

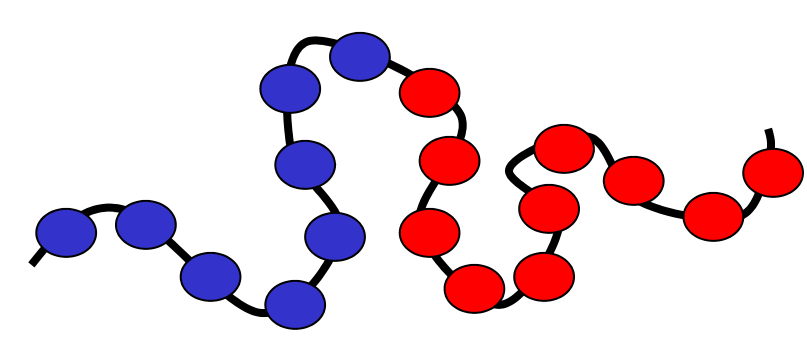
Synthesis and Thermo-responsive Characterization of Poly(2-(dimethylamino)ethyl methacrylate) Polymers



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Polymer Basics

Polymers are made of covalently bonded units called monomers that come together and form long molecules



Polymer structure can be modified to achieve homopolymers or diblock copolymers

Designing Polymers for Applications



Plastic bottles are polymers designed to contain liquids

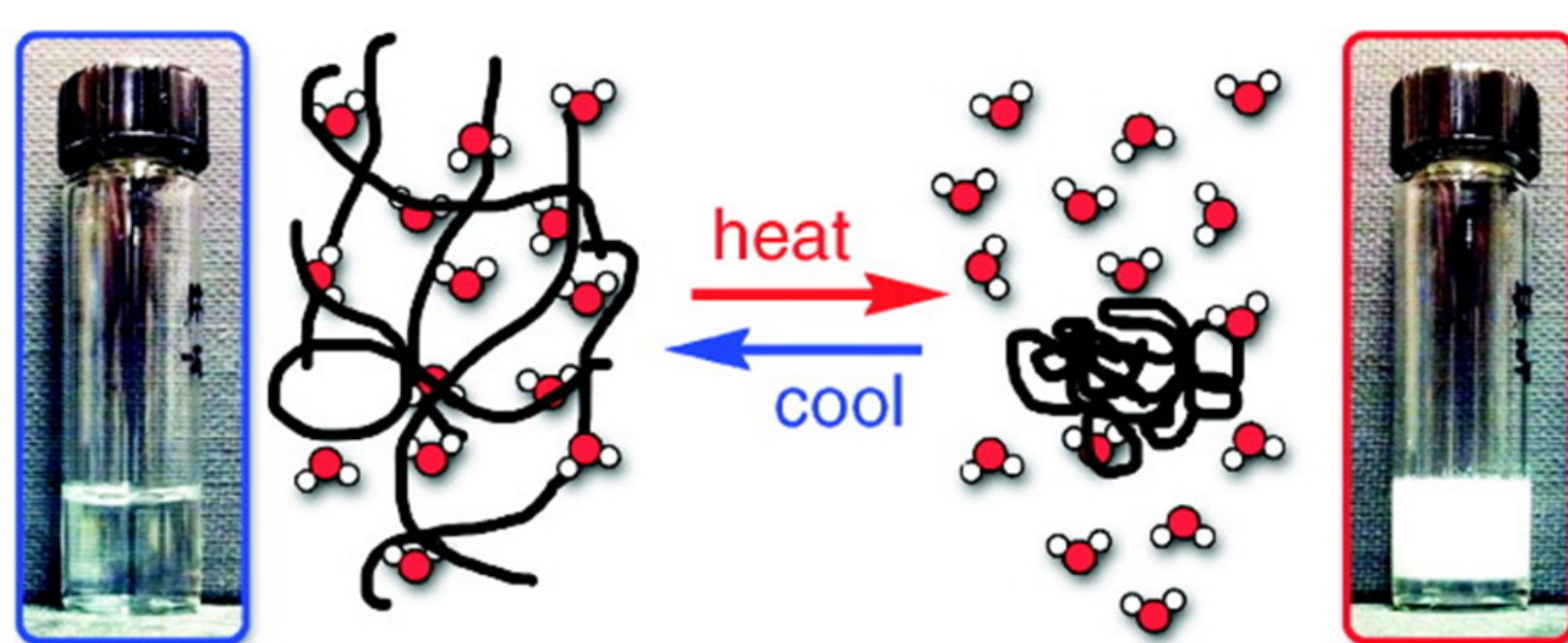
Some polymers are engineered to withstand stress, like polymers used in plastic furniture



<http://www.apartentherapy.com/plastics-170303>

"Smart" Polymers

"Smart" polymers have the unique ability to aggregate under certain conditions such as pH, temperature, and/or concentration



