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Phase Separation Behavior and Crew-Cut Micelle Formation of Polystyrene-*b*-poly(acrylic acid) Copolymers in Solutions

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ABSTRACT: Static light scattering was used to study the phase separation behavior of homopolystyrene and polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) in DMF as a function of added water content. It was found that the critical water content (cwc), at which phase separation starts, depends on both the polymer concentration and the molecular weight. The higher the polymer concentration and the molecular weight, the lower the cwc. For PS homopolymer, phase separation involves the precipitation of the polymer chains. In the copolymer solution, phase separation results in the formation of regular crew-cut micelles consisting of a PS core and a PAA corona; thus, it is preferably referred to as microphase separation. The change of the micelle fraction as a function of water addition can be estimated from the relationship between the cwc and the initial copolymer concentration. The influence of added electrolytes, i.e., NaOH, HCl, NaCl, $CaCl_2$, or $Ca(Ac)_2$, on the self-assembly process of the copolymers in DMF was also explored. Since the micelle cores are highly swollen by DMF in the early stages of their formation, the structures are labile. As the added water content increases, the cores become gradually less swollen and the mobility of the polymer chains in the cores decreases. A study of polymer chain exchange among the micelles was performed by mixing two solutions of micelles of different sizes at different water contents and studying the micelle core size distribution by transmission electron microscopy. It is shown that the copolymer chain exchange within a 1 day period is significant at a water content of 6 wt %, but becomes negligible when the water content is increased to ∼11 wt %.

1. Introduction

Amphiphilic block copolymers undergo self-assembly in a selective solvent to form aggregates of a core−shell structure.[1] Aggregates are frequently referred to as star micelles when the corona-forming blocks are much longer than the core-forming blocks. Aggregates of another kind, namely crew-cut micelles,[2] have been receiving attention recently in this laboratory[3−9] and in others.[10,11] In contrast to star micelles, crew-cut micelles are made from copolymers in which the insoluble blocks are much longer than the soluble blocks. Therefore, they have a rather large core and a relatively short corona; thus, their structure is, in some ways, similar to that of polymer nanospheres,[11] polymer latex particles prepared by emulsion polymerization,[12] and polymer chains grafted onto a solid surface.[13] Since the micelles are prepared from well-defined block copolymers, the core size and the corona dimension can be controlled by varying the block lengths of the copolymers. Furthermore, because the blocks of the copolymer are linked chemically, the density of the corona chains is better defined than that of polymers grafted onto a solid surface or of stabilizer layers on the surface of latex particles. The crew-cut micelles may thus serve as model systems for studies of polymer grafting, latex surfaces, and brushes.

To make the crew-cut micelle solution,[3−9] the block copolymers, e.g., polystyrene-*b*-poly(acrylic acid), are first dissolved in *N*,*N*-dimethylformamide (DMF), a common solvent for both of the blocks. Then, a precipitant for the polystyrene block, i.e., water or methanol, is added to induce the formation of micelles. Finally, the DMF is removed from the micelle solution by dialyzing the resulting solutions against water.[3−6] The structure of the micelles in water is stable because the fraction of the insoluble PS block is high and the core is glassy at room temperature. This makes it possible to study the morphologies by transmission electron microscopy (TEM) and to measure the core sizes directly from the prints.

For polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) diblock copolymers, aggregates with various morphologies have been prepared from copolymers of different compositions.[4,6] When the PAA block content is relatively high, the copolymer chains aggregate to form spherical micelles of low polydispersity. Compared to star micelles, the crew-cut micelles have a low density of coronal chains on the core surface (i.e., a large surface area per corona chain) and a low degree of stretching of the PS chains in the core. As the content of the soluble block (PAA) in the block copolymer decreases, the morphology of the aggregates changes progressively from spheres to cylinders, to bilayers (both vesicles and lamellae), and eventually to large compound micelles. The morphology of the crew-cut aggregates is mainly controlled by three factors, i.e., the stretching (deformation) of the PS chains in the core, the surface tension between the PS core and the solvent, and the inter-corona chain interactions.

The solubilization of homopolystyrene in the micelle cores has also been studied.[6] It was found that the homopolystyrene chains are generally distributed throughout the cores when the homopolystyrene content is relatively low. As the content of added homopolystyrene increases, homopolymer accumulation in the center of the micelle core can be deduced. The addition of homopolystyrene changes the morphologies of the aggregates from either bilayers or cylinders to spheres; this is ascribed mainly to the reduced degree of stretching of the PS blocks in the cores and possibly the effect of mixing entropy, both of which are associated with the solubilization of the homopolystyrene into the micelle cores.

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More recently, it was found that the morphological changes can also be induced by the addition of micro- or millimolar NaCl, $CaCl_2$, $Ca(Ac)_2$, HCl, or NaOH to the DMF solution.[7,8] The effect of added ions on the aggregate morphology is similar to that of changing block copolymer composition. In general, the effects can be ascribed to a change of the repulsive interactions among the corona chains accompanying the addition of ions. In addition to the morphologies which can be produced by varying the copolymer composition in the absence of added ions, i.e., spheres, rods, bilayers, and large compound micelles, aggregates of a new morphology, large compound vesicles (LCVs), are also obtained. The formation of LCVs appears to be a result of kinetic control involving secondary aggregation of many individual vesicles and a subsequent PS wall fusion process. The morphogenic effects of copolymer composition and added ions on the aggregate morphology is also found in the self-assembly system of polystyrene-*b*-poly(ethylene oxide) copolymers.[7,9]

The study of crew-cut aggregates is still in the early phases and many of the fundamental aspects related to their formation as well as the different morphologies still remain unexplored. Because the crew-cut micelles are prepared by adding a precipitant to a homogeneous copolymer solution, a microphase separation process is involved in the course of micellization. Although it has been used to prepare star micelles of copolymers,[14] the addition of a precipitant is not a classical method, and thus it has not been explored before in detail. It has been shown in previous publications[3−9] that this method yields essentially monodisperse micelles and various other morphologies. Therefore, the study of the microphase separation behavior of block copolymers in DMF/water mixtures becomes essential for an understanding of the micellization process. In this paper, we first investigate the microphase separation behavior of PS-*b*-PAA block copolymer solutions as a function of the copolymer concentrations and compositions as well as the presence of added electrolytes. Then, a preliminary study of the relationship between the lability of the micelle structure and the added water content is presented, to verify the conditions under which the formed micelles become structurally frozen aggregates. A parallel study of the thermodynamics of crew-cut micelle formation has been conducted and will be described in a forthcoming paper.[15] Static light scattering and transmission electron microscopy techniques are used.

2. Experimental Section

Polymer Samples. Polystyrene-*b*-poly(acrylic acid) diblock copolymers (PS-*b*-PAA) were synthesized by sequential anionic polymerization of styrene monomer followed by *tert*-butyl acrylate monomer. The polymerization process was carried out in tetrahydrofuran (THF) at −78 °C under nitrogen gas. Before the addition of *tert*-butyl acrylate monomer, an aliquot of the reaction medium was withdrawn to obtain homopolystyrene (PS), which thus had a polystyrene chain length identical to that in the diblock copolymer which was to be synthesized subsequently. A more detailed description of the procedures can be found elsewhere.[6]

The degree of polymerization and the polydispersity of the polymers were measured by size exclusion chromatography (SEC). All the homopolystyrenes and their diblock copolymers in the form of *tert*-butyl acrylate gave one narrow SEC peak. The composition of the block copolymer was determined from FTIR measurements, from which the degree of polymerization of the poly(*tert*-butyl acrylate) was calculated. The as-synthesized block copolymers were hydrolyzed to the acid form (PS-*b*-PAA) in toluene at 110 °C by refluxing overnight in the presence of *p*-toluenesulfonic acid as the catalyst (5 mol % relative to the polyacrylate content). FTIR studies showed that the hydrolysis was essentially complete. The basic characteristics of the polymers are listed in Table 1. The polymer samples are differentiated by the notation developed previously; e.g., PS(500)-*b*-PAA(60) denotes a copolymer containing 500 styrene units and 60 acrylic acid units. PS(180) refers to homopolystyrene with 180 units in the chains.

