

Colloidal Properties of Block Ionomers. 2. Characterization of Reverse Micelles of Styrene-*b*-Methacrylic Acid and Styrene-*b*-Metal Methacrylate Diblocks by Dynamic Light Scattering†

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ABSTRACT: The reverse micelles formed from polystyrene-*b*-poly(methacrylic acid) and polystyrene-*b*-poly(metal methacrylate) block copolymers in solvents selectively good for the polystyrene blocks are investigated by dynamic light scattering (DLS) and viscometry. While the neutralized materials form micelles in all good solvents for the styrene block, the acid materials form micelles only in those solvents which do not interact with the carboxylic acid functionalities of the methacrylate block. The hydrodynamic radii of the micelles increase as the lengths of both the methacrylate and the styrene blocks increase. The aggregation numbers increase as the lengths of the methacrylate blocks increase; they are independent of the lengths of the styrene blocks for the acid materials, but decrease as the lengths of the styrene blocks increase for the neutralized materials. The method of preparation of micellar solutions is shown to have an influence on the characteristics of the resulting micelles. The results obtained by DLS confirm the size-exclusion chromatography determinations reported previously for the neutralized materials.

1. Introduction

Block copolymers, when dissolved in a solvent which is selectively good for one type of block but a nonsolvent for the other, are known to form, under certain conditions, colloidal particles with a micellelike structure by association of several molecules.¹⁻⁴ The micellelike structure is usually described as consisting of a more or less compact core formed by the aggregation of the insoluble blocks, and of a corona formed by the soluble segments emanating from the core. Most of the work reported on the micellar properties of block copolymers involved nonionic block copolymers.¹⁻³ The few studies dealing with ion-containing block copolymers dealt with regular micelles formed in aqueous solutions.⁴ Reverse micelles made from ion-containing block copolymers have received very little attention.^{5,6}

In the first paper of this series,⁶ the micellar properties of ion-containing diblock copolymers of low ion content, or block ionomers, were investigated by size-exclusion chromatography (SEC) and viscometry. The diblock ionomers which were investigated were polystyrene-*b*-poly(metal methacrylate) copolymers with short ionic segments, ca. 6–60 repeat units, and longer polystyrene segments, ca. 170–1100 units. In media of low polarity, which are thermodynamically good for the polystyrene blocks, the block ionomers form reverse micelles comprising an ionic core surrounded by the soluble polystyrene segments. The most significant results obtained so far on the micellar properties of the polystyrene-*b*-poly(metal methacrylates) block ionomers are summarized below. SEC experiments showed the reverse micelles to be very stable. In particular, there was no apparent micelle dissociation–association equilibrium taking place within the time scale of a few days. Moreover, it was shown that the simultaneous presence of micelles and single chains (i.e., molecularly

dissolved chains) in micellar solutions was not a manifestation of micelle–single-chain equilibrium. The single chains were found to have a lower ionic content compared to that of the micellized chains, which explained why they were soluble and did not aggregate. This study also included a systematic investigation of the dependence of block copolymer composition on the micellar characteristics. The aggregation numbers, i.e., the number of chains per micelle, were shown to increase as the length of the insoluble ionic segment increased, but to decrease as the length of the soluble styrene segment increased. The overall size of the micelle increased as the length of the styrene segment increased, and as the aggregation number increased.

The use of the SEC technique for the study of the micellar properties of block ionomers proved to be fruitful, from the point of view of both qualitative and quantitative determinations. For the quantitative determinations of molecular weights (aggregation numbers) and hydrodynamic radii, the SEC columns were calibrated using the universal calibration method.⁷ However, the applicability of this calibration method for quantitative determinations on polymeric micelles remains to be demonstrated by an independent technique.

In the present study, dynamic light scattering (DLS) is used to confirm the SEC determinations reported previously for the polystyrene-*b*-poly(metal methacrylate) series. In addition, many DLS results which complement and extend the characterization of the micellar properties of diblock ionomers are presented. This paper contains results on the effects of varying some of the parameters of the method of preparation of the micellar solutions on the ultimate properties of the micelles. The effect of the solvent in which the block copolymers are dissolved on the micellar characteristics is treated. The stability of micellar solutions under various solvent conditions is investigated as well. Finally, two types of micellar system differing only in the chemical form of the insoluble methacrylate segments are compared: reverse micelles made from polystyrene-*b*-poly(metal methacrylates) copolymers

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Table I
Characteristics of Micelles in DMF and CCl₄ Solutions

sample	DMF solutions				CCl ₄ solutions			
	[η], ^a dL/g	SEC		DLS		[η], dL/g	DLS	
		<i>r</i> _h ± σ, ^a nm	<i>N</i> ^b	<i>r</i> _h , ^c nm	<i>N</i> ^b		<i>r</i> _h , ^d nm	<i>N</i> ^b
PS(170)PMA(9)-Na	0.200	6.9 ± 2.5	6	7	6	0.301	12	20
PS(170)PMA(25)-Na	0.180	16.9 ± 4.2	85	27	343	0.273	42	883
PS(170)PMA(9)-H						0.255	11	19
PS(170)PMA(25)-H						0.205	18	91
PS(440)PMA(7)-Na	0.456	9.9 ± 2.0	3	10	3	0.626	18	12
PS(440)PMA(18)-Na	0.322	19.0 ± 4.6	28	18	36	0.412	24	45
PS(440)PMA(40)-Na	0.263	30.3 ± 7.9	134	31	138	0.316	37	197
PS(440)PMA(7)-Cs	0.440	10.2 ± 2.4	3	14	9	0.797	20	14
PS(440)PMA(18)-Cs	0.332	20.1 ± 5.9	32	21	20	0.413	25	48
PS(440)PMA(40)-Cs	0.277	28.5 ± 7.0	102	28	88	0.332	33	121
PS(440)PMA(7)-H						0.479	20	24
PS(440)PMA(18)-H						0.446	24	42
PS(440)PMA(40)-H						0.361	29	91
PS(1100)PMA(6)-Na	0.900	25.7 ± 6.1	10	23	7	1.02	29	13
PS(1100)PMA(21)-Na	0.665	32.5 ± 7.0	28	30	23	0.941	34	24
PS(1100)PMA(42)-Na	0.603	37.5 ± 7.6	47	36	42	0.816	44	55
PS(1100)PMA(59)-Na	0.539	38.0 ± 8.8	54	37	49	0.798	45	60
PS(1100)PMA(6)-H						0.921	35	26
PS(1100)PMA(21)-H						0.736	45	69
PS(1100)PMA(42)-H						0.700	51	104
PS(1100)PMA(59)-H						0.660	53	119

^a From ref 6, σ is the relative standard deviation of the distribution of radii. ^b Aggregation numbers were obtained from the molecular weights of the micelles calculated from the r_h and [η] values using eq 5. ^c Calculated using eq 4 with σ measured by SEC.⁶ ^d Calculated using eq 4. For the neutralized form, the σ used in the calculation was that measured by SEC in DMF.⁶ For the acid form, the average of the σ 's measured for the neutralized systems was used, i.e., $\sigma = 0.24$.

and those made from polystyrene-*b*-poly(methacrylic acid) copolymers.

