Fluorescence Studies of Naphthalene-Labeled Diblock and Triblock Copolymer Micelles in Organic Media

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ABSTRACT: A-B diblock copolymers of polystyrene-*block*-poly(methyl methacrylate) were prepared by anionic polymerization and labeled with one naphthalene either at the polystyrene block end or at the polystyrene/methyl methacrylate block boundary. B-A-B triblock copolymers of poly(*tert*-butyl methacrylate)-*block*-polystyrene-*block*-poly(*tert*-butyl methacrylate) were prepared by anionic polymerization and labeled with two naphthalenes in the middle of the polystyrene block. Quasi-elastic light scattering was used to study the transition from unimers to micelles as a function of volume percentage of the solvent system 1,4-dioxane/methanol and the steady-state and time-resolved fluorescence and fluorescence depolarization properties were investigated under the same conditions. Changes in all the fluorescence properties seem to be primarily a function of the collapse of the micelle cores. For end-tagged copolymers, the probe most likely resides in the micellar core and the fluorescence properties change dramatically upon the formation of micelles but change little thereafter. As the center-labeled copolymers undergo the transition from unimers to micelles with increasingly compact cores, the changes in fluorescence properties are more continuous than those observed for the end-tagged copolymers.

Introduction

Historically, block copolymer micelles have been studied by employing traditional techniques resulting in a fundamental understanding of many micellar properties.[1] We have recently focused on the application of steady-state and time-dependent fluorescence and fluorescence depolarization to investigate micelle formation, structure, and behavior.[2-4] These more recent techniques (in particular, the time-dependent measurements with nanosecond and picosecond resolution) have proven to be valuable for the investigation of micellar properties at the molecular level.[5-7]

Micelles are formed spontaneously when block copolymers are dissolved in a selective solvent mixture of a thermodynamically good solvent for the block that forms the shell while simultaneously a thermodynamically bad solvent for the block that forms the core. The micellization of block copolymers is a reversible equilibrium process between micelles that are nearly monodisperse in mass and size and nonmicellized polymers called unimers. This equilibrium is a closed association process[8] and is described by $nU \leftrightarrow M$ where n is the association number and U and M represent unimer and micelle, respectively. The association number is the average number of copolymer molecules that form a single micelle and is dependent upon copolymer composition, system temperature, and solvent selectivity.

In our previous paper,[2] fluorescence measurements provided some insight into probe mobility and environment for diblock copolymer micelles in aqueous solution. As part of our continuing effort to understand the behavior of micelles, this paper reports the use of steady-state and time-resolved fluorescence and time-resolved fluorescence depolarization, along with quasi-elastic light scattering, to investigate the behavior of micelles composed of polystyrene-*block*-poly(methyl methacrylate) and poly(*tert*-butyl methacrylate)-*block*-polystyrene-*block*-poly(*tert*-butyl methacrylate). The diblock copolymer samples are strategically labeled with an average of one naphthalene at the styrene end, N-S-MM, or one naphthalene at the block boundary, S-N-MM. The triblock copolymer has on average two naphthalenes attached in the middle of the polystyrene block, BM-S-N2-S-BM. The variety of naphthalene labeling makes these copolymers interesting candidates for comparison in good solvents and selective precipitants where micellization occurs.

Experimental Section

Copolymers. The diblock copolymers were prepared by anionic polymerization in tetrahydrofuran at -78 °C using cumylpotassium as an initiator. Dried and purified styrene was added to the initiator solution resulting in the preparation of living polystyrene blocks. A small amount of polystyryl anion solution was removed and the reaction in this solution was terminated by the addition of degassed methanol. The resultant polystyrene was used in the determination of the molar mass and the distribution of molar masses of the polystyrene block. A single 1,1-diphenylethylene molecule (DPE) was attached to the polystyryl anion to modify its reactivity and *tert*-butyl methacrylate at -78 °C was slowly added to form the second block, which was then terminated by degassed methanol. The copolymer was filtered, precipitated in a water-methanol mixture, dried, and further characterized. The initiator for the triblock copolymer was prepared by reacting naphthalene with potassium metal to form a potassium-naphthalene complex in THF solution. The triblock copolymers were prepared by starting with a short chain of either two or four styrene moieties and adding 2-vinylnaphthalene to the reactive ends. Polystyrene is then polymerized and DPE is added before the poly(*tert*-butyl methacrylate) block. These procedures are described in more detail elsewhere.[9]

Polystyrene-*block*-poly(*tert*-butyl methacrylate) was labeled with an average of one 2-vinylnaphthalene moiety either at the beginning of the polymerization for labeling at the polystyrene end or before the addition of DPE for labeling at the block boundary. Poly(*tert*-butyl methacrylate)-*block*-polystyrene-*block*-poly(*tert*-butyl methacrylate) was labeled with two 2-vinylnaphthalene moieties in the middle of the polystyrene chain. In all cases the naphthalene group distribution is expected to obey a Poisson distribution.[10]

The poly(*tert*-butyl methacrylate) block was hydrolyzed for 5 h at 85 °C in mixture of 6 N aqueous HCl and 1,4-dioxane. The number of moles of HCl was typically about two times greater than that of the resulting methacrylic acid units. The excess water was removed by drying with anhydrous Na_2SO_4. The resultant poly(methacrylic acid) block copolymer was filtered

