

Impact of PDMAEMA Molecular Weight on Smart Properties of mPEG₄₄-block-PDMAEMA

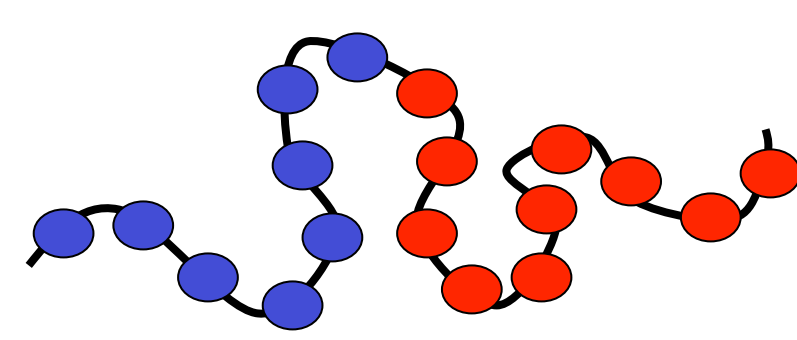


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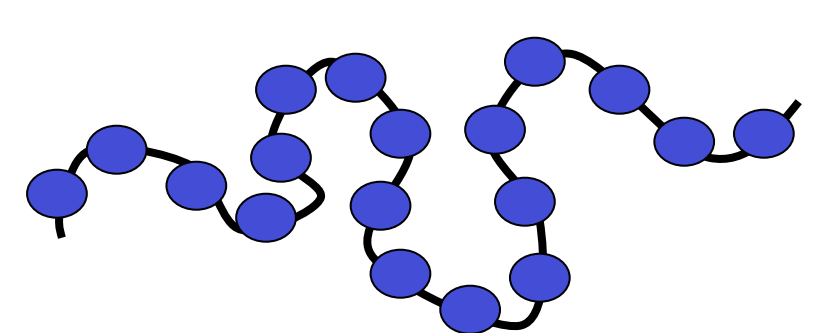
Materials Science Program

Polymer Basics

Polymers are long chains of repeated subunits, called monomers, that are covalently bonded together

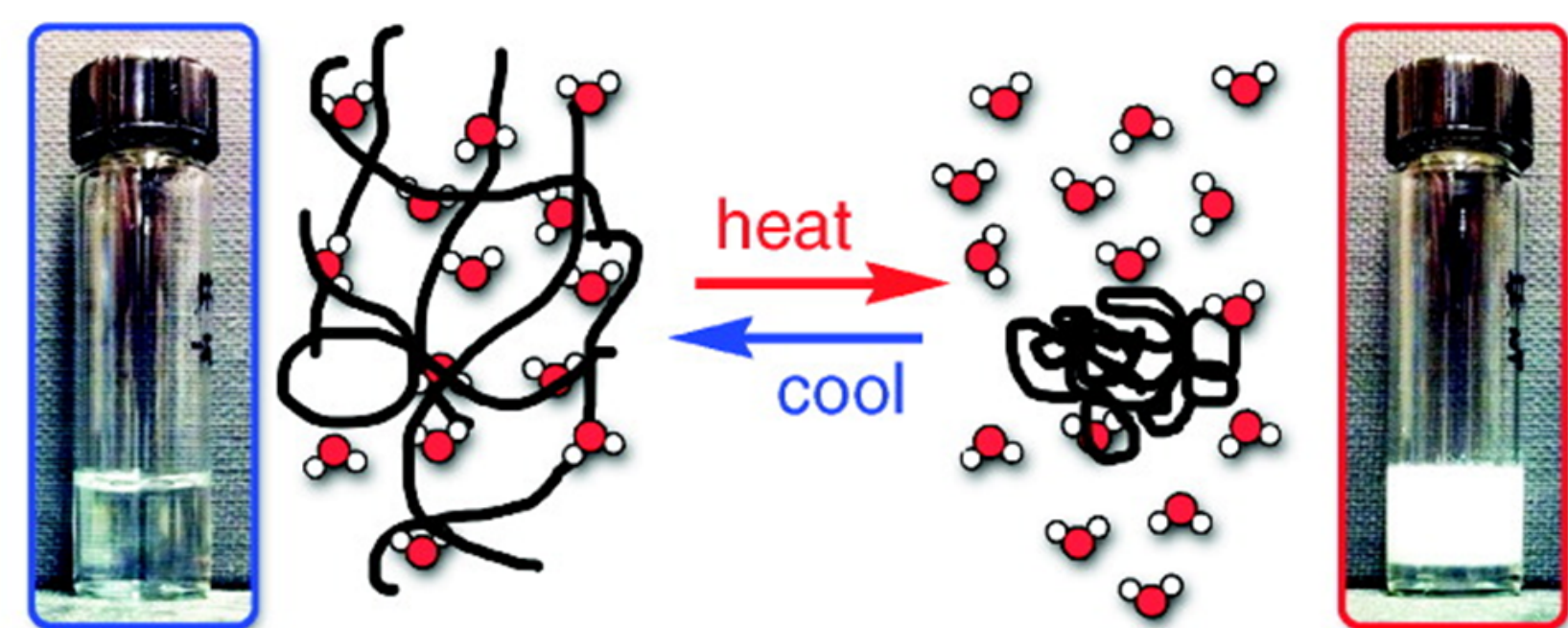


Polymer structure can be altered to generate homopolymers or diblock copolymers.



“Smart” Polymers

“Smart” polymers change properties in response to an external stimulus such as temperature, pH and/or concentration. These polymers will aggregate in response to the external stimuli.



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Cloud point is the temperature in which the smart polymer starts to visibly aggregate.

The smart polymer poly(ethylene glycol)-*block*-poly(2-(dimethylamino)ethyl methacrylate), or mPEG-PDMAEMA, has a cloud point that is controlled based on pH, polymer concentration, ionic strength, and polymer structure.

