A Highly Active Zinc-Based Catalyst System for Lactide Homo- and Copolymerization under Industrially Relevant Conditions

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Content

1 General Information & Methods

All manipulations were carried out with standard Schlenk techniques under argon protection. All solvents and reagents, unless otherwise specified, were purchased from commercial suppliers, and used without additional processing. Toluene, xylene and tetrahydrofuran were refluxed in sodium and distilled under argon. Racemic lactide (*rac*-LA) was recrystallized from toluene once prior to use. *ε*-Caprolactone (*ε*-CL) and *δ*-valerolactone (*δ*-VL) were distilled under vacuum. Cyclohexene oxide (CHO), propylene oxide (PO), glycidyl methacrylate (GMA) and ethylene glycol diglycidyl ether (EGDE) were refluxed over CaH_2 and distilled under argon.

NMR: All ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL-400YH spectrometer at a frequency of 400 MHz.

GPC: The molecular weight (M_n) and polydispersity ($Đ$) of the polymer was determined by gel permeation chromatography (GPC) on a Waters 2414 binary system with a refractive index detector, calibrated with polystyrene standards. The column temperature was maintained at 40 ^{o}C during the test using THF as the eluent at a flow rate of 1.0 mL/min.

MALDI-TOF-MS: MALDI-TOF-MS were acquired in linear mode in a m/z range 1000-10000 using a Bruker microflex LRF-MALDI TOF MS with 2,5-dihydroxybenzoic acid (DHB) as matrix. Samples were dissolved in THF (2-5 mg/mL).

TGA: Thermo Gravimetrical Analysis (TGA) of the complexes was performed with a TG DTA7200 in a temperature range of 30–150 ^{o}C with a heating rate of 10 K min^{-1} followed by 50 min at 150 ^{o}C.

DSC: Differential Scanning Calorimetry (DSC) analysis was performed on NETZSCH DSC 214. The experiments were performed by heating the samples from -70 to 100 ^{o}C (heating and cooling scans were repeated, at least in triplicate, to ensure reproducibility). Also, the measurements were carried out at a heating rate of 10 ^{o}C/min, in nitrogen atmosphere.

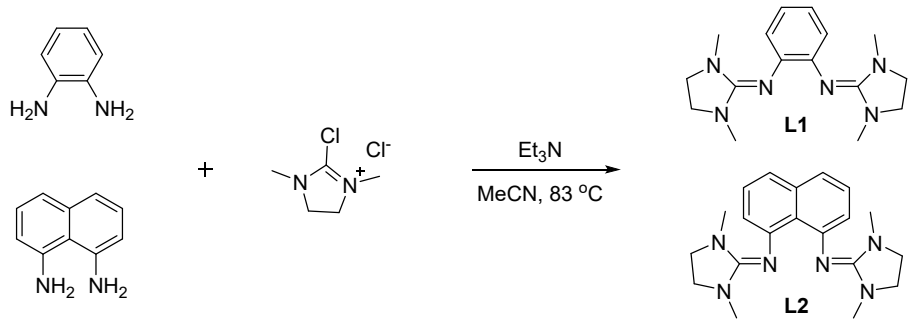
Computational Details: The theoretical calculations were performed via the Gaussian 16 suite of programs.[1] The structures of the studied complexes (denoted by MM1~MM3) were fully optimized at the TPSSh-D3BJ/def2-TZVP level of theory. The

vibrational frequencies of the optimized structures were carried out at the same level. The structures were characterized as a local energy minimum on the potential energy surface by verifying that all the vibrational frequencies were real. The natural bond orbital (NBO) analysis was performed via the NBO 3.1 program[2] implemented in Gaussian 16 to give the natural population analysis (NPA) charge distribution and charge transfer energy for the complexes.

2 Procedural Information

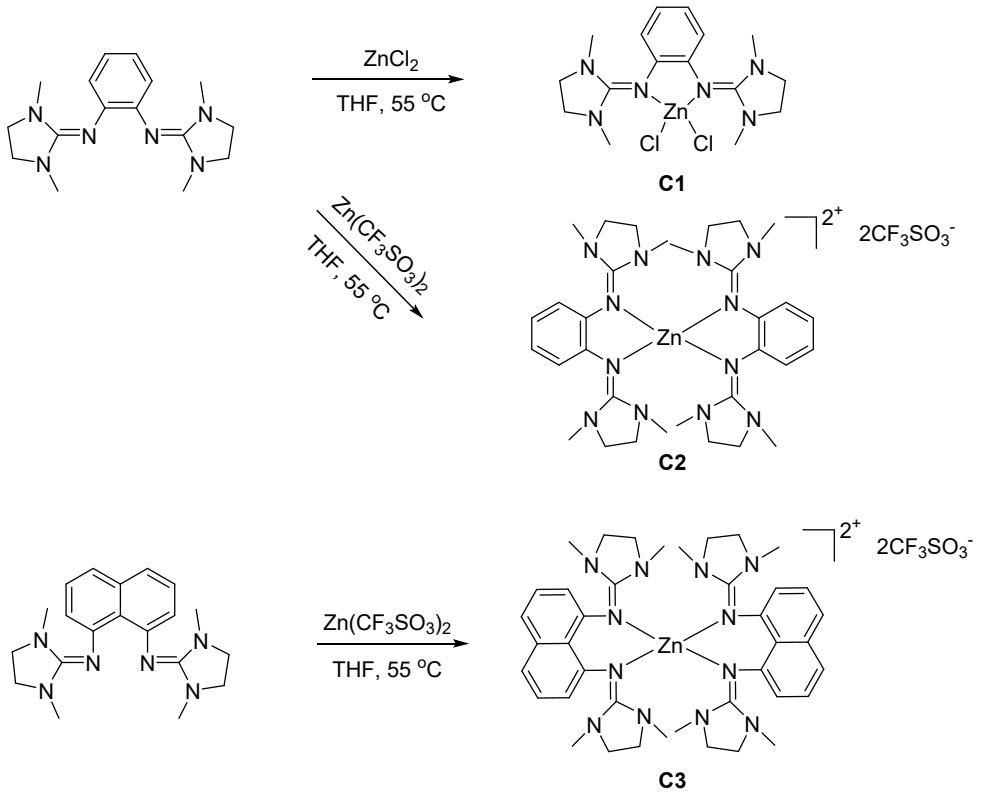
2.1 Complex Synthesis

Guanidine-based ligand and zinc catalyst used were synthesized with reference to the relevant literature.[3,4] The acetonitrile (15 mL) solution of 2-chloro-1,3-dimethylimidazoline (2.53 g, 15 mmol) was added to the acetonitrile (15 mL) solution of 7.5 mmol 1,2-diaminobenzene (**L1**) or 1,8-naphthalenediamine (**L2**) and triethylamine (2.08 mL) at 0 °C. The resulting mixture was refluxed in an oil bath at 83 °C overnight. After cooling to room temperature, NaOH (60 mmol) was added, and the solvent along with triethylamine was removed by vacuum evaporation. The mixture was deprotonated by adding a solution of KOH (30 mL, 50 wt%) and extracted thrice with acetonitrile (30 mL each time). The resulting organic phase was dehydrated with anhydrous Na_2SO_4 and then distilled under reduced pressure to give the desired ligands.



Scheme S1. Synthesis route for ligands **L1** and **L2**.

Zinc trifluoromethanesulfonate [$Zn(CF_3SO_3)_2$ (0.1454 g, 0.4 mmol)] and the ligand (1 mmol) were separately mixed in 4 mL and 6 mL of THF. The ligand solution was added dropwise to the $Zn(CF_3SO_3)_2$ solution while stirring at 55 °C, forming a white precipitate. The precipitate was filtered and washed three times with THF and diethyl ether before being vacuum-dried into a white powdery solid.



Scheme S2. Synthesis route for complexes **C1**, **C2** and **C3**.

Ligand **L1**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.73−6.78 (m, 4H, ArH), 3.18(s, 8H, N-CH_2), 2.61 (s, 12H, N-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 153.7, 141.6, 122.8, 120.9, 48.0, 34.0 ppm.

Ligand **L2**: δ = 6.70−7.30 (m, 6H, ArH), 3.24 (s, 8H, N-CH_2), 2.59 (s, 12H, N-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = δ 152.0, 147.6, 136.7, 125.7, 121.1, 117.9, 48.9, 35.0 ppm.

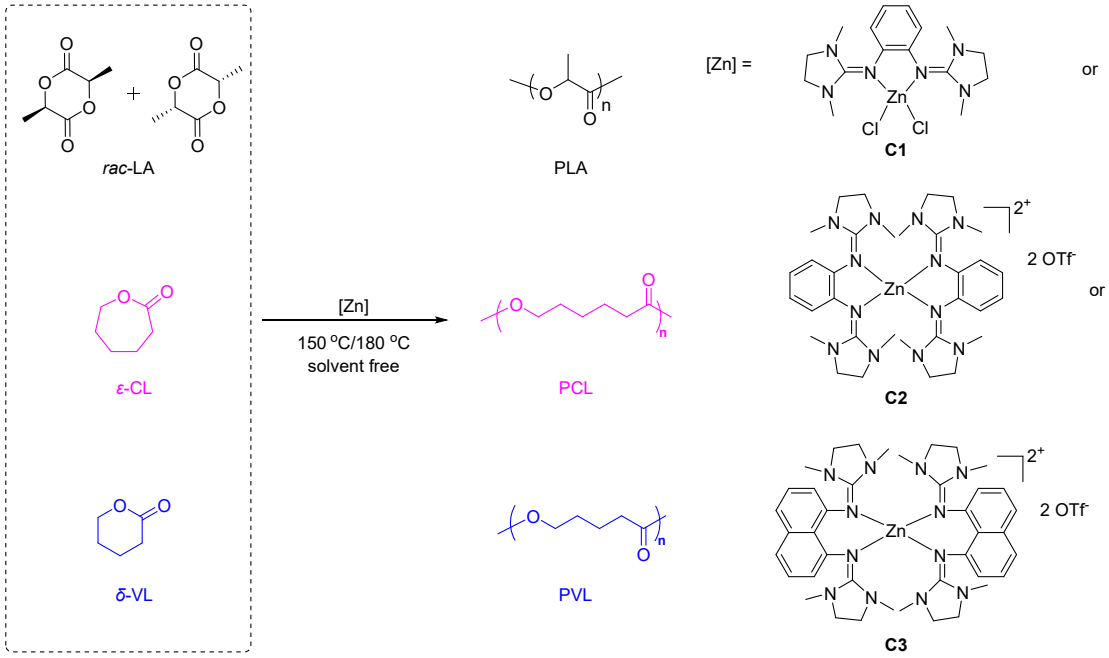
Complex **C1**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.73 (m, 4H, ArH), 3.58-3.52 (d, 8H, N-CH_2), 2.85 (s, 12H, N-CH_3) ppm.^{13}C NMR ($CDCl_3$, 101 MHz): δ = 163.3, 139.6, 120.5, 48.5, 35.7 ppm.

Complex **C2**: ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.95 (m, 4H, ArH), 3.62-3.53 (m, 8H, N-CH_2), 2.57 (s, 12H, N-CH_3) ppm.^{13}C NMR (DMSO-d_6, 101 MHz): δ = 163.0, 137.8, 122.8, 121.6, 48.7, 34.87 ppm.

Complex **C3**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.67−7.34 (m, 12H, ArH), 3.76 (s, 16H, N-CH_2), 2.88 (s, 24H, N-CH_3) ppm.^{13}C NMR ($CDCl_3$, 101 MHz): δ = 158.4, 141.7, 136.6, 126.9, 121.6, 118.6, 115.2, 48.6, 35.2 ppm.

2.2 General Procedure for Homopolymerization of Lactones in Bulk

The types of lactones include *rac*-LA, *ε*-CL and *δ*-VL. Taking a typical polymerization of [*rac*-LA]/[Zn] = 5000/1 as an example: The polymerization was conducted in a 20.0 mL pre-dried tube. The necessary amount of zinc complex (5 μmol), CHO addictive (50 μL) and *rac*-LA (25 mmol) were added in the glove box; the mixture was then transferred to an oil bath with a pre-set temperature and allowed to react for a predetermined time. After cooling to room temperature with water and taking out a small amount of the reaction mixture for ^{1}H NMR analysis, the remaining mixture was dissolved with a small amount of dichloromethane and precipitated with a large amount of ethanol. The polymer that formed was collected, washed multiple times with ethanol, and dried under vacuum at 45 °C for overnight.



Scheme S3. Synthesis route for homopolymerization of different lactone monomers.

2.3 Homopolymerization of *rac*-LA in Solution

The polymerization is carried out in a 20.0 mL pre-dried tube. Appropriate amounts of zinc complex (5 μmol), CHO addictive (50 μL), *rac*-LA (25 mmol) and solution (2.5 mL) were added in the glove box; the mixture was then transferred to an oil bath with a pre-set temperature and allowed to react for a predetermined time. After cooling to room temperature with water and taking out a small amount of the reaction mixture for ^{1}H NMR analysis, the remaining mixture was precipitated with a large amount of

ethanol. The resulting polymer was collected, washed several times with ethanol and dried overnight under vacuum at 45 °C.

2.4 General Procedure for Copolymerization

Take *rac*-LA and ε-CL as an example: The reaction tube was charged sequentially with *rac*-LA, ε-CL, zinc complex, and CHO additive. The resulting mixture was stirred for set hours at a temperature of 150 °C, and then cooled down to room temperature using water. A small portion of the reaction mixture was taken out for ^{1}H NMR analysis, and then the remaining product was dissolved in CH_2Cl_2 and precipitated in ethanol.

