Synthesis of Smart Copolymer PEG-PDMAEMA and Determination of Cloud Point

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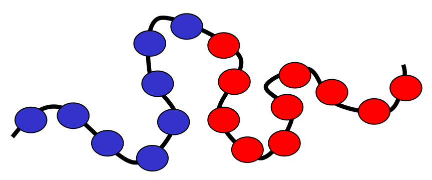
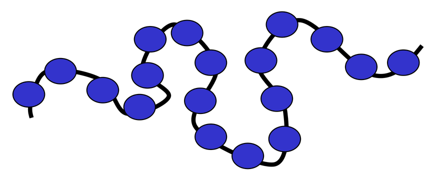
Materials Science Program

Polymer Basics

Polymers are made of covalently bonded repeat units, called monomers, that make up long chains.

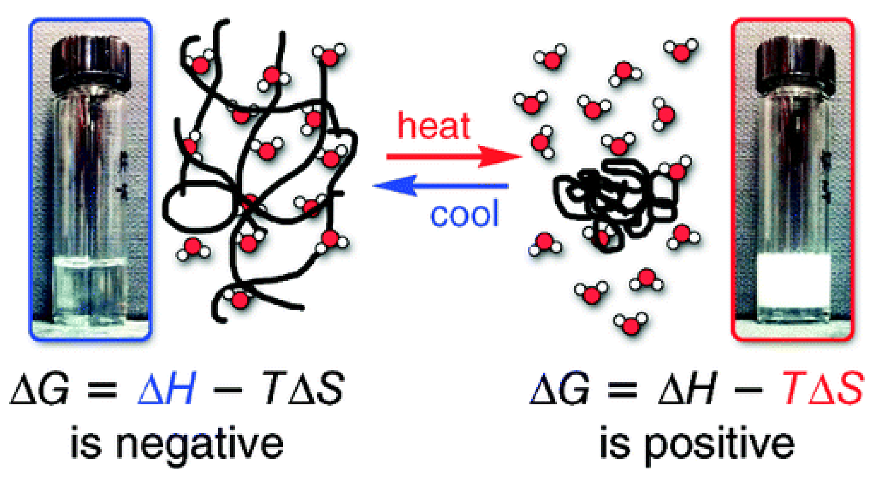




Polymer structure can be modified to achieve homopolymers (one repeat unit) or diblock copolymers (two repeat units segregated into blocks)

"Smart" Polymers

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



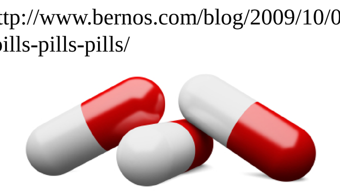
Published in: David E. Bergbreiter; Alexander J. Mijalis; Hui Fu; *J. Chem. Educ.* **2012**, 89, 675-677.

Cloud point is the temperature above which the smart polymer will aggregate and the solution will become cloudy. This is determined by polymer-solvent interactions and ΔG_{mix}

Poly(ethylene glycol) -*block*- Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is a smart polymer and has a cloud point that depends on pH, polymer concentration, ionic strength, and polymer structure.

Smart polymers have a wide array of applications ranging from industry to medicine to cosmetics.

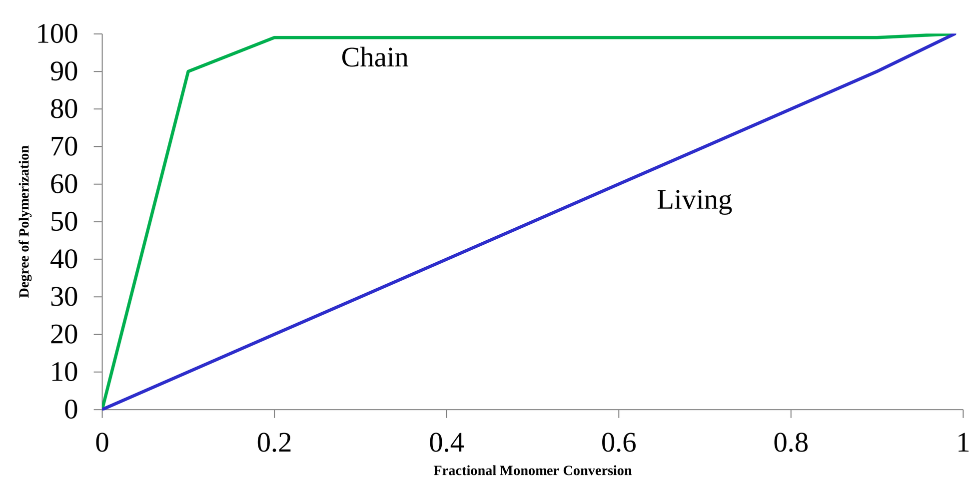
http://www.bernos.com/blog/2009/10/06/pills-pills-pills/



