Fluorescence Energy Transfer Studies of Bulk Styrene–Isoprene Diblock Copolymers and Their Blends with Polyisoprene: Applications to Microphase Separation

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ABSTRACT: Fluorescence energy-transfer measurements of labeled styrene–isoprene diblock copolymers were demonstrated to be sensitive to microphase separation or micelle formation in blends of the copolymers with polyisoprene. Anthracene and carbazole chromophores, serving as energy-transfer acceptors and donors, respectively, were attached to the terminus of the styrene block of the anionically polymerized copolymers. Microphase separation was shown to exist in blends of low molecular weight diblock copolymers with low molecular weight polyisoprene, based on changes in I_A/I_D, the ratio of acceptor to donor fluorescence intensities. However, the gradual increase exhibited in I_A/I_D with increasing block copolymer concentration indicates that a sharp transition, expected of a critical micelle concentration (cmc), is not apparent in these blends or that the cmc occurs at very low block copolymer concentration. The values of I_A/I_D obtained in systems with micelles were compared to a two-state energy-transfer model incorporating the presence of free block copolymer in the homogeneous matrix and block copolymer in micelles; for concentrations at which micelles exist, it was determined that the amount of free block copolymer increases as the total block copolymer concentration increases. The sensitivity of fluorescence lifetime measurements of the carbazole label to microphase separations in the blends was also investigated.

Introduction

In recent years fluorescence energy-transfer experiments have become quite common in the study of solution- and solid-state polymer systems[2-10] as these techniques are very sensitive to both intramolecular and intermolecular interactions. Energy-transfer experiments are well-suited for the study of systems such as bulk-state block copolymers and their blends with homopolymers because the size scale of interest (approximately the dimension of a block of a copolymer chain) corresponds well with the length scale of sensitivity of energy transfer. Previous studies[2,8] have shown that energy transfer is useful in studying micelle formation in block and graft copolymer solutions.

In this paper, nonradiative energy transfer is demonstrated to be useful in studying the morphology or structure (miscibility) of styrene–isoprene block copolymers in blends with polyisoprene. In all cases, block copolymers have the energy donor (carbazole) or acceptor (anthracene) labels located at the terminus of the styrene block. As the efficiency of energy transfer by a Förster mechanism is inversely proportional to the sixth power of the distance between labels,[11] interblock association such as micelle or domain formation should be accompanied[12] by a marked increase in energy-transfer efficiency. This may be monitored by measurement of steady-state fluorescence in the form of the ratio of acceptor to donor fluorescence intensity, I_A/I_D, or by measurement of the fluorescence lifetime, τ_D, of the donor label. A two-state energy-transfer model[2] using I_A/I_D is employed to determine quantitatively the amount of block copolymer in micelles and in the homogeneous polymer matrix. For the systems studied here, the results indicate that at block copolymer concentrations exceeding the phenomenological critical micelle concentration additional block copolymer can partition itself between micelles and the homogeneous matrix.

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 (isoprene), 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 (styrene), the resulting living diblock copolymer was divided into three portions for either terminal attachment of fluorescent groups or termination with 2-propanol.

Anthryl residues were attached by reacting the living polymer anion with 9-(chloromethyl)anthracene which was obtained from Aldrich and dissolved in cyclohexane or toluene. The terminator solutions were deoxygenated by bubbling with N_2 immediately prior to reaction. Carbazole labels were attached in a similar fashion using 9-(4-bromobutyl)carbazole which was prepared by the condensation of sodium carbazole and 1,4-dibromobutane.[13]

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 model compounds, 9-methylanthracene $\epsilon_{369\mathrm{nm}}$ = 7980 M^{-1} cm^{-1} and 9-ethylcarbazole $\epsilon_{294\mathrm{nm}}$ = 16 800 M^{-1} cm^{-1}, were used for comparison. As has been observed in other studies,[2,5,14,15] the absorbance spectra of the attached labels were red-shifted by a few nanometers compared to the chromophores on monomeric analogues. Molecular weight averages were determined by intrinsic viscosity and gel permeation chromatography. Salient characteristics of the diblock copolymers are summarized in Tables I and II.

The 2000 and 9000 MW polyisoprenes (PI) were synthesized in cyclohexane like the block copolymers but without label attachment. Nearly monodisperse PI of 3280, 10 600, and 34 000 MW was purchased from Polymer Laboratories.

