Examining the Viscosity of PEG-PDMAEMA as a Function of Temperature and pH

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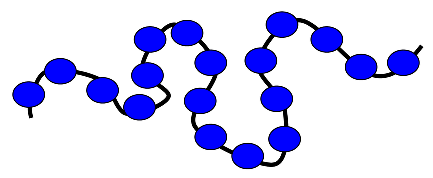
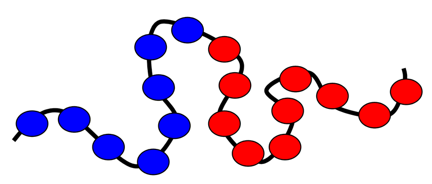
Polymer Basics



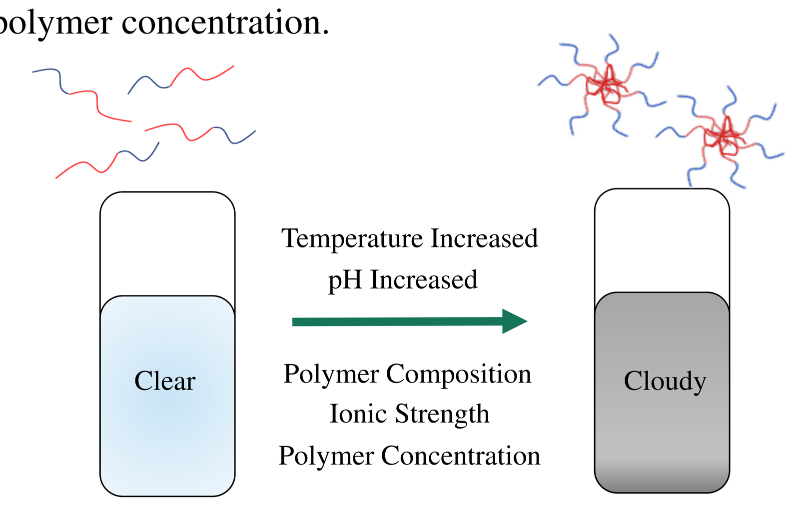
- Polymers are molecular structures which are typically composed of a large number of the same repeating unit. Polymers can also have distinct structures which can affect the properties of the polymer.



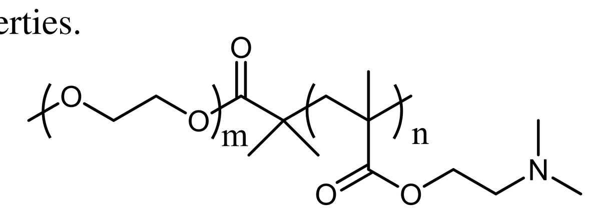
- The polymer structure can be either a homopolymer, a polymer composed of one repeat unit, or a diblock copolymer, which is composed of two different repeating units that are covalently bonded together.

"Smart" Polymers

- "Smart" polymers respond to small changes in the environment in an intriguing way dissimilar to regular polymers. Viscosity is one variable that changes in different conditions of pH, temperature, and polymer concentration.



- Cloud point is the temperature above which the polymer goes from "water loving" (hydrophilic) to "water hating" (hydrophobic) and becoming insoluble.
- PDMAEMA, the smart polymer being tested, has a cloud point that is affected by changes in pH, buffer concentration and polymer concentration. When PDMAEMA is used in a diblock copolymer with poly(ethylene glycol), PEG-PDMAEMA, it changes to take on different properties.

