Polystyrene-Poly(methacrylic acid) Block Copolymer Micelles

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ABSTRACT: Block copolymer micelles formed by diblock and triblock copolymers of styrene and methacrylic acid were characterized in solution in a mixed solvent with 80 vol % of dioxane and 20 vol % of water. Methods of static light scattering, quasielastic light scattering, differential refractometry, viscometry, sedimentation velocity, and densitometry were used. No unattached unimer molecules were observed. Three independent methods were employed for obtaining micellar weights. They agreed well with each other. No anomalous behavior was observed by any method. The micellar solutions were shown to contain almost exclusively single micelles; only a few samples (those producing the largest micelles) contained micellar clusters. The micelles behaved hydrodynamically and thermodynamically as impermeable spheres. The structure of the micellar shell was characterized in some detail. Relations between the aggregation number and the hydrodynamic radius of the micelles on the one hand and the sizes of the styrene and methacrylic acid blocks on the other were presented as scaling type phenomenological equations.

Physicochemical properties of self-assembling molecules are of ever increasing experimental and theoretical interest. This is not only due to the intriguing phenomenon of self-assembling but also due to important applications of such materials in coatings, adhesives, thin films, microfabrication of electronic devices, pharmaceutical and photographic technologies, oil recovery, etc. Among the most important self-assembling systems are polymeric micelles. It is well known that block copolymers, when dissolved in selective solvents, i.e., solvents good for one block but poor for the other, assemble into spherical micelles with a dense core formed by the insoluble blocks and a corona consisting of the soluble blocks. These micelles differ from the more familiar detergent micelles by their larger size and greater stability. Until recently, most studies of block copolymer micelles dealt with copolymers composed of two hydrophobic blocks dissolved in an organic solvent, for example, with copolymers of styrene and hydrogenated butadiene in heptane.[1] Copolymers with hydrophobic and hydrophilic blocks may form micelles in aqueous media. These aqueous micellar systems are potentially useful for applications in the fields of pharmacology, ecology, and agriculture. They may take up and release organic materials from water solutions or may be utilized as delivery vehicles for hydrophobic drugs or pesticides, as scavengers of hydrophobic pollutants, etc. Thus, understanding of the properties of micellar solutions is of great importance from both academic and practical points of view. However, the number of suitable amphiphilic copolymers is quite small and micellar studies devoted to them are scarce.

In our laboratory we have prepared a novel class of micelles that are based on block copolymers of styrene and methacrylic acid. In these copolymers the styrene block is hydrophobic while the methacrylic acid block is hydrophilic. They are mutually incompatible and interact with most solvents differently. Consequently, in aqueous media, the copolymers form micelles in which the styrene segments aggregate into a core and the methacrylic acid blocks become a shell or corona. We have perfected the synthesis of these copolymers having narrow molecular weights distributions and predictable sizes of blocks.[2] More than 20 samples of different molecular weight, block number, and composition were synthesized, which provided a good material base for systematically studying the relationship between the physicochemical properties of the micelles and the structure and composition of the copolymers. In the present paper we report the solution properties of these micellar systems and their dependence on the copolymer structure and composition.

Experimental Section

Materials. Styrene-*tert*-butyl methacrylate diblock and *tert*-butyl methacrylate-styrene-*tert*-butyl methacrylate triblock copolymers were synthesized by sequential anionic polymerization. Using aqueous hydrochloric acid in dioxane at 85 °C for about 5 h the *tert*-butyl groups in the side chain of the diblock and triblock copolymers were hydrolyzed off, resulting in corresponding styrene-methacrylic acid diblock copolymers (SA) and methacrylic acid-styrene-methacrylic acid triblock copolymers (ASA). After the hydrolysis, the solution was dried by anhydrous sodium sulfate, filtered, and precipitated into excess cold hexane. The product was redissolved in dioxane and freeze-dried. Gel permeation chromatography, light scattering, and NMR were used to characterize the copolymers. The detailed procedures of the preparation and characterization of the diblock and triblock copolymers were described elsewhere.[2] Molecular properties of SA and ASA block copolymers are listed in Table 1.

Refractive index increments (dn/dc) were measured with a Brice-Phoenix differential refractometer (Model BP-2000-V). For solutions in mixed solvents, the samples were first subjected to dialysis to establish a dialytic equilibrium using a dialyzer described earlier.[3]

Static Light Scattering. The light scattering measurements were performed on a modified Fica 50 photometer equipped with a mercury lamp, a filter, and a polarizer providing vertically polarized incident light at $\lambda = 546$ nm. The scattered light was registered by a laboratory photometer (Pacific Instruments Model 110), and its output was measured by a Hewlett-Packard multimeter (Model 3438A) which was interfaced to a computer. All light scattering experimental data were analyzed using the Zimm method.

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Table 1. Molecular Properties of Block Copolymers

sample	$M_u \times 10^{-3}$ [a]	W_{PS} [b]	M_w/M_n [c]
SA-1	40.3	0.61	1.09
SA-2	60.3	0.41	1.15
SA-4	29.9	0.83	1.06
SA-5	36.3	0.77	1.05
SA-7	129.7	0.74	1.05
SA-8	181.5	0.74	1.06
SA-9	18.7	0.58	1.07
SA-10	46.7	0.65	1.10
SA-12	68.4	0.52	1.09
SA-20	39.1	0.52	1.05
SA-22	68.9	0.59	1.05
ASA-3	68.8	0.65	1.09
ASA-4	83.0	0.67	1.09
ASA-5	41.6	0.79	1.09
ASA-6	58.2	0.57	1.19
ASA-7	51.2	0.75	1.08
ASA-8	68.7	0.56	1.13
ASA-9	31.2	0.72	1.12
ASA-10	37.7	0.60	1.11
ASA-17	44.6	0.57	1.04
ASA-18	70.0	0.55	1.06

[a] Copolymer after hydrolysis and calculated from the weight of PS block (from GPC) and PS content (from NMR). [b] Weight fraction of styrene units. [c] Polydispersity (from GPC).

