Exchange of Chains between Micelles of Labeled Polystyrene-*block*-poly(oxyethylene) As Monitored by Nonradiative Singlet Energy Transfer

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ABSTRACT: The dynamics of the exchange of chains between micelles formed by diblock copolymers in dilute solution in a selective solvent has been studied using fluorescence measurements. The samples are polystyrene-*block*-poly(oxyethylene) with a single fluorescent label (either naphthalene or pyrene) covalently attached at the junction between the blocks. The critical micelle concentration (cmc) of each sample can be determined from the concentration dependence of the integrated emission intensity, provided the cmc is high enough to permit detection. In order to study the kinetics, micelles of the two differently labeled samples were first prepared at the same concentration, solvent, and temperature, but in two different containers. The contents of the containers were then mixed, and the efficiency of nonradiative singlet energy transfer from naphthalene to pyrene was measured as a function of time. The time dependence of the intensity of the emission from naphthalene can be fitted to a sum of two exponentials, with time constants that differ by at least an order of magnitude. Activation energies are somewhat smaller for the faster process than for the slower process, but in both cases they are on the order of 10^2 kJ mol^{-1} under the conditions where they can be measured. We have not been able to account for this result with a kinetic scheme that assumes the exchange of chains between the micelles takes place exclusively via the population of free chains. This difficulty suggests that an additional mechanism for the exchange of chains may be active.

Introduction

There is a vast literature on the micellization of block copolymers in liquids that are good solvents for one block but poor solvents for the other block.[1−11] Many techniques, such as light scattering, viscosity, and electron microscopy, have been applied to these systems. Fluorescence spectroscopy has also been shown to be very versatile. It can be used for many purposes, including the investigation of the dissolution of small hydrophobic molecules in the core of the micelle,[6,12] detection of the critical micelle concentration (cmc),[5,13] and investigation of the mobility of the micellar core.[14,15] Here we employ two fluorescence probes, naphthalene and pyrene, that are covalently attached to the junction between the blocks in polystyrene−*block*-poly(oxyethylene) (PS−PEO). PS−PEO has been shown to form spherical micelles in water,[4] which is a strong nonsolvent for the polystyrene block. This copolymer also forms micelles in methanol. Most of our study employs a mixed solvent composed of methanol and water.

One purpose of this work is to determine the cmc of the block copolymers using fluorescence. Another purpose is the examination of the dynamics of the exchange of chains between the micelles in dilute solution. Similar dynamical relaxation of micelles formed by common surfactants of low molecular weight has been under extensive investigation.[16] For small surfactants, the dynamics of this process is on the time scale of millisecond or submillisecond, and the chemical relaxation method is commonly employed for its study. The system is subjected to a sudden external change, which induces a perturbation from the original state of equilibrium. The relaxation to the new equilibrium is then monitored by an appropriate method. However, the connection between the apparent relaxation time measured in the experiment and the microscopic rate constant of the unimer−micelle equilibrium was the subject of controversy.[17,18] The detailed analysis of the kinetics by Aniansson and Wall[19] assisted in the resolution of the controversy.

Unlike surfactants of low molecular weight, the dynamic equilibrium between unimers and micelles formed by diblock copolymers is rather slow. Tuzar *et al.*[1] and Price *et al.*[20] reported that the diblock copolymers can have lifetimes in a micelle that are on the order of hours or longer. Recently, Tian *et al.*[21] used sedimentation velocity to investigate the dynamics of the exchange of chains between micelles prepared from diblock copolymers of different sizes, thereby providing a qualitative description of the dynamics.

Halperin and Alexander[22] have given a theoretical description of the relaxation dynamics of polymeric micelles using the chemical relaxation method, such as a temperature jump. By considering the activation energy for several postulated relaxation mechanisms, they concluded that only the mechanism proposed by Aniansson and Wall should be dominant. However, the chemical relaxation method is of marginal use in the study of the dynamic equilibrium of polymeric micelles[23] because a large perturbation of the system is required to produce a change that is detectable with the usual monitoring techniques. In contrast, the theoretical analysis of Halperin and Alexander, or the Aniansson−Wall theory, assumes a small perturbation from the original equilibrium.

One of the methods that can be easily used to monitor the dynamics of the exchange of chains between micelles employs two probes that constitute a Förster pair.[24] One probe is chemically bonded to each diblock copolymer, preferably at the junction between the blocks. In one sample the probe is the Förster donor (D), and in another sample it is the Förster acceptor (A). Separate

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solutions are prepared and equilibrated using each of the labeled samples, thereby producing systems where every micelle contains either D or A, but no micelle contains both D and A. When the two solutions are mixed, the exchange of chains produces a population of micelles that contain both labels, accompanied by an easily measurable increase in the efficiency of nonradiative singlet energy transfer from D to A. This method has been employed by us previously.[25] Procházka *et al.*[26] have reported a similar study. The method provides a convenient way to monitor the exchange of chains,[25,26] and in the long time limit it can also be used to study the equilibrium properties of the system.[13] However, the interpretation of the easily measurable change in the intensity of the fluorescence in terms of the microscopic rate constant of single-chain insertion/expulsion from the micelle is complicated, due to the mechanism of the exchange process itself and also due to the nature of nonradiative singlet energy transfer within a micelle that contains both D and A.

In our previous study[25] and also in the work of Procházka *et al.*,[26] the relaxation is analyzed by empirically fitting the signal with a single exponential decay or with the sum of two exponential decays. We retain this empirical fitting in the present study. However, we also consider further the photophysical process of the nonradiative energy transfer that provides the basis for the measurement. From a few illustrative calculations, we attempt to show how the empirical rate constant obtained from fitting the raw data may be related to the single-chain expulsion rate from the micelle. Also from this analysis, we conclude that the formation of mixed micelles of two differently labeled copolymers in our experiments may be influenced by another process in addition to the transfer of a single chain from one micelle to another.

