

Stereo-electronic Contributions in Yttrium-Mediated Stereoselective Ring-Opening Polymerization of Functional Racemic β -Lactones: ROP of 4-Alkoxyethylene- β - Propiolactones with Bulky Exocyclic Chains

Rama M. Shakaroun,^a Ali Dhaini,^a Romain Ligny,^a Ali Alaaeddine,^b Sophie M. Guillaume (ORCID: 0000-0003-2917-8657),^{a,*} and Jean-François Carpentier (ORCID: 0000-0002-9160-7662)^{a,*}

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General conditions

Material and methods

All manipulations involving organometallic catalysts were performed under inert atmosphere (argon, <3 ppm O₂) using standard Schlenk, vacuum line, and glovebox techniques. Toluene was freshly distilled from Na/benzophenone under argon and degassed thoroughly by freeze-thaw-vacuum cycles prior to use. Isopropyl alcohol was distilled over Mg turnings under argon atmosphere and kept over activated 3–4 Å molecular sieves. Proligands {ONNO^{*t*Bu₂}}H₂, {ONNO^{cumyl₂}}H₂, {ONNO^{Me₂}}H₂ and {ONNO^{Cl₂}}H₂, and precursor Y[N(SiHMe₂)₂]₃(THF)_{1.5}, used to prepare amido yttrium complexes **2a-d**, respectively, were synthesized according to the reported procedures.^{6a,13}

Instrumentation and measurements

¹H (500 and 400 MHz) and ¹³C {¹H} (125 MHz and 100 MHz) NMR spectra were recorded on Bruker Avance AM 500 and Ascend 400 spectrometers at 25 °C. ¹H and ¹³C {¹H} NMR spectra were referenced internally relative to SiMe₄ (δ = 0 ppm) using the residual solvent resonances.

Number-average molar mass ($M_{n,SEC}$) and dispersity ($D_M = M_w/M_n$) values of the PBPL^{FGs} were determined by size-exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL·min⁻¹) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 μm MIXED-D 300 × 7.5 mm columns. The polymer samples were dissolved in THF (*ca.* 2 mg·mL⁻¹). All elution curves were calibrated with polystyrene standards; $M_{n,SEC}$ values of the PBPL^{FGs} were uncorrected for the possible difference in hydrodynamic radius *vs.* that of polystyrene.

The molar mass of PBPL^{FG} samples was also determined by ¹H NMR analysis in CDCl₃ from the relative intensities of the signals of the PBPL^{FG} repeating unit methine hydrogen (δ, ppm): 5.25 –OCH(CH₂OCH(CH₃)₂), PBPL^{CH₂O^{*i*Pr}}; 5.22 –OCH(CH₂OC(CH₃)₃), PBPL^{CH₂O^{*t*Bu}}; 5.20 –OCH(CH₂OSi(CH₃)₂C(CH₃)₃), PBPL^{CH₂OTBDMS}; and of the isopropyl chain-end (δ, ppm): 4.94–4.98 (CH₃)₂CHO–, 1.19–1.25 (CH₃)₂CHO–).

Monomer conversions were calculated from ¹H NMR spectra of the crude polymer samples in CDCl₃ by using the integration (Int.) ratios [Int._{PBPL^{FG}} / (Int._{PBPL^{FG}} + Int._{BPL^{FG}})] of the methine hydrogens of BPL^{FGs} and PBPL^{FGs} (corresponding methine hydrogen signal of the polymers (see above)), and of the monomers (d (ppm) 4.60 BPL^{CH₂O^{*i*Pr}}, 4.55 BPL^{CH₂O^{*t*Bu}}, and 4.65 BPL^{CH₂OTBDMS}).

High resolution Matrix Assisted Laser Desorption Ionization - Time of Flight, MALDI-ToF, mass spectra of the polymers were recorded using an ULTRAFLEX III TOF/TOF spectrometer (Bruker Daltonik GmbH, Bremen, Germany) in positive ionization mode. Spectra were recorded using reflectron mode and an accelerating voltage of 25 kV. A mixture of a freshly prepared solution of the polymer in THF or CH₂Cl₂ (HPLC grade, 10 mg mL⁻¹) and DCTB (*trans*-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene) malononitrile, and a MeOH solution of the cationizing agent (NaI, 10 mg mL⁻¹) were prepared. The solutions were combined in a 1:1:1 v/v/v ratio of matrix-to-sample-to-cationizing agent. The resulting solution (0.25–0.5 μL) was deposited onto the sample target (Prespotted AnchorChip PAC II 384 / 96 HCCA) and air or vacuum dried.

Differential scanning calorimetry (DSC) analyses were performed with a DSC2500 TA Instrument apparatus calibrated with indium using aluminum capsules (40 μL). The thermograms were recorded under a continuous flow of helium (25 mL min⁻¹) according to the following cycles: –80 to 200 °C at 10 °C min⁻¹; 200 to –80 °C at 10 °C min⁻¹; –80 °C for 5 min; –80 to 200 °C at 10 °C min⁻¹; 200 to –80 °C at 10 °C min⁻¹.

Synthesis and characterization of BPL^{CH₂OR} monomers. BPL^{CH₂OR} monomers were synthesized by carbonylation of the corresponding racemic or enantiopure glycidyl ethers (*rac*-/(*S*)-Glyc^{CH₂OR}) using a previously reported procedure.¹ All *rac*-BPL^{CH₂OR} and (*S*)-BPL^{CH₂OR} monomers were stored under argon at –27 °C.

***Rac*/(*S*)-BPL^{CH₂O^{*i*}Pr}.** Using [Salph(Cr(THF)₂)] [Co(CO)₄] (431 mg, 0.47 mmol) and *rac*-Glyc^{CH₂O^{*i*}Pr} (5.51 g, 47.51 mmol, 100 equiv), the carbonylation reaction afforded *rac*-BPL^{CH₂O^{*i*}Pr} which was isolated following a double distillation using a Kügelrohr oven (180 °C, 0.1 torr) as a colorless viscous liquid (4.45 g, 65% yield). ¹H NMR (500 MHz, CDCl₃, 25 °C) δ (ppm): δ 4.60 (dtd, ³J_{H-H} = 6 Hz, ³J_{H-H} = 4 Hz, ³J_{H-H} = 3 Hz, 1H), 3.74 (dd, ²J_{H-H} = 12 Hz, ³J_{H-H} = 3 Hz, 1H), 3.68 – 3.58 (m, 2H), 3.42 (dd, ²J_{H-H} = 16 Hz, ³J_{H-H} = 6 Hz, 1H), 3.35 (dd, ²J_{H-H} = 16 Hz, ³J_{H-H} = 4 Hz, 1H), 1.15 (d, *J* = 6 Hz, 6H) (Figure S1). ¹³C NMR (125 MHz, CDCl₃, 25 °C) δ (ppm): 72.6 (OCH(CH₃)₂), 69.6 (CHOC(O)), 67.4 (CH₂OCH), 39.4 (CH₂C(O)O), 21.8 (CH(CH₃)₂), 21.8 (CH(CH₃)₂) (Figure S2). Carbonylation of (*S*)-BPL^{CH₂O^{*i*}Pr} was performed similarly but starting from (*S*)-Glyc^{CH₂O^{*i*}Pr} and gave (*S*)-BPL^{CH₂O^{*i*}Pr} as a colorless viscous liquid (4.3 g, 63% yield) that displayed NMR spectra identical to those of *rac*-BPL^{CH₂O^{*i*}Pr}.

***Rac*/(*S*)-BPL^{CH₂O^{*t*}Bu}** Using [Salph(Cr(THF)₂)] [Co(CO)₄] (281 mg, 0.31 mmol) and *rac*-Glyc^{CH₂O^{*t*}Bu} (4.03 g, 31.0 mmol, 100 equiv), the carbonylation reaction afforded *rac*-

BPL^{CH₂O^tBu} which was isolated following a double distillation using a Kugelrohr oven (190–200 C, 0.1 torr) as a colorless viscous liquid (3.13 g, 64% yield). ¹H NMR (500 MHz, CDCl₃, 25 C)  (ppm):  4.55 (dtd, ³J_{H-H} = 6 Hz, ³J_{H-H} = 4 Hz, ³J_{H-H} = 3 Hz, 1H), 3.66 (dd, ²J_{H-H} = 11 Hz, ³J_{H-H} = 3 Hz, 1H), 3.54 (dd, ²J_{H-H} = 11 Hz, ³J_{H-H} = 4 Hz, 1H), 3.37 (dd, ²J_{H-H} = 16 Hz, ³J_{H-H} = 6 Hz, 1H), 3.31 (dd, ²J_{H-H} = 16 Hz, ³J_{H-H} = 5 Hz, 1H), 1.15 (s, 9H) (Figure S1). ¹³C NMR (125 MHz, CDCl₃, 25 C)  (ppm):  167.9 (C=O), 74.3 (OC(CH₃)₃), 69.6 (CHOC(O)), 63.6 (CH₂OC), 39.4 (CH₂C(O)O), 27.2 (C(CH₃)₃) (Figure S2). ESI-MS *m/z*_{found} = 181.0833 vs. *m/z*_{calculated} = 181.0835. Carbonylation of (*S*)-BPL^{CH₂O^tBu} was performed similarly but starting from (*S*)-Glyc^{CH₂O^tBu} and gave (*S*)-BPL^{CH₂O^tBu} as a colorless viscous liquid (3.0 g, 61% yield) that displayed NMR spectra identical to those of *rac*-BPL^{CH₂O^tBu}.

