

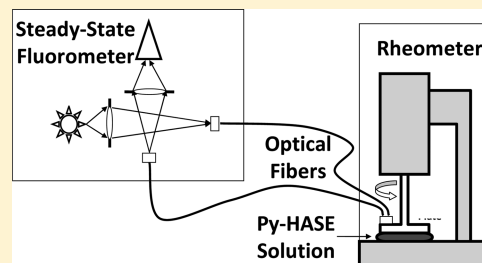
Interactions between Hydrophobically Modified Alkali-Swellable Emulsion Polymers and Sodium Dodecyl Sulfate Probed by Fluorescence and Rheology

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S Supporting Information

ABSTRACT: The interactions between a pyrene-labeled hydrophobically modified alkali-swellable emulsion (Py-HASE) polymer and the anionic surfactant sodium dodecyl sulfate (SDS) in aqueous solution were investigated with a fluorometer, a rheometer, and a combination of both instruments to probe the fluorescence of the polymer while the solution was being sheared. Different amounts of SDS were added to two solutions with Py-HASE concentrations of 8 and 57 g/L. The pyrene monomer and excimer decays of the Py-HASE solutions were acquired and globally fitted according to the fluorescence blob model (FBM) and the model free (MF) analysis. Both models yielded the same molar fractions of pyrenes that were isolated, aggregated, or forming excimer by diffusion. The average number of pyrenes per micelle, $\langle n \rangle$, was determined according to the FBM and found to equal 2.0 at the SDS concentration corresponding to a maximum in solution viscosity. For a Py-HASE concentration of 57 g/L, the solution viscosities at different SDS concentrations were measured from the Newtonian plateau regions and were found to peak at an SDS concentration of 11 mM. The steady-state fluorescence spectra were acquired at SDS concentrations of 0.1, 6.0, 11.1, and 17 mM while the 57 g/L Py-HASE solution was sheared. Although the solutions of Py-HASE and SDS were found to shear-thin substantially with the solution viscosity decreasing by up to 4 orders of magnitude, no change was observed in the fluorescence spectra acquired at shear rates ranging from 0.005 to 500 s⁻¹. The overlap of the fluorescence spectra under conditions where the solution viscosity decreased by 4 orders of magnitude suggested that the rearrangement of the hydrophobes from inter- to intramolecular associations that leads to shear-thinning occurs on a time scale that is much faster than that over which the rheology experiments are being conducted.



INTRODUCTION

Hydrophobically modified water-soluble polymers (HMWSPs) are known for their ability to form polymeric networks in aqueous solution where the water-soluble chains are held together by interpolymeric aggregates of hydrophobes.^{1–8} The polymeric network generated in aqueous solutions of HMWSPs leads to a large enhancement in the solution viscosity which explains why they are often referred to as associative thickeners (ATs). Considering that the network of HMWSPs results from physical interactions between the hydrophobes, the connecting points of the network are thus transient and susceptible to disruption induced by an external trigger such as the application of a shear or the addition of surfactants to the HMWSP solution.^{1–8} In turn, changes in the network architecture lead to dramatic changes in the solution viscosity, which contribute to the rich rheological behavior observed with aqueous solutions of HMWSPs. These intriguing rheological properties have spurred intense scientific interest and have led to numerous industrial applications in cosmetics, paints, and enhanced oil recovery to name but a few.^{1–8}

The three main families of ATs result from the hydrophobic modification of cellulose, ethoxylated urethane polymers (HEURs), and alkali swellable emulsion copolymers

(HASEs). From a purely academic point of view, HEURs might be regarded as the better behaved ATs as HEUR solutions yield a single relaxation time in dynamic rheological experiments⁹ that is defined by the disengagement rate of an elastically active chain bridging two well-defined rosette micelles constituted of ~20–30 HEUR polymers.^{10–12} As with all ATs, the viscoelastic properties of AT solutions depend critically on the hydrophobe used to prepare a given AT.^{9,11,13} In fact, the preparation of a polymer having the same chemical composition and architecture as that of a given AT but where the hydrophobes have been replaced by a methyl group will have no thickening activity when dissolved in water.^{11,13} Consequently, techniques capable of probing selectively the behavior of the hydrophobes at the molecular level are of great interest to rationalize the viscoelastic performance of the AT solution probed at the macroscopic level with a rheometer. Unfortunately, very low amounts of the hydrophobe are usually present in an AT solution, as larger amounts would lead to solubility issues in water. Consequently, techniques used to

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study the behavior of the hydrophobe of an AT need to be extremely sensitive. For this reason, fluorescence has been used extensively to probe the behavior of the hydrophobic dye pyrene incorporated into an AT in lieu of the hydrophobe.^{7,14} Besides being hydrophobic (the solubility of pyrene has been determined to equal 6×10^{-7} M in water),¹² pyrene is ideally suited to probe the associative strength of pyrene-labeled ATs (Py-ATs) because of the sensitivity of its fluorescence to the polarity of its local environment and its ability to form an excimer upon encounter between an excited and a ground-state pyrene.^{7,14–17} In water, hydrophobic pyrenes form ground-state pyrene aggregates that lead to the instantaneous formation of excimer upon direct excitation with UV light. In turn, addition of a surfactant to an aqueous solution of Py-AT targets the hydrophobic pyrene aggregates and provides a hydrophobic environment where the aggregated pyrene labels are solvated and can form excimer over time by diffusive encounters. The interactions of pyrene with itself or with a surfactant can be characterized qualitatively by steady-state and time-resolved fluorescence, and numerous Py-ATs have been characterized in this manner in studies whose results have been summarized in a number of reviews.^{7,14,15}

However, recent developments in the analysis of fluorescence decays acquired with pyrene-labeled polymers based on the fluorescence blob model (FBM)^{18,19} and model free analysis (MFA)^{17,20} have enabled a much more detailed and quantitative description of the behavior of the pyrene labels used as hydrophobes for an AT. The present study takes full advantage of these improved analytical features to probe the behavior of a HASE sample whose hydrophobes were replaced with the chromophore pyrene. Since this HASE sample contained 12 μmol of pyrene hydrophobes/g of polymer, it is referred to as Py-HASE12 in this report. With no surfactant, the pyrene pendants of Py-HASE12 were aggregated in water and pyrene excimer was generated by direct excitation of ground-state pyrene aggregates. Addition of SDS to the Py-HASE12 solution induced the formation of mixed micelles at higher SDS concentration where pyrene pendants form excimer by diffusion and the rheological behavior of the solution was altered. The negatively charged SDS surfactant was selected to enhance the interactions between SDS and the pyrene hydrophobes, as electrostatic repulsion between SDS and the polyacrylate backbone of HASE reduces backbone–SDS interactions at low SDS concentrations and high solution pH. The molar fractions of the different pyrene species present in solution and the average number of pyrenes per SDS micelle were retrieved by global analysis of the pyrene monomer and excimer fluorescence decays, while the effect of shear rate on the solution viscosity was investigated by rheology as a function of SDS concentration. This study provides evidence that the change in the rheological behavior of the solution induced by the addition of SDS is due to the rearrangement of the hydrophobes that led to the disruption of the polymeric network. Additionally, the network relaxation time τ_r of the Py-HASE12 and SDS solutions was determined from the viscosity profiles obtained as a function of shear rate. The trend obtained by plotting τ_r as a function of SDS concentration was similar to that of the solution zero-shear viscosity. Finally, coupling of the rheometer and fluorometer enabled the acquisition of the fluorescence spectra of Py-HASE12 and SDS solutions under shear. The overlap of the fluorescence spectra acquired at shear rates ranging from 0.005 to 500 s^{-1} suggests that application of shear does not affect the fraction of aggregated pyrenes but

rather the nature of these aggregates that are formed intermolecularly at low shear and intramolecularly at high shear. This study represents one of the very few examples in the literature where the behavior of an AT probed at the molecular level by the fluorescence of the pyrene hydrophobe is correlated to the macroscopic behavior of the AT solution probed by rheology.^{21–23}

