Smart Polymer-Grafted Silica Particles: Synthesis and Characterization of Smart Properties

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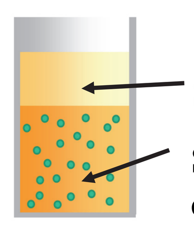
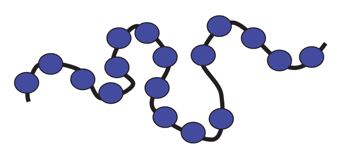
Polymer and Colloid Basics

- Colloids are insoluble particles between 1 and 1000 nanometers in size suspended in a liquid.
- Colloids do not settle out or take a long time to settle out noticeably.



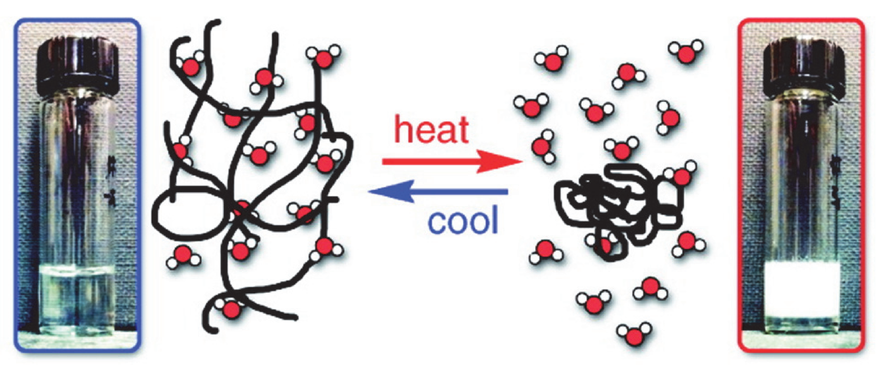
https://en.wikipedia.org/wiki/Colloid#/media/File:ColloidalStability.png



- Polymers are long chains of covalently bonded repeat units, called monomers.
- Polymers are both naturally occurring and synthetic

"Smart" Polymers

- "Smart" materials change properties in response to an external stimulus.

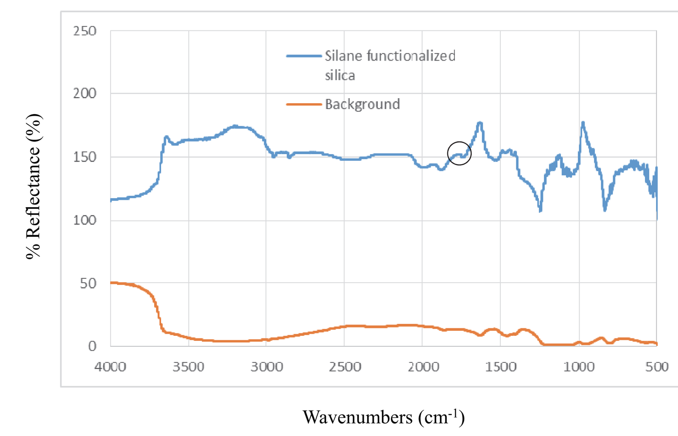


Published in: David E. Bergbreiter; Alexander J. Mijalis; Hui Fu; *J. Chem. Educ.* **2012**, 89, 675-677. Copyright © 2012 The American Chemical Society and Division of Chemical Education, Inc.

- Certain smart polymers become water-insoluble upon heating. The temperature at which it becomes insoluble is the cloud point.

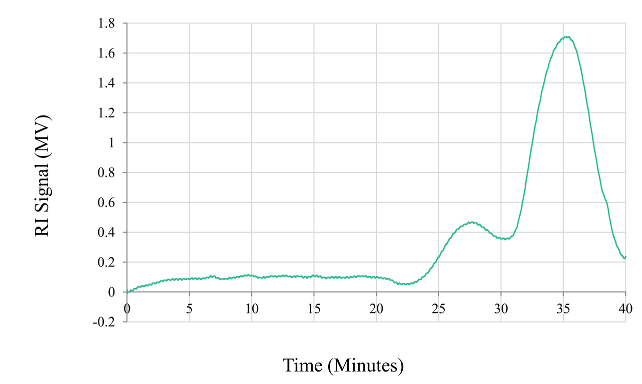
Functionalized SiO_2 Characterization

- Infrared Spectroscopy is used to ensure functionalization occurs.
- Peaks on the graph show different functional groups; double peaks around 1700 cm^{-1} indicate carbonyl group from silane.



