Colloidal Properties of Block Ionomers. 1. Characterization of Reverse Micelles of Styrene-*b*-Metal Methacrylate Diblocks by Size-Exclusion Chromatography†

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ABSTRACT: The colloidal properties of polystyrene-*b*-poly(metal methacrylate) AB diblock ionomers are studied by size-exclusion chromatography (SEC). In solvents selectively good for the polystyrene blocks, the ionomers form species that show the characteristics of reverse micelles and that are very stable in solution. This high stability allows the use of SEC for the complete characterization of this micellelike system. SEC experiments show that there is no apparent micelle dissociation–association equilibrium taking place within the time scale of a few days. By combining intrinsic viscosity and SEC measurements, molecular weights, molecular weight distributions, aggregation numbers, and hydrodynamic radii of the micelles have been determined. The effects on these parameters of varying the lengths of the polystyrene or the ionic blocks are investigated systematically. The presence of spherical micelles is confirmed by electron microscopy. For some of the systems, the aggregation numbers are compared with those determined by small-angle X-ray scattering in the solid state.

1. Introduction

It is well-known that when block copolymers in some composition regions are placed in a selective solvent, i.e., a good solvent for one type of block (usually the major component) but a nonsolvent for the other (usually the minor component), colloidal particles or polymeric micelles are formed as a result of the association of the insoluble segments.[1-4] In many cases, micelles as well as molecularly dissolved chains, or single chains, are found in solution, suggesting the possibility of a dynamic equilibrium between the two. The size, the aggregation number (the number of chains per micelle), and the rate of micelle formation and dissociation depend on various parameters, among them the chemical and structural characteristics of the copolymer, the selectivity of the solvent, and the temperature.

A wide range of micelle-forming block copolymers have been studied. These copolymers can be classified according to the solubility properties of the constituent blocks as lipophilic or amphiphilic. The lipophilic class contains polymers that are essentially soluble only in nonpolar organic solvents, for example, polystyrene–polyisoprene copolymers; the micellar properties of such systems have been extensively covered in the literature.[1,2] Amphiphilic block copolymers contain both hydrophilic and lipophilic segments. Depending on the hydrophilic and lipophilic contents, these copolymers can form regular micelles in aqueous media or reverse micelles in nonpolar solvents. The class of amphiphilic block copolymers is subdivided into nonionic (e.g., polystyrene–poly(ethylene oxide)) and ion-containing (e.g., polystyrene–poly(4-vinylpyridinium alkyl halides)). The micellar properties of nonionic amphiphilic block copolymers have been studied both in aqueous[5] and in nonpolar environments.[6] For the ion-containing amphiphiles, the micellar properties in aqueous media have been reviewed;[4] however, reverse micelles have received very little attention.[7]

Block ionomers are ion-containing amphiphiles of (usually) low ion content.[4,8] The lipophilic segment being the major component, the solubility of block ionomers is governed primarily by the solubilities of the lipophilic block. The presence of the short ionic segment, however, has a profound effect on the state of aggregation of the blocks, which, in turn, affects the solution properties. Since the ionic blocks often show a very low solubility in the good solvents for the lipophilic blocks, block ionomers readily form reverse micelles comprising a compact ionic core surrounded by the soluble lipophilic segments.

Block ionomers have received much attention recently in this laboratory[9,10] and in several others.[7,11-23] Most studies, however, focused on the morphology of the microphase-separated domains in the solid state as well as on the mechanical properties. Very little information is available on their solution properties. Some triblock ionomers were found to form gels in nonpolar solvents,[21,23] as a result of the association of the ionic end blocks. Reverse micelles of a series of polystyrene–poly(2-vinylpyridinium hydrochloric acid) diblock ionomers were briefly described.[7] In this study, the apparent molecular weight of the micelles was determined by light scattering. The aggregation number was found to increase as the length of the ionic segment increases. The aggregation number for blocks with short ionic segments (less than four repeat units) was ca. 10–12, whereas aggregation numbers of ca. 50–60 were observed for chains with longer ionic segments (4–9 repeat units).

The present work was undertaken to explore the unusual solution properties of some block ionomer micelles in nonpolar solvents. The materials of the present study are diblock copolymers based on polystyrene and poly(metal methacrylate). These copolymers have short ionic segments, ca. 10–60 repeat units, and longer polystyrene segments, ca. 200–1000 units. Due to the very different solubilities of the poly(metal methacrylate) and the polystyrene blocks, these copolymers form reverse micelles in all solvents in which polystyrene is soluble, and micellization is observed for diblocks with ionic segments as short as ca. 10 units. Another interesting aspect of the micelles made from these block ionomers is their very high stability in a wide range of solvents. The micelles are so stable that they can be separated from the single chains by fractional precipitation in benzene/methanol mixtures containing as much as 26% methanol. These particular

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Table I
Characteristics of Micelles by SEC and Viscometry in DMF

sample	$[\eta]$,[a] dL/g	micellized chains, %	$\bar{M}_n$[b] × 10^3, g/mol	$\bar{M}_w$[b] × 10^3, g/mol	$\bar{M}_w/\bar{M}_n$	aggregation no. from $\bar{M}_n$	$r_h \pm \sigma$,[c] nm
PS(170)PMA(9)-Na	0.200	72	150	400	2.7	8	6.9 ± 2.5
PS(170)PMA(25)-Na	0.180	89	2000	3500	1.8	98	16.9 ± 4.2
PS(440)PMA(7)-Na	0.456	40	150	230	1.5	3	9.9 ± 2.0
PS(440)PMA(18)-Na	0.322	73	1800	2900	1.6	38	19.0 ± 4.6
PS(440)PMA(40)-Na	0.263	86	8200	16000	2.0	160	30.3 ± 7.9
PS(440)PMA(7)-Cs	0.440	43	170	290	1.7	4	10.2 ± 2.4
PS(440)PMA(18)-Cs	0.332	70	2300	4300	1.9	46	20.1 ● 5.9
PS(440)PMA(40)-Cs	0.277	88	6600	10000	1.5	120	28.5 ± 7.0
PS(1100)PMA(6)-Na	0.900	20	1200	2200	1.8	10	25.7 ● 6.1
PS(1100)PMA(21)-Na	0.665	45	3700	5200	1.4	32	32.5 ± 7.0
PS(1100)PMA(42)-Na	0.603	48	6200	8400	1.4	53	37.5 ± 7.6
PS(1100)PMA(59)-Na	0.539	54	7500	11000	1.5	62	38.0 ± 8.8

[a] Intrinsic viscosities of the micellar solutions free of single chains. [b] The standard deviation of repeat determinations was ca. 5–8%. [c] σ is the standard deviation of the distribution. The standard deviation of repeat determinations of r_h was ca. 1–2%.

properties and others described below and in subsequent papers of this series allow the use of a very wide range of techniques and experimental conditions for the complete characterization of the micellar system. The micellar properties of block ionomers are not only interesting in themselves but also in view of their potential solution applications, for example, the solubilization, the dispersion and the stabilization of polar materials in nonpolar media, and the emulsion of water in hydrophobic solvents.

Among the techniques used to study polymeric micelles, chromatography has received some attention.[24-34] The determination of molecular weights by size-exclusion chromatography (SEC) was attempted on two occasions. In one study,[25] the micellar molecular weight obtained agreed well with that determined by static light scattering, while the agreement was poor in the other.[24] No other attempt to determine the molecular weight of block copolymer micelles using SEC was reported. In these two studies the SEC columns were calibrated by using the universal calibration method,[35] which consists of relating the product of the intrinsic viscosity, $[\eta]$, and molecular weight, M, to the elution volume of narrow molecular weight standards. The universal calibration method is based on the concept that the elution of polymer molecules in SEC columns is governed by their hydrodynamic volumes, which are proportional to the product $[\eta]M$ for spherical molecules. In view of the variable success of the results mentioned above, the applicability of the universal calibration method in SEC for the determination of the molecular weight of highly branched systems such as polymer micelles is still an open question.

In the present study, SEC is used to study the various characteristics of reverse micelles made from block ionomers. Several SEC experiments are devoted to probing the possible existence of a micelle–single chain equilibrium. Molecular weights, aggregation numbers, and hydrodynamic radii of the micelles are determined in dimethylformamide (DMF) solvent as a function of the length of the polystyrene and of the ionic segments. A detailed description of the procedure used to calculate these physical parameters is provided. In addition, the existence of spherical micelles is confirmed by electron microscopy (EM), and the aggregation number of the micelles in solution is compared with that determined in the solid state by small-angle X-ray scattering (SAXS).

