Interactions between a Series of Pyrene End-Labeled Poly(ethylene oxide)s and Sodium Dodecyl Sulfate in Aqueous Solution Probed by Fluorescence

Shaohua Chen and Jean Duhamel

Institute for Polymer Research, Department of Chemistry, University of Waterloo

Introduction

Hydrophobically modified ethoxylated urethanes (HEUR) polymers represent a very important family of commercial associative thickeners (AT) which have found many applications.[1,2] In laboratory setting, hydrophobically end-capped monodisperse poly(ethylene oxide)s (PEOs) are often used as model HEUR polymers having a well-defined chemical architecture. The hydrophobic chromophore pyrene has also been used as a model hydrophobe in a number of instances to label the ends of PEO chains and fluorescence has been applied to investigate the behavior of pyrene end-labeled PEOs (PEO-Py$_2$) in aqueous solution.[3-6] The use of pyrene as a hydrophobic label has two major advantages. First, an excited pyrene can form an excimer upon encounter with a ground-state pyrene.[7] The pyrene excimer emits at wavelengths that are different from the emission of the excited pyrene monomer so that excimer emission can be easily detected and used to provide information about pyrene association.[8] Second, the emission spectrum of the excited pyrene monomer is sensitive to the polarity of its microenviroment and can be used to identify the nature of the environment where pyrene is located.[9]

Although the interactions between PEO-Py$_2$ and the surfactant sodium dodecyl sulfate (SDS) have been previously investigated in aqueous solution using steady-state fluorescence,[3-6] the details of these interactions are still not fully understood due to the following reasons. First, analysis of the steady-state fluorescence spectra only yields qualitative information about the pyrene labels and this information cannot be easily exploited to describe the kinetics of pyrene excimer formation, and consequently, the hydrophobic interactions between pyrene groups and SDS in solution. Second, all earlier studies focused on the behavior of a single PEO-Py$_2$ sample and did not report on the effect of chain length on these interactions. Third, no detailed investigation has been carried out on the behavior of PEO-Py$_2$ constructs at high SDS concentrations where SDS micelles are formed. This study provides an in-depth investigation of the parameters obtained from the analysis of the fluorescence decays acquired with solutions of a series of PEO(X)-Py$_2$ (Scheme 1) and SDS at various SDS concentrations.
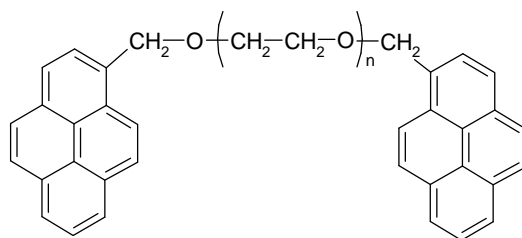
Scheme 1. Chemical structure of the PEO(X)-Py$_2$ samples. n equals 45, 113, 227, and 375 for PEO(X)-Py$_2$ with X = 2, 5, 10, and 16.5 K, respectively.

Steady-state Fluorescence Experiments

    All fluorescence experiments with the PEO(X)-Py$_2$ samples were carried out with a pyrene concentration of 2.5×10^{-6} M. The trends of the fluorescence spectra observed with all PEO(X)-Py$_2$ samples are similar. Figure 1 shows the trends of the I_E/I_M and I_1/I_3 ratios obtained for all PEO(X)-Py$_2$ samples as a function of SDS concentration.
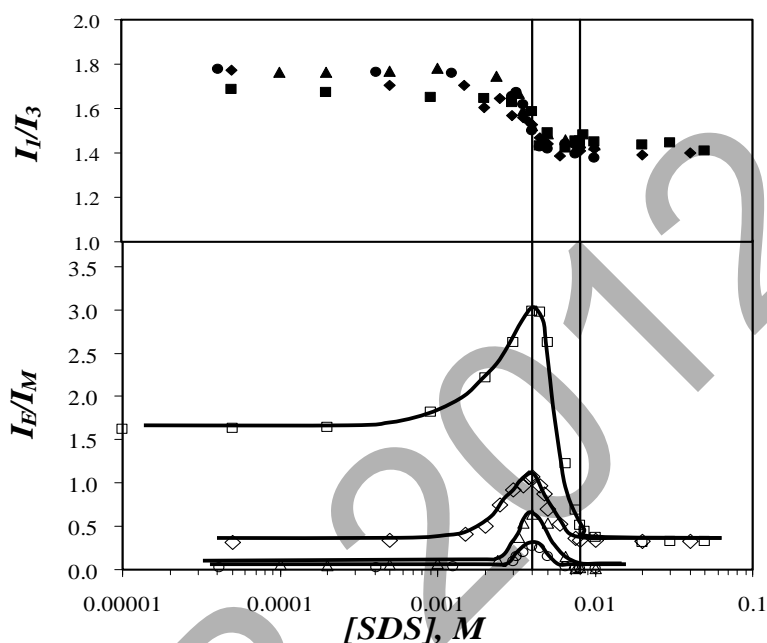

Figure 1. Plot of I_E/I_M (bottom panel) and I_1/I_3 (top panel) vs. SDS concentration for PEO(2K)-Py$_2$ (square), PEO(5K)-Py$_2$ (diamond), PEO(10K)-Py$_2$ (triangle) and PEO(16.5K)-Py$_2$ (circle).

