

Electronic Supplementary Information

For

Synthesis of Mononuclear Magnesium Bis(alkoxide) Complex and Its Reactivity in Ring-Opening Copolymerization of Cyclic Anhydrides with Epoxides

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1. Experimental Details

General

All reactions involving air-sensitive materials were carried out in a nitrogen-filled glovebox. Di-*tert*-butyl-phenylmethanol (HOR) were synthesized according to previously published procedures.¹ *n*-Butyl-*sec*-butylmagnesium (0.7 M solution in hexane) was purchased from Sigma and used as received. All non-deuterated solvents were purchased from Aldrich and were of HPLC grade. The non-deuterated solvents were purified using an MBraun solvent purification system. C₆D₆ and CDCl₃ were purchased from Cambridge Isotope Laboratories. *rac*-Lactide was obtained from Sigma Aldrich and purified by recrystallization from toluene, following by drying over P₂O₅ for 72 h, as previously described.^{2, 3} CHO was purchased from Aldrich and purified by distillation by CaH₂. Anhydrides were purchased from Aldrich and purified by crystallization from toluene. All solvents were stored over 3 Å molecular sieves. Complexes were characterized by ¹H and ¹³C NMR, X-ray crystallography, and elemental analysis. NMR spectra for metal complexes were recorded at the Lumigen Instrument Centre (Wayne State University) on an Agilent 400 and 600 MHz spectrometers in C₆D₆ at room temperature. Chemical shifts and coupling constants (*J*) were reported in parts per million (δ) and Hertz respectively. Elemental analysis was performed under ambient air-free conditions by Midwest Microlab LLC.

The molecular weights (M_n and M_w) and the molecular mass distribution (\mathfrak{D}) of polymer samples were measured by gel permeation chromatography (GPC) at 30 °C using THF as the solvent, a flow rate of the eluent of 1 mL min⁻¹, and narrow polystyrene standards as the reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000–1000000 Å). GPC analyses were done at the Department of Chemistry and Biology of the University of Salerno.

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 polymer samples were ionized in positive ion mode using the MALDI ion source. The mass range was set to m/z 200 – 5000. The laser power was 12% and 18 laser shots were used for each scan. Mass spectra were calibrated externally using a mix of peptide clusters in MALDI ionization positive ion mode. A linear calibration was applied. The polymer samples were dissolved in THF at a

concentration of 1 mg/mL. The cationization agent used was potassium trifluoroacetate (Fluka, > 99 %) dissolved in THF at a concentration of 5 mg/mL. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg/mL. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry.

Preparation of Mg(OR)₂(THF)₂ (1)

A 1 mL solution of HOR (138 mg, 0.63 mmol, 2.0 equiv.) in diethyl ether and a 1 mL solution of Mg(n-butyl)(sec-butyl) (45 mg, 0.32 mmol, 1 equiv.) in hexane were prepared. The solution of HOR was then added dropwise to a stirring solution of Mg(n-butyl)(sec-butyl). 0.5 ml of THF was then added to the reaction mixture. The reaction mixture was stirred for 2 hours, upon which the volatiles were removed *in vacuo*. The resulting oily solid was extracted to diethyl ether, filtered and concentrated *in vacuo* to about 0.5 ml. X-ray quality crystals were obtained from a saturated diethyl ether solution of Mg(OR)₂(THF)₂ kept at -35 °C (176 mg, 0.29 mmol, 91%). ¹H NMR (C₆D₆, 600 MHz) δ 8.18 (d, ³J_{HH} = 7.6 Hz, 2H), 7.95 (d, ³J_{HH} = 8.2 Hz, 2H), 7.38 (td, ³J_{HH} = 6.5 Hz, ⁴J_{HH} = 1.8 Hz, 2H), 7.26 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.8 Hz, 4H), 7.22 (t, ³J_{HH} = 7.0 Hz, 2H), 3.77 (m, 8H), 1.36 (s, 36H), 1.25 (m, 8H); ¹³C{¹H} NMR (C₆D₆, 150 MHz) δ 154.30, 130.50, 129.79, 127.11, 126.03, 125.49, 84.58, 70.99, 43.62, 32.25, 25.57. Anal. Calcd for C₃₈H₆₂MgO₄: C, 75.17; H, 10.29. Found: C, 74.85; H, 9.95.

Preparation of Mg(OR)(sec-butyl)(THF)₂ (2)

A 1 mL solution of HOR (142 mg, 0.64 mmol, 1.0 equiv.) in diethyl ether and a 0.92 mL solution of Mg(n-butyl)(sec-butyl) (89 mg, 0.64 mmol, 1.0 equiv.) in hexane were prepared. The solution of HOR was then added dropwise to a stirring solution of Mg(n-butyl)(sec-butyl). 0.5 ml of THF was then added to the reaction mixture. The reaction mixture was stirred for 2 hours, upon which the volatiles were removed *in vacuo*. X-ray quality crystals were obtained from a saturated hexane solution of Mg(OR)(sec-Bu)(THF)₂ kept at -35 °C (254 mg, 0.57 mmol, 89%). ¹H NMR (C₆D₆, 600 MHz) δ 8.14 (d, ³J_{HH} = 8.2 Hz, 1H), 7.93 (d, ³J_{HH} = 8.2 Hz, 1H), 7.43 (m, 1H), 7.24 (m, 2H), 3.62 (m, 8H), 2.15 (m, 2H), 1.78 (d, ³J_{HH} = 7.81 Hz, 3H), 1.42 (t, ³J_{HH} = 7.2 Hz, 3H), 1.35 (s, 18H), 1.26 (m, 8H), 0.19 (q, ³J_{HH} = 7.4 Hz, 1H); ¹³C{¹H} NMR (C₆D₆, 150 MHz) δ 153.59, 129.35, 128.81, 126.08,

124.92, 124.29, 83.47, 68.66, 42.48, 33.10, 31.03, 24.82, 22.02, 19.11, 17.13. Anal. Calcd for $C_{38}H_{62}MgO_4$: C, 72.88; H, 10.87. Found: C, 72.92; H, 10.65.

Preparation of $Mg(OR)_2(THF)_2$ (1**) via the reaction of $Mg(OR)(sec\text{-}butyl)(THF)_2$ (**2**) with HOR**

A 1 mL solution of HOR (176.2 mg, 0.397 mmol, 1.0 equiv) in diethyl ether and a 1 mL solution of $Mg(OR)(sec\text{-}butyl)(THF)_2$ (**2**, 87.0 mg, 0.395 mmol, 1.0 equiv.) in THF were prepared. The solution of HOR was then added dropwise to a stirring solution of $Mg(OR)_1(sec\text{-}butyl)(THF)_2$. The reaction mixture was stirred for 2 hours, upon which the volatiles were removed *in vacuo*. Colorless crystals of **1** were obtained from a saturated diethyl ether solution kept at $-35\text{ }^\circ\text{C}$ (228.5 mg, 0.376 mmol, 95%). The nature and purity of the product was confirmed by its ^1H NMR spectrum, identical to the spectrum of **1** described above.

