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Utilizing Solvatochromic Dyes to Probe Phase Changes in Stimuli Responsive Nanogels

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Abstract: Stimuli responsive polymers have gained much attention due to their broad-ranging applications and have been considered as potential smart delivery systems for bioactive molecules. By building functionalized polymers that are thermally responsive, synthesizing novel solvatochromic dyes and covalently incorporating them into the polymer, one may be able to efficiently probe the "coil-to globular" phase transition that a smart polymer undergoes. Tracking the "swelling" behavior of these smart materials with solvatochromic dyes in different temperatures and solvent polarities can allow for the correlations between structure and function. In this research, the smart polymers are present as sub-micron sized hydrogels (cross-linked polymers) that we call nanogels. The absorption and fluorescence properties of the solvatochromic dye will be studied in solvents of varying polarities. In addition, fluorescence from the dye-labeled nanogels will be characterized above and below the lower critical solution temperature (LCST) to demonstrate that they can be used to probe real-time changes in the phase of a polymer. This project is supported by the National Science Foundation Research Experience for Undergraduates (REU) Award No. CHE-1460653.

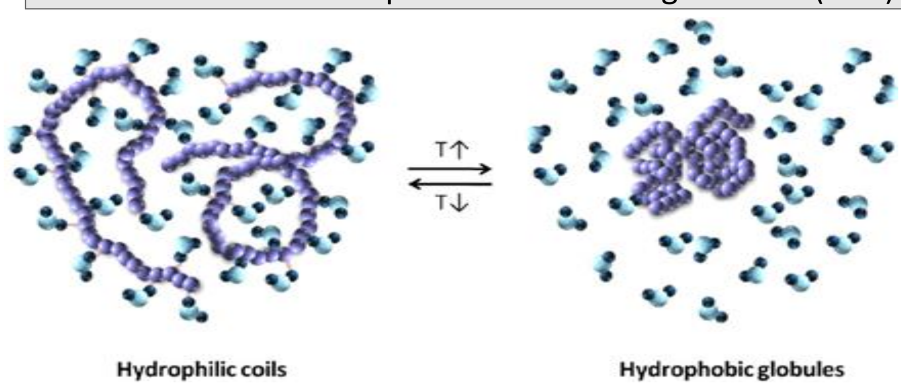
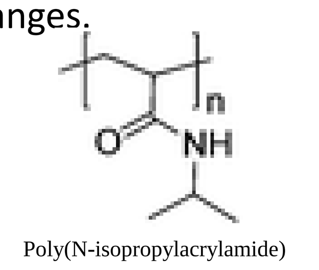
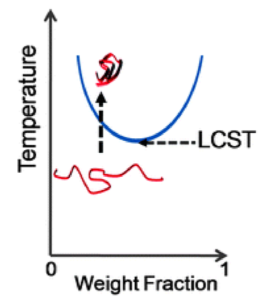


Fig. 1: *The "coil-to-globular" phase change that a smart polymer undergoes depends on temperature[1].*

Background Information

- Solvatochromic dyes: change color in an array of variant environments and report real time changes.
- Stimuli responsive polymers: adapt to the environment in which they are located as well as changing conditions[2].
  - They respond to these alterations by undergoing phase changes.
  - Lower critical solution temperature (LCST): Below this value, polymers swell and are soluble. Above, polymers shrink and become hydrophobic[3].
  - Acrylamide nanogels will be observed due to the fact that the isopropyl amine group can undergo a phase transition that is triggered by temperature changes.





Aims

To: (i) Synthesize novel solvatochromic dyes and (ii) covalently incorporate them into nanogels to track phase changes in the stimuli responsive materials.