Free Polymer Characterization

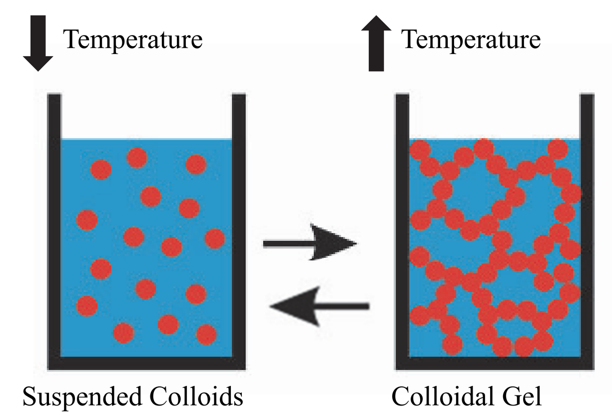
- GPC (gel permeation chromatography) is used to characterize non-grafted polymers.
- This confirms that the ATRP was successful.



- NMR (nuclear magnetic resonance) is used to further characterize the free polymer.

Smart Polymer Grafted Colloids

- By grafting polymers from colloids, characteristics of both can be used and unwanted characteristics can be minimized.

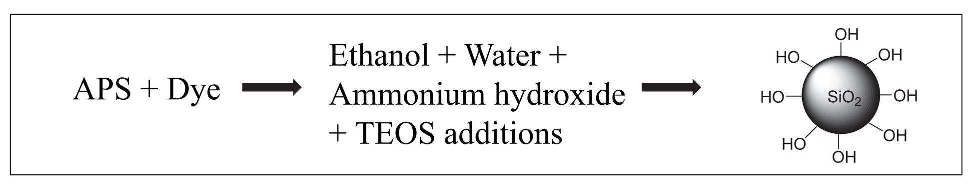


http://soft-matter.seas.harvard.edu/images/thumb/4/47/780px-Wiki_SolGel1.jpg/300px-780px-Wiki_SolGel1.jpg

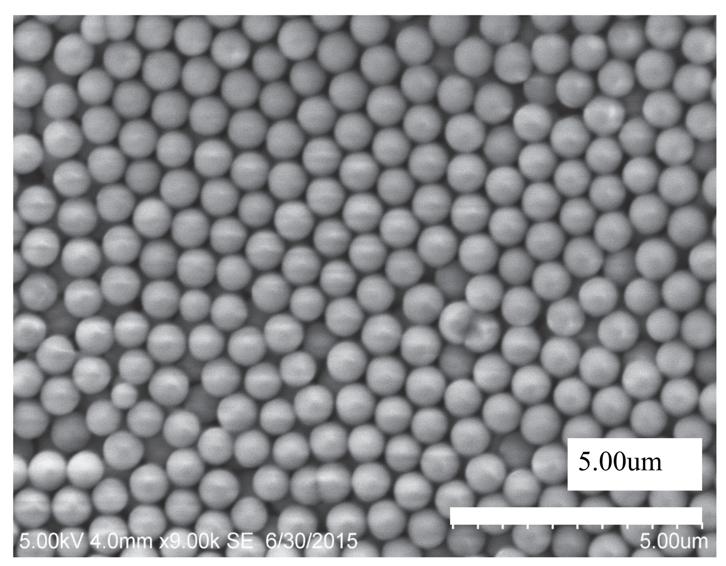
- PDMAEMA or poly(2-(dimethylamino)ethyl methacrylate) was selected because the cloud point can be tuned from 30ºC to 85ºC by changing its structure and other parameters.
- By grafting PDMAEMA from colloids we can create a colloidal suspension that will suspend and aggregate controllably and reversibly via external stimuli.
- Smart polymer-grafted silica has potential applications in 3D printing and enhanced oil recovery (EOR).

