Chain Exchange Kinetics of Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) Micelles in THF/Cyclopentane Mixtures

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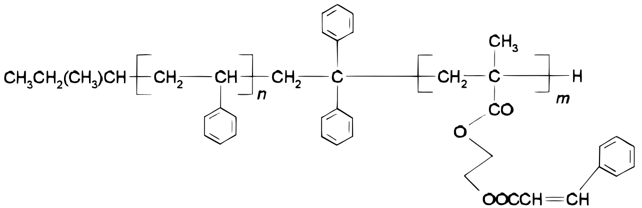
ABSTRACT: Two to three pyrene groups were attached to the PCEMA block of polystyrene-*block*-poly-(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) to yield PS-*b*-PCEMA−Py. Both PS-*b*-PCEMA and PS-*b*-PCEMA−Py formed micelles with PCEMA cores and PS shells in THF/cyclopentane (CP) mixtures with sufficiently high CP contents. Mixing such micelles led to chain exchange between different micelles, which increased the pyrene monomer fluorescence intensity at the cost of excimer emission. The data of pyrene monomer fluorescence intensity increase with time and were fitted to a two-exponential-term function. The average lifetime obtained was used to characterize the micelle chain exchange rate. Investigated were the effect of varying solvent composition, temperature, micelle concentration, and the length of both the PS and PCEMA blocks on the chain exchange rate.

I. Introduction

Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) samples form spherical micelles with PCEMA cores and PS shells in THF/cyclopentane (CP) mixtures with sufficiently high CP contents.[1−3] The core of these micelles can be cross-linked photochemically to prepare either star polymers or nanospheres depending on whether the PS or the PCEMA block is much longer.[1,2] This method has proven to be extremely robust in producing star polymers with a high number of arms, high molar masses, and narrow size distributions.[1,2] Upon contacting a solid substrate, such as silica, with a PS-*b*-PCEMA micellar solution, the micelles can be adsorbed and disintegrate on the substrate to form diblock monolayers or brushes.[4−6] In such a monolayer, the insoluble PCEMA block spreads on the solid substrate like a melt and the soluble PS block stretches into the solution phase. Brush formation should be useful in modifying the surface properties of solid substrates.[7−10]



PS-*b*-PCEMA

In all of these applications, optimizing the relaxation rate of micelles is of critical importance. In the case of cross-linking star micelles to produce star polymers, the micelles should be stable on the time scale of PCEMA cross-linking so that UV irradiation only “locks in” and does not perturb the structure of a micelle. This “locking in” allows control of the number of arms in the final star polymer by tuning the aggregation number, *f*, of the star micelles, where *f* follows a theoretical scaling relation,[11] as recently verified by our group.[2] This locking in also allows one to deduce the *f* numbers of the star micelles by determining the molar mass of the star polymer. The determination of the molar mass of a star polymer is much easier because a star polymer is stable in most organic solvents. On the other hand, the molar mass of a star micelle has to be determined in the mixed solvent in which the micelle is prepared. In the case of brush formation from PS-*b*-PCEMA micelles, we found that polymer brushes form on silica only in THF/CP with CP volume fractions, f_{CP}, between ∼67% and ∼90%. With a CP content above ∼92%, some of the micelles adsorbed intact onto the silica.[6] This suggests that f_{CP} affects the stability of the micelles. At $f_{CP} > 92\%$, some of the micelles were too stable to disintegrate onto the silica to form a brush.

This research was targeted at a systematic study of the factors, such as variation in temperature, solvent composition, and diblock composition, which affect the stability of PS-*b*-PCEMA micelles in THF/CP. For this, micelles were prepared from PS-*b*-PCEMA and PS-*b*-PCEMA−Py, where PS-*b*-PCEMA−Py denotes a PS-*b*-PCEMA sample randomly tagged with two or three pyrenyl groups in the PCEMA block. The micelles were then mixed and pyrene monomer fluorescence intensity was monitored. Less stable micelles were expected to undergo chain exchange rapidly. This should lead to a rapid increase in the pyrene monomer emission intensity at the cost of excimer emission, because chain mixing decreases pyrene concentration in the micellar cores. The kinetic information obtained should help to improve the preparation of polymer brushes and star polymers from PS-*b*-PCEMA micelles.

