Institute for Polymer Research

Quality of Solvent Toward a Polymer of Intrinsic Microporosity (PIM) Determined by Fluorescence

Steve Chen

Department of Chemistry

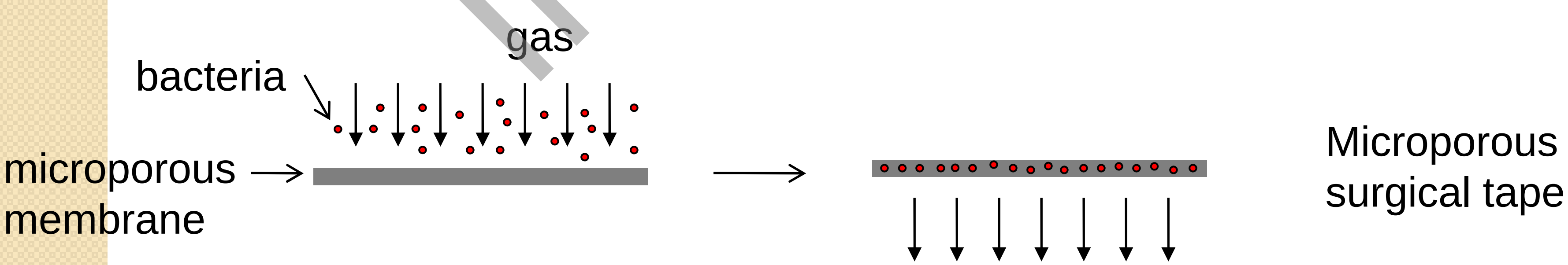
Supervisor: Prof Jean Duhamel

IPR Seminar

May 10th, 2011

Microporous materials

- A material containing pores with diameters less than 2 nm;
- Inorganic materials: zeolites, activated carbons;
- Applications: membranes for gas separations and water purification

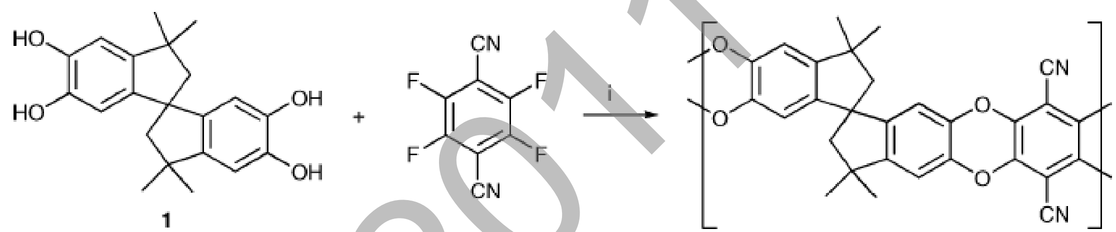


Polymers of Intrinsic Microporosity (PIMs)

- Rigid and contorted macromolecules;
- Inability to pack space efficiently;
- Step-growth polymerization;
- Applications: heterogeneous catalysis, membrane separations, hydrogen storage and the adsorption of organic compounds

Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Fritsch, D. *Macromolecules* **2008**, 41, 1640-1646.

PIM and the Monomer

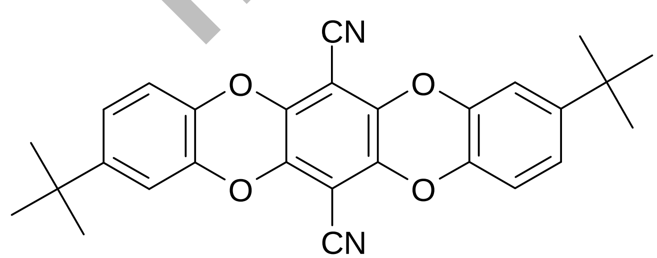


[a] Reagent and conditions: K_2CO_3, DMF, 65 °C, 48 h.

PIM

MW = 63,000 g/mol

Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Fritsch, D. *Macromolecules* **2008**, 41, 1640-1646.



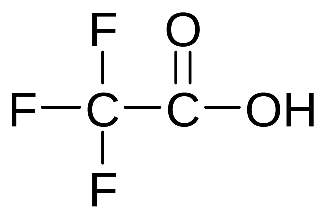
Monomer

Solubility of PIM

- Soluble: chloroform, dichloromethane (DCM), THF;
- Insoluble: DMF, ether, acetone, etc.
- DCM was used as a solvent in this study

Quencher

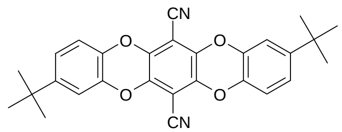
- trifluoroacetic acid (TFA)

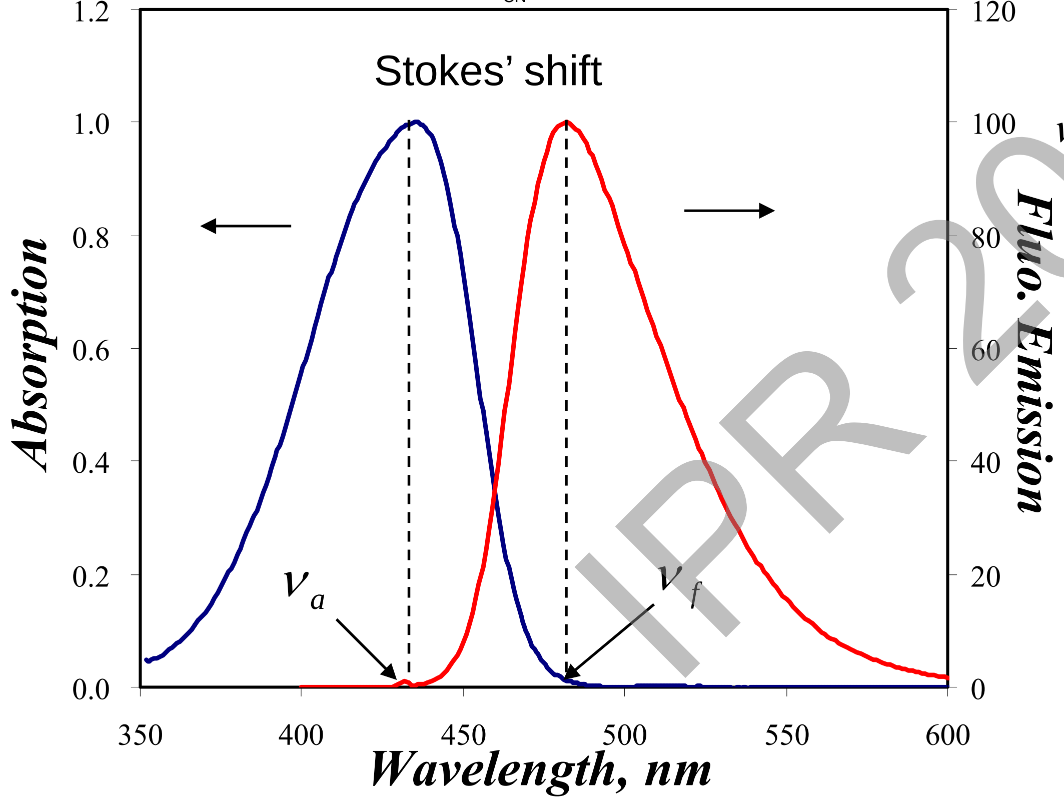


- Strong acid;
- A fluorescence quencher, the quenching efficiency is solvent dependent.*

* Bunce, N.J.; Bergsma, M.D. *J. Org. Chem.* **1980**, 45, 2083-2086.

PIM Monomer Fluorescence and Stokes' shift





Lippert Equation

$$\nu_a - \nu_f = \frac{2}{hc}\left(\frac{\varepsilon - 1}{2\varepsilon - 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\frac{(\mu_E - \mu_G)^2}{a^3} + const$$

h – Planck's constant;
c – the speed of light;
a – the radius of the solvent cavity in which the fluorophore resides;
ε – dielectric constant;
n – refractive index;
ν_a, ν_f – in cm^{-1}
μ_G, μ_E – dipole moments of the ground and excited states

Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, Plenum Publishers: New York, 1983.

