

Exchange of Polymer Molecules between Block Copolymer Micelles Studied by Emission Spectroscopy. A Method for the Quantification of Unimer Exchange Rates

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ABSTRACT: Amphiphilic block copolymers, composed of poly(sodium methacrylate) (PMANa) as the water soluble sequence and poly((dimethylamino)ethyl methacrylate) (PDMAEMA) as the hydrophobic sequence, were anionically synthesized. Due to their amphiphilic character, these polymers aggregate into micelles in aqueous solutions. Of particular interest is the possibility of exchange of free chains, called unimers, between micelles and the bulk and the quantification of the exchange rate. The exchange of unimers between the micellar aggregates was determined spectroscopically. A donor molecule, naphthalene, was covalently bound to the hydrophobic blocks of the copolymers, while the acceptor, pyrene, was dissolved in aggregates built up from an identical, but unlabeled, copolymer. The energy transfer from an excited donor to a ground-state acceptor, with subsequent emission from the acceptor, was used to follow the migration of donor-labeled chains into micelles containing the dissolved acceptor. These data were analyzed according to a kinetic model, and the respective kinetic parameters could be determined. The influence of the relative composition of the block copolymer on the exchange rate was investigated to illustrate the usability of the kinetic model. While keeping the relative amount of comonomers as well as the molecular weights constant, the molecular architecture was also studied: hence the diblock (PDMAEMA-*b*-PMANa) and the corresponding triblocks (PDMAEMA-*b*-PMANa-*b*-PDMAEMA) and (PMANa-*b*-PDMAEMA-*b*-PMANa) were investigated.

1. Introduction

Aggregation of surfactants such as amphiphilic block copolymers is a crucial phenomenon that controls various applications, e.g., emulsions, dispersions, and systems for drug delivery, and has been extensively treated in the literature.^{1–21} These micelle-like systems can be characterized according to a number of parameters, such as the concentration needed for the onset of aggregation (cmc), the average number of polymer molecules in an aggregate (N_a), the hydrodynamic radius (R_H), and the average residence time of one single polymer molecule, i.e., a unimer, in an aggregate. The last parameter is of interest for the determination of the time scale needed to equilibrate a specific block copolymer system upon mixing with another micellar system. Even though the micellar entity itself is thermodynamically stable, its unimers might exchange with copolymer molecules in the bulk phase and copolymer molecules aggregated in other micelles.

One method to study the exchange of individual molecules between the micelles is to make use of nonradiative energy transfer from an excited fluorescent probe donor (D) to a ground-state fluorescent probe acceptor (A).^{3,10,12,20,22} Specifically, exciting D and monitoring the emission of A will be a measure of the efficiency of the energy transfer between the two molecules. If the D molecules are confined in aggregates initially not containing any A molecules and vice versa for the A molecules, an emission intensity of A increasing with time will be indicative of an exchange of A and D molecules between the aggregates. This method has been reported to be successful in some copolymer–micellar systems,^{3,10,12,20,22} where both D and A were

covalently bound to the copolymers.

Cantú *et al.*²³ proposed a kinetic model for the exchange of unimers between polymeric aggregates and used this model on light scattering data. In a study of polystyrene-*block*-poly(ethylene oxide), however, Wang *et al.* could not combine the model of Cantú with their own model for photophysical events.²⁰ This mismatch between the models was assumed to stem from the existence of exchange mechanisms other than redistribution of unimers, e.g., via exchange of molecules between colliding micelles, and has been discussed theoretically.²⁴

In this contribution we report steady-state fluorescence measurements on poly((dimethylamino)ethyl methacrylate)-*block*-poly(sodium methacrylate) (PDMAEMA-*b*-PMANa) systems, where the donor molecule, naphthalene, is covalently bound to the PDMAEMA block and the acceptor molecule, pyrene, is dissolved in the micellar aggregates formed by an unlabeled copolymer. The aim of this article is to quantify the unimer exchange kinetics. This was achieved by measuring the acceptor emission intensity as a function of time, where the change in intensity is due to energy transfer from an excited donor to the ground-state acceptor. These measurements, together with the proposed kinetic model, allow a quantitative estimation of the exchange kinetics.

