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Critical Micelle Lengths for Ionic Blocks in Solutions of Polystyrene-*b*-poly(sodium acrylate) Ionomers

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ABSTRACT: Polystyrene-*b*-poly(sodium acrylate) ionomers were found to form very stable reverse micelles in organic solvents such as tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidinone (NMP), and toluene. The micellar solutions in THF and NMP were investigated by size exclusion chromatography (SEC). Peaks were seen corresponding to both micelles and functionalized single chains; in some cases, homopolystyrene was observed as a separate peak. The single chains were thought to arise from an equilibrium solubilization of species with very short ionic chain lengths below a "critical micelle length" (CML). A computer model was developed in which the relative amounts of micelles and single chains were fitted to the experimentally obtained values using the molecular weight heterogeniety of the ionic block and the CML as the fitting parameters. The value of the CML was found to vary between 2 and 3 units of the ionic block and to be insensitive to the length of polystyrene block between 190 and 2300 units. The effects of counterions and solvents were found to be generally negligible. It is suggested that the CML is a more useful concept in these systems because of the very high free energy of micellization, which contrasts with the much lower value of that parameter for the hydrophobic core micelles. The materials were prepared by sequential anionic polymerization of styrene and *tert*-butyl acrylate in THF at −78 °C using the α-methylstyryllithium–LiCl initiator system as reported by Teyssié et al., followed by hydrolysis and neutralization.

Introduction

In the study of low molecular mass amphiphiles, both micelles and reverse micelles have received considerable attention.[1–6] One of the fundamental and extremely useful concepts, especially for the regular micelles, is that of the critical micelle concentration, cmc.[7] Below that concentration, the molecules of the amphiphile are present in the solvent as unimolecular species; above that concentration, they begin to associate to form micelles in solvents of high dielectric constant, such as water, and reverse micelles in media of low dielectric constants. Extensive experimental and theoretical studies have been performed in this area over many decades. It is known, for example, that the cmc is a sensitive function of a number of variables, one of the most important for regular micelles being the chain length of the hydrophobic segment.

When block copolymers are dissolved in solvents which are selective for one of the components, micelle-like aggregates are also known to form.[8] Although these have received much less attention than their low molecular mass counterparts, a considerable amount of information has been accumulated on these systems. The vast majority of block copolymers studied to date are hydrophobic, and in these systems the distinction between a micelle and a reverse micelle is not relevant. Furthermore, in these nonionic materials, the driving force for phase separation is usually very much smaller than in the ionic amphiphiles of low molecular mass, so that a minimum block length, usually very much larger than 1, is needed for phase separation.

Block copolymers are usually prepared by anionic polymerization techniques, as a result of which the molecular mass distributions are usually quite narrow.[9] Because of this low polydispersity and usually moderate to high molecular masses, the concept of the cmc has been shown to be useful for block copolymer micelles also.[10] Amphiphilic nonionic block copolymers are known, e.g. styrene-*b*-(ethylene oxide), and have received some attention.[11,12] Here the similarity to the ionic systems is more clear.

Block copolymers possessing one or more ionic segments have been studied very much less extensively than their nonionic counterparts, yet they also represent an ideal bridge between the low molecular mass amphiphiles and the block copolymer aggregates. They form micelle-like aggregates of two different types, depending on the relative block lengths and the solvents employed. In media of high dielectric constant, e.g. water, species with short nonionic and long ionic segments, i.e. block polyelectrolytes, for micelle-like aggregates with a hydrophobic core and an ionic corona. The small amount of work on these systems has been reviewed by Selb and Gallot,[13] and only very few studies have been carried out since then in solution,[14–18] in addition, some interest has also been evoked by their very unusual surface behavior.[19–22] Materials with short ionic and long nonionic systems, which in media of low dielectric constant form aggregates analogous to reverse micelles, are also known and can be referred to as block ionomers. Their solution properties have received still less attention[23,24] than those of the block polyelectrolytes. They are of interest, among other reasons, because of the ease with which they absorb water from organic media into their water pool,[25] which suggests a range of possible applications.

It should be pointed out that in this paper, as in the preceding and subsequent publications dealing with ionic block copolymers, the terms block ionomers and block polyelectrolytes will be used in accordance with the nomenclature suggested by Rinaudo and Eisenberg.[26] Ionomers are taken to be materials in which the properties are governed by strong ionic interactions over molecular dimensions, i.e. by the ionic aggregates or multiplets[27] in media of low dielectric constant. Polyelectrolytes, on the other hand, are taken to be materials in which the properties are governed by long-range electrostatic interactions in media of high dielectric constant. Thus, the

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same type of ionic block copolymers could be prepared either as block ionomers, as is done in this work, or as block polyelectrolytes in aqueous solution, as will be reported in future publications.

One of the publications mentioned above represents the first systematic study of block ionomers in solution.[23] It dealt with reverse micelles formed from block copolymers of styrene, the major component, connected to short segments of sodium methacrylate. The micelles were shown to be extremely stable, in that they could be studied by size exclusion chromatography (SEC). While single chains were observed, it was shown that no single chain–micelle equilibrium was involved over the time scale of the experiment; single chains could be separated from the aggregates both by SEC and by selective precipitation methods, and the initial micelle/single chain ratios were not reestablished when the micelles were allowed to stand for extended periods, even in refluxing THF. It was also shown that the ion content of the single chains was considerably lower than that of the micellized block ionomers. This was due, in part, to the presence of some styrene homopolymer, but also to the fact that the single chains of the functionalized copolymer present in solution had a very much lower ion content than the micelles. In another part of the study, the relative amounts of single chains and aggregates were determined as a function of the styrene and ionic block lengths. In an attempt to explain qualitatively the trends observed, it was postulated that block copolymer chains containing less than a critical number of ionic groups were solubilized.

The present work addresses itself to a detailed study of the micelle–single chain equilibrium in block ionomers in solution. It is shown that because of the high free energy of micellization of the ionic groups in solvents of low dielectric constant, critical micelle concentrations are extremely low for ionic blocks of reasonable lengths. Another factor which needs to be kept in mind is that even the narrowest molecular weight distributions accessible by the best techniques have a polydispersity index of the order of 1.05, which by absolute standards is relatively broad. Thus, even if only relatively short ionic chains are involved, a broad molecular heterogeneity is represented when compared with low molecular mass amphiphiles, which are truly monodisperse. Thus, the range of cmc values can be enormous. Therefore, the concept of a critical micelle length, CML, is shown to be much more useful for these systems than the cmc.

