Synthesis, Characterization, and Testing of PEG-PDMAEMA Diblock Smart Polymers

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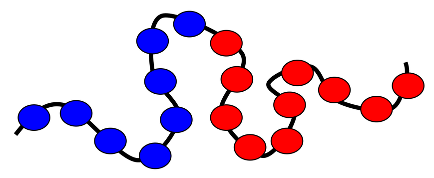
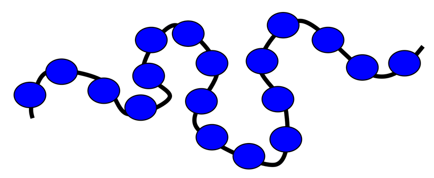
Polymer Basics

Polymers are made of covalently bonded repeat units, called monomers, that make up long chains.

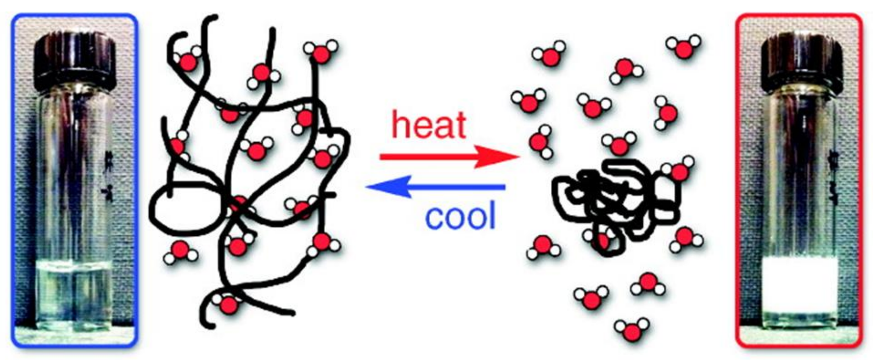




Polymer structure can be modified to achieve homopolymers, polymers made of a single repeat unit, or diblock copolymers, polymers containing two different repeat units on each end.

"Smart" Polymers

"Smart" polymers have the unique ability to dramatically change their properties under certain conditions. One property that can change is their solubility when the conditions such as pH, temperature, and/or concentration change.



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Cloud point is the temperature above which the 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 pH, polymer concentration, and ionic strength. When used in the diblock copolymer poly(ethylene glycol) or PEG-PDMAEMA, it maintains smart polymer properties and gains additional functionalities.

Applications

Smart polymers have a potential future in the field of chemical enhanced oil recovery (EOR). Conventional methods are inefficient, leaving up to 65% of oil in the underground reservoirs. EOR increases the oil yields through the injection of water, polymer, and a surfactant. These additives help oil move towards the pump where it can then be recovered.

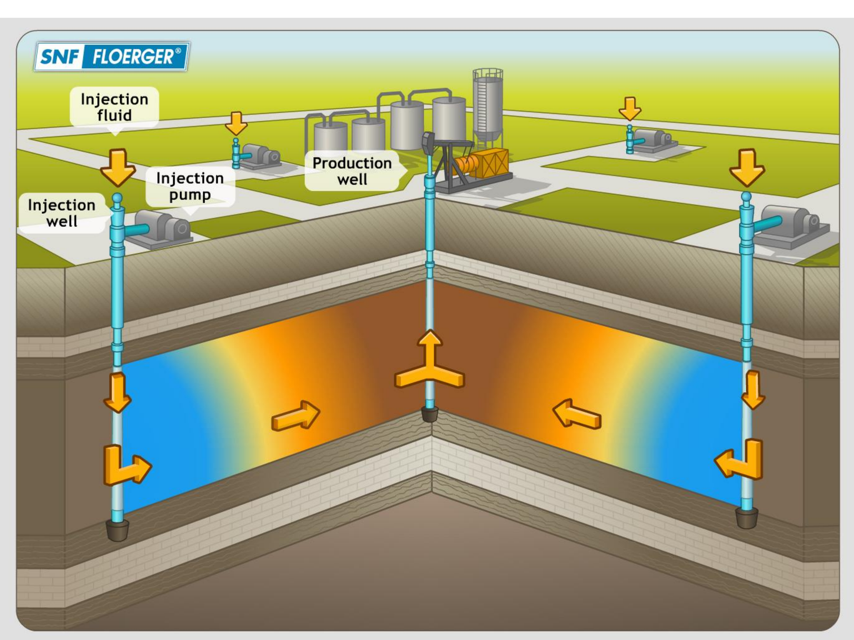
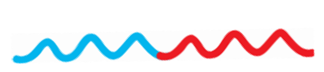


Image from http://www.2b1stconsulting.com/eor/

The addition of polymer to the water increases the viscosity and makes it closer to that of oil. Similar viscosities will mix better. In the case of EOR, better mixing moves more oil to the pump area.