2. Experimental Section

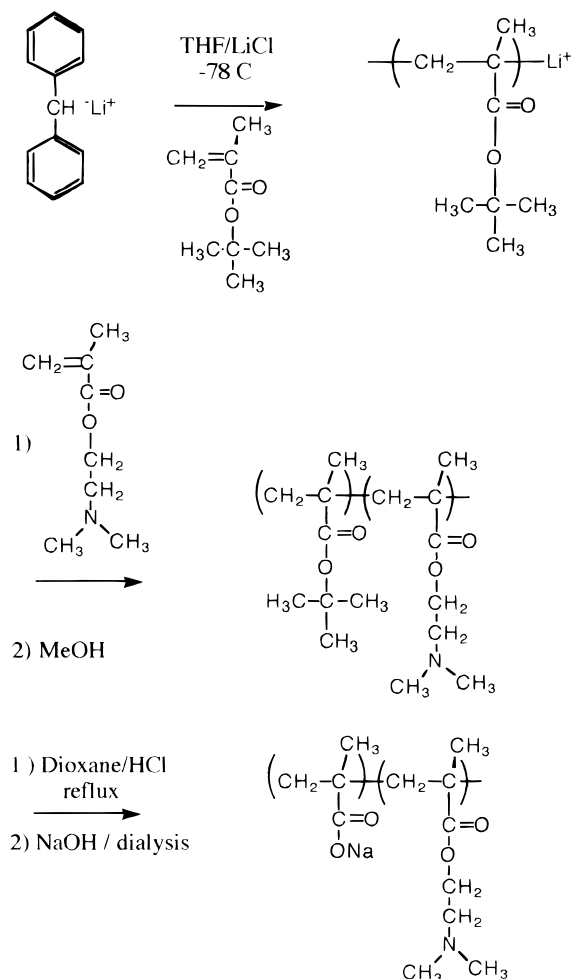
2.1. Materials. Pyrene (ACROS Janssen) was twice recrystallized from absolute ethanol. 1-(Bromomethyl)naphthalene (Aldrich) was purified by sublimation prior to use. Borax buffer solution (0.01 *m*, pH = 9) was prepared from sodium tetraborate decahydrate (ACROS), which was used as received. Distilled water of Milli-Q quality was used for all solutions.

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Scheme 1. Schematic Presentation of the Anionic Synthesis of the Diblock Copolymers Used

The block copolymers were anionically synthesized according to Scheme 1.^{25,26} THF containing LiCl (10-fold molar concentration of the initiator) was titrated by (diphenylmethyl)lithium at -78°C until a persistent yellow color was observed. The required amount of this initiator was then transferred to the medium, followed by the purified *tert*-butyl methacrylate. An aliquot was withdrawn for characterization, and (dimethylamino)ethyl methacrylate was injected. The copolymerization was finally quenched with degassed methanol. The triblock copolymers were synthesized according to the same procedure, with the exception that sodium naphthalene was used as initiator.

Labeling was carried out by reacting the copolymer dissolved in THF (10% w/w) with the purified 1-(bromomethyl)naphthalene (1/1 chain/label molar ratio) for 24 h at 50°C . After removal of the THF, the copolymers were hydrolyzed by reflux in 1/5 v/v HCl/dioxane for 24 h, neutralized with excess NaOH, and finally dialyzed. The label is thus bound to the chain through a quaternary ammonium and is randomly distributed. Rodrigues *et al.*⁴ have studied poly(styrene-*b*-ethylene oxide) copolymer micellization in various methanol/dichloroethane mixtures by nonradiative energy transfer between naphthalene and pyrene. Various copolymers were covalently labeled at the poly(styrene) free end with either naphthalene or pyrene and with pyrene at the junction between poly(styrene) and poly(ethylene oxide). After mixing of the naphthalene-tagged chains with the pyrene-tagged chains, no difference in quenching efficiency was observed as a function of pyrene localization. Rodrigues *et al.* concluded that the free ends of the insoluble block do not concentrate in the center of the core but are distributed throughout the core in the same way as the junction points. This means that the fact that the naphthalene moiety is randomly distributed over the hydrophobic block does

not influence the photophysics of the donor–acceptor pair used in the present investigation.

The hydrolyzed and neutralized copolymers were purified over a silica column by eluting the impurities with THF and then recovering the polymers with water. The structures and abbreviations of the polymers are shown in Figure 1, and their characteristics are compiled in Table 1.