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Table I
Characterization Data for Diblock and Triblock Copolymers

copolymer[a]	$10^{-3}M_W$[b]	$10^{-3}M_{WS}$[b]	M_n/M_W[b]	mol % S[c]
N-S-MM	100.6	38.8	1.07	46.0
S-MM1	94.0	35.4	1.09	47.0
S-N-MM	54.4	22.8	1.15	48.0
S-MM2	50.4	24.4	1.09	57.0
BM-S-N2-S-BM	61.9	32.8	1.08	60.0
BM-S-BM	61.5	33.0	1.19	52.0

[a] S-MM1, S-MM2, and BM-S-BM are the unlabeled copolymers used in preparing mixed micelles (see text). [b] M_W and M_n refer to the parent *tert*-butyl polymer and M_{WS} refers to the molecular weight of polystyrene block, all measured by SEC. [c] Molar percent of polystyrene measured by NMR.

and precipitated in cold hexane then redissolved in 1,4-dioxane with subsequent freeze-drying of the solution. The degree of hydrolysis was estimated by NMR in a deuterated 1,4-dioxane/methanol mixture with tetramethylsiloxane as a reference standard. The hydrolyzed copolymer was esterified with diazomethane to prepare the poly(methyl methacrylate) block.

The molar mass and molar mass distribution of the copolymers were determined by size-exclusion chromatography, SEC, in THF. The value of the molar mass, M_W, obtained from SEC was compared to M_W obtained from static light scattering. The lengths of both blocks were determined by SEC from a comparison of M_W of the polystyrene block with that of the final copolymer. The relative content of styrene and methacrylate was obtained from NMR. The molecular characteristics of the samples are given in Table I.

Micelle Preparation. The method of micelle preparation is critical if aggregation is to be avoided. For N-S-MM and S-N-MM, the desired amount of methanol was added at once to a solution of unimer in 1,4-dioxane to make the appropriate micelle solutions. Solutions of BM-S-N2-S-BM unimers were prepared by adding the required weight of copolymer to a 80/20 vol % mixture of 1,4-dioxane/methanol. To form solutions of micelles, methanol was added at once to a solution of unimers in 1,4-dioxane/methanol. Slow addition of the methanol can lead to turbidity and/or precipitation. Once formed, the micelles in this study are stable for many weeks.

Solvents. Spectral grade 1,4-dioxane and methanol were used as purchased (Aldrich).

Fluorescence Spectroscopy. Steady-state fluorescence spectra were recorded on a SPEX Fluorolog fluorimeter system described elsewhere[11] and a Photon Technology International LS-100 luminescence spectrophotometer described as follows. The light source is a 5-kW peak power pulsed Xe lamp. Both the excitation and emission monochromator have 1200 lines/mm, 4 nm/mm dispersion, 0.5 nm/step minimum resolution, and a wavelength range of 200–1000 nm. The grating is blazed at 300 nm for the excitation monochromator and 500 nm for the emission monochromator. The detector is a R928 PMT with a wavelength range of 200–930 nm. Emission spectra for naphthalene-tagged polymers were collected with an excitation wavelength of 293 nm and span the range 310–510 nm.

Lifetime measurements were performed by the method of time-correlated single photon counting as described elsewhere.[2] Monomer emission was collected at 340 nm, and excimer emission was collected at 410 nm. The multichannel buffer has 8192 channels and the time resolution is ca. 27 ps per channel for lifetime measurements and ca. 6.7 ps per channel for depolarization measurements. Fluorescence was detected through a Glan-Thompson polarizer located between the sample and monochromator. Lifetime measurements were made with the polarizer at the magic angle (54.7°) to ensure the proper ratio of parallel-to-perpendicular intensity was observed, while the polarizer was rotated between horizontal and vertical for depolarization measurements. Other experimental details and mathematical treatment of lifetime data have been described in previous publications.[2,3]

The time-resolved anisotropy, $r(t)$, was computed by performing a channel-by-channel calculation using the fluorescence decays collected at vertical and horizontal polarizations from

$$r(t) = \frac{I_V(t) - GI_H(t)}{I_V(t) + 2GI_H(t)} \quad (1)$$

where $I_V(t)$ and $I_H(t)$ are the fluorescence decays collected at vertical and horizontal polarization respectively and G is the instrumental anisotropy. The G-factor corrects for the polarization dependence of the monochromator.[12] $r(t)$ was computed from I_V and I_H in three ways that are described in more detail in the Results section. In general, the depolarization data were fit by using a multiexponential function described by

$$r(t) = (r_0 - r_\infty)\sum A_{r_i} \exp(-t/\tau_{r_i}) + r_\infty \quad (2)$$

where τ_{r_i} are the effective rotational correlation times of the distinguishable depolarization modes, A_{r_i} are the preexponential factors, r_0 is the initial anisotropy, and r_∞ is the residual anisotropy.

