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Responsive Polymer Grafts for Patternable Self-Oscillating Gel

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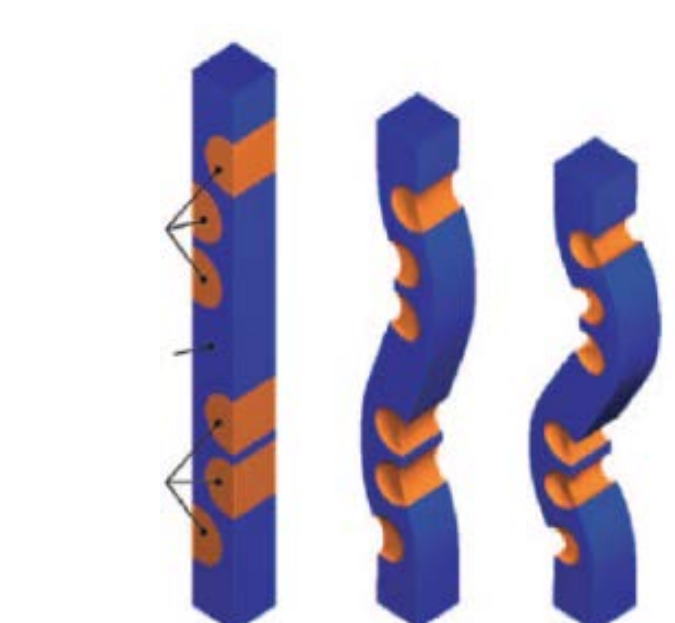
Responsive Polymer Grafts for Patternable Self-Oscillating Gels

MOTIVATION

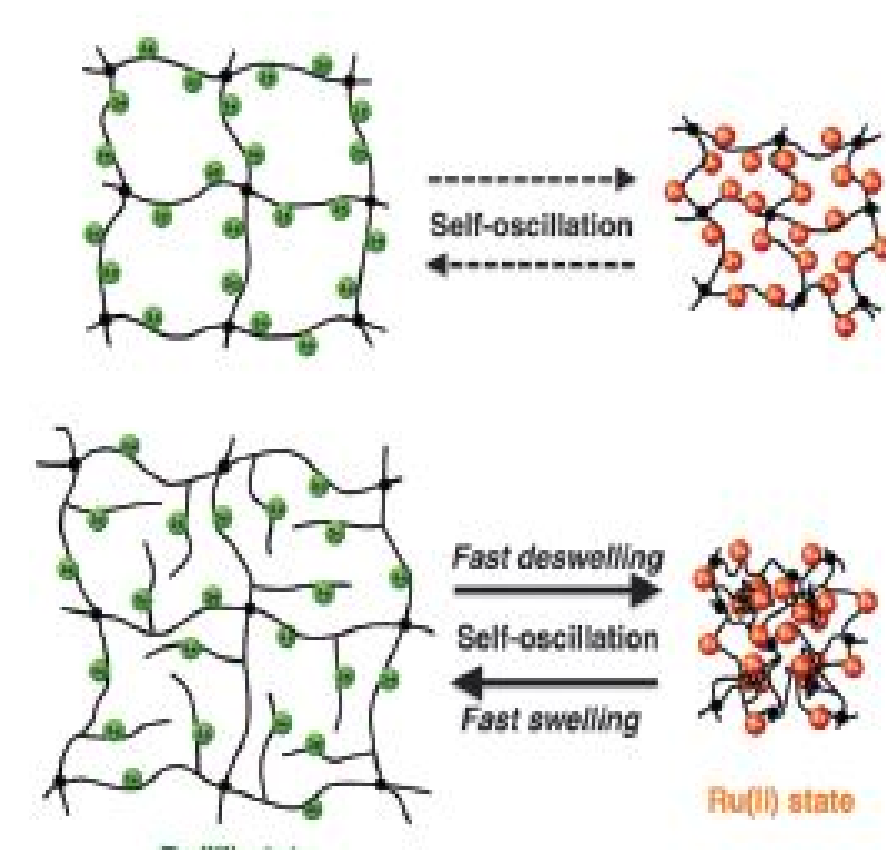
- Polymers that experience drastic changes in their physical properties in the presence of environmental stimulus (temperature, pH, light, humidity, etc) are called **responsive polymers**.
- Responsive materials hold great potential as sensors and actuators that function autonomously. For example, pumps or stirrers for microfluidic devices in lab-on-a-chip applications.

