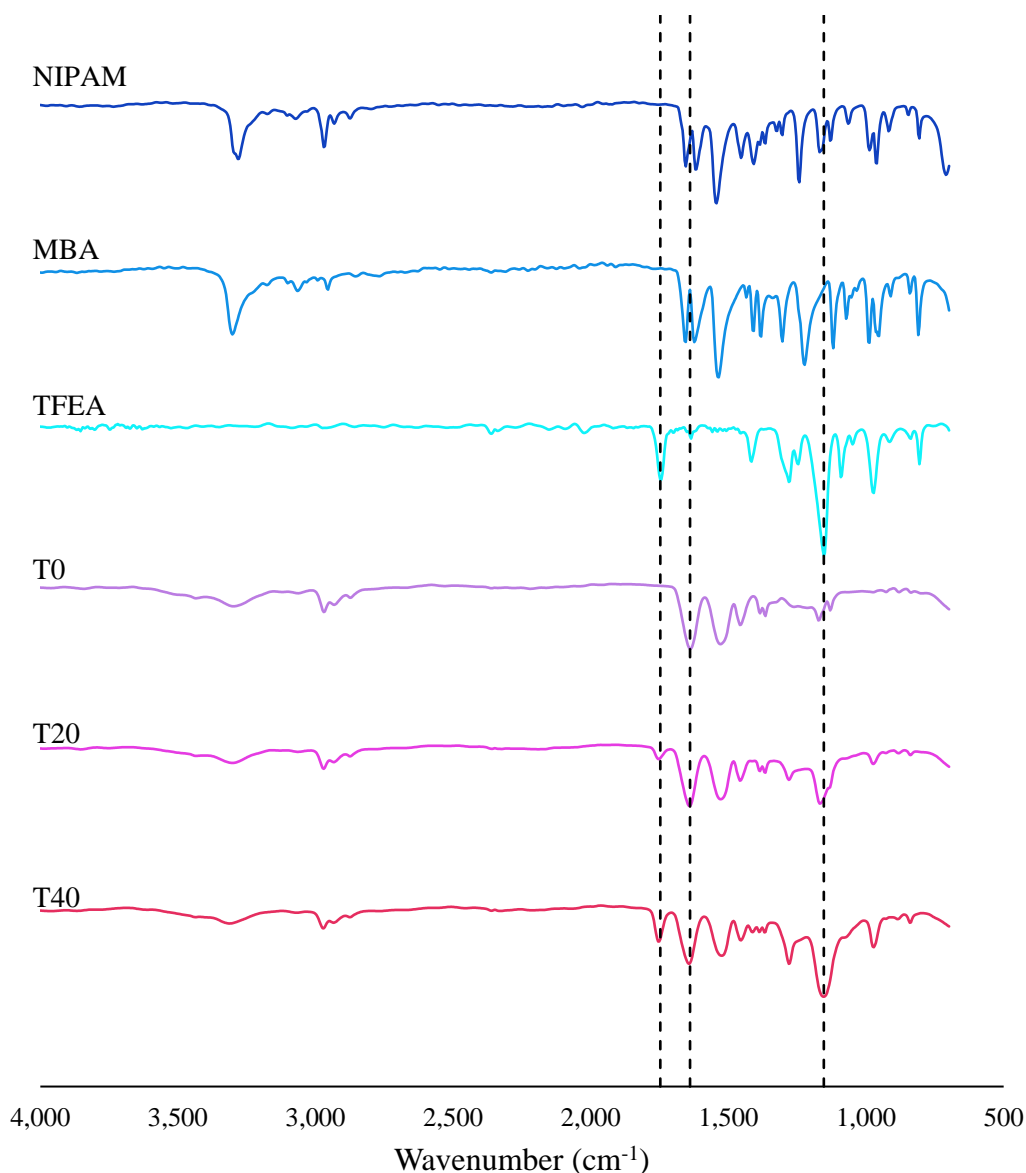


Assessing the Perfluoroalkyl Acid-Induced Swelling of Förster Resonance Energy Transfer-Capable Poly(*N*-Isopropylacrylamide) Microgels