Orientation Polarizability (Δf)

spectral shifts due to reorientation of the solvent molecules ←

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon - 1} - \frac{n^2 - 1}{2n^2 + 1}$$

→ redistribution of electrons

↓

reorientation of the solvent dipoles and redistribution of the electrons in the solvent molecules

For solvent mixture:

$$\varepsilon_{mix} = f_1\varepsilon_1 + f_2\varepsilon_2$$

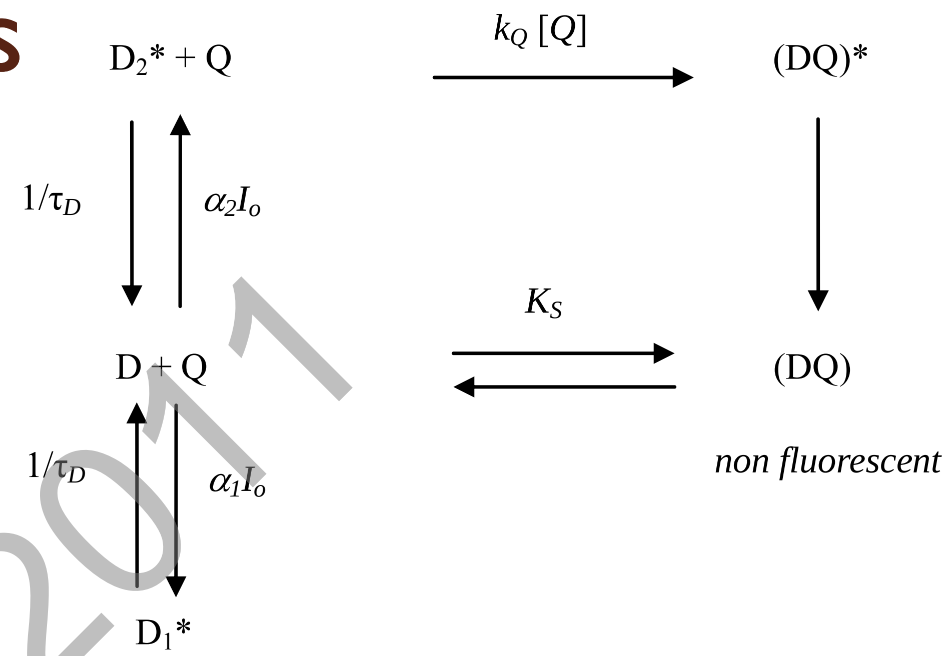
$$n_{mix}^2 = f_1 n_1^2 + f_2 n_2^2$$

f_1 and f_2 are the volume fractions of each solvent.

Fung, S. Y.; Duhamel, J.; Chen, P. *J. Phys. Chem. A* **2006**, 110, 11446-11454.

Quenching Pathways

Dynamic, static and protective quenching



D - chromophore

Q - quencher

k_Q - quenching rate constant by diffusion

K_S - association constant

α_1 and α_2 - the molar fractions of the chromophore which are not quenched and quenched by diffusion

$$f_a = \frac{\alpha_2}{\alpha_1 + \alpha_2}$$

f_a - Fraction of chromophores accessible to the quencher

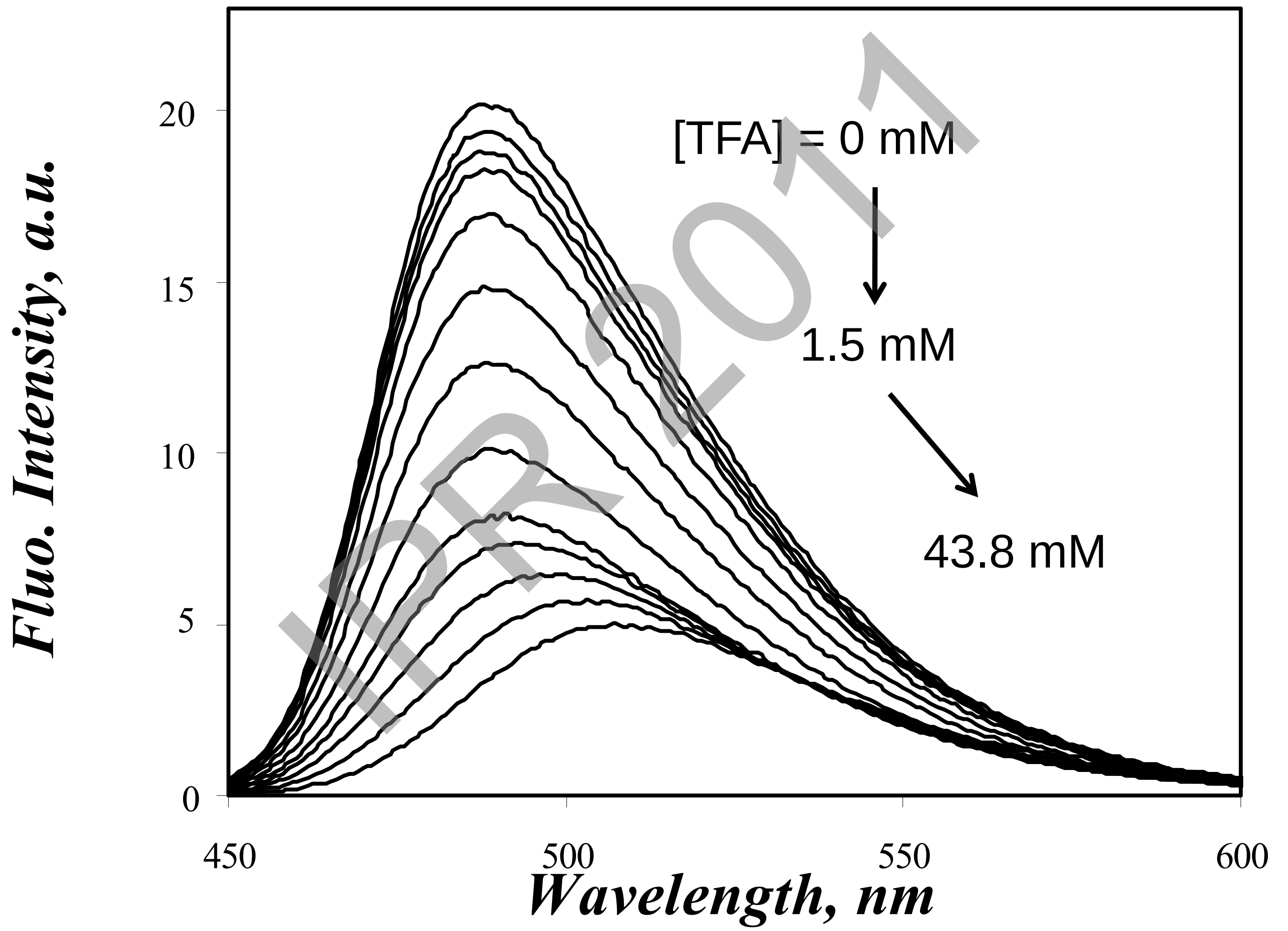
$$\frac{I_{TRo}}{I_{TRo} - I_{TR}} = \frac{I_{TRo}}{\Delta I_{TR}} = \frac{1}{f_a}\frac{1 + k_Q \tau_D [Q]}{k_Q \tau_D [Q]} = \frac{1}{f_a} + \frac{1}{f_a k_Q \tau_D}\frac{1}{[Q]} \longrightarrow k_Q \text{ and } f_a$$

$$\frac{I_{SSo}}{I_{SS}}\left(1 - f_a + \frac{f_a}{1 + k_Q \tau_D [Q]}\right) = 1 + K_S [Q] \longrightarrow K_S$$