BACKGROUND

- Self-oscillating gels are a class of responsive polymer materials that exhibit autonomous swell and deswell oscillations. These gels are driven by the Belousov-Zhabotinsky (BZ) reaction and operate by converting chemical energy to mechanical energy¹ (like “synthetic metabolism”).
- Printing allows for control of chemical and mechanical behavior through patterning of BZ gel patches.

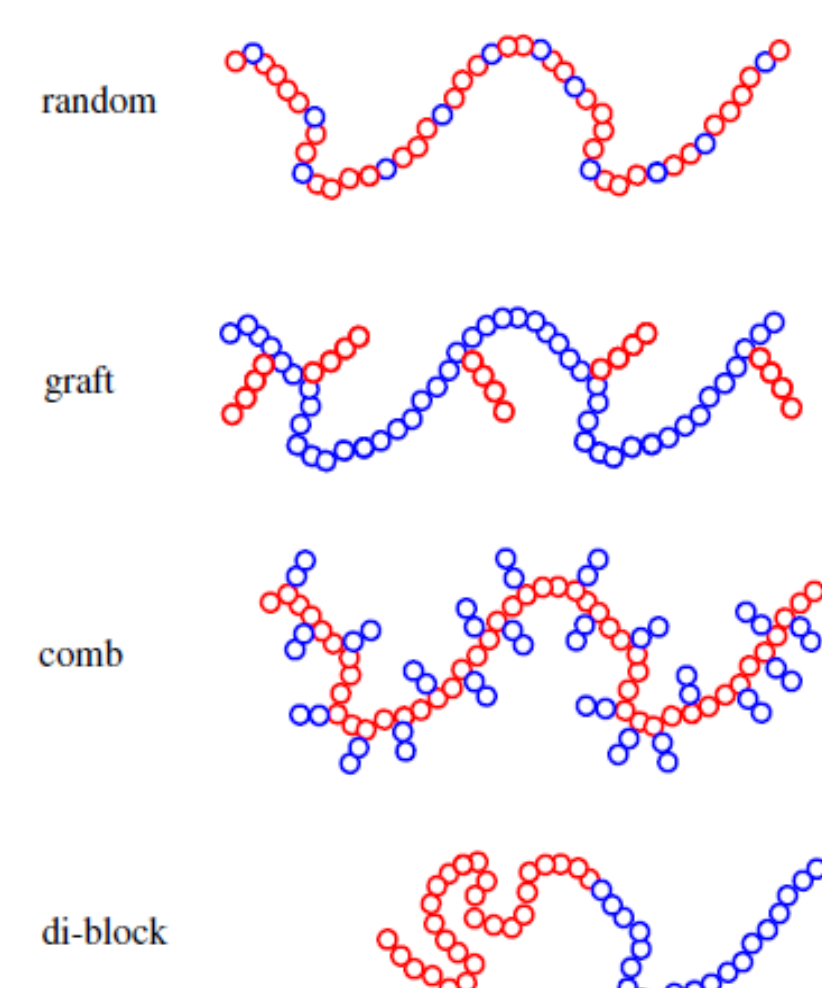


Westbrook and Qi. *J. Intell. Mater. Syst. Struct.* 19 2008

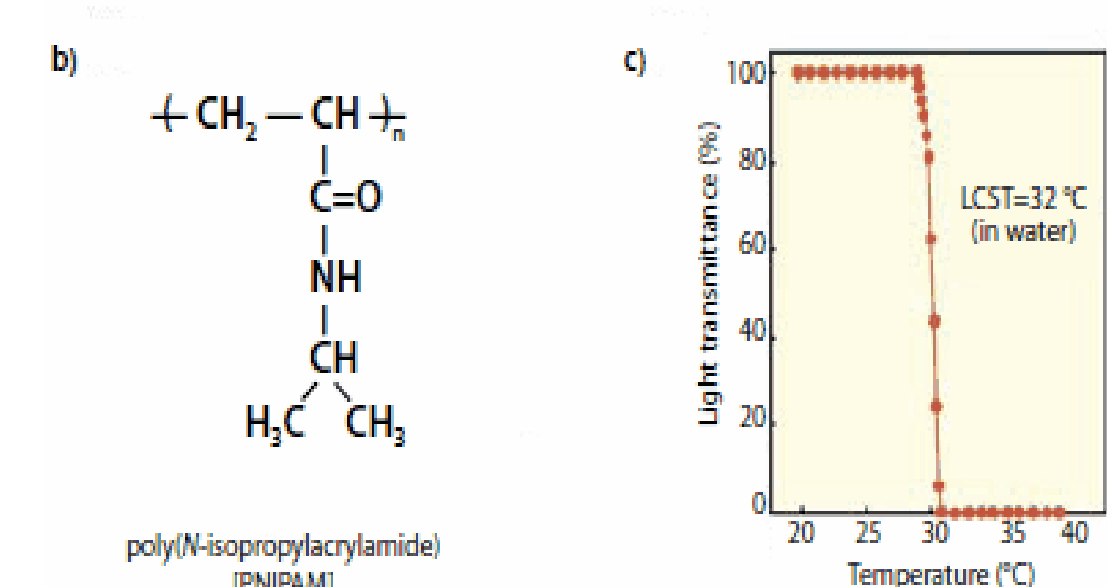
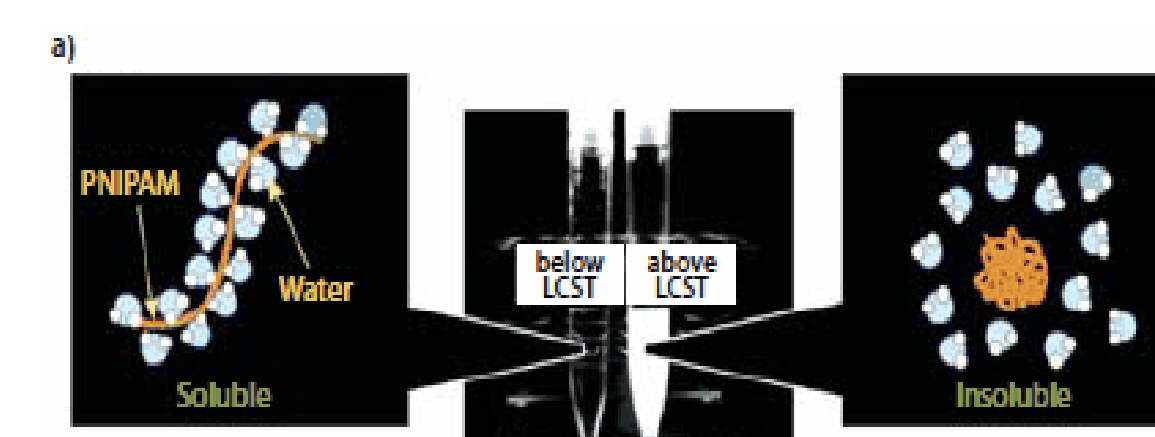


Mitsunaga, Okeyoshi, Yoshida, *Chem. Commun.*, 2013, 49, 4935

- Recently a printable BZ gel based on gelatin was developed¹. Gelatin, however poses some challenges for long term implementation
 - It degrades in BZ solution over time (12-24hrs).
 - Polymer chain composition/properties cannot be easily modified.
- Poly-N-isopropylacrylamide (PNIPAm) is a well studied thermoresponsive polymer known to exhibit lower critical solution temperature (LCST) at 32° C in water.
 - Below 32 ° C, it becomes miscible.
 - Above 32 ° C, it becomes immiscible.
- This thermoresponsive property could potentially be harnessed to produce a thermally reversible gel that could be patterned through printing.
- There are many types of copolymers: random, graft, comb, and di-block.
- PNIPAm graft type copolymers should be able to be designed to produce reversible physical crosslinks (leading to gelation).



Ruixue Liu et al., *Colloid Polym Sci*, Vol 287, 2009



Okano et al., *Material Matters*, 5.3, 56, 2010

PRIMARY AIM

Develop a synthetic, thermally reversible gel using responsive graft copolymers, that can be easily patterned through printing technologies.

