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Nonradiative Energy Transfer in Chromophore-Tagged PS–PEO Diblock Copolymers

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Summary: Nonradiative energy transfer fluorescence was used to investigate the micelle behavior of polystyrene-*b*-poly(ethylene oxide) diblock copoly- mers tagged with either donor naphthalene or acceptor pyrene in solutions and solid films. The effects of the variation in the solvency and micelle collision frequency caused by changing the total block copolymer concentration and the difference in the micelle concentration between polystyrene–poly(ethylene oxide) block copolymers labeled with two different chromophores on the chain release and exchange of micelles were observed. It was noted that the chain exchange of the polymer micelles is clearly observed when the concentration difference and the total micelle concentration are sufficiently large. In the case of the solid film, the NRET efficiency is increased as the molecular weight of the matrix polystyrene homopolymer added is increased.

Keywords: chain dynamics and release; naphthalene and pyrene chromophore; non-radiative energy transfer; polymer micelles; polystyrene–poly(ethylene oxide) diblock copolymer

Introduction

Polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) block copolymers are known to form spherical micelles in water or selective organic solvents. In a hydrophilic solvent, the hydrophobic PS block of PS-*b*-PEO is located at the micelle core and the hydrophilic PEO block resides at the micelle corona at concentrations above the critical micelle concentration (cmc). Among the several experimental techniques available for studying micellar characteristics, fluorescence spectroscopy is known to be a quite versatile and powerful tool due to its high sensitivity in dilute solution.[1–9] The nonradiative energy transfer (NRET) method has been frequently used to investigate the conformational properties of block copolymers in solution and a few organic materials in thin solid films. As the emission spectrum of a naphthalene chromophore overlaps with the absorption spectrum of a pyrene chromophore, these two chromophores are used as the NRET pair and the excitation energy of the naphthalene molecules is transferred by dipole-dipole interaction to the pyrene molecules within a critical distance called the Förster's radius (R_o) of 28 Å.[11] Extensive efforts have been made to study block copolymer micelles through both experimental investigation[1–10] and theoretical analysis due to their potential applications in such fields as drug delivery systems, enhanced oil recovery, and the stability of colloidal suspensions. However, there have been a few detailed studies on micelle kinetics or dynamic phenomena in dilute solutions.[3–8]

The self-assembly of block copolymers is also observed in solid thin films. If a small amount of a block copolymer is mixed with matrix homopolymers, the block copolymer forms domain like micelles in a selective solvent system. The fluorescence of chromophores inside the domain could conceivably be used to obtain information about the shape and size of the microdomains in solid films.

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In the present study, we report on the release and exchange of micelles in a dilute methanol-rich methanol/1, 2-dichloroethane (DCE) mixed solvent using PS– PEO diblock copolymers tagged with naphthalene (energy donor) and pyrene (energy acceptor) at each block junction point. The effects of the variation in the solvency and micelle collision frequency caused by changing the total block copolymer concentration and the difference in the micelle concentration between the PS–PEO block copolymers on the chain release and exchange of micelles are investigated by employing the NRET method in dilute solution. The NRET efficiency is also investigated in order to understand the effect of the molecular weight of the homopolymer matrix inside the block copolymer/homo polymer mixture on the degree of packing of the domain (PEO block) in the thin solid film.

Experimental Part

Preparation of Chromophore Tagged Block Copolymers

PS–PEO diblock copolymers labeled with naphthalene and pyrene at each block junction were prepared by anionic polymerization. The characteristics of the block copolymers are summarized in Table 1 and the polydispersity indices were found to be quite narrow, i.e. below 1.05.

Preparation of Micelle Solution

An equimolar mixture of naphthalene and pyrene tagged PS–PEO diblock copolymers (5N4 and 5P2) was dissolved in a small quantity of 1, 2-dichloroethane (DCE) (Aldrich), and methanol was added to obtain micelle solutions with several different concentrations. The initial micelle solutions (3.4×10^{-6} M) were prepared so as to have concentrations above the cmc and volume ratios of methanol to DCE of 98:2 and 84:16 were used to investigate the effect of the solvent quality.

Preparation of Solid Film

Equimolar quantities of 5N4 (7.2 mg) and 5P2 (5.5 mg) were mixed with homopolystyrene (1.0 g) (Polymer Source) with three different molecular weights, viz. 2.5 K, 32 K, and 200 K, respectively. Toluene (7 ml) was added to dissolve the polymers and the sample solutions were spin-coated on a glass substrate with a rotation speed of 1,500 rpm. The mixture films were then annealed at 130°C for 24 h in a vacuum.