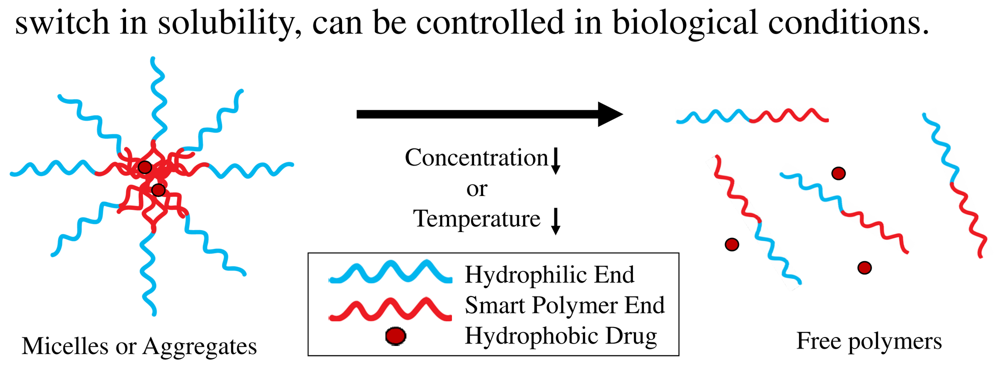


PEG-PDMAEMA

Applications

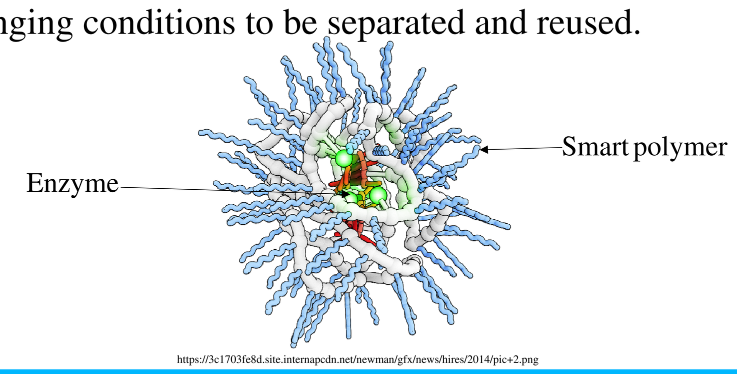
Smart Polymer Drug Delivery

- Smart polymers are of interest for drug delivery and other biomedical applications because smart properties, such as the switch in solubility, can be controlled in biological conditions.



