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Block Ionomer Complexes with Polystyrene Core-Forming Block in Selective Solvents of Various Polarities. 1. Solution Behavior and Self-Assembly in Aqueous Media

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ABSTRACT: The self-assembly behavior of cationic block copolymers of polystyrene-*block*-poly(*N*-ethyl-4-vinylpyridinium bromide) (PS-*b*-PE4VP) with the constant length of PS block (100 units) and varying lengths of ionic PE4VP block (100−500 units) in aqueous dispersions was studied by fluorescence spectroscopy and sedimentation velocity techniques. The values of cmc for PS-*b*-PE4VP copolymers were within the range 10^{-7}−10^{-6} M and only slightly increased as the ionic chain length increased. At the concentrations above cmc, a coexistence of the micelles and micellar clusters formed by PS-*b*-PE4VP copolymers was observed. The distribution of copolymer chains between the micelles and micellar clusters was found to be independent of copolymer concentration and length of ionic PE4VP block but dependent on the concentration of the elementary salt in the solution. Interaction of PS-*b*-PE4VP micellar aggregates with the oppositely charged surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT), was studied. In contrast to homopolyelectrolyte−surfactant systems that form only stoichiometric insoluble complexes, the formation of insoluble nonstoichiometric and stoichiometric PS-*b*-PE4VP/AOT complexes was observed. The composition of insoluble PS-*b*-PE4VP/AOT complexes strongly depends on the length of ionic PE4VP block. Such a difference in behavior of block copolymer-based complexes has been attributed to the presence of block copolymer micelles upon interaction with surfactant ions compared to the individual polymer chains that interact with the surfactant in the case of ionic homopolymer.

Introduction

The behavior of amphiphilic block copolymers in aqueous solutions has received considerable attention in recent decades. This interest is sustained due to the opening of new areas of application of block copolymers in gene and drug delivery systems, microreactors for chemical synthesis and catalysis, polymer detergents and reagents for stabilization of colloid dispersions, etc.[1−9] A wide range of nonionic,[10−13] anionic,[14−17] cationic,[18,19] and amphoteric[20,21] amphiphilic block copolymers have been synthesized, and their solution behavior and self-assembly have been extensively characterized. The recent examples are block copolymers of polystyrene (or its derivatives) with poly(ethylene oxide),[6,22−27] poly(4-vinylpyridine),[18] poly(acrylic acid),[28−32] and poly(methacrylic acid)[33] blocks that have been studied in aqueous and nonaqueous media.

Lately, a new direction in the study of amphiphilic block copolymers has been launched. This research is focused on the design of supramolecular structures produced via binding of block copolymers with various complementary counterparts, including natural and synthetic polyelectrolytes, surfactants, or other block copolymers.[34−37] Block copolymer micelles with the core from interpolyelectrolyte[34] or polyelectrolyte−surfactant[35] complexes as well as onion-type micelles, consisting of several different types of polymer layers,[36] should be mentioned as the examples of such novel structures. Many of these studies utilize block copolymers containing at least one nonionic hydrophilic block such as poly(ethylene oxide). As a result, supramolecular structures formed by such block copolymers frequently produce stable dispersions in aqueous environment due to the effect of the water-soluble blocks.

Much less is known about the supramolecular complexes of block copolymers, containing hydrophobic nonionic blocks, which are insoluble in water. Our previous publication has reported that the interaction of polystyrene-*block*-poly(sodium acrylate) micelles with *N*-cetylpyridinium bromide ions results in the formation of water-insoluble complexes.[37] The resulting materials, termed “block ionomer complexes”, have a unique microheterogeneous structure combining (i) segregated crystalline domains from surfactant ions immobilized on polyion chains, (ii) sodium carboxylate ion pairs, and (iii) amorphous polystyrene segments. The microstructure and properties of such materials can be varied by changing the polyion and surfactant ratio as well as the lengths of the copolymer blocks. The present work extends the studies on the block ionomer complexes by evaluating the solution behavior of micelles formed by cationic amphiphilic block copolymers in the presence of the oppositely charged anionic surfactant. For this purpose a series of block copolymers of polystyrene-*block*-poly(*N*-ethyl-4-vinylpyridinium bromide) (PS-*b*-PE4VP) with the fixed length of PS block (100 units) and varying lengths of PE4VP block (100−500 units) were utilized. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was used as anionic surfactant reacted with PS-

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b-PE4VP block copolymers to form the block ionomer complexes. The self-assembly behavior of PS-*b*-PE4VP copolymers in aqueous dispersions is investigated by fluorescence spectroscopy and the sedimentation velocity technique. The formation of insoluble nonstoichiometric and stoichiometric block ionomer complexes upon interaction of the micellar aggregates of PS-*b*-PE4VP copolymers and AOT ions is demonstrated. The following paper will report on the solution behavior of such block ionomer complexes in organic solvents.[38]

Experimental Section

Materials. Block copolymers of styrene and 4-vinylpyridine were synthesized by sequential anionic polymerization generally following the previously described procedure.[39] The block lengths of these copolymer samples were 100 for PS and 100, 200, and 490 for poly(4-vinylpyridine), respectively. The polydispersity indexes were 1.12 for all synthesized samples. The 4-vinylpyridine units were exhaustively quaternized by ethyl bromide to obtain cationic PS-*b*-PE4VP block copolymers. The reaction was carried out in 5% copolymer solution in a tetrahydrofuran−methanol (70/30, v/v) mixture for 40 h at 60 °C using a 10-fold excess of ethyl bromide relative to 4-vinylpyridine. The PS-*b*-PE4VP copolymers were precipitated in ethyl ether and dried in a vacuum at 60 °C for 48 h. The degree of quaternization of PE4VP block was determined by IR spectroscopy using characteristic bands of absorption of quaternized (1640 cm^{-1}) and nonquaternized (1600 and 1415 cm^{-1}) repeating units.[39,40] In all samples the degree of quaternization was above 90%. Diblock copolymer samples are denoted as PS(100)-*b*-PE4VP(*x*), where (100) represents the degree of polymerization of PS and (*x*) represents the degree of polymerization of the PE4VP. The homopolymer poly(4-vinylpyridine) with $P_w = 480$ was purchased from Polysciences, Inc., and exhaustively quaternized by ethyl bromide to obtain PE4VP(480). The procedure of quaternization was similar to that used for the block copolymers, except for using pure methanol as a solvent for the synthesis. The degree of quaternization was not less than 90% as determined by IR spectroscopy. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT), pyrene, tetrahydrofuran, ethyl ether, and methanol were purchased from Sigma-Aldrich Co. and used without further purification.

Preparation of Aqueous Dispersions of Block Copolymers. All samples of PS-*b*-PE4VP appeared to be insoluble in water at room temperature, which was due to slow rates of dissolution of these samples. Therefore, aqueous dispersions of these block copolymers were prepared using the dialysis method. Initially, samples of PS-*b*-PE4VP were dissolved in a dimethylformamide−methanol (80/20, v/v) mixture at concentration of polymer from about 25 to 40 g/L. After that, distilled water was added to the mixture dropwise until the content of water reached 67 vol %. Finally, the water−organic mixture obtained was dialyzed against distilled water using membrane tubing. The concentration of PS-*b*-PE4VP after dialysis was determined by two independent methods: (1) UV spectroscopy, using absorption band of PE4VP units at 259 nm, and (2) gravimetrically. The results of both methods were consistent within the experimental error. The final concentrations of block copolymers in aqueous dispersions were approximately 4−7 g/L.