EXPERIMENTAL SECTION

Materials. Py-HASE12 was prepared by DOW Chemical Corp. using emulsion polymerization. The synthesis of Py-HASE12 has been described elsewhere.^{24,25} The chemical structure of the polymer is shown in Figure 1. It contained 12

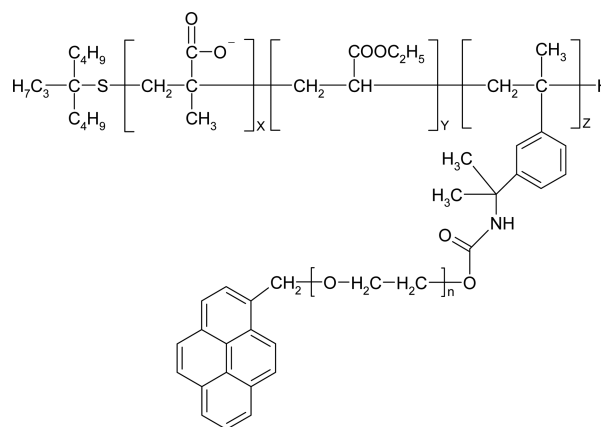


Figure 1. Chemical structure of Py-HASE12 with X:Y:Z = 40:59:0.2.

μmol of pyrene/g of polymer.^{21,26} The method of purification, the preparation of the aqueous polymer solution, and the determination of the polymer concentration in aqueous solution were conducted according to published procedures.^{21,25,26} SDS was purchased from EM Science and used as received.

Steady-State Fluorescence Measurements. All steady-state fluorescence emission spectra were obtained using a Photon Technology International (PTI) fluorometer with a continuous Ushio UXL-75Xe xenon arc lamp as the light source and a PTI 814 photomultiplier detection system. To avoid the inner filter effect, all fluorescence spectra were acquired with a triangular cell purchased from Hellma using the front face geometry.²⁷ The Py-HASE12 solutions were excited at a wavelength of 344 nm. The fluorescence intensities of the pyrene monomer (I_M) and excimer (I_E) were determined by integrating the fluorescence spectra from 372 to 378 nm for the pyrene monomer and from 500 to 530 nm for the pyrene excimer. The I_1/I_3 ratio which reflects the polarity of the microenvironment where pyrene is located was determined by taking the ratio of the fluorescence intensity of the first (I_1) and third (I_3) peaks of the pyrene monomer at 374 and 385 nm, respectively.

Time-Resolved Fluorescence Measurements. The fluorescence decay profiles were obtained by the time-correlated single-photon counting technique (TC-SPC) on an IBH time-resolved fluorometer using the front face geometry.²⁷ The excitation source was an IBH 340 nm LED used with a 500 kHz repetition rate. All fluorescence decays were acquired over 1024 channels ensuring a minimum of 20 000 counts at their maximum. All solutions were excited at 344 nm, and the emission wavelength of the pyrene monomer and excimer was

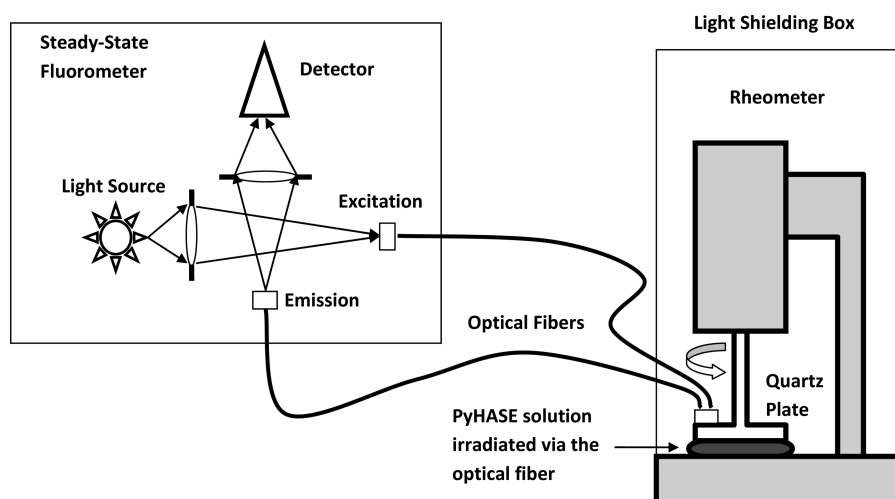


Figure 2. Experimental setup enabling the acquisition of fluorescence spectra of a Py-HASE solution under shear in the rheometer.

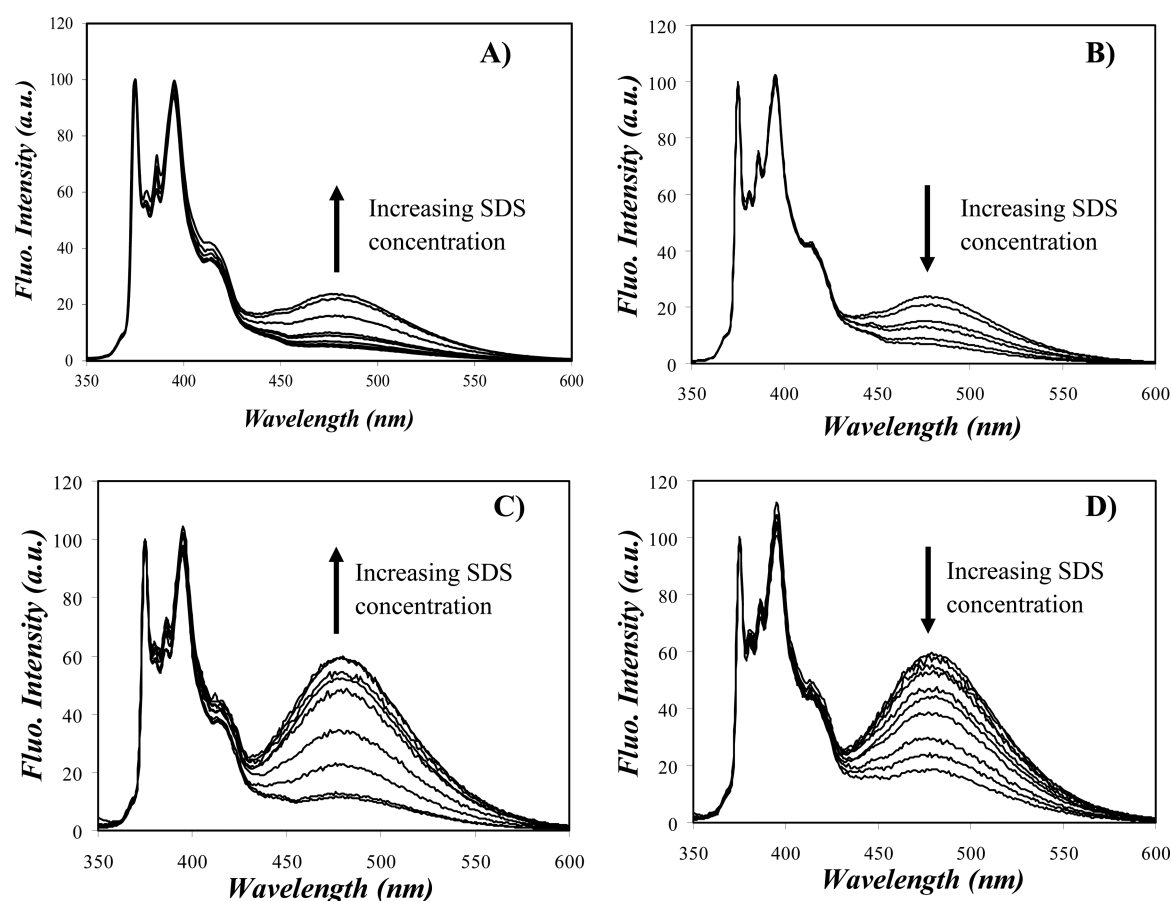


Figure 3. Fluorescence emission spectra of an 8 g/L Py-HASE12 solution (top) with SDS concentrations ranging (A) from 0 to 3.5 mM and (B) from 3.5 to 50 mM and a 57 g/L Py-HASE12 solution (bottom) with SDS concentrations ranging (C) from 0 to 10 mM and (D) from 10 to 100 mM. The solution is a 0.01 M Na_2CO_3 aqueous solution at pH 9. All spectra were normalized at 375 nm.

