Rheology Under the Microscope:
Tracking Changes of a Networked Associative Polymer Under Shear at the Molecular Level

Howard Siu

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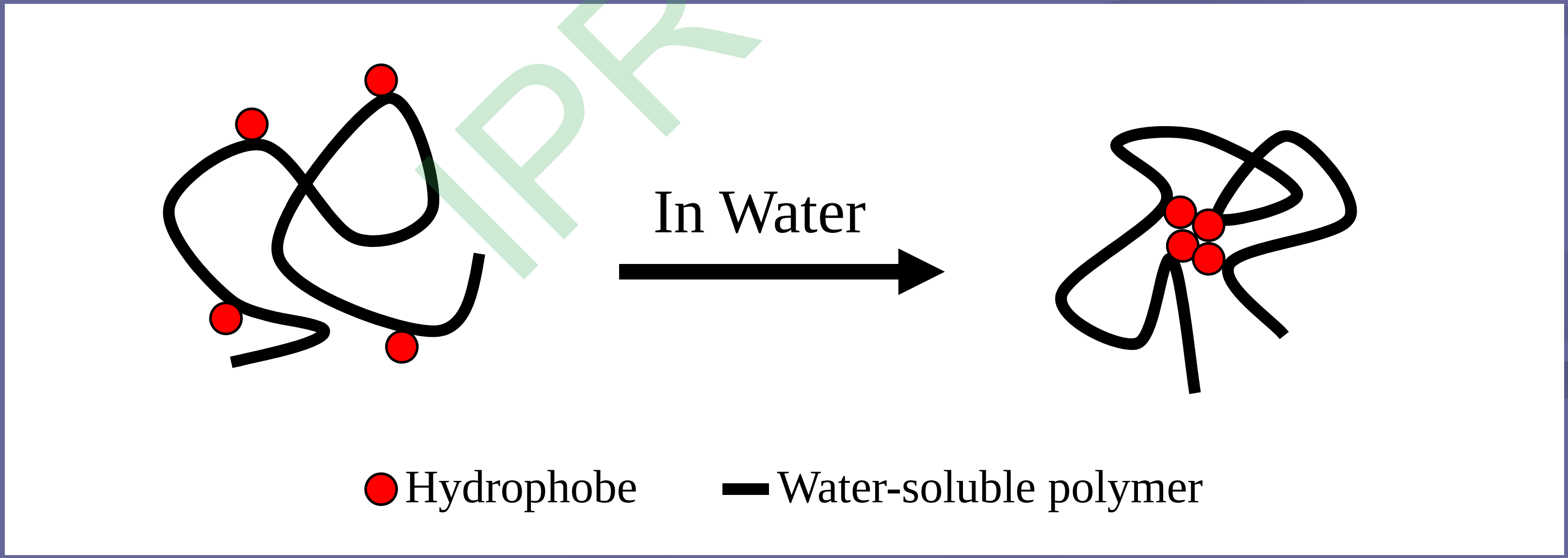
Outline

- Associative polymers (APs)
- Pyrene labelled APs
- Fraction of aggregated pyrenes (f_{agg}) (Py-PDMA)
- Application to Py-HASE system
- Combined fluorometer/rheometer system
- Conclusions

Associative Polymers

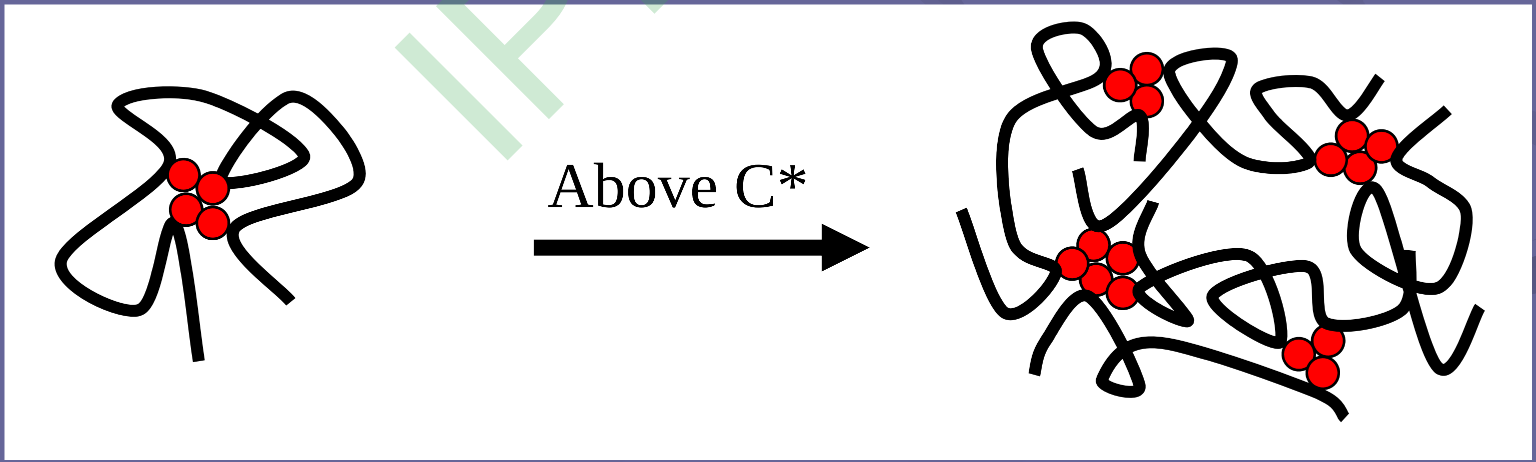
- Water-soluble polymers with a small amount (<5 mol%) of hydrophobic pendants
- In water, hydrophobes cluster to form aggregates



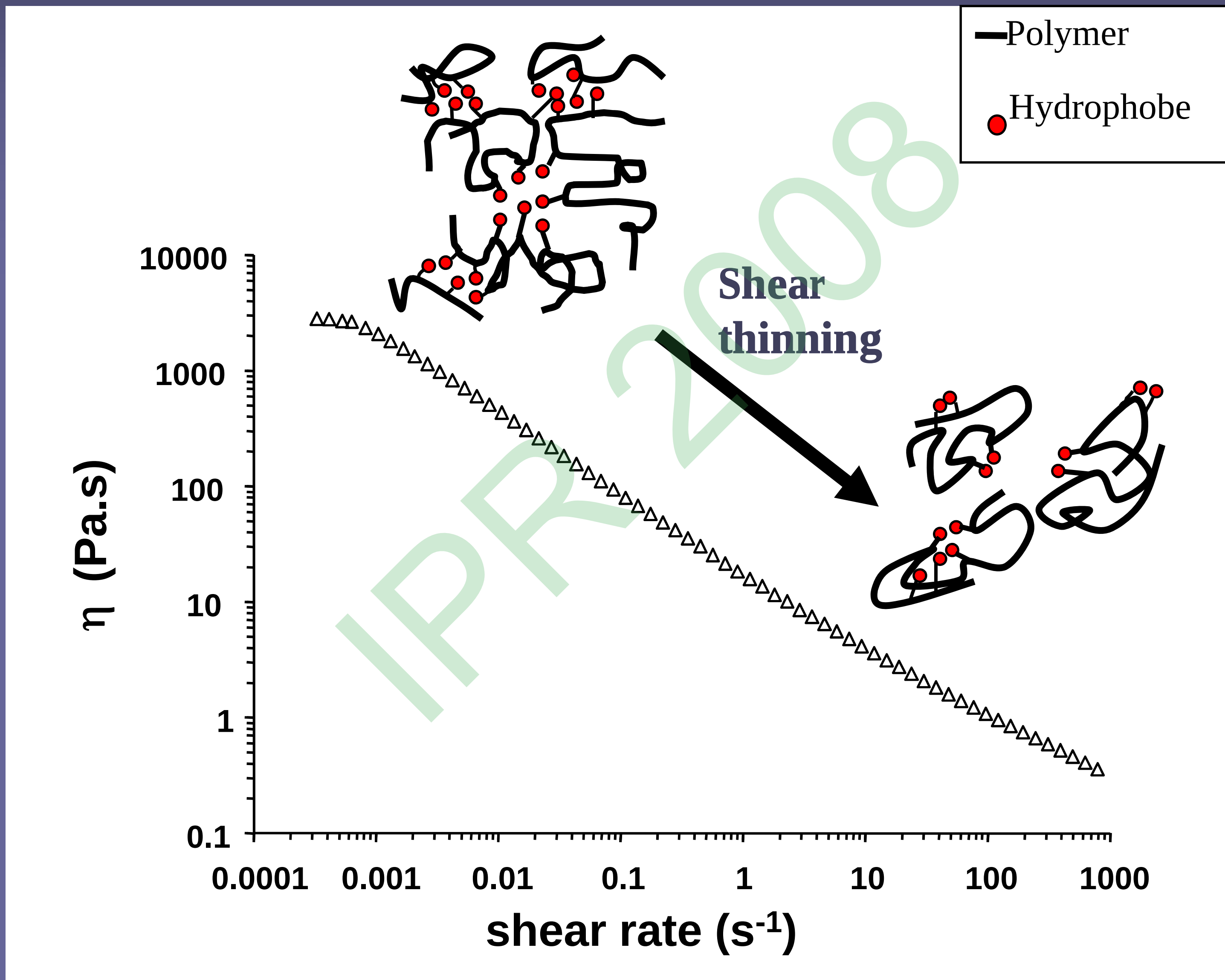
Associative Polymers

- Above C* (semi-dilute regime), intermolecular bridging creates a polymeric network that increases the solution viscosity

