**Hydrophobic and Elastic Forces Experienced by a Series of Pyrene End-Labeled Poly(ethylene oxide)s Interacting with Sodium Dodecyl Sulfate Micelles**

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**ABSTRACT**

A series of pyrene end-labeled poly(ethylene oxide)s (Py2-PEO(*x*) with *x* equal to 2, 3.4, 5, 6, 7.8, and 10 kg.mol) were synthesized and their interactions with SDS micelles were characterized by steady-state and time-resolved fluorescence. Pyrene excimer formation (PEF) indicated that both pyrenyl ends were located in a same SDS micelle whereas absence of PEF reflected bridging of two SDS micelles by a Py2-PEO molecule having its pyrenyl end groups in separate micelles. PEF efficiency was characterized from the excimer-to-monomer fluorescence intensity ratio (*I*E/*I*M) which was determined as a function of PEO chain length and salt concentration. More detailed information about the PEF process was obtained by fitting the monomer and excimer fluorescence decays globally according to the Model Free Analysis (MFA). MFA yielded the average rate constant <*k*> of PEF and the molar fraction (*f*free) of pyrenyl labels that did not form excimer, thus reflecting the extent of bridging undergone by the Py2-PEO constructs. Bridging was inferred for the two longest Py2-PEO constructs but not for the shorter Py2-PEO(2K) sample, since *f*free was large and small for the former and latter constructs, respectively. The most interesting behavior was observed for Py2-PEO(6K) where a substantial increase in *f*free was detected upon addition of a minute amount of NaCl. The Py2-PEO(6K) construct marked the boundary between the regimes where bridging would or would not occur with or without salt, respectively. This observation led to a quantitative analysis of the energies involved in restraining the two end groups of a Py2-PEO construct in a same SDS micelle and in extending a PEO chain to bridge two SDS micelles occupied by one pyrenyl end of a Py2-PEO construct. The theoretical energy calculations were found to predict fairly accurately the *f*free trends obtained experimentally by the MFA of the Py2-PEO fluorescence decays.

**INTRODUCTION**

Hydrophobically modified water-soluble polymers (HMWSPs) are water-soluble macromolecules bearing a small number of hydrophobes. The ability of HMWSPs to associate in water via their hydrophobic pendants either intra- or intermolecularly or with other amphiphilic compounds, that can be organic (surfactants, drugs, latex particles) or inorganic (clay or silica particles), has found numerous applications in the pharmaceutical, paint, food, and mining industry, to name but a few, where they serve as solution thickeners or thinners,[[1]](#endnote-1)-,[[2]](#endnote-2),[[3]](#endnote-3) colloidal stabilizers,[[4]](#endnote-4)-,[[5]](#endnote-5),[[6]](#endnote-6),[[7]](#endnote-7) or flocculants.[[8]](#endnote-8) In one way or another, all these applications rely on the ability of the macromolecules to act as molecular springs that will extend or recoil depending on the amount of stress being applied to the system.[[9]](#endnote-9),[[10]](#endnote-10),[[11]](#endnote-11),[[12]](#endnote-12),[[13]](#endnote-13),[[14]](#endnote-14)

For instance, associative thickeners form an interpolymeric network in water where aggregates of hydrophobic pendants are bridged by water-soluble polymers (WSPs).9-,10,11,12 Under the proper conditions, the network extends throughout the solution, thickening it greatly. But application of a shear to the solution extends the WSP chains to the point where their recoiling force exceeds the adhesion force of the hydrophobes to the hydrophobic aggregates. This situation leads to the disengagement of the hydrophobes, recoiling of the WSPs, and rearrangement of the hydrophobes into hydrophobic aggregates that are formed intramolecularly. This substantial disruption of the polymeric network is associated with a massive shear thinning of the solution. Similarly HMWSPs used as colloidal stabilizers adsorb at the surface of hydrophobic particles such as latex via their hydrophobic groups while the WSP chains spread in the aqueous phase. Encounters between two stabilized particles lead to the interpenetration of the stabilizing polymer layers which reduces the free volume available to each chain resulting in their recoiling that is entropically unfavorable, the overall process ensuring colloidal stabilization.13,14

In view of its relevance to diverse fields of polymer science, the characterization of the elastic force of individual macromolecules in solution constitutes an important goal. Several techniques have been developed over the years to achieve it. Magnetic and optical tweezers,[[15]](#endnote-15)-,[[16]](#endnote-16),[[17]](#endnote-17),[[18]](#endnote-18) atomic force microscopes,[[19]](#endnote-19)-,[[20]](#endnote-20),[[21]](#endnote-21),[[22]](#endnote-22) and surface force apparatus[[23]](#endnote-23)-,[[24]](#endnote-24),[[25]](#endnote-25) have been employed to probe the elastic or recoiling force of macromolecules in solution. They typically involve the tethering of a macromolecule of interest, typically a linear chain, to two macroscopic surfaces, which can be molecularly flat silica or mica substrates or spherical nanosized objects with a large curvature radius of several 100’s of nm such as latex or silica particles.15-,16,17,18,19,20,21,22,23,24,25 Tethering of the macromolecules can be achieved via simple adsorption of the macromolecule to the surfaces or the formation of bonds between the macromolecule and the substrate that are either covalent or physical between a receptor and a ligand (streptavidin and biotin is an often used example).15-,16,17,18,19,20,21,22,23,24,25 Upon tethering the linear chain to the two substrates and pulling the substrates apart, the force experienced by the stretching macromolecule is being recorded to generate a force-versus-displacement plot whose analysis provides information about the spring constant or modulus of a single macromolecule.15‑,16,17,18,19,20,21,22,23,24,25

