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Critical Micellization Phenomena in Block Polyelectrolyte Solutions

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ABSTRACT: Critical micelle concentrations (cmc's) were measured for a range of block copolyelectrolytes based on styrene (the insoluble block) and sodium acrylate. The lengths of the styrene blocks ranged from 6 to 110, while those of the polyelectrolyte ranged from ca. 300 to ca. 1400. The fluorescent probe technique was utilized with pyrene as a probe molecule, and the data were treated by five different methods. cmc results were interpolated for a constant polyelectrolyte block length of 1000 units. It was found that changing the insoluble block length from 6 to 110 lowered the cmc from 1.6×10^{-5} to 5×10^{-8} M. By contrast, changing the soluble block length from 300 to 1400 typically changed the cmc values by less than a factor of 2. For very short PS block lengths, the cmc decreased very rapidly with increasing length of the insoluble block. By contrast, for higher block lengths (above 12) the drop in the cmc was much more gradual. The results are compared with those of previous studies of block copolymer micelles and theories of block copolymer micellization. The following publication treats the results within a new theoretical framework.

Introduction

Micellization phenomena have been an important area of research in colloid science for a long time. Initially, most of the work centered on low molecular mass amphiphiles,[1-4] but in the last few decades, micelles made of block copolymers have also received considerable attention.[5-9] In solvents which are selective for one of the blocks, copolymers form aggregates which contain rather dense cores of the insoluble blocks, surrounded by diffuse outer shells (coronas) formed from the soluble blocks. The morphologies and the behavior of the block copolymer micelles resemble, in many respects, those of the low molecular mass amphiphiles. In both systems one can distinguish several different types of micelles; for example, aggregation can occur to form cores which are small and spherical or long and rodlike.[10-12] Other types of structural variations have also been encountered. For example, in low molecular mass amphiphiles as well as amphiphilic block copolymers, one can speak of either regular micelles, consisting of a hydrophobic core surrounded by the ionic or other hydrophilic species, or of inverse micelles, consisting of a hydrophilic core and hydrophobic corona.[13,14]

Critical Micellization Phenomena. Micellization of both low molecular mass amphiphiles and amphiphilic block copolymers is a process in which critical phenomena are important.[2,15,16] Thus, when low molecular mass amphiphiles are studied as a function of the total concentration, it is observed that micelles exist only above a certain minimum concentration, i.e., the critical micelle concentration (cmc). The cmc can, most conveniently, be defined as that concentration below which only single chains are present but above which both single chains and micellar aggregates can be found. Similar critical phenomena are observed when micellization is investigated as a function of temperature. If, for example, above a certain temperature one finds only single chains, while below that temperature both single chains and micelles coexist, then we can speak of a critical micelle temperature (cmt). Similarly, critical micelle solvent concentrations can also be involved. In general, block copolymer amphiphiles exhibit the same types of phenomena. However, it should be noted that, in general, critical micelle phenomena in block copolymer systems occur at very much lower concentrations than in low molecular mass amphiphiles.[17-20]

Because of the importance of the micellization process in a wide range of industries, a lot of attention has been devoted not only to experimental studies of micelles but also to thermodynamic and theoretical investigations. Micelle formation requires the presence of two opposing forces: an attractive force between the amphiphiles leading to aggregation and a repulsive force that prevents unlimited growth of the micelles into a distinct macroscopic phase. Aggregation of low molecular mass amphiphiles has been described by different thermodynamic approaches, such as the phase separation model, the mass action law model, the multiple equilibrium model, etc.[21] It was found that the micellization process of block copolymers as well as some low molecular mass amphiphiles is sufficiently cooperative to yield colloidal particles with a narrow size distribution and a high aggregation number. The micellization process in these systems obeys the scheme of closed association.[22,23] In terms of this model, the standard Gibbs free energy of micellization, $\Delta G°$, per mole of copolymer chains, is given by

$$\Delta G° = RT \ln \mathrm{cmc}$$

The thermodynamic factors responsible for the association of block copolymers in organic solvents are different from those for amphiphiles in aqueous media. Micelle formation by amphiphiles is mainly due to a positive standard entropy of micellization.[24] In this case, an attractive force arises from the hydrophobic interactions which are a result of a reorganization of the structure of water which takes place when the hydrocarbon units are removed from it. On the other hand, for block copolymers in selective organic solvents, it was shown that the enthalpy contribution to the free energy change is solely responsible for the association.[25]

Methods of cmc Determination. Many techniques are available for the determination of critical micelle concentrations. In principle, one can use any physical property which depends on the particle size or the number of particles. Most frequently, breaks or discontinuities in

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plots of such properties as the surface tension, electrical conductivity, osmotic pressure, interfacial tension, or light scattering as a function of concentration have been used for this purpose. Critical micelle concentrations can also be determined from the change in the spectral characteristics of some dye probes added to the surfactant solution.

Since the cmc's of block copolymers are normally much lower than those of low molecular mass surfactants, cmc determinations using some of the above techniques to the study of micellar properties as well as the determination of the onset of block copolymer micellization has been made in recent years.[15,19] However, there are still relatively few studies devoted to the determination of cmc values for block copolymer micelles. Light scattering is known to be one of the most powerful techniques for the determination of the size, shape, and aggregation numbers of micelles (by static light scattering) as well as values of the diffusion coefficient of the micelles (by dynamic light scattering). However, scattering techniques are able to detect the onset of micellization only if the cmc occurs in a concentration region where this technique is sensitive. For block copolymers in water, this is not often the case. Moreover, light scattering experiments, as was shown for PS-*b*-PEO copolymers in aqueous solutions by Winnik and co-workers,[26] can be complicated by phenomena of secondary association. Furthermore, for hydrocarbon/hydrocarbon block copolymers in organic solvents, Tuzar et al.[27] found that the light scattering data, namely, the concentration dependence of the diffusion coefficient and of the apparent mass-average molecular mass, strongly deviate from the pattern predicted by the model of closed association. This phenomenon can also be explained by the appearance of unstable particles much larger than the common micelles in the concentration region of cmc. Size-exclusion chromatography (SEC) has also been used to determine the single chain and micellar fractions of block copolymers in organic solvents[10,28,29] but occasionally suffers from the drawback of adsorption on the column support.

Recently, it has been shown that fluorescence techniques can be a valuable tool for the investigation of many micellar properties, including micelle formation, micelle–unimer equilibrium, micelle structure as well as chain dynamics, and kinetics of micelle formation and dissociation.[30–32] The techniques include steady-state and time-resolved fluorescence[19,33–35] and fluorescence depolarization,[36,37] along with quenching experiments[38–40] and energy transfer studies.[41,42] The studies of the fluorescence from polarity-sensitive probes such as pyrene yield information on the onset of micellization as well as micelle structure. Thus, a method developed by Wilhelm et al.[19] for the determination of the values of the cmc for PS-*b*-PEO copolymers in water is based on the fluorescent probe technique. This method is of particular importance for the present work.

cmc of Small Amphiphiles. Many investigations have been performed which concerned themselves with determining the values of the cmc in various systems of low molecular mass surfactants, and much effort was devoted to elucidation of the various factors (e.g., chemical structure, hydrophobic chain length, solvent content, presence of added electrolyte, nature of ionic group, temperature, etc.) that determine the concentration at which micelle formation becomes significant, especially in aqueous media.[1,17] For nonionic and ionic surfactants in water, linear relationships have often been observed between the logarithm of the measured cmc values and the number of C atoms in the hydrophobic "tail" of the surfactant.[1–4] In general, the cmc decreases as the number of carbon atoms in the hydrophobic group increases, up to about 16 C atoms. It has also been observed that ionic surfactants have much higher cmc's than nonionic surfactants containing equivalent hydrophobic groups. Also, surfactants containing more than one hydrophilic group in the molecule show higher cmc's than those with only one hydrophilic group and the same hydrophobic group. cmc values in aqueous solutions also reflect the degree of binding of the counterion to the micelle, increased binding of the counterion causes a decrease in the cmc of the surfactant.[43]

Micellization of Nonionic Block Copolymers. While there is extensive information on the micellization of low molecular mass amphiphiles, much less work has been done on block copolymers in this context. The studies on block copolymer micelles concern the nature of the core, the corona, and the solvent. For nonionic block copolymers, one can consider two kinds of systems. The first, to be reviewed here only very briefly, involves block copolymers containing two different hydrophobic segments, while the second kind consists of amphiphilic block copolymers.