There have been several dynamic studies of block copolymer micelles. Theoreticians have been mainly concerned with the description of relaxation experiments in which the equilibrium state of a system is slightly shifted by either a temperature jump or a minor solvent composition change.[12,13] Most experiments were, however, performed by introducing profound perturbations to a system, e.g., to induce micelle formation from a micelle-free system or vice versa.[14,15] Recently, fluorescence experiments have been carried out to study micelle chain exchange under equilibrium conditions.[16−18] In such experiments, diblock copolymers, which were otherwise identical except for their different labeling by fluorescence donor and acceptor groups, were used to prepare micelle solutions separately at an equal con-

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Table 1. Characteristics of the PS-*b*-PCEMA and PS-*b*-PCEMA−Py Samples Used

laboratory code	(n/m) by NMR	$\bar{M}_w/\bar{M}_n$ by GPC	$10^{-4}\ \bar{M}_w$ by LS	n	m	m_{Py}
75-43	1.73	1.14	1.90	75	43	1.5
222-42	5.3	1.08	3.4	2.2×10^2	42	2.0
222-42[a]						1.3
302-37	8.2	1.10	4.1	3.0×10^2	37	2.3
270-23	12.0	1.10	3.4	2.7×10^2	23	3.7
264-75	3.5	1.19	4.7	2.6×10^2	75	2.4

[a] Sample used for examining the effect of different labeling densities.

centration. The solutions were then mixed and the exchange of chains between different micelles caused the fluorescence intensity of the donor to decrease and that of the acceptor to increase with time due to increasing energy transfer efficiencies, despite the fact that the donor was excited constantly. Since the micelles, formed from chains labeled with different chromophores, were assumed to be thermodynamically equivalent, these experiments were believed to be performed under micelle equilibrium conditions. The method used here is very similar, except that the monomer intensity increases at the cost of excimer emission, rather than increasing the acceptor fluorescence intensity at the cost of donor intensity, as was the case in prior work.

II. Experimental Section

PS-*b*-PCEMA Samples. Five PS-*b*-PCEMA samples, as shown in Table 1, were used in this study. A polymer is denoted by two numbers separated by a hyphen, *n*-*m*, where *n* and *m* represent the numbers of styrene and CEMA units in a diblock, respectively. The first three diblocks in Table 1 have similar *m* values and the last three have similar *n* values. The synthesis and characterization of these polymers have been described in detail previously[1] and will thus not be repeated here. Shown in Table 1 are the results of sample characterization obtained from NMR, GPC, light scattering, and UV spectrophotometry. All samples used had low polydispersity.

Preparation of 1-Pyrenebutyryl Chloride. This compound was prepared by reacting pyrenebutyric acid (Aldrich, 97%) with $SOCl_2$ in benzene, following a literature method.[19] The product was purified by recrystallization from toluene/hexane (v/v = 1/1).

PS-*b*-PCEMA−Py Samples. To prepare PS-*b*-PCEMA−Py, polystyrene-*block*-poly(2-hydroxylethyl methacrylate), ~5 wt % in pyridine, was reacted with 1-pyrenebutyryl chloride added dropwise as a solution in pyridine (roughly 10 times the amount calculated for a given labeling density) for 10 h. Three molar equivalents of cinnamoyl chloride (Aldrich, 98%) was then added and the mixture was left to react for an additional 10 h. The polymers were purified by precipitation in methanol containing a trace of NaOH to remove the free 1-pyrenebutyryl chloride. The absence of free pyrene in the end product was indicated by GPC analysis using a UV detector at 342 nm. The number of pyrene groups attached to each chain, m_{Py}, as listed in Table 1, was determined by UV absorption analysis of the labeled samples by assuming that the attached pyrene groups had the same molar extinction coefficient, $2.95 \times 10^4\ cm^{-1}\ M^{-1}$, as pyrenebutyric acid (Aldrich, 97%) in THF at 342 nm.