While these single molecule force spectroscopy experiments are most informative as they measure the recoiling force of a macromolecule directly, it is also fair to state that the macromolecules, which are generally a few nanometers in length, are always confined to the interstitial space separating two much larger macroscopic surfaces. To the best of our knowledge, the ability to probe the extension or recoiling force of a macromolecule floating freely in solution has not been reported yet. We propose herein an experiment based on pyrene excimer fluorescence/formation (PEF) to accomplish this goal by end-labeling a series of monodisperse poly(ethylene oxide)s with the dye pyrene (Py2-PEO(*x*) where *x* is the number average molecular weight of the polymer equal to 2.0, 3.4, 5.0, 6.0, 7.8, and 10 kg.mol) and monitoring their PEF efficiency as a function of salt concentration and polymer molecular weight as the pyrene labels interact with sodium dodecyl sulfate (SDS) micelles. The strong hydrophobicity of the pyrene labels drives their incorporation into the hydrophobic interior of negatively charged SDS micelles. If the two pyrenyl ends are associated with two different SDS micelles, electrostatic repulsion between the micelles induces the stretching of the PEO chain until the recoiling force overcomes the binding force of pyrene to the SDS micelles, at which point the chain recoils and brings the two pyrenyl ends inside a same SDS micelle where they can form an excimer. By carefully monitoring the conditions in terms of salt concentration and PEO chain length where a switch from SDS micelles occupied by mostly one pyrenyl group to SDS micelles occupied by mostly two pyrenyl ends occurred, the energy necessary to pull a pyrenyl end out of an SDS micelle was estimated to equal 2.3 ± 0.8 zJ (1 zJ = 10 J). This study represents the first example where PEF is being employed to probe the intramolecular force experienced by the two ends of a polymer chain freely floating in solution as its ends are pulled apart by the repulsive electrostatic force generated by two negatively charged SDS micelles. It is expected to open a new family of single molecule force spectroscopy experiments based on the use of PEF.

**EXPERIMENTAL**

*Chemicals*: The poly(ethylene oxide) samples were purchased from Polymer Source, Dorval, Québec. The number average molecular weight, dispersity, functionalization, and average end-to-end distance at equilibrium (*r*EE-eq) in water of the Py2-PEO samples are listed in Table 1 and their chemical structure is shown in Figure 1.

**Table 1.** Number average molecular weight (*M*n), dispersity (*Ð*), functionalization, and average end-to-end distance at equilibrium of the Py2-PEO samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Polymer | PEO *M*n (kg∙mol1) | *Ð**(= M*w*/M*n*)* | Functionalization\* | Average end-to-end distance at equilibrium (*r*EE-eq, nm)\*\* |
| Py2-PEO(2K) | 2.0 | 1.05 | 1.98 | 3.75 |
| Py2-PEO(3.4K) | 3.4 | 1.04 | 1.78 | 4.89 |
| Py2-PEO(5K) | 5.0 | 1.08 | 1.97 | 5.94 |
| Py2-PEO(6K) | 6.0 | 1.03 | 1.88 | 6.50 |
| Py2-PEO(7.8K) | 7.8 | 1.04 | 1.77 | 7.41 |
| Py2-PEO(10K) | 10.0 | 1.05 | 1.72 | 8.39 |

\*Determined by UV absorbance measurements of pyrene at 344 nm in THF using Equation 1 with ε(344 nm) = 42,700 M∙cm. A functionalization of 2.0 represents complete pyrene labeling.

\*\* Determined through Equation 6.[[26]](#endnote-26)



**Figure 1.** Chemical structure of the Py2-PEO constructs.

Dichloromethane (DCM, HPLC-grade), *p*-toluenesulfonyl chloride (reagent), trimethylamine (puriss), diethyl ether (anhydrous, reagent), 1-pyrenemethanol (98 %), pyrene (98 %), sodium hydride (60 wt% dispersion in mineral oil), and thallium chloride (99 %) were purchased from Aldrich. HPLC grade ethanol, sodium chloride (reagent), tetrahydrofuran (THF, distilled in glass), and sodium dodecyl sulfate (SDS, OmniPur) were purchased from Fisher Chemicals, ACP, Caledon, and Calbiochem, respectively. Beside pyrene which was re-crystallized three times from ethanol, all other chemicals were used as received. MilliQ water with a resistivity of 18.2 M.cm at 24 °C was used in all experiments.

*Synthesis of pyrene-labeled PEO* (*Py2-PEO*): The synthesis of the Py2-PEO constructs has been described in details in earlier publications31,32 and has been summarized in Supporting Information (SI).

*Gel permeation chromatography*: A Viscotek VE 2001 gel permeation chromatography (GPC) instrument equipped with PolyAnalytik SupeRes mixed bed columns and with a TDA 305 triple detector array (differential refractive index (DRI), light scattering, and absorption) was employed for the characterization of all Py2-PEO samples using THF as the eluent with a flow rate of 1 mL/min. The pyrenyl labels of the Py2-PEO samples were probed with a 2600 UV detector module which was set at 342 nm where the pyrenyl labels absorb. The GPC column was thermostated at 35 °C. The DRI and absorption detectors were used to obtain the traces shown in Figure S2 for the sample Py2-PEO(6K). In Figure S2, the sample eluted at the same elution volume for the DRI and absorption detectors indicating that it had been successfully labeled and no absorption was observed in the region corresponding to low molecular weight species demonstrating that all non-attached pyrenyl groups had been removed.

*UV-Vis absorption measurements*: The pyrene content (**Py) of the Py2-PEO samples was determined by using a Varian Cary 100 Bio spectrophotometer to measure the absorbance at 342 nm of a Py2-PEO solution in THF of known massic concentration (*c*M). The absorbance (*A*) of the Py2-PEO solution was compared to the molar absorbance coefficient (**) of 1-pyrenemethanol in THF equal to 42,700 M.cm at 342 nm from which the pyrene content of the samples was determined (**Py = *A*/(*c*M*×*)). The pyrene content of the samples was used in Equation 1 to determine the functionalization (*f*) of the Py2-PEO samples which was reported in Table 1. In Equation 1, *M*n and *M*Py are the number average molecular weight of the PEO sample and the molar mass of 1-pyrenemethoxide (231 g.mol).

  (1)

The absorbance of the Py2-PEO solutions for all fluorescence experiments equaled 0.1 ensuring that the pyrene concentration in the solution was around 2.3×10 M. With an SDS concentration of 15 mM, a concentration of 1.15×106 M Py2-PEO molecules implied that the probability of having more than one Py2-PEO chain per SDS micelle was less than 0.5% of the probability of having one Py2-PEO molecule per micelle (see calculation in SI). In other words, the fluorescence signal was that of single Py2-PEO chains bound to SDS micelles.

