

Synthesis and Characterization of a Reversible and Tunable Smart Polymer



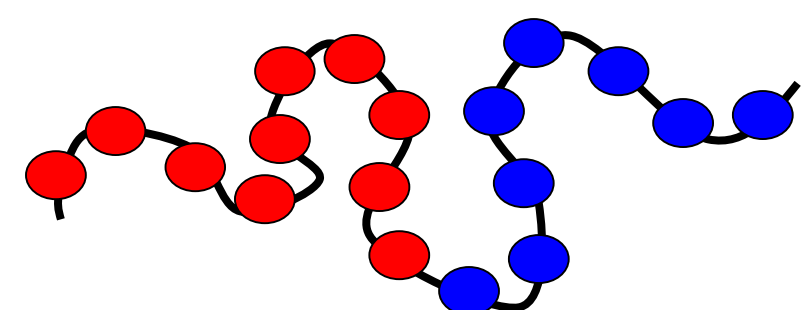
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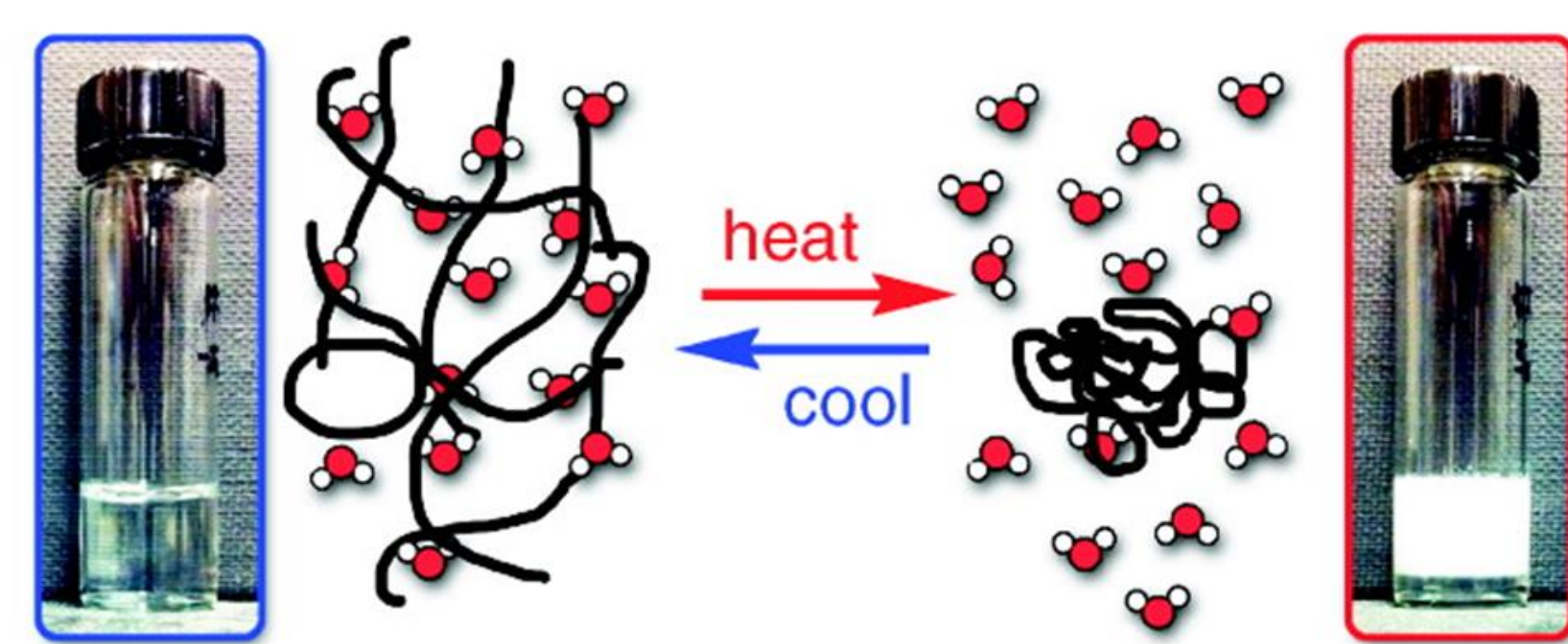
Materials Science

What is a "smart" polymer?

- Polymers are made of covalently bonded repeat units, called monomers, that make up long chains. The structure can be controlled to achieve a diblock copolymer with two different repeat units connected in blocks.



- "Smart" polymers are polymers that can change their properties under certain conditions. Solubility is one property that can change when the conditions such as pH, temperature, and/or polymer concentration change.