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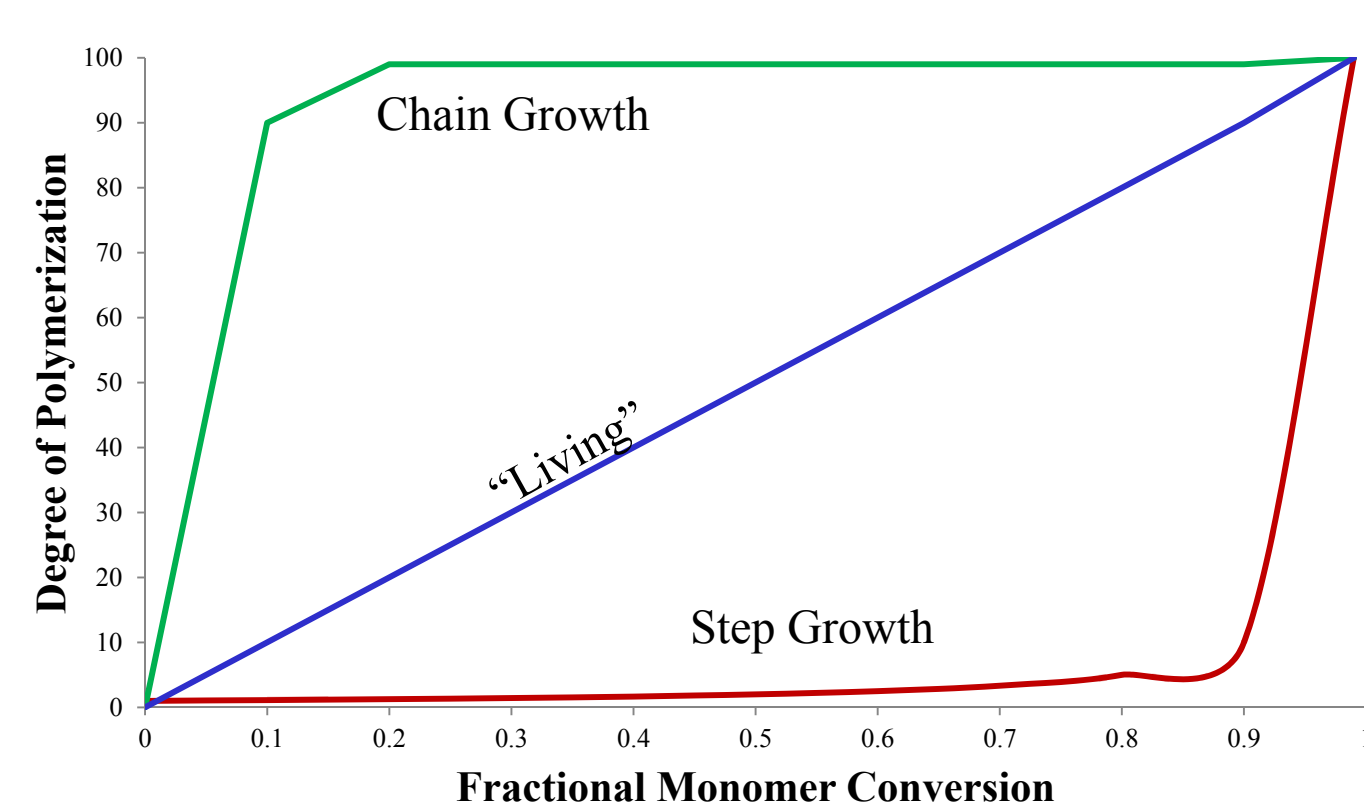
Cloud point:

- Is the temperature above which the smart polymers will aggregate and cause the solution to become cloudy
- At this temperature, interaction with other polymer chains becomes more favorable than interactions with the solution

Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is a smart polymer and has a cloud point that depends on pH, concentration, and polymer structure

Polymerization Mechanisms

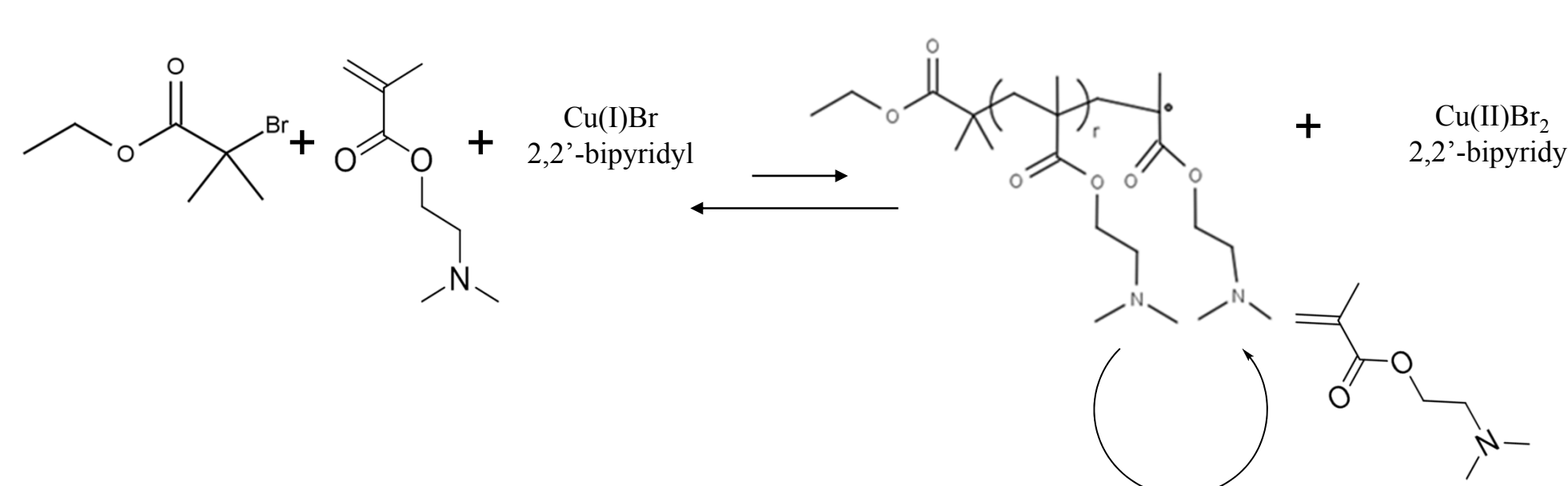
Polymers can be synthesized by different mechanisms: Chain Growth, "Living", or Step Growth



- "Living" polymerizations have a more controlled growth mechanism which will result in a polymer with more well-defined smart polymer characteristics
- PDMAEMA was synthesized using Atom Transfer Radical Polymerization (ATRP) which is a "living" polymerization method

PDMAEMA Polymerizations

ATRP of Linear PDMAEMA Polymer



- By varying the relative amounts of initiator:monomer and time of reaction one can control the molecular weight of the polymer
- Utilizing the equilibrium, one can control the speed of the reaction by adding Cu(II) and/or changing temperature

