Comparing the Dynamics of Encounter Between the Chain Ends or Random Intra-Chain Segments with Pyrene Labeled Polymers in Solution

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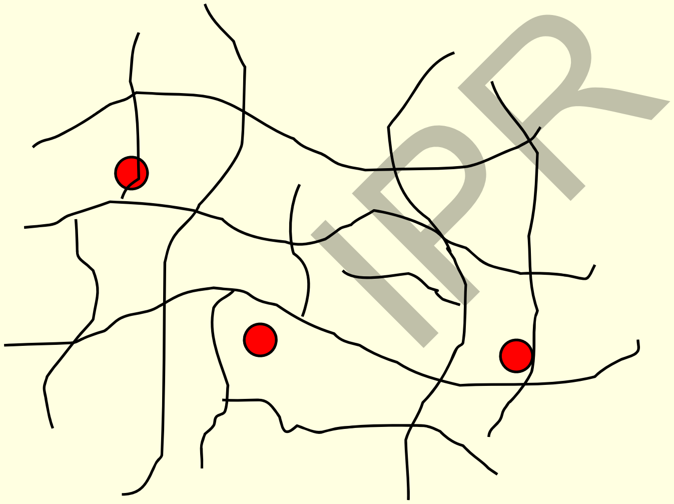
Outline

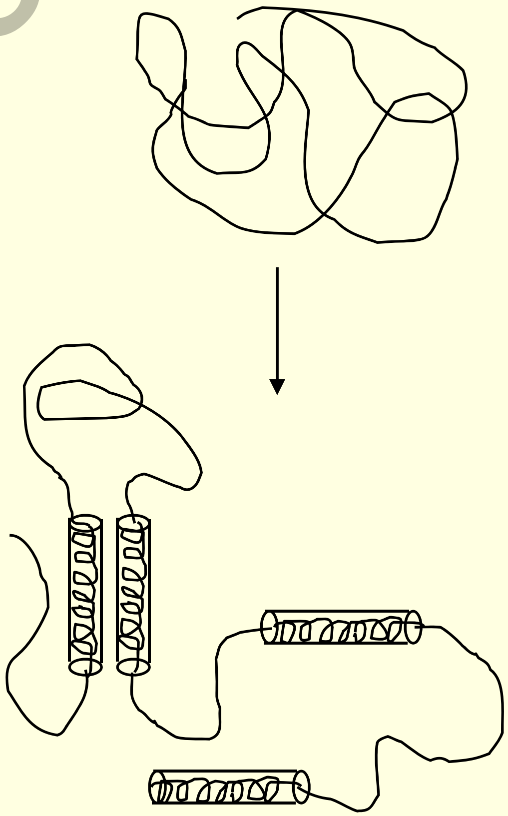
- Background:
  - Studying polymer chain dynamics
  - Pyrene fluorescence
  - Comparing different labeling methods
  - Analysis methods:
    - Birks Scheme
    - The fluorescence blob model (FBM)
- Experiment
  - Comparing the information obtained on the dynamics of polystyrene chains as a function of solvent viscosity
- Results and Conclusions

Why Study Polymer Chain Dynamics?

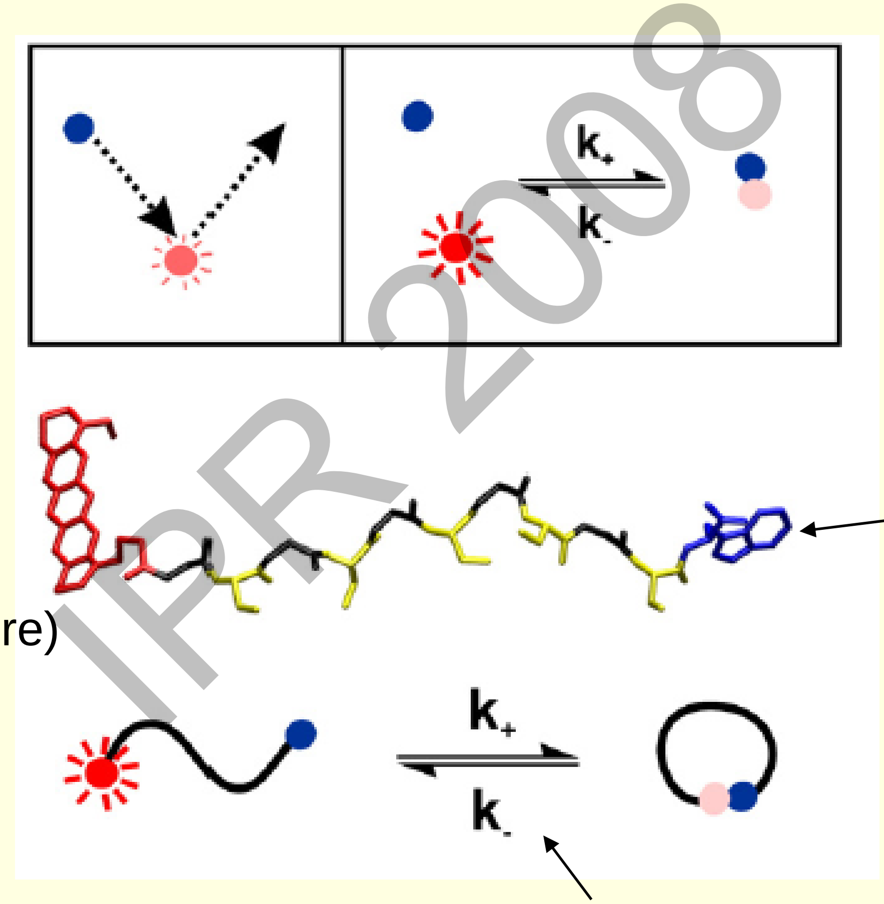
- Cross-linked gels - used in drug delivery, Li-ion batteries



- Protein folding



Cyclization of End-labeled Peptides



Chromophore
(oxazine fluorophore)

Quencher
(Tryptophan)

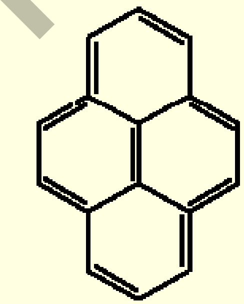
Rate of end-to-end cyclization and ring opening

Neuweiler, H.; Lollmann, M.; Doose, S.; Sauer, M. *J. Mol. Biol*. **2007**, *365*, 856-869.