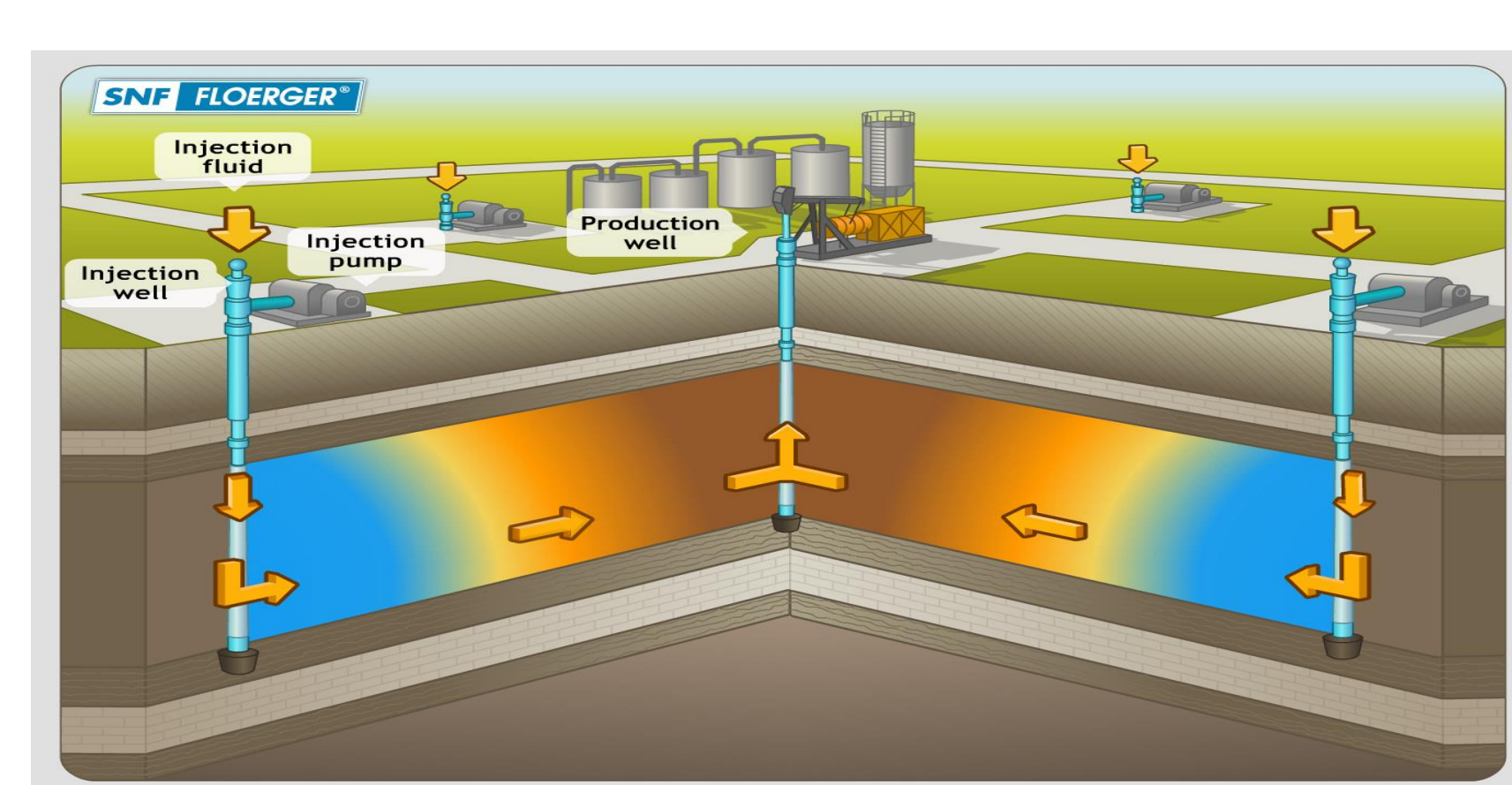
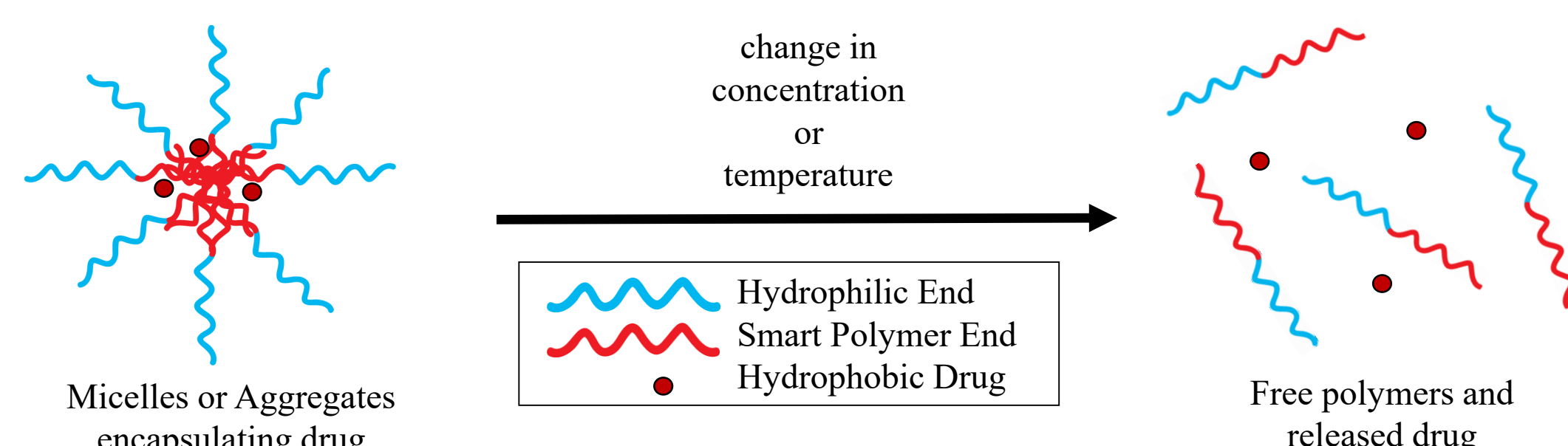


