## **Supporting Information**

## **Enzyme-catalyzed Quantitative Chain-end Functionalization of Poly(ethylene**

## glycol)s under Solventless Conditions

Kwang Su Seo<sup>1</sup>, Marcela Castano<sup>2,</sup> Madalis Casiano<sup>3</sup>, Chrys Wesdemiotis<sup>2,3</sup>, Matthew L. Becker<sup>2</sup>, Judit E. Puskas<sup>1,2,3,\*</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, <sup>2</sup>Department of Polymer Science and <sup>3</sup>Department of Chemistry, The University of Akron, Akron, Ohio 44325

jpuskas@uakron.edu



Figure S1. MALDI-ToF mass spectrum of the reaction product at DVA/TEG = 6 after 1 hour reaction time (cationizing salt: NaTFA). [DVA] = 4.61 mol/L, [TEG] = 0.77 mol/L, [CALB] =  $7.6 \times 10^{-5}$  mol/L.



**Figure S2.** <sup>1</sup>H NMR spectra of HO-TEG-OH (top) and V-TEG-V (bottom) (solvent: DMSO-d<sub>6</sub>). [DVA] = 4.61 mol/L, [TEG] = 0.77 mol/L, [CALB] =  $7.6 \times 10^{-5}$  mol/L.

<sup>1</sup>H NMR: (**a**) 4.55 ppm; (**b**) 3.50 ppm; (**b**') 4.22ppm; (**c**) 3.46 ppm; (**c**') 3.60 ppm; (**d**) 3.50 ppm; (**e**) 4.87 ppm; (**e**') 4.65 ppm; (**f**) 7.24 ppm; (**g**) 2.45 ppm; (**h**) 1.62 ppm; (**i**) 2.32 ppm.



**Figure S3.** <sup>13</sup>C NMR spectrum of telechelic vinyl-functionalized TEG (solvent: DMSO-d<sub>6</sub>).

<sup>13</sup>C NMR: (**B**) 63.09 ppm; (**C**) 68.34 ppm; (**D**) 69.81 ppm; (**E**) 97.76 ppm; (**F**) 141.17 ppm; (**G**)
170.15 ppm; (**H**) 33.02 ppm; (**I**) 23.76/23.45 ppm; (**J**) 32.67 ppm; (**K**) 172.60 ppm.



Figure S4. MALDI-ToF mass spectrum of the product at DVA/MeO-PEG-OH<sub>1100</sub> = 5. [DVA] = 5.30 mol/L, [MeO-PEG-OH<sub>1100</sub>] = 1.06 mol/L; [CALB] =  $6.9 \times 10^{-4} \text{ mol/L}$ .



**Figure S5.** NMR spectra of the product of the reaction of DVA (5.0 eq.) with MeO-PEG-OH<sub>1100</sub>: (top) <sup>1</sup>H NMR spectrum and (bottom) <sup>13</sup>C NMR spectrum (solvent: DMSO-d<sub>6</sub>). [DVA] = 5.30 mol/L, [MeO-PEG-OH<sub>1100</sub>] = 1.06 mol/L; [CALB] =  $6.9 \times 10^{-4}$  mol/L.

<sup>1</sup>H NMR: (b) 4.14 ppm; (c) 3.60 ppm; (d) 3.50 ppm; (e) 3.45 ppm; (f) 3.37 ppm; (g) 3.22 ppm;
(h) 2.32 ppm; (i) 1.56 ppm; (j) 2.44 ppm; (k) 7.18 ppm (l) 4.64 ppm, (l') 4.85 ppm.

<sup>13</sup>C NMR: (**A**) 63.12 ppm; (**B**) 68.04 ppm; (**C**) 70.01 ppm; (**D**) 67.00 ppm; (**E**) 71.79 ppm; (**F**)

57.98 ppm; (G) 73.11 ppm; (H) 23.86 ppm; (I) 33.00 ppm; (J) 23.83 ppm; (K) 170.06 ppm; (L)

141.51 ppm (**M**) 98.08 ppm.



**Figure S6.** MALDI-ToF mass spectrum of the product of the reaction of DVA/ HO-PEG-OH<sub>1000</sub> at t = 2 hours. [DVA] = 5.31 mol/L, [HO-PEG-OH<sub>1000</sub>] = 0.27 mol/L; [CALB] =  $1.6 \times 10^{-4}$  mol/L.

The representative peak at m/z 1362.0 in the major distribution corresponds to the sodium complex of the 23-mer of telechelic vinyl-functionalized HO-PEG-OH<sub>1000</sub>. The calculated monoisotopic mass for this peak [ $m/z = 23 \times 44.03$  (C<sub>2</sub>H<sub>4</sub>O repeat unit) + 326.14 (C<sub>16</sub>H<sub>22</sub>O<sub>7</sub> end groups) + 22.99 (Na<sup>+</sup>)] is 1361.82 Da.