set at 375 and 510 nm, respectively. To reduce potential scattered light, cutoff filters at 370 and 495 nm were used to obtain the fluorescence decays of the pyrene monomer and excimer, respectively. A time per channel of 2.04 ns/channel was used for the acquisition of the monomer and excimer decays of all solutions. For the analyses of the decays, reference decays of degassed solutions of PPO [2,5-diphenyloxazole] in cyclohexane ($\tau = 1.42$ ns) for the pyrene monomer and BBOT

[2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene] in ethanol ($\tau = 1.47$ ns) for the pyrene excimer were used to obtain the instrument response function (IRF) via the MIMIC method.²⁸ The fluorescence decays were fitted globally according to the FBM and MFA using the Marquardt–Levenberg algorithm²⁹ as has been reported earlier.^{17–22} They are described in detail in the Supporting Information.

Viscosity Measurements. The viscosity of the 8 g/L Py-HASE12 aqueous solution was determined with an Ubbelohde viscometer at 25 ± 0.1 °C. The viscosity of the 57 g/L Py-HASE12 aqueous solution was measured at room temperature (26 ± 1 °C) with a stress-controlled Paar Physica DSR 4000 rheometer interfaced with a USD 200 tower. A parallel-plate geometry with a 25 mm diameter plate was used with a gap width of 1 mm for all samples. All data points were recorded within the sensitivity range of the instrument as specified by the manufacturer. The shear rate was varied from 0.0001 to 1000 s^{-1} . This range of shear rates was divided into three domains to account for the dramatic increase in the acquisition time of the rheological data for smaller shear rates and allow the operator to acquire the rheological data within a reasonable time. The three ranges of shear rates were from 0.0001 (or smaller) to 0.001 s^{-1} , from 0.001 to 0.1 s^{-1} (or 1 s^{-1}), and from 0.1 (or 1 s^{-1}) to 1000 s^{-1} . The rheological data with shear rates below 0.001 s^{-1} typically took more than 10 h to acquire. During this period, water was carefully added along the edge of the metal plate of the rheometer with a syringe to compensate for the gradual loss of water due to evaporation. The viscosity measurements in this range of shear rates were repeated two to three times to confirm their reproducibility. The data obtained at different times and over different ranges of shear rates were combined to yield a continuous profile of viscosity versus shear rate over the shear rate range of 0.0001 to 1000 s^{-1} .

Joint Rheometer–Fluorometer Measurements. The setup combining the steady-state fluorometer and the rheometer is illustrated in Figure 2.³⁰ The joint rheometer/fluorometer apparatus allows the simultaneous investigation of the Py-HASE12 solution by fluorescence and rheology. The rheometer was enclosed inside a light-proof box, and the light signals corresponding to the excitation and emission of the fluorometer were delivered via fiber optic cables. A parallel-plate geometry was used with a gap width of 1 mm between the 25 mm diameter quartz plate at the top and the metal plate at the bottom. The fluorescence spectra of the solutions were acquired at fixed shear rates after the solution viscosity had reached a constant value at the target shear rate. The detailed description for the joint setup and the specifications of the fiber optic cables have been presented earlier.³⁰

RESULTS AND DISCUSSION

Two Py-HASE12 concentrations of 8 and 57 g/L were used to investigate the interaction of SDS with the pyrene pendants of the polymer in 0.01 M Na_2CO_3 solution at pH 9. Under these conditions, the overlap concentration (C^*) of Py-HASE12 has been determined to equal 2.4 g/L. Consequently, both concentrations are greater than C^* , indicating that the results obtained with these concentrations describe the behavior of the polymer solution in the semidilute regime. Addition of SDS to the polymer solution altered the fluorescence spectrum of Py-HASE12, demonstrating that the SDS molecules interact with the pyrene groups. The fluorescence spectra of Py-HASE12 normalized at 374 nm are shown in Figure 3. The trends observed at both polymer concentrations are similar. For the 8 g/L Py-HASE12 concentration, panels A and B of Figure 3 indicate that the excimer intensity relative to that of the monomer increases for SDS concentrations increasing from 0 to 3.5 mM and decreases for SDS concentrations increasing from 3.5 to 50 mM. Similarly, the excimer intensity increases in Figure 3C for the 57 g/L Py-HASE12 concentration when the

SDS concentration is raised from 0 to 10 mM but decreases in Figure 3D when the SDS concentration is further increased from 10 to 100 mM. The fluorescence spectra shown in Figure 3 were used to determine the I_1/I_3 and I_E/I_M ratios according to the procedures described in the Experimental Section.

Figure 4 shows the I_E/I_M and I_1/I_3 ratios obtained for the two Py-HASE12 solutions as a function of SDS concentration. The

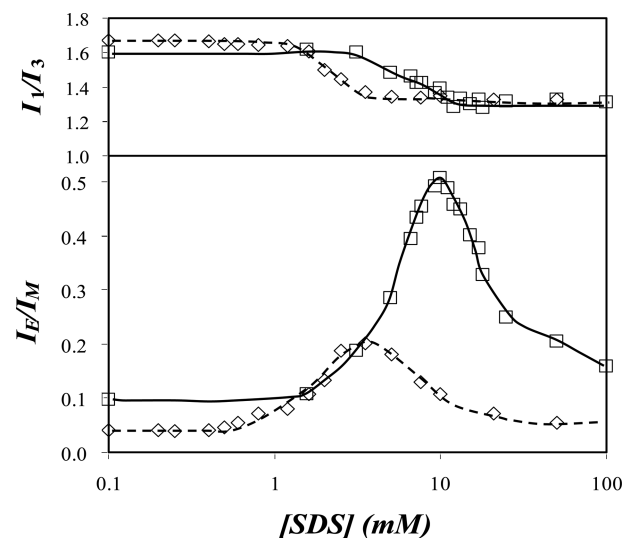


Figure 4. Plot of I_E/I_M (bottom panel) and I_1/I_3 (top panel) vs SDS concentration for Py-HASE12 at 8 g/L (\diamond) and 57 g/L (\square). All samples were excited at 344 nm.

I_1/I_3 ratio of molecular pyrene reflects the polarity of its local environment.³¹ Although this effect is lost if pyrene is substituted in the 1-position with an alkyl chain,³² the effect is partially restored if the methylene group in the β -position along the alkyl chain is replaced with a heteroatom such as the oxygen atom found in the chemical structure of Py-HASE12 shown in Figure 1.³³ Consequently, the I_1/I_3 ratio was used to assess the nature of the environment surrounding the pyrene labels of Py-HASE12 as SDS was added to the solution.