Lactide polymerization

Dichloromethane/toluene/THF solution of 10 μmol catalyst was mixed with a solution containing 100 equivalents (144 mg) of lactide in dichloromethane/toluene (total volume of the reaction was 10 mL, $[\text{LA}] = 0.1\text{ M}$). Reaction was stirred in room temperature (and $60\text{ }^\circ\text{C}$ for toluene) for a given time (Table S1 and S3), after which it was stopped by adding 2-5 mL of methanol. PLA was precipitated in methanol and washed with excess methanol to remove all the impurities. For further purification, the polymer was dissolved using minimal amount of DCM and then added to 20 mL of methanol to precipitate pure PLA. Excess methanol was decanted, and the polymer was dried for 1 hour under vacuum. The reaction with 200 and 300 equivalents of lactide (0.2 M and 0.3 M, respectively) in dichloromethane and toluene solutions was carried out in a similar fashion (Table S1), as well as the experiments with benzyl alcohol (as a co-catalyst, Table S2). The resulting polymer was characterized by ^1H NMR spectroscopy, to determine the nature of the end groups and polymerization degree. The methine region was also analyzed by homonuclear decoupled ^1H NMR, to determine the tacticity of the polymer.

Copolymerization of epoxides with cyclic anhydrides

In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with the anhydride. Subsequently, a solution of catalyst, cocatalyst and epoxide in 1 mL

of toluene was added. The reaction mixture was stirred at 110 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy. At the end of the polymerization, the product was dissolved in CH₂Cl₂, precipitated in wet hexane and dried under vacuum oven. All analyses were performed on crude samples.

Table S1. Catalytic reactions employing Mg(OR)₂(THF)₂ (**1**) with *rac*-lactide in different solvents.^a

Entry	solvent	Eq of lactide	Time (h)	Temp (°C)	^b Conversion %	^c M _n th (10 ³)	^d M _n ^{exp} (10 ³)	^d Đ
1	DCM	100	0.5	24	35	5.0	11.2	1.87
2	DCM	100	1.0	24	56	8.1	4.7	2.26
3	DCM	100	1.5	24	75	10.8	6.3	1.79
4	DCM	200	0.5	24	26	7.5	4.3	1.96
5	DCM	200	1.0	24	47	13.5	7.8	1.79
6	DCM	200	1.5	24	70	20.2	11.7	2.16
7	DCM	300	0.5	24	20	8.6	14.0	2.08
8	DCM	300	1.0	24	43	18.6	4.1	2.56
9	DCM	300	1.5	24	65	28.1	15.7	2.12
10	Toluene	100	1.0	24	40	5.8	7.7	2.09
11	Toluene	100	2.0	24	85	12.2	5.1	2.82
12	Toluene	100	3.0	24	97	14.0	6.1	3.03
13	Toluene	200	1.0	24	31	8.9	17.9	2.26
14	Toluene	200	2.0	24	75	21.6	13.2	2.12
15	Toluene	200	3.0	24	89	25.7	2.1	4.89
16	Toluene	300	1.0	24	20	8.6	17.1	1.96
17	Toluene	300	2.0	24	66	28.5	21.5	1.90
18	Toluene	300	3.0	24	82	35.5	14.9	1.96
19	Toluene	100	1.0	60	70	10.1	10.2	2.52
20	Toluene	100	3.0	60	100	14.4	6.8	2.41
21	Toluene	200	1.0	60	65	18.7	7.7	2.90
22	Toluene	200	3.0	60	91	26.2	7.8	2.26
23	Toluene	300	1.0	60	40	17.3	20.4	1.92
24	Toluene	300	3.0	60	81	35.0	10.5	2.36
25	THF	100	1.0	24	55	7.9	3.7	1.81
26	THF	200	1.0	24	47	13.5	7.3	1.53
27	THF	300	1.0	24	44	19.0	n.d. ^e	n.d. ^e

^aReaction conditions: [Mg] = 10 μmol; solvent = 10 mL. ^bConversion of lactide determined by ¹H NMR spectroscopy (400 MHz, CDCl₃) of the reaction mixture. ^cCalculated M_n of PLA (in g mol⁻¹) = 144.14 x ([LA]/[Mg]) x conversion LA ^dExperimental M_n (corrected using factor 0.58) and Đ values were determined by GPC analysis in THF using polystyrene standards. ^eNot determined (due to the insufficient amount of material).

Table S2. Catalytic reactions employing **1** with *rac*-lactide and PhCH₂OH as a co-catalyst. The reactions were conducted in DCM, under the same reaction conditions^a as in Table S1.

Entry	1:PhCH ₂ OH	Eq of lactide	Time (h)	^b Conversion %	^c M_n^{th} (10 ³)	^d M_n^{exp} (10 ³)	^d \bar{D}
1	1:1	100	0.25	80	5.8	3.4	1.34
2	1:1	200	0.25	69	10.0	3.3	1.36
3	1:1	300	0.25	56	12.1	3.0	1.45
4	1:10	300	0.25	100	3.9	3.4	1.48

^aReaction conditions: [Mg] = 10 μmol; DCM = 10 mL. ^bConversion of lactide determined by ¹H NMR spectroscopy (400 MHz, CDCl₃) of the reaction mixture. ^cCalculated M_n of PLA (in gmol⁻¹) = 144.14 x ([LA]/([Mg]+[PhCH₂OH])) x conversion LA ^dExperimental M_n (corrected using factor 0.58) and \bar{D} values were determined by GPC analysis in THF using polystyrene standards

Table S3. Catalytic reactions employing **2** with *rac*-lactide. The reactions were conducted under the same reaction conditions^a as in Table S1.

Entry	solvent	Eq of lactide	Concentration of lactide (M)	Time (h)	^b Conversion %	^c M_n^{th}	^d M_n^{exp}	^d \bar{D}
1	DCM	100	0.1	1.0	42	6.1	16.8	2.14
2	DCM	200	0.2	1.0	30	8.6	18.1	1.92
3	DCM	300	0.3	1.0	22	9.5	20.1	1.84
4	Toluene	100	0.1	1.0	32	4.6	24.8	1.83
5	Toluene	200	0.2	1.0	26	7.5	12.2	1.70
6	Toluene	300	0.3	1.0	19	8.2	13.9	1.66
7	THF	100	0.1	1.0	41	5.9	n.d. ^d	n.d. ^d
8	THF	200	0.2	1.0	32	9.2	8.7	1.51
9	THF	300	0.3	1.0	23	9.9	7.5	1.58

^aReaction conditions: [Mg] = 10 μmol; solvent = 10 mL. ^bConversion of lactide determined by ¹H NMR spectroscopy (400 MHz, CDCl₃) of the reaction mixture. ^cCalculated M_n of PLA (in gmol⁻¹) = 144.14 x ([LA]/[Mg]) x conversion LA ^dExperimental M_n (corrected using factor 0.58) and \bar{D} values were determined by GPC analysis in THF using polystyrene standards. ^eNot determined (due to the insufficient amount of material).