Quasielastic Light Scattering (QELS). A Brookhaven Instruments Corp. multiangle light scattering goniometer with a He–Ne laser light source was used to measure the intensity fluctuations of the scattered light at 90°. The autocorrelation function of the photocurrent was determined using a Brookhaven Instruments Corp. BI-2030 72-channel, four-bit digital correlator. The experimental data were treated by the cumulant method.[4] For both static and dynamic light scattering measurements, dust-free samples were prepared by filtering through a 0.45-μm filter. The micellar solution concentration was in the range of 10^{-5}–10^{-3} g/mL (depending on the micellar mass).

Intrinsic viscosity was measured by a Ubbelohde type viscometer with a photoelectric registration of flow times. The highest concentrations were about 0.01 g/mL.

Sedimentation Velocity. The sedimentation velocities of micelles were measured at 52 000 rpm using a Beckman Spinco Model E ultracentrifuge with a titanium AN-H rotor, Kel-F cell, and sapphire windows. For a given sample, sedimentation coefficients were measured at several concentrations and then extrapolated toward zero concentration.

Density was measured by an Anton Paar digital precision density meter (Model DMA 02c). The temperature was controlled using a Tronac precision temperature controller (Model 1040) capable of maintaining the temperature constant within 0.001 °C. The density increments and partial specific volumes of the micellar solutions were evaluated using routine calculations.

All experiments were performed at 25 °C.

Results and Discussion

The existence of micelles in solution can usually be detected from its bluish color by the naked eye. Both pure dioxane and water are nonsolvents for styrene and methacrylic acid diblock and triblock copolymers. However, these copolymers very easily dissolve in dioxane and water mixtures rich in dioxane. When water content is under about 5%, the copolymer dissolves molecularly. With more water present, the solution is micellar. For a given copolymer the micellar properties depend on the composition of the solvent. In order to be able to compare micelles made from different copolymers, the same mixture of 80% dioxane and 20% water (by volume) (80D/20W) was used for preparing all micellar solutions. All but two solutions had a clear bluish tint. The two exceptions, SA-7 and SA-8, which had the largest unimer weight and a high polystyrene content, exhibited extremely high turbidity.

Table 2. Light Scattering of Micelles in 80/20 Dioxane/Water

sample	$M_{LS} \times 10^{-6}$	$A_2 \times 10^6$ (mol mL/g^2)	R_g (nm)	N_{ag}	$A_2M/[\eta]$
SA-1	4.7	13.0	11.0	116	3.2
SA-2				70[a]	
SA-4	10.1	3.4	12.9	338	3.7
SA-5	12.5	2.9	16.1	344	2.7
SA-7	121.5	1.6	65.5	936	
SA-8	292.5	3.1	93.7	1612	
SA-9				59[a]	
SA-10	10.4	3.8	15.1	223	2.6
SA-12	11.7	5.0	27.9	171	1.5
SA-20	3.3	10.2	11.6	84	1.4
SA-22	30.5	3.3	39.3	443	3.5
ASA-3	7.8	5.0	17.1	113	2.0
ASA-4	20.1	2.9	47.3	242	2.7
ASA-5	2.9	6.7	7.0	70	1.7
ASA-6	1.9	17.7	7.7	33	1.2
ASA-7	3.3	8.9	10.9	65	2.7
ASA-8	2.9	18.4	11.9	42	1.9
ASA-9				42[a]	
ASA-10	1.0	16.5	5.1	27	1.0
ASA-17	2.2	20.9	12.1	49	1.7
ASA-18	9.8	4.7	33.7	140	1.8

[a] Calculated from M_h.

To obtain correct micellar weights and second virial coefficients from static light scattering measurements, the refractive index increment used in the calculation must be measured at constant chemical potential, $(dn/dc)_\mu$, i.e., after the sample was dialyzed against excess solvent to reach a dialytic equilibrium. For a given mixed solvent, the refractive index increment depends on the composition of the copolymer. Thus, the experimental $(dn/dc)_\mu$ values of micellar solutions of different block copolymers were correlated with their compositions and yielded the following relation, with W_{PS} being the weight fraction of styrene units:

$$(dn/dc)_\mu = 0.067 + 0.112W_{PS} \tag{1}$$

In a separate series of experiments, we measured the refractive increments at constant composition of the solvent mixture $(dn/dc)_m$ and obtained the relation

$$(dn/dc)_m = 0.086 + 0.080W_{PS} \tag{2}$$

From eqs 1 and 2 it is possible to obtain information about preferential adsorption in our micellar system. This calculation is presented in the Appendix. From light scattering measurements, we have obtained values of the micellar weights, the apparent radius of gyration R_g, and the second virial coefficients. They are presented in Table 2. Figure 1 is a typical Zimm plot. Anionically prepared block copolymers, while having quite narrow distributions of molecular weights, exhibit a more heterogeneous chemical composition than the corresponding random copolymers with the same overall composition. However, the chemical heterogeneity of micelles that are made from a considerable number of unimers is much smaller than the heterogeneity of the unimers. (Unimers in any given micelle have a distribution of chemical composition approaching the overall distribution.) Consequently, light scattering yields the true values of weight-average micellar mass, and no correction for sample heterogeneity is needed.[5,6]