Static and Dynamic Fluorescence Spectroscopy

All of the photostationary fluorescence spectra were obtained on a RF-5000 spectrofluorophotometer (Shimadzu) at 25°C. Lifetime data were obtained on a K2 phase and modulation fluorometer (ISS) at the same temperature. A xenon arc lamp was used as a standard light source for both machines. *p*-Terphenyl ($\tau = 1.05$ ns) was used as a reference in methanol solution for the analysis of the donor naphthalene lifetimes. The emissions of naphthalene and pyrene were scanned using a 305 nm cut-on filter to separate them from the excitation frequency. The fluorescence lifetimes were determined by a nonlinear least-squares program (ISS187), which minimizes the value of χ^2 for an exponentially good fit. For the NRET experiments, the emission spectra of equimolar mixtures of

Table 1.
Characterization of PS–PEO diblock copolymers used in this study.

Samples	M_n (g/mol)[a)]	PS/PEO (Weight Ratio)[b)]	Chromophores
5N4	9,200	60/40	Naphthalene
5P2	7,000	78/22	Pyrene
5O3	8,400	62/38	None

[a)] M_n (PS) $= 5.1 \times 10^3$ g/mol (by GPC).
[b)] ^{1}H-NMR ($CDCl_3$) analysis.

the naphthalene and pyrene tagged block copolymers were collected using a donor naphthalene excitation wavelength of 290 nm. The emission was collected at 337 and 377 nm, which are the emission peaks for naphthalene and pyrene, respectively, simultaneously for 2 h in the dynamic experiments. The bandwidths were all fixed at 3.0 nm for both excitation and emission.

Dynamic Light Scattering and Viscosity Measurements

The scattered light of an argon ion laser (Model 95 of Lexel Laser Inc.) was measured at an angle of 90° and a wavelength of 514.5 nm in a constant temperature bath fixed at 25°C. The hydrodynamic diameter (D_H) of the PS–PEO diblock copolymer micelles was calculated using the Stokes-Einstein equation; $D_H = k_B T/3\pi\eta D$ where k_B is the Boltzman constant, T is the absolute temperature, η is the solvent viscosity, and D is the diffusion coefficient. The viscosity was measured on the chromophore-free polymer using an Ubbelohde viscometer in a constant temperature bath at 25°C. The aggregation number of the micelles was calculated using an equation for spherical particles; $[\eta] = 10\pi\ NR_H^3/3N_{agg}M_n$ where $[\eta]$ is the intrinsic viscosity of the block copolymer micelles, N is the Avogadro number, and M_n is the molecular weight of the polymer forming the micelle. The solvent ratio of methanol/DCE in this experiment was also 98:2 by volume.

Results and Discussion

Micelle Characterization

The cmc of the PS–PEO block copolymers in the methanol/DEC mixed solvent was determined to be 3.2×10^{-7} M and hydrodynamic diameters of micelles were 80∼100 nm using fluorescence and dynamic light scattering experiments, as shown in Table 2. Viscosity was measured on six different concentrations, which showed an intrinsic viscosity of 726 mL/g and an aggregation number of 94 polymer units per one micelle.

Table 2.
Basic characterization of micelles prepared in present study.[a]

Polymer	D_H	cmc
	mm	M
5P2	84	–
5N4	96	–
Equimolar mixture of 5P2 and 5N4	84	3.2×10^{-7}

[a] Volume ratios of methanol/DCE mixed solvent are all 98/2.

The lifetime measurements made by the phase-modulation device provide clearer information about the quantitative relationship between the micelles and unimers in the dilute micellar solution. Table 3 indicates the lifetimes of the tagged naphthalene when the concentration is above the cmc. As only 5N4 diblock copolymers without 5P2 polymers exist in the micellar and unimer phase, no NRET occurs. The two different lifetimes represent the proportion of the unimers and micelles, respectively. It is thought that the naphthalene chromophores existing in the unimer chains of lower microviscosity have shorter lifetimes than those trapped in the micellar phase. When the polymer concentration is near the cmc, it is observed that the fraction (0.742) of the unimer is larger than the fraction (0.258) of the micelle.

Table 4 indicates the lifetimes of the tagged naphthalene when NRET appears at a concentration above the cmc. In this case, although two kinds of chromophores exist in the micelle solution, the chromophores are actually located in four kinds of phases (i.e. the donor and acceptor of the unimer and micelle phases, respectively). The lifetimes in Table 4 present the

Table 3.
Lifetimes of tagged naphthalene without NRET.