***Rac*-(*S*)-BPL^{CH₂OTBDMS}.**² Using [Salph(Cr(THF)₂)] [Co(CO)₄] (246 mg, 0.27 mmol) and *rac*-Glyc^{CH₂OTBDMS} (5.57 g, 29.64 mmol, 100 equiv) afforded *rac*-BPL^{CH₂OTBDMS} which was isolated following a double distillation using a Kugelrohr oven (140 C, 0.1 torr) as a colorless viscous liquid (3.8 g, 60% yield). ¹H NMR (500 MHz, CDCl₃, 25 C)  (ppm): 4.65–4.46 (m, 1H), 4.02 (dd, ²J_{H-H} = 12 Hz, ²J_{H-H} = 3 Hz, 1H), 3.82 (dd, ³J_{H-H} = 12 Hz, ³J_{H-H} = 3 Hz, 1H), 3.53–3.28 (m, 2H), 0.91 (s, 9H), 0.09 (s, 6H) (Figure S1). ¹³C NMR (125 MHz, CDCl₃, 25 C)  (ppm): 171.7 (C=O), 74.8 (CHOC(O)), 63.9 (CH₂OTBDMS), 37.4 (CH₂C(O)O), 25.7 Si(CH₃)₂C(CH₃)₃, 15.7 Si(CH₃)₂C(CH₃)₃, –4.9 Si(CH₃)₂C(CH₃)₃ (Figure S2). Carbonylation of (*S*)-BPL^{CH₂OTBDMS} was performed similarly but starting from (*S*)-Glyc^{CH₂OTBDMS} and gave (*S*)-BPL^{CH₂OTBDMS} as a colorless viscous liquid (3.65 g, 58% yield) that displayed NMR spectra identical to those of *rac*-BPL^{CH₂OTBDMS}.

References

- ¹ a) J. A. Schmidt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, **2005**, *127*, 11426–11435; b) J. W. Kramer, G. W. Coates, *Tetrahedron* **2008**, *64*, 6973–6978.
- ² R. M. Shakaroun, H. Li, P. Jehan, A. Alaaeddine, J.-F. Carpentier, S. M. Guillaume, *Polym. Chem.*, **2020**, *11*, 2640–2652.

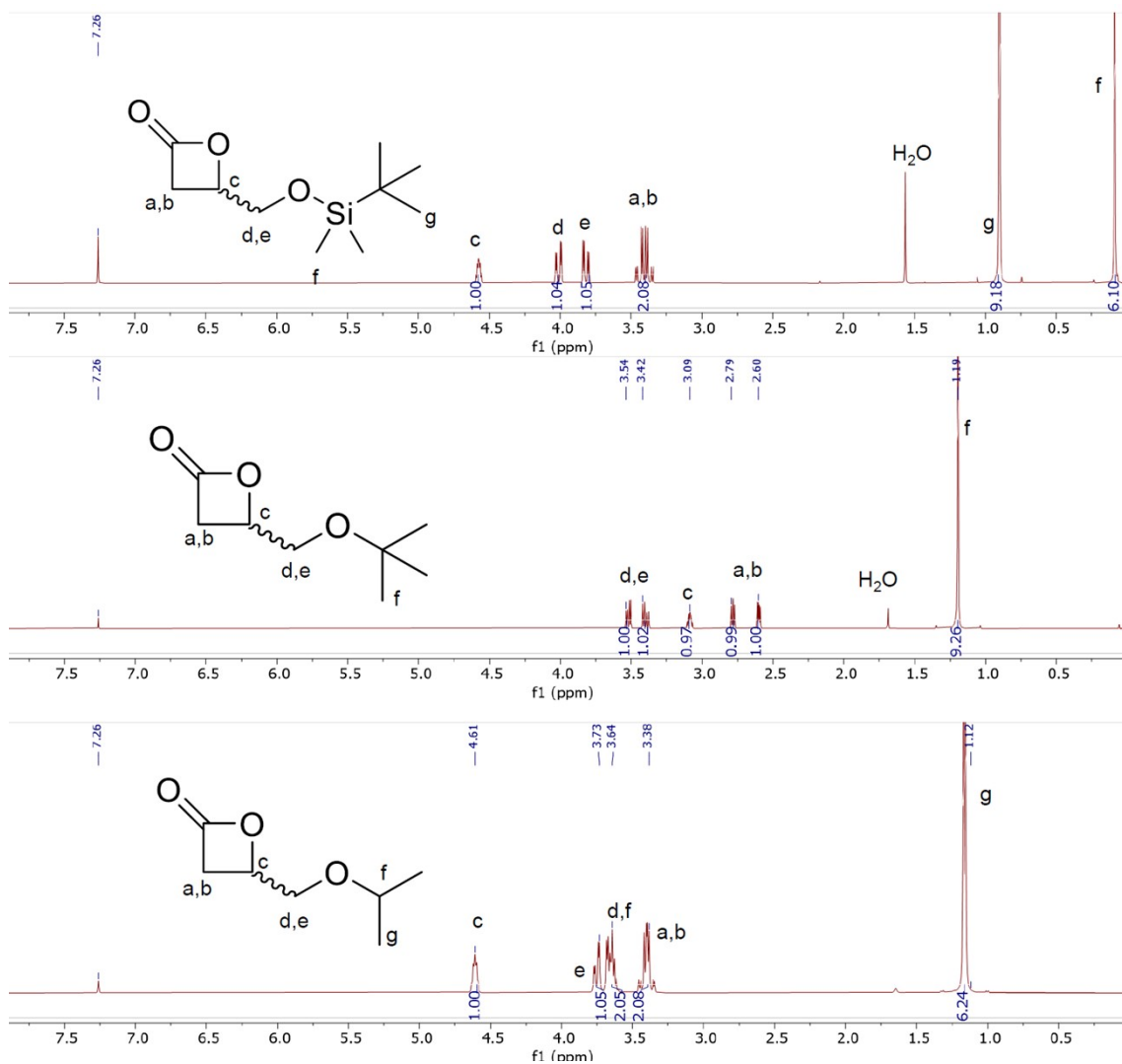


Figure S1. ¹H NMR spectra (500 MHz, CDCl₃, 23 °C) of *rac*-BPL^{CH2OTBDMS}, *rac*-BPL^{CH2OtBu}, *rac*-BPL^{CH2OiPr} monomers (from top to bottom).

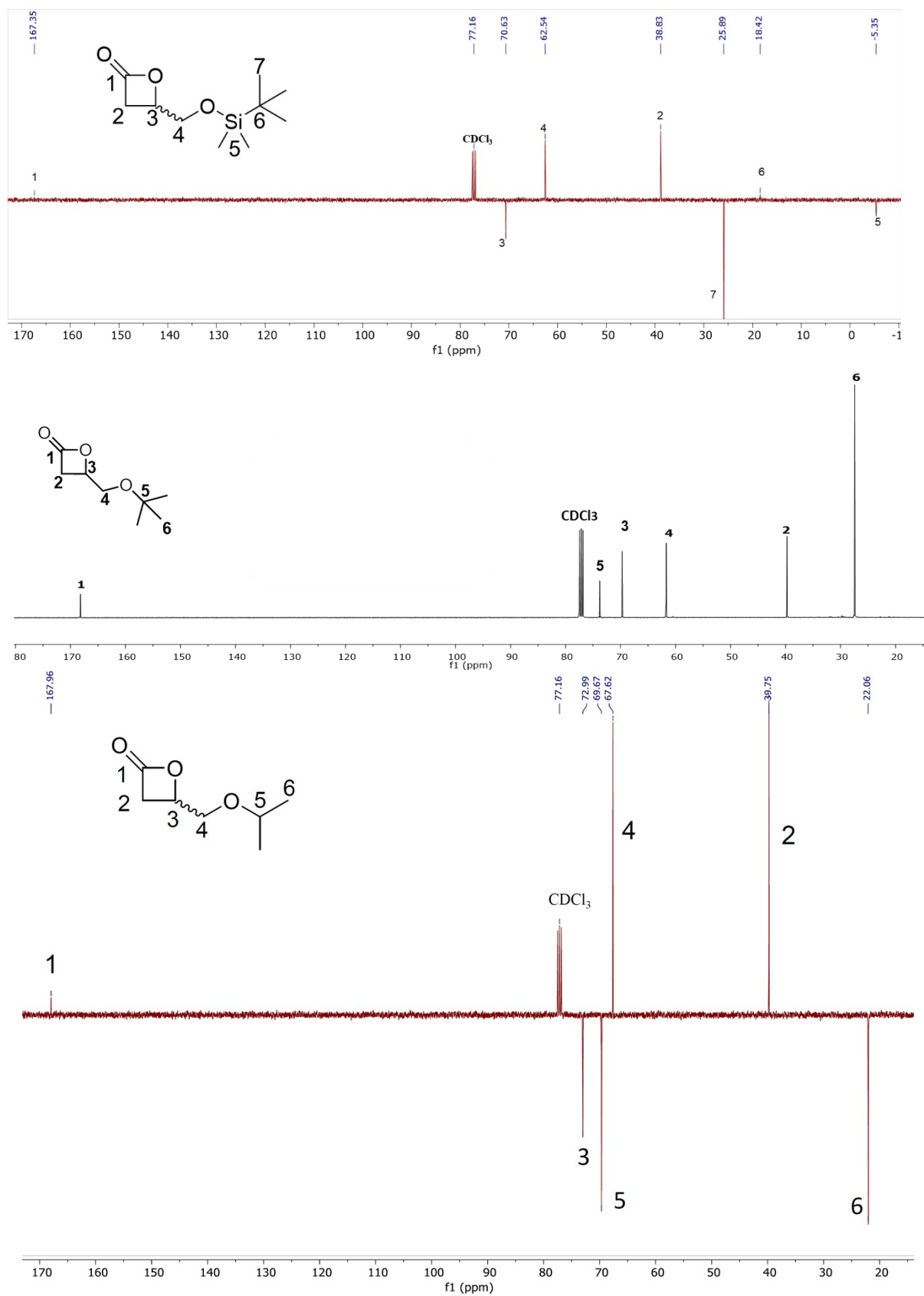


Figure S2. J-MOD / $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, CDCl_3 , 25 °C) of $\text{rac-BPL}^{\text{CH}_2\text{OTBDMS}}$, $\text{rac-BPL}^{\text{CH}_2\text{OtBu}}$, and $\text{rac-BPL}^{\text{CH}_2\text{OiPr}}$ monomers (from top to bottom).

