# Viscosity Testing of PEG-PDMAEMA and Preliminary ARGET ATRP Synthesis

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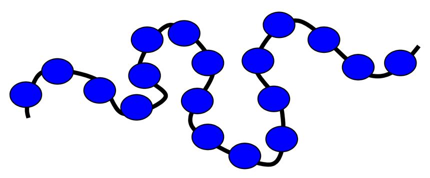
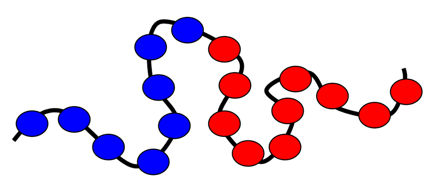
## Polymer Basics

- Monomers are small molecules that are bonded together to make polymers.
- Polymers can have distinct structures which can affect the properties of the polymer.

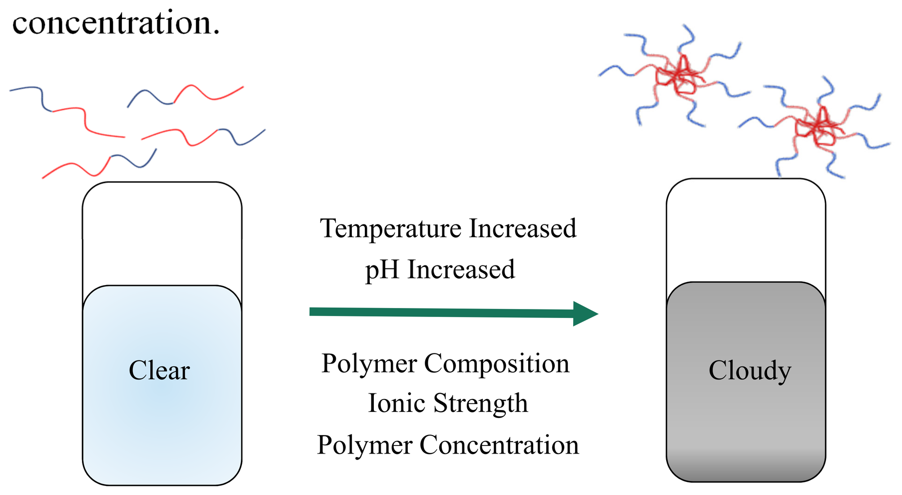


- The polymer structures that are being studied can either be a homopolymer, a polymer composed of one repeating unit, or a diblock copolymer, which is composed of two repeating blocks that are covalently bonded together.

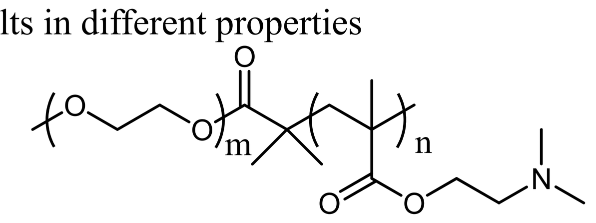


## "Smart" Polymers

- "Smart" polymers respond to small changes in the environment in an intriguing way dissimilar to regular polymers. Viscosity, which is a fluid's resistance to flow, 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 soluble (hydrophilic) to insoluble (hydrophobic).
- Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is the smart polymer that is being tested. Different conditions such as pH, buffer concentration, and polymer concentration will affect the cloud point of PDMAEMA. When it is used as a diblock copolymer with poly(ethylene glycol), PEG-PDMAEMA, the structure results in different properties

