Supporting information for:

Copolymerization of cyclic esters, epoxides and anhydrides by a bimetallic salen aluminum complex. Evidences of a dual role of the monomers in the reaction mixture.

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Experimental Section

Materials and Methods.

Generals. All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster glove-box or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed three times to vacuum–nitrogen cycles.

Reagents and Solvents. Benzene, hexane and toluene (Sigma-Aldrich) were distilled under nitrogen over sodium/benzophenone. The aluminum precursor $AlMe_3$ was purchased from Sigma-Aldrich and was used as received. Deuterated solvents were dried over molecular sieves. Cyclohexene oxide (CHO), ε-caprolactone (ε-CL), β-butyrolactone (β-BL) were purchased from Sigma-Aldrich and freshly distilled over CaH_2. L-lactide (L-LA) was purchased from Sigma-Aldrich and dried in vacuo over P_2O_5 for 72 h, and afterward stored at −20 °C in a glovebox. *i*PrOH was purified by distillation over sodium. All other chemicals were commercially available and used as received unless otherwise stated. The synthesis of complex **1** was performed according the published procedure.[1]

NMR analysis. NMR spectra were recorded on Bruker Advance 250, 300, 400 and 600 MHz spectrometers at 25 °C, unless otherwise stated. Chemical shifts (δ) are expressed as parts per million and coupling constants (J) in hertz. ^1H NMR spectra are referenced using the residual solvent peak at $\delta = 7.16$ for C_6D_6 and $\delta = 7.27$ for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at $\delta = 128.06$ for C_6D_6 and $\delta = 77.23$ for $CDCl_3$.

Thermal analysis. Melting points (T_m) and Glass transition temperature (T_g) of the polymers were measured by differential scanning calorimetry (DSC) using a DSC 2920 apparatus manufactured by TA Instruments under a nitrogen flux of 50 mL min^{-1} with a heating and cooling rate of 10 °C min^{-1} in the range −10 to 200 °C. All calorimetric data were reported for the second heating cycle.

MALDI-ToF-MS Analysis. Mass spectra were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The samples were ionized in positive ion mode using the MALDI ion source. Samples were dissolved in THF (1 mg/mL), 2,5-dihydroxybenzoic acid (DHBA) was used as the matrix material, and potassium trifluoroacetate was added to facilitate ionization. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry.

References.

[1] F. Isnard, M. Lamberti, L. Lettieri, I. D'auria, K. Press, R. Troiano and M. Mazzeo*, Dalton Trans.*, **2016**, *45*, 16001-16010.

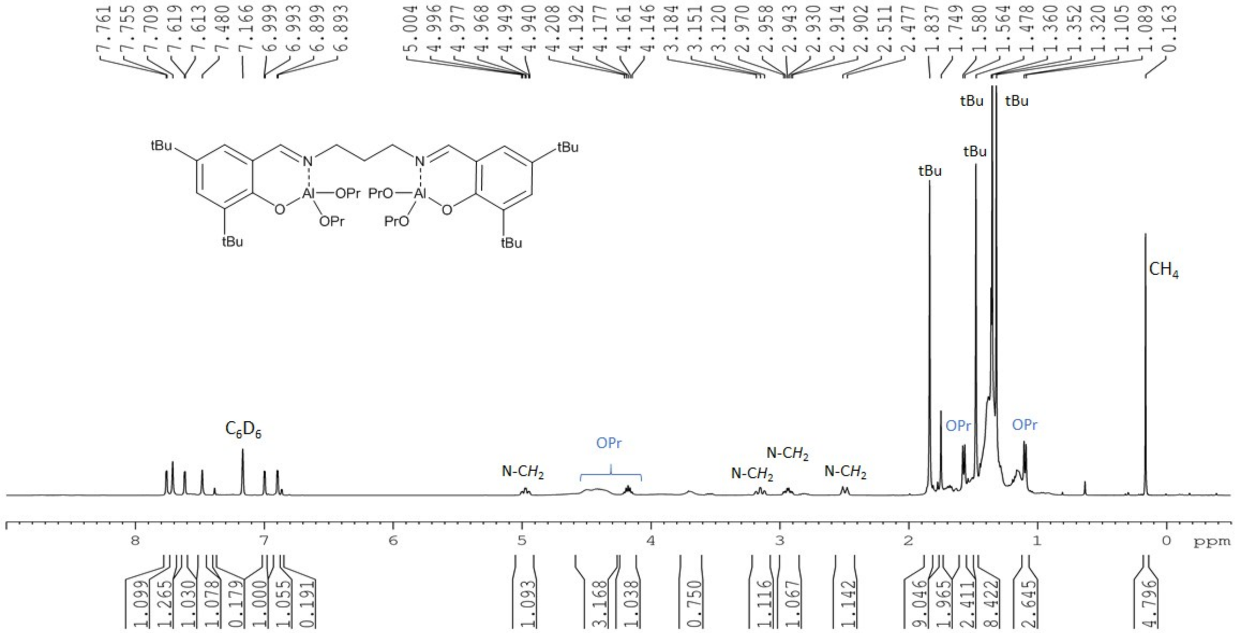


Figure S1. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of the alcoholysis of **1**.

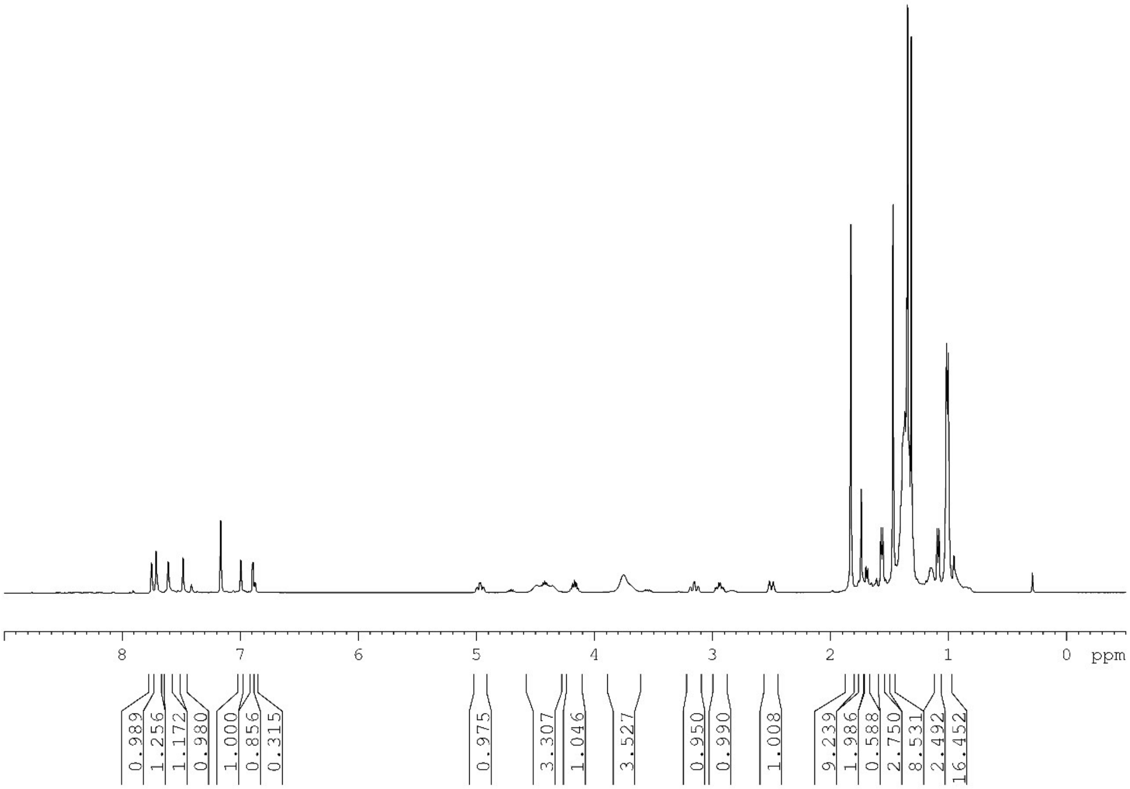


Figure S2. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of the isopropoxide derivative of **1** synthesized from $Al(OiPr)_3$.

