1144 *Macromolecules* **2006,** *39,* 1144−1155

Associations between a Pyrene-Labeled Hydrophobically Modified Alkali Swellable Emulsion Copolymer and Sodium Dodecyl Sulfate Probed by Fluorescence, Surface Tension, and Viscometry

Howard Siu and Jean Duhamel*

Institute for Polymer Research, Department of Chemistry, University of Waterloo,
Waterloo, Ontario N2L 3G1, Canada

Received September 7, 2005; Revised Manuscript Received November 16, 2005

ABSTRACT: A hydrophobically modified alkali swellable emulsion copolymer labeled with pyrene (Py-HASE) was studied by fluorescence, surface tensiometry, and viscometry at concentrations ranging from 0.01 g/L (lower than the overlap concentration, $C^* = 2.4$ g/L) to 10 g/L (above C^*) in the presence of the anionic surfactant sodium dodecyl sulfate (SDS). The results obtained by the three techniques lead to the conclusion that binding of SDS onto Py-HASE proceeds in four different stages which are separated by three SDS transition concentrations. The values of the SDS transition concentrations are little affected by the Py-HASE concentration at low Py-HASE concentration but are shifted to higher SDS concentrations at high Py-HASE concentration. The average number of pyrenes per mixed micelle could be determined from the analysis of the fluorescence decays which established a maximum average capacity of pyrenes per mixed micelle of 2.4 ± 0.5 independent of the polymer concentration. For a Py-HASE concentration of 6.0 g/L, the average number of pyrenes per mixed micelle was found to take the optimal value of 2.0 at the SDS concentration where the solution viscosity peaked. This study constitutes the first example where fluorescence experiments are being used to rationalize the spike in viscosity exhibited by an associative thickener solution upon addition of a surfactant.

Introduction

Hydrophobically modified alkali swellable emulsion copolymers (HASEs) are a major type of associative polymers with numerous industrial applications[1−3] such as in paint formulations,[4] paper coatings,[5] and more recently as glycol-based aircraft anti-icing fluids.[6−8] HASEs are typically terpolymers made of mainly methacrylic acid and ethyl acrylate in roughly equal proportions with a small percentage of a hydrophobically modified macromonomer (HMM).[9] The HMM, usually an α-methylstyrene connected via a urethane linker to a poly(ethylene oxide) (PEO) chain end-capped with a hydrophobic moiety, causes the aggregation of HASEs in aqueous solution. The hydrophobic moieties of HASEs associate in alkaline aqueous media to form transient/reversible clusters[1] which, at concentrations greater than the overlap concentration, form polymeric networks that greatly increase the solution viscosity.[10,11] Because of the nature of the weak intermolecular forces holding the hydrophobic clusters together, the clusters can be disrupted by applying a shearing force, which alters the network and results in a drastic decrease in the viscosity of the solution. This effect, called shear thinning, is one reason for the commercial success of HASEs as viscosity modifiers used in paints, coatings, and aircraft anti-icing fluids.[1−8]

Since the rheological properties of HASEs are tied to the existence of hydrophobic aggregates, some efforts have been spent on understanding their microstructure. The Winnik group in Toronto used fluorescence to characterize the hydrophobic aggregates of a HASE copolymer with a HMM made of 32 ethylene oxide units and a $C_{20}H_{41}$ alkyl hydrophobe.[12] Their experimental results could be rationalized by assuming the presence of several types of hydrophobic domains. Some domains contained 60−80 $C_{20}H_{41}$ hydrophobes whereas others were mixed structures containing both $C_{20}H_{41}$ hydrophobes and ethyl acrylate monomers. Optimization of the HASE solution properties for commercial applications requires that the many factors that influence the rheological properties of the HASE solutions be characterized. This was done in a number of studies where the effect of the methacrylic acid content in the backbone,[3] the number of carbons in the alkyl hydrophobe,[13−17] the level of ethoxylation of the HMM,[13,18] the pH,[18,19] and the addition of salts[15,16] on the HASE solution properties were investigated.

Because the interesting rheological properties of HASE solutions arise essentially from the associations taking place between their hydrophobes, the effect that water-soluble molecules such as anionic[17,20,21] and neutral[21,22] surfactants and cyclodextrins[23] have on the properties of HASE solutions when they interact with the hydrophobes of HASEs has also been reported. These interactions have been monitored by calorimetry,[17,20,21] rheology,[21,22] and light scattering.[23] Such techniques provide information on how the hydrophobically modified water-soluble polymer (HMWSP) responds in solution to the addition of a surface active molecule. However, it is clear that for such studies techniques that report directly on the behavior of the hydrophobe interacting with a surfactant would be much more informative. With this in mind, we initiated a series of studies where the hydrophobe of a HASE copolymer was replaced by the hydrophobic chromophore pyrene (Figure 1a) to yield Py-HASE.[11,24−27] To demonstrate that switching the alkyl chains typically used as hydrophobes for HASEs to pyrene would yield a HASE copolymer whose properties would mimic those of nonfluorescent HASEs, we recently established that the hydrophobic pyrene confers to Py-HASE a rheological behavior which is very similar to that of nonfluorescent HASEs.[11]

Pyrene was chosen as the hydrophobe because it responds to its local environment in two ways. First, the fluorescence spectrum of the pyrene monomer is sensitive to the polarity of

---

* To whom correspondence should be addressed.

10.1021/ma0519563 CCC: $33.50

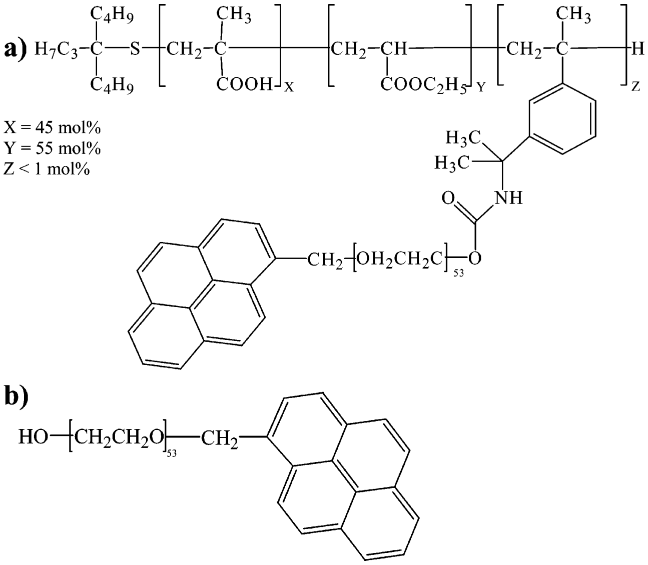


Figure 1. Chemical structure of (a) Py-HASE and (b) Py-PEO surfactant.

its local environment,[28,29] although this effect is weaker for a pyrene pendant attached to a polymer than for a free pyrene molecule.[30,31] Second, after absorption of a photon, an excited monomer can encounter a ground-state pyrene to form an excimer.[32] The high pyrene concentration found in the pyrene aggregates formed by Py-HASEs in aqueous solutions facilitates excimer formation on a rapid time scale. Time-resolved fluorescence experiments performed on the pyrene monomer and excimer can distinguish between those excimers which are formed quickly inside a pyrene aggregate and those which are formed slowly by diffusion. This information can be used to determine quantitatively the fraction of pyrene pendants of Py-HASEs which are aggregated, f_{agg}.[11,24−27] In the present study, we have monitored f_{agg} for different Py-HASE concentrations as increasing amounts of sodium dodecyl sulfate (SDS) are added to the solution. Combining these results with those obtained by surface tensiometry and viscometry lead to a scheme where the binding of SDS onto Py-HASE occurs in four well-defined stages.

Experimental Section

Chemicals. The pyrene-labeled HASE (Py-HASE) was synthesized at the Dow Chemical Corp. (previously UCAR Emulsions Systems) and had a pyrene content of 36 μmol of pyrene per gram of polymer determined by UV-vis adsorption spectroscopy. The chemical composition of Py-HASE is given in Figure 1a. Information about the molecular weight of HASE copolymers is difficult to obtain. It has been determined only once by researchers at DOW who performed static light scattering experiments on HASE solutions where the hydrophobes of the HASE copolymers were capped with cyclodextrin.[23] They found molecular weights in the range of $(1-2) \times 10^5$ g/mol. Since Py-HASE was prepared following the same protocol established at DOW for nonfluorescent HASEs, it is assumed that the molecular weight of Py-HASE lies in the same $\sim(1-2) \times 10^5$ g/mol range.

The macromonomer of Py-HASE was prepared from the anionic polymerization of ethylene oxide initiated with the 1-pyrenemethoxide anion.[33] This poly(ethylene oxide) molecule terminated at one end with pyrene is referred to as Py-PEO (Figure 1b). All Py-HASE and Py-PEO samples were studied in a 0.01 M Na_2CO_3, pH 9 solution.

Hexanes (HPLC grade, EMD), tetrahydrofuran (HPLC grade, EMD), NaOH (BDH), HCl (ACS Reagent, Fisher Scientific), sodium carbonate (Na_2CO_3, EMD), and sodium dodecyl sulfate (SDS, EM Science) were used as received. 3,4-Dimethylbenzophenone (Aldrich, >99%) was recrystallized twice in ethanol. Milli-Q water with a resistivity of over 18 MΩ·cm was used to make all aqueous solutions. Spectra/Por membranes having a cutoff value of 3500 g/mol were used for dialysis.

Sample Preparation. Py-HASE was obtained as a latex dispersion in an aqueous solution. Before performing fluorescence measurements, Py-HASE needed to be purified from all small molecule impurities, especially unreacted pyrene. The water was removed under vacuum, and the recovered solid was dissolved in THF. The polymer was precipitated using hexanes as the nonsolvent. The supernatant was decanted, and the precipitate was then redissolved in THF. The precipitation procedure was repeated two more times to ensure that the Py-HASE was freed of most small molecule impurities. After purification, the THF was removed under vacuum and the Py-HASE was dissolved in a 0.01 M Na_2CO_3, pH 9 solution. Small amounts of 1 M NaOH and HCl were added to adjust the pH to 9. Once the polymer solution was adjusted to pH 9, the solution was then dialyzed for over a week against the 0.01 M Na_2CO_3, pH 9 solution in order to remove any residual THF. Care was taken throughout the preparation of the Py-HASE sample to never completely dry the polymer as cross-linking between methacrylic acid monomers may occur.[34]

Py-PEO was purified by precipitation with hexanes. The Py-PEO sample was dried, and solutions were prepared by dissolving the required masses of purified Py-PEO into the 0.01 M Na_2CO_3, pH 9 solution.

UV−vis Absorption. UV−vis absorption spectra were obtained with a Hewlett-Packard 8452A diode array spectrophotometer using a spectrophotometer cell with a 1 cm path length.