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Table I
Polymer Characterization—Molecular Weight

sample	first block M_v	first block M_n	first block M_w	block copolymer M_n	block copolymer 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]

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

Table II
Polymer Characterization—Weight Fraction Polystyrene and Label Efficiency

sample	wt fraction polystyrene[a]	label efficiency[a] anthracene	label efficiency[a] carbazole
IS3/3	0.54	0.78	0.86
IS 10/11	0.52	0.55	0.51

[a] Based on UV–vis absorbance measurements.

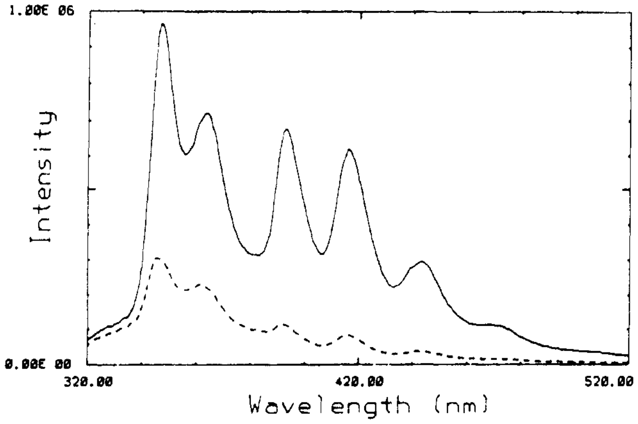

Figure 1. Fluorescence spectra of labeled IS10/11 in 9000 MW polyisoprene: —, 2.0% block copolymer; - - -, 0.15% block copolymer.

Bulk polymer films were prepared by casting polymer solutions with a concentration of 3–4 wt % polymer onto 1 in. by 1 in. polished quartz or UV grade silica slides. The films were allowed to air-dry for 12–24 h and then vacuum dried at room temperature for at least 24 h. The cast films had a thickness of typically 30 but no more than 60 μm.

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. The excitation wavelength employed was 294 nm. Emission was viewed from the front of the solid sample.

Fluorescence lifetimes were obtained 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 which is described elsewhere.[16] 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.[17] Carbazole label lifetimes were measured using a narrow bandpass optical filter with peak transmission at either 341 or 360 nm.

Results and Discussion

The behavior of terminally labeled diblock copolymers IS3/3 and IS10/11, whose characteristics are given in Tables I and II, was investigated in a number of blends with PI of various molecular weights and over a wide concentration range. The PI matrix forms an environment that is selective toward the isoprene blocks. The styrene blocks reduce unfavorable interactions with the matrix by segregating to form solid-state "micelles".[18] This type of phase separation brings the labeled ends of the block copolymer in proximity; hence, energy transfer is enhanced. Figure 1 demonstrates the effect increased energy transfer has on the fluorescence spectra obtained from the labeled block copolymers. With an increase in IS10/11 concentration and a concurrent increase in the amount of microphase separated block copolymer (micelles with styrene cores), there is an increase in high wavelength (acceptor) fluorescence relative to low wavelength (donor) fluorescence. The two peaks apparent between 340 and 370 nm are from the carbazole labels while the three peaks apparent between 385 and 460 nm are from the anthracene labels.[2] Given that virtually all (generally ≥98% for the conditions tested in this study) of the fluorescence observed at 345 nm is associated with the carbazole label while virtually all of the fluorescence observed at 442 nm is associated with the anthryl label,[2] it is convenient to choose the ratio of fluorescence intensity at 442 nm to that at 345 nm to represent I_A/I_D, the ratio of acceptor to donor fluorescence intensity.

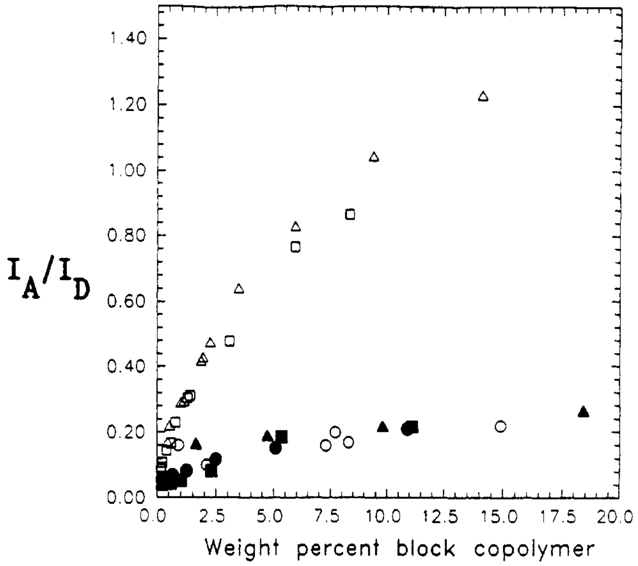

Figure 2. Labeled block copolymer concentration dependence of energy-transfer efficiency in blends of IS3/3 with polyisoprene: (■) M_{PI} = 2000; (○) M_{PI} = 3280; (●) M_{PI} = 9000; (□) M_{PI} = 10 600; (△) M_{PI} = 34 000; (▲) blend with unlabeled block copolymer.

