Supporting Information

Catalyzed Chemical Synthesis of Unnatural Aromatic Polyhydroxyalkanoate (PHA) and Aromatic-Aliphatic PHAs with Record-High Glass-Transition and Decomposition Temperatures

Andrea H. Westlie and Eugene Y.-X. Chen*

Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, United States.

Corresponding Author; email: eugene.chen@colostate.edu

Table of Contents

Experimental Section

Materials. All syntheses and manipulations of air- and moisture-sensitive chemicals and materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line or in an inert gas (Ar or N_2)-filled glovebox. HPLC-grade organic solvents were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through activated alumina (for DCM) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene-d_6 was dried over sodium/potassium alloy and filtered, whereas CD_2Cl_2 and $CDCl_3$ were dried over CaH_2, vacuum-distilled and stored over activated Davison 4 Å molecular sieves.

Yttrium chloride YCl_3 and lanthanum chloride $LaCl_3$ were purchased from Sigma-Aldrich Chemical Co. and used as received. Benzyl alcohol was purchased from Alfa Aesar Chemical Co., purified by distillation over CaH_2, and stored over activated Davison 4 Å molecular sieves. Dimethyl succinate, sodium methoxide, and 3-chloroperoxybenzoic acid (*m*CPBA, 70–75%) were purchased from Fisher Scientific Co. and used as received. Dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate was purchased from TCI chemicals and used as received. Benzyl bromide was purchased from Acros Organics and used as received. Literature procedures were employed for the preparation of *rac*-8DL^{Me} [1] and *rac*-8DL^{Bu}.[2] The yttrium and lanthanum complexes were prepared according to their respective literature procedures: $Y[N(SiHMe_2)_2]_3(THF)_2$, $La[N(SiHMe_2)_2]_3(THF)_2$,[3] and complexes **1**,[4] **2**-**4**,[1,3,5] and **5**.[1]

Synthesis of Monomers

Dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate. A solution of sodium methoxide (185 mL, 5.4 M, 1.0 mol) was added to dimethyl succinate (73.1 g, 0.5 mol) in one portion, and the mixture was heated under reflux for 24 h. A thick pink-colored precipitate was then formed and remained throughout the reaction. The methanol was removed using evaporator, a 2*N* sulfuric acid solution (500 mL) was added to the residue, and the mixture was stirred vigorously for 4 h. The solid was collected by filtration and washed several times with water. The air-dried product was a pale-buff powder, which was recrystallized from 300 mL ethyl acetate. The filtrate was chilled to give cream to pink-cream colored crystals of the title compound, 37.1 g (65 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.12 (s, 1H), 3.79 (s, 3H), 3.18 (s, 2H).

Dimethyl 1,4-dibenzyl-2,5-dioxocyclohexane-1,4-dicarboxylate. To a stirred suspension of K_2CO_3 (33.6 g, 0.263 mol) in 250 mL DMF under N_2 was added dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (20 g, 87.6 mmol). After 15 min stirring at room temperature, benzyl bromide (60.0 g, 0.35 mol) was added dropwise. After 24 h, the mixture was concentrated in vacuo, dissolved in 200 mL of H_2O, and extracted with CH_2Cl_2 (150 mL x 3). The combined organic layers were washed twice with 10% $Na_2S_2O_3$ solution, washed once with saturated NaCl, dried with anhydrous Na_2SO_4, and evaporated. The solid was washed with hexanes to give 34.5 g (96%) of the title compound as a 2:1 mixture of diastereomers. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.8 Hz, 1H, Ar-*H*), 7.65 – 7.39 (m, 1*H,* Ar-*H*), 7.22 (dd, *J* = 7.4, 4.3 Hz, 5H, Ar-*H*), 7.06 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 6.95 (dd, *J* = 6.3, 2.9 Hz, 2H, Ar-*H*), Major diastereomer: 3.64 (s, 6H, *Me*O), 3.18 (dt, *J* = 13.6, 8.6 Hz, 2H, CH_2), 2.88 (t, *J* = 16.1 Hz, 2H, CH_2), 2.68 (d, *J* = 15.2 Hz, 2H, CH_2), 2.26 (d, *J* = 16.4 Hz, 2H, CH_2). Minor diastereomer: δ 3.58 (s, 6H, *Me*O), 3.20 (dd, *J* = 36.7, 22.7 Hz, 4H, CH_2), 2.86 (d, *J* = 15.6 Hz, 2H, CH_2), 2.68 (d, *J* = 15.2 Hz, 2H, CH_2).

***Trans*-2,5-dibenzylcyclohexane-1,4-dione.** To a stirred suspension of dimethyl 1,4-dibenzyl-2,5-dioxocyclohexane-1,4-dicarboxylate 5 g, 12.2 mmol) in 5 mL methanol and 15 g crushed ice, 20 mL of concentrated H_2SO_4 was added. After 15 min of stirring at room temperature, the mixture was heated to 100 °C for 48 h. The acidic solution was cooled to room temperature, neutralized with aq. NaOH (pH 6-7), and extracted with CH_2Cl_2 (150 mL x 3). The combined organic layers were washed twice with saturated NaCl, dried with anhydrous Na_2SO_4, and evaporated. The residue was purified by recrystallization in DCM/hexanes to afford 3.07 g (86%) of the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 8H, Ar-*H*), 7.08 (dd, *J* = 16.4, 6.5 Hz, 2H, Ar-*H*), 3.30 – 3.13 (m, 2H, CH_2), 2.88 – 2.78 (m, 2H, CH_2), 2.63 (dd, *J* = 11.9, 9.7 Hz, 4H, CH_2), 2.49 (dd, *J* = 15.0, 11.2 Hz, 2H, CH_2).

***Trans*-4,8-dibenzyl-1,5-dioxocane-2,6-dione (*meso*-8DL^{Bn}).** To a solution of the *meso*-2,5-dioxocylcolexane-1,4-dicarboxylate (10 g, 34.2 mmol) in 300 mL of CH_2Cl_2 was added *m*-CPBA (25.3 g, 70%, 17.7 mmol) in one portion. The pale-yellow solution was stirred at room temperature in the dark for 48 h. The obtained white suspension was diluted with 200 mL of CH_2Cl_2, washed with saturated $NaHCO_3$ solution (100 mL x 3), which contained 5% $Na_2S_2O_3$, dried with anhydrous Na_2SO_4, and evaporated. After recrystallization of the residue (11.6 g) from hexanes/DCM (5/1) and recrystallization from toluene 7.2 g of pure *meso*-8DL^{Bn} was obtained (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.2 Hz, 5H, Ar-*H*), 7.16 (t, *J* = 6.9 Hz, 5H, Ar-*H*), 5.37 – 5.07 (m, 2H, BnC*H*O-C=O), 3.05 (dd, *J* = 14.1, 7.6 Hz, 2H, CH_2), 2.90 – 2.76 (m, 4H, CH_2), 2.50 (dd, *J* = 13.0, 7.5 Hz, 2H, CH_2).

***Cis*-4,8-dibenzyl-1,5-dioxocane-2,6-dione (*rac*-8DL^{Bn}).** The filtrate from the above purification step of *trans*-2,5-dibenzylcyclohexane-1,4-dione was purified by column chromatography to give the *cis*-dione in ~90% racemic content. To a solution of the *trans*-2,5-dibenzylcyclohexane-1,4-dione (1.5 g, 5.13 mmol) in 100 mL of CH_2Cl_2 was added *m*-CPBA (3.8 g, 70%, 15.4 mmol) in one portion. The yellow solution was stirred at room temperature in the dark for 48 h. The obtained white suspension was diluted with 100 mL of CH_2Cl_2, washed with saturated $NaHCO_3$ solution (50 mL x 3), which contained 5% $Na_2S_2O_3$, dried with anhydrous Na_2SO_4, and evaporated. After recrystallization of the residue from hexanes/DCM and recrystallization from toluene 0.4 g of pure *rac*-8DL^{Bn} was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.36 – 7.19 (m, 61H), 5.46 – 5.33 (m, 9H), 3.11 (dd, *J* = 14.1, 7.6 Hz, 9H), 2.94 (dd, *J* = 14.1, 6.1 Hz, 9H), 2.71 (dd, *J* = 11.3, 10.1 Hz, 9H), 2.46 (dd, *J* = 11.3, 3.5 Hz, 9H).

General polymerization procedures. Polymerizations were performed in 5.5 mL glass reactors inside the inert glovebox at RT. The reactor was charged with a predetermined amount of catalyst and/or initiator and solvent (as specified in the polymerization tables) in a glovebox. The mixture was stirred at RT for 10 min, and the polymerization was initiated by rapid addition to an 8DL monomer. After a desired time period, the polymerization was immediately quenched by addition of 0.5 mL of benzoic acid/chloroform (10 mg mL^{-1}) and a 0.02 mL of aliquot was taken from the reaction mixture and prepared for ^1H NMR analysis to obtain the percent monomer conversion data. The quenched mixture was then precipitated into 50 mL of cold methanol while stirring, filtered, washed with cold methanol to remove any unreacted monomer, and dried in a vacuum oven at RT overnight to a constant weight.

Specific conditions for copolymerization runs summarized in Table 3. Statistical copolymerizations: run 15, 8DL = 0.95 mmol [1/1 *rac*-DL^{Me} (0.0819 g) : *meso*-DL^{Bn} (0.154 g)], $V_{solvent}$ = 0.95 mL, RT; run 16, 8DL = 0.80 mmol [5/1 *rac*-DL^{Me} (0.115 g) : *meso*-DL^{Bn} (0.043 g)], $V_{solvent}$ = 0.80 mL, RT; run 19, 8DL = 0.37 mmol [(5/1 *meso*-DL^{Bn} (0.100 g) : *rac*-DL^{Bu} (0.0158 g)], $V_{solvent}$ = 0.4 mL, RT; run 20, 8DL = 0.339 mmol [(10/1 *meso*-DL^{Bn} (0.100 g) : *rac*-DL^{Bu} (0.008 g)], $V_{solvent}$ = 0.4 mL, RT. Sequential block copolymerizations: run 17, 8DL = 0.58 mmol [(1/1 *rac*-DL^{Me} (0.05 g) : *meso*-DL^{Bn} (0.094 g)], RT. Tapered block copolymerization: run 18, 8DL = 0.58 mmol, [(1/1 *rac*-DL^{Me} (0.05 g) : *meso*-DL^{Bn} (0.094 g)], RT.