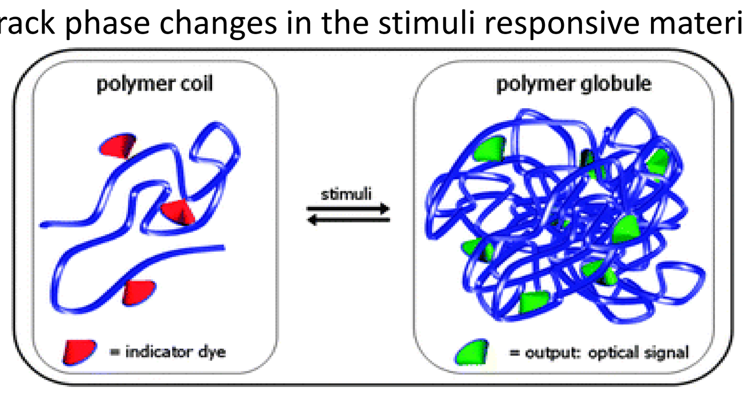


Fig. 2: *A dye is used to label the polymer and allows the coil to globular change to be imaged[4]. The wavelength (color) of fluorescence is altered as the polymer changes from the hydrated (coil), to the collapsed globule phase.*

Experimental Procedure

1.

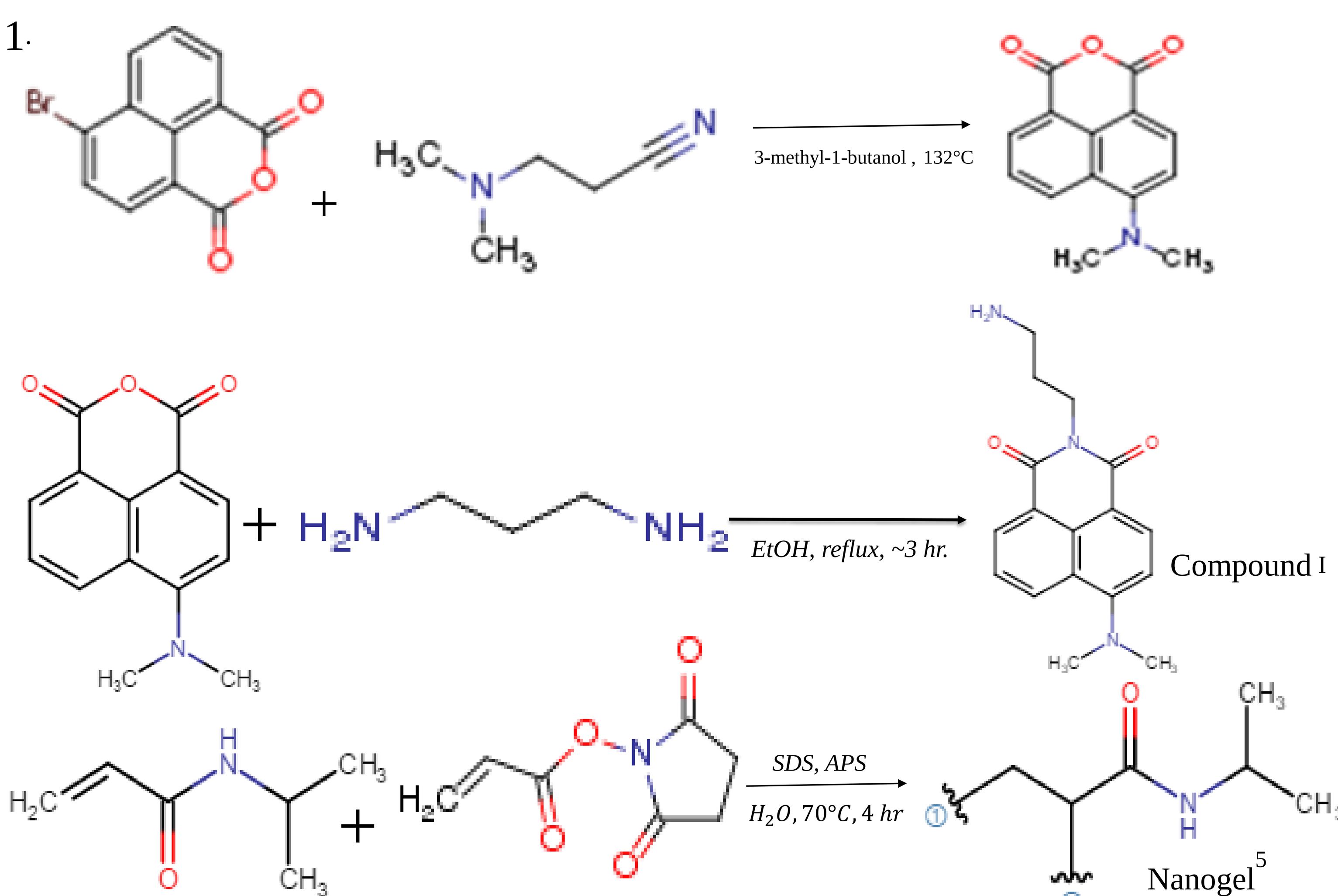


Fig. 3. *Synthesis of the solvatochromic dye (compound I) and