

Institute for Polymer Research
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Symposium documents for

Howard Siu

Abstract

Presentation

Characterization of the Aggregation Made by Short PEO Chains Labeled at One End by the Fluorophore Pyrene

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Associative polymers are an important group of polymers used in industry. In particular, two families of associative polymers, HASE and HEUR polymers (Figure 1a), are the main types of viscosity modifiers used in the paints and coatings industries. The peculiar viscoelasticities of these polymer families are rooted in the hydrophobic interactions of the hydrophobically end-capped poly(ethylene oxide) (hyd-PEO) groups which are common to both types of associative polymers. Thus, characterization studies of the aggregation properties of hyd-PEO are likely to yield important information on the associations of the HASE and HEUR polymers.

One technique that is often employed in characterizing HASE and HEUR systems is fluorescence. To gain direct information on the hydrophobic interactions, the hydrophobe can be replaced by a hydrophobic fluorophore. Pyrene is a common choice since it has the ability to complex with itself to create different fluorescence species called excimers. By monitoring the fluorescence of the various pyrene species, an idea of the amount of association between hydrophobes can be gained.

This seminar will focus on the characterization of the aggregation properties of a short poly(ethylene oxide) chain of 53 units in length capped at one end by the fluorophore pyrene (Py-PEO) (see Figure 1b). Several features of the associations of Py-PEO in water will be characterized such as the onset concentration of aggregation of Py-PEO and the sizes of these aggregates using fluorescence as well as other techniques such as surface tensiometry and light scattering.

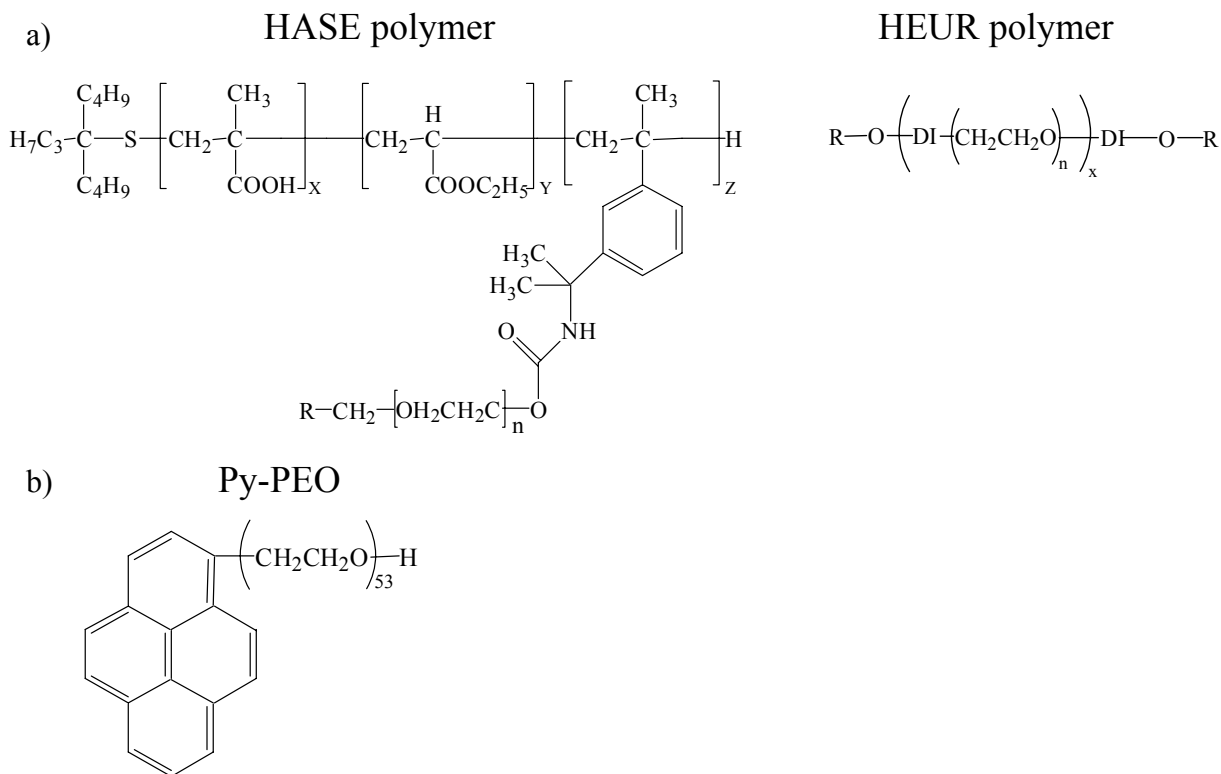


Figure 1: a) HASE and HEUR polymer structures with R and DI representing the hydrophobic group and diisocyanate linker, respectively; b) Structure of Py-PEO.

