Supporting Information

Self-Association of a Thermosensitive Amphiphilic Block Copolymer Poly(*N*-isopropylacrylamide)-*b*-Poly(*N*-vinyl-2-pyrrolidone) in Aqueous Solution upon Heating

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Size exclusion chromatograms for PNIPAM-*b*-PNVP block copolymer and its precursor samples. Figure S1 shows SEC elution curves for a NIPAM-*b*-PNVP block copolymer sample (x = 0.31) and its precursor (the PNIPAM homopolymer). The curve for the copolymer (the blue dotted curve) has a long tail at the longer retention time side but not any peak around the region where the elution curve for the precursor (the red curve) has the peak. This indicates that the copolymerization reaction took place effectively, and almost no PNIPAM homopolymer remained in the sample, as expected from the mechanism of organotellurium-mediated living radical polymerization.[1] Similar SEC curves were obtained for other NIPAM-*b*-PNVP block copolymer samples used in this study.

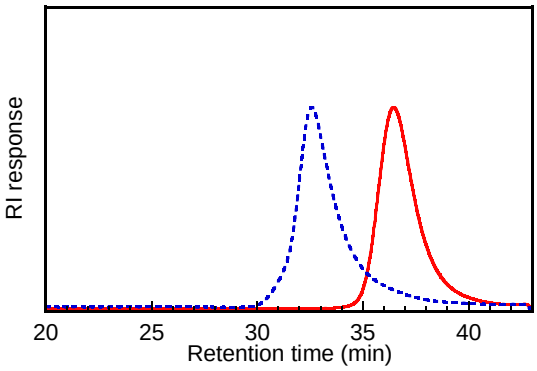

Figure S1. SEC elution profiles for a NIPAM-*b*-PNVP block copolymer sample (x = 0.31, ----) and its precursor (PNIPAM homopolymer, —), detected by the excess refractive index.

Calculation of the Radius of Gyration for the Bilayer Vesicle.[2] The vesicle consists of a spherical (hydrophobic) shell and (hydrophilic) brushes inside and outside the shell, as shown in Figure S2. The thicknesses of the shell and inner and outer brushes are denoted as a, H_i, and H_o, and the inner and outer radii of the shell as $R \pm a/2$. The radius R is related to the molar mass M_{shell} of the block chain forming the shell by the equation

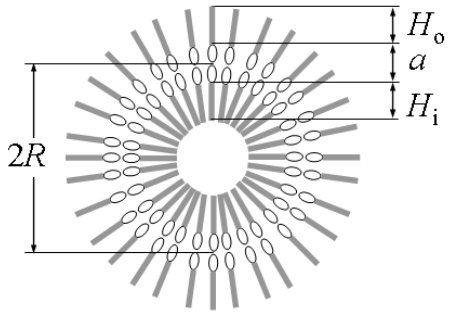

Figure S2. Schematic diagram of the vesicle model.

$$4\pi c_{in}^{shell} a(R^2 + \tfrac{1}{12}a^2) = \frac{(m_i + m_o)M_{shell}}{N_A} \tag{S1}$$

where c_{in}^{shell} is the mass concentration of the hydrophobic block chain inside the shell, m_i and m_o are the numbers of chains in the inner and outer brushes, respectively, and N_A is the Avogadro constant. On the other hand, the thicknesses of the brushes, H_i, and H_o, are related to the molar mass M_{brush} of the block chain forming the shell by the equation[3]

$$H_i = \kappa \frac{m_i^{1/3} M_{brush}}{R'^{2/3}}, \quad H_o = \kappa \frac{m_o^{1/3} M_{brush}}{R''^{2/3}} \tag{S2}$$

where κ is a constant, and R' and R'' are defined by

$$R' \equiv R - \tfrac{1}{2}a, \quad R'' \equiv R + \tfrac{1}{2}a \tag{S3}$$

The light-scattering square radius of gyration $\langle S^2 \rangle^*$ of the vesicle is given by