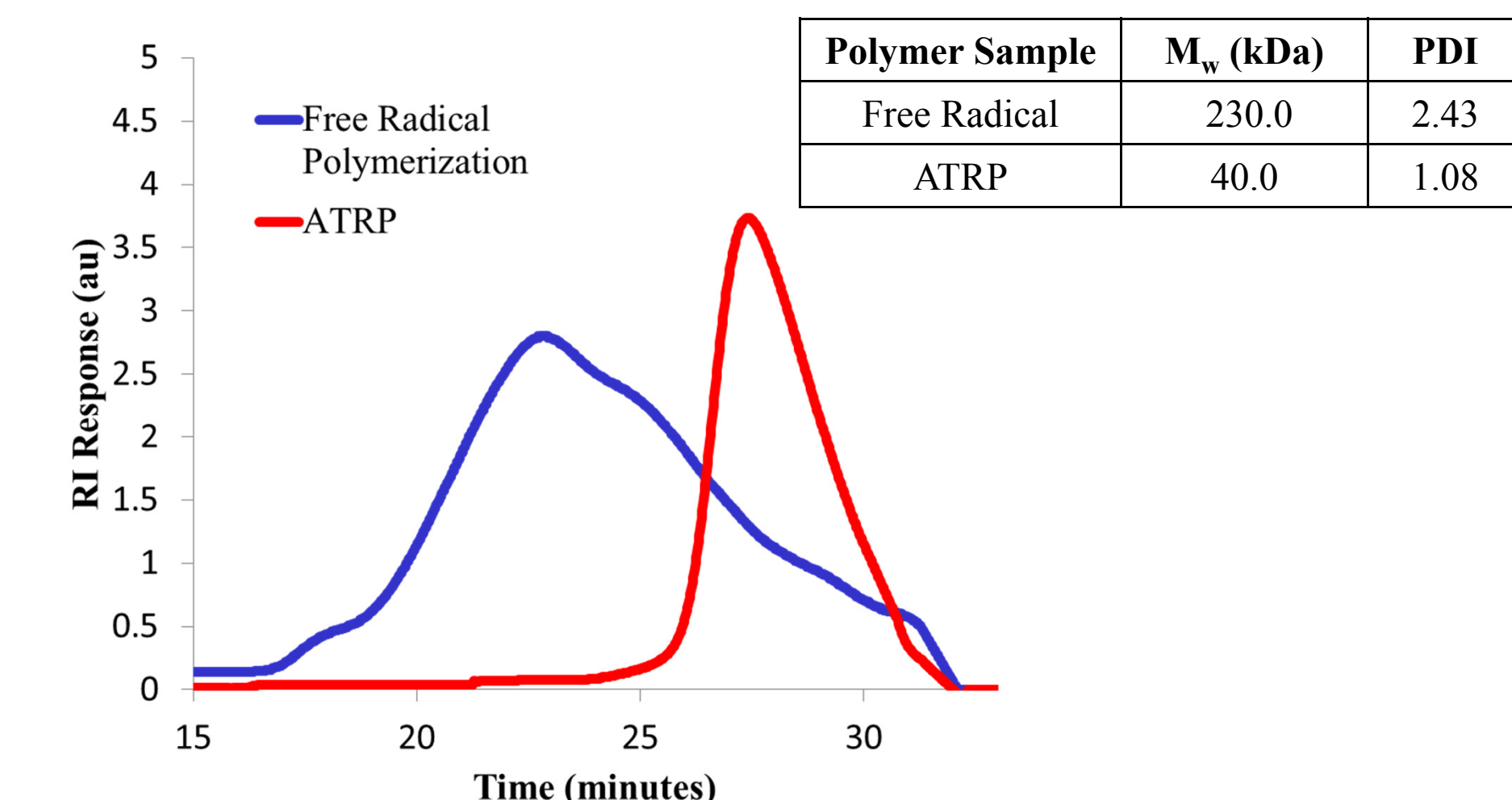
Smart polymers need to have a narrow distribution of chain lengths in order to have similar smart properties for each chain

Polydispersity index (PDI) is a measure of the distribution of polymer chain lengths