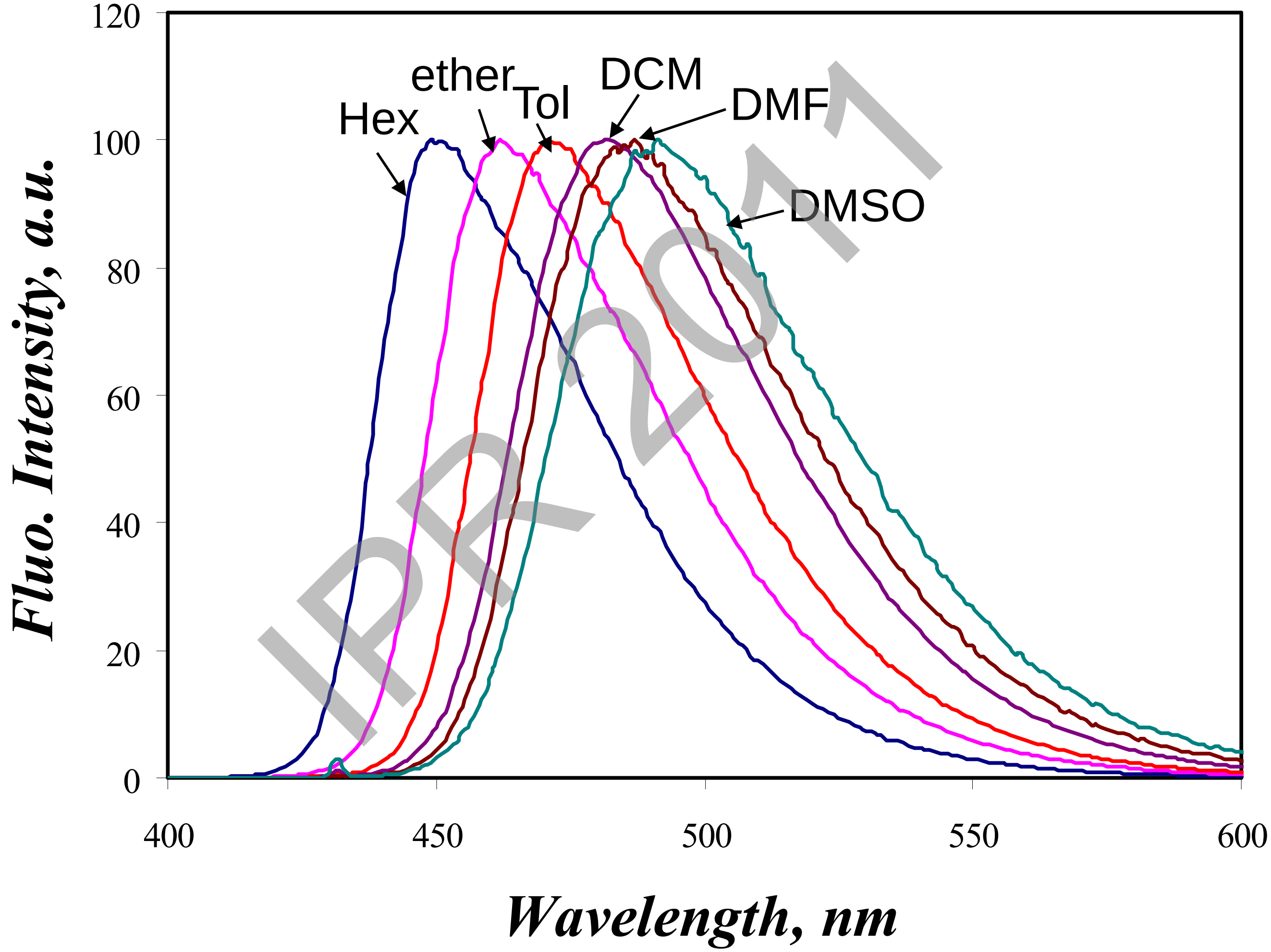
Siddique, B.; Duhamel, J. *Langmuir* **2011**, *ASAP*.

