Optimizing Polymer Fluorescence for Explosives Detection

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Optimizing Polymer Fluorescence for Explosives Detection

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Abstract

Pyrene is commonly used for explosives detection, as when mixed with polystyrene, the fluorescence intensity of the resulting film can be used as an indicator of the presence of nitro-aromatic, nitro-ether, or nitro-amine explosives\textsuperscript{[5]}. Previous studies\textsuperscript{[5]} have tested a three-component system including pyrene, polystyrene, and a salt, tetrabutylammonium hexafluorophosphate (TBAHP). From these previous studies, it has been seen that vapor pressure of the preparation area is a governing factor in the formation of excimers, which are instrumental in achieving and maintaining fluorescence intensity. In this study, three parameters – solution concentration, film thickness, and molecular weight of polystyrene are examined to determine the effect of film processing on fluorescence results. The results from this study show that excimer formation (and thereby excimer fluorescence) is directly proportional to both concentration and thickness, but will plateau at higher concentrations. This plateau may indicate of a quenching behavior of the films at higher concentrations, but instead may represent an inflection point for fluorescent behavior. Results also confirmed that molecular weight of polystyrene does not appear to directly affect excimer formation. Film polarity was proven to be inversely proportional to excimer fluorescence. That is, a less polar film will result in higher fluorescence. It is suggested in future quenching studies that 192K molecular weight at 4.77wt% or 6.34wt% would provide the greatest initial fluorescence, and is therefore the best choice.
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1. Introduction

In the current age, few of the technological advancements hold as much importance for national security as explosives detection and prevention. Explosives detection technology is a much-needed technology with the ever-present threat of terrorism. Sniffer dogs, while a predominant method for bomb-detection, often cannot detect explosives with odorless vapors or low vapor pressures. (1) Current technology exists to detect most explosives, with Cornell University recently developing a conjugated polymer system to detect RDX (1,3,5-Trinitroperhydro-1,3,5-triazine), with a very low vapor pressure explosive, and has gone undetected with many systems. This technology requires chemical interaction with the RDX rather than reactionary mechanisms. (2) Current technology can also only detect based upon vapor pressure or bulk mechanisms. Polymer films which detect based upon fluorescence mechanisms (due to vapor pressure mechanisms) can also detect based upon quantity of polymer, leading to a bridging of these two methods. (3) The field of polymer film explosives detection requires new polymers that increase fluorescence yields. (3)

Polymer films consisting of macromolecular conjugated copolymers exhibit semiconducting properties, as their saturated sigma bonds and unsaturated pi bonds act as a “molecular wire”\(^\text{[10]}\). As a result of this electronic phenomenon, certain copolymers exhibit special optical, electrochemical, and chemical properties. Polymers which exhibit fluorescent behavior (an optical behavior caused by electron excitation resulting in emission of light) are labeled as fluorophores. Fluorophores exhibit two fluorescent peak ranges: a monomer range and an

![Figure 1: Excimer and Monomer Excitation](image-url)

**Figure 1: Excimer and Monomer Excitation.** Excimer ranges correspond with an intermolecular distance of 0.4nm to 1 nm, while monomers correspond to intermolecular distances >1nm.
excimer range. The monomeric range denotes lower wavelength emissions, while the excimer range is a longer wavelength emission, exciting to a lower energy state, as seen in Figure 1 \(^\text{[10]}\). Excimer and monomers also differ by the intermolecular distance between PY molecules, as excimers are those where the distance is between 0.4 nm and 1 nm, and monomers exist where the distance is greater than 1 nm \(^\text{[5]}\).

Explosive vapors diffuse within the polymer film with a transient flow, as seen by the approximation in Figure 2, which shows diffusion concentration (parts/100) of vapor as a function of distance from surface (x) and time (t). This model shows \(C(x,t)\) vs. \(x\) as time approaches infinity. Over time, the amount of vapor within the film will follow the trend shown in this figure. Further quenching experiments should also follow this trend, as the amount of fluorescence quenching will coincide with the diffusion of the vapor.

![Figure 2: Concentration of Vapor vs. Distance from Surface. This is an approximate representation of general diffusion of a vapor within a film.](image)

Polymer films involving fluorophores employed in testing to detect nitro-aromatic, nitroamine, and nitroether explosives. Such explosive substance are used in military explosive devices and unexploded landmines \(^\text{[11]}\). These nitrogen-based explosives, due the nature of
nitrogen, are electron deficient, and will readily accept the displaced electrons as caused by excitation of the fluorophore (this effect of a lack of fluorescence is called “quenching”). The detection of any explosives is directly related to the magnitude of excitation, thus the optimization of the initial fluorescence of the polymer film allows for the greatest quenching of the polymer in the presence of nitro-based explosives. The fluorophore pyrene has been utilized in thin-film polymers for detection of explosives, with a monomer peak range of 370-400nm\textsuperscript{[5]} and an excimer peak range of 420-600nm. In previous experiments at the University of Connecticut run by Hyun-Sook Jang\textsuperscript{[5]}, a 3-component system had been tested consisting of polystyrene (PS), pyrene (PY), and the salt tetrabutylammonium hexafluorophosphate (TBAHP). During this study, it was seen that the inclusion of the salt may be deleterious to the formation of excimer; hence, a 2-component system was devised by eliminating salt from the system. Initial trials with the 2-component system were completed in Fall 2012 to determine the effects of polymer concentration, film thickness, and polystyrene molecular weight on polymer fluorescence were investigated using this system.

