Aggregation and Critical Micelle Concentrations of Polystyrene-*b*-poly(sodium acrylate) and Polystyrene-*b*-poly(acrylic acid) Micelles in Organic Media

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ABSTRACT: Block copolymer micelles formed from polystyrene-*b*-poly(sodium acrylate) (PS-*b*-PANa) and polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) were characterized in organic solvents. The critical micelle concentrations (cmc's) were determined for one block copolymer series in which PS blocks of 660 units were attached to either relatively short PANa or PAA blocks ranging in length from 2.6 to 18 units. The cmc's for these block copolymers in toluene, tetrahydrofuran (THF), and chloroform were found to range from ca. 1×10^{-7} to 5×10^{-9} M. The *a* and *b* constants in the relation $\log C_i = aN_i^{1/3} + b$, where C_i is the cmc for a monodisperse polymer and N_i is the insoluble block length were evaluated and correlated to the polymer−solvent interaction parameters for the present systems as well as for several other block copolymer micelles. The PS(660)-*b*-PANa(*x*) series was also investigated by size exclusion chromatography (SEC) in THF. Two peaks in the SEC chromatograms could be distinguished, one corresponding to micellized block copolymers and the other to unassociated chains. The position of the latter peak was the same as that of the PS homopolymer, which was also present. These micelles were also characterized by static and dynamic light scattering (SLS and DLS). The effect of the soluble (PS) block length on the aggregation was investigated by SLS in THF. For this study, three additional PS-*b*-PANa series containing PS block lengths of 190, 630, and 2300 units attached to PANa blocks ranging in lengths from 4.2 to 69 units were characterized. The aggregation numbers ($N_{\rm agg}$) were found to be influenced significantly by the soluble PS block length ($N_{\rm PS}$). The $N_{\rm agg}$ and the calculated core radii ($R_{\rm c}$) were found to scale with the block lengths as $N_{\rm agg} \propto N_{\rm PANa}^{0.5}N_{\rm PS}^{-0.6}$ and $R_{\rm c} \propto N_{\rm PANa}^{0.5}N_{\rm PS}^{-0.2}$.

1. Introduction

Micelles formed from amphiphilic low molecular weight surfactants and block copolymers have vast application in areas such as detergency,[1] oil recovery,[2] drug-delivery systems,[3] and catalysis,[4] among others. For such applications, an understanding of certain parameters such as the critical micelle concentration (cmc), the aggregation number, the size, and the stability is first required. The use of block copolymers is advantageous in many cases since micelle systems can be created to achieve the desired properties by changing the nature and/or the length of the blocks. Thus, in recent years, considerable effort has been devoted to the characterization of block copolymer micelles, and the subject has been reviewed.[5−8]

The cmc is an important thermodynamic parameter describing the concentration above which micelles form. Cmc values have been determined for several nonionic block copolymers in aqueous[9−12] and in organic media.[13,14] The thermodynamics of micelle formation have been obtained from the temperature dependence of the cmc[15,16] or from the concentration dependence of the critical micelle temperature (cmt) which is the temperature below which micelles form.[17−24]

Cmc values have also been determined for ionic block copolymer micelles. Two types of micelles can be distinguished depending on the solvent nature in which micellization occurs, block polyelectrolyte and block ionomer micelles. In aqueous media, one obtains block polyelectrolyte micelles in a which a non-ionic core is surrounded by an ionic corona. These systems have been characterized by several techniques.[7,25−29] The cmc values have been determined for some of these systems such as polystyrene-*b*-poly(4-vinylpyridinium ethyl bromide) (PS-*b*-P4VPEtBr)[25] and polystyrene-*b*-poly(sodium acrylate) (PS-*b*-PANa).[29,30] In organic solvents, one obtains block ionomer micelles in which the micelle core is ionic and is surrounded by a non-ionic corona.

Investigations of the cmc's of block ionomers are scarce. These systems are of interest because of their stability[31] and their possible applications in areas such as the preparation of semiconductor particles[32] and as microreactors.[4] A recent preliminary study has shown that for a block ionomer series, PS(660)-*b*-PANa(*x*) in tetrahydrofuran (THF), the cmc values decreased from 2.5×10^{-8} to 5.4×10^{-9} M when the number of repeat units in the insoluble PANa block (*x*) increased from 2.6 to 14 units.[33] The present study further explores the effects of several parameters on these low cmc values and on certain micellar characteristics such as the aggregation numbers and micelle sizes.

There are several methods which have been used to evaluate the cmc's of block copolymer micelles. These methods include fluorescence spectroscopy,[9,12,29,30] osmometry,[13,17] viscosity,[13] and light scattering.[10,15,16,33] Recently, a method was developed to determine the cmc's of polydisperse block copolymer micelles of low cmc by static light scattering (SLS).[34] This method is based on the theory of Gao and Eisenberg[35] which accounts for the effects of polydispersity in block copolymers. It should be mentioned that, more recently, the influence of polydispersity on the micellization of triblock copolymers of PEO-*b*-PPO-*b*-PEO and PPO-*b*-PEO-*b*-PPO in aqueous solutions have been theoretically examined by Linse.[36] In the theory of Gao and

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Eisenberg, the cmc was found to depend on the length and polydispersity of the insoluble block.[35] For instance, an increase in the polydispersity index results in a decrease in the cmc. The single-chain concentration was also found to increase with the total polymer concentration, in contrast to monodisperse systems in which the single-chain concentration remains constant above the cmc. The effect of polydispersity on the cmc was found to decrease as the dependence of the cmc on the insoluble block length decreased. This dependence could be evaluated from the value of the constant a in the equation, $\log C_i \propto aN_i^{1/3}$, where C_i refers to the cmc for a monodisperse polymer and N_i is the number of repeat units in the insoluble block.

The SLS method which has been proposed takes into account these effects of polydispersity on the cmc, i.e., the change in the single-chain concentration with total concentration and the polydispersity of the insoluble block.[34] SLS is a convenient technique for the evaluation of the cmc, since it is sensitive to the apparent weight-average molecular weight ($M_{\mathrm{w,app}}$) of the particles in solution.[37] By measuring the $M_{\mathrm{w,app}}$ for block copolymer micelles as a function of concentration (c), three different regions can be distinguished, the micelle region ($c \gg$ cmc), the transition region of micelles to single chains ($c \sim$ cmc), and the single chain region ($c \leq$ cmc). In general, the cmc can be evaluated from the onset of the single-chain region. Unfortunately, in many block copolymer systems, the single-chain region cannot be measured due to the low value of the cmc. For such cases, an extrapolation method using an equation developed by Debye can be used.[37] This equation, as well as the method mentioned above, describe the cmc values for block copolymers which have a weak dependence of the cmc on the insoluble block length as well as for monodisperse block copolymers.[34] However, for block copolymers that have a strong dependence of the cmc on the insoluble block length and that are polydisperse, only the proposed method was able to evaluate the cmc.

Since the present paper focuses on the association of block ionomer micelles, the following sections will briefly describe some of the relevant results pertaining to these systems. It should first be noted that for some block ionomer micelles, such as those investigated in the present paper, when the glass transition temperature of the micelle core is above the temperature of measurement, “frozen” structures result, i.e., the exchanges between single chains and micelles are extremely reduced or nonexistant.

Micellization of block ionomers has been studied extensively in this laboratory[31,38−44] as well as in others.[45−48] Block ionomer micelles have been shown to possess several characteristic features. For instance, they have been found to be extremely stable.[31,38] This stability allows for the characterization of the micelles by SEC.[31,39] In general, two peaks could be identified from the SEC chromatograms, one corresponding to the micellized block copolymer and the other due to block copolymers present as single chains. In addition, in some cases, polystyrene homopolymer was eluted as a separate peak. The peak containing a lower ionic content arises from the polydispersity in the lengths of the ionic blocks, which, for narrow molecular weight distributions, such as 1.10, are broad compared to truly monodisperse chains. This result can be understood from the concept of a threshold length for micellization, i.e, a critical micelle length (cml) which has been proposed.[39] For instance, very short ionic block lengths, below the cml, remain soluble and unassociated while longer ionic block lengths, above the cml, prefer micellization at concentrations typical of SEC measurements (i.e., ca. 2 mg/mL). The cml was found by computer modeling of SEC chromatograms to vary between 2 and 3 ionic block units, independent of the PS block length, which ranged from 190 to 2300 units.

Additional studies have concentrated on the characterization of block ionomer micelles by still other techniques. The dependence of the micellar characteristics on the block copolymer composition of polystyrene-*b*-poly(metal methacrylate) and polystyrene-*b*-poly(methacrylic acid) was systematically investigated by SEC, DLS, and viscometry.[31,38] Small-angle X-ray scattering (SAXS) studies also probed the dependence of the core radius on the insoluble and soluble block lengths in the solid state and in solution for block ionomers with an non-ionic PS block attached to an ionic block consisting of poly(cesium acrylate),[42] poly(cesium methacrylate),[42] or poly(quaternized 4-vinylpyridine).[43] The scaling relations of the star model[49] were found to describe the systems.[41,42] A ^{2}H NMR study investigated the dynamics of PS segments in the corona.[40] It was found that segments near the core had a restricted mobility compared to those further from the core or to single chains in solution. The effect of different degrees of neutralization of the block forming the micelle core on the micellization was also probed by SAXS and SLS.[44] From a solution of PS-*b*-PAA present as single chains, micellization was found to begin at ca. 7% neutralization of the PAA block with cesium hydroxide.

The purpose of the present paper is to characterize block copolymer micelles formed from polystyrene-*b*-poly(sodium acrylate) and polystyrene-*b*-poly(acrylic acid) in organic solvents. The paper is divided into three parts. The first two parts focus on the aggregation of two block copolymer series in which a PS block of constant length (660 units) is attached to either PANa or to PAA blocks of relatively short lengths, ranging from 2.6 to 21 units. In the first part, the cmc values for these block copolymer micelles are reported as a function of the nature of the solvent and the core block, i.e., salt versus acid forms. The second part concentrates on the characterization of the block copolymer micelles by SEC in THF and by SLS and DLS in different solvents. In the third part of this paper, the aggregation behavior of three additional block ionomer series consisting of 190, 630, and 2300 PS units attached to various PANa blocks ranging in length from 4 to 67 units are examined by SLS in THF. This latter part extends the results obtained from a previous SEC study[39] on these samples.

