SUPPORTING INFORMATION

Rediscovering the Isospecific Ring-Opening Polymerization of Racemic Propylene Oxide with Dibutylmagnesium

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EXPERIMENTAL SECTION

General Experimental Details. All reactions were performed under argon with rigorous exclusion of moisture and air using standard Schlenk and glove box techniques. $^{n}Bu_2Mg$ was purchased from Sigma Aldrich as a 1.0 M solution in heptane and used without further purification. Propylene oxide (PO) was also purchased from Sigma Aldrich and was dried over calcium hydride and distilled prior to use.

Instruments. *NMR:* ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance 300 spectrometer with a QNP probe head (^{1}H: 300 MHz, ^{13}C: 75 MHz) or Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz). The calibration of the spectra were carried out on referenced with residual solvent shifts ($CDCl_3$, ^{1}H = 7.26, ^{13}C = 77.16) and were reported as parts per million relative to $SiMe_4$. All the NMR samples were measured at 297 K. *Mass-spectrometry*: ESI-TOF spectra were recorded using a Waters Q-Tof micro mass spectrometer. *GPC* measurements were performed on an HP1090 II chromatograph with a DAD detector (Hewlett–Packard) at 40 °C with a flow of 0.9 ml/min and THF as the eluent. The columns used of the measurements were connected three PSS SDV gel columns with molecular weight ranges of 102, 103, and 104 g/mol. Number average molecular weights (M_n) and MWDs (M_w/M_n) of polymers were measured relative to polystyrene standards. *Differential scanning calorimetry* (DSC) measurement was performedon a DSC 1 STARe device from Metler Toledo. The heating and cooling rate was 10 °C /min. Ramp method was used for these analyses and 10-15 mg samples were taken. The *optical rotation* of the polymer was measured at room temperature with a tungsten halogen lamp using a Modular Circular polarimeter (Anton Paar, MCP-200), cell length 1 dm, measurement accuracy 0.001° in THF solution. The specific rotation was measured and compared to the reported values.[1] *Infrared spectroscopy* analysis was performed using the ATR-IR spectrometer Nicolet 6700 (Thermo Electron), spectral range of 4000-400 cm^{-1} and maximum resolution 0.5 cm^{-1}. *Powder X-Ray Diffraction* data were collected on a Stoe STADI-P powder diffractometer equipped with a position sensitive detector using Ge(111) monochromatized Cu-Kα1 radiation (λ = 1.54056 Å, 40 kV, 40 mA). The sample was cooled with liquid nitrogen and carefully grinded to obtain a fine powder. A specimen of the powder was fixed between two polymeric foils and finally measured in transmission geometry. The diffraction data were collected in the range of 2° and 60° of 2θ by a step wide of 0.1° and a counting time of 100 s per step. Primary data treatment was done with the PanalyticalHighScorePlus Software package. Peak positions and profile were fitted with Pseudo-Voigt functions. Cell indexing was done with the implemented Treor feature.[2] Cell parameters were refined by least-square methods.

General Procedure for the Polymerization of *rac*-PO. The polymerizations with different catalyst to monomer ratios were performed as follows: Under argon atmosphere 10 g (0.172 mol.) of dry *rac*-PO was added to an oven-dried Schlenk flask containing a stirring bar. The flask was cooled in an icy water bath. The amount of $^{n}Bu_2Mg$ (1 M in heptane) corresponding to each particular catalyst to monomer ratio) was added dropwise to the Schlenk flask containing the cold PO with an air-tight syringe, and the resulting mixture was stirred for 10 minutes. Then, the reaction mixtures were heated at 40 °C and stirred for the required period of time for complete conversion. Unreacted PO was removed under vacuum and the reaction was quenched with 10 ml of water acidified with HCl. The resulting polymer was filtered off and dried overnight under vacuum. The conversion was determined by the mass of the dry polymer. After that, the polymer was dissolved in boiling acetone and filtrated hot through neutral alumina. The filtrated solution was stored at 0 °C for 6 hours. The resulting white precipitate was filtrated and dried in vacuum until a constant weight. These polymers were characterized by ^{1}H, ^{13}C and DEPT. Data concerning molecular weights and the polydispersity indices of the polymer samples were determined by using a GPC analysis and number average molecular weights (M_n) and polydispersity (M_w/M_n) of polymers were measured relative to polystyrene standards (Table 1). The glass-transition temperature (T_g) and melting-transition temperature (T_m) of the polymers were obtained from DSC analysis. The amorphous part of the polymer was collected form the filtrated acetone solution. The solvent was evaporated through rotary evaporator and dried overnight under vacuum a viscus liquid product was obtained. It was characterized by ^{1}H, ^{13}C and DEPT.

Polymerization of *rac*-PO with a 200:1 monomer to catalyst ratio. The reaction was performed following the standard procedure using 10 g (0.172 mol.) of dry *rac*-PO

and 0.86 ml (0.86 mmol) of $^{n}Bu_2Mg$ (1 M in heptane). The polymer was obtained as a white solid (9.4 g, 93 % yield). After recrystallization in acetone a crystalline white powder was obtained (8.7g, 86 % yield). For the crystalline part (Figures S1-S6): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 3.50-3.58 (m, 2H), 3.36-3.43 (m, 1H), 1.13 (d, 6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 75.67, 73.57, 17.60. For the amorphous part (Figures S7-S9): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 3.52 (m), 3.38 (m), 1.11 (bs). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 75.53, 75.38, 75.34, 75.14, 73.42, 72.94, 72.32, 17.45, 17.34

Determination of Polymerization Kinetics. In order to determine the reaction kinetics, polymerizations were carried out using 0.86 ml (0.86 mmol) of $^{n}Bu_2Mg$, and 10 g of PO at 40 °C under an argon atmosphere in a sealed round-bottom Schlenk flask. At different time intervals, 0.3 ml aliquots were taken from the reaction mixture with an airtight syringe, and carefully dissolve in a previously cold CDCl3 (0°C) containing NMR tube. The samples obtained at various time intervals were analyzed by ^{1}H NMR for the determination of conversion. The $\ln\{[M]_0/[M]_t\}$ ratio was calculated by integration of the peak corresponding to the methine proton for the polymer and monomer. Apparent rate constants were obtained from the slopes of the best fit line.

Determination of the Polymerization Kinetics with Respect to the Catalyst

In order to determine the kinetic regime, with respect to the catalyst, the polymerizations were carried out using a defined quantity (1.72 mmol, 0.86 mmol, 0.43 mmol and 0.28 mmol) of $^{n}Bu_2Mg$, with 10 g (0.172 mol) of PO at 40 °C under an argon atmosphere in a sealed round-bottom Schlenk flask. At different time intervals, 0.2 ml aliquots were taken from the reaction mixture with an airtight syringe, and carefully dissolve in a previously cold $CDCl_3$ (0°C) containing NMR tube. The NMR tube was sealed immediately and analyzed through ^{1}H NMR for the determination of conversion. Initial rates depending on [catalyst] were determined by the Plots of [polymer] versus time (Table S1) using ^{1}H NMR analysis of aliquots taken at defined intervals. Reaction order of catalyst for the polymerization PO was determined by the plot of the initial rate versus the concentration of catalyst (Figure S15).

Table S1. Experimental data used for the plots to determine the rate law.

