# Predicting the Fraction of Mixing Between Latex Particles

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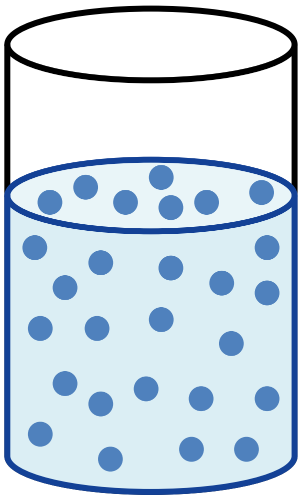
BASF We create chemistry

# Introduction



- Latex:
    - Stable dispersion of polymer particles in an aqueous solution

- Applications:
    - Products: gloves and tires
    - Additives: adhesives and paper coatings
    - Films: paints and coatings

*Tire tread*, <http://mrg.bz/q7fSMj>.

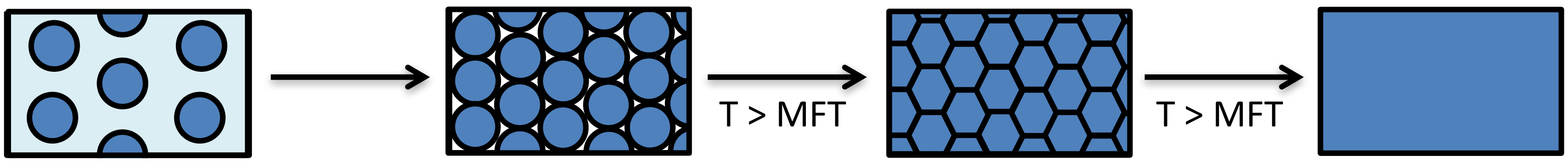
*Painted boards*, <http://mrg.bz/q7fSMj>.

# Film Formation from a Latex Dispersion

Stage 1: Water Evaporation

Stage 2: Particle Deformation

Stage 3: Coalescence



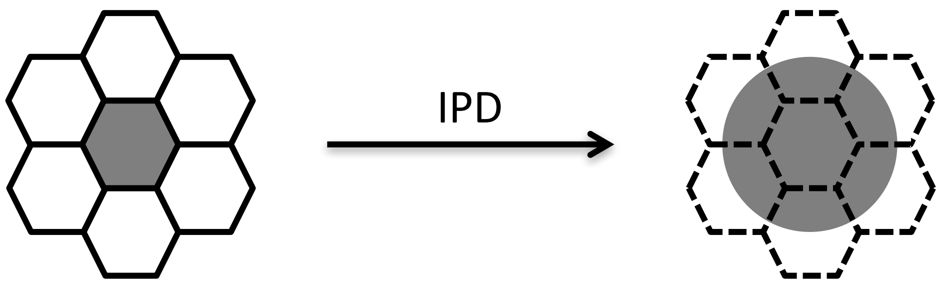

- Poor Mechanical Properties
- Good Mechanical Properties

- The minimum film formation temperature (MFT) must be reached before polymer chains can interdiffuse (MFT ≈ $T_g$)[1]
- Interparticle polymer diffusion (IPD) during the coalescence of latex particles produces a homogeneous film
- Mechanical properties are highly dependent on the extent of IPD[2]

1. Zhao, C., Wang, Y., Hruska, Z., Winnik, M. Molecular Aspects of Latex Film Formation: An Energy-Transfer Study; *Macromolecules* **1990**, 23, 4082-4087.
2. Gauthier, C.; Guyot, A.; Perez, J.; Sindt, O. Film Formation and Mechanical Behavior of Polymer Laticies. *Film Formation in Waterborne Coatings,* Chapter 10, **1996,** 163-178. Washington, DC: American Chemical Society.

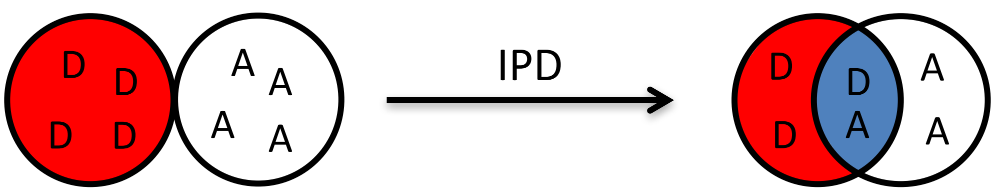
# Quantification of IPD

## Small Angle Neutron Scattering (SANS)




- Deuterated polymers are expensive
- Requires a neutron source
- Small particles only

## Fluorescence Resonance Energy Transfer (FRET)

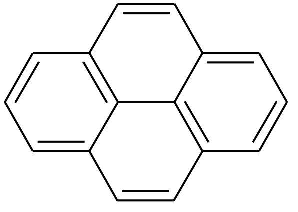



- Both latexes must be labeled with dyes
- Requires time-resolved fluorescence

# Probing IPD:

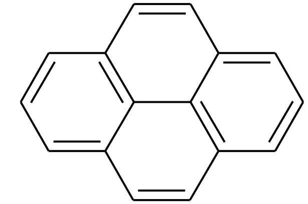
# Pyrene Excimer Fluorescence (PEF)

- A simpler method to probe the degree of interparticle polymer diffusion (IPD) in latex films[1]
- Using  a fluorescently-labeled latex with an emission that changes depending on the degree of IPD
- A single fluorophore pyrene (Py) can be used
  - Only one fluorescently-labeled latex is required
- Steady-state fluorescence can be used

