



# 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

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## ■ Background:

- Studying polymer chain dynamics
- Pyrene fluorescence
- Comparing different labeling methods
- Analysis methods:
  - Birks Scheme
  - The fluorescence blob model (FBM)

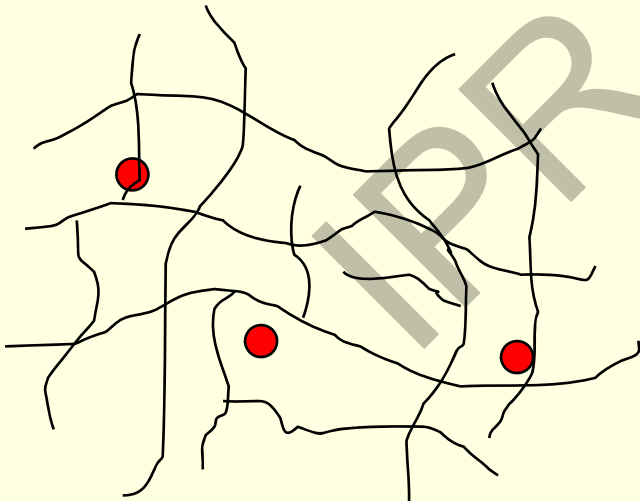
## ■ Experiment

- Comparing the information obtained on the dynamics of polystyrene chains as a function of solvent viscosity

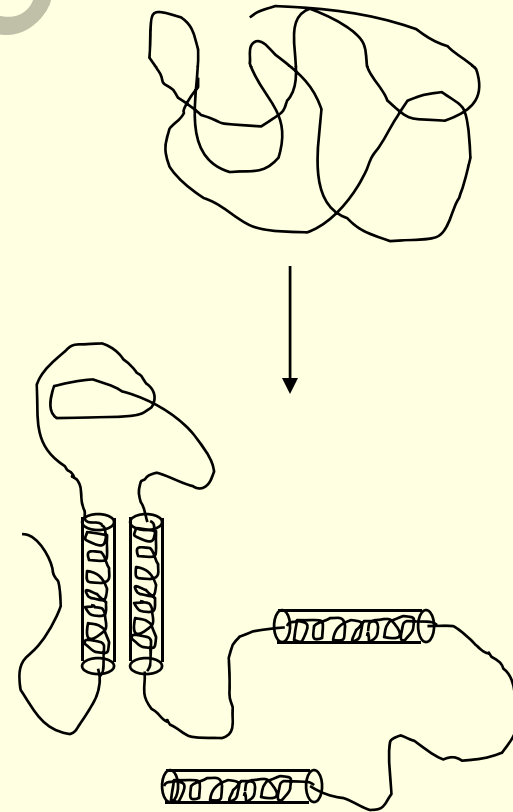
## ■ Results and Conclusions

# Why Study Polymer Chain Dynamics?

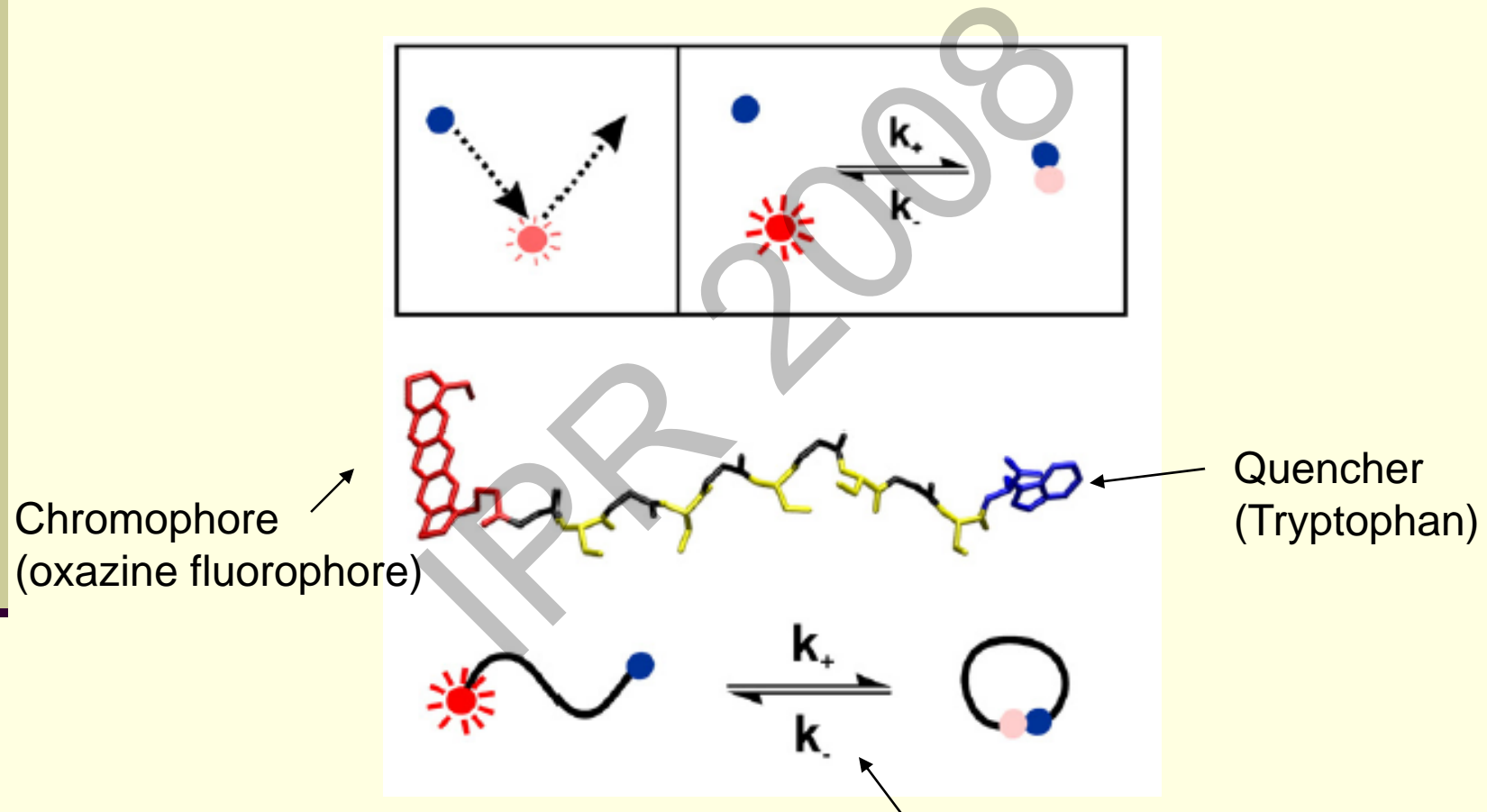
- Cross-linked gels - used in drug delivery, Li-ion batteries