Aqueous dispersions can be also obtained by direct dissolution of PS-*b*-PE4VP in water at elevated temperatures (close to the boiling point of water) under continuous stirring for 3−10 days. However, in the case of PS(100)-*b*-PE4VP(100) sample the dispersions obtained by heating in water for as long as 10 days were turbid indicating that the dissolution was not complete. In contrast, PS(100)-*b*-PE4VP(100) dispersions prepared through dialysis method were practically transparent. Therefore, the dialysis technique appears to be more appropriate for preparation of aqueous dispersions of PS-*b*-PE4VP copolymers, particularly those containing relatively short PE4VP blocks. The results described further referred to PS-*b*-PE4VP dispersions prepared using the dialysis technique.

Methods and Instrumentation. Steady-state fluorescent spectra were recorded using a Shimadzu RF5000U spectrofluorimeter with the bandwidth of 3 nm for excitation and 1.5 nm for emission. For emission spectra λ_{ex} was 339 nm, and for excitation spectra λ_{em} was 374 nm. Pyrene was used as the fluorescent probe. The sample solutions were prepared by adding known amounts of pyrene in acetone to empty vials. After acetone evaporation aqueous solutions of PE4VP or dispersions of PS-*b*-PE4VP of various concentrations were added to the vials. The final pyrene concentration was 5×10^{-7} M, i.e., slightly below the saturation concentration of pyrene in water at 22 °C. These samples were stirred overnight at the room temperature. All measurements were performed at room temperature using air-equilibrated solutions.

UV spectra of block copolymers were recorded using a Shimadzu UV-160 spectrophotometer.

Sedimentation velocity measurements were performed using Beckman model E analytical ultracentrifuge in the scanning mode at $\lambda = 280$ nm and $\omega = 48\,000$ rpm at room temperature. The sedimentation coefficients were calculated at several concentrations of the block copolymer in the solution and then extrapolated to zero concentration.

Results and Discussion

Association of PS-*b*-PE4VP Copolymers in Aqueous Solutions. The association of PS-*b*-PE4VP block copolymers in aqueous solutions was examined by fluorescence technique using pyrene as a probe. This method is based on the sensitivity of the probe to the hydrophobicity and polarity of its microenvironment.[12,14,22,28] In the presence of micelles or similar supramolecular aggregates, pyrene is solubilized within the interior of the hydrophobic part ("core") of such aggregates. As a result, significant changes in the spectroscopic properties are observed upon transfer of the probe from aqueous environment to the nonpolar environment of the micelle core.[41] Such changes are exemplified in Figure 1, which presents typical emission and excitation spectra recorded for pyrene in the aqueous solutions of PS(100)-*b*-PE4VP(200) at various concentrations of the block copolymer. First, the quantum yield of the fluorescence elevated as the concentration of the polymer increased. This effect was exhibited by an increase in the intensity of the fluorescence maximum at $\lambda = 372$ nm (I_1) in the emission spectra (panel A). Second, the vibrational fine structure of the emission spectra underwent changes. This effect was best characterized by the decrease in the ratio of the intensity of the vibrational band one to the vibrational band three (I_1/I_3), which was consistent with the decrease in polarity of the environment of the probe (panel A). Finally, in the excitation spectra one can see the red shift of the (0,0) band from 333 to 338 nm (characterized by change of I_{338}/I_{333} intensity ratio) upon the increase of the block copolymer concentration (panel B). Overall, these changes in the emission and excitation spectra are indicative of the partitioning of pyrene between aqueous and hydrophobic environment. Similar behavior was observed with all PS-*b*-PE4VP samples studied in this work as well as other nonionic[12,22] and anionic[14,28] block copolymers containing a PS hydrophobic block, which were reported previously.

All the key parameters characterizing the fluorescent properties of pyrene discussed above (I_{338}/I_{333} ratio, I_1, and I_1/I_3 ratio) changed sharply in a rather narrow range of PS(100)-*b*-PE4VP(200) concentrations and then leveled off (Figure 2). As the concentration of PS-*b*-PE4VP increased above the cmc, the progressive incorporation of pyrene within the core of the micelles took

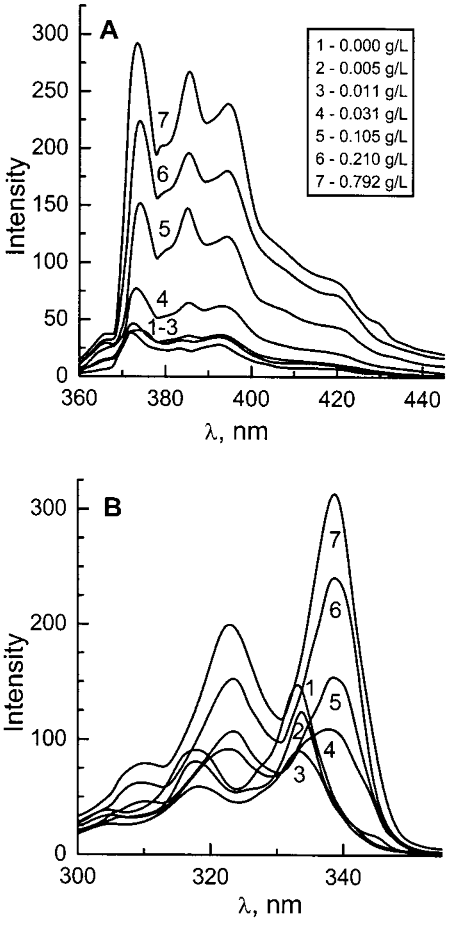

Figure 1. (A) Fluorescence spectra and (B) excitation spectra of pyrene (5×10^{-7} M) in aqueous solutions of PS(100)-*b*-PE4VP(200) at different polymer concentrations. $\lambda_{ex} = 339$ nm; $\lambda_{em} = 372$ nm; $T = 22$ °C.

place, which resulted in the changes of the fluorescent properties. In contrast, in the aqueous solution of the homopolymer PE4VP only a slight decrease in I_1/I_3 ratio and practically no changes in other spectroscopic characteristics of pyrene were observed as the polymer concentration elevated (Figure 2). The I_1/I_3 ratio was used to characterize the polarity of pyrene environment. This value measured for pyrene in a copolymer-free aqueous solution was approximately 1.8. As the concentration of the copolymer increased, the I_1/I_3 value decreased to approximately 1.12, suggesting incorporation of the probe in the hydrophobic PS core (Figure 2a). This value was close to that reported for polystyrene-*block*-poly(sodium acrylate), PS-*b*-PAA (I_1/I_3 = 1.05–1.12),[28] and polystyrene-*block*-poly(ethylene oxide), PS-*b*-PEO ($I_1/I_3 \approx 1.2$),[22] micelles. For the comparison, the I_1/I_3 value for pyrene in hexane is 0.6.[41]

It has to be noted that the determination of a true onset of aggregation is a rather delicate problem. In the present work, two different methods were used to obtain cmc values from the original fluorescence spectra that yielded four numbers, all of which clustered in the Δ log cmc range of 0.05–0.4 for the different samples. It is also worth to point out that cmc determinations were performed on samples equilibrated at room temperature for at least 24 h and compared with the results obtained for samples equilibrated at 37 °C for the same period of time. The experimental values obtained for both sets of polymer solutions were the same within experimental error. At first, the cmc values for all PS-*b*-PE4VP samples were determined from the concentration dependence of the fluorescence intensity I_1 (cmc$_1$) as well as excitation I_{338}/I_{333} ratio (cmc$_2$) by a simple procedure involving crossover points in the low concentration range as indicated in Figure 2b,c.[42] However, the change in the fluorescent signal can be influenced not only by the polymer association but also by the partitioning of the fluorescent probe between the aqueous and the hydrophobic phases.[22,28] The accurate inspection of data in Figure 2b,c reveals some steady increases in both I_1 and I_{338}/I_{333} values below cmc. This effect may be due to binding of pyrene with PS chains of the single block copolymer molecules, called "unimers". As previously reported, PS blocks in the unimers can collapse, forming a unimolecular micelle "core", which can bind hydrophobic compounds.[22,28] This can affect the cmc values determined from I_1 and I_{338}/I_{333} data, resulting in the shift of these values compared to the "true" block copolymer cmc.[22,28] To estimate the true values of cmc corresponding to the onset of formation of the multimolecular micelles in these systems, the approach proposed by Wilhelm et al. was used.[22] According to this

