Supporting Information

Stereoselective Ring-Opening Polymerization of *rac*-Lactide Using Organocatalytic Cyclic Trimeric Phosphazene Base

Shaofeng Liu, Huaike Li, Na Zhao, and Zhibo Li*

Key Laboratory of Biobased Polymer Materials, Shandong Provincial Education Department; School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

*E-mail: zbli@qust.edu.cn

General Considerations.

All moisture/oxygen sensitive reactions/compounds were performed using standard Schlenk techniques or glovebox techniques in an atmosphere of high-purity nitrogen. THF, DCM, toluene was purified by first purging with dry nitrogen, followed by passing through columns of activated alumina. *rac*-LA was purchased from TCI and recrystallized from toluene. All other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Reaction temperatures were controlled using an IKA temperature modulator.

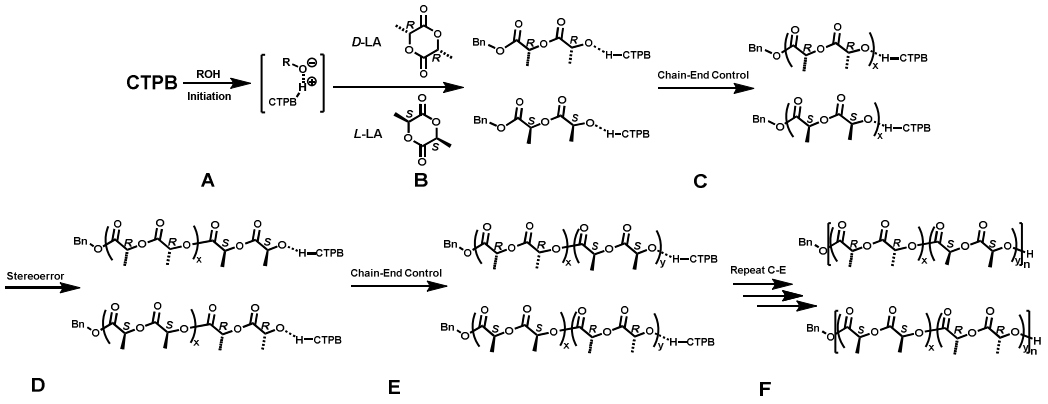
NMR spectra were recorded on Bruker AV500 FT-NMR spectrometer. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) measurements were carried out on Bruker BIFLEX III equipped with a 337 nm nitrogen laser. α-Cyano-4-hydroxycinnamic acid was used as the matrix and sodium chloride as the cationizing agent. The GPC measurements of PLAs were collected on Agilent 1260 Infinity using THF as the eluent (flow rate: 1 mL min^{-1}, at 40 °C) and polystyrenes as standard. Differential scanning calorimetry (DSC) was performed using a TA differential scanning calorimeter DSC25 that was calibrated using high purity indium at a heating rate of 5 °C/min. Melting temperature were determined from the second scan at a heating rate of 5 °C/min following a slow cooling rate of 3 °C/min to remove the influence of thermal history.

General procedure for polymerization of *rac*-LA (Table 1, run 5). *rac*-LA (0.360 g, 2.5 mmol) was dissolved in toluene (16.2 g) in a Schlenk flask sealed with a rubber cap. The solution was then cooled to -75 °C. A solution of **CTPB** (30.0 mg, 25 μmol) and BnOH (2.6 μL, 25 μmol) in toluene (10 g) was then added through a needle to initiate the polymerization. After the desired polymerization time, acetic acid was added to quench the reaction and a small part of solution was taken and dried for ^{1}H NMR characterization to determine the conversion. The other solution was poured into methanol (100 mL) to precipitate polymer.