- Protein folding



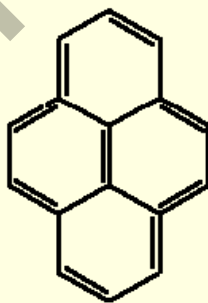
# Cyclization of End-labeled Peptides



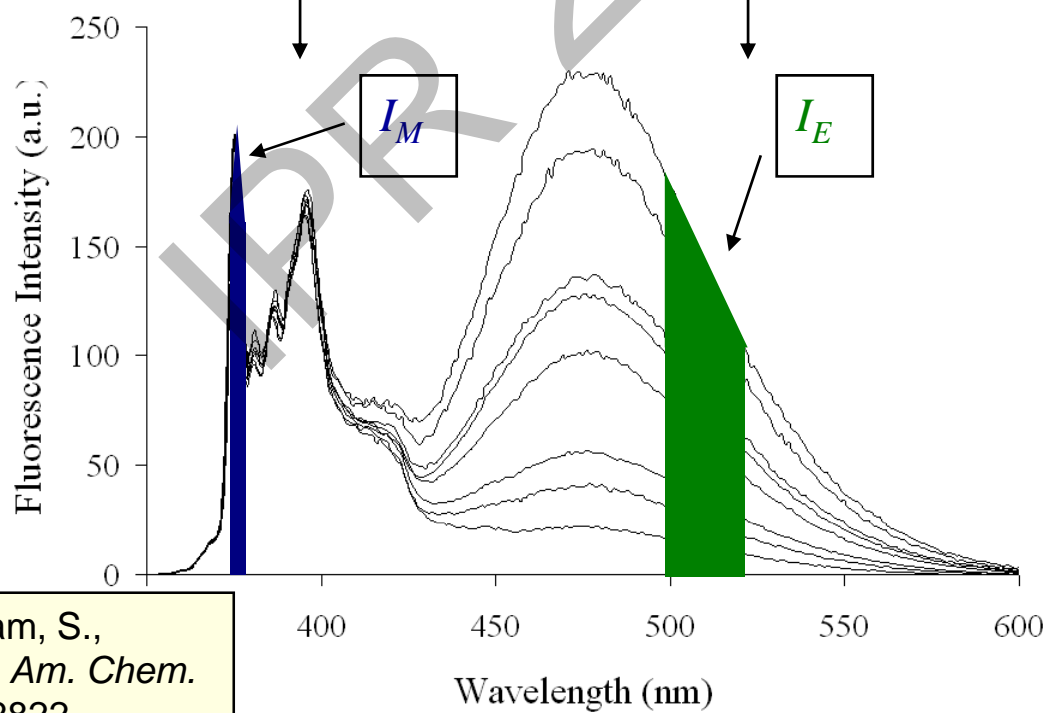
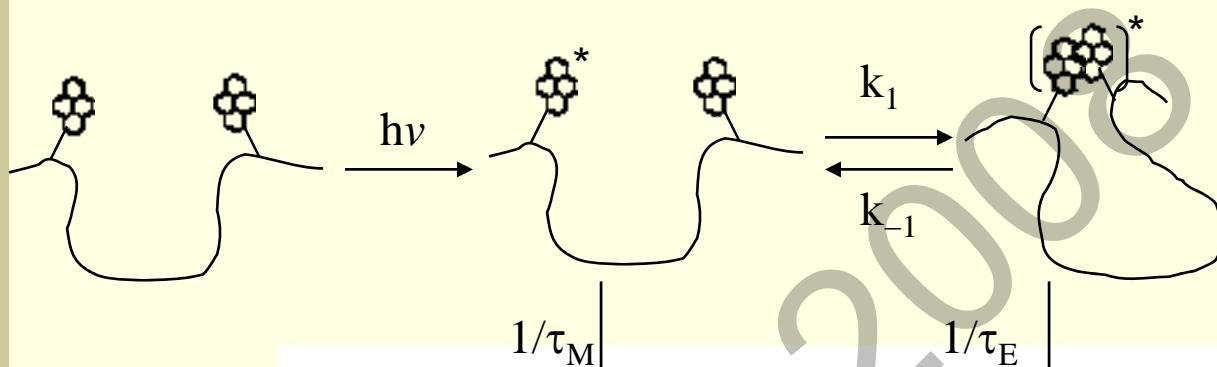
# Probing Polymer Chain Dynamics

- 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

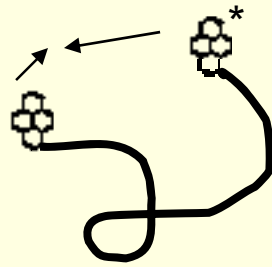


# Pyrene Fluorescence

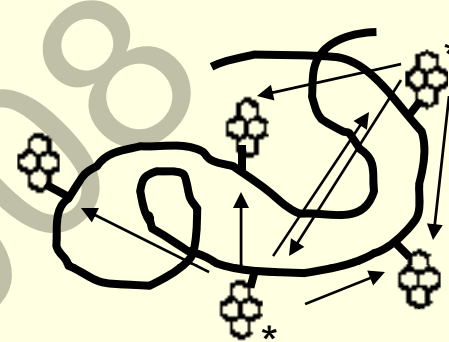


Duhamel, J., Kanagalingam, S.,  
O'Brien, T., Ingratta, M. *J. Am. Chem.  
Soc.* **2003**, *125*, 12810-12822.

# End-Labeling vs. Random Labeling



V.S.