2. Experimental Section

2.1. Materials. The preparation and characterization of the materials is described in detail elsewhere.[36] Thus, only a summary of the procedure will be given here for convenience. The diblock copolymers were synthesized by sequential anionic polymerization of styrene monomer followed by *tert*-butyl methacrylate monomer, using *n*-butyllithium as initiator. The polymerization was performed in tetrahydrofuran (THF), at −78 °C, and under a nitrogen atmosphere. A small amount of high molecular weight contaminant was observed on SEC chromatograms when the *tert*-butyl methacrylate monomer was polymerized directly from the living polystyryllithium chains. No high molecular weight contaminant was detectable, however, when the polystyryllithium chains were reacted with diphenylethylene (DPE) before introducing the *tert*-butyl methacrylate monomer. After this initial finding, capping of the polystyryllithium chains with DPE was performed on a routine basis.

The apparatus used for the polymerization allows the withdrawal of reaction mixture in the course of the synthesis. After the polystyrene block was formed, a fraction of the solution was withdrawn for further characterization. The withdrawal procedure was repeated several times as the poly(*tert*-butyl methacrylate) block was being polymerized. Thus, for a given constant polystyrene block length, a series of diblocks with poly(*tert*-butyl methacrylate) segments of lengths varying between ca. 10 and ca. 60 units were isolated.

Polystyrene-*b*-poly(methacrylic acid) copolymers were obtained by acid-catalyzed hydrolysis of the *tert*-butyl methacrylate segments in toluene at 80 °C using *p*-toluenesulfonic acid as the catalyst.[17] Acetic acid was used as the cosolvent to maintain the solubility of the polymer as hydrolysis proceeded. The polymer was recovered and purified by repeated precipitation in methanol, methanol/water mixtures, or water, depending on the composition of the diblocks.

The molecular weight of the polystyrene block was measured by SEC in THF using narrow molecular weight polystyrene standards. The precision in the number of repeat units per block is on the order of 5%. The polydispersity index was found to vary from 1.1 to 1.2. The *tert*-butyl methacrylate contents of the nonionic precursors were determined by FT-IR and by nonaqueous titration in THF/water mixtures for the acid. Details are given elsewhere.[36]

The composition of the diblocks is given in Table I, along with a tabulation of the results discussed below. The abbreviations used to indicate the copolymer composition are illustrated in the following example: PS(440)PMA(18)-H indicates a polystrene chain of 440 units joined to a polymethacrylate chain of 18 units, with H denoting the acid form. Neutralized forms will be indicated by Na or Cs.

2.2. Preparation of the Micelles. The diblocks in the acid form were dissolved in benzene/methanol (90/10, v/v) mixtures, where only single chains are found. The concentration of the polymer was 0.03 g of polymer/mL of solvent. The acid was neutralized by addition of stoichiometric amounts of methanolic solutions of NaOH or CsOH. The solutions were stirred for 1 h, and the solvent was stripped by freeze-drying. The process was completed by vacuum-drying at 80 °C for several days. Micellar solutions were obtained by dissolution of the dried powder in the desired solvent.

2.3. Size-Exclusion Chromatography. The SEC measurements were performed on a Varian Model 5010 liquid chromatograph equipped with a refractive index detector. The detector was interfaced with a Varian DS-604 computer with SEC application software. Preliminary studies of the micellar solutions in THF were performed on 10^4-, 10^5-, and 10^6-Å Ultrastyragel (Waters) SEC columns connected in series. Molecular weights and hydrodynamic radii of the micelles were determined in DMF by using a mixed-bed column (Shodex) and a 10^3-Å Ultrastyragel column (Waters) connected in series. HPLC-grade DMF and THF were used as received. A series of five narrow molecular weight linear polystyrene standards ranging in molecular weight from 1.0×10^4 to 1.3×10^6 were used for the calibration of the columns. Measurements were performed at 25 °C. Micellar solutions for molecular weight determinations were obtained by dilution of the solutions prepared for viscometry measurements to concentrations in the range of 0.5–1 mg/mL. Solutions were filtered through membrane filters with a nominal pore size of 0.5 μm before injection.

2.4. Viscometry. Solution flow times were measured by using standard Ubbelohde viscometers at 25.0 °C in HPLC-grade DMF. Measurements were made by successive dilutions of solutions in the concentration range 10–0.2 mg/mL. Plots of η_{sp}/C and ln (η_r/C) versus concentration were extrapolated to infinite dilution to obtain the intrinsic viscosity. Solutions were prepared 1 day in advance and were filtered through membrane filters with a nominal pore size of 0.5 μm before measurements.

2.5. Fractionation of Micellar Solutions. Micelles and single chains of diblock ionomers PS(440)PMA(40)-Na and PS(1100)PMA(42)-Na were separated by conventional fractional precipitation as follows.[37] The block ionomers (0.5 g) were dissolved in 100 mL of benzene, and 35 mL of methanol was added to achieve a methanol content of 26% by volume. The resulting cloudy solutions were warmed until they cleared and were then allowed to cool slowly to room temperature with stirring. After 1 day, the insoluble polymer fraction had settled as a gel layer at the bottom of the flask. The clear supernatant liquid was decanted and the gel treated a second time with the same volume and concentration of the benzene/methanol mixture. The micellar and single-chain fractions were isolated by freeze-drying of the gel fraction and of the combined supernatant fractions, respectively.

When needed for FT-IR measurements, the isolated fractions were acidified by treatment with HCl in THF for 1 h. The solvent was evaporated and the polymer dried in a vacuum oven at 80 °C for several days.

2.6. FT-IR. FT-IR spectra were recorded on an AQS-20 FT-IR spectrometer (Analect Instruments). Spectra were recorded from thin films, prepared by pressing powders at 140 °C between smooth aluminum plates.

2.7. Electron Microscopy. Electron micrographs were recorded on a JEOL-CX100-TEMSCAN analytical transmission electron microscope operated under 80 kV. The samples were prepared as follows: the block ionomer was dissolved in benzene to a concentration of 0.10 mg/mL. A few drops were spread on a microscope slide, which was frozen and then freeze-dried under vacuum. The sample was shadowed with gold/platinum and coated with carbon. The resulting film was floated on distilled water and fished out onto a copper grid.

3. Results and Discussion

The Results and Discussion section of this paper is divided into seven parts. In the first part, typical SEC chromatograms of solutions of the diblock ionomers are presented to illustrate the main features of the system. This is followed by considerations of the possibility of a micelle–single chain equilibrium in the system. In the third part, the chemical composition of the single chains is compared to that of the micelles. Then the proportion of micellized materials found in micellar solutions as a function of block ionomer composition is examined. In part five, the determination of intrinsic viscosities, of molecular weights, and of hydrodynamic radii of the micelles is described. Finally, in parts six and seven, EM and SAXS data are compared with SEC results.

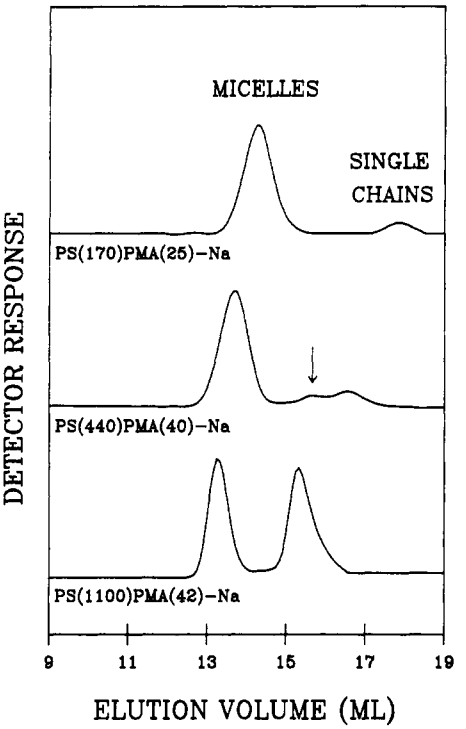

Figure 1. Representative SEC chromatograms of micellar solutions for the three series of block ionomers using DMF as the eluent.

