

**Synthesis and extensive study of end-to-end
cyclization of monodisperse pyrene-labeled
poly(ethylene oxide) (PEO)**

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IPR Seminar

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Outline

- Introduction
- Pyrene and pyrene-labelled PEO
- Synthesis
- Results
- Conclusions and future work
- Acknowledgements

INTRODUCTION

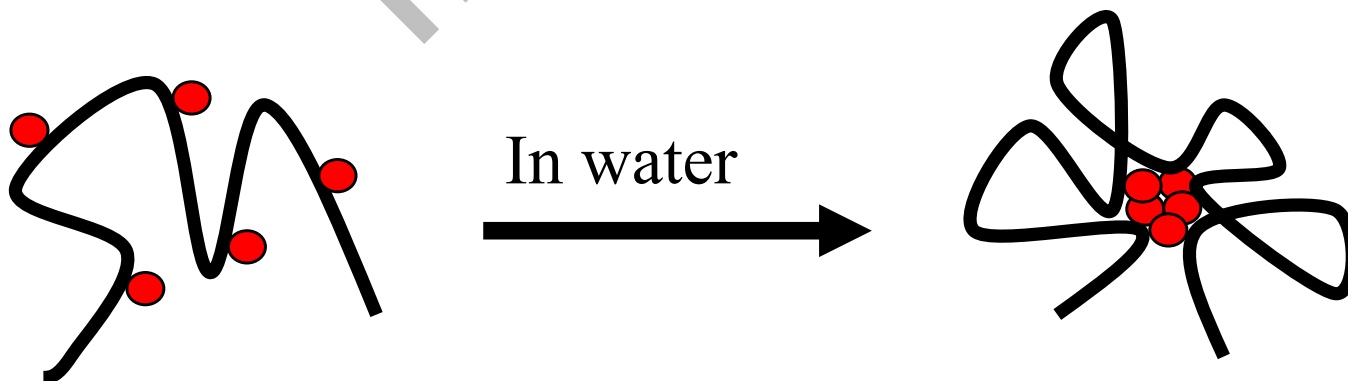
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Associative Polymers

- Water-soluble polymers with a small amount ($<5 \text{ mol}\%$) of hydrophobic pendants

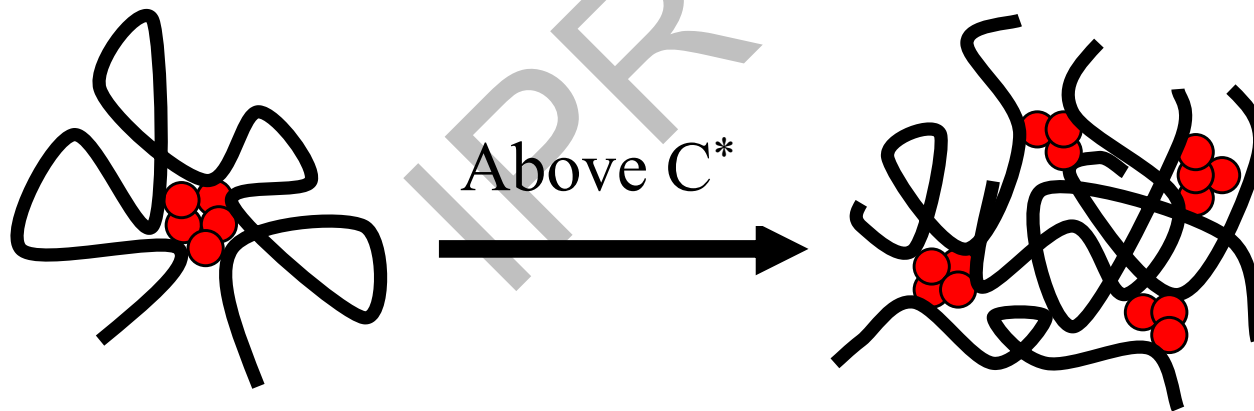


- In water, hydrophobes cluster to form aggregates



Associative Polymers

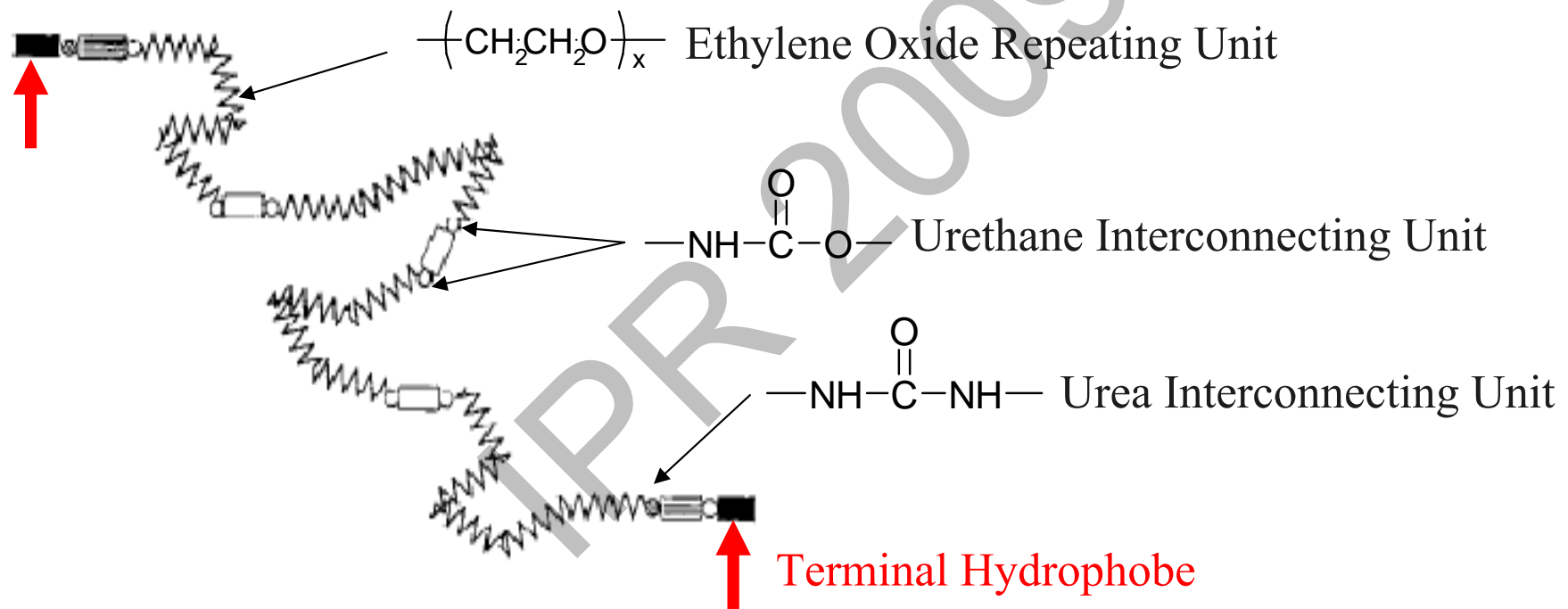
- Above C^* (semi-dilute concentration), a polymeric network created by intermolecular bridging, the solution viscosity increases



- Applications – paints, coatings, dispersants, drug delivery, etc.

HEUR Polymers

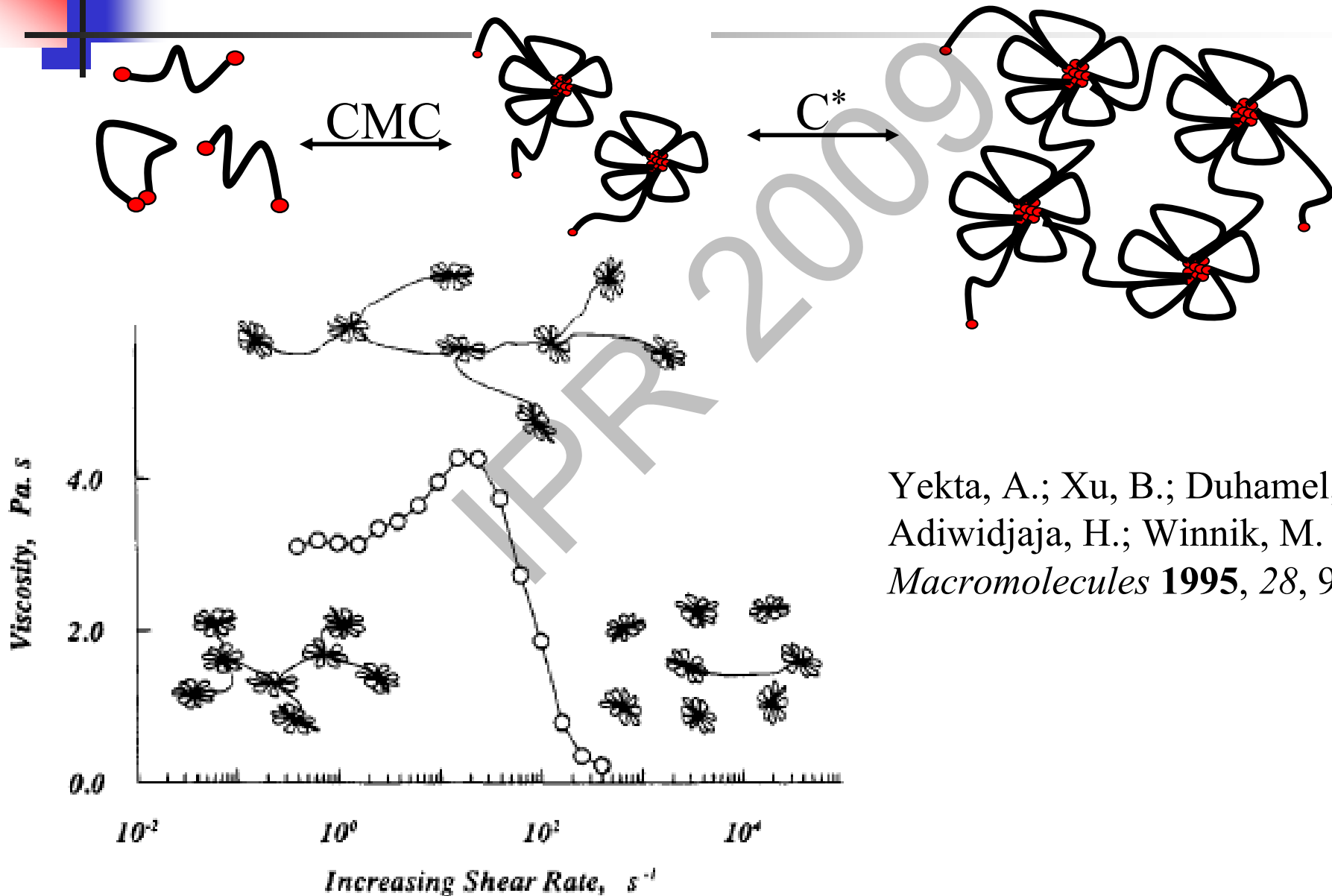
- Hydrophobically modified Ethoxylated URethane (HEUR) polymer



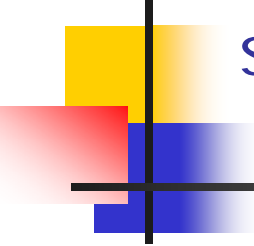
Wetzel, W. H.; Chen, M.; Glass, J. E. *Hydrophilic Polymers, Performance with Environmental Acceptability*, Ed. Glass, J. E. Advances in Chemistry Series 248, American Chemical Society, Washington, DC, **1996**, 163.

- Hydrophobically modified PEO belongs to the HEUR family

Network and Viscoelastic Behaviors of HEUR Polymer in Water



Yekta, A.; Xu, B.; Duhamel, J.;
Adiwidjaja, H.; Winnik, M. A.
Macromolecules **1995**, *28*, 956.



Advantages of using hydrophobically end-capped PEO to study the long-range polymer chain dynamics (LRPCD)

- **A well-defined architecture**

The position of the hydrophobic groups is known – at chain ends

- **A fixed distance between end hydrophobes**

Using a monodisperse PEO ($PDI = M_w/M_n \leq 1.1$) as the polymer backbone

Hydrophobically end-capped PEO is an ideal model system to investigate the chain dynamics

LRPCD are best studied in organic solvents where no aggregation takes place between hydrophobic pendants.