Information about the micellar size can also be derived from the quasielastic light scattering measurements. The average translational diffusion coefficient of micelles in solution, D, was measured at an angle of 90° and evaluated

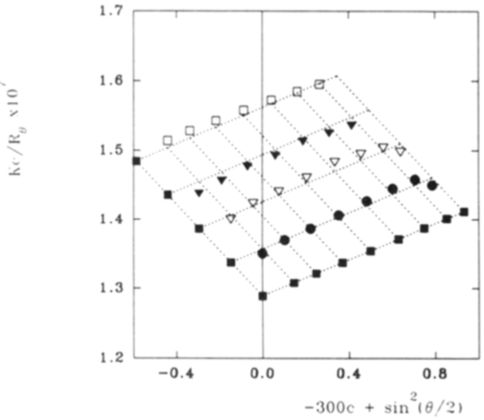

Figure 1. Zimm plot of copolymer ASA-3 micellar solution in 80D/20D at 25 °C: (●) $c = 4.890 \times 10^{-4}$ g/mL; (▼) $c = 9.780 \times 10^{-4}$ g/mL; (▽) $c = 1.467 \times 10^{-3}$ g/mL; (□) $c = 1.956 \times 10^{-3}$ g/mL; (■) $c = 0$ or $\theta = 0$.

Table 3. Micellar Weights from QELS and Intrinsic Viscosity

sample	$D \times 10^8$ (cm^2/s)	R_h (nm)	[η] (mL/g)	$M_h \times 10^{-6}$
SA-1	5.09	24.7	19.1	5.0
SA-2	4.08	30.8	43.7	4.2
SA-4	5.05	24.9	9.4	10.4
SA-5	4.29	29.3	13.6	11.7
SA-7	1.88	67.0		
SA-8	1.44	87.5		
SA-9	9.01	13.9	15.3	1.1
SA-10	4.42	28.5	15.1	9.6
SA-12	3.33	37.7	38.5	8.8
SA-20	5.26	23.9	24.6	3.5
SA-22	2.45	51.4	29.0	29.4
ASA-3	4.72	26.6	19.6	6.1
ASA-4	3.26	38.6	21.6	16.7
ASA-5	7.81	16.1	11.6	2.3
ASA-6	6.17	20.4	28.8	1.9
ASA-7	6.62	19.0	11.0	3.9
ASA-8	5.26	23.9	28.6	3.0
ASA-9	10.10	12.5	9.6	1.3
ASA-10	9.11	13.8	16.5	1.0
ASA-17	6.10	20.6	26.9	2.1
ASA-18	3.61	34.9	25.2	10.6

from the first cumulant. The hydrodynamic radius R_h can then be found using the Stokes–Einstein relation.

$$R_h \equiv kT/(6\pi\eta D) \tag{3}$$

where η is the viscosity of the solvent (1.737 cP for the 80D/20W mixture at 25 °C) and k and T have their usual meanings. No concentration dependence of D was observed within our concentration range. D and R_h values are compiled in Table 3.

As we will show below, the micelles can be modeled by hydrodynamically impermeable spheres. For such spheres, the intrinsic viscosity is related to other properties of the solution as

$$[\eta] = 2.5\phi_h/c \equiv 2.5V_hN_A/M \equiv 2.5(4\pi R_h^{\,3}N_A)/(3M) \tag{4}$$

where ϕ_h is the hydrodynamically active volume fraction of the solute particles in solution, V_h is the hydrodynamically active volume of a single impermeable spherical particle, c is the concentration of the particles (in mass/volume units), N_A is the Avogadro number, and M is the molecular weight of the particle. R_h is the hydrodynamic radius of the particle defined by the last identity in eq 4. For impermeable spheres it is reasonable to equate it with R_h, defined by eq 3. Then, we can combine viscosity and QELS measurements (eqs 3 and 4) and obtain hydrodynamic micellar weights M_h.

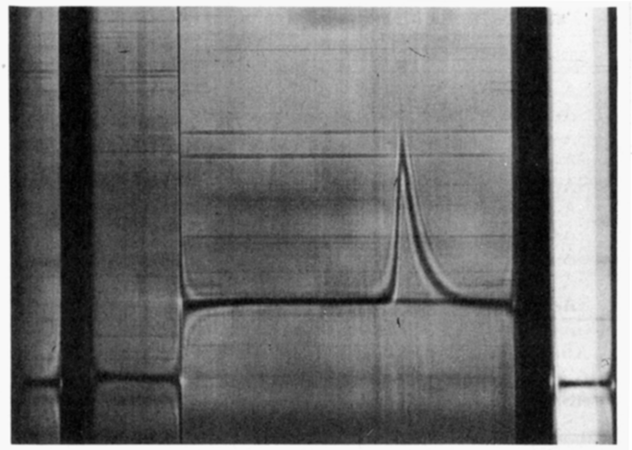

Figure 2. Sedimentation velocity experiment. Diblock copolymer micelle SA-5 in 80D/20W (c = 5 mg/mL, 52 000 rpm, 45 min at full speed).

$$M_h = 10\pi N_A[kT/(6\pi\eta D)]^3/(3[\eta]) \tag{5}$$

Values of M_h and [η] are compiled in Table 3.

