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Detection of the rate of exchange of chains between micelles formed by diblock copolymers in aqueous solution

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Summary

A fluorescence method is described for the measurement of the rate of exchange of chains between micelles formed by diblock copolymers in aqueous solution. The method requires two samples of the diblock copolymer. One sample is labelled with a Förster donor, the other sample is labelled with a Förster acceptor. Successful application of the method is demonstrated with diblock copolymers composed of polystyrene and poly(ethylene oxide). The donor and acceptor are naphthalene and pyrene, respectively. The label is covalently attached to the copolymers at the junction points between the two blocks. Solutions with micelles are formed independently by the two labelled samples. At the time of mixing of the two solutions, no micelle contains both a donor and an acceptor. Micelles containing both types of labels may be formed at later times as a consequence of the exchange of labelled chains. The efficiency of nonradiative singlet energy transfer from naphthalene to pyrene is measured as a function of time after mixing of the two solutions. At 60° C the rate constant deduced from the time dependence of the fluorescence is on the order 10^{-5} s^{-1}. At ambient temperature, however, no exchange can be detected, presumably because of the difficulty in extraction of a polystyrene block from the glassy core.

Introduction

Diblock copolymers of polystyrene and poly(ethylene oxide) can form micelles in water if the block of poly(ethylene oxide) is much longer than the block of polystyrene (1,2). The formation of micelles by diblock copolymers in selective solvents is, in many respects, analogous to the formation of micelles by small amphiphilic molecules in aqueous solution. With small molecules, the formation of micelles is reversible. For some systems, such as sodium dodecyl sulfate, the residence time for an amphiphilic molecule to be in a particular micelle is on the order of 10^{-5} s (3). There is little information on the rates of the comparable processes involving micelles formed by diblock copolymers. If the temperature of the measurements is far below the glass transition temperature of the core formed by the insoluble blocks of the copolymer, the rate might be so slow that equilibration of the micelles would be difficult. Indeed, some experimental results indicate that the equilibrium between free chains and the chains in the micelles may not be obtained under certain conditions (4,5). Simulations of the self-assembly of diblock copolymers in dilute solution also find that the micelles equilibrate slowly under certain conditions (6).

Direct measurement of the exchange in these systems is difficult, in part because of the very low concentration of free chains that is in equilibrium with the micelles. Here we report a method for monitoring the rate of exchange of chains *in situ*, using diblock copolymers with chemically bonded fluorescence probes.

Materials

The characteristics of the diblock copolymers used in the experiments are presented in Table I. The method used for the preparation of the diblock copolymers with a fluorescent label at the junction point has been presented previously (7,8). Stock solutions of P_N (2.0×10^{-2} g l^{-1}) and P_P (2.7×10^{-2} g l^{-1}) were prepared by solution of the appropriate copolymer in distilled, deionized water at 60 – 70° C, and cooled overnight. The solutions for study of the time dependence of Förster transfer are prepared by mixing any two stock solutions at room temperature. Fluorescence emission spectra are measured with an SLM-8000C spectrofluorometer.

TABLE 1

Characterization of the Diblock Copolymers

Sample	M_n, PS block	M_n, PEO block	Label
P_N	4500	11,000	Naphthalene
P_P	4500	19,000	Pyrene
P_U	4500	14,000	None

Results and Discussion

Emission and excitation spectra (not shown here) exhibit no unusual features for the two stock solutions separately. The diblock copolymers in the stock solutions do not exhibit any tendency for excimer formation.

Figure 1 depicts the emission spectrum immediately after mixing 20 ml of the stock solution of P_N with 5 ml of the stock solution of P_P. Excitation is at 290 nm, which is at the maximum of the excitation band for naphthalene. The emission band near 340 nm is from naphthalene, and the emission band near 400 nm is from pyrene. In Figure 1 the 400 nm band is due mainly to direct excitation of pyrene at 290 nm. The energy transfer in this case is small, based on the comparison of the intensity of the naphthalene emission in Figure 1 with the naphthalene emission