*Steady-state fluorescence measurements*: The steady-state fluorescence (SSF) spectra of all 15 mM SDS aqueous solutions with 1.15×106 M Py2-PEO or 0.5×106 M molecular pyrene were acquired with a Photon Technology International LS-100 steady-state fluorometer equipped with an Ushio UXL-75 Xenon lamp and a PTI 814 photomultiplier detection system. The solutions were not degassed. The fluorescence intensity ratio of the peak at 375 nm over that at 390 nm yielded the ratio *I*1/*I*3 which reflected the polarity of the environment experienced by the pyrenyl labels. The ratio *I*E/*I*M of the excimer to monomer fluorescence intensity represented the efficiency of the Py2-PEO solutions at forming excimer. It was calculated by taking the integral of the fluorescence signal between 500 and 530 nm and between 372 and 378 nm for the pyrene excimer (*I*E) and monomer (*I*M), respectively.

*Time-resolved fluorescence measurements*: The time-resolved fluorescence (TRF) decays of 1.15×106 M Py2-PEO or 0.5×106 M molecular pyrene in 15 mM SDS aqueous solutions were acquired with an IBH Ltd. time-resolved fluorometer using an IBH 340 nm nanoLED. A 344 nm excitation wavelength was selected with the excitation monochromator and the decays were acquired at 375 nm with a 370 nm cut-off filter for the monomer and 510 nm with a 480 nm cut-off filter for the excimer. The cut-off filters minimized unwanted scattered light. The fluorescence decays were collected until the maximum point in the decay reached 20,000 counts at a time-per-channel of 2.04 ns/ch and a repetition rate of 500 kHz. Along with each decay, an instrument response function was also acquired.

*Fluorescence decay analysis*: The pyrene monomer and excimer fluorescence decays of the Py2-PEO samples were analyzed globally with the Model Free Analysis (MFA) using Equations S4 and S5 given in SI, respectively. The MFA has been described in detail in numerous publications and reviews.[[27]](#endnote-27),[[28]](#endnote-28) More details about the use of Equations S4 and S5 are provided in SI. The MFA retrieves the molar fractions *f*free, *f*diff, and *f*agg of the pyrene species that are unable to form an excimer (*Py*free\*) because they are located in two different SDS micelles, and as such, emit with the natural lifetime of pyrene (**M) as if they were free in solution, form excimer by diffusive encounters (*Py*diff\*) with an average rate constant <*k*> because they are located inside a same SDS micelle, and are aggregated (*E0*\*), form excimer instantaneously upon absorption of a photon, and emit with a lifetime **E0. The derivation of the molar fractions *f*free, *f*diff, and *f*agg and the average rate constant <*k*> from the parameters (pre-exponential factors and decay times) retrieved from the MFA is described in SI.

The fluorescence decays of the 15 mM SDS solutions with 0.5×10 M pyrene quenched by thallium cations[[29]](#endnote-29) were fitted with Equation 2 derived by Tachiya.[[30]](#endnote-30)

 (2)

In Equation 2, *f*M(*t*) represents the fluorescence decay of pyrene in SDS micelles without quencher. The function *f*M(*t*) was biexponential, with a long decay time of 181 ± 5 ns obtained with a pre-exponential contribution that was larger than 90% representing isolated pyrenes in SDS micelles. The shorter decay time was attributed to the residual presence of metal cations in the SDS sample that quenched the fluorescence of pyrene. Using *f*M(*t*) in the analysis enabled one to account for this problem. The parameters used for *f*M(*t*) were listed in Table S20 and were fixed in the analysis with Equation 2. The parameters *A*2, *A*3, and *A*4 used in Equation 2 are defined in Equation 3,

   (3)

where *k* and *k’* are the rate constants for the binding and dissociation of thallium cations to and from the SDS micelles, respectively, *k*q is the quenching rate constant for an excited pyrene located inside a micelle with one quencher, and [*Q*]w represents the concentration of thallium cations in water. Considering that the average number <*n*> of quenchers bound to micelles equals *k*×[*Q*]w/*k*’, an expression for <*n*>, *k*q, and *k*’ is provided in Equation 4 based on the parameters *A*2, *A*3, and *A*4 given in Equation 3.

    (4)

**RESULTS**

The fluorescence spectra of all the Py2-PEO samples were acquired at a polymer concentration of 1.15×10 M and with NaCl concentrations of 0.00, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40, and 0.50 M with 15 mM SDS. As shown in an earlier report,31 interactions between SDS and the PEO backbone are not expected to be relevant at the low PEO concentration (< 12 mg.L) used in these experiments implying that interactions occur principally between the pyrenyl labels and the SDS micelles. This earlier study31 also found that without salt, interactions between SDS and Py2-PEO constructs began at an onset SDS concentration of 0.4 mM. These interactions were demonstrated by an increase in PEF corresponding to the formation of mixed micelles containing several Py2-PEO and SDS molecules. As the SDS concentration was further increased, PEF passed through a maximum before decreasing as the Py2-PEO constructs distributed themselves into different mixed micelles. At SDS concentrations greater than the CMC of SDS, PEF remained constant corresponding to a state where Py2-PEO molecules were isolated inside SDS micelles. The SDS concentration of 15 mM was selected in the present study as it was sufficiently above the CMC of SDS at all salt concentrations, thus ensuring that Py2-PEO molecules isolated in SDS micelles would be probed.

Representative spectra are shown in Figure 2A and B. The SSF spectra displayed the typical features of an excimer-forming pyrene-labeled macromolecule, with sharp fluorescence peaks between 375 and 410 nm and a broad structureless emission centered at 480 nm, both spectral features being characteristic of the pyrene monomer and excimer, respectively. The *I*1/*I*3 ratios of all fluorescence spectra were found to equal 1.41 ± 0.02 which is typical for a 1-pyrenemethoxide group associated with SDS micelles.[[31]](#endnote-31)-,[[32]](#endnote-32),[[33]](#endnote-33) Figure 2A indicates that the Py2-PEO constructs can be classified into two categories depending on whether they are short (2.0, 3.4, 5.0, and 6.0 K) or long (7.8 and 10 K) as the short and long constructs do and do not form excimer, respectively. Since the *I*1/*I*3 ratio indicated that the pyrenyl end groups were associated with SDS micelles, the trend shown in Figure 2A demonstrated that the two ends of the short and long constructs were located in a same micelle or in two different micelles where excimer formation was and was not allowed, respectively. As salt was added to the solutions, excimer formation decreased substantially as shown in Figure 2B for Py2-PEO(3.4K). These trends were summarized in Figures 3A and B by plotting the *I*E/*I*M ratios obtained for all SSF spectra as a function of salt concentration and construct molecular weight, respectively.

|  |  |
| --- | --- |
| A) | B) |

**Figure 2.** Fluorescence spectra of A) the Py2-PEO constructs without salt ([NaCl] = 0 M, from top to bottom: *M*n = 3.4, 2.0, 5.0, 6.0, 7.8, and 10.0 K) and B) of Py2-PEO(3.4K) in the presence of increasing concentration of salt (from top to bottom: [NaCl] = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40, and 0.50 M).