In study in Fall of 2012, two important data ratios were investigated for fluorescence effectiveness: $I_{\text{exc}}/I_{\text{mon}}$ and $I_2/I_3$. $I_{\text{exc}}/I_{\text{mon}}$ represents the ratio of excimer versus monomer formation, and thereby the ratio of their fluorescence. Fluorescence quenching is influenced primarily by excimer fluorescence (an effective representation of the ratio of their fluorescence), and a low ratio of excimer to monomer fluorescence may not show a great quenching efficiency\textsuperscript{1}. The $I_2/I_3$ ratio represents the fluorescence ratio of $I_1$ (373 nm) over $I_3$ (384 nm), and is directly related to the polarity of the solvent environment\textsuperscript{[5]}. It has been inferred from the most recent study that fluorescence quenching is also governed by a self-quenching mechanism, but little is known about this possible phenomena. This inference is based on a conclusion from the first part of this study (Fall 2012) of the relationship between fluorescence and concentration. In this, there appears a linear proportionality between the two until higher concentrations, at which point the relationship appears to approach a horizontal asymptote. The study in Fall 2012 also related these data ratios in relation to the molecular

\footnotesize\textsuperscript{1} Excimer formation is controlled by diffusion in solution state\textsuperscript{[2][4][5]}. 
weight of the polymer (polystyrene), but showed no clear correlation between molecular weight and excimer excitation or polarity.

Film preparation was another focus of the study in fall 2012. Films were prepared at room temperature (25°C), high temperature (100°C), and room temperature demountable cell (see Appendix, Figure 14). The two first preparation methods were observed to mark the effects of heat upon film formation and evaporation rate. With these methods, the substrates were cleaned and dried, and 100µL of solution was collected in a pipette. This was ejected onto the substrate, and a spackle knife was use to uniformly smooth the solution across the substrate. The THF within the solution evaporated out of the film, leaving the polymer. The demountable cells were fabricated using a pipette and spackle knife as well, and were used in order to optimize uniform thickness for thickness comparison. The study found that a link exists between crystallinity (as attained by different temperature preparations) of the polymer and its excimer fluorescence [3]. The correlation that exists between local stiffness/modulus of the polymer and excimer fluorescence, which shows that fluorescence decreases with stiffness. This was inferred from the higher excimer fluorescence of the high-temperature films, both in the concentration study and the molecular weight study. Higher temperature preparations lead to a faster evaporation rate within the film, and therefore higher vapor pressure of the evaporating THF. This heightened vapor pressure caused greater order and packing within the polymer during formation (and with greater order and packing leads to greater crystallinity).

Unfortunately, in this previous study, a lack of film uniformity and ineffective measurement techniques led to unsuccessful thickness measurements.

This study will detail further investigation into the molecular weight effect on polymer fluorescence and polarity, as well as continue the investigation into the effects of film thickness. In order to investigate any self-quenching effects, a higher concentration (8.27wt %) was added to the testing matrix from the last study. A new preparation method, spin casting, will be employed, with the hopes of solving any problems with film uniformity seen in the previous study. Specifically, this study was designed to test the fluorescence of control samples of PY-PS films in order to see the implications of a 2 component system varying (1) concentration of polymer within solution (1.67wt%, 3.27wt%, 4.77wt%, 6.34wt%, and 8.27wt%)and (2)
molecular weights of polystyrene. From this, it will be extrapolated the fundamental understanding of excimer formation as a result of polymer molecular weight and film preparation. Spin casting will be used in place of previous fabrication methods to ensure film uniformity, such that any thickness effect can be investigated.
2. Materials and Experiments

2.1. Materials and Procedure

2.1.1. Materials Selection

This study worked with 202.25 molecular weight pyrene (as the fluorophore) paired with one of five separate molecular weights of polystyrene (2500, 35,000, 192,000, 350,000, and 900,000 g/mol). All materials were procured from Sigma-Aldrich.

