Tuning of the Exchange Dynamics of Unimers between Block Copolymer Micelles with Temperature, Cosolvents, and Cosurfactants

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ABSTRACT: The dynamics of unimer exchange between aqueous micelles, formed by two amphiphilic block copolymers, i.e., poly(styrene-*b*-sodium methacrylate) and poly(*tert*-butylstyrene-*b*-sodium methacrylate), has been investigated by steady-state fluorescence spectroscopy. The kinetics are so slow at room temperature that no exchange could be detected over several hours, while at 60 °C the exchange rate constants could be estimated. These results corroborate our previous findings that the rate is slowed down by increasing the hydrophobicity of the core. In addition to the temperature, the exchange can also be tuned by the addition of either a cosolvent or a cosurfactant. The efficiency of these additives to speed up the exchange process is related to their water solubility and their compatibility with the hydrophobic core of the micelles. The most pronounced effect on the exchange process is observed when the water solubility is low and the mixing of the additive with the hydrophobic core is favorable.

1. Introduction

When dissolved in a solvent selective for one of the constitutive components, amphiphilic block copolymers self-assemble into micelles in a manner similar to classical surfactants. Compared with classical surfactants, the exchange rate of amphiphilic block copolymer molecules, unimers, between the aggregates is substantially slowed down. On one hand, if the rate is slowed down too much, block copolymers will be of limited use for applications that require a quite fast unimer release. For instance, adsorption from a selective solvent onto surfaces, which is a prerequisite for the stabilization of solid dispersions, has been shown to be driven by the ease of unimer release.[1] On the other hand, slow exchange rates do open new opportunities, e.g., drug delivery.

Both theoretical and experimental studies on the aggregation behavior of block copolymers in aqueous solutions,[2−23] as well as studies of the exchange of unimers between aqueous block copolymer micelles,[24−34] have been very active research domains in the recent years. Special attention has been paid to poloxamers, i.e., di- or triblock copolymers of ethylene oxide and propylene oxide, and block copolymers of polystyrene as the hydrophobic block. The former have an exit rate of approximately 10^3 s^{-1},[28] which is slow in comparison with what is found for ordinary micelles,[35−38] while poly(styrene-*b*-ethylene oxide) copolymers exchange so slowly, that a significant rate only could be determined at elevated temperatures.[26] In other words, the exchange rate of copolymer molecules between block copolymer micelles can, roughly, be expected to be found in the range between 10^3 s^{-1} and 0.

Recently, the exchange kinetics of poly(dimethylaminoalkyl methacrylate-*b*-sodium methacrylate) copolymers, determined by nonradiative energy transfer, were reported.[33,34] The unimer exchange kinetics were in between those of poloxamers and polystyrene-based copolymers and could be related to the hydrophobic character of the aminated block, the composition, and the architecture of the copolymer. Any increase of the copolymer hydrophobicity, by changing either the copolymer composition or the aminated monomer, slows down the exchange.

In this study, the influence of the hydrophobic character on the unimer exchange rate has been further elaborated on by replacing the hydrophobic methacrylate block by blocks with varying lipophilicity, i.e., styrene and *tert*-butylstyrene. According to earlier reports on polystyrene copolymers, extremely slow exchange rates are expected.[26,27] The possibility to tune the exchange rate by changing the temperature or addition of a cosolvent or cosurfactant is investigated and discussed in detail.

2. Experimental Section

2.1. Materials. Pyrene (Acros Janssen) was twice recrystallized from absolute ethanol. Distilled water of Milli-Q quality was used for all solutions.

Triton X-100 (Tx-100) (Acros Janssen), sodium dodecyl sulfate (SDS) (BDH, specially pure), toluene, and 1,4-dioxane (dioxane) (both from Rathburn, PA quality) were used as received.

2.2. Block Copolymer Synthesis. The anionic synthesis of poly(styrene-*b*-sodium methacrylate) copolymers has been reported by Desjardins et al.[39] and Ramireddy et al.[40] Desjardins et al. highlighted the need for end-capping the polystyrene with 1,1-diphenylethylene; otherwise, side reactions were observed. The labeling procedure was described by Ramireddy et al. and was applied in the present study. The method used differs from their only by the type of initiator used, i.e., α-methylstyrene (αMeS) in combination with *sec*-butyllithium.[41] This initiator is preferred, compared to cumylpotassium,[40] since it is formed in situ and does not require any preliminary synthesis. In addition, the used initiator can easily be extended to other poly(styrene-*b*-alkyl methacrylate) co-

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polymers.[42,43] As a drawback, initiators based on lithium as counterion yield homo[44] or block[45] copolymers of tBMA with a broader molecular weight distribution, i.e., about 1.3, than that of the ones based on potassium, i.e., 1.1.[40,44] This problem can be circumvented by the addition of LiCl, which forms a μ-complex with the propagating species, as shown by Varshney et al.[44] for homopolymers and the present study for block copolymers.

