Dynamics of Poly((dimethylamino)alkyl methacrylate-*block*-sodium methacrylate) Micelles. Influence of Hydrophobicity and Molecular Architecture on the Exchange Rate of Copolymer Molecules

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ABSTRACT: The dynamic stability of the micellar aggregates formed by amphiphilic block copolymers, i.e., poly((dimethylamino)alkyl methacrylate-*b*-sodium methacrylate), has been investigated by steady-state fluorescence spectroscopy and size exclusion chromatography. The dynamics of exchange of block copolymer molecules between the micelles, formed in aqueous solution, depend on a manifold of factors, e.g., alkyl substituent in the hydrophobic block, the relation between the hydrophobic and hydrophilic blocks, and the architecture of the block copolymer. All copolymers investigated show a slow unimer exchange with an exchange rate constant on the order of 10^{-3} s^{-1}, with a difference of a factor of 20 between the fastest and the slowest exchange. It is possible to tune the exchange rate in a controlled way; for instance, an extension or branching of the alkyl chain slows down the exchange rate. The same effect is observed when the hydrophobic/hydrophilic balance of these copolymers is increased or when either the hydrophilic or the hydrophobic moiety of diblocks is divided into two external blocks, leading to a triblock copolymer.

1. Introduction

Amphiphilic block copolymers combine the advantages of water-soluble polymers, e.g., they are sensitive to cooperative transitions, and those of ordinary surfactant systems, in particular a high dissolving capability of hydrophobic species in aqueous solutions. Such block copolymers, forming micellar structures, have been extensively treated in the literature[1−29] and can be described by 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 in an aggregate. The latter is of importance for the understanding of the stability of the system. In contrast to classical low molecular weight surfactants, which are known to easily exchange,[30−32] the exchange between unimers and micelles of block copolymers is substantially slowed down. Among the block copolymers, poloxamers, i.e., poly(ethylene oxide-*block*-propylene oxide-*block*-ethylene oxide), have an exchange rate constant larger than 3×10^3 s^{-1} in aqueous solution, which is slow in comparison with what is found for ordinary micelles (exchange rate constant between 10^6 and 10^8 s^{-1}),[33] while block copolymers based on polystyrene as hydrophobic block have an even slower exchange rate.[10,14,25]

Ideally, the exchange rate should be tunable in such a way that the requirement for a slower or a faster exchange could be achieved according to the desired application. For this purpose, amphiphilic block copolymers show more potential than classical low molecular weight surfactants that offer less possibilities to tune their exchange rate.

Although extensive literature exists on block copolymers with poly(propylene oxide)[19,33−48] or polystyrene[2,4−11,13,21,25,49−52] as the hydrophobic block, few data on the dynamics of their micellar aggregates are available. Light scattering,[5−9,19,21,35−37,41,42,44−47,51,53,54] NMR,[33,38,48,55,56] calorimetry,[41,43,44] and fluorescence methods[2−7,9,10,21,25,47,49,50,52,57,58] are frequently used for the investigation of aggregating block copolymers. The theory of aggregation phenomenon in block copolymer systems has been treated in the literature,[1,4,12,59−61] as well as the exchange of polymer molecules between the aggregates.[21,26,62]

One method for studying the exchange of polymer 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).[3,10,11,21,25] 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, upon excitation of D, 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,[3,10,11,21,25] where both D and A were covalently bound to the copolymers. Recently we presented a simplified approach,[63] based on the models developed by Cantú *et al.*[54] and Wang *et al.*,[21] suitable for the study of the exchange of copolymer unimers between block copolymer micellar aggregates.

In this contribution we report on the characterization of the aggregation behavior of poly((dimethylamino)-alkyl methacrylate)-*block*-poly(sodium methacrylate) (PDAxMA-*b*-(PMA)Na) systems. For the steady-state fluorescence measurements, the donor molecule, naphthalene, was covalently bound to the hydrophobic sequence, while the acceptor, pyrene, was molecularly

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dissolved in aggregates formed by unlabeled copolymers. The aqueous micellar solutions of the block copolymers were also investigated by size exclusion chromatography (SEC).

The emphasis in this study is put on the influence of the relative composition of the block copolymers on the exchange process of block copolymer molecules between the micellar aggregates, and the possibilities for tuning the exchange rate by changing the composition or architecture of the block copolymer. While keeping the relative amount of comonomers as well as the molecular weights constant, the molecular architecture was studied; hence, the diblock PDMAEMA-*b*-(PMA)Na and its corresponding triblocks PDMAEMA-*b*-(PMA)Na-*b*-PDMAEMA and (PMA)Na-*b*-PDMAEMA-*b*-(PMA)Na were investigated as well as the diblocks PDMAPMA-*b*-PMANA and PDMAMEMA-*b*-(PMA)Na and the triblock PDMAMEMA-*b*-(PMA)Na-*b*-PDMAMEMA (DMAEMA, DMAPMA, and DMAMEMA stand for (dimethylamino)-ethyl methacrylate, (dimethylamino)propyl methacrylate, and [2-(dimethylamino)-1-methyl]ethyl methacrylate, respectively).

2. Experimental Section

2.1. Materials. Pyrene (ACROS Janssen) was twice recrystallized from absolute ethanol. 1-(Bromomethyl)naphthalene (Aldrich) was purified by sublimation and dried by azeotropic evaporation from dry toluene 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.

(Dimethylamino)propyl methacrylate (DMAPMA) and (dimethylamino)ethyl methacrylate (DMAMEMA) were synthesized by esterification of methacryloyl chloride and the parent tertiary aminoalcohol in dichloromethane in the presence of triethylamine. All of these reagents were vacuum distilled over calcium hydride. The reaction was carried out under dry nitrogen. This reaction is very exothermic, and care was taken to avoid pressure buildup. The reagents were transferred through stainless steel capillaries or with glass syringes through a rubber septum. Typically, with all reagents and solvents cooled to 0 °C, 200 mL of dichloromethane was added, followed by 0.22 mol of methacryloyl chloride and thereafter 0.18 mol of aminoalcohol. Finally, triethylamine was slowly added. The highly exothermic reaction was allowed to proceed for 2 h and then quenched by addition of a 10% aqueous solution of sodium carbonate. The organic phase was washed two times with a 10% aqueous solution of sodium carbonate and finally with water. After removal of the dichloromethane, the monomer was distilled over calcium hydride under vacuum. The monomers were stored under nitrogen at −20 °C. The final yield was 75 and 50% for DMAPMA and DMAMEMA, respectively.