$V_{Methanol}$:V_{DCE}	$C^{a)}$	$\tau_i^{b)}$	$f_N^{c)}$	χ^2
	(10^{-6} M)	nsec		
98:2	4.36	39.3 91.7	0.742 0.258	2.38

[a] Total polymer concentration.
[b] Lifetimes of naphthalene.
[c] Fraction of emission spectrum corresponding to each lifetime.

Table 4.
Lifetimes of donor naphthalene with NRET.

$V_{Methanol}$:V_{DCE}	$C^{a)}$ (10^{-6} M)	$\tau_i^{b)}$ nsec	$f_N^{c)}$	χ^2
98:2	12.3	40.6	0.142	3.54
	6.32	55.8	0.304	6.01
84:16	12.3	28.9	0.268	6.92
	6.32	29.2	0.343	4.98

[a] Total polymer concentration.
[b] Lifetimes of naphthalene.
[c] Fraction of emission spectrum corresponding to each lifetime.

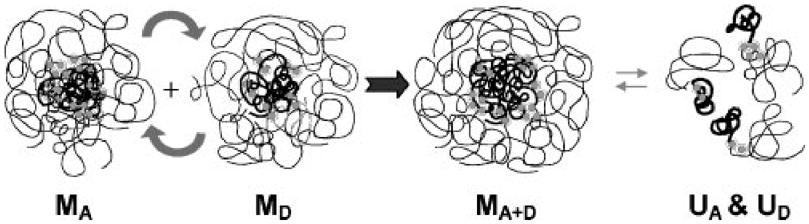
averaged data of the tagged naphthalenes existing as unimers and those that did not transfer their excited energy in the micellar phase. In the case where the concentration is high, viz. 12.3×10^{-6} M, the lifetime value is decreased from 55.8 to 40.6 nsec, as expected. In the case where the better solvent is used (e.g. methanol:DCE = 84:16 by vol.), the lifetime value is low and almost independent of the variation of the concentration. The lifetime data in Table 4 also show that the chromophores in the relatively good methanol/DCE solvent are more flexible and those in the micelle core phase are looser than those in the poorer solvent.

Chain Release as a Function of Solvency

The experimental scheme concerning the chain release of the block copolymer micelles is illustrated in the right part of Scheme 1. A micellar batch solution, whose concentration is 3.4×10^{-6} M, containing an equimolar mixture of the 5P2 and 5N4 block copolymers, was prepared. The MeOH/DCE mixed solvent had an initial volume ratio of 98/2 and was diluted with three solvents, viz. pure methanol, methanol/DCE (70/30 v/v) mixed solvent, and methanol/DCE (50/50 v/v) mixed solvent. Figure 1(a) shows the resulting photostationary fluorescence emissions of naphthalene and pyrene obtained after exciting the naphthalene chromophores for the NRET experiment. The fluorescence data show the different degrees of chain release according to the solvent quality. When the solvency for both blocks is better, the pyrene peak resulting from NRET is more noticeably reduced. This result implies that the block copolymer chains which are aggregated into micelles are released to form unimers by the addition of the good cosolvent and that the chain release of the block copolymer micelle is more efficient in the good solvent. Figure 1(b) shows the *in-situ* time-dependant emissions of naphthalene (337 nm) and pyrene (377 nm) observed while exciting the naphthalene chromophores. The pyrene emission is the highest in the case where pure methanol solvent is used, however, the NRET phenomena is not observed when the methanol/DCE (50/50 v/v) mixed solvent is used, as shown in Figure 1(b). This result also demonstrates that the number of micelles is decreased and the chain release is more efficient in the good solvent. The nearly constant dynamic data obtained from the beginning point show that the chain release rate is quite fast within few milliseconds and that the equilibrium state is established as soon as the diluent solvent is added.

Chain Exchange Between Polymeric Micelles

The experimental scheme for the chain exchange between the polymer micelles is



Scheme 1.
Experimental scheme depicting the chain release and exchange of polymer micelles containing donor-acceptor chromophores in dilute solution.