Extensive studies of the hydrocarbon/hydrocarbon block copolymers were performed by Price and co-workers on systems such as the polystyrene-*b*-poly(ethylene/propylene) (PS-*b*-PEp) copolymers in *n*-decane and in *N*,*N*-dimethylacetamide[10] as well as on polystyrene-*b*-polyisoprene (PS-*b*-PI) in *n*-hexadecane.[10–12] These systems were studied by a wide range of techniques, including gel permeation chromatography, electron microscopy, ultracentrifugation, light scattering, and membrane osmometry. It was shown that the micelles have a very narrow size distribution, and, depending on the block length as well as preparative conditions, spherical micelles as well as extended wormlike aggregates can be formed. The study of the critical micelle concentration at different temperatures yielded information on the enthalpic contribution to the free energy change which is responsible for micelle formation. The effect of the polystyrene block length (which forms the micelle core) on the thermodynamic stability of PS-*b*-PI copolymers in *n*-hexadecane was also studied.[44] The values of ΔG° and ΔH° were found to be strongly dependent on the molecular mass of the polystyrene block, both becoming more negative as the molecular mass increased. The important role of the block lengths in the copolymer was also seen in a study of the dynamics of micelle dissociation in stopped-flow fluorescence measurements.[45] Many other investigations indicate that the copolymer structure and the solvent composition and temperature markedly influence the free chain–micelle equilibrium, the micelle structure, and the dynamics of the unimer-micelle exchange.[46–49]

Of great relevance to the present work are the studies on nonionic diblock copolymers containing a hydrophobic and a hydrophilic segment. Micelle formation in these systems has been studied in different polar and nonpolar solvents, and micellar properties, such as the size of the aggregates, the occurrence and values of the critical micelle concentration, the structure of the micelles, etc., have been investigated to some extent as a function of the molecular parameters of the copolymer and the solvent.[50–58] Static and dynamic light scattering studies as well as electron microscopy measurements of amphiphilic diblock and triblock copolymers with a polystyrene core suggested that micelles exist in two narrowly distributed populations.[26,59] A detailed analysis of PS-*b*-PEO micelles in water revealed normal spherical core–shell micelles and loose micellar clusters consisting of tens of micelles. A fluorescent probe study gave the values of the critical micelle concentrations for these systems.[19] Micelles based on block copolymers of polystyrene and poly(methacrylic acid) have also received attention recently. These systems will be treated below along with their ionic counterparts.

Micellization of Ionic Block Copolymers. The present section of this brief review deals with ionic block copolymers. Micelles with an ionic core (block ionomers) based on block copolymers of polystyrene and neutralized poly(methacrylic or polyacrylic acid) (PMAA or PAA) have been investigated extensively in this laboratory.[29,60–63] It was shown that block copolymers consisting of short segments of poly(sodium methacrylate) attached to long PS chains yielded extremely stable reversed micelles in organic solvents.[60] Size-exclusion chromatography allowed the determination of the aggregation numbers which were in good agreement with those determined by the dynamic light scattering.[61] In another study,[62] the partition coefficient of water was determined between water in the hydrocarbon solvent and water in the micelle core. It was shown also that Gibbs free energies for the transfer of water from the solvent to the core were linearly related to the Gibbs free energies calculated from the solubility of the water in the various solvents. In the most recent study[29] it was shown that the critical micelle length (cml) is a more convenient concept than the critical micelle concentration in these systems. The value of cml, i.e., the length below which the ionic block becomes soluble in a solvent like THF at a particular total polymer concentration, is on the order of 2–3 units and is independent of the polystyrene block length in the corona. Other studies on these systems are underway.

Many studies were performed on ionic block copolymers in which the hydrophobic segments form the core and the ionic segments are in the corona.[9,64–67] While most of these studies concerned themselves with systems in which the ionic chains have a high charge density, some studies were devoted to the systems with a low charge density in the corona. Thus, in one of those studies block copolymers of polystyrene–*n*-poly(*tert*-butylstyrene) in dimethylformamide were compared with those containing 3.2% sulfonated polystyrene.[68] It was shown by static and dynamic light scattering and viscometry that block copolymers containing ionic groups in the corona have a much larger overall size despite their smaller aggregation numbers when compared to the nonionic polymers. This behavior can be interpreted as arising from the repulsion effect of the ionic charges on the polymer in the corona.

Micelles prepared from block polyelectrolytes, i.e., systems with a hydrophobic core and an ionic corona in aqueous solutions, have also received attention. The first studies on these systems by Selb and Gallot[64] dealt with PS-*b*-poly(4-vinylpyridinium) copolymers in water–methanol–LiBr mixtures. The micellization process was studied using static light scattering, viscometry, and sedimentation velocity. It was shown that micelles exhibit a starlike structure, and the micellization process as well as micelle behavior was found to be strongly dependent on the solvent composition, temperature, salt concentration, and insoluble polystyrene block length.

It should be pointed out that the behavior of block polyelectrolyte systems is considerably more complicated when compared with 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 small ions, as well as the charge density along the chain and the degree of neutralization. Thus, the formation and properties of PS-*b*-PMAA micelles, such as their ability to solubilize and release hydrophobic species, were found to be strongly dependent on pH and ionic strength; micelle behavior in this system was found to depend significantly on the hydrophobic interactions in the poly(methacrylic acid) shell at low pH.[65–67] Quasi-elastic light scattering (QELS) and viscosity measurements indicate that, at low ionic strength and at rather high degrees of ionization of the carboxylic groups of the PMAA block, the electrostatic repulsion of highly charged sperical micelles results in the formation of long-range order in micelle solutions.[67]

Theories of Micellization in Block Copolymers. Not surprisingly, block copolymer micelles, in view of their complex behavior, have received considerable theoretical attention.[69–77] Most of the theoretical studies dealt with the calculation of the micelle core radius, the shell thickness, and the aggregation number; some of the theories also allowed the prediction of the critical micelle concentration.[69,70,75–77] In general, one can use different approaches to describe micelle properties. Thus, the mean-field model assumes a constant shell density, i.e., uniform concentration of polymer segments within the shell, independent of the distance from the micellar core.[69–71] Theories based on this model can be applied only to micelles with a large core size. Another approach, i.e., the star model, assumes that the segment concentration in the shell decreases with increasing distance from the micellar center.[72] This theory fits the experimental data concerning the systems containing a small core and a large corona much better by comparison with the mean-field approach. It should be noted, however, that the results obtained by Xu and Winnik[78] for PS–PEO diblock and PS–PEO–PS triblock copolymer micelles in water provide good support for these two very different models for copolymers with large cores. In this study, the star model was incorporated into the analysis of QELS data to obtain aggregation numbers and core radii. These parameters were then used to test the validity of the mean density model by calculation of the interaction parameter of PEO with water and of PEO with PS. The data obtained were found to be in very good agreement with values in the literature.

To calculate detailed micelle properties, one needs to describe the free energy of the system and to minimize it using scaling approaches. The various theories use for the minimization procedure either the total Gibbs free energy of the system[71] or the Gibbs free energy of the isolated micelle.[23,76]

Thus, the critical micelle concentration of the symmetric diblock copolymers in the homopolymer matrix was investigated by Liebler et al.[70] and the treatment extended for the case of asymmetric triblock copolymers by Balsara et al.[79] This approach provides a numerical prediction for the cmc under the conditions of strong segregation and shows the cmc dependence on the number of units in the insoluble block as well as on the interaction parameter. Recently another approach based on a simulation of a cubic lattice of micelle formation under conditions of relatively weak segregation was developed.[80] It demonstrated also that the cmc is strongly affected by variation in the size of the insoluble block.

One of the most extensive thermodynamic treatments of block copolymer micelles has been proposed by Nagarajan and Ganesh.[76] It considered the copolymer–solvent system to be a multicomponent solution consisting of solvent molecules, singly dispersed copolymer molecules, and micelles. By minimizing the free energy of this system, an expression for the equilibrium size distribution of micelles was obtained. The analysis of micellization in the pseudo phase approximation allowed one to visualize the influence of different molecular parameters on the size of the equilibrium micelles and to calculate micelle parameters, including the cmc, as a function of the copolymer and solvent characteristics. This theory predicts that the micelle size is influenced not only by the insoluble block but also by the solvent compatible block. The theory of Nagarajan and Ganesh dealing with diblock copolymers was extended and modified for the case of triblock copolymers by Prochàzka, Tuzar, and Kratochvil.[81] Results obtained showed that the association number of micelles of a diblock copolymer is substantially higher than that for micelles of a triblock copolymer of a comparable molar mass and composition and in the same selective solvent.

The fundamental theoretical understanding of the behavior of block copolymer micelles containing a polyelectrolyte block is still not as far advanced as that for neutral block copolymers. The studies which provide analytical scaling approximations have been developed for polyelectrolytes end-grafted to solid surfaces as well as to small colloidal particles.[82–84] Another study was concerned with the behavior of block copolymers composed of a neutral polymer joined to a polyelectrolyte and described the system under conditions of weak and strong segregation.[35] In that study, on the basis of the mean-field model, it was found that strongly charged diblocks in dilute solutions did not form stable micelles by contrast to weakly charged block copolymers. However, it should be pointed out that this study described micelle formation, accompanied by counterion condensation from the point of view of the mean-field model, which can fit only "crew-cut" micelles with short extended "hairs" sticking out from a relatively large core.

Purpose of the Present Study. The present publication is devoted to the investigation of the micellization of polystyrene-*b*-poly(sodium acrylate) in aqueous solution using the fluorescent probe technique. Specially, the purpose of this paper is the detailed examination of the influence of the molecular parameters of ionic block copolymers, especially the hydrophobic block length, on the onset of micellization. This is a part of an extensive study of ion-containing block copolymer micelles. In a future publication other aspects of the present system will be explored, such as the dependence of the cmc on the ionic block length, pH, and salt effect.

Experimental Section

Materials. The block copolymers of polystyrene-*b*-poly(*tert*-butyl acrylate) were synthesized by anionic polymerization in THF at −78 °C, as described previously in detail.[29] *sec*-Butyllithium was used as the initiator, LiCl was added to serve as a stabilizer for the poly(*tert*-butyl acrylate) living end, and α-methylstyrene was used as the end-capping agent of the poly(styryllithium) anion. A series of copolymers with an identical polystyrene block length and varying poly(*tert*-butyl acrylate) block lengths were obtained by several sequential additions of *tert*-butyl acrylate to the same block of polystyrene, each of which was followed by the withdrawal of a certain amount of polymer solution. The polymers were precipitated into water and dried under vacuum at 80 °C.