Fluorescence Measurement. All fluorescence measurements were carried out using a Photon Technology International Alpha Scan system equipped with a 75-W xenon lamp. Excitation and emission spectra were reported as they were recorded without correcting for the wavelength-dependent lamp emission and photomultiplier tube response efficiency. For all measurements, the excitation and emission slit widths used were 4.5 and 5.5 nm, respectively. Emission spectra were obtained by exciting at 343 nm.

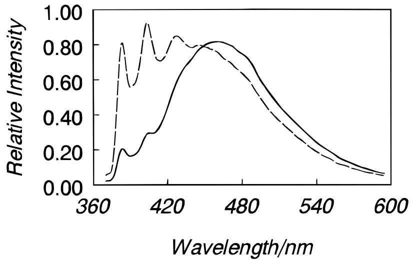


Figure 1. Normalized fluorescence spectra of 270-23-Py (0.10 mg/mL) before (—) and after (···) mixing with an equal volume of 270-23 solution (1.00 mg/mL) in CP.

Room-Temperature Micelle Mixing Kinetics. PS-*b*-PCEMA and PS-*b*-PCEMA−Py micelles, each at 1.00 mL and 1.50 mg/mL in THF/CP unless otherwise specified, were mixed. The pyrene emission intensity was monitored at 398 nm as a function of time.

High-Temperature Micelle Mixing Kinetics. Three small prongs were formed in a glass tube, with inner and outer diameters of 8.5 and 11 mm, approximately 4 cm above the bottom end. The bottom end was then sealed. After tube cleaning, a stirring bar and 1.00 mL of a PS-*b*-PCEMA−Py solution, $c_{Py} = 0.150$ mg/mL, were added. Also added was 1.00 mL of a PS-*b*-PCEMA solution, $c_{Py} = 1.50$ mg/mL, sealed in a thin ampule with an outer diameter of 6.5 mm. The ampule was supported on the three prongs so as not to touch the PS-*b*-PCEMA−Py solution. The PS-*b*-PCEMA−Py solution was frozen, allowing the tube to be sealed under slight vacuum without loss of solvent. Each sealed system was then equilibrated in the temperature-regulated fluorescence cell holder for 30 min at the appropriate temperature. The cell holder has a depth of 8 cm to ensure uniform heating of both the PS-*b*-PCEMA and the PS-*b*-PCEMA−Py micellar solutions. The inner ampule was then broken by shaking, which initiated mixing and started the experiment.

Specific Refractive Index Increment, dn_r/dc. Measurement of the refractive index increment, Δn_r, of a polymer solution in a mixed solvent, relative to the solvent at constant chemical potential, required the dialysis of the solution against the solvent. This was done by first introducing 5.00 mL of a polymer solution into a dialysis tube (Spectra/Por 4). The tube was equilibrated with the appropriate solvent (150 mL) for 48 h. Changes in polymer concentration due to dialysis were monitored by UV spectrophotometry at 274 nm.

The Δn_r values at 488 nm were determined using a differential refractometer (Precision Instruments Company) equipped with a band-pass filter at room temperature. The specific refractive index increment, ν, or dn_r/dc, where n_r and c represent the refractive index and concentration of a polymer solution, respectively, was obtained from the slope of the Δn_r-vs-c plot.

Light Scattering Measurements. Light scattering studies of the micelles were performed on a Brookhaven Model 9025 light scattering instrument equipped with a 150−mW argon ion laser operated at 488 nm. For static light scattering measurements, the micellar concentration used was typically between 0.300 and 5.00 mg/mL and the scattering angles were between 25 and 140°. For dynamic light scattering experiments, solutions of concentrations of ~0.1 mg/mL were used. Dynamic light scattering data were analyzed following the method of cumulants.[20] The densities and viscosities of THF/CP mixtures were determined following our previous method.[21] The viscosities of THF/CP mixtures at $f_{CP} = 100$, 0.96, 0.90, and 0.82 are 0.493, 0.487, 0.480, and 0.466 cP, respectively. The refractive indices at the D-line of sodium, 589.3 nm, were measured by a Fisher refractometer and found to be invariant around 1.414 at the above solvent compositions.