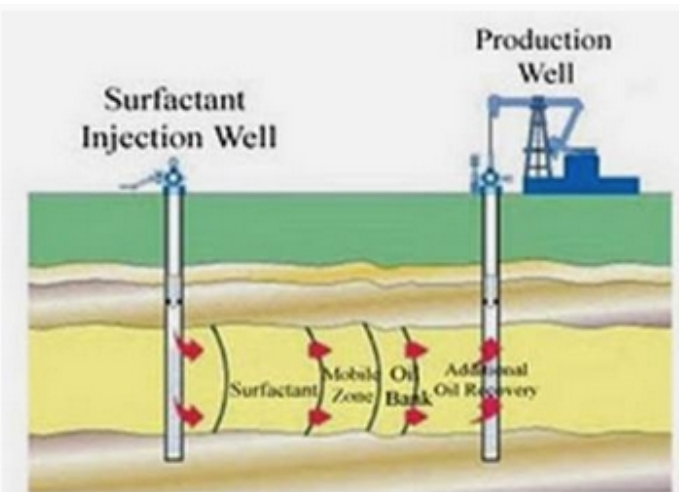
Potential Applications

Smart polymers have a wide array of applications ranging from drug delivery to enhanced oil recovery.

<http://www.bernos.com/blog/2009/10/06/pills-pills-pills/>



- Smart polymers have the potential to enhance the efficiency of drug delivery systems and lessen adverse effects by controlling drug delivery through the use of external stimuli such as pH or light.

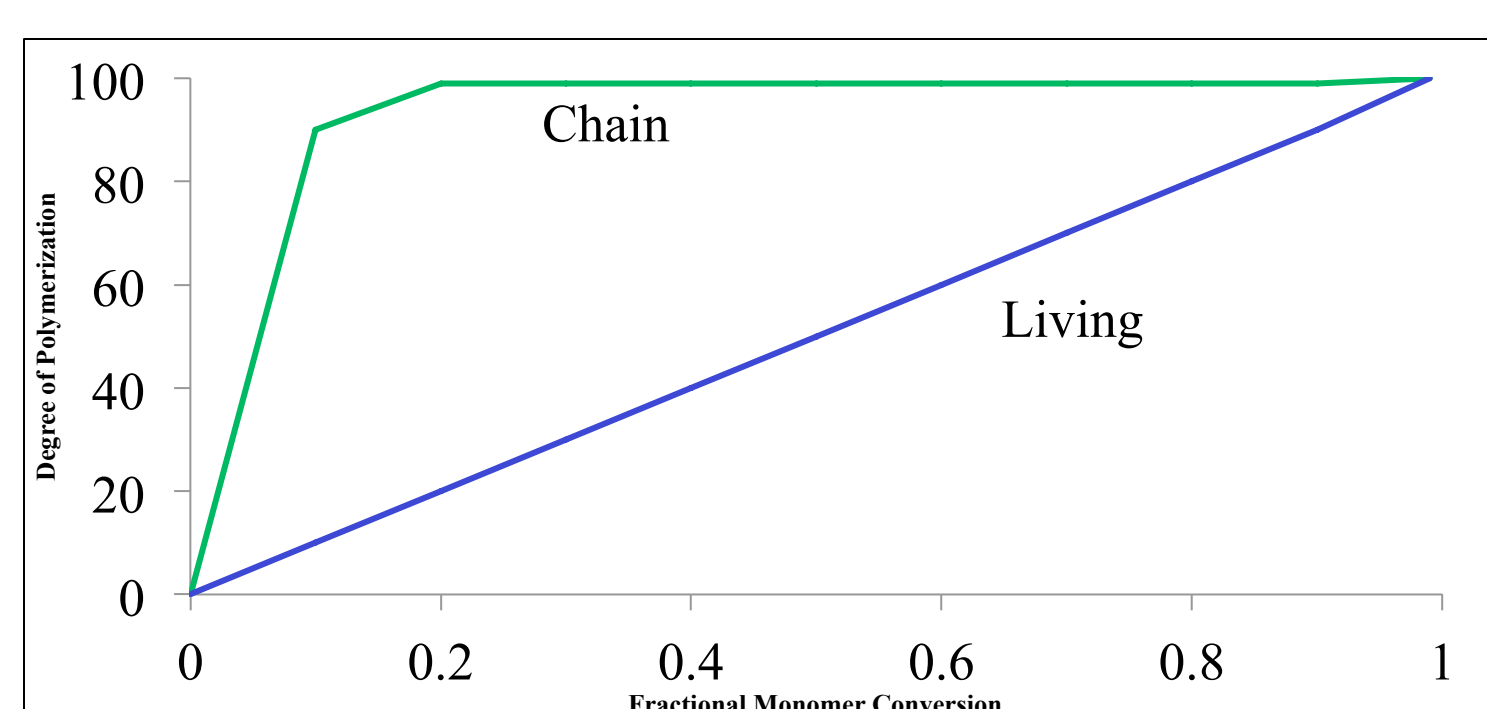


<http://www.energyandcapital.com/articles/enhanced-oil-recovery-market-booming/3190>

- Smart polymers have the potential to recover more oil than conventional chemical flooding by adding polymer to the water that is normally injected, which increases viscosity and in turn sweeps more oil through.