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- Cloud point is the temperature above which the thermoresponsive smart polymer will change its solubility and form aggregates.
- Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is a smart polymer that changes its cloud point when conditions change, such as temperature, pH, polymer concentration, and ionic strength.
- When combined into a diblock copolymer with poly(ethylene glycol), the newly formed polymer, PEG-PDMAEMA, retains the smart polymer properties of PDMAEMA and acquires properties based on its new diblock structure.

What can smart polymers do?

- Many smart polymers are being researched for drug delivery and other biomedical applications due to their ability to change properties under conditions of pH and temperature, such as the ones in the biological environment, to release drugs.
- The cloud point of this copolymer can be fine-tuned based on its structure to control the stimuli-responsive behavior.

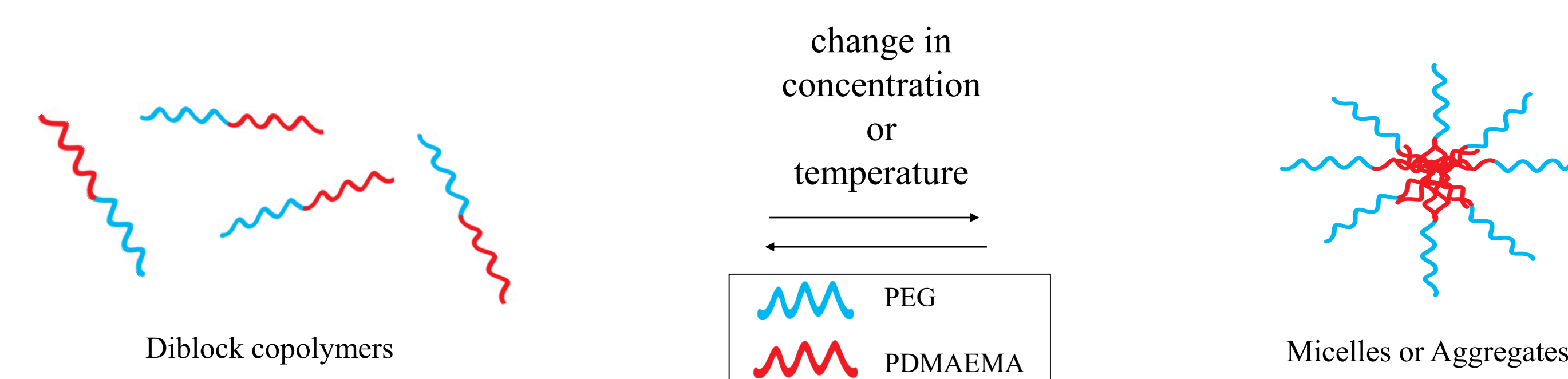


<http://www.2b1stconsulting.com/eor/>

- Two thirds of the oil in the United States are trapped in oil reservoirs due to the limits of conventional oil recovery techniques. Once conventional techniques are exhausted, chemical enhanced oil recovery (EOR) methods are implemented.