Naphthalene-labeled and unlabeled poly(styrene-*b*-sodium methacrylate) (S_NM and SM, respectively) and poly(*tert*-butylstyrene-*b*-sodium methacrylate) (tBS_NM and tBSM, respectively) copolymers were synthesized as follows. Styrene (S), *tert*-butylstyrene (tBS), αMeS, and *tert*-butyl methacrylate (tBMA) were first vacuum-distilled from calcium hydride and then stored under a nitrogen atmosphere at −20 °C. Before polymerization, all monomers were diluted with an equal volume of toluene. Triethylaluminum (1 M in toluene) was added to tBMA until a yellowish green color was observed. Fluorenyllithium was added drop by drop to S, tBS, and αMeS until a persistent orange color was observed. The monomers were recovered by distillation under reduced pressure. 1,1-Diphenylethylene was dried and redistilled over *sec*-butyllithium just before polymerization. 2-Vinylnaphthalene was purified by sublimation and dried by azeotropic distillation of toluene prior to use.

Lithium chloride was flame-dried under vacuum just prior to polymerization and stored under nitrogen. THF was purified by reflux over a freshly prepared sodium−benzophenone complex.

Polymerization was carried out under dry nitrogen in flasks equipped with three-way stopcocks capped with rubber septa. All glassware was flamed under vacuum before use. Solutions were transferred via stainless steel capillaries or with glass syringes through the septa.

After introduction of a 10-fold molar excess of LiCl, with respect to the initiator, into the reactor, THF and a few droplets of αMeS were added. The solution was cooled to −78 °C and drop by drop titrated with *sec*-butyllithium until a persistent orange/red color was observed. The required amount of the initiator was added to the polymerization medium, followed by S, whereupon the polymerization was performed for 30 min. Polystyrene chains were end-capped with 1,1-diphenylethylene, and an aliquot was withdrawn for characterization, followed by tBMA addition. The final copolymer concentration was 50 g/L. The copolymerization reaction was quenched with degassed methanol after 2 h. The copolymer was recovered by precipitation in water, and the comonomer conversion was close to completion.

The naphthalene labeling was carried out by adding 1 molar equivalent of 2-vinylnaphthalene just before 1,1-diphenylethylene, all other steps being the same. tBS copolymers were synthesized according to the same procedure.

2.3. Copolymer Characterization. Size exclusion chromatography (SEC) was carried out in THF at 35 °C, using a Hewlett-Packard 1050 liquid chromatograph equipped with four PLGel Columns (100, 500, 1000, and 10 000 Å) and a Hewlett-Packard 1047A refractive index detector. Polystyrene standards were used for calibration. The copolymer compositions were analyzed before hydrolysis by ^{1}H NMR with a Brüker AN 400 superconducting magnet equipment.

2.4. Hydrolysis. The tBMA block was hydrolyzed by refluxing the copolymer overnight in a 5/1 v/v dioxane/37% HCl solution. The hydrolyzed copolymers were recovered by solvent distillation under vacuum and redissolution in aqueous NaOH. Finally, the copolymers were purified by dialysis against demineralized water. The characteristics of the copolymers are reported in Table 1.

Table 1. Characteristics of the Diblock Copolymers Used in This Contribution

polymer[a]	M_n	φ	M_w/M_n	cmc [mg/L]	cmc [μM]	C [g/L]
SM	2800−8000	0.48	1.10	9	0.8	1.2
S_NM	2500−6800	0.50	1.10	7	0.75	1.2
tBSM	4000−6400	0.55	1.10	2	0.19	0.8
tBS_NM	3400−6200	0.48	1.15	2	0.21	0.8

[a] S, M, and tBS stand for styrene, sodium methacrylate, and *tert*-butylstyrene, respectively, while subscript N refers to naphthalene-labeled blocks. M_n is the molecular weight of the each block before hydrolysis. The first weight is for the hydrophobic and the second for the hydrophilic block. φ is the molar ratio of the hydrophobic to hydrophilic monomers. C is the concentration used in this study.

3. Fluorescence Measurements

The determination of the critical micelle concentration (cmc) and the steady-state fluorescence measurements were performed as reported elsewhere,[33,34] except for some minor modifications. First, no Borax buffer was used, as the hydrophobic blocks under consideration are insensitive to the pH. Second, the aqueous solutions were, in addition to stirring, also sonicated at 50 °C for 30 min. The solutions of the naphthalene-labeled block copolymer and pyrene dissolved in unlabeled block copolymer micelles, equal in copolymer concentration, were mixed, whereupon the required amount of cosolvent or cosurfactant was added. The cosurfactants were added in small amounts from an aqueous stock solution, 6 mM of surfactant, to prevent dilution effects. The dilution never exceeded 4%.

The solutions were preheated in the same water-bath used for the temperature control of the fluorimeter, to prevent temperature gradients.

The model used for the calculation of the exchange rates, based on the models of Cantú et al.[46] and Wang et al.,[29] has been reported earlier.[33,34] The fluorescence intensity data are fitted by

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

where I_0 takes account for the emission intensity at time $t = 0$ and $\xi_{D\to A}$ 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.

