Fluorescence Resonance Energy Transfer (FRET) in Polymer Films and Polymer Blends

Neda Felorzabihi, Jeffrey C. Haley,
Pablo Froimowicz, Ghasem R.
Bardajee and Mitchell A. Winnik

Department of Chemical Engineering and Chemistry
University of Toronto

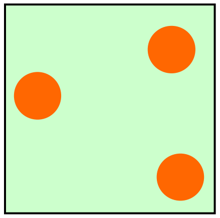
IPR Symposium, Waterloo
May 15, 2007

Introduction

- Polymer blends → a route to obtain new high performance materials

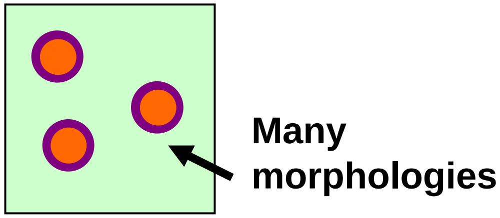
- Blend systems:
  - Two immiscible polymers →

    matrix/dispersed



  - Three immiscible polymers →

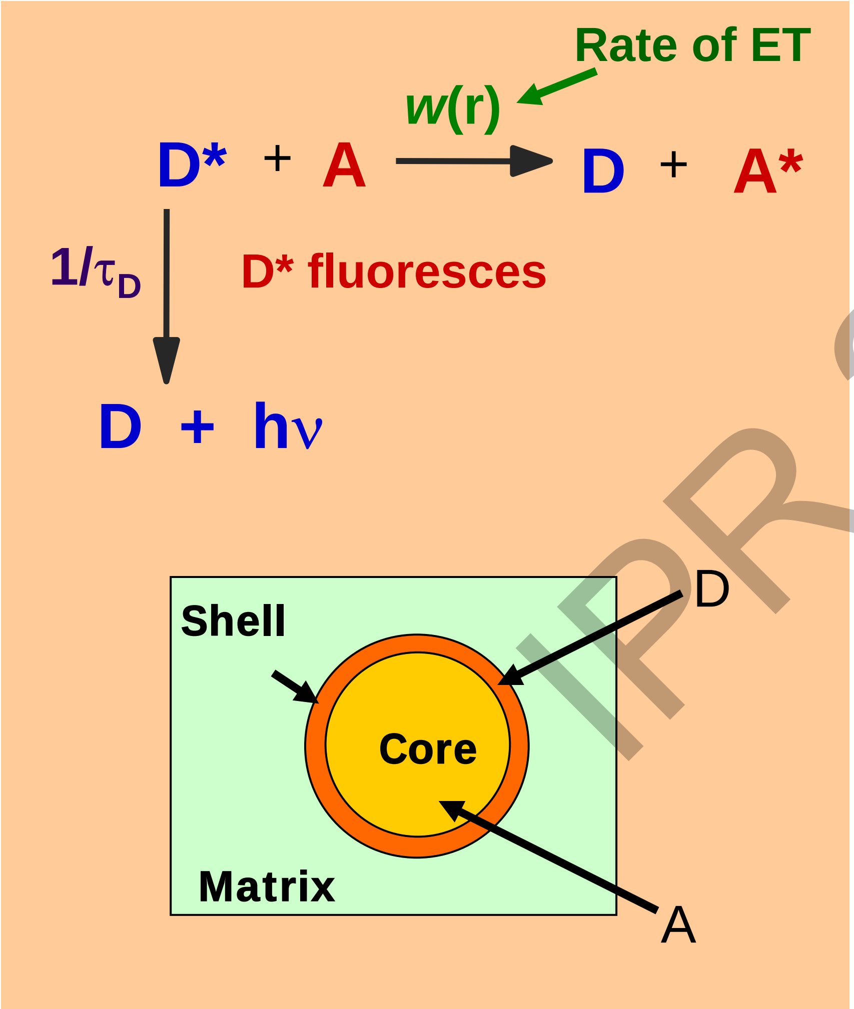
    core/shell (composite/droplet)

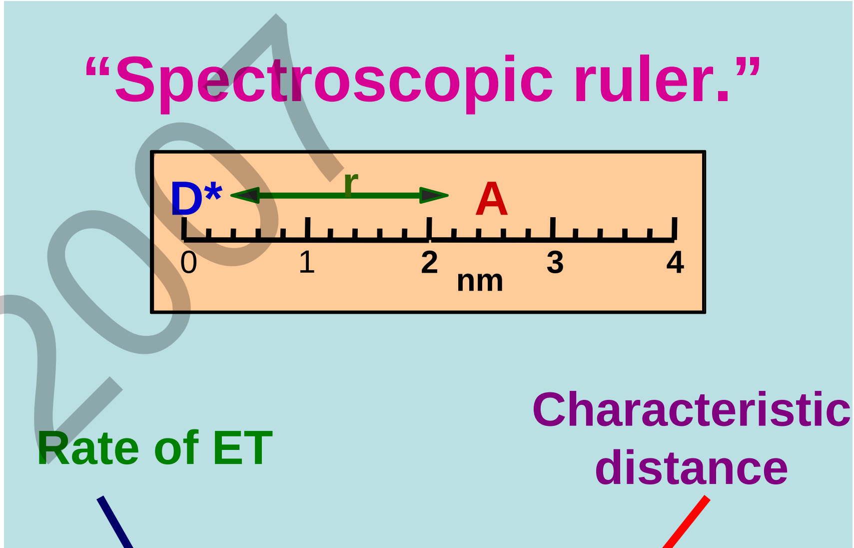


I am interested in core/shell structures

- I want to use core/shell 3-component blends as a means of studying partial miscibility and interfaces between the components.

Fluorescence Resonance Energy Transfer (FRET)



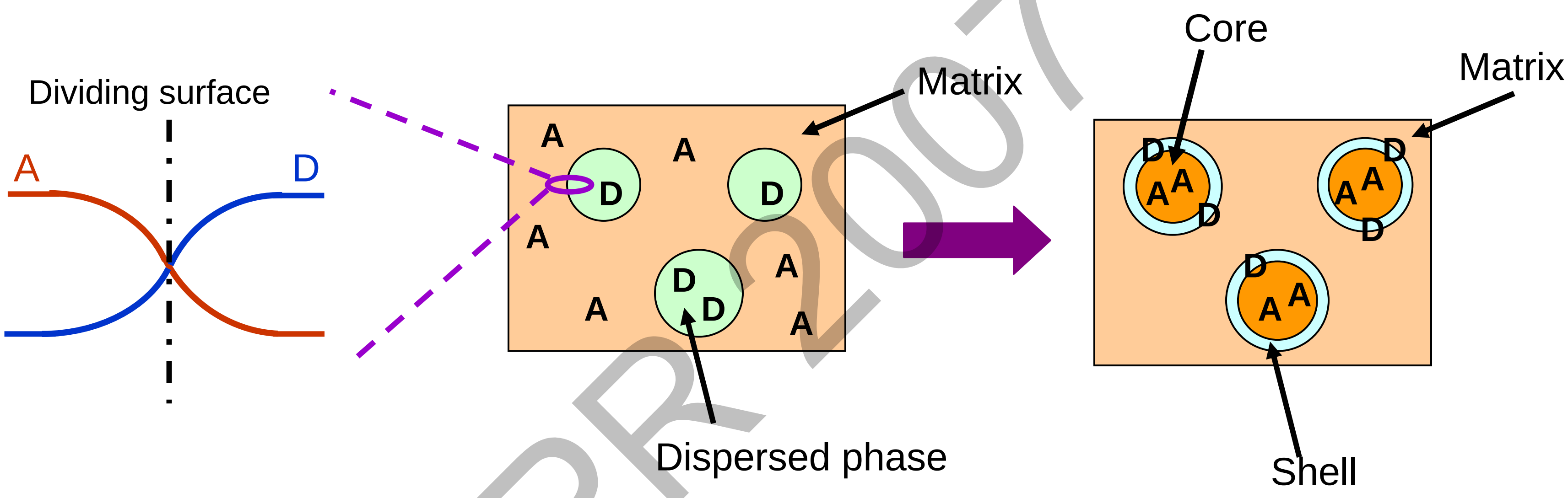


$$w(r) = \frac{3}{2}\kappa^2 \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

$$w(r) \sim r^{-6}$$

Long Term Goal

- To obtain information about the interface between the components of a polymer blend.



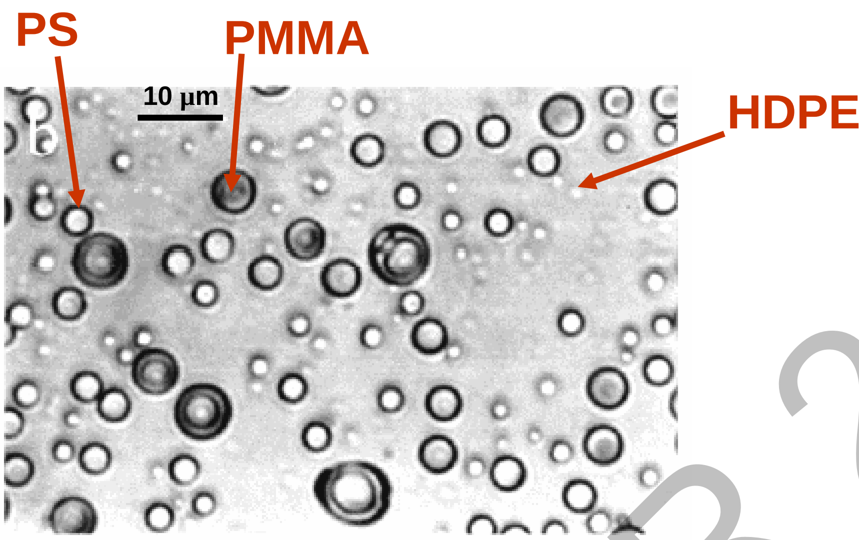
- Our group uses FRET to study polymer-polymer interfaces.
- This technique works well for block copolymers.
- It has not yet been used for the quantitative study of polymer blends.

Steps to Meet Our Goals

1. Study core/shell morphology development in a ternary blend.
2. Select the chromophores (D and A) based on spectroscopic properties.
3. Synthesize dye-labeled polymers.
4. Test our models for fitting the experimental data.
5. Determine key parameters.
6. Carry out FRET experiments on polymer blends.

1. Study core/shell morphology development in a ternary blend

Study of Core/Shell Morphology Development in PS/PMMA/HDPE Blend



Ternary blend of PS/PMMA/HDPE (5/5/90), after 90 min. mixing

Reigneier, J. and Favis, B. *Macromolecules* (2000), 33, 6998.

