Electronic Supplementary Information for:

Facile synthesis of chain end functionalized polyethylenes via epoxide ring-opening and thiol-ene addition click chemistry

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Figure S1¹H NMR of 1,3-PS (A, CDCl₃) and KPS (B, D₂O)



Figure S2¹H NMR of v-PE2 (1,2-Dichlorobenzene-d4, assignments similar to

v-PE1; inset: calculation of vinyl group selectivity)



Figure S3¹H NMR spectrum of carboxy-t-PE1 (1,2-Dichlorobenzene-d4,



assignments similar to carboxy-t-PE)

Figure S4 ¹³C NMR spectrum of v-PE1 (1,2-Dichlorobenzene-d4)



Figure S5 ¹³C NMR spectrum of v-PE2 (1,2-Dichlorobenzene-d4, assignments



similar to v-PE1)

Figure S6 ¹³C NMR spectrum of e-PE (1,2-Dichlorobenzene-d4)





Figure S7 ¹³C NMR spectrum of 2-hydroxy PE (1,2-Dichlorobenzene-d4)

Figure S8 ¹³C NMR spectrum of chloro-t-PE (1,2-Dichlorobenzene-d4)





Figure S9¹³C NMR spectrum of azide-t-PE (1,2-Dichlorobenzene-d4)

Figure S10 ¹³C NMR spectrum of carboxy-t-PE (1,1,2,2-Tetrachloroethane-D2)



Figure S11 ¹³C NMR spectrum of sulfo-t-PE (1,2-Dichlorobenzene-d4, carbons



labelled with *h* and *i* not found)

Figure S12 ¹³C NMR spectrum of diol-PE (1,2-Dichlorobenzene-d4)



Figure S13 ¹³C NMR spectrum of NH₂-t-PE (1,2-Dichlorobenzene-d4)



Figure S14 ¹³C NMR spectrum of PE-*b*-PEG (1,2-Dichlorobenzene-d4)



Figure S15 ¹³C NMR spectrum of TMS-t-PE (1,2-Dichlorobenzene-d4)



Figure S16 ¹³C NMR spectrum of PE-S-OH (1,2-Dichlorobenzene-d4)



Figure S17 ¹³C NMR spectrum of AO-t-PE (1,1,2,2-Tetrachloroethane-D2)



Figure S18 FT-IR spectrum of e-PE

Peaks: a $(3040 \text{ cm}^{-1}) \text{ C-H}$ (in epoxy group) stretching, b (2918 cm^{-1}) and c (2849 cm^{-1}) C-H stretching, d $(1470 \text{ cm}^{-1}) \text{ C-H}$ bending (CH_2) , e (914 cm^{-1}) and f $(848 \text{ cm}^{-1}) \text{ C-O-C}$ (in epoxy group) stretching, h $(719 \text{ cm}^{-1}) \text{ C-C}$ out of plane bending



Figure S19 FT-IR spectrum of 2-hydroxy PE

Peaks: a (3363 cm^{-1}) O-H stretching, b (2918 cm^{-1}) and c (2849 cm^{-1}) C-H stretching, d (1473 cm^{-1}) C-H bending (CH_2) , e (1376 cm^{-1}) C-H bending (CH_3) , f (1133 cm^{-1}) C-O

stretching, g (719cm⁻¹) C-C out of plane bending



Figure S20 FT-IR spectrum of chloro-t-PE

Peaks: a (3405 cm^{-1}) O-H stretching, b (2918 cm^{-1}) and c (2849 cm^{-1}) C-H stretching, d (1473 cm^{-1}) C-H bending (CH₂), e (1066 cm^{-1}) C-O stretching, f (719 cm^{-1}) C-C out of plane bending



Figure S21 FT-IR spectrum of azide-t-PE

Peaks: a (3388 cm⁻¹) O-H stretching, b (2918 cm⁻¹) and c (2848 cm⁻¹) C-H stretching, d (2104 cm⁻¹) N=N=N stretching, e (1462 cm⁻¹) C-H bending (CH₂), f (1274 cm⁻¹), g (1084 cm⁻¹) C-O and C-N stretching, h (719cm⁻¹) C-C out of plane bending



