Electronic Supplementary Information

Design and Synthesis of Thermoresponsive Aliphatic Polyethers with Tunable Phase Transition Temperature

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1. Experimental

1-1. Materials

(*S*)-epichlorohydrin (>99.0%, enantiomeric excess (*e.e.*) >99.0%) was purchased from Sanyo Fine Co., Ltd., and used as received. (*RS*)-epichlorohydrin (>99.0%), 2-methoxyethanol (>99.0%), 2-ethoxyethanol (>99.0%), ethylene glycol monopropyl ether (>98.0%), diethylene glycol monomethyl ether (99.0%), diethylene glycol monoethyl ether (>99.0%), and boron trifluoride – ethyl ether complex (BF_3-Et_2O; >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd., (TCI) and used as received. *n*-Butanol (>98.0%; *n*-BuOH), glycidyl methyl ether (>85%; MeGE) and glycidyl isopropyl ether (>96.0%; *i*PrGE) were purchased from TCI and purified by distillation under vacuum over calcium hydride, which were then stored under an argon atmosphere. *t*-Bu-P_4 (in *n*-hexane as 1.0 mol L^{-1} solution) was purchased from the Sigma-Aldrich Chemicals Co. and used as received. Commercially-available dry toluene (Kanto Chemical Co., Inc., >99.5%, water content, <0.001%) was further purified by an MBRAUN MB SPS Compact solvent purification system equipped with a MB-KOL-C column and a MB-KOL-A column. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl glycidyl ether ($MeEO_3GE$) was prepared according to a reported method and purified by distillation under vacuum over calcium hydride.[1]

1-2. Instruments

The polymerization was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, O_2 <1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 moisture probe and an MB-OX-SE 1 oxygen probe, respectively. The optical rotations were measured at 25 °C by a Jasco DIP-1000 digital polarimeter equipped with a sodium lamp (589 nm) using a 50 mm path length cell. The SEC in THF was performed at 40 °C using a Shodex GPC 101 system (DU-H 2130 Intelligent HPLC pump, RI-71S Intelligent RI detector, and ERC-3125) equipped with a Shodex K-G guard column (4.6 mm × 10 mm; particle size, 8 μm) and two Shodex K-805L columns (linear; particle size, 10 μm; 8.0 mm × 300 mm; exclusion limit, 4×10^4) at the flow rate of 1.0 mL min^{-1}. The number-average molecular weight ($M_{\text{n,SEC}}$) and molecular weight distribution (M_w/M_n) of the polymers were calculated on the basis of a polystyrene (PSt) calibration. The optical purity of the monomers was determined by a chiral HPLC analysis using a DAICEL CHIRALPAK IC column (flow rate, 1.0 mL min^{-1}; solvent, *n*-hexane/EtOH = 95/5 (v/v), temp., 25 °C; detector, RI). The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL ECS400 instrument, and the chemical shifts are referenced to the internal standard of tetramethylsilane (0 ppm). The thermal properties of the samples in the bulk were measured during the second heating under a nitrogen atmosphere from −100 to 100 °C at the heating rate of 10 °C min^{-1} and cooling rate of −10 °C min^{-1} by a Bruker AXS DSC 3100 differential scanning calorimeter. The turbidimetry analysis was performed at $\lambda = 500$ nm with the heating and cooling rates of 1.0 °C min^{-1} using a Jasco V-550 spectrophotometer equipped with a Jasco ETC-505T temperature controller. For the turbidity measurement, the sample was dissolved in deionized water, then the solution degassed at room temperature for 30 min. The dynamic light scattering (DLS) measurement was performed using a Delsa Nano HC Zeta Potential and Submicron Particle Size Analyzer with a solid state laser ($\lambda = 658$ nm, $\theta = 15$ °).

1-3. Synthesis

Synthesis of (*R*)-methoxy glycidyl ether ((*R*)-MeGE). A typical monomer synthesis procedure is as follows (Procedure A): Under a nitrogen atmosphere, (*S*)-epichlorohydrin (170 mL, 2.17 mol) was dropwise added to a mixture of methanol (133 mL, 3.27 mol) and BF_3-Et_2O (33.6 mL, 273 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with water, then extracted with dichloromethane (50 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, then concentrated by rotary evaporation. The residue was purified by distillation using a 10-cm Vigreux column (b.p. 67 °C / 2.6 kPa) to give 126.5 g of a colorless liquid. This material (126.5 g) was dropwise added to a 45.6 wt% NaOH aqueous solution (220 g) at 0 °C. The reaction mixture was warmed to 20 °C and stirred for 2 h. The mixture was extracted with dichloromethane (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, then concentrated by rotary evaporation. The residue was purified by distillation (b.p. 75 °C / 73 kPa) to give (*R*)-MeGE (30.2 g) as a colorless liquid. Yield: 15.8%. >99 %*ee*. $[\alpha]_D = -2.5°$ (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.84-3.81 (dd, $J = 3.2, 14.8$ Hz, 1H, $-CH_2OCH_3$), 3.43-3.39 (s, 3H, −OC*H*$_3$), 3.37-3.30 (m, 1H, −C*H*$_2$OCH$_3$), 3.19-3.12 (m, 1H, −OC*H*(CH$_2$OCH$_3$)CH$_2$−), 2.83-2.78 (t, *J* = 4.6 Hz, 1H, −OCH(CH$_2$OCH$_3$)C*H*$_2$−), 2.65-2.60 (m, 1H, −OCH(CH$_2$OCH$_3$)C*H*$_2$−). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* (ppm) 73.1 (−*C*H$_2$OCH$_3$), 59.1 (−O*C*H$_3$), 50.7 (−O*C*H−), 44.0 (−OCH(CH$_2$OCH$_3$)*C*H$_2$−).

Synthesis of (*RS*)-ethoxy glycidyl ether (EtGE). Procedure A was used for the reaction of (*RS*)-epichlorohydrin (38.8 mL, 495 mmol) and ethanol (125 mL, 2.14 mol) with BF$_3$-Et$_2$O (1250 µL, 10.1 mmol) and a 45.6 wt% NaOH aqueous solution (55.8 g) to produce EtGE as a colorless liquid (9.8 g, b.p. 125 °C). Yield: 19.4%. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) 3.75-3.69 (dd, *J* = 2.8, 14.4 Hz, 1H, −C*H*$_2$OCH$_2$CH$_3$), 3.62-3.50 (m, 2H, −CH$_2$OC*H*$_2$CH$_3$), 3.42-3.34 (m, 1H, −C*H*$_2$OCH$_2$CH$_3$), 3.19-3.13 (m, 1H, −OC*H*(CH$_2$OCH$_2$CH$_3$)CH$_2$−), 2.83-2.78 (t, *J* = 4.6 Hz, 1H, −OCH(CH$_2$OCH$_2$CH$_3$)C*H*$_2$−), 2.64-2.59 (m, 1H, −OCH(CH$_2$OCH$_2$CH$_3$)C*H*$_2$−), 1.25-1.19 (t, *J* = 7.6 Hz, 3H, −OCH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* (ppm) 71.3 (−*C*H$_2$OCH$_2$CH$_3$), 66.7 (−O*C*H$_2$CH$_3$), 50.8 (−O*C*H−), 44.2 (−OCH(CH$_2$OCH$_2$CH$_3$)*C*H$_2$−), 15.1 (−OCH$_2$*C*H$_3$).

Synthesis of (*R*)-ethoxy glycidyl ether ((*R*)-EtGE). Procedure A was used for the reaction of (*S*)-epichlorohydrin (38.8 mL, 495 mmol) and ethanol (125 mL, 2.14 mol) with BF$_3$-Et$_2$O (1250 µL, 10.1 mmol) and a 45.6 wt% NaOH aqueous solution (45.9 g) to produce (*R*)-EtGE as a colorless liquid (8.0 g, b.p. 125 °C). Yield: 15.8%. >99 %*ee*. $[\alpha]_D = -2.8°$ (*c* 1.0, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) 3.75-3.69 (dd, *J* = 2.8, 14.4 Hz, 1H, −C*H*$_2$OCH$_2$CH$_3$), 3.62-3.50 (m, 2H, −CH$_2$OC*H*$_2$CH$_3$), 3.42-3.34 (m, 1H, −C*H*$_2$OCH$_2$CH$_3$), 3.19-3.13 (m, 1H,

$-OC\mathit{H}(CH_2OCH_2CH_3)CH_2-$), 2.83-2.78 (t, *J* = 4.6 Hz, 1H, $-OCH(CH_2OCH_2CH_3)C\mathit{H}_2-$), 2.64-2.59 (m, 1H, $-OCH(CH_2OCH_2CH_3)C\mathit{H}_2-$), 1.25-1.19 (t, *J* = 7.6 Hz, 3H, $-OCH_2C\mathit{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 71.3 ($-\mathit{C}H_2OCH_2CH_3$), 66.7 ($-O\mathit{C}H_2CH_3$), 50.8 ($-O\mathit{C}H-$), 44.2 ($-OCH(CH_2OCH_2CH_3)\mathit{C}H_2-$), 15.1 ($-OCH_2\mathit{C}H_3$).

Synthesis of (*RS*)-2-methoxyethyl glycidyl ether (MeEOGE). Procedure A was used for the reaction of (*RS*)-epichlorohydrin (35.6 mL, 454 mmol) and 2-methoxyethanol (154 mL, 1.95 mol) with BF_3-Et_2O (1120 μL, 9.1 mmol) and a 45.6 wt% NaOH aqueous solution (47.7 g) to produce (*RS*)-MeEOGE as a colorless liquid (18.3 g, b.p. 50 °C / 1.0 kPa). Yield: 30.5%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 3.84-3.79 (dd, *J* = 3.2, 15.2 Hz, 1H, $-CHC\mathit{H}_2O-$), 3.75-3.52 (m, 4H, $-CH_2O(C\mathit{H}_2)_2OCH_3$), 3.46-3.36 (m, 4H, $-CHC\mathit{H}_2O-$, $-OC\mathit{H}_3$), 3.21-3.15 (m, 1H, $-OC\mathit{H}(CH_2O(CH_2)_2OCH_3)CH_2-$), 2.82-2.78 (t, *J* = 4.6 Hz, 1H, $-OCH(CH_2O(CH_2)_2CH_3)C\mathit{H}_2-$), 2.64-2.59 (m, 1H, $-OCH(CH_2O(CH_2)_2CH_3)C\mathit{H}_2-$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 72.1 ($-\mathit{C}H_2OCH_3$), 71.9 ($-\mathit{C}H_2CH_2OCH_3$), 70.6 ($-OCH(\mathit{C}H_2OCH_2CH_2OCH_3)CH_2-$), 59.0 ($-O\mathit{C}H_3$), 50.8 ($-O\mathit{C}H-$), 44.2 ($-OCH(CH_2OCH_2CH_2OCH_3)\mathit{C}H_2-$).

Synthesis of (*R*)-2-methoxyethyl glycidyl ether ((*R*)-MeEOGE). Procedure A was used for the reaction of (*S*)-epichlorohydrin (35.6 mL, 454 mmol) and 2-methoxyethanol (154 mL, 1.95 mol) with BF_3-Et_2O (1120 μL, 9.1 mmol) and a 45.6 wt% NaOH aqueous solution (42.0 g) to produce (*R*)-MeEOGE as a colorless liquid (12.5 g, b.p. 68 °C / 1.0 kPa). Yield: 20.8%. >99 %*ee*. $[\alpha]_D = -3.9°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 3.84-3.79 (dd, *J* = 3.6, 18.8 Hz, 1H, $-\mathrm{CHC}\mathit{H}_2\mathrm{O}-$), 3.75-3.52 (m, 4H, $-\mathrm{CH_2O(C}\mathit{H}_2)_2\mathrm{OCH_3}$), 3.46-3.36 (m, 4H, $-\mathrm{CHC}\mathit{H}_2\mathrm{O}-$, $-\mathrm{OC}\mathit{H}_3$), 3.21-3.15 (m, 1H, $-\mathrm{OC}\mathit{H}\mathrm{(CH_2O(CH_2)_2OCH_3)CH_2}-$), 2.82-2.78 (t, J = 4.8 Hz, 1H, $-\mathrm{OCH(CH_2O(CH_2)_2OCH_3)C}\mathit{H}_2-$), 2.64-2.59 (m, 1H, $-\mathrm{OCH(CH_2O(CH_2)_2CH_3)C}\mathit{H}_2-$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ (ppm) 72.1 ($-\mathit{C}\mathrm{H_2OCH_3}$), 71.9 ($-\mathit{C}\mathrm{H_2CH_2OCH_3}$), 70.6 ($-\mathrm{OCH(}\mathit{C}\mathrm{H_2OCH_2CH_2OCH_3)CH_2}-$), 59.0 ($-\mathrm{O}\mathit{C}\mathrm{H_3}$), 50.8 ($-\mathrm{O}\mathit{C}\mathrm{H}-$), 44.2 ($-\mathrm{OCH(CH_2OCH_2CH_2OCH_3)}\mathit{C}\mathrm{H_2}-$).

