Electronic Supplementary Information

Green synthesis of well-defined linear poly(hydroxyl thioether) direct from epoxide in water†

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I. Experimental Section

Synthesis of monomers

Synthesis of 2-[4-(hydroxymethyl)-phenoxymethyl] epoxide (*p*HMPE). In a 500 mL round-bottomed flask equipped with a magnetic stirrer, 4-hydroxybenzyl alcohol (31.0 g, 0.25 mol), K_2CO_3 (69.0 g, 0.5 mol), and KI (8.3 g, 50 mmol) were dispersed into 200 mL of CH_3CN, and the mixture was heated to reflux for 2 h, then epichlorohydrin (46.0 g, 0.5 mol) was added dropwise to the mixture and stirred at 90 °C for further 12 h. Upon cooling, the reaction mixture was filtered, the solvent was removed from the filtrate, and 100 mL of CH_2Cl_2 was added to dissolve the solid residue. The solution was washed with distilled water (3×30 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The solid crude was purified by column chromatography on silica gel using PE/EA (2:3) as an eluent to afford the product ***p*HMPE** as a white powder (26.1 g, 58%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.23-7.21(d, 2H, *phenyl*), 6.91-6.90 (d, 2H, *phenyl*), 5.07-5.04 (t, 1H, PhCH$_2$O*H*), 4.43-4.41 (d, 2H, OPhC*H*$_2$OH), 4.30-4.28 and 3.82-3.79 (d, 2H, CHC*H*$_2$OPh), 3.32 (s, 1H, CH$_2$OC*H*CH$_2$), 2.84-2.82 and 2.71-2.69 (d, 2H, C*H*$_2$OCH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.57, 135.38, 128.37, 114.55, 69.37, 62.97, 50.21, 44.22. MS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{10}H_{12}O_3$ 203.0684, found: 203.0673. ATR-IR (cm^{-1}): 3329 and 3244 (ν_{O-H}), 2925 and 2868 (ν_{C-H}), 1608 and 1583 (ν_{Ph-H}), 1240 (ν_{Ph-O}), 1003 (ν_{C-O}).

Synthesis of 2-[4-(hydroxymethyl)-phenoxymethyl] thiirane (*p*HMPT). In a 25 mL of round-bottomed flask equipped with a magnetic stirrer, ***p*HMPE** (3.6 g, 20.0 mmol) and KSCN (3.88 g, 40.0 mmol) were dispersed into 10 mL of water, and the mixture containing a large amount of undissolved ***p*HMPE** was stirred at 5 °C for 2 d, which was then washed with water (10 mL) and the solid was dissolved in CH_2Cl_2 (30 mL). The solution was washed with distilled water (3×30 mL), and the organic layer was dried with Na_2SO_4,

filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using PE/EA (2:1) as an eluent to afford ***p*HMPT** as a white powder (2.1 g, 54%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.23-7.21 (d, 2H, *phenyl*), 6.91-6.90 (d, 2H, *phenyl*), 5.07-5.04 (t, 1H, PhCH$_2$O*H*), 4.43-4.41 (d, 2H, OPhC*H*$_2$OH), 4.15-4.12 and 3.99-3.95 (d, 2H, CHC*H*$_2$OPh) 3.34 (s, 1H, CH$_2$OC*H*CH$_2$), 2.66-2.64 and 2.45-2.43 (d, 2H, C*H*$_2$OCH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.45, 135.43, 128.39, 114.63, 72.57, 62.96, 32.82, 24.22. MS (ESI) *m/z*: [M+Na]$^+$ calcd. for $C_{10}H_{12}SO_2$ 219.0456, found: 219.0444. ATR-IR (cm^{-1}): 3329 and 3244 (ν_{O-H}), 2925 and 2868 (ν_{C-H}, alkyl), 1608-1583 (ν_{Ph-H}), 1240 (ν_{Ph-O}), 1003 (ν_{C-O}).

Synthesis of 2-[2-(hydroxymethyl)-phenoxymethyl] epoxide (*o*HMPE). In a 250 mL round-bottomed flask equipped with a magnetic stirrer, 2-hydroxybenzyl alcohol (6.2 g, 50 mmol), K_2CO_3 (13.8 g, 0.1 mol), and KI (1.7 g, 10 mmol) were dispersed into 80 mL of CH_3CN, epichlorohydrin (9.2 g, 0.1 mol) was then added dropwise after 1 h, and the reaction mixture was further refluxed at 90 ^{o}C for 12 h. Upon cooling, the reaction mixture was filtered, the solvent was removed from the filtrate, and 30 mL of CH_2Cl_2 was added to dissolve the solid residue. The solution was washed with distilled water (3×10 mL), the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using PE/EA (2:1) as an eluent to give ***o*HMPE** as colorless oil (5.6 g, 62%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.40-7.38 (d, 2H, *phenyl*), 7.21-7.19 (d, 2H, *phenyl*), 6.97-6.93 (m, 2H, *phenyl*), 5.0 (s, 1H, PhCH$_2$O*H*), 4.52 (s, 2H, PhC*H*$_2$OH), 4.33-4.30 and 3.88-3.85 (d, 2H, CHC*H*$_2$OPh), 3.34-3.32 (d, 1H, C*H*CH$_2$OPh), 2.85-2.83 and 2.73-2.71 (d, 2H, C*H*$_2$OCH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 155.44, 131.11, 128.02, 127.48, 121.01, 111.87, 69.27, 58.22, 50.29, 44.16.

Synthesis of 2-[3-(hydroxymethyl)-phenoxymethyl] epoxide (*m*HMPE). In a 250 mL round-bottomed flask equipped with a magnetic stirrer, 3-hydroxybenzyl alcohol (5.0 g, 40 mmol), K_2CO_3 (11.0 g, 80 mmol), and KI (1.3 g, 8 mmol) were dispersed into 50 mL of CH_3CN, and the mixture was heated to reflux for 1 h. Then epichlorohydrin (7.4 g, 80 mmol) was added dropwise into the mixture and stirred at 90 ^oC for futher 12 h. Upon cooling, the reaction mixture was filtered and the solvent was removed from the filtrate. The crude product was dissolved in 30 mL of CH_2Cl_2, washed with distilled water (3×10 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using PE/EA (2 : 1) as an eluent to afford ***m*HMPE** was obtained as colorless oil (4.6 g, 65%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.25-7.22 (t, 2H, *phenyl*), 6.92-6.89 (m, 2H, *phenyl*), 6.83-6.80 (d, 1H, *phenyl*), 5.20-5.18 (t, 1H, PhCH$_2$O*H*), 4.48-4.46 (d, 2H, PhC*H*$_2$OH), 4.32-4.29 and 3.82-3.79 (d, 2H, C*H*$_2$OCH), 3.33-3.31 (m, 1H, C*H*CH$_2$OPh), 2.85-2.83 and 2.72-2.70 (d, 2H, C*H*$_2$OCH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 158.68, 144.83, 129.62, 119.33, 113.00, 69.27, 63.20, 50.21, 44.22.

Synthesis of 2-[4-(hydroxyethyl)-phenoxymethyl] epoxide (*p*HEPE). In a 250 mL round-bottomed flask equipped with a magnetic stirrer, 4-hydroxyphenethyl alcohol (5.5 g, 40 mmol), K_2CO_3 (11.0 g, 80 mmol), and KI (1.3 g, 8 mmol) were dispersed into 60 mL of CH_3CN, and epichlorohydrin (7.4 g, 80 mmol) was then added dropwise to the mixture and further refluxed at 90 ^oC for 12 h. Upon cooling to room temperature, the reaction mixture was filtered and the solvent was removed from the filtrate. The crude product was dissolved in 30 mL of CH_2Cl_2, washed with distilled water (3×10 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure to get the crude product, which was purified by column chromatography on silica gel using PE/EA (5:1 to 1:1) as an eluent, affording ***p*HEME** as a white powder (5.2 g, 67%). ^{1}H NMR (500 MHz,

DMSO-d_6, ppm) δ 7.13-7.11 (d, 2H, *phenyl*), 6.87-6.85 (d, 2H, *phenyl*), 4.59 (t, 1H, $PhCH_2CH_2O\mathit{H}$) 4.28-4.26 and 3.80-3.76 (d, 2H, $CHC\mathit{H}_2OPh$), 3.56-3.53 (t, 2H, $CH_2C\mathit{H}_2OH$), 3.31-3.29 (m, 1H, $C\mathit{H}CH_2OPh$), 2.84-2.82 and 2.70-2.68 (d, 2H, $C\mathit{H}_2OCH$), 2.66-2.63 (d, 2H, $C\mathit{H}_2CH_2OH$). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.00, 132.26, 130.29, 114.69, 69.36, 62.87, 50.24, 44.22.

Synthesis of 2-[4-(2-methoxyethoxy)-phenoxymethyl] epoxide (*p*MEPE). In a 250 mL round-bottomed flask equipped with a magnetic stirrer, 4-(2-methoxyethoxy) phenol (3.4 g, 20 mmol), K_2CO_3 (5.5 g, 40 mmol), and KI (0.7 g, 4 mmol) were dispersed into 60 mL of CH_3CN, and epichlorohydrin (3.7 g, 40 mmol) was then added dropwise to the mixture and further refluxed at 90 ^oC for 12 h. Upon cooling to room temperature, the reaction mixture was filtered, and the solvent was removed from the filtrate to give solid crude product, which was dissolved in 20 mL of CH_2Cl_2, washed with distilled water (3×10 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using PE/EA (2:1) as an eluent to afford ***p*MEPE** as a white powder (3.1 g, 69%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 6.89-6,85 (m, 4H, *phenyl*), 4.25-4.22 and 3.77-3.74 (m, 2H, $CHC\mathit{H}_2OPh$), 4.02-4.00 (m, 2H, $PhOC\mathit{H}_2CH_2OCH_3$) 3.63-3.61 (m, 2H, $PhOCH_2C\mathit{H}_2OCH_3$), 3.32 (s, 1H, $C\mathit{H}CH_2OPh$), 3.30-3.28 (m, 3H, $PhOCH_2CH_2OC\mathit{H}_3$), 2.83-2.81 and 2.69-2.67 (d, 2H, $C\mathit{H}_2OCH$). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 153.21, 152.80, 115.89, 115.76, 70.95, 69.87, 67.74, 58.61, 50.28, 44.21. ATR-IR (cm^{-1}): 2970 ($\nu_{C–H}$, methyl), 2925 and 2868 ($\nu_{C–H}$, methylene), 1608 and 1583 (ν_{Ph-H}), 1225 (ν_{Ph-O}), 1003 (ν_{C-O}). MS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{12}H_{16}O_4$ 247.1138, found: 247.0947.

Synthesis of 2-[4-[(*tert*-butoxycarbonylamino)methyl]-phenoxymethyl] epoxide (*p*BAPE). A 250 mL round-bottomed flask was charged with 4-hydroxybenzylamine (6.2 g, 50 mmol) dissolved in 80 mL of CH_2Cl_2. Dibutyldicarbonate (10.9 g, 50 mmol) was

added to the solution and stirred at 25 °C for 5 h. The reaction mixture was washed with distilled water (3×20 mL) and the organic layer was dried with Na_2SO_4, filtered, then concentrated under reduced pressure, and a white solid was obtained (10.7 g, 96%). The white solid (10.7 g, 48 mmol) was directly dissolved in 100 mL of CH_3CN, K_2CO_3 (13.2 g, 96 mmol) and KI (1.6 g, 9.6 mmol) were added to this solution, and the mixture was heated to reflux for 1 h. Then, epichlorohydrin (8.8 g, 96 mmol) was added dropwise into the mixture and stirred at 90 ^oC for further 12 h. Upon cooling, the reaction mixture was filtered and the solvent was removed from the filtrate. The solid crude product was dissolved in 30 mL of CH_2Cl_2, washed with distilled water (3×10 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using PE/EA (2:1) as an eluent to afford ***p*BAPE** as a white powder (16.1 g, 60%). ^1H NMR (500 MHz, DMSO-d_6, ppm) δ 7.30 (s, 1H, $CH_2NHCOOC(CH_3)_3$), 7.16-7.14 (d, 2H, *phenyl*), 6.90-6.88 (d, 2H, *phenyl*), 4.30-4.27 and 3.81-3.78 (dd, 2H, $CHCH_2OPh$), 4.05-4.04 (d, 2H, $CH_2NHCOOC(CH_3)_3$), 3.32-3.30 (m, 1H, $CHCH_2OPh$), 2.84-2.82 and 2.70-2.69 (dd, 2H, CH_2OCH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.55, 156.21, 133.04, 128.72, 114.73, 78.15, 69.39, 50.20, 44.22, 43.26, 28.73. ATR-IR (cm^{-1}): 3450 (ν_{N-H}), 2995 and 2970 (ν_{C-H}, methyl), 2925 and 2868 (ν_{C-H}, methylene), 1608 and 1583 (ν_{Ph-H}), 1240 (ν_{Ph-O}), 1003 (ν_{C-O}). MS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{15}H_{21}NO_4$ 302.1569, found: 302.1365.