Naphthalene, covalently bound to the hydrophobic block of the copolymers, was used as excitation donor and unbound pyrene as acceptor. Recently, attention has been paid to the partitioning and mobility of dissolved pyrene between block copolymeric micelles in aqueous solutions.[47−49] It was shown, by dilution experiments, that pyrene was able to leave the micelles formed by a polystyrene-based block copolymer, even at temperatures below the T_g of the core.[47,48] The partitioning between the micellar subphase and the aqueous bulk yields 98−100% of the pyrene molecules to be located in the micelles at higher (1 g/L) block copolymer concentrations. At low concentrations (5 mg/L), however, as much as 25−50% of the pyrene is dissolved in the aqueous phase.[47] These results suggest that the conclusion made in previous articles,[33,34] i.e., that the pyrene does not leave the host micelle during the measurements, holds for the studied concentration range (at least 0.8 g/L) but might not be valid if extended to very low copolymer concentrations. To confirm the applicability of eq 1, control measurements were performed. First, the mobility of pyrene was controlled in the same way as in previous publications;[33,34] i.e., solutions of high concentration of the unlabeled tBSM and high pyrene concentration were used. No effects of pyrene migration

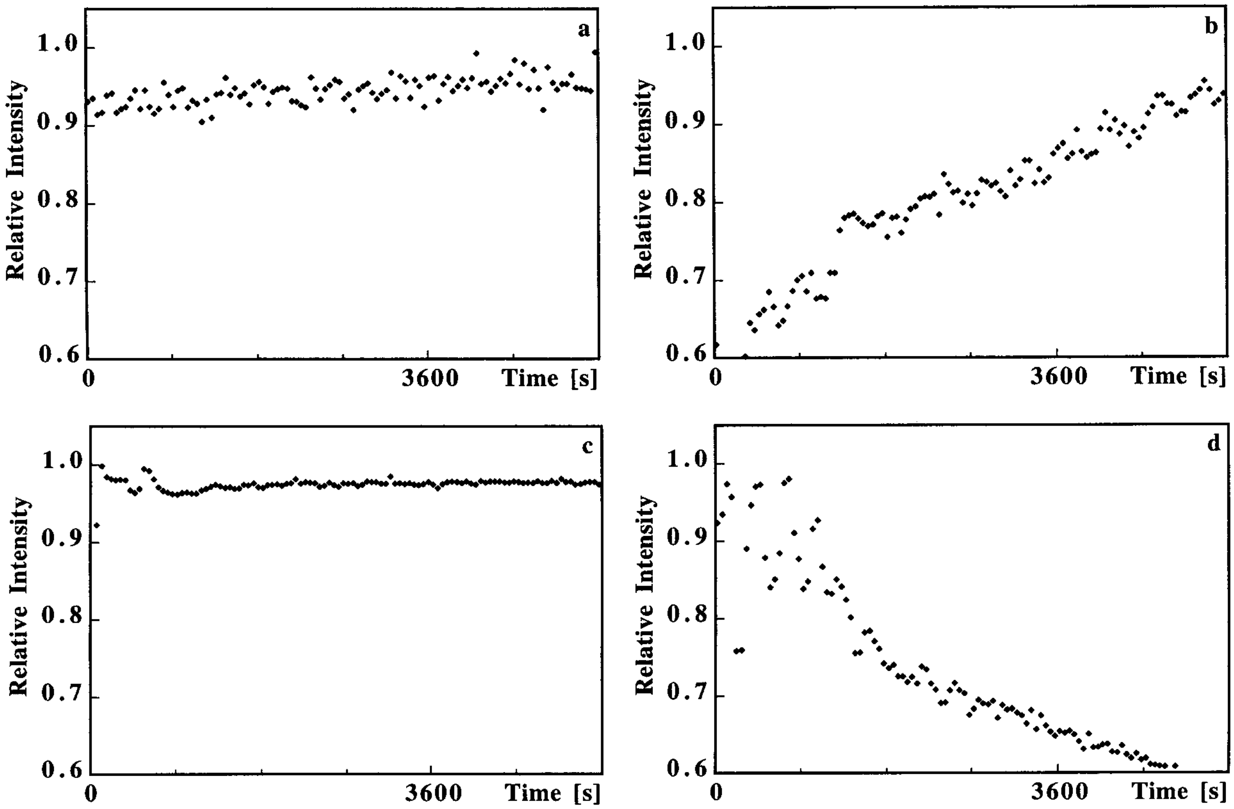

Figure 1. Time dependence of the fluorescence intensity (dots) for pyrene dissolved in tBSM block copolymer micelles in energy transfer, dilution, and quenching experiments: (a) tBSM, 0.8 g/L, energy transfer from naphthalene to pyrene; (b) tBSM, 4 mg/L, pyrene molecularly dissolved in block copolymer micelles; (c) tBSM, 0.2 g/L, 10 mM TlCl, pyrene molecularly dissolved in block copolymer micelles; (d) tBSM, 4 mg/L, 10 mM TlCl, pyrene molecularly dissolved in block copolymer micelles. All measurements were performed at 20 °C.

were detected during 4 h of measurements, indicative for very low pyrene mobility.