Steady-State Fluorescence. The steady-state emission spectra were obtained using a Photon Technology International LS-100 steady-state fluorometer with a pulsed xenon flash lamp, except those acquired for the 2.5 and 6.0 g/L Py-HASE solutions for which the fluorometer was fitted with a Ushio UXL-75Xe xenon arc lamp and a PTI 814 photomultiplier detection system resulting in a much improved detection. Since the wavelength response of the two detectors differs, only the relative trends of the results of the 2.5 and 6.0 g/L Py-HASE solutions obtained by fluorescence were considered and not the absolute values. For Py-HASE concentrations above 1 g/L, fluorescence measurements were performed with a front face geometry using a Hellma triangular cell in order to avoid the inner filter effect during fluorescence measurements.[35] For all other Py-HASE concentrations, the emission spectra were acquired using a right angle geometry. The steady-state fluorescence spectra of Py-PEO were acquired with the usual right angle geometry using a fluorescence microcell (Hellma) with an inner cross section of 3×3 mm^2. All fluorescence measurements were performed with aerated solutions since attempts at degassing the solutions by bubbling nitrogen led to excessive foam and bubble formation. The emission spectra were acquired by exciting the sample at 344 nm. The I_E/I_M ratios were determined by integrating the fluorescence intensity from 372 to 378 nm for the pyrene monomer, I_M, and from 500 to 530 nm for the pyrene excimer, I_E. To determine the I_1/I_3 ratios which describe the polarity of the medium surrounding pyrene, the intensity of the first, I_1, and third, I_3, peaks of the pyrene monomer was taken at 374 and 385 nm, respectively.

Time-Resolved Fluorescence. The fluorescence decay profiles were obtained by a time-correlated single photon counter manufactured by IBH Ltd. using a 5000F coaxial nanosecond flash lamp filled with H_2 gas. All solutions were excited at 344 nm. The emission wavelength was set at 374 and 510 nm for the pyrene monomer and excimer decays, respectively. To reduce potential stray scattered light, cutoff filters at 370 and 495 nm were used to acquire the monomer and excimer decays, respectively. For Py-HASE samples with concentrations larger than 1 g/L, the front face geometry was used to acquire the fluorescence decays. For all other Py-HASE concentrations, the decays were acquired with the right angle geometry. All fluorescence decays were acquired on aerated samples. All decays were collected over 1024 channels with a minimum of 40 000 and 15 000 counts taken at the maximum of the monomer and excimer decays, respectively, to ensure a high signal-to-noise ratio. Deoxygenated solutions of PPO [2,5-diphenyloxazole] in cyclohexane ($\tau = 1.42$ ns) and BBOT [2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene] in ethanol ($\tau = 1.47$ ns) were used as references for the monomer and excimer decays, respectively. The decays of the reference compounds were used to determine the true instrument response function of the IBH fluorometer by using the MIMIC method.[36] All measured decays were deconvoluted from the lamp profile and fitted to the desired function using a least-squares analysis. The monomer and excimer fluorescence decays were fitted either separately with sums of exponentials or globally using the fluorescence blob model (FBM).[25,26] The equations used to fit the fluorescence decays have been described in detail.[25,26] They are also given in the Supporting Information (SI). The resulting fits were described as “good” when the χ^2 was smaller than 1.3, and the residuals and the autocorrelation function of the residuals were randomly distributed around zero.

Surface Tension. All surface tension measurements were done with a DuNuoy ring tensiometer manufactured by Central Scientific Co., Inc. The platinum−iridium ring used in these measurements had a ring radius to wire radius ratio of 53.4. The measurements were corrected using a correction factor obtained from a chart supplied by the manufacturer. The procedure used to carry out the surface tension measurements has been reported in an earlier publication.[33]

Viscosity. The viscosity of the Py-HASE aqueous solutions was measured with an Ubbelohde viscometer at 25 ± 0.1 °C.

Aggregation Number of SDS Micelles. The aggregation number of SDS micelles in the 0.01 M Na_2CO_3, pH 9 solution was determined from the quenching studies of pyrene by 3,4-dimethylbenzophenone in SDS micelles following the micellar quenching model outlined by Turro and Yekta.[37]

Results

The behavior of the Py-HASE solutions was monitored as a function of increasing SDS concentrations at Py-HASE concentrations of 0.01, 0.1, 1.0, 2.5, 6.0, and 10 g/L. The overlap concentration, C^*, of Py-HASE was determined to equal 2.4 g/L in a 0.01 M Na_2CO_3, pH 9 solution by taking the inverse of the intrinsic viscosity.[38] This value is reasonable since C^* was found to equal 3.3 g/L in a 0.01 M Na_2CO_3, pH 9 solution containing 0.05 M KCl. The presence of additional salt screens the charges on the polyelectrolyte Py-HASE backbone, resulting in a shrinking of the polymer coil which leads to a larger C^* value. The C^* value of 2.4 g/L indicates that the trends obtained with Py-HASE concentrations of 2.5, 6.0, and 10 g/L reflect the behavior of the polymer in the semidilute regime.

Upon addition of SDS to a 10 g/L Py-HASE solution, the fluorescence spectrum of the solution is strongly altered, as shown in Figure 2. For SDS concentrations ranging from 0 to 8.0 mM, Figure 2a demonstrates that the decrease in monomer fluorescence intensity is mirrored by a concomitant increase in excimer intensity when SDS is added to the solution. For SDS concentrations larger than 8.5 mM, the trend reverses and the monomer intensity increases at the expense of the excimer intensity. Similar trends were observed at all Py-HASE concentrations studied in the present work. These results can be summarized by plotting the I_E/I_M ratio for each Py-HASE concentration as a function of SDS concentration.

The I_E/I_M ratio gives information about the relative amount of pyrene excimer being produced. For all Py-HASE concentrations, the general behavior of I_E/I_M as a function of SDS concentration is similar, as shown in Figure 3. With little to no SDS, I_E/I_M takes a low value that remains constant with SDS concentration. Since the pyrene pendants of Py-HASE are known to be mostly aggregated in aqueous solution,[11,24−27] this result indicates that the initial addition of SDS does not affect the pyrene aggregates. The low I_E/I_M values obtained in this range of SDS concentrations is due to the low quantum yield of fluorescence of the pyrene aggregates.[27] Past a critical onset SDS concentration, I_E/I_M increases sharply, showing that beyond this onset concentration the surfactant begins to interact with the pyrene aggregates forming mixed micelles where the pyrene pendants form excimer by diffusion with a higher fluorescence quantum yield.[27] At a critical SDS concentration I_E/I_M peaks, and further addition of SDS prompts I_E/I_M to drop. This drop is due to the compartmentalization of the pyrene pendants into a large number of mixed micelles which prevents encounters between pyrenes located in different mixed micelles.

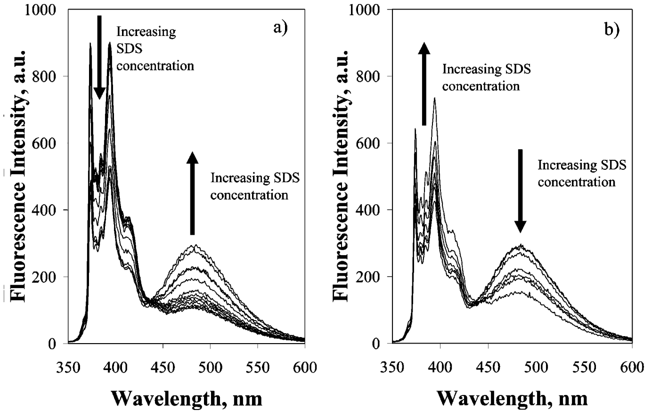


Figure 2. Fluorescence emission spectra of a 10 g/L Py-HASE in 0.01 M Na_2CO_3, pH 9 solution with SDS concentrations ranging from 0 to 8 mM (a) and from 9 to 50 mM (b). All samples were excited at 344 nm.

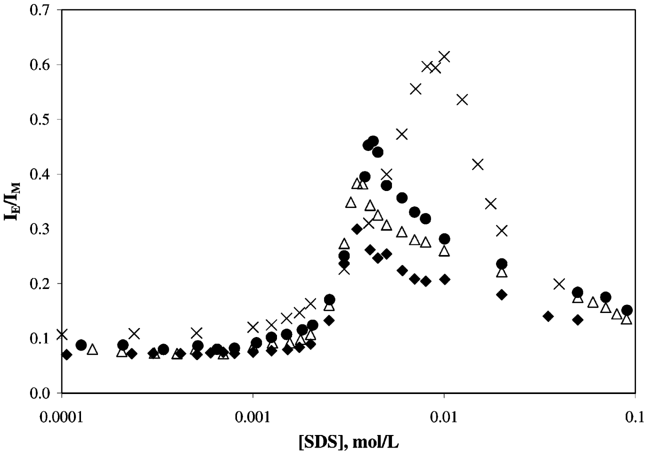


Figure 3. Plot of I_EI_M vs SDS concentration for Py-HASE at 0.01 (◆), 0.1 (△), 1 (●), and 10 (×) g/L in 0.01 M Na_2CO_3 solution at pH 9, $\lambda_{ex} = 344$ nm.

