

Supporting Information

Metal-Catalyzed Stereoselective Ring-Opening Polymerization of Functional β -Lactones: Methylene-Alkoxy Fluorinated Polyhydroxyalkanoates Unveil the Role of Non-Covalent Interactions

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Figure S17. DSC thermogram (heating rate = 10 °C min⁻¹, second heating cycle –80 to +200 °C) of a syndio-enriched PBPL^{CH₂OCF₂CHF₂} (*P_r* = 0.79) prepared by ROP of *rac*-BPL^{CH₂OCF₂CHF₂} with the **1c**/*i*PrOH system (Table 1, entry 15).

Figure S18. DSC thermogram (heating rate = 10 °C min⁻¹, second heating cycle –80 to +200 °C) of a syndio-enriched PBPL^{CH₂OCF₂CHF₂} (*P_r* = 0.86) prepared by ROP of *rac*-BPL^{CH₂OCF₂CHF₂} with the **1d**/*i*PrOH system (Table 1, entry 18).

Figure S19. DSC thermogram (heating rate = 10 °C min⁻¹, second heating cycle –80 to +200 °C) of an iso-enriched PBPL^{CH₂OCF₂CHF₂} polymer (*P_r* = 0.09) prepared by ROP of (*S*)-BPL^{CH₂OCF₂CHF₂} mediated by the **1d**/*i*PrOH system (Table 1, entry 2).

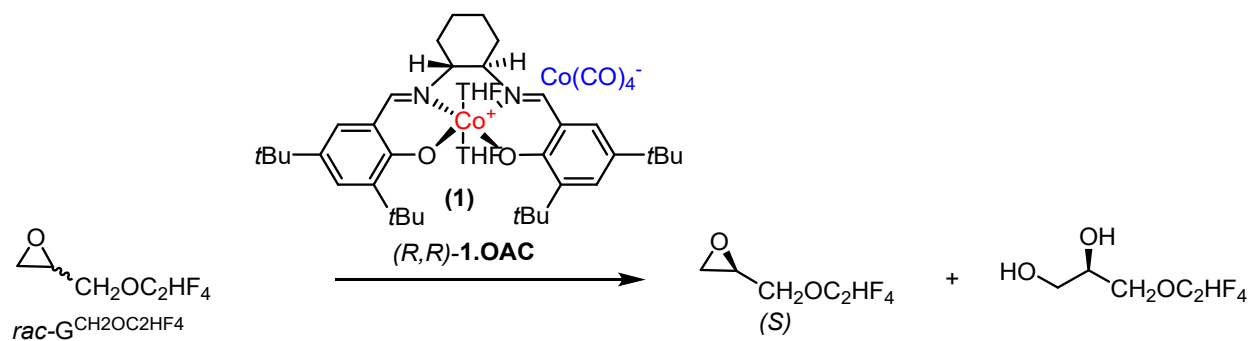
Figure S20. TGA thermogram of a PBPL^{CH₂OCF₂CHF₂} prepared from the ROP of (*rac*)-BPL^{CH₂OCF₂CHF₂} mediated by complex **1d** in the presence of *i*PrOH (Table 1, entry 5). T_d is the degradation temperature at 5wt% loss of the polymer.

Figure S21. TGA thermogram of a PBPL^{CH₂OCF₂CHF₂} prepared from the ROP of (*S*)-BPL^{CH₂OCF₂CHF₂} mediated by complex **1d** in the presence of *i*PrOH (Table 1, entry 2). T_d is the degradation temperature at 5wt% loss of the polymer.

Figure S22. TGA thermogram of a PBPL^{CH₂OCF₂CHF₂} prepared from the ROP of (*rac*)-BPL^{CH₂OCF₂CHF₂} mediated by complex **1d** in the presence of *i*PrOH (Table 1, entry 3). T_d is the degradation temperature at 5wt% loss of the polymer.

Synthesis of enantio-enriched (*S*)-G^{CH₂OCF₂CHF₂}

The synthesis of enantio-enriched (*S*)-G^{CH₂OCF₂CHF₂} was performed through hydrolytic kinetic resolution (HKR) of the *racemic* epoxide.ⁱ performed using 5mol% of chiral (salen)Co^{III} complex **1.OAc** (Jacobsen's catalyst ((*R,R*)-**1**)), in the presence of 2mol% acetic acid and 50wt% water (Scheme S1). The thus recovered (*S*)-G^{CH₂OCF₂CHF₂} was separated from the diol co-product by distillation (1.6 g, 40%). It was then characterized by NMR and chiral chromatography; incomplete separation of the two enantiomers' peaks allowed us to assess only > 90% ee purity (Figure S1).



Scheme S1. Isolation of enantio-enriched (*S*)-G^{CH₂OCF₂CHF₂} (> 90% ee) by hydrolytic kinetic resolution (HKR) of *rac*-G^{CH₂OCF₂CHF₂}.

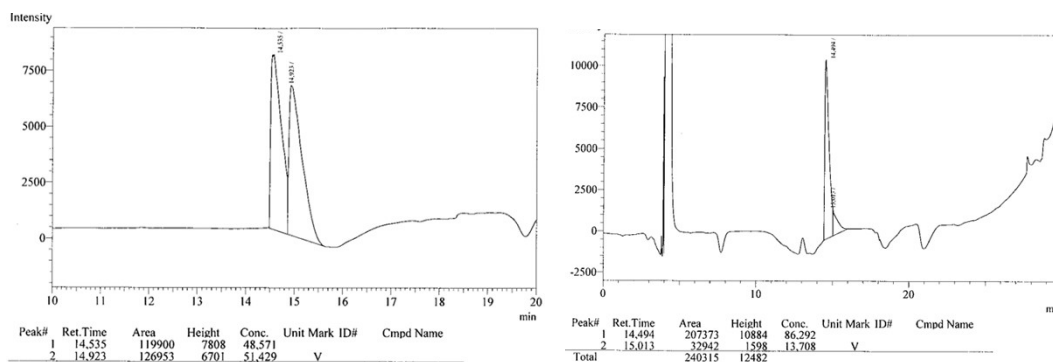


Figure S1. Separation of enantiomers of G^{CH₂OCF₂CHF₂} (left: a racemic mixture; right: the product isolated from hydrolytic kinetic resolution) using chiral gas chromatography (performed on a CPG/FID VARIAN CP-3380 chromatograph equipped with a Chiralsil-Dex CB Varian CP7502 Chrompack).

