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Investigation of Polystyrene–Poly(ethylene oxide) Block Copolymer Micelle Formation in Organic and Aqueous Solutions by Nonradiative Energy Transfer Experiments

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ABSTRACT: Micelle formation in tetrahydrofuran–methanol, 1,2-dichloroethane–methanol, tetrahydrofuran–water, and water solutions by PS–PEO diblock copolymers was studied by the fluorescence spectroscopy. For this purpose, a series of PS–PEO copolymers was labeled by the phenanthrene or anthracene groups at the block junctions. The chromophore contents in copolymers were determined by the absorbance spectroscopy using suitable model compounds. When micelles were present, intramicellar nonradiative energy transfer could be observed. For the PS–PEO copolymer (M_n = 114 000, 93 weight % PEO) we find the onset of micelle formation in water in the range of 10 × 10^{-3} g/L (9 × 10^{-8} M).

Introduction

Amphiphilic block and graft copolymers consisting of hydrophilic and hydrophobic parts have become subjects of numerous studies on their solution, solid state, and surface properties.[1,2] Nonionic polystyrene–poly(ethylene oxide) block copolymers (PS–PEO) are characterized by their ability to associate in various organic and aqueous solutions. The PS–PEO copolymers are known to form micelles in water when the length of the hydrophilic PEO part is significantly longer than that of the polystyrene part. In analogy to the low molecular weight surfactants, the critical micelle concentration (CMC) can be defined for the amphiphilic block copolymers as the onset of intermolecular chain association.

Fluorescence techniques appear to be useful tools for the characterization of polymer solutions. For example, the fluorescence probe technique has been used by Winnik's group[3] to study the CMC of polystyrene–poly(ethylene oxide) diblock and triblock copolymers in water. Recently, the synthesis of well-defined chromophore labeled block copolymers[4–11] extended the ability of fluorescence techniques to report on various aspects of polymer micelle formation like, for instance, the nature of micelle interface[9] or the exchange dynamics in polymer micelles.[11]

In our previous publication[12] we described the synthesis of polystyrene–poly(ethylene oxide) diblock copolymers bearing anthracene or phenanthrene groups at the block junctions. We studied solutions of these copolymers in water and in 1,2-dichloroethane–methanol mixtures by fluorescence spectroscopy. When micelles containing both donor (phenanthrene) and acceptor (anthracene) groups were present (e.g. in water), the intramicellar nonradiative energy transfer was observed.

In the present work we have studied the micellization of labeled PS–PEO copolymers in mixtures of various solvents. We demonstrate here that the evolution of nonradiative energy transfer between donor and acceptor groups as a function of the copolymer concentration in water can yield information on the copolymer critical micelle concentration. In order to characterize more precisely the phenanthrene labeled copolymers, a suitable model molecule reflecting the copolymer structure has been synthesized and its spectral characteristics examined.

Experimental Section

Materials. Styrene and ethylene oxide monomers were purified as described earlier.[13]

Tetrahydrofuran, THF (Aldrich), was fractionally distilled over $\mathrm{CuCl_2}$ and sodium metal, degassed, and stirred over sodium metal in the presence of benzophenone until the violet color of the sodium benzophenone complex appeared. All other highest purity grade solvents were distilled before use. Dry nitrogen (Air Liquide, N5) was used during the polymerization and in the preparation of reagents.

The preparation of fluorescent monomers, 1-(2-anthryl)-1-phenylethylene and 1-(9-phenanthryl)-1-phenylethylene, has been described recently.[8] They were sublimed in vacuo (10^{-5} Torr) just before use.

Synthesis of the Model Compound. The usual high vacuum/nitrogen purge technique was used during the synthesis of 5-methyl-3-(9-phenanthryl)-3-phenylheptan-1-ol (Scheme 1, compound 4).

First, 250 mL of anhydrous THF was cryodistilled into the reactor at −78 °C. Then 5.2 mL (6.8 mmol) of 1.3 M *s*-BuLi and 2.2 g (7.9 mmol) of 1 dissolved in 20 mL of anhydrous THF were transferred into the reactor. The dark green color of the carbanion 2 appeared immediately after the monomer addition, confirming that the reaction between monomer and initiator is very fast. After ca. 30 min at −78 °C, 7 g (159 mmol) of ethylene oxide was cryodistilled into the reactor and the system was allowed to come slowly to room temperature. The reaction mixture was then stirred for another 3 days. During this period, a slow discoloration of the solution was observed. Alkoxide anion 3 was then deactivated by the addition of methanol.

The TLC analysis (ethylacetate/hexane, volume ratio 4/6) of the crude reaction product showed that it contained two main constituents: 5-methyl-3-(9-phenanthryl)-3-phenylheptan-1-ol, 4 (R_f = 0.43) and the unreacted starting monomer 1 (R_f = 0.70). The desired alcohol 4 was isolated by column chromatography (Merck silica gel 60, particle size 0.040–0.063 mm) with ethyl acetate/hexane (volume ratio 4/6) mixture. In total, 1.69 g of white crystals (65% according to *s*-BuLi) were obtained, mp 69–71 °C.