Results Obtained by Steady-State Fluorescence

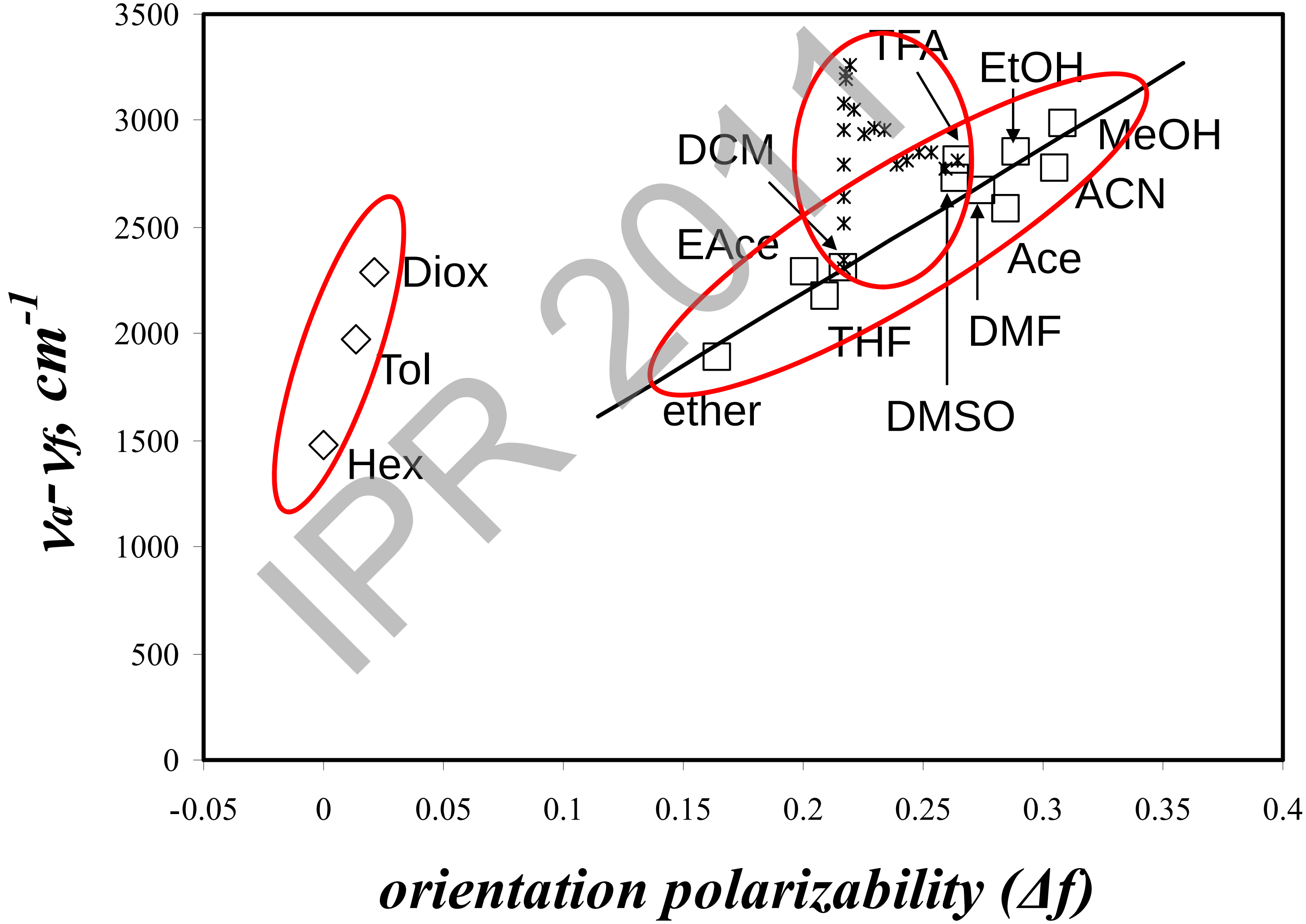
PIM in DCM with TFA



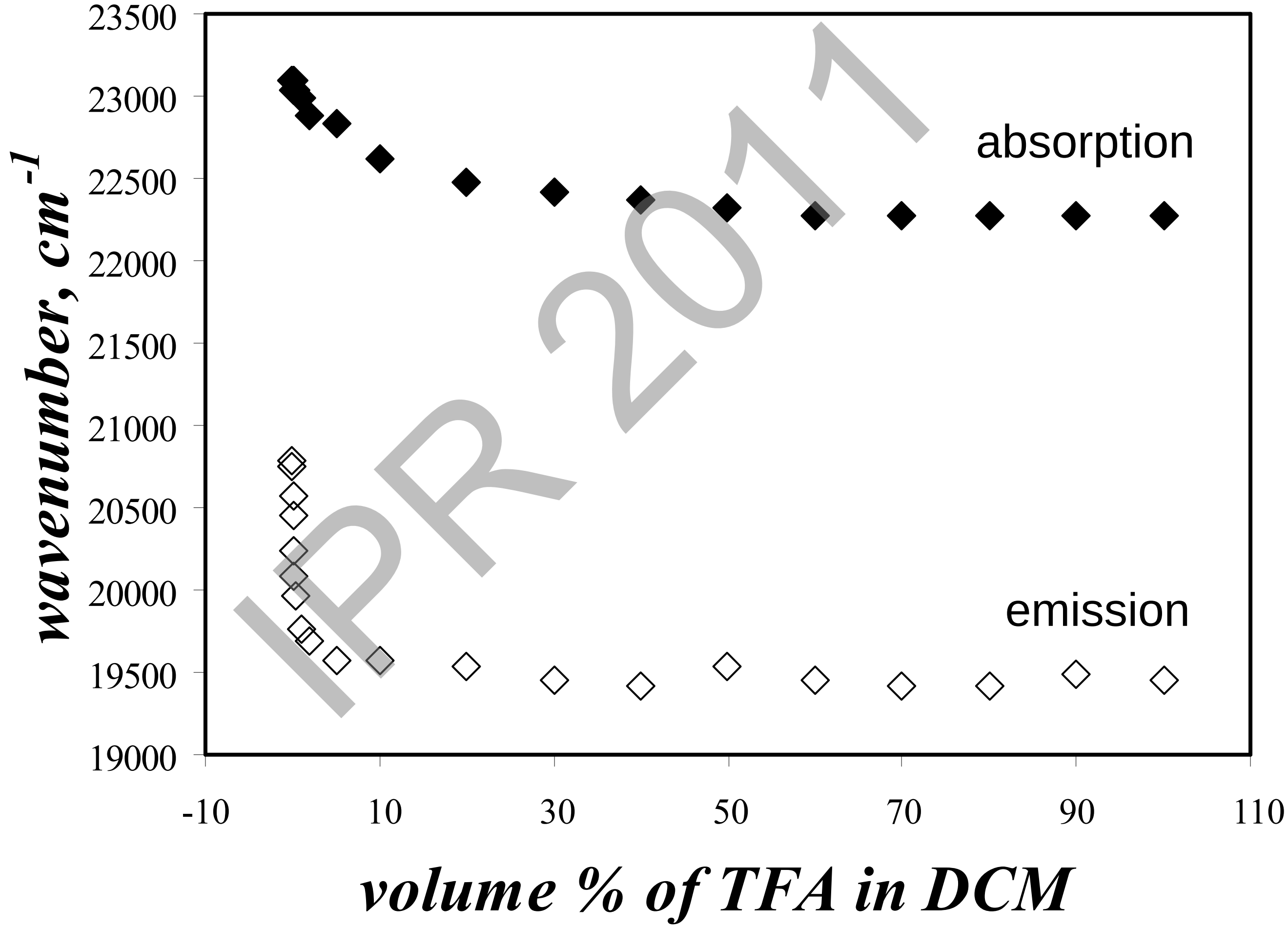
Solvent Effects on Monomer Fluorescence