Second, dilution experiments as described by Teng et al.[49] were performed and are reported in Figure 1. When performing the energy-transfer experiments at high concentration of the copolymer, no increase in pyrene emission intensity was detected at room temperature (Figure 1a). When diluting a solution of unlabeled tBSM and pyrene-loaded tBSM by a factor of 200, however, an increase of the emission intensity is seen (Figure 1b). To understand this, one has to assume that migration of pyrene from the micelles into the bulk phase, so maintaining equilibrium conditions, leads to a lower degree of pyrene self-quenching. The number of pyrene molecules per micelle is indeed quite high, i.e., about 20, and self-quenching can certainly not be excluded. This result would then point in the direction of a detectable pyrene mobility. Teng et al. also performed combined dilution and quenching measurements.[49] By diluting a solution of a micelle-forming block copolymer with a solution containing Tl^+ ions, this is an efficient pyrene fluorescence quencher; they followed the fluorescence intensity decrease, due to quenching by Tl^+, as a function of time. From their results, they concluded that pyrene has a rather high mobility inside the micelles and that pyrene migration between the polymeric micelles must be substantial. Similar experiments were performed with tBSM as the micelle-forming block copolymer. When diluting the initial solution, i.e., 0.8 g/L, by a factor of 4, no intensity decrease was detected as a function of time (Figure 1c), while at a dilution factor of 200, the intensity decrease (Figure 1d) was of the same order as the increase in Figure 1b. Evidently, the results shown in Figure 1a,c suggest an immobile pyrene molecule dissolved in the tBSM micelle, while the results shown in Figure 1b,d suggest the contrary, that pyrene has a substantial mobility in this system.

This ostensible discrepancy can be rationalized and understood. An extensive discussion on the influence of a possible probe migration on the use of eq 1 has been published elsewhere.[34] To set the discussion further, there are two important factors to take into account: The partition of pyrene between the micelles and the kinetics of the pyrene exchange process. The partition, first, will ensure a certain distribution of pyrene between the micellar subphase and the aqueous bulk. As reported by Stepanek et al., it can be assumed that at 0.8 g/L tBSM about 98−100% of the pyrene molecules are dissolved in the micelles, while at 4 mg/L, between 25% and 50% of the pyrene will be in the aqueous phase.[47] Upon dilution, pyrene will be displaced from the micelles to the bulk to maintain equilibrium conditions. If one assumes the diffusion of pyrene inside the micelles to be independent of the micelle concentration, the consequence will be that the pyrene diffusion is not really fast in the micelles, as seen from the slow fluorescence intensity changes in Figure 1b,d. Second, the kinetics of the exchange require, at equilibrium conditions, that the pyrene rate of exit of the micelle must equal that of entry, i.e., $x_{PY}k_{exit} = k_{entry}[PY]_{aq}$, where x_{PY} is the average number of pyrene molecules in the micelle and $[PY]_{aq}$ the pyrene concentration in the aqueous bulk. The rate of the exchange process will depend on both the ratio between k_{exit} and k_{entry}, on one hand, and the values on x_{PY} and $[PY]_{aq}$, on the other hand. To have an efficient pyrene exchange between the