Experimental Details

Materials. Styrene, benzene, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), 2-(1-phenylethenyl)naphthalene (**1**), and 1-phenyl-1-(1-pyrenyl)ethylene (**2**) were carefully purified as described previously.[27–29] Potassium amyloxide (1.7 M in toluene) (Callery Chemical Co., Pittsburgh) was used as received. Methanol, of HPLC grade, was purchased from Fisher. Water was distilled and deionized (Milli-Q grade).

Polymerization. *sec*-Butyllithium-initiated polymerizations of styrene were carried out in benzene (10–12 vol % styrene) at room temperature in all-glass reactors using breakseals and standard high-vacuum techniques.[30] Fluorescent labeling of poly(styryl)lithium with **1** or **2** was achieved as described previously.[29] The resulting diarylalkyllithium was functionalized with excess ethylene oxide in benzene overnight. Dimethyl sulfoxide (0.5–1/1 vol/vol, DMSO/benzene) and potassium amyloxide (0.14–0.46 equiv relative to lithium) were added to the polymeric lithium alkoxide solution to promote ethylene oxide polymerization which was effected at 30–50 °C for 7–9 days. After termination with 0.1 N methanolic HCl and addition of water, the copolymer was isolated by extraction with chloroform. The chloroform layer was washed with saturated aqueous NaCl and dried over anhydrous $MgSO_4$. After removal of the chloroform, a THF solution of the copolymer was precipitated from solution by addition of petroleum ether.

The synthesis of the diblock copolymer, PS–PEO, with one chromophore covalently attached at the junction point has been reported elsewhere.[29] The characteristics of the samples used in these experiments are presented in Table 1. The two chromophores, naphthalene and pyrene, form a pair for Förster energy transfer, with a Förster radius (R_0) of 2.8 nm.[31] The slight differences in the molecular weights of corresponding blocks in the two samples are not important, as will be shown later.

Table 1. Characterization of the Samples[a]

sample	M_n(PS)	M_n(PEO)	M_n(PS–PEO)	M_w/M_n	label
5-P-19	4.4×10^3	19×10^3	25×10^3	1.14	pyrene
5-N-19	5.5×10^3	22×10^3	28×10^3	1.12	naphthalene

[a] M_n (in 10^3 g mol^{-1}) was determined by SEC for the PS block and by NMR for the PEO block. M_w/M_n was determined by SEC, using calibration with polystyrene standards.

Solutions. The samples are not easily dissolved in water, but they dissolve almost instantly in methanol at ambient temperature at a concentration of 0.6 g L^{-1}. As the amount of water increases in mixed solvents of methanol and water, dissolution requires more time. For the highest concentration of water used here (75:25 methanol:water by volume), the solutions were prepared by gentle heating (at 40 °C) for no longer than 5 h.

Fluorescence. The steady-state fluorescence spectroscopy was performed on an SLM 8000C fluorometer. Right-angle geometry was used in all of the measurements. The excitation was at 290 nm for the kinetic measurements, with slits of 4 mm for excitation and emission. The same conditions were used for the measurements of the intensity of the emission from the naphthalene-labeled samples as a function of concentration of the copolymer. For the pyrene-labeled sample, the excitation was at 350 nm, using an emission slit of 1 mm.

In the kinetic measurements, the two labeled samples, both at the same concentration, are equilibrated separately at the temperature that will be used for the measurement. Then appropriate amounts of the two samples are mixed in the optical cell and placed in the temperature-controlled sample chamber in the fluorometer. The ratio of the labels in the mixed sample is denoted by α, defined as 1:α = naphthalene:pyrene. The temperature control in the equilibration of the separate solutions and in the fluorometer is ±1 °C.

Dynamic Light Scattering. Dynamic light scattering measurements were made with an argon ion laser (Model 95 from Lexel Laser Inc.), operated at 514 nm (vertically polarized) in a light-control mode to adjust the power. The goniometer used was purchased from Brookhaven Instruments (BI-200SM), equipped with a BI-2030AT digital correlator for the photon correlation spectroscopy measurements. The scattered light was collected without any polarizer. The sample cell (12 mm o.d. cylindrical cell) was immersed in the refractive index matching liquid (filtered decalin), insulated by a brass thermostat, and the temperature was controlled within ±0.1 °C. The sample preparation methods are the same as for the fluorescence measurements, except the solvent was prefiltered using a Gelman Science membrane filter (0.2 μm pore size). The sample solutions were filtered again through the same filter before they were transferred to the cell. The measurements were carried out at three different angles: 60, 90, and 125°. The data were analyzed using cumulants, double exponential, and CONTIN methods.

