### Supporting Information

#### **Preparation of Water-soluble Hyperbranched Polymers with Tunable**

### Thermosensitivity using Chain-growth CuAAC Copolymerization

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# Experimental

**Materials.** AB<sub>2</sub> monomers with oligo(ethylene oxide) (EO<sub>x</sub>) dangling side group, AB<sub>2</sub>-EO<sub>3</sub> and AB<sub>2</sub>-EO<sub>7.5</sub> were synthesized according to previous report.<sup>1</sup> Ascorbic acid (Alfa Aesar,  $\geq$  99%), copper(II) sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O, BDH, ACS grade), dimethylformamide (DMF, Sigma-Aldrich,  $\geq$  99.8%), ethyl ether (EMD Millipore  $\geq$  99%), *N*,*N*,*N*',*N*''-pentamethyldiethylenetriamine (PMDETA, Sigma-Aldrich, 99%), dimethyl sulfoxide-d6 (DMSO-*d*<sub>6</sub>, Alfa Aesar, 100%), were used as received.

**Instrumental Methods.** The THF size exclusion chromatography (SEC) was equipped with Polymer Standards Services (PSS) columns (guard,  $10^5$ ,  $10^3$ , and  $10^2$  Å SDV columns) at 35 °C with THF flow rate = 1.00 ml/min, a differential refractive index (RI) detector (Wyatt Technology, Optilab T-rEX) using PSS WinGPC 7.5 software. The apparent molecular weights were calculated based on linear poly(methyl methacrylate) (PMMA) standards. The detectors employed to measure the absolute molecular weights of hyperbranched polymers in THF SEC were the RI detector and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN HELEOS II) with the light wavelength at 658 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology with the pre-measured dn/dc = 0.0896 for all hyperbranched polymers. <sup>1</sup>H nuclear magnetic resonance (NMR) was acquired on a Bruker 500 MHz spectrometer at 25 °C using CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as solvent. FT-IR was conducted using a Thermo Nicolet IR 200 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector, mid-IR source (4000-400 cm) and Ge on KBr beam splitter. Dynamic light scattering (DLS) equipped with a Zetasizer Nano-ZS (He-Ne laser wavelength at 633 nm) and an autotitrator (Malvern Instruments) was used to study the temperature dependence of hydrodynamic diameter  $(D_{\rm h})$ of  $HB-((EO_{7.5})_x-r-(EO_3)_{1-x})$ and HB-((EO7.5)x-r- $(EO_3)_{1-x}$ -cap-eEO<sub>3</sub> in aqueous solution. The solution was heated or cooled in steps and stabilized at each predetermined temperature for 15 min.

**CuAAC polymerization of AB**<sub>2</sub> monomers in one pot. Typical procedures in the polymerization of AB<sub>2</sub>-EO<sub>7.5</sub> monomer using molar ratios of  $[AB_2-EO_{7.5}]_0$ :  $[CuSO_4 \cdot 5H_2O]_0$ : [ascorbic acid]<sub>0</sub> = 50 : 1 : 5 are described. CuSO<sub>4</sub> · 5H<sub>2</sub>O (5.0 mg, 0.02 mmol) and AB<sub>2</sub>-EO<sub>7.5</sub> monomer (0.70 g, 1.0 mmol) and 2 ml DMF were charged in a 10 ml flask. This flask immersed in a thermostatic oil bath at 45 °C was capped with rubber septa and bubbled with nitrogen gas for 40 min before the ascorbic acid (17.6 mg, 0.1 mmol) was quickly added into the flask to initiate the polymerization. Samples were collected using deoxygenated syringes at each predetermined interval and were quenched by exposure to air and the addition of a

trace amount of PMDETA. One portion was diluted by THF and then passed through a flash alumina column for SEC measurement. The polymerization was stopped at 15 hours before the addition of 2 equiv. of PMDETA ligand to exact the Cu catalyst out of the polymer. The hyperbranched polymers in DCM were then passed through a flash alumina column before being precipitated in ethyl ether three times. The procedures for polymerization of AB<sub>2</sub>-EO<sub>3</sub> at various ratios were similar to those described above.

**End-capping of hyperbranched polymer**. Typical procedures for synthesizing HB-EO<sub>3</sub>-*cap*-eEO<sub>3</sub> were as follows: HB-EO<sub>3</sub> (0.2 g, 0.52 mmol of -N<sub>3</sub>), ay-eEO<sub>3</sub> (0.34 g, 1.04 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (5 mg, 0.02 mmol) and 2 mL DMF were charged in a 10 mL flask. The mixture was degassed by three freeze-pump-thaw cycles, and then the ascorbic acid (17.6 mg, 0.1 mmol) was added into flask. The flask was sealed under vacuum and the click reaction was carried out in an oil bath at 45 °C. The reaction was stopped at 4 hours before the addition of 2 equiv. of PMDETA ligand to exact the Cu catalyst out of the polymer. The hyperbranched polymers in DCM were then passed through a flash alumina column before being precipitated in diethyl ether three times. The final dried product was colorless with a yield around 80%.

**Micellar aggregate of HB-EO<sub>3</sub> in water.** Hyperbranched polymer HB-EO<sub>3</sub> was dissolved in THF to make a 2 mg/mL stock solution before being added dropwise into 10 mL deionized water. Mild magnetic stirring was applied for 30 min at room temperature to induce assembly of the HB-EO<sub>3</sub>. After stirring, the THF was removed using dialysis (COMW: 6–8000 g/mol) against DI water (changing water every 4 h for 24 h).



**Figure S1.** (A) SEC traces of hyperbranched copolymers produced from CuAAC copolymerization of AB<sub>2</sub>-EO<sub>7.5</sub> and AB<sub>2</sub>-EO<sub>3</sub> with THF as the SEC mobile phase; (B) the weight fraction of AB<sub>2</sub>-EO<sub>3</sub> in hyperbranched copolymer as a function of conversion.



**Figure S2**. SEC traces of hyperbranched copolymers HB- HB-((EO<sub>7.5</sub>)<sub>0.25</sub>-*r*-(EO<sub>3</sub>)<sub>0.75</sub>) and HB-((EO<sub>7.5</sub>)<sub>0.25</sub>-*r*-(EO<sub>3</sub>)<sub>0.75</sub>)-*cap*-eEO<sub>3</sub> after end capping with alkyne-terminated EO<sub>3</sub>, THF was the SEC mobile phase using RI detector.



Figure S3. Hydrodynamic diameter  $(D_h)$  of HB-EO<sub>7.5</sub> in water and THF.



**Figure S4**. Hydrodynamic diameter  $(D_h)$  of HB-EO<sub>3</sub> in water.



Figure S5. (A) SEC traces with THF as the mobile phase and (B) hydrodynamic diameter  $(D_h)$  in water of HB-((EO<sub>3</sub>)<sub>0.42</sub>@(EO<sub>7.5</sub>)<sub>0.58</sub>), HB-((EO<sub>3</sub>)<sub>0.42</sub>-*r*-(EO<sub>7.5</sub>)<sub>0.58</sub>) and HB-((EO<sub>7.5</sub>)<sub>0.58</sub>@(EO<sub>3</sub>)<sub>0.42</sub>).

# References

1. Shi, Y.; Cao, X.; Luo, S.; Wang, X.; Graff, R. W.; Hu, D.; Guo, R.; Gao, H., *Macromolecules* **2016**, *49* (12), 4416-4422.