ⁱⁱ Scott E. Schaus, Bridget D. Brandes, Jay F. Larrow, Makoto Tokunaga, Karl B. Hansen, Alexandra E. Gould, Michael E. Furrow, and Eric N. Jacobsen, *J. Am. Chem. Soc.* 2002, 124, 7, 1307–1315. Highly Selective Hydrolytic Kinetic Resolution of Terminal Epoxides Catalyzed by Chiral (salen)Co^{III} Complexes. Practical Synthesis of Enantioenriched Terminal Epoxides and 1,2-Diols. <https://doi-org.passerelle.univ-rennes1.fr/10.1021/ja016737l>

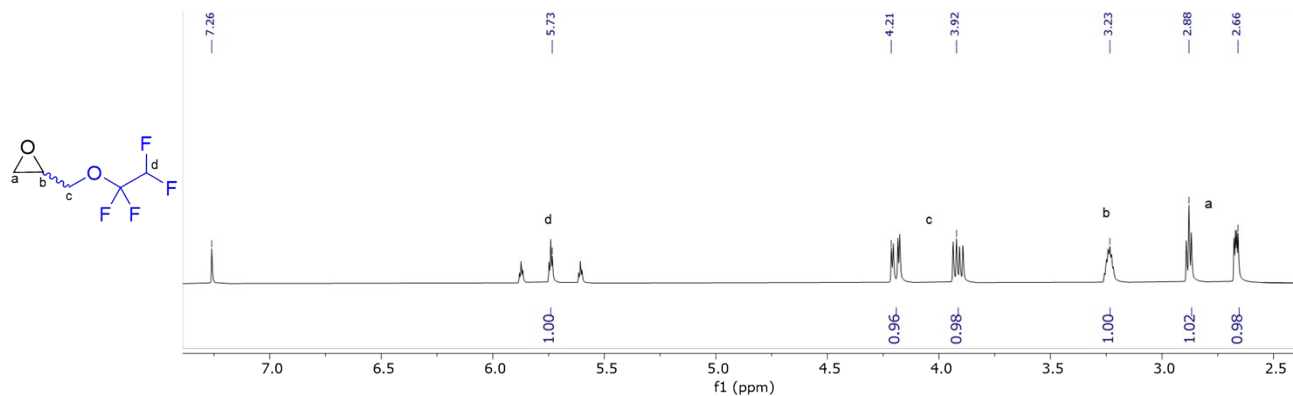


Figure S2. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of *racemic* 2-((1,1,2,2-tetrafluoroethoxy)methyl)oxirane (*rac*- $\text{G}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$).

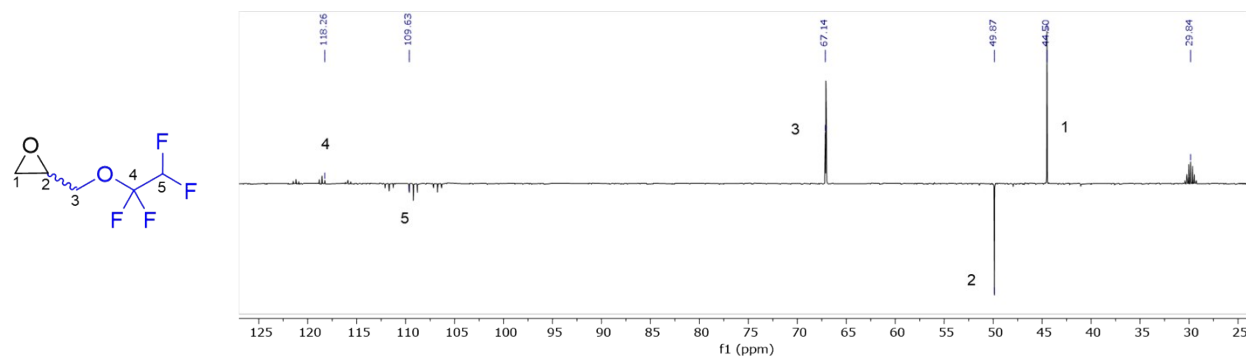


Figure S3. ^{13}C J-MOD NMR spectrum (100 MHz, $(\text{CD}_3)_2\text{CO}$, 25 °C) of *racemic* 2-((1,1,2,2-tetrafluoroethoxy)methyl)oxirane (*rac*- $\text{G}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$).

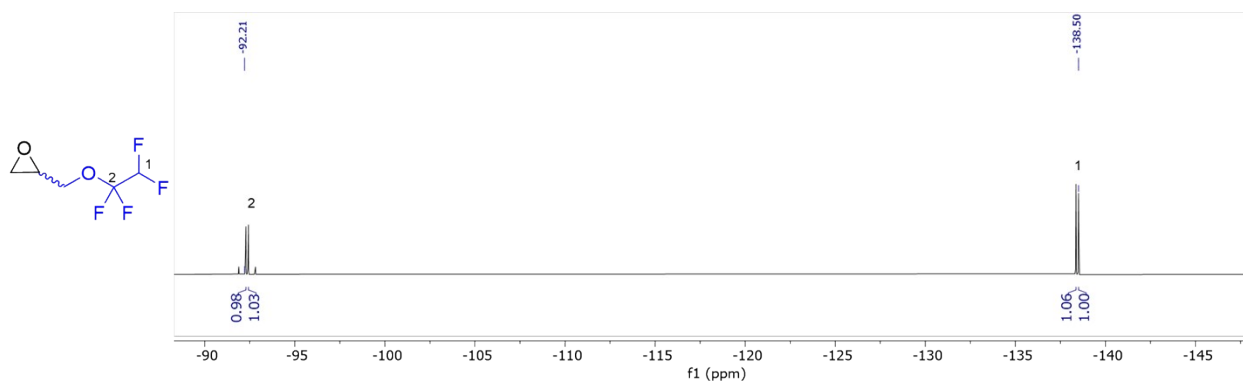


Figure S4. ^{19}F NMR spectrum (376 MHz, $(\text{CD}_3)_2\text{CO}$, 25 °C) of *racemic* 2-((1,1,2,2-tetrafluoroethoxy)methyl)oxirane (*rac*- $\text{G}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$).