    The change in I_1/I_3 indicates that the pyrene pendants experience a more apolar environment as SDS is added to the solution. 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 1 as a function of SDS concentration. At very low SDS concentrations, I_E/I_M remains constant for each PEO(X)-Py$_2$ sample. The I_E/I_M ratio decreases dramatically with polymer molecular weight due to a decrease in the concentration of pyrene aggregates present in solution with increasing PEO chain length.[10] At low SDS concentrations, the I_E/I_M ratio of all PEO(X)-Py$_2$ samples increases with increasing SDS concentration and peaks at 4 mM. I_E/I_M was found to increase as SDS targeted the pyrene aggregates to form mixed micelles. The alkyl tails of the SDS molecules bound to the pyrene aggregates reduce the strength of the pyrene-pyrene interactions which enabled the pyrene groups to form excimer by diffusion with a higher fluorescence quantum yield than that of the excimer generated by the direct excitation of a pyrene aggregate. However, a 2.5×10^{-6} M solution of a PEO(2K) chain labeled at

a single end with pyrene (PEO(2K)-Py$_1$) that did not form pyrene aggregates also exhibited an increase in I_E/I_M with increasing SDS concentration.[11] For the PEO(2K)-Py$_1$ construct that cannot form intramolecular pyrene excimer, the increase in I_E/I_M is certainly due to intermolecular pyrene excimer formation that is being promoted upon addition of SDS. Therefore, the increase in I_E/I_M observed in Figure 1 results from a combination of both the low fluorescence quantum yield of the pyrene excimer formed by direct excitation of a pyrene aggregate and intermolecular pyrene excimer formation induced by the presence of SDS which brings together different polymer chains. After I_E/I_M peaks at [SDS] = 4 mM, 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 between pyrene groups located in different micelles. I_1/I_3 remains constant for SDS concentrations larger than 4 mM indicating that the pyrene groups are located in the hydrophobic interior of the mixed micelles. Since all pyrene groups are properly solvated inside the SDS micelles, the drop in I_E/I_M past [SDS] = 4 mM can be attributed to the decrease in the average number of pyrenes per mixed micelle in this range of SDS concentration.[10,11] For SDS concentrations larger than the CMC of SDS in water (~ 8 mM), the I_E/I_M ratio of all PEO(X)-Py$_2$ samples plateaus. However, the I_E/I_M ratios of PEO(2K)-Py$_2$ and PEO(5K)-Py$_2$ plateau at a larger value than those of PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$ with the I_E/I_M ratios of the latter taking values close to zero. This observation is a result of the PEO(2K)-Py$_2$ and PEO(5K)-Py$_2$ being too short to allow the SDS micelles to separate the two pyrene end-groups into two different SDS micelles. Consequently, pyrene excimer is formed intramolecularly by diffusional encounter inside a same SDS micelle. However, the PEO chains of PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$ being longer allow the pyrene groups to be isolated in different SDS micelles in a process that prevents any pyrene excimer formation.