Since Py-PEO has a structure similar to that of many non-ionic surfactants, surface tensiometry should be capable of determining the critical micelle concentration (CMC) in water. For Py-PEO, the surface tension is shown in Figure 2 to drop at 0.001 g/L, from which concentration it steadily decreases upon further addition of Py-PEO until reaching a plateau at 10 g/L. Simple light scattering as well as excimer lifetime measurements indicate that micelles are being formed at concentrations above 0.003 g/L, implying that the CMC occurs at a concentration close to 0.001 g/L as observed from surface tensiometry. At concentrations above 10 g/L, dynamic light scattering

measurements showed a bimodal distribution indicating that larger aggregates are created. A potential scheme to describe the system would be that below a concentration of 0.003 g/L, only singular Py-PEO species exist in the bulk. At Py-PEO concentrations between 0.003 and 10 g/L, Py-PEO micelles are formed, which, at concentrations above 10 g/L, cluster to form larger aggregates (see Figure 2). From steady-state fluorescence spectroscopy experiments, it can be concluded that these larger aggregates consist of loosely associated Py-PEO micelles whose structure remains unchanged. This idea has also been proposed by the group of Jeanne François using poly(ethylene oxide) end-labeled with alkyl chains.¹

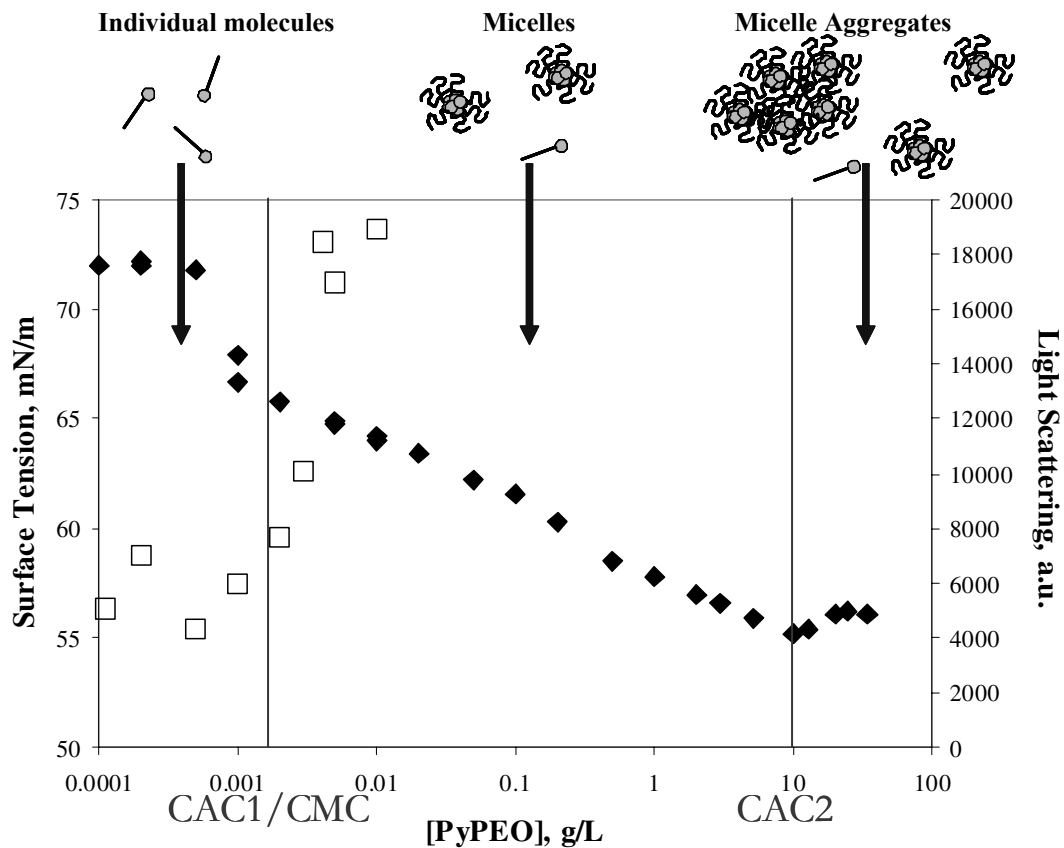


Figure 2: Py-PEO aggregation scheme in water with surface tension (◆) and light scattering (□) data.

Using Py-PEO as the surfactant, each micelle can be considered to act as a single fluorescent excimer species. Upon addition of an external hydrophobic quencher such as dodecyl pyridinium chloride (DPC), the excimer intensity is found to obey Equation 1 which was originally proposed by Turro and Yekta (see Figure 3):²