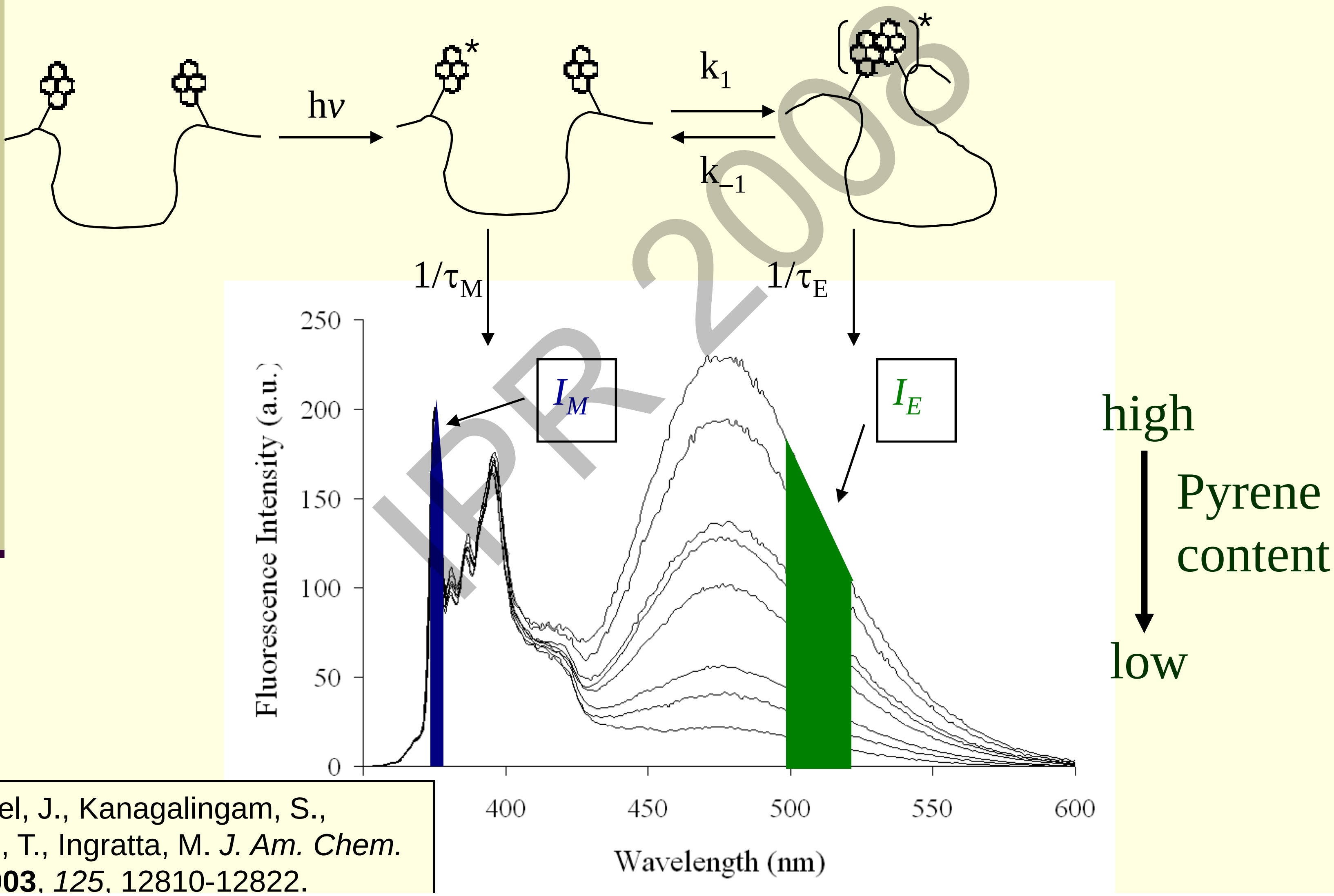
Probing Polymer Chain Dynamics

- Idea: The lifetime an excited chromophore acts as a timer for the motions of the polymer
- Encounters between a chromophore and its quencher represent collisions of monomer units

Chromophore of Choice = Pyrene

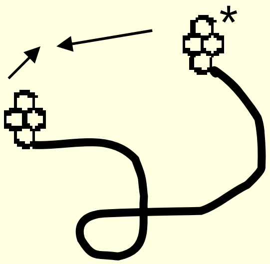


Pyrene Fluorescence



Duhamel, J., Kanagalingam, S., O'Brien, T., Ingratta, M. *J. Am. Chem. Soc.* **2003**, *125*, 12810-12822.

End-Labeling vs. Random Labeling



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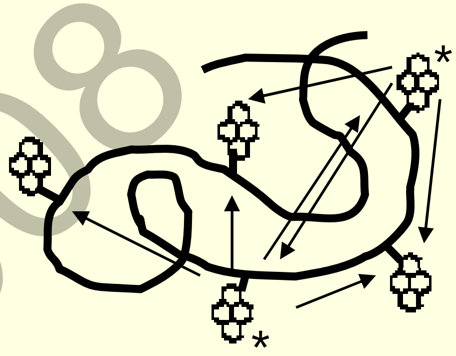
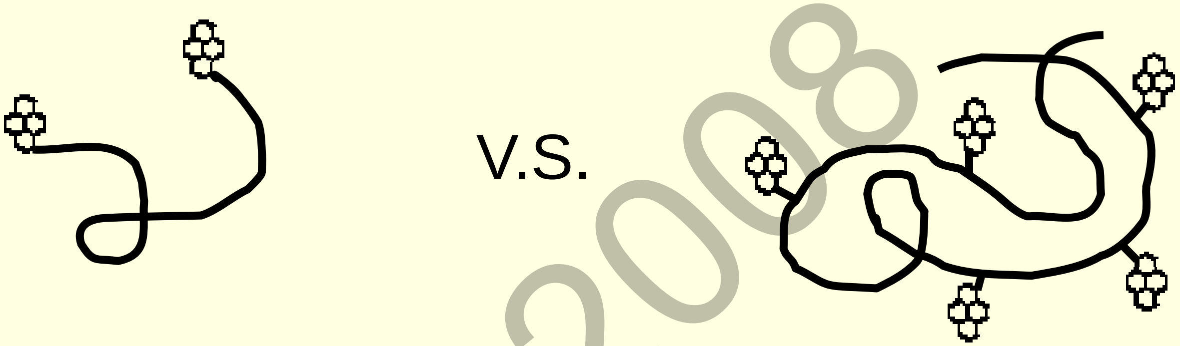
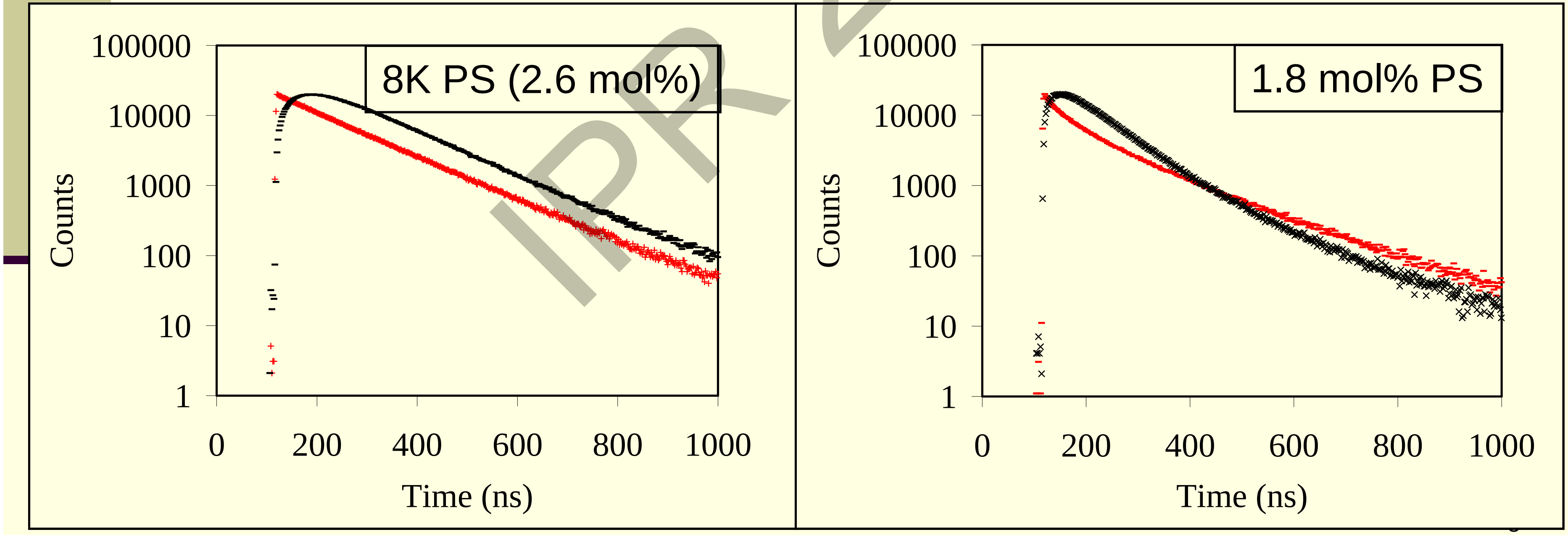