The diblock copolymers were anionically synthesized as described elsewhere, and only a brief description will be given here.[64]

Before polymerization, the monomers were purified with triethylaluminium. The glass reactor containing the required amount of LiCl (10/1 LiCl/initiator molar ratio) was flame dried under vacuum, purged with nitrogen, added with the required amount of tetrahydrofuran (THF), and cooled to −78 °C. (Diphenylmethyl)lithium was added drop by drop until a persistent yellow color was observed, followed by the required amount of initiator. After 1 h of polymerization of *tert*-butyl methacrylate, a small sample was taken for characterization, after which the aminated monomer was injected. The copolymerization medium was divided in two parts, one being quenched with methanol and the other with 1-(bromomethyl)-naphthalene (1/1 chain/label molar ratio). Lithium naphthalenide was used as a bifunctional initiator for the synthesis of the triblock copolymers.

As an exception, the DMAEMA and DMAPMA based copolymers, i.e., SC184, SC240, SC495, SC704, and SC367, were quenched with methanol and labeled afterward in THF (10% (w/w)) with purified 1-(bromomethyl)naphthalene (1/1 chain/label molar ratio) for 24 h at 50 °C.

After removal of 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 characterization of the polymerized products was performed by SEC and NMR. SEC was performed at 35 °C in THF added with 1% (v/v) triethylamine, using a Hewlett-Packard 1050 liquid chromatograph equipped with two PLGel columns (1000 and 10000 Å, respectively) and a Hewlett-Packard 1047A refractive index detector. Poly(methyl methacrylate) standards were used for calibration. ^{1}H NMR spectra were recorded at 400 MHz with Bruker AM 400 superconducting magnet equipment. More details of the characterization are given elsewhere.[64]

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

2.2. Methods. The critical micelle concentration (cmc) was determined for each block copolymer by light scattering with a BI-200 photogoniometer (Brookhaven Instruments) equipped with a BI-2030 128 channel digital correlator (Brookhaven) and an Ar-ion laser (Lexel model 95), emitting vertically polarized light at 488 nm. All measurements were performed at 20 ± 0.1 °C.

The scattered light intensity was measured at 90° as a function of decreasing copolymer concentration. The concentration at which the scattering by the micelles disappeared, Figure 2, is defined as the cmc, Table 1. This method will, which should be stressed, only give an indicative cmc, as the transition in scattered light intensity is not sharp. Nevertheless, as the purpose of the cmc determination is to ensure that the concentrations used for the kinetic measurements are well above the cmc, this method is adequate.

Naphthalene and pyrene were chosen as donor and acceptor, respectively, for the steady-state fluorescence measurements, because of their favorable spectral properties.[63] The naphthalene concentration equals the copolymer concentration (one label per block copolymer) and is between 0.25 and 1 mM, while the pyrene concentration was typically 5−10 μM. At 395 nm, the naphthalene emission intensity is low while pyrene displays an intense fluorescence at this wavelength. Furthermore, the emission spectrum of naphthalene overlaps well with the absorption spectrum of pyrene and the two chromophores have a Förster radius of 29 Å.[65] The preparation of the samples for steady-state fluorescence studies has been described elsewhere.[63]

Steady-state emission spectra were recorded in the right-angle mode on a SPEX Fluorolog 1680 combined with a SPEX spectroscopy laboratory coordinator DM1B, as described earlier.[63] The slits used gave a bandwidth of approximately 2 nm.

The model used for the calculation of the exchange rate constants, based on the models of Cantú *et al.*[54] and Wang *et al.*,[21] has been reported earlier.[63] In short, the data are fitted by

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

where I_0 accounts for the emission intensity at time $t = 0$ and $\xi_{D\rightarrow A}$ is a measure of the efficiency of the energy transfer from the donor to the acceptor. k is the rate constant for exchange of copolymer unimers between the copolymer aggregates.

Recently, Wang *et al.* presented a theoretical framework for exchange kinetics in a spherical geometry.[62] According to their treatment, one has to take into account the recapture process, yielding a more complicated expression for the true escape rate