- Material

	Mw (g/mol)	Mn (g/mol)	MI (g/10 min)
HDPE	79000	24000	2.2
PS	230,000	140,000	7.5
PMMA	11,900	7,800	-

- MMA and styrene for synthesizing dye-labeled PMMA and PS

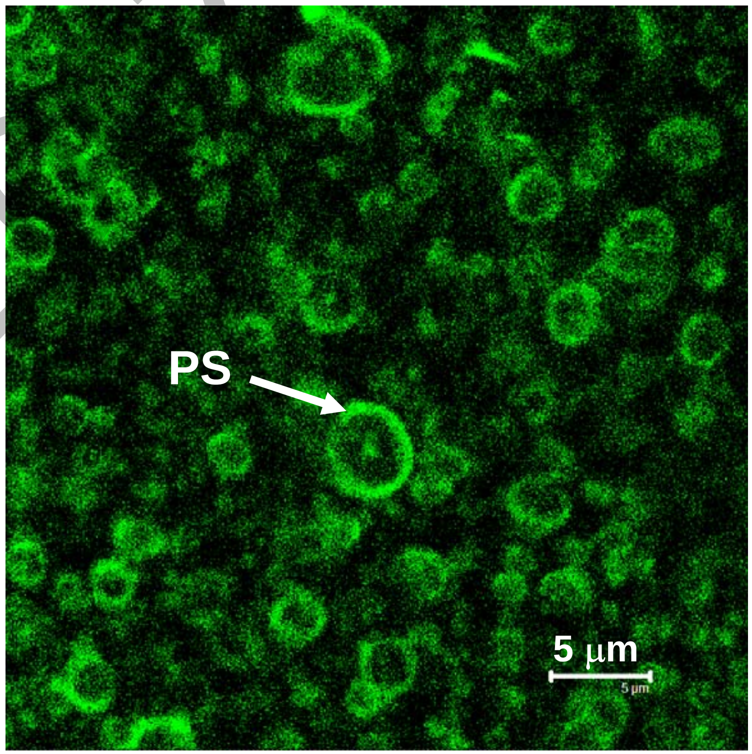
PS/PMMA/HDPE Blend Preparation

- Blend Preparation
  - Solution precipitation
  - Melt mixing in a twin screw extruder (at 200 °C and 200 rpm). Then quenching the samples in cold water

PS is labeled with an HY dye,

λ_{ex} = 488 nm

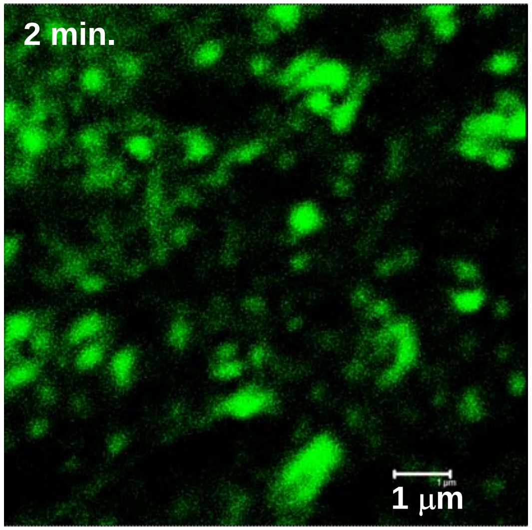
80/20 (14+86) HDPE/(PS+PMMA)

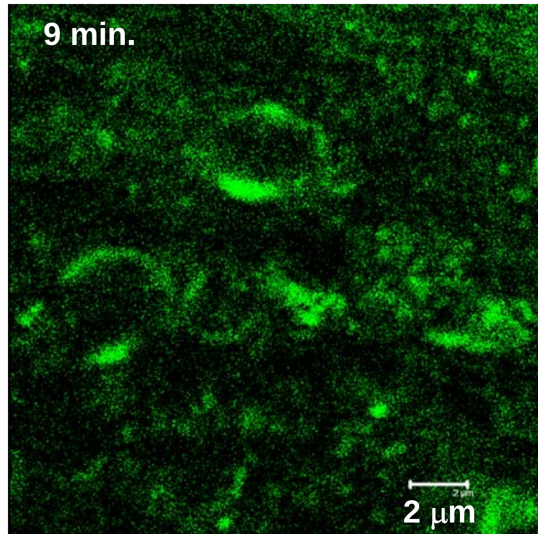


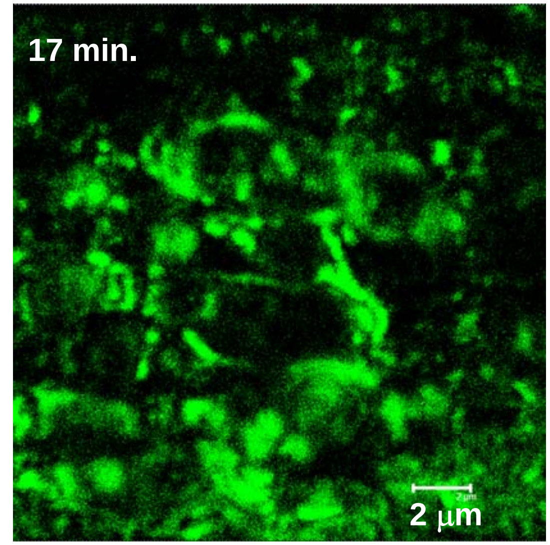
Blend at 60 min. of mixing

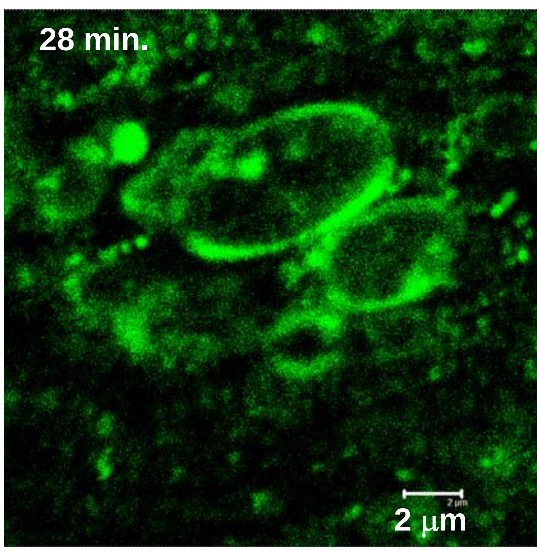
Image depth: 7-10 μm

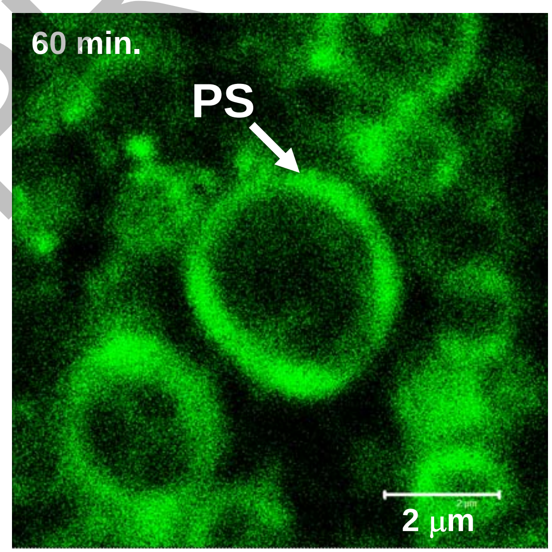
Effect of Mixing Time on Morphology Development









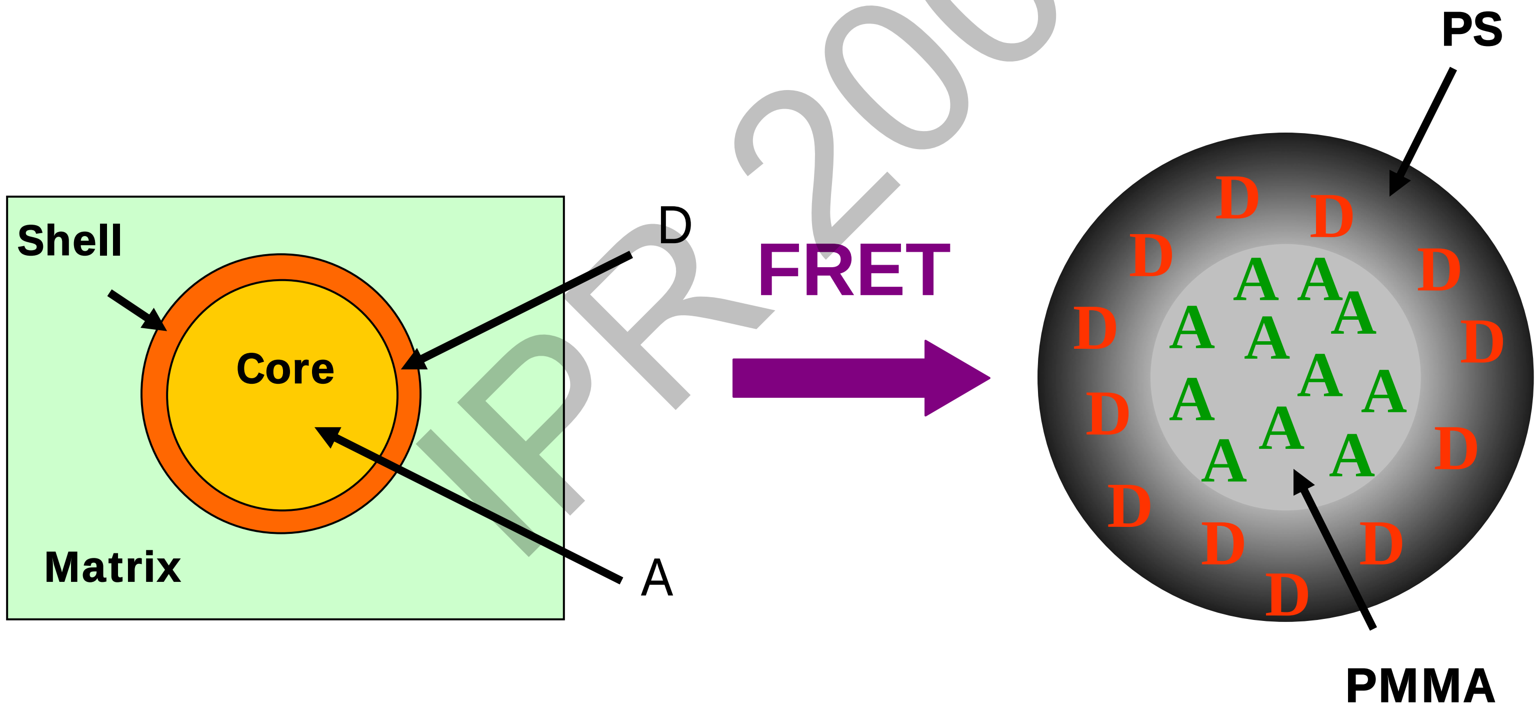


80/20 (14+86)
HDPE/(PS+PMMA)