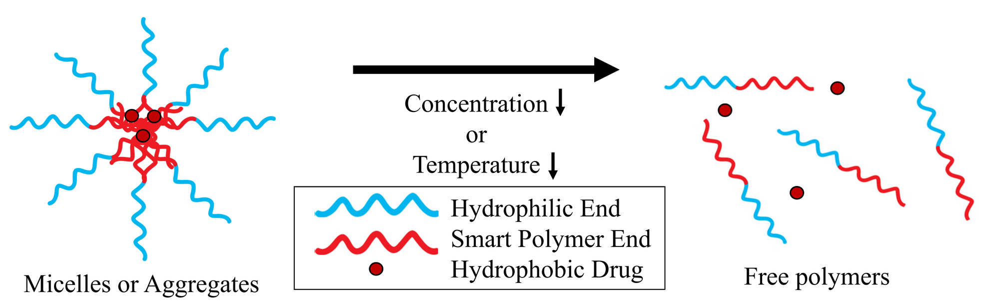


**PEG-PDMAEMA**

## 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.



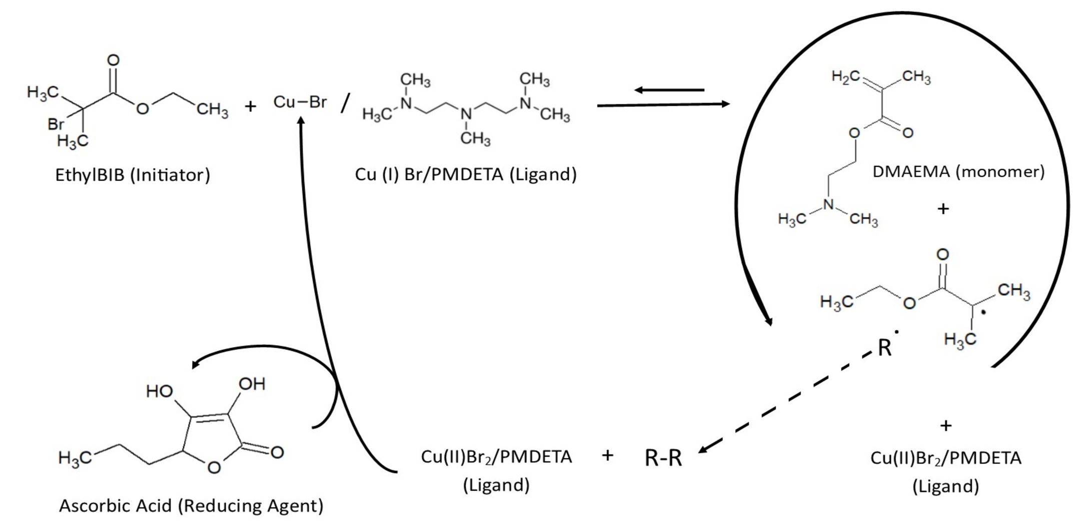

**Applications in Disperse Dye Removal**

- Smart polymers have the potential to remove hydrophobic contaminants from water such as dispersed dyes by using the polar, or hydrophilic functional groups of the polymer to interact with water while using the hydrophobic functional groups of the polymer to attach to the hydrophobic molecules in the dispersed dyes.
- Using a smart polymer allows for the potential to recover the smart material for reuse.

[Digital image]. (n.d.). Retrieved March/April, 2018, from https://mediacdn.grabone.co.nz/asset/xzEuejtlyd/box=615x0Click to add text

## Polymer ARGET ATRP Synthesis

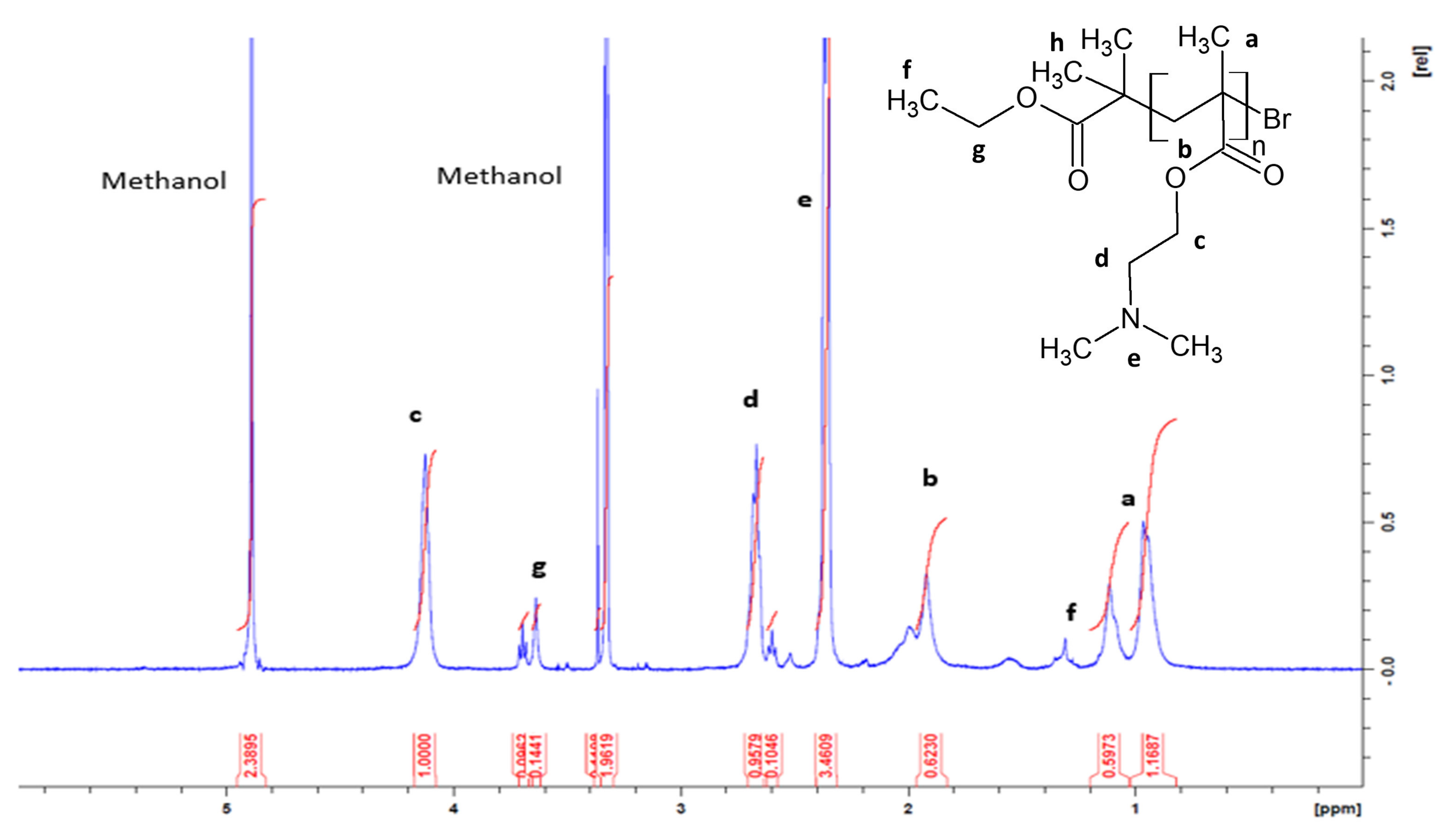
- Activators ReGenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) is used to synthesize the PDMAEMA linear homopolymer. Molecular weight can be controlled by changing the ratio of initiator to monomer. A narrow molecular weight distribution can be achieved by limiting termination through the regeneration of the deactivating Cu(I)Br species using ascorbic acid, the reducing agent.




