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Supporting Information

Selective ring-opening polymerization of glycidyl ester: a versatile synthetic platform for glycerol-based (co)polyethers

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Experimental Section

Materials

Benzyl alcohol (BA; Energy Chemical, 99%), (R)-(-)-glycidyl butyrate (*R*GB; Energy Chemical, 97%), (S)-(+)-glycidyl butyrate (*S*GB; Energy Chemical, 95%), *tert*-butyl glycidyl ether (^{t}BGE; Aldrich, 99%), and dichloromethane (CH_2Cl_2; Guangzhou Chemical Reagent, AR) were dried over calcium hydride (CaH_2) and (vacuum-)distilled. 1,4-Benzenedimethanol (BDM; Aladdin, 99%) was dried by azeotropic distillation of purified THF prior to use. Ethylene oxide (EO; Aldrich, 99%) was first condensed from a metal cylinder into a Schlenk flask by cooling the flask at 0 °C under vacuum and dried by stirring with sodium hydride (NaH) at 0 °C for 4 h, then vacuum-transferred into a graduated flask pre-charged with *n*-BuLi and stirred at 0 °C for 1 h before finally cryo-distilled into the reaction flask. Propylene oxide (PO; Aldrich, 99%) was stirred with NaH overnight and cryo-distilled into a storage flask. Neutral alumina (Aladdin, AR) were washed with CH_2Cl_2 and vacuum-dried prior to use. Methanol (CH_3OH; Guangzhou Chemical Reagent, AR), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; TCI, 98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; TCI, 98%), triethylborane (Et_3B; TCI, 1.0 mol L^{-1} in THF), and 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene) (^{t}BuP$_2$; Aldrich, 2.0 mol L^{-1} in THF) were used as received.

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker AV400 NMR spectrometer using deuterated chloroform ($CDCl_3$), dimethyl sulfoxide (DMSO-d_6) or methanol-d_4 as the solvent and tetramethylsilane as the internal standard. ^{1}H NMR spectra were used to calculate number-average molar mass ($M_{n,NMR}$) by comparing the integrals of signals from end groups and polymer main bodies.

Size exclusion chromatography (SEC) coupled with a refractive index (RI) detector was conducted in THF at 35 °C using two identical PLgel MIXED-C columns at a flow rate of 1.0 mL min^{-1}. Calibration was done with a series of narrowly dispersed polystyrene (PS) standards to obtain the apparent number-average molar mass ($M_{\mathrm{n,SEC}}$) and molar mass distribution ($Đ_{\mathrm{M}}$) of the (co)polyethers. For polyglycerols or other (co)polyethers that are poorly soluble in THF, SEC was conducted in *N*,*N*-dimethylformamide (DMF) with LiBr (0.05 mol L^{-1}) at 50 °C with the same flow rate using three successively connected Styragel columns (HR2, HR4, HR6). A series of narrowly dispersed polystyrene (PS) standards were used for calibration.

Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) measurement was performed on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer (Bruker, Germany). Samples were dissolved in THF (10 mg mL^{-1}, CH_3OH was used for polyglycerols) and mixed with a solution of sodium trifluoroacetate in THF (10 mg mL^{-1}) in a volume ratio of 5:1. This solution was then mixed with a solution of matrix, 2,5-dihdroxybenzoic acid in THF (20 mg mL^{-1}), in a volume ratio of 1:20. Then, 0.4 μL of the final solution was spotted on the target plate (dried-droplet method). The reflective positive ion mode was used to acquire the mass spectra of the samples. Calibration was done externally with poly(methyl methacrylate) standards using the nearest neighbor positions.

Thermosensitivity in aqueous solution was estimated by cloud points measurements conducted in deionized water at a polymer concentration of 1.0 mg mL^{-1} using the optical transmittance of a light beam (λ = 600 nm) in a U-3010 spectrophotometer. The intensities of the transmitted light were recorded versus the temperature of the sample cell at a heating rate of 1 K min^{-1}.

Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC204F1 system in a nitrogen flow. The sample was heated to 200 °C at a rate of 10 °C min^{-1}, kept at this temperature for 5 min to remove thermal history, cooled to −80 °C at a rate of 10 °C min^{-1}, kept at this temperature for 10 min, and then heated again to 200 °C at a rate of 10 °C min^{-1}. The glass transition temperature (T_g) was acquired on the second heating run.

Wide angle X-ray diffraction (WAXD) data were collected on X'pert Powder diffractometer (with Bragg Brentano geometry) over the 2θ range of 0-90° with a scan speed of 12°/min and a step size of 0.013° at room temperature.

The DFT calculations were performed at B3LYP-D3(BJ)[1, 2]/defTZVP[3] level with PCM solvent model (ethyl acetate), in Gaussian 16 package[4].

The CYLview20[5] was used to depicted the 3D structures.

Polymer Synthesis

(1) PRGB by ROP of RGB in bulk

A typical procedure of entry 3 is as follows (Table 1). A round-bottom reaction flask was dried with a heat gun on a vacuum line and transferred into a glovebox where purified BA (49.7 μL, 0.48 mmol), *R*GB (2.0 mL, 14.32 mmol), Et_3B (1.0 mol L^{-1}, 120 μL, 0.12 mmol), and ^{t}BuP_2 (2.0 mol L^{-1}, 12 μL, 0.02 mmol) were successively loaded. The mixture was stirred at room temperature (RT) for 36 h, then a small aliquot was withdrawn for ^{1}H NMR and SEC measurements. Conv.(*R*GB) = 100%, $M_{n,th}$ = 4.4 kg mol^{-1}. $M_{n,SEC}$(THF) = 3.9 kg mol^{-1}, $Đ_M$ = 1.09. White solids (crystallized P*R*GB) appeared when the reaction mixture was stirred for another 36 h at RT, indicating the semicrystalline nature of the polymer. The crude product was dissolved in CH_3OH containing a few drops of acetic acid, and slowly precipitated again when the methanol solution was allowed to stand overnight at -20 °C. After the supernatant was removed, a colorless and viscous liquid product was obtained at RT and dried in vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): 7.35-7.28 ($C_6H_5CH_2O$−P*R*GB−), 4.53 ($C_6H_5CH_2O$−P*R*GB−), 4.28-4.04 (−$OCH_2CH(CH_2OCOC_3H_7)O$−), 3.94 (−P*R*GB−$CH(CH_2OCOC_3H_7)OH$), 3.72-3.50 (−$OCH_2CH(CH_2OCOC_3H_7)O$−), 2.30 (−$OCH_2CH(CH_2OCOCH_2CH_2CH_3)O$−), 1.64

(−$OCH_2CH(CH_2OCOCH_2C\mathit{H}_2CH_3)O$−), 0.94 (−$OCH_2CH(CH_2OCOCH_2CH_2C\mathit{H}_3)O$−); $M_{n,NMR}$ = 4.5 kg mol^{-1}.

(2) PsGC by methanolysis treatment of PRGB

P*R*GB (0.3 g, 2.1 mmol of carboxylic ester groups) described in (1) and TBD (14.1 mg, 0.10 mmol) was dissolved in CH_3OH (2.5 mL) at RT. The mixture was stirred at RT for 12 h before a small aliquot was withdrawn for ^1H NMR analysis to determine the degree of methanolysis (100%). The crude product was precipitated in THF, collected, and dried in vacuum. $M_{n,SEC}$(DMF) = 10.0 kg mol^{-1}, $Đ_M$ = 1.11. ^1H NMR (600 MHz, DMSO-d_6): 7.30 ($C_6\mathit{H}_5CH_2O$−P*s*GC−), 4.48 ($C_6H_5C\mathit{H}_2O$−P*s*GC−), 3.61-3.30 (−$OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2OH)O$−); $M_{n,NMR}$ = 2.3 kg mol^{-1}.

Entry 2, 4~10 followed the same polymerization and methanolysis procedures as entry 3.

(3) P(PO-co-sGB) by random copolymerization of mixed PO and sGB

A typical procedure of entry 14 in Table 1 is as follows. To a pre-dried reaction flask was successively loaded *s*GB (3.2 mL, 22.9 mmol), PO (1.6 mL, 22.9 mmol), BA (47.3 μL, 0.46 mmol), Et_3B (1.0 mol L^{-1}, 182.9 μL, 0.18 mmol), and ^{t}BuP_2 (2.0 mol L^{-1}, 22.9 μL, 0.05 mmol). The reaction mixture was stirred at RT with aliquots withdrawn in different time intervals for ^1H NMR and SEC analysis. The reaction was finally quenched after 18 h by addition of a few drops of acetic acid. Conv.(*s*GB) = 100%, Conv.(PO) = 100%. $M_{n,SEC}$(THF) = 10.5 kg mol^{-1}, $Đ_M$ = 1.09. The crude product was diluted with CH_2Cl_2 and stirred with neutral alumina to remove the catalyst residuals. After filtration and evaporation of the solvent, a colorless and viscous liquid product was obtained and dried in vacuum. ^1H NMR (600 MHz, $CDCl_3$): 7.35-7.31 ($C_6\mathit{H}_5CH_2O$−), 4.54 ($C_6H_5C\mathit{H}_2O$−), 4.26-4.07 (−$OCH_2CH(C\mathit{H}_2OCOC_3H_7)O$−), 3.92 (−$C\mathit{H}(CH_2OCOC_3H_7)OH$ or −$C\mathit{H}(CH_3)OH$), 3.69-3.33 (−$OC\mathit{H}_2C\mathit{H}(CH_2OCOC_3H_7)O$−, −$OC\mathit{H}_2C\mathit{H}(CH_3)O$−), 2.30 (−$OCH_2CH(CH_2OCOC\mathit{H}_2CH_2CH_3)O$−), 1.64

$(-OCH_2CH(CH_2OCOCH_2C\mathit{H}_2CH_3)O-)$, 1.13 $(-OCH_2CH(C\mathit{H}_3)O-)$, 0.95 $(-OCH_2CH(CH_2OCOCH_2CH_2C\mathit{H}_3)O-)$; $M_{\mathrm{n,NMR}}$ = 10.8 kg mol^{-1}.