<table>
<thead>
<tr>
<th>Polystyrene</th>
<th>Pyrene</th>
<th>Tetrahydrafuron</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Polystyrene structure" /></td>
<td><img src="image" alt="Pyrene structure" /></td>
<td><img src="image" alt="Tetrahydrafuron structure" /></td>
</tr>
</tbody>
</table>

Table 1: Experiment Materials

2.1.2. Design of Experiment

The solutions were prepared at 5 concentrations, expanded upon below:

<table>
<thead>
<tr>
<th>Weight % PS-PY:</th>
<th>8.27 wt%</th>
<th>6.34 wt%</th>
<th>4.32 wt%</th>
<th>3.27 wt%</th>
<th>1.66 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS(g)</td>
<td>0.1011</td>
<td>0.1011</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PY(g)</td>
<td>0.1999</td>
<td>0.1999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF (mL)</td>
<td>3.75</td>
<td>5.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight Conc. (g/L)</td>
<td>80.3</td>
<td>60.2</td>
<td>40.1</td>
<td>30.1</td>
<td>15.1</td>
</tr>
</tbody>
</table>

Table 2: Solution Concentrations

2.1.3. Film Preparation

Polymers were mixed into THF using magnetic stirrers on a hot plate (on spin setting) for approximately one hour or until polymer was visibly mixed into the solution. After solution preparation, vials were covered in aluminum foil to prevent setting for approximately one hour or until polymer was visibly mixed into the solution. After solution preparation, vials were covered in aluminum foil to prevent setting for approximately one hour or until polymer was visibly mixed into the solution.
expiration of the solution due to light exposure. Several solutions were fabricated by diluting previous made solutions (dilutions shown in Table 2)².

The films were then prepared using a spin caster to promote film uniformity. 40μL of solution were placed on each 1”x1” slide and placed into the spin caster. Parameters for the spin casting can be found in Table 3.

<table>
<thead>
<tr>
<th>Excitation Range</th>
<th>350-600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step Size</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>Slit Size</td>
<td>14</td>
</tr>
<tr>
<td>Excitation</td>
<td>350 nm</td>
</tr>
<tr>
<td>Exposure Time</td>
<td>0.5 s</td>
</tr>
</tbody>
</table>

Table 3: This table is filler until spin casting parameters are known.

2.2. Characterization

2.2.1. Design of Characterization Experiment

2.2.1.1. Fluorescence Measurement

The films were characterized to measure fluorescence and thickness³. Fluorolog tests were conducted on a Fluorolog 3 machine using the following parameters (see Appendix, Figure 4):

<table>
<thead>
<tr>
<th>Excitation Range</th>
<th>350-600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step Size</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>Slit Size</td>
<td>14</td>
</tr>
<tr>
<td>Excitation</td>
<td>350 nm</td>
</tr>
<tr>
<td>Exposure Time</td>
<td>0.5 s</td>
</tr>
</tbody>
</table>

Table 4: Fluorolog 3 Testing Parameters

2.2.1.2. Thickness Measurements

² Samples in Fall 2012 were prepared from raw, undiluted materials. Fabrication using dilution was suggested by graduate student Hyunsook Jang in Spring 2013 as a means to more efficiently use supplies.
³ Thickness in order to compare with concentration effect
⁴ Slit size varied in previous studies, but was maintained in the given procedures
Thickness measurements were initially conducted using a tabletop scanning electron microscope (SEM) with the samples perpendicular to the image detector in order to obtain micro scale photos for measurement. This method proved faulty, however, as the samples very rarely lay precisely 90° to the detector, and minor changes in angle created large slant, and therefore inaccurate thickness measurements. Therefore, thickness measurements were mainly captured with Atomic Force Microscopy (AFM) to encourage highest data accuracy.

AFM proved to have some issues, with irregularity in measurements due to porous films, or uneven folds due to the cutting of the film. However, measurements were far more consistent and reliable with the AFM measurements than the SEM measurements (see Appendix, Figure 33).
3. Results and Discussion

Fall 2012

3.1. Fluorescence as a Function of Polymer Concentration

Figures for Reference:

Figure 3: Fluorescence Results for 350K MW PS. (a) Solution, Normalized, (b) Compiled High Temperature (100C), Normalized, (c) Compiled Room Temperature (25C), Normalized, (d) Compiled Demountable Cell, Normalized.
3.1.1. $I_{\text{exc}}/I_{\text{mon}}$ and $I_1/I_3$