Table 1. Molecular Characteristics of Homopolystyrene and of Polystyrene-*b*-poly(acrylic acid) Diblock Copolymers

polystyrene (PS)	M_w/M_n	copolymer (PS-*b*-PAA)	M_w/M_n
PS(86)	1.09	170-*b*-33	1.08
PS(170)	1.07	410-*b*-25	1.05
PS(390)	1.05	390-*b*-41	1.06
PS(500)	1.04	500-*b*-60	1.04
PS(1140)	1.05	1140-*b*-165	1.06

Static Light Scattering. Light scattering experiments were performed on a DAWN-F multiangle laser photometer (Wyatt Technology, Santa Barbara, CA) equipped with a He−Ne laser (632.8 nm). The polymer solutions were prepared by dissolving polymers into *N*,*N*-dimethylformamide (DMF). The DMF (Aldrich) was used as received without any further purification. According to the manufacturer, the water content is less than 0.02%. The solutions with different concentrations were obtained by stepwise dilution of a more concentrated solution. The solutions were filtered through a membrane filter with nominal pore size of 0.45 μm. Deionized water (Milli Q) was added to the polymer/DMF solutions with a microsyringe. The experiments were performed at room temperature. The scattered light intensity was recorded 15 min after the addition of water and mixing of the solution.

Transmission Electron Microscopy (TEM). A Philips EM410 microscope was used for the studies. To prepare TEM samples, a drop of dilute aqueous solutions (about 1 mg/mL) was deposited onto copper EM grids, which had been precoated with a thin film of Formvar (poly(vinylformaldehyde) plastic) and then coated with carbon. The aqueous solution was allowed to stay about 2 min on the copper grid and then was blotted away with a strip of filter paper. Finally, the samples were shadowed with palladium/platinum alloy at an angle of ∼35°.

3. Results and Discussion

3.1. Phase Separation of Polymer/DMF/Water Solutions. DMF is a common solvent for both blocks of the polystyrene-*b*-poly(acrylic acid) copolymers. The dissolution of the copolymers in DMF as single chains has been confirmed by static light scattering measurement of the molecular weight. Because water is a good solvent for poly(acrylic acid), but a precipitant for polystyrene, as water is added to the copolymer/DMF solution, the solvent becomes progressively worse for the polystyrene block. Eventually, the copolymer solution undergoes microphase separation and the polystyrene chains aggregate, which is reflected in a sudden change in the scattered light intensity.

3.1.1. Addition of Water to Homopolystyrene/DMF Solutions. Before exploring the microphase separation behavior of the copolymer/DMF solutions resulting from the addition of water, it is useful to study the homopolystyrene (homo-PS) solutions because the major component of the PS-*b*-PAA copolymers is polystyrene. Figure 1 presents experimental curves of the scattered light intensity from the PS(170) homopolymer solutions as a function of added water content. For each solution, as long as the water content is relatively low, the scattered light intensity changes only very little, implying that the polymer chain dimensions do not change appreciably. However, when the water content reaches some critical value, the scattered light intensity

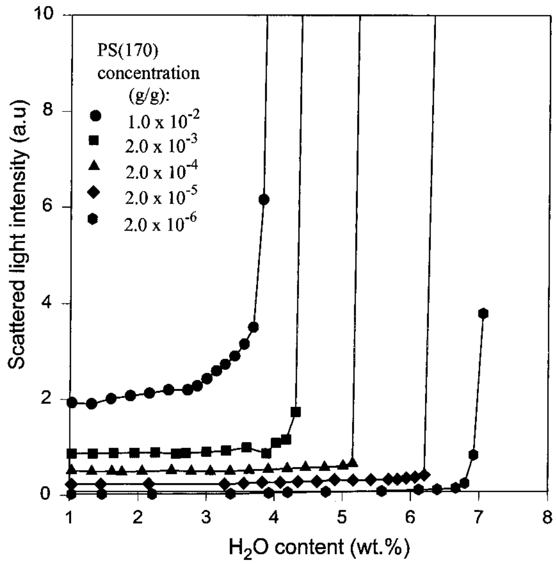

Figure 1. Scattered light intensity as a function of added water content in PS(170)/DMF solutions of different concentrations.

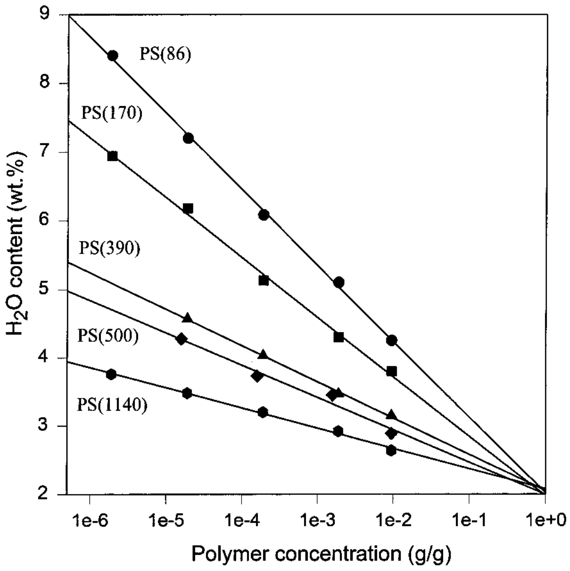

Figure 2. Plot of the critical water content versus polymer concentration for solutions of homopolystyrene of different molecular weights.

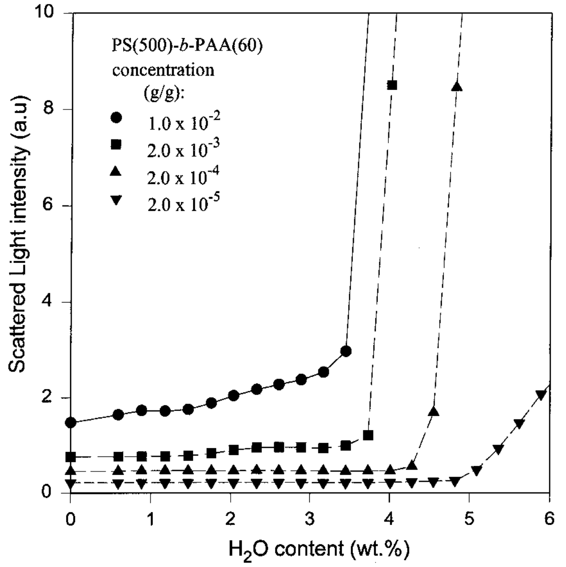

Figure 3. Scattered light intensity as a function of added water content in PS(500)-*b*-PAA(60)/DMF solutions of different concentrations.

increases rapidly. The drastic increase in the scattered light intensity indicates that a phase separation has occurred. For the more concentrated solutions, the solutions turns cloudy at that point; a PS-rich phase is observed on the bottom of the light scattering vials after the solutions are allowed to stand for a few hours. Figure 1 also shows that the onset of phase separation shifts to higher water contents as the initial polymer concentration in DMF decreases, indicating that the polymer chains in more dilute solution remain soluble to a higher water content; as might be expected, the solubility of homo-PS decreases as the water content increases.