 The trends presented in Figure 3A showed a general decrease in *I*E/*I*M with increasing salt concentration for the shorter Py2-PEO constructs. The longer Py2-PEO(7.8K) and Py2-PEO(10K) constructs yielded a very low *I*E/*I*M ratio for all salt concentrations in agreement with the fluorescence spectra shown in Figure 2A. The effect of the degree of polymerization (DP) of the samples was illustrated in Figure 3B where *I*E/*I*M was plotted as a function of *M*n for each salt concentration. Here again, the transition from Py2-PEO constructs having an *M*n value smaller or greater than 7.0 K was very clear with *I*E/*I*M taking a very low value for Py2-PEO(7.8K) and Py2-PEO(10K) at all salt concentrations. While the general trend of the *I*E/*I*M ratio shown in Figure 3B was to decrease with increasing DP, it was also noticeable that the *I*E/*I*M ratio of Py2-PEO(2K) was smaller than that of Py2-PEO(3.4K) for most salt concentrations. This result was due to the short 3.8 nm end-to-end distance at equilibrium (*r*EE-eq in Table 1, see Equation 6)26 of Py2-PEO(2K) being similar in size to the 3.5 nm diameter of an SDS micelle in water (see Equation 11 to determine the diameter of SDS micelles). Due to its short size, the PEO segment of Py2-PEO(2K) must be associated with the SDS micelle thus allowing the pyrene labels to probe the entire micellar interior. By contrast, the 4.9 nm *r*EE-eq value of Py2-PEO(3.4K) is larger than the diameter of an SDS micelle without salt suggesting that some sections of the PEO chain might be out of the micelle and solvated in water, thus pulling the two pyrenyl groups anchored in a same micelle closer to each other. This situation would reduce the volume probed by the pyrenyl labels in the micellar interior, and would result in more efficient excimer formation as observed for Py2-PEO(3.4K) in Figure 3. As the PEO chain increased in size, the pyrenyl end groups became freer to probe the entire micellar interior and the *I*E/*I*M ratio decreased. When the PEO chain reached an *M*n value larger than 6.0 K, the average end-to-end distance became much larger than the size of an SDS micelle and the restoring force experienced by the long Py2-PEO constructs having their two pyrenyl end groups in a same micelle overcame the adhesion force of the pyrenyl labels bound to the micellar interior. It induced the release of the recoiled PEO chain which sprang open and was long enough to sustain the extension induced by the electrostatic repulsion of the two SDS micelles encapsulating the two hydrophobic pyrenyl ends.

|  |  |
| --- | --- |
| A) | B) |

**Figure 3.** Plot of *I*E/*I*M as a function of A) salt concentration for the Py2-PEO constructs with an *M*n value of () 2.0 K, () 3.4 K, ( ) 5.0 K, (**×**) 6.0 K, () 7.8 K, and () 10.0 K and B) *M*n for salt concentrations of () 0.00, () 0.02, () 0.04, () 0.06, ( ) 0.08, ( ) 0.10, () 0.20, () 0.30, (**×**) 0.40, and (**+**) 0.50 M.

 While the trends described in Figures 3A and B are most certainly the result of an interplay between the elastic force of the PEO chains and the electrostatic repulsion experienced by the pyrenyl ends encapsulated inside two negatively charged SDS micelles, it remained difficult to conclude whether the decrease in *I*E/*I*M observed with increasing salt concentration in Figure 3A was solely due to the progressive bridging of two SDS micelles by the Py2-PEO chains as the addition of salt screened the charged micelles allowing them to come nearer to each other. As is well established in the scientific literature, both the size and microviscosity of SDS micelles increase with increasing salt concentration.[[34]](#endnote-34),[[35]](#endnote-35) Both effects combine to reduce the formation of excimer by diffusive encounters between the two pyrenyl ends located in a same micelle, as a larger micelle decreases the local concentration [*Py*]loc of pyrene labels inside an SDS micelle and an increased viscosity decreases the bimolecular rate constant (*k*diff) of diffusive encounters between two pyrenyl labels located inside a same micelle. To accurately probe the bridging of two SDS micelles by a Py2-PEO chain, the contributions to the *I*E/*I*M ratio from the kinetics of pyrene excimer formation reflected by the product *k*diff×[*Py*]loc and the state of the two pyrenyl labels of the Py2-PEO constructs being either both inside a same micelle and capable of forming excimer by diffusion (*Py*diff\*) or isolated inside two different micelles and unable to form excimer (*Py*free\*) needed to be determined. To this end, the pyrene monomer and excimer TRF decays of the Py2-PEO constructs were acquired and analyzed globally according to the MFA. To date, the MFA is the only available TRF decay analysis that provides information reliably about the kinetics and the state of the pyrenyl labels of a macromolecule in solution such as those of the Py2-PEO constructs. An example of the quality of the fits can be seen in Figure S3. In all cases, the **2 parameter was less than 1.3 and the residuals and autocorrelation of the residuals were randomly distributed around zero indicating a good fit. The pre-exponential factors and decay times retrieved from the MFA of the TRF decays are listed in Tables S2-19 in SI.