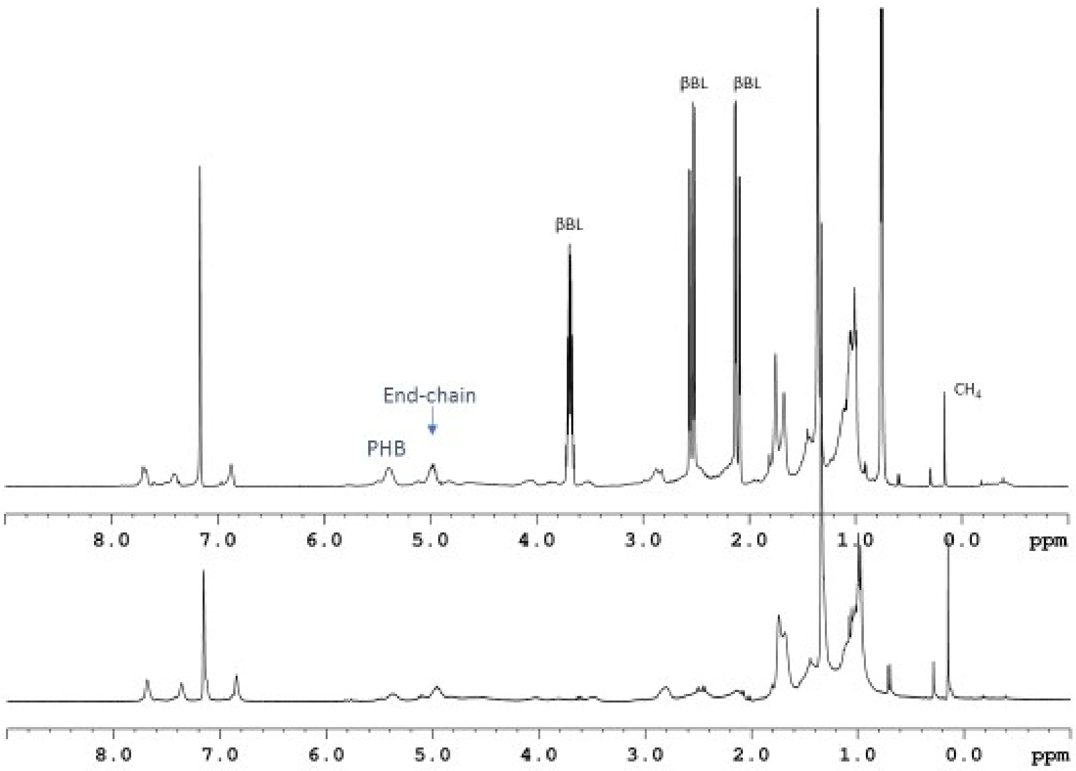


Figure S3. ^{1}H NMR spectrum (C_6D_6, 300 MHz, 298 K) of the propagating species of **1**-PHB. Up: After addition of β-BL, showing the increase of the signal of the polymer PHB.

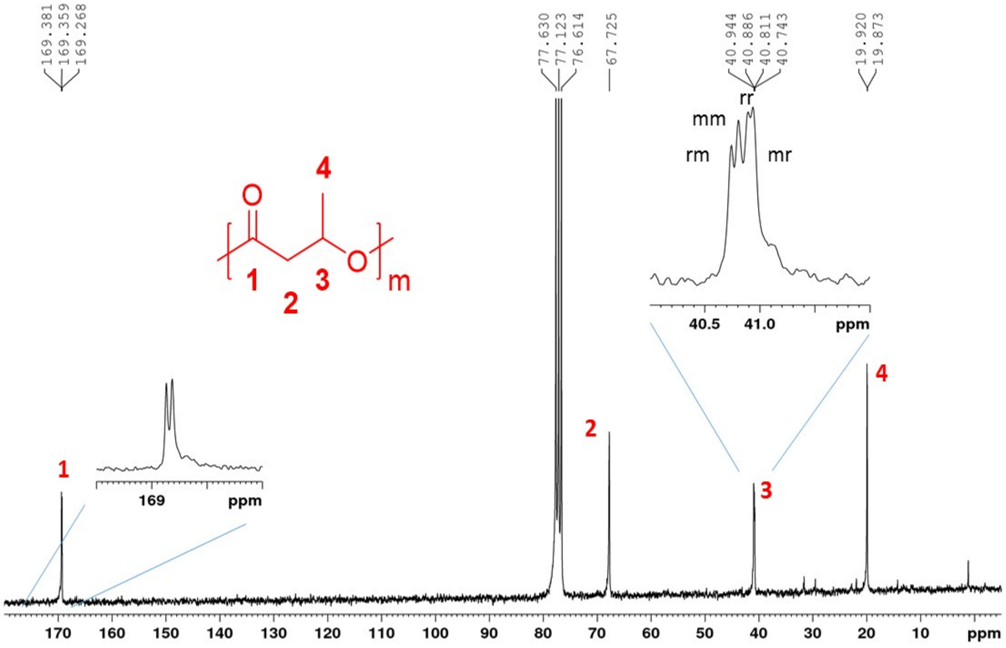


Figure S4. ^{13}C NMR spectrum (63 MHz, $CDCl_3$, 298 K) of the atactic PHB (run 5 of Table 1).

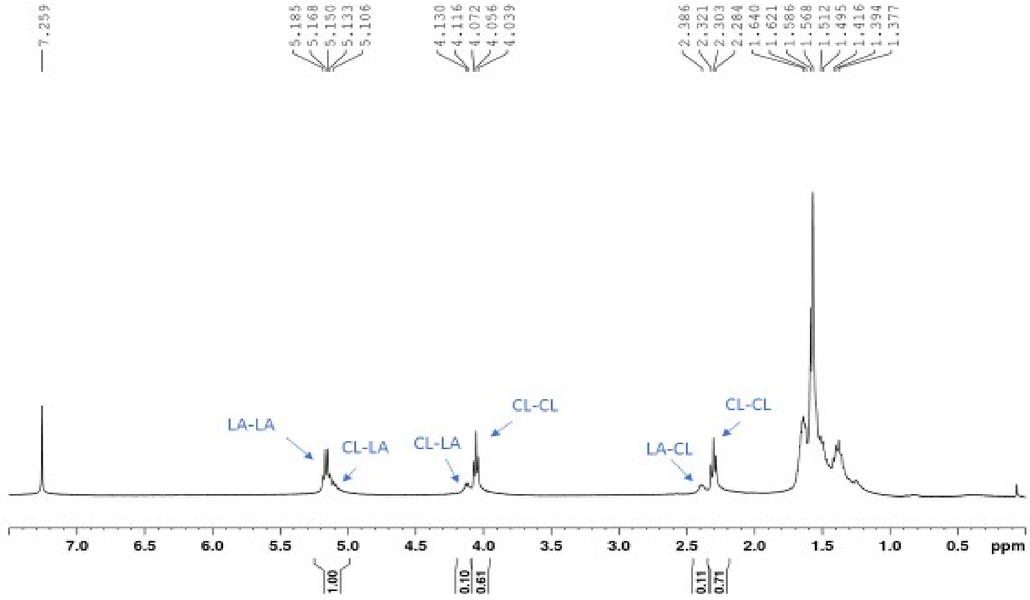


Figure S5. ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298 K) of ε-CL/L-LA copolymer.

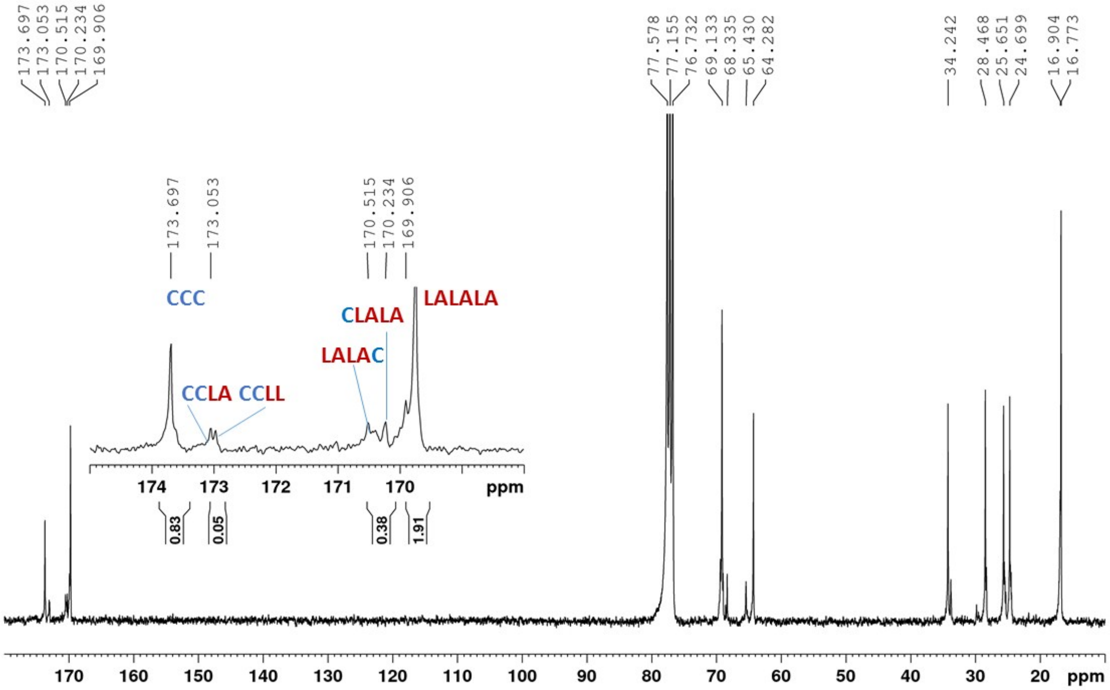


Figure S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of ε-CL/L-LA copolymer.

