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Registry No. Hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5.

Fluorescence Energy Transfer Studies of Styrene–Isoprene Diblock Copolymer Solutions[†]

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ABSTRACT: Micelle formation in solutions of chromophore-labeled styrene–isoprene diblock copolymers in selective solvent systems has been investigated using nonradiative energy transfer techniques. Energy transfer donor (carbazolyl or naphthyl) or acceptor (anthryl) chromophores were attached to anionically polymerized block copolymers and used to study micellar solutions as parameters such as concentration, solvent composition, temperature, and molecular weight were varied. Dramatic increases in I_A/I_D, the ratio of acceptor to donor fluorescence intensity, accompanied the formation of micelles. As the solvent quality worsens for the labeled blocks through either a reduction in temperature or the addition of a nonsolvent, micelles are detected first in the more concentrated solutions, consistent with expectations of a phenomenological critical micelle concentration (cmc). The high sensitivity of energy transfer experiments was also demonstrated; multimolecular micelles are observed at very low copolymer concentrations, near 10^{-3} g/L, where turbidimetry is insensitive to micelle formation. With the use of a two-state energy transfer model, it was determined for the block copolymer systems under investigation that at concentrations exceeding the cmc additional copolymer apparently partitions itself between micelles and the homogeneous solution phase. Single photon counting measurements were also performed to observe changes in fluorescence lifetimes of both donors and acceptors upon micellization. Measured lifetimes of anthryl units nearly doubled in micelles due to the time lag caused by the energy transfer process.

Introduction

Heterogeneous structure, such as the existence of multimolecular micelles, occurs in diblock copolymer solutions when the solvent is selective for one of the blocks. A number of studies[2-21] on both diblock and triblock copolymers using techniques such as intrinsic viscosity measurement, light scattering, small-angle X-ray scattering, neutron scattering, and electron microscopy have detailed conditions under which multimolecular aggregates occur. These micelles are formed by aggregation of the precipitated or less soluble blocks into cores surrounded by a shell of the more soluble blocks. For triblock copolymers the solvent must be preferential toward the end blocks.[22]

Temperature has a significant influence on micellar solutions. Typically, at high temperatures the equilibrium between micelles and unassociated chains favor the latter. Upon lowering the temperature, micelles begin to

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form at what has been termed the critical micelle temperature, cmt.[4] As with the critical micelle concentration (cmc), the cmt may be a phenomenological observation signifying the temperature at which micelles may be detected by a given technique. As the temperature is lowered, the radius of gyration of the particles often decreases due to collapse of the cores while the apparent molecular weight increases as the number of chains per micelle rises.

In analogy to decreasing the temperature of the system, a selective precipitant may be added to a block copolymer solution in order to form micelles. In solutions containing high amounts of precipitant, most copolymer molecules tend to form micelles; however, ultracentrifugation shows that some unassociated chains remain in solution.[5] Between the regions of high temperature (or relatively nonselective solvent), where unassociated copolymer dominates, and low temperature (or high fraction of selective precipitant), where the majority of polymers aggregate, block copolymer behavior is complex and may be a function of concentration and composition.[5]

This paper reports the use of fluorescence energy transfer measurements to characterize the formation of micelles in diblock copolymer solutions. Nonradiative energy transfer techniques have been used to investigate the compatibility of polymer blends,[23-27] to assess other aspects of polymer solution behavior such as the extent of interpenetration in semidilute solution,[28,29] and to investigate the structure of colloidal polymer systems.[30] (A review of some of the energy transfer studies of polymer systems has been published recently.[31]) The compatibility studies involve labeling one polymer with a "donor" chromophore and a second with an "acceptor" species. Energy absorbed by the donor may be transferred by a Förster mechanism[32] to the acceptor provided that the distance separating the chromophores is relatively short, typically, a few nanometers. The relative intensities of donor and acceptor emission, after excitation of the donor moieties, may then provide a measure of the average spacing between chromophores and hence a characterization of the compatibility of appropriately labeled polymers.

The nonradiative energy transfer technique has recently been used to investigate dilute solution properties of a polystyrene–poly(methyl methacrylate) graft copolymer. Watanabe and Matsuda[33] observed changes in the fluorescence spectrum of labeled graft copolymer that corresponded to intermolecular and intramolecular interactions. The polymers were labeled with fluorene on the chain backbone and pyrene at the ends of the grafts. Their investigation also demonstrated the sensitivity of the energy transfer technique below concentrations at which other experimental methods lose their utility. The extreme sensitivity of fluorescence methods, even in solutions which are quite dilute, is known in general.[34,35] Recently, unidirectional energy transfer was investigated in block copolymers of 2-vinylnaphthalene and vinyldiphenylanthracene,[36] and fluorescence decay measurements have been used to probe further the nature of naphthalene-labeled polymer colloids.[37]

In this study, the solution behavior of several styrene–isoprene diblock copolymers, of similar composition but different molecular weight, is studied by using nonradiative energy transfer. Additionally, different donor–acceptor pairs are used in examining the solutions. Proper choice of labels is important in the design of these experiments. The terminal units of either the polystyrene or polyisoprene blocks are labeled with either donor or acceptor chromophores. Accordingly, the separation between the donor (carbazolyl, naphthyl) and acceptor (anthryl) units is greatly reduced upon micellization. As the efficiency of energy transfer by a Förster mechanism is inversely proportional to the sixth power of the distance between labels,[32] micelle formation should be accompanied by a marked increase in energy transfer. This is monitored by measurement of the ratio of acceptor to donor fluorescence intensity, I_A/I_D. The dependence of energy transfer efficiency on polymer concentration, molecular weight, and temperature is demonstrated in solvent environments including pure selective solvents and binary solvent mixtures.

Table I
Polymer Characterization—Molecular Weight

	first block			block copolymer	
sample	M_v	M_n	M_w	M_n	M_w
IS3/3	3.6×10^3 [a]	2.7×10^3 [b]	3.5×10^3 [b]	5.2×10^3 [b]	6.5×10^3 [b]
IS10/11	$1.0_2 \times 10^4$ [a]			$2.1_6 \times 10^4$ [b]	$2.5_7 \times 10^4$ [b]
SI44/32	$4.4_3 \times 10^4$ [c]				

[a] Based on intrinsic viscosity measurement of polyisoprene in dioxane at 34 °C; Θ conditions.[40]. [b] Measurements made on a portion of the unlabeled block copolymer; measurements made by Wayne Willkomm using GPC at the University of Minnesota. [c] Based on intrinsic viscosity measurements of polystyrene in cyclohexane at 34.5 °C; Θ conditions.[39]

Experimental Section

Materials. Block copolymers were synthesized in capped beverage bottles with N_2 atmosphere by sequential anionic polymerization; cyclohexane was the solvent and *sec*-butyllithium the initiator. Following formation of the first block, an aliquot of the reaction mixture was removed and terminated with either 2-propanol or methanol for molecular weight characterization. Following reaction of the second monomeric species, the resulting diblock copolymer, still retaining its living ends, was divided into portions for either terminal attachment of chromophores or termination with 2-propanol.

Naphthyl or anthryl residues were attached by reacting the living polymer anion with 1-(chloromethyl)naphthalene or 9-(chloromethyl)anthracene (both from Aldrich) dissolved in cyclohexane or toluene. The terminator solutions were deoxygenated by bubbling with N_2 immediately prior to reaction. Carbazole labels were attached similarly by using 9-(4-bromobutyl)carbazole that was prepared by condensation of sodium carbazole and 1,4-dibromobutane.[38] A sample of anthryl-terminated polystyrene was prepared by the same methods.

In order to remove unreacted fluorescent residues, the polymer was cleaned by repeated dissolution in either toluene or cyclohexane and precipitation in methanol. The composition of the block copolymer and the extent of labeling were determined by UV–vis absorbance spectroscopy. Absorbance measurements were performed with an IBM UV–vis 9410 double-beam spectrophotometer. The extinction coefficients of 1-methylnaphthalene, $\epsilon_{277\text{nm}} = 5900\ \text{M}^{-1}\ \text{cm}^{-1}$, 9-methylanthracene, $\epsilon_{369\text{nm}} = 7980\ \text{M}^{-1}\ \text{cm}^{-1}$, and 9-ethylcarbazole, $\epsilon_{294\text{nm}} = 16\,800\ \text{M}^{-1}\ \text{cm}^{-1}$, in toluene were used for comparison. As expected, the absorbance spectra of the attached labels were red-shifted by at most a few nanometers. Molecular weight averages were determined by intrinsic viscosity and gel permeation chromatography. Polymer characterization is given in Tables I and II.