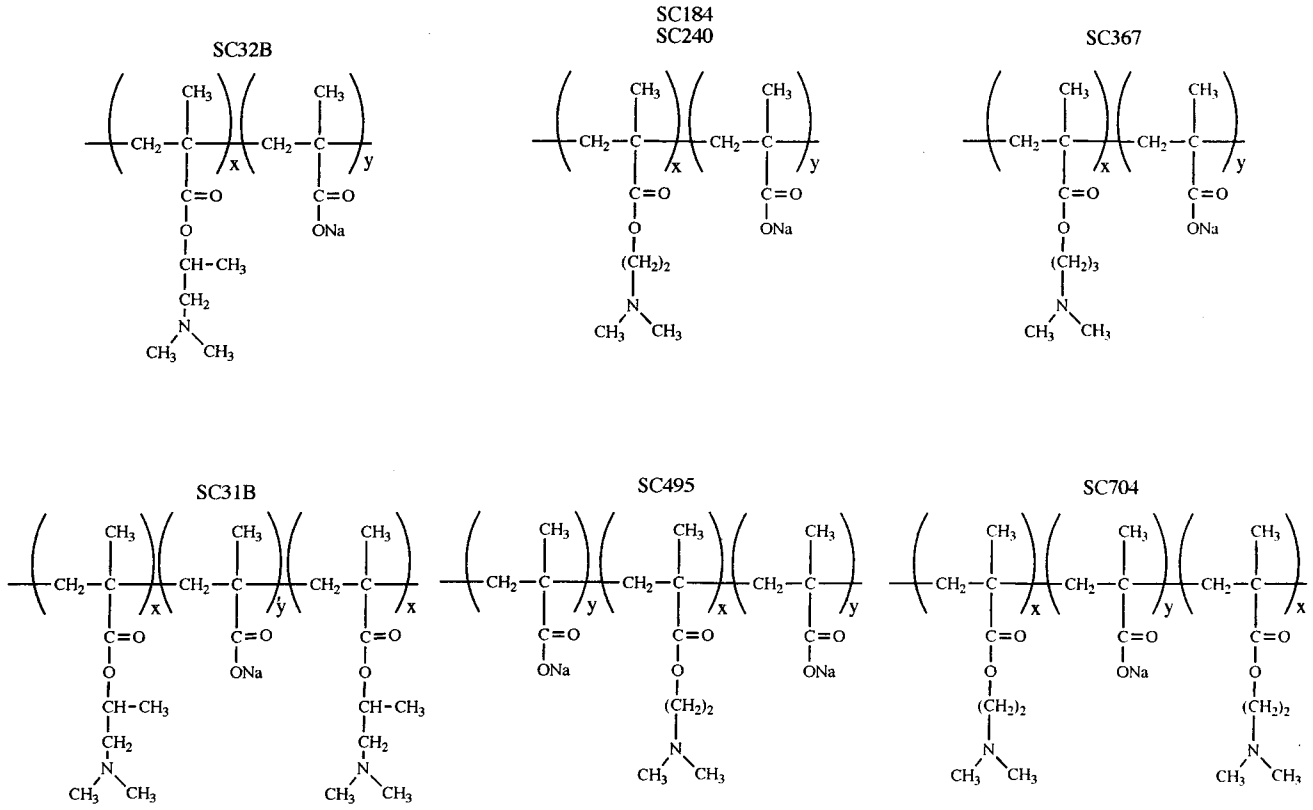

Figure 1. Structures and abbreviations of the block copolymers used in this investigation.

Table 1. Characteristics of the Different Copolymers Used in This Article[a]

polymer	M_n^x, M_n^y	*x*/*y*	M_w/M_n	cmc (mg/L)	cmc (μM)	*C* (g/L)
		(Dimethylamino)ethyl Methacrylate/Sodium Methacrylate				
SC184	3600, 7000	23/49	1.10	120	11.2	5.0
SC240	2400, 2900	15/20	1.10	15	2.8	5.0
SC495	3500, 3600	23/25	1.10	115	10.8	5.0
SC704	1800, 7000	11/49	1.10	150	14.2	5.0
		(Dimethylamino)propyl Methacrylate/Sodium Methacrylate				
SC367	2600, 4300	15/30	1.10	26	3.8	2.5
		[2-(Dimethylamino)-1-methyl]ethyl Methacrylate/Sodium Methacrylate				
SC32B	3500, 5300	20/37	1.05	25	2.8	2.5
SC31B	1500, 5500	9/39	1.10	24	2.8	5.0

[a] For abbreviations and the meaning of *x* and *y*, see Figure 1. M_n^x and M_n^y denote the molecular weights of the hydrophobic and hydrophilic blocks, respectively, of the copolymer before hydrolysis (for the triblock copolymer the M_n of *one* block is given), and *C* is the actual concentration used for the different copolymers.

constant. The purpose of the present investigation, however, is to estimate the exchange rate constants for several micellar block copolymer systems. From this point of view, a recaptured unimer has not left its host micelle and does not contribute to the observed exchange.

SEC was carried out at 24 °C, with a 0.1 M $NaNO_3$, 0.025 M tris(hydroxymethyl)aminomethane, and 0.001 M EDTA aqueous solution as eluent. The initial pH was basic due to the tris(hydroxymethyl)aminomethane and was adjusted to pH 9 with HCl. For the SEC measurements, a Waters model 600E liquid chromatograph was equipped with a TosoHaas TSKgel G4000 PW_{xl} and a UV detector (Waters 486). The various copolymers were analyzed at a flow rate of 0.5 mL/min at the same concentrations as those used for the steady-state fluorescence measurements. Poly(sodium methacrylate) standards were used for calibration.

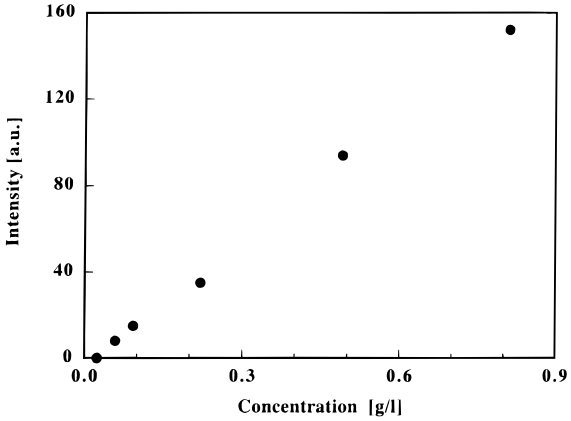

Figure 2. Example of light scattering intensities used for the determination of the cmc. The scattering of the pure borax buffer solution was subtracted.

All calculations were performed on a Macintosh Performa 5200 Power PC within the framework of KaleidaGraph 3.0 (Abelbeck Software).

3. Results and Discussion

In order to collect information on the micellization of block copolymers and particularly on the dynamic stability of the micelles, two different methods have been employed in this study: time dependence of the steady-state fluorescence intensity and size exclusion chromatography. Both methods report on the exchange characteristics of the block copolymer micellar aggregates, and one purpose of this study is to reveal if these two methods correlate.

The time dependence of the steady-state fluorescence intensity is the most direct measure of the exchange kinetics of the micelles, allowing the quantification of the exchange rate constant of block copolymer molecules between the polymeric micelles.