The selection of the present system was based on the consideration that of all the anionically polymerizable monomers, *tert*-butyl acrylate is expected to yield, after hydrolysis and neutralization, the most hydrophilic ionic group, i.e. one which has the smallest volume per ionic repeat unit. Clearly, the acrylate anion is considerably smaller than those based on methacrylic acid, vinylpyridine, or *p*-carboxystyrene. This system, therefore, should represent a baseline system for the study of ion-core micelles.

Theoretical Section

The first part of this section will explore, in an approximate way, the thermodynamics of the formation of reverse micelles from block ionomers in media of low dielectric constant. The second part will be devoted to modeling of the association process which allows the determination of the ionic block length at the solubility limit for single chains from SEC data.

Empirical relationships for the cmc as a function of the hydrocarbon chain length for micellization processes involving low molecular mass amphiphiles in water suggest that the relationship is of the form[28]

$$\log_{10} \mathrm{cmc} = n_c(\Delta G^{h}{}_{m}/2.3RT) + K \qquad (1)$$

where n_c is the hydrocarbon chain length and $\Delta G^{h}{}_{m}$ is the Gibbs free energy of micellization per mole of repeat units of methylene groups for the hydrocarbon component, R and T are the gas constant and temperature, respectively, and K contains all the constant terms of the equation. It does not seem unreasonable to invoke an equation of a similar form for the aggregation of block ionomers in organic solvents, i.e.

$$\log_{10} \mathrm{cmc} = n_i(\Delta G^{i}{}_{m}/2.3RT) + K' \qquad (2)$$

where n_i is the number of repeat units in the ionic block, $\Delta G^{i}{}_{m}$ is the free energy of aggregation per mole of ionic groups, and K' has a similar significance as K above. Clearly many factors are neglected in this primitive treatment, but a semiquantitative evaluation does give an appreciation for the relative importance of the most important factors involved.

One factor of interest is the rate at which the cmc changes with n_i. A quantitative estimate of this factor can be obtained by differentiating the cmc equation, i.e.

$$\mathrm{d} \log_{10} \mathrm{cmc}/\mathrm{d}n_i = \Delta G^{i}{}_{m}/2.3RT \qquad (3)$$

The free energy of aggregation of the ionic groups is given by

$$\Delta G^{i}{}_{m} = \Delta H^{i}{}_{m} - T\,\Delta S^{i}{}_{m} \qquad (4)$$

In nonionic block copolymer systems, it has been suggested[10] that the enthalpy contribution to the free energy is responsible for the association. Since the micellization in the present system involves assembly of ionic species, it seems reasonable that the free energy will also be governed primarily by the enthalpy term. The latter, in turn, is expected to be at least of the order of a strong hydrogen bond, i.e. −20 kJ/mol. Thus, one obtains

$$\mathrm{d} \log_{10} \mathrm{cmc}/\mathrm{d}n_i \approx -20000/2.3 \times 8.3 \times 300 = -3.5 \qquad (5)$$

This, in turn, suggests that for an increase in the ionic block of one unit, the cmc will drop by 3.5 orders of magnitude. For low molecular mass amphiphiles in water, the observed drop in log cmc as a function of the alkyl chain length is ca. one-tenth that value.[28] Naturally, if $\Delta G^{i}{}_{m}$ were greater than −20 kJ/mol, the drop would be larger.

Another factor that should be recalled is that low molecular mass amphiphiles are chemically monodisperse, while the block copolymers under study here are quite heterogeneous by comparison, even if they are close to the best that can be produced by anionic techniques for such short ionic block lengths. Thus, for example, a block copolymer containing an average of five ionic repeat units with a Gaussian distribution and a polydispersity index of 1.1, will contain 1% of blocks of one unit, 4% of two, 11% of three, 21% of four, 25% of five, 21% of six, 11% of seven, 4% of eight, and 1% of nine. Thus, the range of cmc values represented by these species covers more than 30 orders of magnitude if they were present individually as monodisperse materials. Obviously they are now, and most copolymer systems used to prepare aggregates will contain both species which are above the cmc and those which are below. When such a system is dissolved in a solvent for the nonionic component, the chains with very short ionic blocks would be present as single chains at all reasonable polymer concentrations.

The data to be presented later in this paper were acquired mostly by SEC, which employs concentrations of 2 g/L or $\approx 10^{-5}$ mol/L. At that concentration, it is clear that chains with ionic block lengths below a certain value should be soluble. Furthermore, the thermodynamic arguments presented above suggest that a change of polymer concentration of 3.5 orders of magnitude is accompanied by a change in the cutoff point for solubility by one ionic unit. It should be borne in mind, however, that experimental errors associated with the determination of that cutoff point are of the order of one unit. Therefore, for a particular block copolymer, it seems far more reasonable to speak of a critical micelle length (CML) than a critical micelle concentration, especially over the relatively narrow concentration ranges employed in the study of block ionomer micelles, and it is this concept which will be employed.

As will be shown, the ionic block lengths at the solubility limit are very short. The nonionic block lengths, by contrast, can be quite long, so that nonionic to ionic block length ratios frequently are in the range of 100:1 to 1000:1. Currently available analytical tools do not allow the precise determination of such short ionic block lengths in the polymers studied here, i.e. styrene and sodium acrylate. It is much more convenient to investigate the relative amounts of micelles and single chains for various average ionic block lengths, while keeping the nonionic block length constant. From this relative amount one has to calculate the solubility limit or CML for the particular family of ionomer blocks. Such a calculation necessarily involves some assumptions.

One of these involves the chain length distribution of the ionic block. In this work, three types of distributions are used, i.e. Poisson, continuous Gaussian which allows for the chains containing fractional repeat units, and discontinuous Gaussian distribution which accepts only integers. This should provide an idea of the effect of the assumed distribution on the CML. Still other distributions could, of course, have been taken, but the results, as will be shown, are not very sensitive to the details of the distribution, as long as its width is allowed to vary. In the Gaussian distribution assumption, the polydispersity index is assumed to be identical for all the ionic block lengths for the same PS family.

A second assumption involves the dependence of the cutoff on the nonionic block length and other parameters. Here it is assumed that the cutoff length (CML) depends only on the PS block length for a given solvent and temperature. Thus, for a family consisting of an identical PS block and of varying ionic block lengths, the CML is taken to be identical. Finally, all the chains above the CML are taken to be in the micelles, while those at and below that length are taken to be soluble.

