210 *Macromolecules* **1998,** *31,* 210−212

Characterization by Fluorescence Energy Transfer of the Core of Polyisoprene−Poly(Methyl Methacrylate) Diblock Copolymer Micelles. Strong Segregation in Acetonitrile

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Micelle formation by block copolymers, when dissolved in a solvent selective for one of the blocks, has been studied for many years.[1,2] Theoretical models have been developed to describe the structure of both "star-like" and "crew-cut" micelles.[3] Recently, block copolymer micelles have investigated as vehicles for small-molecule delivery[4] and for surface modification.[5] These applications emphasize the need for more detailed understanding of the parameters that control structure and dynamics of the micelles and micelle-solubilized materials in solution. One would like to learn how dynamics of exchange with the outside relate to the core morphology.[6,7] The exchanging species can be the diblock chains (unimers), and/or core-dissolved molecules. The techniques of small-angle X-ray[8,9] and small-angle neutron scattering[10,11] have often been used to obtain structural information about block copolymer micelles. In this work we wish to show how the technique of direct dipole−dipole energy transfer (DET) can be utilized to characterize the morphology of the micellar core. By morphological characterization we mean a determination of geometric and compositional characteristics of the core, particularly at the core−corona interface.

Recently, Martin and Webber have applied DET measurements to the study of polystyrene−poly(methacrylic acid) block copolymer micelles in dioxane−water mixtures where the polystyrene block was doubly labeled with naphthalene and anthracene.[12] However, sample heterogeneity did not allow the authors to analyze the data quantitatively to extract morphological information. In the past we have presented qualitative experimental results showing that the micellar core may swell in the presence of mixed solvents.[13] Since then, we have perfected the theoretical methodology for the analysis of data obtained in DET experiments, allowing for extraction of more detailed morphological information from the fluorescence decay data.[14] A fuller investigation of the PI−PMMA micellar system using other experimental techniques in addition, such as dynamic and static light scattering, will be reported in a future publication.[15]

Synthesis of PI−PMMA diblock copolymers labeled at the junction with a single fluorescent chromophore has been described earlier, employing a strategy first reported by Quirk.[16,17] The architectural structures of the samples are presented in Chart 1. Our donor chromophore (D) is phenanthrene, the acceptor chromophore (A) is anthracene, and the polymers are singly labeled. The PI block composition is 40% 1,2-addition, 55% 3,4-addition, and 5% 1,4-addition.

The PI−PMMA samples have the following number-averaged degrees of polymerization of (N_{PI}:N_{PMMA}) 150:470 (D-labeled), 150:550 (A-labeled), and 125:485 (unlabeled), respectively. In acetonitrile (CH_3CN), a modestly good solvent for PMMA, PI is insoluble and comprises the micellar core. Dynamic light scattering studies indicate that dilute CH_3CN solutions of the three samples have micellar hydrodynamic radii (R_H) of 21.6, 25.3, and 22.3 nm, respectively.

To utilize DET to characterize the core, the A- and/or D-labeled chains need to be randomly mixed in any given micelle. When the labeled polymers were dissolved separately in acetonitrile and then mixed as solutions, much less energy transfer was observed by steady-state fluorescence measurements than when the two polymers were premixed in a good solvent for both blocks (CH_2Cl_2), dried, and then dissolved in acetonitrile. This result indicates that the micelles do not exchange polymers on a time scale of weeks, even though the micelle core has a T_g well below room temperature. We also observed some sensitivity of the micelle size (DLS) to sample preparation conditions. Thus, to obtain reproducible results, the D- and A-labeled polymers were first dissolved in CH_2Cl_2. The solvent was then evaporated in a N_2(g) stream to yield a thin film which was dried under vacuum at 50 °C. The solid mixture, when dissolved in acetonitrile, led to the desired mixed micelles, with, as we will show, D and A restricted to the core−corona interface. For the DET experiments reported here, the total polymer concentration was kept at 0.25 wt %.

All fluorescence decay measurements employed the single photon timing technique, at 22−25 °C, on solutions deoxygenated by gentle bubbling with argon (15 min). The donor was excited at 300 nm, and its emission was monitored at 348 nm. Figure 1 displays fluorescence decay curves ($I_D(t)$) of the micellar solutions, where the fraction of A-labeled polymer increases from 0 (curve a) to 0.74 (curve g). Note that in the absence of acceptors, decay is exponential, with a donor lifetime (t_D) of 45.5 ns. In the presence of acceptors, the donor decay is faster because of energy transfer.