Absolute Molecular Weight Measurements. Measurements of polymer absolute weight-average molecular weight (M_w), number average molecular weight (M_n), and dispersity indices ($Đ = M_w / M_n$) were performed via gel-permeation chromatography (GPC). The GPC instrument consisted of an Agilent HPLC system equipped with one guard column and three PLgel 5 μm mixed-C gel permeation columns and coupled with a Wyatt DAWN HELEOS II multi (18)- angle light scattering detector and a Wyatt Optilab TrEX dRI detector; the analysis was performed at 40 °C using chloroform as the eluent at a flow rate of 1.0 mL min^{-1}, using Wyatt ASTRA 7.1.3 molecular weight characterization software. The refractive index increment (d*n*/d*c*) of P3H4PhB was determined to be 0.1079 ± 0.0004 mL g^{-1}, and d*n*/d*c* of P3HHp was determined to be 0.0292 ± 0.0010 mL g^{-1}, obtained by batch experiments using Wyatt Optilab TrEX dRI detector and calculated using ASTRA software. Polymer solutions were prepared in chloroform and injected into dRI detector by Harvard Apparatus pump 11 at a flow rate of 0.30 mL min^{-1}. A series of known concentrations were injected and the change in refractive index was measured to obtain a plot of change in refractive index versus change in concentration ranging from 0.4 to 5.0 mg/mL. The slope from a linear fitting of the data was the d*n*/d*c* of the polymer. Random and diblock specimens d*n*/d*c* values were calculated based on weighted average with respect to co-monomer composition. For GPC data presented in Figure 3, the GPC instrument consisted of an Agilent HPLC system equipped with one guard column and three PL-gel 5 μm mixed-C gel permeation columns running THF as eluent at 1.0 mL/min at 40 °C. The

detectors used were a Wyatt Technology TrEX differential refractometer (dRI) and a Wyatt Technology miniDAWN Treos light scattering detector (MALS). The d*n*/d*c* values were determined experimentally, through analysis of known-concentration samples, to be 0.1572 mL g^{-1} for P3H4PhB.

Spectroscopic Characterizations. The isolated low molecular weight samples were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI−TOF MS); the experiment was performed on Microflex-LRF mass spectrometer (Bruker Daltonics, Billerica, MA) operated in positive ion, reflector mode using a Nd:YAG laser at 355 nm and 25 kV accelerating voltage. A thin layer of a 1% NaI solution was first deposited on the target plate, followed by 0.6 µl of both sample and matrix (dithranol in chloroform). External calibration was done using a peptide calibration mixture (4 to 6 peptides) on a spot adjacent to the sample. The raw data was processed in the FlexAnalysis software (version 3.4.7, Bruker Daltonics).

NMR spectra were recorded on a Bruker AV-III 400 MHz spectrometer (400 MHz, ^{1}H; 100 MHz, ^{13}C). Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to $SiMe_4$. The [*rr*] (the syndiotactic triad made up of two adjacent *rac* diads probability of *rac* linkages between 3HPhB units) value of P3H4PhB was calculated according to the integration area of *rr*, *mr,* and *rm* triads [A([*rr*]), A([*mr*]), A([*rm*])] of the carbonyl group region at δ169.2 ppm, that is [*rr*] = A([rr])/[A([*rr*]), A([*mr*]), A([*rm*])].

Single-crystal X-ray diffraction intensities were collected on a Bruker D8 Venture Diffractometer using CuKa (1.542 Å) radiation at 100 K. Crystallographic data for the structure of *meso*-DL^{Bn} have been deposited with the Cambridge Crystallographic Data Center (CCDC 2004305).

Thermal analysis. Melting transition (T_m) and glass transition (T_g) temperatures were measured by differential scanning calorimetry (DSC) on an Auto Q20, TA Instrument. All T_m and T_g values were obtained from a second scan after the thermal history was removed from the first scan, unless noted otherwise. The second heating rate was 5 °C/min and cooling rate was 5 °C/min unless indicated otherwise in the polymerization tables. This heating and cooling rate was used because of the relatively low crystallinity of the resultant polymer and also as a standard condition to compare other chemically synthesized PHAs in our lab. Decomposition temperatures (T_d, defined by the temperature of 5 % weight loss) and maximum rate decomposition temperatures (T_{max}) of the polymers were measured by thermal gravimetric analysis (TGA) on a Q50 TGA Analyzer, TA Instrument. Polymer samples were heated from ambient temperatures to 700 °C at a heating rate of 10 °C min^{-1}. Values of T_{max} were obtained from derivative (wt %/°C) vs. temperature (°C) plots, while T_d and T_{onset} values (initial and end temperatures) were obtained from wt % vs. temperature (°C) plots.

Mechanical Analysis. Tensile stress/strain testing was performed by an Instron 5966 universal testing system (10 k*N* load cell) on dog-bone-shaped test specimens (ASTM D638 standard; Type V) prepared *via* compression molding using a Carver Bench Top Laboratory Press (Model 4386) equipped with a two-column hydraulic unit (Carver, Model 3912, maximum force 24000 psi). Isolated polymer materials were loaded between non-stick Teflon paper sheets into a stainless-steel mold with inset dimensions 30 × 73.5 × 0.87 mm fabricated in house, and compressed between two 6" × 6" steel electrically heated platens (EHP) clamp force 5000 psi, at temperature 70 °C. Specimens for analysis were cut using an ASTM D638-5-IMP cutting die (Qualitest) to standard dimensions. From each compression molding procedure using the stainless-steel mold described, two ASTM D638-5 standard dog-bone shaped specimens could be cut. To reduce the amount of materials needed for mechanical testing while examining their reprocessability, the measured dog-bone specimens were reprocessed for subsequent trials rather than virgin materials prepared for each measurement. Thus, the workflow would proceed as follows: virgin materials were compression molded to yield two new specimens and measured using the Instron instrument to the point of failure, before reprocessing the material in a subsequent round of compression molding to yield two reprocessed specimens to be again measured to the point of failure. Mechanical behavior was averaged for all the specimens measured for each individual species investigated. Thickness (0.85 ± 0.01 mm), width (3.18 mm), and grip length (26.4 ± 0.2 mm) of the measured dog-bone specimens were measured for normalization of data by the Bluehill measurement software (Instron). Test specimens were affixed into the screw-tight grip frame. Tensile stress and strain were measured to the point of material break at a grip extension speed of 10.0 mm min^{-1} at ambient conditions.

Additional Figures

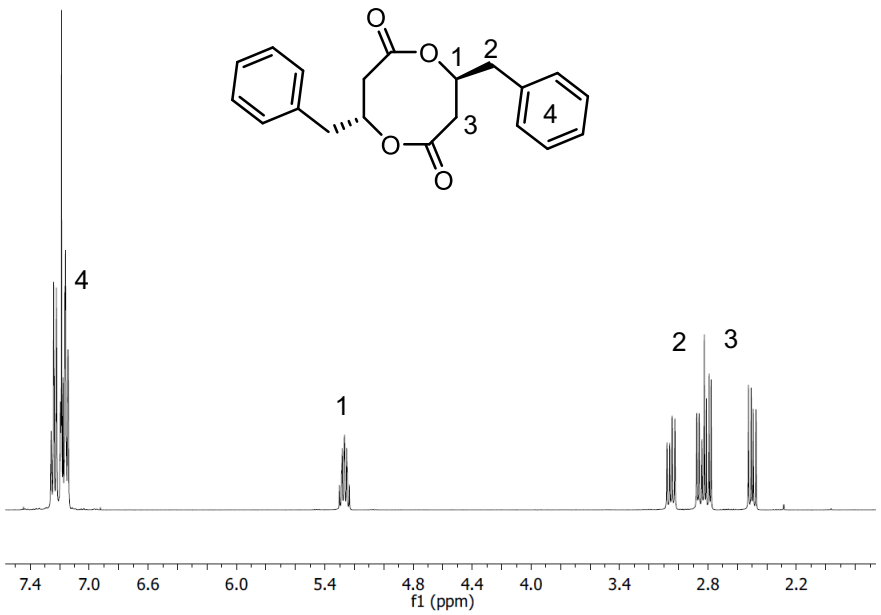

Figure S1. ^{1}H NMR ($CDCl_3$, 23 °C) of *meso*-DL^{Bn}.

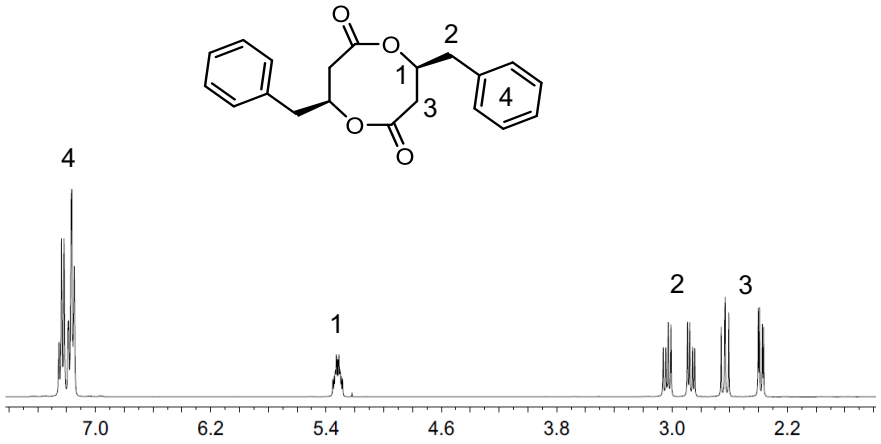

Figure S2. ^{1}H NMR ($CDCl_3$, 23 °C) of *rac*-DL^{Bn}.

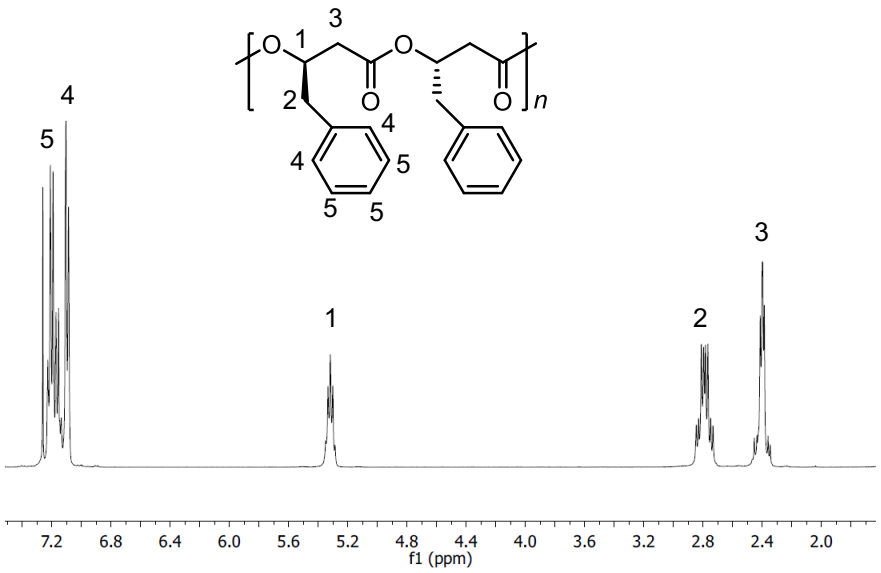

Figure S3. ^{1}H NMR ($CDCl_3$, 23 °C) of *st*-P3H4PhB.