It is recognized that the acrylate blocks are, in some cases, very short (e.g. sample 1b which contains, on the average, only 1.1 ionic units, see below). Therefore, only a very small amount of acrylate monomer is added to the polystyrene anion in the crossover step to produce such samples. Thus, given the operative rates of initiation and propagation, it is very likely that some PS chains might not initiate acrylate sequences at some compositions (see discussion section). This is also possible if a small fraction of the PS chains are terminated by impurities, which is expected even in the best copolymerization procedures. Thus, some styrene homopolymer is expected to be present. This homopolymer fraction is obviously not expected to participate in the micellization process. If the amount of homopolymer is known, its effect can be taken into account in the modeling. If the SEC does not allow the determination of the homopolymer content, it is treated as a fitting parameter.

The fitting parameters involved in the modeling are, thus, the CML, the value of the ionic block polydispersity index (for Gaussian distributions), and the amount of nonionic homopolymer if the latter cannot be separated from the functionalized single chains with ionic block lengths below the CML. With the above assumptions and fitting parameters, the plot of the percentage of micelles in the micelle–single chain mixture is fitted using an iteration procedure in a very simple BASIC program on a PC.

Experimental Section

Reagents and Solvents. Styrene and α-methylstyrene were dried over calcium hydride (CaH_2) for 24 h, distilled under vacuum, and stored under nitrogen at −20 °C. They were then treated with fluorenyllithium for 15 min and distilled under vacuum (mechanical pump) just before polymerization. *tert*-Butyl acrylate (*t*BuA) was also dried over CaH_2 for 24 h, vacuum distilled, and stored under nitrogen in the dark at −20 °C. It was diluted with toluene and then treated with a 10% triethylaluminum solution in hexane until a persistent greenish-yellow color was observed.[29] Finally, it was distilled under vacuum prior to polymerization.

Tetrahydrofuran (THF) was purified by refluxing over sodium benzophenone complex under nitrogen (a blue-violet color indicating a solvent free of oxygen and moisture). It was further distilled under dry nitrogen over poly(styryllithium). Toluene was distilled after refluxing over CaH_2 for several days.

LiCl (99.99%+) was obtained from Aldrich. It was dried under vacuum overnight at 130 °C in a glass reactor which was to be used for the block copolymerization.

The initiator used in this study was the reaction product of *sec*-butyllithium with a few units of α-methylstyrene. It was prepared in the glass reactor which was to be used for the polymerization. A deep purple red color developed in the THF at room temperature.

Polymerization. The anionic block copolymerization of styrene and *t*BuA was carried out under nitrogen atmosphere in a previously flamed glass reactor, employing the procedure described recently by Teyssié et al.[30] LiCl was first introduced into the glass reactor and dried as described above. The monomers, solvent, and initiator were transferred by a syringe and capillary techniques. A typical synthesis involved introducing 0.68 g (1.6×10^{-2} mol) of LiCl into the flask. THF (1000 mL) and α-methylstyrene (2 mL) were then charged into the reactor. After the LiCl had completely dissolved in the THF, the solution was cooled to −20 °C; it was then titrated with *sec*-BuLi until a light red color developed, which was followed by the addition of 1.2 mL of *sec*-BuLi (1.3 M). After 15 min, the solution was cooled to −78 °C; 30 g of styrene was added dropwise by means of a stainless steel capillary accompanied by vigorous stirring. The dark red color of the initiator solution changed quickly to a deep orange-yellow color. A few minutes after the last drop of styrene was added, the color changed back to dark red, indicating the end of the styrene polymerization.[31] However, the polymerization was allowed to proceed for 10 min beyond that point. An aliquot (100 mL) of the reaction medium was withdrawn for analysis by size exclusion chromatography (SEC) in order to determine the degree of polymerization of the polystyrene block. *t*BuA (0.2 g) was then added to the polymerization medium as a dilute solution (75% (v/v) in toluene). Upon addition of a few drops of the *t*BuA solution, the red color of the living poly(styryllithium) anions changed instantaneously to a light yellow color. After 5 min, an aliquot of 200 mL of the reaction medium was withdrawn as the first block copolymer with the shortest of *t*BuA sequence attached to the polystyrene block. Subsequent stepwise additions of *t*BuA in 1-mL amounts were continued after withdrawals of 200 mL of solution at each step. This procedure allowed the preparation of a series of polystyrene-*b*-poly(*tert*-butyl acrylate) copolymers with the same polystyrene block length but with varying poly(*tert*-butyl acrylate) lengths. The polymers were recovered by precipitation into methanol or a methanol/water mixture (80/20 (v/v)) and were dried under vacuum at 80 °C for 48 h.

Hydrolysis. The block copolymers were hydrolyzed to polystyrene-*b*-poly(acrylic acid) (PS–PAA) by using *p*-toluenesulfonic acid as the catalyst (5 mol % relative to the polyacrylate content).[32] They were dissolved in toluene, the catalyst was added, and the solution heated at reflux overnight. After cooling, the polymers were precipitated into cold methanol, washed several times with methanol, and dried under vacuum at 50 °C for 48 h. Hydrolysis was found to be complete from a FTIR study (see results section).

Neutralization. The dried copolymers of PS–PAA were dissolved in benzene/methanol (90/10 (v/v)). The polymer concentration was about 2% (w/w). The acid content was neutralized by addition of a stoichiometric amount of $NaOCH_3$. The $NaOCH_3$ solution was prepared by reacting Na with CH_3OH in THF. The polymer solution was stirred for 30 min and the methanol was stripped off under vacuum. The material was recovered by freeze-drying. It was subsequently dried at 60 °C for 48 h. Micellar solutions were obtained by dissolving the dried powder in the desired solvent.

One sample was neutralized separately with LiOH, NaOH, KOH, CsOH, $Ba(OH)_2$, NH_4OH, $N(CH_3)_4OH$, and NBu_4OH to prepare the block ionomers with different counterions.

Size Exclusion Chromatography. The SEC measurement was performed at room temperature on a Varion 5010 liquid chromatography apparatus equipped with a refractive index detector. THF was used as eluent at a flow rate of 1 mL/min. The column was a progel-TSK G4000 HXL from Supelco, Inc. One run was also made on PL gel 10^3 Å obtained from Polymer Lab. The system was calibrated with monodisperse polystyrene. The concentration of injected polymer solution was about 2 mg/mL. The solution was filtered through membrane filters before injection. The number and weight average molecular weight of the polystyrene block and the final copolymer were calculated by a Varian DS-604 computer with SEC application software. The possible adsorption of the polymer by the column will be discussed later.

Some samples were analyzed on a Waters CV-150 high temperature SEC equipped with a refractometer and a viscometer as detector. *N*-Methylpyrrolidinone (NMP) was used as eluent. The temperature of the column compartment was set at 90 °C. The chromatographic results from the refractometer will be discussed by comparison with those obtained at room temperature with THF also using refractometric detection.