fluorescent polymer (nanogel)[5].*

2. Purify compound. Column chromatography and a chromatotron were employed.

Results

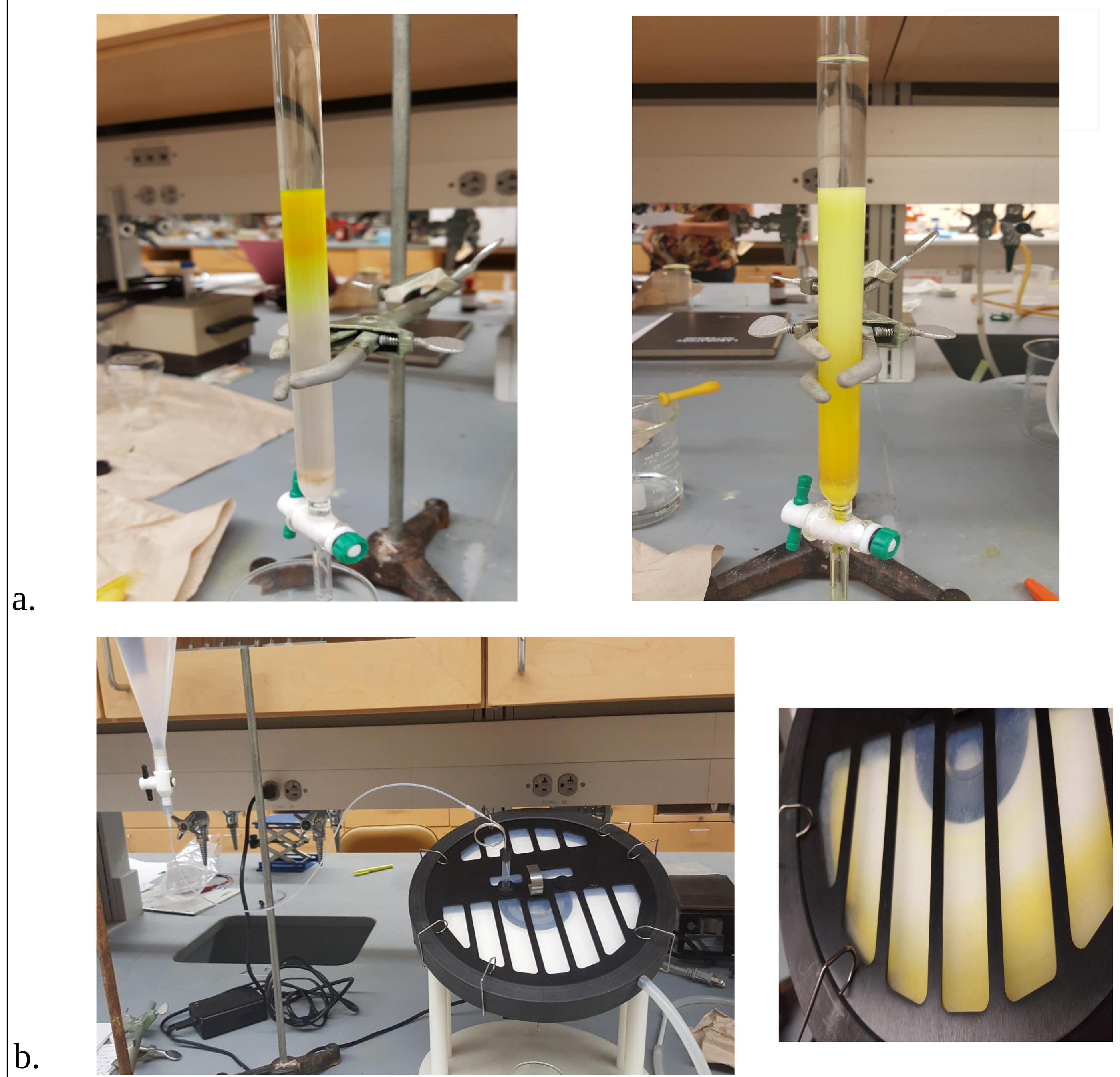
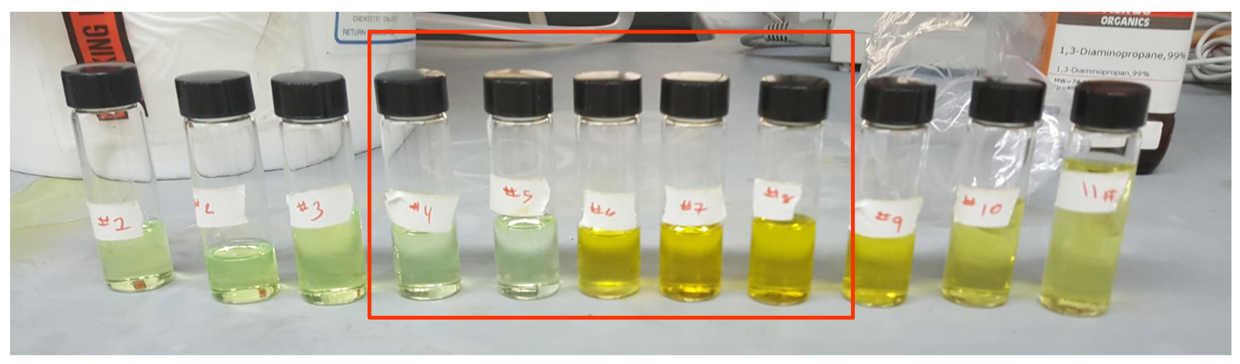