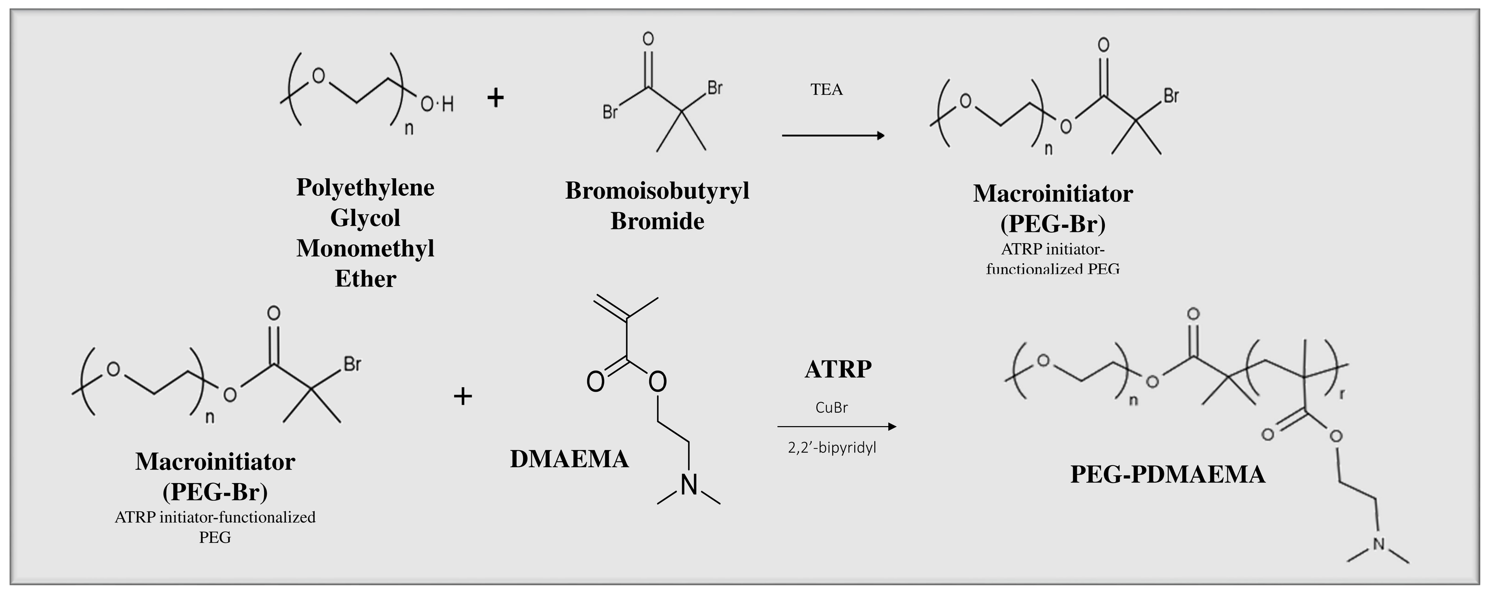
Reversible Biocatalyst

- Smart polymers can also be used for a soluble/insoluble biocatalyst. Using the phase separation that smart polymers offer, they can be bound to the enzyme molecule through covalent bonding. When the reaction is completed, the smart polymer catalyst is then precipitated by changing conditions to be separated and reused.