(4) P(PO-co-rGC) by methanolysis treatment of P(PO-co-sGB)

P(PO-*co*-*s*GB) (0.54 g, 2.67 mmol of carboxylic ester groups) described in (3) and TBD (17.4 mg, 0.13 mmol) was dissolved in CH_3OH (4.0 mL). The mixture was stirred at RT for 12 h before a small aliquot was withdrawn for ^{1}H NMR analysis to determine the degree of methanolysis (100%). $M_{\mathrm{n,SEC}}$(THF) = 6.3 kg mol^{-1}, $Đ_{\mathrm{M}}$ = 1.08. The crude product was diluted with CH_3OH and stirred with cation-exchange resin (Dowex50WX4) to remove the catalyst residuals. After filtration and evaporation of the solvent, a colorless and viscous liquid product was obtained and dried in vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): 7.34-7.33 $(C_6\mathit{H}_5CH_2O-)$, 4.55 $(C_6H_5C\mathit{H}_2O-)$, 3.93 $(-C\mathit{H}(CH_2OH)OH$ or $-C\mathit{H}(CH_3)OH)$, 3.76-3.34 $(-OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2OH)O-$, $-OC\mathit{H}_2C\mathit{H}(CH_3)O-)$, 1.13 $(-OCH_2CH(C\mathit{H}_3)O-)$; $M_{\mathrm{n,NMR}}$ = 6.7 kg mol^{-1}.

Entry 11~13 followed the same polymerization and methanolysis procedures as entry 14.

(5) PrGB-b-P^{t}BGE by block copolymerization of rGB and ^{t}BGE

To a pre-dried reaction flask was successively loaded *r*GB (2.5 mL, 17.9 mmol), BA (26.5 μL, 0.26 mmol), Et_3B (1.0 mol L^{-1}, 102.3 μL, 0.102 mmol), and ^{t}BuP$_2$ (2.0 mol L^{-1}, 12.8 μL, 0.026 mmol). After the reaction mixture was stirred at RT for 48 h, a small aliquot was withdrawn for ^{1}H NMR and SEC measurements. Conv.(*r*GB) = 100%, $M_{\mathrm{n,th}}$(P*r*GB) = 10.2 kg mol^{-1}. $M_{\mathrm{n,SEC}}$(THF) = 7.6 kg mol^{-1}, $Đ_{\mathrm{M}}$ = 1.12. Then ^{t}BGE (2.53 mL, 17.9 mmol) was added and the new reaction mixture was stirred at RT for another 48 h before the addition of a few drops of acetic acid to quench the polymerization. Conv.(^{t}BGE) = 100%, $M_{\mathrm{n,th}}$(P^{t}BGE) = 9.1 kg mol^{-1}. $M_{\mathrm{n,SEC}}$(THF) = 13.0 kg mol^{-1}, $Đ_{\mathrm{M}}$ = 1.09. The crude product was diluted with CH_2Cl_2 and stirred with neutral alumina to remove the catalyst residuals. After filtration and evaporation of the solvent, a viscous liquid product was obtained and dried in vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): 7.35-7.29 $(C_6\mathit{H}_5CH_2O-)$, 4.53 $(C_6H_5C\mathit{H}_2O-)$, 4.26-4.07

$(-OCH_2CH(C\mathit{H}_2OCOC_3H_7)O-)$, 3.69-3.33 $(-OCH_2CH(C\mathit{H}_2OCOC_3H_7)O-$, $-OCH_2CH(C\mathit{H}_2O-CC_3H_9)O-)$, 2.30 $(-OCH_2CH(CH_2OCOC\mathit{H}_2CH_2CH_3)O-)$, 1.64 $(-OCH_2CH(CH_2OCOCH_2C\mathit{H}_2CH_3)O-)$, 1.16 $(-OCH_2CH(CH_2O-CC_3\mathit{H}_9)O-)$, 0.95 $(-OCH_2CH(CH_2OCOCH_2CH_2C\mathit{H}_3)O-)$; $M_{n,NMR}$ = 18.9 kg mol^{-1}.

(6) PSGC-b-P^{t}BGE by methanolysis treatment of PRGB-b-P^{t}BGE

P(*R*GB-*b*-^{t}BGE) (0.50 g, 1.82 mmol of carboxylic ester groups) described in (5) and TBD (12.7 mg, 0.09 mmol) was dissolved in CH_3OH (4.0 mL). The mixture was stirred at RT for 12 h before a small aliquot was withdrawn for ^{1}H NMR analysis to determine the degree of methanolysis (100%). $M_{n,SEC}$(DMF) = 22.9 kg mol^{-1}, $Đ_M$ = 1.10. The crude product was diluted with CH_3OH and stirred with cation-exchange resin (Dowex50WX4) to remove the catalyst residuals. After filtration and evaporation of the solvent, a white solid product was obtained and dried in vacuum. ^{1}H NMR (600 MHz, methanol-*d*$_4$): 7.35-7.29 $(C_6\mathit{H}_5CH_2O-)$, 4.54 $(C_6H_5C\mathit{H}_2O-)$, 3.75-3.40 $(-OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2OH)O-$, $-OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2O-CC_3H_9)O-)$, 1.20 $(-OCH_2CH(CH_2O-CC_3\mathit{H}_9)O-)$; $M_{n,NMR}$ = 14.3 kg mol^{-1}.

(7) PRGB-b-PEO by block copolymerization of RGB and EO

ROP of *R*GB followed the same procedure as (5). Conv.(*R*GB) = 100%, $M_{n,th}$(P*R*GB) = 10.2 kg mol^{-1}. $M_{n,SEC}$(DMF) = 12.1 kg mol^{-1}, $Đ_M$ = 1.12. Then EO (1.6 mL, 30.7 mmol) was cryo-distilled into the flask at -20 °C. The new reaction mixture was slowly warmed up to RT and stirred for another 5 h to obtain a white solid. Conv.(EO) = 100%, $M_{n,th}$ (PEO) = 5.3 kg mol^{-1}. $M_{n,SEC}$(DMF) = 22.2 kg mol^{-1}, $Đ_M$ = 1.15. The crude product was dissolved in CH_2Cl_2 containing a few drops of acetic acid and precipitated with *n*-hexane. A white solid was then collected and dried in vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): 7.35-7.29 $(C_6\mathit{H}_5CH_2O-)$, 4.53 $(C_6H_5C\mathit{H}_2O-)$, 4.26-4.07 $(-OCH_2CH(C\mathit{H}_2OCOC_3H_7)O-)$, 3.78-3.50 $(-OC\mathit{H}_2C\mathit{H}(C\mathit{H}_2OCOC_3H_7)O-$, $-OC\mathit{H}_2C\mathit{H}_2O-)$, 2.30

(−OCH$_2$CH(CH$_2$OCOC*H*$_2$CH$_2$CH$_3$)O−), 1.64 (−OCH$_2$CH(CH$_2$OCOCH$_2$C*H*$_2$CH$_3$)O−), 0.95 (−OCH$_2$CH(CH$_2$OCOCH$_2$CH$_2$C*H*$_3$)O−); $M_{\mathrm{n,NMR}}$ = 16.1 kg mol^{-1}.

(8) PsGC-b-PEO by methanolysis treatment of PRGB-b-PEO

The methanolysis of P(*R*GB-*b*-EO) followed the same procedure as described in (6), achieving a degree of methanolysis of 100%. $M_{\mathrm{n,SEC}}$(DMF) = 25.2 kg mol^{-1}, $Đ_{\mathrm{M}}$ = 1.12. ^{1}H NMR (600 MHz, methanol-*d*$_4$): 7.35-7.29 (C$_6$*H*$_5$CH$_2$O−), 4.55 (C$_6$H$_5$C*H*$_2$O−), 3.78-3.48 (−OC*H*$_2$C*H*(C*H*$_2$OH)O−, −OC*H*$_2$C*H*$_2$O−). $M_{\mathrm{n,NMR}}$ = 10.8 kg mol^{-1}.