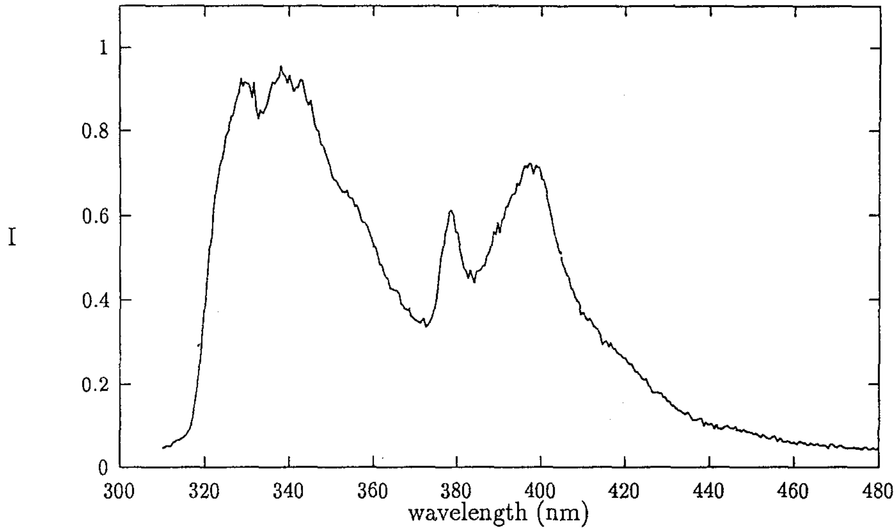

Figure 1. Emission spectrum at ambient temperature immediately after mixing the two stock solutions to give a solution with 1.6×10^{-2} g l^{-1} of P_N and 5.4×10^{-3} g l^{-1} of P_P. Excitation is at 290 nm.

from a solution that contains only P_N. The emission spectra do not change when the solution is held at ambient temperature for several days.

When a similar solution is heated to 60° C for several hours, and then cooled to ambient temperature for measurement of the emission, it shows a decrease in the intensity of the emission from naphthalene, and an increase in the emission from pyrene. Figure 2 presents four examples of these emission spectra, where the time at 60° C is 0–97 hr. The change in the shape of the emission spectrum is due primarily to the increase in the efficiency of energy transfer from naphthalene to pyrene, as a consequence of an exchange of chains between micelles as illustrated in Eq. (1)–(4). The processes represented by the last two equations produce micelles that contain both naphthalene and pyrene. When a micelle contains both labels, the efficiency of Förster nonradiative energy transfer is increased due to the closer approach of the donor to the acceptor.

$$(P_N)_x \rightarrow (P_N)_{x-1} + P_N \tag{1}$$

$$(P_P)_x \rightarrow (P_P)_{x-1} + P_P \tag{2}$$

$$(P_N)_{x-1} + P_P \rightarrow (P_N)_{x-1}P_P \tag{3}$$

$$(P_P)_{x-1} + P_N \rightarrow (P_P)_{x-1}P_N \tag{4}$$

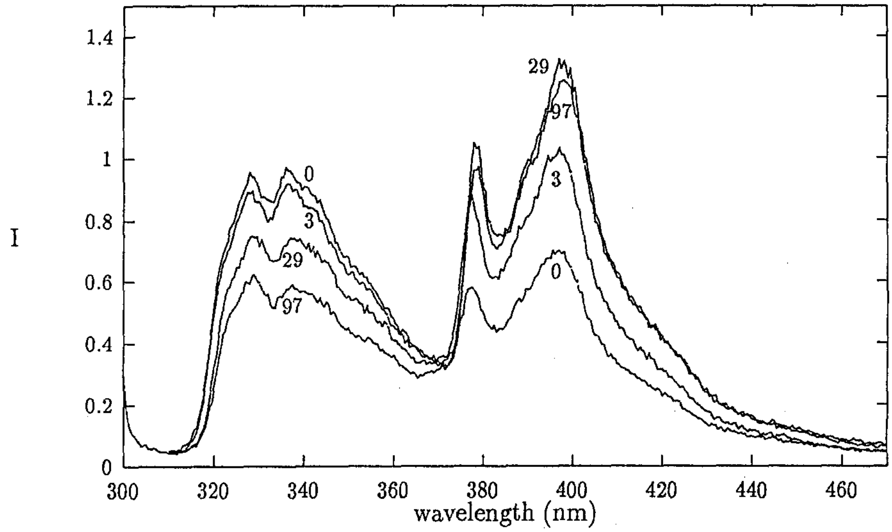

Figure 2. Emission spectra at ambient temperature for a solution with 1.6×10^{-2} g l^{-1} of P_N and 5.4×10^{-3} g l^{-1} of P_P. The times the solution was held at 60° C are 0, 3, 29, and 97 hr, as indicated for each curve.

Two additional factors, other than the change in the efficiency of nonradiative singlet energy transfer, contribute to the time dependence of the shapes of the emission spectra. One factor is due to self-quenching by pyrene, which is most important at zero time, where the concentration of pyrene in a micelle has its maximum value. The influence of pyrene self-quenching can be documented separately by the experiment shown in Figure 3. The absence of naphthalene negates any influence of Förster transfer from naphthalene to pyrene in this experiment. The increase in the intensity of pyrene emission arises from the exchange of chains between micelles of P_P and micelles of P_U. This process distributes the pyrene labels over a larger number of micelles, and thereby decreases the maximum concentration of pyrene in the micelles. Self-quenching is reduced, and the emission intensity increases. The importance of this effect can be assessed by measurements of the type presented in Figure 3.

The second complicating factor is the adsorption of the copolymer onto the walls of the container after prolonged heating. This process is readily apparent as a reduction in the intensity of the total emission spectrum after heating at 60° C for several days. The material can be recovered from the walls of the container by using a good solvent for both blocks, such as dichloroethane.