Entry	$[PO]_o$ (mol)	[Catalyst] (mmol)	Initial rate[a] (mol^{-1} h^{-1})
1	0.172	0.28	0.00515
2	0.172	0.43	0.00576
3	0.172	0.86	0.0079
4	0.172	1.72	0.01059

NMR SPECTRA

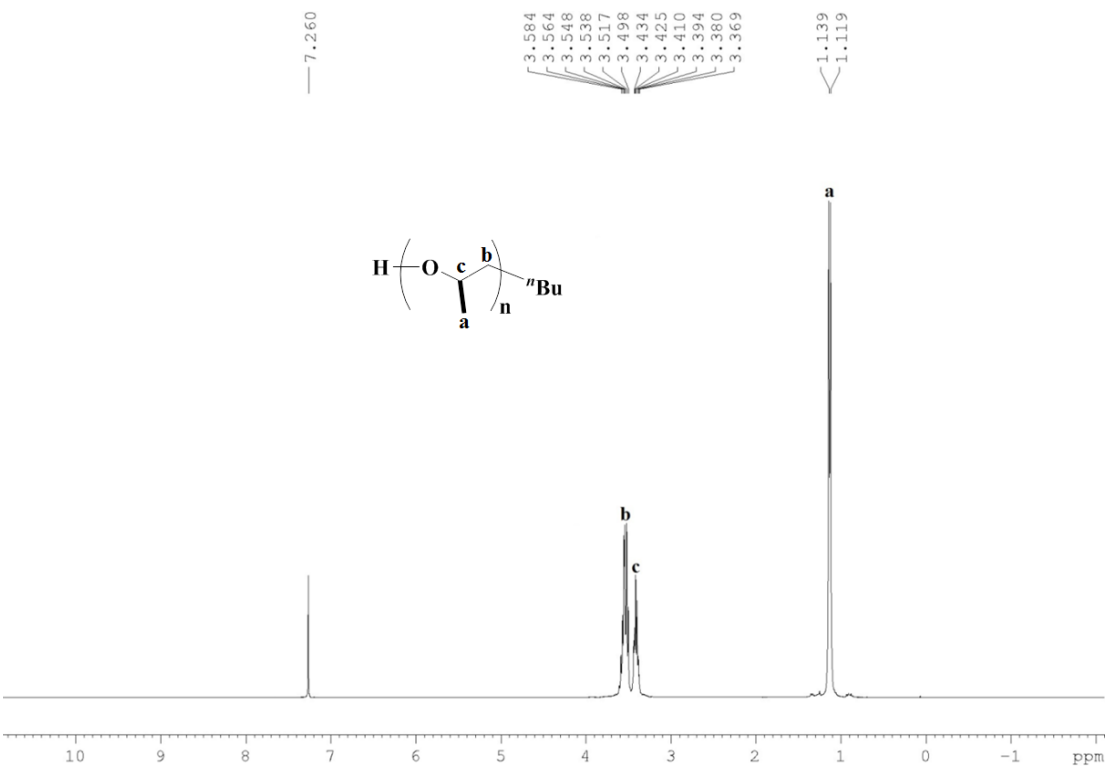
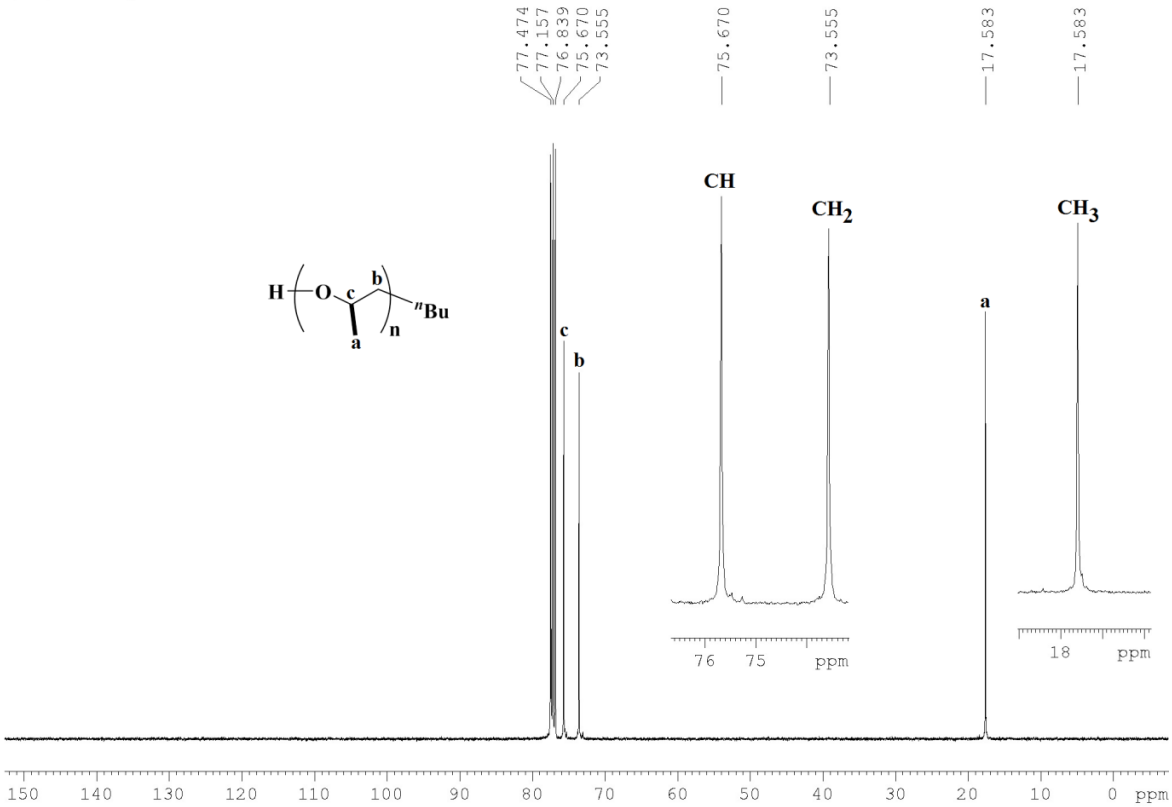


Figure S1. ^{1}H NMR ($CDCl_3$) spectrum of isotactic crystalline poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.



FigureS2. ^{13}C NMR ($CDCl_3$) spectrum of isotactic crystalline poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

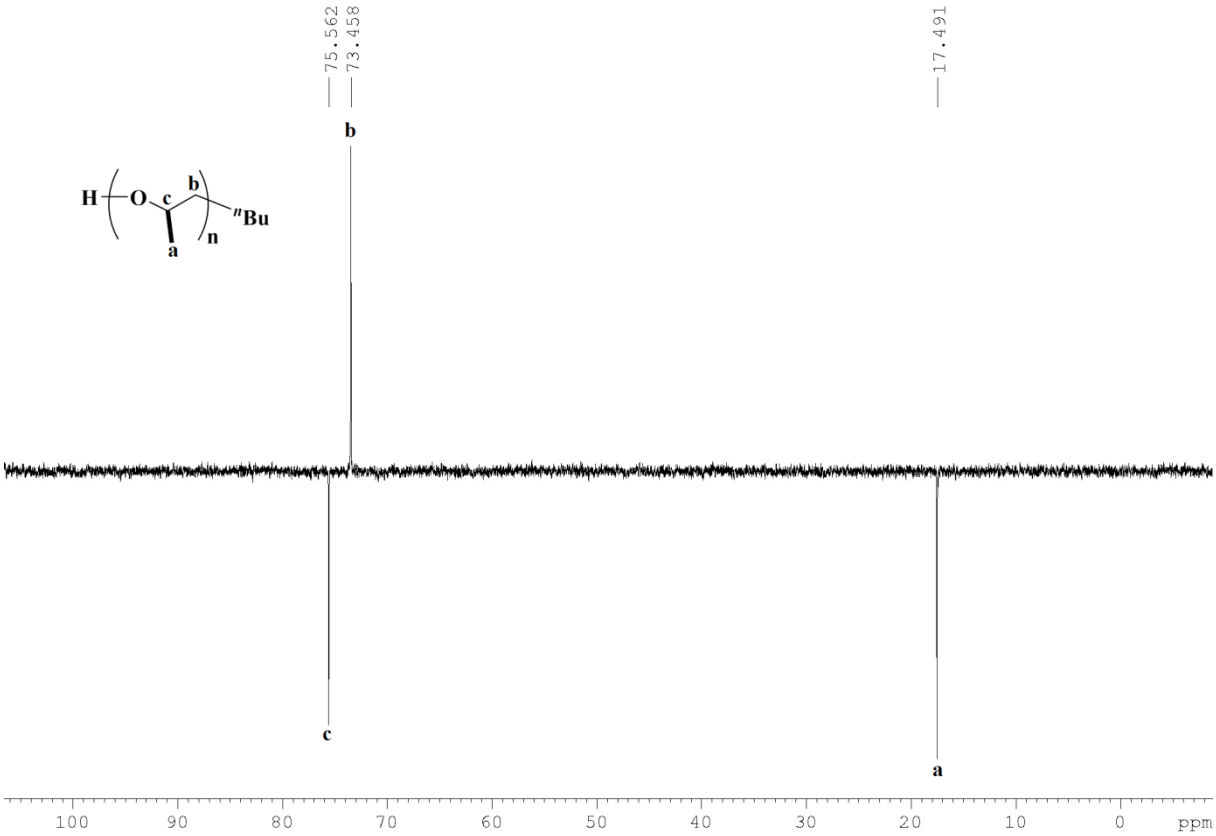


Figure S3. DEPT NMR ($CDCl_3$) spectrum of isotactic crystalline poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

