Use of Pyrene Excimer Fluorescence to Probe Polymer Chain Diffusion between Latex Particles during Film Formation

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Introduction

Latex:

- Stable dispersion of polymer particles in an aqueous solution

Applications:

- Products such as gloves and balloons
- Additive to glues and paper coatings
- Paints and coatings
**Film Formation from a Latex Dispersion**

**Stage 1:**
Water Evaporation

**Stage 2:**
Particle Deformation

**Stage 3:**
Coalescence

- Interparticle polymer diffusion (IPD) during coalescence of the latex particles produces a homogeneous film.

- The minimum film formation temperature (MFT) must be reached before polymer chains can interdiffuse ($\text{MFT} \approx T_g$)\(^1\)

# Background

- Previous studies of latex film formation by Winnik\textsuperscript{1-2} have primarily used fluorescence resonance energy transfer (FRET) to probe IPD

- Two dyes used: Phenanthrene as a donor and anthracene as an acceptor

- Time resolved fluorescence decays are obtained for various annealing times

\[ I_D(t) = B_1 \exp \left[ -\frac{t}{\tau_D} - P \left( \frac{t}{\tau_D} \right)^{\frac{1}{2}} \right] + B_2 \exp \left( -\frac{t}{\tau_D} \right) \]

Proposal

- Develop a simpler method to probe the minimum film formation temperature (MFT) and the degree of interparticle polymer diffusion (IPD) in latex films

- Use a fluorescently-labelled latex with an emission that changes depending on the degree of IPD

- A single fluorophore pyrene (Py) can be used, thus only a single fluorescently-labelled latex must be prepared
Pyrene Excimer Fluorescence

hv + Py + Py → Py* + Py → (Py Py)*

Monomer Emission

Excimer Emission

$I_E/I_M$ – a measure of the amount of excimer formed
Interparticle Polymer Diffusion

At $t=0$:
- High $C_{Py}$
- Lots of excimer formation
- High $I_E/I_M$ ratio

At $t>0$:
- Low $C_{Py}$
- Minimal excimer formation
- Low $I_E/I_M$ ratio
Pyrene Labeled Monomer (PyLM)

- Water solubility can be tuned by varying the length of the oligo(ethylene glycol) unit
- Copolymerized with \( n \)-butyl methacrylate to yield a pyrene labeled poly(butyl methacrylate) latex (Py-PBMA Latex)

1-pyrenylmethoxy-2-ethoxy-2-ethoxy-2-ethoxy methacrylate (Py-\( \text{EG}_3 \)-MA)
1-Pyrenylmethoxy-2-Ethoxy-2-Ethoxy-2-Ethanol

\[ \text{Br} + \text{AgO}_2 \text{, 2 eq.} \quad \text{CH}_2\text{Cl}_2 \quad \text{1 eq.} \]

1.05 eq.
2-(1-Pyrenylmethyloxy)ethyl Methacrylate (Py-EG-MA)

1 eq. + 1.5 eq. \[\text{DMAP} \quad \text{CH}_2\text{Cl}_2\] \[\rightarrow\]

Py

9.0 1.0 1.0 2.0 2.0 10.0 2.7
Low solids content (2 g \(n\)-butyl methacrylate in 66 mL H\(_2\)O)

Surfactant: 50 mg dioctyl sodium sulfosuccinate (AOT) (0.8 mol\%, based on monomer)
- Less surfactant used led to unstable particles, and the formation of coagulum (up to 40 wt\% of the monomer used)
- More surfactant led to very small particles

Initiator: 5 mg ammonium persulfate (APS) (0.15 mol\%, based on monomer)

Conditions: 80 °C for 3 hours, stirred at 550 RPM

90 – 100 nm particle size, \(d_1/d_2 < 1.05\)

<table>
<thead>
<tr>
<th>Reaction Volume (mL)</th>
<th>Particle Diameter (nm)</th>
<th>(d_1/d_2)</th>
<th>(M_n) (kg/mol)</th>
<th>(\bar{D})</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>95</td>
<td>1.04</td>
<td>510</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Emulsion Containing Py-EG$_3$-MA

- **Initial Charge**
  - 63 mL deionized water with 58 mg AOT and 5 mg APS

- **Monomer Feed**
  - 2.1 g BMA, 0.3 g Py-EG$_3$-MA (5 mol%) and 20 mg AOT was emulsified with 1 mL deionized water

- Monomer was fed in over 3 hours at 80 °C with a stirring rate of 550 rpm

- Reaction was stopped immediately after to help prevent the formation of low molecular weight pyrene containing species

- Particle size of 118 nm with a d$_1$/d$_2$ of 1.04

- Pyrene labelling level of 1.9 mol%
Py-PBMA Latex GPC Trace

![Graph showing DRI and Abs. (a.u.) vs. Retention Volume (mL)]