The molecular weights and the molecular weight distributions of the polymers were determined by size-exclusion chromatography (SEC) in THF. The lengths of the poly(*tert*-butyl acrylate) blocks were calculated by subtraction of the molecular weight of the polystyrene block from those of the block copolymers. For one series of copolymers, the compositions were also determined by ^{1}H NMR; the values are in good agreement with those obtained by SEC.

The polymers were hydrolyzed by refluxing in 1 M HCl in 1,4-dioxane for more than 10 h, after which the solvent and the HCl were removed by evaporation at 60 °C. The polymers were redissolved in methanol and neutralized by adding the polymer solution to 0.2 M NaOH in isopropyl alcohol. The polymer precipitated on neutralization. The neutralized polymers were then filtered and washed with isopropyl alcohol until the filtrate became neutral and were dried under vacuum at 80 °C. The solid-state ^{13}C NMR spectra of the polymers showed that the peak at 175 ppm, due to the carbon of the ester carbonyl, shifted to 188 ppm, a chemical shift characteristic of the carbon of an ionized carboxylate, while the two peaks of the quaternary carbon and methyl carbon of the *tert*-butyl ester groups at 81 and 27 ppm, respectively, disappeared. This indicates that the hydrolysis and the neutralization were complete.

Sample Preparation. All solutions were prepared by dissolving the block copolymer in doubly distilled deionized water (Milli Q) to give solutions of final concentrations from 2.0 to 10.0 mg/mL. The polymer–water mixtures, in sealed glass ampules, were heated with stirring for 20–24 h 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 from 10^{-4} to 10^{-2} mg/mL. Dilutions were performed with water or with a 0.02 M buffer solution (sodium phosphate at pH 9).

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 to give final pH values of 9–9.5. 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.[85,86] To each flask was added a measured amount of a stock solution, followed by doubly distilled water. The flasks were heated with stirring 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 samples ranged in polymer concentration from 10^{-6} to a maximum of 1–5 mg/mL. In parallel experiments, lower pyrene concentrations were also studied (8.0×10^{-8} and 1.2×10^{-7} M) to check the influence of probe concentration on fluorescence data and the resulting cmc values.

Aqueous Size-Exclusion Chromatography. The SEC measurements were performed at room temperature on a liquid chromatography apparatus equipped with an LKB 2248 HPLC pump and a Waters 410 differential refractometer. The column was an OHpak SB-80M from Shodex. The neutralized polymers were dissolved in 0.1 M NaCl to a concentration of about 2 mg/mL. The solutions were filtered through a 0.5-μm membrane filter before injection. Aqueous NaCl solutions of different concentrations were used as the eluent at 1 mL/min.

Viscometry. The viscosity measurements were carried out on an Ubbelohde viscometer at 25.0 °C. The block polyelectrolyte solutions in pure water were filtered through a 0.5-μm membrane and kept at temperatures of 25, 80, and 100 °C for varying times. The viscosities of the solutions were measured at 25.0 °C as a function of storage time at these different temperatures.

Fluorescence Measurements. Steady-state fluorescent 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. For lower pyrene

Table I. Molecular Characteristics of Block Copolymers and Their Apparent cmc Values in Aqueous Solutions

sample	M_w/M_n			
PS-*b*-PANa	PS block	total	CMC_1 (mol/L)	CMC_2 (mol/L)
6-*b*-400	1.18	1.10	4.2×10^{-5}	2.5×10^{-5}
6-*b*-1000		1.16	1.8×10^{-5} [a]	1.6×10^{-5}
			1.5×10^{-5}	1.3×10^{-5}
11-*b*-350	1.13	1.06	4.3×10^{-6}	3.4×10^{-6}
11-*b*-1030		1.06	2.0×10^{-6}	1.5×10^{-6}
14-*b*-270	1.16	1.09	2.7×10^{-6}	2.5×10^{-6}
			3.6×10^{-6}	2.2×10^{-6}
14-*b*-620		1.11	2.0×10^{-6}	1.9×10^{-6}
			2.1×10^{-6}	1.7×10^{-6}
23-*b*-300	1.14	1.06	8.0×10^{-7}	3.7×10^{-7}
23-*b*-780		1.05	8.9×10^{-7}	7.1×10^{-7}
			5.1×10^{-7}	3.5×10^{-7}
23-*b*-1400		1.13	6.9×10^{-7}	5.2×10^{-7}
			4.7×10^{-7}	2.5×10^{-7}
28-*b*-330	1.09	1.05	1.2×10^{-6}	7.9×10^{-7}
			8.5×10^{-7}	5.9×10^{-7}
28-*b*-1560		1.07	7.2×10^{-7}	5.6×10^{-7}
			5.4×10^{-7}	4.0×10^{-7}
40-*b*-520	1.13	1.07	2.9×10^{-7}	2.1×10^{-7}
			2.6×10^{-7}	1.9×10^{-7}
40-*b*-2420		1.19	2.2×10^{-7}	1.7×10^{-7}
			1.7×10^{-7}	1.3×10^{-7}
86-*b*-390	1.09	1.21	1.6×10^{-7}	8.0×10^{-8}
			1.3×10^{-7}	8.9×10^{-8}
86-*b*-900		1.15	1.2×10^{-7}	6.3×10^{-8}
			1.1×10^{-7}	6.2×10^{-8}
110-*b*-380	1.08	1.10	8.0×10^{-8}	6.6×10^{-8}
			6.3×10^{-8}	5.0×10^{-8}
110-*b*-2360		1.21	5.7×10^{-8}	4.7×10^{-8}
			3.9×10^{-8}	4.1×10^{-8}

[a] All cmc determinations were performed at least in duplicate. Only one value is given if the results agree within less than 0.05 log units; all values are reported if the disagreement is worse.

concentrations, the signal-to-noise ratio was improved significantly by using a 2 s/0.5 nm or 4 s/0.5 nm integration time.

Results and Discussion

Size-Exclusion Chromatography. All polystyrenes and their copolymers with *tert*-butyl acrylate in THF gave one narrow SEC peak, with the polydispersity index (M_w/M_n) between 1.05 and 1.15. All the polymers used in the present study are listed in Table I, which shows the block lengths and polydispersities, along with other results to be discussed later. After hydrolysis and neutralization, the block polyelectrolytes (PS-*b*-PANa) in 0.1 M NaCl gave two peaks in the SEC chromatograms, in contrast to the behavior of poly(sodium acrylate) homopolymer which gave a single peak. The chromatograms are shown in Figure 1. The peak at the higher elution volume (8.6 mL) is located at almost the same position as that of homopoly(sodium acrylate) of comparable molecular weight. Therefore, it is assigned to molecularly dissolved single chains. The peak at the lower elution volume (7.4 mL) corresponds to an apparent molecular weight of 3×10^5 (as calibrated against homopoly(sodium acrylate)) and is attributed to the aggregates (regular micelles). Because of the star nature of the micelle, the real particle weight may be much higher.

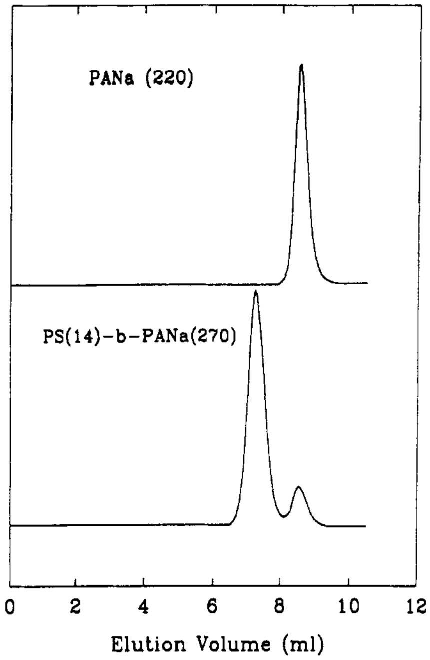

Figure 1. Size-exclusion chromatograms of poly(sodium acrylate) and block polyelectrolyte PS-*b*-PANa in 0.1 M NaCl.

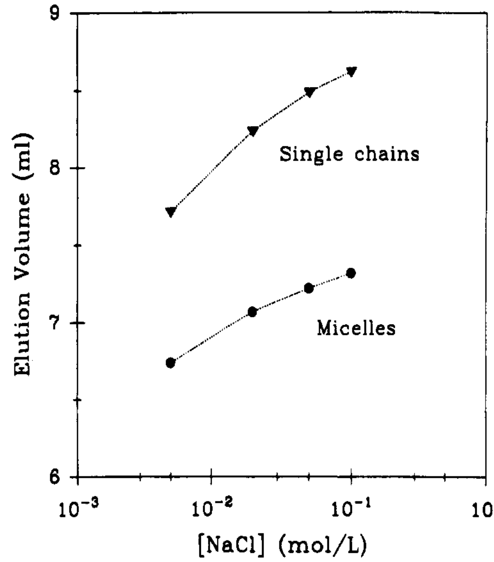

Figure 2. Elution volumes of PS(14)-*b*-PANa(270) as a function of NaCl concentration.

As the concentration of NaCl in the eluent was decreased, both the micelle peak and the single chain peak shifted to lower elution volumes due to the so-called polyelectrolyte effect, i.e., chain expansion caused by the electrostatic repulsion in pure water or aqueous solutions of low salt concentration. The elution volumes of both peaks are plotted as a function of the salt concentration in Figure 2. It is clear that the salt effect is more pronounced for the single chains than for the micelles. This can be explained by the fact that the polymer chains in the corona of the micelles are already expanded by the steric exclusion and, because of the polyelectrolyte chains in their vicinity, are already at a somewhat elevated salt content. Effects due to microsalt addition are therefore less significant.