$$PDI = \frac{M_w}{M_n}$$

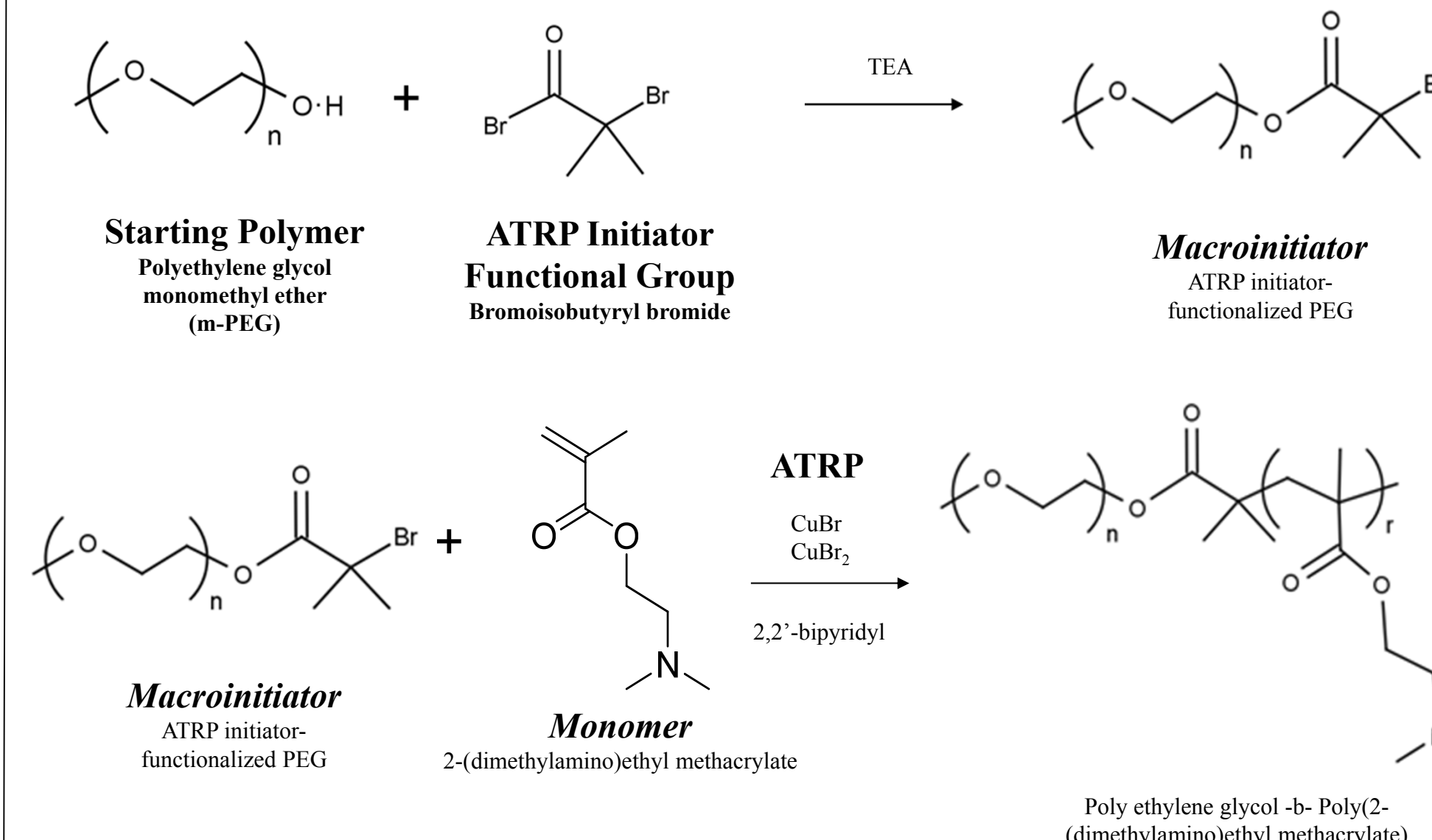
If PDI

- = 1, all polymers are the same chain length
- < 1.5, good PDI for ATRP
- > 1.5, typical for chain growth polymerization

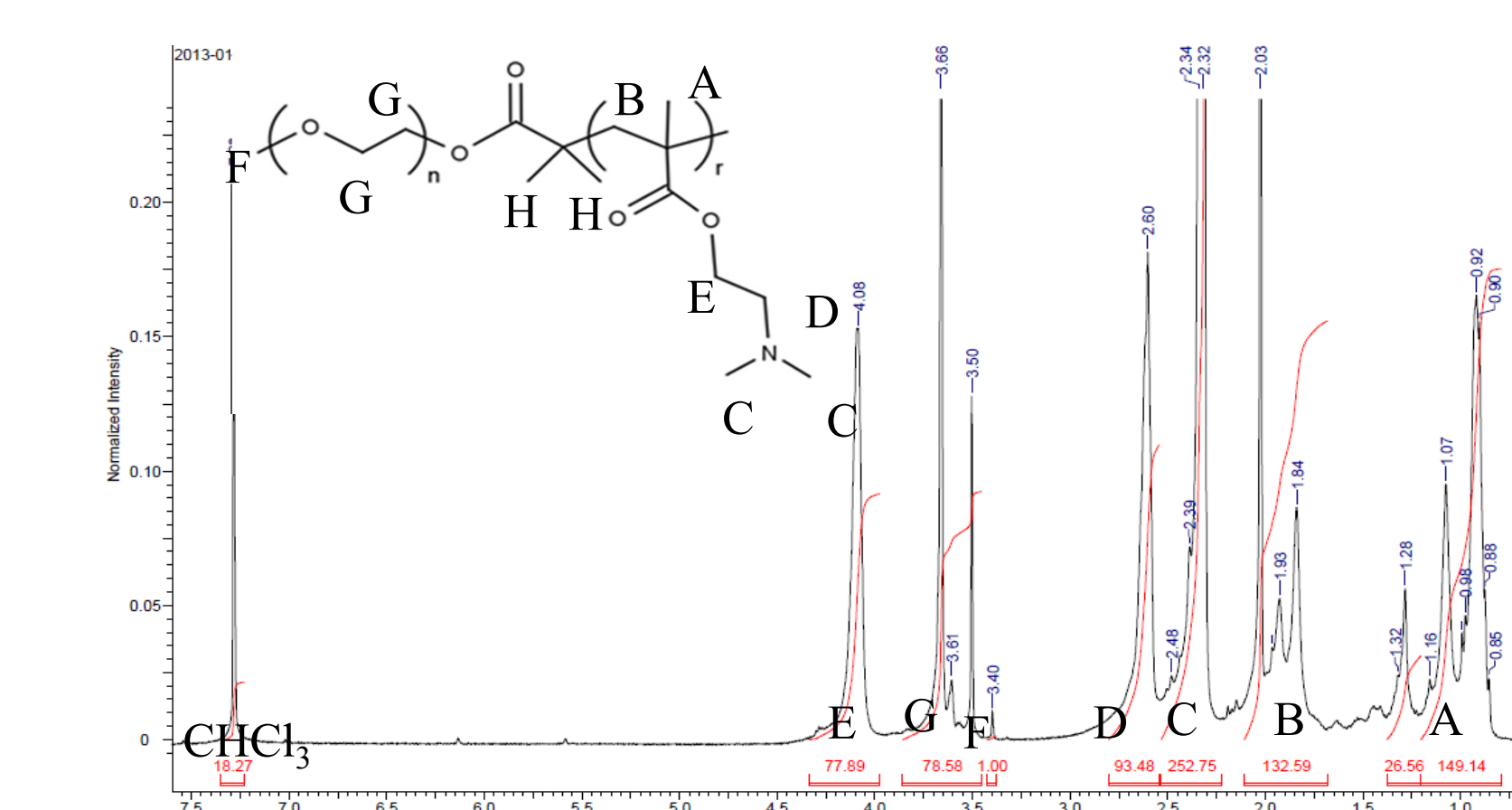


Gel Permeation Chromatography (GPC) separates polymers based on molecular weight and can be used to determine relative molecular weight and PDI

ATRP of Diblock PDMAEMA Copolymer



Molecular weight was controlled by varying the ratio of monomer:macroinitiator and polymerization time



Proton Nuclear Magnetic Resonance Spectroscopy (¹H-NMR) is a way to calculate molecular weight by measuring and comparing the integration of protons in the polymer chains

$$E \rightarrow \frac{77.89}{2 \text{ protons}} = 38.95 \frac{1}{\text{proton}}$$

$$G \rightarrow \frac{78.58}{4 \text{ protons}} = 19.65 \frac{1}{\text{proton}}$$

