pNIPAM-PEG-AAc Microgels Explored with Light Scattering

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My current research involves exploring the physical properties of microgels made from (poly)n-isopropylacrylamide crosslinked with polyethylene glycol and copolymerized with acrylic acid (pNIPAM-PEG-AAc). These microgels show dramatic controllable size changes both as a function of temperature and solvent pH: pNIPAM transitions from hydrophilic at low temperatures (<30 °C) to hydrophobic at higher temperatures (>30 °C) due to an increase in mixing enthalpy, and acrylic acid ionizes above its pK_a of 4.4, drawing counterions into the microgel and swelling it.

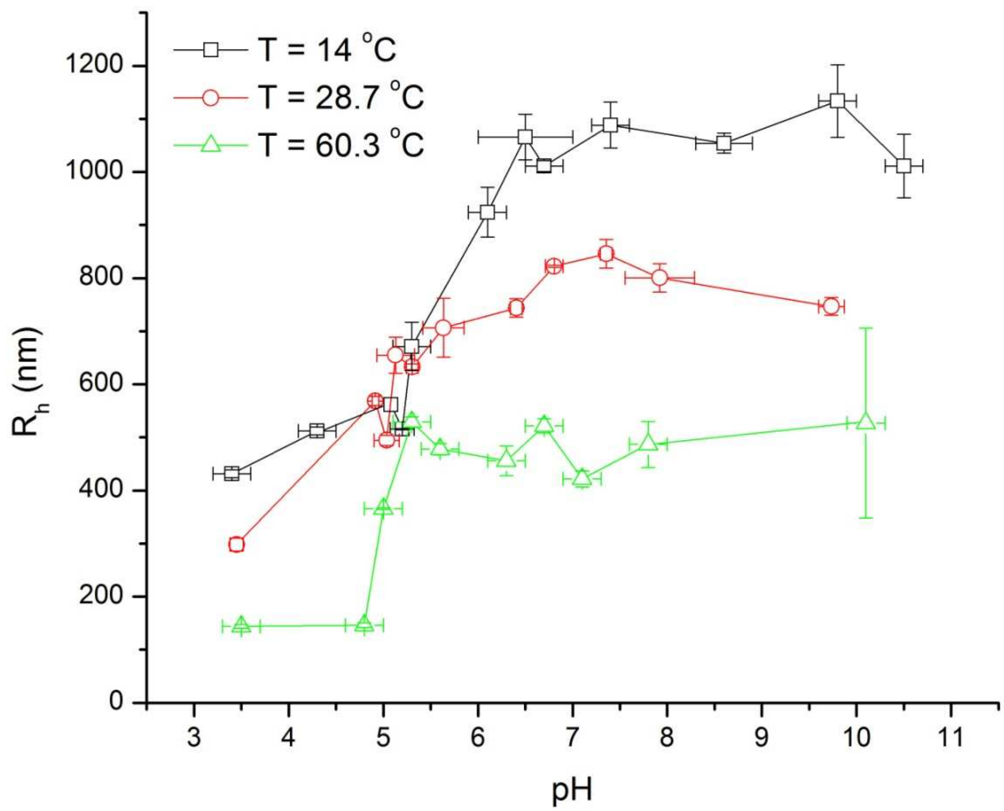

Figure 1: Hydrodynamic radius of pNIPAM-PEG-AAc microgels in water as a function of pH for 3 different temperatures. The particles swell (higher R_h) with increasing pH and decreasing temperature and span an entire order of magnitude in size, from about 200 nm to 2000 nm across. Hydrodynamic radius was obtained from dynamic light scattering measurements using the Stokes-Einstein equation for spherical particles, relating diffusion coefficient to size.

The eventual goal of this project is to study the glass transition, if any, of these microgels, using their tunable properties to probe different sizes and softness of the microgels. The swollen microgels are more deformable than in their deswollen state, and can be packed to very high generalized volume fraction $\zeta = NV_0$, where N is the number of particles and V_0 is the volume of the particles measured in the dilute state. For dilute suspensions of particles, $\zeta = \phi$, the conventional volume fraction; however, ζ can be extended to very concentrated packing of deformable particles that decrease in size as they push on one another. Some previous experiments with VP microgels made by another member of the group, Benjamin Sierra-Martin, showed liquid-like behavior of those microgels even at ζ approaching 100.

Size characterization of dilute suspensions of these microgels has been done in the lab's light scattering apparatus, a 3D dynamic light scattering apparatus made by LS Instruments. A He-Ne laser with wavelength $\lambda_0 = 632.8$ nm is split into 2 beams that are focused onto a small scattering volume within the sample. The scattered light is collected through 2 pinholes and guided through optical fibers to two avalanche photodiodes. The angle at which light is collected can be changed by a motorized goniometer, giving an angle range from between θ = 20° to θ = 140°. This arrangement creates two simultaneous scattering experiments with identical scattering vector $\vec{q} = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$, which are cross-correlated to obtain an intensity correlation function that is insensitive to contributions from multiple scattering.

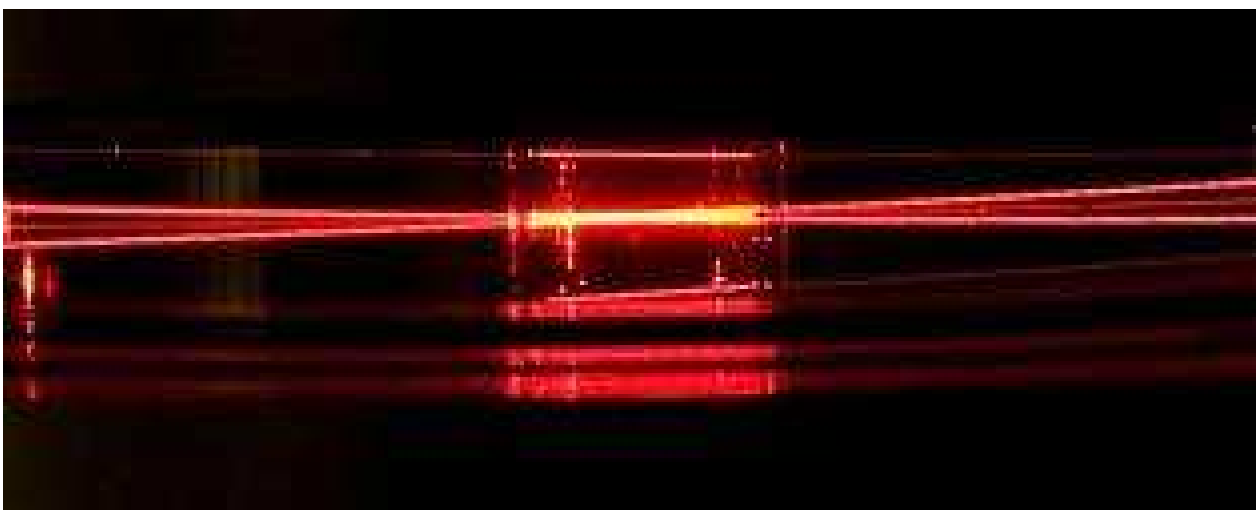

**Figure 2: The focused laser beams intersecting in the scattering volume of a sample.
http://www.lsinstruments.ch/services/technology/3d_cross-correlation_light_scattering/
Retrieved 06-21-2011**