Table S1. Kinetic studies for ROP of *L*-LA using **CTPB**/BnOH.[a]

Run	Time (min)	Conv.[b]	$M_{n,theor}$[c] (kDa)	$M_{n,GPC}$[d] (kDa)	$Đ$[d]
1	15	31	4.5	3.6	1.25
2	30	51	7.4	8.8	1.19
3	60	75	10.9	13.0	1.12
4	90	86	12.5	13.1	1.35
5	120	93	13.5	13.9	1.58

[a]Conditions: $[L\text{-LA}]_0/[\text{BnOH}]_0/[\text{CTPB}]_0 = 100/1/1$; 2.5 mmol monomer in 30 mL toluene, -75 °C. [b]Determined by ^{1}H NMR. [c]$M_{n,theor} = M_{LA}$ (144.13 g·mol^{-1}) ×($[LA]_0$:$[I]_0$) ×conversion + M_{BnOH} (108.14 g·mol^{-1}). [d]Determined by GPC at 40 °C in THF relative to PS standards, using a correcting factor of 0.58.



Scheme S1. Proposed mechanism for the stereoselective ROP of *rac*-LA with **CTPB**/BnOH at -75 °C. **A**: initiation process; **B**: the first ring-opening reaction; **C**: chain propagation; **D**: stereoerror reaction at the chain end; **E**: chain propagation; **F**: repeating of **C-E** processes.

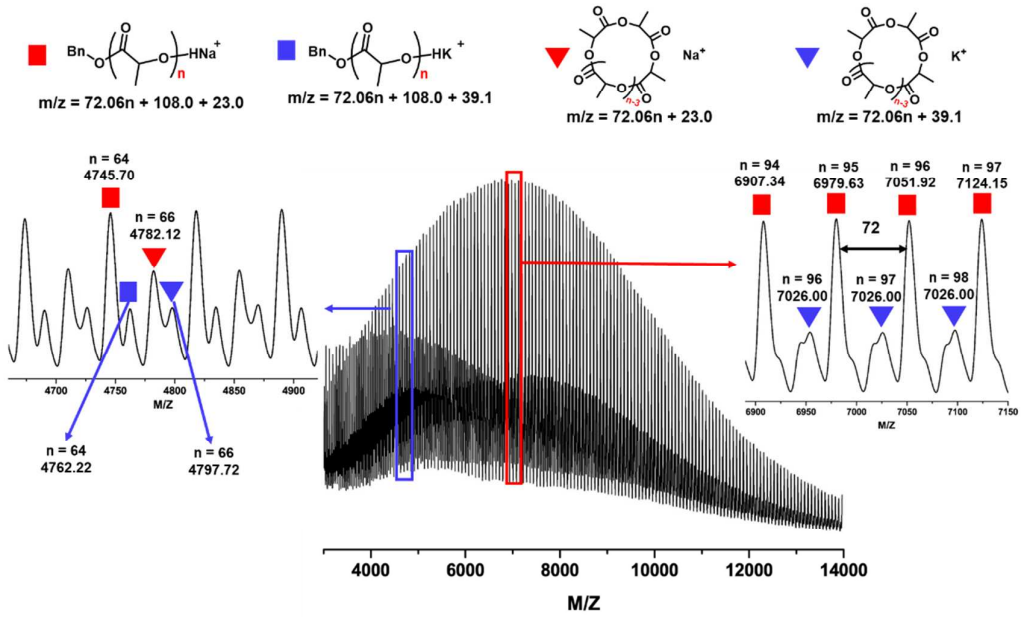


Figure S1. MALDI-TOF mass spectrum of PLA sample obtained in Table 1 run 1.