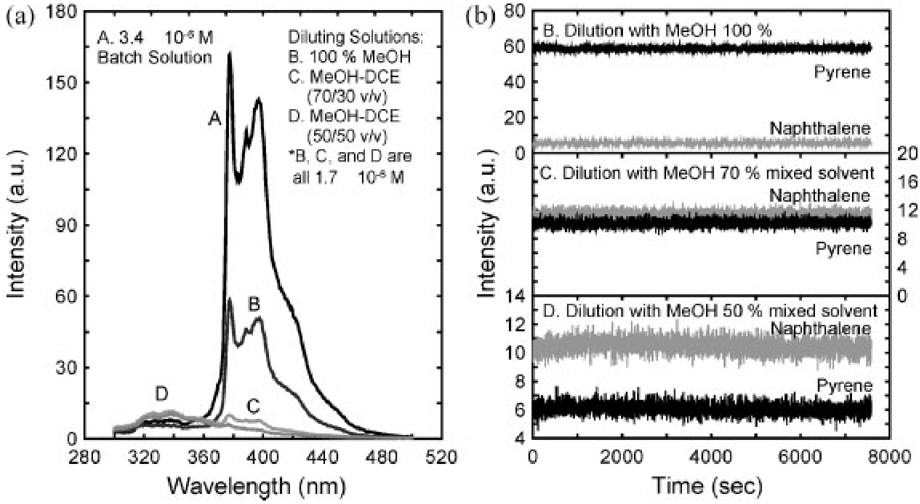


Figure 1.

(a) Photostationary and (b) *in-situ* time-dependent naphthalene (donor) and pyrene (acceptor) emission spectra of equimolar mixture of 5P2 and 5N4 according to solvent quality. The excitation wavelength is fixed at 290 nm for all of the experiments and emission wavelengths for the dynamic measurements were set at 337 and 377 nm.

illustrated in Scheme 1. Figure 2 shows the time-dependent naphthalene intensity after adding the different concentrations of 5P2 micelle solutions to the 5N4 micelle solution at a concentration of 6×10^{-6} M. The volume ratios of the methanol/DCE mixed solvent are all 98/2 and the volumes of all the micelle solution are same. As the concentration of the 5P2 solution is increased, the naphthalene emission is rapidly decreased (A, B, and C in Figure 2), however, when the concentration of the 5P2 solution is above a certain threshold, the naphthalene decay rates become lower again (D and E in Figure 2). It is thought that the difference in concentration between the two micellar solutions causes the micelles in the more highly concentrated solution to be released more easily than those in the lower concentration solution, and that the unimers released from the micelles rearrange and enter into a new micelle. Figure 2 also suggests that reducing the concentration difference between the two micellar solutions causes the release rates to diminish. As the concentration of the micellar solutions is very low in this experiment, it is thought that the effect of the frequency of the collisions resulting from the total micellar concentration is negligible.

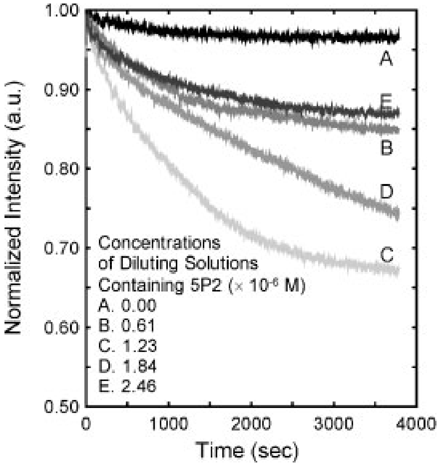


Figure 2.

Naphthalene donor emission intensity as a function of time after adding the diluting solutions containing 5P2 with different concentrations. The initial concentration of the basis solution containing 5N4 is 6×10^{-6} M. The volume ratios of the methanol/DCE mixed solvent are all 98/2.

To determine the specific factors affecting the chain exchange of the polymer micelles, the NRET phenomena were investigated according to the molar ratio and the

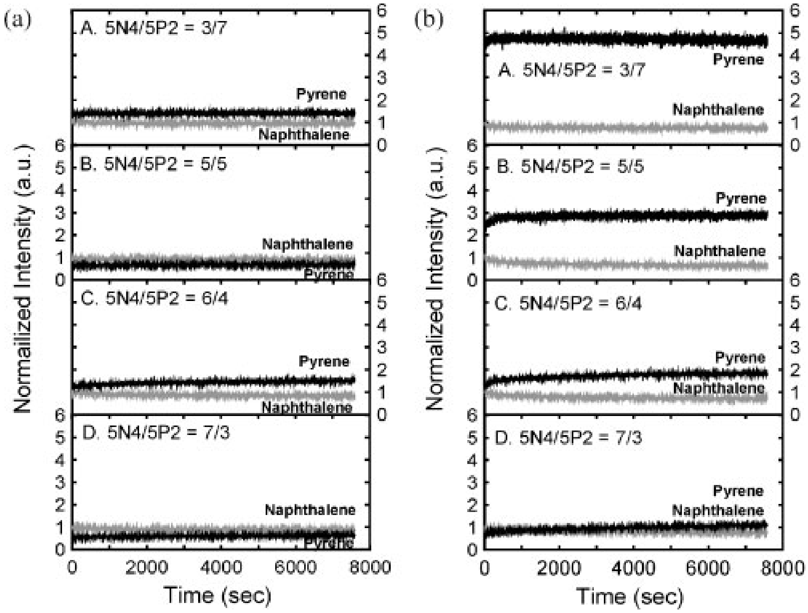


Figure 3.
Time-dependent naphthalene (donor) and pyrene (acceptor) emission spectra according to the molar ratio of 5N4 and 5P2. The total concentrations are constant at 3×10^{-6} M (a) and 7×10^{-6} M (b).

