

Supporting Information

Controlling the Response of Color Tunable Poly (*N*-Isopropylacrylamide) Microgel-Based Etalons with Hysteresis

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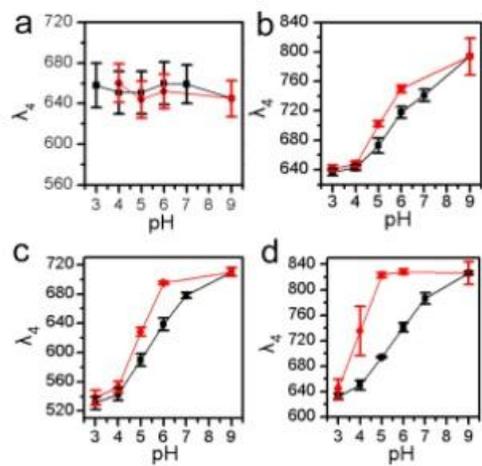
1. Experimental

Materials: *N*-isopropylacrylamide was obtained from TCI (Portland, Oregon) and purified by recrystallization from hexane ($\geq 98.5\%$, Sigma-Aldrich) prior to use. *N*, *N*'-methylenebisacrylamide (BIS) (99%), acrylic acid (AAc) (99%) ammonium persulfate (APS) (98%) and ammonium chloride ($\geq 99.5\%$) were purchased from Sigma-Aldrich (Oakville, Ontario). Ammonium hydroxide was obtained from Anachemia Canada Inc (Mississauga, Ontario), while hydrochloric acid was purchased from Caledon Laboratories Ltd (Georgetown, Ontario). Sodium chloride, sodium hydroxide, potassium chloride, potassium hydroxide were obtained from EMD (Mississauga, Ontario). These chemicals without details were used as received. Glass substrates (25mm \times 25mm) were provided by Fisher (Ottawa, Ontario). Deionized (DI) water was filtered to have a resistivity of 18.2 M Ω and was produced by a Milli-Q Plus system (Millipore Co.). Au (99.99%) and Cr (99.999%) were purchased from ESPI Company and MRCS Canada (Edmonton), respectively.

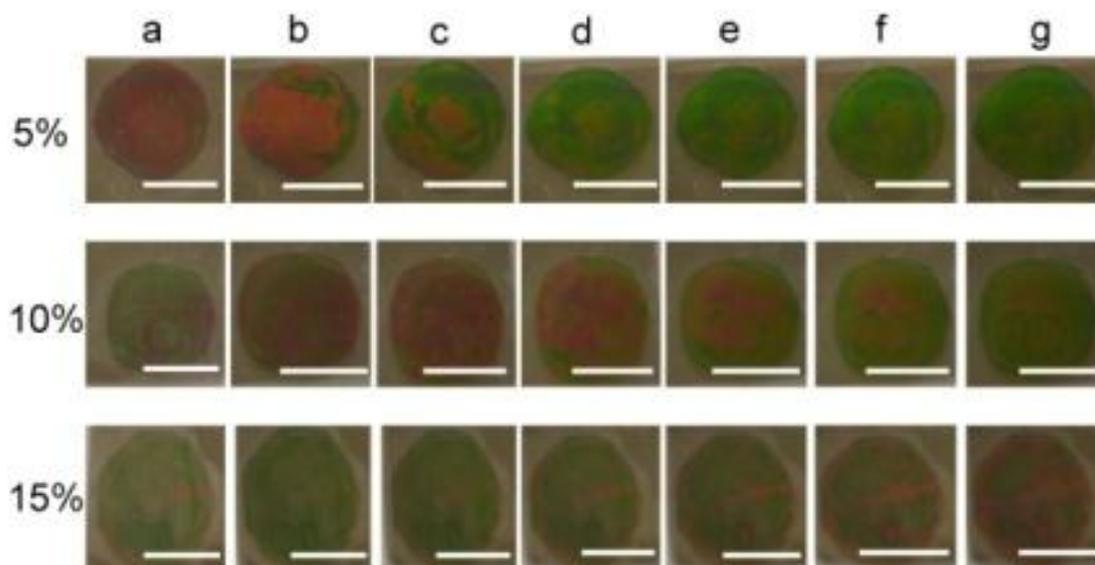
Microgel Synthesis: Microgels were prepared as previously described.¹ A 3-neck flask was fitted with a reflux condenser, nitrogen inlet, and temperature probe (as above), and charged with a solution of NIPAm (11.9 mmol) and BIS (0.703 mmol) in 99 mL DI water, previously filtered through a 0.2 μ m filter. The solution was purged with N₂ gas and allowed to heat to 70 °C for ~1 hour. AAc (1.43 mmol) was added to the heated reaction mixture in one aliquot. The reaction was then initiated with a solution of APS (0.2 mmol) in 1 mL of DI water. The reaction proceeded at 70 °C for 4 hours under N₂ atmosphere. The resulting suspension was allowed to cool overnight, and then it was filtered through a Whatman #1 paper filter to remove any large aggregates. The microgel solution was then distributed into centrifuge tubes and purified via centrifugation at ~8300 rpm to form a pellet, followed by removal of the supernatant and resuspension with DI water, 6x. The resultant microgels had a hydrodynamic diameter (D_H) = 1105 \pm 133 nm in DI water at 25 °C. Microgels with varying AAc concentration were synthesized in the same manner by keeping the total monomer concentration the same and varying the percent NIPAm in the reaction to accommodate the varying AAc amounts.