<table>
<thead>
<tr>
<th></th>
<th>Demountable Cell, 0.1 thickness</th>
<th>Demountable Cell, 0.2 thickness</th>
<th>HT (100°C) Film</th>
<th>RT (25°C) Film</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_{\text{exc}}/I_{\text{mon}}$</td>
<td>$I_{\text{exc}}/I_{\text{mon}}$</td>
<td>$I_{\text{exc}}/I_{\text{mon}}$</td>
<td>$I_{\text{exc}}/I_{\text{mon}}$</td>
<td>$I_{\text{exc}}/I_{\text{mon}}$</td>
</tr>
<tr>
<td>1.67wt%</td>
<td>4.4013</td>
<td>4.9308</td>
<td>3.8176</td>
<td>2.0196</td>
<td>1.1671</td>
</tr>
<tr>
<td>3.27wt%</td>
<td>N/A</td>
<td>N/A</td>
<td>7.9532</td>
<td>3.2163</td>
<td>1.7046</td>
</tr>
<tr>
<td>4.77wt%</td>
<td>20.4493</td>
<td>10.6305</td>
<td>15.8384</td>
<td>8.5641</td>
<td>2.4973</td>
</tr>
<tr>
<td>6.34wt%</td>
<td>2.3530</td>
<td>2.6384</td>
<td>13.6917</td>
<td>13.0267</td>
<td>3.3557</td>
</tr>
<tr>
<td></td>
<td>$I_1/I_3$</td>
<td>$I_1/I_3$</td>
<td>$I_1/I_3$</td>
<td>$I_1/I_3$</td>
<td>$I_1/I_3$</td>
</tr>
<tr>
<td>1.67wt%</td>
<td>0.3561</td>
<td>0.3731</td>
<td>0.8225</td>
<td>0.3767</td>
<td>0.3636</td>
</tr>
<tr>
<td>3.27wt%</td>
<td>N/A</td>
<td>N/A</td>
<td>0.6842</td>
<td>0.4897</td>
<td>0.6446</td>
</tr>
<tr>
<td>4.77wt%</td>
<td>0.4384</td>
<td>0.2629</td>
<td>0.6122</td>
<td>0.7767</td>
<td>0.7765</td>
</tr>
<tr>
<td>6.34wt%</td>
<td>0.4260</td>
<td>0.4610</td>
<td>0.6041</td>
<td>0.7899</td>
<td>0.8049</td>
</tr>
</tbody>
</table>

Table 5: I-Ratios for Concentration Effect. The five different types of samples (Demountable Cells (0.1 and 0.2mm thick), High Temperature (100°C), Room Temperature (25°C) and Solution)

The highest $I_{\text{exc}}/I_{\text{mon}}$ value occurs in the 6.34wt% (room temperature) and 4.77wt% (demountable cell and high temperature) films, and the lowest in the 1.67wt% (high temperature and room temperature) and 6.34wt% (demountable cell). This is concurrent with the pre-established observation that lowest concentration will produce the least fluorescence (before any possible effects of self-quenching). The solution results suggest that the self-quenching effects are not evident in solution, as the results exhibited a trend of the excimer ratio being proportional to the concentration.
Overall, the 4.77wt% film had the most consistently high excimer ratio, suggesting that the combined effects of concentration and self-quenching for this concentration produce the greatest fluorescence.


I_3 < I_1 for all samples, which suggests the film is fairly non-polar, and polarity decreases with concentration.

![Graphs showing fluorescence intensity ratios](image)

**Figure 4: I-Ratios to observe effect of Polymer Concentration. (a) I_{exc}/I_{mon}, (b) I_1/I_3.**

3.1.2. Solution vs. Solid

The solution showed fluorescence of low intensity (<1000), while the demountable films exhibited fluorescence intensity of over 2,000,000. This is possibly due to the randomized excitation of the molecules. As liquid molecules have greater mobility than solid, the molecules in the solution would have a greater range of motion. Therefore, when excited, they may choose not to excite in the direction of the monitor.
3.2. Film Thickness Measurements and Discrepancies

Note: While demountable cells were made for all concentrations using 350,000 g/mol molecular weight PS, it was impossible to measure them using the AFM, as film porosity and solidification made the surface too irregular to measure.

<table>
<thead>
<tr>
<th></th>
<th>6.34wt%</th>
<th>4.77wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1mm</td>
<td>3.531 μm</td>
<td>2.08μm</td>
</tr>
<tr>
<td></td>
<td>3.546μm</td>
<td>2.146μm</td>
</tr>
<tr>
<td></td>
<td>3.539μm</td>
<td>2.379μm</td>
</tr>
<tr>
<td></td>
<td>3.597μm</td>
<td>2.158μm</td>
</tr>
<tr>
<td></td>
<td>3.642μm</td>
<td></td>
</tr>
<tr>
<td>0.2mm</td>
<td>~7μm</td>
<td>7.184μm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.391μm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.141μm</td>
</tr>
</tbody>
</table>

Table 6: Measured AFM Results. AFM proved unreliable due to experimental technique and film porosity. Therefore, measurements are not truthfully representative of film thickness.

