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Micellization in Block Polyelectrolyte Solutions. 2. Fluorescence Study of the Critical Micelle Concentration as a Function of Soluble Block Length and Salt Concentration

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ABSTRACT: Critical micelle concentrations (cmcs) of block polyelectrolyte micelles formed from poly(styrene-*b*-sodium acrylate) in aqueous and NaCl salt solutions were investigated by fluorescence measurements of solubilized pyrene. The measurements were made for a range of PS block lengths (6 to 110 units) and of PANa block lengths (15–2400 units). For the series consisting of 11 and 23 units of PS, which had been prepared with a wide range of PANa lengths, the cmc was found to pass through a maximum as a function of the soluble (PANa) block length. It was observed that as the length of the PS block increased, the dependence of the log cmc versus the PANa block length decreased. For all samples except the PS(6) series at low salt concentrations, the log cmc values were found to decrease linearly as a function of the square root of the NaCl concentration ($\sqrt{C_s}$) which was varied from 0.10–2.5 M. The shape of the gradient d(log cmc)/d($\sqrt{C_s}$) versus the log of the number of PANa units was found to follow a curve of the same shape for the block polyelectrolyte micelles consisting of 6, 11, and 23 units of PS. The behavior of the curve was explained on the basis of polyelectrolyte conformations.

1. Introduction

Block copolymer micelles have been the subject of increasing attention in recent years.[1–8] The number of papers dealing with micellization in nonionic micellar systems composed of block copolymers has been relatively large, especially for systems soluble in organic solvents. By comparison to this extensive body of literature, much less work has been done on block copolymer amphiphiles in aqueous solutions, in spite of the fact that these systems have extensive potential uses, e.g. in pharmaceutical applications as drug carrier systems which can be used in vivo.[9,10] Two types of block copolymer micelles in aqueous solutions can be distinguished, i.e. those with hydrophobic cores and hydrophilic but nonionic coronas, and those with hydrophobic cores and polyelectrolyte coronas. Recently considerable work has been performed on the characterization of nonionic block copolymers in water.[11–15] The behavior of the block polyelectrolytes has received only very little attention experimentally[16–19] and only two theoretical papers deal directly with such systems.[20,21]

A previous publication from this laboratory dealt with the micellization phenomena, specifically the critical micelle concentrations (cmcs), in an aqueous block polyelectrolyte copolymer system, poly(styrene-*b*-sodium acrylate).[22] A review of the revelant block copolymer literature is also contained in that publication. These micelles, which are the subject of the present work, consist of PS cores surrounded by polyelectrolyte PANa coronas. It is necessary to keep in mind that the behavior of block polyelectrolyte systems is considerably more complicated than that of copolymer micelles containing nonionic water-soluble blocks. Micellar behavior is strongly influenced by the polyelectrolyte nature of the outer shell, which, in turn, is affected by the presence and nature of the small ions, as well as the charge density along the chain and the degree of neutralization.

Micelles of block polyelectrolytes, i.e., systems with a hydrophobic core and an ionic corona in aqueous solutions, have been studied to some extent. The earliest studies on these systems, by Selb and Gallot,[16,17] dealt with PS-*b*-poly(4-vinyl-*N*-ethylpyridinium bromide) (PS-*b*-P4VPEtBr) copolymers in water–methanol–LiBr mixtures. The micellization process was studied using static light scattering (SLS), viscometry, and sedimentation techniques. It was shown that the micelles exhibit a star-like structure, and the micellization process as well as micelle behavior was found to be strongly dependent on the solvent composition, temperature, salt concentration, and the insoluble polystyrene block length. The results indicated that the equilibrium between single chains and micelles shifted to lower polymer concentrations as the salt content was increased. The magnitude of the effect was found to depend on the length of the PS block. Thus, we can conclude that the parameters of micellization of block polyelectrolytes are influenced by variables such as block length, salt content, temperature, and pH. These variables cannot always be considered independently, since a change in one parameter, e.g. pH, can sometimes cause a change of the effect of another parameter, e.g. ionic strength, on the properties of the system.

The micellization of block copolymers composed of poly(methacrylic acid-*b*-9-vinylphenanthrene) and poly(methacrylic acid-*b*-(dimethylamino)styrene) in aqueous solutions has been investigated by fluorescence measurements by Morishima et al.[23,24] There are also several fluorescence studies dealing with the hydrophobic associations in aqueous solutions of copolymers where one of the components consists of a polyelectrolyte, such as methacrylic acid-*co*-9-vinylphenanthrene[25] and 2-acrylamido-2-methylpropanesulfonic acid (AMPS)-*co*-styrene.[26] The micelle-like hydrophobic domains for copolymers of AMPS with different hydrophobic mono-

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mers were also studied by viscosity, ^{1}H NMR, surface tension, and electron microscopy.[27]