http://www.sephora.com/water-fuse-smart-gel-bb-P377560

Polymerization Mechanisms

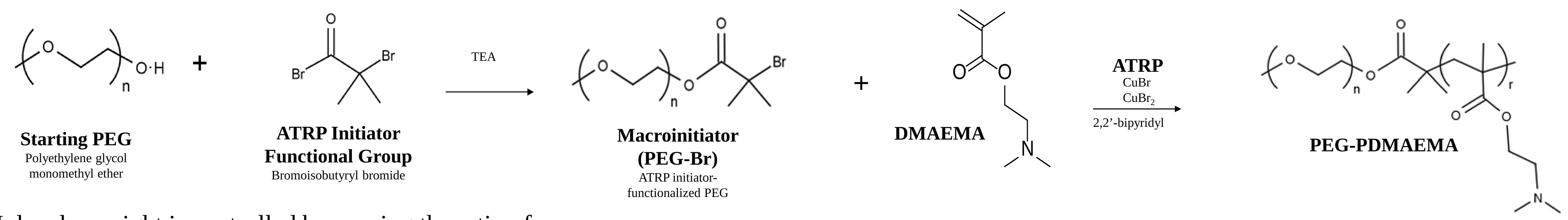
Chain growth polymerization is widely used to synthesize industrial polymers. This method is much quicker, but produces less uniform product than living polymerization.



"Living" polymerizations have a more controlled growth mechanism which will result in a polymer with more highly-defined smart polymer characteristics

PDMAEMA was synthesized using Atom Transfer Radical Polymerization (ATRP) or a subset of "living" polymerization

ATRP of Polymer Diblock



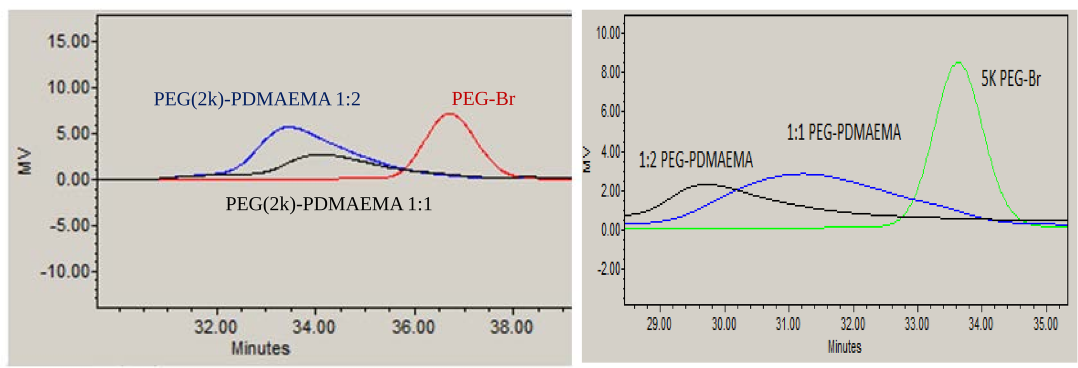
Molecular weight is controlled by varying the ratio of monomer:macroinitiator and polymerization time