General cascade O-S ER/AAROP procedure

Cascade O-S ER/AAROP of epoxide with KSCN

Synthesis of poly(2-[4-(hydroxymethyl)-phenoxymethyl] thioether) (P*p*HMPT). In a 10 mL of Schlenk tube, 1 mL of water was added to disperse the powder monomer ***p*HMPE** (360 mg, 2.0 mmol) and dissolve KSCN (388 mg, 4.0 mmol), the mixture was stirred at 40 ^oC for 12 h, and the white viscous solid appeared gradually, which was washed

with distilled water and dissolved in 2 mL of DMF. Then, the solution was poured into an excess of water (40 mL) to separate out a white viscous precipitate, which was dissolved in DMF (2 mL) again, and the solution was added dropwise into EA (40 mL) to afford polythioether **P*p*HMPT** as a white solid (174.4 mg, 48%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.16-7.14 (d, *phenyl*), 6.82-6.80 (d, *phenyl*), 5.05-5.03 (s, 1H, PhCH$_2$O*H*), 4.38 (d, 2H, PhO*CH*$_2$OH), 4.14-4.12 and 4.07-4.05 (d, 2H, CH$_2$CHSC*H*$_2$OPh), 3.22 (s, 1H, CH$_2$C*H*SCH$_2$OPh), 3.02 (s, 2H, C*H*$_2$CHSCH$_2$OPh). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.43, 135.36, 128.34, 114.61, 69.65, 46.39, 33.97. ATR-IR (cm^{-1}): 3329 (ν_{O-H}), 2925 and 2868 (ν_{C-H}, alkyl), 2051 ($\nu_{C\equiv N}$), 1608 and 1583 (ν_{Ph-H}), 1240 (ν_{Ph-O}), 1003 (ν_{C-O}), 818 (ν_{C-S}).

When KSCN was replaced by Bu$_4$NSCN in the above case, the yield of **P*p*HMPT** was reached up to 85%.

Synthesis of poly(2-[2-(hydroxymethyl)-phenoxymethyl] thioether) (P*o*HMPT). A 10 mL of Schlenk tube was charged with monomer ***o*HMPE** (360 mg, 2.0 mmol) and KSCN (388 mg, 4.0 mmol), and 1 mL water was added. The mixture was stirred at 40 °C for 12 h, and the white viscous precipitate was produced. The solid was dissolved in DMF (2 mL), and then the solution was dropped into 40 mL of water for precipitation twice, affording polythioether **P*o*HMPT** (162.2 mg, 45%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.34-7.32 (d, 1H, *phenyl*), 7.12-7.10 (d, 1H, *phenyl*), 6.88-6.80 (d, 2H, *phenyl*), 4.96 (d, 1H, PhCH$_2$O*H*), 4.50-4.48 (d, 2H, PhC*H*$_2$OH), 4.17 and 4.05-4.01 (m, 2H, CH$_2$CHSC*H*$_2$OPh), 3.20 (s, 1H, CH$_2$C*H*SCH$_2$OPh), 3.01 (s, 2H, C*H*$_2$CHSCH$_2$OPh). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 154.80, 130.57, 127.61, 126.96, 120.48, 111.08, 68.75, 58.01, 46.07, 30.80.

Synthesis of poly(2-[3-(hydroxymethyl)-phenoxymethyl] thioether) (P*m*HMPT). The synthetic procedure was similar with that of **P*o*HMPT**, and **P*m*HMPT** was obtained

as a white viscous solid (165.7 mg, 46%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.17-7.15 (d, 1H, *phenyl*), 6.86-6.84 (d, 2H, *phenyl*), 6.72 (s, 1H, *phenyl*), 5.17-5.15 (d, 1H, PhCH$_2$O*H*), 4.43-4.41 (d, 2H, PhC*H*$_2$OH), 4.15 and 4.07 (d, 2H, CH$_2$CHSC*H*$_2$OPh), 3.23 (s, 1H, CH$_2$C*H*SCH$_2$OPh), 3.02 (s, 2H, C*H*$_2$CHSCH$_2$OPh). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 158.07, 144.25, 129.12, 118.88, 112.58, 69.06, 62.73, 45.80, 30.77.

Synthesis of poly(2-[4-(hydroxyethyl)-phenoxymethyl] thioether) (P*p*HEPT). A 10 mL of Schlenk tube was charged with monomer ***p*HEPE** (388 mg, 2.0 mmol) and KSCN (388 mg, 4.0 mmol), 1 mL water was added as a solvent. The mixture was stirred at 40 °C for 12 h, and the white viscous solid was obtained, which was dissolved in DMF (2 mL), and the solution was added into an excess of water (40 mL) to gain white viscous precipitate. The filtered precipitate was dissolved again in DMF (2 mL), and then dropped into EA (40 mL) to afford **P*p*HEPT** as a white viscous solid (221.1 mg, 57%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.03-7.01 (d, 2H, *phenyl*), 6.75-6.73 (m, 2H, *phenyl*), 4.59-4.57 (t, 1H, PhCH$_2$CH$_2$O*H*), 4.11 and 4.03-4.01 (m, 2H, CH$_2$CHSC*H*$_2$OPh), 3.53-3.51 (m, 2H, PhCH$_2$C*H*$_2$OH), 3.21 (s, 1H, CH$_2$C*H*SCH$_2$OPh), 3.00 (s, 1H, C*H*$_2$CHSCH$_2$OPh), 2.62-2.59 (t, 2H, PhC*H*$_2$CH$_2$OH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 156.84, 132.23, 130.24, 114.75, 69.64, 62.89, 46.39, 38.64, 33.97.

Synthesis of poly([2-hydroxymethyl] thioether) (PHMT). A 10 mL of Schlenk tube was charged with monomer **HME** (296 mg, 4.0 mmol), KSCN (776 mg, 8.0 mmol), and water (2 mL), and the solution was stirred at 40 °C for 1 h. After decanting the supernatant, the white viscous precipitate was obtained. The precipitate was dissolved in 2 mL of DMF, and then added to 40 mL of EA to afford polythioether **PHMT** as a white viscous solid (287.2 mg, 97%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 4.92 (s, 1H, CHSCH$_2$*OH*), 3.73-3.71 and 3.51-3.49 (m, 2H, CHSC*H*$_2$OH), 3.35 (s, 1H, CH$_2$C*H*SCH$_2$OH), 2.89-2,86 (d, 2H, C*H*$_2$CHSCH$_2$OH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 63.17, 46.40, 33.97. ATR-IR

(cm^{-1}): 3329 (ν_{O-H}), 2925 and 2868 (ν_{C-H}, alkyl), 2051 ($\nu_{S-C\equiv N}$).

Large-scale synthesis of poly([2-hydroxymethyl] thioether) (PHMT). In a 250 mL of round-bottomed flask equipped with a magnetic stirrer, **HME** (20.0 g, 0.27 mol) and KSCN (52.4 g, 0.54 mol) were dispersed in water (135 mL), and the solution was stirred at 40 °C for 12 h. After the reaction finished, the solid was separated and dissolved in DMF (30 mL), the solution was added to a large amount of water (600 mL) to obtain white precipitate, which was again dissolved in DMF (30 mL) and then added to 600 mL of EA to give polythioether **PHMT** (14.1 g, 71%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 4.92 (s, 1H, CHSCH$_2$*OH*), 3.73-3.71 and 3.51-3.49 (m, 2H, CHSC*H*$_2$OH), 3.35 (s, 1H, CH$_2$C*H*SCH$_2$OH), 2.89-2,86 (d, 2H, C*H*$_2$CHSCH$_2$OH). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 63.17, 49.46, 33.97.

Cascade O-S ER/AAROP of epoxide with KSCN and quaternary ammonium salt

Various cocatalysts were used for cascade O-S ER/AAROP. For example, in presence of TBAC, the reaction of ***p*HMPE** and KSCN was carried out as the presented conditions and procedures.

Synthesis of poly(2-[4-(hydroxymethyl)-phenoxymethyl] thioether) (P*p*HMPT) with cocatalyst TBAC. In 10 mL of Schlenk tube, the monomer ***p*HMPE** with hydroxyl group (360 mg, 2.0 mmol), KSCN (388 mg, 4.0 mmol), and TBAC (111.2 mg, 0.4 mmol) were dispersed into water (1 mL), and the mixture was stirred at 40 °C for 12 h. After cooling to room temperature, the white viscous solid was obtained, which was washed with distilled water, then dissolved in DMF (2 mL), and the solution was added to water (40 mL) for precipitation. Finally, the separated precipitate was again dissolved in DMF (2 mL), and then dropped into EA (40 mL) to afford polythioether **P*p*HMPT** (324.1 mg, 90%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.16-7.14 (d, 2H, *phenyl*), 6.82-6.80 (d, 2H, *phenyl*), 5.05-5.03 (s, 1H, PhOCH$_2$*OH*), 4.38 (d, 2H, PhO*CH*$_2$OH), 4.14-4.12 and 4.07-4.05 (d, 2H,

CH_2CHSCH_2OPh), 3.22 (s, 1H, CH_2CHSCH_2OPh), 3.02 (s, 2H, CH_2CHSCH_2OPh). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.43, 135.36, 128.34, 114.61, 69.65, 46.39, 33.97.

Synthesis of poly(2-[4-(2-methoxyethoxy)-phenoxymethyl] thioether) (P*p*MEPT). In 10 mL of Schlenk tube, the monomer ***p*MEPE** without hydroxyl group (448 mg, 2.0 mmol), KSCN (388 mg, 4.0 mmol), and TOAB (218.4 mg, 0.4 mmol) were dispersed into 1 mL of water. The mixture was stirred at 40 ^oC for 12 h, and the white viscous solid was formed, which was dissolved in THF (2 mL), and the solution was poured into an excess of water (40 mL) to gain white viscous solid. The precipitate was dissolved again in THF (2 mL), and then dropped into CH_3OH (40 mL) to afford **P*p*MEPT** as a white solid, which was dried under vacuum at 60 ^oC to a constant weight (358.5 mg, 80%). ^1H NMR (500 MHz, DMSO-d_6, ppm) δ 6.76-6.74 (d, 4H, *phenyl*), 4.06-3.96 (m, 4H, $CHSCH_2OPhOCH_2CH_2$), 3.58-3.56 (s, 2H, $CH_2CH_2OCH_3$), 3.27-3.25 (d, 3H, $CH_2CH_2OCH_3$), 3.19 (s, 1H, $CH_2CHSOPh$), 2.99 (s, 1H, CH_2CHSCH_2OPh). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 153.22, 152.62, 115.97, 115.66, 70.92, 70.14, 67.70, 58.60, 46.34, 33.95. ATR-IR (cm^{-1}): 2970 ($\nu_{C–H}$, methyl), 2925 and 2868 ($\nu_{C–H}$, methylene), 2051 ($\nu_{C\equiv N}$),1608 and 1583 (ν_{Ph-H}), 1003 (ν_{C-O}), 818 (ν_{C-S}).

Synthesis of poly(2-[4-[(*tert*-butoxycarbonylamino)methyl]-phenoxymethyl] thioether) (P*p*BAPT). A 10 mL of Schlenk tube was charged with the monomer ***p*BAPE** without hydroxyl group (558 mg, 2.0 mmol), KSCN (388 mg, 4.0 mmol), and TOAB (218.4 mg, 0.4 mmol), 1 mL water was added as a solvent. The mixture was stirred at 40 ^oC for 12 h, and the white viscous precipitate was produced. The solid was dissolved in THF (2 mL), and then the solution was dropped into 40 mL of water for precipitation. The precipitate was dissolved again in THF (2 mL), and then dropped into the solution of PE/EA = 10:1 (44 mL) to give **P*p*BAPT** as a white solid, which was dried under vacuum at 60 ^oC to a constant weight (479.8 mg, 86%). ^1H NMR (500 MHz, DMSO-d_6, ppm) δ 7.23-7.21

(s, 1H, CH_2NHCOO), 7.08-7.06 (d, 2H, *phenyl*), 6.78-6.76 (s, 2H, *phenyl*), 4.12-4.04 (m, 4H, $CHSCH_2OPhCH_2NH$), 3.22 (s, 1H, CH_2CHSCH_2OPh), 2.99 (s, 2H, CH_2CHSCH_2OPh), 1.38-1.27 (m, 9H, $COOC(CH_3)_3$). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.40, 156.18, 133.00, 128.70, 114.74, 78.13, 69.64, 46.34, 43.28, 33.95, 28.71. ATR-IR (cm^{-1}): 3340 (ν_{N-H}), 2970 (ν_{C-H}, methyl), 2925 and 2868 (ν_{C-H}, methylene), 2051 ($\nu_{C\equiv N}$), 1608 and 1583 (ν_{Ph-H}), 1003 (ν_{C-O}), 818 (ν_{C-S}).

Cascade O-S ER/AAROP of epoxide with Bu_4NSCN

Synthesis of poly(2-phenoxymethyl thioether) (PPMT). In a 10 mL of Schlenk tube, **PME** (150 mg, 1.0 mmol) and Bu_4NSCN (600 mg, 2.0 mmol) were dissolved in 0.5 mL of water, the mixture was stirred at 40 °C for 12 h, and the white viscous solid appeared as the reaction progressed. The solid was washed with water and dissolved in THF (1 mL), and the solution was added to water (40 mL) for precipitation. The obtained precipitate was again dissolved in THF (1 mL), and the solution was added dropwise into CH_3OH (40 mL) to afford polythioether **PPMT** as a white solid, which was dried under vacuum at 60 °C to a constant weight (93.4 mg, 62%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.17 (s, 2H, *phenyl*), 6.86-6.82 (d, 3H, *phenyl*), 4.08 (d, 2H, $CHSCH_2OPh$), 3.21 (s, 1H, CH_2CHSCH_2OPh), 2.99 (s, 2H, CH_2CHSCH_2OPh). ^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 158.49, 129.91, 121.30, 114.94, 69.54, 46.18, 33.97.