- Pros
  - *Relatively* un-complicated analysis
  - k_{cy} is quantitative
- Cons
  - Only short, mono-disperse chains can be used

- Pros
  - Can use higher MW, polydisperse polymers; usually easier to synthesize
- Cons
  - Excimer formation is *complicated*
  - Analysis is often considered *qualitative*

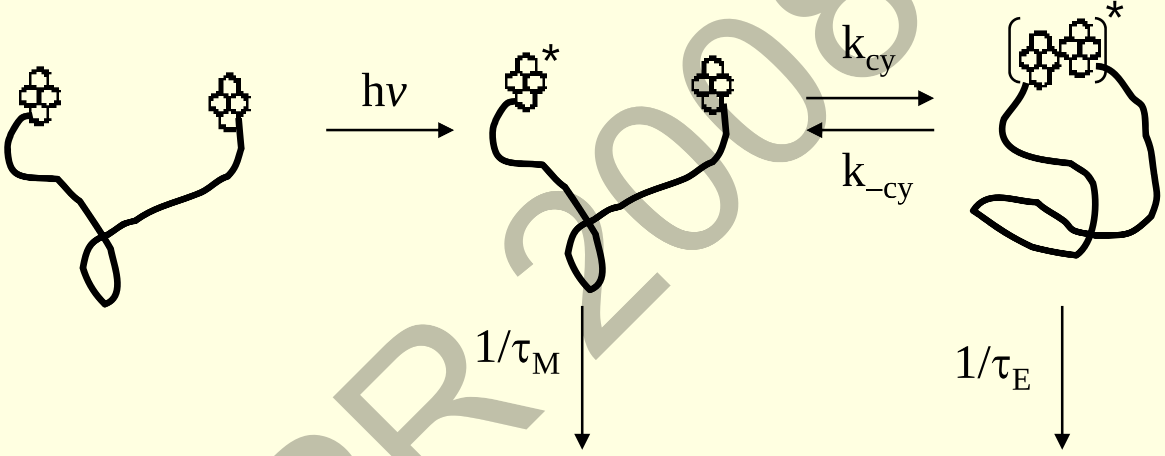
End-Labeling vs. Random Labeling





Py-Polystyrene in toluene

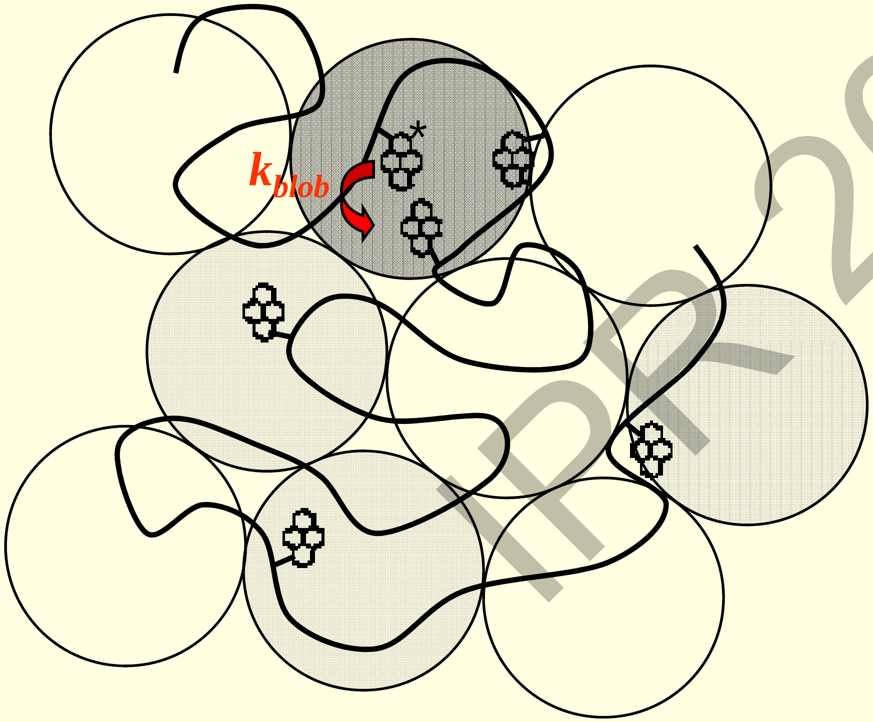
Birks’ Scheme for Excimer Formation



Parameters retrieved:
k_{cy}, k_{-cy}
τ_E

Where k_{cy} gives information on the flexibility and conformation of the backbone.

Fluorescence Blob Model (FBM): Polymer ⟶ Blobs



k_{blob} = rate constant for excimer formation within a blob

$\langle n \rangle$ = average number of ground state pyrenes per blob (quenchers per blob)

N_{blob} = number of units per blob

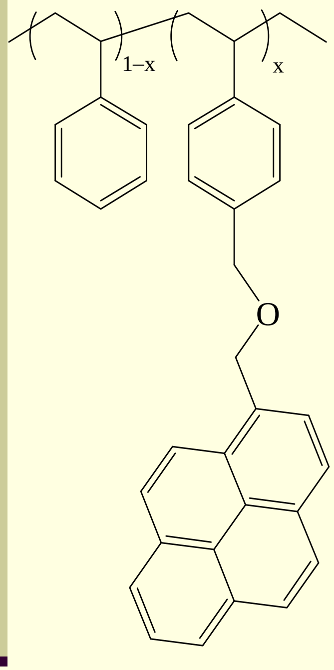
Experiment:

- Previous work showed changing the way pyrene is attached appears to have a strong affect on excimer formation*

- Two Goals:
  - Comparison of the excimer formation of end-labeled vs. randomly labeled Py-PS
  - How does excimer formation change as a function of *solvent viscosity*

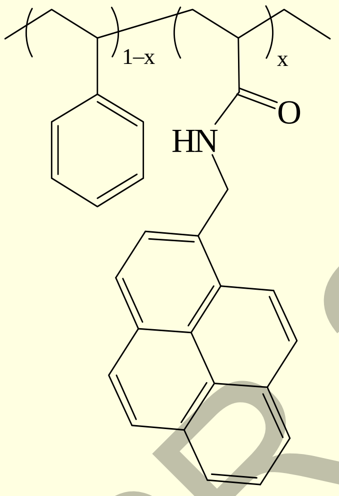
* Ingratta, M.; Duhamel, J. *Macromolecules* **2007**, *40*, 6647-6657.