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

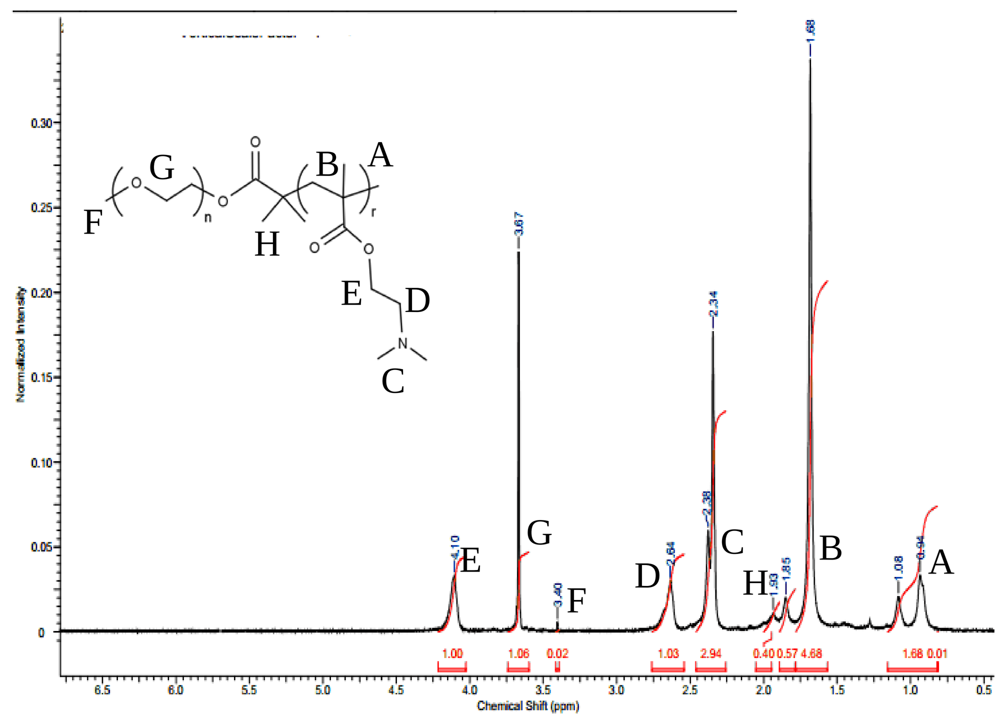
$$PDI = \frac{M_w}{M_n}$$

A PDI of 1 indicates that all polymers are the exact same length (impossible to attain outside of nature). Synthetic polymers have a PDI greater than 1. A good PDI for living polymerization is less than 1.2



Gel Permeation Chromatography (GPC) uses a series of columns with different sized pores inside to separate molecules based on their size. It is used to determine the PDI of the diblock sample. The molecular weights given by GPC are relative to polystyrene standards.

Sample	PDI	Mn(GPC)	Mn(NMR)
PEG(2k)-Br	1.10	4100g/mol	1900g/mol
PEG(2k)-PDMAEMA (1:1)	1.08	21300g/mol	8700g/mol
PEG(2k)-PDMAEMA (1:2)	1.08	28000g/mol	15500g/mol
PEG(5k)-Br	1.01	13100g/mol	5600g/mol
PEG(5k)-PDMAEMA (1:1)	1.18	52400g/mol	26800g/mol
PEG(5k)-PDMAEMA (1:2)	1.14	81500g/mol	49300g/mol



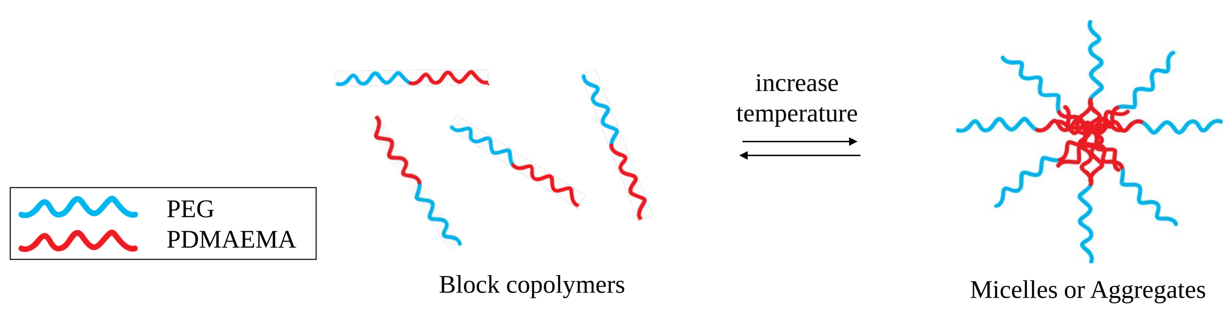
Proton Nuclear Magnetic Resonance Spectroscopy (H^1-NMR) is a way to calculate molecular weight by measuring and comparing the integration of protons in the polymer chains