Due to the presence of rotamers in the molecule, the ^{1}H NMR study was performed at an elevated temperature (60 °C). It has confirmed the existence of two diastereoisomers.

^{1}H NMR ($\mathrm{CDCl_3}$ at 60 °C), δ/ppm: 8.70–7.14 (m, 14H, aromatic protons), 3.35 (s, 1H, –OH), 3.50 (m, 2H, –$\mathrm{CH_2}$–O–), 2.80 (m, 2H, R–C(Ar)–$\mathrm{CH_2}$–C–O–), 2.38 (d, J = 5 Hz, 2H, R–$\mathrm{CH_2}$–C(Ar)–R′–O–), 1.12 (m, 1H, R–CH(R′)–R″), 0.88 (m, 2H, R–$\mathrm{CH_2}$–R′–C(Ar)–R″–O–), 0.55 (t, J = 7Hz, 3H, $\mathrm{CH_3}$–R–C(Ar)–R′–O–), 0.40 (d, J = 6 Hz, 3H, $\mathrm{CH_3}$–CH(R)–R′).

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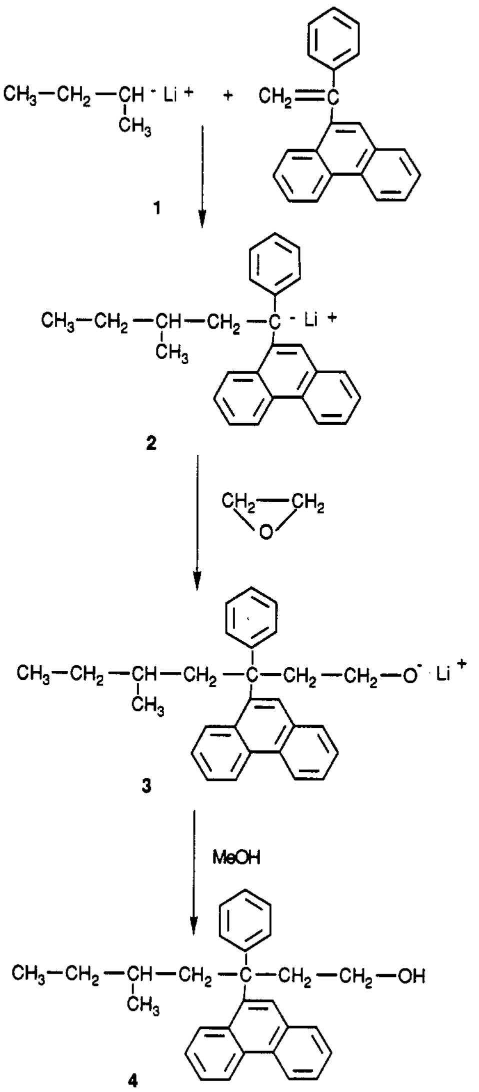
Scheme 1



IR (film), ν/cm^{-1}: 3400 (m, OH), 2900 (s, CH_3), 1600 (w, C=C), 1490 (m), 1450 (m), 1380 (w), 1040 (m, C—O), 750 (s).

UV (tetrahydrofuran), λ_{max}/nm (ϵ/L·mol^{-1}·cm^{-1}): 298 (11 000), 286 (10 200), 277.5 (13 300), 255.5 (50 500), 210 (7500).

Instrumentation. Thin layer chromatography (TLC) was carried out on silica gel 60F (254) precoated sheets. UV–VIS spectra were recorded on a Beckman DU-7 spectrophotometer. Fluorescence spectra were obtained on a Perkin-Elmer LS-5B spectrometer. Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 spectrometer.

The polymer gel permeation chromatography (GPC) analyses were performed on an ALC/GPC 150C chromatograph (Millipore-Waters) equipped with four Microstyragel columns (10^4, 10^3, 500, and 100 Å) using both the refractive index and UV detectors. For the UV detector, 298- and 357-nm wavelengths were chosen to detect phenanthrene and anthracene labeled (co)polymers, respectively. Samples of living polystyrenes were removed before the addition of the chromophore monomers and quenched in methanol and their molecular weights determined by the GPC analysis. The molecular weights of the copolymers were found both by the absorbance measurements and by the GPC/^{1}H NMR analyses.

The composition of the copolymers was determined by the 250-MHz ^{1}H NMR on Bruker AC 250-F using $CDCl_3$ as a solvent. The content of PEO was calculated from the ratio of the intensities of the CH_2CH_2 signal (at 3.6 ppm) and of the aromatic signal (at 6.4–7.2 ppm).

The micelle size was measured by the quasielastic light scattering using a Coultronics N4 apparatus.