## ■ Pros

- *Relatively* un-complicated analysis
- $k_{cy}$  is quantitative

## ■ Cons

- Only short, mono-disperse chains can be used

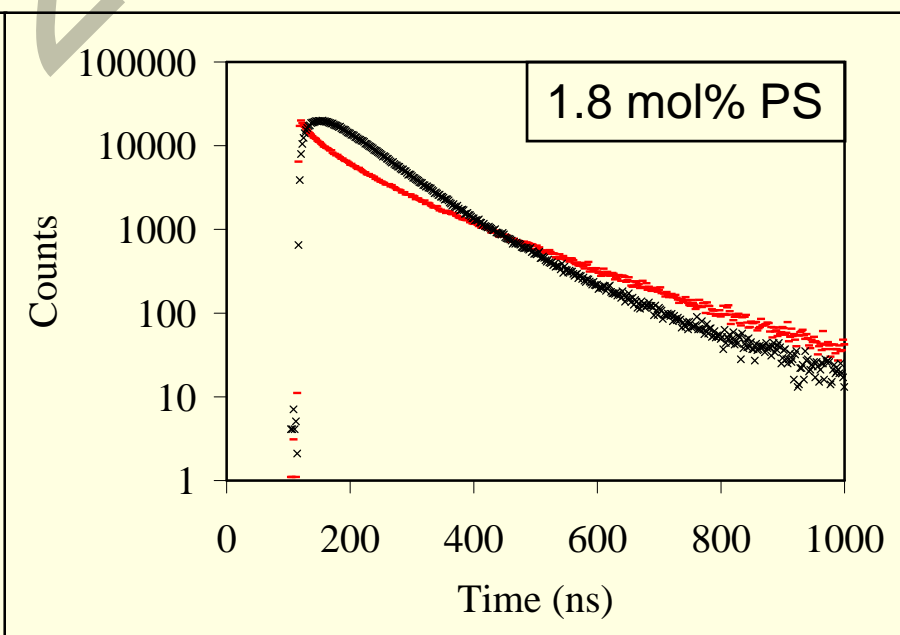
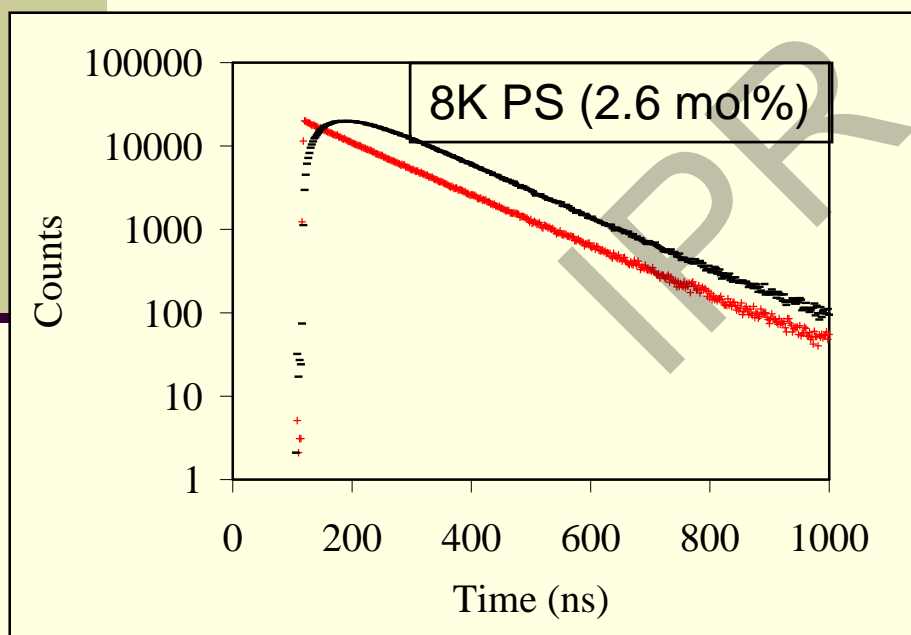
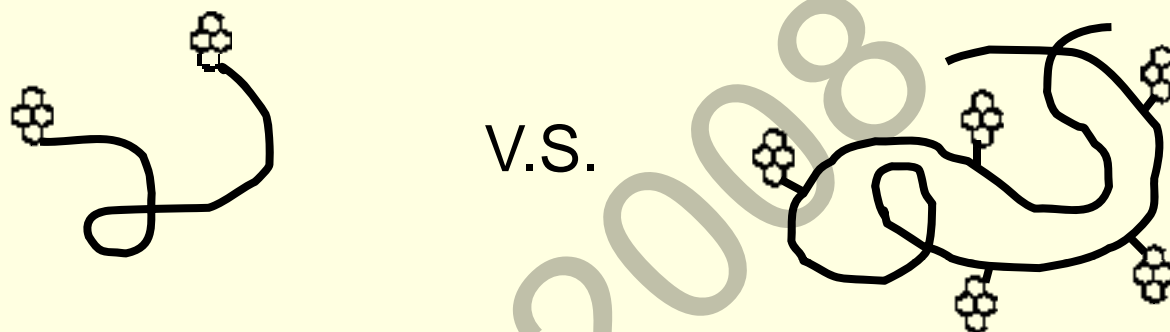
## ■ Pros

- Can use higher MW, polydisperse polymers; usually easier to synthesize

## ■ Cons

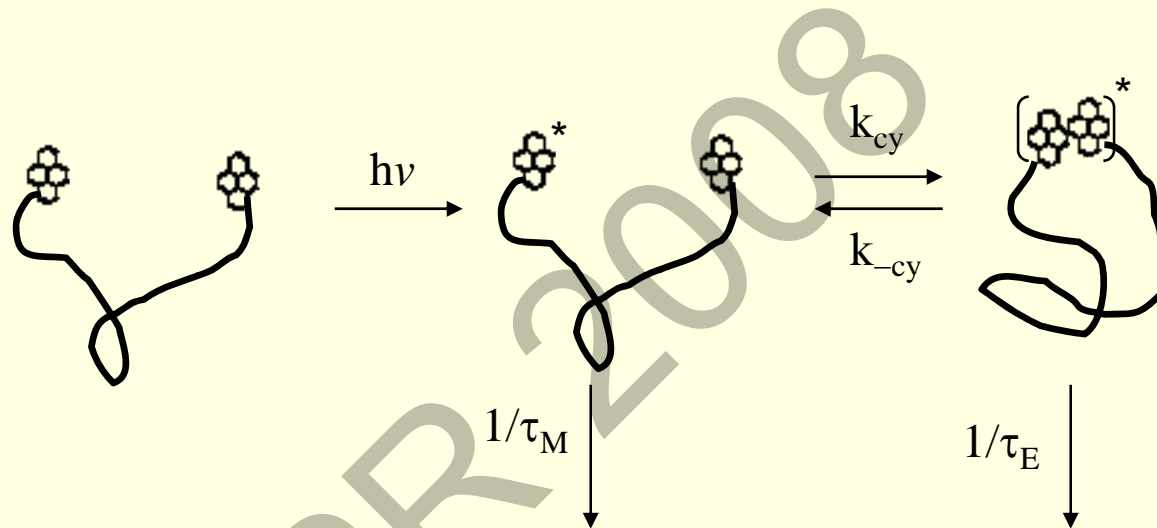
- Excimer formation is *complicated*
- Analysis is often considered *qualitative*

# End-Labeling vs. Random Labeling



Py-Polystyrene in toluene

# Birks' Scheme for Excimer Formation



Parameters retrieved:

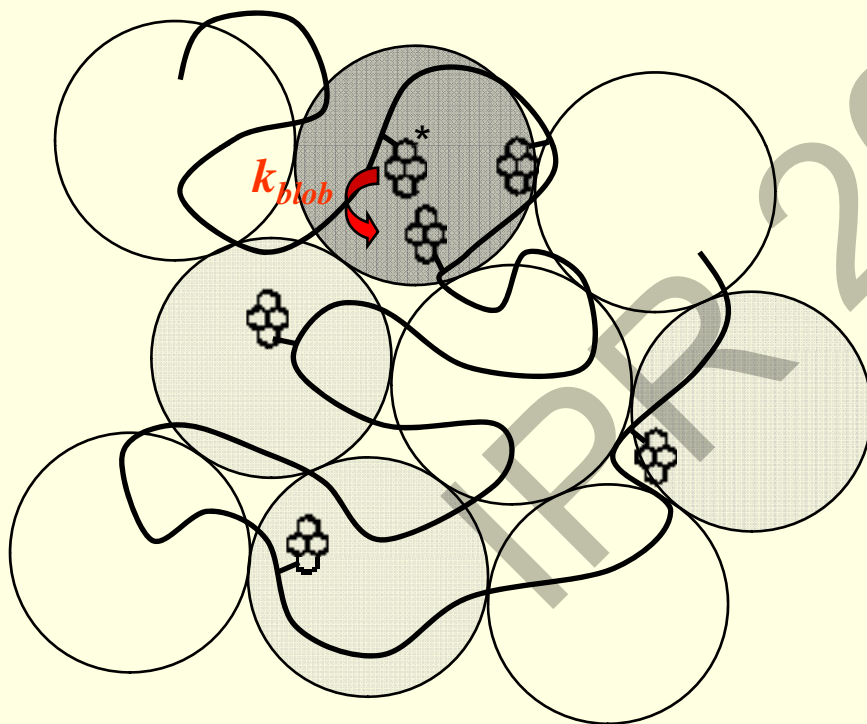
$k_{cy}$ ,  $k_{-cy}$

$\tau_E$

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

# Fluorescence Blob Model (FBM): Polymer $\rightarrow$ Blobs

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$k_{blob}$  = 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