Figure 22 FT-IR spectrum of carboxy-t-PE

Peaks: a (3500-3100 cm⁻¹) Hydroxyl (left, broad) and carboxyl (right, sharp) O-H stretching, b (2918 cm⁻¹) and c (2849 cm⁻¹) C-H stretching, d (1678 cm⁻¹) C=O stretching, e (1614 cm⁻¹) C=C (Aromatic) stretching, f (1490-1450 cm⁻¹) C-H bending & C=C (Aromatic) stretching (CH₂), g (1300-1100 cm⁻¹) C-O stretching, h (750-710 cm⁻¹) C-C out of plane bending & C-H (Aromatic) out of plane bending



Figure S23 FT-IR spectrum of sulfo-t-PE

Peaks: a (3387 cm^{-1}) O-H stretching, b (2918 cm^{-1}) and c (2849 cm^{-1}) C-H stretching, d (1473 cm^{-1}) C-H bending (CH₂), e (1377 cm^{-1}) O=S=O asymmetrical stretching, f (1158 cm^{-1}) O=S=O symmetrical stretching, e (1072 cm^{-1}) C-O stretching, h (719 cm^{-1}) C-C out of plane bending



Figure S24 FT-IR spectrum of diol-PE

Peaks: a (3383 cm⁻¹) O-H stretching, b (2918 cm⁻¹) and c (2849 cm⁻¹) C-H stretching, d

 $(1473 \text{ cm}^{-1}) \text{ C-H}$ bending (CH₂), e $(1072 \text{ cm}^{-1}) \text{ C-O}$ stretching, f $(719 \text{ cm}^{-1}) \text{ C-C}$ out of

plane bending



Figure S25 FT-IR spectrum of NH₂-t-PE

Peaks: a (3295 cm⁻¹, broad) O-H & N-H stretching, b (2918 cm⁻¹) and c (2849 cm⁻¹) C-H stretching, d (1576 cm⁻¹) N-H bending, e (1473 cm⁻¹) C-H bending (CH₂), f (1319 cm⁻¹) C-N stretching, g (1126 cm⁻¹) C-O stretching , h (719cm⁻¹) C-C out of plane bending



Figure S26 FT-IR spectrum of PE-b-PEG

Peaks: a (3480 cm⁻¹) O-H stretching, b (2917 cm⁻¹) and c (2848 cm⁻¹) C-H stretching,

d (1470 cm⁻¹) C-H bending (CH₂), e (1114cm⁻¹) C-O-C stretching



Figure S27 FT-IR spectrum of TMS-t-PE

Peaks: a (2918 cm⁻¹) and b (2849cm⁻¹) C-H stretching, c (1470 cm⁻¹) C-H bending (CH₂), d (1088 cm⁻¹) C-O stretching, e (816 cm⁻¹) Si-O symmetric stretching vibration in Si-O-C structure (?), f (719 cm⁻¹) C-C out of plane bending



Figure S28 FT-IR spectrum of PE-S-OH

Peaks: a (3373 cm^{-1}) O-H stretching, b (2918 cm^{-1}) and c (2849 cm^{-1}) C-H stretching, d (1472 cm^{-1}) C-H bending (CH₂), e (1048 cm^{-1}) C-O stretching, f (719 cm^{-1}) C-C out of plane bending



Figure S29 FT-IR spectrum of AO-t-PE

Peaks: a (3647 cm⁻¹) phenolic hydroxyl O-H stretching, b (2918 cm⁻¹) and c (2849 cm⁻¹)

C-H stretching, d (1740 cm⁻¹) C=O (ester) stretching, e (1473 cm⁻¹) C-H bending (CH₂), f (1159 cm⁻¹) C-O stretching, i (719cm⁻¹) C-C out of plane bending



Figure S30 GPC curves of v-PE1, e-PE and TMS-t-PE



Figure S31 GPC curves of e-PE, 2-hydoxy-PE, chloro-t-PE and azide-t-PE



Figure S32 GPC curves of carbpxy-t-PE, sulfo-t-PE, diol-PE, NH₂-t-PE and PE-*b*-PEG



Figure S33 GPC curves of v-PE2, PE-t-OH, and AO-t-PE



Figure S34 DSC heating curves of Cef-PEs (all derived from v-PE1)



Figure S35 DSC heating curves of v-PE2, PE-S-OH, AO-t-PE