Figure 4 shows the fluorescence spectra of a 6.4 mg/L solution (equivalent to a 2.5×10^{-6} mol/L concentration of pyrene) of a poly(ethylene oxide) (PEO) chain made of 53 ethylene oxide monomers and terminated at one end with a 1-pyrenyl unit (Py-PEO, see Figure 1b).[33] The spectra shown in Figure 4 have several features which are worth pointing out. When no SDS is present in solution, the fluorescence spectrum of Py-PEO shown in Figure 4a exhibits no excimer emission. At an SDS concentration of 4.2 mM, the fluorescence spectrum presented in Figure 4b indicates that the monomer intensity has decreased and the characteristic broad and structureless emission of the pyrene excimer has appeared. At larger SDS concentrations, the fluorescence intensity of the pyrene monomer increases whereas no excimer can be found in the fluorescence spectrum shown in Figure 4c. Another interesting aspect of the fluores-

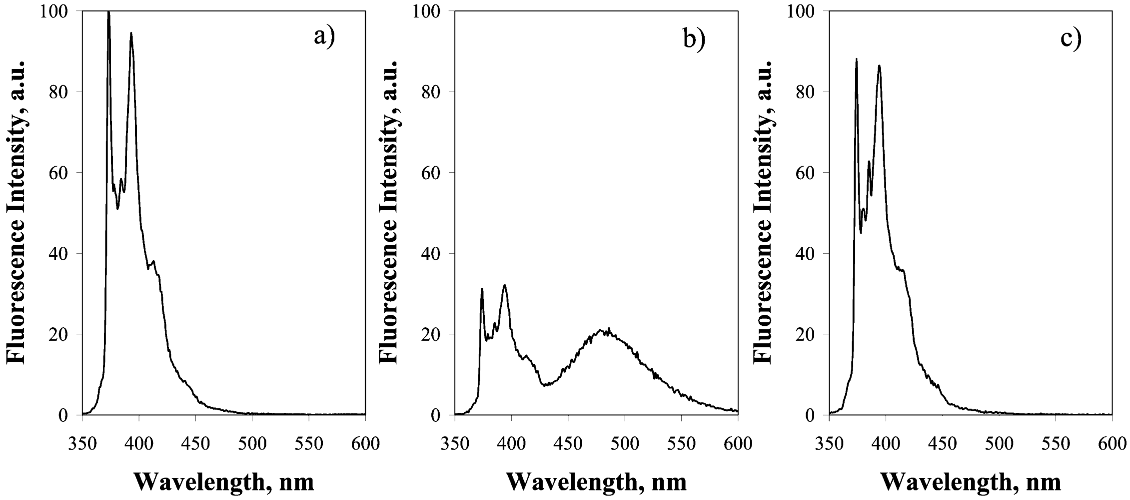


Figure 4. Fluorescence emission spectra of 0.006 g/L Py-PEO in 0.01 M Na_2CO_3, pH 9 solution with 0 (a), 4.2 (b), and 8 mM (c) SDS. All three samples were excited at a wavelength of 344 nm.

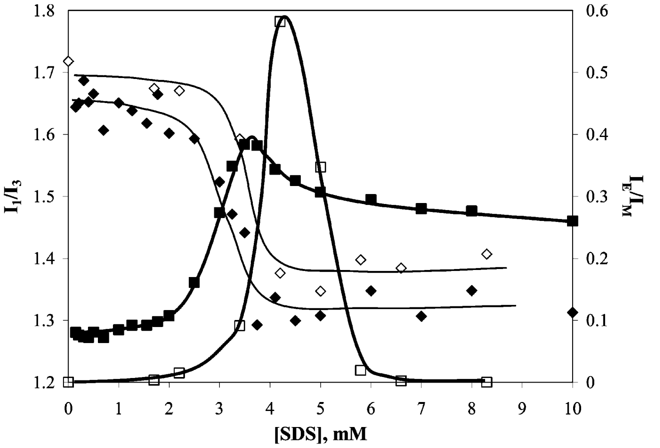


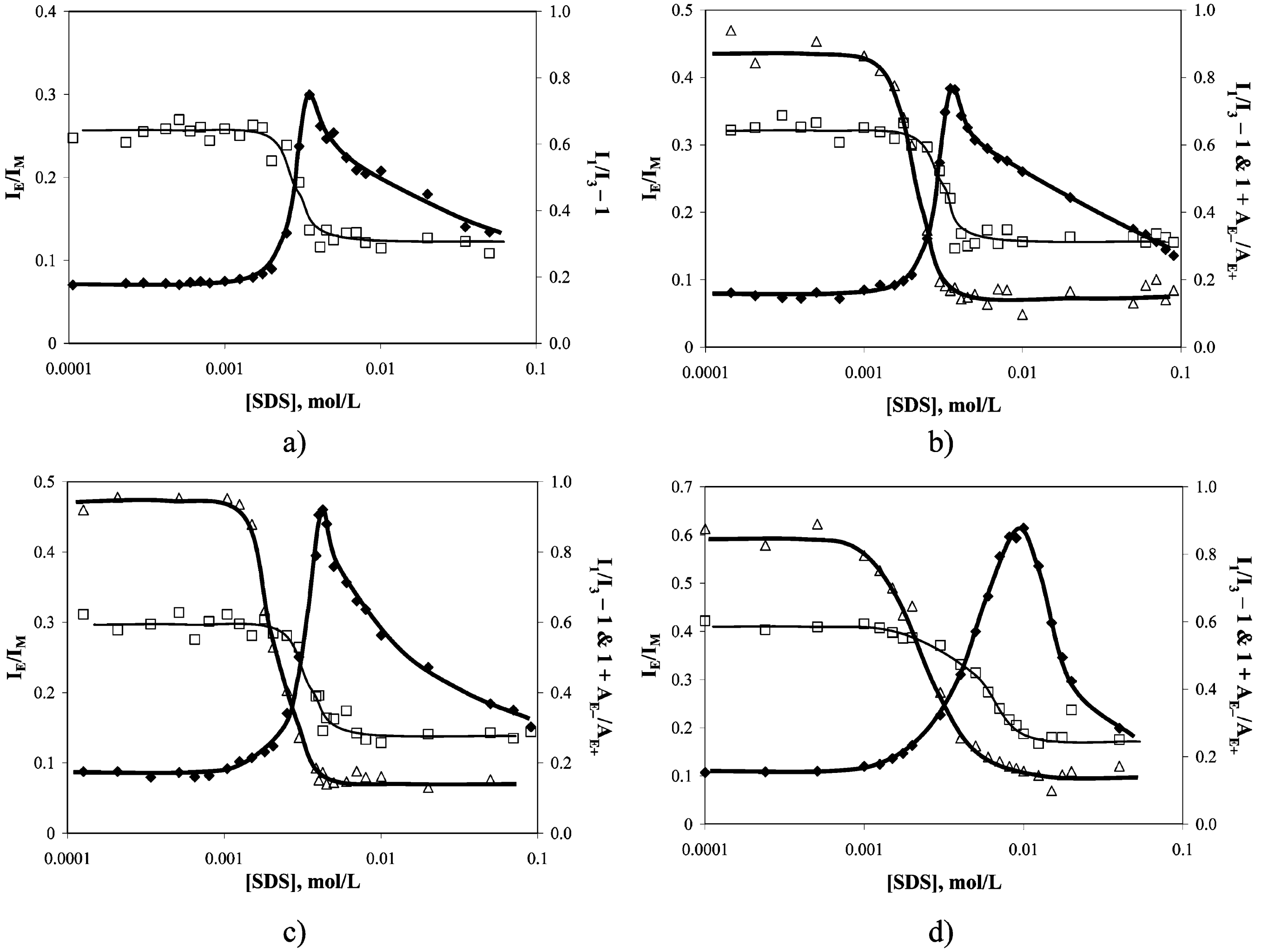
Figure 5. I_1/I_3 (◇ and ◆) and I_E/I_M (☐ and ■) obtained by steady-state fluorescence of 0.006 g/L Py-PEO corresponding to a [Py] of 2.4 × 10^{-6} mol/L (hollow) and 0.1 g/L Py-HASE corresponding to a [Py] of 3.6 × 10^{-6} mol/L (filled) in a 0.01 M Na_2CO_3 aqueous solution kept at pH 9 as a function of SDS concentration.

cence spectra presented in Figure 4 revolves around the relative intensities of the first, I_1, and third, I_3, peaks of the pyrene monomer emission. The relative intensity of the third peak with respect to the first one is larger for SDS concentrations equal to 4.2 and 8.0 mM. Since the I_1/I_3 ratio of the pyrene monomer is known to respond to the polarity of the local environment of the probe, these changes in the I_1/I_3 ratio suggest that the 1-pyrenyl pendants interact with the amphiphilic SDS molecules at high SDS concentrations.

Figure 5 compares the behavior of Py-HASE with that of Py-PEO. The concentrations of pyrene pendants in both samples are similar, being 2.5 × 10^{-6} mol/L and 3.5 × 10^{-6} mol/L for the 6.4 mg/L Py-PEO and the 0.1 g/L Py-HASE solution, respectively. Despite the fact that Py-PEO was used to generate the side chain of the Py-HASE copolymer, Py-PEO and Py-HASE exhibit drastically different I_E/I_M vs [SDS] profiles. At a Py-PEO concentration of 2.5 × 10^{-6} mol/L, very few Py-PEO chains are aggregated, and the fluorescence spectrum obtained in aqueous solution with no SDS is that of the pyrene monomer. The I_E/I_M maximum occurs at an SDS concentration of 4.2 mM, larger than the CMC,[39] indicating that the formation of SDS micelles generates hydrophobic domains in the solution that pull in the pyrene end groups of Py-PEO. The pyrene concentration inside the SDS micelles is large, and excimer is being formed. As more pyrenes are drawn into the micelles, more excimer forms and the I_E/I_M ratio increases, passes through a maximum, and decreases as the 1-pyrenyl end groups of the Py-PEO chains are compartmentalized into numerous micelles. Eventually the I_E/I_M ratio reaches zero when all pyrene groups are distributed individually inside SDS micelles.

A rather different behavior is observed for Py-HASE. Since the local concentration of pyrene pendants inside the polymer coil remains high even at low Py-HASE concentration, the I_E/I_M ratio never equals zero in aqueous solution without SDS. An increase in I_E/I_M reflecting an increase in excimer formation by diffusion confirmed by the time-resolved fluorescence experiments presented afterward is observed at SDS concentrations smaller than the CMC. In other words, the enhancement of excimer formation for Py-HASE is not induced by the formation of hydrophobic domains at the CMC of SDS as for Py-PEO, but rather is triggered by the binding of SDS onto the Py-HASE copolymer. This observation leads to the conclusion that despite the presence of negative charges along the Py-HASE backbone that should repel the negatively charged SDS molecules, SDS binds more strongly onto Py-HASE than Py-PEO. Surface tension and time-resolved fluorescence measurements presented later suggest that the stronger binding of SDS onto Py-HASE might be due to the presence of highly hydrophobic pyrene aggregates in the polymer coil of Py-HASE. As more SDS is added to the Py-HASE solution, the I_E/I_M ratio increases, passes through a maximum, and decreases as the pyrene pendants distribute themselves into more numerous SDS micelles. However, the I_E/I_M ratio of Py-HASE never reaches zero at high SDS concentration because the local concentration of pyrene inside the polymer coil remains high and excimer formation occurs even though past the SDS concentration where the I_E/I_M ratio peaks, free micelles are certainly being formed.

