Fluorescence Studies of Polymer Micelles: Intracoil Direct Energy Transfer

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ABSTRACT: Doubly tagged polystyrene (PS) or polystyrene–poly(methacrylic acid) (PS–PMA) polymers have been prepared by anionic polymerization. These polymers may be represented by the structure N-PS$_n$-A or N-PS$_n$-A–PMA where N and A represent a naphthalene or anthracene chromophore and n is the degree of polymerization (n = 40 or 283). Direct energy transfer (DET) from the N to the A group has been studied in micelles composed entirely of the tagged micelle or mixed micelles which contain ca. 1 wt % of tagged polymer. While DET clearly demonstrated the different end-to-end distances of the two PS segments, very strong environment effects on the fluorescence properties of both chromophores frustrated efforts to elucidate any modification in the end-to-end distribution in going from homogeneous solution to PS films to micelle structures. On the other hand, these complexities demonstrated that there is considerable heterogeneity present in an amphiphilic polymer micelle in mixed organic and aqueous solvents in which it equilibrates. These complexities are also a function of the details of the micelle preparation. Thus the use of fluorescently tagged polymers has permitted a much more molecular view of the process of polymer micelle formation.

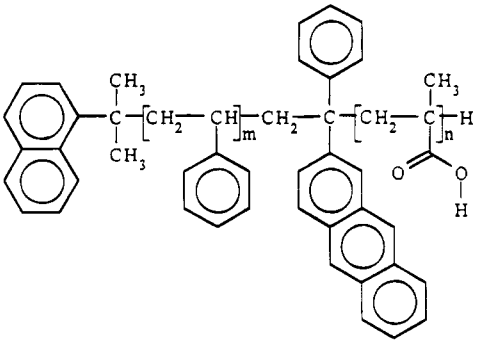
Introduction

In recent years considerable effort has been directed to the study of block copolymer micelles. Such self-assembling systems have potential applications in many areas including solar energy conversion, drug delivery,[1] and surface modification.[2] This interest has also produced a variety of methods to fluorescently label the constituent polymers of a micelle.[3] The judicious use of fluorescence techniques can elucidate the process of micelle formation and the structure of the resultant micelle on a molecular level. Structural information on this level is a prerequisite for rational design of polymer micelle.

When diblock copolymers consisting of a hydrophobic block and a hydrophilic block are allowed to self-assemble in an aqueous environment, it is assumed that the hydrophobic blocks of the individual copolymers will aggregate to form a micelle core while the hydrophilic blocks extend into solution to form the shell. It is our intent to use energy transfer methods to understand the formation and structure of the micelle core by observing the collapse and aggregation of the core-forming blocks. As will be discussed, the change in the fluorescence spectra has also demonstrated that during the process of micelle preparation by dialysis the micelle is highly disordered and similar to a high-concentration solution of polymer in an organic solvent, despite the presence of micelles according to light scattering.

The doubly labeled, diblock copolymer indicated in Chart 1 was chosen as a probe to be placed within an otherwise well-characterized, unlabeled micelle. We also have available the analogous polymer without the poly(methacrylic acid) (PMA) segment (i.e., N-PS$_n$-A) for comparison. The naphthalene and anthracene are located on opposite ends of the polystyrene (PS) block and act as a donor–acceptor pair, able to undergo direct energy transfer (DET) by the well-known Förster dipole–dipole mechanism. Our presumption is that this labeled copolymer acts representatively of the micelle-forming

Chart 1



copolymers (unimers), that is, if the hydrophobic blocks collapse, the tagged unimer hydrophobic blocks will likewise collapse, resulting in an observable increase in DET. We have found that the naphthyl probe fluorescence spectrum and lifetime are very sensitive to the environment such that the naphthalene fluorescence spectrum has provided insight to the disordered nature of the swollen micelle in dioxane:water mixtures.

Experimental Section

Materials. All materials listed here were prepared for use in the polymerization or dialysis procedures. Both styrene (Aldrich) and *tert*-butyl methacrylate (Rohm Tech Monomers) were each passed through an Al_2O_3 column to remove the inhibitor. Tetrahydrofuran (THF), styrene, and *tert*-butyl methacrylate were stirred over and cryodistilled from calcium hydride (−40 mesh). THF was twice distilled from a purple sodium/naphthalene complex. Styrene was treated with dibutyl magnesium, and *tert*-butyl methacrylate was treated with diisobutyl aluminum hydride and triethyl aluminum slightly above −78 °C. Each was then cryodistilled directly into modified pressure equalizing dropping funnels and stored under nitrogen. High-purity nitrogen was passed through activated 3 Å molecular sieves, manganese(II) oxide (regenerated as needed by passing hydrogen through the column at 350 °C), and calcium hydride. Methanol, used for termination, was cryodistilled into a similar funnel and stored under nitrogen. Spectroscopic grade 1,4-dioxane (Aldrich; referred to as dioxane hereafter) was used as received. Dialysis tubing (Spectra/Por) was washed with deionized water before use.

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Initiator Synthesis. Arylmethide anions have been prepared by a variety of methods and have been used as polymerization initiators with good results.[4] Although Pearson et al.[5] have shown that the product of the reaction of α-methoxymethylnaphthalene with potassium in THF at 25 °C is diamagnetic, this naphthylmethide anion did not initiate the polymerization of styrene sufficiently rapidly in our case to produce a satisfactorily monodisperse PS sample. The naphthalene analog of cumyl potassium, described below, was used instead as the initiator to label the PS free end.

1-(1-Hydroxy-1-methylethyl)naphthalene (1). A 10 mL (65.8 mmol) quantity of 1-acetonaphthone was dissolved in 150 mL of diethyl ether in a 500 mL, two-neck round bottom flask equipped with a pressure equalizing dropping funnel and fitted with a rubber septum and a protected reflux condenser. A 138 mL (98 mmol) quantity of 1.4 M methyllithium in ether (Aldrich) was transferred to the funnel by use of a cannula and nitrogen pressure. This was slowly added to the stirred ketone over a 20 min period. A light green color indicated an excess of methyllithium. This was refluxed for an additional 1 h, and then the reaction was carefully quenched with an excess of water. The ether layer was made acidic using HCl, neutralized with $NaHCO_3$, dried using $MgSO_4$, and filtered. After the solvent was removed, the crude product was recrystallized from benzene, filtered, and washed with cold pentane to yield white, fibrous crystals (>98%), mp 81–86 °C. ^{1}H NMR (acetone-d_6): δ 9.01 (m, 1 H, aromatic), 7.95 (m, 1 H, aromatic), 7.82 (d, J = 10.6 Hz, 1 H, aromatic), 7.68 (d, J = 10.3 Hz, 1 H, aromatic), 7.50 (m, 3 H, aromatic), 4.30 (s, 1 H, -OH), 1.84 (s, 6 H, -CH_3).

1-(1-Methoxy-1-methylethyl)naphthalene (2). A 12 g (64.4 mmol) quantity of **1** was dissolved in 300 mL of THF employing the above setup without the funnel. About 2 g of NaH was slowly added to the stirred solution. An excess was added once the H_2 evolution ceased such that solid NaH settled on the bottom of the flask. A 8.1 mL (130 mmol) quantity of methyl iodide was added at once, and the mixture was stirred at room temperature overnight. (Methyl tosylate works as well, but the excess is difficult to remove.) This mixture was then acidified, neutralized, and isolated as above. The crude, oily product was put through an Al_2O_3 column, eluted with hexane to remove the starting material (>90% yield). ^{1}H NMR (acetone-d_6): δ 8.95 (m, 1 H, aromatic), 7.84 (m, 2 H, aromatic), 7.44 (m, 4 H, aromatic), 2.95 (s, 3 H, -OCH_3), 1.73 (s, 6 H, -CH_3). MS (CI+): m/z 200 (M^+), 185 ($M^+ - CH_3$), 169 ($M^+ - OCH_3$).