3 Ligand and Complex Characterization

3.1 Ligand Characterization

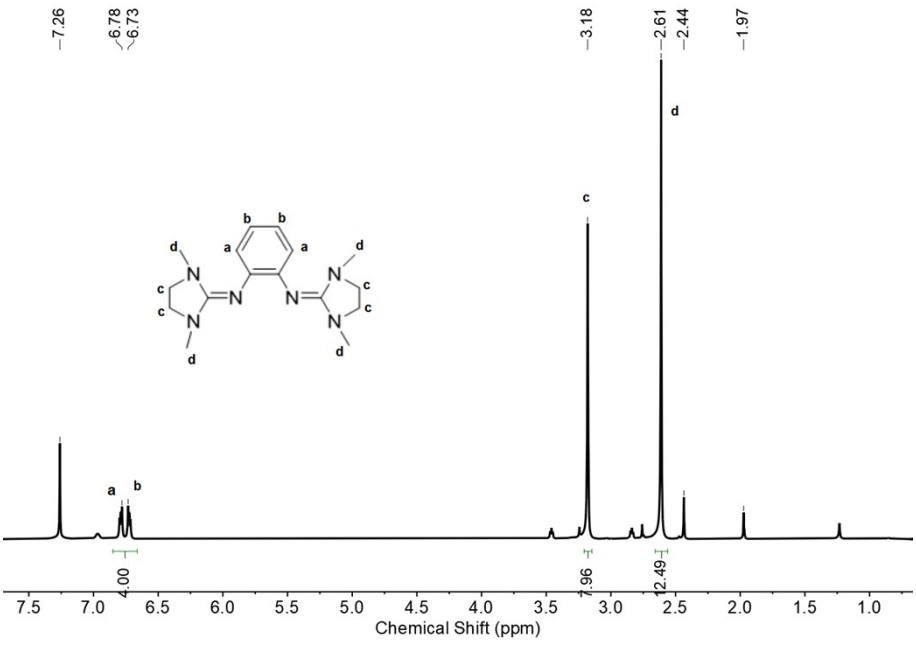


Figure S1. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of ligand **L1**.

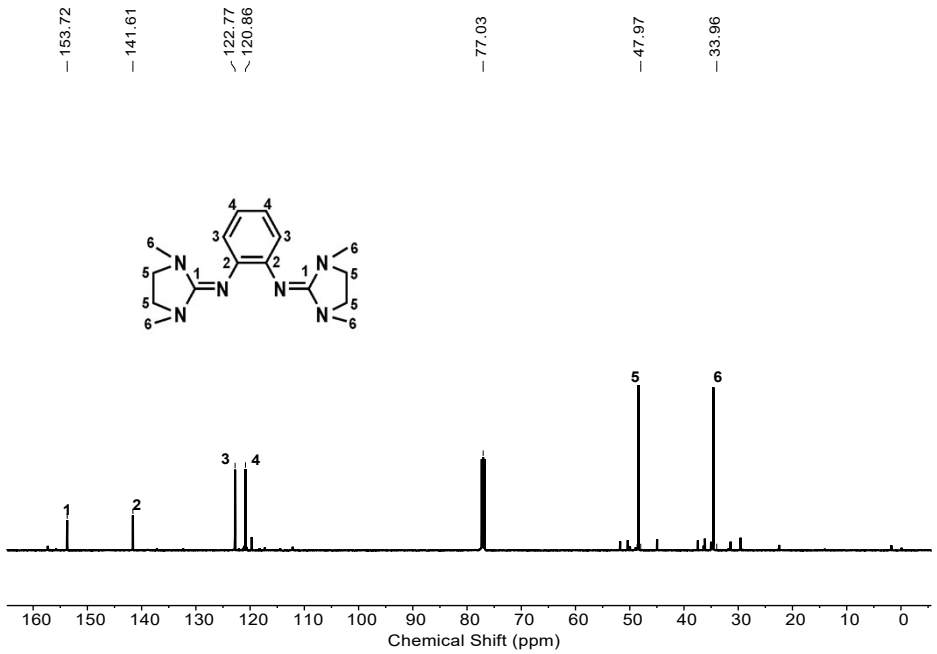


Figure S2. ^{13}C-NMR spectrum ($CDCl_3$, 101 MHz) of ligand **L1**.

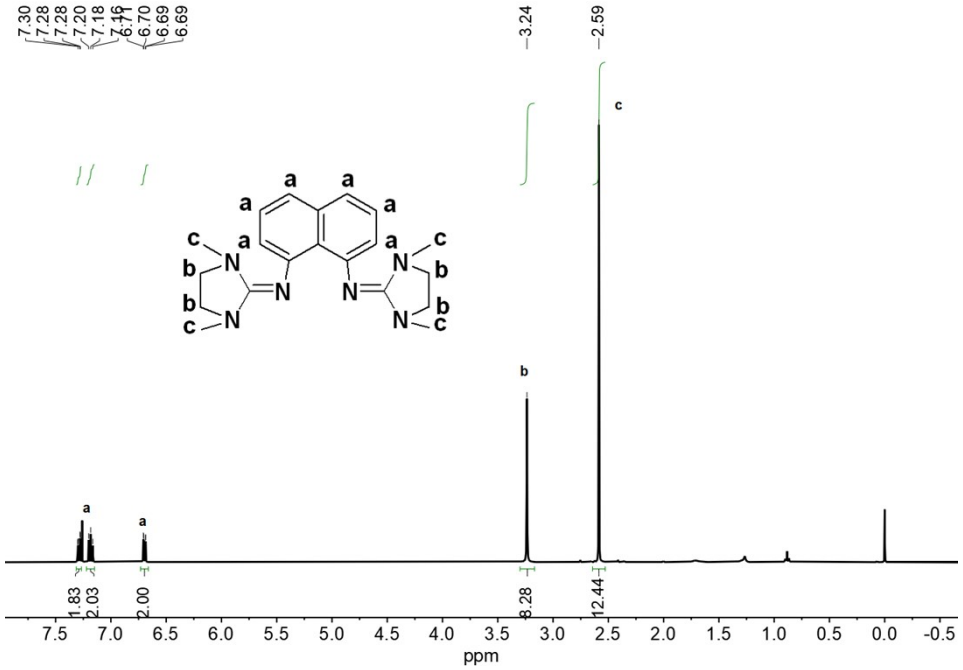


Figure S3. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of ligand **L2**.

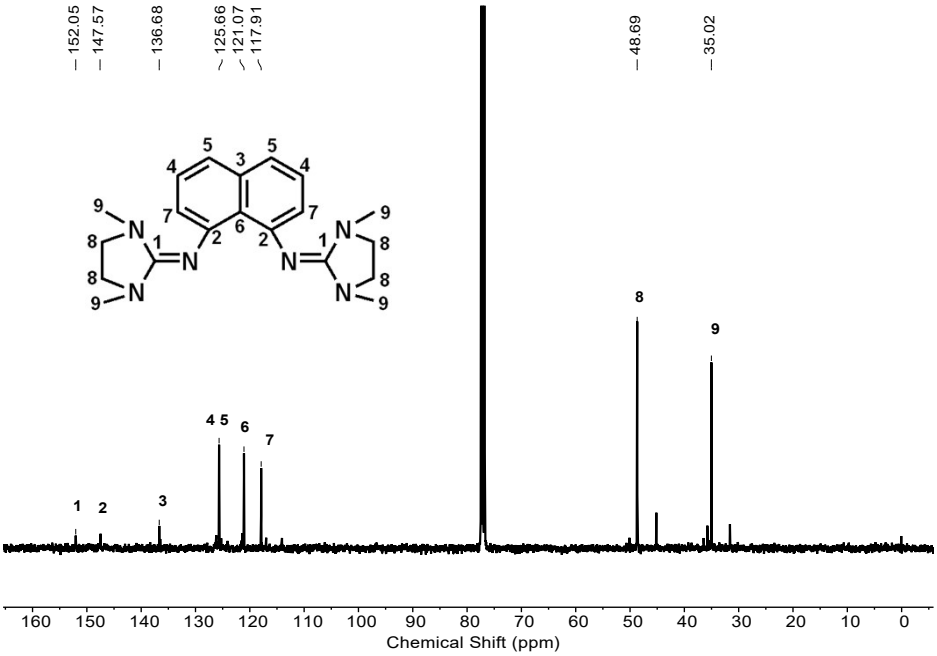


Figure S4. ^{13}C-NMR spectrum ($CDCl_3$, 101 MHz) of ligand **L2**.

3.2 Complex Characterization

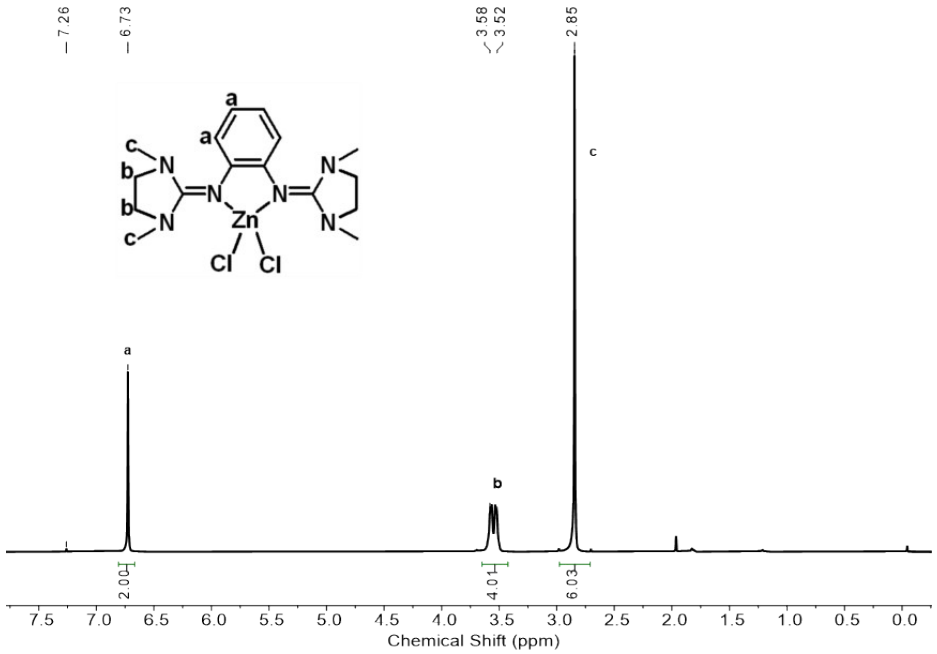


Figure S5. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of catalyst **C1**.

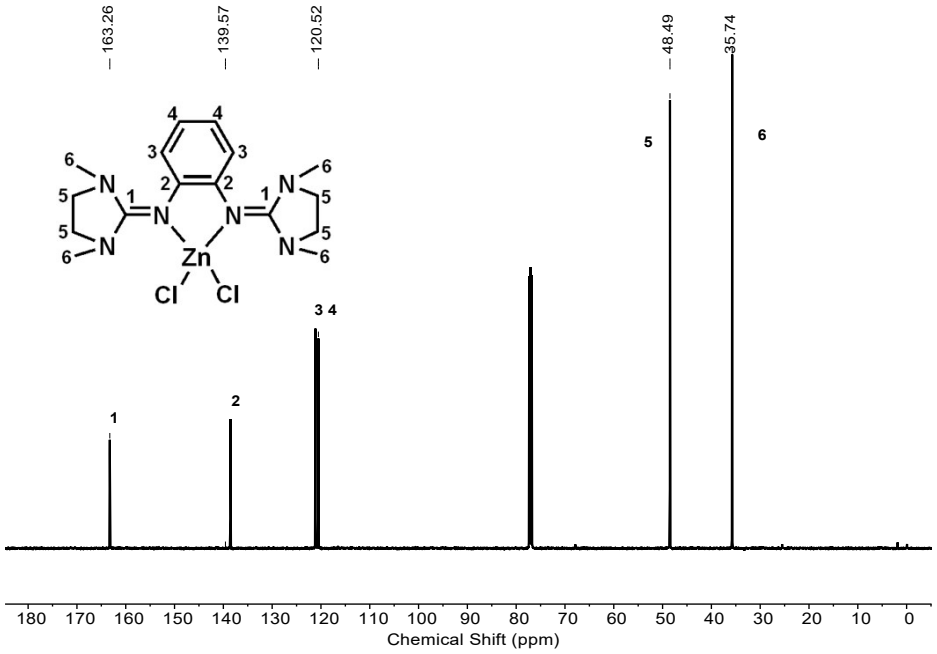


Figure S6. ^{13}C-NMR spectrum ($CDCl_3$, 101 MHz) of catalyst **C1**.

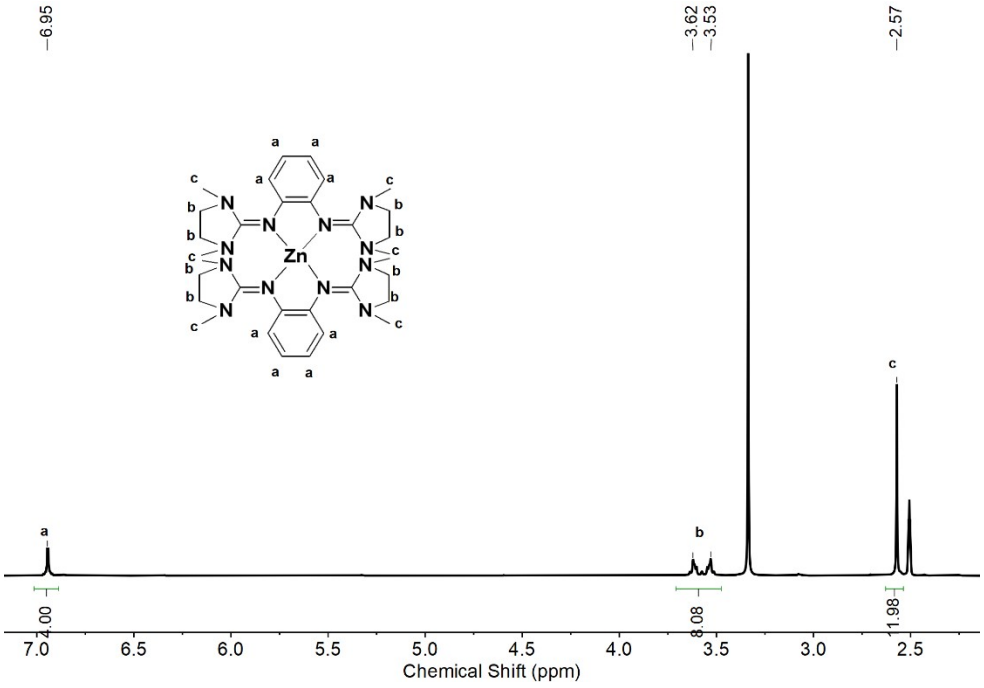


Figure S7. ^{1}H-NMR spectrum (DMSO-d_6, 400 MHz) of catalyst **C2**.