<table>
<thead>
<tr>
<th></th>
<th>6.34wt%</th>
<th>4.77wt%</th>
<th>3.27wt%</th>
<th>1.67wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol% PS-PY</td>
<td>6.37%</td>
<td>4.80%</td>
<td>3.29%</td>
<td>1.67%</td>
</tr>
<tr>
<td>Thickness (0.1mm cell) (Calculated)</td>
<td>μm</td>
<td>9.43</td>
<td>7.105</td>
<td>4.87</td>
</tr>
<tr>
<td>Thickness (0.1mm cell) (Measured Average)</td>
<td>μm</td>
<td>3.571</td>
<td>2.19</td>
<td>----</td>
</tr>
<tr>
<td>Percent Difference</td>
<td>90.13%</td>
<td>105.76%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness (0.2mm cell) (Calculated)</td>
<td>μm</td>
<td>17.81</td>
<td>13.42</td>
<td>9.20</td>
</tr>
<tr>
<td>Thickness (0.1mm cell) (Measured Average)</td>
<td>μm</td>
<td>7</td>
<td>7.239</td>
<td>----</td>
</tr>
<tr>
<td>Percent Difference</td>
<td>87.14%</td>
<td>59.84%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7: Calculated Thicknesses. This table compares the AFM values for thickness measurement with the calculation of thickness as derived from the total mass of polymer.

Thicknesses were calculated by finding the volume percent and multiplying it by the cell depth, as it is assumed that evaporation will cause shrinkage in the depth and not width.
of length of the cell. Any inconsistency between the calculated thicknesses and measured thicknesses is explained by inconsistency in solution concentration or film porosity.

3.3. Correlations between Molecular Weight and Excimer Ratio

Figures for Reference

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5 PS-PY content may have dissociated from the THF in the solution, causing the concentration to be lower than expected in the films
Figure 5: Molecular Weight Comparison of Normalized Fluorescence. (a) 2500MW PS, (b) 35K MW PS, (c) 192K MW PS, (d) 350K MW PS, (e) 900K MW PS
3.3.1. Correlations between Concentration and Molecular Weight with Polarity

<table>
<thead>
<tr>
<th>Molecular Weight (g/mol)</th>
<th>Preparation Type</th>
<th>3.27wt%</th>
<th>6.34wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>RT</td>
<td>0.6428</td>
<td>0.5315</td>
</tr>
<tr>
<td></td>
<td>HT</td>
<td>0.8215</td>
<td>0.5536</td>
</tr>
<tr>
<td>35,000</td>
<td>RT</td>
<td>0.5472</td>
<td>0.4571</td>
</tr>
<tr>
<td></td>
<td>HT</td>
<td>0.7150</td>
<td>0.5508</td>
</tr>
<tr>
<td>192,000</td>
<td>RT</td>
<td>0.5344</td>
<td>0.4362</td>
</tr>
<tr>
<td></td>
<td>HT</td>
<td>0.6678</td>
<td>0.4772</td>
</tr>
<tr>
<td>350,000</td>
<td>RT</td>
<td>0.8159</td>
<td>0.5207</td>
</tr>
<tr>
<td></td>
<td>HT</td>
<td>0.7271</td>
<td>0.6005</td>
</tr>
<tr>
<td>900,000</td>
<td>RT</td>
<td>0.3775</td>
<td>0.4220</td>
</tr>
<tr>
<td></td>
<td>HT</td>
<td>0.5369</td>
<td></td>
</tr>
</tbody>
</table>

Table 8: $I_1/I_3$ Values for varying molecular weights and two concentrations (3.27wt% and 6.34wt%)

The higher concentrations showed a lower $I_1/I_3$ ratio, suggesting that they are more hydrophobic than the lower concentrations, suggesting that the degree of hydrophobia directly relates to the amount of polymer in the film. There does not seem to be a trend between molecular weight of polystyrene and hydrophobia, as values do not follow a discernible trend with respect to molecular weight.
Figure 6: Plots representing Polarity versus molecular weight of polystyrene (a) and concentration (b). Polarity shows little dependence on molecular weight of PS, and an inverse proportionality to concentration.
3.3.2. $I_{\text{peak}}$ Values:

<table>
<thead>
<tr>
<th></th>
<th>3.27wt%</th>
<th>6.34wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HT</td>
<td>RT</td>
</tr>
<tr>
<td>2.5K</td>
<td>246804</td>
<td>177241</td>
</tr>
<tr>
<td>35K</td>
<td>229650</td>
<td>295324</td>
</tr>
<tr>
<td>192K</td>
<td>164526.7</td>
<td>206198.7</td>
</tr>
<tr>
<td>350K</td>
<td>838589</td>
<td>769605</td>
</tr>
<tr>
<td>900K</td>
<td>N/A</td>
<td>272310.7</td>
</tr>
</tbody>
</table>

Table 9: $I_{\text{peak}}$ Values. These values represent the highest fluorescence intensity reached during a fluorolog test.

Figure 7: $I_{\text{peak}}$ Values. These values represent the highest fluorescence intensity reached during a fluorolog test. Values for 350K MW PS were abnormally higher than other result of a new fluorescence lamp.

As the films for 350,000 MW were prepared well before those for any other molecular weight, and the lamp was changed before the molecular weight comparisons, and a new lamp will produce a larger stream of light toward the sample. This may explain the abnormal peak intensity of the 350K MW samples.
3.3.3. Solution vs. Solid

Figure 8: Solution Data for 3.27wt% (a) and 6.34wt% (b), as made with 350K MW PS.