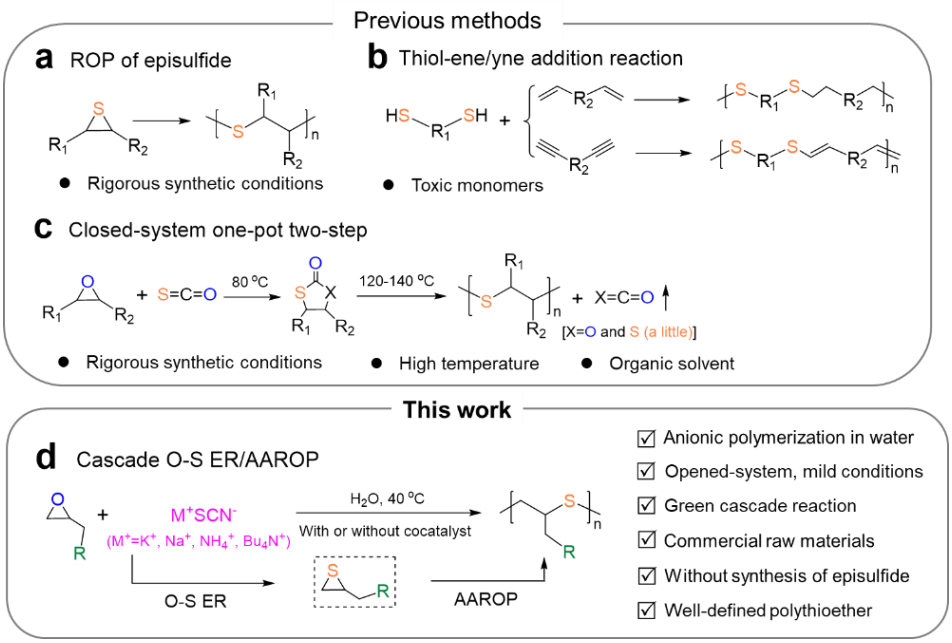
Chain end-capping and chain-extending reactions

Synthesis of poly(2-hydroxymethyl thioether) ethyl propionate (PHMT-EP). In a 10 mL Schlenk tube equipped with a magnetic stirrer, **HME** (296 mg, 4.0 mmol) and KSCN (776 mg, 8.0 mmol) were dissolved in water (2 mL) and the solution was stirred at 40 °C for 0.5 h, Next, HCl (0.2 mL) was added and stirred for further 0.5 h to terminate the reaction, affording the end-functionalized polythioether, **PHMT-SH**. Subsequently, excess ethyl acrylate (1 mL, 10.0 mmol) was added to the solution of purified **PHMT** in DMF (2

mL) and stirred at 30 °C for 12 h. After the reaction finished, the solution was added to water (40 mL) for precipitation, the white precipitate was dissolved in DMF (2 mL), and then dropped into EA (40 mL) to afford the end-capped polythioether **PHMT-EP** as a white solid (168.5 mg, 57%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 4.92 (s, CHSCH$_2$*OH*), 4.03-4.01 (d, SCH$_2$COOC*H*$_2$CH$_3$), 3.73-3.71 and 3.51-3.49 (m, CHSC*H*$_2$OH), 3.35 (s, CH$_2$C*H*SCH$_2$OH), 2.89-2,86 (d, C*H*$_2$CHSCH$_2$OH), 1.99 (s, SCH$_2$COOCH$_2$C*H*$_3$). ATR-IR (cm^{-1}): 3329 (ν_{O-H}), 2925 and 2868 ($\nu_{C-H,}$ alkyl), 2051 ($\nu_{C\equiv N}$), 1240 ($\nu_{C=O}$ of ester).

Synthesis of block copolythioether. In a 10 mL Schlenk tube equipped with a magnetic stirrer, **HME** (22.6 mg, 0.3 mmol) and KSCN (356 mg, 3.7 mmol) were dissolved in water (0.5 mL) and the solution was stirred at 40 °C for 0.5 h. Next, ***p*HMPE** (275 mg, 1.5 mmol) was added to the reaction mixture and stirred at 40 °C for further 12 h, and the white viscous solid was precipitated out. The solid was washed with distilled water and dissolved in DMF (2 mL), the solution was dropped to water (40 mL) for precipitation. The precipitate was dissolved again in DMF (2 mL), and the solution was dropped to EA (40 mL) to give block polymer **PHMT**-*b*-**P*p*HMPT** as a white solid (210 mg, 91%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.16-7.14 (d, *phenyl*), 6.82-6.80 (d, *phenyl*), 5.05-5.03 (s, PhOCH$_2$O*H*+CHCH$_2$O*H*), 4.38 (d, PhO*CH*$_2$OH), 4.14-4.12 and 4.07-4.05 (d, CH$_2$CHSC*H*$_2$OPh), 3.73-3.71 and 3.51-3.49 (m, CHSC*H*$_2$OH), 3.22 (s, CH$_2$C*H*SCH$_2$OPh), 3.02-2.88 (s, CH$_2$CHSC*H*$_2$OPh+C*H*$_2$C*H*S). ATR-IR (cm^{-1}): 3329 (ν_{O-H}), 2925 and 2868 (ν_{C-H}, alkyl), 2051 ($\nu_{C\equiv N}$), 1608-1583 (ν_{Ph-H}), 1240 (ν_{Ph-O}), 1003 (ν_{C-O}), 818 (ν_{C-S}).

II. Supplementary Data and Discussion



Scheme S1 Synthetic methods to polythioethers. (a) ROP of episulfide. (b) Thiol-ene/yne click polymerization. (c) Reaction of COS and epoxide using organic base as catalyst. (d) Green cascade O-S ER/AAROP from epoxide direct to polythioether.

Note S1. Characteristics of epoxides and episulfides

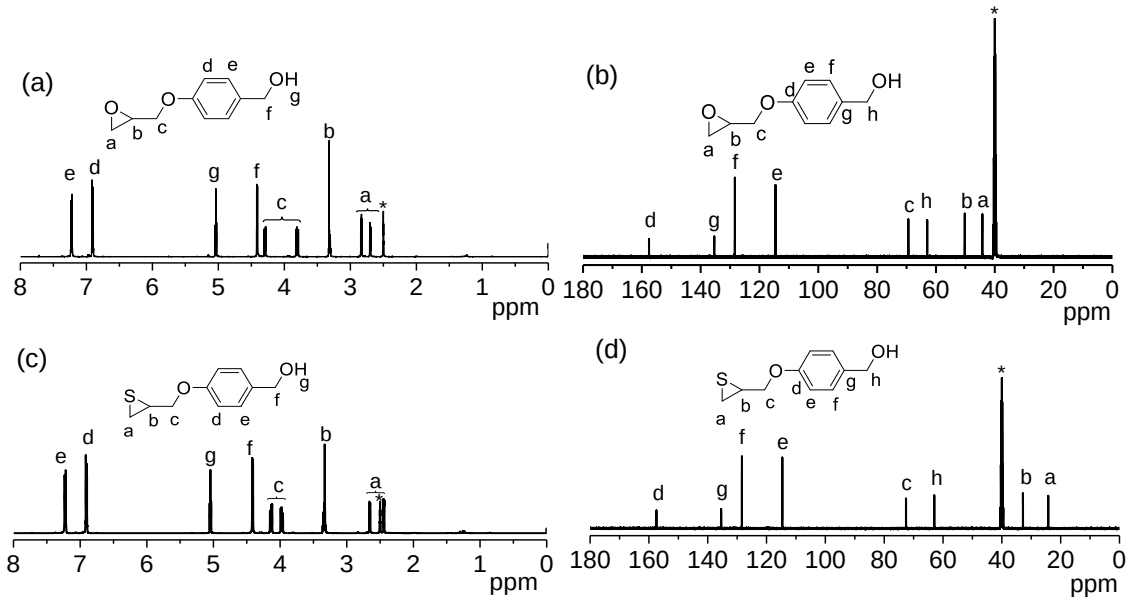


Fig. S1 ^{1}H (a,c) and ^{13}C (b,d) NMR spectra of ***p*HMPE** (a,b) and ***p*HMPT** (c,d) in DMSO-d_6.

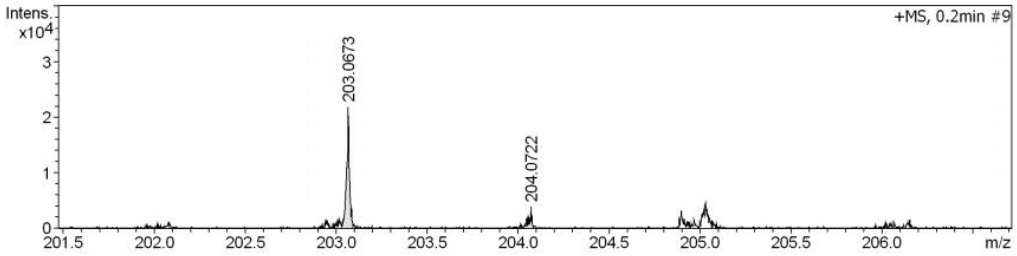


Fig. S2 ESI mass spectrum of ***p*HMPE**.

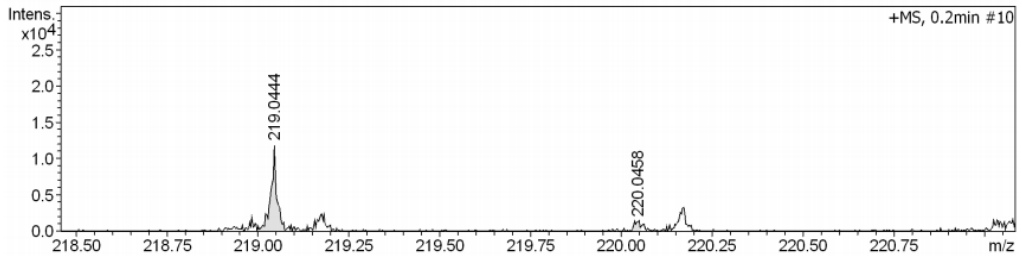


Fig. S3 ESI mass spectrum of ***p*HMPT**.

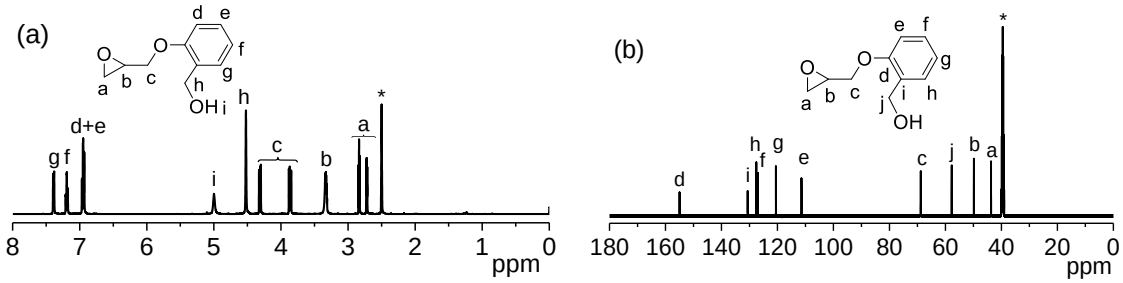


Fig. S4 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of ***o*HMPE** in DMSO-d_6.

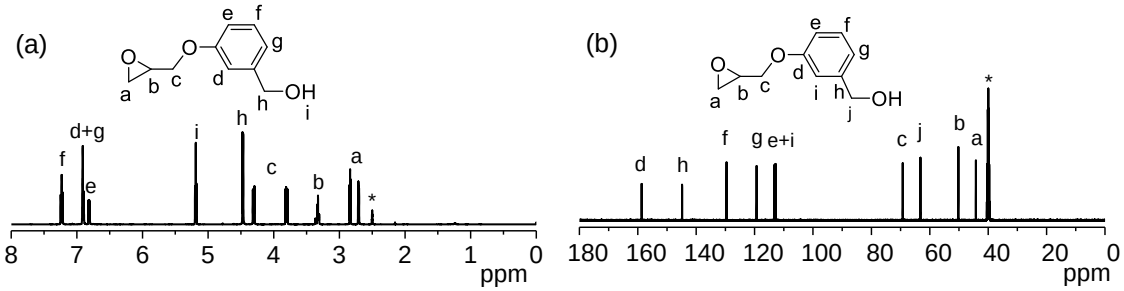


Fig. S5 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of ***m*HMPE** in DMSO-d_6.

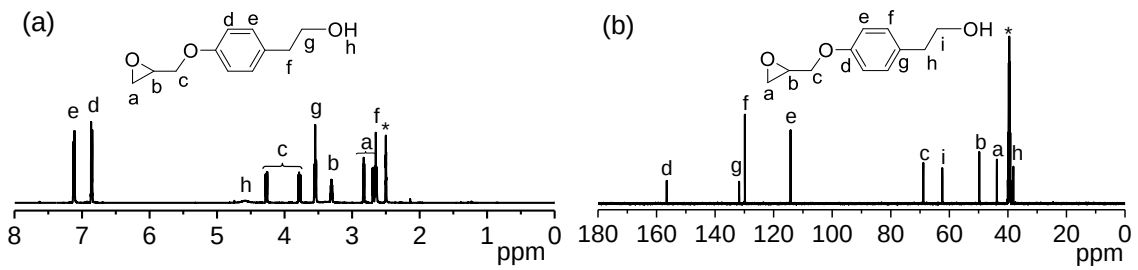


Fig. S6 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of ***p*HEPE** in DMSO-d_6.