It is worth recalling that the block copolymers with long polystyrene blocks and short poly(sodium acrylate) or poly(sodium methacrylate) blocks form reverse micelles in organic solvents such as toluene, THF, DMF, etc.[29,60-63] The SEC of those block copolymers also showed a micelle peak and a single-chain peak. Thus, as might be expected, the same type of ionic block copolymers can be used to prepare either reverse micelles in organic solvents or regular micelles in water by changing the relative block lengths and methods of sample preparation.

The dependence of the fraction of micelles and single chains in the micellar solution on the total polymer concentration is shown in Figure 3. It can be seen that both single-chain and micelle concentrations increase with

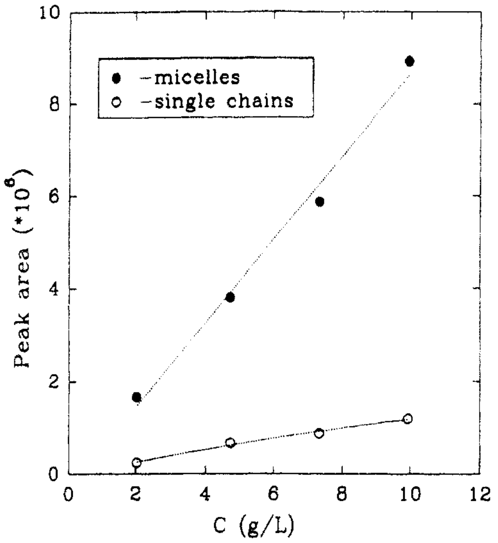

Figure 3. SEC peak area of micelles and single chains as a function of PS(14)-*b*-PANa(270) concentration.

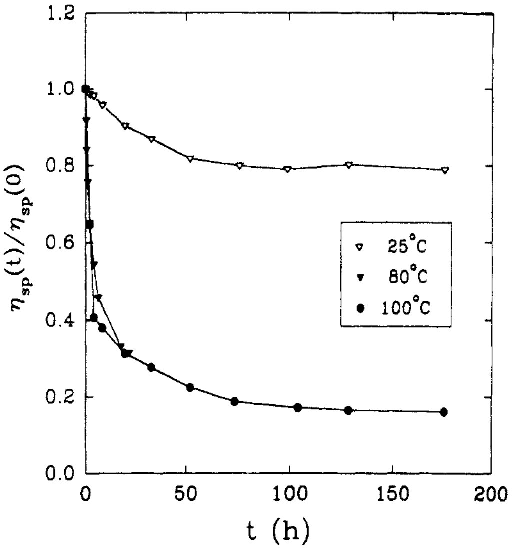

Figure 4. Viscosity of PS(40)-*b*-PANa(620) in water as a function of the storage at 15, 80, and 100 °C.

increasing polymer concentration. This increase might seem surprising because, according to the closed association model of micellization,[22,23] the total concentration of single chains above the critical micelle concentration should remain constant with increasing polymer concentration. However, this phenomenon can be understood in the light of the mixed micellization model.[87] A new version of this model along with interpretation of the present data in light of this model is presented in the subsequent paper in this issue.

In a previous publication[29] dealing with a SEC of block ionomer (reverse) micelles, SEC traces were used to calculate the so-called critical micelle lengths for the insoluble ionic blocks. In the present case, the critical micelle length concept is not as useful because of the smaller free energy of micellization. Furthermore, serious column adsorption problems do not allow more than semiquantitative estimates to be obtained from the present SEC data. However, the present results do allow us to conclude unambiguously that both micelles and single chains are present in a solution of these block copolymers over wide ranges of polymer and salt concentrations.

Dependence of cmc and Viscosity on Thermal History. As was pointed out in the introduction, block copolymer micelles in aqueous solutions tend to associate to form supermicellar aggregates, which show behavior similar to that of the secondary aggregates of micelles from nonionic surfactants in water.[88] This phenomenon was observed for both nonionic[26,59] and ionic[67] block copolymers. As was suggested from the results of the quasi-elastic light scattering study for block polyelectrolyte micelles of poly(styrene-*b*-sodium methacrylate) at pH 9, the repulsion of the highly stretched polyelectrolyte chains in the shell leads to the formation of partially organized structures in solution, which can be considered as clusters of structurally organized micelles.[67] While the detailed mechanism of this type of aggregation has not been elucidated completely, it can be related to multiple chain entanglement, as has been shown for homopolyelectrolytes.[89]

One of the purposes of the present study was to determine whether this type of aggregation influences the cmc. To detect such aggregates and to investigate the kinetics of the disentanglement process in a preliminary way, both light scattering and viscosity can be used. In the present study it was noted that freshly prepared solutions of PS-*b*-PANa are more viscous than those after storage. The fresh solutions also show some heterogeneity in that small particles of gel can be detected, especially for copolymers with rather long poly(sodium acrylate) blocks. This is related to the dissolution process and depends on the ionic block length as well as the aggregation number of micelles.

In an attempt to find out how quickly the dissociation of these higher order aggregates proceeds, the viscosity of the solutions was monitored as a function of the residence time at three different temperatures; 25, 80, and 100 °C. Polymer solutions were heated for different periods, followed by cooling to room temperature and immediate viscosity measurements. The results of these experiments are shown in Figure 4. As can be seen, the viscosity decreases with time, and initially the decay is much more rapid at 80 and 100 °C than at 25 °C. A plateau is reached after ca. 80 h, the plateau for 100 °C being much lower than that for 25 °C. Logarithmic plots (not shown) also suggest that the plateau is real. It is seen that the solutions kept at 25 °C are very different from those kept at 100 °C for comparable time scales. This implies that the final state depends on the thermal history. Further studies need to be performed to understand this effect in detail.

Since it was of interest to see whether the cmc was affected by the phenomena which give rise to the thermal history observed here, the cmc's of the systems prepared in different ways were determined. cmc determinations were performed on samples stored at room temperature for ca. 1–40 h, and the results, compared with those performed for samples which had been heated at 100 °C for 1, 10, 24, and 48 h. The heating was performed in sealed ampules. While the detailed results of the cmc studies will not be presented until later, it is worth pointing out at this time that the cmc values obtained for all the above samples were the same within experimental error. It should be mentioned that the experimental values obtained for unheated polymer solutions show more scatter than those for the heated samples, but the averages are the same. These data indicate that thermal history does not have any effect on the cmc values. This also shows that the phenomena which are responsible for the viscosity changes with time are not related to any aspect of the micelle–single chain equilibrium. It is much more likely that the drop of the viscosity with time of storage is related to the disruption of some supermolecular aggregates which exist as a result of entanglements of the highly charged polyelectrolyte chains.

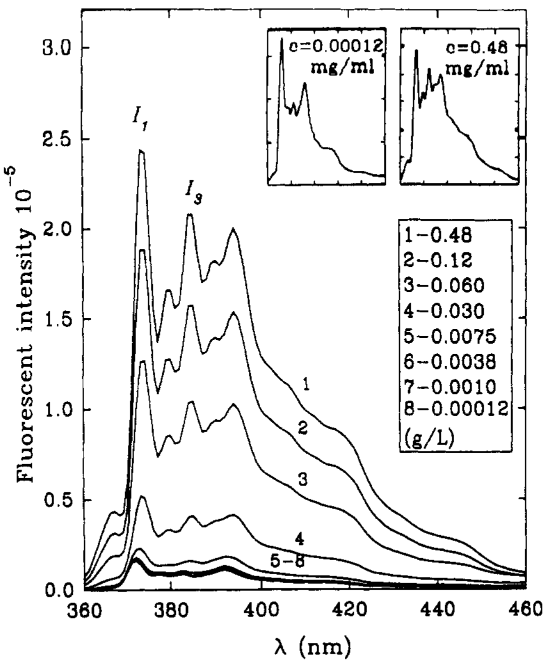

Figure 5. Fluorescence spectra of pyrene (5×10^{-7} M) in aqueous solutions of PS(23)-*b*-PANa(300) at different concentrations, λ_{em} = 339 nm. Insets show spectra at the highest and lowest concentrations adjusted to give the same peak height for I_1.

Fluorescence Probe Study. Information about the onset of micellization of the block copolymer systems was derived from steady-state fluorescent probe studies. Pyrene was chosen as the fluorescent probe because of its photophysical and other properties.[30] It is strongly hydrophobic, and its solubility in water is very low. In the presence of a hydrophobic phase or microphase such as that found in micelles or similar macromolecular systems, pyrene is preferentially solubilized into the interior of the hydrophobic regions of these aggregates.[31-35] In recent years, pyrene has been successfully employed as a fluorescent probe in the study of low and high molecular weight regular micelles,[19,37-39] water-soluble macroaggregates,[90,91] polysoaps,[40,92] membranelike systems of phospholipid dispersions,[31,93,94] self-assembling monolayers,[95,96] etc., to mention just a few examples. These studies focused on the dynamics of quenching of pyrene monomer fluorescence,[38,39] excimer and exciplex formation processes,[33,65-67,90,92] fluorescence depolarization,[36,37] and an analysis of the vibrational fine structure of the pyrene emission spectra.[19,31,86] In the present study steady-state pyrene fluorescence was employed to detect the formation of the hydrophobic regions of the micellar cores.