The rate of DET (w) depends on the D−A separation distance (r). For dipole−dipole interaction, Förster[18] showed that $w = (r/R_0)^{-6}/t_D$, where R_0 is a constant that depends on the spectral characteristics of D and A. For the pair under consideration, R_0 is (2.3 ± 0.1) nm.[12,19] Because closely spaced pairs decay faster than those further apart, the donor fluorescence decay ($I_D(t)$) contains information about the distribution of distances. The pair-distribution is in turn related to morphology. If we presume that the morphology is one in which the micelle core has a smooth surface (interface thickness $\ll R_0$), then DET is restricted to the surface of a sphere. According to Klafter and Blumen[20] under such circumstances

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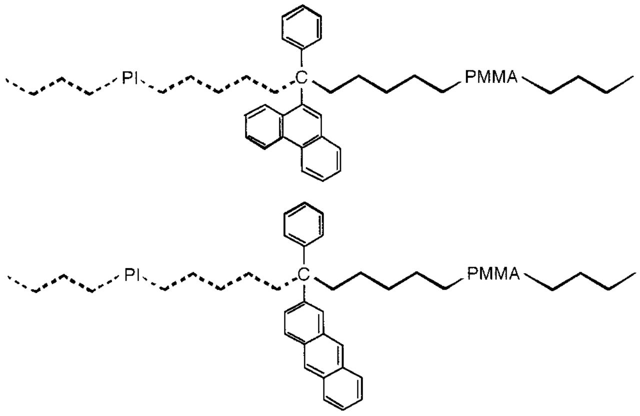
Chart 1



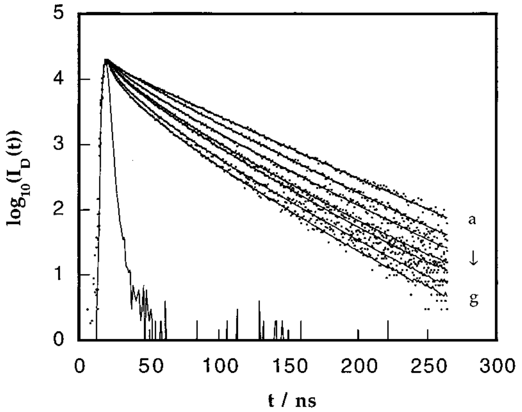


Figure 1. Time-resolved fluorescence decay profiles of 0.25 wt % PI−PMMA micellar solutions. The donor chromophore, phenanthrene, is excited at 300 nm. Donor emission is observed at 348 nm. The fraction of the acceptor dye, anthracene, is varied from 0 (trace a) to 0.74 (trace g).

$$I_D(t) = I_D(0)\exp\{(-t/\tau_D)\}\exp\{-g(t)\}$$
$$g(t) = P(-t/\tau_D)^{\beta} \quad (1)$$

where P is a parameter proportional to the local concentration of acceptors (c_A), and $\beta = \Delta/6$.

Here Δ is the dimensionality of the system in which DET takes place. Equation 1 is strictly valid only if $\Delta = 1$, 2, or 3. For the surface of a perfect sphere $\Delta = 2$. If the interface becomes more diffuse (on the scale of R_0), the fit of data to eq 1 would yield values of $\Delta > 2$ and one would have to use the more complete DET theory.[14,21] When D and A are attached to the surface of a perfect sphere of radius R_{core}

$$g(t) = P(-t/\tau_D)^{1/3} \qquad P = 0.339\, f_A N_{agg}(R_0/R_{core})^2 \quad (2)$$

where $f_A = c_A/(c_A + c_D)$ is the mole fraction of acceptor labeled chains and N_{agg} is the micelle aggregation number.