Another study of block polyelectrolytes, by Valint and Bock,[28] explored the enhanced rheological properties of poly(*tert*-butylstyrene-*b*-styrenesulfonate) as compared to the random copolymer and to poly(styrenesulfonate) and attributed the behavior to the micellization of the block copolymer. More recently, poly(styrene-*b*-methacrylic acid) (PS-*b*-PMAA) copolymers were studied by time-resolved fluorescence as well as by other methods such as dynamic light scattering (DLS),[18,19,29,30] SLS,[30] sedimentation velocity,[30] and viscometry.[30] Most of the effort in that work was devoted to the acidic PS-*b*-PMAA systems, but a part of the study dealt with polyelectrolytes. It was shown that the formation and properties of PS-*b*-PMAA micelles, as well as their ability to solubilize and release hydrophobic species, were strongly dependent on pH and ionic strength.[19] Dynamic light scattering and viscosity measurements indicated that at low ionic strength and at rather high degrees of ionization of the carboxylate groups of the PMAA block, the electrostatic repulsion of highly charged spherical micelles results in the formation of long-range order in the micelle solutions.[19] An analysis of the autocorrelation curves gave a broad spectrum of correlation times with two well-separated maxima. A fast-diffusion mode was described as the so-called "collective diffusion", which was also observed in semidilute polyelectrolyte solutions[31] and in latex particles where a certain degree of long-range order is assumed.[32,33] The slow motion may correspond to the individual diffusion of clusters of structurally organized micelles.

Some comments concerning the theoretical treatment of systems relevant to the block polyelectrolyte micelles are in order. It should be pointed out that even for homopolyelectrolytes, both theoretical approaches as well as the interpretation of experimental data are rather complicated because of the multicomponent nature of the polyelectrolyte solutions.[34-36] Hence, various approximations and assumptions are used in theoretical treatments to simplify the situation. Therefore, it is completely beyond the scope of the present publication to attempt anything more than a qualitative application of some of the theoretical concepts in the discussion section.

Since the present study deals with micellization phenomena in block polyelectrolytes, studies which consider polyelectrolyte chains grafted onto flat surfaces or onto spherical colloids can be useful for the interpretation of micellar properties. Some studies provide numerical solutions of the electrostatic mean-field equations coupled to polymer elasticity for polyions grafted to flat surfaces.[37,38] A recent study by Pincus[39] provided analytical scaling laws for the case of polyelectrolytes end-grafted to flat surfaces as well as to small colloidal particles. It was shown in that study that the distribution of charges on macromolecules yields a layer force which is considerably less sensitive to the Debye screening by added electrolytes. Very recent publications by Ronis[40] considered the conformational behavior of polyelectrolyte chains attached to a spherical colloid. In these studies, the conformational equilibrium of the polyelectrolyte was examined using a combination of mean-field approximations and Monte Carlo methods. It was shown that polyelectrolyte chains exhibit both rod-like and coil-like behavior at different distances from the colloid core and that the extent of each type of behavior depends on the core size, the aggregation number, and the screening length, which depends on salt content. This study will be invoked in the Results and Discussion section.

There are only two theoretical studies which deal with the micellization of block polyelectrolytes; those of Marko and Rabin[20] and of Dan and Tirrell.[21] The first theory describes the microphase-separation properties of charged-neutral diblocks using the mean-field approach of Joanny and Leibler[41] to describe micelle formation and the properties of the micelles. Due to the large energy cost of contacts between the neutral block and the solvent, it is favorable for the chains to aggregate; however Coulomb repulsion sets a preferred size for these aggregates, which take the form of spherical micelles. The critical micelle concentration, critical micelle size, and aggregation number were calculated in the long-chain limit. Two situations were considered: the weakly charged case, where there is no charge condensation either for the isolated chains or for the micelles, and the case of highly charged diblocks, for which counterion condensation on the micelles reduces their Coulomb energy. It was shown that when strong condensation occurs, the osmotic pressure of the confined counterion strongly stretches the polyelectrolyte chains in the corona. It should be pointed out that this theory is based on the mean-field approach, which assumes a rather long insoluble block and a short soluble block, i.e. "crew cut" micelles. For this case, the theory predicts that highly charged diblocks will not form stable micelles with high aggregation numbers and that micelle formation will predominantly occur in dilute solutions of weakly charged diblocks. Therefore, according to the theoretical prediction of Marko and Rabin,[20] micellization of highly charged block polyelectrolytes in dilute salt solutions will not occur unless the charged block is short as compared to the hydrophobic block forming the micelle core. This situation is very different from the case of neutral copolymers in selective nonpolar solvents, where "star-like" micelles have been obtained.

In the theory by Dan and Tirrell,[21] scaling relations for block copolymer micelles in the region of moderate salt concentration were investigated. In this salt concentration region, the range of excluded volume interactions is higher than that of the electrostatic correlation length and the configuration of the polymer chain is a function of both factors. Therefore this region lies between the low salt concentration where electrostatic effects dominate and the high salt concentration where the screening effects reduce the range of electrostatic interactions and the conformation of charged chains in block polyelectrolyte micelles is indistinguishable from that of neutral ones. It is found that the aggregation number, cmc, and chemical potential of the micellar solution are dominated by the core block properties and are identical, within a logarithmic factor, to those calculated for micelles of neutral diblock copolymers in a nonpolar, highly selective solvent. It is also suggested that changes in salt concentration do not affect either the cmc or the aggregation number, though the corona size decreases with increasing salt concentration.