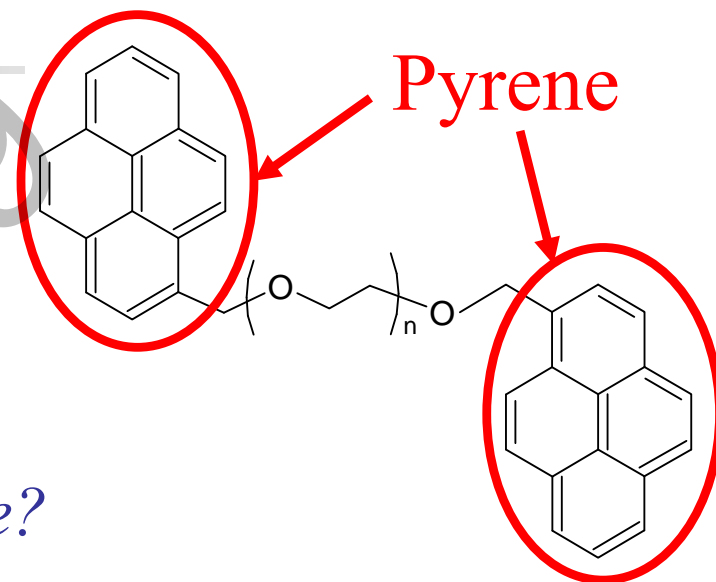
***PYRENE AND PYRENE-
LABELLED PEO***

Pyrene and Pyrene-labelled PEO

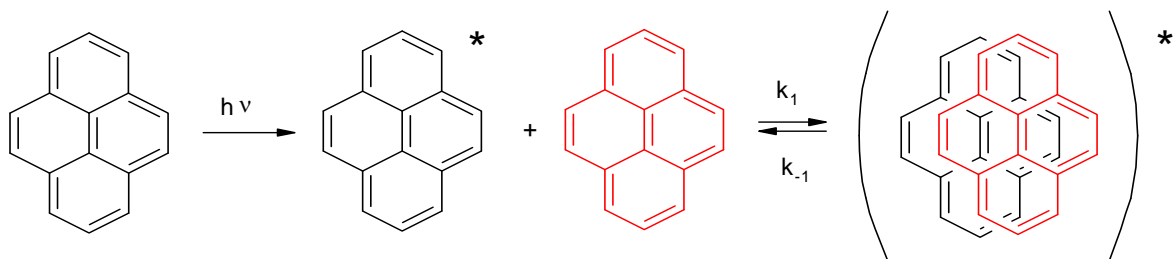
Pyrene – an ideal chromophore

- Highly hydrophobic (0.3-0.7 μ M in water)
- Large extinction coefficient
- Good quantum yield
- Long lifetime
- Isolated excited monomer fluoresces around 375nm and shifts to 480nm when associates with ground-state pyrene to form an excimer

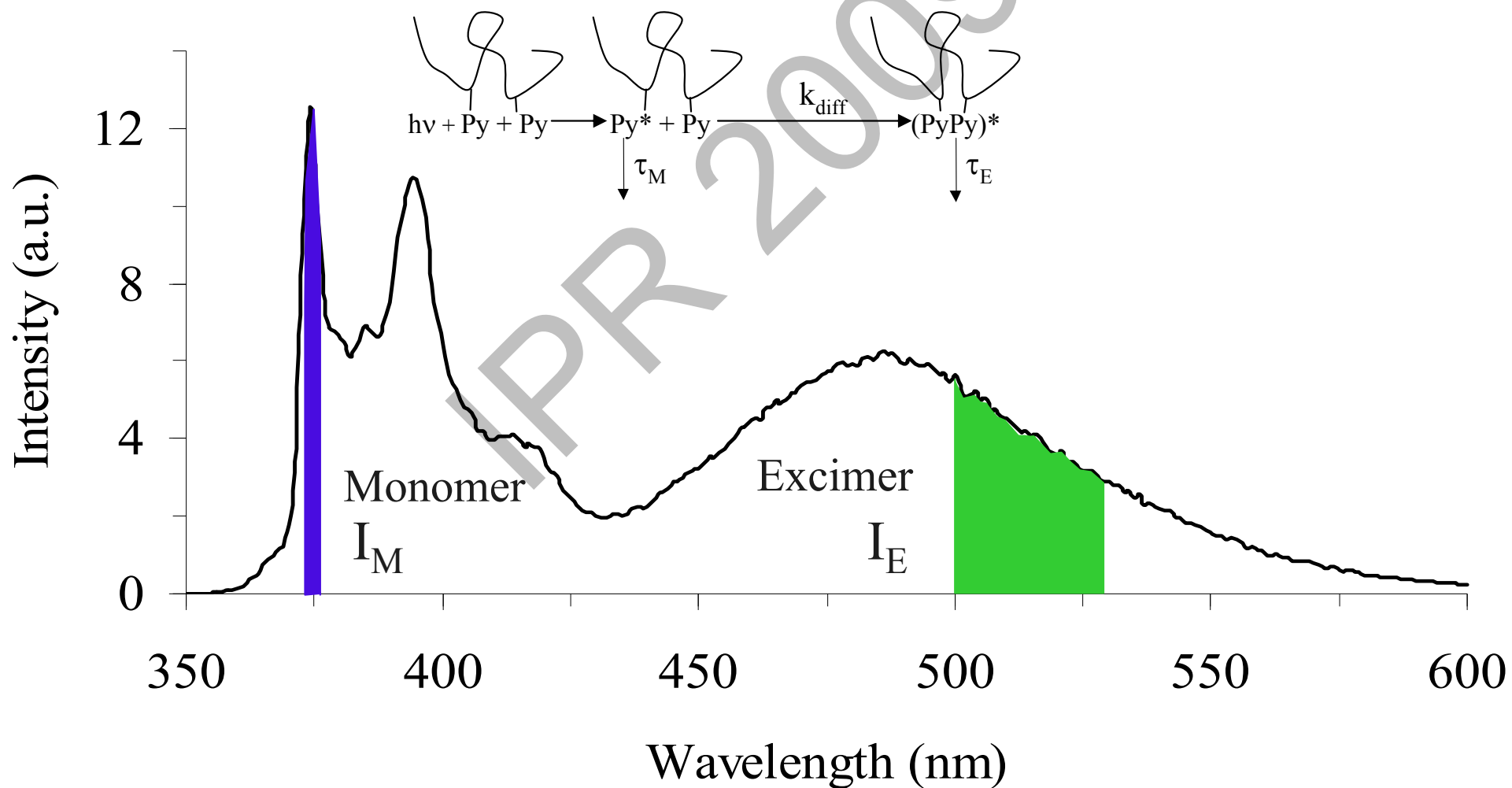
Why Use Pyrene?



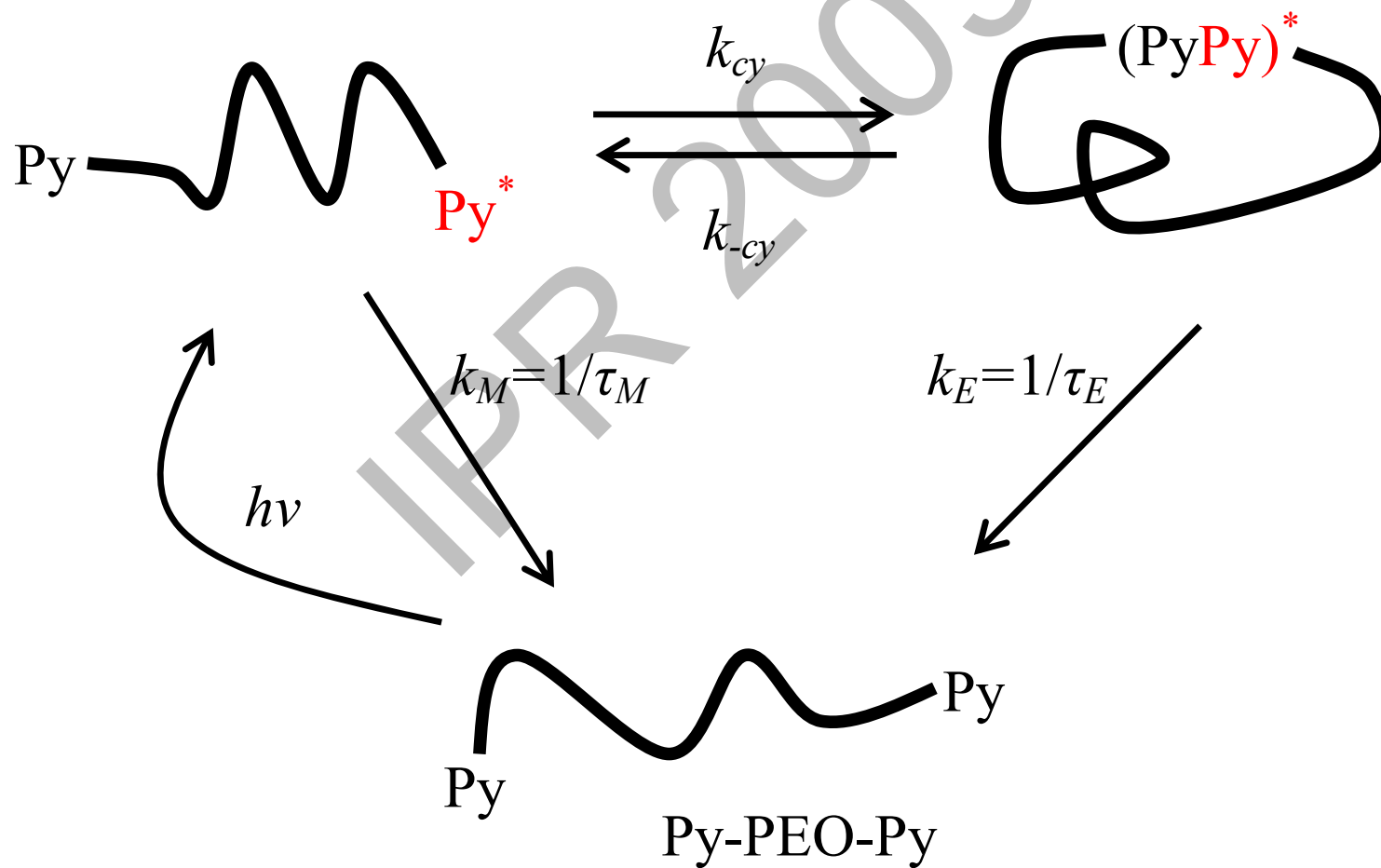
Pyrene (the hydrophobe) end-labelled PEO