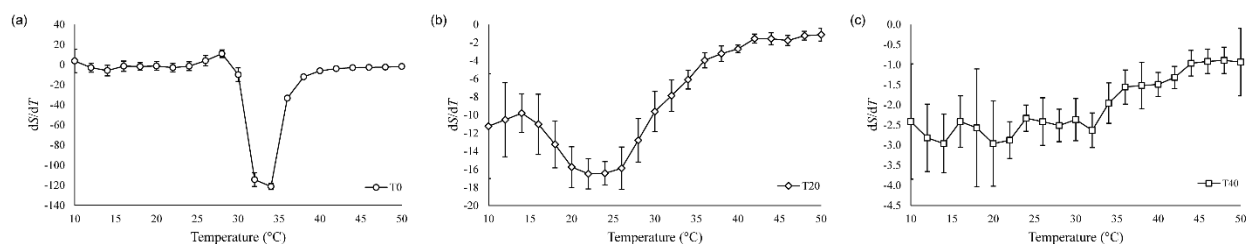
Dustin T. Savage,¹ J. Zach Hilt¹ and Thomas D. Dziubla¹

¹ University of Kentucky, College of Engineering, 512 Administration Drive, 177 F. Paul Anderson Tower, Lexington, KY 40506

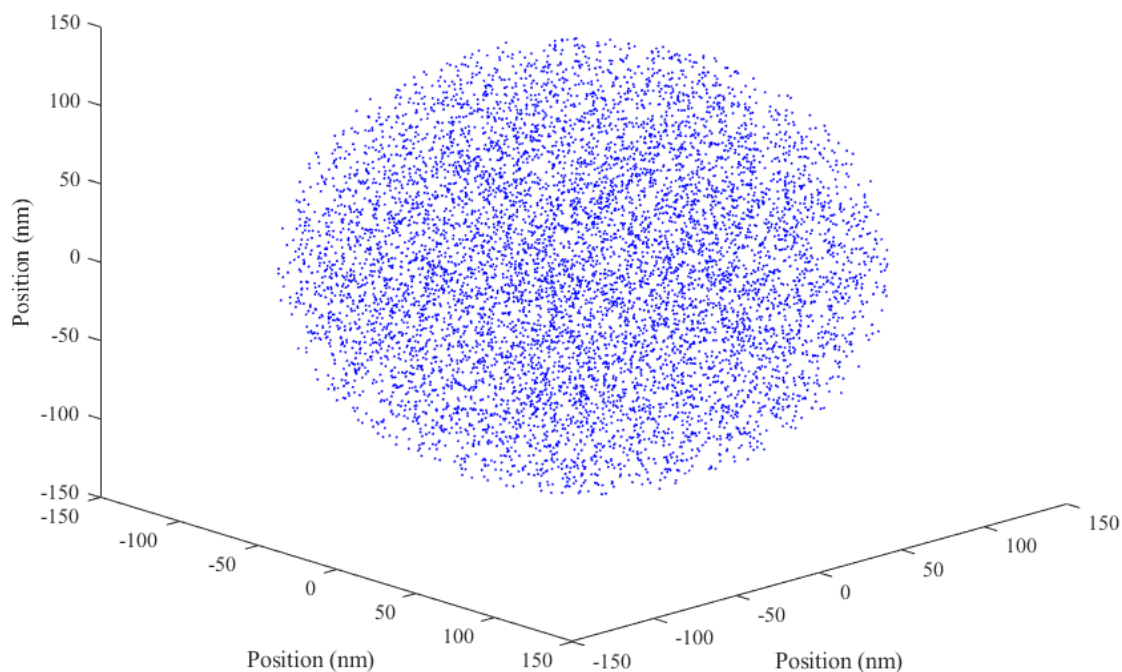
Correspondence to: Thomas D. Dziubla (E-mail: thomas.dziubla@uky.edu)



Supplementary Figure 1: Fourier-transform infrared spectra for the monomers and resulting microgels synthesized. Dashed lines are guides representing 1,748 cm^{-1} (carbonyl), 1,639 cm^{-1} (amide I), and 1,153 cm^{-1} (CF_x) from left to right.