For each solution, a critical water content (cwc) can be defined as the water content at which phase separation starts; it is obtained from the intercept of the nearly horizontal and vertical straight line segments of the light scattering curve. A plot of the cwc as a function of polymer concentration for different PS homopolymers is given in Figure 2. A linear relationship is found between the cwc and the logarithm of the polymer concentration, which has been seen in other polymer/solvent/precipitant systems.[16] The cwc decreases as the polymer concentration increases. For a specific polymer concentration, the cwc decreases as the polymer molecular weight increases. It is well known that the solubility of a polymer is related to its chain length. This is the case here also, as can be seen by following horizontally across the plot for any water content. Figure 2 also shows that the relationship between the cwc and the polymer concentration changes with the molecular weight of the polymers. The higher the molecular weight, the larger the slope d[log C]/d[cwc] of the lines. This means that the higher the molecular weight, the stronger the effect of water on solubility. Finally, it is noteworthy that all the straight lines intersect at a polymer concentration of ~1 g/g (which corresponds to the density of the bulk phase) at a water content about 2 wt %. This may indicate that even if the molecular weight and the concentration of polystyrene become very high, the polymer will not phase separate from a DMF/water mixture for a water content less than 2 wt %. Obviously, the solution behavior of polystyrene/DMF/water mixtures is complex but quite interesting. However, since the primary object of present paper is the study of micellization of block copolymers, the topic of solubility of homopolystyrene in this mixed solvent will not be pursued further here.

3.1.2. Addition of Water to PS-*b*-PAA/DMF Solutions. For PS homopolymer solution at any reasonable polymer concentration, phase separation occurs when the added water content reaches a certain level. For the block copolymers, the phenomena show some similarity to the case of homo-PS. As can be seen in Figure 3, when water content is relatively low for all of the solutions, the intensity of scattered light changes only little. At some critical value, the increase of the intensity becomes very steep for all polymer concentrations. The drastic change in the intensity indicates that phase separation has occurred. In contrast to homo-PS solutions, where the polymer chains collapsed and precipitated out, the solutions of diblock copolymers were found to be very stable after microphase separation. This occurs because of the formation of micelles, with the polystyrene blocks of the copolymers aggregating to form the micelle core, and the PAA blocks to form

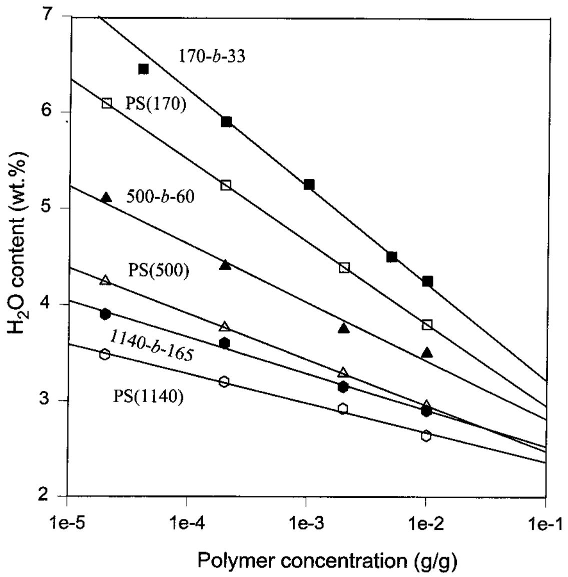

Figure 4. Plot of the critical water content versus polymer concentration for solutions of homopolystyrenes and of PS-*b*-PAA block copolymers of different molecular weights.

the corona. Because both DMF and water are good solvents for acrylic acid, the hydrophilic interactions between the PAA segments and the solvent prevent the particles from precipitating through secondary aggregation. Figure 3 also shows that as the initial copolymer concentration decreases, the microphase separation shifts to a higher water content, which means that the copolymer solubility in DMF/water mixtures decreases as the water content increases.

As in the case of homo-PS solutions, the cwc can be obtained from the light scattering curves in Figure 3 for copolymer solutions of different concentrations. Figure 4 shows a plot of the cwc against the logarithm of the polymer concentration for copolymers of different molecular weight. For convenience, the data for some of the homopolystyrene solutions are also shown in this plot. It is found that here also a linear relationship exists between the cwc and the logarithm of the block copolymer concentrations. One can see that the onset of phase separation of the corresponding diblock copolymer solutions (with the same polystyrene segment length and concentration as that of the homopolymer) always occurs at a higher water content. Because both water and DMF are good solvents for PAA blocks, it is reasonable to believe that the interactions between the solvent and the acrylic acid units prevent the collapse of the copolymer molecules from the solution until a higher water content is reached. The linear relationship has only a slightly different slope (smaller d[log *C*]/d[cwc]) compared to that of the corresponding homo-PS solutions, probably due to the large weight fraction of polystyrene in the block copolymers. Furthermore, for a specific polymer concentration, the cwc decreases with an increase of the PS block length. This implies that the copolymers with longer PS blocks start to form micelles at a lower water content than shorter blocks do. Because the solvent–PS (Flory–Huggins) interaction parameter, χ, increases as the water content increases, from a thermodynamic point of view, the micelles form at χ values which decrease with increasing PS block length and/or polymer concentration.

3.1.3. Addition of Water to Polymer Mixtures in DMF Solutions. In a previous paper,[6] it was reported that PS homopolymer can be solubilized into the micelle cores during micellization of the copolymers, by dissolving the homopolymer in the copolymer/DMF solutions before the addition of water. Therefore, it is of interest to study the phase separation of the solutions composed of two different polymers in DMF as the addition of water progresses. For this purpose, four different polymer mixtures were prepared from PS(500)-*b*-PAA(60) and PS(170), PS(500)-*b*-PAA(60) and PS(1140), PS(1140)-*b*-PAA(165) and PS(180), and PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33), respectively. The weight ratio of the two selected polymers in the mixtures was one to one. We chose the above polymer combinations because of the large differences in their critical water contents.

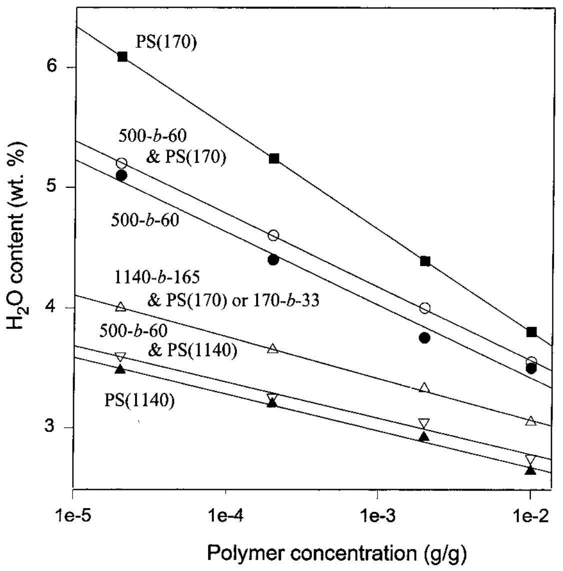

Figure 5. Plot of the critical water content versus total polymer concentration in solutions of polymer mixtures.