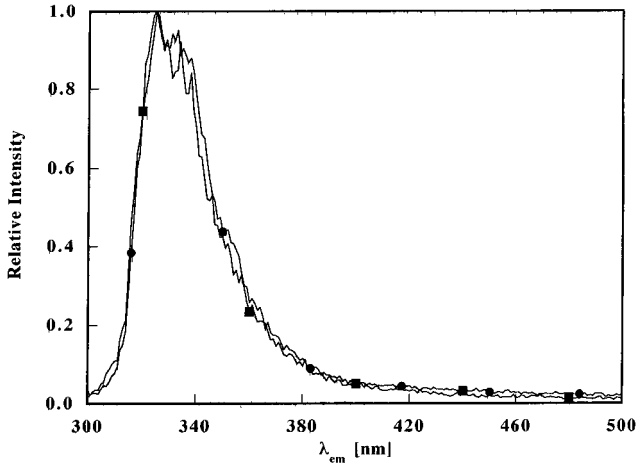

Figure 3. Steady-state fluorescence spectra of SC32B (●) and SC367 (■), labeled by two different methods.

It should be pointed out that two labeling procedures have been followed. On the one hand, SC184, SC240, SC495, SC704, and SC367 were labeled after polymerization by quaternization of the dimethylamino moiety with 1-(bromomethyl)naphthalene in a 1/1 chain/label ratio. The label is thus bound to the chain through a quaternary ammonium and is randomly distributed. On the other hand, SC31B and SC32B were labeled during polymerization by deactivating the living anions with 1-(bromomethyl)naphthalene. The label is in this case bound through a carbon−carbon bond and is located at the end of the DMAMEMA block. Since no difference in the emission spectra of naphthalene has been observed between polymers labeled by the two procedures, Figure 3, it can be concluded that the difference in labeling procedure does not influence the spectral properties of naphthalene. The difference in location, i.e., random distribution vs the free end of the PDMAMEMA block, could affect the distribution of the label within the aggregate. Rodrigues *et al.*[4] studied poly(styrene-*b*-ethylene oxide) copolymer micellization in various methanol/dichloroethane mixtures by nonradiative energy transfer between naphthalene and pyrene. The copolymers were covalently labeled at the polystyrene free end with either naphthalene or pyrene and with pyrene at the junction between polystyrene 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. In the present study, any difference is even less likely, since the naphthalene is randomly distributed and not specially localized at the junction. Finally, in case of influence of the naphthalene localization on the quenching efficiency, $\xi_{D\rightarrow A}$ should systematically be higher for one labeling procedure compared to the other one. No such trend is observed in the present study. Therefore, the results obtained with the two kinds of labeling can be directly compared.

The SEC measurements also give information on the exchange between micelles and unimers. When the exchange rate is low compared to the flow rate, micelles and unimers are observed as distinct species. When these two rates become comparable, the resolution of the elution peaks for the unimers and the micelles may decrease to the point where the peaks coalesce with formation of a not well-separated peak. Finally, if the exchange rate is much faster than the elution rate, only the unimer peak is observed; hence, only qualitative conclusions may be drawn from SEC measurements.

3.1. Pyrene as Immobile Probe. The use of eq 1 requires that the pyrene acceptor probes are stationary in their host micelles for the time frame of the experiment. As this cannot be assumed a priori, it is necessary to experimentally assure that this requirement is fulfilled. If the pyrene molecules would migrate between the block copolymer micelles, however, the influence on the usage of eq 1 can be evaluated. Assume that the donor-labeled block copolymers exchange with rate constant k, as given in eq 1, and the pyrene molecules with rate constant k_{py}. In the following, A denotes the micelles composed of naphthalene-labeled block copolymers and B the micelles of unlabeled polymers, containing the pyrene molecules. Energy transfer from an excited naphthalene to a ground-state pyrene can occur due to two different mechanisms: one labeled polymer can migrate from an A to a B micelle, or a pyrene molecule can migrate from a B to an A micelle. These two exchange processes will be independent from each other. The situation of exchanging donor and acceptor molecules was treated for labeled polymers by Wang *et al.*,[21] and their kinetic expressions can be used in a modified form for the present. The time dependence of the number of naphthalene-labeled copolymers in B micelles and pyrene in A micelles will, if the initial concentrations of A and B micelles are equal, be given by

$$n_N^B = \frac{n_N^{tot.}}{2}(1 - \exp(-kt))$$

$$n_{py}^A = \frac{n_{py}^{tot.}}{2}(1 - \exp(-k_{py}t)) \qquad (2)$$

where n_N^B is the number of naphthalene moieties in B micelles, $n_N^{tot.}$ is the total number of naphthalene molecules, n_{py}^A is the number of pyrene molecules in A micelles, and $n_{py}^{tot.}$ is the total number of pyrene molecules. The measured fluorescence intensity of pyrene excited by energy transfer from naphthalene will be a function of n_N^B and n_{py}^A, and the relative importance of the pyrene migration is given by the ratio

$$\frac{n_{py}^A}{n_N^B + n_{py}^A} = \frac{n_{py}^{tot.}(1 - \exp(-k_{py}t))}{n_N^{tot.}(1 - \exp(-kt)) + n_{py}^{tot.}(1 - \exp(-k_{py}t))} \qquad (3)$$

Assuming that the efficiency of energy transfer between a pyrene molecule in an A micelle and naphthalene is similar to that in a B micelle, and keeping in mind that $n_N^{tot.}$ is about 50 times larger than $n_{py}^{tot.}$, it can be concluded that the pyrene exchange has to be significantly faster than the exchange of naphthalene-labeled block copolymers, if the pyrene exchange should have any impact within the time frame of the experiments.