The intensity of the third peak (I_3) of the pyrene monomer emission in Figure 3 was found to increase with respect to the first peak (I_1) at intermediate SDS concentrations but remained constant at a lower or higher value for lower and higher SDS concentrations, respectively. This behavior is captured in the top panel of Figure 4. At low SDS concentration, the I_1/I_3 ratio equals 1.66 ± 0.01 and 1.61 ± 0.01 for the Py-HASE12 concentrations of 8 and 57 g/L, respectively. These I_1/I_3 ratios indicate that the pyrene pendants are located in the aqueous solution at low SDS concentration. The lower I_1/I_3 ratio obtained for the concentrated Py-HASE12 solution reflects the decrease in solution polarity due to the presence of a larger amount of polymer. At high SDS concentration, the I_1/I_3 ratio equals 1.33 ± 0.01 regardless of the polymer concentration. The drop in the I_1/I_3 ratio from ~ 1.61 – 1.66 at low SDS concentration to 1.33 at high SDS concentration reflects a decrease in the polarity of the local environment probed by pyrene, confirming that the pyrenyl pendants associate with the apolar dodecyl tails of the SDS surfactants as SDS is added to the Py-HASE12 solution.²² Since the pyrenyl labels probe the environment provided by the SDS surfactants at high SDS concentration, the pyrene pendants are now isolated from the rest of the solution and they only report on the interior of the

SDS micelles. Consequently, the pyrene labels no longer feel the change in polymer concentration and the I_1/I_3 ratio takes the same value of 1.33 for both polymer concentrations characteristic of the hydrophobic interior of the SDS micelles.

The I_E/I_M ratio describes qualitatively the efficiency of pyrene excimer formation, and its behavior is shown in the bottom panel of Figure 4 as a function of SDS concentration. At low SDS concentrations, most pyrene groups associate in solution and I_E/I_M remains constant, suggesting that SDS does not interact with the pyrene aggregates certainly due to electrostatic repulsions between the SDS surfactants (CMC = 4 mM in 0.01 M Na_2CO_3 aqueous solution at pH 9) and the Py-HASE12 polymer coils. This conclusion is similar to what has been observed by isothermal calorimetry.^{34,35} The low I_E/I_M ratio obtained in the plateau region corresponding to the low SDS concentration regime is due to the low fluorescence quantum yield of the pyrene excimer formed via the direct excitation of a pyrene aggregate.^{36–38} With more SDS added into the polymer solution, I_E/I_M increases as SDS targets the pyrene aggregates to form mixed micelles where the excimer is now generated by diffusive encounters between pyrene groups.

The hydrophobic alkyl tails of the SDS molecules enable sufficient mobility for the pyrenyl moieties to adopt the proper stacking required for excimer formation, thus endowing the excimer with a higher fluorescence quantum yield—around 4.5 times larger than the excimer generated from the direct excitation of pyrene aggregates.³⁶ After I_E/I_M peaks at the critical SDS concentrations of 3.5 and 10 mM for Py-HASE12 concentrations of, respectively, 8 and 57 g/L, further addition of SDS results in a decrease of I_E/I_M due to the distribution of the pyrene pendants into different mixed micelles which hinders the diffusional encounters of pyrene groups located in different micelles.

I_1/I_3 remains constant for SDS concentrations larger than the critical SDS concentration at the I_E/I_M peak ($[\text{SDS}]_p^{I_E/I_M}$), suggesting that the pyrene groups are all located in the less polar environment provided by the hydrophobic domains of the mixed micelles. Therefore, the drop in I_E/I_M past $[\text{SDS}]_p^{I_E/I_M}$ can be attributed to the decrease in the average number of pyrenes per mixed micelle in this range of SDS concentration.^{22,39,40} Figure 4 also shows that the profile of I_E/I_M versus SDS concentration obtained for the 57 g/L Py-HASE12 solution shifts to higher SDS concentration when compared with the profile obtained with the lower polymer concentration. These effects were also observed with a Py-HASE36 sample.²² They are due to the increase in the number of pyrene groups present in a more concentrated Py-HASE solution, which requires more SDS to interact with the more numerous pyrene pendants.

While the analysis of the fluorescence spectra acquired with solutions of Py-HASE12 and SDS provides a qualitative description of the processes affecting the hydrophobic pyrenyl moieties in solution, quantitative information about the actual molar fractions of pyrene species present in solution can be obtained through the analysis of the monomer and excimer fluorescence decays. To this end, the monomer and excimer fluorescence decays of Py-HASE12 were acquired at both polymer concentrations with different SDS concentrations. The decays were fitted globally with the FBM and MF analysis which is described in the Supporting Information. The fits were good with χ^2 smaller than 1.30, and residuals and autocorrelation functions of the residuals randomly distributed around zero. The parameters including the decay times and

pre-exponential factors retrieved from the analyses are listed in Table S1 of the Supporting Information. According to these parameters, the molar fractions of aggregated pyrenes (f_{agg}), pyrenes forming excimer by diffusional encounter (f_{diff}), and isolated pyrenes that do not form excimer (f_{free}) were determined using eqs 6–15 according to procedures described in previous papers.^{20,26,41} The fractions are listed in Table S2 (Supporting Information) and plotted as a function of SDS concentration in Figure 5. Both FBM and MF analyses yielded

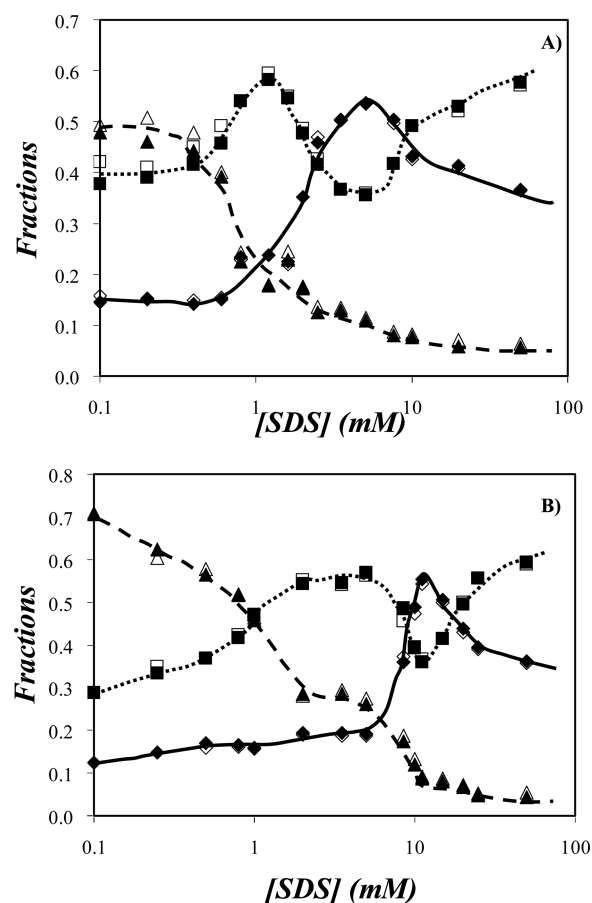


Figure 5. Fractions f_{diff} (◆ and ◇), f_{free} (■ and □), and f_{agg} (▲ and △) as a function of SDS concentration for Py-HASE12 at polymer concentrations of (A) 8 and (B) 57 g/L. The filled and hollow symbols indicate that the pyrene monomer and excimer decays were globally fitted with the FBM or MF analysis, respectively.

identical trends when the molar fractions f_{diff} , f_{free} , and f_{agg} were plotted as a function of SDS concentration, demonstrating excellent agreement between the two analyses as found in other studies.^{20,22}