III. Results and Discussion

Micelle Mixing Experiment. Illustrated in Figure 1 is the comparison between the fluorescence spectra of 270-23-Py before and after mixing with an equal

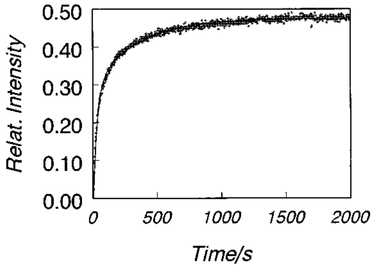
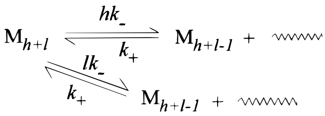


Figure 2. Pyrene monomer fluorescence intensity increase with time after 302-37 and 302-37-Py micelles were mixed at $f_{CP} = 0.90$. The experimental data points were fitted to eq 2 as shown by the solid line. The micellar solutions were each at 1.00 mL and the concentrations of 2.00 and 0.40 mg/mL, respectively.

volume of a 270-23 solution in cyclopentane. Upon establishing chain exchange equilibrium, the pyrene excimer fluorescence intensity at ~475 nm decreased and the structured monomer emission at 382, 398, and 423 nm increased. This was caused by the pyrene concentration decrease inside the micellar cores.

Illustrated in Figure 2 is the increase in pyrene monomer fluorescence intensity with time after mixing 302-37-Py and 302-37 solutions at the CP volume fraction, f_{CP}, of 0.90 at room temperature. If we allow M_{h+l} to denote a micelle containing h PS-*b*-PCEMA−Py chains and l PS-*b*-PCEMA chains and assume that a micelle can increase or decrease in size only by uptaking or rejecting one chain at a time,[12] the general kinetic scheme for such a system is



(1)

where h and l can assume values anywhere between zero and infinity, ∿ represents a PS-*b*-PCEMA chain, ∿Py represents a PS-*b*-PCEMA−Py chain, and k_+ and k_- are rate constants for chain uptake and rejection, respectively. Coefficients h and l are added in front of k_- as the chance for a chain to exit is proportional to the total number of chains of a particular type present. A solution of eq 1 based on some assumptions which are not valid for the current system has been published.[22] Aside from this, eq 1 cannot be solved, in general, to obtain an analytical expression for the pyrene monomer fluorescence intensity, $I(t)$ at time t.

Therefore, in this study, the increase in pyrene monomer fluorescence intensity at time t relative to that at time zero, $I_{Py}(t) - I_{Py}(0)$ or $\Delta I(t)$, has been fitted to the following empirical equation:

$$\Delta I(t) = a_0 - a_1 \exp(-t/\tau_1) - a_2 \exp(-t/\tau_2) \qquad (2)$$

where τ_1 and τ_2 are defined as the two relaxation times of micelles. The average relaxation time

$$\langle \tau \rangle = \frac{a_1\tau_1 + a_2\tau_2}{a_1 + a_2} \qquad (3)$$

should give an indication of how rapidly the micelle chains mix under various experimental conditions. Figure 2 shows the best fit of the $\Delta I(t)$ data by eq 2. In all cases, eq 2 fitted the experimental data well, yielding correlation coefficients very close to 1.000.

The Aniansson and Wall theory[12] describing micelle relaxation also yields two micellar relaxation times.