Names and Structures



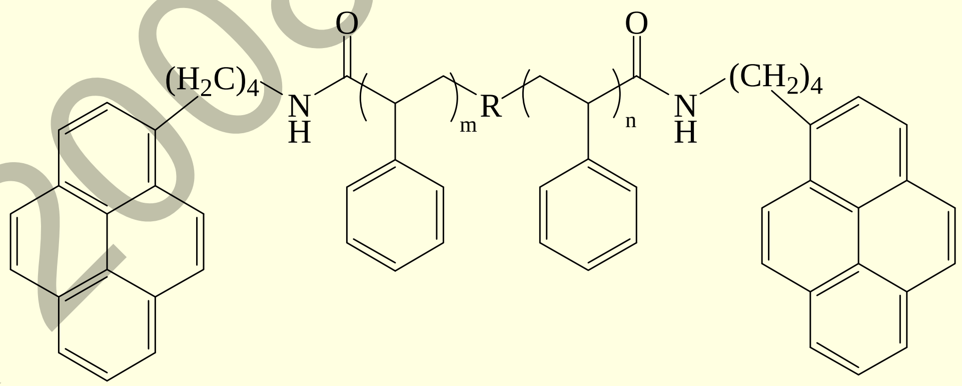
CoE-PS

Copolymer - Ether linker



CoA-PS

Copolymer- Amide linker



Where m+n = 30, 45 and 80 units

PS(X)Py$_2$

End-labeled with
a longer Amide linker

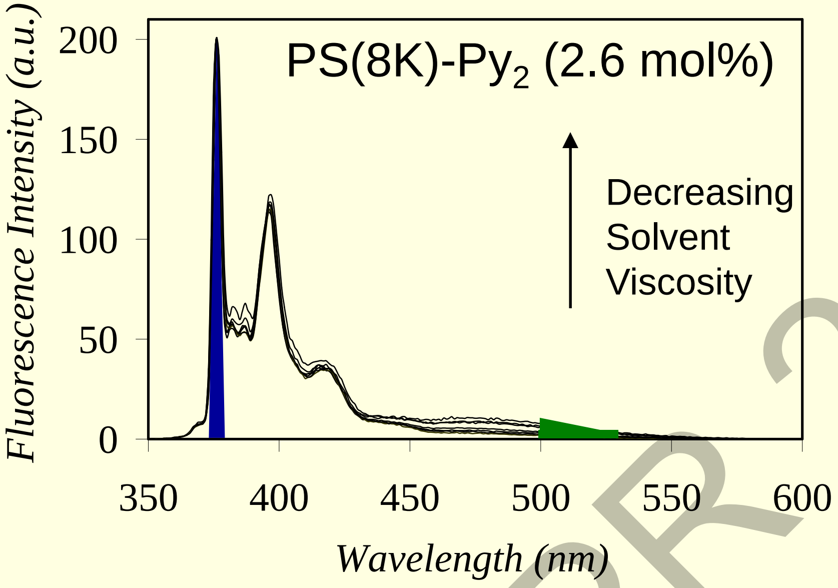
Polymers and Solvents

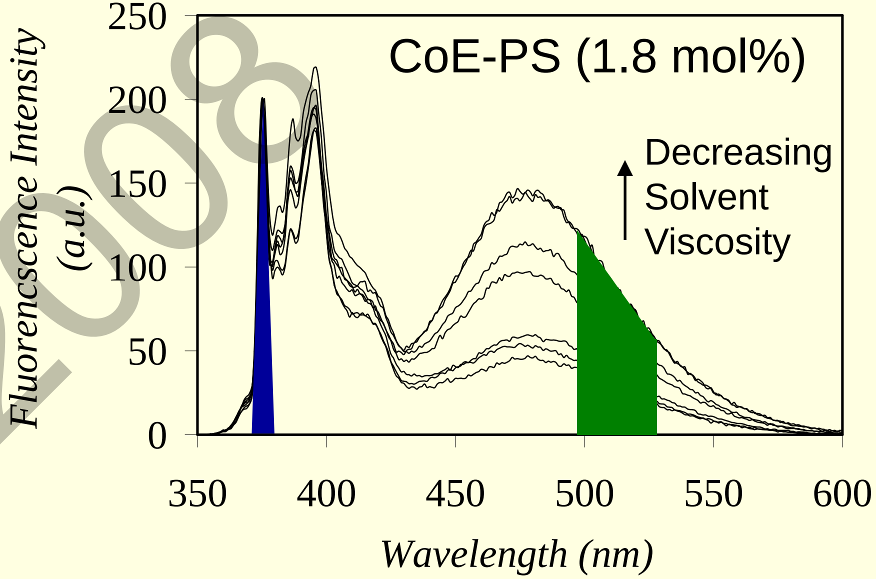
Sample	x, mol % Py	λ_{Py}, μmol·g^{-1}	M_n, kg·mol^{-1}	PDI
CoE-PS	1.5	141	35	1.81
	1.8	169	45	1.87
	3.2	284	32	1.99
	4.8	412	16	1.85
	5.1	436	34	1.80
	6.4	533	46	1.65
CoA-PS	1.1	105	43	1.88
	2.5	230	39	2.04
	3.7	331	55	1.90
	5.0	437	28	1.88
	5.2	459	34	1.96
	6.4	550	39	1.91
PS(X)Py$_2$	2.6	250	8.0	1.09
	4.6	444	4.5	1.12
	6.9	667	3.0	1.10

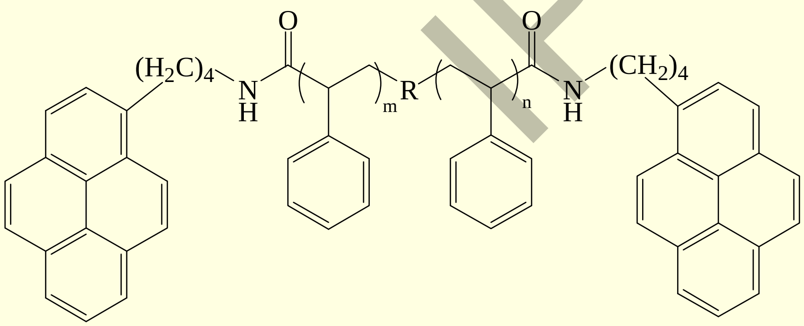
Solvent	η, mPa·s	$[\eta]_{40K}$, L/g	± [η], L/g	Solvent Quality
Methyl Ethyl Ketone (MEK)	0.41	0.0178	0.0002	poor
Dichloromethane (DCM)	0.41	0.0248	0.0004	good
Tetrahydrofuran (THF)	0.46	0.0246	0.0014	good
Toluene	0.56	0.0259	0.0003	good
N,*N*-Dimethylformamide (DMF)	0.79	0.0192	0.0003	poor
Dioxane	1.18	0.0241	0.0001	good
N,*N*-Dimethylacetamide (DMA)	1.92	0.0221	0.0007	mediocre

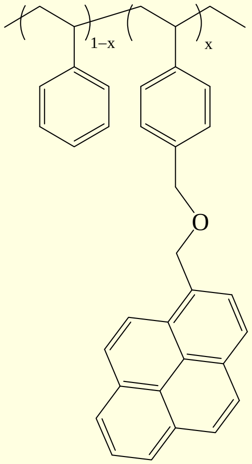
Results

Steady-State Spectra









Example I_E/I_M values for PS(X)Py$_2$

Solvent	I_E/I_M		
	3K	4.5K	8K
DMA	0.030	0.024	0.010
Toluene	0.094	0.080	0.034
MEK	0.114	0.080	0.046