Figure 2 summarizes the energy-transfer experiments on blends of IS3/3 with PI of various molecular weight along with a corresponding "control" experiment of labeled block copolymer blended with unlabeled block copolymer. With regard to the pure block copolymer data, the abscissa refers to the concentration of labeled block copolymer needed to match the labeled content in the block copolymer/homopolymer blend.[19] This figure illustrates a significant similarity in I_A/I_D between the blends with PI of 9000 or lower molecular weight and the blend

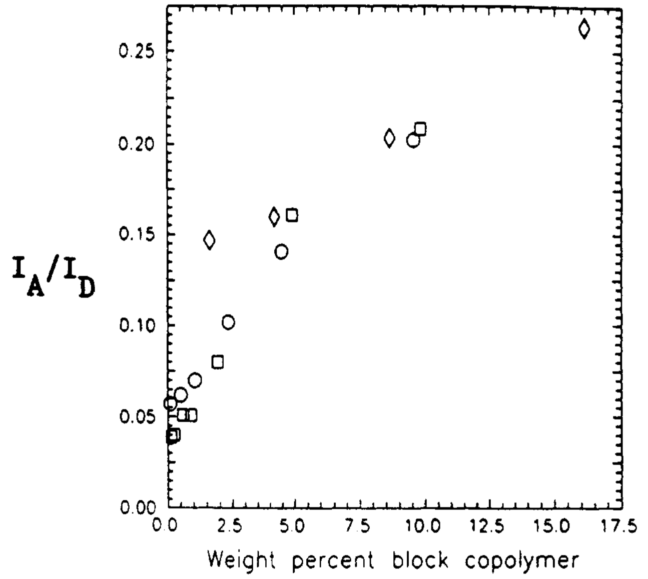

Figure 3. Comparison of energy-transfer efficiency in blends of labeled IS3/3 with 2000 MW polyisoprene (□), 9000 MW polyisoprene (○), and unlabeled block copolymer (◇).

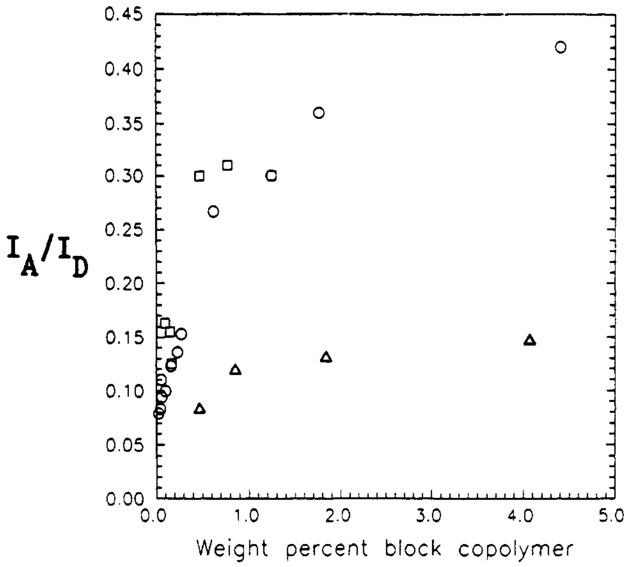

Figure 4. Comparison of energy-transfer efficiency in blends of labeled IS10/11 with 2000 MW polyisoprene (□), 9000 MW polyisoprene (○), and unlabeled IS10/11 (△).

with unlabeled block copolymer; I_A/I_D is approximately equal for all of these blends of a given label content irrespective of the materials in the blend and exhibits a relatively small dependence on weight percent block copolymer. This small dependence of I_A/I_D on the amount of block copolymer for blends with 9000 or lower molecular weight PI is illustrated more clearly in Figure 3 which covers a much smaller range of I_A/I_D than shown in Figure 2. [The data for the 3280 MW PI blend were not included in Figure 3 as the label content in this system does not exactly match those for the 2000 and 9000 MW polyisoprene blends at equal block copolymer contents. (See ref 19.)]