Results and Discussion

Formation of Micelles. The size of the micelle in a selective solvent is mainly controlled by the size of the insoluble block, if the core of the micelle is not swollen by solvent. Since both of the components of our solvents, methanol and water, are poor solvents for polystyrene, we anticipate negligible swelling of the core of the micelle in these systems. Under this condition, a very rough approximation of Leibler's theory,[32] in which we assume the size of the micelle is controlled completely by the penalty due to the deformation of the insoluble block, provides a rough estimate of about 46 as the preferred number of chains in a micelle. We have used a characteristic ratio of 10 for the polystyrene block[33,34] and a density of 1.07 g cm^{-3}. The radius of the core of the micelle is 4.5 nm in this simple model. When other energetic contributions are taken into account, the estimate of the number of chains in the

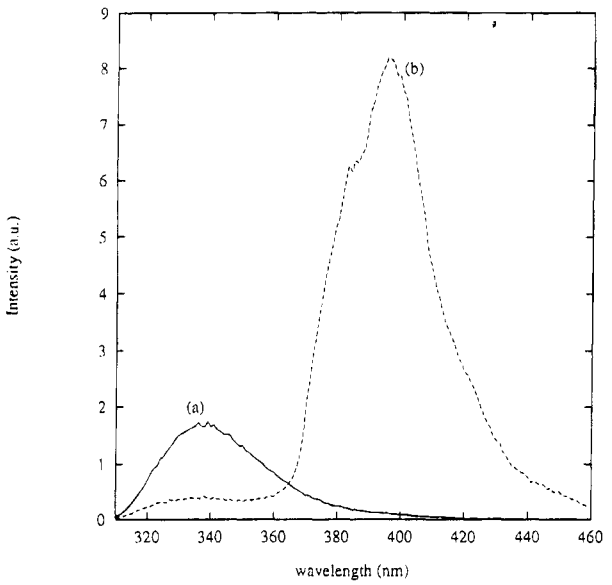

Figure 1. Emission spectra from the excitation of the naphthalene-labeled copolymer at a concentration of 0.060 g L^{-1} in (a) methanol and in (b) methanol containing the pyrene-labeled copolymer, also at a concentration of 0.060 g L^{-1}.

micelle should increase, and hence the simple model produces a lower limit for the size of the micelle. This estimate can be compared with the result obtained by Duhamel *et al.*[35] for a PS-*block*-PMMA (poly(methyl methacrylate)) in dioxane/methanol. The molecular weights of the PS and PMMA blocks were 11 000 and 26 000, respectively, and the association number was reported as 140 in a solvent of composition 30:70 dioxane:methanol by weight. Since dioxane is a good solvent for PS, the core may be swollen in this system. Thus our estimate of the size of the PS–PEO micelle is roughly correct.

The formation of micelles by the diblock copolymers in methanol can be demonstrated using fluorescence. Solutions of each differently labeled sample are prepared at a concentration of 0.12 g L^{-1}, which produces concentrations of naphthalene and pyrene of 4.4×10^{-6} and 5.0×10^{-6} M, respectively. If the chains are molecularly dispersed, the average spacing of the chromophores is over 100 times larger than R_0 for the naphthalene–pyrene pair, leading to the expectation that nonradiative singlet energy transfer should be unmeasurable in mixtures of the two solutions if the diblock copolymers do not associate. Figure 1 depicts the emission spectrum from the naphthalene-labeled sample alone and from the equilibrated solution that also contains the pyrene-labeled sample. The efficiency of nonradiative singlet energy transfer is very high in the mixed solution at a total concentration of 0.12 g L^{-1}. The chains are not molecularly dispersed but are instead confined to geometries that produce much smaller separations of the junctions between the blocks. Based on the behavior of similar systems in the literature, these geometries are identified as micelles.

Dynamic Light Scattering Results. Dynamic light scattering measurements were performed in methanol at 25 °C at two concentrations of the diblock copolymer, 1.1 and 0.11 g L^{-1}. At 1.1 g L^{-1}, the measurements show that the particles present in the solution have a very low polydispersity and a hydrodynamic radius of 36 nm. At 0.11 g L^{-1}, a species with a hydrodynamic radius less than 10 nm (presumably the free chain) is also detected. Its concentration is about 10% of the total

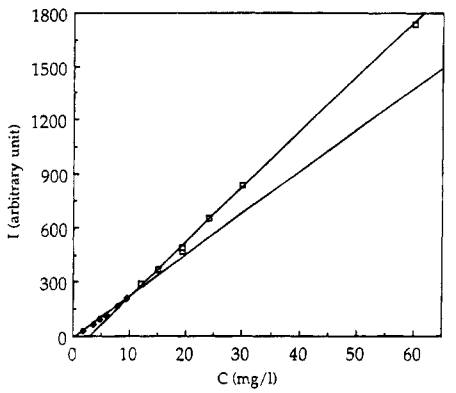

Figure 2. Integrated emission intensity as a function of concentration for the naphthalene-labeled copolymer in methanol.

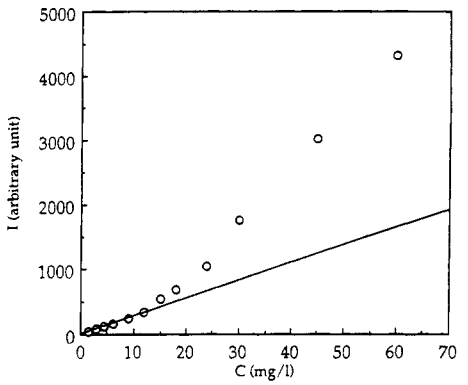

Figure 3. Integrated emission intensity as a function of concentration for the pyrene-labeled copolymer in methanol.

concentration (0.11 g L^{-1}), which implies a critical micelle concentration of about 0.01 g L^{-1}, consistent with the value deduced from the analysis of the fluorescence reported below.

Similar measurements were performed for the sample in a mixed solvent (80:20 methanol:water by weight) at 30 °C at a concentration of 1.23 g L^{-1}. These measurements reveal that addition of water to the solvent produces an increase in the effective hydrodynamic radius of the particles to 55 nm, accompanied by an increase in polydispersity of the particles. Analysis of the size distribution yields two populations at 46 and ~110 nm. Similar phenomena have been reported by Xu *et al.*[4] They suggest the larger particle may be a cluster of micelles.