- Used in paints and coatings as colloidal stabilizers and viscosity modifiers



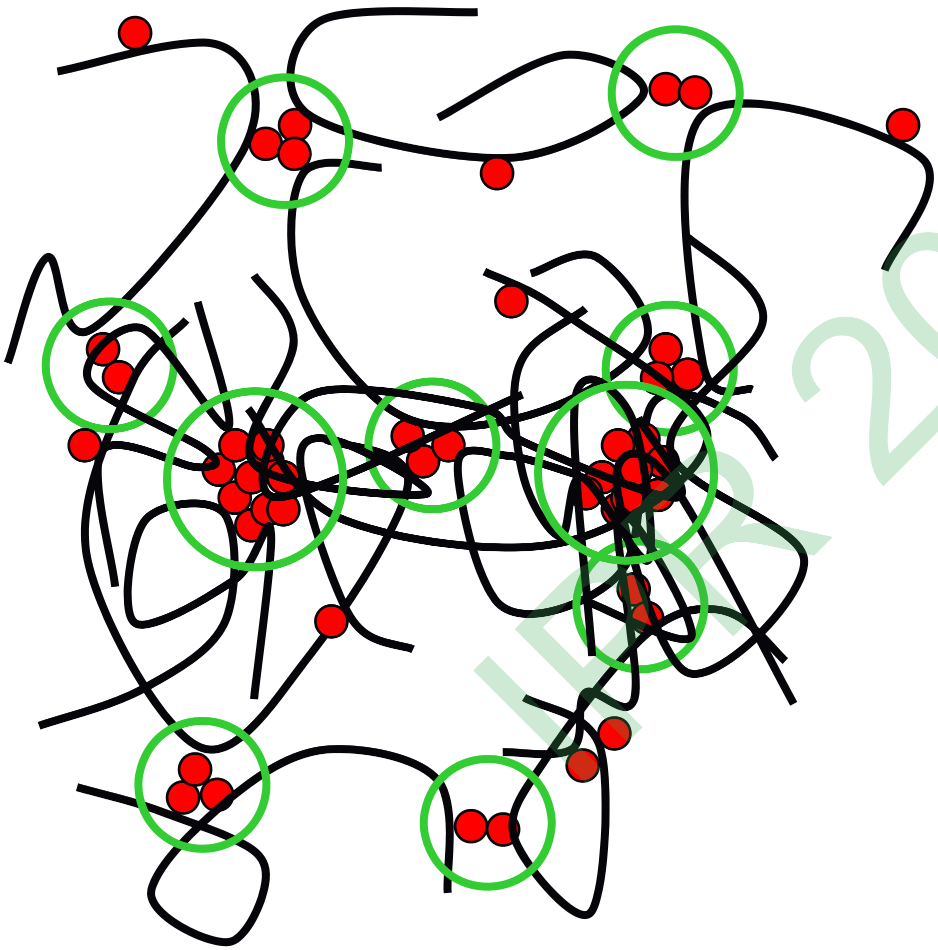
Rheology (Flow/Deformation) of AP Solutions



Important Parameters in Modeling Rheology of AP Solutions

- Residence time of hydrophobes in aggregates
- Average number of hydrophobes per aggregate (N_{agg})
- Overall level of association of hydrophobes in solution (f_{agg})

Defining the Network by N_{agg} and f_{agg}



- f_{agg} gives the fraction of hydrophobes in aggregates
- Knowing f_{agg} and N_{agg} gives the # of junction points, thus the extent of network
- For same f_{agg}, having high N_{agg} values results in a less extended network

Thus, it is essential to know both f_{agg} and N_{agg} in order to characterize the network effectively

Determination of f_{agg} and N_{agg}

- N_{agg} can be determined for a pyrene labelled AP by fluorescence quenching studies*

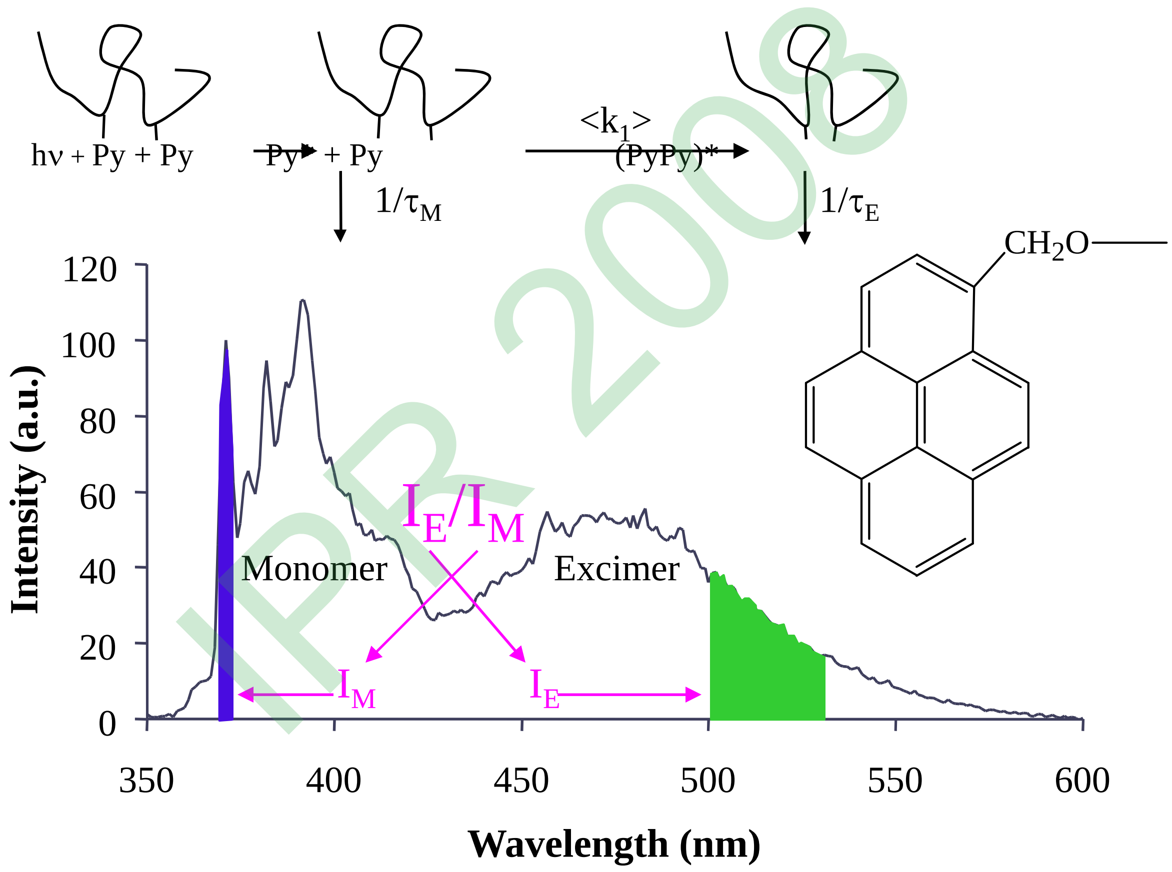
- Recently f_{agg} parameter has been determined by fluorescence measurements for pyrene labelled APs**

- N_{agg} has also been determined for a pyrene labelled AP from fluorescence, using f_{agg} and information obtained from the fluorescence blob model (FBM)**