Assuming that the labels do not cause any extra interaction or phase separation, in the case of the bulk block copolymer samples the labeled block copolymer will be dispersed homogeneously throughout the unlabeled copolymer. Of course, the bulk block copolymer samples are expected to form a lamellar microstructure so the labels will reside only in the polystyrene and interphase regions (roughly one-half of the volume of the bulk block copolymer). Given the similarity of I_A/I_D values in the blends of labeled block copolymer with PI of 9000 or lower molecular weight and the blend of labeled and unlabeled block copolymer and given the fact that I_A/I_D is not very sensitive to labeled block copolymer concentration in comparison to the systems containing higher molecular weight PI, it can be concluded that there is not significant microphase separation in the blends of IS3/3 with PI of 9000 or lower molecular weight. Instead, it is likely that much of the small increase in I_A/I_D with copolymer (label) content is associated with a slight increase in nonradiative energy-transfer efficiency as more labels are added to the system and the average separation distance between labels decreases.

In contrast to the data for the lower molecular weight PI blends, the data shown in Figure 2 for blends of IS3/3 with polyisoprene of 10 600 or 34 000 molecular weight exhibit a very large increase in I_A/I_D with increasing weight percent block copolymer. This increase is consistent with significant microphase separation of the styrene blocks in these blends. Obviously, the molecular weights of PI and the blocks constituting the copolymer are very important in determining the miscibility of the styrene blocks with the PI matrix. (The sensitivity of the phase behavior to molecular weight in such systems has been predicted theoretically[18,20] and demonstrated experimentally[21-23] by other techniques.) Effects of PI microstructures may also be important for the systems studied here as the polyisoprene samples purchased from Polymer Laboratories may differ in microstructure from the PI synthesized for this study. These effects will be studied in a future investigation. However, taken by itself, it is clear that PI molecular weight is key to the morphology developed in these systems.

Figure 4 summarizes a more limited energy-transfer study performed on blends of IS10/11 with PI of molecular weight 2000 and 9000 and with unlabeled IS10/11. As in Figure 2, with regard to the pure block copolymer data, the abscissa refers to the concentration of labeled block copolymer needed to match the label content in the block copolymer/homopolymer blend. For the case of the IS10/11-PI blends there is a large increase in I_A/I_D with increasing weight fraction of block copolymer. These results are similar to those given in Figure 2 for the IS3/3 blends with the 10 600 and 34 000 molecular weight PI and again indicate significant microphase separation. A comparison of the data in Figures 2 and 4 also illustrates the importance of block length in determining miscibility of diblock copolymers added to homopolymer. While IS3/3 is seemingly quite miscible with PI of molecular weight as high as 9000, IS10/11 exhibits significant phase separation when added to even 2000 molecular weight PI.

It is interesting to note that in Figures 2 and 4 there is no abrupt transition in I_A/I_D with increasing block copolymer content to serve as evidence of a critical micelle concentration (cmc). Either a cmc (in the classical sense) is not present in these systems, or it occurs at very low block copolymer concentrations not sampled by these studies.

While it has been noted that nonradiative energy transfer can contribute to the slight increases of I_A/I_D with increasing block copolymer content for the homogeneous or nearly homogeneous systems, it should be made clear that little of the increase in I_A/I_D with increasing block copolymer content observed in Figures 2–4 can be attributed to the effects of radiative energy transfer. The upper bound of the extent of radiative energy transfer may be estimated by calculating the absorbance of the acceptor labels. For example, for the systems in Figure 4, the maximum total label concentration is about 1.1 × 10^{-3} M; thus, the anthracene label content is about 0.5 × 10^{-3} M. At the peak in the absorbance spectrum, the extinction coefficient of 9-methylanthracene is about 8 × 10^{-3} M^{-1} cm^{-1}. For a path length (film thickness) of 30 μm, the maximum absorbance calculated from Beer's law, $A = \epsilon cl$, is $A = 0.012$. Therefore, it is clear that less than 2% of the carbazole emission is transferred radiatively to the anthracene labels.

An important question associated with micelle formation of diblock copolymers in blends with homopolymers concerns the degree to which additional copolymer above an effective cmc contributes to the formation of new micelles or to free, unassociated block copolymer dissolved in the homopolymer matrix. Leibler et al.[18] have addressed this issue theoretically and have concluded that not all added block copolymers in excess of the effective cmc form new micelles; instead, some of the additional polymer remains unassociated, resulting in an increase in the homogeneous phase entropy.