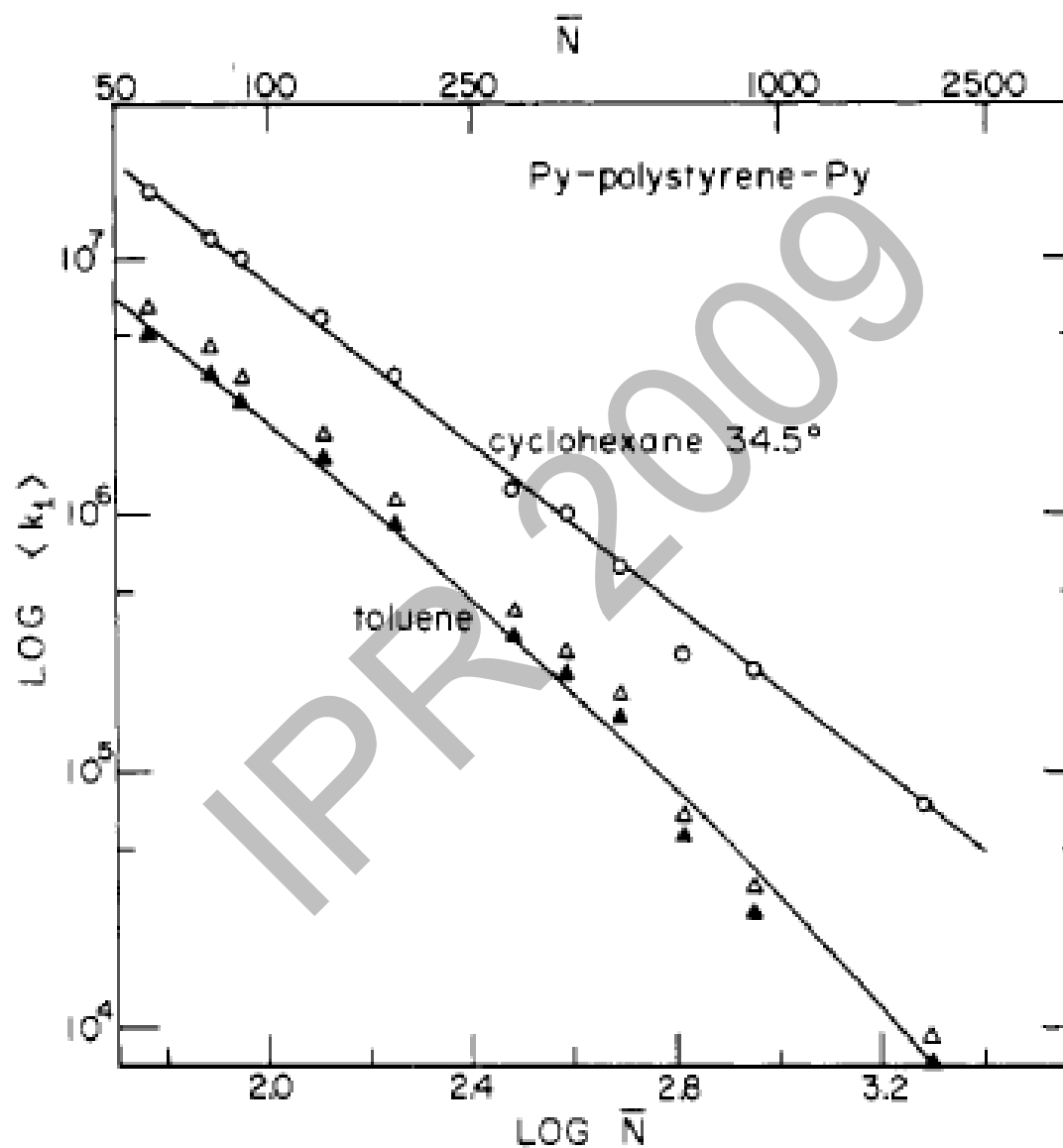
Pyrene Fluorescence



Birks' Scheme

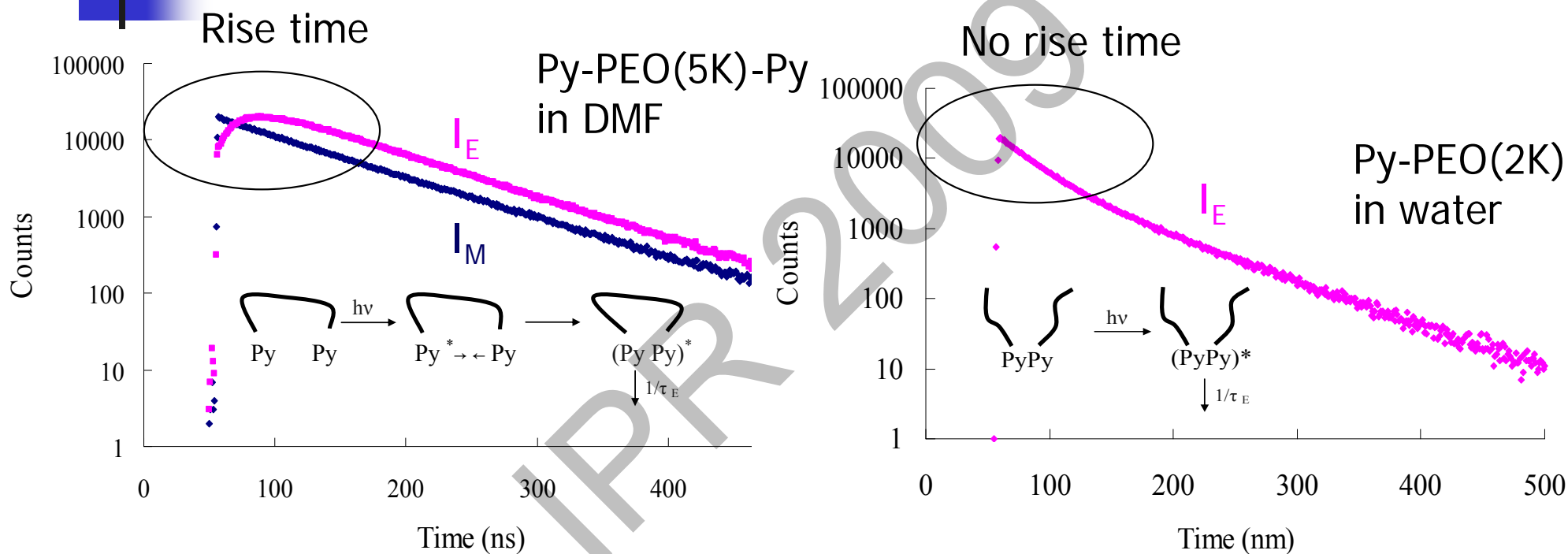


Birks' Scheme



Winnik M. A. *Acc. Chem. Res.* **1985**, 18, 73-79.

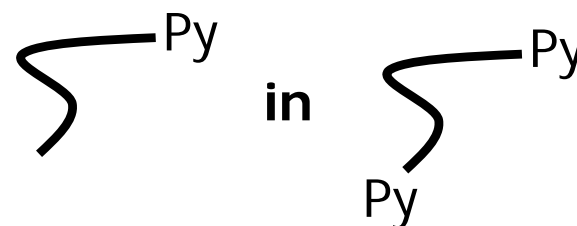
Birks' Scheme



$$I_M(t) = a_{M1} \exp(-t/\tau_1) + a_{M2} \exp(-t/\tau_2) + a_M \exp(-t/\tau_M)$$

$$I_E(t) = a_{E1} \exp(-t/\tau_3) + a_{E2} \exp(-t/\tau_4)$$

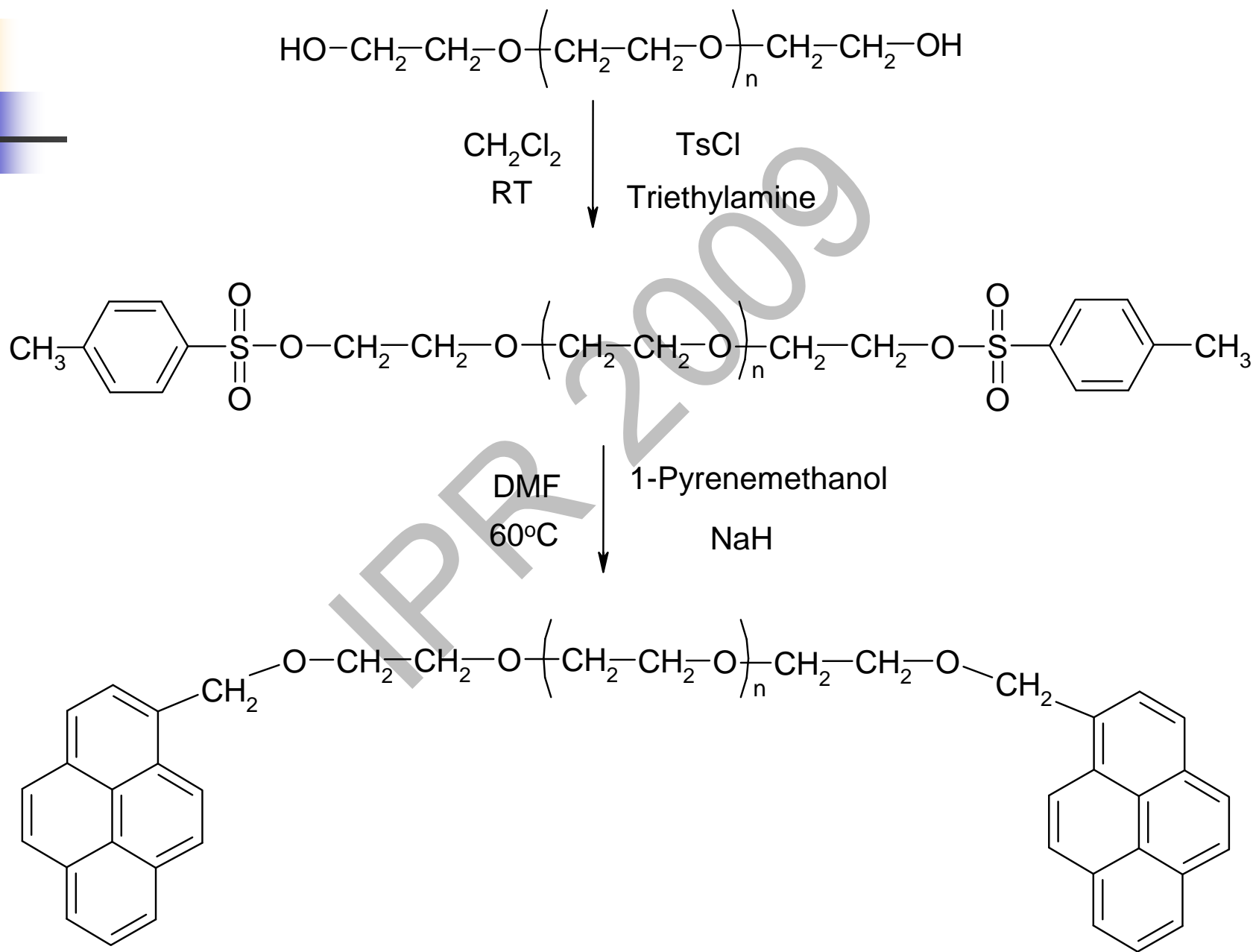
$$\tau_1 = \tau_3 \quad \tau_2 = \tau_4 \quad a_{E1} = -a_{E2}$$



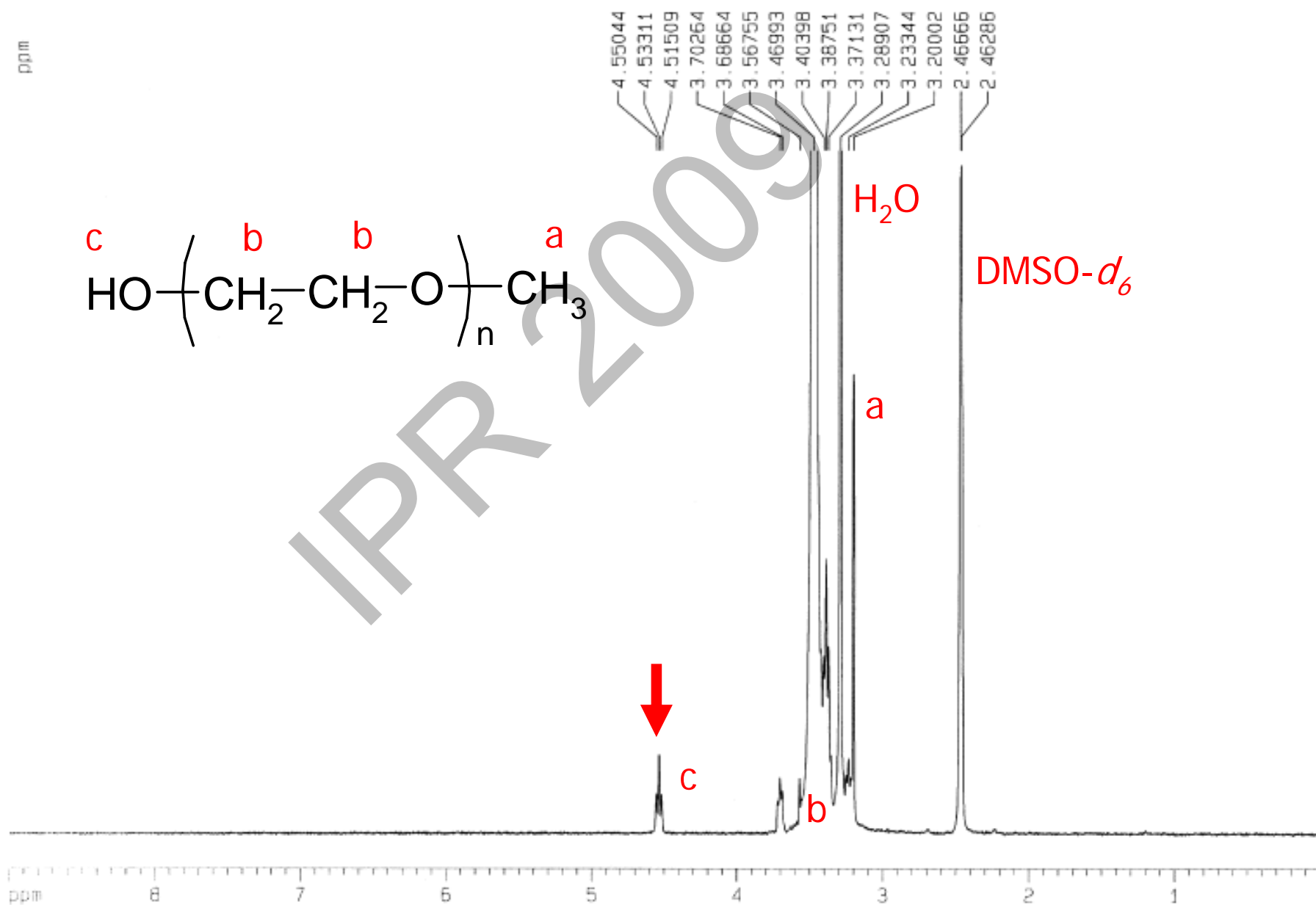
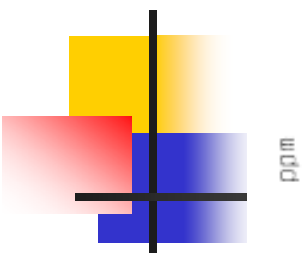
SYNTHESIS

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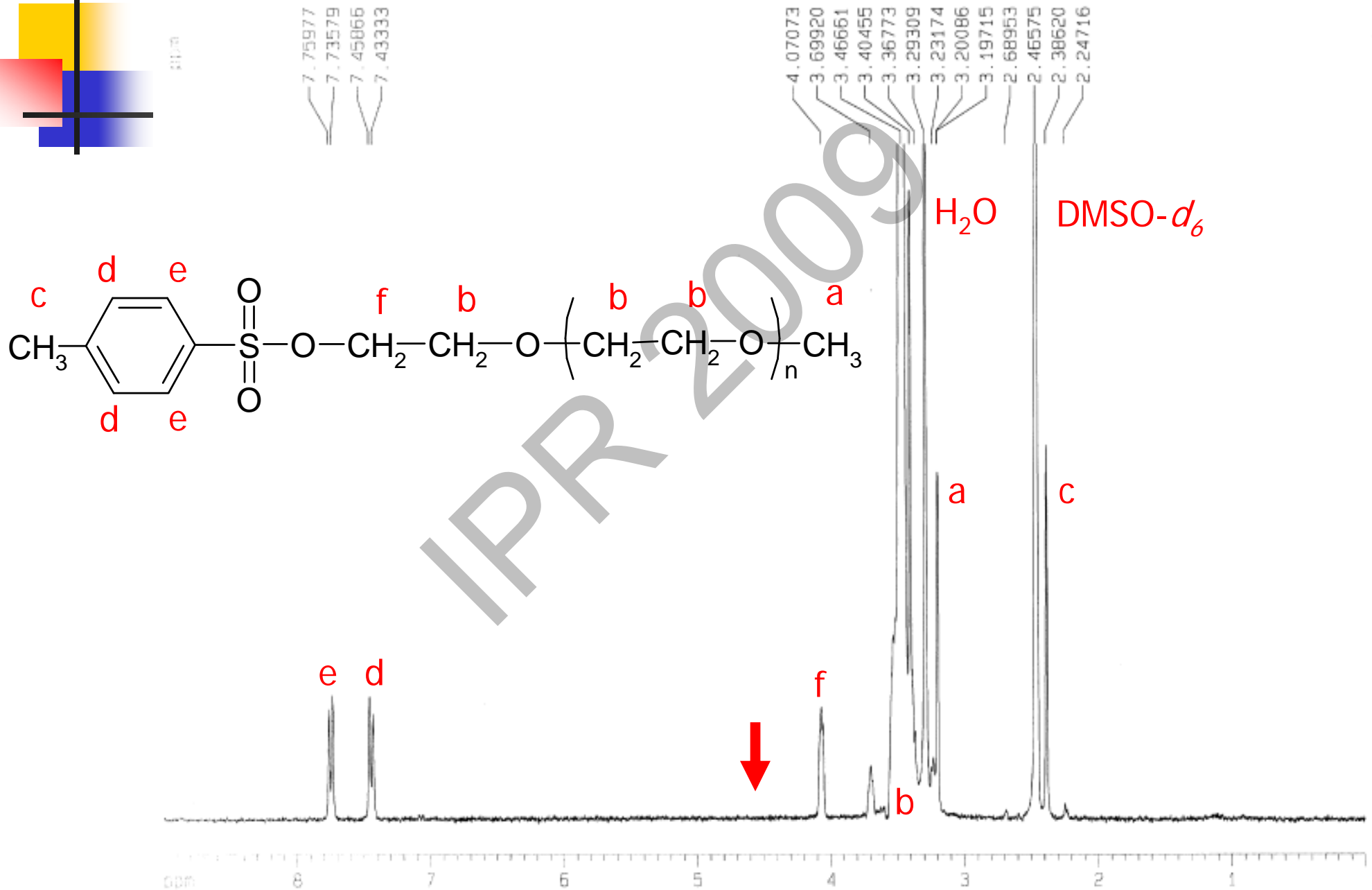
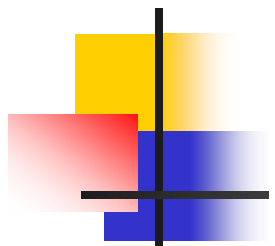
Overall Scheme