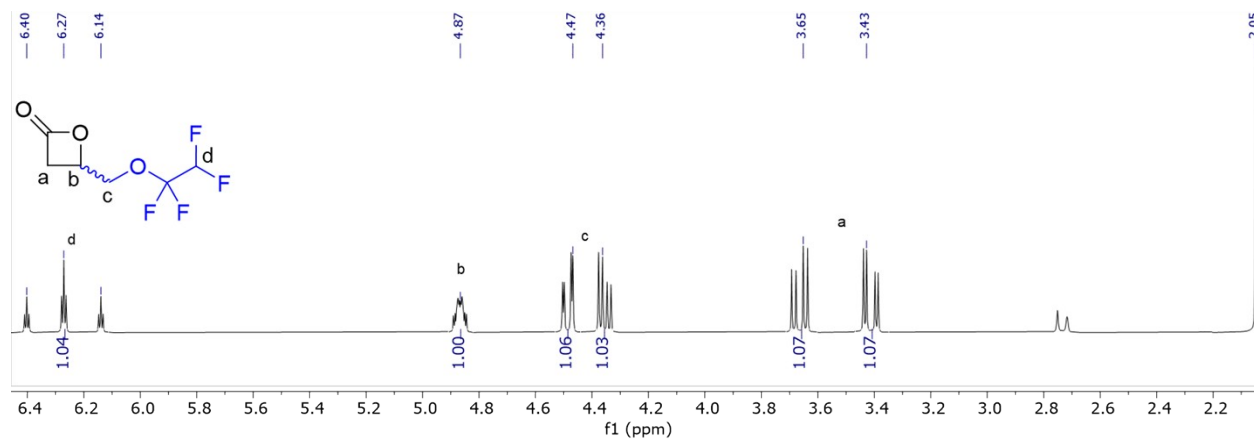


Figure S5. ¹H NMR spectrum (500 MHz, (CD₃)₂CO, 25 °C) of *racemic* 4-((1,1,2,2-tetrafluoroethoxy)methyl)oxetan-2-one (*rac*-BPL^{CH₂O}CF₂CHF₂).

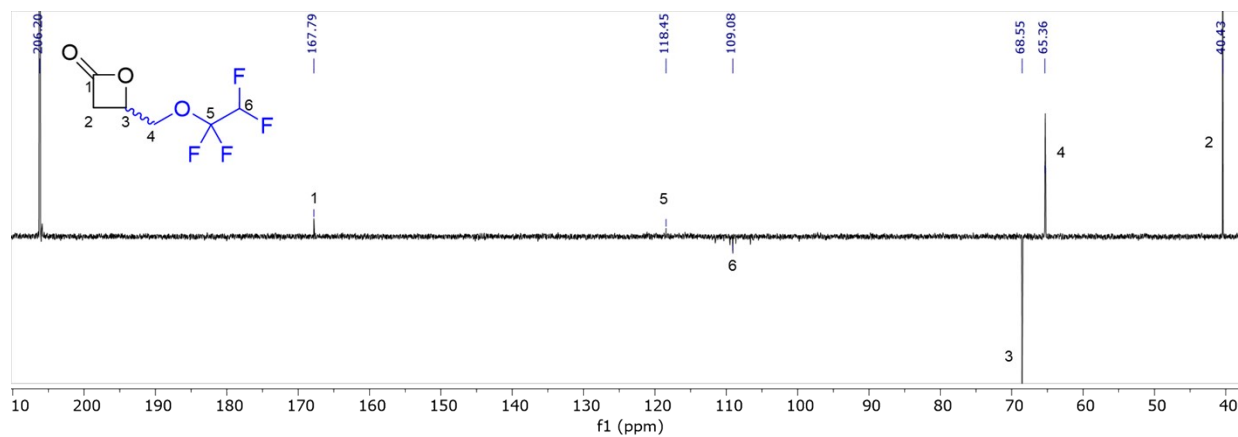


Figure S6. ¹³C J-MOD NMR spectrum (125 MHz, (CD₃)₂CO, 25 °C) of *racemic* 4-((1,1,2,2-tetrafluoroethoxy)methyl)oxetan-2-one (*rac*-BPL^{CH₂O}CF₂CHF₂).

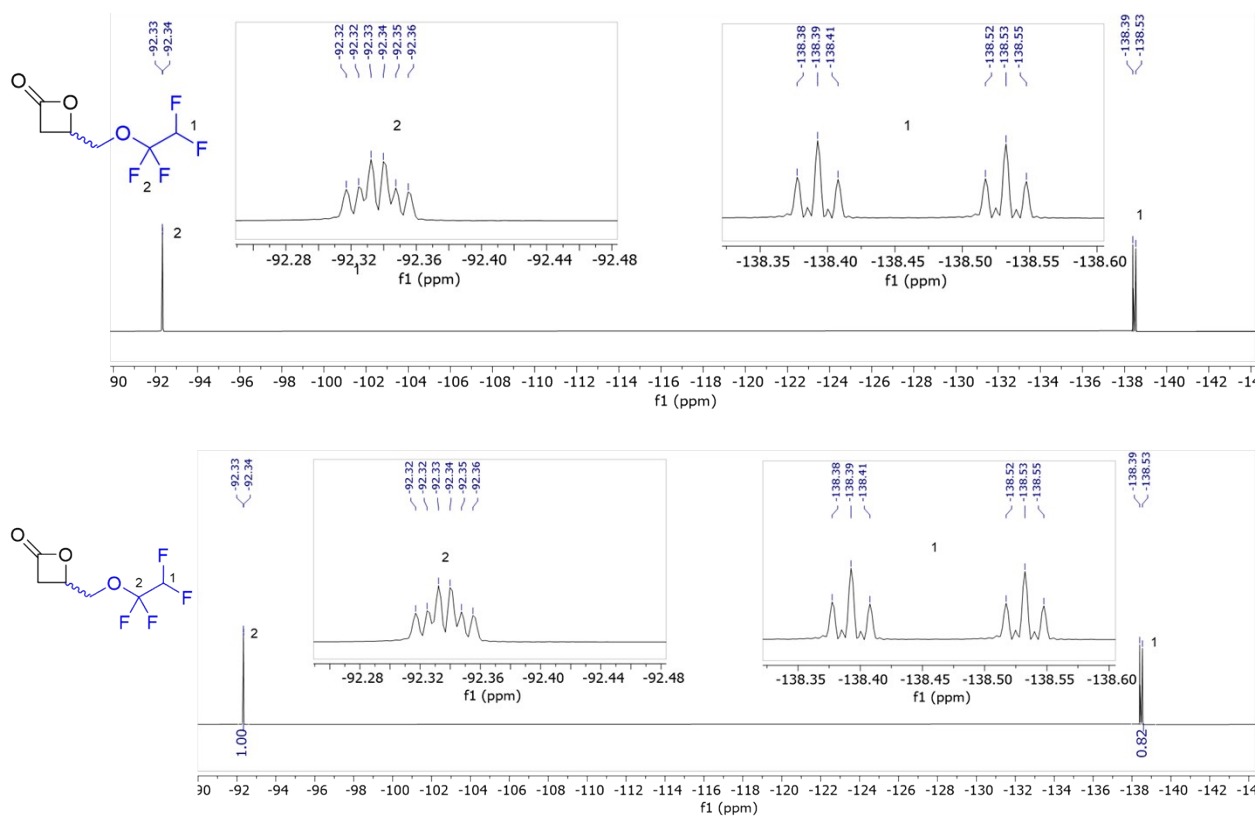


Figure S7. ^{19}F NMR spectrum (470 MHz, $(\text{CD}_3)_2\text{CO}$, 25 $^\circ\text{C}$) of *racemic* 4-((1,1,2,2-tetrafluoroethoxy)methyl)oxetan-2-one (*rac*-BPL $^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$).