At small SDS concentrations, Figure 5 shows that the most populated state of the pyrene pendants is that of the aggregated pyrenes and that the molar fraction f_{agg} increases from 0.48 (± 0.02) to 0.63 (± 0.03) with an increase in Py-HASE12 concentration from 8 to 57 g/L. With more SDS added to the solution, f_{agg} drops dramatically, suggesting that SDS is targeting the pyrene aggregates. At high SDS concentrations, f_{agg} decreases to around 0.05 (± 0.01) for both polymer solutions, confirming the disappearance of the pyrene aggregates for large SDS concentrations where the pyrene groups are solvated inside mixed micelles constituted of themselves and SDS molecules. However, f_{agg} remains larger

than zero at high SDS concentration, suggesting that some residual pyrene aggregation is still present in the mixed micelles, as has been found previously.²² Figure 5 also indicates that, at low SDS concentrations, not all pyrene excimer is formed by direct excitation of the pyrene aggregates, and that some pyrene excimer is generated by diffusive encounters between excited and ground-state pyrenes. The fraction of pyrene forming excimer via diffusion, f_{diff} , is small at low SDS concentrations found to equal 0.14 (± 0.01) and 0.11 (± 0.01) for polymer concentrations of 8 and 57 g/L, respectively.

With an increase in SDS concentration, f_{diff} increases and peaks at an SDS concentration ($[\text{SDS}]_p^{\text{diff}}$) where most pyrene groups are incorporated into mixed micelles and pyrene excimer is formed by diffusion. The molar fraction f_{diff} at $[\text{SDS}]_p^{\text{diff}}$ of 5.1 and 11.1 mM was found to equal 0.53 (± 0.01) and 0.55 (± 0.00) for the polymer concentrations of 8 and 57 g/L, respectively. The SDS concentration at $[\text{SDS}]_p^{\text{diff}}$ is very close to $[\text{SDS}]_p^{I_E/I_M}$ found to equal 3.5 and 10 mM at Py-HASE12 concentrations of 8 and 57 g/L. Increasing the SDS concentration past $[\text{SDS}]_p^{\text{diff}}$ results in a drop in f_{diff} as the pyrene pendants distribute themselves into different micelles, as reflected by the decrease in the I_E/I_M ratio observed in Figure 4 for high SDS concentrations. At very high SDS concentration, pyrene excimer is still formed by diffusion but with a reduced number of pyrene pendants, since a majority of pyrene pendants are isolated in individual mixed micelles (f_{free} is large for large SDS concentrations in Figure 5).

Although pyrene is a hydrophobe that tends to aggregate in aqueous solution, a significant fraction of pyrenes that do not form excimer, f_{free} , is found at low SDS concentrations. The values for f_{free} at low SDS concentration equal 0.38 (± 0.03) and 0.26 (± 0.03) for the polymer concentrations of 8 and 57 g/L, respectively. The larger f_{free} value obtained at the lower Py-HASE12 concentration is expected, as it reflects a decrease in intermolecular aggregation following a decrease in pyrene concentration. With a continuous increase in SDS concentration, the value of f_{free} first increases, then decreases, before increasing again past the SDS concentration where f_{diff} peaks ($[\text{SDS}]_p^{\text{diff}}$). This behavior can be rationalized as follows. At low SDS concentration, SDS targets the pyrene aggregates and expels pyrene moieties into the bulk solution where they act as isolated pyrenes.²² With more SDS added to the solution, these free pyrene groups are “pulled back” into the mixed micelles which are generated between SDS molecules and the pyrene pendants. For SDS concentrations larger than $[\text{SDS}]_p^{\text{diff}}$, f_{free} increases because more pyrene groups are isolated in different SDS micelles. This rationale has been corroborated by earlier surface tension experiments²² and has also been observed for the interactions between HEUR and SDS.⁴²

As stated earlier, the interactions between HMWSPs and surfactants result in solutions that exhibit particularly interesting viscoelastic properties.^{39,43–47} Such properties were observed for the Py-HASE12 solution having a concentration of 57 g/L whose zero-shear viscosity was found to increase dramatically upon SDS addition. Figure 6 shows the variation of the solution viscosity as a function of shear rate for a 57 g/L aqueous solution of Py-HASE12 with varying concentrations of SDS. In order to correlate the trends obtained from the rheological behavior of the polymer solutions and its associative behavior characterized by fluorescence, the SDS concentrations used for the rheological experiments covered the whole range of SDS concentrations used in the fluorescence experiments (see Figure 3C). A small

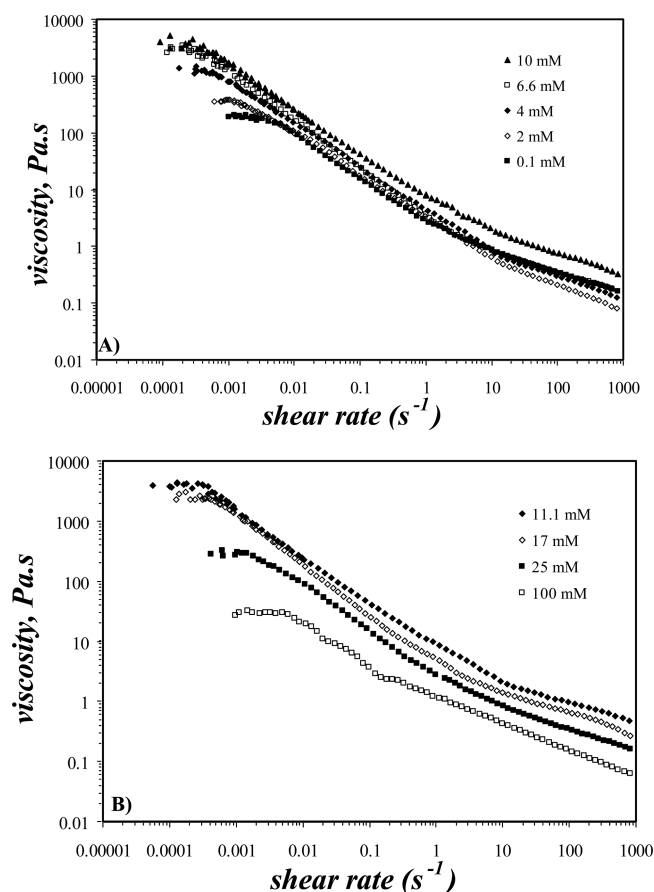


Figure 6. Steady-shear viscosity as a function of shear rate for Py-HASE12 at 57 g/L with SDS concentrations ranging from (A) 0.1 to 10 mM and (B) 11.1 to 100 mM.

Newtonian regime is observed for all samples at low shear rates where the viscosity remains constant with shear rate and is taken as the zero-shear viscosity, η_0 . No indication of shear-thickening was observed in the viscosity profiles shown in Figure 6.