Image depth: 7-10 μm

Blend System

- Using core/shell structures to study miscibility and interfaces in 3-component polymer blends by FRET



2. Select the chromophores (D & A) based on spectroscopic properties.

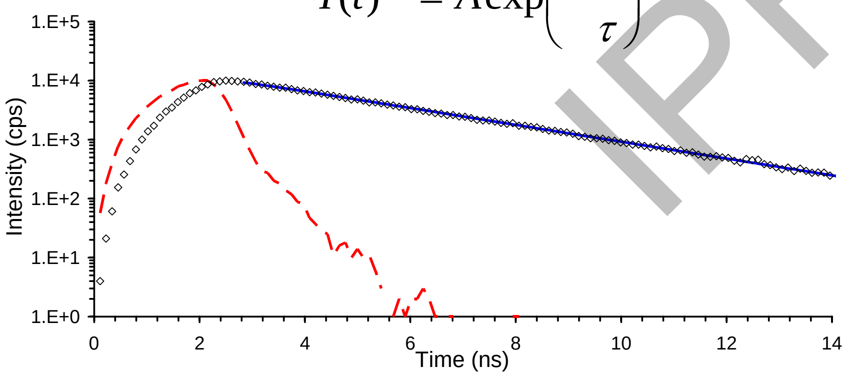
Systematic Study of Fluorescence Decay of Coumarin Dyes in Polymer Films

I need to find the proper donor dyes for my FRET experiments.

$$D^* + A \longrightarrow D + A^*$$

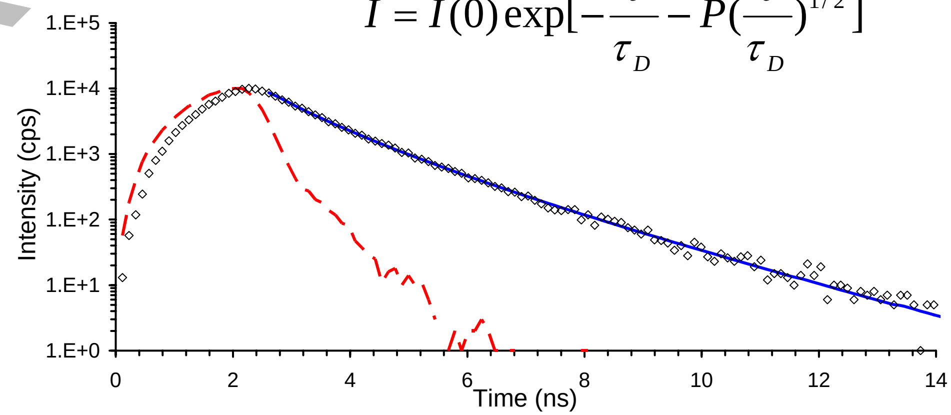
- The donor dye should have an exponential fluorescence decay profile in polymer matrices.

$$I(t) = A\exp\left(-\frac{t}{\tau}\right)$$



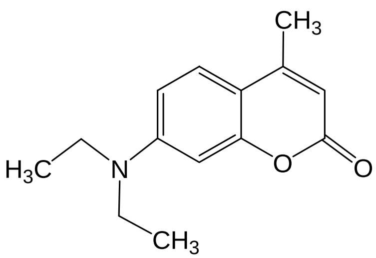
Exponential decay

$$I = I(0)\exp[-\frac{t}{\tau_D} - P(\frac{t}{\tau_D})^{1/2}]$$

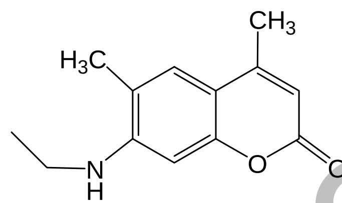


Non-Exponential decay

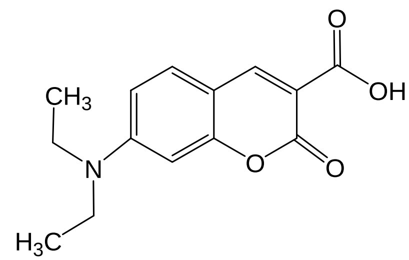
Selected Amino-Coumarin Donor Dyes



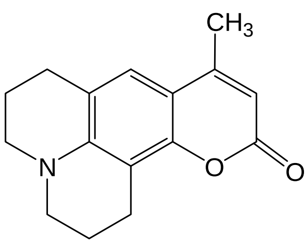
(a) Coumarin-1



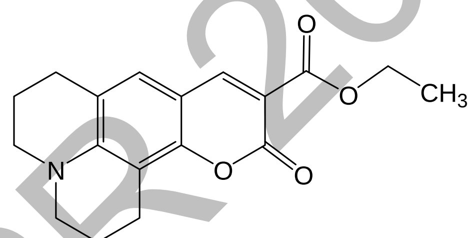
(b) Coumarin-2



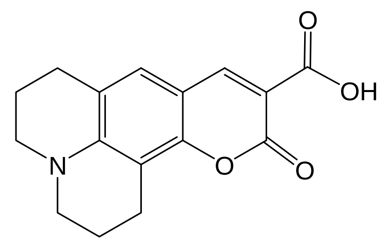
(c) Coumarin-3



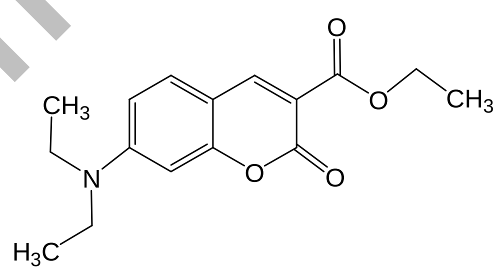
(d) Coumarin-102



(e) Coumarin-314

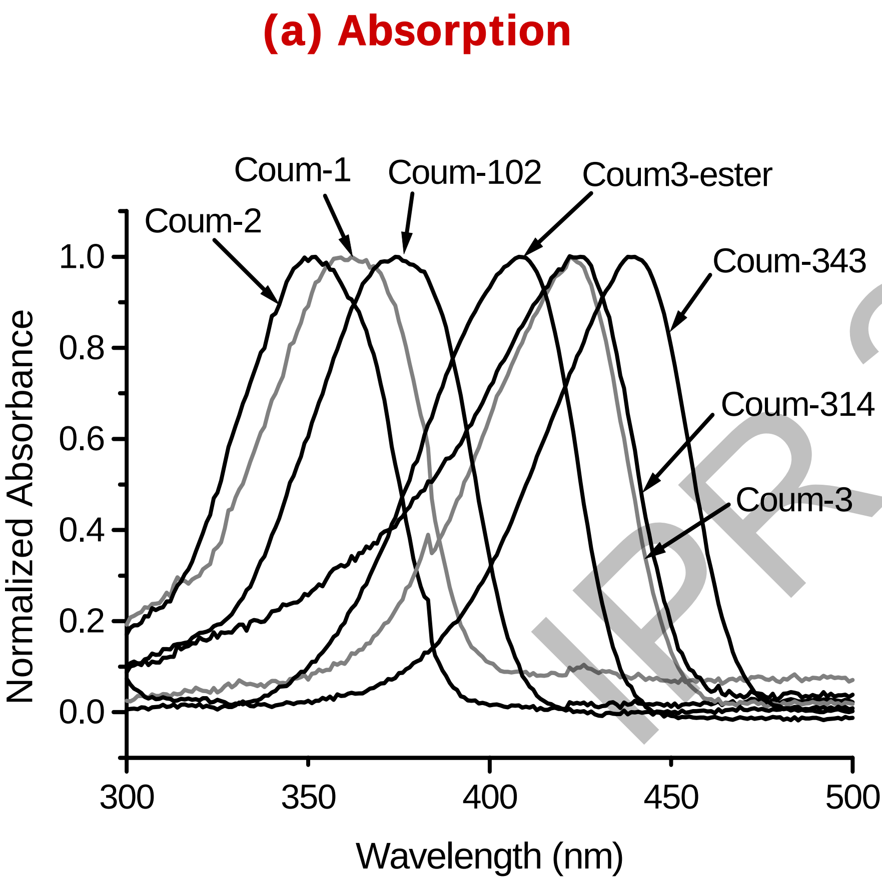


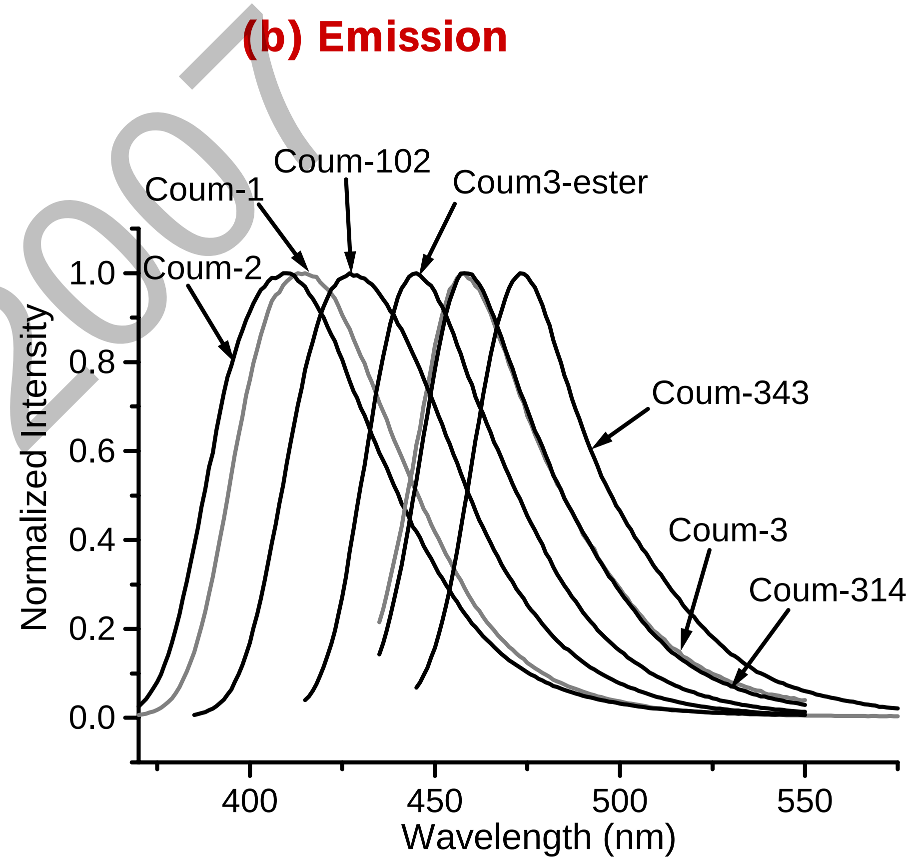
(f) Coumarin-343



(g) Coumarin-3-ester

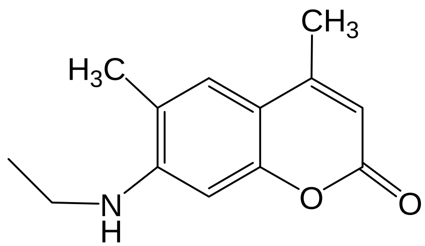
Absorption & Emission Spectra of Coumarin Dyes in Ethyl acetate