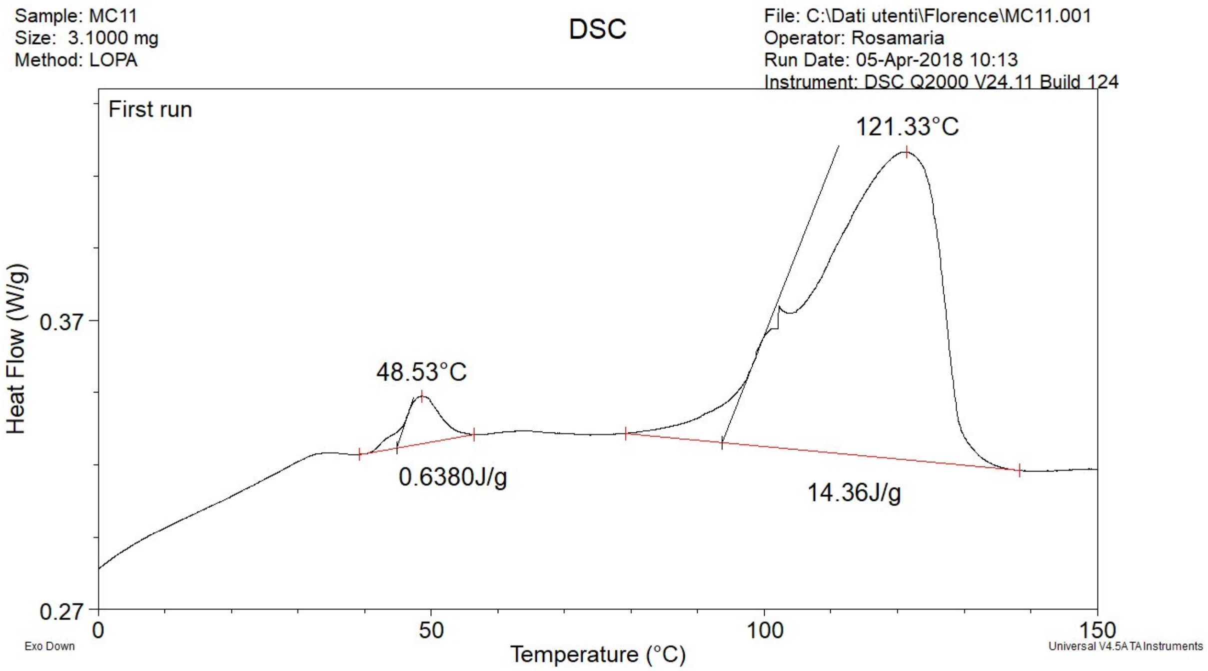


Figure S7. DSC thermogram of PCL/PLA copolymer.

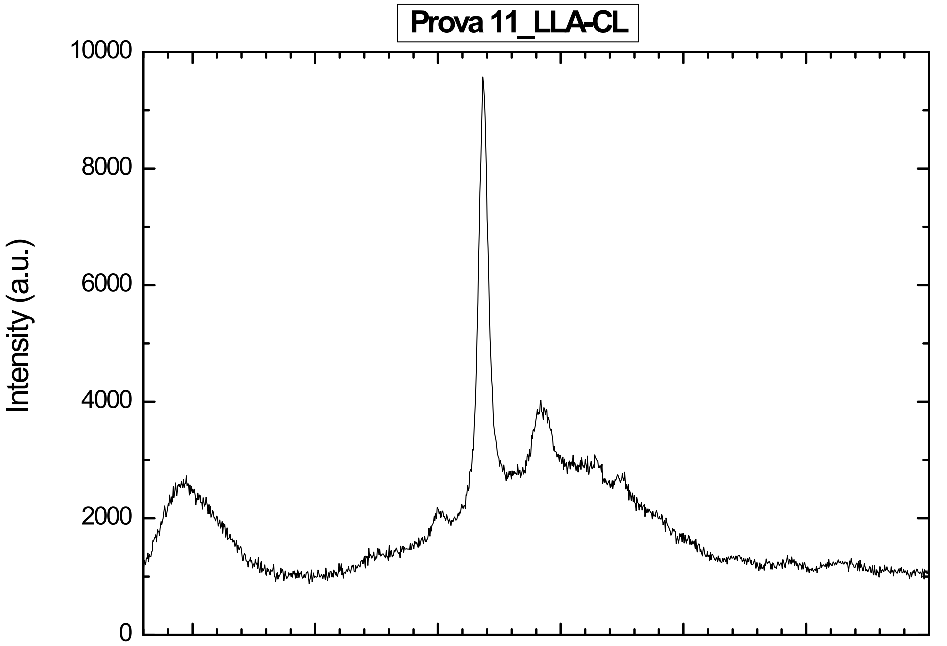


Figure S8. WAXD analysis of the PCL/PLA copolymer.

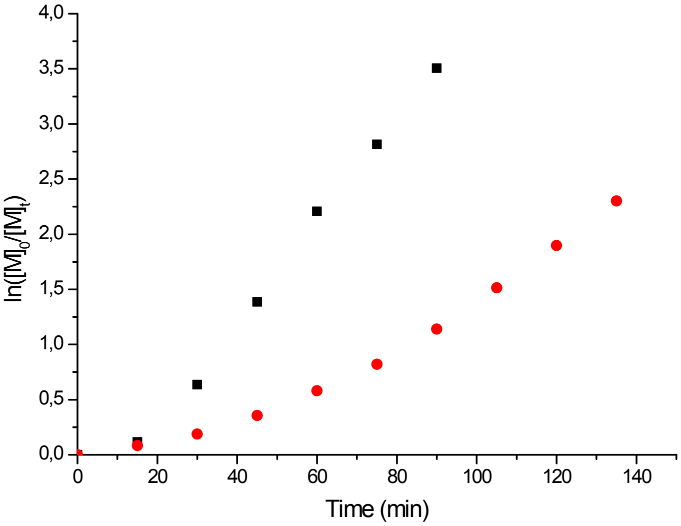


Figure S9. Plot of ln($[M]_0/[M]_t$) vs time depicting a reaction order of unity with respect to L-LA (black solid squares) and ε-CL (red solid circles) concentration ($R^2 = 0.993$ for L-LA and $R^2 = 0.991$ for ε-CL).

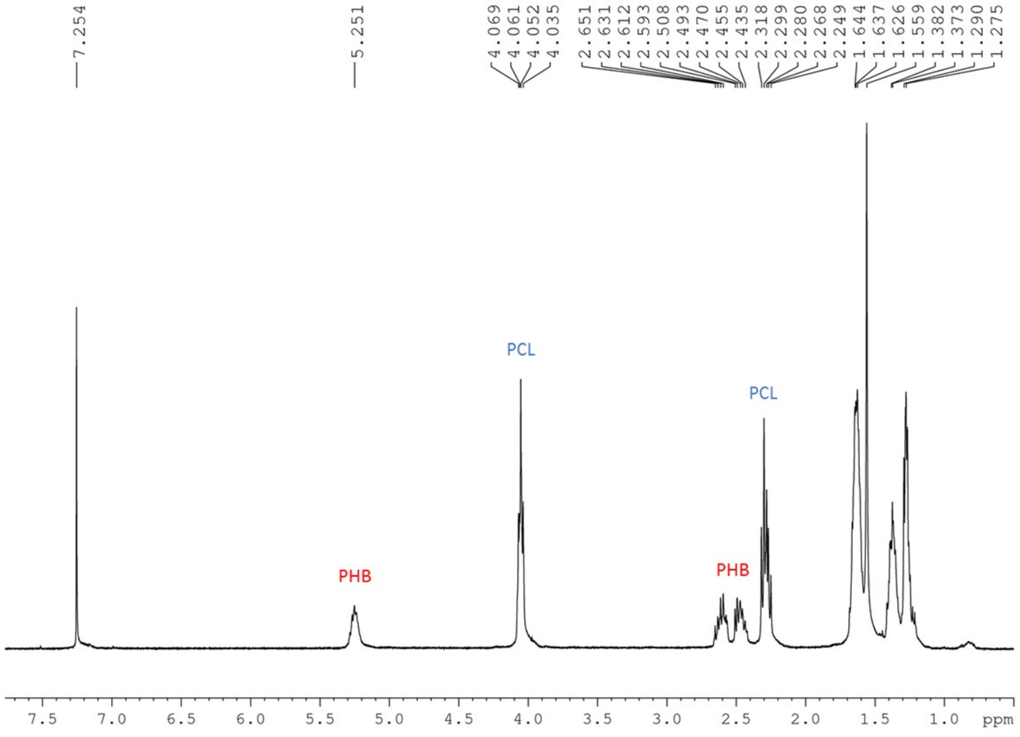


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of poly[HB-co-CL].

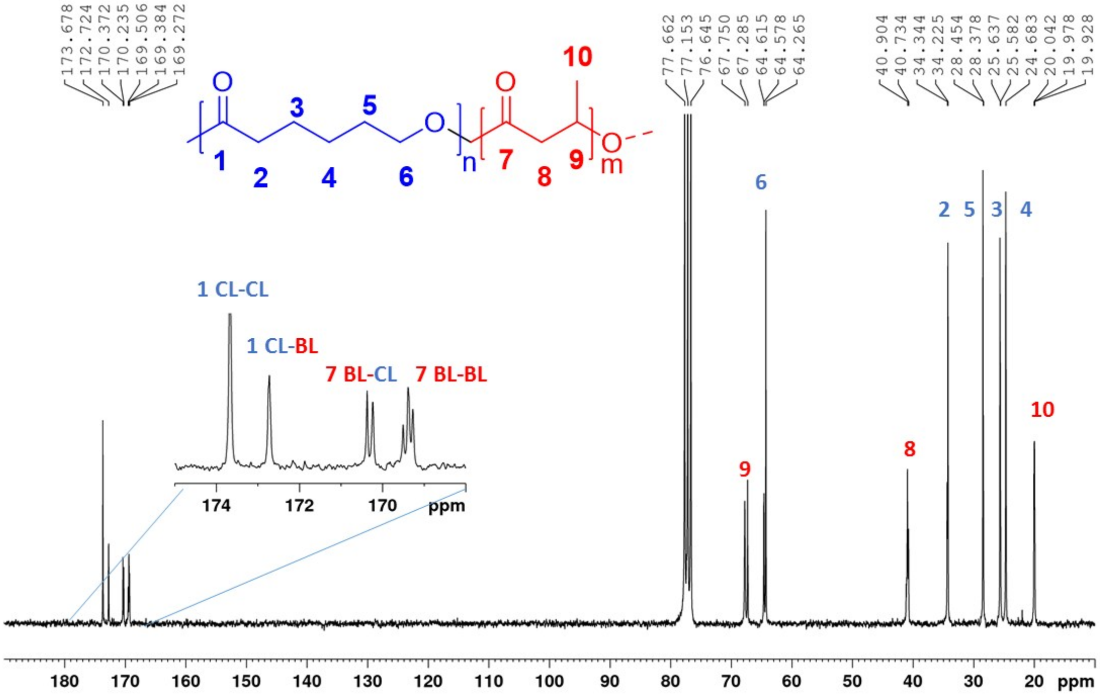


Figure S11. ^{13}C NMR spectrum (63 MHz, $CDCl_3$, 298 K) of poly[HB-co-CL].