Polymerization Mechanisms

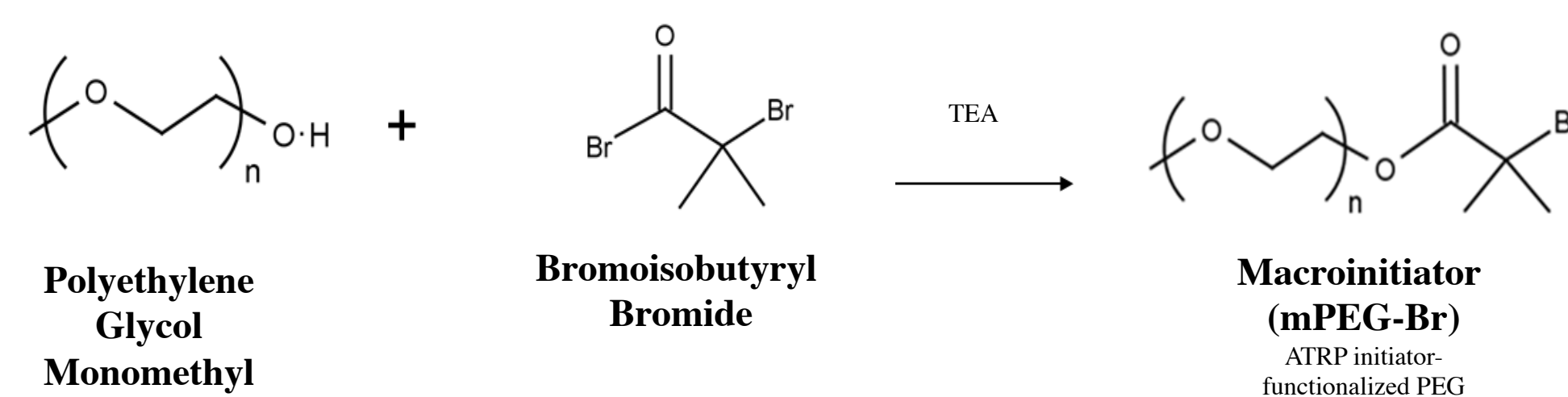
Two types of polymerization mechanisms are chain and living polymerization. Chain polymerization occurs much faster, but doesn't allow for the precision and control that “living” polymerization does.



Living polymerizations have a more controlled growth mechanism which allows for more fine-tuned control over the smart polymer characteristics and properties.

PDMAEMA was synthesized using Atom Transfer Radical Polymerization (ATRP) which is a subset of “living” polymerization.

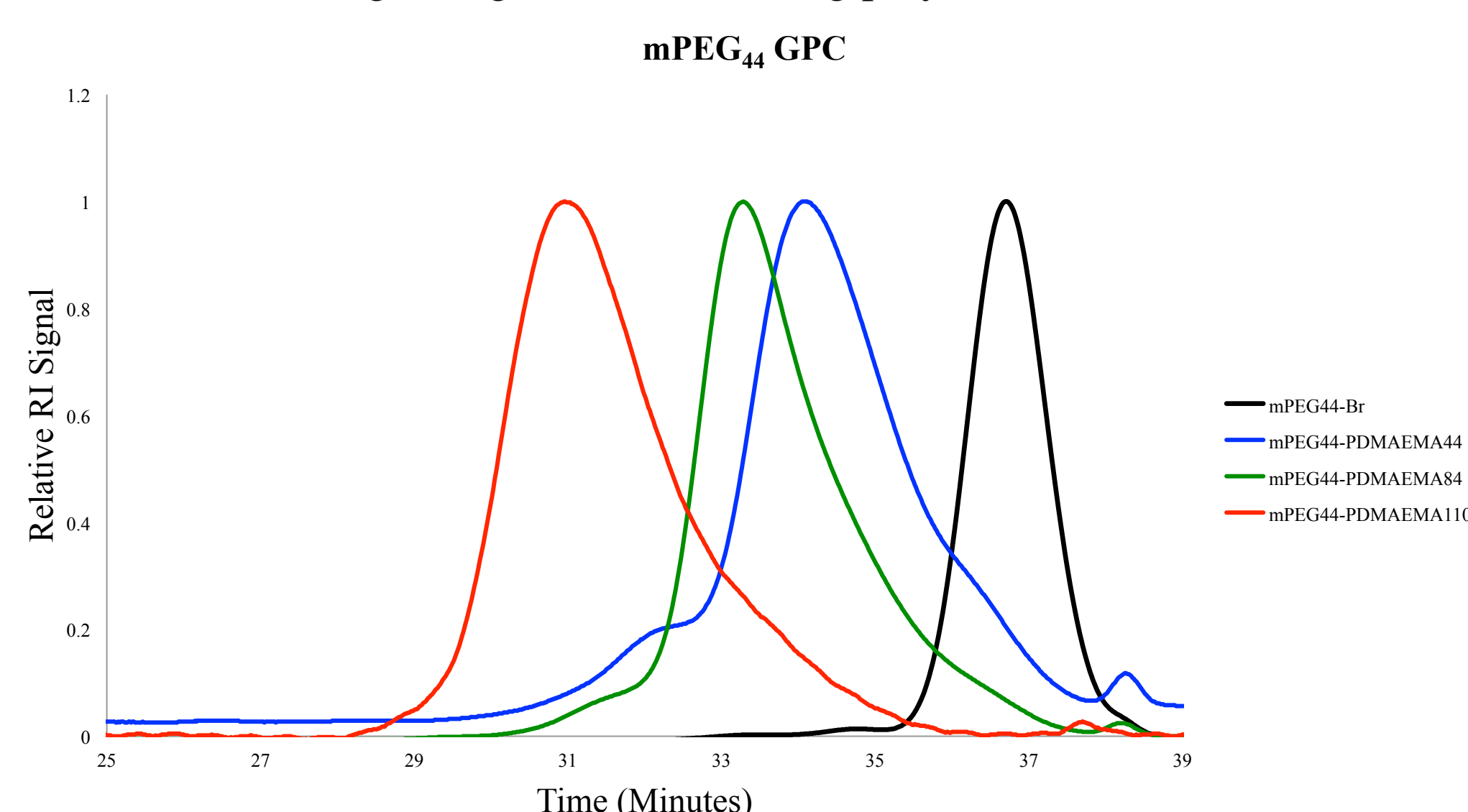
Synthesis and Characterization of Diblock Copolymer