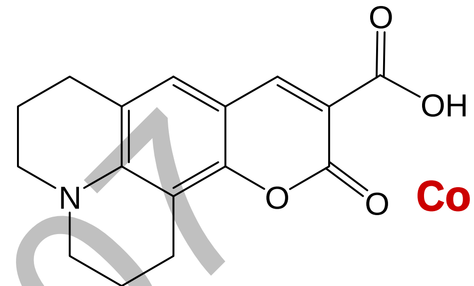




Fluorescence Decays

Coumarin-2

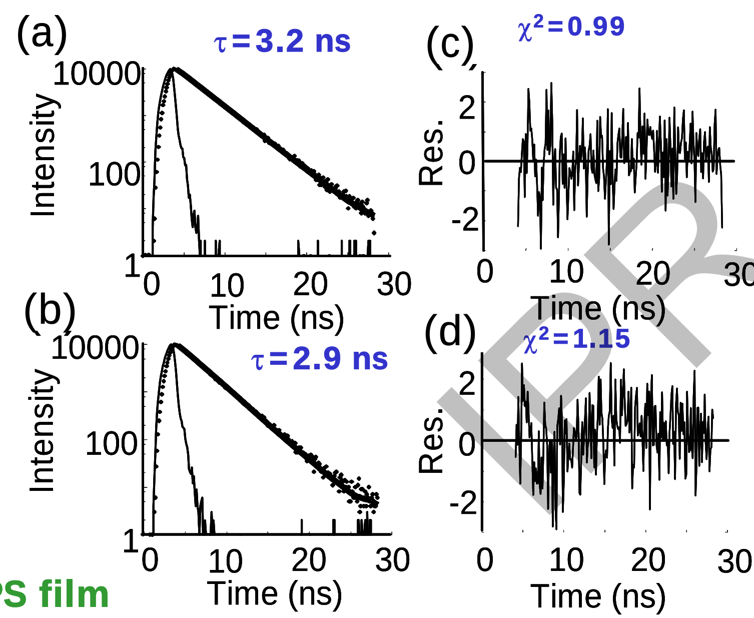




Coumarin-343

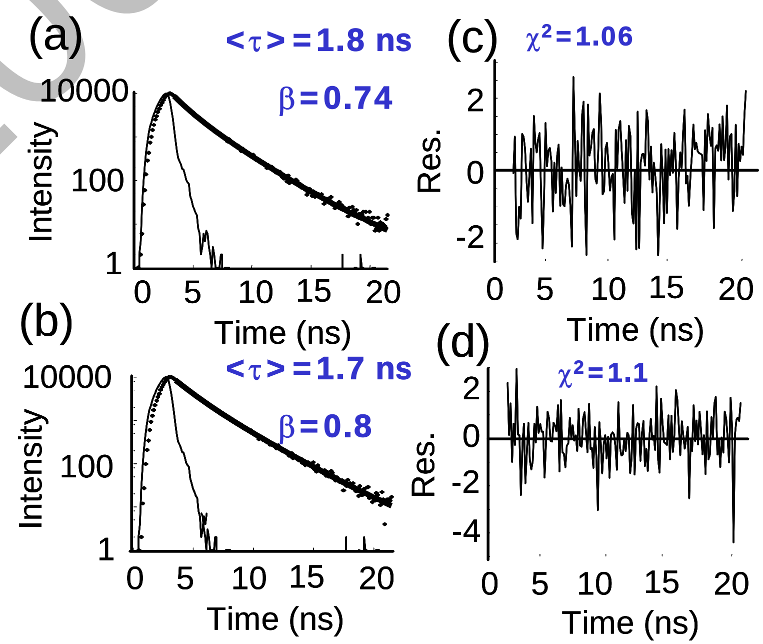
In PMMA film

In PS film



$$I(t) = A\exp\left[-\left(\frac{t}{\tau}\right)\right]$$

In PMMA film



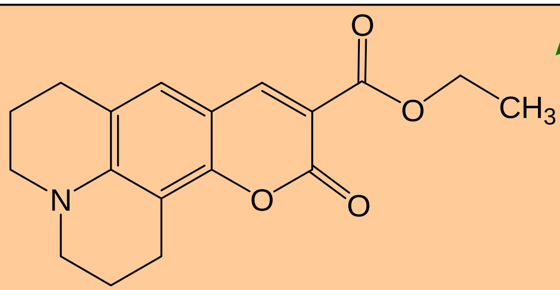
In PS film

$$I(t) = A\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$

Selected Donors and Acceptor Dyes

Donors

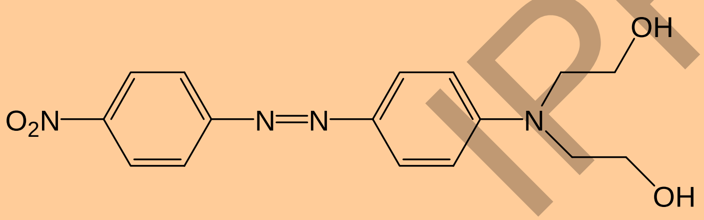
Model dyes



(a) Coumarin-314

λ_{Abs}=425 nm

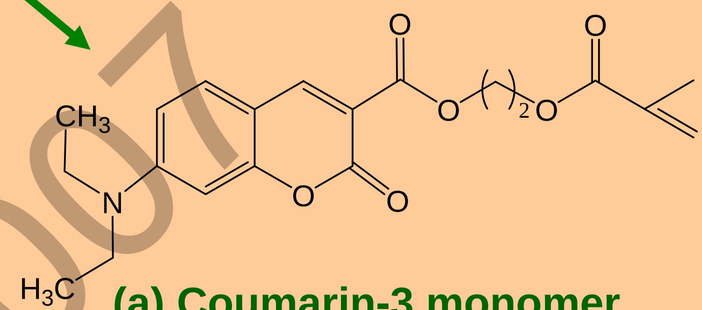
λ_{Em}=458 nm



(b) Dispersed red 19

λ_{Abs}=491 nm

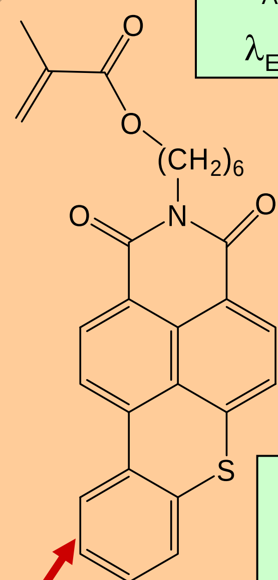
Functional dyes



(a) Coumarin-3 monomer

λ_{Abs}=416 nm

λ_{Em}=441 nm



(b) HY monmer

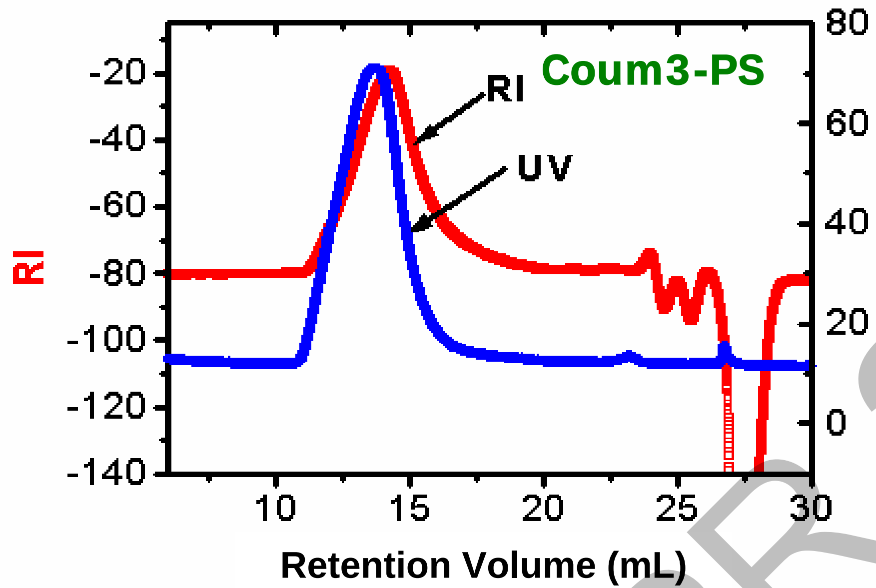
λ_{Abs}=455 nm

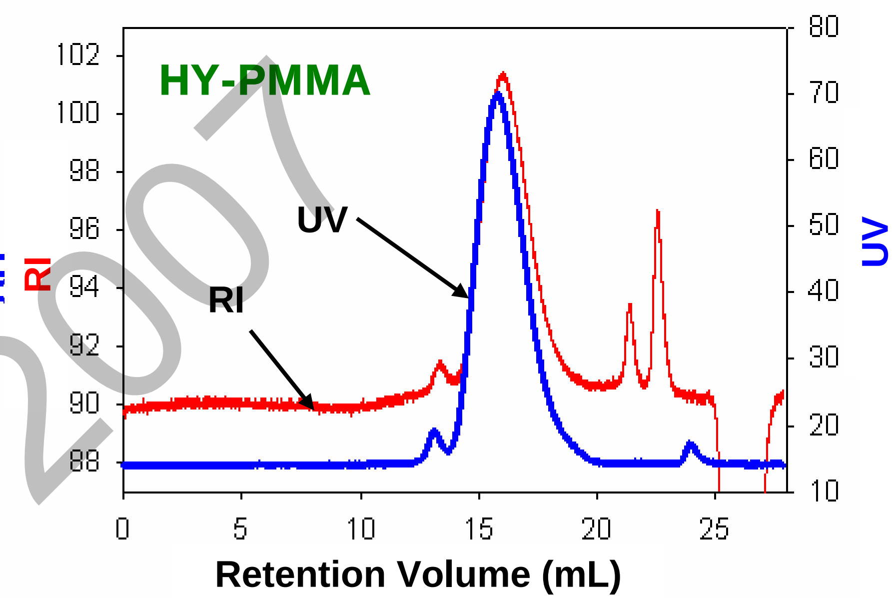
λ_{Em}=508 nm

Acceptors

3. Synthesizing dye-labeled polymers

Characterization of Dye-Labeled PS and PMMA





- UV-vis results:
  - Dye incorporation into polymer

HY-labeled PMMA: 0.099 mmol/g
HY-Labeled PS: 0.0202 mmol/g
Coum3-labeled PS=0.009 mmol/g