The third method used in this study to evaluate the micellar weights is a combination of sedimentation velocity and QELS. In all sedimentation velocity experiments the observed sedimentation profiles were unimodal (Figure 2). No slow unimer boundary was detected for any sample. The shape of the sedimentation boundaries is affected by the diffusion, polydispersity, and concentration of the solute. In our case, the shape of the boundary did not change appreciably with the change of concentration. It is therefore reasonable to conclude (i) that the shape of the peak reflects mainly the sedimentation and diffusion processes and is not unduly influenced by the self-sharpening effect and (ii) that the narrow peaks indicate that the polydispersity of the micelles is moderate at most. The sedimentation coefficients span the range (3.8–20.1) $\times 10^{-13}$ s^{-1}.

The concentration dependence of the sedimentation coefficients can be well described by the standard relation

$$1/s = (1/s_0)(1 + k_sc) \tag{6}$$

where s and s_0 are the sedimentation coefficients at finite and vanishing concentration, respectively, c is the micellar concentration, and k_s is a characteristic coefficient of the concentration dependence. Figure 3 is the plot of the reciprocal sedimentation coefficient versus concentration from which s_0 and k_s were derived. By combining the sedimentation coefficients with the diffusion coefficients D obtained from QELS measurements, the micellar weights M_s were calculated using the Svedberg equation

$$s_0/D = M_s(1 - \bar{v}\rho)/RT \tag{7}$$

where $\bar{v}$ is the partial specific volume of the micelle and ρ is the density of the solvent. The partial specific volumes were calculated from the measured densities of the solvent and the micellar solutions. The results were correlated with the compositional parameter W_{PS}, yielding

$$\bar{v} = 0.94W_{PS} + 0.73(1 - W_{PS}) \tag{8}$$

In the Appendix it is shown that the values of $(1 - \bar{v}\rho)$ are only marginally affected by preferential adsorption in this particular solvent mixture and that relation 8 is quite satisfactory. Values of M_s, s_0, k_s, and $\bar{v}$ are compiled in Table 4.

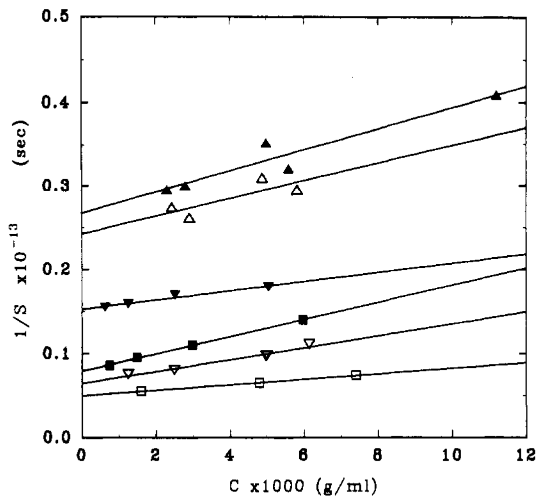

Figure 3. Plot of $1/s$ versus concentration for some micellar solutions: (■) SA-2; (□) SA-5; (△) SA-9; (▽) ASA-3; (▼) ASA-5; (▲) ASA-9.

Table 4. Sedimentation Behavior of Micelles in 80/20 Dioxane/Water Solutions

	$s_0 \times 10^{13}$ (s^{-1})	k_s (mL/g)	$\bar{v}$ (mL/g)	$M_s \times 10^{-6}$
SA-1	12.4	80.0	0.858	5.4
SA-2	12.6	128.0	0.816	4.9
SA-5	20.1	66.1	0.892	15.0
SA-9	4.1	43.8	0.852	0.9
SA-10	15.0	59.6	0.867	8.1
SA-12	16.3	89.4	0.839	9.2
SA-20	10.0	86.5	0.839	3.6
SA-22	30.6	66.4	0.854	26.5
ASA-3	15.4	109.0	0.867	7.8
ASA-5	6.6	35.9	0.896	2.9
ASA-6	6.9	76.2	0.850	2.3
ASA-7	8.1	21.5	0.888	3.7
ASA-8	7.2	69.5	0.848	2.8
ASA-9	3.8	49.2	0.881	1.1
ASA-10	3.7	82.1	0.856	0.9
ASA-17	6.7	41.8	0.850	2.3
ASA-18	13.7	32.9	0.846	7.5

QELS and sedimentation velocity measurements also shed light on the polydispersity of micelles in solution. For all the samples, the decay curves in the QELS experiments had a shape very close to a single-exponential function. The D values estimated from the single-exponential fitting and from the first cumulant fitting were very close to each other; the difference for the majority of the samples was in the range 0.1–1.5%, and in the worst case it was within 2.5%. From the cumulant method the polydispersities, defined as the relative variance of D, were estimated and found to be around 0.05. These observations seemingly implied that all samples have narrow micellar size distributions. However, while the peak profiles of sedimentation velocity experiments were rather narrow for most samples, some samples (SA-12, SA-22, ASA-4, and ASA-18) had discernibly broad peaks. Thus, while the QELS method is not sensitive enough for distinguishing small size differences among particles, sedimentation velocity measurement is an excellent method, offering more direct and perceptible pictures of the polydispersity behavior of the micelles in solutions.