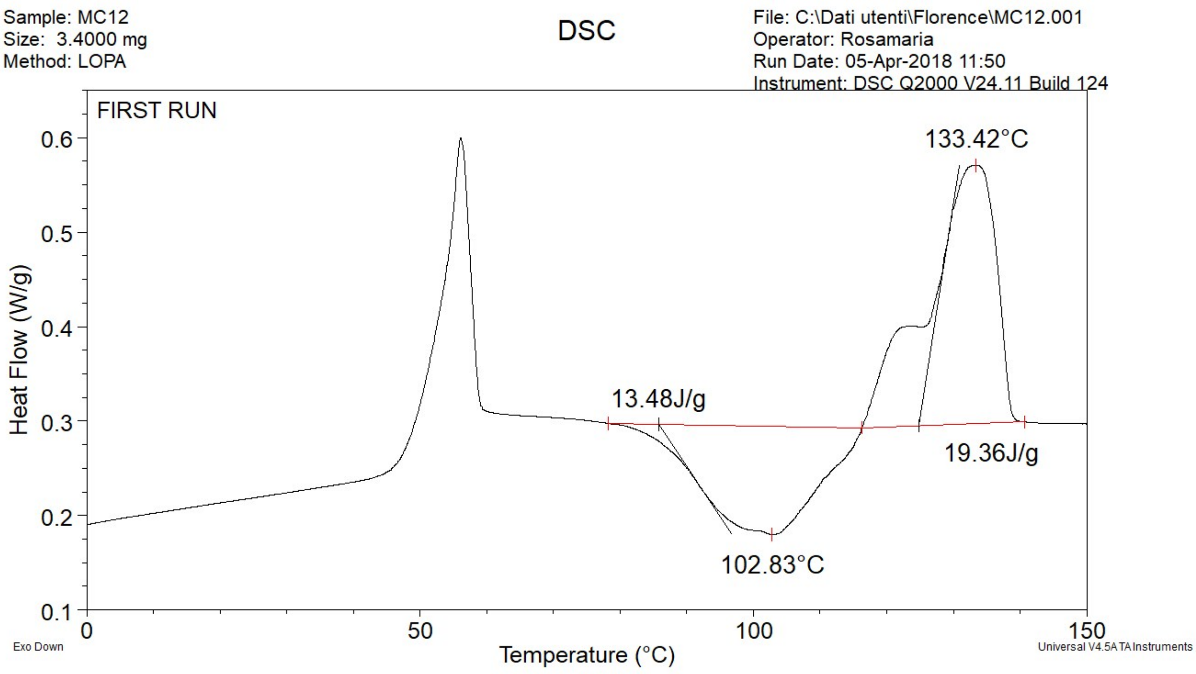


Figure S12. DSC thermogram of PHB/PLA copolymer.

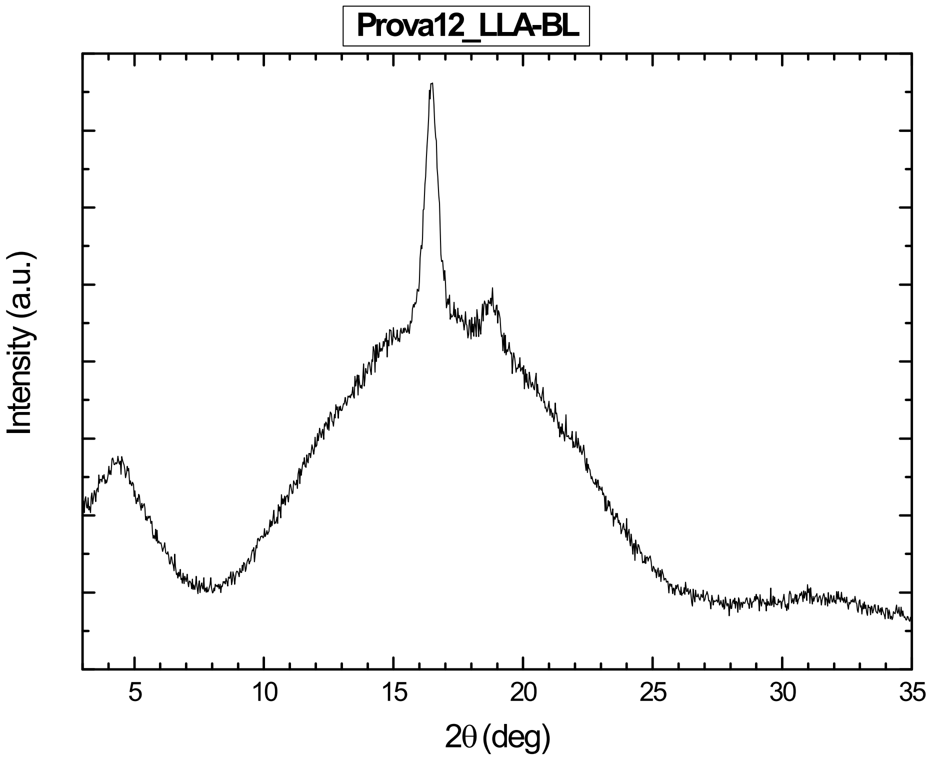


Figure S13. WAXD analysis of PHB/PLA copolymer.

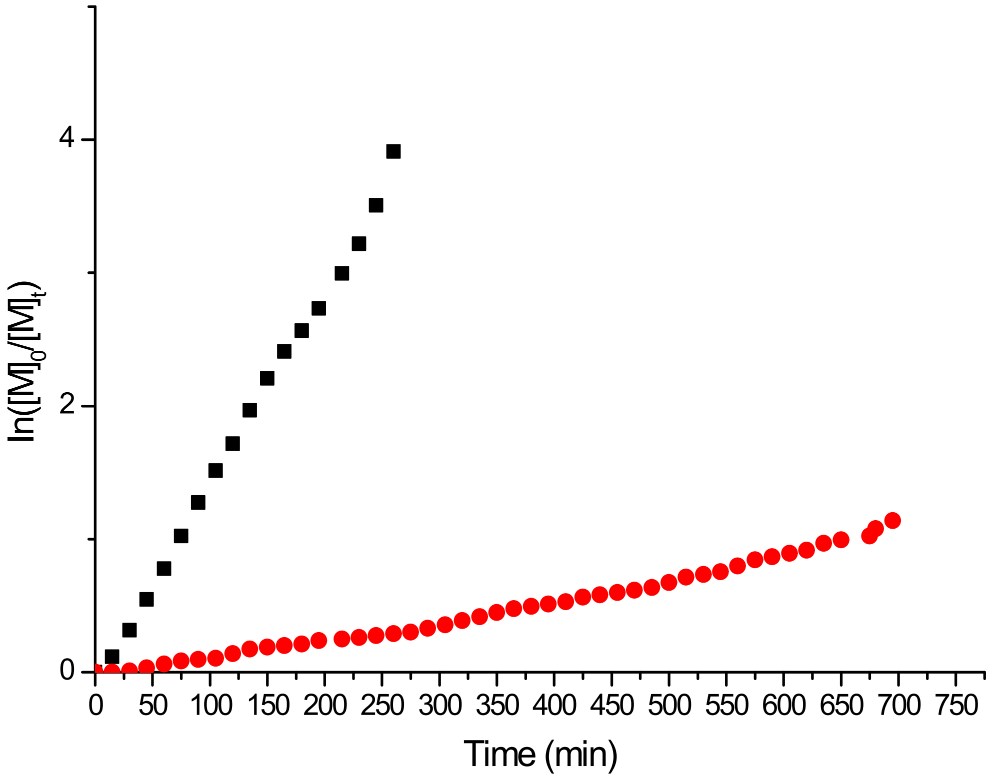


Figure S14. Plot of ln([M]$_0$/[M]$_t$) vs time depicting a reaction order of unity with respect to L-LA (black solid squares and β-BL (red solid circles) concentration. (k_{app} = 0.0147 min^{-1} R^2 = 0.9968 for L-LA and k_{app} = 0,00134 R^2 = 0.9916 for poly- β-BL).

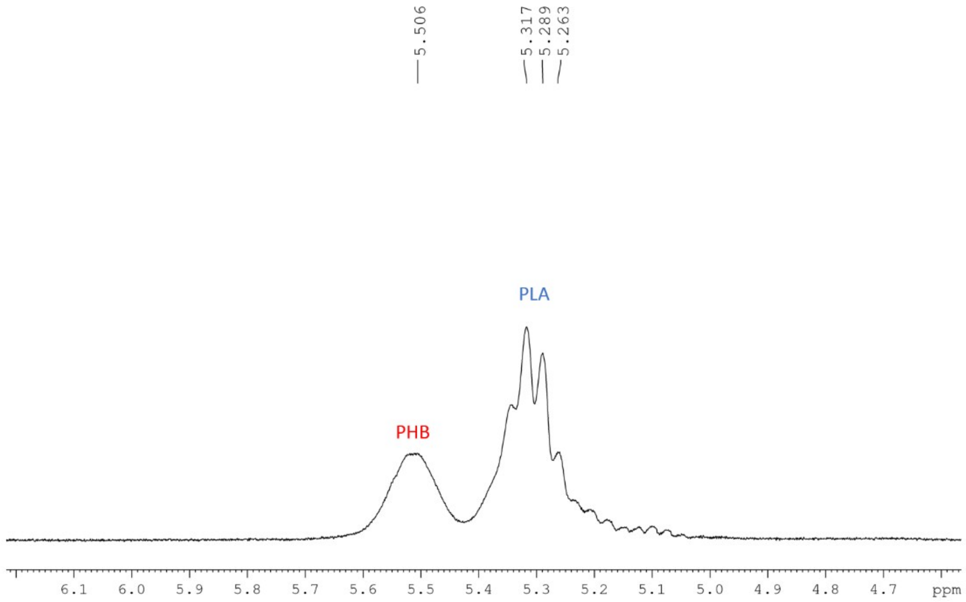


Figure S15. ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298 K) of co-polymer of β-BL and L-LA obtained in run 3 of Table 2.