3.1. Features of the Chromatograms. Figure 1 shows typical chromatograms of diblock ionomer solutions. One example of each of the three series of block copolymers considered in this study is represented on this figure. The chromatograms reveal the presence of peaks of very different elution volumes. For the series PS(170) and PS(1100) (top and bottom traces) two peaks are observed. The peak at the higher elution volume is seen at the same location as that due to the nonionic precursor and is therefore assigned to molecularly dissolved chains or single chains. The second peak has a lower elution volume; it therefore corresponds to a polymer of higher molecular weight and is attributed to micelles.

For the series PS(440) (middle chromatogram), beside the micelle and single chain peaks, a third peak located between the single chain and the micellar peaks is observed. It is indicated by an arrow in Figure 1. It is also seen as a shoulder to the single-chain peak in Figures 2 and 3. This peak is due to a contaminant of intermediate molecular weight and was present also on chromatograms of the other diblocks of this series (PS(440)). It was also observed on chromatograms of the nonionic polystyrene-*b*-poly(*tert*-butyl methacrylate) precursors. Consequently, this contaminant is not due to an incomplete hydrolysis or to a side reaction caused by hydrolysis, nor is it related to the process of neutralization. It should be noted that copolymers of this series were the only ones prepared without end-capping of the living polystyrene block before the *tert*-butyl methacrylate monomer was added. Diblocks of the series PS(170) and PS(1100) were prepared with DPE capping of the styrene blocks, and chromatograms for those series did not show this contaminant.

The formation of a contaminant of this type was noticed before when methyl methacrylate monomer was reacted with living polystyrene.[38] Its formation was explained as due to a reaction between living polystyrene chains and the ester functionality of the methyl methacrylate mono-

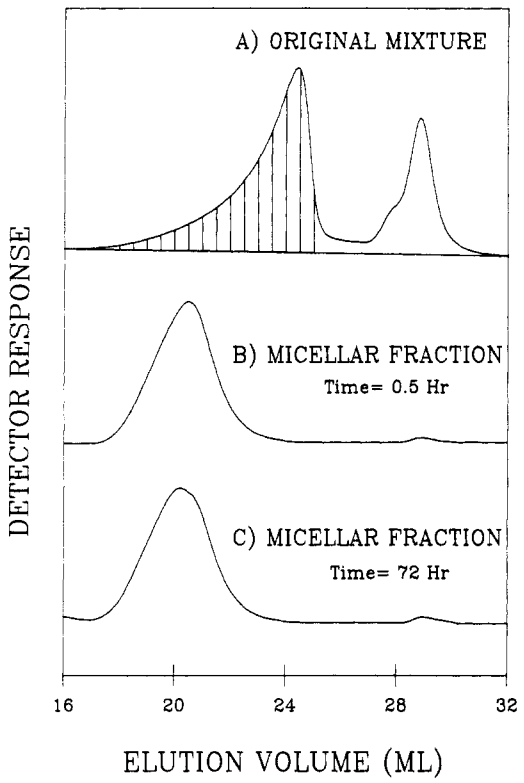

Figure 2. Isolation of the micellar peak of PS(440)PMA(18)-Na by SEC. (A) The shaded area shows the fraction collected and reinjected immediately (B) and after 72 h (C). THF was the eluent.

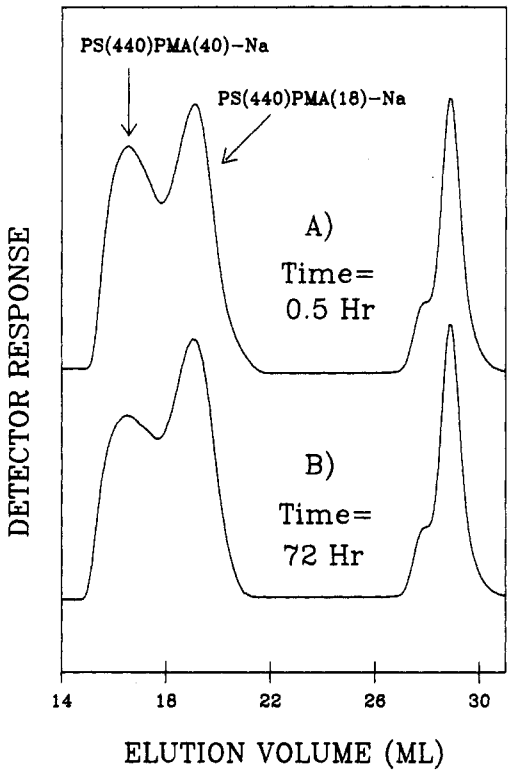

Figure 3. SEC of a mixture of micelles of different sizes as a function of time. THF was the eluent.

mer, leading to polystyrene branches on the poly(methyl methacrylate) blocks and, consequently, to a contaminant of higher polystyrene content. This side reaction was prevented by decreasing the reactivity of the living polystyrene chains by addition of DPE before introducing the methacrylate monomer. It has been suggested that the *tert*-butyl group of the *tert*-butyl methacrylate monomer makes the carbonyl moiety more "protected";[17] for this reason, the carbonyl group of the *tert*-butyl methacrylate monomer should be less susceptible to attack by polystyrene living chains. It appears from the present chromatographic results, however, that the presence of the *tert*-butyl group is not sufficient to eliminate this side reaction in our system.

It is difficult to determine if the high molecular weight contaminant participates in the micellization process. However, it appears from a consideration of the peak areas of the chromatograms that a high proportion of this contaminant is not incorporated into micelles. The higher polystyrene content present in this contaminant might account for its low propensity to micellize. Whether the contaminant participates in micellization or not, the perturbation introduced by its presence in the micelles may be considered negligible because of its relatively low concentration.

The reproducibility of the chromatograms was very good. The elution volume of the micelles as well as the relative proportion of micelles to single chains (as calculated from the areas under the peaks) remained constant in periodic injections performed over a 72-h time period from freshly prepared THF and DMF solutions. Therefore, the method of preparation, i.e., the dissolution of dry powders of the diblock ionomers, leads to stable micellar solutions.

It was of interest to verify if the presence of a solvent of high polarity affects the stability of the micelles. Water (up to 5% by volume) was added to the micellar solutions, and aliquots were injected periodically. The elution volumes recorded from these "wet" solutions were shifted slightly to lower values when compared to "dry" solutions but remained constant as a function of time. In addition, the relative proportion of micelles to single chains was not affected by the presence of water. Therefore, it appears that the stability of the micelles in solutions is considerable even in the presence of a polar cosolvent.

3.2. Possibility of a Micelle–Single Chain Equilibrium. In this section, the possible existence of a micelle–single chain equilibrium in the micellar solutions made from block ionomers is explored by means of several SEC experiments. The simultaneous presence of micelles and single chains has been observed by SEC for nonionic block copolymer micelles[24,25,27,28,32] and by sedimentation for ion-containing amphiphilic block copolymer micelles in aqueous solutions.[4] In some of these cases, this was interpreted as a manifestation of a dynamic equilibrium between single chains and micelles paralleling the behavior of small amphiphile molecules, except that the rate of the micelle formation and dissociation is considerably slower.[2,31,32]

The following experiment was designed to determine whether or not the presence of a single-chain peak on the chromatograms is a manifestation of a dynamic equilibrium between single chains and micelles. In this experiment, SEC was used to separate micelles from single chains. This separation was performed by collecting the fraction corresponding to micelles at the outlet of the SEC instrument. The single chain–free micellar fraction was then reinjected at different times in order to ascertain whether the presence of a dynamic equilibrium would reestablish the original single-chain population. Figure 2 shows the chromatogram of the concentrated solution from which the micellar fraction was collected (A) and the results when it was reinjected at different times (B and C). The fraction collected and reinjected is indicated by the shaded area in chromatogram A. The higher polymer concentration used for this run was sufficient to overload the column as manifested by the spreading of the micellar

peak. The area of the single-chain peak in the original mixture corresponds to 28% of the total area of the peaks. Chromatogram B indicates that immediately after fractionation a very small amount of single chains is found since the area of the single-chain peak corresponds to 2% of the total area of the peaks. The presence of single chains in this chromatogram might be due to incomplete separation; the chromatogram in A shows clearly that the trace between the two peaks does not reach the base line. If the micellar fraction is allowed to stand 3 days, the area of the single-chain peak is seen to increase very slightly to 5% of the total area. This increase being within experimental error, it cannot be attributed to a manifestation of a dynamic equilibrium. A long-term storage of the solution for further studies was not attempted because of the unknown effect on the micelles of solvent degradation.