2.2. Methods. Naphthalene and pyrene were chosen as donor and acceptor, respectively, due to their favorable spectral properties. At the excitation wavelength, 280 nm, the pyrene absorption is low at the concentrations used, typically $1\text{--}5\ \mu\text{M}$ pyrene, as compared to that of naphthalene²⁷ ($\epsilon_{\text{pyrene},280} = 1500\ \text{M}^{-1}\ \text{cm}^{-1}$, $\epsilon_{\text{naphthalene},280} = 6600\ \text{M}^{-1}\ \text{cm}^{-1}$). The naphthalene concentration equals the copolymer concentration (one label per block copolymer) and is between 0.5 and 1 mM. At the emission wavelength, 395 nm, the naphthalene emission intensity is low while pyrene displays an intense fluorescence. Furthermore, the emission spectrum of naphthalene overlaps well with the absorption spectrum of pyrene and the two chromophores have a Förster radius of 2.9 nm.²⁸

Aqueous samples of the naphthalene-tagged block copolymers were prepared by weighing the polymer and dissolving it in a Borax aqueous buffer solution. For the untagged polymers, a known volume, corresponding to a final pyrene concentration in the range $1\text{--}10\ \mu\text{M}$, of a pyrene stock solution in absolute ethanol was introduced into a volumetric flask. The ethanol was removed by suction, and a known mass of the polymer was added to the flask and dissolved in Borax. The pyrene-containing solutions were allowed to stir overnight to ensure complete dissolution of pyrene. The copolymer concentrations in the donor and acceptor solutions were equal.

Steady-state emission spectra of both solutions were recorded separately, with 280 and 320 nm as excitation wavelengths and emission wavelengths up to 500 nm. For the measurements of the fluorescence intensity as a function of time, a known volume of the naphthalene-tagged polymer solution was introduced into a quartz cuvette. An equal volume of the pyrene-containing solution of the untagged polymer was pipetted directly into the cuvette, and the measurements were started immediately. The excitation wavelength was 280 nm and the emission wavelength 395 nm. The intensity at the emission wavelength was recorded every tenth second for at least 2 h.

The emission spectra were recorded in the right-angle mode on a SPEX Fluorolog 1680 combined with a SPEX Spectroscopy Laboratory Coordinator DM1B. The slits used gave a bandwidth of approximately 2 nm. The temperature was held constant at 20°C by a standard water-bath connected to the cell compartment of the fluorometer. All calculations were performed on a Macintosh Performa 5200 Power PC within the framework of KaleidaGraph 3.0 (Abelbeck Software). The critical micelle concentrations (cmc) of the block copolymers were determined by light-scattering measurements, as reported elsewhere.²⁹

3. Theory

Cantú *et al.* presented a kinetic model for the exchange of polymer molecules between aggregates,²³ which was fitted to light scattering data:

$$\begin{cases} \frac{dn_D}{dt} = k_+^D C_D (n_D + n_A) - k_-^D n_D \\ \frac{dn_A}{dt} = k_+^A C_A (n_D + n_A) - k_-^A n_A \end{cases} \quad (1)$$

where D and A stand for the donor and acceptor molecules, respectively, k_- and k_+ are the rate constants for a polymer molecule to exit and enter a micelle, respectively, C is the concentration of unaggregated molecules, and $(n_D + n_A)$ is the total number of D and acceptor (A) molecules in a micelle. The expression for the time dependence of the distribution of A molecules is analogous to eq 1.