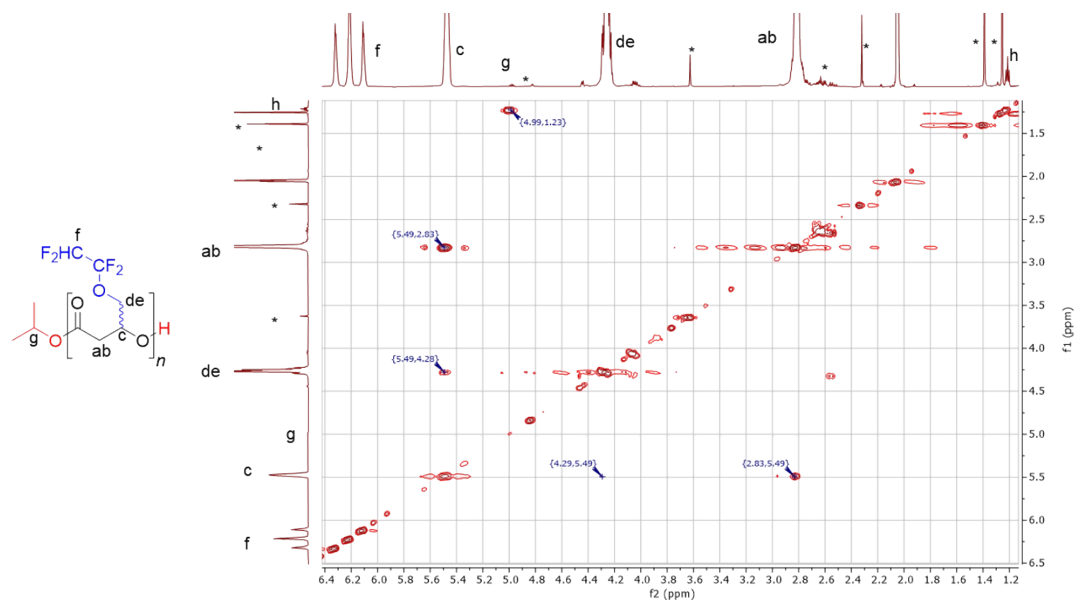


Figure S8. ^1H - ^1H COSY NMR spectrum (500 MHz, $(\text{CD}_3)_2\text{CO}$, 25 °C) of a PBPL $^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ polymer prepared from the ROP of $\text{rac-BPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ mediated by the **1c**/*i*PrOH (1:1) catalyst system (Table 1, entry 10). * stands for resonances of residual solvent and/or catalyst.

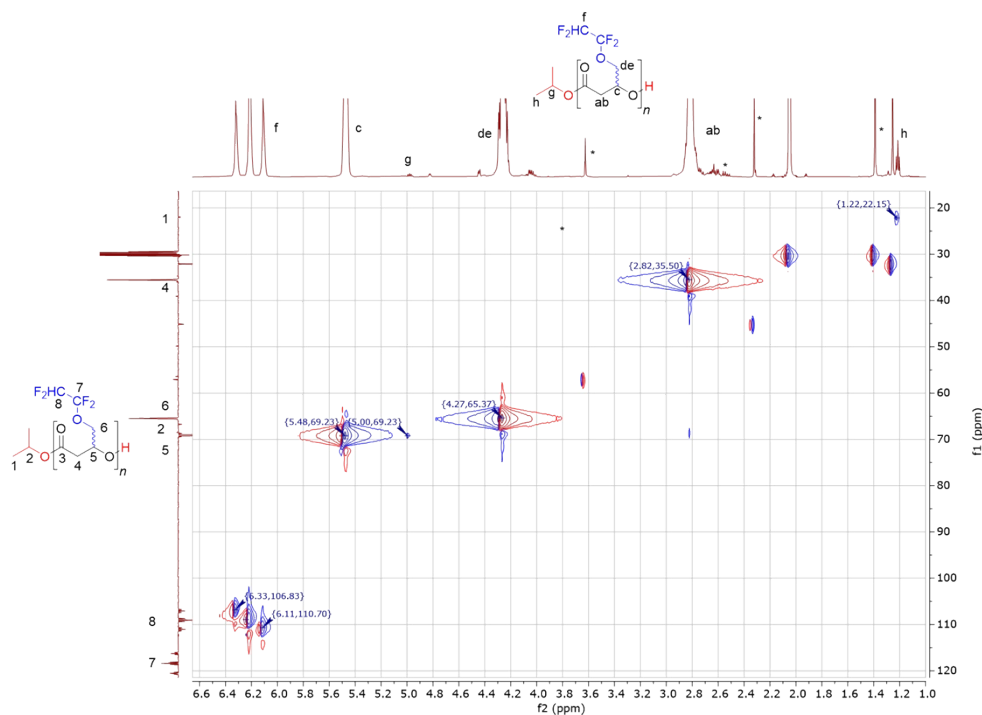


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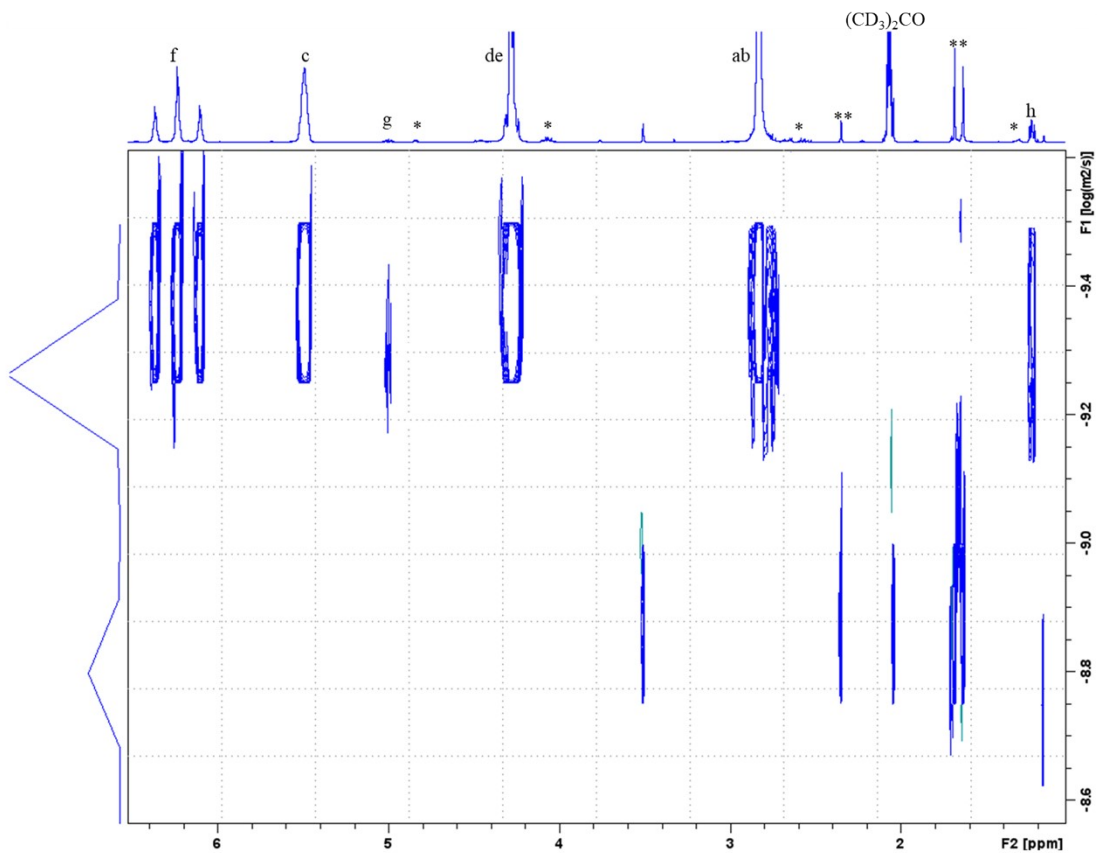