Typical emission and excitation spectra of aqueous solutions of PS-*b*-PANa block copolymers at various concentrations in the presence of 5×10^{-7} M pyrene are shown in Figures 5 and 6. Both kinds of spectra, emission and excitation, are characteristic of pyrene monomer fluorescence in specific microenvironments. With increasing polymer concentration in an aqueous solution of pyrene, several significant changes in the fluorescence can be observed. First, there is an increase in the quantum yield of the fluorescence. Also, there are changes in the vibrational fine structure of the emission spectra. Finally, one can see a shift of the (0,0) band from 333 to 338.5 nm in the excitation spectra. These changes accompany the transfer of pyrene molecules from a water environment to the hydrophobic micellar cores and thus provide information on the location of the pyrene probe in the system.

An enhancement of the quantum yield of pyrene fluorescence can be seen from an increase in the fluorescent intensity *I* with increasing polymer concentration; it is worth recalling that the pyrene concentration is constant. This increase in *I* reflects the increase of the lifetime of the excited state of the pyrene, which is significantly different for the different probe surroundings.[19,86] Quantum yields of a fluorophore are mainly a function of the polarity of the solvating environment, but usually other contributions such as quenching, internal conversion, intersystem crossing, energy transfer, photochemical reactions, and complex formation in the excited state may also affect the quantum yield. In our case these additional factors can be neglected.

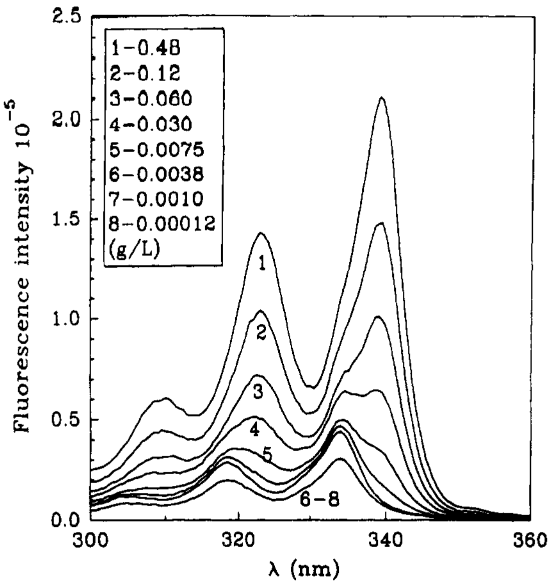

Figure 6. Excitation spectra of pyrene (5×10^{-7} M) in aqueous solutions of PS(23)-*b*-PANa(300) at different concentrations, λ_{ex} = 390 nm.

Pyrene is one of the few condensed aromatic hydrocarbons which shows significant fine structure in its monomer fluorescence spectra in solution. As was shown by Nakajima[97] and Kalyanasundaram[86] the vibrational fine structure intensities undergo significant perturbations on going from nonpolar solvents to polar solvents with a high dipole moment and a high dielectric constant. The intensity ratio between the first and third highest energy (frequency) emission peaks, known as the I_1/I_3 ratio, has been shown to correlate well with solvent polarity. The I_1 peak, which arises from the (0,0) transition from the lowest excited electronic state, is a "symmetry-forbidden" transition that can be enhanced by the distortion of the π-electron cloud. On the other hand, the I_3 peak is not forbidden and thus is relatively solvent-insensitive. In a wide variety of aromatic hydrocarbons, as has been shown earlier[98] (Ham effect), forbidden vibronic bands in weak electronic transitions show marked intensity enhancements under the influence of solvent polarity. Thus, the ratio (I_1/I_3) serves as a measure of the polarity of the environment.[86] These values range from 1.9 for water, to 0.95 for a polystyrene film, and to about 0.5 for nonpolar solvents such as hexane and are thus very helpful for determining the location of the pyrene probe in the micelles.

Much information on the onset of block copolymer aggregation can also be obtained from the analysis of pyrene excitation spectra. As was shown by Wilhelm et al.,[19] the concentration dependence of the I_{338}/I_{333} ratios of the (0,0) band of pyrene is more sensitive to the critical micelle concentration than lifetime measurements or fluorescent emission. Moreover, it was indicated that the concentration dependence of the excitation spectra is

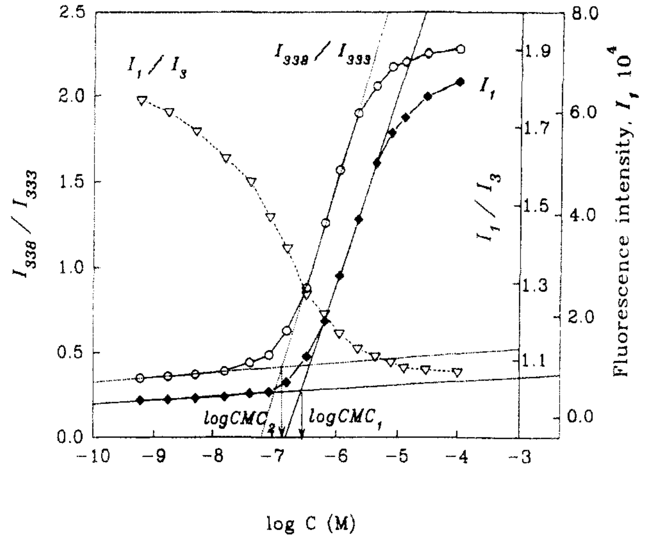

Figure 7. Plots of the fluorescence intensity I_1 and intensity ratios I_1/I_3 (from pyrene emission spectra) and I_{338}/I_{333} as a function of PS(23)-*b*-PANa(780). Values of cmc$_{\text{app}}$ are indicated by arrows.

sensitive to a true onset of aggregation.

Plots of the fluorescent intensity I, the I_1/I_3 peak height ratio from emission spectra, and the intensity ratio I_{338}/I_{333} from excitation spectra are shown in Figure 7 as a function of the copolymer concentration. These values remain fairly constant or change only slightly below a certain concentration; above that concentration they change substantially, reflecting the partitioning of the pyrene between the aqueous and micellar phases once the latter is formed.

Below the critical micelle concentration, there are no micelles present in the system and the pyrene fluorescence spectrum corresponds to that in water, with an I_1/I_3 ratio of about 1.6–1.8. As the polymer concentration increases above the cmc, pyrene is progressively solubilized into the hydrophobic interior, as illustrated by the drastically decreased I_1/I_3 ratio in the intermediate region of polymer concentration. The I_1/I_3 values of about 1.05–1.12 for the higher concentration regions of PS-*b*-PANa copolymer indicate that the location of the pyrene probe is primarily in the nonpolar environment of the micellar core. These ratios were found to be almost independent of the length of the polystyrene block for the range of 6–110 units.

It was shown before for low molecular weight detergents[86] that, above the critical micelle concentration, the I_1/I_3 values remain fairly constant and independent of the surfactant concentration, or of the length of the hydrocarbon chain, but that they depend on the nature of detergent. It was suggested that these values can be taken as a measure of the compactness of the micellar core and head-group structures as well as the extent of surface charge. Another explanation can also be sought in terms of the extent of water penetration into these micellar systems.[99] The I_1/I_3 values for PS-*b*-PANa were found to be very similar to those for ionic detergents (sodium laurate, 1.042; sodium lauryl sulfate, 1.136) but below those for nonionic detergents (Triton X-100, 1.30) or cationic detergents with large counterions (dodecyltrimethylammonium chloride, 1.37). The I_1/I_3 values for PS-*b*-PANa lie slightly below those for PS-*b*-POE diblock copolymers[19] which is probably a result of the greater degree of compactness of the polystyrene core in block copolymers containing a charged polyelectrolyte rather than POE chains in the outer shell.

The ratios of I_{338}/I_{333} are obtained from the (0,0) bands of the pyrene excitation spectra. At low polymer concentrations, this ratio takes the value characteristic of pyrene in aqueous media, while at high concentrations it takes the value of pyrene in a hydrophobic environment. It should be noted that these ratios are reproducible for different pyrene concentrations (8×10^{-8}–6×10^{-7} M) and different block copolymer samples; they are very useful in comparing different block copolymer systems.

cmc Determination from Fluorescence Data. As was shown above, the quantum yield of probe fluorescence I and the ratios I_1/I_3 and I_{338}/I_{333} show substantial changes with polymer concentration. In these plots, major changes in slope are related to the onset of micellization and provide a quantitative method of cmc determination. It should be stressed that the determination of a true onset of aggregation is a rather complex question. In the present publication, three different ways were used to obtain cmc values from the original fluorescence spectra, which gave five numbers, all of which fell into a Δlog cmc range of 0.01–0.3 for the different samples.