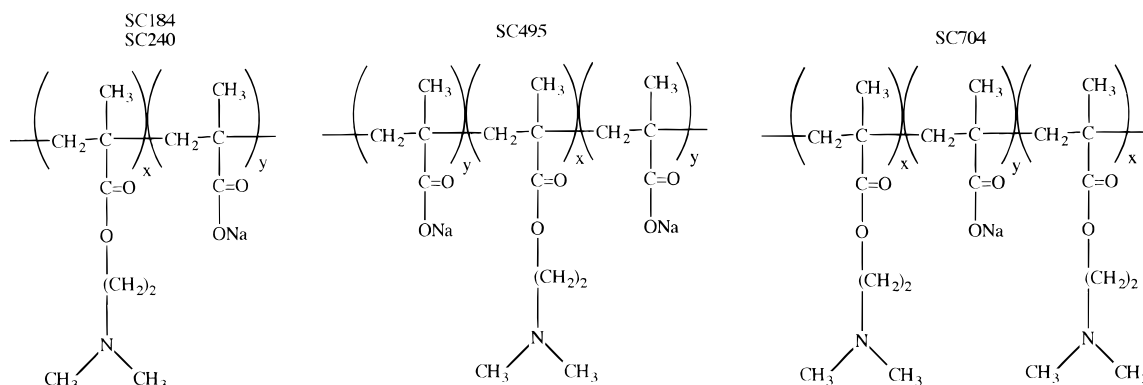


Figure 1. Structures and abbreviations of the copolymers used in this investigation.

Table 1. Characteristics of the Different Copolymers Used in This Contribution^a

polymer	M_n	x/y^b	M_w/M_n	cmc (mg/L)	C (g/L)
SC184	10 700	24/49	1.1	120	5.0
SC240	5 300	15/20	1.1	15	5.0
SC495	10 600	23/25	1.1	115	5.0
SC704	10 600	11/49	1.1	150	5.0

^a For abbreviations, see Figure 1. ^b See Figure 1 for meaning of x and y .

Equation 1 was further elaborated on by Wang *et al.*²⁰ to treat the case when the macromolecules labeled with a donor and an acceptor, respectively, have the same rate constants of exchange. For the time evaluation of the number of donor molecules present in a micelle that initially did not contain any D molecules, n_D^A , eq 1 can now be written as

$$n_D^A = \frac{N_A}{\alpha + 1} [1 - \exp(-kt)] \quad (2)$$

where N_A is the total concentration of polymer chains not labeled with the donor, α is the ratio of N_A to N_D (the number of donor-labeled polymers, $N_A = \alpha N_D$), and k is the rate constant for the exit of a polymer molecule from a micelle. Wang and co-workers combined eq 2 with a model taking the integrated intensity from time-resolved fluorescence measurements into account.²⁰ It was needed, however, to include exchange mechanisms other than migration via the bulk, if this combined model was to be applied to their data.

When applying steady-state emission spectroscopy, no model for the integrated emission intensity is needed, since this property is directly measured. Furthermore, if only the donor is covalently attached to the copolymer and the acceptor molecule is exclusively dissolved in micelles built up from unlabeled polymer molecules, a simplified approach is possible. If the acceptor molecule is stationary in its host micelle during the time of the measurements, the only migration process that will occur is the exchange of unimers between the micelles. Mixing two solutions, of which one contains the donor-labeled polymer only, and the other the unlabeled polymer and the acceptor molecule, will lead to a situation where the measured intensity increase of the acceptor emission upon excitation of the donor solely stems from the migration of donor-labeled molecules to micelles containing the acceptor molecule. Furthermore, if the two solutions are equal in copolymer concentration, the number of donor-labeled polymer molecules in such a micelle will be described by a rearrangement of eq 2. The fluorescence intensity at time t , I_t , which is proportional to the number of excited

donor molecules in the micelles with acceptor molecules, will in such a case be given by

$$I_t = I_0 + \frac{\xi_{D \rightarrow A}}{2} [1 - \exp(-kt)] \quad (3)$$

where I_0 represents the emission intensity at time $t = 0$ and $\xi_{D \rightarrow A}$ is a measure of the efficiency of the energy transfer from donor to acceptor. Ideally, for normalized emission spectra, I_0 should be zero and $\xi_{D \rightarrow A}$ unity. Deviations in the value of the former can be due to spectral overlap between the donor and acceptor emission and/or absorption spectra, while deviations in the value of the latter can be due to the size of the aggregate—in a large aggregate the probability for energy transfer will be lower than in a small one. Values below unity for $\xi_{D \rightarrow A}$ can also be due to a difference in loci between the donor and the acceptor in an aggregate, as the donor is bound to the hydrophobic block and the acceptor is free to take any locus in the micelle. Nevertheless, a fit of eq 3 will yield a quantitative measure of the exchange kinetics and was used in the evaluations of the emission intensity data. It should be mentioned that normalization of the spectra is not necessary. Using the raw data only results in a scaling of the parameters I_t and I_0 —for normalized spectra these parameters will be constrained within $\{0, 1\}$. The value estimated for k is, of course, independent of whether the spectra are normalized or not. In the present study, all spectra were normalized before evaluation.