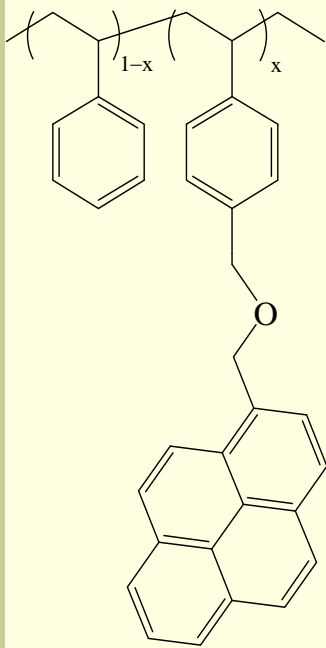
# Experiment:

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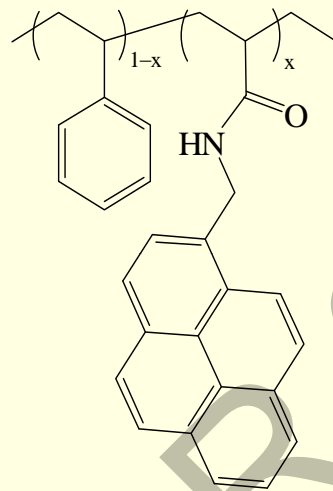
- Previous work showed changing the way pyrene is attached appears to have a strong affect on excimer formation\*
- Two Goals:
  - Comparison of the excimer formation of end-labeled vs. randomly labeled Py-PS
  - How does excimer formation change as a function of *solvent viscosity*

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

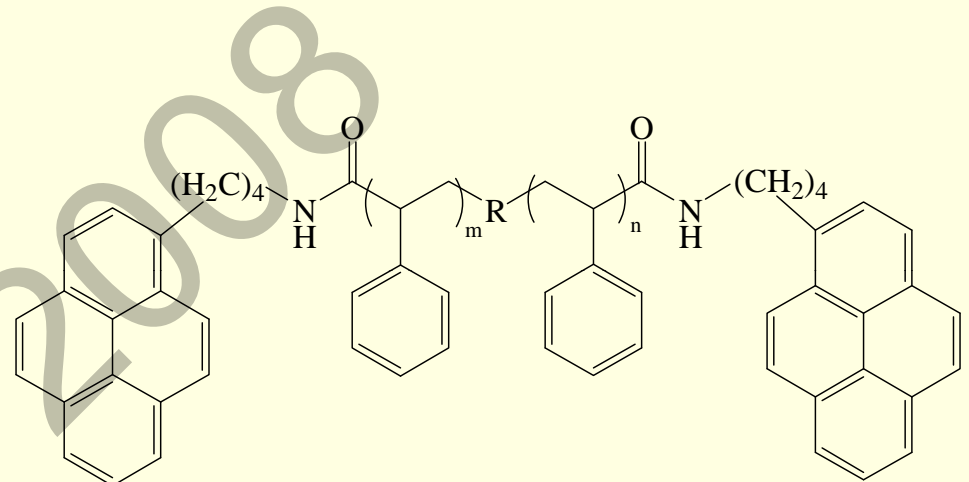
# Names and Structures



**CoE-PS**  
Copolymer - Ether linker



**CoA-PS**  
Copolymer- Amide linker



Where  $m+n = 30, 45$  and  $80$  units

**PS(X)Py<sub>2</sub>**  
End-labeled with  
a longer Amide linker

# Polymers and Solvents

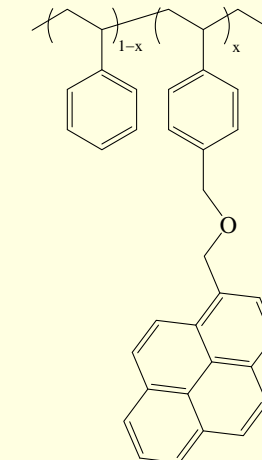
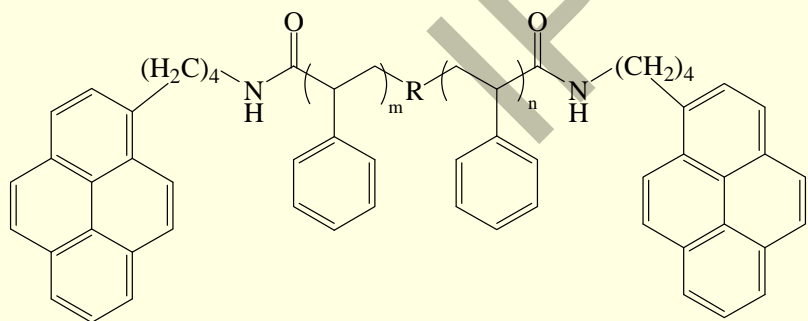
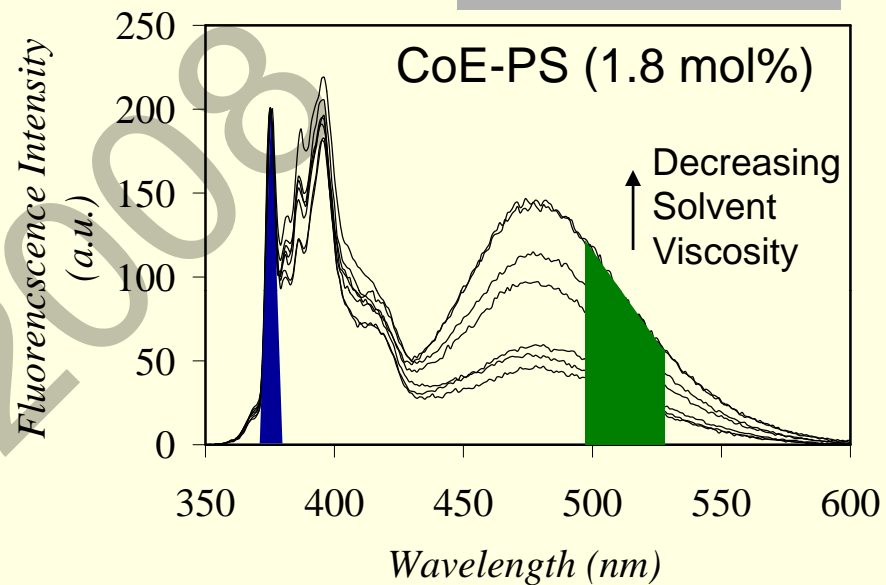
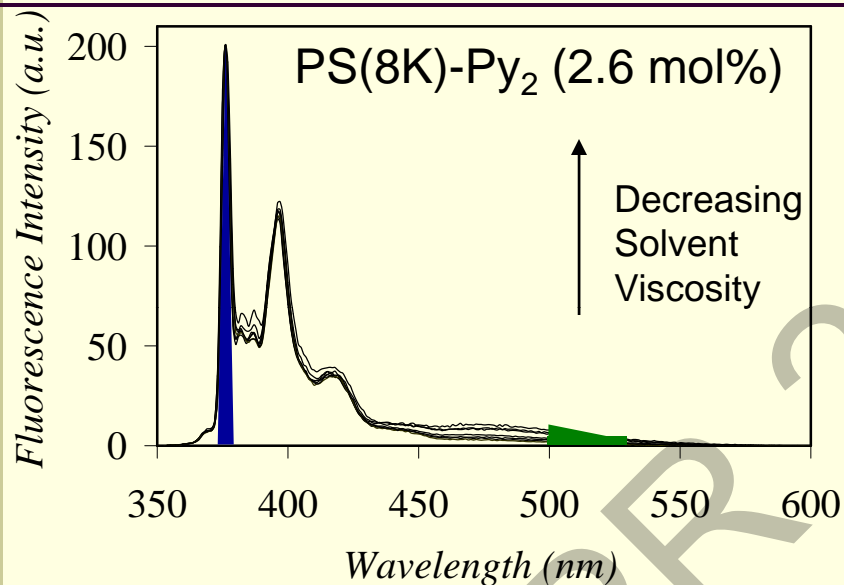
Sample	x, mol % Py	$\lambda_{Py}, \mu\text{mol}\cdot\text{g}^{-1}$	$M_n, \text{kg}\cdot\text{mol}^{-1}$	PDI
CoE-PS	1.5	141	35	1.81
	1.8	169	45	1.87
	3.2	284	32	1.99
	4.8	412	16	1.85
	5.1	436	34	1.80
	6.4	533	46	1.65
CoA-PS	1.1	105	43	1.88
	2.5	230	39	2.04
	3.7	331	55	1.90
	5.0	437	28	1.88
	5.2	459	34	1.96
	6.4	550	39	1.91
PS(X)Py <sub>2</sub>	2.6	250	8.0	1.09
	4.6	444	4.5	1.12
	6.9	667	3.0	1.10

