Zn(II) and Cu(II) formamidine complexes: Structural, kinetics and polymer tacticity studies in ring-opening polymerization of ε-caprolactone and lactides

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Supplementary Information

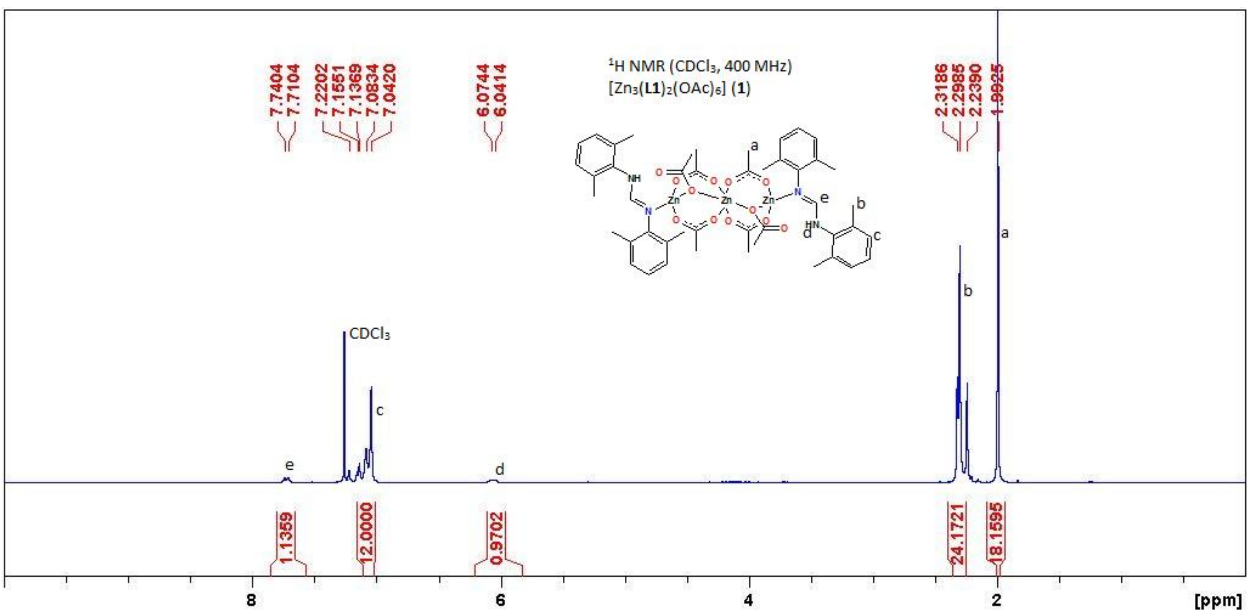


Figure S1. ^{1}H NMR spectrum of complex **1** in $CDCl_3$ at room temperature.