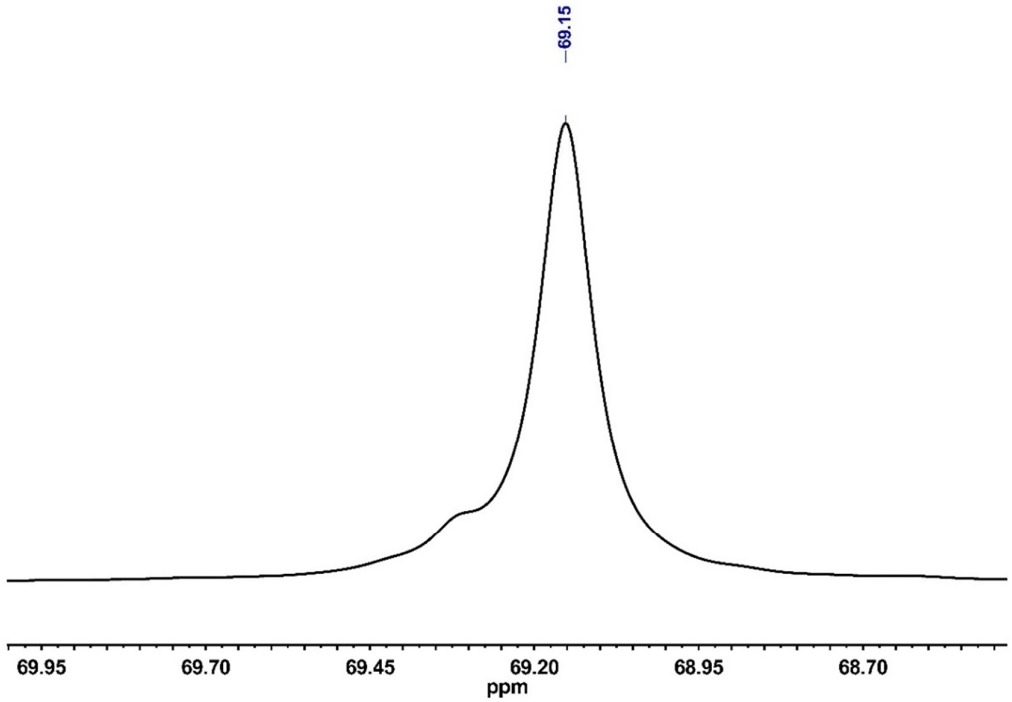


Figure S2. ^{13}C NMR ($CDCl_3$) spectrum of PLA produced by **CTPB**/BnOH in Table 1, run 7.

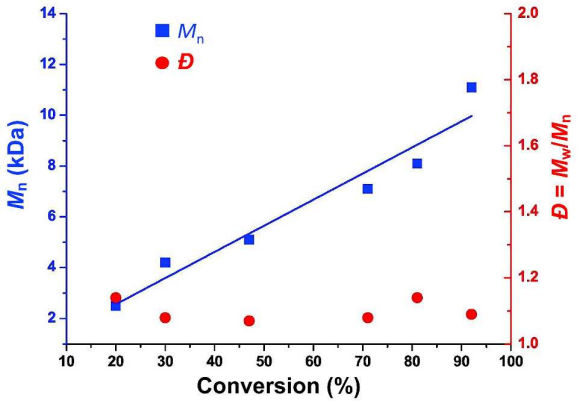


Figure S3. M_n vs. monomer conversions (blue) and dispersities (red) of resulted PLAs in Table 1 runs 2–7.