Five different methods were used to determine the cmc values. In the first and second, data from both original emission (I) and excitation (I_{338}/I_{333}) spectra were treated, at first, by a simple procedure involving points of intersection of extrapolated straight line segments, which yields apparent cmc values. These will be referred to as cmc$_1$ and cmc$_2$, respectively. In another procedure, the excitation spectra were treated using a deconvolution process, with the resulting data yielding cmc values as intersection points in a plot of the intensity ratios vs concentration; these will be referred to as cmc$_3$. Finally, the sigmoidal curves, obtained from the original and the deconvoluted excitation spectra, were treated using the approach suggested by Wilhelm et al.,[19] which takes into account the partitioning of pyrene in the micellar and aqueous phases; the cmc values obtained this way will be called cmc$_4$ and cmc$_5$, respectively. These procedures will be discussed in greater detail below.

cmc$_1$, cmc$_2$, and cmc$_3$ are all apparent cmc's, collectively referred to as C_{app}; those were determined from the concentration dependence of the fluorescence intensities I as well as the I_{338}/I_{333} ratios. They were taken as the intersection of straight line segments, drawn through the points at the lowest polymer concentrations, which lie on a nearly horizontal line, with that going through the points on the rapidly rising part of the plot. An example is shown in Figure 7. It should be recalled that the I_1/I_3 ratios were used only to ascertain the location of the pyrene probe; they were not used as a cmc determination procedure because these values depend on the wavelength of excitation. Thus, when the excitation wavelength, λ_{ex}, is 339 nm, the plot of the I_1/I_3 ratio is shifted in favor of the pyrene in a hydrophobic environment, but when $\lambda_{\text{ex}} = 333$ nm, it is strongly weighted toward pyrene in an aqueous medium. The apparent cmc values obtained from excitation spectra (cmc$_2$), in most cases, lie slightly below those from emission spectra (cmc$_1$); usually the difference falls into a Δlog cmc range of 0.1–0.3. A summary of the C_{app} values determined by the different methods described above for the various samples is given in Table I.

An alternative method of data treatment consisted of the deconvolution of the excitation spectra using a nonlinear curve-fitting program (Peak Fit). The excitation spectra were fitted to a sum of four Gaussian peaks, as shown in Figure 8, with maxima at 306, 322, 333 (characteristic of pyrene in an aqueous environment), and 338.5 nm (characteristic of pyrene in a hydrophobic environment). Since the deconvolution procedure, on occasion, gave deconvoluted plots in which the maxima for the third

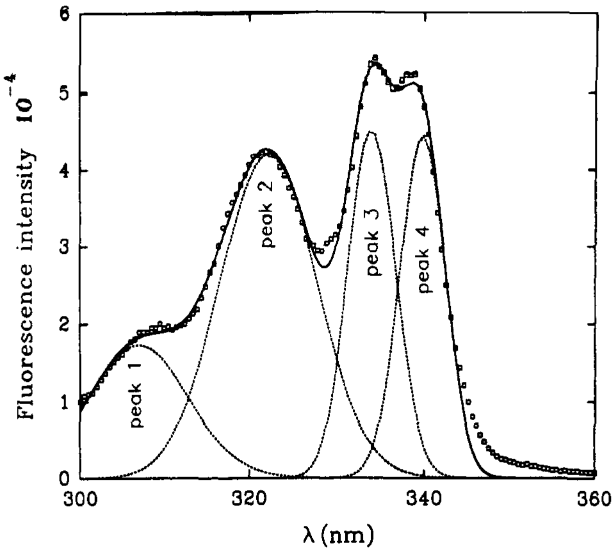

Figure 8. Deconvoluted excitation spectra of pyrene (5 × 10^{-7} M) in an aqueous solution of PS(23)-*b*-PANa(780) at $c \approx 0.11$ g/L.

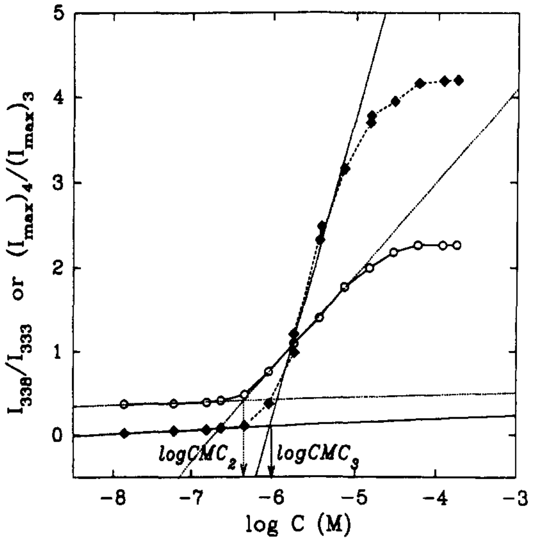

Figure 9. Plots of intensity ratios obtained from nondeconvoluted (○) and deconvoluted (◆) excitation spectra of PS(23)-*b*-PANa(300).

and fourth peaks were not exactly at 333 and 338 nm, the ratios of intensities of the maxima of these peaks (I_{max4}/I_{max3}) were taken. These data, as well as the ratios I_{338}/I_{333} from the nondeconvoluted spectra as a function of the polymer concentration, are shown in Figure 9. It should be mentioned that, in an alternative procedure, the ratios of the peak areas rather than absolute peak highs were taken from the deconvolution data. The cmc values obtained by these two procedures were identical. This is not surprising in view of the nearly identical half-widths of these two peaks. Therefore, only results from the peak maxima plots are given.

From results such as those presented in Figure 9, the cmc values are obtained by the procedure described in the connection with Figure 5. These values (called cmc$_3$) are in good agreement with those obtained from the emission spectra (cmc$_1$). The data for Figure 9 were chosen because they give the worst deviation between cmc$_1$ and cmc$_3$. A comparison of these values is given in Table II for all the samples for which deconvolutions were performed.

It is tempting to identify the cmc values obtained as described above with the true onset of polymer aggregation. However, in cmc determinations, a number of factors need to be borne in mind. First of all, the polymer concentration ranges over 6–7 orders of magnitude. In the region of the apparent onset of micellization, the number of dye molecules present can equal or exceed the number of polymer molecules. Hence, 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. For example, polysoaps form only intramolecular (i.e., single chain) micelles. These systems have no multimolecular association, and consequently no cmc. In this case, the changes in the fluorescent signal are caused only by the partitioning of the fluorescent probe into different domains.[100] Hence, as soon as a new microphase or domains with properties which are significantly different from those in the bulk are formed, the pyrene probe will be present in both environments in accordance with the value of its equilibrium constants for those environments.

Hence, for the determination of the true onset of micellization in block copolymers, the influence on the data of the pyrene–unimer and the pyrene–micelle equilibria should be considered. The determination of the real onset of aggregation might also be complicated due to the existence of the monomolecular micelles in the concentration region below the critical micelle concentration. As was shown before,[64,101] in selective solvents, the insoluble block of the single-chain polymer may collapse to form these structures. This effect can be pronounced, especially for block copolymers with rather long polystyrene block lengths. In this case, collapsed polystyrene blocks can be treated like a microphase which can bind pyrene molecules preferentially in comparison with the bulk solution. The problem of single-chain micelles will be discussed below.

For the determination of the cmc as well as for the estimation of the effect of single chains, one needs to have a detailed understanding of the partitioning of the pyrene probe between the polystyrene and the aqueous phases. In this connection, one should first determine whether the apparent cmc values depend on the pyrene concentration. For this reason, several experiments were repeated with pyrene concentrations of 2 × 10^{-7} and 8 × 10^{-8} M. It should be noted that, for the lowest pyrene concentration, the sensitivity of the method is not high, and the scatter in the data is much greater than for other pyrene concentrations, so a longer integration time was used to accumulate spectra. The C_{app} values obtained from the excitation spectra using different pyrene concentrations are identical within experimental error.

In order to estimate the effect of the interaction of the pyrene with the polystyrene core of the micelle on the fluorescence data, the approach suggested by Wilhelm et al.[19] was used. These authors showed that the concentration dependence of the excitation spectra was sensitive to the true onset of block copolymer association. The ratio of pyrene in the micellar and water phases was calculated from the excitation spectra using the following equation:

$$\frac{[\mathrm{Py}]_m}{[\mathrm{Py}]_w} = \frac{F - F_{min}}{F_{max} - F}, \qquad \text{where } F = I_{338}/I_{333}$$

F_{min} and F_{max} correspond to the magnitudes of the I_{338}/I_{333} ratios in the flat regions at low and high polymer concentrations in plots of the type shown in Figure 9.

Pyrene binding to the micelles is described as a simple partition equilibrium between the micellar PS phase, which is taken to be spherical, and the water phase. Using this model, data from the excitation spectra can be recalculated.

Table II. Comparison of cmc Values As Determined by All Methods along with Partition Coefficients (K_ν) for Pyrene between the Aqueous Phase and Micellar Core

sample PS-*b*-PANa	cmc_1 (mol/L)	cmc_2 (mol/L)	cmc_3 (mol/L)	cmc_4 (mol/L)	cmc_5 (mol/L)	K_ν ($\times 10^{-5}$)
11-*b*-350	4.3×10^{-6}	3.4×10^{-6}	4.8×10^{-6}	2.8×10^{-6}	4.6×10^{-6}	1.9
23-*b*-300	8.0×10^{-7}	3.7×10^{-7}	9.2×10^{-7}	3.5×10^{-7}	8.3×10^{-7}	1.9
23-*b*-780	8.9×10^{-7}	7.1×10^{-7}	9.9×10^{-7}	4.4×10^{-7}	8.7×10^{-7}	2.2
23-*b*-1400	6.9×10^{-7}	5.2×10^{-7}	8.5×10^{-7}	4.3×10^{-7}	7.2×10^{-7}	2.5
40-*b*-520	2.9×10^{-7}	2.1×10^{-7}	3.2×10^{-7}	1.4×10^{-7}	3.0×10^{-7}	2.3
86-*b*-390	1.6×10^{-7}	8.0×10^{-8}	2.2×10^{-7}	6.9×10^{-8}	1.5×10^{-7}	2.4