It should also be noted that it was shown[63] that, within the time frame of the steady-state fluorescence measurements, the exchange of naphthalene-tagged chains between micelles does not occur through fusion−

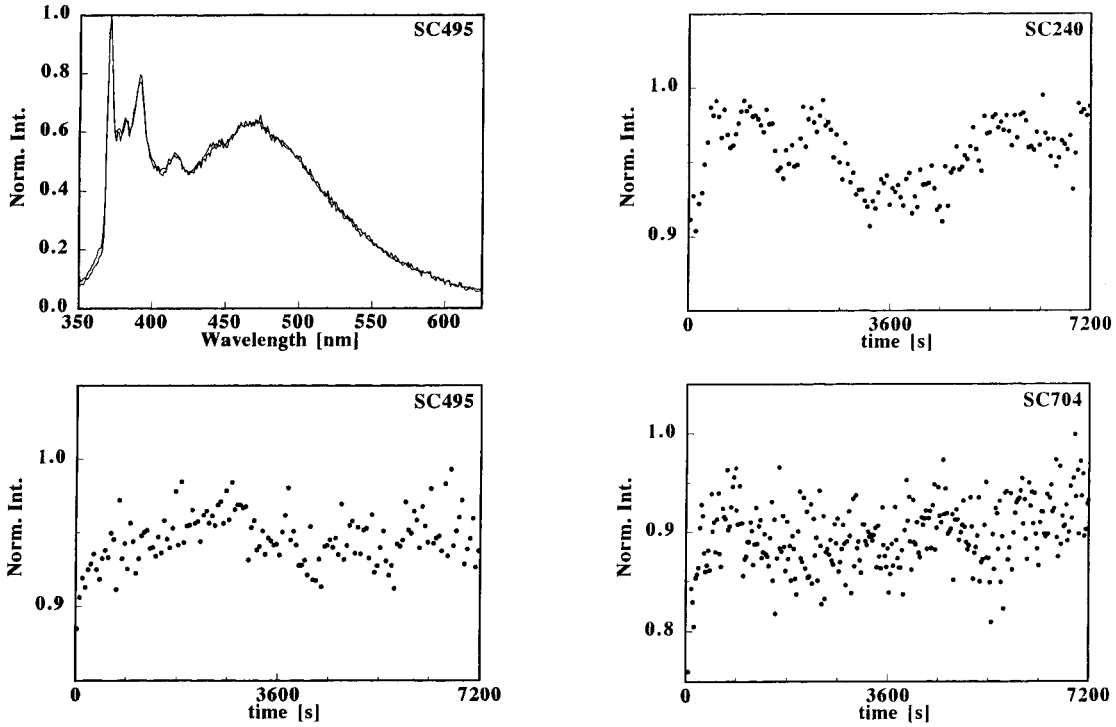

Figure 4. Control measurements for the possibility that pyrene should migrate between the block copolymer micelles. The steady-state emission spectra (upper left) were recorded on a solution containing 100 μM pyrene and 5 g/L SC495 and 3 h after mixing this solution with a 5 g/L SC495 solution without pyrene. The three other spectra show the fluorescence intensity at 395 nm as a function of time for the indicated block copolymers. The excitation wavelength was 320 nm.

fission of micelles but rather through unimer exchange via the Aniansson−Wall mechanism.[66−68] This mechanism allows the change of the aggregation number only in steps consisting of addition or subtraction of a single surfactant, which is in agreement with the theoretical predictions of Halperin and Alexander.[69] Due to the repulsive interactions between the outer layers, the fusion of two polymeric micelles is much more energetically unfavorable than the release of one unimer from one micelle and its reentry in the other one. This theory was developed for uncharged block copolymers, and since the hydrophilic block in the present study is a polyelectrolyte, the fusion−fission mechanism is even more unlikely. Furthermore, Tian *et al.* have also reported experimental evidences in favor of unimer-driven exchange between micelles of block copolymers.[14] The conclusion is that *if* pyrene migrates between the micelles, it has to be via the bulk.

The mobility of the micelle-dissolved pyrene molecules was investigated as described earlier.[63] From the steady-state emission spectra, it could be concluded that the pyrene excimer emission intensity did not decrease within the time frame of the experiments, and, similarly, the emission from the pyrene locally excited state did not increase, Figure 4. The initial rise of the emission intensity of the locally excited state seen in Figure 4 is most probably due to the mixing of the two samples. If the rise were due to pyrene migration, this fast migration would lead to a complete redistribution of the pyrene molecules within less than 10 min and make it impossible to follow an intensity increase during several hours in some cases; see section 3.2 and Figure 5. This result may seem unexpected, as the residence time of a pyrene molecule in low molecular weight surfactant micelles is shown to be on the order of milliseconds.[70] There is, however, evidence for a different behavior in block copolymer micelles. Cao *et al.* studied the pyrene migration between micelles formed by triblock copolymers of methacrylic acid and styrene.[2] They also found a very long equilibration time in a similar type of experiment as mentioned here; more than a week was needed to reach equilibrium. In their study, a rapid initial decrease of the pyrene excimer emission intensity was also observed. The explanation given, that some of the pyrene is dissolved in the swollen corona shell and therefore exchanges faster,[2] could also be true for the present systems. An argument against this is the difference in solvent: Cao *et al.* used a dioxane/water mixture to prepare their block copolymer micelles, while the present investigation only treats aqueous systems. Even after dialysis, some dioxane could be left in the micelle, influencing the pyrene locus and exchange.

In order to explain the long residence time of pyrene in block copolymer micelles, one must remember that the hydrophobic volume of the polymeric micelles used in this investigation are order of magnitudes larger than for, e.g., an sodium dodecyl sulfate (SDS) micelle. This huge difference in hydrophobic volume will make pyrene bulk migration less probable. Furthermore, the hydrophilic part of the block copolymer amphiphiles used is a polymer, also leading to a large shell volume difference as compared to conventional surfactants. The possibility for a polymeric micelle to recapture a pyrene molecule, leaving the hydrophobic domain of the micelle, is therefore much larger than for a conventional surfactant micelle. Also the size of the hydrophobic core is shown to be of importance for the exchange rate,[25] with a lower escape rate for larger cores, as well as the interactions between the hydrophobic core and the hydrophilic chain.[14,28,71,72] Finally, it has been pointed out that polymeric micelles show a higher dissolving capacity than conventional micelles.[27] This is in agree-