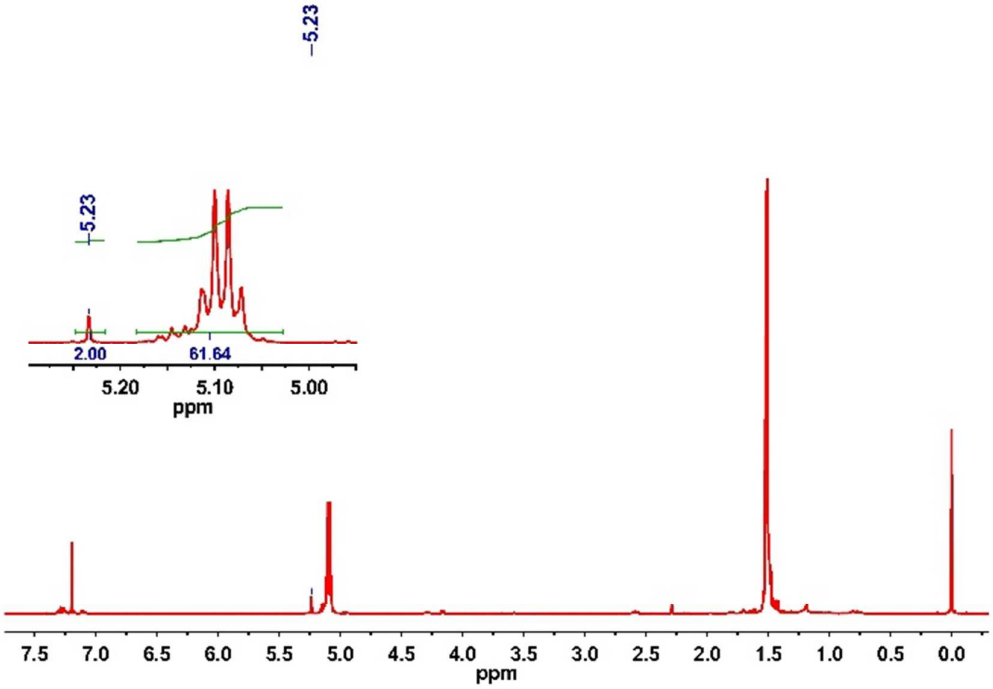


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of PLA sample produced in Table 1 run 3.

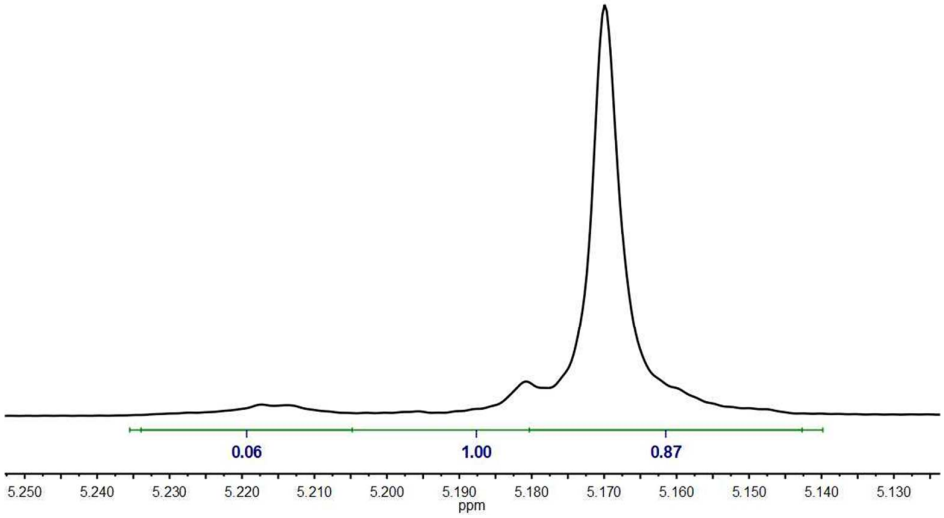


Figure S5. Homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of PLA sample produced with $[LA]_0/[I]_0/[B]_0 = 500/1/1$ (Table 1 run 10, $P_i = 0.91$).