Recently, in an energy-transfer study of micelle formation in diblock copolymer solution,[2] a two-state energy-transfer model was developed to determine the extent to which the block copolymer above an effective cmc contributed to the formation of new micelles in solutions. In this two-state model,[25] labels in micelles are assumed to undergo energy transfer with an efficiency, E, while those unassociated in solution experience negligible energy transfer. In the absence of energy transfer, I_A/I_D may be related to the ratio of quantum yields and fraction of light absorbed by either the acceptor or donor chromophores

$$\frac{I_A}{I_D} = \frac{\Phi_A f_A}{\Phi_D f_D} \tag{1}$$

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

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

If a fraction, Y/W, of block copolymer chains, and hence labels, are unassociated and experience negligible energy transfer, and a fraction, $(1 - Y/W)$, are associated in micelles and experience energy transfer, the previous two expressions may be combined to give

$$\frac{I_A}{I_D} = \frac{\Phi_A f_A}{\Phi_D f_D}\left(\frac{Y}{W}\right) + \frac{\Phi_A(f_A + f_D E)}{\Phi_D f_D(1 - E)}\left(1 - \frac{Y}{W}\right) \tag{3}$$

This last expression may be rearranged to yield the following:

$$\frac{I_A}{I_D} = \frac{\Phi_A(f_A + f_D E)}{\Phi_D f_D(1 - E)} + \left(\frac{Y}{W}\right)\left[\frac{\Phi_A f_A}{\Phi_D f_D} - \frac{\Phi_A(f_A + f_D E)}{\Phi_D f_D(1 - E)}\right] \tag{4}$$

With eq 4, I_A/I_D may be plotted against $1/W$. If all additional block copolymer above an effective cmc contributes to form new micelles and none forms additional unassociated chains beyond those present at the effective cmc (implying that Y is the cmc), then a linear plot should result. Examples of such plots are given in Figure 5. It is apparent that the data in Figure 5 do not fit well to straight lines; this indicates that for the systems investigated some of the additional block copolymer above the effective cmc goes to form free, unassociated chains in the homogeneous phase.

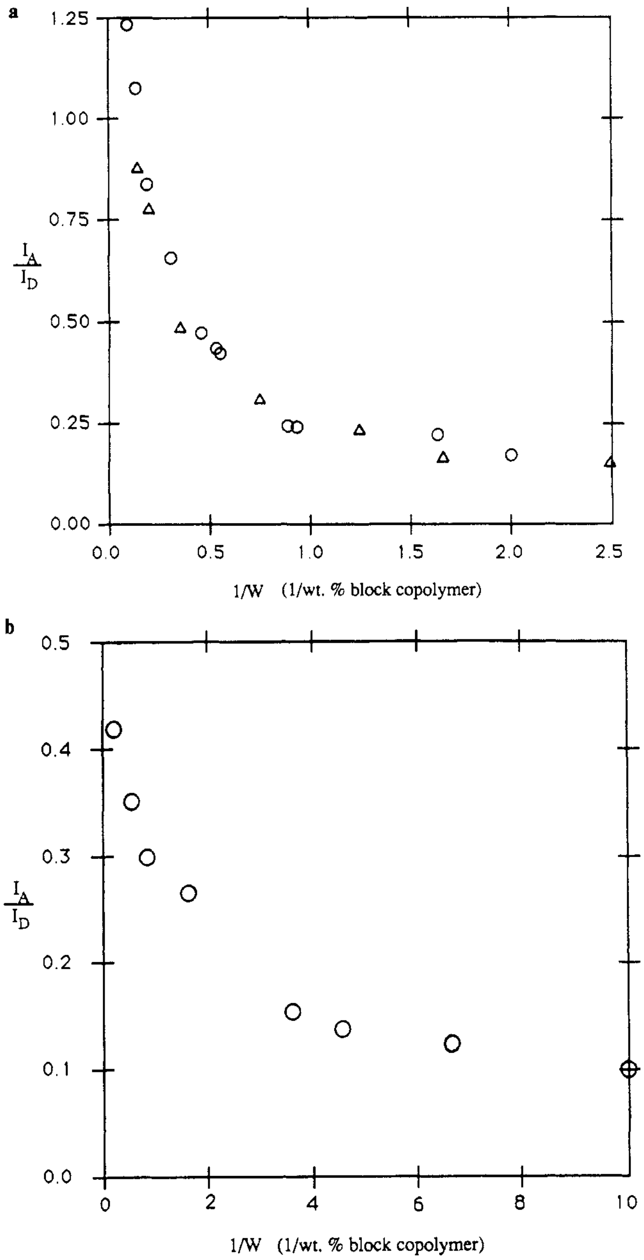

Figure 5. (a) Test of I_A/I_D for blends of IS3/3 with 34 000 MW (○) and 10 600 MW (△) polyisoprene by the two-state energy-transfer model given by eq 4. (b) Test of I_A/I_D for blends of IS10/11 with 9000 MW polyisoprene by the two-state energy-transfer model given by eq 4.