2. Experimental Section

2.1. Materials. Synthesis and Hydrolysis of Block Copolymers. The preparation and characterization of the block ionomers is described in detail in paper 1 of this series.⁶ 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. It was found necessary to react the poly(styryllithium) chains with diphenylethylene before addition of the *tert*-butyl methacrylate monomer in order to avoid a side reaction leading to a small but detectable amount of high molecular weight contaminant. The polymerization was performed in tetrahydrofuran (THF), at -78 °C, under a nitrogen atmosphere. The apparatus used for the polymerization allows the withdrawal of aliquots of the 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. 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 determination of number of repeat units per block is of 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. The composition of the diblocks studied is given in Table I, along with a tabulation of the most important quantitative results to be discussed below. The abbreviations used to indicate the copolymer composition are illustrated in the following example: PS(440)PMA(18)-H indicates a polystyrene chain of 440 units joined to a polymethacrylate chain of 18 units, H denoting the acid form. Neutralized forms will be indicated by Na or Cs.

Solvents. The solvents used in the preparation and study of micellar solutions were HPLC grade dimethylformamide (DMF) and tetrahydrofuran (THF) (both from Anachemia), and spectrograde carbon tetrachloride, toluene, benzene, cyclohexane, and methanol (American Chemicals). All solvents were used as received, unless stated otherwise.

2.2. Preparation of the Micellar Solutions. Acid Form. Micellar solutions of the block copolymers in the acid form were prepared as described below. The polystyrene-poly(methacrylic acid) copolymers were dissolved in freshly distilled THF, which had been dried with CaH₂. It should be pointed out that the acid form of the block ionomers dissolves completely as single chains in THF for the copolymer composition range studied. The concentrations of polymer were 0.025 g/mL. The solutions were stirred for 1 h and then filtered through a membrane filter with nominal pore size of 0.2 μ m. The solutions were cast by allowing the solvent to evaporate slowly overnight in a dish protected from atmospheric dust. The resulting films were further dried in a vacuum oven at 80 °C for several days. Micellar solutions were obtained by dissolution at room temperature of the cast copolymers in solvents such as CCl₄, toluene, and cyclohexane.

Neutralized Form. Micellar solutions of the block copolymers in the neutralized form were prepared as follows: the diblocks in the acid form were dissolved in benzene/methanol (90/10, v/v) mixtures, where only single chains are present. The concentration of the polymer was 0.03 g/mL. The poly(methacrylic acid) blocks were neutralized by addition of stoichiometric amounts of methanolic solutions of NaOH or CsOH. The solutions were stirred for 1 h. The micelles formed upon neutralization were then isolated as a powder by stripping the solvent by freeze-drying. The process was completed by vacuum-drying at 80 °C for several days. Micellar solutions were obtained by dissolution at room temperature of the dried powder in any

good solvent for the styrene block.

Any deviation from the standard procedures described above for the preparation of micelles in the acid or neutralized forms will be indicated in the text.

2.3. Micelle Characterization. Measurements were performed at 25.0 °C. For each block copolymer, a stock micellar solution was prepared by dissolving the dry polymer in the desired solvent to a concentration of ca. 0.01 g/mL. These solutions were stirred overnight at room temperature before any measurements were performed. Micellar solutions studied by different techniques were obtained by dilution of the stock solutions to the desired concentration. All determinations were obtained within a few days after the stock solutions were prepared.

Dynamic Light Scattering. DLS studies on micellar solutions were carried out on a Brookhaven Instruments Corp. photon correlation spectrometer with a BI-2030 digital correlator and a Spectra Physics 120 helium/neon laser with a wavelength of 632.8 nm. The scattering angle was always 130°. The index matching solvent was toluene. Samples were filtered through membrane filters with nominal pore size of 0.5 μm before measurement of the diffusion constant. Solutions were measured in the concentration range 0.2–5 mg/mL and the radii obtained by extrapolation to infinite dilution, unless stated otherwise. The standard deviation of repeat measurements at a given concentration was typically less than 2%.

The normalized time correlation function of the electric field of scattered light, $g(\theta, \tau)$, was assumed to be in the form of a cumulant expansion

$$g(\mathbf{q}, \tau) = \exp(-\Gamma\tau) \{1 + (\mu_2/2)\tau^2 + \dots\} \quad (1)$$

where only the first (Γ) and second (μ_2) moments were calculated. The effective translational diffusion coefficient (D_T) measured by DLS is related to Γ through the expression

$$D_T = \Gamma/q^2$$

where q is the absolute value of the scattering vector \mathbf{q} :

$$q = (4\pi n/\lambda_0) \sin(\theta_s/2)$$

where n is the refractive index of the medium, λ_0 the wavelength of the incident light, and θ_s the scattering angle.

The hydrodynamic radius of the particle, $r_{h,DLS}$, is calculated from the translational diffusion coefficient extrapolated to zero concentration, D_0 , using the well-known Stokes-Einstein relationship

$$r_{h,DLS} = kT/6\pi\eta D_0 \quad (2)$$

where k is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent medium. In general, the radius calculated from DLS measurements can be related to the actual average radius of the distribution, r_h , by⁸

$$r_{h,DLS} = \frac{\overline{r_h^6}}{\overline{r_h^5}} = \frac{\int r_h^6 P(r_h) dr_h}{\int r_h^5 P(r_h) dr_h} \quad (3)$$

where $P(r_h)$ is the distribution of radii for the system. Assuming a Gaussian distribution, eq 3 becomes⁹

$$r_{h,DLS} = r_h \frac{(1 + 5\sigma^2 + 45\sigma^4 + 15\sigma^6)}{(1 + 10\sigma^2 + 15\sigma^4)} \quad (4)$$

where σ is the relative standard deviation of the distribution of radii for the particles. For the present study, σ values were calculated from the SEC chromatograms.⁶

It has been shown^{10,11} that the hydrodynamic radii of polymer molecules of various structures and chemical compositions can be related to the molecular weights, M , by

$$r_h^3 = 3[\eta]M/10N_A\pi \quad (5)$$

where $[\eta]$ is the intrinsic viscosity of the solution and N_A is Avogadro's number. Finally, the aggregation number of the micelles is calculated by dividing the molecular weight of the micelles by that of a single chain.