2. Experimental Section

Synthesis. The block copolymers were prepared by sequential anionic polymerization; the details are given in ref 39. For convenience, only a brief summary is given here. The copolymers were synthesized by polymerizing the styrene monomer, followed by addition of *tert*-butyl acrylate. The initiator was the reaction product of *sec*-butyllithium with a few drops of α-methylstyrene. The polymerization was carried out in tetrahydrofuran (THF) at −78 °C under an atmosphere of nitrogen. The apparatus employed for the polymerization allowed the withdrawal of the reaction mixture during the course of the synthesis. Therefore, for a given constant polystyrene block length, a series of diblocks was obtained with poly(*tert*-butyl acrylate) segments of different lengths. Aliquots of the reaction mixtures were withdrawn for characterization after the polystyrene block was formed and every time

Table 1. Composition and Polydispersity Index of the PS Homopolymers and the Block Copolymers

PS(x)-*b*-PANa(*y*)	P.I.[a]	PS(x)-*b*-PANa(*y*)	P.I.[a]
190-*b*-0	1.12	630-*b*-0	1.10
190-*b*-10	1.10	630-*b*-4.2	
190-*b*-24	1.13	630-*b*-18	1.12
		630-*b*-31	1.12
660-*b*-0	1.05	2300-*b*-0	1.12
660-*b*-2.6		2300-*b*-4.6	
660-*b*-4.7		2300-*b*-31	
660-*b*-8.9		2300-*b*-69	1.12
660-*b*-14			
660-*b*-18			
660-*b*-21	1.05		

[a] The P.I. for samples with very short ester blocks were not measured.

following addition of the second monomer. Polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) was obtained by acid-catalyzed hydrolysis of the *tert*-butyl acrylate segments in toluene at 110 °C using *p*-toluenesulfonic acid as the catalyst. The PS-*b*-PAA was recovered and purified by repeated precipitations into cold methanol. The samples were then dried in a vacuum oven at 50 °C for 48 h. The composition of the copolymers was determined by either FT-IR using copolymers in the ester form or by titration of the acid. Table 1 summarizes the composition of the block copolymers and the polydispersity indexes (P.I.) of the PS homopolymer and the ester form of the block copolymer. The molecular weight of the polystyrene block was determined with a precision of ±5% by size exclusion chromatography in THF using narrow molecular weight polystyrene standards.

For neutralization of the PS-*b*-PAA, a known amount of the dry copolymer was dissolved in benzene/methanol (90/10 (v/v)) at a concentration of 2% (w/w). The acid samples were neutralized by the addition of a stoichiometric amount of $NaOCH_3$, which was prepared by reacting Na with methanol in THF. The solutions were stirred for 30 min, and the diblock ionomers were recovered by freeze drying. The samples were then further dried at 60 °C for 48 h under vacuum. Abbreviations are used to indicate the copolymer composition; for example, PS(660)-*b*-PANa(8.9) represents a polystyrene chain of 660 units joined to a poly(sodium acrylate) chain of 8.9 units; PAA denotes poly(acrylic acid).

Size Exclusion Chromatography. The SEC measurements were performed in THF and at room temperature on a Varian 5010 liquid chromatography apparatus equipped with a refractive index detector. The molecular weights and polydispersity indexes of the PS and the PS-*b*-poly(*tert*-butyl acrylate) were evaluated using a Varian DS-604 computer with SEC application software. The flow rate was 1.0 mL/min. Two columns were used in series, Progel-TSK G2000-HXL and G4000 HXL (Supelco Inc.) with effective molecular weight ranges from 10^2 to 10^4 g/mol and from 10^2 to 8×10^6 g/mol, respectively. The columns were calibrated using five polystyrene standards of narrow molecular weight distributions. The concentrations of the polymer solutions were ca. 2 mg/mL, and they were filtered (0.45 μm pore size) prior to injection. To determine the percent of micelles for the PS(660)-*b*-PANa block ionomers, the samples were injected in triplicate.

Sample Preparation for Light Scattering. For the light-scattering experiments, toluene and THF were distilled over calcium hydride and sodium benzophenone complex, respectively, while chloroform (spectrograde) was dried with molecular sieves. The polymer solutions were prepared by dissolving the dried block copolymer in the distilled or filtered solvent (0.2 μm PTFE filters, Chromatographic Specialties) and the solutions were stirred. Prior to the measurements, the polymer solutions were filtered through 0.45 μm PTFE filters directly into dust-free scintillation vials or into test tubes for the SLS and DLS measurements, respectively. Measurements at different concentrations were performed by diluting the filtered polymer solution with filtered solvent. The dilutions were followed by the weighing of the solutions with an analytical balance having a precision of ±0.001 g. Typical initial polymer concentrations for the SLS measurements were in the range 2×10^{-3}–2×10^{-5} g/mL, depending on molecular weight of the sample. For the DLS measurements the concentration range used was ca. (2−5) × 10^{-3} g/mL.

Table 2. Specific Refractive Index Increments of PS(660)-*b*-PANa(*x*) in Different Solvents at 630 nm

PS(660)-*b*-PANa(*x*)	solvent	d*n*/d*c* (mL/g)
4.7	toluene	0.105 ± 0.007
21	toluene	0.111 ± 0.006
14	chloroform	0.174 ± 0.01
21	chloroform	0.167 ± 0.01

Static Light-Scattering Measurements. Light-scattering experiments were performed using a DAWN-F multiangle laser photometer (Wyatt Technology, Santa Barbara, CA) at 25 °C, which operates at 15 angles, from 26 to 137°, and is equipped with a He−Ne laser (632.8 nm). The data were acquired and processed with the accompanying software. A minimum of four concentrations was used to determine the weight-average molecular weight, radius of gyration, and second virial coefficient with the aid of a Zimm plot. The measurements were performed at least in duplicate for each sample; the average value is reported. The error in the weight-average molecular weight was estimated to be less than 10%.

The specific refractive index increment (d*n*/d*c*) was determined using the Wyatt/Optilab 903 interferometric refractometer and accompanying software at a wavelength of 630 nm. The cell constant was determined by calibration with different concentrations of sodium chloride (99.999%, Aldrich) solutions. Eight to ten concentrations were measured for each d*n*/d*c* determination. These values are given in Table 2. It was found that these values were the same as those of PS; the literature values for toluene, THF, and chloroform are 0.110, 0.194, and 0.170 mL/g, respectively.[50]

Light scattering from a dilute polymer solution, when the particle size is greater than approximately $\lambda/20$, has been described by[51]

$$Kc/R(\theta) = \frac{1}{P(\theta)M_{\mathrm{w}}} + 2A_2c + ... \qquad (1)$$

where K is the optical constant, $(2\pi^2(n\,\mathrm{d}n/\mathrm{d}c)^2/\lambda_0^4N_{\mathrm{av}})$, n is the refractive index of the solvent, λ_0 is the wavelength in vacuum, N_{av} is Avogadro's constant, c is the concentration, $R(\theta)$ is the Rayleigh ratio at the angle of measurement, $P(\theta)$ is the particle scattering function, M_{w} is the weight-average molecular weight, and A_2 is the second virial coefficient. This equation can be solved graphically with a Zimm plot,[52] in which $Kc/R(\theta)$ is plotted as a function of $\sin^2(\theta/2) + kc$, where k is a scaling factor. By extrapolating to zero concentration as well as zero angle, the intercept gives the inverse M_{w} and the corresponding slopes of these two lines yield A_2 and R_{g}.

For block copolymers, M_{w} refers to an apparent weight-average molecular weight ($M_{\mathrm{w,app}}$) because of the chemical heterogeneity of the copolymer.[53] However, since d*n*/d*c* values for the block copolymer were found to be the same as literature values for homopolystyrene (Table 2), $M_{\mathrm{w,app}}$ is close to the true M_{w}. The constancy of the d*n*/d*c* is most likely due to the small weight fraction of the insoluble block.[54]

Certain micellar parameters, such as the aggregation numbers (N_{agg}), core radii (R_{c}), and surface area per chain (S/N_{agg}), can be calculated from the value of the M_{w}. For instance, the aggregation numbers were evaluated from the ratio of the molecular weight of the micelles to that of the unassociated block copolymer. For the PS-*b*-PANa block ionomers in THF, the core radii were determined from N_{agg} using the following relation for the core volume (V_{c}):

$$V_{\mathrm{c}} = {}^4/_3\pi R_{\mathrm{c}}^{\,3} = N_{\mathrm{agg}}N_{\mathrm{B}}MW/(\rho N_{\mathrm{av}}) \qquad (2)$$

where N_{B}, MW, and ρ are the number of repeat units, the repeat unit molecular weight, and the density of the PANa block, respectively. The density of the PANa block was evaluated from pycnometric measurements to be 2.05 g/mL. From the R_{c} and N_{agg} values, the surface area per chain

(S/N_{agg}), given as

$$S/N_{agg} = 4\pi R_c^2/N_{agg} \quad (3)$$

can be calculated.

The cmc values were determined from the Debye equation,[37] which was developed for monodisperse surfactants and has been previously used in the determination of cmc's for block copolymer micelles.[34,55] It can be described as

$$Kc/R(0) = c/[M_w(s) \times \text{cmc} + M_w(\text{mic}) \times (c - \text{cmc})] + 2A_2(c - \text{cmc}) \quad (4)$$

where $R(0)$ is the Rayleigh ratio extrapolated to zero angle and $M_w(s)$ and $M_w(\text{mic})$ are the weight-average molecular weights of the single chains and the micelles, respectively. The $Kc/R(0)$ values were plotted as a function of concentration and the cmc was evaluated from fitting the resulting curve using the program Peak Fit (Jandel Scientific). It should be noted that when the cmc is evaluated for polydisperse block copolymer micelles, the cmc in eq 4 should be replaced by the concentration of single chains which has been found to change with total polymer concentration. The reader is referred to a previous publication for details concerning this procedure.[34]

Dynamic Light-Scattering Measurements. Dynamic light-scattering studies were performed on a Brookhaven Instruments Corp. photon correlation spectrometer with a BI-2030 digital correlator and a Spectra Physics 120 helium/neon laser with a wavelength of 632.8 nm. The scattering angle used was 90°. A refractive index matching bath of filtered Decalin (0.2 μm) surrounded the scattering cell, and the temperature was controlled to 25 °C.