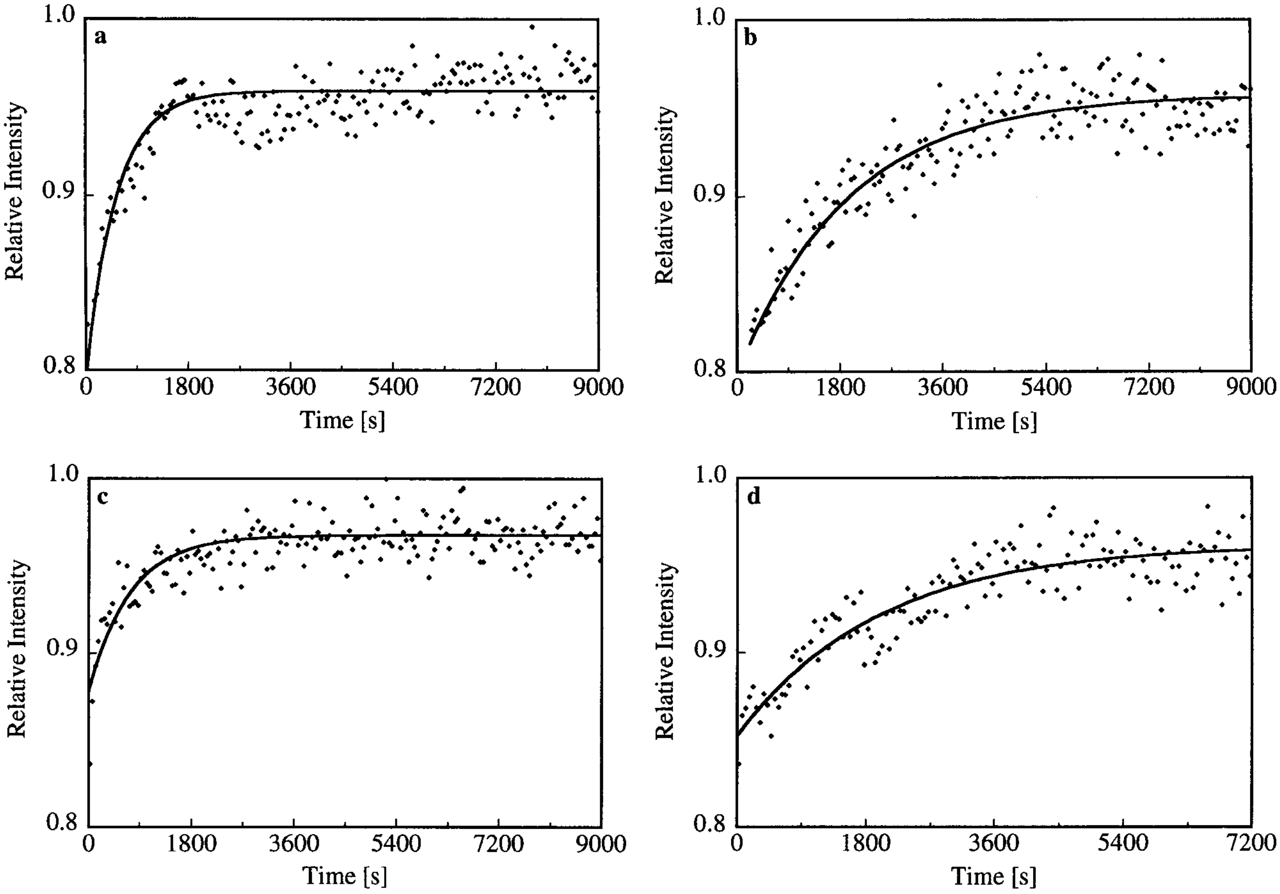

Figure 2. Time dependence of the fluorescence intensity (dots) and the curve based on the fitting of eq 1 to the experimental data (line): (a) SM, 60 °C; (b) tBSM, 60 °C; (c) tBSM with toluene 1:1, 20 °C; (d) tBSM with SDS 1:1, 20 °C. The results of the fittings are compiled in Table 2.

block copolymer micelles, a rather high bulk concentration of pyrene is a necessity, but $[PY]_{aq}$ is very low for the undiluted samples. This means that, even if the partition allows a possible migration of pyrene, the kinetics will not favor a migration. The diffusion of pyrene inside the micelles is slow, and more important, the pyrene concentration in the bulk phase is too low. This explains why no effects of pyrene migration or redistribution in the undiluted samples of tBSM are detected in the energy-transfer experiments. No effects are found in the dilution experiments either, as long as the dilution is not too extensive, while effects are found for high dilution factors, when $[PY]_{aq}$ is considerably larger.

This conclusion is in harmony with other reports. Investigations on similar block copolymer systems show that the equilibration time of the pyrene partitioning can be as long as a week.[50] Together with the long equilibration time, there are other important factors pointing toward low pyrene mobility between the block copolymer micelles. The low mobility makes it not straightforward to compare present micellar systems with micelles of low molecular weight surfactants. For instance, the influence of the hydrophobic volume,[51] interactions between the hydrophobic core and the hydrophilic block,[15,20,27,52] and the higher dissolving capacity of polymeric micelles[11] have to be taken into account. Data from the literature and our own experimental evidence validate the usage of eq 1 for the data evaluation for the systems investigated in the present study. It should be stressed, though, that this is due to the investigated block copolymer concentrations, leading to a zero concentration of pyrene in the aqueous bulk. Under other experimental conditions, the situation can be different, as reported recently.[47−49]

4. Results and Discussion

The unimer exchange rate constants were determined as described earlier.[33,34] Some representative increases of the steady-state fluorescence intensity as a function of time are shown in Figure 2 together with the fits of eq 1 to the data.