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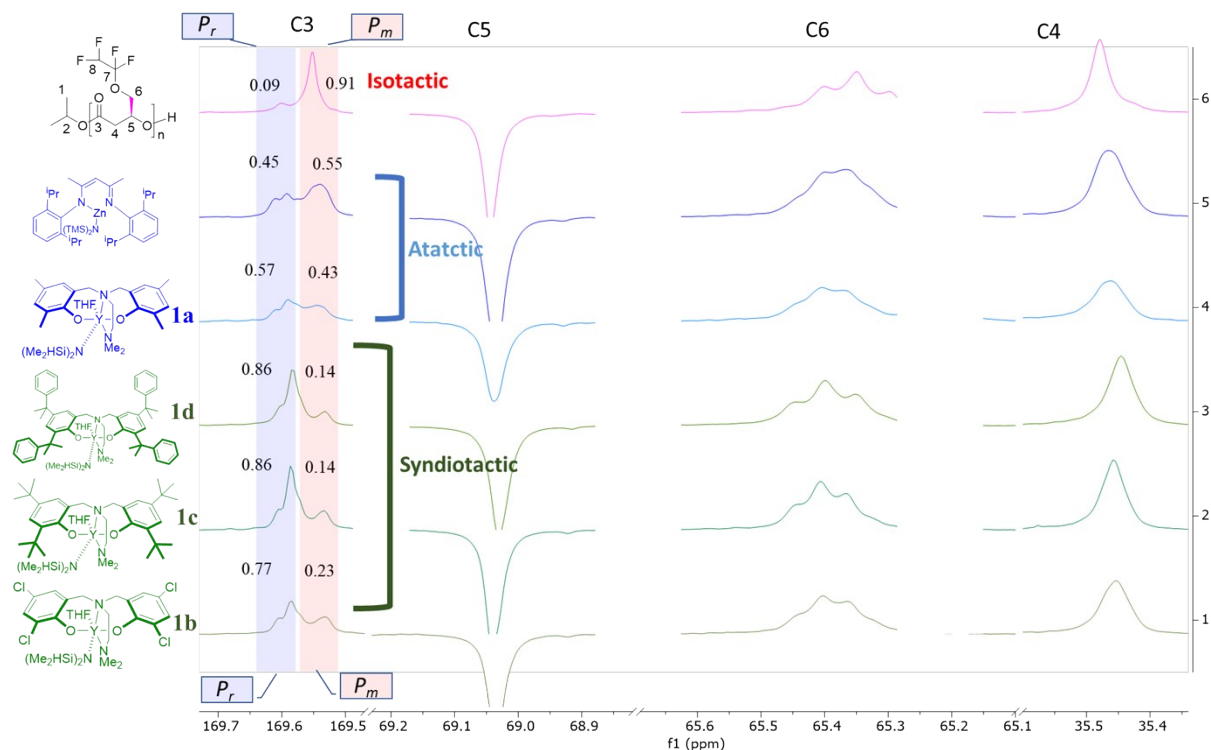


Figure S11. Zoomed regions of the ^{13}C J-MOD NMR spectra (100 MHz, $(\text{CD}_3)_2\text{CO}$, 23 °C) of $\text{PBPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}_s$ prepared by ROP of $\text{rac-BPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$, except for the top spectrum of enantiopure (*S*)- $\text{BPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ (Table 1, entry 2), mediated by the $(\text{BDI})\text{Zn}(\text{NTMS}_2)$, **1a**, **1d**, **1c**, or **1b**/*i*PrOH (1 : 1) catalyst systems, respectively (Table 1, entries 2, 3, 5, 8 and 18).

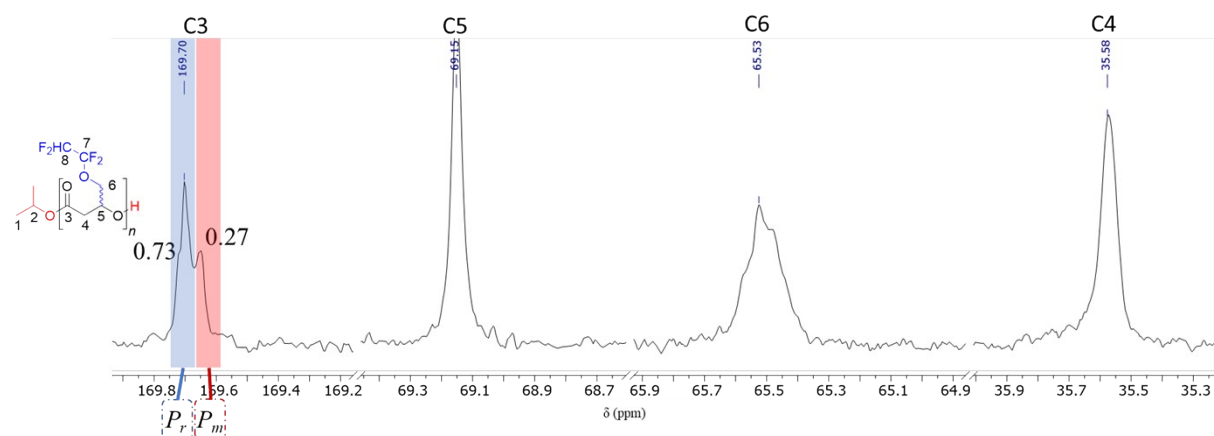


Figure S12. Zoomed regions of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, $(\text{CD}_3)_2\text{CO}$, 23 °C) of a $\text{PBPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ polymer prepared by ROP of $\text{rac-BPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ mediated by the **1b**/*i*PrOH (1 : 1) catalyst system (Table 1, entry 18).