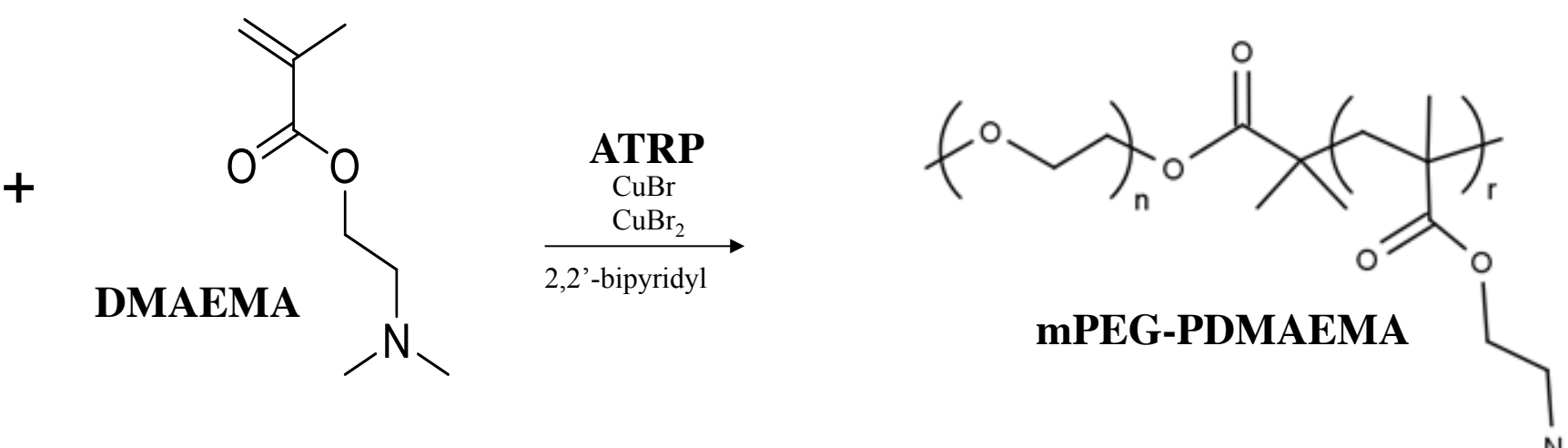
Properties of smart polymers depend on chain length and molecular weight. The more uniform the chain lengths, the more uniform the properties will be.

Smart polymer chains with similar length allows the chains to respond to external stimuli in the same way which allows for greater control over the behavior of the smart polymer.

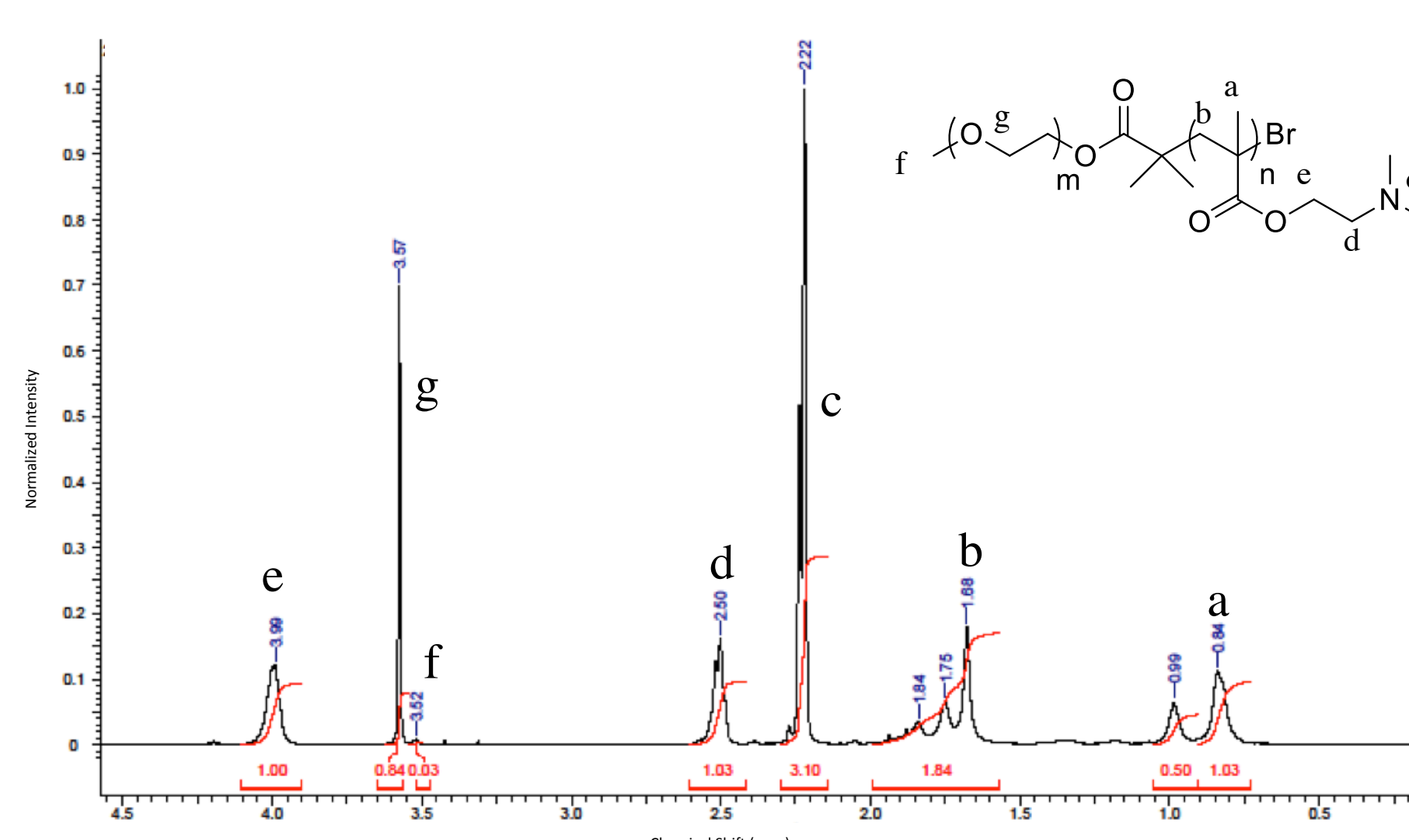
The measure of distribution of polymer chain lengths is known as the polydispersity index, or PDI. A PDI of 1 means that all of the polymers have the same length. A good PDI for living polymerization is less than 1.2.