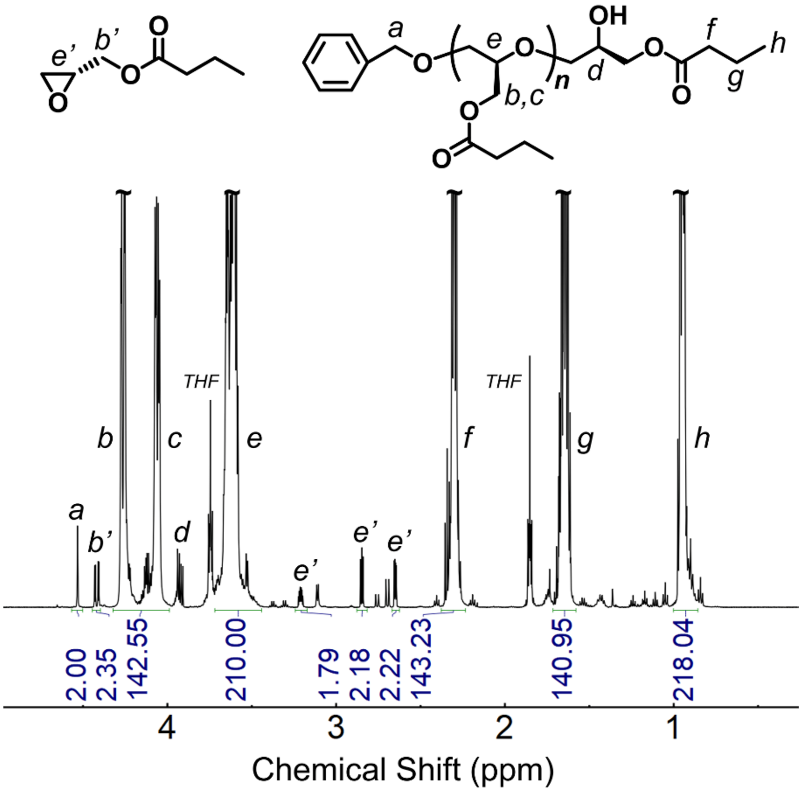

Figure S1. ^{1}H NMR spectrum (in $CDCl_3$; crude product) of BA-initiated P*R*GB (DP = 70; entry 1 in Table 1) obtained after the ROP of *R*GB proceeds for 9 days at room temperature.

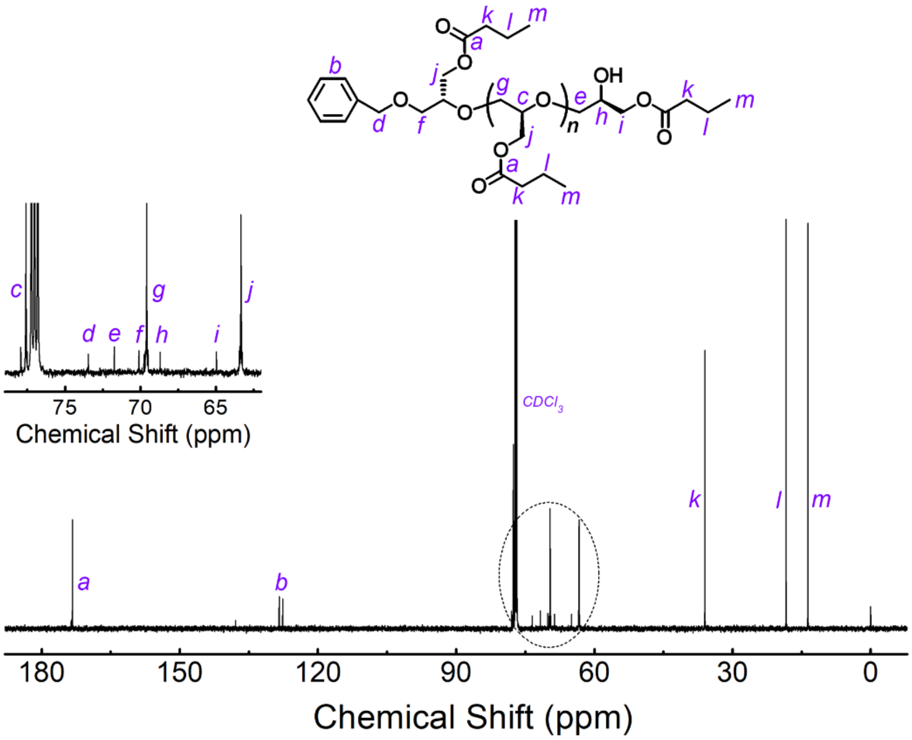

Figure S2. ^{13}C NMR spectrum (in $CDCl_3$) with an enlarged area of a P*R*GB with a DP of 30 (the isolated product of entry 3 in Table 1).

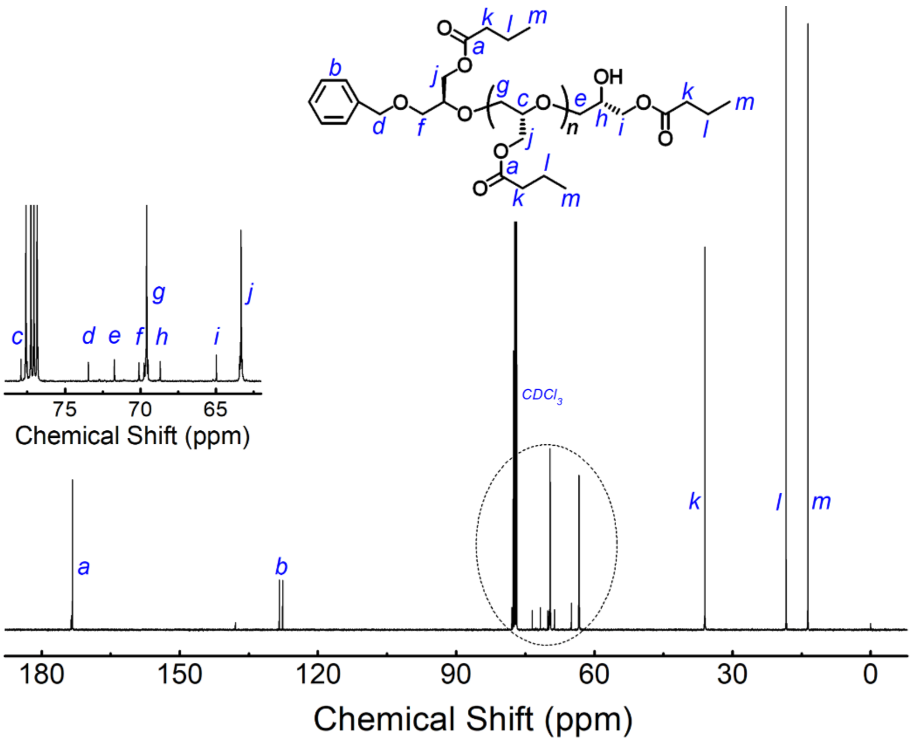

Figure S3. ^{13}C NMR spectrum (in CDCl$_3$) with an enlarged area of a P*S*GB with a DP of 30 (the isolated product of entry 5 in Table 1).

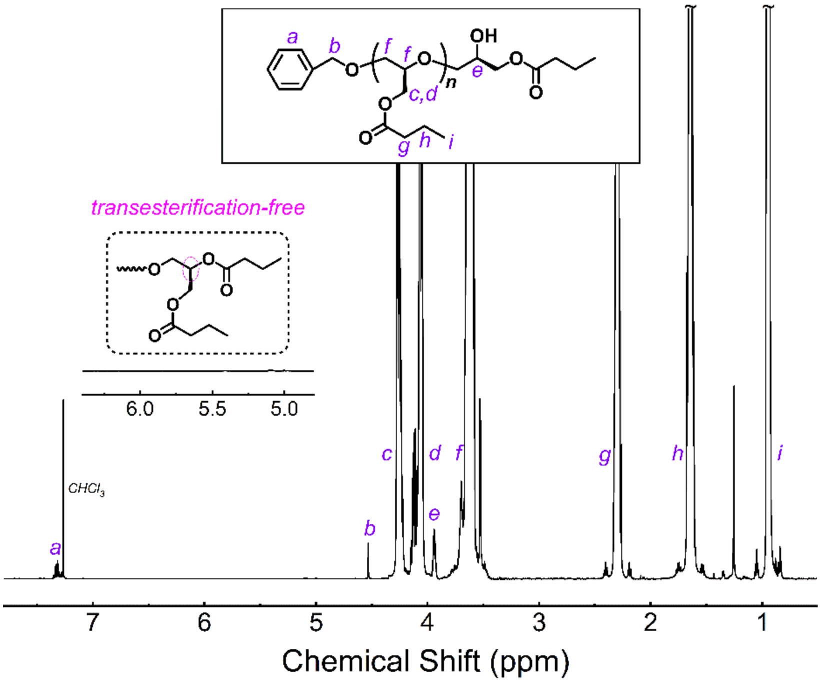

Figure S4. ^{1}H NMR spectrum (in CDCl$_3$) with an enlarged area of a P*R*GB with a DP of 280 (the isolated product of entry 4 in Table 1).

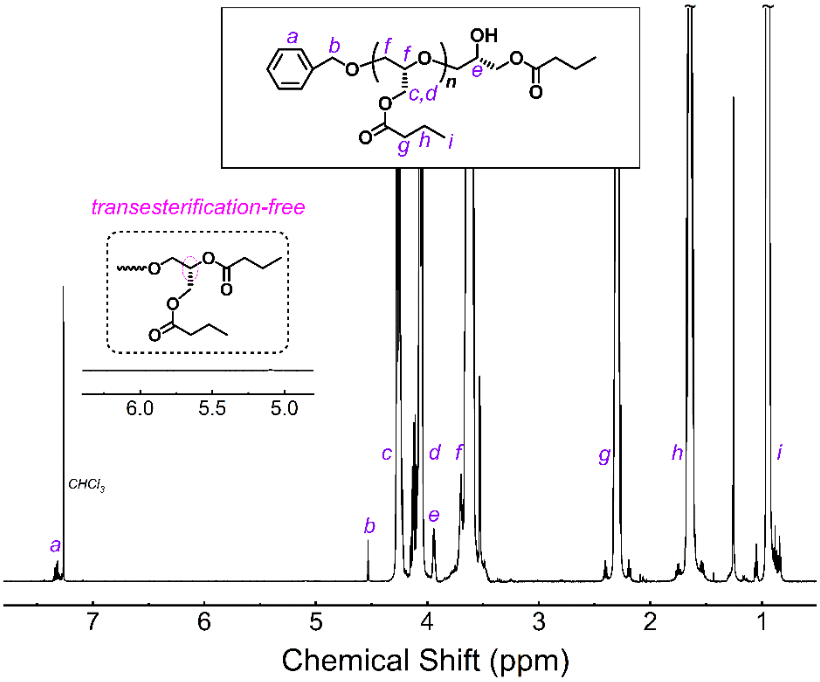

Figure S5. ^{1}H NMR spectrum (in $CDCl_3$) with an enlarged area of a P*S*GB with a DP of 280 (the isolated product of entry 7 in Table 1).