Having established that most our micellar solutions have a narrow distribution of micellar weights, we feel comfortable in comparing the micellar weights obtained by the three methods (each method yielding a possibly different average of molecular weights). Indeed, the three sets of micellar weights are quite close to each other. Especially, the micellar weights calculated from the static light scattering matched those from QELS and viscosity measurements very well. For most of the samples the discrepancy was within 10%. This agreement proved the reliability of the above-measured micellar weights. From the micellar weights and the corresponding unimer molecular weights, the aggregation number N_{ag} can be obtained. In the calculation of N_{ag}, the micellar weights used were those from static light scattering measurements. Values of N_{ag} are listed in Table 2. The aggregation numbers vary from tens to a few hundreds except for samples SA-7 and SA-8. For these two samples, N_{ag} was around 1000; this explains the large turbidity of the micellar solutions. The aggregation numbers of micelles formed from diblock copolymers are usually larger than those formed from triblock copolymers of a comparable size. The copolymers of higher molecular weight and/or higher styrene content also have larger aggregation numbers, as theory predicts.[7,8]

Modeling the Micelles. While the micellar weights are rather large, the intrinsic viscosities of micellar solutions are quite small, indicating that the micelles are considerably compact. Thus, it seems reasonable to model the micelles as concentric spheres with a homogeneous (possibly swollen) spherical polystyrene core surrounded by a hydrodynamically impermeable spherical shell of poly(methacrylic acid). Our experimental values of the second virial coefficient A_2, which drop significantly with increasing micellar weight, provide a strong justification for this model.

According to thermodynamic models based on excluded volume of particles, for hard noninteracting particles, the second virial coefficient A_2 is related with the particle mass M as

$$A_2 = uN_A/(2M^2) \qquad (9)$$

where u is the excluded volume. Thus A_2 is inversely proportional to the square of the particle mass. This is quite close to what we have observed. For impermeable, spherical particles, u is given as[9]

$$u = 8V_h \qquad (10)$$

For such particles, by combining eqs 4, 9, and 10, the relation between particle weight M, the second virial coefficient A_2, and intrinsic viscosity $[\eta]$ can be expressed as

$$MA_2/[\eta] = 1.6 \qquad (11)$$

The values of $MA_2/[\eta]$ were calculated and are included in Table 2. These values vary from 1.0 to 3.7. While this represents a rather strong justification for the model of impermeable spherical particle, it also points out that the total neglect of contact interactions between micelles is not quite appropriate.

Polydispersity of the Micelles. On the basis of the shape of the sedimentation velocity boundary profiles, we assume that for most samples the solution contains mainly individual micelles, while for several samples micellar clusters are also present. Another useful indication of significant presence of micellar clusters is the comparison of the experimental apparent radius of gyration with its value estimated from the concentric sphere model. Similar information may be obtained from the experimental R_g/R_h ratio.

The theory of light scattering[10,11] leads to the following expression for the apparent radius of gyration $R_{g,cal}$ of particles composed of two materials having different

Table 5. Theoretical and Experimental Values of Radius of Gyration and Its Ratio to R_h

	experimental			dry core			swollen core		
	R_h (nm)	R_g (nm)	R_g/R_h	R_c (nm)	$R_{g,cal}$ (nm)	$R_{g,cal}/R_h$	R_c (nm)	$R_{g,cal}$ (nm)	$R_{g,cal}/R_h$
SA-1	24.7	11.0	0.45	10.44	11.32	0.46	13.15	12.78	0.52
SA-4	24.9	12.9	0.52	14.92	12.46	0.50	18.80	15.23	0.61
SA-5	29.3	16.1	0.55	15.63	13.79	0.47	19.69	16.53	0.56
SA-7	67.0	65.5	0.98	32.91	30.31	0.45	41.46	35.84	0.53
SA-8	87.5	93.7	1.07	44.10	40.29	0.46	55.57	47.75	0.55
SA-10	28.5	15.1	0.53	13.89	13.64	0.48	17.50	15.81	0.55
SA-12	37.7	27.9	0.74	13.41	17.55	0.47	16.90	19.06	0.51
SA-20	23.9	11.6	0.49	8.79	11.24	0.47	11.08	12.26	0.51
SA-22	51.4	39.3	0.76	19.25	22.78	0.44	24.25	25.24	0.49
ASA-3	26.6	17.1	0.64	12.62	12.54	0.47	15.90	14.48	0.54
ASA-4	38.6	47.3	1.23	17.48	17.47	0.45	22.02	20.15	0.52
ASA-5	16.1	7.0	0.43	9.68	8.23	0.51	12.20	10.00	0.62
ASA-6	20.4	7.7	0.38	7.54	9.17	0.45	9.50	10.10	0.50
ASA-7	19.0	10.9	0.57	9.94	8.92	0.47	12.52	10.63	0.56
ASA-8	23.9	11.9	0.50	8.63	10.76	0.45	10.88	11.80	0.49
ASA-10	13.8	5.1	0.37	6.22	6.57	0.48	7.83	7.46	0.54
ASA-17	20.6	12.1	0.59	7.92	9.39	0.46	9.98	10.40	0.50
ASA-18	34.9	33.7	0.97	12.88	15.98	0.46	16.23	17.53	0.50

refractive increments

$$R^2_{g,cal} = R^2_{g,A} W_A (dn/dc)_A/(dn/dc) + R^2_{g,B} W_B (dn/dc)_B/(dn/dc) + \Delta^2 (dn/dc)_A (dn/dc)_B W_A W_B/(dn/dc)^2 \quad (12)$$