By performing calculations using eq 4 and values of E determined from the intercepts of the curves in Figure 5, it is possible to estimate values of Y, or the amount of copolymer present in the homogeneous matrix, at concentrations where micelles exist. (The assumption that E is independent of concentration above the cmc is equivalent to assuming that the micelle structure is independent of polymer concentration for the range of concentrations studied.) Given appropriate estimates[26] of the intercept (with an estimated error of less than 5%) in Figure 5b, the value of E for the IS10/11-9000 MW PI system is calculated to be 0.097_2. Using this value of E and values of Φ and f determined[27] in ref 2 in combination with eq 4, the dependence of Y on block copolymer

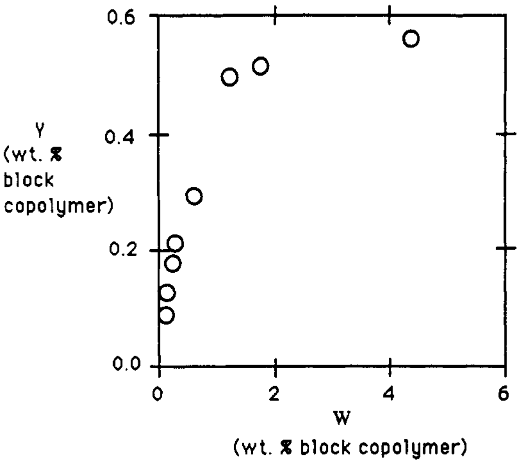

Figure 6. Dependence of the concentration of unassociated IS10/11 (Y) on total IS10/11 concentration (W) in 9000 MW polyisoprene as calculated from eq 4 and using data in Figures 4 and 5b.

concentration for the IS10/11–9000 MW PI system was calculated and is given in Figure 6. These results are consistent with the interpretation that, for the system under consideration, a substantial amount of the block copolymer exceeding the cmc partitions itself into the homogeneous matrix phase instead of micelles. This amount increases with increasing copolymer concentration above the cmc although the effect is relatively small at concentrations exceeding 1 wt % block copolymer.

A similar conclusion concerning the partitioning of block copolymer into the homogeneous matrix phase at concentrations exceeding the cmc has been reached recently by Kinning et al.[21] on styrene–butadiene diblock copolymer–polystyrene blends using a combination of small-angle X-ray scattering and electron microscopy. Kinning et al. reported that the predicted[18,20] values of the critical micelle concentration are 1–2 orders of magnitude smaller than those observed experimentally. Additionally Kinning states that "...the volume fraction of free copolymer in the matrix increases markedly for these blends as the overall concentration of copolymer increases".[21] This is consistent with the energy-transfer observations reported here. As the copolymer concentration increases, some of the chains enter the micellar phase while some remain unassociated. Those which participate in micelles presumably experience energy transfer; therefore, they contribute to the acceptor emission intensity. Those chains that remain unassociated are on average widely separated and transfer no energy or transfer energy inefficiently in comparison to the block copolymers in micelles; hence, for block copolymers in the homogeneous matrix phase, donor emission should predominate. The overall effect of such partitioning between the micellar phase and the homogeneous matrix phase is an increase in the amount of acceptor fluorescence relative to donor fluorescence.

It should be noted that the experimental studies by Kinning et al.[21] were performed above the glass transition temperature of both component polymers. This should allow for a close approach to equilibrium. The energy-transfer studies reported here were performed at room temperature which is above the glass transition temperature of only the polyisoprene block, and therefore these studies may not exactly duplicate the equilibrium conditions studied by Kinning et al.[21] It is possible that nonequilibrium states which were created in the solvent casting procedure used in making the films remained in the blends used in the energy-transfer studies. Future work will involve measurements at elevated temperatures so that equilibrium states may be studied. This work may require the use of other chromophores as it has been determined that the anthracene label can exhibit chemical instability if maintained at high temperatures for long time periods.[28]

Table III
Comparison of Observed Donor Fluorescence Lifetimes in Blends of Block Copolymer IS3/3 and IS10/11 with 9000 MW Polyisoprene

wt % block copolymer[a]		label concn $M \times 10^{-4}$	A_1	A_2	τ_1, ns	τ_2, ns	$\langle\tau\rangle$, ns
IS10/11	0.1	0.17	0.45	0.76	13.7_4	2.1_6	11.3
IS10/11	1.0	1.54	0.52	0.80	12.5_5	2.3_5	11.2
IS10/11	10.0	15.6	0.62	0.62	9.7_4	2.4_9	8.3
IS3/3	4.0	4.7	0.52	0.71	13.2_6	1.9_5	11.4
IS3/3	10.0	12.0	0.60	0.67	12.9_2	2.3_6	11.1

[a] Equal weight mixtures of anthracene-labeled and carbazole-labeled block copolymers.