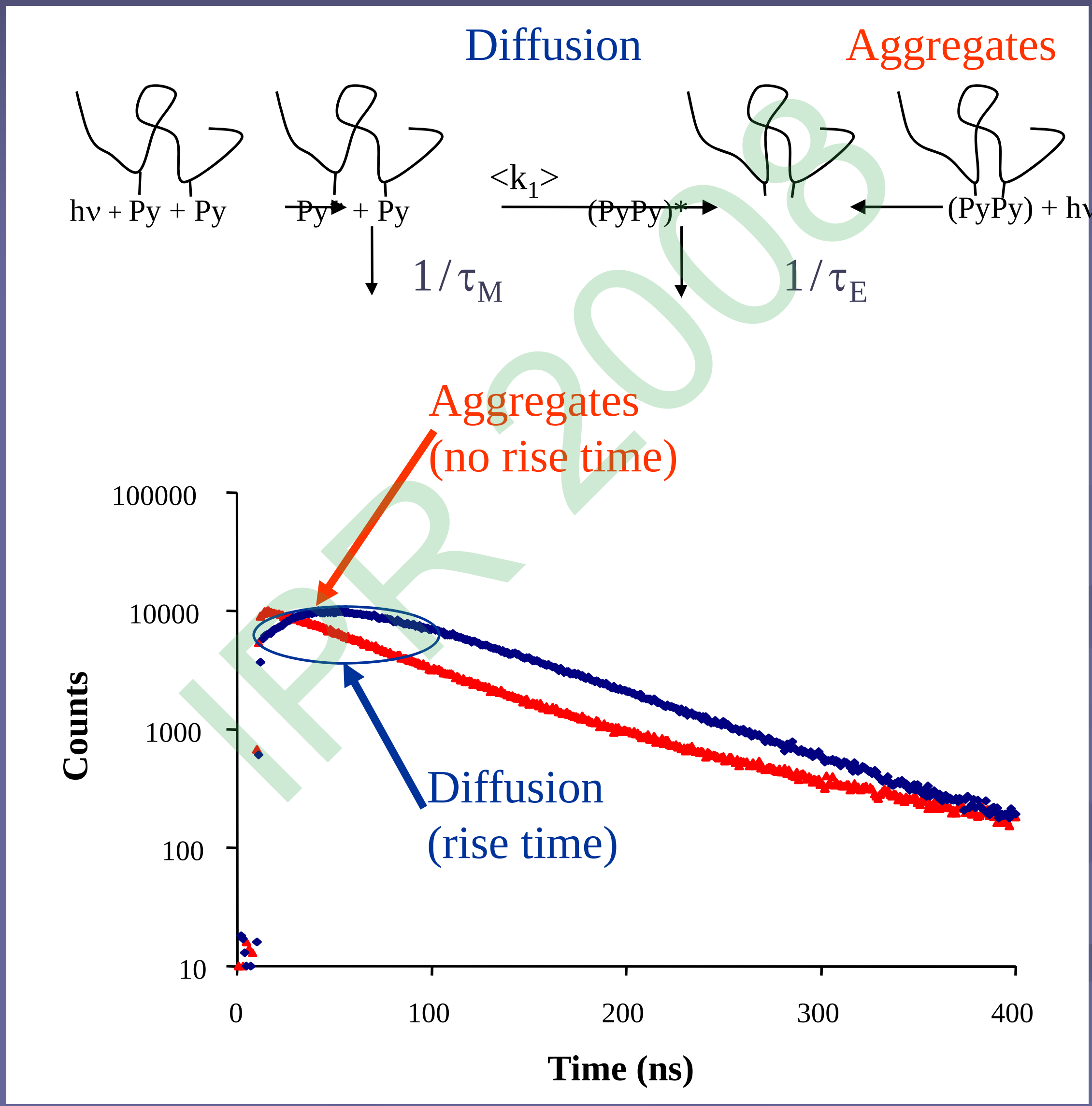
*Siu, H.; Prazeres, T. J. V.; Duhamel, J.; Olesen, K.; Shay, G. *Macromolecules* **2005**, *38*, 2865.

**Siu, H.; Duhamel, J. *Submitted to J. Phys. Chem. B, Manuscript # JP-2008-011059*

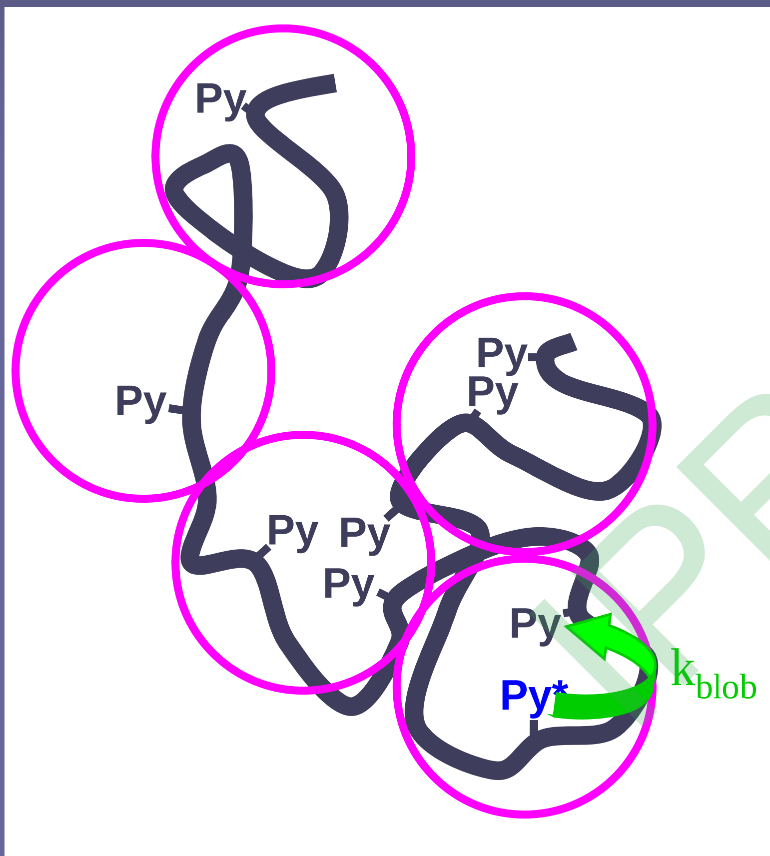
Pyrene Fluorescence



Excimer Lifetime Decays



The Fluorescence Blob Model (FBM)



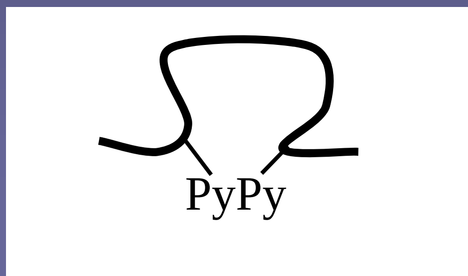
Blob = Volume probed by an excited pyrene can probe

<n>: Average number of pyrenes per blob

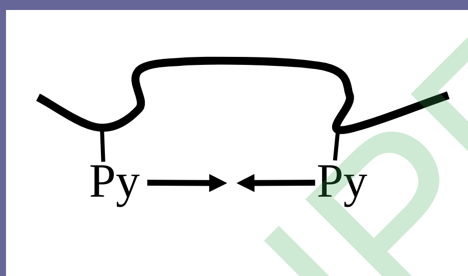
k_{blob}: Rate of encounter of excited pyrene with one ground-state pyrene

The fluorescence blob model is useful to model diffusional encounters of pyrene pendants attached to a polymer

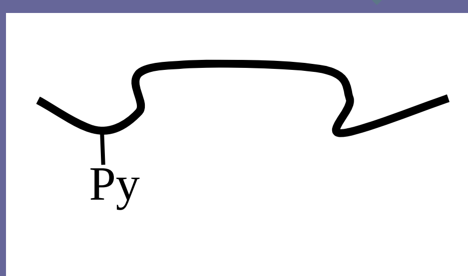
Pyrene Species Present in Solution



f_{agg}: Fraction of associated pyrene pendants in solution



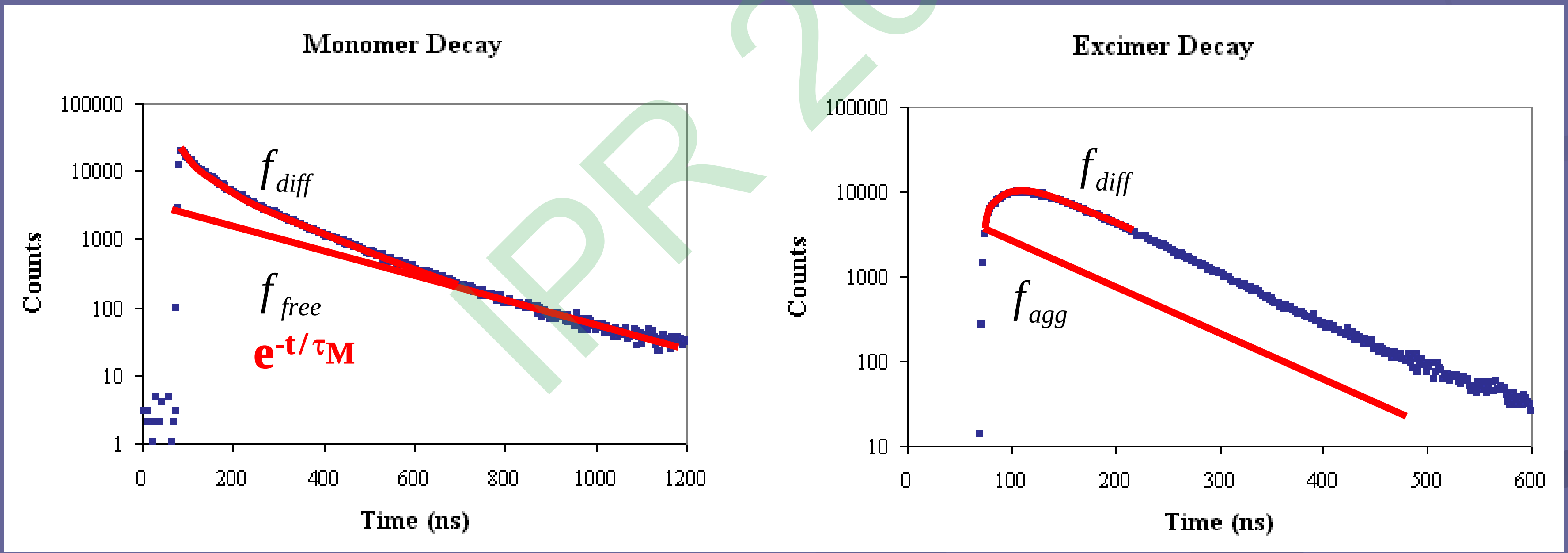
f_{diff}: Fraction of pyrenes forming excimer via diffusion (FBM)



f_{free}: Fraction of pyrenes that never form excimer (e^{-t/τ_M})