Fluorescence Measurements. Corrected, steady-state emission spectra were measured by using a Spex fluorolog spectrophotometer with a bandwidth of 4.5 nm for both excitation and emission; excitation wavelengths of 294 (IS3/3 and IS10/11 copolymers) or 278 nm (SI44/32 copolymer) were employed. Spectrophotometric grade solvents (Aldrich) were used as received. When binary solvent mixtures were required, the samples were prepared from stock solutions of the polymer in the better solvent and these were diluted with the other solvent to the desired concentration and composition. Dilutions were performed by using volumetric pipettes, flasks, and, when very dilute solutions were needed, microsyringes. Temperature control of flu-

Table II
Polymer Characterization—Weight Fraction of Polystyrene and Label Efficiency

sample	wt fractn polystyrene[a]	label efficiency[a]		
		anthracene	naphthalene	carbazole
IS3/3	0.54	0.78		0.86
IS10/11	0.52	0.55		0.51
SI44/32	0.58–0.60	0.50	0.10[b]	

[a] Based on UV–vis absorbance measurements. [b] The substantial overlap of the absorbance spectra of naphthalene and polystyrene reduces the precision of this measurement.

orescence solutions was achieved through the use of a thermostated cell holder and refrigerated water bath. Temperature in the cell was measured directly by using a calibrated thermocouple. The sample solutions were air-equilibrated.

Fluorescence lifetimes were obtained by using time-correlated single photon counting (TCSPC) techniques at Argonne National Laboratory. Fluorescence was excited with weak, 10-ps, 305-nm light pulses obtained by frequency-doubling the output of an argon-ion pumped cavity-dumped dye laser. Fluorescence emission was collected at right angles to the excitation and was time-resolved by using a TCSPC system that is described elsewhere.[41] The TCSPC system, which has an instrument response function of 60-ps fwhm, was operated time-forward at a count rate of 5 kHz (1% of the laser repetition rate), and data were collected to 10 000 counts in the peak channel. The fluorescence decays were fit to single or double exponential decays by using an iterative nonlinear least-squares fitting program. Carbazole label lifetimes were measured by using a narrow band-pass optical filter with peak transmission at either 341 or 360 nm, and the anthracene label lifetimes were determined by using only that part of the signal which had a wavelength greater than 440 nm.

Results and Discussion

A. Photophysics of Labeled Block Copolymers. Before considering the energy transfer experiments, the photophysics of the system must be addressed. The absorbance spectra of the labeled polymers are red-shifted compared to the spectra of the model compounds, and the peaks are broadened. Figure 1 compares the absorbance spectra of labeled polymers and model chromophores. The emission spectra are also changed somewhat as shown in Figure 2.

In view of the fact that neither the absorbance nor the fluorescence spectra of the labeled polymers are identical with those of the low molecular weight analogues, it is prudent to calculate the expected value for R_0, the critical energy transfer distance. R_0 may be calculated from[32]

$$R_0^6 = 8.78 \times 10^{-25} \kappa^2 \Phi_D n^{-4} \int \frac{f_D(\nu)\epsilon_A(\nu)}{\nu^4}\, d\nu \qquad (1)$$

where ν is a wavenumber, $\epsilon_A(\nu)$ is the molar extinction coefficient of the energy acceptor, $f_D(\nu)$ is the fluorescence spectrum of the energy donor normalized so that $\int f_D(\nu)\, d\nu = 1$, Φ_D is the fluorescence quantum yield of the donor, n is the refractive index of the solvent, and κ^2 is an orientation factor which has a value of 2/3 in low viscosity solutions. In cyclohexane, the monomeric analogues 9-ethylcarbazole and 9-methylanthracene were found to have $R_0 = 28.9$ Å which compares well to the tabulated value[32] of $R_0 = 28.75$ Å for 9-methylcarbazole and 9-methylanthracene. The polymer samples IS10/11 and IS3/3 were calculated to have R_0 values of 28.8 and 28.1 Å, respectively. (The quantum yield of the donor was assumed to be 0.51, the quantum yield of 9-methylcarbazole.[42]) Thus, R_0 is relatively unaffected by the shifts found in the electronic spectra of the polymer-bound labels.

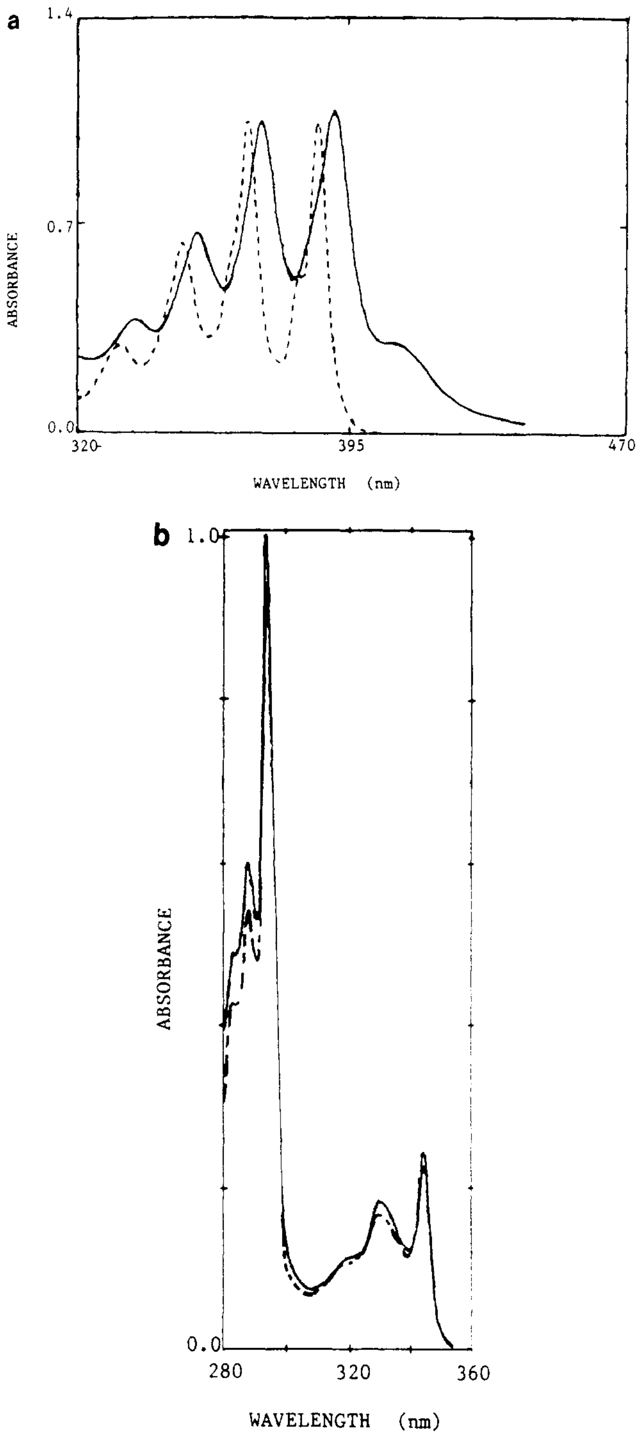

Figure 1. (a) Absorbance spectra (referenced to pure toluene) of 0.021 g/L 9-methylanthracene: (- - -) and 5.20 g/L anthracene-labeled IS10/11 (—) in toluene. (b) Absorbance spectra (referenced to pure cyclohexane) of 0.0080 g/L 9-ethylcarbazole (- - -) and 2.13 g/L carbazole-labeled IS10/11 (—) in cyclohexane.