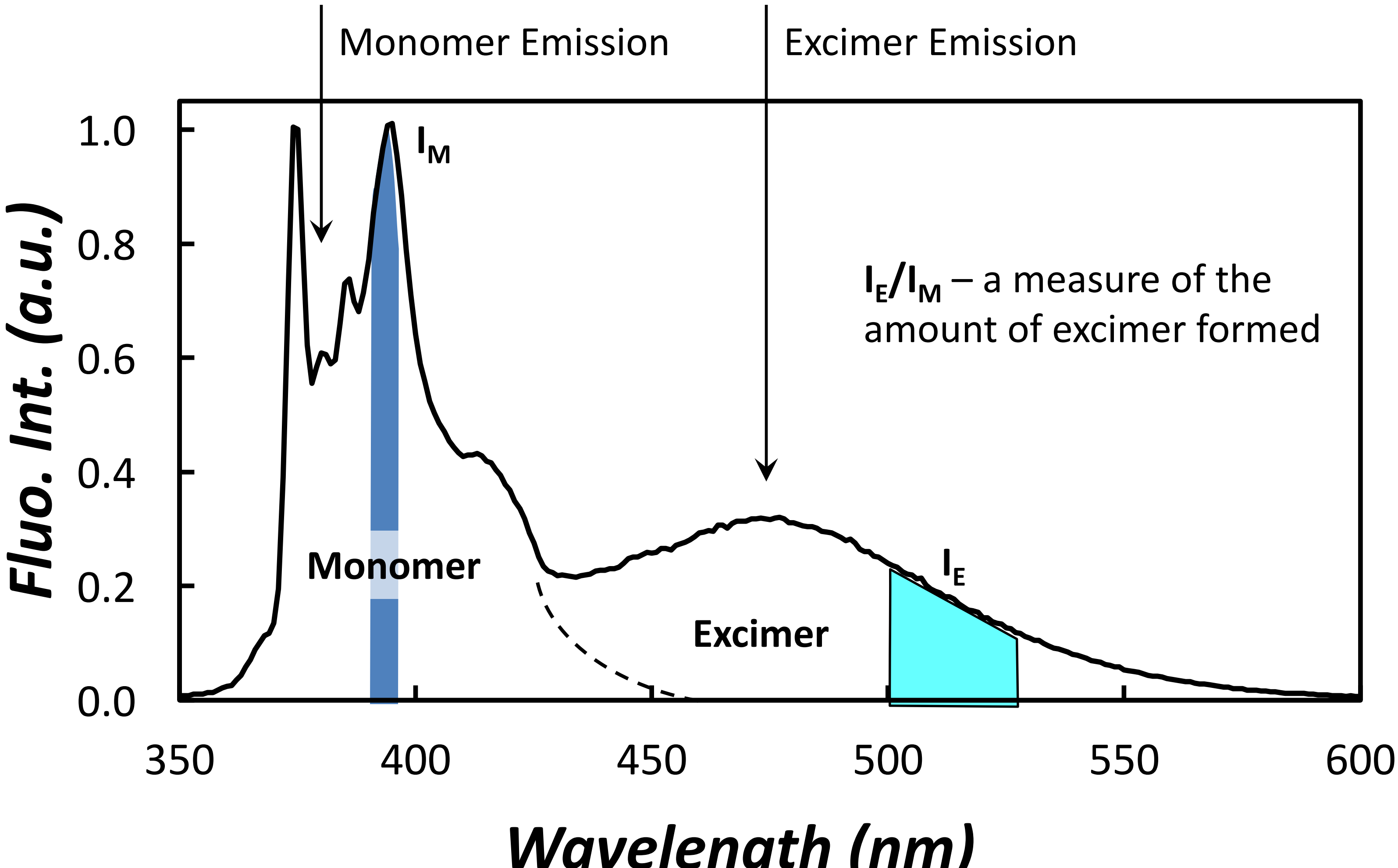


1. Casier, R.; Gauthier, M.; Duhamel, J. Using Pyrene Excimer Fluorescence to Probe Polymer Diffusion in Latex Films. *Macromolecules* **2017**, *50*, 1635–1644.

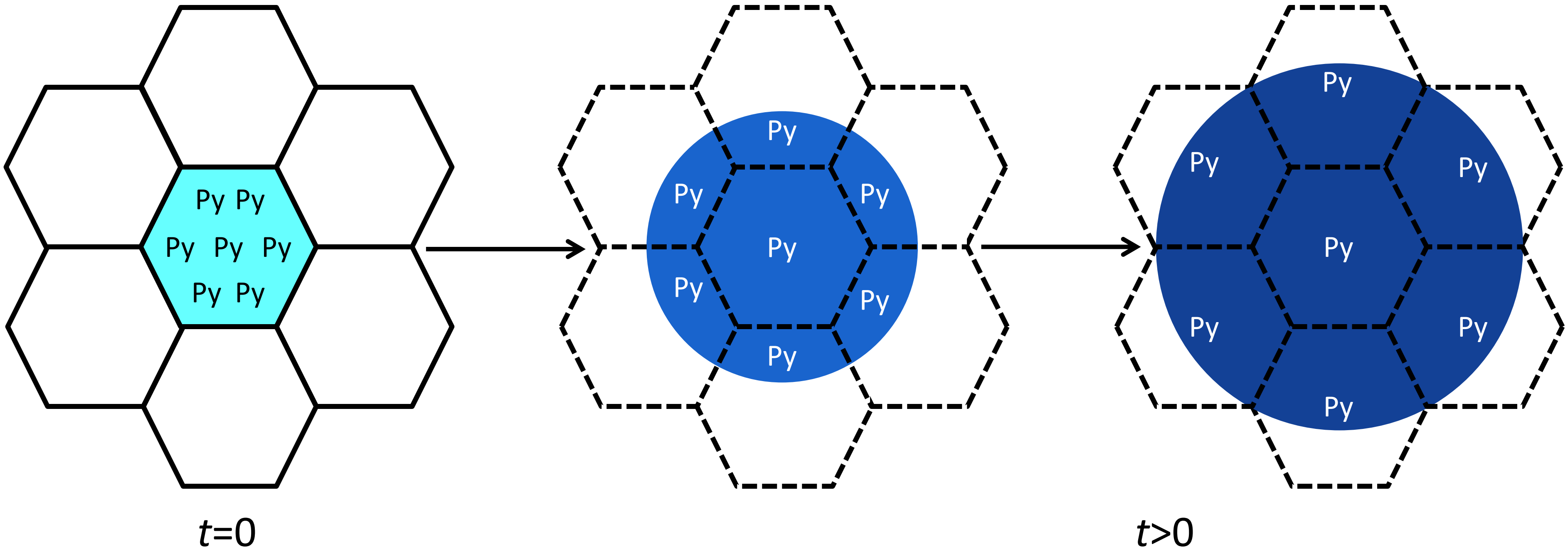
# Pyrene Fluorescence



$$Py + Py \xrightarrow{h\nu} Py^* + Py \longrightarrow (PyPy)^* \xleftarrow{h\nu} (PyPy)$$



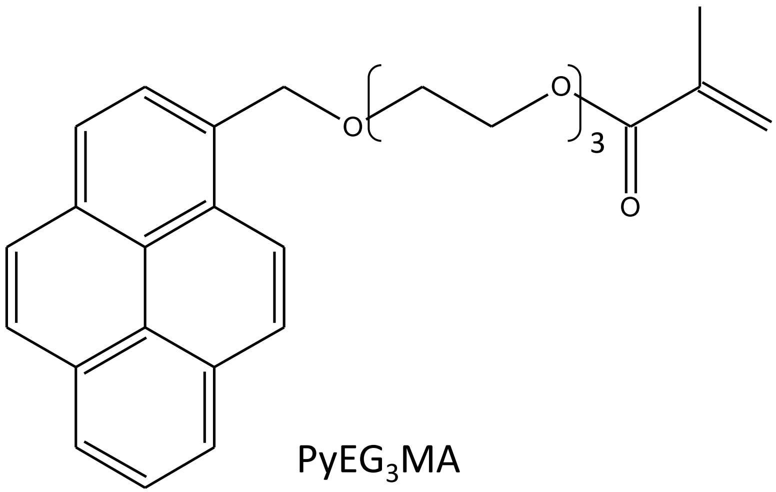
# Interparticle Polymer Diffusion using PEF




- High $C_{py}$
- Lots of excimer formation
- High $I_E/I_M$ ratio

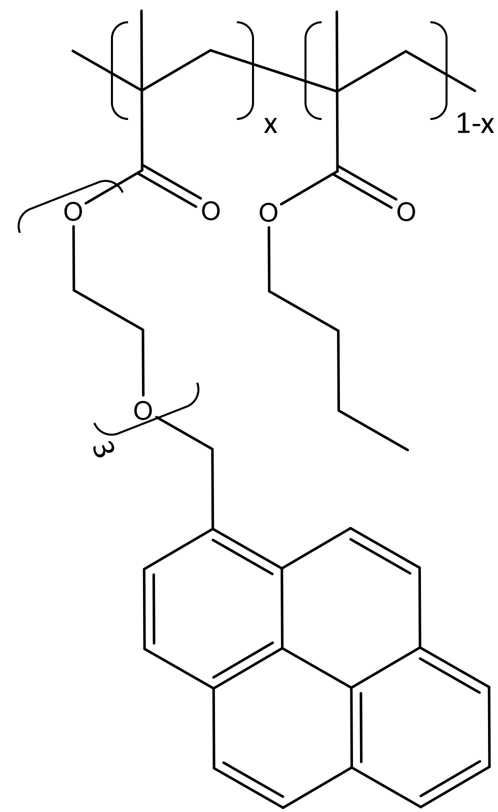
- Low $C_{Py}$
- Little excimer formation
- Low $I_E/I_M$ ratio