Polymerization. The copolymers were prepared by anionic polymerization in THF under nitrogen at −78 °C using cumylpotassium as initiator. A detailed description of the polymerization procedure is given elsewhere.[12,13]

Study of Micellar Solutions by Fluorescence Spectroscopy. Phenanthrene (donor) and anthracene (acceptor) constitute a suitable donor–acceptor pair for the nonradiative energy transfer (NRET) experiments. The phenanthrene emission spectrum overlaps the absorption spectrum of anthracene. The excitation energy absorbed by phenanthrene can therefore be nonradiatively transferred to anthracene. Changes in NRET efficiency between the phenanthrene and anthracene chromophores depend on their mutual proximity. According to the theory of Förster,[14] the NRET efficiency (E) can be related to the separation R of donor and acceptor by the expression

$$E = \frac{R_0^{\,6}}{R_0^{\,6} + R^6} \tag{1}$$

where R_0 (Förster's radius) is the characteristic distance at which the rate of energy transfer and inherent rate of deactivation of the donor are equal. For the phenanthrene–anthracene pair R_0 is 22 Å.[15] In dilute solutions of labeled copolymers in good solvents for both blocks, the labels are separated by a distance that is too large to permit any NRET. As the solvent system becomes poorer for one block and the copolymer concentration exceeds the CMC, the copolymer chains associate and the NRET becomes eventually observable. In our experiments, we used the ratio of intensities of the anthracene emission at 425 nm (I_f(A)) and that of the phenanthrene emission at 370 nm (I_f(D)) as a measure of the NRET efficiency.

In the first series of experiments we studied the micelle formation by PS–PEO copolymers in various solvent (tetrahydrofuran–methanol, 1,2-dichloroethane–methanol, tetrahydrofuran–water) mixtures. In these mixtures, tetrahydrofuran (THF) and 1,2-dichloroethane (DCE) are good solvents for both sequences while methanol and water are selective solvents for the PEO blocks. First, stock solutions (5 g/L) of block copolymers in THF or DCE were prepared. Then, 100 μL of these solutions were injected into the corresponding solvent mixtures in order to obtain the concentration 0.09 g/L for the copolymer couple C-20 and C-21, and the concentration 0.02 g/L for the couple C-15 and C-17. Sample solutions were excited at 299 nm, and the emission spectra were collected between 335 and 535 nm.

In the second series of experiments we have determined the CMC values of phenanthrene and anthracene labeled pairs of copolymers in water solutions. To accomplish that, we followed the evolution of the I_f(A)/I_f(D) ratio as a function of increasing copolymer concentration. Examined solutions were prepared by injecting calculated volumes (in microliters) of copolymer stock solutions (5 g/L in THF) into 10 mL of distilled water.

Results and Discussion

Model Compound for Absorbance Measurements. Polymers containing strongly absorbing chromophore groups such as phenanthrene, anthracene, or pyrene can be analyzed by the UV spectroscopy. By using Beer's law, one can easily find the degree of labeling of the polymer chains. Further, if the exact number of chromophore units per polymer chain is known, one can estimate the polymer molecular weight. Potential sources of error include the choice of suitable model compound. In order to diminish this error, we prepared a phenanthrene group containing low molecular weight compound, 5-methyl-3-(9-phenanthryl)-3-phenylheptan-1-ol.

The structure of the model compound molecule reflects the chemical environment of the phenanthrene group in the PS–PEO copolymer. The hydrophobic aliphatic part of the molecule represents the PS part of the copolymer molecule. The reaction of *s*-BuLi with the 1,1-diaryl molecule (fluorescent monomer) proceeds quantitatively without homopolymerization.[16] We used a 15% excess of the fluorescent monomer to assure that the reaction mixture did not contain any unreacted *s*-BuLi initiator. Further, it is known that polymeric organolithium com-

Table 1. Molar Absorption Coefficients (ϵ) of Phenanthrene Containing Monomer and Model Compounds in Various Solvents and at Different Wavelengths

	solvent			
	THF	*n*-hexane	1,2-DCE	MeOH
	Fluorescent Monomer			
λ_{max} (nm)	298	298	300	
ϵ_{max} (L mol^{-1} cm^{-1})	15 400	11 500	18 500	
	Model Compound			
λ_{max} (nm)	298	296.5	299	296.5
ϵ_{max} (L mol^{-1} cm^{-1})	11 000	10 900	10 900	10 600
ϵ_{297} (L mol^{-1} cm^{-1})	10 300	10 800	9400	10 500
ϵ_{298} (L mol^{-1} cm^{-1})	11 000	9500	10 600	9300
ϵ_{299} (L mol^{-1} cm^{-1})	10 300	7250	10 900	7300

pounds react with ethylene oxide quantitatively without side reactions to give the corresponding hydroxyethylated products.[17] We used this fact to introduce the hydroxyethyl group into our model compound.

The molar absorption coefficients (ϵ) of the model compound in various solvents were determined according to Beer's law in solutions of known concentration. Their values are collected in Table 1. We observe a relatively small difference in peak maxima (up to 2.5 nm) depending on the type of solvent. This is not surprising as it is known that the $\pi \rightarrow \pi^*$ electronic transitions of conjugated aromatic systems are little affected by the solvent polarity. It is imperative to use the correct value of (ϵ) in the polymer molecular weight calculations. Small shifts in peak maxima can have a dramatic effect on the values of molar absorption coefficients and, consequently, on the calculated molecular weights.