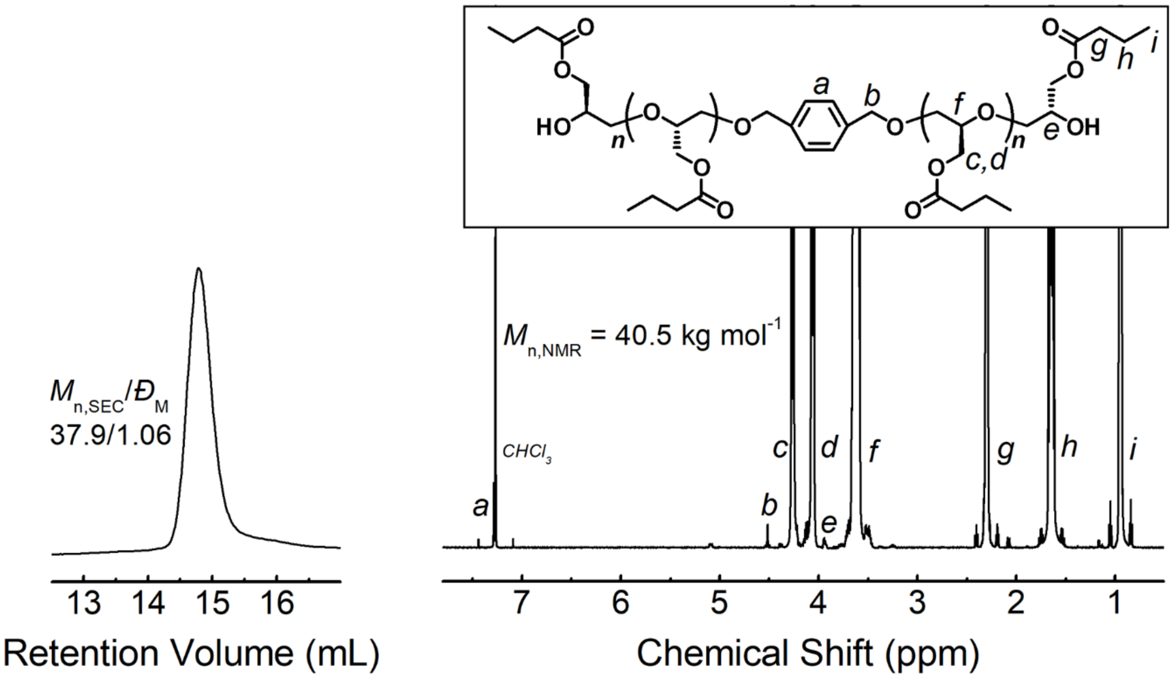

Figure S6. SEC trace (left; RI signals, THF, 35 °C, PS standards; with $M_{\mathrm{n,SEC}}$ and $Đ_{\mathrm{M}}$ noted; crude product) and ^{1}H NMR spectrum (right; in $CDCl_3$; with $M_{\mathrm{n,NMR}}$ noted; isolated product) of BDM-initiated P*R*GB with a DP of 280 (entry 9 in Table 1).

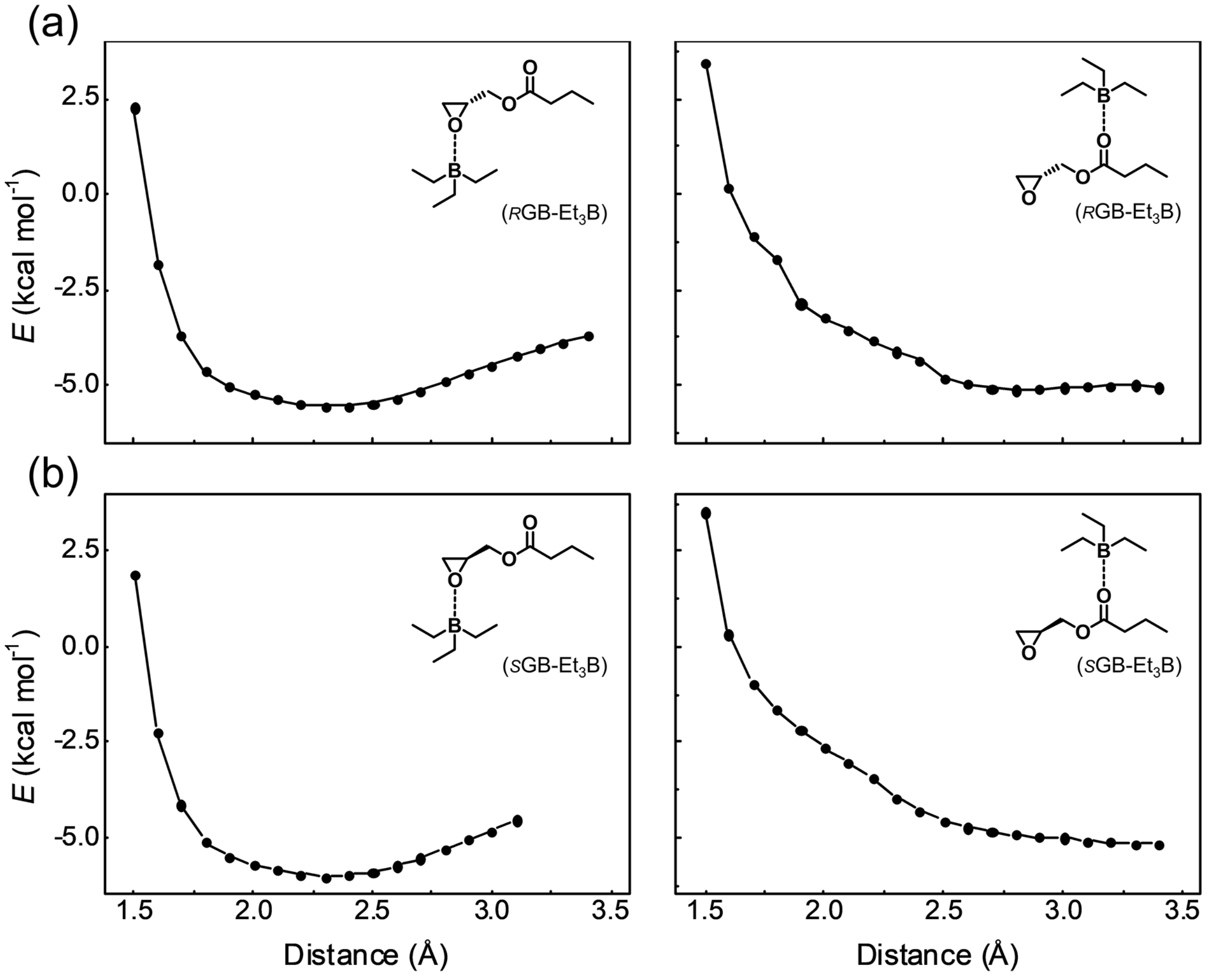

Figure S7. DFT calculated interaction energy versus atom distance for (a) *R*GB-Et$_3$B and (b) *S*GB-Et$_3$B pairs under B3LYP-D3(BJ)/defTZVP level with PCM solvent model (ethyl acetate).

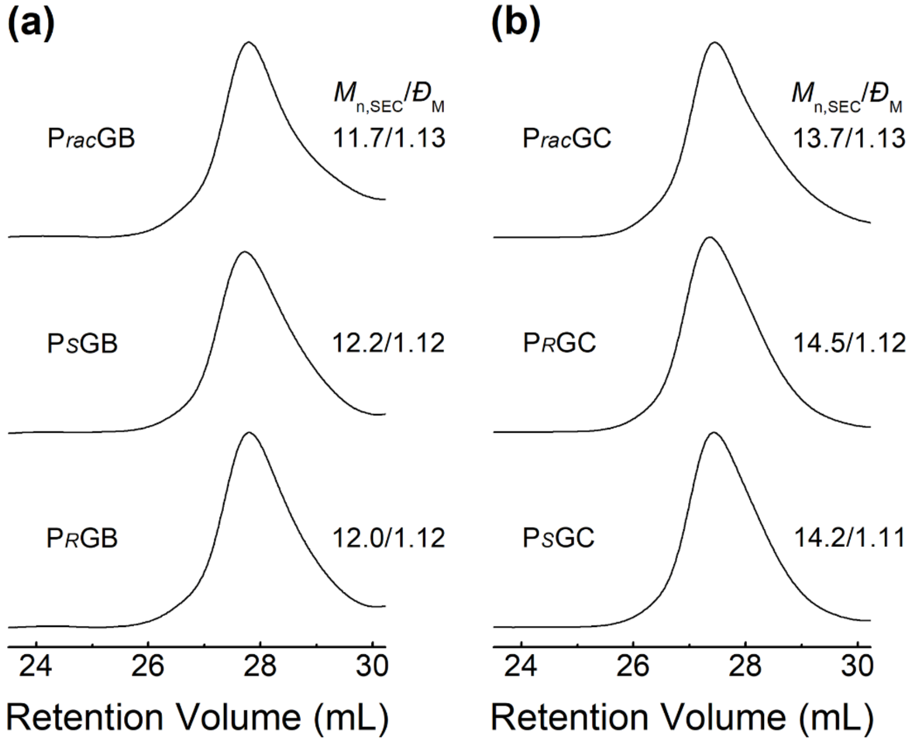

Figure S8. SEC traces (RI signals, DMF, 50 °C, PS standards; with $M_{n,SEC}$ and $Đ_M$ noted; isolated product, DP = 70) of (a) P*R*GB (entry 2 in Table 1), P*S*GB (entry 6 in Table 1), P*rac*GB (entry 10 in Table 1) and (b) the corresponding P*S*GC, P*R*GC, P*rac*GC obtained by TBD-catalyzed methanolysis of the pendent butyrate groups.