# Pyrene Labeled Latex




PyEG$_3$MA

- Hydrophobicity of the monomer was controlled by varying the length of the oligo(ethylene glycol) unit



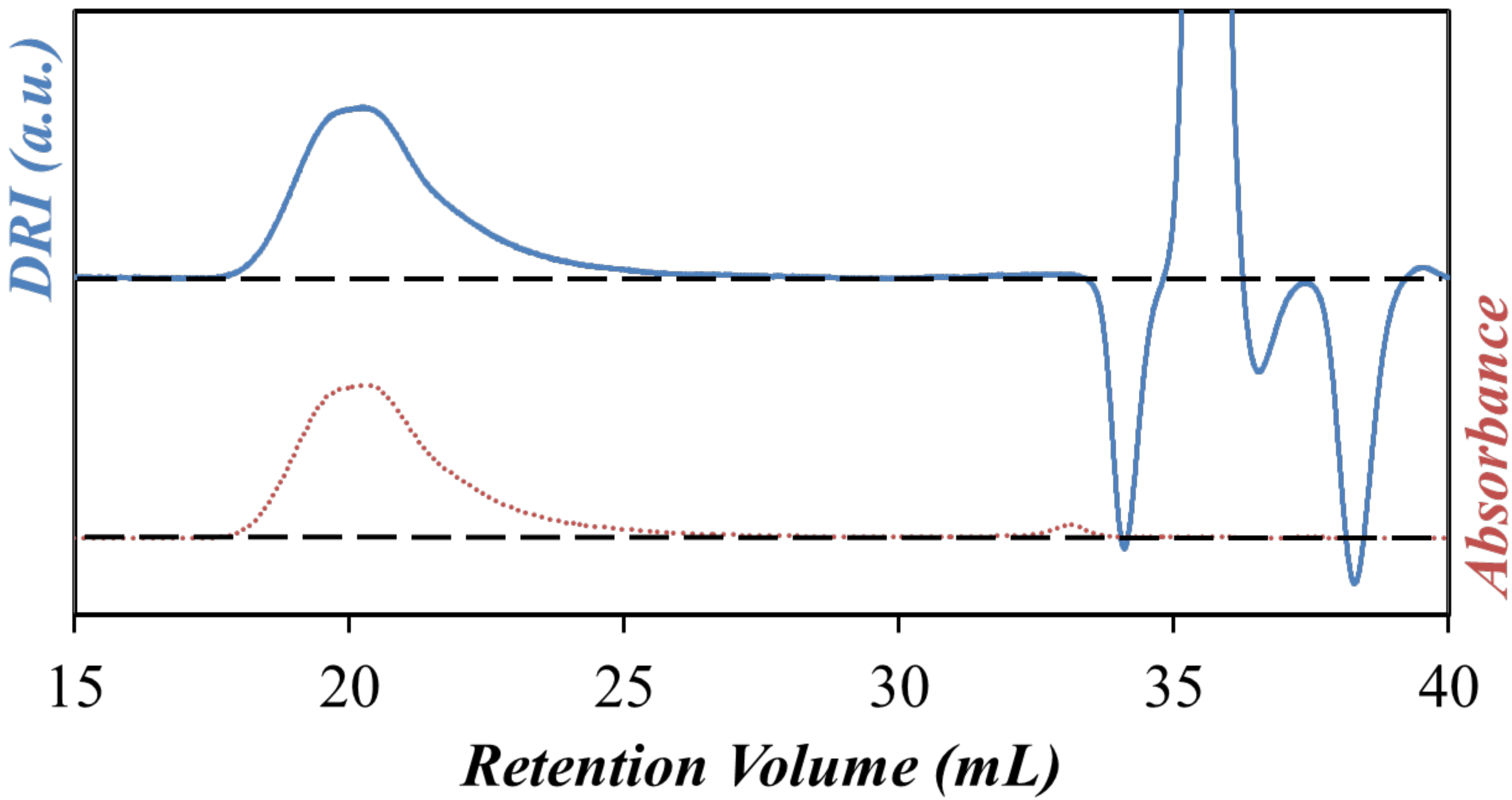

- Semi-batch emulsion process

- Copolymerized with *n*-butyl methacrylate (BMA) to yield a poly(*n*-butyl methacrylate) randomly labeled with pyrene (Py-PBMA)

Py-PBMA Latex

# GPC: Py-PBMA-Latex-1

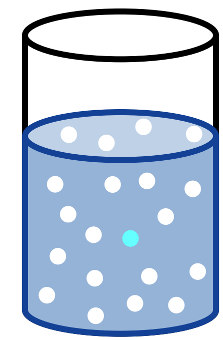
| Sample | PyLM | PyLM Incorporated (mol%) | Particle Size (nm) | PSD | $M_w$ (kg/mol) | Đ |
|---|---|---|---|---|---|---|
| Py-PBMA-Latex-1 | $PyEG_3MA$ | 1.9 | 118 | 1.04 | 820 | 1.9 |
| Py-PBMA-Latex-2 | $PyEG_3MA$ | 1.8 | 120 | 1.04 | 360 | 1.8 |