Static and Quasi-elastic Light Scattering (QELS). The weight-average molar masses of copolymers were measured by a Sofica 42000 system as described elsewhere.[13] The apparent hydrodynamic diameter, D_H, of both micelles and unimers was measured with a Brookhaven BI 2030 system with a 72-channel correlator. The association number for the micelles in this study is in the range 50–250, depending on the solvent selectivity and copolymer concentration. The scattering angle was 90° and the temperature was 25 °C. A He–Ne laser operating at 632.8 nm was used as a light source. The mathematical treatment of data is described elsewhere.[2,3]

NMR. NMR measurements were performed on a General Electric Q E 300 (300 MHz) spectrometer.[2] The nonhydrolyzed polymers were dissolved in $CDCl_3$ and the hydrolyzed polymers were dissolved in mixtures of deuterated 1,4-dioxane/methanol.

Results and Discussion

Characterization of Polymer Solutions by QELS. As noted above, aggregation was always a potential problem when making micelles with the polymers in this study. Before any photophysical measurements were performed, QELS was used to ensure that each solution was monodisperse in either unimers or micelles. The sensitivity of QELS to the presence of particles larger than unimers in solution makes it relatively easy to determine whether unimers, micelles, or aggregates are present for a given solvent composition.[2] The dispersity of sizes for each sample solution is a critical factor in the determination of the presence of micelles or aggregates (micelles are monodisperse and aggregates typically are not). We prepared unimer or micelle solutions that had polydispersities on the order of 0.02–0.09.[14] From the QELS data, it is clear that we could determine whether or not a given solution contained unimers, micelles, aggregates, or some combination of the above and the data presented here are always derived from monodisperse solutions of unimers or micelles.

Values of the hydrodynamic diameter, D_H, corresponding to unimers are found in a good solvent. As soon as micelles are present in a solution, even as low as ca. 10–20 wt %, the calculated D_H corresponds approximately to that of micelles. Figure 1 shows values of D_H as a function of the volume percent of methanol for S-N-MM. Mixtures with less than 45 vol % methanol are good solvents for both blocks of S-N-MM and the sample dissolves molecularly. The values of D_H are approximately constant and correspond to that of unimers. A sudden increase with increasing content of methanol is observed in the region of 45–55 vol % methanol, corresponding to the onset of micellization (the solution still contains a high percentage of unimers;[2] see later discussion of excimer lifetime measurements). In the region of 55 vol % methanol and above, the values of D_H increase slightly with methanol.

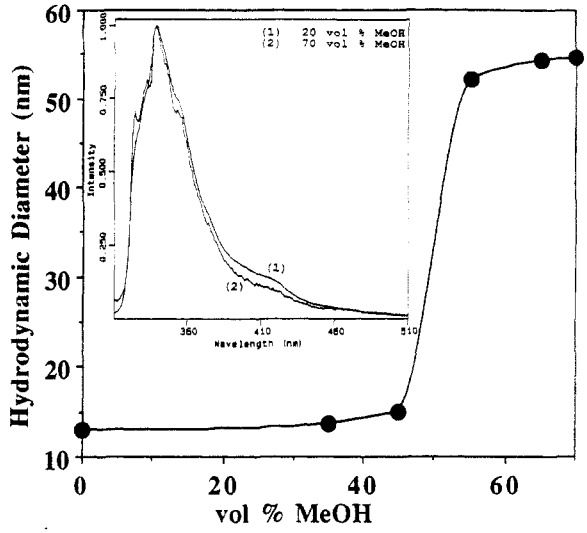

Figure 1. Apparent hydrodynamic diameter, D_H, for S–N–MM in 1,4-dioxane/methanol mixtures as a function of volume percentage of methanol. Inset: Steady-state fluorescence spectra for S–N–MM in 1,4-dioxane with 20 and 70 vol % methanol (curves 1 and 2, respectively). The concentration of copolymer in all solutions was in the range 2–3 mg/mL.

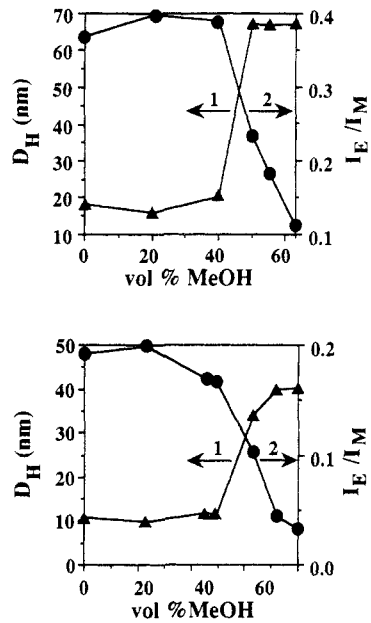

Figure 2. Hydrodynamic diameter, D_H (curve 1), and excimer-to-monomer fluorescence intensity, I_{410}/I_{340} (curve 2), for N–S–MM (top) and BM–S–N2–S–BM (bottom) as functions of volume percent of methanol. The concentration of copolymer in all solutions was in the range 2–4 mg/mL.

This is most likely an indication of the start of precipitation. If more than 70 vol % methanol is added, precipitation occurs and is clearly visible by eye.

The QELS data for BM–S–N2–S–BM and N–S–MM exhibit the same overall trends as those previously described for S–N–MM (see Figure 2, curve 1). There are slight differences in the onset of micellization and more significant differences in D_H (also see Table II). However, these variations are consistent with the differences in M_W and molar percent of the styrene block for these polymers (compare Tables I and II).