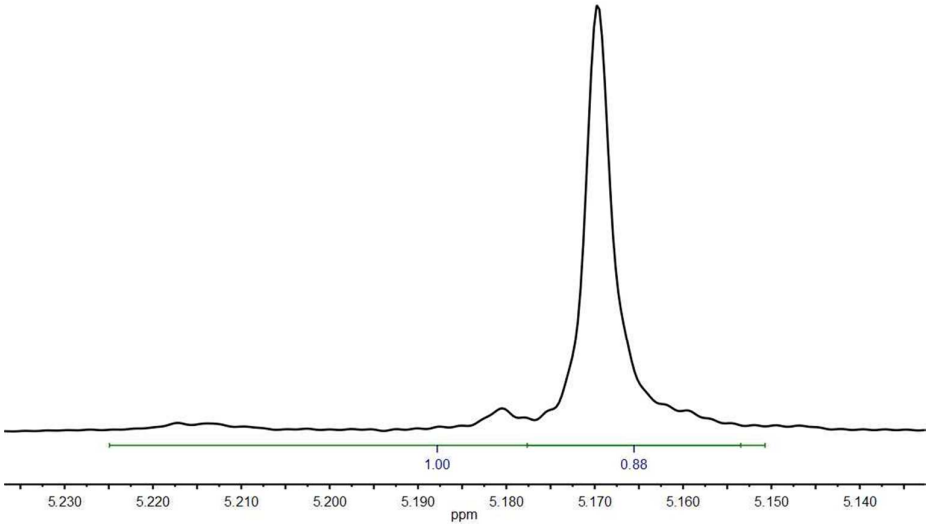


Figure S6. Homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of PLA sample produced with $[LA]_0/[I]_0/[B]_0 = 1000/1/10$ (Table 1 run 13, $P_i = 0.92$).

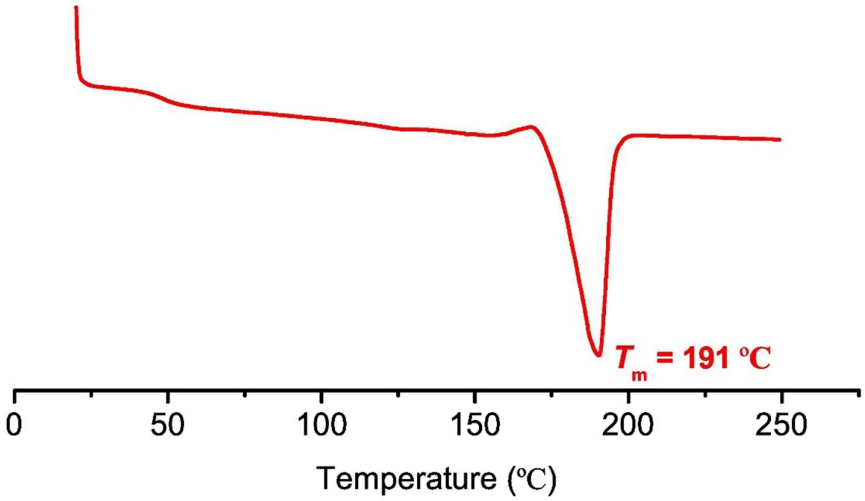


Figure S7. Thermal analysis (heating rate of 5 °C/min, 2nd scan) of PLA prepared in toluene with $[LA]_0/[I]_0/[B]_0 = 500/1/1$ (Table 1 run 10).

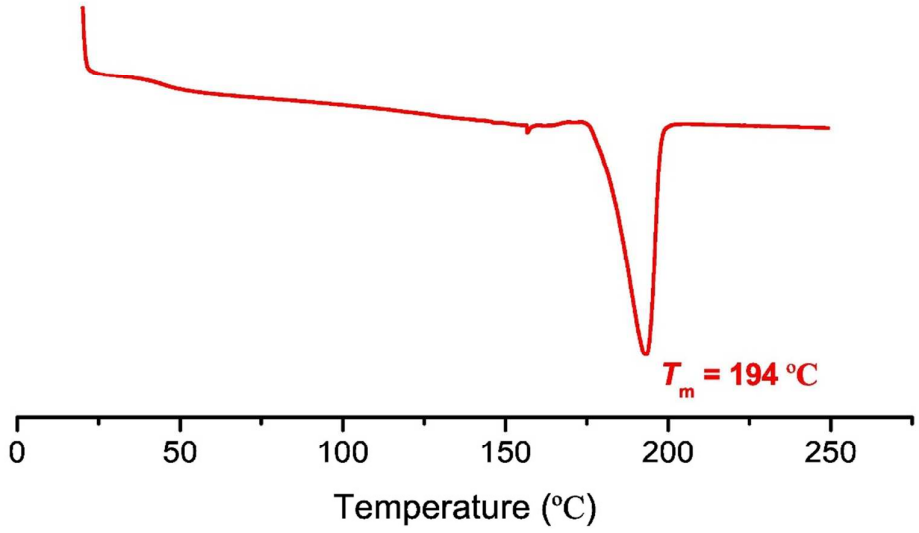


Figure S8. Thermal analysis (heating rate of 5 °C/min, 2nd scan) of PLA prepared in toluene with $[LA]_0/[I]_0/[B]_0 = 1000/1/10$ (Table 1 run 13).