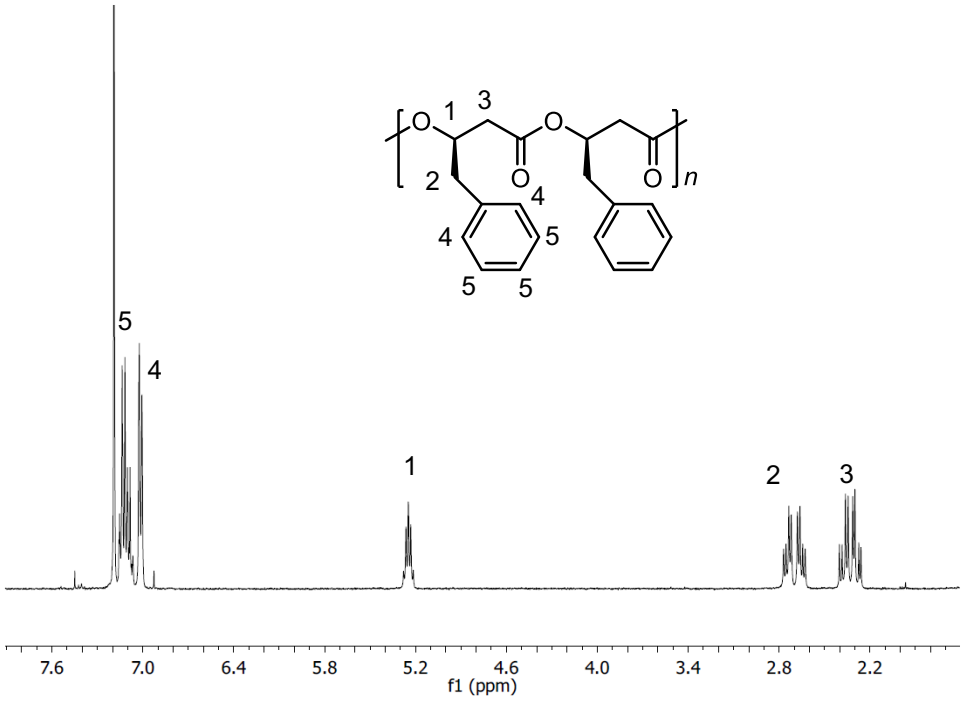

Figure S4. ^{1}H NMR ($CDCl_3$, 23 °C) of *it*-P3H4PhB.

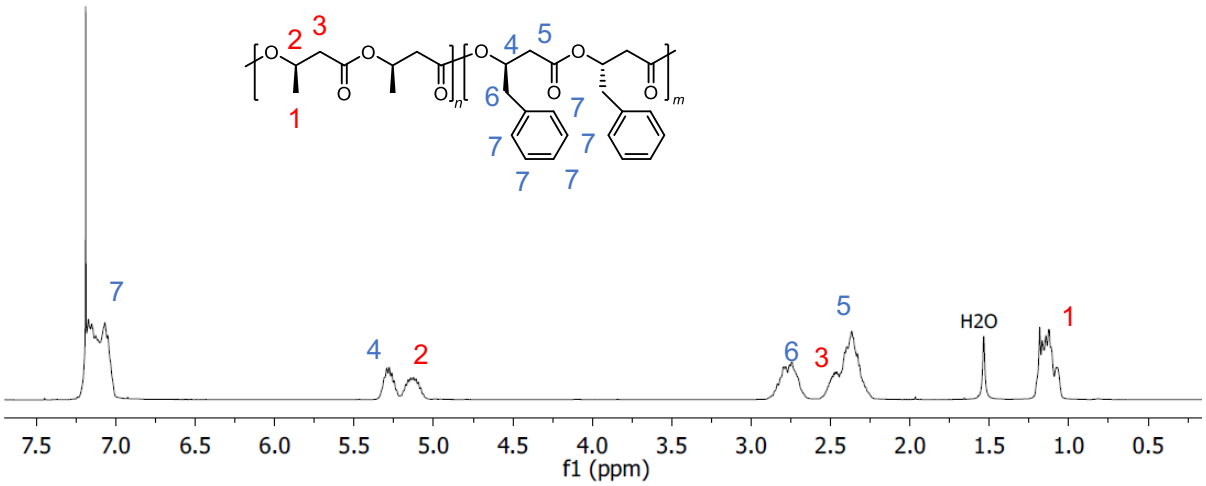

Figure S5. ^{1}H NMR ($CDCl_3$, 23 °C) of random copolymer P3H4PhB-*co*-P3HB (48% *rac*-8DL^{Me} incorporation). (Note: H_2O in $CDCl_3$ at 1.56 ppm)

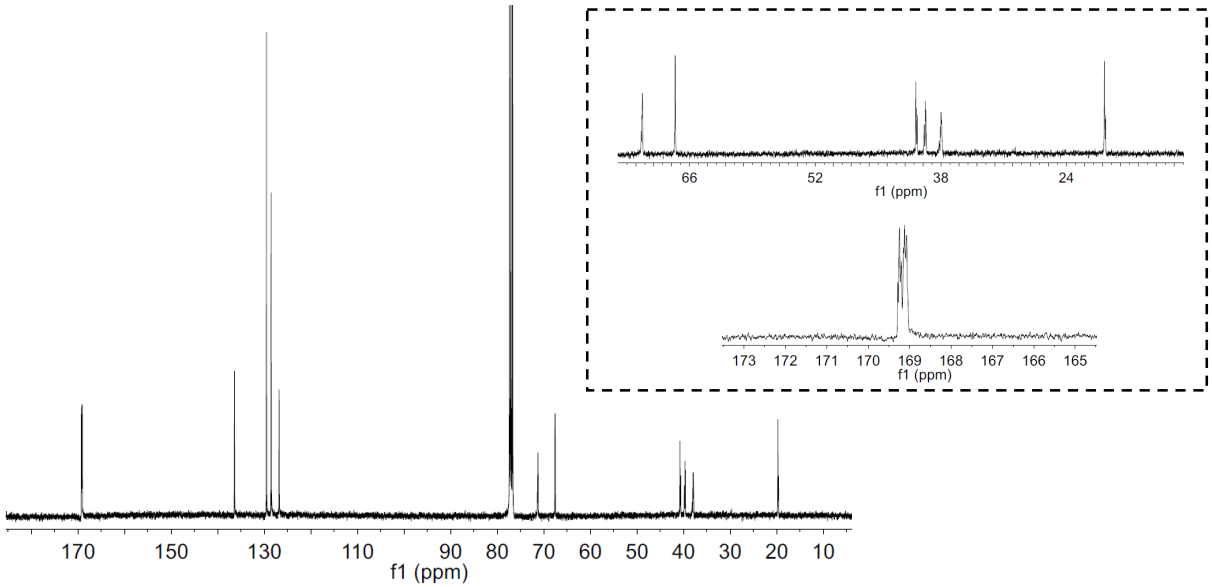

Figure S6. ^{13}C NMR (CDCl3, 23 °C) of random copolymer P3H4PhB-*co*-P3HB (48% *rac*-8DL^{Me} incorporation).

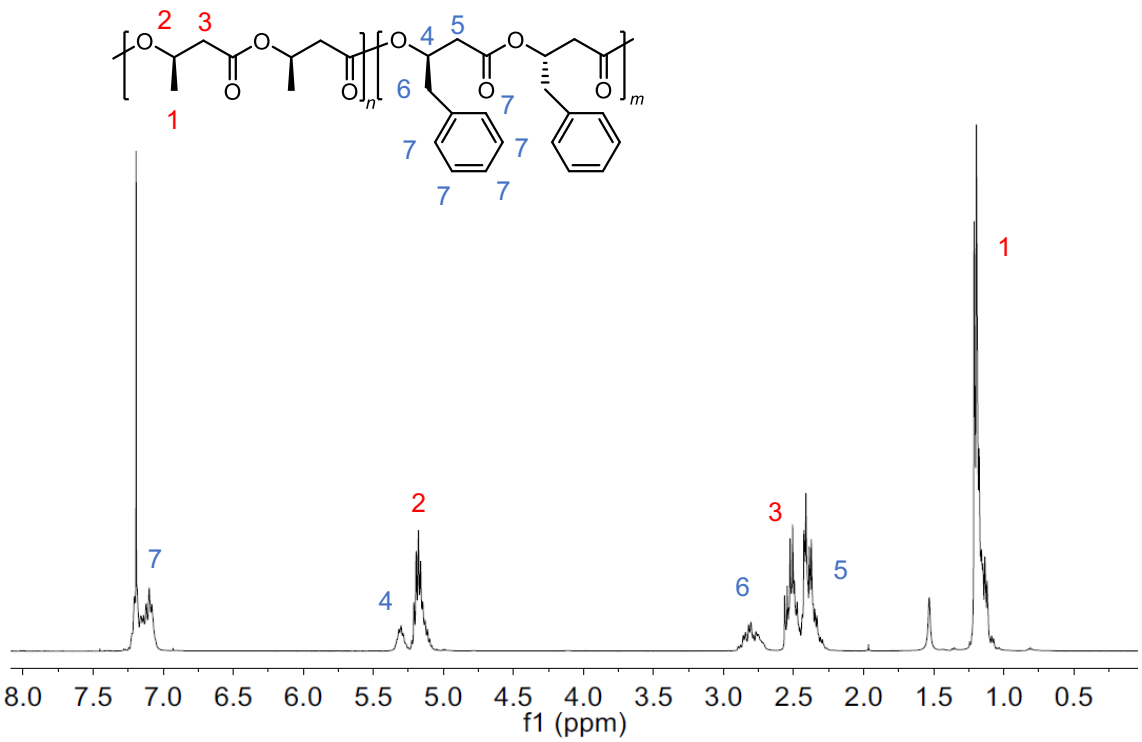

Figure S7. ^{1}H NMR ($CDCl_3$, 23 °C) of random copolymer P3H4PhB-*co*-P3HB (80% *rac*-8DL^{Me} incorporation). (Note: H_2O in $CDCl_3$ at 1.56 ppm).