B. Energy Transfer—Steady-State Intensity Studies. Two types of energy transfer experiments were used in the study of block copolymer solution behavior. First, intermolecular energy transfer experiments in which transfer necessarily occurred between two different polymer chains were done; multimolecular association caused an increase in the likelihood of energy transfer. Polymers used were IS3/3 and IS10/11 with either carbazolyl donor or anthryl acceptor at the ends of the styrene blocks. Second, the naphthalene–anthracene chromophore pair, with units located at the ends of the isoprene blocks in polymer SI44/32, was used with an excitation

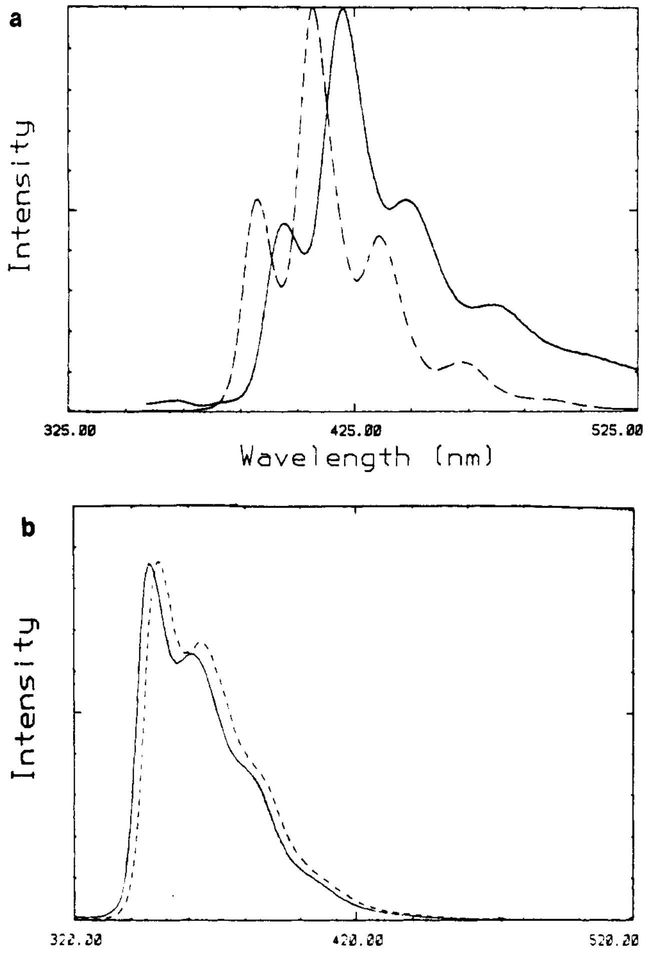

Figure 2. (a) Corrected fluorescence spectra of 9-methylanthracene (- - -) and anthracene-labeled IS10/11 (—) in cyclohexane. (Peak intensities have been normalized.) (b) Corrected fluorescence spectra of 9-ethylcarbazole (—) and carbazole-labeled IS10/11 (- - -) in cyclohexane. (Peak intensities have been normalized.)

wavelength chosen such that the styrene block could absorb appreciable amounts of excitation energy. Therefore, the extent of energy transfer was sensitive to both intermolecular and intramolecular interactions as both the naphthyl label and the styrene block could serve as energy donors.

B.1.a. Carbazole- and Anthracene-Labeled Block Copolymers—Energy Transfer Data. The behavior of terminally labeled styrene–isoprene block copolymers IS3/3 and IS10/11 was investigated at several low concentrations in either binary mixtures of cyclohexane and heptane of various compositions or pure heptane. In dilute cyclohexane solutions, the block copolymers are, on average, widely separated. There are relatively few interpolymeric contacts and, consequently, little opportunity for energy transfer. As heptane is added to the solution, the solvent environment becomes selectively poor for the styrene blocks and causes the styrene blocks to contract, and eventually micelle formation is induced. The micelle cores are composed of styrene blocks with fluorescent labels at the ends; therefore, the efficiency of energy transfer is increased because the labels are in closer proximity. Figure 3 shows the enhancement in energy transfer as the heptane content is increased. The relatively wide separation and lack of overlap between the anthracene peak at 442 nm and the carbazole peak at 345 nm allows easy characterization of I_A/I_D, the anthracene (acceptor) to carbazole (donor) fluorescence intensity ratio.

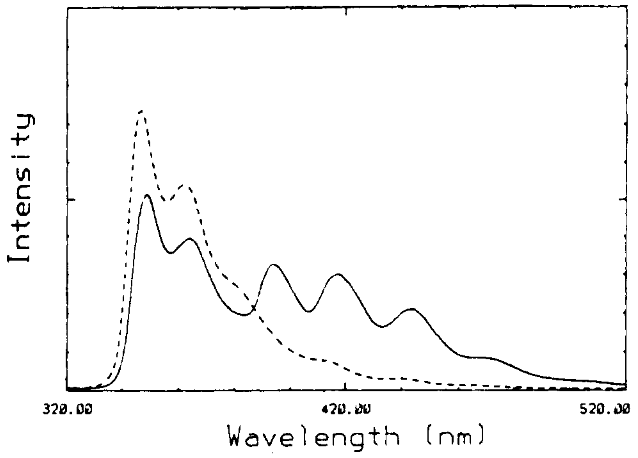

Figure 3. Corrected fluorescence spectra of labeled IS10/11 in mixed solvents (concentration = 2.23 g/L): (- - -) cyclohexane; (—) 10:90 cyclohexane/heptane.

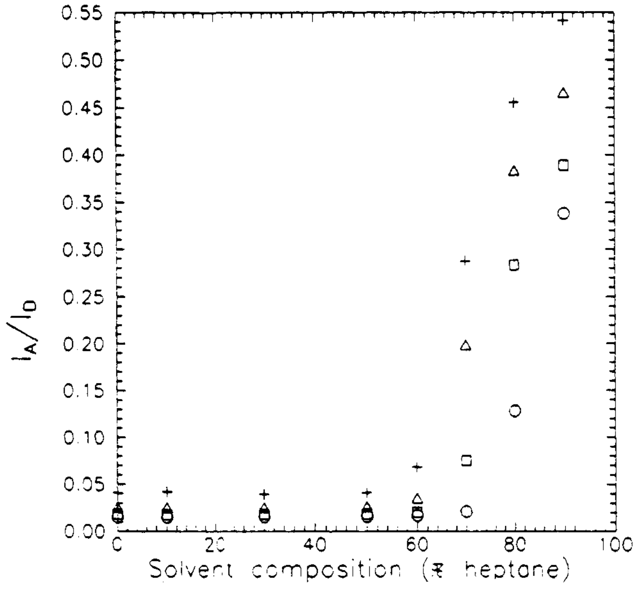

Figure 4. Dependence of anthracene to carbazole fluorescence intensity ratio on solvent composition for a range of concentrations of block copolymer IS10/11 in cyclohexane/heptane solutions: 0.10 g/L (○); 1.09 g/L (△); 0.50 g/L (□); 2.23 g/L (+).

Figure 4 summarizes the effect of solvent composition on energy transfer and additionally demonstrates the concentration dependence of I_A/I_D. Clearly, the value of I_A/I_D, taken as the ratio of intensities at 442 and 345 nm, increases with concentration. Several factors may contribute to this.

One of these is that there is some probability of energy transfer occurring because Brownian motion of the polymer chains causes an acceptor labeled polymer to come close to an excited donor. The mean diffusion length, r, may be estimated for the polymer coils as $r = (2D\tau)^{1/2}$ where D is the sum of donor and acceptor diffusion coefficients and τ is the lifetime of the donor excited state. A survey of diffusion coefficients for polymers of similar molecular weight in solvents of similar viscosity from *Polymer Handbook*[43] indicates that D will not exceed 10^{-6} cm^2/s. τ is approximately 9.7 ns which leads to an estimation of $r \approx 20$ Å. In the most concentrated solution examined, polymer coils are present at a concentration of about 10^{-4} M which suggests that the average separation between coils is approximately 140 Å.[44] While it is recognized that some diffusional energy transfer may occur, its contribution to changing the emission spectrum is probably minor.

Another phenomenon that may affect the fluorescence measurements is radiative energy transfer. The importance of this factor increases with increasing label concentration. As the donor fluorescence spectrum necessarily overlaps the acceptor absorbance spectrum, there is a chance that donor emission will be absorbed by the acceptor. The probability of this event, which may adversely affect interpretation of fluorescence spectra, may be reduced by lowering the total absorbance of the accepting species.