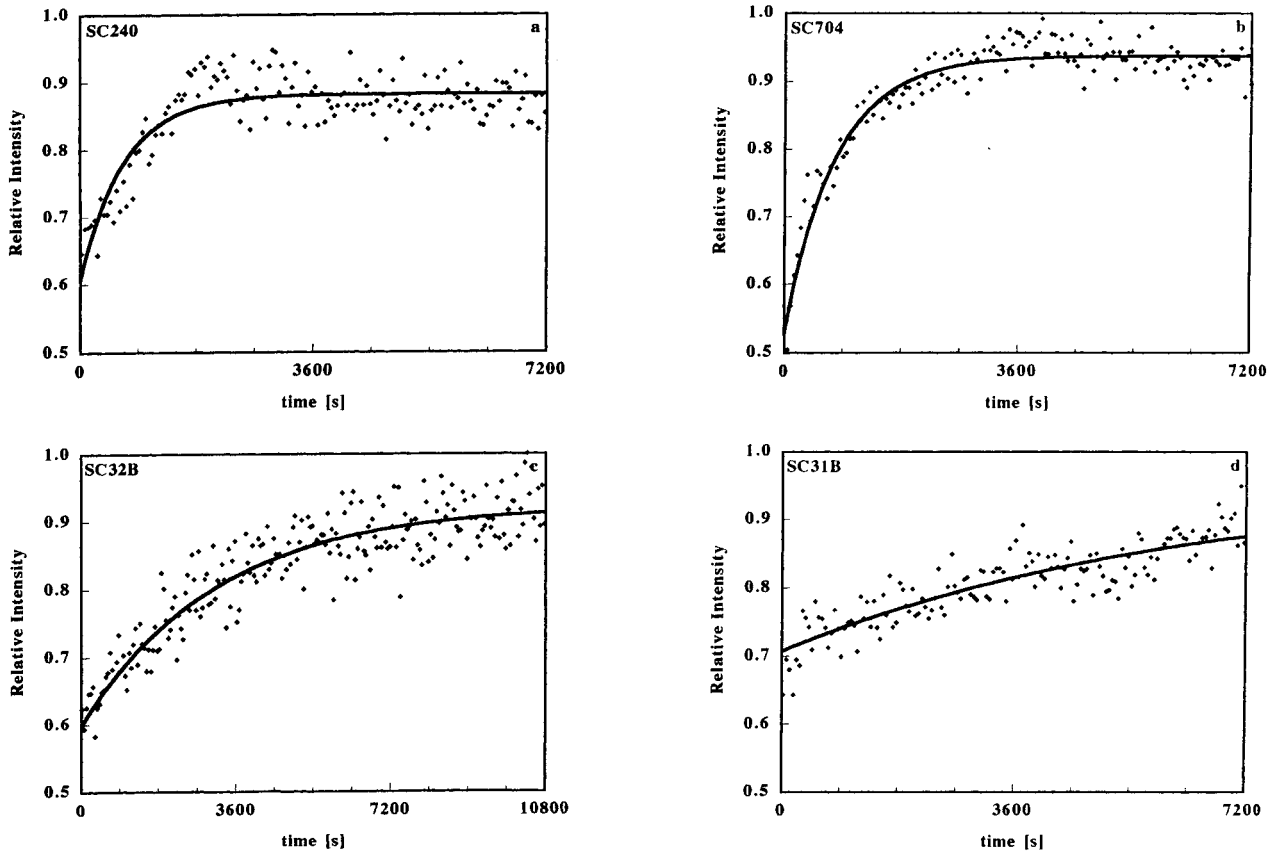

Figure 5. Fluorescence intensity as a function of time (dots) and the curve based on the fitting of eq 1 to the experimental data (line): (a, top left) SC240; (b, top right) SC704; (c, bottom left) SC32B; (d, bottom right) SC31B. All measurements performed at 20 °C. The results of the fittings are compiled in Table 2.

Table 2. Numerical Results of the Fittings of Equation 1 to the Pyrene Emission Intensity Data as a Function of Time at 20 °C[a]

polymer	I_p	$\xi_{D\rightarrow A}$	$k \times 10^3$ (s^{-1})
SC184	0.77	0.33	2.43 ± 0.17
SC240	0.61	0.55	1.48 ± 0.01
SC495	0.79	0.14	0.50 ± 0.11
SC704	0.53	0.82	1.28 ± 0.03
SC367	0.79	0.26	1.35 ± 0.10
SC32B	0.60	0.65	0.32 ± 0.01
SC31B	0.71	0.56	0.13 ± 0.02

[a] See text for further explanations.

ment with the finding that pyrene does not leave its host polymeric micelle for the systems studied.

As the pyrene exchange between the block copolymer micelles is slow on the time scale of amphiphilic unimer exchange, we conclude that eq 1 holds for the evaluation of the present data.

3.2. Critical Micelle Concentrations and Unimer Exchange Rate Constants. Figure 5 shows some representative examples of the kinetic measurement together with the fitting of eq 1 to the experimental data. The calculated exchange rate constants, k, are listed in Table 2.

Two poly((dimethylamino)ethyl methacrylate) containing diblock copolymers with a difference in their hydrophobic/hydrophilic balance have been synthesized, i.e., SC184 and SC240, Table 1. It is clear from Table 2 that the more hydrophilic diblock copolymer (SC184) exchanges much faster between micelles, approximately two times faster, than the more hydrophobic counterpart (SC240). Tian *et al.*[14] have shown that the rate controlling process would be the escape of the unimers from the micelles. In order to escape, the hydrophobic block has first to escape from the core, whereupon the unimer has to diffuse out of the outer layer of the micelle to the bulk solution. The reptation of the hydrophobic block is slowed down by increasing the molecular weight, and the probability of recapture of the unimer is proportional to the corona thickness. This means that any increase in molecular weight of either block should slow down the exchange rate, and SC184 should exhibit a lower exchange rate, the molecular weight of both its hydrophilic and hydrophobic blocks being higher. In fact, this way of viewing polymeric micelles is too static, and the hydrophobic/hydrophilic balance should also be considered when forecasting trends in the unimer exchange rate constants. The hydrophilic block will tend to diffuse to the bulk solution to increase its entropy, whereas the hydrophobic block will prefer to stay in the micellar core to avoid any unfavorable contact with water. The final behavior of the unimer will be a compromise between these two antagonistic tendencies. The effect of the hydrophobicity is also reflected in the cmc values: increasing the hydrophobic/hydrophilic ratio with a factor of 1.6 decreases the cmc with a factor of 4, Table 1. This strong dependence of cmc on the relative length of the hydrocarbon tail of traditional surfactants is well-known,[12,55,59,61,68,73,74] even though additional factors, e.g., the size of the head group,[75] also play an important role.