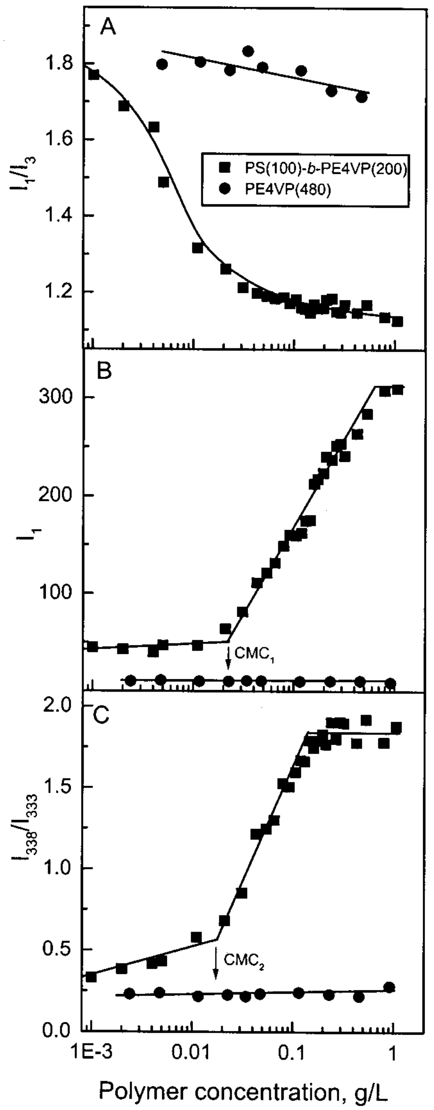

Figure 2. Dependencies of fluorescence intensity I_1 and intensity ratio I_1/I_3 (from pyrene emission spectra) and I_{338}/I_{333} (from pyrene excitation spectra) as a function of PS(100)-*b*-PE4VP(200) or PE4VP(480) concentrations. Vertical arrows indicate cmc values. [Py] = 5.0×10^{-7} M, $\lambda_{ex} = 339$ nm, $\lambda_{em} = 374$ nm, $T = 22$ °C.

method, the ratio of pyrene in the micellar ([Py]$_m$) and water ([Py]$_w$) phases can be expressed as follows:

$$\frac{[\mathrm{Py}]_m}{[\mathrm{Py}]_w} = \frac{F - F_{\min}}{F_{\max} - F} \tag{1}$$

where $F = I_{338}/I_{333}$ or I_1, $F_{\min}$ and $F_{\max}$ are the I_{338}/I_{333} or I_1 values determined at the zero copolymer concentration and at the saturating copolymer concentration, respectively. Pyrene binding to the micelles was described as simple partition equilibrium between the micellar PS phase, which is assumed to be spherical, and the water phase. Using this model, the data from the original fluorescence spectra can be recalculated and linearized utilizing following equations:

$$\frac{[\mathrm{Py}]_m}{[\mathrm{Py}]_w} = \frac{K_{\nu 1}\omega_{ps}c}{1000\rho_{ps}} \quad \text{below cmc} \tag{2}$$

or

$$\frac{[\mathrm{Py}]_m}{[\mathrm{Py}]_w} = \frac{K_{\nu 2}\omega_{ps}(c - \mathrm{cmc})}{1000\rho_{ps}} \quad \text{above cmc} \tag{3}$$

where $K_{\nu 1}$ and $K_{\nu 2}$ are the equilibrium constants for the partitioning of pyrene between aqueous and polystyrene phases below and above cmc, c is the total copolymer concentration in g/L, ω_{ps} is the weight fraction of PS in the copolymer, and ρ_{ps} is the density of the PS core in the micelle (which was assumed to have the same value as that of the bulk PS, 1.04 g/mL).[28]

Figure 3 presents the plots of the [Py]$_m$/[Py]$_w$ ratio determined from fluorescence excitation and emission spectra using eq 1 vs the copolymer concentration. These plots can be fitted by two straight lines, which intersect at cmc. If below cmc there were no binding of pyrene to the block copolymer unimers, the [Py]$_m$/[Py]$_w$ value should equal zero. However, the low but finite values of [Py]$_m$/[Py]$_w$ at this range of polymer concentrations suggest that there is a small contribution to the pyrene signal due to pyrene association with PS-*b*-PE4VP unimers or to premicellar aggregates. In this case equilibrium constants for the partitioning of pyrene between aqueous and polystyrene phases below and above cmc can be calculated by using eqs 2 and 3.

The cmc values determined using this approach from emission and excitation data are referred to as cmc$_3$ and cmc$_4$, respectively. The cmc$_3$ and cmc$_4$ data obtained for various samples of PS-*b*-PE4VP are summarized in Table 1. As is seen in Table 1, cmc values for PS-*b*-PE4VP copolymers determined by various methods were very small and had an order of $10^{-7}-10^{-6}$ M. The analysis of cmc$_1$ and cmc$_2$ values presented in Table 1 suggests that these two methods are in good agreement with each other. Furthermore, with few exceptions the cmc$_3$ and cmc$_4$ data were in a reasonable agreement with the cmc$_1$ and cmc$_2$ data. (In the case of PS(100)-*b*-PE4VP(490) cmc$_3$ and cmc$_4$ were 3−4 times higher than cmc$_2$. Furthermore, the cmc$_3$ value for PS(100)-*b*-PE4VP(100) was approximately twice higher than cmc values obtained for this polymer by three other methods.)

The analysis of the data on cmc indicates that the increase in the length of the ionic PE4VP block from 200 to 490 units is accompanied by severalfold increase in the cmc value. A similar trend in the dependency of cmc on the length of ionic block was observed earlier for other amphiphilic block copolymers.[14,29] Such a trend may be explained by two factors. First, as the length of the ionic PE4VP block is increased, the shielding of the hydrophobic PS block in the unimer may become more effective. Second, the longer PE4VP block is, the stronger is the electrostatic repulsion of the PE4VP chains in the micelle corona. Both factors provide for negative contributions to micellization and increasing of cmc by, on one hand, stabilizing unimers in solutions and, on the other hand, destabilizing multimolecular micelles. It is interesting to compare the cmc values obtained for PS-*b*-PE4VP copolymers in this work with similar data for other PS-containing block copolymers determined by the same method. The cmc values for various block copolymers are presented in Table 2. On the basis of these data, the cmc values of PS-containing block copolymers can be ranked in the following order: PS-*b*-PEO < PS-*b*-PAA < PS-*b*-PE4VP ~ PS-*b*-poly(sulfonated isoprene), PS-*b*-SPI. This ranking probably reflects the decrease in the stability of the micelles due to additional contribution of electrostatic repulsion within the micellar corona upon the change of the solubilizing block from nonionic (PEO) to ionic (PAA, PE4VP, SPI). An increase in charge density of the ionic block upon the change from the weak polyelectrolyte (PAA) to strong polyelectrolytes (PE4VP, SPI) further reinforces the increase of cmc values of corresponding block copolymers due to the electrostatic repulsion.