When we fit the data of Figure 1 to expression 1, two fitting parameters, β and P, are recovered. Figure 2 shows a plot of the recovered values of exponent b as a function of mole fraction (f_A) of acceptor labeled polymers. We obtain $\beta = 0.345 \pm 0.034$. This corresponds to a dimensionality of $\Delta = 2.07 \pm 0.20$. Within experimental uncertainty, $\Delta = 2.0$. This means that the interface is sharp, on the scale of <1 nm ($<0.5R_0$). Figure 3 shows the fit of data to eq 2, where it is assumed that $\beta = {}^1/_3$. P is proportional to f_A, as expected from eq 2. From the slope, we obtain the product $N_{agg}(R_0/R_{core})^2 = 9.00 \pm 0.15$. To extract the two unknowns (N_{agg}, R_{core}), another independent relationship is needed. Since from the value of β we have indication of a near-perfect spherical core, we assume that the core is comprised only of the insoluble PI block. $M_n^{PI} = (10.3 \pm 0.6) \times 10^3$ g/mol (from gel permeation chromatography (GPC)) with a density of bulk PI, $\rho_{PI} = 0.913$ g/cm^3. In this case, the expression

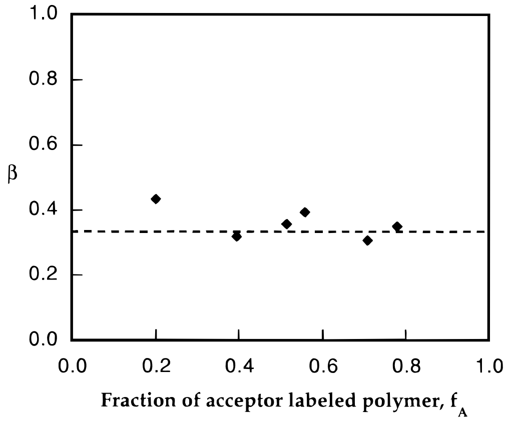


Figure 2. Recovered values of the exponent parameter β obtained by fitting data of Figure 1 to eq 1 of the text. The donor lifetime τ_D is fixed at 45.5 ns. The mean value of the recovered dimensionality $\Delta = 6\beta = 2.07 \pm 0.20$. The dashed line shows $\beta = {}^1/_3$ ($\Delta = 2.0$, the perfect sphere).

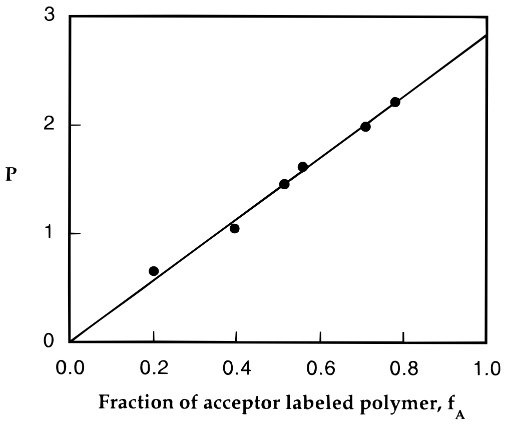


Figure 3. Plot of the recovered values of parameter P, vs mole fraction of acceptor labeled polymer (f_A) obtained by fitting data of Figure 1 to eq 2 of the text. The donor lifetime τ_D is fixed at 45.5 ns. Slope = 0.339 $N_{agg}(R_0/R_{core})^2 = 3.05 \pm 0.05$.

$$N_{agg} = \frac{4\pi R_{core}^{3}\rho_{PI}N_{AV}}{3M_n^{PI}} \quad (3)$$

where N_{AV} is Avogadro's number, gives us the desired second relationship. Combining the two relations for N_{agg}, we obtain $R_{core} = (7.6 \pm 0.9)$ nm, and $N_{agg} = 98 \pm 24$. The largest contribution to the error limits is uncertainty in the GPC determination of M_n^{PI}, with the balance due to uncertainty in the value of R_0.

In summary, one is able to utilize the technique of direct nonradiative energy transfer (DET) to characterize morphology of the core of block copolymer micelles in selective solvents. For the PI−PMMA/CH_3CN systems considered here, the PI segments strongly segregate from the solvent by forming a sharp interface with a compact spherical shape. The sharp interface, together with the macromolecular size of the PI block, results in immeasurably slow rates of intermicellar exchange. We plan to investigate how presence of additional components such as PI homopolymer or PI-miscible solvents affect the core morphology and exchange dynamics of the system.

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