	HY-PS	HY-PMMA	Coum3-PS
Mn	321,000	5600	300,000
PDI	1.63	1.81	1.88
D_p	57	49	-

4. Determine Key parameters

Determination of the Förster Distance (R_0) From Spectral Overlap Method

$$K^{RET} = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

$$R_0 = \frac{9000(\ln 10)\kappa^2 \Phi_D}{128\pi^5 N n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

$$\kappa^2 = (\cos\theta_{DA} - 3\cos\theta_D \cos\theta_A)^2$$

$$R_0 = 0.2108[\kappa^2 n^{-4}\Phi_D J(\lambda)]^{1/6}$$

$$J(\lambda) = \sum_a^b F(\lambda)\varepsilon(\lambda)\lambda^4$$

FL spectrum of donor

Extinction coefficient spectrum of acceptor

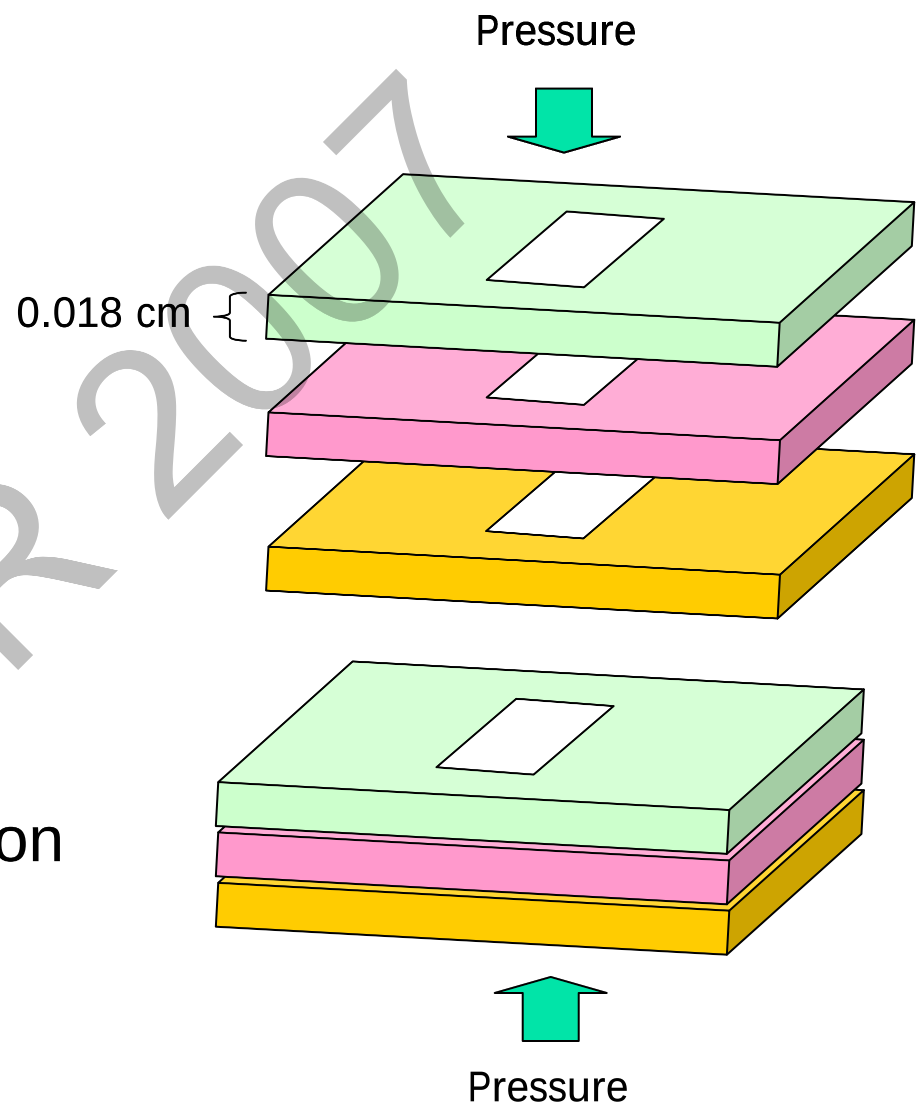
Determination of Extinction Coefficient of Acceptors in Polymer Films