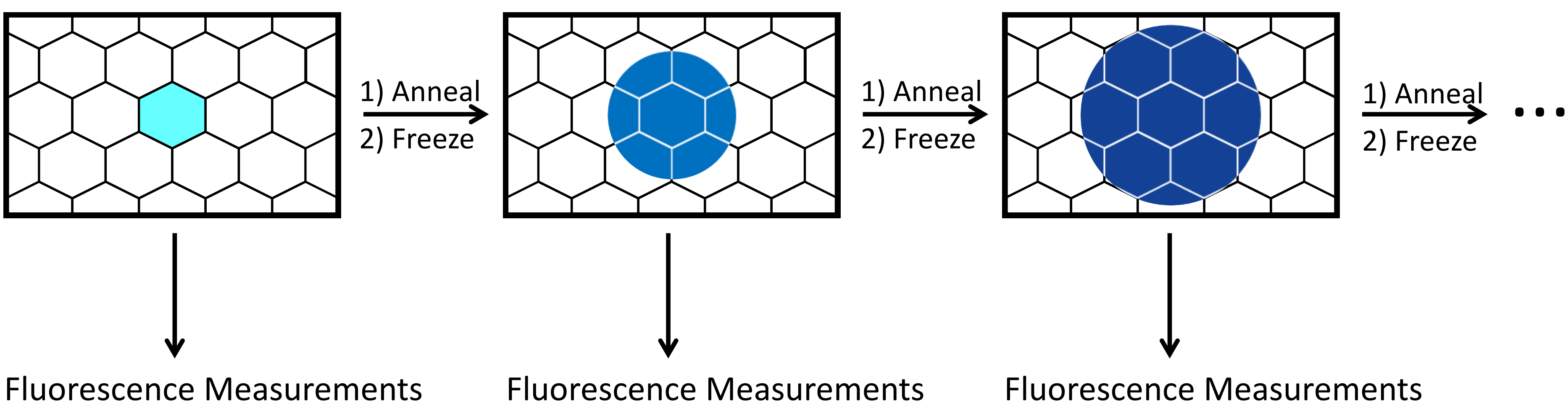


# Film Preparation and Annealing

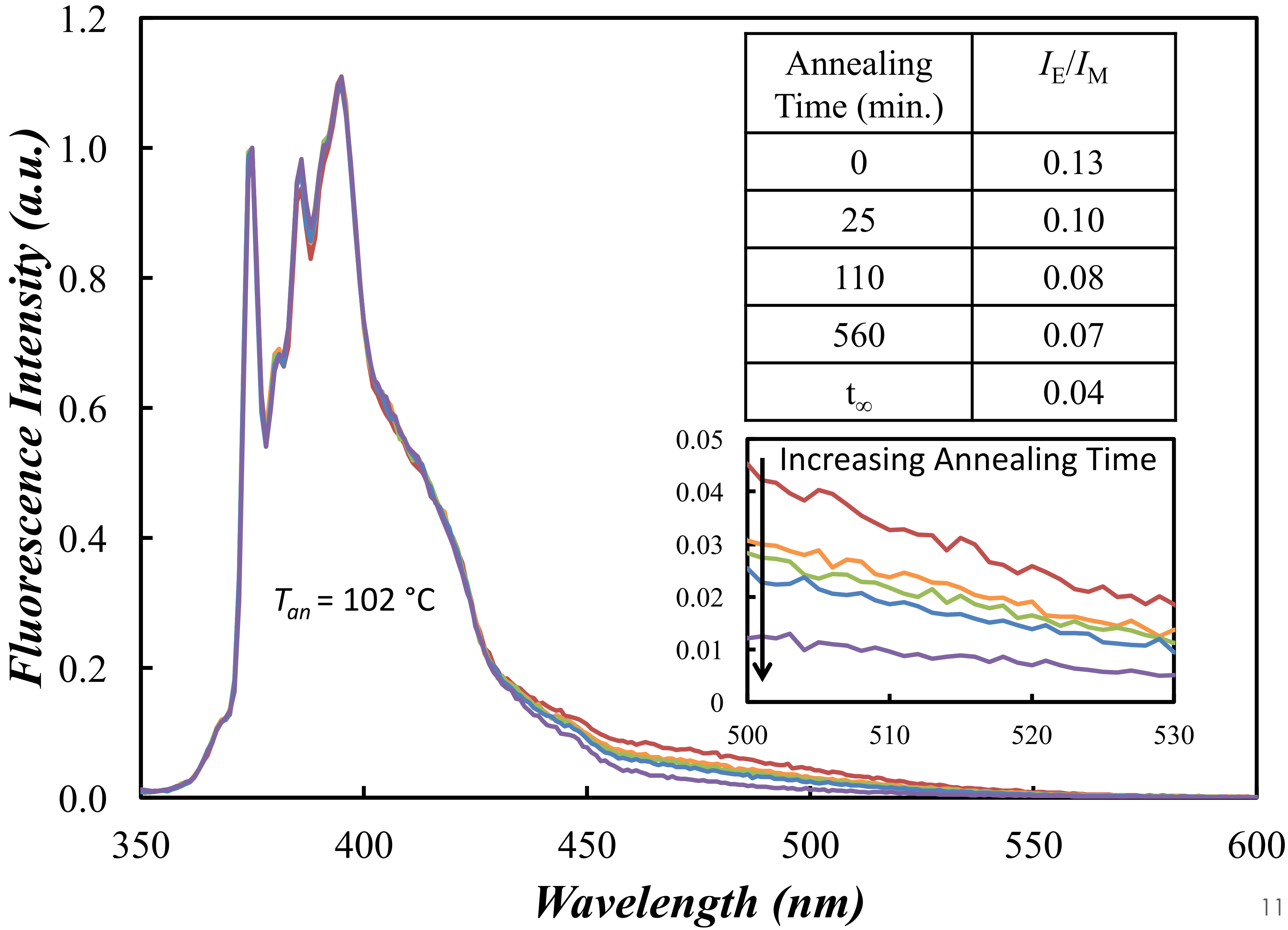
- A film was prepared from a mixture of 5 wt% Py-PBMA-latex in 95 wt% PBMA-latex

| Film | Latex | Latex Pyrene Content (mol%) | Particle Size (nm) | *PSD* | $M_w$ (kg/mol) | *Đ* | Weight Fraction |
|---|---|---|---|---|---|---|---|
| **1** | Py-PBMA-Latex-1 | 1.9 | 118 | 1.04 | 820 | 1.9 | 0.05 |
| | PBMA-Latex-1 | 0 | 95 | 1.04 | 1,000 | 2.0 | 0.95 |
| **2** | Py-PBMA-Latex-2 | 1.8 | 120 | 1.04 | 360 | 1.8 | 0.05 |
| | PBMA-Latex-2 | 0 | 119 | 1.04 | 320 | 1.7 | 0.95 |