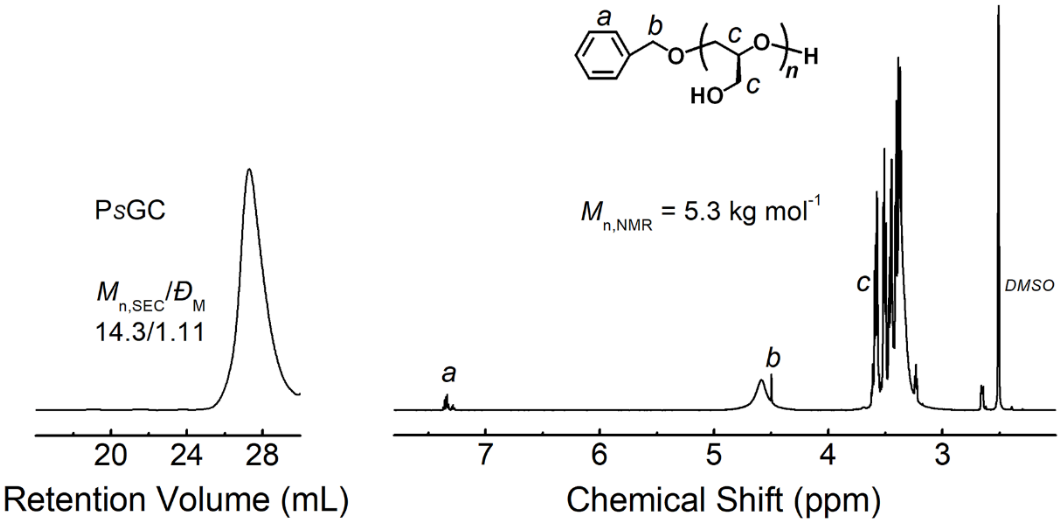

Figure S9. SEC trace (left, RI signals, DMF, 50 °C, PS standards; with $M_{n,SEC}$ and $Đ_M$ noted; crude product) and ^{1}H NMR spectrum (right; in DMSO-d_6; with $M_{n,NMR}$ noted; isolated product) of P*S*GC obtained by DBU-catalyzed methanolysis of the parent P*R*GB (DP = 70; the isolated product of entry 2 in Table 1).

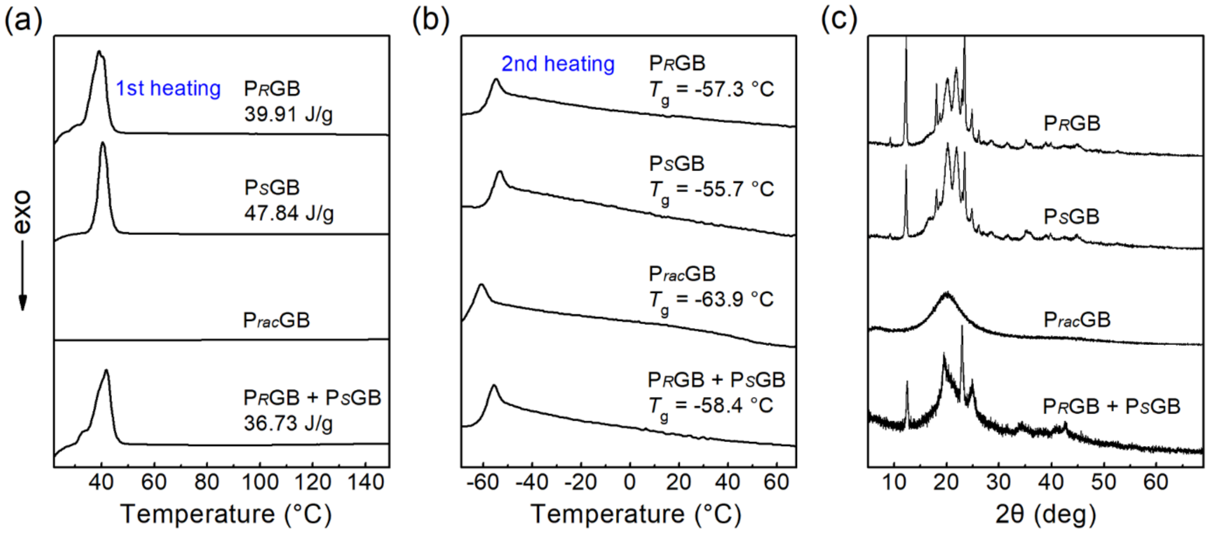

Figure S10. DSC traces (left: 1st heating; middle: 2nd heating; DP = 70) and WAXD profiles (right) of BA-initiated P*R*GB (entry 2 in Table 1), P*S*GB (entry 6 in Table 1), P*rac*GB (entry 10 in Table 1) and the 1:1 blend of two enantiomeric PGBs.

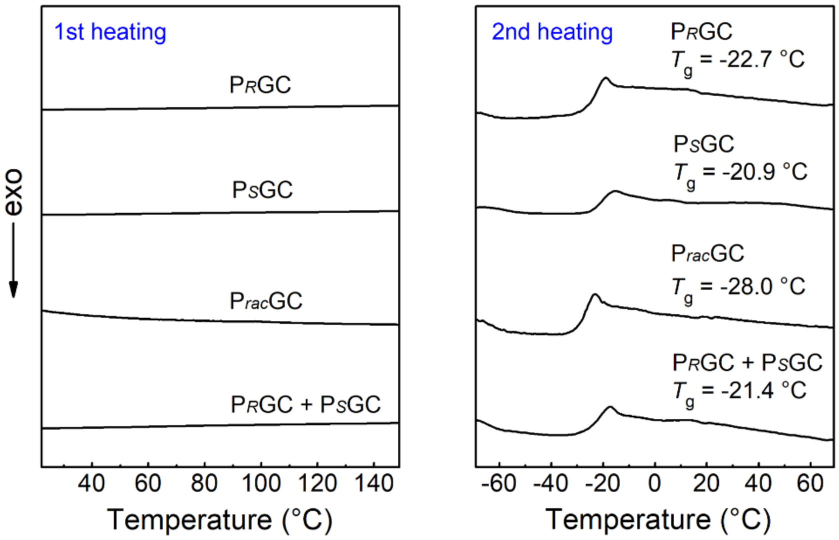

Figure S11. DSC traces (left: 1st heating; right: 2nd heating; DP = 70) of P*R*GC, P*S*GC, P*rac*GC and the 1:1 blend of two enantiomeric PGCs.

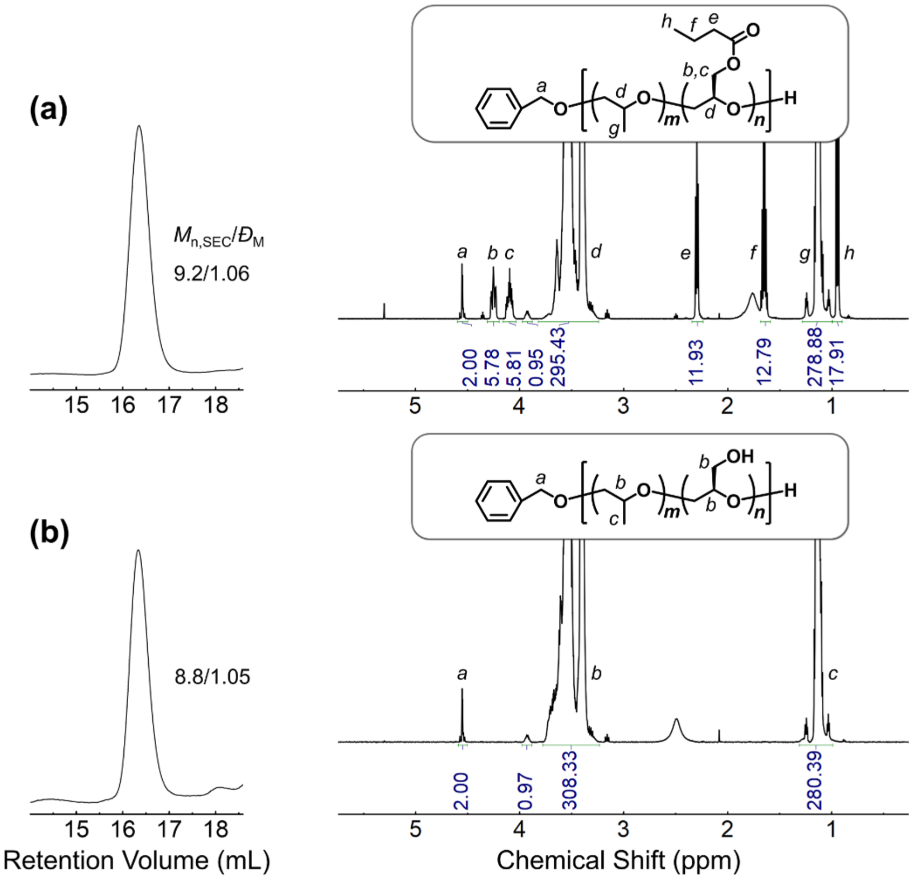

Figure S12. SEC traces (RI signals, THF, 35 °C, PS standards) and ^{1}H NMR spectra (in CDCl$_3$) of (a) P(PO$_{95}$-*co*-*S*GB$_5$), corresponding to entry 11 in Table 1, and (b) P(PO$_{95}$-*co*-*R*GC$_5$) obtained after the methanolysis treatment.