Characterization of the Copolymers. We prepared several PS–PEO diblock copolymers with anthracene or phenanthrene labels at the junction between the two blocks. Direct evidence of the chromophore incorporation into a copolymer chain comes from the comparison of the absorption spectra of starting anthracene containing monomer and resulting (co)polymer. The absorption maxima are in the latter case blue-shifted for about 7–10 nm.[12] Further, the refractive index and UV detector GPC curves of all examined copolymers are virtually superimposable.

Characteristic data of synthesized copolymers are presented in Table 2. We notice that the values of molecular weights found by the GPC/NMR analyses and absorbance measurements are in a fairly good agreement.

Determination of the Micelle Sizes. Uniform micellar solutions were prepared by the stepwise dialysis technique. This technique permits one to obtain the aqueous micellar solutions of PS–PEO block copolymers of a large compositional variety without the formation of secondary aggregates. Typically, the copolymers are dissolved in a good solvent for both blocks such as tetrahydrofuran. This water-soluble solvent is subsequently replaced by water in a dialysis apparatus.

Values of hydrodynamic radii of the micelles prepared from one type of copolymer or mixed micelles prepared from pairs of anthracene and phenanthrene labeled copolymers are given in Table 3. The observed micelle sizes are comparable to those obtained by the measurement of nonlabeled PS–PEO copolymers.[18] The presence of a single chromophore group in the copolymer molecule does not have any significant effect on the measured micelle size.

Table 2. Characterization of Chromophore Labeled Polystyrenes and PS–PEO Block Copolymers

	samples, label					
	C-12, Ant	C-13, Phe	C-15, Phe	C-17, Ant	C-20, Phe	C-21, Ant
	M_n(CPG)					
M_n(PS)^a	16 500	21 000	10 000	12 000	8 000	8 000
M_n(PS-M)^a	16 500	21 000	10 000	12 500	8 000	8 000
M_n(Cop)^b	50 000	33 500	25 000	28 000	114 000	114 000
	M_n(UV) in THF					
M_n(PS-M)^c	15 500	22 000	10 500	13 000		
M_n(PS-M)^d		21 000	10 000			
M_n(Cop)^c	51 000	37 000	23 000	30 500	125 000	106 000
M_n(Cop)^d		35 000	22 000		116 000	
	M_n(UV) in 1,2-DCE					
M_n(Cop)^e	54 500	41 000	32 000	40 000	137 000	96 500
M_n(Cop)^f		37 000	29 000		126 000	
weight % PEO^b	67	37	60	57	93	93
$M_w/M_n{}^a$	1.15	1.15	1.16	1.18	1.25	1.23

[a] Calculation of the number-average molecular weight (M_n) and the ratio of weight-average to number-average molecular weight (M_w/M_n) is based on the evaluation of GPC chromatograms using polystyrene standards. [b] Calculation of the total copolymer molecular weight and of the content of PEO (w % PEO) is based both on the GPC and ^{1}H NMR analyses. [c] Obtained from absorbance measurements in THF by using the following: ϵ = 11 800 L mol^{-1} cm^{-1} (9-methylphenanthrene[8]) at 298 nm; ϵ = 5790 L mol^{-1} cm^{-1} (methyl 7-(2-anthryl)heptanoate[8]) at 358 nm. [d] Obtained from absorbance measurements in THF by using the following: ϵ = 11 000 L mol^{-1} cm^{-1} (5-methyl-3-(9-phenanthryl)-3-phenylheptan-1-ol) at 298 nm. [e] Obtained from absorbance measurements in DCE by using the following: ϵ = 11 800 L mol^{-1} cm^{-1} (9-methylphenanthrene[8]) at 298 nm; ϵ = 5790 L mol^{-1} cm^{-1} (methyl 7-(2-anthryl) heptanoate[8]) at 358 nm. [f] Obtained from absorbance measurements in DCE by using the following: ϵ = 10 900 L mol^{-1} cm^{-1} (5-methyl-3-(9-phenanthryl)-3-phenylheptan-1-ol) at 299 nm.