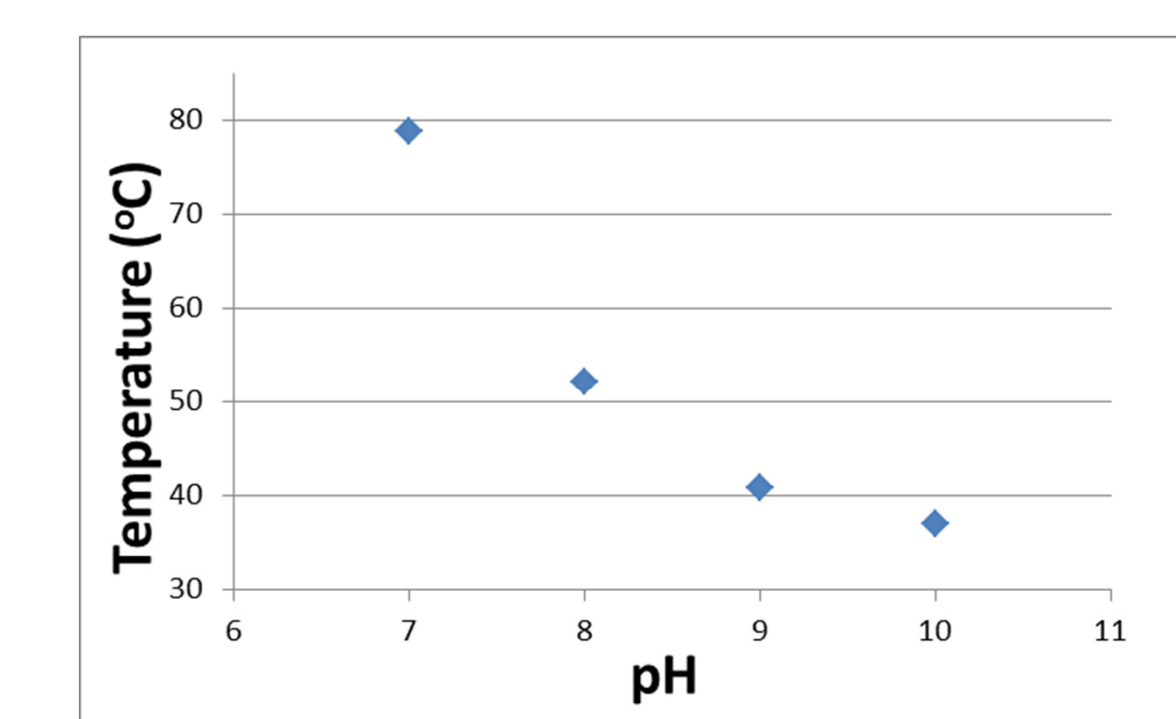
$$\frac{n}{r} = \frac{19.65}{38.95} = \frac{1.00}{1.98}$$

The PDMAEMA chain is ~2x the length of the PEG chain

Thermo-responsive Study Results

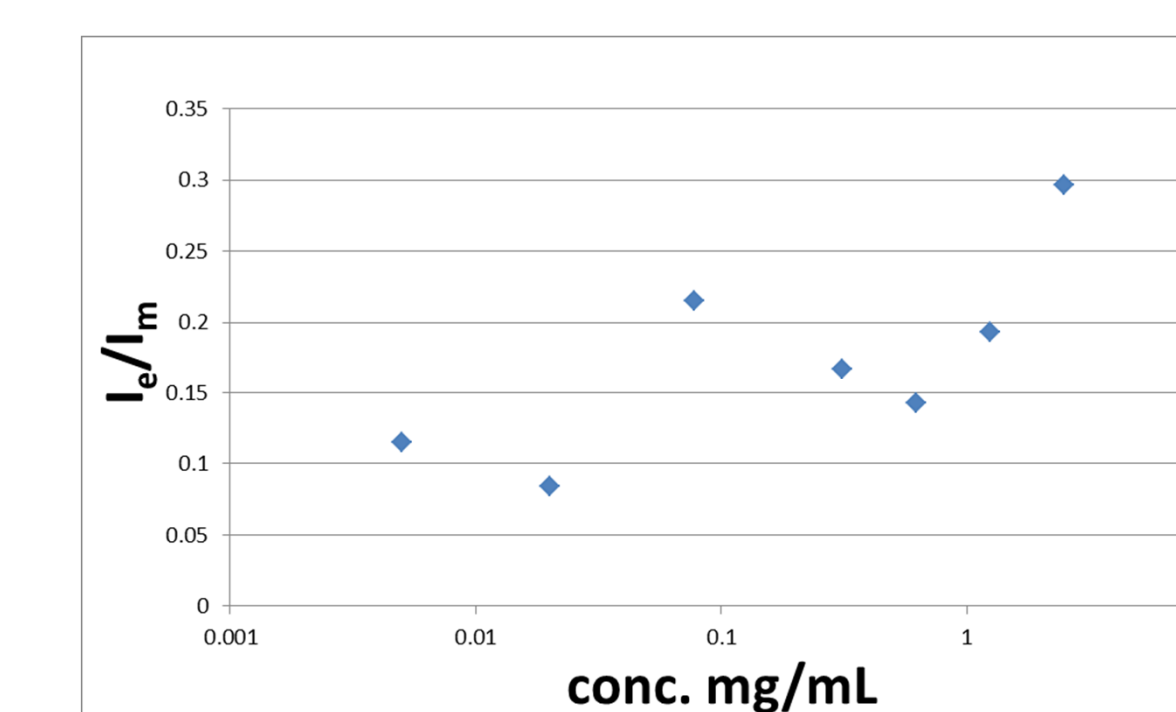
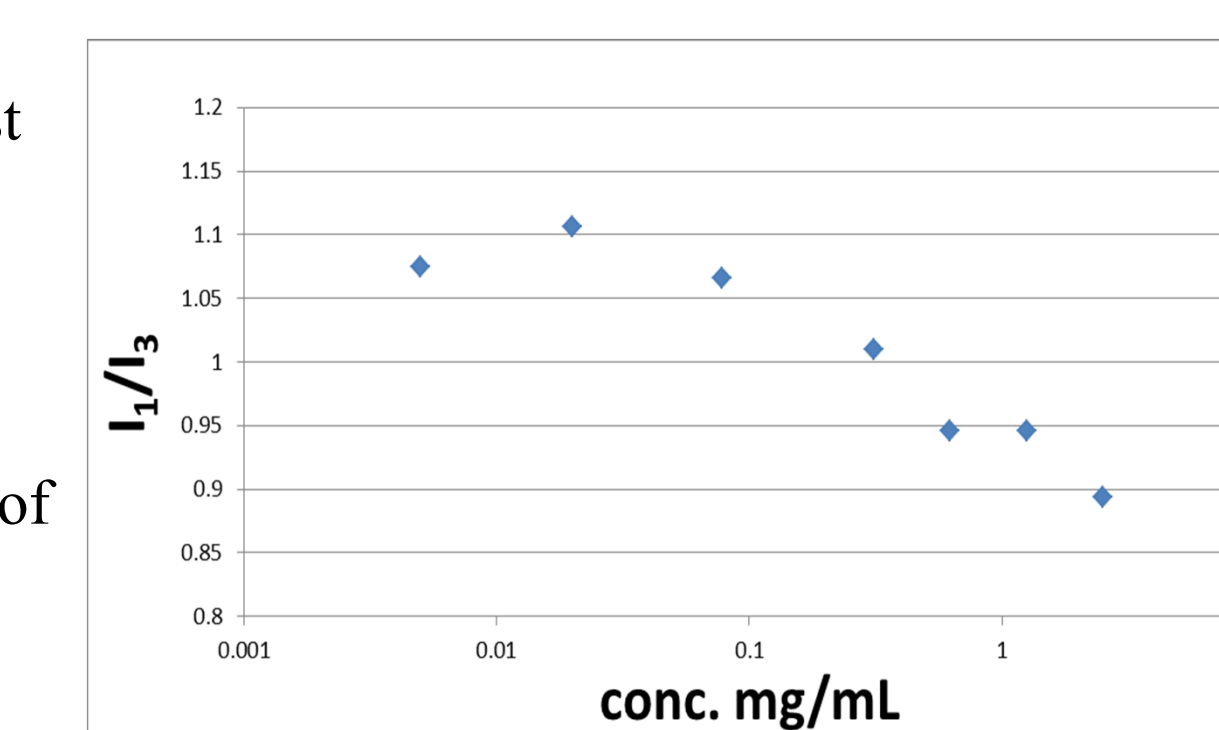
Linear Polymer