Here $R_{g,A}$ and $R_{g,B}$ are the radii of gyration of the materials A and B, W_A and W_B are their mass fractions, $(dn/dc)_A$ and $(dn/dc)_B$ are their refractive increments, (dn/dc) is the refractive increment for the composite particles and Δ is the distance between the centers of mass of the two materials. Obviously, the overall refractive increment can be expressed as

$$dn/dc = W_A (dn/dc)_A + W_B (dn/dc)_B \quad (13)$$

For concentric spheres Δ is zero. Then, for our micelles $R^2_{g,cal}$ reads

$$R^2_{g,cal} = [R^2_{g,PS} W_{PS} (dn/dc)_{PS} + R^2_{g,MA} (1 - W_{PS})(dn/dc)_{MA}]/(dn/dc) \quad (14)$$

where the subscripts PS and MA refer to the polystyrene and the poly(methacrylic acid), respectively.

Assuming that the density of polystyrene segments in the core is homogeneous (a good assumption), that the methacrylic segments are homogeneously distributed in the shell (an acceptable assumption for particles behaving as impermeable spheres and having as low an intrinsic viscosity as our micelles), and that the outer diameter of the shell is equal to the hydrodynamic radius of the micelle R_h, we can write

$$R_c = [3MW_{PS}\bar{v}_{PS}/4\pi N_A \phi_{PS}]^{1/3} \quad (15)$$

$$R^2_{g,PS} = (3/5)R_c^{\,2} \quad (16)$$

$$R^2_{g,MA} = (3/5)(R_h^{\,5} - R_c^{\,5})/(R_h^{\,3} - R_c^{\,3}) \quad (17)$$

Equation 15 relates the core radius R_c with the micellar mass M, the weight fraction of polystyrene in the unimer W_{PS}, the specific volume of polystyrene $\bar{v}_{PS}$, and the volume fraction of the polymer within the core ϕ_{PS}. We have performed the calculations for two extreme assumptions about the core swelling: (1) The cores are not swollen at all ($\phi_{PS} = 1$). (2) The swelling is extensive ($\phi_{PS} = 0.5$). It is shown in the Appendix that the latter assumption may be quite realistic. For both assumptions we have calculated the R_c and $R_{g,cal}$ values and presented them together with the experimental value of R_g and R_h in Table 5. While the R_c values for the swollen model are 26% larger than those for the unswollen model, the difference between the $R_{g,cal}$ values is less. For most of our samples, the agreement between the experimental and calculated values is very good, some R_g values being closer to the swollen-core model and others to the dry-core model. However, for several samples, the experimental values are 2 times (or even more) larger than the calculated ones. These are samples SA-7, SA-8, SA-12, SA-22, ASA-4, and ASA-18. For the same samples, sedimentation velocity experiments indicated significant polydispersity.

A more direct indication of the same phenomenon is obtained from the experimental ratio R_g/R_h. For homogeneous spheres, the theoretical value of this ratio is 0.775. However, for the model of concentric spheres with the refractive increments appropriate for our blocks, the ratio is between 0.45 and 0.50 (depending on W_{PS}) for the dry-core model and between 0.50 and 0.60 for the swollen-core model. These low values are due to the fact that the more strongly scattering polystyrene is segregated in the small micellar core. The experimental value of R_g/R_h is quite close to this range for most of our samples with the exception of our culprits, samples SA-7, SA-8, SA-12, SA-22, ASA-4, and ASA-18, for which the ratio is in the range 0.74–1.23. We explain these values by the presence of micellar clusters. We have estimated the R_g/R_h ratio for a dumbbell formed by two micelles touching each other to be about 0.90. Other small clusters yielded similar values. (Longer linear clusters led to much larger values.) The experimental R_g values are z averages. Thus, they are strongly influenced by the presence of clusters, and the R_g/R_h value may approach that of the cluster even if the dominant species in the solution are still individual micelles. Consequently, the ratio R_g/R_h provides a very sensitive indication of micellar agglutination.

Structure of Micelles. Having established that the micelles in solutions of samples SA-7, SA-8, SA-12, SA-22, ASA-4, and ASA-18 are partially agglutinated, we will exclude these samples from further consideration. We will now evaluate for the remaining samples the overall volume fraction of the polymer in the micelle ϕ_{pol}, its fraction in the shell ϕ_{shell}, the average coiling ratio of the shell chains C_r, and the area of the surface of the core per tethered chain A_c. The evaluation will be done for both the dry-core model ($\phi_{PS} = 1$) and the swollen-core model ($\phi_{PS} = 0.5$). The fractions ϕ_{pol} and ϕ_{shell} were obtained from the following relations;

$$\phi_{pol} = 3M\bar{v}/4\pi N_A R_h^{\,3} \quad (18)$$

$$\phi_{shell} = 3M(1 - W_{PS})\bar{v}_{MA}/4\pi N_A (R_h^{\,3} - R_c^{\,3}) \quad (19)$$

where $\bar{v}$ is the specific volume of the copolymer from Table 4, the specific volume of poly(methacrylic acid) $\bar{v}_{MA}$ = 0.73 mL/g (from eq 8), and R_c has been obtained from eq 15.