It was found that all solutions gave curves of the scattered light intensity versus the added water content which are very similar to those shown previously in Figures 1 and 3. Figure 5 shows a plot of the cwc from the solutions of polymer mixtures as a function of the logarithm of the total polymer concentration. One can see that the cwc decreases as the total polymer concentration increases. Again a linear relationship is found. The cwc of the solution of mixed polymers depends mainly on the component polymer which has the lower critical water content alone. For example, for comparable concentrations, the solution of the mixture of PS(500)-*b*-PAA(60) and PS(170) has a cwc which is only slightly higher than that of the solution of PS(500)-*b*-PAA(60) alone. The solution of PS(500)-*b*-PAA(60) and PS(1140) mixture has a cwc which is only slightly higher than that of PS(1140) alone but much lower than that of PS(500)-*b*-PAA(60) alone. Furthermore, if one considers that the cwc is plotted against the total polymer concentration in Figure 5 and that each polymer component in the mixtures accounts for 50% of the total concentration, the cwc of the solution of the mixed polymers is almost identical to that of the solution of the component polymer having the lower cwc alone.

On the basis of the above results, one can deduce that if one wishes to incorporate homopolystyrene into the copolymer micelle cores, the homo-PS should have a higher cwc than that of the block copolymer. Otherwise, the homo-PS chains will precipitate first from the solution as the water content increases, without becoming incorporated into the PS core of the copolymer micelle. The cwc can be increased by decreasing the polymer concentration and/or molecular weight. This is consistent with the results of previous papers[17] on the solubilization of a homopolymer into micelle cores, which reported that within certain limits, the solubilization of a homopolymer is possible only when the homopolymer has a lower molecular weight than that of the core-forming block of the copolymer.

3.1.4. Dependence of the Degree of Micellization on the Water Content. It is clear from the above that for a copolymer solution of a certain initial concentration, when the water content is below a critical value, the copolymer chains are unassociated. At the critical water content, the copolymers start to associate, and as the addition of water progresses further, more and more copolymer chains associate to form micelles and the concentration of the copolymers in single-chain form decreases. Thus, it is of interest to see how the micelle fraction of the copolymers depends on the change of water content beyond the critical value.

According to the plots in Figure 4, the relationship between the cwc and the initial copolymer concentration, C_0, can be expressed as

$$\mathrm{cwc} = -A \log C_0 + B \tag{1}$$

or

$$C_0 = \exp[2.303(B - \mathrm{cwc})/A] \tag{2}$$

where A and B are constant for a specific copolymer. At the critical water content, the copolymer concentration represents actually the critical micellization concentration (cmc), which depends on the polymer molecular weight and the water content. As the added water content increases further, more and more copolymer chains form micelles. However, the concentration of the unassociated polymer chains, cmc, still obeys the relationship of eq 1. Thus, we have

$$\mathrm{cmc} = \exp[2.303(B - \%\ \mathrm{H_2O})/A] \tag{3}$$

where % H_2O represents the water content in the solution. It is worthy of note that the molecular weight distribution of the block copolymer should also have an effect on the micellization behavior or the critical micellization concentration as shown in an earlier study.[18] However, in the present simplified treatment, we do not consider the polydispersity in the copolymer molecular weight.

The micelle fraction can be defined as a ratio of the associated polymer to the total polymer, $(C_0 - \mathrm{cmc})/C_0$. A combination of eqs 2 and 3 yields the following relationship:

$$\begin{aligned}(C_0 - \mathrm{cmc})/C_0 &= 1 - \exp[2.303(\mathrm{cwc} - \%\ \mathrm{H_2O})/A] \\ &= 1 - \exp(-2.303\Delta\mathrm{H_2O}/A) \end{aligned} \tag{4}$$

where ΔH_2O represents the increment of added water above the cwc. When the value of ΔH_2O is zero (or less), the ratio of $(C_0 - \mathrm{cmc})/C_0$ equals zero, because all the copolymer chains are unassociated in the solution when the water content is below the cwc. Figure 6 shows a plot of the micelle fraction against the increment of the water content for different block copolymers. It is clear that the micelle fraction depends on the copolymer molecular weight and the water content. For copolymers with longer PS chains, the micellization is completed within a narrower range of the water increments. However, the copolymers with shorter PS block length show a broader water increment range needed for a complete micellization. Since the value of the solvent–PS interaction, the χ parameter, is a function of the water content, this means that, even for an individual copolymer solution, the micelles may be formed at a value of the χ parameter which is slightly different from micelle to micelle. However, as will be seen in section 3.3, at this water content range, the structure of the micelles is not frozen. A dynamic equilibrium between the micelles and copolymer unimers exists. Therefore, the structural parameters of the micelles can still change in response to the slightly changed solvent environment. As a result, the slight increase of the value of the χ parameter during micellization may not affect the core size distribution appreciably since it has been found that the formed micelles are generally monodisperse.

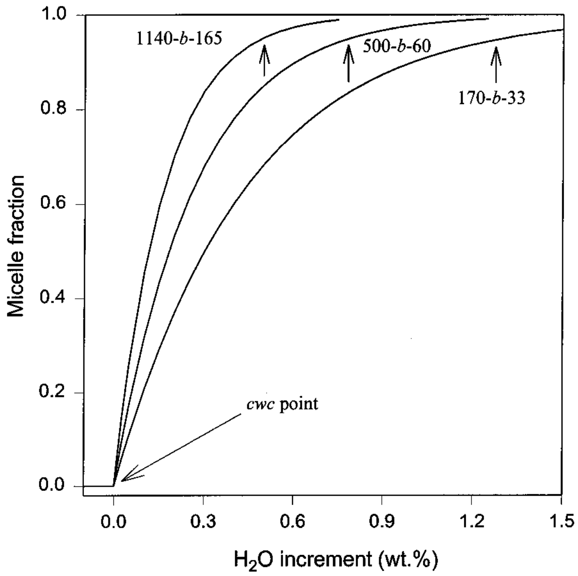

Figure 6. Plot of the micelle fraction as a function of the water increment beyond the critical water content. Arrows indicate 95% micellization.

3.2. Phase Separation of Polymer/DMF/Water Solutions Containing Electrolytes. Recently, it has been found that small amounts of added electrolytes, e.g., HCl, $CaCl_2$, or NaCl, can have a very strong effect on aggregate morphologies.[7,8] Electrolytes in aqueous solution are added to the copolymer/DMF solutions before adding more deionized water to induce the PS block aggregation. As a typical example, for a 1 wt % PS(410)-*b*-PAA(25) solution, without any added HCl, the aggregates are spherical micelles; when the added HCl concentrations are 210, 240, and 270 μM, the aggregates are rodlike micelles, vesicles, and large compound vesicles, respectively. In this section, we mainly discuss the influence of the added electrolytes on the microphase separation behavior of the copolymer solutions. In particular, we emphasize the state of the copolymers upon dissolution in the presence of added electrolytes and some water, but not enough to induce PS block aggregation. In order to connect the present study with the morphogenic effect of added electrolytes on the aggregates,[7,8] the experimental conditions and the concentration range of the added electrolytes are designed specifically to be similar to those under which the aggregates of different morphologies are formed.