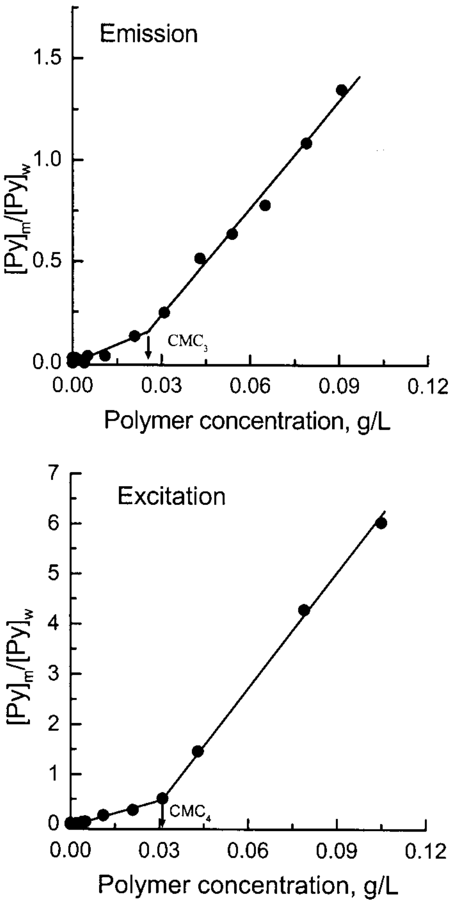

Figure 3. Plots of [Py]$_m$/[Py]$_w$ vs concentration of PS(100)-*b*-PE4VP(200) in aqueous solution determined from emission and excitation spectra of pyrene. Vertical arrows indicate cmc values. [Py] = 5.0×10^{-7} M, λ_{ex} = 339 nm, λ_{em} = 374 nm, T = 22 °C.

Table 1 also presents the partitioning equilibrium constants $K_{\nu 1}$ and $K_{\nu 2}$. These constants correspond to

Table 1. Micellar Characteristics of PS-*b*-PE4VP Copolymers in Aqueous Solutions

	copolymer		
solution properties	PS(100)-*b*-PE4VP(100)	PS(100)-*b*-PE4VP(200)	PS(100)-*b*-PE4VP(490)
cmc$_1$, mol/L	4.0×10^{-7}	5.1×10^{-7}	1.7×10^{-6}
cmc$_2$, mol/L	3.0×10^{-7}	3.0×10^{-7}	8.7×10^{-7}
cmc$_3$, mol/L	8.0×10^{-7}	5.3×10^{-7}	3.5×10^{-6}
cmc$_4$, mol/L	4.6×10^{-7}	5.7×10^{-7}	2.2×10^{-6}
$K_{\nu 1}$[a]	7.5×10^{4}	3.8×10^{4}	6.4×10^{4}
$K_{\nu 2}$[a]	2.7×10^{5}	9.3×10^{4}	2.4×10^{5}
S, Sv (micelles)[b]	5.0	7.5	4.9
w, mol % (micelles)[c]	32	29	26
S, Sv (micellar clusters)[b]	10.4	19.0	8.2
w, mol % (micellar clusters)[c]	68	71	74

[a] Presented values of partitioning constants were calculated from the data of emission spectra. [b] Sedimentation coefficients were determined in 0.2 M NaCl solutions. The sedimentation coefficient for PE4VP(480) under the same conditions is 1.8 Sv. [c] Values of molar fractions of chains (*w*) incorporated in various types of aggregates determined in 0.2 M NaCl were independent of polymer concentrations above the cmc within the experimental error.

Table 2. Apparent cmc Values of Various Amphiphilic Block Copolymers in Aqueous Solutions

block copolymer	cmc, M	ref
PS(100)-*b*-PE4VP(490)[a]	2.2×10^{-6}	present study
PS(86)-*b*-PAA(390)[b]	1.5×10^{-7}	28
PS(110)-*b*-PAA(380)[b]	8.0×10^{-8}	28
PS(58)-*b*-SPI(206)	1.5×10^{-6}	14
PS(135)-*b*-SPI(824)	1.1×10^{-6}	14
PS(108)-*b*-PEO(400)	3.5×10^{-8}	22

[a] cmc$_4$. [b] cmc values determined at pH 9 when PAA segment is almost neutralized.

the pyrene binding with the PS chain of the unimers or partitioning of pyrene in the PS core of the multimolecular micelles. The comparison of these data for various samples of PS-*b*-PE4VP suggests that the length of ionic block had no significant effect on the partitioning of pyrene in PS-*b*-PE4VP micelles. Moreover, the $K_{\nu 2}$ values for PS-*b*-PE4VP micelles are in the same range as those values reported for other block copolymer micelles with the PS core: PS-*b*-PAA ($K_\nu = (1.7-2.2) \times 10^5$),[28] PS-*b*-poly(methacrylic acid), PS-*b*-PMA ($K_\nu = 2.2 \times 10^5$),[33a] PS-*b*-PEO ($K_\nu = 3 \times 10^5$),[22] and PS-*b*-SPI ($K_\nu = (1.6-3.1) \times 10^5$).[14] Thus, the partitioning of pyrene in the micelles of PS-containing block copolymers is mainly determined by hydrophobic PS and is not affected by the chemical nature of the hydrophilic block. Similarly, in the case of unimers the length of the ionic PE4VP block had only weak influence on the $K_{\nu 1}$ values (Table 1). Remarkably, the $K_{\nu 1}$ values are only 3−4 times lower than the corresponding $K_{\nu 2}$ values; in other words, the binding of the probe with the copolymer unimers was several times less effective than binding of this probe with the micelles. Such a tendency was exhibited for all PS-*b*-PE4VP samples studied in this work. To explain such behavior, we hypothesize that the PS blocks might undergo in the aqueous environment the transition from the coil to a more condensed conformation, which reassemble into the core of the micelle. In this case, even a single PS-*b*-PE4VP chain can be considered as a monomolecular micelle able to bind the pyrene molecules. A gradual decrease of I_1/I_3 value in the concentration region below cmc (Figure 2a) provides evidence of pyrene partitioning in such monomolecular PS-*b*-PE4VP micelles. One may expect that the ability of pyrene to bind to block copolymer unimers should depend on the length of PS block. Indeed, previous reports indicated that pyrene does not bind to the individual polymer chains in the case of copolymers with PS block shorter than 40 units.[28] Conversely, the length of PS block was relatively long (100 units) in the studied PS-*b*-PE4VP copolymers. Furthermore, another factor such as polydispersity of the polymer samples is worth consideration upon interpretation of these data. Although the length differences of individual chains will be mutually compensated in the micelles and the polydispersity of the studied copolymer samples was very low, it is possible that some loose premicellar aggregates of copolymer chains with longer PS blocks (or shorter PE4VP blocks) might exist below experimentally determined cmc. Partitioning of pyrene in such loose aggregates might also result in the appearance of finite slope of $[\mathrm{Py}]_\mathrm{m}/[\mathrm{Py}]_\mathrm{w}$ ratio plots (see Figure 3) at polymer concentrations below the cmc.