Determination of Pyrene Fluorescence Fractions

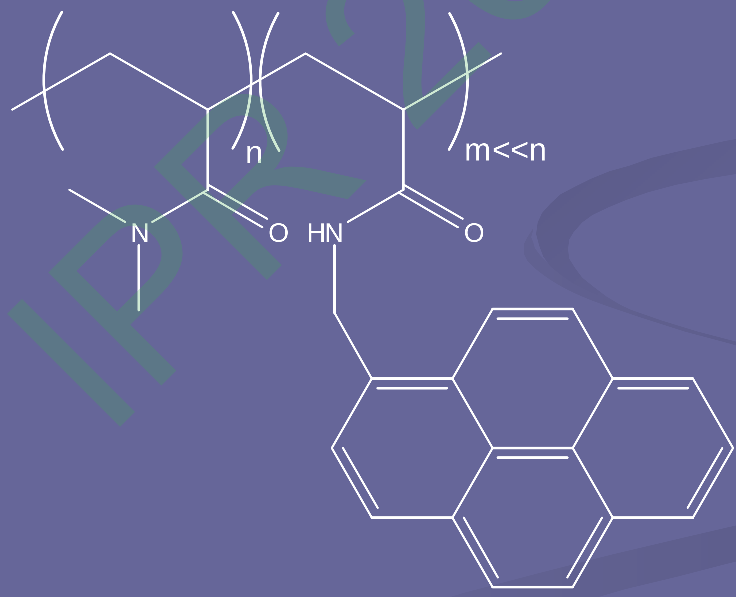
By relating the curvature of the monomer decay to the rise time of the excimer decay, the fractions f_{agg}, f_{free}, and f_{diff} can be determined.



Siu, H.; Duhamel, J. *Macromolecules* (Technical Note) **2004**, *37*, 9287.

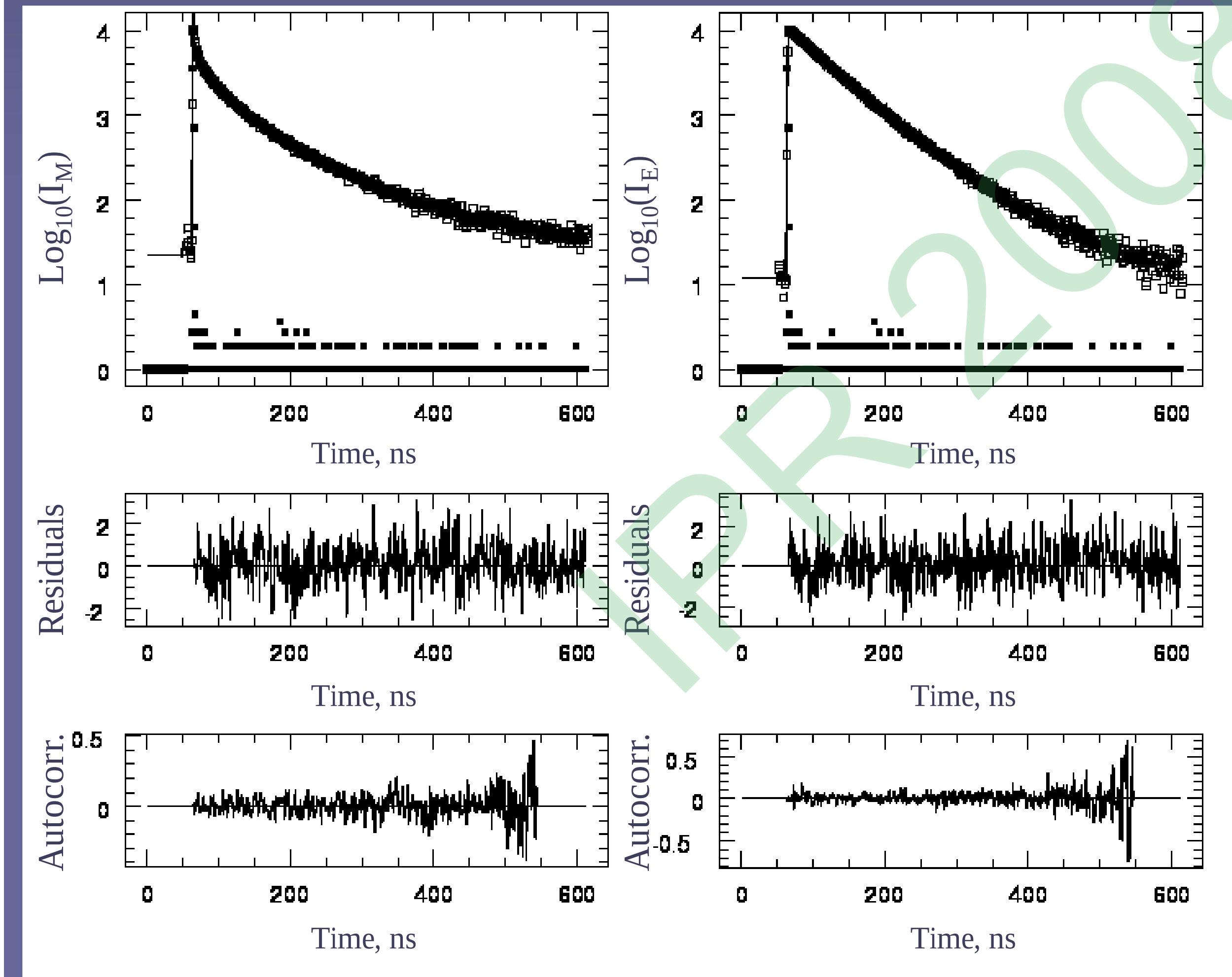
Ideal Case Scenario

Pyrene randomly labelled onto poly(*N*,*N*-dimethyl acrylamide) (PyPDMA)



Analysis of Fluorescence Decays

Monomer Decay Excimer Decay



[Py-PDMA] = 0.09 g/L

645 μmol pyrene/g polymer

Monomer

λ_{ex} = 340 nm

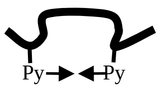
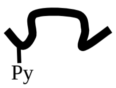
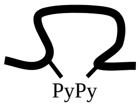
λ_{em} = 375 nm

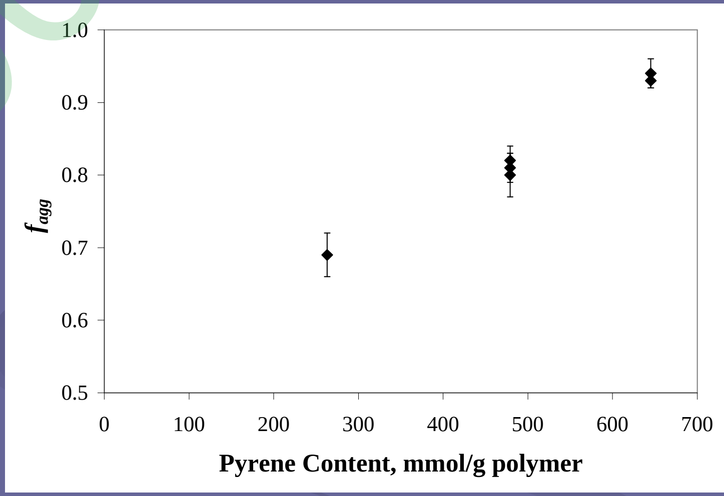
Excimer

λ_{ex} = 340 nm

λ_{em} = 510 nm

Py-PDMA Pyrene Fractions

Pyrene Content µmol/g	OD	[Py-PDMA] g/L	 f_{diff}	 f_{free}	 f_{agg}
645	1	0.09	0.07 ± 0.01	0.00 ± 0.00	0.93 ± 0.01
	30	2.2	0.06 ± 0.01	0.00 ± 0.00	094 ± 0.02
479	0.1	0.01	0.18 ± 0.03	0.02 ± 0.00	0.80 ± 0.03
	0.7	0.08	0.18 ± 0.02	0.02 ± 0.00	0.81 ± 0.02
	15	1.8	0.17 ± 0.02	0.01 ± 0.00	0.82 ± 0.02
263	30	4.8	0.25 ± 0.02	0.06 ± 0.01	0.69 ± 0.03



Model was able to determine the pyrene fractions in solution

N_{agg} for Py-PDMA

- Knowing the total pyrene concentration and the fractions of the species we can obtain $[Py_{diff}]_0$, $[Py_{agg}]_0$

