Supporting Information for:

Physical Aging and Phase Behavior of Multi-Responsive Microgel Colloidal Dispersions

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Experimental

Materials. The monomer *N*-isopropylacrylamide (NIPAm, Aldrich) was purified by re-crystalllization from n-hexane (J. T. Baker). Acrylic acid (AAc, Fluka), *N,N'*-methylene bisacrylamide (BIS, Aldrich) and ammonium persulfate (APS, Sigma) were used as received. Water for polymerizations, purification, and dispersion preparations was distilled, and deionized to a resistivity of 18 MΩ·cm (Barnstead E-Pure system), and filtered through a 0.2 μm filter to remove particulate matter.

Synthesis and purification of pNIPAm-AAc microgel particles. PNIPAm-AAc microgels were synthesized by ammonium persulfate (APS)-initiated surfactant-free radical precipitation copolymerization of *N*-isopropylacrylamide (NIPAm, monomer), acrylic acid (AAc, co-monomer), and *N,N'*-methylene bisacrylamide (BIS, cross-linker) in de-ionized water at 60 °C under N_2 blanket for 4 hours.[1] A typical synthetic protocol is as follows. PNIPAm-AAc microgels were prepared with a 8.4:1.5:0.1 molar ratio of comonomers (NIPAm:AAc:BIS). NIPAm (1.8 g), BIS (0.03 g), and AAc (0.2 g) were dissolved in 100 mL of de-ionized water and filtered through 0.8 μm filter to remove particulate matter. De-ionized water (25 mL) was used to transfer and wash throughout filtration. After introduction of monomer solution into a 250 mL three-neck, round bottom flask equipped with thermometer, condenser/N_2 outlet, stir bar, and N_2 inlet, the reaction vessel was purged with N_2 for 1 hour while being heated from 22 °C to 60 °C. The monomer solution (125 mL) was then maintained at 60 °C for 15 min at a stir rate of 450 rpm. An APS (0.05 g, 5 mL) aqueous solution was then added to the monomer solution via syringe with an in-line 0.2 μm filter to initiate the polymerization. The polymerization was allowed to proceed at 60 °C for 4 hours. After polymerization, the resultant turbid reaction mixture was first filtered through 5.0 μm filter paper to remove flocculate, and then centrifuged at a relative centrifugal force (RCF) of 15, 422 × g for 1 hour to separate unreacted monomers, oligomers, and initiator from the microgels, followed by removal of the supernatant solution and re-dispersion of microgel pellets by shaking with fresh deionized water. The centrifugation and redispersion process was repeated for four cycles. After purification, the microgel dispersion was lyophilized at –42 °C under 45×10^{-3} mbar for 48-72 hours. The freeze-dried product was hygroscopic white powder.

Preparation of pNIPAm-AAc microgel dispersions. Aqueous buffers were prepared using recipes from the buffer calculator developed by R. Beynon at the University of Liverpool.[2] The microgel dispersions were prepared by first dispersing the pNIPAm-AAc powder in deionized water followed by shaking for one week. After centrifugation at a RCF of 15, 422 × g for 1 hour, the supernatant solution was removed, then the designated aqueous buffer was added and the microgels were redispersed in the buffer via shaking for 48 hours. After another centrifugation to remove the buffer aliquot, the designated amount of the aqueous buffer was added to adjust the weight concentration of microgel dispersions, followed by shaking for another 48 hours. The pH values were measured by a model 430 pH meter (Corning Corp.) with an Accumet probe (Cole-Palmer). The ionic strength was controlled by adding the appropriate amount of NaCl based on the buffer calculation. Because ionic strength is proportional to the conductivity, the ionic strength of pH buffers was determined by measuring the conductivity of corresponding pH buffers. The conductivity was measured with a Pinnacle 541 conductivity meter (Corning Corp.) with a "3 in 1" Combo w/RJ probe (Corning Corp.). The conductivity measured for all aqueous buffers was 1.48 ± 0.20 mS/cm.

Preparation of pNIPAm-AAc microgel aging samples. The dispersions were introduced into 5.0 × 2.0 × 0.1 mm VITROTUBE™ rectangular capillaries (Fiber Optic Center, Inc.) by capillary force at room temperature, and then sealed with Epoxy Putty™ (ITW Devcon®) resin. In some cases for very viscous dispersions, the

samples were heated above the melting temperature in order to fill the capillary. The dispersions were then allowed to age at room temperature for set periods of time prior to measurements being performed. Note that for any sample aged over 30 days, the evaporation of water cannot be completely eliminated. Thus some small amounts of evaporation could influence the phase behavior of microgel dispersions aged for longer than 30 days.

Tracking particles by video microscopy. Bright-field images (transmission mode) were taken with an inverted Olympus IX-71 microscope equipped with a 100× oil immersion objective and Andor™ LUCA camera with an electron multiplying charge-coupled device (EMCCD). The sample temperature was controlled with a temperature stage (Physitemp) as well as an objective heater (Bioptechs) to within ±0.1 °C. Typically, after being thermally equilibrated at a specific temperature for 30 minutes, images were recorded from the middle layer of microgel assemblies, ~50 μm away from both the upper and lower walls to minimize perturbations from the glass surface. Andor™ iQ 3.0 software were used to monitor and record the motion of microgels at a recording rate of 30 frames/s. To enable quantification of particle motion, the microgel positions in an image time series acquired *via* video microscopy were analyzed using a modified version of the particle tracking code originally developed by Crocker and Grier[3] in the IDL 6.0 (ITT Visual Information Solutions) programming environment.

ζ potential of microgel particles. A Malvern Zetasizer was used to determine the ζ potential of pNIPAm-AAc microgel particles in the very dilute regime (0.0002 wt%) at 20 °C. The ζ potential is shown in Figure S1 as a function of pH.

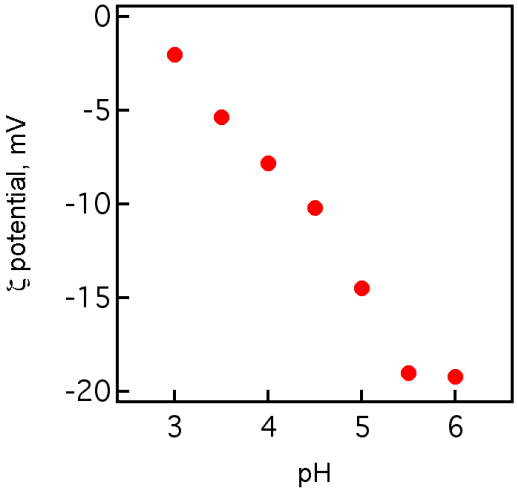

Figure S1. The ζ potential of pNIPAm-AAc microgel particles (0.0002 wt%) from pH 3.0 to 6.0. With increasing pH, the absolute value of the ζ potential increases due to deprotonation of AAc units on the microgels.

References.

1. Meng, Z.; Cho, J. K.; Debord, S.; Breedveld, V.; Lyon, L. A., *J. Phys. Chem. B* **2007,** *111*, 6992-6997.
2. Beynon, R. Buffer Calculator http://www.liv.ac.uk/buffers.
3. Crocker, J. C.; Grier, D. G., *J. Colloid Interface Sci.* **1996,** *179* (1), 298-310.