

Supporting Information for Reversible Gold “Locked” Synthetic Vesicles Derived from Stimuli-Responsive Diblock Copolymers

*Adam E. Smith, Xuewei Xu, Daniel A. Savin, and Charles L. McCormick**

Department of Polymer Science and Department of Chemistry and Biochemistry, The
University of Southern Mississippi, Hattiesburg, MS 39406

Experimental Section

Materials. The synthesis of P(DMAEMA₁₆₅-*b*-NIPAM₄₃₅) follows a procedure previously reported by our group.¹ O-[2-(3-Mercaptopropionylamino)ethyl]-O'-methylpolyethylene glycol (PEG-SH, 5,000 g/mol) and cysteamine were purchased from Aldrich and used as received.

Preparation and AuNP-“locking” of Vesicles. P(DMAEMA₁₆₅-*b*-NIPAM₄₃₅) was dissolved directly in HPLC grade water at a concentration of 0.01 wt% (0.1 mg/mL). The pH was subsequently adjusted to 7 using 0.1 N HCl or NaOH. Self-assembly of the block copolymers was then induced by increasing the temperature to 50 °C (1.0 °C/min). After 30 min, 2 µL of a preheated solution of sodium tetrachloroaurate (III) dihydrate solution (NaAuCl₄) at pH 6.5 was added to the copolymer solution at 50 °C to give a DMAEMA to Au ratio of 10 to 1 as discussed in previous work.² The mixed solution was allowed to stir at 50 °C for 48 h prior to being cooled to room temperature for analysis.

Ligand Exchange Reaction to Reverse Cross-linking. In order to reverse AuNP-“locking”, 1 mL of AuNP cross-linked vesicle solution was reacted with an appropriate volume of 1 mM cysteamine or 1 mM PEG-SH to yield a thiol to DMAEMA ratio of 10. The mixture was allowed to stir for 48 h prior to centrifugation at 13,000 rpm for 1 hr to remove liberated P(DMAEMA₁₆₅-*b*-NIPAM₄₃₅) from the thiol-stabilized AuNPs. After removal of the supernatant, the AuNPs were redispersed in 1.0 mL of HPLC grade water for analysis.

Characterization. DLS studies were conducted using a Malvern Instruments Zetasizer Nano series instrument equipped with a 4 mW He-Ne laser operating at $\lambda = 632.8$ nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system. Dispersion Technology Software 5.03 (Malvern Instruments) was used to record and analyze the data.

DLS was performed using incident light at 633 nm from a Spectra Physics HeNe operating at 40 mW. The angular dependence of the autocorrelation functions were measured using a Brookhaven Instruments BI-200SM goniometer with an avalanche photodiode detector and TurboCorr correlator. Correlation functions were analyzed according to the method of cumulants using the companion software. All data reported correspond to the diffusion coefficient corresponding to the average decay rate obtained from the second cumulant fit.

The hydrodynamic radius (R_H) was calculated from the diffusion coefficient using the Stokes-Einstein relation. Static light scattering (SLS) experiments in this study were performed on aqueous polymer solutions with the same concentration and light scattering instrument as described above to determine the radius of gyration (R_g). The scattered intensity was analyzed using a Brookhaven TurboCorr correlator and the companion software. Solutions were prepared by dissolving the polymer into purified water to a concentration of 0.01 wt%. Samples were agitated to ensure complete dissolution and then filtered through a 0.45 μ m PVDF syringe-driven filter (Millipore) directly into the scattering cell. Samples were then sonicated and allowed to reach thermal equilibrium prior to measurements.

Transmission electron microscopy measurements were conducted using a JEOL JEM-2100 electron microscope at an accelerating voltage of 200 kV. The specimens were prepared by placing a 5 μ L drop of solution on a carbon-coated copper grid followed by water evaporation at 25 °C overnight.

- 1 A. E. Smith, X. Xu, T. U. Abell, S. E. Kirkland, R. M. Hensarling and C. L. McCormick, *Macromolecules*, 2009, **42**, 2958-2964.
- 2 Y. Li, A. E. Smith, B. S. Lokitz and C. L. McCormick, *Macromolecules*, 2007, **40**, 8524-8526.