- The Cu(I)Br is necessary to limit termination, but it becomes $Cu(II)Br_2$ when exposed to oxygen. ARGET ATRP uses the reducing agent instead of just adding more Cu(I)Br. The benefits of this reaction as opposed to traditional ATRP is that there is significantly reduced concentrations of heavy metal catalysts and the tolerance of oxygen is greatly improved.

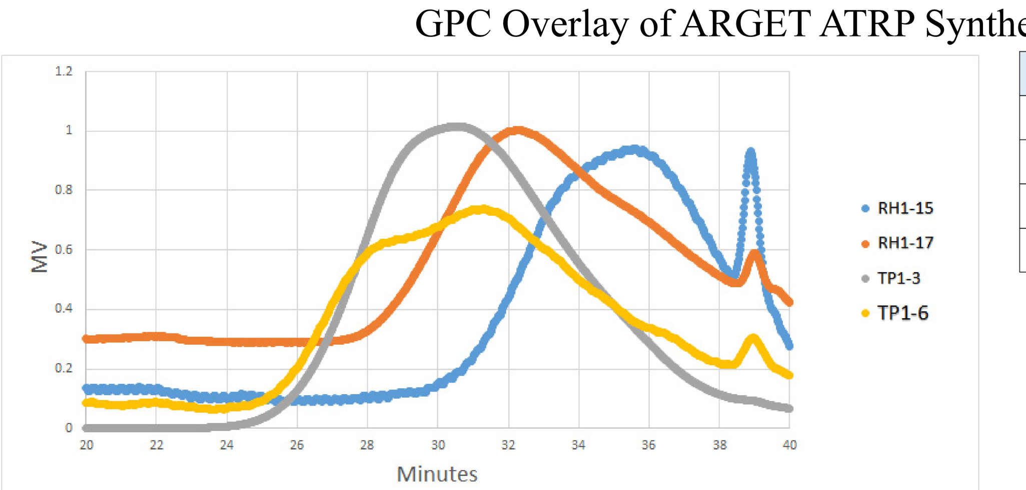
## Polymer Characterization

$^1$H-NMR of Linear PDMAEMA Homopolymer

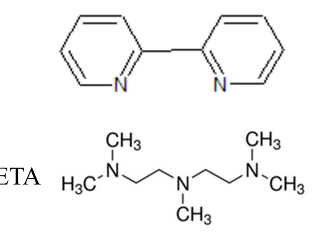



- Proton Nuclear Magnetic Resonance Spectroscopy ($^1$H-NMR) is a tool to figure out the structure of the polymer. The peaks correspond to the groups of hydrogens on the structure which can be affected by the location and the neighboring atoms.