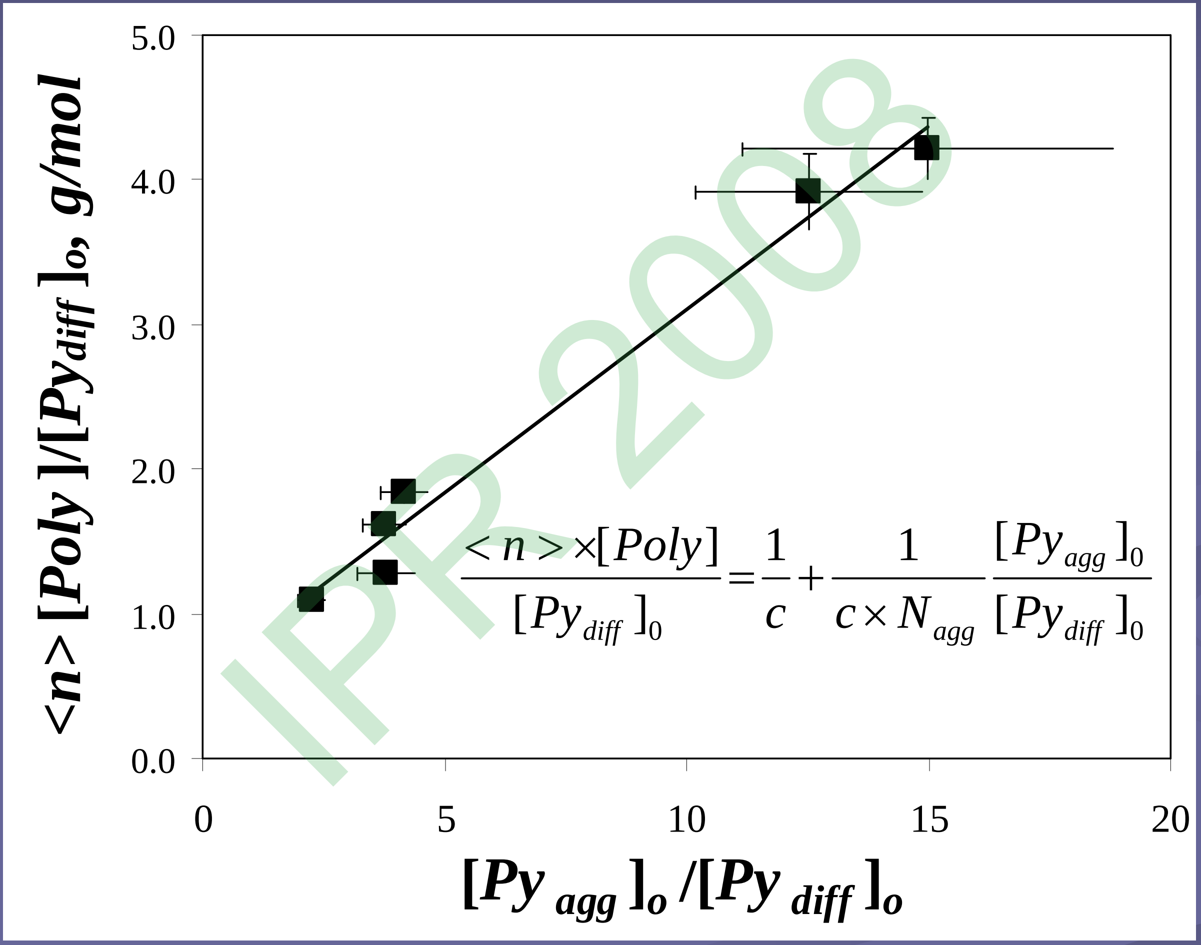
- From FBM we obtain $<n>$, which is the number of ground-state pyrene species per blob or:

$$<n> = \frac{[Py_{diff}]_0 + [Py_{agg}]_0 / N_{agg}}{[blob]}$$

- Assuming $[blob] = c \times [Poly]$, we can rearrange to get:

$$\frac{<n> \times [Poly]}{[Py_{diff}]_0} = \frac{1}{c} + \frac{1}{c \times N_{agg}} \frac{[Py_{agg}]_0}{[Py_{diff}]_0}$$

N_{agg} for Py-PDMA (cont'd)



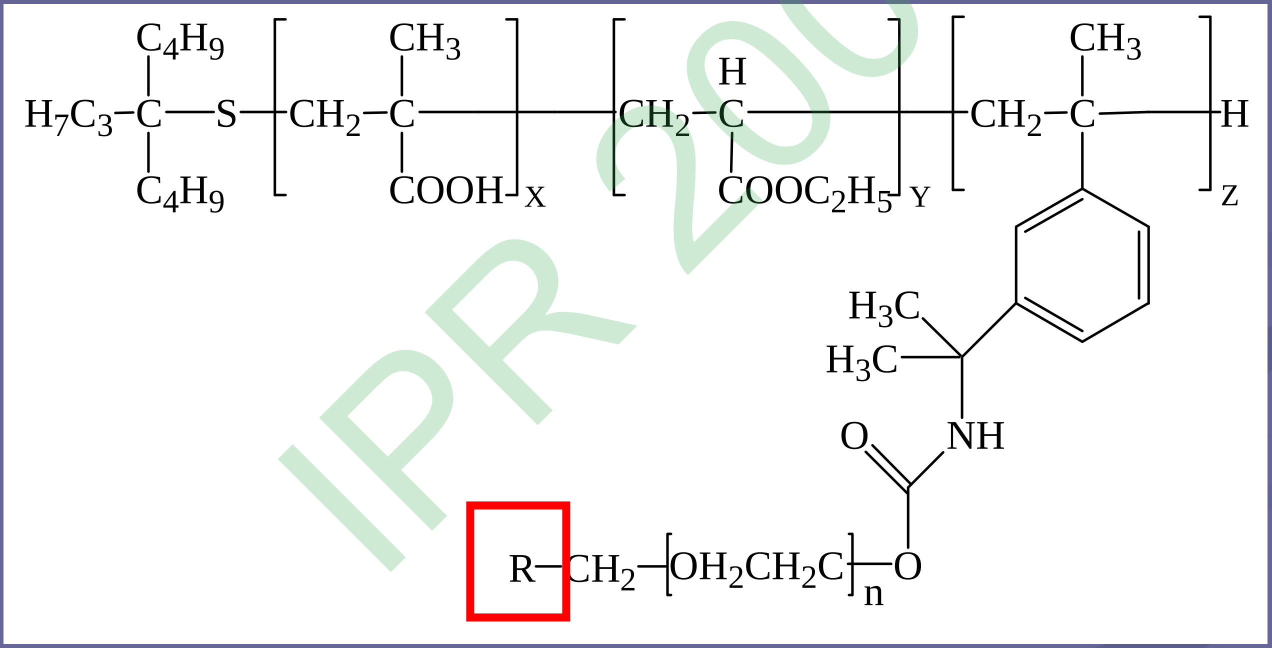
From the slope and intercept: $N_{agg} = 3.1 \pm 1.6$

Application to HASE System

- Apply method used to determine f_{agg} and N_{agg} for Py-PDMA system to Py-HASE associative polymer system
  - More industrially relevant system (HASE polymer used in latex paints as thickening agent)
  - Relate f_{agg} and N_{agg} to physical properties of Py-HASE solutions under sheared conditions