Critical Micelle Concentration. The cmc for the block copolymers in methanol can be determined by measuring the total emission intensity as a function of concentration over the range 0.001–0.030 g L^{-1}. The optical density at the wavelength of excitation does not exceed 0.1 at these concentrations. If the chains experience the same environment throughout this range, one expects a linear dependence of the intensity on the concentration. Figures 2 and 3 depict the actual integrated intensity as a function of the concentration of the naphthalene-labeled and pyrene-labeled copolymers, respectively. Transitions are seen (weakly for the copolymer labeled with naphthalene, strongly for the copolymer labeled with pyrene), at which the integrated intensity deviates from the linear dependence. The cmc, identified with the concentration at which the transition occurs, is 0.009 ± 0.002 g L^{-1} for the naphthalene-labeled sample and 0.012 ± 0.001 g L^{-1} for the pyrene-labeled sample. The ratio of these two cmc's is about

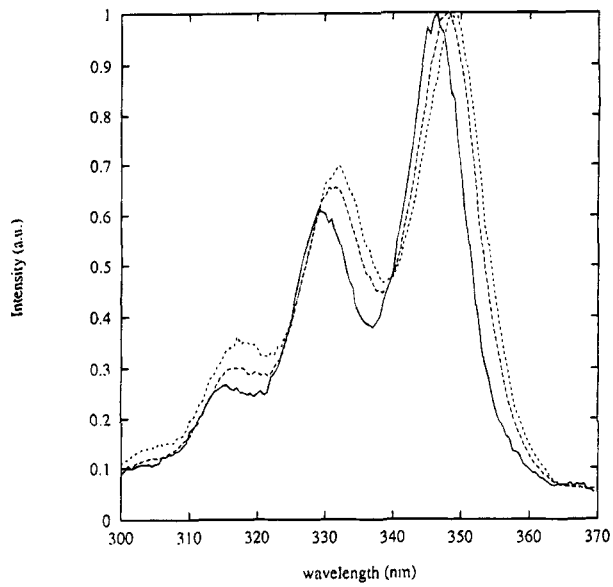

Figure 4. Excitation spectra for the pyrene-labeled copolymer in methanol at concentrations of (—) 0.009, (- - -) 0.045, and (•••) 0.060 g L^{-1}. The emission is monitored at 390 nm, and the excitation slit is 2 mm.

the same as the ratio of the molecular weights of the PS blocks in the two samples.

For the pyrene-labeled sample, the transition at the cmc is also reflected in the excitation spectra. When the concentration is less than 0.012 g L^{-1}, the maximum in the excitation spectrum is at 346 nm. At high concentrations, the maximum is shifted to the red, as shown in Figure 4. The size of the shift is much smaller than the shift reported for free pyrene when it is dissolved in water *vs* free pyrene located in the core of a micelle.[5] It has also been reported that when pyrene is transferred from water into the interior of a hydrophobic micellar core, there is a change in the fine structure in the emission spectrum, as manifested most strongly in the ratio of intensities denoted by I_1/I_3. No such change in I_1/I_3 was detected upon the formation of micelles in our system. This result is not surprising, because the pyrene in our sample is covalently attached to the junction between the blocks. When the system forms micelles, the pyrene is confined to the interface between the core and the corona and remains exposed to the polar solvent. In contrast, when free pyrene is used as a probe, it may enter the core of the micelle, where it is completely shielded from solvent.

Application of this method to the determination of the cmc in the mixed solvents is limited by the ability to detect the fluorescence at concentrations near the cmc. Since the cmc decreases when water is added to methanol, the method can be applied only when the concentration of water is small. Figure 5 depicts the experiment for the pyrene-labeled sample in 95:5 methanol:water at 40 °C. The cmc is about 0.003 g L^{-1}. The values reported here for the cmc are similar in magnitude to the values reported by Wilhelm *et al.*[5] For example, their sample with $M_n = 3700$ for the PS block and $M_n = 10\,400$ for the PEO block was reported to have a cmc of 0.0016 g L^{-1} in water.

Kinetic Data. The emission bands from naphthalene and pyrene are distinct enough so that the intensity at 338 nm can be considered to arise only from naphthalene under most of the conditions of our measurements. Figure 6 depicts the raw data in four experiments in which the intensity at 338 nm is monitored

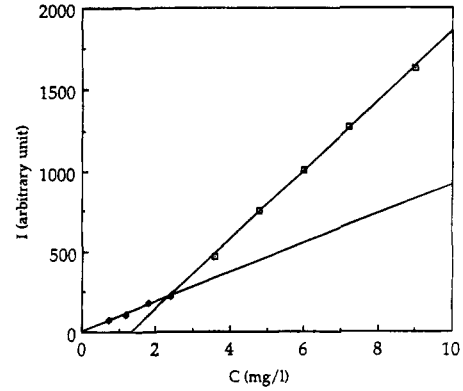

Figure 5. Integrated emission intensity as a function of concentration for the pyrene-labeled copolymer in 95:5 methanol:water (by volume) at 40 °C.