3.2.1. Addition of NaOH(aq) to Polymer/DMF Solutions. It was found that the phase separation

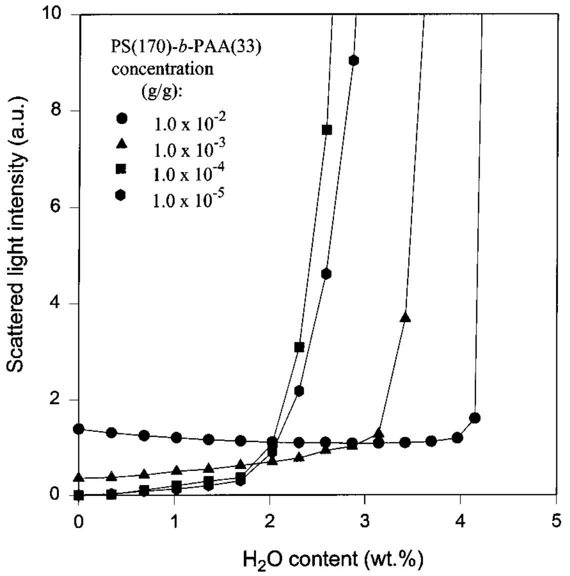

Figure 7. Scattered light intensity from PS(170)-*b*-PAA(33)/DMF solutions of different concentrations as a function of added water content introduced by adding 0.030 M NaOH aqueous solution.

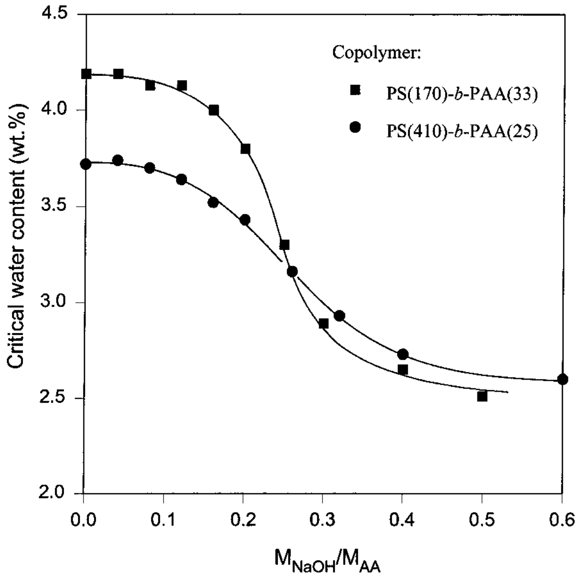

Figure 8. Plot of the critical water content as a function of molar ratio of the added NaOH to the acrylic acid units (AA) of the PS(410)-*b*-PAA(25) copolymers, M_{NaOH}/M_{AA}. The initial copolymer concentration is 1 wt %.

behavior of PS(170) homopolymer solution did not change at all when 0.010 M NaOH(aq) was added instead of pure water. This is not surprising, because polystyrene is nonionic, so the effect of the added electrolyte on polymer chain dimension should be very limited. However, for the block copolymers, the phase separation behavior becomes more complicated. Figure 7 shows a plot of the scattered light intensity against the water content for the addition of 0.030 M NaOH(aq) to PS(170)-*b*-PAA(33) copolymer/DMF solutions of different polymer concentrations. For the 1 wt % copolymer solution, the scattered light intensity increases rapidly when the water content reaches 4.2 wt %, which is similar to the behavior when adding deionized water. However, for more dilute solutions, the scattered light intensity starts to increase rapidly at much lower water contents than those observed when deionized water is added.

Considering the fact that NaOH has almost no effect on the phase separation of the homopolystyrene solutions, the different phase separation behavior of the copolymer solution should be related to the neutralization of the acrylic acid units (to sodium acrylate) by the NaOH. It is known that PS-*b*-PANa diblock copolymers in DMF form reverse micelles, which have a PANa block core and a PS corona.[19] The degree of reverse micellization depends on the degree of neutralization of the PAA blocks.[20] In the present system, as the addition of NaOH(aq) progresses, more and more acrylic acid units become neutralized; in addition, the water content also increases. For NaOH solutions of the same concentration, the degree of neutralization of the PAA blocks increases much faster for the more dilute polymer solutions than that of the more concentrated solutions. Therefore, in the more concentrated copolymer solutions, when the water content reaches some critical point for the PS block precipitation, the neutralization degree of the PAA blocks could be still low. A low degree of neutralization of the PAA blocks does not lead to the formation of reverse micelle-like aggregates.[19] As a result, the microphase separation resulting from the addition of NaOH(aq) is similar to that resulting from the addition of deionized water. However, for a more dilute copolymer solution, before the water content reaches the critical point for the PS block precipitation, the degree of neutralization of the PAA blocks could already be very high. A high degree of neutralization of the PAA blocks leads to the formation of reverse micelles. Naturally, both mechanisms of aggregation lead to an increase in the scattered light intensity.

It is of interest to study the relationship between reverse micellization and the degree of neutralization of the PAA blocks. Because reverse micellization also increases the scattered light intensity, it is difficult to determine the position of cwc for the PS block aggregation from the curves in Figure 7. However, although the formation of reverse micelles increases the scattered light intensity, the appearance of the solutions is almost clear because of the small core sizes of the reverse micelles. By contrast, the onset of the PS block aggregation can be observed by a turbid appearance of the solutions. Because the solubility of the PS blocks is very sensitive to the water content, as a good approximation, the water content at which the solution starts to become turbid represents the critical point for the PS block aggregation. For this experiment, the initial copolymer concentration in DMF was 1 wt %. NaOH(aq) in different amounts was first added to the copolymer solutions in different vials. Then, deionized water was added right until the solutions became cloudy. This study is based on the fact that the cwc is a function of the molecular weight of the PS block (cf. Figure 2). At a constant polymer concentration, the higher the molecular weight, the lower the cwc. If the polymers are unassociated, the cwc is determined by the molecular weight of the polymer single chains. When the copolymer chains become associated to form star type reverse micelles, the cwc is then determined by the molecular weight of the reverse micelles rather than that of the polymer single chains. The only difference is that the copolymer chains are linear before aggregation but become a star type after the formation of reverse micelles. The much higher apparent molecular weight of the reverse micelles results in phase separation at a lower water content.

Figure 8 shows a plot of the cwc (or water content at the cloud point) versus the molar ratio of the added

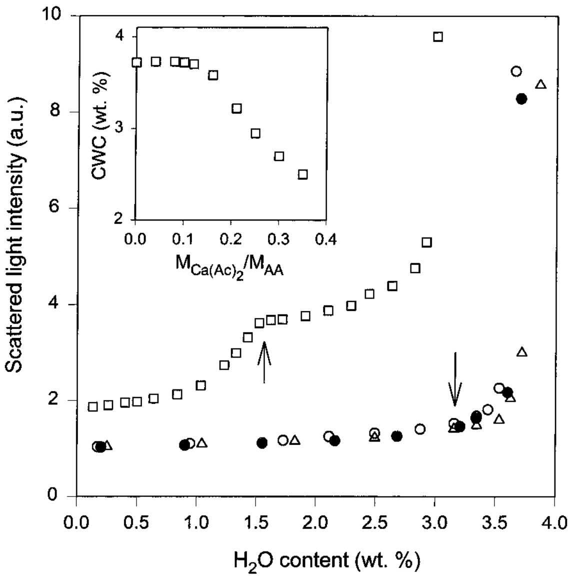

Figure 9. Scattered light intensity as a function of added water content from 1 wt % PS(410)-*b*-PAA(25)/DMF solutions. The arrows indicate the positions after which deionized water was added instead of the aqueous electrolyte solutions. The concentrations of added electrolytes at the points indicated by the arrows were 0.54 mM ($R = 0.1$) for HCl (△), 21 mM ($R = 4.0$) for NaCl (●), 0.54 mM ($R = 0.1$) for $CaCl_2$ (○), and 1.4 mM ($R = 0.25$) for $Ca(Ac)_2$ (□), respectively. The insert is a plot of the critical water content as a function of the molar ratio of added $Ca(Ac)_2$ to the acrylic acid (AA) units from the copolymers, $M_{Ca(Ac)2}/M_{AA}$.