Like in the concentration comparison, the solution came in at very low intensity (<8000), while the films measured in the hundreds of thousands. Again, this can be attributed to the randomized excitation of the molecules\(^6\).

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\(^6\) As liquid molecules have greater mobility than solid, the molecules in the solution would have a greater range of motion. Therefore, when excited, they may choose not to excite in the direction of the monitor.
Spring 2013

3.1. Correlations between Polarity and Excimer Fluorescence

During testing in spring 2013, there was an observed trend between polarity ($I_1/I_3$) and excimer fluorescence ($I_{exc}/I_{mon}$), as seen in example Figure 9 (350K).

![Figure 9: $I_1/I_3$ vs. Excimer Ratio](image)

This inverse relationship suggests that a less polar (hydrophobic) film will produce a higher excimer ratio. As a less polar environment will have a more even distribution of charge, therefore a more even electron density for fluorescence is maintained, and overall excimer fluorescence is higher.

3.2. Fluorescence as a Function of Concentration

Results of concentration effect studies supported the results from Fall 2012: that concentration and $I_{exc}/I_{mon}$ are linearly related until concentrations >5wt%, where a plateau appears to form. This trend was seen in both room and high temperature films in Fall 2012 (Figure 10).
Figure 10: Excimer Ratio Behavior as a function of Concentration. (a) Excimer ratios from Fall 2012, which shows a general upward trend of proportionality. (b) Plateau behavior of excimer ratio as a function of concentration from studies of Spring 2013.

Possible reasoning for this plateau is undetermined, but implied that the polymer molecules within the film may act as self-quenchers for their fluorescence. That is, the polymer may act as an electron acceptor at higher concentrations, as more material may heighten the electron deficiency by decreasing the number of shared electrons. An alternate reasoning is that the plateau may only be a temporary stagnation of fluorescence increase, as suggested by
the mathematical approximation in Figure 11\(^7\). This approximation implies that fluorescence will continue to increase with concentration past the tested concentrations.\(^8\)

![Mathematical Approximation of Fluorescence vs. Concentration (350K)](image)

**Figure 11: Mathematical Approximation of Fluorescence vs. Concentration (350K).** This plot shows a fourth-order polynomial relationship between concentration and thickness. The solid line and markers denote the tested concentrations, while the dotted line denotes theoretical values based on the mathematical extrapolation.

### 3.3. Thickness Effect vs. Concentration Effect

The observation of the correlation between film thickness and fluorescence was important to note, as the thicknesses could help to explain the earlier seen relation between concentration and fluorescence. The concentration effect either originated in (1) molecular interactions due to the overall quantity of the polymers or (2) in a physical effect due to the amount of polymer within any given vertical cross section. Correlations between excimer ratios. film thickness overlaid with excimer ratio vs. concentration can be seen in Figure 12a (350K molecular weight). Figure 12b demonstrates that there is little mathematical difference between concentration effect and thickness effect, suggesting that the concentration effect could be in large part due to the thickness, supporting the supposition (2) above. Also shown is a graph denoting concentration vs. thickness, which exhibits direct proportionality (Figure 12a) between the two. In this

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\(^7\) this plot was created with an assumed intercept of \((0,0)\)

\(^8\) Further studies should be conducted with higher concentrations to confirm any furthered trend.
study, all thickness and concentration graphs showed that thickness could be modeled as a fourth-order polynomial function of concentration, as seen by the approximation.

![Graph showing thickness vs. concentration](image)

**Figure 12:** Comparisons of Concentration and Thickness. (a) Concentration vs. Thickness, which shows fourth-order polynomial ratio proportionality. (b) Comparison of Excimer Ratio Results (Normalized) of the Concentration effect to the Thickness effect. Results align, suggesting that the two effects originate from the same interactions.

### 3.4. Molecular Weight Effect

In Spring 2013, the molecular weight effect on fluorescence was re-investigated, as seen below in Figure 13.
Figure 13: I-Ratios for the molecular weight effect. (a) Excimer ratio versus molecular weight. The plot shows no general trend between molecular weight and excimer ratio (the lines going downward). (b) Polarity versus molecular weight. The plot shows no general trend between molecular weight and polarity ratio (the lines going downward). (c) Thickness versus concentration for different molecular weights. The plot shows no distinct correlation between thickness and concentration correlation and different molecular weights. It suggests that each molecular weight will have its own correlation function for thickness as a function of concentration.
This study reaffirmed the theory that molecular weight is not directly proportional to fluorescence. 192K performed higher than expected given a hypothetical proportional relationship (i.e. that excimer fluorescence is $\propto$ to molecular weight), and 350K performed lower given this preliminary presumption. Looking at the relationships given in Figures 13, it can be inferred that results within each molecular weight is consistent, but there is no proportionality between molecular weight and fluorescence results or thickness.
4. Conclusions