Particle Synthesis

- Silica particles were picked because the size and functionality can be controlled.
- The Stöber growth process allows for controlled particle growth around a fluorescent dye (FITC or RITC).



- Incorporation of dye allows for characterization with confocal microscopy.
- Target particle size is 800-1000nm, this allows for proper characterization and helps particles exhibit similar characteristics when grafted with smart polymer.

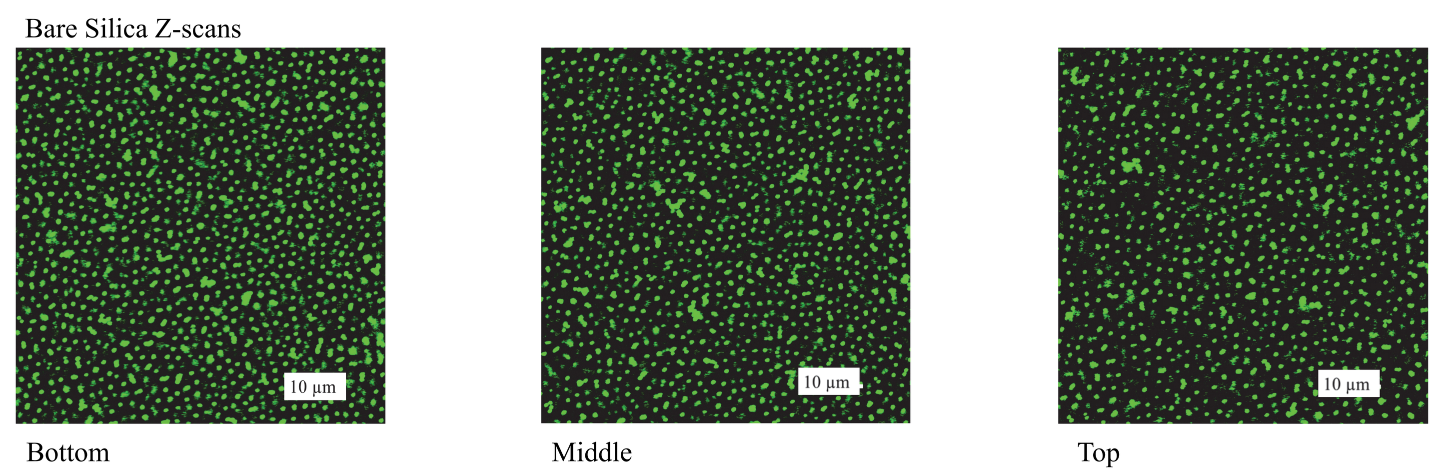


- Scanning electron micrograph of cleaned unfunctionalized silica
- 5.00kV, 4.0 mm WD, 9k x magnification, secondary electrons