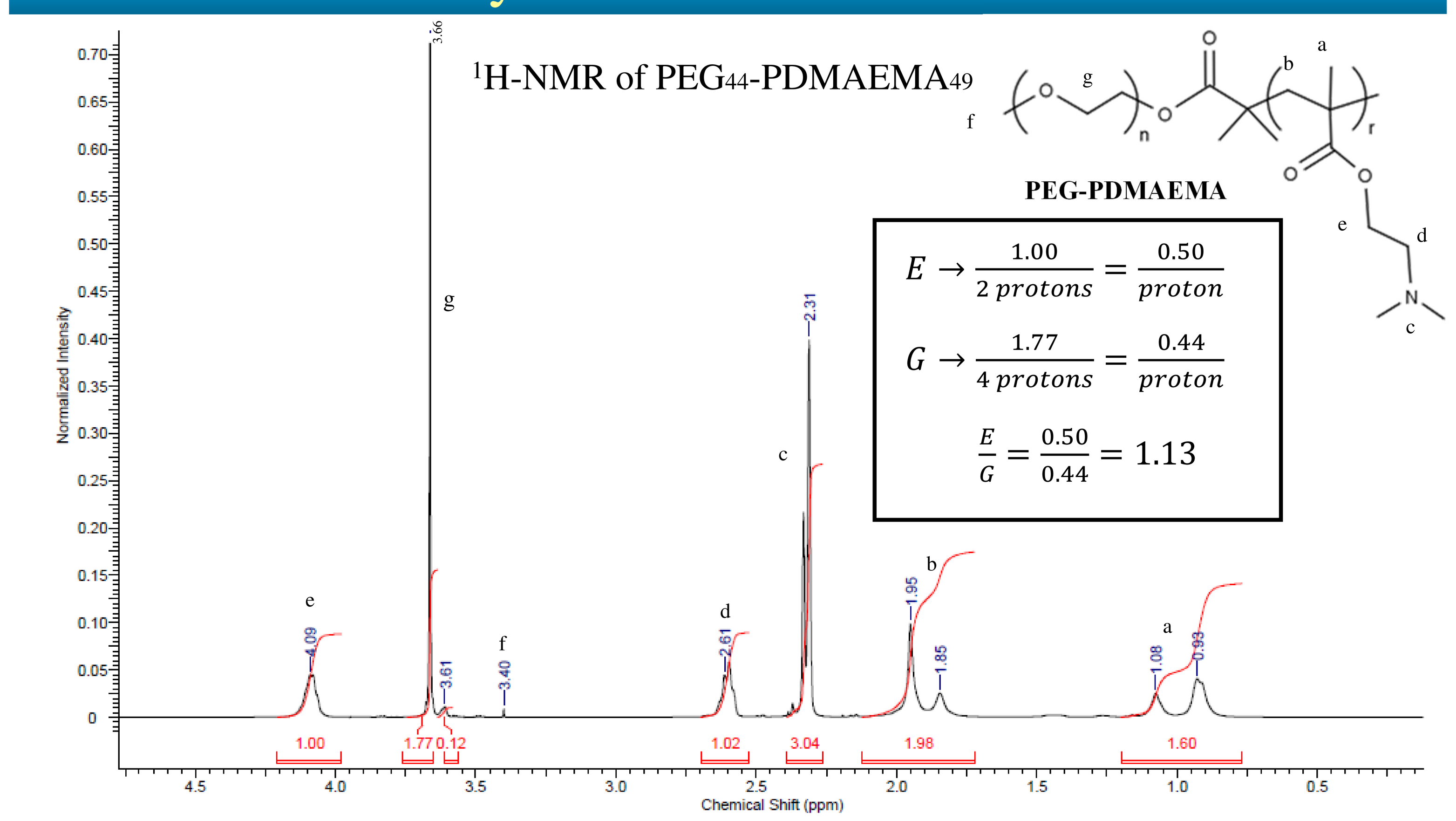
Polymer Synthesis

- A "living" polymerization method has a more controlled growth and offers increased uniformity compared to the commonly used chain polymerization. This results in a lower distribution of polymer chain length and molecular weight, making its properties and behaviors more predictable.

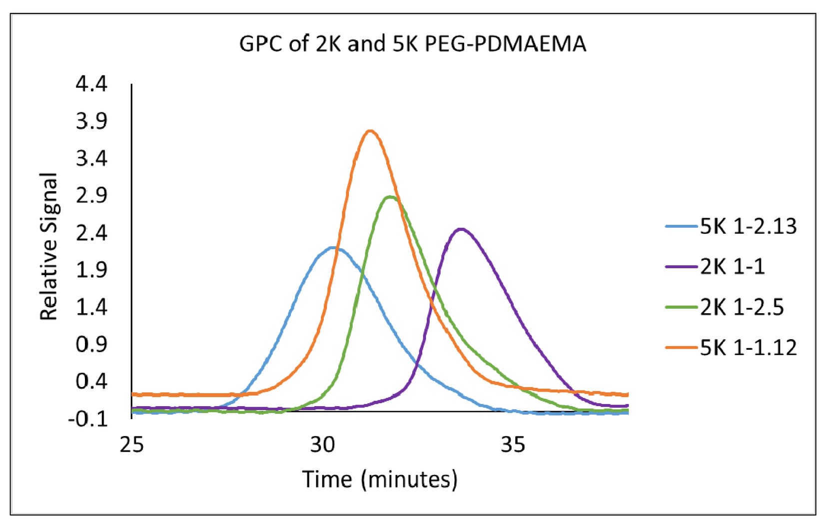


- Atom Transfer Radical Polymerization (ATRP) is used to synthesize the diblock copolymer, PEG-PDMAEMA. The molecular weight can be controlled by changing the ratio of the monomer (DMAEMA) to the initiator (PEG-Br) as well as polymerization time.

Polymer Characterization



- One way to determine molecular weight is through Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR Spectroscopy). This instrument works by comparing the relative amounts of hydrogen atoms present in the polymer chains.
- All peaks are integrated relative to peak E. A comparison of E from the PDMAEMA block to G on the PEG block shows that the PDMAEMA is about 1.1 times longer.



- Another instrument that aids in characterization is Gel Permeation Chromatography (GPC) which measures the polydispersity index (PDI). This is a measure of the distribution of polymer chain lengths.

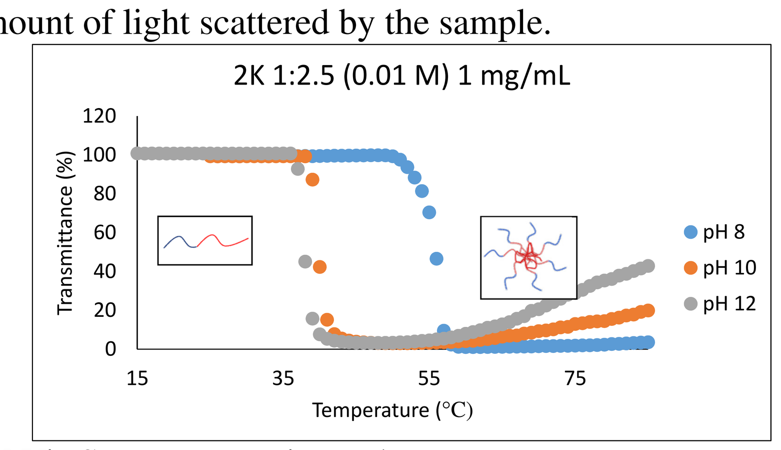
Sample	PDI	Relative Mn (GPC) (kDa)	Mn (NMR) (kDa)
2K PEG-PDMAEMA 1:1	1.09	24.4	10.1
2K PEG-PDMAEMA 1:2.5	1.14	38.4	19.5
5K PEG-PDMAEMA 1:1	1.13	49.4	25.0
5K PEG-PDMAEMA 1:2.13	1.20	67.9	43.1

- The GPC is able to estimate molecular weight based on the retention time of the sample, and then compare it to a standard retention time and corresponding molecular weight.