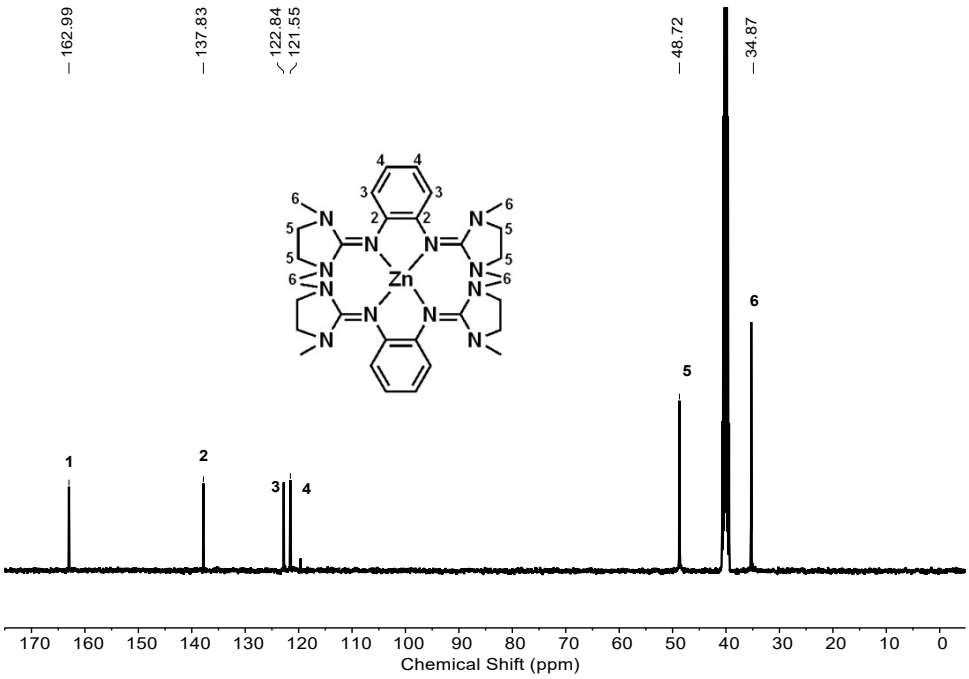


Figure S8. ^{13}C-NMR spectrum (DMSO-d_6, 101 MHz) of catalyst **C2**.

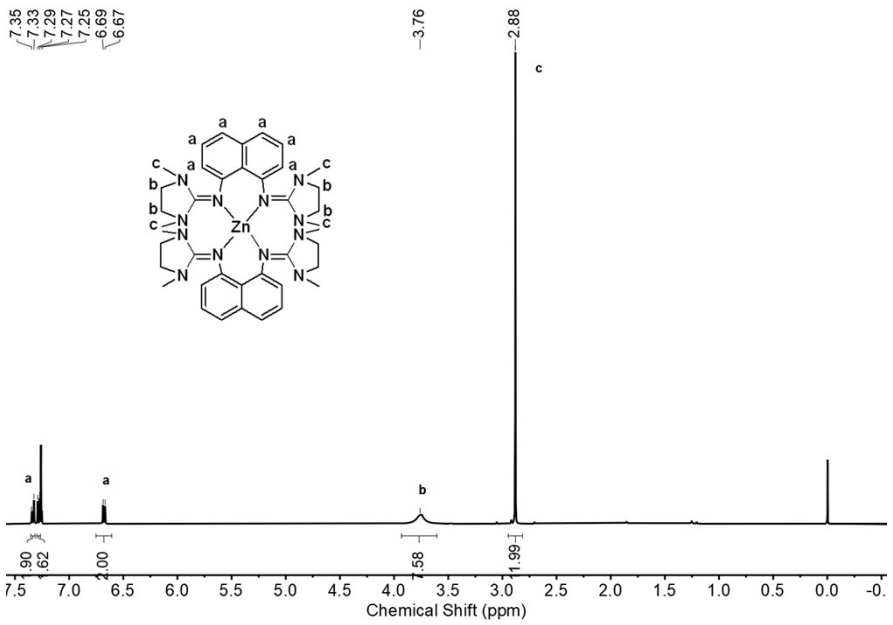


Figure S9. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of catalyst **C3**.

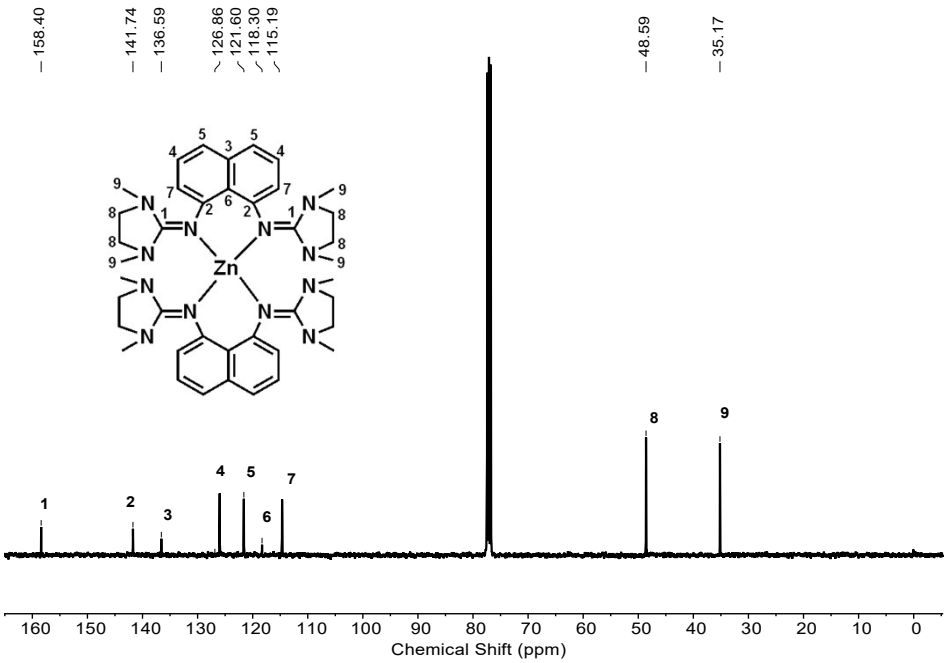


Figure S10. ^{13}C-NMR spectrum ($CDCl_3$, 101 MHz) of catalyst **C3**.

4 Thermogravimetric Analysis

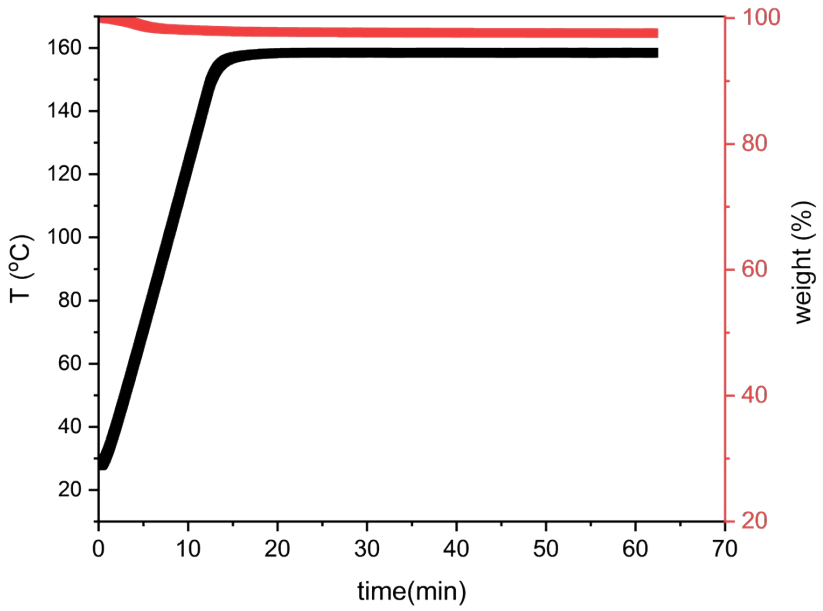


Figure S11. TGA measurement of complex **C2** at 150 °C.

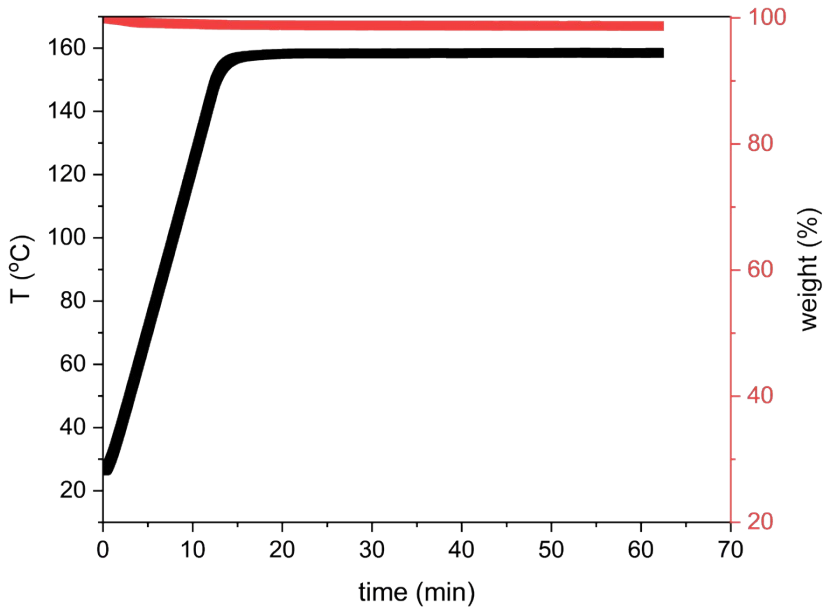


Figure S12. TGA measurement of complex **C3** at 150 °C.

5. Polymerization Details

5.1 NMR Characterization of PLA

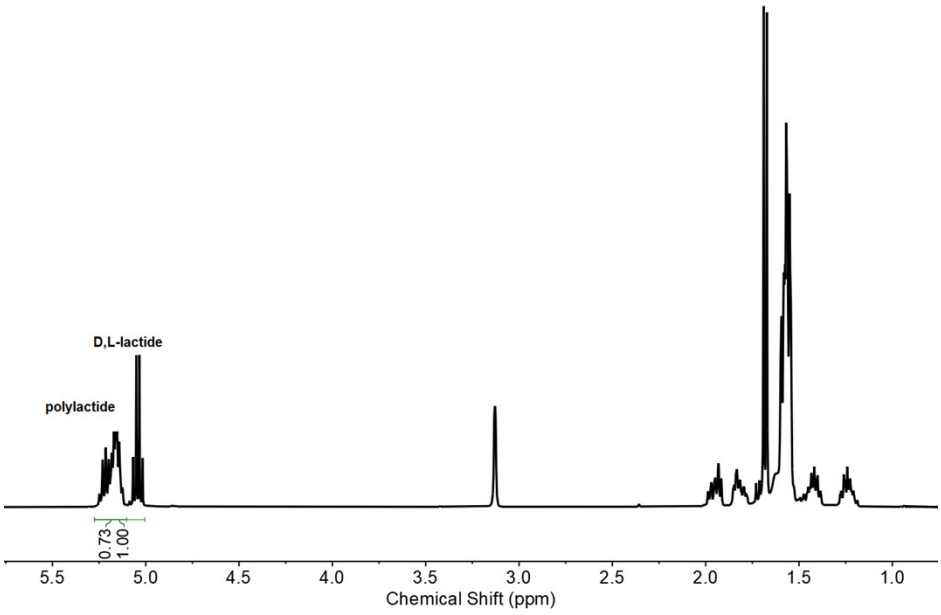


Figure S13. Example of ^{1}H NMR spectrum of lactide polymerization. Conditions: catalyst **C1**, [LA]/[Cat.] = 5000/1, [CHO] = 50 μL, 150 °C, 70 min (Table 1, entry 1).

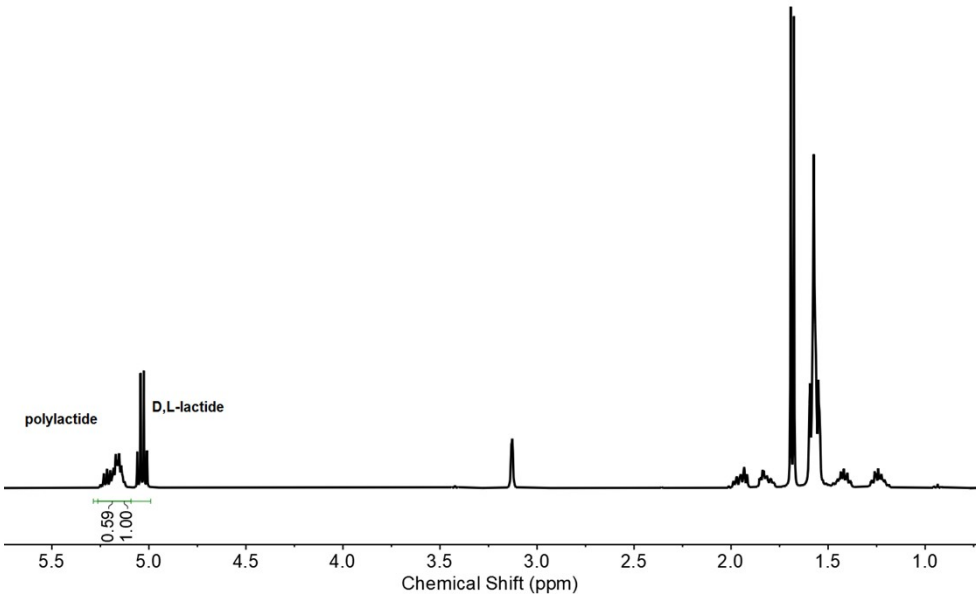


Figure S14. Example of ^{1}H NMR spectrum of lactide polymerization. Conditions: catalyst **C2**, [LA]/[Cat.] = 5000/1, [CHO] = 50 μL, 150 °C, 30 min (Table 1, entry 2).

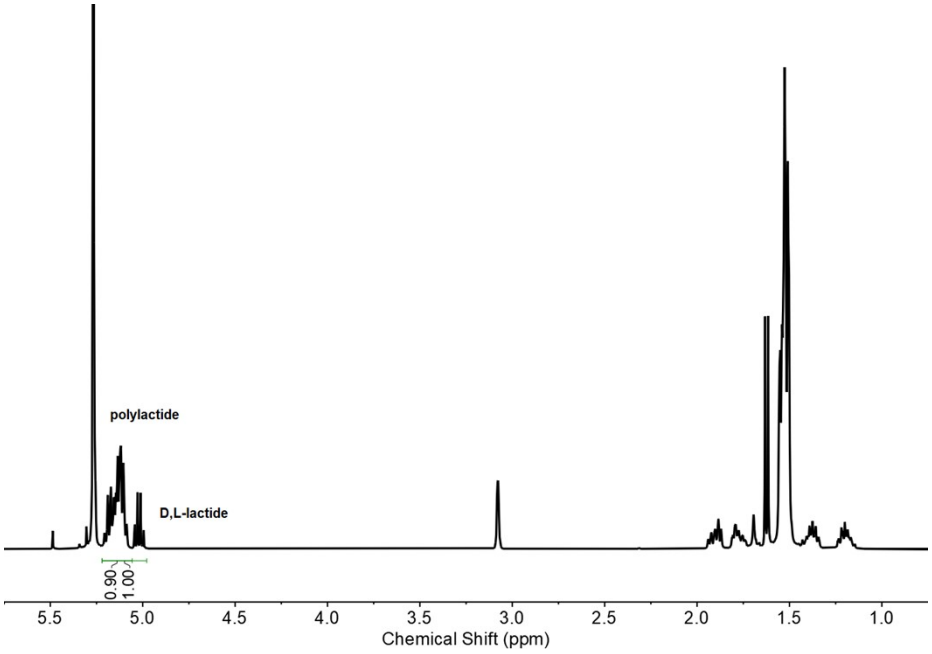


Figure S15. Example of ^{1}H NMR spectrum of lactide polymerization. Conditions: catalyst **C3**, [LA]/[Cat.] = 5000/1, [CHO] = 50 μL, 150 °C, 30 min (Table 1, entry 4).