The ratio of the first to the third monomer peaks, the I_1/I_3 ratio, can be used as an indicator of the polarity of the local environment of the pyrene pendants,[28,29] although it is not as sensitive to the polarity of the local environment of a pyrene pendant as it is for molecular pyrene.[30,31] The profiles of the I_1/I_3 ratio as a function of SDS concentration shown in Figure 5 exhibit similar features for Py-PEO and Py-HASE. At low SDS concentrations, the I_1/I_3 ratio of Py-HASE takes a value of 1.62 ± 0.02 averaged for all polymer concentrations. This value is close to that of 1.69 ± 0.03 obtained for Py-PEO (Figure 5). The high I_1/I_3 value obtained for Py-PEO and Py-HASE at low SDS concentrations implies that the pyrene pendants experience the polar environment of the aqueous solution. The



a) b) c) d)

Figure 6. Plot of I_E/I_M (◆), $I_1/I_3 - 1$ (□), and $1 + A_{E-}/A_{E+}$ (△) vs SDS concentration for Py-HASE in 0.01 M Na_2CO_3 solution at pH 9. The Py-HASE concentrations were (a) 0.01, (b) 0.1, (c) 1, and (d) 10 g/L.

slightly lower I_1/I_3 value obtained for Py-HASE might be due to the presence of stretches of contiguous hydrophobic ethyl acrylate monomers in the HASE backbone which could provide a slightly more hydrophobic environment for the pyrene pendants than that of the PEO backbone of Py-PEO. Beyond a critical onset SDS concentration, I_1/I_3 drops sharply, indicating that the pyrene monomers are being incorporated into the hydrophobic interior of the SDS micelles. I_1/I_3 plateaus at a value of 1.30 ± 0.02 for Py-HASE at the same SDS concentration where I_E/I_M peaks. This I_1/I_3 value is also similar to that of 1.38 ± 0.02 obtained for Py-PEO at high SDS concentration. Here again, the I_1/I_3 value of Py-HASE is lower than that of Py-PEO, certainly due to the higher hydrophobicity of the HASE backbone.

In this study which focuses on the hydrophobic pendants of Py-HASE, we refer to the critical aggregation concentration of pyrene (CAC_{Py}) as the SDS concentration where individual pyrene monomers are incorporated inside mixed micelles composed of SDS and pyrene molecules. Because the pyrene monomers are incorporated inside the mixed micelles over a rather small range of SDS concentration, CAC_{Py} was determined by taking the inflection point of the I_1/I_3 vs [SDS] profiles in Figure 6. The resulting CAC_{Py} values are listed in Table 1. CAC_{Py} is shown to increase slightly with increasing Py-HASE concentration. As will be demonstrated later on, the incorporation of individual pyrene pendants into mixed micelles follows the breakup of the pyrene aggregates through targeted binding of individual SDS molecules. Increased Py-HASE concentrations require larger amounts of SDS to break up the more numerous pyrene aggregates before they are incorporated inside the mixed micelles which results in the higher CAC_{Py} values observed with increasing Py-HASE concentration in Table 1.

Table 1. CAC_{Py} Values Where the Pyrene Pendants Are Incorporated Inside Mixed Micelles

[HASE], g/L	CAC_{Py}, mM	[HASE], g/L	CAC_{Py}, mM
0.01	3.0	2.5	4.3
0.1	3.1	6.0	4.7
1.0	3.5	10	5.0

To assess the nature of the process of excimer formation in solution, the pyrene excimer decays of the Py-HASE solutions were acquired over a range of SDS concentrations and fitted with a sum of three exponentials. The resulting preexponential factors and decay times are listed in Table SI.2 as Supporting Information (SI). The ratio of the negative preexponential factor, corresponding to the rise of the excimer decay, over the sum of the positive ones, corresponding to the decay of the excimer, or the A_{E-}/A_{E+} ratio, is an indicator of the mode of formation of the pyrene excimers. A pyrene excimer can be formed via two pathways. Direct excitation of a pyrene aggregate generates an excimer quasi-instantaneously, and only a decay component is observed in the excimer decay. In other words, the A_{E-}/A_{E+} ratio equals zero. When the excimer is formed exclusively by diffusion, the Birks' scheme predicts that the A_{E-}/A_{E+} ratio equals −1.0.[32] In most examples of excimer formation between

Table 2. SDS Concentrations at the Onset and Plateau of I_1/I_3, I_E/I_M, and A_{E-}/A_{E+}, Initial and Plateau Values of I_1/I_3, A_{E-}/A_{E+}, and Peak Value of I_E/I_M for Py-HASE in 0.01 M Na_2CO_3 Solution at pH 9

[HASE], g/L	initial I_1/I_3 [SDS] → 0 M	initial I_E/I_M [SDS] → 0 M	initial A_{E-}/A_{E+} [SDS] → 0 M	onset $[SDS]_{I1/I3}$, mM	onset $[SDS]_{IE/IM}$, mM	onset $[SDS]_{A_{E-}/AE+}$, mM
0.01	1.62 ± 0.02	0.07 ± 0.00	N/A	2.4	2.2	N/A
0.1	1.65 ± 0.02	0.08 ± 0.00	−0.10 ± 0.05	2.2	2.0	1.4
1	1.61 ± 0.02	0.09 ± 0.00	−0.06 ± 0.02	2.6	2.3	1.2
2.5	1.63 ± 0.01	0.08 ± 0.00[a]	N/A	2.4	2.3	N/A
6[b]	1.69 ± 0.02	0.06 ± 0.00[a]	N/A	2.2	1.6	N/A
10[b]	1.59 ± 0.01	0.11 ± 0.00	−0.16 ± 0.05	2.3	2.3	1.1

[HASE], g/L	peak I_E/I_M	plateau I_1/I_3 [SDS] → ∞	plateau A_{E-}/A_{E+} [SDS] → ∞	[SDS] at I_E/I_M peak, mM	plateau $[SDS]_{I1/I3}$, mM	plateau $[SDS]_{A_{E-}/A_{E+}}$, mM
0.01	0.30	1.30 ± 0.02	N/A	3.5	3.8	N/A
0.1	0.38	1.33 ± 0.02	−0.85 ± 0.04	3.6	4.5	3.1
1	0.46	1.28 ± 0.01	−0.85 ± 0.02	4.2	4.6	3.6
2.5	0.40[a]	1.34 ± 0.02	N/A	5.5	6.5	N/A
6[b]	0.36[a]	1.41 ± 0.02	N/A	7.1	7.8	N/A
10[b]	0.61	1.27 ± 0.04	−0.86 ± 0.03	8.5	10.7	5.5

[a] A different lamp and detector were used for 2.5 and 6 g/L; thus, the overall values of the ratios cannot be compared (only critical SDS concentrations). [b] Plateau and onset values were difficult to determine due to stretched profile.

pyrenyl moieties covalently attached onto a polymer backbone, the A_{E-}/A_{E+} ratio takes an intermediate value between 0.0 and −1.0. Depending on how close the A_{E-}/A_{E+} ratio is from one of these two values, conclusions can be drawn on whether excimer formation occurs mainly by direct excitation of a pyrene aggregate or via diffusional encounters between pyrene pendants. The A_{E-}/A_{E+} ratio could not be obtained at a Py-HASE concentration of 0.01 g/L because the low fluorescence intensity of both the monomer and excimer prevented acquisition of their fluorescence decays within a reasonable time span (<4 h). Consequently the A_{E-}/A_{E+} trace of the 0.01 g/L Py-HASE solution is missing in Figure 6. For the other Py-HASE solutions, an A_{E-}/A_{E+} value of −0.11 ± 0.04 averaged over all Py-HASE concentrations was retrieved at low SDS concentrations. This value is close to 0.0, indicating that the pyrene excimers are being formed primarily by direct excitation of ground-state pyrene aggregates. Past a SDS concentration that is lower than the SDS concentration corresponding to the onset of the drop in I_1/I_3, the A_{E-}/A_{E+} ratio decreases rapidly to more negative values, implying that SDS is interacting with the pyrene aggregates by "melting" the associations between pyrenes. At the same SDS concentration where I_1/I_3 plateaus and I_E/I_M peaks, A_{E-}/A_{E+} also plateaus to a value of −0.85 ± 0.03. This value is close to −1.0, demonstrating that the majority of pyrene excimers are being formed via diffusional encounters of pyrene monomers. The cumulated results for the initial and plateau values of I_1/I_3 and A_{E-}/A_{E+}, the corresponding SDS concentrations for their onset and plateau value, the peak I_E/I_M value, and the onset and peak SDS concentrations for I_E/I_M are summarized in Table 2.

The monomer and excimer fluorescence decays of Py-HASE were acquired at concentrations of 0.1, 1.0, and 10 g/L with varying amounts of SDS. Global analysis of the decays was carried out using the fluorescence blob model (FBM).[25−27] As shown in Figure 7, the fits of the monomer and excimer decays were good with the residuals and the autocorrelation function of the residuals randomly distributed around zero. The parameters retrieved from these analyses are listed in Table SI.3 of the SI. Using the parameters obtained by the global analysis of the monomer and excimer fluorescence decays, the fractions of aggregated pyrenes, f_{agg}, pyrenes forming excimer via diffusion, f_{diff}, and isolated pyrenes, f_{free}, were determined following the procedure described in the SI and in ref 26. These parameters are listed in Table SI.4 of the SI and are plotted as a function of SDS concentration in Figure 8.

At low SDS concentrations, substantial aggregation occurs in the Py-HASE system with f_{agg} values of 0.53 ± 0.05, 0.70 ± 0.06, and 0.61 ± 0.05 for polymer concentrations of 0.1, 1.0, and 10 g/L, respectively. Above a certain SDS concentration, f_{agg} is found to decrease rapidly, which indicates that SDS is breaking up the pyrene aggregates. At high SDS concentrations, f_{agg} plateaus at 0.07 ± 0.01, 0.08 ± 0.01, and 0.09 ± 0.01 for the Py-HASE concentrations of 0.1, 1.0, and 10 g/L, respectively. While a high concentration of SDS does reduce f_{agg} of Py-HASE to lower values, f_{agg} never reaches 0.0. The nonzero values of f_{agg} obtained at high SDS concentrations is consistent with the A_{E-}/A_{E+} ratio being more positive than −1.0, which both indicate that some residual pyrene aggregation is still occurring even at high SDS concentration.

In Py-HASE solutions containing low SDS concentrations, the fraction of pyrenes forming excimer by diffusion is small with f_{diff} values of 0.17 ± 0.01, 0.11 ± 0.04, and 0.18 ± 0.03 for Py-HASE concentrations of 0.1, 1.0, and 10 g/L, respectively. This is a consequence of most pyrene pendants being aggregated in this range of SDS concentrations. Beyond an onset SDS concentration, f_{diff} experiences a sharp increase that peaks at a critical concentration. In this concentration range, SDS binds onto the pyrene aggregates generating mixed micelles where excimer formation can occur by diffusion. At the peak, values of f_{diff} are 0.70, 0.67, and 0.72 for Py-HASE concentrations of 0.1, 1.0, and 10 g/L, respectively. For each polymer concentration, the SDS concentration where f_{diff} peaks is very close to the SDS concentration where the I_E/I_M ratio peaks. At SDS concentrations beyond that where f_{diff} peaks, increasing numbers of SDS micelles are being formed and the pyrene pendants distribute themselves into different micelles in a process that hinders the diffusional encounters between pyrene pendants, resulting in a decrease of f_{diff}.