- The Beer Lambert Law

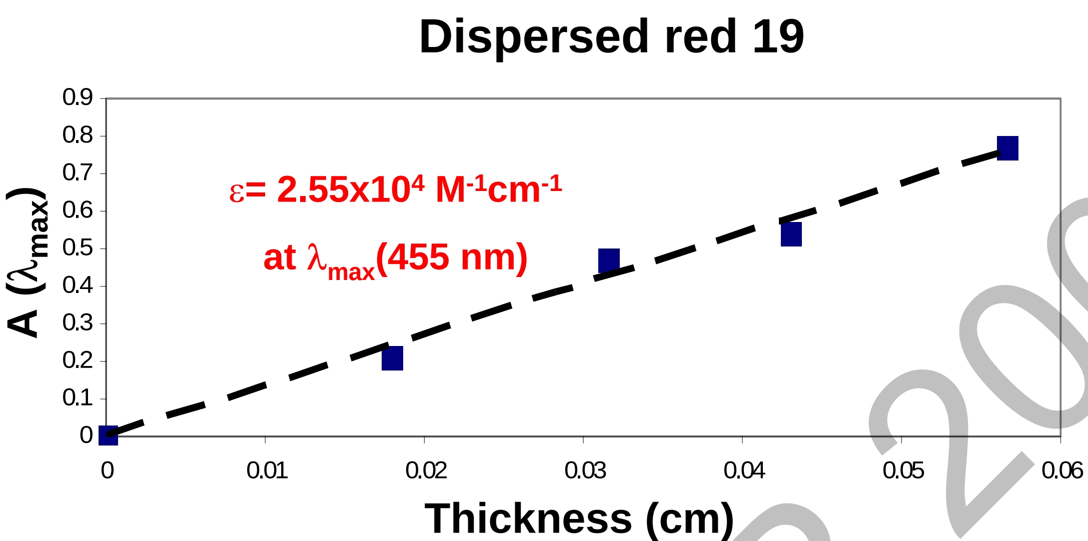
$$A = \varepsilon C_A d$$

C_A=0.53 mM

- I varied film thickness instead of dye concentration

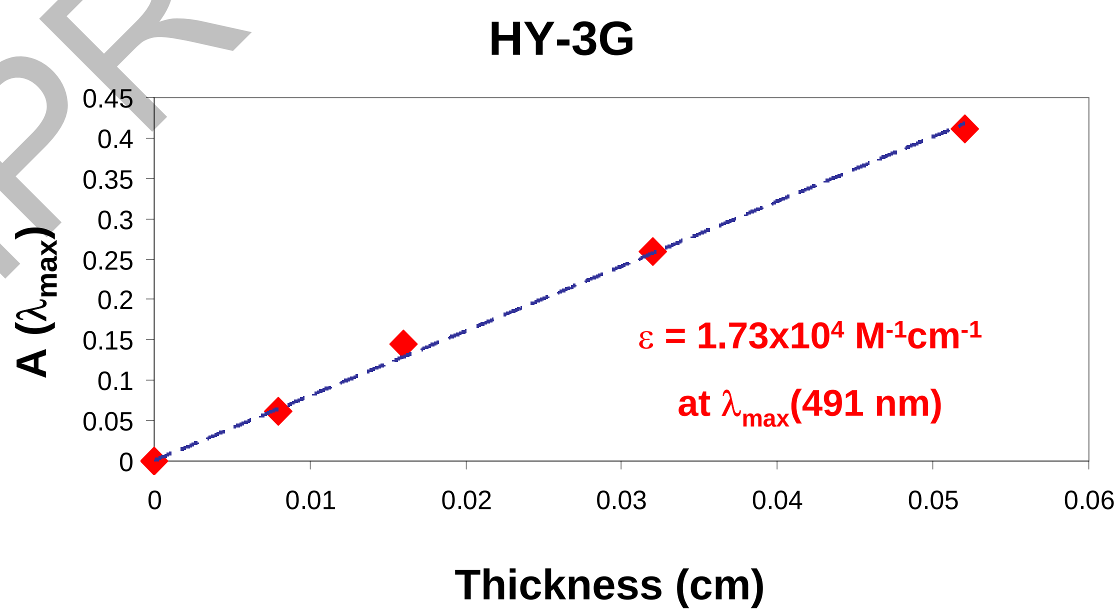


Beer's Law Plots for Two Acceptor Dyes

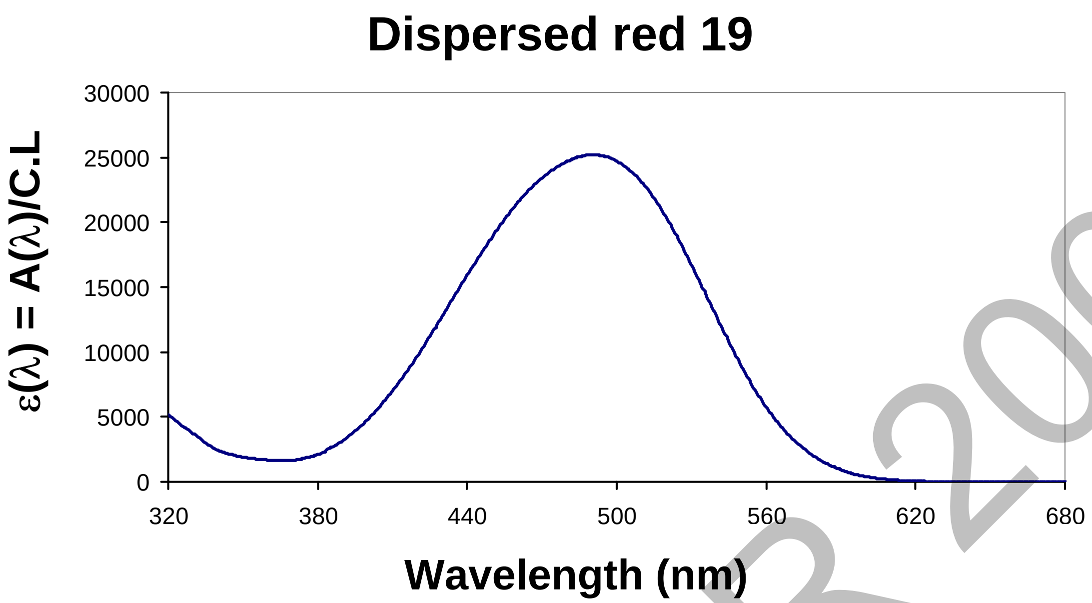


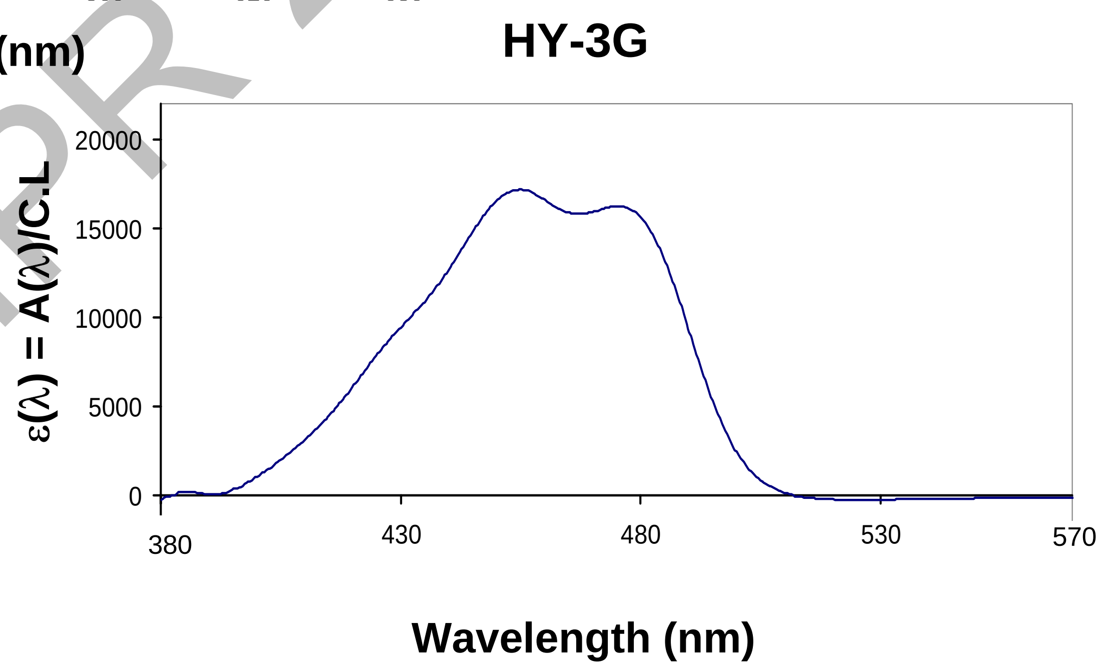
I varied film thickness instead of dye concentration.

$$A = \varepsilon C_A d$$



$\varepsilon(\lambda)$ Spectra for R_0 Calculations



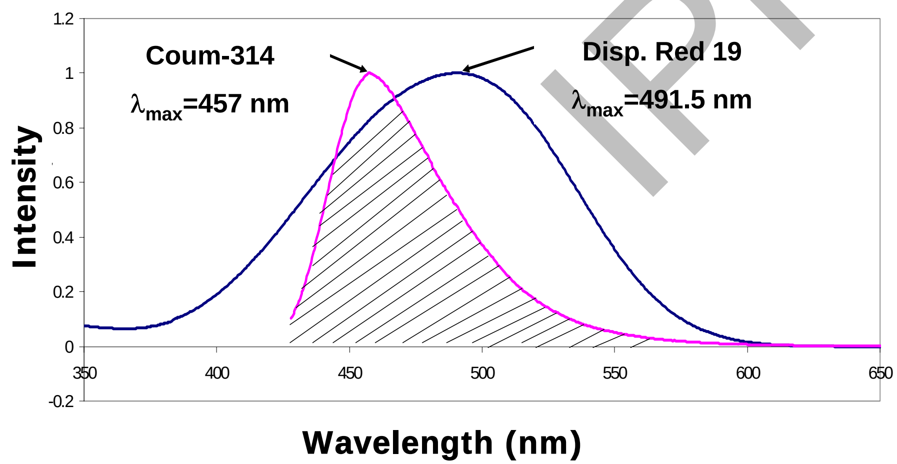


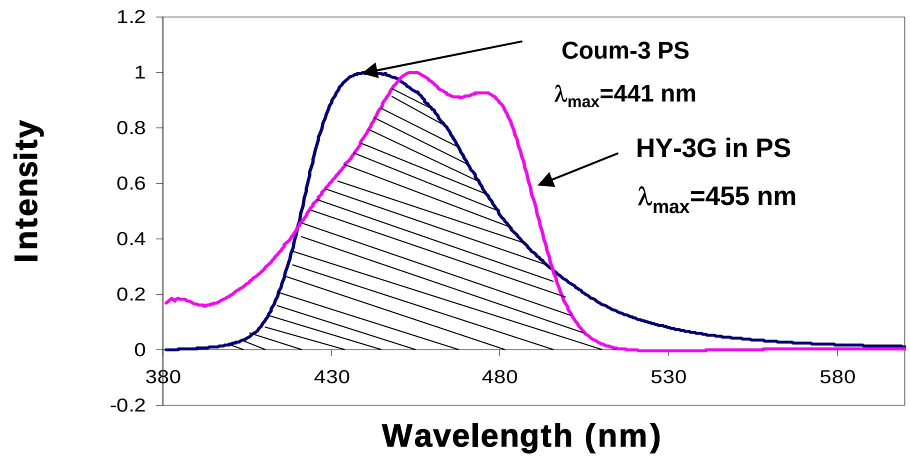
Spectral Overlap Calculation

$$J(\lambda) = \sum_{a}^{b} F(\lambda)\varepsilon(\lambda)\lambda^4$$

$$J(\lambda)_{coum-314/disp.red19} = 2.16E15$$

$$J(\lambda)_{coum-3,PS/HY-3G,PS} = 1.03E15$$





Determination of Quantum Yields

a) Coumarin -314 in PMMA film

$$\Phi_x = \Phi_{ref} \frac{n_x^2 (1-10^{-A_{ref}(\lambda)}) \int F_x(\lambda) d(\lambda)}{n_{ref}^2 (1-10^{-A_x(\lambda)}) \int F_{ref}(\lambda) d(\lambda)}$$

$$\Phi_{D,coum-314} = 0.68\,*$$

$$n_{PMMA} = 1.49$$

$$n_{ethanol} = 1.36$$

$$\frac{\Phi_z}{\Phi_y} = \frac{n_z^2 \tau_z}{n_y^2 \tau_y}$$

$$\tau_{coum-314,EtOH} = 3.63$$

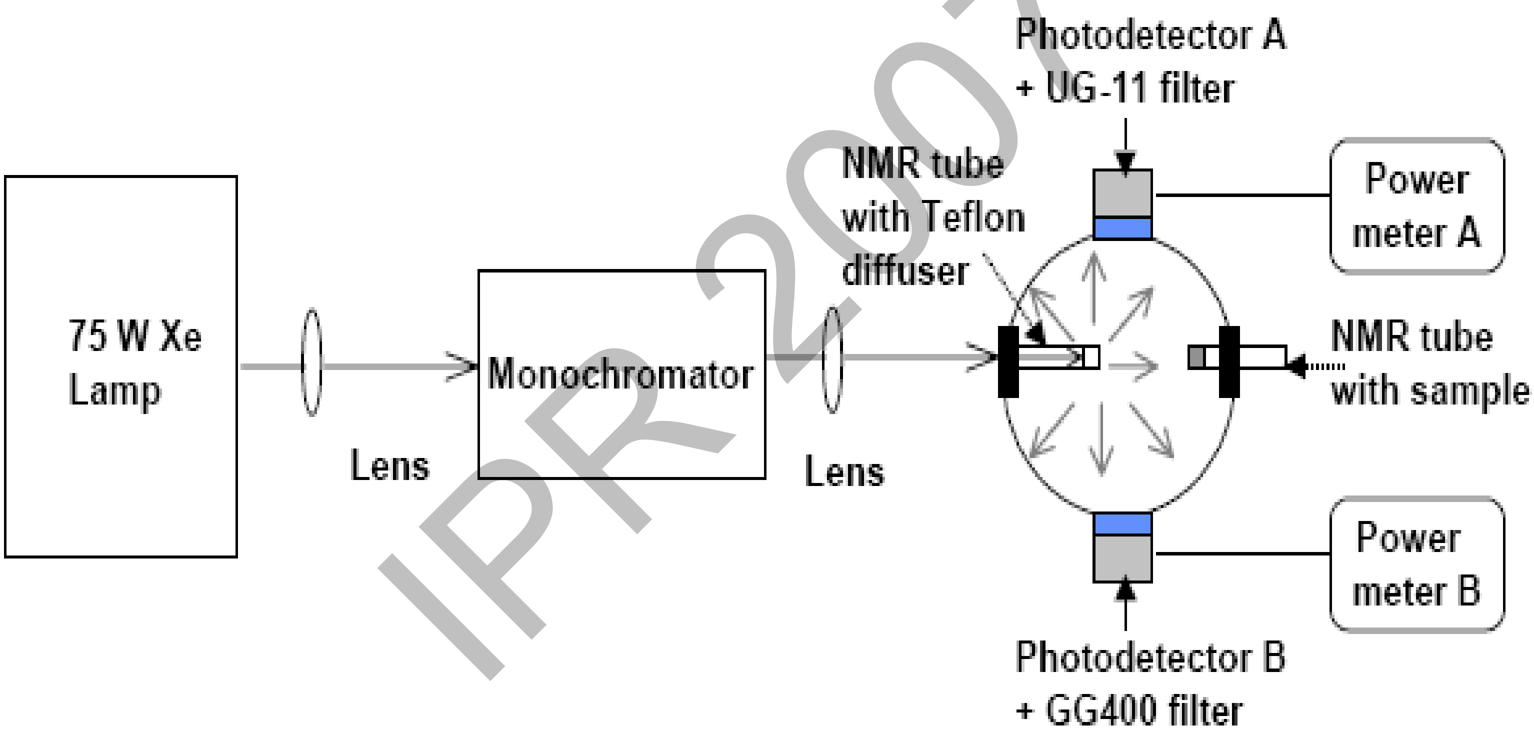
$$\tau_{coum-314,PMMA} = 3$$

$$\Phi_{coum-314,PMMA} = 0.675$$

* Jones et al., J. Phys. Letters (1983), 10, 189.