4.1. Influence of Copolymer Hydrophobicity and Temperature. The aggregation in aqueous solution of poly(S-*b*-methacrylic acid) copolymers, often in combination with a cosolvent, has been extensively studied by Webber and co-workers.[27,50,53−56] They have demonstrated, by sedimentation velocity studies, that, in the absence of cosolvent, the micellar core is apparently glassy and, consequently, that the escape of unimers is frozen.[27] As far as block copolymers based on polystyrene are concerned, the only quantitative determination of the exchange rate of unimers between micelles in aqueous solution was reported for poly(styrene-*b*-ethylene oxide) (SEO) copolymers.[26] Only when the sample was heated to 60 °C, a measurable exchange was detected. In the present study, it was as well necessary to heat the SM and tBSM solutions to 60 °C in order to measure the exchange rate (Table 2). This confirms the observation of Tian et al. that, at room temperature, the exchange rate of polystyrene-based block copolymers is too slow to be measured.[27]

Table 2. Numerical Results of the Fittings of Eq 1 to the Pyrene Emission Intensity as a Function of Time

	I_p	$\xi_{D->A}$	$k \times 10^3$ [s^{-1}]
		SM	
60 °C 0:1[a]	0.80	0.33	1.85 ± 0.06
		tBSM	
60 °C 0:1[a]	0.80	0.32	0.52 ± 0.02
dioxane 1:1[a]	0.91	0.10	0.61 ± 0.05
toluene 1:1[a]	0.88	0.18	1.36 ± 0.06
toluene 4:1[a]	0.54	0.76	2.08 ± 0.07
SDS 1:1[a]	0.85	0.22	0.51 ± 0.02
SDS 2:1[a]	0.86	0.21	3.83 ± 0.27
Tx-100 2:5[a]	0.81	0.25	0.32 ± 0.02
Tx-100 1:1[a]	0.63	0.69	10.75 ± 0.41

[a] 0:1, 1:1, 2:1, 4:1, and 2:5 stand for the molar ratio between the additive and the copolymer. At room temperature, no exchange of unimers was detected for systems without added cosolvent or cosurfactant. The systems with added cosolvent or cosurfactant were investigated at room temperature.

In a preceding study on poly(dimethylaminoalkyl methacrylate-*b*-sodium methacrylate),[34] a direct link between the exchange rate and the hydrophobicity of the block copolymer was demonstrated: The higher the hydrophobic character of the copolymer, the slower the exchange. This is also observed in the present study; neither SM nor tBSM shows any measurable exchange at room temperature. At 60 °C, however, both block copolymers show an exchange. The exchange rate constant is substantially smaller for tBSM compared to that of SM (Table 2). The latter exchanges almost 4 times faster than the former. This might be surprising, if comparing directly with micelles of low molecular weight surfactants. One should keep in mind that the influence of the hydrophobic volume[51] and the dissolving capacity[11] is of crucial importance, which explains the seemingly small difference between the exchange rate constants.

From the difference in hydrophobic character between these two blocks, as expressed by their Flory−Huggins interaction parameters (vide infra), the different exchange rates are as expected. Another parameter of interest in this context is the glass transition temperature, T_g, of the hydrophobic block. The reference values found for S and tBS are approximately 100 and 130 °C, respectively,[57] far too high to explain the observed exchange at 60 °C. One must keep in mind, however, that the T_g is a function of molecular weight and that the molecular weight of the hydrophobic blocks of the polymers used in this study is quite low. For tBS, Malhotra et al. determined the molecular weight dependence of the T_g (K) to be $446 - 7.3 \times 10^5/M_n$,[58] for molecular weights in the range $(1-4) \times 10^4$. For the actual tBSM block copolymer, the molecular weight of the tBS block is 1 order of magnitude lower, making the use of a linear relationship very uncertain.[59] To overcome this problem, an expression proposed by O'Driscoll and Sanayei can be used. They used an expression of the form $T_g = T_{g,\infty} - K/X_n^{2/3}$, with K a polymer-specific constant and X_n the number-average chain length.[59] For poly(styrene), $K = 404$ was used, which applied to the SM block copolymer of this study yields the T_g of the core to be approximately 50 °C.

It is possible to use the data given by Malhotra et al.[58] to calculate the parameters necessary to apply the model proposed by O'Driscoll and Sanayei[59] to the core of tBSM. For an expression using the molecular weight instead of the chain length, i.e., $T_g = T_{g,\infty} - K/M_n^{2/3}$, the parameters $T_{g,\infty}$ and K were determined to 442.5 K and 60.7, respectively. From the M_n given in Table 1, T_g can be estimated to be in the range 45−58 °C for hydrophobic tBS core in this study.

Not only the influence of the molecular weight on the T_g is of importance for the unimer exchange. Also, the next-to-corona part of the core, as well as the presence of a hydrophilic layer round the core, will play a role.[15,54] The chains located in the outer core are much more mobile due to a less dense packing caused by corona interactions. This effect will be of relatively more importance for a hydrophobic block of low molecular weight, and if the hydrophobic block is short enough, no part of the core will be in the glassy state.

The observation of a unimer exchange at 60 °C in the present systems, therefore, conforms with a T_g substantially lower than 100 °C in the present systems, and the conclusion is that, for both block copolymers, the T_g is higher than 20 °C and lower than 60 °C.