Table 3. Values of Measured (R_h) and Calculated (R_m) Micellar Hydrodynamic Radii for the Micellar Solution of Labeled Diblock Copolymers and Their 1/1 Mixtures in Water

samples	N_{PS}	N_{POE}	% PEO	R_h (Å)	R_m (Å)	R_h/R_m
C-12	159	761	67	210	120	1.75
C-13	202	284	37	210	69	3.04
C-15	96	341	60	190	69	2.75
C-17	115	364	57	220	73	3.01
C-20	77	2409	93	400	214	1.87
C-21	77	2409	93	410	214	1.91
C-12 + C-15				200		
C-15 + C-17				210		
C-20 + C-21				410		
C-21 + C-15				380		
C-20 + C-17				360		

Also, we have tested the key predictions of the Halperin's star model theory[19] in our micelle systems. According to this model, the PS–PEO diblock copolymer micelle radius (R_m) can be related to the lengths of PS (N_{PS}) and PEO (N_{PEO}) blocks. In the case of $N_{PEO} \gg N_{PS}$, the micellar radius is given by

$$R_m \approx N_{PS}{}^{0.16} N_{PEO}{}^{0.6} \qquad (2)$$

From Table 3 we can see that the values of the measured micelle radii R_h are twice or three times larger than the R_m values calculated according to the star model theory. These results are in good agreement with the results reported by the Winnik group.[18] We would like to note, however, that we have tested the micelle characteristics in water for a very large number of PS–PEO block copolymers having very different compositions[20] and found that the star model predictions are not completely satisfactory for the description of PS–PEO aqueous system. We will comment on these results in more detail in the future.

Finally, we show that mixed uniform micelles can be prepared by stepwise dialysis of the mixture of two

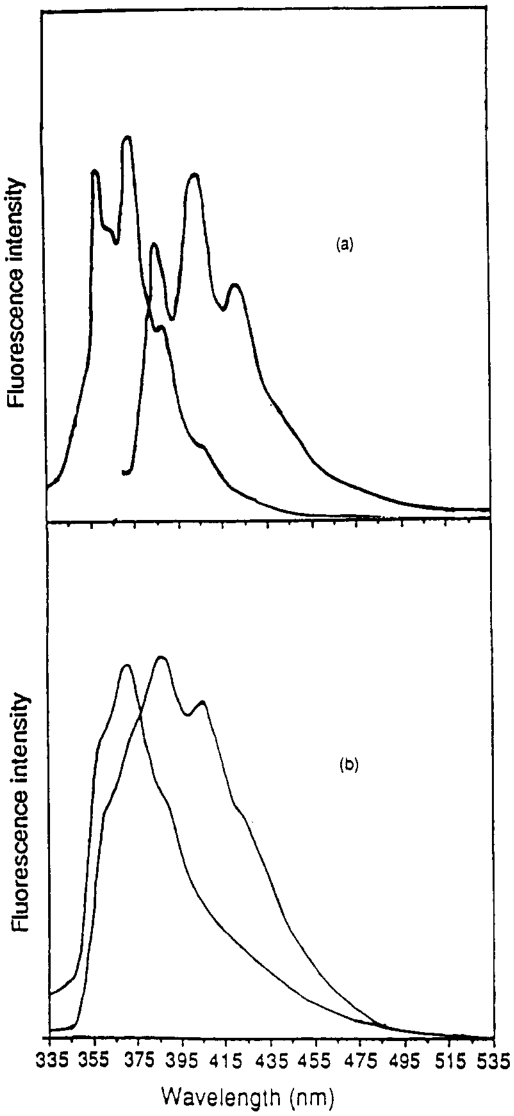


Figure 1. (a) Superimposed fluorescence spectra of phenanthrene labeled copolymer C-15 (λ_{ex} = 299 nm, 0.02 g/L, left curve) and anthracene labeled copolymer C-17 (λ_{ex} = 357 nm, 0.02 g/L, right curve) solutions in DCE. (b) Superimposed fluorescence spectra of a C-15 and C-17 mixture (1:1 mole ratio, 0.02 g/L) excited at 299 nm in DCE (left curve) and in a 10:90 vol % DCE-methanol mixture (right curve).

differently labeled copolymers. We confirm the possibility of forming mixed micelles as reported by Munk et al.[21] The hydrodynamic radius of the mixed micelle prepared from two copolymers differing in their molecular weight is found to have an intermediate value.

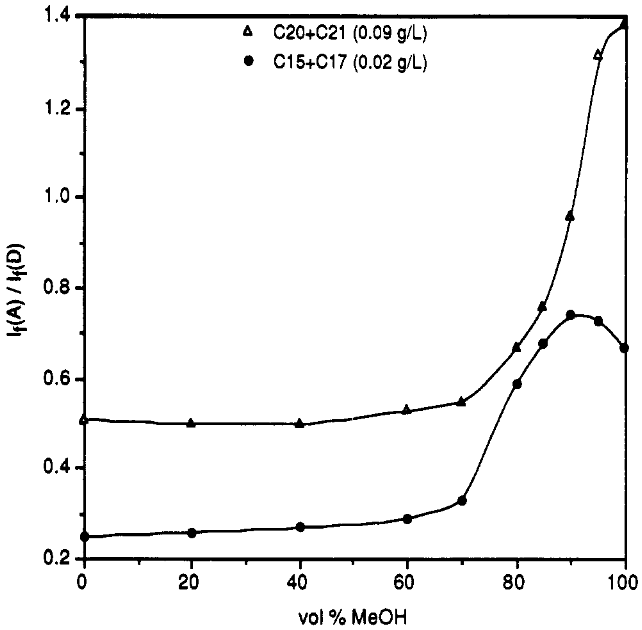


Figure 2. $I_f(A)/I_d(D)$ evolution as a function of solvent composition in DCE-methanol solutions containing equimolar quantities of phenanthrene and anthracene labeled copolymers: circles, copolymers C-15 and C-17 (0.02 g/L); triangles, copolymers C-20 and C-21 (0.09 g/L).