In these experiments, the probability of radiative energy transfer was minimized by using a fairly low anthryl label content and a front surface geometry for the fluorescence experiments. Extinction coefficients for the anthryl-labeled polymer are about 0.2 L g^{-1} cm^{-1} at the maxima in the absorbance spectrum (370 and 389 nm). The front surface geometry presents a maximum effective path length of about 0.1 cm of solution through which the emission must pass. For the samples with the highest concentration of anthryl-labeled polymer, about 1 g/L, the absorbance (A) due to anthracene may be estimated as A = 0.02; therefore, under the conditions most favorable to radiative transfer less than 5% of the energy transfer occurs by radiative means.

The most convincing argument that there is little occurrence of either diffusive or radiative energy transfer comes from the fluorescence spectra for the cyclohexane solutions where micelles are not expected. Figure 3 shows that there is very little anthracene emission in the absence of micelles. Because the carbazolyl labels account for most of the absorption of light, little anthracene fluorescence is expected in the absence of energy transfer.

In addition to the small effect in solutions which do not contain micelles, polymer concentration affects the fluorescence behavior of the micellar systems in a more dramatic way. As evidenced in Figure 4, the more concentrated solutions exhibit a substantially higher I_A/I_D. Assuming that the structure of the micelle does not depend on polymer concentration,[16] the increase in I_A/I_D is indicative of an increase in the number of chains in the micelles relative to the number of unassociated chains. This is not inconsistent with the classic model of micelle formation which suggests that cmc is equal to the concentration of unassociated chains. If this model were operative, above the cmc virtually all of the polymer added to the system would go into micelles. At concentrations closer to the cmc, a greater fraction of the polymer in the system is unassociated; therefore, donor fluorescence is more prominent and I_A/I_D is reduced.

For all concentrations in Figure 4, the point of onset of the increase in I_A/I_D occurs at a composition of roughly 60% heptane. For the highest concentration, 2.23 g/L, micellization appears to begin at a composition of just over 50% heptane; the lowest concentration solution, 0.10 g/L, does not appear to contain micelles until the solvent contains just under 70% heptane. Although location of the precise composition of the break in the I_A/I_D curves is somewhat subjective, the observed behavior is consistent with expectations: micelles appear at lower heptane contents when the polymer concentration is higher.

Above 60% heptane, as more heptane is added, I_A/I_D increases. This may be due to an increase in the aggregation number, that is, the number of chains in a micelle, and/or due to contraction of the core of the micelle. Either phenomenon would enhance energy transfer. It is reasonable to expect that both an increase in aggregation number and a decrease in the core size occur. A study of a similar SI block copolymer in mixtures of a selective (decane) and nonselective (*trans*-decalin) solvent indicated that large polydisperse aggregates formed at solvent compositions intermediate between pure selective solvent, which contained compact micelles, and the nonselective solvent, which contained dissociated chains.[14] Additionally, light scattering has shown that the apparent molecular weight observed from a micelle-forming block copolymer system increases as thermodynamic conditions worsen.[5]

Table III
Apparent Optical Density (Turbidity) of IS10/11 Block Copolymer Solutions (Cyclohexane/Heptane) of Various Concentrations

vol fractn heptane	opt density of polymer solns rel to air			
	0.10 g/L	0.50 g/L	1.08 g/L	2.26 g/L
0.00	0.043	0.045	0.046	0.051
0.10		0.045	0.047	0.054
0.30		0.045	0.048	0.054
0.50		0.046	0.047	0.057
0.60	0.043	0.045	0.047	0.057
0.70		0.045	0.050	0.069
0.80		0.048	0.055	0.069
0.90	0.044	0.049	0.055	0.073

A measurement of block copolymer solution turbidity was obtained for comparison. Table III shows the observed optical density of the polymer solutions at λ = 500 nm. For the higher polymer concentrations, >1 g/L, only very small increases in the turbidity accompany the formation of micelles. For the lowest polymer concentration, 0.1 g/L, no change in optical density is detected upon micellization. Thus, energy transfer can be much more sensitive than turbidity to the presence of micelles at low block copolymer concentrations.

Given the significant sensitivity of the energy transfer technique to micelles at low block copolymer concentrations, an attempt was made to determine the cmc of block copolymer IS10/11 in heptane (actually heptane which contains a small amount of cyclohexane). In this case, the cmc should be much below 0.1 g/L where there is no chance of turbidimetry exhibiting sensitivity. Dilute polymer solutions were prepared by adding small amounts of a stock solution to spectrophotometric grade heptane. The stock solution consisted of 1.06 g/L IS10/11 in 90:10 heptane/cyclohexane.

As shown in Figure 5, there is a significant reduction in I_A/I_D with decreasing polymer concentration over the range of concentrations from about 1 g/L down to about 10^{-3} g/L; over this range I_A/I_D drops from about 0.47 to 0.18. Below 10^{-3} g/L there is apparently a reduction in the concentration dependence which could be interpreted as a plateau in I_A/I_D with block copolymer concentration. However, below about 10^{-2} g/L, the fluorescence emission is rather weak and the signal-to-noise ratio is diminished. The apparent plateau in this system occurs at $I_A/I_D = 0.15 \pm 0.01$, which is well above the values of I_A/I_D observed in the cyclohexane/heptane mixtures absent of micelles in Figure 4. The relatively high values of I_A/I_D at low concentrations in Figure 5 are indicative of the background noise making a substantial contribution to measured intensities I_A and I_D. Although there is little sensitivity below 10^{-3} g/L due to the extreme dilution of the labels, it is clear that the cmc should be at or below 10^{-3} g/L for IS10/11 in heptane.

The extremely low value for the cmc is similar to that reported by Watanabe and Matsuda[33] for a polystyrene-poly(methyl methacrylate) (PS-PMMA) graft copoly-

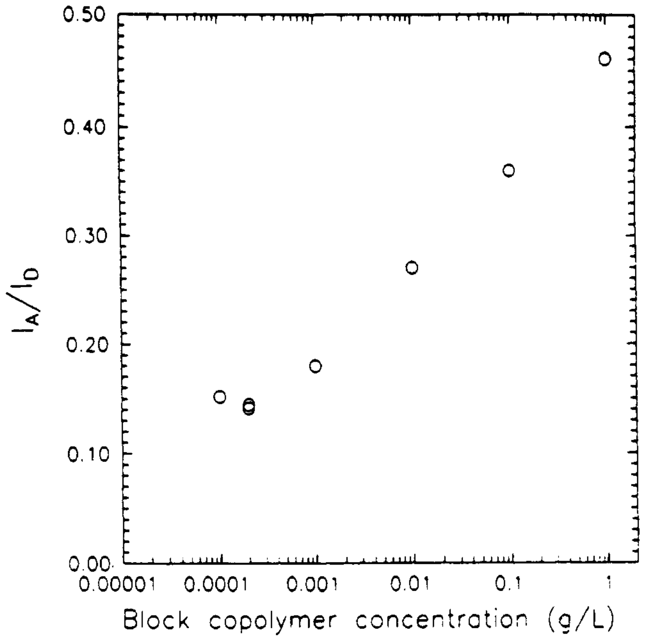

Figure 5. Concentration dependence of I_A/I_D from block copolymer IS10/11 in heptane.

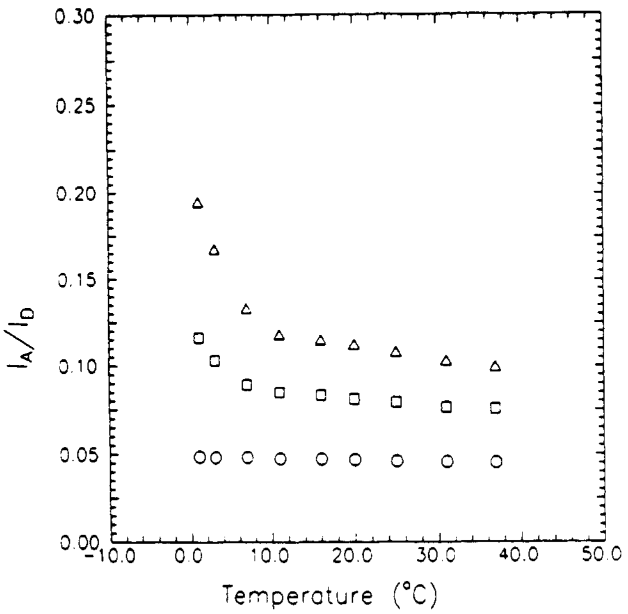

Figure 6. Temperature dependence of I_A/I_D for block copolymer IS3/3 at several concentrations in heptane: 1.41 g/L (△); 1.01 g/L (□); 0.23 g/L (○).

mer solution. They measured energy transfer from fluorene (labeled at the chain backbone) to pyrene (labeled at the end of the grafts). Further, they verified by light scattering that the energy transfer increase was not due solely to a change in intramolecular conformations that also affected their results as both donor and acceptor chromophores were on the same polymer.