4.2. Influence of Cosolvents and Cosurfactants. The presence of a cosolvent is known to strongly influence the exchange of unimers between micelles in aqueous solutions of poly(styrene-*b*-methacrylic acid) copolymers.[27] When dissolved in a dioxane/water mixture, the copolymer molecules exchange between micelles only if the water content is lower than 20% v/v, and the influence of dioxane on tBSM was expected to be similar. If approximately one dioxane molecule is added per copolymer chain, that is 80 μM dioxane with the copolymer concentrations used in this study, an exchange rate constant comparable to the one observed at 60 °C in the absence of cosolvent is reached, but already at room temperature. The very low amount of cosolvent needed to induce unimer exchange can be rationalized in terms of the length of the hydrophobic block. In the study of Tian et al.,[27] where a much weaker effect of the cosolvent was observed, the hydrophobic block consists of 220 S units, while in the present study, the hydrophobic block carries 27 tBS units. Tian et al. concluded that the unimer exchange is very sensitive to the length of the hydrophobic (and hydrophilic) block, and it is logical that the amount of cosolvent needed in the present study is much lower than in theirs.

Addition of 80 μM toluene, i.e., in a 1:1 molar ratio toluene:polymer, induces an exchange at room temperature with a rate constant about 2 times larger than when dioxane was added (Table 2). Because of its poor miscibility with water, toluene almost exclusively dissolves in the micellar core. This tendency is less pronounced for dioxane, which is miscible with water up to 82%.[60] Moreover, in contrast to classical surfactants, block copolymers selectively dissolve cosolvents, as demonstrated by Nagarajan et al.[61]

The strength of the interactions between the hydrophobic block and the solubilizate has an effect not only on the partition of the solubilizate between water and the micellar core[15,61] but also on the hydrophobic block mobility inside the core. The interactions between the solubilizate and the core, given by the Flory−Huggins interaction parameter χ_{sc}, are related to the matching of their Hildebrand−Scatchard solubility parameters, δ:

$$\chi_{SC} = (\delta_s - \delta_c)^2 V_s / k_B T \tag{2}$$

where δ_s and δ_c are the solubility parameters for the solubilizate and the hydrophobic block, respectively, V_s is the molecular volume of the solubilizate (Table 3),

Table 3. Flory−Huggins Interaction Parameter χ_{sc} of Poly(tBS) with Several Additives[a]

additive	δ_s [cal/cm^3]$^{1/2}$	$V_s \times 10^{24}$ [cm^3]	χ_{sc}
dioxane	10	141	~0.28
toluene	8.9	176	~0.016
SDS	7.8	350	~0.22
Tx-100	~8.2	360	~0.057

[a] δ_s and V_s denote the Hildebrand−Scatchard solubility parameter and the molecular volume of the solubilizate, respectively.

and k_B is the Boltzmann constant. A low χ_{sc} is indicative for a strong interaction, and consequently, the two compounds will mix more easily. Unfortunately, the solubility parameter for poly(tBS) is not known. Nevertheless, it can be roughly estimated by analogy with benzene ($\delta = 9.2$), toluene ($\delta = 8.9$), and ethylbenzene ($\delta = 8.8$).[61] It turns out that substituting benzene with an alkyl group decreases the solubility parameter. This decrease depends, however, on the size of the alkyl chain. In reference to toluene and ethylbenzene, an additional methylene group in the substituent results in a decrease in δ of 0.1 unit. From this follows that δ of *tert*-butylbenzene can be estimated to be approximately 8.6. Since the solubility parameter of polystyrene (9.1) is close to that of benzene (9.2),[61] a reasonable estimate of δ of poly(tBS) is 8.6. The estimation of χ_{sc} for poly(tBS) with toluene and dioxane (Table 3) shows that the former is by far the better solvent for the copolymer, giving rise to a better mixing of toluene in the micellar core.[15,61] In addition, when the solubility parameters of the cosolvent and the hydrophobic polymer are close, a higher degree of swelling of the latter is observed, as reported by Yu et al.[62] This agrees with the higher efficiency of toluene in improving the unimer exchange. Further addition of toluene, up to 320 μM, causes a further increase of the exchange, but to a lesser extent.

When a cosurfactant is added to the block copolymer solution, mixed micelles are formed. The formation of mixed aggregates of classical surfactants has been extensively studied.[46,63−71] These mixed aggregates will have their own characteristics, sometimes closely related to the two surfactants used, but sometimes differing, e.g., increasing or decreasing, aggregation numbers, change in counterion binding, and changed dissolving behavior.[65,68,69,71]

The addition of SDS to aggregating block copolymer systems has been discussed in the literature.[3,9,72] At low SDS:polymer ratio, the surfactant dissolves in the block copolymer micelles, strongly influencing their characteristics. At higher SDS concentrations, the mixed micelles resemble more the features of an ordinary SDS micelle, interacting with the block copolymer.[72] To our best knowledge, the influence of classical surfactants on the dynamics of micellar solutions of block copolymers, e.g., the rate of intermicellar exchange, has not yet been explored. Addition of 80 μM SDS (ratio 1:1 SDS:polymer) speeds up the exchange rate by the same extent as dioxane does. In contrast to when cosolvents are added, no leveling off is observed upon further increasing the concentration of SDS. If, instead of the negatively charged SDS, the neutral Tx-100 is added, the rate is even more affected. As was observed for dioxane and toluene, the increase of the exchange rate is related to the solubility of the solubilizate in the bulk. In the case of cosurfactants, the cmc should rather be considered. There is indeed a good correlation between the cmc's, 0.2 mM for Tx-100[73] and 8 mM for SDS,[74] and the exchange rate increase. The higher the cmc, the more surfactant molecules in the bulk, and the minor the influence on the rate. Nevertheless, the higher tendency of Tx-100 to micellize does not necessarily mean that mixed aggregates with the block copolymers will be formed.