Surfactants are molecules with a hydrophilic head and a hydrophobic tale. When placed at the interface of water and oil, they will align and decrease the interfacial tension, which also allows for better mixing.

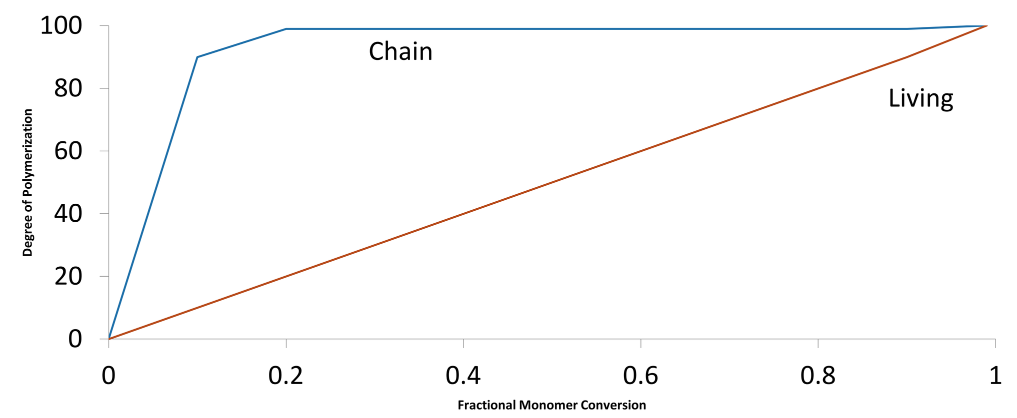


PEG block Hydrophilic head

PDMAEMA block Reversibly hydrophobic tail

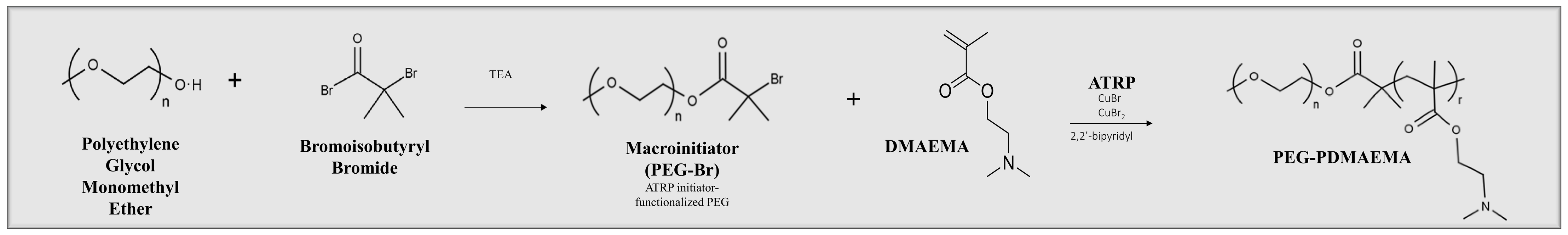
PEG-PDMAEMA potentially serves as both the polymer and the surfactant in EOR. Because it has a dual purpose, it can reduce the amount of additives to the oil. This offers many benefits including decreased cost and waste while providing an adaptable system that can be tuned to the needs of different EOR locations. The smart functionality of the PEG-PDMAEMA allows the oil mixture to be separated after recovery and to reuse the smart polymer surfactant.

Polymer Synthesis and Characterization



Synthesis can be achieved using either chain or "living" polymerization methods. The living method has a more controlled growth and therefore increases uniformity. This results in a lower distribution of polymer chain length and molecular weight. This way, the properties are more similar and more defined for all chains. The more similar the properties of each polymer, the more consistent and predictable the behavior will be.