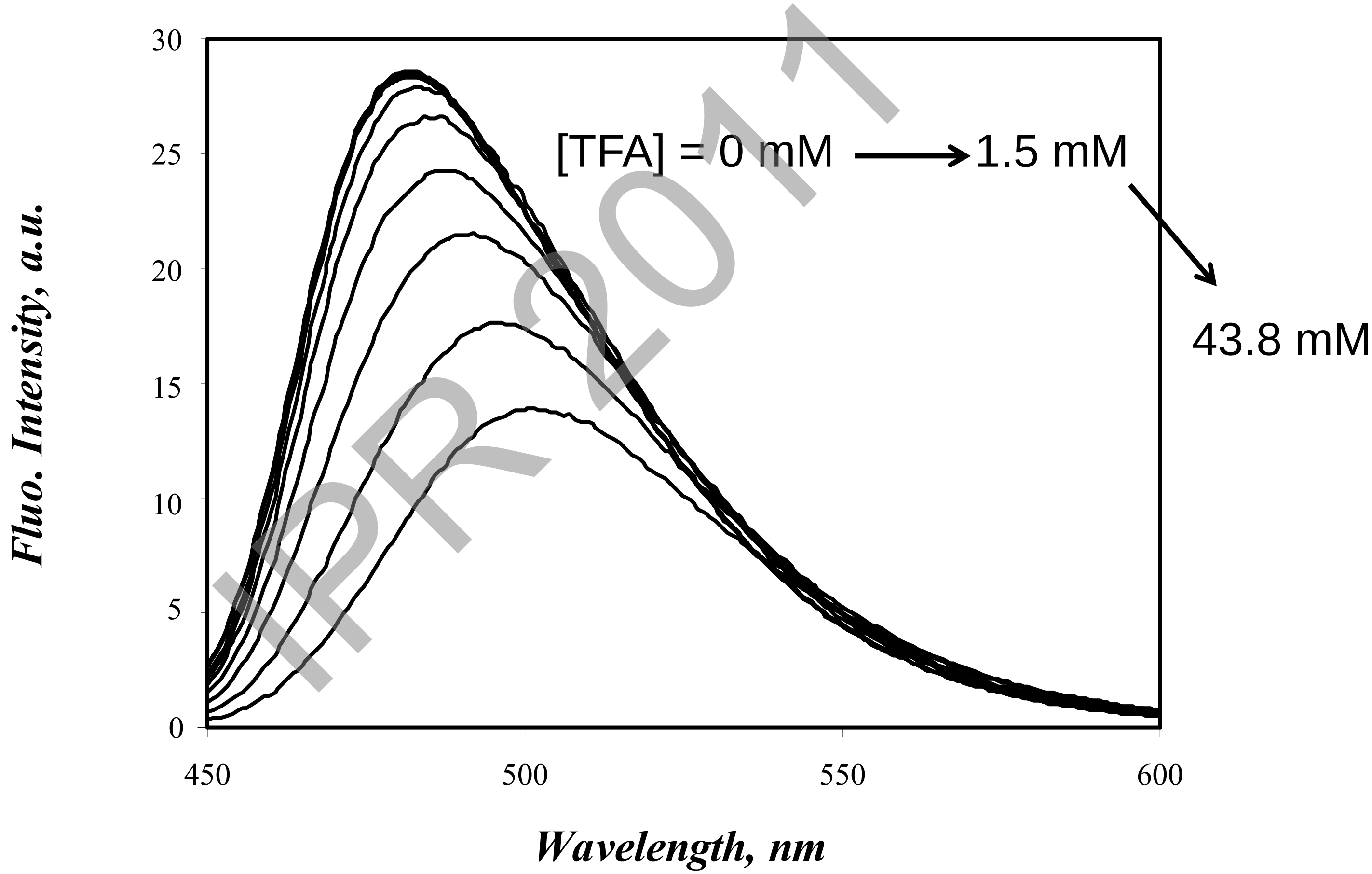
Lippert plot of PIM monomer



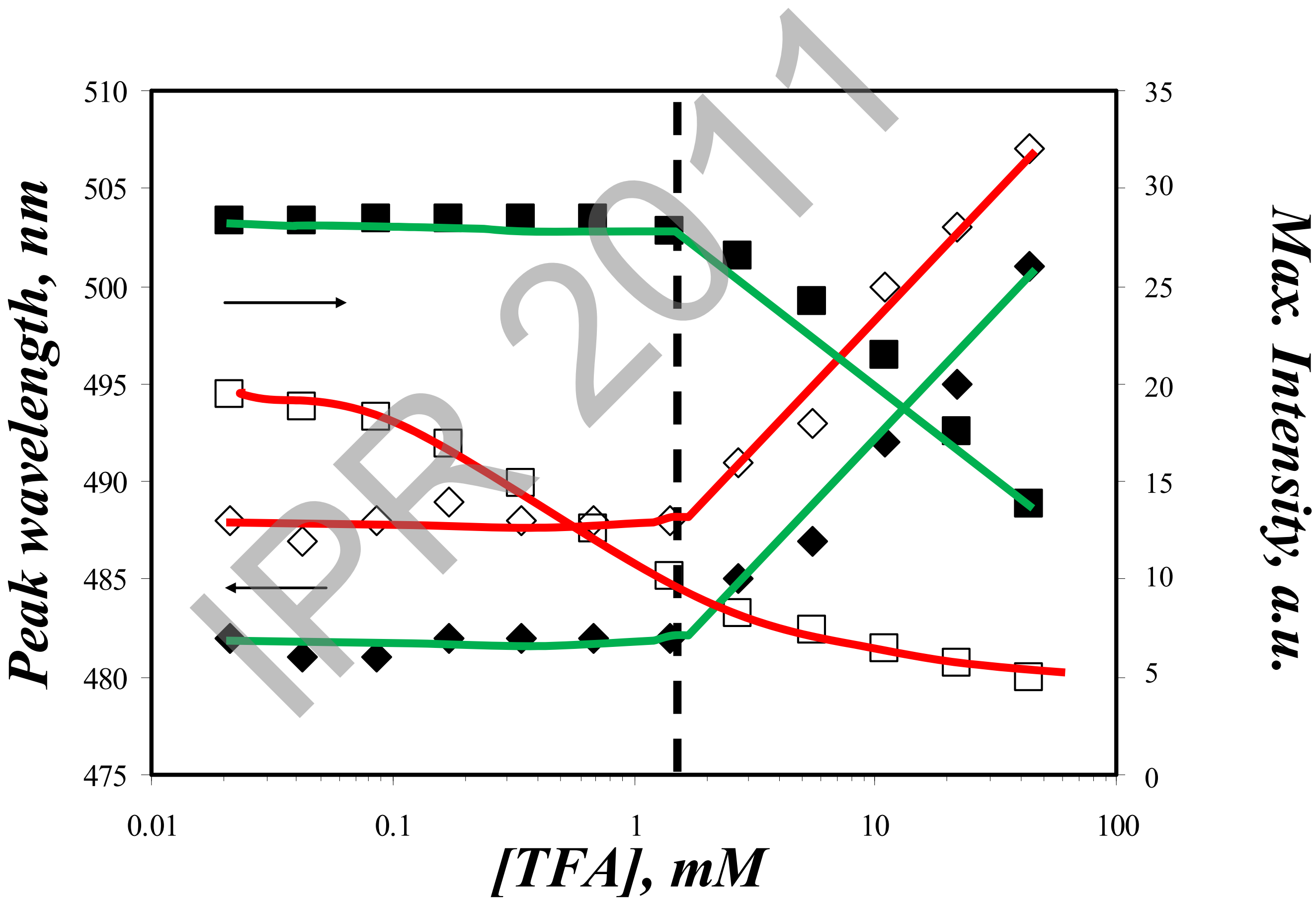
Positions of the ABS and Emission Peaks of Monomer in DCM and TFA