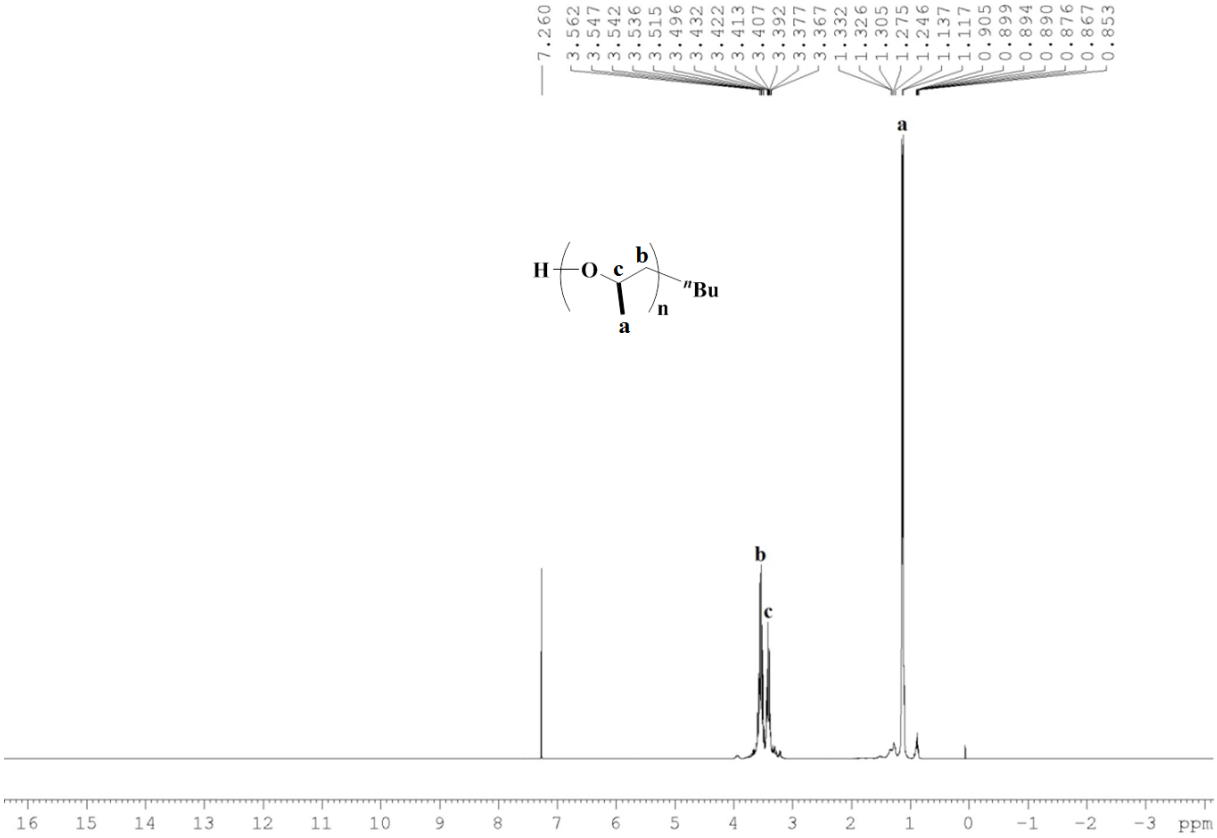


Figure S4. ^{1}H NMR ($CDCl_3$) spectrum of crude poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

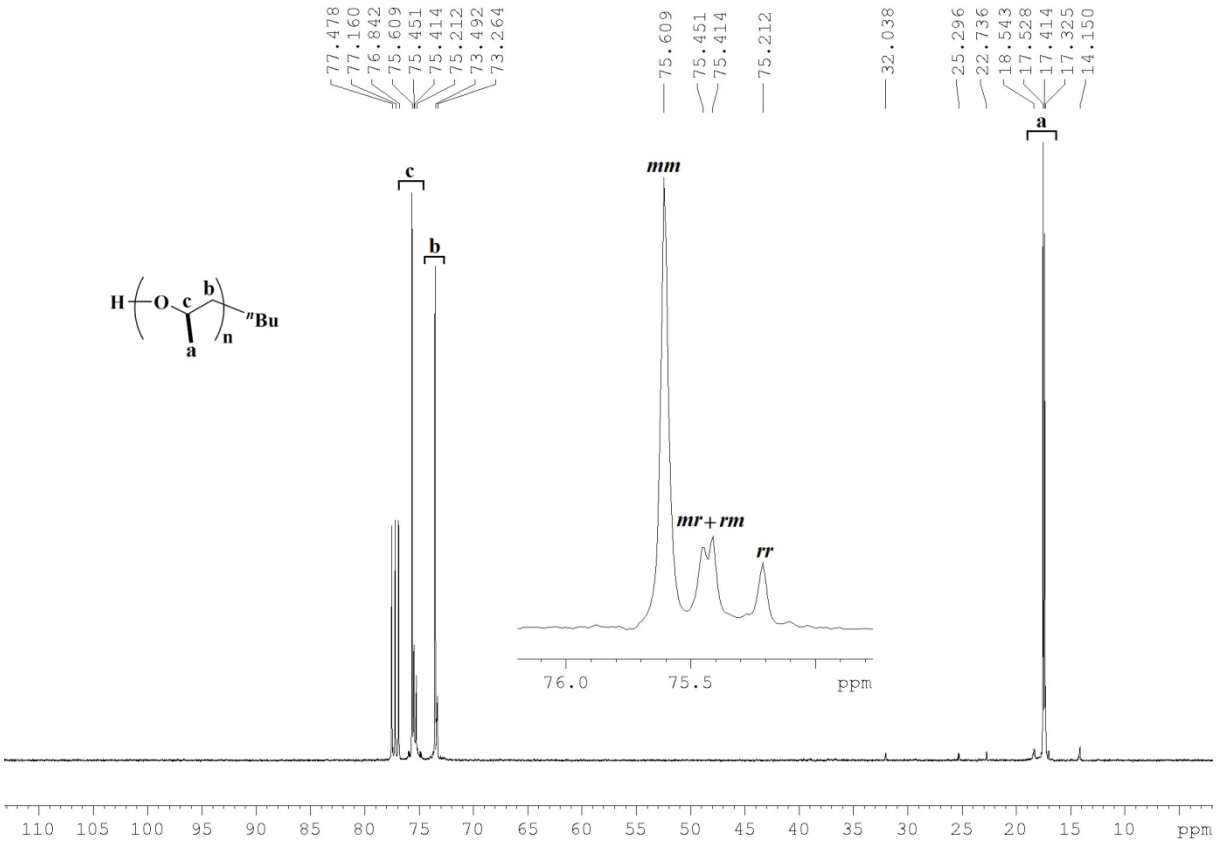


Figure S5. ^{13}C NMR ($CDCl_3$) spectrum of crude poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