One caveat about the preparation of **2** is that the reaction temperature must be kept low (ca. 25 °C), and no distillation of the product (initiator precursor) should be attempted. **2** readily eliminates methanol at elevated temperatures. The result is an impurity (1-methyl-1-naphthylethylene) that can possibly add to the PS chain. **2** was reacted just as its cumyl analog to form the initiator. Potassium, freshly cut under mineral oil and washed with hexane, was placed in the reaction vessel and sublimed to form a mirror. THF was distilled in and **2** added. A deep red-orange color appeared immediately. The solution was stirred overnight at room temperature and then filtered and transferred to a similar pressure equalizing dropping funnel. A fraction of this was titrated with acetanilide to calculate the molarity. Another portion was terminated with degassed methanol for structural analysis. ^{1}H NMR (acetone-d_6): δ 8.18 (m, 1 H, aromatic), 7.90 (m, 1 H, aromatic), 7.74 (m, 1 H, aromatic), 7.50 (m, 4 H, aromatic), 3.78 (m, 1 H, -CH), 1.38 (d, 6 H, CH_3). MS (CI^+): m/z 170 (M^+), 155 ($M^- - CH_3$), 140, 129 ($M^+ - CH(CH_3)_2$).

Monomer Synthesis. This monomer, 1-(2-anthryl)-1-phenylethylene (**3**), has been described previously[6] but is presented here in brief to emphasize slight changes made to the procedure. A 5.0 g (22.7 mmol) quantity of 2-acetylanthracene from the acylation reaction of anthracene and acetic anhydride[7] was dissolved in 85 mL of THF and placed in a three-neck, round bottom flask equipped with a septum, protected condenser, and pressure equalizing dropping funnel. A 15.13 mL (45.4 mmol) quantity of 3.0 M phenylmagnesium bromide (Aldrich) was transferred by cannula to the funnel and slowly added to the ketone. This was refluxed for an additional 30 min and then separated, acidified, neutralized, and dried as before. The solvent was removed, and the remaining solid was refluxed in acetic acid for 15 min. The acetic acid was removed by rotoevaporation and the residue put through an Al_2O_3 column eluted with hexane. A final recrystallization from ethanol yielded 1.5 g of yellow, crystal plates, mp 179–181 °C (lit.[6] mp 178–180 °C). A 1.25 mol excess of **3**/mol of initiator was dissolved in THF and transferred, using a cannula, to a dropping funnel. ^{1}H NMR (chloroform-d_3): δ 8.39 (s, 1 H, aromatic), 8.36 (s, 1 H, aromatic), 7.96 (m, 4 H, aromatic), 7.44 (m, 8 H, aromatic), 5.67 (d, J = 0.7875 Hz, 1 H, =CH_2), 5.56 (d, J = 0.7775 Hz, 1 H, =CH_2).

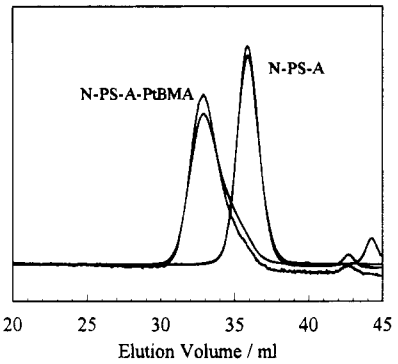


Figure 1. Gel permeation chromatography of N-PS-A and N-PS-A–PtBMA. Both differential refractive index (with higher maxima in plot) and fluorescence detection (λ_{ex} = 340 nm, λ_{em} = 420 nm) are shown.

Copolymer Synthesis and Characterization. It is necessary in a study such as this to assure that each polymer contains a single donor and acceptor pair. Winnik, Quirk, and others[6,8] have demonstrated the utility of 1-aryl-1-phenylethylene compounds, which reliably place a single aryl group at the junction of the PS and the poly(*tert*-butyl methacrylate) (PtBMA) blocks. The PtBMA block readily undergoes an acid-catalyzed elimination reaction (hydrolysis) which produces isobutylene and a water soluble PMA block. A simple structural substitution using naphthalene in place of the phenyl group in cumyl methyl ether was chosen as the initiator precursor, **2**. All indications suggest that **2**, when reacted with potassium, behaves similarly to cumyl potassium, placing a single naphthalene at the PS free end. Two types of polymers were synthesized for this study: one having a low molecular weight PS block, N-PS_{40}-A–PMA (degree of polymerization for the styrene block is 40), and another having a much higher molecular weight PS block, N-PS_{283}-A–PMA (DP_{PS} = 283). Both PMA blocks were comparable in DP to their respective PS blocks (cf. Table 1). This method of polymerization has been described previously.[9]

THF, after being distilled into the completely assembled and flame-treated reactor, was purged with nitrogen and treated with a small amount of the initiator to react with any remaining impurities that would terminate or otherwise alter the polymerization. The solution temperature was lowered to −78 °C, and the calculated amounts of the initiator and monomers were then added in turn. Each monomer was added dropwise and allowed to react for 20–30 min. A 1.25 molar excess of **3** was used to ensure complete labeling. The reaction flask was set up to allow an aliquot to be withdrawn after the initial PS block was formed. The aliquot was terminated with methanol and used for molecular weight determination. Removal of this aliquot before the addition of **3** produces a naphthalene-end labeled PS homopolymer (N-PS). Removal of this sample after the addition of **3** produced a PS homopolymer (N-PS-A) identical with the PS block of the final copolymer. The final copolymer was also terminated with a small amount of methanol and precipitated in 60% methanol/water. As shown in Figure 1, the precipitation in methanol/water was adequate to remove most of the excess **3**. The tailing to lower molecular weights for the N-PS-A–PtBMA is expected for sequential anionic polymerization but could also represent a

Table 1. GPC Results for Diblock Copolymer Synthesis

	RI[a]		fluorescence[b]	
polymer	$\langle M\rangle_n$[c]	PD	$\langle M\rangle_n$	PD
N-PS	7300	1.03		
N-PS_{40}-A	4200	1.06	4200	1.06
N-PS_{40}-A−PtBMA[d]	11 500	1.10	11 500	1.12
N-PS_{283}-A	29 500	1.03	29 500	1.04
N-PS_{283}-A−PtBMA[d]	53 000	1.12	51 000	1.13
PS	26 800	1.06		
Ps−PtBMA[d]	48 100	1.06		

[a] Differential refractive index detection. [b] Fluorescence detection: λ_{ex} = 340 nm filter, λ_{em} = 420 monochrometer. [c] Number-average molecular weight (g/mol) and polydispersity: PD = $\langle M\rangle_w/\langle M\rangle_n$, computed from the PS calibration curve and taking the RI signal to be proportional to the concentration of polymer, as is standard procedure. [d] The molecular weight of the PtBMA polymers was determined using the PS calibration curve such that these values cannot be considered absolute.

small component (ca. 5%) of N-PS-A that did not propagate. The copolymer was allowed to air-dry overnight and fully dry under vacuum at room temperature. Other unlabeled copolymers, polystyrene-*block*-poly(*tert*-butyl methacrylate), needed for this study were synthesized by the same procedure, using cumyl potassium for the initiator and omitting **3**. No adverse side reactions were observed due to the later omission. In fact, it has ceased to be a practice in our laboratories to use the 1,1-diphenylethylene to modify the reactivity of the polystyryl anion. The *tert*-butyl group of the methacrylate monomer may be bulky enough such that the initiation by the polystyryl anion occurs without nucleophilic attack of the carbonyl carbon.

To hydrolyze the PtBMA block, each copolymer was dissolved in a minimum of dioxane in a two-neck, round bottom flask equipped with a protected reflux column and a purge valve; 2 mol equiv of HCl/ester group was added and the system flushed with nitrogen. The solution was brought to a slight reflux (80−90 °C) and allowed to react for 5 h. The solution was dried with $MgSO_4$, filtered, and precipitated in cold hexane. The bulk of the solvent was decanted and the remaining mixture filtered. This further removed any trace amounts of **3** from the polymer sample that might interfere with the fluorescence results. The polymer was removed from the filter while still wet and allowed to dry overnight. Each polymer or polymer mixture was then freeze-dried from 1,4-dioxane.

The GPC system used consisted of four Waters Millipore μStyragel columns (10^5, 10^4, 10^3, 500 Å) using both differential refractive index and fluorescence detection (filter, λ_{ex} = 340 nm; monochrometer, λ_{em} = 420 nm). The analog output of both detectors was collected on a Hewlett-Packard computer, transferred, and analyzed by software written for an ×86-based computer. THF was used for the mobile phase at a flow rate of 1.5 mL/min. Polystyrene standards (Scientific Polymer Products) were used for calibration. The GPC results for the various aliquots and copolymers described above are collected in Table 1.