The cloud point temperature was found to decrease with increasing pH



Diblock Copolymer

The ratio between the first and third peaks in the pyrene fluorescence decreases with increasing polymer concentration because of the formation of micelles in the solution

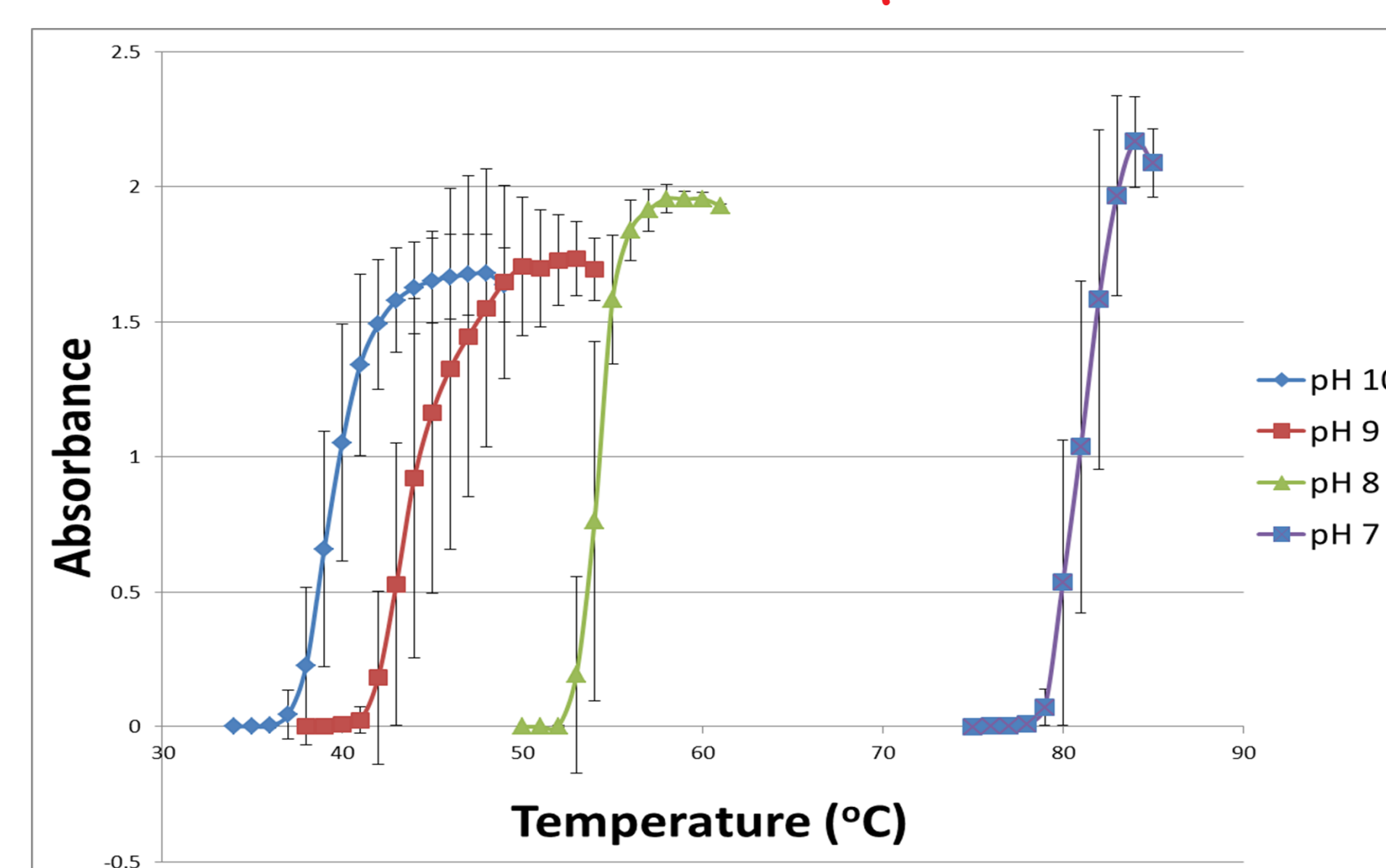
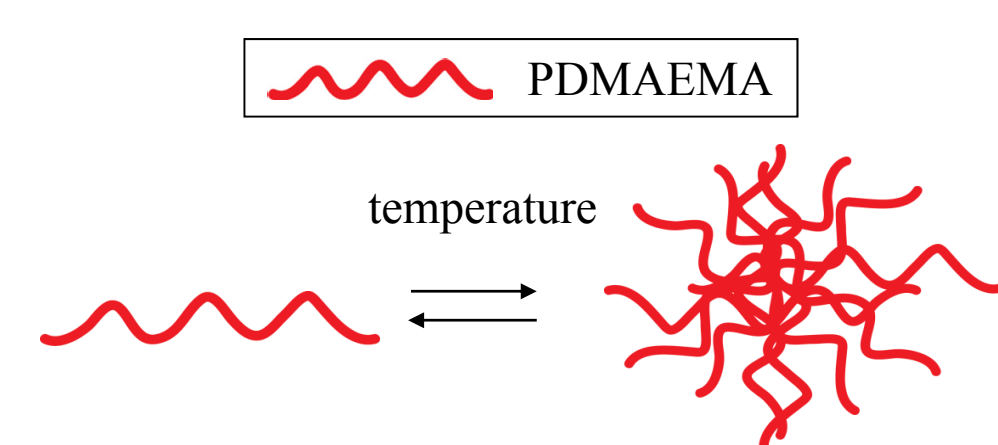