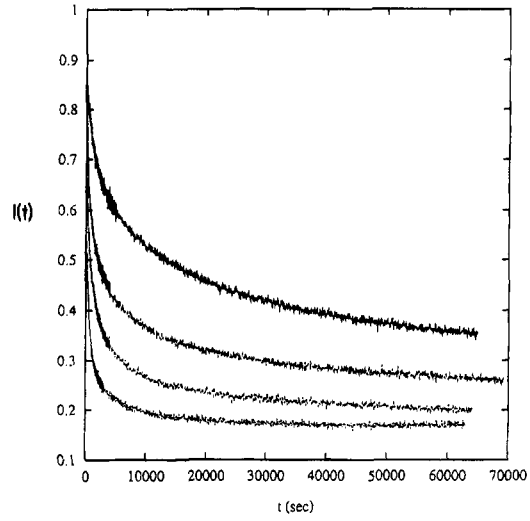

Figure 6. Normalized fluorescence emission at 338 nm in 90:10 methanol:water when the total concentration of copolymer is 0.120 g L^{-1} and $\alpha = 0.5$. The temperature is 25, 30, 35, and 40 °C, respectively, from top to bottom.

after mixing preequilibrated samples of the naphthalene-labeled and pyrene-labeled copolymers at different temperatures. The intensity is normalized by division of the measured intensity by the intensity from the naphthalene sample alone at the concentration used in the measurement. The normalized intensity decreases with time, due to the formation of micelles that contain both naphthalene and pyrene, in which the efficiency of nonradiative singlet energy transfer from naphthalene to pyrene is high. There is an initial very fast decay, which is followed by further decay at a much slower rate. In some instances, the second process is so slow that a plateau value is not achieved until several days (or longer) after mixing. This second slow process becomes more important in the overall decay as the temperature decreases.

Three compositions of mixed solvents were investigated at $\alpha = 0.5$ and a total copolymer concentration of 0.120 g L^{-1}. The decays were fitted to the equation

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \quad (1)$$

in which there are four adjustable parameters, A_1, τ_1, A_2, and τ_2. The subscripts for the relaxation times are assigned so that $\tau_1 < \tau_2$. The last term in eq 1, A_3, is a fixed constant. The samples that are completely mixed always reach the same intensity (0.17) as $t \to \infty$. For some of the decays, the intensities do not reach that

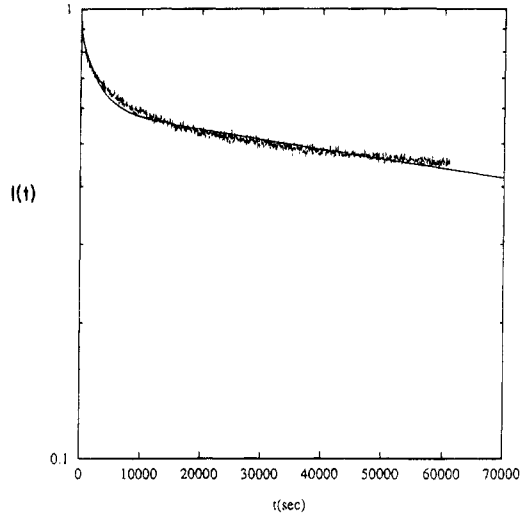

Figure 7. Illustrative fit to eq 1, using data at 30 °C in 85:15 methanol:water.

Table 2. Fitting Parameters for the Kinetic Decays

solvent[a]	T, °C	τ_1 (10^3 s)	fraction[b]	τ_2 (10^3 s)	$\langle\tau\rangle$ (10^3 s)
95:5	23	0.500 ± 0.019	0.57	8.2 ± 0.2	3.8
	25	0.245 ± 0.010	0.64	3.22 ± 0.07	1.32
	30			0.532 ± 0.012	0.53
	35			0.275 ± 0.010	0.28
	40			0.210 ± 0.012	0.21
90:10	25	2.67 ± 0.05	0.43	74.0 ± 0.9	43.6
	30	1.04 ± 0.02	0.58	45.9 ± 0.5	19.9
	35	0.700 ± 0.010	0.68	21.4 ± 0.3	7.3
	40	0.215 ± 0.005	0.71	3.08 ± 0.09	1.04
85:15	23	4.08 ± 0.15	0.18	316 ± 8	260
	30	2.52 ± 0.08	0.40	127 ± 2	77
	35	1.69 ± 0.03	0.49	88 ± 1	46
	40	1.10 ± 0.02	0.53	48.9 ± 0.6	23.6

[a] Methanol:water by volume. [b] Fraction of the decay due to the faster of the two time-dependent processes, when the two processes could be resolved. (Not resolved at 30–40 °C in 95:5 methanol:water.)

plateau value during the time we could record, because the decay of $I(t)$ is very slow. However, they have the same infinite time intensity as checked later after a long period of mixing. Thus it is reasonable to fix A_3 at that constant value.

Figure 7 depicts an illustrative fit. The fitting with eq 1 is not always satisfactory, especially when the decay is slow. The values of A_1, τ_1, A_2, and τ_2 obtained from the fit are summarized in Table 2. In 95:5 methanol:water, the initial fast decay is unmeasurable with our technique, as shown in Figure 8. The normalized intensities start at values smaller than 1, due to the initial very fast decay that cannot be measured in the experiment. The inability to obtain information on the initial fast process caused us to fit the data obtained at 30, 35, and 40 °C in 95:5 methanol:water to eq 2 instead of eq 1.

$$I(t) = A_2 \exp(-t/\tau_2) + A_3 \qquad (2)$$

It can also be seen that the curves in Figure 8 approach the same value of $I(t)$ as $t \to \infty$. This result supports assignments of A_3 as 0.17. Attempts to fit the data to a stretched exponential did not produce a satisfactory fit.

The fluorescence from the free naphthalene-labeled chains will not be quenched even when the system reaches the completely randomized state. If the residual intensity were due to the free unimer chains in the solution, one would see a change in the residual intensity at different temperatures and different solvent compositions. In contrast, the experimental results suggest that in most cases the cmc is so small that the contribution from the free unimer chains can be ignored. Therefore the residual fluorescence is mainly from the naphthalene in the mixed micelles that are produced by complete randomization of the labeled chains.