Synthesis of (*RS*)-2-ethoxyethyl glycidyl ether (EtEOGE). Procedure A was used for the reaction of (*RS*)-epichlorohydrin (32.1 mL, 410 mmol) and 2-ethoxyethanol (171 mL, 1.76 mol) with $\mathrm{BF_3\text{-}Et_2O}$ (1010 µL, 8.2 mmol) and a 45.6 wt% NaOH aqueous solution (67.0 g) to produce EtEOGE as a colorless liquid (28.0 g, b.p. 76 °C / 1.0 kPa). Yield: 46.7%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ (ppm) 3.84-3.81 (dd, J = 3.2, 15.2 Hz, 1H, $-\mathrm{C}\mathit{H}_2\mathrm{O(CH_2)_2OCH_2CH_3}$), 3.75-3.50 (m, 6H, $-\mathrm{CH_2O(C}\mathit{H}_2)_2\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 3.47-3.39 (m, 1H, $-\mathrm{C}\mathit{H}_2\mathrm{O(CH_2)_2OCH_2CH_3}$), 3.21-3.15 (m, 1H, $-\mathrm{OC}\mathit{H}\mathrm{(CH_2O(CH_2)_2OCH_2CH_3)CH_2}-$), 2.82-2.78 (t, J = 4.8 Hz, 1H, $-\mathrm{OCH(CH_2O(CH_2)_2OCH_2CH_3)C}\mathit{H}_2-$), 2.64-2.59 (m, 1H, $-\mathrm{OCH(CH_2O(CH_2)_2OCH_2CH_3)C}\mathit{H}_2-$), 1.25-1.19 (t, J = 3.6 Hz, 3H, $-\mathrm{OCH_2C}\mathit{H}_3$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ (ppm) 72.1 ($-\mathit{C}\mathrm{H_2OCH_2CH_3}$), 70.8 ($-\mathit{C}\mathrm{H_2CH_2OCH_2CH_3}$), 69.8 ($-\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 66.7 ($-\mathrm{OCH(}\mathit{C}\mathrm{H_2OCH_2CH_2OCH_2CH_3)CH_2}-$), 50.8 ($-\mathrm{O}\mathit{C}\mathrm{H}-$), 44.2 ($-\mathrm{OCH(CH_2OCH_2CH_2OCH_3)}\mathit{C}\mathrm{H_2}-$), 15.2 ($-\mathrm{O}\mathit{C}\mathrm{H_3}$).

Synthesis of (*R*)-2-ethoxyethyl glycidyl ether ((*R*)-EtEOGE). Procedure A was used for the reaction of (*R*)-epichlorohydrin (32.1 mL, 410 mmol) and 2-ethoxyethanol (171 mL, 1.76 mol) with BF_3-Et_2O (1010 μL, 8.2 mmol) and a 45.6 wt% NaOH aqueous solution (51.7 g) to produce (*R*)-EtEOGE as a colorless liquid (20.5 g, b.p. 76 °C / 1.0 kPa). Yield: 34.2%. >99 %*ee*. $[\alpha]_D = -4.2°$ (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.84-3.81 (dd, J = 3.2, 15.2 Hz, 1H, $-CH_2O(CH_2)_2OCH_2CH_3$), 3.75-3.50 (m, 6H, $-CH_2O(CH_2)_2OCH_2CH_3$), 3.47-3.39 (m, 1H, $-CH_2O(CH_2)_2OCH_2CH_3$), 3.21-3.15 (m, 1H, $-OCH(CH_2O(CH_2)_2OCH_2CH_3)CH_2-$), 2.82-2.78 (t, J = 4.8 Hz, 1H, $-OCH(CH_2O(CH_2)_2OCH_2CH_3)CH_2-$), 2.64-2.59 (m, 1H, $-OCH(CH_2O(CH_2)_2OCH_2CH_3)CH_2-$), 1.25-1.19 (t, J = 3.6 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 72.1 ($-CH_2OCH_2CH_3$), 70.8 ($-CH_2CH_2OCH_2CH_3$), 69.8 ($-OCH_2CH_3$), 66.7 ($-OCH(CH_2OCH_2CH_2OCH_2CH_3)CH_2-$), 50.8 ($-OCH-$), 44.2 ($-OCH(CH_2OCH_2CH_2OCH_2CH_3)CH_2-$), 15.2 ($-OCH_2CH_3$).

Synthesis of (*RS*)-propoxy ethyl glycidyl ether (PrEOGE). Procedure A was used for the reaction of (*RS*)-epichlorohydrin (29.3 mL, 375 mmol) and ethylene glycol monopropyl ether (51.6 mL, 449 mmol) with BF_3-Et_2O (4.6 mL, 37.5 mmol) and a 45.6 wt% NaOH aqueous solution (38.8 g) to produce PrEOGE as a colorless liquid (17.5 g, b.p. 37 °C / 5.0 Pa). Yield: 29.2%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.84-3.81 (dd, J = 3.2, 15.2 Hz, 1H, $-CH_2O(CH_2)_2OCH_2CH_2CH_3$), 3.74-3.56 (m, 4H, $-CH_2O(CH_2)_2OCH_2CH_2CH_3$), 3.47-3.39 (m, 3H, $-CH_2O(CH_2)_2OCH_2CH_2CH_3$), 3.21-3.13 (m, 1H, $-OCH(CH_2O(CH_2)_2OCH_2CH_2CH_3)CH_2-$), 2.81-2.77 (t, J = 5.2 Hz, 1H, $-OCH(CH_2O(CH_2)_2OCH_2CH_2CH_3)CH_2-$), 2.63-2.59 (m, 1H,

$\mathrm{-OCH(CH_2O(CH_2)_2OCH_2CH_2CH_3)C}\mathit{H}_2\mathrm{-}$), 1.55-1.44 (m, 2H, $\mathrm{-O\ CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_3$), 0.84-0.77 (t, *J* = 7.6 Hz, 3H, $\mathrm{-OCH_2CH_2C}\mathit{H}_3$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): *δ* (ppm) 73.0 ($\mathrm{-CH_2OCH_2CH_2O}\mathit{C}\mathrm{H_2CH_2CH_3}$), 72.0 ($\mathrm{-CH_2OCH_2}\mathit{C}\mathrm{H_2O(CH_2)_2CH_3}$), 70.7 ($\mathrm{-CH_2O}\mathit{C}\mathrm{H_2CH_2O(CH_2)_2CH_3}$), 70.0 ($\mathrm{-}\mathit{C}\mathrm{H_2O(CH_2)_2O(CH_2)_2CH_3}$), 50.8 ($\mathrm{-O}\mathit{C}\mathrm{H-}$), 44.3 ($\mathrm{-OCH(CH_2O(CH_2)_2O(CH_2)_2CH_3)}\mathit{C}\mathrm{H_2-}$), 22.8 ($\mathrm{-OCH_2}\mathit{C}\mathrm{H_2CH_3}$), 10.5 ($\mathrm{-OCH_2CH_2}\mathit{C}\mathrm{H_3}$).

Synthesis of (*RS*)-2-(methoxyethoxy)ethyl glycidyl ether (**MeEO$_2$GE).** Procedure A was used for the reaction of (*RS*)-epichlorohydrin (26.6 mL, 340 mmol) and diethylene glycol monomethyl ether (48.1 mL, 408 mmol) with $\mathrm{BF_3\text{-}Et_2O}$ (4.2 mL, 34.0 mmol) and a 45.6 wt% NaOH aqueous solution (36.9 g) to produce MeEO$_2$GE as a colorless liquid (18.2 g, b.p. 90 °C / 4.0 Pa). Yield: 30.0%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): *δ* (ppm) 3.83-3.77 (dd, *J* = 3.2, 15.2 Hz, 1H, $\mathrm{-C}\mathit{H}_2\mathrm{O(CH_2)_2O(CH_2)_2OCH_3}$), 3.75-3.50 (m, 8H, $\mathrm{-CH_2O(C}\mathit{H}_2\mathrm{)_2O(C}\mathit{H}_2\mathrm{)_2OCH_3}$), 3.47-3.34 (m, 4H, $\mathrm{-C}\mathit{H}_2\mathrm{O(CH_2)_2O(CH_2)_2OCH_3}$, $\mathrm{-CH_2O(CH_2)_2O(CH_2)_2OC}\mathit{H}_3$), 3.20-3.13 (m, 1H, $\mathrm{-OC}\mathit{H}\mathrm{(CH_2O(CH_2)_2O(CH_2)_2OCH_3)CH_2-}$), 2.82-2.77 (t, *J* = 4.4 Hz, 1H, $\mathrm{-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_3)C}\mathit{H}_2\mathrm{-}$), 2.64-2.59 (m, 1H, $\mathrm{-OCH(CH_2O(CH_2)_2O(CH_2)_2OCCH_3)C}\mathit{H}_2\mathrm{-}$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): *δ* (ppm) 72.1-70.3 ($\mathrm{-}\mathit{C}\mathrm{H_2OCH_2}\mathit{C}\mathrm{H_2OCH_2}\mathit{C}\mathrm{H_2OCH_3}$), 71.0-70.4 ($\mathrm{-CH_2O}\mathit{C}\mathrm{H_2CH_2O}\mathit{C}\mathrm{H_2CH_2OCH_3,}$), 59.0 ($\mathrm{-CH_2O(CH_2)_2O(CH_2)_2O}\mathit{C}\mathrm{H_3}$), 50.8 ($\mathrm{-O}\mathit{C}\mathrm{H-}$), 44.1 ($\mathrm{-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)}\mathit{C}\mathrm{H_2-}$).

Synthesis of (*RS*)-2-(ethoxyethoxy)ethyl glycidyl ether (**EtEO$_2$GE).** Procedure A was used for the reaction of (*RS*)-epichlorohydrin (24.6 mL, 315 mmol) and diethylene glycol monoethyl ether (50.7 mL, 378 mmol) with BF_3-Et_2O (3.9 mL, 31.5 mmol) and a 45.6 wt% NaOH aqueous solution (38.4 g) to produce $EtEO_2GE$ as a colorless liquid (20.1 g, b.p. 110 °C / 4.0 Pa). Yield: 34.2%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.82-3.76 (dd, J = 3.2, 15.2 Hz, 1H, $-CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 3.75-3.50 (m, 10H, $-CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 3.47-3.39 (m, 1H, $-CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 3.21-3.15 (m, 1H, $-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)CH_2-$), 2.82-2.77 (t, J = 4.8 Hz, 1H, $-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)CH_2-$), 2.64-2.59 (m, 1H, $-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)CH_2-$), 1.25-1.19 (t, J = 7.2 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 72.0 ($-CH_2OCH_2CH_2O(CH_2)_2OCH_2CH_3$), 71.0-70.4 ($-CH_2OCH_2CH_2O(CH_2)_2OCH_2CH_3$), 69.8 ($-CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 66.6 ($-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)CH_2-$), 51.0 ($-OCH-$), 44.3 ($-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)CH_2-$), 15.2 ($-OCH_2CH_3$).

Synthesis of (*R*)-2-(ethoxyethoxy)ethyl glycidyl ether ((*R*)-$EtEO_2GE$). Procedure A was used for the reaction of (*S*)-epichlorohydrin (24.6 mL, 315 mmol) and diethylene glycol monoethyl ether (50.7 mL, 378 mmol) with BF_3-Et_2O (3.9 mL, 31.5 mmol) and a 45.6 wt% NaOH aqueous solution (32.1 g) to produce (*R*)-$EtEO_2GE$ as a colorless liquid (15.2 g, b.p. 110 °C / 4.0 Pa). Yield: 25.3%. >99 %*ee*. $[\alpha]_D = -3.5°$ (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.82-3.76 (dd, J = 3.2, 15.2 Hz, 1H, $-CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 3.75-3.50 (m, 10H, $-CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 3.47-3.39 (m, 1H, $-CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 3.21-3.15

(m, 1H, $-OC\mathit{H}(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)CH_2-$), 2.82-2.77 (t, J = 4.8 Hz, 1H, $-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)C\mathit{H}_2-$), 2.64-2.59 (m, 1H, $-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)C\mathit{H}_2-$), 1.25-1.19 (t, J = 7.2 Hz, 3H, $-OCH_2C\mathit{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 72.0 ($-CH_2OCH_2\mathit{C}H_2O(CH_2)_2OCH_2CH_3$), 71.0-70.4 ($-CH_2O\mathit{C}H_2CH_2O(\mathit{C}H_2)_2OCH_2CH_3$), 69.8 ($-CH_2O(CH_2)_2O(CH_2)_2O\mathit{C}H_2CH_3$), 66.6 ($-\mathit{C}H_2O(CH_2)_2O(CH_2)_2OCH_2CH_3$), 51.0 ($-O\mathit{C}H-$), 44.3 ($-OCH(CH_2O(CH_2)_2O(CH_2)_2OCH_2CH_3)\mathit{C}H_2-$), 15.2 ($-OCH_2\mathit{C}H_3$).