The rate constant <*k*> retrieved from the MFA of the decays and equivalent to the product *k*diff×[*Py*]loc was plotted as a function of salt concentration and the *M*n value of the Py2-PEO constructs in Figures 4A and B, respectively. While the <*k*> values plotted as a function of salt concentration showed a general decreasing trend with increasing salt concentration when considering a single Py2-PEO construct, a more detailed analysis was difficult to achieve since the trends appeared somewhat erratic when all Py2-PEO samples were compared. For instance, Py2-PEO(2K) yielded the smallest <*k*> value at all salt concentrations and Py2-PEO(3.4K) yielded the highest and lowest <*k*> value at 0 and 0.5 M salt concentration, respectively. Interestingly, much clearer trends were obtained after plotting the <*k*> values as a function of *M*n in Figure 4B.

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| --- | --- | --- |
| A) | B) |  C) |

**Figure 4.** Plots of A) <*k*> as a function of salt concentration for the Py2-PEO constructs with an *M*n value of () 2.0 K, () 3.4 K, ( ) 5.0 K, (**×**) 6.0 K, () 7.8 K, and () 10.0 K, B) <*k*> as a function of *M*n for salt concentrations of () 0.00, () 0.02, () 0.04, () 0.06, ( ) 0.08, ( ) 0.10, () 0.20, () 0.30, (**×**) 0.40, and (**+**) 0.50 M, and C) *f*free as a function salt concentration (same symbols as in Figure 4A).

Regardless of the length of the Py2-PEO construct, the <*k*> values in Figure 4B were the largest at 0 M salt and continuously decreased with increasing salt concentration until taking the lowest value at 0.5 M salt. This trend is reasonable since the SDS micelles are smaller and more fluid at 0 M salt, conditions that favor excimer formation between two pyrenyl labels located inside a same micelle.33,34 As the salt concentration increased, the SDS micelles increased in size and their interior became more viscous,33,34 both effects contributing to a reduction in the rate of excimer formation as clearly illustrated in Figure 4B. The profiles of the <*k*> values also paralleled those found for the *I*E/*I*M ratios in Figure 3B, showing a maximum in the <*k*> profiles that shifted to higher Py2-PEO molecular weights with increasing salt concentration. As for the *I*E/*I*M ratios, this behavior is certainly related to the comparable sizes of the shorter Py2-PEO constructs and the SDS micelles whose dimension increases with increasing salt concentration. It is noticeable that the maximum <*k*> value passed through a maximum for the Py2-PEO(3.4K) solution without salt because the 3.8 nm *r*EE-eq of Py2-PEO(2K) in Table 1 was comparable to the 3.5 nm diameter of the SDS micelles without salt and Py2-PEO(2K) must therefore have been engulfed by the micelles resulting in slower excimer formation since the interior of an SDS micelle is much more viscous than water. As the salt concentration increased and the SDS micelles grew in size, the 4.9 nm *r*EE-eq of Py2-PEO(3.4K) became comparable to the 4.7 nm diameter of the SDS micelle for a 0.5 M salt concentration. It now became Py2-PEO(3.4K)’s turn to be engulfed inside the larger SDS micelles which resulted in a noticeable reduction in <*k*> with a maximum <*k*> value for a 0.5 M salt concentration occurring for Py2-PEO(5K).

 As mentioned earlier, one obvious advantage of the MFA of the TRF decays is that this procedure deconvolutes the contributions arising from the kinetics of pyrene excimer formation with <*k*> and the different states occupied by the different pyrenyl labels. The resulting trends, such as the one shown in Figure 4B, become much more straightforward to interpret compared to those obtained by SSF which combine both contributions. Another clear-cut trend is that obtained by plotting *f*free as a function of salt concentration in Figure 4C. Since *f*free is the molar fraction of those pyrenyl labels that do not form excimer, it represents the fraction of pyrenes that are isolated inside an SDS micelle. Consequently, *f*free reflects the extent of bridging of two SDS micelles by a single Py2-PEO chain. Based on the trends shown in Figure 4C, the short Py2-PEO constructs with an *M*n value of 2.0, 3.4, and 5.0 K had a low *f*free fraction that increased slightly with increasing salt concentration. These constructs appeared to be too short to bridge two micelles resulting in low *f*free values. It would be possible however for the longer chains of the molecular weight distribution (MWD) of these shorter Py2-PEO constructs to bridge two micelles at high salt concentration thanks to the screening of the negatively charged micelles, thus resulting in the slight increase observed for *f*free. By contrast, the longer Py2-PEO(7.8K) and Py2-PEO(10K) constructs had a large *f*free value that decreased slightly with increasing salt concentration. These larger constructs were long enough to bridge two SDS micelles in a process that isolated the pyrenyl labels and thus prevented them from forming excimer resulting in a large *f*free value. However the size of the SDS micelles is known to increase with increasing salt concentration.33,34 The larger dimension of the SDS micelles at high salt concentration enabled the shorter chains of the MWD of the long Py2-PEO constructs to accommodate the two pyrenyl end groups which resulted in residual excimer formation and a decrease in *f*free.

 The most remarkable trend in Figure 4C was that displayed by Py2-PEO(6K). As was described in Figure 3B, Py2-PEO(6K) had a chain length that placed this construct right at the boundary before bridging could take place and no excimer was formed. This conclusion based on the analysis of the *I*E/*I*M ratios was however complicated by the fact that an *I*E/*I*M ratio combined the contributions of the kinetics and states of the pyrene labels. By separating both contributions through the MFA of the TRF decays, a much clearer trend was found for the *f*free fraction of Py2‑PEO(6K). *f*free showed a sharp increase at low salt concentration upon addition of just 0.02 M NaCl implying that most pyrenyl end groups of Py2-PEO(6K) were located inside a same micelle in the absence of salt, but that the resulting conformation of this molecule was greatly strained resulting in the build-up of a large restoring potential energy. Addition of a small amount of salt sufficiently reduced the electrostatic repulsion between two SDS micelles to enable a substantial fraction of the longer chains of the MWD of Py2-PEO(6K) to bridge two different micelles that would accommodate each pyrenyl end group. Further addition of salt enabled more chains to bridge and *f*free continued increasing until it reached 0.1 M salt. Above that salt concentration, the continued increase in micellar size and decrease in electrostatic repulsion, which would allow Py2-PEO(6K) chains to have their pyrenyl end groups in a same or two different SDS micelles, respectively, competed against each other leading to more-or-less constant *f*free values for NaCl concentrations above 0.1 M.