Using the various techniques described in the Experimental Section for micelle preparation, we attempted to define more precisely the point at which micellization begins. However, for all three polymers in this study it was impossible to form micelles without aggregation in a range that roughly corresponds to 40–50 vol % methanol,

Table II
Micelle Properties

copolymer	vol % MeOH	D_H	r_∞
N-S-MM	0	18.3	0
	20	15.9	0
	40	20.1	0
	50[a]	67.2	0.068
	55	67.0	0.068
	63	67.2	0.068
S-N-MM	0	12.9	0
	20		0
	35	13.7	0
	45	15.0	0
	50[a]	52.0	
	55		0.022
	65	54.2	0.089
	70	54.5	0.104
BM-S-N2-S-BM	0	10.8	0
	20	9.8	0
	40	11.7	0.01
	43	11.6	
	55[a]	34.1	0.063
	63	40.0	0.14
	70	40.1	0.14

[a] Initial solvent composition at which micelles form.

depending on the polymer. For these solvent compositions, the QELS measurements indicated that the samples were highly polydisperse and contained a component with a very large hydrodynamic diameter. The samples appeared slightly milky, which is typical of large aggregates, while concurrently having the bluish tint typical of monodisperse micelles. Presumedly this is an example of "anomalous micellization".[15] Thus none of our measurements were made in the region between "primarily unimers" and "primarily micelles".

Steady-State Fluorescence. In a previous publication,[2] we discussed how the head-to-tail oligomerization of several 2-vinylnaphthalene monomers at the end of the polystyrene block results in the possibility of a coplanar "sandwich" arrangement of neighbor-pendant naphthalene groups. These groups are the proper distance from each other for excimer formation and if there is sufficient rotational freedom of pendant fluorophores and mobility of polymer chains, efficient excimer formation is achieved.[16] In the present study, there is on average one naphthalene per chain (see later discussion on depolarization of mixed micelles) except in the case of BM–S–N2–S–BM where there are two per chain. Because the naphthalene group distribution follows a Poisson distribution,[10] some chains have multiple naphthalenes that can form excimers and there was measurable excimer formation for all samples studied. For S–N–MM, there is a statistically significant number of chains that may not have multiple naphthalenes since there are on average less than one naphthalene per chain. This is illustrated in Figure 1 (inset) for S–N–MM in two solvent mixtures. This polymer has the weakest excimer fluorescence and the exhibits the least sensitivity of steady-state fluorescence spectra to solvent changes. A plot of I_{410}/I_{340} (not shown) follows the same trend as that of N–S–MM (see later discussion) except that the value of this ratio for S–N–MM is smaller for each solvent composition. On the basis of the time-dependent fluorescence it seems likely that excimers in this system are formed almost exclusively from contact pairs.

Figure 3 shows the steady-state spectra for N–S–MM. The steady-state emission spectrum in 1,4-dioxane is composed of both the monomer emission close to 340 nm and a broad excimer peak with a maximum at ca. 390 nm. A considerably less intense excimer peak is observed for BM–S–N2–S–BM (spectrum not shown), suggesting that

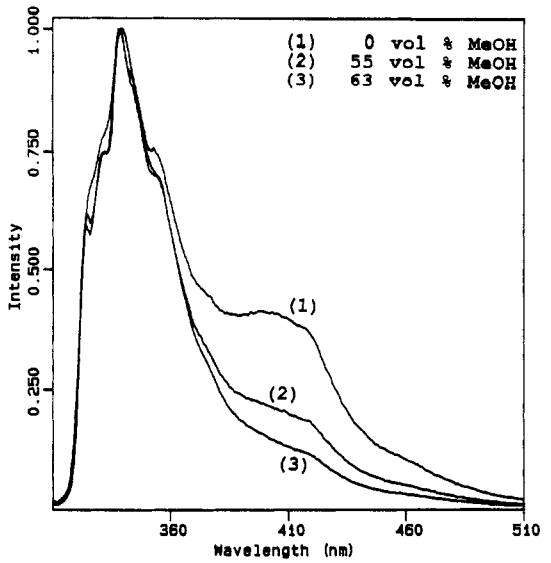

Figure 3. Steady-state fluorescence spectra for N-S-MM in 1,4-dioxane with 0, 55, and 63 vol % methanol (curves 1, 2, and 3, respectively). Excitation at 293 nm.

there are fewer multiple naphthalenes in the middle of the chain and/or that those capable of forming diffusional excimers experience a more restricted environment than naphthalene at the end of a chain, even when in a good solvent. We cannot discount the possibility that the naphthalenes separated by the central styryl groups may form excimers. The time-dependent data discussed later imply the existence of this mechanism. In all cases, comparison of I_E/I_M is complicated by the fact that the statistical distribution of naphthalene pairs may be slightly different for the different polymers.