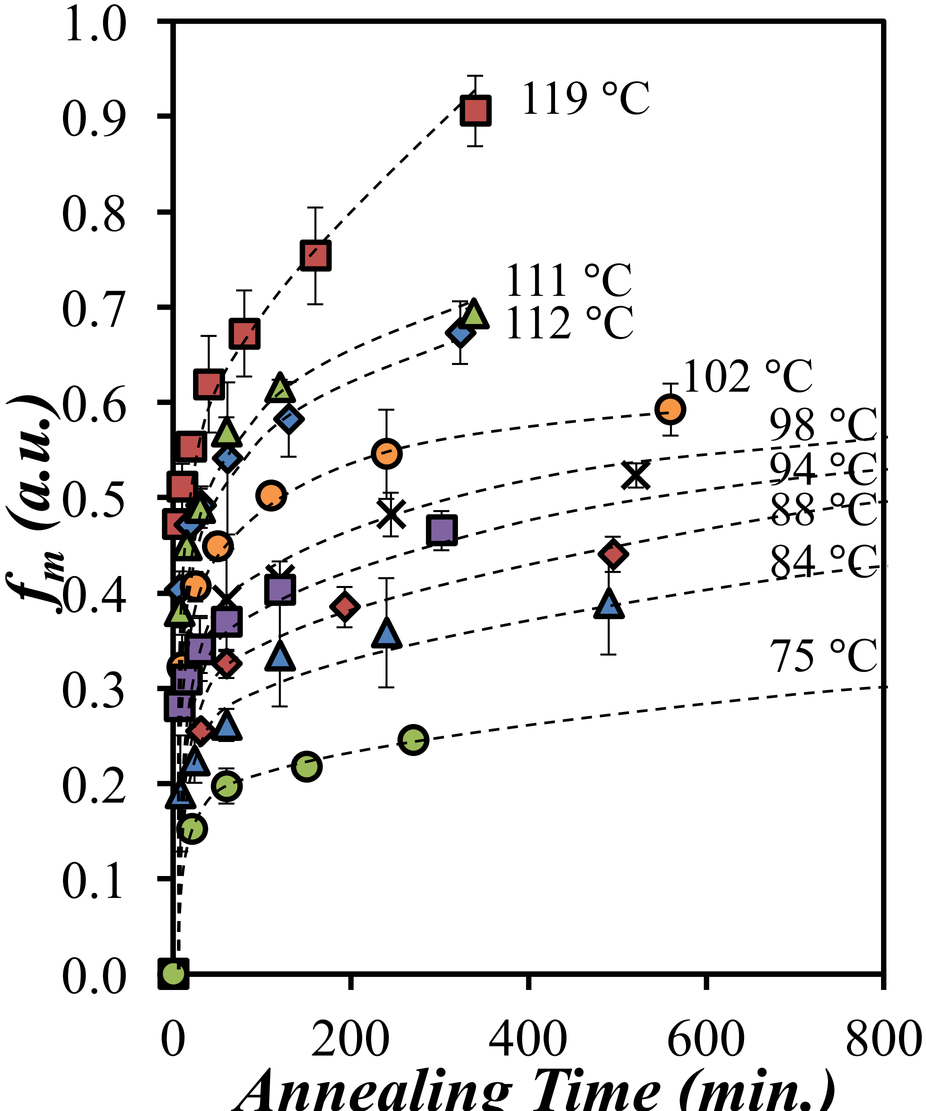
# Steady-State Fluorescence: Film 1



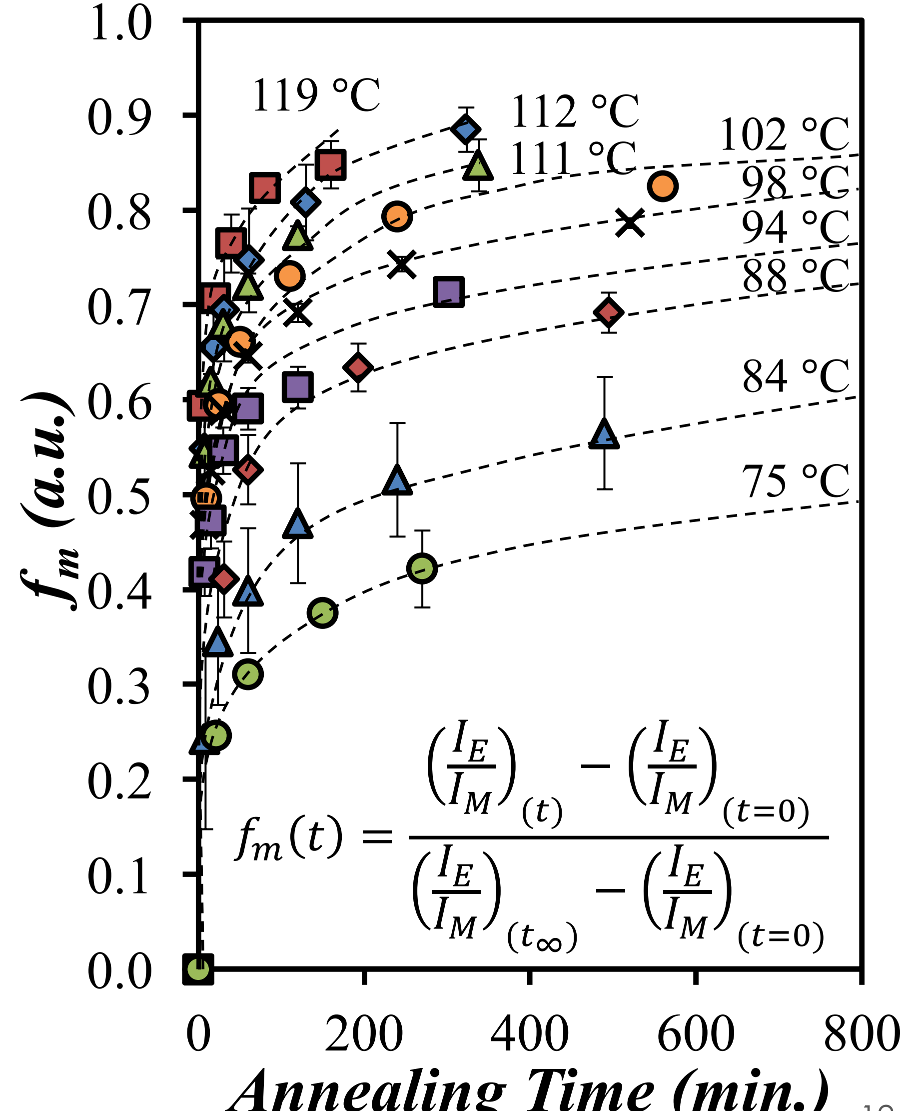

| Annealing Time (min.) | $I_E/I_M$ |
|---|---|
| 0 | 0.13 |
| 25 | 0.10 |
| 110 | 0.08 |
| 560 | 0.07 |
| $t_\infty$ | 0.04 |