Characterization of PS-*b*-PE4VP Micellar Aggregates by Sedimentation. The micellar aggregates formed by PS-*b*-PE4VP copolymers at the concentrations above cmc were studied utilizing the sedimentation velocity technique. This method enables to obtain direct information about the hydrodynamic characteristics of the polymer species present in the solution. The micelles formed by PS-*b*-PE4VP block copolymers can be ascribed as systems with a hydrophobic PS core and a corona formed by strongly charged PE4VP chains. In the absence of elementary salt or at low salt concentration polyelectrolyte chains expand due to electrostatic repulsion of the charges along the polymer backbone. This phenomenon is known as the polyelectrolyte effect. Electrostatic interactions are known to have a major contribution to the micelle formation in block polyelectrolyte solutions, particularly when salt concentrations are very low.[29,30] As the salt concentration increases, the low molecular mass counterions mask the polyelectrolyte charges and the electrostatic repulsion in the corona decreases, resulting in the increase of the aggregation number of the micelle. As the salt concentration reaches approximately 0.1−0.2 M, the contribution of the electrostatic repulsion becomes negligible and, therefore, aggregation number does not change significantly upon further addition of salt.[30]

To suppress the polyelectrolyte effect, the hydrodynamic properties of PS-*b*-PE4VP micelles were initially studied utilizing 0.2 M NaCl solutions. Characteristic sedimentation profiles of PE4VP(480) homopolymer and PS-*b*-PE4VP copolymers in 0.2 M NaCl solution are shown in Figure 4A−D. For all block copolymers studied these profiles revealed two distinct steps. These data suggest that two types of polymer species (**I** and **II**) characterized by different velocity of sedimentation were present in the PS-*b*-PE4VP copolymer solutions. The sedimentation coefficients for these two types of species

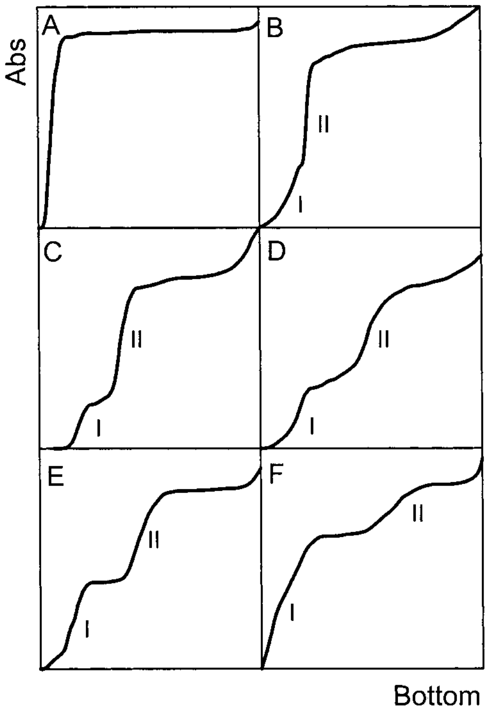

Figure 4. Sedimentation profiles of (A) PE4VP(480) in 0.2 M NaCl solution and block copolymers micellar solutions: (B) PS(100)-*b*-PE4VP(490) in 0.2 M NaCl, (C) PS(100)-*b*-PE4VP(100) in 0.2 M NaCl, (D) PS(100)-*b*-PE4VP(200) in 0.2 M NaCl, (E) PS(100)-*b*-PE4VP(200) in 0.05 M NaCl, and (F) PS(100)-*b*-PE4VP(200) in 0.01 M NaCl. $\lambda = 280$ nm, $\omega = 48\ 000$ rpm, $t = 26-38$ min; $T = 22$ °C. Sedimentation steps I and II correspond to micelles and micellar clusters, respectively (see text).

appeared to be significantly higher than those expected for individual macromolecules. Since the block copolymer samples used in this work exhibited a rather narrow molecular weight distributions and since the concentrations of the block copolymers were above the cmc, these species can be ascribed as multimolecular aggregates. The "light" fraction (**I**) with lower sedimentation velocity was assigned to PS-*b*-PE4VP micelles, while the "heavy" fraction (**II**) with higher sedimentation velocity was assigned to the micellar clusters. The sedimentation coefficients and molar fractions of PS-*b*-PE4VP chains incorporated in both types of aggregates are summarized in Table 1. These results indicate that in 0.2 M NaCl the relative portions of macromolecules incorporated into the micelles and micellar clusters were practically the same for all block copolymers (approximately 30% of micelles vs 70% of micellar clusters), i.e., independent of the length of PE4VP block. It is important to note that the dilution of the block copolymer solutions up to 20 times did not change these portions either. However, upon variation of the ionic strength the distribution of the copolymer chains between the micelles and micellar clusters changed significantly. Sedimentation profiles of PS(100)-*b*-PE4VP(200) copolymer recorded at various salt concentrations in the solution are shown in Figure 4D–F. The increase of length of ionic PE4VP block has practically no effect on the micellization of PS-*b*-PE4VP copolymers. The molar fractions of both micelles and micellar clusters components were calculated from the sedimentograms, and these data are presented in Figure 5. As is seen from this figure, an increase of NaCl concentration from 0.01 to 0.2 M resulted in the progressive decrease of the portion of the micelles and increase of the portion of the micellar clusters. At the same time, the values of the sedimentation coefficients of both components remained practically unchanged within the experimental error (data not shown). These results suggest that the increase of the salt concentration did not affect the composition of the micelles and micellar clusters and resulted only in the change of a relative number of particles of each type. Specifically, the relative portion of the micellar clusters increases as the salt content increases.

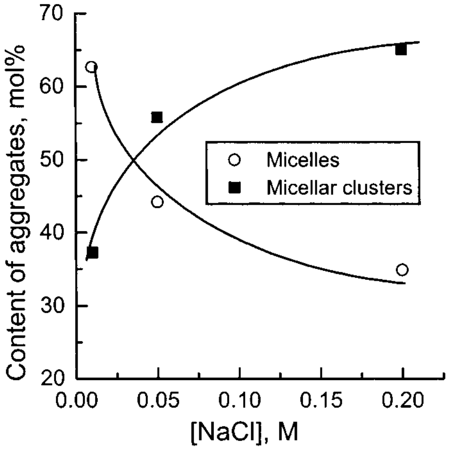

Figure 5. Distribution of PS(100)-*b*-PE4VP(200) macromolecules between micelles and micellar clusters upon NaCl concentration in solution. Copolymer concentration is 0.12 g/dL, $T = 22$ °C.

The nature of micellar clusters observed in this study is not clear. One possibility is that the micellar clusters represent loose aggregates formed via association of individual micelles. For instance, formation of such loose PS-*b*-PEO micellar clusters has been described, which was attributed to hydrogen-bonding and hydrophobic interactions between PEO blocks of the block copolymers.[23,26] In this case the association of the micelles did not appear to be accompanied by any structural transitions affecting the micelle core. However, an alternative possibility upon association of the micelles would be the fusion and reorganization of micellar cores as well as possible change in the micelle morphology. Such association can be affected by both thermodynamic and kinetic factors, the most important of which are the copolymer concentration, effective charge of the corona-forming blocks (for block copolymers with polyelectrolyte chains), the solvent composition, and the route of solution preparation.[43]

Unfortunately, this study cannot directly discriminate between the two alternative mechanisms of the cluster formation. However, some preliminary considerations can be reported. Specifically, it is known that if the core-forming insoluble block is characterized by high glass transition temperature, the micelle core can be "frozen"; i.e., there will be no or little exchange of individual chains between the micelles. This situation is likely for the PS-based block copolymers studied in this work. Therefore, we believe that the fusion of the micelle cores in the micellar clusters is unlikely. It is more likely that the micelles form clusters due to the relatively weak van der Waals attractive interactions between the polymer chains in the micelle corona and core. Since the corona-forming PE4VP block is a strong polyelectrolyte with a high charge density, it condenses with the low molecular mass counterions. The counterion condensa-