$$\langle S^2 \rangle^* = \frac{\left[\begin{array}{l} \nu_{brush} A_i H_i^3 \left(\tfrac{2}{3}R'^4 - R'^3 H_i + \tfrac{4}{5}R'^2 H_i^2 - \tfrac{1}{3}R' H_i^3 + \tfrac{2}{35}H_i^4\right) \\ + \tfrac{1}{5}\nu_{shell} c_{in}^{shell}(R''^5 - R'^5) \\ + \nu_{brush} A_o H_o^3 \left(\tfrac{2}{3}R''^4 + R''^3 H_o + \tfrac{4}{5}R''^2 H_o^2 + \tfrac{1}{3}R'' H_o^3 + \tfrac{2}{35}H_o^4\right) \end{array}\right]}{\bar{\nu}(m_i + m_o)(M_{shell} + M_{brush})/4\pi N_A} \tag{S4}$$

where ν_{brush} and ν_{shell} are refractive index increments of the brush and shell chains, respectively, $\bar{\nu}$ is the weight-average refractive index increment of the copolymer sample, and A_{i} and A_{o} are calculated by

$$\begin{cases} A_{\text{i}}\left(\frac{2}{3}R'^2 - \frac{1}{2}R'H_{\text{i}} + \frac{2}{15}H_{\text{i}}^2\right)H_{\text{i}}^3 = \dfrac{m_{\text{i}}M_{\text{brush}}}{4\pi N_{\text{A}}} \\ A_{\text{o}}\left(\frac{2}{3}R''^2 + \frac{1}{2}R''H_{\text{o}} + \frac{2}{15}H_{\text{o}}^2\right)H_{\text{o}}^3 = \dfrac{m_{\text{o}}M_{\text{brush}}}{4\pi N_{\text{A}}} \end{cases} \tag{S5}$$

Equations for the Particle Scattering Functions. The particle scattering function $P(k)$ for the random coil chain (or the Gaussian chain) is given by[4]

$$P_{\text{chain}}(k) = 2\frac{\exp(-k^2\langle S^2\rangle) - 1 + k^2\langle S^2\rangle}{\left(k^2\langle S^2\rangle\right)^2} \tag{S6}$$

where $\langle S^2\rangle$ is the square radius of gyration of the chain. On the other hand, $P(k)$ for the random aggregate or randomly branching polymer synthesized from f-functional monomers is given by the cascade theory[5]

$$P_{\text{random branch}}(k) = \frac{1-(f-1)\alpha}{1+\alpha}\frac{1+\alpha\,\mathrm{e}^{-k^2b^2/6}}{1-(f-1)\alpha\,\mathrm{e}^{-k^2b^2/6}} \tag{S7}$$

where b is the unimer bond length and a is the fraction of reacted functional groups being related to the weight average aggregation number M_{w}/M_0 (M_{w}: the weight average molar mass; M_0: the unimer molar mass) by

$$\alpha = \frac{\left(M_{\text{w}}/M_0\right)-1}{1+(f-1)\left(M_{\text{w}}/M_0\right)} \tag{S8}$$

Equations S6 and S7 do not consider the excluded volume effect. This effect is only important at low k, and may affect $\langle S^2\rangle$ in eq S6 and b in eq S7 at the fitting of the low k scattering profile.

According to Pedersen and Gerstenberg,[6-8] the particle scattering function $P_{\text{star}}(k)$ of the star micelle is calculated by

$$P_{\text{star}}(k) = \left[f_{\text{core}}E_{\text{core}}(k) + \left(1-f_{\text{core}}\right)E_{\text{corona}}(k)\right]^2 + \frac{\left(1-f_{\text{core}}\right)^2}{m_{\text{star}}}\left[E_{\text{chain}}^2(k) - E_{\text{corona}}^2(k)\right] \tag{S9}$$