Monomer in DCM with TFA



Different Quenching Observed with the Polymer and the Monomer

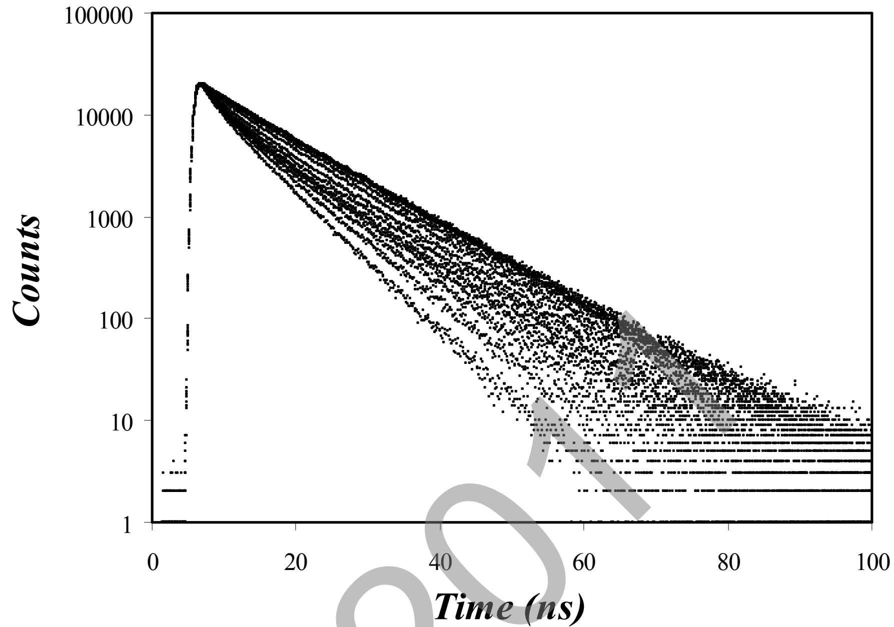


polymer – the hollow symbols, monomer – the solid symbols

Results Obtained by Time-Resolved Fluorescence

Polymer

λ_{ex} = 438 nm
λ_{em} = 500 nm



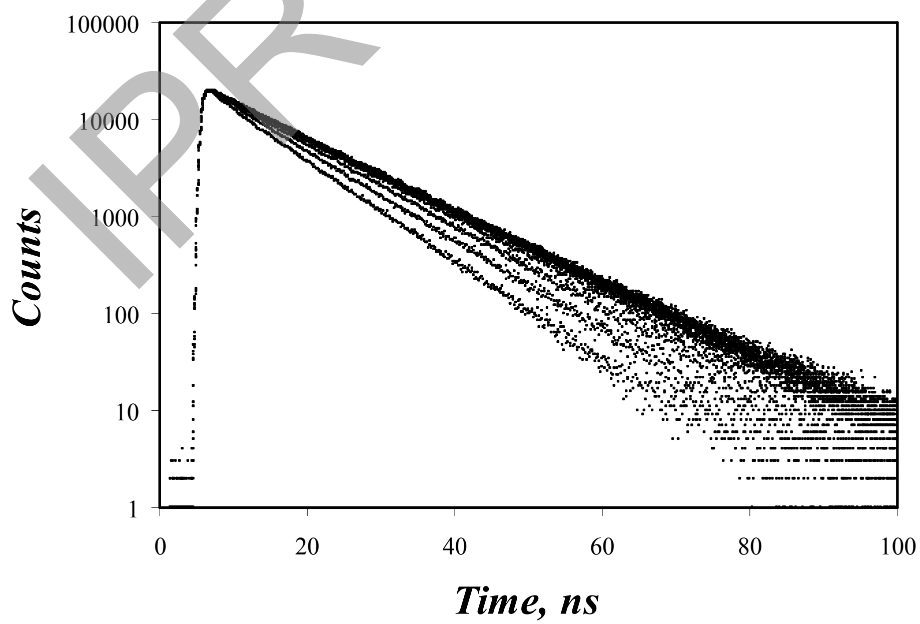
[TFA] = 0 mM

↓

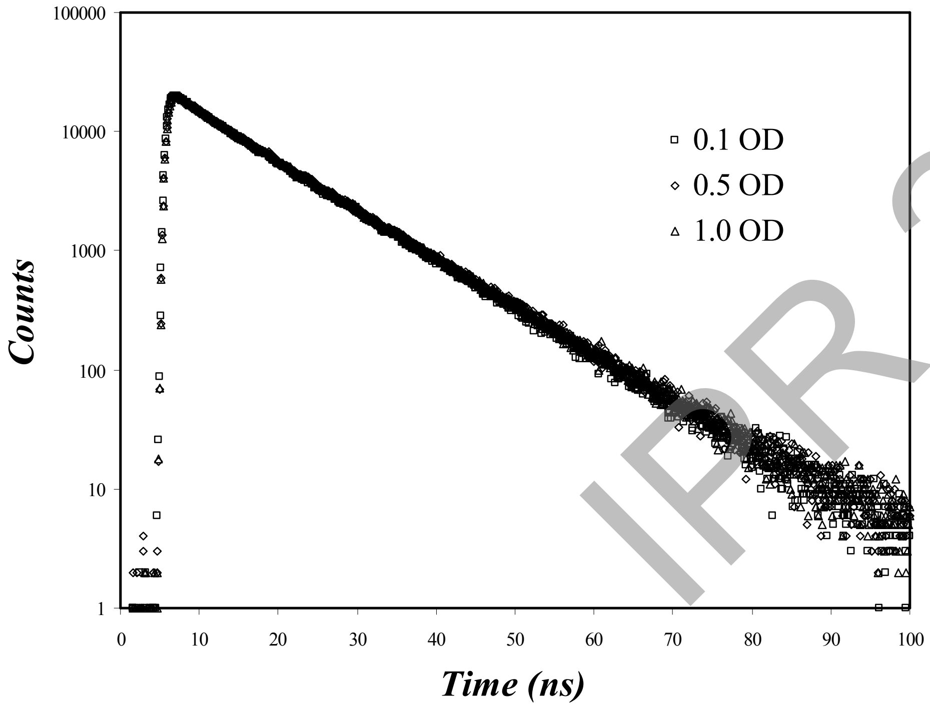
43.8 mM

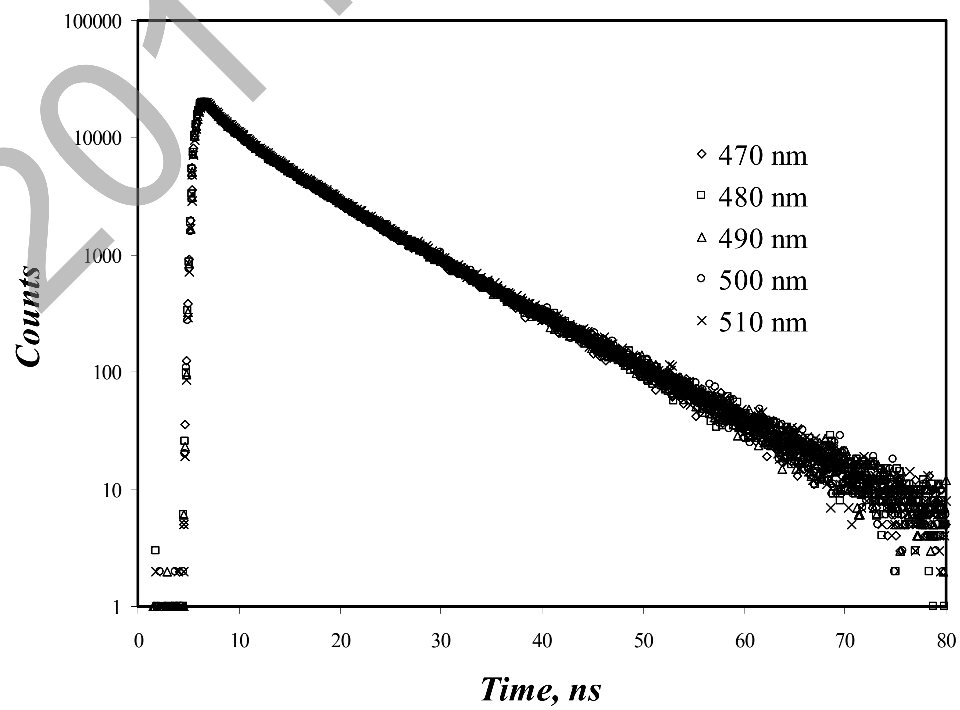
Monomer

λ_{ex} = 433 nm
λ_{em} = 500 nm



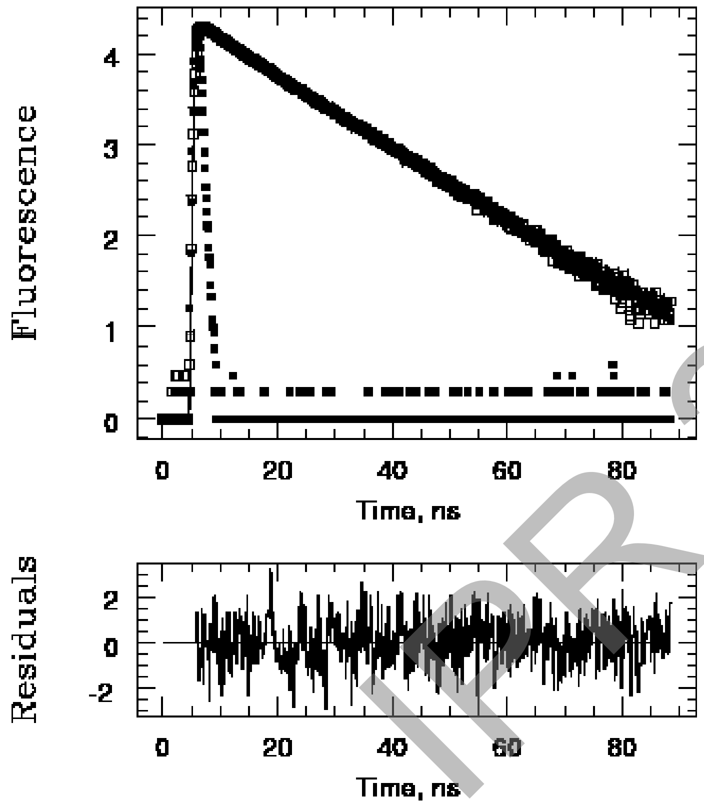
Effect of Concentration and Emission Wavelength on PIM