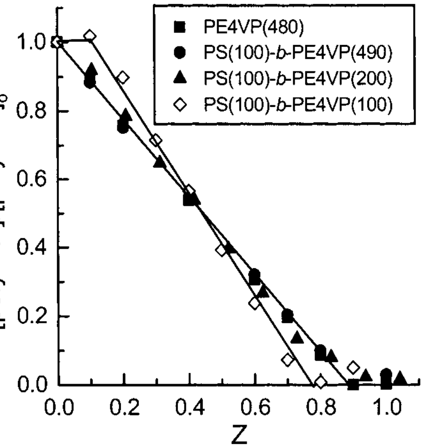

Figure 6. Relative portion of polymer ([polymer]/[polymer]$_0$) remaining in supernatant after titration of the PE4VP or PS-*b*-PE4VP polymers by AOT as a function of the composition of the mixture *Z*. Initial concentrations were 0.01 base-mol/L for PE4VP(480) and PS(100)-*b*-PE4VP(490) and 0.007 base-mol/L for PS(100)-*b*-PE4VP(200) and PS(100)-*b*-PE4VP(100) copolymers; [NaCl] = 0.2 M; T = 22 °C; [polymer] is the equilibrium polymer concentration in the supernatant; [polymer]$_0$ is the initial polymer concentration in the solution.

tion decreases the electrostatic energy and repulsive contributions, thus favoring the micellar cluster formation. Furthermore, the condensation of counterions elevates as the elementary salt concentration increases. This can explain the apparent increase of the relative portion of the micellar clusters upon increase of the NaCl concentration from 0.05 to 0.2 M. Taking into account that dilution does not affect the relative ratio of the micelles and micellar clusters, one can assume that the cluster formation is kinetically controlled; i.e., there is no equilibrium between these structures. A more detailed understanding of the structure of micelles and micellar clusters as well as kinetic vs thermodynamic aspects of their behavior requires a separate comprehensive study, which is beyond the scope of the present publication. However, the existence of two types of the block copolymer aggregates is an important consideration in the reactions of these block copolymers with oppositely charged surfactants ions leading to the formation of block ionomer complexes.

Interaction of PS-*b*-PE4VP Copolymers with AOT. It is well-known that mixing of the solutions of polyelectrolytes with the surfactants of opposite charge results in the formation of polymer–surfactant complexes.[44,45] Mixing of AOT and PE4VP-containing polymer solutions was accompanied by an increase in the turbidity of the system followed by the phase separation. To analyze the distribution of the polymer molecules between the phases, the precipitate was removed by centrifugation, and the concentration of the polymer in the supernatant was determined by the UV spectroscopy technique using the characteristic absorption band of PE4VP repeating units at 259 nm. Figure 6 shows the dependencies of the relative portion of polymer remaining in supernatant after addition of the surfactant as a function of the composition of the mixture, Z. Z is expressed as the ratio of the concentration of AOT to the total base-molar concentration of ionic groups of the corresponding polycation, Z = [AOT]/[PE4VP]$_0$. The data are presented for all the block copolymers and PE4VP homopolymer.

As is seen in the figure, the PS(100)-*b*-PE4VP(100) containing systems exhibited different behavior than the systems containing two other block copolymers or the homopolymer. The behavior of the PS(100)-*b*-PE4VP-(100)/AOT mixtures will be discussed later in this section. In the case of the other studied systems, the polymer concentrations in the supernatants decreased linearly as the amount of surfactant added increased. This behavior suggests that the insoluble complexes PS-*b*-PE4VP/AOT or PE4VP/AOT were formed. Furthermore, the linear character of the dependencies presented in Figure 6 unambiguously suggests that the composition of the complexes formed, φ (defined as the ratio of AOT ions to repeating units of the polycation in the complex), remained constant for the entire range of the compositions of the mixture. These compositions of the complexes were determined from the results of the phase analysis as the points of intersection of the linear dependencies with the abscissa in Figure 6 (since φ = Z when the titration is complete, i.e., [polymer]/[polymer]$_0$ = 0). Alternatively, the compositions were determined directly from the data of the elemental analysis as a ratio of S to N contents in the precipitate. Both φ values obtained are presented in Table 3. Generally, these values are in good agreement with each other, with the exception of PE4VP for which approximately 20% difference between the phase analysis and elemental analysis was observed. Furthermore, both sets of composition data revealed the same trend. Specifically, in the cases of PS(100)-*b*-PE4VP(490) and PS(100)-*b*-PE4VP(200) and PE4VP homopolymer the compositions of the complexes precipitating from solution are close to stoichiometric; i.e., complexes contain almost equivalent amounts of surfactant ions and PE4VP units.

In contrast, the analysis of the data for PS(100)-*b*-PE4VP(100)/AOT mixtures suggests that the precipitate contained the nonstoichiometric complex with the composition approximately equal to 0.8. This is a striking difference compared to behavior of regular homopolymer–surfactant complexes, which are always stoichiometric, as they precipitate. In the case of relatively long polyions (e.g., several hundreds of repeating units), the precipitate can coexist in equilibrium with the soluble nonstoichiometric complex of a characteristic composition φ_{ch}, usually not exceeding 0.25–0.3. When a polyion is short (e.g., 100 repeating units or less), the precipitate of the stoichiometric complex coexists in equilibrium with the free polyion in solution.[46–48] Such a critical dependence of the pattern of the complex formation on the length of the polyion chain observed in the case of homopolymers is explained by the cooperative character of the surfactant association with the oppositely charged polyions. In these systems the charged headgroups of the surfactant form ion pairs with polyion units, while the surfactant tails segregate into hydrophobic

Table 3. Compositions of Insoluble Complexes Formed in PS-*b*-PE4VP/AOT and PE4VP/AOT Mixtures

	polymer			
method of determination	PE4VP	PS(100)-*b*-PE4VP(100)	PS(100)-*b*-PE4VP(200)	PS(100)-*b*-PE4VP(490)
phase analysis	0.9	0.8	0.9	0.9
elemental analysis	1.1	0.8	0.9	1.0

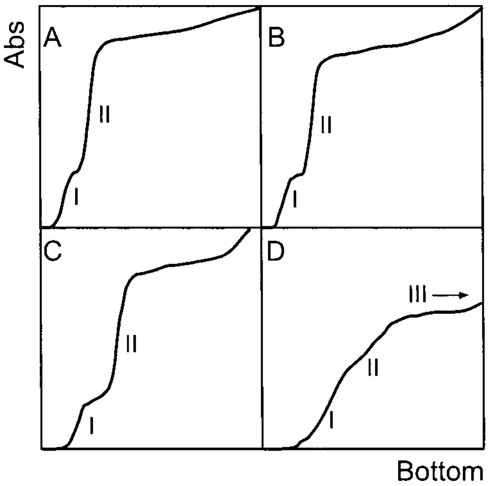

Figure 7. Sedimentation profiles of PS(100)-*b*-PE4VP(100) in mixtures with AOT at various Z: (A) $Z = 0.025$, (B) $Z = 0.050$, (C) $Z = 0.075$, and (D) $Z = 0.100$. Concentration of PS(100)-*b*-PE4VP(100) was 0.007 base-mol/L, $\lambda = 280$ nm, $\omega = 48\,000$ rpm, $t = 24$ min, [NaCl] = 0.2 M, $T = 22$ °C.