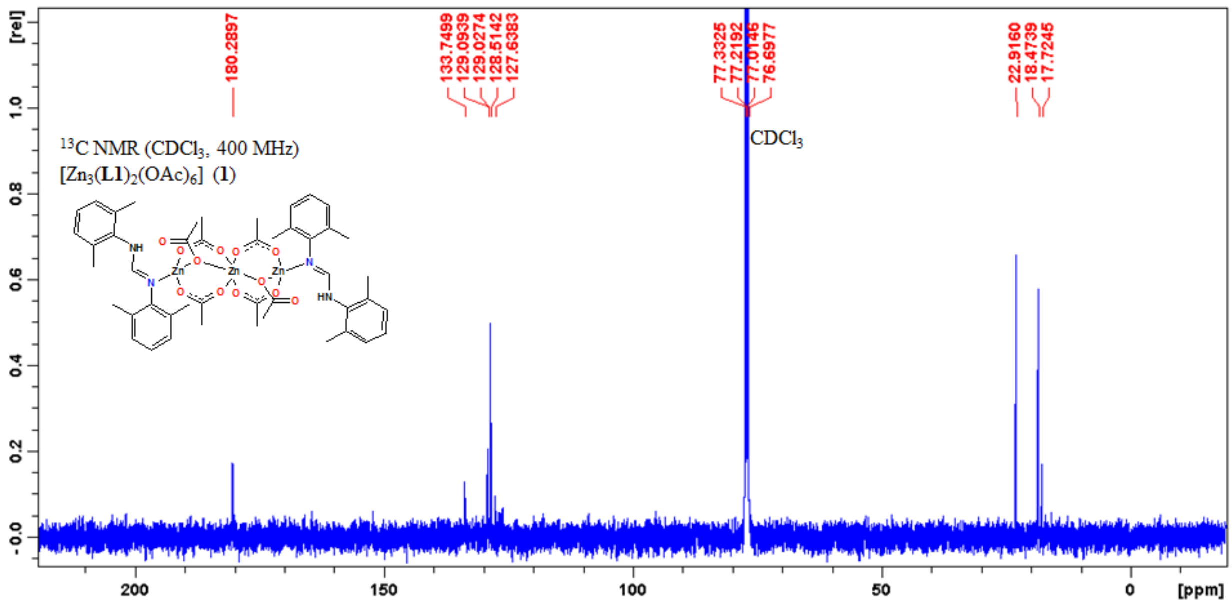


Figure S2. ^{13}C NMR spectrum of complex **1** in CDCl$_3$ at room temperature.

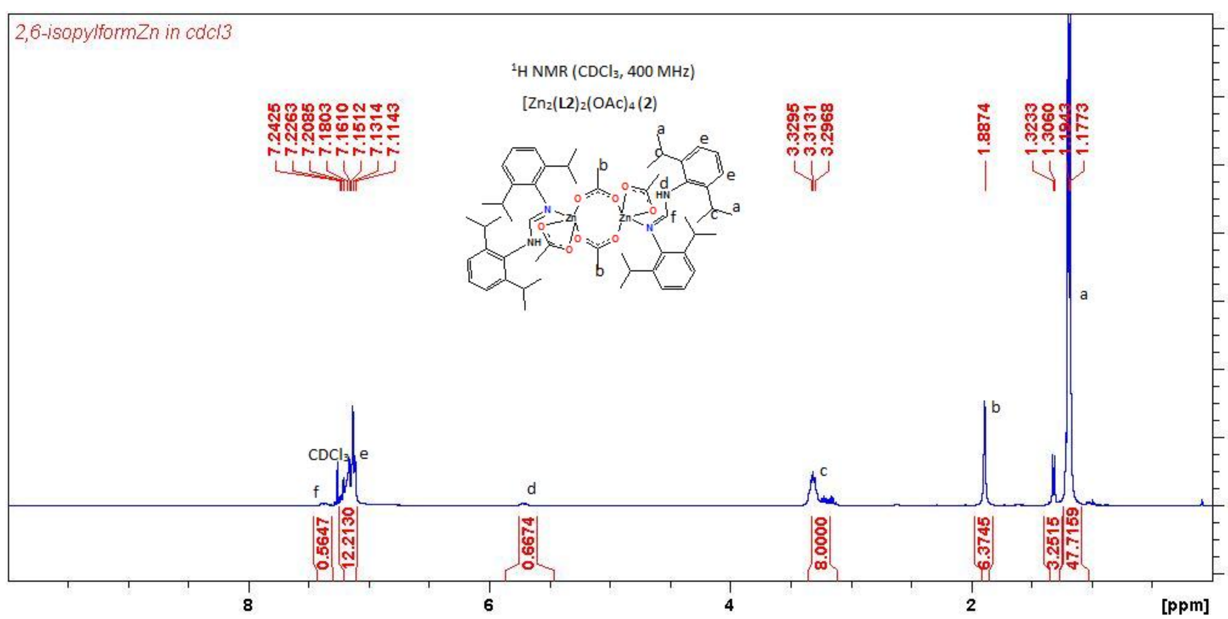


Figure S3. ^{1}H NMR spectrum of complex **2** in CDCl$_3$ at room temperature.