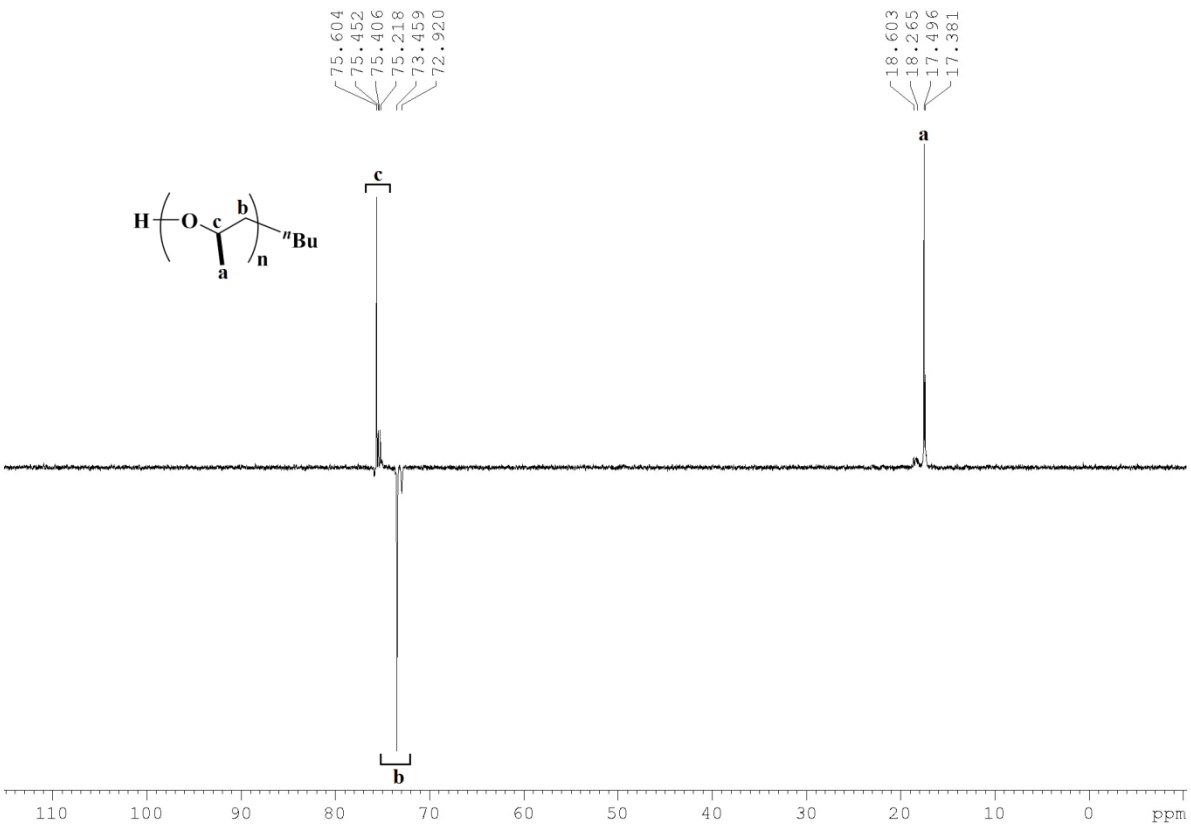


Figure S6. DEPT NMR ($CDCl_3$) spectrum of crude poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

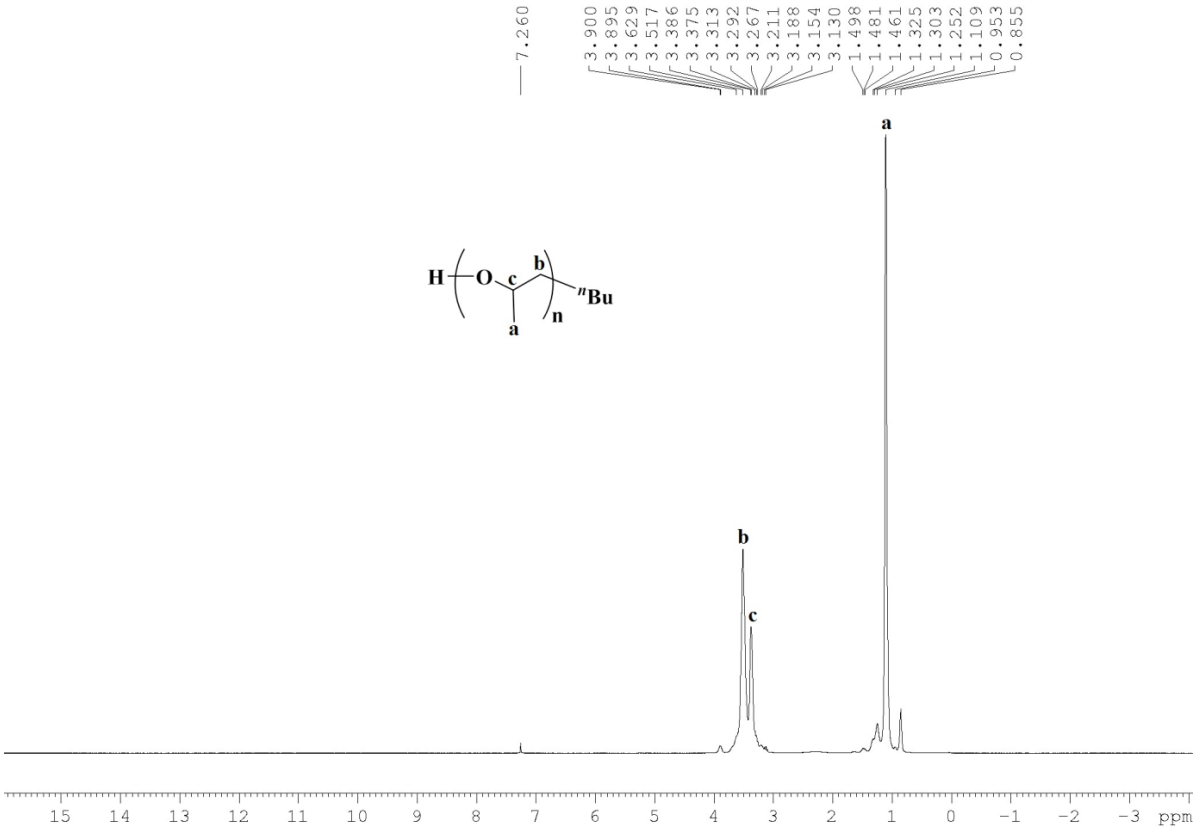


Figure S7. ^{1}H NMR ($CDCl_3$) spectrum of atactic, amorphous poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

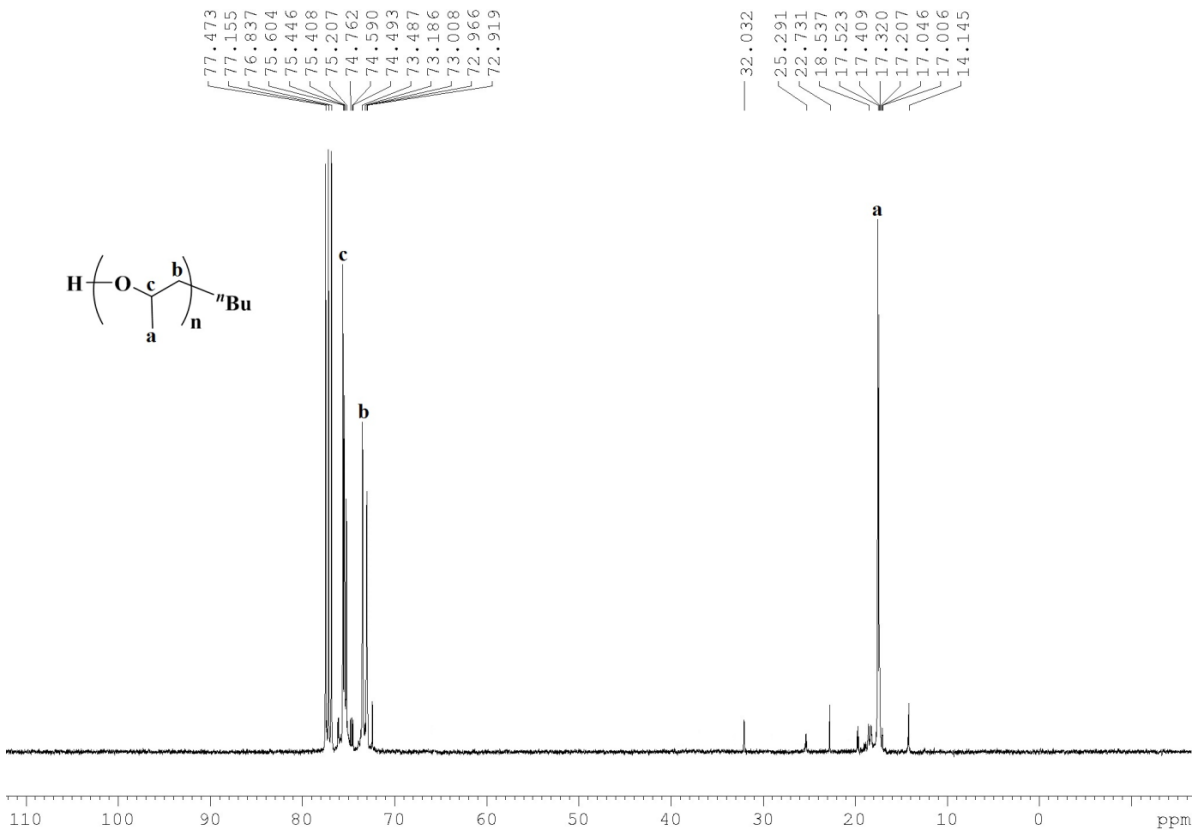


Figure S8. ^{13}C NMR ($CDCl_3$) spectrum of atactic, amorphous poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