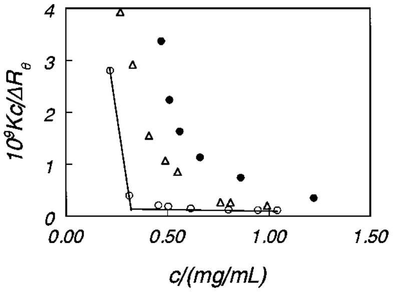


Figure 3. At a scattering angle of 90°, $Kc/\Delta R_\theta$ are plotted as a function of polymer concentration for 75-43 ($f_{CP} = 0.82$, ●), 222-42 ($f_{CP} = 0.82$, Δ), and 302-37 ($f_{CP} = 0.76$, ○).

Table 2. Critical Micellar Concentrations of the Diblocks in mg/mL at Different f_{CP}'s

polymer	$f_{CP} = 0.96$	$f_{CP} = 0.90$	$f_{CP} = 0.82$
75-43		<0.03	0.58
222-42		0.044	0.47
302-37		0.041	0.21
270-23	0.10	1.00	
264-75		0.060	

Since the present experiment is different from theirs and also the pyrene monomer emission intensity is nontrivially related to the mass change of a given species, the τ_1 and τ_2 values here are different from those described by Aniansson and Wall.

Critical Micelle Concentrations. The current study was aimed at obtaining a qualitative understanding of how various factors affect micellar chain exchange kinetics. Even so, experiments should be carried out under conditions as identical as possible. This required that all solutions were above their critical micelle concentrations (cmc's) so that all experiments involved the mixing of micellar solutions.

Light scattering was used to establish the cmc for the diblocks in different THF/CP mixtures. As the concentration, c, of a diblock increased (Figure 3), $Kc/\Delta R_\theta$ decreased initially very rapidly, where K is the optical constant of our light scattering system and ΔR_θ is the Rayleigh ratio. Above the cmc, $Kc/\Delta R_\theta$ decreased more slowly. The cmc value was defined as the concentration at the intersection between the two $Kc/\Delta R_\theta$-vs-c lines at low and high concentrations. Illustrated in Figure 3 are the $Kc/\Delta R_\theta$-vs-c data for three samples in different solvent mixtures. The cmc values for other diblocks and in other solvents are summarized in Table 2. The general trend is that the cmc decreases sharply with increasing f_{CP}.

The method used here for the cmc determination may yield values greater than the true values. As far as the micelle mixing kinetic experiments are concerned, this overestimation should not matter, because the use of the polymer solutions with concentrations above these overestimated cmc's guarantees that micellar solutions are mixed. For a more accurate determination of the cmc's from light scattering experiments, a method developed by Khougaz et al. could have been used.[23]

Effect of Solvent Composition Change. Illustrated in Table 3 are the relaxation times of 302-37 and 264-75 micelles in different CP/THF mixtures. The general trend is that the micelle chain exchange rate increased as the THF content increased. This is reasonable, since THF swells and plasticizes the PCEMA core. This is also in agreement with the previous observation that some PS-*b*-PCEMA micelles became so stable at high f_{CP} values that they did not disintegrate to form polymer brushes.[6]

Table 3. Effect of Solvent Composition Change on Micelle Chain Exchange Kinetics[a]

f_{CP}	$10^{-2}\tau_1$/s	$10^{-2}\tau_2$/s	$10^{-2}\langle\tau\rangle$/s	dn_r/dc (mL/g)	f	R_G/nm	R_h/nm
			302-37				
1.00	3.64	16.5	10.9	0.1913	84	35	41
0.96	0.31	4.3	1.94	0.1886	57	25.5	36
0.90	0.268	1.02	0.50	0.1883	40	20.2	31
0.82	0.071	0.30	0.270	0.1880	40	20.3	31
0.76	0.071	0.32	0.285				
			264-75				
0.96	3.1	3.1	3.1				
0.90	0.94	1.33	1.37				
0.82	0.58	4.8	1.05				
0.76	0.56	1.27	0.72				

[a] The micelle concentration used was 1.50 mg/mL for both PS-*b*-PCEMA and PS-*b*-PCEMA−Py.