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. A mixed-bed (Shodex) column and a 10³-Å Ultrastaygel (Waters) SEC column connected in series were used when the eluent was DMF. Details regarding the determination of the hydrodynamic radii of micelles by SEC in DMF solutions are given elsewhere.⁶ Studies of the micellar solutions in THF were performed on 10⁴-, 10⁵-, and 10⁶-Å Ultrastaygel (Waters) columns connected in series. The determination of the proportion of micelles versus single chains in CCl₄ solutions was performed on a 10⁴-Å Ultrastaygel (Waters) column. Solutions in the concentration range of 0.5–1 mg/mL were filtered through membrane filters with nominal pore size of 0.5 μm before injection.

Viscometry. Solution flow times were measured using standard Ubbelohde viscometers. Measurements were made by successive dilutions of solutions in the concentration range 0.2–10 mg/mL. Solutions were filtered through 0.5- μm membrane filters before measurements. Plots of η_{sp}/C and $\ln \eta_r/C$ versus concentration were extrapolated to infinite dilution to obtain the intrinsic viscosity. The intrinsic viscosities were corrected for the presence of single chains in micellar solutions by following a mathematical procedure described in detail previously.⁶ Therefore, the intrinsic viscosities reported in Table I correspond to those of micellar solutions containing only micelles.

3. Results and Discussion

This part of the paper is divided into four sections. In the first section, the concentration dependence of the diffusion coefficient of micelles made from the block copolymers is covered briefly. Then the hydrodynamic radii and the aggregation numbers of the micelles in DMF and CCl₄ solutions are discussed. In the third section, the effect of changing the method of preparation on the micellar characteristics is examined. Finally, the stability of the micelles in pure nonpolar solvents and in mixtures containing a small amount of polar solvent is discussed.

3.1. Concentration Dependence of the Diffusion Coefficient. In order to correct for any possible interparticle interactions, the translational diffusion coefficients were extrapolated to infinite dilution to yield D_0 . The concentration dependence of D_T can be approximated by

$$D_T = D_0(1 + k_d C) \quad (6)$$

where k_d is the diffusion virial coefficient and C the concentration. The linear concentration dependence of the diffusion coefficient of the micellar solutions was analyzed in terms of eq 6, and the results for both DMF and CCl₄ solutions are summarized in Figure 1. This figure shows that k_d values approach zero for D_0 larger than ca. $7 \times 10^{-8} \text{ cm}^2/\text{s}$, which corresponds to particles with $r_{h,DLS}$ lower than ca. 30 nm. However, for particles with D_0 values lower than ca. $7 \times 10^{-8} \text{ cm}^2/\text{s}$ (i.e., with $r_{h,DLS}$ larger than ca. 30 nm), k_d values become significant and decrease as the size of the micelle increases. Negative k_d values result in decreasing D_T with concentration, or in an apparent increase in radius as the concentration increases. A rapid change in the value of k_d with radius is expected in the range $0.2 < qr_{h,DLS} < 4$.¹² For the present system, the values of $qr_{h,DLS}$ are in the range 0.2–1.4, and a variation in k_d with radius is therefore not surprising.

3.2. Hydrodynamic Radii and Aggregation Numbers. The hydrodynamic radii and the aggregation numbers of the micelles made from the block copolymers in the neutralized and acid forms to be discussed in this section are summarized in Table I. Note that this table also contains results determined earlier by SEC.⁶ The results obtained for the neutralized copolymers will be presented first, followed by the results for the acid

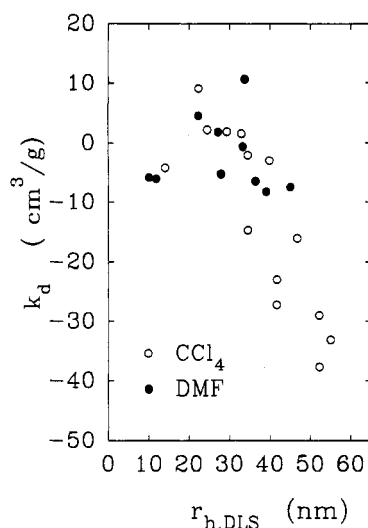


Figure 1. Diffusion virial coefficient versus hydrodynamic radius for DMF and CCl_4 micellar solutions.

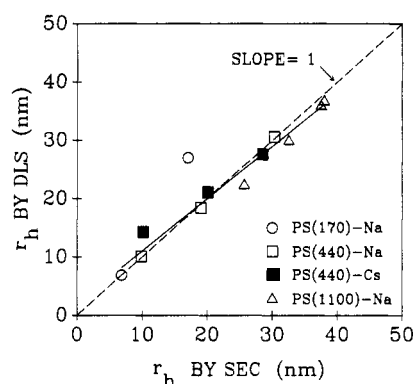


Figure 2. Comparison of the hydrodynamic radii determined by DLS and by SEC in DMF for micellar solutions prepared from the neutralized materials.

materials. Finally, the hydrodynamic radii in a common solvent of the micelles made from the copolymers in the neutralized and acid forms will be compared.

3.2.1. Copolymers in the Neutralized Form. Comparison of DLS and SEC Results in DMF. Figure 2 shows a comparison of the hydrodynamic radii of micelles which have been determined by DLS and SEC in DMF solutions. The plot is constructed from the data in Table I. A line of slope 1 corresponding to a perfect agreement between the results of the two techniques is also included. The plot shows that, with the exception of one point corresponding to sample PS(170)PMA(25)-Na, all points approach closely the line of slope 1. A linear regression performed on the points (except for that corresponding to sample PS(170)PMA(25)-Na) gives a slope of 0.899 and a coefficient of correlation equal to 0.988. The line fitting the points is reproduced on the figure. Thus, for most samples, the radii determined by DLS and SEC techniques agree very closely; this confirms the validity of the SEC determinations.