Solvent	$\eta, \text{mPa}\cdot\text{s}$	$[\eta]_{40\text{K}}, \text{L/g}$	$\pm [\eta], \text{L/g}$	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
<i>N,N</i> -Dimethylformamide (DMF)	0.79	0.0192	0.0003	poor
Dioxane	1.18	0.0241	0.0001	good
<i>N,N</i> -Dimethylacetamide (DMA)	1.92	0.0221	0.0007	mediocre

# Results

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# Steady-State Spectra



# Example $I_E/I_M$ values for PS(X)Py<sub>2</sub>

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

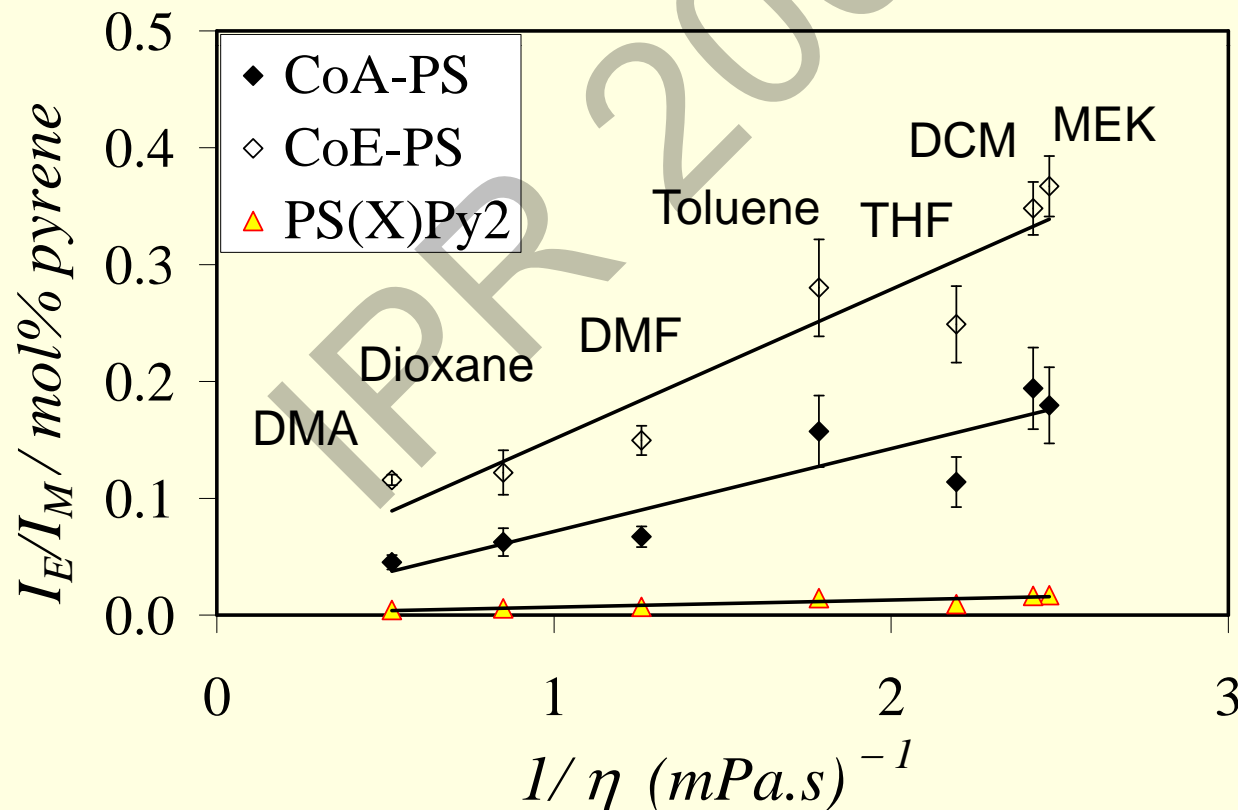
Decreasing Viscosity

$I_E/I_M$  / 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

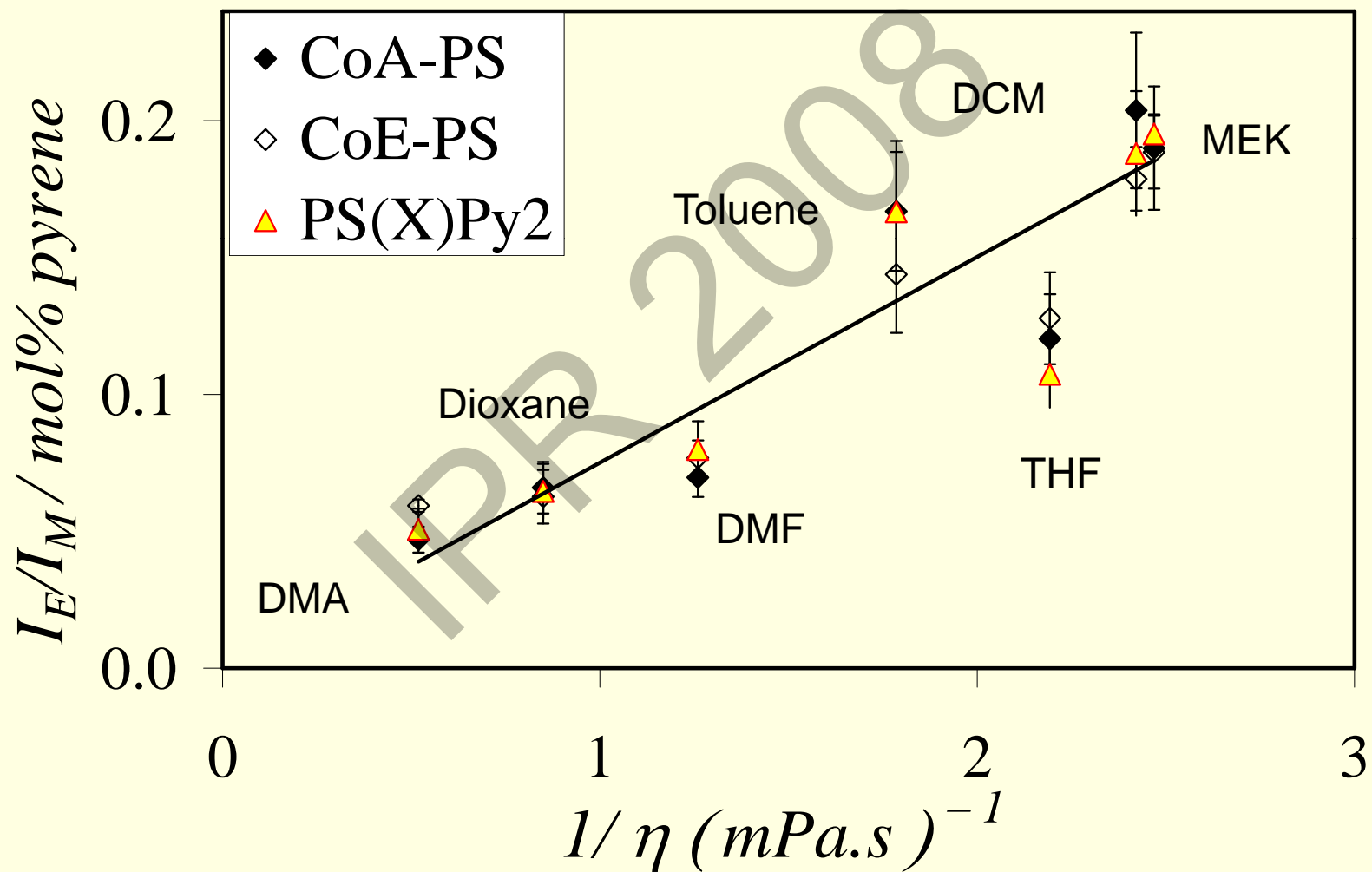


# How do we compare the data?

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- 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<sub>2</sub>, CoE-PS, and CoA-PS series

# Steady-State Fluorescence: $I_E/I_M$



## Steady-State Fluorescence: $I_E/I_M$

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

Where

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

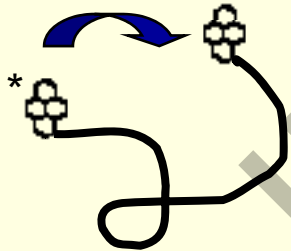
Therefore,  $I_E/I_M \propto k_{diff}[Py]_{loc} \propto 1/\eta$

# Time-Resolved Fluorescence

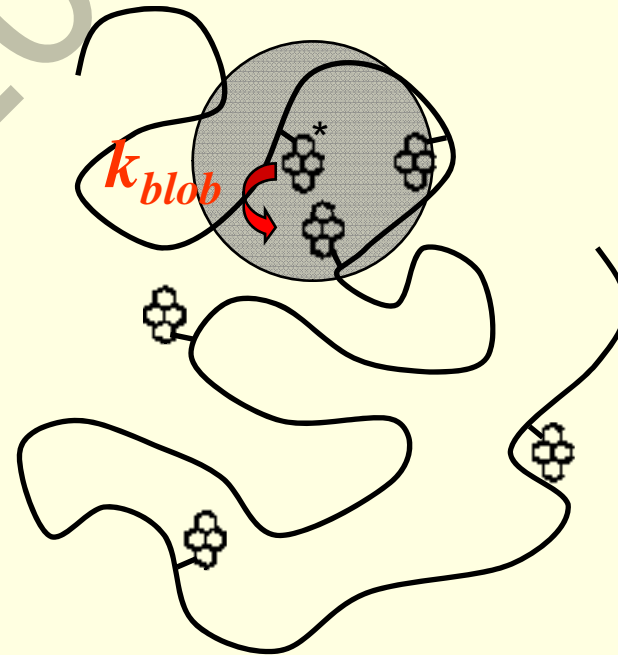
$$k_{cy} = k_{diff}^c \times \frac{1}{V_{coil}}$$

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

$k_{cy}$



$k_{blob}$

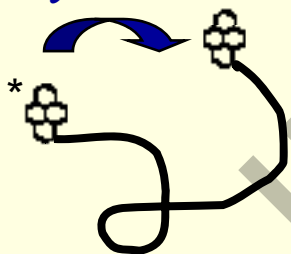


# Time-Resolved Fluorescence

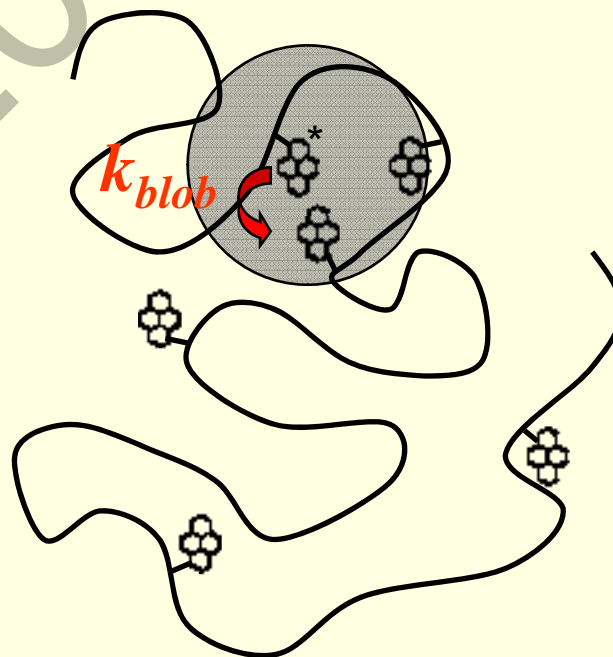
$$k_{cy} = k_{diff}^c \times \frac{1}{V_{coil}}$$

