Synthesizing and Characterizing Triblocks of the Smart Polymer PDMAEMA

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The Power of AND

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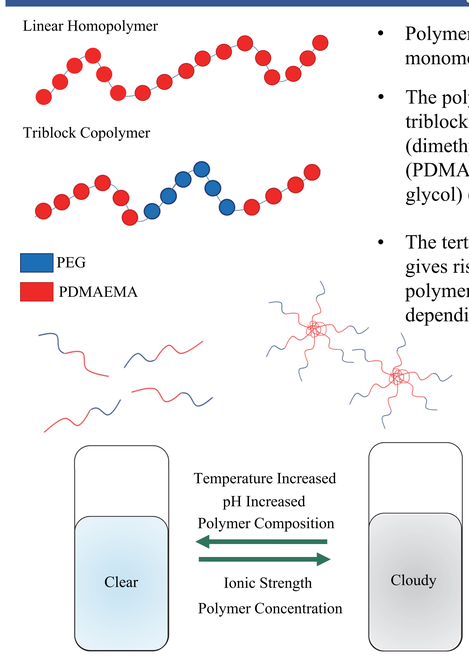
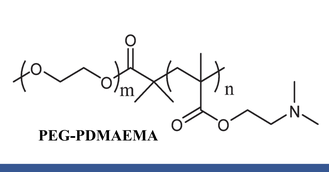
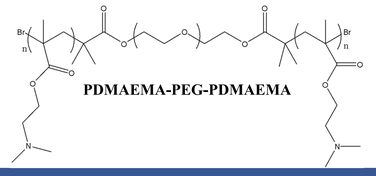
"Smart" Polymers



- Polymers are covalently bonded molecules, or monomers, that have repeating units.
- The polymer composition of interest is linear triblock copolymers consisting of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) on both ends of poly(ethylene glycol) (PEG).
- The tertiary amine group on the PDMAEMA gives rise to these "smart" polymers. Smart polymers are able to switch their properties depending on the external stimuli.
- The external stimuli which can affect the properties of the polymer are temperature, pH, ionic strength and polymer concentration
- Properties that are tested and observed are viscosity, interfacial tension and water solubility. These properties are caused by the stimuli-responsive PDMAEMA.
- Synthesizing PDMAEMA-containing block copolymers with controlled architecture can lead to unique structures which result in various properties.

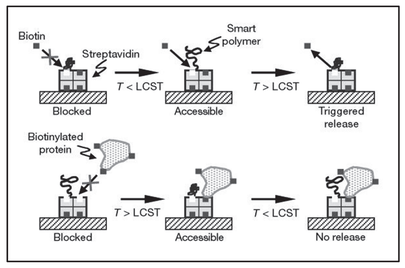




Applications

Tissue Engineering: Molecular Gates and Switches

- Smart polymers are of interest for their potential to have shape-memory capabilities. The swelling of the polymer in response to temperature will allow for active sites of protein to be blocked or unblocked.
- An increase in temperature will signal the polymer to swell and allow the covering of the active site to prevent binding.



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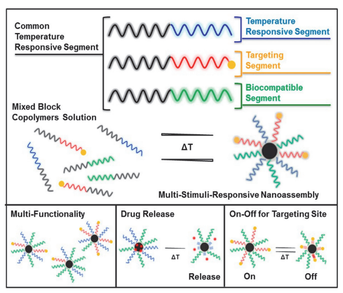
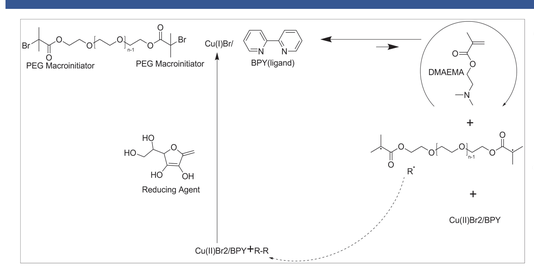
Pharmaceutical: Drug Delivery



http://www.mdpi.com/polymers/polymers-0800380/article_deploy/html/images/polymers-08-00380-g012.png

- Smart polymers are of interest for their potential to be used in drug delivery. The polymer's ability to switch its properties allows for different structures such as a network of chains or a micelle. These structures are prompted by temperature and pH.
- PDMAEMA switches from hydrophobic to hydrophilic depending on the environment whereas the PEG remains hydrophilic which causes changes in structure. This allows for encapsulation and targeted release of drug.
- The pH and temperature at which it encapsulates and releases the drug can be modified by changing polymer composition.

Polymer Synthesis and Characterization

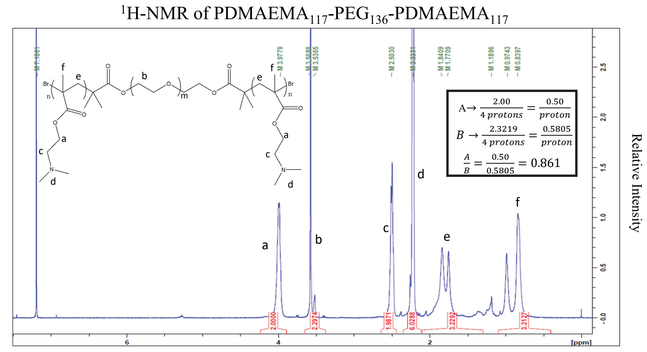


- To synthesize PDMAEMA triblocks, Activator ReGenerated Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) is used.
- Since less amount of copper is used than ATRP, it is easy to prepare, inexpensive, and an environment-friendly process.
- To control the molecular weight, the monomer (DMAEMA) was changed to initiator ratio.
- To prepare the triblocks, macroinitiator of 2k or 6k molecular weight PEG was used. To prepare the diblocks, macroinitiator of 2k or 5k molecular weight PEG was used.
- The diblock and triblock products were characterized by NMR and GPC.
- To calculate the consistency of the polymer chain lengths, measurement of dispersity was needed, and it was obtained by Gel Permeation Chromatography (GPC).