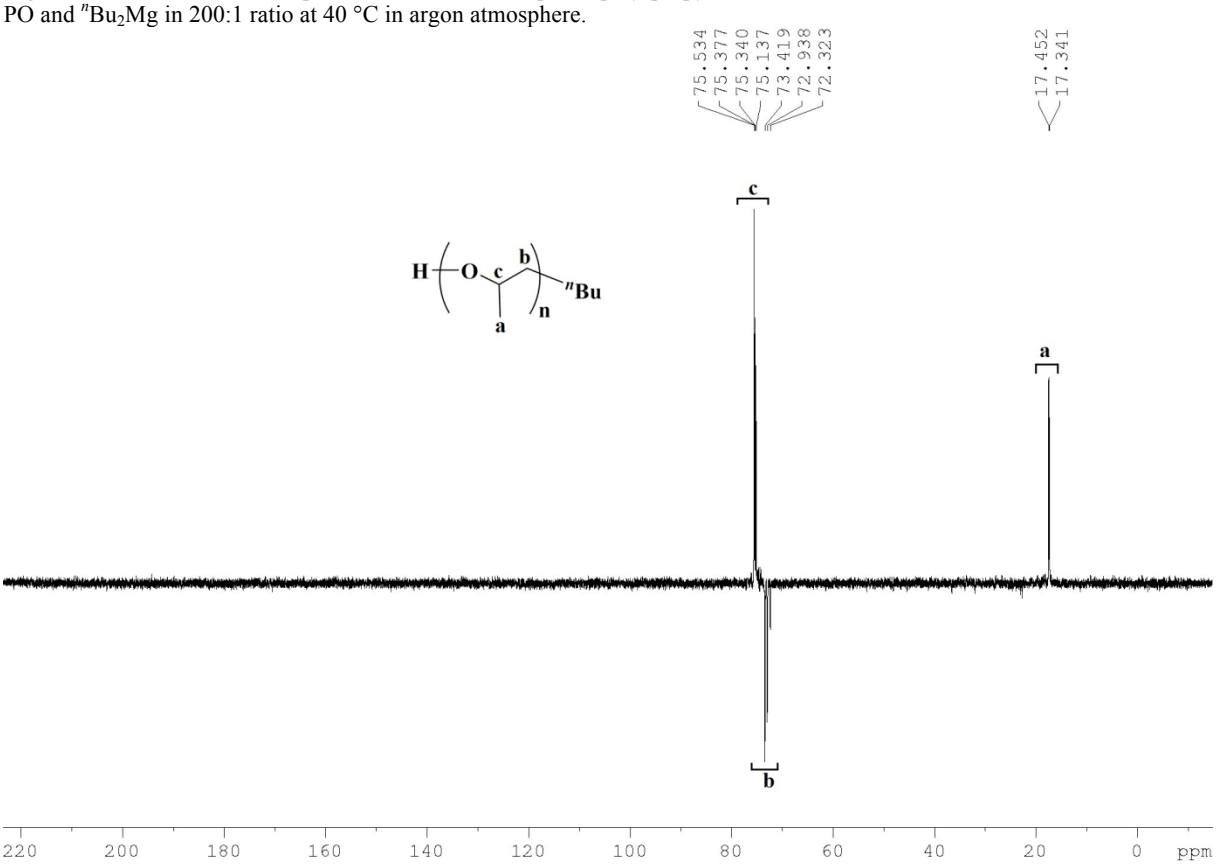


Figure S9. DEPT NMR ($CDCl_3$) spectrum of atactic, amorphous poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

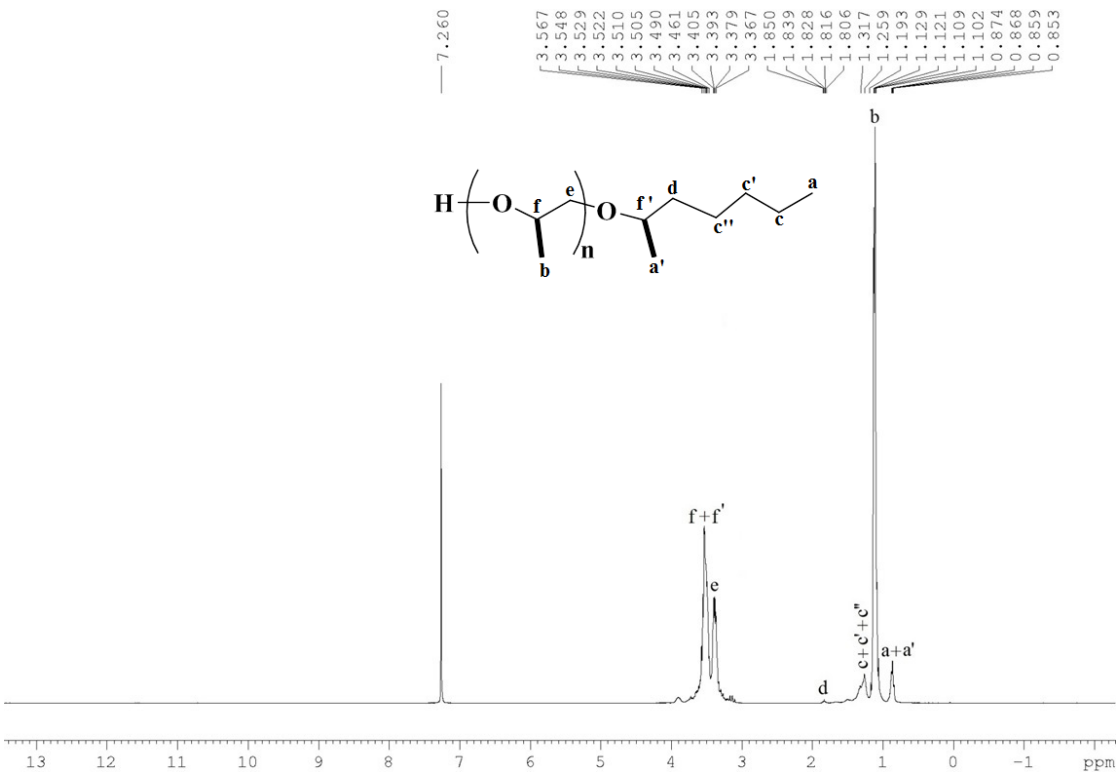


Figure S10. ^{1}H NMR ($CDCl_3$) spectrum of poly(propylene oxide) obtained from a reaction between PO and $^{n}Bu_2Mg$ in 30:1 ratio at 40 °C in argon atmosphere.