In the previous publication from this laboratory, an extensive study was described which dealt with the cmc in the poly(styrene-*b*-sodium acrylate) (PS-*b*-PANa) block copolymer system in aqueous solutions as a function of the PS block length.[22] Several families of block copolymers were investigated, with the PS chain length ranging from 6−110 units, and the PANa chains ranging from ca. 300−1400 units. The results were interpolated for a PANa block length of 1000 units. It was found that changing the insoluble block length from 6–110 units lowered the cmc values from 1.6×10^{-5}–5×10^{-8} M. For very short PS block lengths, the cmc decreased very rapidly with increasing length of the insoluble block. By contrast, for higher PS block lengths (above 12), the drop in the cmc was much more gradual. A subsequent publication interpreted the results in terms of a model of mixed micellization of polydisperse block copolymers in which the insoluble blocks are assumed to adopt a spherical collapsed conformation.[42] The relationship between the cmc of each component and the length of the insoluble block was obtained, and the single chain fraction of the block copolymer was calculated as a function of the total polymer concentration. The molecular weight distributions of the single chain and the micellar fractions were also determined.

The present publication is devoted to the exploration of the effect of the polyelectrolyte block length and the salt concentration on the cmc values. The micellization phenomena are investigated by fluorescence spectroscopy for a rather wide range of block lengths where the polystyrene block length ranged from 6–110 units and the poly(sodium acrylate) block length ranged from 15–2400 units. The influence of low molecular weight salt concentration on the cmc values of the block copolymers is also explored. The subsequent paper, directly following this one, will deal with the characterization of the block polyelectrolyte micelles by static light scattering as a function of PS and PANa block lengths, and salt concentration.[43]

2. Experimental Section

2.1. Materials. The poly(styrene-*b*-sodium acrylate) block polyelectrolytes were prepared as described in a previous publication.[44] First, the poly(styrene-*b*-*tert*-butyl acrylate) block copolymers were synthesized by anionic block copolymerization in THF at −78 °C in presence of LiCl. *sec*-Butyllithium was used to initiate the styrene polymerization. After the end capping of the polystyrene blocks by α-methylstyrene, a certain amount of the *tert*-butyl acrylate monomer was added to make the first block copolymer. The reaction mixture was partially withdrawn after 5 min and more *tert*-butyl acrylate was added. This sequence of operations was repeated successively. This procedure allows the preparation of a series of copolymers with the same polystyrene block length and varying poly(*tert*-butyl acrylate) block lengths. The polymers were precipitated into water and dried under vacuum at 80 °C. The polymers were hydrolyzed for more than 10 h in dioxane at 100 °C in the presence of 1 M HCl. The poly(styrene-*b*-acrylic acid) copolymers were then obtained by freeze drying the reaction solution. The poly(styrene-*b*-sodium acrylate) copolymers were prepared by redissolving the acid form of the copolymers in methanol and neutralizing by adding the polymer solution to 0.2 M NaOH in isopropyl alcohol.

Three to four different copolymers were easily obtained for each series, which was the usual case of the present study. When more extensive studies were needed, eight different copolymers were made for each series. In these cases, special precautions had to be taken, especially in regard to the extremely high purity of the monomers and the strict prevention of the deactivation of the living polymer chains in the reactor during the repeated additions of the monomers and the withdrawals of polymer solution.

The molecular weight, composition, and polydispersity index were determined by size exclusion chromatography (SEC) on the polystyrenes and the poly(styrene-*b*-*tert*-butyl acrylate) copolymers. For one series of copolymers, the compositions were also determined by ^{1}H NMR; the values were in good agreement with those obtained by SEC. The complete hydrolysis and neutralization of the polymers were confirmed by solid state ^{13}C NMR. The abbreviations used indicate the copolymer composition; for example, PS(23)-*b*-PANa(44) represents a polystyrene chain of 23 units joined to a poly(sodium acrylate) chain of 44 units.

2.2. Sample Preparation for Fluorescence. All solutions were prepared by dissolving the block copolymers in doubly distilled deionized water (Millipore Milli-Q) to give solutions of final concentrations ranging from 2.0–10.0 mg/mL. The polymer–water mixtures in sealed glass ampules were heated with stirring for 5 days at 100 °C to dissolve the polymer. An alternative procedure, used in the early stages of the work, involved stirring the samples for 5–6 h at room temperature to dissolve the polymers without heating. The solutions prepared as described above were used as stock solutions for further dilutions to obtain secondary stock solutions of concentrations ranging from 10^{-4} to 10^{-2} mg/mL. Dilutions were performed with water or with NaCl solutions as required.

All stock solutions had initial pH values of 9–11. To be sure of complete microsalt elimination and of complete ionization of the polyelectrolyte block, the solutions of high pH were dialyzed against water at room temperature to give final pH values between 9 and 9.5. Polymer concentrations after dialysis were determined by potentiometric titrations with 0.05–0.1 M HCl.

Sample solutions for the fluorescence investigation were prepared by adding known amounts of pyrene in acetone to each of a series of empty flasks, following which the acetone was evaporated. The amount of pyrene was chosen so as to give a pyrene concentration in the final solution of 5.0×10^{-7} M, slightly below the saturation concentration of pyrene in water at 22 °C.[45,46] To each flask was added a measured amount of a stock solution, followed by deionized water. The flasks were heated and stirred for 2 h at 40–50 °C to equilibrate the pyrene and the micelles; subsequently, the solutions were cooled and stirred overnight at room temperature. The polymer concentrations ranged from 10^{-6} to a maximum of 5 mg/mL.