A significant fraction of isolated pyrenes, f_{free}, is obtained for Py-HASE solutions at low SDS concentrations with f_{free} values of 0.32 ± 0.05, 0.19 ± 0.03, and 0.21 ± 0.02 for Py-HASE concentrations of 0.1, 1.0, and 10 g/L, respectively. Past an onset SDS concentration, f_{free} spikes to significantly higher values close to 0.45. The lower values of f_{free} obtained at low SDS concentrations are restored at the critical SDS concentration where f_{agg} plateaus and f_{diff} and I_E/I_M peak, beyond which the amount of isolated pyrenes slowly increases as more micelles are created and the pyrenes are compartmentalized more efficiently. The spike in f_{free} occurring at intermediate SDS concentrations will become relevant in explaining the surface

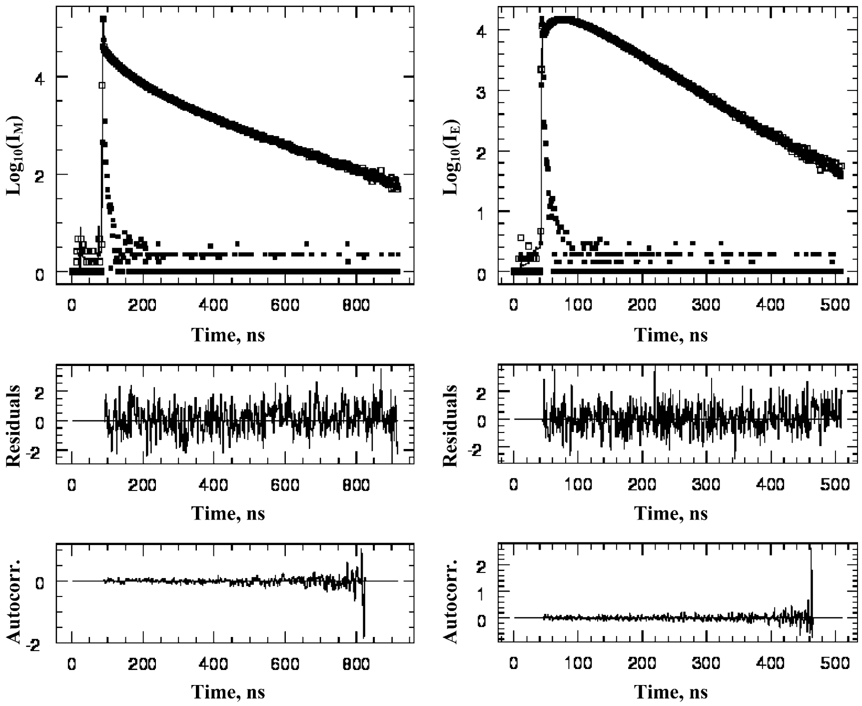


Figure 7. Monomer acquired at 375 nm (left) and excimer acquired at 510 nm (right) fluorescence decays of a 10 g/L Py-HASE in 0.01 M Na_2CO_3, pH 9 solution with 9 mM SDS. The decays were fitted globally using the fluorescence blob model (FBM), giving a χ^2 value of 1.06.

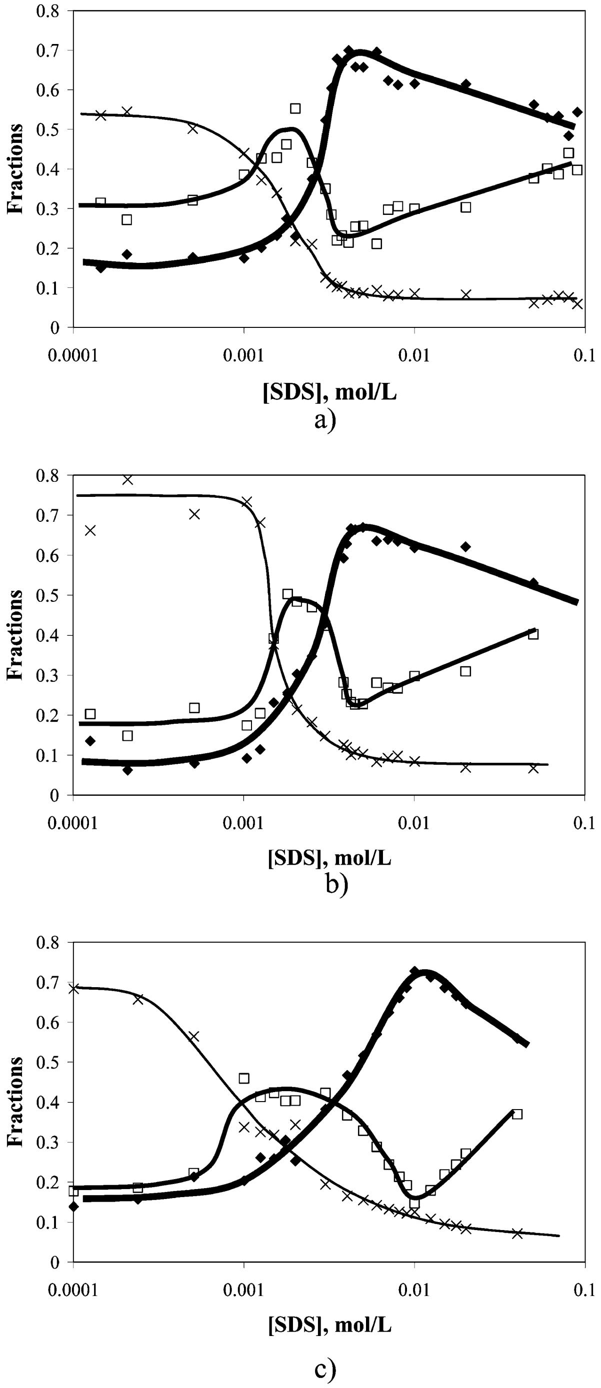
tension results presented later. The cumulated results of those critical SDS concentrations where the fractions of the pyrene species, f_{agg}, f_{diff}, and f_{free}, increase, decrease, or plateau are listed in Table 3.

The amphiphilic composition of SDS and Py-HASE implies that both species are surface active. Thus, the interactions taking place between SDS and Py-HASE could be probed by performing surface tensiometry experiments. The surface tension of several polymer solutions with Py-HASE concentrations of 0, 0.01, 0.1, 1.0, and 10 g/L was measured as a function of SDS concentration, and the resulting profiles are shown in Figure 9. An increase of the Py-HASE concentration in SDS-free solutions results in a decrease of the surface tension as shown by the table inset in Figure 9. The drop of surface tension observed for the solutions containing increasing quantities of Py-HASE confirms that Py-HASE is surface active.

At very dilute polymer concentrations such as 0.01 g/L, the surface tension profile as a function of SDS concentration is identical to that of the basic solution with no polymer being present, indicating that at low polymer concentrations the presence of polymer cannot be detected by surface tension measurements. The surface tension vs [SDS] profiles are typical of what is expected of a surfactant. Below the critical micellar concentration (CMC) of SDS in the basic solution, addition of SDS lowers the surface tension up to the CMC where micelles form and the surface tension plateaus. According to the profiles shown in Figure 9, the CMC of SDS in the 0.01 M Na_2CO_3, pH 9 solution equals 3.5 mM.

At Py-HASE concentrations greater than 0.01 g/L, a drastic decrease in the surface tension is observed with respect to the solution containing no polymer at SDS concentrations smaller than the CMC. Incidentally, this drop takes place at SDS concentrations where the Py-HASE/SDS solutions exhibit increased amounts of isolated pyrenes (i.e., f_{free} goes through a maximum in Figure 8). These isolated pyrenes are expelled into the aqueous medium since the I_1/I_3 ratio remains close to the value of 1.6 found for the pyrene monomer of Py-HASE in aqueous solution. These results suggest that the isolated pyrenes present in water increase the hydrophobic surface exposed by Py-HASE to water, making Py-HASE more surface active, and resulting in a drop in surface tension. For Py-HASE concentrations lower than or equal to 1.0 g/L, further addition of SDS leads to a recovery of the surface tension of the Py-HASE solutions at SDS concentrations near the CMC of SDS. This is due to the formation of mixed micelles between pyrene pendants and SDS which drive the free pyrenes back inside the micelles and out of the water phase (cf. f_{free} in Figure 8 which decreases to a minimum for an SDS concentration located at the I_E/I_M maximum). The Py-HASE copolymer becomes less surface active, and the surface tension recovers to near its value obtained with no polymer present in solution. For the highest Py-HASE concentration of 10 g/L, large amounts of pyrene pendants are present in the solution, and they cannot be all accommodated inside the mixed micelles at the CMC of SDS. Indeed, f_{free} for the Py-HASE concentration of 10 g/L reaches its minimum value at a SDS concentration of 10 mM, close to 3 times larger than the 3.5 mM CMC of SDS. When all pyrene pendants are located inside the mixed micelles for SDS concentrations larger than 0.01 M, the surface tension of the Py-HASE solution tends to that of the solution with no polymer.

The solutions with polymer concentrations in the dilute regime (0.1 and 1.0 g/L) exhibit a significantly steeper drop of about 25 mN/m in surface tension than the drop experienced by the concentrated Py-HASE solution (10 g/L) whose surface tension drops by only 10 mN/m. This attenuation of the surface tension drop observed with the 10 g/L Py-HASE solution can be rationalized by the fact that more polymer chains are packed at the surface when the polymer solution is in the semidilute concentration regime. When the hydrophobic aggregates are broken up upon addition of SDS, Py-HASE still becomes more surface active but has little access to the already crowded surface. Consequently, the limited accessibility to the surface leads to a weaker decrease in the surface tension of the semidilute solution. For each Py-HASE concentration, the SDS concentrations where the surface tension drops, recovers, and plateaus are listed in Table 4.



a)

b)

c)

Figure 8. f_{agg} (×), f_{diff} (◆), and f_{free} (□) as a function of SDS concentration for Py-HASE in 0.01 M Na_2CO_3 solution at pH 9 at polymer concentrations of (a) 0.1, (b) 1.0, and (c) 10 g/L.

Discussion

Although the solutions prepared with different polymer concentrations exhibit similar features, it is noticeable that those obtained with the 10 g/L series appear to be "smeared out" compared to those obtained at more dilute polymer concentrations. This effect is clearly illustrated in Figure 3 where the I_E/I_M vs [SDS] profiles are overlapped for four Py-HASE concentrations. As the Py-HASE concentration approaches and exceeds C^*, the I_E/I_M profile broadens with the peak shifting toward higher SDS concentrations, as seen in Table 2. Since the spike in I_E/I_M shown in Figure 3 results from the interaction between SDS and the pyrene pendants of Py-HASE, these observations imply that more SDS is required at higher polymer concentrations to yield the same I_E/I_M response as that observed at the lower Py-HASE concentrations.