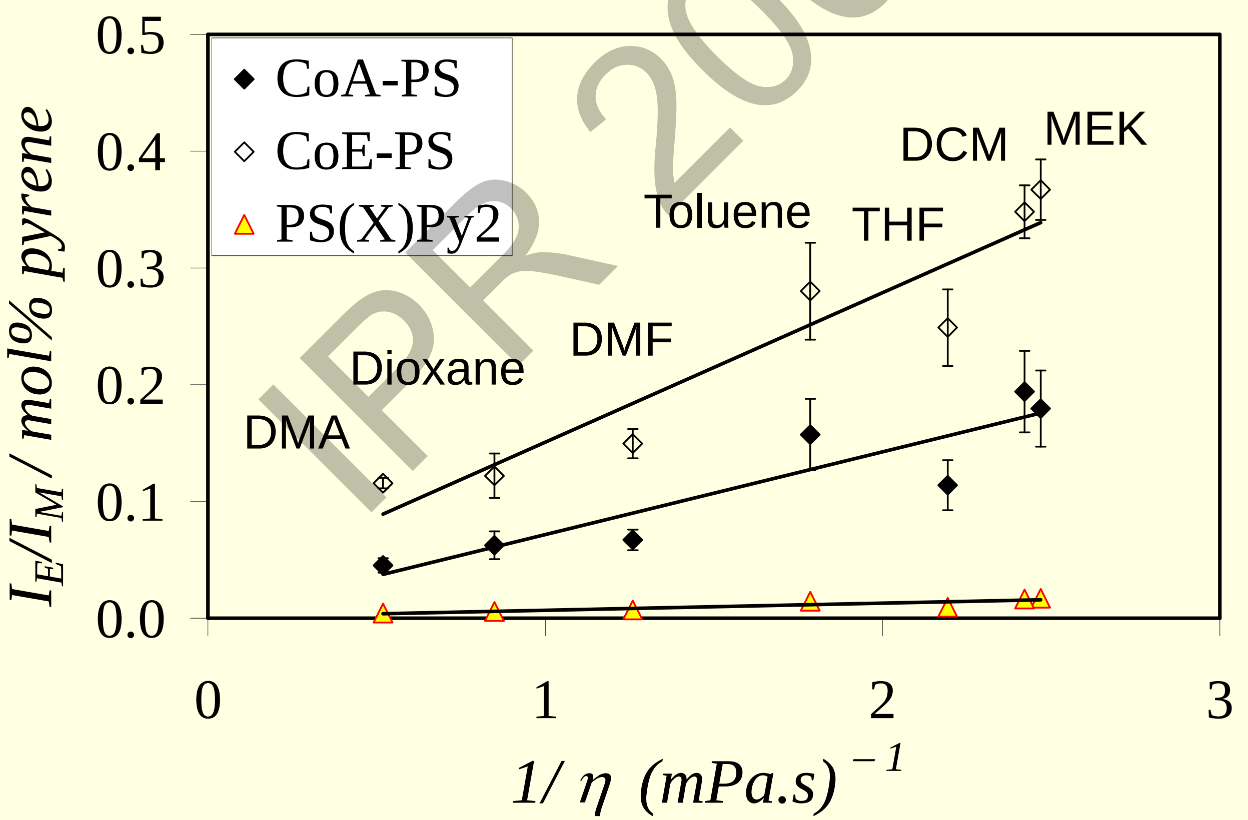
Decreasing Viscosity

I_E/I_M / mol% pyrene

Solvent	I_E/I_M / *mol% pyrene*			Average	STDEV
	3K	4.5K	8K		
DMA	0.004	0.005	0.004	0.004	0.001
Toluene	0.014	0.017	0.013	0.015	0.002
MEK	0.017	0.017	0.018	0.017	0.001

Steady-State Fluorescence: I_E/I_M

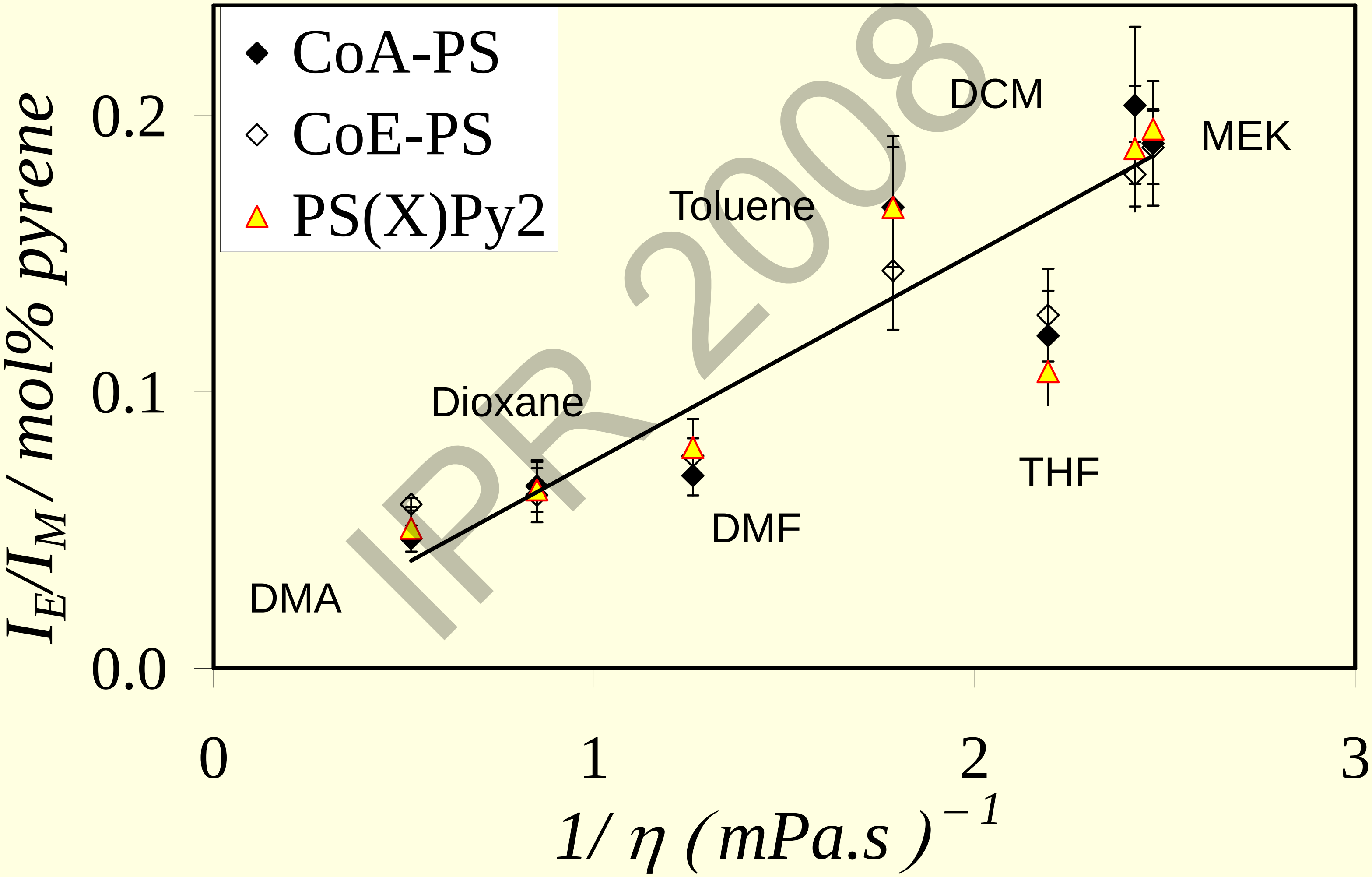
- Different pyrene contents – normalized by dividing by mol% pyrene



How do we compare the data?

- Determine the average ratio between the series (relative to CoA-PS) and normalize by that factor.
    - *i.e.* the trends were multiplied by a scaling factor that equaled 11.2, 0.49, and 1.0 for the PS(X)-Py_2, CoE-PS, and CoA-PS series

Steady-State Fluorescence: I_E/I_M



Steady-State Fluorescence: I_E/I_M

$$\frac{I_E}{I_M} = \kappa \frac{\phi_E^o}{\phi_M^o} \tau_M \boxed{k_{diff} [Py]_{loc}}$$

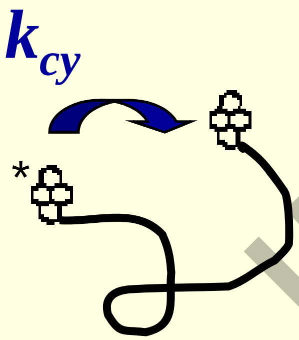
Where $$k_{diff} = \frac{2RT}{3\eta}$$

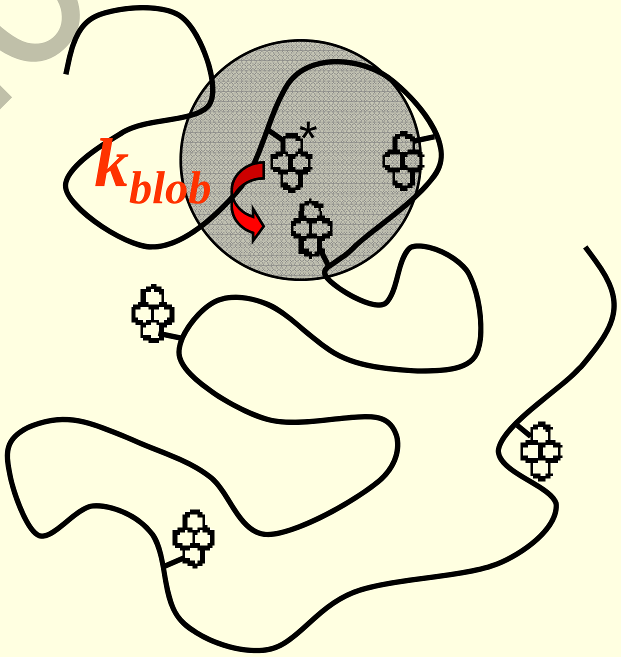
Therefore, $I_E/I_M \propto k_{diff}[Py]_{loc} \propto 1/\eta$