 The effects observed in Figure 4C could be readily rationalized by invoking a balance between the presence or absence of bridging between SDS micelles by a single Py2-PEO chain which could be influenced by the PEO chain length and the ionic strength of the solution. In turn, these parameters are known to control, respectively, the elastic force of the spring-like PEO chain as it extends or recoils with respect to its equilibrium average end-to-end distance (*r*EE-eq)[[36]](#endnote-36) and the electrostatic repulsion between two negatively charged SDS micelles located at the chain ends of a linear PEO chain.[[37]](#endnote-37) In fact, the salt concentration where *f*free increased in Figure 4C for a given Py2-PEO construct was expected to mark the point where the restoring energy of the recoiled chain with its two ends in a same SDS micelle would overcome the repulsive electrostatic energy between two micelles leading to their bridging. How this insight could be harnessed to quantitatively describe the interactions between the Py2-PEO constructs and the SDS micelles is described hereafter.

**DISCUSSION**

The conclusions that were reached from the analysis of the fluorescence spectra and decays suggested that the interactions between the Py2-PEO samples and the SDS micelles were the result of an interplay between the repulsive electrostatic energy (*E*elec) applied by the negatively charged SDS micelles bridged by a Py2-PEO chain and the restoring elastic energy (*E*elas) of an extended PEO chain. The balance between *E*elas and *E*elec and its implications on the conformation of the Py2-PEO constructs are schematically depicted in Figure 5. *E*elas increases when the two pyrenyl ends are forced closer or further from each other compared to their equilibrium end-to-end distance *r*EE‑eq. An *r*EE value smaller than *r*EE-eq would occur if the two hydrophobic ends of a PEO chain were forced to remain inside a same micelle of diameter *d*mic with *r*EE ~ *d*mic because *E*elec that would be obtained if the two pyrenyl ends were located inside two different micelles would induce a too large *E*elas response. Similarly, an *r*EE value larger than *r*EE-eq would be obtained for a PEO chain whose pyrenyl ends were forced into two negatively charged SDS micelles because their presence inside a same micelle would generate an *E*elas energy that would be too large. This balance between *E*elas and *E*elec is reflected in the trends obtained for *f*free in Figure 4C. For instance, *r*EE-eq listed in Table 1 for Py2-PEO(7.8K) and Py2-PEO(10K) would result in a restoring energy that would be too large to have both ends of these constructs in a same micelle. However *r*EE-eq for these constructs appears to be also large enough to result in weak electrostatic repulsion between two SDS micelles each occupied by one of the two pyrenyl end groups. These observations hold for the longer Py2-PEO constructs at all NaCl concentrations.

By contrast, *r*EEeq is small enough for Py2-PEO(2K) to ensure that both pyrenyl groups are located inside a same micelle regardless of salt concentration. But the increase in *f*free observed in Figure 4C upon increasing the salt concentration for the Py2-PEO constructs having intermediate *M*n values of 3.4, 5.0, and 6.0 K suggests that there must exist a salt concentration where a transition takes place between a regime at low salt concentration where *E*elas would be larger than *E*elec upon bridging two micelles to a regime at high salt concentration where *E*elas would become smaller than *E*elec due to screening of the negatively charged micelles which reduces the intermicellar distance. Bridging, as defined by an increase in *f*free in Figure 4C, would be allowed at the salt concentration for which *E*elas would equal *E*elec. In order to determine the energy necessary for bridging two SDS micelles with a single Py2-PEO chain, *E*elas and *E*elec needed to be determined as a function of *r*EE for a given Py2-PEO construct and salt concentration to establish the condition where *E*elas would equal *E*elec. The expression for *E*elas is given in Equation 5 assuming that the Py2-PEO constructs are molecular springs with a spring constant equal to 3*k*B*T*/*r*EE-eq2, where *d* is the displacement from *r*EE-eq.35

  (5)



**Figure 5.** Depiction of the balance between the repulsive electrostatic force between the negatively charged surfactant micelles and the elastic restoring force of a PEO chains.

Based on Equation 5, *r*EE-eq must be known to calculate *E*elas for a given *d* value. The expression of *r*EE-eq is given in Equation 6 for a PEO chain of number average molecular weight *M*n in water where *N*K and *l*K represent the number and length of Kuhn segments equal to 0.0141×*M*­n and 0.707 nm, respectively.17 The corresponding *r*EE-eq values were listed in Table 1 for all Py2-PEO constructs.

  (6)

 An expression for *E*elec was provided in Equation 7 by viewing the SDS micelles as charged spheres which are brought together from a very far distance (*x*→∞) to a distance *d* from one another.36

 (7)

In Equation 7, ** is the inverse of the Debye length (= ** given in Equation 8), *Z* is the interaction constant whose expression is given in Equation 9, and *R* is the sphere radius (Equation 11).

  (8)

  (9)

In Equations 8 and 9, **o is the permittivity of vacuum (8.854×10-12 C2Jm), ** is the dielectric constant of the solution,[[38]](#endnote-38) *k*B is Boltzman’s constant (=*R*/*N*A), *e* is the electronic charge (*e* = 1.602×10 C), *I* is the ionic strength of the solution, and **o is the potential of the isolated surface whose expression is given in Equation 10.

  (10)

In Equation 10, ** is the charge density equal to the number of free charges per SDS micelles divided by the surface of the micelle. The surface of the micelles could be determined from the radius of the SDS micelles (*R*M) calculated by using Equation 11 where *N*agg is the aggregation number of the SDS micelles at a given salt concentration whose values have been published33,[[39]](#endnote-39) and *V*Tail is the volume occupied by the hydrocarbon chain of an SDS molecule (350 Å3).[[40]](#endnote-40)

  (11)

The ionic strength of the solution *I* was calculated as the sum of the ionic strength of the surfactant solution *I*S and the salt *I*NaCl. Since both the sodium and chloride ions of NaCl are monovalent and fully dissociated, *I*NaCl was simply taken as the salt concentration. The SDS solution presented three distinct species in solution, namely the sulfate ions, the sodium ions, and the charged micelles. The equilibrium between these three species had to be accounted for. The calculation of *I*S was carried out according to a published procedure.[[41]](#endnote-41) The full calculation of *I*S is given in the SI.