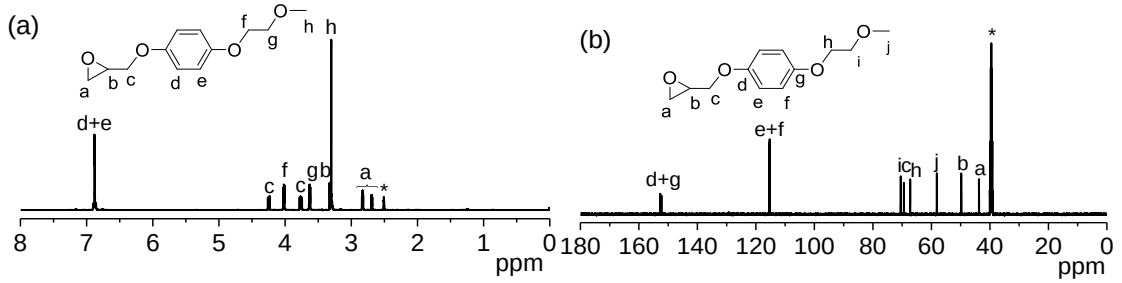


Fig. S7 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of ***p*MEPE** in DMSO-d_6.

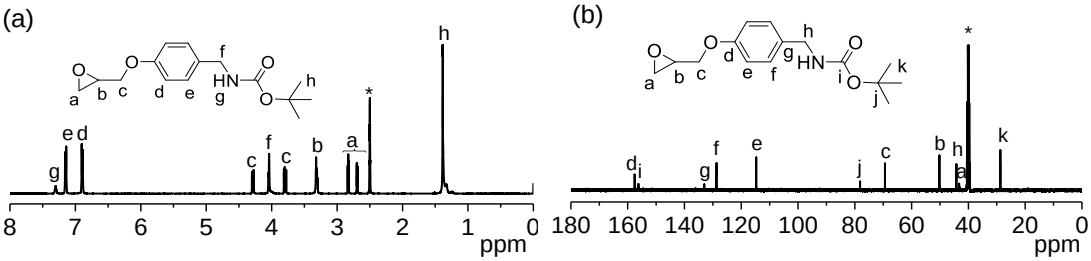


Fig. S8 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of ***p*BAPE** in DMSO-d_6.

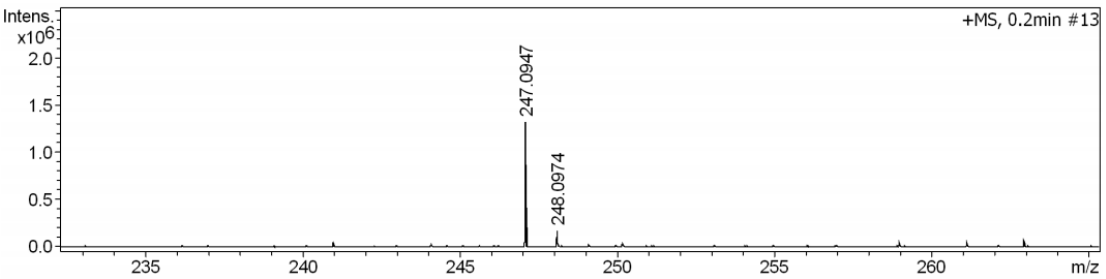


Fig. S9 ESI mass spectrum of ***p*MEPE**.

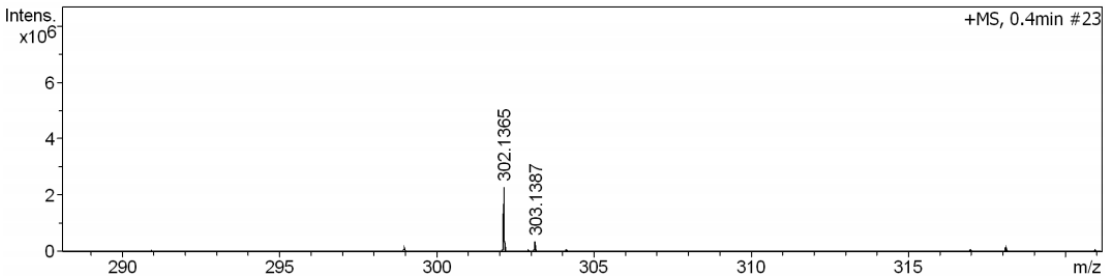


Fig. S10 ESI mass spectrum of ***p*BAPE**.

Note S2. Optimization of O-S ER/AAROP of ***p*HMPE** and KSCN/TBAC to **P*p*HMPT**

Table S1 Cascade O-S ER/AAROP of ***p*HMPE** and KSCN in the presence of TBAC[a]

Run	[***p*HMPE**]:[KSCN]:[TBAC] (molar ratios)	Time (h)	M_n[b] (kDa)	$Đ$[b] (M_w/M_n)	Yield (%)
1	1:2:0.05	12	9.2	1.16	78
2	1:2:0.2	12	10.2	1.15	90
3	1:2:1	12	11.2	1.18	95
4	1:2:0.2	2	5.1	1.14	18
5	1:2:0.2	4	8.3	1.18	45
6	1:2:0.2	8	9.6	1.17	79
7	1:2:0.2	24	10.8	1.19	93

[a]Polymerization conditions: using water as solvent, $[M]_0$ = 2 mol L^{-1} means dispersing 2 mmol of ***p*HMPE** in 1 mL of water, temperature = 40 °C. [b]Determined by GPC in THF, calibrated with polystyrene standards.

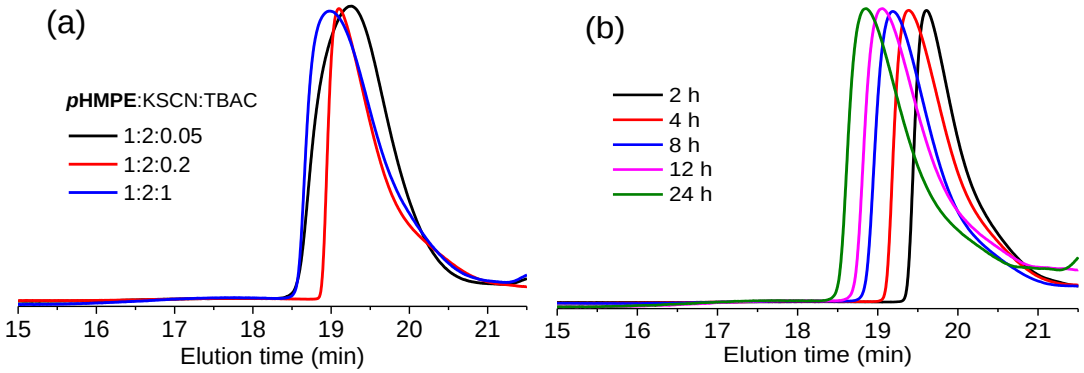


Fig. S11 GPC traces of **P*p*HMPT** prepared with different contents of TBAC (a) and with 0.2 eq TBAC at different time (b) using THF as eluent.

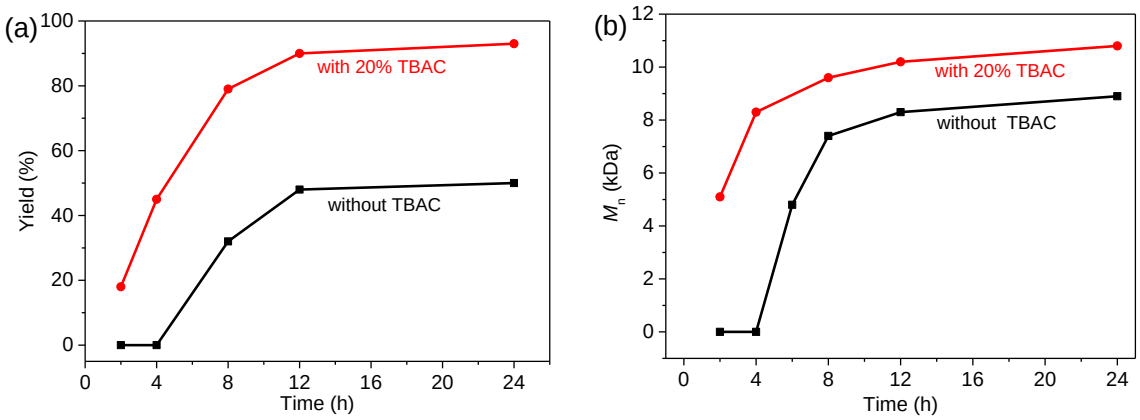


Fig. S12 Yield (a) and M_n (b) of ***Pp*HMPT** varied with reaction time at 40 °C.

Note S3. The pK_a values of different anions

Table S2 The p*K*a value of different anions

Anion	$\Delta_f H_m^\Theta$ (kJ mol^{-1}, 298.15 K)	$\Delta_f G_m^\Theta$ (kJ mol^{-1}, 298.15 K)	ΔG_2 (kJ mol^{-1}, 313.15 K)	pK_a (313.15 K)
$^-$SCN	76.44	92.71	93.53	15.6
I^-	-55.19	-51.57	-51.39	8.6
Br^-	-121.55	-103.96	-103.07	-17.2
Cl^-	-167.159	-131.228	-129.42	-21.6
OH^-	-229.99	-158.28	-154.67	-25.8

$\Delta_f H_m^\Theta$ is the standard molar enthalpy of formation, and $\Delta_f G_m^\Theta$ is the standard molar free energy of formation, both come from the standard thermodynamic list.

ΔG_2 was calculated according to equation 1:[1]

$$\frac{\Delta G_2}{T_2} - \frac{\Delta_f G_m^\Theta}{T_1} = \Delta_f H_m^\Theta \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (1)$$

T_1=298.15 K, T_2=313.15 K.

The pK_a values were calculated according to equation 2:

$$pK_a = \frac{\Delta G_2}{2.303RT} \quad (2)$$

where ΔG_2 (in kJ mol^{-1}) was the Gibbs free energy of difference anion in Table S2, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (313.15 K).

Note S4. GPC traces of **P*p*HMPT** prepared with various cocatalysts

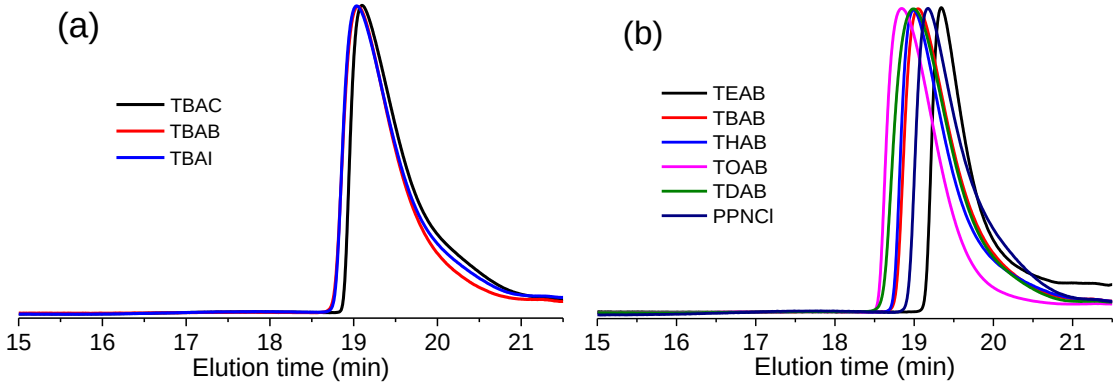


Fig. S13 GPC traces of **P*p*HMPT** prepared by adding various cocatalysts with different halogen anions (a) and different ammonium cations (b) using THF as eluent.

Note S5. GPC traces of polythioethers prepared by various monomers

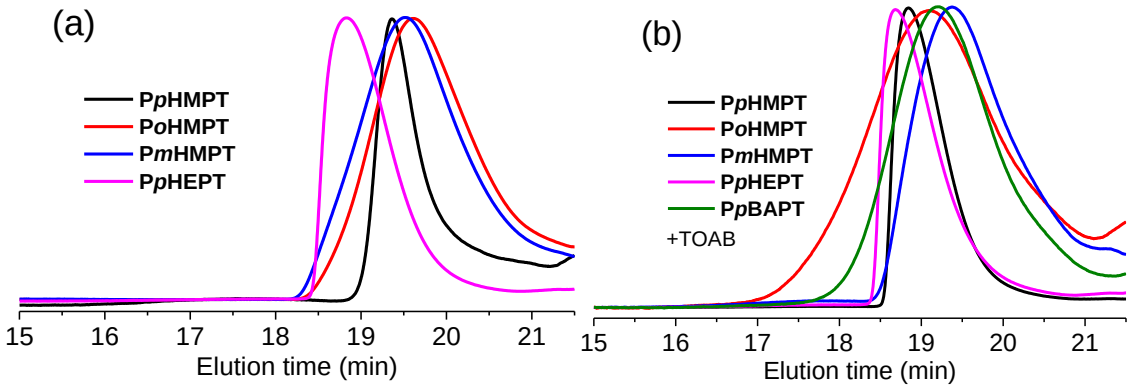


Fig. S14 GPC traces of various polythioethers without (a) and with (b) TOAB using THF as eluent.

