Synthesis and Application of Smart Polymers in Architectural Coatings

The Power of AND | University of Wisconsin Eau Claire

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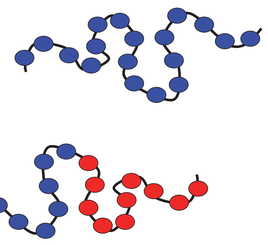
Materials Science and Engineering

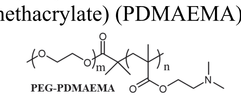
Introduction to Polymers

- Polymers are formed through the linking of many repeating small molecules
- The polymer structures that are being studied are diblock copolymers, which are composed of two repeating blocks that are covalently bonded together.

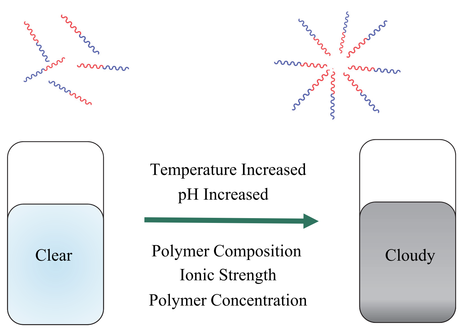


Smart Polymers

- "Smart" polymers vary from traditional polymers in the way they respond to small triggers in the environment.
- Smart diblock copolymers have a Polyethylene Glycol (PEG) end and a Poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) end.



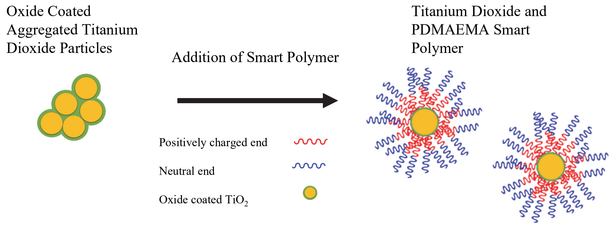
- PDMAEMA was chosen because it switches properties based on pH and temperature.
- Changes in pH, buffer concentration, and polymer concentration will affect the cloud point and other properties of PDMAEMA.



- Cloud point is the temperature above which the polymer goes from soluble (hydrophilic) to insoluble (hydrophobic).
- Cloud point affects solubility, viscosity, interfacial activity, and other properties.

Applications

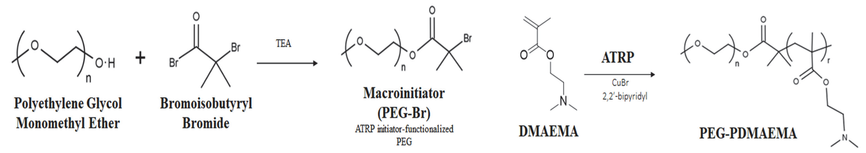
- The architectural coating industry uses additives in their paints, primers, and stains to produce certain pigments or other effects.
- Titanium dioxide particles are used to scatter light and to make coatings opaque. Production is expensive and hard on the environment.
- Uniform dispersion of titanium dioxide will reduce cost and improve the opacity of the coatings.



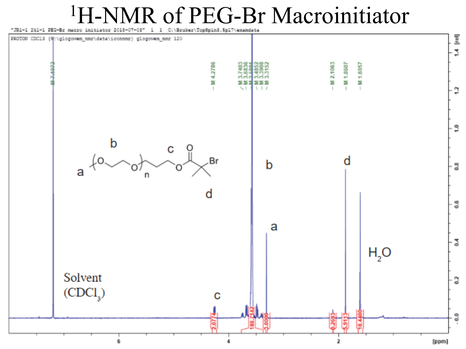
- Smart polymers are predicted to improve the dispersion of oxide coated titanium dioxide particles.
- PDMAEMA smart polymer would reduce production costs by lowering the quantity of particles needed for even color.
- The PDMAEMA ends are predicted to attach to the silicon oxide-coated titanium dioxide as a function of pH.
- The neutral PEG end will physically prevent the copolymer coated particles from aggregating.

Polymer ATRP Synthesis

- Atom Transfer Radical Polymerization (ATRP) was used to synthesize PDMAEMA diblock copolymers.
- Molecular weight was controlled through changing the ratio of initiator to monomer.
- Using ATRP resulted in copolymers with controlled molecular weight and narrow molecular weight ranges.