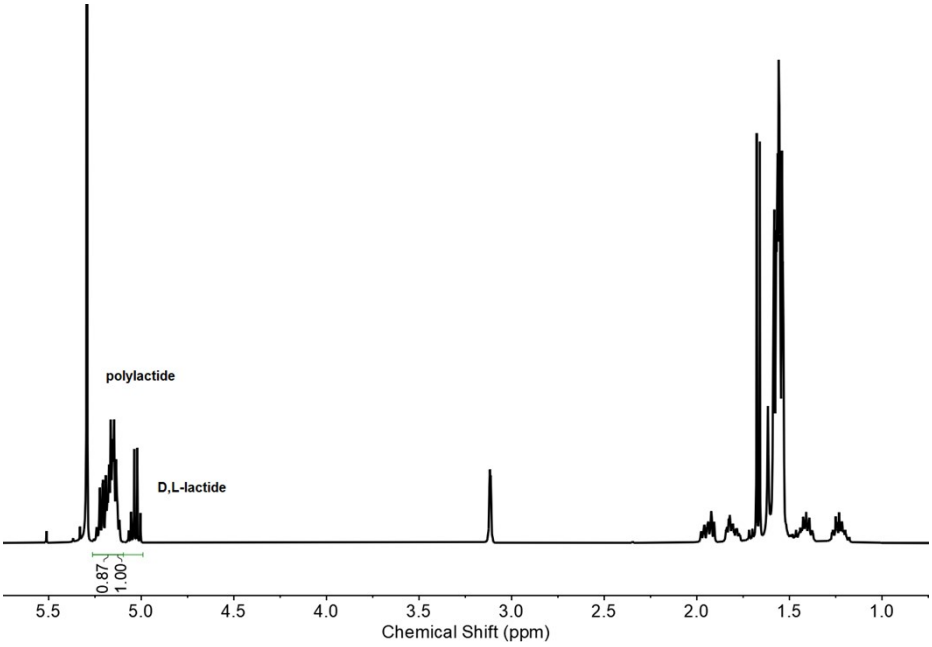


Figure S16. Example of ^{1}H NMR spectrum of lactide polymerization. Conditions: catalyst **C2**, [LA]/[Cat.] = 10000/1, [CHO] = 100 μL, 180 °C, 50 min (Table 2, entry 2).

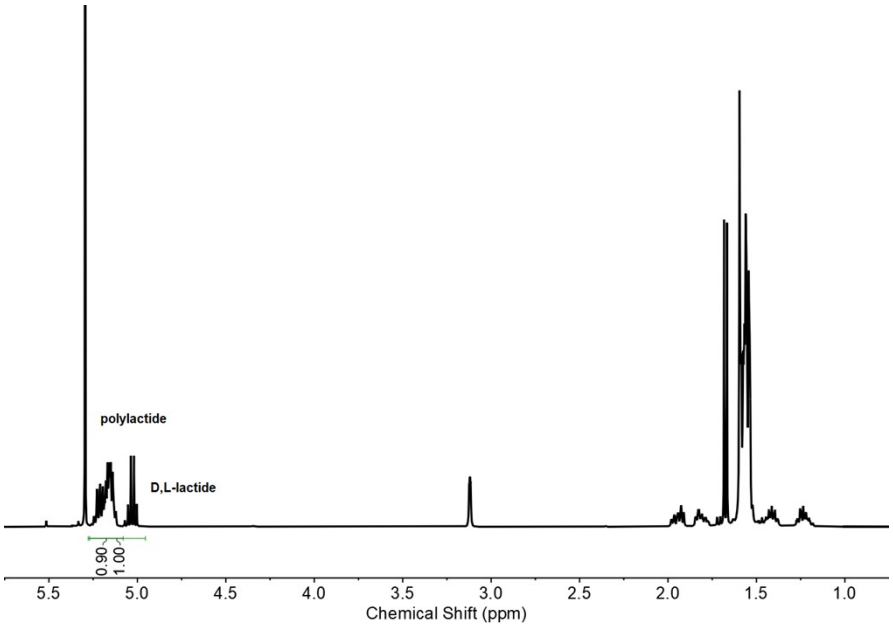


Figure S17. Example of ^{1}H NMR spectrum of lactide polymerization. Conditions: catalyst **C3**, [LA]/[Cat.] = 10000/1, [CHO] = 100 μL, 180 °C, 30 min (Table 2, entry 4).

The parameter P_m is the tetrad probability to give *meso* enchainment between monomer units and is determined from the methine region of the homonuclear decoupled ^{1}H NMR spectrum: [mmm] = $P_m^2 + (1 - P_m)P_m/2$, [mmr] = [rmm] = $(1 - P_m)P_m/2$, [rmr] = $(1 - P_m)^2/2$, and [mrm] = $[(1 - P_m)^2 + P_m(1 - P_m)]/2$.

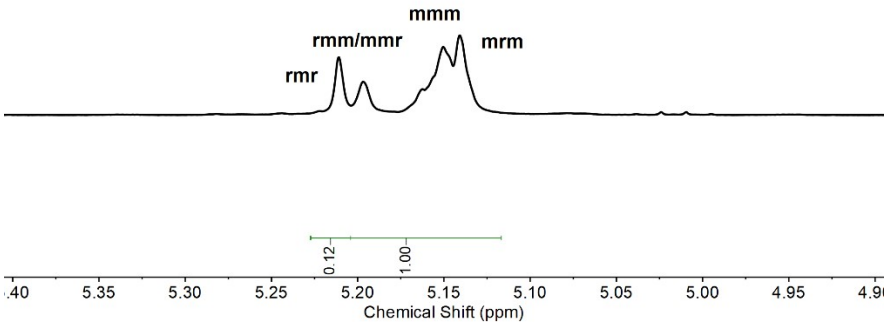


Figure S18. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA), P_m = 0.51. (Table 1, entry 1).

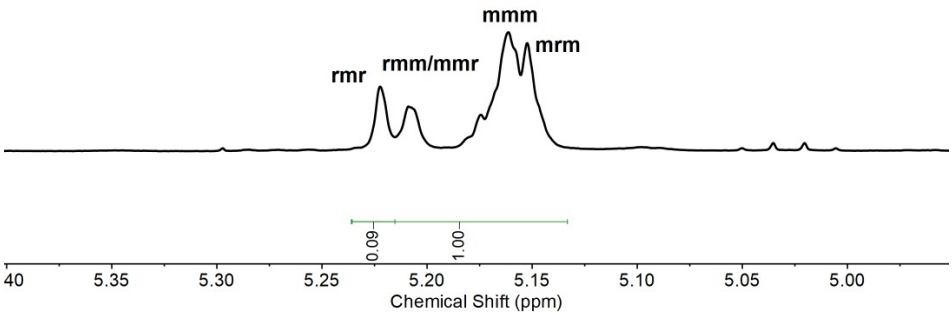


Figure S19. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA), P_m = 0.58. (Table 1, entry 2).

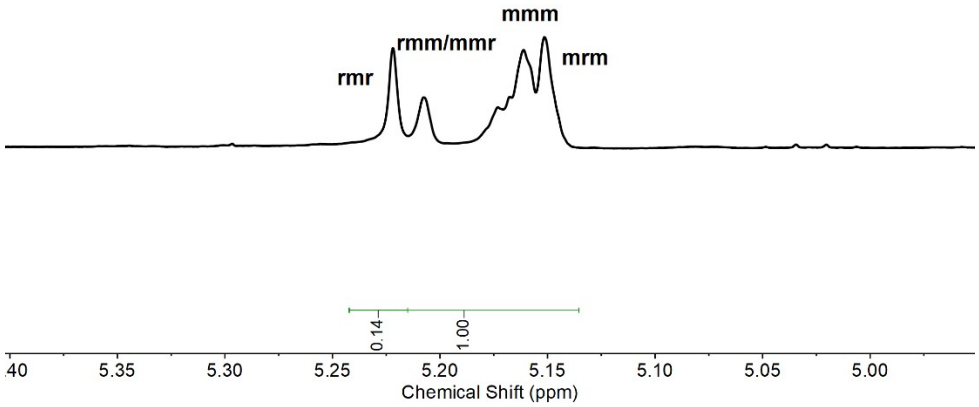


Figure S20. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA), P_m = 0.47. (Table 1, entry 3).

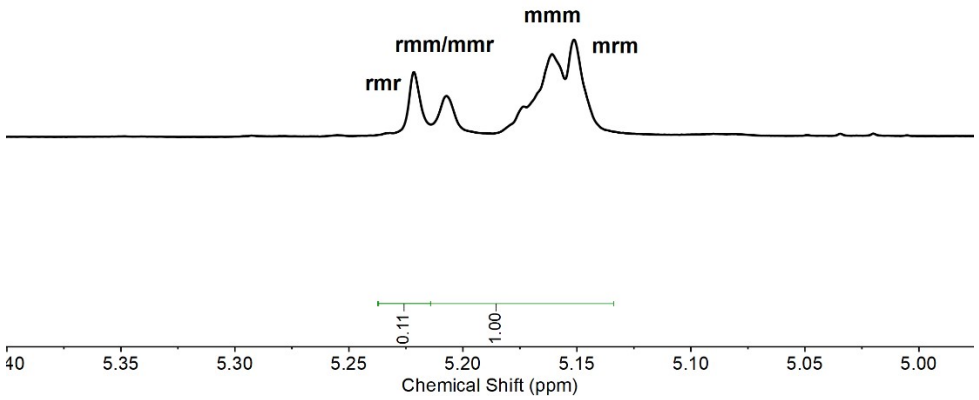


Figure S21. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA), P_m = 0.53. (Table 2, entry 4).

5.2 Homopolymerization Results of *rac*-LA

Table S1. ROP of *rac*-LA catalyzed by different catalyst/epoxide catalytic systems.[a]

Entry	Cat.	LA:epoxide:Cat.	t/ min	Conv.[b]/%	TOF[c]/ h^{-1}	M_n[d]/ kg/mol	$Đ$[d]
1	**C2**	1000:0:1	120	trace	-	-	-
2	**C2**	1000:300:1	50	81	972	19.7	1.34
3[e]	**C3**	5000:1000:1	15	56	11200	26.6	1.58
4[f]	**C3**	5000:1000:1	15	94	18800	5.0	1.33
5[g]	**C3**	5000:1000:1	15	71	14200	12.4	1.27
6	**C3**	5000:1000:1	15	78	15600	26.7	1.29
7	**C3**	5000:300:1	15	trace	-	-	-
8	**C3**	5000:300:1	40	54	4050	12.8	1.36
9	**C3**	5000:500:1	15	9	1800	7.9	1.22
10	**C3**	5000:500:1	40	58	4350	23.8	1.36

[a] Conditions: 150 °C, 0.01 mmol [Zn], epoxide=CHO. [b] According to ^{1}H NMR. [c] Turnover frequency (TOF) = mol of monomer consumed per mole of Zn per hour, in h^{-1}. [d] Experimental M_n values determined by GPC in THF *vs.* polystyrene standards using a correcting factor of 0.58.[5] [e] epoxide = PO. [f] epoxide = GMA. [g] epoxide = EGDE.

Table S2. R OP of *rac*-LA catalyzed by **C3** upon different solvents.[a]

Entry	solvent	Conv.[b]/%	TOF[c]/h^{-1}	M_n/(kg/mol)[d]	$Đ$[d]
1	toluene	trace	-	-	-
2	xylene	19	1900	7.8	1.21
3[e]	diphenyl ether	trace	-	-	-
4	diphenyl ether	40	4000	8.5	1.23

[a] Condition: LA/**C3** = 5000/1, [Zn] = 5 μmol, [CHO] = 50 μL, 30 min, solvent = 2.5 mL, T(toluene) = 100 °C, T(diphenyl ether) and T(xylene) = 150 °C. [b] According to ^{1}H NMR. [c] Turnover frequency (TOF) = mol of monomer consumed per mole of Zn per hour, in h^{-1}. [d] Experimental M_n values determined by GPC in THF *vs.* polystyrene standards using a correcting factor of 0.58.[5] [e] Without CHO.

5.3 Kinetic Study

Table S3. Kinetic study of ROP of *rac*-LA catalyzed by complex **C2** and **C3**.[a]

Catalyst	t/min	Conv.[b]/%	TOF[c]/h^{-1}	M_n/(kg/mol)[d]	$Đ$[d]
C2	18	39	6500	18.0	1.22
	25	57	6840	18.6	1.18
	30	59	5900	24.5	1.22
	45	78	5200	21.4	1.32
	50	81	4860	19.2	1.38
C3	10	70	21000	27.3	1.26
	13	75	17310	25.6	1.47
	15	78	15600	26.7	1.29
	20	85	12750	28.4	1.36
	30	90	9000	22.2	1.48

[a] Condition: LA/[Zn] = 5000/1, [Zn] = 5 μmol, [CHO] = 50 μL, 150°C. [b] According to ^{1}H NMR. [c] Turnover frequency (TOF) = mol of monomer consumed per mole of Zn per hour, in h^{-1}. [d] Experimental M_n values determined by GPC in THF *vs.* polystyrene standards using a correcting factor of 0.58.[5]

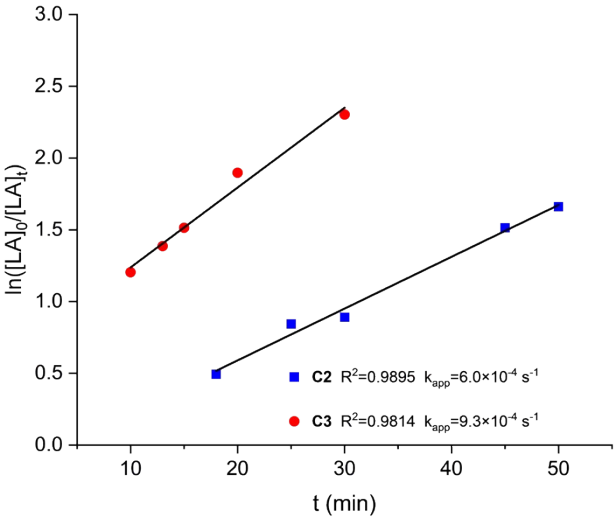


Figure S22. Kinetic plots for ROP of *rac*-LA with **C2** and **C3** (Table S2).