4. Results and Discussion

From the emission spectra, Figure 2, it can be concluded that the emission of naphthalene overlaps with the emission of pyrene up to wavelengths beyond 400 nm. This means that the ideal value of zero for I_0 cannot be expected in these systems, as there will also be a detectable emission from naphthalene at 395 nm at time zero. Furthermore, even if the probability of excitation of pyrene is rather low at $\lambda_{ex} = 285$ nm, some pyrene molecules will be excited directly and not due to energy transfer from an excited naphthalene. This will also cause I_0 to take a value higher than zero.

In order to ensure that an increased acceptor emission intensity does not originate from acceptor molecules migrating to micelles containing the donor, control measurements were performed. Solutions containing 1–10 μ M pyrene showed no pyrene excimer emission. A solution of 100 μ M pyrene dissolved in unlabeled SC704, however, showed a broad emission band cen-

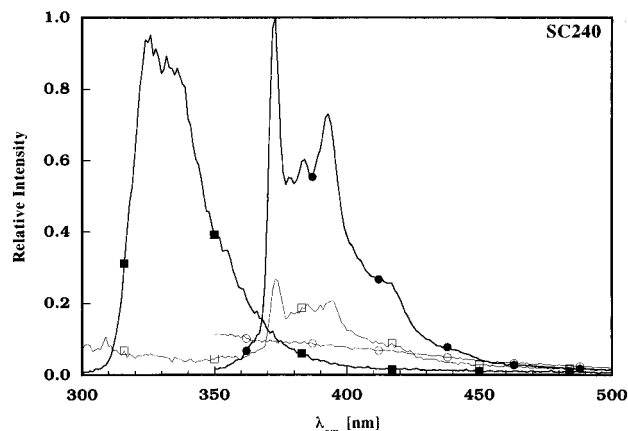


Figure 2. Steady-state emission spectra: (■) micelles of SC240 labeled with naphthalene at the PDMAEMA block, excited at 280 nm; (□) micelles of SC240 labeled with naphthalene at the PDMAEMA block, excited at 320 nm; (○) micelles of unlabeled SC240 with pyrene, excited at 280 nm; (●) micelles of unlabeled SC240 with pyrene, excited at 320 nm. The spectra with the thicker lines show the experimental situation for the measurements of the pyrene emission intensity as a function of time, when pyrene is excited by energy transfer from naphthalene excited at 280 nm.

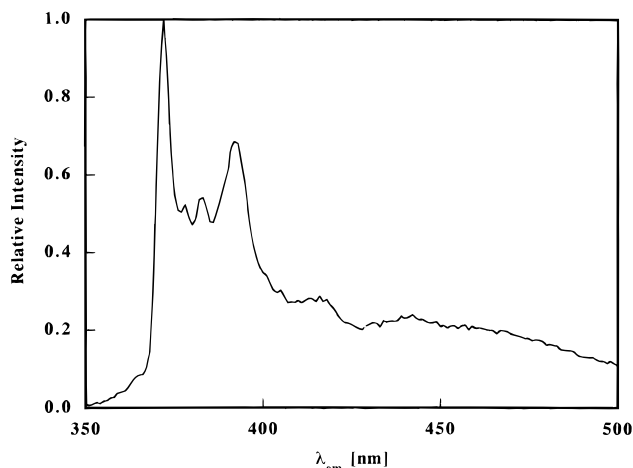


Figure 3. Steady-state emission spectrum of a 100 μ M pyrene solution, dissolved in unlabeled SC704.

tered around 480 nm, characteristic for pyrene excimer emission, Figure 3.

There are three possible mechanisms for dissolved pyrene to migrate from one host micelle to another: (i) via the bulk, (ii) via collision and fusion of two micelles with subsequent mixing of their contents before separating into two micelles, or (iii) via solubilization in a so-called "unimolecular micelle", i.e., a single block copolymer molecule where the hydrophilic part has collapsed around the hydrophobic part, which can diffuse via the bulk.