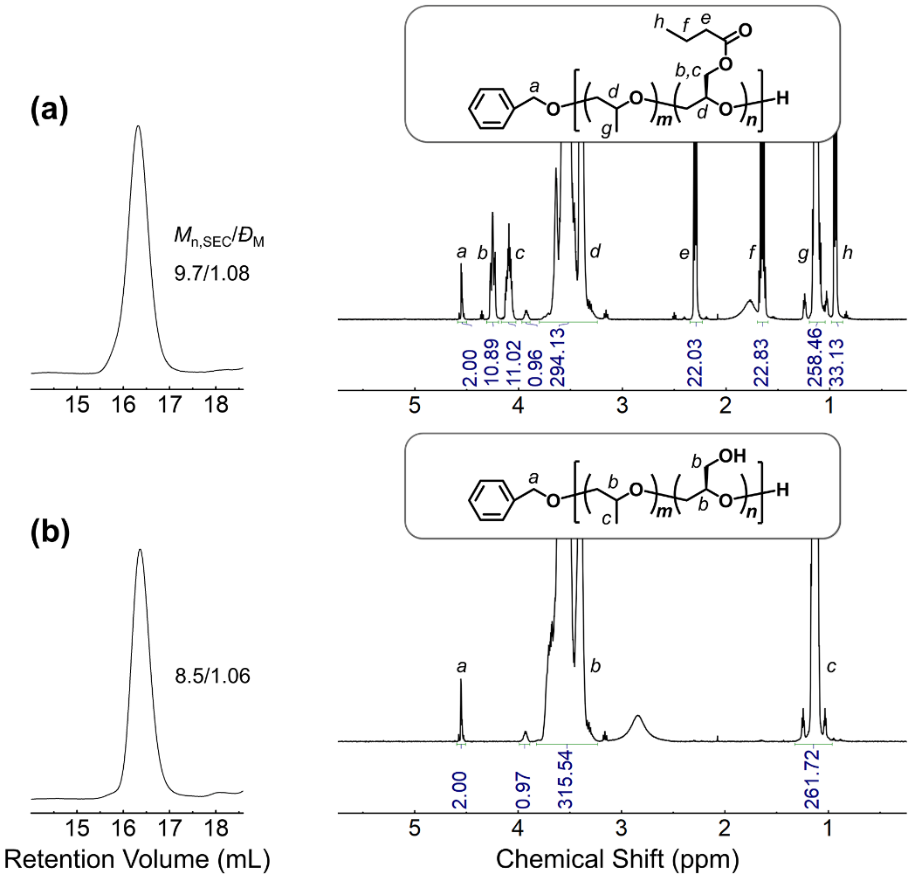

Figure S13. SEC traces (RI signals, THF, 35 °C, PS standards) and ^{1}H NMR spectra (in $CDCl_3$) of (a) P(PO$_{90}$-*co*-*S*GB$_{10}$), corresponding to entry 12 in Table 1, and (b) P(PO$_{90}$-*co*-*R*GC$_{10}$) obtained after the methanolysis treatment.

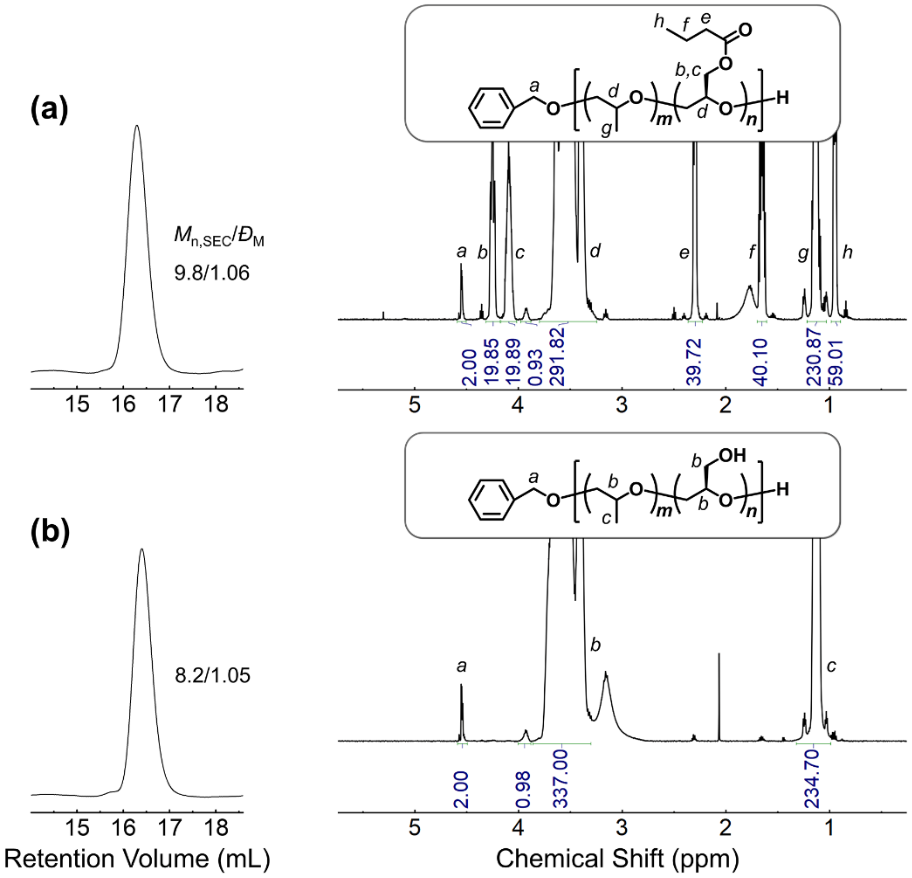

Figure S14. SEC traces (RI signals, THF, 35 °C, PS standards) and ^{1}H NMR spectra (in CDCl$_3$) of (a) P(PO$_{80}$-*co*-*S*GB$_{20}$), corresponding to entry 13 in Table 1, and (b) P(PO$_{80}$-*co*-*R*GC$_{20}$) obtained after the methanolysis treatment.

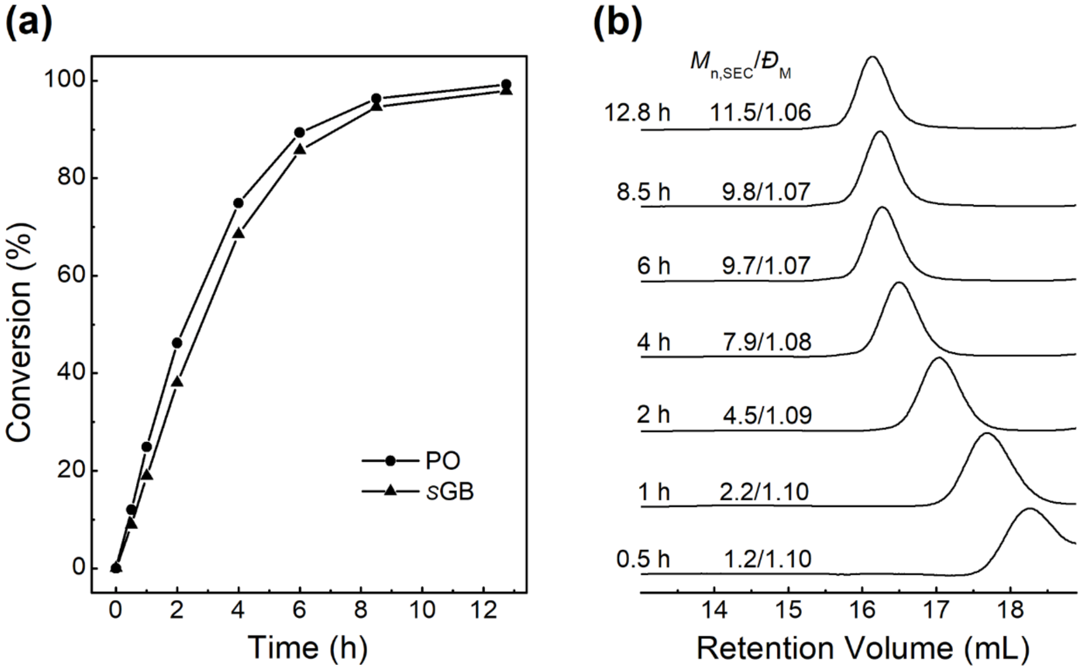

Figure 15. (a) Plots of monomer conversion versus time for the copolymerization of PO and *s*GB with a molar feed ratio of 50/50 (entry 14 in Table 1). (b) SEC traces of copolyethers obtained from the aliquots withdrawn at different reaction times with $M_{n,SEC}$ and $Đ_M$ noted.