Figure 2 (curve 2) demonstrates the similarities and differences in the ratio of excimer-to-monomer intensity, I_E/I_M, for N-S-MM and BM-S-N2-S-BM, respectively. For the case of BM-S-N2-S-BM, I_E/I_M decreases before micelles are present and then more abruptly after micelles form, while N-S-MM shows no change until micelles form. This difference may reflect the affect of different locations for the probes and indicates that a partial collapse of the coil may precede micelle formation for BM-S-N2-S-BM. (Depolarization data support this assertion; see later.) At the highest percentage of methanol, there is some excimer emission from contact pairs (see later discussion) for both BM-S-N2-S-BM and N-S-MM, with $I_E/I_M = 0.025$ and 0.11, respectively. For N-S-MM, the lack of change in excimer formation before the sudden decrease in I_E/I_M in the 40–45 vol % methanol region may be the result of having naphthalene at the end of the polymer chain where it is more difficult to restrict probe motions until they are located in the micelle core. Apparently for N-S-MM above 50 vol % methanol, most fluorophores are trapped in micelle cores. As more methanol is added the micelle cores become even more compact and the excimer intensity further decreases. This drop continues for higher additions of methanol even though the values of D_H (also see Table II) remain constant for these same additions. At high percentages of methanol, there is no diffusional excimer formation due to low mobility in a compact micelle core (see later time-dependent results). A small fraction of fluorophores does form excimers from "contact pairs" for which no significant segmental rotation is required to produce the necessary cofacial geometry.

Time-Resolved Fluorescence. We have previously shown that the quenching of monomer fluorescence by excimer formation is a good means for investigating

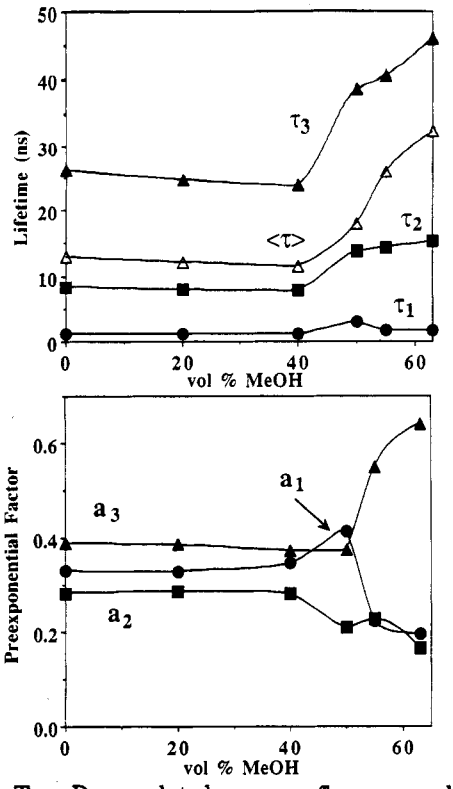

Figure 4. Top: Deconvoluted monomer fluorescence lifetimes, τ_1, τ_2, τ_3, and $\langle\tau\rangle$. Bottom: Preexponential factors, A_1, A_2, and A_3. Both for N-S-MM as a function of volume percent of methanol. Excitation at 293 nm; emission at 340 nm.

polymer chain dynamics.[2,3] We noted that this may be illustrated by plotting the lifetime components, τ_i, and the corresponding preexponential factors, A_i, as a function of solvent composition. While this presentation of the data illustrates nicely the onset of micelle formation, it is impossible to ascribe a precise physical meaning to the individual lifetime components except for the longest one, which corresponds to the behavior of unquenched probes. For all these polymer and solvent combinations there is always a very fast lifetime component observed (τ_1, ca. 1 ns), which is quite common for polymer systems containing pendant fluorophores covalently bound to a polymer chain.[17] For S-N-MM, only small changes in the lifetimes and preexponential factors are observed (decay curves not shown). This is a result of very weak excimer emission concurrent with minimal monomer quenching. This is not the case for the other two polymers. The lifetimes and corresponding preexponential factors for N-S-MM as functions of solvent composition are plotted in Figure 4 along with the average lifetime $\langle\tau\rangle$.[18] (Similar data for BM-S-N2-S-BM are not shown.) The increase in the lifetime components, primarily $\tau_{2,3}$ in the region 40–50 vol % methanol, as well as the change in the corresponding coefficients, $A_{2,3}$, illustrate the changes in the fluorescence decays that accompany micelle formation for this sample. $\tau_{2,3}$ change between 40 and 50 vol % methanol while $A_{2,3}$ change most dramatically above 50 vol %. Changes in $\langle\tau\rangle$ illustrate how sensitive fluorescence decays are to changes in probe environment, particularly with respect to monomer quenching, and follow the same trends as were observed from QELS.