The experiment described above shows that the behavior of the fractionated solution is very different from that of the original solution. In the original solution a relatively large single-chain peak is observed, even when the micellar solution is prepared only a few minutes before injection. On the other hand, in the fractionated solution, a very small single-chain peak is seen. These results suggest that the single chains in the original solution are not involved in a micelle–single chain equilibrium; if they were, the single-chain population of the fractionated solution should grow rapidly to the original proportion, which is not the case. Therefore, this experiment shows that the presence of a single-chain peak in the chromatograms of unfractionated solutions is not a manifestation of a dynamic equilibrium.

This experiment, however, does not exclude the occurrence in these systems of an equilibrium involving single chains at very low concentrations (i.e., <1–2% of the total peak areas). Therefore, another experiment is necessary to probe this possibility. The proposed experiment is based on the following considerations: the existence of a micelle–single chain equilibrium implies that micelles dissociate to single chains and that single chains associate to form micelles, the rates of the dissociation and association processes being equal when equilibrium is reached. If the rates of formation and dissociation are not negligible, a given single chain can be found successively in different micelles. Moreover, if micelles made of single chains of type A are mixed with micelles made of single chains of type A*, it is expected that after a certain period of time all micelles will have exchanged single chains and will contain single chains of both A and A* types. The same would be true if a fusion–fission type mechanism were operative.

The possible existence of the above equilibration mechanisms was explored by SEC in the following experiment: micelles of different elution volumes were mixed together in THF at room temperature, and the chromatograms of aliquots were recorded after different mixing times, as shown in Figure 3. In the case of a system where the rates of the formation and dissociation (or fusion–fission) processes are not negligible, the micelles would exchange single chains and the bimodal shape of the chromatogram would be expected to disappear, resulting in a single micellar peak with an elution volume between those of the starting micelles. Conversely, if the rates are negligible, the bimodal shape of the chromatogram would be retained. Figure 3 shows that at room temperature, even after 3 days, the bimodal shape of the chromatogram is retained and the elution volumes of the micellar peaks remain unchanged. The same experiment was repeated in boiling THF with a similar result. Therefore, the dynamics of this micellar system are extremely slow.

The rates at which the micelle formation and dissociation processes take place have an important implication with respect to the applicability of the universal calibration method in SEC for the determination of the molecular weight of the micelles. The universal calibration curve relates the elution volume of a polymer molecule to its hydrodynamic volume. When the rate of micelle formation and dissociation is low with respect to the time scale of a SEC run, the hydrodynamic volume of the micelles remains constant during the elution process and, consequently, the elution volume of the micelles is determined by its hydrodynamic volume. In this case, sharp micellar peaks are observed on chromatograms,[24,27,28,30] and the calibration curve should be applicable provided the separation mechanisms of the standards and of the micelles are similar (i.e., size exclusion). When the rates are not negligible, however, the dynamic equilibrium continuously perturbs the elution process, which is manifested by broad peaks on chromatograms.[24,27,28,30] In the latter situation, the elution volume of the micelles cannot be related to a specific hydrodynamic volume, and the calibration curve is not applicable. Therefore, meaningful molecular weight determinations are possible only for micellar systems characterized by very low rates of micelle formation and dissociation; this is the case for the block copolymers studied in this work.

In spite of the fact that the colloidal particles of the present study are not subject to a micelle–single chain equilibrium over a reasonable time scale, it is still tempting to retain the word micelle to describe the particles, especially in view of the structural and behavioral similarities of the present aggregates to other block copolymer micelles to which the term has been applied in the literature.[39]

3.3. Composition of the Single Chains. Since the occurrence of single chains in these micellar solutions is not a consequence of a dynamic equilibrium, their chemical nature becomes interesting. In order to ascertain whether the chemical compositions of the single chains and of the micellized chains are similar, the single chains and micelles were separated by conventional solution fractionation. Figure 4 shows the SEC chromatograms recorded in DMF of the original mixture (top trace) as well as of the micellar and single-chain fractions (middle and bottom traces, respectively) for sample PS(1100)PMA(42)-Na. This shows that the separation is very good, although not complete. Furthermore, the successful separation of the two species under the experimental conditions is, again, another manifestation of the stability of the micelles formed by these diblock ionomers.

Infrared spectroscopy was used to compare qualitatively the composition of the single-chain fraction with that of the original mixture. The single-chain fractions of PS(440)PMA(40)-Na and PS(1100)PMA(42)-Na were acidified and their FT-IR spectra recorded. In both cases, the spectra showed a marked decrease of the carbonyl band of the carboxylic acid group (around 1705 and 1743 cm^{-1}) in going from the original mixtures to the single-chain fractions. This is shown in Figure 5. In the case of PS(1100)PMA(42)-H (Figure 5A), the carboxyl band of the single-chain component disappears completely and the spectrum is very similar to that of homopolystyrene. For the single-chain component of PS(440)PMA(40)-H (Figure 5B), in addition, a band at 1733 cm^{-1}, corresponding to the carbonyl stretching of an ester group, is observed.

From these experiments it is obvious that the chemical compositions of the single chains and the micelles are

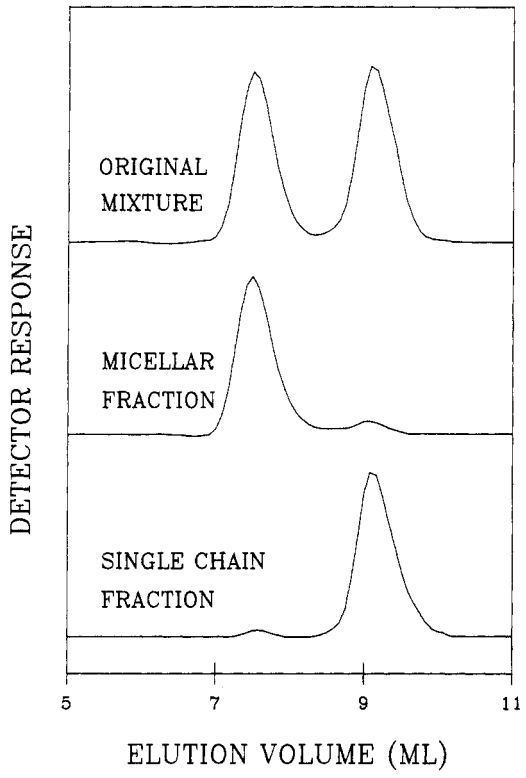

Figure 4. SEC chromatograms of the original mixture and of the micellar and single-chain fractions isolated by solution fractionation for sample PS(1100)PMA(42)-Na. DMF was the eluent.

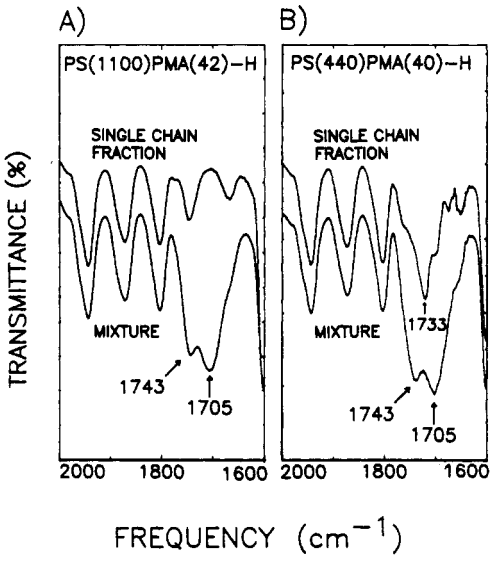

Figure 5. FT-IR spectra comparing the methacrylate content of the micelle–single chain mixture and of the single-chain fraction for (A) PS(1100)PMA(42)-H and (B) PS(440)PMA(40)-H.

different. The ion content in the single chains is significantly lower than that in the micelles. Three types of single chains can be envisaged. The first category includes chains with very short ionic segments, for which thermodynamics does not favor micellization. The second category comprises chains that are not functionalized at all; i.e., they are styrene homopolymers. Their presence is due to the introduction of impurities which deactivate the living chains in the course of polymerization. The presence of homopolystyrene is strongly suspected in the case of the series PS(1100). Finally, a third category of single chains includes chains bearing ester functionalities in the ionic segment. These ester functionalities are due either to incomplete hydrolysis or to accidental esterification during the various steps during which the hydrolyzed copolymer is in the presence of an alcohol. In summary, the presence of single chains in this micellar system is not a manifestation of a dynamic equilibrium between the micelles and the single chains but is a manifestation of compositional heterogeneities and of ionic block length polydispersity. This problem might conceivably be alleviated by improving the conditions and the procedures associated with the various steps involved in the preparation of these block ionomers. It should be borne in mind, however, that the block copolymers of the present study contain one very short block and that preparing short blocks of narrow molecular weight distribution attached to long blocks is expected to be very difficult. Nevertheless, the presence of the single chains does not prevent the complete characterization of the micelles by SEC.