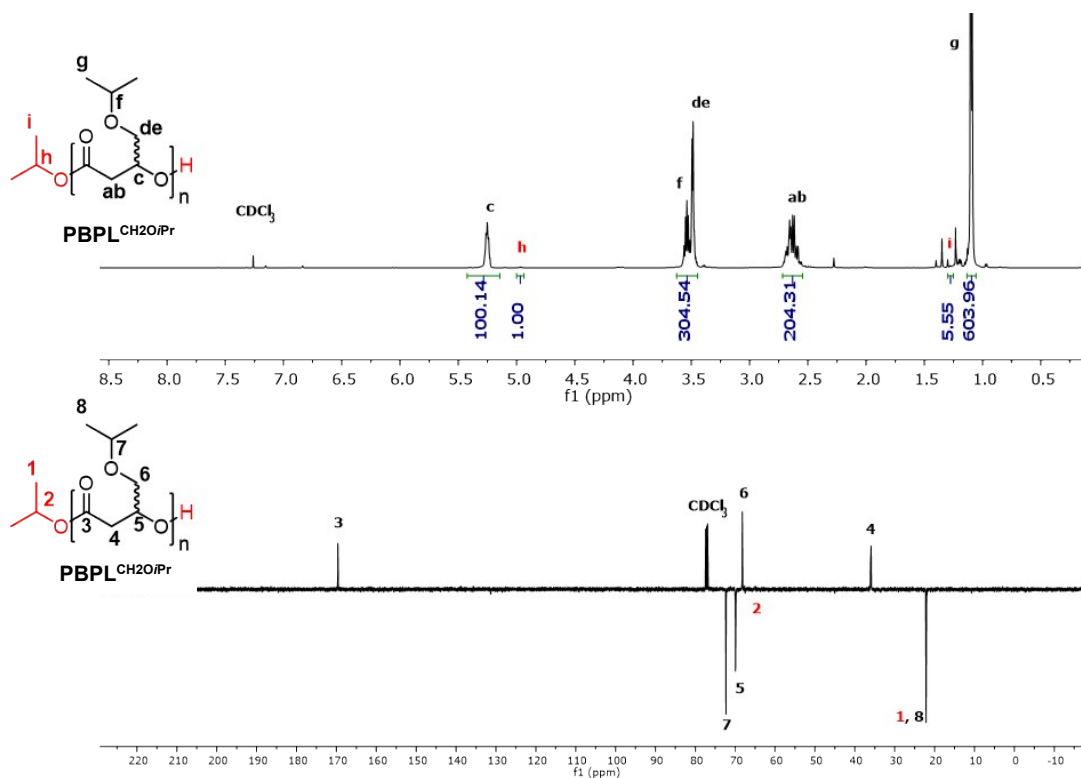


Figure S3. ^1H (500 MHz, CDCl_3 , 25 °C) (top) and J-MOD (125 MHz, CDCl_3 , 25 °C) (bottom) NMR spectra of a syndio-enriched $\text{PBPL}^{\text{CH}_2\text{O}i\text{Pr}}$ prepared from the ROP of $\text{rac-BPL}^{\text{CH}_2\text{O}i\text{Pr}}$ mediated by the **2b**/*i*PrOH (1:1) system (Table 1, entry 6).

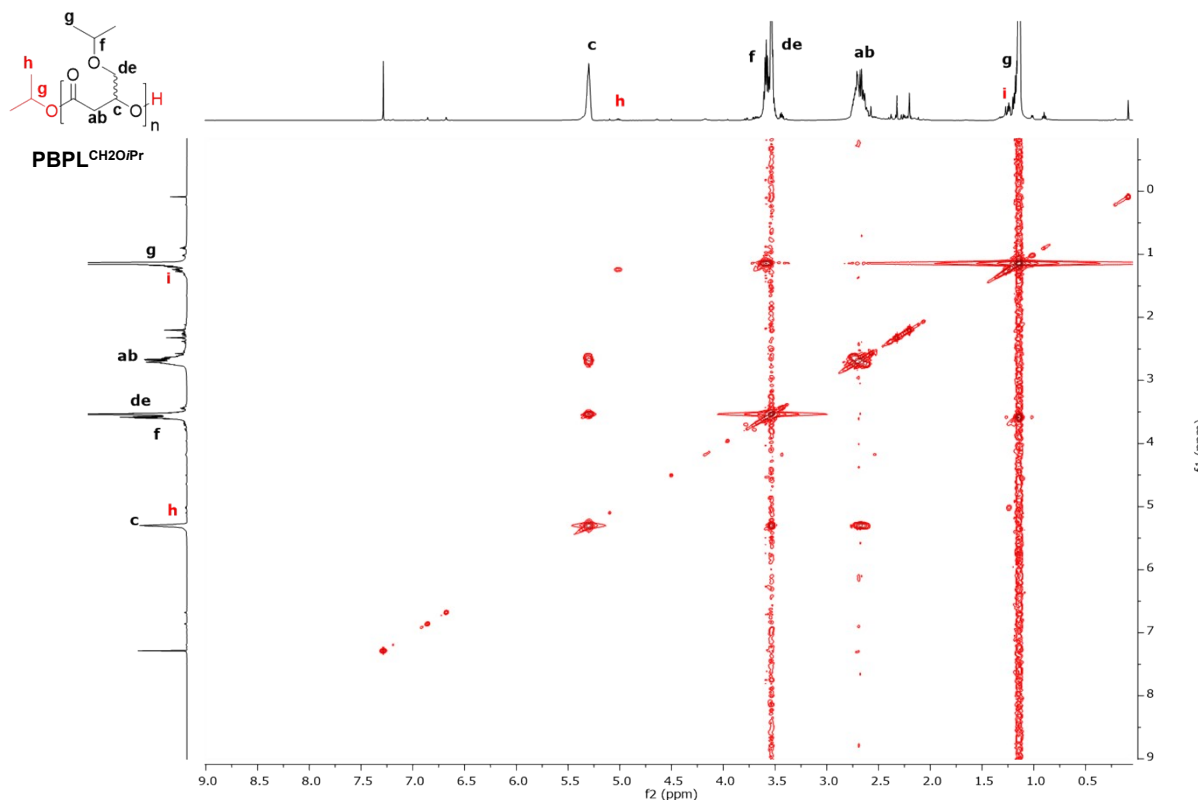


Figure S4. ^1H - ^1H COSY NMR spectrum (500 MHz, CDCl_3 , 25 °C) of a syndio-enriched $\text{PBPL}^{\text{CH}_2\text{O}i\text{Pr}}$ (Table 1, entry 6).

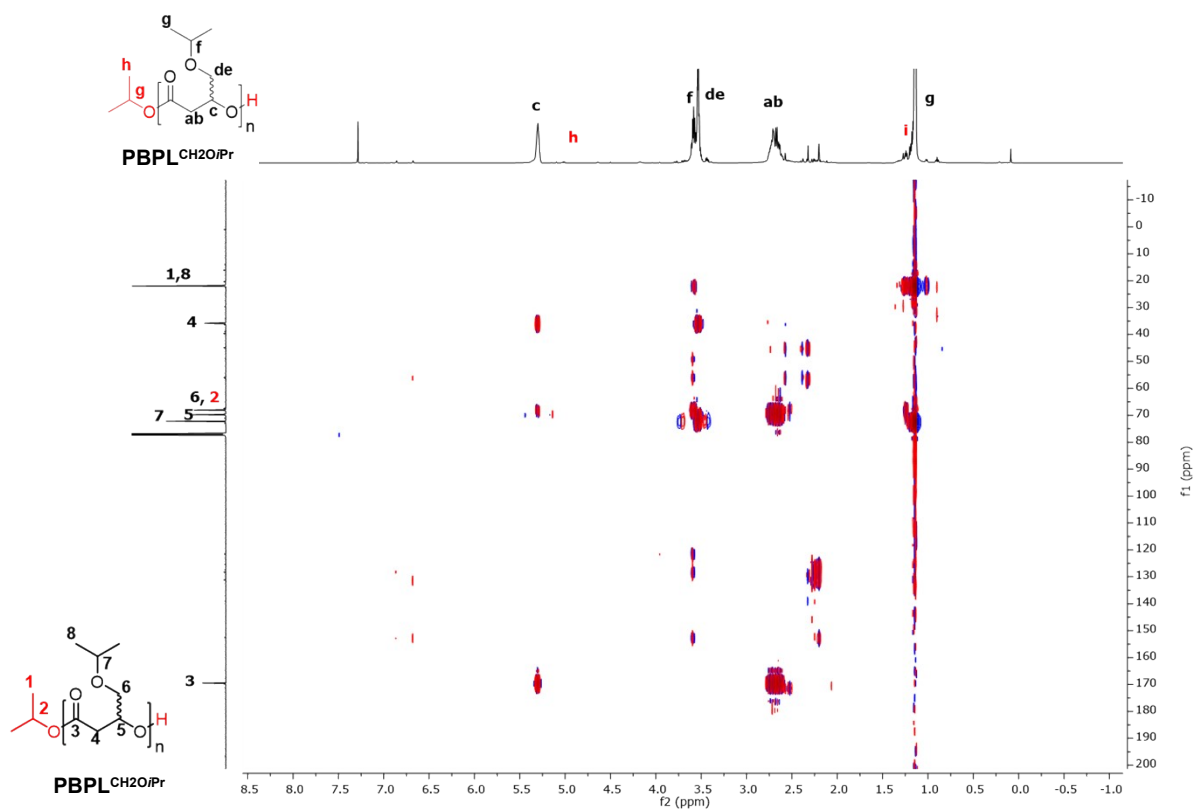


Figure S5. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a syndio-enriched PBPL $^{\text{CH}_2\text{O}i\text{Pr}}$ (Table 1, entry 6).