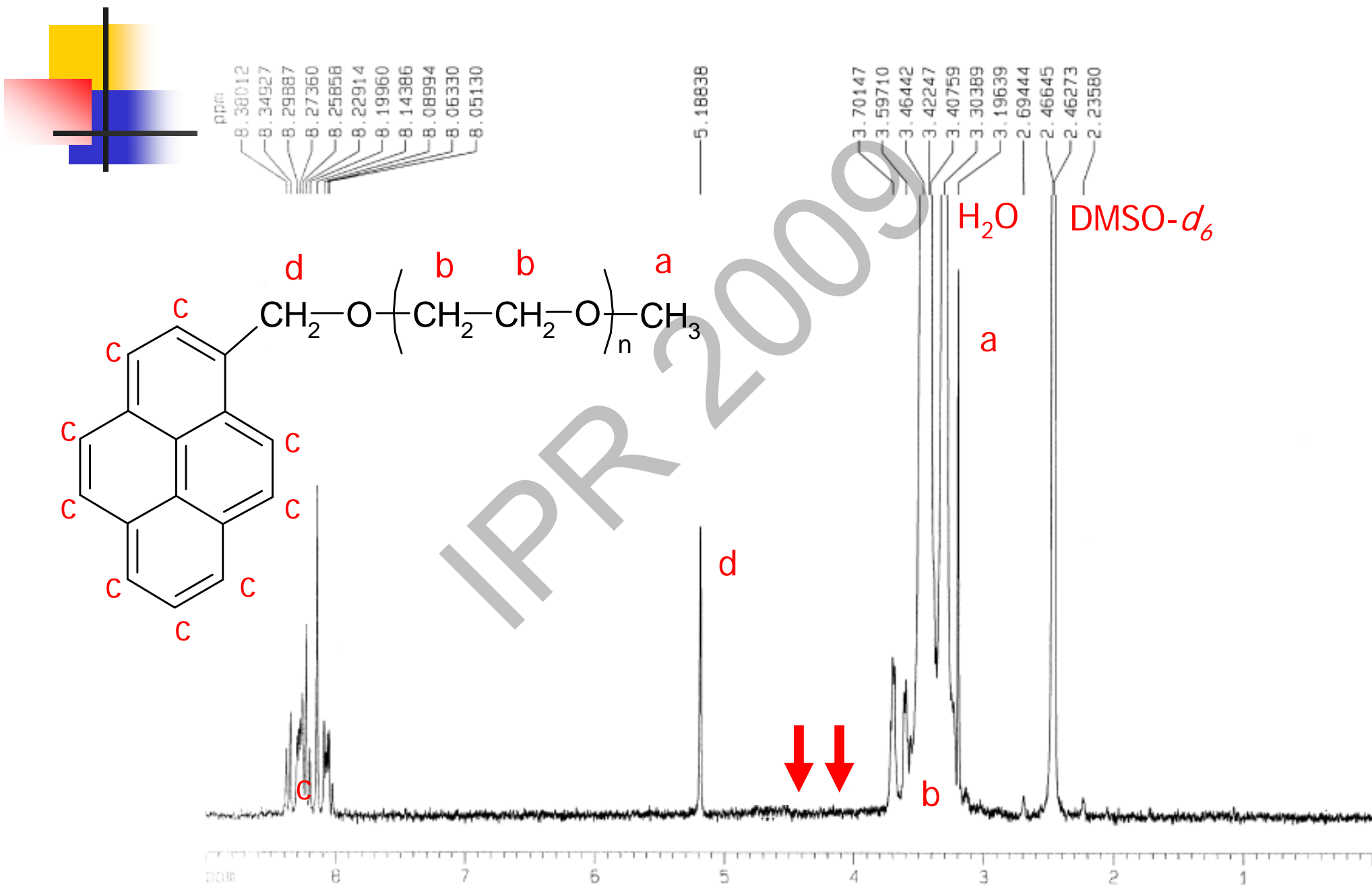
^1H NMR Characterization – PEO



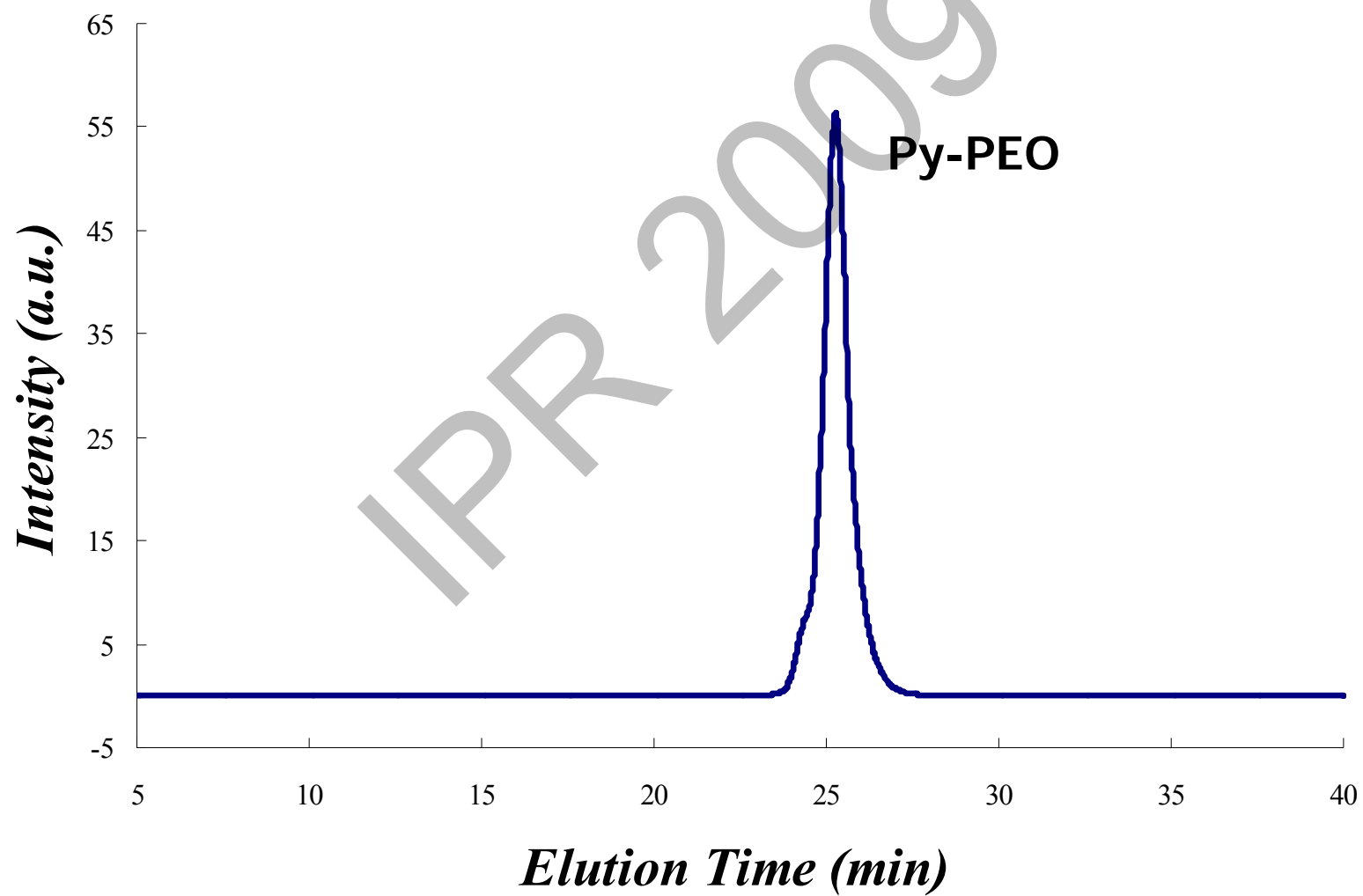
^1H NMR Characterization – Tos-PEO



^1H NMR Characterization – Py-PEO



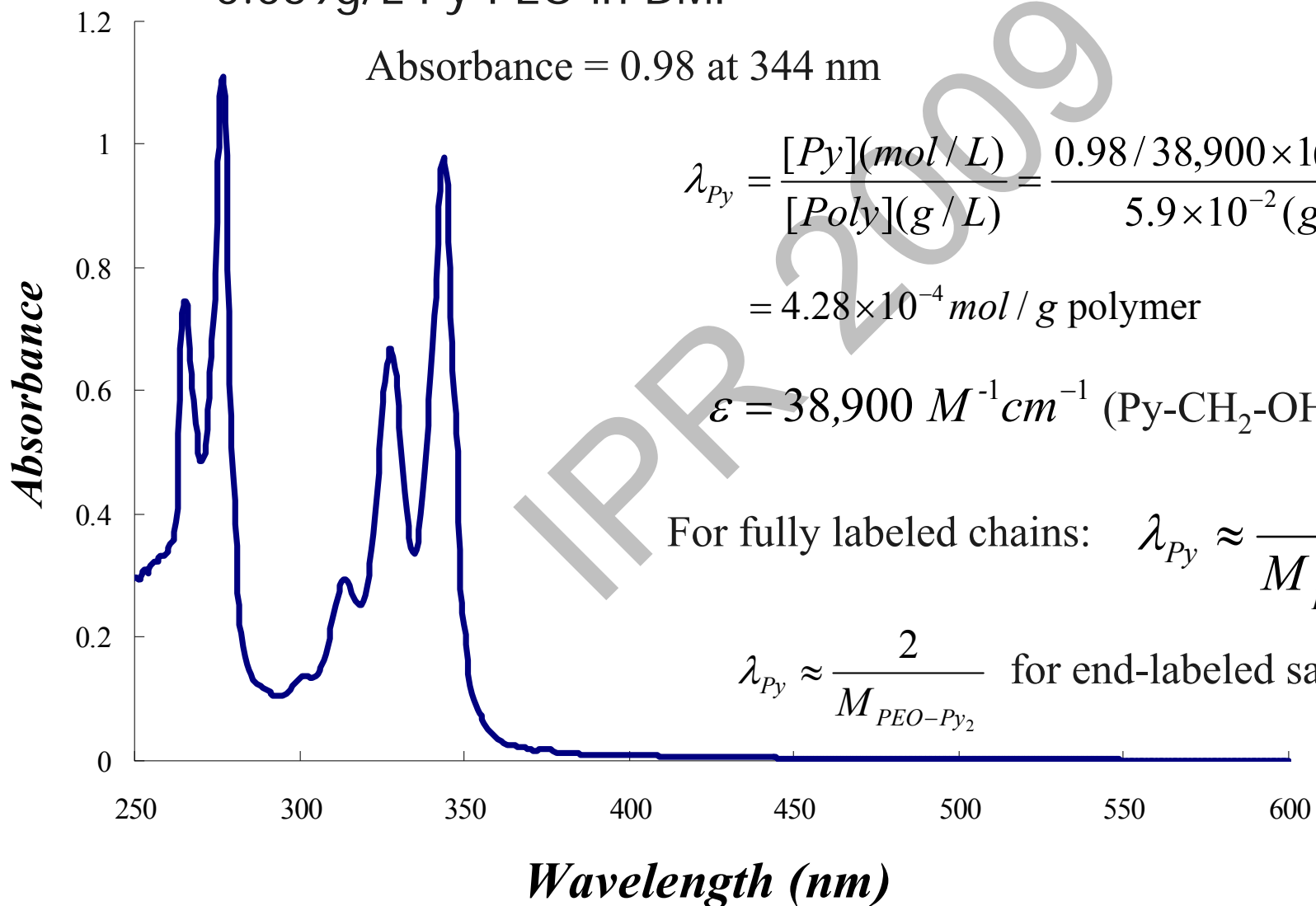
GPC Characterization



UV-Vis Characterization

0.059g/L Py-PEO in DMF

Absorbance = 0.98 at 344 nm



$$\lambda_{Py} = \frac{[Py](mol/L)}{[Poly](g/L)} = \frac{0.98 / 38,900 \times 1(mol/L)}{5.9 \times 10^{-2}(g/L)}$$