Etalon Fabrication: Microgel-based etalons were fabricated as previously described.² Briefly, glass coverslip (25 \times 25 mm) was rinsed by ethanol and dried by N₂ gas, followed by deposition of Cr (2 nm) and Au (15 nm), using a Torr International Inc. (New Windsor, NY) thermal evaporation system Model THEUPG. The Cr/Au coated substrates were annealed at 250 °C for 3 h using a Thermolyne muffle furnace (Thermo Fisher Scientific, Ottawa, Ontario). After being subsequently rinsed with ethanol and dried with N₂ gas, the substrate was placed onto a hot plate set to 30 °C along with the tube containing a concentrated microgel pellet (from centrifugation). A homogeneous "monolithic" microgel film was deposited on the Au substrate, using the "paint on" protocol. The microgel layer was allowed to dry for 2 h, followed by copious rinsing with DI water. The microgel-coated substrate was then soaked in DI water overnight at ~30 °C, and then rinsed with DI water again. The microgel-coated surface was then dried with N₂ gas and another Cr/Au layer (2 nm Cr, 15 nm Au) was added to the microgel layer. The etalons were then soaked in DI water overnight at 30 °C prior to use.

Characterization: Reflectance spectra were collected by a Red Tide USB650 spectrometer, using a reflectance probe connected to a LS-1 tungsten light source (Ocean Optics, Dunedin). The spectra were collected over a wavelength range of 400–1000 nm and analyzed by Ocean Optics Spectra Suite Spectroscopy software. Photographs were taken using a Nikon camera equipped with a 40 mm Nikon macrolens. Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano S series dynamic light scattering instrument (United Kingdom). Microgel solutions were diluted in DI water and equilibrated at 25 °C.



SI Figure 1. λ_4 as a function of pH increasing (black curve) and decreasing (red curve) for the etalon made by pNIPAm-co-XAAc, X= (a) 0% (b) 5%, (c) 10%, and (d) 15% mol. The pH solutions were made with HCl/KOH/KCl (I.S. 2 mM). The average λ_4 from three spectra obtained from different regions of the same etalon is shown with the error bars indicating \pm one standard deviation.



SI Figure 2. Photographs of pNIPAm-*co*-AAc microgel-based etalons (fabricated as circles) with 5%, 10% and 15% AAC in (a) pH 9.0 initially, and (b) 0, (c) 5, (d) 10, (e) 15, (f) 20, and (g) 30 min after being immersed in pH 6.0 I.S. 2 mM adjusted with KCl. The scale bars in the photographs are 0.5 cm.

SI Figure 2 shows the pNIPAm-*co*-5%AAc microgel-based etalon changes color from red to green upon switching the pH of the solution from 9.0 to 6.0. Then, the color is stable visually, after ~10 min. However, the pNIPAm-*co*-10%AAc microgel-based etalon took 20 min to reach a stable color, while the pNIPAm-*co*-15%AAc microgel-based etalon took significantly longer, e.g., compare the photograph for pNIPAm-*co*-15%AAc microgel-based etalon after 30 min with pNIPAm-*co*-10%AAc microgel-based etalon after 5 min. We acknowledge here that while the visual color appears to be stable, we still do observe spectral peak shifts. Therefore, SI Figure 2 proves that pNIPAm-*co*-15%AAc microgel-based etalon exhibits the strongest hysteresis in response to pH.

References

1. C. D. Sorrell and M. J. Serpe, *Anal. Bioanal. Chem.*, 2012, **402**, 2385.
2. C. D. Sorrell, M. C. D. Carter and M. J. Serpe, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1140.