NaOH molecules to the acrylic acid units (or the degree of neutralization of the PAA blocks). As can be seen, for both PS(170)-*b*-PAA(33) and PS(410)-*b*-PAA(25) copolymers, when the neutralization degree is relatively low, e.g., less than 10%, the cwc does not change very much, indicating that the copolymers before the onset of microphase separation were still dispersed as single chains. As the degree of neutralization of the PAA blocks increases, the cwc decreases, implying the formation of reverse micelle-like aggregates and also showing that the extent of the aggregation (or the aggregation number) increases. For different copolymers, the detailed shapes of the curve of cwc versus the neutralization degree are somewhat different, which may be related to the copolymer composition, the block lengths of both the PS and the PAA, etc.

3.2.2. Addition of Other Electrolytes to the Copolymer/DMF Solutions. In this section, we explore the effect of other added electrolytes on the microphase separation behavior of the copolymer solutions. The electrolytes used for this study are HCl, NaCl, $CaCl_2$, and $Ca(Ac)_2$ because they show a strong morphogenic effect on the crew-cut aggregates.[7,8] The aqueous electrolyte solutions were added to the copolymer/DMF solutions. The scattered light intensity was monitored after each addition. After the concentration of added electrolytes in the copolymer solution reached a predetermined level, deionized water was added until microphase separation occurred.

Figure 9 shows a plot of the scattered light intensity versus the water content from a 1 wt % copolymer solutions during the addition of different electrolyte solutions. The copolymer is PS(410)-*b*-PAA(25). The arrows indicate the positions after which only deionized water was added instead of the electrolyte solutions. The concentrations of added electrolytes at the indicated points were 0.54 mM ($R = 0.1$) for HCl, 21 mM ($R = 4.0$) for NaCl, 0.54 mM ($R = 0.1$) for $CaCl_2$, and 1.4 mM ($R = 0.25$) for $Ca(Ac)_2$. R is the molar ratio of added electrolyte equivalents to acrylic acid units from the copolymers. Generally, when HCl, $CaCl_2$, or NaCl was used, the curves of the scattered light intensity vs the water content are similar to that obtained by adding only deionized water. When only deionized water is added, the cwc of this solution is 3.7 wt %. For the addition of HCl, the same cwc is obtained as for the addition of deionized water. For the case of $CaCl_2$ or NaCl addition, the microphase separation occurs at a water content which is only slightly lower than that when HCl or deionized water is used. Therefore, one can conclude that, at least for the present concentration levels of added electrolytes, no reverse micelle-like aggregation occurs prior to the normal micellization resulting from the water addition.

When $Ca(Ac)_2$ solution is added, the microphase separation behavior is more complicated. As shown in Figure 9, the curve of the scattered light intensity as a function of the water content can be divided into different regions. First, when the water content was below 0.8 wt % (corresponding to a $Ca(Ac)_2$ concentration of 0.7 mM or $R = 0.13$), the intensity does not change very much during the addition of the $Ca(Ac)_2$ solution. Second, in the range of the water content from 0.8 to 1.6 wt % (or a concentration of $Ca(Ac)_2$ from 0.7 to 1.4 mM, corresponding to $R = 0.13-0.25$), the intensity increases continuously. The third region extends from a water content of 1.6 to 3 wt %, the region in which deionized water is added instead of the $Ca(Ac)_2$ solution. The scattered light intensity first increases slowly and then more rapidly at a water content around 3 wt %. At that point, the solution turns turbid, indicating that the PS chains are collapsing. The cwc is apparently lower than those for the other electrolytes, which suggests that reverse micellization of the copolymers has taken place to some extent before the PS chains collapse. Therefore, the increase of the scattered light intensity in the second region (ca. 0.8−1.6 wt % water) reflects the formation of reverse micelle-like aggregates.

In order to understand at what concentration of added $Ca(Ac)_2$ the copolymers start to form the reverse micelles, it is of interest to examine how the cwc for PS block aggregation changes as a function of the added $Ca(Ac)_2$ concentration. The insert in Figure 9 shows a plot of the relationship between the cwc and the molar ratio R of added $Ca(Ac)_2$ to the acrylic acid (AA) units in the solution. Below $R = 0.12$ (i.e., below a molar concentration of $Ca(Ac)_2$ of 0.65 mM), the cwc does not change appreciably with R. However, when R exceeds 0.12, the cwc starts to decrease as the concentration of added $Ca(Ac)_2$ increases, indicating that the copolymers start to form reverse micelle-like aggregates when the concentration of the added $Ca(Ac)_2$ is about 0.65 mM ($R = 0.12$).

The formation of reverse micelle-like aggregates is most likely related to the interaction of the added $Ca(Ac)_2$ with acrylic acid units, leading to the formation of calcium acrylate. As the added $Ca(Ac)_2$ concentration increases, the fraction of calcium acrylate in the PAA segments increases. As a result, the PAA blocks become less soluble and finally aggregate to form reverse micelles. It is worth recalling that the addition of $CaCl_2$ did not cause the formation of reverse micelle-like aggregates (Figure 9). One possible reason is that the highest concentration of added $CaCl_2$ in this study was

0.54 mM, i.e., below the critical concentration for the reverse micelle formation.

3.3. Preliminary Studies of Polymer Chain Exchange Kinetics between Micelles. So far, we have explored the phase separation behavior of the polymer/DMF/water solution with and without added electrolytes. For the PS-*b*-PAA copolymer solution, the phase separation corresponds to the formation of the block copolymer micelles with PS cores. It has been suggested in previous papers[4−6] that in the early stages of micellization, the micelle cores are swollen with DMF. When DMF concentration in the cores is high, the micelle structures could be quite labile. As the water concentration increases, the DMF concentration in the micelle cores decreases as does the mobility of the polymer chains. At some point during the water addition, the micelles become frozen on the time scale of the experiment, and retain their structural integrity in the process of further water addition and subsequent dialysis.

An important aspect of copolymer micelle studies involves the dynamics of the chain exchange between micelles. An equilibrated system must be in dynamic equilibrium, with the micelles exchanging chains with one another. For small-molecule amphiphiles, the chain exchange is very fast. However, in copolymer micelles, it is usually slow for reasons such as the high molecular weight and the consequent low mobility of the chains in the core, as well as the low cmc. The dynamic process of chain exchange between star micelles has been studied by several methods, including fluorescence[21,22] and sedimentation velocity measurements.[23,24] The process was found to depend, among other things, on the degree of incompatibility of the solvent and the insoluble block. For example, for micelles of the polystyrene-*b*-poly(methacrylic acid) (PS-*b*-PMAA) copolymers in dioxane/water mixtures,[23] the chain exchange (or micelle hybridization) was investigated by mixing two solutions of micelles made from two different copolymers and studying the changes of the micelle sizes by the method of sedimentation velocity. The rate of hybridization was found to be significant over the time scale of hours when the solvent composition was 80/20 (v/v) for dioxane/water. In this case, the high rate of the chain exchange is mainly due to the fact that the PS core is swollen with dioxane and that the cmc is relatively high. However, when the water content in the solvent mixtures was increased to above 30%, chain exchange between the micelles was negligible over a period of several days, and the micelle structures were considered to be "frozen". The decreased rate of chain exchange or micelle hybridization at higher water contents was ascribed to a decreased cmc and the low degree of swelling of the PS cores.