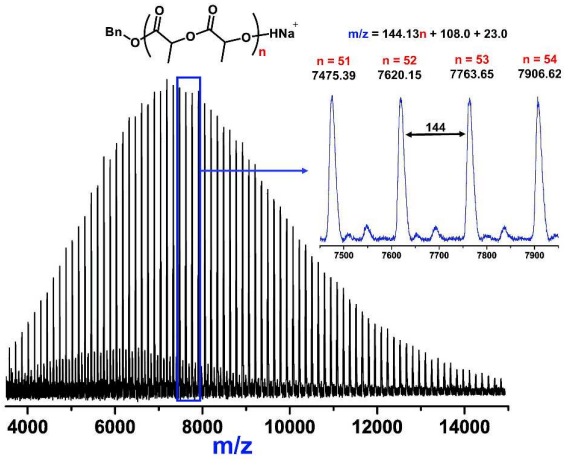


Figure S9. MALDI-TOF mass spectrum of PLA sample obtained in Table 1 run 7.

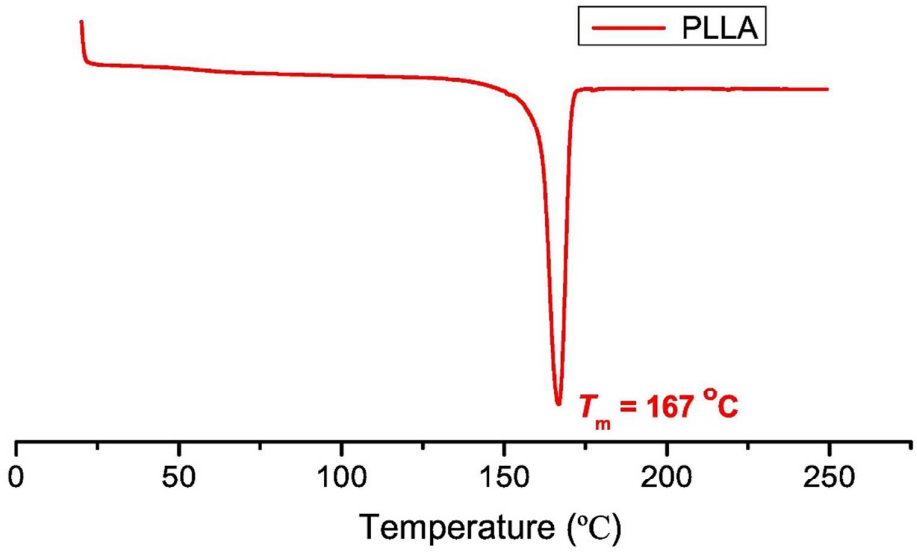


Figure S10. Thermal analysis (heating rate of 5 °C/min, 2nd scan) of PLLA prepared in toluene with $[L\text{-LA}]_0/[I]_0/[B]_0 = 100/1/1$ (Table S1 run 5).