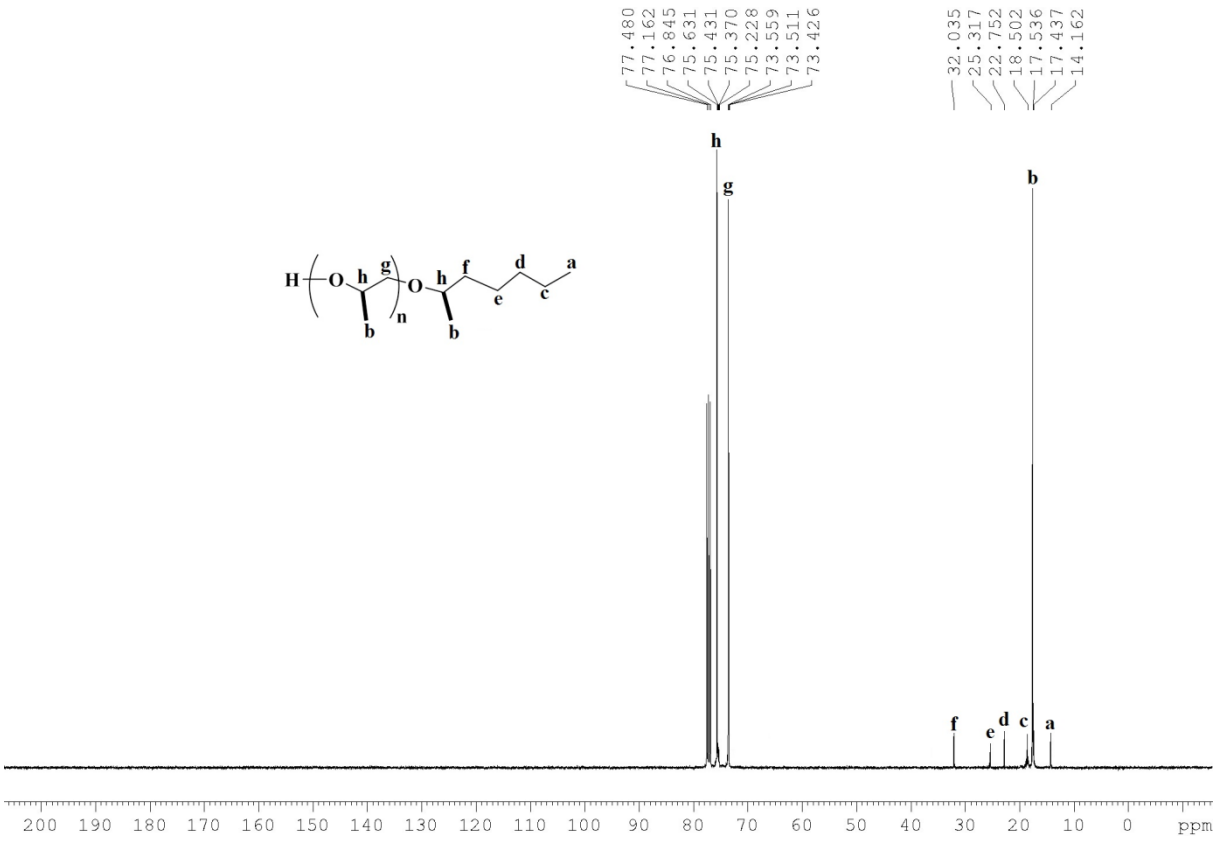


Figure S11. ^{13}C NMR ($CDCl_3$) spectrum ofpoly poly(propylene oxide) oligomer obtained from a reaction between PO and $^{n}Bu_2Mg$ in 30:1 ratio at 40 °C in argon atmosphere.

KINETIC STUDIES

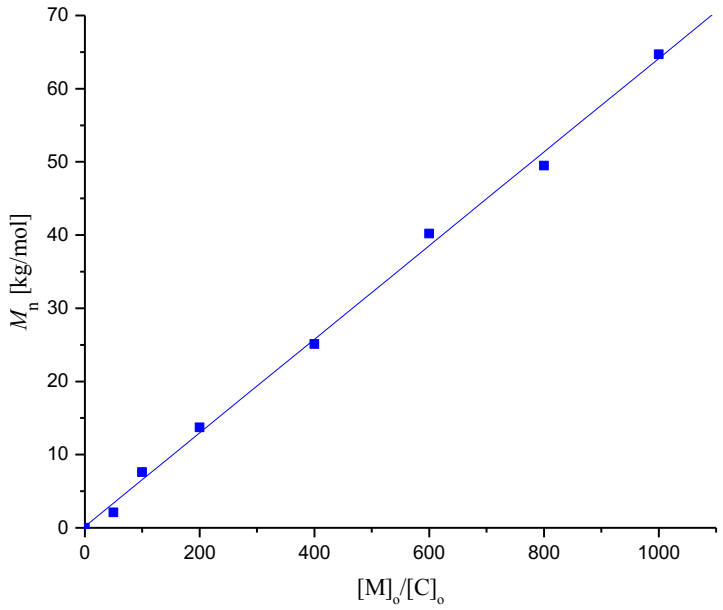


Figure S12. Plot of M_n vs. $[M]_0/[C]_0$ for PO using catalyst $^nBu_2Mg$.

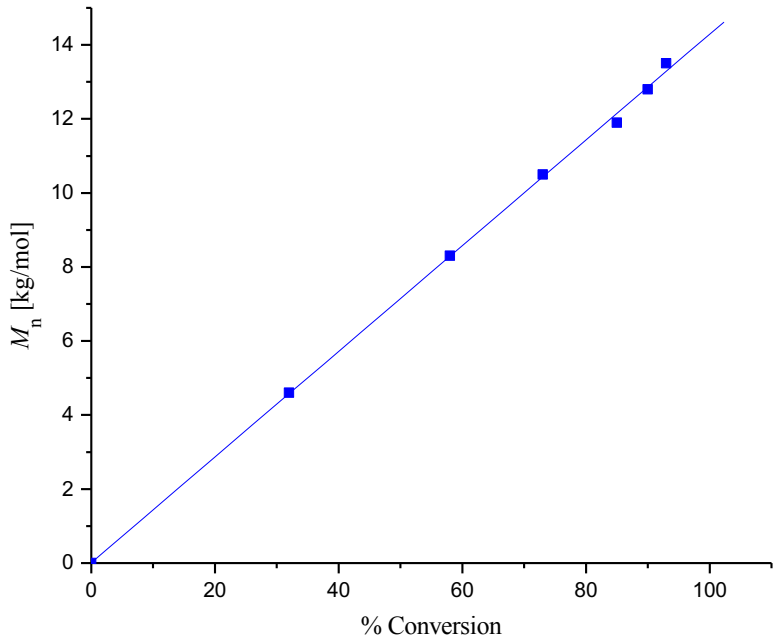


Figure S13. Plot of M_n vs. % Conversion for POusing $^nBu_2Mg$: $[M]_o/[C]_o$ = 200 at 40 °C.

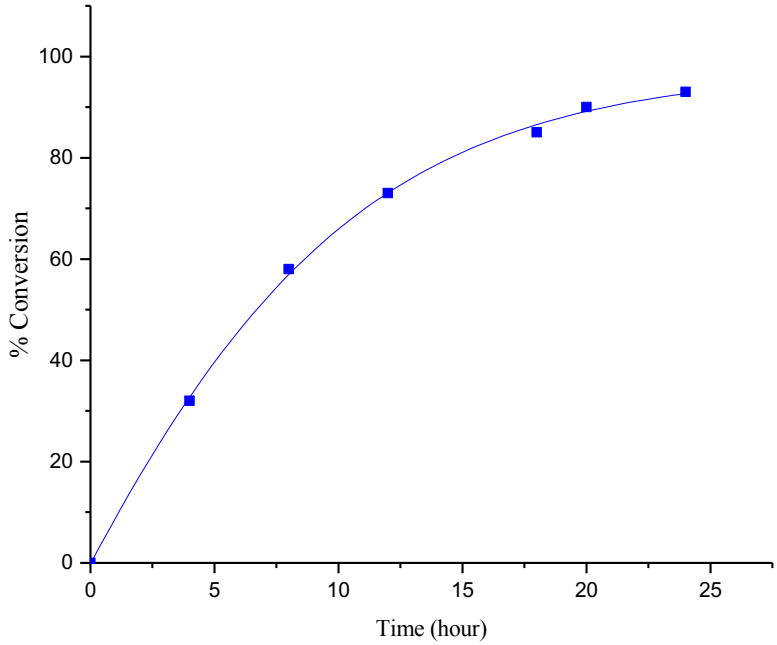


Figure S14. Plot of Conversion vs. time for PO using $^{n}Bu_2Mg$: $[M]_o/[C]_o$ = 200 at 40 °C.