Synthesis of poly(MeGE). A typical polymerization procedure is as follows (Procedure B): *t*-Bu-P_4 (113 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 113 μmol) was added to a stirred mixture of MeGE (501 μL, 5.67 mmol), *n*-butanol (113 μL as 1.0 mol L^{-1} stock solution in toluene, 113 μmol) in toluene (1540 μL). After stirring at room temperature for 20 h, the polymerization was terminated by adding an excess amount of benzoic acid. The reaction mixture was purified by passing through an alumina column (eluent: THF) to give poly(MeGE)$_{7k}$ (360 mg) as a colorless viscous liquid. Yield: 71.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.69-3.39 (m, $CH_3CH_2CH_2C\mathit{H}_2O-$, $-OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2OCH_3)O-$), 3.39-3.32 (m, $-OCH_2CH(CH_2OC\mathit{H}_3)O-$), 1.53 (m, 2H, $CH_3CH_2C\mathit{H}_2-$), 1.35 (m, $CH_3C\mathit{H}_2-$), 0.91 (t, J = 7.2 Hz, $C\mathit{H}_3-$). $M_{n,NMR}$ = 4,570 g mol^{-1}; $M_{n,SEC}$ = 5,190 g mol^{-1}; M_w/M_n = 1.04.

Synthesis of poly(EtGE). Procedure B was used for the polymerization of EtGE (529 μL, 4.90 mmol) with *n*-butanol (97.9 μL as 1.0 mol L^{-1} stock solution in toluene, 97.9 μmol) and *t*-Bu-P_4

(294 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 294 μmol) in toluene (1040 μL) to produce poly(EtGE)$_{5k}$ as a colorless viscous liquid (350 mg). Yield: 69.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.80-3.40 (m, $CH_3CH_2CH_2CH_2O-$, $-OCH_2CH(CH_2OCH_2CH_3)O-$), 1.53 (m, 2H, $CH_3CH_2CH_2-$), 1.35 (m, CH_3CH_2-), 1.18 (t, $J = 6.8$ Hz, $-OCH_2CH(CH_2OCH_2CH_3)O-$), 0.91 (t, $J = 7.6$ Hz, CH_3-). $M_{n,NMR} = 5{,}290$ g mol^{-1}; $M_{n,SEC} = 9{,}560$ g mol^{-1}; $M_w/M_n = 1.04$.

Synthesis of poly(*i*PrGE). Procedure B was used for the polymerization of *i*PrGE (544 μL, 4.30 mmol) with *n*-butanol (86.1 μL as 1.0 mol L^{-1} stock solution in toluene, 86.1 μmol) and *t*-Bu-P_4 (86.1 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 86.1 μmol) in toluene (1010 μL) to produce poly(*i*PrGE)$_{6k}$ as a colorless viscous liquid (390 mg). Yield: 77.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.90-3.30 (m, $CH_3CH_2CH_2CH_2O-$, $-OCH_2CH(CH_2OCH(CH_3)_2)O-$), 1.53 (m, $-CH_3CH_2CH_2-$), 1.35 (m, CH_3CH_2-), 1.20-1.15 (m, $-OCH_2CH(CH_2OCH(CH_3)_2)O-$), 0.91 (t, $J = 8.0$ Hz, CH_3-). $M_{n,NMR} = 6{,}380$ g mol^{-1}; $M_{n,SEC} = 6{,}250$ g mol^{-1}; $M_w/M_n = 1.05$.

Synthesis of poly(MeEOGE). Procedure B was used for the polymerization of MeEOGE (483 μL, 3.78 mmol) with *n*-butanol (75.7 μL as 1.0 mol L^{-1} stock solution in toluene, 75.7 μmol) and *t*-Bu-P_4 (75.7 μL as 1.0 mol L^{-1} stock solution in toluene, 75.7 μmol) in toluene (879 μL) to produce poly(MeEOGE)$_{7k}$ as a colorless viscous liquid (350 mg). Yield: 69.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.68-3.45 (m, $CH_3CH_2CH_2CH_2O-$, $-OCH_2CH(CH_2OCH_2CH_2OCH_3)O-$), 3.39-3.35 (m, $-OCH_2CH(CH_2OCH_2CH_2OCH_3)O-$), 1.53 (m, 2H, $CH_3CH_2CH_2-$), 1.35 (m, CH_3CH_2-), 0.91 (t, $J = 7.6$ Hz, CH_3-). $M_{n,NMR} = 6{,}620$ g mol^{-1}; $M_{n,SEC} = 6{,}290$ g mol^{-1}; $M_w/M_n = 1.04$.

Synthesis of poly(EtEOGE). Procedure B was used for the polymerization of EtEOGE (493 µL, 3.42 mmol) with *n*-butanol (68.4 µL as 1.0 mol L^{-1} stock solution in toluene, 68.4 µmol) and *t*-Bu-P_4 (68.4 µL as 1.0 mol L^{-1} stock solution in *n*-hexane, 68.4 µmol) in toluene (738 µL) to produce poly(EtEOGE)$_{7k}$ as a colorless viscous liquid (380 mg). Yield: 75.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.80-3.40 (m, $CH_3CH_2CH_2C\mathit{H}_2O-$, $-OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2CH_3)O-$), 1.53 (m, 2H, $CH_3CH_2C\mathit{H}_2-$), 1.35 (m, $CH_3C\mathit{H}_2-$), 1.20 (t, J = 6.8 Hz, $-OCH_2CH(CH_2OCH_2CH_2OCH_2C\mathit{H}_3)O-$), 0.91 (t, J = 7.6 Hz, $C\mathit{H}_3-$). $M_{n,NMR}$ = 7,480 g mol^{-1}; $M_{n,SEC}$ = 7,180 g mol^{-1}; M_w/M_n = 1.04.

Synthesis of poly(PrEOGE). Procedure B was used for the polymerization of PrEOGE (502 µL, 3.12 mmol) with *n*-butanol (62.4 µL as 1.0 mol L^{-1} stock solution in toluene, 62.4 µmol) and *t*-Bu-P_4 (62.4 µL as 1.0 mol L^{-1} stock solution in *n*-hexane, 62.4 µmol) in toluene (622 µL) to produce poly(PrEOGE)$_{10k}$ as a colorless viscous liquid (390 mg). Yield: 77.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.68-3.36 (m, $CH_3CH_2CH_2C\mathit{H}_2O-$, $-OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2CH_2CH_3)O-$), 1.65-1.52 (m, $-CH_3CH_2C\mathit{H}_2-$, $-OCH_2CH(CH_2OCH_2CH_2OCH_2C\mathit{H}_2CH_3)O$), 1.35 (m, $CH_3C\mathit{H}_2-$), 1.20 (t, J = 6.8 Hz, $-OCH_2CH(CH_2OCH_2CH_2OCH_2CH_2C\mathit{H}_3)O-$), 0.91 (t, J = 7.6 Hz, $C\mathit{H}_3-$). $M_{n,NMR}$ = 9,830 g mol^{-1}; $M_{n,SEC}$ = 7,950 g mol^{-1}; M_w/M_n = 1.04.

Synthesis of poly($MeEO_2GE$). Procedure B was used for the polymerization of $MeEO_2GE$ (474 µL, 2.84 mmol) with *n*-butanol (28.4 µL as 1.0 mol L^{-1} stock solution in toluene, 28.4 µmol) and *t*-Bu-P_4 (28.4 µL as 1.0 mol L^{-1} stock solution in *n*-hexane, 52.6 µmol) in toluene (604 µL) to produce poly(MeEO$_2$GE)$_{9k}$ as a colorless viscous liquid (380 mg). Yield: 75.7%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 3.70-3.43 (m, CH$_3$CH$_2$CH$_2$C*H*$_2$O–, −OC*H*$_2$C*H*(C*H*$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_3$)O–), 3.40-3.37 (m, −OCH$_2$CH(CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OC*H*$_3$)O–), 1.53 (m, 2H, CH$_3$CH$_2$C*H*$_2$–), 1.35 (m, CH$_3$C*H*$_2$–), 0.91 (t, J = 7.2 Hz, C*H*$_3$–). $M_{\mathrm{n,NMR}}$ = 8,820 g mol^{-1}; $M_{\mathrm{n,SEC}}$ = 9,700 g mol^{-1}; $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.03.

Synthesis of poly(EtEO$_2$GE). Procedure B was used for the polymerization of (*RS*)-EtEO$_2$GE (483 μL, 2.63 mmol) with *n*-butanol (52.6 μL as 1.0 mol L^{-1} stock solution in toluene, 52.6 μmol) and *t*-Bu-P$_4$ (52.6 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 52.6 μmol) in toluene (464 μL) to produce poly(EtEO$_2$GE)$_{10k}$ as a colorless viscous liquid (380 mg). Yield: 75.7%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 3.70-3.40 (m, CH$_3$CH$_2$CH$_2$C*H*$_2$O–, −OC*H*$_2$C*H*(C*H*$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$CH$_3$)O–), 1.53 (m, 2H, CH$_3$CH$_2$C*H*$_2$–), 1.35 (m, CH$_3$C*H*$_2$–), 1.21 (t, J = 6.8 Hz, −OCH$_2$CH(CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$C*H*$_3$)O–), 0.91 (t, J = 7.6 Hz, C*H*$_3$–). $M_{\mathrm{n,NMR}}$ = 9,910 g mol^{-1}; $M_{\mathrm{n,SEC}}$ = 11,800 g mol^{-1}; $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.04.

Synthesis of poly(MeEO$_3$GE). Procedure B was used for the polymerization of (*RS*)-MeEO$_3$GE (469 μL, 2.27 mmol) with *n*-butanol (69 μL as 1.0 mol L^{-1} stock solution in toluene, 69 μmol) and *t*-Bu-P$_4$ (69 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 69 μmol) in toluene (302 μL) to produce poly(EtEO$_2$GE)$_{8k}$ as a colorless viscous liquid (246 mg). Yield: 47.0%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 3.29-3.75 (−OC*H*$_2$C*H*(C*H*$_2$O(C*H*$_2$C*H*$_2$O)$_3$C*H*$_3$)O–),1.47-1.56 (m, CH$_3$CH$_2$C*H*$_2$CH$_2$O–), 1.28-1.39 (m, CH$_3$C*H*$_2$CH$_2$CH$_2$O–), 0.86-0.95 (t, J = 7.6 Hz, C*H*$_3$–). $M_{\mathrm{n,NMR}}$ =

7,600 g mol^{-1}; $M_{\mathrm{n,SEC}}$ = 6,700 g mol^{-1}; $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.05.

Synthesis of isotactic poly(MeGE) (poly[(*R*)-MeGE]). Procedure B was used for the polymerization of (*R*)-MeGE (501 μL, 5.67 mmol) with *n*-butanol (57.0 μL as 1.0 mol L^{-1} stock solution in toluene, 57.0μmol) and *t*-Bu-P$_4$ (57.0 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 57.0 μmol) in toluene (1660 μL) to produce poly[(*R*)-MeGE]$_{9\mathrm{k}}$ as a colorless viscous liquid (380 mg). Yield: 75.4%. $[\alpha]_{\mathrm{D}}$ = −35.7 ° (*c* 1.0, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) 3.69-3.39 (m, $\mathrm{CH_3CH_2CH_2C}H_2\mathrm{O}$–, $-\mathrm{OC}H_2\mathrm{C}H(\mathrm{C}H_2\mathrm{OCH_3})\mathrm{O}-$), 3.39-3.32 (m, $-\mathrm{OCH_2CH(CH_2OC}H_3)\mathrm{O}-$), 1.53 (m, 2H, $\mathrm{CH_3CH_2C}H_2-$), 1.35 (m, $\mathrm{CH_3C}H_2-$), 0.91 (t, *J* = 7.2 Hz, $\mathrm{C}H_3-$). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* (ppm) 78.8 ($-\mathrm{OCH_2}C\mathrm{H(CH_2OCH_3)O}-$), 72.7 ($-\mathrm{OCH_2CH(}C\mathrm{H_2OCH_3)O}-$), 70.0 ($-\mathrm{O}C\mathrm{H_2CH(CH_2OCH_3)O}-$), 59.3 ($-\mathrm{OCH_2CH(CH_2O}C\mathrm{H_3)O}-$). $M_{\mathrm{n,NMR}}$ = 8,890 g mol^{-1}; $M_{\mathrm{n,SEC}}$ = 10,100 g mol^{-1}; $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.04.