The time scale of the exchange can be estimated from the time dependence of I_A/I_D, which is the ratio of the maximum intensities of the emission bands near 400 nm and 340 nm. Figure 4 depicts an example of this procedure. The Figure contains two sets of data, each obtained at 60° C, but with different initial

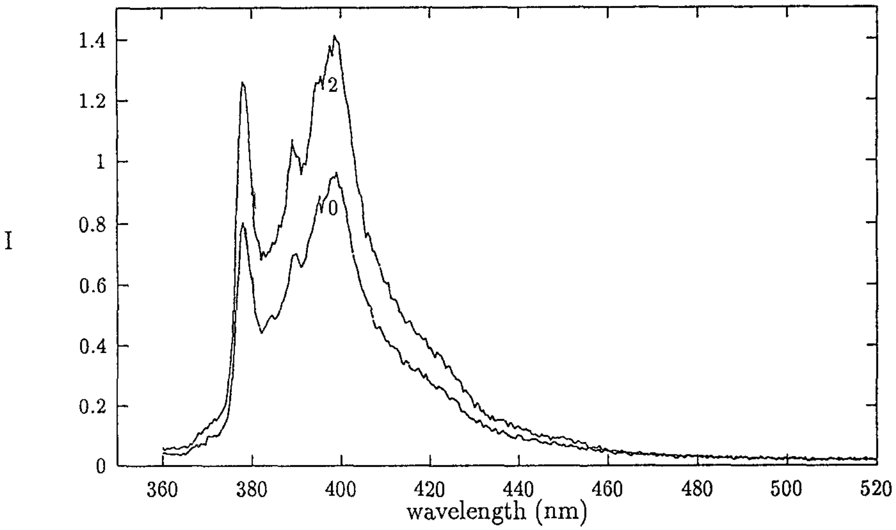

Figure 3. Emission spectra at ambient temperature for a solution with equal concentrations (10.4×10^{-3} g l^{-1}) of P_P and P_U immediately after mixing (0) and after having been at 70° C for 2 hr (2).

concentrations of P_N and P_P. Both sets of data are fitted to an exponential function, with an apparent rate constant of about 1.7×10^{-5} s^{-1}. We use the word "apparent" in describing the rate constant because the process involves several steps such as depicted in Eqs. (1)–(4). If the rate determining step for the entire process is the extraction of a chain from a micelle, the apparent rate constant should be most sensitive to the rates of the processes depicted in Eq. (1) and (2).

Conclusion

The time dependence depicted in Figures 2 and 4 can be interpreted as follows. When naphthalene and pyrene are situated in separate micelles in the solution, the efficiency of energy transfer is small due to the low concentration. Micelles containing both labels are produced as a consequence of the exchange of chains between micelles. Nonradiative singlet energy transfer occurs in the micelles that contain both labels. Our results shown that there is negligible exchange of chains over a period of several days when the micelles are held at ambient temperature. Exchange on a time scale of hours is seen when the temperature is 60° C. The very slow exchange of chains between micelles at ambient temperature can be attributed to the glassy nature of the core of polystyrene. When the exchange is fast enough to be observed, the time dependence of the shape of the emission spectrum permits a determination of the rate for the process.

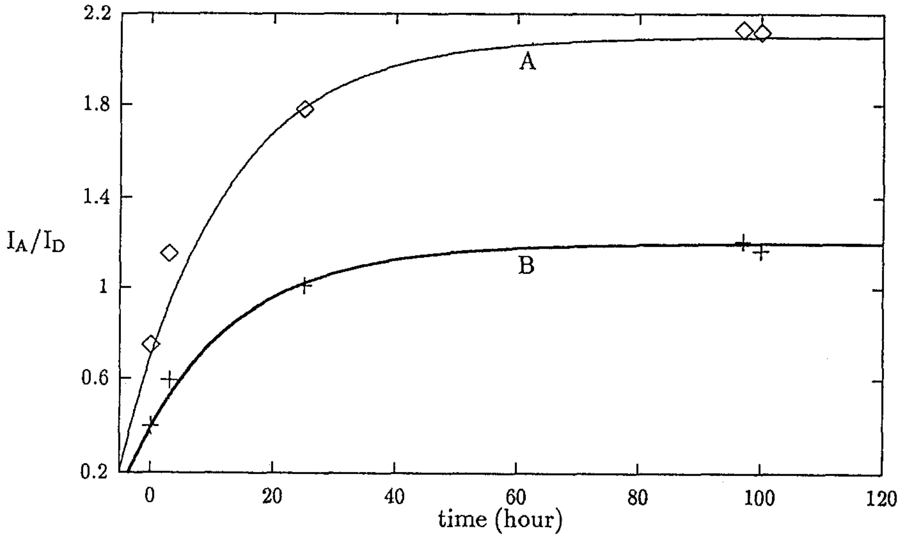

Figure 4. Time dependence of I_A/I_D at 60° C for solutions that contain 1.6×10^{-2} g l^{-1} of P_N, and P_P at a concentration of (A) 5.4×10^{-3} g l^{-1} or (B) 2.4×10^{-3} g l^{-1}.

Acknowledgments

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