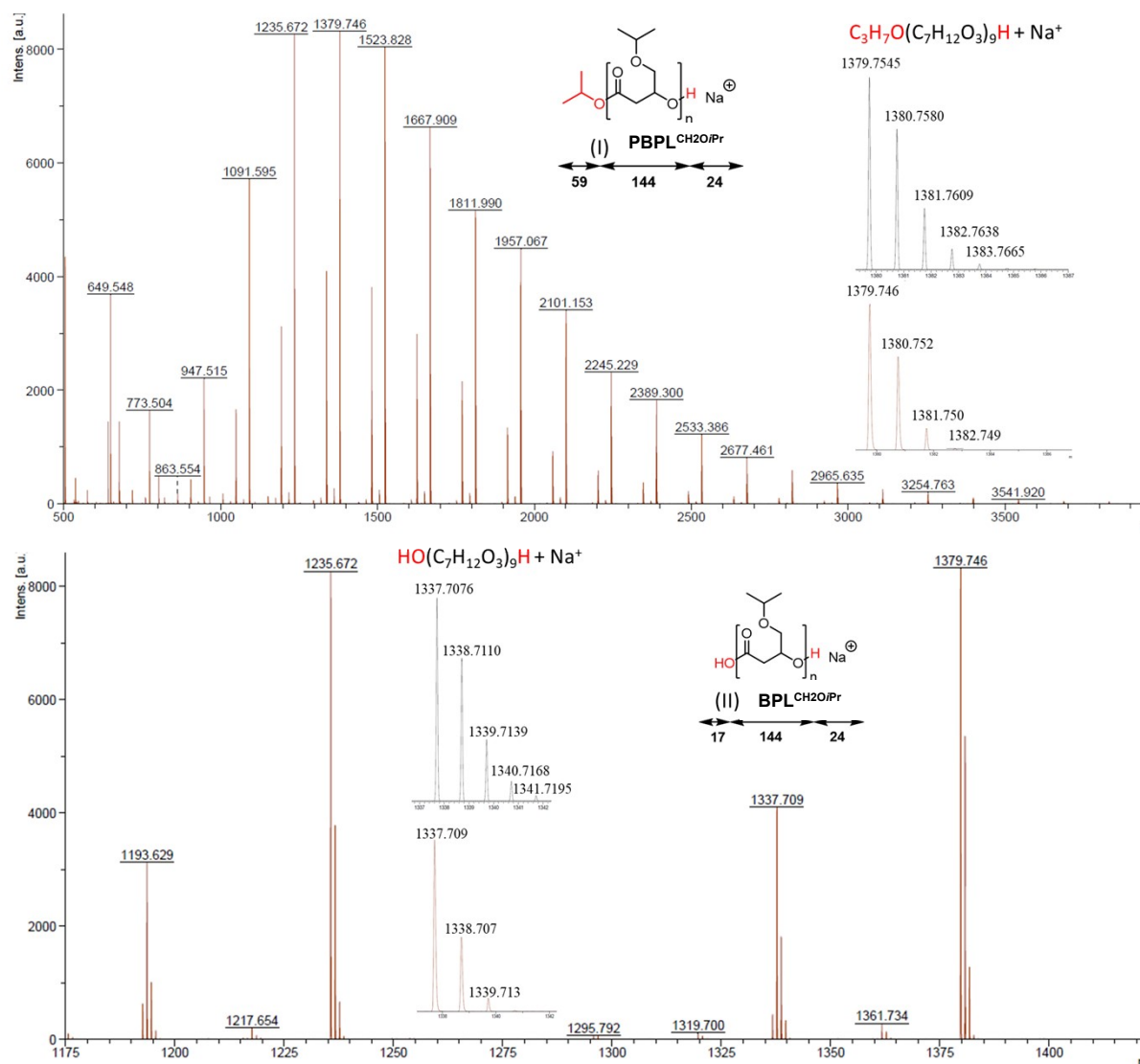


Figure S6. MALDI-ToF mass spectrum (DCTB matrix, ionized by Na^+) of a $PBPL^{CH_2O*i*Pr}$ (Table 1, entry 1), showing populations **I** (major, top) and **II** (minor, bottom) showing a repeating unit of m/z 144 corresponding to the $BPL^{CH_2O*i*Pr}$ monomer unit. Right and middle zoomed regions correspond to the simulated (top) and experimental (bottom) spectra for populations **I** and **II**, respectively. The major population (**I**) corresponds to α -isopropoxy, ω -hydroxyl telechelic $PBPL^{CH_2O*i*Pr}$ chains ionized by Na^+ , as confirmed by the close match with the corresponding isotopic simulation of $[(CH_3)_2CHO(COCH_2CH(CH_2OC_3H_7)O)_nH] \cdot Na^+$ with, for example, $m/z_{\text{calculated}} = 1379.7545$ vs. $m/z_{\text{found}} = 1379.746$ for $n = 9$. The minor population (**II**) corresponds to α -carboxylic, ω -hydroxy telechelic $PBPL^{CH_2O*i*Pr}$ chains ionized by Na^+ , as confirmed by the close match with the corresponding isotopic simulation illustrated for $[HO(C_7H_{12}O_3)_nH] \cdot Na^+$ with, for example, $m/z_{\text{calculated}} = 1337.7076$ vs. $m/z_{\text{found}} = 1337.709$ for $n = 9$. This latter population likely results from hydrolysis during the MS sample preparation/ionization.

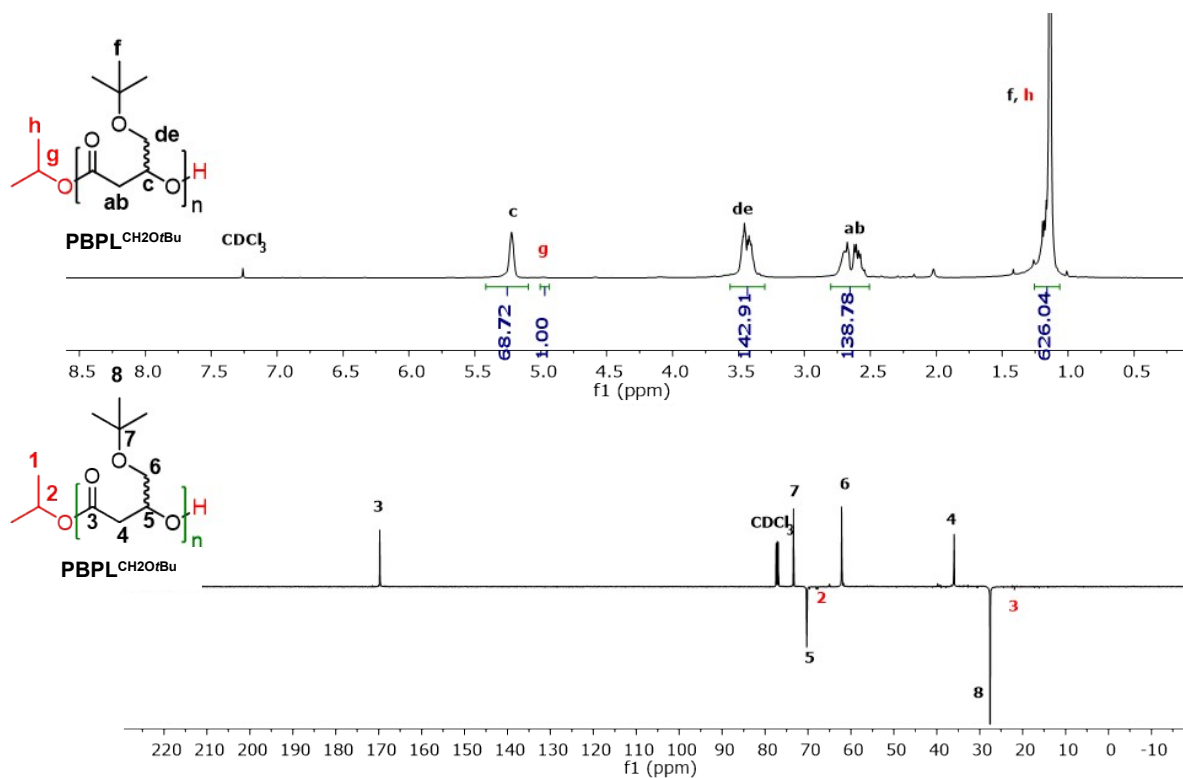


Figure S7. ¹H (500 MHz, CDCl₃, 25 °C) (top) and J-MOD (125 MHz, CDCl₃, 25 °C) (bottom) NMR spectra of a syndio-enriched PBPL^{CH₂OrBu} prepared from the ROP of *rac*-BPL^{CH₂OrBu} mediated by the **2a**/*i*PrOH system (Table 2, entry 11).