Sample	2K 1:2.5	5K 1:2	6K Br-PEG-Br	6K 1:1:1
Total Mn (NMR) (kDa)	19.5	47.9	6.0	42.7
Relative Mn (GPC) (kDa)	38.4	67.5	27.7	73.6
$Đ_m$ (dispersity)	1.14	1.21	1.03	1.35

- Proton Nuclear Magnetic Resonance (H-NMR) spectroscopy was used to characterize the synthesis by ensuring proper molecular structure as well as to determine molar ratio.

^{1}H-NMR of PDMAEMA$_{117}$-PEG$_{136}$-PDMAEMA$_{117}$

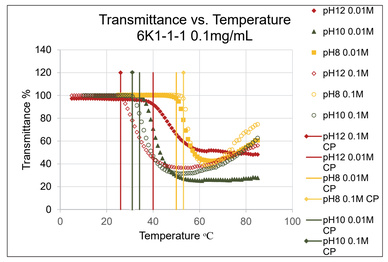


- Each peak corresponds to protons which has a specific chemical shift on the x axis which is caused by the chemical and electronic environment of the proton. Letters were assigned arbitrarily to match the integration of the peak to polymer.
- The integrations were taken for each peak. A ratio was determined from values obtained for the peak from a PEG block and a PDMAEMA block which gives the molar ratio.
- A successful synthesis is determined by obtaining a molar ratio and structure that corresponds to the target ratio and target structure.

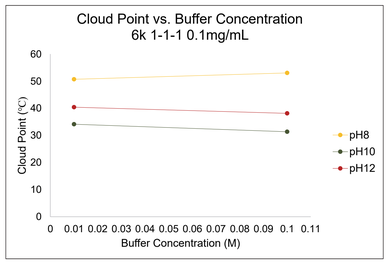
Polymer Characterization

Ultra-Violet Visible Light Spectroscopy (UV-Vis)

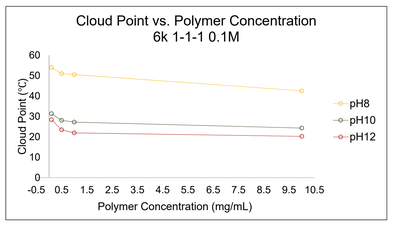
- UV-Vis Spectroscopy is a technique that can be used to measure the drop in transmittance of the aqueous polymer solution which is called the cloud point (CP).
- UV-Vis spectroscopy was used to determine how the cloud point of PDMAEMA is affected by changing PDMAEMA molecular weight, pH level, polymer concentrations, and buffer concentrations.



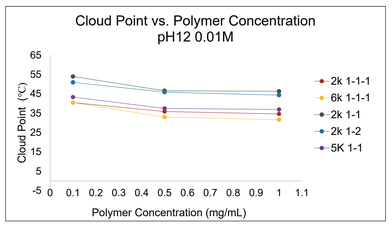
- Higher pH level (pH12) needs lower temperature to switch from soluble to insoluble.



- Buffer concentration at 0.1M and 0.01M is graphed.
- In general, the cloud point increases with decreasing buffer concentration.



- Polymer concentration at 0.1, 0.5, 1, and 10mg/mL is plotted.
- Lower polymer concentration (0.1mg/mL) shows higher cloud point.

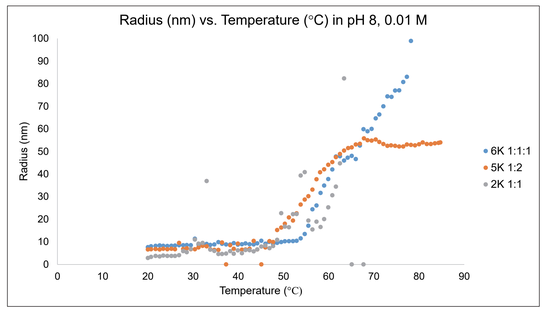


- Triblock copolymers show lower cloud points than diblock copolymers.
- The cloud point decreases with increasing molecular weight.

Dynamic Light Scattering (DLS)

- DLS is an instrument used to measure the average size of objects as a function of temperature.
- DLS studies were done to determine the temperature at which the polymer forms micelles or aggregates. Comparisons of this data were made with UV-Vis data to determine when the polymer exhibits its switching, or smart, properties.
- The effect of temperature from 20-85℃ was tested with various pH of pH 8, 10 or 12 and buffer concentration of 0.1M or 0.01M.
- Temperature ramp using a set polymer concentration and buffer concentration determined the formation of aggregates.

Triblock and Diblock Micelle Radius with DLS



- A comparison of micelle and aggregation size is made between a triblock and diblocks of the same pH and concentration. Temperature at which these sizes are formed are also recorded.
- The temperature at which the polymer switches from soluble to insoluble corresponds to the cloud point obtained from UV-Vis.
- The triblock and diblocks of different PEG molecular weights appear to switch from soluble to insoluble at around the same temperature. It appears that lower molecular weight PEG results in aggregates instead of micelles.

Conclusions & Future Work

- UV-Vis was used to determine cloud point.
- Lower pH level results in higher cloud point.
- Triblock copolymers switch from soluble to insoluble at lower temperature than diblock copolymers.
- Triblock copolymers form micelles vs. larger aggregates for 2k diblock copolymers in pH 8, 0.01M concentration.
- Future goals aim to continue measuring triblocks and compare smart properties to diblocks, as well as synthesize PDMAEMA smart polymers of brush and block architecture.

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