A volume of the pyrene-containing sample yielding the spectrum shown in Figure 3 was mixed with an aliquot part unlabeled SC704 solution of identical concentration but without added pyrene. If pyrene was able to migrate between the micelles, the excimer emission intensity should decrease as a function of time, while the monomer emission intensity should increase. The measurement shows that the monomer emission intensity remains constant for at least 2 h, Figure 4. This proves that pyrene is stationary in its host micelle within this time frame. Furthermore, this finding also has implications for the understanding of how the exchange of block copolymer molecules between the

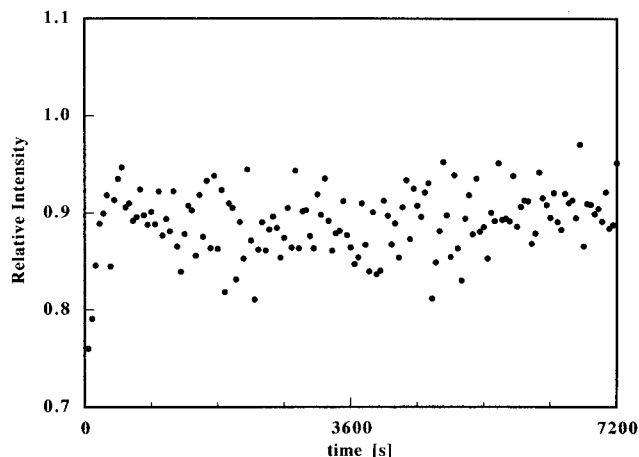


Figure 4. Pyrene monomer emission intensity, measured at 372 nm, as a function of time. The measured solution was a mixture of equal amounts of unlabeled SC704 with and without added pyrene. See text for further explanation.

micelles occurs. If two micelles built up by the block copolymers were to fuse and mix their contents with subsequent fission, this would have been seen in the pyrene excimer experiment. So, mechanism (ii) can be ruled out, and only the exchange of copolymer molecules via the bulk has to be considered. This is easy to rationalize, as the concentration is low and the micelles have a quite high negative charge density, leading to efficient electrostatic repulsion and diminishing the frequency of collision of two micelles.

Moreover, for a micellar solution in equilibrium, the concentration of unaggregated molecules is constant and close to the cmc, at least at low concentrations. So, when a copolymer molecule exits its micelle, it or any bulk-dissolved copolymer will enter a micelle. The rate of exit and entry will be equal for a system in equilibrium ($k_{\text{exit}} = k_{\text{entry}}[\text{copolymer}]_{\text{bulk}}$) with the exit as the rate-determining step. So, even if the model leading to eq 3 only predicts a first-order exchange and not the mechanism for the exchange, it can, for the present systems, be concluded that the exchange rate equals the exit rate for one copolymer molecule from its micelle. The residence time equals $1/k_{\text{exit}}$, which is identical to $1/k$ from eq 3.

The measurements of the emission intensity as a function of time, Figure 5, show that the method utilized works well. Applying eq 3 to the data resulted in good fits, Figure 5, and the numerical results are given in Table 2. For the two triblocks, it was found that ξ_{D-A} takes a much higher value for SC704 than for SC495. The results for the two diblocks, however, show that there is no correlation between hydrophilicity and energy transfer efficiency. SC184, being more hydrophilic, yields a lower value for ξ_{D-A} than SC240, which should be indicative of a less effective naphthalene penetration with increasing hydrophobicity of the polymer. More likely, ξ_{D-A} depends on structural factors.

The exchange kinetics, on the other hand, is, as expected, a function of hydrophilicity. The numerical results for the exchange rate constant, Table 2, confirm that the more hydrophilic molecule migrates faster between the aggregates.

5. Conclusions

The exchange of block-copolymer molecules between micellar aggregates was measured by means of steady-state emission spectroscopy. Attaching a donor co-

