Supporting information

Unconventional transitions of poly(N-isopropylacrylamide) upon heating in the presence of multiple non-covalent interactions

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1. **Synthesis of PNIPAM via AIBN initiated free radical polymerization.** NIPAM monomer (1.0 g) and AIBN (4.4 mg) were dissolved with THF (3.0 mL), and the mixture was placed in a preheated oil bath at 60 ℃ for 20 h. The resulting polymer was isolated and purified by repeated precipitation in hexane and dried under vacuum, M_n = 67,000 g/mol, PDI = 1.8

2. **^{1}H-NMR Measurements.**

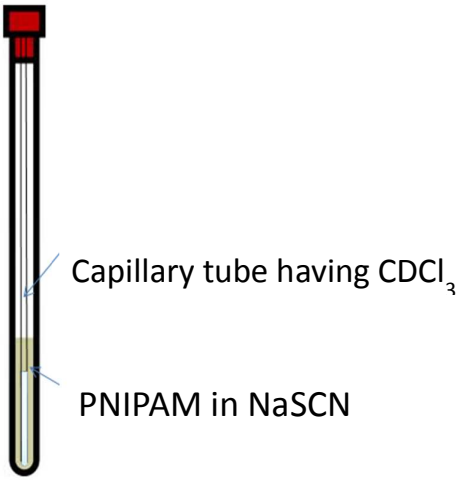

Figure S1. The illustration depicting ^{1}H-NMR measurement: the mixed solution of PNIPAM and sodium salt was in the NMR tube, and $CDCl_3$ containing 0.03% TMS was in the inner of the concentric capillary tube.

Stock solutions of PNIPAM (10.0 mg/mL) and sodium salts aqueous (2.0 M) were prepared using D_2O as solvent, respectively. All the testing samples have PNIPAM of 3.0 mg/mL, and the range of sodium salt concentrations is from 0.01 M to 1.0 M. ^{1}H-NMR spectra for PNIPAM under different sodium salts concentration were obtained on a 300 MHz NMR spectrometer. ^{1}H-NMR spectra were recorded with NMR tubes adapted with coaxial inserts (as shown in Figure S1). $CDCl_3$ containing 0.03% TMS was in the inner of the concentric capillary tube, while the mixed solution of PNIPAM and sodium salt was in the outer capillary tube. As such, the TMS control was never exposed to PNIPAM or varying salt concentrations.

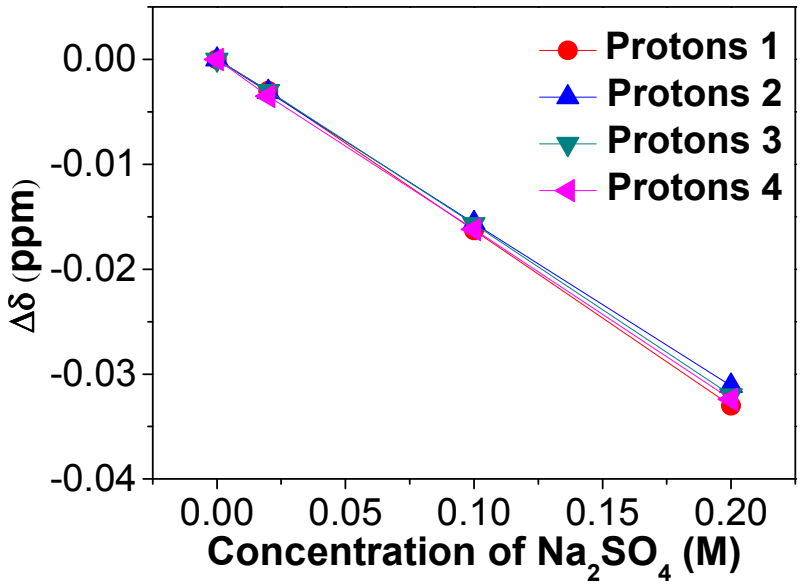

Figure S2. Chemical shift changes for the protons of **1-4** in PNIPAM with the concentration of Na_2SO_4 at 27 °C.