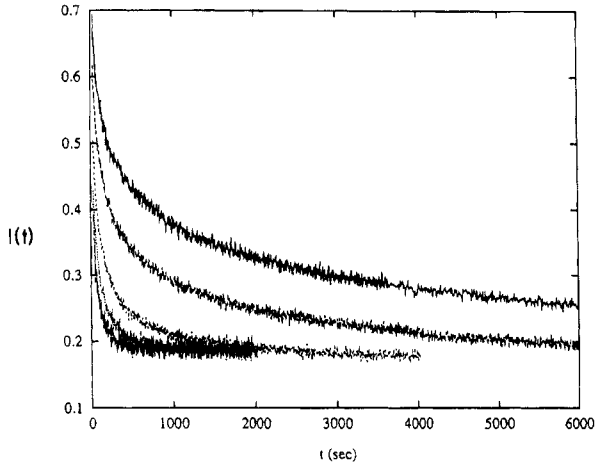

Figure 8. Experimental decays of the fluorescence in 95:5 methanol:water at 23, 25, 30, 35, and 40 °C. The decay becomes faster as the temperature increases.

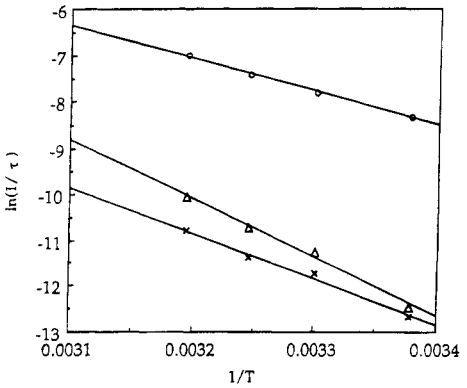

Figure 9. Arrhenius plot for (○) τ_1, (×) τ_2, and (△) $\langle\tau\rangle$ in 85:15 methanol:water.

Table 3. Activation Energies (kJ mol^{-1})

solvent[a]	from τ_1	from τ_2	from $\langle\tau\rangle$
90:10	123	159	189
85:15	59	83	107

[a] Methanol:water by volume.

Activation energies can be estimated from the temperature dependence of the relaxation times in Table 2. Figure 9 presents a plot of $\ln(1/\tau)$ *vs* $1/T$ for the data in 85:15 methanol:water. The activation energies in this medium and in 90:10 methanol:water are on the order of 10^2 kJ mol^{-1}, as shown in Table 3. The difficulty in measuring the fast decay components in 95:5 methanol:water produces strong curvature in $\ln(1/\tau_2)$ *vs* $1/T$, and therefore no activation energies are tabulated for this medium. In the two mixed solvents for which the comparison can be made, the activation energy for the slower process (with relaxation time τ_2) is larger than the activation energy for the faster process (with relaxation time τ_1).

A puzzling feature of the activation energies is the observation that they decrease upon adding sufficient

water to the medium to bring the solvent from 90:10 to 85:15 methanol:water. The rates themselves decrease as water is added to the system (Table 2), as expected. Apparently, an attempt to understand the solvent effect on the rates must include a consideration of the entropy of activation, which increases as the solvent becomes richer in water.

Analysis of the Kinetics. In a micelle that contains mainly chains of type D, the efficiency of energy transfer from D to A may change in a complicated fashion as the number of acceptors in the micelle increases in the sequence 1, 2, ... Thus it is possible that the mechanism of the exchange of chains between micelles may follow a simple kinetic model, yet the measured decay using the energy transfer method may be quite complicated. For this reason we performed the following analysis of the results using a simple kinetic model of the exchange of chains but accounting for the energy transfer mechanism realistically.

We examined the application of the simple kinetic model described by Cantú *et al.*,[36] which assumes the formation of the mixed micelles containing two different chromophores is achieved by the transfer of single chains from one micelle to another via the pool of free chains and the rate-controlling step is the release of a single chain from the micelle. Diffusion of the free chains from one micelle to another is considered to be a fast process. The second assumption is reasonable since the distance that the free chains must diffuse is on a microscopic scale; thus the time scale of the diffusion cannot be longer than a few seconds. This model neglects the potential importance of micelle–micelle collisions and may not be able to describe the experimental results if those collisions are important.

Assuming the two differently labeled chains are the same, it is easy to show that the growth (or decay) of the population of chains of either type D or type A in the mixed micelles follows a simple exponential function. The results are

$$n_D^D = \frac{N_D}{\alpha + 1}[1 + \alpha \exp(-k_{-1}t)] \quad (3)$$

$$n_A^D = \frac{N_D \alpha}{\alpha + 1}[1 - \exp(-k_{-1}t)] \quad (4)$$

where n_D^D and n_A^D are the concentrations of chains of type D and A in the mixed micelles that are initially composed of type D chains only, N_D is the total concentration of type D chains at zero time, α is the ratio of the total concentration of type A to type D, and k_{-1} is the rate constant for extraction of the chains from the micelle.

For micelles that are initially composed of type A, the time dependence of the concentrations are

$$n_D^A = \frac{N_A}{\alpha + 1}[1 - \exp(-k_{-1}t)] \quad (5)$$

$$n_A^A = \frac{N_A}{\alpha + 1}[\alpha + \exp(-k_{-1}t)] \quad (6)$$

where N_A is the total concentration of A type chains at zero time. At all times, $N_D = n_D^D + n_D^A$ is constant, noting that $N_A = \alpha N_D$.

These equations hold under the condition that the system is in a thermodynamic equilibrium state and the two types of chains, D and A, are thermodynamically equivalent species. The growth of the mixed micelles only depends on one rate constant, k_{-1}.