Time-Resolved Fluorescence

$$k_{cy} = k_{diff}^{c} \times \frac{1}{V_{coil}}$$

$$k_{blob} = k_{diff}^{b} \times \frac{1}{V_{blob}}$$

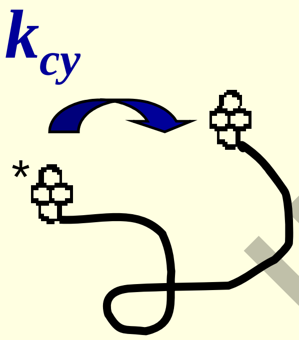


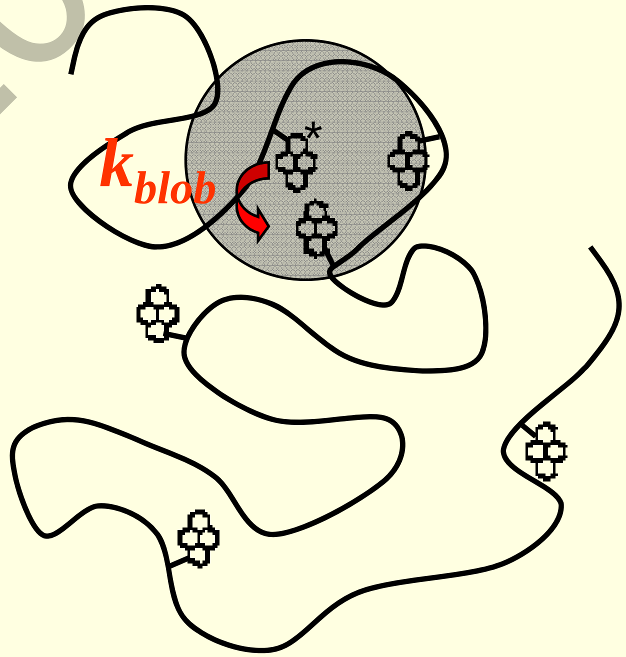


Time-Resolved Fluorescence

$$k_{cy} = k_{diff}^{c} \times \frac{1}{V_{coil}}$$

$$k_{blob}\langle n\rangle = k_{diff}^{b} \times \frac{\langle n\rangle}{V_{blob}}$$





Time-Resolved Fluorescence

$$k_{cy} = k^{c}_{diff} \times \frac{1}{V_{coil}}$$

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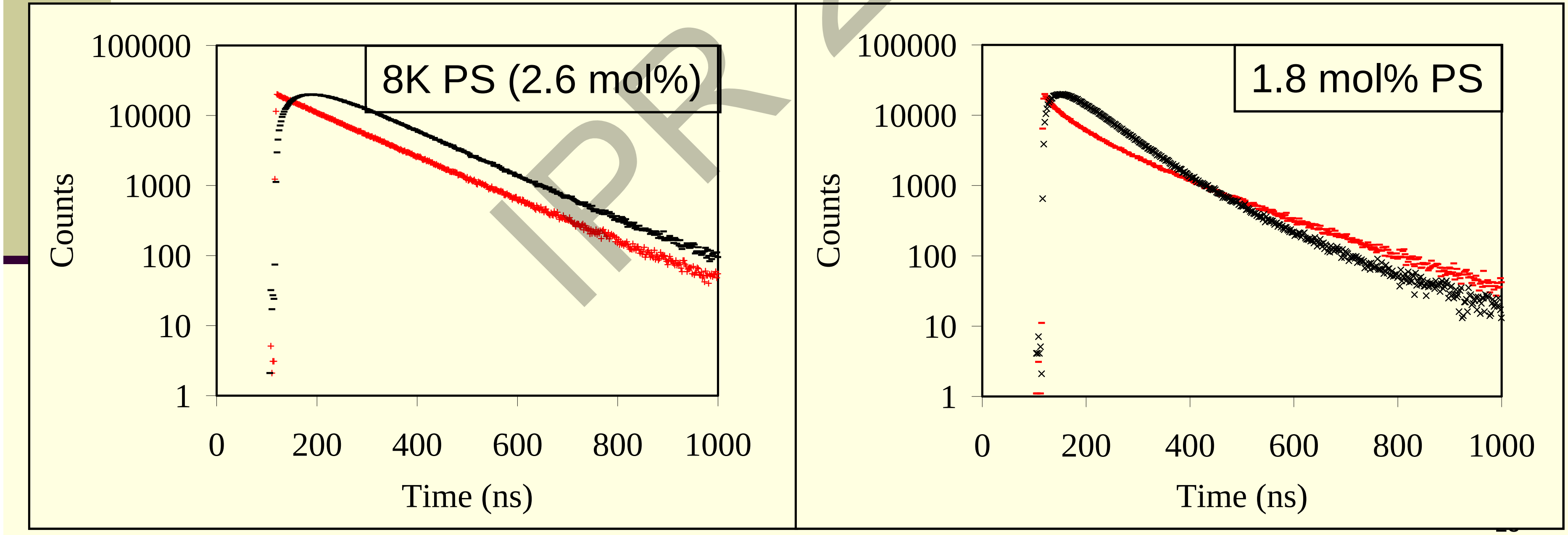
$$k_{blob}\langle n\rangle = k^{b}_{diff} \times \frac{\langle n\rangle}{V_{blob}}$$