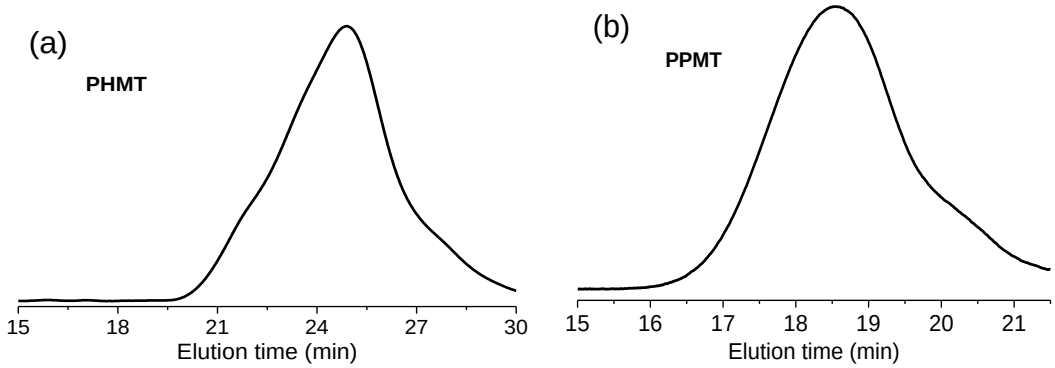


Fig. S15 GPC traces of **PHMT** using DMF as eluent (a) and **PPMT** using THF as eluent (b).

Table S3 Cascade O-S ER/AAROP or AAROP of different monomers with TBAT

Entry	monomer	[monomer]/[TBAT] (molar ratio)	M_n[a] (kDa)	$Đ$[a]	Yield (%)
1	***p*HMPE**	1 : 2	7.8	1.16	85
2	***p*HMPE**	1 : 1	crosslinked	/	/
3	***p*HMPE**	1 : 0.01	crosslinked	/	/
4	***p*HMPT**	1 : 1	6.4	1.13	87
5	***p*HMPT**	1 : 0.01	/	/	/
6	**PME**	1 : 2	12.8	1.62	62
7	**PME**	1 : 0.01	2.8	2.92	50
8	**PMT**	1 : 1	25.7	1.53	59
9	**PMT**	1 : 0.01	/	/	/

Reaction conditions: water as solvent, $[M]_0$ = 2 mol L^{-1} means dispersing 2 mmol of monomer in 1 mL of water, temperature = 40 °C. [a] Determined by GPC in THF, calibrated with polystyrene standards. $Đ$ = M_w/M_n.

Note S6. Dynamic monitoring cascade reaction by ^{1}H NMR spectroscopy

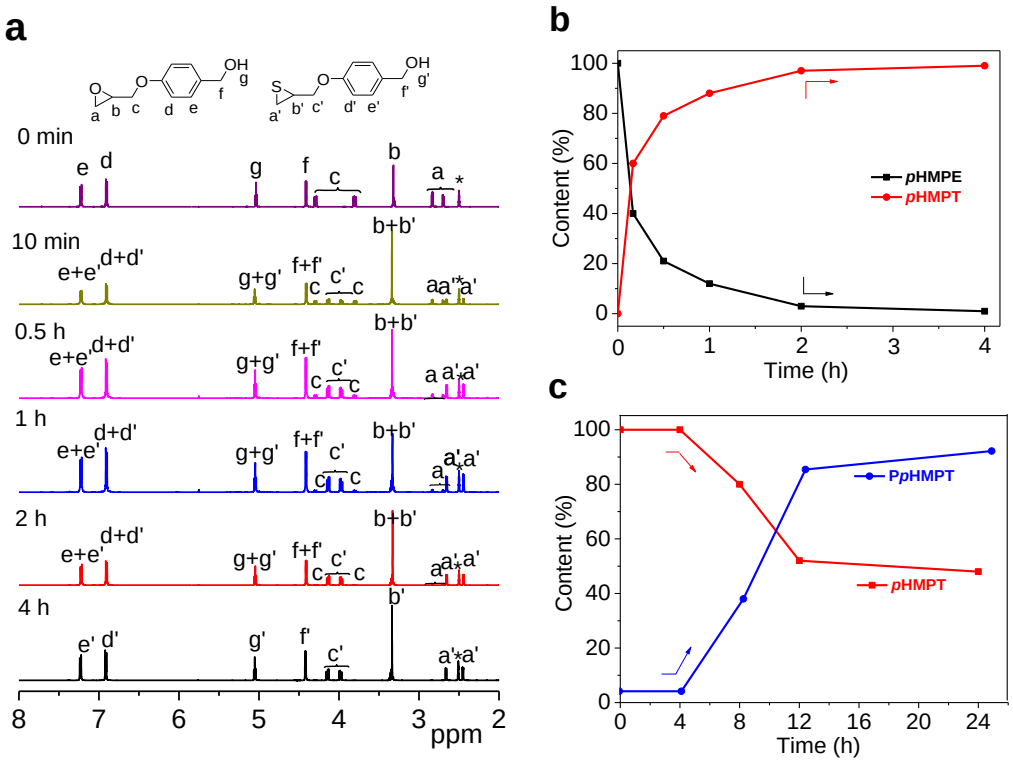


Fig. S16 (a) ^{1}H NMR spectra for monitoring the change of **pHMPE** to **pHMPT** within 4 h in DMSO-d_6. (b) Variation of **pHMPE** and **pHMPT** contents as reaction time within 4 h. (c) Variation of **pHMPT** and **PpHMPT** contents as reaction time within 24 h.

Additional support for the mechanism of cascade O-S ER/AAROP of **HME** and KSCN was provided by the *in-situ* ^{1}H NMR analysis. **HME** was rapidly consumed as revealed by the dramatic decrease in proportion from 100% to 65% within 5 min (Fig. S17). Meanwhile, the proportion of generated **HMT** was 35%, which increased to 45% after 10 min. Subsequently, **HMT** was rapidly consumed and the proportion decreased to 8%, while the proportion of generated **PHMT** was 47%. These results indicated that **PHMT** was produced by AAROP of the *in-situ* formed **HMT** when it reached a certain of concentration. Prolonging the reaction time to 40 min, the remained **HME** was 10% and no **HMT** residue was detected, because the generated **HMT** rapidly converted to **PHMT** (Fig. S18). Due to the better solubility of monomer, polymerization was completed within 1 h. Compared ^{1}H NMR spectrum of **PHMT** in Fig. 5e, the positions of proton peaks were obviously shifted toward higher field in Fig. S17, which could attribute to the presence of inorganic salt KSCN that affected shimming the magnetic field when *in situ* ^{1}H NMR monitoring the cascade O-S ER/AAROP process of **HME** and KSCN.

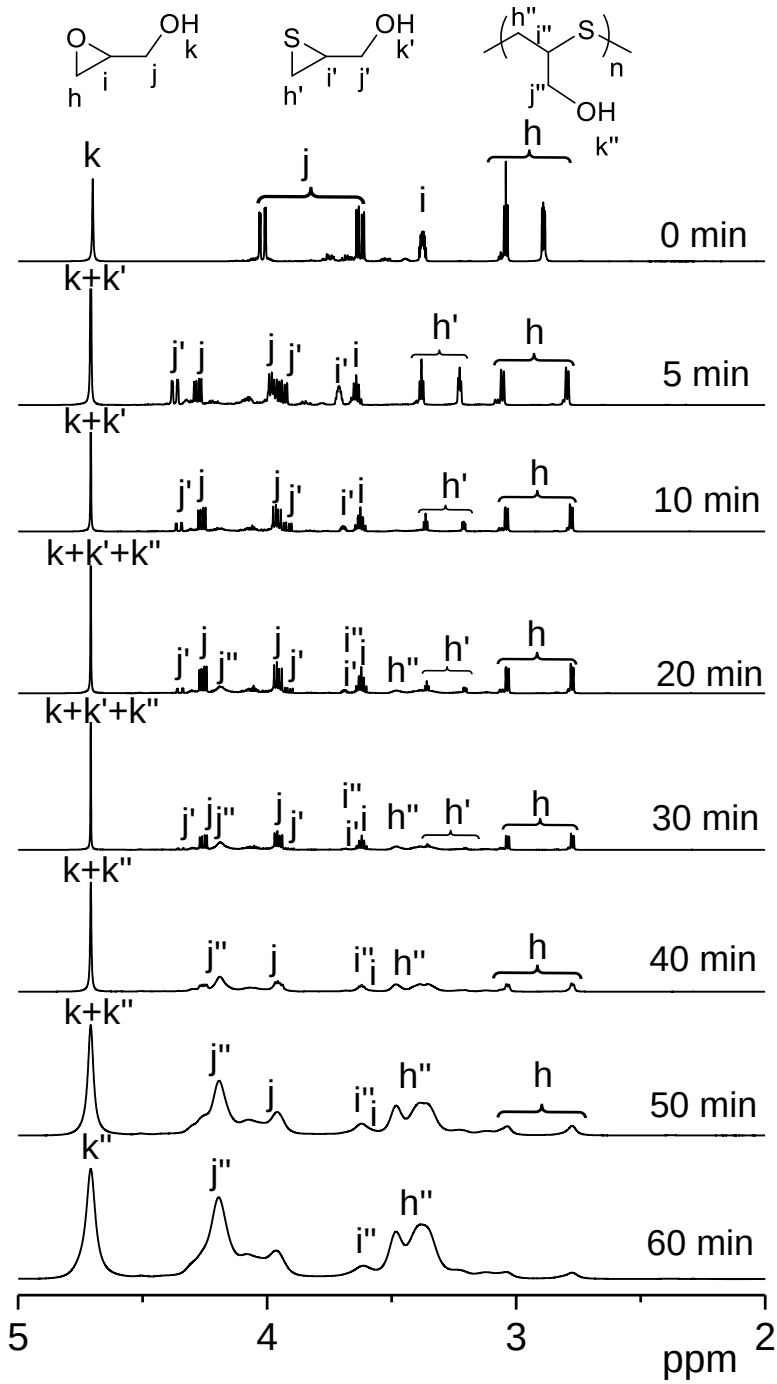


Fig. S17 *In-situ* ^{1}H NMR spectra of **HME**, **HMT**, and **PHMT** within 1 h in D_2O at 40 ^{o}C.

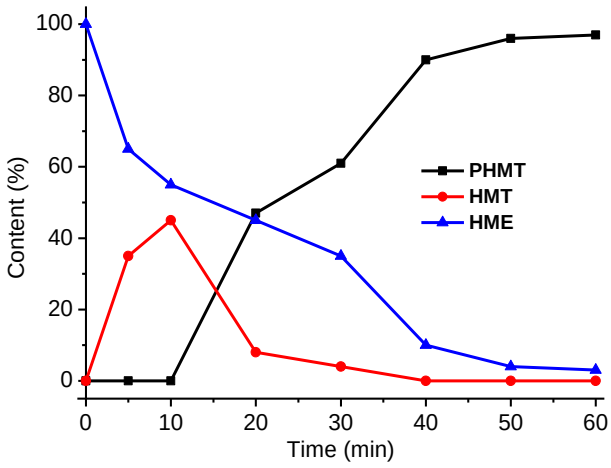


Fig. S18 Variation in the contents of **HME**, **HMT**, and **PHMT** with reaction time.

Note S7. Mimicking AAROP of intermediate episulfides

The cascade O-S ER/AAROP process was disassembled into plausible two stages, i.e. (A) O-S ER of epoxide with sulfo reagent (such as KSCN) to form episulfide, and (B) AAROP of episulfide initiated by sulfanion to afford well-defined polythioether, as shown in Fig. 1c. It is wonderful to find that reaction temperature is a key factor to control O-S ER/AAROP of epoxide containing hydroxyl group (***p*HMPE**) with KSCN detaining in the first stage by regulating temperature below 25 °C, which can effectively prevent proceeding to polythioether from AAROP of episulfide (route **i**), and the resultant episulfide ***p*HMPT** could be separated from the reaction mixture in good yield. With ***p*HMPT** in hand, AAROP of ***p*HMPT** in the presence of KSCN was investigated at 40 °C. Unexpectedly, polymerization did not occur (Table S4), which was contrary to the real-time procedure in cascade reaction. This result might due to the deviated apparent chemical circumstance in the mimicked second stage from the actual cascade reaction process. Astonishingly, the pH value of water in the mimicked second stage for plausible AAROP of ***p*HMPT** (pH≈7) was much lower than that in the cascade reaction process starting from ***p*HMPE** (pH≈13), simply tested by the pH indicator strips (Fig. 4a). Although the pH value of water for O-S

ER of ***p*HMPE** with KSCN (route **i**) was also up to 13, AAROP of the formed ***p*HMPT** could not be performed below 25 ^{o}C. Furthermore, automatically monitoring the pH value variation in the cascade O-S ER/AAROP process of **HME** was carried out (Movie S1), which showed that the pH value rapidly increased from 7 to 13 in 2 min as the addition of **HME** to KSCN aqueous solution, and then maintained high pH value in the whole cascade reaction procedure (Fig. 4b). Unlike the fictitious AAROP of ***p*HMPT** at the mimicked second stage with low pH value, the rapidly increased pH value at the O-S ER stage created a strong alkaline circumstance that attributed to the generated $^{-}$OH by hydrolysis of ring-opened oxyanion,[2] and this is yet another key factor to trigger subsequent AAROP reaction of intermediate episulfide (such as ***p*HMPT**). The difference in the pH value of water can roughly estimate the cascade reaction, for example, cascade O-S ER/AAROP of ***p*HMPE** in the presence of KSCN or NaSCN with higher pH value (pH≈13) exhibited better performance than that of NH_4SCN (pH≈11) (Table 1), which manifested that the existence of $^{-}$SCN is essential for cascade O-S ER/AAROP. On the basis of this discovery, AAROP of episulfide ***p*HMPT** was initially attempted by KSCN (pH≈7), using appropriate amount of KOH as alkaline reagent (pH≈13), or Lewis base TBAC (pH≈7), but polymerization failed relying on just strong alkalinity and only KSCN or TBAC in water at 40 ^{o}C (Table S4), meaning that solely KSCN, OH^- (pK_a = -25.8), or TBAC can not initiate AAROP of ***p*HMPT**. Subsequently, we tried to simulate the chemical circumstance (pH≈13) in one-pot cascade reaction by adding KSCN as initiator and KOH as alkaline reagent to the opened-system for AAROP of ***p*HMPT** under the same conditions. Surprisingly, **P*p*HMPT** was indeed formed with M_n of 8.2 kDa in 56% yield at [***p*HMPT**]/[KSCN]/[KOH] of 1:1:0.1 (route **ii**, Table S4), demonstrating that sufficient alkalinity would effectively enhance the nucleophilicity of anion, which is no doubt vital for AAROP.[2] If the proportion of KSCN decreased to 0.01, AAROP of ***p*HMPT** still proceeded reasonably to produce