The reason why the radii determined by DLS and SEC for sample PS(170)PMA(25)-Na (the sample with the highest ratio of ionic to nonionic groups) do not agree might be related to the presence in solution of micelles of nonspherical shape. As was mentioned earlier, the micellar solutions are prepared by dissolution of powders. In view of the very high stability of the micelles,⁶ it is very likely that the solid-state morphology is retained to some extent upon dissolution. It is known from solid-state studies that the shape of the microphase-separated

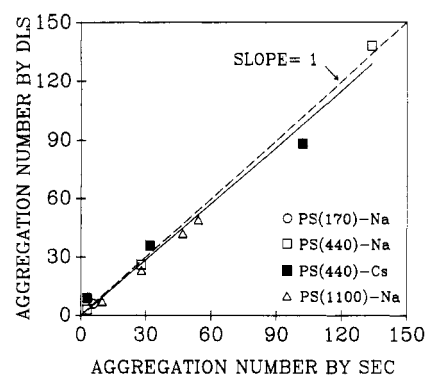


Figure 3. Comparison of the aggregation numbers determined by DLS and by SEC in DMF for micellar solutions prepared from the neutralized materials.

domains of nonionic block copolymers is largely dependent upon the composition of the copolymer.¹³ At low volume fraction of the minor component, spherical domains of the minor component in a continuous matrix of the major component are commonly observed. As the content of the minor component is increased, however, the shape of the domains of the minor component progressively changes to nonspherical shapes like cylinders and lamellae. The average ion content of sample PS(170)-PMA(25)-Na is low enough that, based on morphological results obtained for nonionic block copolymers, spherical ionic domains would be expected. However, in a recent investigation,¹⁴ electron microscopy results showed the presence of cylindrical morphologies of the ionic domains for block ionomers with ionic contents of ca. 10%. Therefore, because of the higher ion content (13 mol %) of this sample compared to the others, and because of the particular way the micellar solutions are prepared, it is possible that for this particular sample a portion of the micelles are not spherical in shape. If this is the case, it is not surprising that a large deviation is observed for this sample, since the equation used to calculate the radius from DLS data, i.e., eq 1, assumes spherical shape.

Figure 3 compares the aggregation numbers of the micelles in DMF solutions obtained from the two techniques. These are calculated from the r_h values discussed above using eq 5 and are summarized in Table I. The point corresponding to sample PS(170)PMA(25)-Na is not included in the plot, the aggregation number determined by DLS being very far out of range. The other points lie along the line of slope equal to 1. The slope calculated for the line fitting the points is 0.963, with a coefficient of correlation equal to 0.992.

Comparison of DLS Results in DMF and CCl_4 . The hydrodynamic radius of micelles made from block ionomers depends on several parameters. The most important of these are the length (or molecular weight) of the soluble block, the aggregation number (which depends largely on the length of the ionic segment), and the "affinity" of the solvent for the soluble segments, which determines the degree of swelling of the soluble corona. In solvents of similar affinity for the soluble blocks, the hydrodynamic radii of micelles made from a block copolymer of a given composition should be comparable if the aggregation numbers are similar. On the other hand, if the radii are not comparable, it can be concluded unambiguously that the aggregation numbers are different. In solvents of different affinities for the soluble block, however, a difference in the hydrodynamic radii is expected for micelles of identical aggregation numbers, since the degree of swelling of the corona is different. Therefore, for solvents of different affinities, a meaningful comparison

Table II
Micellar Characteristics of Sample PS(440)PMA(40)-Na in Various Solvents

solvent	solvent properties (25 °C)		micellar characteristics	
	Mark-Houwink parameter ^a	dielectric constant ^b	$r_{h,DLS}$, nm	aggregation no.
toluene	0.73	2.4	36.5	
THF	0.72	7	36.9	
CCl ₄	0.73	2.2	36.6	197
DMF	0.60	37	30.6	138
cyclohexane	0.50	2.0	28.3	

^a Reference 15. ^b Reference 16.

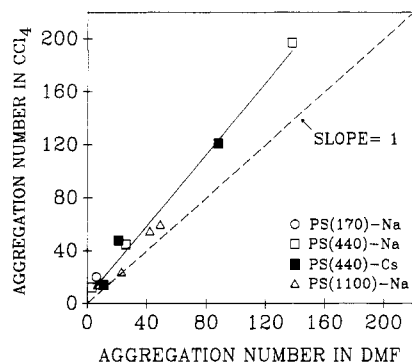


Figure 4. Comparison of the aggregation numbers determined by DLS in CCl₄ and in DMF for micellar solutions prepared from the neutralized materials.

of the micellar characteristics should be based on the aggregation numbers.

The effect of the affinity of the solvent for the soluble block is illustrated in Table II, where the micellar characteristics of sample PS(440)PMA(40)-Na in various solvents are listed. The parameter used to evaluate the solvent affinity with respect to the soluble block is the Mark-Houwink a exponent, which is an experimental parameter with a value proportional to the expansion of the chains in the solvent. In solvents of similar affinity, such as toluene, THF, and CCl₄, the hydrodynamic radii are similar, within experimental error, which implies that the aggregation numbers are also the same. In solvents of lower affinity like DMF, or in a θ solvent like cyclohexane, the radii are smaller. The aggregation number in DMF, however, is lower than in CCl₄, which shows that the decrease in the hydrodynamic radius observed in going from CCl₄ to DMF might not be due solely to a decrease in solvent affinity with respect to the soluble segments, but also to a decrease in the aggregation number.

Larger aggregation numbers of micelles are observed in CCl₄ compared to those found in DMF, as shown in Figure 4. It should be noted, however, that the aggregation numbers in CCl₄ were calculated from eq 4 using the σ values calculated from SEC traces recorded in DMF.¹ In view of this approximation, two extreme situations can be envisaged: either the σ values in the two solvents are similar, in which case the aggregation numbers in CCl₄ are actually larger than those in DMF, or the aggregation numbers in the two solvents are similar, in which case the σ values are substantially and systematically larger in CCl₄ compared to those in DMF. The latter hypothesis can be rejected by comparing the square root of the ratio μ_2/Γ^2 (cf. eq 1), which is a measure of the standard deviation in the diffusion constant for micelles in DMF and CCl₄ solutions. The comparison shows that the ratios are not systematically larger in CCl₄ compared to those in DMF. Therefore, as a first approximation, the σ values in the two solvents are similar, and the aggregation numbers in CCl₄ are actually larger than those in DMF.