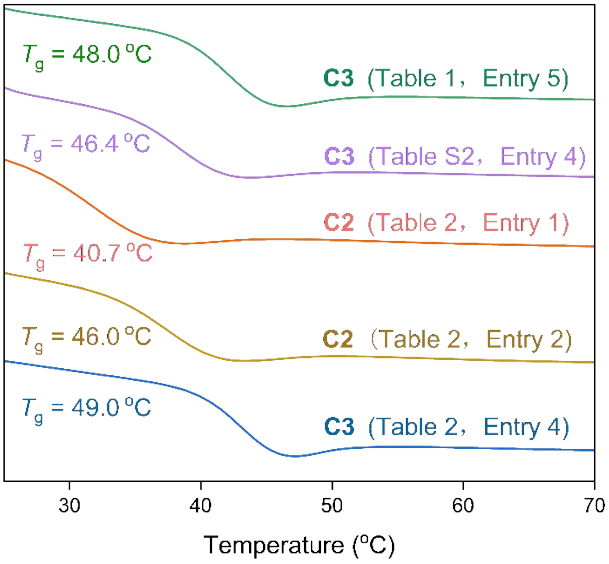


Figure S23. DSC traces for the obtained PLA.

5.4 Computational Results

Table S4. Selected NPA charges and charge transfer energies of the complex cations in **C1**, **C2**, and **C3** (NBO 3.1, TPSSh/def2-TZVP GD3BJ)

Cation	Zn-N [Å]	NPA charge [e units] Zn	Charge transfer energies [kcal/mol] N→Zn
C1	1.4878, 1.8207	0.84602	36, 38
C2	1.6906, 1.6905, 1.6906, 1.6906	0.82528	36, 36, 36, 36
C3	1.9124, 1.5984, 1.5989, 1.9092	0.80656	33, 35, 35, 33

5.5 MALDI-TOF-MS Spectra

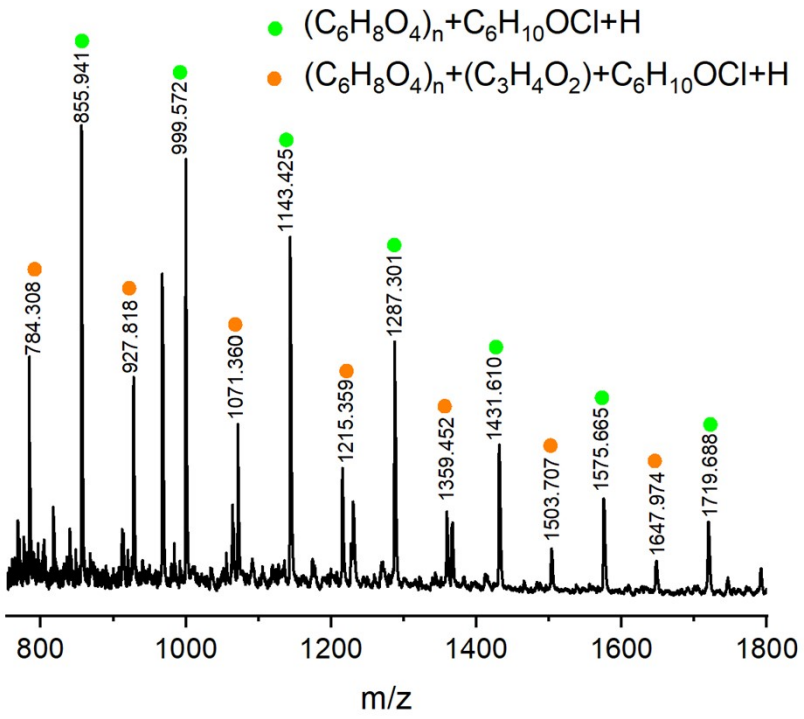


Figure S24. The MALDI-TOF mass spectrum of the PLA obtained using **C1** (entry 1, Table 1).

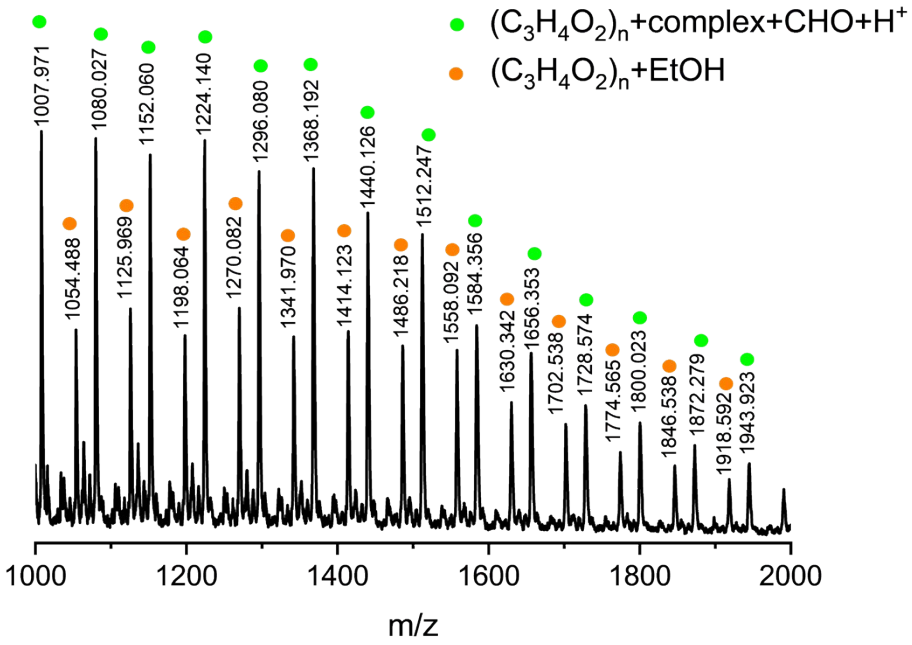


Figure S25. The MALDI-TOF mass spectrum of the PLA obtained using **C3** (entry 4, Table 2).

5.6 Proposed mechanism

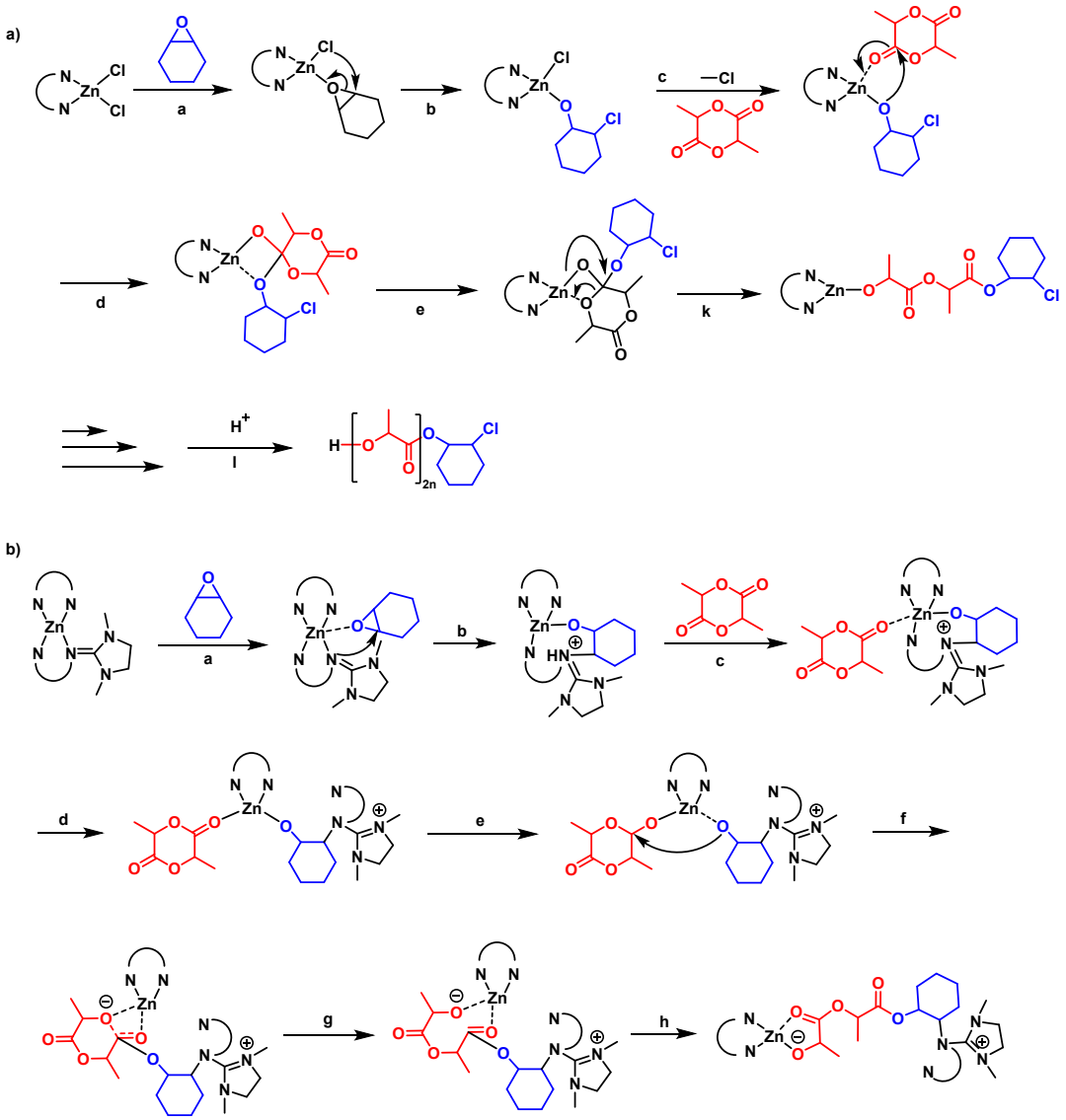


Figure S26. Proposed reaction mechanism for the PLA formation in the presence of catalyst **C1** (a) and **C3** (b).

5.7 Homopolymerization Results of Lactones

Table S5. ROP of different lactones catalyzed by **C3**.[a]

Entry	monomer	M:Cat.	t /h	Conv.[b] /%	TOF[c] /h^{-1}	M_n[d] (kg/mol)	$Đ$[d]	T_g/T_m[e] /°C
1	ε-CL	5000:1	2.5	63	1260	66.0	1.34	-44.0/54.9
2[f]	δ-VL	1000:1	5	83	166	18.0	1.29	-42.5/52.7

[a] Condition: [Zn] = 0.01 mmol, [CHO] = 0.3 mL, 150 °C. [b] According to ^{1}H NMR. [c] Turnover

frequency (TOF) = mol of monomer consumed per mole of Zn per hour, in h^{-1}. [d] Experimental M_n values determined by GPC in THF *vs.* polystyrene standards using a correcting factor of 0.56 for *ε*-CL, 0.57 for *δ*-VL.[5] [e] Determined by DSC. [f] [CHO] = 0.5 mL.

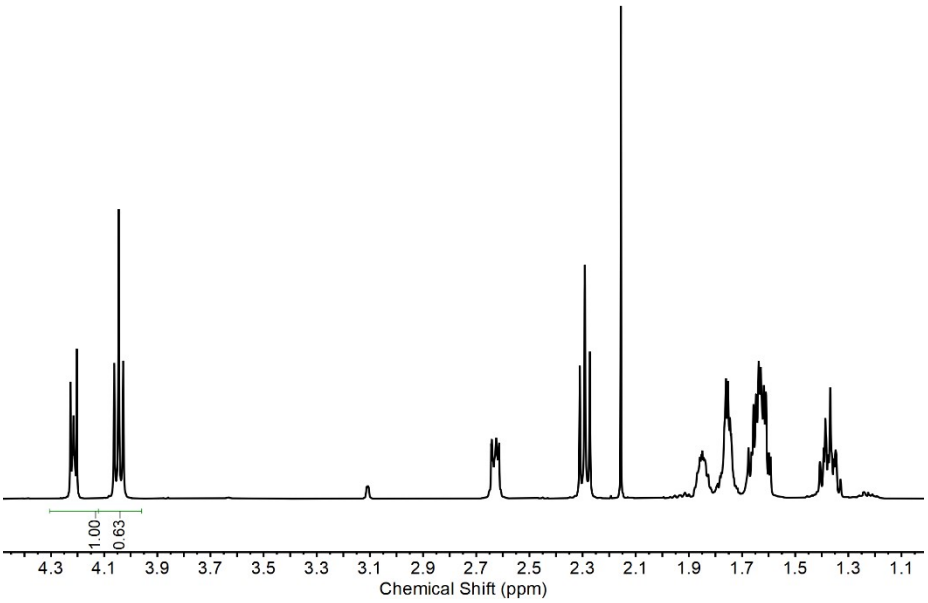


Figure S27. ^{1}H NMR spectrum of *ε*-CL polymerization. Conditions: catalyst **C3**, [*ε*-CL]/[Cat.] = 5000/1, [CHO] = 0.3 mL, 150 °C, 2.5 h (Table S5, entry 1).

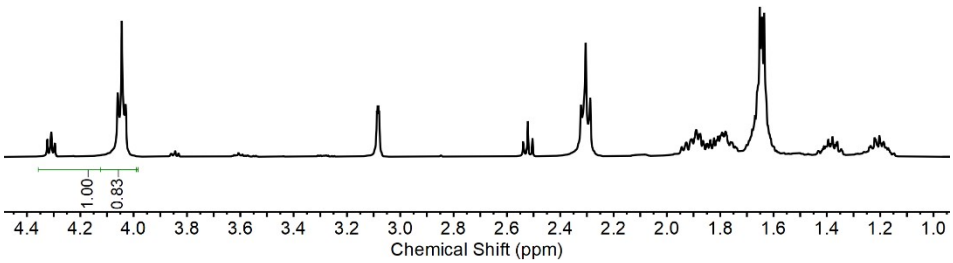


Figure S28. ^{1}H NMR spectrum of *δ*-VL polymerization. Conditions: catalyst **C3**, [*δ*-VL]/[Cat.] = 1000/1, [CHO] = 0.5 mL, 150 °C, 5 h (Table S5, entry 2).