# Fraction of Mixing

*Film 1: $M_w$ = 820 kg/mol*

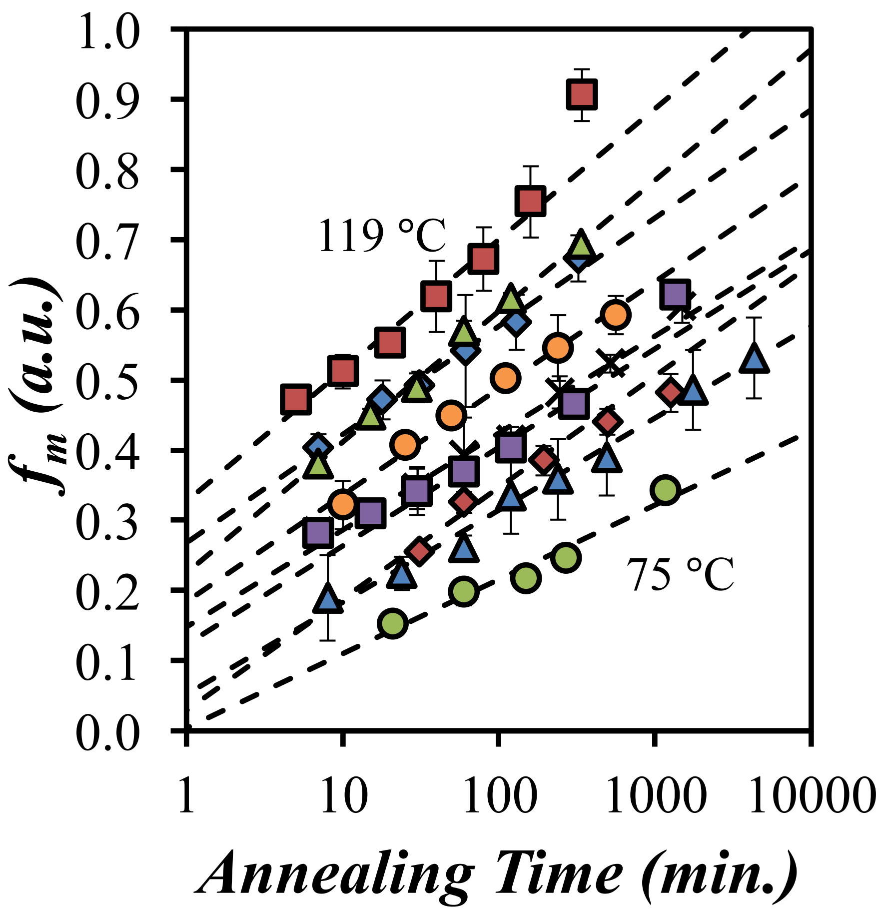



*Film 2: $M_w$ = 360 kg/mol*

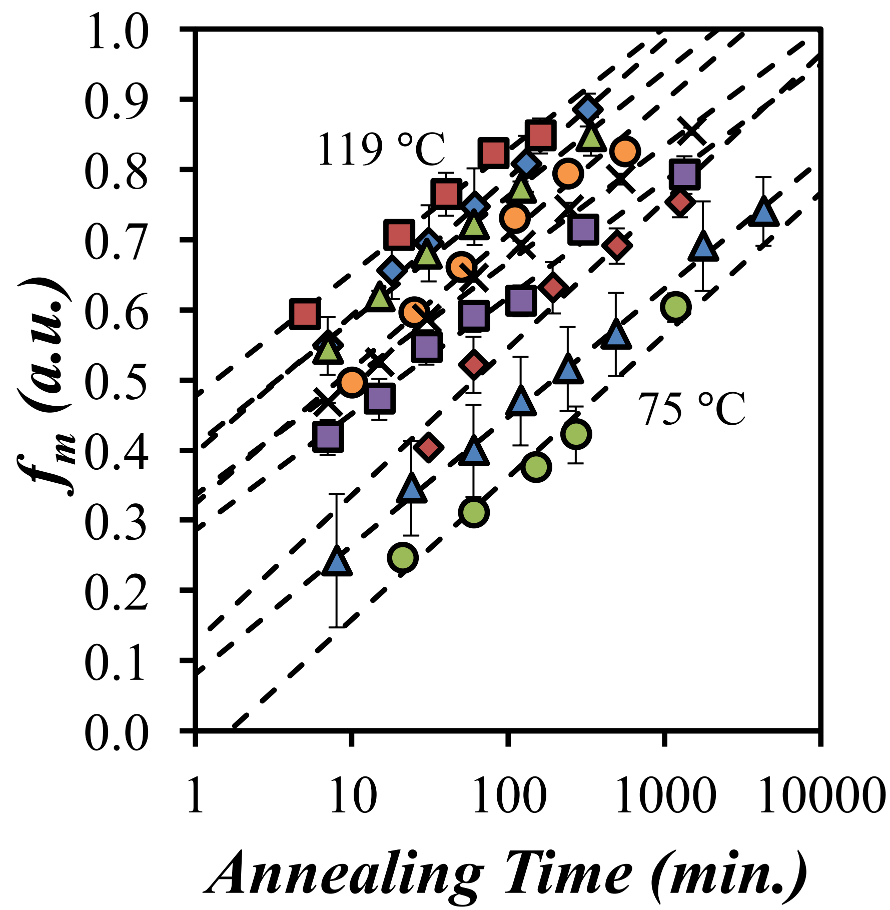


# Fraction of Mixing: Linear Trend

*Film 1: $M_w$ = 820 kg/mol*



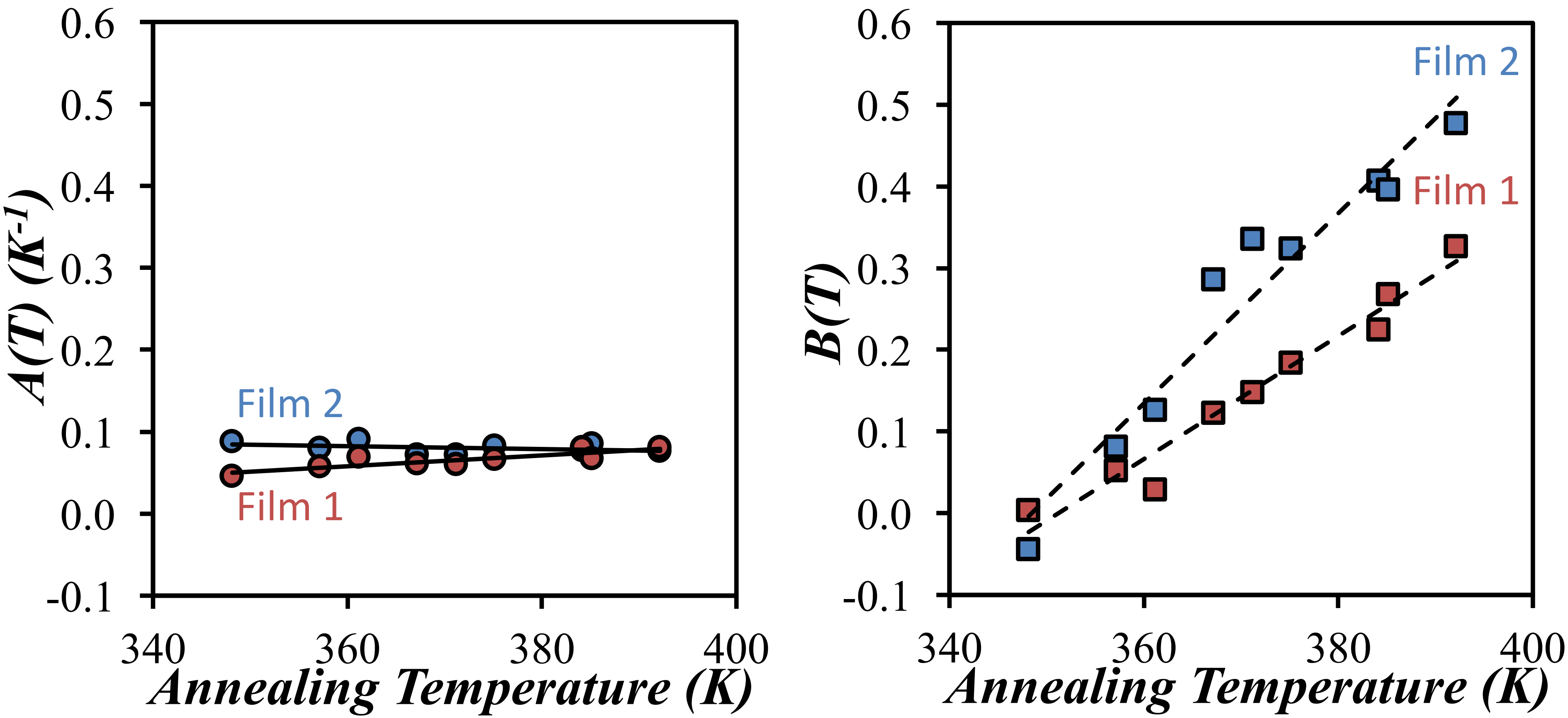

*Film 2: $M_w$ = 360 kg/mol*




$$f_m\left(T,t_{an}\right)=A\left(T\right)\cdot\ln(t_{an})+B\left(T\right)$$

# $f_m$: Slopes and Intercepts

$$f_m\left(T,t_{an}\right)=A\left(T\right)\ln(t_{an})+B\left(T\right)$$



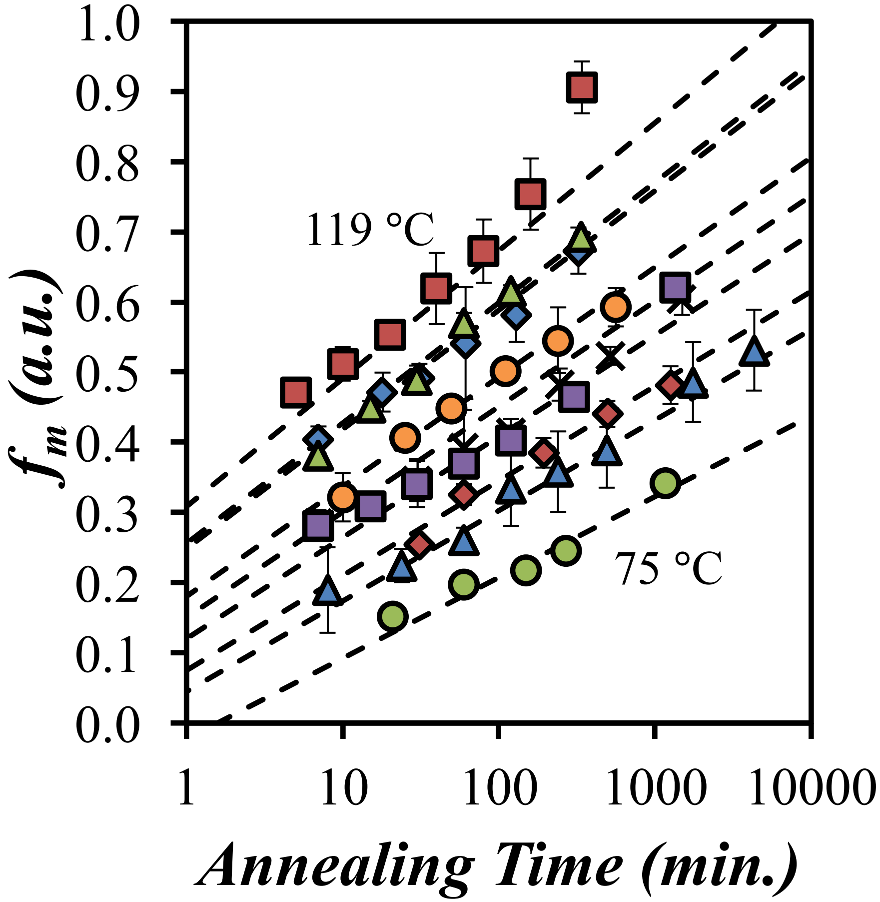

Film 1: $f_m\left(T,t_{an}\right)=\left(6.71\times10^{-4}T-0.184\right)\ln\left(t_{an}\right)+\left(7.74\times10^{-3}T-2.65\right)$