FTIR Spectroscopy. The FTIR spectroscopy was carried out on Perkin-Elmer 16PC apparatus. For qualitative analysis, polymer films were cast on a KBr window. The spectra of the films were recorded. For quantitative measurements, the spectra of polymer solutions in CCl_4 were recorded with a KBr cell (optical path = 15 μm).

As the carbonyl C═O of poly(*tert*-butyl acrylate) gives a very strong and narrow absorption band in the infrared region at 1730 cm^{-1}, FTIR spectroscopy can be used to subsequently determine the polyacrylate content of the copolymers. The procedure consisted in calibrating a KBr cell homopoly(*tert*-butyl acrylate) solution in CCl_4 and determining the absorbance of a solution of the copolymer PS–P*t*BuA of known concentration in the same cell. In order to obtain the extinction coefficient of the C═O, the absorbance at 1730 cm^{-1} was plotted as a function of the concentration of homopoly(*tert*-butyl acrylate) (Figure 1). A straight line was obtained as expected from the Beer–Lambert law. The extinction coefficient, which is 0.384 OD L/g was obtained from the slope. Thus the weight fraction of poly(*tert*-butyl acrylate) in the copolymers was calculated from

$$f_{PA} = A_{1730}/0.384C \qquad (6)$$

where *C* is the copolymer concentration in g/L.

Titration. The poly(acrylic acid) content of one series of copolymers PS–PAA was determined by titration with 0.0138 M NaOH/MeOH. A known weight of PS–PAA was dissolved in toluene/MeOH (9:1 (v/v)). The end point was determined by a pH meter.

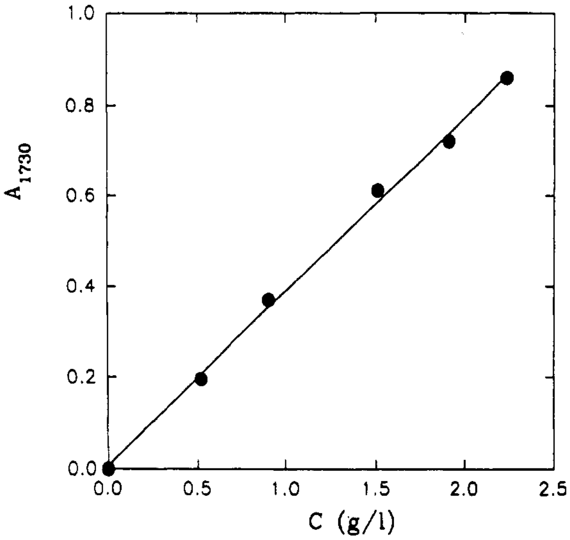

Figure 1. Absorbance at 1730 cm^{-1} as a function of the concentration of poly(*tert*-butyl acrylate).

Table I
Composition of Block Copolymers of Polystyrene-*b*-poly(*tert*-butyl acrylate)

sample no.	molar fraction of poly(*t*BuA)[a]	molar fraction of poly(acrylic acid)[b]	composition[c]	M_w/M_n[d]
1a			190-*b*-0	1.12
1b	0.0057	0.0056	190-*b*-1.1	
1c	0.019	0.018	190-*b*-3.8	
1d	0.050	0.042	190-*b*-10	1.10
1e	0.112	0.103	190-*b*-24	1.13
2a			630-*b*-0	1.10
2b	0.0066		630-*b*-4.2	
2c	0.028		630-*b*-18	1.12
2d	0.047		630-*b*-31	1.12
2e	0.121		630-*b*-87	1.13
3a			2300-*b*-0	1.12
3b	0.0020		2300-*b*-4.6	
3c	0.013		2300-*b*-31	
3d	0.029		2300-*b*-69	1.12
3e	0.076		2300-*b*-190	1.12

[a] From FTIR. [b] From titration. [c] From SEC and FTIR; *m*-*b*-*n* stands for *m* units of styrene and *n* units of *tert*-butyl acrylate. [d] From SEC. Samples with very short ester blocks were not measured.

Results

Composition of the Block Copolymers. The compositions of the copolymers as determined by FTIR spectroscopy and/or titration are presented in Table I. For the first series, it is clear that the values obtained by both techniques are in close agreement, which confirms that the hydrolysis of the ester moieties to carboxylic acid groups was essentially complete. The quantitative conversion is also supported by FTIR spectra. Figure 2 shows the spectra of a block copolymer (sample 1e) in the ester form, the acid form, and the sodium salt form. It is evident that after hydrolysis, the absorption band at 1730 cm^{-1} due to ester C═O stretching vibration becomes a broad doublet absorption band at 1738 and 1710 cm^{-1}, characteristic of carboxylic acids. Furthermore, a band at 1150 cm^{-1} from C—O stretching of the ester, disappears completely after hydrolysis. After neutralization with $NaOCH_3$, the C═O band around 1730 cm^{-1} shifts totally to 1582 cm^{-1}, again indicating essentially complete hydrolysis and neutralization.

Size Exclusion Chromatograms. All the polystyrenes and their copolymers with *tert*-butyl acrylate gave one narrow SEC peak. The polydispersity index (M_w/M_n) varied between 1.10 and 1.13 as shown in Table I. The

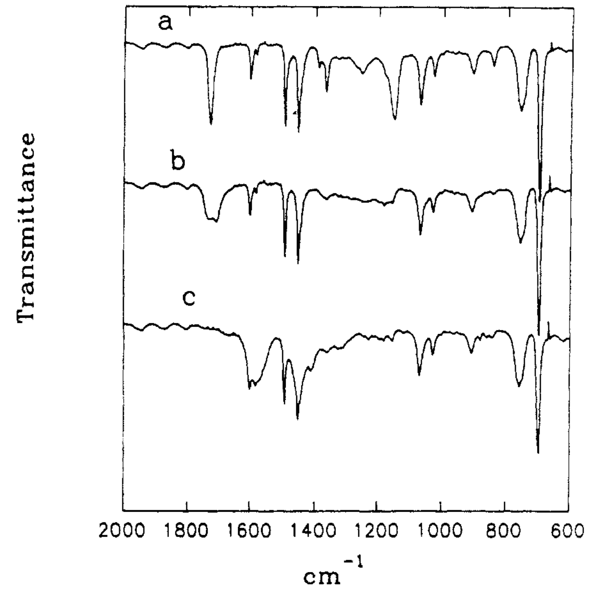

Figure 2. FTIR spectra of polystyrene-*b*-poly(*tert*-butyl acrylate) (a), polystyrene-*b*-poly(acrylic acid) (b), and polystyrene-*b*-poly(sodium acrylate) (c).