 The average number *c* of charges per micelles was estimated by conducting a quenching study of pyrene in SDS micelles by thallium cations. Aqueous solutions of 0.5×10 M pyrene in 15 mM SDS were prepared with increasing concentration of thallium chloride and their fluorescence decays were acquired and fitted with Equation 2. The lifetime of pyrene (**M)and the parameters *A*2, *A*3, and *A*4 retrieved from this analysis were listed in Table S21. The parameters *A*2, *A*3, and *A*4 were used to calculate *k*q, *k*’, and most importantly <*n*> which was plotted as a function of thallium concentration in Figure 6A. The plots in Figure 6A yielded straight lines whose slope could be related to the binding constant *K* of thallium cations to SDS micelles according to Equation 12. The micelle concentration in Equation 12 is given by the quantity ([SDS] – CMC)/*N*agg where *N*agg and CMC at each salt concentration have been determined earlier33,33,38 and the SDS concentration equals 15 mM in these experiments. A plot of *K* versus NaCl concentration is provided in Figure 6B. As the ionic strength of the solution increased, *K* decreased substantially.

  (12)

 The determination of the charge per micelle *c* assumed that sodium or thallium cations would bind similarly to the SDS micelles. It also assumed that the binding constant *K* represented the binding of those sodium cations that were the counterions of the SDS molecules involved in the SDS micelles for a given NaCl concentration. Using the *K* values listed in Figure 6B, *c* could be determined with Equation 13. The *c* values were plotted in Figure 6C as a function of salt concentration. The charge per micelle increased with increasing salt concentration reflecting the weaker binding of the sodium cations to the SDS micelles at high ionic strength.

  (13)

|  |  |  |
| --- | --- | --- |
| A) | B) | C) |

**Figure 6.** Plots of A) <*n*> as a function of thallium concentration for salt concentrations of () 0.00, () 0.01, () 0.03, () 0.05, ( ) 0.07, () 0.09, ( ) 0.10, () 0.20, () 0.30, (**×**) 0.40, and (**+**) 0.50 M. Plots of B) *K* and C) ( ) *c* and ( ) *N*agg as a function of salt concentration.

Combining Equations 5 – 13 enabled the calculation of *E*elas (Equation 5) and *E*elec (Equation 7) as a function of the distance separating the pyrene labels (*d*) for each Py2-PEO construct and salt concentration. Figure 7 describes the trends obtained by plotting *E*elas and *E*Elec as a function of *d*.

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**Figure 7**: A plot of *E*elec (─) as a function of the distance *d* separating two micelles (from right to left: [NaCl] = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09, 0.10, 0.20, 0.30, 0.40, and 0.50 M), and *E*elas (---) as the polymer was stretched to a distance *d* from *r*EE-eq (from left to right: *M*n = 2.0, 3.4, 5.0, 6.0, 7.8, and 10.0 K). (1 zJ = 1021 J).

To determine *E*Py, the binding energy of a pyrenyl label to an SDS micelle, *E*elas and *E*elec were compared when both pyrenyl ends were located either inside one same micelle or in two different micelles. In order for the pyrenyl groups to be held inside one micelle, the energy *E*Py required to remove a pyrene from an SDS micellehad to be greater than or equal to *E*elas of the polymer. When the pyrenyl ends were held inside one micelle, *E*elas(*d*mic) was calculated by setting *d*mic = 2×*R*M in Equation 5 where *R*M was the radius of the hydrophobic micellar interior (see Equation 11) and it was plotted in Figure 8A as a function of salt concentration. At any given salt concentration, *E*elas(*d*mic) increased with increasing chain length of the Py2-PEO construct. This increase in *E*elas corresponded to the penalty of constraining the two ends of a PEO chain of increasing length inside a same SDS micelle. Considering that Py2-PEO(6K) was the longest construct that kept its two ends in a same micelle for a solution without salt, these conditions would represent the largest *E*elas(*d*mic) where bridging would be avoided, corresponding to an energy of 1.41 zJ (1 zJ = ×1021 J) reflecting a lower estimate for *E*Py. By contrast, the high *f*free values obtained for Py2PEO(7.8K) suggested that this construct always bridged, so that the energy *E*elas(*d*mic) = 1.84 zJ required to hold the pyrenes within one micelle was larger than *E*Py. As a result, *E*Py, estimated from the energy required to pull one pyrenyl group out of a micelle to induce bridging, could be estimated to equal 1.6 (±0.3) zJ.

|  |  |  |
| --- | --- | --- |
|  | B) | C) |

**Figure** **8**: *E*elas as a function of salt concentration when A) Py2-PEO is bridging adjacent micelles (*E*elas(*d*eq)) and B) the pyrenyl ends occupy the same micelle (*E*elas(*d*mic)), and C) the difference in *E*elas if the pyrenyl ends were to move from adjacent micelles to one (*ΔE*elas = *E*elas(*d*eq) – *E*elas(*d*mic)). Py2-PEO *M*n = () 2.0 K, () 3.4 K, ( ) 5.0 K, (**×**) 6.0 K, () 7.8 K, and () 10.0 K. (1 zJ = 1021 J).

A)

Assuming that equilibrium for bridging was reached when the two pyrenyl ends were separated by a distance *d*eq where the elastic energy required to spread apart the two ends of a Py2-PEO molecule from *d*mic to *d*eq equaled the energy involved in bringing an SDS micelle from the bulk (*d* → ∞) to *d*eq, *d*eq could be obtained by setting *E*elas(*d*eq) equal to *E*elec(*d*eq). In turn, this condition represented the distance (*d*=*d*eq) where the traces for *E*elas and *E*elec would intercept in Figure 7. This analysis led to a set of *E*elas(*d*eq) values for each Py2-PEO construct which were plotted as a function of salt concentration in Figure 8B. Using the trends obtained for *f*free in Figure 4C, the highest energy observed for bridging was for Py2-PEO(7.8K) without salt with an energy of 2.67 zJ in Figure 8B. However, knowing that Py2-PEO(6K) without salt did not bridge two SDS micelles suggested that the energy of 3.46 zJ required for bridging in Figure 8B was greater than *E*Py. The upper and lower estimates for *E*Py determined for bridging (2.67 < *E*Py < 3.46 zJ) and nonbridging (1.41 < *E*Py <1.84 zJ) were similar in magnitude, leading to the conclusion that *E*Py took a value around 2.3 (±0.8) zJ. Although this value is quite small, it appears to be consistent with the so-named *transient network theory* which defines the bonding potential for a hydrophobe to a micelle.11,[[42]](#endnote-42) The bonding potential (*E*­m), or the energy required to pull a hydrophobe from the interior of a micelle, is typically described via the disengagement rate (*β*0) defined in Equation 14, where ω0 is the characteristic frequency of thermal vibration of the polymer.