Time-resolved Fluorescence Experiments

The monomer and excimer fluorescence decays of PEO(X)-Py$_2$ were acquired at different SDS concentrations. The decays were fitted globally with the "model free" (MF) analysis except for PEO(16.5K)-Py$_2$ at low SDS concentration. The fits of the decays were good with all χ^2 smaller than 1.30, and residuals and autocorrelation functions of the residuals randomly distributed around zero. The parameters obtained from the fits were used to determine the molar fractions of aggregated pyrenes (f_{E0}), pyrenes forming excimer by diffusional encounter (f_{diff}), isolated pyrenes that do not form excimer (f_{free}) and the average rate constant of excimer formation ($<k>$). The fractions f_{diff}, f_{free}, and f_{E0} and the rate constant $<k>$ are plotted as a function of SDS concentration in Figure 2A-D.
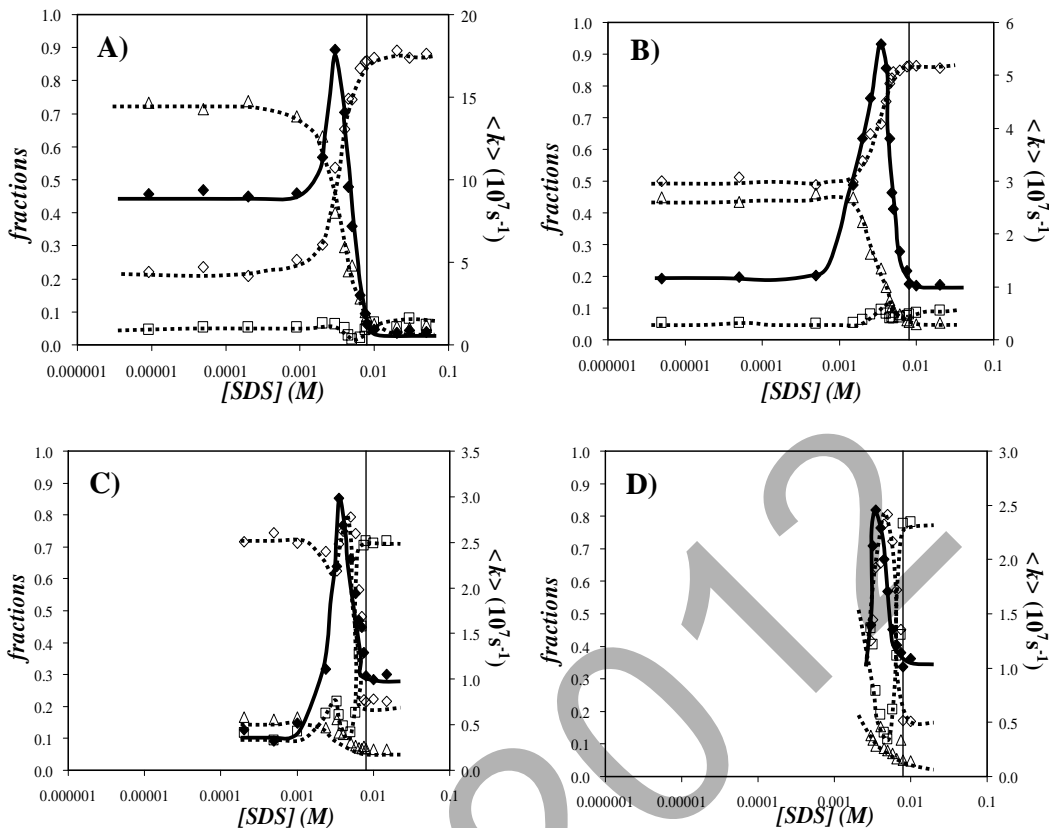
Figure 2. Fractions f_{diff} ($\diamondsuit$), f_{free} ($\square$), and f_{E0} ($\triangle$) and $<k>$ ($\blacklozenge$) as a function of SDS concentration for (A) PEO(2K)-Py$_2$, (B) PEO(5K)-Py$_2$, (C) PEO(10K)-Py$_2$, and (D) PEO(16.5K)-Py$_2$. The vertical line represents the CMC of SDS in water.

At small SDS concentrations, Figure 2 shows that in water most of the pyrene pendants are associated for PEO(2K)-Py$_2$ and the molar fraction f_{E0} decreases with increasing PEO chain length. For each sample, addition of a sufficient amount of SDS to the solution results in a drop of f_{E0} suggesting that SDS is disrupting the pyrene aggregates. At high SDS concentrations, f_{E0} decreases to around 0.05 for all PEO(X)-Py$_2$ samples confirming the disappearance of the pyrene aggregates for large SDS concentration. Figure 2 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 an excited and a ground-state pyrene. With an increase in SDS concentration, f_{diff} increases for PEO(2K)-Py$_2$ and PEO(5K)-Py$_2$ until it reaches a maximum value at the CMC of SDS in water above which it remains constant. However for PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$, f_{diff} decreases after passing through a maximum at an SDS concentration of 5 mM. Further addition of SDS results in a drop in f_{diff} as the pyrene pendants distribute themselves into different micelles in a process that decreases the $I_{\text{E}}/I_{\text{M}}$ ratio. At SDS concentrations higher than the CMC of SDS in water, PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$ form little excimer. For PEO(2K)-Py$_2$ and PEO(5K)-Py$_2$, f_{free} remains small over the entire range of SDS concentrations within