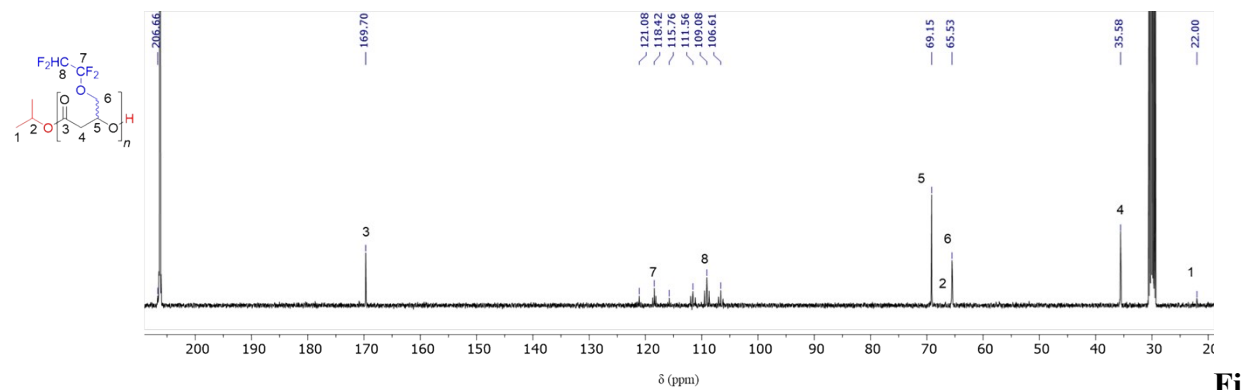


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$, 25 °C) spectrum of a $\text{PBPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ polymer prepared from the ROP of $\text{rac-BPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ mediated by the **1b**/*i*PrOH (1:1) catalyst system (Table 1, entry 18).

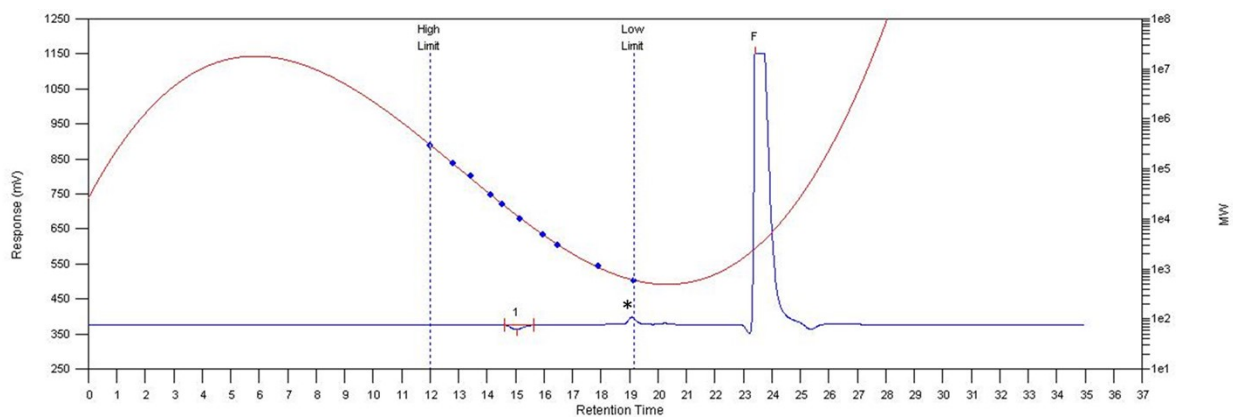


Figure S14. SEC trace of an isolated $\text{PBPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ prepared by ROP of $\text{rac-BPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ prepared from **1c**/*i*PrOH (Table 1, entry 10). * stands for residual ligand ($\approx 600 \text{ g}\cdot\text{mol}^{-1}$).

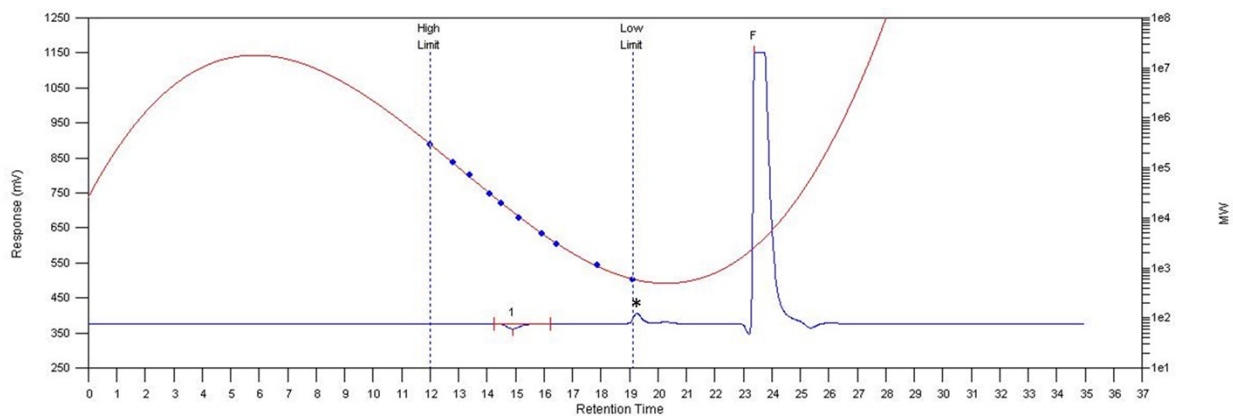


Figure S15. SEC trace of an isolated $\text{PBPL}^{\text{CH}_2\text{OCF}_2\text{CHF}_2}$ prepared from **1d**/*i*PrOH (Table 1, entry 18). * stands for residual ligand ($\approx 600 \text{ g}\cdot\text{mol}^{-1}$).