 (14)

From Equation 14, it can be seen that the rate of disengagement depends on the ratio of *E*m over *k*B*T* (= 4.11 zJ). In turn, the obtained *E*Py value of 2.3 zJ (*E*Py/*k*B*T* ~ 0.56) lands in the expected order of magnitude for a hydrophobe that is bound to the interior of a micelle but is still readily exchangeable. For the sake of comparison, an *E*Py >> *k*B*T* would lead to a disengagement rate approaching zero which would forbid pyrene from leaving a micelle, and the pyrene pendants would be unable to redistribute themselves among the micelles. On the other hand, an *E*Py << *k*B*T* would imply that the hydrophobic pyrene ends move freely in and out of the micelle as the polymer diffuses throughout the solution and would spend a significant amount of time outside the micelles leading to a high fraction of free pyrene, even for the low molecular weight Py2-PEO. The conditions *E*Py >> *k*B*T* and *E*Py << *k*B*T* are thus not representative of the experimental observations, namely that the pyrenyl end groups are bound to the SDS micelles (*I*1/*I*3 = 1.41 ± 0.02) but can redistribute themselves among the micelles relatively easily based on the changes in *I*E/*I*M observed in Figure 4.

 In Figure 8C the difference in energies (*ΔE*elas = *E*elas(*d*eq) – *E*elas(*d*mic)) acting on the pyrenyl ends before and after bridging occurred was obtained by subtracting *E*elas(*d*mic) when both ends occupied a single micelle from *E*elas(*d*eq) when bridging occurred. Based on this definition, a negative *ΔE*elas would correspond to a conformation in which a Py2-PEO molecule would prefer to bridge two micelles. For example, the positive *ΔE*elas of Py2‑PEO(2K) in Figure 8C predicts that the energy representing a polymer conformation where both ends are located inside one micelle is lower than the energy representing a conformation where the polymer would bridge two micelles. Based on this interpretation of *ΔE*elas, Py2-PEO(2K) cannot bridge two micelles as observed experimentally from the low *f*free values reported in Figure 4C. On the other hand, the negative *ΔE*elas of Py2‑PEO(7.8K) and Py2-PEO(10K) indicates that the conformation where the polymer bridges two micelles always has a lower energy and is thus favored. These predictions matched the results obtained by the MFA which demonstrated a consistently low *f*free value for Py2-PEO(2K) as a function of salt concentration and a consistently high *f*free value for the Py2-PEO constructs with an *M*n of 7.8 and 10K. *ΔE*elas in Figure 8C and *f*free in Figure 4C were also in good agreement for Py2‑PEO(6K), where *E*elas(*d*mic) was predicted to be lower than *E*elas(*d*eq) in the solution without salt suggesting that both ends were in a same micelle and accordingly, *f*free was found to be low in Figure 4C. When salt was added to the solution, it quickly became more favourable for the ends to bridge two micelles as *ΔE*elas turned negative for salt concentrations greater than zero and *f*free increased. Similar trends were also observed for Py2-PEO(3.4K), where the energy calculations predicted no bridging at low salt concentration and a possibility of bridging at high salt concentrations as reflected by *f*free in Figure 4C. Py2-PEO(5K) might be the only construct whose behavior reflected by *f*free in Figure 4C did not match the predictions based on *ΔE*elas in Figure 8C. Experimentally, Py2-PEO(5K) would be expected to behave more like Py2-PEO(3.4K) but was predicted to behave more like Py2-PEO(6K) theoretically. This apparent discrepancy might be attributed first to the fact that the calculation of *ΔE*elas can still be improved, and second that the Py2-PEO(5K) construct being at a regime boundary might be more sensitive to dispersity effects. Unfortunately, the PEO(5K) substrate used to prepare the Py2-PEO(5K) sample had the highest dispersity of all other constructs. Nevertheless the overall trends determined from the theoretical energy calculations for *ΔE*elas in Figure 8 seemed to match fairly well the trends observed experimentally with the *f*free values obtained by the MFA in Figure 4C supporting the validity of these relatively simple calculations.

**CONCLUSIONS**

This study represents the first example in the scientific literature where PEF is applied to probe the intermolecular forces experienced by an isolated polymer chain freely floating in solution. These fluorescence experiments took advantage of the high sensitivity of fluorescence to probe the Py2-PEO constructs under conditions that were so dilute that interactions took place principally between the pyrenyl end groups and the SDS micelles and not between PEO and SDS molecules, and that the probability of having more than one Py2-PEO construct per SDS micelle was minuscule ensuring that the fluorescence signal emanated from isolated Py2-PEO molecules. The encapsulation of the pyrenyl labels inside SDS micelles provided a tool to adjust the extent of stretching on a PEO chain by carefully adjusting the PEO chain length and the solution ionic strength. Furthermore the MFA could satisfyingly separate the contributions to PEF between the kinetics experienced by the pyrenyl labels and their physical state, either located both in a same micelle or separated in two different micelles. In particular, the MFA of the fluorescence decays yielded the molar fraction *f*free that represented the extent of bridging for the Py2-PEO constructs. The fact that theoretical calculations of the forces experienced by the pyrenyl groups predicted fairly closely the bridging of a Py2-PEO construct having a given chain length and immersed in a solution of known ionic strength suggests that PEF can be applied to probe the intramolecular forces of macromolecules freely floating in solution. This feature represents a major departure from the set up typically used to conduct single molecule force spectroscopy experiments that always require tethering a macromolecule to a macroscopic surface, and thus provides an additional experimental means to study intramacromolecular forces in solution.

**SUPPORTING INFORMATION**

Synthesis of the Py2-PEO constructs, probability of micellar occupancy, equations for the model free analysis of the fluorescence decays, parameters retrieved from the fluorescence decay analyses, calculations of the electrostatic and elastic energies.

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