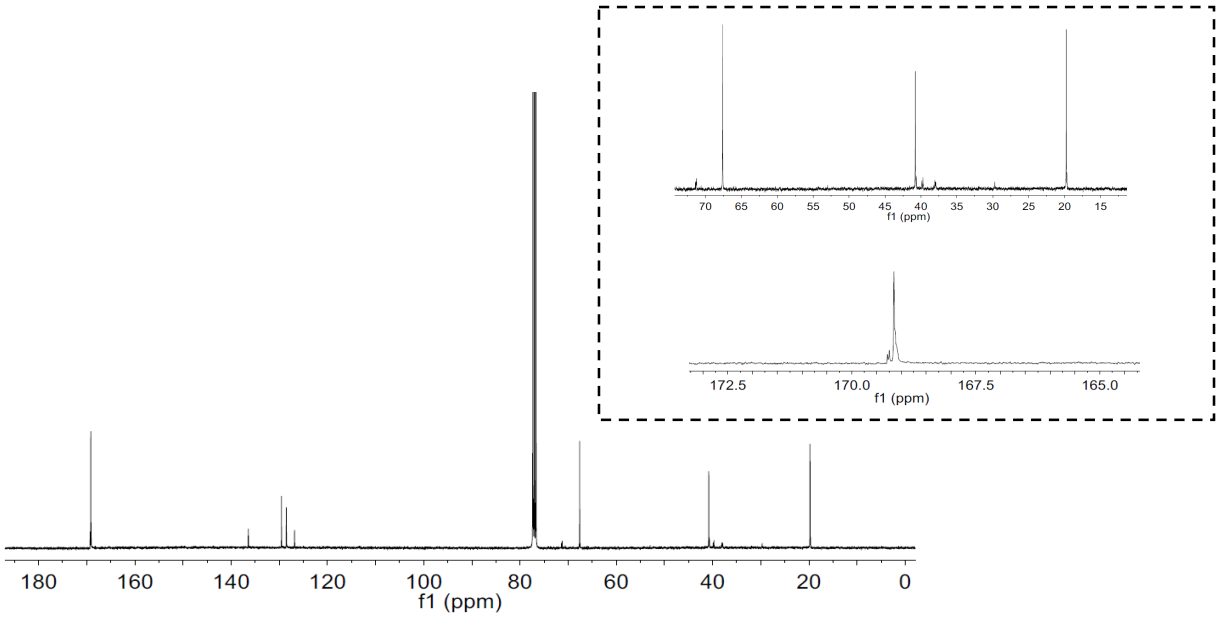

Figure S8. ^{13}C NMR (CDCl3, 23 °C) of random copolymer random copolymer P3H4PhB-*co*-P3HB (80% *rac*-8DL^{Me} incorporation).

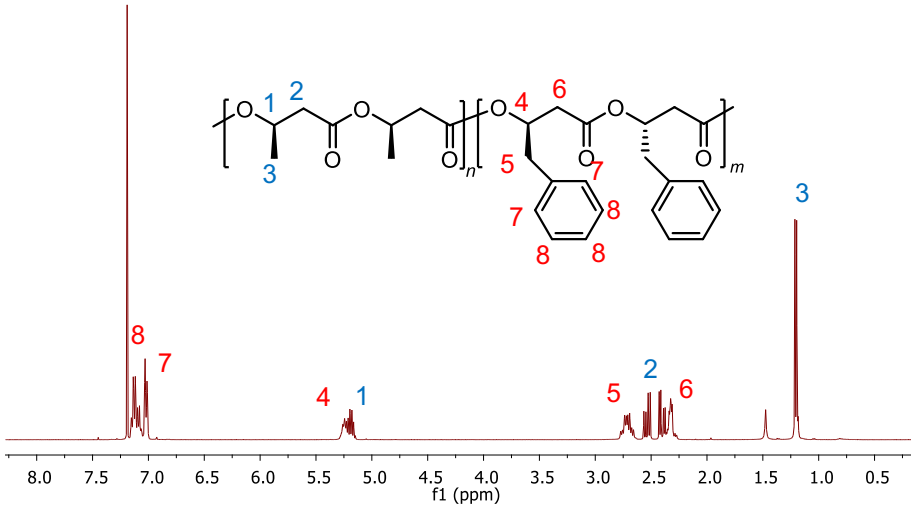

Figure S9. ^{1}H NMR ($CDCl_3$, 23 °C) of stereoblock copolymer *it*-P3HB-*b*-*st*-P3H4PhB. (Note: H_2O in $CDCl_3$ at 1.56 ppm).

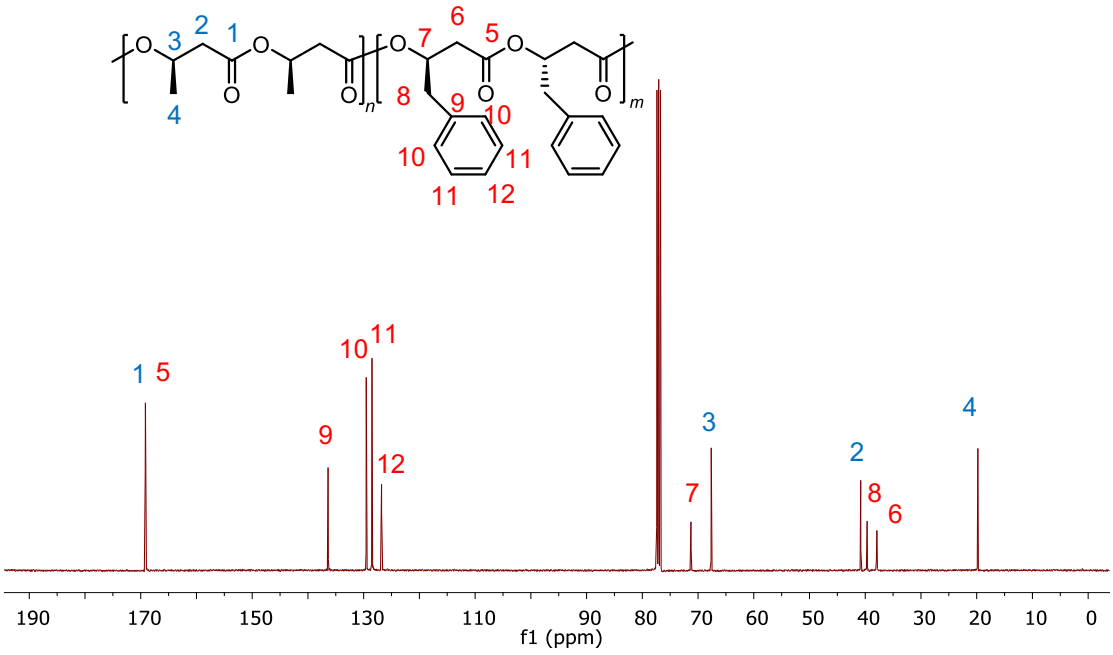

Figure S10. ^{13}C NMR ($CDCl_3$, 23 °C) of stereoblock copolymer *it*-P3HB-*b*-*st*-P3H4PhB.

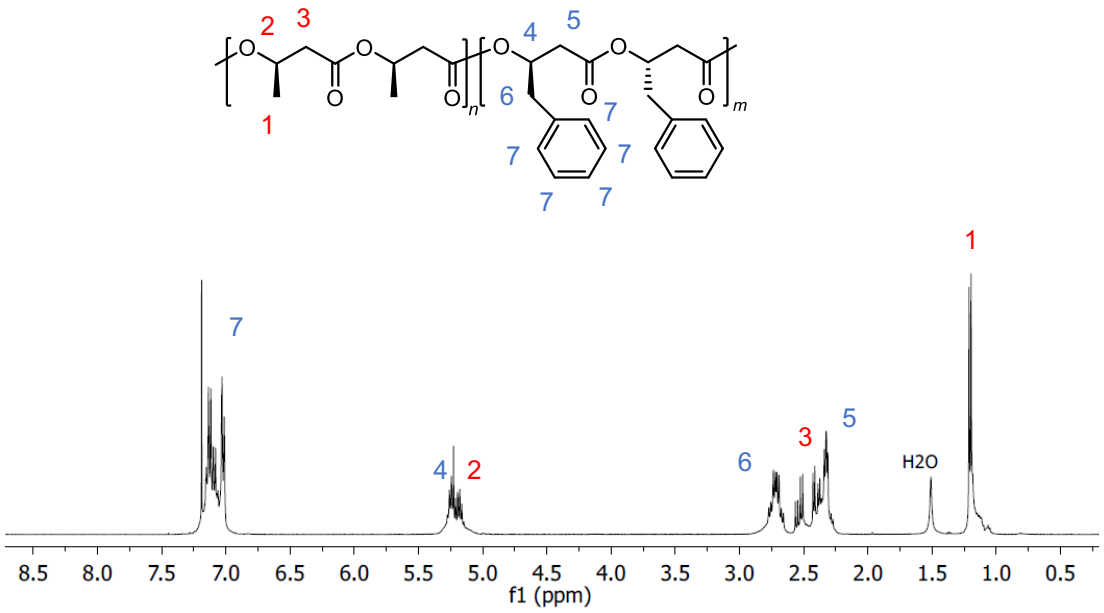

Figure S11. ^{1}H NMR ($CDCl_3$, 23 °C) of tapered block copolymer *it*-P3HB-*b*-*st*-P3H4PhB. (Note: H_2O in $CDCl_3$ at 1.56 ppm).

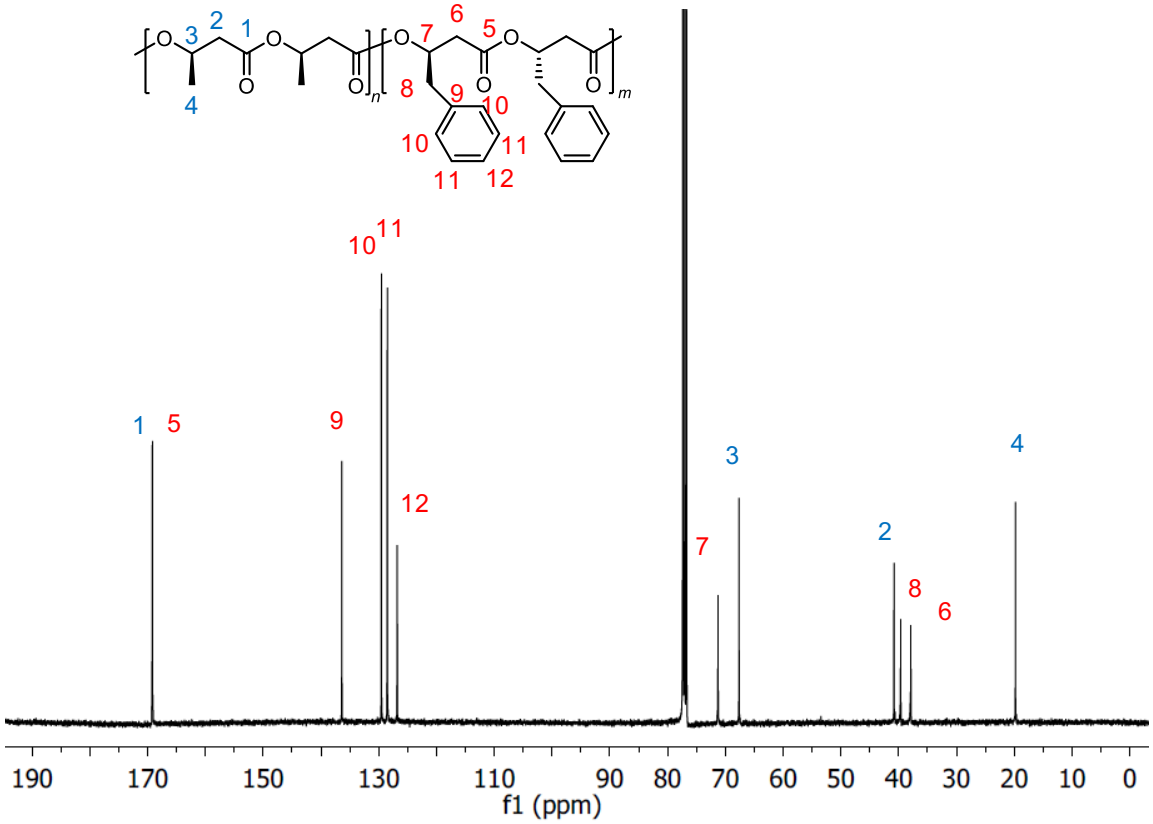

Figure S12. ^{13}C NMR (CDCl3, 23 °C) of tapered block copolymer *it*-P3HB-*b*-*st*-P3H4PhB.