Synthesis of isotactic poly(EtGE) (poly[(*R*)-EtGE]). Procedure B was used for the polymerization of (*R*)-EtGE (529 μL, 4.90 mmol) with *n*-butanol (97.9 μL as 1.0 mol L^{-1} stock solution in toluene, 97.9 μmol) and *t*-Bu-P$_4$ (294 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 294 μmol) in toluene (1040 μL) to produce poly[(*R*)-EtGE]$_{5\mathrm{k}}$ as a colorless viscous liquid (350 mg). Yield: 69.5%. $[\alpha]_{\mathrm{D}}$ = −26.3 ° (*c* 1.0, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) 3.80-3.40 (m, $\mathrm{CH_3CH_2CH_2C}H_2\mathrm{O}$–, $-\mathrm{OC}H_2\mathrm{C}H(\mathrm{C}H_2\mathrm{OC}H_2\mathrm{CH_3})\mathrm{O}-$), 1.53 (m, 2H, $\mathrm{CH_3CH_2C}H_2-$), 1.35 (m, $\mathrm{CH_3C}H_2-$), 1.18 (t, *J* = 6.8 Hz, $-\mathrm{OCH_2CH(CH_2OCH_2C}H_3)\mathrm{O}-$), 0.91 (t, *J* = 7.6 Hz, $\mathrm{C}H_3-$). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* (ppm) 78.8 ($-\mathrm{OCH_2}C\mathrm{H(CH_2OCH_2CH_3)O}-$), 70.6-69.8

($-OCH_2CH(CH_2OCH_2CH_3)O-$), 66.7 ($-OCH_2CH_3$), 15.2 ($-OCH_2CH_3$). $M_{n,NMR}$ = 5,430 g mol^{-1}; $M_{n,SEC}$ = 7,320 g mol^{-1}; M_w/M_n = 1.04.

Synthesis of isotactic poly(MeEOGE) (poly[(*R*)-MeEOGE]). Procedure B was used for the polymerization of (*R*)-MeEOGE (483 μL, 3.78 mmol) with *n*-butanol (37.8 μL as 1.0 mol L^{-1} stock solution in toluene, 37.8 μmol) and *t*-Bu-P_4 (37.8 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 37.8 μmol) in toluene (955 μL) to produce poly[(*R*)-MeEOGE]$_{13k}$ as a colorless viscous liquid (360 mg). Yield: 68.2%. $[\alpha]_D$ = −20.5 ° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.68-3.45 (m, $CH_3CH_2CH_2CH_2O-$, $-OCH_2CH(CH_2OCH_2CH_2OCH_3)O-$), 3.39-3.35 (m, $-OCH_2CH(CH_2OCH_2CH_2OCH_3)O-$), 1.53 (m, 2H, $CH_3CH_2CH_2-$), 1.35 (m, CH_3CH_2-), 0.91 (t, J = 7.6 Hz, CH_3-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 78.8 ($-OCH_2CH(CH_2OCH_2CH_2OCH_3)O-$), 71.9-70.0 ($-OCH_2CH(CH_2OCH_2CH_2OCH_3)O-$), 59.0 ($-OCH_3$). $M_{n,NMR}$ = 13,000 g mol^{-1}; $M_{n,SEC}$ = 10,700 g mol^{-1}; M_w/M_n = 1.05.

Synthesis of isotactic poly(EtEOGE) (poly[(*R*)-EtEOGE]). Procedure B was used for the polymerization of (*R*)-EtEOGE (493 μL, 3.42 mmol) with *n*-butanol (34.2 μL as 1.0 mol L^{-1} stock solution in toluene, 34.2 μmol) and *t*-Bu-P_4 (34.2 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 3.42 μmol) in toluene (807 μL) to produce poly[(*R*)-EtEOGE]$_{15k}$ as a colorless viscous liquid (370 mg). Yield: 73.6%. $[\alpha]_D$ = −21.0 ° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.80-3.40 (m, $CH_3CH_2CH_2CH_2O-$, $-OCH_2CH(CH_2OCH_2CH_2OCH_2CH_3)O-$), 1.53 (m, 2H, $CH_3CH_2CH_2-$), 1.35 (m, CH_3CH_2-), 1.20 (t, J = 6.8 Hz, $-OCH_2CH(CH_2OCH_2CH_2OCH_2CH_3)O-$), 0.91 (t, J = 7.6 Hz,

$\mathrm{C}\mathit{H}_3-$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ (ppm) 78.8 ($-\mathrm{OCH_2}\mathit{C}\mathrm{H(CH_2O(CH_2)_2OCH_2CH_3)O}-$), 71.4-69.8 ($-\mathrm{O}\mathit{C}\mathrm{H_2CH(}\mathit{C}\mathrm{H_2O(}\mathit{C}\mathrm{H_2)_2OCH_2CH_3)O}-$), 66.5 ($-\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 15.2 ($-\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$). $M_{\mathrm{n,NMR}}$ = 15,100 g mol^{-1}; $M_{\mathrm{n,SEC}}$ = 12,900 g mol^{-1}; $M_\mathrm{w}/M_\mathrm{n}$ = 1.07.

Synthesis of isotactic poly(EtEO$_2$GE) (poly[(*R*)-EtEO$_2$GE]). Procedure B was used for the polymerization of (*R*)-EtEO$_2$GE (483 µL, 2.63 mmol) with *n*-butanol (52.6 µL as 1.0 mol L^{-1} stock solution in toluene, 52.6 µmol) and *t*-Bu-P$_4$ (52.6 µL as 1.0 mol L^{-1} stock solution in *n*-hexane, 52.6 µmol) in toluene (464 µL) to produce poly[(*R*)-EtEO$_2$GE]$_{10\mathrm{k}}$ as a colorless viscous liquid (380 mg). Yield: 75.7%. $[\alpha]_\mathrm{D}$ = −14.3 ° (*c* 1.0, $\mathrm{CHCl_3}$). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ (ppm) 3.70-3.40 (m, $\mathrm{CH_3CH_2CH_2C}\mathit{H}_2\mathrm{O}-$, $-\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}\mathrm{(C}\mathit{H}_2\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{OC}\mathit{H}_2\mathrm{CH_3)O}-$), 1.53 (m, 2H, $\mathrm{CH_3CH_2C}\mathit{H}_2-$), 1.35 (m, $\mathrm{CH_3C}\mathit{H}_2-$), 1.21 (t, *J* = 6.8 Hz, $-\mathrm{OCH_2CH(CH_2OCH_2CH_2OCH_2CH_2OCH_2C}\mathit{H}_3\mathrm{)O}-$), 0.91 (t, *J* = 7.6 Hz, $\mathrm{C}\mathit{H}_3-$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ (ppm) 78.8 ($-\mathrm{OCH_2}\mathit{C}\mathrm{H(CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3)O}-$), 71.4-69.8 ($-\mathrm{O}\mathit{C}\mathrm{H_2CH(}\mathit{C}\mathrm{H_2O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2OCH_2CH_3)O}-$), 66.5 ($-\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 15.2 ($-\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$). $M_{\mathrm{n,NMR}}$ = 9,640 g mol^{-1}; $M_{\mathrm{n,SEC}}$ = 6,770 g mol^{-1}; $M_\mathrm{w}/M_\mathrm{n}$ = 1.05.

Synthesis of poly(MeEOGE-*st*-EtEOGE). Procedure B was used for the polymerization of MeEOGE (242 µL, 1.89 mmol) and EtEOGE (273 µL, 1.89 mmol) with *n*-butanol (37.8 µL as 1.0 mol L^{-1} stock solution in toluene, 37.8 µmol) and *t*-Bu-P$_4$ (37.8 µL as 1.0 mol L^{-1} stock solution in *n*-hexane, 37.8 µmol) in toluene (923 µL) to produce poly(MeEOGE$_{0.50}$-*st*-EtEOGE$_{0.50}$)$_{14\mathrm{k}}$ as a colorless viscous liquid (390 mg). Yield: 75.6%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ (ppm) 3.70-3.45 (m,

$CH_3CH_2CH_2CH_2O$–, –$OCH_2CH(CH_2OCH_2CH_2OCH_3)O$–, –$OCH_2CH(CH_2OCH_2CH_2OCH_2CH_3)O$–), 3.39-3.35 (m, –$OCH_2CH(CH_2OCH_2CH_2OCH_3)O$–), 1.53 (m, 2H, $CH_3CH_2CH_2$–), 1.35 (m, CH_3CH_2–), 1.20 (t, J = 6.8 Hz, –$OCH_2CH(CH_2OCH_2CH_2OCH_2CH_3)O$–), 0.91 (t, J = 7.6 Hz, CH_3–). $M_{n,NMR}$ = 13,700 g mol^{-1}; $M_{n,SEC}$ = 10,900 g mol^{-1}; M_w/M_n = 1.04.

Synthesis of poly(MeEOGE-*b*-EtEOGE). First, poly(MeEOGE) ($M_{n,NMR}$ = 6,680, M_w/M_n = 1.05) was prepared according to Procedure B using MeEOGE (242 μL, 1.89 mmol, first monomer) with *n*-butanol (37.8 μL as 1.0 mol L^{-1} stock solution in toluene, 37.8 μmol) and *t*-Bu-P_4 (37.8 μL as 1.0 mol L^{-1} stock solution in *n*-hexane, 37.8 μmol) in toluene (439 μL). Complete monomer conversion was verified by ^1H NMR measurement of an aliquot of the polymerization mixture. (*RS*)-EtEOGE (273 μL, 1.89 mmol, second monomer) and toluene (484 μL) were added to the polymerization mixture to further continue the polymerization. After stirring for 24 h at room temperature, the mixture was purified according to procedure B to produce poly($MeEOGE_{0.50}$-*b*-$EtEOGE_{0.50}$)$_{14k}$ as a colorless viscous liquid (400 mg). Yield: 79.6%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.70-3.45 (m, $CH_3CH_2CH_2CH_2O$–, –$OCH_2CH(CH_2OCH_2CH_2OCH_3)O$–, –$OCH_2CH(CH_2OCH_2CH_2OCH_2CH_3)O$–), 3.39-3.35 (m, –$OCH_2CH(CH_2OCH_2CH_2OCH_3)O$–), 1.53 (m, 2H, $CH_3CH_2CH_2$–), 1.35 (m, CH_3CH_2–), 1.20 (t, J = 7.2 Hz, –$OCH_2CH(CH_2OCH_2CH_2OCH_2CH_3)O$–), 0.91 (t, J = 7.6 Hz, CH_3–). $M_{n,NMR}$ = 13,600 g mol^{-1}; $M_{n,SEC}$ = 11,500 g mol^{-1}; M_w/M_n = 1.06.