As most measurement techniques lose their sensitivity to the cmc at very low polymer concentrations, relatively few cmc values in polymer systems have been reported. A general exception to this is the study of polymeric surfactants in aqueous solutions where changes in surface tension are used to infer changes in molecular association.[44,45] Even in systems like these, detection of micelle formation must be verified by other methods, such as light scattering,[45] although some of the quantitative capabilities may be lost at such dilutions.[33] The present results and those of Watanabe and Matsuda[33] suggest that nonradiative energy transfer may become useful in identifying cmc's in very dilute polymer systems.

In addition to the studies on IS10/11, a second diblock copolymer with terminally labeled styrene blocks, IS3/3, was also investigated. While the composition of the polymer was roughly the same as the first SI diblock copolymer, the molecular weight (see Table I) was much lower compared to IS10/11. Because IS3/3 did not appear to form micelles in cyclohexane/heptane mixtures, micellization experiments were performed in pure heptane.

In order to induce micelle formation of IS3/3 at low concentration, where diffusive or radiative energy transfer are negligible, the solution temperature was lowered. (See Figure 6.) At high temperatures, I_A/I_D is relatively constant. The slight increase in I_A/I_D with temperature is probably due to the temperature dependence of the fluorescence of individual labels rather than to any significant changes in intermolecular interactions. As the temperature is lowered, the environment becomes progressively worse for the polystyrene blocks and, eventually, micelle formation occurs.

In addition to determining the critical micelle temperature, cmt, at which micelle formation for a particular polymer concentration occurs, this experiment brackets the cmc for a given temperature. At 11 °C it appears that no micelles have formed in any of the solutions; however, at 7 °C, the 1.41 g/L solution begins to exhibit a more pronounced increase in I_A/I_D. Because neither of the other samples shows this increase, it is clear that at 7 °C the cmc must fall between 1.01 and 1.41 g/L. Similarly, at 3 °C, the cmc must fall between 0.23 and 1.01 g/L. Thus, although there are circumstances in which the energy transfer technique cannot accurately bracket the critical micelle concentration (e.g. at extremely dilute concentrations in which the fluorescence signal is too weak and at high concentrations in which diffusive or radiative energy transfer contributions might mask the energy transfer due to micelle formation), it can be a sensitive technique for determining the cmc over a rather broad range of conditions.

B.1.b. Carbazole- and Anthracene-Labeled Block Copolymers—Test of Block Copolymer Partitioning above the CMC by a Two-State Energy Transfer Model. A simple two-state model of energy transfer has been devised to relate I_A/I_D to the parameters of the micellar system such as quantum yields, energy transfer efficiencies, and critical micelle concentration. Labels in the micelles are assumed to undergo energy transfer with an efficiency, E, while those not in micelles experience no energy transfer. In the absence of energy transfer, I_A/I_D may be calculated from the ratio of quantum yields and fraction of light absorbed by either the acceptor or donor chromophores:

$$\frac{I_A}{I_D} = \frac{\Phi_A f_A}{\Phi_D f_D}$$

where Φ is the fluorescence quantum yield and f is the fraction of light absorbed by either the acceptors (subscript A) or donors (subscript D). If energy transfer occurs with an efficiency, E, the intensity of the acceptor fluorescence is increased by adding a fraction of the energy absorbed by the donors and the intensity of donor fluorescence is reduced accordingly.

$$\frac{I_A}{I_D} = \frac{\Phi_A(f_A + f_D E)}{\Phi_D f_D(1 - E)}$$

If a fraction, Y/W, of polymer chains and hence labels

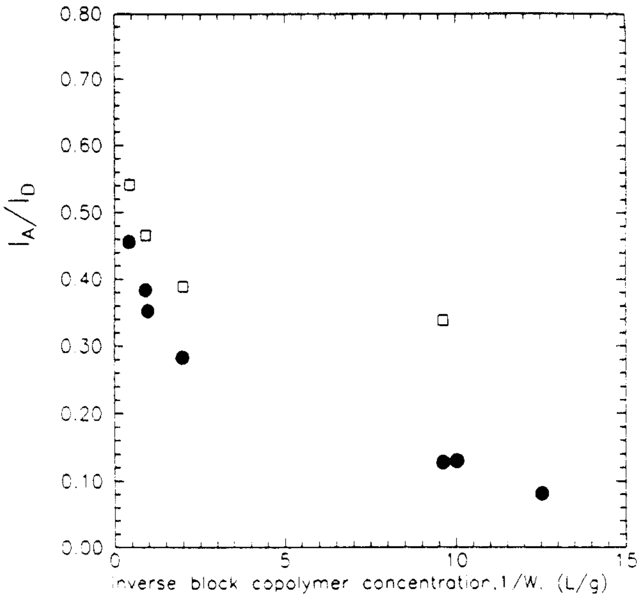

Figure 7. Anthracene to carbazole fluorescence intensity ratio for IS10/11 micellar systems in several cyclohexane/heptane systems as a function of inverse IS10/11 concentration: 20:80 cyclohexane/heptane (●); 10:90 cyclohexane/heptane (□).

are unassociated and experience no energy transfer and a fraction, $(1 - Y/W)$, of polymer chains are in micelles and experience energy transfer, the previous two expressions may be combined to give

$$\frac{I_A}{I_D} = \frac{\Phi_A f_A}{\Phi_D f_D}\left(\frac{Y}{W}\right) + \frac{\Phi_A (f_A + f_D E)}{\Phi_D f_D (1 - E)}\left(1 - \frac{Y}{W}\right)$$

This last expression may be rearranged to yield the following:

$$\frac{I_A}{I_D} = \frac{\Phi_A f_A + \Phi_A f_D E}{\Phi_D f_D (1 - E)} + \frac{Y}{W}\left(\frac{\Phi_A f_A}{\Phi_D f_D} - \frac{\Phi_A (f_A + f_D E)}{\Phi_D f_D (1 - E)}\right) \tag{2}$$

The constants f_A and f_D are easily determined for this system, and Φ_A/Φ_D may be determined from the value of I_A/I_D at concentrations below the cmc. When I_A/I_D is plotted as a function of $1/W$, the intercept, if identifiable, can be used to solve for E, and then Y may be determined. If at values of W exceeding the cmc the plot of I_A/I_D versus $1/W$ yields a line of constant slope, then Y is independent of W and would be equivalent to the cmc. Under such conditions, it could be concluded that above the cmc additional copolymer partitions exclusively into micelles.

Shown in Figure 7 are examples of plots of I_A/I_D as a function of $1/W$. The data are for IS10/11 samples in 10:90 and 20:80 cyclohexane/heptane mixtures and correspond to the fluorescence results given in Figures 4 and 8. It is apparent that the data in Figure 7 do not fit well to a straight line; therefore, for these particular copolymer/solvent systems, the data are inconsistent with the assumption that virtually all additional copolymer in excess of the cmc forms micelles. Instead, the curvature in Figure 7 is consistent with an increase in "free" copolymer concentration (in the homogeneous solution phase) as copolymer concentration increases above the cmc.