$$E \rightarrow \frac{1.0}{2\ \text{protons}} = .5\ \frac{1}{\text{proton}}$$
$$G \rightarrow \frac{1.02}{4\ \text{protons}} = .255\ \frac{1}{\text{proton}}$$
$$\frac{E}{G} = \frac{.5}{.255} = \frac{1.96}{1.00}$$

All of the peaks were integrated relative to the E peak of PDMAEMA labeled above.

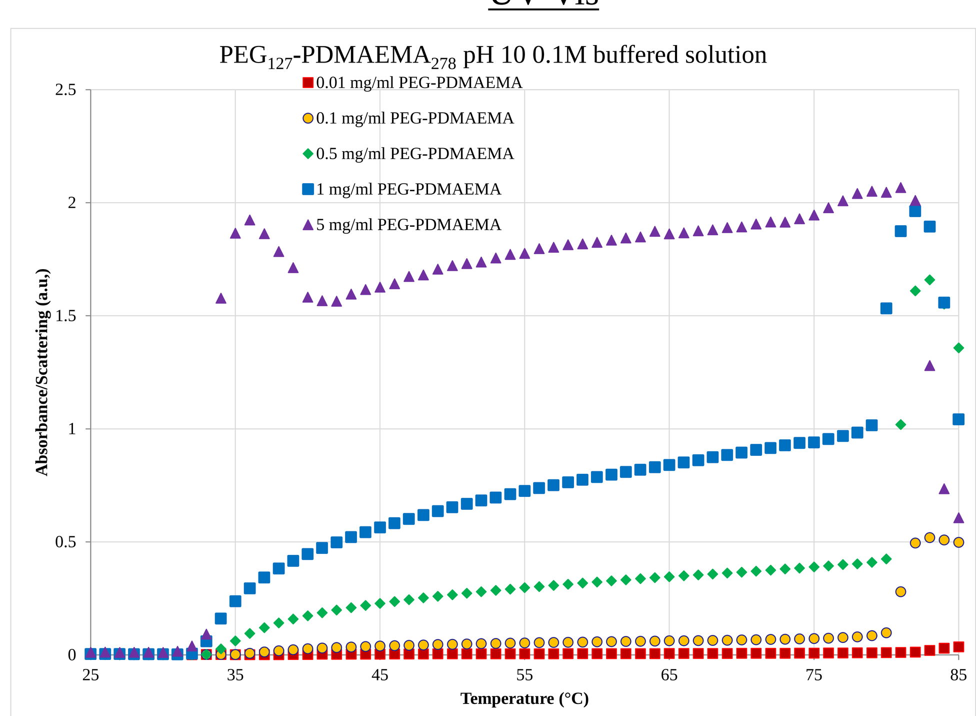
The PDMAEMA chain is ~2x the length of the PEG chain for this diblock.