The correlation function ($G_2(t)$) for a single-exponential decay can be given as a function of time (t) by[56]

$$G_2(t) = B(1 + \beta \exp(-2\Gamma t)) \quad (5)$$

where B is the baseline, β is an optical constant which depends on the instrument, and Γ is the decay rate for the process. This rate is given by

$$\Gamma = Dq^2 \quad (6)$$

where D is the translation diffusion coefficient and q is the absolute value of the scattering vector:

$$q = 4\pi n/(\lambda_0 \sin(\theta/2)) \quad (7)$$

The diffusion coefficient for spherical particles is related to the hydrodynamic radius (R_h) by the Stokes–Einstein equation:

$$D = k_B T/6\pi\eta R_h \quad (8)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent medium. In general, the diffusion coefficients should be extrapolated to zero concentration. However, for the present system, the DLS results were found to be independent of concentration, probably due to the relatively small particle radius (<30 nm).[38]

3. Results and Discussion

This section is divided into three parts. The first part concentrates on the cmc's of two series of block copolymers, PS(660)-*b*-PANa(x) and PS(660)-*b*-PAA(x). The effects of the solvent and the insoluble block (length and nature) on the cmc's are investigated. As an application of the mixed micelle model,[35] the distributions of the block copolymers present as single chains and in the micellar fractions are evaluated. Correlations of the constants describing the dependence of the log C_i on the $N_i^{1/3}$ are made with the polymer–solvent interaction parameter for the present system as well as for other block copolymer micelle systems previously investigated. The second part addresses other aspects of aggregation. The percent of micelles in solution for the PS(660)-*b*-PANa(x) block ionomer series are evaluated in THF by SEC. Also, the aggregation numbers, second virial coefficients, and micelle radii, for the PS(660)-*b*-PANa(x) and PS(660)-*b*-PAA(x) series as a function of the insoluble block length for different solvents are investigated. The third part deals with the effect of the soluble PS block length on the micellization of three additional PS(x)-*b*-PANa(y) block ionomer series in THF. These block ionomers were composed of PS block lengths of 190, 630, and 2300 units, attached to PANa blocks of various lengths. The scaling relation between the aggregation number and the calculated core radius with the PS and PANa block lengths are explored.

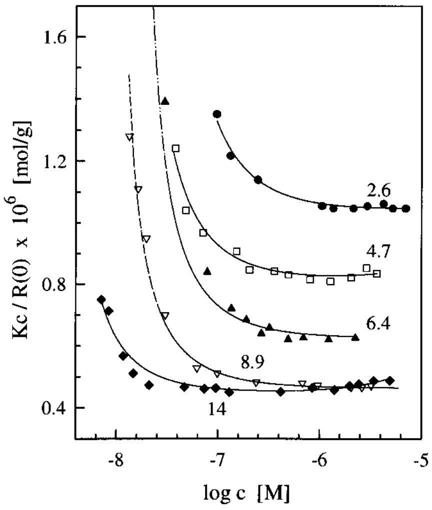

Figure 1. Plots of $Kc/R(0)$ used in cmc determinations for PS-(660)-*b*-PANa(x) for different PANa block lengths in THF.

3.1. **Cmc's for PS(660)-*b*-PANa(x) and PS(660)-*b*-PAA(x) Block Copolymer Micelles.** *3.1.1. Solvent and Insoluble Block Effects.* The cmc values for PS(660)-*b*-PANa(x) and PS(660)-*b*-PAA(x) were evaluated for different PANa and PAA block lengths ranging from 2.6 to 18 units. Typical data obtained from SLS for the PS-*b*-PANa series in THF are presented in Figure 1. The lines shown are the fits used to determine the cmc values; this will be discussed in more detail in the subsequent paragraph. From the behavior of the $Kc/R(0)$ values as a function of concentration, two regions can be distinguished. At high concentrations, the scattered intensity is predominantly due to the presence of micelles. In this region, extrapolation of the $Kc/R(0)$ values to zero concentration gives the inverse weight-average molecular weight of all the particles in solution ($M_{w,\text{total}}^{-1}$), and the slope of this line is proportional to the second virial coefficient. At intermediate concentrations, the transition region is observed in which micelles dissociate to single chains. In this region, the $Kc/R(0)$ values increase with decreasing total concentration; this trend represents a decrease in $M_{w,\text{total}}$. For instance, for the PS(660)-*b*-PANa(8.9) block ionomer (Figure 1), the micelle region occurs at a concentration ca. >1 × 10^{-7} M, and the transition region occurs at a concentration ca. <1 × 10^{-7} M. It should be noted that the region which corresponds to the existence of predominantly single chains, i.e., c < cmc, was not attained in these measurements because the sensitivity of the instrument did not allow measurement at such low concentrations.

The cmc values for the PS(660)-*b*-PANa(x) and PS(660)-*b*-PAA(x) block copolymers were evaluated by fitting the

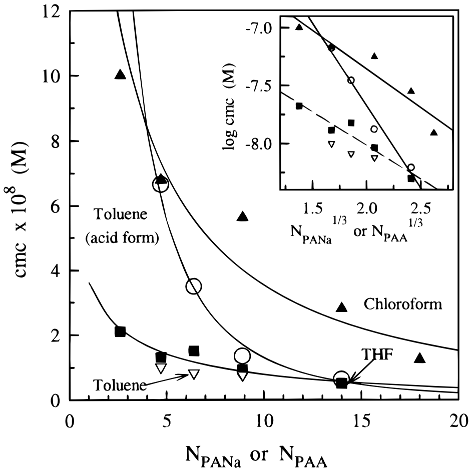

Figure 2. Cmc values of PS(660)-*b*-PANa(x) in chloroform, THF, and toluene and of PS(660)-*b*-PAA(x) in toluene, as a function of the insoluble block length. The inset represents the data plotted as the log of the cmc as a function of $N_{\text{PANa}}^{1/3}$.

$Kc/R(0)$ values as a function of concentration using the Debye equation (eq 4). The details of this procedure were given in the Experimental Section. Typical fits obtained for these block copolymers are depicted in Figure 1 as solid lines. As discussed in a previous publication, the sensitivity of the cmc's evaluated by this method falls within a 20% error limit.[34] The agreement of the lines with the data points shows that the Debye equation gives a good representation of the micelle and transition regions. A similar procedure was also followed for the acid block copolymers in toluene and good agreement was also observed. Previously, the cmc's for this PS-*b*-PANa block ionomer series were investigated by SLS in THF.[34] The Debye equation was found to fit the light-scattering curves because of relatively weak dependence of the cmc on the insoluble block length and also because of the low polydispersity of the PANa blocks. Therefore, for the present system, the effects of polydispersity on the cmc are not significant.

Figure 2 summarizes the cmc values determined for PS(660)-*b*-PANa(x) and PS(660)-*b*-PAA(x) as a function of the insoluble block length, i.e., N_{PANa} or N_{PAA}. It should be noted that the cmc's could not be evaluated for PANa block lengths higher than 14 units in THF and toluene or higher than 18 units in chloroform because of their low magnitude. In general, it was found that as the length of the insoluble block increased, the cmc values decreased. This result is expected, since the solubility of the single chains decreases with increasing insoluble block length; thus, micellization occurs at lower concentrations. It is interesting to examine the effect of solvent on the cmc values for the PS(660)-*b*-PANa(x) block ionomers. The cmc's were found to decrease in the order chloroform > THF ~ toluene. It should be noted that the difference (on a linear scale) between the cmc's in chloroform and those in THF or toluene decreased as the insoluble block length increased.

The cmc's for PS(660)-*b*-PAA(x) were investigated only in toluene (Figure 2). The cmc values for PS(660)-*b*-PAA(x) show an interesting trend. First, for PANa block lengths of ca. 5 units, the cmc values for the acid form are similar to those of the salt form in chloroform, while at ca. 14 units, the cmc values are similar to the those of the salt form in THF. From the trend of the dashed line, it is expected that for PANa block lengths lower than 4.6 units, the cmc values for the acid form might be larger than those for the salt form in chloroform; for block lengths greater than 14 units, the cmc values for the acid form apparently converge with those for the salt form in THF.

It is interesting to compare the magnitude of the present cmc values with those previously measured for other block copolymer systems. First, it should be recognized that the cmc's depend on both the soluble and insoluble block lengths. However, cmc's for different systems can be characterized by certain typical cmc ranges. The cmc's for some block copolymer systems will be given here for illustrative purposes. For instance, if one considers the mirror image system of the present block ionomer, i.e., PS(x)-*b*-PANa(1000) block polyelectrolytes in water, the cmc's have been found to range from ca. 2×10^{-5} to 6×10^{-8} M for insoluble PS block lengths ranging from 6 to 110 units.[29] The cmc values for PS-*b*-PEO and PEO-*b*-PS-*b*-PEO in water for approximately this PS block length range were found to be slightly lower.[57] The cmc values for PS-*b*-PI in *n*-hexadecane for various PI block lengths were found to range from ca. 3×10^{-4} to 8×10^{-6} M for insoluble PS block lengths ranging from 67 to 120 units.[18] Thus, for comparable insoluble block lengths, the cmc's for the present systems represent the lowest values which have yet been reported. There are clearly systems with lower cmc values for comparable block lengths; however, we have not found any reports describing a systematic study.

3.1.2. Theoretical Applications of the Mixed Micelle Model. The mixed micelle model developed for block copolymer micelles considers the effects of the polydispersity of the insoluble block on the cmc. The cmc for a monodisperse block copolymer (C_i) is given as[35]

$$\log C_i = aN_i^{1/3} + b \qquad (9)$$

where a and b are constants and N_i is the number of repeat units in the insoluble block. This relation was found to describe the cmc values of PS-*b*-PI in *n*-hexadecane and those of PS-*b*-PANa in water.[35] The effect of the polydispersity on the cmc depends on the magnitude of the a constant, which is a measure of the dependence of the log C_i on the insoluble block length. In the present system, since the effect of polydispersity has been found not to be significant,[34] the cmc evaluated by the Debye equation is close to C_i and the relation can be investigated directly.