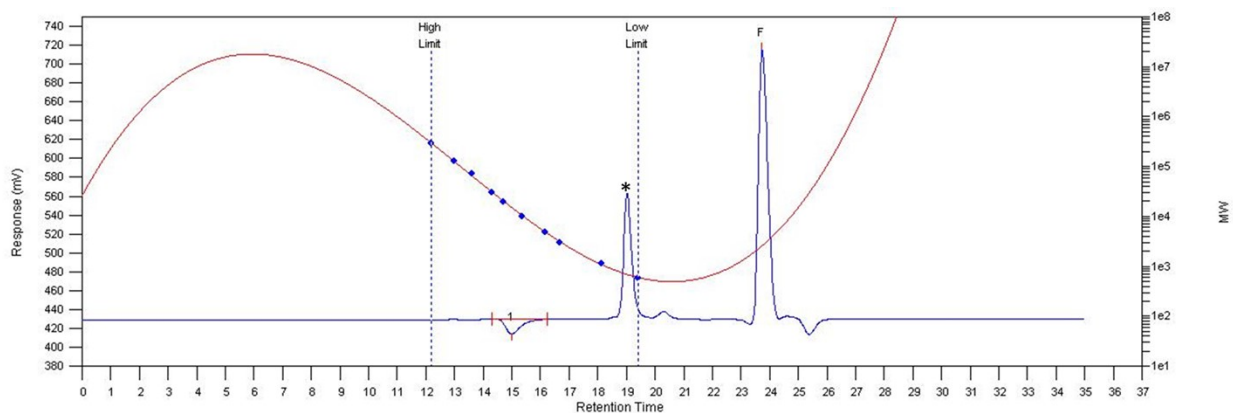


Figure S16. SEC trace of an isolated PBPL^{CH₂OCF₂CHF₂} prepared from **1d**/*i*PrOH (Table 1, entry 2). * stands for residual ligand ($\approx 600 \text{ g}\cdot\text{mol}^{-1}$).

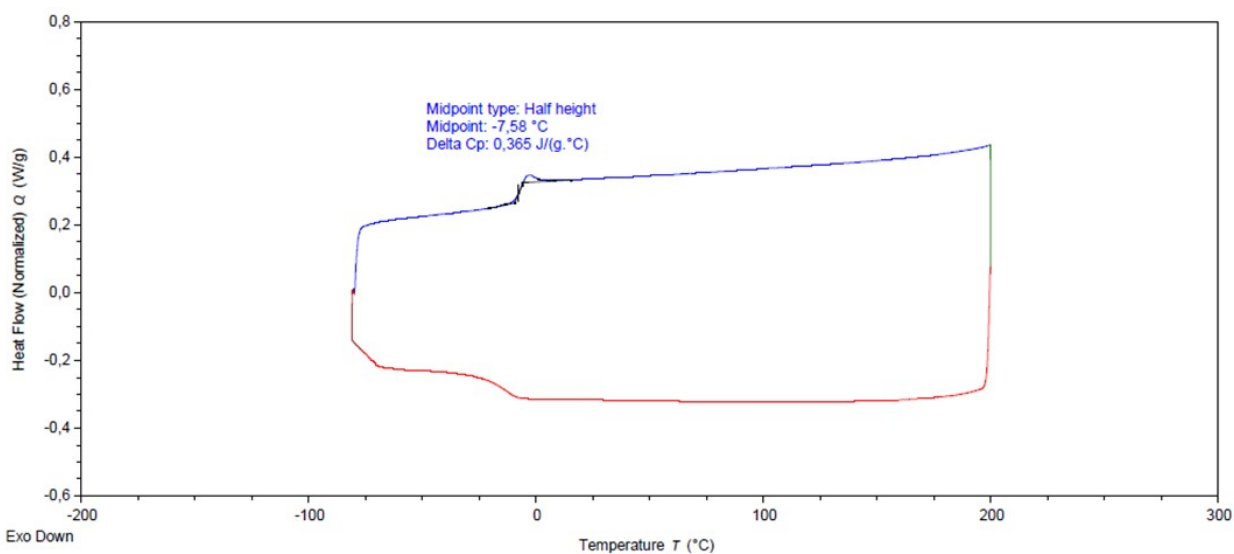


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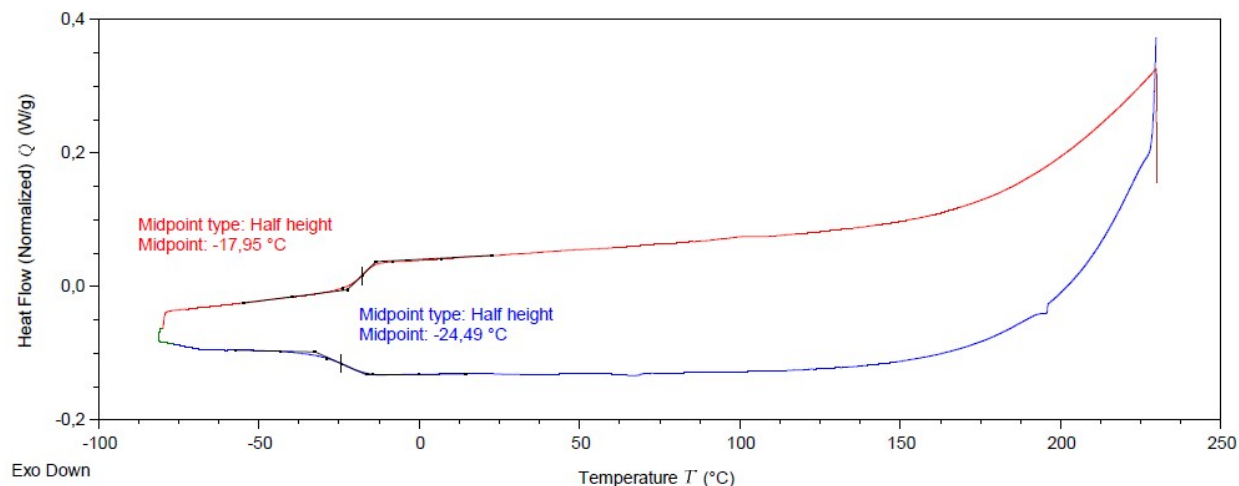