Retention Volume (mL)
Removal of Unbound Pyrene

- Only polymer-bound pyrene can be used to probe interparticle polymer diffusion during film formation

- If any free pyrene remains, the diffusion of the small pyrene-containing molecules will be measured

- Dialysis (50 kg/mol MWCO) was used to remove low molecular weight species while maintaining a stable emulsion

- A mixture of 20 vol% ethanol in water containing 2.5 mM AOT was used to accelerate the removal of the hydrophobic PyLM
Dialysis of the Py-PBMA Latex

- The pyrene content of the dialysate was measured by steady-state fluorescence
- Particle size remained unchanged after dialysis
After Dialysis

\[ \text{M}_n: 430 \text{ kg/mol} \quad \mathcal{D}: 1.9 \]
A film was prepared from a mixture of 5 wt% Py-PBMA-latex in 95 wt% PBMA-latex

<table>
<thead>
<tr>
<th>Latex Sample</th>
<th>Py Content (mol%)</th>
<th>Particle Diameter (nm)</th>
<th>d₁/d₂</th>
<th>Mₙ (kg/mol)</th>
<th>Đ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBMA</td>
<td>0</td>
<td>95</td>
<td>1.04</td>
<td>510</td>
<td>2.0</td>
</tr>
<tr>
<td>Py-PBMA</td>
<td>1.9</td>
<td>118</td>
<td>1.04</td>
<td>430</td>
<td>1.9</td>
</tr>
</tbody>
</table>

After the film had dried for 3 hours under nitrogen:
1. Annealed in a glass tube submerged in an oil bath
2. Rapidly cooled to room temperature with an aluminum block
3. Analysed by steady-state fluorescence
Steady-State Fluorescence

$T_{an} = 82 \, ^\circ C$

<table>
<thead>
<tr>
<th>Annealing Time (min.)</th>
<th>$I_E/I_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.22</td>
</tr>
<tr>
<td>7</td>
<td>0.19</td>
</tr>
<tr>
<td>30</td>
<td>0.17</td>
</tr>
<tr>
<td>120</td>
<td>0.16</td>
</tr>
<tr>
<td>$t_{\infty}$</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Increasing Annealing Time.
Fraction of Mixing

\[ f_m(t) = \frac{(\frac{I_E}{I_M})_{(t)} - (\frac{I_E}{I_M})_{(t=0)}}{(\frac{I_E}{I_M})_{(t=\infty)} - (\frac{I_E}{I_M})_{(t=0)}} \]

Annealing Time (min.)

Py

Py

Py

Py

149 °C

114 °C

82 °C

Annealing Time (min.)
Polymer Chain Diffusion Coefficient ($D$)

- Concentration profile of molecules diffusing out of a spherical particle of radius $R$ using Fick’s law:

$$C_{Py}(r, t, D) = \frac{C_0}{2} \left[ \text{erf} \left( \frac{R + r}{\sqrt{2Dt}} \right) + \text{erf} \left( \frac{R - r}{\sqrt{2Dt}} \right) \right] - \frac{C_0}{r} \left( \frac{Dt}{\pi} \right)^{1/2} \left[ \exp \left( \frac{(R - r)^2}{4Dt} \right) - \exp \left( - \frac{(R + r)^2}{4Dt} \right) \right]$$

Calculated $f_m$: 

$$f_m^{calc}(t) = \frac{M_t}{M_\infty}$$

Where $M_t$ is the mass that has diffused across the particle interface at time $t$.

$$M_t = M_\infty - \int_0^R C_{Py}(r, t, D) \cdot 4\pi r^2 dr$$

$$M_\infty = \frac{4}{3} \pi R^3 C_0$$

$$f_m^{calc}(t) = 1 - \frac{\int_0^R C_{Py}(r, t, D) \cdot 4\pi r^2 dr}{\frac{4}{3} \pi R^3 C_0}$$

By setting $f_m^{calc}$ equal to the experimental $f_m$ and numerically integrating $C_{Py}$, the diffusion coefficient $D$ can be found.

$$f_m(t) = \frac{\left(\frac{I_E}{I_M}\right)_t - \left(\frac{I_E}{I_M}\right)_{t=0}}{\left(\frac{I_E}{I_M}\right)_{t=\infty} - \left(\frac{I_E}{I_M}\right)_{t=0}}$$
Diffusion Coefficients

![Graph showing diffusion coefficients at different temperatures.]

- **D (nm\(^2\).s\(^{-1}\))**
- **f\(_m\) (a.u.)**
- Temperatures: 82 °C, 114 °C, 149 °C
Summary

Determine the degree of interparticle polymer diffusion

- Using a single fluorescently-labelled latex
- Quantitatively analysed by steady-state fluorescence

Current areas of improvement:
- low pyrene labeling levels
- the removal of unbound pyrene
Acknowledgements

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