We are defining the coiling ratio C_r as a ratio $(R_h - R_c)/L_s$ between the thickness of the micellar shell $(R_h - R_c)$ and the length of fully stretched poly(methacrylic acid) blocks L_s. The latter quantity is calculated from the mass of the block and the bond lengths and bond angles of the backbone. Finally, the area A_c is given as

$$A_c = 4\pi R_c^{\,2}/nN_{ag} \quad (20)$$

where $n = 1$ for diblock copolymers and $n = 2$ for triblock ones. The relevant data are assembled in Table 6.

It is remarkable that for either model the values of ϕ_{shell}, C_r, and A_c for all samples fall in a relatively narrow range. Possibly, an approximately constant optimum value of one of these values may be an important factor among

Table 6. Structural Parameters of Micelles

			dry core			swollen core		
	$\phi_{\text{pol}} \times 10^2$	L_s	$\phi_{\text{shell}} \times 10^2$	C_r	A_c (nm^2)	$\phi_{\text{shell}} \times 10^2$	C_r	A_c (nm^2)
SA-1	10.6	32.69	3.8	0.44	11.77	4.1	0.35	18.69
SA-4	23.4	10.57	4.1	0.94	8.31	5.6	0.58	13.19
SA-5	17.5	17.37	3.9	0.79	8.94	4.7	0.55	14.19
SA-10	15.4	34.00	5.1	0.43	10.92	5.9	0.32	17.34
SA-20	8.0	39.04	3.5	0.39	11.55	3.7	0.33	18.34
ASA-3	14.2	25.04	4.7	0.56	8.85	5.3	0.43	14.05
ASA-5	24.6	9.09	5.4	0.71	8.48	7.5	0.43	13.46
ASA-6	7.5	26.03	2.9	0.49	10.99	3.1	0.42	17.44
ASA-7	16.9	13.31	4.0	0.68	9.66	4.9	0.49	15.33
ASA-8	7.1	31.44	2.8	0.49	11.13	3.0	0.41	17.67
ASA-10	13.0	15.68	4.9	0.48	9.09	5.4	0.38	14.43
ASA-17	8.4	19.94	3.3	0.64	8.02	3.5	0.53	12.73

those controlling the aggregation number and, through it, the structure of the micelles. We plan to study this topic in more detail.

Relation between Micellar and Unimer Properties. Since we have measured a relatively large number of copolymer samples, we may try to correlate the aggregation number and the hydrodynamic size of the micelle with the size of both copolymer blocks. Again, we have eliminated from our regression analysis the misbehaving samples SA-7, SA-8, SA-12, SA-22, ASA-4, and ASA-18. The remaining samples yielded the following relations (standard deviations are given in parentheses).

Diblock micellar solution:

$$N_{\text{ag}} = 0.40 N_{\text{PS}}^{1.89} N_{\text{MA}}^{-0.86} \quad (13\%) \qquad (21)$$

$$R_{\text{h}} = 0.347 N_{\text{PS}}^{0.71} N_{\text{MA}}^{0.09}\ \text{nm} \quad (6\%) \qquad (22)$$

Triblock micellar solutions:

$$N_{\text{ag}} = 0.041 N_{\text{PS}}^{1.62} N_{\text{MA}}^{-0.41} \quad (29\%) \qquad (23)$$

$$R_{\text{h}} = 0.162 N_{\text{PS}}^{0.56} N_{\text{MA}}^{0.30}\ \text{nm} \quad (9\%) \qquad (24)$$

While the correlations expressed by eqs 21–24 are quite acceptable, it should be kept in mind that the ranges of values of the polymerization degrees of polystyrene and poly(methacrylic acid), N_{PS} and N_{MA}, respectively, were not broad enough for a satisfactory statistical analysis. Nevertheless, the basic results are clear: (1) The aggregation numbers of diblock copolymers are much larger than those of triblock copolymers of comparable unimer mass and composition. (2) Aggregation numbers increase steeply with the length of the core forming block but decrease with the length of the shell-forming block. (3) The effect of the length of the shell-forming block on the hydrodynamic radius is only moderate due to the compensation of two factors—decrease of the aggregation number but increase of the shell depth with the increasing length of the shell-forming block.

Our scaling exponents for N_{PS} in eqs 21 and 23 are larger than those predicted theoretically by Halperin and Alexander.[12] They are also larger than the experimental values reported by Nagarajan and Ganesh[7] for poly(ethylene oxide)/poly(propylene oxide) micelles. Of course, the discrepancies could be ascribed to an inadequate theoretical treatment, to differences in the experimental systems, to experimental errors, or most probably, to a combination of all of these.

Conclusions

1. The methods of static light scattering, quasielastic light scattering, viscometry, and sedimentation velocity can successfully be used for characterization of styrene/methacrylic acid block copolymer micelles in mixed solvent systems.
2. Unattached unimer molecules were not detected. Thus, the critical micelle concentration is below the detection limit of our experimental methods (sedimentation velocity and static light scattering).
3. Sedimentation velocity is the choice method for detecting the polydispersity of micellar solutions. Combined measurements of R_{g} and R_{h} may provide the same information. The QELS method is not sensitive enough for this purpose.
4. The polydispersity of micellar solutions depended mainly on the micellar size: solutions with smaller micelles were rather monodisperse while large micelles had a tendency to form clusters.
5. The micelles in the 80D/20W solvent behave thermodynamically and hydrodynamically as impermeable spheres.
6. The micellar cores are quite swollen in the 80D/20W solvent.
7. Detailed information was found about the structure of the micellar shell.
8. Tentative scaling relations for the aggregation number and hydrodynamic radius were obtained.