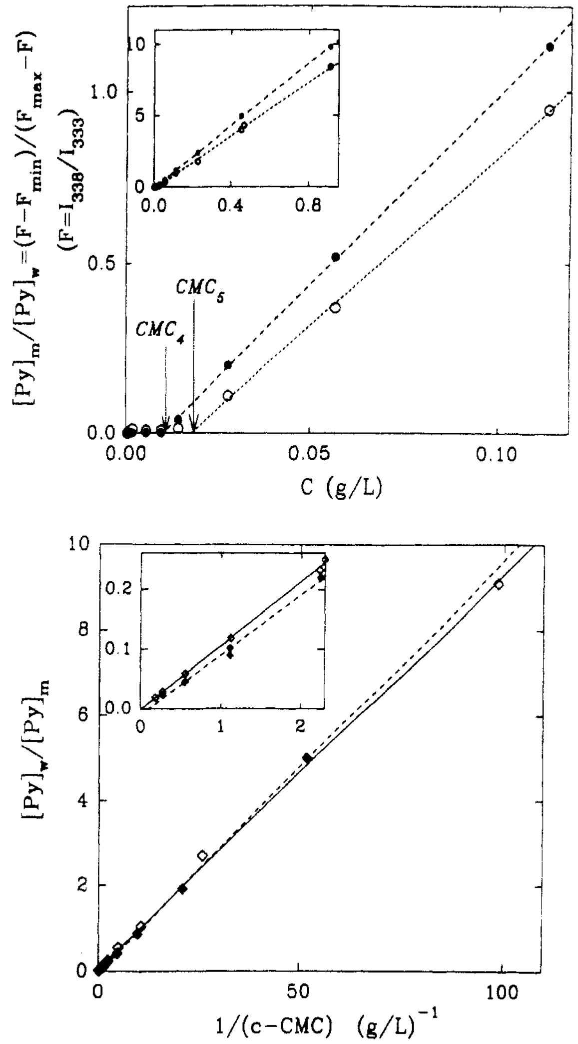

Figure 10. (a) Plot of $(F - F_{min})/(F_{max} - F)$ vs concentration PS(23)-*b*-PANa(300) from the data of nondeconvoluted (●) and deconvoluted (○) excitation spectra. The inset shows all the data, including those at highest concentration. (b) Plot of $[Py]_w/[Py]_m$ vs $(c - cmc)^{-1}$ for PS(23)-*b*-PANa(300) from the data of nondeconvoluted (◆) and deconvoluted (◇) excitation spectra. cmc_4 and cmc_5 are chosen as the cmc values. The inset shows an enlargement of the area near the origin.

These data were linearized with the following equation:

$$\frac{[Py]_m}{[Py]_w} = \frac{K_\nu \chi_{PS}(c - cmc)}{1000\rho_{PS}} \qquad (1)$$

where K_ν is the equilibrium constant for the partitioning of the pyrene between the aqueous and the micelle core phases, c is the total polymer concentration in g/L, χ_{PS} is the weight fraction of PS in the polymer, and ρ_{PS} is the density of the PS core of the micelle, which was assumed to have the same value as that of bulk polystyrene (1.04 g/mL).

When the data from both the original and the deconvoluted excitation spectra are plotted according to eq 1, it is seen that they can be fitted by two intersecting straight lines. An example is shown in Figure 10a for PS(23)-*b*-PANa(300). This sample was selected because it shows the largest discrepancy between the two cmc values. Both plots (obtained from the original and the deconvoluted excitation spectra data) have the same slope for polymer concentrations above the cmc. The only difference is in the value of the intercept on the concentration axis, which give the cmc's, which differ by ca. 0.2 log units. From the slope of the plots at higher concentrations, K_ν can be calculated. The K_ν values calculated for different block copolymers are shown in Table II. All the K_ν values are on the order of $(1.7-2.2) \times 10^5$. When one compares these values with those obtained by Wilhelm et al.[19] for PS-*b*-POE copolymers (3×10^5) and by Almgren[102] for sodium dodecyl sulfate (SDS) micelles (1.2×10^5), it is seen that the equilibrium constants for partitioning of pyrene between the aqueous and micellar phases for PS-*b*-PANa copolymers lie between those for the PS-*b*-POE and the SDS systems, but the differences are not large. The value of K_ν indicates that partitioning of pyrene into the hydrophobic micellar core phase is strongly favored.

Below cmc, the value of $[Py]_m$, as can be seen from Figure 10a, is zero for copolymers with short polystyrene blocks, which means that pyrene is not bound to the isolated polymer chains. However, for copolymers with polystyrene block lengths of more then 40 units, the value of $[Py]_m$ increases slightly with polymer concentration. This low but finite value of $[Py]_m$ is due to the pyrene associated with the collapsed single polystyrene chains, which behave like a microphase in terms of their interaction with pyrene.

The cmc values obtained by fitting the data to eq 1 can be confirmed by replotting those as a function of the inverse polymer concentration $[1/(c - cmc)]$, as can be seen in Figure 10b. These plots show straight lines without any curvature which verifies the accuracy of the cmc determination.

As shown in Table II, data treatment which takes into account the partitioning of the pyrene between aqueous and micellar phases gives, in most cases, cmc values (cmc_4 and cmc_5) which are smaller than the apparent cmc's. It should be recalled that the C_{app} values were determined directly from the intersection points of plots of the concentration dependence of the same original and deconvoluted fluorescence data (cmc_2 and cmc_3). It should also be noted that the cmc values calculated from the deconvoluted excitation spectra agree very well with the those calculated from the original emission spectra. One can see that the deconvolution procedure provides the more valid input for each of the components from the excitation spectra than data from the undeconvoluted spectra. Hence, when combined with a fitting procedure which takes into account the interaction of the pyrene with the polystyrene core, it gives the true values for the partitioning of the probe into the micellar and aqueous phases and, consequently, it gives the true onset of aggregation. For the subsequent part of the presentation, the values of cmc_5 were chosen which, in all cases, are found to be, within experimental error, the same as the

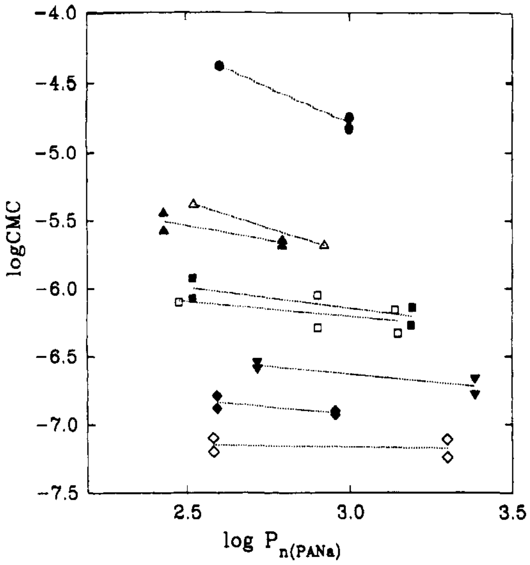

Figure 11. cmc dependence of PS-*b*-PANa block length for different PS block lengths: $P_{n,PS}$ = 6 (●), 11 (△), 14 (▲), 23 (□), 28 (■), 40 (▼), 86 (◆), 110 (◇).

cmc values from the original emission spectra (cmc$_l$).

Block Length Dependence of cmc. Since the aim of the present study is the determination of the critical micelle concentration as a function of the insoluble block length, in this case polystyrene, it is of importance to compare the micellization by keeping the polyelectrolyte block length constant and varying only the polystyrene block length. For synthetic reasons, this is not feasible, since, as was pointed out before, the polymers are synthesized as a series starting with the styrene segments. Thus, one prepares a series of block copolymers, for example, of 40 units of PS, with varying lengths of poly(acrylic acid). Therefore, to keep the polyelectrolyte block length approximately constant, we resort to the expedient of studying polyelectrolyte block length near a chain length of 1000 and interpolating the value of the cmc for 1000 acrylic acid units. Thus, the data that will be presented are given for each PS length for different polyelectrolyte block lengths in the vicinity of 1000.

The dependencies of the cmc values (cmc$_5$ and cmc$_l$) of the PS-*b*-PANa copolymers with different PS block lengths on the PANa length are presented in Figure 11. It is seen that, for a given polystyrene block length, only a slight lowering of the cmc values can be observed when the PANa block length is increased from ca. 300 to ca. 1400 units. The slope of the plot of log cmc as a function of the log of the ionic block length [d(log cmc)/d(log $P_{n,PANa}$)] is approximately −1 for a PS block length of 6 and increases gradually to approximately zero for a PS block length of 110. This aspect will be discussed in a future publication. On the other hand, a substantial change in the cmc's occurs within a narrow range of PS block length. An increase of the PS block length from 6 to 110 units decreases the cmc values by about 2.5 orders of magnitude.

It should be pointed out that under the experimental conditions (pH = 9 and low ionic strength, i.e., without added salt) the polyelectrolyte block is stretched significantly. Under those conditions, the influence of the length of the soluble block, which ranges from ca. 300 to ca. 1400 units, probably does not have a strong effect on the onset of micellization. The effects of polyelectrolyte chain length, as well as those of salt addition and pH changes, on the cmc values of these block copolyelectrolytes will be the subject of a future publication.