Figure 5 (top) shows several typical monomer decay curves for N-S-MM in a good solvent (curves 1, 2), with 50 vol % methanol (curve 3) and with 55 and 63 vol % methanol (curves 4, 5, respectively) where micelles with compact cores are present. The decay observed in good solvents is typical of monomer fluorescence quenched by

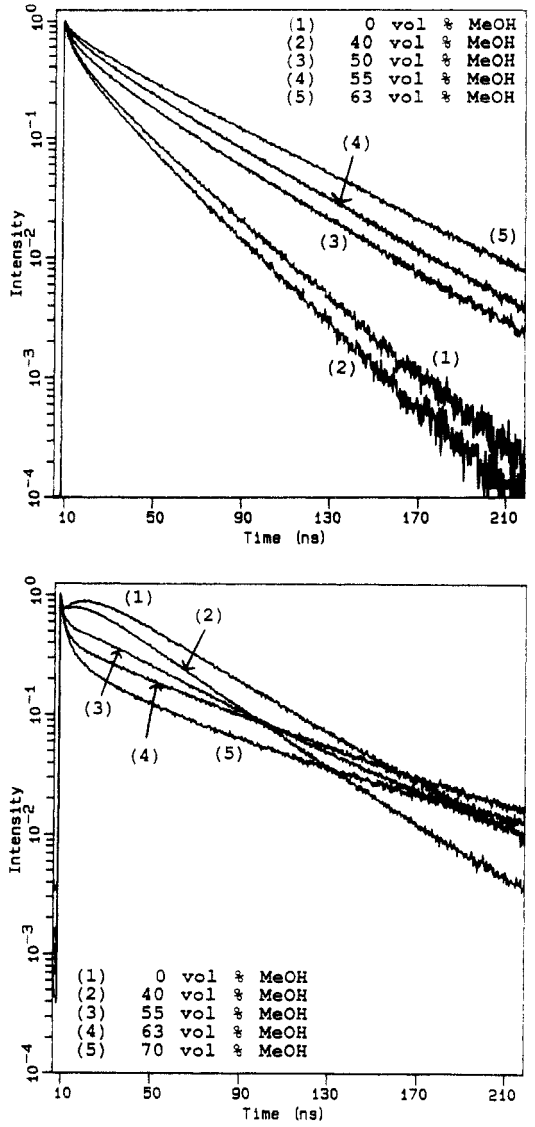

Figure 5. Top: Time-resolved monomer fluorescence decays for N-S-MM at 0, 40, 50, 55, and 63 vol % methanol (curves 1, 2, 3, 4, and 5, respectively). Excitation at 293 nm; emission at 340 nm. Bottom: Time-resolved excimer fluorescence decays for BM-S-N2-S-BM at 0, 40, 55, 63, and 70 vol % methanol (curves 1, 2, 3, 4, and 5, respectively). Excitation at 293 nm; emission at 410 nm.

excimer formation, although it cannot be uniquely ascribed to this mechanism. Excimer formation is controlled by the rotational diffusion of pendant naphthalene groups and the dynamics of the polymer backbone. Increasing the amount of methanol when only unimers are present shortens the lifetime, which seems to be a general effect for naphthalenic systems when the overall polarity of the medium is increased. Once micelles form, there is far less quenching and the average lifetime increases significantly. Presumably this is the result of the fluorophores being trapped in nonpolar micelle cores with extremely high microviscosity. BM-S-N2-S-BM exhibits similar behavior, except there is a smaller short-lifetime component in the decay (decay curves not shown).

When comparing the decay curves for the time-dependent excimer fluorescence at 410 nm for these polymers in a good solvent with those in selective solvents, obvious differences are evident. (In this comparison we determined that there is no significant monomer/excimer spectral overlap at this wavelength.) In a good solvent (unimers only), the excimer decay curve for BM-S-N2-S-BM shows an obvious buildup along with a very fast component (Figure 5 (bottom), curves 1 and 2). When only micelles with compact cores are present, the decay is multiexponential with a rapid initial decay (curves 4 and 5). The absence of a buildup implies that excimers that form are present as "contact pairs" for which no significant segmental rotation is required to produce the necessary cofacial geometry. Curves 1 and 2 appear to represent a combination of these two cases. Since these curves represent unimers in good solvents, this behavior is most likely a result of more than one type of excimer formation mechanism. The rapidly decaying component has the same lifetime (ca. 100 ps) and same preexponential factor (ca. 0.5) for the case of a good solvent where the buildup is present and in a selective precipitant where no excimers are formed from probe motions. We are unsure of the origin of this component. We speculate that certain naphthalenic orientations lead to a rapidly quenched species that emits in this region, while others lead to the normal cofacial naphthalene excimer. This implies that even in a good solvent there are contact pairs for which no significant segmental rotation is necessary to produce the required cofacial geometry. This rapidly decaying component was observed to some degree for *all* our polymers. The relatively large importance of a diffusional mechanism for BM-S-N2-S-BM when compared to N-S-MM (decay curves not shown) suggests that excimer formation can occur from naphthalenes separated by the central styryl units. As was discussed above, the steady-state excimer emission from BM-S-N2-S-BM is less intense than that from N-S-MM, which probably reflects the different mechanisms of excimer formation for these two polymers.

Time-Resolved Fluorescence Depolarization for Mixed Micelles. The final fluorescence technique used in this study is time-resolved fluorescence depolarization. This type of measurement is sensitive to probe motions and provides additional data concerning the formation of micelles while yielding insight into the local probe environment.[19] Because fluorescence depolarization measurements focus on the motion of individual naphthalene groups and not on pairs (as is the case for excimer measurements), the problem of comparing chains with less than two naphthalenes in close proximity to those with two or more is eliminated and a better comparison of changes in probe mobility for all three polymers can be made. From depolarization measurements, changes in residual anisotropy, r_∞, rotational correlation times, τ_{r_i}, and corresponding preexponential factors, A_{r_i}, may be obtained from fitting the anisotropy decays and have the potential to provide more detailed information concerning probe motions.