Polymer Thermoresponsive Study

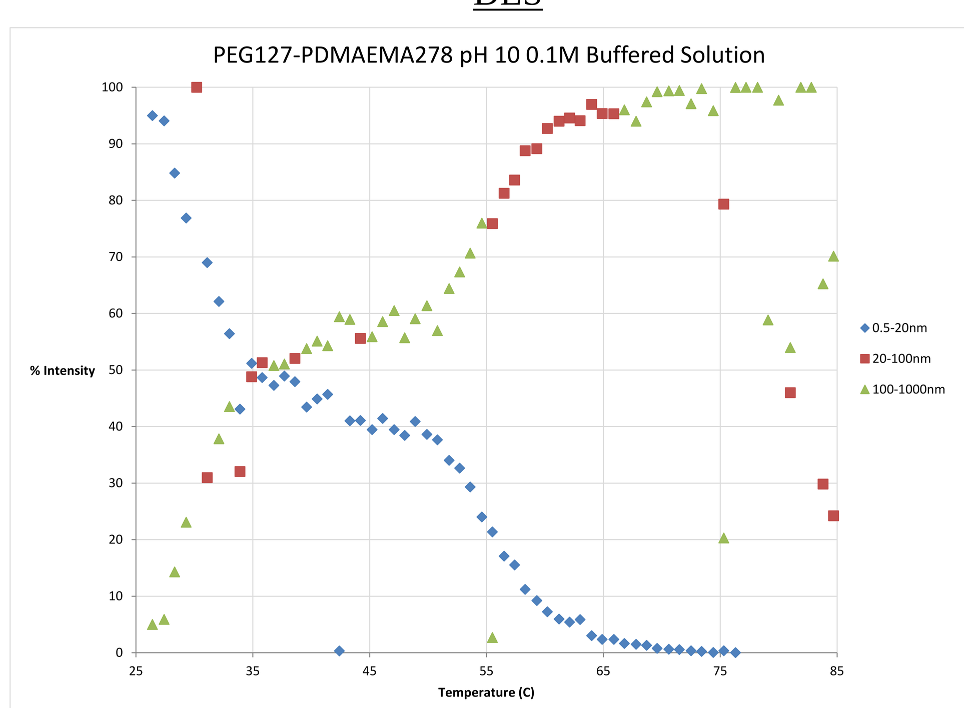


- PDMAEMA diblock copolymers will create micelles/aggregates depending on polymer concentration and temperature
- UV-Vis spectroscopy is used to measure presence of micelles/aggregates in solution
- "Absorbance" in the UV-Vis occurs when micelles or aggregates are formed
- Dynamic light scattering (DLS) uses light to determine the size of our polymer micelles or aggregates in solution.
- The plot below shows that as temperature increases, aggregation is occurring. DLS gives us the size of these aggregates.