[TFA] = 2 mM

Analysis of Fluorescence Decays



PIM in DCM,

λ_{ex} = 438 nm,

λ_{em} = 500 nm,

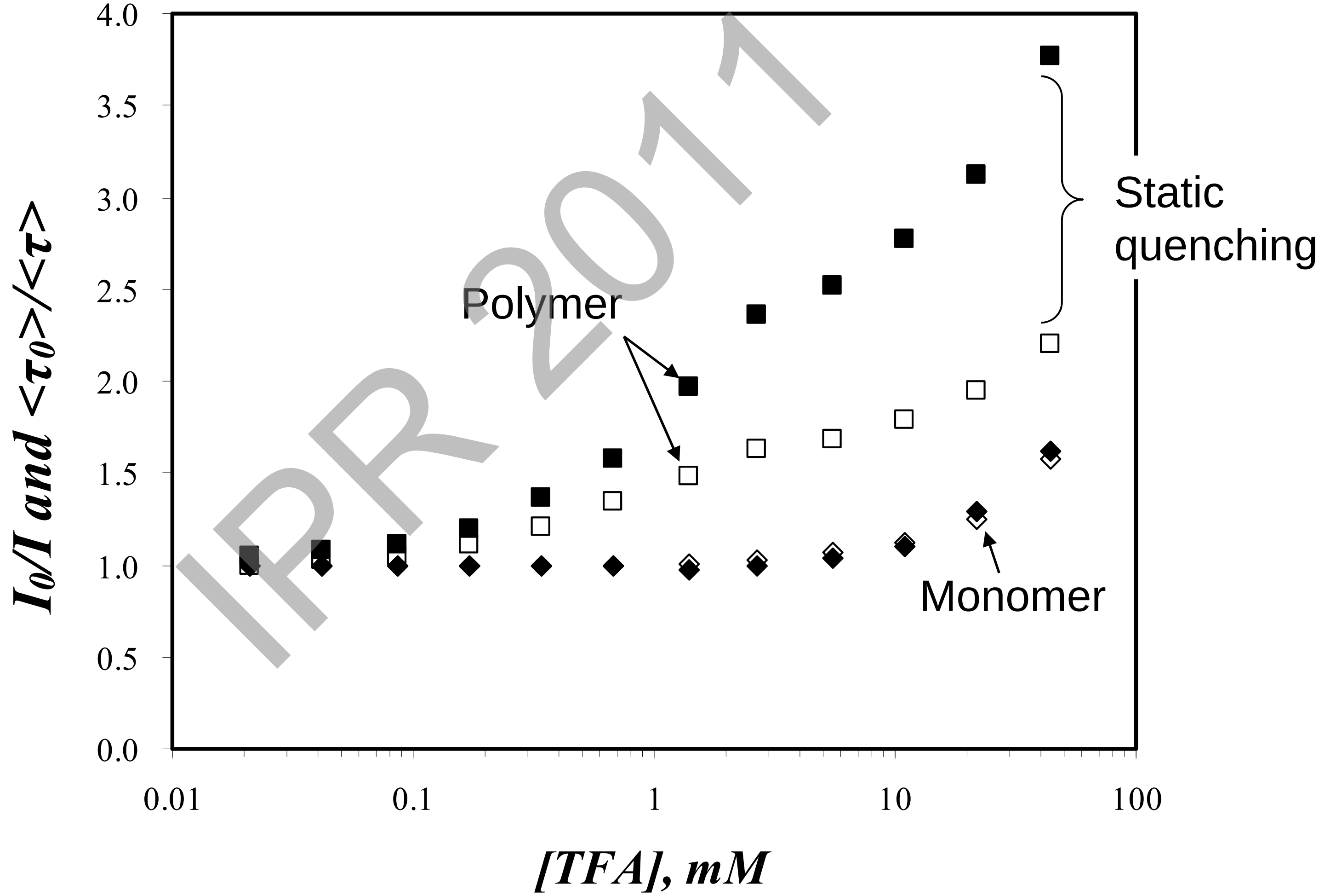
TPC = 0.118 ns/ch,

χ^2 = 1.12

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$$

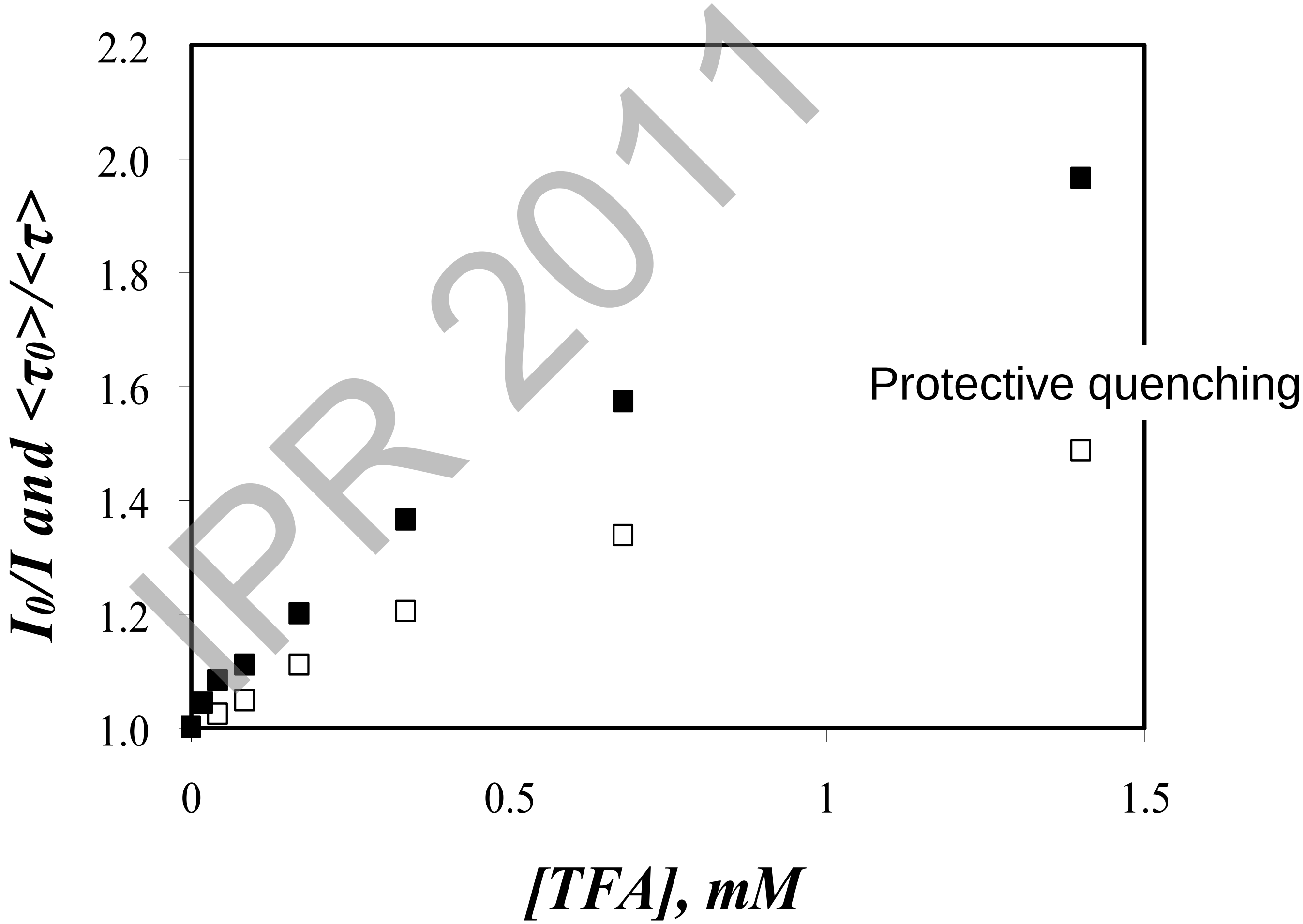
$$\langle \tau \rangle = \tau_1 \times A_1 + \tau_2 \times A_2 + \tau_3 \times A_3$$

Steady-State and Time-Resolved Fluorescence Results



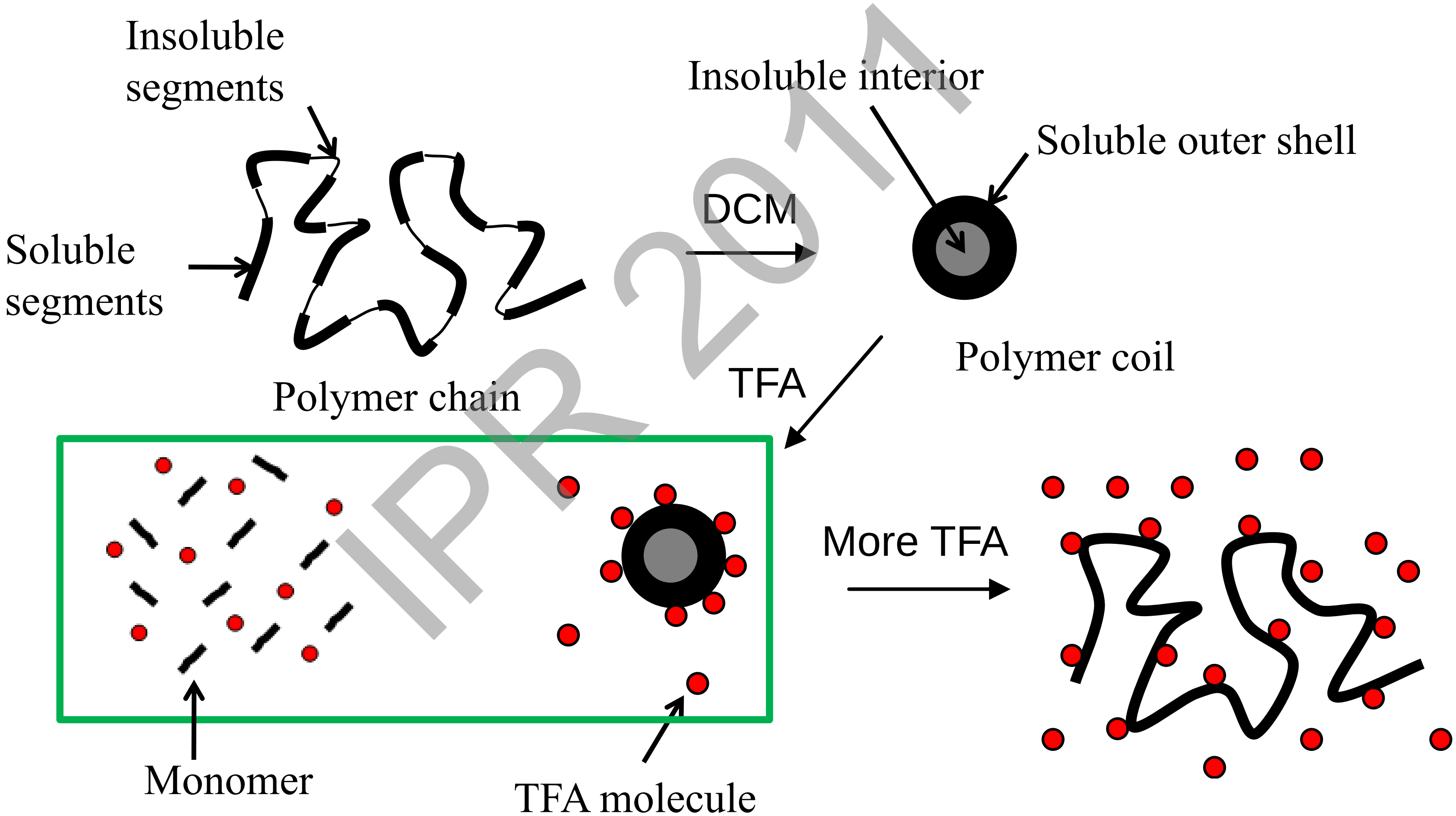
$\langle \tau_0 \rangle / \langle \tau \rangle$ – the hollow symbols, I_0/I – the solid symbols