Fluorescence Measurements. Figure 1a shows the fluorescence spectra of anthracene (C-15) and phenanthrene (C-17) labeled copolymers in DCE. Emission spectra of the phenanthrene and anthracene labeled copolymers are very similar to those of the model compounds, 5-methyl-3-(9-phenanthryl)-3-phenylheptan-1-ol and 2-methylanthracene, respectively. The fluorescence spectra of equimolar mixtures of C-15 and C-17 copolymers in DCE and in 10/90 vol % DCE-methanol solvent mixture are presented in Figure 1b. In DCE which is a good solvent for both blocks we do not see any significant energy transfer. When the mixture of C-15 and C-17 copolymers in DCE is irradiated by the 299-nm light, we observe a small increase in the emission intensity at 405 nm (Figure 1b, left curve) as compared to that of the phenanthrene labeled C-15 copolymer (Figure 1a, left curve). This can be explained by the fact that the absorption of the anthracene at 299 nm is very small but not zero. We verify that this increase was due to the anthracene emission. The right curve in Figure 1b shows what happens when a solvent mixture contains large amounts of a PEO selective solvent (such as a 10/90 vol % DCE-methanol mixture). In this case, the donor and acceptor groups approach each other (micelle formation) and the energy transfer becomes evident as the phenanthrene emission intensity (maximum at 370 nm) decreases and, at the same time, the anthracene emission intensity increases (maximum at 425 nm). In our experiments, we used the ratio of anthracene emission intensity at 425 nm to that of phenanthrene at 370 nm to examine the NRET efficiency as a function of the solvent mixture composition. The intensity of anthracene emission was measured at 425 nm rather than 405 nm in order to make the overlap of the donor and acceptor emission spectra as small as possible.

It is important to note that there are no significant spectral shifts in the anthracene or phenanthrene emission due to changes in the solvent mixture compositions (in both DCE-methanol and THF-methanol systems).

Figures 2 and 3 show that the ratio $I_f(A)/I_f(D)$ depends strongly on the solvent composition. In mixtures rich in good solvent for both blocks (THF or DCE) the copolymer is molecularly dissolved (unimers) and we do not observe any significant energy transfer due to the micelle formation.[22] As the solvent mixture becomes richer in a PEO selective solvent, e.g. when the solvent mixture contains about 75 vol % of methanol, the copolymer chains start to associate and the $I_f(A)/I_f(D)$ ratio increases sharply. In organic solvent mixtures, the relation between the onset of the micelle formation and the copolymer composition is not well-defined. The higher PEO content in the block copolymer seems to favor the micelle formation at higher PEO selective solvent content. Our results appear to be in very good agreement with the results of Rodrigues et al.[23] who studied the PS-PEO diblock copolymers labeled by a naphthalene or pyrene chromophore in DCE-methanol solvent mixtures.

A full explanation of the behavior of the PS-PEO block copolymers in organic solvent-water systems (such as THF-water) is rather difficult. Even at high water

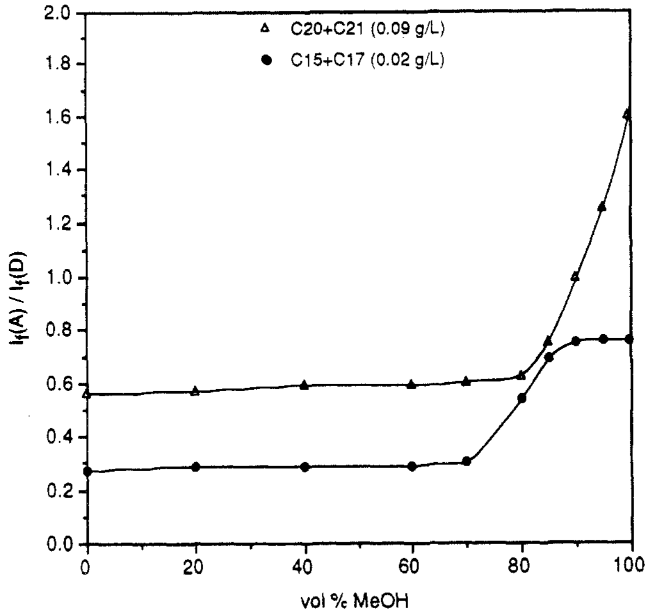


Figure 3. $I_f(A)/I_f(D)$ evolution as a function of solvent composition in THF–methanol solutions containing equimolar quantities of phenanthrene and anthracene labeled copolymers: circles, copolymers C-15 and C-17 (0.02 g/L); triangles, copolymers C-20 and C-21 (0.09 g/L).