Fig.4: Compound I was purified by (a) column chromatography as well as by (b) a chromatotron. 1,4-Dioxane and methanol were solvents of choice.



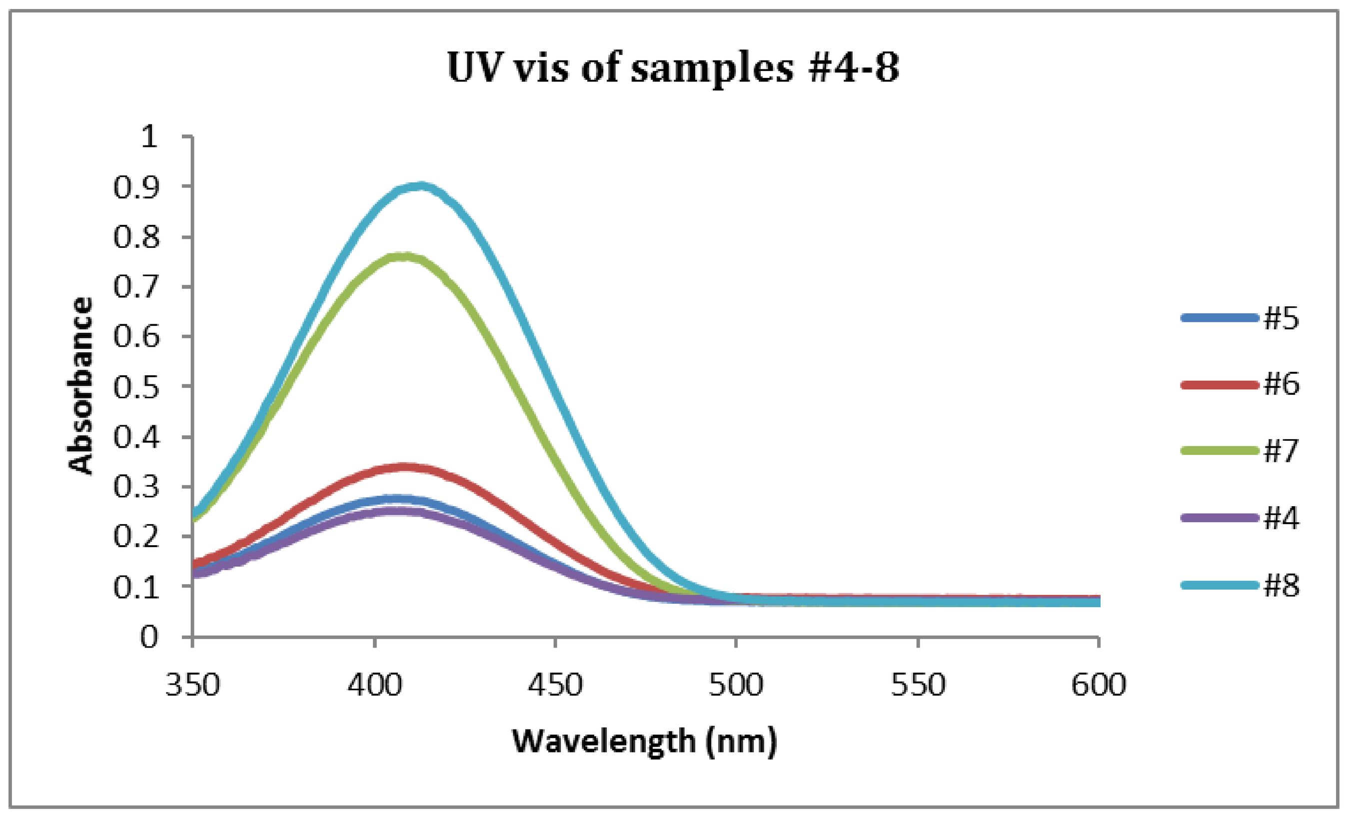


Fig. 5: UV vis Absorption spectra of compound I after column chromatography (samples #4-#8).

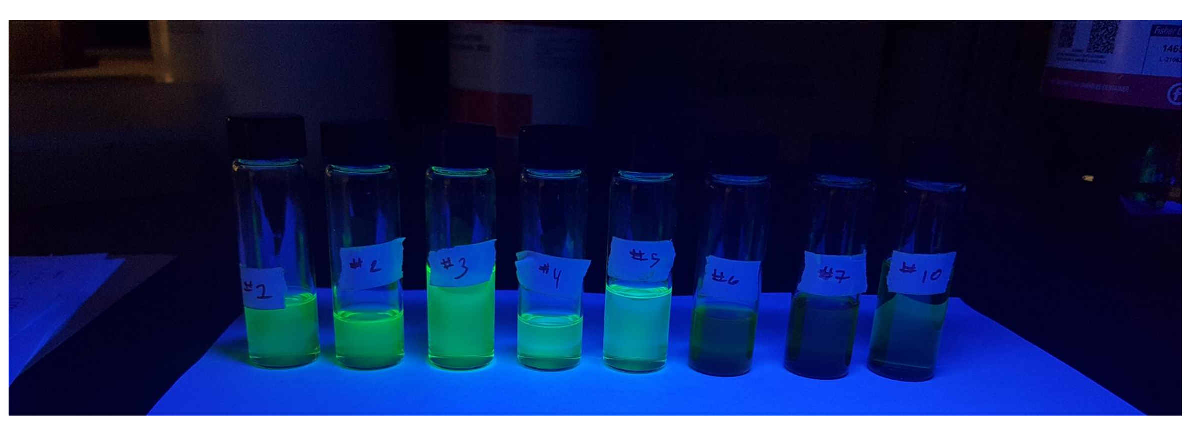


Fig. 6: Compound I under long UV wavelength after being purified by column chromatography.