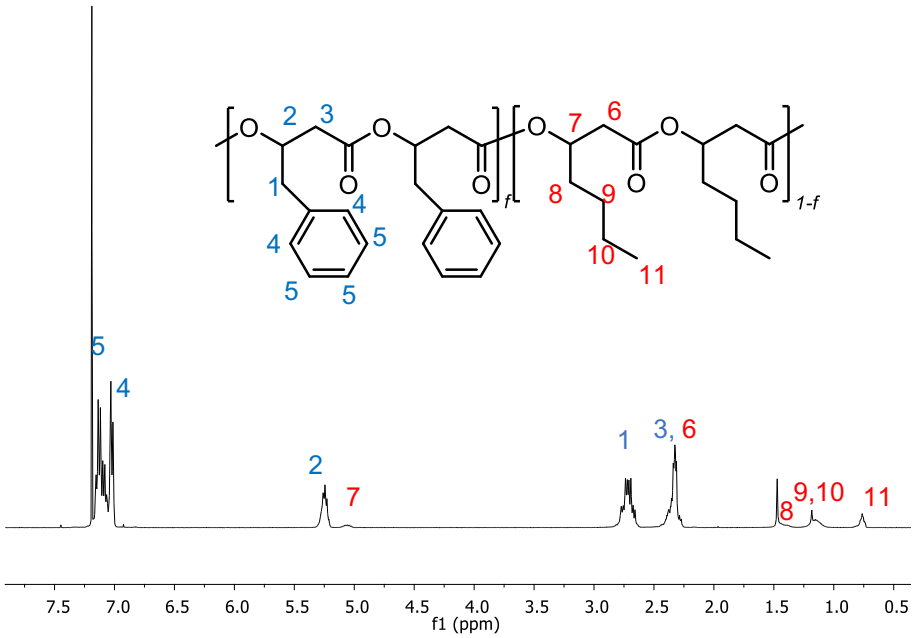

Figure S13. ^{1}H NMR ($CDCl_3$, 23 °C) of P3H4PhB-*co*-P3HHp (8.1% *rac*-DL^{Bu} incorporation). (Note: H_2O in $CDCl_3$ at 1.56 ppm).

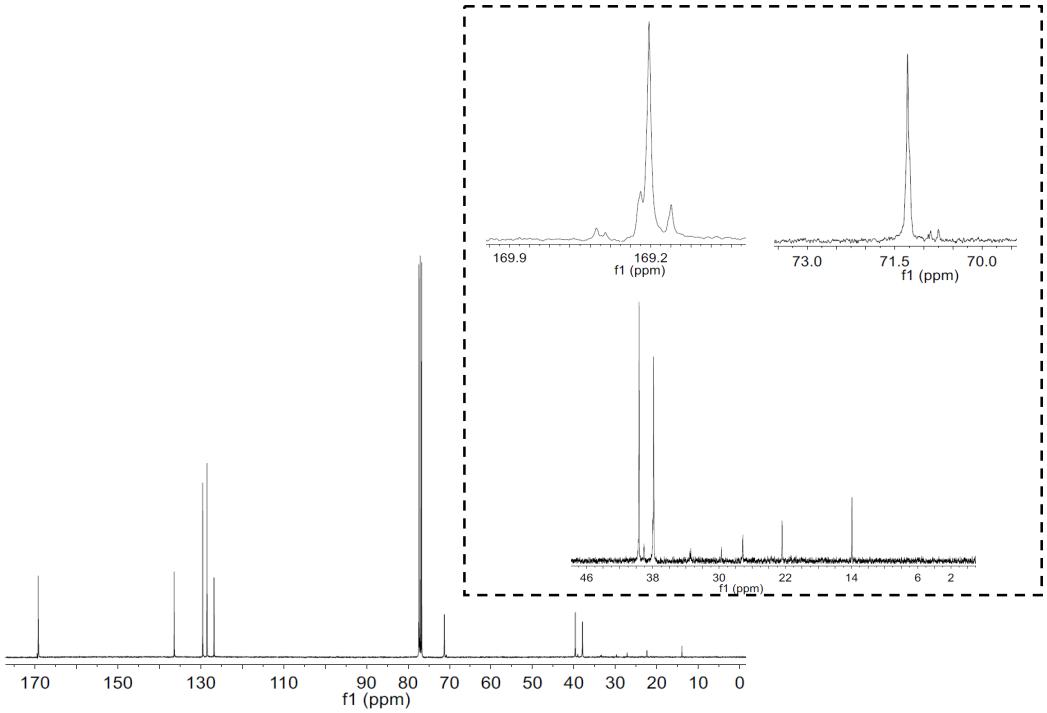

Figure S14. ^{13}C NMR ($CDCl_3$, 23 °C) of random copolymer P3H4PhBB-*co*-P3HHp (8.1% *rac*-DL^{Bu} incorporation).

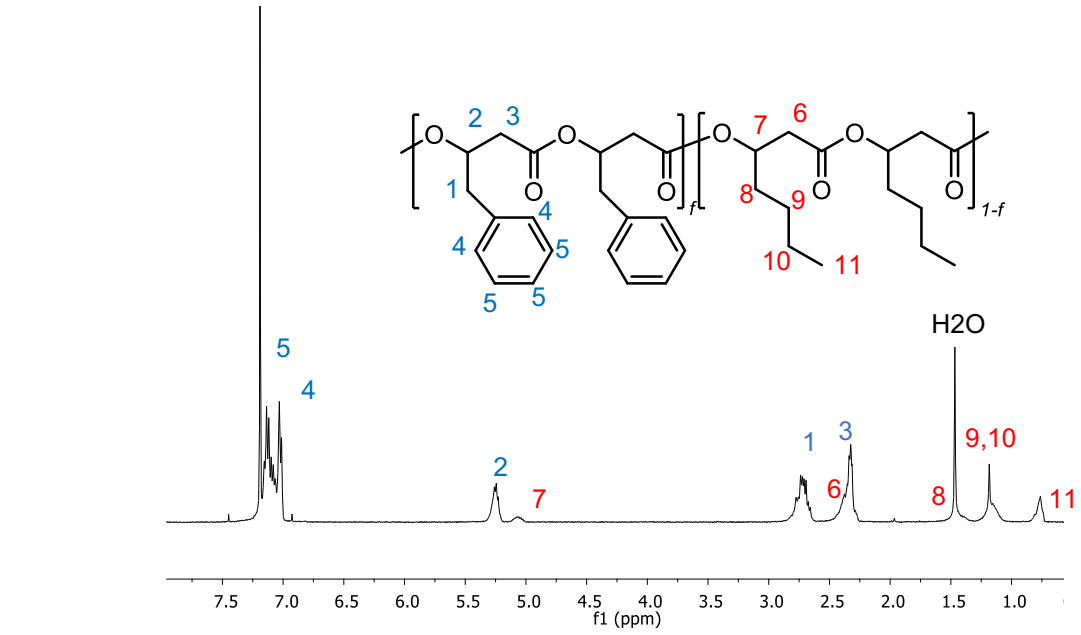

Figure S15. ^{1}H NMR ($CDCl_3$, 23 °C) of P3H4PhB-*co*-P3HHp (15.6% *rac*-DL^{Bu} incorporation). (Note: H_2O in $CDCl_3$ at 1.56 ppm)

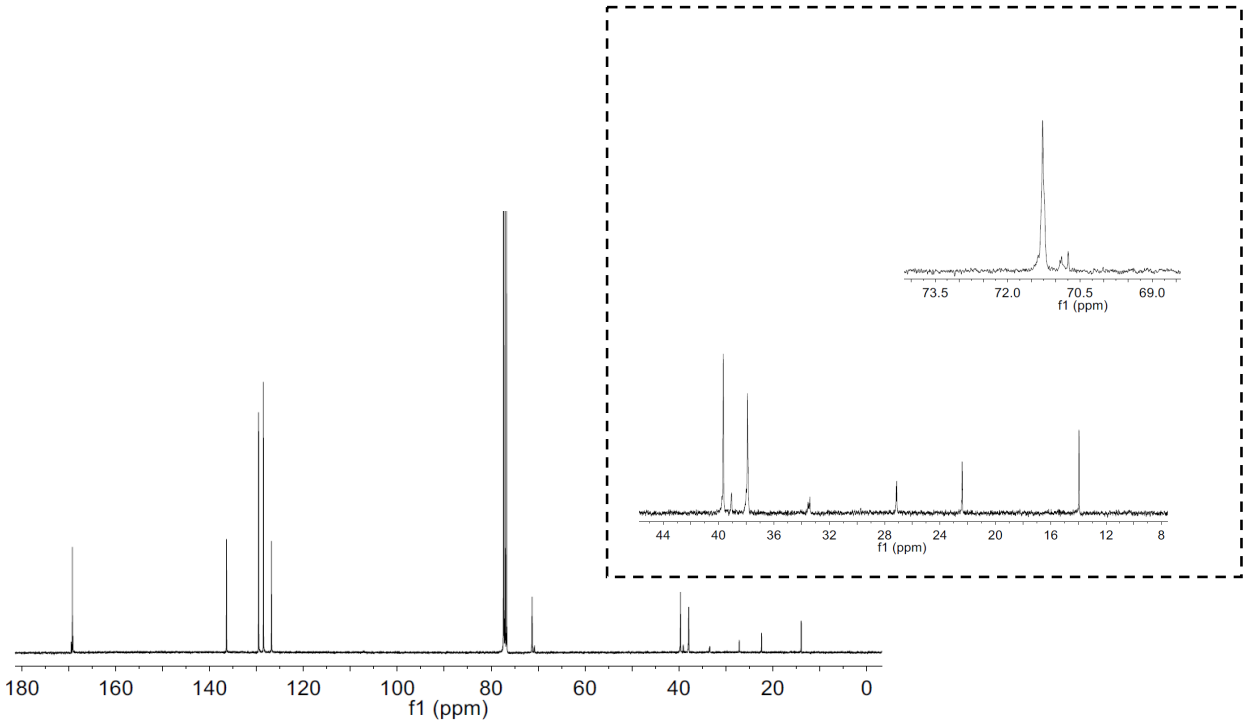

Figure S16. ^{13}C NMR ($CDCl_3$, 23 °C) of random copolymer P3H4PhBB-*co*-P3HHp (15.6% *rac*-DL^{Bu} incorporation).