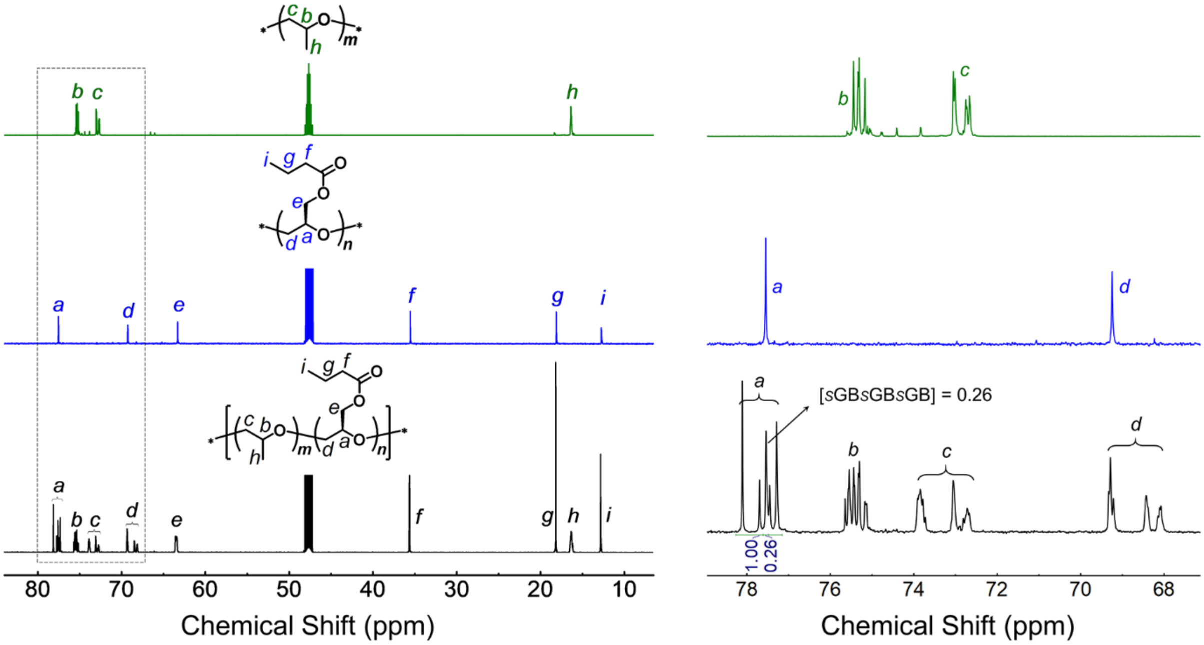

Figure S16. (Left) ^{13}C NMR spectra (in methanol-d_4) with (right) an enlarged area of PPO, P*s*GB and P(PO$_{50}$-*co*-*s*GB$_{50}$) (entry 14 in Table 1), respectively.

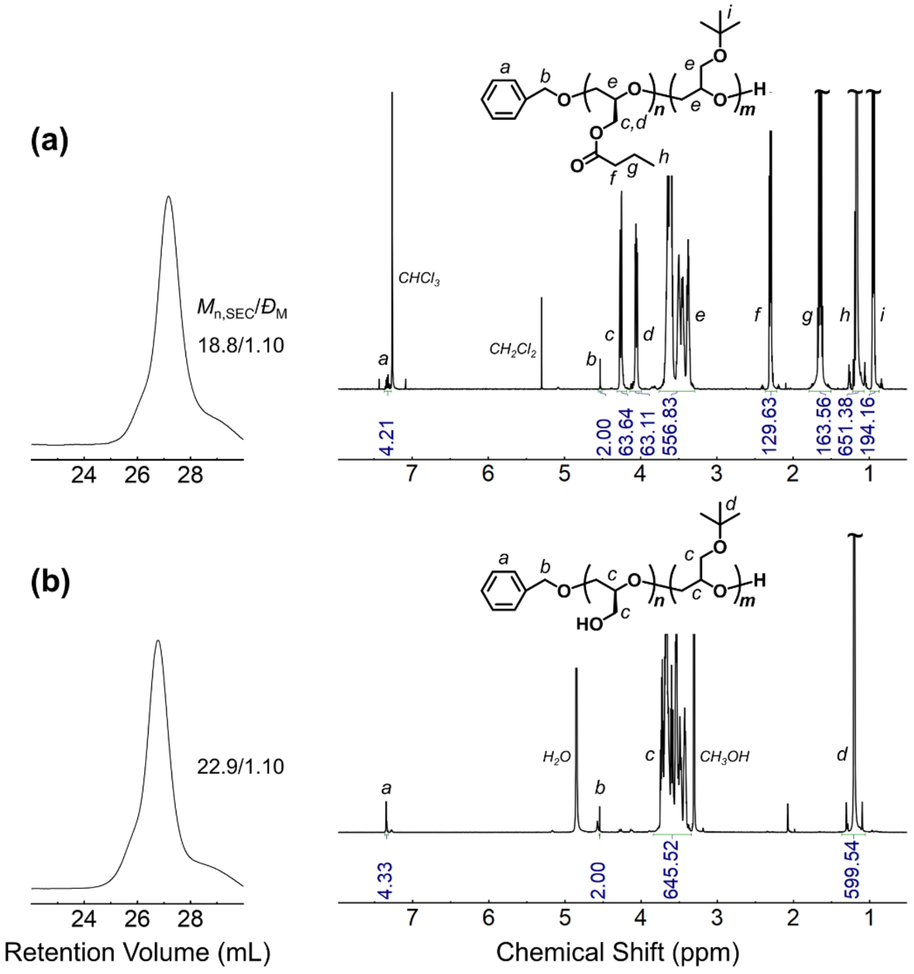

Figure S17. SEC traces (RI signals, DMF, 50 °C, PS standards) and ^{1}H NMR spectra (upper: in $CDCl_3$; down: in methanol-d_4) of (a) P*R*GB-*b*-P^{t}BGE block copolymer, corresponding to entry 15 in Table 1, and (b) P*S*GC-*b*-P^{t}BGE obtained after methanolysis treatment of the P*R*GB block.

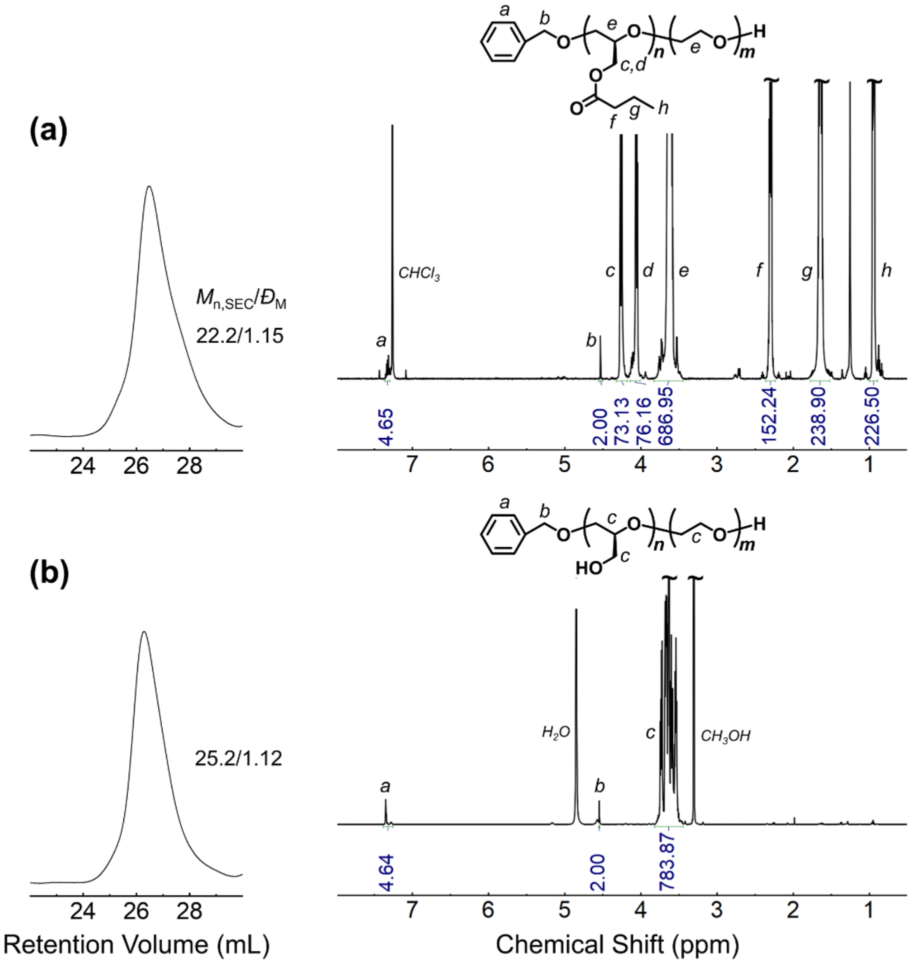

Figure S18. SEC traces (RI signals, DMF, 50 °C, PS standards) and ^{1}H NMR spectra (upper: in $CDCl_3$; down: in methanol-d_4) of (a) P*R*GB-*b*-PEO diblock copolymer, corresponding to entry 16 in Table 1, and (b) P*S*GC-*b*-PEO obtained after methanolysis treatment of the P*R*GB block.

References

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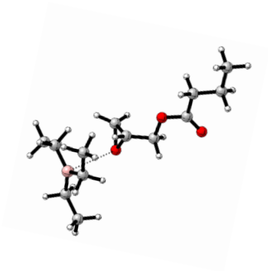
(5) CYLview20; Legault, C. Y., Université de Sherbrooke, 2020.

Cartesian coordinates

3D structures and the associated Cartesian coordinates for the calculated interactions between Et$_3$B and the epoxy groups of GBs at the minimum *O-B* distance of 2.2 Å and the interactions between Et$_3$B and the carbonyl groups at the same distance.