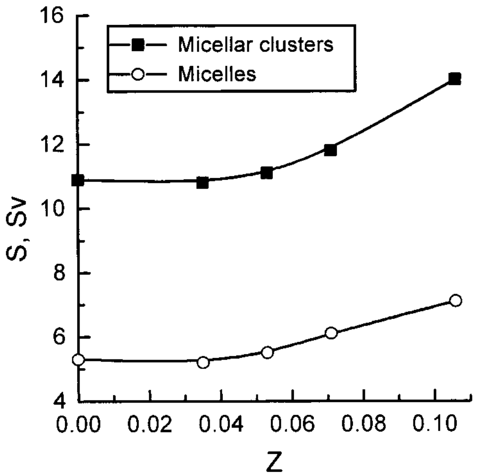

Figure 8. Dependencies of sedimentation coefficients of PS(100)-*b*-PE4VP(100) block copolymer in aqueous solution in the presence of AOT upon the composition of mixture Z. Concentration of PS(100)-*b*-PE4VP(100) was 0.007 base-mol/L, [NaCl] = 0.2 M, $T = 22$ °C.

domains.[44-46] The driving force of such binding is the release of counterions, originally associated with the surfactants and polyions, into the external media, which is accompanied by a substantial entropy gain. It was shown that there is some critical amount of surfactant molecules that needs to associate to allow for the cooperative interaction with the polyion chain.[47,48] This amount can be considered as an aggregation number of a minimal surfactant domain formed in a polymer–surfactant complex. This number depends on the structure of the surfactant domain and has a minimal number of approximately 100 in the case of a spherical micelle. Thus, if the polymerization degree of the polyion is significantly higher than the critical aggregation number, the complex of the polyion with surfactant domain can still be soluble due to the presence of the lyophilizing segments of the polyion chain that are not neutralized by surfactant. If the polyion is too short, formation of the soluble complex becomes impossible, and the complex always precipitates. The increase in the amount of the surfactant in the range of $\varphi_{\mathrm{ch}} < Z < 1$ results in a decrease of the soluble complex portion and an increase of the stoichiometric complex portion. At $Z = 1$ all polyion chains become entrapped in the stoichiometric complex, which remains the only product of the reaction.

Obviously, such a behavior is not the case for the PS(100)-*b*-PE4VP(100)/AOT system. No phase separation was detected in this system in the range of the compositions of the mixture $0 < Z \leq 0.1$. At $0.1 < Z \leq 0.75$ a linear decrease of the block copolymer concentration in the solution was observed (Figure 6). Finally, at $Z \geq 0.75$ the precipitation of the block ionomer was complete, and no copolymer was detected in the supernatants. In view of such unusual behavior the mixtures of PS(100)-*b*-PE4VP(100) and AOT were examined in greater detail by the sedimentation velocity technique at $0 < Z \leq 0.1$. The sedimentation profiles obtained in this study are presented in Figure 7. These profiles exhibited two distinct steps corresponding to two different types of species designated in this study as the "light" and "heavy" fractions. The distribution of the block copolymer molecules between these species was ca. 30 mol % in the light fraction and ca. 70 mol % in the heavy fraction. Such a distribution pattern was similar to the distribution of the block copolymer between the micelles and micellar clusters in the absence of AOT (Figure 4C). Therefore, it is reasonable to describe these fractions as the products of the reaction of AOT with the micelles (light fraction) and micellar clusters (heavy fraction). The dependencies of the sedimentation coefficients for both types of species as a function of the composition of the mixture in the range $0 < Z < 0.1$ are presented in Figure 8. These dependencies suggest that an increase of AOT content was accompanied by a gradual increase of the sedimentation coefficients for each type of species. This behavior clearly suggests that nonstoichiometric complexes are formed between PS(100)-*b*-PE4VP(100) aggregates and AOT molecules, which form stable aqueous dispersions. Importantly, in this range of the compositions of the mixture neither new sedimentation steps were apparent on the sedimentograms nor the relative portions of the light and heavy fractions changed. This result is consistent with an assumption that AOT ions distribute evenly between PS(100)-*b*-PE4VP(100) micelles and micellar clusters at $0 < Z < 0.1$. However, at $Z = 0.1$ the sedimentation profiles changed dramatically. In this case sedimentograms revealed three steps (third step shown by arrow in Figure 7D). For example at $Z = 0.1$ sedimentation coefficients corresponding to these steps were ca. 8, 14, and 40 Sv, respectively. There were no distinct boundaries between these steps, indicating a broad distribution of PS(100)-*b*-PE4VP(100) chains between various types of aggregates. Overall, on the basis of this study, $Z = 0.1$ can be considered as a critical point at which the onset of disproportionation and formation of insoluble PS(100)-*b*-PE4VP(100)/AOT complexes occurs.

Therefore, the interaction of AOT with PS(100)-*b*-PE4VP(100) copolymer appears to be markedly different from the interactions of this surfactant with the block copolymers having longer PE4VP chains as well as with the PE4VP homopolymer. Formation of the dispersed nonstoichiometric complexes with the block copolymer having the shortest ionic chain which does not precipitate at $0 < Z < 0.1$ is unexpected. This is even more surprising in the view of the fact that the block copolymers with longer ionic chain form stoichiometric complexes that precipitate over the entire range of the compositions of the mixture.

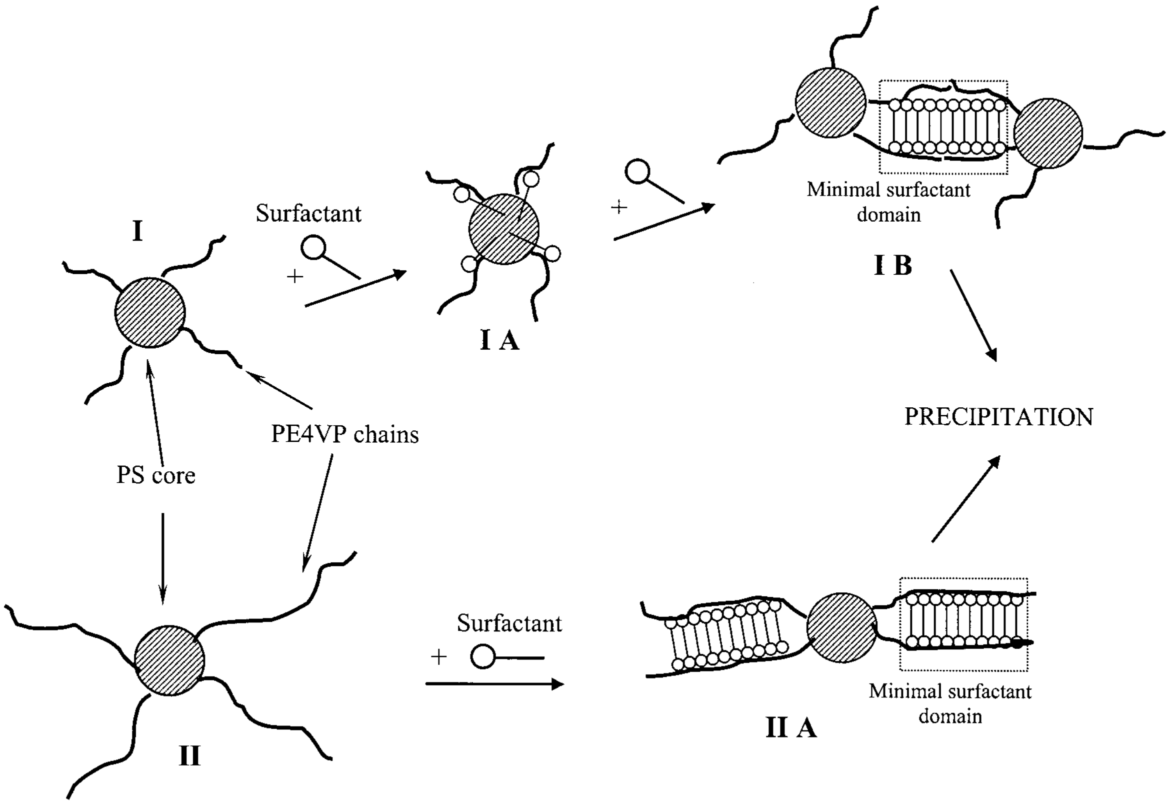

Figure 9. Schematic representation of interactions between PS-*b*-PE4VP micelles and AOT: (**I**) block copolymer micelle with short ionic PE4VP chains (100); (**II**) block copolymer micelle with long ionic PE4VP chains (200, 490).