Film 2: $f_m\left(T,t_{an}\right)=\left(-0.172\times10^{-4}T+0.144\right)\ln\left(t_{an}\right)+\left(1.16\times10^{-2}T-4.05\right)$

# Predicting $f_m$: Time and Temperature

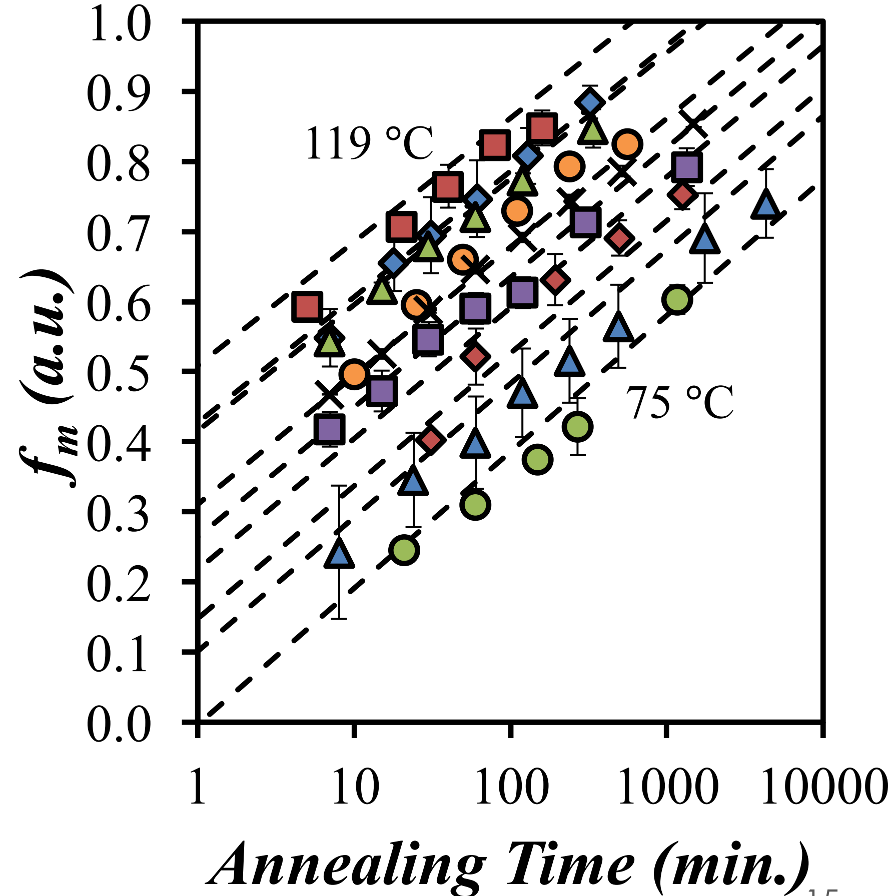
*Film 1: $M_w$* = 820 kg/mol

$$f_m(T, t_{an}) = \left(6.71\times10^{-4}T - 0.184\right)\ln\left(t_{an}\right) + \left(7.74\times10^{-3}T - 2.65\right)$$




*Film 2: $M_w$* = 360 kg/mol

$$f_m(T, t_{an}) = \left(-0.172\times10^{-4}T + 0.144\right)\ln\left(t_{an}\right) + \left(1.16\times10^{-2}T - 4.05\right)$$



# Applications

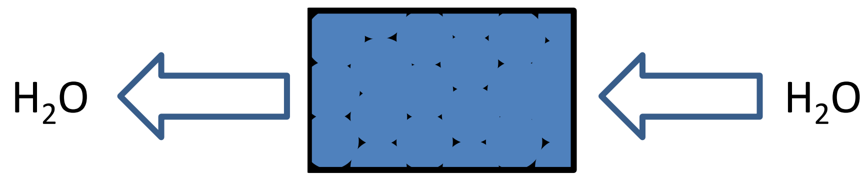
- The **properties** of a film are directly related to the extent of coalescence[1]

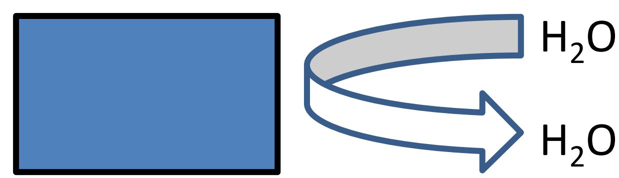
$$f_m(T, t_{an}) = A(T)\ln(t_{an}) + B(T) \quad \Rightarrow \quad \boxed{t_{an} = \exp\left(\frac{f_m^{\ desired} - B(T)}{A(T)}\right)}$$

- Predict the coalescence time required to reach a specific $f_m$.

Example:

- Abrasion resistance
  - Mechanically robust
  - Low $f_m \approx 0.4$
    - Film 1 (102 °C) $t_{an}$ = 34 min.
- Corrosion resistance
  - Void-free
  - High $f_m \approx 0.95$
    - Film 1 (102 °C) $t_{an}$ = 3 months

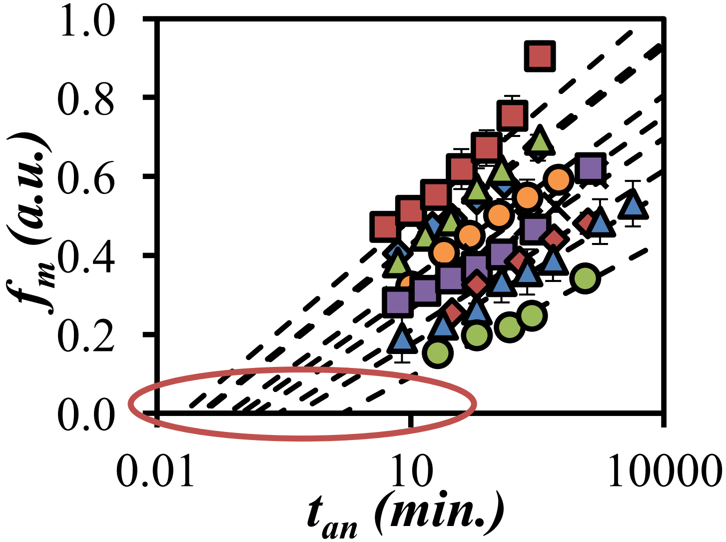


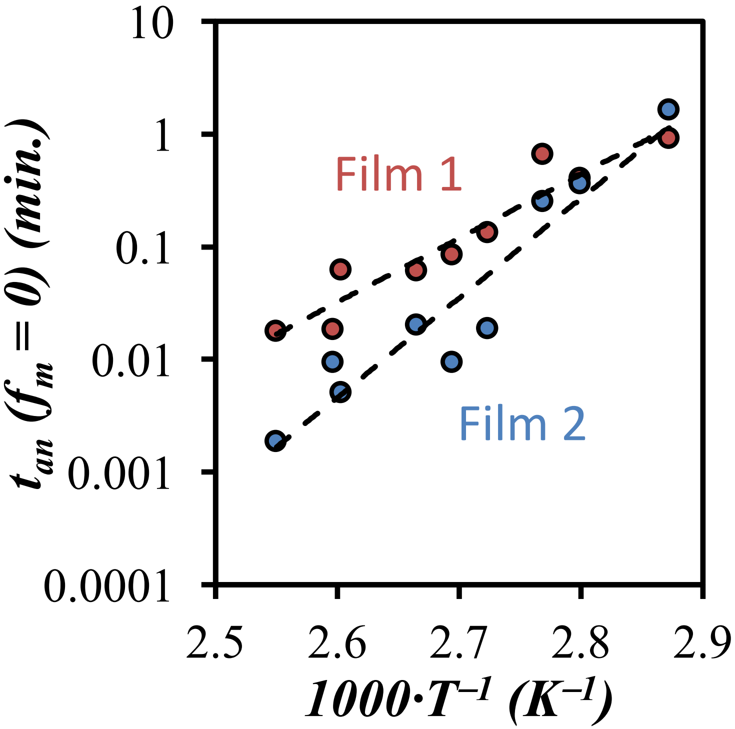





1. Gauthier, C.; Guyot, A.; Perez, J.; Sindt, O. Film Formation and Mechanical Behavior of Polymer Laticies. *Film Formation in Waterborne Coatings,* Chapter 10, **1996,** 163-178. Washington, DC: American Chemical Society.