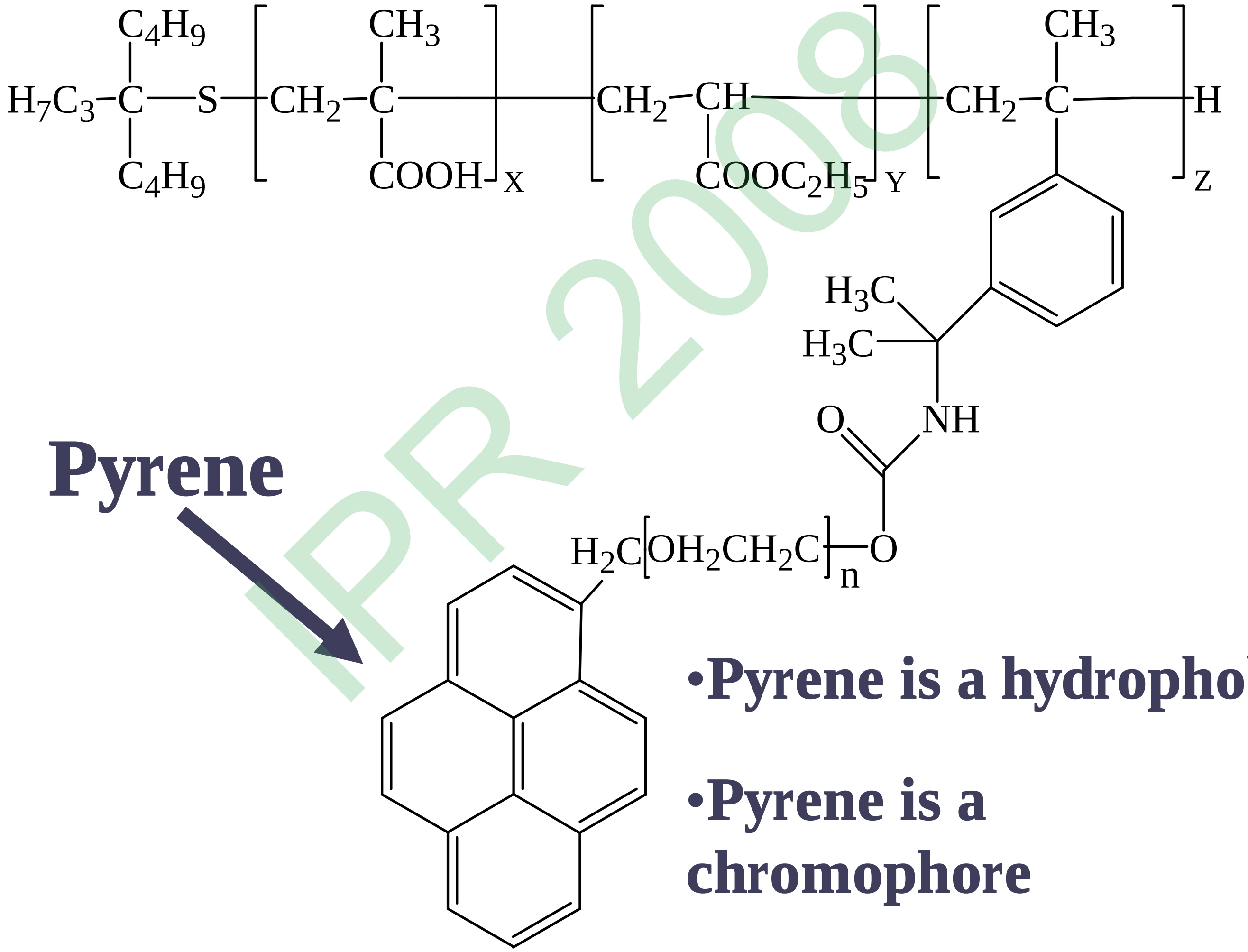
HASE Polymers

- Hydrophobically modified Alkali Swellable Emulsion (HASE) polymer



- Polymer properties can be fine tuned by controlling ratio of X:Y:Z, PEO length n, and hydrophobe R

Pyrene Labelled HASE Polymer



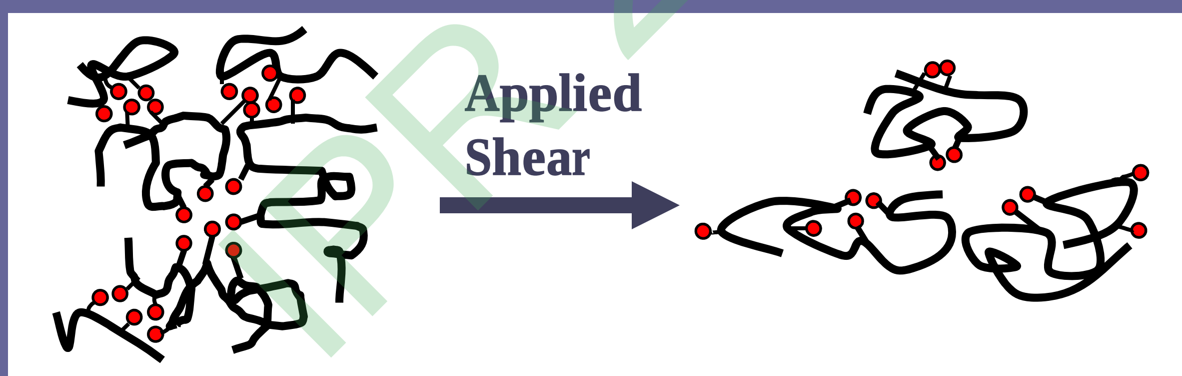
Pyrene

- **Pyrene is a hydrophobe**
- **Pyrene is a chromophore**

Proposed Study
Effect of Shear on Level of Association

Application of shear breaks up hydrophobic aggregates

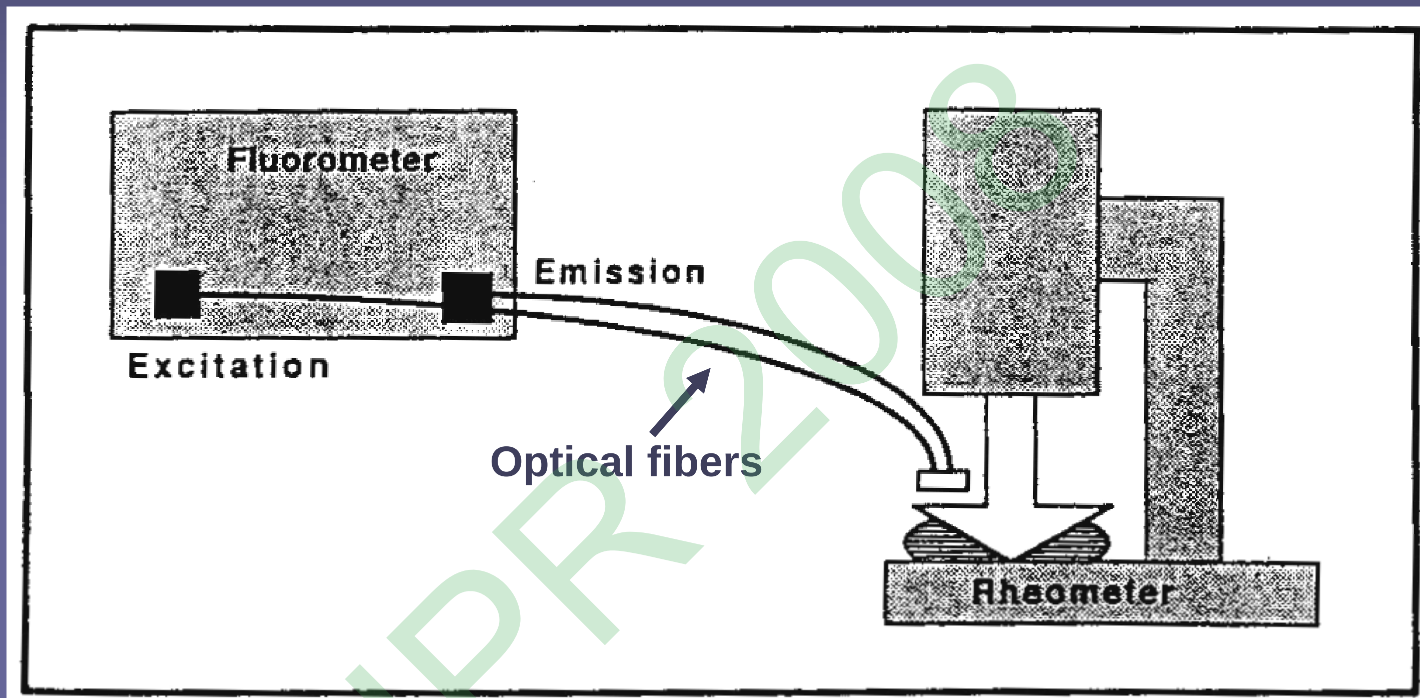
- Disrupts network leading to a drop in viscosity (shear thinning)



Break up of aggregates leads to a change in network

Goal: Map the changes in level of association (f_{agg} and N_{agg}) while the system is under shear using the proposed setup

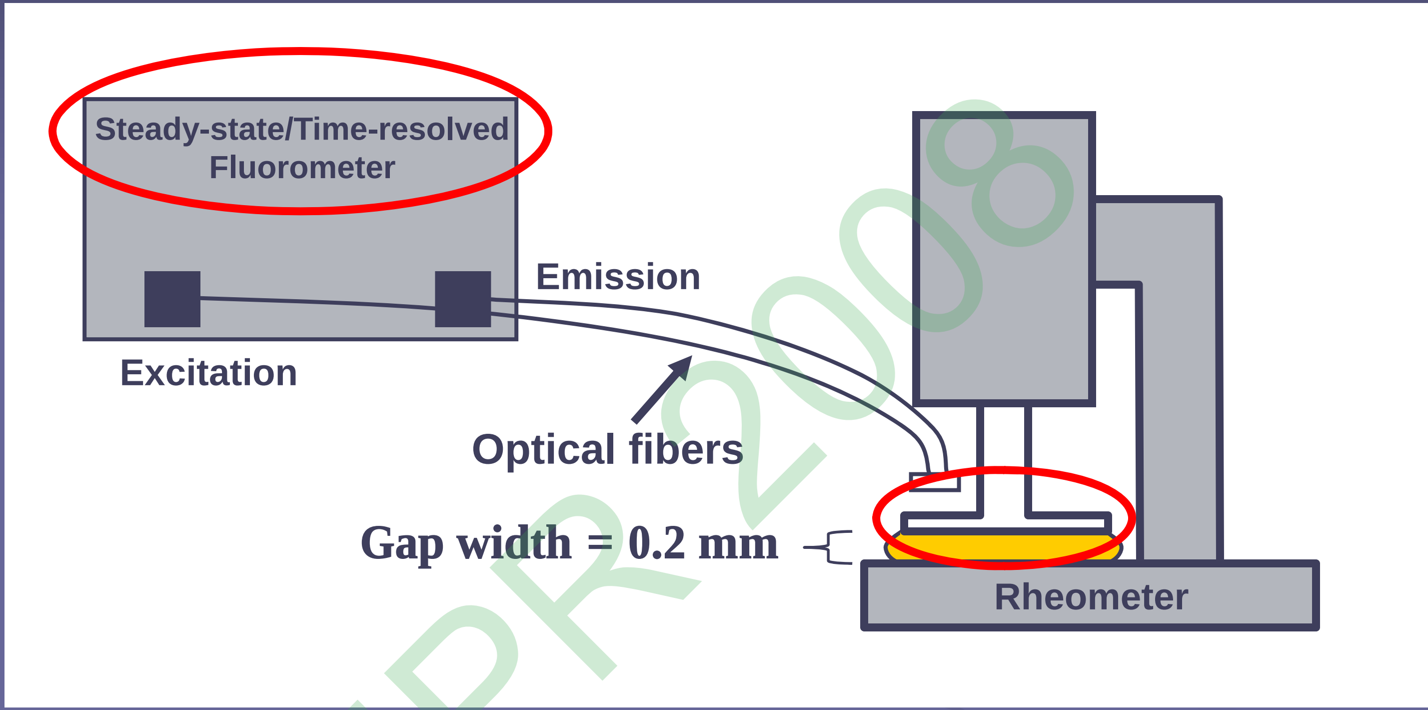
Example of Fluorometer / Rheometer Setup



