Supplementary Information for

Cross-Linkable Multi-Stimuli Responsive Hydrogels for Direct-Write 3D Printing

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Calculation of M_n

Number average molecular weight was calculated using ¹H NMR and an example for a copolymer of PiPGE-*stat*-PAGE-*b*-PiPGE-*stat*-PAGE is given. The M_n of PEG is 8k Da which corresponds to approximately 182 ethylene glycol units per macroinitiator. If we use Figure S3 as the example spectrum then the number of isopropyl and allyl glycidyl ether units can be calculated by finding the PEG to PiPGE and PEG to PAGE ratio. The integration for the peak at 2 ppm corresponds to the methyl groups on iPGE and is usually set to 1. The peaks between 3.2 and 3.9 correspond to protons e-m and were integrated to a value of 8, and the peaks at 4, 5.1 to 5.3, and 5.9 ppm corresponding to proton a-d equaled a total of 0.125. Since iPGE and AGE have peaks that overlap in the 3.5 ppm region, their contribution to the overall integration must be subtracted as shown below.

$$\frac{182 \text{ ethylene glycol units}}{\left(\frac{6 \text{ PiPGE CH}_3}{4 \text{ PEG CH}_2}\right) * (8 - 1 - 0.125)} = 17.6 \text{ iPGE units}$$

Then, the integrations for PAGE allyl and vinyl protons at 4, 5.1 to 5.3, and 5.9 ppm can be summed and multiplied by the number of iPGE units to give the number of AGE units as shown below.

$$0.125 * \frac{6 PiPGE CH_3}{5 PAGE CH_2 + CH} * 17.6 = 2.6 AGE units$$

Supplementary Experimental Details

Synthesis of poly(allyl glycidyl ether)-b-poly(ethylene glycol)-b-poly(allyl glycidyl ether) (PAGE-b-PEGb-PAGE)

PEG (10 g, 1.25 mmol, M_n = 8,000 g/mol) was dried under reduced pressure in a reaction vessel at 50 °C overnight. THF (100 mL) was added under an argon atmosphere to dissolve PEG at room temperature. Potassium naphthalenide solution was titrated into the flask until a slight green color persisted, indicating that the hydroxyl groups of the PEG have been fully deprotonated. The reaction vessel was then warmed to 30 °C and AGE (4 mL, 34 mmol) was added via buret. The reaction was left to stir for 48 h and was quenched with degassed acidic methanol (10 mL, 1 v/v % acetic acid). The reaction mixture was concentrated under reduced pressure and added to cold diethyl ether to precipitate. The resulting suspension was poured into centrifuge tubes and spun at 4400 rpm for 10 min. The supernatant was decanted and resulting material was dried in a vacuum oven to afford a white solid. ¹H NMR (500 MHz, CDCl₃): δ 5.86-5.95 (m, 1 H, CH₂-CH=CH₂), 5.15-5.30 (m, 2 H, CH₂-CH=CH₂), 4.01 (s, 2 H, O-CH₂-CH=CH₂), 3.47-3.89 (m, 4 H, + 5 H, PEG backbone, PAGE backbone). M_n = 10800 g/mol (determined by ¹H NMR 500 MHz, CDCl₃). Φ = 1.11 (determined by SEC using RI detection and CHCl₃ as eluent).

Synthesis of poly(ethyl glycidyl ether)-*b*-poly(ethylene glycol)-*b*-poly(ethyl glycidyl ether) (PEGE-*b*-PEGE)

PEG (10 g, 1.25 mmol, M_n = 8,000 g/mol) was dried under reduced pressure in a reaction vessel at 50 °C overnight. THF (100 mL) was added under an argon atmosphere to dissolve PEG at room temperature. Potassium naphthalenide solution was titrated into the flask until a slight green color persisted, indicating that the hydroxyl groups of the PEG have been fully deprotonated. The reaction vessel was then warmed to 50 °C and EGE (4.8 mL, 44 mmol) was added via buret. The reaction was left to stir for 48 h and was quenched with degassed acidic methanol (10 mL, 1 v/v % acetic acid). The reaction mixture

was concentrated under reduced pressure and added to cold diethyl ether to precipitate. The resulting suspension was poured into centrifuge tubes and spun at 4400 rpm for 10 min. The supernatant was decanted and resulting material was dried in a vacuum oven to afford a white solid. ¹H NMR (500 MHz, CDCl₃): δ 3.48-3.92 (m, 4 H, + 7 H, PEG backbone, PEGE backbone), 1.18-1.19 (m, 3 H, O-CH₂CH₃). M_n = 11300 g/mol (determined by ¹H NMR 500 MHz, CDCl₃). D = 1.11 (determined by SEC using RI detection and CHCl₃ as eluent).

