Supporting Information

Enzyme-catalyzed Quantitative Chain-end Functionalization of Poly(ethylene glycol)s under Solventless Conditions

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**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 × 10⁻⁵ mol/L.
**Figure S2.** $^1$H NMR spectra of HO-TEG-OH (top) and V-TEG-V (bottom) (solvent: DMSO-$d_6$). [DVA] = 4.61 mol/L, [TEG] = 0.77 mol/L, [CALB] = $7.6 \times 10^{-5}$ mol/L.

$^1$H NMR: (a) 4.55 ppm; (b) 3.50 ppm; (b') 4.22 ppm; (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. $^{13}$C NMR spectrum of telechelic vinyl-functionalized TEG (solvent: DMSO-d$_6$).

$^{13}$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$_{1100}$ = 5. [DVA] = 5.30 mol/L, [MeO-PEG-OH$_{1100}$] = 1.06 mol/L; [CALB] = 6.9 × 10^{-4} mol/L.
Figure S5. NMR spectra of the product of the reaction of DVA (5.0 eq.) with MeO-PEG-OH\textsubscript{1100}: (top) \textsuperscript{1}H NMR spectrum and (bottom) \textsuperscript{13}C NMR spectrum (solvent: DMSO-d\textsubscript{6}). [DVA] = 5.30 mol/L, [MeO-PEG-OH\textsubscript{1100}] = 1.06 mol/L; [CALB] = 6.9 \times 10^{-4} mol/L.

\textsuperscript{1}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\textsuperscript{'}) 4.85 ppm.

\textsuperscript{13}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\textsubscript{1000} at \(t = 2\) hours. \([\text{DVA}] = 5.31\ \text{mol/L}; \ [\text{HO-PEG-OH}\textsubscript{1000}] = 0.27\ \text{mol/L}; \ [\text{CALB}] = 1.6 \times 10^{-4}\ \text{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\textsubscript{1000}. The calculated monoisotopic mass for this peak \([m/z = 23 \times 44.03 \ (\text{C}_2\text{H}_4\text{O} \ \text{repeat unit}) + 326.14 \ (\text{C}_{16}\text{H}_{22}\text{O}_7 \ \text{end groups}) + 22.99 \ (\text{Na}^+)\] is 1361.82 Da.