Our previous investigation of micelles in aqueous media[3] focused in part on mixed micelles with 20 wt % labeled polymer and 80 wt % unlabeled polymer in order to eliminate energy migration effects. The three samples we are investigating here also have the potential to exhibit depolarization due to energy migration. Mixed micelles were formed from N-S-MM/S-MM1, S-N-MM/S-MM2, and BM-S-N2-S-BM/BM-S-BM. The data for each polymer is given in Table I. We prepared the mixed micelles by dissolving the solid samples in the required mass ratios of tagged and untagged polymers in a 80/20 vol % 1,4-dioxane/methanol mixture and adding the methanol as in the standard preparation. We observed that only in the case of S-N-MM was there a measurable difference in the residual anisotropy. The residual anisotropy for the pure micelle at 63% methanol is 0.03 lower than that for the mixed micelle at the same solvent composition. This difference is small and implies that

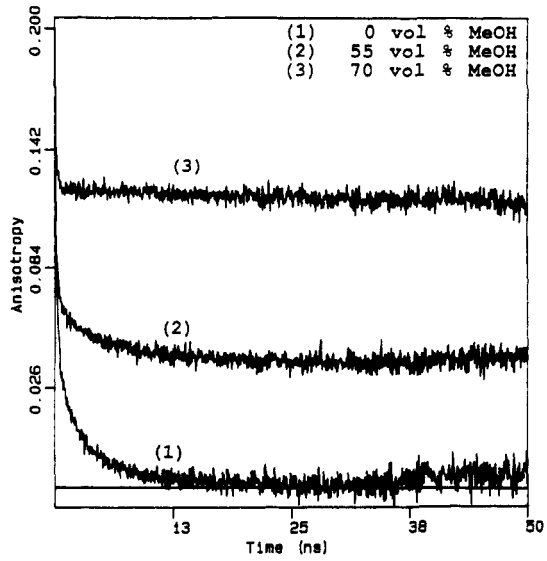

Figure 6. Anisotropy decays for BM-S-N2-S-BM in 1,4-dioxane with 0, 55, and 70 vol % methanol (curves 1, 2, and 3, respectively). Excitation at 293 nm; emission at 340 nm.

energy migration has no significant effect on the interpretation of our results. Since our signal-to-noise ratio is higher for the pure micelles, we report those data in detail.

Time-Resolved Fluorescence Depolarization for Pure Labeled Micelles. In this study, we focus on changes in r_∞ that are unaffected by any uncertainty associated with finding r_0 (see eq 2). However, a few points should be made concerning the estimation of r_0. For naphthalene in 1,4-dioxane at 77 K for which the motions of naphthalene essentially cease, r_0 was ca. 0.34, which is lower than the theoretical value of 0.4 for parallel absorption and emission transition dipole moments. As we have previously discussed,[3] this discrepancy may be a consequence of the complicated photophysics of naphthalene derivatives. In the present case, the accuracy of r_0 is limited by the experimental setup and the difficulties involved in making measurements of this type. Laser instability during measurements (typically 2 h for one anisotropy curve) together with the wavelength dependence of the microchannel plate[12] result in a small uncertainty in the determination of time zero. For very fast anisotropy decays, even small shifts in the beginning of the decay corresponding to the width of one channel (ca 6.7 ps) may cause considerable errors in the estimation of r_0.

Representative anisotropy decays for BM-S-N2-S-BM are shown in Figure 6. The increase in r_∞ with each addition of methanol is clearly visible. Also noteworthy is the change in the decays over the initial 10 ns. As methanol is added and r_∞ increases, the initial rate of decay becomes more rapid. An examination of τ_{r_i} and A_{r_i} (see eq 2) provides no additional information without pressing the limits of our system and data analysis. We generally observe a very fast partial depolarization occurring in ca. 50 ps, which increases in dominance (according to its corresponding preexponential factor), while a longer τ_{r_i} of ca. 3 ns remains unchanged as its preexponential factor decreases. For the largest volume fraction of methanol, only the τ_{r_i} of ca. 50 ps remains. An examination of the anisotropy decays for both N-S-MM and S-N-MM shows similar trends.

Figure 7 shows a plot of r_∞ as a function of added methanol for all three polymers (also see Table II). r_∞ for N-S-MM (curve 1) is constant and equal to ca. zero before micellization (up to 60/40 vol % 1,4-dioxane/methanol).

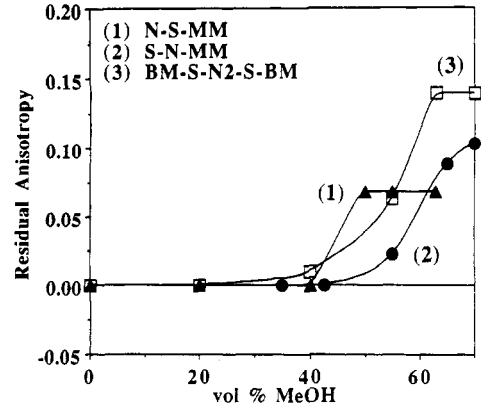

Figure 7. Residual anisotropy as functions of volume percent of methanol for N-S-MM (curve 1), S-N-MM (curve 2), and BM-S-N2-S-BM (curve 3).