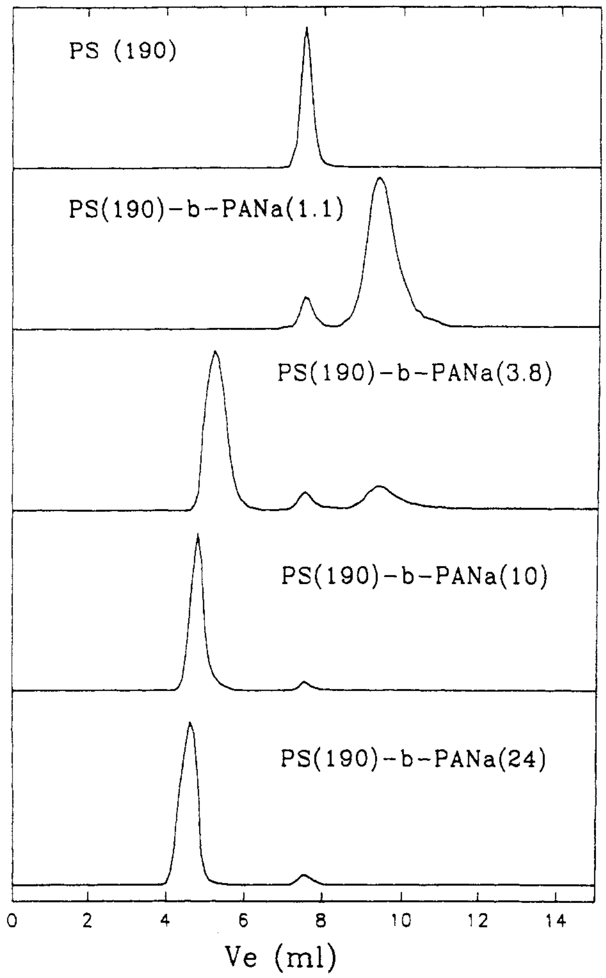

Figure 3. Size exclusion chromatograms of one series of block ionomers PS(190)-*b*-PANa(*x*). Where *x* is the length of the polyacrylate block.

copolymers in the acid form could only be partially eluted from the column and were not studied further. By contrast, for the copolymers in sodium salt form, well-defined chromatograms were obtained, and adsorption of materials by the column was not a problem. This was ascertained from the fact that the ratio of the total peak area (A in arbitrary units for the system) to the polymer concentration (C in g/L) for the block ionomers was approximately equal to that found for polystyrene. (A/C = (1.60 ± 0.14) × 10^6 for PS(190)-*b*-PANa, (1.80 ± 0.11) × 10^6 for PS(630)-*b*-PANa, (1.75 ± 0.09) × 10^6 for PS-(2300)-*b*-PANa, and (1.87 ± 0.14) × 10^6 for polystyrene.) Also, the elution volumes and the peak areas were reproducible. One sample was analyzed on two different columns (Supelco and PL). The same peak area ratio of micelles to single chains was obtained on both columns. For copolymers with polystyrene blocks shorter than those investigated here, serious column adsorption problems were found. Data for those series are not reported.

Figure 3 shows the chromatograms of one series of copolymers (series 1) in the sodium salt form, along with homopolystyrene of the same chain length as that of the PS block of the copolymers as reference. The polystyrene block had 190 units, and the poly(sodium acrylate) blocks contained 1.1, 3.8, 10, or 24 units. The evolution of the chromatograms is noteworthy. For copolymer 1b, which has an average of 1.1 units attached to the polystyrene block, two peaks are observed. The peak at the lower elution volume (7.5 mL) is located at the same position as that for the homopolystyrene. It was therefore assigned to homopolystyrene of 190 units. Surprisingly, the second peak at 9.5 mL has higher elution volume than that of the homopolystyrene. If the separation were based only on size exclusion, the size or molecular weight of the component eluted at this volume should be much smaller than that of the homopolystyrene. This is impossible, since no chain scission can have taken place in the column or during the hydrolysis and neutralization. This peak, however, can be attributed to the free block copolymer which does not participate in the micellization process. Its elution is delayed, possibly either by some temporary adsorption process or by interaction with the ionic group of other single chains leading to reversible trapping by the packing material of the SEC column. Similar adsorption behavior of colloidal particles by an SEC column has also been mentioned by Tuzar et al.[33] A comparable retardation has also been found for random copolymers of styrene with acrylic acid.[34]

When the length of ionic block increases to 3.8, the peak at 9.5 mL decreases dramatically while that of the homopolystyrene is reduced only slightly. A third peak appears at 5.2 mL, a much lower elution volume than that of the two other peaks. This peak corresponds to an apparent molecular weight of about 200 000 (as calibrated against PS standards) and is attributed to the aggregates (reverse micelles). The real molecular weight may be much higher. A subsequent publication will deal with the size characterization of these micelles in a manner analogous to that performed previously for the styrene-*b*-poly(metal methacrylate) micelle system.[23,24] When the length of ionic block is increased further to 10 and 24 units, the peak of the free block copolymer at 9.5 mL disappears, while the peak of homopolystyrene at 7.5 mL decreases further. At the same time, the micelle peak shifts to 4.8 and 4.6 mL, respectively. This evolution of the chromatograms means that not only the weight fraction but also the size of micelle increases with increasing length of the ionic block for the same polystyrene block length. This behavior parallels that found in the case of polystyrene-*b*-poly(sodium methacrylate).[23] Similar results were obtained for the series PS(630)-*b*-PANa (sample 2) in the present study.

In the series PS(2300)-*b*-PANa (sample 3), only two peaks are observed, since the homopolystyrene is not separated from the free block copolymers. This overlap occurs probably because the polystyrene block is long

Table II
Weight Percentage of Micelles of Polystyrene-*b*-poly(sodium acrylate) Determined by SEC Analysis

sample no.	composition	wt % homopolystyrene	wt % free block copolymers	wt % micelles
1a	190-*b*-0	100	0	0
1b	190-*b*-1.1	7.85	92.2	0
1c	190-*b*-3.8	5.38	14.6	80.0
1d	190-*b*-10	3.61	0	96.4
1e	190-*b*-24	3.34	0	96.7
2a	630-*b*-0	100	0	0
2b	630-*b*-4.2	3.63	19.1	77.3
2c	630-*b*-18	3.07	1.79	95.1
2d	630-*b*-31	1.69	0	98.3
2e	630-*b*-87	1.70	0	98.3
3a	2300-*b*-0	100		0
3b	2300-*b*-4.6	32.1		67.9
3c	2300-*b*-31	17.2		82.8
3d	2300-*b*-69	15.8		84.2
3e[a]	2300-*b*-190			

[a] This sample is not completely soluble in THF.

enough to reduce the retardation effect to such an extent that the size exclusion effect is predominant.