With the value of the diblock copolymer SC184 being set as a reference, the effect of the molecular architecture has been investigated. While the molecular weight and the chemical composition are kept unchanged as compared to SC184, two different triblock copolymers

have been synthesized. One copolymer has hydrophilic outer ends, i.e., SC495, while the other, SC704, has two hydrophobic outer blocks. The cmc is not changed substantially when compared to that of SC184: for SC495 it is more or less identical, while for SC704 it is only approximately 25% higher. The triblock copolymer with hydrophobic end blocks could, in principle, bridge two micelles, leading to a gel-like network, giving rise to a high viscosity. Since this is not observed even at much higher concentrations than the one presented here, and since well-defined objects are detected by light scattering, all of the hydrophobic outer blocks are considered to be aggregated in the same micelle.

The qualitative agreement observed in the dependence of the cmc and the exchange kinetics on the hydrophobic/hydrophilic balance of diblocks becomes less obvious, however, when the triblocks are considered. The triblock copolymers are exchanging slower than the diblocks, i.e., decreasing the exchange rate constant by a factor of 2 and 6 for SC704 and SC495, respectively, which is in contrast to the small variation in the cmc. Evidently, the copolymer architecture affects the dynamics of the copolymer exchange.

In the case of a triblock copolymer with two hydrophobic outer blocks, the escape of the unimer from the micelle can only occur if both blocks are released. Since their molecular weight is lower than for SC184, it is reasonable to assume that each block should be released faster than for SC184. Therefore, this step should be favored. Nevertheless, the free hydrophobic block, which is now exposed to the aqueous solution, will tend to reenter into the micellar core, unless in the meantime the other block is withdrawn from the micellar core.

The reverse triblock copolymer, with the two hydrophilic outer blocks, forms more stable micelles. Upon micellization, the hydrophobic central block localizes within the core and both outer blocks are exposed to the aqueous phase. In order to release the triblock copolymer from its host micelle, one of the hydrophilic outer ends will have to be transported through the hydrophobic region of the micelle, a highly unfavorable process. Another factor, also leading to a slower exchange, is the splitting-up of the hydrophilic block into two shorter blocks. This architectural change leads to a lower tendency for the unimer to dissolve into the bulk.

Substitution of *n*-propyl for the ethyl substituent in the poly((dimethylamino)ethyl methacrylate) hydrophobic block results logically in a more hydrophobic diblock copolymer, i.e., SC367, when compared at the approximately the same hydrophobic/hydrophilic comonomer balance to the SC184 sample. Indeed, due to the lower water solubility of DMPAMA compared to DMAEMA, both the cmc and the unimer exchange rate constant, k, are substantially decreased to a point where they are closer to those of the more hydrophobic SC240. The branching of the propyl substituent from normal (SC367) to the isopropyl structure (SC32B) does not intrinsically change the hydrophobic/hydrophilic balance, and the cmc remains accordingly unchanged, Table 1. It is, however, noteworthy that the exchange rate constant is decreased by a factor of 4. This indicates that a minute change in the molecular structure of the hydrophobic comonomer may have a pronounced effect on the packing of the micellar core.

Still considering PDMAMEMA as the hydrophobic block, a triblock consisting of a central hydrophilic block, i.e., SC31B, has been compared with the diblock SC32B. There is a remarkable parallelism in the characteristic features of these two samples with respect to the copolymers based on (dimethylamino)ethyl methacrylate, i.e., SC184 and SC704. No change in the cmc is observed, whereas the exchange of the copolymer molecules becomes two times slower for the triblock copolymers as compared to the diblock.

Comparing the results obtained with those found for micelles buildup of conventional surfactants, some striking differences are observed. The cmc's of alkyltrimethylammonium chloride surfactants with 12, 14, and 16 carbon atoms in the hydrophobic tail, respectively, is 16, 4.5, and 1.4 mM, respectively.[30] Thus, the cmc decreases by a factor of 2 upon increasing the hydrophobic tail by one methylene group. The changes in the cmc values for the amphiphilic block copolymers used in this investigation, Table 1, are much smaller; compare, e.g., SC184 with SC240 and SC32B. The lowering in cmc with increasing hydrophobic tail length, however, is also for conventional surfactants not linear, e.g., the alkyltrimethylammonium chloride series. As the relative importance of an additional methylene group is greater for the shorter chains, the lowering will be more pronounced when going from 12 to 14 carbons than when going from 14 to 16. This is also reflected in the relative increase of the hydrophobic volume when extending the hydrophobic tail; the increase is approximately 15 and 13% for the two cases. Also structural factors, e.g., branching of the chains, influence the cmc.

The variation in cmc for the block copolymers can be understood in the following way. When going from SC184 to SC240, with a lowering of the cmc by a factor of 4, a decrease the hydrophobic volume occurs but, more important, also a pronounced increase in hydrophobic character. As discussed above, at least for these block coplymers, the balance between the hydrophobic and hydrophilic blocks is of greater importance than the hydrophobic volume of the tail. For the comparison of SC184 with SC32B, however, this balance difference is at first sight not enough to explain the lowering of the cmc. Also a notable influence of the branching of the (dimethylamino)alkyl group as well as the influence of the hydrophilic block, which is much longer for SC184, should be pointed out and allows the conclusion that, for such large amphiphiles as block copolymers, the changes in cmc when changing one or more of the physical parameters of the molecule do not follow as simple relationships as is the case for conventional surfactants.

