Supplementary Information

Reversibly Interchangeable, Chain-Wrapped Micelles and Vesicles of an Amphiphilic Rod–Coil Block Copolymer**

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Experimental Section

Micelles and vesicles A $PHIC_{189}$-*b*-$P2VP_{228}$ rod–coil block copolymer was dissolved in toluene by stirring for 12 h.

Polymer solutions were drop-coated on carbon-coated copper grids for energy-filtering TEM (EF–TEM, EM 912 OMEGA [ZEISS, S-4700]) and Si wafers for AFM analysis. The TEM specimens were exposed to I_2 vapor for 3h in a closed container. The DLS was performed at 25 °C using DLS/Malvern Instrument, PCS. The absorption spectra was recorded on a UV spectrophotometer (CARY 1E).

Synthesis of Au NPs. $HAuCl_4$ (0.3 equiv. per P2VP pyridine unit of a block copolymer) was dispersed in the solutions of micelles and vesicles, respectively, followed by stirring for 24 h to complete complexation. Into the solution was added 5 equiv. of $H_2O{\cdot}N_2H_4$. As the

solutions turned deep purple, they were stirred further for 5 h and then centrifuged for 10 min at 3000 rpm to remove the salts and the precipitates.

DLS results

Aggregation behaviors of the $PHIC_{189}$-*b*-$P2VP_{228}$ block copolymer was studied by dynamic light scattering (DLS) from a solution of the copolymer in toluene, a selective solvent for the rod-like PHIC block. Figure S1 shows the hydrodynamic diameter (D_h) estimated from the DLS data of the copolymer solutions (0.5-6.0 mg/mL).

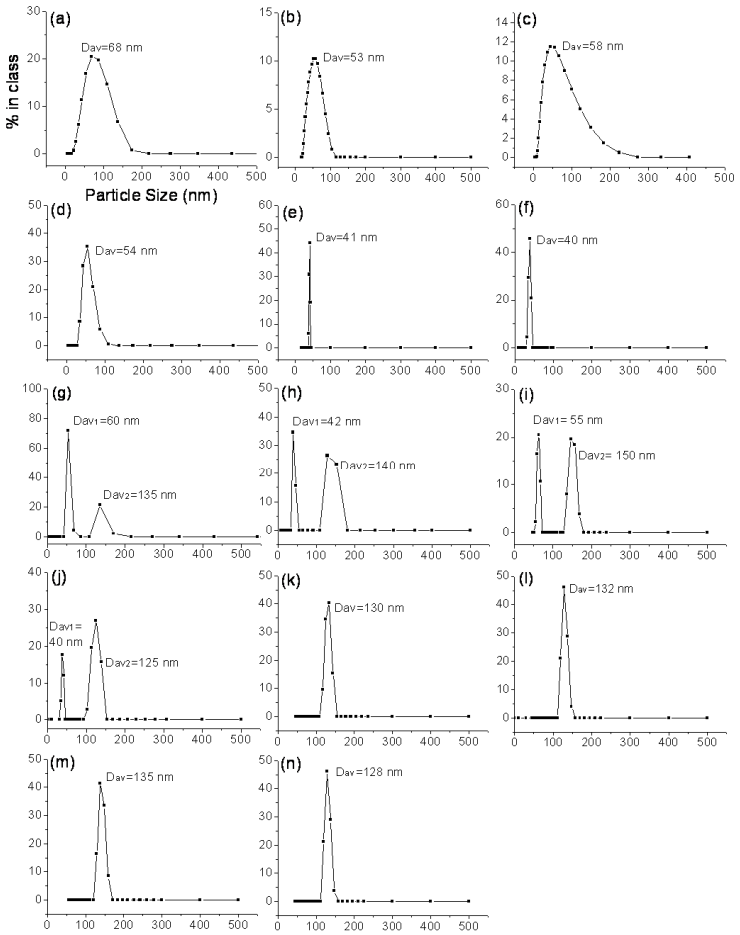

Figure S1. Dynamic light scattering (DLS)-measured particle size distributions of PHIC-*b*-P2VP rod-coil block copolymer at different concentrations in toluene. (a) 0.5 mg/mL, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0, (g) 3.4, (h) 3.6, (i) 3.8, (j) 4.0, (k) 4.5, (l) 5.0, (m) 5.5, (n) 6.0.

The reversibility indicates that each aggregate structure is thermodynamically favored over the other structure in each concentration range. Figure S2 shows the representative diagram showing the reversibility in size change and their corresponding DLS particle size distributions.