Table 4. Micelle Chain Exchange Kinetic Data of 302-37 at Different Temperatures[a]

T/°C	$10^{-2}\tau_1$/s	$10^{-2}\tau_2$/s	$10^{-2}\langle\tau\rangle$/s	R_h/nm
		$f_{CP} = 1.00$		
22	4.1	15.9	10.4	41
30	3.4	10.1	7.9	37
40	1.15	7.6	5.5	35
45	0.18	6.8	4.2	33
50	0.10	3.2	2.7	
		$f_{CP} = 0.96$		
22	0.33	1.95	0.93	
30	0.124	1.38	1.03	
40	0.155	0.96	0.65	
45	0.066	0.70	0.47	
50	0.176	0.40	0.30	

[a] The concentrations of 302-37 and 302-27-Py were 1.50 and 1.150 mg/mL, respectively.

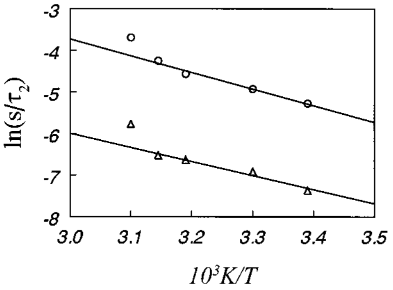


Figure 4. Plot of $\ln(s/\tau_2)$-vs-K/T, where s and K denote second and Kelvin, for 302-37 at $f_{CP} = 1.00$ (Δ) and $f_{CP} = 0.96$ (○), respectively.

Table 5. Effect of Varying 302-37 and 302-37-Py Concentrations, c_M and c_{Py}, at $f_{CP} = 0.90$ on Micelle Chain Exchange Kinetics

c_M/(mg/mL)	c_{Py}/(mg/mL)	c_{Py}/c_M	$10^{-2}\tau_1$/s	$10^{-2}\tau_2$/s	$10^{-2}\langle\tau\rangle$/s
2.00	0.050	0.025	0.188	1.48	0.79
2.00	0.100	0.050	0.36	1.34	0.73
2.00	0.200	0.100	0.089	0.93	0.48
2.00	0.400	0.200	0.082	0.80	0.43
0.50	0.100	0.200	0.082	0.73	0.39
1.00	0.100	0.100	0.091	0.81	0.46
4.00	0.100	0.025	0.129	1.32	0.69
1.50	0.461	0.307	0.061	0.71	0.36
1.50	0.75	0.50	0.056	0.62	0.20
1.50	1.07	0.72	0.075	1.05	0.36
1.50	1.50	1.00	0.27	1.02	0.50

The only exception to the rule is the data for 302-37 at $f_{CP} = 0.76$. A close examination of Table 3 shows that $\tau_1 = 7.1$ s in this case. It is thus possible that the initial rapid increase in pyrene monomer fluorescence intensity with time was not captured and that the a_1 term observed was smaller than the true value.

The scattering results of 302-37 micelles clearly indicate that the change in the micelle chain mixing rate was not caused by a drastic change in micellar size or aggregation number. In fact, the micelle size did not change at all with a f_{CP} increase from 0.82 to 0.90, while the relaxation rate slowed down by a factor of 2.

Since our previous transmission electron microscopic (TEM) studies have demonstrated that no cylindrical micelles were present for $f_{CP} < 0.97$ for 302-37,[2] the increase in the f number at $f_{CP} = 0.96$ was caused by an increase in the size of the spherical micelles. At $f_{CP} = 1.00$, the R_h/R_G value decreased sharply. This is in agreement with our previous TEM observation which showed that some short cylindrical micelles formed in pure CP.

Effect of Temperature Change. Table 4 clearly shows that the chain exchange rate increased for 302-37 micelles as temperature increased at both $f_{CP} = 1.00$ and $f_{CP} = 0.96$. An increase in polymer chain mobility with temperature is expected.