5.8 Copolymerization Details

Table S6 Copolymerization of different lactones catalyzed by complex **C3**.[a]

Entry	monomers		M1:M2:Cat.	t	Conv./%[b]		M_n/$Đ$[c]	T_g[d]	T_m[d]
	M1	M2		/h	M1	M2		/°C	/°C
1[e]	CL	VL	700:700:1	5	24	48	8.7/1.08	-[h]	-
2[f]	CL	VL	700:700:1	5	98	92	21.4/1.40	/	19.6
3[f,g]	CL	VL	700:700:1	4	98	88	20.1/1.48	/	18.6
4	CL	LA	1000:1000:1	4	31	>99	17.6/1.40	15.1	/
5[g]	CL	LA	1000:1000:1	3.5	88	>99	12.3/1.39	-12.9	19.0
6	VL	LA	700:1000:1	5	43	89	6.3/1.22	23.4	/

[a] Condition: 150 °C, [Zn] = 0.01 mmol, [CHO] = 0.5 mL. [b] According to ^{1}H NMR. [c] Experimental M_n values determined by GPC in THF *vs.* polystyrene standards. The unit of M_n is kg/mol. [d] Determined by DSC. [e] Without CHO. [f] [CHO] = 0.3 mL. [g] Performed at 180 °C. [h] Not determined.

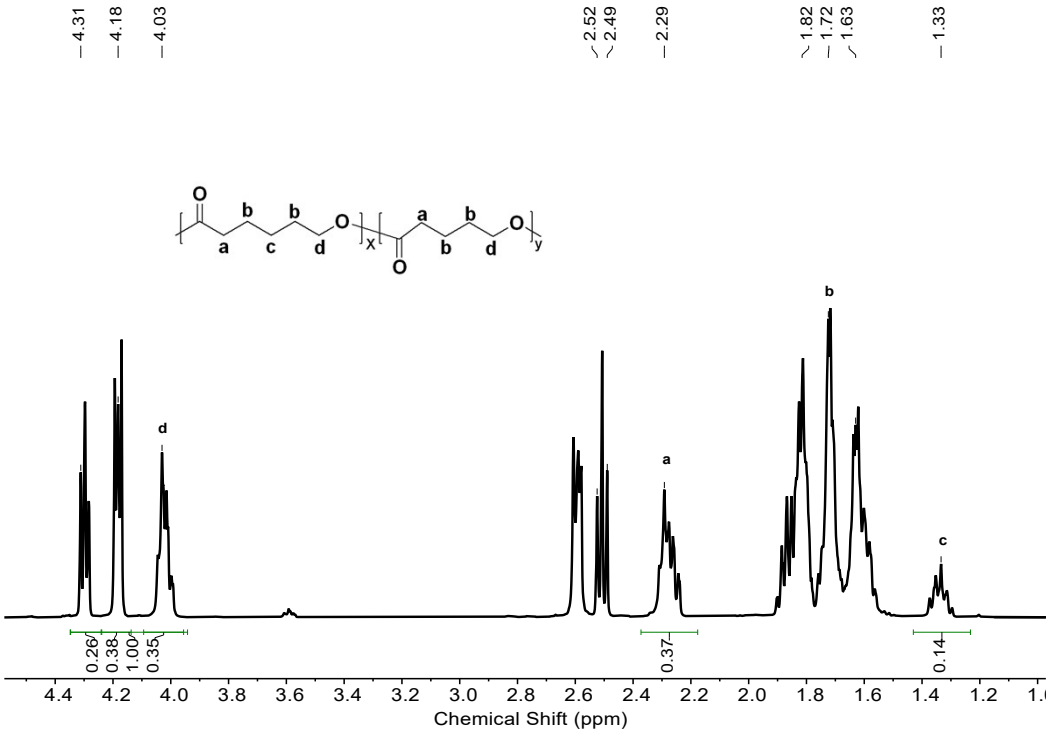


Figure S29. ^{1}H NMR spectrum of copolymerization. Conditions: catalyst **C3**, 150 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 1).

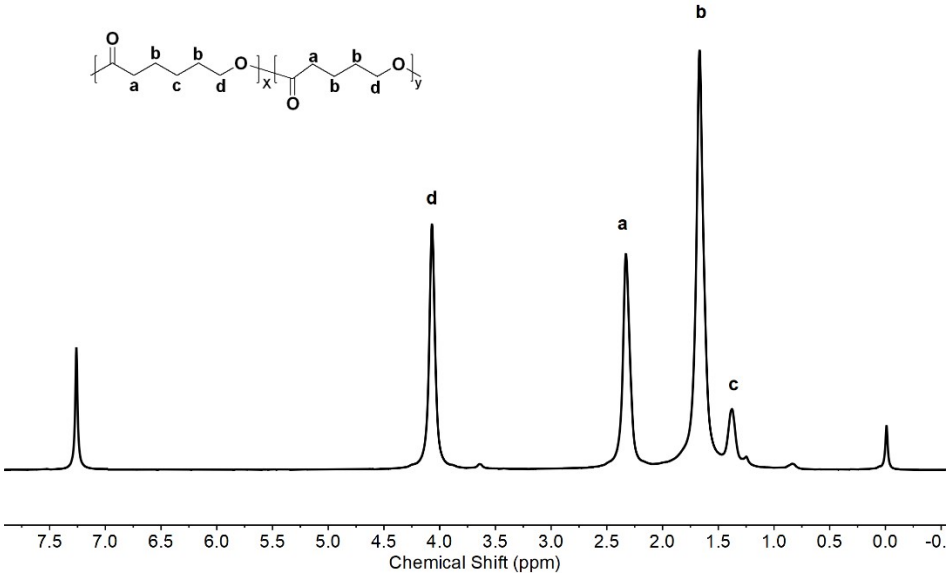


Figure S30. ^{1}H NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, 150 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 1).

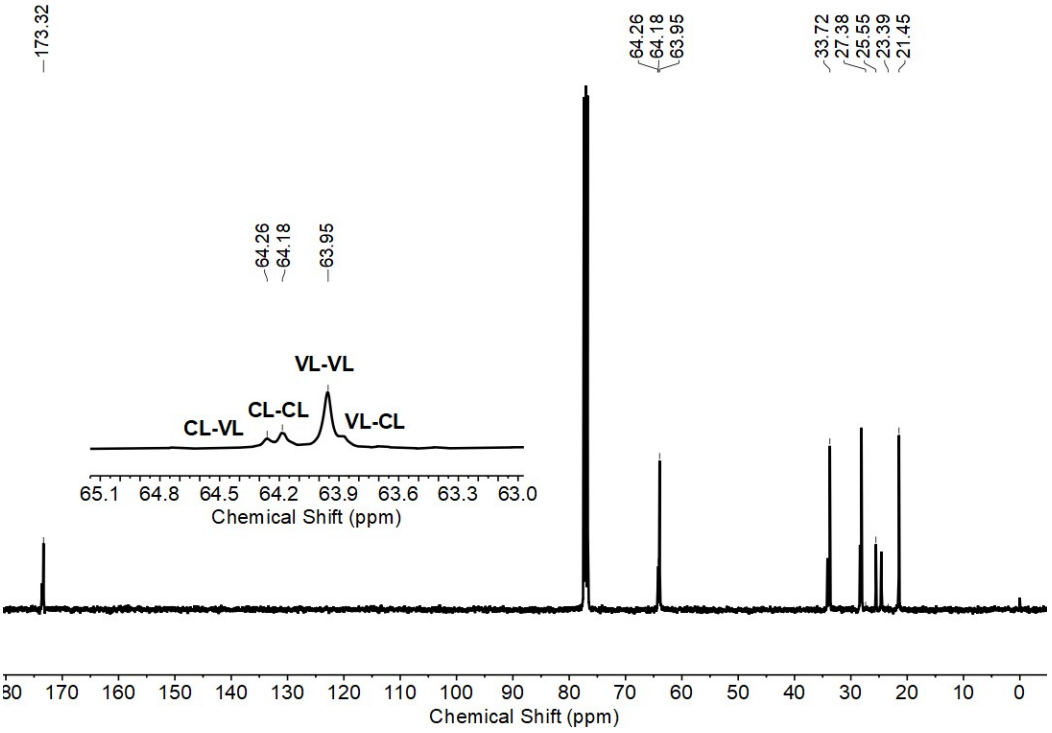


Figure S31. ^{13}C NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, 150 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 1).

Calculating the randomness of CL and VL copolymerization: the average sequence length (L) and the randomness (R) are calculated according to the following equations, where L_{CL} and L_{VL} represent the sequence lengths of CL and VL chain segments, respectively.[6]

$$L_{CL} = \frac{I_{cc} + I_{vc}}{I_{vc}} \quad \text{(Eq. 1)}$$

$$L_{VL} = \frac{I_{vv} + I_{cv}}{I_{cv}} \quad \text{(Eq. 2)}$$

$$R = \frac{1}{L_{CL}} + \frac{1}{L_{VL}} \quad \text{(Eq. 3)}$$

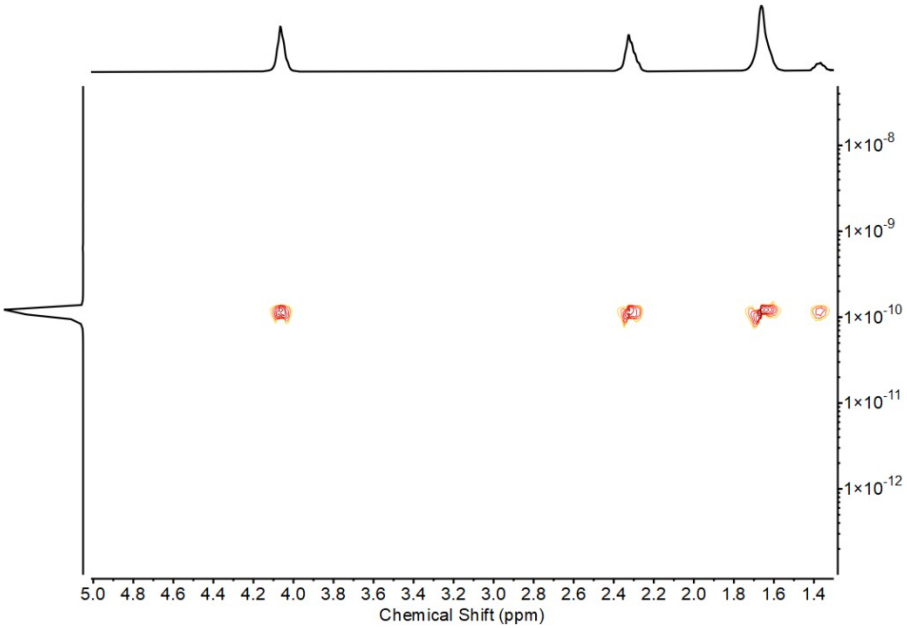


Figure S32. DOSY NMR spectrum ($CDCl_3$) of the PVL/PCL copolymer. Conditions: catalyst **C3**, 150 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 1).

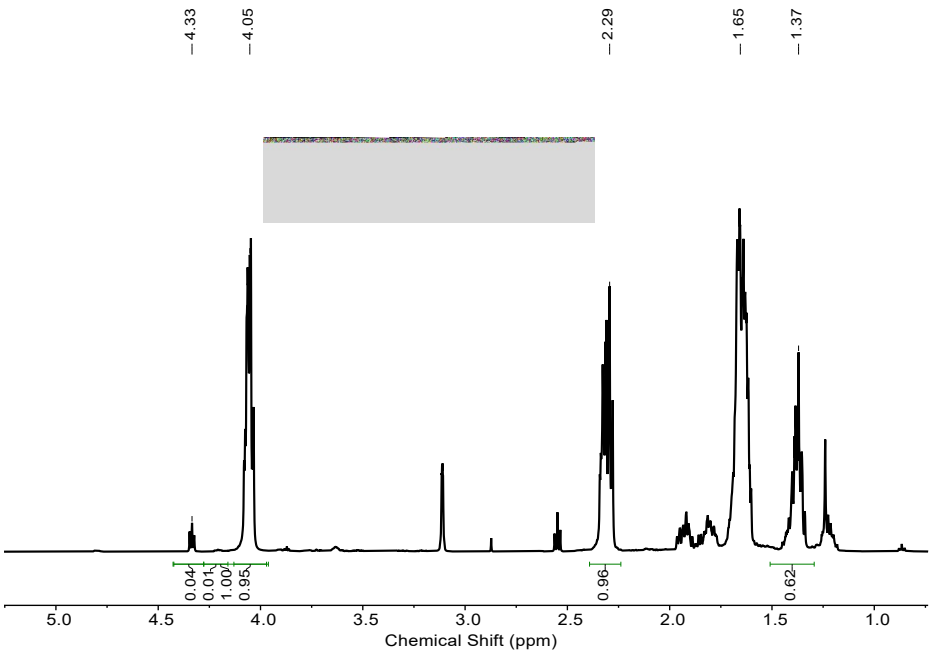


Figure S33. [1]H NMR spectrum of copolymerization. Conditions: catalyst **C3**, [CHO] = 0.3 mL, 150 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 2).

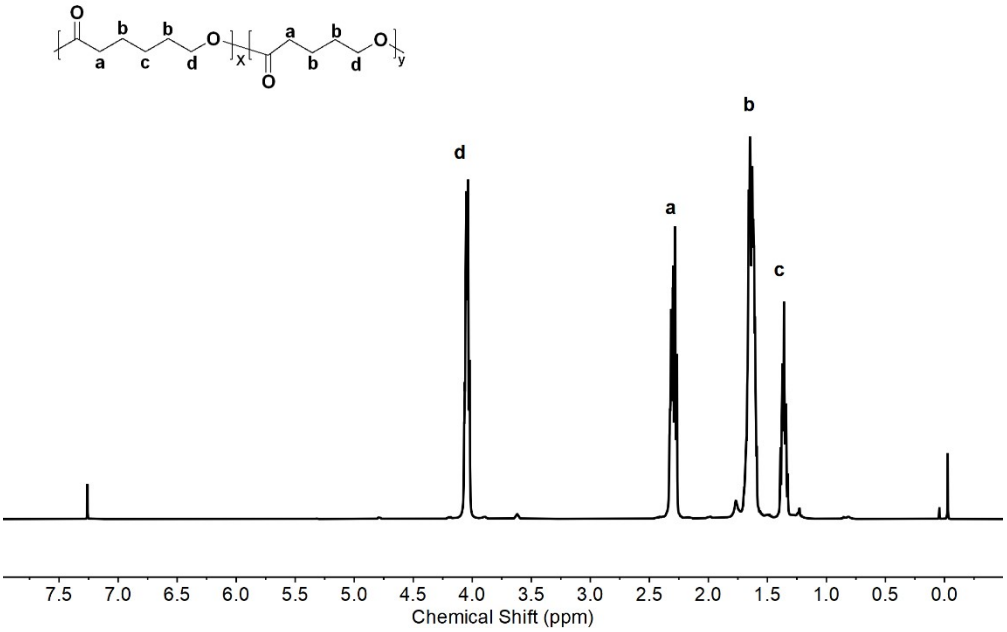


Figure S34. [1]H NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.3 mL, 150 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 2).