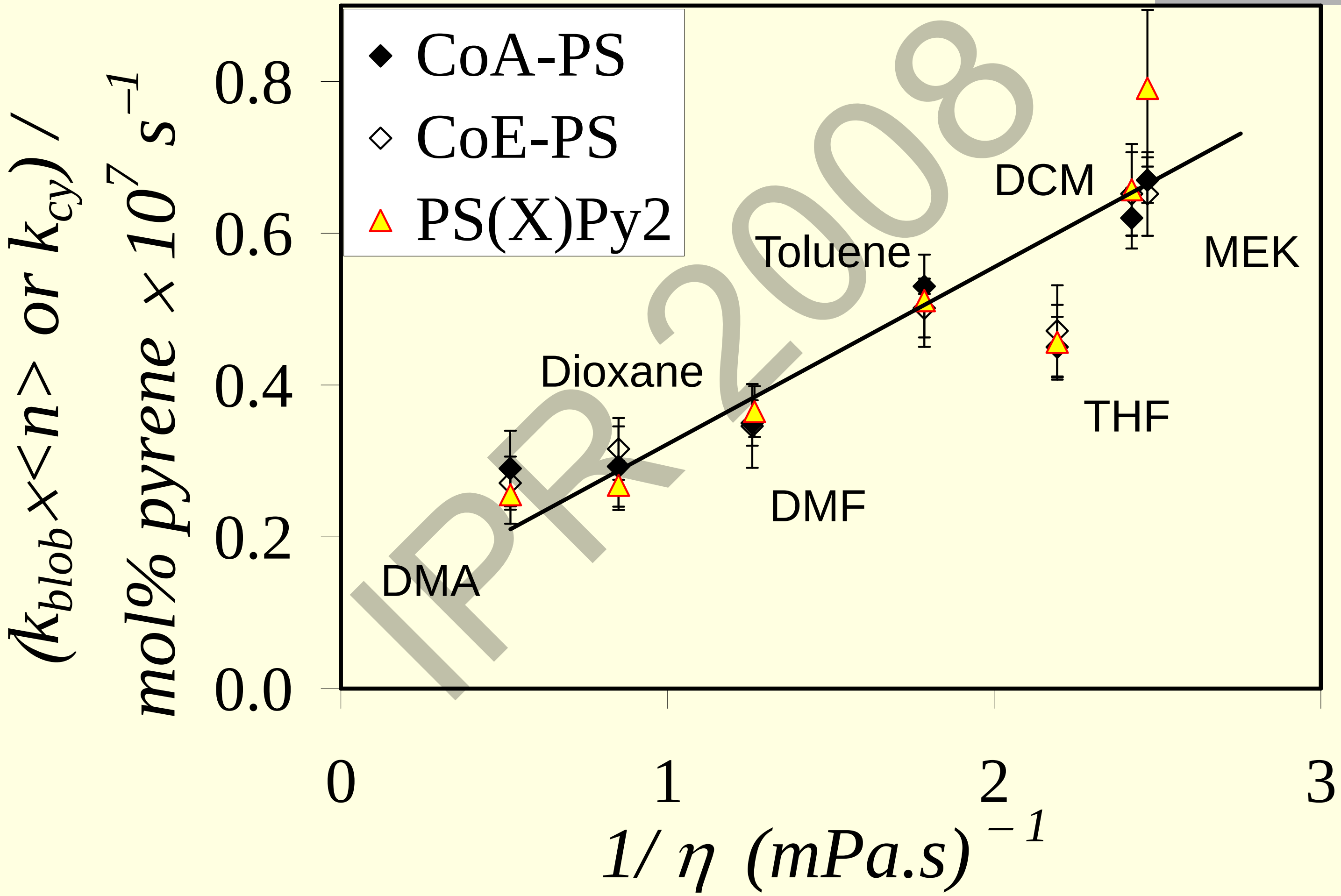
Py-Polystyrene in toluene

Time-Resolved Fluorescence

$$k_{cy} = k_{diff}^{c} \times \frac{1}{V_{coil}} \qquad k_{blob}\langle n \rangle = k_{diff}^{b} \times \frac{\langle n \rangle}{V_{blob}}$$

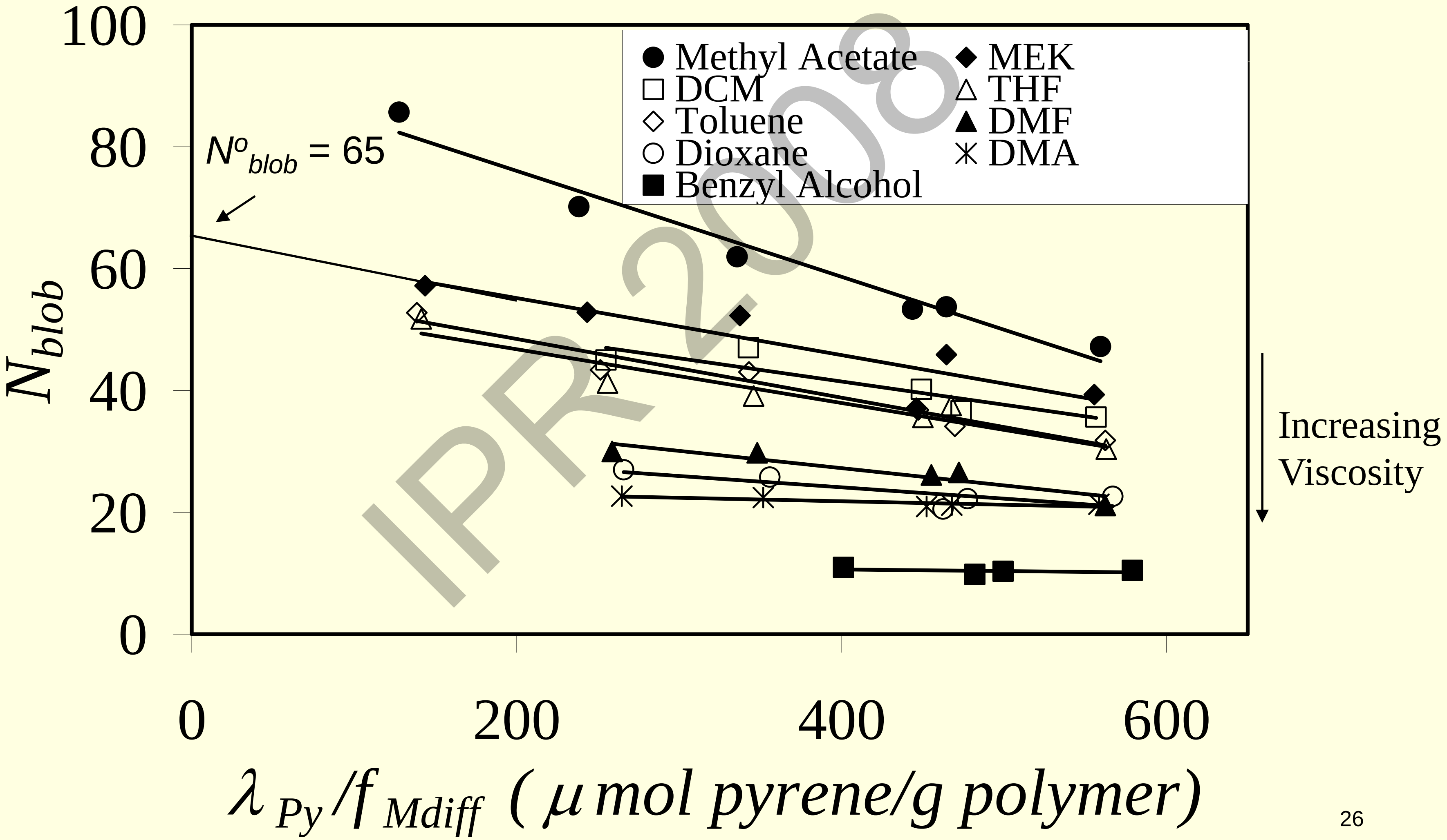
- Follow the same treatment as for the I_E/I_M's to normalize the trends
  - Divide by mol% labeling
  - Normalize scale according to CoA-PS