The inset of Figure 2 shows the data plotted according to eq 9; the resulting linear regressions are also presented as curves in the main plot of the cmc versus the insoluble block length in Figure 2. The agreement with this relation was found to be satisfactory for PS-*b*-PANa in THF and for PS-*b*-PAA in toluene. For the neutralized copolymer in chloroform the data showed more scatter in the linear regression. Also, it should be noted that for PS-*b*-PANa in toluene, not enough cmc values were determined to obtain a meaningful regression. The values for the a and b constants are given in Table 3. It should be noted that plots of log cmc versus the insoluble block length also gave satisfactory linear regressions; this fact may be due to the weak dependence of the cmc on N_{PANa} or N_{PAA}. Thus, the dependence of the log cmc on $N_{\text{PANa}}^{1/3}$ or $N_{\text{PAA}}^{1/3}$ for the present systems is not very sensitive; however, the $N_{\text{PANa}}^{1/3}$ or $N_{\text{PAA}}^{1/3}$ dependence is consistent with the theory.

The molecular weight distribution of the block copolymer molecules present as single chains (S) and

Table 3. Summary of the *a* and *b* Constants for Different Block Copolymer Micelles and the Hildebrand Solubility Parameters[50] Used in the Evaluation of Core–Solvent Interactions

block copolymer					δ (cal/cm^3)$^{1/2}$		
core	corona	solvent	a	b	core	corona	solvent
PANa	PS	chloroform	−0.66	−6.03	ca. 16[f]	9.1	9.3
PANa	PS	THF	−0.58	−6.86	ca. 16[f]	9.1	9.1
PAA	PS	toluene	−1.42	−4.83	ca. 11[f]	9.1	8.9
PVP	PS[a]	toluene	−1.66[a]	−0.90[a]	ca. 10[f]	9.1	8.9
PS	PANa[b]	water	−0.68[e]	−4.02[e]	9.1	ca. 16[f]	24
PS	PI[c]	*n*-hexadecane	−1.65[e]	3.55[e]	9.1	8.0	7.7
PS	PEO[d]	water	−0.45	−5.26	9.1	10.5	24

[a–d] Evaluated from data given in refs 34, 18, 29, and 57, respectively. [a,e] *a* and *b* constants determined in refs 34 and 35, respectively. [f] Calculated values based on ref 60 (see text).

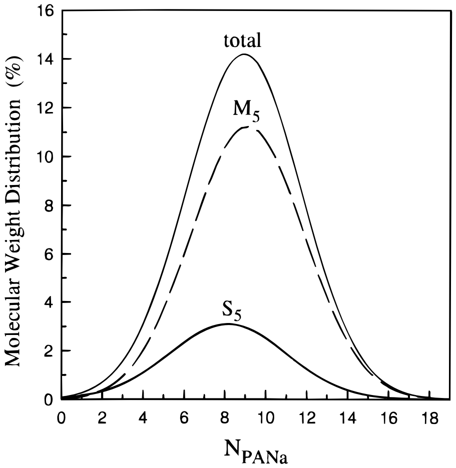

Figure 3. Molecular weight distribution of the single chains (*S*) and the micelle fraction (*M*) at 5 times the cmc for PS-(660)-*b*-PANa(8.9) in THF.

present in the micelle fraction (M) can be calculated from the mixed micelle model.[35] Figure 3 gives such a plot for PS(660)-*b*-PANa(8.9) in THF. The total molecular weight distribution of all the polymer chains is given as a solid curve (total). The distributions of the single chains and micelle fraction are given as a percentage of the total distribution for a concentration of 5 times the cmc (denoted by subscripts in the figure). The distributions of the single chains and micelle fractions were found to overlap extensively for the block ionomer. It should be noted that the N_{PANa} value for the peak maxima are somewhat lower for the single-chain fraction than the micelle fraction. The lack of segregation between the single chain and micelle fractions is due to the relatively weak dependence of the cmc on the insoluble block length as expressed in the low value of the constant a (−0.58) in eq 9. For the acid form at these concentrations, the distributions for the single chains and micelle fractions were found to be slightly more segregated at low PAA block length compared to the salt form (graph not shown). This fact was due to larger dependence of the log cmc on the insoluble block length ($a = -1.4$).

3.1.3. Correlations of the a and b Constants with Interaction Parameters. In general, micellization theories have considered three contributions to the total free energy of a micelle, that of the core, the shell, and the core/shell interface.[8] It is of interest to correlate these contributions to the quality of the solvent for the core and for the shell blocks using the Flory–Huggins interaction parameter (χ). This section describes the results of such a correlation. Table 3 summarizes the *a* and *b* values determined for the present system as well as those previously determined for other systems.[34,35] It should be noted that certain theories, such as that of Nagarajan and Ganesh,[58] allow the calculation of the interaction parameters from the micellar parameters such as aggregation numbers, core radii, etc. We have tried to extract the χ values for PS(660)-*b*-PANa-(x) in THF by these approaches; however, the interaction parameter between the polymer forming the core and the solvent ($\chi_{\mathrm{core-sol}}$) was found to decrease progressively as the insoluble PANa block length increased. The PS–THF interaction parameter was nearly constant, with a value of 0.5.

Since not all χ values are known for the different systems listed in Table 3, it is necessary to estimate these values. The polymer–solvent interaction parameter (χ_{ps}) can be described as a sum of entropic and enthalpic contributions.[59] The entropic contribution for nonpolar systems and polar systems in the absence of specific polymer–solvent interactions is given as a constant, ca. 0.34. The enthalpic contribution can be estimated from the values of the Hildebrand–Scatchard solubility parameters (δ); the χ_{ps} is thus given by[60]

$$\chi_{\mathrm{ps}} = (\delta_{\mathrm{s}} - \delta_{\mathrm{p}})^2 V_{\mathrm{s}}/RT + 0.34 \qquad (10)$$

where δ_{s} and δ_{p} are the solubility parameters for the solvent and polymer, respectively, V_{s} is the molar volume of the solvent, and R is the gas constant. This equation provides a qualitative indication of the interaction parameters. It should be noted that for polar systems with specific interactions between the components, the intermolecular forces between molecules should also be taken into account.[50]

To evaluate the quality of the estimate of the χ values calculated from eq 10, comparison can be made with χ values which are available in the literature. For instance, the calculated and the literature χ values for PS in different solvents are given below:[50]

solvent	T (°C)	χ_{exp}	χ_{cal}
water	162	4.4	5.0
formamide	162	4.1	5.0
ethylene glycol	162	3.8	4.4
methanol	162	2.2	1.7
n-hexadecane	183	1.2	0.73
toluene	27	0.43	0.35

The average difference between the experimental and estimated χ values was 22%. From this comparison, the χ values evaluated from eq 10 can be used qualitatively to illustrate the general trends in the χ values but not for quantitative predictions. It should also be noted that for this illustration, the δ values at 25 °C were employed. In general the δ values change with temperature; however, this dependence is not known for many systems.

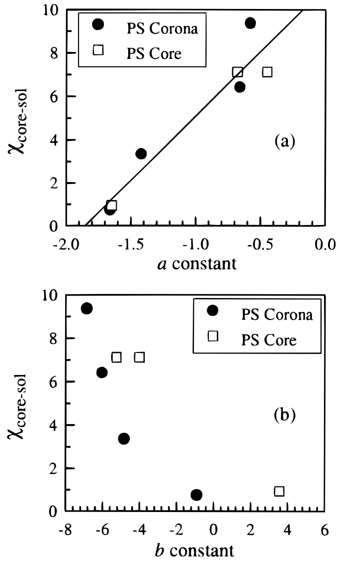

Figure 4. Correlations of the *a* and *b* constants with the interaction parameters of the polymer forming the core and the solvent.

The literature values for the solubility parameters for the solvents and polymers are given in Table 3.[59] It should be noted that these values are not available for PAA, PVP, and PANa. However, they can be evaluated from group contributions of the cohesive energy (E_{coh}) and the molar volume (V) from

$$\delta = (E_{\text{coh}}/V)^{0.5} \tag{11}$$

The E_{coh} were evaluated from the tables of van Krevelen or Fedors.[61] For PANa, the value of Na was not known; thus, as an approximation, the value for Cd was used. The values are also given in Table 3.

In the following paragraphs, the correlations of the *a* and *b* are discussed first for block copolymers having a soluble PS block (PS-*b*-PANa, PS-*b*-PAA, and PS-*b*-P4VP) followed by block copolymers having the same insoluble block, i.e., PS (PS-*b*-PI, PS-*b*-PANa, and PS-*b*-PEO). The trends of the *a* and *b* constants with the estimated $\chi_{\text{core-sol}}$ values are illustrated in Figure 4a,b respectively. The *a* and *b* values plotted are for polymer/solvent systems having a PS corona and a PS core. The line shown in Figure 4a is a linear regression through all the points.

The correlation between the *a* constants and the $\chi_{\text{core-sol}}$ values was considered for block copolymer micelles having a soluble PS block in a good solvent, i.e., PS-*b*-PANa in THF and in chloroform, PS-*b*-PAA in toluene, and PS-*b*-P4VP in toluene (Table 3). For these block copolymers, the estimated $\chi_{\text{core-sol}}$ values were found to decrease according to the nature of the insoluble block in the following order: PANa (in THF) (9.4) > PANa (in chloroform) (6.4) > PAA (3.4) > P4VP (0.74), where the numbers in parentheses are the estimated $\chi_{\text{core-sol}}$ values. The absolute magnitude of the *a* constants were found to increase in the following order: PANa (in THF) (0.58) ~ PANa (in chloroform) (0.66) < PAA (1.42) < P4VP (1.66). This trend is opposite to that of the $\chi_{\text{core-sol}}$ values, i.e., the polymers with the largest $\chi_{\text{core-sol}}$ have the smallest dependence (i.e., the smallest absolute value of *a*) of log C_i on $N_i^{1/3}$. This qualitative trend is shown in Figure 4a.