All NMR measurements were performed on a Bruker AC-250 spectrometer (250 MHz). The spectra were referenced to residual solvent protons. A ratio of the area under the aromatic region and the *tert*-butyl peak for the unhydrolyzed sample is compared to the ratio derived from the GPC data (Figure 1). This comparison shows the mole fraction of styrene per unimer (x) to be as follows: For N-PS_{40}-A−PMA, x_{NMR} = 0.45 and x_{GPC} = 0.42; for N-PS_{283}-A−PMA, x_{NMR} = 0.47 and x_{GPC} = 0.63. The hydrolysis is shown to be complete by the disappearance of the *tert*-butyl peak at δ 1.41 in $CDCl_3$.

UV−vis spectra were taken on a Hewlett-Packard 8451A diode array spectrophotometer. A Beers law calculation, using 2-methylanthracene as a model compound, shows that the number of **3** monomer residues per unimer is 1.078 ± 0.064 for N-PS_{40}-A−PMA and 0.963 ± 0.082 for N-PS_{283}-A−PMA. Absorbance by PS and scattering prohibited a similar calculation for naphthalene.

Micelle Preparation and Characterization. It is essential to obtain a random distribution of the doubly labeled copolymers with the unlabeled copolymers in the micelle. Two methods were used. (1) Copolymer mixtures were mixed as dry solids, dissolved in dioxane, and freeze-dried, and this mixed solid was added to the 80:20 dioxane:water mixture described below. (2) The two polymers were added as dry solids to the 80:20 dioxane:water mixture. In a typical preparation 40 mg of the unlabeled copolymer with a total molecular weight of 48 100 g/mol was mixed with ca. 0.1 mg of the labeled copolymer. The former copolymer formed micelles with an aggregation number[10] of ca. 200 unimers/micelle.

All polymer samples were dissolved initially in 15 mL of 80% 1,4-dioxane/water (the latter was 0.1 M in either LiCl or NaCl), filtered through a 0.45 μm filter, and dialyzed by 10% increments into solutions richer in the aqueous salt solution. The dialysis was carried out using a length of dialysis tubing closed at one end and with the other end modified so that an aliquot could be removed after each dialysis step without allowing dust to contaminate the sample. The assembly was placed in the desired 1,4-dioxane/water mixture, and each step was allowed to proceed for at least 3 h with vigorous stirring of the outer solution.

Quasi-elastic light scattering (QELS) was performed on a Brookhaven BI-2030AT system described elsewhere.[9] All samples were filtered through a 0.45 μm filter before measurement. In all cases, the autocorrelation function was sufficiently monoexponential that a first-order fit of the data was used to compute the hydrodynamic diameter.

Fluorescence Techniques. Steady-state fluorescence and time-correlated single-photon counting have been described in detail elsewhere.[9,11] All samples were measured without removal of atmospheric oxygen. Steady-state fluorescence spectra were measured using a SPEX Fluorolog 2 instrument containing a 450 W Xe lamp, a Hammamatsu R508 photomultiplier, and double-grating monochrometers on both the excitation and emission sides of the sample compartment. The spectral data were collected on a SPEX DM3000 controller unit interfaced with the Fluorolog instrument. All steady-state spectra were corrected for the emission monochrometer/PMT wavelength dependence before calculations.

Time-resolved fluorescence decay measurements were performed by the method of single-photon counting (SPC). The frequency-doubled output of a Nd:YAG laser pumps a Rhodamine 6G dye laser. This output was again doubled resulting in an excitation pulse (λ = 293 nm) with an instrumental response width (fwhm) of 74 ps and a repetition rate of 1.9 MHz. Fluorescence emission was measured using magic angle (54.7°) detection and recorded in a 8192 channel buffer. Software based on the Levenberg−Marquardt minimization method[12] was used to perform the iterative reconvolution to find the best multiexponential fit of the decay data.

Results and Discussion

DET in Homogeneous Solution. The use of sequential, anionic polymerization produces well-defined block copolymers with a narrow distribution of molecular weight and predictable molecular weights (Table 1, Figure 1). The use of a functionalized initiator (**2**) and a single-addition monomer (**3**) labels unimers in a 1:1 ratio which, when isolated, should exhibit intracoil DET uncomplicated by other photophysical processes. The 1-naphthyl and 2-anthryl donor−acceptor pair has an R_0 of ca. 21 Å,[13] which is the characteristic distance between the two chromophores at which DET and all other intrinsic decay processes of the excited state have an equal probability of occurring.

The steady-state fluorescence spectra (λ_{ex} = 293 nm) show both characteristic naphthalene and anthracene emission from N-PS-A (Figure 2). The anthracene emission is a result of both DET and direct excitation. A model compound, 2-methylanthracene in 1,4-dioxane,

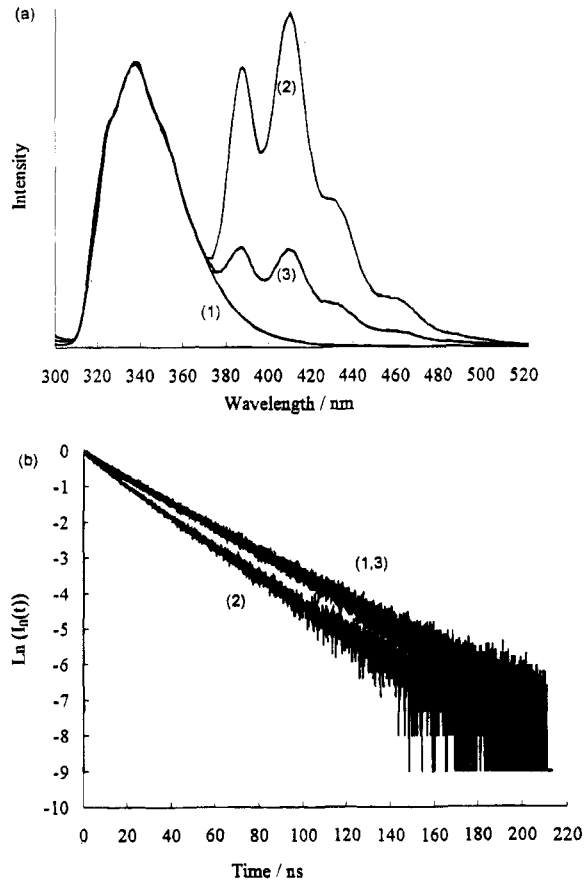


Figure 2. Fluorescence in dioxane solutions of (1) N-PS, (2) N-PS_{40}-A, and (3) N-PS_{283}-A for both steady-state (a) and time-resolved (b) emission (λ_{ex} = 293 nm). The time-resolved emission is observed at 340 nm. The steady-state spectra are scaled to be equal at 340 nm and are not corrected for the instrumental response.

has a non-negligible extinction coefficient at the wavelength for naphthalene excitation ($\epsilon_A(293)$ = 466 M^{-1} cm^{-1}, $\epsilon_N(293)$ = 4229 M^{-1} cm^{-1}). Methods exist for measuring the efficiency of DET, denoted by χ, from steady-state excitation and emission spectra by comparing each to a corresponding absorbance spectrum.[14,15] These techniques require the absorbance of naphthalene at 293 nm to be known precisely. Since micelle solutions exhibit a large amount of light scattering in this region, application of such data analysis is not feasible. Another complication arises from the dialysis procedure. Since it is not a constant volume process, the final micelle concentration is not necessarily the same as the original concentration. This prevents the calculation of predicted absorbances for the individual chromophores from the initial sample weights and volumes.