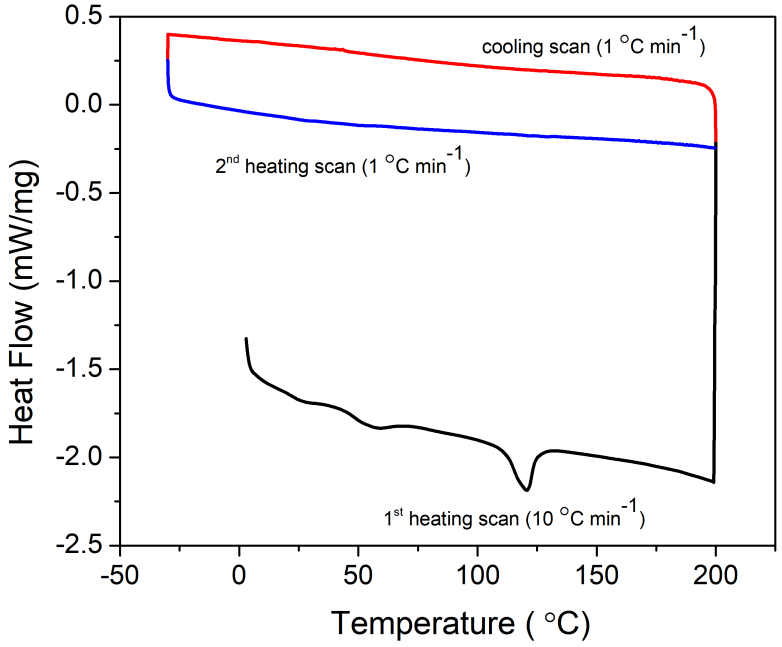

Figure S17. DSC curve of *it*-P3H4PhB ([*mm*]>99%). First heating scan (black curve: 10°C min^{-1}) followed by cooling scan (red curve: 1°C min^{-1}) and second heating scan (blue curve: 1°C min^{-1}). An endotherm visible in the first scan at 126 °C for T_m, but no T_c or T_m visible in the cooling or heating scan.

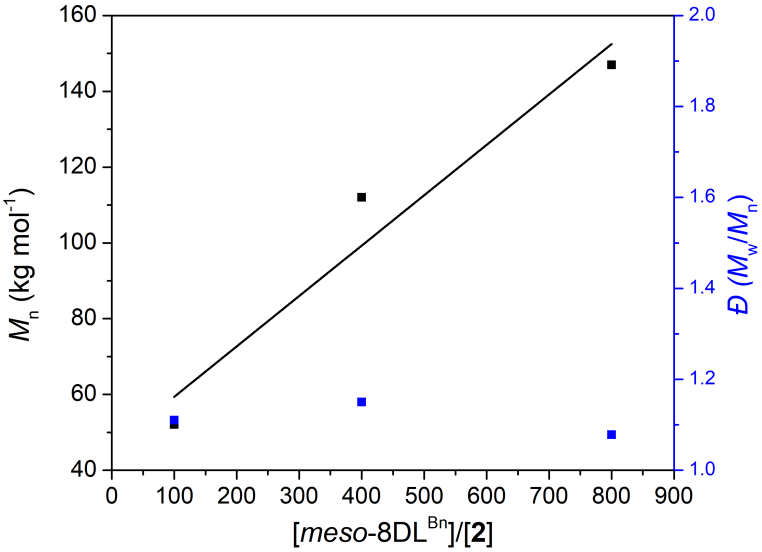

Figure S18. Plots of M_n and $Đ$ values of *st*-P3H4PhB produced by racemic complex **2** at varied [*meso*-8DL^{Bn}]/[**2**] ratios. Conditions: [*meso*-8DL^{Bn}] = 0.77 M (0.100 g in 0.4 mL DCM); RT; [**2**]/[BnOH] = 1/1).

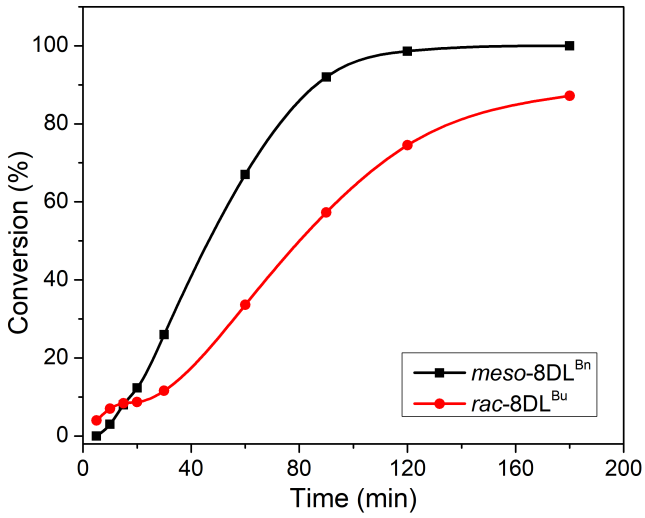

Figure S19. Time-conversion plots in the polymerization of *meso*-8DL^{Bn} and *rac*-8DL^{Bu} (5/1 ratio, in DCM, RT, [8DL]/[**2**]/BnOH = 800/1/1).

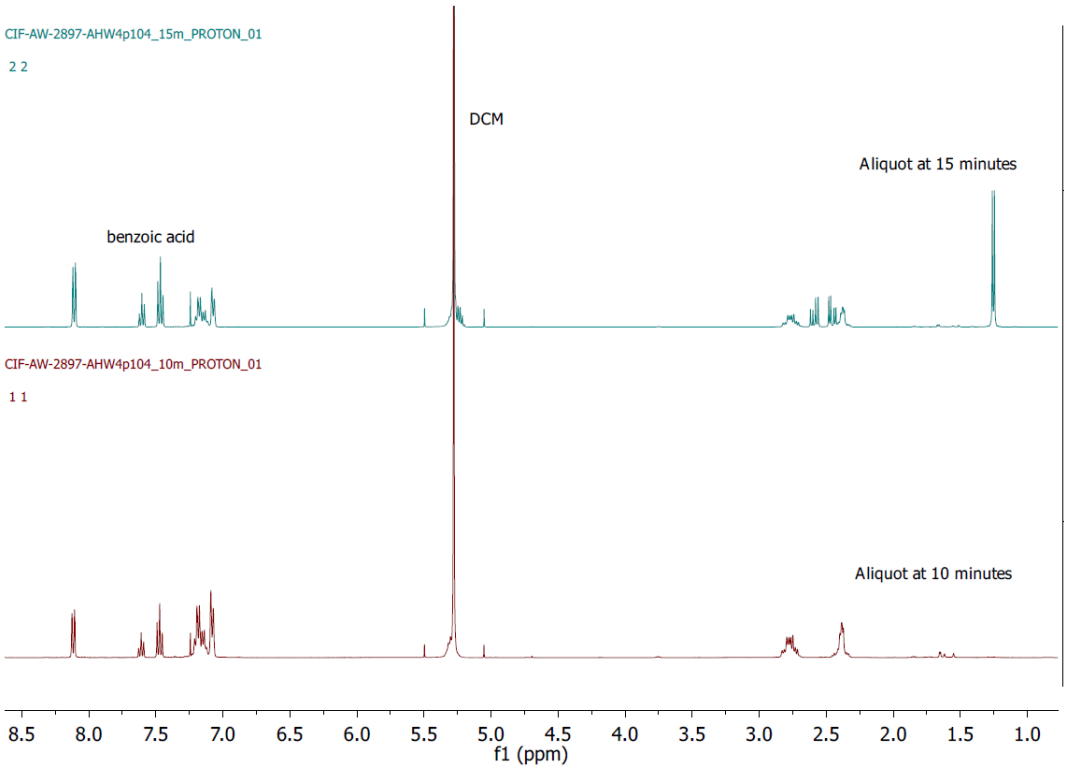

Figure S20. ^{1}H NMR of sequential block copolymer produced with *meso*-8DL^{Bn} added first and *rac*-8DL^{Me} added second.

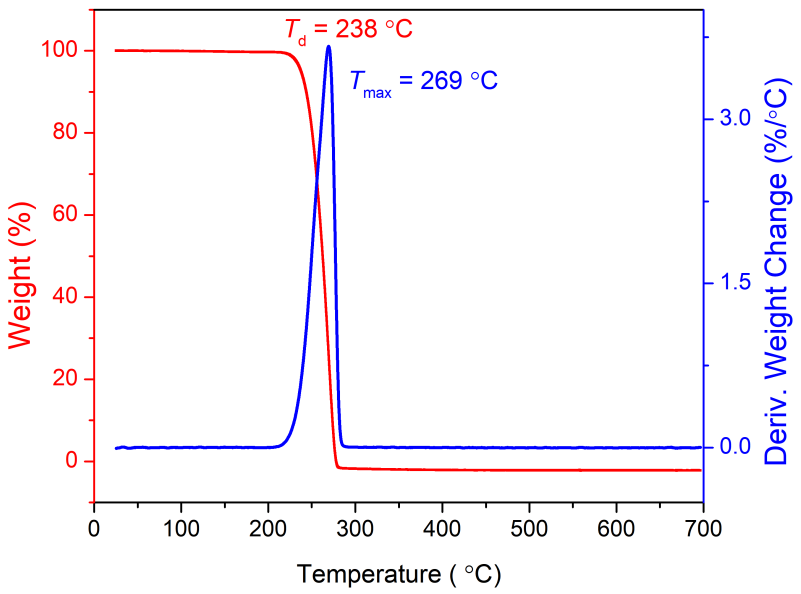

Figure S21. TGA curve of random copolymer P3H4PhB-*co*-P3HB (M_n = 58.9 kg mol^{-1}, $Đ$ = 1.16, 48% incorporation of 3HB units).