The magnitude of the *b* constants for the block copolymers having a constant soluble PS block can also be correlated to the polymer–solvent interaction parameters (Figure 4b). The *b* constants are expected to reflect the interaction between the soluble block and the solvent as well as the free energy of the core/shell interface. The free energy of the interface arises from the interactions between the core and the shell region which consists of the soluble block and the solvent. Therefore, $\chi_{\text{core-sol}}$ also contributes to the magnitude of the *b* constant. The $-b$ values were found to change in the following order: PANa (in THF) (6.86) > PANa (in chloroform) (6.03) > PAA (4.83) > P4VP (0.90). For these samples, the values for the interaction parameter between the polymer forming the corona and the solvent ($\chi_{\text{corona-sol}}$) are expected to be similar in magnitude since they reflect the interaction between PS and either THF or toluene. Therefore, the $\chi_{\text{core-sol}}$ values must contribute significantly to the values of the *b* constants. The observed trends in $-b$ parallel those observed for $\chi_{\text{core-sol}}$ given above. Thus, the polymers with the largest $\chi_{\text{core-sol}}$ values have the largest $-b$ values, as is in the case of the block ionomer micelles. As a result, micellization for these samples occurs at lower concentrations.

The *a* and *b* constants for the other block copolymer systems (Table 3) having the same insoluble block can also be correlated to the polymer–solvent interaction parameters. For instance, the constants for the block copolymers having a PS core can be considered. The three systems are PS-*b*-PANa and PS-*b*-PEO in water and PS-*b*-PI in *n*-hexadecane. The *a* values for the block copolymers in water, PS-*b*-PANa (−0.68) and PS-*b*-PEO (−0.45), were found to be similar in magnitude. The PS-*b*-PI in *n*-hexadecane system, in comparison to PS-*b*-PANa and PS-*b*-PEO in water, had a larger dependence of the log C_i on the insoluble block length ($a = -1.65$) and a larger *b* value (3.55), thus a higher cmc than the block copolymers in water. These values reflect the weaker interaction between the PS core with *n*-hexadecane compared to that with water.

3.2. Aggregation of PS(660)-*b*-PANa(*x*) and PS(660)-*b*-PAA(*x*) Block Copolymer Micelles. *3.2.1. Size Exclusion Chromatography.* In the course of the SEC characterization of the PS(660)-*b*-PANa(*x*) block ionomer micelles in THF, two peaks with different elution volumes were observed in the chromatograms. Two peaks have been observed in previous SEC studies of block ionomer micelles,[31,39] which, as was discussed in the Introduction, are due to micellized and unassociated polymer chains. In the present study, the position of the unassociated polymer chains was the same as that of the corresponding polystyrene homopolymer, PS(660). It has been found in a previous study that the unassociated polymer arises from some PS homopolymer as well as from the presence of block ionomer chains containing a lower ion content than those in the micelles.[31] The presence of the latter species has been postulated to arise from the polydispersity of the ionic block, with the block ionomers of very short ionic block lengths being preferentially soluble as single chains. Above the cml, which has been evaluated to be ca. 2–3 units[39] for concentrations used in the SEC experiments, the block ionomers favor micellization.

The weight percent of micellized chains in the block ionomers was determined from the relative areas of the micellized and the unassociated chains in the chromatograms. These values were determined in triplicate, and the average and the standard error values are given in Table 4. It is important to establish that no significant adsorption of the PS(660)-*b*-PANa(*x*) block ionomers

Table 4. Summary of the Percent of Micellized Chains and the Weight-Average Molecular Weights for PS(660)-*b*-PANa(*x*) and PS(660)-*b*-PAA(*x*) in Different Solvents

		$10^{-6}M_w$ (g/mol)					
		toluene		THF		chloroform	
PS(600)-*b*-X	micellized chains (%)	total	micelle	total	micelle	total	micelle
PANa(*x*)							
2.6	21 ± 1	1.1	5.0	0.76	3.4	0.30	1.4
4.7	65 ± 4	1.4	2.2	1.2	1.9	0.60	1.0
6.4	79 ± 3	1.8	2.2	1.6	2.0	0.66	0.92
8.9	84 ± 1	2.1	2.4	2.2	2.6	1.1	1.4
14	82 ± 2	2.2	2.7	2.2	2.7	1.6	2.2
18	87 ± 1	2.5	2.9	2.8	3.2	2.2	2.9
21	88 ± 2	2.8	3.2	2.9	3.3		
PAA(*x*)							
4.7		0.46	0.66				
6.4		0.61	0.76				
8.9		1.4	1.6				
14		2.2	2.7				

occurred on the SEC columns. The amount of adsorption was evaluated from the percent difference in the ratio of the peak areas to the concentration of injected polymer for the PS(660) and the block ionomers. It was found that the percent difference was below 10%, with the exception of PS(660)-*b*-PANa(2.6) in which the difference was 15%.

The weight percent of micellized chains was found to increase as the length of the insoluble block increased. Unfortunately, in the present chromatograms, the relative contributions of the PS homopolymer and of the block ionomer containing low ionic content to the area of unassociated chains can not be distinguished. However, in view of the synthetic procedure, the PS content is expected to be constant for the block ionomer series; thus, the observed changes in the percent of micellized chains are due to the decrease in the amount of the block ionomers of low ion content. For PANa block lengths above ca. 8.9 units, the weight percent of micellized chains seems to be constant at ca. 88%. From this value, the amount of PS homopolymer is estimated to be ca. 12%.

3.2.1.1. Comparison of the cmc and the cml Concept. In view of the SEC results, it is useful to discuss the cmc results previously obtained (section 3.1.2) in light of the cml concept. Previously, it was established by using the mixed micelle model that there was very little segregation in the molecular weight distribution of the single chain and micelle fractions (Figure 3). Thus, at concentrations of the SEC experiment, no fractionation is to be expected. However, the SEC chromatograms show that as the insoluble block length increases for short ionic block lengths, the weight percentage of chains which micellize increases. The phenomenon can be understood by noting that the mixed micelle model is valid only for collapsed insoluble blocks.[35] Thus, deviations are expected for block lengths which are shorter than the minimum length required for collapse. In these cases, the cml concept is operative: it was previously found that at the concentrations used in SEC, very little micellization occurs for insoluble block lengths less than 2−3 units.[39] Support for this view comes from a consideration of monochelics, i.e., polymer chains containing one ionic unit at the end, such as carboxylate-terminated polystyrene (PS(100)−COONa), studied in THF.[62] For this system, it has been found that the cmc was ca. 1 × 10^{-4} M, or 1 mg/mL, which was similar to the concentrations used in SEC measurements (2 mg/mL). Therefore, the present findings are consistent with the notion that in the SEC experiments, the concentrations used were above the cmc values for collapsed blocks but below those for very short uncollapsed blocks.

3.2.2. Static Light Scattering. The PS(660)-*b*-PANa(*x*) and PS(660)-*b*-PAA(*x*) reverse micelles were characterized by SLS in order to determine the aggregation numbers and second virial coefficient values. The light-scattering data were analyzed from Zimm plots obtained in the micelle region, i.e., at high concentrations (see Figure 1). In general, from these plots, information can be obtained on the weight-average molecular weight (M_w), the second virial coefficient (A_2), and the radius of gyration (R_g) of the particles in solution. In the present case, the R_g values could not be evaluated since the particles sizes were smaller than the wavelength of incident light. This section will present the results obtained by SLS on the block copolymer micelles by first discussing the weight-average molecular weights and the aggregation numbers and second the A_2 values.

The weight-average molecular weight which was obtained by SLS is an average value for the solutes present in solution. As was previously discussed, the SEC chromatograms of these block copolymer solutions show peaks for both micellized and unmicellized block copolymer chains. The total weight-average molecular weight ($M_{w,total}$) can thus be described as

$$M_{w,total} = f_{mic}M_w(mic) + (1 - f_{mic})M_w(s) \qquad (12)$$

where f_{mic} is the mass fraction of micellized chains. For the molecular weight of the single chains, the value for PS(660) was used. Since the cmc was much lower than the concentrations used, the M_w(mic) required no correction for the cmc values. The $M_{w,total}$ and M_w(mic) values and the calculated aggregation numbers are given in Tables 4 and 5, respectively.

The aggregation numbers (N_{agg}) of the micelles were investigated in different solvents. Figure 5 shows the N_{agg} values plotted for PS(660)-*b*-PANa(*x*) in toluene, THF, and chloroform and for PS(660)-*b*-PAA(*x*) in toluene, as a function of the insoluble block length, i.e., either N_{PANa} or N_{PAA}. The lines represent linear regressions through the data, shown to illustrate the general trends observed. It should be noted that the N_{agg} values for the sample with the shortest insoluble block length, PS(660)-*b*-PANa(2.6), are not represented on the graph. The N_{agg} values for this sample were found to be much larger than those of the other samples. For instance, the N_{agg} values for PS(660)-*b*-PANa(2.6) in toluene, THF and chloroform were 72, 49, and 20, respectively (Table 5). These large values may result from the adsorption of some of the polymer on the SEC columns (section

Table 5. Summary of the Results Obtained for PS(660)-*b*-PANa(*x*) and PS(660)-*b*-PAA(*x*) by SLS and DLS in Different Solvents

composition	toluene			THF			chloroform		
PS(660)-*b*-X	N_{agg}	10^4A_2 (mL mol/g^2)	D_h (nm)	N_{agg}	10^4A_2 (mL mol/g^2)	D_h (nm)	N_{agg}	10^4A_2 (mL mol/g^2)	D_h (nm)
PANa(*x*)									
2.6	72	0.56	46	49	0.70	49	20	0.70	48
4.7	31	0.65	46	27	0.75	47	15	0.77	44
6.4	32	0.58	47	29	0.50	50	13	0.58	50
8.9	35	0.52	53	37	0.56	53	20	0.79	53
14	38	0.64	54	39	0.38	52	31	0.68	50
18	40	0.37	57	46	0.40	56	41	0.65	55
21	45	0.36	59	47	0.31	52			57
PAA(*x*)									
4.7	9.6	0.69							
6.4	11	0.75							
8.9	23	0.28							
14	39	0.39							

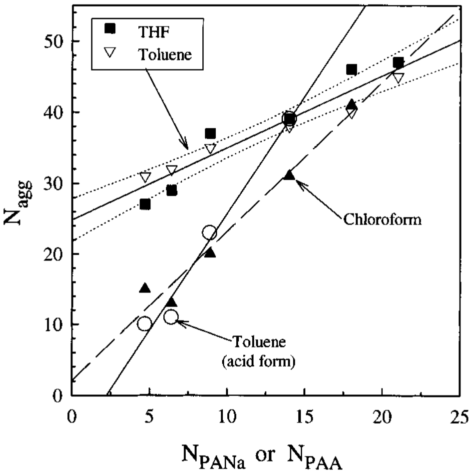

Figure 5. Aggregation numbers for PS(660)-*b*-PANa(*x*) and PS(660)-*b*-PAA(*x*) in different solvents plotted as a function of the insoluble block length. The solid and the dashed lines represent linear regressions and 95% confidence intervals.