One startling result found in Figure 3 is that a 3 orders of magnitude change in polymer concentration only doubles the I_E/I_M ratio at its peak value. For pyrene molecules in solution, the I_E/I_M ratio is supposed to increase linearly with pyrene concentration.[32] This trend is clearly not observed for the Py-HASE polymer, with or without SDS in solution. To qualitatively rationalize this effect, one must consider the two regimes depicted in Figure 3, namely, the one at low SDS concentration, where the pyrene hydrophobes seem to be unaffected by the presence of SDS, and the one at higher SDS concentration, where the pyrene hydrophobes are incorporated inside mixed micelles. In the regime corresponding to low SDS concentrations, the negatively charged polymer coils repel one another in a process which inhibits the intermolecular formation of excimer. Excimer formation, even at the semidilute concentration of 10 g/L, occurs mostly intramolecularly. Thus, the I_E/I_M ratio increases only slightly upon increasing the Py-HASE concentration 1000-fold. This result is confirmed by a recent study which found that excimer formation occurs mostly intramolecularly for Py-HASE concentrations smaller than 10 g/L.[11] At higher SDS concentrations where the pyrene pendants are solubilized inside the mixed micelles (i.e., at and past the I_E/I_M peak), the I_E/I_M ratio is controlled by the largest number of pyrene pendants which can be accommodated by a mixed micelle. If the size of the mixed micelles remains the same, the same average number of pyrene pendants can be incorporated inside the micelles, and the I_E/I_M ratio does not change regardless of Py-HASE concentration. These considerations rationalize the fact that the I_E/I_M ratio remains relatively constant with Py-HASE concentration. Nevertheless, the I_E/I_M ratio increases slightly (2-fold) upon the 1000-fold increase in Py-HASE concentration. This is presumably due to an increase of residual intermolecular associations which are promoted as the Py-HASE concentration is increased.

The analysis of the monomer and excimer fluorescence decays was based on the fluorescence blob model (FBM). Within the framework of the FBM, a blob is defined as the volume probed by an excited chromophore during its lifetime.[40] In the case of a polymer chain labeled with a chromophore in solution, a blob represents that portion of the polymer coil that is being probed by the excited chromophore. This definition of a blob applies to the pyrene pendants of Py-HASE at low SDS concentrations. However, at the high SDS concentrations where all the pyrene pendants of Py-HASE are incorporated inside mixed micelles, the nature of the blob might change, as a blob may turn into a mixed micelle. That this might be happening is supported by the observation that at the SDS concentration where the I_E/I_M ratio peaks the average number of pyrenes per blob, $\langle n \rangle$, changes little (2.4 ± 0.5) over the range of Py-HASE concentrations studied. It seems that increasing the Py-HASE concentration 100-fold from 0.1 to 10 g/L does not lead to a higher number of pyrene pendants per blobs when the I_E/I_M ratio peaks. It suggests that the blobs cannot accommodate large numbers of pyrene pendants, as would be expected from the finite volume of a mixed micelle. Furthermore, the fact that the pyrene pendants are concentrated in a few micelles when I_E/I_M peaks implies that at this SDS concentration, very few free SDS micelles are present.

The above discussion strongly suggests that at the I_E/I_M peak the parameter $\langle n \rangle$ represents the average number of hydrophobic pendants per mixed micelles. In this case, a few relationships are expected to unfold. For instance, at the SDS concentration

Table 3. Onset and Other Critical SDS Concentrations of f_{agg}, f_{diff}, f_{free}, and Their Associated Values for Py-HASE in 0.01 M Na_2CO_3 Solution at pH 9

[HASE], g/L	initial f_{agg}	initial f_{diff}	initial f_{free}	onset $[SDS]_{f_{agg}}$, mM	onset $[SDS]_{f_{diff}}$, mM	onset $[SDS]_{f_{free}}$, mM
0.1	0.53 ± 0.05	0.17 ± 0.01	0.32 ± 0.05	0.7	3.7	1.0[a]
1	0.70 ± 0.06	0.11 ± 0.04	0.19 ± 0.03	1.2	4.5	1.2
10[b]	0.61 ± 0.05	0.18 ± 0.03	0.21 ± 0.02	N/A	10	N/A

[HASE], g/L	plateau f_{agg}	plateau $[SDS]_{f_{agg}}$, mM	peak $[SDS]_{f_{diff}}$, mM	minimum $[SDS]_{f_{free}}$, mM
0.1	0.07 ± 0.01	3.9	3.7	3.5
1	0.08 ± 0.01	4.2	4.5	4.5
10[b]	0.09 ± 0.01	N/A	10	10

[a] f_{free} value could only be approximated for Py-HASE = 0.1 g/L. [b] Plateau and onset values were difficult to determine due to skewed profile.

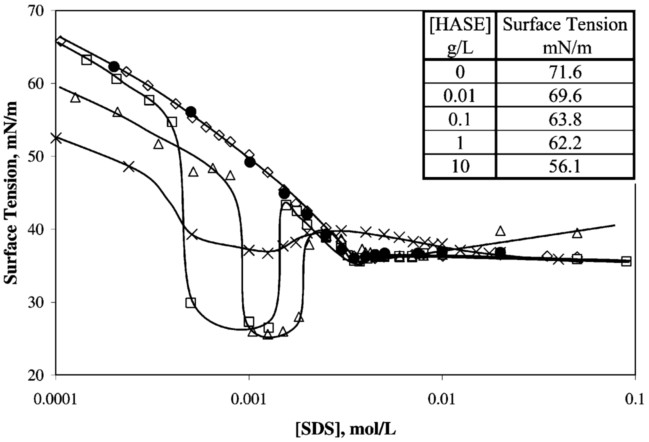


Figure 9. Surface tension of Py-HASE in 0.01 M Na_2CO_3 solution at pH 9 with SDS without (●) and with Py-HASE at concentrations of 0.01 (◇), 0.1 (□), 1 (△), and 10 g/L (×). Inset: surface tension of Py-HASE solutions without SDS.

where the I_E/I_M ratio peaks, $\langle n \rangle$ should be given by eq 1, if all micelles present in solution are mixed micelles, i.e., associated with the pyrene pendants of Py-HASE.

$$\langle n \rangle = \frac{[\text{Py}]}{[\text{micelle}]_{\text{IE/IM}}} \tag{1}$$

In eq 1, [Py] and $[\text{micelle}]_{\text{IE/IM}}$ are the concentrations of the pyrene pendants which are accounted for by the FBM, i.e., those pyrenes that form excimer via diffusion, and micelles at the SDS concentration where the I_E/I_M ratio peaks, respectively. The expressions of [Py] and $[\text{micelle}]_{\text{IE/IM}}$ are given by eqs 2 and 3, respectively.

$$[\text{Py}] = \lambda[\text{Py-HASE}]\, f_{\text{diff}} \tag{2}$$

$$[\text{micelle}]_{\text{IE/IM}} = \frac{[\text{SDS}]_{\text{IE/IM}} - \text{CAC}_{\text{Py}}}{N_{\text{agg}}} \tag{3}$$

In the above equations, λ is the pyrene content of the polymer in moles of pyrene per gram of polymer, CAC_{Py} is the critical aggregation concentration of SDS in the sodium carbonate solution where the pyrene pendants are incorporated inside the mixed micelles, $[\text{SDS}]_{\text{IE/IM}}$ is the SDS concentration where the I_E/I_M ratio peaks, and N_{agg} is the aggregation number of SDS molecules per micelle. The CAC_{Py} values are listed in Table 1. Substituting the expressions for [Py] and $[\text{micelle}]_{\text{IE/IM}}$ into $\langle n \rangle$ and solving for N_{agg} gives

$$N_{\text{agg}} = \frac{\langle n \rangle([\text{SDS}]_{\text{IE/IM}} - \text{CAC}_{\text{Py}})}{\lambda[\text{Py-HASE}]\, f_{\text{diff}}} \tag{4}$$

Equation 4 holds only under the assumption that no free SDS micelle exists in solution. According to the above discussion, it is believed to be obeyed at $[\text{SDS}]_{\text{IE/IM}}$. Equation 4 should be applied for Py-HASE concentrations where $[\text{SDS}]_{\text{IE/IM}}$ is well separated from the CAC. Equation 4 was used at Py-HASE concentrations of 1.0, 2.5, 6.0, and 10 g/L. Within experimental error, N_{agg} remained constant as a function of Py-HASE concentration and equal to 44 ± 8 SDS units per mixed micelle. The relatively large scatter in the N_{agg} values obtained at different Py-HASE concentrations is due to the fact that the calculation of N_{agg} in eq 4 uses $\langle n \rangle$ and f_{diff} which are obtained from the FBM analysis of the fluorescence decays of those pyrene monomers that form excimer by diffusion. Accurate $\langle n \rangle$ and f_{diff} values are obtained with the FBM when the fraction $f_{diff}/(f_{diff} + f_{free})$ is greater than 0.85. All FBM analyses resulted in a maximum fraction ratio value around 0.70, substantially smaller than 0.85, which led to the spread observed in the N_{agg} values.

The N_{agg} value of SDS micelles in a 0.01 M Na_2CO_3, pH 9 solution without polymer was determined by monitoring the quenching of molecular pyrene by 3,4-dimethylbenzophenone in the micellar solution and applying the Turro−Yekta procedure.[37] SDS solutions with concentrations of 6, 8, and 10 mM were prepared without polymer, and an N_{agg} value of 60 was obtained (see Figure SI.1 in the SI). Consequently, the mixed micelles made of about 44 ± 8 units are smaller than the free SDS micelles.

One major implication of the above study is that, as SDS interacts with the pyrene pendants of HASE, the ill-defined blob turns into a well-defined mixed micelle for SDS concentrations larger than that where the I_E/I_M ratio peaks ($[\text{SDS}]_{\text{IE/IM}}$). Thus, and maybe most importantly for rheological applications, the blob model can be used to directly measure the average number of pyrene pendants per mixed micelle, $\langle n \rangle$, for the Py-HASE system, at SDS concentrations larger than $[\text{SDS}]_{\text{IE/IM}}$, even when free SDS micelles exist.