$$= 4.28 \times 10^{-4} mol/g \text{ polymer}$$

$$\epsilon = 38,900 M^{-1}cm^{-1} \text{ (Py-CH}_2\text{-OH in DMF)}$$

For fully labeled chains: $\lambda_{Py} \approx \frac{1}{M_{py-PEO}}$

$$\lambda_{Py} \approx \frac{2}{M_{PEO-Py_2}} \text{ for end-labeled samples}$$



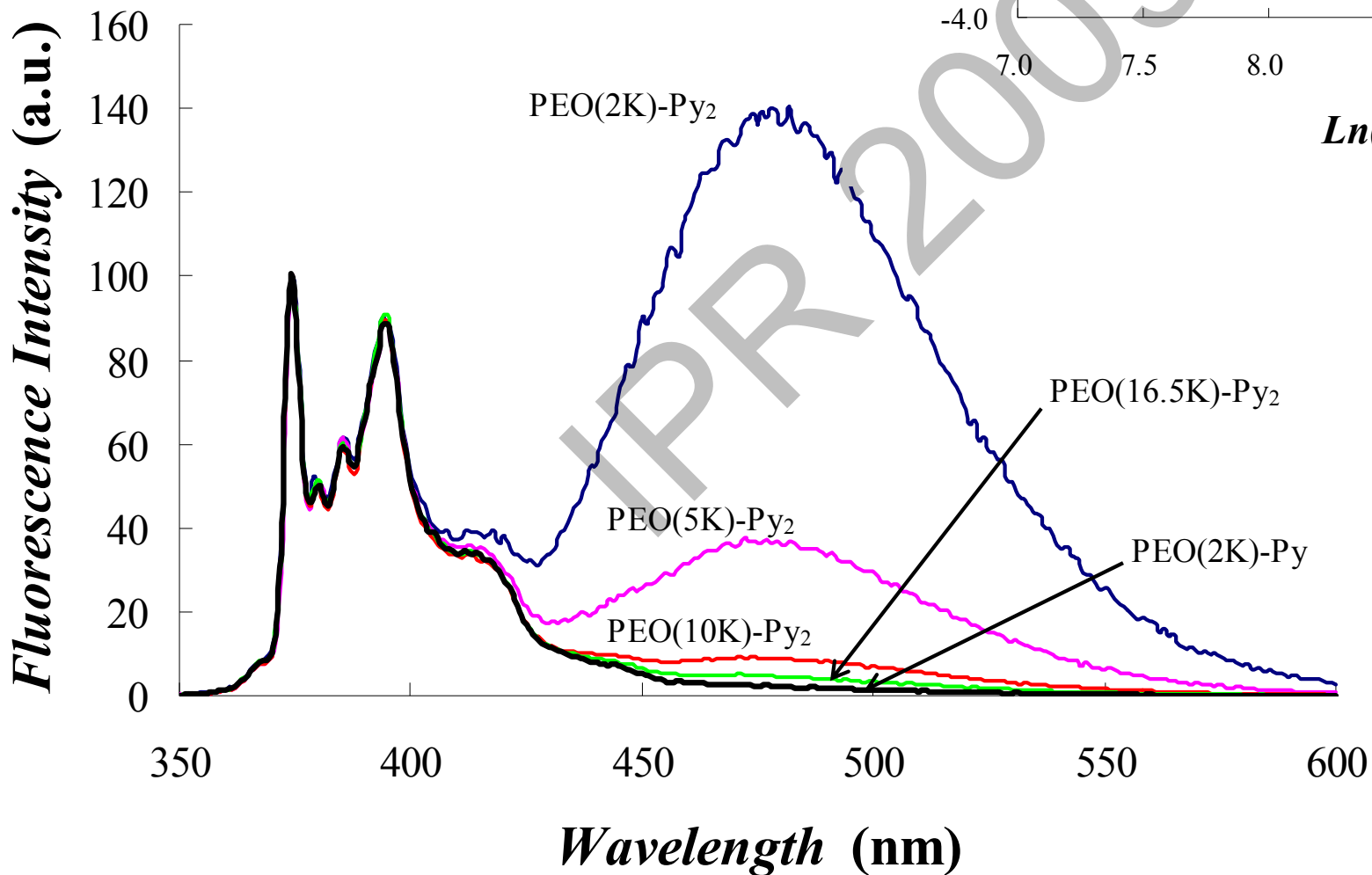
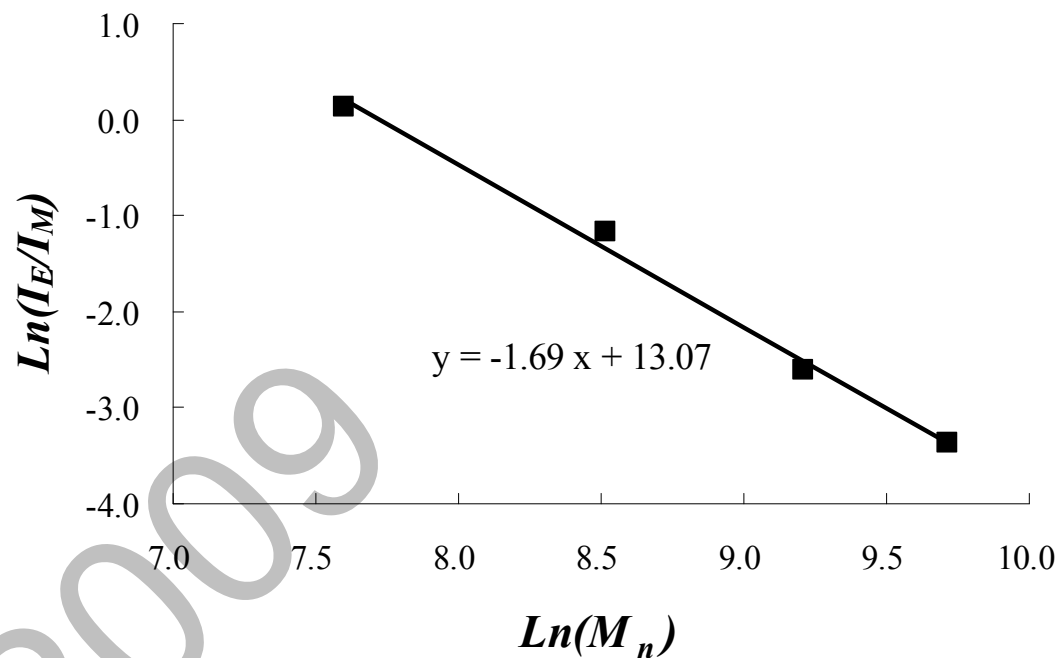
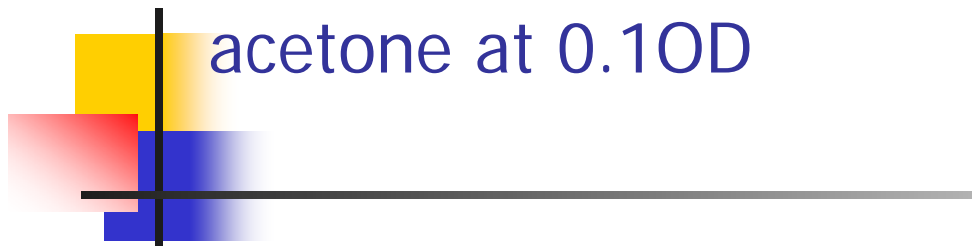
Samples

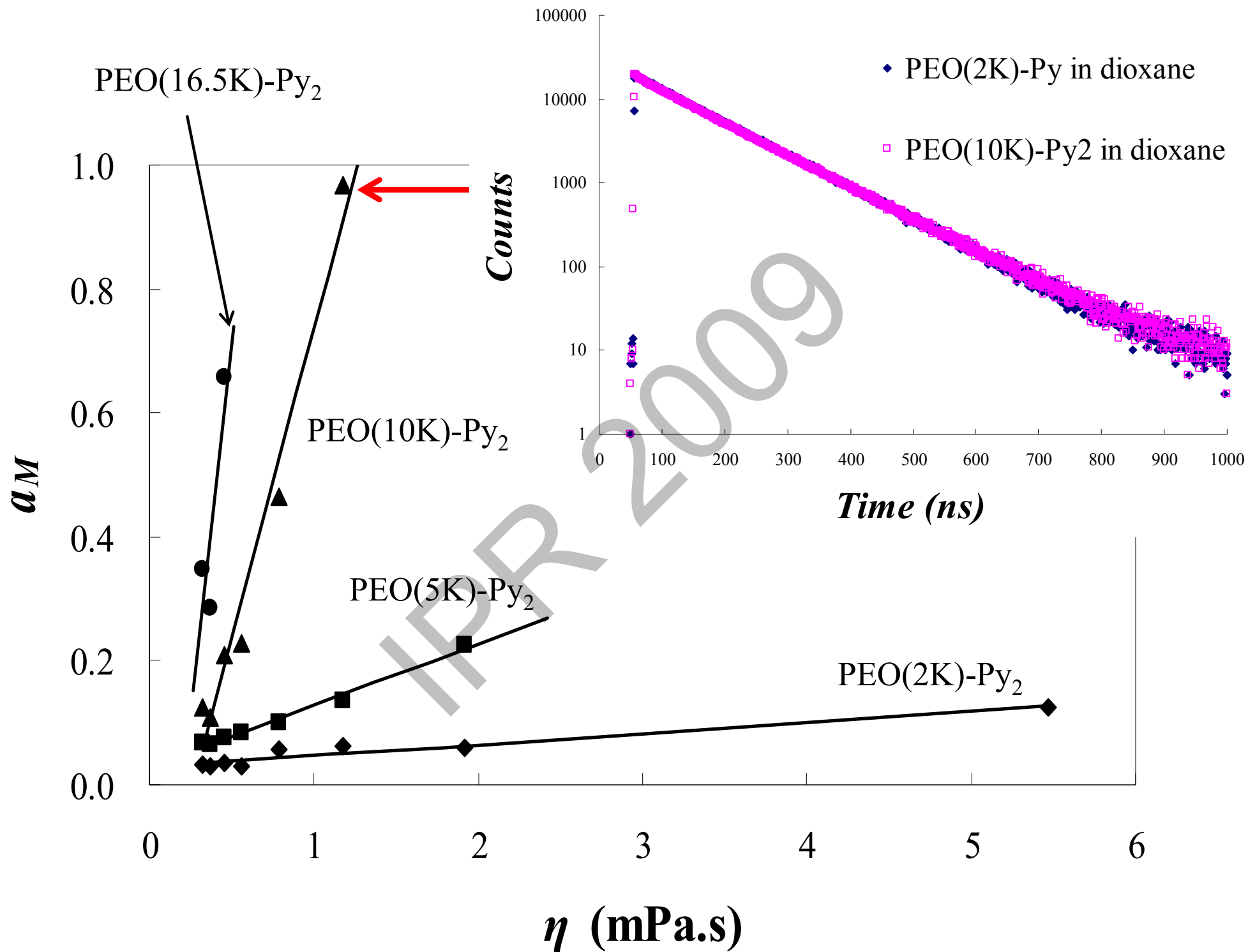
Sample	Mn (PEO) (g/mol)	PDI
PEO(2K)-Py	2,000	1.05
PEO(2K)-Py ₂	2,000	1.10
PEO(5K)-Py ₂	5,000	1.08
PEO(10k)-Py ₂	10,000	1.05
PEO(16.5k)-Py ₂	16,500	1.05