Polymer Thermoresponsive Study

UV-Vis Studies on 2K PEG-PDMAEMA

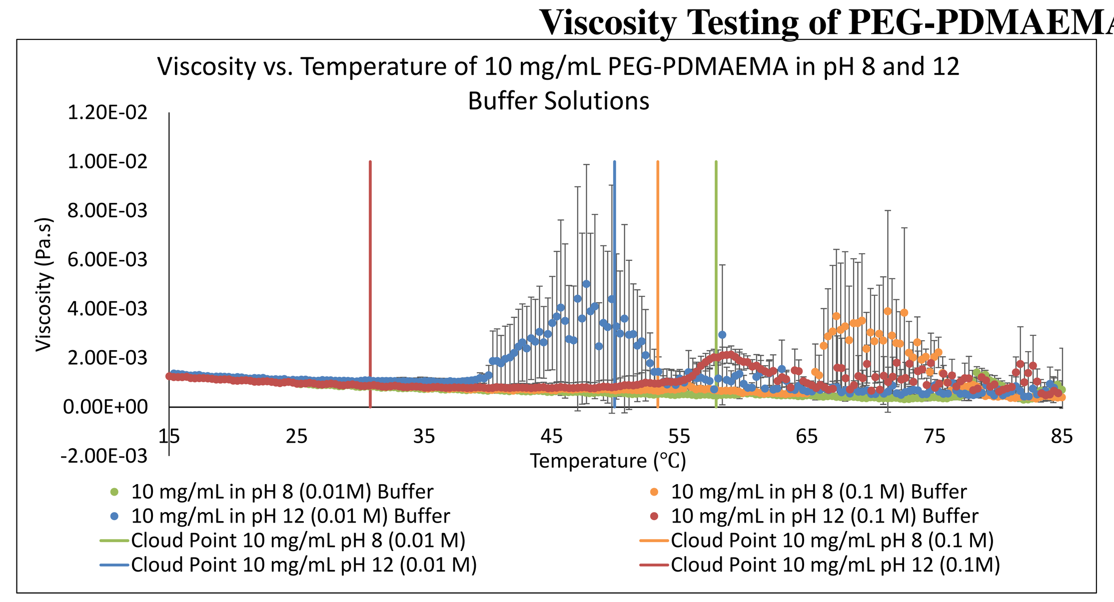
- The change in solubility of the diblock causes both visual and quantitative changes in polymer solutions. When the diblock transitions from soluble to insoluble, the solution becomes cloudy changing the amount of light scattered by the sample.



2K 1:2.5 (0.01 M) 1 mg/mL	
pH	Cloud Point (°C)
8	53.40
10	38.59
12	36.71

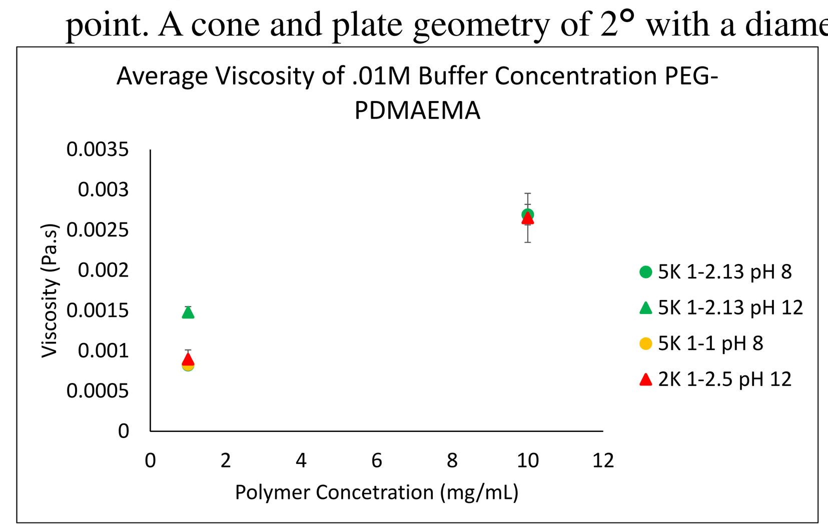
- UV-Vis Spectroscopy is used to:
  - Determine the cloud point of PEG-PDMAEMA.
  - Verify that as pH increases, cloud point decreases.
  - Understand how PDMAEMA molecular weight affects the smart properties of PEG-PDMAEMA.
- The effect of pH and polymer concentration on cloud point is consistent regardless of smart polymer molecular weight. As smart polymer molecular weight increases, the cloud point decreases under more basic conditions.