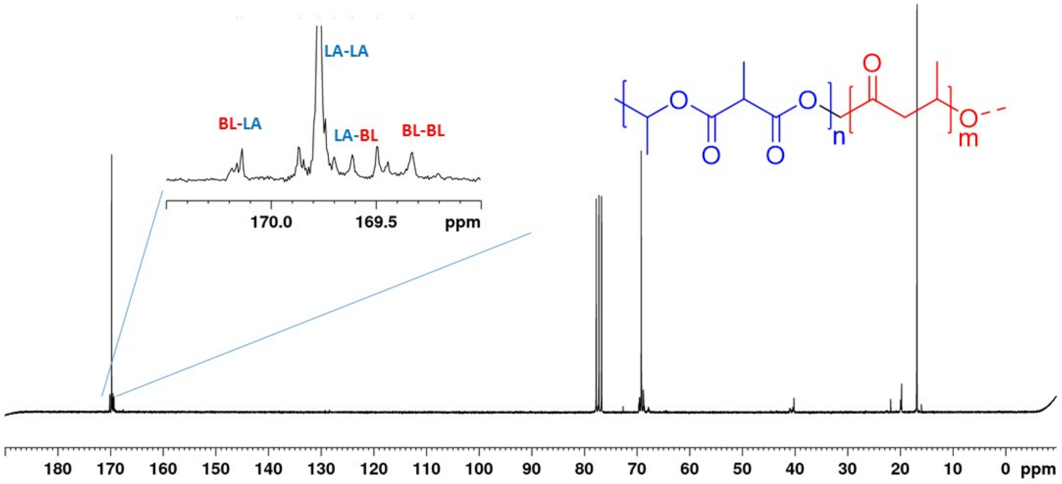


Figure S16. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of poly[LA-co-HB] obtained in entry 3 of Table 2.

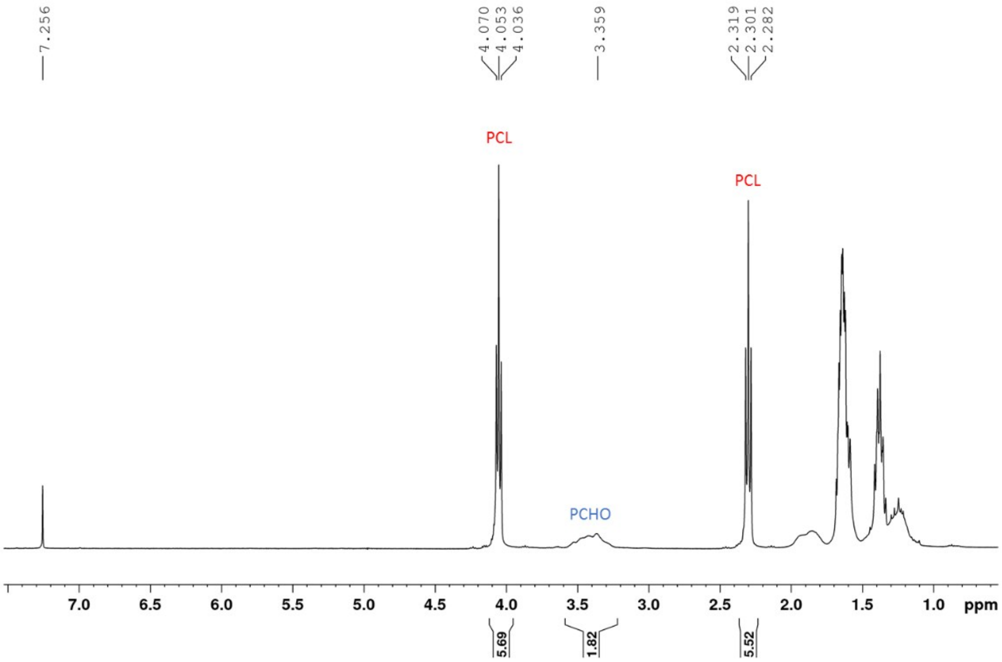


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of co-polymer of CHO and ε-CL.

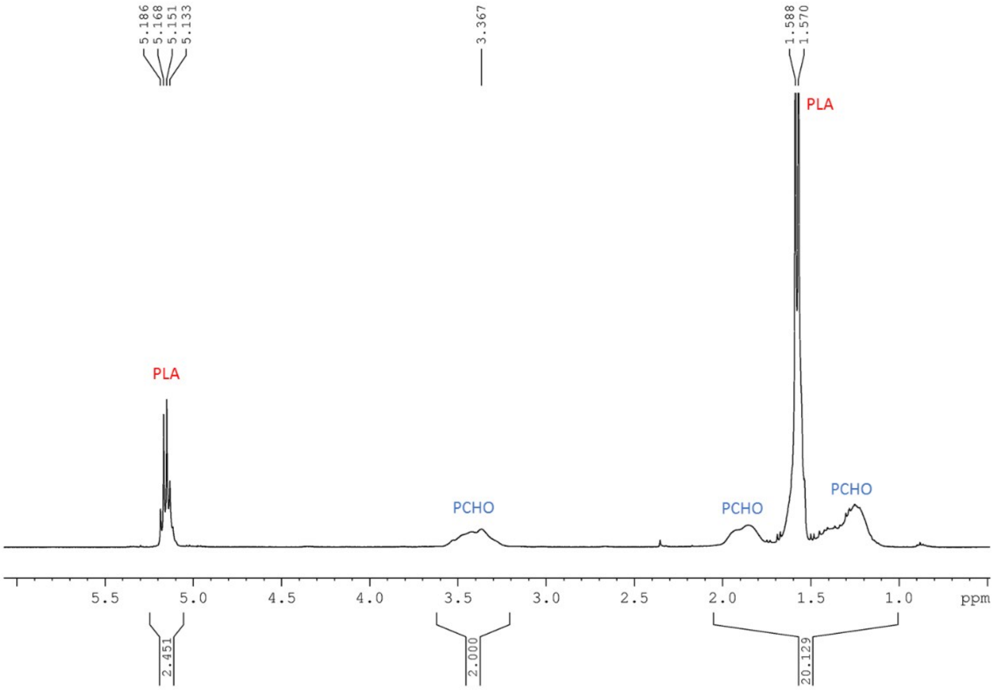


Figure S18. ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298 K) of co-polymer of CHO and L-LA.

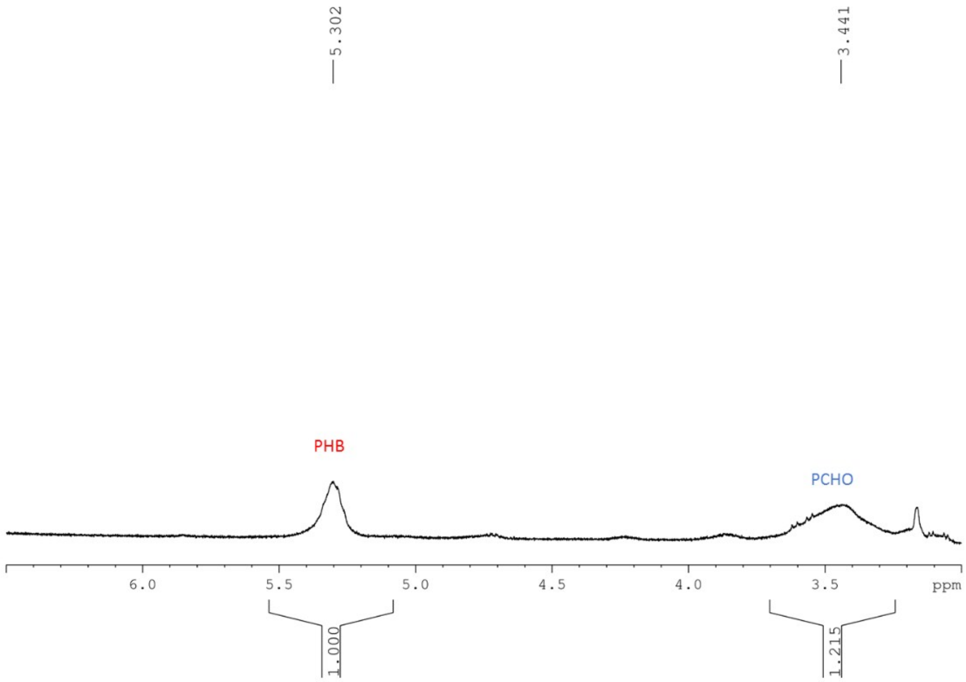


Figure S19. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of co-polymer of CHO and β-BL.