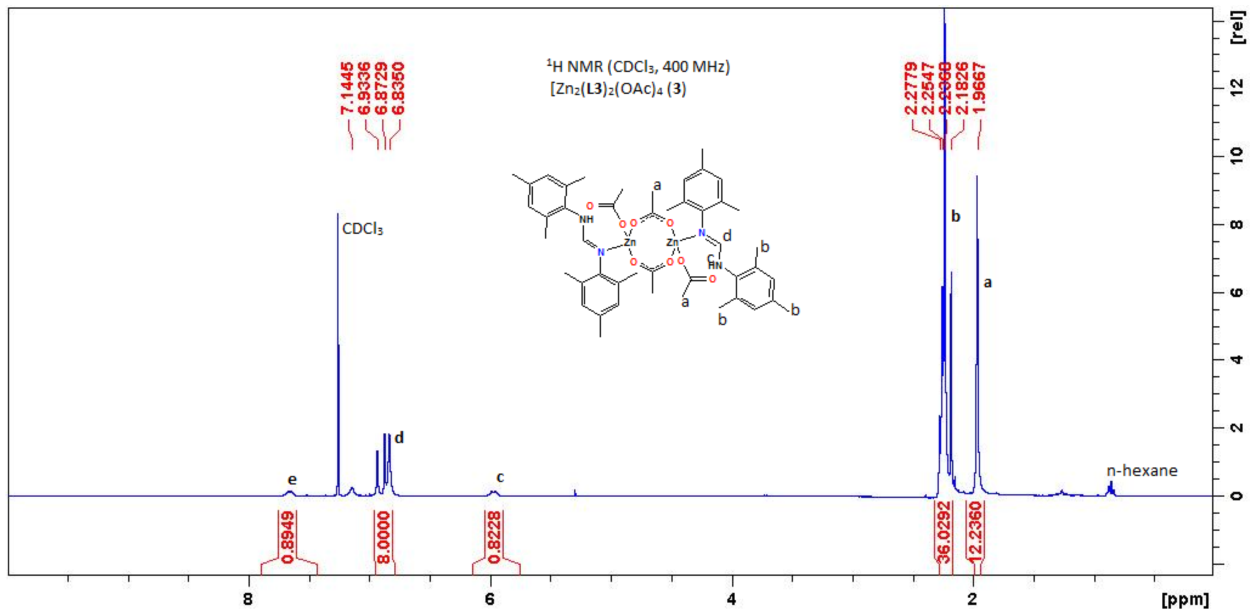


Figure S4. ^{1}H NMR spectrum of complex **3** in $CDCl_3$ at room temperature.