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experimental error. However, increasing the SDS concentration past 5 mM for PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$ results in a dramatic increase of f_{free} as more pyrene groups are isolated in different SDS micelles. At small SDS concentrations, addition of SDS results in an increase of $<k>$ due to two effects. First, SDS melts the pyrene aggregates of the short PEO(X)-Py$_2$ constructs to allow more pyrene excimer to be formed by diffusion. Second, adding SDS is expected to bring pyrene groups of different chains into a same micelle so that intra- and intermolecular pyrene excimer formation takes place by diffusional encounter between many pyrene units located in a same micelle which results in a larger $<k>$. After the maximum, $<k>$ decreases and plateaus at the CMC of SDS in water. The decrease in $<k>$ is due to the separation of the pyrene pendants into different SDS micelles. Interestingly, for SDS concentrations larger than the CMC, $<k>$ takes a constant value of $9.6(\pm1.1)\times10^{-6}$ s^{-1} for all PEO(X)-Py$_2$ samples, suggesting that it represents the rate constant for pyrene excimer formation that occurs intramolecularly inside an SDS micelle and that it is independent of the polymer chain length.

The results that were obtained so far have been summarized schematically in Figure 3 to describe the interactions taking place between SDS and the PEO(X)-Py$_2$ samples. Figure 3 consists of two sequences of binding stages that apply for the short-chain samples on the one hand, and the long-chain samples on the other hand. At low SDS concentrations, SDS molecules target the pyrene pendants and bring them together to form mixed micelles, which results in an increase of the I_E/I_M ratio. Due to the stronger hydrophobic interactions between the pyrenes attached onto the short-chain samples and the shorter distance separating the pyrene end-groups, it is more difficult to separate them inside the different hydrophobic domains that are created in solution upon addition of SDS, which leads to a larger I_E/I_M observed than that of the longer chain samples. With excess amounts of SDS, free SDS micelles are formed and the pyrene end-groups of the shorter chain samples cannot be isolated into different SDS micelles. This effect results in intramolecular excimer formation inside a same SDS micelle. On the other hand, most pyrene end-groups attached onto the longer chain PEOs can be successfully separated and the PEO backbone can interact with the surface of the SDS micelles to decrease the electrostatic repulsion between two micelles and further insulate the hydrophobic domains of the micelles from the aqueous phase.
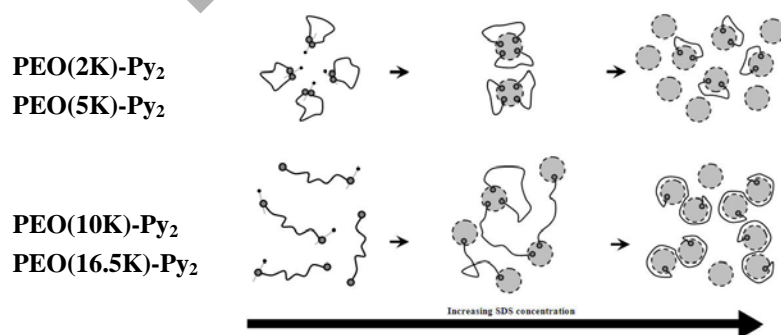

Figure 3. Schematic overview of the interactions between SDS and PEO(X)-Py$_2$ as a function of SDS concentration.

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Conclusions

The interactions between SDS and a series of PEO(X)-Py$_2$ constructs were investigated in aqueous solution by steady-state and time-resolved fluorescence methods. The fractions of the different excited pyrene species were calculated at different SDS concentrations. Increasing SDS concentration past the CMC resulted in a significant increase of f_{free} for PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$ as most pyrene groups became isolated in different SDS micelles. However the PEO(2K)-Py$_2$ and PEO(5K)-Py$_2$ samples were too short to allow SDS micelles to isolate the pyrene ends and pyrene excimer was still formed by intramolecular diffusion of the pyrene end-groups inside the SDS micelles. A scheme describing the interactions between SDS and the short and long PEO(X)-Py$_2$ constructs was proposed to rationalize the fluorescence results.

References

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Institute for Polymer Research

University of Waterloo

Probing the Interactions between a Series of Pyrene End-Labeled Poly(ethylene oxide)s and Sodium Dodecyl Sulfate in Aqueous Solution

Shaohua Chen
Supervisor: Prof Jean Duhamel
Department of Chemistry

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Associative Polymers

• Water-soluble polymers with a small amount (<5 mol%) of hydrophobic pendants

● Hydrophobe   — Water-soluble polymer

• In water, hydrophobes cluster to form aggregates

In water

•Applications – paints, coatings, dispersants, drug delivery, etc.