In view of the above, the viscosity, η, of a solution containing 6.0 g/L of Py-HASE was measured as the SDS concentration was progressively increased. The steady-state fluorescence spectra and time-resolved fluorescence decays of the solutions were acquired. The average number of pyrene per mixed micelle, $\langle n \rangle$, is plotted as a function of [SDS] in the top panel of Figure 10, whereas the [SDS] dependence of the I_E/I_M ratio and η are plotted in the bottom panel of Figure 10. The dependence of the I_E/I_M ratio with [SDS] is similar to the plots shown in Figure 3. The I_E/I_M ratio peaks at an SDS concentration of 7.1 mM between the maxima obtained for the solutions containing 2.5 and 10 g/L of Py-HASE which peaked at 5.5 and 8.5 mM, respectively. The η vs [SDS] profile is also typical of what is expected from the interactions of a surfactant and a hydropho-

Table 4. SDS Concentrations for the Surface Tension Drop, Recovery, and Plateau, and Minimum and Plateau Surface Tensions for Py-HASE in 0.01 M Na_2CO_3 Solution at pH 9

[HASE], g/L	onset $[SDS]_{drop}$, mmol/L	onset $[SDS]_{recovery}$, mmol/L	plateau [SDS], mmol/L	minimum surface tension, mN/m	plateau surface tension, mN/m
0	N/A	N/A	3.7	36	36
0.01	N/A	N/A	3.7	36	36
0.1	0.5	1.6	3.7	27	36
1	1.0	2.0	4.2	26	36
10	0.5^a	2.0	N/A	37	N/A

[a] Surface tension drop was difficult to determine due to smoother response drop.

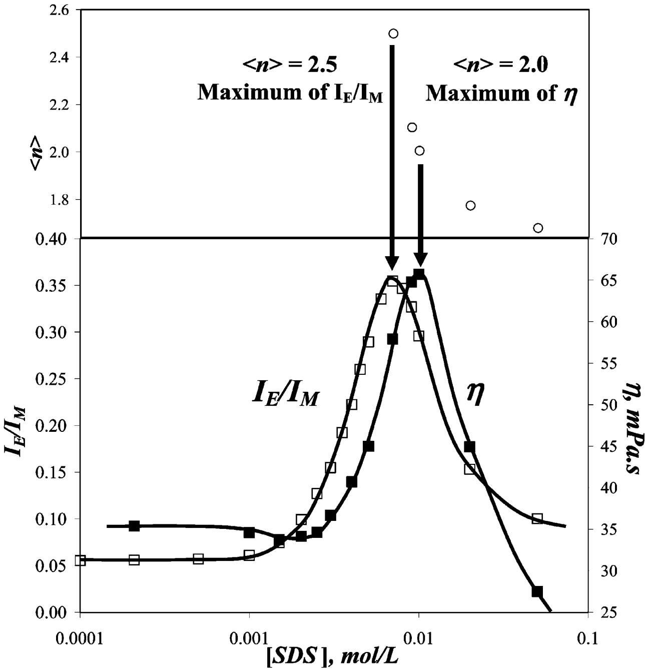
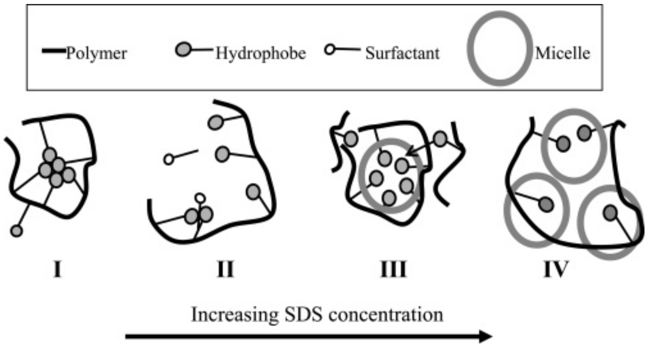


Figure 10. Values of $\langle n \rangle$ (top panel) and I_E/I_M and η (bottom panel) plotted as a function of [SDS] for a Py-HASE concentration of 6.0 g/L in 0.01 M Na_2CO_3 solution at pH 9.

bically modified polymer.[41−43] At low SDS concentrations, the associations between pyrene groups occur mostly intramolecularly, as suggested in two earlier publications.[11,24] The addition of SDS seems to promote the intermolecular formation of pyrene excimer which leads to an increase in the I_E/I_M ratio and a concomitant increase of the cross-linker density, resulting in the increase of η. When further SDS is added to the solution, the hydrophobes are separated inside different micelles; excimer formation is inhibited, leading to a decrease in the number of intermolecular cross-linkers which is accompanied by a decrease in the solution viscosity.

Interestingly, the I_E/I_M vs [SDS] and η vs [SDS] profiles do not peak at the same SDS concentration. Whereas the I_E/I_M ratio peaks at a SDS concentration of 7.1 mM, η takes its maximum value for a higher SDS concentration of 10 mM. An explanation for this shift in the two traces can be found in the value of $\langle n \rangle$ plotted as a function of [SDS] in the top panel of Figure 10. At the SDS concentrations where I_E/I_M and η pass through a maximum, $\langle n \rangle$ was found to equal 2.5 and 2.0, respectively. An $\langle n \rangle$ value of 2.5 corresponds to the maximum pyrene loading with minimum formation of pyrene aggregates since at the SDS concentration where the I_E/I_M ratio passes through a maximum, f_{agg} takes a small value (cf. Tables 1−3). Since pyrene aggregates have been found to be weak emitters,[27] their quasi-absence leads to a high I_E/I_M ratio. However, in terms of forming a polymeric network held together with aggregates of pyrene pendants, an $\langle n \rangle$ value of 2.5 is not expected to be optimal, since only two pyrene pendants in a given mixed micelle are required to form an efficient cross-link. When $\langle n \rangle$ takes its optimal value of 2, the chains are expected to maximize their conformations to form the largest possible polymeric aggregates. The formation of large polymeric aggregates is expected to result in a maximum in viscosity. Indeed, an $\langle n \rangle$ value of 2 was obtained for the SDS concentration corresponding to the maximum value of η in Figure 10. The good qualitative agreement obtained between the η vs [SDS] and the $\langle n \rangle$ vs [SDS] profiles shown in Figure 10 suggests that our analysis of the fluorescence decays with the FBM is appropriate. To the best of our knowledge, it is also the first example that such a satisfying quantitative agreement between the results obtained by fluorescence and viscometry is reached when dealing with the associations of a surfactant and a pyrene-labeled water-soluble associative thickener.

Scheme 1. Regimes for the Binding of SDS to Py-HASE in Alkaline Aqueous Solution



Combining the results obtained by fluorescence, surface tensiometry, and viscometry, Scheme 1 might be proposed to describe the binding of SDS to Py-HASE. This scheme consists of four SDS concentration binding regions. Region I represents the low SDS concentration regime before the ratio A_{E-}/A_{E+} and the fraction f_{agg} drop and where no interactions between SDS and the pyrene aggregates occur. In region I, the unassociated pyrene pendants are exposed to water ($I_1/I_3 = 1.62 \pm 0.02$) or are associated into ground-state pyrene aggregates. Since the I_E/I_M ratio increases very little upon increasing the polymer concentration by 3 orders of magnitude, it was concluded that the aggregates are predominantly intramolecular in nature.

Region II is the SDS concentration regime delimited at the lower end by the onset concentration where A_{E-}/A_{E+} and f_{agg} drop and at the higher end by the onset concentration where the I_1/I_3 ratio drops. In region II, SDS interacts with the pyrene aggregates. It is unlikely that SDS associates with other sections of Py-HASE since an earlier microcalorimetry study established that SDS targets mostly the aggregates made of the hydrophobic end groups of the macromonomers when the PEO spacer exhibits a degree of ethoxylation larger than 10.[20] As a matter of fact, the degree of ethoxylation of Py-PEO used to prepare Py-HASE equals 53 (Figure 1). Addition of SDS to the solution melts the ground-state pyrene aggregates by ejecting lone pyrenes into the water and facilitating excimer formation by diffusional encounters. The burst of isolated pyrenes caused by the disruption of intramolecular pyrene aggregates results in a more surface active Py-HASE coil as probed by surface tension measurements (Figure 9). No SDS interacts with these isolated pyrenes ($I_1/I_3 \sim 1.6$), implying that SDS molecules target preferentially the pyrene aggregates.

Region III marks the incorporation of the pyrene pendants into mixed micelles. For all Py-HASE concentrations studied, it is delimited at the low end by the SDS concentration where the I_1/I_3 ratio begins to drop and at the higher end where the I_1/I_3 and A_{E-}/A_{E+} ratios and the f_{agg} fraction plateau accompanied by the peak of f_{diff} and I_E/I_M. In this region, the formation of mixed micelles occurs. The pyrene aggregates are solubilized into the micelles so that very few ground-state pyrene aggregates remain in solution. Isolated pyrenes are drawn back into mixed micelles made of SDS and pyrene pendants, thereby causing the polymer to become less surface active (the surface tension increases in Figure 9) and enhancing pyrene associations (I_E/I_M increases in Figure 6). In this SDS concentration regime, it is assumed that very few free SDS micelles exist. For Py-HASE concentrations in the semidilute regime, intermolecular aggregation in region III is enhanced as demonstrated by an increase in viscosity.

In region IV, all of the pyrenes are incorporated into mixed micelles. Increasing the surfactant concentration leads to the formation of extra micelles which allows the pyrenes to distribute themselves among the growing number of micelles. This causes a decrease in the average number of pyrenes per micelle, $\langle n \rangle$, and the I_E/I_M ratio drops. This result is general and has been reported for numerous pyrene-labeled associative polymers.[44−51] For solutions in the semidilute concentration regime, the redistribution of the pyrenes favors initially the formation of intermolecular cross-links which results in an increase of viscosity, as established by viscosity measurements in Figure 10. Further addition of SDS leads the average number of hydrophobes per micelle to drop below 2, resulting in the decrease of the viscosity of the solution, as observed in Figure 10.

Regardless of the SDS concentration, the semidilute Py-HASE solutions yield trends which are “smeared” compared to those obtained for dilute polymer concentrations. In particular, the plateau regions found in the dilute samples for many of the parameters are difficult to determine for the semidilute case. In some circumstances, such as the f_{agg} behavior for the 10 g/L sample, there is no plateau region to speak of. This smearing could be a consequence of the relative number of SDS molecules to pyrene hydrophobes present in solution. In terms of concentration of hydrophobes in solution, a 1.0 g/L Py-HASE solution has a pyrene concentration of 36 μM since the pyrene content of Py-HASE, λ, equals 36 μmol of pyrene per gram of polymer. The onset concentration of SDS interacting with the pyrene aggregates occurs approximately at 1 mM (cf. $[SDS]_{fagg}$ in Table 3). This means that for dilute samples the concentration of hydrophobes is less than 4 mol % that of SDS. Thus, formation of mixed micelles is unaffected by the presence of the hydrophobes, which explains why SDS begins to interact with Py-HASE at the same SDS concentrations for all the dilute polymer solutions ([Py-HASE] < 1 g/L). For the semidilute polymer solution having a polymer concentration of 10 g/L, the hydrophobe concentration is 360 μM, which represents 36 mol % of the SDS concentration of 1 mM where binding occurs in the dilute solutions. Consequently, the large number of hydrophobes present requires a greater amount of SDS to create the same effect as that observed for the more dilute Py-HASE solutions, and the transitions appear broader than those observed in the dilute regime.