We also determined the hydrodynamic radii, R_h, of 302-37 micelles at $f_{CP} = 1.00$ at different temperatures, and the results are shown in Table 4. Since these R_h values were obtained without correcting for the CP viscosity decrease with increasing temperature, the R_h values at higher temperatures should be lower than the true values. It is, therefore, likely that R_h changed little with temperature. Thus, a micellar structure change with temperature was not the major cause for the increased micelle chain mixing rate.

While the variation in τ_2 values exhibited a clear trend, some irregularity was found for the τ_1 values. This again is attributed to the experimental difficulties associated with capturing the rapidly rising monomer fluorescence intensity term. For this, we did not treat the τ_1 data for the activation energy of this process. Illustrated in Figure 4 are the $\ln(s/\tau_2)$-vs-K/T data at the two f_{CP} values, where s and K denote seconds and Kelvin, respectively. Excluding the points at 50 °C, the data at the other temperatures were fitted to the Arrhenius equation to yield the activation energies, E_a, of 28 and 33 kJ/mol for $f_{CP} = 1.00$ and $f_{CP} = 0.96$, respectively. The reason for the deviation of the data at 50 °C from the Arrhenius plot is not known. It may be related to the fact that CP boils at this temperature.

The E_a values at the two solvent compositions may be the same within experimental error. If a trend had to be assigned, this surprising increase in E_a with the addition of the better solvent for PCEMA would be in agreement with the trend observed by Wang et al.[17] for another system.

Effect of Polymer Concentration Change. Different diblock copolymers have different labeling densities. Micelle mixing kinetics of different polymers can be performed at different polymer concentrations. To compare the mixing kinetics of micelles of different diblocks, the effect of varying chain labeling density and polymer concentration needed to be examined. Table 5 shows the effect of varying the 302-37 and 302-37-Py concentrations, c_M and c_{Py}, on the τ_1 and τ_2 values.

Increasing c_M increased the relaxation times, opposite to the effect of increasing c_{Py}. Also shown in Table 5 and Figure 5 is the variation in these relaxation times as a function of c_{Py}/c_M or α. At the same α value, τ_2 and $\langle\tau\rangle$ values measured at different c_M and c_{Py} matched closely. The τ_1 values are not considered here again because of the larger experimental errors involved in their determination. Thus, a reasonable assumption is

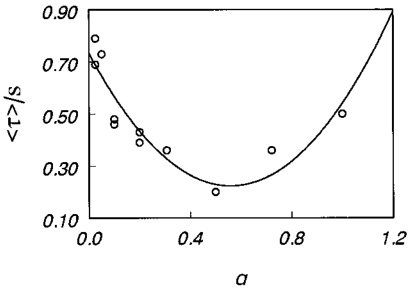


Figure 5. Effect of varying α, c_{Py}/c_M, on the relaxation time $\langle\tau\rangle$ of 302-37 micelles at f_{CP} = 0.90.

Table 6. Effect of Varying PS and PCEMA Lengths on Micelle Chain Exchange Kinetics, Where Both PS-*b*-PCEMA and PS-*b*-PCEMA−Py Micelles Were at 1.50 mg/mL Unless Otherwise Labeled

sample	$10^{-2}\tau_1$/s	$10^{-2}\tau_2$/s	$10^{-2}\langle\tau\rangle$/s	*f*	R_G/nm	R_h/nm
			f_{CP} = 0.90			
75-43[a]	1.22	15.9	11.6			
222-42	0.52	5.9	2.68	63	20.0	37.5
302-37	0.121	1.50	0.52	40	20.2	30.8
270-23	1.25	26.6	20.6	44	23.7	24.7
264-75	0.94	1.33	1.37	87	27.8	41.4
270-23[b]	0.49	20.8	17.6			
			f_{CP} = 0.96			
302-37	0.31	4.3	1.94			
270-23	0.024	1.45	0.326			
264-75	3.1	3.1	3.1			

[a] Sample solubility too low for *f* determination. [b] PS-*b*-PCEMA and PS-*b*-PCEMA−Py micelles were at 5.00 mg/mL.

that the rate of micelle mixing is largely determined by α and not by the absolute c_M and c_{Py} values.