The ratios between the "excimer" and "monomer" peaks do not show a specific trend that is comparable to literature

More data points with samples of lower concentration could reveal more significant trends and allow conclusions to be drawn

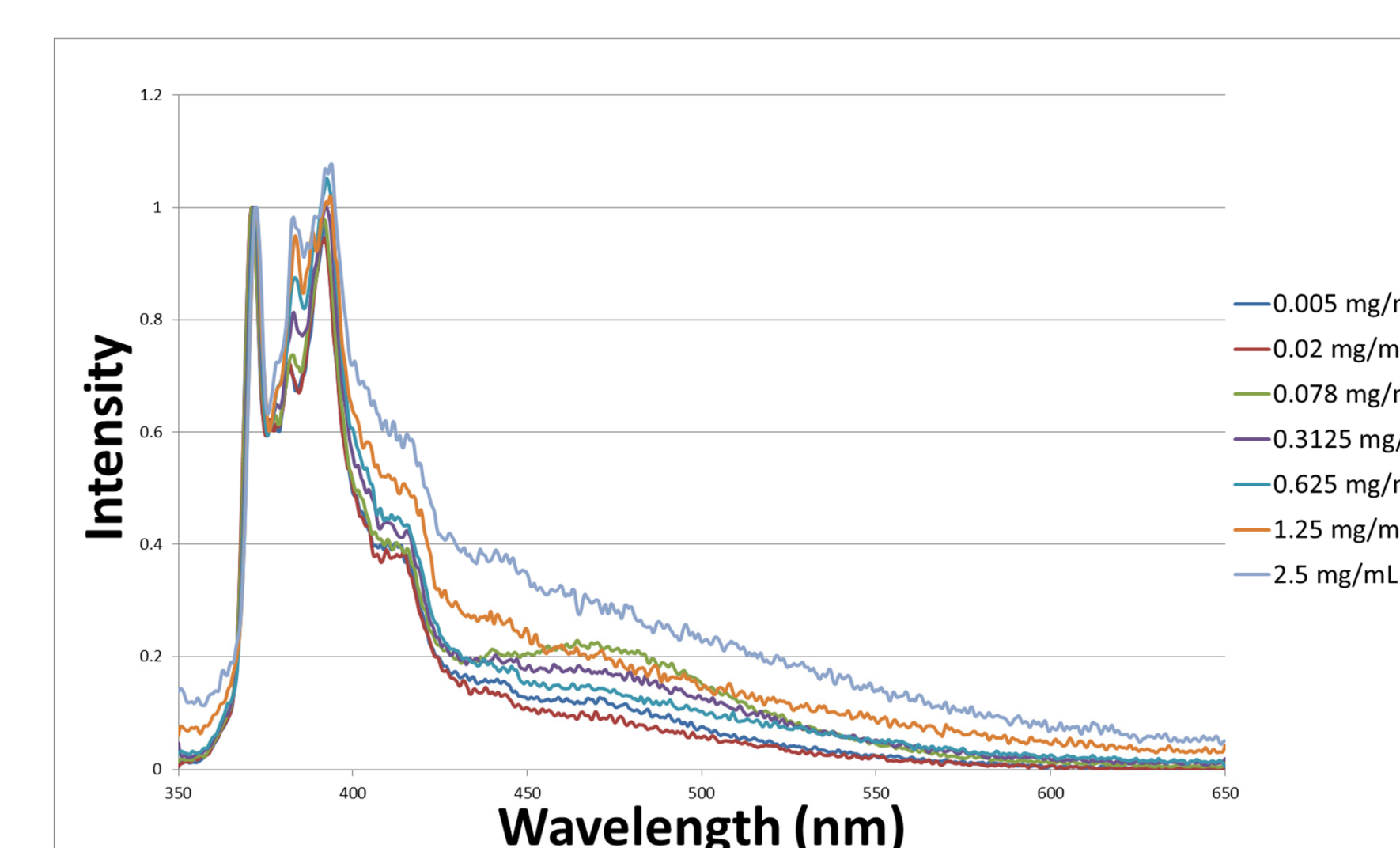
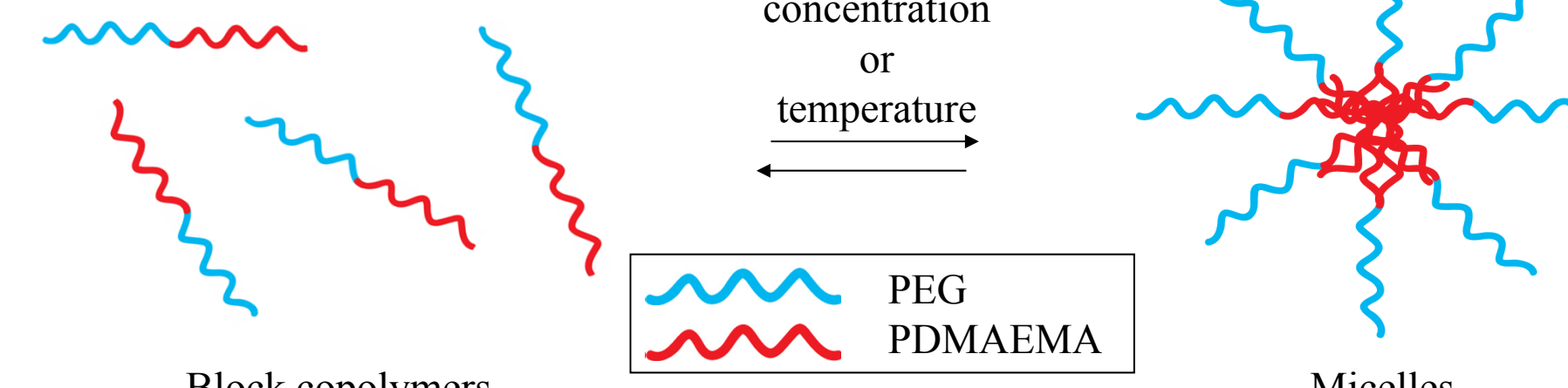
Polymer Thermo-responsive Study