Gel Permeation Chromatography (GPC) is a characterization method used to determine the molecular weight of a polymer and the molecular weight distribution. This is done by running the polymer in solution through columns that separate the polymers by size and measuring the molecular weight distribution by the time it takes to run through the column.



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

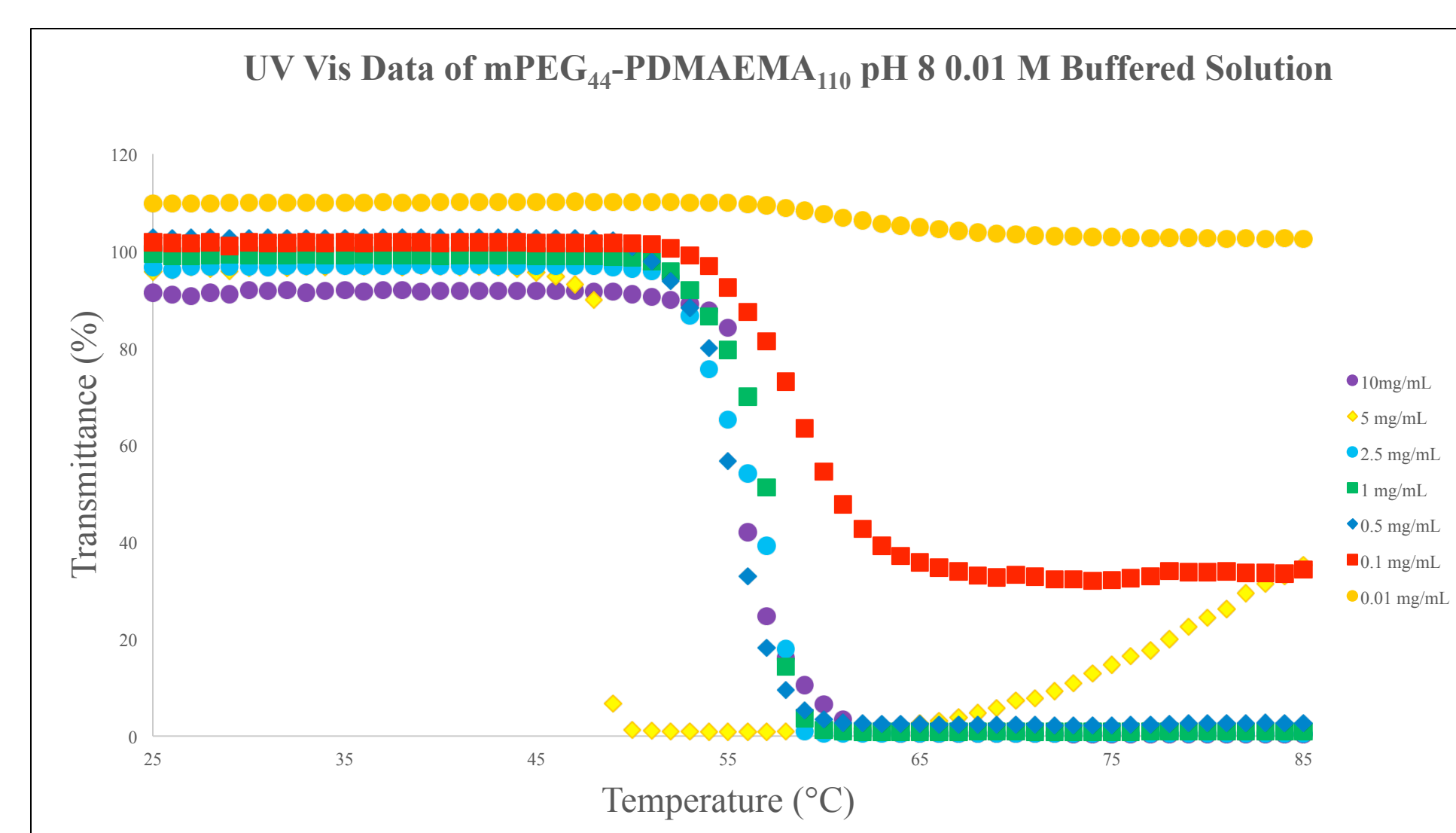
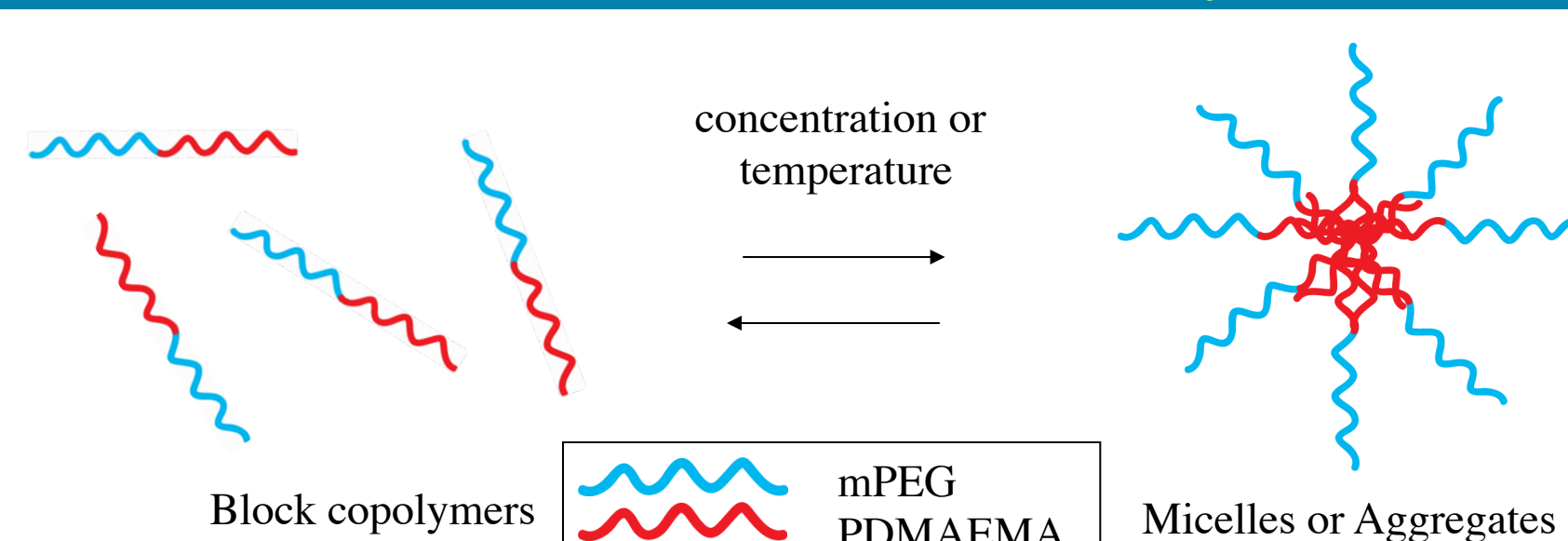