2. ^1H and ^{13}C NMR Spectra of complexes 1 and 2

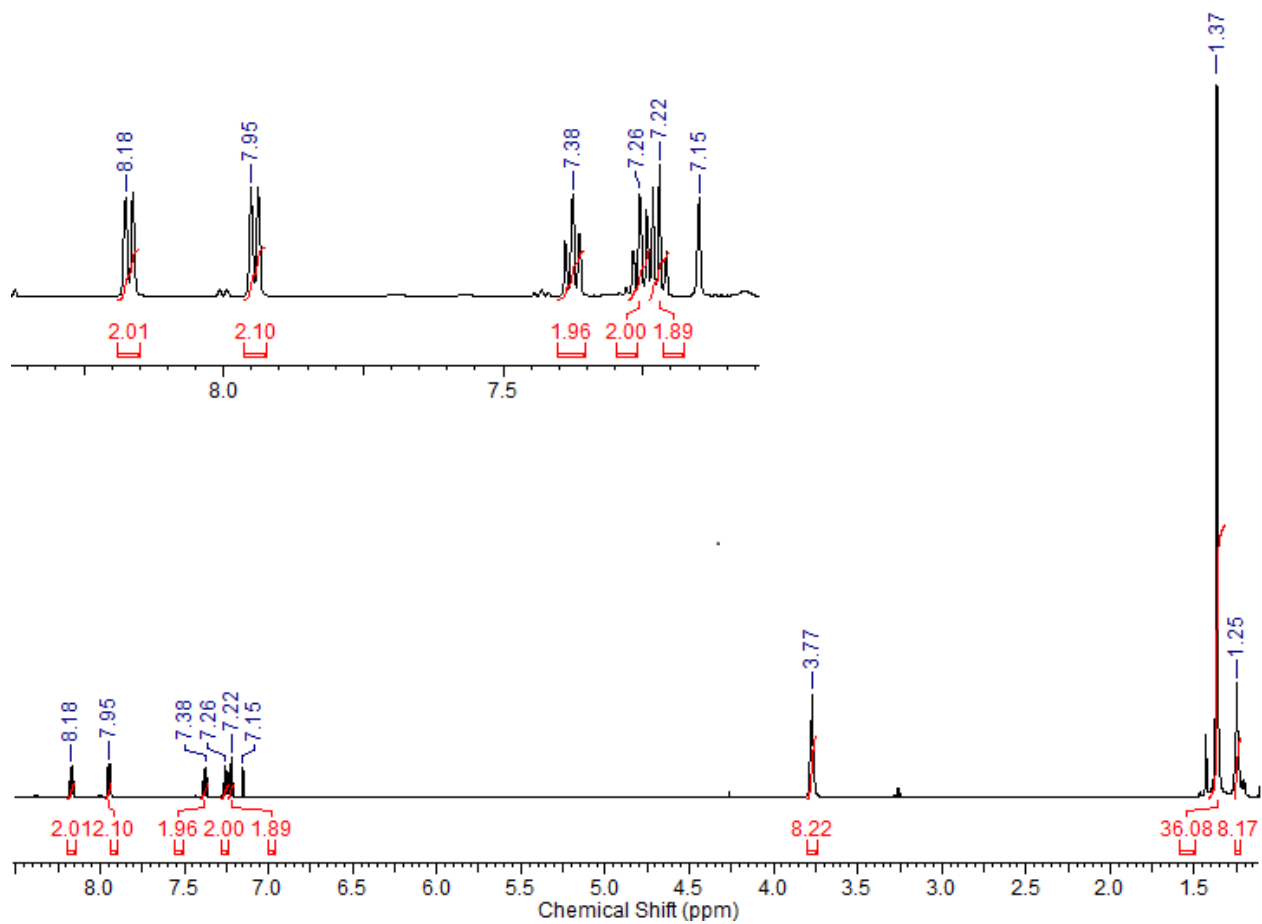


Figure S1. ^1H NMR of $\text{Mg}(\text{OR})_2(\text{THF})_2$ (**1**) (C_6D_6 , 600 MHz).

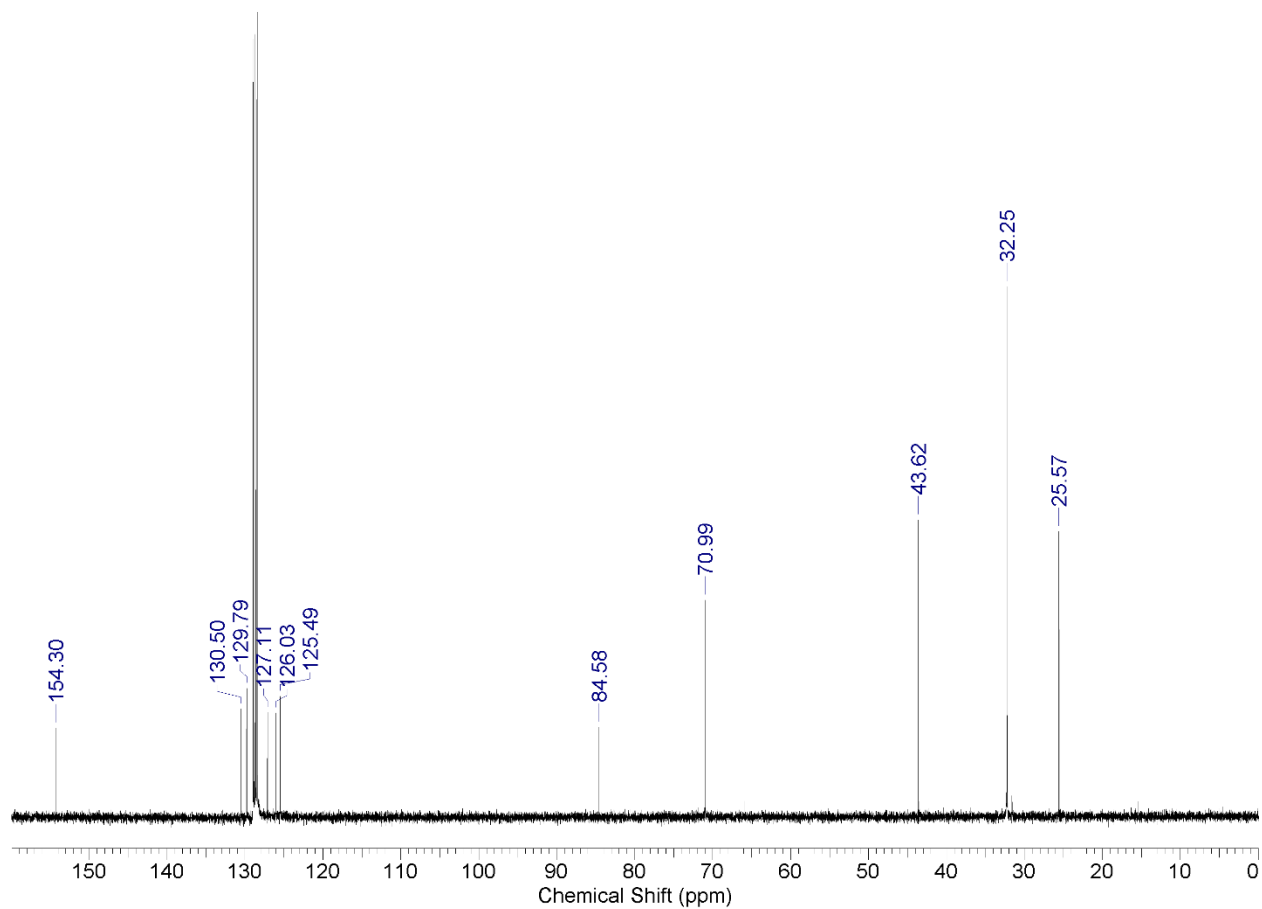


Figure S2. ^{13}C NMR of $\text{Mg}(\text{OR})_2(\text{THF})_2$ (**1**) (C_6D_6 , 150 MHz).