Figure 6 demonstrates that the addition of SDS up to a concentration of 11.1 mM for the 57 g/L Py-HASE12 aqueous solution increases η_0 20-fold from 200 to 4000 Pa·s. Further addition of SDS results in a dramatic decrease in η_0 to 30 Pa·s for an SDS concentration of 100 mM. Figure 6 also shows that, when shear is applied to the solutions, the viscosity remains constant at low shear rate before decreasing dramatically with increasing shear rate. This effect is referred to as shear-thinning, which is a common effect for associating polymers and has been widely reported before.^{9,13,21,45–48}

Generally, shear-thinning is due to a transition from intermolecular to intramolecular associations resulting from the “pull-out” and rearrangement of the hydrophobes. The results shown in Figure 6 have two implications: first, pyrene is an efficient hydrophobe that behaves similarly to other non-fluorescent hydrophobes such as the alkyl chains typically used in commercial HASEs as has been already shown for pyrene-labeled HASE²¹ and HEUR;²⁶ second, interactions between SDS and the pyrene groups result in a progressive change in the rheological behavior of the polymer solution. Figure 6 also demonstrates that shear-thinning occurs at a lower onset shear rate for solutions having a higher viscosity, an observation which had been made earlier for solutions of Py-HASEs having

different pyrene contents²¹ and for solutions of SDS and HASE with a C₂₀H₄₁ hydrophobe.⁴⁷

To better correlate the results obtained by the fluorescence and viscosity measurements, the I_E/I_M ratios, the average number of pyrene pendants per mixed micelle, $\langle n \rangle$, retrieved from the global analysis of the monomer and excimer decays of the Py-HASE12 solutions using the FBM, and the zero-shear viscosity were plotted together in Figure 7 as a function of SDS

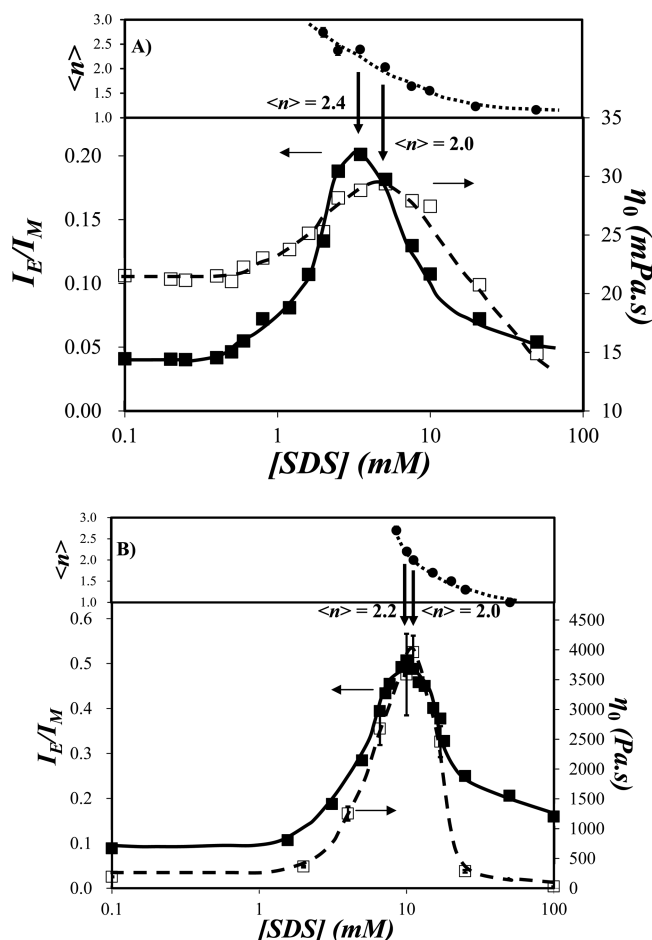


Figure 7. Values of $\langle n \rangle$ (top panel) and I_E/I_M and η (bottom panel) plotted as a function of SDS concentration for a Py-HASE12 concentration of (A) 8 and (B) 57 g/L. Symbols: $\langle n \rangle$ (●), I_E/I_M (■), and η_0 (□).

concentration for the two polymer concentrations. At a Py-HASE12 concentration of 8 g/L, an Ubbelohde viscometer was used to measure η_0 , since the solutions were much less viscous than the 57 g/L Py-HASE12 solutions. The viscosity profiles obtained for both polymer concentrations as a function of SDS concentration are typical of solutions where interactions between a surfactant and HMWSPs take place.^{22,39,44}

At low SDS concentrations, the associations between pyrene groups are most likely intrapolymeric in nature.^{22,39} The addition of SDS enhances intermolecular pyrene excimer formation which reflects enhanced networking and results in an increase in solution viscosity. Beyond the SDS concentration where the viscosity peaks, the hydrophobes are separated between different micelles which reduces the networking ability of Py-HASE12. As a result, the viscosity drops progressively to values that are lower than those obtained for the Py-HASE12 solution without SDS, as shown in Figure 7 for both polymer

concentrations. In Figure 7A, the error bars acquired with the 8 g/L Py-HASE12 solution containing SDS are not shown because they are all smaller than the symbols.

For SDS concentration around ($[SDS]_p^{I_E/I_M}$), the I_1/I_3 ratios shown in Figure 4 indicate that the pyrene pendants are incorporated into the SDS micelles where they distribute themselves randomly according to a Poisson distribution. The solubilization of the pyrene pendants in the interior of the mixed micelles is also reflected by the low f_{agg} value obtained at SDS concentrations larger than ($[SDS]_p^{I_E/I_M}$) in Figure 5. Consequently, the parameter $\langle n \rangle$ retrieved from the analysis of the fluorescence decays with the FBM at SDS concentrations greater than ($[SDS]_p^{I_E/I_M}$) yields the average number of pyrenes per mixed micelles. It is plotted in Figure 7 as a function of SDS concentration.

Starting from ($[SDS]_p^{I_E/I_M}$), $\langle n \rangle$ decreases from a value of 2.8 to a value of 1.0 as the SDS concentration increases. Interestingly, $\langle n \rangle$ equals ~2.0 for those SDS concentrations where η_0 passes through a maximum. The optimal networking ability of a HMWSP in the presence of surfactant micelles is usually attained when each mixed micelle contains 2 hydrophobes per micelle on average, as has been observed for mixtures of hydrophobically modified hydroxyethylcellulose and different alkyltrimethylammonium bromide surfactants by using pyrene as an external probe.⁴⁰ The fact that the $\langle n \rangle$ value of 2.0 found at an SDS concentration where η_0 peaks in the present experiments and earlier ones²² represents a nice correlation between the results obtained by fluorescence and rheology. Past the SDS concentration of $[SDS]_p^{I_E/I_M}$, $\langle n \rangle$ appears to decrease toward unity at high SDS concentration.

The relaxation time (τ_r) of the polymeric network probed by rheology reflects the relaxation of individual polymer chains. Under shear, relaxation of the polymeric network results in a decrease in solution viscosity. Since the rheological behavior of HASEs is much more complex than that of HEURs, τ_r needed to be approximated. In the case of the 57 g/L Py-HASE12 solution, τ_r for each SDS concentration was taken as the inverse of the shear rate obtained at the intercept between the horizontal line defined by the zero-shear viscosity η_0 and the oblique line where η scales as $\dot{\gamma}^{-\alpha}$ corresponding to the shear-thinning part of the plots given in Figure 6. A plot of τ_r as a function of SDS concentration is presented in Figure 8. The

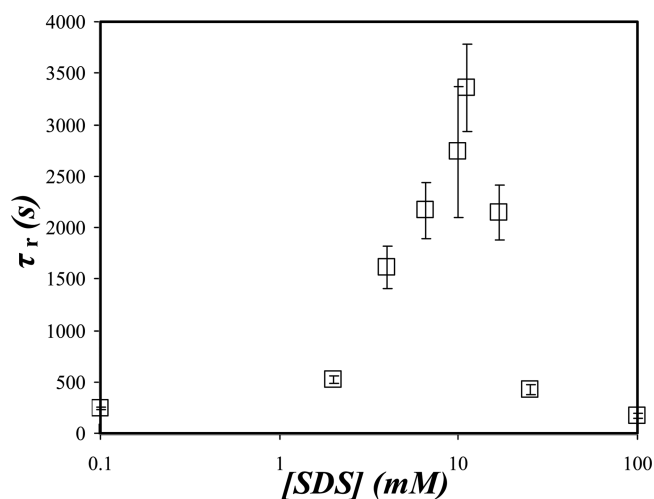


Figure 8. Plot of τ_r as a function of SDS concentration for the 57 g/L Py-HASE12 solution.

trend obtained for τ_r is similar to that obtained for the solution viscosity shown in Figure 7B. The data shown in Figure 8 indicate that τ_r increases with increasing SDS concentration until it passes through a maximum at an SDS concentration of 11.1 mM where all pyrene pendants are located in the hydrophobic domains formed by SDS. Further increase in SDS concentration results in a significant decrease in τ_r .