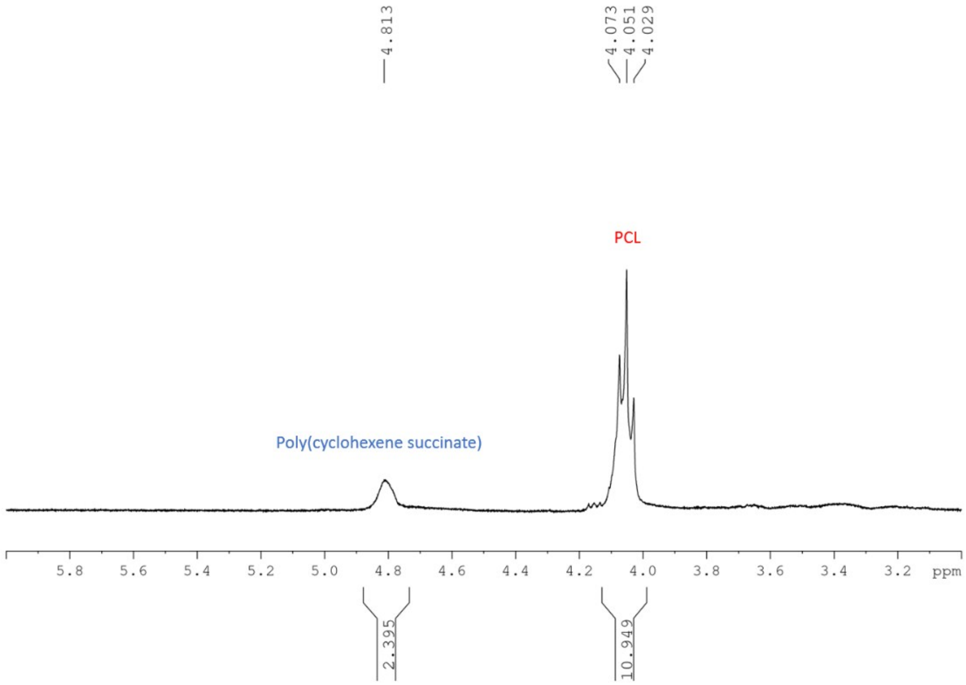


Figure S20. ^{1}H NMR spectrum (250 MHz, $CDCl_3$, 298 K) of poly(cyclohexene succinate-co-caprolactone).

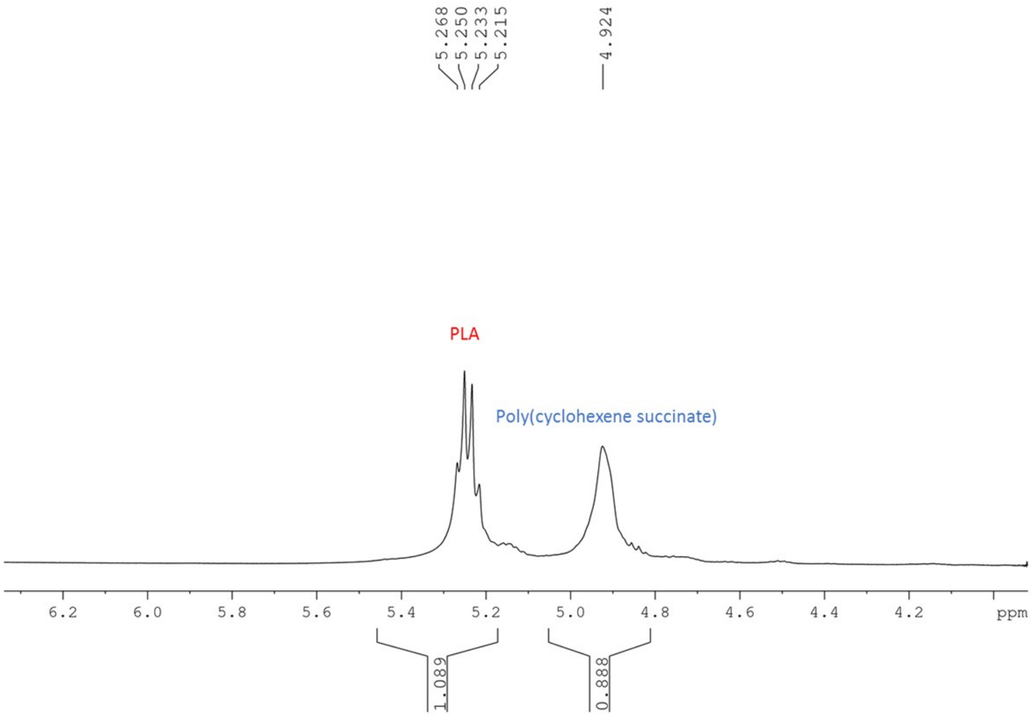


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of poly(cyclohexene succinate-co-lactide).

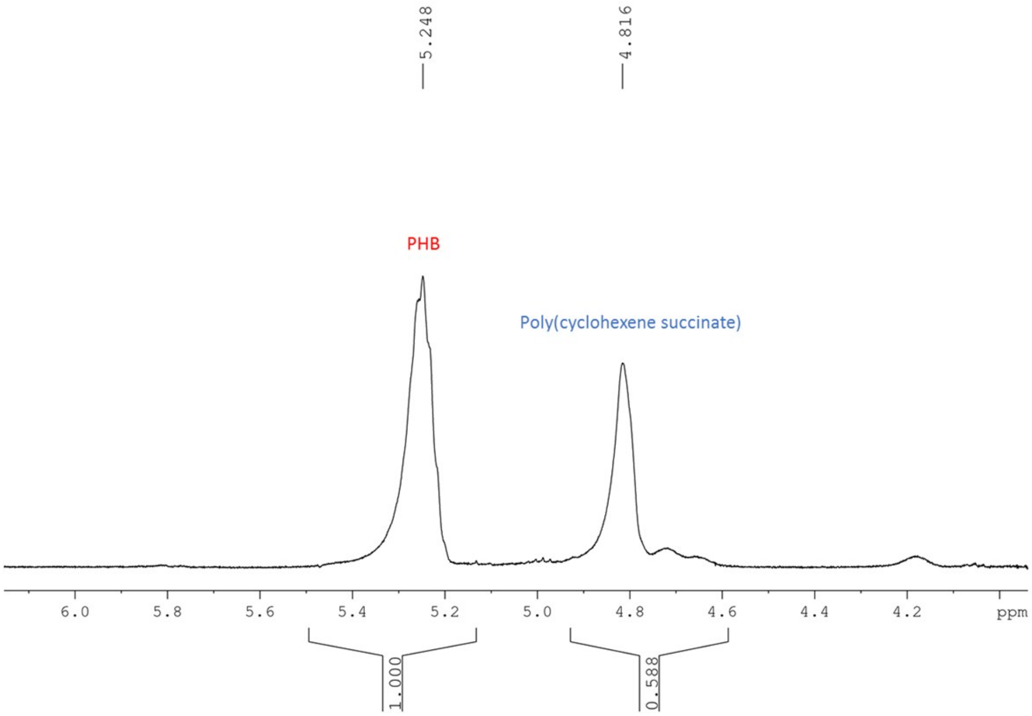
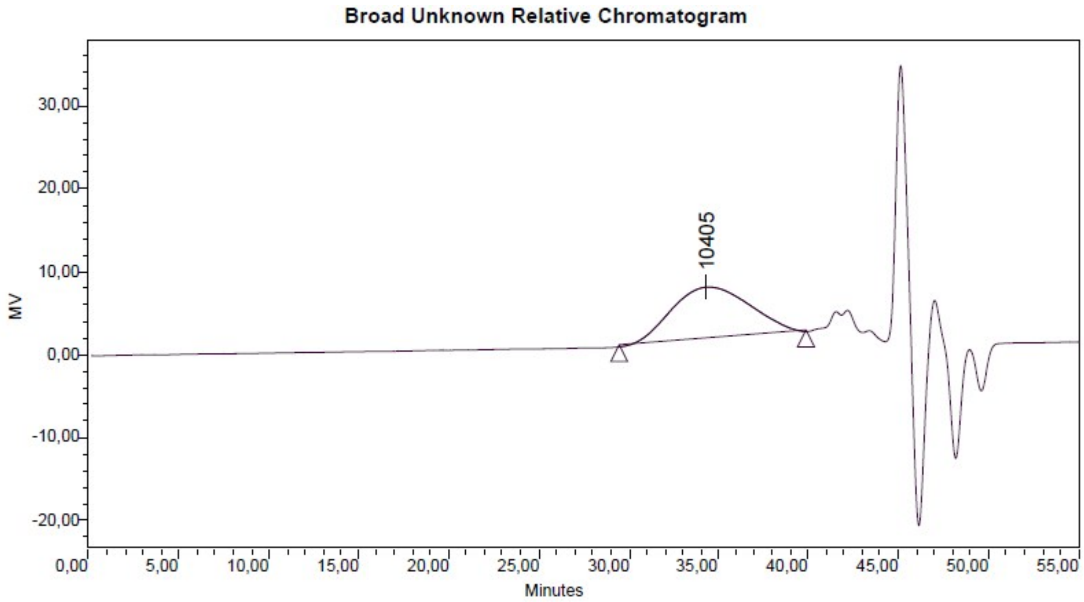