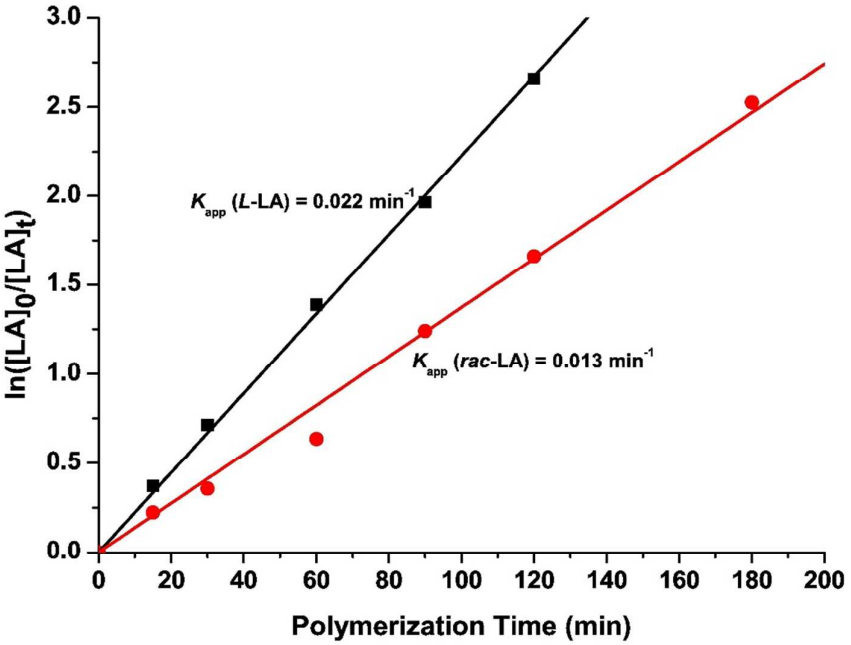


Figure S11. Kinetic plots of the *L*-LA and *rac*-LA conversions versus the reaction time: (black) *L*-LA, (red) *rac*-LA.

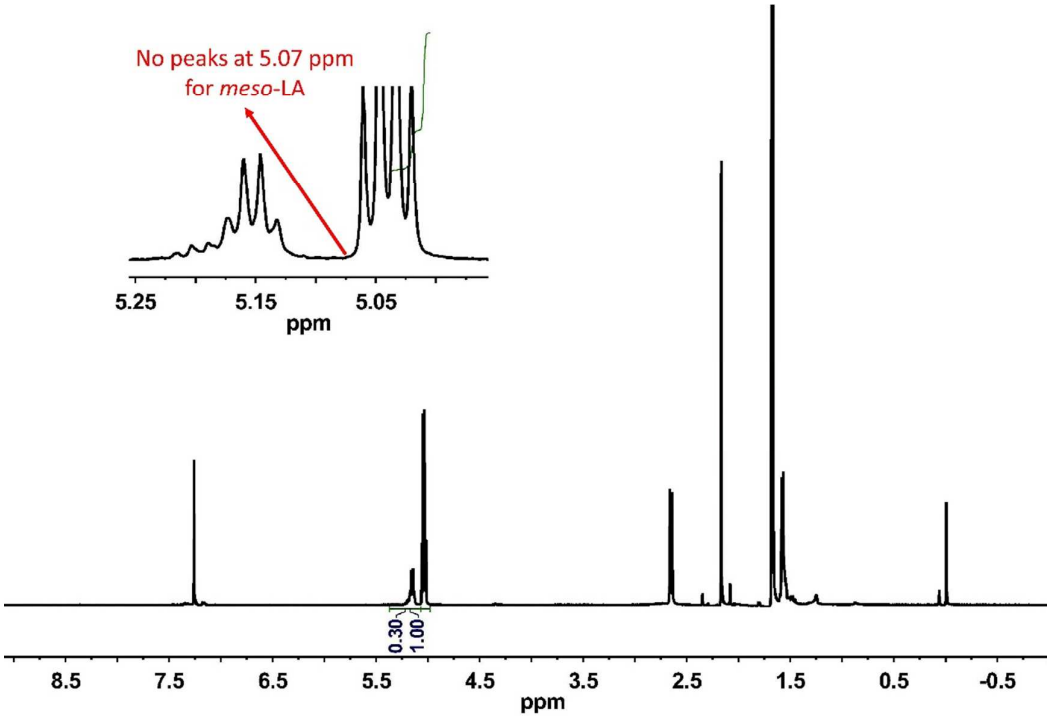


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of polymerization solution sample for conversion calculation in Table 1 run 3.