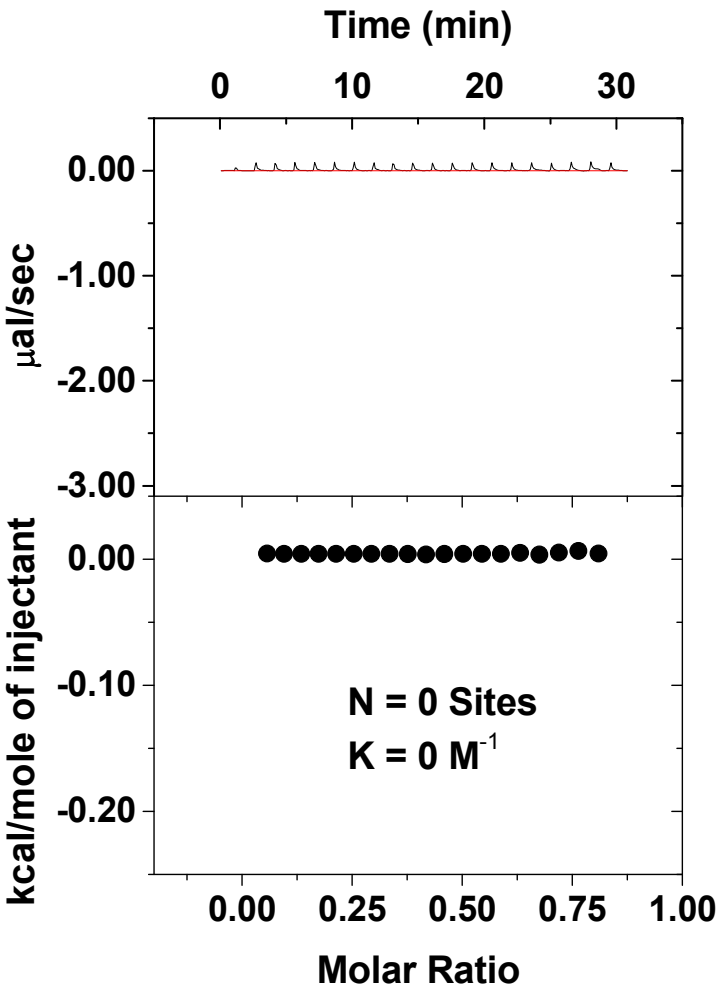

Figure S3. ITC titration curve for Na_2SO_4 solution to PNIPAM at 27 °C.

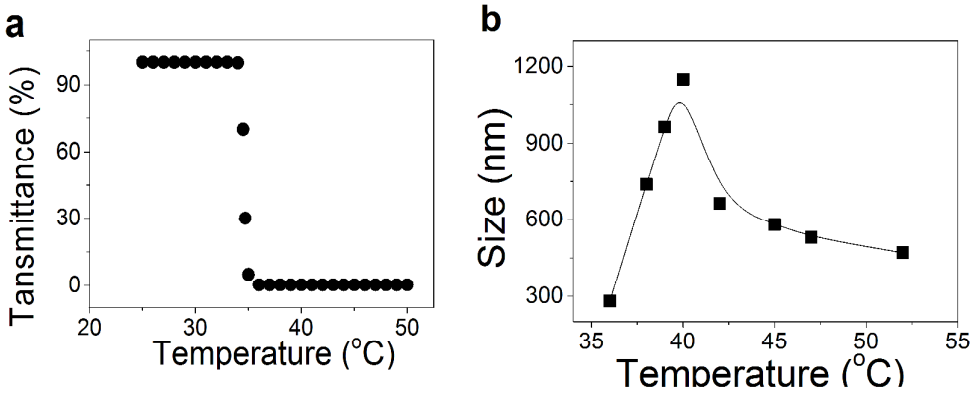

Figure S4. (**a**) The variation of transmittance of PNIPAM aqueous solution in the presence of NaSCN with temperature. (**b**) The variation of the size for the formed PNIPAM nanoparticles in the presence of NaSCN with temperature.

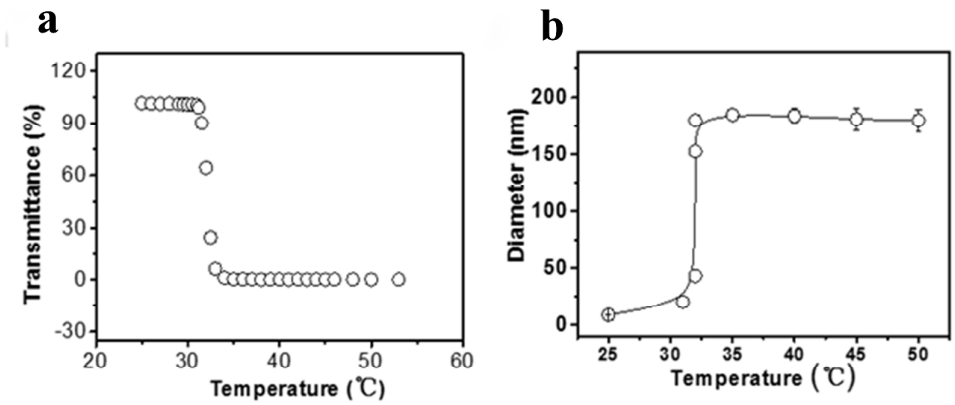

Figure S5. (**a**) The variation of transmittance of PNIPAM aqueous solution with temperature. (**b**) The variation of the size for the formed PNIPAM nanoparticles in water with temperature.