4.1. Fall 2012

- The fluorescence ($I_{\text{exc}}/I_{\text{mon}}$) is directly proportional to polymer concentration, with 6.34wt% being the highest $I_{\text{exc}}/I_{\text{mon}}$ ratio in all cases except the high temperature films and the demountable cell.
- There exists a connection between local stiffness and modulus of the polymer and fluorescence, which states that fluorescence decreases with stiffness. This explains the higher fluorescence of the high-temperature films, both in the concentration study and the molecular weight study.
- The solution samples saw a decrease in hydrophilia with concentration, while both the room temperature and high temperature films saw an increase in hydrophilia with concentration.
- The thickness study showed very little, as AFM measurements failed to accurately measure 2/4 samples. A cell, in which the thickness could be measured along an open side rather than an irregular center portion, would provide uniformity in the cell preparation, rather than the irregularity that the razor blades provided.
- In the molecular weight study, there seemed no distinct correlation between molecular weights and excimer ratio or fluorescence. The excimer ratio for the 900k MW and 192 MW polystyrene films appeared higher than the others, but further testing is required to confirm this affect.
- The high temperature films in this part of the study showed again higher excimer ratios than their room temperature counterparts.

4.2. Spring 2013

- Film concentration and thickness are directly proportional to excimer ratio (overall fluorescence).
- Concentration effect is partially due to the thickness of the film.
- Further tests are required to confirm if fluorescence plateaus at higher concentrations.
- A less polar solution will produce stronger fluorescence due to greater electron density.
• Results suggest that a solution made from 192K molecular weight polystyrene at 4.77 wt% or 6.34 wt% would provide the greatest fluorescence.
5. Appendices

5.1. Equipment and Materials

Figure 14: Demountable Cell for Films. This fabrication substrate was used during tests for Fall 2012 and proved useful, but not completely effective.

Figure 15: Atomic Force Microscopy. AFM works by scanning a very sharp (end radius ca. 10 nm) probe along the sample surface, carefully maintaining the force between the probe and surface at a set, low level. Usually, the probe is formed by silicon or silicon nitride cantilever with a sharp integrated tip, and the vertical bending (deflection) of the cantilever due to forces acting on the tip is detected by a laser focused on the back of the cantilever. The laser is reflected by the cantilever onto a distant photo detector. The movement of the laser spot on the photo detector gives a greatly exaggerated measurement of the movement of the probe. This set-up is known as an optical lever. The probe is moved over the sample by a scanner, typically a piezoelectric element, which can make extremely precise movements. The combination of the sharp tip, the very sensitive optical lever, and the highly precise movements by the scanner, combined with the careful control of probe-sample forces allow the extremely high resolution of AFM. (Taken from AFM: A Beginner’s Guide)
Figure 16: Fluorolog 3 Operation. A fluorolog produces a proton beam, which is filtered by an excitation spectrometer. The sample then reacts to the given radiation. A sensor records the incoming radiation from the sample and maps it to a computer.

5.2. Fall 2012

5.2.1. Preparation Method Investigation

Figure 17: The Correlation between I-Ratios and Concentration. (a) Excimer Ratio, (b) Polarity Ratio.

5.2.2. Molecular Weight Effect
Figure 18: The Correlation between I-Ratios and Molecular Weight. (a) Excimer Ratio, (b) Polarity Ratio.

3.3.4. Concentration Profiles
3.3.4.1. Compiled Plots

3.3.4.1.1. Solution

![Graph showing compiled plots for different wt% solutions.](image-url)

The graph displays intensity (y-axis) against wavelength (nm) (x-axis) for different wt% solutions. The graph includes plots for 6.34 wt%, 4.77 wt%, 1.67 wt%, and 3.27 wt% solutions.
Figure 19: Fluorescence of Solution Samples. (a) Normalized, (b) Unnormalized.
3.3.4.1.2. Film

(a) Intensity vs. Wavelength (nm)

- 3.27wt%
- 1.67wt%
- 6.34wt%
- 4.77wt%

(b) Intensity vs. Wavelength (nm)

- 6.34wt%
- 1.67wt%
- 4.77wt%
- 3.27wt%
Figure 20: Compiled Room Temperature Samples, 350K. (a) Normalized, (b) Unnormalized.
Figure 21: Compiled High Temperature (100C) Samples, 350K. (a) Normalized, (b) Unnormalized.