Supplementary Figure 2: Derivative of the z-average diameter with respect to temperature for (a) T0, (b) T20, and (c) T40 microgels. Minima roughly indicate the position of the respective lower critical solution temperature for each microgel. Values were calculate using finite difference.



Supplementary Figure 3: An example model of dye locations within a collapsed microgel holding a z-average diameter of 270.9 nm. The sphere shown contains a simulated 0.01 mol% theoretical load of AEMA. Each dye is randomly drawn; successive iterations of the same simulation will result in slightly different dye locations relative to this image.

Dye positions were simulated with:

$$r_n = \frac{r_1 U^{1/3}}{\sqrt{x_n^2 + y_n^2 + z_n^2}}$$

$$x = x_n r_n$$

$$y = y_n r_n$$

$$z = z_n r_n$$

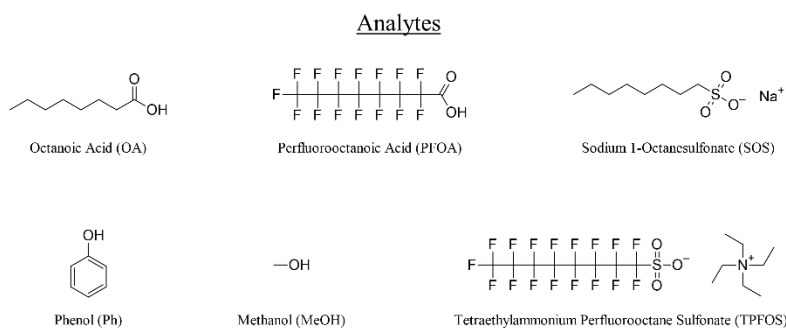
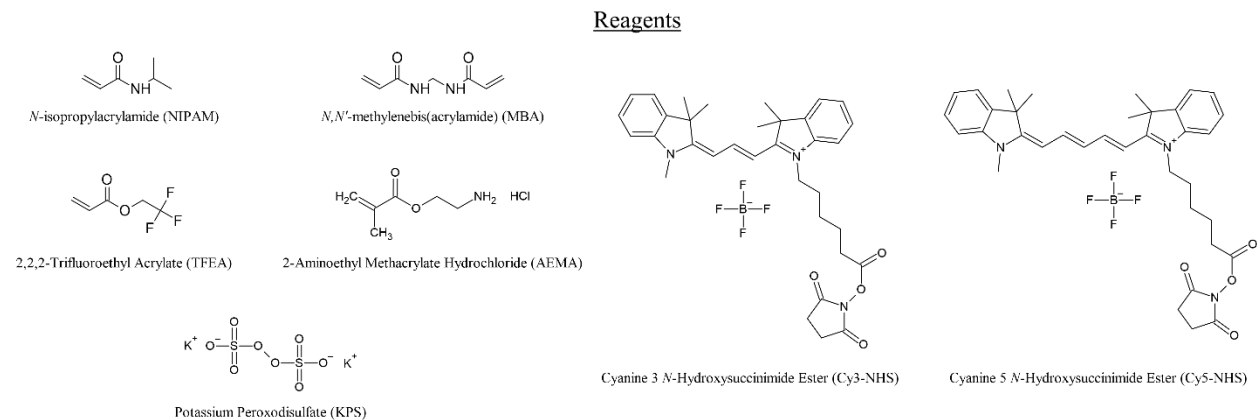
Where x_n , y_n , and z_n are normally distributed random variables, U is a uniformly distributed random variable, r_1 is the collapsed nanoparticle radius, and x , y , and z are the cartesian coordinates for the n th dye. The number of dyes for a given microgel collapsed volume (p) was estimated via:

$$p = \frac{fV_1}{V_m}$$

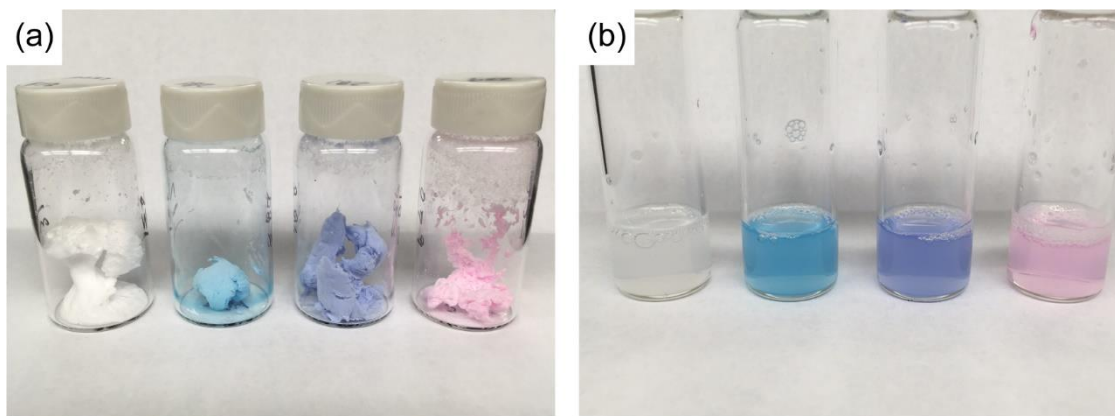
Using f as the anchor loading fraction, V_1 as the collapsed microgel volume, and V_m as the average monomer volume (126.9 \AA^3). When simulating the swollen state, a sham dye population was inserted with:

$$f_{sham} = \frac{pV_m}{V_2}$$

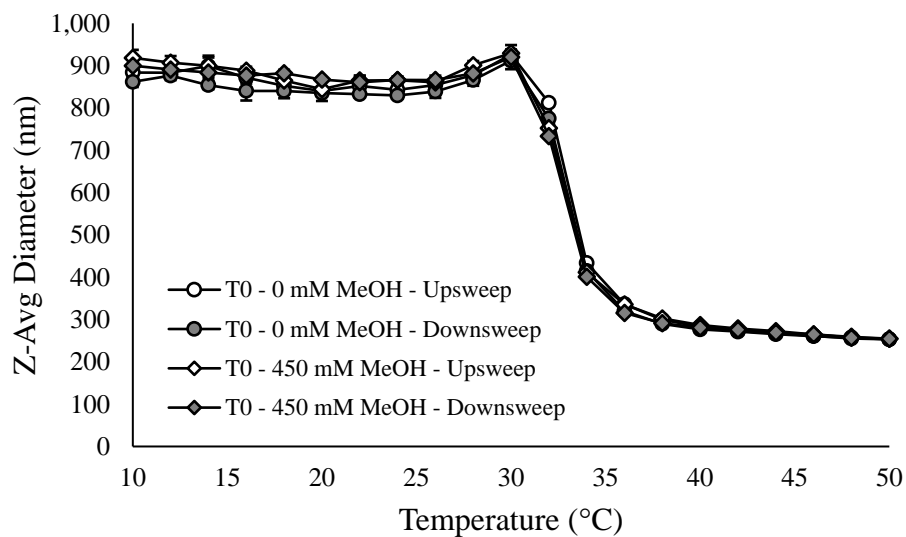
Where V_2 is the volume of the swollen microgel.



Supplementary Figure 4: Chemical structures of synthesis reagents and analytes tested throughout the study.



Supplementary Figure 5: Pictures of microgels that are (a) dry and (b) dispersed in water at 2 mg mL⁻¹. From left to right: T0 microgels, microgels dyed with Cy5, Cy3 and Cy5, and Cy3.



Supplementary Figure 6: Temperature response of T0 microgels in water alone (circles) and exposed to 450 mM methanol (diamonds). Upsweeps progressing from 10 °C to 50 °C are colored white, and downsweeps from 50 °C to 10 °C are gray.