Steady-state fluorescence measurements of AP solutions located inside a rheometer

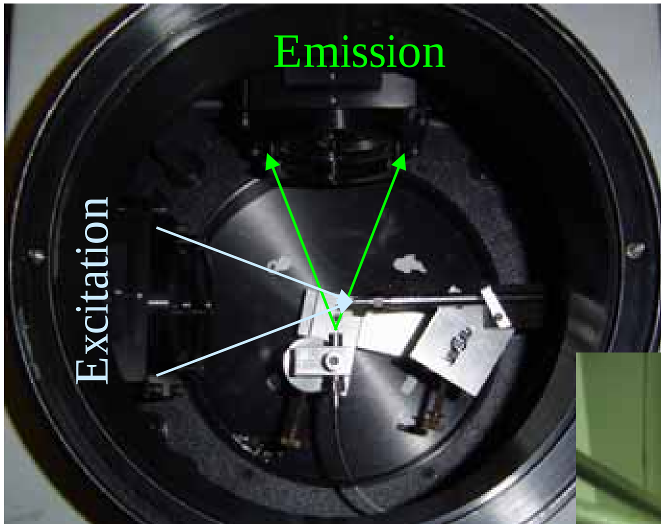
Richey, B.; Kirk, A.B.; Eisenhart, E.K.; Fitzwater, S.; Hook, J. *J. Coat. Technol.* **1991**, *63*, 31.

Proposed Fluorometer/Rheometer Setup

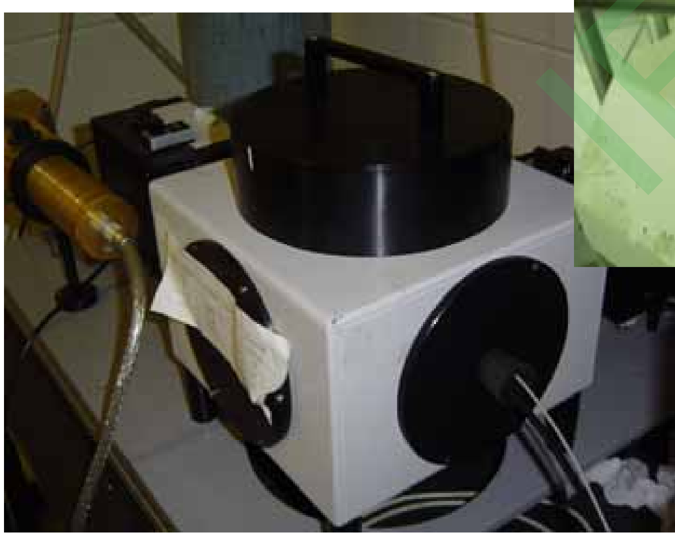


Steady-state and time-resolved fluorescence measurements of pyrene labeled HASE solutions located inside a rheometer