$$\ln\left(\frac{I_{E0}}{I_E}\right) = \frac{[Q]}{[M]} = \frac{[DPC] \times N_{agg}}{[Py-PEO] - CMC} \quad (1)$$

where I_E and I_{E0} are the intensities with and without quencher, respectively, and $[Q]$ and $[M]$ are the quencher and micelle concentrations, respectively. The micelle concentration for Py-PEO can be expressed as the difference between the surfactant concentration ($[Py-PEO]$) and the CMC divided by the number of surfactant molecules per micelle (N_{agg}). From this quenching study, carried out with several Py-PEO concentrations, a N_{agg} value of 20 ± 2 Py-PEO per micelle is determined. Since the micellar structure remains unchanged even after undergoing aggregation into larger structures, the Py-PEO concentrations used for this study are considered to be valid. By comparing the size of the micelles obtained by dynamic light scattering measurements with estimated sizes based on various conformations of the poly(ethylene oxide) corona, it can be concluded that the Py-PEO micelles, consisting of 20 ± 2 Py-PEO per micelle, have a pyrene core surrounded by a compact poly(ethylene oxide) corona. This conclusion differs from the extended chains proposed by the François group possibly stemming from the differences between pyrene and alkyl hydrophobic groups.

From this study, the aggregation of short poly(ethylene oxide) chains labeled at one end with pyrene (Py-PEO) has been investigated. From the results, it is found that

Py-PEO formed micelles at the very low concentration of 0.003 g/L but also undergoes a secondary aggregation into larger structures at 10 g/L. The micelles formed by Py-PEO are determined to consist of 20 ± 2 Py-PEO molecules having a PEO corona existing in a compact coiled state. It is hoped that the knowledge obtained from this study can be applied to modeling the associations of HASE and HEUR polymers to better understand those systems.