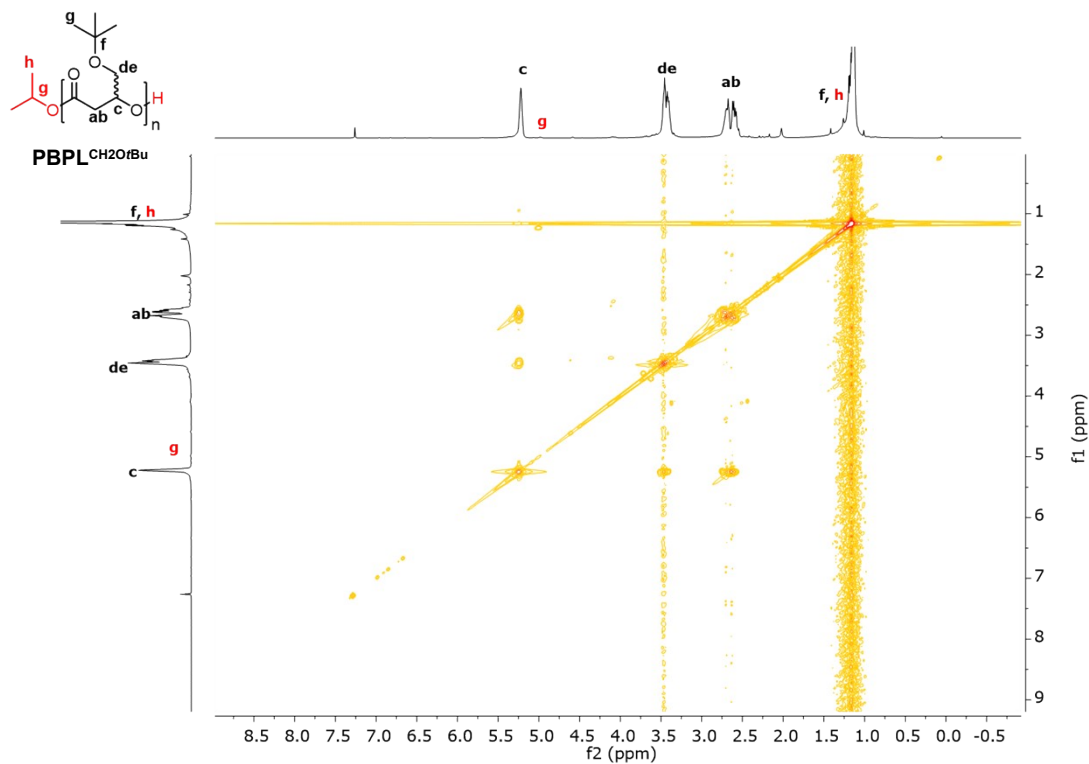


Figure S8. ¹H-¹H COSY NMR spectrum (500 MHz, CDCl₃, 25 °C) of a syndio-enriched PBPL^{CH₂OrBu} (Table 2, entry 11).

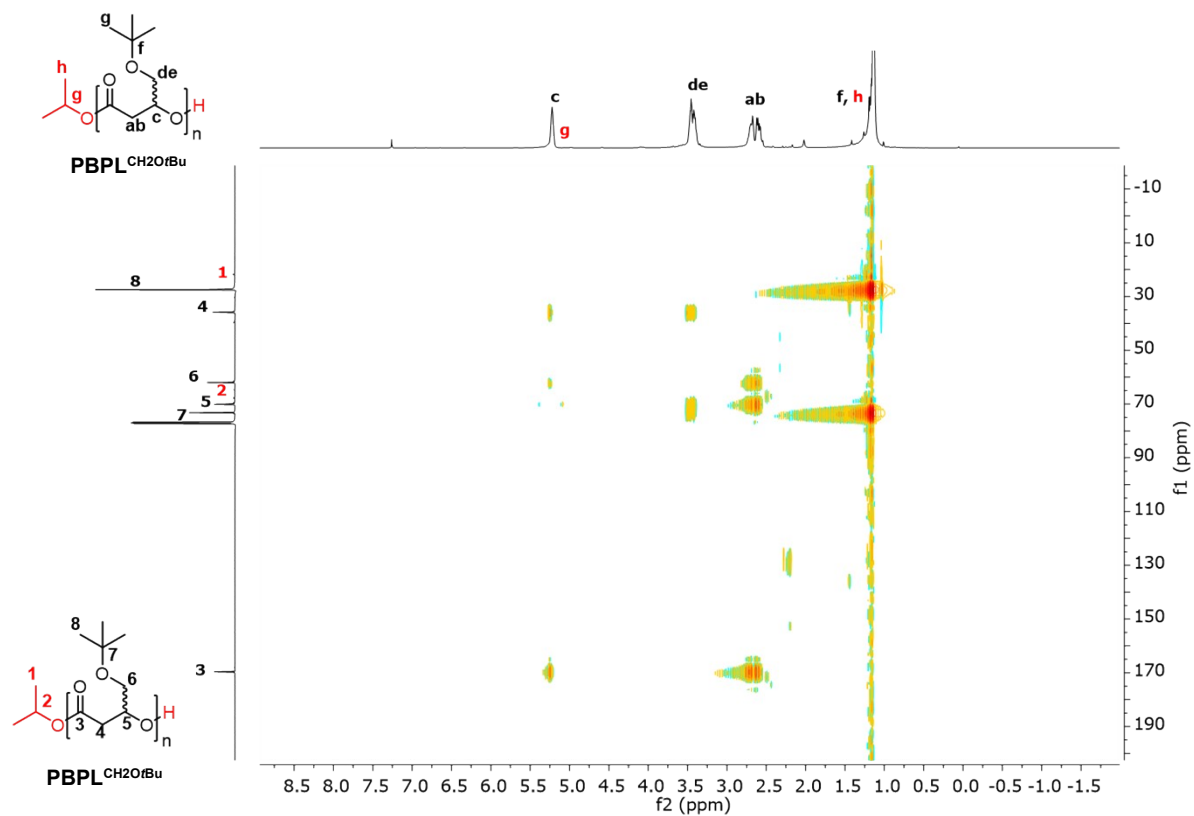


Figure S9. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of a syndio-enriched PBPL-CH₂OtBu (Table 2, entry 11).

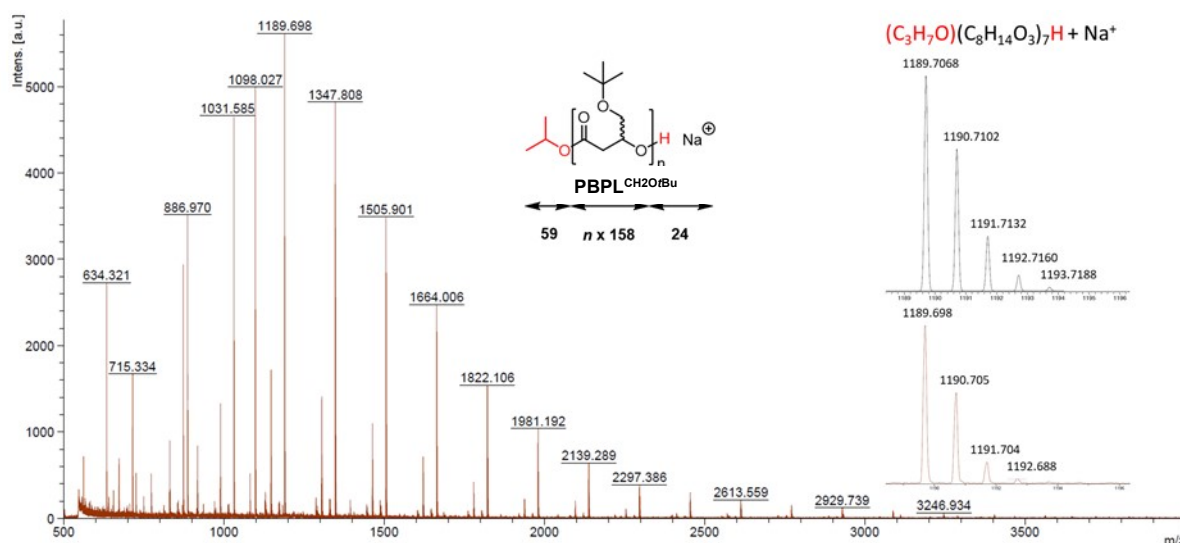


Figure S10. MALDI-ToF mass spectrum (DCTB matrix, ionized by Na^+) of a $\text{PBPL}^{\text{CH}_2\text{O}t\text{Bu}}$ (Table 2, entry 5). Right zoomed regions correspond to the simulated (top) and experimental (bottom) spectra of the main population (Table 2, entry 5). The expected population of macromolecules having a repeating unit of m/z 158, corresponding to α -isopropoxy, ω -hydroxyl telechelic $\text{PBPL}^{\text{CH}_2\text{O}t\text{Bu}}$ chains ionized by Na^+ is clearly observed. This is confirmed by the close match with the corresponding isotopic simulations, as illustrated for $[(\text{CH}_3)_2\text{CHO}(\text{COCH}_2\text{CH}(\text{CH}_2\text{OC}_4\text{H}_9)\text{O})_n\text{H}]\cdot\text{Na}^+$ with, for example, $m/z_{\text{calculated}}$ 1189.7068 vs. m/z_{found} 1189.698 for $n = 7$.