The trends presented in Figures 5B, 7B, and 8 suggest that, when SDS is added into the Py-HASE12 solution, SDS molecules interact with the pyrene aggregates by replacing pyrene units that are ejected into the solution. This process enhances their ability to network by interacting with other pyrenyl pendants or mixed micelles, and in turn results in the observed increase in the viscosity of the solution and the relaxation time of the polymeric network. At higher SDS concentrations, the pyrenes are isolated in different hydrophobic junctions formed by SDS in a process that decreases the average number $\langle n \rangle$ of hydrophobes per junction. While interactions between the pyrenyl pendants and the SDS molecules first promote intermolecular bridging of the polymeric network, a point is reached where further increase in [SDS] disrupts the network and both solution viscosity and network relaxation time decrease.

Since the shear-thinning effect shown in Figure 6 results from a rearrangement of the conformation of the polymer chains in solution, the setup shown in Figure 2 was used to acquire the fluorescence spectra of the polymer solutions under shear in an effort to probe this rearrangement. The samples with a Py-HASE12 concentration of 57 g/L were used at SDS concentrations of 0.1, 6, 11.1, and 17 mM which cover the whole range of SDS concentrations shown in Figure 7B. The steady-state emission spectra of the Py-HASE12 solutions were acquired for the SDS concentrations mentioned above using the joint setup at shear rates ranging from 0 to 500 s^{-1} . Figure 9 presents the fluorescence spectra obtained at a SDS concentration of 11.1 mM, which is the concentration where η_0 peaks ($[\text{SDS}]_p^{\eta_0}$) in Figure 7B and an optimal polymeric network is formed according to the $\langle n \rangle$ value of 2.0 retrieved from the analysis of the fluorescence decays. For comparison purposes, the fluorescence spectrum of the solution was also

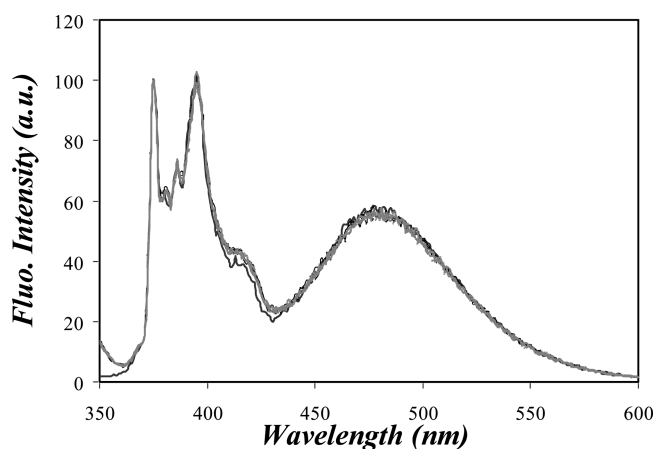


Figure 9. Fluorescence emission spectra normalized at 375 nm of 57 g/L Py-HASE12 solution with a SDS concentration of 11.1 mM acquired in a triangular fluorescence cell (thick black solid line) and with shear rates of 0 (thin black solid line), 0.005 (black dashed line), 0.05 (black dotted line), 1 (gray solid line), 10 (gray dashed line), and 500 (gray dotted line) s^{-1} .

acquired in the spectrofluorometer using a triangular quartz cell having the front face geometry to minimize the inner filter effect. All spectra were normalized at 375 nm.

As demonstrated in Figure 9, the emission fluorescence spectra acquired at all shear rates with the setup shown in Figure 2 overlapped perfectly, even with the one acquired with the fluorescence cell. In this latter case, the acquisition of the fluorescence spectrum was carried out without an optical fiber, resulting in less light scattering being detected at 350 nm. Since the fluorescence spectra reflect the arrangement of the pyrene pendants in the solution, this lack of change in the fluorescence spectra is remarkable, as it occurs over a range of shear rates where the solution viscosity decreases by over 4 orders of magnitude, from 4000 Pa·s at $\dot{\gamma} \sim 0 \text{ s}^{-1}$ to 0.4 Pa·s at $\dot{\gamma} = 500 \text{ s}^{-1}$.

The ratios I_E/I_M and I_1/I_3 determined from the emission spectra of the Py-HASE12 solution at four SDS concentrations were plotted in Figure 10 as a function of shear rate. Again,

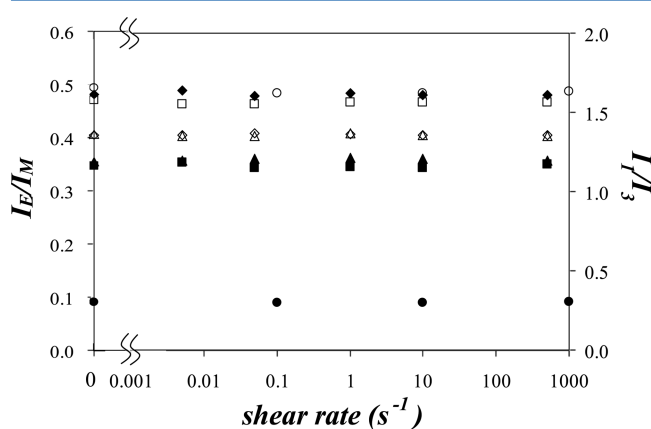


Figure 10. I_E/I_M (filled symbols) and I_1/I_3 (hollow symbols) of 57 g/L Py-HASE12 solution with SDS concentrations of 0.1 (circle), 6.0 (square), 11.1 (diamond), and 17 (triangle) mM.

although the viscosity at each SDS concentration dropped by several orders of magnitude with an increase in shear rate (see Figure 6), the I_E/I_M and I_1/I_3 ratios were all independent of shear rate. This result suggests that the overall arrangement of the pyrene pendants in the solution does not change and that the polarity of the local environment surrounding the pyrene groups remains constant when the solution is under shear. These results are similar to those obtained in other experiments carried out by this laboratory using the joint setup with the rheometer and the steady-state and time-resolved fluorimeters for solutions of Py-HASE65 (a HASE sample having the chemical structure shown in Figure 1 with a pyrene content of $65 \mu\text{mol}\cdot\text{g}^{-1}$) at various polymer concentrations.³⁰ These experiments also showed that f_{agg} remained constant at different shear rates despite a significant change in the macroscopic viscosity of the solution.