Micelle Stability. As with the PS-*b*-PMANa micelles, micelles of block ionomers of polystyrene-*b*-poly(sodium acrylate) are also very stable. This was confirmed by keeping their THF solution in an ultrasonic bath for 15 min at room temperature. The elution volumes of the micelles as well as the peak area ratios of micelles to single chains remained unchanged. This was true even after storing the solution for a week after sonication. Similar behavior was also observed when the micellar solutions in xylene were heated at reflux under a nitrogen atmosphere for 3 days. Therefore, it appears that the micelle stability is excellent.

Weight Percentage of Micelles in the Block Ionomers. From the SEC peak areas, one obtains the weight percentage of micelles for the different series of copolymers. These are presented in Table II. In general, the weight percentage of micelles increases with increasing length of the ionic block. In the case of the first series of copolymers (samples 1a–1e), it should be noted that the percentage of micelles jumps from 0% to 80.0% when the average length of PANa changes from 1.1 to 3.8. This means that the length of the ionic block is critical for the formation of the reverse micelle, as was to be expected.

Effects of the Counterions, Solvent, and Temperature on the Micellization. One sample in the acid form (sample 2b, 630-*b*-4.2) was neutralized with different metal hydroxides and with ammonium hydroxide. The neutralized samples were analyzed by SEC at 90 °C with NMP as eluent. The results are as follows:

counterions	Li^+	Na^+	K^+	Cs^+	Ba^{2+}	NH_4^+	$(CH)_3)_4N^+$	$(n\text{-}C_4H_9)_4N^+$
micelle % (w/w)	59.7	69.0	71.9	66.4	65.3	59.0	69.0	71.6

The weight percentage of micelle is independent of the nature of the counterions except for Li^+ and NH_4^+, which give 59.7% and 59.0%, respectively. The rest of samples involving the six other counterions give 68.9 ± 2.4% as the weight percentage of micelles.

For the study of the effect of solvent and temperature, one series of samples was analyzed by SEC with NMP as eluent at 90 °C. The results are compared with those obtained with THF at room temperature in Table III. With the exception of sample 1b, the effects of solvent and temperature on the micellization are negligible.

Table III
Weight Percentage of Micelles of Polystyrene-*b*-poly(sodium acrylate) in NMP at 90 °C and in THF at Room Temperature

sample no.	composition	wt % micelles in NMP at 90 °C	wt % micelles in THF at room temperature
1a	190-*b*-0	0	0
1b	190-*b*-1.1	20.5	0
1c	190-*b*-3.8	77.5	80.0
1d	190-*b*-10	92.4	96.4
1e	190-*b*-24	95.5	96.7

Computer Modeling. With the assumptions given in the Theoretical Section, the modeling was done on a PC computer by using a BASIC program. Three parameters, i.e. the CML, the polydispersity index (PI) for the ionic block (for the Gaussian distribution), and the mole fraction of homopolystyrene (only in the case of the PS(2300)-PA–Na series), were adjusted until an optimum fitting of experimental points was obtained. The quality of the fits was judged from a calculation of the standard deviation (SD) for all the points. Calculations were stopped when a minimum SD was obtained. The fitted curves for the experimental points of the three series of block ionomers using the continuous Gaussian distribution are shown in Figures 4 and 5. The fitting parameters for all the distributions are given in Table IV and will be discussed below.

Discussion

It is clear that the block ionomer aggregates (or reverse micelles) can be formed even from very short ionic blocks and that at these short block lengths, single chain solubility is a very strong function of the block length. While it is recognized that the equation relating the cmc to the ionic block length given in the Theoretical Section represents an oversimplification, it is nonetheless instructive to explore the consequences of that relation when applied to the systems under study here.

Under existing experimental conditions, the SEC instrument operates at a concentration of 10^{-5} mol/L, and values for the CML between 2 and 3 are obtained independent of the PS length. For the continuous Gaussian fit, an average value of 2.7 is obtained. Inserting this number into the equation, one can calculate the constant K' to be 4.5; thus, the complete equation becomes

$$\log_{10} \text{cmc} = n_i\,(-20000/2.3RT) + 4.5 \qquad (7)$$

At 298 K, $20000/2.3RT$ is equal to 3.5. Therefore

$$\log_{10} \text{cmc} = -3.5n_i + 4.5 \qquad (8)$$

This suggests that for $n_i = 1$, the cmc is 10 mol/L, for $n_i = 2$, it is ca. 3×10^{-3}, and for $n_i = 3$ it is 10^{-6}. It reaches 3×10^{-24} at $n_i = 8$, at which point it loses physical significance since only about one chain would be expected to be present as a single chain per liter of solution. At the other extreme, gelation phenomena have been observed at moderate concentrations for telechelics, i.e. polymer chains containing single ions at each end, which suggests aggregation. The equation is thus not unreasonable. It is worth noting that for a $\Delta G_m{}^i$ of −30 kJ/mol, the drop in the cmc with n_i is much steeper and reaches ca. 3×10^{-23} already at $n_i = 6$.

For the continuous Gaussian distribution, the CML values obtained by computer modeling for the three series are 2.9, 2.7, and 2.7, practically independent of the length of polystyrene block between 190 and 2300 units. Sodium