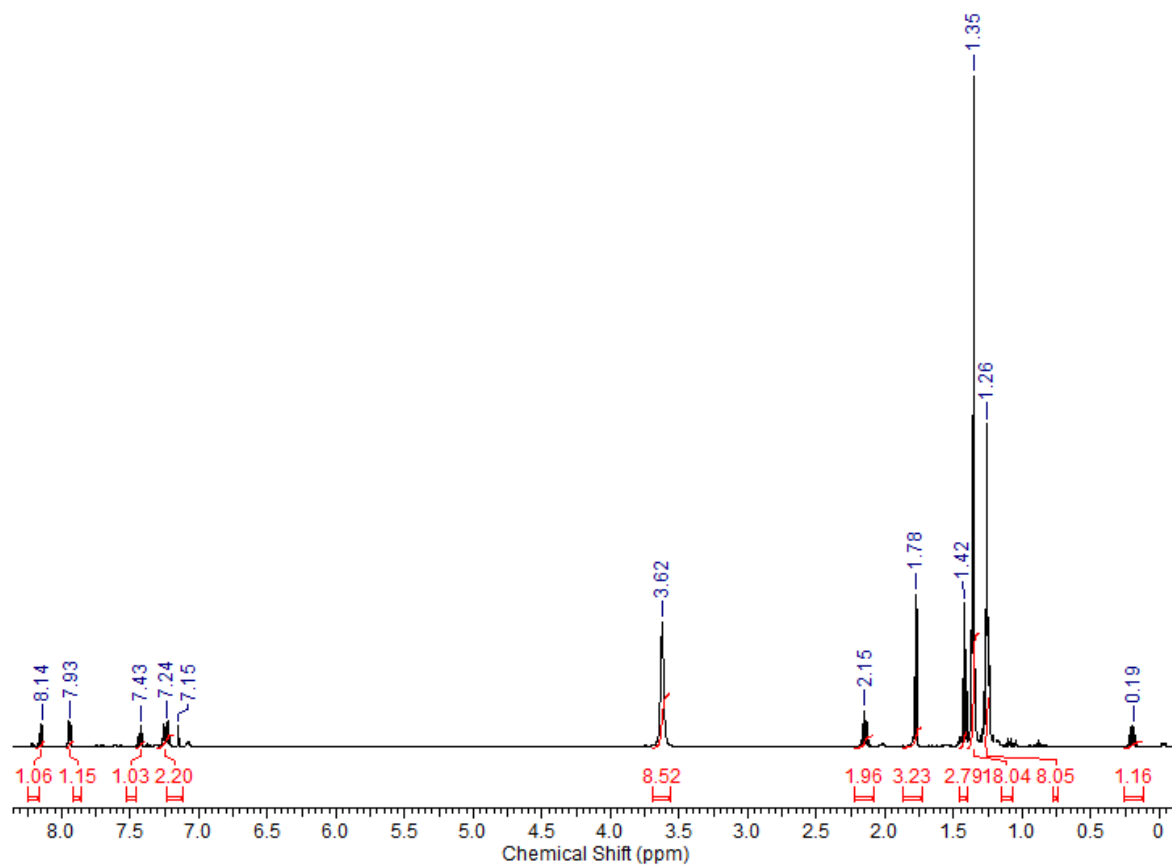


Figure S3. ^1H NMR of $\text{Mg}(\text{OR})(\text{sec-butyl})(\text{THF})_2$ (**2**) (C_6D_6 , 600 MHz).

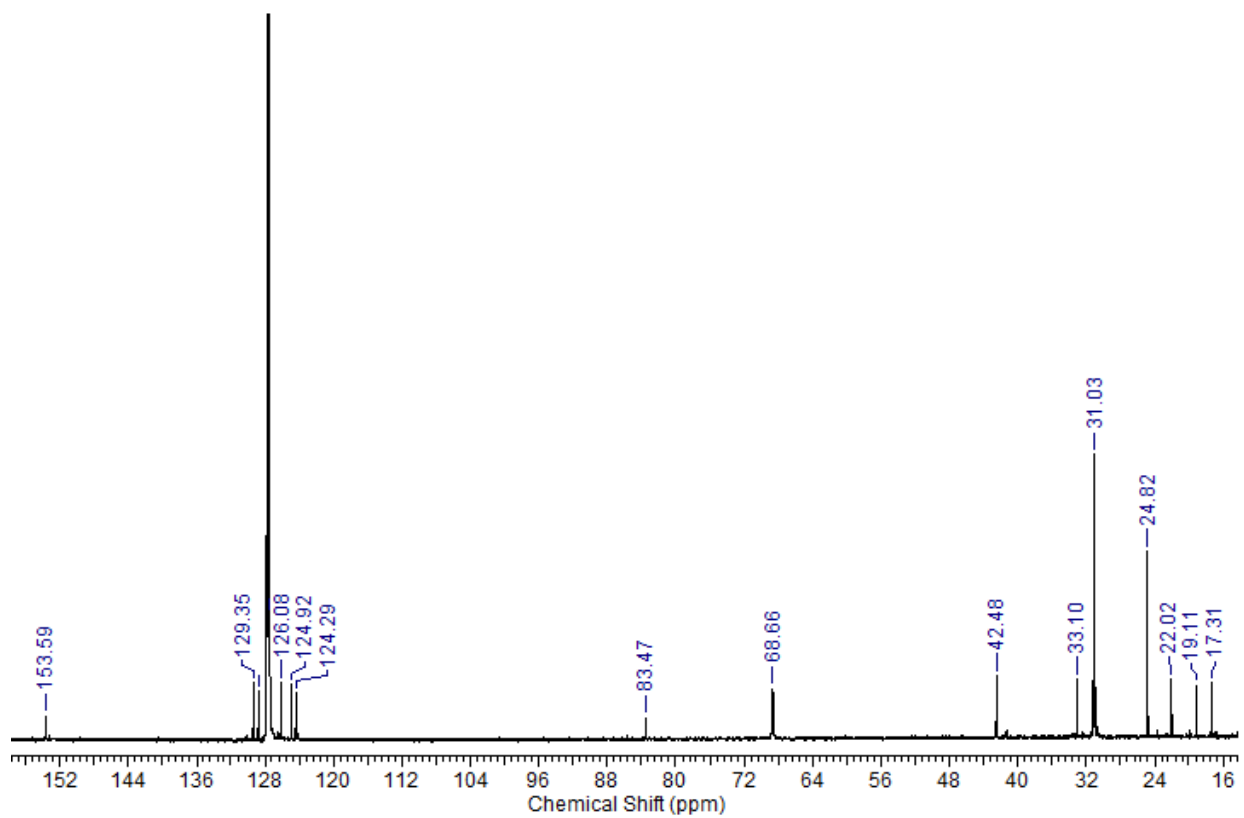


Figure S4. ^{13}C NMR of $\text{Mg}(\text{OR})(\text{sec-butyl})(\text{THF})_2$ (**2**) (C_6D_6 , 150 MHz).

3. X-ray crystallographic details

The structures of $\text{Mg}(\text{OR})_2(\text{THF})_2$ (**1**) and $\text{Mg}(\text{OR})(\text{sec-Bu})(\text{THF})_2$ (**2**) were determined by X-ray crystallography. A Bruker APEXII/Kappa three circle goniometer platform diffractometer with an APEX-2 detector was used for data collection. A graphic monochromator was employed for the wavelength selection ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The data were processed, and the structure was solved using the APEX-2 software. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically. The structure of **1** exhibited crystallographic C_2 symmetry, containing only half of the molecule in the asymmetric unit. The structure of **2** contained disordered sec-butyl group; the disorder was modeled using two alternating positions. Detailed crystal and structure refinement data are given in Table S2.