To gain useful information from the steady-state fluorescence spectra, we chose the following approach. A steady-state emission spectrum was taken of a dilute, equimolar solution (OD_{293} < 0.1) of the two model compounds, 1-methylnaphthalene and 2-methylanthracene in 1,4-dioxane. Assuming similar quantum yields and extinction coefficients for the model compounds and the polymer-bound chromophores, this spectrum should give a reasonable estimate of the relative emission from direct excitation of both chromophores at 293 nm (note that at high dilution DET for the model compounds is eliminated, unlike the polymer). The total area under the fluorescence emission spectrum is the sum of the contributions from each chromophore is given by

$$I = I_N + I_A \tag{1}$$

where

$$I_N = K\phi_N^{mod}P_N \tag{2}$$

$$I_A = K\phi_A^{mod}P_A \tag{3}$$

ϕ_N^{mod} and ϕ_A^{mod} are the fluorescence quantum yields, and P_N and P_A are the fractions of the light adsorbed by the naphthalene and anthracene model compounds, respectively. K is a unitless, instrumental constant. For the case in which DET occurs (denoted by primes) between the two chromophores on the polymer, the area under the fluorescence spectrum is given by[16]

$$I' = I'_N + I'_A \tag{4}$$

where

$$I'_N = K'\phi_N^{poly}[(1 - \chi_{SS})P_N] \tag{5}$$

$$I'_A = K'\phi_A^{sens}(P_A + \chi_{SS}P_N) \tag{6}$$

and χ_{SS} is the efficiency of DET. All spectra are corrected for the instrumental wavelength dependence and recorded in ratio mode ($I = I_{fl}/I_0$, where I_0 is the incident light intensity at the excitation wavelength). ϕ_A^{sens} is the quantum yield of the sensitized anthracene fluorescence, which could be different than directly excited anthracene (see later discussion), and ϕ_N^{poly} is the quantum yield of the polymer-bound naphthalene.

One can use eqs 2 and 3 to obtain P_N and P_A, which upon substitution in (5) and (6) and rearrangement yields

$$\frac{I'_A}{I'_N} = \frac{\dfrac{\phi_A^{sens}\phi_N^{mod}I_A}{\phi_A^{mod}\phi_N^{poly}I_N} + \chi_{SS}\dfrac{\phi_A^{sens}}{\phi_N^{poly}}}{(1 - \chi_{SS})} \tag{7}$$

or

$$\chi_{SS} = \frac{1 - R\dfrac{I_AI_N'}{I_A'I_N}}{1 + \dfrac{\phi_A^{sens}I_N'}{\phi_N^{poly}I_A'}} \tag{8}$$

In eq 8 R accounts for the difference in quantum yield of the model and the polymer-bound chromophore, i.e.,

$$R = \frac{\phi_A^{sens}\phi_N^{mod}}{\phi_A^{mod}\phi_N^{poly}} \tag{9}$$

If I_A = 0 and R = 1, then the well-known equation due to Holden and Guillet is obtained.[17] We find this ratio to be very close to unity in comparing directly excited naphthalene or anthracene on the N-PS or N-PS-A polymer with the model compounds.

Liu and Guillet (LG) have carried out similar evaluations of energy transfer for doubly tagged naphthalene-PMMA-anthracene polymers in different solvents and for different degrees of polymerization for the PMMA block (ranging from 70 to 111).[15] They compared two methods, one based on the quenching of the naphthalene fluorescence (like eq 11 discussed later) and a

Table 2. DET Efficiency Comparison

polymer	in 1,4-dioxane χ_{SS}	in 1,4-dioxane χ_{tr}	in 1,4-dioxane χ_{LG}[a]	in PS film, χ_{SS}	theoretical χ[b]
N-PS_{40}-A	0.153	0.248	0.207	0.154	0.171
N-PS_{283}-A	−0.026[c]	0.056	0.045	−0.005[c]	0.013

[a] Using the Liu−Guillet treatment of steady-state emission data (cf. ref 15). [b] Assuming Gaussian chain statistics and a Flory characteristic ratio of 10. [c] Negative values have no physical meaning but are presented for comparison of methods.

second method based on the anthracene fluorescence intensity obtained by direct excitation and sensitization. If we denote by $I_A(\lambda_{dir})$ and $I_A(\lambda_{sens})$ the intensity of the anthracene fluorescence by direct excitation (340 nm) and sensitization (293 nm) and denote by $P_N(\lambda_{sens})$ the fraction of light absorbed by the naphthalene, then they derive[18]

$$\chi_{LG} = \frac{1}{P_N(\lambda_{sens})}\left[\frac{I_A(\lambda_{sens})(1-10^{-OD(\lambda_{dir})})\dfrac{\phi_A^{dir}}{\phi_A^{sens}}}{I_A(\lambda_{dir})(1-10^{-OD(\lambda_{sens})})} - 1 + P_N(\lambda_{sens})\right] \quad (10)$$

where the $1 - 10^{-OD(\lambda)}$ terms correct for the fraction of light absorbed at the two different wavelengths. We have also modified the LG expression by the factor $\phi_A^{dir}/\phi_A^{sens}$, which is assumed by LG to be unity. However in a heterogeneous system such as the polymer micelles discussed here, this may not be the case, as stated above.

Dilute solutions of N-PS, N-PS_{40}-A, and N-PS_{283}-A in dioxane were prepared with OD <0.1. The steady-state spectrum in Figure 2a shows similar naphthalene emission for all samples and vibronically resolved emission for anthracene. Figure 2b shows nearly monoexponential decays. This suggests that the naphthalene is in a homogeneous environment. In this case χ_{tr} can be computed from (see Appendix)[19]

$$\chi_{tr} = 1 - \frac{\langle \tau_{NA} \rangle}{\langle \tau_N^0 \rangle} \quad (11)$$

The fluorescence decay exhibits little naphthalene lifetime shortening for N-PS_{283}-A which is consistant with ineffective DET. The steady-state fluorescence for this latter polymer has a clear anthracene emission, which can be attributed to direct excitation of anthracene. A low value of χ is expected from a Gaussian chain analysis of the end-to-end distance (see Table 2). The χ values obtained from the various data analysis methods are collected in Table 2. There is substantial disagreement between the values. It should be noted that in comparing solution-phase data to solids end-to-end diffusion of the PS coil increases the amount of DET observed.[20] Our values of χ_{SS} obtained by these methods are similar to χ (equivalent to χ_{tr} in the above) obtained by LG for similar polymers in CH_2Cl_2 (but with $n = 70$) but is substantially higher than their E values (equivalent to χ_{SS} in the above).

DET in PS Thin Films. A 1−3 mg portion of N-PS or the N-PS_n-A polymers in 5−7 mL of a 10 wt % solution of 280k PS in dioxane was used to cast films either by simply allowing the solvent to evaporate or by spin-casting. Residual dioxane was removed by air-drying at room temperature. The fluorescence spectra excited at 293 nm are very similar to those in pure dioxane (see Figure 2) with similar χ_{SS} values computed using model compounds. In the films the coils are expected to be in a θ-condition with a more collapsed coil than in a good solvent like dioxane. However it is not surprising that a slightly collapsed but immobilized coild produces a DET efficiency similar to a mobile coil in a good solvent.

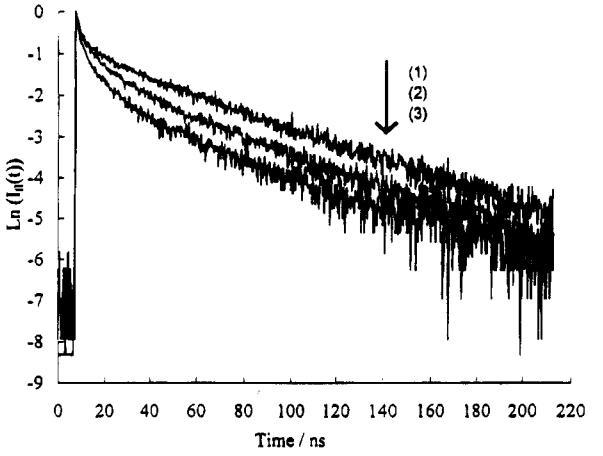


Figure 3. Fluorescence decay of naphthalene (λ_{obs} = 340 nm) in cast PS films of (1) N-PS, (2) N-PS_{40}-A, and (3) N-PS_{283}-A. The values of the average lifetimes ($\langle \tau_D \rangle$ in Appendix) are 21.4, 15.6, and 10.5 ns, respectively (λ_{ex} = 293 nm).

The time dependence of the naphthalene fluorescence is extremely nonexponential in PS films (see Figure 3). This effect persisted in films swollen in dioxane vapor and redried, which should serve to anneal the film. However no systematic study was made of annealling the PS films. While the average lifetime is always shorter for the N-PS_n-A than the N-PS, the lifetime is shorter for N-PS_{283}-A than N-PS_{40}-A which is inconsistent with the χ_{SS} results. This implies that the end-to-end distribution function is not independent of the local inhomogeneities that result in a nonexponential lifetime (see Appendix). Possibly the difference in these local inhomogeneities is the result of the difference in the molecular weight of the PS segments of these polymers. The unhappy consequence of this result is that the time-dependent data cannot be used in any direct way to test models for the end-to-end distance ($P(R)$ in Appendix). As is also discussed in the Appendix, the comparison of steady-state χ_{SS} values is complex such that similar χ_{SS} values do not necessarily imply similar end-to-end distribution.