Time-Resolved Fluorescence

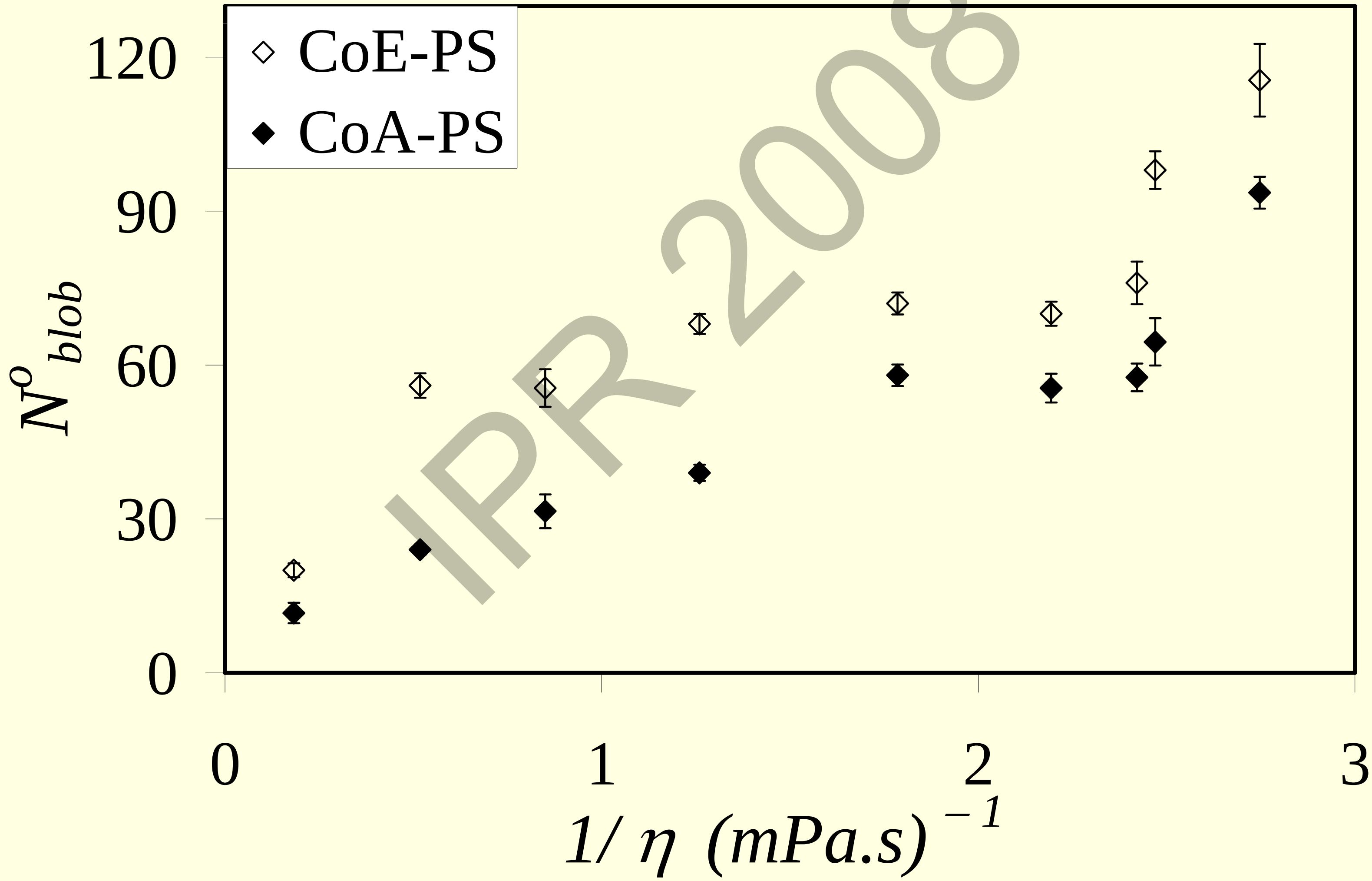


Ingratta, M.; Duhamel, J. *Accepted for publication, J. Am. Chem. Soc.*

N_{blob} vs. Pyrene content: CoA-PS



N_{blob} vs. $1/\eta$



Conclusions

- The rate of excimer formation is inversely proportional to the solvent viscosity
- The *trends* obtained using randomly or end-labeled Py-PS are *identical* using the common methods to evaluate excimer formation
- Since random labeling has a stronger excimer formation, allows for the use of more viscous solvents, stiffer or longer polymers that are not accessible using end-labeling
- FBM result - N_{blob} increases with a decrease in solvent viscosity

Acknowledgements

- Supervisor, Jean Duhamel
- Lab Colleagues
- OGSST, NSERC

Thanks!

Questions / Comments?

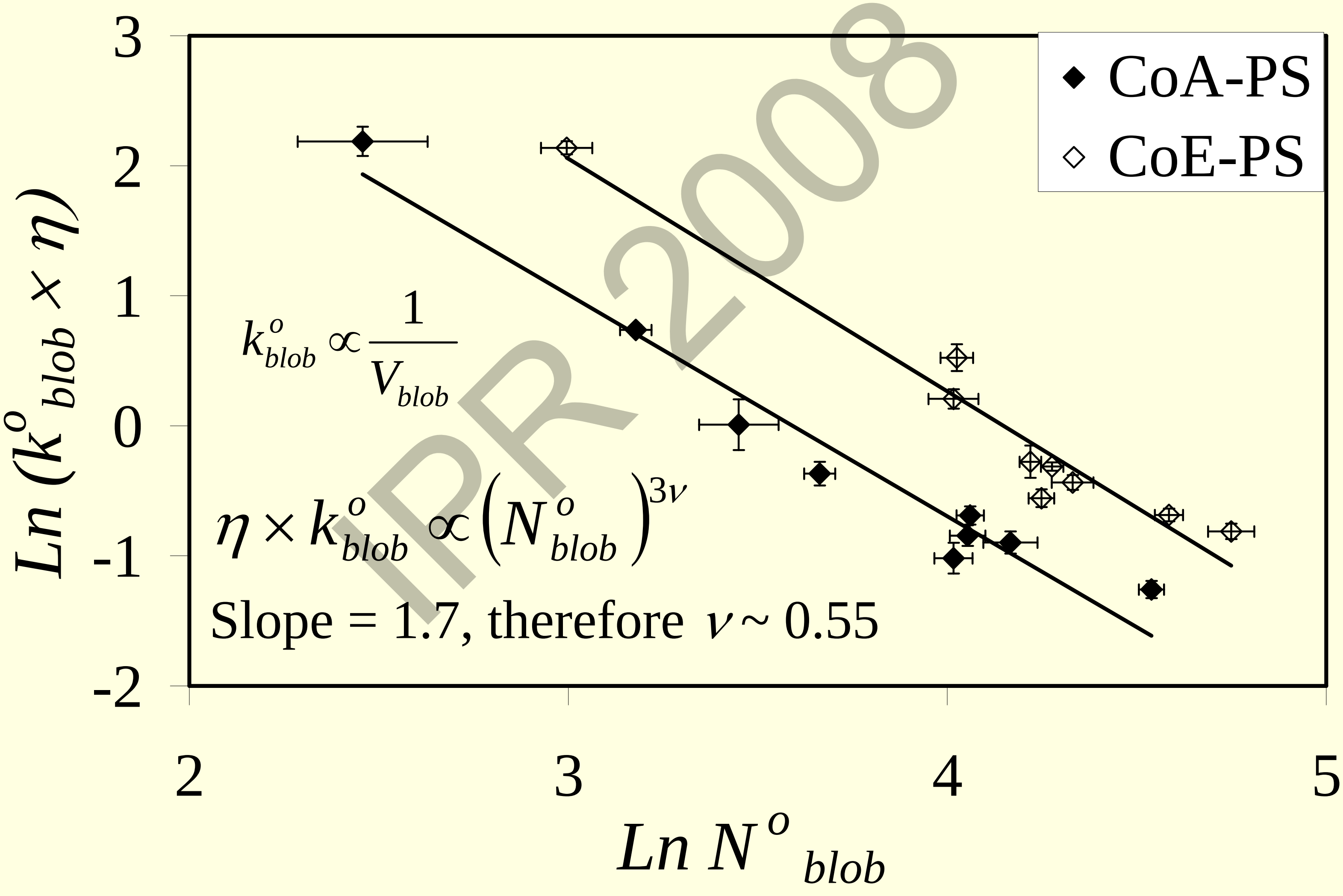
$$[Py^*]_{(t)} = \left[Py^*_{diff}\right]_{(t=0)} \exp\left[-\left(A_2 + \frac{1}{\tau_M}\right)t - A_3\left(1 - \exp(-A_4 t)\right)\right] + \left[Py^*_{free}\right]_{(t=0)} \exp(-t/\tau_M)$$

$$A_2 = \langle n \rangle \frac{k_{blob} k_e [blob]}{k_{blob} + k_e [blob]} \qquad A_3 = \langle n \rangle \frac{k^2_{blob}}{\left(k_{blob} + k_e [blob]\right)^2}$$

$$A_4 = k_{blob} + k_e [blob]$$

$$N_{blob} = \frac{\langle n \rangle}{\lambda_{Py} / f_{Mdiff} \left[M_{Py}(x) + M(1-x) \right]}$$

Scaling laws



$$k^o_{blob} \propto \frac{1}{V_{blob}}$$

$$\eta \times k^o_{blob} \propto \left(N^o_{blob}\right)^{3\nu}$$

Slope = 1.7, therefore $\nu \sim 0.55$