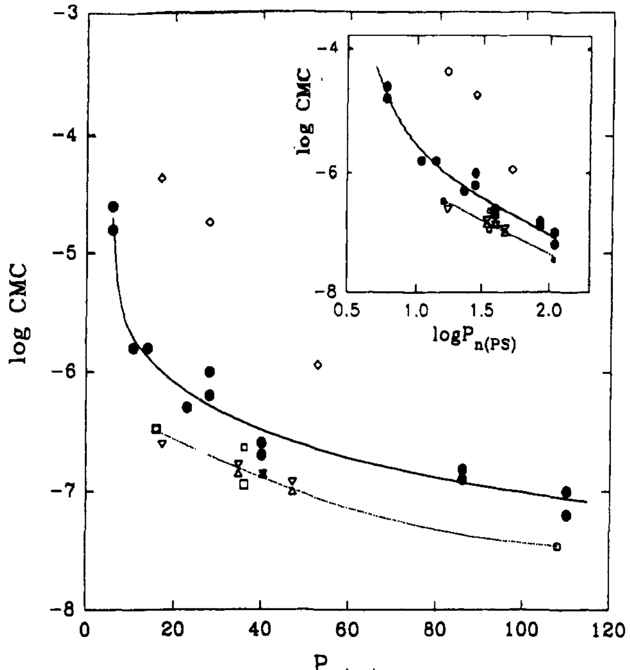

Figure 12. cmc dependence on an insoluble block length for (●) PS-*b*-PANa (PANa block length = 1000), (□,▫) PS-*b*-PEO diblocks and (△,▽) triblocks, calculated by various methods (see ref 19), and (◇) PEO-*b*-PBO-*b*-PEO (see ref 54). The inset shows a log–log plot of the data.

The dependence of the cmc of PS-*b*-PANa copolymers on the length of an insoluble polystyrene block is presented in Figure 12. One can see that for the rather short PS blocks (6–30 units) the cmc's decrease drastically. However, when the PS block length reaches ca. 40 units, the slope decreases more gently. It is seen that these data, even when plotted logarithmically, do not give a linear dependence between the cmc and the PS block length over the entire range. This suggests that the free energy of micellization is not proportional to the length of the insoluble block. Its dependence on PS chain length shows a curvature which becomes more pronounced for the lower PS block lengths. The strong dependence of the cmc on the insoluble block length is not surprising in view of the fact that the driving force for the micellization of the amphiphilic block copolymers as well as for low molecular mass surfactants is believed to arise predominantly from hydrophobic interactions, the result of which is a reorganization of the structure of water which takes place when the hydrophobic units are removed from it.

Comparison with Other cmc Studies on Block Copolymer Micelles. It is interesting to compare the results on the onset of micellization presented in this publication with data on cmc's specifically and micelle formation generally for other block copolymer systems. Correlations of the results with those for low molecular mass surfactants and with the theoretical relations are also of interest.

It should be pointed out that the present investigation is the first extensive systematic study on the influence of the insoluble block length in block copolymers on the cmc values of regular micelles. In most of the previous studies on the onset of micellization of block copolymers, the role of the molecular characteristics was not considered in such detail. Usually, the polymers studied had different lengths of both blocks, which made the evaluation of the cmc dependence as a function of any one variable rather complicated.

The cmc's obtained by Wilhelm et al.[19] involved three PS–PEO diblock copolymers in which the PEO block length varied from 150 to 400 units while the PS block length varied from 16 to 100 units. The same complications were involved in the study of PEO–PS–PEO[19] and PEO–poly(butylene oxide)–PEO (PEO–PBO–PEO)[54] triblock copolymers. However, in view of the present finding concerning the weak dependence of the onset of micellization on the length of the soluble block, one can, for comparative purposes, neglect this dependence and plot the experimental values of the cmc's for the copolymers mentioned above on the same graph as those for the copolymers of the present study. These comparisons are presented in Figure 12. It is seen that the cmc values for copolymers containing PEO as the soluble block lie below those for PS-*b*-PANa but that the plot of log cmc vs block length has generally the same slope. Since these polymers differ only in the nature of the hydrophilic block, the difference in the cmc's shows that the nature of the soluble block has only a weak influence on the cmc values. The change of the soluble block from ionic with a rather high charge density to nonionic does not influence the slope of the curve of log cmc vs PS block length. Furthermore, as one can see from the data of Wilhelm et al.,[19] there seems to be only a very weak dependence on polymer architecture; i.e., the cmc's of diblocks of PS–PEO and of triblocks of PEO–PS–PEO seem to fall on the same curve. This probably suggests that the onset of micellization is determined mainly by the nature and the length of the hydrophobic block. Polymer architecture, as can be seen from the theoretical model of Prochàzka[81] as well as from the experimental studies,[101,102] has an influence on the values of association number. By contrast, a change of the nature of the insoluble block, for example, for PEO–PBO–PEO triblock copolymers,[54] shows that both the absolute values of cmc's and the shape of the plot of the cmc values vs the insoluble block length are very different. This is also shown in Figure 12.

The influence of the molecular characteristics of block copolyelectrolytes on micelle formation was considered by Selb and Gallot for PS-*b*-poly(4-vinyl-*N*-ethylpyridinium bromide) diblock and triblock copolymers.[9,64,103] It was shown that the higher the PS block length, the shorter the range (in terms of water/methanol composition) of existence of unassociated single molecules. It was also shown that the degree of association decreases with increasing the length of the soluble block but that it increases with increasing the PS block length. From the results of intrinsic viscosity and sedimentation studies, it was shown that the multimerization process depends more strongly on the length of the insoluble block than on that of the soluble block.

The influence of the molecular mass ratio of the blocks on aggregation was also explored using fluorescence measurements by Morishima et al.[104,105] They observed that the enhancement of the fluorescence intensity of ANS (sodium 8-anilino-1-naphthalenesulfonate), a classical hydrophobic fluorescence probe, in the presence of block copolymers of poly(methacrylic acid)-*b*-poly(9-vinylphenanthrene)[104] or poly(methacrylic acid)-*b*-poly[(dimethylamino)styrene][105] in an aqueous medium is greater when the hydrophobic block is longer. The interpretation of the experimental results of the fluorescence intensity as well as of fluorescence quenching agrees with the expected variation of the dependence of the size of hydrophobic domains on the ratio of the block lengths of the copolymers.

It should be pointed out that, for most low molecular mass surfactants in aqueous solutions, the free energy of micellization is proportional to the length of the alkyl chain.[1,3,4] Many investigators have developed empirical equations relating the cmc to the various structural units in the surface-active agents. Thus, for homologous straight-chain ionic surfactants in an aqueous medium, a relation between the cmc and the number of carbon atoms, N, in the hydrophobic chain was found to be of the form[1]

$$\log \mathrm{cmc} = A - BN$$

where A and B depend on the specific ion type and the temperature. However, as was mentioned in the Introduction, it has also been found that when the number of carbon atoms in a straight-chain hydrophobic part of the surfactant exceeds 16, the chain-length dependence of the cmc becomes weaker. When the number of methylene groups exceeds 22, the value of the cmc becomes substantially independent of the alkyl chain length.[107]

In spite of the many experimental studies of block copolymer micelles in selective solvents which have been reported in the literature, there are only a few systematic comparisons between the experimental data and theoretical calculations. This is particularly true for studies of the onset of micellization. Illustrative calculations of the micellar properties, including cmc values, have been carried out by Nagarajan and Ganesh as a function of the copolymer and solvent characteristics.[76] The cmc values predicted on the basis of the pseudo phase approximation for poly(propylene oxide)-*b*-PEO (PPO-*b*-PEO) micelles in water, range from e^{-38} for a PPO chain length of 111 units to e^{-298} for a PPO chain length of 1945 units. As can be seen, the calculated cmc values lie considerably below the experimentally accessible range. It is interesting, however, that the shapes of the theoretical and experimental curves do show a strong resemblance for PPO–PEO and PBO–PEO systems. However, PS-*b*-PEO micelles cannot be treated with the same scaling relations because of the difference in the nature of the core.

The theoretical approaches concerning copolymers which contain a polyelectrolyte block are of great relevance to the systems under investigation here. Thus, the theoretical treatment developed by Marko and Rabin[77] for block copolyelectrolytes, based on the mean-field model, can be used to fit the experimental cmc vs PS block length results presented above. This approach considers the micelle properties to be determined by a balance of the corona–solvent interphase energy, minimized for large micelles, with Coulomb repulsion, minimized for isolated chains. In terms of this theory, the logarithm of the cmc should be proportional to $N^{2/3}$ (where N is the number of units in the insoluble block). A more thorough discussion of theoretical aspects of this problem is given in the subsequent publication.

Conclusions

This work represents the first systematic study of the insoluble block length dependence of the cmc of block polyelectrolytes.

Sample synthesis involved the production of a series of samples with an identical polystyrene block length and varying polyelectrolyte segments. This procedure made it possible, by interpolation, to obtain the cmc of a series of block copolymers with identical interpolated polyelectrolyte block lengths and varying PS block lengths in the range from 6 to 110; the polyacrylate block lengths varied from ca. 300 to ca. 1400.

The fluorescence probe technique was applied to determine the cmc values using pyrene as the fluorescence probe. Five different ways of experimental data treatment were explored to obtain the cmc values. It was shown that the best results were obtained from emission fluorescent spectra as well as from deconvoluted excitation fluorescent spectra. The data treatment also took into account the partitioning of pyrene between the micelle cores and the aqueous phase.

Changing the insoluble block length from 6 to 110 lowered the cmc from 1.6×10^{-5} to 5×10^{-8}. By contrast, changing the soluble block length from 300 to 1400 typically changed the cmc values by less than a factor of 2. For very short PS block lengths, the cmc decreased very rapidly with increasing the length of the insoluble block. For higher block lengths (above 12) the drop in the cmc was much more gradual.

The publication immediately following this paper deals with theoretical aspects of the cmc data interpretation. A future publication will be devoted to the effect of other parameters (polyelectrolyte block length, ionic strength of solution, pH, temperature) on the cmc values.

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