2. Additional Tables

Table S1. *t*-Bu-P$_4$-catalyzed ring-opening polymerization of various glycidyl ether monomers [a]

sample ID	monomer	$[M]_0$/ $[n\text{-BuOH}]_0$/ $[t\text{-Bu-P}_4]$	time (h)	$M_{n,theo}$ [b] (g mol^{-1})	$M_{n,NMR}$ [c] (g mol^{-1})	M_w/M_n [d]
poly(MeGE)$_{2k}$	MeGE	25/1/1	12	2,280	2,290	1.08
poly(MeGE)$_{4k}$		50/1/1	20	4,480	4,570	1.04
poly(MeGE)$_{5k}$		56/1/1	20	5,010	4,940	1.03
poly(MeGE)$_{7k}$		75/1/1	20	6,680	6,840	1.04
poly(MeGE)$_{9k}$		100/1/1	24	8,890	8,990	1.04
poly(EtGE)$_{2k}$	EtGE	25/1/1	12	2,630	2,630	1.05
poly(EtGE)$_{5k}$		50/1/3	20	5,180	5,290	1.04
poly(*i*PrGE)$_{6k}$	*i*PrGE	50/1/1	20	5,880	6,380	1.05
poly(MeEOGE)$_{3k}$	MeEOGE	25/1/1	12	3,380	3,480	1.09
poly(MeEOGE)$_{5k}$		37/1/1	12	4,960	4,860	1.05
poly(MeEOGE)$_{7k}$		50/1/1	20	6,680	6,620	1.04
poly(MeEOGE)$_{10k}$		75/1/1	20	9,990	9,930	1.04
poly(MeEOGE)$_{14k}$		100/1/1	24	13,700	13,500	1.06
poly(EtEOGE)$_{4k}$	EtEOGE	25/1/1	12	3,730	3,890	1.06
poly(EtEOGE)$_{5k}$		34/1/1	12	5,040	5,030	1.04
poly(EtEOGE)$_{7k}$		50/1/1	20	7,380	7,480	1.04
poly(EtEOGE)$_{11k}$		75/1/1	20	11,000	11,200	1.04
poly(EtEOGE)$_{13k}$		100/1/1	24	14,700	13,100	1.05
poly(PrEOGE)$_{10k}$	PrEOGE	50/1/1	20	8,080	9,830	1.04
poly(MeEO$_2$GE)$_{9k}$	MeEO$_2$GE	50/1/2	20	8,880	8,820	1.03
poly(EtEO$_2$GE)$_{5k}$	EtEO$_2$GE	25/1/1	12	4,830	4,930	1.06
poly(EtEO$_2$GE)$_{10k}$		50/1/1	20	9,590	9,910	1.04
poly(MeEO$_3$GE)$_{8k}$	MeEO$_3$GE	33/1/1	20	7,340	7,600	1.05

[a] Polymerization condition: Ar atmosphere; solvent, toluene; initiator, *n*-butanol; $[M]_0 = 2.5$ mol L^{-1}; temp., 27 °C; conv., >99%. [b] Calculated from ($[M]_0/[n\text{-BuOH}]_0$) × (conv.) × (M.W. of monomer) + (M.W. of initiator). [c] Determined by ^{1}H NMR in CDCl$_3$. [d] Determined by SEC in THF using polystyrene standards.

Table S2. Polymerization of various optically pure epoxide monomers [a]

sample ID	monomer	$[\mathrm{M}]_0$/ $[n\text{-BuOH}]_0$/ $[t\text{-Bu-P}_4]$	time (h)	$M_{\mathrm{n,theo.}}$ [b] (g mol^{-1})	$M_{\mathrm{n,NMR}}$ [c] (g mol^{-1})	$M_{\mathrm{w}}/M_{\mathrm{n}}$ [d]	$[\alpha]_{\mathrm{D}}$ [e] (°)
poly[(*R*)-MeGE]$_{9\mathrm{k}}$	(*R*)-MeGE	100/1/1	24	8,890	8,990	1.04	– 35.7
poly[(*R*)-EtGE]$_{5\mathrm{k}}$	(*R*)-EtGE	50/1/3	20	5,180	5,430	1.04	– 26.3
poly[(*R*)-MeEOGE]$_{13\mathrm{k}}$	(*R*)-MeEOGE	100/1/1	24	13,300	13,100	1.05	– 20.5
poly[(*R*)-EtEOGE]$_{15\mathrm{k}}$	(*R*)-EtEOGE	100/1/1	24	14,700	15,100	1.07	– 21.0
poly[(*R*)-EtEO$_2$GE]$_{10\mathrm{k}}$	(*R*)-EtEO$_2$GE	50/1/1	20	9,590	9,640	1.05	– 14.3

[a] Polymerization condition: Ar atmosphere; solvent, toluene; initiator, *n*-butanol; $[\mathrm{M}]_0 = 2.5$ mol L^{-1}; temp., 27 °C; conv., >99%. [b] Calculated from $([\mathrm{M}]_0/[n\text{-BuOH}]_0)$ × (conv.) × (M.W. of monomer) + (M.W. of initiator). [c] Determined by ^{1}H NMR in CDCl$_3$. [d] Determined by SEC in THF using polystyrene standards. [e] Specific rotation ($[\alpha]_{\mathrm{D}}$) was measured in CHCl$_3$ (*c* 1.0, CHCl$_3$).

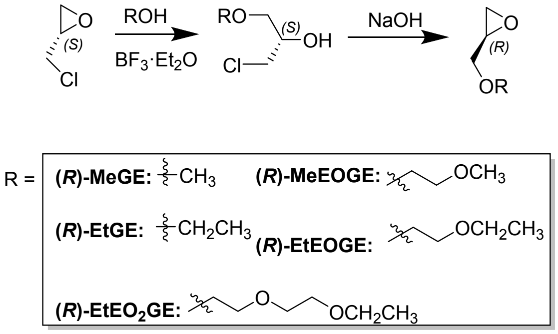
Table S3. Molecular characteristics and properties of atactic and isotactic poly(MeGE)s, poly(EtGE)s, poly(MeEOGE)s, poly(EtEOGE)s, and poly(EtEO$_2$GE)s

sample ID	$M_{\mathrm{n,NMR}}$ [a] (g mol^{-1})	$M_{\mathrm{w}}/M_{\mathrm{n}}$ [b]	T_{cp} [c] (°C)	T_{g} [d] (°C)	T_{c} [e] (°C)	T_{m} [d] (°C)
poly(MeGE)$_{9\mathrm{k}}$	8,990	1.04	63.6	– 64.5	-	-
poly[(*R*)-MeGE]$_{9\mathrm{k}}$	8,990	1.04	62.7	– 64.8	– 3.0	– 23.0
poly(EtGE)$_{5\mathrm{k}}$	5,290	1.04	12.5	– 68.5	-	-
poly[(*R*)-EtGE]$_{5\mathrm{k}}$	5,430	1.04	11.7	– 67.6	7.3	31.7
poly(MeEOGE)$_{14\mathrm{k}}$	13,500	1.06	83.9	– 72.8	-	-
poly[(*R*)-MeEOGE]$_{13\mathrm{k}}$	13,090	1.05	84.8	– 74.3	– 3.2	26.9
poly(EtEOGE)$_{13\mathrm{k}}$	13,100	1.05	39.5	– 75.8	-	-
poly[(*R*)-EtEOGE]$_{15\mathrm{k}}$	15,130	1.07	39.9	– 73.9	-	-
poly(EtEO$_2$GE)$_{10\mathrm{k}}$	9,910	1.04	56.0	– 78.3	-	-
poly[(*R*)-EtEO$_2$GE]$_{10\mathrm{k}}$	9,640	1.05	56.7	– 77.5	-	-

[a] Determined by ^{1}H NMR in CDCl$_3$. [b] Determined by SEC in THF using polystyrene standards. [c] Determined by turbidimetric analysis for a 1 wt% aqueous polymer solution. [d] Glass transition temperature (T_{g}) and melting temperature (T_{m}) were determined by DSC analysis during the second heating (heating rate, 10 °C min^{-1}). [e] Crystallization temperature (T_{c}) was determined by DSC analysis during the first cooling (cooling rate, 10 °C min^{-1}).

3. Additional Scheme

Scheme S1. Synthesis of optically-pure glycidyl ethers



4. Additional Figures

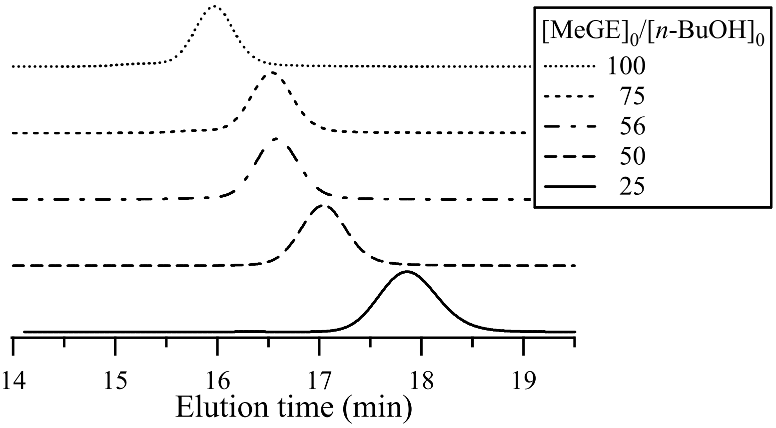


Figure S1. SEC traces of poly(MeGE)s with various molecular weights (eluent, THF; flow rate, 1.0 mL min^{-1}).

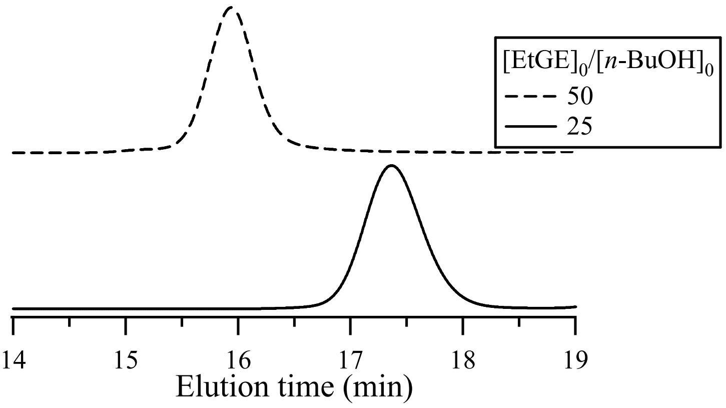


Figure S2. SEC traces of poly(EtGE)s with various molecular weights (eluent, THF; flow rate, 1.0 mL min^{-1}).

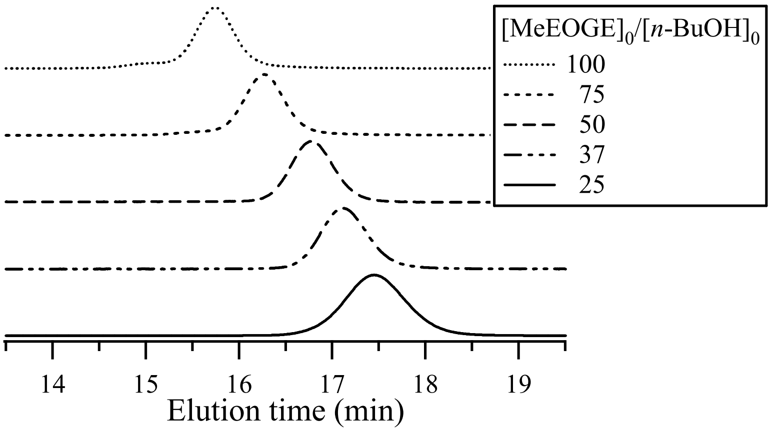


Figure S3. SEC traces of poly(MeEOGE)s with various molecular weight (eluent, THF; flow rate, 1.0 mL min^{-1}).

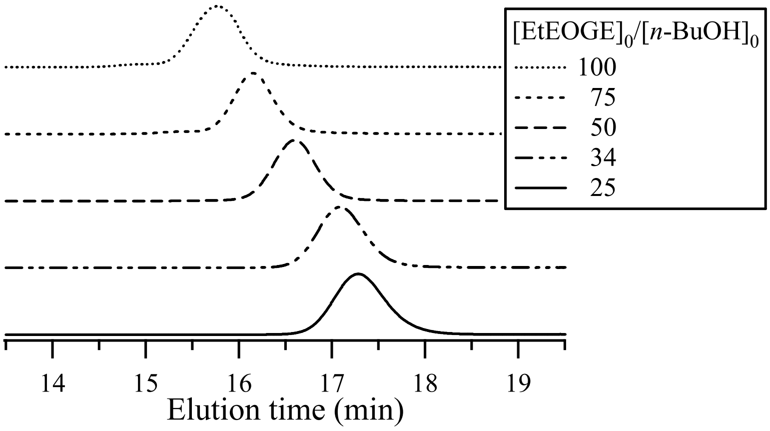


Figure S4. SEC traces of poly(EtEOGE)s with various molecular weights (eluent, THF; flow rate, 1.0 mL min^{-1}).

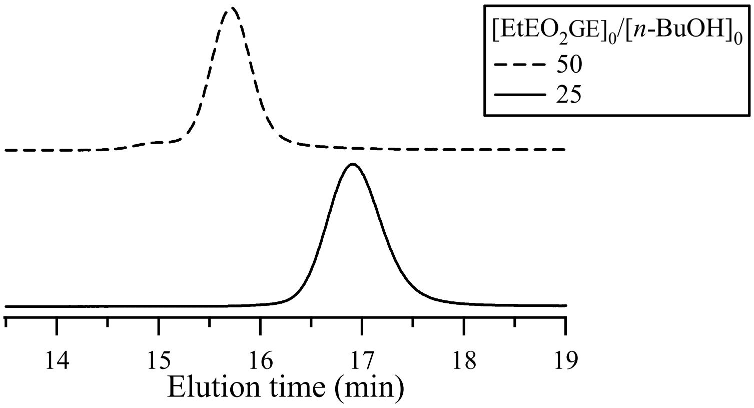


Figure S5. SEC traces of poly($EtEO_2GE$)s with various molecular weights (eluent, THF; flow rate, 1.0 mL min^{-1}).