To explain the striking difference in the behavior of the block copolymer-based and homopolymer-based complexes, we considered the interaction of AOT with the corona of the block copolymer micelles or micellar aggregates present in the aqueous dispersions. A schematic representation of the possible steps in the formation of PS-*b*-PE4VP−AOT complexes is shown in Figure 9. This scheme assumes that in the case of PS(100)-*b*-PE4VP(100) systems (Figure 9, **I**) the length of the polycation chains in the corona is insufficient to form a complex with the minimal surfactant domain within one block copolymer micelle. This effect can be even more pronounced if, as a result of sterical constrains, parts of the PE4VP chains in the corona adjacent to the surface of the PS core become unavailable for the reaction with the surfactant. It is possible that in such system at low concentration of AOT ($0 < Z < 0.1$) the surfactant molecules can loosely bind with the micelles through a combination of hydrophobic interactions with the PS core and electrostatic interactions with the PE4VP corona (Figure 9, **IA**). This results in a partial contraction of the polycation chains in the corona and the increase in the sedimentation coefficients of both the micelles and micellar clusters observed in the sedimentation experiments. As the surfactant concentration increases, the amount of the surfactant ions bound with the micelles also increases. At a critical point $Z = 0.1$ the contraction of the corona reaches the degree after which the corona loses the ability to keep the micelles and micellar clusters in dispersed state. Above this point the formation of minimal surfactant domain is possible through the confluence of several micelles (Figure 9, **IB**). As a result, the aggregation and precipitation of the insoluble complex become favorable. The resulting complex represents a kind of a collapsed network in which several block copolymer micelles are interconnected through their coronas and the surfactant domains.

In the case of PS(100)-*b*-PE4VP(200) and PS(100)-*b*-PE4VP(490), the PE4VP chains are sufficiently long, and the complexes between the polyion and the minimal surfactant domain can form within one block copolymer micelle; i.e., the aggregation of several micelles is not required (Figure 9, **IIA**). In such systems the disproportionation is observed, and the stoichiometric complexes form in the entire range of the compositions of the mixture, $0 < Z < 1$, like in the case of the regular homopolymer-based complexes.

Formation of the insoluble nonstoichiometric complexes has been previously reported for the anionic PS-*b*-PAA block copolymers and a cationic surfactant, *N*-cetylpyridinium bromide.[37] The current work presents the second example of such unusual behavior observed in the mixtures of the cationic PS-*b*-PE4VP block copolymer and an anionic surfactant, AOT. It appears that the precipitation of the nonstoichiometric complexes is a general phenomenon for the block ionomer complexes formed by block copolymers containing hydrophobic and ionic blocks with surfactant of opposite charge. As discussed for the PS-*b*-PE4VP-based systems in this paper and as previously discussed for the PS-*b*-PAA-based system elsewhere,[37] the self-assembly of these block copolymers into micelles in aqueous media is a key for understanding of the peculiarities of their interaction with the surfactants. The presence of the block copolymer micelles results in a somewhat different mechanism of formation of such block ionomer complexes compared to the mechanism of formation of the homopolymer-based complexes. An accurate comparison of the results obtained in this work with the PS-*b*-PAA/*N*-cetylpyridinium bromide study reported earlier[37] also suggests certain difference in the behavior of these two types of systems. In particular, in the case of PS-*b*-PAA with very long ionic chains (900 repeating units) the insoluble nonstoichiometric complexes were obtained at $Z < 1$. Furthermore, the composition of the complexes was adjusted in a broad range by varying the amounts of the surfactant added to this complex. As a result, the complex ionomer materials of various compositions containing a surfactant domain, carboxylate ion pairs, and PS segments were obtained. Conversely, in the case of the PS-*b*-PE4VP with long ionic blocks mixed with the AOT, the insoluble stoichiometric complexes were the only products of the reaction. This difference is most likely due to the fact that PE4VP is a strong polybase, with a constant charge density, while PAA is a weak polyacid that can change the degree of ionization and charge density in response to the changes in pH and polarity of the environment. As the block ionomer complex is formed with PS-*b*-PAA, the COO^- groups of the PAA chains are transferred in the less polar environment, which can result in a local p*K* increase and protonation of these groups. Therefore, at least a portion of COO^- groups in PS-*b*-PAA does not require the biding of surfactant cations to be neutralized. As a result, an electroneutral precipitate can be formed with nonstoichiometric amounts of surfactant ions.

Conclusions

The fluorescence and sedimentation velocity techniques were used to characterize the self-assembly behavior of a series of cationic PS-*b*-PE4VP block copolymers in aqueous media. The studied block copolymers had an identical PS block length (100 units) and ionic PE4VP blocks lengths varying from 100 to 490 units. The values of cmc for PS-*b*-PE4VP copolymers are within the range of $10^{-7}-10^{-6}$ M and are of the same order of magnitude as those reported for other amphiphilic block copolymers with the PS block of similar length. The increase of length of ionic PE4VP block in the range studied has practically no effect on the onset of aggregation in PS-*b*-PE4VP systems. The cmc values for PS-containing block copolymers can be ranked in the following order: PS-*b*-PEO (nonionic) < PS-*b*-PAA (weak polyelectrolyte) < PS-*b*-PE4VP ∼ PS-*b*-SPI (strong polyelectrolyte), which can be explained by different contributions of the electrostatic repulsion within the micellar corona to the stability of these block copolymer micelles.

At the concentrations above cmc PS-*b*-PE4VP copolymers form two types of aggregates representing micelles and micellar clusters. Mutual transformations between micelles and micellar clusters seem to be primarily under kinetic control. The molar fractions of polymer chains in both types of micellar aggregates were found to be independent of the copolymer concentration and the length of the ionic PE4VP block. However, the relative portion of the micellar clusters increased as salt concentration in the system increased.

Interaction of PS-*b*-PE4VP micellar solutions with oppositely charged surfactant AOT led to formation of block ionomer complexes. In contrast to the common polyelectrolyte–surfactant complexes, formation of insoluble nonstoichiometric and stoichiometric complexes was observed. The composition of insoluble PS-*b*-PE4VP/AOT complexes strongly depended on the length of ionic PE4VP block. It appears that the precipitation of the nonstoichiometric complexes is a general phenomenon for the block ionomer complexes formed by block copolymers containing hydrophobic and ionic blocks with surfactant of opposite charge. In the case of block copolymer with the shortest ionic block, PS(100)-*b*-PE4VP(100), the formation of stable aqueous dispersions of nonstoichiometric complexes was observed in the deficiency of the surfactant in the mixture ($Z < 0.1$). Such complexes represent the products of interaction between PS-*b*-PE4VP micelles or micellar clusters and AOT ions. The observed peculiarities in the formation of block ionomer complexes are the result of interaction of surfactant ions with already preformed multimolecular copolymer aggregates in contrast to the interaction with individual chains in the case of ionic homopolymer. The relative rigidity of the micellar aggregates might restrict the interactions of polyion chains with the surfactant headgroups and be a reason for formation of electroneutral precipitates with a nonstoichiometric amount of surfactant ions.

Overall, the simplicity of preparation, unique self-assembly behavior, and the wide variety of available surfactant components make these systems very promising in addressing various theoretical and practical problems, particularly in the design of novel polymeric materials.

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