

Effect of crosslinking density on excimer formation in pyrene-labeled poly(N,N-dimethylacrylamide) gels

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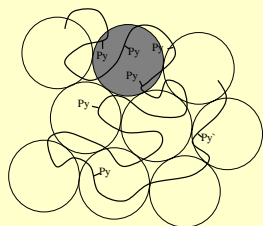
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Introduction

Several studies of pyrene-labeled PDMA (Py-PDMA) have been conducted using a fluorescence blob model (FBM). These studies described the effect that polymer concentration and solvent quality towards the polymer have on the volume probed by an excited pyrene during its lifetime. In turn, these measurements provide information on the Long Range Polymer Chain Dynamics (LRPCD) of PDMA.

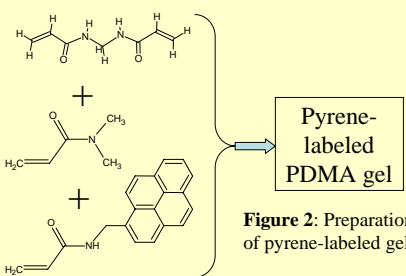
The ability of the FBM to describe the LRPCD of PDMA under various conditions led us to investigate how the crosslinker density of a Py-PDMA gel affects LRPCD as probed by the FBM. This poster describes a set of experiments conducted with a set of pyrene-labeled PDMA gels where the polymer content of the *bis*-acrylamide crosslinker was increased from 2.5 to 4.2 mol%.

Fluorescence Blob Model (FBM)

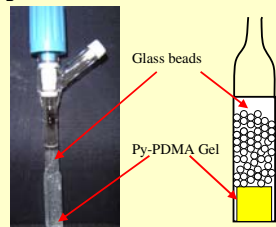
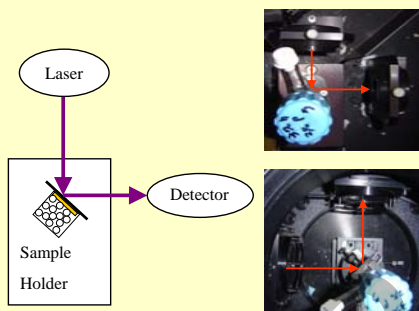


k_{blob} = rate constant for excimer formation by diffusion
 $\langle n \rangle$ = number of ground state pyrenes per blob quenchers per blob

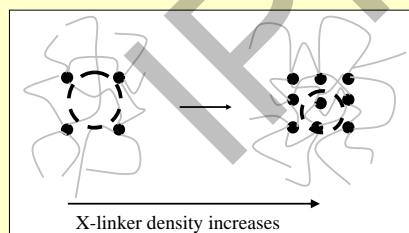
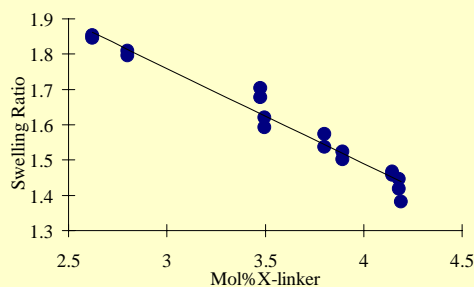
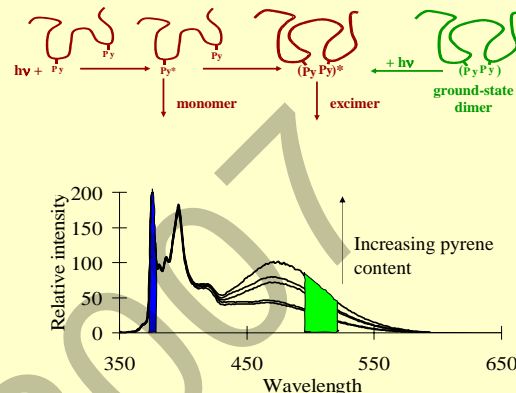
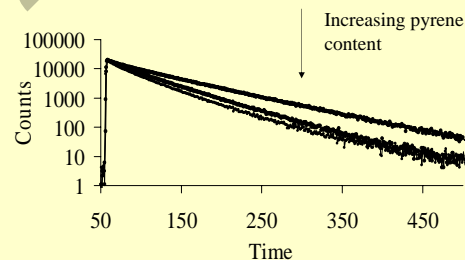
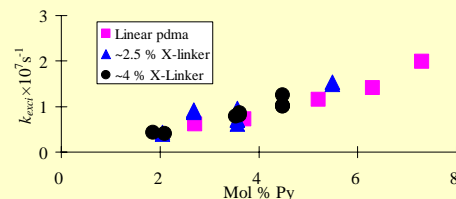
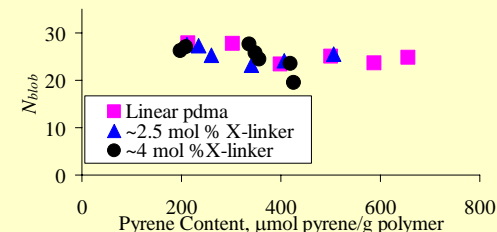
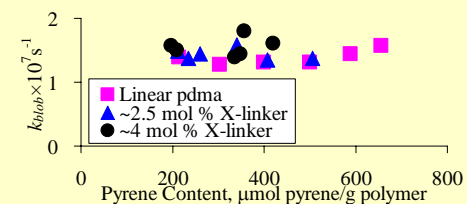
$k_{[blob]}$ = rate of pyrene exchange between blobs \times blob concentration per polymer coil
 N_{blob} = dimethylacrylamide monomer units / blob

Figure 1: Fluorescence Blob Model.

Figure 2: Preparation of pyrene-labeled gel

Sample Measurement


Figure 3: Sample cells.

Figure 4: Spatial arrangement of the fluorescence cell with respect to the excitation source and emission detection in the steady-state (top) and time-resolved (bottom) fluorometer

Results


Figure 5: Effect of X-linker density on blob size.

Figure 6: Swelling Ratio vs. mol% of X-linker in gel.

Figure 7: Steady-state fluorescence spectra of PDMA gel with ~4 mol% of X-linker with different pyrene contents.

Figure 8: Monomer fluorescence decays of X-linked PDMA gel with ~4% X-linker.

Figure 9: Plot of the apparent rate constant for excimer formation (k_{exc}) vs. mol% pyrene

Figure 10: N_{blob} vs. Pyrene content.

Figure 11: k_{blob} vs. Pyrene content.

Conclusions and Future Work

- The FBM analysis of the time-resolved fluorescence decays shows that with up to 4 mol% X-linker, the volume probed by an excited pyrene remains unchanged compared to linear PDMA.

- Interestingly, 4 mol% X-linker in the PDMA gel means that there is a X-link every 25 monomer units on average, i.e. the same number of monomers as found for the N_{blob} of PDMA with no X-linkers.

- Future work will include using acetone as a solvent instead of DMF, since an excited pyrene probes a larger volume in acetone compared to DMF, resulting in a larger N_{blob} value.

- Prepare gels having a higher X-linker density.

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