As will be discussed later, the preparation of micelles by dialysis from 80:20 vol % dioxane:water demonstrated very strong perturbation of the naphthalene fluorescence spectra for dioxane contents ≥50 vol %. We attempted to reproduce this behavior in PS films by swelling the film in dioxane vapor or exposing the film to dioxane:water mixtures. In no case was this spectral perturbation observed. It will be argued later that these spectral perturbations are the result of naphthalene-PMA segment interactions in a dioxane-rich environment.

Copolymer Micelles from N-PS_n−PMA. While the main focus of this study is to observe DET in mixed micelles, it is interesting to know how these doubly labeled copolymers behave as homomicelles. It is reasonably safe to assume that N-PS_{283}-A−PMA will form micelles that are similar to the unlabeled copolymers (PS−PMA) because of their similar structures and molecular weights. The micelles of N-PS_{283}-A−PMA have a hydrodynamic diameter (D_h) of 80.7 nm, which

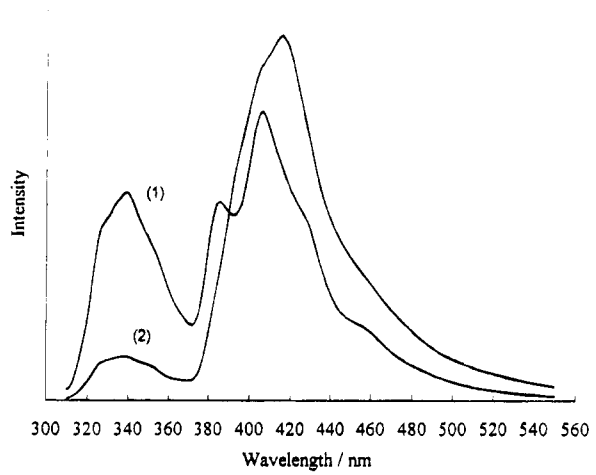


Figure 4. Steady-state spectra of micelles formed from (1) N-PS_{283}-A-PMA and (2) N-PS_{40}-A-PMA in pure H_2O (λ_{ex} = 293 nm).

is comparable to the unlabeled block copolymer homomicelles with a D_h of 70.1 nm. Since, in the N-PS_{40}-A-PMA case, the driving force for phase separation is weaker due to the shorter blocks, it is not known if these form well-structured micelles. For typical higher molecular weight polymers, the solid is first dissolved in 80 vol % 1,4-dioxane/water and dialyzed. At this point of initial dissolution, micelles are present, and it has been anticipated that the cores are swollen with 1,4-dioxane (this will be expanded on later).[10] However, N-PS_{40}-A-PMA dissolves molecularly in 80% 1,4-dioxane/water, giving an immeasurably weak QELS signal. Dialysis from this point into aqueous solutions produces ill-defined aggregates (D_h = 543 nm, polydispersity, PD = 0.54, where PD < 0.10 is expected for well-behaved micelles[10]). When directly dissolving N-PS_{40}-A-PMA in varying concentrations of 1,4-dioxane/water, one finds that the 60–70% range contains preformed micelles ($D_h \approx 20$–25 nm). Dialysis from this point produces relatively ill-defined aggregates (D_h = 29 nm, PD = 0.17).

Steady-state and time-dependent fluorescence do not have the potential to provide straightforward structural analytical information due to the proximity of many naphthalene chromophores with concomitant energy migration between naphthalene donors before sensitization of the anthracene. For micelles formed from pure N-PS_{283}-A-PMA or N-PS_{40}-A-PMA, the anthracene emission dominates the naphthalene emission (see Figure 4). The time-dependent fluorescence of the N-PS_{40}-A-PMA homomicelle is much faster at both 340 nm (naphthalene) and 410 nm (anthracene) than in the mixed micelle but is also devoid of the very fast component observed in mixed micelles (see later) or PS films. The decay of the N-PS_{283}-A-PMA homomicelle is much slower at 340 nm, which is expected given the fact that a significant fraction of the naphthalene groups are located far from the anthryl group. Despite the similarity of the average lifetime for the anthracene (cf. 5.7 and 6.9 ns, respectively) for these two micelles, for N-PS_{283}-A-PMA there is a long-lived component that is similar to the naphthalene, which indicates continued sensitization of the anthracene at long times by relatively distant naphthalene groups (see Figure 5). This could be also a contribution from naphthalene excimers, which would be expected in the 400 nm region. However the excimer fluorescence is definitely a minor component of the total fluorescence in the anthracene region. In no case is a rise time observed for the anthracene decay, which demonstrates that a significant fraction of the anthracene fluorescence arises from either direct excitation (estimated as ca. 10%) and/or sensitization from naphthalene groups in close proximity.

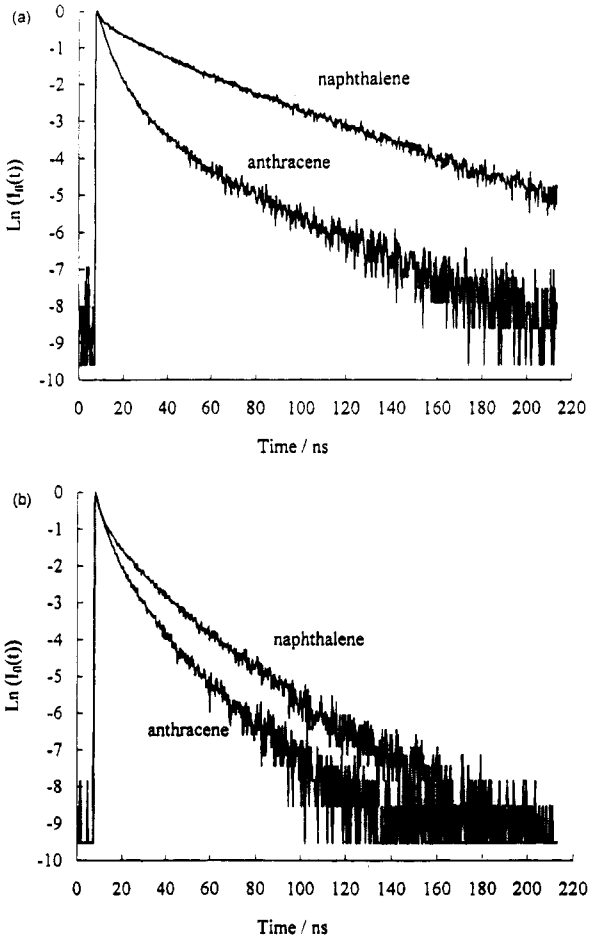


Figure 5. Time-resolved fluorescence for (a) N-PS_{283}-A-PMA and (b) N-PS_{40}-A-PMA homomicelles (λ_{ex} = 293 nm). Naphthalene emission observed at 340 nm and anthracene at 420 nm.

Mixed Micelles of PS-PMA/N-PS_n-A-PMA: (1) Micelle Formation. The mixed micelles for both types of doubly labeled unimers have QELS results identical with those of the unlabeled homomicelles ($D_h \approx 70$ nm). For such a low loading, the physical properties of the micelles are expected to be dominated by the major component. It is assumed that micelles made with N-PS or N-PS-A contain these homopolymers within the core since no aggregation is observed and PS is not soluble in 80% 1,4-dioxane/water. D_h is observed to change as the dialysis proceeds (Figure 6). Assuming a constant aggregation number (closed association), this is a result of the expansion and contraction of the PMA shell as a function of the effective pH[21] and solvent mixture.