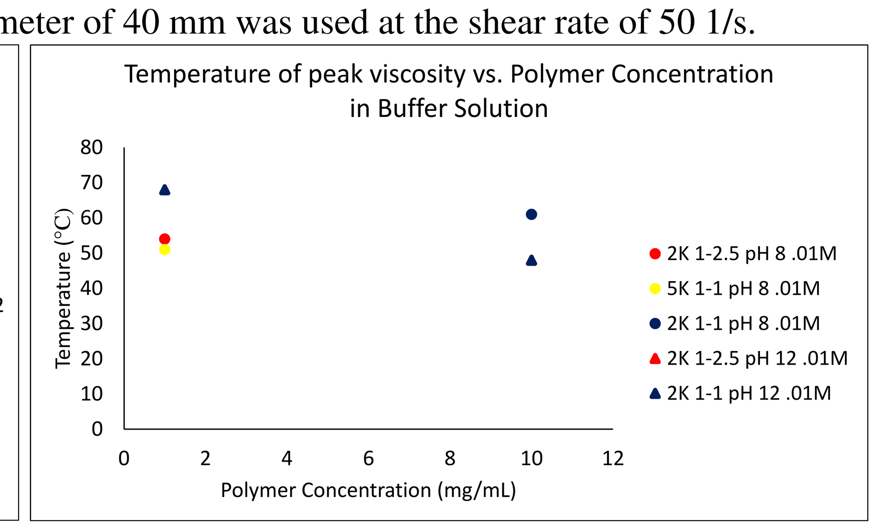
Viscosity Testing of PEG-PDMAEMA



- This graph depicts the viscosity of PEG-PDMAEMA at various pH, polymer concentrations, and buffer concentrations.
- Each vertical line represents the cloud point of each polymer solution.
- The viscosity of the polymer solution changes near or after the cloud point.

- Rheological studies were done to measure the viscosity as a function of temperature below and above the cloud point. A cone and plate geometry of 2° with a diameter of 40 mm was used at the shear rate of 50 1/s.





- The graph above (left) shows the average viscosity of different PEG-PDMAEMA molecular weights. An increase in polymer concentration results in a higher average viscosity. At lower polymer concentration (1 mg/mL) the highest molecular weight results in a higher average viscosity.
- The graph above (right) shows the temperature at which the polymer solution's viscosity first peaked for different PEG-DMAEMA molecular weights.
- For both graphs color represents different molecular weights and shape represents different pH.

Conclusions

- PEG-PDMAEMA is a smart polymer with properties that respond to external stimuli.
- Samples are synthesized to achieve uniformity through "living" polymerization. They are characterized for PDI and molecular weight using GPC and ^{1}H-NMR.
- The effect of smart polymer molecular weight on cloud point as a function of pH and polymer concentration was determined.
- Viscosity studies were performed on PEG-PDMAEMA.

Future Projects and Research Goals

- Change polymer architecture to determine impact on properties.
- Test thermoresponsiveness as a function of PEG molecular weight.
- Perform further rheology studies to understand changes near the cloud point.

Acknowledgments

- Dr. Anthony Wagner
- Elizabeth Stubbs
- Cristian Naxi
- Materials Science and Engineering Program
- Elizabeth Laskowski
- Petroleum Research Foundation (PRF) Grant Number 54467-UNI7

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