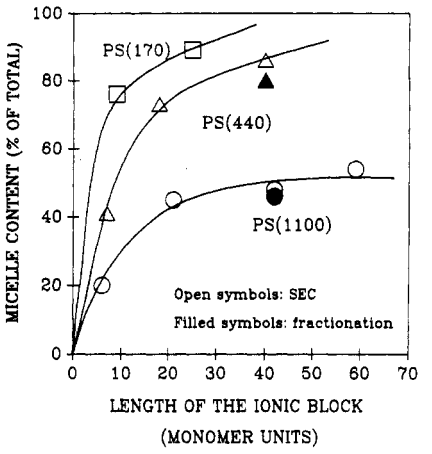

Figure 6. Proportion of micellized chains as a function of the length of the poly(sodium methacrylate) for the three series of block ionomers, as determined from SEC chromatograms in DMF and from solution fractionation.

It is worth noting that a difference in the chemical composition of the single chains and of the micelles was reported recently for aqueous solutions of polystyrene-*b*-poly(ethylene oxide).[34] In this system, the single chains had a lower content of the insoluble block (styrene) in comparison to that in the micelles, which parallels the trend observed for the present block ionomer system.

3.4. Proportion of Micellized Materials. An advantageous aspect of studying micelles by SEC is that the chromatograms give the proportion of polymer chains in solution found as micelles or single chains. The proportions of micellized material are determined from the relative peak areas in the chromatograms. In this study, this proportion was also determined for two samples from the weights of the micelle and single-chain fractions isolated by solution fractionation. The results obtained by the two methods agree reasonbly well, as shown in Figure 6. Therefore, the procedure of determining the proportion of micelles directly from the area of the peaks in the chromatograms is justified.

The proportion of diblock ionomer found as micelles or single chains varies considerably as a function of the copolymer composition, as is also illustrated in Figure 6. One trend observed in this figure is that the proportion of micellized material increases with the length of the (insoluble) ionic segment. The proportion of micelles reaches values of about 90% at the highest ion contents for diblocks of the series PS(170) and PS(440). For the series PS(1100), however, the proportion of micelles levels off at approximately 50%. This behavior is anomalous and suggests that, for this specific series, a significant

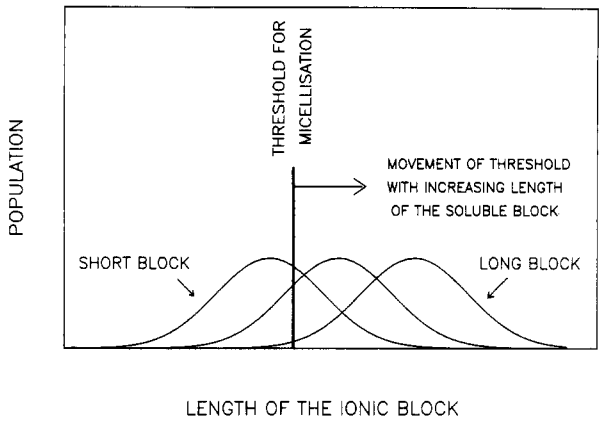

Figure 7. Schematic representation of the effect on the proportion of micellized chains of changing the length of the ionic block and of increasing the length of the polystyrene block.

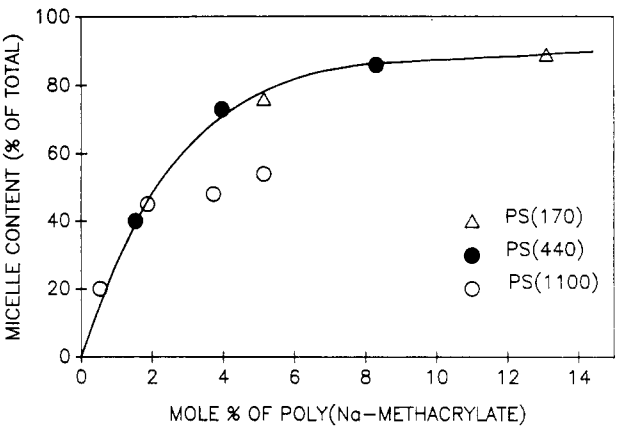

Figure 8. Proportion of micellized chains as a function of the mole percent of poly(sodium methacrylate) for the three series of block ionomers, as determined from SEC chromatograms.

proportion of living chains was killed in the course of the anionic polymerization. This interpretation is supported by the FT-IR result obtained on the single-chain fraction, which was mentioned in the previous section.

Another trend seen in Figure 6 is that, for a given length of the ionic segment, the proportion of micelles decreases as the length of the (soluble) polystyrene block increases. It is clear also that, on a per monomer unit basis, the effect on the proportion of micelles of varying the length of the ionic segment is more pronounced than the effect of varying the length of the nonionic segment. For example, for the diblocks of the series PS(440), the proportion of micelles varies from 40% to 86% when the length of the ionic segment is increased from 7 to 40 monomer units, i.e., by 33 units. On the other hand, the proportion of micelles is decreased by only 20%, on average, when the polystyrene segment is increased from 170 to 440 monomer units, i.e., 270 units.

The dependence of micelle formation upon the block lengths has been investigated for lipophilic[40] as well as amphiphilic ion-containing[41] diblock copolymers. These studies show that, at an identical temperature and solvent composition, micellization is very much a function of the overall copolymer composition. Thus, for a given length of the soluble block, micellization was only observed above a certain "threshold" length of the insoluble segment. The value of this threshold length depends on the length of the soluble block.

As was mentioned before, the simultaneous presence of micelles and single chains in solution is probably due to the polydispersity of the ionic end blocks, the single chains being the chains with very short ionic blocks while the micelles contain the chains with the longer ionic blocks. The progressive increase in the proportion of micelles as the length of the ionic block is increased is also an indication of polydispersity. If the poly(sodium methacrylate) blocks were monodisperse, a sharp increase in the proportion of micelles would be observed above a certain threshold length of the ionic block. What is observed, in fact, is a progressive increase in the proportion of micelles.

The explanation proposed for the trends observed in Figure 6 is illustrated in Figure 7, which shows three hypothetical distributions of ionic end block lengths for a constant styrene length, along with a hypothetical micellization threshold. For a given length of the polystyrene block, the threshold is fixed at a certain value, as mentioned above. When the average degree of polymerization of the ionic segment is increased, the distribution of segment lengths is shifted in such a way that the proportion of chains with the ionic segment longer than the threshold value increases. Consequently, the proportion of micelles increases as the average length of the ionic segment is increased. When the length of the ionic segment is kept constant and the length of the styrene block is increased, it is the threshold value that is shifted to a higher value, as indicated by the arrow. The effect is to reduce the number of chains with the minimal length required for micellization. Therefore, the proportion of micelles decreases. Note that the actual ionic block length distribution is not known, and it is not necessarily symmetrical.

In summary, the proportion of micellized materials is proportional to the ionic content of the block ionomer. This is illustrated in Figure 8, which shows a plot of the proportion of micelles against the mole percent of poly(sodium methacrylate). Note that most points (except for two of the PS(1100) series with the longest methacrylate blocks) lie on a single curve.

3.5. Intrinsic Viscosities, Molecular Weights, and Hydrodynamic Radii of the Micelles. 3.5.1. Choice of Solvent. The choice of solvent for the quantitative determinations by SEC was dictated by the following observations: in THF, some of the micelles of larger hydrodynamic volumes were eluted completely outside of the elution volume range of the standards; these micelles had smaller elution volumes than all of the standards, even of standards with a hydrodynamic volume comparable to or larger than that of the micelles and of standards at the exclusion limits of the columns. This unexpected behavior, however, was not observed in DMF, where all micelles eluted within the range of the standards. Therefore, DMF was selected for the quantitative determinations. The exact reason for the abnormal behavior observed in THF is unknown. It is suspected, however, that, for the micelles of larger hydrodynamic volumes, the mechanism of separation might not be only size exclusion. It is possible that a secondary separation mechanism, such as that effective in hydrodynamic chromatography,[42] might be operative.