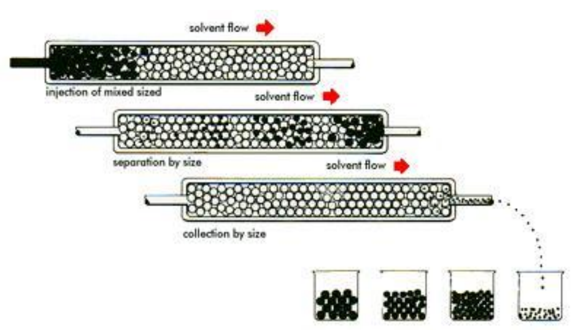
PDMAEMA is synthesized using a living polymerization called Atom Transfer Radical Polymerization (ATRP). By varying the ratio of monomer to initiator and the polymerization time, the molecular weight can be controlled.



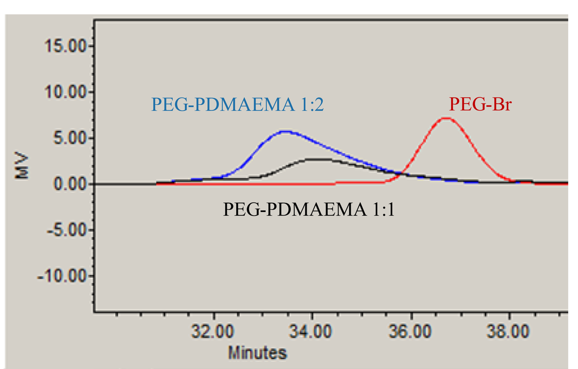
One way to test uniformity of the synthesized polymer is to measure the polydispersity index (PDI). It is a measure of the distribution of polymer chain lengths. A PDI of 1 indicates that all polymers are the exact same length. Living polymerization can achieve a PDI less than 1.2 for synthetic polymers.

Sample	PDI	Relative Mn (GPC)	Mn (NMR)
PEG-Br	1.10	4100	1900
PEG-PDMAEMA 1:1	1.08	21300	8700
PEG-PDMAEMA 1:2	1.08	28000	15500

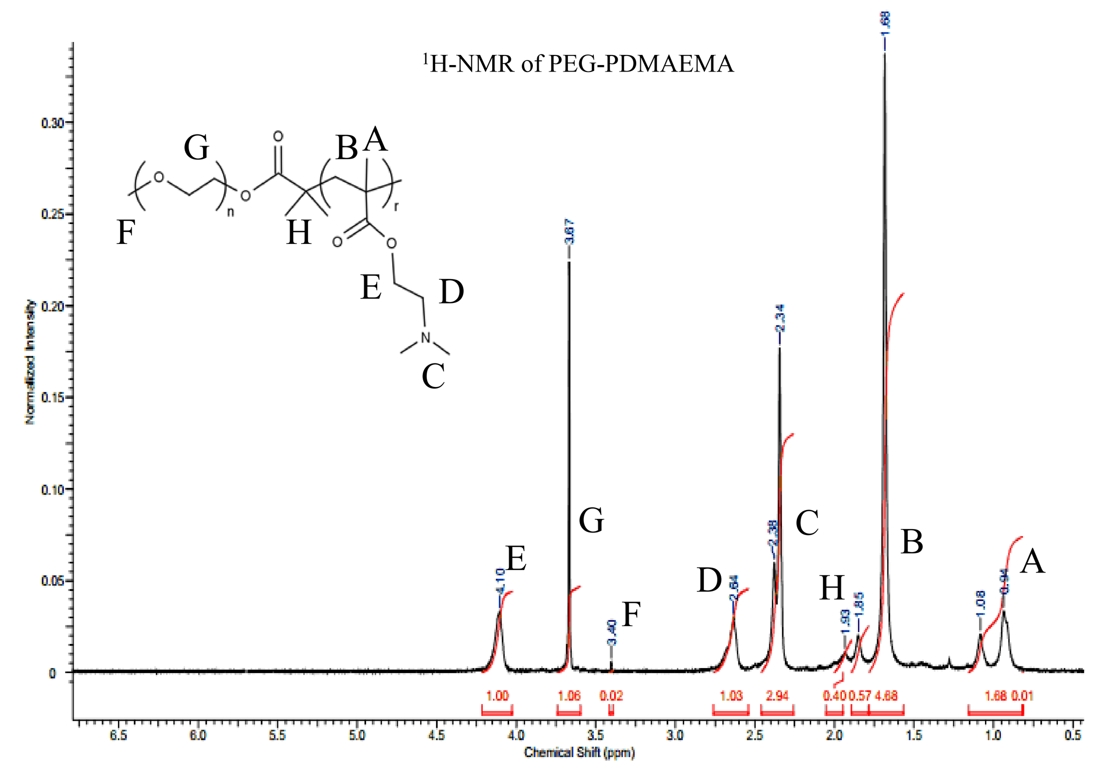
Gel Permeation Chromatography (GPC) is a method to measure PDI as well as relative molecular weight. It uses a series of columns with different sized pores to separate molecules based on size. The smaller the molecule, the more time it will take to go through the columns.