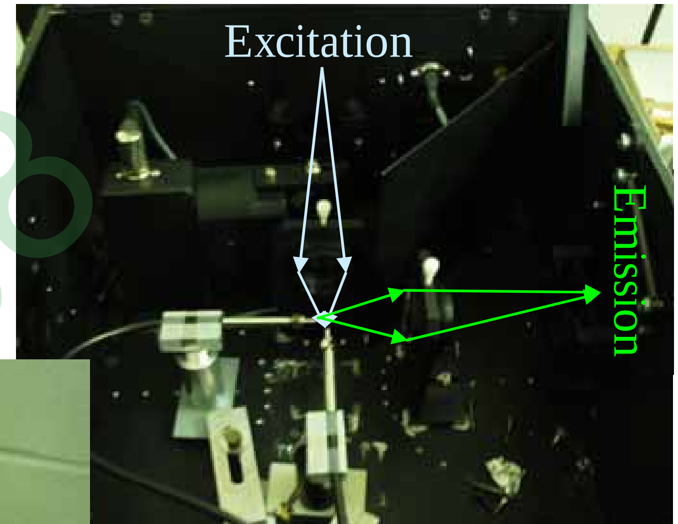
Experimental Coupled Setup



Single Photon Counter



Rheometer Site

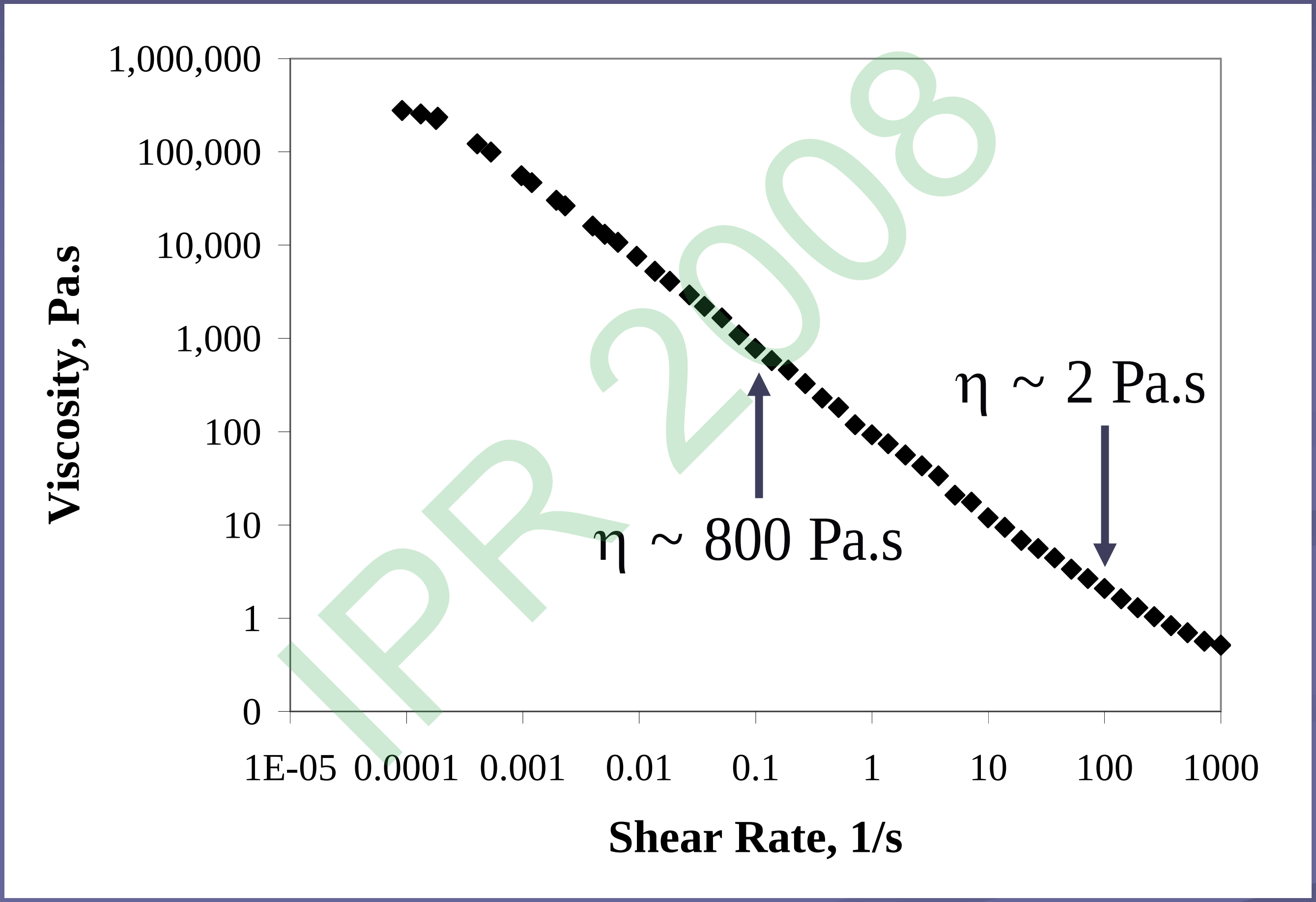


Steady-State Fluorometer

Experimental Conditions

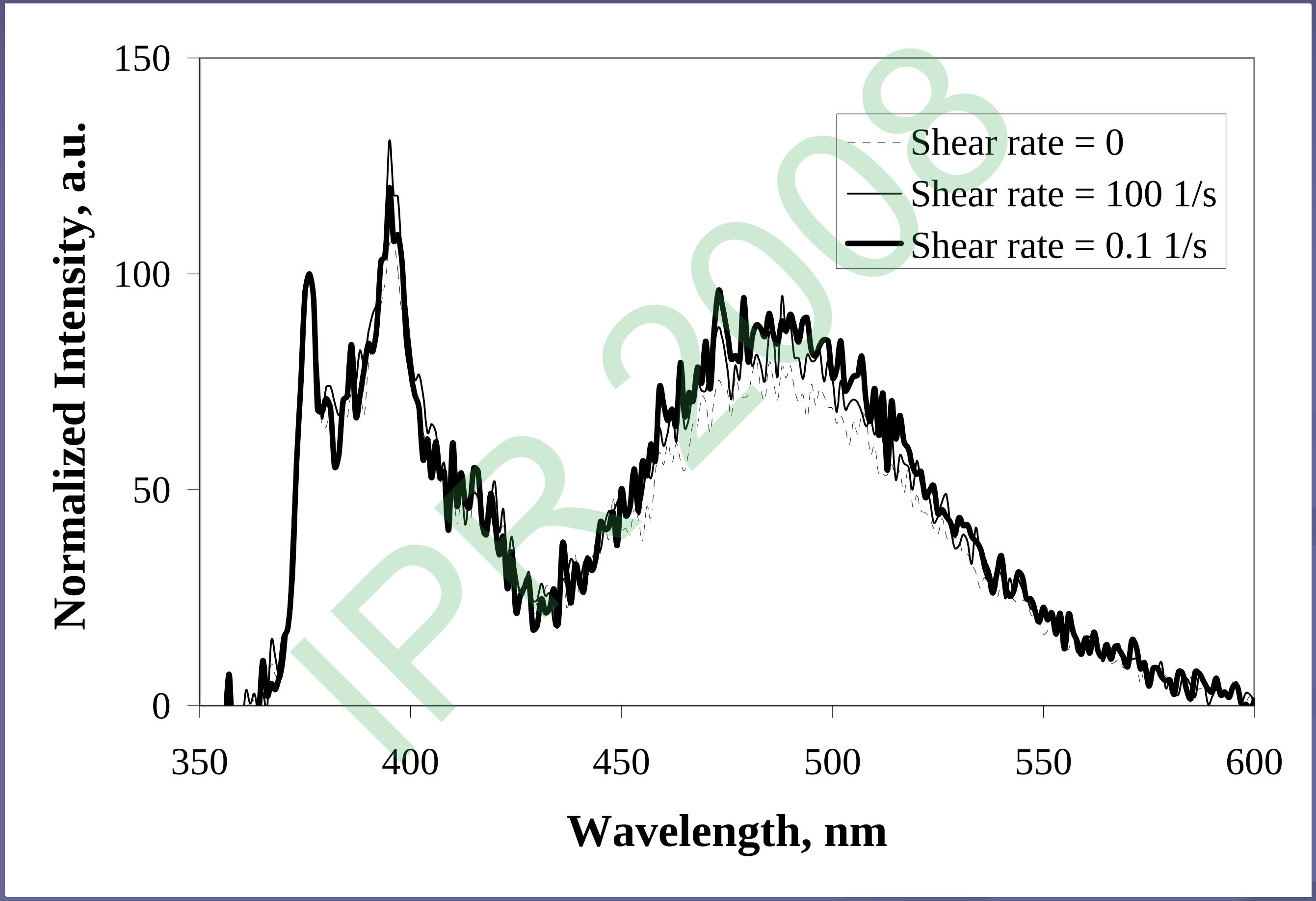
- Py-HASE with a pyrene content of 65 μM pyrene/g polymer
- Solvent is 0.01 M Na_2CO_3, pH 9 solution
- [Py-HASE] = 5 w/w%

Rotation Experiment for Py-HASE



0.2 mm gap width between plates

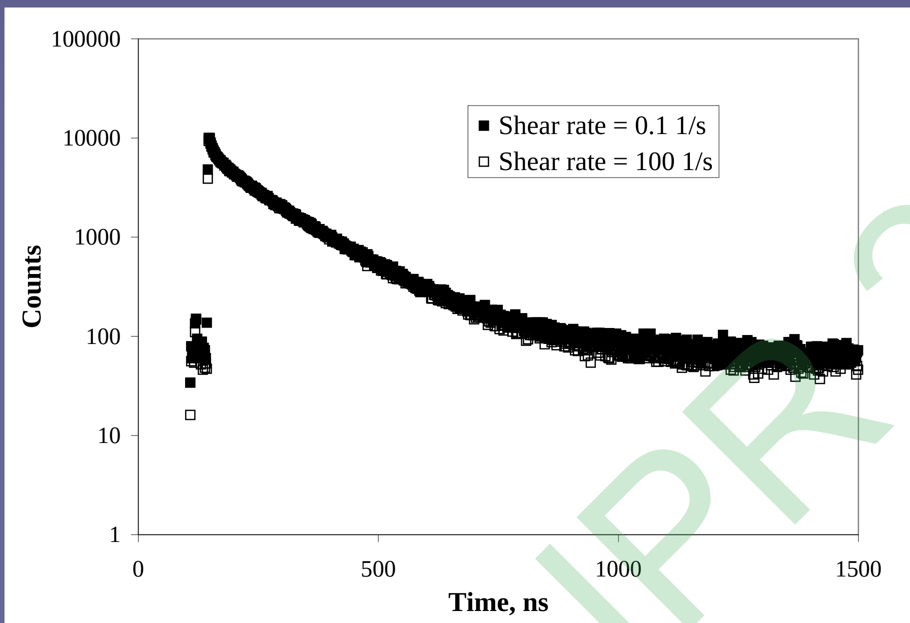
Preliminary Steady-State/Rheometer Data



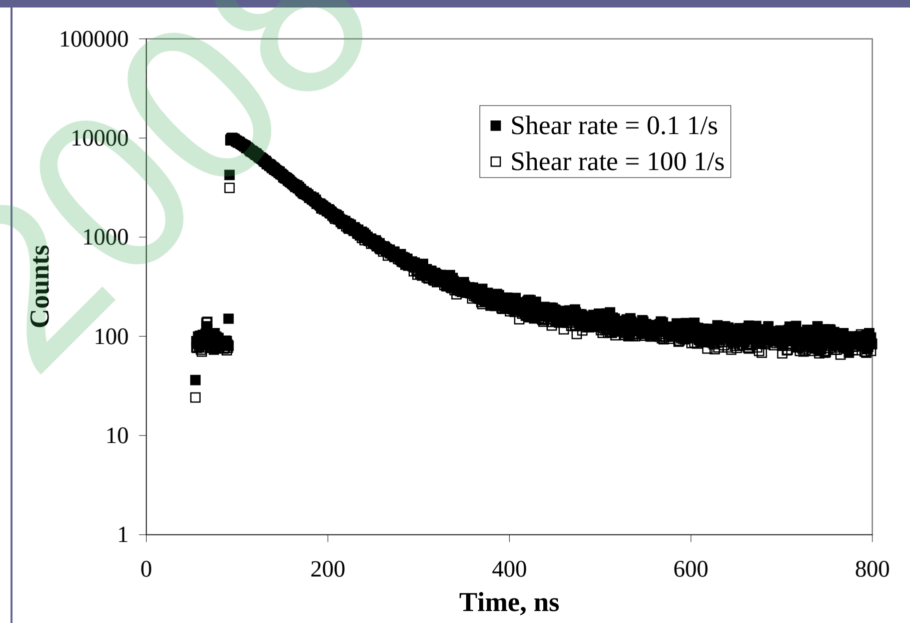
Little change in steady-state fluorescence despite 400x drop in viscosity

Preliminary SPC / Rheometer Data

Monomer Decay



Excimer Decay



Monomer and excimer fluorescence decays also exhibit LITTLE DIFFERENCE despite change of 400x in viscosity (f_{agg} and N_{agg} likely are unchanged)!

Conclusions for Fluorometer–Rheometer Experiments

- Concept for both single photon counter and steady-state fluorometer coupled with the rheometer proven to be feasible
  - Optimization of procedure/setup is required to improve signal to the detector
  - Need to build a more permanent setup

Conclusions for Fluorometer–Rheometer Experiments (cont'd)

- Little change observed in time-resolved and steady-state preliminary data indicating that little to no change in f_{agg} and N_{agg} with change in shear rate
  - Implies a switching between intra- and intermolecular associations with formation/disruption of network (energy transfer experiment)
  - More measurements varying setup parameters (measurement depth, gap width, concentration, etc.) need to be performed to verify this results
  - Introduce latex particles (found to affect steady-state spectra in the presence of shear according to Richey et al.)

Acknowledgements

- Dr. Jean Duhamel
- DOW Chemical for the Py-HASE and PyPEO
- Telmo Prazeres
- Duhamel and Gauthier Lab Groups

QUESTIONS?