Measuring Quantum Yield using Integrating Sphere

b) Coumarin-3 PS film



$$\Phi_{D,coum\text{-}3PS} = ?$$

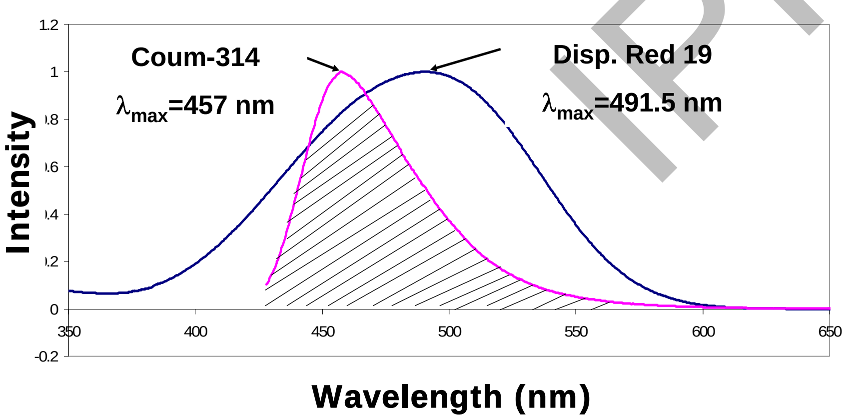
By Gisela Schulz, S. Holdcroft, Simon Fraser University

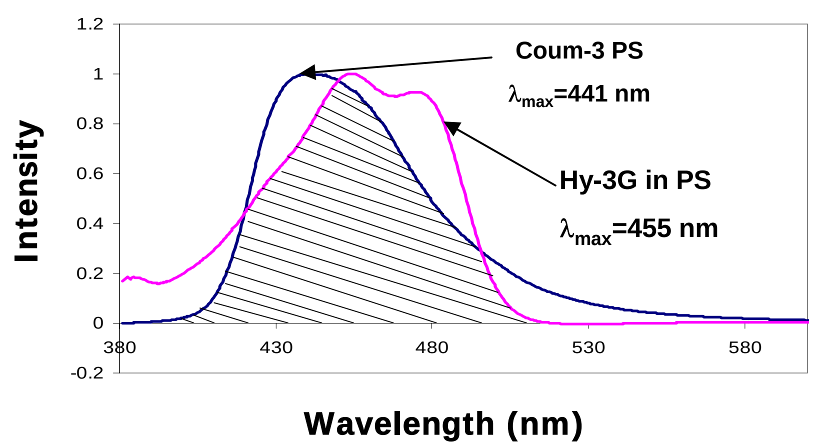
Förster Distance for Coum-314 in PMMA & Coum-3 PS (Spectral Overlap Method)

$$R_0 = 0.2108[\kappa^2 n^{-4} \Phi_D J(\lambda)]^{1/6}$$

$$R_0, coum-314PMMA = 4.8 \text{ nm}$$

$$R_0, coum-3PS = ?$$

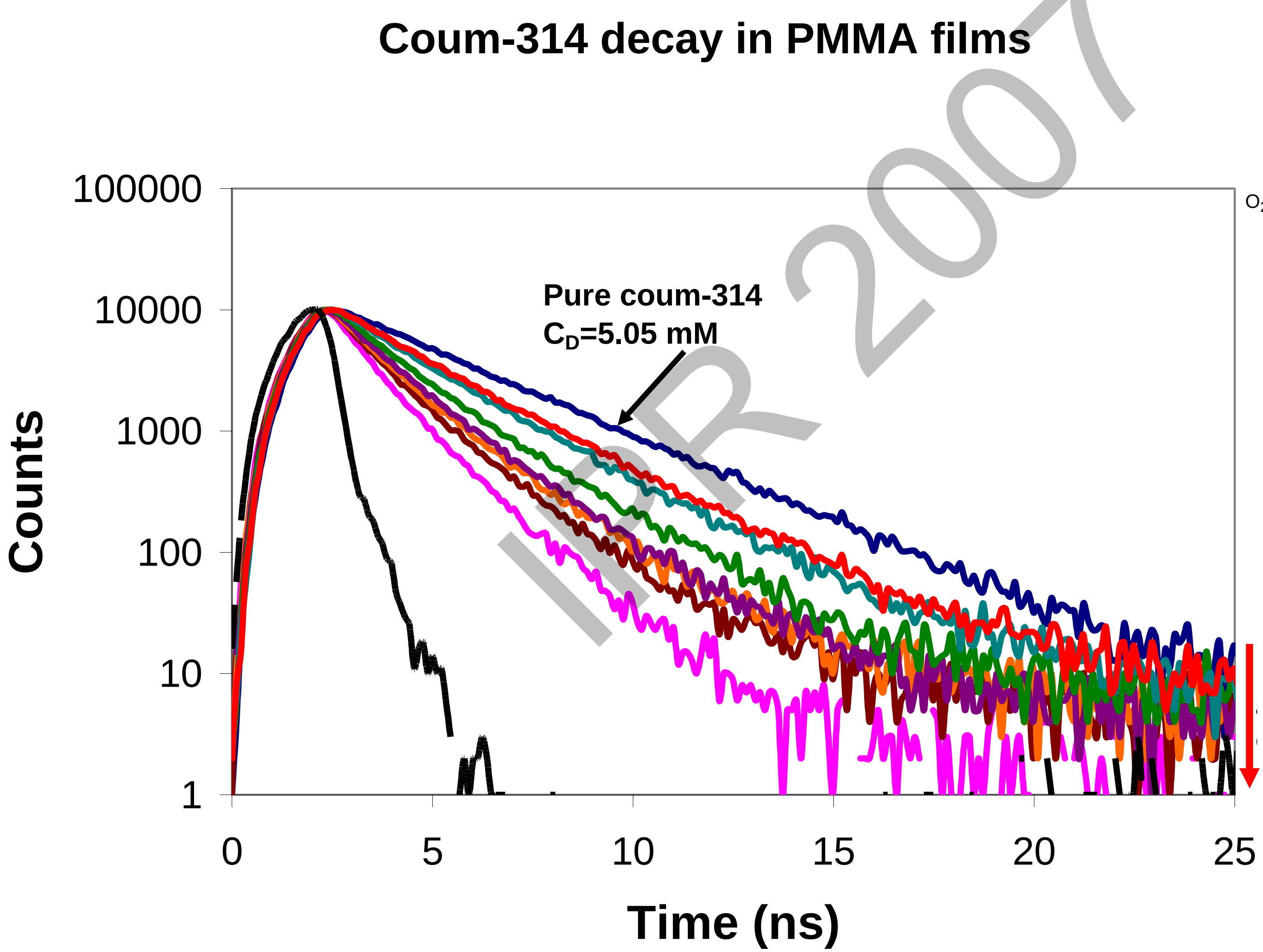


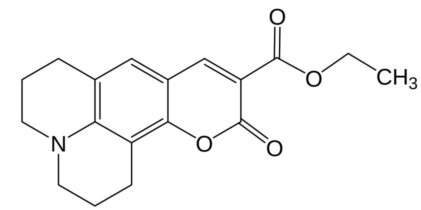


5. Test our models for fitting the experimental data

$$D^* + A \xrightarrow{\text{FRET}} D + A^*$$

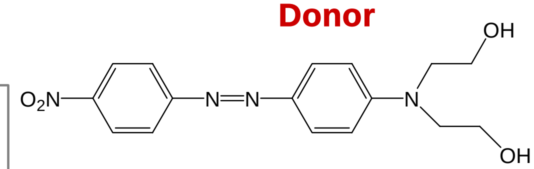
Fluorescence Decay Measurements for Coum-314/Dispersed Red 19 in PMMA Films





Coum-314

Donor



Dispersed red-19

Acceptor

Increasing acceptor concentration

C_a=0 - 4.5 mM

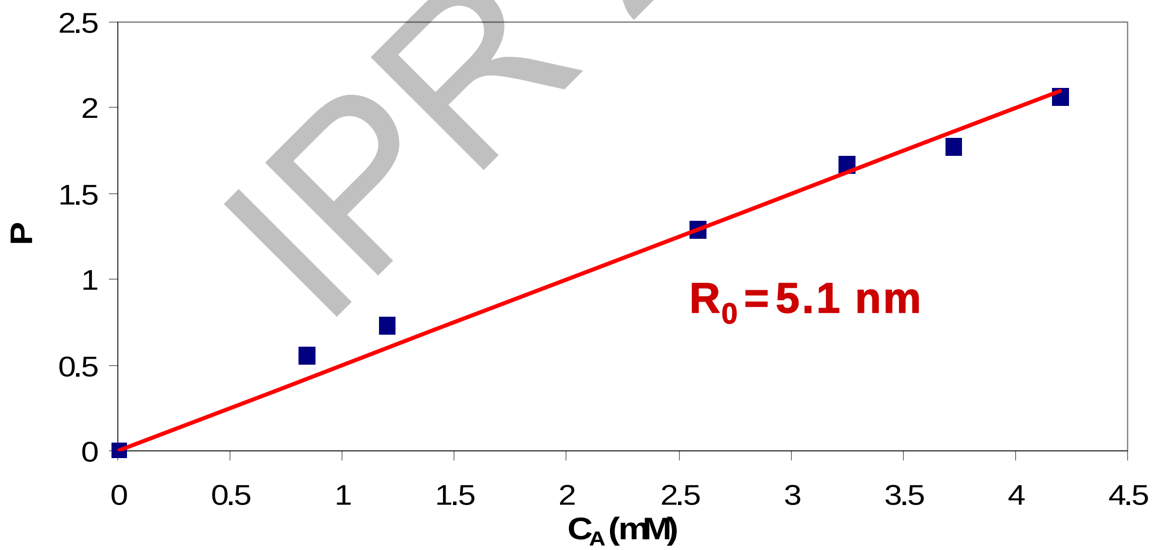
Fluorescence Decay Measurements for Coum-314/Dispersed Red 19 in PMMA Films (Cont'd)

- Förster Model

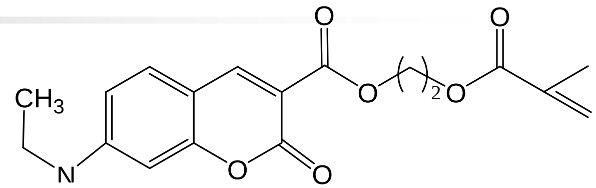
$$I = I(0)\exp[-\frac{t}{\tau_D} - P(\frac{t}{\tau_D})^{1/2}]$$

$$P = \frac{4}{3000}\pi^{3/2} N_A \langle \frac{3}{2}\kappa^2 \rangle^{1/2} R_0^3 C_A$$