2

Hydrophobically Modified Ethoxylated Urethane (HEUR) Polymers

with R' =

Key structure of HEUR

3

Network of HEUR in Aqueous Solution

CMC   C*   high c

4

Sodium Dodecyl Sulfate (SDS)

CH_3 CH_2 CH_2 CH_2 CH_2 CH_2 O — SO_3^- Na^+
CH_2 CH_2 CH_2 CH_2 CH_2 CH_2

CMC

At 25° C,
➢critical micelle concentration (CMC) = 8.2 mM
➢aggregation number (N_{agg}) = 62
➢microviscosity = 20 mPa.s
➢hydrophobic radius = 1.7 nm

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Pyrene and Pyrene End-labeled PEO

Pyrene – an ideal chromophore

• Highly hydrophobic

• Large extinction coefficient

• Good quantum yield

• Long lifetime

CH_2 — O — (CH_2 — CH_2 — O)$_n$ — CH_2

PEO(X)-Py$_2$

n equals 45, 113, 227, and 375 for PEO(X)-Py$_2$ with X = 2, 5, 10, and 16.5 K, respectively

• Isolated excited monomer fluoresces around 375nm and shifts to 480nm when associates with ground-state pyrene to form an excimer

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Pyrene Fluorescence Spectra

PEO(2K)-Py$_1$ ... PEO(2K)-Py$_2$

Global Analysis
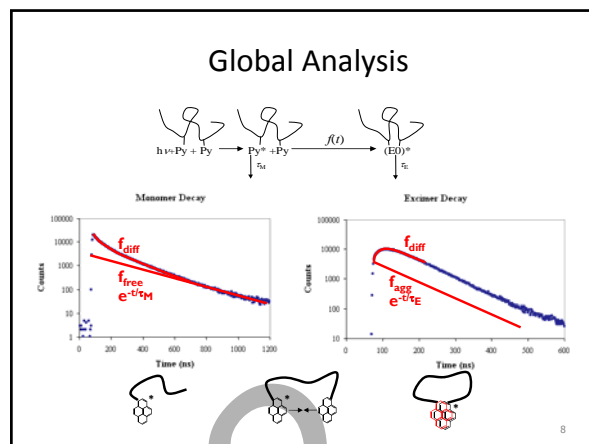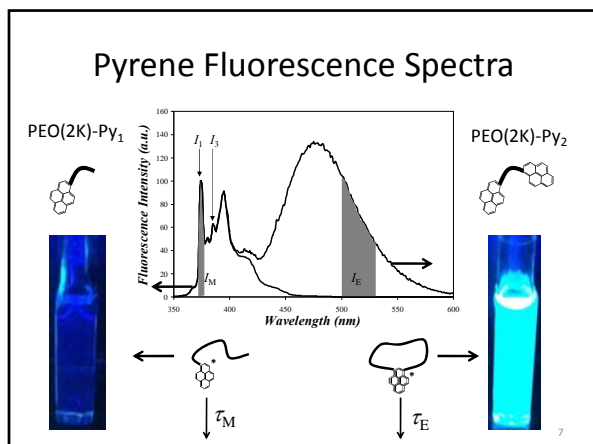
Interactions between PEO(X)–Py$_2$ and SDS Probed by Isothermal Titration Calorimetry (ITC), Potentiometry with an SDS Selective Electrode and Conductivity Measurements

Interactions between PEO and SDS Probing by ITC

titrant: 0.2 M SDS solution

PEG75: M_n = 3,350 g/mol
CAC: critical aggregation concentration
C$_2$: saturation concentration
C$_m$: critical concentration

Dai, S.; Tam, K. C. *J. Phys. Chem. B* **2001**, *105*, 10759-10763.
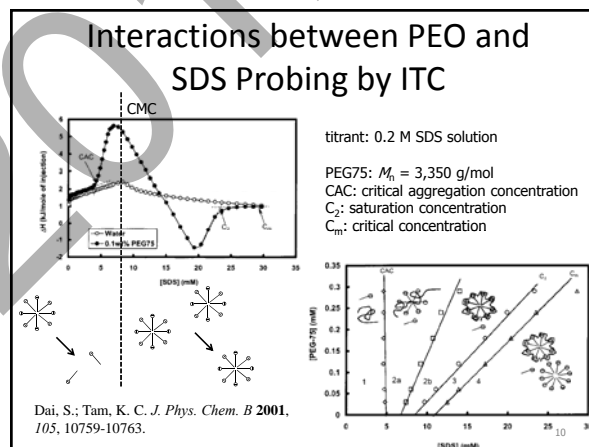
Polymer Concentrations Used in This Study

➤**For fluorescence:**

[Py] = 0.1 OD = 2.5×10^{-6} M ⟶ [PEO(X)-Py$_2$] = 1.25×10^{-6} M

➤**For ITC, etc:**

polymer concentration, C_p = 0.1 wt%,

[PEO(2K)-Py$_2$] = 5.0×10^{-4} M
[PEO(5K)-Py$_2$] = 2.0×10^{-4} M
[PEO(10K)-Py$_2$] = 1.0×10^{-4} M
[PEO(16.5K)-Py$_2$] = 6.1×10^{-5} M