Steady-State and Time-Resolved Fluorescence Results

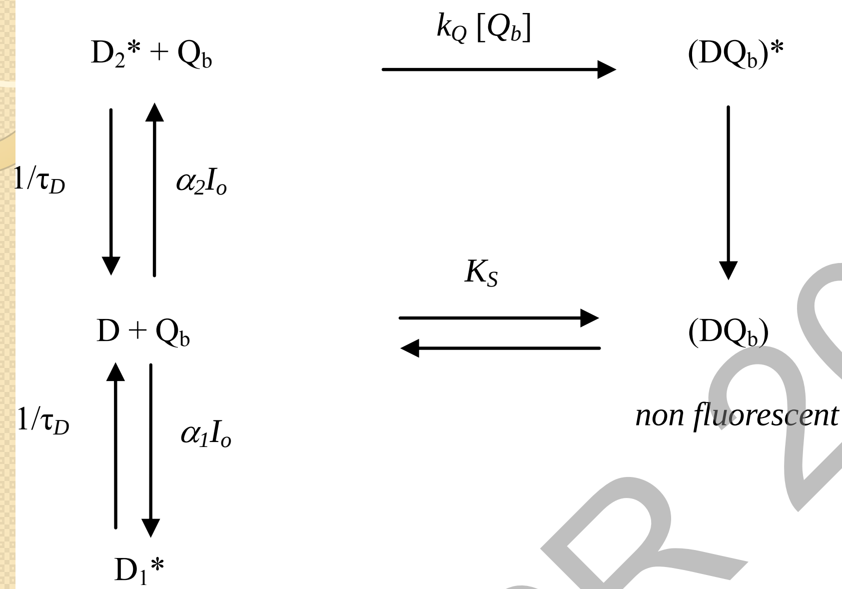


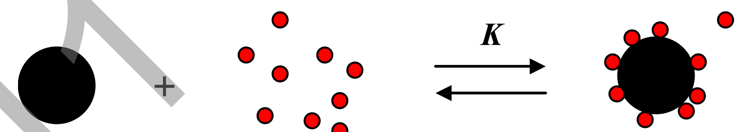
$\langle \tau_0 \rangle / \langle \tau \rangle$ – the hollow symbols, I_0/I – the solid symbols

Mechanism of the Quenching of PIM by TFA



Quenching Pathways of PIM by TFA





$$D + Q_f \underset{}{\overset{K}{\rightleftharpoons}} Q_b$$

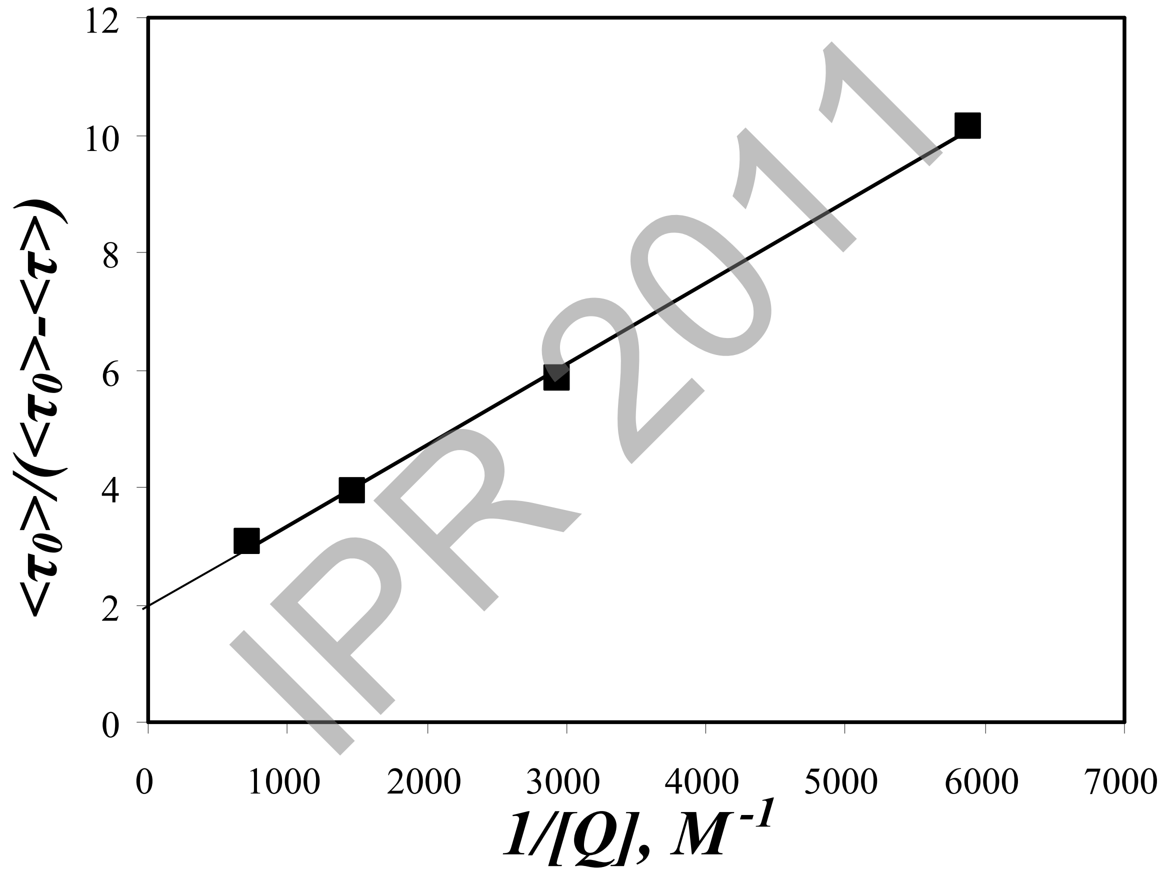
$$\frac{<\tau_o>}{<\tau_o> - <\tau>} = \frac{1}{f_a} + \frac{1}{f_a k_Q \tau_D} \times \frac{1+K[D]}{K[D]} \times \frac{1}{[Q]}$$

$$K = \frac{[Q_b]}{[D][Q_f]} = \frac{[Q_b]}{[D]([Q]-[Q_b])}$$

$$\frac{I_o}{I}\left(1 - f_a + \frac{f_a(1+K[D])}{1+k_Q \tau_D K[D][Q]}\right) = 1 + \frac{K_s K[D]}{1+K[D]}[Q]$$

K is unknown!

Determination of f_a



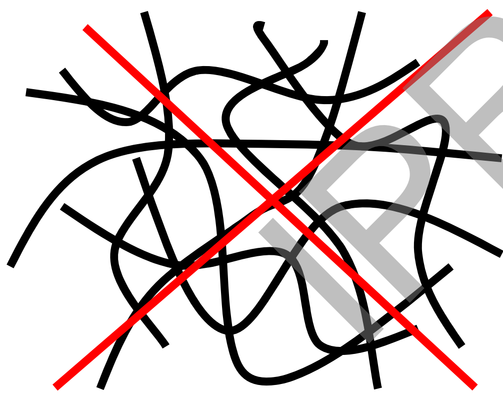
f_a was found to equal 0.51 ⟶ 49 % of the PIM segments are not exposed to the solvent

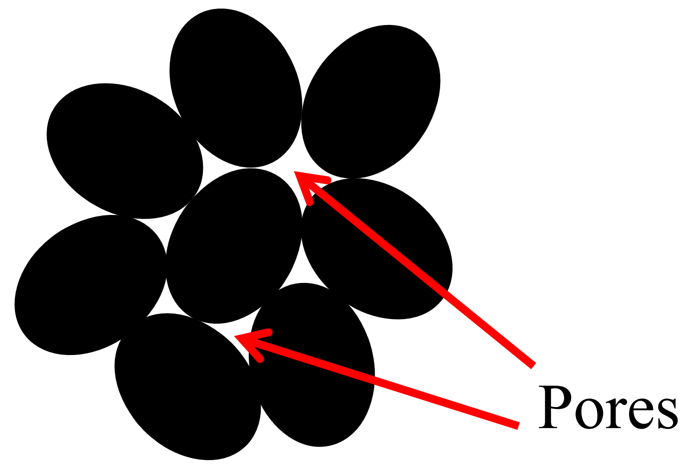
Conclusions

- The fluorescence intensity of the PIM polymer solution is strongly reduced by addition of up to 2 mM TFA, while the intensity of the monomer doesn't change;
- TFA was bound to the outer shell of the PIM polymer coil due to the poor solubility of PIM in DCM;
- Further addition of TFA enhances the solubility of PIM in DCM;

Conclusions

- The pores of PIM membrane are formed by stacking of the domains formed by polymer coils.





Acknowledgement

- Dr Jean Duhamel;
- Dr Detlev Fritsch;
- Duhamel Lab Members;
- Petroleum Research Fund (ACS)
- NSERC

IPR

Institute for Polymer Research

Questions/Comments?