Supporting Information for

Efficient Formation of Multicompartment Hydrogels
by Stepwise Self-Assembly of Thermoresponsive ABC Triblock Terpolymers

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Experimental

Materials. We prepared three PON triblock terpolymers and one NON triblock copolymer. PON triblock terpolymers were prepared using a combination of anionic and reversible addition-fragmentation chain transfer (RAFT) polymerizations. The detailed description of the synthesis of PON triblock terpolymers has been published earlier.\(^1\) NON triblock copolymer was synthesized by RAFT polymerization from a \(\alpha,\omega\)-dihydroxy-\(\text{PEO}\) precursor (\(M_n = 20 \text{ kDa}\)) following a reported procedure.\(^2\) The hydroxyl end-groups of PEO were coupled to the chain transfer agent (CTA), \(\text{S-1-docecyl-S'(a,\alpha'-dimethyl-\alpha'''-acetic acid) trithiocarbonate}\) to give the macroinitiator \(\text{CTA-PEO-CTA}\). The macroinitiator \(\text{CTA-PEO-CTA}\) was then used to grow PNIPAm blocks by RAFT polymerization. The resulting \(\text{CTA-NON-CTA}\) triblock copolymer had the trithiocarbonate end groups on both ends and they were removed by aminolysis and Michael addition to afford the final NON triblock copolymers.\(^3\) The product of each reaction step was confirmed by \(^1\text{H}\) NMR spectroscopy and characterized by size exclusion chromatography (SEC) (Figures S1).

Sample Preparation. All the polymer solutions were prepared by the thin-film hydration method. Appropriate amounts of bulk polymer were dissolved in \(\text{CH}_2\text{Cl}_2\), followed by evaporation of the solvent to yield a thin film on the walls of the vial. The thin film was then hydrated with a defined amount of water, and the resulting mixture was stirred at room temperature for at least 1 month before further characterization.

Rheology. Rheological measurements were performed using an AR-G2 rheometer with a Couette geometry that contains the sample in a 1 mm concentric cylindrical gap between a cup with a diameter of 30 mm and a bob with a diameter of 28 mm. About 15 mL of the sample was first loaded on the cup at room temperature (25 °C). This amount filled the gap as the bob was lowered. The temperature was controlled using Peltier temperature controller. To avoid any water evaporation from the sample, the whole fixture assembly was covered with a metal cover with a wet sponge. Dynamic frequency sweeps were examined in the linear viscoelastic regime, as determined by dynamic strain sweep experiments. The temperature dependences of \(G'\) and \(G''\) were measured with a frequency of 10 rad/s, and a heating rate of 1 °C/min.

CryoTEM: CryoTEM samples were prepared using the Vitrobot system (FEI company). To prepare the sample at 25 °C, a drop of micelle solution (ca. 5 \(\mu\)L) was placed onto a lacy Formvar carbon-supported TEM grid in the climate chamber of the Vitrobot system, where the temperature was kept at 25 °C and the relative humidity was kept at 100%. To prepare the sample at 50 °C, the micelle solution was heated in an oil bath at 50 °C for 10 min and a drop of the resulting hydrogel was placed onto a lacy Formvar carbon-supported TEM grid in the climate chamber of the Vitrobot system, where the temperature was kept at 50 °C and the relative humidity was kept at 100%. The excess solution was blotted with the filter paper and the sample was quickly plunged into a reservoir of liquid ethane cooled by liquid nitrogen. The vitrified samples were then stored in liquid nitrogen until they were transferred to a cryogenic sample holder and examined with a FEI Tecnai Spirit BioTWIN TEM instrument operated at an acceleration voltage of 120 kV at about –178 °C. The phase contrast was enhanced by acquiring images at a nominal underfocus of 10–15 \(\mu\)m.
Figure S1. SEC traces of PEO, CTA-PEO-CTA, CTA-NON-CTA(10-20-10), NON(10-20-10). THF/N,N,N',N'-tetramethylethylenediamine was used as the eluting solvent at a flow rate of 1.0 mL/min.

Figure S2. Photographs of PON(3-25-10) solutions at varying polymer concentrations and the indicated temperatures.
Figure S3. Dynamic shear moduli ($G'$ and $G''$) as a function of frequency for the 5 wt% PON(3-25-10) solution measured at a strain $\gamma = 2\%$ and three indicated temperatures.
Figure S4. Temperature-dependent dynamic shear moduli ($G'$ and $G''$) for PON(3-25-10) solutions with different concentrations at a frequency $\omega = 10$ rad/s and heating rate of 1 °C/min. The 5 wt% PON(3-25-10) solution was measured at a strain $\gamma = 2\%$. The 2 wt% and 1 wt% PON(3-25-10) solutions were measured at a strain $\gamma = 50\%$ for the low temperatures and $\gamma = 2\%$ for the high temperatures.
Figure S5. Temperature-dependent dynamic shear moduli ($G'$ and $G''$) for NON(10-20-10) solutions with different concentrations at a frequency $\omega = 10$ rad/s and heating rate of 1 °C/min. The 10 wt% and 5 wt% NON(10-20-10) solutions were measured at a strain $\gamma = 50\%$ for the low temperatures and $\gamma = 2\%$ for the high temperatures. The 2 wt% NON(10-20-10) solution was measured at a strain $\gamma = 50\%$. 
Figure S6. CryoTEM images of 5 wt% NON(10-20-10) aqueous solution prepared at (a) 25 ºC and (b) 60 ºC.

References and Notes

(3) Qiu, X. P.; Winnik, F. M. Macromol. Rapid Commun. 2006, 27, 1648-1653