Isothermal Titration Curves

Electromotive Force (EMF) Versus SDS Concentration

1.25×10⁻⁶ M PEO(2K)-Py₂, PEO(5K)-Py₂ and PEO(10K)-Py₂

1.0×10⁻⁴ M PEO(10K)

1.0×10⁻⁴ M PEO(10K)-Py₂

SDS bind to pyrene

titrant: 0.8 M SDS solution

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Solution Conductance Versus SDS Concentration

titrant: 0.8 M SDS solution

Dominguez, A.; Fernandez, A.; Gonzalez, N.; Iglesias, E.; Montenegro, L. *J. Chem. Ed.* **1997**, *74*, 1227-1231.

14
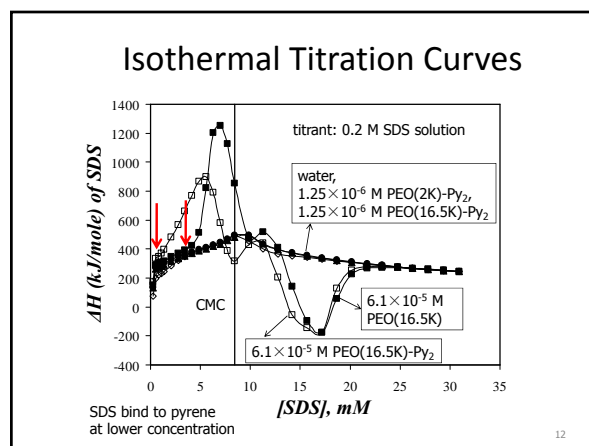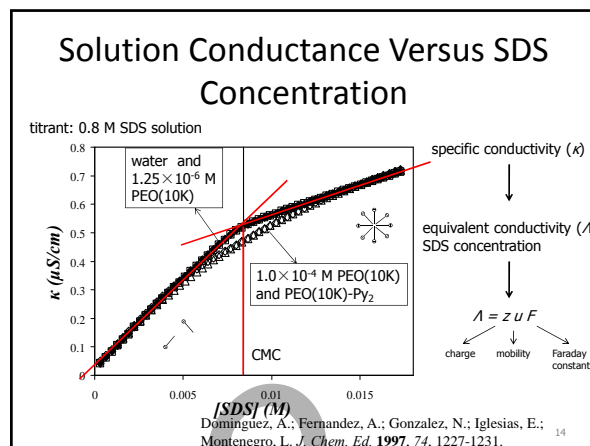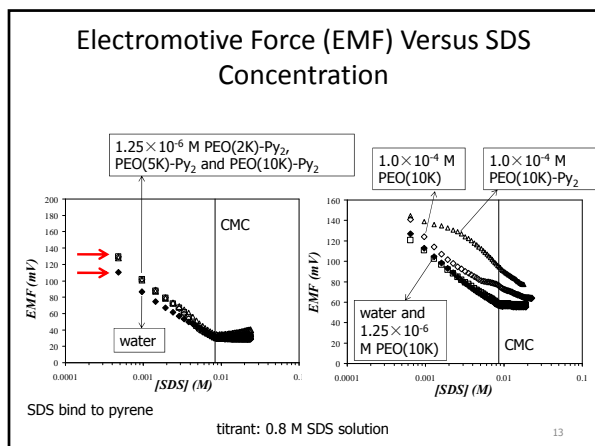
Interactions between PEO(X)–Py₂ and SDS Probed by Fluorescence

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Steady-state Spectra of 1.25×10⁻⁶ M PEO(5K)-Py₂ with SDS

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I_E/I_M and I_1/I_3 versus SDS Concentration

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Fractions and <k> versus SDS Concentration

18

3

Schematic Overview of the Interactions between SDS and PEO(*X*)-Py$_2$ as a Function of SDS Concentration

PEO(2K)-Py$_2$ and PEO(5K)-Py$_2$

PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$

CMC

Increasing SDS concentration

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Probing Pyrene Excimer Formation inside Micelle

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Steady-state Spectra of PEO(*X*)-Py$_2$ at SDS Concentrations above CMC

Fluo. Intensity (a.u.)