Synthesis of poly(isopropyl glycidyl ether)-*stat*-poly(allyl glycidyl ether)-*b*-poly(ethylene glycol)-*b*-poly(isopropyl glycidyl ether)-*stat*-poly(allyl glycidyl ether) (PiPGE-*stat*-PAGE-*b*-PEG-*b*-PiPGE-*stat*-PAGE)

PEG (10 g, 1.25 mmol, M_n = 8,000 g/mol) was dried under reduced pressure in a reaction vessel at 50 °C overnight. THF (100 mL) was added under an argon atmosphere to dissolve PEG at room temperature. Potassium naphthalenide solution was titrated into the flask until a slight green color persisted, indicating that the hydroxyl groups of the PEG have been fully deprotonated. The reaction vessel was then warmed to 30 °C AGE (0.72 mL, 6.1 mmol) and iPGE (3.3 mL, 26 mmol) were added via burets. The reaction was left to stir for 48 h and was quenched with degassed acidic methanol (10 mL, 1 v/v % acetic acid). The reaction mixture was concentrated under reduced pressure and added to cold diethyl ether to precipitate. The resulting suspension was poured into centrifuge tubes and spun at 4400 rpm for 10 min. The supernatant was decanted and resulting material was dried in a vacuum oven to afford a white solid. ¹H NMR (500 MHz, CDCl₃): δ 5.88-5.97 (m, 1 H, CH₂-CH=CH₂), 5.16-5.28 (m, 2 H, CH₂-CH=CH₂), 3.99 (s, 2 H, O-CH₂-CH=CH₂), 3.47-3.89 (m, 4 H, + 5 H, + 6 H, PEG backbone, PAGE backbone, PiPGE backbone), 1.14-1.21 (d, 6 H, O-CH-2CH₃). M_n = 10700 g/mol (determined by ¹H NMR 500 MHz, CDCl₃). \tilde{D} = 1.11 (determined by SEC using RI detection and CHCl₃ as eluent).

Synthesis of poly(ethyl glycidyl ether)-*stat*-poly(allyl glycidyl ether)-*b*-poly(ethylene glycol)-*b*-poly(ethyl glycidyl ether)-*stat*-poly(allyl glycidyl ether) (PEGE-*stat*-PAGE-*b*-PEGE-*stat*-PAGE)

PEG (10 g, 1.25 mmol, M_n = 8,000 g/mol) was dried under reduced pressure in a reaction vessel at 50 °C overnight. THF (100 mL) was added under an argon atmosphere to dissolve PEG at room temperature. Potassium naphthalenide solution was titrated into the flask until a slight green color persisted, indicating that the hydroxyl groups of the PEG have been fully deprotonated. The reaction vessel was then warmed to 30 °C AGE (3.1 mL, 26 mmol) and EGE (1.8 mL, 15 mmol) were added via burets. The reaction was left to stir for 48 h and was quenched with degassed acidic methanol (10 mL, 1 v/v % acetic acid). The reaction mixture was concentrated under reduced pressure and added to cold diethyl ether to precipitate. The resulting suspension was poured into centrifuge tubes and spun at 4400 rpm for 10 min. The supernatant was decanted and resulting material was dried in a vacuum oven to afford a white solid. ¹H NMR (500 MHz, CDCl₃): δ 5.88-5.89 (m, 1 H, CH₂-CH=CH₂), 5.14-5.27 (m, 2 H, CH₂-CH=CH₂), 3.98 (s, 2 H, O-CH₂-CH=CH₂), 3.48-3.89 (m, 4 H, + 5 H, + 7 H, PEG backbone, PAGE backbone, PEGE backbone), 1.18 (m, 3 H, O-CH-CH₃). M_n = 11300 g/mol (determined by ¹H NMR 500 MHz, CDCl₃). ϑ = 1.11 (determined by SEC using RI detection and CHCl₃ as eluent).

Supplementary Figures







Figure S2. PAGE_{18.5}-*b*-PEG₁₈₁-*b*-PAGE_{18.5} (polymer 1) 15 wt % concentration hydrogel



7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm Figure S3. ¹H NMR spectrum of PiPGE-*stat*-PAGE-*b*-PiPGE-*stat*-PAGE (polymer **3**) triblock (500 MHz, 293 K, CDCl₃)



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