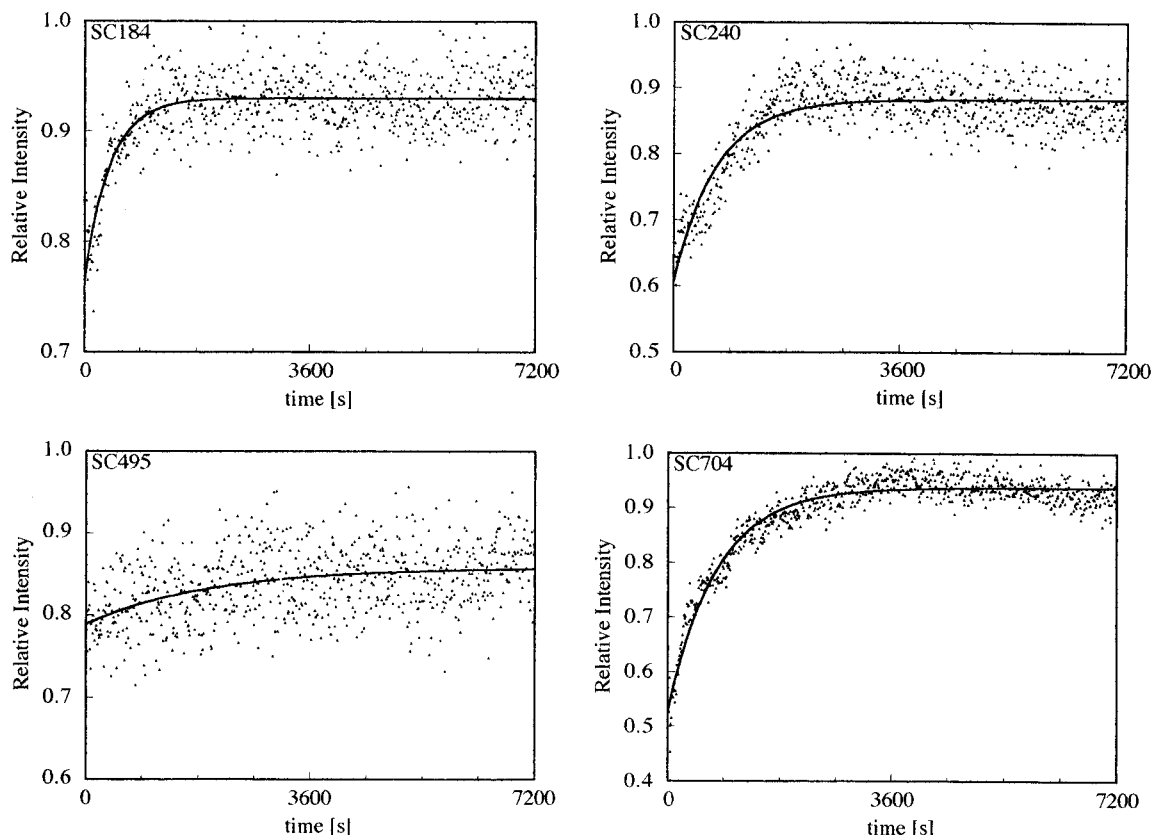


Figure 5. Pyrene emission intensity as a function of time (dots) and the curve based on the fitting of eq 3 to the experimental data (line).

Table 2. Numerical Results of the Fit of Eq 3 to the Pyrene Emission Intensity Data as a Function of Time at 20 °C

polymer	I_0	ξ_{D-A}	k (s ⁻¹)
SC184	0.77	0.33	$2.43 \times 10^{-3} \pm 1.7 \times 10^{-4}$
SC240	0.61	0.55	$1.48 \times 10^{-3} \pm 7 \times 10^{-6}$
SC495	0.79	0.14	$5.03 \times 10^{-4} \pm 1.15 \times 10^{-4}$
SC704	0.53	0.82	$1.28 \times 10^{-3} \pm 2.9 \times 10^{-5}$

valently to the hydrophobic block allowed the detection of the exchange as an increase of the acceptor molecule emission intensity with time. By applying a simple kinetic model, it was possible to estimate the exchange rate constant. The estimated exchange rate constants show that the exchange of polymer molecules between the aggregates is very slow as compared to ordinary surfactant micelles, i.e., on the order of 10^{-3} s⁻¹ for the polymers used in this study and 10^6 – 10^8 s⁻¹ for ordinary surfactants.^{30–34} On the other hand, amphiphilic block copolymers containing polystyrene as the hydrophobic block and poly(ethylene oxide) as the hydrophilic block were found to exhibit negligible exchange at room temperature.¹⁰

It is possible to correlate the obtained results both to structural properties of the copolymers and to differences in their hydrophobicity. These trends are under study and will be the subject of a forthcoming paper.²⁹

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