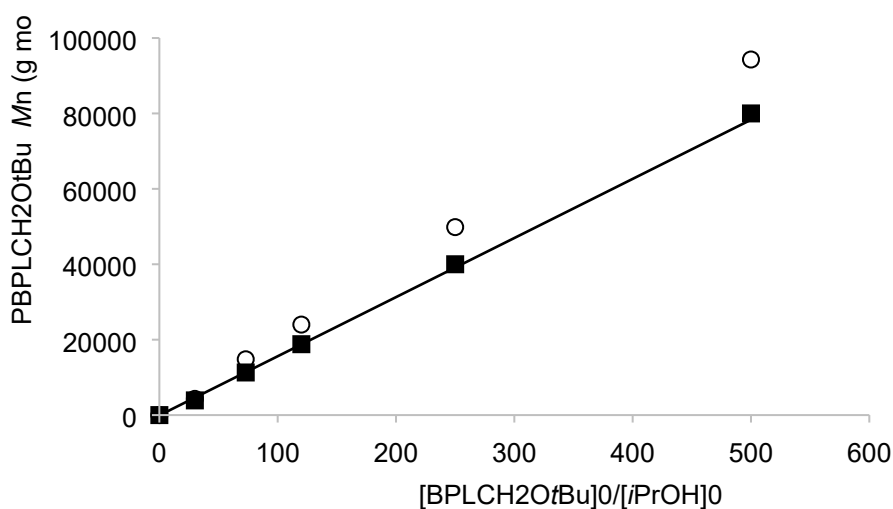


Figure S11. Variation of $M_{n,\text{NMR}}$ (■), $M_{n,\text{SEC}}$ (○), and $M_{n,\text{theo}}$ (solid line) values of $\text{PBPL}^{\text{CH}_2\text{O}t\text{Bu}}$ synthesized from the ROP of $\text{rac-BPL}^{\text{CH}_2\text{O}t\text{Bu}}$ mediated by the **2b**/*i*PrOH (1:1) system as a function of the monomer loading/conversion (Table 2, entries 5–9).

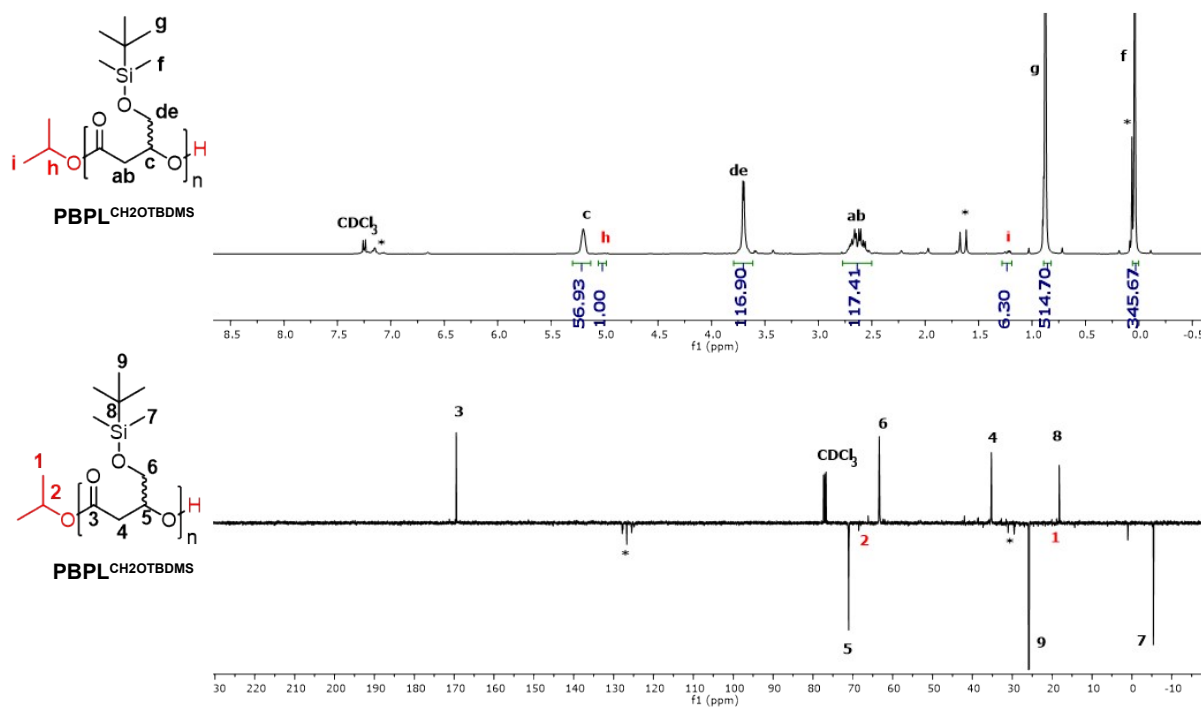


Figure S12. ¹H (500 MHz, CDCl₃, 25 °C) (top) and J-MOD (125 MHz, CDCl₃, 25 °C) (bottom) NMR spectra of a syndio-enriched PBPL^{CH2OTBDMS} prepared from the ROP of *rac*-BPL^{CH2OTBDMS} mediated by the **2a**/*i*PrOH (1:1) system (Table 3, entry 7); * stands for residual monomer, toluene and water resonances.

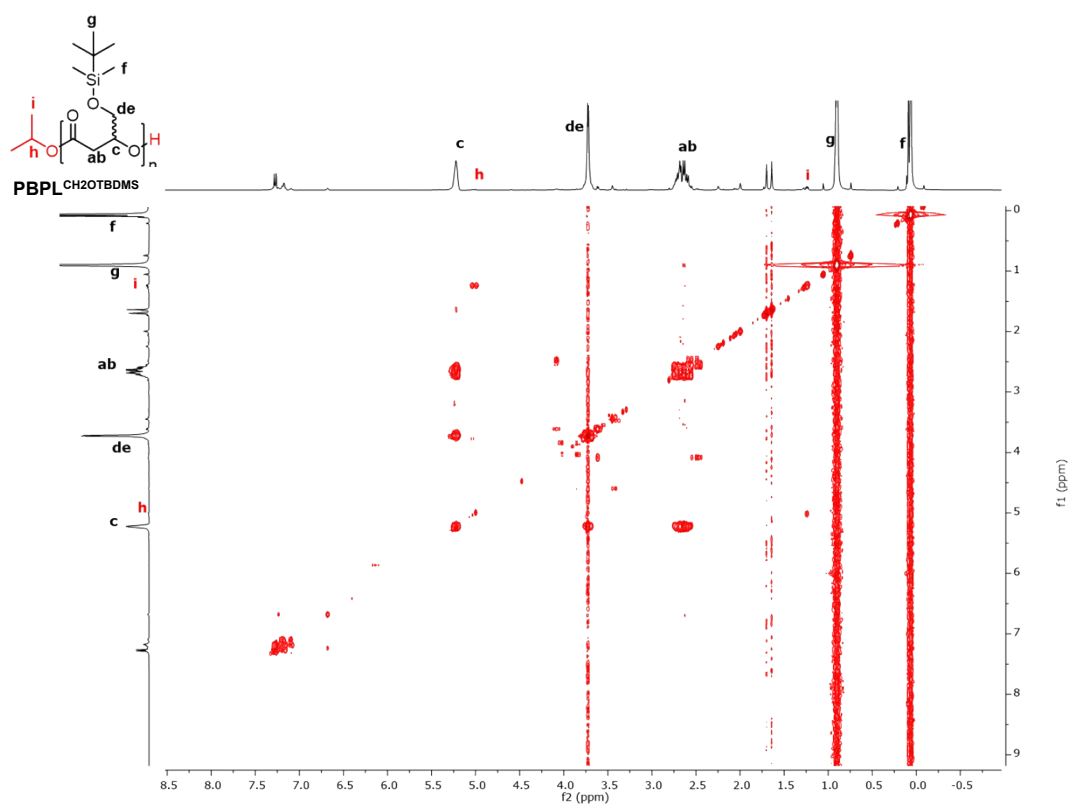


Figure S13. ¹H-¹H COSY NMR spectrum (500 MHz, CDCl₃, 25 °C) of a syndio-enriched PBPL_{CH2OTBDMS} (Table 3, entry 7).