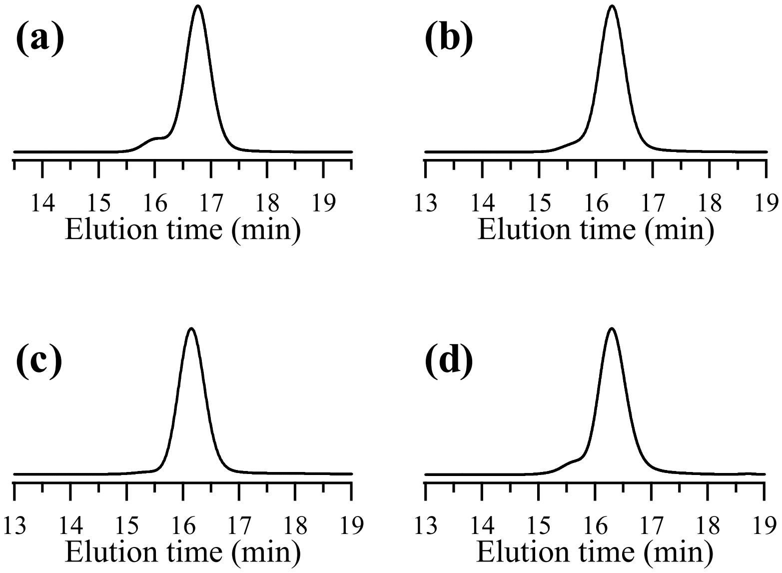


Figure S6. SEC traces of (a) poly(*i*PrGE)$_{6k}$, (b) poly(PrEOGE)$_{10k}$, (c) poly($MeEO_2GE$)$_{9k}$, and (d) poly($MeEO_3GE$)$_{8k}$ (eluent, THF; flow rate, 1.0 mL min^{-1}).

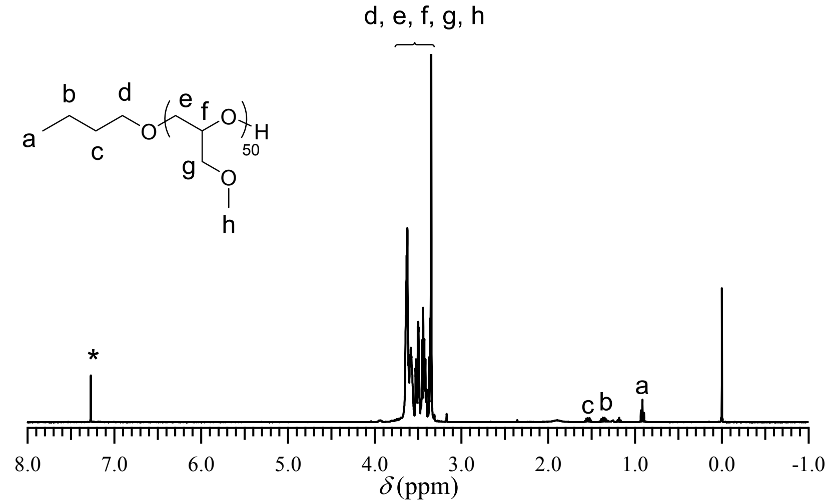


Figure S7. ^{1}H NMR spectrum of poly(MeGE)$_{4k}$ in CDCl$_3$ (400 MHz). The asterisks indicate the solvent peaks.

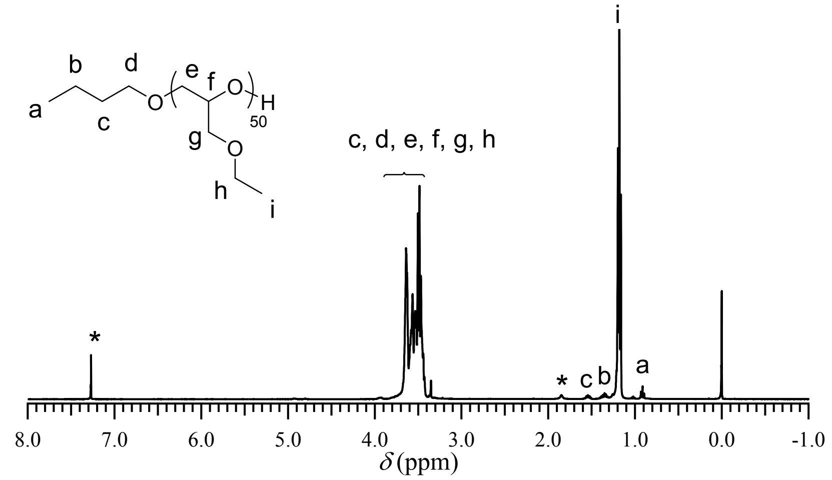


Figure S8. ^{1}H NMR spectrum of poly(EtGE)$_{5k}$ in CDCl$_3$ (400 MHz). The asterisks indicate the solvent peaks.

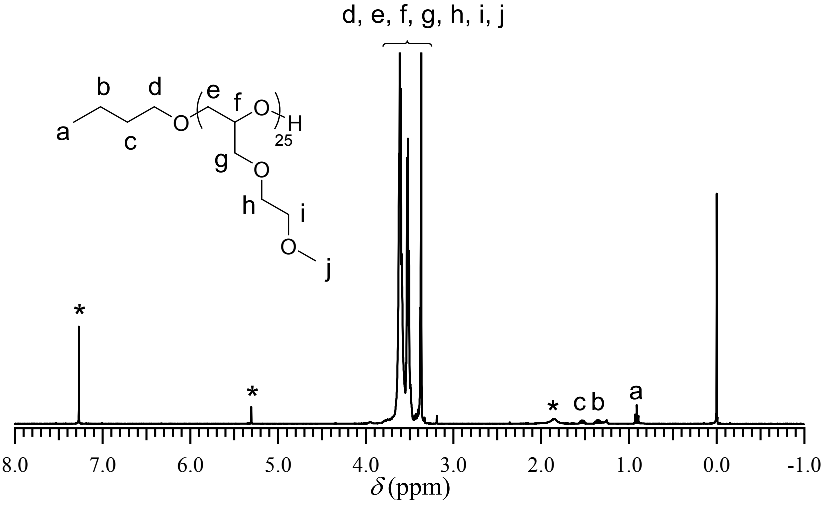


Figure S9. ^{1}H NMR spectrum of poly(MeEOGE)$_{3k}$ in CDCl$_3$ (400 MHz). The asterisks indicate the solvent peaks.

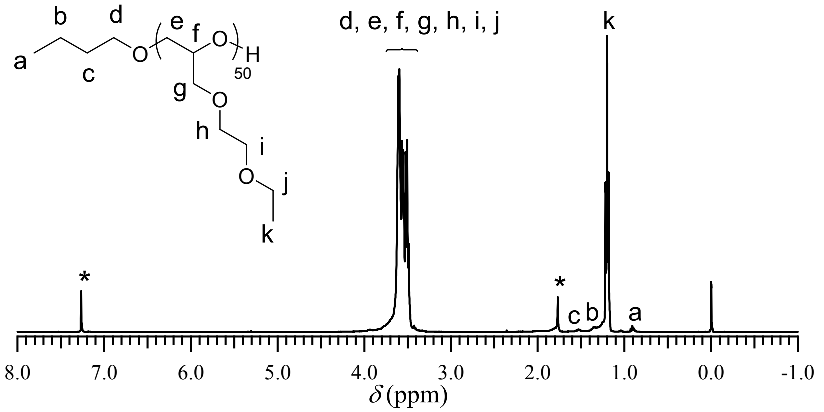


Figure S10. ^{1}H NMR spectrum of poly(EtEOGE)$_{7k}$ in CDCl$_3$ (400 MHz). The asterisks indicate the solvent peaks.

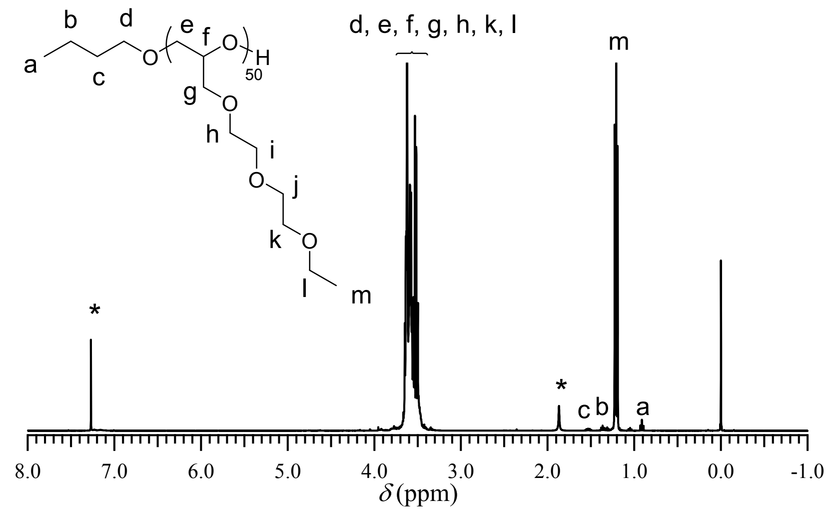


Figure S11. ^{1}H NMR spectrum of poly(EtEO$_2$GE)$_{10k}$ in CDCl$_3$ (400 MHz). The asterisks indicate the solvent peaks.

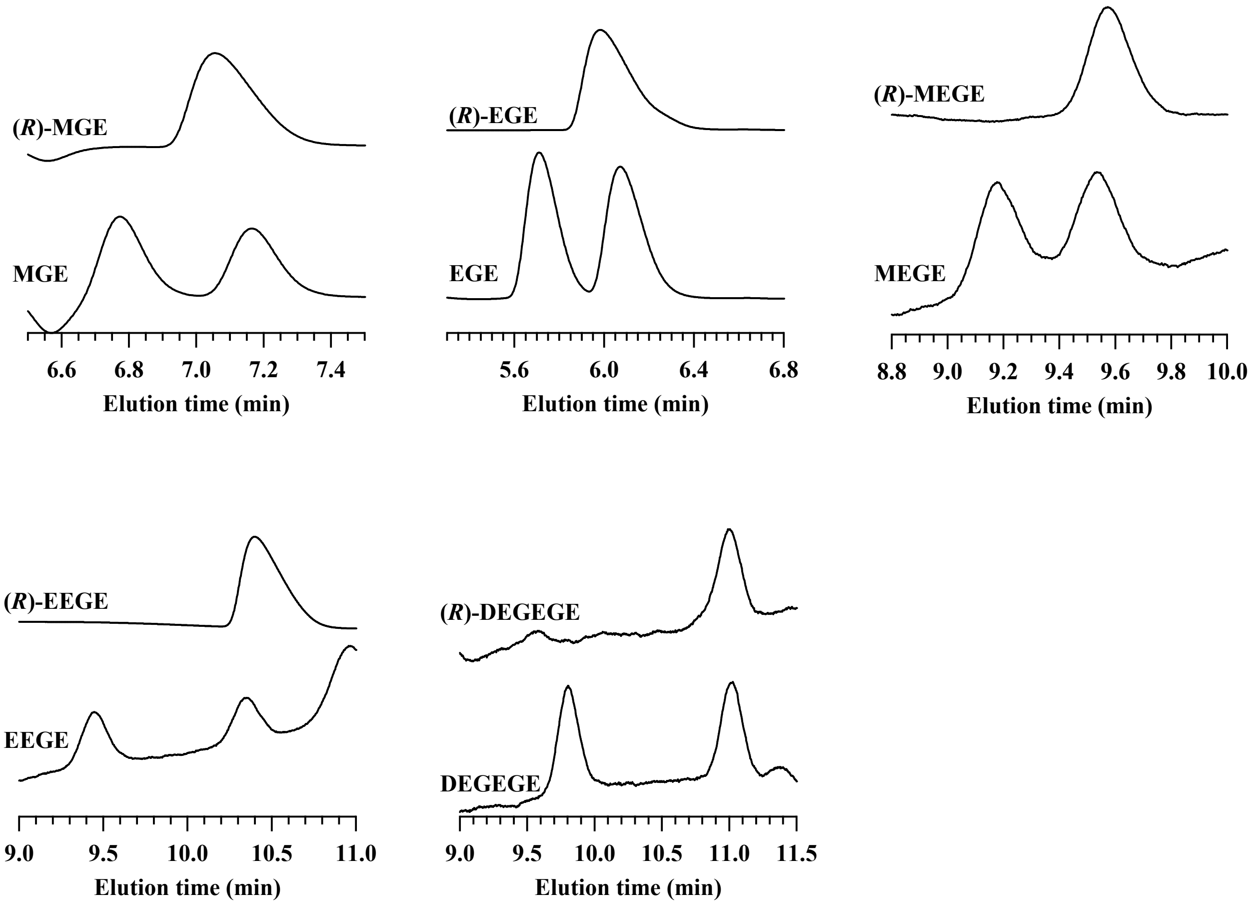


Figure S12. Chiral HPLC chromatograms of racemic and optically pure glycidyl ethers (column, CHIRALPAK IC; mobile phase, *n*-hexane/ethanol = 95/5 v/v; flow rate, 1.0 mL min^{-1}).