The different micellar characteristics observed in CCl₄ and in DMF are probably related to another important parameter of the solvent, the affinity of the solvent for the ionic blocks. A qualitative evaluation of this affinity is given by the dielectric constants of the solvents, which are listed in Table II. This table shows that DMF, in particular, has a much higher dielectric constant and therefore a higher affinity than CCl₄ for the ionic blocks. Several mechanisms by which the affinity of the solvent for the ionic block could influence the characteristics of the micelles are discussed below.

SEC experiments⁶ showed that there was no apparent micelle dissociation-association equilibrium taking place during the time scale of a few days in THF solutions. There is no reason to believe that this is not also the case in CCl₄, or in DMF, because the chromatographic behavior of the micelles in THF, CCl₄, and DMF is comparable. For example, sharp micellar peaks are obtained in all solvents. In addition, when the micelles are separated from the single chains, chromatograms of the micellar fraction show the presence of a very small peak from residual single chains that does not grow significantly with time.⁶ Moreover, the solubility properties of triblock ionomers are similar in those different solvents.¹⁷ When dry powders of triblock ionomers consisting of a polystyrene mid block and poly(sodium methacrylate) end blocks are placed in THF, CCl₄, or DMF, they are found to be insoluble. In addition, the extent of swelling of these triblocks is very limited and does not appear to change over several weeks for all three solvents. Therefore, a micelle dissociation-association equilibrium in very unlikely also in CCl₄ or DMF and is therefore not a factor which could account for the different micellar characteristics in the two solvents.

The larger aggregation numbers in CCl₄ compared to those in DMF could be a manifestation of the higher solubility of the chains in DMF compared to CCl₄. The copolymer chains could be more soluble in DMF because of the higher solubility of the ionic segments in that solvent. The consequence of this higher solubility would be that, upon dissolution of the powder, more chains among those having short ionic segments (present due to the polydispersity of the ionic blocks) would be leached out of the micelles in DMF when compared to those in CCl₄. As a consequence, the proportion of single chains in the solutions should be significantly higher in DMF. However, the proportion of single chains in the two solvents, as measured from the area under the peaks on SEC chromatograms in DMF⁶ and in CCl₄, is not significantly different, within experimental error. Therefore this possibility should be rejected as well.

Finally, a mechanism which would account for the larger aggregation numbers in CCl₄ is proposed. This mechanism involves the affinity of the solvent for the ionic core without, however, involving a dissociation-association equilibrium. The affinity of the solvent for the ionic segments determines the extent to which solvent molecules are present in the ionic cores and, therefore, the extent by which the glass transition temperature (T_g) of the ionic cores is lowered due to plasticization by the solvent molecules. It is worth noting that a rearrangement of the micelles is possible only if the T_g of the cores is around or below the temperature of the solution. Therefore, because of its effect on the glass transition of the cores, the affinity of the solvent for the ionic segments will determine whether or not micelles can reorganize significantly upon dissolution. The driving force for reorganization of the aggregates upon dissolution is the change in the volume fraction of the ionic and nonionic components in going

from the solid state to the solution. The morphology present in the solid state depends roughly on the volume fraction of the immiscible components. Upon dissolution, however, the styrene component of the aggregates swells extensively, which changes drastically the relative volume fractions of the two components. As a result of this change in volume fraction, the morphology achieved in the solid state might be thermodynamically unstable upon dissolution. As mentioned earlier, a reorganization of the aggregates is possible only if the glass transition temperature of the insoluble ionic cores is depressed by plasticization by the solvent molecules. It is very likely that DMF plasticizes the cores more efficiently than CCl_4 because of its very much higher dielectric constant without, however, leading to solubility. This might be sufficient to allow a significant rearrangement of the micelles in DMF, in particular of some of the very large aggregates, the presence of which would contribute very strongly to the scattering in CCl_4 . It is conceivable, for example, that upon dissolution in DMF large micelles could convert, because of the swelling phenomenon and of the plasticization of the ionic cores, into smaller micelles by a fissionlike mechanism.

3.2.2. Copolymers in the Acid Form and Comparison with Neutralized Materials. For the polystyrene-*b*-poly(metal methacrylate) ionomers, reverse micelles were observed in all solvents in which polystyrene is soluble. For the polystyrene-*b*-poly(methacrylic acid) copolymers, however, reverse micelles were observed only in solvents in which polystyrene is soluble and which do not contain a functional group able to interact by hydrogen bonding with the carboxylic acid functionalities of the methacrylate blocks. Therefore, for the copolymer in the acid form, reverse micelles are observed in solvents like CCl_4 , toluene, cyclohexane, etc., but not in these solvents when methanol is added to them, or in THF, dioxane, DMF, etc. The results obtained for CCl_4 solutions are presented below.

It should be noted that the r_h values for the materials in the acid form were calculated from eq 4 using a value of σ which is the average of the σ 's measured for the neutralized materials by SEC in DMF, i.e., $\sigma = 0.24$. However, the DLS data show that, in general, in going from the neutralized to the acid materials a slight but significant reduction of the square root of the ratio μ_2/Γ^2 (cf. eq 1) is observed. Therefore, the radii and aggregation numbers reported for the acid materials in Table I should be regarded as minimum values. A value of $\sigma = 0.20$ might possibly be a better estimate, as suggested by the DLS data. The effect of using this lower value of σ would be to increase the r_h values by ca. 6% and to increase the aggregation numbers by ca. 19%.

Figures 5 and 6 summarize the various results obtained in CCl_4 solutions for the micelles made from the diblock copolymers where the insoluble methacrylate segments are in the acid form. For comparative purposes, the results obtained in CCl_4 for the neutralized materials are also included. General trends are considered first, followed by a comparison of the hydrodynamic radii or of the aggregation numbers for the acid and neutralized systems.

Figure 5 shows that the hydrodynamic radii of the micelles increase as the length of the styrene and of the methacrylic acid segments increases. Identical general trends are observed also for the neutralized materials. Figure 6 shows that the aggregation numbers increase as the length of the poly(methacrylic acid) block increases. The length of the soluble polystyrene segment, however, does not appear to affect the aggregation numbers significantly. This contrasts with the trend observed for the neutralized

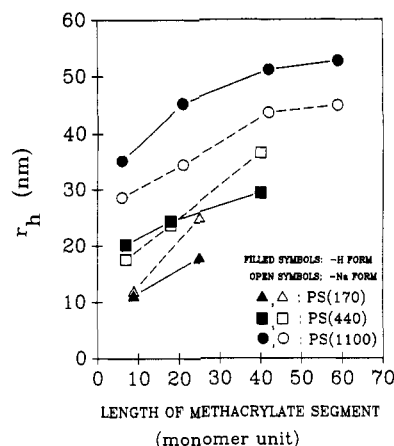


Figure 5. Hydrodynamic radius versus the length of the methacrylate segment for micelles prepared from the acid and neutralized materials, as determined by DLS in CCl_4 .