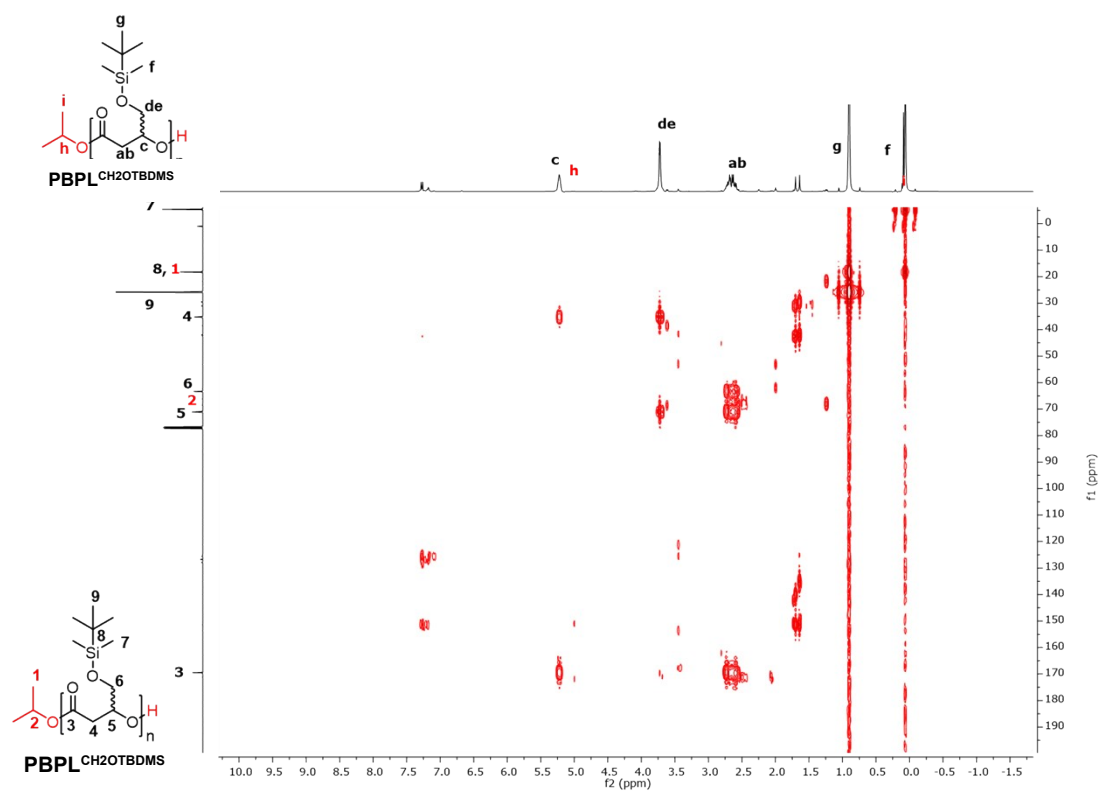


Figure S14. ^1H - ^{13}C HMBC NMR spectrum (500 MHz, CDCl_3 , 25 °C) of a syndio-enriched PBPL-CH₂OTBDMS (Table 3, entry 7).

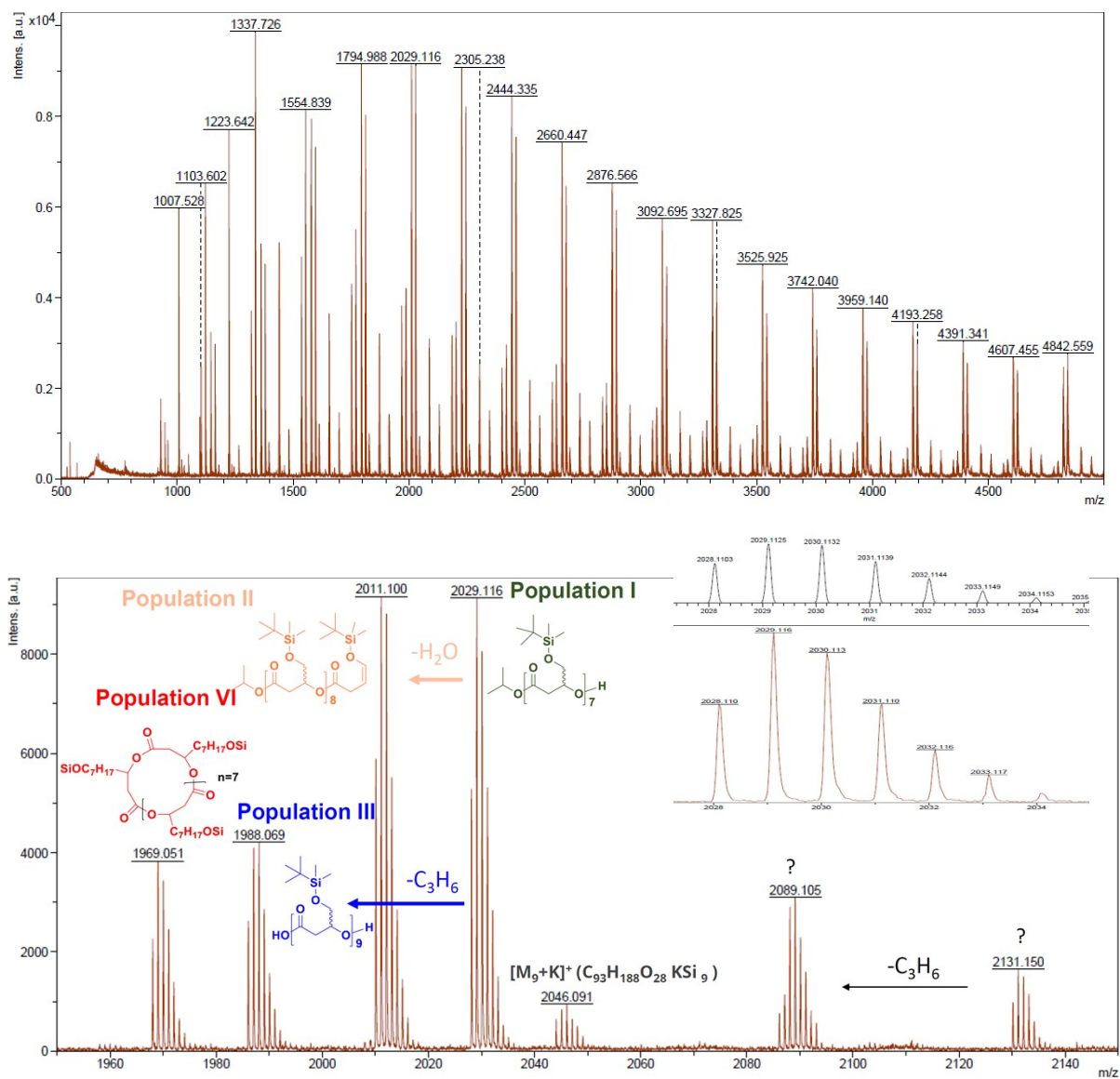


Figure S15. MALDI-ToF mass spectrum (DCTB matrix, ionized by Na⁺) (top, full spectrum; bottom, detail of the region for DP = 7-9) of a low molar mass PBPL^{CH₂OTBDMS} ($M_{n,NMR} = 4000$, $M_{n,SEC} = 6300$ g.mol⁻¹) prepared from the ROP of 25 equiv of *rac*-BPL^{CH₂OTBDMS} with the **2a**/*i*PrOH (1:1) system (entry not reported in Table 3). The major populations observed (**I**) corresponds to α-isopropoxy,ω-hydroxyl telechelic PBPL^{CH₂OTBDMS} chains ionized by Na⁺ (see the zoomed regions featuring the simulated (top) and experimental (bottom) spectra). The minor populations (**II-IV**) most likely arise from hydrolysis during the MS sample preparation/ionization.

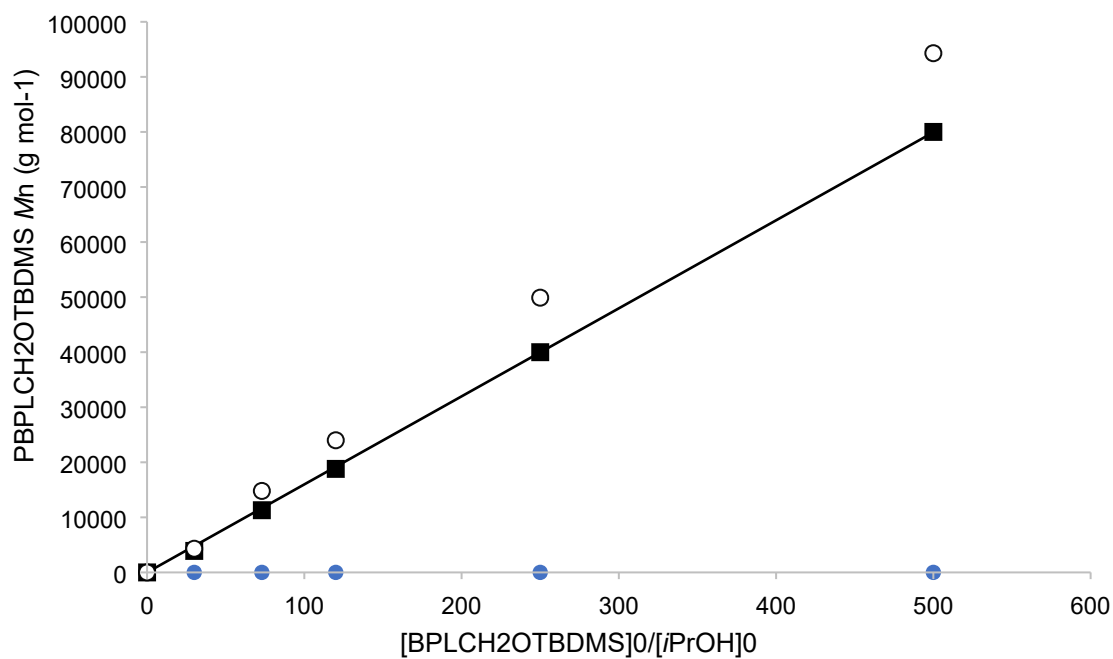


Figure S16. Variation of $M_{n,NMR}$ (●), $M_{n,SEC}$ (○), and $M_{n,theo}$ (solid line) molar mass values of PBPL^{CH2OTBDMS} synthesized from the ROP of *rac*-BPL^{CH2OTBDMS} mediated by the **2b**/*i*PrOH (1:1) catalyst system as a function of the BPL^{CH2OTBDMS} monomer loading/conversion (Table 3, entries 2–7).