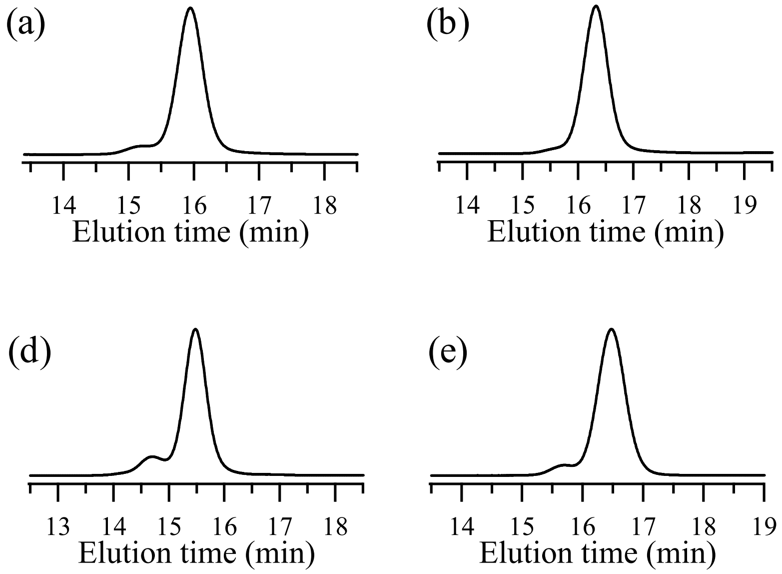


Figure S13. SEC traces of (a) poly[(*R*)-MeGE]$_{9k}$, (b) poly([(*R*)-EtGE]$_{5k}$, (c) poly[(*R*)-MeEOGE]$_{13k}$, (d) poly[(*R*)-EtEOGE]$_{15k}$, and (e) poly[(*R*)-EtEO$_2$GE]$_{10k}$ (eluent, THF; flow rate, 1.0 mL min^{-1}).

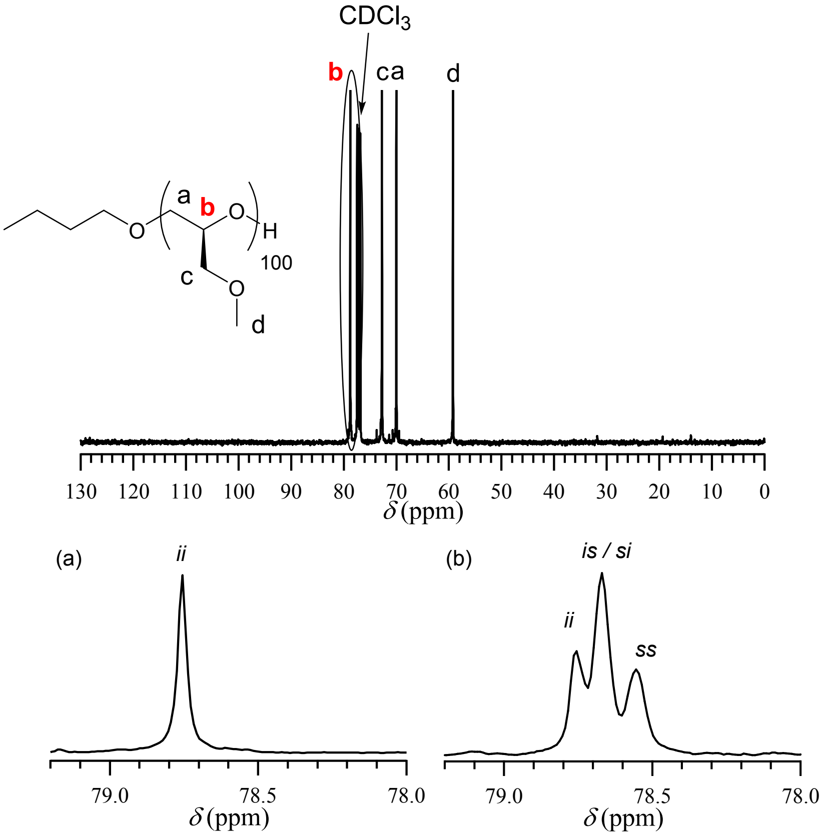


Figure S14. ^{13}C NMR spectra of poly[(*R*)-MeGE]$_{9k}$ and the expanded methine carbon region of (a) poly[(*R*)-MeGE]$_{9k}$ (b) and poly(MeGE)$_{9k}$ in CDCl$_3$ (100 MHz).

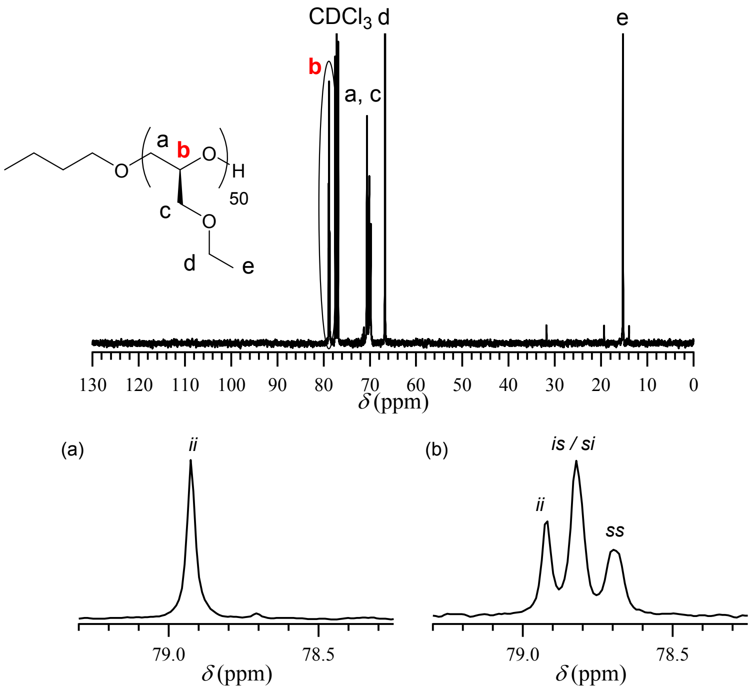


Figure S15. ^{13}C NMR spectra of poly([(*R*)-EtGE]$_{5k}$ and the expanded methine carbon region of (a) poly([(*R*)-EtGE]$_{5k}$ and (b) poly(EtGE)$_{5k}$ in CDCl$_3$ (100 MHz).

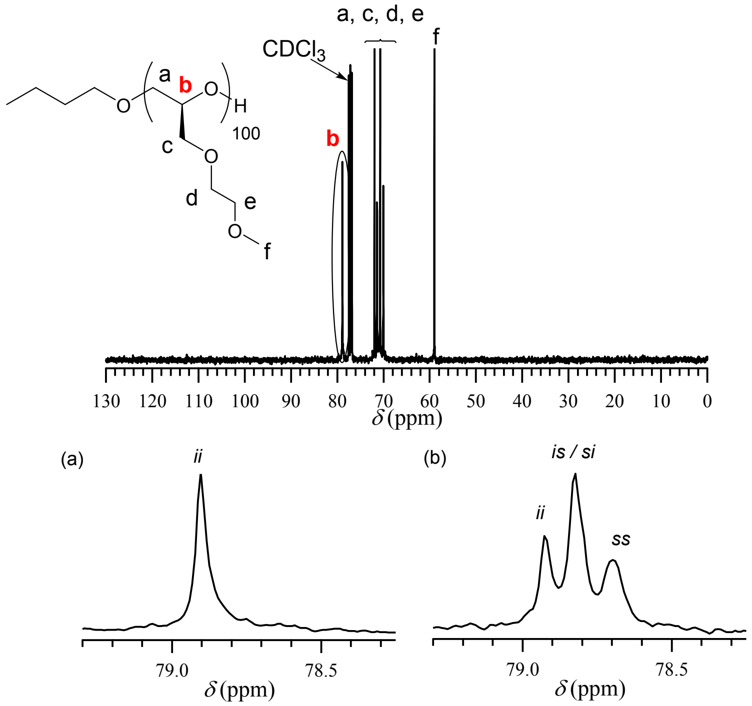


Figure S16. ^{13}C NMR spectra of poly[(*R*)-MeEOGE]$_{13k}$ and the expanded methine carbon region of (a) poly[(*R*)-MeEOGE]$_{13k}$ and (b) poly(MeEOGE)$_{14k}$ in CDCl$_3$ (100 MHz).

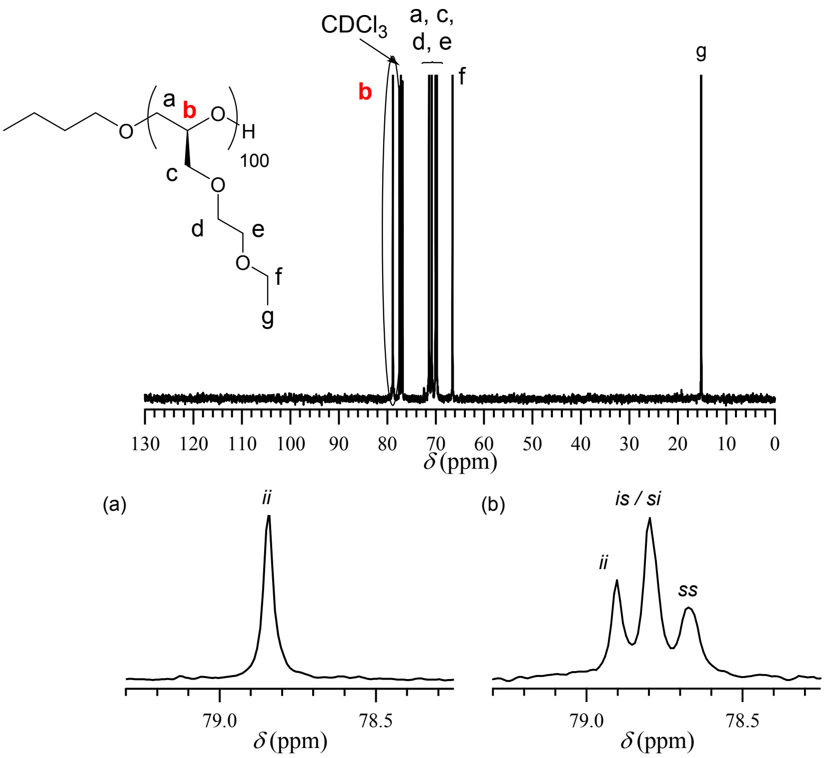


Figure S17. ^{13}C NMR spectra of poly[(*R*)-EtEOGE]$_{15k}$ and the expanded methine carbon region of (a) poly[(*R*)-EtEOGE]$_{15k}$ and (b) poly(EtEOGE)$_{13k}$ in CDCl$_3$ (100 MHz).