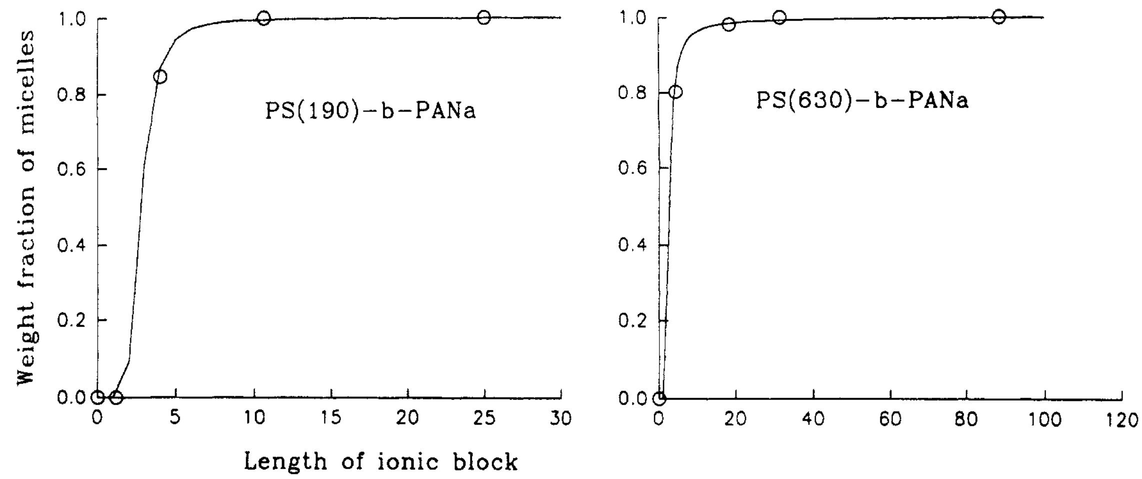

Figure 4. Weight fraction of micelles (after exclusion of homopolystyrene) as a function of the length of ionic block for PS(190)-*b*-PANa and PS(630)-*b*-PANa.

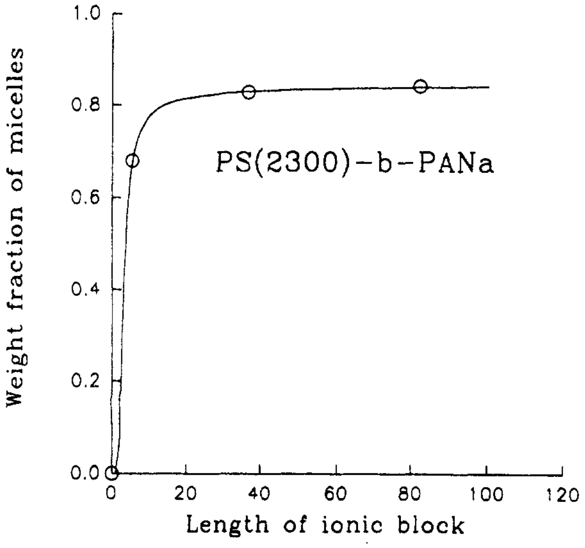

Figure 5. Weight fraction of micelles as a function of the length of ionic block for PS(2300)-*b*-PANa.

Table IV
Fitting Parameters Obtained from the Computer Modeling

series	distribution	CML	PI	F_{PS}	SD
PS(190)-*b*-PANa	cont Gaussian	2.9	1.07		0.37×10^{-2}
	discont Gaussian	2	1.13		2.17×10^{-2}
		3	1.02		0.39×10^{-2}
PS(630)-*b*-PANa	Poisson	2	*a*		2.90×10^{-2}
	cont Gaussian	2.7	1.19		0.36×10^{-2}
	discont Gaussian	2	1.40		0.84×10^{-2}
		3	1.05		0.89×10^{-2}
PS(2300)-*b*-PANa	Poisson	2	*a*		1.89×10^{-2}
	cont Gaussian	2.7	1.32	0.16	0.17×10^{-2}
	discont Gaussian	3	1.14	0.16	0.56×10^{-2}
	Poisson	3	*a*	0.16	1.31×10^{-2}

[a] For the Poisson distribution, the PI varies with chain length of the polyacrylate block. Since this is an intrinsic part of the distribution, the values are not reported here.

salts of low molecular weight organic acids, such as sodium propionate, are not soluble in THF. This suggests that somewhere below a polystyrene block length of ca. 190, the CML should decrease as the polystyrene block length decreases. Unfortunately, a study of the materials with short polystyrene blocks was impossible since they were seriously adsorbed by the column during SEC analysis.

As has been pointed out in the literature,[8] adsorption of block copolymers in a selective solvent by the column packing material may be serious. As was mentioned before, the columns employed here did not adsorb the three series of copolymers significantly. However, it was still of interest to see what effect selective adsorption would have on the CML. In calculating the CML, the most serious error is likely to be introduced if some of the material (either micelles or single chains) is adsorbed for the sample which contains substantial amounts of both micelles and single chains. To explore the effect of selective column adsorption of ca. 10% of one or the other component, the CML was recalculated for the continuous Gaussian distribution after arbitrarily moving the point PS(630)-*b*-PANa(4.2) up and down by 10%, i.e., to a percentage of micelles of 85% and 69%, respectively. Since selective adsorption for the longer chains is probably even less serious than for this sample, the other values were left unmodified. The results are as follows:

mode of calculation	CML	PI	SD
point moved 10% down	3.2	1.18	3.69×10^{-3}
no movement	2.7	1.19	3.60×10^{-3}
point moved 10% up	2.0	1.22	3.86×10^{-3}

While it is known that the molecular weight distribution of polymers prepared by anionic polymerization under ideal conditions is of the Poisson type,[35] two other distributions were also studied to explore the effect of the type of distribution on the CML. This was needed since it is unlikely that the distribution for the ionogenic systems used here are indeed of the Poisson type. For the continuous Gaussian distribution, the minimum standard deviation is easy to ascertain and is also given in Table IV. For the discontinuous Gaussian, a fairly broad minimum region is found, so two values of the CML are reported. For the CML of 3, the value of PI is unreasonably low, although the minimum SD (for the PS(190) series) is lower than that for a CML of 2. Both are reported. The discrepancy (2 vs 3) should be taken as the uncertainty for the CML for this calculation. If the PI were known, the uncertainty in the CML would decrease.

For the continuous Gaussian distribution, the PI values obtained by computer modeling for the length of the polyacrylate blocks increase with increasing degree of polymerization of PS. This can be understood from the fact that the concentration of living centers in the synthesis of copolymers with the longer PS blocks is lower than that with the shorter PS blocks. Therefore, the chance of deactivation of the living chains due to the introduction of impurities at the time of the addition of *t*BuA is higher in the former case, resulting in a broader distribution of the lengths of polyacrylate blocks. The higher chance of deactivation can also explain the higher percentage of homopolystyrene in the case of the PS(2300)PA–Na series, i.e. 16% compared to 3.3% and 1.7% in the other two cases. In addition, the higher the molecular weight, the higher the viscosity; this causes poorer mixing and more local polymerization during the introduction of the *t*BuA monomer because of its extremely fast polymerization rate.[36] This therefore should result in a broader distribution of poly(*t*BuA) block lengths.