UV-Vis

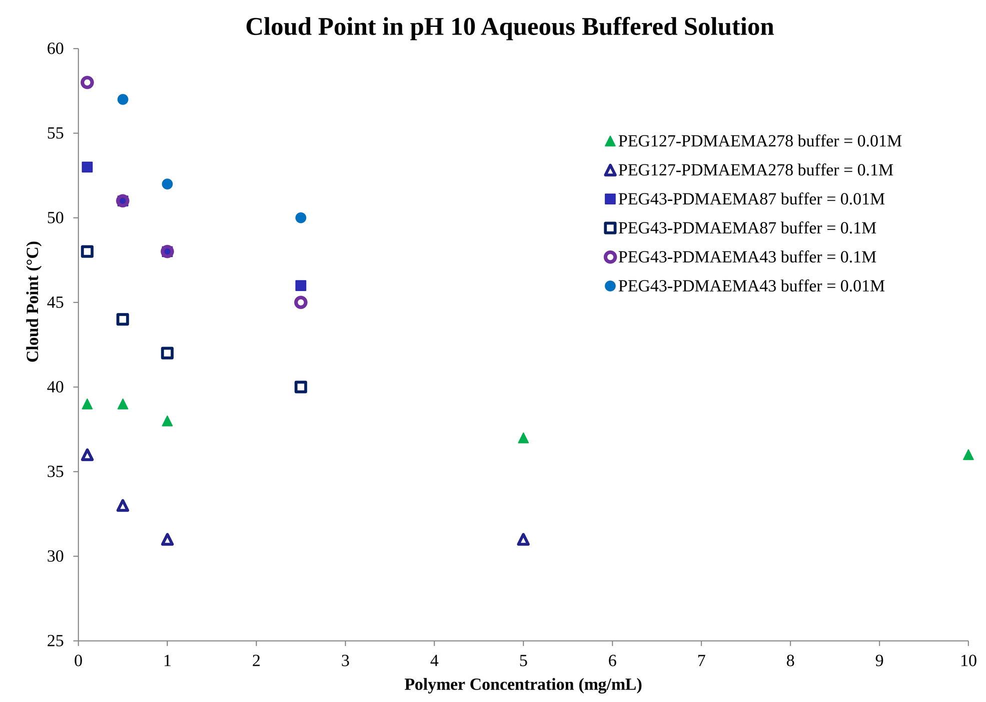


DLS



Summary of Thermoresponsive Studies

Due to the smart polymer nature of PEG-PDMAEMA the cloud point of a polymer solution can be controlled using a number of different external stimuli.

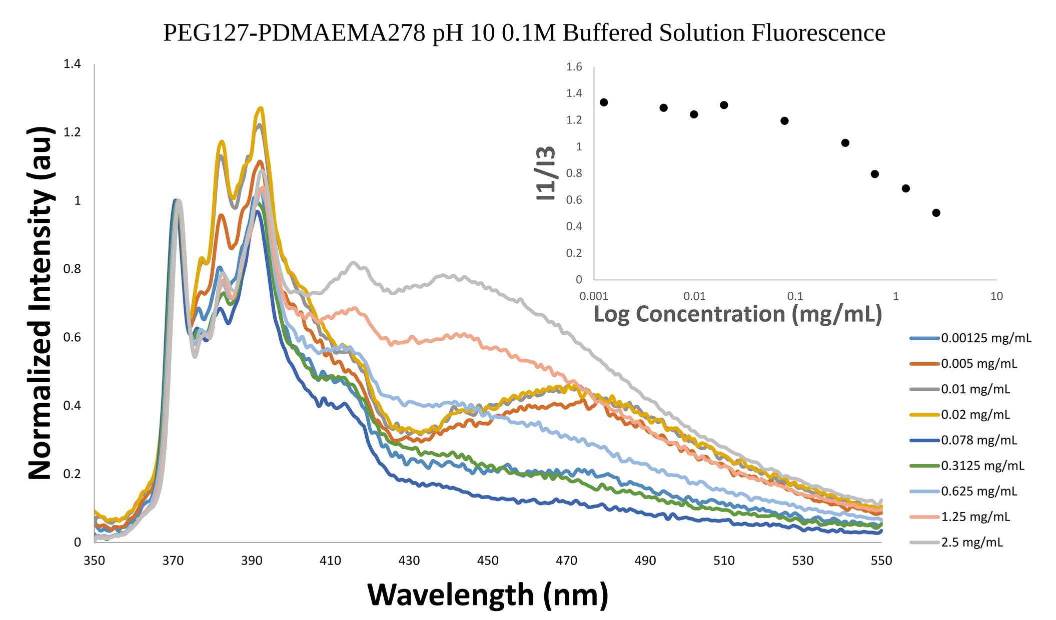


The data above shows that the cloud point of a polymer solution can be controlled using the following:

- Molecular weight of both PEG & PDMAEMA
- Polymer chain length ratios
- Buffer concentration

Fluorescence Studies

- The fluorescent dye used, pyrene, fluoresces differently when exposed to a hydrophobic or hydrophilic environment.
- Using pyrene, the micelle/aggregate formation can be detected by comparing peaks in the fluorescence spectra.
- The relative intensities of peak 1 to peak 3 is related to polarity. I1 increases with polarity. (peak 1 at 372 nm and peak 3 at 383 nm)
- As concentration of polymer increases, the pyrene moves to a less polar environment due to aggregate formation.



Fluorescence shows PEG-PDMAEMA aggregates at room temperature as the concentration increases

Conclusions

- NMR and GPC were used to verify the structure and find MW of the diblock
- UV-Vis and DLS were used to test the thermoresponsive behavior
- Cloud points were observed as a function of pH and polymer concentration
- Fluorescence studies with varying polymer concentrations have been started

Future Projects and Research Goals

- Test thermoresponsiveness as a function of pH and ionic strength
- Test aggregation due to temperature using fluorescence studies
- Continue to study aggregate size using dynamic light scattering

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