3.2.1) which would lead to a smaller percent of micelles and therefore larger N_{agg} values.

The N_{agg} values for PS(660)-*b*-PANa(*x*) in toluene were found to be very similar to those in THF, and a single line represented the increase of N_{agg} with N_{PANa} for these two solvents; the dotted lines shown in the plot represent the 95% confidence limits. The N_{agg} values in chloroform were found to be lower than those in toluene or THF for low ionic block lengths; however, at higher ionic block lengths, the N_{agg} values approached those of toluene or THF. For PS(660)-*b*-PAA(*x*) in toluene, the N_{agg} values were found to be equal to those in chloroform at ca. 4.7 units and to those in toluene or THF at 14 units. These PANa block lengths also correspond to those at which the cmc values were observed to be the same (Figure 2). A comparison of Figures 2 and 5 suggests that the trends in the N_{agg} values with increasing insoluble block length for these systems were found to be essentially opposite to those previously observed in the log cmc values, which seems reasonable.

It is of interest to investigate the trends in Figure 5 and the points at which the lines cross. For instance, at an insoluble block length of 5 units, the N_{agg} values decrease in the order PANa in toluene ~ PANa in THF > PAA in toluene ~ PANa in chloroform. On the other hand, if the trends are extrapolated to higher insoluble block lengths, such as 25 units, the N_{agg} values decrease in a different order, PAA in toluene > PANa in chloroform ~ PANa in toluene ~ PANa in THF. It should be noted that the trends which are observed in the aggregation numbers for these samples which have relatively short insoluble block lengths (0.4–3 mol %) may not necessarily be indicative of the behavior for higher ionic block lengths. For instance, a recent paper probed the effect of different degrees of neutralization on the micellization of two block copolymer samples, PS(600)-*b*-PAA(34) and PS(600)-*b*-PAA(45).[44] In that study, the aggregation numbers in toluene for the acid block copolymers were found to be lower than those of the sodium neutralized samples. Therefore, caution should be exercised when extending the present trends to longer insoluble block lengths.

The quality of the solvent for the block copolymer can be determined from the second virial coefficient values. These values represent an average quantity over all the particles in solution and are given in Table 5. In general, it was found that the A_2 values decreased as the total molecular weight of the particles in solution increased. This trend is expected since, in general, the solvent quality decreases as M_w increases. However, the error in the A_2 values can be significant for such low values, i.e., in the 10^{-5} mL mol/g^2 range. The average values and standard deviations in the different solvents were found to be similar in toluene (0.5 ± 0.1), in THF (0.5 ± 0.2), and in chloroform (0.7 ± 0.1) (values given as $\times 10^{-4}$ mL mol/g^2). Similarly, the average A_2 value for PS(660)-*b*-PAA(*x*) in toluene was $(0.5 \pm 0.2) \times 10^{-4}$ mL mol/g^2. These A_2 values were found to be significantly lower than those for linear PS of the same weight-average molecular weight. For instance, A_2 for PS in toluene[63] at a M_w of 2×10^6 g/mol is 2.5×10^{-4} mL mol/g^2, which is higher by a factor of 5 than those determined for the reverse micelles.

3.2.3. Dynamic Light Scattering. The hydrodynamic diameters (D_h) for PS(660)-*b*-PANa(*x*) were determined from DLS data using eq 8. These values are summarized in Table 5 for the block ionomers in toluene, THF, and chloroform. The D_h values were found to be very similar in these three solvents. The D_h for block copolymer micelles are expected to depend on the length of the soluble block, the quality of the solvent, and the aggregation number. The former two parameters affect the size of the PS coronal chains, while the latter parameter affects the core size. The size of the polymer chains can be described by the empirical Mark–Houwink parameter, which, for Θ solvents, has a value of 0.50. The values for this coefficient for PS in toluene, THF and chloroform are ca. 0.74, 0.72, and 0.75.[50] Thus, the expansion of the PS corona in these solvents is expected to be very similar.

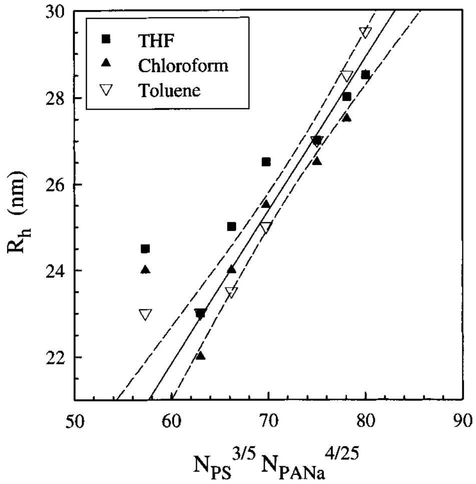

Figure 6. Hydrodynamic radii for PS(660)-*b*-PANa(*x*) in different solvents plotted according to the scaling relation of the star model.

The R_h values of the block copolymer micelles have been described by the star model,[49] which addresses block copolymer micelles which have a small core and a relatively large corona. The R_h scales as

$$R_h \sim aN_A^{3/5}N_B^{4/25} \qquad (13)$$

where a is the length of a monomer unit and N_A and N_B are the number of monomer units in the soluble and insoluble blocks, respectively. The R_h values plotted according to this relation are given in Figure 6. The solid and the dashed lines represent the linear regression through the data for the three solvents and the 95% confidence limits, respectively. The slope and intercept of the line were 0.35 and 0.68, respectively, with a correlation coefficient of 0.94. This scaling prediction thus adequately describes the R_h values, with the exception of those for the PS(660)-*b*-PANa(2.6) block copolymers, which were omitted in the linear regression analysis. At this point it is not clear why these R_h values deviate from the line; however, it may be possible that for these samples, the PANa block is not sufficiently long to adopt a collapsed conformation. Consequently, the insoluble block would exist in an extended conformation, which might result in larger micelle size.

The R_h values can be used to calculate the A_2 values for hard spheres. These A_2 values are given as[64]

$$A_2 = 16\pi N_{av}R^3/3M_w(\text{mic})^2 \qquad (14)$$

where R is the equivalent thermodynamic radius. It was found that the A_2 values were in the same range as those measured by SLS (Table 5). For instance, for PS(660)-*b*-PANa(*x*) in toluene, the average of the measured and the calculated values were $(0.5 \pm 0.2) \times 10^{-4}$ and $(0.23 \pm 0.09) \times 10^{-4}$ mL mol/g^2, respectively. The thermodynamic intermicellar interactions are thus close to those for hard spheres.

3.3. Effect of PS Block Lengths on the Aggregation of PS-*b*-PANa Block Ionomers. In this part of the paper, a description is given of the effects of the soluble block lengths on the aggregation of PS-*b*-PANa block ionomers in THF as investigated by SLS. The composition and polydispersity indexes of the block ionomers are given in Table 1. The PS block lengths investigated had 190, 630, and 2300 units, attached to PANa blocks ranging in length from 4.2 to 69 units. The results obtained on the block ionomers are given in Table 6. The weight percent of micellized chains given in this table was determined by SEC in a previous study.[39] From these values, the weight-average molecular weight of the micelles and the aggregation numbers were evaluated as described in the previous section (3.2.2).

Figure 7 illustrates a plot of the N_{agg} values as a function of the PANa block length for different PS block lengths. Included in this figure are the values for the PS(660)-*b*-PANa(*x*) block ionomers discussed in the previous section. From the trends, it can be concluded that for a constant PANa block length, the N_{agg} values decrease as the length of the PS block increases. This decrease in the N_{agg} values was more pronounced for longer PANa block lengths. Thus, the soluble block length was found to influence the aggregation numbers significantly.

The PS(190)-*b*-PANa(24) sample had a much higher aggregation number (590) than the other samples investigated. The mole percent of the ionic block for this sample was 11%, much higher than that of the other samples investigated, which ranged from 0.20 to 5%. It is possible that this sample forms aggregates having a nonspherical morphology. For polymers containing an ionic phase such as the segmented ionene systems[65] and block ionomers of poly(*n*-hexyl methacrylate)-*b*-poly(cesium methacrylate),[66] the cylindrical or lamellar morphology has been observed in bulk at an ionic content of ca. 10%. In non-ionic block copolymers such as PS-*b*-PI, the transition from spherical to cylindrical morphology has been observed at a higher mole percent (ca. 17 mol %).[67,68] The morphological change occurs at lower mole percent for the ionic systems compared to the non-ionic systems due to the larger interaction parameter between the two blocks.[69]

It was of interest to determine the scaling relation between the aggregation numbers and the PS and PANa block lengths. The PS(190)-*b*-PANa(24) block copolymer sample is omitted from the present discussion, for reasons discussed above. Since the PS block length was found to influence the N_{agg} values, theories such as the star model[49] could not be employed. The effect of the soluble and insoluble blocks on N_{agg} are considered in the mean field theories of Whitmore and Noolandi[70] and of Nagarajan and Ganesh.[58] The N_{agg} values can be described by

$$N_{agg} \propto N_{PANa}^{\alpha}N_{PS}^{\beta} \qquad (15)$$

where α and β are constants. The β constant was determined from a plot of log N_{agg} versus log N_{PS} for a constant PANa block length of 10 units. The β constant was evaluated to be −0.64. Similarly, the α constant was determined from the slope of a plot of log N_{agg} versus log N_{PANa} for constant PS block lengths. Since the α values were found to vary with the PS length, for instance, they were 0.82, 0.38, and 0.36 for PS block lengths of 630, 660, and 2300 units, respectively, the average value was employed (0.52). A linear relationship between the N_{agg} values and $N_{PANa}^{0.5}N_{PS}^{-0.6}$ was found with a correlation coefficient of 0.83 (graph not shown).