For the two series, PS(190)-*b*-PANa (sample 1) and PS-(630)-*b*-PANa (sample 2), the weight fraction of homopolystyrene has been determined by SEC analysis. The results in Table II show that the weight fraction of homopolystyrene decreases with the length of polyacrylate block. This behavior can be interpreted by considering that the initiation by polystyryllithium of *tert*-butyl acrylate is incomplete when the amount of monomer is very low and that further additions of the monomer complete the initiation progressively. The final residue of homopolystyrene, 3.3% and 1.7% in the two cases, is due to the deactivation of polystyryllithium during the introduction of the monomer *t*BuA.

With respect to the counterion effect, Li^+ and NH_4^+ give a lower percentage of micelles than the other counterions which have been studied. It is known that due to its small size, Li^+ can undergo specific interactions with solvents such as THF, DMF, CH_3CN, and DMSO, etc., resulting in a better solubility of its salts in these solvents. It is very likely that NMP is also able to solvate the Li^+ in the block ionomers, making them also more soluble as single chains. As for the NH_4OH neutralized sample, the reason for its lower micelle percentage is not well understood at present. The fact that all the other counterions give almost the same weight percentage of micelles implies that the free energy of micellization, $\Delta G^i{}_m$, does not depend much on the type of counterion, unless some specific interactions such as solvation are involved.

Conclusions

The present study has demonstrated that the length of ionic block is critical for the formation of reverse micelles of block ionomers of polystyrene-*b*-poly(sodium acrylate). Because of the high Gibbs free energy of micellization and the finite molecular weight distribution of the ionic blocks, a small fraction of chains of low ion content are expected to be soluble as single chains. This leads to the introduction of the concept of critical micelle length (CML). The value of the CML for this copolymer system has been determined by computer modeling using values of relative amounts of micelles and single chains for block copolymers of different polystyrene lengths and different ionic lengths. This concept is not expected to be operative for block copolymer micelles with hydrophobic cores in which the critical micelle concentration (cmc) is expected to vary much more weakly with the length of the insoluble non ionic block; therefore, the concept of the cmc should remain valid and useful. The value of CML in the present system has been found to vary between 2 and 3 ionic repeat units and to be insensitive to the length of polystyrene block between 190 and 2300 units. The effects of counterions on the micellization have been shown to be insignificant, except for Li^+ and NH_4^+, which give lower weight percentages of micelles, possibly because of improved solvation. The effect of temperature changes in the range of 25–90 °C is also not significant.

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References and Notes

(1) Tanford, C. *The Hydrophobic Effect: formation of micelles and biological membranes*; John Wiley & Sons: New York, 1980.
(2) Lindman, B.; Wennerstrom, H. *Top. Current Chem.* **1980**, *87*, 1.
(3) Eicke, H. F. *Top. Current Chem.* **1980**, *87*, 86.
(4) Fendler, J. H. *Membrane Mimetic Chemistry*; John Wiley & Sons: New York, 1982.
(5) Luisi, P. L.; Straub, B. E., Eds. *Reverse Micelles*; Plenum: New York, 1984.
(6) Pileni, M. P., Ed. *Structure and Reactivity in Reverse Micelles*; Elsevier: New York, 1989.
(7) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; NSRDS-NBS 36; U.S. Government Printing Office: Washington, DC, 1971.
(8) Price, C. In *Developments in Blocks Copolymers 1*; Goodman, I., Ed.; Elsevier Applied Sciences Publisher: London, U.K., 1982; Chapter 2.
(9) Szwarc, M. *Ions and Ion Pairs in Organic Reactions*; Wiley-Interscience: New York, 1972, Vol. 1; 1974, Vol. 2.
(10) Price, C. *Pure & Appl. Chem.* **1983**, *55*, 1563.
(11) Xu, R.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. *Macromolecules* **1992**, *25*, 644.
(12) Cogan, K. A.; Gast, A. P. *Macromolecules* **1991**, *24*, 6512.
(13) Selb, J.; Gallot, Y. In *Developments in Block Copolymers 2*; Goodman, I., Ed.; Elsevier Applied Science Publisher: London, U.K., 1985; Chapter 2.
(14) Tuzar, Z.; Webber, S. E.; Ramireddy, C.; Munk, P. *Polym. Prepr.* **1991**, *32*, 525.
(15) Cao, T.; Munk, P.; Ramireddy, C.; Tuzar, Z.; Webber, S. E. *Macromolecules* **1991**, *24*, 6300.
(16) Prochazka, K.; Kiserow, D.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 454.
(17) Kiserow, D.; Prochazka, K.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 461.
(18) Ramireddy, C.; Tuzar, Z.; Prochazka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992**, *25*, 2541.
(19) Zhu, J.; Eisenberg, A.; Lennox, R. B. *J. Am. Chem. Soc.* **1991**, *113*, 5583.
(20) Zhu, J.; Lennox, R. B.; Eisenberg, A. *Langmuir* **1991**, *7*, 1579.
(21) Zhu, J.; Hanley, S.; Eisenberg, A.; Lennox, R. B. *Makromol. Chem., Macromol. Symp.* **1992**, *53*, 211.
(22) Zhu, J.; Lennox, R. B.; Eisenberg, A. *J. Phys. Chem.* **1992**, *96*, 4727.
(23) Desjardins, A.; Eisenberg, A. *Macromolecules* **1991**, *24*, 5779.
(24) Desjardins, A.; van de Ven, T. G. M.; Eisenberg, A. *Macromolcules* **1992**, *25*, 2412.
(25) Gao, Z.; Desjardins, A.; Eisenberg, A. *Macromolecules* **1992**, *25*, 1300.
(26) Eisenberg, A.; Rinaudo, M. *Polym. Bull.* **1990**, *24*, 671.
(27) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(28) Myers, D. *Surfactant Science and Technology*; VCH Publishers, Inc.: New York, 1988.
(29) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *15* (2), 127.
(30) Hautekeer, J. P.; Varshney, S. K.; Fayt, R.; Jacobs, C.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1990**, *23*, 3893.
(31) Teyssie, Ph.; Jerome, R.; Ouhadi, T.; Fayt, R. US Patent 4,461,874, 1984.
(32) Long, T. E.; Allen, R. D.; McGrath, J. E. *Chemical Reactions on Polymers*; Benham, J. L., Kinstel, J. F., Eds.; ACS Symposium Series 364; American Chemical Society: Washington, DC, 1988; Chapter 19.
(33) Prochazka, K.; Bendar, B.; Tuzar, Z.; Kocirik, M. *J. Liq. Chromatog.* **1989**, *12*, 1023.
(34) Spychaj, T. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1991**, *48*, 199.
(35) Elias, H.-G. *Macromolecules*; Plenum Press: New York, 1977; Vol. 2, Chapter 18.
(36) Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442.