(2) Steady-State Spectral Changes during Dialysis. Freeze-drying the mixed labeled and unlabeled polymers from 100% dioxane is assumed to produce a homogeneous mixture of the unimers. The steady-state spectra for all samples (including N-PS) in 80% to ca. 50% 1,4-dioxane/water solutions show a broadened, red-shifted naphthalene emission when using this method. A somewhat less perturbed spectrum is observed if the initial samples are mixed as dry solids, dissolved directly in 80% 1,4-dioxane/water, and dialyzed (these are compared in Figure 7a). The multiexponential character of the fluorescence decay is also accentuated

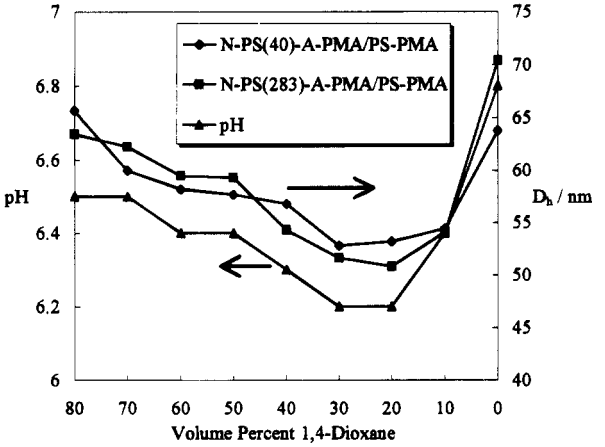


Figure 6. Apparent hydrodynamic diameter (D_h) of the micelle and pH of the micelle solution as a function of dioxane concentration for N-PS_{283}-A/PS−PMA and N-PS_{40}-A/PS−PMA micelles. The pH is measured in the dioxane:water mixture.

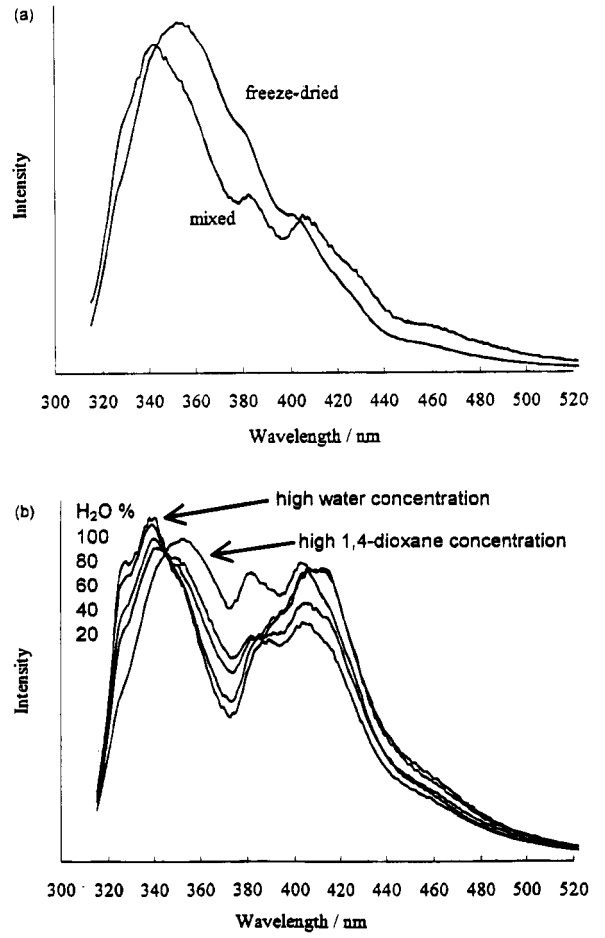


Figure 7. Steady-state emission (λ_{ex} = 293 nm) for N-PS_{283}-A−PMA/PS−PMA comicelles (a) in 80% dioxane/water when the initial preparation is performed by freeze-drying or mixing the solid polymer samples or (b) recorded at 20% increments in dioxane/water concentration from 80% to 0%.

for the mixed and freeze-dried samples. This spectrum becomes a normal superposition of naphthalene and anthracene when the H_2O content is above 50% (see Figure 7b for N-PS_{40}-A−PMA). Similar observations are made for all other tagged polymers during the dialysis. The average naphthalene fluorescence lifetime increases at a H_2O content of ca. 60% dioxane (Figure 8), especially for the two N-PS_n-A−PMA polymers and N-PS. As stated above, attempts to reproduce this

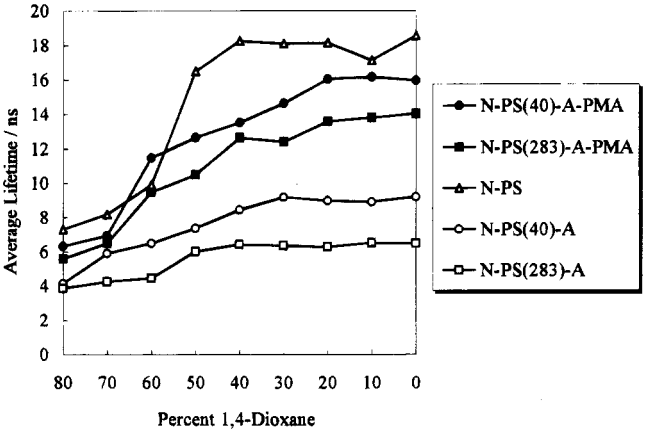


Figure 8. Average lifetime for the naphthalene decay as a function of dioxane:water vol % for species indicated.

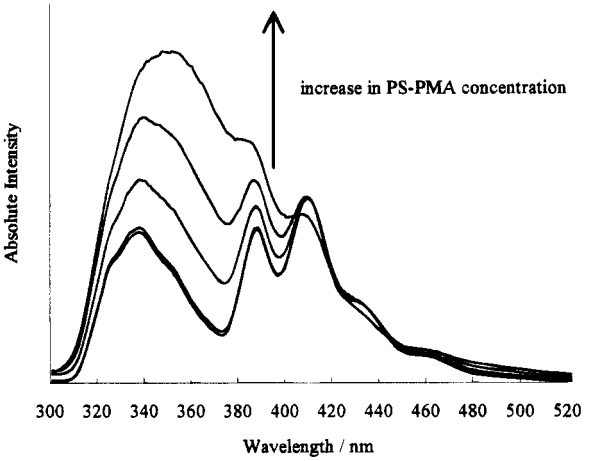
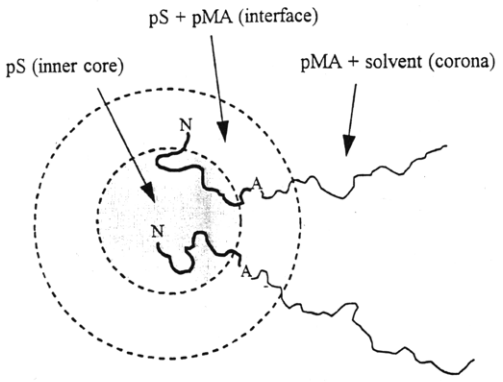


Figure 9. Steady-state emission (λ_{ex} = 293 nm) spectra as a function of PS−PMA concentration in dioxane. For a constant N-PS_{40}-A concentration, the PS−PMA concentrations are 0.00, 0.44, 8.97, 23.45, and 72.40 mg/mL. Note the constant anthracene emission maxima at 410 nm for all but the highest concentration.

spectral modification in environments such as dry or dioxane-swollen PS films were unsuccessful, although the nonexponential decay character of naphthalene emission in a PS film resembles that in a micelle. Other model systems such as an analogous, "all-methyl" system (1-methylnaphthalene in 50% acetic acid/toluene) also failed to show similar red-shifted emission. However, when any of our polymers is dissolved in a concentrated (ca. 70 wt %) dioxane solution of the unlabeled copolymer, the same broadened, red-shifted naphthalene emission is observed (Figure 9). This is not a result of excimer formation because the emission maximum is ca. 350 nm (not 410 nm) and there is minimal and constant concentration of N-PS-A. The red shift does exhibit a dependence on the concentration of the unlabled PS−PMA polymer (Figure 9). To test if this is a peculiarity of our particular polymer, another copolymer (N_1-PS−PMA), synthesized using cumyl potassium and 1-vinylnaphthalene,[22] was tested under the same conditions. In 80% 1,4-dioxane/water the micelles prepared by method 1 (freeze-dried N_1-PS−PMA/PS−PMA sample) show the red shift emission while the micelles produced by method 2 do not. Evidently the detailed comixing of polymers to form mixed micelles can depend strongly on sample history, which in this case is primarily the preparation of the solid sample.

Thus we conclude that the red-shifted naphthalene fluorescence is a result of the interaction with PMA

Chart 2



segments in a dioxane-rich environment (note that this experiment could not be carried out with pure PMA because of poor solubility in dioxane). Since the analogous effect was not observed for a model compound in acetic acid/toluene, we speculate that this must be the result of the simultaneous interaction of many acid groups with the fluorophore. However the more important implication is that at dioxane contents down to 30 vol % the local environment of the micelle must be similar to a concentrated PS–PMA solution. In other words, the strong segregation into a core and corona structure has not occurred. Thus we envision a structure much more like a "droplet" containing the number of chains of the final micelle but without the strong phase separation of the naphthalene units from the PMA part of the polymer (see Chart 2).

