Supporting Information

Sticky Ends in a Self-Assembling ABA Triblock Copolymer: The Role of Ureas in Stimuli-Responsive Hydrogels

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Estimation of degree of polymerization (*DP*) by ¹H NMR spectroscopy: To complement the estimates of M_n made *via* GPC, degree of polymerization (and hence, M_n) was calculated using ¹H NMR. A sample calculation is as follows: Let 'x' equal the integration per proton for iPGE. Let 'y' equal the integration per proton for PEO. Using **Figure S1** as a sample spectrum, this gives the equations 6x = 1 for the 6 protons that contribute to the isopropyl resonance at 1.1 ppm, and 4y + 6x = 8.78 for the 4 PEO protons and 6 iPGE protons that contribute to the polyether backbone 1

resonances between 3.3-3.9 ppm. Solving these equations yields $x = \overline{6}$ and $y \approx 1.95$ This gives a y

PEO:PiPGE molar ratio of $\overline{x} = 11.7:1$. With a known M_n for PEO of 8.0 kg mol⁻¹ and the monomer 8000

mass of ethylene oxide (44.05 g mol⁻¹), the average number of PEO repeat units is $\overline{44.05} \approx 182$. 182

Dividing this by the ratio of PEO to iPGE, we obtain $\overline{11.7} \approx 15.6$ total repeat units of iPGE, or 15.6

 $\overline{2}$ = 7.8 repeat units per block (rounded up to 8).

Estimation of degree of functionalization (f_n) for polymers 1-U and 1-bisU: The efficiency of DCC-mediated esterification was estimated by integrating the polymer chain-end methyne proton (δ 4.9 ppm, DMSO- d_{δ}) and the *boc* methyl protons (δ 1.4 ppm, DMSO- d_{δ}) against the iPGE methyl protons (δ 1.1 ppm, DMSO- d_{δ}). Using the known *DP* (8) of the PiPGE blocks, the iPGE methyl resonance was calibrated to $8 \times 2 \times 6 = 96$. This resulted in integrations of 1.8 for the methyne proton and 16.7 for the *boc* methyl protons (spectra not shown). Division by the theoretical integrations of 2 and 18 gave estimates of $f_n \approx 90\%$ and 93%, respectively. TFA-catalyzed deprotection was quantitative as indicated by the complete disappearance of the *boc* methyl protons. To estimate degree of functionalization for subsequent coupling with *p*-tolyl isocyanate or tolylene-2,4-diisocyanate, the aromatic protons (δ 6.9-7.6 ppm, (CD₃)₂CO) were integrated against the chain-end methyne proton (δ 5.1 ppm, (CD₃)₂CO). Division by the theoretical values for the integrations, followed by multiplying the yield of the esterification and deprotection steps, gave f_n estimates of $f_n \approx 82-91\%$ for polymer 1-U and 90-93% for 1-bisU. In the case of polymer 1-U and polymer 1-bisU, the aryl methyl protons (δ 2.2-2.3 ppm, (CD₃)₂CO) were also used to estimate f_n .

Hydrogel preparation for rheological experiments: All polymer sol-gels were prepared using a "sandwich" technique: Approximately half of the desired mass of water was added to a small vial, followed by the desired mass of polymer and finally the remaining mass of water. All solutions were incubated at 0-5 °C for 72 h prior to temperature-ramp measurements, with daily stirring. Using the temperature-ramp data, a solution was defined as any region where the storage modulus (*G*') was less than the loss modulus (*G*''). Conversely, a gel was defined as any region where *G*' > *G*". Based on qualitative observations, a viscous solution was defined as any region where *G*' <

G" and *G*" \geq 10 Pa. The gelation temperature (T_{gel}) was defined as the point of modulus crossover, where *G* becomes greater than *G*".



Scheme S1. Anionic ring-opening polymerization of iPGE from PEO macroinitiator. (i) Potassium naphthalenide (1.0 M in THF), 50 °C, THF. (ii) (1) iPGE, 50 °C, 48 h. (2) 1% v/v AcOH:MeOH, 50 °C, 10 min.









Figure S4. Overlaid thin-film IR spectra of polymer 1, polymer 1-U, and polymer 1-bisU (black, red, and blue, respectively). Inset: Closeup of region between 1200-1800 cm⁻¹.

Figure S5. Normalized GPC traces of polymer 1, polymer 1-U, and polymer 1bisU, eluted in CHCl₃ (stabilized with 0.1% v/v triethylamine).

Figure S6. Temperature-ramp experiment for 25 wt% polymer 1. Strain amplitude = 1%; radial frequency = 6 rad s⁻¹.

Figure S7. Temperature-ramp experiment for 25 wt% polymer 1-U. Strain amplitude = 1%; radial frequency = 6 rad s⁻¹.

Figure S8. Temperature-ramp experiment for 25 wt% polymer 1-bisU. Strain amplitude = 1%; radial frequency = 6 rad s⁻¹.

Figure S9. Plot of viscosity *vs.* shear rate for 25 wt% polymer 1. The solution behaves as a free-flowing liquid at 25 °C, and viscosity remains nearly constant.

Figure S10. Dynamic oscillatory strain test for 25 wt% polymer 1, conducted at 25 °C. Angular frequency = 6 rad s⁻¹.

Figure S11. Oscillatory frequency sweep test for 25 wt% polymer 1, conducted at 25 °C (1% strain amplitude).

Figure S12. Oscillatory frequency sweep test for 25 wt% polymer 1-U, conducted at 25 °C (1% strain amplitude).

Figure S13. Oscillatory frequency sweep test for 25 wt% polymer 1-bisU, conducted at 25 °C (1% strain amplitude).

Figure S14. Oscillatory strain sweep test (angular frequency, $\omega = 6$ rad s⁻¹) for 25 wt% polymer 1, conducted at 25 °C. The material is fluidlike, and hence does not possess a measurable yield stress.

Figure S15. Overlay of polymer 1 (black), polymer 1-U (red), and polymer 1-bisU (orange and purple) baseline-shifted thermograms between 150-200 °C.

Figure S16. DSC thermogram of polymer 1-bisU heated from 0 °C, showing PEO melting transition centered at 52 °C, and one urea melting transition centered at 170 °C.

Figure S17. DSC thermogram of polymer 1-U.

Figure S18. DSC thermogram of polymer 1.

Figure S19. Baseline-corrected IR spectra (1615-1715 cm⁻¹) of 23 wt% polymer 1-bisU in D₂O at temperatures between 5-50 °C.

Figure S20. 25 wt% solutions/gels at 21 °C. "a" = polymer 1; "b" = polymer 1-U; "c" = polymer 1-bisU.