3.3.4.1.3. Demountable Cells

(a)
Figure 22: Compiled (Average) Demountable Cell (350k MW PS) Samples, 350K. (a) Normalized, (b) Unnormalized.
By Concentration

3.3.4.1.4. Room Temperature

Figure 23: Room Temperature Samples, 350K MW PS. (a) 4.77wt%, Normalized, (b) 4.77wt%, Unnormalized, (c) 6.34wt%, Normalized, (d) 6.34wt%, Unnormalized
Figure 24: Room Temperature Samples, 350K MW PS. (a) 3.27wt %, Normalized, (b) 3.27wt %, Unnormalized, (c) 1.67wt %, Normalized, (d) 1.67wt %, Unnormalized
3.3.4.1.5. High Temperature (100°C)

Figure 25: High Temperature Samples, 350K MW PS. (a) 4.77wt%, Normalized, (b) 4.77wt%, Unnormalized, (c) 6.34wt%, Normalized, (d) 6.34wt%, Unnormalized
Figure 26: High Temperature Samples, 350K MW PS. (a) 3.27wt %, Normalized, (b) 3.27wt %, Unnormalized, (c) 1.67wt %, Normalized, (d) 1.67wt %, Unnormalized
3.3.4.1.6. Demountable Cells

Figure 27: Demountable Cell Samples, 350K MW PS. (a) 4.77wt %, Normalized, (b) 4.77wt %, Unnormalized, (c) 6.34wt %, Normalized, (d) 6.34wt %, Unnormalized, (e) 1.67wt %, Normalized, (f) 1.67wt %, Unnormalized
3.3.5. Molecular Weight

3.3.5.1. Comparison by Molecular Weight

Figure 28: Molecular Weight Comparisons, Varying Concentrations. (a) 2.5K MW PS, Normalized, (b) 2.5K MW PS, Unnormalized, (c) 35K MW PS, Normalized, (d) 35K MW PS, Unnormalized
Figure 29: Molecular Weight Comparisons, Varying Concentrations. (a) 192K MW PS, Normalized, (b) 192K MW PS, Unnormalized, (c) 350K MW PS, Normalized, (d) 350K MW PS, Unnormalized, (e) 900K MW PS, Normalized, (f) 900K MW PS, Unnormalized
Figure 30: Molecular Weight Comparisons. (a) 3.27wt%, Normalized, (b) 3.27wt%, Unnormalized, (c) 6.34wt%, Normalized, (d) 6.34wt%, Unnormalized.
3.3.5.3. Comparison by Preparation Method

Figure 31: Preparation Method Comparisons. (a) Room Temperature (25C), Normalized, (b) Room Temperature (25C), Un-normalized, (c) High Temperature (100C), Normalized, (d) High Temperature (100C), Un-normalized.
Solution:

Figure 32: Solution Samples. (a) 6.34wt%, Unnormalized, (b) 6.34wt%, Normalized, (c) 3.27wt%, Unnormalized, (d) 3.27wt%, Normalized.
Figure 33: SEM Thickness Measurements for Varying Concentrations. (a) 2.5K MW PS, (b) 192K MW PS, (c) 350K MW PS, (d) 900K MW PS.
Figure 34: Plots for 2.5K MW PS. (a) Excimer Ratio vs. Concentration, (b) Thickness vs. Concentration, (c) Polarity Ratio vs. Concentration, (d) Excimer Ratio vs. Thickness, (e) Excimer Ratio vs. Polarity Ratio, (f) Polarity Ratio vs. Thickness
Figure 35: Plots for 192K MW PS. (a) Excimer Ratio vs. Concentration, (b) Thickness vs. Concentration, (c) Polarity Ratio vs. Concentration, (d) Excimer Ratio vs. Thickness, (e) Excimer Ratio vs. Polarity Ratio, (f) Polarity Ratio vs. Thickness
Figure 36: Plots for 192K MW PS. (a) Polarity Ratio vs. Thickness, (b) Thickness vs. Concentration, (c) Excimer Ratio vs. Polarity Ratio, (d) Excimer Ratio vs. Thickness
Figure 37: Plots for 900K MW PS. (a) Excimer Ratio vs. Concentration, (b) Thickness vs. Concentration, (c) Polarity Ratio vs. Concentration, (d) Excimer Ratio vs. Thickness, (e) Excimer Ratio vs. Polarity Ratio, (f) Polarity Ratio vs. Thickness
Figure 38: Plots for 2.5K MW PS. (a) Excimer Ratio vs. Concentration, (b) Polarity Ratio vs. Concentration, (c) Thickness vs. Concentration
Figure 39: Plots for 35K MW PS. (a) Excimer Ratio vs. Concentration, (b) Polarity Ratio vs. Concentration, (c) Thickness vs. Concentration
Figure 40: Plots for 192K MW PS. (a) Excimer Ratio vs. Concentration, (b) Polarity Ratio vs. Concentration, (c) Thickness vs. Concentration
Figure 41: Plots for 350K MW PS. (a) Excimer Ratio vs. Concentration, (b) Polarity Ratio vs. Concentration, (c) Thickness vs. Concentration.
Figure 42: Plots for 900K MW PS. (a) Excimer Ratio vs. Concentration, (b) Polarity Ratio vs. Concentration, (c) Thickness vs. Concentration
6. References