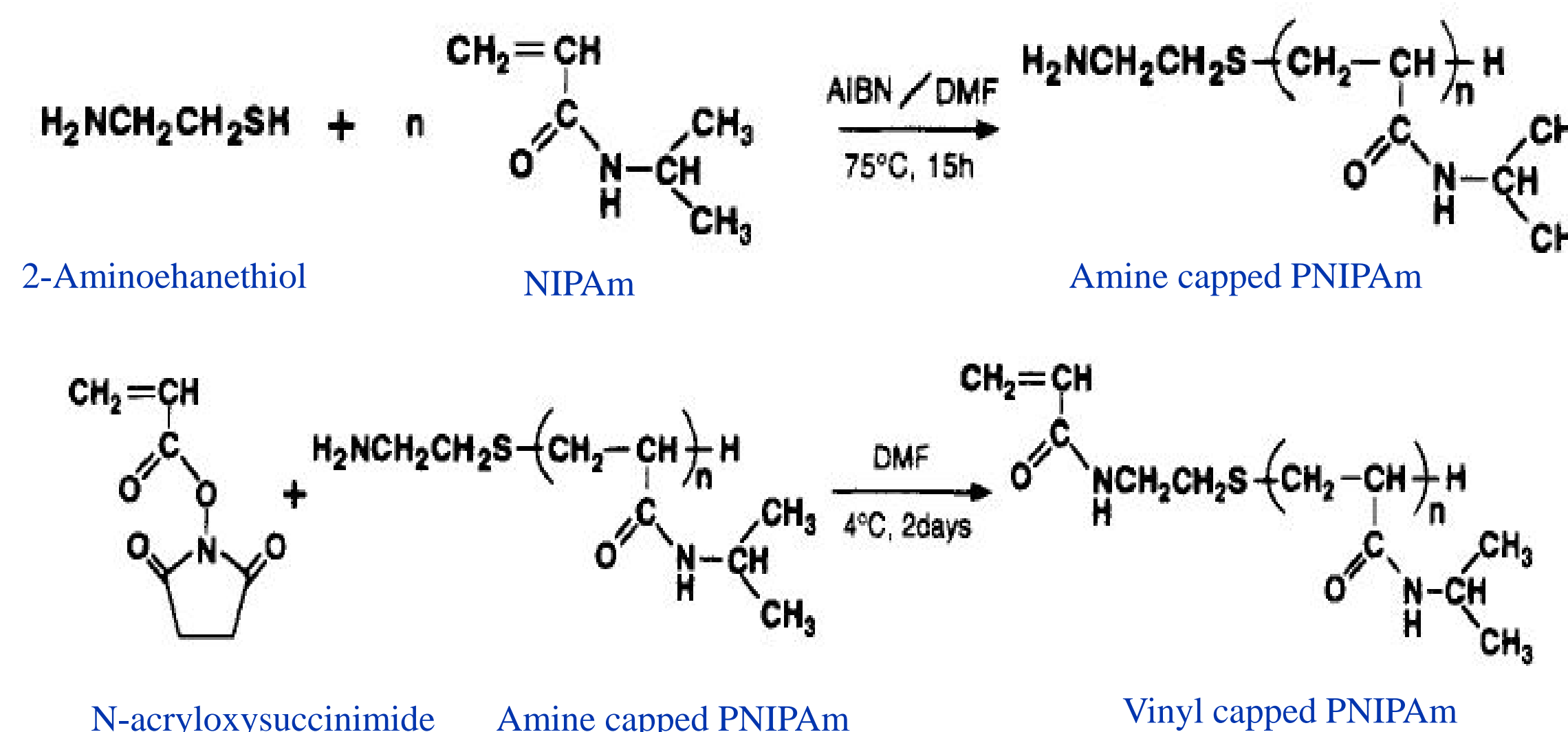
APPROACH

- A procedure from the literature for the synthesis of PNIPAm grafts was adopted.²
- N-isopropylacrylamide (NIPAm) was polymerized with amine functionality. The amine was then converted into a vinyl-capped PNIPAm using an amide condensation reaction between the amino groups in PNIPAm and N-acryloxysuccinimide (NAS).

EXPERIMENTAL / PROCEDURE

Procedure Summary

- NIPAm was mixed with 2-aminoethanethiol(AESH), N,N'-Azobisisobutyronitrile(AIBN) in N,N-Dimethylformamide(DMF).
- The solution was freeze-pump-thawed to remove any oxygen that might prevent the polymerization.
- The oxygen-free solution was water-bathed at 75 °C with stirring.
- After heating for 15 hours, the product was precipitated in acetone/hexane solution.
- The precipitated powders were mixed with NAS in DMF solution.
- After keeping the solution at 4 °C for 2 days, the product was precipitated in acetone/hexane solution.



²Kaneko, Y., Sakai, K., Kikuchi, A., Yoshida, R., Sakurai, Y., & Okano, T. (1995). Influence of freely mobile grafted chain length on dynamic properties of comb-type grafted poly(n-isopropylacrylamide) hydrogels. *Macromolecules*, 28, 7717-7723.