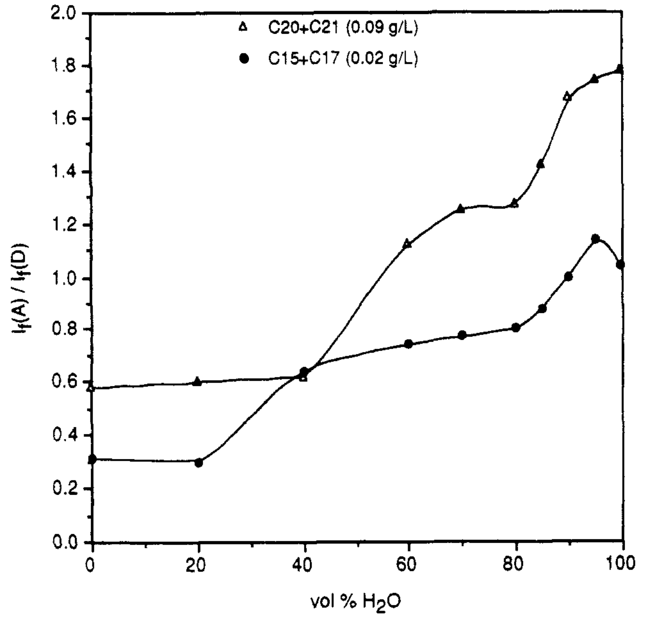


Figure 4. $I_f(A)/I_f(D)$ evolution as a function of solvent composition in THF–water solutions containing equimolar quantities of phenanthrene and anthracene labeled copolymers: circles, copolymers C-15 and C-17 (0.02 g/L); triangles, copolymers C-20 and C-21 (0.09 g/L).

contents the PS core is probably plasticized by the organic solvent. In the THF–water system (Figure 4) we can clearly distinguish two different transitions. The first one which is observed at higher water contents (around 80 vol %) might correspond to the micellization process in analogy to the phenomena observed in organic solvent systems (DCE–methanol or THF–methanol, Figures 2 and 3). We suppose that the second one which appears at much lower water contents (ca. 20–40 vol %) can be attributed to the aggregation behavior of the PEO chains in water containing solutions. This seems reasonable as there are numerous reports in the literature showing that in aqueous solutions the clustering of PEO molecules occurs.[24]

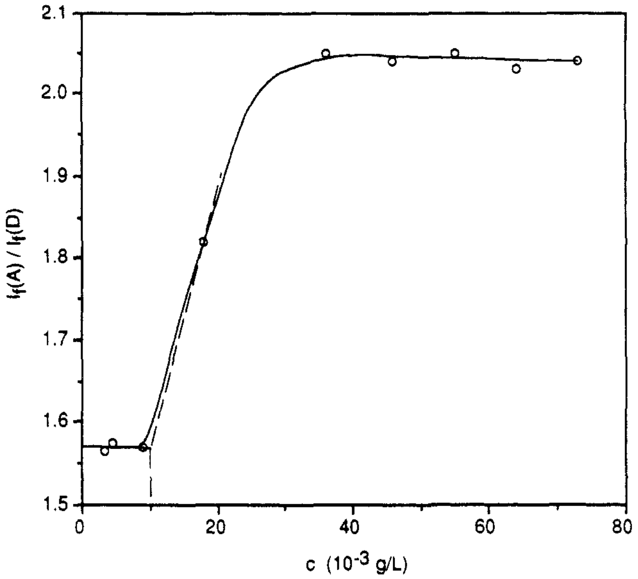


Figure 5. $I_f(A)/I_f(D)$ evolution as a function of copolymer concentration in water solution. The solution contains equimolar quantities of C-20 and C-21 copolymers.

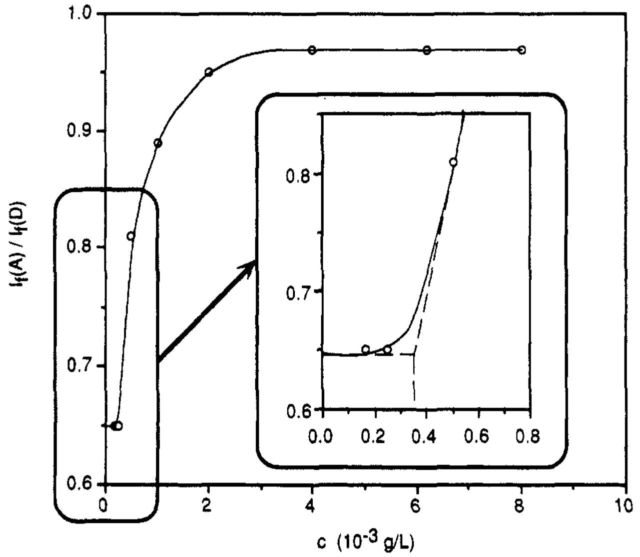


Figure 6. $I_f(A)/I_f(D)$ evolution as a function of copolymer concentration in water solution. The solution contains equimolar quantities of C-15 and C-17 copolymers.