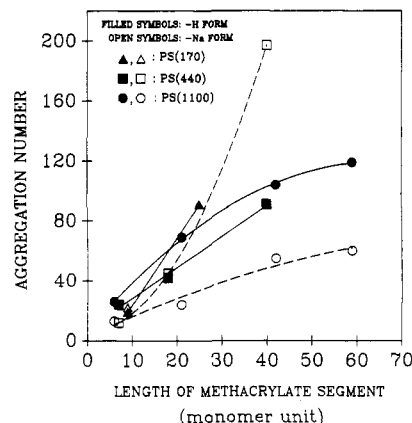


Figure 6. Aggregation number versus the length of the methacrylate segment for micelles prepared from the acid and neutralized materials, as determined by DLS in CCl_4 .

materials in CCl_4 and in DMF,⁶ for which the effect of the length of the styrene block is pronounced. For the neutralized form, the aggregation numbers for a given length of the ionic segment decrease as the length of the polystyrene segment increases. The point corresponding to sample PS(170)PMA(25)-Na is not included in Figure 6, the aggregation number being very far out of range.

A comparison of the hydrodynamic radii (Figure 5) of the two systems shows that, at similar composition, the hydrodynamic radii of the micelles are often different for the acid and the neutralized forms. The radii are larger for the acid form for the series PS(1100). For the series PS(440) and PS(170), the radii are close at low methacrylate contents, but the difference is large for the higher methacrylate contents. The deviation observed for sample PS(170)PMA(25)-Na was accounted for earlier (section 3.2.1); therefore, for this sample, the very large difference between the acid and neutralized forms should be regarded with caution. A comparison of the aggregation numbers (Figure 6) would lead essentially to identical conclusions and is therefore omitted.

The different characteristics noted above for the micelles prepared from the copolymers in the acid or the neutralized forms might be due to at least two factors. Both the chemical nature of the insoluble blocks and the methods of preparation of the micellar solutions are drastically different. Unfortunately, since both of these parameters are varied simultaneously, it is difficult to establish their relative contribution. However, the method of preparation certainly plays a very important role. The

micelles with the methacrylate segment in the acid form are prepared by casting solutions of single chains. Under these conditions, the morphology achieved in the powders is probably closer to true equilibrium. Further discussion on the effect of the method of preparation is presented in the next section.

3.3. Effect of the Method of Preparation. In this section, the reproducibility of the characteristics of micellar solutions prepared by the standard methods is discussed first. Then, several results showing the influence of the method of preparation on the micellar characteristics are presented.

3.3.1. Reproducibility. The standard methods of preparation of the micellar solutions involve two distinct steps. The first step consists in isolating powders or films of the block copolymers by freeze-drying in the case of the neutralized materials or by casting for the polymers in the acid form. The second step involves dissolution of these materials in a suitable solvent. The reproducibility of the micellar characteristics for each of these steps is discussed below.

The reproducibility of the dissolution process was investigated by measuring the radii of micelles in solutions which had been prepared separately but under identical conditions from the same powder. For example, $r_{h,DLS}$ values of 39.1 and 39.8 nm were determined for two micellar solutions prepared from sample PS(440)PMA(40)-Na in DMF (note: numbers are given to three significant figures, which reflects the high precision of the comparative measurements; the accuracy should not be taken as better than two significant figures). Therefore, the dissolution of the neutralized materials yields reproducible values. The same conclusion applies also to micelles made from the block copolymers in the acid form.

The reproducibility for the first step of the method of preparation was verified for the neutralized materials by neutralizing and isolating two samples independently but under identical conditions. After redissolution in toluene, $r_{h,DLS}$ values of 31.3 and 29.4 nm were determined for samples of PS(440)PMA(18)-Na. In the case of micelles in the acid form, the following $r_{h,DLS}$ values were determined for samples which had been cast independently and redissolved in toluene at concentrations of ca. 5.0 mg/mL: 13.3 and 13.8 nm for samples of PS(170)PMA(9)-H; 34.7 and 34.8 nm for samples of PS(440)PMA(40)-H. Therefore, both steps of the standard methods of preparation lead to reproducible micellar parameters.

3.3.2. Micellar Characteristics and Method of Preparation. So far, only micellar solutions obtained by following the standard methods have been described. Several experiments were performed in order to evaluate the effect of changes in the method of preparation on the micellar characteristics. In the case of the copolymers in the neutralized form, the effect of the concentration of the polymer at the time of neutralization and the effect of the nature of the solvent in which the neutralization is taking place were investigated. Moreover, the characteristics of the micelles obtained upon neutralization were compared to those found after freeze-drying and redissolution. In the case of materials in the acid form, micelles were prepared using a different method. The results for the systems in the neutralized form are presented first, followed by the results for the systems in the acid form.

3.3.2.1. Copolymers in the Neutralized Form. Effect of Polymer Concentration. The concentration of the polymer at the time of neutralization was varied to ascertain whether this parameter had an influence on micellar characteristics. For example, samples of PS(440)-

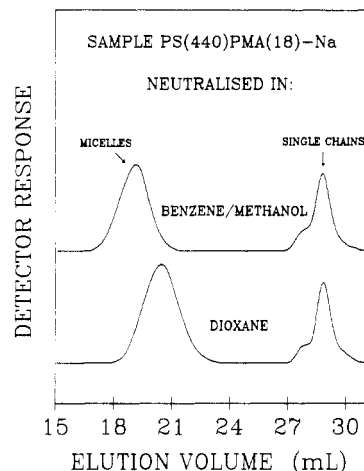


Figure 7. SEC chromatograms of samples of PS(440)PMA(18)-Na prepared by neutralization in different solvents. These chromatograms recorded in THF illustrate the effect of the medium in which neutralization takes place on the micellar characteristics.

PMA(18)-Na neutralized at polymer concentrations of 0.03 and 0.003 g/mL gave hydrodynamic radii of 29.4 and 30.8 nm in toluene. Moreover, SEC chromatograms recorded in THF showed micellar peaks of similar shapes and elution volumes (19.04 and 19.16 mL) for the two samples. Therefore, the concentration of polymer at the time of neutralization does not have a significant influence on the micellar characteristics in the concentration range studied.