GPC Overlay of ARGET ATRP Syntheses




| Linear PDMAEMA Homopolymer | PDI |
|---|---|
| RH 1-15 | 1.45 |
| RH 1-17 | 1.49 |
| TP 1-3 | 1.79 |
| TP 1-6 | 2.21 |

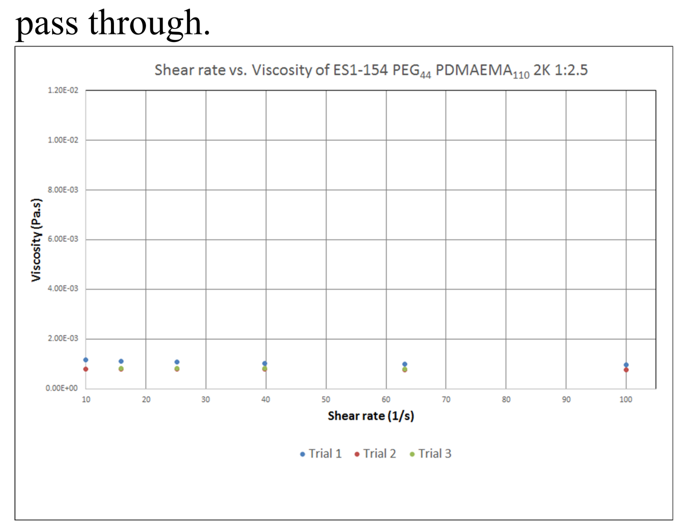



- The uniformity of the chain lengths of the polymer is indicated by the polydispersity index (PDI). The GPC estimates molecular weight based on the time it takes the sample to pass through the four columns (retention time), and then compares it to a standard retention time and corresponding weight average molecular weight (Mw). PDI is calculated by dividing the weight average molecular weight by number average weight (Mn). The uniformity of a polymer tells what type of properties it will have. In the table shown above, different ligands which were 2,2'-Bipyridine and PMDETA were used in different syntheses. The purpose of the overlaid data was to observe which ligand resulted in the best polymer uniformity.

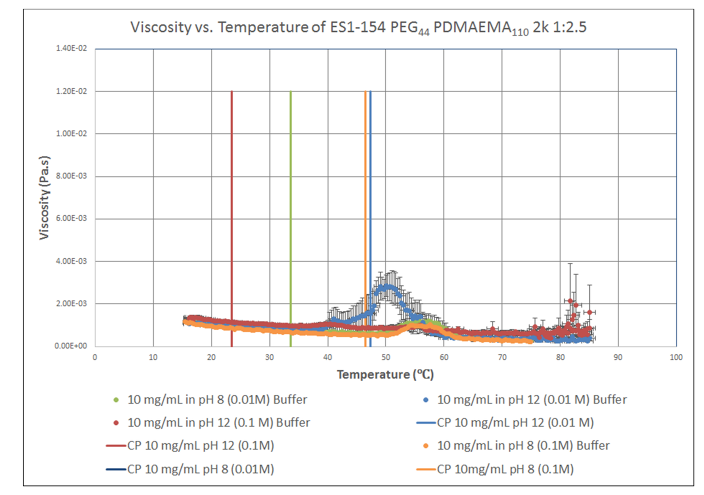
## Viscosity Testing using Rheometry

**Viscosity Testing of PEG-PDMAEMA using a Rheometer**

- The rheometer is an instrument used to measure viscosity, or a fluid's resistance to flow.
- Rheological studies were done to measure the viscosity as a function of temperature or strain rate. A cone and plate geometry of 2° with a diameter of 40 mm was used.
- UV-Visible spectroscopy tests the "cloudiness" of a polymer sample by transmitting light through it. As the polymer clumps towards its cloud point temperature, it doesn't allow as much light to pass through.