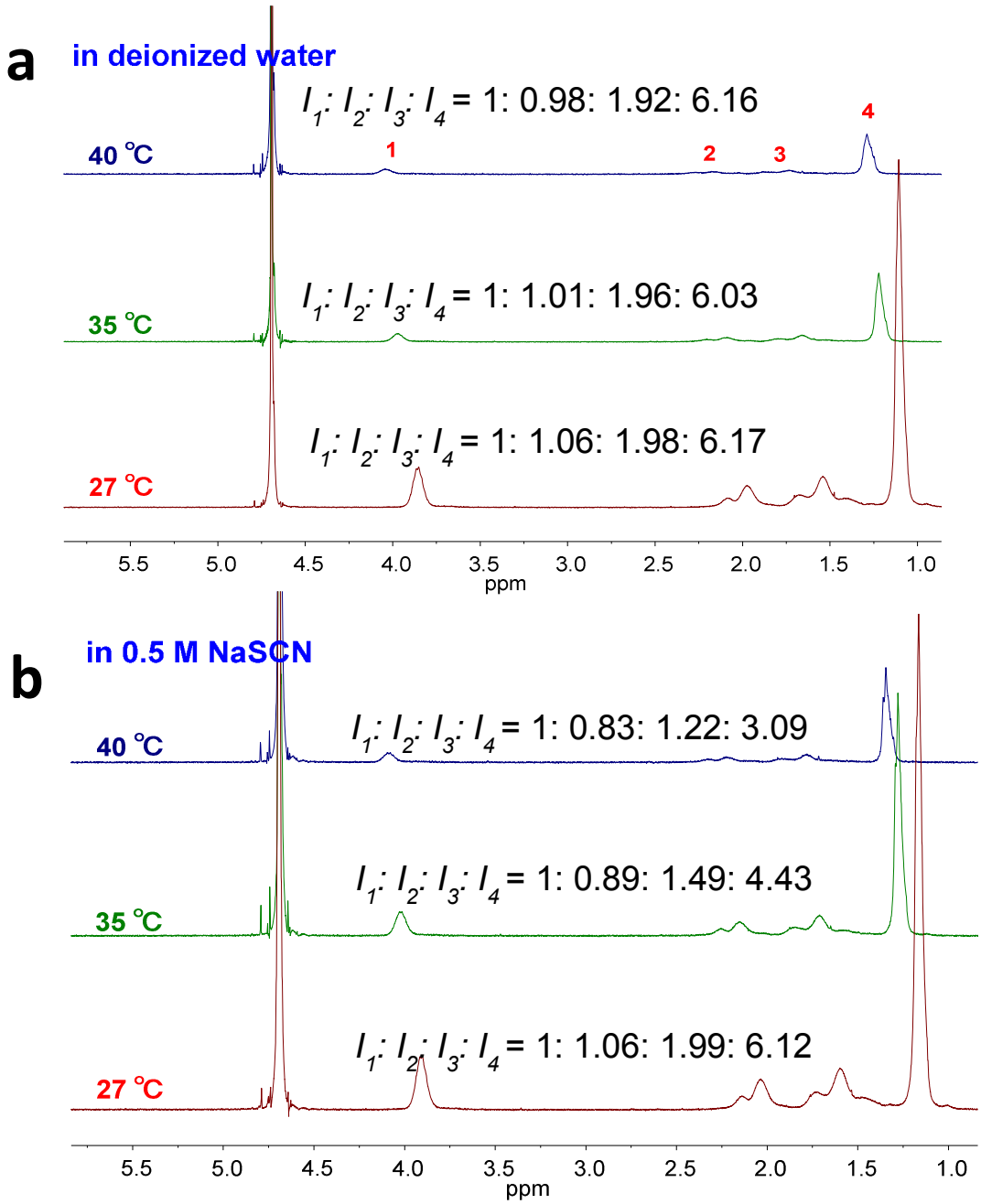

Figure S6. ^{1}H NMR spectra of PNIPAM (3.0 mg/mL) in DI water and NaSCN solution (0.5 M) at 27, 35, and 40 ºC.

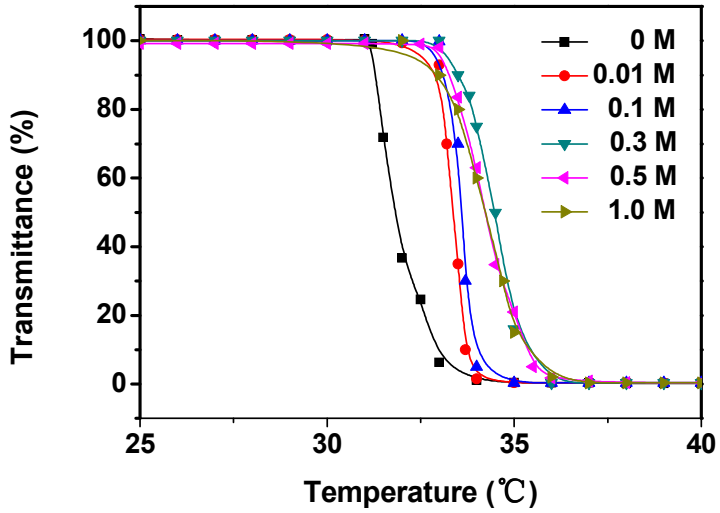

Figure S7. The transmittance changes of PNIPAM aqueous solution (3.0 mg/mL) with temperature at different concentrations of NaSCN.