P*p*HMPT (Table S4), demonstrating that KSCN was initiator for AAROP and excessive KSCN was mainly to ensure the completion of O-S ER of epoxides while no negative effect on AAROP. When inorganic base KOH was switched to organic base TBAC, AAROP of ***p*HMPT** was also performed successfully to yield **P*p*HMPT** with M_n of 6.7 kDa in 50% yield (route **ii**, Table S4), but could not be conducted at 25 °C (Table S4) even if other conditions are the same as above. Different from KOH, TBAC bearing bulky ammonium cation promoted AAROP of ***p*HMPT** mainly by improving the solubility of monomer and enhancing the nucleophilicity of anion $^-$SCN.[3] Certainly, Bu_4SCN (pH≈7) exhibited more effect on AAROP of ***p*HMPT** than the combinant of KSCN and TBAC, which afforded **P*p*HMPT** with high yield of 87% (route **ii**, Table S4), and Bu_4SCN even effectively underwent the cascade O-S ER/AAROP of **PME** without hydroxyl group (Fig. 1d), but the mixture of KSCN and TBAC can not. Therefore, strong inorganic base or bulky ammonium cation could enhance the nucleophilicity of anion $^-$SCN to facilitate polymerization. Briefly, both strong nucleophilicity and appropriate temperature are two decisive factors for cascade O-S ER/AAROP of epoxide.

Table S4 AAROP of ***p*HMPT** under different conditions[a]

Run	[***p*HMPT**]/[KSCN]/[KOH]/[TBAC]	M_n[b] (kDa)	$Đ$[b] (M_w/M_n)	Yield (%)
1	1 : 1 : 0 : 0	/	/	/
2	1 : 0 : 0.1 : 0	/	/	/
3	1 : 0 : 0 : 0.2	/	/	/
4	1 : 1 : 0.1 : 0	8.2	1.11	56
5	1 : 0.01 : 0.1 : 0	6.3	1.19	48
6	1 : 1 : 0 : 0.2	6.7	1.12	50
7[c]	1 : 1 : 0 : 0.2	/	/	/
8[d]	1 : 0 : 0 : 0	6.4	1.13	87

[a]Polymerization conditions: using water as solvent, $[M]_0$ = 2 mol L^{-1} means dispersing 2 mmol of monomer in 1 mL of water, temperature = 40 °C, reaction time = 12 h. [b]Determined by GPC in THF, calibrated with polystyrene standards. [c]Reaction temperature = 25 °C. [d][***p*HMPT**]/[Bu_4NSCN] = 1:1.

Note S8. Characterization of **P*p*HMPT** and **PHMT** by NMR and IR

To reveal the backbone structure of the synthesized polythioethers, elemental analysis of **P*p*HMPT**, **PHMT**, and **PPMT** was performed. The contents of C、H, and S were measured by Vario EL Cube, and the content of O was measured by Flash Smart. As shown in Table S5, the measured contents of C, H, S, and O in polythioethers were close to those calculated from the optimum structures. Of significance, the deviation of sulfur contents between the determined values by elemental analysis and the calculated values in polythioethers was 0.1~0.2%, indicating the produced polythioethers with highly pure thioether repeat units but without the mixed ether repeat units on the backbone.

Table S5 Elemental analysis data of polythioethers

Polythioether	C_{found} (%)	H_{found} (%)	S_{found} (%)	O_{found} (%)	C_{calcd}[a] (%)	H_{calcd}[a] (%)	S_{calcd}[a] (%)	O_{calcd}[a] (%)
PHMT	32.97	6.37	29.22	16.52	32.92	6.40	29.26	14.63
PPMT	63.28	6.42	18.7	10.20	63.22	6.43	18.73	9.37
P*p*HMPT	58.56	6.33	15.58	16.88	58.57	6.35	15.62	15.62

[a]Element content calculated from the structure of thioether units.

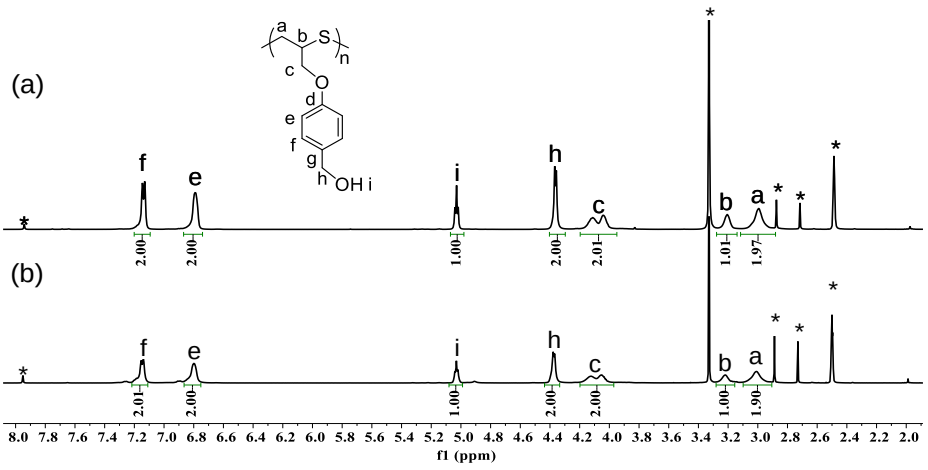


Fig. S19 ^{1}H NMR spectra of **P*p*HMPT** by cascade O-S ER/AAROP from ***p*HMPE** (a) and AAROP of ***p*HMPT** (b) in DMSO-d_6.

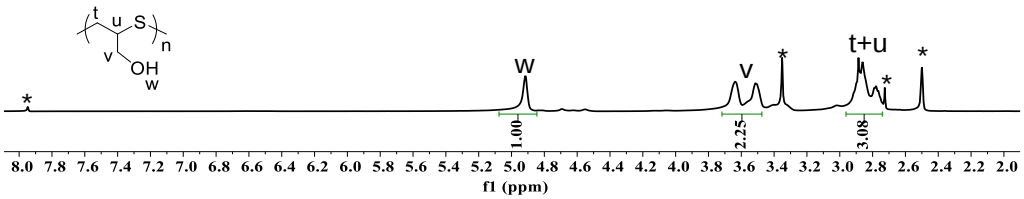


Fig. S20 ^{1}H NMR spectrum of **PHMT** in DMSO-d_6.

In ^{13}C NMR spectrum of **P*p*HMPT** (Fig. S21), a peak signal belonging to the carbon on -SCN (C_i) was located at 129.85 ppm,[4] and of significance, compared to ***p*HMPE** and ***p*HMPT**, the stretching vibration band attributed to the new included S-C≡N in the end of **P*p*HMPT** backbone was observed at 2051 cm^{-1} in FT-IR spectrum (Fig. S22),[5] suggesting that SCN$^-$ attacked methylene on thiirane ring of ***p*HMPT** to generate the ring-opened sulfanion and form C-S bond in the other end, which is consistent with the proposed polymerization mechanism. The characteristic peaks of aromatic ring (Ph-H) at 1608-1583 cm^{-1}, ether bond (Ph-O and C-O) at 1240 cm^{-1} and 1003 cm^{-1}, and C-S bond at 818 cm^{-1} were observed, attesting to the presence of phenyl group and polysulfide linkage in **P*p*HMPT**. In addition, the characteristic O-H stretching bands appeared at 3329 cm^{-1} in FT-IR spectra of ***p*HMPE**, ***p*HMPT**, and **P*p*HMPT**, indicating the successful reservation of hydroxyl group on side chain of polymers.

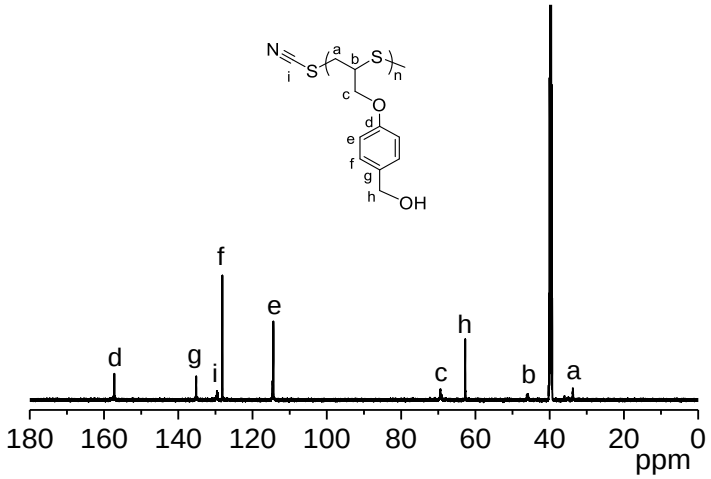


Fig. S21 ^{13}C NMR (150 MHz) spectrum of **P*p*HMPT** (M_n=4.8 kDa) when the coherent accumulation number added up to 1024 in DMSO-d_6.

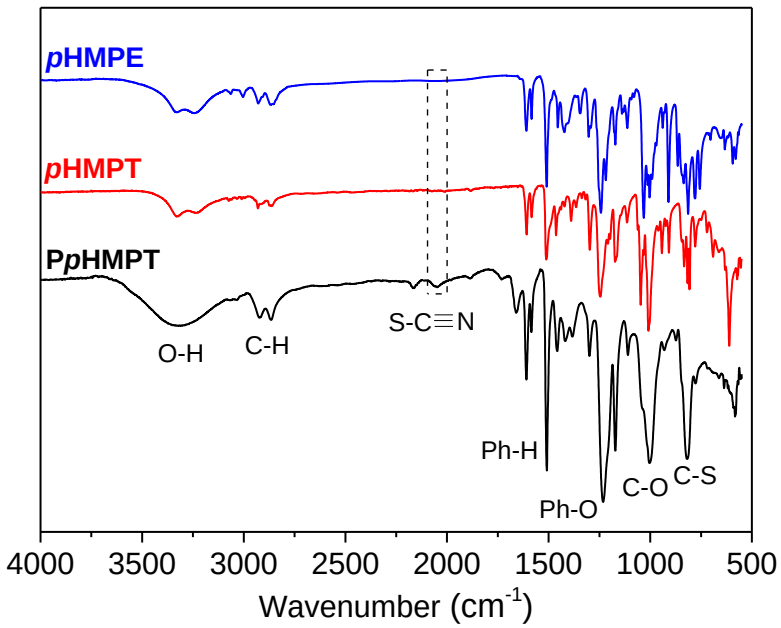


Fig. S22 FT-IR spectra of ***p*HMPE**, ***p*HMPT**, and **P*p*HMPT**.

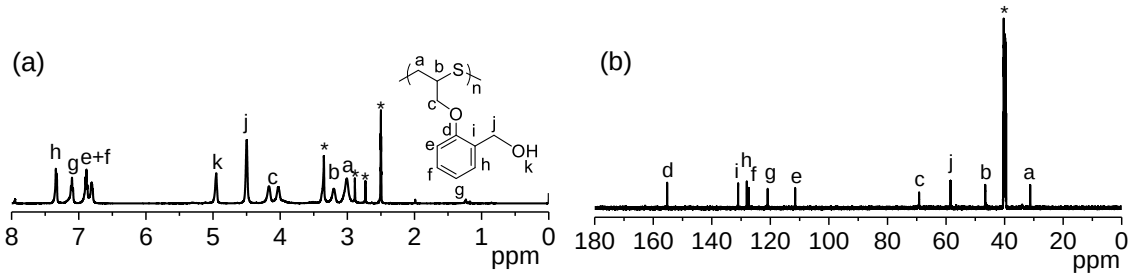


Fig. S23 ^{1}H (a) and ^{13}C (b) NMR spectra of **P*o*HMPT** in DMSO-d_6.

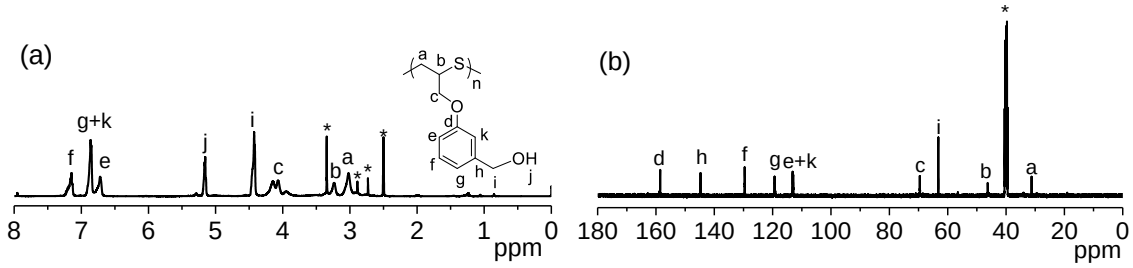


Fig. S24 ^{1}H (a) and ^{13}C (b) NMR spectra of **P*m*HMPT** in DMSO-d_6.