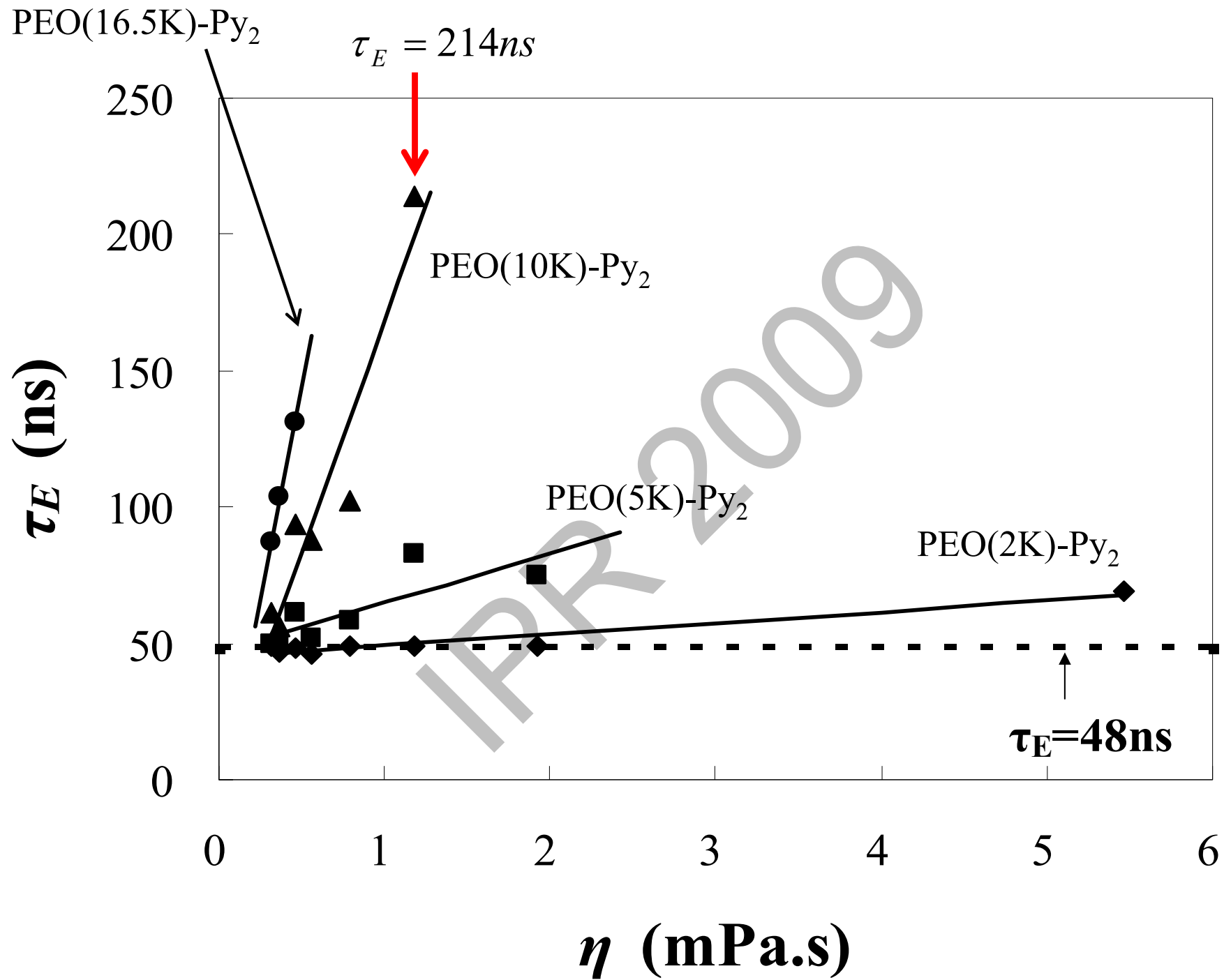
RESULTS

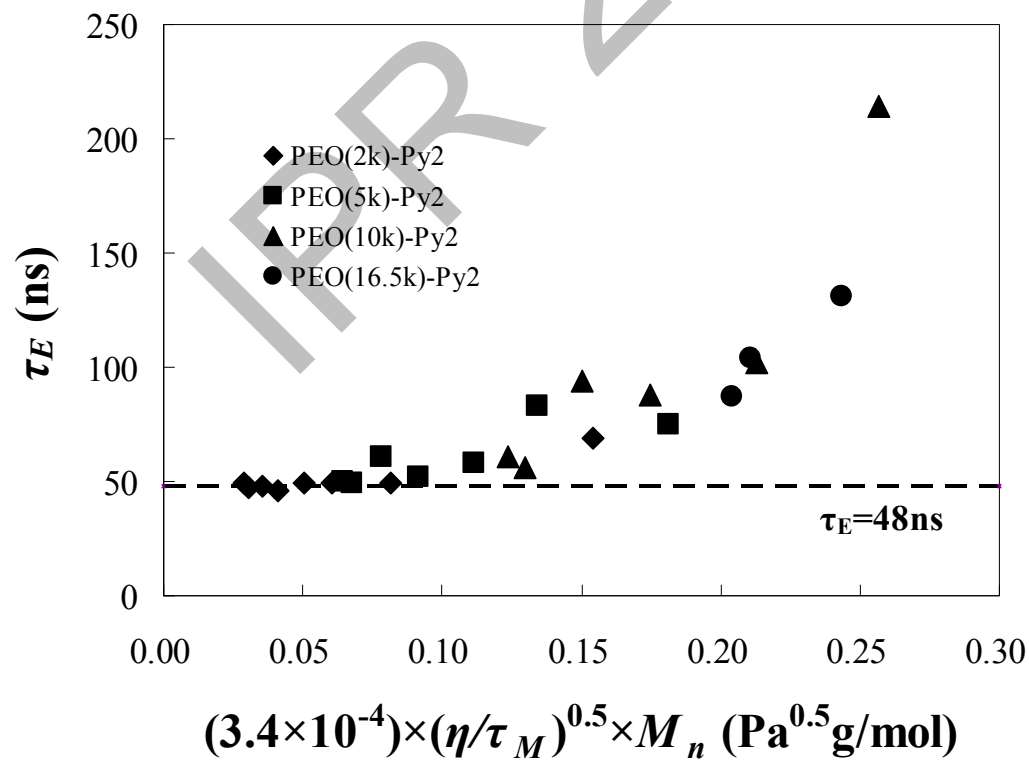
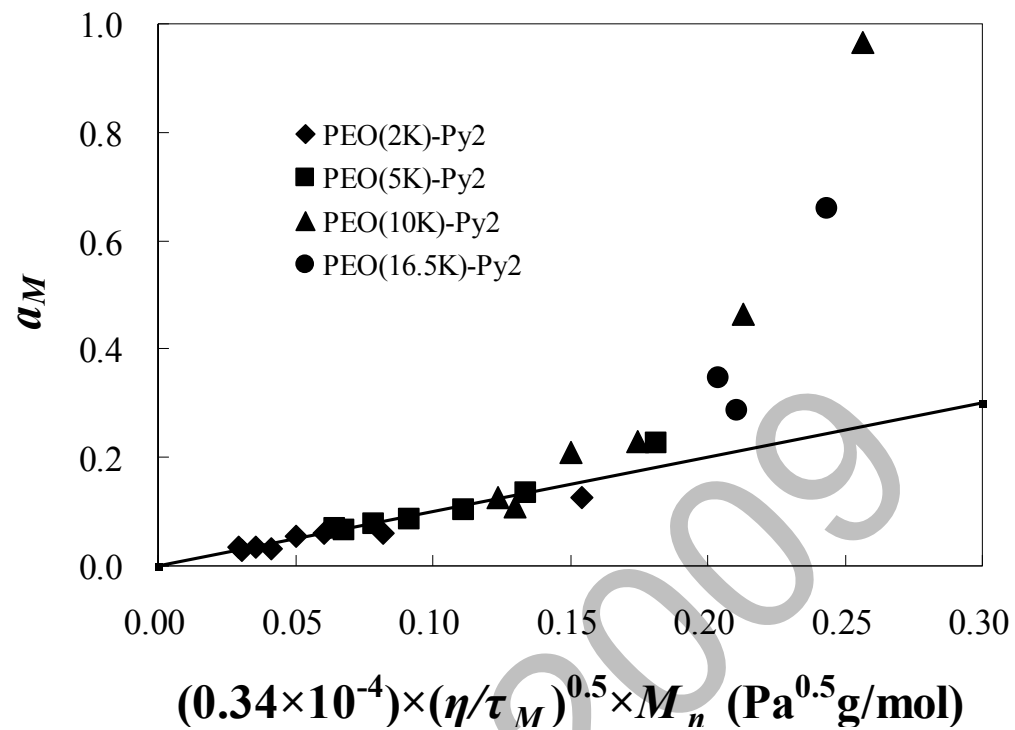
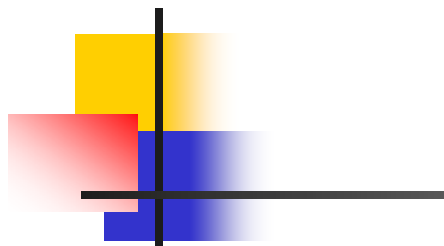
PART 1 – Birks' Scheme

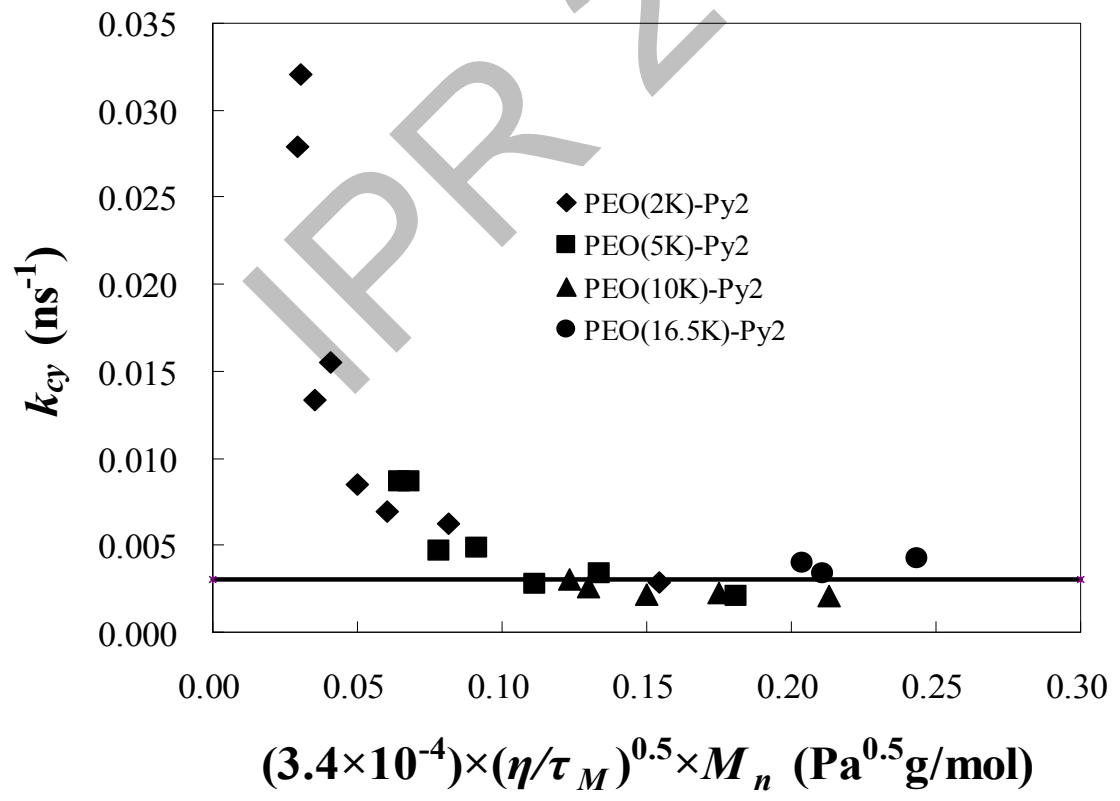
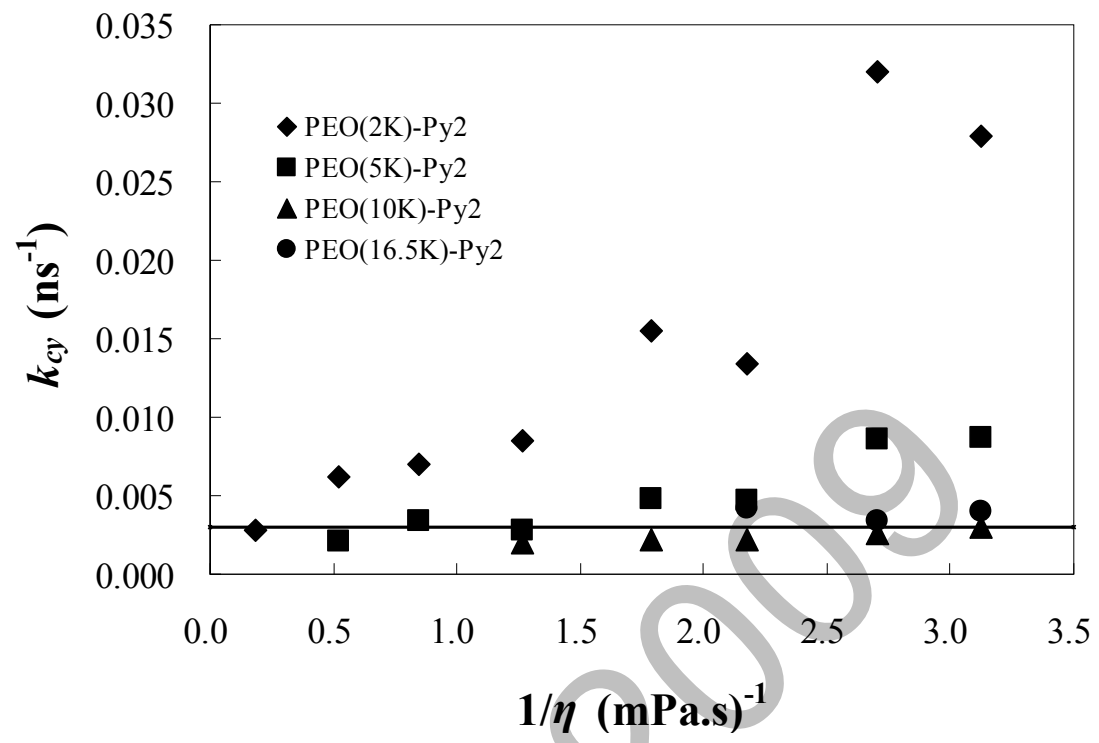
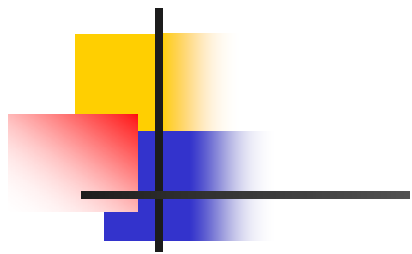
Pyrene end-labeled and mono-labeled PEOs in acetone at 0.10D