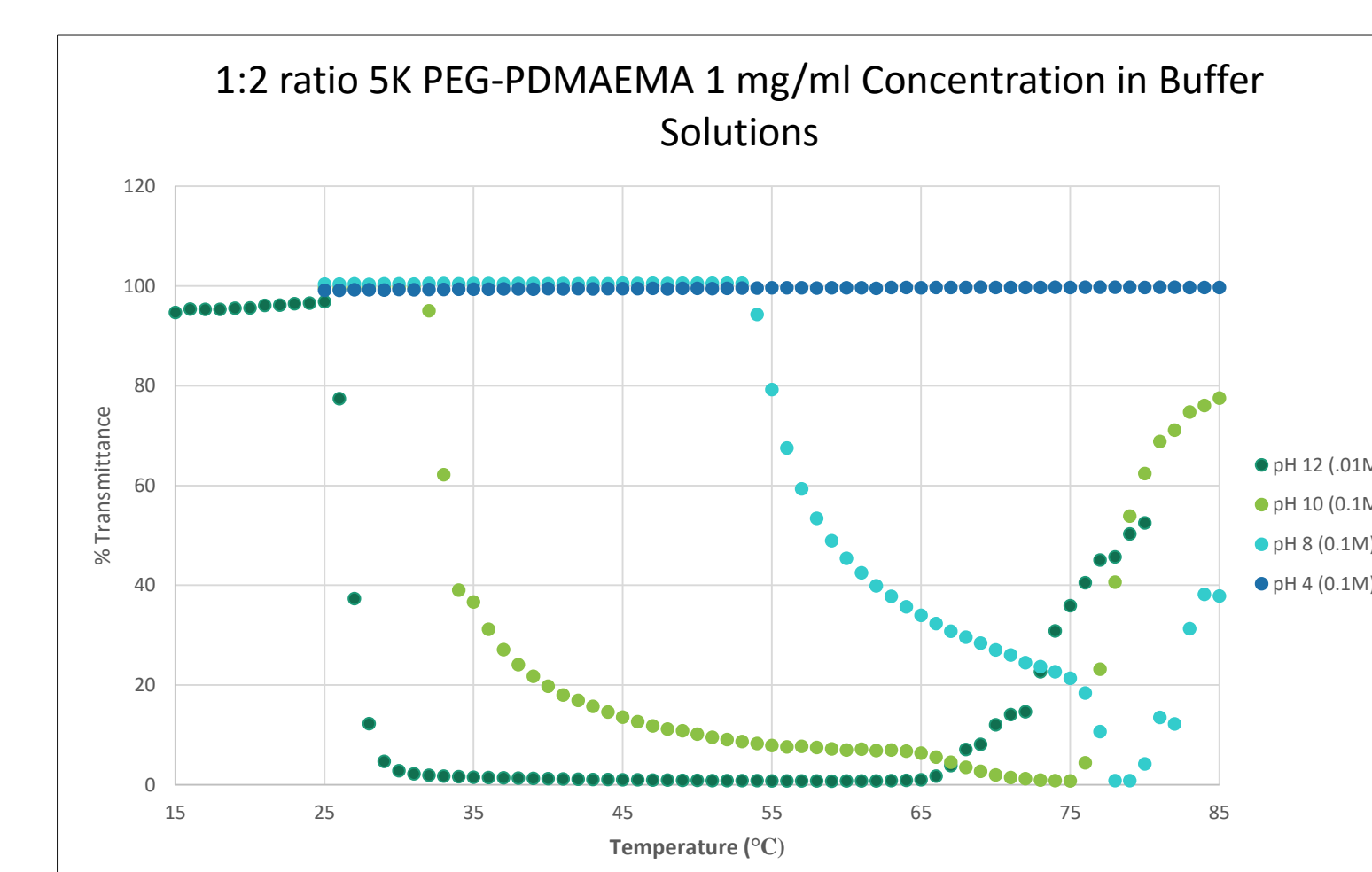
- A mixture of water, surfactants, and polymers is injected into the underground oil reservoir
- The oil and chemical mixture is pumped out and collected above ground
- The mixture is allowed to cool and the oil naturally separates from the polymer and water

Polymer Thermoresponsive Study



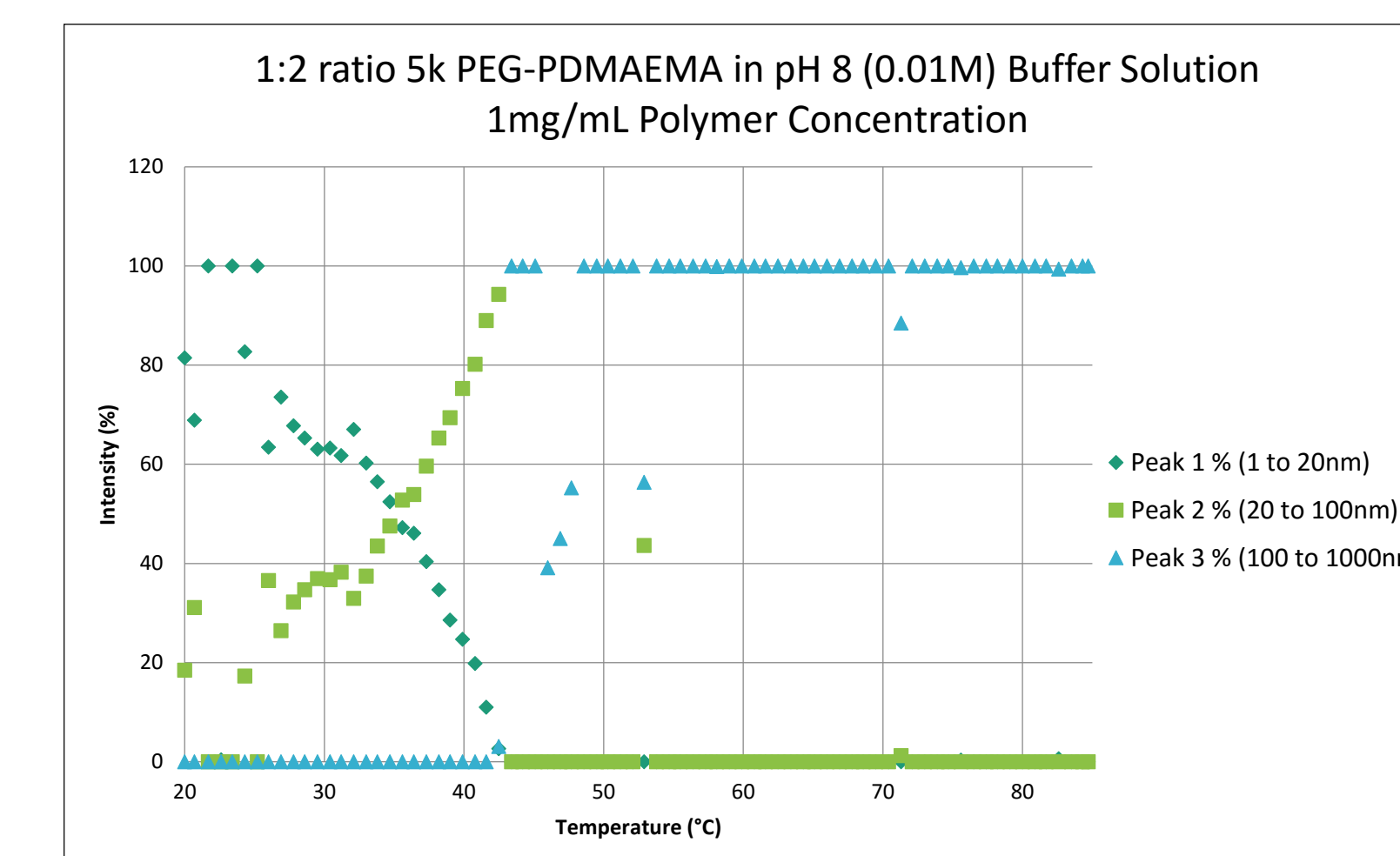
- UV-Vis Spectroscopy and Dynamic Light Scattering are two ways to test PEG-PDMAEMA's smart properties.