It is possible to criticize the use of eq 4 with the data from Figures 2 or 4 on the grounds that the assumption used in formulating eq 4 that no energy transfer occurs between the free block copolymers in the homogeneous phase is not strictly correct. The nonradiative energy-transfer efficiency, E^*, between labels in a homogeneous blend is based on the following equation

$$E^* = \frac{R_0^{\,6}}{R_0^{\,6} + R_{\mathrm{DA}}^{\,6}} \tag{5}$$

where R_0 is the critical overlap distance defining a 50% energy-transfer efficiency between labels and R_{DA} is the average separation distance between donor and acceptor molecules. The average separation distance between labels has been expressed[29] as $R_{\mathrm{DA}} = 6.5[\text{labels}]^{-1/3}$ where the label concentration has units of moles/liter and R_{DA} is in angstroms. For the case of the blend of IS10/11 with 9000 MW PI, E^* remains well below 1% for block copolymer concentrations below 4.4 wt %, the highest concentration of IS10/11 used in the study of that system. (See Figures 4, 5b, and 6.) Ignoring the small energy-transfer efficiency in the homogeneous phase by no means invalidates the conclusion drawn from the data that not all of the additional block copolymer in excess of the cmc forms micelles.

Besides the steady-state fluorescence studies reported above, a limited study was undertaken to investigate the advantages and/or disadvantages afforded by the measurement of fluorescence lifetimes in the investigation of diblock copolymer–homopolymer blends. Carbazole label lifetimes were measured for several systems: bulk copolymer in the absence of any anthracene-labeled copolymer and IS3/3 or IS10/11 blended with 9000 MW PI.

In the bulk, the excited-state lifetime of carbazole-labeled block copolymer was measured to be 12.5 ns. When both carbazole- and anthracene-labeled block copolymers were blended with PI, the measured carbazole lifetime was reduced. This may be interpreted as evidence of the energy-transfer process quenching the carbazole emission. Measured lifetimes of the carbazole label from a number of blends of both IS3/3 and IS10/11 are given in Table III. A double-exponential fit was used to characterize the carbazole label decay curves; however, there is no reason to believe that the double-exponential fit has any particular photophysical significance.[17] Because heterogeneous systems may be expected to have complex behavior, quantitative interpretations may be possible if the decay curves can be compared consistently.

To do this, an average lifetime $\langle \tau \rangle$ may be calculated[6,30]

$$\langle \tau \rangle = (\sum A_i \tau_i^2) / \sum A_i \tau_i \qquad (6)$$

where A_i is the preexponential coefficient for a given lifetime τ_i. With such an analysis, the preexponentials tend to compensate for changes in the lifetimes; hence, the average lifetimes obtained are not strongly dependent upon the details of the fitting.

As shown in Table III, there does not appear to be a significant trend in the data from blends of either polymer IS10/11 or polymer IS3/3; however, for the few observations, it might be concluded that IS3/3 shows slightly longer $\langle \tau \rangle$'s than IS10/11 blends. This may suggest that IS10/11 is more segregated in these blends than is IS3/3. With greater phase segregation, the carbazole labels transfer energy more effectively; therefore, their fluorescence is quenched, that is, their lifetimes are reduced. It is also clear that the lifetimes of the carbazole labels in all of the blends are shorter than the lifetime of the labels in the absence of anthracene. This suggests that both IS10/11 and IS3/3 may exhibit some phase separation in the blends with polyisoprene.

This particular observation differs from the steady-state fluorescence results which suggested that while the IS10/11 blend with 9000 MW polyisoprene had extensive phase separation, the IS3/3 blend did not. This may be due to several factors including the following: fluorescence lifetime measurements in the form of single photon counting experiments may be more sensitive to effects of modest phase separation than steady-state fluorescence, or the complexity of the fluorescence lifetimes of heterogeneous systems is such that it is possible for the averaged lifetimes from extensively phase-separated system and a modestly phase-separated or nearly homogeneous system to appear to be quite similar. Obviously, given their complex nature, further detailed research will be necessary to determine how to utilize most fully fluorescence lifetimes in order to complement information from steady-state fluorescence measurements in studies of block copolymer–homopolymer blends.