In the following, we explore the lability of the crew-cut micelle structure as a function of the water content, a process controlled by kinetics of polymer chain exchange. The copolymers PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33) were used in this part of the study. On the basis of the results of light scattering studies, these two polymers form micelles at different water contents. As shown in Figures 4−6, for a 1 wt % copolymer solution, PS(1140)-*b*-PAA(165) copolymers start to form micelles at a water content of ∼3 wt %, and when water content reaches about 3.5 wt %, more than 95% of the copolymer chains are present as micelles. However, PS(170)-*b*-PAA(33) copolymers start to form micelles only at a water content of ∼4.3 wt %, and only when water content reaches about 5.5 wt % are more than 95% of the copolymer chains aggregated. Furthermore, as shown in Figure 5, for the solutions of these two copolymer mixtures, the cwc is mainly determined by the fraction of the PS(1140)-*b*-PAA(165) copolymer. Therefore, as water is added to a solution of these two copolymers, the PS(1140)-*b*-PAA(165) copolymer starts to form micelles at a lower water content, and PS(170)-*b*-PAA(33) starts to form micelles at a higher water content. Some of the latter polymer would be expected to be solubilized into the micelles of the former; this will be discussed below.

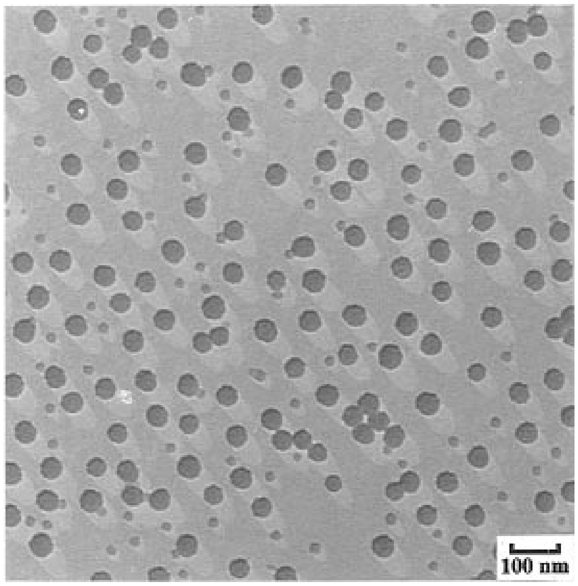

Figure 10. TEM picture of the spherical micelles from mixed copolymers of PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33) resulting from an uninterrupted water addition at a rate of 0.4 wt % per 10 s until 25 wt % water in the solution.

Figure 10 shows a TEM picture of the aggregates made from a mixture of PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33). The total initial copolymer concentration was 2 wt % with an equal weight of each of the two copolymers. The aggregates were prepared by the addition of water at a rate of 0.4 wt % per 10 s until 25 wt % water had been added. The resulting solution was then dialyzed against water to remove the DMF. A bimodal distribution of micelle sizes is seen. The larger particles have an average diameter of 48 nm, while the smaller particles have an average diameter of 24 nm. For each copolymer alone, the average spherical micelle core diameters are 38 and 25 nm for PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33), respectively.[4,5] Therefore, the particles with smaller sizes are most likely formed from PS(170)-*b*-PAA(33), while the micelles with the larger diameters are formed from both PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33). In the early stages, one can expect that as the addition of water progresses, PS(1140)-*b*-PAA(165) copolymers start to form micelles first. Once these micelles are formed, PS(170)-*b*-PAA(33) copolymer chains can partition between the swollen micelles of PS(1140)-*b*-PAA(165) and the solvent, because the previously formed large PS micelle cores provide a better environment for the PS segments of the PS(170)-*b*-PAA(33) chains. Therefore, the formation of the larger particles is a result of the incorporation of PS(170)-*b*-PAA(33) chains into the micelle cores of the PS(1140)-*b*-PAA(165).

The bimodal distribution of the micelle sizes in Figure 10 appears also to be a result of a kinetically-controlled process of polymer chain exchange. As was mentioned

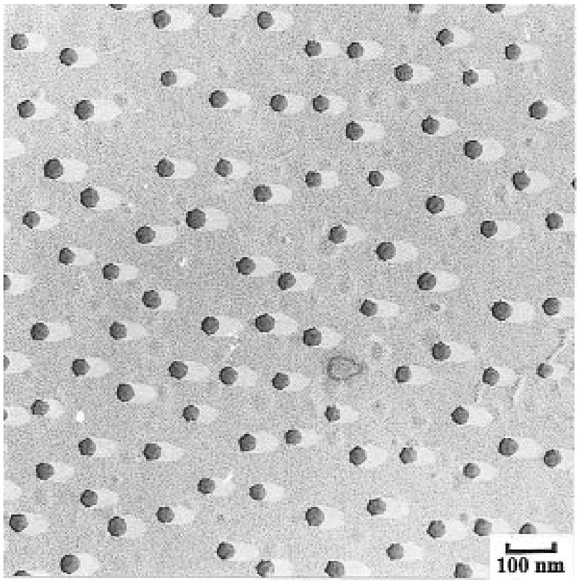

Figure 11. TEM picture of the spherical micelles from the same mixed copolymers as for the micelles in Figure 10, with the water addition interrupted for 1 day at 5 wt %.

above, once the micelles of PS(1140)-*b*-PAA(165) copolymers are formed, PS(170)-*b*-PAA(33) copolymer chains partition between the PS micelle cores of PS(1140)-*b*-PAA(165) and the solvent. When the added water content exceeds some value, single chains of PS(170)-*b*-PAA(33) copolymers can also aggregate to form micelles (with smaller core sizes). However, the copolymer chain exchange among the micelles driven by the mixing entropy should homogenize the micelle sizes. The final state of the system depends on the rate of water addition. If water is added slowly, the rate of the polymer chain exchange remains relatively high for longer periods. As a result, the size distribution of aggregates can become monomodal instead of bimodal. On the other hand, if the water addition is fast, before an equilibrium resulting from polymer chain exchange can be established, the micelle cores are already frozen due to the decrease of the mobility of polymer chains in the cores as the water content increases. Therefore, micelles with two populations of the sizes are obtained.

In order to verify that chain exchange kinetics are operative in the above experiment, aggregates were also prepared in a different way. The same solution was used as for the aggregates in Figure 10, but after 5 wt % water had been added, the addition of water was stopped for 1 day and then continued until 25 wt % water was added. A TEM picture of the aggregates is shown in Figure 11. The distribution of the aggregates is monomodal with an average diameter of 41 nm. It is noteworthy that the average diameter of the micelle cores is larger than those made from either PS(1140)-*b*-PAA(165) or PS(170)-*b*-PAA(33) alone; this increase in size is probably caused by an increased polydispersity of the PS segments in the mixture of the two copolymers.[25]

That the rate of copolymer chain exchange depends on the water content provides a way to study the conditions under which the micelles become structurally frozen. The experiment is based on mixing two solutions of micelles of different sizes (which had been prepared separately from different copolymers) at different water contents. If the mobility of polymer chains is significant at a particular water content, chain exchange between different micelles will change the sizes of the micelles over the time scale of the experiment. If, on the other hand, the mobility of the polymer chains is low, the chain exchange process is very slow so that the micelles will retain their structural integrity. For this experiment, two stock copolymer/DMF solutions were prepared, which contained either 2 wt % PS(1140)-*b*-PAA(165) or 2 wt % PS(170)-*b*-PAA(33) copolymers. After the addition of water to the separate solutions reached different predetermined values, aliquots of each of the two solutions were withdrawn and mixed. The mixed solutions at those specific water contents were stirred for 1 day to allow polymer chain exchange and partition over that time scale. Then, the addition of water was continued until the water concentration in the solution was 25 wt %. Finally, the aggregates were isolated into water by dialyzing the resulting solutions against water to remove the DMF. The micelle sizes were analyzed by TEM.