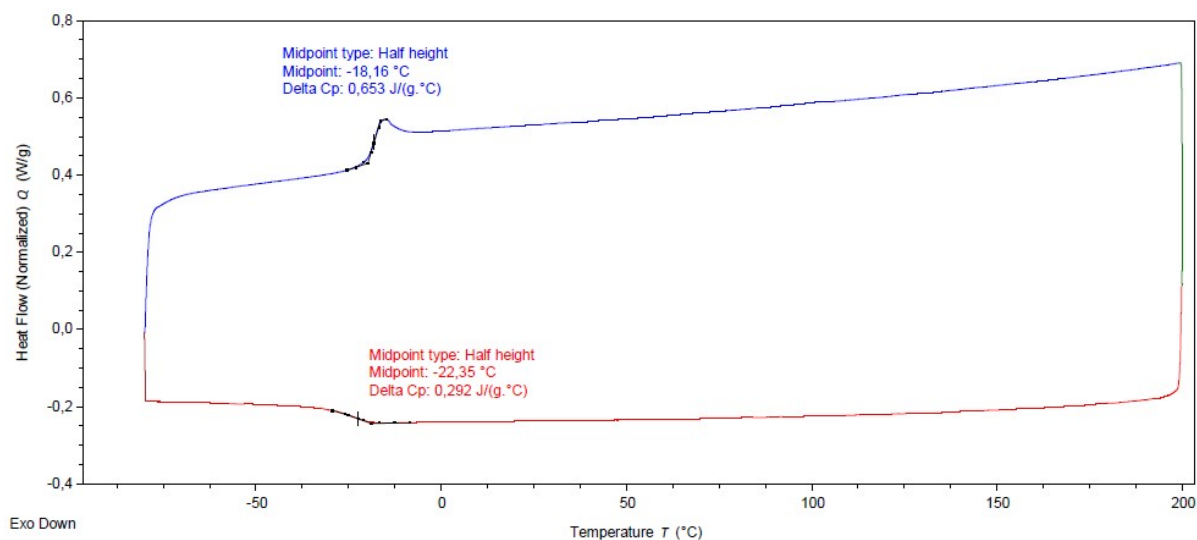


Figure S17. DSC thermogram (heating rate = 10 °C min⁻¹, second heating cycle –80 to 200 °C) of a syndio-enriched PBPL^{CH₂O/*i*Pr} ($P_r = 0.86$) prepared by ROP of *rac*-BPL^{CH₂O/*i*Pr} with the **2b**/*i*PrOH system (Table 1, entry 8).

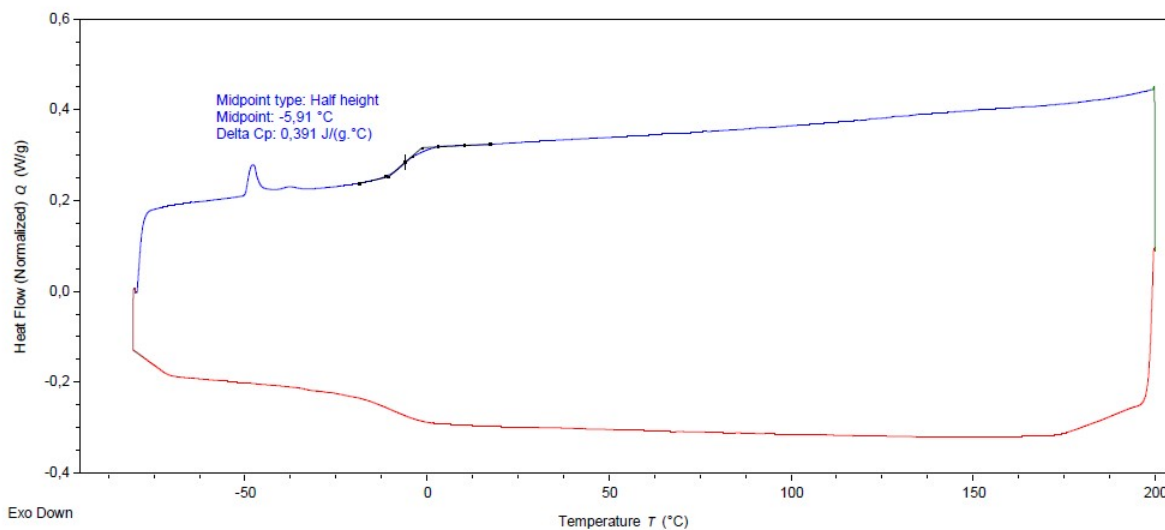


Figure S18. DSC thermogram (heating rate = 10 °C min⁻¹, second heating cycle –80 to 200 °C) of a syndio-enriched PBPL^{CH₂O/*Bu*} ($P_r = 0.84$) prepared by ROP of *rac*-BPL^{CH₂O/*Bu*} with the **2b**/*i*PrOH system (Table 2, entry 5).

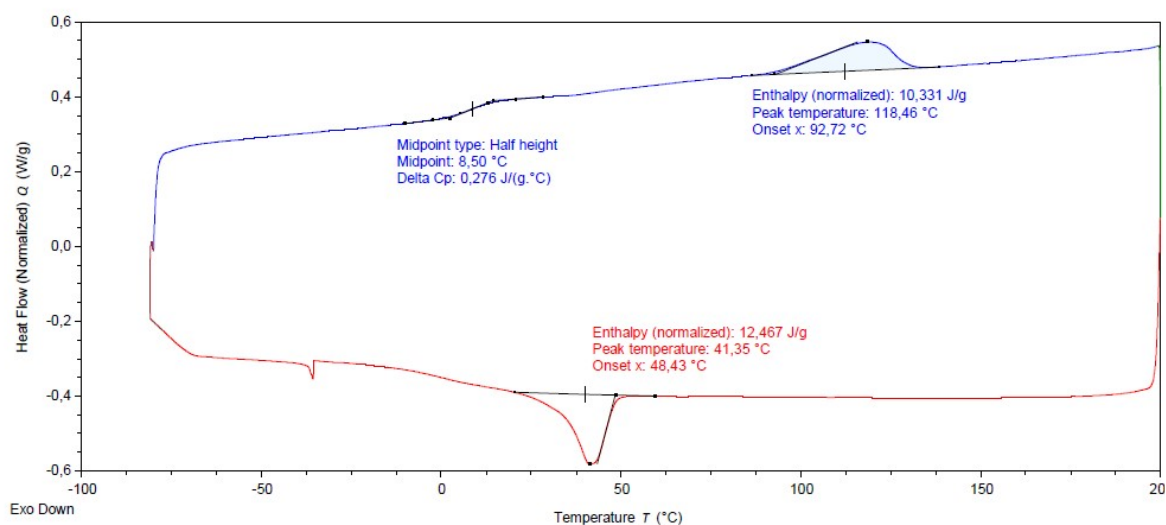


Figure S19. DSC thermogram (heating rate = 10 °C min⁻¹, second heating cycle –80 to 200 °C) of a syndio-enriched PBPL^{CH₂OTBDMS} ($P_r = 0.81$) prepared by ROP of *rac*-BPL^{CH₂OTBDMS} with the **2b**/*i*PrOH system (Table 3, entry 6).

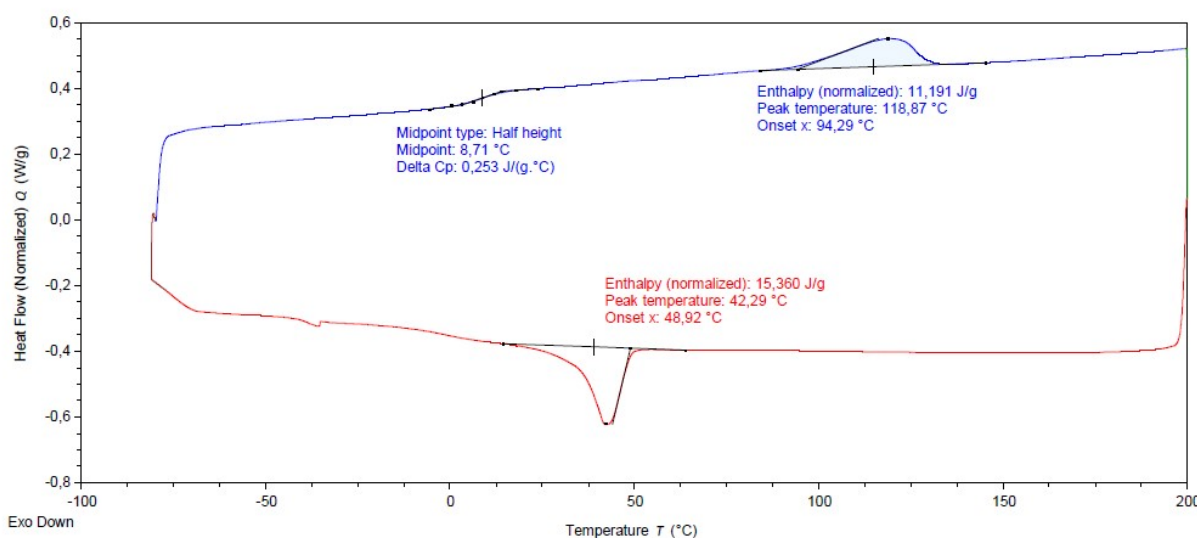


Figure S20. DSC thermogram (heating rate = 10 °C min⁻¹, second heating cycle –80 to 200 °C) of a syndio-enriched PBPL^{CH₂OTBDMS} ($P_r = 0.81$) prepared by ROP of *rac*-BPL^{CH₂OTBDMS} with the **2b**/*i*PrOH system (Table 3, entry 7).