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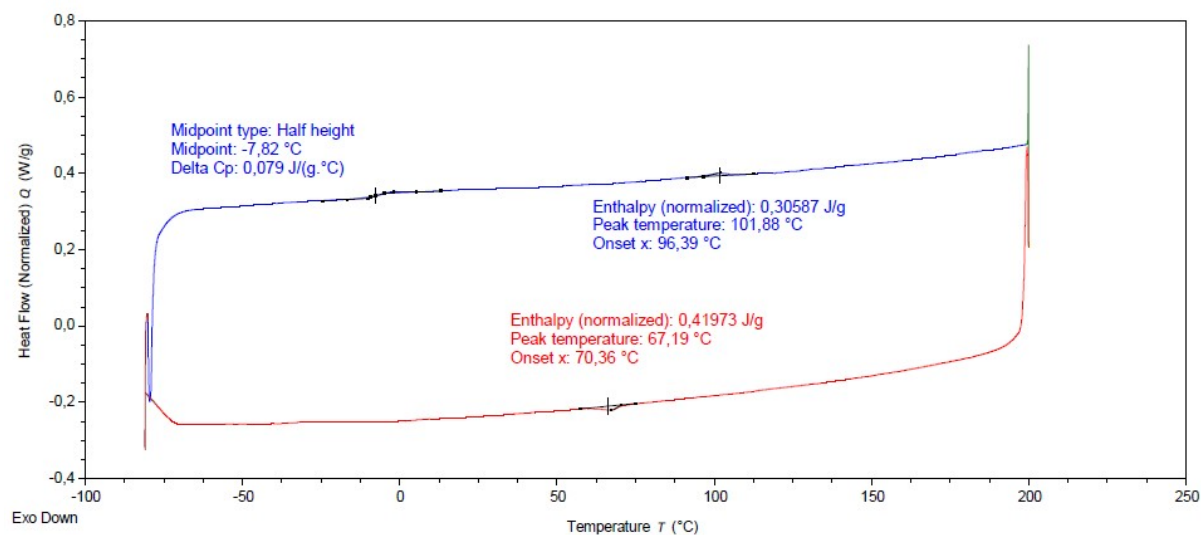


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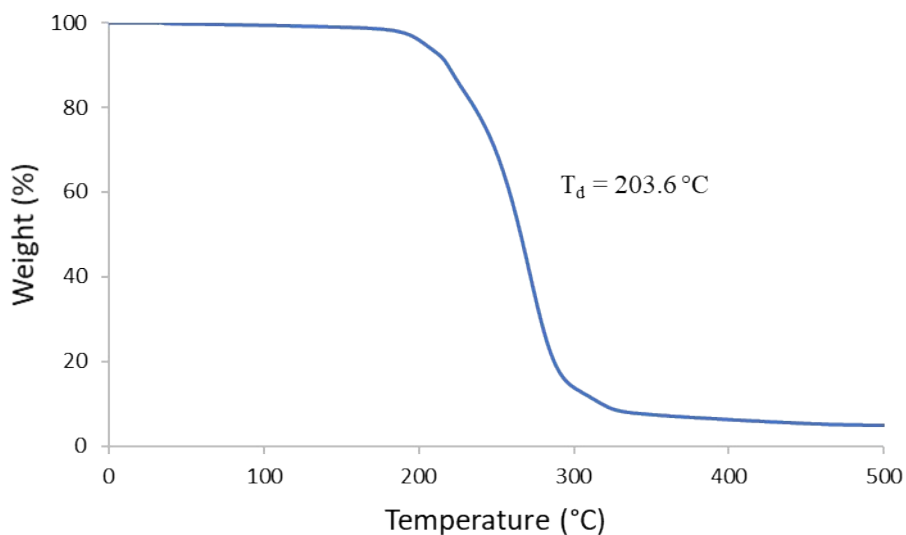


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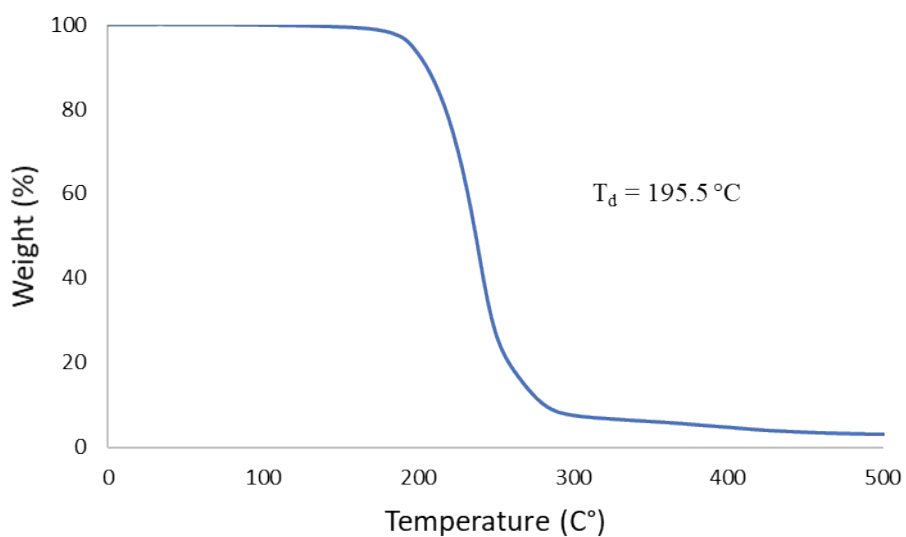


Figure S21. TGA thermogram of a PBPL^{CH₂OCF₂CHF₂} prepared from the ROP of (*S*)-BPL^{CH₂OCF₂CHF₂} mediated by complex **1d** in the presence of *i*PrOH (Table 1, entry 2). T_d is the degradation temperature at 5wt% loss of the polymer.

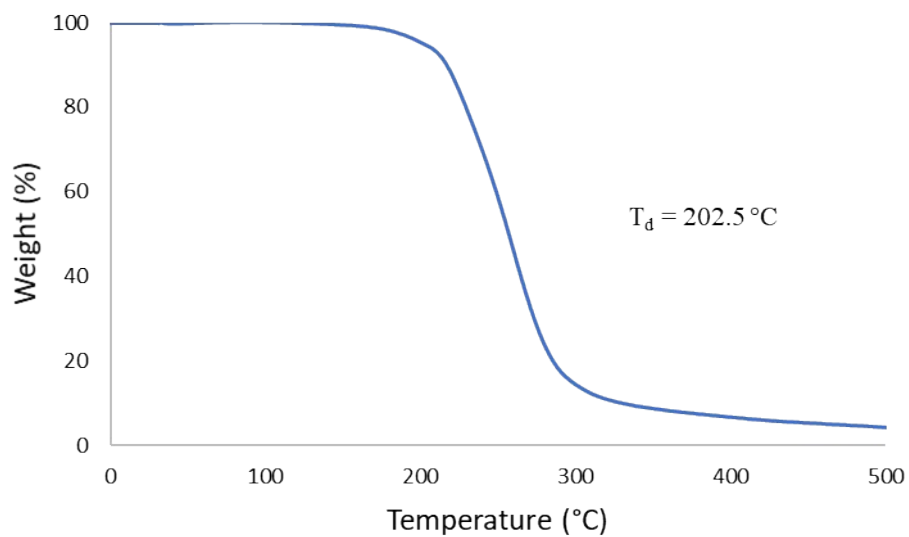


Figure S22. TGA thermogram of a PBPL^{CH₂OCF₂CHF₂} prepared from the ROP of (*rac*)-BPL^{CH₂OCF₂CHF₂} mediated by complex **1d** in the presence of *i*PrOH (Table 1, entry 3). T_d is the degradation temperature at 5wt% loss of the polymer.