With a turn now to the exchange rate constant k and by comparison of the present results with those obtained for conventional surfactant micelles, the results reported by Malliaris *et al.* are useful.[30] The escape rate constants for two alkylpyridinium chloride surfactants, with 10 and 12 carbons in the hydrophobic tail, respectively, dissolved in alkyltrimethylammonium chloride micelles, see above, were determined. All escape rate constants, when migration occurred, were on the order of 10^5 s^{-1}.[30] Increasing the hydrocarbon tail with two methylene groups, decreased the escape rate constant by a factor of 5−15, strongly depending on the relation between the tail length of the migrating alkylpyridinium ion and that of the alkyltrimethylammonium surfactant, forming the micelle. In view of this, the lowering of k, when going from SC184 to SC32B, can be understood.

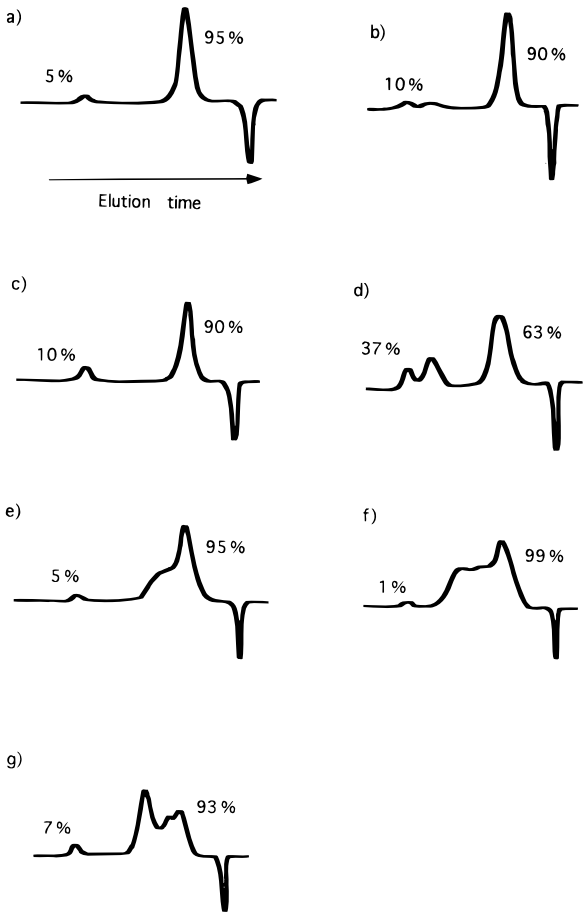

Figure 6. SEC chromatograms of (a) SC184, (b) SC240, (c) SC704, (d) SC495, (e) SC367, (f) SC32B, (g) SC31B. The relative proportion of the aggregated species and the unimers are given next to their corresponding peak for each chromatogram.

Evidently, not only tail length or head group play a role for the exchange process of block copolymer unimers between micelles but also other factors, such as micellar aggregation number and shape.

3.3. Size Exclusion Chromatography. All chromatograms together with the micelle/unimer ratios are shown in Figure 6. For some block copolymers, more than one aggregated species have been observed. This might emanate from a distribution of aggregate species or from different types of micelles. This effect will be discussed elsewhere.[76] Arbitrarily, all types of aggregation will be reported as aggregates, and only the ratio between aggregates and unimers is considered.

In the case of (dimethylamino)ethyl methacrylate copolymers, there is a good agreement between SEC and fluorescence. Approximately, 5, 10, 10, and 37% aggregates are observed by SEC for SC184, SC240, SC704, and SC495, respectively, Figures 6a−d. This corresponds to the trend measured by fluorescence, as, to some extent, the increase in aggregate content observed by SEC is proportional to the decrease of the exchange rate constant measured by fluorescence. Nevertheless, SEC affords only a rough estimate, as it cannot discriminate between similar exchange rate constants, as for SC240 and SC704.

In the case of SC367, in addition to the well-separated micellar peak (5%), some fronting of the unimer peak is observed. This is an indication that some micelles are breaking apart at a rate comparable to the flow rate. Therefore, it is not possible to quantify them correctly. It can only be concluded that the aggregates represent more than 5%. Thus, SC367 should exchange slower than SC184, but it is not possible to discriminate it from SC240, SC704, and SC495 by SEC measurements only.

In the case of SC32B and SC31B, the main micellar peak and the unimers peak are not fully resolved. Most likely, the micelles break apart during elution. This is comparable to the situation found for SC367, except that the micellar peaks are more conspicuous for SC32B and, particularly, for SC31B. Even though the micelle peak cannot be quantified, clearly SC31B and SC32B exchange slower than the other copolymers. Moreover, since the micelle peak is dominating for SC31B, it is clear that it exchanges slower than SC32B.

4. Conclusions

Fluorescence and SEC measurements of the micelles formed by (dimethylamino)alkyl methacrylate copolymers have shown that the exchange of block copolymer molecules between the micelles in aqueous solution can be tuned by changing the composition, the molecular architecture, and the alkyl spacer.

Increasing the hydrophobicity of the copolymer, either through the composition or through the monomer, slows down the exchange due to the less favorable interactions with the aqueous bulk. The splitting-up of either the hydrophobic or the hydrophilic block into two outer blocks, resulting in a triblock copolymer, also decreases the exchange rate constant. In the former case, both outer blocks have to be released simultaneously prior to the unimer migration. The probability for escape is thus reduced and the exchange slowed down. In the latter case, the central hydrophobic block is most likely in the micellar core. Its reptation is slowed down, as is the exchange rate. Branching of the alkyl substituent also leads to a decreased unimer exchange rate constant.

Finally, good qualitative agreement between SEC and fluorescence has been observed. This suggests that if one wants to distinguish trends in the dynamical stability of the micellar aggregates, the simpler SEC method can be used within certain limits. For a more precise determination, however, more exact methods are necessary, e.g., the fluorescence intensity increase due to energy transfer as function of time.

The possibility of tuning the exchange rate with means other than changing the composition or the architecture of the block copolymers, e.g., by changing the counterion or by additives, is under investigation.[77]

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