)-*b*-P4VP·MeI(85) crew-cut micelles prepared using method 2, which has an average surface area per chain (15 nm^2) similar to that of the PS(933)-*b*-P4VP·MeI(82) crew-cut micelles prepared using method 2 (16 nm^2).

The structure of the crew-cut micelles is similar to that of polyelectrolytes grafted onto a solid surface[23,24] as well as that of polymer latex particles.[25] It is anticipated that crew-cut micelles can serve as model systems for the studies of polyelectrolyte grafting and latex emulsions. Since crew-cut micelles can be prepared from well-characterized block copolymers, the control of composition and structure can be achieved simply by varying the length of the blocks. The core size and the corona thickness of block copolymer crew-cut micelles are determined by the insoluble and soluble block lengths, respectively. The surface area per chain for the crew-cut micelles is also much better defined than that of polymers grafted onto a solid surface. If the dependence of the critical micelle concentration (cmc) on the insoluble block length for the block ionomer crew-cut micelles in water is assumed to be similar to that of the block polyelectrolyte poly(styrene-*b*-sodium acrylate) (short styrene block and long ionic block) micelles in water,[26,27] the cmc's of PS(933)-*b*-P4VP·MeI(82) and PS(575)-*b*-P4VP·MeI(85) in water are expected to be on the order of 10^{-11} and 10^{-10} M, respectively. Fluroescent dyes and other guest molecules may be introduced to the crew-cut micelles either by solubilization or by incorporating via covalent bond into the block ionomers during synthesis.

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