(3) DET in Mixed Micelles. Since the naphthalene emission spectra changes during the dialysis process, the R_0 value for naphthalene to anthracene DET is not constant. The change in this value can be calculated from spectroscopic information,[13,23] but one must then estimate a value for the refractive index and fluorescence quantum yield for naphthalene in this complicated, microheterogeneous environment. When R_0 varies, a change in χ_{SS} is not necessarily indicative of coil collapse or expansion. Therefore no conclusions about chain conformation can be drawn from the data in the 80–30 vol % dialysis region. No reliable χ_{tr} values are obtained from the time-resolved fluorescence decay because these decays are strongly multiexponential and suggest that naphthalene is located in a heterogeneous environment.[24] Because of this extreme environmental sensitivity of naphthalene fluorescence, more quantitative data analysis such as fitting the decay data to modified forms[25] of a distribution function for the N–A separation is not possible.

Using the steady-state methods described earlier, χ_{SS} can be obtained for all four probe polymers in the comicelle. These results are plotted as a function of dioxane content (Figure 10) for the range 30–0 vol % dioxane for which the naphthalene is not subject to the red shift discussed earlier. Very little change of χ_{SS} with composition is observed. For N-PS_{298}-A or N-PS_{283}-A–PMA, the χ_{SS} values are low and on the orde of that observed in pure dioxane or PS films (note that for $\chi_{SS} \approx 0.05$ there is very large relative error). For N-PS_{40}-A or N-PS_{40}-A–PMA, a smaller χ_{SS} value is obtained for the former than the latter (cf. 0.08 and 0.14 in 100% water). For N-PS_{40}-A, this value is lower than observed for pure dioxane or PS film (see Table 2), but this may also be a result of the heterogeneous distribution of lifetimes (see Appendix). On the basis of the χ_{SS} values, one would conclude that the N to A distance is slightly

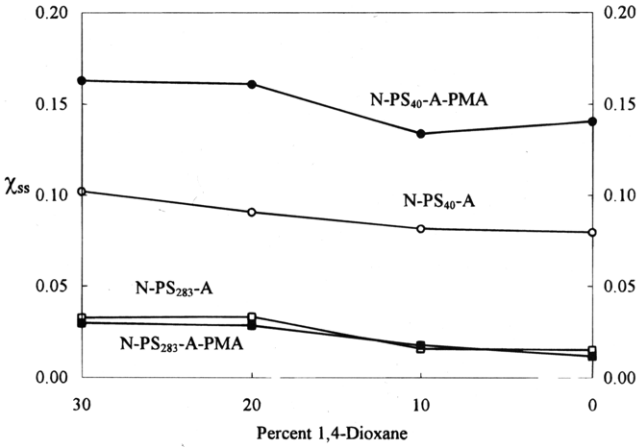


Figure 10. Steady-state DET efficiency (χ_{SS}) for N-PS_{40}-A, N-PS_{40}-A–PMA, N-PS_{283}-A, and N-PS_{283}-A–PMA in PS–PMA mixed micelles.

smaller for N-PS_{40}-A–PMA (in the interfacial region) than N-PS_{40}-A in the micelle core. However, as is discussed next in comparing the sensitized and directly excited anthracene fluorescence spectra, it seems likely that DET for N-PS_{40}-A–PMA is dominated by a minority of probe molecules located in a disordered interfacial region (see Chart 2). Therefore no straightforward interpretation of the end-to-end distance of the PS segment for N-PS_{40}-A–PMA is possible. For N-PS_{283}-A and N-PS_{283}-A–PMA, we conclude that there is no significant change in this dimension for chains located in the core and at the interface.

(4) Comparison of Sensitized and Directly Excited Anthracene Fluorescence. Evidence for heterogeneity of the interfacial region also emerges from a comparison of the anthracene spectrum for N-PS_{40}-A and N-PS_{40}-A–PMA when directly excited at 340 nm or sensitized at 293 nm. For the former polymer these spectra are essentially identical with respect to the apparent vibronic resolution (see Figure 11a). For the latter the sensitized anthracene fluorescence is distinctly less resolved (Figure 11b). Since χ_{SS} is higher for N-PS_{40}-A–PMA than N-PS_{40}-A (see previous subsection), we conclude that DET is enhanced for those naphthalene–anthracene pairs that are in a region that is not typical for the PS core. This is represented in Chart 2. The sensitized anthracene fluorescence is much weaker for N-PS_{283}-A or N-PS_{283}-A–PMA such that the comparison is more difficult, but it would appear that there is no large difference between sensitized and directly excited anthracene. We presume that this is a result of the long PS chain; it is very improbable that the naphthalene end will return to the interfacial region. It is also possible that the interfacial region experienced by the N-PS_{283}-A–PMA probe may be sharper. Like any "probe" study, if the probe molecule differs from the phase that is to be characterized, there may be some degree of phase separation, and hence the probe molecule may not "report" a typical environment. However we re-emphasize that the perturbed fluorescence spectra observed for high dioxane contents, discussed above, were observed for all tagged polymers in micelles.

Summary

The original objective of this research was to obtain the time dependence of the naphthalene donor fluorescence in N-PS_n-A or N-PS_n-A–PMA polymers in various environments, including polymer micelles, in order to

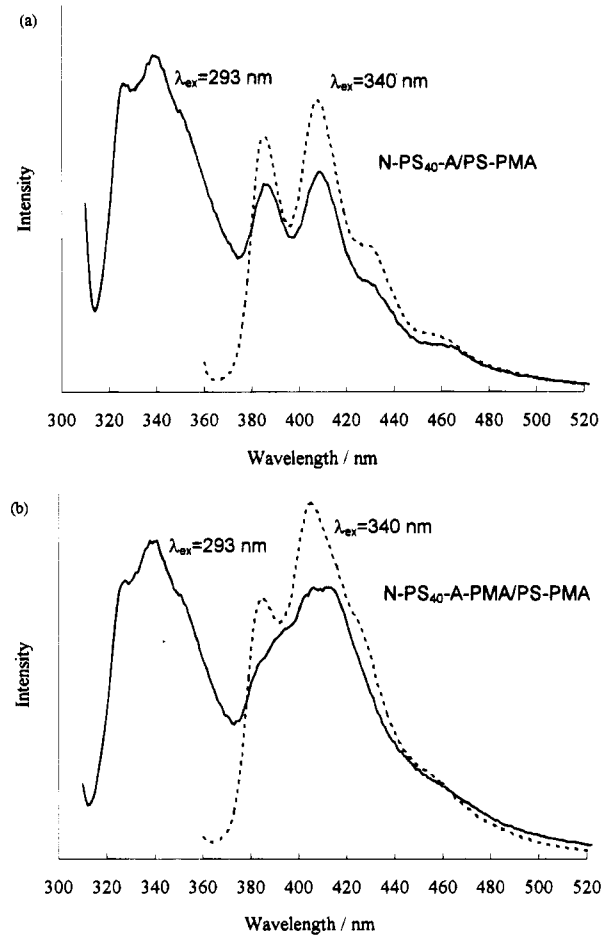


Figure 11. Comparison of sensitized and directly excited anthracene fluorescence (λ_{ex} = 293 and 340 nm, respectively) for (a) N-PS_{40}-A/PS–PMA and (b) N-PS_{40}-A–PMA/PS–PMA comicelles in water.

model the distribution of end-to-end distances. The sensitivity of the naphthalene fluorescence to local inhomogeneities has prevented this objective from being achieved. To the extent that the direct energy transfer data can be interpreted, there is no evidence for a significant modification in the N–A separation in micelles compared to films or in a good solvent. The spectral difference in the anthracene fluorescence upon direct excitation vs naphthalene sensitization also demonstrates the strong heterogeneity for the anthryl moiety, at least in N-PS_{40}-A–PMA/PS–PMA micelles.