The dependence of the core radii (R_c, calculated from eq 2), on the PS and PANa block lengths was also investigated. It should be noted that eq 2 is valid only for micelles which have solvent-free cores. Recently the core radii for similar block ionomers were determined

Table 6. Summary of SLS Results for PS(*x*)-*b*-PANa(*y*) in THF

PS(*x*)-*b*-PANa(*y*)	micellized chains (%)[39]	$10^{-6}M_w$ (g/mol) total	$10^{-6}M_w$ (g/mol) micelle	N_{agg}	R_g (total) (nm)	10^4A_2 (mL mol/g^2)
190-*b*-10	96	2.55	2.64	130	42	0.35
190-*b*-24	97	12.6	13.0	590	85	1.1
630-*b*-4.2	77	1.03	1.32	20	54	0.42
630-*b*-18	95	5.05	5.31	79	50	0.50
630-*b*-31	98	6.92	7.04	100	50	0.56
2300-*b*-4.6	68	3.84	5.54	23	58	
2300-*b*-31	83	8.23	9.89	41	65	0.40
2300-*b*-69	84	12.5	14.8	60	68	0.54

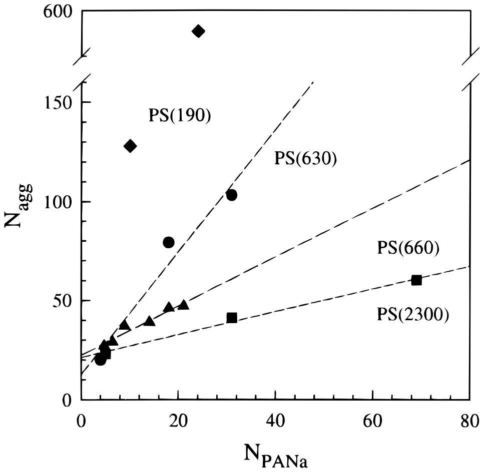

Figure 7. Aggregation numbers of PS(*x*)-*b*-PANa(*y*) in THF plotted as a function of the PANa block length for different PS block lengths.

by SAXS in solution (toluene and THF) and in the solid state.[71] The R_c values for these two states were found to agree, indicating the solvent-free nature of these ionic cores in solution. The R_c values are expected to obey the same scaling relation given in eq 15 with different α and β values. The values for the α and β constants were determined in the same manner as those for the N_{agg} scaling relation. The β constant was evaluated from a log−log plot of R_c versus N_{PS} for a N_{PANa} value of 10 units and was found to be −0.22. The α constant for PS block lengths of 630, 660, and 2300 units were 0.61, 0.45, and 0.45, respectively. The average value (0.50) was used to evaluate the scaling relation. The main part of Figure 8 shows the plot of R_c as a function of $N_{PANa}^{0.5}N_{PS}^{-0.2}$. The solid line corresponds to the linear regression having a correlation coefficient of 0.95. The intercept and slope of the line were −0.03 and 2.4, respectively. It is to be expected that the correlation coefficient for scaling relations involving the radius are better than those involving N_{agg}, since the calculation of R_c involves the cube root of N_{agg} (eq 2).

For the present block ionomer system, the scaling relations of N_{agg} and R_c were found to depend significantly on the length of the PS block length. The theory of Nagarajan and Ganesh[58] has predicted a significant dependence of the micellar parameters on the soluble block for systems in which the solvent is very good for the soluble block. This appears to be applicable to the present case, where THF is a good solvent for PS. The micellar parameters for PEO-*b*-PPO block copolymers in water were modeled in that theory.[58] It was found that N_{agg} and R_c scaled as $N_{agg} \propto N_{PPO}^{0.73}N_{PEO}^{-0.51}$ and $R_c \propto N_{PPO}^{0.73}N_{PEO}^{-0.17}$. The magnitude of the dependence on the length of the soluble block (PEO) was found to be similar to the present system ($N_{agg} \propto N_{PANa}^{0.5}N_{PS}^{N-0.6}$ and $R_c \propto N_{PANa}^{0.5}N_{PS}^{-0.2}$).

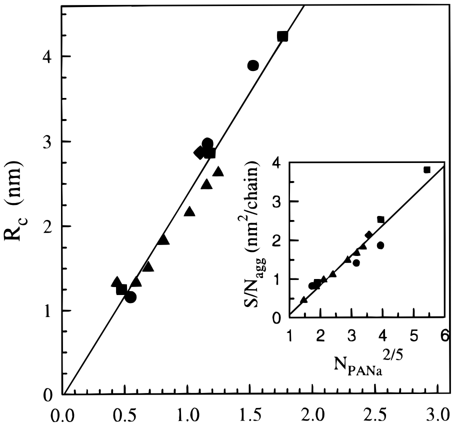

Figure 8. Calculated core radii for the PS(*x*)-*b*-PANa(*y*) samples investigated in THF plotted as a function of the PS and PANa block lengths for the series with PS block lengths of 190 (◆) , 630 (●), 660 (▲) and 2300 (■) units. The inset is a plot of the surface area per chain as a function of $N_{PANa}^{2/5}$.

Table 7. Comparison of Aggregation Numbers Determined by SLS and SAXS[41]

composition	SLS (Na, THF)	SAXS (Cs, toluene)
PS(190)-*b*-PA(10)-Na or Cs	130	120
PS(190)-*b*-PA(24)-Na or Cs	590	88
PS(630)-*b*-PA(4.2)-Na or Cs	20	34
PS(630)-*b*-PA(18)-Na or Cs	79	86
PS(630)-*b*-PA(31)-Na or Cs	100	140
PS(2300)-*b*-PA(69)-Na or Cs	41	110

The scaling relation of another micellar parameter, the surface area per chain (S/N_{agg}), calculated from eq 3 was also investigated. It was found that S/N_{agg} was proportional to $N_{PANa}^{2/5}$, as predicted by the star model.[49] The inset of Figure 8 shows this scaling relation, in which the regression coefficient was 0.94. The intercept and slope of the line were −0.68 and 0.76, respectively. From this result, it can be seen that the soluble (PS) block length has no effect on the surface area per chain values.

The micellization of similar block ionomers has been investigated in a previous SAXS study.[41] The block ionomers were composed of PS blocks attached to either poly(cesium acrylate) (PACs) or poly(cesium methacrylate) (PMACs). The samples were measured in toluene at a concentration of ca. 0.05 g/mL, which was much higher than those used in the present SLS study (ca. 0.02−2 mg/mL). The composition of several of these block ionomers were identical with those given in Table 6, with the exception that a Cs counterion was used in the samples studied by SAXS.

The N_{agg} values for the block ionomers as determined by both SLS and SAXS are given in Table 7. In general, satisfactory agreement was obtained between the two methods with the exception of two samples. For instance, the N_{agg} value for PS(190)-*b*-PACs(24) was found to be significantly smaller by SAXS than by SLS. The lower value by SAXS is probably due to the fact that a spherical morphology was assumed in the calculations, whereas by SLS it was suggested that the sample most likely has a nonspherical morphology. The PS(2300)-*b*-PANa(69) sample was found to be significantly larger by SAXS compared to that evaluated by SLS. This difference is not fully understood at this time but may be related to sample preparation conditions. It should also be noted that the present study found a strong influence of the soluble block length on N_{agg}, while by SAXS the N_{agg} were found to be independent of the PS block length. Excluding these two samples, a plot of N_{agg} values determined by SLS versus those determined by SAXS had a slope close to unity (1.1) when the linear regression was passed through the origin (graph not shown).

4. Conclusions

The aggregation of two block copolymer series, PS(660)-*b*-PANa(*x*) and PS(660)-*b*-PAA(*x*), was investigated by SLS, SEC, and DLS. The cmc's were determined for the salt form in toluene, THF, and chloroform and for the acid form in toluene. These values were found to decrease as the insoluble block length increased. In general, the cmc values ranged from 1×10^{-7} to 5×10^{-9} M. The *a* and *b* constants in the relation $\log C_i = aN_i^{1/3} + b$ were determined for these systems. The value of the *a* constant for the block ionomer system was relatively small (ca. −0.6) which is reflected in a weak dependence of the cmc on the PANa block length. As a consequence, very little segregation was found in the molecular weight distributions of the block copolymers present as single chains in solution and those in the micelle fraction.

For the present systems as well as for several other block copolymer micelles the *a* and *b* constants were correlated with estimated interaction parameters between the polymer forming the core and the solvent, $\chi_{\mathrm{core-sol}}$. It was found that the absolute magnitude of the *a* values were inversely proportional to the $\chi_{\mathrm{core-sol}}$ values, while the $-b$ values were proportional to the $\chi_{\mathrm{core-sol}}$ values. This result shows that when the interaction between the polymer forming the micelle core and the solvent is strong (large incompatibility), the dependence of the cmc on the insoluble block length is weak (small absolute value of *a*), and the cmc values are low (small *b* value).

The mixed micelle model describes the cmc values for block copolymers which have collapsed insoluble blocks. For insoluble blocks which have lengths less than the minimum length required for collapse, the cml concept seems valid. These chains, which are ca. 2−3 units long, are expected to have cmc's which are larger than those assuming collapsed insoluble blocks.

Other aspects of aggregation such as the aggregation numbers, second virial coefficient values, and the hydrodynamic radii were also investigated. The trends in the aggregation numbers with increasing insoluble block lengths were found to be opposite to those observed for the cmc values. The hydrodynamic radii for PS(660)-*b*-PANa(x) in toluene, THF, and chloroform were found essentially to be the same, since the expansion of PS in these solvents is expected to be similar.