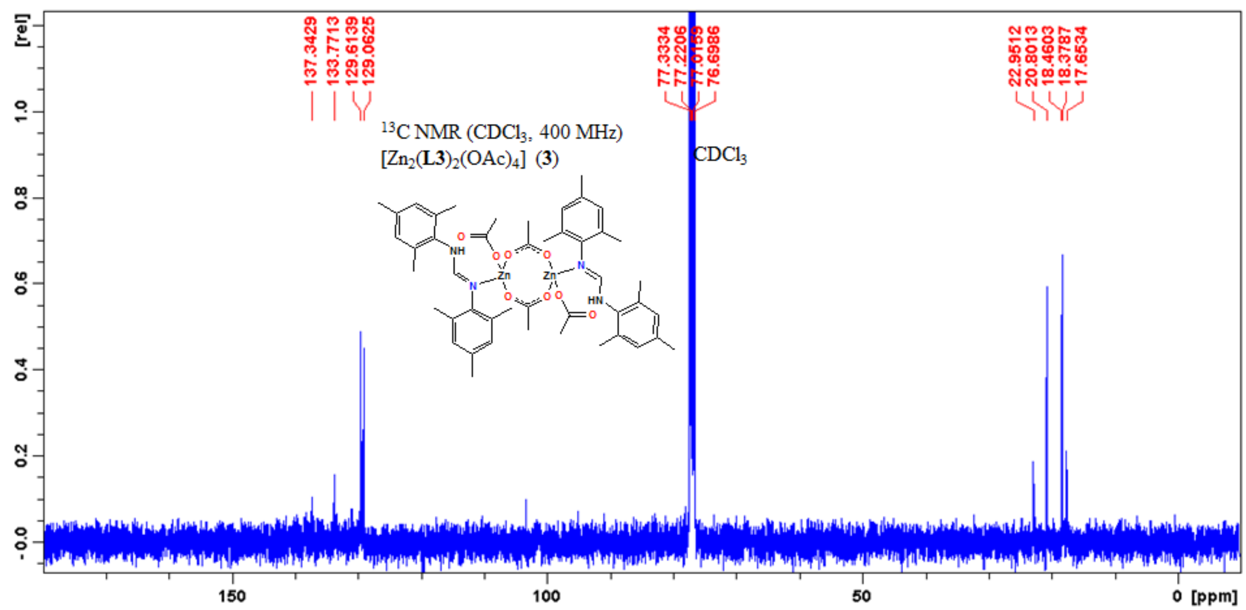


Figure S5. ^{13}C NMR spectrum of complex **3** in $CDCl_3$ at room temperature.

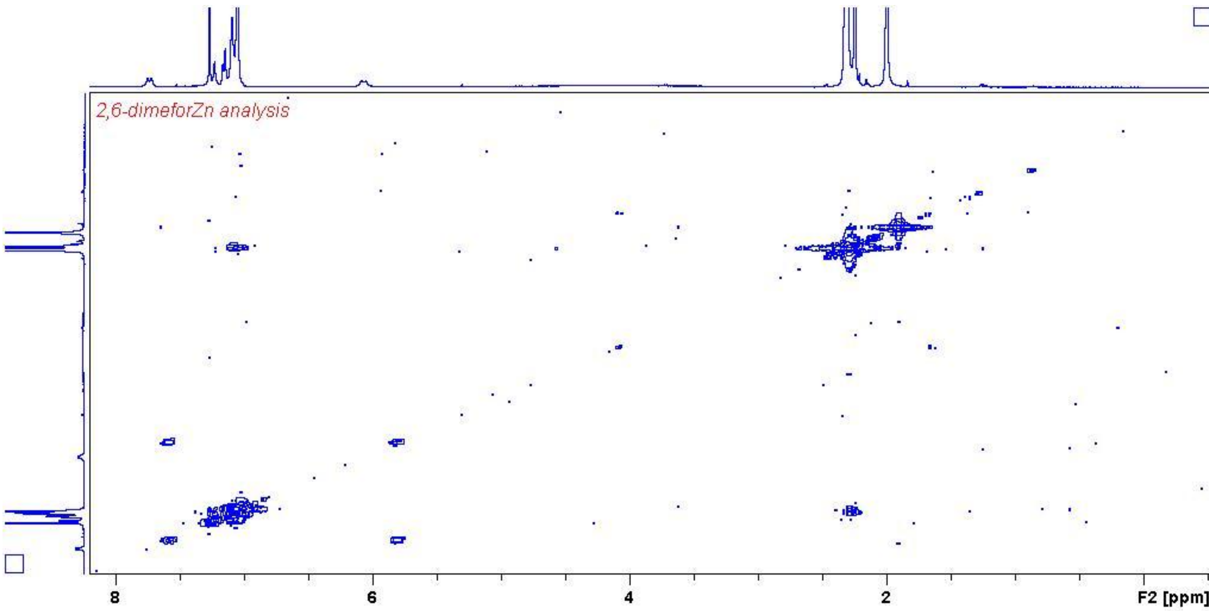


Figure S6. COSY NMR spectrum of complex **1** in $CDCl_3$ at room temperature**.**