By performing appropriate calculations using eq 2 and values of E determined from the intercepts of the curves in Figure 7, it is possible to estimate values of Y, or the amount of copolymer present in the homogeneous solution phase, at concentrations above the cmc. (The assumption that E is independent of concentration above the cmc is equivalent to assuming that micelle structure is independent of polymer concentration for the range of concentrations studied. Results by Bluhm and Malhotra[16] on styrene–isoprene diblock copolymers of similar molecular weight and composition in heptane suggest this assumption may be valid.) Given appropriate estimates[47] of the intercepts (with an estimated error less than 10%) in Figure 7, the values of E (the energy transfer efficiency in the micelles) are calculated to be 0.11_4 in the 20:80 cyclohexane/heptane mixture and 0.16_6 in the 10:90 cyclohexane/heptane mixture. (It is reasonable that the calculated transfer efficiency is higher in the more selective solvent.) Using these values of E and values of Φ and f determined[48] as described above in combination with eq 2, the dependence of Y on polymer concentration (for concentration above the cmc) in the 20:80 cyclohexane/heptane system was calculated and is given in Figure 9. These results are consistent with the interpretation that, for the IS10/11 systems under consideration, a substantial amount of the block copolymer exceeding the cmc (using the data in Figure 8, the cmc is estimated to be about 0.03 g/L for the 20:80 cyclohexane/heptane mixture) partitions itself into the homogeneous

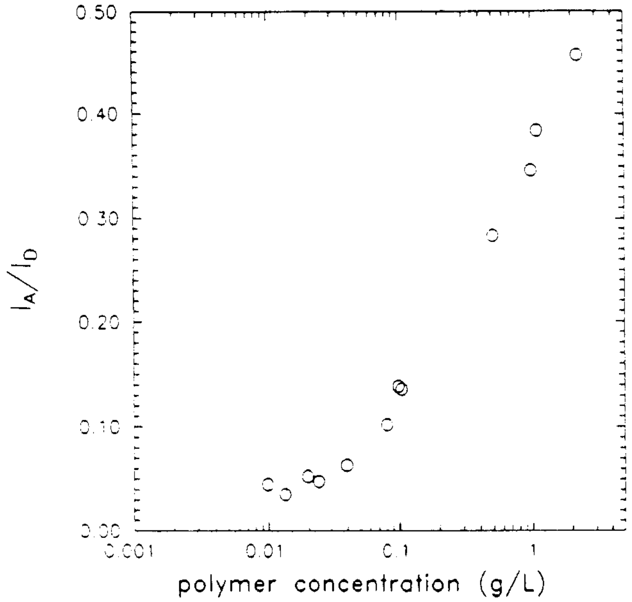

Figure 8. Concentration dependence of anthracene to carbazole fluorescence intensity ratio for IS10/11 in cyclohexane/heptane (20:80) mixture.

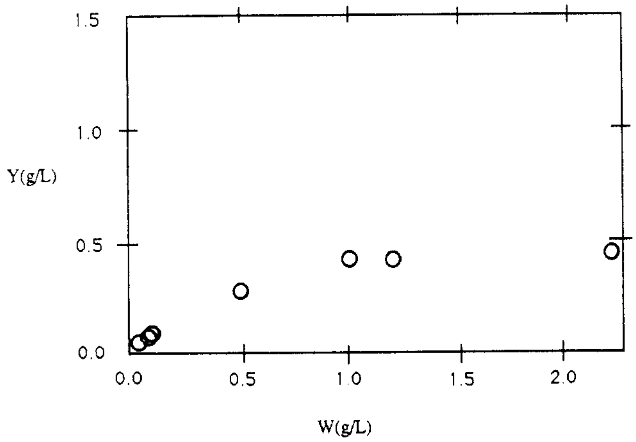

Figure 9. The dependence of IS10/11 concentration unassociated in solution (Y) on total IS10/11 concentration (W) in 20:80 cyclohexane/heptane mixtures as calculated from eq 2 and using data in Figure 7. (The estimated cmc for this system 0.03 g/L.)

solution phase instead of micelles. This amount increases with increasing copolymer concentration above the cmc.

It should be noted that a theoretical study by Munch and Gast[49] concerning micelle formation in block copolymer solutions, based on the developments for bulk blends of block copolymers with homopolymers has recently been published.[50] As their theoretical study and the systems modeled by it are not strictly applicable to the system under investigation in this study (the theory employs solvent molecules that are considerably larger than those used here and assumes athermal interactions between solvent and the repeat units of the block making up the corona of the micelles, resulting in much higher predicted cmc's than those obtained here), no quantitative comparison between experimental results and theoretical predictions will be attempted. However, the results presented by Munch and Gast[49] predict that the free copolymer concentration increases at concentrations exceeding the cmc. While this increase in free copolymer concentration is almost negligible for systems exhibiting high cmc's (>0.10 volume fraction), it becomes increasingly important for systems with decreasing cmc's. The experimental systems studied here had cmc's below 0.001 volume fraction and, if extrapolation of the Munch–Gast approach is permissible, may be expected to exhibit the type of increase in free copolymer concentration shown in Figure 9. Future studies will concern not only the appropriate modification of approaches such as those of Munch and Gast[49] to allow for quantitative comparison of theory and experiment but also the experimental study of other block copolymer systems that may not exhibit the same level of partitioning of block copolymer between homogeneous solution and micelles found in the IS10/11 systems.

B.2. Naphthalene- and Anthracene-Labeled Block Copolymers. SI44/32 was used to examine further the role energy transfer can play in investigation of polymer solution structure. SI44/32 is labeled at the isoprene ends with either naphthalene or anthracene, with the anthryl label serving as acceptor. However, both the naphthyl labels and the styrene blocks may act as donors. The strong overlap of the absorption spectra of the naphthyl labels and the styrene blocks complicates the analysis as both intramolecular and intermolecular energy transfer may be possible. In this respect, SI44/32 is more similar in its character to that of the graft copolymers studied by Watanabe and Matsuda[33] than to the anthryl- and carbazolyl-labeled IS3/3 and IS10/11.

Solutions were composed of two parts (by weight) anthryl-labeled polymer to one part naphthyl-labeled polymer. As the styrene block molecular weight was high and because phenyl units absorb weakly at the excitation wavelength 278 nm, the styrene blocks absorbed a significant fraction of the excitation energy.

Although the styrene blocks may absorb an appreciable fraction of light, the fluorescence spectrum in the short wavelength region has a substantial contribution from naphthalene emission. One reason for this is that the quantum yield of polystyrene is relatively low. Furthermore, energy transfer from polystyrene to naphthalene may occur; $R_0 \approx 10.5$ Å for the polystyrene/1-methylnaphthalene pair.[32] Emission from the naphthalene labels is strongest in the range from 320 to 340 nm; this is the same location as the polystyrene excimer peak. Thus, both components contribute to the donor fluorescence signal. Fortunately, the anthryl (acceptor) labels absorb relatively little light at the excitation wavelength. Additionally, acceptor emission is rather far removed from the donor emission; therefore, interpretation of the energy transfer experiments is reasonably straightforward.

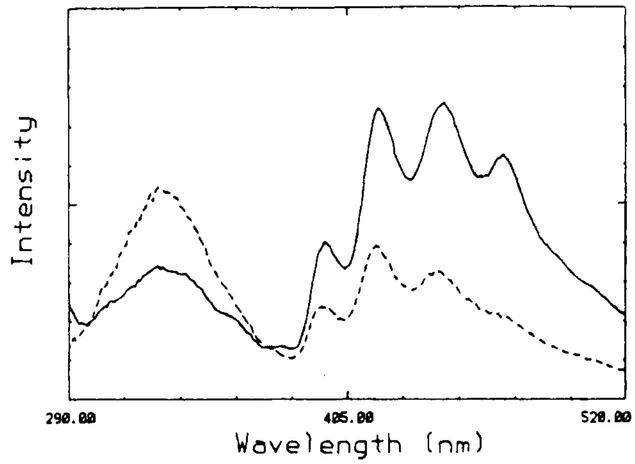

Figure 10. Corrected fluorescence spectra of labeled SI44/32 in dioxane/ethanol mixtures (concentration = 17.1 g/L): (- - -) 95% dioxane, 70 °C; (—) 61% dioxane, 25 °C.