total concentration of the 5P2 and 5N4 mixed micelle solution. Figure 3(a) shows that the effect on the chain exchange is not so high in the dilute solution, such as that with a total concentration of 3×10^{-6} M (*i.e.* the effects of the concentration differences and collision frequency is not very noticeable.) The NRET spectra in Figure 3(b) taken at a higher total concentration of 7×10^{-6} M clearly show that the micellar collision frequency increases as the total concentration is increased. The average equilibration times of the naphthalene emission in Figure 3(b) are determined to be (A) 1,000.5, (B) 1,336.8, (C) 2,764.5, and (D) 9,704.3 s from the equation $I = I_0 + A_1\exp(t/\tau_1) + A_2\exp(t/\tau_2)$ and $<\tau> = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$. It is thought that, as the total concentration is increased, the number of exchangeable micelle chains is increased and the 5P2 chains, which are somewhat shorter than the 5N4 ones, move more rapidly. About the intensity differences between the pyrene and naphthalene emissions of the same molar ratio differences (i.e. comparison between 7:3 and 3:7), it is thought that the quantum yield of pyrene attached to the 5P2 chains is relatively higher than that of naphthalene and, as the number of movable 5P2 chains is increased, the probability of new micelles being formed with the 5N4 unimers is also increased.

Energy Transfer in Solid Film

The NRET method was also applied to solid films in order to investigate the effect of the molecular weight of the homopolymer on the micelle (domain) formation of block copolymers in a block/homo polymer mixture. The molecular weights of the polystyrene homopolymer used in the present study were 2.5 K, 32 K, and 200 K. As the polystyrene molecular weight is increased from 2.5 K and 32 K to 200 K, the energy transfer efficiency (I_A/I_D) is increased from 2.09 and 2.43 to 2.67, respectively, as shown in Figure 6. It is thought that as the molecular weight is increased, the micelles containing an equimolar mixture of chro-

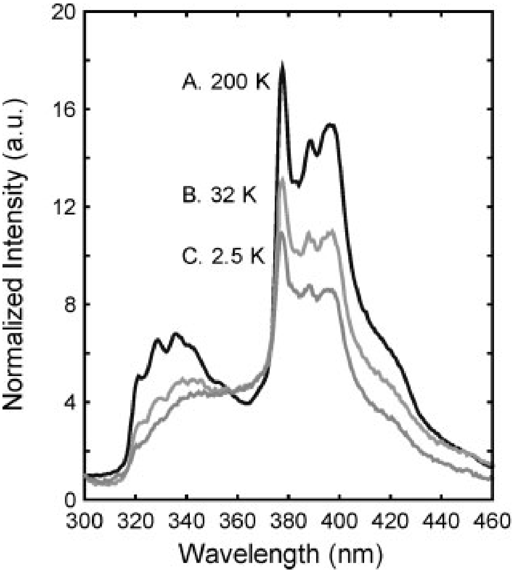


Figure 4.
Variations of naphthalene and pyrene emission spectra according to the molecular weight of the matrix polystyrene homopolymers.

mophores transform from wet-brush micelles, in which the polystyrene penetrates into the core region of the micelle, to dry-brush micelles where there is no appreciable penetration of the homopolymer, thus tightening up the micelles.

Conclusions

The nonradiative energy transfer of polystyrene-poly(ethylene oxide) block copolymers tagged with either naphthalene or pyrene at the block junction point was successfully observed in dilute solution and solid films. The lifetime of the naphthalene emission in a dilute solution suggested that micelles and unimers coexist with a certain ratio which is dependent on the solvent quality. The dynamic and static emissions of naphthalene, which transferred its energy to pyrene, were also investigated, in order to determine the effect of the variation of the outer conditions, such as the solvent quality, the difference in concentration between the respective chromophore-tagged micelle solutions, and the total polymer concentration, on the chain release and exchange of micelles. In the solid film, the naphthalene and pyrene emissions brought about through energy transfer were also observed, in order to determine the effect of the molecular weight on the domain packing of the block copolymers, using three kinds of polystyrene homopolymers as the matrix polymer. From these results, it was successfully demonstrated that NRET is a useful tool to study nanostructures as well as the chain dynamics of polymeric micelles.

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