Effect of Neutralizing Medium. The effect on the micellar characteristics of the nature of the medium in which the polymer is neutralized is illustrated in Figure 7. This figure shows chromatograms of micellar solutions of samples of PS(440)PMA(18)-Na, which were obtained by neutralization and freeze-drying in benzene/methanol and in dioxane, followed by redissolution in THF. The traces show that the elution volume, and therefore the hydrodynamic radius, of the micelles prepared in benzene/methanol is significantly larger than that of the sample prepared in dioxane. A confirmation of the trend observed above was obtained by comparing the radii measured by DLS for samples of PS(440)PMA(18)-Cs prepared by neutralization and freeze-drying in benzene/methanol and in dioxane, followed by redissolution in DMF. The $r_{h,DLS}$ of the sample prepared in a benzene/methanol mixture was 28 nm, while it was 23 nm when prepared from dioxane. Therefore, it can be concluded that the medium in which neutralization takes place has a significant effect on the characteristics of the micelles.

Effect of Freeze-Drying. It is also of interest to compare the characteristics of the micelles formed directly upon neutralization with those obtained by the standard method, i.e., freeze-drying of the neutralized solution and redissolution of the powders. For sample PS(440)PMA(18)-Na, the value of $r_{h,DLS}$ for the micelles obtained in benzene/methanol directly upon neutralization was 14 nm. This value is significantly lower than that determined for micellar solutions prepared by the standard method (30–37 nm, cf. Table I).

In order to confirm this preliminary observation, the characteristics of micelles formed directly upon neutralization in DMF were compared with those prepared by the standard method (i.e., dissolution of powders) in DMF solutions. The SEC results are presented first, followed by those obtained by DLS. Figure 8 shows SEC chromatograms recorded from micellar solutions prepared by the standard method (traces labeled "freeze-dried") and chromatograms which were obtained directly from the

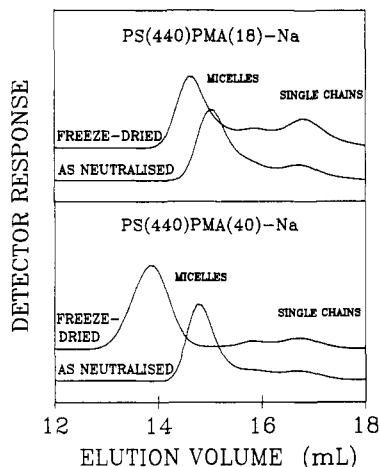


Figure 8. SEC chromatograms comparing the elution volumes of micelles prepared by the standard method to those obtained directly upon neutralization in DMF.

DMF solutions in which the neutralization was performed (traces labeled "as neutralized"). It is clear from a comparison of the elution volumes that the sizes of the micelles present at the time of neutralization and after freeze-drying differ considerably, as was expected from the preliminary result in benzene/methanol mentioned in the previous paragraph. The r_h values calculated from SEC traces for the "as neutralized" PS(440)PMA(18)-Na and PS(440)PMA(40)-Na were, respectively, 13 and 15 nm, corresponding to aggregation numbers of 7 and 14. The hydrodynamic radii determined by SEC for the "as neutralized" materials were confirmed by DLS, which gave r_h values of 11 and 16 nm, corresponding to aggregation numbers of 4 and 16, in fair agreement with the SEC results. When the standard method of preparation was used, the values of r_h for samples PS(440)PMA(18)-Na and PS(440)PMA(40)-Na were 19 and 30 nm, corresponding to aggregation numbers of 28 and 134 (cf. Table I). Therefore, the sizes (and aggregation numbers) of the micelles formed upon neutralization are considerably smaller than those of micelles prepared from the freeze-dried neutralized solutions. This observation implies that there is a considerable reorganization of the micelles upon isolation; this reorganization, however, appears not to be reversible upon dissolution.

3.3.2.2. Copolymers in the Acid Form. In the case of materials in the acid form, the effect of the r_h values of preparing micelles by different methods was also investigated. The standard method used to prepare micellar solutions from copolymers in the acid form was to cast THF solutions of the diblocks. The dried films were then redissolved in a suitable solvent. An alternative but more tedious method of preparing micelles for these copolymers is to start from a solution of single chains, like that obtained in a mixture of toluene/methanol (85/15, v/v), and to distill off the methanol under reduced pressure. As the polar component is removed, the poly(methacrylic acid) blocks become progressively more insoluble and polymeric micelles form. The micelles formed in this manner for sample PS(440)PMA(18)-H gave a $r_{h,DLS}$ of 21 nm, while the micelles obtained by dissolution of cast film in toluene gave a $r_{h,DLS}$ of 30 nm. Therefore, micelles formed directly in solution are smaller than those obtained by dissolution of cast films. Those results, therefore, parallel those observed for the neutralized materials. Therefore, the characteristics of the micelles are very dependent on the detailed manner by which the micellar solutions are prepared. In particular, drying of micelles

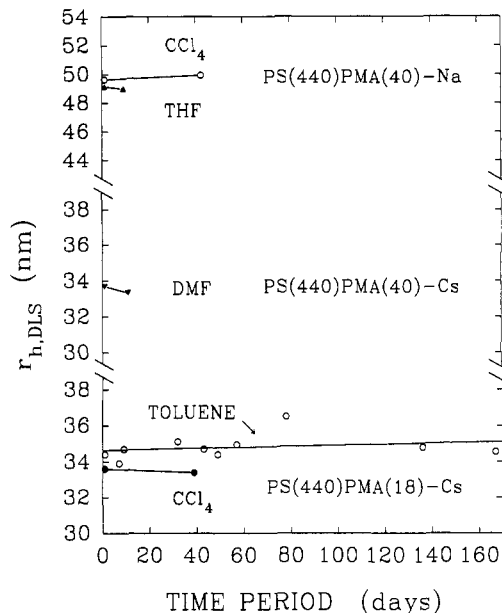


Figure 9. Hydrodynamic radius as a function of time for micelles in solvents of low polarity.

and subsequent redissolution leads to a significant enlargement of the micelles.

3.4. Stability of Micellar Solutions. In this section, the stability of the micelles is probed by several experiments. The stability in media of low polarity is discussed first, followed by the results for micellar solutions to which a small amount of a polar solvent has been added.

