Studying the Effects of Varying pH and Temperature on the Smart Polymer mPEG-*block*-PDMAEMA

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Polymers

- Polymers are made up of many small, repeating units called monomers, that bond together in a chainlike fashion.
- Polymer structure can be controlled such that different types are made, like homopolymers - polymers made of a single repeat unit, or copolymers -that contain two different monomers.

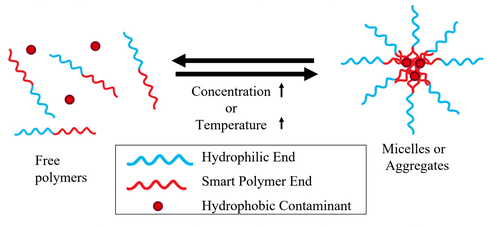
"Smart" Polymers

- "Smart polymers" change their mechanical properties in response to changes in stimuli, such as pH, temperature, and polymer concentration.

- We chose to focus on the viscoelastic properties when determining the effects of various stimuli for these polymers in an aqueous solution. Viscoelasticity refers to the material acting both like a solid and a liquid.
- Poly(2-dimethylamino)ethyl methacrylate-block-poly(ethylene glycol)-block-poly(2-dimethylamino)ethyl methacrylate, or PDMAEMA-PEG-PDMAEMA, is a tri-block copolymer with viscoelastic properties that depend on polymer composition, temperature, pH, and polymer concentration.

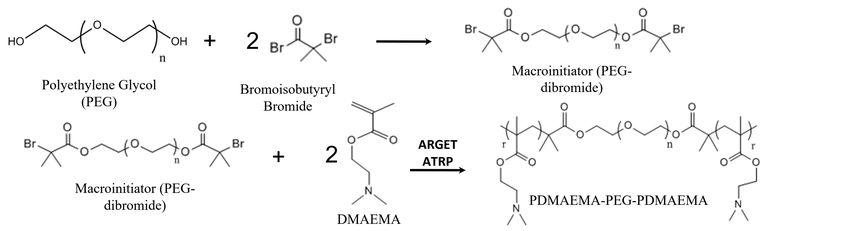
Applications

- When a polymer has one end that is hydrophobic and one end that is hydrophilic, it is a polymeric surfactant.
- Hydrophilic means it is attracted to water.
- Hydrophobic means it is repelled by water.



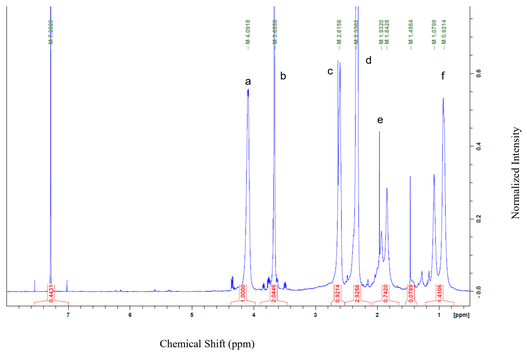
- Smart polymers can be used as environmentally cleaner fracking fluid for better oil recovery.
- Underground is much warmer than aboveground.
- Smart polymers would be hydrophilic aboveground and be able to be pumped underground with water.
- The change in temperature underground would turn the polymer hydrophobic, surrounding the oil and bringing more oil back to the surface.
- The polymer would change back to hydrophilic at the surface releasing the oil while also becoming reusable.

Polymer Synthesis and Characterization



- PDMAEMA-PEG-PDMAEMA is synthesized by using a process called Activators ReGenerated by Electron Transfer Atom Transfer Radical Polymerization, or ARGET ATRP.
- This "living" polymerization method has more control over forming precise polymer chains than traditional polymerization methods. This results in the polymer chain lengths and molecular weight being more consistent, making properties and behaviors more predictable.
- The PEG can be bought and then functionalized to make macroinitiator with various molecular weights.
- Varying the ratio of monomer to initiator controls the molecular weight of PDMAEMA during ARGET ATRP.

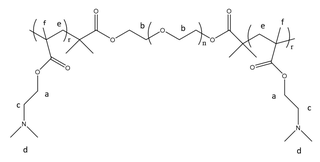
^{1}H-NMR of 2K PDMAEMA-PEG-PDMAEMA



$$A \rightarrow \frac{1.00}{2\ protons} = \frac{0.50}{proton}$$

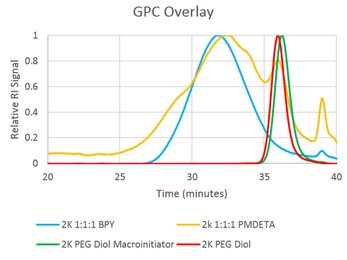
$$B \rightarrow \frac{2.04}{4\ protons} = \frac{0.51}{proton}$$

$$\frac{A}{B} = \frac{0.50}{0.51} = 0.98$$



- Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR) is a tool commonly used to determine molecular weight, structure, and purity. The integrations of the peaks (relative amounts of the protons present in the polymer chains) are compared, and then the molecular weight can be calculated.
- All peaks are integrated relative to 'A'. A comparison of 'A' from the PDMAEMA block to 'B' on the PEG block shows that the PDMAEMA is about the same length as the PEG.