Summary

Steady-state fluorescence energy-transfer studies involving isoprene–styrene diblock copolymers labeled at the terminus of the styrene blocks have been demonstrated to be very sensitive to the phase behavior of blends of the copolymers with homopolymers. In particular, these results indicate that the molecular weights of the blocks constituting the block copolymer and the molecular weight of the homopolymer play a controlling role in the phase behavior, in agreement with conclusions drawn by others, both theoretically[18,20] and experimentally.[21-23] These results have also shown that above an effective cmc, additional block copolymer partitions itself between micelles and the homogeneous matrix phase, in agreement with conclusions reached recently on related systems by Kinning et al.[21]

Having demonstrated the sensitivity of these techniques, work is ongoing concerning their more general applicability. By the careful construction of labeled diblock copolymer systems, it should be possible to investigate other important issues concerning these blends, such as the level of homopolymer present in the micelle core, interpenetration of the micelle corona by homopolymer, and differences in blends studied at high temperature under equilibrium conditions versus blends observed under conditions where morphology may be affected by processing conditions such as solvent casting or shear flow.[31] Furthermore, these techniques are being investigated for studying compatibilization phenomena[32,33] involving blends of block copolymers and two homopolymers. Investigations of the utility of fluorescence lifetime measurements in the study of these systems are also continuing.

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these materials. Some of the effects may be indicative of the solvent-casting procedures used in preparing the blends and may be related to the fact that the measurements were taken below the glass temperature of the polystyrene blocks. Nevertheless, these results illustrate the sensitivity of energy transfer to the phase behavior of these systems.

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(26) In the particular case of Figure 5b, it is relatively easy to estimate a value of the y intercept with small error. (It was taken to be 0.475.) However, readers who may be doing similar studies are warned against trying to reduce the error by obtaining 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, radiative energy transfer, not to mention a change in gross microphase-separated structure, may invalidate the approach defined and used in this study. Care was used in the present study to employ concentrations low enough to minimize such effects but high enough to allow a reasonable estimate of the y intercept in Figure 5b.

(27) For the IS10/11 systems studied here, f_A/f_D was taken to be 0.11_4 as in ref 2. Φ_A/Φ_D (actually not true quantum yields as the left-hand side of eq 4 is a ratio of intensities rather than quantum yields) was determined in ref 2 to be 3.95 in a cyclohexane/heptane solution; in the absence of accessible fluorescence data below the cmc in a blend of IS10/11 in 9000 MW PI, it was assumed that 3.95 was a reasonable estimate for Φ_A/Φ_D in the blend.

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Registry No. PI, 9003-31-0; (isoprene)(styrene) (block copolymer), 105729-79-1.

Flow and Diffusion through Random Suspensions of Aggregated Rods: Application to Proteoglycan Solutions

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ABSTRACT: Flow and point-solute diffusion through random distributions of rods and model rod assemblages with small volume fraction is considered. The effect of steric interactions on the rod orientation distribution in the assemblages is calculated. The method of averaged equations is used to calculate the effective diffusion coefficient and the flow permeability in both distributions of rods and rod assemblages. We discuss the application to biopolymer aggregates, particularly proteoglycans, and consider dependence on polymer concentration and the effect of aggregation.

1. Introduction

As a model for transport in biopolymer solutions, we consider flow and diffusion in random distributions of rods and rod assemblages with small volume fraction.

Long-chain, highly charged polyions have an important effect on the physicochemical properties of connective tissue, which are reviewed by Grodzinsky.[1] The polyions influence the diffusion of both small ions and larger solutes and resist the flow of water, enhancing the tissue's ability to withstand rapid deformation. The fixed charges on the polymers produce a large swelling pressure, giving tissues such as cartilage a load-bearing ability, and cause electrokinetic phenomena such as electroosmosis and streaming potentials, in which electric fields and ion fluxes are coupled to pressure gradients and solvent flow.

The glycosaminoglycans (GAGs) are an important component of connective tissue, often occurring in aggregates known as proteoglycans (PGs). There are two stages of aggregation: first, GAG side chains (chondroitin sulfate and keratan sulfate) are attached to a core protein to form a "PG monomer", and second, PG monomers are bound to a hyaluronate molecule to form a PG aggregate. The PG aggregate has a complicated branched structure (see Figure 1) and can contain up to 40 000 GAG side chains. Although the function of PGs is not well understood, the resulting inhomogeneity in the GAG concentration has a potentially large effect on the properties of the tissue. For example, the large variation of the viscosity of PG solutions with the proportion of monomers aggregated has been measured experimentally.[2]

In this study the GAG side chains are idealized as cylinders. Several workers have used the ad hoc rod-in-cell model to investigate flow[3,4] and point-solute diffusion[5]

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