3.4.1. Media of Low Polarity. For the neutralized materials, the stability of micelles in solvents of low polarity is illustrated in Figure 9. This figure shows a plot of the hydrodynamic radii of the micelles as a function of time for representative samples. Note that the hydrodynamic radii plotted are $r_{h,DLS}$ values measured at a fixed concentration, ca. 5 mg/mL. This figure shows that, in solvents such as toluene and CCl_4 , the radii of the micelles are constant over a period of time exceeding several weeks. In particular, a micellar solution of sample PS(440)PMA(18)-Cs in toluene was monitored over a period of 167 days. For this solution, the average $r_{h,DLS}$ and associated standard deviation calculated from all measurements recorded over that time scale were 34.7 ± 0.8 nm (or $\pm 2\%$). The stability of the micelles was excellent not only in stable and hydrophobic solvents like toluene and CCl_4 but also in less stable and hygroscopic solvents like THF and DMF. In THF and DMF, no significant change in hydrodynamic radius was noticed over a period of ca. 10 days. Studies over longer time scales would probably have shown the effect of solvent degradation, particularly in DMF solutions. The latter solvent is known to degrade to formic acid under certain conditions, which could acidify and therefore change the chemical nature and solubility properties of the ionic segments. Note that the acid form of the block copolymer is soluble as single chains in DMF as well as in other solvents having a functional group capable of forming hydrogen bonds.

In the above experiments, not only the radii but also the intensity of the scattered light was reasonably constant with time. Combining these two observations leads to the conclusion that the micelles have constant radii and that the number of micelles remains constant with time.

The same conclusions apply also to micelles made from materials in the acid form in solvents like CCl_4 or toluene.

3.4.2. In the Presence of a Polar Additive. The stability of micelles in solutions to which a polar solvent

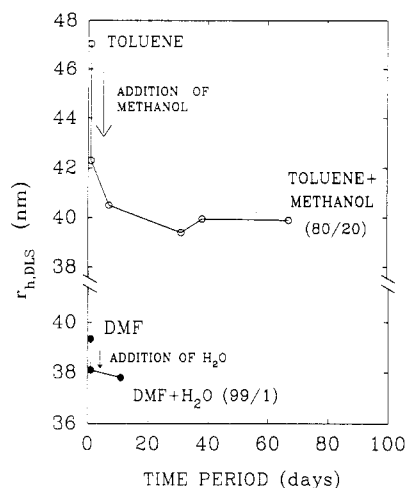


Figure 10. Hydrodynamic radius as a function of time for micellar solutions to which a polar solvent was added.

had been added was also monitored. Figure 10 shows the effect on the $r_{h,DLS}$ of sample PS(440)PMA(40)-Na of adding methanol (20% v/v) to a toluene solution and of adding water (1% v/v) to a DMF solution. This plot shows that upon addition of a polar solvent the hydrodynamic radii are reduced significantly. However, after this initial decrease, the hydrodynamic radii remain reasonably constant over long periods of time. Further experiments would be required to determine whether or not the decrease in the radius of the micelles upon addition of a polar cosolvent is solely due to the decrease of the quality of the solvent toward the polystyrene blocks. As shown earlier when the DLS results in DMF and CCl_4 were compared for the neutralized materials, the aggregation numbers of micelles prepared from the same materials appeared to decrease as the dielectric constant of the solvent increased, i.e., as the affinity of the solvent for the ionic blocks increased. Therefore, the decrease in the radius of the micelles upon addition of a polar cosolvent might be due to a combined effect of the decrease in solvent affinity toward the styrene segments and of a decrease in aggregation number.

In the case of micelles prepared from copolymers in the acid form, the addition of a polar cosolvent like methanol to toluene or CCl_4 solutions leads to the complete disruption of the micelles above a certain proportion of polar solvent.

4. Conclusions

Dynamic light scattering is used in various experiments to confirm and extend the results obtained previously by size-exclusion chromatography on reverse micelles made from block ionomers. For the poly(styrene)-*b*-poly(metal methacrylate) materials, the hydrodynamic radii and aggregation numbers of the reverse micelles in DMF solutions are similar when determined by either SEC or DLS, therefore confirming the earlier SEC determinations.⁶

DLS shows the reverse micelles prepared from the neutralized materials have larger aggregation numbers in CCl_4 compared to those in DMF. This difference is explained as due to the very different affinities of CCl_4 and DMF for the ionic cores. DMF, which has a very much higher dielectric constant than CCl_4 , can plasticize the ionic cores. This plasticization makes possible a rearrangement of the micelles upon dissolution in DMF, which is less likely in CCl_4 . Therefore, the nature of the solvent can play a significant role in the characteristics of the micelles.

While the neutralized materials form reverse micelles in all solvents in which polystyrene is soluble, micellization is observed for the acid materials only in those good solvents for polystyrene which do not contain a functional group able to interact by hydrogen bonding with the carboxylic acid functionalities of the methacrylate blocks.

For the poly(styrene)-*b*-poly(methacrylic acid) copolymers, the hydrodynamic radii determined in CCl_4 increase as the length of both the styrene and the methacrylate blocks increase, a behavior which is similar to that of the neutralized materials. The aggregation numbers increase as the length of the methacrylate segment increases, but seem to be independent of the styrene block length, in contrast to the behavior observed for the neutralized materials.⁶

The hydrodynamic radii and the aggregation numbers of the micelles prepared from the acid or neutralized materials are often very different for identical copolymer block lengths. The differences observed between the two series of materials result from the different methods used to prepare the neutralized and acid forms of the micelles, and possibly from the different chemical natures of the insoluble segments.

Several aspects of the methods of preparation of the micellar solutions are investigated using DLS. The methods of preparation yield reproducible micellar characteristics for both the neutralized and the acid materials. For the neutralized materials, the concentration at the time of neutralization has no effect on the micellar characteristics, while the nature of the solvent in which the neutralization is performed has a significant effect. For both the acid and the neutralized materials, the micelles formed directly in solution are smaller than those prepared after drying of the micellar solution and dissolution, thus showing the strong influence of sample preparation history on final micellar characteristics.

Finally, DLS shows that the reverse micelles made from the neutralized materials are stable for several days in various pure or mixed solvent systems. The micelles made from the acid materials are stable in solvents like CCl_4 or toluene.

Several investigations are in progress to characterize block ionomers further. In solution, reverse micelles are studied by static light scattering, small-angle X-ray scattering, and NMR spectroscopy. The NMR investigation¹⁸ probes the interaction of polar solvents with the ionic cores. The surface properties and the melt rheology of these materials are also under investigation.

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Registry No. DMF, 68-12-2; THF, 109-99-9; MeOH, 67-56-1; CCl₄, 56-23-5; water, 7732-18-5; toluene, 108-88-3; cyclohexane, 110-82-7.