3.5.2. Intrinsic Viscosities. The intrinsic viscosities measured on micellar solutions contain contributions from micelles and single chains. In order to obtain a meaningful molecular weight for the micelles from the SEC calibration procedure, the intrinsic viscosity to be used in the calculations must be that corresponding to a solution free of single chains. The method used to evaluate the intrinsic viscosity of such a micellar solution from viscometric measurements on a micellar solution containing both micelles and single chains is illustrated below.

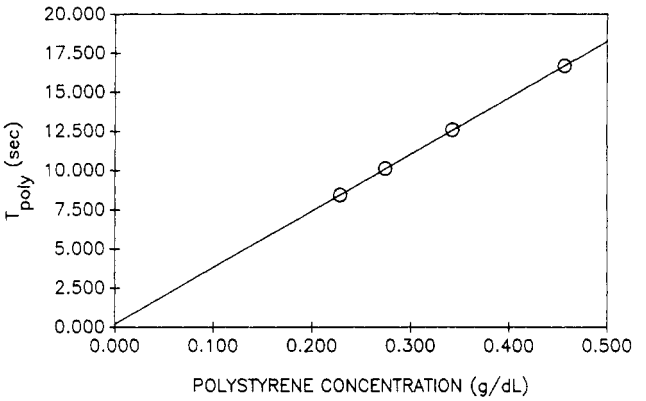

Figure 9. Flow time contribution of a polymer versus its concentration in DMF. The polymer is PS(440).

Einstein[43] showed that the viscosity, η, of a solution of spheres is given by

$$\eta = \eta_0(1 + 2.5\phi) \quad (1)$$

where η_0 is the viscosity of the pure solvent and ϕ the volume fraction of the spheres in solution. Poiseuille's law relates the viscosity of a solution to the time t required for a given volume of that solution to flow through a capillary by equation

$$\eta = A\rho t \quad (2)$$

where A is a constant for a given capillary and ρ is the density of the solution. Combining eqs 1 and 2 yields

$$A\rho t = A\rho_0 t_0(1 + 2.5\phi) \quad (3)$$

Assuming $\rho \sim \rho_0$ for dilute solutions, eq 3 simplifies to

$$t = t_0(1 + 2.5\phi)$$

$$t = t_0 + t_0(2.5\phi)$$

$$t = t_0 + t_{poly} \quad (4)$$

Equation 4 shows that the time t required for a very dilute polymer solution to flow through a capillary is the sum of the flow time contributions of the solvent, t_0, and of the polymer, t_{poly}. Measurement on the pure solvent allows the determination of t_0. Therefore, t_{poly} can be calculated for any polymer concentration, and a plot of t_{poly} as a function of concentration can easily be constructed. Such a plot is found in Figure 9. This plot was obtained for a solution containing the homopolystyrene block precursor of the diblock series PS(440). It shows essentially that, in a dilute solution, the flow time contribution of the polymer is a simple linear function of the polymer concentration. The interparticle interactions being negligible in dilute solutions, the plot is linear and extrapolates to $t_{poly} \sim 0$ at zero polymer concentration.

The micellar solutions of the present study contain two polymeric species, micelles and single chains. In this context eq 4 becomes

$$t = t_0 + t_{\text{single chain}} + t_{\text{micelle}} \quad (5)$$

where $t_{\text{single chain}}$ and t_{micelle} are the flow time contributions of the single chains and micelles, respectively. Since, again, the experiment takes place in dilute solutions and there are no specific interactions between single chains and micelles, $t_{\text{single chain}}$ and t_{micelle} are linearly proportional to the concentration of single chains and micelles in the solution.

In order to calculate the intrinsic viscosity of a micellar solution free of single chains, the value of t_{micelle} must be known. The value of t_{micelle} can be calculated from eq 5 provided $t_{\text{single chain}}$ can be estimated. As discussed above, the single chains are very similar in terms of chemical composition to the styrene block precursor. Therefore, it is reasonable to approximate the value of $t_{\text{single chain}}$ from the flow time–concentration relationship of the corresponding styrene block precursor solution (cf. Figure 9). This is possible because the concentration of single chains in micellar solution is known from the total mass of the polymer originally placed in solution and from the fraction of material that is in the form of single chains (calculated from the relative areas under the peaks in SEC chromatograms; cf. section 3.4). Therefore, the flow time contribution of the single chains can be evaluated for any concentration from a plot like that in Figure 9. Finally, the intrinsic viscosity of the single-chain-free micellar solution is calculated from the values of t_{micelle}.

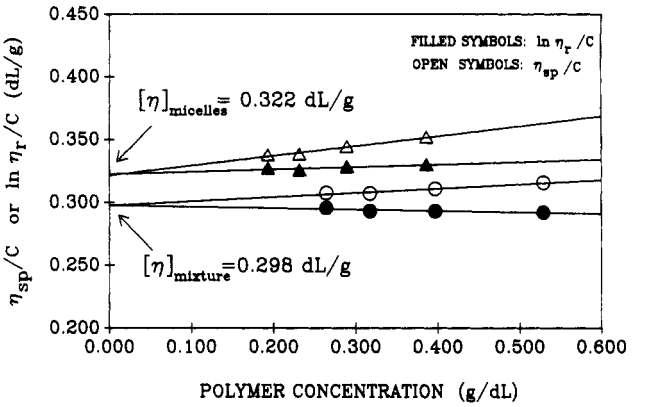

Figure 10. Intrinsic viscosity of a DMF solution containing single chains and micelles with and without corrections for the presence of single chains. The sample is PS(440)PMA(18)-Na.

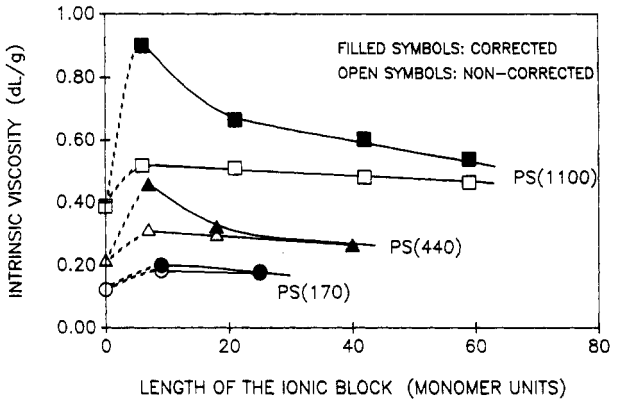

Figure 11. Intrinsic viscosity versus the length of the ionic block for the three series of block ionomers with and without corrections for the presence of single chains, in DMF.

Figure 10 illustrates the effect on the intrinsic viscosity of correcting for the presence of single chains in micellar solutions. The intrinsic viscosity of the micellar solution free of single chains is higher than that of the mixture. This is not surprising because the intrinsic viscosity of the micellar solution is higher than that of the single-chain solution.

Figure 11 summarizes the viscometric results obtained for the three series of block ionomers. The intrinsic viscosities of the micellar solutions with and without corrections for the presence of single chains are included for comparison. As mentioned above, the intrinsic viscosities of the micellar solutions free of single chains are larger than those for the mixtures. The difference between the corrected and the uncorrected values is related to the proportion of single chains in the solution. It appears

that when the proportion of micellized chains is large (i.e., over 70% of the material), the effect of correcting for the presence of single chains is negligible. This correction, however, is significant and cannot be neglected when the proportion of micelles is lower.

The intrinsic viscosity of the micelles is governed primarily by the length of the soluble styrene segment and to a lesser extent by the length of the ionic segment. As the length of the styrene segment increases, the intrinsic viscosity of the micelles increases dramatically (from bottom to top in Figure 11). This trend simply reflects the one observed for the intrinsic viscosities of the polystyrene precursors. However, in general, as the length of the ionic segment increases for a given polystyrene segment length, the intrinsic viscosity decreases (from left to right in Figure 11). Also, as will be shown below, as the length of the ionic segments increases for a given series, the aggregation number increases. Therefore, the decreasing intrinsic viscosity appears to be related to an increase in aggregation number. A possible explanation for this observation is provided below.