2.3. Fluorescence Measurements. Steady-state fluorescence spectra were measured using a SPEX Fluorolog 2 spectrometer in the right-angle geometry (90 ° collecting optics) with a bandwidth of 0.5 mm for both excitation and emission. For the fluorescence measurements, 3 mL of solution was placed in a 1.0 cm square quartz cell. All spectra were run on air-equilibrated solutions. For fluorescence emission spectra, λ_{ex} was 339 nm, and for excitation spectra, λ_{em} was 390 nm. For samples with a pyrene concentration of 5.0×10^{-7} M, spectra were accumulated with an integration time of 1 s/0.5 nm. An increase of the integration time to 2 or 4 s/0.5 nm for this pyrene concentration did not improve the signal-to-noise ratio.

3. Results and Discussion

3.1. Influence of Ionic Block Length on the cmc. The synthetic procedure allows the preparation of a series of diblock copolymers with an identical styrene block length and varying ionic block lengths. Table 1 lists the samples prepared and used in this study. The cmc values for each member of eight such series were determined from fluorescence measurements using previously established techniques.[47] Since the PS block length remains constant throughout a given series, one can observe directly the effects of the ionic block length on the cmc values. For this study, the PS block lengths ranged from 6–110 units, while the ionic block lengths ranged from 15–2400 units.

In the current discussion, an attempt will be made to explain qualitatively the cmc behavior versus the ionic block length in terms of two trends. Quantitative reasoning is premature, since, to the best of our knowledge, no model has been developed for the present systems in all its ramifications, i.e., water-soluble micelles composed mainly of a small insoluble PS core and a corona formed from polyelectrolyte chains of

Table 1. Composition and Polydispersity Index of the Poly(styrene-*b*-sodium acrylate) Copolymers

PS(X)-*b*-PANa(Y)	M_w/M_n	PS(X)-*b*-PANa(Y)	M_w/M_n
6-*b*-89	1.09	23-*b*-780	1.05
6-*b*-180	1.10	23-*b*-1400	1.13
6-*b*-400	1.10		
6-*b*-1000	1.16	28-*b*-73	1.06
		28-*b*-330	1.05
11-*b*-15	1.13	28-*b*-1600	1.07
11-*b*-69	1.07		
11-*b*-160	1.04	40-*b*-82	1.07
11-*b*-350	1.06	40-*b*-180	1.09
11-*b*-1030	1.06	40-*b*-520	1.07
		40-*b*-2400	1.19
14-*b*-130			
14-*b*-270		86-*b*-100	1.11
14-*b*-620	1.11	86-*b*-190	1.11
		86-*b*-390	1.21
23-*b*-29	1.10	86-*b*-900	1.15
23-b-44	1.08		
23-b-81	1.08	110-*b*-380	1.10
23-*b*-160	1.04	110-*b*-2400	1.21
23-*b*-300	1.06		

varying lengths, in a broad range of salt concentrations. Figure 1 illustrates the cmc behavior for two series of block polyelectrolytes with PS block lengths of 11 and 23 units. Two points are given for the cmc values which represent the values determined from the excitation and the emission spectra. These two series have been specifically selected for illustrative purposes, since for each series a relatively large number of samples has been synthesized, which cover a wide range of ionic block lengths (15−1400 units). Thus, they are well suited to show the general trends which will be discussed below.

Figure 1 shows that for both PS series, the log cmc values increase with the ionic block length (N_{PANa}) for relatively short ionic chains. As the PANa chain length increases, the cmc values eventually pass through a maximum, after which the values decrease with increasing ionic chain length, in a pattern which resembles a parabolic profile. For the sake of convenience, the left side of the figure (parabola) will subsequently be referred to as the short ionic block region (SIBR), and the right side as the long ionic block region (LIBR). This type of parabolic behavior as a function of many parameters is well-known and generally occurs when two mechanisms or trends oppose one another.[48,49] More pertinently, from scaling concepts, this kind of behavior is also expected when a system crosses a boundary between two specific regimes. In each of these ionic block length regions (SIBR and LIBR), a particular regime will dictate the conformational behavior of the micelle corona. A full mathematical treatment of these two regimes is considerably beyond the scope of the present paper (and should be undertaken by theoreticians). Moreover, as previously stated, the only primary parameter that varies in the micellar system is the length of the ionic block. Also, as will be seen in the following publication, the aggregation numbers for the PS(11) and PS(23) series do not change significantly with PANa block length.[43] Thus, presumably, both types of behavior in these two regimes must be related to the polyelectrolyte nature of the ionic chain segments and to the total length of the chain.

Intuitively, for any PS block length in the SIBR, the ionic chain must have a minimum length in order for the molecule to be able to form a micelle. For very short PS block lengths, a single ionic unit might suffice, but for long hydrophobic blocks, this minimum length will undoubtedly be longer. For the purpose of illustration, it is useful to take an extreme case which, while possibly unrealistic, is highly illustrative. The copolymer PS(11)-*b*-PANa(1) might well be soluble in water in micelle form, since its total chain length is typical of those of low molecular weight surfactants.[6] Now, it is reasonable to inquire what would be the effect on the cmc value if a second ionic unit were added to the diblock, then a third, etc. Presumably, with increasing ionic block length, the block polyelectrolyte present in single chain form will become more soluble. Therefore, the cmc values should increase with each added ionic unit, and thus generally with the ionic chain length of the diblock. This type of behavior has, indeed, been observed for low molecular weight surfactants and for PEO systems.[6] The increase in the cmc values in the SIBR can be understood within this framework.