Table S4. Experimental crystallographic parameters for **1** and **2**.

complex	1	2
formula	C ₃₈ H ₆₂ MgO ₄	C ₂₇ H ₄₈ MgO ₃
Fw, g/mol	607.21	448.98
temperature	100(2)	100(2)
cryst syst	orthorhombic	monoclinic
space group	<i>Fdd2</i>	<i>P21/c</i>
color	Colorless	Colorless
Z	16	4
<i>a</i> , Å	21.017(2)	8.7017(3)
<i>b</i> , Å	36.775(4)	27.6498(10)
<i>c</i> , Å	9.2521(10)	11.5771(4)
<i>α</i> , deg	90.00	90.00
<i>β</i> , deg	90.00	104.557(2)
<i>γ</i> , deg	90.00	90.00
<i>V</i> , Å ³	7151.0(13)	2696.03(16)
<i>d</i> _{calcd} , g/cm ³	1.128	1.094
<i>μ</i> , mm ⁻¹	0.086	0.089
2 <i>θ</i> , deg	51.48	55.20
<i>R</i> ₁ ^{<i>a</i>} (all data)	0.1009	0.0712
<i>wR</i> ₂ ^{<i>b</i>} (all data)	0.1065	0.1344
<i>R</i> ₁ ^{<i>a</i>} [(<i>I</i> >2 <i>σ</i>)]	0.0525	0.0496
<i>wR</i> ₂ ^{<i>b</i>} [(<i>I</i> >2 <i>σ</i>)]	0.0917	0.1218
GOF (<i>F</i> ²)	1.004	1.014

^a $R_1 = \sum ||F_o - |F_c|| / \sum |F_o|$. ^b $wR_2 = (\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$. ^c $GOF = (\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

4. Selected Characterization Data for PLA

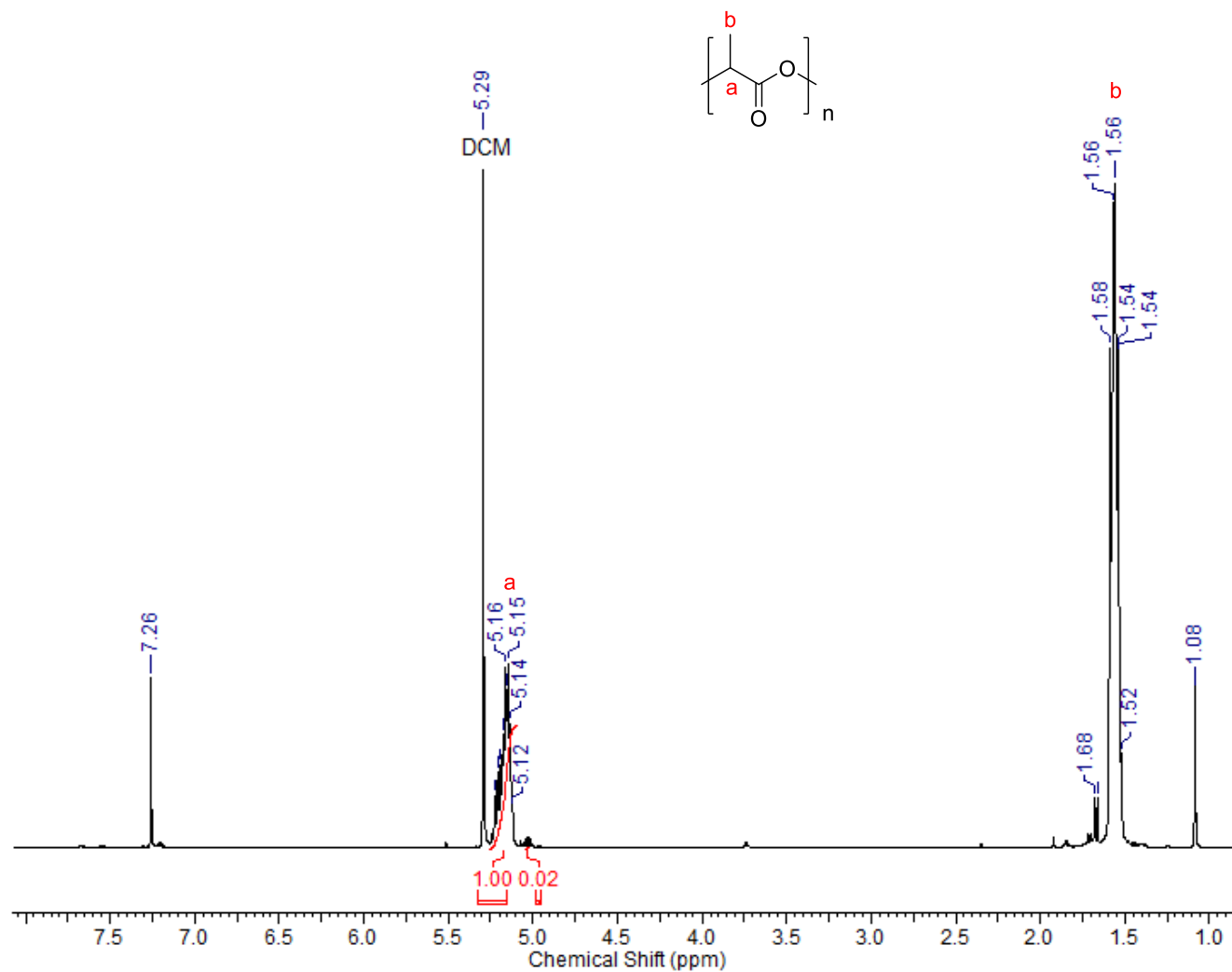


Figure S5. Typical ^1H NMR spectrum demonstrating conversion of lactide to PLA.