Sample	PDI	Mn (kDa)	Mw (kDa)
2K PEG Diol	1.02	12.46	12.73
2K PEG Diol Macroinitiator	1.02	11.65	11.90
2K 1:1:1 BPY	1.36	38.46	52.16
2K 1:1:1 PMDETA	1.60	36.44	58.42



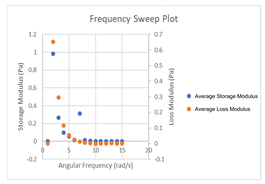
- Gel Permeation Chromatography (GPC) gives the polydispersity index (PDI) of samples, which is the relative distribution of relative polymer chain lengths.
- GPC can also be used to determine reaction completion by comparing GPC data from different samples - such as 2K 1:1:1 BPY and the 2K Macroinitiator, which have no overlapping peaks, indicating reaction completion.

Conclusions and Future Research Goals

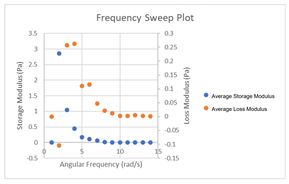
- PDMAEMA-PEG-PDMAEMA and PEG-PDMAEMA are smart polymers - various stimuli can change their properties.
- The effect of changing pH, temperature, and polymer concentration changes the viscoelastic properties of the polymer, causing it to behave more like a solid or a liquid.
- BPY (Bipyridine) proved to be a more effective ligand than PMDETA in 2K triblock copolymer synthesis.
- Characterization of triblock copolymers will include UV-Vis and cloud point studies, dynamic light scattering, and rheology for both viscosity and viscoelasticity testing.

Frequency Sweep Studies of PEG-PDMAEMA 2K 1:2.5

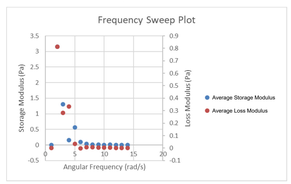
- The rheometer was used to determine storage (G') and loss (G") moduli. The temperature was set to 25C. The data was collected for four different polymer samples that had different pH solutions and buffer concentrations and strain percentages determined by previous experiments. The study used either pH 8 or 12, and the buffer concentrations were 0.1M and 0.01M. Using the rheometer, three trials of the same sample were run. Angular frequency (rad/s) vs storage and loss moduli was graphed.



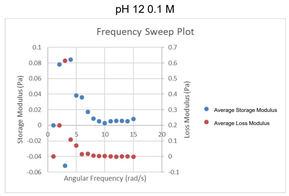
pH 12 0.01 M



pH 12 0.1 M



pH 8 0.01 M

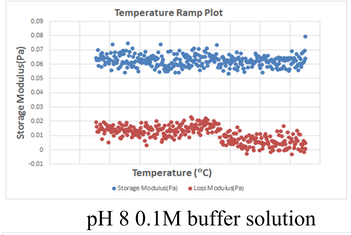


pH 8 0.1 M

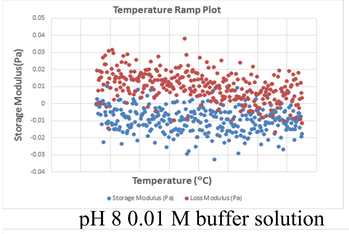
- At low frequencies, there is greater variation in G' and G", and increasing frequency results in a leveling off of the moduli.
- Determining the effect of pH, polymer composition, polymer concentration, and buffer concentration on G' and G" as a function of frequency is ongoing.

Temperature Ramp Studies of PEG-PDMAEMA 2K 1:1

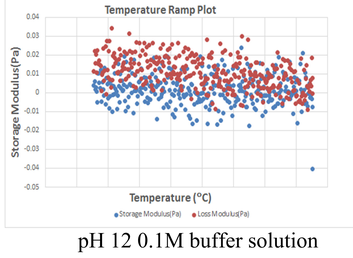
- For temperature ramp studies, the temperature range was set to 15-85C. The data was collected for four different aqueous polymer samples that had different buffer concentration and pH. The study focused more on the aqueous polymer samples with a ratio of 10mg/ml polymer concentration, while changing the buffer concentration between 0.1M and 0.01M and changing pH between 8 and 12. Three trials of the same sample were run using the rheometer and a plot of temperature vs. storage and loss moduli was graphed.



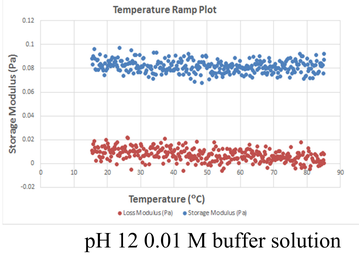
pH 8 0.1M buffer solution



pH 8 0.01 M buffer solution



pH 12 0.1M buffer solution



pH 12 0.01 M buffer solution

- For 10 mg/ml samples, G' and G" values are similar across the entire temperature range measured.
- Determining the effect of pH, polymer composition, polymer concentration, and buffer concentration on G' and G" as a function of temperature is ongoing.

Acknowledgments

- Anthony Wagner
- Elizabeth Laskowski
- Materials Science and Engineering Program
- UW System Applied Research Grant
- UWEC Differential Tuition

Celebration of Excellence in Research and Creative Activity