Here, f_{core} is the contrast factor of the core, given by

$$f_{\text{core}} \equiv \frac{xn_{\text{NIPAM}}}{xn_{\text{NIPAM}} + (1-x)n_{\text{NVP}}} \tag{S10}$$

with the content (the mole fraction) x of the NIPAM monomer unit in the copolymer chain and the numbers of electrons n_{NVP} and n_{NIPAM} of the NVP and NIPAM monomer units, respectively ($n_{\text{NVP}} = n_{\text{NIPAM}} = 60$). Furthermore, in eq S9, E_{core}, E_{corona}, and E_{chain} are time-averaged amplitudes of the scattering electric field from the core, the corona, and each coronal chain, respectively, given by

$$E_{\text{core}}(k) = 3\frac{\sin(kR_{\text{core}}) - kR_{\text{core}}\cos(kR_{\text{core}})}{(kR_{\text{core}})^3} \tag{S11}$$

$$E_{\text{corona}}(k) = \frac{1-\exp\left(-k^2\langle S^2\rangle_{\text{corona}}\right)}{k^2\langle S^2\rangle_{\text{corona}}}\frac{\sin\left[k\left(R_{\text{core}} + \langle S^2\rangle_{\text{corona}}^{1/2}\right)\right]}{k\left(R_{\text{core}} + \langle S^2\rangle_{\text{corona}}^{1/2}\right)} \tag{S12}$$

$$E_{\text{chain}}^2(k) = 2\frac{\exp(-k^2\langle S^2\rangle_{\text{corona}}) - 1 + k^2\langle S^2\rangle_{\text{corona}}}{\left(k^2\langle S^2\rangle_{\text{corona}}\right)^2} \tag{S13}$$

where $\langle S^2\rangle_{\text{corona}}$ is the square radius of gyration of the coronal chain in the star micelle.

Finally, the particle scattering function $P_M(k)$ of the sphere with a molar mass M and radius R_M is given by[4]

$$P_M(k) = \left[3\frac{\sin(kR_M) - kR_M\cos(kR_M)}{(kR_M)^3}\right]^2 \tag{S14}$$

The radius R_M is related to M by

$$R_M = \left(\frac{3M}{4\pi N_{\text{A}} c_{\text{in}}^{\text{sphere}}}\right)^{1/3} \tag{S15}$$

with $c_{\text{in}}^{\text{sphere}}$ being the copolymer mass concentration inside the sphere. We assume that the size distribution (the weight fraction) of the polydisperse spheres is expressed by the log-normal distribution:

$$w(x)\mathrm{d}x = \tfrac{1}{\sqrt{\pi}}\exp\left(-x^2\right)\mathrm{d}x \tag{S16}$$

Here x is defined by

$$x \equiv \sigma^{-1}\ln\left(M/M^{\circ}\right) \tag{S17}$$

with $M° \equiv (M_w M_n)^{1/2}$ and $\sigma \equiv 2\ln(M_w/M_n)$, where M_w and M_n are the weight and number average molar masses of the polydisperse spheres, respectively. The particle scattering function of the polydisperse spheres $P_{sphere}(k)$ is given by

$$P_{\text{sphere}}(k) = M_{\text{w}}^{-1} \int M P_M(k) w(x) \mathrm{d}x \tag{S18}$$

Cryogenic Transmission Electron Microscopy. Cryogenic transmittance electron microscopic observation was made on an aqueous solution of a PNIPAM-*b*-PNVP sample (x = 0.28, $c = 1 \times 10^{-5}$ g/cm^3) quenched from ca. 45 °C using liquid nitrogen by JEOL JEM-1011 at 100 kV. As shown in Figure S3, we observed spherical objects in the image of the copolymer solution, and their sizes are comparable to $\langle S^2 \rangle^{1/2}$ at the corresponding temperature.

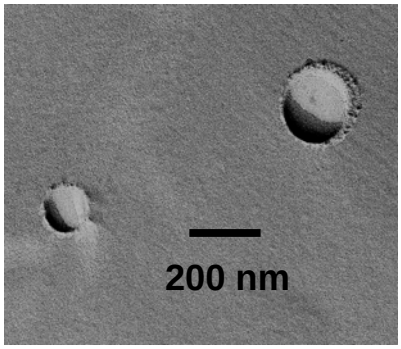

Figure S3. Cryogenic transmission electron micrograph for an aqueous solution of a PNIPAM-*b*-PNVP sample (x = 0.28 in Table 1) quenched from ca. 46 °C.

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