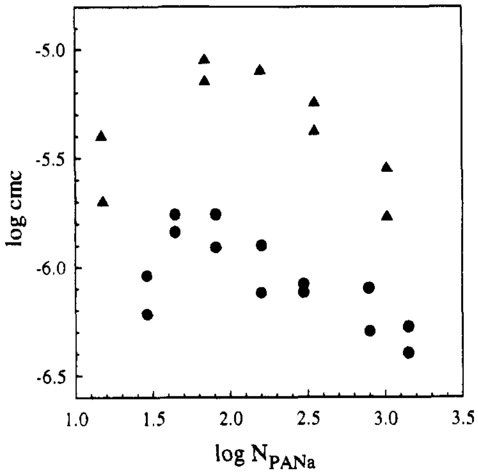

Figure 1. Effect of the ionic block length on the cmc values for PS-*b*-PANa series with PS block lengths of 11 (▲) and 23 (●) units.

Due to the polyelectrolyte nature of segments in the micelle corona, the trend of increasing cmc with increasing ionic block length cannot go on indefinitely. To explore the behavior for longer ionic chains, it is useful to proceed to the opposite side of the plot, i.e. to the LIBR of the graph (Figure 1). In this region, the cmc values were found to decrease with increasing polyelectrolyte chain length. As will be shown later in the following publication devoted to the results of static light scattering experiments, the aggregation numbers in 2.5 M NaCl for the series consisting of 11 and 23 units of PS are ca. 70 and 150, respectively.[43] Therefore, for these micelles, the crowding around the PS core is quite high. Qualitatively, this fact implies that the charge density as well as the total polyelectrolyte and counterion concentrations are very large in the vicinity of the core. It is expected that above a certain PANa length, the high charge will result in extensive screening. This results in a decrease in the PANa chain solubility since it is known that the solvent quality for polyelectrolytes decreases with increasing ionic strength of the solution.[34−36] Hence, it is not unreasonable to expect the same type of behavior will be operative with increasing ionic chain length, since it is equivalent to an effective increase of the ion content in the aqueous solution. The decrease in the quality of the solvent with increasing polyelectrolyte chain length should eventually lead to a decrease in the cmc values with increasing polyelectrolyte block length in this region. The maximum in the cmc occurs at the point at which the two trends described above balance each other. It should be

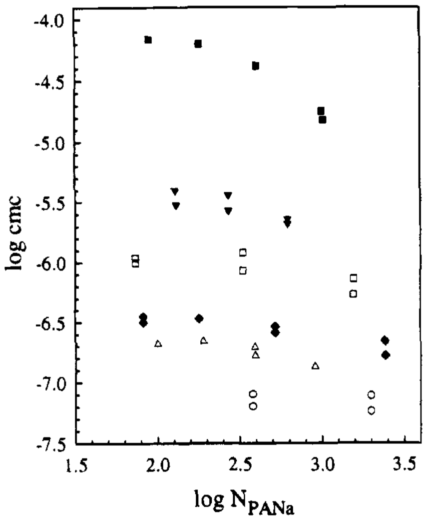

Figure 2. Effect of the ionic block length on the cmc values for various PS-*b*-PANa copolymer series with PS block lengths of 6 (■), 14 (▼), 28 (□), 40 (◆), 86 (△), and 110 (○) units.

mentioned that the same type of behavior has been predicted for colloid crystals, where melting occurs if the charge of the colloid is increased beyond a certain critical value, due to the screening by the counterions.[50]

The decrease in the cmc values with increasing polyelectrolyte chain length can also be visualized using the model of Ronis.[40] In this model, the extent of rod-like conformations of the polyelectrolyte chain near the core will decrease with an increase in salt content and/or the ionic block length. Therefore, a PANa block which has a considerable coil-like conformation will be more affected by counterions as compared to one with a considerable rod-like conformation. The application and implications of this model in relation to the present micellar systems will be discussed more extensively later, i.e. in section 3.2 where the effect of added salt on the cmc behavior is described.

Figure 2 shows the results for six additional block copolymer series having relatively long ionic block lengths. The observed curvature in the plots of log cmc versus soluble block length substantiates to some extent the presence of the two opposing trends discussed previously. The LIBR is not observed in these samples since the ratio of the PS to PANa block length is relatively high compared to the samples based on the PS series of 11 and 23 units. It is expected that if the two factors are operative and effectively opposing one another, the position of the maximum along with its width (or the flatness of the parabola) should reflect the balance between the two. The position of the maximum would be expected to move to higher ionic block lengths as the PS block is increased. It should be noted that the effect of the soluble block length on the cmc values decreases as the PS block length increases. This result was also observed previously in the first paper of this series.[22]

The dependence of the cmc as a function of the soluble block length for different insoluble block lengths can be evaluated from the slopes of the curves presented in two previous figures. Figure 3 shows a plot of d(log cmc)/d(log N_{PANa}) against the log of the PS block length (log N_{PS}) for a PANa block length of 1000 units. This figure shows that the effect of the PANa block length on the cmc decreases as the PS block length increases. In fact, for very long PS block lengths the slope of the curve approaches zero. This result suggests that the micellization of block copolymers for short insoluble block lengths depends on the block length of the soluble block. However, for long insoluble block lengths, the micellization is dominated by the properties of the insoluble block.