E → 1.0/2 protons = .50/proton
G → 0.84/4 protons = 0.21/proton
E/G = 0.50/0.21 = 2.4/1.0
1.0 mPEG : 2.4 PDMAEMA

All peaks were integrated relative to the E peak. The integrations of each refers to the total number of hydrogens for each signal. The ratio of mPEG to PDMAEMA was determined by comparing the ratio of integration of the G (mPEG) peak to the E (PDMAEMA) peak.

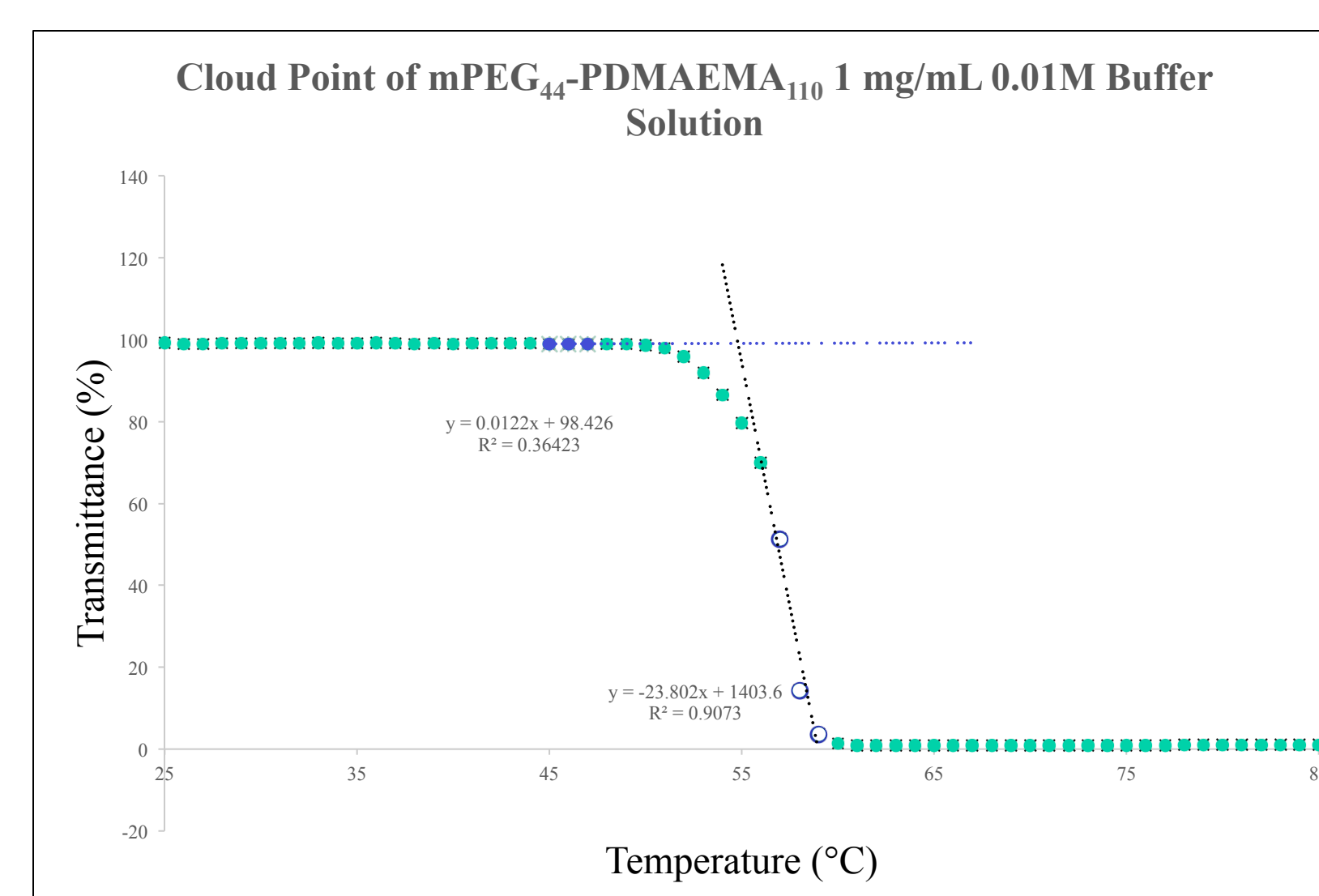
Sample	Polydispersity Index (PDI)	M _n by NMR (kDa)
mPEG ₄₄	1.01	2.0
mPEG ₄₄ -PDMAEMA ₄₄	1.13	8.9
mPEG ₄₄ -PDMAEMA ₈₄	1.09	15.1
mPEG ₄₄ -PDMAEMA ₁₁₀	1.15	19.3