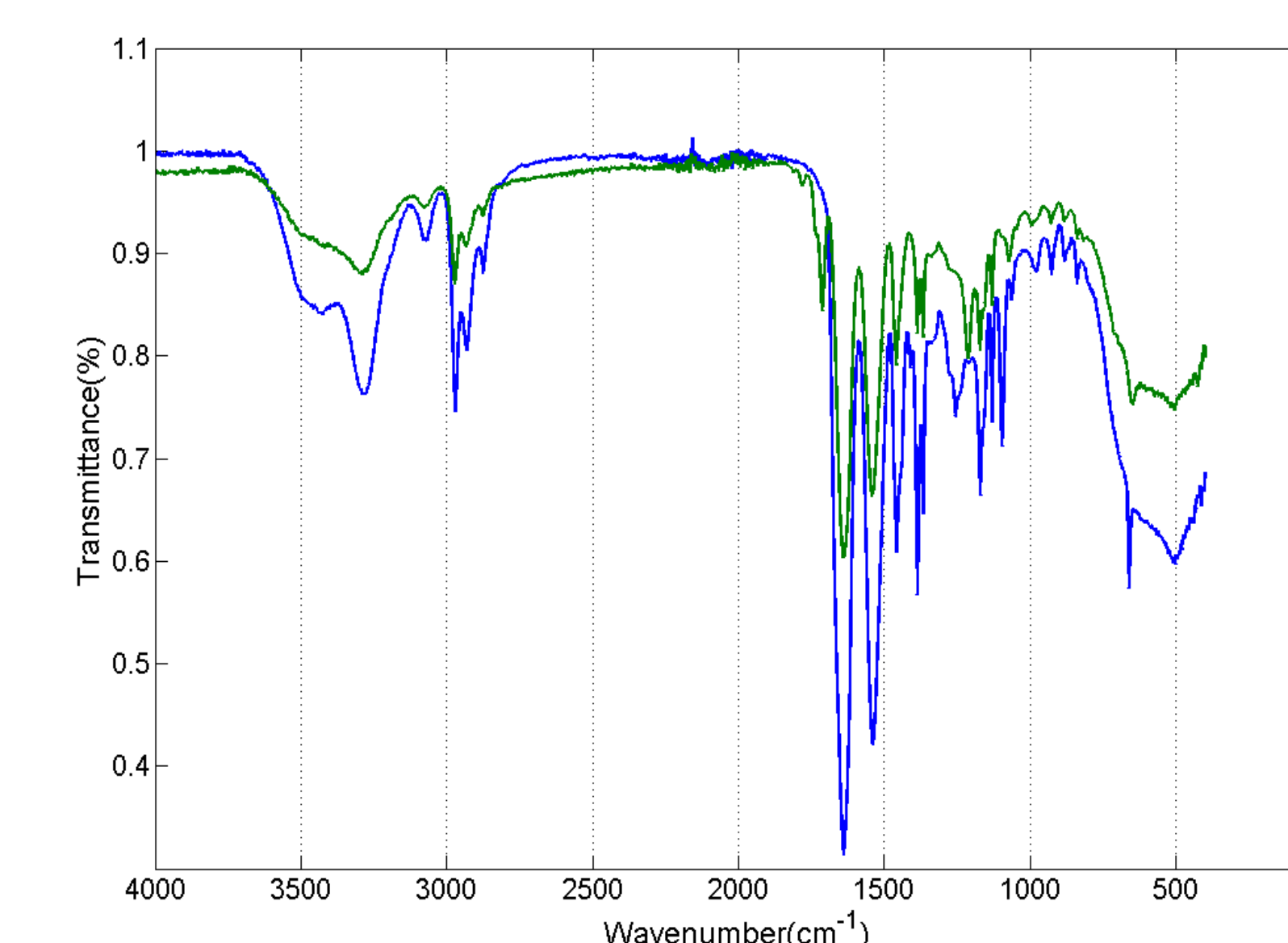
Precipitation

- The precipitation procedure in diethyl ether as specified², produced unusable product.
- Instead, the product, either amine capped or vinyl capped PNIPAm, was dissolved in sufficient amount of acetone and added **drop wise** into hexane while vigorously **stirring**.
- The optimal ratio of PNIPAm to hexane solution was PNIPAm:hexane=1:100.
- Lower ratio resulted in sticky precipitation.