PDMAEMA will reversibly change water-solubility as a function of both pH and temperature



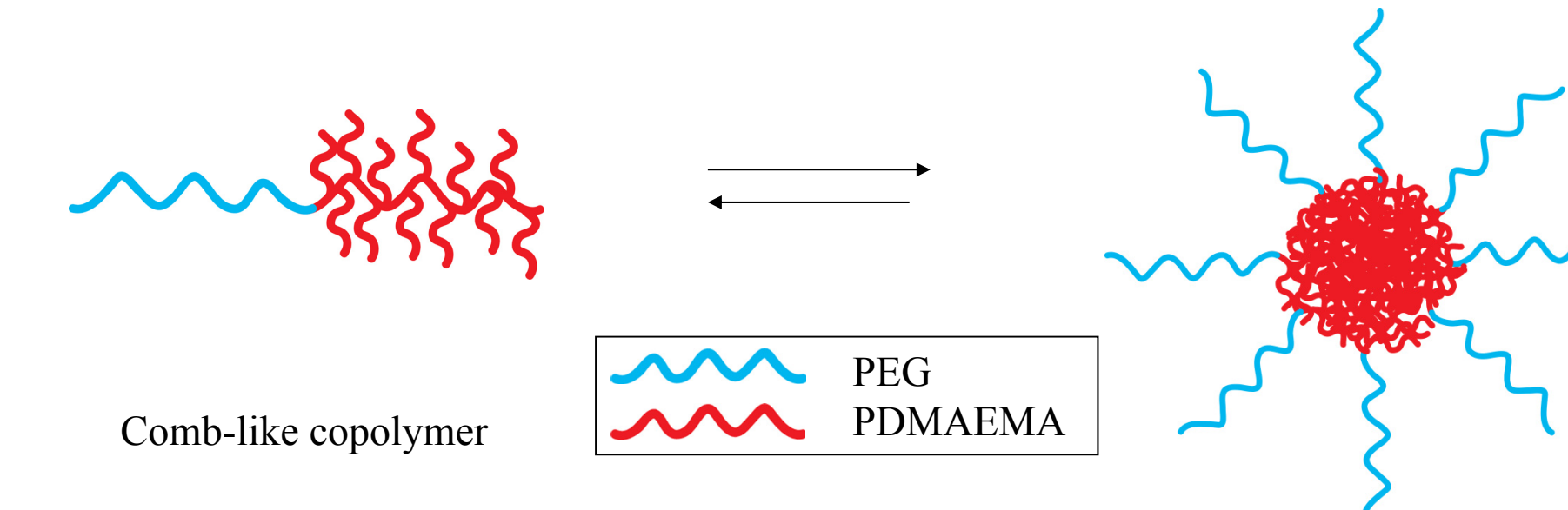
UV-Visible Light Spectroscopy measures the ability of a substance in solution to either absorb or transmit light. In the case of PDMAEMA, light that is not able to pass through the solution is reported as absorbance. When PDMAEMA reaches its cloud point the measured absorbance will increase significantly.

PDMAEMA diblock copolymers will create micelles depending on polymer concentration and temperature



Using a fluorescent molecule called pyrene, the micelle formation concentration can be found by comparing peaks in the fluorescence spectra. When the micelle is created, the pyrene molecules will join the PDMAEMA in the micelle. The pyrene fluoresces differently when it is in a hydrophobic or hydrophilic environment, so measuring the pyrene fluorescence gives information about the polymers in solution.

Future Projects and Research Goals



Conclusions

- PDMAEMA is a smart polymer that reversibly self-assembles in aqueous solution as a function of pH, temperature, or concentration for both homopolymers and diblock copolymers
- UV-Visible Light Spectroscopy is an effective way to study how linear PDMAEMA will respond to temperature changes in aqueous solution
- Linear PDMAEMA with a molecular weight of ~50 kDa has decreasing cloud points with increasing pH
- Measuring the fluorescence of pyrene allows for the determination of solution behavior of diblock copolymers
- Short term future goals include continuing diblock fluorescence studies to find critical micelle formation concentration and thermo-responsive studies of the diblock copolymer
- Long term future goals include synthesis of comb polymers and thermo-responsive studies to determine the effect of architecture on reversible self-assembly

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