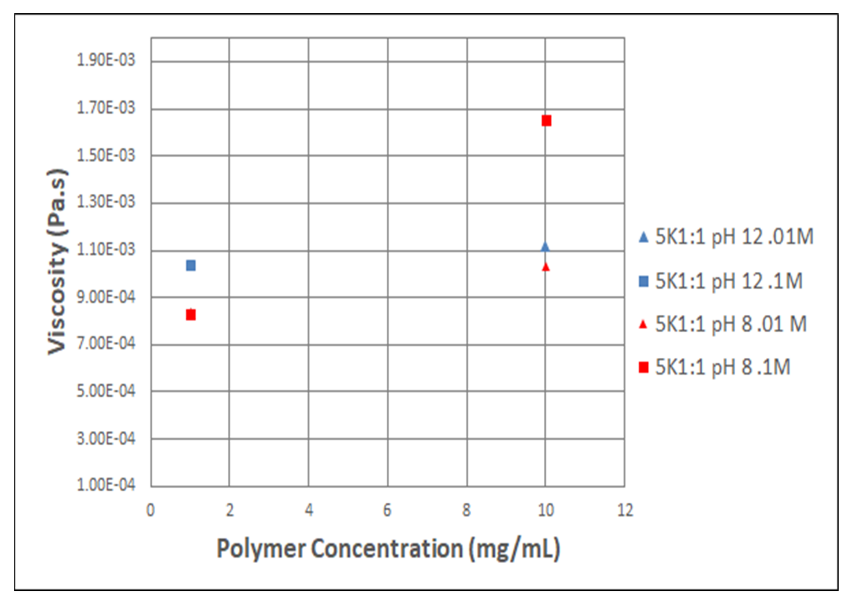


The graph shown above is the steady state viscosity test of smart polymer $PEG_{44}$-$PDMAEMA_{110}$. Here the viscosity stays constant even when shear rate increases.

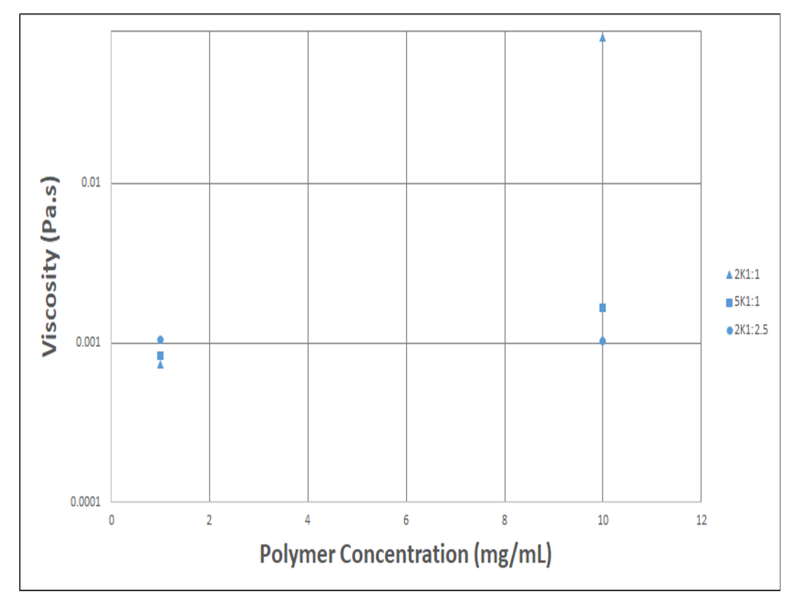


The graph shown above is a compilation of temperature ramp tests where viscosity is dependent on temperature. Viscosity increases rapidly above cloud point.

## Viscosity vs. Concentration Graphs




The graph above is a compilation of steady state data that compares $PEG_{127}$-$PDMAEMA_{127}$ which is made in concentrations of 1 mg/mL and 10mg/mL. It was tested in pH 8 and pH 12 buffers and compares the viscosity of the polymer solutions as a function of strain rate. Viscosity increases with increasing polymer concentration, but in this case, there is not enough evidence that viscosity depends on pH.




The graph shows $PEG_{44}$-$PDMAEMA_{44}$, $PEG_{127}$-$PDMAEMA_{127}$, and $PEG_{44}$-$PDMAEMA_{110}$ made in concentrations of 1 mg/mL and 10 mg/mL with viscosity testing in different pH 12 buffer solutions. The graph compares the viscosity of the polymer compositions as a function of strain rate. The effect of polymer composition is more noticeable at 10 mg/mL. Again, increasing polymer concentration increases viscosity.

## Conclusions

- PDMAEMA is a smart polymer with properties that respond to external stimuli.
- Samples are characterized for PDI and molecular weight using GPC and $^1$H-NMR.
- ARGET ATRP synthesis methods produced PDMAEMA homopolymers.
- Rheological studies were performed on varying polymer compositions, polymer concentrations (1 mg/mL and 10 mg/mL) along with different buffer concentrations (0.1 M and 0.01 M) and different pH (8 and 12).

## Future Projects and Research Goals

- Figure out which ligand works better in ARGET ATRP homopolymer synthesis
- Compare the diblock copolymer characteristics from ATRP and ARGET ATRP to see which one is better
- Decide temperature testing for viscosity and cloud points on the new diblock copolymers

## Acknowledgments

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