By simple manipulation of eq 1, it can be shown that the specific viscosity, η_{sp}, of a solution of spheres is given by

$$\lim_{\phi \to 0} (\eta_{sp}) = 2.5\phi \tag{6}$$

where ϕ is the volume fraction of the spheres. Since the volume fraction of the spheres is equal to the concentration of the spheres, C, divided by their density, ρ, eq 6 can be modified to

$$[\eta] = \lim_{C \to 0} (\eta_{sp}/C) = 2.5/\rho \tag{7}$$

Equation 7 shows that the intrinsic viscosity is inversely proportional to the density of the sphere. Therefore, the decreasing intrinsic viscosity as the ionic segment length increases could be related to an increase in micelle density as the aggregation number increases.

The change in intrinsic viscosity with the aggregation number for the micelles can be compared to that observed for star polymers as the number of arms is varied. It was observed that for a constant arm molecular weight, the intrinsic viscosity was nearly independent of the number of arms.[44,45] However, this conclusion applies to stars having ca. 4–15 arms, while the aggregation numbers for the micelles range from 3 to over 100 chains.

3.5.3. Molecular Weights. The first step in the determination of the molecular weights of the micelles is the construction of a SEC universal calibration curve.[35] This calibration procedure is necessary since both the chemical compositions and the structures of the samples are different from those of the standards. The intrinsic viscosities and the elution volumes of the polystyrene standards are used to construct a plot of log ($[\eta]M$) versus the SEC elution volume, as shown in Figure 12. Then the elution volume of the micellar peak is measured, and the $[\eta]M$ product corresponding to that elution volume is determined from the universal calibration equation. Finally, the molecular weight M of the micelles is obtained when this product is divided by the independently measured intrinsic viscosity of the micellar solution.

This procedure, however, provides only a peak molecular weight and does not give any indication of the molecular weight distribution. Such information can be obtained from the "slice" analysis[46] of the chromatogram, as illustrated in Figure 13. In this figure, a typical peak is presented as a series of slices, with label A of the abscissa giving the elution volume. With the universal calibration

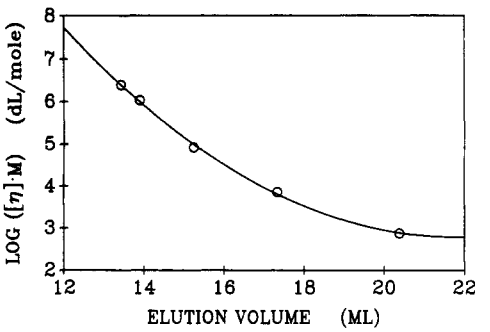

Figure 12. SEC universal calibration curve for the molecular weight determination of the micelles in DMF.

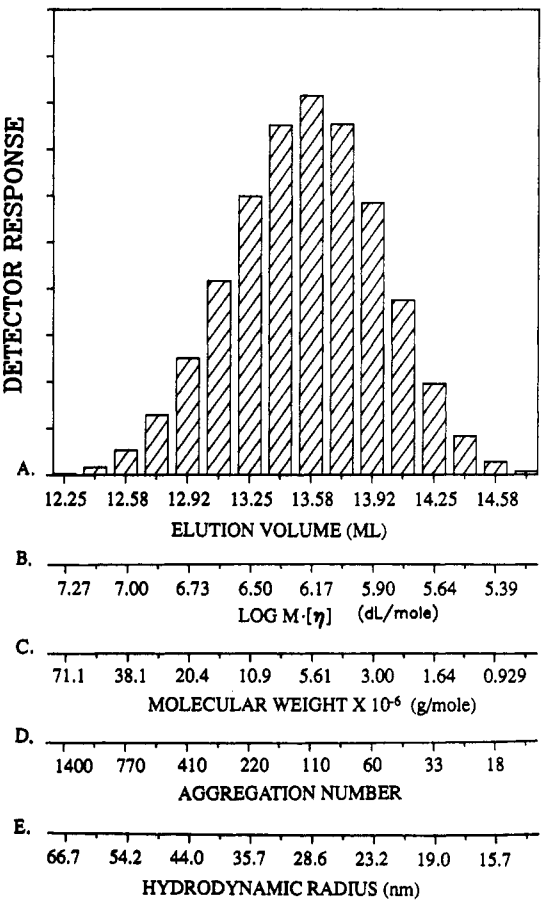

Figure 13. Slice analysis of the SEC micellar peak for the determination of molecular weights and the hydrodynamic radius for sample PS(440)PMA(40)-Na. Detector response versus (A) elution volume, (B) log $[\eta]M$, (C) molecular weight, (D) aggregation number, and (E) hydrodynamic radius.

equation, the elution volume can be transformed into the product $[\eta]M$, as shown in label B. Then, the $[\eta]M$ product is divided by $[\eta]$ to express the slice analysis in terms of M, as shown in label C. Finally, from the area and the M values of each slice, the number- and weight-average molecular weights (M_n and M_w) as well as the polydispersity ratio, M_w/M_n, are calculated. The distribution in aggregation numbers is illustrated by label D. The calculation of label E is explained later.

In order to confirm that reasonable molecular weights are calculated by using this procedure, a comparison was made of the molecular weight averages obtained for a polystyrene block precursor, PS(440), by conventional calibration and by the universal calibration method. The M_n, M_w, and M_w/M_n were, respectively, 45 400, 49 500, and 1.09 by conventional calibration, and 45 600, 53 700, and 1.18 by the universal calibration method. Therefore,

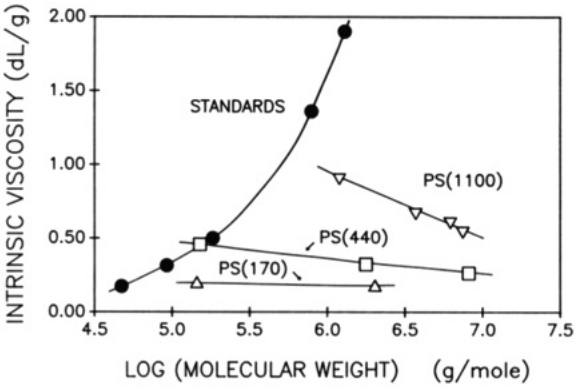

Figure 14. Intrinsic viscosity versus molecular weight for standards and micelles in DMF.

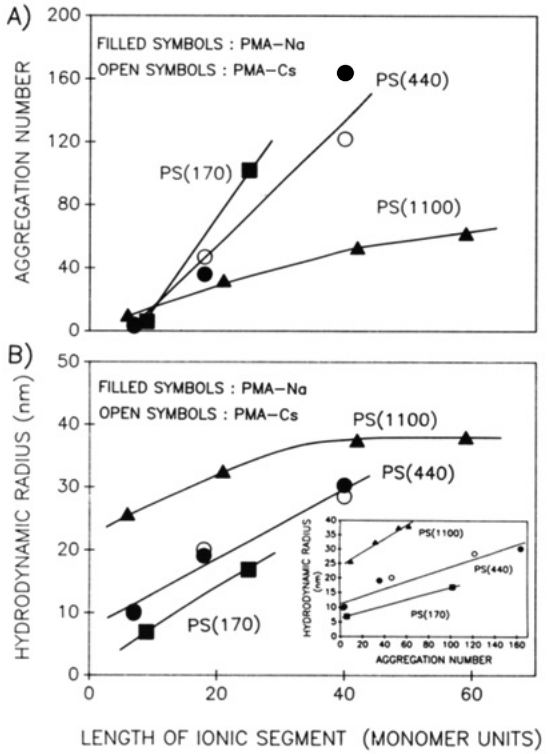

Figure 15. Aggregation number (A) and hydrodynamic radius (B) versus the length of the poly(metal methacrylate) block for the three series of block ionomers.

the procedure seems to yield acceptable results for narrow molecular weight distribution polymers. The micelles, however, have polydispersity indices that are much larger. Fortunately, however, the change in $[\eta]$ as a function of molecular weight is small for micelles when compared to linear polystyrene, as can be seen from Figure 14. Consequently, the use of an average $[\eta]$ for computations over the whole distribution is acceptable in the case of the micelles as well. Figure 14 also shows that the intrinsic viscosity of the micelles decreases with increasing molecular weight (or aggregation number), as mentioned earlier.

The molecular weights and aggregation numbers of the micelles are summarized in Table I. The influence of the length of each block on the aggregation number of the micelles is illustrated in Figure 15A. For a given polystyrene block length, the aggregation numbers increase as the length of the insoluble ionic segments increases. However, for a constant ionic block length, the aggregation numbers decrease as the length of the soluble styrene block increases. Similar general trends were observed for micelles made from amphiphilic[47,48] and lipophilic[40] block copolymers.