This is expected since the probe is located at the end of the polystyrene block and retains all of its mobility until micelles form. As the solvent composition changes from good to poor with the addition of the precipitant, no change in probe mobility is observed preceding micellization. Once micelles form and the naphthalene is located in the core, it appears that there is some minimum amount of free volume associated with naphthalene such that a continuing increase in r_∞ is not observed, even though the excimer study suggests that the core continues to become more compact. We speculate that the ability of two bulky groups to form excimers by the static mechanism may be influenced by the 1,4-dioxane content of the core, while the depolarization is unaffected. In other words, the 1,4-dioxane content of the core has a different effect on the equilibrium distribution of pairs of naphthalenes and naphthalene mobility. The r_∞ data for S-N-MM (curve 2) indicate that there is no restriction of motion before micellization occurs. Once micelles form, there is a small initial increase in r_∞. Since the naphthalene is presumably located in the core/shell region, this small increase in r_∞ may reflect a more fluid environment in this region at a low volume of selective precipitant. At higher volume percent of methanol, the value of r_∞ is greater than that for N-S-MM, which may be a consequence of "stretching" the methacrylate chain ends. How changes in the shell affect naphthalene located in the core/shell region is the subject of a new pH study using the methacrylic acid analogue of this polymer (S-N-MA) and will be the subject of a future publication.

The fluorescence polarization of BM-S-N2-S-BM exhibits unique solvent dependence (curve 3). From 20 vol % methanol until micelles form, there is an increase in r_∞, indicating there is significant coil collapse, similar to the I_{410}/I_{340} behavior (see Figure 2, curve 2, bottom). Once micelles initially form, r_∞ is nearly the same as that for N-S-MM and as the core becomes more compact the value of r_∞ continues to rise. The high value (compared to the other polymers) of r_∞ at 70 vol % may again be the result of changes in the methacrylate shell, such as "stretching" of the chain ends.

It was originally hoped that fitting the anisotropy decays using eq 2 would yield more detailed information concerning probe environment, but this was not the case. The fitting of these data was performed three ways: (1) the fluorescence decays collected at vertical and horizontal polarizations were used to directly compute $r(t)$, (2) the decays were deconvoluted by using three exponentials with variable lifetimes and preexponential factors as usual, and these data were used to compute $r(t)$, and (3) the decays were deconvoluted by fitting up to 35 fixed exponentials

and these deconvoluted data were used to compute $r(t)$.[12] While the last method is generally agreed to be superior for this type of work, there are problems with it and the other two methods. In all cases, the time shift between the instrument response function and sample decay leads to a significant uncertainty in the short rotational correlation times, τ_{r_1}. We consistently found a fast τ_{r_1} of 10–60 ps, where the variance of 10–60 ps represents the different methods of computing and fitting $r(t)$. A lifetime component in this range was seen for every sample we measured under every condition and may be explained in the following manner. Our current system setup does not allow excitation at 320 nm where the weak 0–0 band of the S_o–S_1 absorption of naphthalene is located. Our excitation at 293 nm produces the S_2 excited state and a partial internal depolarization of the emission takes place during the rapid vibrational relaxation to the vibrational states of S_1. This same partial depolarization was observed for anthracene under similar circumstances.[5] However, the values for the longer components $\tau_{r_{2,3}}$ and $A_{r_{2,3}}$ are the nearly same when comparing the results obtained from the different methods of computation outlined previously. These components did not vary with solvent composition in any way that further elucidates micellar properties and we do not discuss these results.

Summary

The data from steady-state and time-resolved fluorescence and fluorescence depolarization measurements are consistent with a model for N–S–MM where naphthalene resides in the micelle core. This is evidenced by the very limited changes observed in the fluorescence properties once micelles form. For BM–S–N2–S–BM and S–N–MM the data show that naphthalene probes experience a much broader range of changing fluorescence properties with addition of methanol. For S–N–MM it is likely that naphthalene resides in an outer core or core/shell region (i.e., a more fluid environment) since the naphthalene motions are restricted in a less severe manner when micelles first form and then in a more gradual manner with the continued addition of precipitant. Data for BM–S–N2–S–BM indicate significant coil collapse before micelles form. Once micelles are present, the residual anisotropy continues to increase to a relatively high value. Results from mixed micelles indicate that there is very little naphthalene-to-naphthalene energy migration for any of the polymers. The behavior of $r(t)$ and r_∞ demonstrates that for all cases the rotational mobility of the naphthalene probe is greatly inhibited in the micelle core. This is consistent with the diminution of excimer fluorescence under these same conditions. While there are differences observed for probes located at different positions on the polymer chains, in general the data demonstrate a severe loss of mobility of pendant groups and of chain segments on all parts of the polymer chain that are expected to form the micelle core.

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(18) This quantity is defined by $\langle \tau \rangle = \sum_{i=1}^{3} a_i \tau_i$.

(19) The motion of pendant groups cannot be treated separately since, in the relatively dense cores, probe motion is strongly influenced by the motion of chain segments.