The knowledge of the growth of the mixed micelles alone cannot predict the time dependence of $I_D(t)/I_0$, where $I_D(t)$ denotes the intensity of the fluorescence by the donors in the mixed system in the experiment and I_0 is the intensity of the fluorescence in a system that contains only chains of type D. In addition, one needs to know the relative fluorescence intensity of a donor in a mixed micelle composed of varying ratios of chains of type A and type D with respect to the intensity of the fluorescence from the donor in the absence of any acceptors. Since both the donors and acceptors in our sample are covalently attached to the junction between the blocks, they can be considered to be confined on a surface of a spherical micellar core with a radius of R. The survival probability of an excited donor molecule in such a system has been considered previously.[35,37] Following Duhamel *et al.*,[35]

$$\phi(t) = \exp\left[-\frac{t}{\tau_D} - f_A x_n \frac{\Gamma(2/3)}{4}\left(\frac{R_0}{R}\right)^2\left(\frac{t}{\tau_D}\right)^{1/2}\right] \quad (7)$$

where f_A is the fraction of the chains that are labeled with acceptors, x_n is the average number of chains in a micelle, and τ_D is the lifetime of the fluorescence from the donor. The relative intensity from the donor with respect to the intensity in the absence of any acceptors is simply

$$q(f_A) = [\int_0^\infty \exp(-t/\tau_D)\, dt]^{-1} \int_0^\infty \exp\left[-\frac{t}{\tau_D} - f_A x_n \frac{\Gamma(2/3)}{4}\left(\frac{R_0}{R}\right)^2\left(\frac{t}{\tau_D}\right)^{1/2}\right] dt \quad (8)$$

Given R_0/R and x_n, the functional form of $q(f_A)$ can be computed numerically from eq 8.

With the functional form of $q(f_A)$, the time dependence of I_D/I_0 in the mixed solutions can be calculated from the model as

$$\frac{I_D(t)}{I_0} = \frac{1}{N_D(0)}[n_D^D q[n_A^D/(n_D^D + n_A^D)] + n_D^A q[n_A^A/(n_A^A + n_D^A)]\} \quad (9)$$

This expression ignores the contribution from any free chains in the system. $I_D(t)/I_0$ depends on the functional form of $q(f_A)$ and the rate constant, k_{-1}, as well as on the ratio of the two types of chains, α.

For the experimental system studied here, we could estimate the functional form of $q(f_A)$ if x_n and R_0/R are known, using eq 8. Since our knowledge of x_n and R_0/R is subject to substantial uncertainty, we prefer instead to determine $q(f_A)$ experimentally, using solutions with a constant concentration of chains of type D and variable concentrations of chains of type A. When the mixed systems have equilibrated, the measured fluorescence intensity (divided by the intensity in the absence of acceptors) as a function of α is equivalent to $q(f_A)$. We have assumed that the contribution from the free chains is negligible. Figure 10 depicts the experimentally determined $q(f_A)$ in 95:5 methanol:water at ambient temperature. The solid line is the best fit to the theoretical model, eq 8, with R_0 assigned its known value of 2.8 nm. The size of the micelle, which specifies both x_n and R, was varied in order to produce the best fit. The values used, $x_n = 71$ and $R = 5.2$ nm, are in

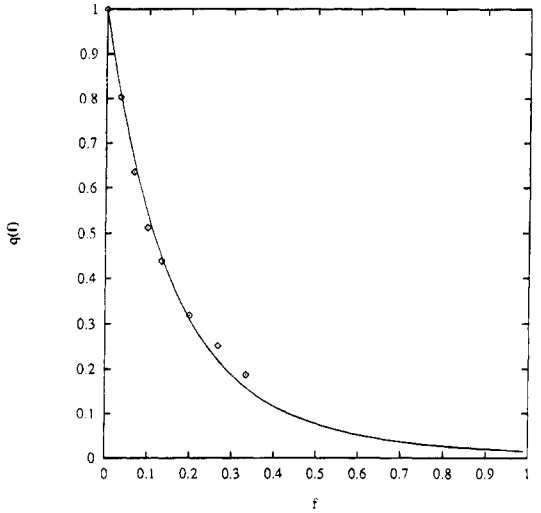

Figure 10. Experimentally measured $q(f_A)$ (◇) in the 95:5 methanol:water system at ambient temperature. The solid line is the best fit to the data using eq 8 with $x_n = 71$, $R = 5.2$ nm, and $R_0 = 2.8$ nm.

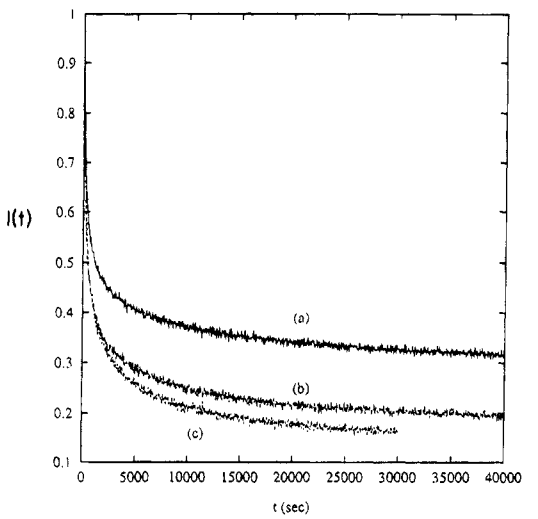

Figure 11. Measured fluorescence decays at 35 °C in 90:10 methanol:water, a total concentration of 0.120 g L^{-1}, and α of (a) 0.25, (b) 0.50, and (c) 1.00.

the range expected, using the simple model of micellization that was described at the beginning of this article. Therefore it seems likely that eq 8 is a reasonable approximation for the photophysical events within the mixed micelle.