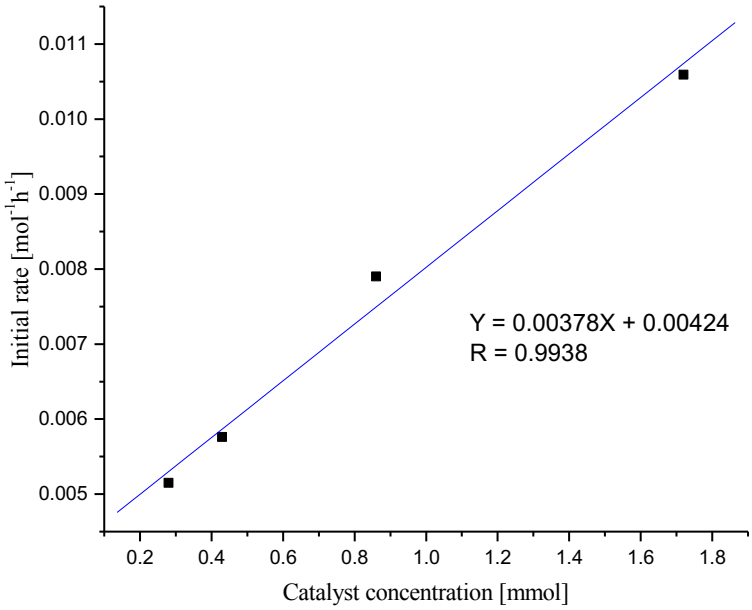


Figure S15. Plot of the initial rate vs. the concentration of catalyst for poly(propylene oxide) using $^{n}Bu_2Mg$ catalyst at 40 °C.

DSC THERMOGRAMS

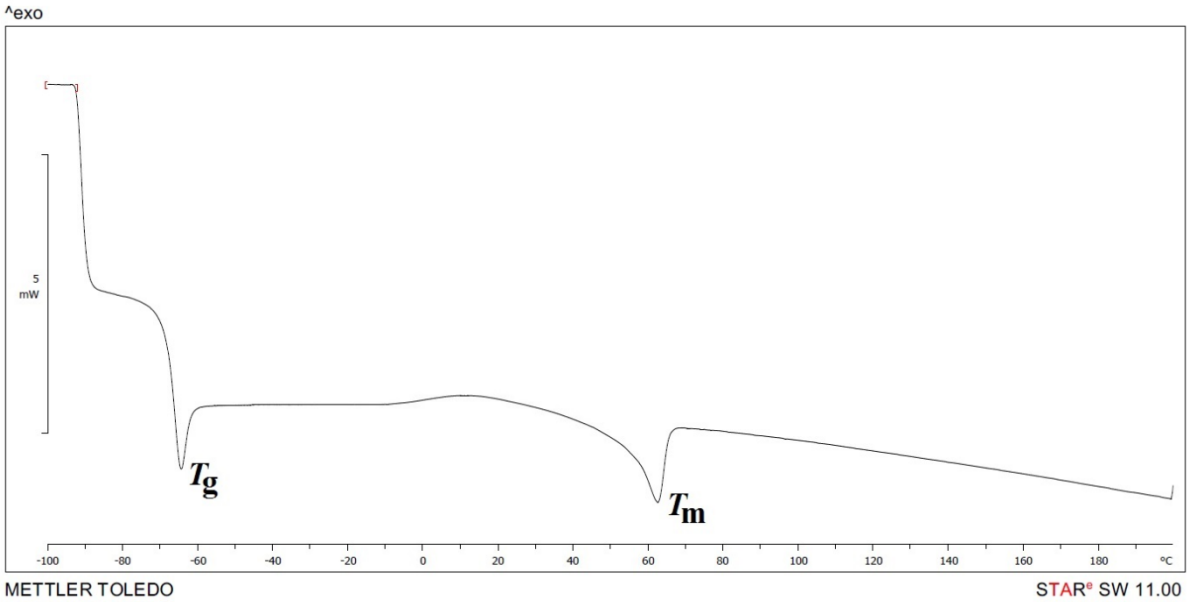


Figure S16. Differential scanning calorimetry (DSC) graph of isotactic poly(propylene oxide) obtained from a reaction between *rac*-PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere.

X-RAY POWDER DIFFRACTION

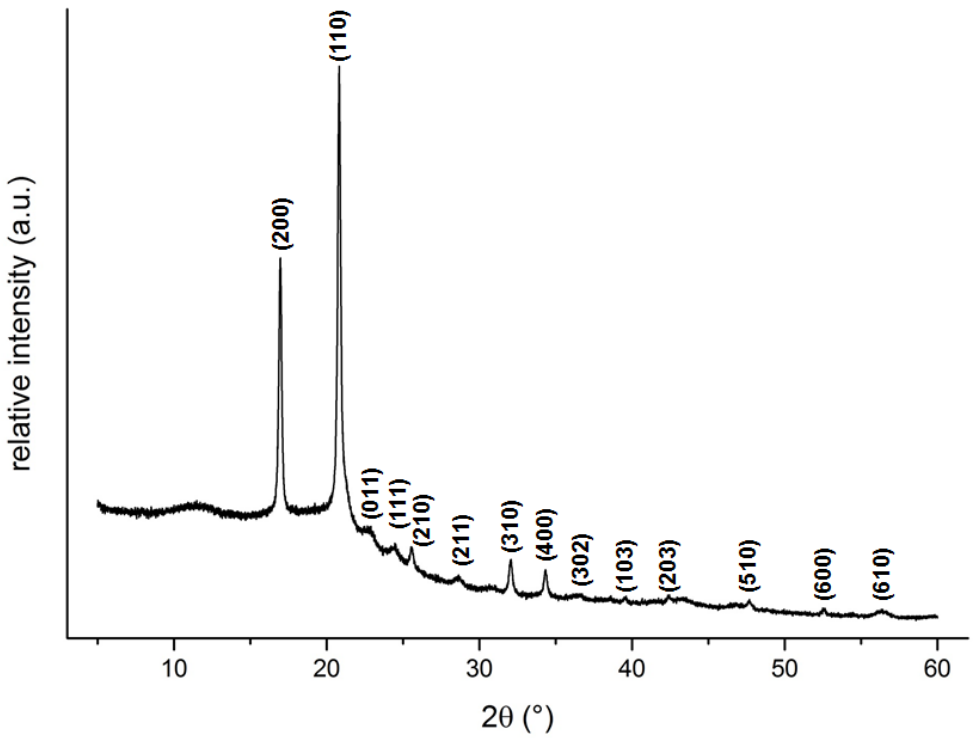


Figure S17. Powder X-ray diffraction pattern of the crude PPO obtained from a reaction between *rac*- PO and $^{n}Bu_2Mg$ in 200:1 ratio at 40 °C in argon atmosphere; orthorhombic cell with a = 10.39(5) Å, b = 4.67(2) Å, c = 6.98(3) Å; space group $P2_12_12_1$.

Table S2. Summary of profile fits and cell indexing for crystalline and crude poly(propylene oxide)

Sample Name	Crystalline PPO	Crude PPO
Profile	pseudo-Voigt	pseudo-Voigt
Rexp	1.669	2.184
Rp	2.337	1.97
Rwp	3.392	2.566
GOF	2.032	1.175
Index Method	Treor	Treor
Figure of Merit (FOM)	93	51
Number of Indexed Peaks	9	8
Number of unindexed lines	1	2
a [Å]	10.47(3)	10.44(2)
b [Å]	4.72(2)	4.67(1)
c [Å]	7.03(3)	6.97(1)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å^3]	347.17	338.65

Table S3. Indexed reflection peaks for crystallinepoly(propylene oxide) after precipitation in acetone

Position[°2θ]	**d-spacing [Å]**	**I_{Rel}**	**h**	**k**	**l**
16.94	5.23	61.7	2	0	0
20.78	4.27	100.00	1	1	0
20.91	4.25	12.6	2	0	1
22.82	3.89	2.2	0	1	1
24.40	3.65	2.3	1	1	1
25.52	3.49	4.8	2	1	0
28.57	3.12	1.7	3	0	1
30.64	2.92	0.6	2	0	2
32.00	2.79	7.9	3	1	0
34.29	2.61	5.5	4	0	0
36.37	2.47	1.0	3	0	2
38.44	2.34	0.5	0	2	0
39.45	2.28	0.7	1	0	3
41.33	2.18	0.7	1	2	1
42.34	2.13	1.2	2	0	3
43.31	2.09	1.3	0	1	3
46.60	1.95	0.7	3	0	3
47.13	1.93	0.2	1	2	2
47.60	1.91	1.6	5	1	0

48.30	1.88	0.3	3	2	1
52.50	1.74	1.0	6	0	0
54.20	1.69	0.3	6	0	1
56.27	1.63	1.2	6	1	0

Table S4. Indexed reflection peaks for crude poly(propylene oxide) before precipitation in acetone