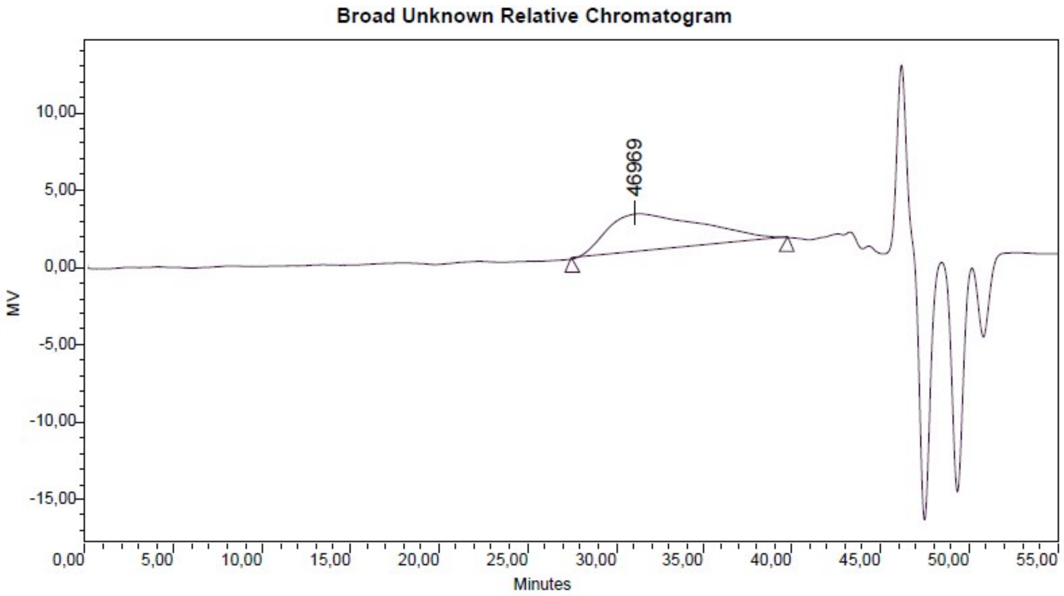
Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of poly(cyclohexene succinate-co-butyrolactone).



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		7378	11275	10405	15930	20602	1,528158	1,412860	1,827242

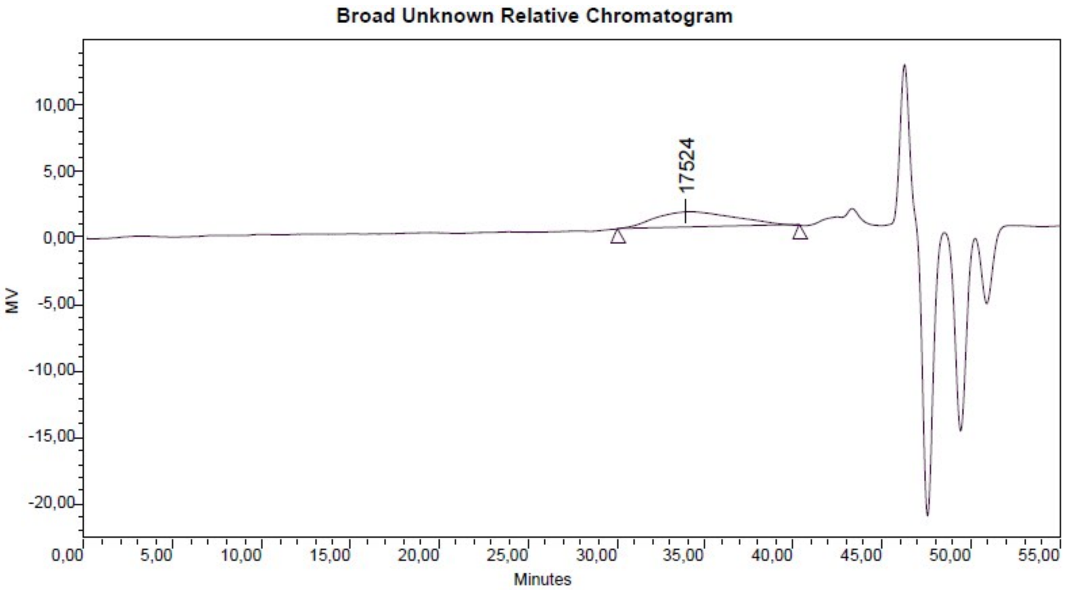
Figure S23. GPC profile of the PCHO block from Table 3, Entry 1. PCHO, check at 70% conversion of CHO, no PCL block.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		19429	38378	46969	60461	79184	1,975265	1,575438	2,063294

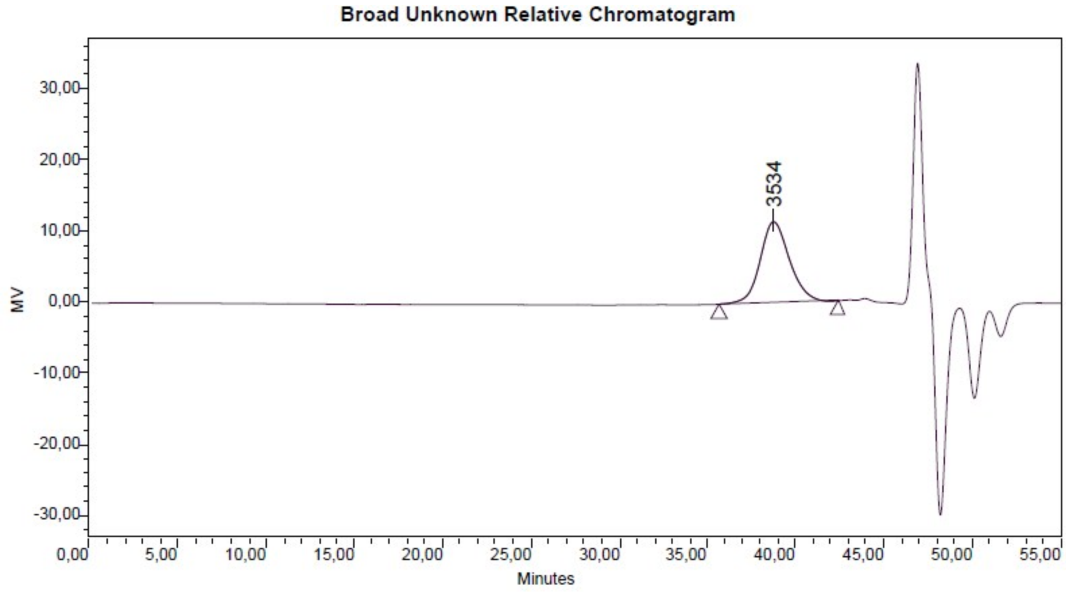
Figure S24. GPC profile of PCHO/PCL polymer from Table 3, Entry 1.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		11047	17088	17524	23877	30098	1,546845	1,397248	1,761309

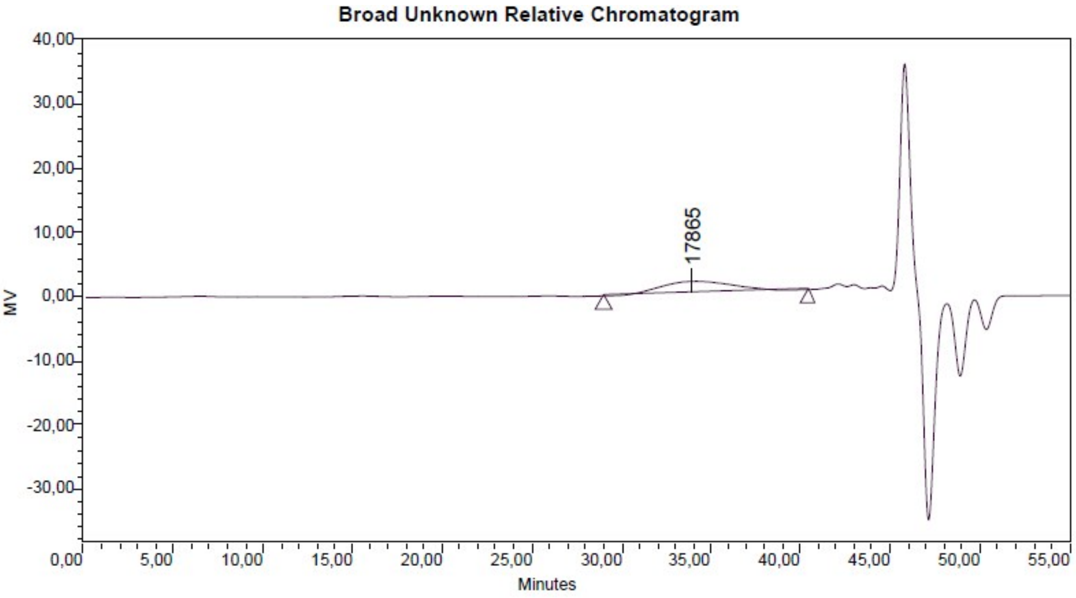
Figure S25. GPC profile of PCHO/PLA from Table 3, Entry 2.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		3226	3524	3534	3830	4155	1,092305	1,086968	1,179098