However, if we combine eq 8 with the kinetic scheme that is presented in eqs 1–4, we are unable to produce a fit to the experimentally measured decay kinetics. The decay calculated using eq 9 is nonexponential, but it could be fitted to the sum of two exponential decays with lifetimes that differ by only a factor of 2–3. In the experimental measurements, the two relaxation lifetimes could differ by 1 or 2 orders of magnitude.

There are a few aspects of the measured behavior that can be recovered from the model. The infinite time value for the intensity, which is 0.17 from the experiment, is predicted to be 0.16 from the model when α = 0.5. The theoretical scheme predicts that the total concentration should not be a factor, which is consistent with our observation that kinetic curves obtained at concentrations of 0.24 and 0.12 g L^{-1} in 90:10 methanol: water are superimposable. At constant concentration, the decays are not very sensitive to the ratio of mixing, α, as shown in Figure 11. The simple theory would predict that the decay rates should vary by ~30%.

The existence of two largely different relaxation lifetimes in the measured kinetic curves is also reported by Procházka *et al.*[14] Their micelles are nearly monodisperse in size. Thus the existence of two relaxation lifetimes cannot be attributed to the possible existence of two micellar sizes in solution. On the other hand, the mismatch between the two labeled copolymers is too small to account for the difference in the two relaxation times, based on the values of the cmc determined for the two samples. We are led to the conclusion that the mixing of the chains in the micelles may take place by another mechanism, such as micelle–micelle collision, in addition to the transfer of free chains between independent micelles.

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References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Adv. Colloid Interface Sci.* **1976**, *6*, 201.
(2) Booth, C.; Naylor, T. D.; Price, C.; Rajab, N. S.; Stubbersfield, R. G. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2353.
(3) Price, C.; Kendall, K. D.; Stubbersfield, R. B.; Wright, B. *Polym. Commun.* **1983**, *24*, 326.
(4) Xu, R.; Winnik, M. A.; Hallet, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 87.
(5) Wilhelm, M.; Zhao, C.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 1033.
(6) Cao, T.; Munk, P.; Ramireddy, C.; Tuzar, Z.; Webber, S. E. *Macromolecules* **1991**, *24*, 6300.
(7) Linse, P.; Malmsten, M. *Macromolecules* **1992**, *25*, 5434.
(8) Quintana, J. R.; Villacampa, M.; Katime, I. A. *Macromolecules* **1993**, *26*, 601.
(9) Quintana, J. R.; Villacampa, M.; Katime, I. A. *Macromolecules* **1993**, *26*, 606.
(10) Zhou, Z.; Chu, B.; Peiffer, D. G. *Macromolecules* **1993**, *26*, 1876.
(11) Nguyen, D.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1994**, *27*, 5090.
(12) Hruska, Z.; Piton, M.; Yekta, A.; Duhamel, J.; Winnik, M. A.; Riess, G.; Croucher, M. D. *Macromolecules* **1993**, *26*, 1825.
(13) Caldérara, F.; Hruska, Z.; Hurtrez, G.; Lerch, J.-P.; Nugay, T.; Riess, G. *Macromolecules* **1994**, *27*, 1210.
(14) Procházka, K.; Kiserow, D.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 454.
(15) Kiserow, D.; Chan, J.; Ramireddy, C.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 5338.
(16) Zana, R. In *Surfactants in Solution*; Mittal, K. L., Botherel, P., Eds.; Plenum Press: New York, 1986; Vol. 4.
(17) Muller, N. *J. Phys. Chem.* **1972**, *76*, 3017.
(18) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffman, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, *80*, 905.
(19) Aniansson, E. A. G.; Wall, S. N. *J. Phys. Chem.* **1974**, *78*, 1024.
(20) Price, C.; Hudd, A. L.; Booth, C.; Wright, B. *Polymer* **1982**, *23*, 650.
(21) Tian, M.; Qin, A.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z.; Procházka, K. *Langmuir* **1993**, *9*, 1741.
(22) Halperin, A.; Alexander, S. *Macromolecules* **1989**, *22*, 2403.
(23) Bendář, B.; Edwards, K.; Almgren, M.; Tormod, S.; Tuzar, Z. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 785.
(24) Förster, Th. *Ann. Phys.* **1948**, *2*, 55.
(25) Wang, Y.; Balaji, R.; Quirk, R. P.; Mattice, W. L. *Polym. Bull.* **1992**, *28*, 333.
(26) Procházka, K.; Bednář, B.; Mukhtar, E.; Svoboda, P.; Trěná, J.; Almgren, M. *J. Phys. Chem.* **1991**, *95*, 4563.
(27) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071.
(28) Quirk, R. P.; Ma, J.-J. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 2031.
(29) Quirk, R. P.; Kim, J.; Rodrigues, K.; Mattice, W. L. *Makromol. Chem., Macromol. Symp.* **1991**, *463*, 42.

(30) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(31) Berlmann, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973.
(32) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(33) Sato, H.; Tanaka, Y.; Hatada, K. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 181.
(34) Kawamura, T.; Uryu, T.; Matsuzaki, K. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 661.
(35) Duhamel, J.; Yekta, A.; Ni, S.; Khaykin, Y.; Winnik, M. A. *Macromolecules* **1993**, *26*, 6255.
(36) Cantú, L.; Cori, M.; Salina, P. *J. Phys. Chem.* **1991**, *95*, 5981.
(37) Klafter, J.; Blumen, A. *J. Chem. Phys.* **1984**, *80*, 875.

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