The effect of the soluble block on the aggregation of four PS(*x*)-*b*-PANa(*y*) block ionomer series was investigated in THF. For these block ionomers, the PS block lengths were either 190, 630, 660, or 2300 units, attached to PANa blocks of various lengths, ranging from ca. 2.6 to 69 units. The aggregation numbers increased as the PANa block length increased and decreased as the length of the soluble block increased. The aggregation numbers and core radii for these four series could be described by $N_{\mathrm{agg}} \propto N_{\mathrm{PANa}}{}^{0.5}N_{\mathrm{PS}}{}^{-0.6}$ and $R_{\mathrm{c}} \propto N_{\mathrm{PANa}}{}^{0.5}N_{\mathrm{PS}}{}^{-0.2}$, respectively. The surface area per chain was found to be proportional to $N_{\mathrm{PANa}}{}^{2/5}$ as has been predicted by the star model.

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References and Notes

(1) Myers, D. *Surfaces, Interfaces, and Colloids. Principles and Applications*; VCH Publishers: New York, 1991.

(2) Langevin, D. In *Reverse Micelles Biological and Technological Revelance of Amphiphilic Structures in Apolar Media*; Luisi, P. L.; Straub, B. E., Eds.; Plenim Press: New York, 1982; p 287.

(3) (a) Petrak, K. *Brit. Polym. J.* **1990**, *22*, 213. (b) Kataoka, K.; Kwon, G. S.; Yokoyama, M.; Okano, T.; Sakurai, Y. *J. Controlled Release* **1993**, *24*, 119.

(4) (a) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975. (b) Khmelnitsky, Y. L.; Levashov, A. V.; Klyachko, N. L.; Martinek, K. *Russ. Chem. Rev.* **1984**, *53*, 319. (c) Luisi, P. L.; Giomini, M.; Pileni, M. P.; Robinson, B. H., *Biochim. Biophys. Acta* **1988**, *947*, 209.

(5) Price, C. In *Development in Block Copolymers*; Goodman, I., Ed.; Elsevier Applied Science: London, U.K., 1982; Vol. 1, pp 39−80.

(6) Riess, G.; Hurtrez, G.; Bahadur, P. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1985; Vol 2, pp 324−434.

(7) Selb, J.; Gallot, Y. In *Development in Block Copolymers*; Goodman, I., Ed.; Elsevier Applied Science: London, U.K., 1985; Vol. 2, pp 27−96.

(8) Tuzar, Z.; Kratochvil, P. *Surf. Colloid. Sci. Ser.* **1993**, 1−83.

(9) Wilhelm, M.; Zhao, C. L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J. L.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 1033.

(10) Nicholas, C. V.; Luo, Y.-Z.; Deng, N.-J.; Attwood, D.; Collett, J. H.; Price, C.; Booth, C. *Polymer* **1993**, *34*, 138.

(11) Wanka, G.; Hoffmann, H.; Ulbricht W. *Macromolecules* **1994**, *27*, 4145.

(12) Nakashima, K.; Anzai, T.; Fujimoto, Y. *Langmuir* **1994**, *10*, 658.

(13) Sikora, A.; Tuzar, Z. *Makromol. Chem.* **1983**, *184*, 2049.

(14) Vagberg, L. J. M.; Cogan, K. A.; Gast, A. P. *Macromolecules* **1991**, *24*, 1670.

(15) Quintana, J. R.; Villacampa, M.; Munoz, M.; Andrio, A.; Katime, I. A. *Macromolecules* **1992**, *25*, 3125.

(16) Quintana, J. R.; Villacampa, M.; Katime, I. A. *Macromolecules* **1993**, *26*, 601.

(17) Price, C. *Pure Appl. Chem.* **1983**, *55*, 1563.

(18) Price, C.; Chan, E. K. M.; Stubbersfield, R. B. *Eur. Polym. J.* **1987**, *23*, 649.

(19) Price, C.; Chan, E. K. M.; Stubbersfield, R. B. *Eur. Polym. J.* **1987**, *23*, 649.

(20) Zhou, Z.; Chu, B. *J. Colloid Interface Sci.* **1988**, *126*, 171.

(21) Price, C.; Stubbersfield, R. B.; El-Kafrawy, S.; Kendall, K. D. *Bri. Polym J.* **1989**, *21*, 391.

(22) Quintana, J. R.; Villacampa, M.; Munoz, M.; Andrio, A.; Katime, I. A. *Macromolecules* **1992**, *25*, 3125.

(23) Linse, P.; Malmstem, M. *Macromolecules* **1992**, *25*, 5434.

(24) Zhou, Z.; Chu, B.; Peiffer, D. G. *Macromolecules* **1993**, *26*, 1876.

(25) Selb, J.; Gallot, Y. In *Polymeric Amines and Ammonium Salts*; Goethals, E. J., Ed.; Pergamon Press: New York, 1980; p 205.

(26) Morishima, Y.; Itoh, Y.; Hashimoto, T.; Nozakura. S.-I. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2007.

(27) (a) Cao, T.; Munk, P.; Ramireddy, C.; Tuzar, Z.; Webber, S. E. *Macromolecules* **1991**, *24*, 6300. (b) Kiserov, D.; Prochazka, K.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 461.

(28) Khougaz, K.; Astafieva, I.; Eisenberg, A. *Macromolecules,* in press.

(29) Astafieva, I.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7339.

(30) Astafieva, I.; Khougaz, K.; Eisenberg, A. *Macromolecules,* in press.

(31) Desjardins, A.; Eisenberg, A. *Macromolecules* **1991**, *24*, 5779.

(32) (a) Möller, M. *Synth. Met.* **1991**, *41*−43, 1159. (b) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *J. Am. Chem. Soc.* **1992**, *114*, 7295. (c) Moffitt, M.; McMahon, L.; Pessel, V.; Eisenberg, A. *Chem. Mater.* **1995**, *7*, 1185.

(33) Tuzar, Z.; Konak, C.; Stepanek, P.; Kratochvil, P.; Prochazka, K. *Polymer* **1990**, *31*, 2118.

(34) Khougaz, K.; Gao, Z.; Eisenberg, A. *Macromolecules* **1994**, *27*, 6341.

(35) Gao, Z.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7353.

(36) Linse, P. *Macromolecules* **1994**, *27*, 6404.

(37) Elias, H. G. In *Light Scattering from Polymer Solutions;* Huglin, M. B., Ed.; Academic Press: New York, 1972; Chapter 9.

(38) Desjardins, A.; van de Ven, T. G. M.; Eisenberg, A. *Macromolecules* **1992**, *25*, 2412.

(39) Zhong, X. F.; Varshney, S. K; Eisenberg, A. *Macromolecules* **1992**, *25*, 7160.

(40) Gao, Z.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 794.

(41) Nguyen, D.; Varshney, S. K.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1994**, *27*, 5086.

(42) Nguyen, D.; Williams, C. E.; Eisenberg, A.; *Macromolecules* **1994**, *27*, 5090.

(43) Nguyen, D.; Zhong, X. F.; Williams, C. E; Eisenberg A. *Macromolecules* **1994**, *27*, 5173.

(44) Khougaz, K.; Nguyen, D.; Williams, C. E.; Eisenberg, A. *J. Can. Chem.*, in press.

(45) Schwab, F. C.; Hellwell, I. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 435.

(46) Phoon, C. L.; Higgins, J. S.; Burchard, W.; Peiffer, D. G. *Makromol. Rep.* **1992**, *A29*, 179.

(47) Zhou, Z.; Chu, B.; G. Wu; Peiffer, D. G. *Macromolecules* **1993**, *26*, 2968.

(48) Zhou, Z.; Peiffer, D. G.; Chu, B. *Macromolecules* **1994**, *27*, 1428.

(49) (a) Zhulina, E. B.; Birshtein, T. M. *Poly. Sci. USSR* **1985**, *27*, 570. (b) Halperin, A. *Macromolecules* **1987**, *20*, 2943.

(50) Brandup, J., Immergut, E. H., Eds. *Polymer Handbook*; 3rd ed.; John Wiley and Sons: New York, 1989.

(51) Huglin, M. B., Ed. *Light Scattering from Polymer Solutions*; Academic Press: New York, 1972.

(52) Zimm B. H. *J. Chem. Phys.* **1948**, *16*, 1099.

(53) Benoit, H.; Froelich, D. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: New York, 1972; Chapter 11.

(54) Kratochvíl, P. *Classical Light Scattering from Polymer Solutions;* Jenkins, A. D., Ed.; Elsevier Science Publishers: New York, 1987.

(55) (a) Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 1491. (b) Hilfiker, R.; Chu, B.; Zhongde, X. *J. Colloid Interface Sci.* **1989**, *133*, 176.

(56) Brown, W. *Dynamic Light Scattering: The Method and Some Applications*; Oxford University Press: New York, 1993.

(57) Wilhelm, M.; Zhao, C. L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J. L.; Riess; G., Croucher, M. D. *Macromolecules* **1991**, *24*, 1033.

(58) Nagarajan, R.; Ganesh, K. *J. Chem. Phys.* **1989**, *90*, 5843.

(59) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters;* CRC Press: Boca Raton, FL, 1983.

(60) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1986.

(61) Bicerano, J. *Prediction of Polymer Properties*; Marcel Dekker: New York, 1993; Chapter 5.

(62) Zhong, X. F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 1751.

(63) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980**, *13*, 657.

(64) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953.

(65) Feng, D.; Wilkes, G. L.; Stark, J. E.; Lier, C. M. *J. Macromol. Sci. Chem.* **1989**, *A26*, 1151.

(66) Venkateshwaran, L. N. ; York, G. A.; DePorter, C. D.; McGrath, J. E. ; Wilkes, G. L. *Polymer* **1992**, *33*, 2277.

(67) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

(68) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.

(69) (a) Leibler, L. *Macromolecules* **1980**, *13*, 1602. (b) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.

(70) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.

(71) Nguyen, D.; Williams, C. E.; Eisenberg, A., to be published.

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