Characterizing the Dimensions and Dynamics of Pyrene Labeled Macromolecules in Solution

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Outline

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  • Pyrene Excimer Fluorescence
• Dendritic Constructs
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• Acknowledgments
Introduction

- Polymers with complex architecture can be separated into 4 categories. These topologies include:

  Star  Hyperbranched/ Dendritic  Brush/ Comb  Networks/ Gels
Encapsulation of metal nanoparticles for catalytic reactions

\[ \text{CO}_2 + \text{H}_2 + \text{co} \rightarrow \text{H}_2\text{O} + \text{CO} \]

0.19 M NaHCO\(_3\) @ -0.8 V

A - Covalent bond
B - Cleavable bond
C - Non-covalently internal
D - Non-covalently external
E + F - Associated dendrimer


Fluorescence

Pyrene was chosen because of its interesting characteristics:

- High molar extinction coefficient
- High quantum yield
- Excimer formation *

\[ M + \text{hv} \rightarrow M^* + M \xrightarrow{<k>} (MM)^* \]

\[ \tau_M^{-1} \]

\[ \tau_E^{-1} \]

- \( M^* \) = Excited pyrene
- \( M \) = Ground state pyrene monomer
- \( (MM)^* \) = Pyrene excimer
- \( <k> \) = average rate constant of excimer formation
Steady-State (SS) Fluorescence

SS fluorescence measures the intensity of the monomer and excimer emission.

The monomer emission produces several fluorescence peaks between 375 nm and 410 nm.

Excimer emission produces a broad structureless emission which is centered around 480 nm.
Monomer and excimer excited at 344 nm.

Fluorescence of monomer monitored as a function of time at 375 nm.
Immediate decay of the monomer is seen.

Fluorescence of excimer monitored as a function of time at 510 nm.
Rise time is seen because of the time required for an excited pyrene to encounter a ground state pyrene.

\[ \langle k \rangle = k_{diff} \times [Py]_{loc} \]
Bis(hydroxymethyl)propionic acid dendrimers

$\text{Py}_x \text{G(N)}$

Synthesized by Prof. A. Adronov and S. A. McNelles from Department of Chemistry and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, Canada
Bis(hydroxymethyl)propionic acid dendrimers

G4

G5

G6

$P_y x G(N)$

Synthesized by Prof. A. Adronov and S. A. McNelles from Department of Chemistry and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, Canada
Bis(hydroxymethyl)propionic acid dendrons

\( \text{Py}_{64} \text{G}(6) \)-spacer

\( \text{Py}_{64+1} \text{G}(6) \)-spacer

Synthesized by Prof. A. Adronov and S. A. McNelles from Department of Chemistry and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, Canada
Determining $<L_{Py}^2>$ - Average of the squared end-to-end distance separating every two pyrene labels

\[
<k> = k_{\text{diff}} \times [Py]_{\text{loc}} = k_{\text{diff}} \times \frac{2^N - 1}{V_{\text{dendron}}}
\]

\[
[Py]_{\text{local}} = \frac{(2^N - 1)}{\frac{4}{3} \pi r^3}
\]

\[
r = \left( \frac{\langle L_{Py}^2 \rangle}{2^2} \right)^{\frac{1}{2}} \quad \Rightarrow \quad \langle L_{Py}^2 \rangle^{\frac{1}{2}} = n^2 \times l
\]

Assume $V_{\text{dendron}}$ is a sphere.
Example Calculation for G3

\[ \langle L_{py}^2 \rangle = n \times l^2 \]

\[ \frac{\langle L_{py}^2 \rangle}{l^2} = n \]

\[ \frac{\langle L_{py}^2 \rangle}{l^2} = \frac{(2a+1)+2(2a+1+b)+4(2a+1+2b)}{7} \]

\[ \frac{\langle L_{py}^2 \rangle}{l^2} = \frac{2a+1+4a+2+2b+8a+4+8b}{7} \]

\[ \frac{\langle L_{py}^2 \rangle}{l^2} = \frac{14a+10b+7}{7} \]

\[ \frac{\langle L_{py}^2 \rangle}{l^2} = 1 + 2a + \frac{10b}{7} \]
Determining $<L_{Py}^2>$

\[
< L_{Py}^2 > = l^2 \left( 1 + 2a + b \frac{N \times 2^N - 2^{N+1} + 2}{2^N - 1} \right)
\]

\[
< L_{Py}^2 > = l^2 \left( 1 + 2a + b \frac{258}{63} + c \frac{112}{63} \right)
\]