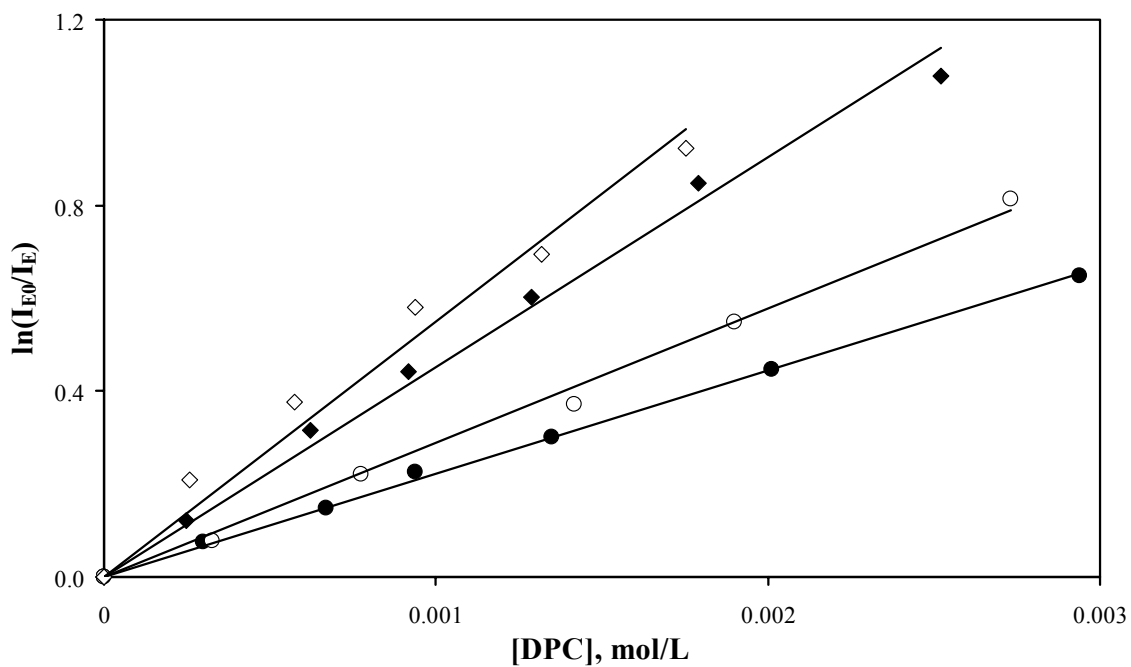


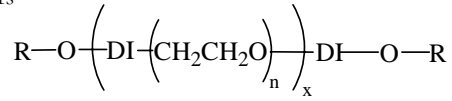
Figure 3: Quencher DPC concentration study at Py-PEO concentrations of 15 (\diamond), 44 (\blacklozenge), 100 (\circ) and 149 (\bullet) g/L.

References

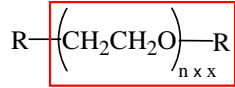
1. Beaudoin, E.; Borisov, O.; Lapp, A.; Billon, L.; Hiorns, R.C.; François, J. *Macromolecules* **2002**, *35*, 7436 – 7447.
2. Turro, N.J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951 – 5952.

HEUR Polymers

- Hydrophobically modified Ethoxylated Urethane (HEUR) polymers



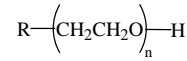
- DI represent diisocyanate linkages, effect is usually disregarded



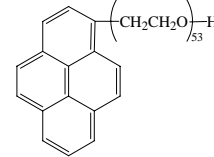
- The properties depend on the ratio of hydrophobe (R) size : hydrophilic chain (n × x) size

Proposed Model Compound (Py-PEO)

- Nature of HASE and HEUR networking based on aggregation of hydrophobically end-labeled PEO chains

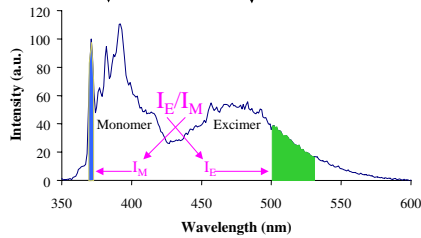
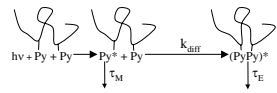


- Study of this component gives insight on HASE/HEUR aggregation

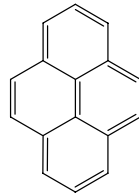


Model compound (Py-PEO) should act like a surfactant

Pyrene Fluorescence



R = Pyrene



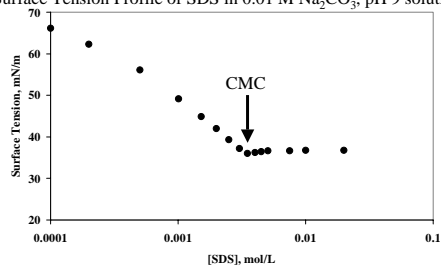
Studies of Py-PEO

- Determine the onset concentration of aggregation of Py-PEO
 - Surface tension
 - Light scattering
 - Time-resolved fluorescence of excimer
- Determine the number of Py-PEO per aggregate, N_{agg}
 - Micellar quenching studies using dodecyl pyridinium chloride (DPC)
 - Verify using dynamic light scattering (DLS)