Plot of P versus Acceptor Concentration for Coum-314 in PMMA Films

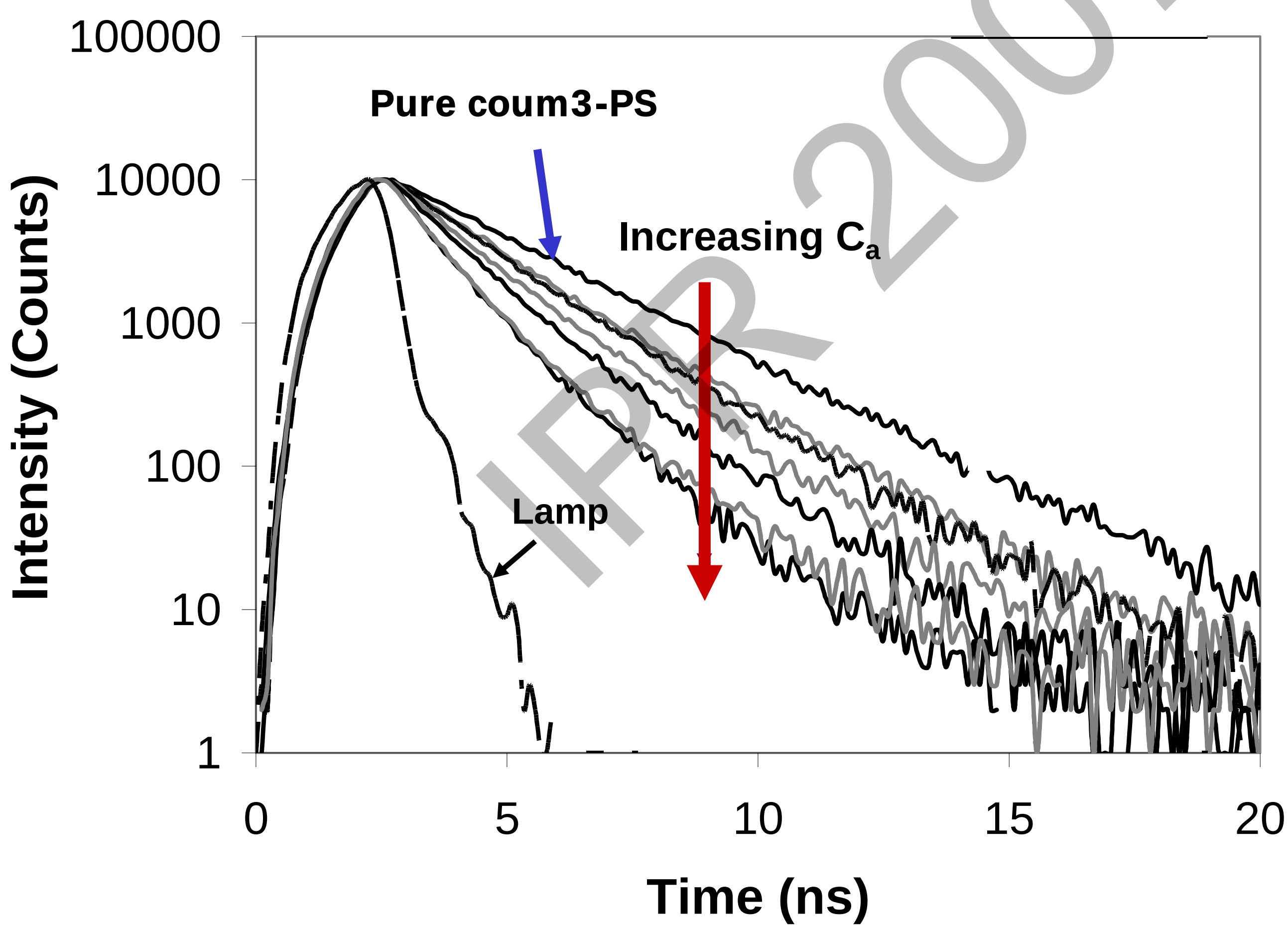


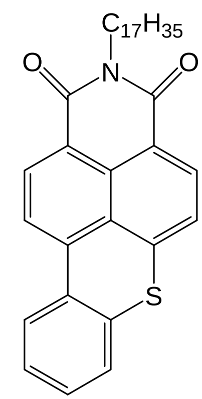
Fluorescence Decay Measurements for Coum-3 PS & HY-3G in PS Films



Coum-3 Monomer

Donor





HY-3G

Acceptor

C_a=0 - 5.72 mM

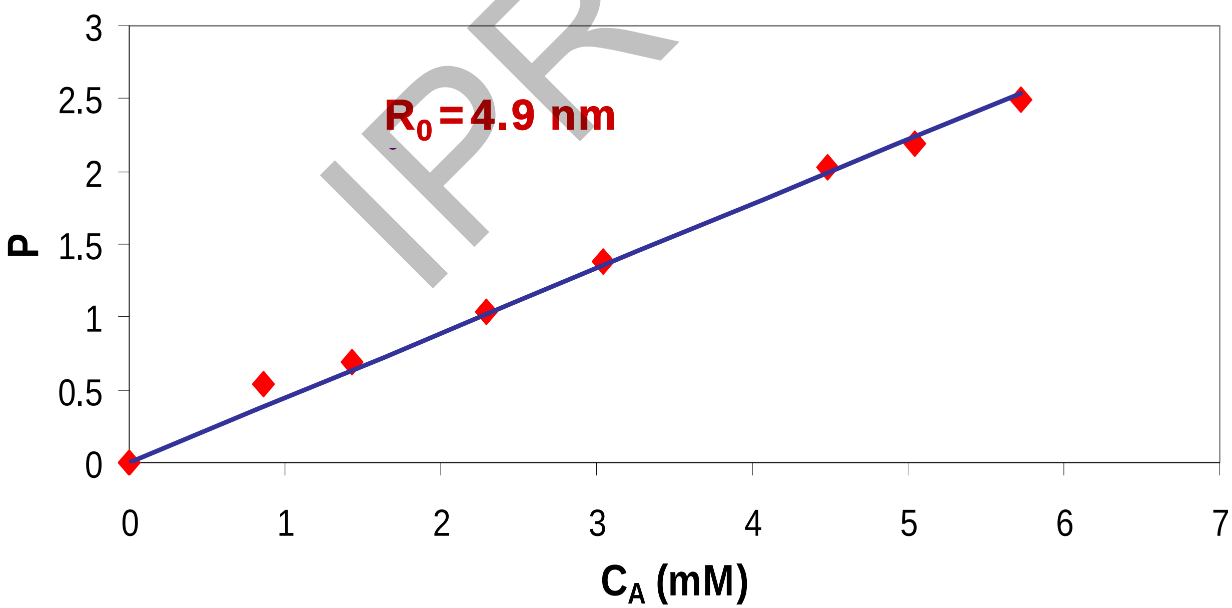
Fluorescence Decay Measurements for Coum-3 PS & HY-3G in PS Films (Cont'd)

- Our Generalized Förster Model

$$I(t) = A\exp\left[-\left(\frac{t}{\tau}\right)^{\beta} - P\sqrt{\frac{t}{<\tau>}}\right]$$

$$P = \frac{4}{3000}\pi^{3/2} N_A \langle\frac{3}{2}\kappa^2\rangle^{1/2} R_0^3 C_A$$

Plot of P versus Acceptor Concentration for Coum-3-PS & HY-3G dyes



Summary

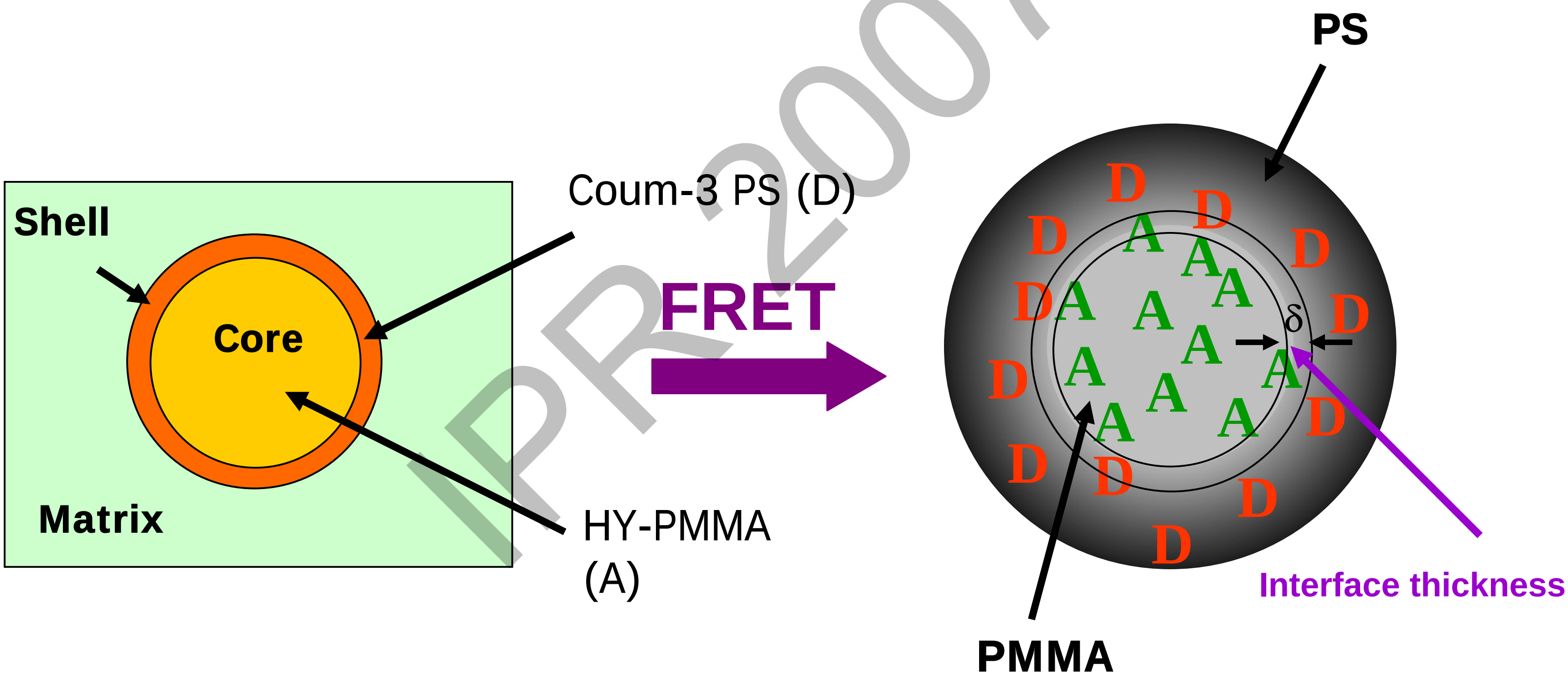
- Core/shell morphology development within the dispersed phase for ternary polymer blend of HDPE/PS/PMMA.
  - Formation of dispersed particles of PMMA in a PS shell in a HDPE matrix upon melt mixing (t>30 min).

- Systematic study of the fluorescence decay of coumarin dyes in polymer films and solutions (In press, *J. Polym. Sci,. B*).
  - Many of the dye-polymer pairs exhibit exp. decays with $\tau_D \approx 3$ ns. These dyes are well suited for FRET in Polymers.

- Testing our Generalized model by comparing R_0 values obtained from spectral overlap method and FRET.

Future Work

- To carry out FRET experiments on (PS/PMMA/HDPE) blends using Monte Carlo simulations.



Thank you for your attention