Lucy Wingard

Chem 69A

Lab 1

Temperature Responsive Polymeric Hydrogel Synthesis

In this experiment we aimed to synthesize two polymeric hydrogels with temperature responsive properties via radical polymerization, which have a wide range of use in the biomedical field.

Experimental

Materials:

- N-isopropylacrylamide (NIPA)
- N,N'-methylenebisacrylamide (BIS)
- ammounium persulfate (APS)
- N,N,N,N'-tetramethylethylenediamine (TEMED)
- Acetone
- Distilled water

Procedure A:

Day 1

1. To a 4 mL glass vial, add
    - 0.0972 g NIPA
    - 0.045 g BIS
    - 0.0044 g APS
2. Add 1 mL acetone and 1 mL dH_2O, sonicate until dissolved
3. Degas for 15 minutes with N_2
4. Add 1 drop TEMED, sonicate for 30 seconds then leave at room temperature for 1 week

Day 2

5. Flush vial with dH_2O many times, until white gel turns clear and colorless
6. Put vial in freezer in attempt to get gel completely clear
7. Put vial in 45^{o}C rotovap bath until color change is observed

Procedure B:

Day 1

1. To a 4 mL glass vial, add
    - 0.1114 g NIPA
    - 0.0045 g BIS
    - 0.0016 g APS
2. Add 2 mL dH_2O, sonicate until dissolved
3. Degas for 15 min with N_2
4. Add 1 drop TEMED, sonicate for 30 seconds then leave at room temperature for 1 week

Day 2

5. Remove excess solvent from vial and add 1 mL dH_2O to the vial
6. Put vial in refrigerator to observe a color change

Results & Discussion

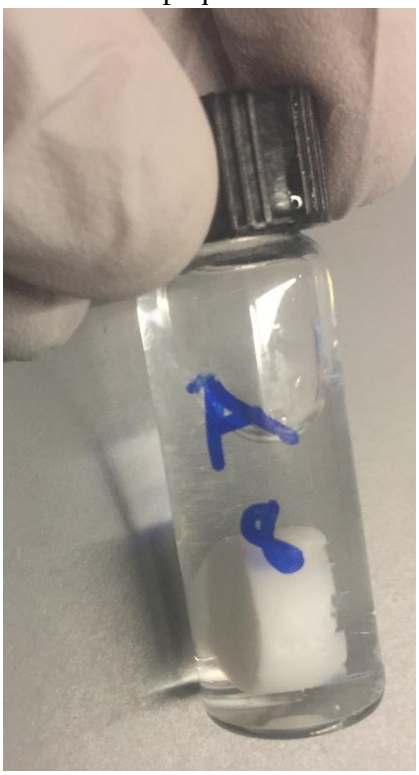
Observations

- NIPA, BIS, APS- all white, crystalline solids
- H_2O, TEMED and acetone- clear and colorless solutions

Day 1 procedures for A and B had the same observations:

- Solution remained clear and colorless after solids dissolved
- While degassing, solution cooled and condensation appeared on outside of vial
- No change to solution appearance after addition of TEMED
  Day 2- A
- Opaque white gel at bottom of vial with thin, clear layer on top. Layer of clear solution filling vial
- Gel slowly turned colorless with successive H_2O rinses
- Almost completely clear and colorless after sitting in freezer for 5 minutes

- Gel turned opaque white when heated in water bath



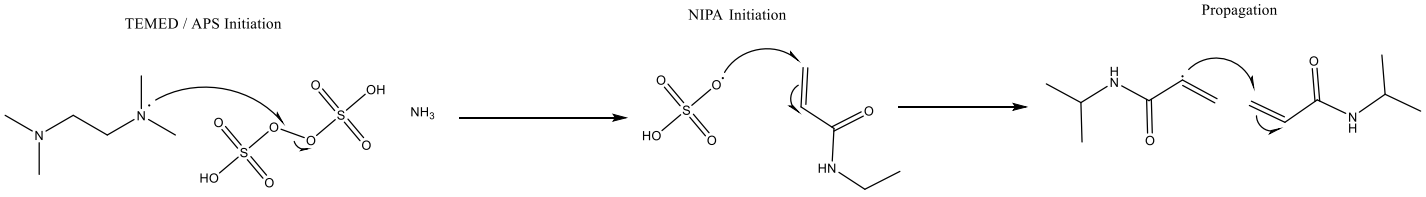
Day 2- B (observations from another lab group due to complications in my experiment)

- White precipitate present in clear solution after week at room temperature
- Sample B placed in 46ºC water bath to promote hydrogel formation

Unfortunately, upon return to the lab for the second week no change was discovered in vial B, when a white precipitate should have been expected. The lack of product can likely be attributed to an insufficient amount of BIS or APS in reaction; while measuring such small

amounts of reactants, it's possible that the mass reading was influenced by air pressure differences on the balance recording a higher mass of reagent than what was on the scale. An insufficient amount of BIS would have limited the potential of hydrogel formation because there would not have been enough double bonds available to act as a crosslinker between monomers. Similarly, an insufficient amount of APS in solution would have prevent product formation because the radical propagation would not have enough a sufficient concentration of APS to provide free radicals used in monomer linking. Alternatively, too high a concentration of APS would cause a too-rapid radicalization of monomers, resulting in polymer chains so short that they are unable to be cross linked into a successful gel lattice. In other lab groups, it was observed that Gel B was colorless at cold temperatures (0^{o}C) and opaque white at room temperature, indicating a temperature responsiveness in the porosity of the gel network.

From Procedure A, a hydrogel was successfully synthesized. During the week at room temperature, the reagents underwent radical polymerization to form a covalently linked polymer. First, before adding the radicalizing agent (TEMED), it was important to degas the solution with 15 minutes of nitrogen; this prevented any atmospheric oxygen that might have been dissolved in solution from reacting in the radical propagation cycle. TEMED and APS serve as co-initiators for radicalization, with TEMED catalyzing the radicalization of the more abundant APS. Monomers of NIPA are then radicalized forming long chains, which are randomly cross linked by BIS forming the gel lattice. Gel A was observed to change color (from clear and colorless to an opaque white) when heated- contracting the gel network and becoming more solid (less "space" for water between linked chains).



Conclusion

This lab examined the synthesis of two polymeric hydrogels via radical polymerization. As indicated by the color change when Gel A was heated and cooled, the polymer network showed a temperature responsiveness in how "porous" or "solid" the network was. Though experimental error prevented my group from obtaining the product of Gel B, observation of another group's gel showed a similar temperature response, at a different temperature range than Gel A (shifted about 40^{o}C cooler, with more porous clear gel at 0C and a "solid" white gel around room temperature). These temperature sensitive hydrogels have a wide range of application in the biomedical field. Temperature responsive polyacryclamide hydrogels have can be blood compatible and used for controlled drug deliveries in medical applications. Because these hydrogels can be biologically recognized by living systems, they can be used in promoting protein synthesis, as seen in the use of Epogen to stimulate red blood cell production for dialysis patients. Using hydrogels for medical purposes is becoming an increasingly important field, as indicated by the acquirement of GelTex Pharmaceuticals for $1 billion in 2000.