Conclusions

A wide range of Py-HASE concentrations were studied in the presence of the surfactant SDS. The binding of SDS to the polymer was monitored using both traditional and global fluorescence analysis techniques as well as surface tensiometry and viscometry. From the parameters obtained by the global analysis of the fluorescence decays, the fraction of aggregated pyrene pendants was determined quantitatively. The combination of all results obtained by the fluorescence and surface tension measurements leads to Scheme 1 which describes the binding of SDS to Py-HASE by assuming the existence of four SDS concentration regions. At low SDS concentrations, no interaction between SDS and the pyrene pendants occurred. As more SDS was added, the SDS targeted the pyrene aggregates, resulting in the aggregates breaking apart and releasing isolated pyrenes into the solution. At even higher SDS concentrations, micelles formed, further melting the remaining pyrene aggregates and drawing in individual pendants into the micelles. This resulted in an increase of excimer formation and an increase in solution viscosity at semidilute polymer concentrations. Finally, at excess surfactant concentrations, all the pyrenes were incorporated into the micelles, and as more SDS was added, the average number of pyrenes per micelle dropped as the pyrenes distributed themselves among more micelles. This last stage is accompanied by a peak maximum followed by a drop in solution viscosity.

From these experiments, a significant difference was observed in the way SDS interacted with Py-HASE, whether the polymer solution was in the dilute or semidilute concentration regime. For dilute polymer solutions ([Py-HASE] < 1 g/L), the micelle formation and binding of SDS to the pyrene aggregates is independent of polymer concentration. This is due to the low amount of hydrophobes present in solution compared to the SDS concentration when SDS begins to interact with them. For semidilute polymer solutions, the concentration of hydrophobes is significant enough to affect the range of SDS concentrations where binding and micelle formation take place. Consequently, extra SDS is required to solubilize the pyrene pendants, and the transitions are observed for most parameters to occur at higher SDS concentrations than for the dilute Py-HASE solutions. It is important to note though that, despite the wide range of Py-HASE concentrations studied, the average number of pyrenes per blob, $\langle n \rangle$, remained constant at the I_E/I_M maximum. This observation led to the conclusion that the blob defined by the FBM is equivalent to a mixed micelle at high SDS concentrations. This implied that the parameter $\langle n \rangle$ represents the average number of pyrenes per mixed micelle, and since $\langle n \rangle$ remains constant and equal to 2.4 ± 0.5 at the SDS concentration where I_E/I_M peaks regardless of Py-HASE concentration, this value represents the maximum capacity of mixed micelles to host pyrene pendants.

Knowledge that $\langle n \rangle$ represents the average number of Py-HASE hydrophobes per mixed micelle was shown to have a major implication for rationalizing the complex rheological behavior of a Py-HASE/SDS solution. The viscosity of a 6 g/L Py-HASE solution measured as a function of SDS concentration was found to peak at a SDS concentration where $\langle n \rangle$ equaled 2.0. An $\langle n \rangle$ value of 2.0 is expected to result in an optimally branched polymeric network which should yield large polymeric aggregates and solution viscosities, as observed experimentally. That this was indeed the case for the Py-HASE/SDS solution is an important result since it is the first example of its kind.

The combination of these results obtained by fluorescence, surface tensionmetry, and viscometry provides a deeper understanding of the process of SDS binding onto Py-HASE. Such information will become extremely useful in explaining the macroscopic viscoelastic behavior of the Py-HASE/SDS system in future studies.

Acknowledgment. J.D. and H.S. are thankful for funding from NSERC and CFI. J.D. is thankful for the funding associated to his being awarded a Tier-2 Canada Research Chair.

Supporting Information Available: Fitting the excimer fluorescence decays with a sum of exponentials and fitting the fluorescence decays with the fluorescence blob model. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) English, R. J.; Gulati, H. S.; Jenkins, R. D.; Khan, S. A. *J. Rheol.* **1997**, *41*, 427−444.
(2) Abdala, A. A.; Olesen, K.; Khan, S. A. *J. Rheol.* **2003**, *47*, 497−511.
(3) Jenkins, R. D.; DeLong, L. M.; Bassett, D. R. *Hydrophobic Polymers. Performance with Environmental* Acceptability, Glass, J. E., Ed.; Advances in Chemistry 248; American Chemical Society: Washington, DC, 1996; pp 425−447.
(4) Jenkins, R. D.; Bassett, D. R.; Shay, G. D.; Smith, D. E.; Argyropoulos, J. N.; Loftus, J. E. WO 93/24544, 1993.
(5) El-Sherbiny, S.; Xiao, H. *Ind. Eng. Chem.*, in press.
(6) Jenkins, R. D.; Bassett, D. R.; Lightfoot, R. H.; Boluk, M. Y. WO9324543, 1993.
(7) Jenkins, R. D.; Bassett, D. R.; Lightfoot, R. H.; Boluk, M. Y. USP 5681882, 1997.
(8) Carder, C. H.; Garska, D. C.; Jenkins; R. D.; McGuiness, M. J. USP 5708068, 1998.
(9) Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424.
(10) Schultz, D. N., Glass, J. E., Eds. *Polymer as Rheology Modifiers*; ACS Symposium Series 462; American Chemical Society: Washington, DC, 1991.
(11) Prazeres, T. V. J.; Duhamel, J.; Olesen, K.; Shay, G. *J. Phys. Chem. B* **2005**, *109*, 17406−17416.
(12) Horiuchi, K.; Rharbi, Y.; Spiro, J. G.; Yekta, A.; Jenkins, R. D.; Bassett, D. R. *Langmuir* **1999**, *15*, 1644−1650.
(13) Dai, S.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* **2000**, *33*, 7021−7028.
(14) Tam, K. C.; Guo, L.; Jenkins, R. D.; Bassett, D. R. *Polymer* **1999**, *40*, 6369−6379.
(15) Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* **1997**, *30*, 3271−3282.
(16) Guo, L.; Tam, K. C.; Jenkins, R. D. *Macromol. Chem. Phys.* **1998**, *199*, 1175−1184.
(17) Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Langmuir* **2000**, *16*, 2151−2156.
(18) Tam, K. C.; Farmer, M. L.; Jenkins, R. D.; Bassett, D. R. *J. Polym. Sci., Part B*: *Polym. Phys.* **1998**, *36*, 2275−2290.
(19) Kumacheva, E.; Rharbi, Y.; Winnik, M. A.; Guo, L.; Tam, K. C.; Jenkins, R. D. *Langmuir* **1997**, *13*, 182−186.
(20) Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* **2000**, *33*, 1727−1733.
(21) Seng, W. P.; Tam, K. C.; Jenkins, R. D. *Colloids Surf., A* **1999**, *154*, 365−382.
(22) Olesen, K. R.; Bassett, D. R.; Wilkerson, C. L. *Prog. Org. Coat.* **1998**, *35*, 161−170.
(23) Islam, M. F.; Jenkins, R. D.; Bassett, D. R.; Lau, W.; Ou-Yang, H. D. *Macromolecules* **2000**, *33*, 2480−2485.
(24) Prazeres, T. J. V.;Beingessner, R.; Duhamel, J.; Olesen, K.; Shay, G.; Bassett, D. R. *Macromolecules* **2001**, *34*, 7876−7884.
(25) Siu, H.; Duhamel, J. *Macromolecules* **2004**, *37*, 9287−9289.
(26) Siu, H.; Duhamel, J. *J. Phys. Chem. B* **2005**, *109*, 1770−1780.
(27) Siu, H.; Duhamel, J. *Macromolecules* **2005**, *38*, 7184−7186.
(28) Dong, D. C.; Winnik, M. A. *Can. J. Chem.* **1984**, *62*, 2560−2565.
(29) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.
(30) Winnik, F. M.; Regismond, S. T. A. *Colloids Surf., A* **1996**, *118*, 1−39.
(31) Duhamel, J. In *Molecular Interfacial Phenomena of Polymer and Biopolymers*; Chen, P., Ed.; Woodhead: New York, 2005.
(32) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; p 351.
(33) Siu, H.; Prazeres, T. V. J.; Duhamel, J.; Olesen, K.; Shay, G. *Macromolecules* **2005**, *38*, 2865−2875.
(34) Grant, D. H.; Grassie, N. *Polymer* **1960**, *1*, 125−134.
(35) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum Publishers: New York, 1999; pp 52−54.
(36) James, D. R.; Demmer, D. R. M.; Verrall, R. E.; Steer, R. P. *Rev. Sci. Instrum.* **1983**, *54*, 1121−1130.
(37) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951−5952.
(38) Regalado, E. J.; Selb, J.; Candau, F. *Macromolecules* **1999**, *32*, 8580−8588.
(39) The CMC of SDS in 0.01 M Na_2CO_3 solution at pH 9 equals 3.5 mM, as determined by surface tension measurements.
(40) Mathew, A. K.; Siu, H.; Duhamel, J. *Macromolecules* **1999**, *32*, 7100−7108.
(41) Magny, B.; Iliopoulos, I.; Zana, R.; Audebert, R. *Langmuir* **1994**, *10*, 3180−3187.
(42) Iliopoulos, I.; Wang, T. K.; Audebert, R. *Langmuir* **1991**, *7*, 617−619.
(43) Iliopoulos, I.; Olsson, U. *J. Phys. Chem.* **1994**, *98*, 1500−1505.
(44) Anghel, D. F.; Toca-Herrera, J. L.; Winnik, F. M.; Rettig, W.; v. Kliting, R. *Langmuir* **2002**, *18*, 5600−5606.
(45) Winnik, F. M.; Regismond, S. T. A.; Goddard, E. D. *Langmuir* **1997**, *13*, 111−114.
(46) Quina, F.; Abuin, E.; Lissi, E. *Macromolecules* **1990**, *23*, 5173−5175.
(47) Maltesh, C.; Somasundaran, P. *Langmuir* **1992**, *8*, 1926−1930.
(48) Hu, Y.-Z.; Zhao, C.-L.; Winnik, M. A.; Sundararajan, P. R. *Langmuir* **1990**, *6*, 880−883.
(49) Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 912−917.
(50) Winnik, M. A.; Bystryak, S. M.; Siddiqui, J. *Macromolecules* **1999**, *32*, 624−632.
(51) Winnik, F. M.; Winnik, M. A.; Tazuke, S. *J. Phys. Chem.* **1987**, *91*, 594−597.

MA0519563