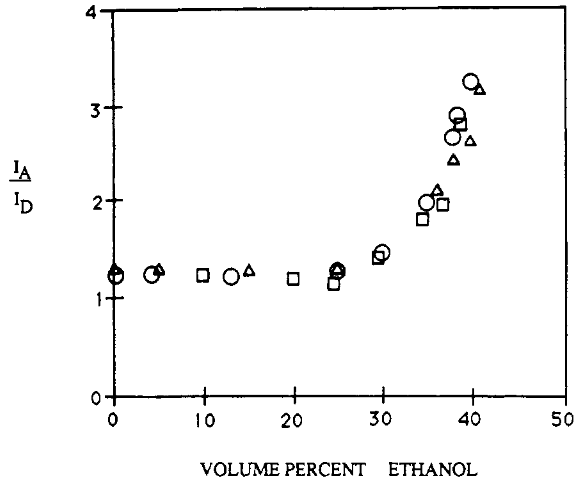

Figure 11. Ratio of acceptor to donor fluorescence intensity for labeled SI44/32 solutions (dioxane/ethanol). Concentration: 8.1 g/L (□); 17.1 g/L (△); 32.3 g/L (○).

Typical corrected fluorescence spectra are shown in Figure 10 for both homogeneous (relatively little energy transfer) and heterogeneous (increased energy transfer) solution systems. The emission intensities at 414 and 324 nm were taken to be representative of the acceptor and donor, respectively, with a correction for the overlap of donor and acceptor emission bands.

Figure 11 shows I_A/I_D for solutions of different concentrations in dioxane–ethanol mixtures of varying composition. Pure dioxane solutions are expected to be homogeneous. Verification of this comes from comparing I_A/I_D from the dioxane system to I_A/I_D from other solutions having the same polymer concentration and label content in a nonselective solvent such as tetrahydrofuran. I_A/I_D is the same in these cases. Figure 11 shows a significant increase in energy transfer with increasing ethanol content beginning at about 25% ethanol and continuing to the point of precipitation. As the ethanol volume fraction passes 25%, micelles form having isoprene cores surrounded by a shell of polystyrene; concurrently, energy transfer increases. This behavior parallels that observed in the case of IS3/3 and IS10/11 described earlier and also that reported by Watanabe and Matsuda.[33]

This micellization may cause an increase in energy transfer by two mechanisms. First, aggregation of chains brings a greater number of styrene blocks, forming the corona,

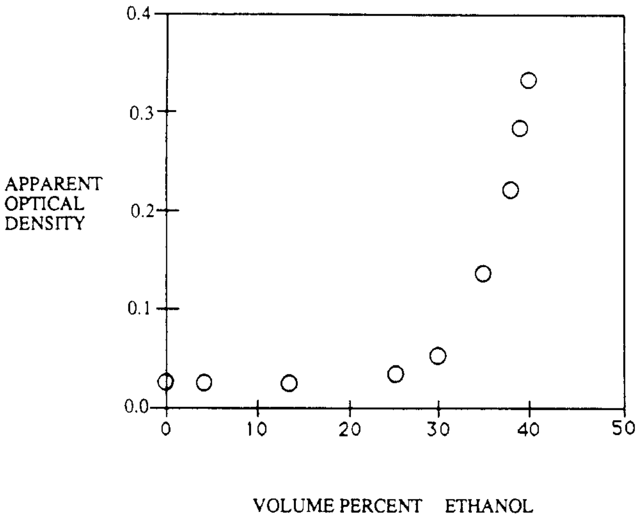

Figure 12. Apparent optical density at 500 nm for 32.3 g/L solution (dioxane/ethanol) of block copolymer SI44/32.

near a given anthracene label in the core. Thus, in addition to receiving some energy through intramolecular transfer from the styrene block on the chain on which the anthracene resides, the anthryl group may begin to accept energy from other styrene blocks in the aggregate. Second, the worsening solvent environment causes the polymer chains to contract. As the excluded volume of a chain decreases, its segments, as well as any labels, must come in closer proximity. Contraction of the chains, particularly of the isoprene blocks, must decrease the average separation between styrene block and anthracene label. As more ethanol is added to the system, energy transfer increases further presumably because of an increase in the number of micelles and an increase in the number of chains in a micelle and/or because the coils continue to contract. Of course, the presence of naphthyl units also allows for greater intermolecular energy transfer of the type seen in the carbazole-containing systems described in the previous section.

Figure 12 corroborates the energy transfer data by showing the apparent optical density of the solutions as a function of volume fraction of precipitant. The apparent optical density of the polymer solutions in the binary solvent, relative to pure binary solvent, was measured at a wavelength at which neither the polymers nor the labels absorb an appreciable amount of light. A sharp increase in the apparent absorbance is observed at a solvent composition that corresponds well with the point of increase in I_A/I_D.

Figure 13 shows the temperature dependence of I_A/I_D. Because I_A and I_D change with temperature independent of changes in energy transfer characteristics, the data are normalized by dividing by I_A/I_D obtained from homogeneous solutions at the same temperature. As expected[5,51] the solutions containing more precipitant show a break in I_A/I_D at higher temperatures.

While Figures 11 and 13 demonstrate that both cmc's and cmt's can be determined in the SI44/32 systems, it is clear that the change in I_A/I_D is less pronounced in the case of polystyrene/naphthalene to anthracene energy transfer (in SI44/32) than in the case of carbazole to anthracene transfer (in IS3/3 and IS10/11). Although efficient Förster energy transfer is expected even from excimer forming polymers,[44,52] there are several reasons why the change in energy transfer efficiency may be less dramatic in SI44/32. One is that the quantum yield for polystyrene is significantly lower than for carbazole. In addition to reducing the total emission intensity, this also tends to reduce R_0. The lower R_0 for both polystyrene–anthracene transfer and labeled naphthalene–anthracene transfer relative to that expected for the labeled carbazole–anthracene pair reduces the probability of energy transfer in the former system. Additionally, some energy transfer is expected to occur in the SI44/32 system under homogeneous conditions due to intrachain interactions. The random coil conformation of the chain[9] allows energy transfer from polystyrene to anthracene whereas intermolecular transfer is virtually excluded from the homogeneous IS3/3 and IS10/11 solutions barring radiative transfer. By comparison, the experiments that involved transfer from carbazole to anthracene, strictly intermolecular energy transfer, provide easier interpretation and are more sensitive than those in which the styrene blocks absorbed much of the excitation light.

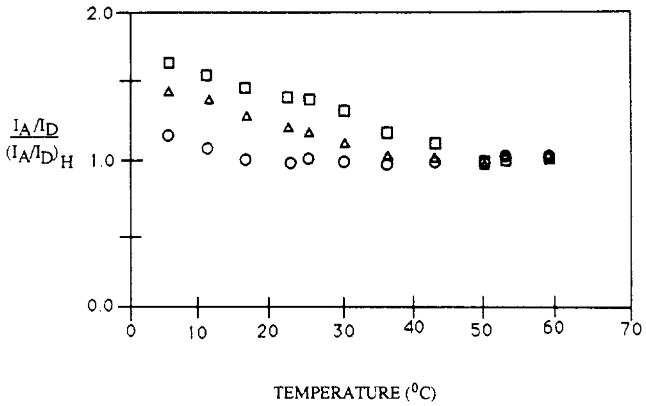

Figure 13. Normalized ratio of acceptor to donor fluorescence for SI44/32 in dioxane/ethanol solutions. The subscript H refers to a homogeneous solution at the same temperature (concentration = 8.1 g/L): 95% dioxane (○); 75% dioxane (△); 67% dioxane (□).

C. Time-Correlated Single Photon Counting (TCSPC) Experiments—Carbazole- and Anthracene-Labeled Block Copolymers. To investigate further the photophysics of the IS3/3 and IS10/11 systems under micelle-forming conditions, TCSPC experiments on polymers and monomeric analogs were performed to obtain fluorescence lifetimes. 9-Methylanthracene was found to have a fluorescence lifetime, τ, of 4.2 ns in cyclohexane and 3.1 ns in heptane; this compares well to a published value of 4.6 ns in cyclohexane.[42] For 9-ethylcarbazole τ = 8.3 ns in cyclohexane while τ = 5.7 ns in heptane. Berlman[42] lists a value of 18.3 ns for 9-methylcarbazole in cyclohexane. When attached to the polymer chains, the lifetimes of both chromophores increase. The carbazolyl-labeled IS3/3 had lifetimes of 9.3 and 7.2 ns in cyclohexane and heptane, respectively. The anthryl-labeled counterpart had lifetimes of 6.0 and 7.1 ns in cyclohexane and heptane. When attached to the ends of block copolymer IS10/11, the carbazole labels had an excited state lifetime of 9.7 ns in cyclohexane. The decay curve for the anthryl-labeled IS10/11 sample in cyclohexane was not quite single exponential in nature; however, when the data were fit to a single exponential, the lifetime was 6.6 ns, close to that obtained for anthryl-terminated IS3/3.