Polymer Structure Characterization



- ^{1}H-NMR (Proton Nuclear Magnetic Resonance) Spectroscopy is a technique used to determine whether or not the functionalized macroinitiator is viable for PEG-PDMAEMA synthesis.
- Peaks correspond to the different hydrogen groups on the structure which is affected by location and neighboring atoms.

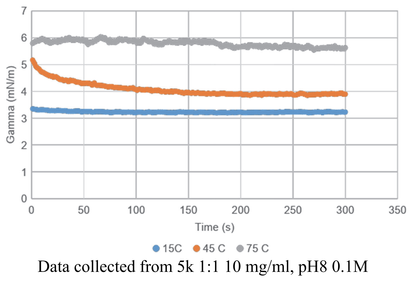
- Polymer composition is represented by molecular weight and proportions of PEG to PDMAEMA.
- PEG-PDMAEMA is synthesized from PEG-Br macroinitiator and DMAEMA ATRP reaction with different average molecular weights of PEG.
- Molecular weights of PEG used were Mn ~ 5,600 (n=127) and Mn ~ 2,000 (n=45).
- Ratio of PEG to PDMAEMA refers to the molar ratio in the diblock copolymer.

Polymer compositions that were tested:

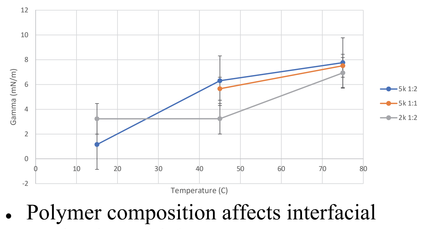
Target diblock copolymers	Mn PEG	n PEG	Mn PDMAEMA	n PDMAEMA	Polydispersity	Resulting diblock copolymers
5k 1:2 PEG:PDMAEMA	5,600	127	43,646	278	1.32	5k 1:2.3 PEG:PDMAEMA
5k 1:1 PEG:PDMAEMA	5,600	127	21,980	140	1.26	5k 1:1.12 PEG:PDMAEMA
2k 1:2 PEG:PDMAEMA	2,000	45	13,188	84	1.09	2k 1:1.90 PEG:PDMAEMA

Interfacial Tension

- Interfacial tension is the tendency of an interface of two liquids to become spherical to make its surface energy as low as possible.
- Ramé-hart Pendant Drop Tensiometer and DROPimage software are used to find interfacial tension in mN/m.



Data collected from 5k 1:1 10 mg/ml, pH8 0.1M

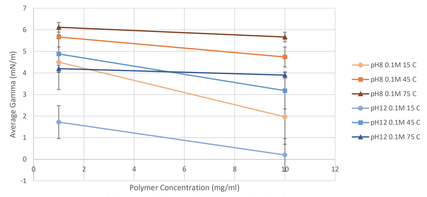


- Polymer composition affects interfacial tension in multiple ways.
- An increase in molecular weight increases interfacial tension.
- An increase in ratio of PDMAEMA to PEG increases interfacial tension.
- Increased temperatures increase IFT.
- Lower temperatures are difficult to quantify trends, further data will need to be collected.

Factors that affect interfacial tension:

- Time
- Temperature
- Buffer pH
- Buffer Concentration
- Polymer Concentration
- Polymer Molecular Weight
- Copolymer Proportions
- Solute/Solvent Interactions
- Droplet Volume (needle gauge)

- Interfacial tension is time dependent until equilibrium is reached due to polymer interactions between liquidus phases.
- Interfacial tension proportionally increases with temperature for polymers dispersed in aqueous solutions.