https://sites.google.com/site/gpclabreport/gpc-how-it-works



The graph shows that PEG-Br, a smaller molecule, takes more time than PEG-PDMAEMA. It also shows how the ratio 1:1 for PEG-PDMAEMA is smaller than that of 1:2. When compared to polystyrene standards, the time difference is used to calculate the relative molecular weight and PDI.



Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR) is a tool to calculate molecular weight. By comparing the integration of protons, (how many there are in the polymer chains) molecular weight can be calculated.

All of the peaks were integrated relative to the E peak of PDMAEMA labeled above.

A comparison of E from the PDMAEMA block to G on the PEG block shows that the PDMAEMA is ~2x longer.

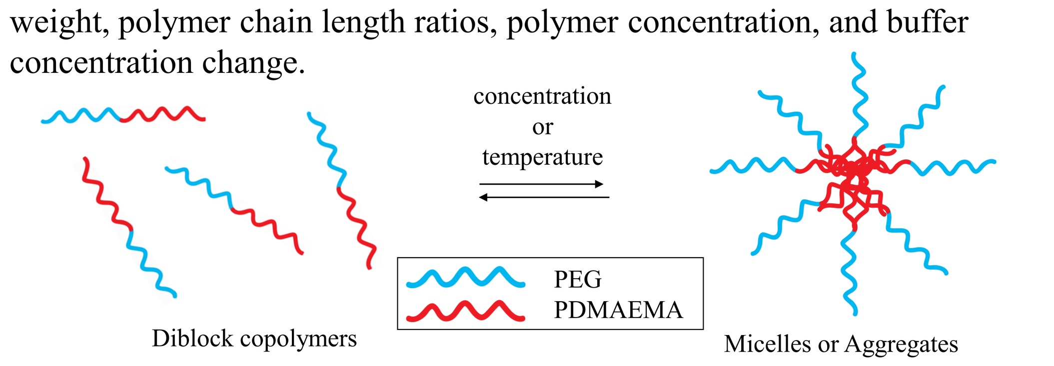
$$E \rightarrow \frac{1.0}{2\ \text{protons}} = .5\ \frac{1}{\text{proton}}$$

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

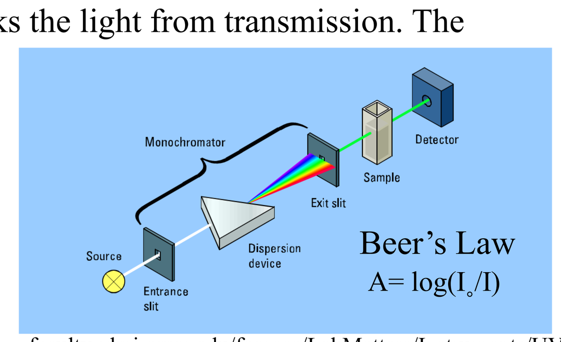
$$\frac{E}{G} = \frac{.5}{.255} = \frac{1.96}{1.00}$$