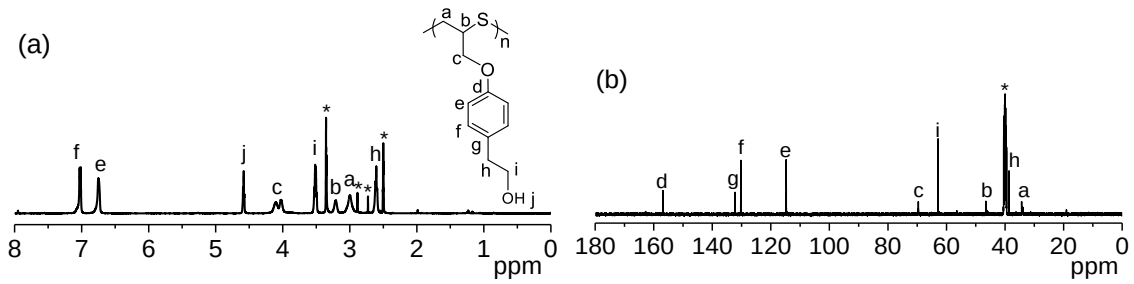


Fig. S25 ^{1}H (a) and ^{13}C (b) NMR spectra of **P*p*HEPT** in DMSO-d_6.

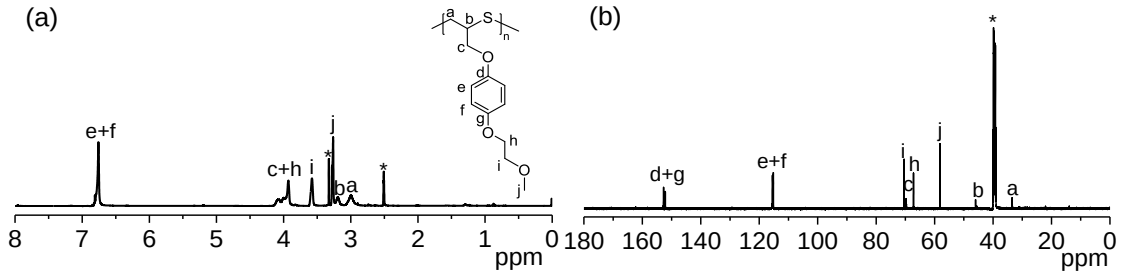


Fig. S26 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of **P*p*MEPT** in DMSO-d_6.

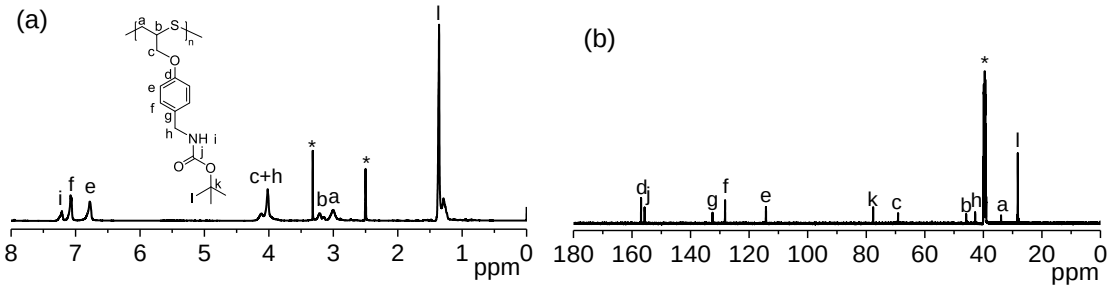


Fig. S27 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of **P*p*BAPT** in DMSO-d_6.

Note S9. End-capping and chain-extending reactions

Cascade O-S ER/AAROP was carried out from **HME** and KSCN at 40 °C in aqueous medium. After 0.5 h, HCl was added and stirred for another 0.5 h to terminate the reaction. Subsequently, the purified **PHMT-SH** was used to react with excess ethyl acrylate in DMF for 12 h at 30 °C, and an end-capped **PHMT-EP** was obtained (Fig. S28a), which was characterized by ^{1}H NMR spectroscopy. Compared to ^{1}H NMR spectrum of **PHMT**, new

signals at 4.04-4.00 (H_a) and 1.99-1.90 ppm (H_b) were observed in ^{1}H NMR spectrum of **PHMT-EP** (Fig. S28c), corresponding to the methylene and methyl protons in a terminal ethyl ester group, while no resonance appeared for the unsaturated H_2C=CH- protons of ethyl acrylate residue, meaning that the thiol active terminal on **PHMT-SH** was formed, and can be end-capped by ethyl acrylate. Hence, this strategy provides a simple method to prepare promising reactive polythioethers with one thiol end group. The degree of polymerization (DP) was calculated by the integrated intensity ratio of $S_d/(S_g/2) = 33$, and thus the molecular weight $M_{n,NMR}$ was 2.97 kDa. Furthermore, the characteristic peak at 1240 cm^{-1} for the C=O of ester group[6] on the end of **PHMT-EP** backbone was also observed in Fourier transform infrared (FT-IR) spectrum (Fig. S29), while no C=O vibration appeared in **PHMT**, demonstrating that the end of **PHMT** was successfully capped by ethyl propionate. Especially, the appearance of the solely absorption band at 2051 cm^{-1} for the vibration of S-C≡N[5] on the backbone of polythioethers further demonstrated the structure of an end group, suggesting that C-S bond formed at the initial end of polythioethers. To further confirm the living feature of AAROP, block copolymer **PHMT-*b*-P*p*HMPT** was synthesized by stepwise addition of **HME** and ***p*HMPE**, as shown in Fig. S28b. Firstly, **PHMT** was prepared by O-S ER/AAROP of **HME** and KSCN at 40 ^{o}C for 0.5 h. Next, ***p*HMPE** was added and stirred at 40 °C for 12 h, and **PHMT-*b*-P*p*HMPT** was obtained with predicted structure detected by ^{1}H NMR spectrum. As shown in Fig. S28c, by integrating the signals of methylene protons (H_c) at 3.63-3.51 ppm on **PHMT** segment and that of methylene protons (H_j) at 4.39 ppm on **P*p*HMPT** segment, the molar ratio of H_c/H_j was calculated to be 1:5, which was compliant with the **HME/*p*HMPE** feed ratio of 1:5, indicating that the well-defined block copolymer was achieved, and AAROP was conducted in a controlled manner. The structure of polysulfides was also verified by IR spectra (Fig. S29). The characteristic peak appeared at 3329 cm^{-1} assigned

to the O-H vibration in side chain, indicating the successful reservation of hydroxyl group on side chain of three polythioethers. The peak at 1608-1583 cm^{-1} belong to the aromatic ring (Ar-H) in IR spectrum of **PHMT**-*b*-**P*p*HMPT** were newly appeared compared to that of **PHMT**, implying that copolymer had phenyl group from **P*p*HMPT** block. The ether bonds at 1240 cm^{-1} (Ph-O) and 1003 cm^{-1} (C-O), and thioether bond (C-S) at 818 cm^{-1} were observed, attesting to the presence of associated groups in **PHMT** and **PHMT**-*b*-**P*p*HMPT**, and also confirmed the success of block copolymerization.

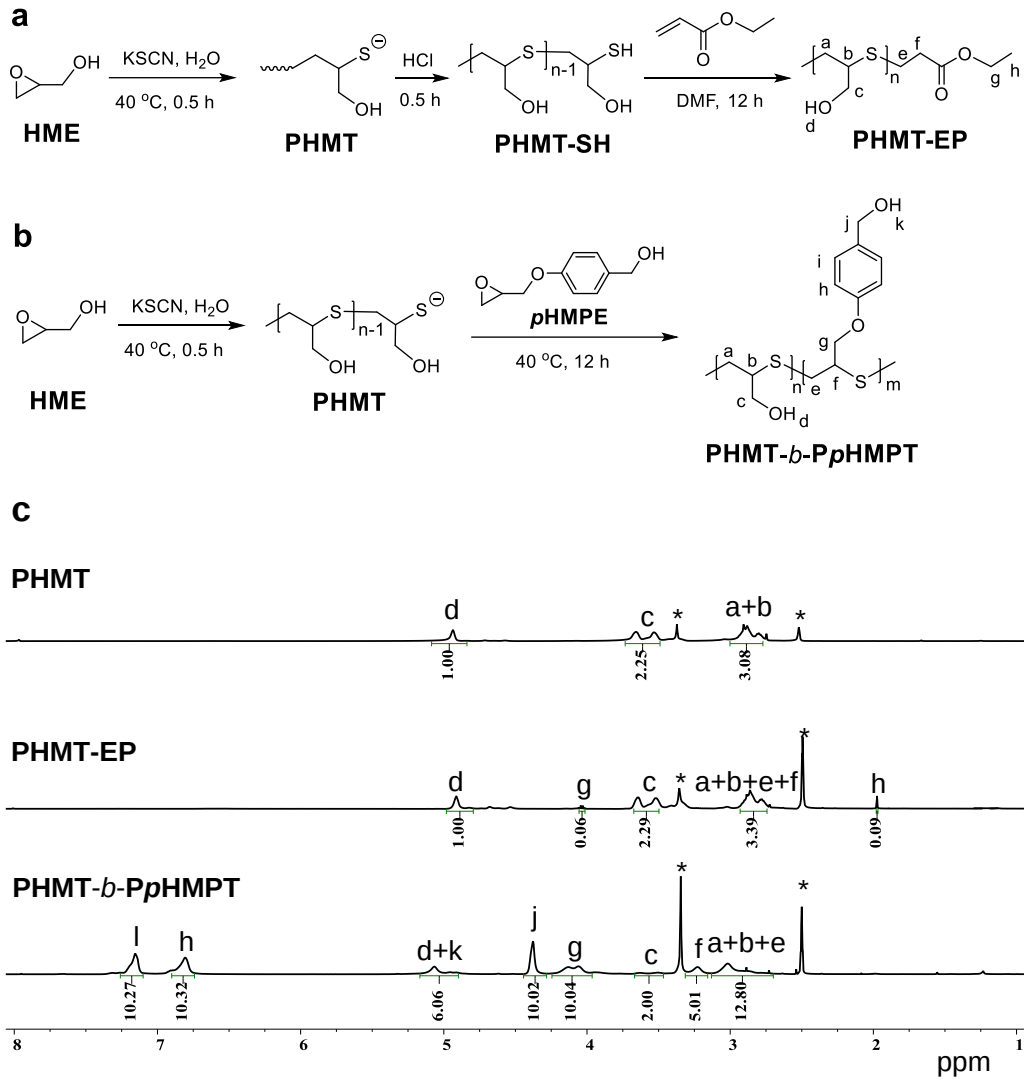


Fig. S28 (a) End-capping reaction for **PHMT-EP**. (b) Chain-extending reaction for block copolymer **PHMT**-*b*-**P*p*HMPT**. (c) Comparing structure of different poly(hydroxyl thioether)s via ^{1}H NMR spectra in DMSO-d_6.

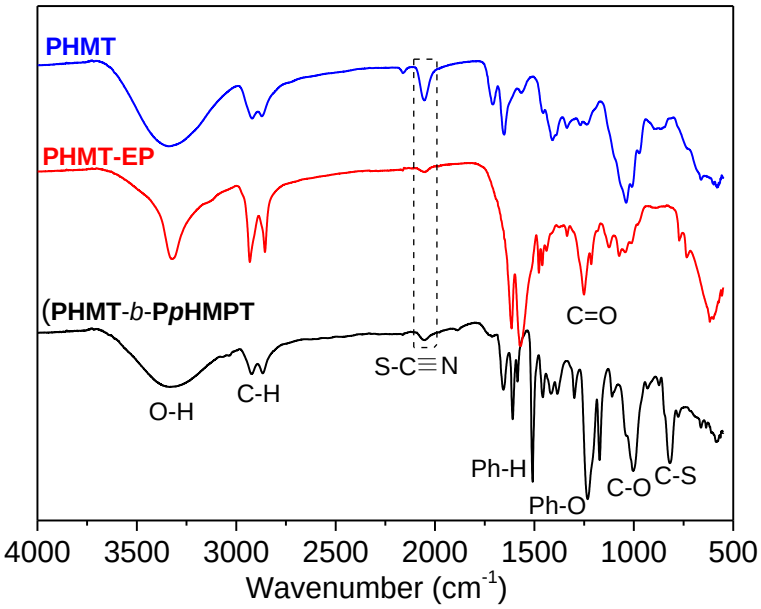


Fig. S29 FT-IR spectra of polythioethers and block copolythioether.