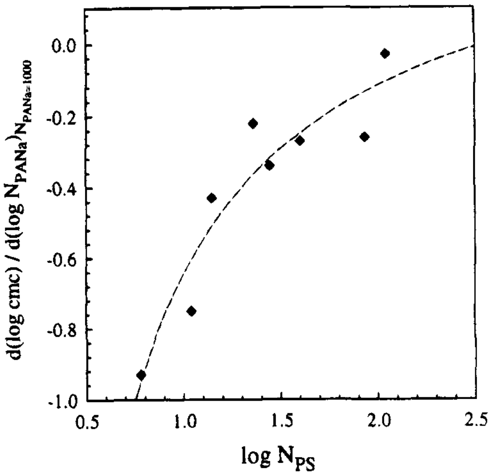

Figure 3. Dependence of the slopes of the curves of log cmc versus log N_{PANa} (for the PANa block length of 1000 units) on the length of the PS block. The line is a fit through the points and is shown as a guide for the eye.

3.2. Influence of Added Salt on the cmc. As was mentioned previously, an increase in the concentration of low molecular weight salt decreases the quality of water as a solvent for polyelectrolytes. This phenomenon will be also encountered in the subsequent paper in connection with the second virial coefficient values determined by SLS of the block polyelectrolyte micelles as a function of salt concentration.[43] As a result of the decrease in solvent quality for the block polyelectrolyte, micelles would be expected to form at a lower concentration, thus the cmc value would decrease. To explore this phenomenon, the effect of a broad range of salt concentrations, 0.10–2.5 M, on the cmc values was performed.

The effect of salt concentration on the cmc behavior was studied for three series of copolymer diblocks as a function of NaCl concentration. NaCl was selected for two reasons; first, there is no specific interaction between the low molecular weight ions and the polyion chains, apart from Coulombic interactions. Second, in solution, the NaCl generates the same cations (Na^+) as those already present as counterions for the polyelectrolyte chains. For this part of the study, the PS block lengths were 6, 11, and 23 units, while the length of the ionic segments ranged from 15–1400 units. Due to the relatively wide range of cmc values obtained for these three copolymer series, the plots of log cmc versus $\sqrt{C_s}$ (where C_s is the NaCl concentration in molar units) are shown, for the sake of clarity, in two separate figures. Figure 4 gives the plots for the block copolymer series with PS block lengths of 11 and 23 units, and Figure 5 shows the results obtained for the copolymer series with a PS block length of 6 units. As can be seen from Figure 4, log cmc decreases linearly with $\sqrt{C_s}$. For the plots given in Figure 5 (for the PS block length of 6 units), at low salt contents ($\sqrt{C_s} \leq 0.3$), a clear departure from linearity can be seen. This behavior will be discussed later.

The linear dependence of log cmc on $\sqrt{C_s}$ is not unexpected, since a wide range of polyelectrolyte properties, notably the free energy of the polyelectrolyte chain, depend on the Debye length, which, in turn, is

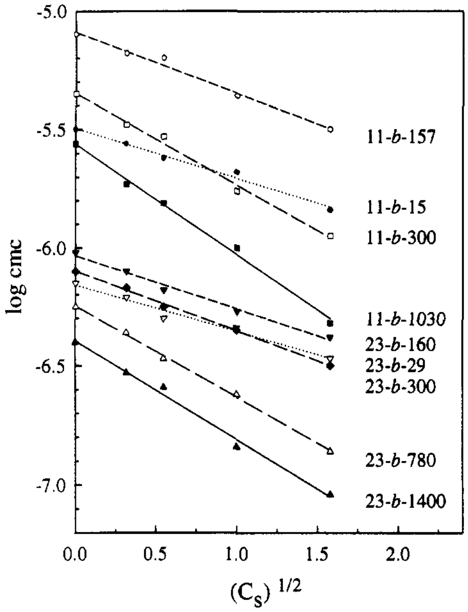

Figure 4. Plots of the log of the cmc versus $C_s^{1/2}$ for two series of block polyelectrolytes with PS block lengths of 11 and 23 units and different ionic block lengths.

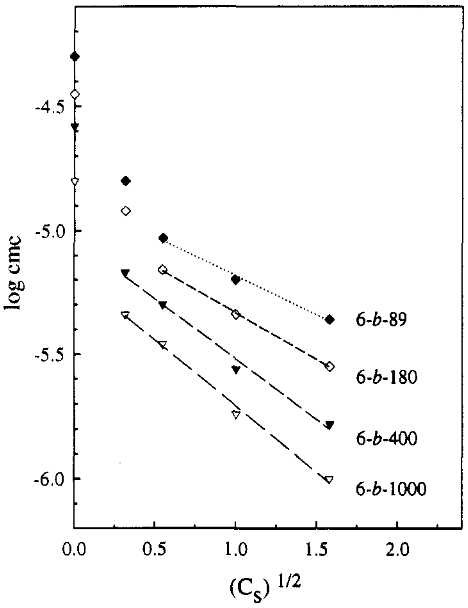

Figure 5. Plots of the log of the cmc versus $C_s^{1/2}$ for the PS(6)-*b*-PANa series.