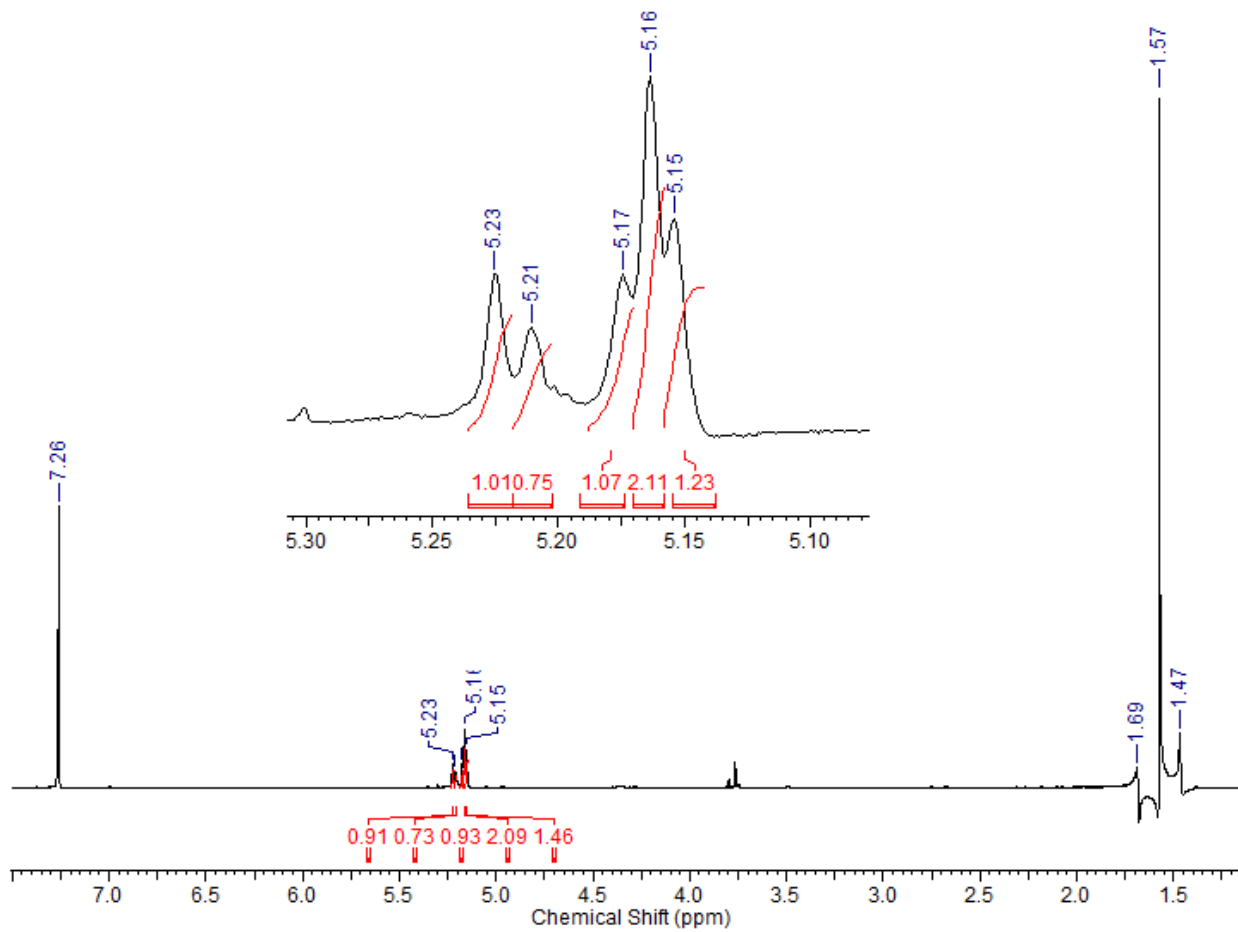


Figure S6. Typical ¹H NMR spectrum of PLA, indicating the atactic nature of the resulting polymer.

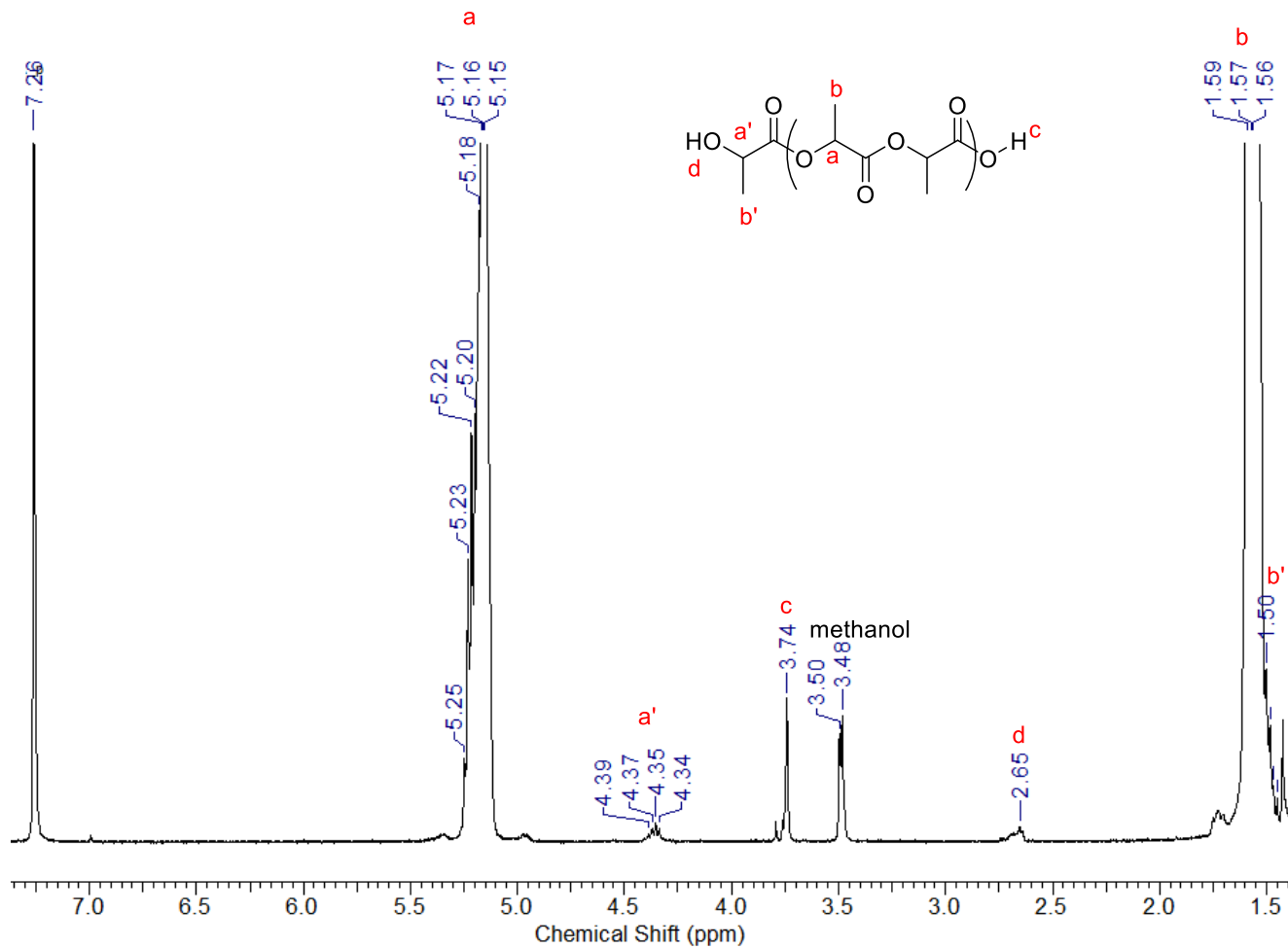
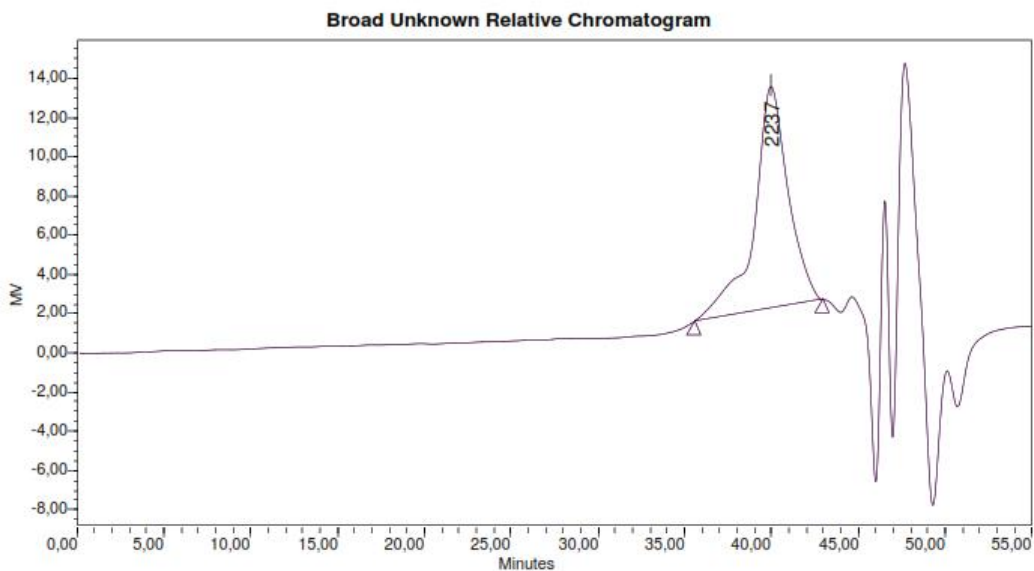


Figure S7. ^1H NMR spectrum demonstrating end group analysis of PLA synthesized by $\text{Mg}(\text{OR})_2(\text{THF})_2$.