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Appendix

Preferential Adsorption on Micelles. When macromolecules or similar entities are dissolved in a mixture of two solvents, one solvent is frequently found in the vicinity of the macromolecule in excess over its concentration in the liquid far away from the macromolecule. This phenomenon is called preferential adsorption.[13,14] It is usually described by a derivative $(\partial w_2/\partial w_3)_\mu$ that expresses the mass of component 2 of the solvent mixture that must be added to the solution together with the unit mass of the polymer (subscript 3) while not disturbing the chemical potentials μ_1 and μ_2 of the solvent components. This derivative is related to the experimentally accessible parameter λ, which is defined as

$$\lambda \equiv -v_2 \phi_1 (\partial w_2/\partial w_3)_\mu \qquad (\text{A1})$$

where v_2 is the partial specific volume of solvent 2 and ϕ_1 is the volume fraction of solvent 1. Experimentally, λ is obtained from the difference of the refractive increments of the polymer measured at constant chemical potential $(\partial n/\partial c_3)_\mu$ and constant solvent composition $(\partial n/\partial c_3)_{\text{m}}$

$$\lambda = [(\partial n/\partial c_3)_\mu - (\partial n/\partial c_3)_{\text{m}}]/(\text{d}n/\text{d}\phi_1) \qquad (\text{A2})$$

where $(\text{d}n/\text{d}\phi_1)$ is the derivative of the refractive index of the solvent mixture with respect to its composition.

Alternately, λ may be obtained from analogous measurements of density ρ

$$\lambda = [(\partial \rho/\partial c_3)_\mu - (\partial \rho/\partial c_3)_{\text{m}}]/(\text{d}\rho/\text{d}\phi_1) \qquad (\text{A3})$$

Note that $(\partial \rho/\partial c_3)_{\text{m}}$ is equal to $(1 - \bar{v}_3 \rho)$. However, this quantity is not the one that should be substituted into the Svedberg equation, eq 7. When mixed solvents are used, $(\partial \rho/\partial c_3)_\mu$ should be used.

In solutions of copolymers, all relevant increments are dependent on the composition of the copolymer. For micellar solutions, in which the two types of polymer chains are spatially segregated, it is reasonable to assume (as we did in eqs 1 and 2) that the increments are linear functions of the composition of the copolymer.

The amount of preferential adsorption depends on the composition of the solvent mixture, but in the present case we are interested only in data related to the 80D/20W solvent. Designating dioxane as component 1, water as component 2, and micelles as component 3, utilizing the experimental value for this 80D/20W mixture ($dn/d\phi_1 = 0.075$), and substituting eqs 1 and 2 into eq A2, we obtain

$$\lambda = -0.25 + 0.43 W_{PS} \qquad \text{(A4)}$$

Thus, parameter λ changes sign at about $W_{PS} = 0.60$. That is what we expect intuitively: copolymers rich in polystyrene adsorb preferentially dioxane while copolymers rich in methacrylic acid adsorb preferentially water. Extrapolating equation A4 to both pure homopolymers and applying appropriate stoichiometry, we find that each styrene unit adsorbs about 1 molecule of dioxane and each methacrylic acid unit adsorbs 1.5 molecules of water. While it must be kept in mind that this estimate is subject to a substantial experimental error and that, in any case, it has been established only for the 80D/20W solvent mixture, it is noteworthy that our preliminary results on the swelling of bulk polystyrene in the 80D/20W solvent quantitatively agree with the 1:1 molar ratio of styrene and dioxane.

We can utilize the above results also for estimating the error committed by using in the Svedberg equation the density increments measured at constant composition instead of constant chemical potential. Two phenomena tend to minimize the error. (1) Water/dioxane mixtures have large negative excess volumes of mixing. The mixture with 65% dioxane exhibits maximum density. Consequently, for any solution in this mixture $(\partial\rho/\partial c_3)_\mu = (\partial\rho/\rho c_3)_m$ because $d\rho/d\phi_1 = 0$. For solvent mixtures close to this composition (e.g., 80D/20W) the differences between these increments will be small. (2) In our 80D/20W mixture, copolymers with $W_{PS} = 0.60$ have vanishing preferential sorption and this sorption remains small for all our copolymer samples.

These expectations are borne out by the quantitative analysis. Combination of eqs A2 and A3 yields

$$(\partial\rho/\partial c_3)_\mu = (\partial\rho/\partial c_3)_m + [(\partial n/\partial c_3)_\mu - (\partial n/\partial c_3)_m][(d\rho/d\phi_1)/(dn/d\phi_1)] \qquad \text{(A5)}$$

Substituting eqs 1, 2, and 8 into this relation together with $\rho = 1.034$ g/mL and $d\rho/d\phi_1 = -0.035$ g/mL, we obtain

$$(\partial\rho/\partial c_3)_\mu = [0.245 - 0.217 W_{PS}] + [0.009 - 0.015 W_{PS}] \qquad \text{(A6)}$$

where the first term is based on the values measured at constant composition and the second term represents the correction for preferential sorption. Substitution of W_{PS} values for our copolymer samples shows that the maximum correction is about 3%; it is much less for most samples. Such a correction is comparable to experimental errors and may be safely neglected.

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