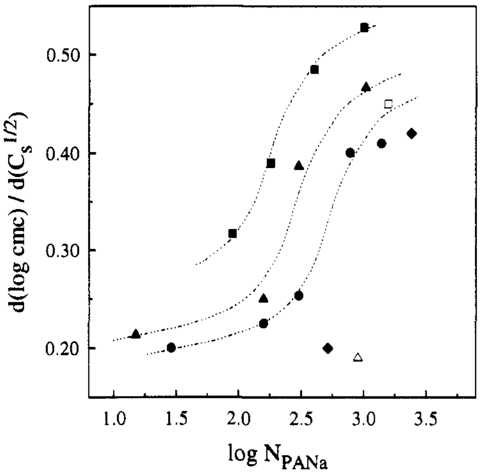

Figure 6. Dependence of the slopes of the plots of log cmc versus $C_s^{1/2}$ for different PANa block lengths: 6 (■), 11 (▲), 23 (●), 28 (□), 40 (◆), and 86 (△).

related to $\sqrt{C_s}$. Figures 4 and 5 show that the slopes of this dependence are a function of the ionic block length. A convenient way to illustrate this effect is to plot the slopes of these lines as a function of the ionic block length. For the series based on copolymers with 6 PS units, the linear portions of the plots from the high salt content region of Figure 5 are used. The slopes, d(log cmc)/ d($\sqrt{C_s}$), for these three copolymer systems as well as values for other copolymers, i.e. PS(28)-*b*-PANa(1600), PS(40)-*b*-PANa(520), PS(40)-*b*-PANa(2400), and PS(86)-*b*-PANa(900), are shown in Figure 6. The sigmoidal nature of the curves is clear for the three diblock copolymer families with PS block lengths of 6, 11, and 23 units. The sigmoidal shape is most evident for the PS block lengths of 11 and 23 units, since more points are available for those series. Some universality in the shape of these lines can be suggested. As a matter of fact, the three smooth curves drawn through the points for the 6, 11, and 23 PS families are identical and are only displaced relative to each other by horizontal and/or vertical shifts. The curves therefore serve only to indicate the similarity of behavior and to guide the eye.

In order to understand the effect of salt on the cmc as a function of the soluble chain length, it is useful to invoke, in a qualitative fashion, the theoretical model recently proposed by Ronis.[40] According to this theory, the conformation of the polyelectrolyte block in a micelle corona can be visualized as being composed of three major regions. In the first region, the polyelectrolyte chains just near the core are in a highly stretched inflexible rod-like conformation. In the second region, further from the core, the ionic chains have a flexible rod-like conformation. Finally, in the region far from the core, the ionic chains approach a random coil conformation. It is convenient to refer to the length of the rod-like region as L_{RR}. The shape of the polyelectrolyte corona will depend on the relative lengths of the L_{RR} and that of the whole PANa block. If the length of the ionic block is less than the theoretical L_{RR}, the micelle will look like a porcupine; by contrast, if the ionic block is longer than the L_{RR}, the outer ends of the polyelectrolyte chains in the corona will approach random coil conformations. According to this model, the L_{RR} value is influenced by three main factors, i.e. the radius of the core (R_c), the length of the ionic block, and the low molecular weight salt concentration in solution (C_s). It was shown that a variation in R_c has little influence on the L_{RR} behavior as compared to the two last parameters mentioned.[40] Furthermore, it was shown that the L_{RR} values should decrease with increasing C_s.

From the aggregation number of the micelles, the local charge density (or counterion concentration), which, in turn, affects the electrostatic repulsion, can be determined. The changeover from one type of chain conformation to another naturally depends also on the ionic chain length. For all reasonable salt contents, there will be a section right near the core which is extended, while further away from the core it becomes a more random coil. One can apply this idea to the present system. For relatively low ionic chain lengths, one can expect the extended form to exist at all reasonable salt contents. Therefore, the effect of added salt for these systems is relatively small, and the addition of salt is not likely to perturb the cmc appreciably. This type of behavior is seen from the initial low slopes of the sigmoidal curves in Figure 6. This working hypothesis could be substantiated if one were able to evaluate the charge density in the vicinity of the core. Using the aggregation number value that will be reported in the following paper, and assuming a rod-like conformation for the short ionic blocks, as well as a certain distribution of the counterions in the corona, along with the phenomenon of counterions condensation on the polyion chains, one can evaluate the concentration of counterions in the corona, which, for short ionic block lengths, is expected to be very high.

One can extend the discussion of chain conformations to the cmc values. The dependence of the cmc on salt concentration is also a function of the PANa block length, as is suggested from the sigmoidal curve in Figure 6. First, it is observed that for relatively short ionic block lengths, the slope of log cmc versus $\sqrt{C_s}$ plots depends only slightly on the ionic block length. This result is not surprising since all of the polyelectrolyte segments are located in the vicinity of the core, where the ionic strength is quite high due to the high concentration of polyions and counterions. Therefore, the addition of salt to the solution will not increase appreciably the ionic strength in the proximity of the core. This fact explains the weak effect of the added salt for relatively short ionic block lengths.

Once a certain minimum chain length is exceeded, the ionic chain at some distance from the core acquires a much larger number of accessible conformations. For this chain, the effect of salt becomes more significant since the value of the L_{RR} is dependent on salt content. This fact is seen in the transition region of the sigmoidal curve (Figure 6), where the cmc change is significant with ionic block length. Again, the chain conformation concept can be extended to cmc values. Thus, as salt is added, the L_{RR} decreases, and for ionic chain length values in this region the effect of added salt on the cmc should be very notable. It seems reasonable to suggest that the transition from low slope to high slope behavior occurs at approximately the chain length of ionic block close to the L_{RR}. At the low end, the sigmoidal curve can be approximated by two straight line segments. For PS chains of 6, 11, and 23 units these intersections lie near the ionic block lengths of 100, 120, and 160 units, respectively. A plot of these values against the number of PS units (not shown here) yields a linear relationship (correlation coefficient = 0.99) between the two parameters.