UV-Visible Spectroscopy



- UV-Vis Spectroscopy is used to determine the cloud point by detecting micelle/aggregate formation and to determine the effect of pH, concentration, and ionic strength on cloud point.

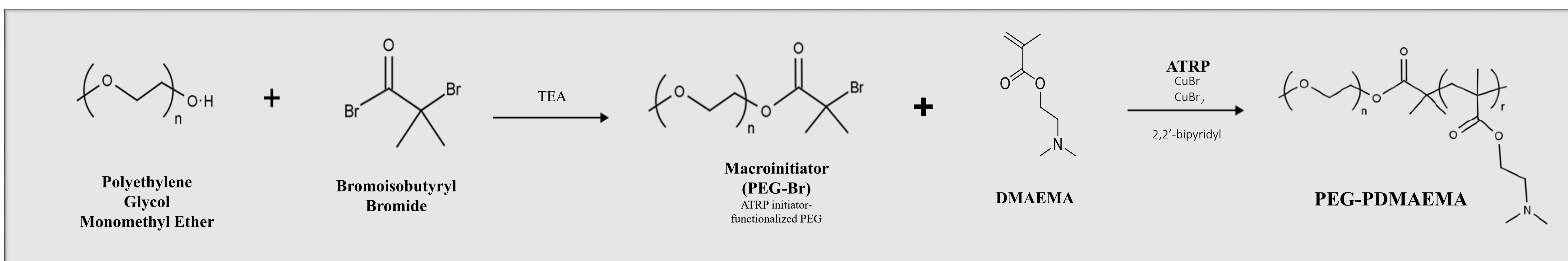
Dynamic Light Scattering



- Dynamic Light Scattering (DLS) is used to determine the cloud point by detecting how light scatters off of the aggregates present and shows how the size of polymers and aggregates changes with temperature.

Polymer Synthesis

- PDMAEMA is synthesized using a living polymerization technique called Atom Transfer Radical Polymerization (ATRP). By varying the ratio of monomer to initiator and the polymerization time, the molecular weight can be tuned.



Polymer Characterization

- Proton NMR and Gel Permeation Chromatography were used to determine whether or not the synthesis was successful as well as compute the weight ratios of the blocks, the molecular weight of the polymer, and the PDI.