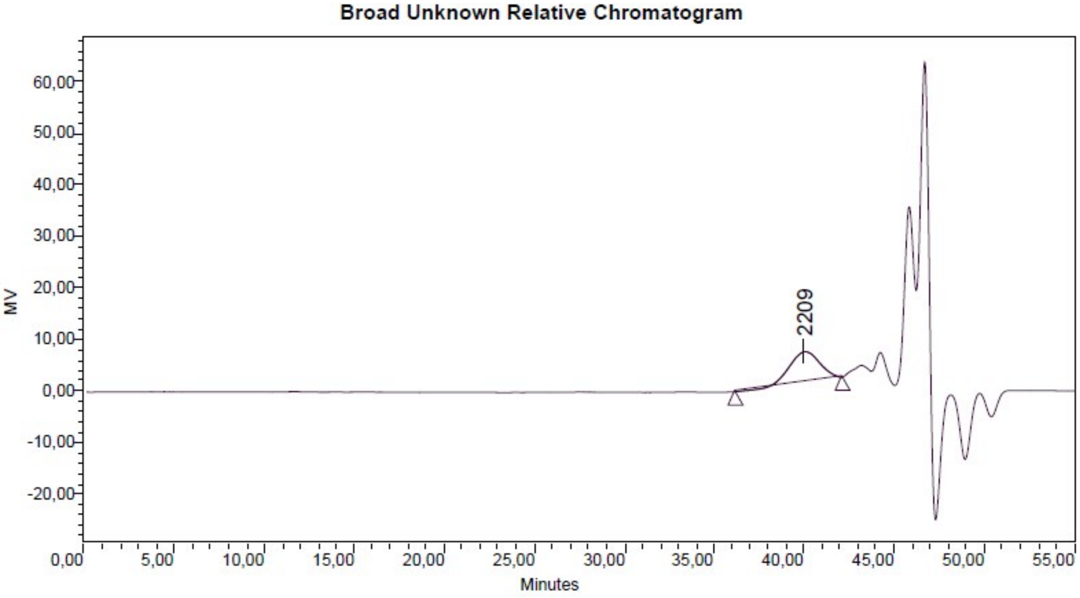
Figure S26. GPC profile of PCHO/PHB from Table 3, Entry 3.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		13271	18830	17865	25227	31576	1,418851	1,339713	1,676884

Figure S27. GPC profile of terpolymer from Table 4, Entry 1.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		2124	2301	2209	2485	2670	1,083213	1,079921	1,160234

Figure S28. GPC profile of the first block of terpolymer from Table 4, Entry 1: poly(cyclohexene succinate) block, check at 57% conversion of SA, no PCL block.

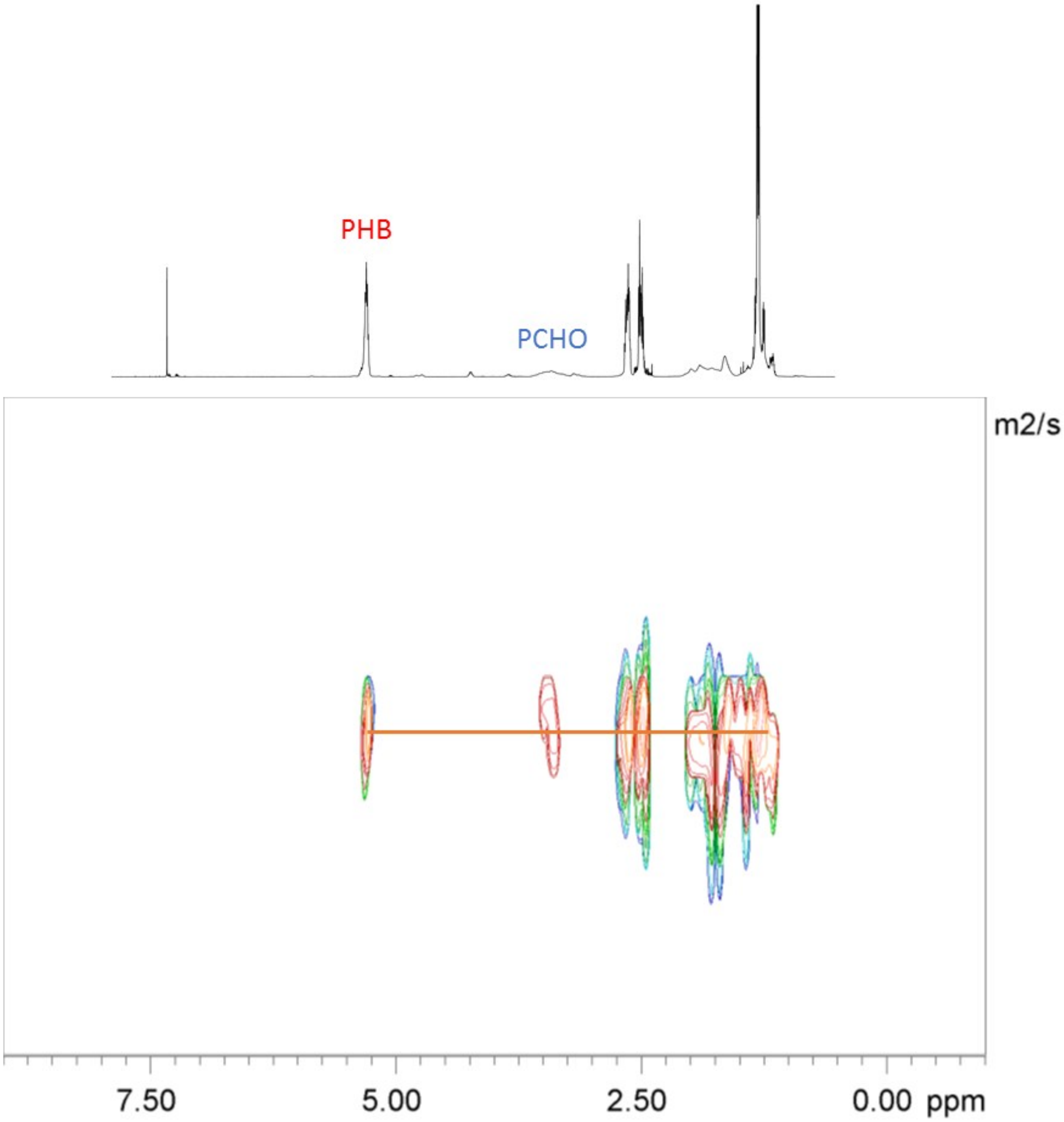


Figure S29. ^{1}H DOSY spectrum (600 MHz, $CDCl_3$, 298K) of the co-polymer from Table 3, Entry 3.

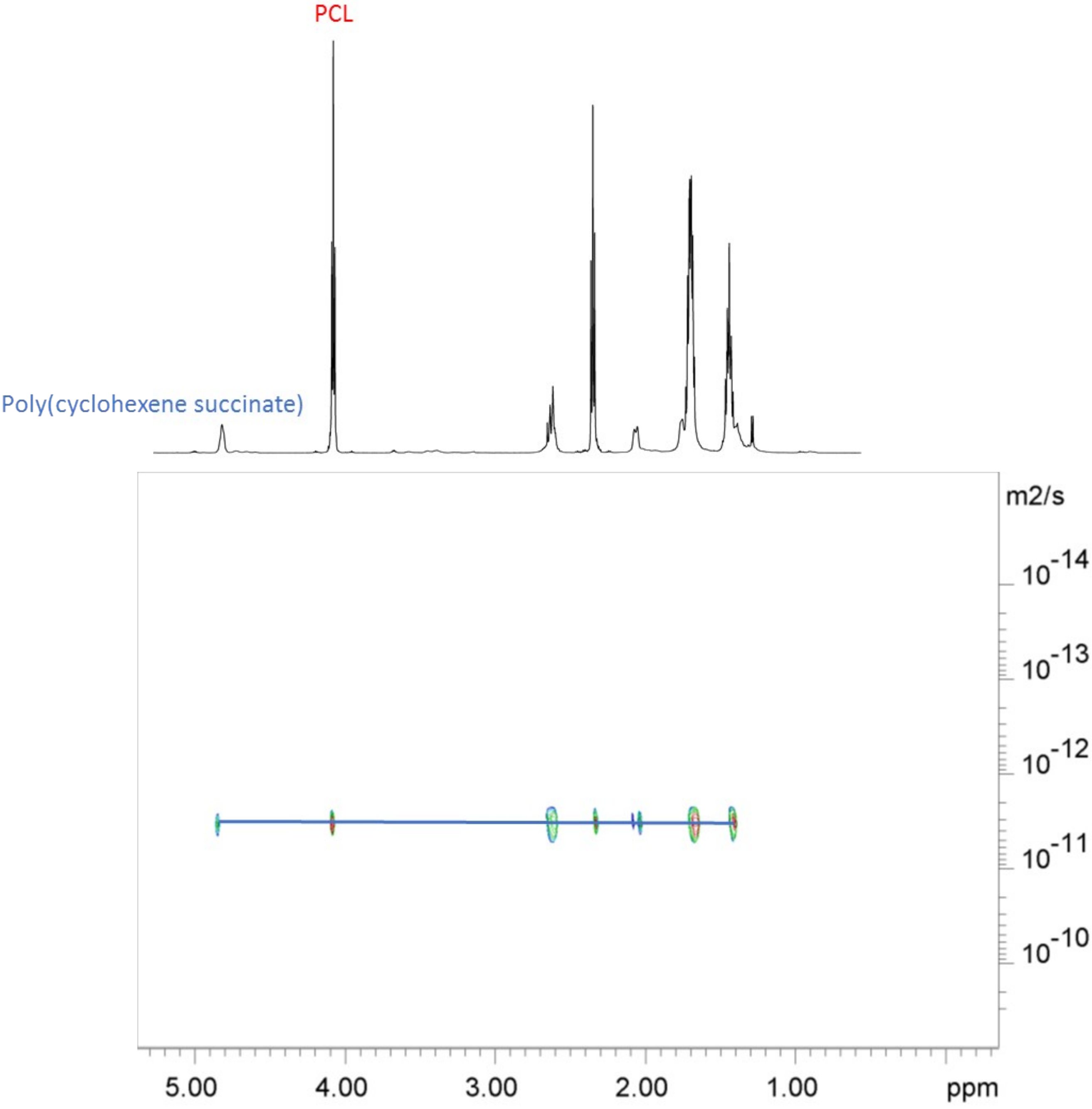


Figure S30. ^{1}H DOSY spectrum (600 MHz, $CDCl_3$, 298K) of the ter-polymer from Table 4, Entry 1.