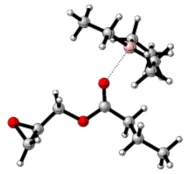


(*R*GB-Et$_3$B)

C	3.2980190	-0.4184950	-0.0542560
O	3.3713910	-1.5972560	-0.3090060
O	2.1239420	0.2510180	-0.0195200
C	0.9378530	-0.5213220	-0.2946660
H	0.9875110	-0.9438700	-1.2984180
H	0.8573050	-1.3373330	0.4248860
C	-0.2206770	0.4231930	-0.1671520

C	-0.7895140	1.1004410	-1.3317680
O	-1.4384940	-0.0553550	-0.7598670
H	-0.3508210	0.8790550	0.8085890
H	-0.3595800	0.9308650	-2.3124780
H	-1.3254960	2.0320310	-1.1976840
C	4.4520900	0.4980410	0.2607630
H	4.4162630	1.3306220	-0.4482090
H	4.2624860	0.9399400	1.2437310
C	5.8114360	-0.1912200	0.2259110
H	5.8117840	-1.0226950	0.9341980
H	5.9676580	-0.6302610	-0.7620240
C	6.9481660	0.7743240	0.5534420
H	6.8261270	1.2045110	1.5506910
H	7.9135140	0.2660940	0.5252980
H	6.9841930	1.5995770	-0.1622000
B	-3.4989870	-0.0704760	0.2619650
C	-4.2200140	0.8071830	-0.8444090
H	-5.2016620	1.0617550	-0.4142870
H	-3.7204910	1.7766380	-0.9464430
C	-3.1026070	0.6026930	1.6441860
H	-3.8931850	0.2947040	2.3459070
H	-2.2020470	0.1279310	2.0489600
C	-3.6104020	-1.6506190	0.1915720
H	-3.4147150	-1.9913930	-0.8295040
H	-4.6759670	-1.8763650	0.3563610
C	-2.7676430	-2.4686830	1.1758160

H	-2.9267900	-3.5437440	1.0561250
H	-1.7010070	-2.2798650	1.0292670
H	-3.0004640	-2.2174620	2.2131290
C	-2.9596400	2.1274560	1.7008180
H	-2.7232910	2.4788640	2.7086920
H	-2.1647750	2.4852480	1.0410850
H	-3.8788880	2.6264890	1.3869610
C	-4.4245210	0.1846440	-2.2292460
H	-4.9365670	0.8668000	-2.9133880
H	-3.4671400	-0.0814510	-2.6840910
H	-5.0186810	-0.7300570	-2.1736190

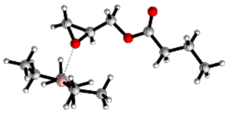


(*R*GB-Et$_3$B)

C	-4.1678240	-1.1535380	-0.0474560
O	-4.2102520	-2.0047240	0.8171340
O	-3.6522190	0.0651060	0.1818200
C	-3.1631650	0.3180020	1.5194260
H	-3.9667410	0.1743970	2.2416340
H	-2.3589790	-0.3829680	1.7457680
C	-2.6751610	1.7368200	1.5347130
C	-3.5525170	2.8290060	1.9548040
O	-2.5433170	2.3091320	2.8421210
H	-1.8531080	1.9590050	0.8602600
H	-4.5747020	2.6068470	2.2439220

H	-3.3684190	3.8326290	1.5877010
B	-4.9991890	-4.1199680	1.2568170
C	-6.3331510	-4.0718810	0.3981290
H	-6.6621050	-5.1204060	0.3219970
H	-6.1128700	-3.7915130	-0.6361500
C	-5.0874640	-3.8353690	2.8143300
H	-5.7103840	-4.6458430	3.2253220
H	-5.6747380	-2.9283350	2.9887760
C	-3.7390070	-4.9007770	0.6944590
H	-2.8214650	-4.4548900	1.0908630
C	-4.6946830	-1.2850780	-1.4475370
H	-3.9772770	-0.8394360	-2.1389910
H	-4.7805530	-2.3456110	-1.6734430
C	-6.0624800	-0.5990830	-1.6086430
H	-6.7560800	-1.0068820	-0.8707040
H	-5.9565060	0.4663470	-1.3931930
C	-6.6283720	-0.7974630	-3.0118430
H	-6.7665240	-1.8585480	-3.2321600
H	-7.5971490	-0.3053870	-3.1137290
H	-5.9589030	-0.3822200	-3.7688750
C	-7.4925780	-3.2245600	0.9315410
H	-8.3536990	-3.2347130	0.2577430
H	-7.8340060	-3.5828870	1.9051190
C	-3.7766980	-3.7576400	3.6026910
H	-3.1412810	-2.9575260	3.2162900
H	-3.9481310	-3.5605590	4.6647090

H	-3.2074870	-4.6874830	3.5313350
H	-7.1907020	-2.1828010	1.0644350
H	-3.7860110	-5.8916940	1.1738980
C	-3.6089820	-5.0882270	-0.8199520
H	-2.7461430	-5.7061820	-1.0833280
H	-4.4947000	-5.5651980	-1.2460260
H	-3.4832920	-4.1283550	-1.3263610

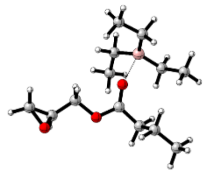


(*s*GB-Et$_3$B)

C	-0.8421610	0.5527970	3.0266290
O	-1.1987520	-0.4845920	3.5350990
O	-0.4021370	0.6319300	1.7530810
C	-0.3364270	-0.6033960	1.0098490
H	0.2551490	-1.3344930	1.5603760
H	-1.3449380	-0.9969580	0.8679110
C	-0.8132520	1.9063360	3.6885680
H	0.2196530	2.2658610	3.6499970
H	-1.3865170	2.5944830	3.0604140
C	-1.3378410	1.9052790	5.1196280
H	-2.3639550	1.5305360	5.1274990
H	-0.7510910	1.2050940	5.7183570
C	-1.2862750	3.2975390	5.7449490
H	-1.6643910	3.2814690	6.7685990
H	-0.2628990	3.6801520	5.7726260
H	-1.8910940	4.0084890	5.1763700

C	0.2939840	-0.2809370	-0.3045510
C	1.1006230	-1.2668150	-1.0246490
O	1.7308270	-0.1914140	-0.3042410
H	-0.1908620	0.5022100	-0.8774550
H	1.1755590	-1.2009730	-2.1034630
H	1.2634190	-2.2491890	-0.5955480
B	2.9660510	1.5374580	-1.1847070
C	3.5916160	1.9168980	0.2222700
H	4.4743450	2.5353250	-0.0061300
H	4.0032480	1.0208120	0.6965800
C	1.7801850	2.4260160	-1.7540450
H	2.2011450	3.4394370	-1.8436780
H	0.9997900	2.5383840	-0.9936360
C	3.7987630	0.6283780	-2.1823560
H	4.3310730	1.3337670	-2.8399960
H	3.1258790	0.0939620	-2.8616940
C	4.8071870	-0.3540920	-1.5781110
H	4.3095970	-1.0672430	-0.9161880
H	5.3320300	-0.9277630	-2.3469420
H	5.5627410	0.1629690	-0.9826200
C	2.6985940	2.6622270	1.2207120
H	3.2248240	2.8816760	2.1541190
H	2.3472600	3.6136790	0.8140910
H	1.8149470	2.0714820	1.4704520
C	1.1519930	2.0323200	-3.0952180
H	0.6975980	1.0387580	-3.0539680

H	0.3694130	2.7315250	-3.4017670
H	1.8975330	2.0047040	-3.8927750



(*s*GB-Et$_3$B)

C	-0.1376970	-0.7710310	0.0772590
O	0.6696500	-0.1833740	-0.6154640
O	-0.8591180	-0.1495270	1.0209660
C	-0.6319180	1.2742900	1.1699690
H	0.4164530	1.4490140	1.4105290
H	-0.8666710	1.7714640	0.2279680
C	-1.5262270	1.7566040	2.2634450
C	-1.1314080	2.8972580	3.0910010
O	-1.0628800	1.5581930	3.6085630
H	-2.5849950	1.5572770	2.1249880
H	-1.8999950	3.5260020	3.5269240
H	-0.1710110	3.3737550	2.9213000
B	0.8991090	0.2351630	-2.8653910
C	2.4258420	0.6425890	-2.7585670
H	2.8034090	0.6497890	-3.7934470
H	2.9837350	-0.1640840	-2.2728840
C	-0.2086370	1.3710380	-2.8681850
H	-0.0468180	1.9210040	-3.8091590
H	0.0097000	2.1051750	-2.0872120
C	0.5238320	-1.1994310	-3.4267690
H	-0.4440360	-1.5230240	-3.0307390

C	-0.4067430	-2.2466810	0.0166170
H	-1.3296120	-2.4773750	0.5475450
H	-0.5322200	-2.5143730	-1.0333040
C	0.7678560	-3.0435360	0.6099440
H	1.6898080	-2.7391070	0.1101770
H	0.8793490	-2.7853140	1.6662160
C	0.5640040	-4.5477660	0.4580530
H	0.4843930	-4.8260820	-0.5954750
H	1.4011010	-5.0996690	0.8890350
H	-0.3485630	-4.8753290	0.9615230
C	2.7634020	1.9779860	-2.0885070
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H	-2.3549190	1.8057290	-2.8115040
H	-1.9538220	0.2924680	-3.6186420
H	2.4028480	1.9937330	-1.0573480
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C	1.5529050	-2.3233440	-3.2741920
H	1.1934010	-3.2686160	-3.6898920
H	2.4895380	-2.0786210	-3.7796030
H	1.7932370	-2.4958850	-2.2229500