If the concept of the CMC is well-defined for low molecular weight surfactants, the situation is more complicated with block copolymers because of their molecular weight and composition polydispersity. In aqueous solutions the increase of the $I_f(A)/I_f(D)$ ratio with the copolymer concentration reflects the onset of the macromolecular chain association. At low concentrations the copolymer chains are molecularly dispersed and we do not observe any important energy transfer. When the chains possessing donor and acceptor groups approach each other to form micelles (at the CMC) we observe a sharp increase in the NRET efficiency (Figures 5 and 6). We have chosen the beginning of this increase to estimate the CMC values by the tangent method. For the copolymer pairs C-15/C-17 and C-20/C-21 we find the CMC values 0.000 35 g/L (1.4×10^{-8} M) and 0.01 g/L (9×10^{-8} M), respectively. We note that the PS–PEO block copolymer with a higher content of PEO, which corresponds to a better solubility in water, has a higher CMC value. The obtained CMC values provide confidence in our study since they agree reasonably well with the CMC values obtained by the fluorescence probe technique (Zhao et al.[3]).

References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Adv. Colloid Interface Sci.* **1976**, *6*, 201.
(2) Riess, G.; Hurtrez, G.; Bahadur, P. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1985, Vol. 2, p 324.
(3) Zhao, C. L.; Winnik, M. A.; Riess, G.; Croucher, M. D. *Langmuir* **1990**, *6*, 514.
(4) Al-Takrity, E. T. B.; Jenkins, A. D.; Walton, D. R. M. *Makromol. Chem.* **1990**, *191*, 3059, 3069 and 3073.
(5) Chen, L.; Winnik, M. A.; Al-Takrity, E. T. B.; Jenkins, A. D.; Walton, D. R. M. *Makromol. Chem.* **1987**, *188*, 2621.
(6) Quirk, R. P.; Perry, S.; Mendicuti, F.; Mattice, W. L. *Macromolecules* **1988**, *21*, 2294.
(7) Leemans, L.; Fayt, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 1554.
(8) Hruska, Z.; Vuillemin, B.; Riess, G.; Katz, A.; Winnik, M. A. *Makromol. Chem.* **1992**, *193*, 1987.
(9) Rodrigues, K.; Kausch, C. M.; Kim, J.; Quirk, R. P.; Mattice, W. L. *Polym. Bull.* **1991**, *26*, 695.
(10) Ni, S.; Juhué, D.; Moselhy, J.; Wang, Y.; Winnik, M. A. *Macromolecules* **1992**, *25*, 496.
(11) Wang, Y.; Balaji, R.; Quirk, R. P.; Mattice, W. L. *Polym. Bull.* **1992**, *28*, 333.
(12) Caldérara, F.; Hruska, Z.; Hurtrez, G.; Nugay, T.; Riess, G.; Winnik, M. A. *Makromol. Chem.* **1993**, *194*, 1411.
(13) Hruska, Z.; Hurtrez, G.; Walter, S.; Riess, G. *Polym. Commun.* **1992**, *33* (11), 2447.
(14) Förster, Th. *Ann. Phys.* **1948**, *2*, 55.
(15) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York and London, 1973.
(16) Yuki, H.; Hotta, J.; Okamoto, Y.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2659.
(17) Quirk, R. P.; Yin, J.; Guo, S.; Hu, X.; Summers, G.; Kim, J.; Zhu, L.; Schock, L. E. *Makromol. Chem., Makromol. Symp.* **1990**, *32*, 47.
(18) Xu, R.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. *Macromolecules* **1992**, *25*, 644.
(19) Halperin, A. *Macromolecules* **1987**, *20*, 2943.
(20) Hurtrez, G. Ph.D. Thesis, Université de Haute-Alsace, Mulhouse, France, 1992.
(21) Munk, P.; Ramirredy, C.; Tian, M.; Webber, S. E.; Prochazka, K.; Tuzar, Z. *Makromol. Chem., Makromol. Symp.* **1992**, *58*, 195.
(22) The referee has brought to our attention that fact that the differences in $I_f(D)/I_f(A)$ values observed for the C-20/C-21 and C-15/C-17 copolymer pairs in organic solvent mixtures (Figures 2 and 3) or in THF–water mixtures (Figure 4) might be significant. These values are about twice as large for the C-20/C-21 copolymer pair. Reasons leading to this phenomenon are not clear. We used equimolar concentrations of donor and acceptor, and we suppose the 100% labeling efficiency. It cannot be excluded, however, that in the case of C-20/C-21 copolymers (unimers as well as micelles) a long PEO chain protects in some way the chromophore groups so that the quenching of fluorescence emissions by ubiquitous impurities or oxygen molecules is to a certain extent limited. In the future, we intend to examine the emission characteristics of labeled PS–PEO copolymers with a fixed PS block length as a function of the varying PEO block length.
(23) Quirk, R. P.; Kim, J.; Rodrigues, K.; Mattice, W. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 87.
(24) Polik, W. F.; Burchard, W. *Macromolecules* **1983**, *16*, 978.