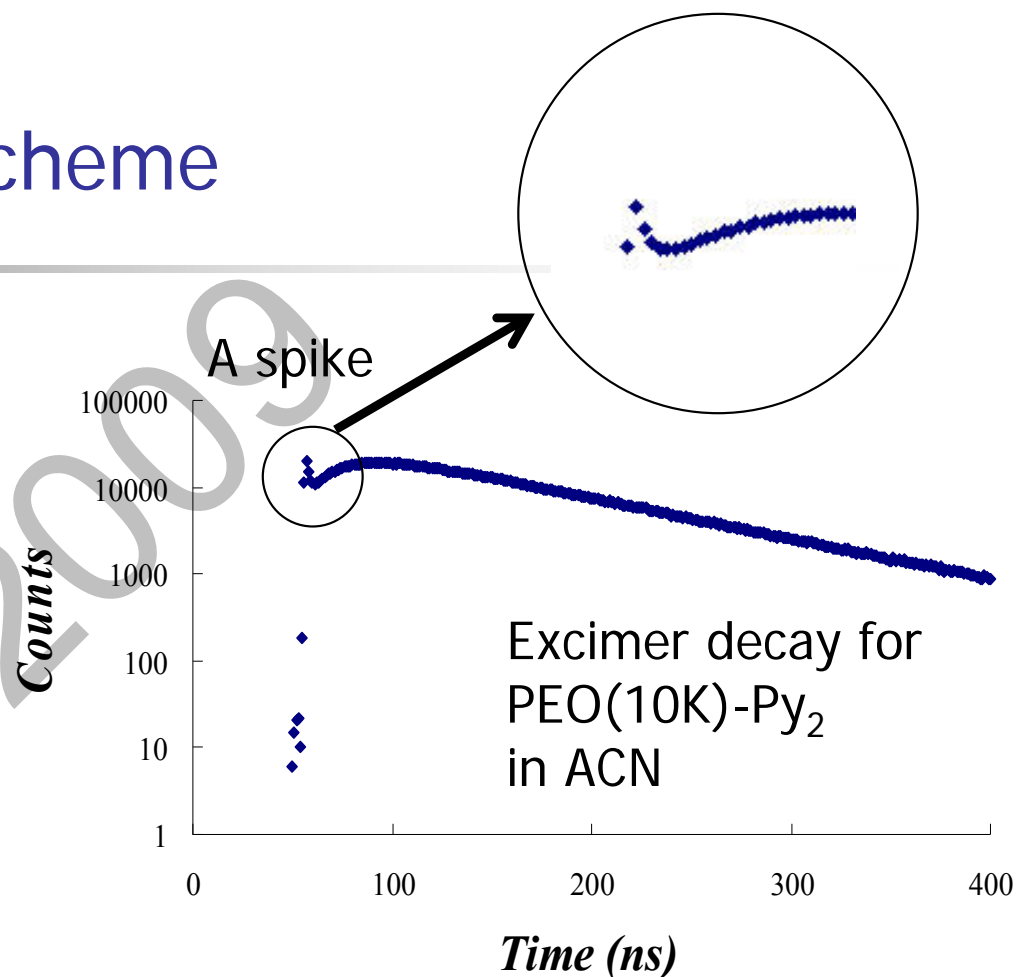






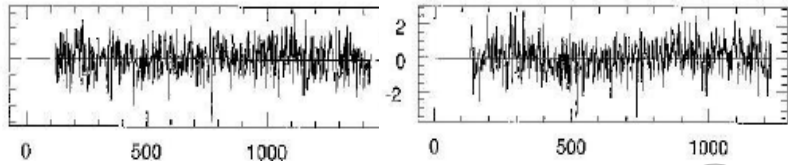
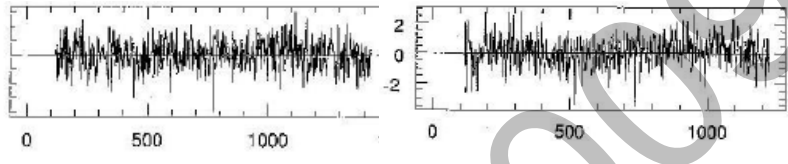
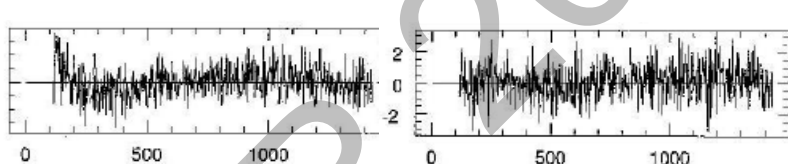
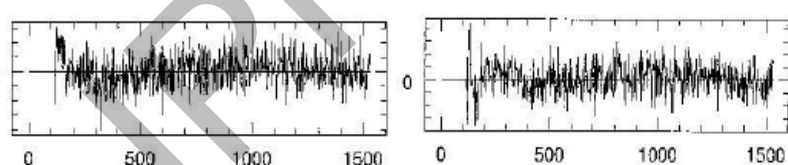
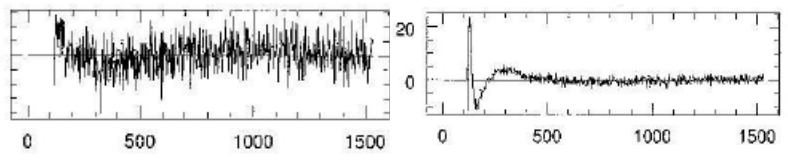
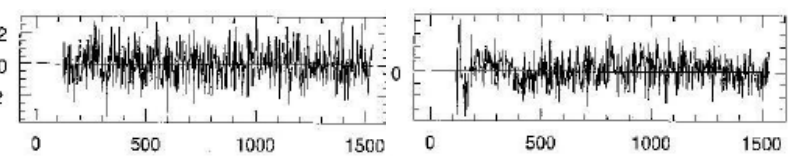
Revisions of Birks' Scheme

- ◆ Ground-state dimer (GSD)¹
- ◆ A short lifetime,¹ $\tau_S = 3.5ns$
- ◆ $a_{E-} = a_{E+}$
- ◆ $\tau_E = 48ns$
- ◆ Biexponential decay for mono-labeled PEO



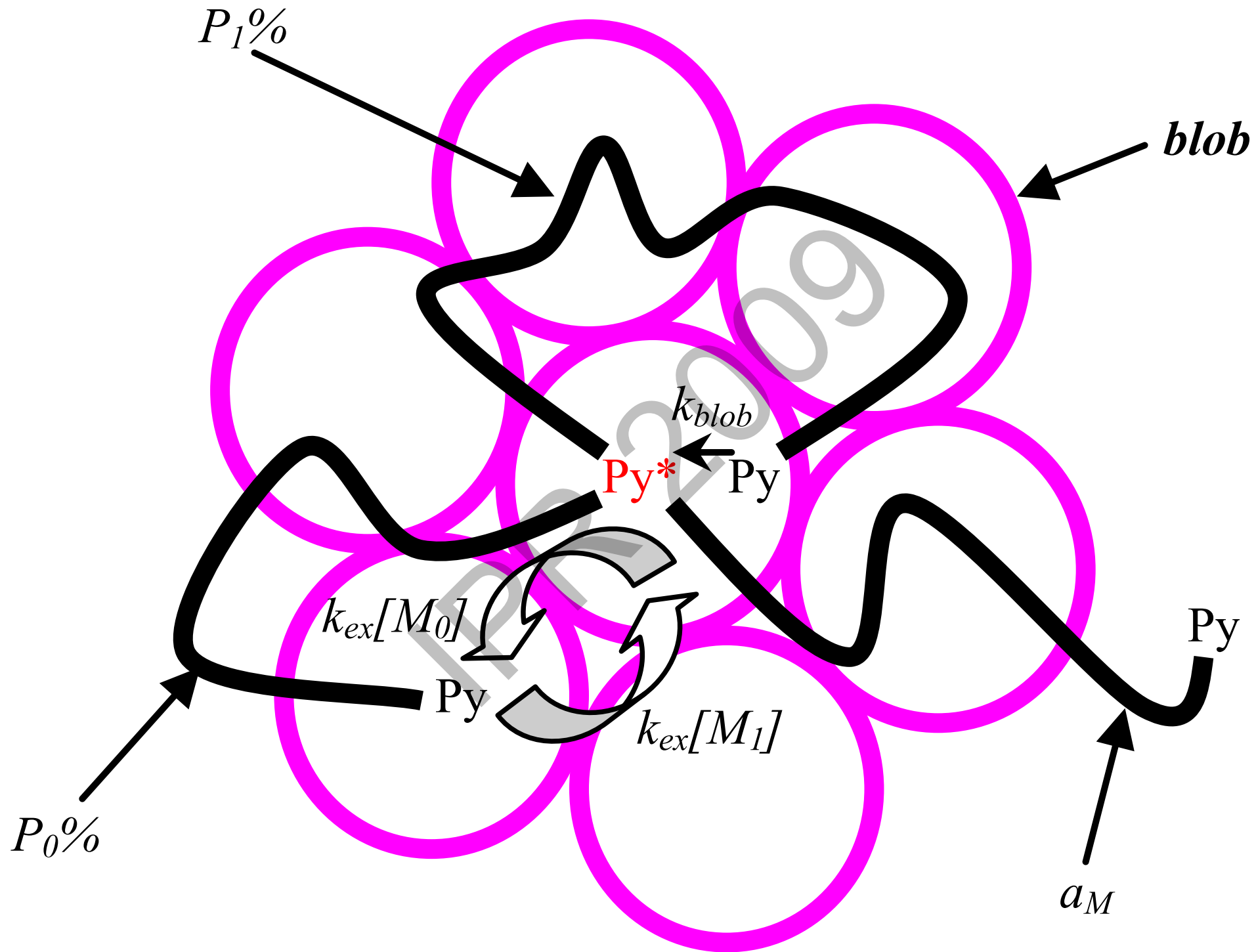
¹ Costa, T.; Seixas de Melo, J.; Burrows H. D. *J. Phys. Chem. B* **2009**, 113, 618-626.

PEO(10K)-Py₂ in DMF, the decays were fitted by various revisions of Birks' Scheme

Program	Fits (Res. vs t, ns; chisq)	Results
no GSD; $a_{E-} \neq a_{E+}$ mexp. m-labeled decay; τ_E is not fixed; no τ_S	 $\chi^2 = 1.03$	Good fits but can not start analysis from max. lamp and τ_E , a_M increase with η
no GSD; $a_{E-} \neq a_{E+}$ mexp. m-labeled decay; τ_E is not fixed; $\tau_S = 3.5ns$	 $\chi^2 = 1.04$	Good fits but τ_E and a_M increase with η
no GSD; $a_{E-} \neq a_{E+}$ mexp. m-labeled decay; $\tau_E = 48ns$; $\tau_S = 3.5ns$	 $\chi^2 = 1.13$	Monomer residuals are not randomly distributed.
GSD; $a_{E-} = a_{E+}$ mexp. m-labeled decay; $\tau_E = 48ns$; $\tau_S = 3.5ns$	 $\chi^2 = 1.21$	Monomer residuals are not randomly distributed.
no GSD; $a_{E-} = a_{E+}$ mexp. m-labeled decay; $\tau_E = 48ns$; $\tau_S = 3.5ns$	 $\chi^2 = 4.37$	Bad fits!
GSD; $a_{E-} = a_{E+}$ bexp. m-labeled decay; $\tau_E = 48ns$; $\tau_S = 3.5ns$	 $\chi^2 = 1.14$	Good fits but a_M increases with η and the excimer residuals are not perfect.