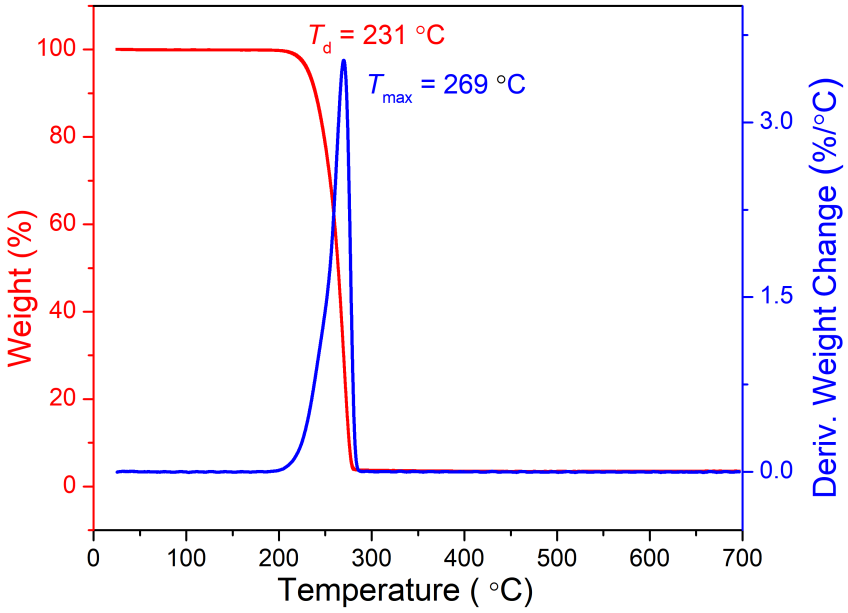

Figure S22. TGA curve of random copolymer P3H4PhB-*co*-P3HB (M_n = 93.3 kg mol^{-1}, $Đ$ = 1.11, 80% incorporation of 3HB units).

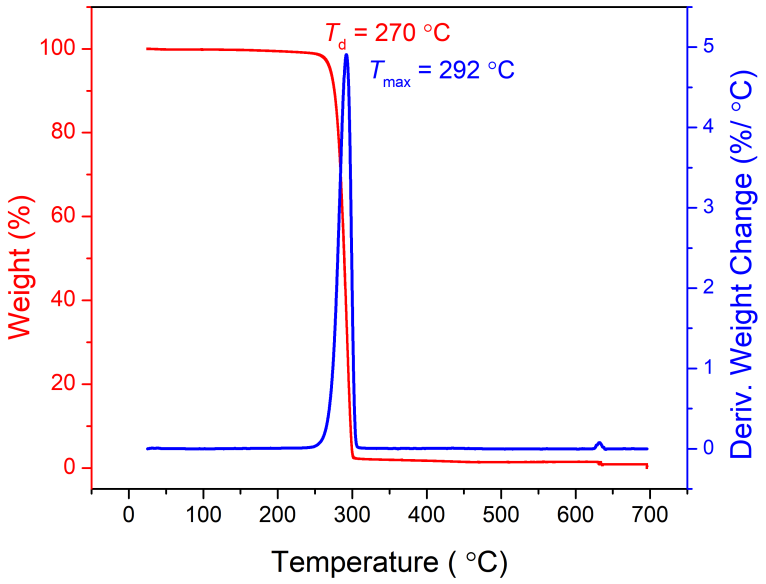

Figure S23. TGA curve of *it*-P3H4PhB ([*mm*] > 99%) (M_n = 64.5 kg mol^{-1}, $Đ$ = 1.29).

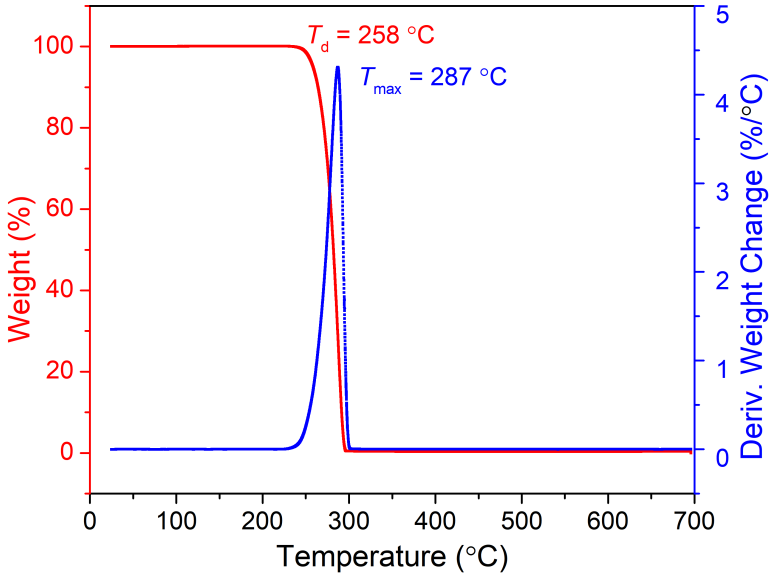

Figure S24. TGA curve of P3H4PhB-*co*-P3HHp (incorporation of 3HHp units derived from *rac*-DL^{Bu} = 9.1%, M_n = 206 kg mol^{-1}, $Đ$ = 1.13, prepared from copolymerization of *meso*-8DL^{Bn}/*rac*-8DL^{Bu} = 10/1, [8DL]/[2]/[BnOH] = 1200/1/1 in DCM at RT).

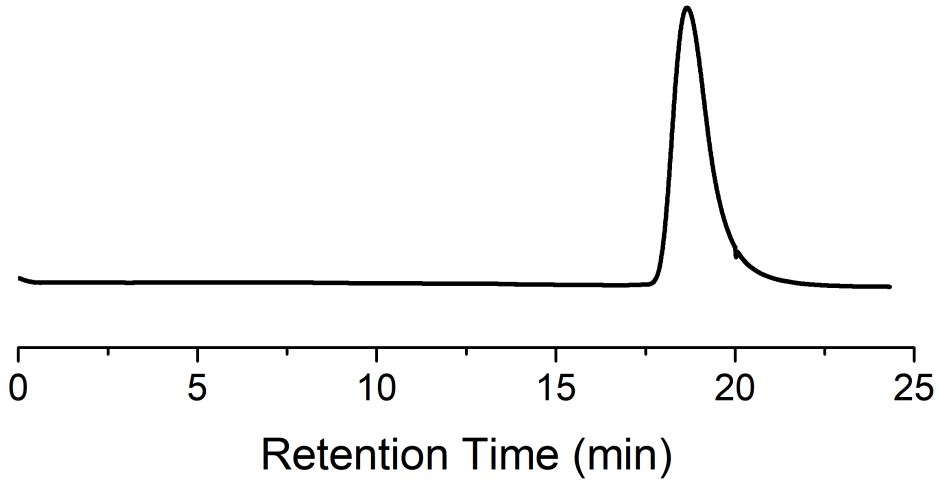

Figure S25. GPC trace of *st*-P3H4PhB by [*meso*-DL^{Bn}]/[**2**] = 400/1 in DCM (M_n = 112 kg mol^{-1}, $Đ$ = 1.15) (Run 3, Table 1).

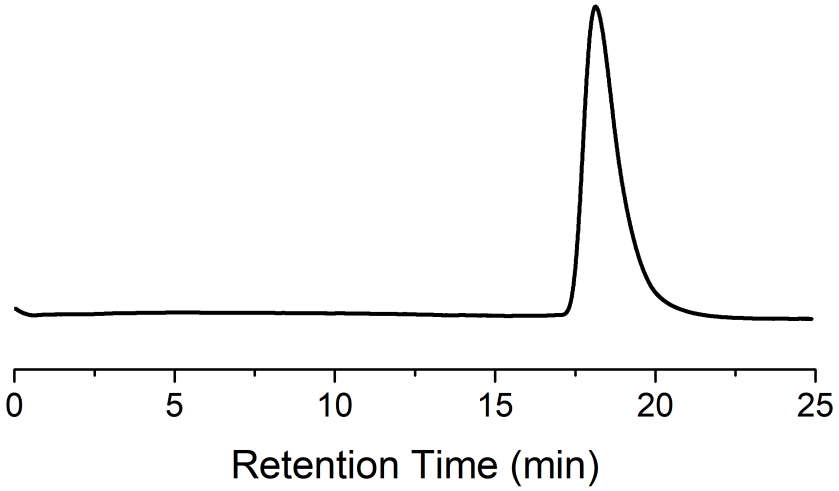

Figure S26. GPC trace of *st*-P3H4PhB by [*meso*-DL^{Bn}]/[**2**] = 800/1 in DCM (M_n = 147 kg mol^{-1}, $Đ$ = 1.19) (Run 4, Table 1).

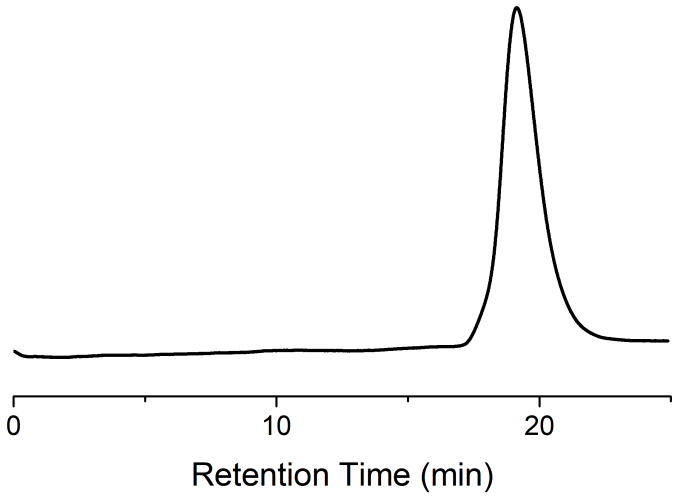

Figure S27. GPC trace of *st*-P3H4PhB by [*meso*-DL^{Bn}]/[**2**] = 400/1 in toluene (M_n = 76 kg mol^{-1}, $Đ$ = 1.16) (Run 10, Table 2).

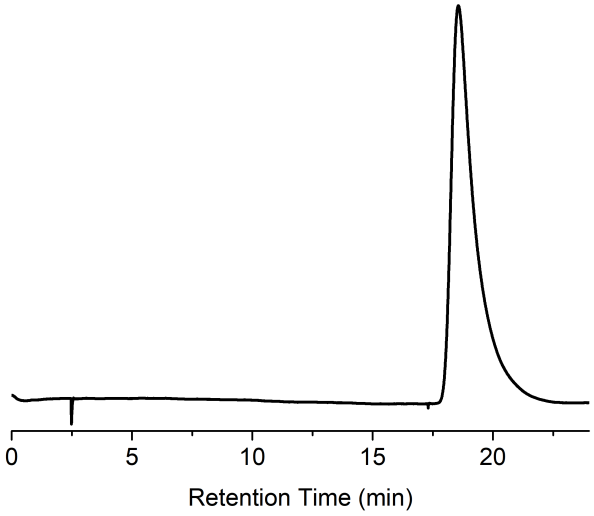

Figure S28. GPC trace of *st*-P3H4PhB by [*meso*-DL^{Bn}]/[**2**] = 800/1 in fluorobenzene (M_n = 119 kg mol^{-1}, $Đ$ = 1.16) (Run 12, Table 2).