\[
< L_{Py}^2 > = l^2 \left( 1 + 2a + b \frac{258}{64} + c \frac{112}{64} + \frac{(a+2.5b+c+d)}{64} \right)
\]

\[
\langle L_{Py}^2 \rangle = n \times l^2
\]
Calculated $<L_{Py}^2>^{1/2}$

<table>
<thead>
<tr>
<th>Generation</th>
<th># of GS pyrenes</th>
<th>$&lt;L_{Py}^2&gt;^{1/2}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>4.5</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>5.4</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>6.2</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>7.0</td>
</tr>
<tr>
<td>5</td>
<td>31</td>
<td>7.7</td>
</tr>
<tr>
<td>6</td>
<td>63</td>
<td>8.5</td>
</tr>
<tr>
<td>6-spacer</td>
<td>63</td>
<td>11.3</td>
</tr>
<tr>
<td>6-spacer</td>
<td>64</td>
<td>11.2</td>
</tr>
</tbody>
</table>

\[ <k> = k_{\text{diff}} \times [Py]_{\text{loc}} = k_{\text{diff}} \times \frac{2^N - 1}{V_{\text{dendron}}} \]

\[ V_{\text{dendron}} = \frac{\pi}{6} \times \left( \frac{L_{Py}}{2} \right)^3 \]

Can this be applied to PBBs?

A polymeric bottle brush (PBB) is a highly branched macromolecule with a high degree of polymerization and high grafting density.
## Pyrene labeled poly(EG$_5$MA)

<table>
<thead>
<tr>
<th>Pyrene Content (x)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.013</td>
<td>92000</td>
<td>140000</td>
<td>1.6</td>
<td>290</td>
</tr>
<tr>
<td>0.027</td>
<td>62000</td>
<td>93000</td>
<td>1.5</td>
<td>190</td>
</tr>
<tr>
<td>0.047</td>
<td>62500</td>
<td>96500</td>
<td>1.6</td>
<td>200</td>
</tr>
<tr>
<td>0.060</td>
<td>37000</td>
<td>55500</td>
<td>1.5</td>
<td>120</td>
</tr>
<tr>
<td>0.11</td>
<td>45000</td>
<td>75000</td>
<td>1.7</td>
<td>140</td>
</tr>
</tbody>
</table>
Steady State Fluorescence Results THF

Decreasing Pyrene Content

Fluorescence Intensity (a.u.) vs. Wavelength (nm)

$I/I_M$ vs. Pyrene Content

Pyrene Content: 0.0, 0.5, 1.0, 1.5, 2.0, 2.5

Fluorescence Intensity (a.u.): 0.0, 0.5, 1.0, 1.5, 2.0, 2.5

Wavelength (nm): 350, 400, 450, 500, 550, 600
Time Resolved Fluorescence Results in THF

\[ N_{blob} = 39 \pm 7 \]

- The number of monomer units within a blob

\[ k_{blob} \times N_{blob} = 0.34 \pm 0.05 \text{ ns}^{-1} \]

- Provides a quantitative measure of the rate constant of pyrene excimer formation
Hyperchem
Hyperchem Results

Hyperchem blob - 20 \times 2 + 1 = 41
Hyperchem Results

Hyperchem blob: $20 \times 2 + 1 = 41$

FBM = $39 \pm 7$
What is $\langle L_{Py}^2 \rangle^{1/2}$ for a blob?

\[
\left\langle L_{Py}^2 \right\rangle = l^2 \times (2a + 1 + b\left(\frac{n+1}{2}\right))
\]

Let $a = 18$ and $b = 2$

From $N_{blob} = 39$ we know $n = 19$

\[
\left\langle L_{Py}^2 \right\rangle^{1/2} = 9.4 \text{ Å}
\]
Results in THF

\[ <k> = k_{\text{diff}} \times [\text{Py}]_{\text{loc}} \]
Conclusions

- $<L_{py}^2>^{1/2}$ was calculated for a series of dendrimers.
- Addition of a spacer reduces the fraction of aggregated pyrene.
- A calibration curve was constructed which relates the dimensions of a dendrimer with the dynamics of its terminal ends.
- Poly(EG$_5$MA) has a rigid backbone in solution.

Future Work

- Synthesize a pyrene labeled poly(MMA) using the EG$_5$ as the pyrene linker.
- Synthesize copolymers with 3, 8, and 12 EG units in the side chain
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