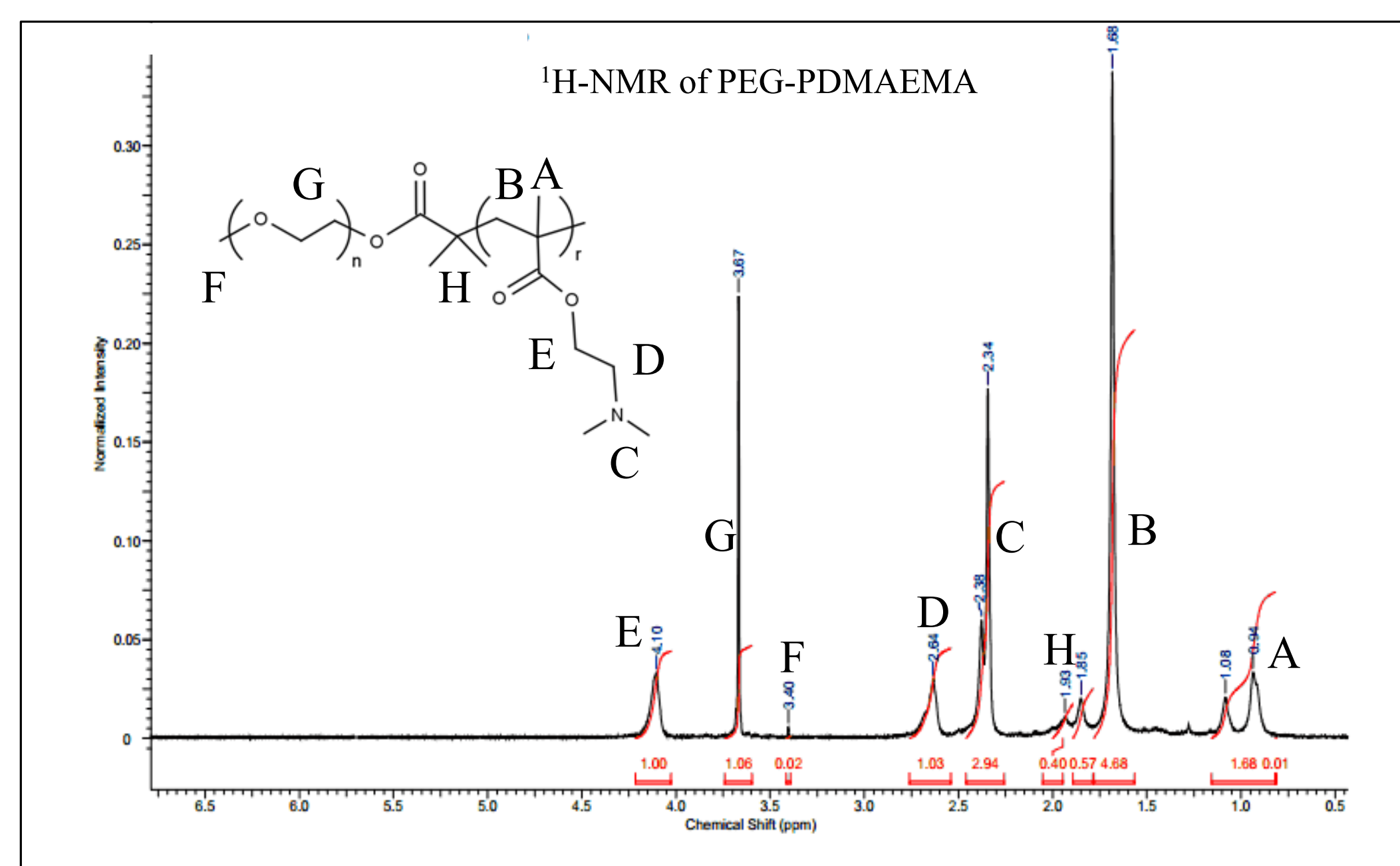
Sample	M _n (NMR) (kDa)	PDI	Molar Ratio
5K PEG-Br	5.6	1.01	-
5K PEG-PDMAEMA 1:1	26.8	1.26	1:1.1
5K PEG-PDMAEMA 1:2	49.3	1.14	1:2.3

- Proton Nuclear Magnetic Resonance Spectroscopy (¹H-NMR) is a technique that was used to calculate molecular weight. It works by comparing the relative amounts of the protons present in the polymer chains allowing for the calculation of the molecular weight.

$$E \rightarrow \frac{1.0}{2 \text{ protons}} = .5 \frac{1}{\text{proton}}$$

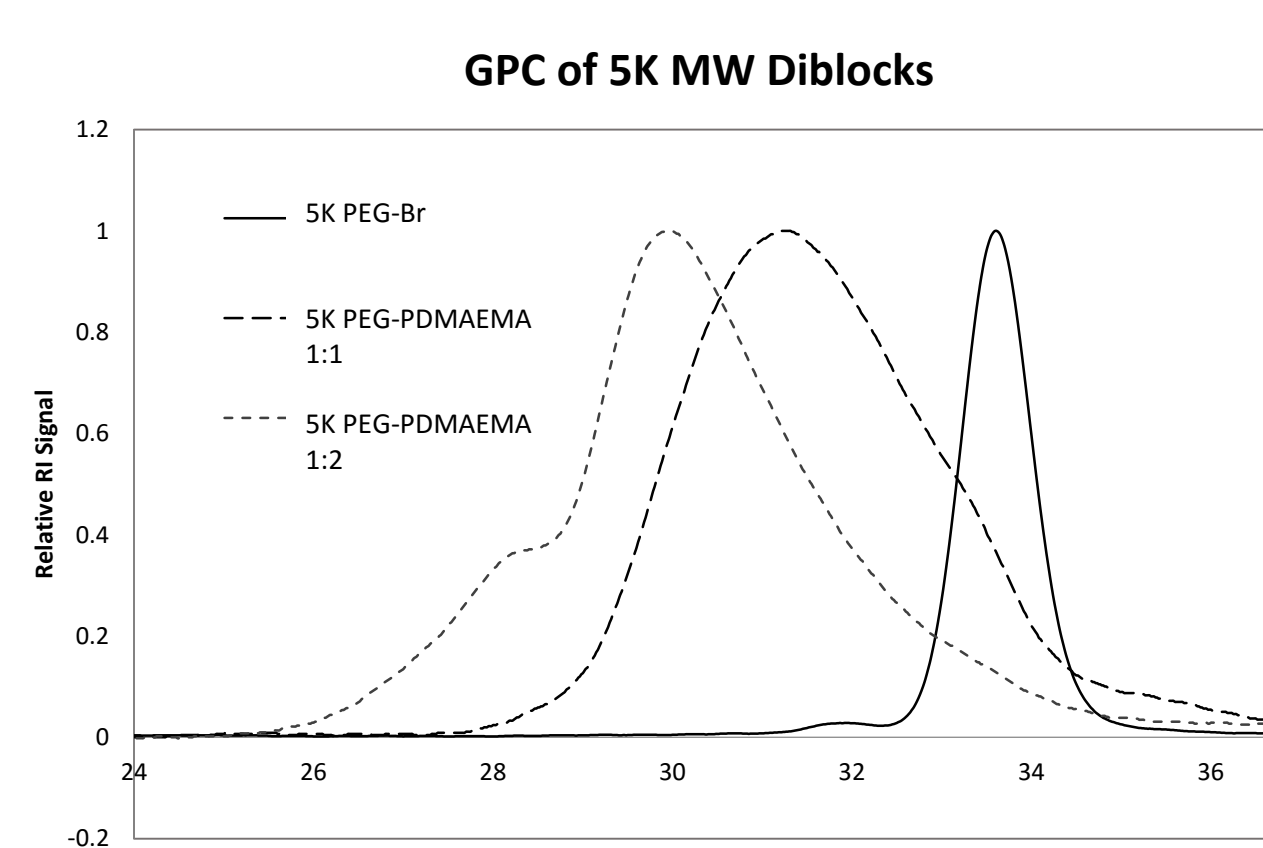
$$G \rightarrow \frac{1.02}{4 \text{ protons}} = .255 \frac{1}{\text{proton}}$$