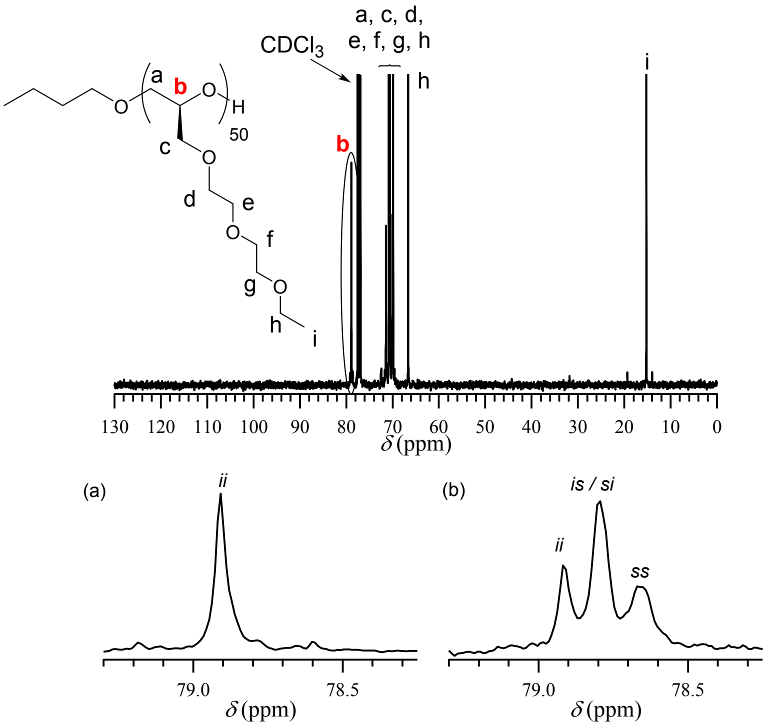


Figure S18. ^{13}C NMR spectra of poly[(*R*)-EtEO$_2$GE]$_{10k}$ and the expanded methine carbon region of (a) poly[(*R*)-EtEO$_2$GE]$_{10k}$ and (b) poly(EtEO$_2$GE)$_{10k}$ in CDCl$_3$ (100 MHz).

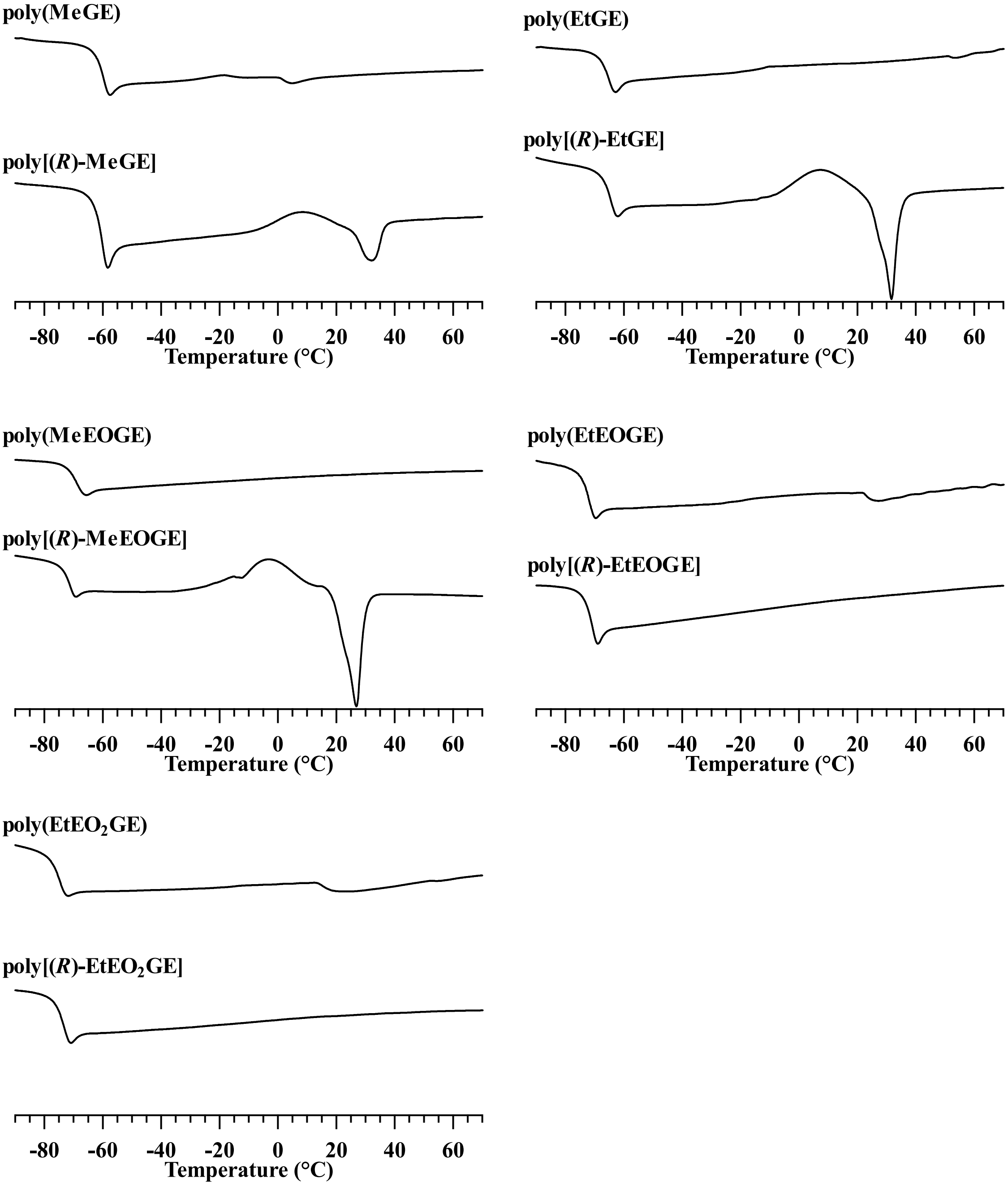


Figure S19. DSC thermogrames of atactic and isotactic poly(MeGE)s, poly(EtGE)s, poly(MeEOGE)s, poly(EtEOGE)s, and poly(EtGEO$_2$GE)s during the second heating (heating rate of 10 °C min^{-1}).

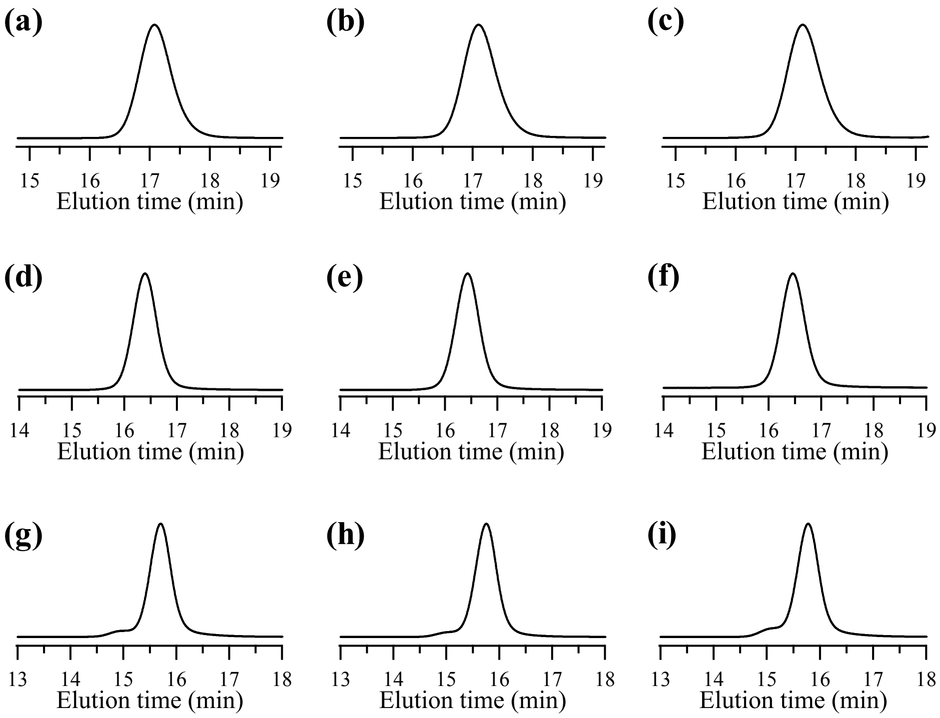


Figure S20. SEC traces of poly(MeEOGE-*st*-EtEOGE)s ([MeEOGE]$_0$/[EtEOGE]$_0$/[*n*-BuOH]$_0$ = (a) 6/19/1, (b) 13/13/1, (c) 19/6/1, (d) 13/37/1, (e) 25/25/1, (f) 37/13/1, (g) 25/75/1, (h) 50/50/1, (i) 75/25/1) (eluent, THF; flow rate, 1.0 mL min^{-1}).

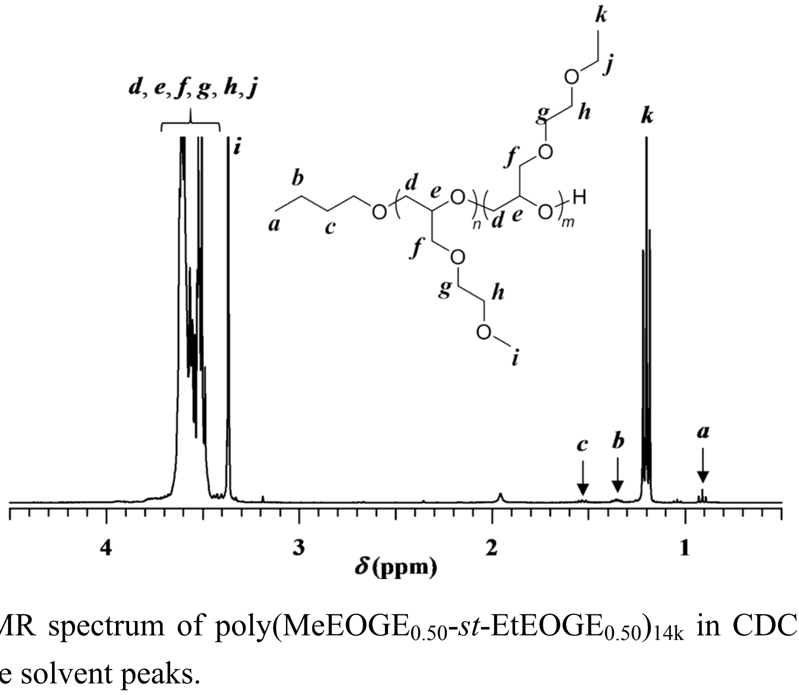


Figure S21. ^{1}H NMR spectrum of poly(MeEOGE$_{0.50}$-*st*-EtEOGE$_{0.50}$)$_{14k}$ in CDCl$_3$ (400 MHz). The asterisks indicate the solvent peaks.

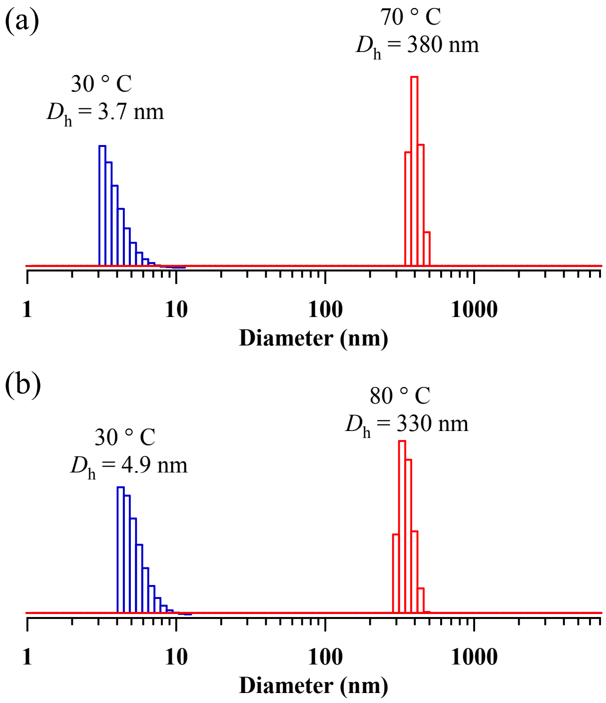


Figure S22. Number-average particle size distributions for the aqueous solution of (a) poly(MeEOGE$_{0.24}$-*b*-EtEOGE$_{0.76}$)$_{18k}$ and (b) poly(MeEOGE$_{0.75}$-*b*-EtEOGE$_{0.25}$)$_{14k}$ at the indicated temperatures.

5. Additional Discussion for Tacticity Effects on Thermal Properties

The lack of the tacticity effect on the thermoresponsive properties is highly significant from practical point of view. It is well known that the tacticity of the resultant polyethers can be affected by the employed polymerization catalyst (or initiator), even when a racemic epoxide monomer is used.[2] Meanwhile, our present results demonstrated that a polyether with the targeted thermoresponsive property can be unambiguously obtained regardless of the polymerization catalyst (or initiator). This is in sharp contrast to the bulk properties of the polyethers. In fact, a number of previous studies reported a significant difference in the polymer properties, such as melting point, glass transition temperature, and crystallinity, between the atactic and stereoregular polyethers. In addition, as shown in Table S3 and Figure S19, the atactic and isotactic poly(MeGE)s, poly(EtGE)s, and poly(MeEOGE)s exhibited a difference in the crystallization ability; the atactic ones did not show any evidence of crystallization and melting by the DSC measurement, while the isotactic ones showed both recrystallization and melting transitions during the second heating process.

6. References

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