SAMPLE INFORMATION			
Sample Name:	FSM105	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	19/09/2019 23.12.42
Vial:	11	Acq. Method:	MG_F1A_R35C_UV254_S19a
Injection #:	1	Date Processed:	20/09/2019 14.05.22
Injection Volume:	100,00 ul	Channel Name:	410
Run Time:	55,00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name:	2019_Settembre19



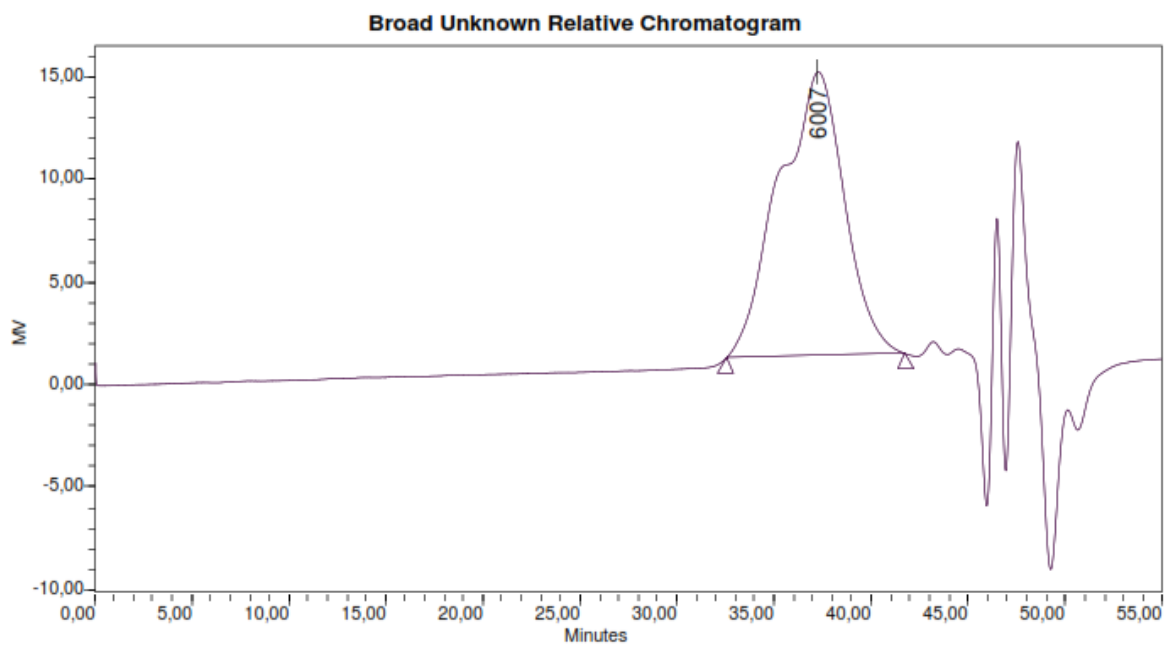
Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	2066	2563	2237	3313	4340	1,240844	1,292320	1,693239

Figure S8. GPC trace of polymer obtained in run 7 of Table 1.

SAMPLE INFORMATION

Sample Name:	FSM106	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	20/09/2019 0.09.42
Vial:	12	Acq. Method:	MG_F1A_R35C_UV254_S19a
Injection #:	1	Date Processed:	20/09/2019 14.05.33
Injection Volume:	100,00 ul	Channel Name:	410
Run Time:	55,00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name:	2019_Settembre19



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	5896	7884	6007	10194	12528	1,337259	1,293016	1,588997

Figure S9. GPC trace of polymer obtained in run 2 of Table 1.

5. Characterization Data for the DHC/LO copolymers

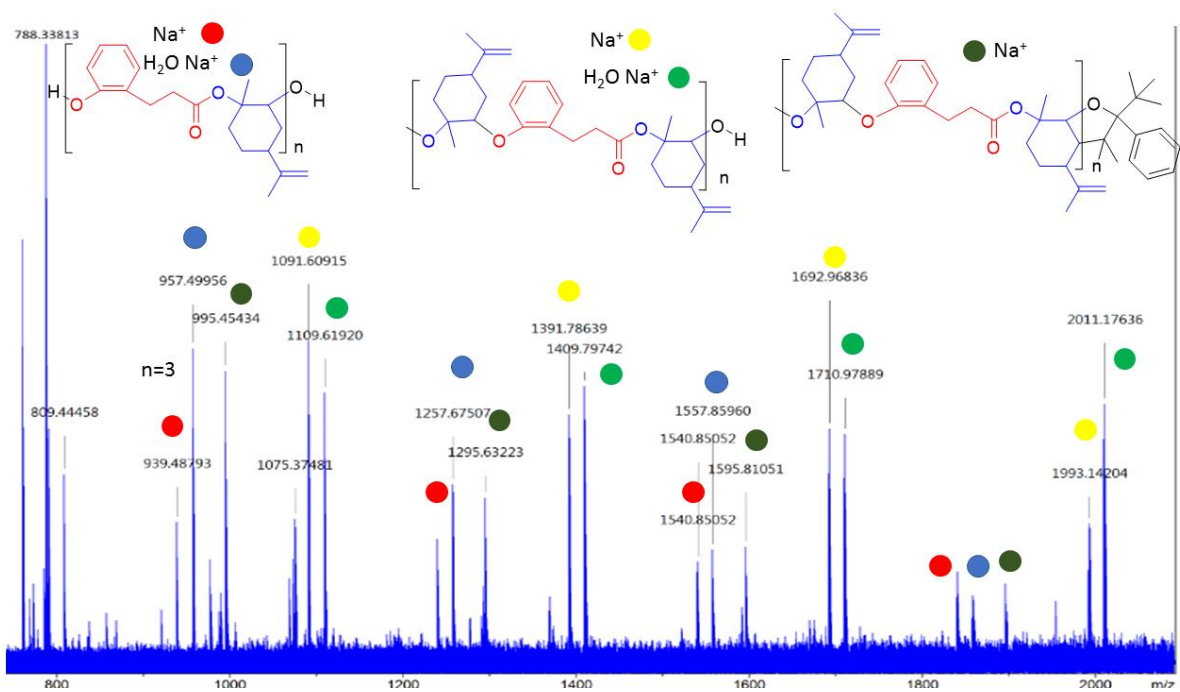


Figure S10. MALDI-ToF-MS spectrum of DCH/LO copolymer synthesized by 1.