# Onset Time for Diffusion

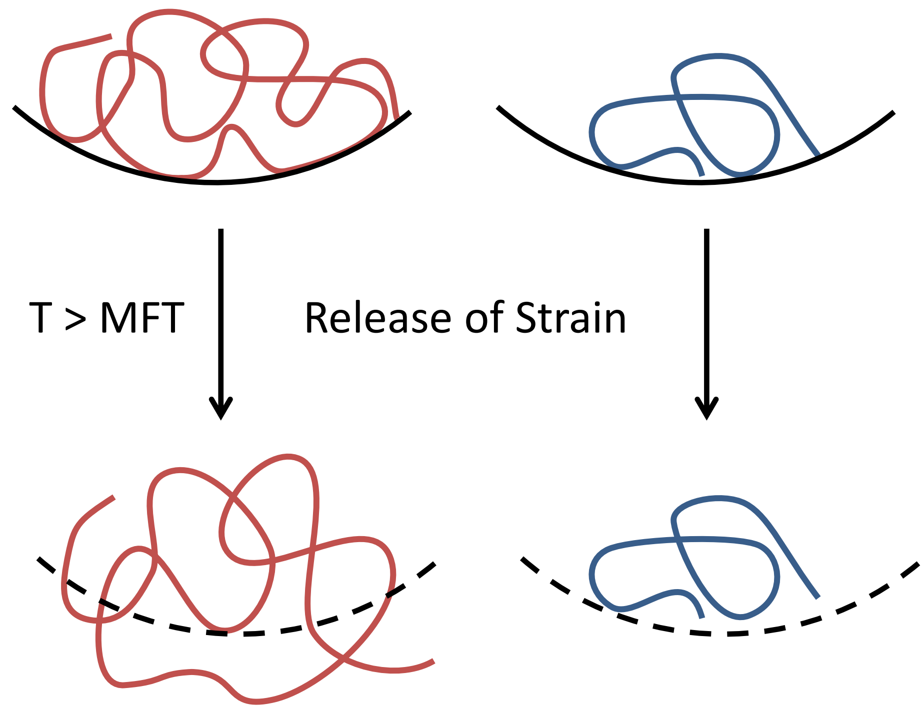



Film 1 ($M_w$ = 820 kg/mol): **$E_a$ = 109 ± 13 kJ/mol**

Film 2 ($M_w$ = 360 kg/mol): **$E_a$ = 169 ± 21 kJ/mol**

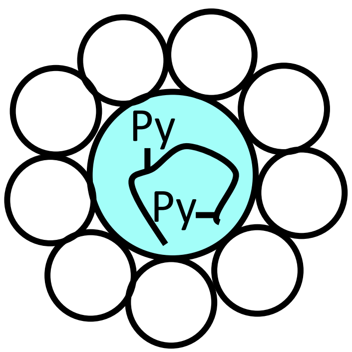
Why do the chains in Film 1 flow sooner?



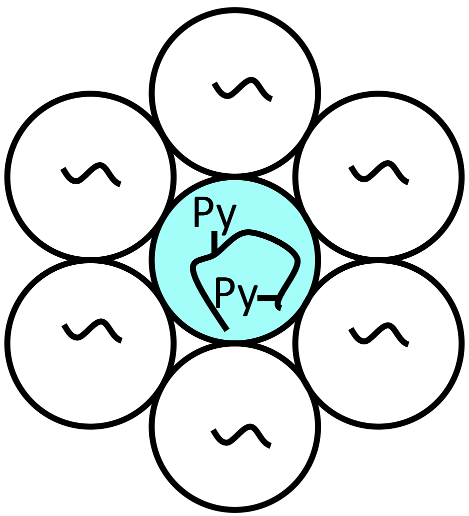
# Future Work

Probe the diffusion between asymmetric latex nanoparticles:

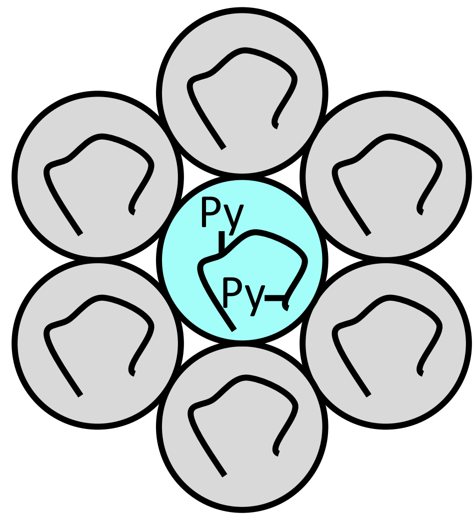
- Particle size



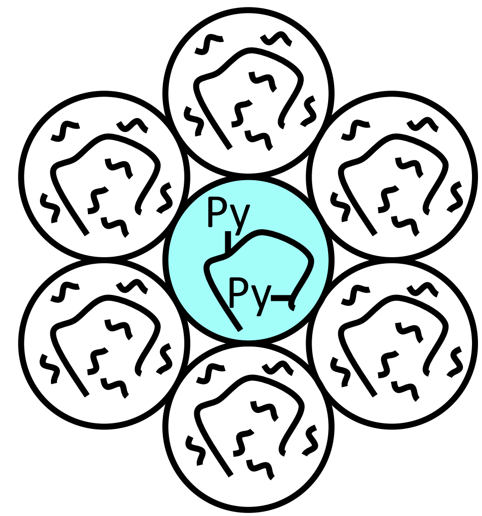

- Molecular weight




- Polymer Type




- Plasticizer Content




Zehou You: Poster Session

Increase pyrene monomer incorporation to enhance excimer formation

# Acknowledgements

Supervisors:

Prof. Jean Duhamel

Prof. Mario Gauthier

All members of the Duhamel and Gauthier groups.

Thank you for your attention!

# Why Use Pyrene Excimer Formation?

| **Requirement** | ***FRET*** | **Pyrene Excimer Formation** |
|---|---|---|
| Instrumentation | Time-resolved fluorometer<br>(complex and expensive) | Steady-state fluorometer<br>(simple and inexpensive) |
| Data Acquisition | ~ 10 minutes per decay | ~ 30 seconds per spectrum |
| Fluorescence Analysis | Decay must be modeled, fitted, and then integrated | $I_E/I_M$ ratio |
| Fluorescently-Labeled Latex | 2<br>(donor labeled, acceptor labeled) | 1<br>(pyrene labeled) |
| Film Composition | 100 wt% labeled-latex | ≤ 5 wt% labeled-latex<br>≥ 95 wt% native-latex |
| Latex Nanoparticles | Symmetrical | Symmetrical or Asymmetrical |