The lifetime of the carbazole labels on IS10/11 was measured as a function of polymer concentration in cyclohexane solutions. (See Table IV.) Carbazole label lifetime increased by about 4.4 ns as the polymer concentration changed from 1 g/L to almost 300 g/L. A similarly striking increase in the lifetime of the carbazole labels was observed when the solvent was changed from cyclohexane (τ = 9.7 ns) to a 10:90 cyclohexane/heptane mix-

Table IV
Fluorescence Lifetime, τ, of the Carbazole Label in IS10/11 as a Function of IS10/11 Concentration[a]

IS10/11 concn, g/L	τ, ns
1	9.7
22	10.2
105	11.7
290	14.1

[a] Solvent is cyclohexane.

Table V
Lifetimes[a] **of Carbazole and Anthracene Labels in Solutions of Block Copolymer IS10/11**

polymer concn, g/L	solvent	carbazole lifetime ($\lambda \simeq 341$ nm), ns	anthracene lifetime ($\lambda \simeq 440$ nm), ns
2.2	cyclohexane	8.5	8.9
2.2	50:50 cyclohexane/heptane		8.8
2.2	30:70 cyclohexane/heptane	7.9	17.1
2.2	10:90 cyclohexane/heptane	7.5	17.2

[a] Measurements made from solutions containing both carbazole-labeled and anthracene-labeled IS10/11. (Note that when measurements were made on solutions containing only anthracene-labeled IS10/11, the anthracene fluorescence lifetime was unchanged within experimental error in going from a cyclohexane solution to a 10:90 cyclohexane/heptane solution.)

ture (τ = 12.6 ns). This may be due to an increase in the local concentration of polymer chains caused by micellization. These results clearly indicate that any fluorescence lifetime analysis of labeled block copolymers that may form micelles must include information on the dependence of lifetime on local polymer concentration; otherwise, faulty conclusions may be reached. It should be noted that polymer IS3/3, which did not form micelles in heptane at room temperature, showed a decrease in the lifetime of the carbazole labels when the solvent was changed from cyclohexane to heptane.

The decay curves of the anthracene labels on polymer IS10/11 were measured and found to show slight non-single exponential character. Nevertheless, when fit to a single exponential decay, no concentration dependence was observed. Additionally, τ changed only slightly when the solvent was changed from cyclohexane to a micelle-forming cyclohexane–heptane mixture. (The change in τ was within the error of the measurements, as defined by a single standard deviation of the measurement in going from a cyclohexane to a 10:90 cyclohexane/heptane mixture.) This indicates that anthracene self-quenching[53] is not significant under conditions of micellization.

When both anthryl- and carbazolyl-labeled polymers were present in the same solution, their behavior was quite interesting and is summarized in Table V. In the 2.2 g/L solution, the carbazole label lifetime decreases by 1 ns as the transition from homogeneous to micellar solution is made. By itself, this decrease that is caused by the quenching of the carbazole labels by the anthracene is not very substantial. However, when considered with the increase in τ observed when only the carbazole labels were in the micelle, there is significant quenching being caused by the anthracene units. Additionally, there is a large increase in the observed lifetime of the anthracene labels under micelle-forming conditions that is not present in the absence of carbazole-labeled block copolymers (direct anthracene excitation).[54] (See discussion above.) In the absence of micelles, the measured lifetime for the anthracene labels is predominantly that which is observed from direct excitation of anthracene. When micelles form, the anthracene emission can arise from two sources, direct excitation and nonradiative transfer from the carbazole labels. As the rate of nonradiative transfer depends upon the spatial separation between labels, there is some finite time following the excitation pulse and preceding the emission from the anthracene that the excitation resides on the carbazole label. Therefore, under micelle forming conditions, the measured lifetime of the anthracene labels is apparently increased due to the time lag caused by the carbazole lifetime.[54] It is interesting to note that the measured lifetime of the anthracene labels under micelle forming conditions is approximately equal to the sum of the lifetimes of the individual components when micelles do not form.

Summary

This investigation has further explored the utility of photophysical methods in the study of polymeric systems. It has been shown that the attachment of chromophores to a polymer chain may change some aspects of their photophysical behavior as evidenced by slight spectral shifts or increased lifetimes; however, these changes do not appreciably alter other mechanisms of their behavior. For example, the critical energy transfer distance, R_0, for a donor–acceptor pair was not changed much by attaching the labels to a polymer chain.

Both steady-state intensity and fluorescence lifetime measurements showed that intermolecular micelle formation is easily detected, even in very dilute block copolymer solutions, by energy transfer experiments. Furthermore, it was seen that block copolymer molecular weight has a profound effect on micelle formation in selective solvent environments as IS10/11 had a cmc at or below 10^{-3} g/L in heptane at room temperature while IS3/3 formed micelles in heptane only at reduced temperature. Additionally, the temperature at which micelles were detected changed with polymer concentration. Analogously, as the solvent quality decreased by the addition of selective precipitant, micelle formation was first detected in higher polymer concentration solutions.

It is evident that fluorescence methods, in particular nonradiative energy transfer experiments, are very sensitive to polymer solution behavior. Intermolecular energy transfer studies may be quite useful in the investigation of multimolecular interactions especially in dilute solutions. The so-called "spectroscopic ruler" is commonly used in the study of intramolecular distances in biological systems[55] and has also been applied to the investigation of intramolecular structure in synthetic polymers.[56] As mentioned by Fredrickson,[57] recent theoretical advances should be instrumental in conferring quantitative precision on energy transfer experiments. This method of investigation is still in its infancy.[58,59]

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(47) In the particular case of Figure 7, it is relatively easy to estimate values of the y intercept with small error. However, readers who may be doing similar studies are warned against trying to lessen the error further by obtaining data on I_A/I_D at high block copolymer concentrations, resulting in data very close to the y intercept in a plot of I_A/I_D vs $1/W$. At high block copolymer concentrations, diffusive and radiative energy transfer may begin to compete with or even overshadow effects on nonradiative energy transfer, thereby invalidating the approach defined and used in this study. Care was used in the present study to employ concentrations low enough to minimize the effects of diffusive and radiative energy transfer but high enough to allow a reasonable estimate of the y intercept in Figure 7.

(48) For the IS10/11 system studied here, f_A/f_D was taken to be 0.011_4 by using data from ref 42. Φ_A/Φ_D (actually not true quantum yields as the left-hand side of eq 2 is a ratio of intensities rather than quantum yields) was determined to be 3.95 by using the fact that, below the cmc in the 20:80 cyclohexane–heptane system, I_A/I_D is approximately 0.045 (see Figure 8).

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(54) One reviewer commented that the high level of fluorescence at 520 nm observed from anthracene-labeled copolymers (see Figures 2a and 10) and the doubling of the fluorescence lifetime of anthracene labeled copolymers in going from a homogeneous solution to a solution containing micelles were evidence of substantial excimer fluorescence. However, it should be noted that others (including Tang, W. T.; Hadziioannou, G.; Smith, B. A.; Frank, C. E. *Polymer* **1988**, *29*, 1313) have noted enhanced fluorescence between 470 and 550 nm of anthracene-labeled polymer as compared to the low molecular weight fluorescence analogue. These measurements were on dilute, homogeneous solutions where excimers could not form. Also, as noted in section C of Results and Discussion and in Table V, the anthracene fluorescence lifetime doubled upon micellization only when solutions contained both carbazole-labeled polystyrene and anthracene-labeled polystyrene (the excitation wavelength, 305 nm, resulted mostly in direct excitation of carbazole labels); when solutions contained only anthracene-labeled IS10/11, the anthracene fluorescence lifetime remained unchanged within experimental error upon micellization. This latter point strongly indicates that excimer fluorescence is not present to any significant degree in any of our systems.

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Registry No. 9-Methylanthracene, 779-02-2; 9-ethylcarbazole, 86-28-2.