Polymer Thermoresponse Study



- “Transmittance” changes when the cloud point of the polymer occurs.
- The graph above shows cloud point as a function of polymer concentration.
- As polymer concentration increases the cloud point of a polymer decreases.
- Transmittance is expected to be high when there are no aggregates formed and the polymer is free in solution because light isn't scattered.
- Once aggregates form they scatter light which makes the transmittance decrease.

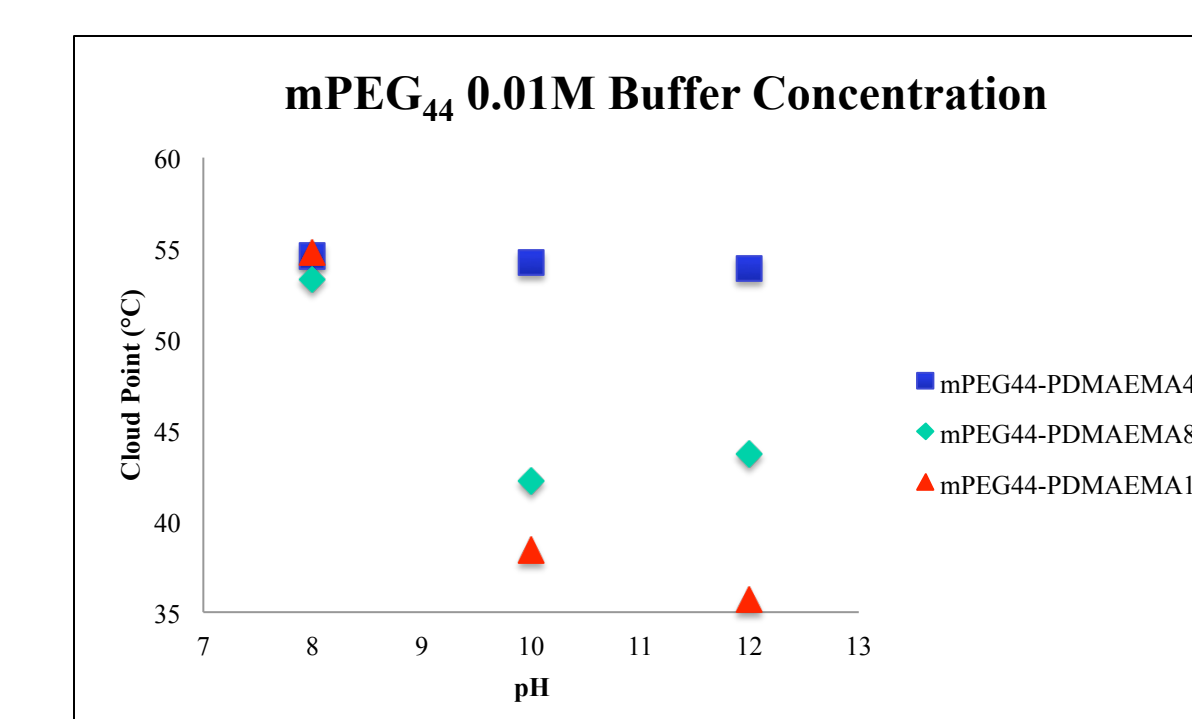
- PDMAEMA diblock copolymers will create micelles/aggregates depending on polymer concentration and temperature
- UV-Vis spectroscopy is used to measure presence of micelles/aggregates in solution