Polymer Thermoresponsive Study

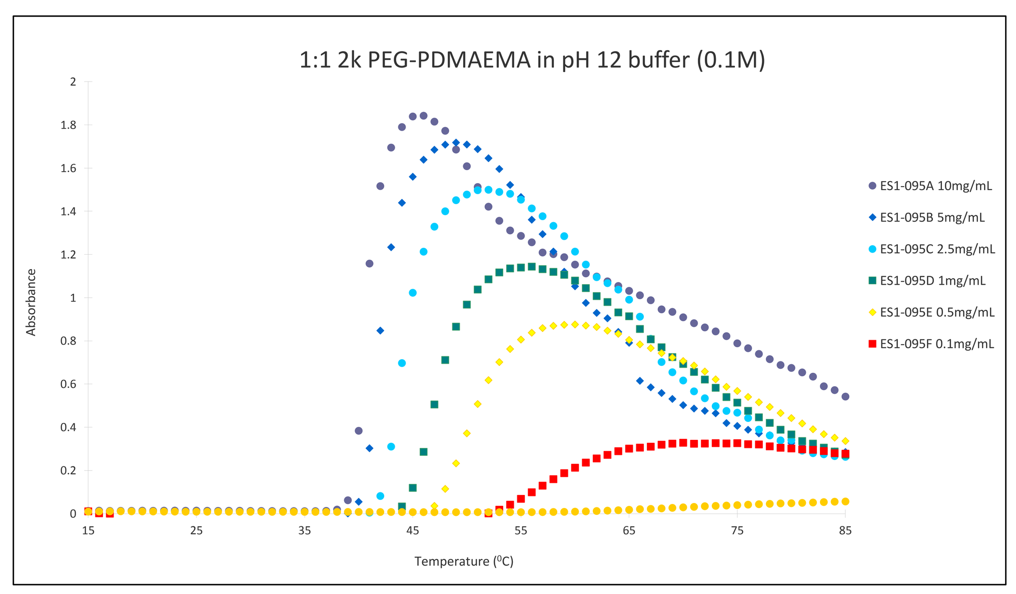
It is important to verify that PEG-PDMAEMA maintains the smart polymer property of changing solubility with temperature. UV-Vis spectroscopy is one tool used to measure the change in cloud point as variables such as molecular weight, polymer chain length ratios, polymer concentration, and buffer concentration change.



UV-Vis reads the absorbance of light by a sample. When polymer reaches its cloud point, aggregates form and blocks the light from transmission. The cloud point can be determined by the absorbance increasing above zero. Beer's Law is used to show how Absorbance (A) varies as a function of the ratio of light in (I_o) to light out (I). Zero absorbance means no aggregates are present and all light passes through the sample.



faculty.sdmiramar.edu/fgarces/LabMatters/Instruments/UV_Vis/Cary50.htm



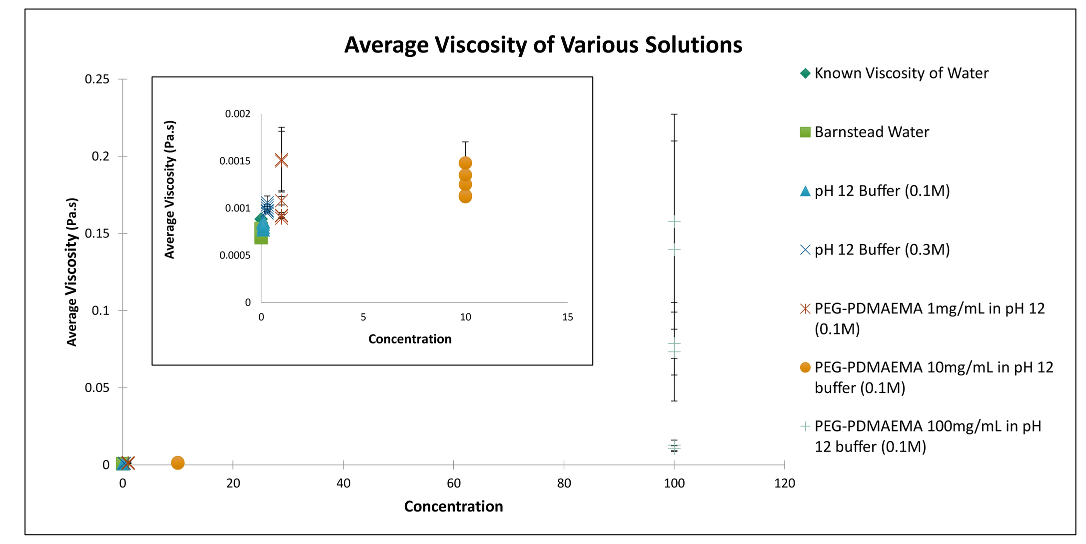
PEG-PDMAEMA thermoresponsive studies look at the change in the cloud point as the concentration changes. An increase in the concentration of polymer has a clear increase in the amount of absorbance/scattering. Increased concentration also lowers the cloud point.

The detection of a cloud point confirms that PEG-PDMAEMA is a smart polymer. The ability to change the cloud point by changing concentration can be useful for applications including EOR.