I_E/I_M

[SDS], M

PEO(2K)-Py$_2$
PEO(5K)-Py$_2$

PEO(10K)-Py$_2$
PEO(16.5K)-Py$_2$

wavelength (nm)

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Birks' Scheme

PEO(2K)-Py$_2$
PEO(5K)-Py$_2$

$$hv + Py \quad Py \longrightarrow (Py^* \quad Py) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (PyPy)^*$$
$$\tau_M^{-1} \qquad \tau_E^{-1}$$
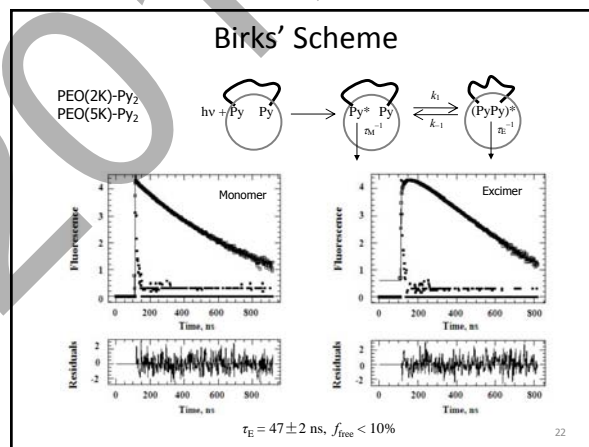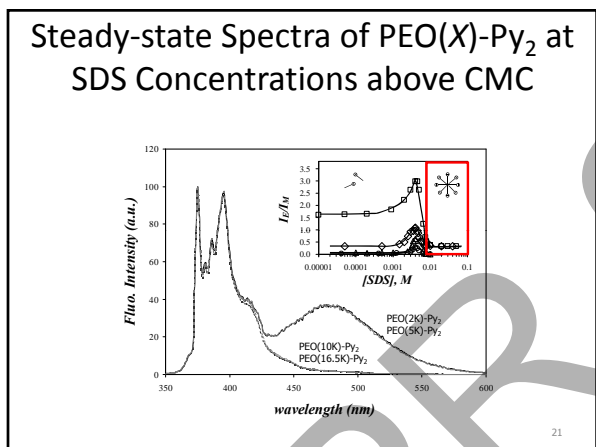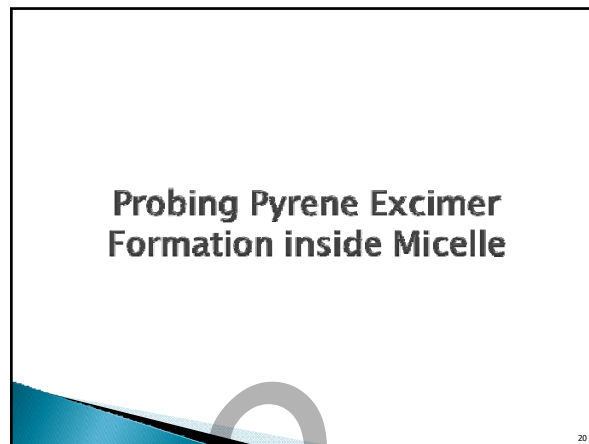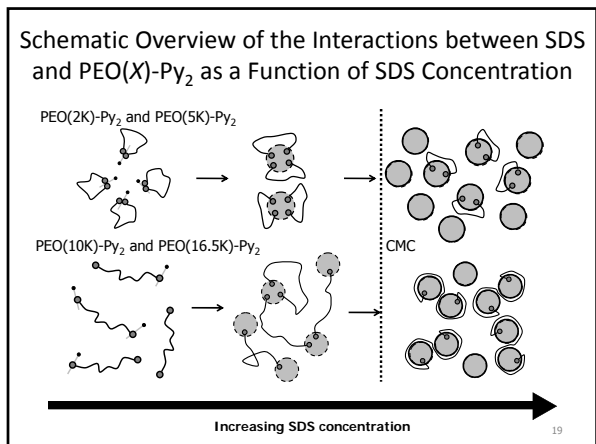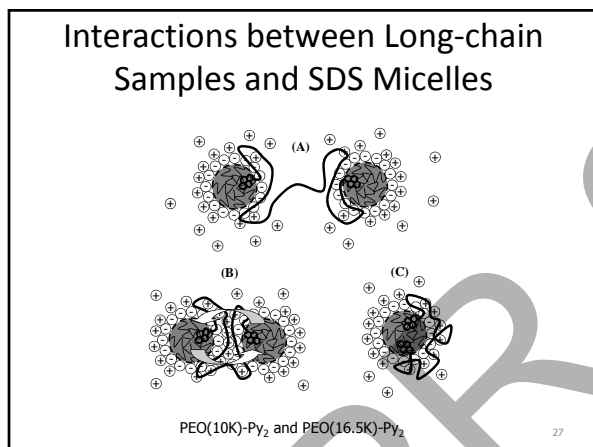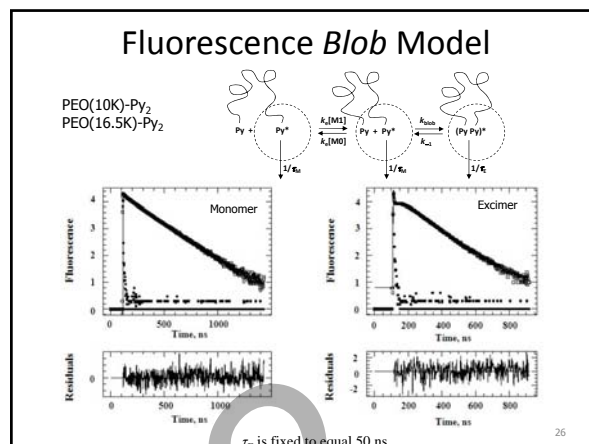
Fluorescence — Monomer