The region of increasing values of d(log cmc)/d($\sqrt{C_s}$) probably coincides with the region over which the rod-like conformation changes to the random coil conformation as a function of salt content. Therefore, in this region, the d(log cmc)/d($\sqrt{C_s}$) values show the greatest variability. However, beyond some length of the ionic block (which depends on the PS block length, but is of the order of 1000 ionic units) the polyelectrolyte chain will be a random coil even at the lowest experimentally accessible microion concentrations. At that point, the effect of added salt on the cmc should level off again, but at a high value consistent with random coil behavior.

It is interesting to note that the relative positions of the low to high slope transitions in Figure 6 can be related to the positions of the maxima previously observed for the plots of cmc versus the ionic block length in Figure 1. These values increase with increasing PS block length. It is suggested that both of these phenomena are related to the different regimes in polyelectrolyte micelle behavior appearing at short and long lengths of the ionic blocks. The transition region from one type of regime to another, depending on the PS block length, can be related to the different type of conformations of the polyelectrolyte chain and thus the solubility.

At this point, some comments are in order on the behavior of block polyelectrolytes containing very short PS blocks at different salt contents. It is found that the dependence of d(log cmc)/d($\sqrt{C_s}$) for the PS block length of 6 units deviates from linearity at low salt concentrations (Figure 5). This behavior is not seen for the series consisting of 11 and 23 styrene units as well as series with longer PS block lengths (not shown here). At this time, we cannot offer a semiquantitative explanation for this behavior. A number of different factors may be responsible for the nonlinearity. One possibility is that the shortness of the PS chain makes it difficult for the PS block to be present as a collapsed coil, as the longer PS blocks probably are. Thus, if the PS is not present as a collapsed coil, the quality of the solvent or the interactions of the solvent with the styrene block become much more important. A change in the quality of water as a solvent for PS is expected as low molecular weight salt is added to the water. The trends suggest that water with added salt is a worse solvent for short PS chains than water without salt.

It should be also mentioned that Selb and Gallot[16] noticed some effects which can be related to the behavior of PS(6)-*b*-PANa at low salt concentrations. Using sedimentation and light scattering experiments, these authors investigated the effect of added salt on the micellization of PS-*b*-P4VPEtBr in water–methanol–LiBr mixtures. Their results indicated that the equilibrium between single molecules and micelles is shifted to lower polymer concentrations as the salt content is increased. For a very low salt concentration (0.01 M LiBr) for PS(27)-*b*-P4VPEtBr(140), only single molecules were present in solution, but micelles appeared when the salt concentration was increased. It also was noticed that beyond a particular salt concentration, a change in the ionic strength had no effect on micellization. The effect of salt concentration was found to be important only for short PS block lengths (less than ca. 30 units). For higher PS block lengths, the unimer–multimer equilibrium was affected much less (if $N_{PS} \cong 30$) or not at all (if $N_{PS} \cong 130$) by changes in salt concentration.

4. Conclusions

The first part of the present study was devoted to an investigation of the critical micelle concentration of block polyelectrolytes formed from a wide range of PS-*b*-PANa copolymers. The PS blocks ranged from 6 to 110 units, while the ionic blocks ranged from 15 to 2400 units. Since the previous publication dealt with the dependence of the cmc on the polystyrene block length for a constant ionic block length of 1000 units, the first parameter investigated in the present study was the ionic block length dependence. Two families of copolymers were studied in detail, i.e. those based on PS block lengths of 11 and 23 units. For both families, it was shown that the cmc initially rose to a maximum value and then dropped off as the ionic chain length increased. This phenomenon is due to the polyelectrolyte nature of the water-soluble block. At low ionic block lengths, the solubility of the block copolymer increased with increasing ionic block length; by contrast, for long ionic blocks, the quality of water as a solvent for the polyelectrolyte block becomes poorer with increasing block length, and the cmc decreased. The dependence of the cmc on the soluble block length was also found to decrease as the length of the insoluble PS block increased.

The influence of low molecular weight salt concentration on the cmc was also investigated. It was shown that log cmc decreased linearly with the square root of the salt concentration for the block polyelectrolytes investigated except for the PS series of 6 units at low salt concentrations. A plot of d(log cmc)/d($\sqrt{C_s}$) versus d(N_{PANa}) for the systems investigated shows a sigmoidal character; initially the values are low, they rise at a certain ionic block length, and then level off at a relatively high value. The initial low value is due to the fact that for very short ionic block lengths the ionic chains are highly extended and the ionic strength in the vicinity of the core is very high. Thus, the addition of salt does not perturb the cmc values appreciably. As the ionic chain length increases, eventually one reaches the point at which the ionic chain no longer behaves as a rigid rod; at that point the cmc becomes very sensitive to the salt concentration. This area is reflected in a very high value of the slope of d(log cmc) versus d($\sqrt{C_s}$). Finally, at very long ionic block lengths, i.e. where the chain already behaves as a highly coiled system, the effect of salt levels off because no further conformational changes are occurring; only the point of onset of coil-like behavior changes. This picture is in qualitative agreement with the model proposed by Ronis.[40]

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