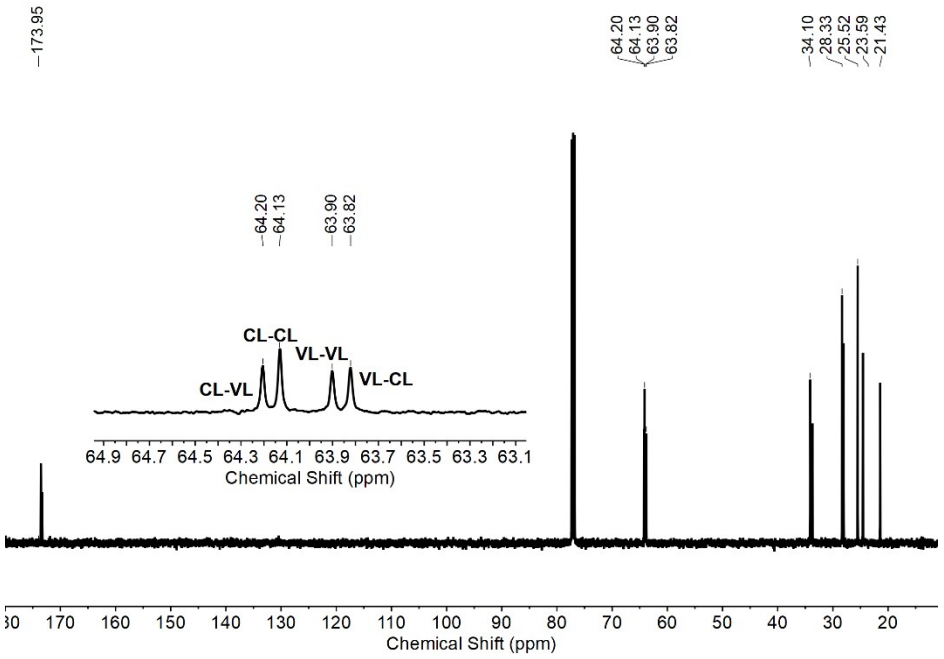


Figure S35. ^{13}C NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.3 mL, 150 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 2).

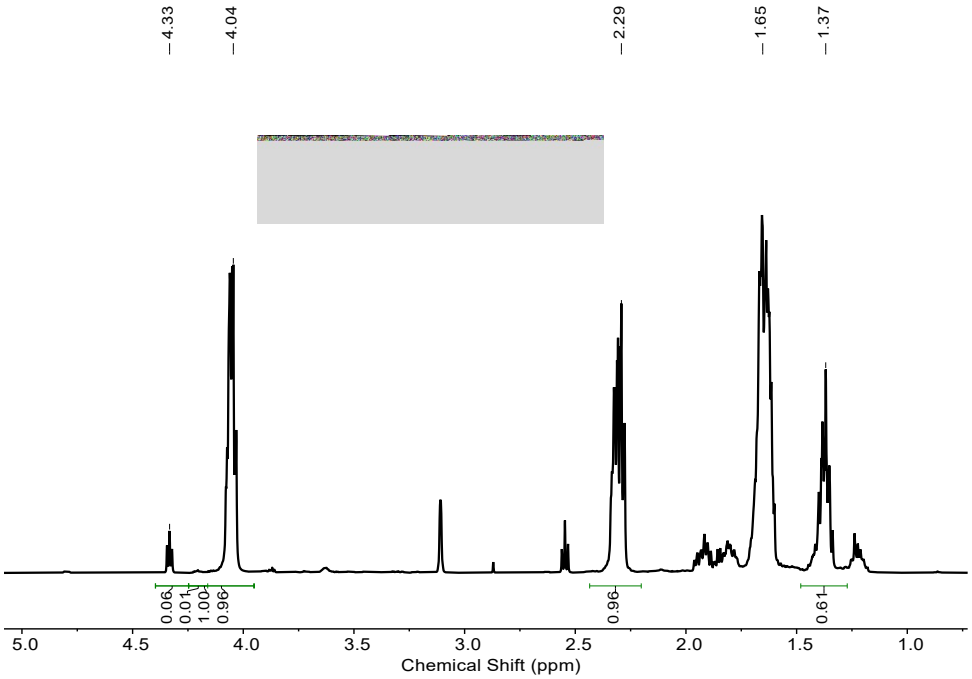


Figure S36. ^{1}H NMR spectrum of copolymerization. Conditions: catalyst **C3**, [CHO] = 0.3 mL, 180 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 3).

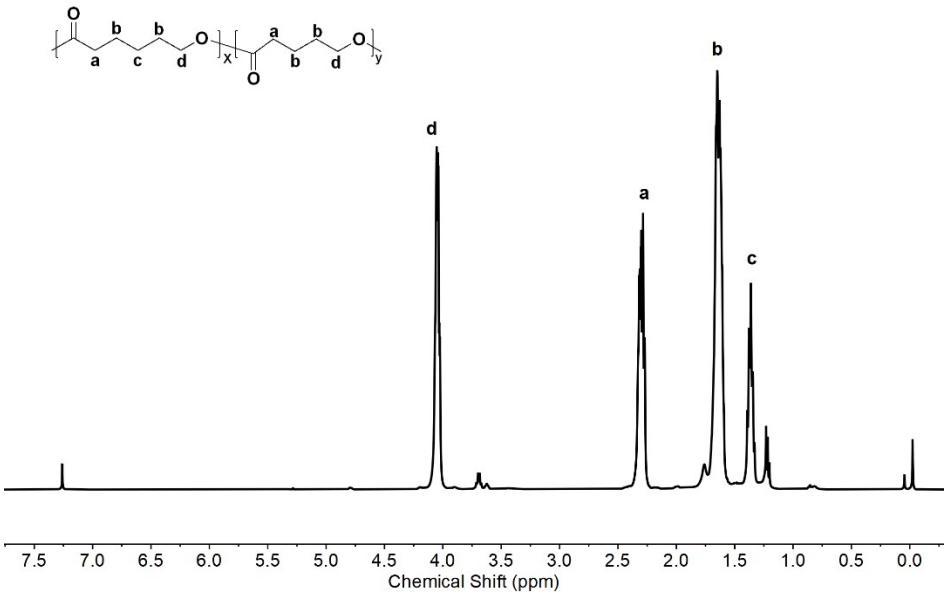


Figure S37. ^{1}H NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.3 mL, 180 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 3).

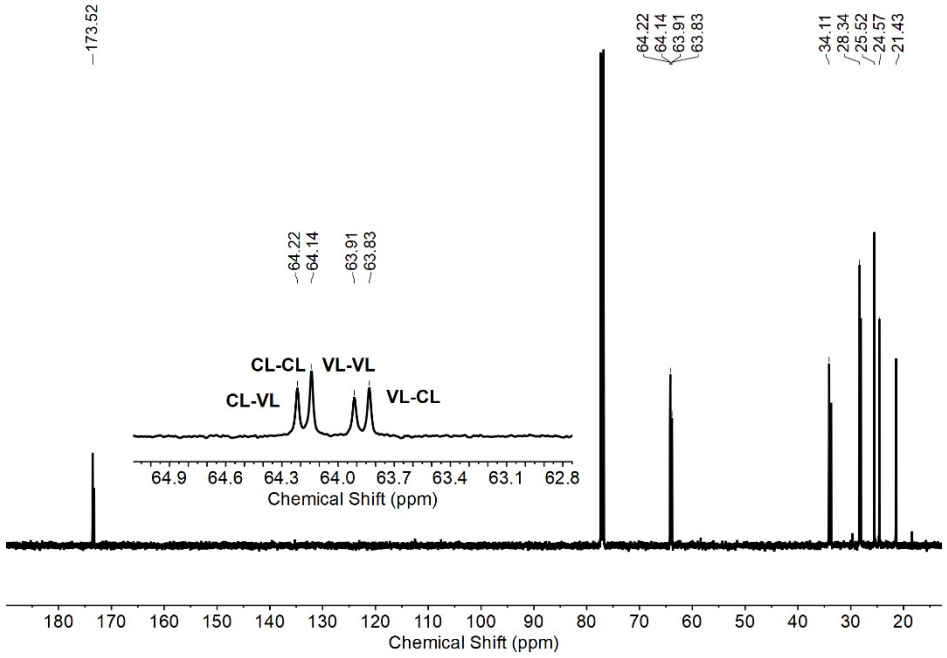


Figure S38. ^{13}C NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.3 mL, 180 °C, [VL]/[CL]/[Cat.] = 700:700:1 (Table 3, entry 3).

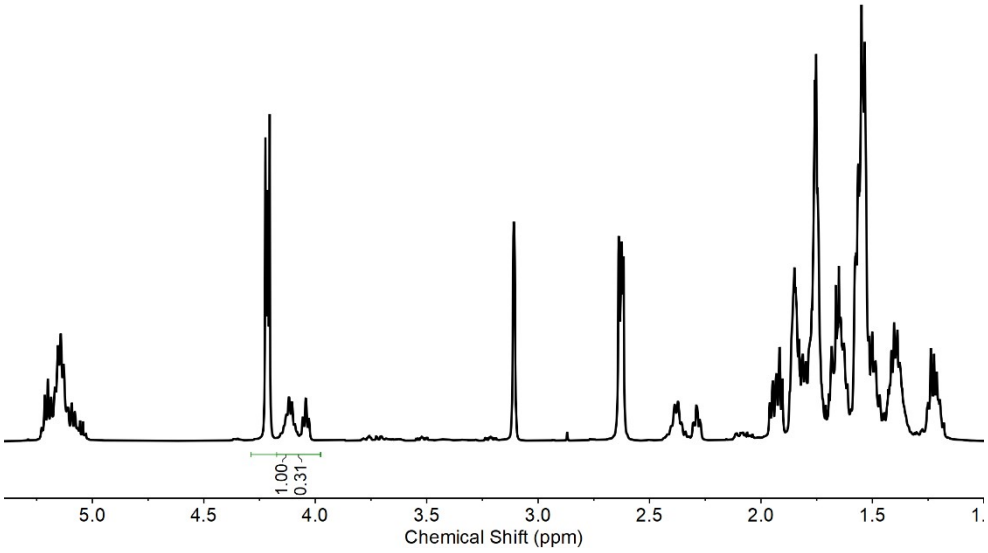


Figure S39. [1]H NMR spectrum of copolymerization. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 150 °C, [CL]/[LA]/[Cat.] = 1000:1000:1 (Table 3, entry 4).

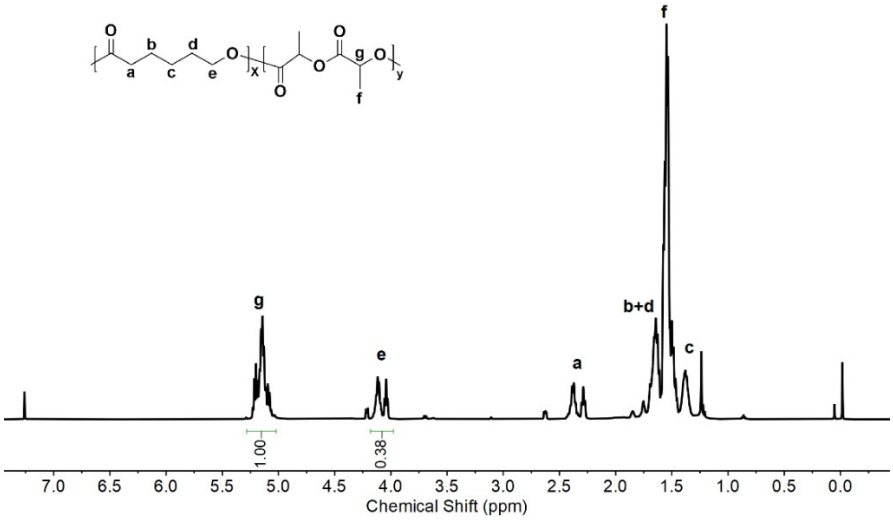


Figure S40. [1]H NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 150 °C, [CL]/[LA]/[Cat.] = 1000:1000:1 (Table 3, entry 4).

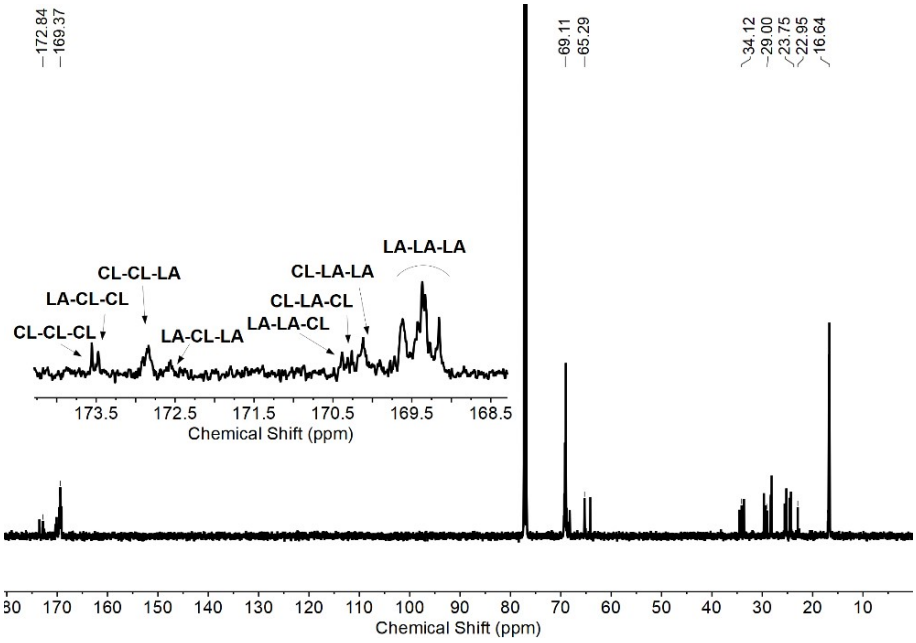


Figure S41. ^{13}C NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 150 °C, [CL]/[LA]/[Cat.] = 1000:1000:1 (Table 3, entry 4).