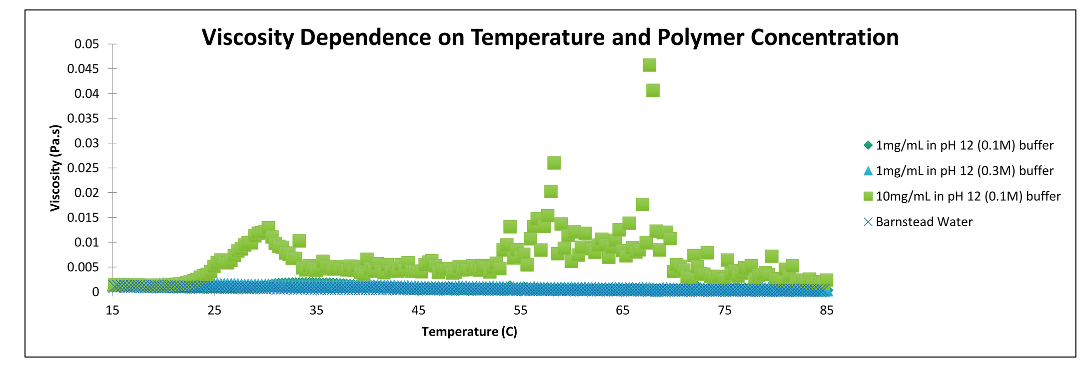
Polymer Testing

In order to determine if PEG-PDMAEMA serves as both a polymer and a surfactant in EOR, testing of how viscosity and interfacial tension change of the aqueous PEG-PDMAEMA solution is needed. This can predict its ability to mix with oil.

Rheology studies the flow of liquids by applying a gradual sheer strain and recording its resistance to flow. In the case of EOR, an increase in the average viscosity will make the solution closer to the viscosity of oil.

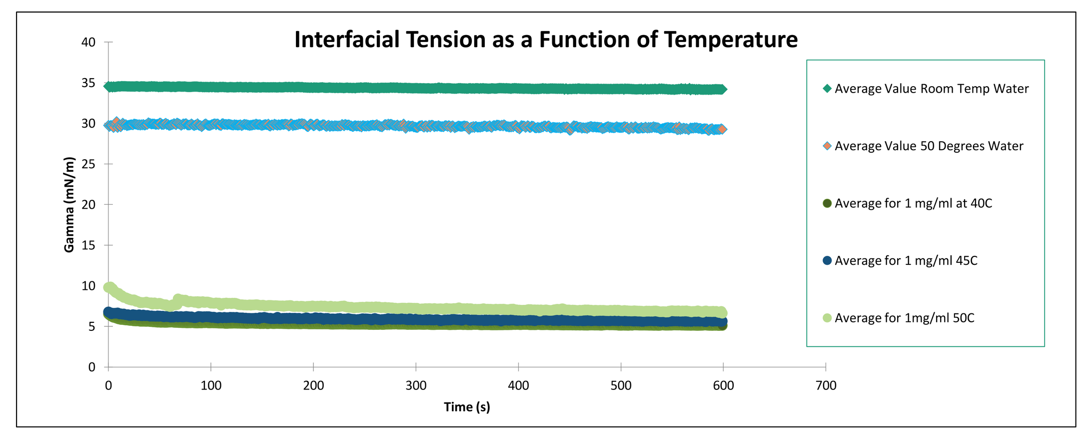


An increase in PEG-PDMAEMA concentration increases the average viscosity as predicted.



Understanding the viscosity of the smart polymer as a function of temperature and concentration is necessary to understand its properties for applications including EOR.

By studying the interfacial tension, a prediction of how PEG-PDMAEMA will act as a surfactant can be made. A lower interfacial tension allows for better mixing and is shown by a lower gamma value. This value comes from the Young-Laplace equation, which describes the relationship between capillary pressures and the interfacial tension between two static fluids.



The graph shows how the addition of PEG-PDMAEMA greatly lowers the interfacial tension of water and oil. The gamma value decreases by ~70%.

Conclusions

- PEG-PDMAEMA is a smart polymer with properties that can be tuned.
- Samples are synthesized to achieve uniformity through living polymerization. They are characterized for PDI and molecular weight using GPC and ^{1}H-NMR.
- UV-Vis spectroscopy shows the cloud point decreases as concentration increases.
- Rheology and tensiometry show that PEG-PDMAEMA increases the ability to mix water and oil by increasing the viscosity and lowering the interfacial tension. Smart properties are still under investigation.

Future Projects and Research Goals

- Change polymer architecture to determine impact on properties
- Test thermoresponsiveness as a function of pH and ionic strength
- Study aggregate size using dynamic light scattering

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