Note S10. Proposed mechanism for cascade O-S ER/AAROP

The proposed cascade reaction to polythioether from epoxide is accomplished in consecutive two steps, involving O-S ER and AAROP in water. Encouraged by the aforementioned results, a possible mechanism for one-pot cascade O-S ER/AAROP was postulated (Fig. S30a). During the O-S ER process, the nucleophilic $^{-}$SCN attacked the methylene site on epoxide ring of ***p*HMPE** to generate the ring-opened transition state of oxyanion **I**, and the continuously generated **I** is bound to a hydrogen proton of water to release $^{-}$OH, which results in a rapid increase in the pH value of reaction mixture.[2] As a result, the intermediate **II** was formed. Subsequently, the ring-opened intermediate **II** was transformed to highly strained oxathiolane intermediate **III** by a ring-closure reaction. Then, the exchange of oxygen to sulfur via ring-opening of oxathiolane allowed to yield 2-[4-(hydroxymethyl)-phenoxymethyl]cyanate sulfanion **IV**.[7] Finally, episulfide ***p*HMPT** was formed by ring-closure reaction with the liberation of $^{-}$OCN group.[8] This process is accompanied by Walden inversion, and the thiirane ring may be closed only in the *trans*

position.[2] According to the previous reports, both the steric and electronic effects affected the attack position of nucleophile.[9] Thanks to the steric hindrance of phenoxymethyl group of ***p*HMPT**, the stronger nucleophilic $^{-}$SCN, rather than the *in-situ* generated $^{-}$OH or $^{-}$OCN in the O-S ER stage, attacked the carbon of methylene on thiirane ring of ***p*HMPT** to form sulfanion **V** and further grow into the stereoregular **P*p*HMPT** chain. Notably, the synergistic effect that both the complexation of cation K^{+} with sulfur atom on thiirane and the hydrogen bond interaction between $^{-}$OH with hydroxyl group on ***p*HMPT** played a key role to activate the thiirane ring and strengthen the nucleophilicity of the more exposed anion $^{-}$SCN, which can favorably to initiate AAROP of ***p*HMPT** and lead the overall chain growth to give **P*p*HMPT**. For AAROP of episulfide, two-component reagents of KSCN and KOH (or bulky cation) were needed, which played the role to activate the thiirane ring of episulfide, as mentioned above. When quaternary ammonium salt was used, the electropositive N^{+} activated the C-S bond, and nucleophilic anion $^{-}$SCN attacked the methylene on thiirane ring of ***p*HMPT** to form sulfanion **V** (Fig. S30b), resulting in a well-defined **P*p*HMPT** with high M_n and good yield, which forcefully verified the proposed polymerization mechanism.

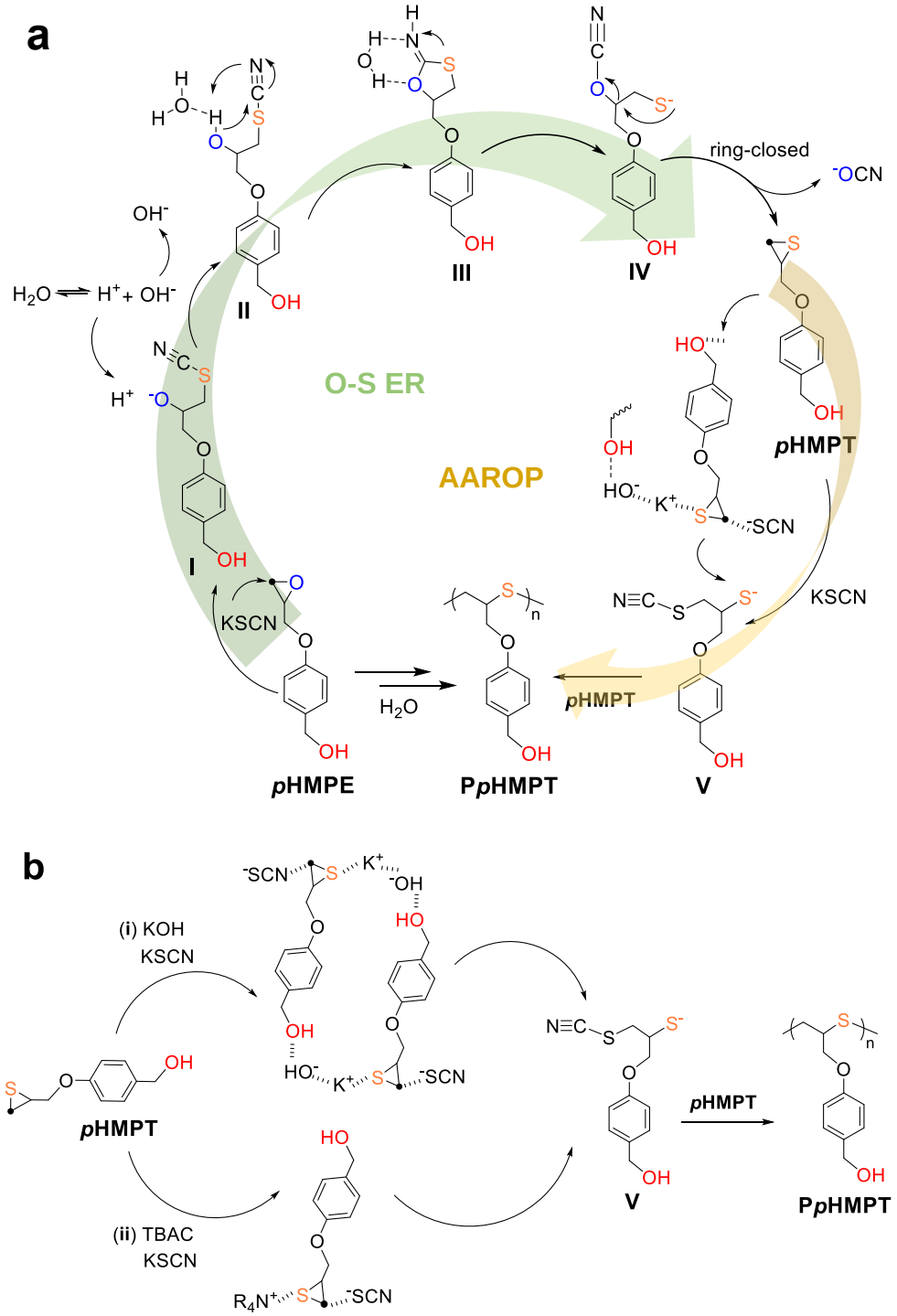


Fig. S30 Proposed reaction mechanism. a, Cascade O-S ER/AAROP from epoxide and KSCN to episulfide and poly(hydroxyl thioether). **b**, AAROP of episulfide to poly(hydroxyl thioether) by KSCN combined with KOH or quaternary ammonium salt.

The dynamic transformation of epoxide to poly(hydroxyl thioether) could be roughly revealed by the whole cascade O-S ER/AAROP process, as depicted in Fig. S31. During

the O-S ER process, epoxide was reacted with thiocyanate to generate episulfide with a reduced solubility, which is easy to form the micelle-like structure in water as the synchronous presence of hydrophilic hydroxyl and hydrophobic thiirane groups in a monomer. Subsequently, small amount of water-soluble thiocyanate anion ($^{-}$SCN) diffused into the hydrophobic inner cavity of the micelle structure and initiated the ring-opening of episulfide to form the living sulfanion (S^{-}) species in a hydrophobic cavity. Crucially, the reactive S^{-} species could maintain the activity due to its hydrophobicity in such hydrophobic cavity that can avoid the interference of protic solvent, and further grow into the active chains, which was finally terminated to form the poly(hydroxyl thioether) in an aggregated clumpy state in water.

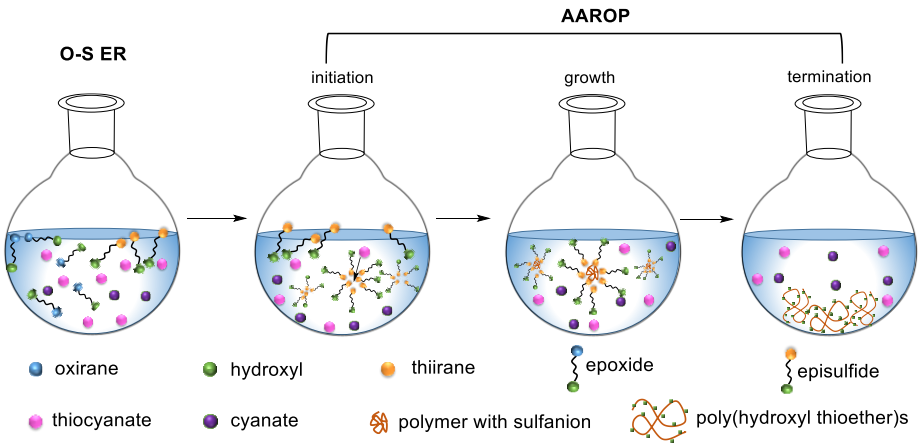


Fig. S31 Schematic representation for dynamic transformation of epoxide to poly(hydroxyl thioether) by cascade O-S ER/AAROP in water.

Note S11. Thermal and mechanical properties

This method was successfully expanded to produce polythioether with different structure of side chains. The thermal properties of polythioethers were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA indicated that all of polythioethers had a high thermal decomposition temperature (T_d > 200

°C) at 5% weight loss (Fig. S32a). Among them, the residual amount of **P*p*HMPT** at 600 °C was about 40%, indicating the good thermal stability. The glass-transition temperature (T_g) of polythioethers was affected by the substituents of epoxides (Fig. S32b). The T_g value of **P*p*HMPT** (T_g = 35 °C) was obviously higher than those of **P*o*HMPT** (T_g = -6 °C) and **P*m*HMPT** (T_g = 3 °C), which is mainly due to that the hydroxyl group on para position of poly(hydroxyl thioether)s had a higher symmetry than that on the ortho or meta position. Comparing with **P*p*HMPT**, **PHMT** (T_g = 33 °C), **P*p*HEPT** (T_g = 27 °C), and **P*p*BAPT** (T_g = 25 °C), the T_g value of **PPMT** was only 17 °C, indicating that the T_g value could be strongly enhanced by the hydrogen bonding interaction between hydroxyl or iminyl groups. Of unique, **P*p*HEPT** presents a melting point (T_m) of 62 °C that is caused by the regular arrangement of side chain and a T_g of 27 °C.

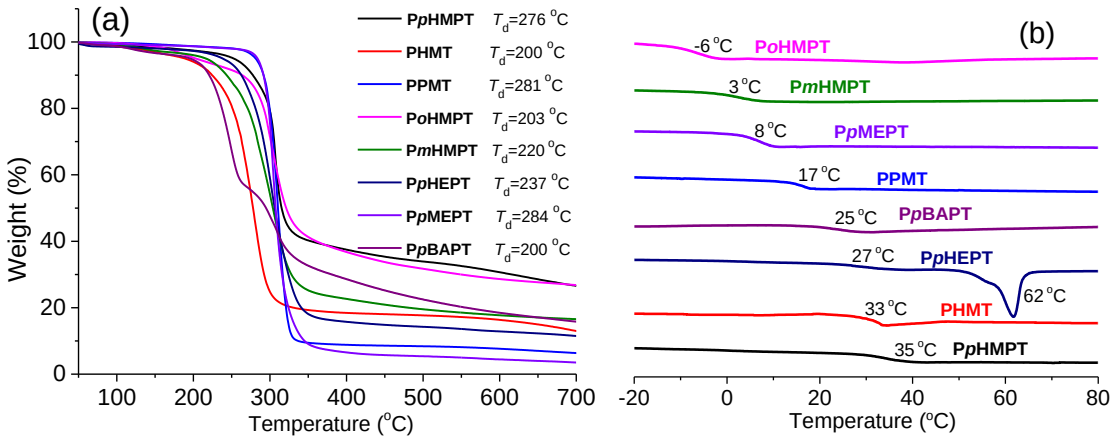


Fig. S32 TGA (a) and DSC (b) curves of polythioethers.

The mechanical properties of representative poly(hydroxyl thioether) **P*p*HMPT** (sample Run 3 in Table 1) were preliminarily investigated by the stress-strain test, as shown in Fig. S33. The results showed that **P*p*HMPT** exhibited a tensile strength of 1.1 MPa and a large elongation at break of 3687%, indicating that this poly(hydroxyl thioether) may be used as a new type of soft thermoplastic elastomer.

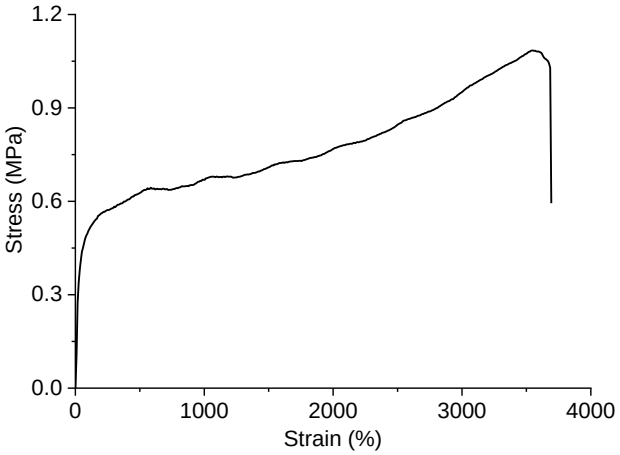


Fig. S33 Stress-strain curve of **P*p*HMPT**.

Note S12. Wastewater treatment

As previously reported, the conventional reaction of KSCN with epoxide only provided episulfide through O-S ER, while producing wastewater contained KOH, KSCN, and KOCN.[10] Here, we described an approach to poly(hydroxyl thioether) by one-pot reaction of epoxide, which avoided the isolation and purification of episulfide, reduced the energy consumption and waste emissions, and the produced wastewater in the cascade O-S ER/AAROP process still contained KOH, KSCN, and KOCN, without the generation of new pollutants. Taking the seawater treatment as reference,[11,12] a proposed way of treating wastewater is first to neutralize the base KOH with hydrochloric acid to give the salt KCl, and then using the membrane crystallization to treat wastewater. This method utilized membrane separation technology to separate the generated water vapor through the membrane, and meanwhile, the liquid water and salts (KCl, KSCN, and KOCN) were left on one side of membrane. Thus, the concentrated crystallization of salts was achieved. This process has low sensitivity to saline concentrations, and owned high selectivity and better energy efficiency.

Legend for Supplementary Movie

Movie S1. Automatically monitoring the pH value variation of cascade O-S ER/AAROP of **HME** with KSCN in aqueous solution by the laboratory pH meter.

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