Position[°2*θ*.]	**d-spacing [Å]**	**I_{Rel}**	**h**	**k**	**l**
16.95	5.225	59.4	2	0	0
20.81	4.264	100.0	1	1	0
21.19	4.189	5.7	2	0	1
22.84	3.891	2.1	0	1	1
24.48	3.633	2.51	1	1	1
25.56	3.482	4.7	2	1	0
28.62	3.116	1.8	3	0	1
30.74	2.906	0.9	2	0	2
32.05	2.791	7.8	3	1	0
34.33	2.610	6.0	4	0	0
36.39	2.467	1.1	3	0	2
38.42	2.341	0.8	0	2	0
39.53	2.278	1.0	1	0	3
41.42	2.178	0.7	1	2	1
42.39	2.130	1.2	2	0	3
43.28	2.089	1.7	0	1	3
47.06	1.929	1.3	1	2	2
47.67	1.906	1.3	5	1	0
52.54	1.740	1.4	6	0	0
56.31	1.632	1.5	6	1	0

IR SPECTRA

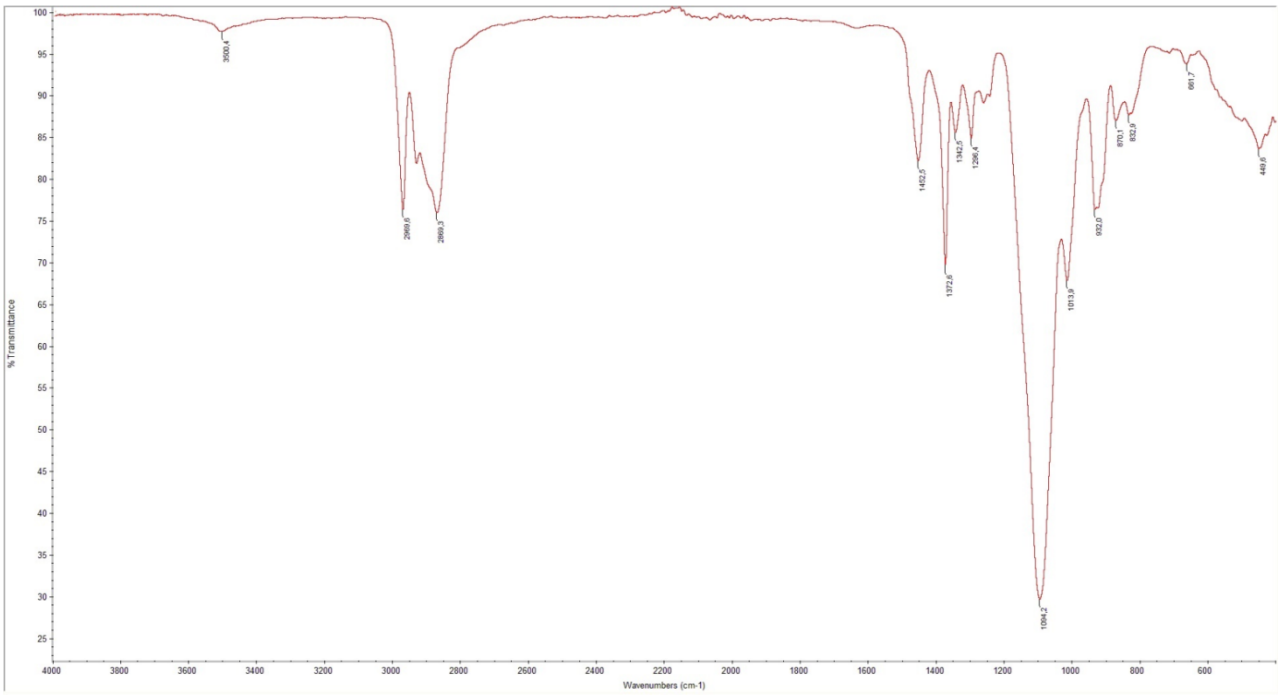
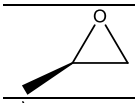
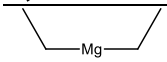
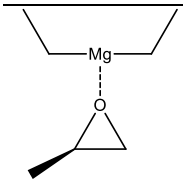
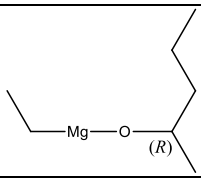


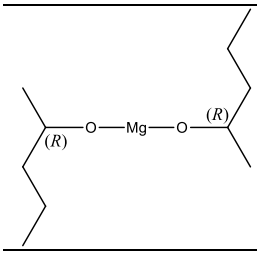
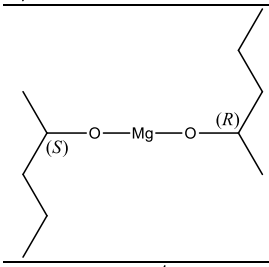
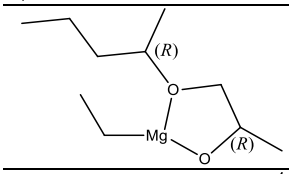
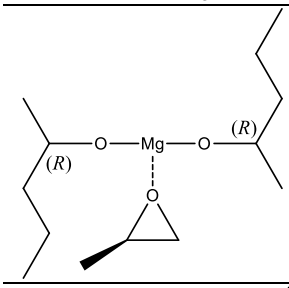
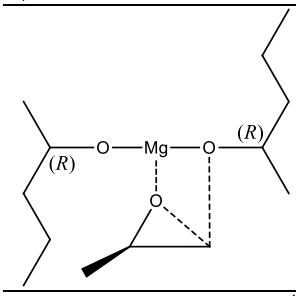
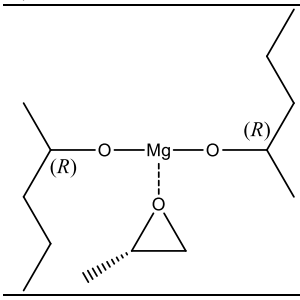
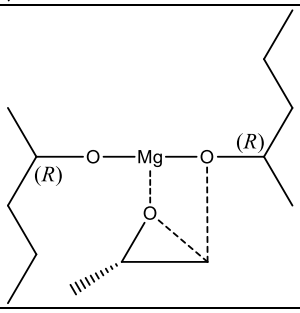
Figure S18. IR spectrum of the crude product obtained from a reaction between PO and $^{n}Bu_2Mg$ in 30:1 ratio at 40 °C in argon atmosphere.

COMPUTATIONAL MODELS AND METHODS

Along with our experimental studies, we also carried out density functional theory computations. All calculations were performed by using the Gaussian 09 program.[3] All structures were optimized at the B3PW91[4] level of density functional theory with the TZVP[5] basis set in gas phase (SVP basis set was used for the large cubane cluster). All optimized structures were characterized as energy minimums without imaginary frequencies by frequency calculations or transition states with only one imaginary frequency. The thermal corrections to Gibbs free energy at 298 K from the frequency analysis are added to the total electronic energy, and we therefore used the corrected Gibbs free energy (ΔG) at 298 K for our discussion.

Table S5. B3PW91/TZVP computed energetic data for the mono-metallic complexes

	HF=-193.106929 ZPE=53.64546 NImag=0	Htot=-193,016098 Gtot= -193,047790
	HF=-358.4632029 ZPE=79.70592 NImag=0	Htot=-358,326494 Gtot=-358,370418
	HF=-551.5878823 ZPE=133.98354 NImag=0	Htot=-551,358498 Gtot=-551,419949
	HF=-551.6720629 ZPE=136.77590 NImag=0	Htot=-551,439534 Gtot= -551,496890

	HF=-744.8755048 ZPE=193.47742 NImag=0	Htot=-744,547476 Gtot= -744,619559
	HF=-744.8754198 ZPE=193.23397 NImag=0	Htot=-744.548449 Gtot= -744,619511
	HF=-744.8357153 ZPE= 193.04967 NImag=0	Htot= -744.508863 Gtot= -744.576225
	HF=-938.014812 ZPE=248.28971 NImag=0	Htot=-937,593810 Gtot= -937,678934
	HF=-937.9659693 ZPE= 247.25583 NImag=1 (-409 cm-1)	Htot= -937,547270 Gtot= -937,630084
	HF=-938.0149377 ZPE=248.41306 NImag=0	Htot=-937,593838 Gtot= -937,678400
	HF=-937.9659385 ZPE=247.12873 NImag=1 (-408 cm-1)	Htot= -937.547353 Gtot= -937,631079

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