$$\frac{E}{G} = \frac{.5}{.255} = \frac{1.96}{1.00}$$

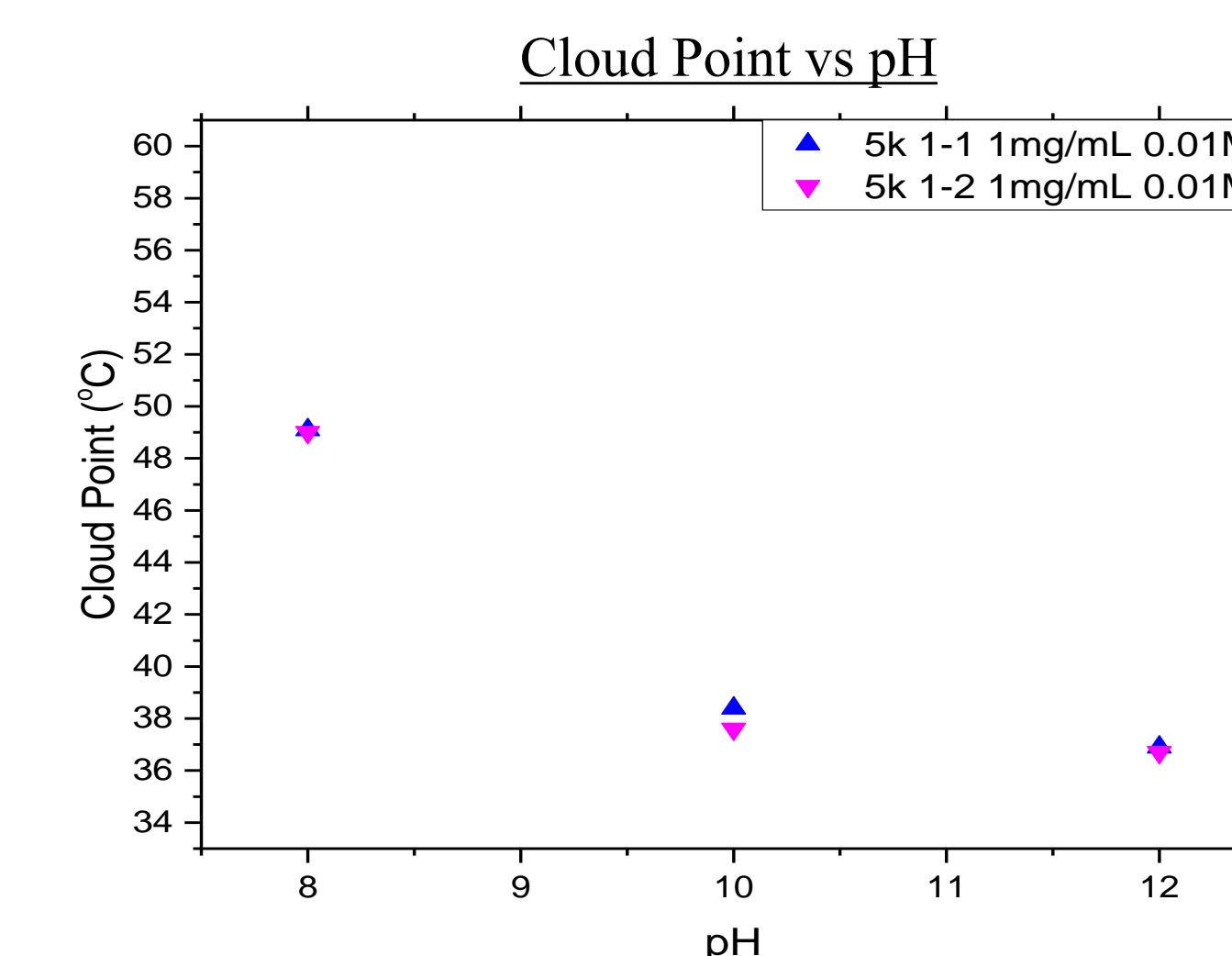


- All peaks are integrated relative to E. A comparison of E from the PDMAEMA block to G on the PEG block shows that the PDMAEMA is about 2x larger.