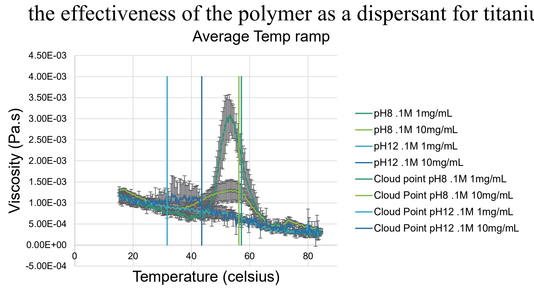


Data collected from 5k 1:2

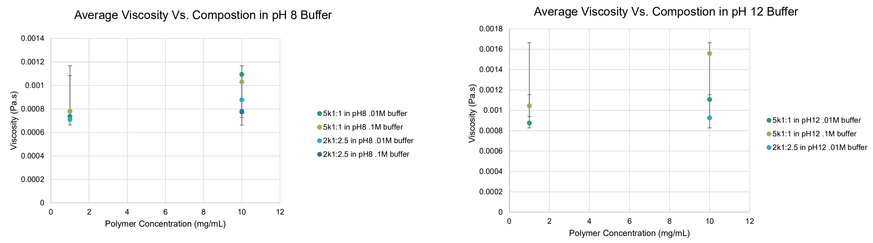
- Increasing polymer concentration decreases interfacial tension due to increased rate of interfacial reactions.
- Increasing pH decreases IFT due to solute solvent interactions.
- Temperature trends are consistent with other data.

Viscosity

- The Rheometer is an instrument that is used to measure viscosity (a fluid's resistance to flow).
- Temperature and pH affect the viscosity of the PDMAEMA in water. This will impact the effectiveness of the polymer as a dispersant for titanium dioxide.

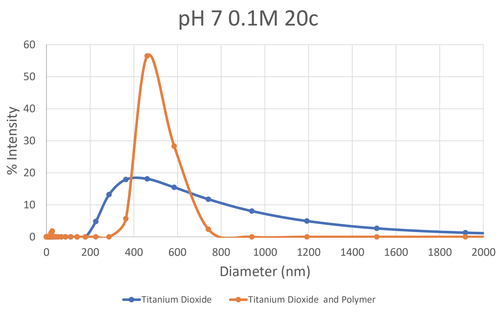


- Viscosity was measured as a function of temperature for 5k 1:1 and 2k1:2.5 PEG-PDMAEMA with different pH and polymer concentration.
- The cloud points for each polymer are depicted by vertical color coded lines which tells us precisely the point where the solution starts to phase separate and become separated.

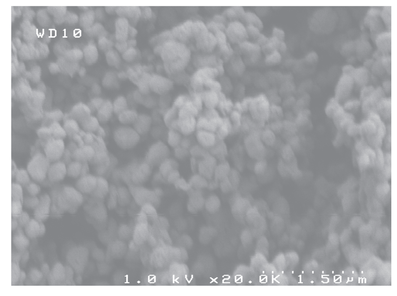


- Viscosity was measured as a function of shear rate and the average was calculated when viscosity plateaued for PEG-PDMAEMA (with a 1:1 molar ratio) copolymer.
- Variables tested include polymer concentration, buffer concentration, and pH. Polymer concentration has shown to result in a higher viscosity whereas the increase in buffer concentration and pH is still inconclusive until further testing

Particle Polymer Solutions



- Dynamic Light Scattering (DLS) scans of silicon oxide coated titanium dioxide particles with 2k 1:2 diblock copolymer.
- Particles and polymer are suspended in pH buffer solution
- DLS is used to analyze particle size to show if particle aggregation is occurring.



- SEM (Scanning Electron Microscope) scan of titanium dioxide particles on aluminum stub.
- Particles analyzed for diameter with ImageJ software.
- Approximate particle diameter of 302nm.

- Aggregation is found to have occurred when the distribution shown by DLS is wider than that of unaggregated particles.

Conclusions

- PDMAEMA copolymers were synthesized using ATRP and characterized with NMR.
- Smart properties of PDMAEMA were tested with tensiometry and rheology.
- Viscosity and interfacial tension changed in response to small changes in temperature and pH.
- DLS is used to show if aggregation occurs between titanium dioxide particles at various pH.
- Interfacial tension of polymers in aqueous solutions will affect how evenly titanium dioxide particles can be dispersed.

Future Projects and Research Goals

- Further testing with the pendant drop tensiometer, DLS, and rheometer to determine viable polymers for testing with titanium dioxide particles.
- ARGET ATRP will be used in favor of ATRP for future synthesis, this process is simpler and is not as sensitive to oxygen contamination with only a slightly higher dispersity on average.

Acknowledgments

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