The sensitivity of the naphthalene fluorescence to environment has demonstrated an unanticipated phenomenon: The polymer micelle does not appear to have a well-defined core–corona structure until the dioxane content in the aqueous solution is ≤30 vol %. Above this dioxane content, the naphthalene fluorescence is perturbed in a way that is consistent with the naphthalene end of the polymer residing in a concentrated dioxane solution of PS–PMA. Note that this observation holds equally well for N-PS_n-A or N-PS_n-A–PMA. This spectral perturbation is most evident for the "method 1" preparation in which a solution of the tagged and untagged polymer is freeze-dried and the micelle prepared by addition of the resultant powder to 80:20 dioxane:H_2O.

In "method 2" the individual dried polymers are added independently to the 80:20 dioxane:H_2O, and the perturbation of the naphthalene fluorescence is much less. We know that the tagged polymers are adding to the untagged polymer micelle because the steady-state and time-dependent fluorescences are not the same as in the N-PS_n-A–PMA homomicelle (see Figures 4 and 5). Thus the degree of disorder in these micelles when swollen by dioxane depends on the sample history and preparation method for reasons that we do not understand. There is no evidence from our work that the micelle prepared by either method and dialyzed to 100% H_2O is different. We can speculate that in method 1 the initially formed micelles reflect the domains formed in the freeze-dried solid, while for method 2 the micelle equilibrates by the exchange of unimers between tagged and untagged micelles. These observations as well as observation of fluorescence quenching[26] suggest that the core–interface boundary is quite disordered on a molecular level.

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Appendix: DET in Doubly Tagged Polymers with a Heterogeneous Distribution of Lifetimes

For an ensemble of polymers with a single donor–acceptor pair, the fluorescence decay of the donor can be written

$$F_D(t) = e^{-k_D t} \int P(R)\, e^{-k_{DET}(R)t}\, dV \qquad (A1)$$

where k_D is the decay rate of the donor, $P(R)$ is the normalized distribution of donor–acceptor separations, and $k_{DET}(R)$ is given by the Förster expression

$$k_{DET}(R) = k_D(R_0/R)^6 \qquad (A2)$$

R_0 implicitly contains the average of the different mutual orientations of the chromophores. In writing this form it is also implicitly assumed that the angular averaging is not a function of the number of polymer segments separating D and A. The separation of the D and A pair is given by R.

The integral of $F_D(t)$ yields the steady-state intensity

$$\langle \tau_D \rangle = \int_0^\infty F_D(t)\, dt = \int P(R) \frac{1}{k_D(1 + (R_0/R)^6)}\, dV \qquad (A3)$$

The symbol $\langle \tau_D \rangle$ is used to emphasize that the integral also represents the average lifetime of the excited state.[27] If the same integral is carried out for the donor without an acceptor, one obtains

$$\langle \tau_D^0 \rangle = \int_0^\infty e^{-k_D t}\, dt = 1/k_D \qquad (A4)$$

The energy transfer efficiency, χ, is given by

$$\chi = 1 - \frac{\langle \tau_D \rangle}{\langle \tau_D^0 \rangle} = \int P(R) \frac{R_0^6}{R^6 + R_0^6}\, dV \qquad (A5)$$

which is a well-known expression relating energy transfer efficiency to a pairwise distribution function.[28] The above demonstrates that one should be able to obtain χ equally well from time-dependent or steady-state measurements. However the above assumes that the fluorescence decay is deconvolved perfectly such that no

ultrafast components are missed. In practice it is often observed that

$$\chi_{tr} < \chi_{SS} \tag{A6}$$

where χ_{tr} is obtained using the time-dependent technique and χ_{SS} is obtained from steady-state fluorescence.

If the donor state is sensitive to local environmental inhomogeneities, but these local effects have no effect on the distribution function, $P(R)$, then we may write

$$F_D(t)_i = e^{-k_D\kappa_i t}\int P(R)\, e^{-k_{DET}(R)t}\, dV \tag{A7}$$

where κ_i is a multiplicative factor that describes the change in lifetime for the ith environment. The energy transfer efficiency for the ith site is given by an equation analogous to eq A5,

$$\chi_i = \int P(R)\frac{R_0^6}{\kappa_i R^6 + R_0^6}\, dV \tag{A8}$$

and the ensemble average χ value is

$$\langle\chi\rangle = \sum_i f_i\chi_i \tag{A9}$$

where f_i is the fraction of a site of type i. Equation A9 reflects the fact that sites with short lifetimes ($\kappa_i \gg 1$) discriminate against the part of the $P(R)$ distribution at large R. We note that a simple extension of eq A5 is not valid, i.e.,

$$\langle\chi\rangle = 1 - \sum_i f_i\frac{\langle\tau_D\rangle_i}{\langle\tau_D^0\rangle_i}$$

$$\neq 1 - \frac{\sum_i f_i\langle\tau_D\rangle_i}{\sum_i f_i\langle\tau_D^0\rangle_i} = 1 - \frac{\langle\tau_D\rangle}{\langle\tau_D^0\rangle} \tag{A10}$$

The equality *is* satisfied in the case that there is only one environment with a modified lifetime, i.e., $f_i = \delta_{i1}$ and $\kappa_1 \neq 1$, and the donor decay is single exponential in the absence of DET. In general the time-dependent data cannot be used in a straightforward way to obtain $\langle\chi\rangle$, and one has to use the steady-state spectra.[29]

On the other hand, according to the assumption of this treatment

$$F_D(t) = \sum_i f_i\, e^{-\kappa_i k_D t}\int P(R)\, e^{-k_{DET}(R)t}\, dV \tag{A11}$$

and

$$F_D^0(t) = \sum_i f_i\, e^{-\kappa_i k_D t} \tag{A12}$$

such that

$$\frac{F_D(t)}{F_D^0(t)} = \int P(R)\, e^{-k_{DET}(R)t}\, dV \tag{A13}$$

According to this expression the ratio on the left-hand side of eq A13 should always decay more slowly for a longer segment separating the donor and acceptor. We do not find this to be true in comparing N-PS_{40}-A and N-PS_{283}-A in PS films or the interior of micelles (see Figure 3). Hence we conclude that the end-to-end distribution and the heterogeneity in lifetime *are* correlated.

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(17) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289.

(18) In ref 15 a correction is also made for the fraction of polymers that are not terminated by the anthryl group. We do not need to make this correction for our polymers. We use low optical densities, so $P_N(\lambda_{sens}) = \epsilon_N(293)/(\epsilon_N(293) + \epsilon_A(293))$. For the model compounds $\epsilon_N(293) = 4229\ M^{-1}\ cm^{-1}$ and $\epsilon_A(293) = 466\ M^{-1}\ cm^{-1}$, so $P_N(293) = 0.901$.

(19) This expression is equivalent to the ratio of the naphthalene fluorescence yields, which was also used by ref 15 to obtain χ.

(20) Private communication, prof. G. Liu. See the following papers that deal with the effect of end-group diffusion on DET: (a) Liu, G.; Guillet, J. E.; Al-Takrity, E. T. B.; Jenkins, A. D.; Walton, D. R. M. *Macromolecules* **1990**, *23*, 4164. (b) Liu, G.; Guillet, J. E. *Ibid.* **1990**, *23*, 2973. (c) Liu, G.; Guillet, J. E. *Ibid.* **1990**, *23*, 2969.

(21) The solvent system was unbuffered, and the pH of the micelle solution was allowed to vary as the dialysis proceeded.

(22) Kiserow, D.; Chan, J.; Ramireddy, C.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 5338.

(23) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1986.

(24) Untagged micelles were examined to evaluate any fluorescence decay that might arise from excitation of the weak tail of the PS component. While a rapidly decaying fluorescence was observed, it was so weak compared to the tagged samples that this cannot be the source of the short lifetime component.

(25) (a) Grinvald, A.; Haas, E.; Steinberg, I. *Z. Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 2273. (b) Liu, G. *Macromolecules* **1993**, *26*, 1144.

(26) Ongoing work by A. Eckert and T. Martin.

(27) This is the average lifetime in the sense that if $F(t) = e^{-t/\tau}$, then $\int_0^\infty e^{-t/\tau}\, dt = \tau$. For a multiexponential decay, $\langle\tau\rangle = \Sigma a_i\tau_i$. Some authors will define an average lifetime as the following first moment: $\tau_{avg} = \int_0^\infty tF_D(t)\, dt/\int_0^\infty F_D(t)\, dt$.

(28) See ref 23, p 308.

(29) In principle an accurate fit of $F_D^0(t)$ to a multiexponential function would yield a valid distribution of f_i and κ_i, which could then be used to test a trial function for $P(R)$. However this seems likely to be subject to considerable error.

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