This observation may seem strange initially, because it is intuitively expected that the rate of chain exchange would increase with the number of micelles present. This may be true of the total chain mixing rate in terms of chains exchanged per unit time in the whole system. Pyrene fluorescence intensity is only sensitive to the pyrene concentration change in each micelle or to the number of chains exchanged per unit time in each micelle. This "relative" chain exchange rate may not depend on how many micelles are present.

The average relaxation time $\langle\tau\rangle$ has a complex dependence on α, as shown in Figure 5. This dependence is difficult to explain without solving eq 1. In this study, the same α value of 1.00 was used to compare the mixing kinetics of micelles formed from different diblocks.

Effect of Varying Pyrene Labeling Densities. Labeling the PCEMA block with pyrene may affect the structure of the micelles formed. As in most fluorescence studies, we assume that this structural perturbation is negligibly small due to the small number of pyrene groups present in each chain. A change in the labeling density also affects the degree of excimer formation and may thus change the micelle relaxation times determined from the current fluorescence experiment.

We compared the kinetics of mixing micelles of 222-42-Py, labeled at the densities of 1.3 and 2.0 pyrene groups per chain, with 222-42 micelles. At f_{CP} = 0.90, the average mixing times for the two systems were 258 and 268 s, respectively. This suggests that that varying the pyrene labeling densities, in the range used in this study, has an insignificant effect on the observed micelle mixing rate.

Effect of PCEMA Length Variation. At an approximately equal PS length for 302-37, 270-23, and 264-75, the results of Table 6 at f_{CP} = 0.96 clearly indicate that the micelle chain exchange rate decreases as the PCEMA length increases. This trend is also obeyed by 302-37 and 264-75 at f_{CP} = 0.90. The decrease in the micelle mixing rate with increased PCEMA length is expected. As the PCEMA block becomes longer, it requires longer times for it to reptate into or out of a micellar core.

The micelle mixing time of 270-23 at f_{CP} = 0.90 was, however, abnormally long. Suspecting that the high cmc of 270-23 at f_{CP} = 0.90 was the cause of this, we attempted the micelle mixing experiment at the 270-23 and 270-23-Py concentration of 5.00 mg/mL. A long mixing time was also obtained. The most likely cause for the abnormally long micelle mixing time of 270-23 at f_{CP} = 0.90 is our failure to capture the fast rising pyrene monomer intensity increase term. At f_{CP} = 0.96, τ_1, was already 2.4 s. This time should be considerably shorter than 2.4 s at f_{CP} = 0.90 instead of the observed 125 s.

Effect of PS Length Variation. Samples 75-43, 222-42, and 302-37 have similar PCEMA lengths and different PS lengths. The results in Table 6 show that the chain exchange rate increases with PS chain length. This trend is counterintuitive, because one would expect chain rejection or incorporation to become more difficult as the corona becomes thicker. One possible explanation is that as the corona block becomes longer, the repulsion between neighboring PS chains increases. This repulsion can be partially offset by the expansion of the PCEMA core due to an increased uptake of THF. The higher fraction of THF in the core will then increase the PCEMA rejection and incorporation rate.

IV. Conclusions

The chain exchange kinetics of PS-*b*-PCEMA micelles was studied as a function of various parameters in THF/CP. As f_{CP} decreased or the temperature increased, the chain exchange rate increased. The chain exchange rate, determined from this method, seems to be affected only by the relative concentrations of the PS-*b*-PCEMA and PS-*b*-PCEMA−Py samples and not by their absolute concentrations. At a fixed PS length, increasing the PCEMA length increased chain exchange rate, while the effect of increasing the PS length at a fixed PCEMA length was found to decrease the exchange rate.

These results clearly suggest that one should use a solvent mixture with a sufficiently high content of the block-selective solvent, CP in this case, to lock in star micelles to prepare star polymers. For polymer brush formation, f_{CP} should be low enough to allow micelle disintegration.

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