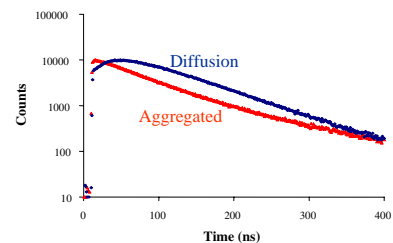
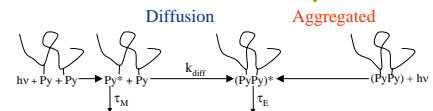
Surface Tension

- Addition of surfactants lowers the surface tension
- At critical micelle concentration (CMC), individual surfactants aggregate into structures called "micelles"

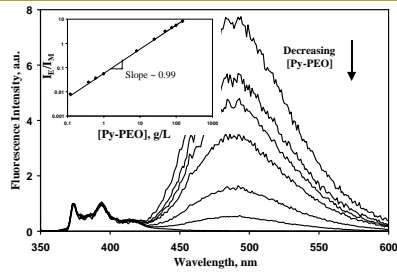
Surface Tension Profile of SDS in 0.01 M Na_2CO_3 , pH 9 solution



Fluorescence Excimer Decays

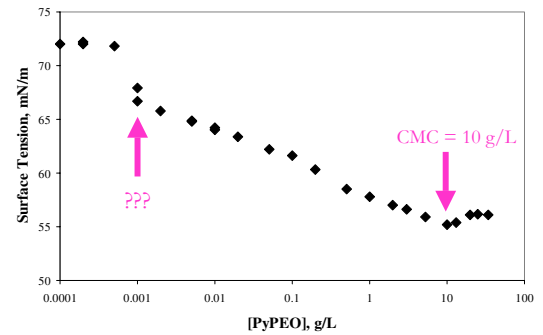


Results: Determining Onset of Aggregation

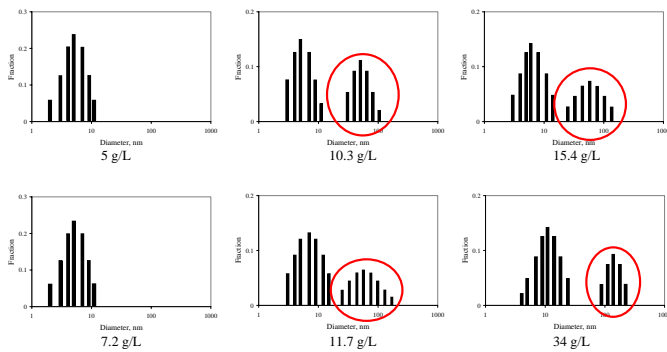


- Addition of Py-PEO (0.1 to 150 g/L) found an almost linear increase of intensity of excimer (I_E) relative to monomer (I_M) fluorescence

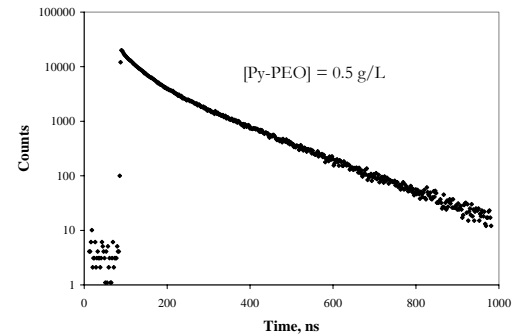
Surface Tension Measurements of Py-PEO



CONTIN Analysis of DLS of Py-PEO



Time-Resolved Excimer Decays of Py-PEO



- Lack of risetime indicates excimers formed via excited aggregates

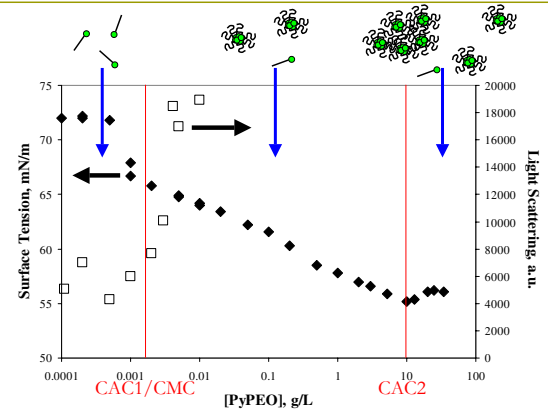
Loose Aggregation of Micelles

- Secondary aggregation occurs with micelles associating together
- Since I_E/I_M trend does not change, assume micelles stay unchanged throughout aggregation process
- The François group proposed a similar system with alkyl end-capped PEO*



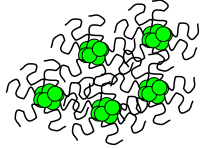
* Baudoïn, E.; Borisov, O.; Lapp, A.; Billon, L.; Hiorns, R. C.; François, J. *Macromolecules* **2002**, *35*, 7436.