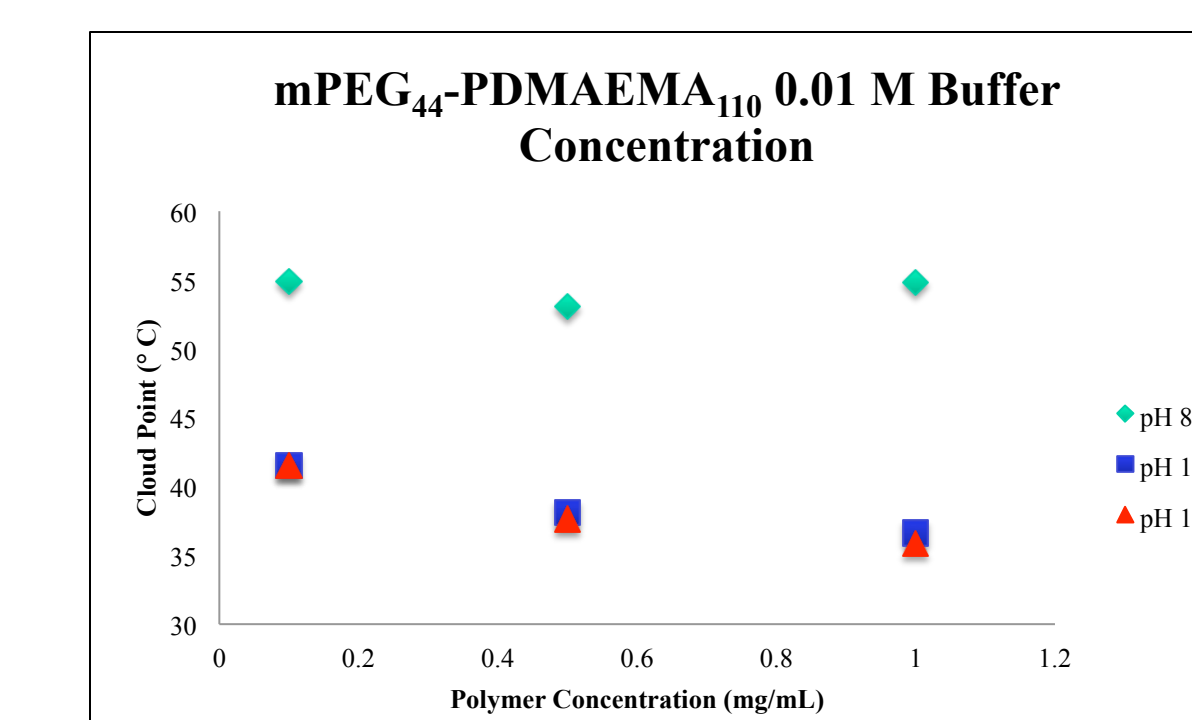
- The graph above shows mPEG-PDMAEMA cloud point at a specific polymer chain length ratio, pH, and buffer concentration
- Cloud point is determined by creating two best fit lines on the transmittance versus temperature graph.
- The first best fit line includes the value with the smallest slope in the graph before it changes.
- The cloud point is determined as the intersection of these two lines.

UV-Vis Studies

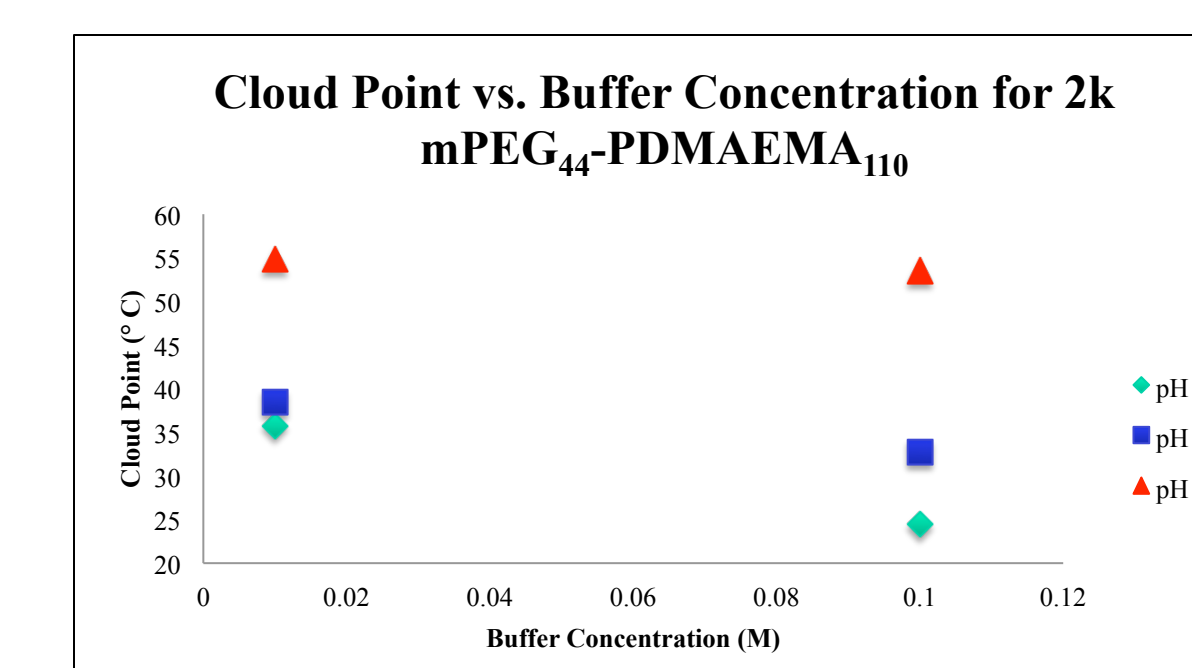
- The cloud point of the mPEG-PDMAEMA smart polymer can be controlled by external stimuli such as pH and buffer concentration.



- Above is a graph that shows cloud point versus pH for 2k 0.01M buffer solution for three different ratios of mPEG:PDMAEMA.
- The general trend of the graph shows that as pH of the solution increases, cloud point decreases.
- The PDMAEMA part of the diblock has a tertiary amine group on the end that can be protonated or deprotonated depending on the pH of the solution that the diblock polymer is in.
- At pH 8 more PDMAEMA is charged so the ratios affect the cloud point less.
- The ratio of mPEG:PDMAEMA also affects the cloud point.



- The graph above shows the relationship between cloud point and polymer concentration at pH 8, 10, and 12.
- The graph above shows for pH 10 and 12 that as polymer concentration increases, the cloud point decreases.
- At pH 8 molecular weight affects the cloud point less because of PDMAEMA being charged more than at pH of 10 and 12.



- The graph above shows cloud point versus buffer concentration for mPEG₄₄-PDMAEMA₁₁₀ at pH 8, 10, and 12.
- The general trend of the graph show that as buffer concentration increases, cloud point of the diblock polymer decreases.

Conclusions

- mPEG-PDMAEMA was characterized using NMR and GPC
- Samples were thermoresponsively studied using UV-Vis spectroscopy.
- Cloud points were observed as a function of pH, polymer concentration, buffer concentration and polymer composition.

Future Projects and Research Goals

- Perform thermo fluorescence studies
- Study aggregate size using dynamic light scattering
- Study how architecture affects cloud point

Acknowledgments

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