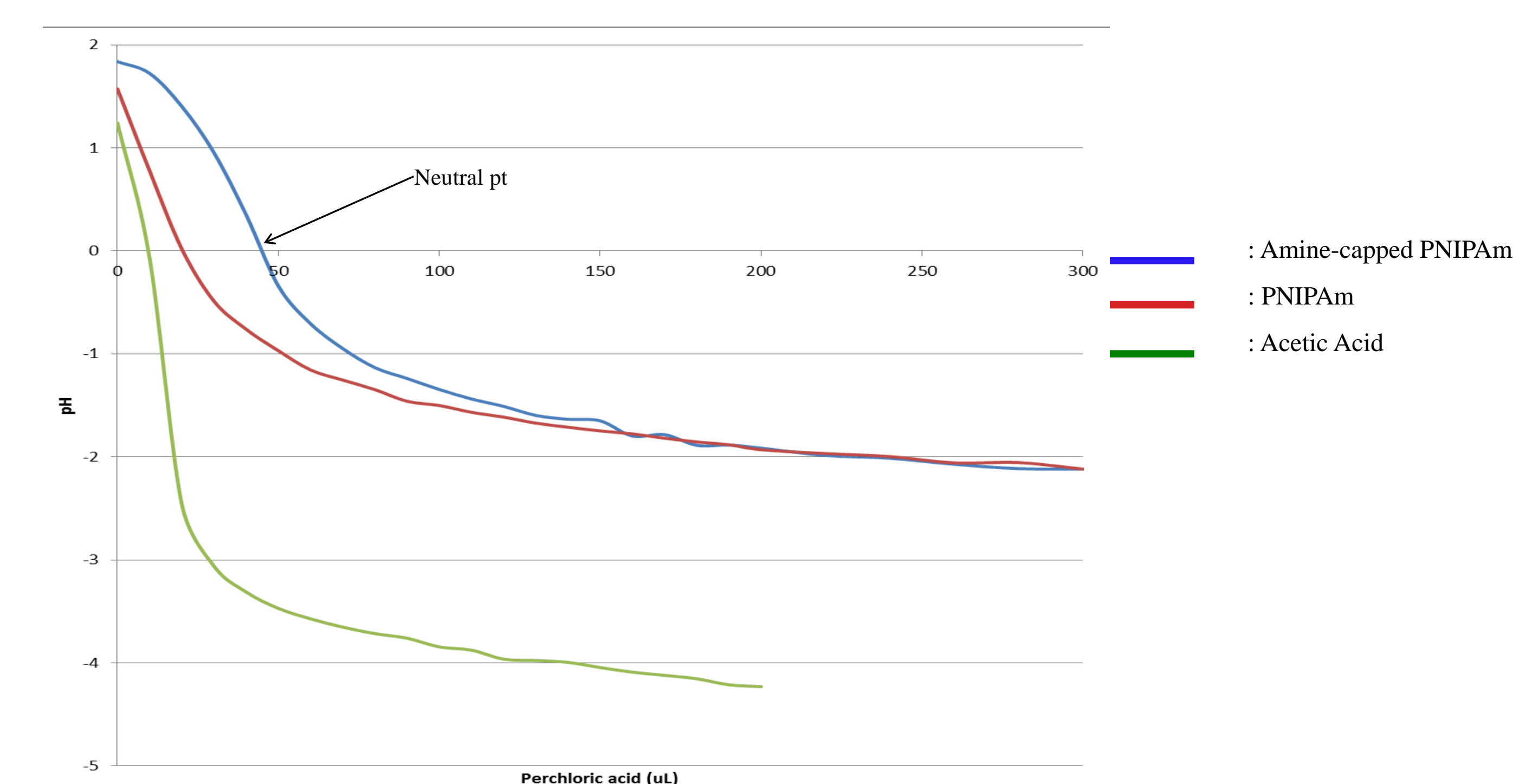
RESULTS

- The formation of amine-capped PNIPAm and vinyl-capped PNIPAm were verified using IR Spectrum.



— : Amine-capped PNIPAm
— : Vinyl-capped PNIPAm

- The average molecular weight of the grafts was determined by the end group titration with acetic acid/perchloric acid.



CONCLUSIONS / FUTURE WORK

- Vinyl-capped PNIPAm grafts with different length was successfully synthesized.
- More characterization is required to confirm the functional group changes.
- Next steps are to polymerize these grafts with a backbone polymer to produce a thermally reversible gel and to incorporate ruthenium complex to run the BZ reaction for its autonomous characteristic.

ACKNOWLEDGEMENT

- This research was supported in part by a grant to Hope College from the Howard Hughes Medical Institute through the Undergraduate Science Education Program.
- Funding provided by the Dean of Natural and Applied Sciences and the Department of Engineering, Hope College

¹Smith, L., Heitfeld, Stone, Vaia, A. (2012). Autonomic Hydrogels through postfunctionalization of gelatin. *Chem. Mater.* 2012, 24, 3074–3080