The size distributions of the spherical micelles from separate solutions of PS(1140)-*b*-PAA(165) and PS(170)-*b*-PAA(33) are shown in Figure 12A,B. Each of the samples shows a single size distribution. The average diameters are 37 and 25 nm for the micelles of the two copolymers, respectively. Because of the relatively narrow size distribution, the regions of the micelle sizes are separated reasonably well. The size distributions of the micelles made by mixing the above two different copolymer micelle solutions at different water contents are shown in Figure 12C−G. When the micelle solutions are mixed at 5 wt % water content (Figure 12C), the micelle size distribution is monomodal with an average core diameter of 41 nm. When the water content at mixing was 6 wt % (Figure 12D), the size distribution of micelles is similar to that of micelles made by mixing solutions at 5 wt % water (Figure 12C); some apparently smaller micelles are seen only very rarely. When the two solutions are mixed at higher water contents, i.e., 7 and 9 wt % (Figure 12E,F), more and more smaller micelles can be seen in the micrographs. Bimodal distributions of the micelle core sizes are clear, indicating that the rate of polymer chain exchange among the micelles of different sizes has slowed down significantly. Finally, when the two micelle solutions are mixed at an added water content of 11 wt % (Figure 12G), the micelles have two populations, the size distribution of which is similar to the sum of the size distributions in Figure 12A,B. Although the two micelle solutions are mixed with each other and allowed to interact for 1 day, the micelles retain their structural integrity. Chain exchange over the time scale of 1 day is therefore negligible, and the structures of the micelles are kinetically frozen.

4. Summary

Phase separation behavior of homopolystyrene and polystyrene-*b*-poly(acrylic acid) copolymers in DMF solution as a function of the added water content has been explored by light scattering. Starting as a homogeneous solution in DMF, the polymers phase separate when the added water content reaches some critical point. The critical water content, cwc, at which the phase separation starts depends on both the polymer concentration and the molecular weight. The higher the polymer concentration and molecular weight, the lower the cwc. The relationship between the cwc and the logarithm of the polymer concentration is linear. Compared to homopolystyrene solutions, the corresponding PS-*b*-PAA diblock copolymer solutions (of the same

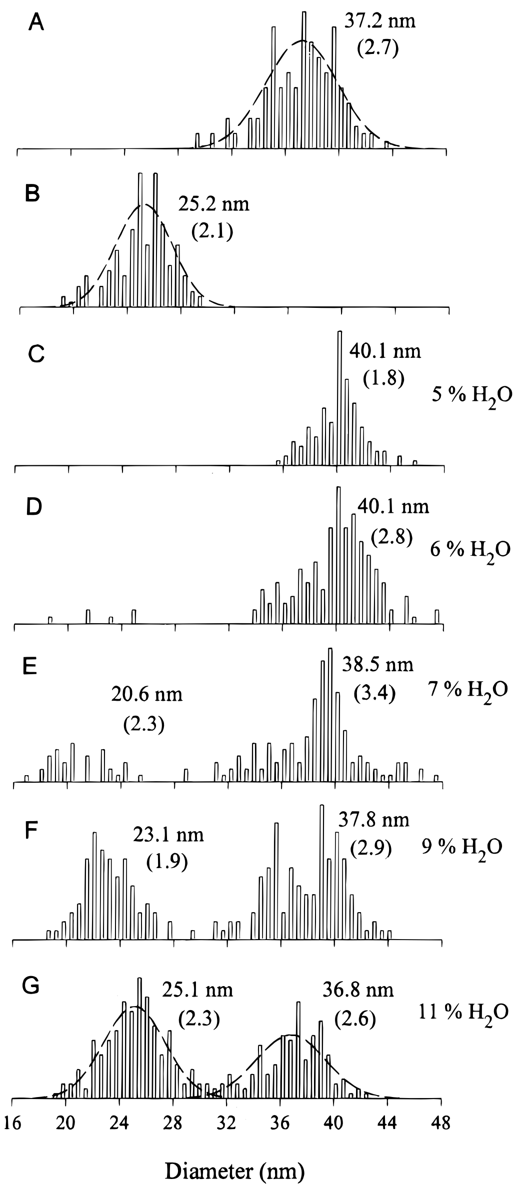

Figure 12. Size distribution of the spherical micelles made from PS(1140)-*b*-PAA(165) (A) and PS(170)-*b*-PAA(33) (B) and made by mixing the above two different copolymer micelle solutions when the added water contents are 5 (C), 6 (D), 7 (E), 9 (F), and 11 wt % (G), respectively. The numbers are the average core diameters with the standard deviations in parentheses for each size distribution. The dashed line represents a Gaussian fit.

polystyrene segment length and concentration as that of the homopolymer) always phase separate at a higher water content. For solutions of mixed polymers, the cwc is largely determined by the component which alone has the lower cwc.

For homopolystyrene/DMF solutions, phase separation involves the precipitation of the polymer chains. For PS-*b*-PAA diblock copolymer solutions, phase separation results in the formation of micelles, with the PS blocks forming the micelle core and the PAA blocks forming the corona. The change of the micelle fraction as the water is added can be estimated from the relationship between the cwc and the initial copolymer concentration. For the three block copolymers used, the ΔH_2O values for 95% micellization are ~0.5% for PS-(1140)-*b*-PAA(165), ~0.8% for PS(500)-*b*-PAA(60), and 1.3% for PS(170)-*b*-PAA(33).

The influence of added electrolytes on the phase separation is related to the interactions between the additives and the PAA segments of the copolymers. When NaOH is added, the PAA segments are neutralized and the copolymers start to form reverse micelle-like aggregates when they are ~10% neutralized. Because the reverse micelle-like aggregates have a much higher apparent molecular weight than the single copolymer chains, they start to separate from the solution at a lower water content than do the single copolymer chains. When $Ca(Ac)_2$ is added, the copolymer chains start to form reverse micelle-like aggregates when the added $Ca(Ac)_2$ concentration is around 0.7 mM, or at a molar ratio R of added $Ca(Ac)_2$ to acrylic acid units of 0.13. The reverse micellization is due to the formation of calcium acrylate, which decreases the solubility of the PAA segments. Within the concentration levels used in this study for the other electrolytes, i.e., 0.54 mM ($R = 0.1$) for HCl or $CaCl_2$, and 21 mM ($R = 4.0$) for NaCl, the copolymers do not form reverse micelle-like aggregates in DMF.

In the early stages of the copolymer micellization, the micelles are highly swollen by DMF, and their structures are labile. As the added water content increases, the micelle cores become gradually less swollen and the mobility of polymer chains in the cores decreases. A preliminary study of the copolymer chain exchange among the micelles has been performed by mixing two micelle solutions of different sizes at different water contents. It is found that when the micelles are formed at a water content of ~4 wt %, the copolymer chain exchange within a 1 day period is still significant when the water content in the solution is increased to 6 wt % but is negligible at a water content of ~11 wt %.

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