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

$k_{cy}$



$k_{blob}$

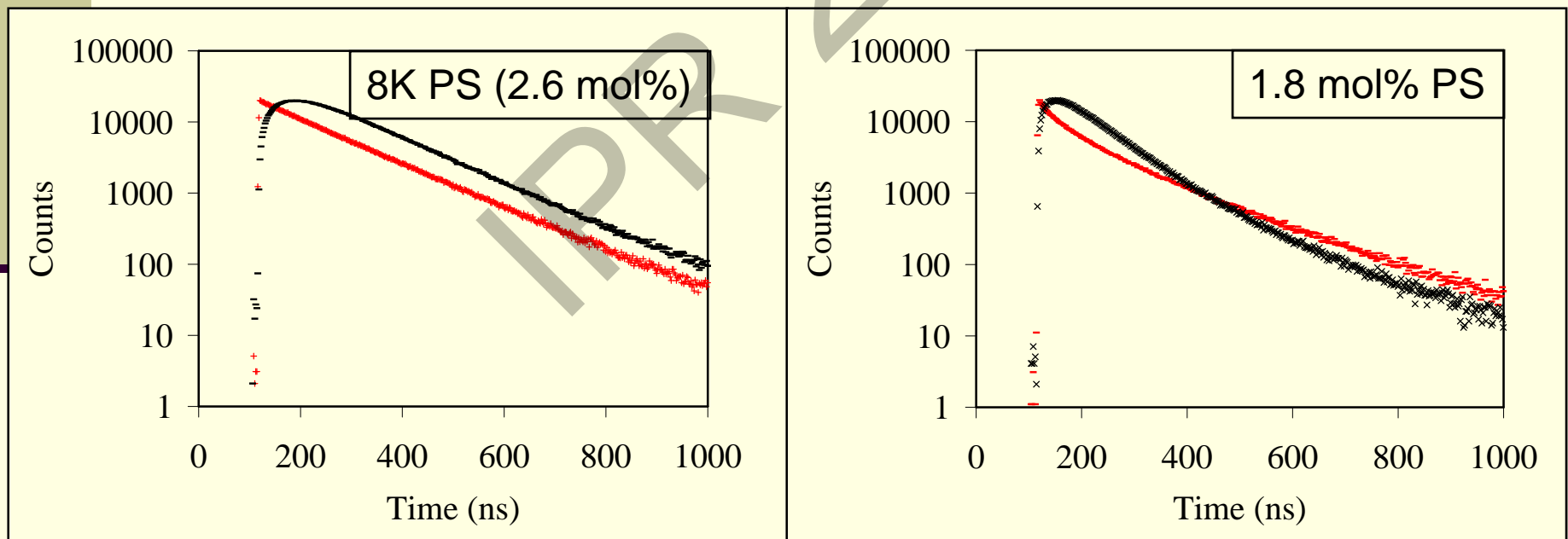


# Time-Resolved Fluorescence

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

V.S.