The shear-thinning effect observed with the aqueous solutions of many ATs^{9,13,21,45–48} is believed to result from a transition between inter- to intramolecular hydrophobic association, and a similar phenomenon is expected to occur for the aqueous solutions of Py-HASE12 and SDS. At extremely low shear rates, the polymer network of Py-HASE12 is not disrupted and the hydrophobic aggregates are unaffected. Therefore, the viscosity does not change and the sample exhibits the Newtonian plateau regime observed in Figure 6. At

a higher shear rate, the polymeric network is extended due to the stretching of the polymer coils by shear. Under those conditions, the physically cross-linked network is deformed until the hydrophobes are pulled out from the hydrophobic junctions. With more hydrophobes escaping from the junctions that bridge the polymer chains intermolecularly, the network collapses, which is accompanied with a shear-thinning effect. However, the hydrophobes which are pulled out from the aggregates are not isolated in solution. The rearrangement of the polymeric network triggered by the applied shear induces these hydrophobes to form intramolecular associations on a time scale that is too fast to be probed by our experimental setup. This process has been discussed by Winnik's group with HEUR polymers which are known to form flowerlike micelles in aqueous solution.^{10–12} For HEURs, the shear-thinning effect can be described as a “bridge-to-loop” transition.^{11,49} At extremely high shear rates, the hydrophobes of the bridging chains are pulled out from the interpolymeric junctions but the overall number of micelles remains the same.^{11,12} These micelles whose hydrophobic cores are severed from the network no longer contribute to the solution viscosity. Indeed, the results shown in Figure 10 suggest that this transition from inter- to intramolecular pyrene association does not affect the association between the hydrophobic pyrenes as the fluorescence spectra of the Py-HASE12 solutions remain unchanged. A schematic describing the change of the Py-HASE polymeric network with SDS under shear is shown in Figure 11. The polymeric network is disrupted under shear via

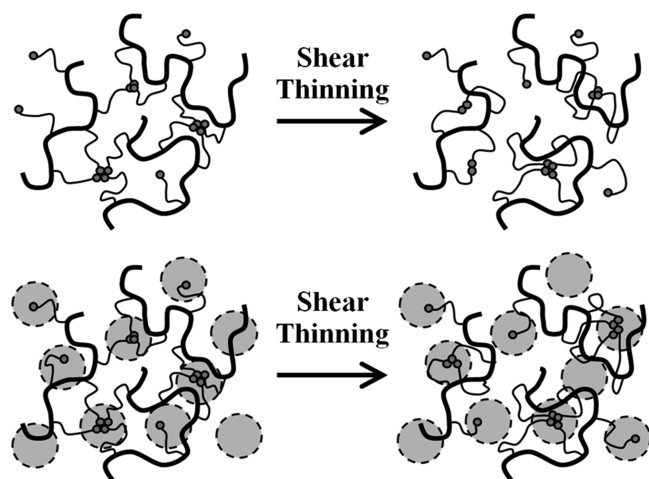


Figure 11. Proposed mechanism for the transition of inter- to intramolecular pyrene interaction of PyHASE solution with and without SDS under a shearing force.

the “pull-out” of pyrene pendants from intermolecular pyrene aggregates or mixed micelles followed by the rearrangement of the polymer coils under shear to enhance intramolecular pyrene interactions. However, this inter- to intramolecular transition does not affect the balance between free pyrene and aggregated pyrene species. Since the balance between isolated and excimer forming pyrenes remains the same under shear regardless of whether pyrene excimer formation occurs intra- or intermolecularly, the I_E/I_M ratio is unaffected. Furthermore, upon addition of SDS, the inter- to intramolecular transition does not affect the microenvironment that pyrene is probing. Therefore, the I_1/I_3 ratio is also unaffected. Consequently, the fluorescence emission spectra remain unchanged under shear.

As the purpose of this study was to correlate the rheological behavior of the Py-HASE-12 solution to the fluorescence response of the pyrene hydrophobes, simple profiles of solution viscosity versus steady shear rate were acquired and presented in Figure 6. It is worth noting that the complex rheological behavior of HASE aqueous solutions has been characterized by probing other aspects of the viscoelasticity of HASE solutions, for example, with oscillatory rheological measurements^{21,46–49} and the superposition of oscillations on steady shear flow.^{13,46–48,50,51} In particular, these latter experiments have revealed the existence of two viscosity regimes for aqueous HASE solutions defined by two critical shear stresses.⁴⁸ The relaxation time of a HASE network was also found to decrease with increasing shear stress.⁴⁸ The interactions of HASEs with different non-ionic surfactants composed of an ethoxylated nonylphenol chain (NPEO_x, where x represents the number of ethylene oxide units) have also been investigated.^{46,50,51} The profiles of zero-shear viscosity versus NPEO_x concentration matched very closely those presented in Figure 7 as a function of SDS concentration, as long as the number x of ethylene oxide units was greater than 6. NPEO₆ was found to be too hydrophobic, and the NPEO₆–HASE mixtures resulted in a markedly different profile. The similarity of the profiles obtained for the zero-shear viscosity and the concentration of SDS and NPEO_x surfactants suggests that the non-ionic surfactants interact with the HASE hydrophobes in the same manner as SDS does, as presented in this study.

CONCLUSIONS

The interactions between Py-HASE12 and the surfactant SDS were investigated at Py-HASE12 concentrations of 8 and 57 g/L in the semidilute regime. The FBM and MF analyses were applied to globally fit the pyrene monomer and excimer fluorescence decays acquired over a wide range of SDS concentrations. The molar fractions representing the different excited pyrene species in solution, namely, f_{diff} , f_{free} , and f_{agg} , were determined, and the results obtained from the two analyses were identical (see Figure 5). At low SDS concentrations, no binding occurs between SDS and the pyrene pendants and most pyrene groups form aggregates. With more SDS being added, SDS targets the pyrene aggregates to produce more isolated pyrenes. At higher SDS concentrations, SDS starts to form mixed micelles with the pyrene pendants and the pyrene aggregates are further decomposed until all pyrene pendants are incorporated into mixed micelles. This behavior results in an increase of the solution viscosity and of the efficiency of pyrene excimer formation, as shown in Figure 7. With excess SDS, the pyrene pendants distribute themselves into different mixed micelles and more isolated pyrenes are generated, severing interpolymeric associations. At this stage, both pyrene excimer formation and solution viscosity were found to decrease significantly with increasing SDS concentration.

For both Py-HASE12 concentrations, the average number of pyrenes per micelle, $\langle n \rangle$, was determined to equal 2.4 and 2.2 at $[SDS]_p^{I_E/I_M}$, suggesting that this $\langle n \rangle$ value represents the maximum pyrene loading capacity of the mixed micelles where most pyrene excimer is formed by diffusion and the least isolated pyrenes are present (see f_{free} in Figure 5). The viscosity of both Py-HASE12 solutions having a concentration of 8 and 57 g/L was found to reach a maximum value at an SDS concentration where $\langle n \rangle$ equals ~ 2.0 in Figure 7, as would be expected for the formation of an optimal polymeric network.

Adding SDS into the 57 g/L Py-HASE12 solution significantly increased the zero shear viscosity of the solution. As often found with AT solutions, shear-thinning was observed at high shear rate in Figure 6 for all solutions studied. However, no change in the fluorescence spectra could be detected as a function of shear rate in Figures 9 and 10 despite the dramatic shear-thinning undergone by the Py-HASE12 solution. The decrease in viscosity is attributed to the polymeric network experiencing a transition from inter- to intramolecular hydrophobic association as increasing shear is applied to the solution. A rationale was proposed in Figure 11 to explain why this transition does not result in a change of the fluorescence spectra. It was suggested that, when shear is applied to the solution, the rearrangement of the chains from interpolymeric bridges to intramolecular loops takes place in a manner that does not affect the balance between those pyrenes that form excimer and those that do not, resulting in a constant I_E/I_M ratio regardless of the amount of shear being applied to the solution. These conclusions could be reached thanks to the dual setup shown in Figure 2 that allows fluorescence measurements to be conducted on the AT solution while it is being sheared. These experiments represent one of the very few examples in the literature where the behavior of an AT solution under shear is being probed simultaneously at the molecular and macroscopic level.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed description of the analysis of the fluorescence decays based on the FBM and MFA and tables summarizing the parameters retrieved from the fits of the fluorescence decays. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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