Supplementary Information for

Colloidal Probes of PNIPAM Grafted SiO_2 in Studying the Microrheology of Thermally Sensitive Microgel Suspensions

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In the supplementary, the synthesis of the thermally sensitive PNIPAM microgels used in the microrheology studies has been described. The characterizations of the microgels' structure, size, and their thermally responsive behaviors have been shown.

The relatively homogeneously crosslinked microgel of PNIPAM are prepared according to our former work (Macromolecules 2012, 45, 15, 6158-6167), and fully dialyzed in deionized water for three weeks before characterizations. The details are as follows. The relatively homogeneously crosslinked microgel of PNIPAM are prepared by precipitation polymerization at 70 °C in water. The purified monomer of NIPAM (1.613 g), the cross-linker of BIS (0.07g), and surfactant of SDS (0.034g) are dissolved in 140 mL of deionized water in a 250 ml three-necked flask with a reflux condenser, put in an oil bath of 40 ºC and, stirred with a magnetic stirring. After nitrogen gas is purged for 1.5 hrs, KPS (0.09 g) is dissolved in 10 ml deionized water and is fed with

an injector. The temperature is gradually raised to 70 °C, another BIS (0.02g) is dissolved in 5 mL deionized water and is fed by a syringe pump at the rate of 20 ml/h. The reaction is continued at the temperature of 70 °C for 4 hrs.

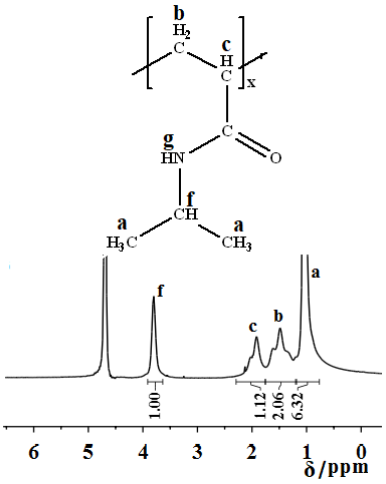

Figure S1. The ^{1}H-NMR (D_2O, 400 MHz) spectrum of the PNIPAM synthesized.

Figure S1 shows the ^{1}H-NMR spectrum of the PNIPAM synthesized. PNIPAM microgels are firstly dried and dissolved in D_2O. The ^{1}H-NMR spectrum is recorded by using Bruker Avance 400, Germany. We have used ChemDraw to simulate the chemical shifts of the constitutional repeating unit of PNIPAM, which has been drawn above the spectrum. From the experimental data, a singlet at 1.0 ppm is attributed from the methyl groups(a), that of the protons of -CH_2 (b) and -CH(c) on the backbone are located at 1.5 and 2.0 ppm, respectively. The -CH in the amide(d) contributes at 3.8 ppm, whose integral area, the proton number, has been normalized to 1. It is observed from the spectrum that proton number ratio among a, b, c, and d is approximately 6:2:1:1, which is in consistent with the chemical structure of the constitutional repeating unit of PNIPAM.

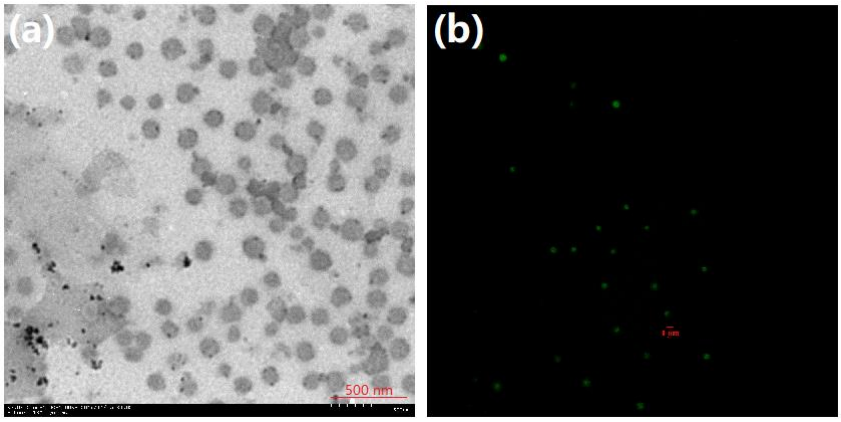

Figure S2. The (a) TEM and (b) confocal images taken for the PNIPAM microgels.

The size and morphology of the PNIPAM microgels are observed by using Transmission Electron Microscope (TEM) and laser confocal scanning microscopy (LCSM). TEM(H-7650) is from HITACHI, Japan, and the results has been shown in Figure S2. The specimen is ultrasonically dispersed in ethanol, dropped onto a copper mesh and the observation is performed after the solvent is evaporated. LCSM (MRC-1024) is from Bio-Rad, USA. The excitation wavelength is 488 nm, and the microgel are labeled with fluorescein sodium salt (FSS) at pH of 3. From both TEM and confocal images in Figure S2, we could observe the PNIPAM microgels synthesized and then used in microrheology studies are of spherical shape, and most of them are sized at 100-200 nm in diameter.

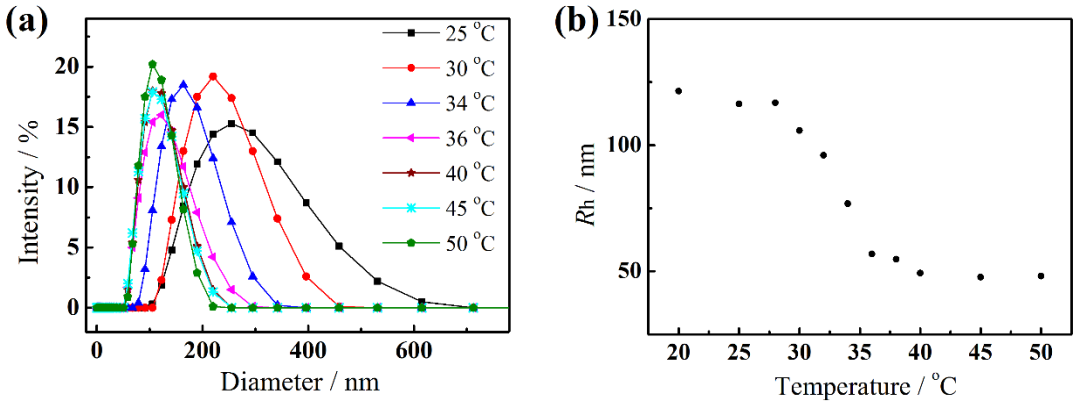

Figure S3. The temperature dependent (a) diameter distribution and (b) average hydrodynamic radius of the PNIPAM microgels in the dispersion.

Zetasizer Nano ZS90 from Malvern, UK, with a 10 mW and 635 nm laser, the scattering angle of 90 º is used to estimate the hydrodynamic size distribution of the synthesized PNIPAM microgels. The temperature is controlled in the range of 20-50 ºC by a precise thermostat, so that the temperature dependence of the size of the microgels can be evaluated. The sample concentration used in light scattering measurement is as dilute as less than 1 wt.%. The temperature dependent of the diameter distribution and the average hydrodynamic radius (Rh) of the PNIPAM microgels are shown in Figure S3. From both graphs we could observe that with the increasing temperature, the microgels shrink to small sizes, an abrupt drop in size is observed around 32 ºC, which is the LCST of PNIPAM.