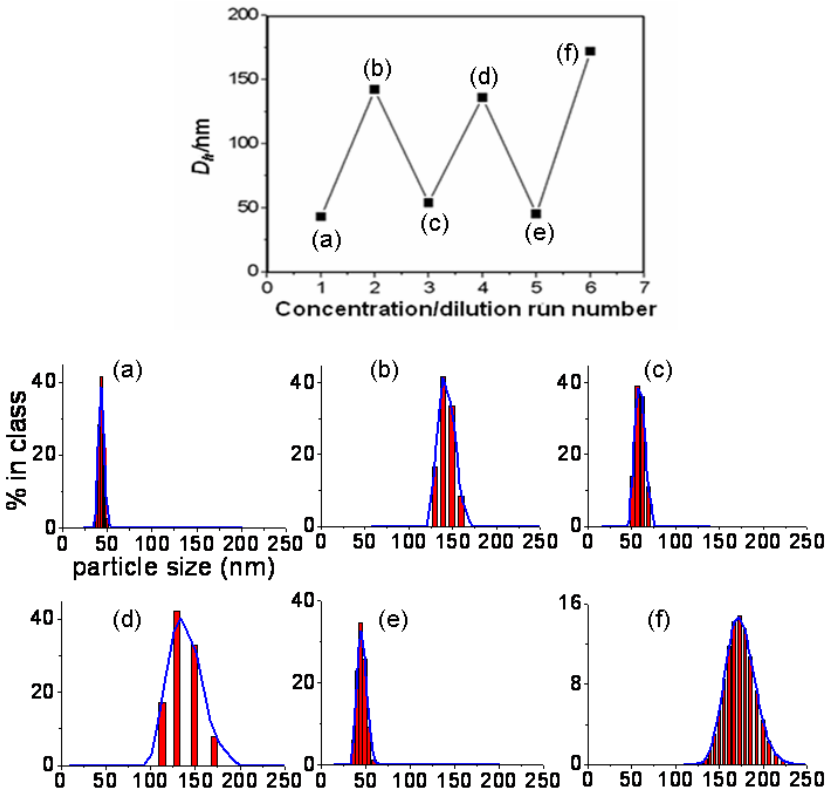

Figure S2. Reversible change in DLS particle sizes/distributions with concentration and dilution cycles between 3.0 (a), (c), and (e) and 6.0 mg/mL (b), (d), and (f).

Synthesis of Au nanoparticles using the micelles/vesicles.

The unique morphologies of the rod–coil micelles and vesicles are expected to allow various applications. We used the P2VP core in the micelles and vesicles as nanoreactors for the synthesis of Au nanoparticles (NPs), which can be performed via coordination of $HAuCl_4$ with the pyridine units of P2VP and subsequent reduction with hydrazine.

The synthesized Au NPs in the micellar and vesicular solutions appeared deep purple. The surface plasmon resonance (SPR) of the resultant Au NP dispersions was obtained from the UV–Vis absorption spectra, as shown in Figure S1a. Only one absorption band centered at 540 nm was observed in Au-micelle solution, whereas two absorption bands centered at 540 and 750 nm were observed in Au-vesicle solution, indicating that spherical Au NPs were synthesized in the micellar solution while Au nanorods were formed in the vesicular solution. It is known that SPRs of Au NPs strongly depend on their shape. The SPRs of spherical Au NPs are generally observed in the range of 500–550 nm.[1] In the case of Au nanowires/nanorods, two SPR absorption bands corresponding to the transverse (T) resonance in the range of 500–550 nm and the longitudinal (L) resonance in the range of 700–800 nm are observed.[2] The TEM images of the Au NPs within the micelles and vesicles also support the shape of Au NPs indicated by the UV–Vis spectra (Figures S1b and S1c).

Higher connectivity of Au NPs in the vesicle may be accounted for by the membrane-like reaction environment of the P2VP core sandwiched between inner and outer PHIC layers. The different morphologies of Au NPs in the micelles and vesicle also indicate that the nano-film consisting of tangential rod-like chains is sufficiently stable to contain guest molecules or nanoparticles, suggesting that the chain-wrapped micelles and vesicles may be suitable for other types of applications.

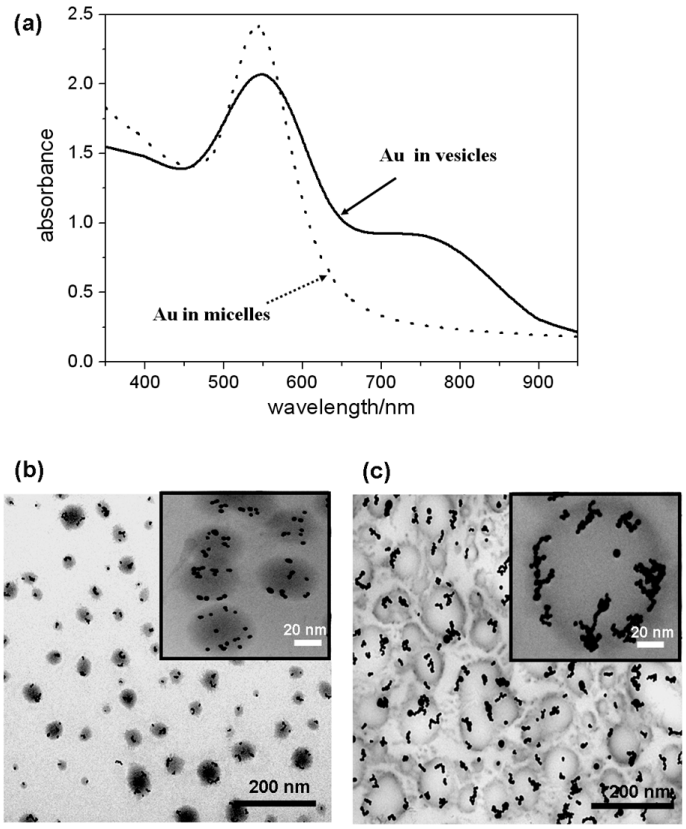

Figure S3. (a) UV–Vis absorption spectra of Au NPs synthesized in the solution of $PHIC_{189}$-*b*-$P2VP_{228}$ micelles (dotted line) and vesicles (solid line). (b) and (c) TEM images of Au NPs synthesized in micelles and vesicles, respectively. The P2VP domains were stained with iodine.

References

1 H. D. Koh, N. G. Kang, J. S. Lee, *Langmuir* **2007**, *23*, 11425.

2 G. A. Wurtz, P. R. Evans, W. Hendren, R. Atkinson, W. Dickson, R. J. Pollard, A. V. Zayats, W. Harrison, C. Bower, *Nano Lett.* **2007**, *7*, 1297.