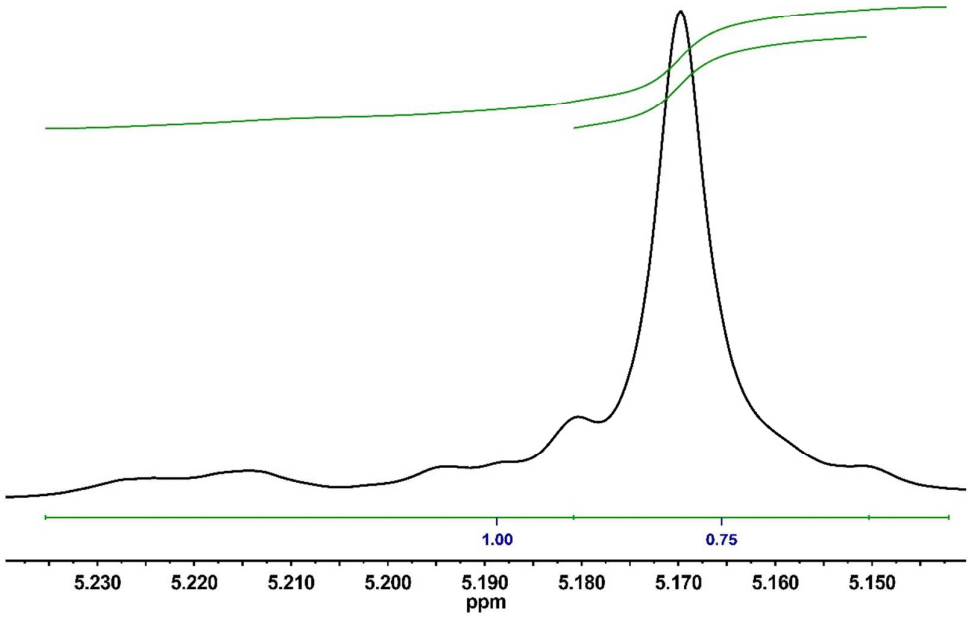


Figure S13. Homonuclear decoupled ^{1}H NMR spectra ($CDCl_3$, 25 °C) of PLA samples produced in THF (Table 1, run 14).

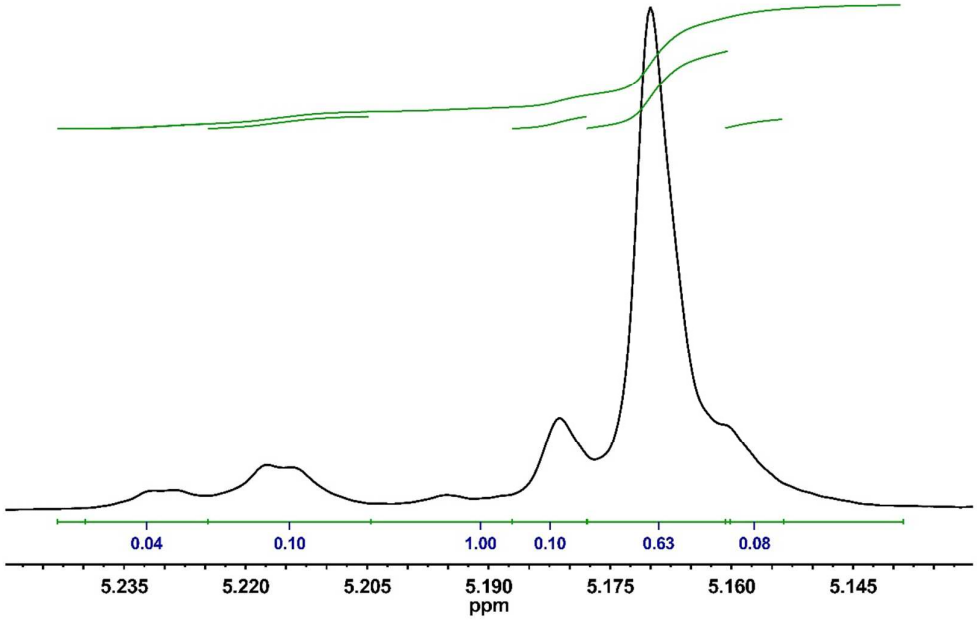


Figure S14. Homonuclear decoupled ^{1}H NMR spectra ($CDCl_3$, 25 °C) of PLA samples produced in DCM (Table 1, run 15).