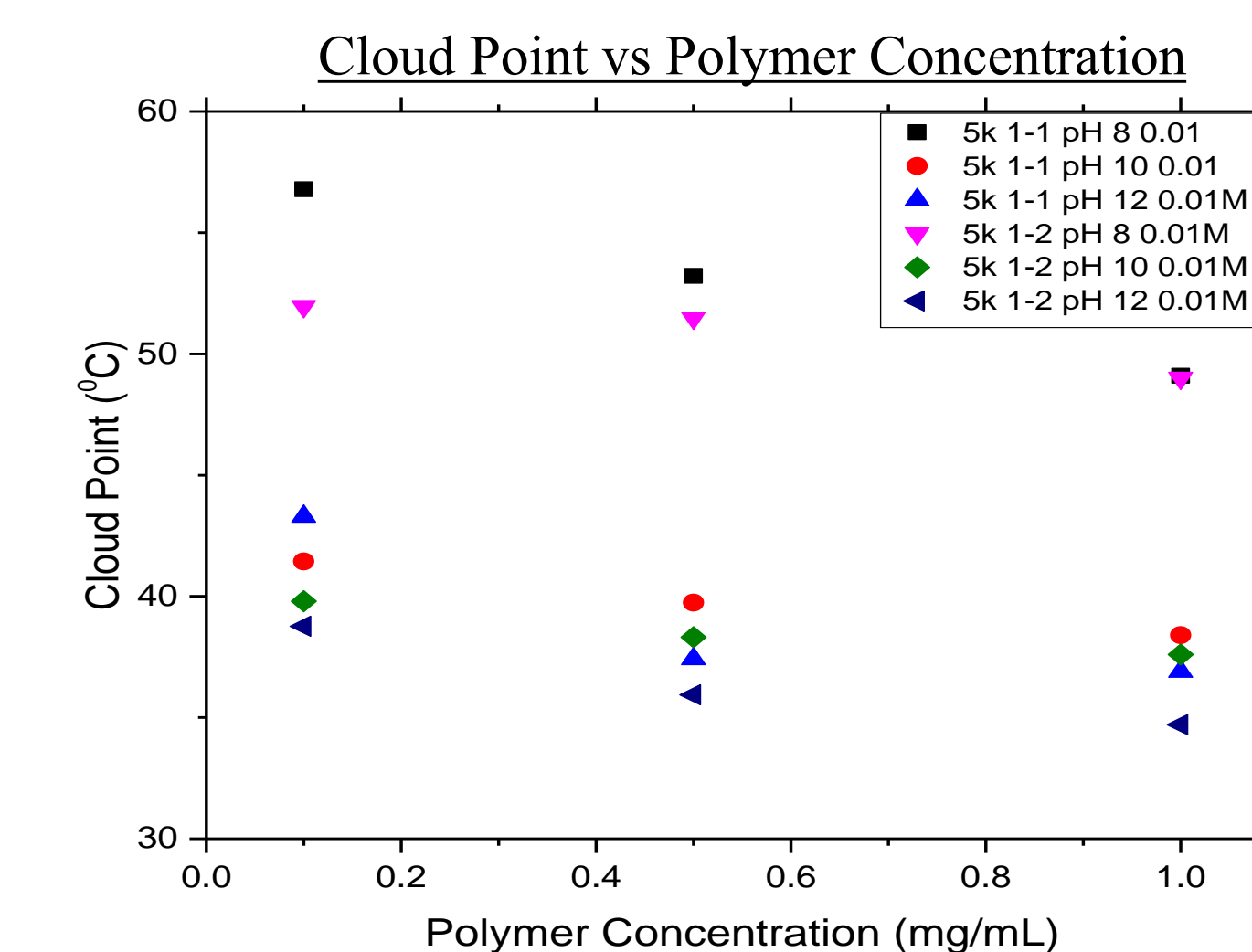
- Gel Permeation Chromatography (GPC) is a method to measure polydispersity index (PDI) as well as relative molecular weight. It estimates molecular weight based on the retention time of the sample, and then compares it to a standard retention time and corresponding molecular weight.



Cloud Point Studies



- The above graph of cloud point vs pH shows that cloud point of a polymer solution can be controlled with pH and the trend that cloud point decreases with an increase in pH.



- The above graph of cloud point vs polymer concentration shows a decrease in cloud point as polymer concentration increases.
- It also shows a decrease in cloud point as the weight of the diblock copolymer increases.

Conclusions

- PEG-PDMAEMA is a smart polymer with properties that respond to external stimuli.
- Cloud points were observed as a function of polymer concentration and pH.
- Samples were studied using UV-Vis spectroscopy as a function of temperature, pH, polymer concentration, and buffer concentration
- Samples were studied using Dynamic Light Scattering as a function of temperature, pH, polymer concentration, and buffer concentration

Future Projects and Research Goals

- Further change polymer architecture to determine impact on properties
- Test thermoresponsiveness as a function of ionic strength

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