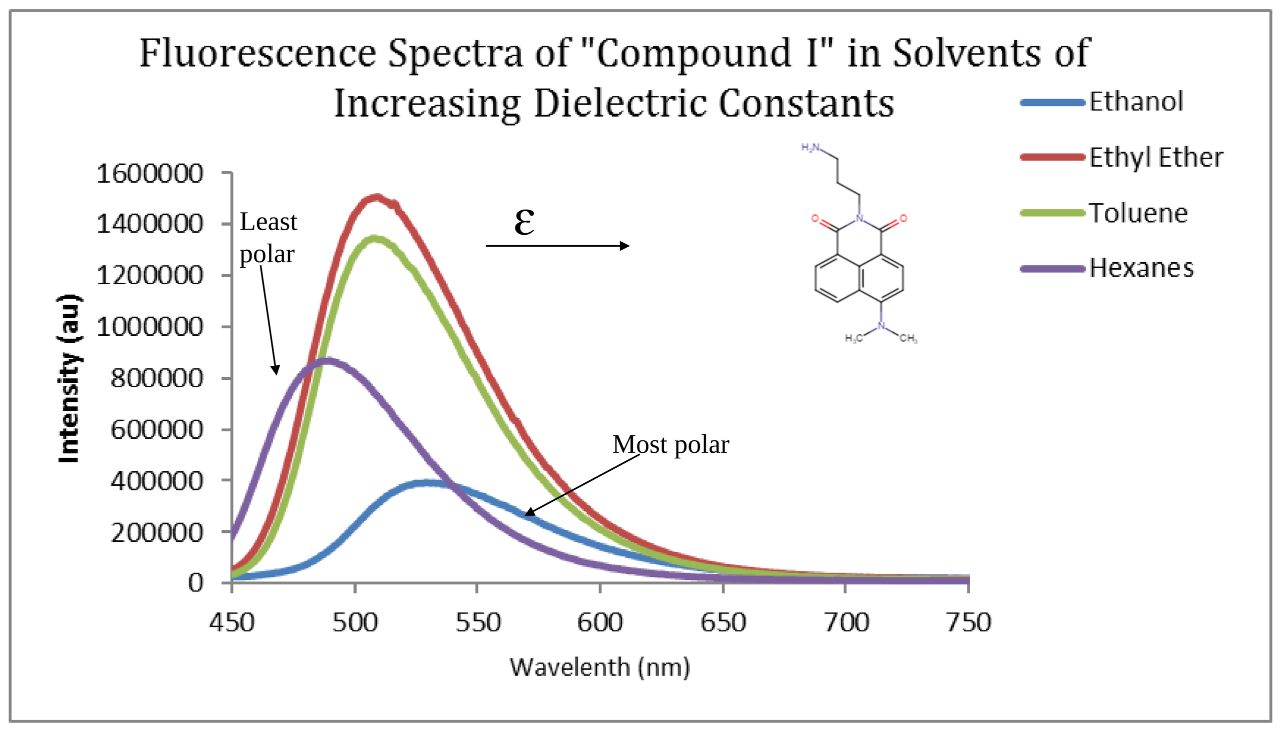


Fig. 4: *Fluorescence spectra of compound I in different solvents at 22° C, with varying polarities as identified by dielectric constants. Methanol (32.70), ethanol (24.3), chloroform (4.81), ethyl ether (4.33), toluene (2.38) and hexanes (1.88). "Red shift" observed for compound in ethanol.*