Calculating the randomness of CL and LA copolymerization: the average sequence length (L) and the randomness (R) are calculated according to the following equations, where L_{CL} and L_{LA} represent the sequence lengths of CL and LA chain segments, respectively.[7]

$$L_{CL} = \frac{I_{CCC} + I_{LCC}}{I_{CCL} + I_{LCL}} \quad \text{(Eq. 4)}$$

$$L_{LA} = \frac{1}{2}\left[\frac{I_{LLL} + \frac{I_{LLC} + I_{CLL}}{2}}{\frac{I_{LLC} + I_{CLL}}{2} + I_{CLC}} + 1\right] \quad \text{(Eq. 5)}$$

$$R = \frac{1}{L_{CL}} + \frac{1}{L_{LA}} \quad \text{(Eq. 6)}$$

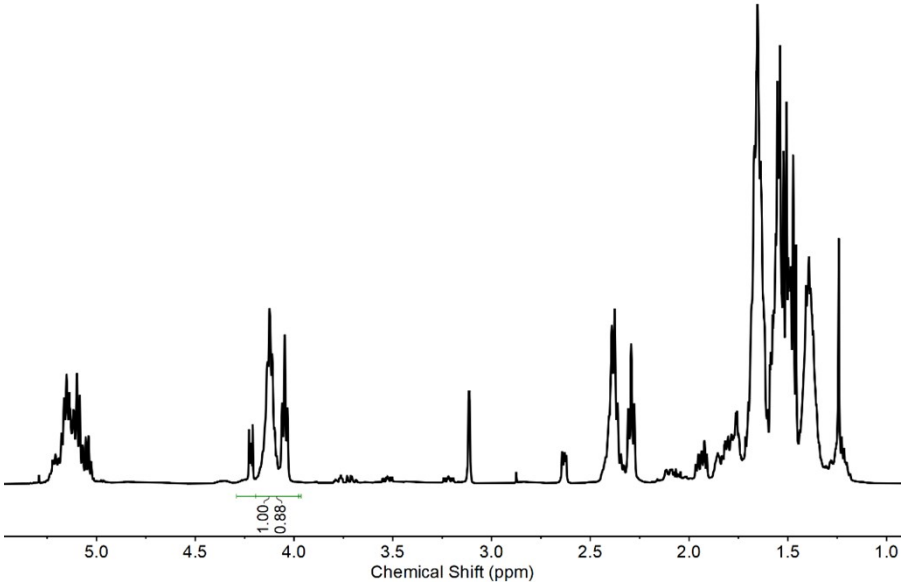


Figure S42. [1]H NMR spectrum of copolymerization. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 180 °C, [CL]/[LA]/[Cat.] = 1000:1000:1 (Table 3, entry 5).

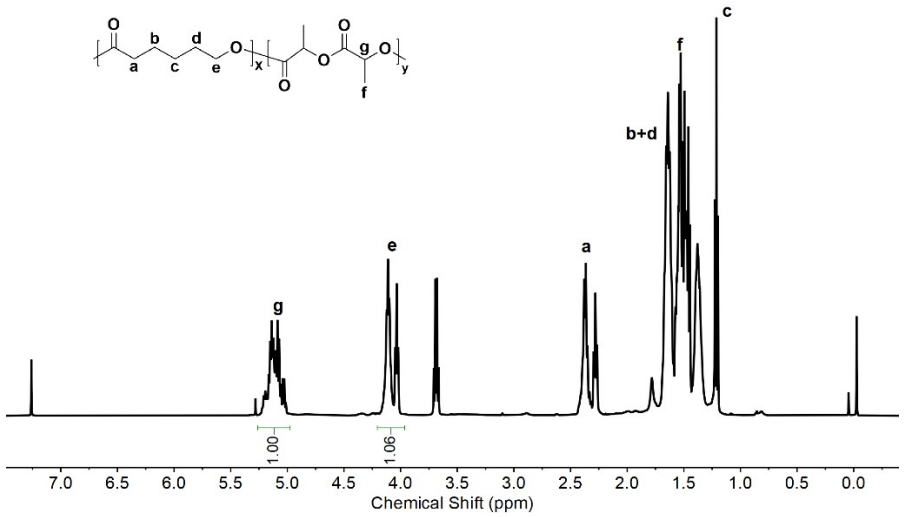


Figure S43. [1]H NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 180 °C, [CL]/[LA]/[Cat.] = 1000:1000:1 (Table 3, entry 5).

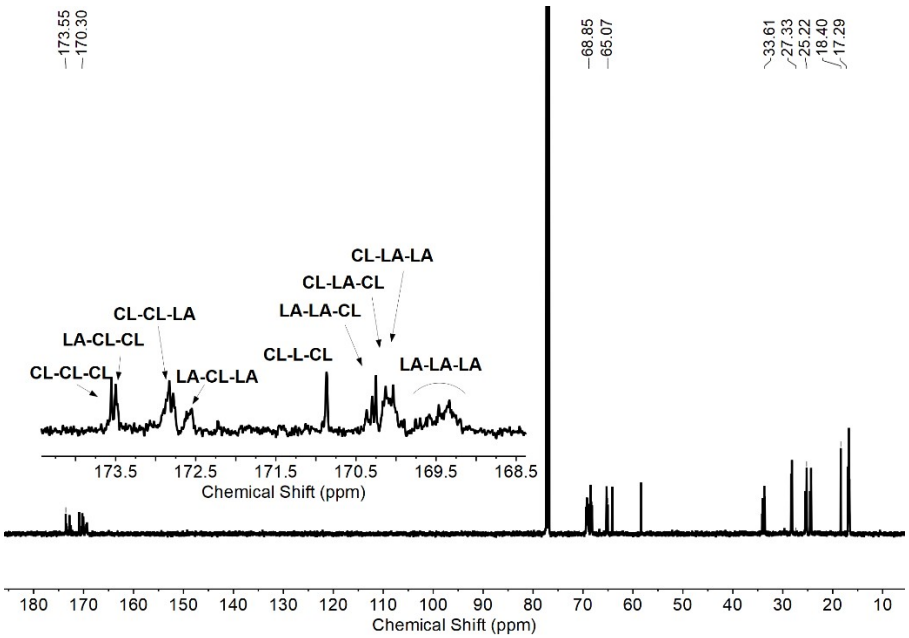


Figure S44. ^{13}C NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 180 °C, [CL]/[LA]/[Cat.] = 1000:1000:1 (Table 3, entry 5).

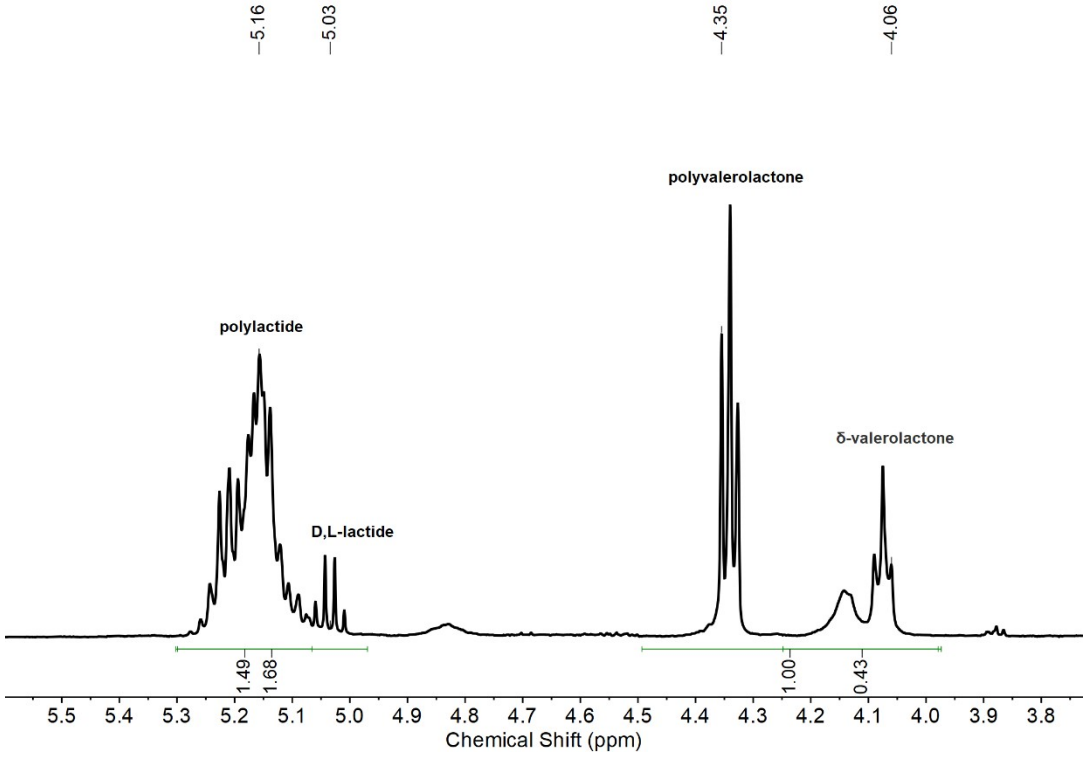


Figure S45. ^{1}H NMR spectrum of copolymerization. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 150 °C, [VL]/[LA]/[Cat.] = 700:1000:1 (Table 3, entry 6).

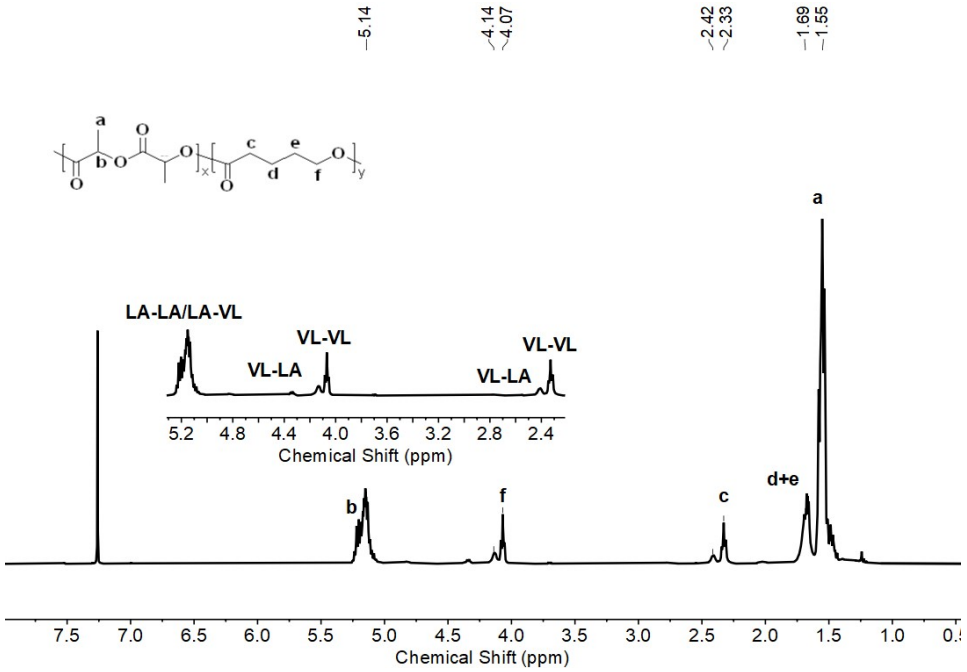


Figure S46. ^{1}H NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 150 °C, [VL]/[LA]/[Cat.] = 700:1000:1 (Table 3, entry 6).

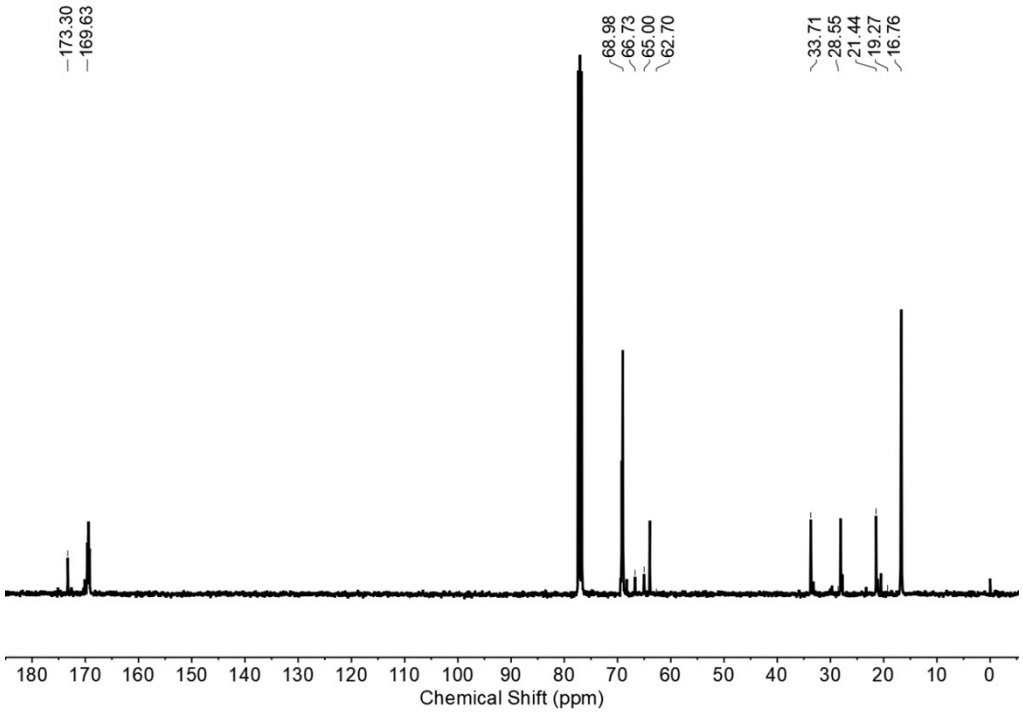


Figure S47. ^{13}C NMR spectrum of copolymerization after purification. Conditions: catalyst **C3**, [CHO] = 0.5 mL, 150 °C, [VL]/[LA]/[Cat.] = 700:1000:1 (Table 3, entry 6).

Calculating the randomness of VL and LA copolymerization: the average sequence length (*L*) and the randomness (*R*) are calculated according to the following equations,

where L_{VL} and L_{LA} represent the sequence lengths of VL and LA chain segments, respectively.[8]

$$L_{LA} = \frac{2LA}{VL - LA} \quad \text{(Eq. 7)}$$

$$L_{VL} = \frac{2VL}{VL - LA} \quad \text{(Eq. 8)}$$

$$R = \frac{1}{L_{LA}} + \frac{1}{L_{VL}} \quad \text{(Eq. 9)}$$

6. References

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