Time, ns

Fluorescence — Excimer

Time, ns

Residuals

Time, ns

Residuals

Time, ns

$\tau_E = 47 \pm 2$ ns, $f_{free} < 10\%$

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End-to-end Distance Distribution of PEO

$Pr(r_{E-E})$

2K

5K

10K

16.5K

r_{E-E} (nm)

$$\Pr(r_{EE}) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 r_{EE}^2} 4\pi r_{EE}^2$$

where $\quad \beta^2 = \dfrac{3}{2N_K l_K^2}$

Kuhn length of PEO $l_K = 0.707$ nm,
the number of segments $N_K = 0.0141 M_n$

Pattanayek, S. K.; Juvekar, V. A. *Macromolecules* **2002**, 35, 9574-9585.

$$R_{blob} = 245.8 \times \sqrt{\tau_M/\eta} + 0.837$$

Chen, S.; Duhamel, J.; Winnik, M. A. *J. Phys. Chem. B* **2011**, *115*, 3289-3302.

0.82 nm

1.04 nm

$R_{SDS} = 1.7$ nm

$R_{blob} = 1.5 \pm 0.6$ nm in SDS micelle

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Problems Encountered When Applying Birks' Scheme to Long-chain Samples

$$hv + Py \quad Py \longrightarrow Py^* \quad Py \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (PyPy)^*$$
$$\tau_M^{-1} \qquad \tau_E^{-1}$$

Samples	PEO(2K)-Py$_2$	PEO(5K)-Py$_2$	PEO(10K)-Py$_2$	PEO(16.5K)-Py$_2$
τ_E (ns)	47±1	48±2	77±2	90±1

Birks' scheme analysis yields parameters that do not reflect the overall kinetics of pyrene excimer formation.

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Fluorescence *Blob* Model

Mathew, A.; Siu, H.; Duhamel, J. *Macromolecules* **1999**, *32*, 7100-7108.

Siu, H.; Duhamel, J. *Macromolecules* **2004**, *37*, 9287-9289.

Chen, S.; Duhamel, J.; Winnik, M. A. *J. Phys. Chem. B* **2011**, *115*, 3289-3302.

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Fluorescence *Blob* Model

PEO(10K)-Py$_2$
PEO(16.5K)-Py$_2$

τ_E is fixed to equal 50 ns

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Interactions between Long-chain Samples and SDS Micelles

PEO(10K)-Py$_2$ and PEO(16.5K)-Py$_2$

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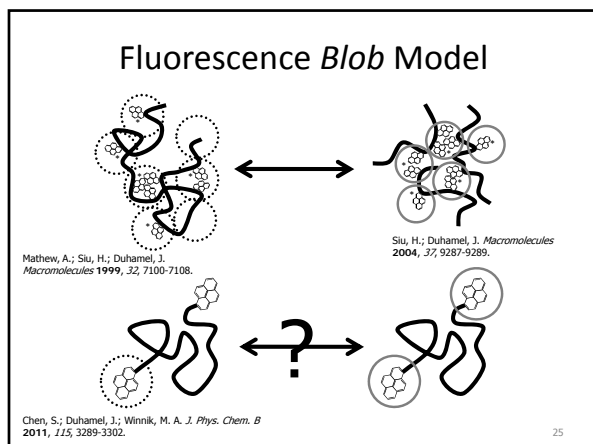
Conclusions

➤Molar fractions of excited pyrene species were determined for PEO(X)-Py$_2$ constructs in water at different SDS concentrations;

➤Increasing SDS concentration past the CMC results in intramolecular pyrene excimer formation inside a micelle for the short-chain samples and isolation of pyrene pendants inside different micelles for the long-chain samples.

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Thank you for your attention!

Questions/Comments?