RESULTS

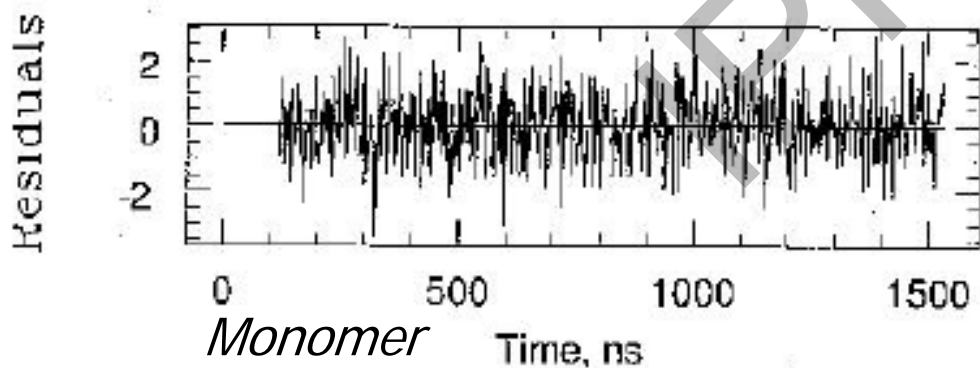
PART 2 – A Blob Model



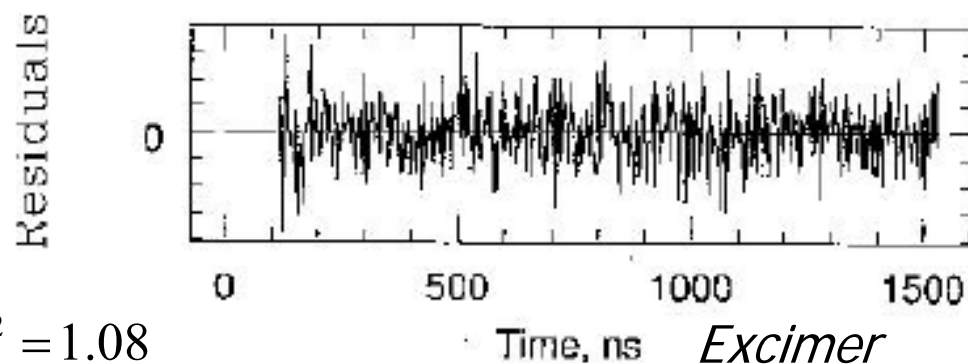
Assumptions and fits of *Blob* Model

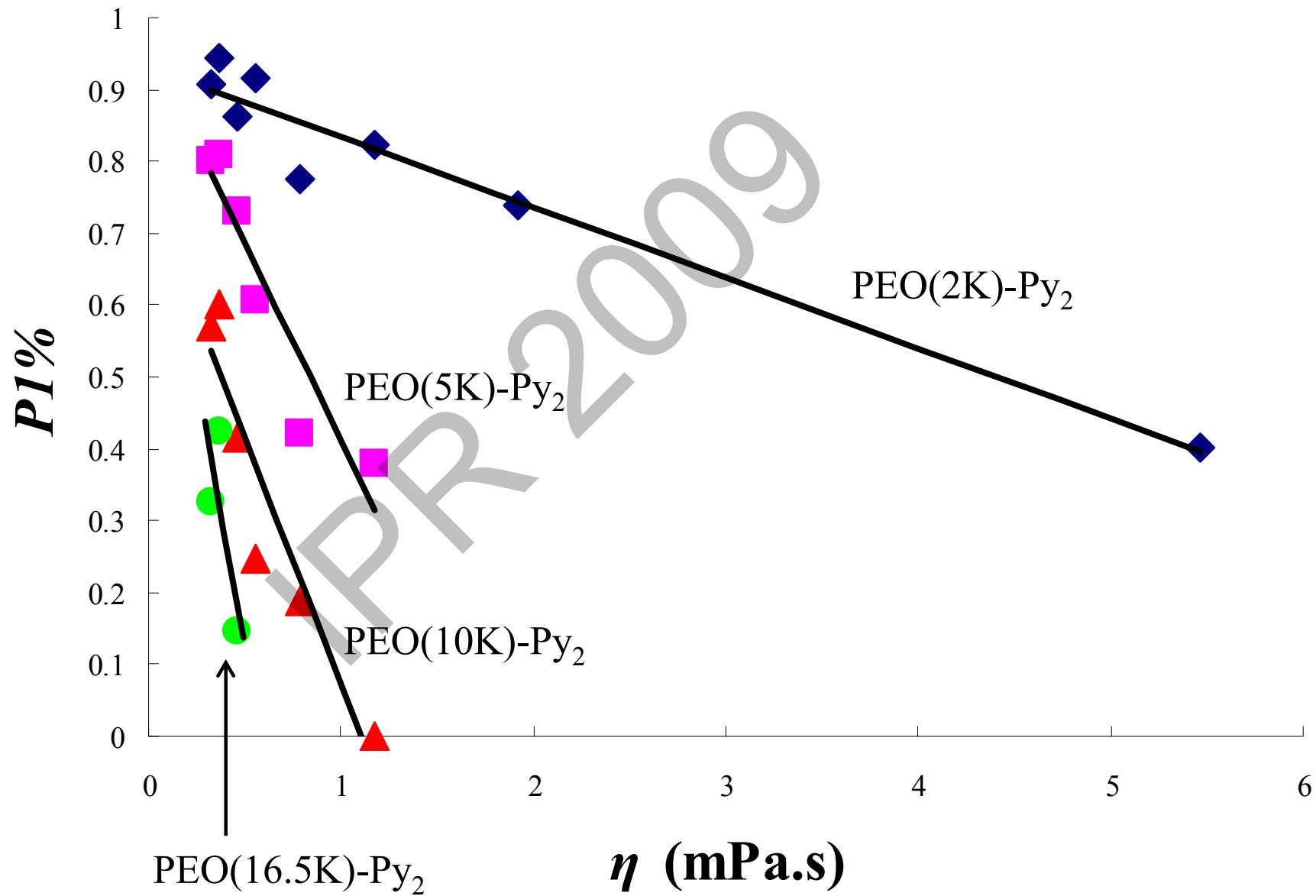
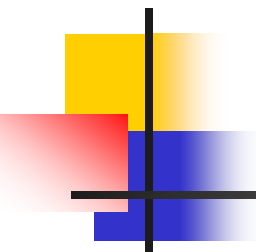
Assumptions: $\tau_S = 3.5ns$; $\tau_E = 48ns$; GSD presents; bexp. decay for mono-labeled PEO; the fraction of τ_{M1} is not fixed but no more than 5% for all samples; all PEO chains end-labeled.

PEO(10K)-Py2 in DMF:

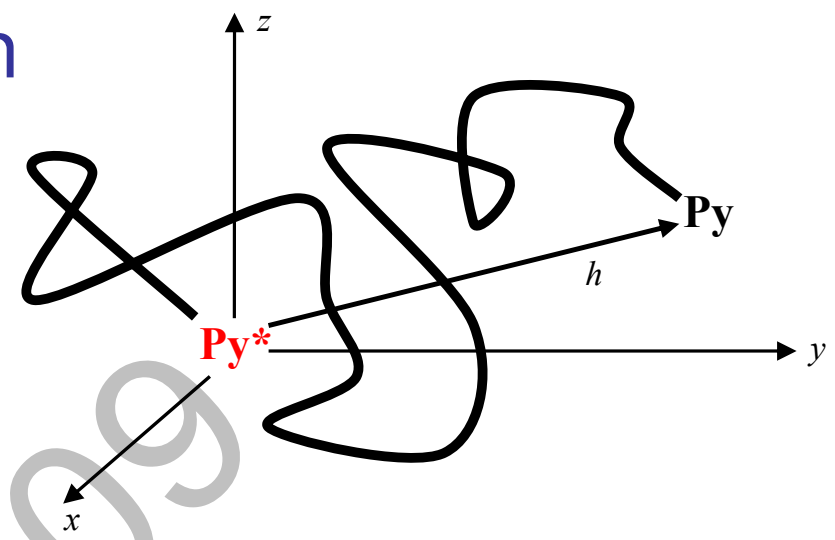
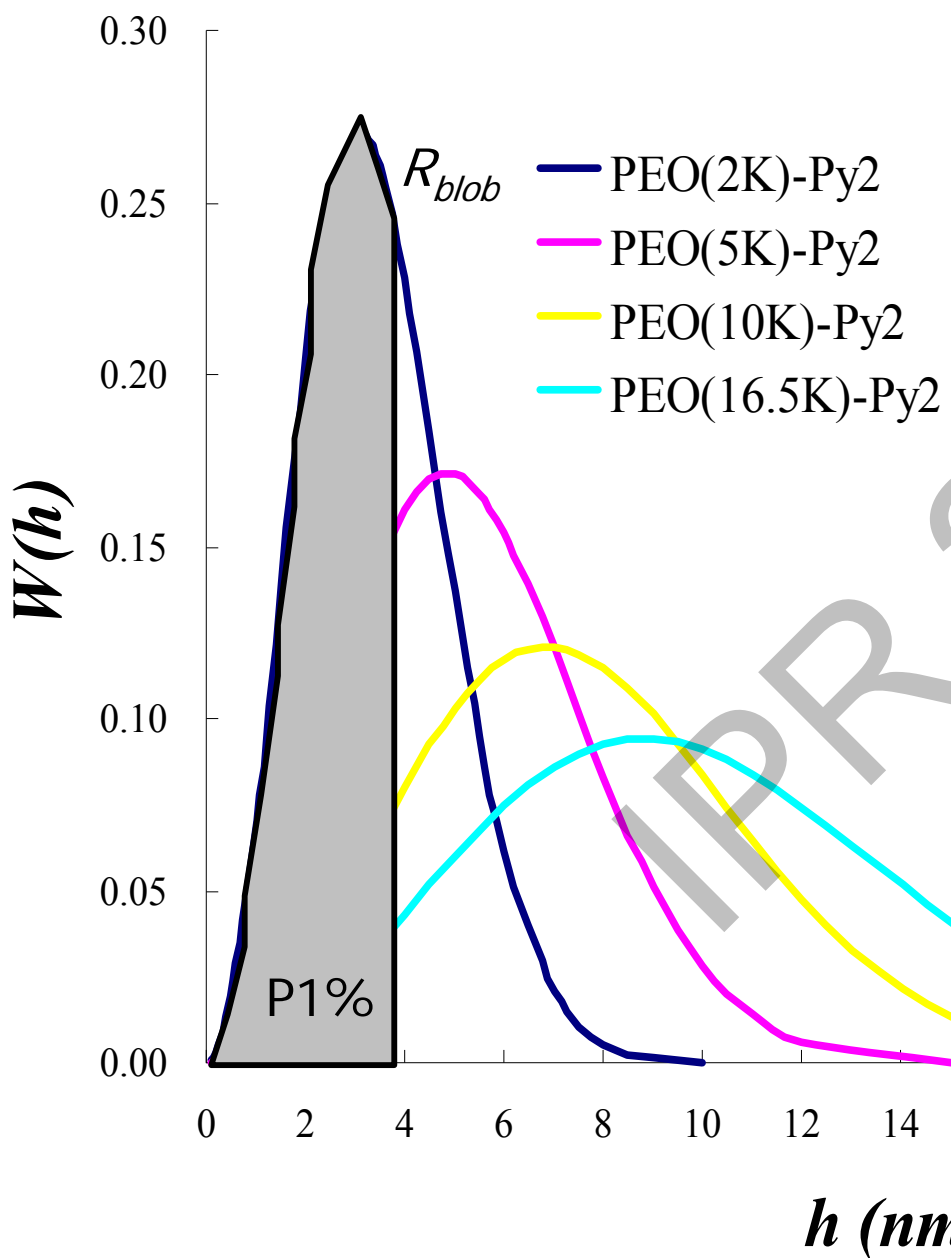


$$\chi^2 = 1.08$$





End-to-end distance distribution



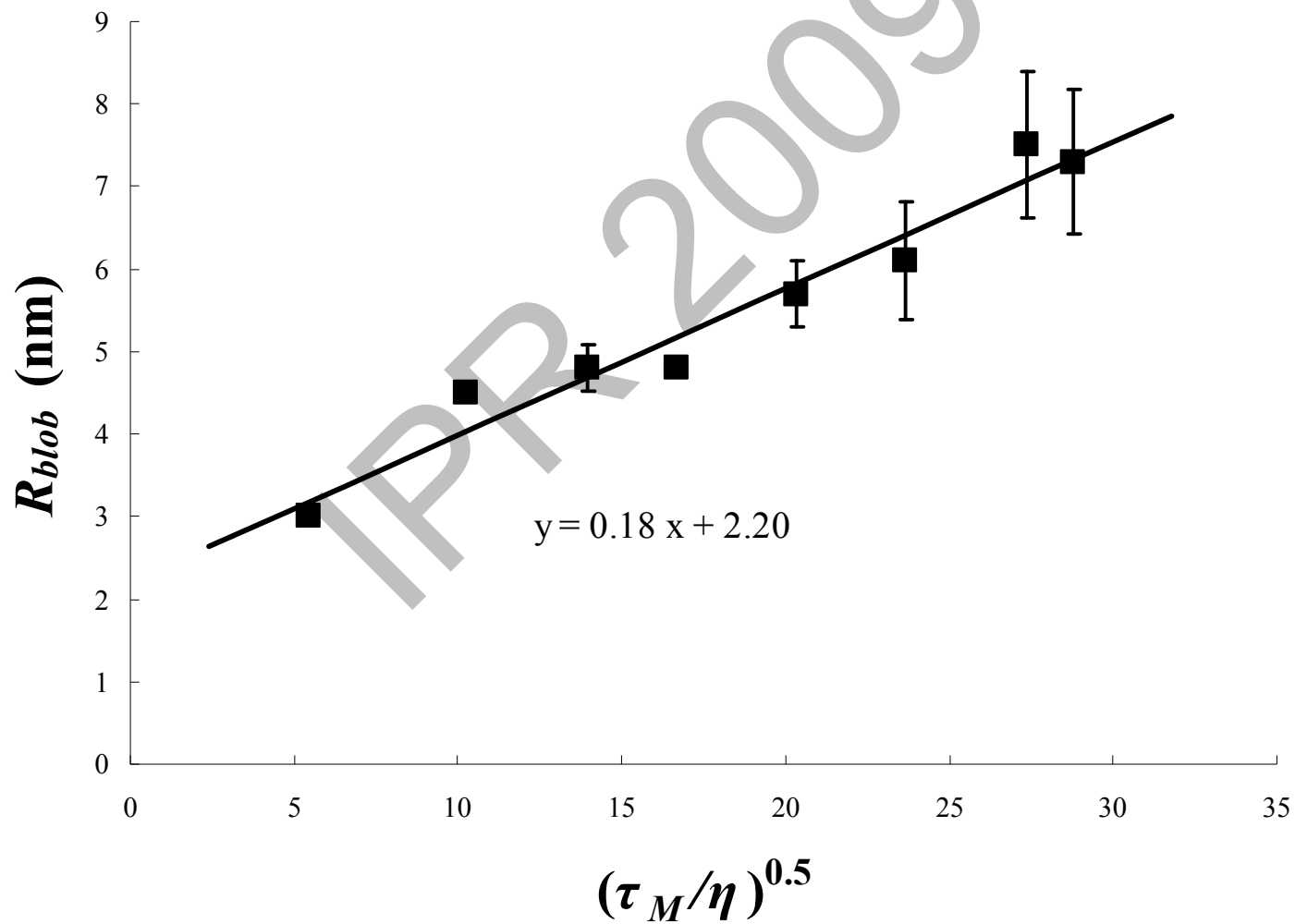
Kuhn length of PEO $l_K = 0.707\text{nm}$,
 the number of segments $N_K = 0.0141M_P^1$

$$W(h) = \left(\frac{\beta}{\sqrt{\pi}} \right)^3 e^{-\beta^2 h^2} 4\pi h^2$$

where $\beta^2 = \frac{3}{2N_K l_K^2}$

¹ Pattanayek, S. K.; Juvekar, V. A. *Macromolecules* **2002**, 35, 9574-9585.

Blob radii (R_{blob}) in organic solvents





Conclusions

- The *blob* model is more comprehensive than Birks' scheme to study this pyrene end-labeled PEO system in organic solvents; Birks' scheme is limited to the excimer formation within one *blob*
- The radii of *blob* in various organic solvents were determined and are proportional to $\sqrt{\tau_M/\eta}$



Future Work

- Study the chain kinetics by *blob* model
- Quantitatively investigate how a quencher reduce the size of *blob*
- Study the effect of backbone stiffness on the size of *blob*
- Characterize the micelle formation of this system in water



Acknowledgements

- Dr. Jean Duhamel
- Dr. Mario Gauthier
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IIPR

Institute for Polymer Research

Questions / Comments?