The tendency of SDS and Tx-100 to form mixed micelles with the tBS-containing block copolymers can also be discussed by extending the approach of Nagarajan to cosurfactants, considering their lipophilic tails as solubilizates.[61] The solubility parameter of the Tx-100 alkyl chain is unknown, but since it is very similar to the poly(tBS) structure and an additional carbon is expected to decrease the solubility parameter by 0.1 or less, δ of Tx-100 should be in the 8.2−8.6 range. This value is closer to that of tBS than the δ of the dodecyl chain of SDS, 7.8.[61] The volumes of the hydrophobic tails are similar, i.e., 360 Å^3 for Tx-100[75] and 350 Å^3 for SDS,[76] and χ_{sc} is more favorable for Tx-100. This means that Tx-100 will form mixed aggregates with tBSM more easily than SDS does. In the worst case, the solubility parameter of Tx-100 will be 0.4 units away from that of tBS, and the χ_{sc} of Tx-100 and poly(tBS) can roughly be estimated to be lower than or equal to 0.057 (see Table 3).

If the additions of 1 equiv of cosolvent or cosurfactant are compared, the following can be mentioned. Dioxane and SDS, which have similar χ_{sc}, increase the rate to the same extent. Toluene is much more efficient, as predicted by its χ_{sc}. Finally, due to the uncertainty on its solubility parameter, the behavior of Tx-100 can only be roughly estimated. Clearly, it should be more efficient than dioxane or SDS, but when compared to toluene, only an approximate prediction can be made; it will be at least as efficient as toluene. It must also be pointed out that any reliable prediction of a low χ_{sc} is particularly difficult, since the solubilizate uptake tends to grow exponentially at small χ_{sc}, as reported by Nagarajan.[61] This uncertainty is also reflected by the fact that the calculated value of χ_{sc} for Tx-100 is larger than that for toluene (Table 3), although addition of Tx-100 induces a much more efficient exchange of unimers (Table 2).

In contrast to the cosolvent behavior, a rather steep increase of the unimer exchange rate is observed upon increasing the concentration of the cosurfactants. In fact, in addition to the swelling of the core, a cosurfactant also perturbs the interface and the corona by its hydrophilic headgroup. This further influences, among other characteristics, the packing of the micelles and the thickness of the corona, as observed for fatty alcohols in solutions of conventional surfactants.[77,78] Finally, the less pronounced influence of the SDS concentration on the rate is probably due to the negative charge, which slows down its incorporation in mixed micelles with tBSM.

5. Conclusions

The direct link between hydrophobicity of the core and the exchange rate constant, reported previously,[33,34] has been confirmed for copolymers based on styrene derivatives. Increasing the hydrophobicity of the copolymer slows down the exchange due to the less favorable interactions with the aqueous bulk. In the present study, the rates are so low that the temperature has to be raised to 60 °C to measure any exchange. This can, at least qualitatively, be related to the T_g of the hydrophobic block, if taking into account that this parameter shows a strong dependence on the molecular weight and that interactions between the corona and the outer core cause the latter to be more mobile.

The kinetics could be tuned by the addition of either a cosolvent, i.e., dioxane or toluene, or a cosurfactant, i.e., SDS or Tx-100. In the former case, the exchange rate is related to the cosolvent−water and cosolvent−core interactions. The cosolvent will accumulate in the most favorable environment, as demonstrated by Nagarajan et al.[61] The same argumentation can successfully be extended to cosurfactants. In contrast to a cosolvent, however, the influence of cosurfactant on the rate does not level off with increasing amount of additive. In fact, the cosurfactant, in addition to the swelling of the core, also perturbs the interface and the corona by its hydrophilic headgroup. This further influences, among other characteristics, the packing of the micelles and the thickness of the corona, as observed for fatty alcohols in solutions of conventional surfactants.[77,78] A cosurfactant with a charge of the same sign as the corona's forms mixed micelles less efficiently, as expected, and thereby exerts a smaller influence on the exchange process.

Finally, it should be mentioned that the unimer exchange kinetics cannot be predicted solely on the basis of the T_g of the equivalent bulk matrix, i.e., the micelle being frozen at temperatures below the T_g and fluid above. Other parameters, e.g., core packing, electrostatic repulsions, core−solvent, and corona−solvent interactions, should be as well considered, as shown for other block copolymer systems.[79,80]

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