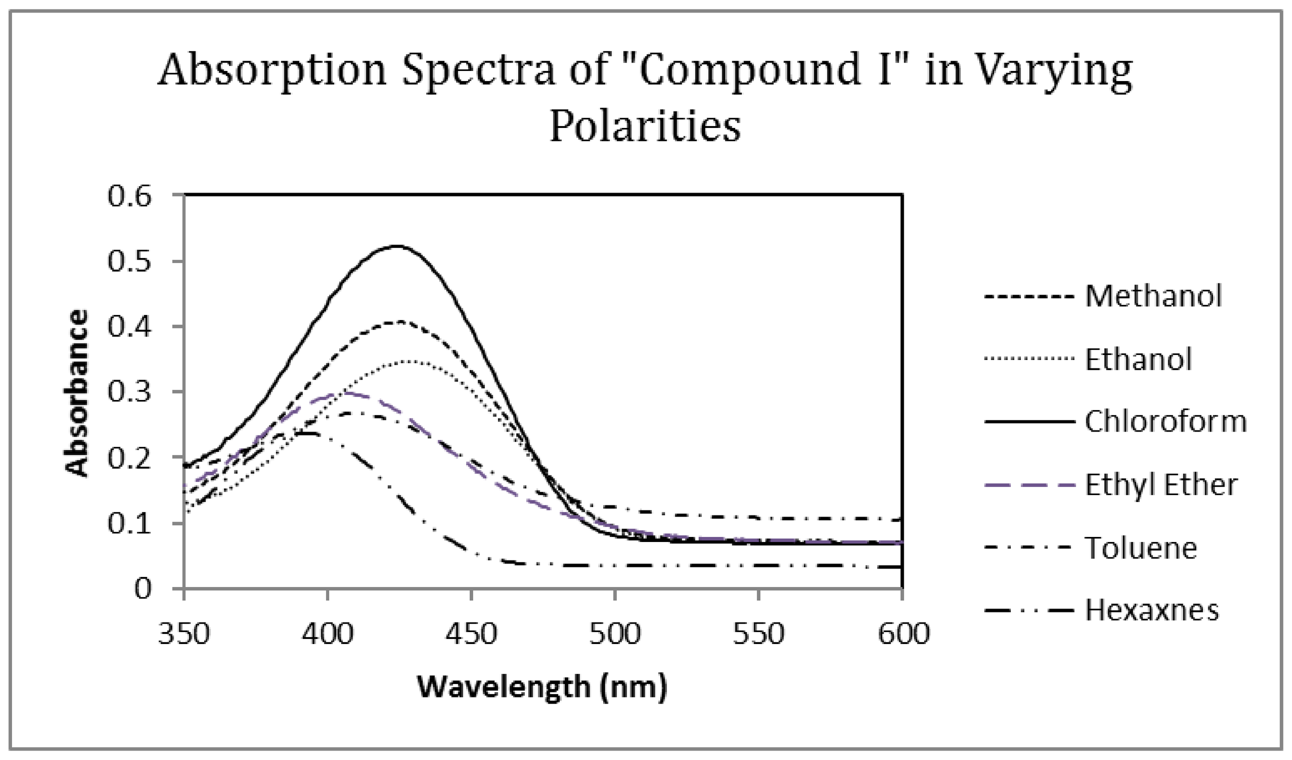


Fig. 6: Absorption spectra of "Compound 1" in solvents of various polarities.

Conclusion:

- A solvatochromic dye small enough to not disrupt the polymer structure as well as a strategy to attach the dye to the polymer were created.
- NAS-NIPAM copolymer was synthesized. This will then lead to actually labeling the polymer with the dye and be able to monitor the structural changes of the polymer in real-time. By being able to measure wavelength we can tell what phase the polymer is in.

Future Work

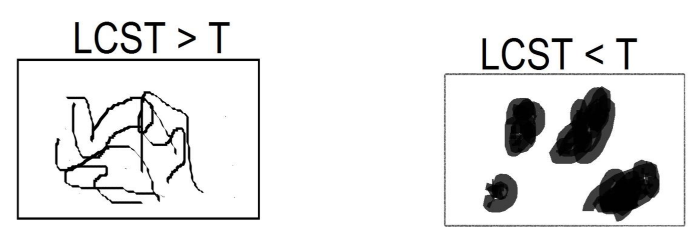


Fig. 7: Polymer is coiled below LCST values and collapsed above it.

To label polymer with synthesized novel solvatochromic dye and measure fluorescence spectra above LCST (32°C) value to be able to observe changes in wavelength and be able to track when the polymer material collapses. LCST can be altered by various stimuli- pH, ionic strength, etc.

References/Acknowledgements

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