Supporting Information

Waterborne polymer nanogels non-covalently crosslinked by multiple hydrogen bond arrays

Yunhua Chen, Nicholas Ballard, and Stefan A. F. Bon*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

E-mail: <u>S.Bon@warwick.ac.uk</u>. Web: www.bonlab.info.

EXPERIMENTAL SECTION

Materials. All chemicals were purchased from Aldrich unless noted otherwise. Ureido-pyrimidinone (UPy) functionalized poly(ethylene glycol) methacrylate (PEGMA) macromonomer was synthesized by the method as described in our previous study.¹ Laurylpolyethoxy (23) methacrylate (LEM-23) was purchased from Bimax and used as received. Deionized water was used in all experiments. Hydrophilic filter (0.2 μ m, Sartorius Minisart) was used to remove the particulate matter.

Preparation of quadruple hydrogen bonding cross-linked nanogel particles. NIPAm (0.2 g), water (30 ml) and SDS (0.0086 g) were placed into a 50 ml roundbottom flask. This mixture was purged with N₂ for 15 min, and then heated to 70 °C. After stabilizing the system for another 15 min, the desired amount of UPy functionalized PEGMA macromonomer (dissolved in chloroform, concentration: 0.1 g/ml) was injected, and then KPS (0.01 g) dissolved in 1 ml of pure water was immediately added to initiate the reaction. The polymerization was allowed to proceed under N₂ atmosphere for 10 h. The resulting nanogel dispersion was filtered through the filter paper above the LCST to remove the small amount of coagulum, and then purified by dialysis for one week against deionized water (twice daily changes of water) to remove surfactant and unreacted monomer. Thermo-responsive P(MEO₂MA-*co*-OEGMA)-UPy nanogel particles were perpared through the same method except using MEO₂MA (0.2 g), OEGMA (0.025 g) as monomers. For comparison, PNIPAm-co-PLEM copolymer system and covalently crosslinked PNIPAm nanogels were also prepared by following the same route above using laurylpolyethoxy (23) methacrylate (LEM-23) macromonomer (0.09 g), and methylenebisacrylamide instead of PEGMA-UPy, respectively.

Synthesis of polystyrene (PS) nanoparticle seeds. PS nanoparticles were prepared through typical emulsion polymerization. St (2 g), NIPAm (0.1 g) and SDS (0.1 g) were dissolved in water (100 ml), and KPS (0.11 g) as initiator. The reaction was allowed to proceed under N_2 atmosphere at 70 °C for 8 h. The latex was purified by dialysis against deionized water.

Preparation of PS-PNIPAm-UPy nanogel particles with non-covalently crosslinked shell. Core-shell nanogel particles were synthesized through seed emulsion polymerization. The purified PS core latex (20 ml, solid content: 1.5 wt%) was diluted with 10 ml of water, and then NIPAm (0.4 g), PEGMA-UPy macromonomer (0.2 g in 2 ml chloroform) were added. KPS (0.01 g) was injected to initiate the polymerization at 70 °C. The reaction was then kept under N₂ atmosphere for 4 h. The obtained core-shell nanogel particles were purified through dialysis against deionized water.

Characterization.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 700 MHz spectrometer using CDCl₃ as solvent. Average particle sizes of the nanogels were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano instrument. All samples are allowed to equilibrate at the desired temperature for 5 min. For the measurement of PNIPAm-*co*-PLEM system, the sample was kept hot after the reaction and then measured at 40 °C, followed by the measurement at 25 °C and back to 40 °C for the next measurement cycle. The UV-Vis spectra were performed on a Perkin Elmer Lamda-45 UV-Vis spectrophotometer. The measurements were conducted at 20 °C. Transmission electron microscope (TEM) observations were conducted on a JEOL 2011 electron microscope with a Cryo attachment.

Table S1. Monomer composition and average hydrodynamic diameter of nanogel

 particles from NGP1 to NGP4.

Sample	UPy macromonomer fraction		$D_{\rm H}$ by DLS		Monomer	Particle
	(mol%)		(nm)		Conversion ^a	Number ^b
	Theoretical	NMR	25 °C	40 °C		
NGP 1	3.3	2.7	240	90	80.4%	3.4×10^{15}
NGP 2	6.4	4.0	201	76	71.5%	6.8×10^{15}
NGP 3	9.4	6.7	161	66	71.4%	1.19×10^{16}
NGP 4	12.1	10.2	136	62	69.4%	1.64×10^{16}

^a Total monomer conversion was determined by gravimetry.

 $^{\rm b}$ We assume that the polymer volume fraction is about 0.7 in the collapsed state of pNIPAm chains at 40 °C.



Fig. S1 (a) Chemical structure of PNIPAm-*co*-PLEM copolymer, (b) Size distribution of the PNIPAm-*co*-PLEM copolymer particles at 40 $^{\circ}$ C. (c) Size distribution of the same sample at 40 $^{\circ}$ C after the cooling cycle to 25 $^{\circ}$ C.



Fig. S2 Volume variation of the NGP1 nanogel particles as a function of heating and cooling measurement number n at 40 °C and 20 °C, respectively.



Fig. S3 TEM image of (a) PS core nanoparticles, (b) PS-PNIPAm-UPy nanogel particles at room temperature.



Fig. S4 Temperature dependent deswelling ratio of PS core and PS-PNIPAm-UPy nanogel particles.

Calculation of the PNIPAm-UPy shell thinckness in PS-PNIPAm-UPy nanoparticles

PS core particle number Ncp in the seed dispersion:

$$N_{cp} = m_o/m_{cp}$$
$$m_{cp} = \frac{3}{4}\pi\rho(\frac{d_{cp}}{2})^3$$
$$N_{cp} = m_o/[\frac{3}{4}\pi\rho(\frac{d_{cp}}{2})^3]$$

Where, ρ and d_{cp} are the density and diameter (90.1 nm as measured by DLS) of the core particles, respectively, m_{cp} is the mass of an individual core particle, m_o is the total mass of the core particles in the seed dispersion. There is no secondary nucleation in the seed precipitation polymerization, so the number of core-shell nanogel particles is the same as Ncp,

$$\frac{3}{4}\pi\rho[(\frac{d_{csp}}{2})^3 - (\frac{d_{cp}}{2})^3]N_{cp} = m_1 - m_o$$

 m_1 is the total mass of the core-shell nanogel particles after the reaction. The solid content and volume of the core-shell nanogel particle dispersion are 1.8 wt% and 30 ml, respectively. We assume that the densities of core and shell part of the nanogel particles are equal (1.1 g/cm⁻³). Hence, in theory the final diameter of the nanogel particles can be obtained, $d_{csp} = 109.6$ nm. The diameter of the core particles and core-shell nanogel particles measured by DLS is 90.1 nm and 115.8 nm at 39 °C, respectively. If we assume that the PNIPAm-UPy shell polymer volume fraction is about 0.7 in the collapsed state,^{2, 3} the diameter of the PS-PNIPAm-UPy nanoparticles should be 108.1 nm with a shell thickness of 18.0 nm, which is greatly consistent to the theoretical value of 109.6 nm.

References

- 1. Y. Chen, N. Ballard, F. Gayet and S. A. F. Bon, *Chem. Commun.*, 2012, 48, 1117-1119.
- 2. J. J. Crassous, M. Siebenburger, M. Ballauff, M. Drechsler, O. Henrich and M. Fuchs, *J. Chem. Phys.*, 2006, **125**, 11.
- 3. J. Crassous, A. Wittemann, M. Siebenbürger, M. Schrinner, M. Drechsler and M. Ballauff, *Colloid & Polymer Science*, 2008, **286**, 805-812.