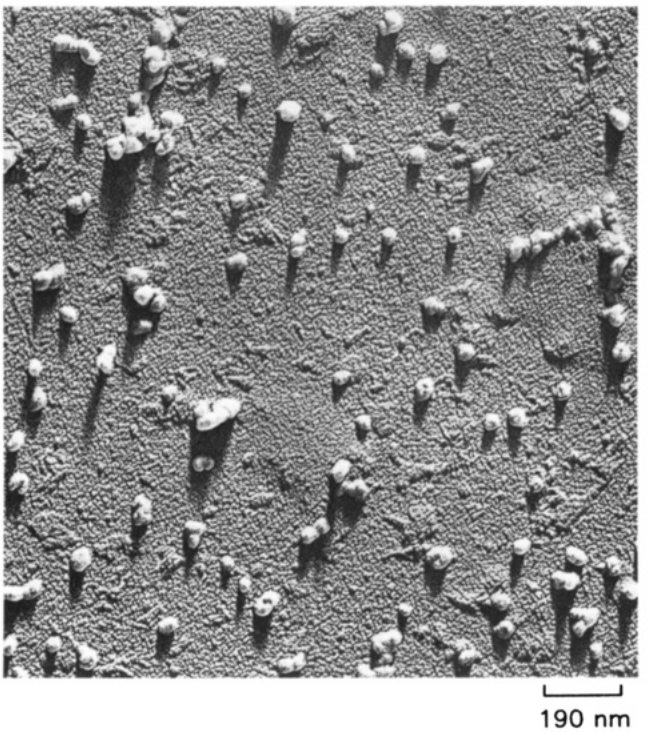

Figure 16. Electron micrograph of the micelles of sample PS(440)PMA(40)-Na.

3.5.4. Hydrodynamic Radii. It has been shown[49,50] that the product $[\eta]M$ is related to the hydrodynamic radius, r_h, of polymer molecules of various structures and chemical compositions. The relation, derived by substituting the density by $(3M)/(4\pi N_a r_h^3)$ in eq 7, is given by

$$[\eta]M = (10/3)N_a\pi r_h^3 \quad (8)$$

where N_a is Avogadro's number. Using eq 8, SEC traces expressed in terms of the product of $[\eta]M$ can be replotted in terms of r_h; this scale is given as the abscissa label E in Figure 13. Average hydrodynamic radii, with the associated standard deviation as calculated from the slice analysis of SEC micellar peaks, are given in Table I.

Figure 15B shows that the hydrodynamic radius increases with the lengths of both the nonionic and the ionic blocks. However, the increase of the radius with the length of the ionic block is not a direct consequence of the increase in the size of that block, as it is when the length of the styrene block is increased. It is, rather, a consequence of the increase in the aggregation number with the length of the ionic block. Therefore, it might be more relevant to plot the hydrodynamic radius against the aggregation number, which combines the effects of the ionic and of the nonionic blocks, as shown in the inset of Figure 15B. The inset shows that, for a given series, the radius increases with the aggregation number. For a given aggregation number, on the other hand, the radius of the micelle is determined mainly by the length of the soluble polystyrene block.

3.6. Electron Microscopy. Figure 16 shows an electron micrograph of the micelles of sample PS(440)PMA(40)-Na. The micrograph shows two types of particles, isolated micelles and aggregates of micelles. These aggregates are probably not present in solution; this was confirmed by dynamic light scattering measurements of the micellar solutions to be published later.[51] These aggregates are probably formed in the process of sample

Table II
Comparison of Aggregation Numbers by SEC and SAXS[52]

sample	aggregation no. from SEC-(Na)	SEC-(Cs)	SAXS-(Cs)	EM-(Na)
PS(170)PMA(9)-Na or -CS	8		87	
PS(170)PMA(25)-Na or -Cs	98		153	
PS(440)PMA(7)-Na or -Cs	3	4	101	
PS(440)PMA(18)-Na or -Cs	38	46	151	
PS(440)PMA(40)-Na or -Cs	160	120	213	250

preparation, as a result of solvent evaporation. Inspection of the isolated particles shows that the micelles are spherical in shape and that they are somewhat polydisperse in size, as was expected from the polydispersity index calculated for this sample by SEC. The average radius with associated standard deviation calculated from these isolated micelles (numbering 63) was 17 ± 5 nm. This radius should be considered as an upper limit to the real radius, as it is suspected that the micelles are not perfectly spherical but are slightly flattened as a consequence of the method of preparation of the sample. The average aggregation number calculated from this radius is 253, which is larger by a factor of ~1.5 when compared with that determined by SEC from M_n. Again, this number should be considered as an upper limit to the real value.

3.7. Comparison of SEC and SAXS[52] Aggregation Numbers. The aggregation numbers measured by SEC in solution and by SAXS in the solid state are compared in this section. As was mentioned earlier, the micellar solutions are obtained by dissolution of the dry powders in the solvent. SAXS measurements, on the other hand, are performed on samples molded from the powders. As might be expected, the SAXS results show that, in the solid state, the ionic blocks are microphase-separated into small spherical ionic domains embedded in a polystyrene matrix. A detailed analysis of the results allowed the determination of the average number of chains per ionic domain. It is interesting to compare this "aggregation number" from the solid-state measurements with that of the micelles in solution, in order to gain some insight into the dissolution process. The data relevant to this discussion are summarized in Table II.

A comparison of the aggregation numbers obtained in the solid state by SAXS with those determined in solution by SEC shows that there is a large difference for the copolymers with the short ionic segments, while the agreement is within a factor of less than 2 for the copolymers with the longest ionic segments. If both the SAXS and the SEC data are correct for their respective environments, the dissolution of the block ionomers with the shortest ionic segment is accompanied by a change in the aggregation number, which is probably the result of leaching of soluble chains upon dissolution. This process is described below. Even before dissolution, it is clear that some of the chains are probably already unassociated with the ionic domains. This is especially true of the unfunctionalized styrene homopolymer, if present, but might also be valid for some chains with extremely short ionic sequences. As was pointed out before, for any styrene length, there is a solubility threshold for single chains as a function of ionic segment length. Below this threshold, the chains are soluble, and the lower the average ionic block length, the larger the proportion of chains below this solubility threshold. These chains, which are probably incorporated into the ionic domains in the solid state, are solubilized on addition of solvent. This decreases the apparent aggregation number, with the effect becoming more important with decreasing block length.

4. Conclusions

Size-exclusion chromatography provides extensive information on the colloidal properties of the diblock ionomers studied here. In solvents selectively good for the nonionic block, the chromatograms show the simultaneous presence of micelles and single chains for all block ionomer compositions. These solutions are stable, as manifested by constant elution volumes and proportions of micelles to single chains. There is no apparent micelle dissociation–association equilibrium taking place within the time scale of a few days. The presence of the single chains is, therefore, not a manifestation of micelle–single chain equilibrium. The single chains have a very low ionic content compared to that of the micellized chains, which explains why they do not aggregate. The proportion of micellized materials is related to the ionic content of the block copolymer.

The intrinsic viscosity of the micellar solution is higher than that of a solution of single chains. The correction of the intrinsic viscosity for the presence of single chains is significant when the proportion of micellized chains is below ca. 70%. The intrinsic viscosity of micellar solutions is mainly determined by the soluble styrene segment and is proportional to its length. For a given length of the styrene block, the intrinsic viscosity decreases as the length of the insoluble ionic segment increases or as the aggregation number increases. This trend is interpreted as an increase in the density of the micelles as the aggregation number increases.

The aggregation number, calculated from the molecular weight of the micelles, increases as the length of the ionic segment increases but decreases as the length of the polystyrene segment increases. The hydrodynamic radius increases as the length of the styrene increases and as the aggregation number increases. The presence of spherical micelles has been verified by electron microscopy. Comparison of the aggregation numbers in solution (SEC) and in the solid state (SAXS) suggests that there is a considerable change in the aggregation number upon dissolution, especially for the ionomers with the shortest ionic blocks. This decrease could be due to leaching of the soluble chains from the micelles upon dissolution.

This micellar system is being investigated by dynamic light scattering in order to confirm and extend the SEC results. This study will be the subject of a future publication[51] and will include a discussion of the effect of preparative conditions on micellar characteristics.

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