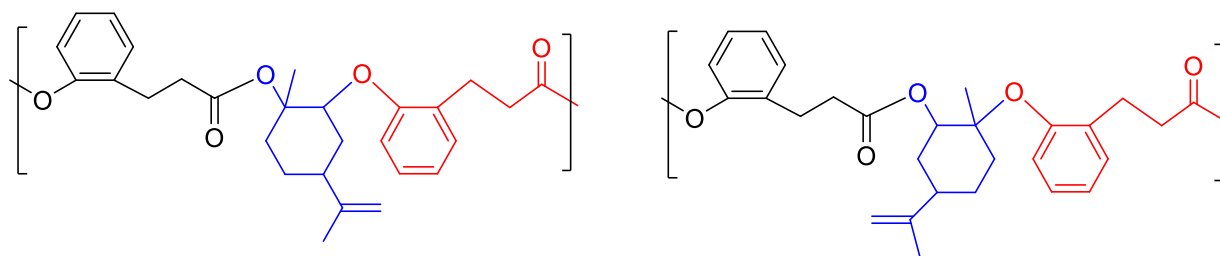


Figure S11. Regioisomers for DCH/LO sequences

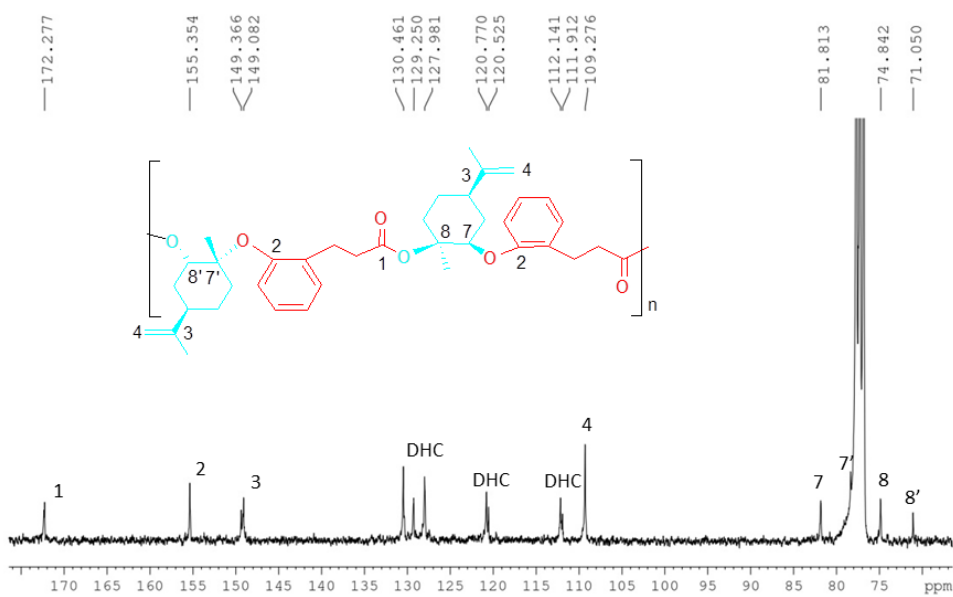


Figure S12. ^{13}C NMR spectrum of DCH/LO copolymer synthesized by **1**.

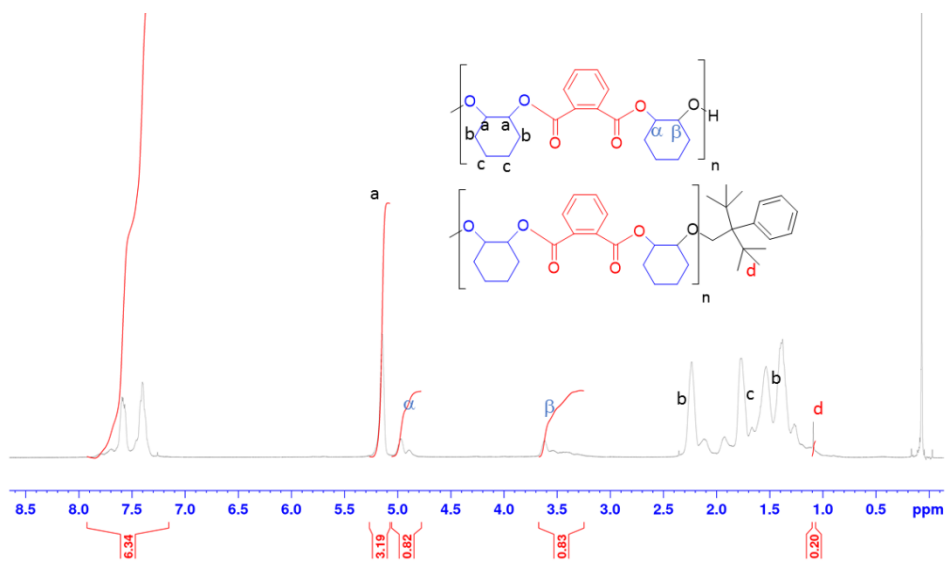


Figure S13. ^1H NMR spectrum of CHO/PA copolymer obtained in the absence of alcohol

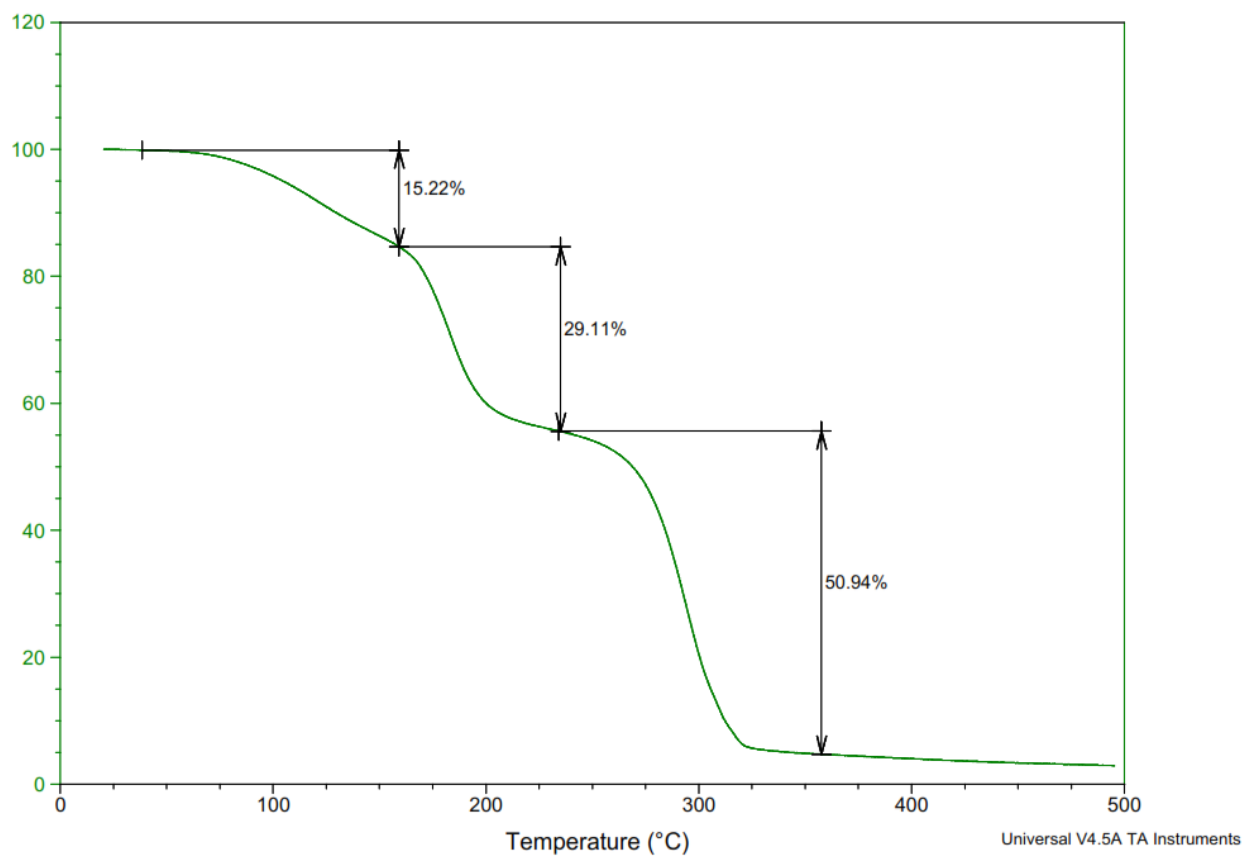


Figure S14 TGA analysis of the of DCH/LO copolymer.

6. References

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