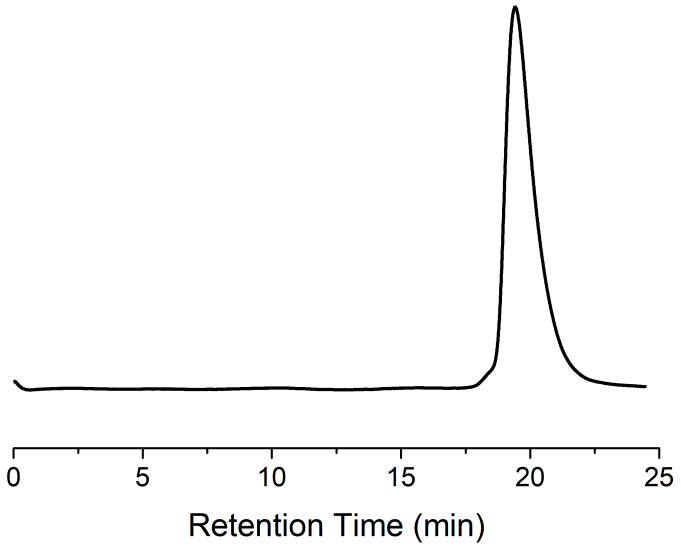

Figure S29. GPC trace of *it*-P3H4PhB by [*rac*-DL^{Bn}]/[**2**] = 100/1 in DCM (M_n = 64.5 kg mol^{-1}, $Đ$ = 1.29).

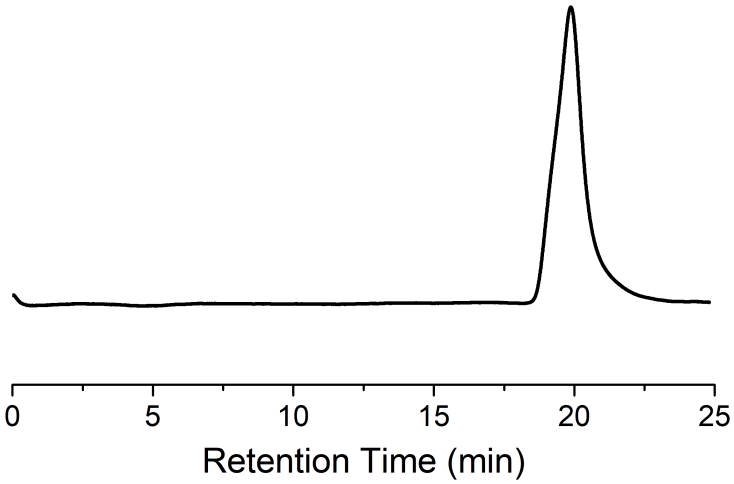

Figure S30. GPC trace of stereoblock copolymer *it*-P3HB-*b*-*st*-P3H4PhB by [DL]/[**2**] = 100/1 (M_n = 84.1 kg mol^{-1}, $Đ$ = 1.08) (Run 17, Table 3).

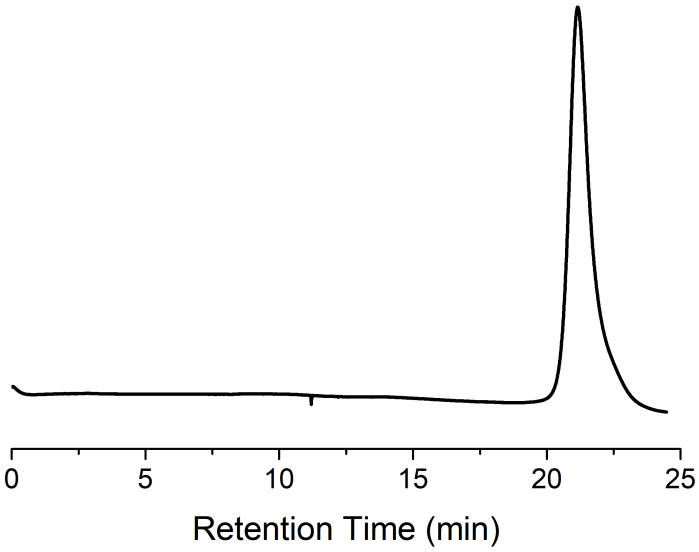

Figure S31. GPC trace of tapered stereoblock copolymer *it*-P3HB-*co*-*st*-P3H4PhB by [DL]/[**2**] = 100/1 (M_n = 18.4 kg mol^{-1}, $Đ$ = 1.22) (Run 18, Table 3).

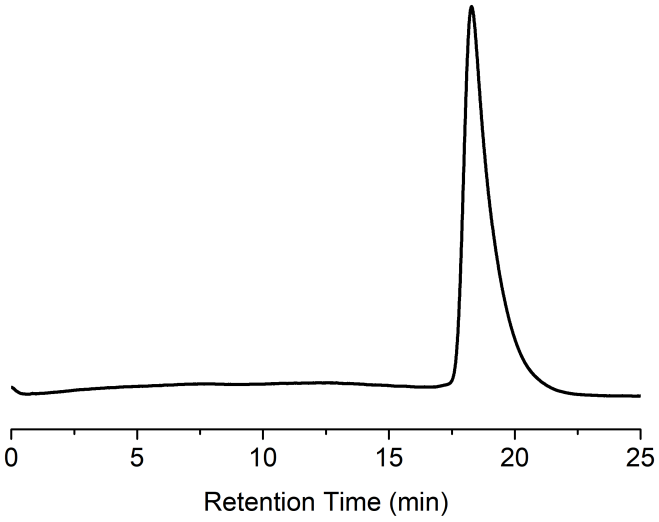

Figure S32. GPC trace of P3H4PhB-*co*-P3HHp (5:1) by [DL]/[**2**] = 800/1 (M_n = 117 kg mol^{-1}, $Đ$ = 1.28) (Run 19, Table 3).

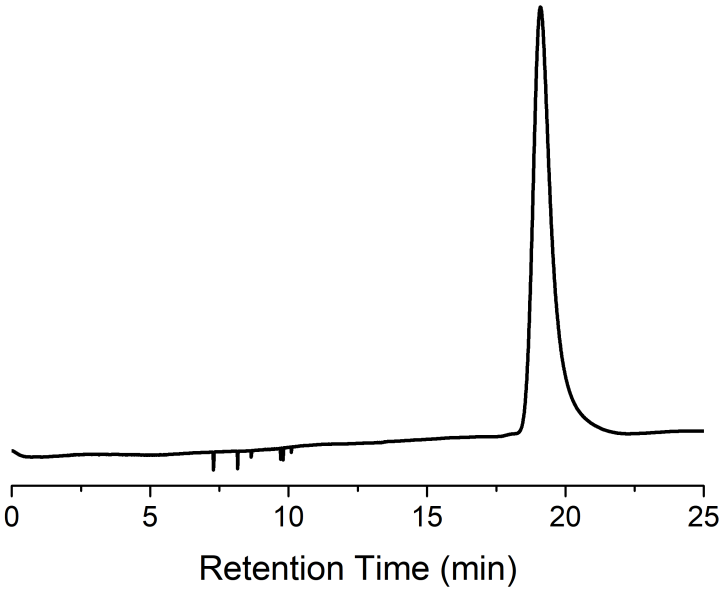

Figure S33. GPC trace of P3H4PhB-*co*-P3HHp (10:1) by [DL]/[**2**] = 800/1 (M_n = 84.0 kg mol^{-1}, $Đ$ = 1.14) (Run 20, Table 3).

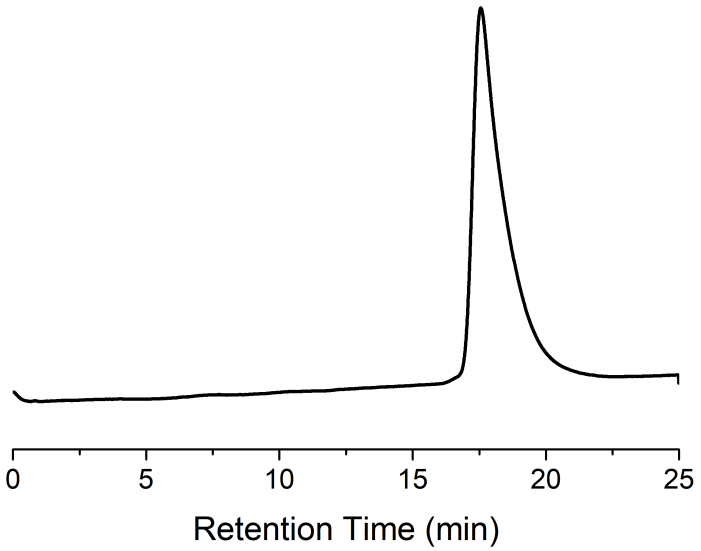

Figure S34. GPC trace of large-scale copolymer P3H4PhB-*co*-P3HHp (5:1) by **2** (M_n = 205 kg mol^{-1}, $Đ$ = 1.21).

Additional Tables

Table S1. Measured tensile behavior of P3H4PhB-*co*-P3HHp (incorporation of *rac*-DL^{Bu} = 15.6%, M_n = 205 kg mol^{-1}, $Đ$ = 1.21) dog-bone shaped specimens (ASTM D638-5).

Specimen	Modulus of Elasticity (Young's Modulus) (MPa)	Tensile Strength (MPa)	% Elongation at Break
1	1220	19.5	195.0
2	1360	22.7	204.6
3	1510	26.0	173.4
Mean	1363 ± 145	22.7 ± 3.25	191 ± 16

References

(1) Tang, X.; Chen, E. Y.-X. Chemical Synthesis of Perfectly Isotactic and High Melting Bacterial Poly(3-Hydroxybutyrate) from Bio-Sourced Racemic Cyclic Diolide. *Nat. Commun.* **2018**, *9*, 2345. https://doi.org/10.1038/s41467-018-04734-3

(2) Tang, X.; Westlie, A. H.; Caporaso, L.; Cavallo, L.; Falivene, L.; Chen, E. Y.-X. Biodegradable Polyhydroxyalkanoates by Stereoselective Copolymerization of Racemic Diolides: Stereocontrol and Polyolefin- Like Properties Research Articles. *Angew. Chem. Int. Ed.* **2020**, *59*, 2–12. https://doi.org/10.1002/anie.201916415

(3) Anwander, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M. Synthesis and Structural Characterisation of Rare-Earth Bis(Dimethylsilyl)Amides and Their Surface Organometallic Chemistry on Mesoporous MCM-41. *J. Chem. Soc. Dalt. Trans.* **1998**, 5, 847–858. https://doi.org/10.1039/a705608g

(4) Lin, M. H.; RajanBabu, T. V. Ligand-Assisted Rate Acceleration in Transacylation by a Yttrium - Salen Complex. Demonstration of a Conceptually New Strategy for Metal-Catalyzed Kinetic Resolution of Alcohols. *Org. Lett.* **2002**, *4*, 1607–1610. https://doi.org/10.1021/ol025809q

(5) Liu, Q.; Meermann, C.; Görlitzer, H. W.; Runte, O.; Herdtweck, E.; Sirsch, P.; Törnroos, K. W.; Anwander, R. Cationic Rare-Earth Metal SALEN Complexes. *J. Chem. Soc. Dalt. Trans.* **2008**, 44, 6170–6178. https://doi.org/10.1039/b808781d