Additional Light Scattering Measurements



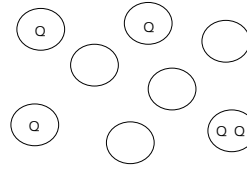
Results of Concentration Study of Py-PEO

- Determined critical micelle concentration (CMC) of Py-PEO to be 0.003 g/L
- Determined second aggregation of micelles (CAC2) of Py-PEO to be 10 g/L
 - Loose aggregates similar to those proposed by the François group



Finding the Aggregation Number, N_{agg}

- Each Py-PEO micelle acts as single excimer species
- Added hydrophobic quencher (Q), distributed amongst micelles

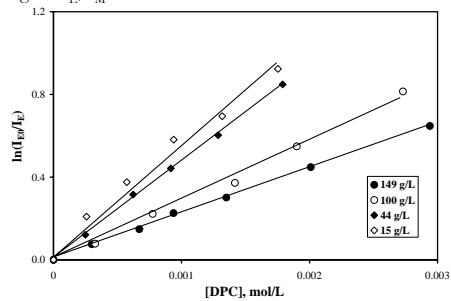


$$\ln\left(\frac{I_{E0}}{I_E}\right) = \frac{[Q]}{[M]} = \frac{[Q] \times N_{agg}}{[Py-PEO] - CMC}$$

- Micelles containing quenchers automatically quenched (i.e. do not fluoresce) reducing intensity of excimer from I_{E0} to I_E

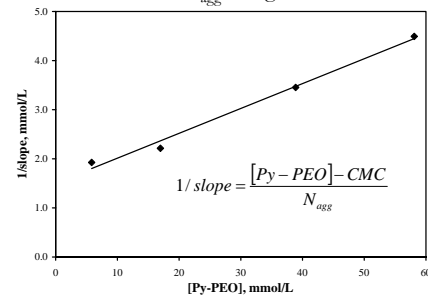
Determination of N_{agg} of Py-PEO Micelles

- Quenched Py-PEO micelles using dodecyl pyridinium chloride (DPC)
- Assumed micelle aggregation did not affect micelle structure
 - No change in I_E/I_M



Determined Value of N_{agg}

- From slopes of each Py-PEO concentration of $\ln(I_{E0}/I_E)$ vs. [DPC], one can determine N_{agg} using:



- N_{agg} determined to be 20 ± 2 Py-PEO per micelle

Comparison of Estimated vs. Measured Sizes

- Dynamic light scattering gave hydrodynamic diameters d_{H1} of 7.2 ± 3.1 nm for single micelles

- Taking into account a loosely-packed pyrene core of 20 units:

- Fully extended PEO corona has d_{H1} of 51 nm
- Unperturbed coiled PEO corona has d_{H1} of 10 nm
- Tightly packed PEO corona has d_{H1} of 6.8 nm



Conclusion:

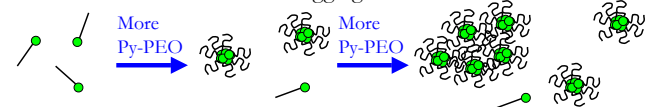
Py-PEO micelles consist of 20 ± 2 Py-PEO units with a compact PEO corona

- Contrary to extended conformation proposed by the François group!
 - François group used long PEO chains

Conclusions

- Py-PEO (53 units) forms micelles at 0.003 g/L (CMC)

- Py-PEO micelles aggregate at 10 g/L (CAC2) but individual micelle structures left intact in aggregate



- Micelles consist of 20 ± 2 Py-PEO units (N_{agg})
 - Collapsed PEO corona





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