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



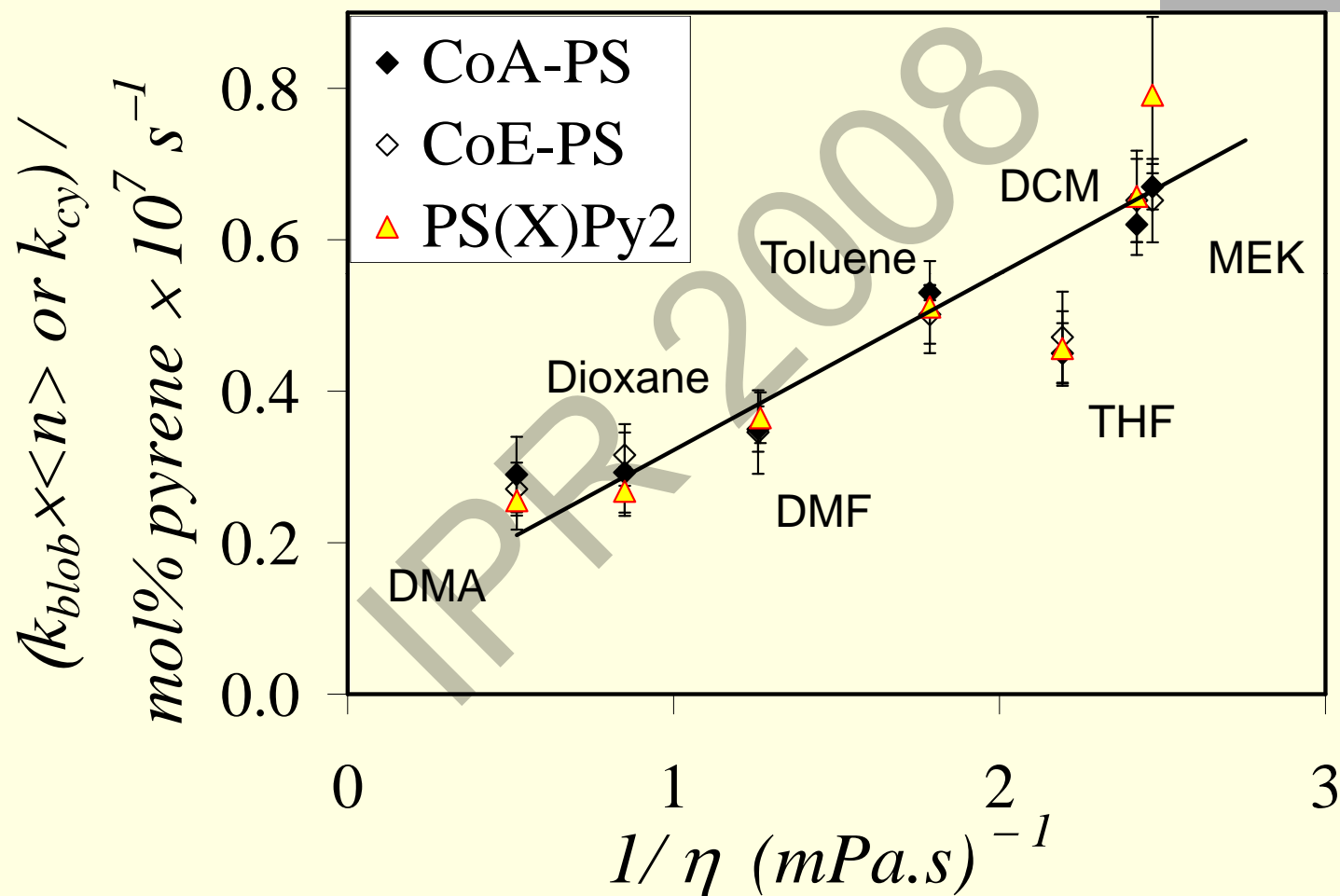
Py-Polystyrene in toluene

# Time-Resolved Fluorescence

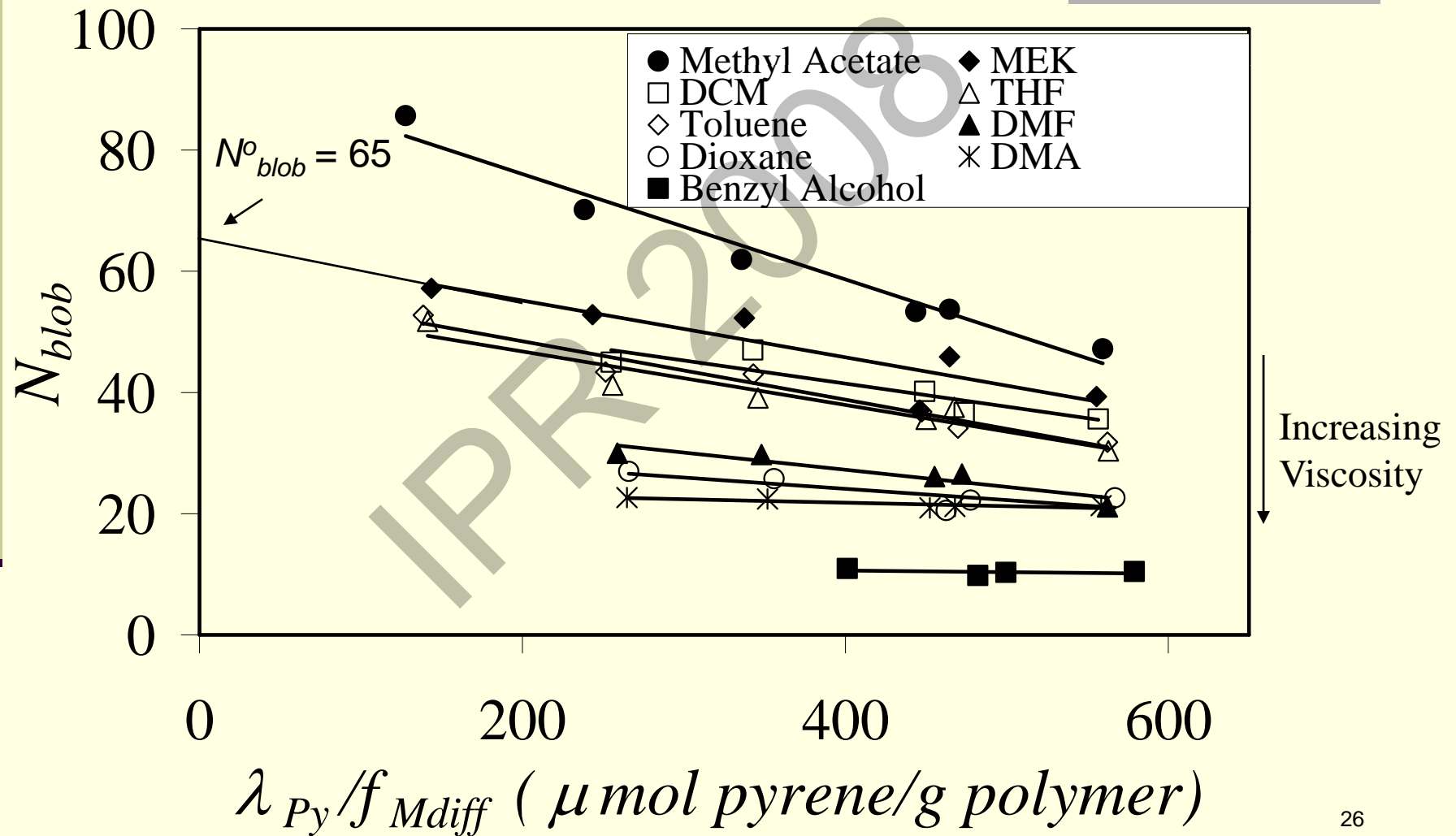
$$k_{cy} = k_{diff}^c \times \frac{1}{V_{coil}} \quad k_{blob} \langle n \rangle = k_{diff}^b \times \frac{\langle n \rangle}{V_{blob}}$$

- 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

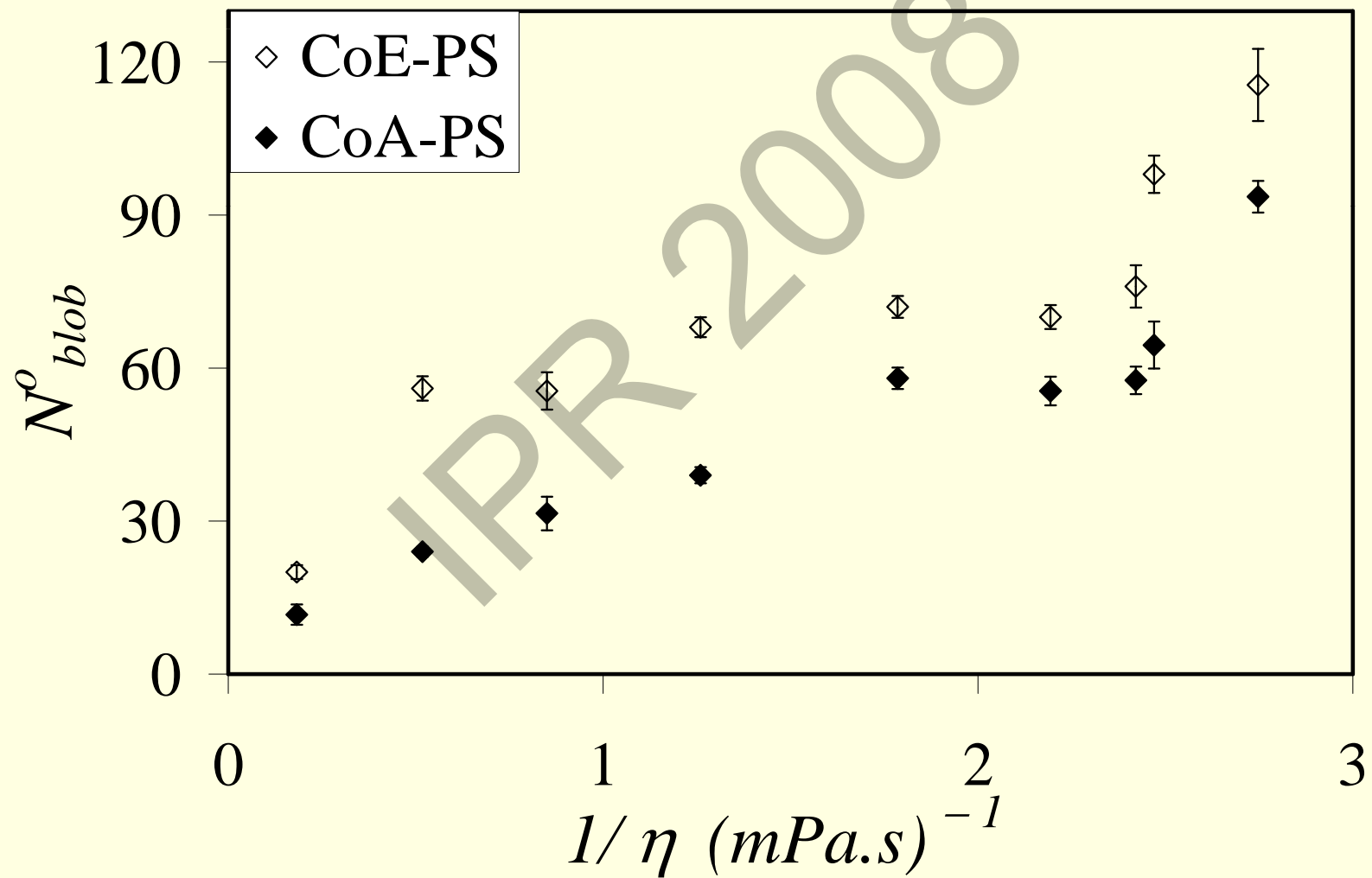
# Time-Resolved Fluorescence



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



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



# Conclusions

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- 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

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

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Thanks!

Questions / Comments?

$$[Py^*]_{(t)} = [Py^*_{diff}]_{(t=0)} \exp\left[-\left(A_2 + \frac{1}{\tau_M}\right)t - A_3(1 - \exp(-A_4t))\right] + [Py^*_{free}]_{(t=0)} \exp(-t/\tau_M)$$

$$A_2 = \langle n \rangle \frac{k_{blob} k_e [blob]}{k_{blob} + k_e [blob]} \quad A_3 = \langle n \rangle \frac{k_{blob}^2}{(k_{blob} + k_e [blob])^2}$$

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

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

# Scaling laws