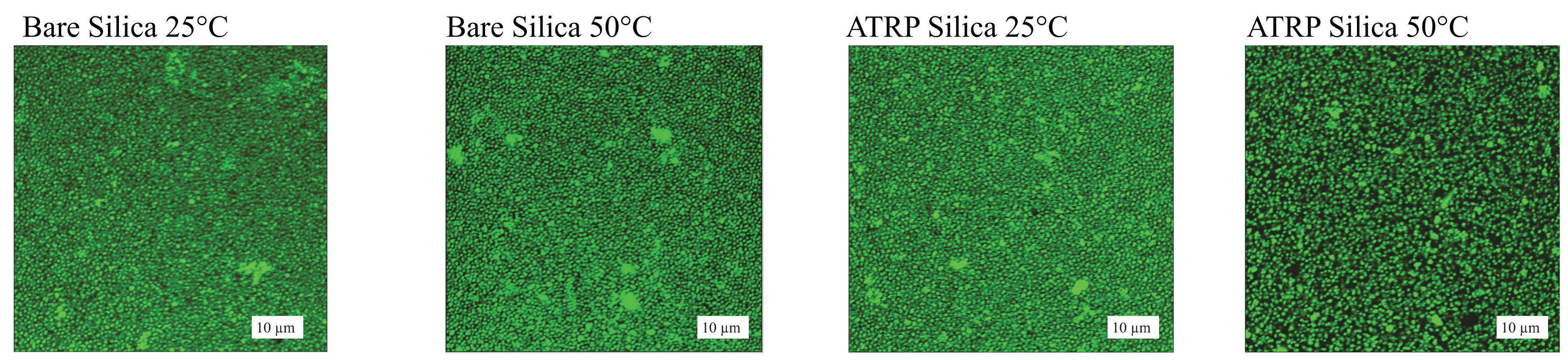
Confocal Microscopy

- Confocal microscopy uses a laser source and a confocal pinhole detector to achieve high resolution light microscope images.
- The dyes used during particle synthesis enable characterization using florescence microscopy. The different dyes can be tracked individually, showing different behavior with and without polymer grafting.

Bare Silica Z-scans

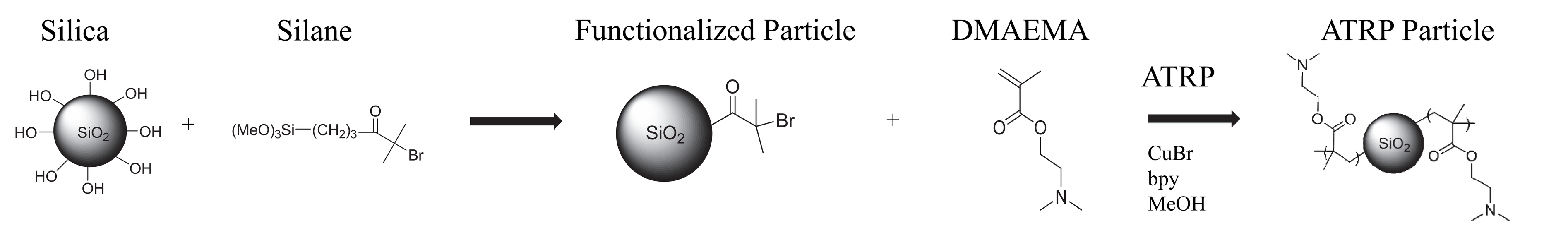


- Fast scan speeds allow for high speed imaging for both time scans and z or height scans of moving particles. Time scans show how dispersed one area is by looking at particle movement. Z scans show aggregation throughout the sample.



- The bare silica time scans show how well the particles are dispersed.
- There is no change between the 25°C and 50°C bare particles.
- ATRP particles at 25°C show similar characteristics to bare particles at 25°C.
- ATRP particles at 50°C aggregate.
- ATRP particles at 50°C are the only particles that show thermoresponsive behavior. Less movement occurs when particles are aggregated and the particles are locked in a more open network.

Silica Functionalization and Grafting-from Polymerization



- The silica particles are first reacted with silane to form a functionalized silica particle
- Proper functionalization with silane is necessary to initiate Atom Transfer Radical Polymerization or ATRP
- ATRP allows for the covalent bonding of PDMAEMA from the silica particles.
- ATRP is a form of "living" polymerization. "Living" polymerizations are more controlled, which results in more well defined smart characteristics.

Conclusions

- Particles of approximately 800nm in size have been successfully grown and characterized by use of the SEM.
- Silica particles were functionalized, polymer grafted, and then characterized using the IR, GPC, and Confocal Microscope.
- Preliminary results indicate thermoresponsive behavior of the PDMAEMA grafted silica particles.

Future Projects and Research Goals

- Study thermoresponsiveness for PDMAEMA grafted particles.
- Study how molecular weight and pH change cloud point.
- Graft particles with branched smart polymer.
- Observe settling rate of aggregated particles.

Acknowledgments

Dr. Doug Dunham
Phil Conor
Materials Science Program
WiscAMP
NSF-MRI
Blugold Commitment

Celebration of Excellence in Research and Creative Activity Spring 2016