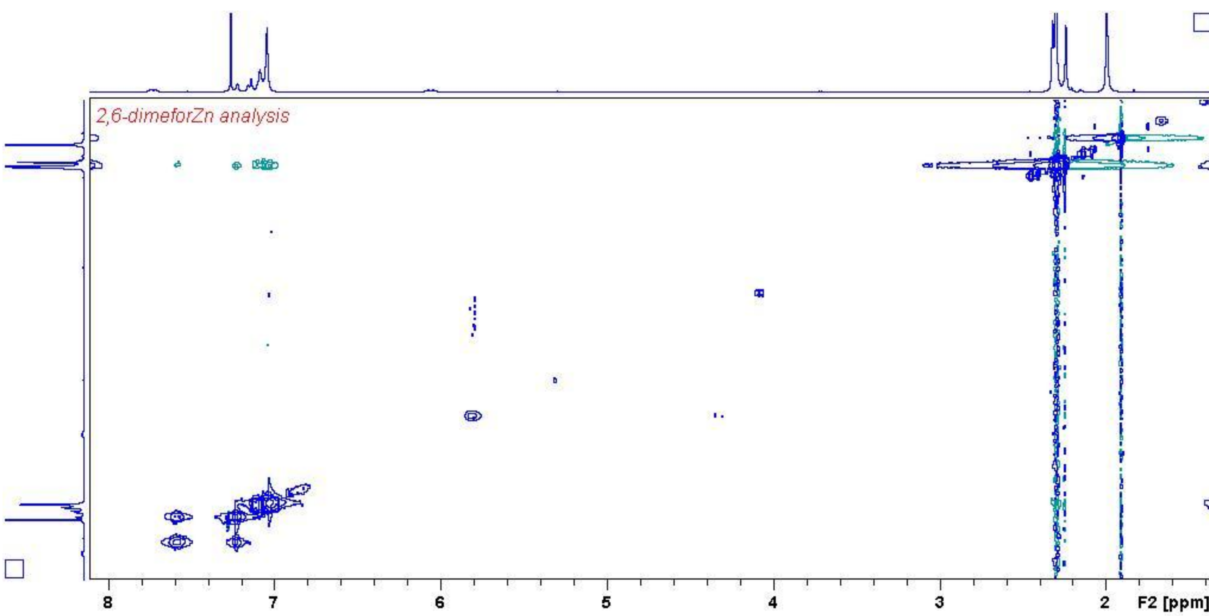


Figure S7. Two dimensional (2D) ^1H-^1H nuclear overhauser effect spectroscopy (NOESY) NMR of complex **1** in $CDCl_3$ at room temperature.

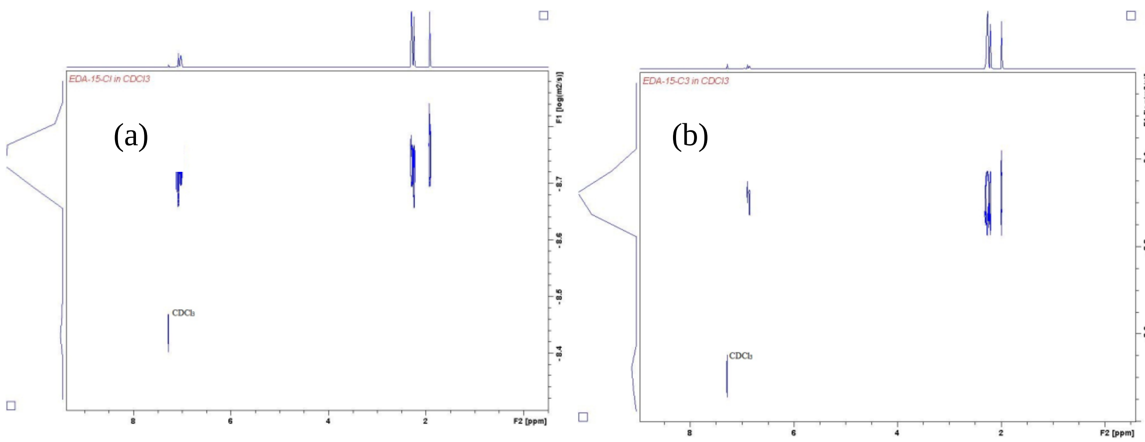


Figure S8. DOSY NMR spectra of complexes (a) **1** and (b) **3**

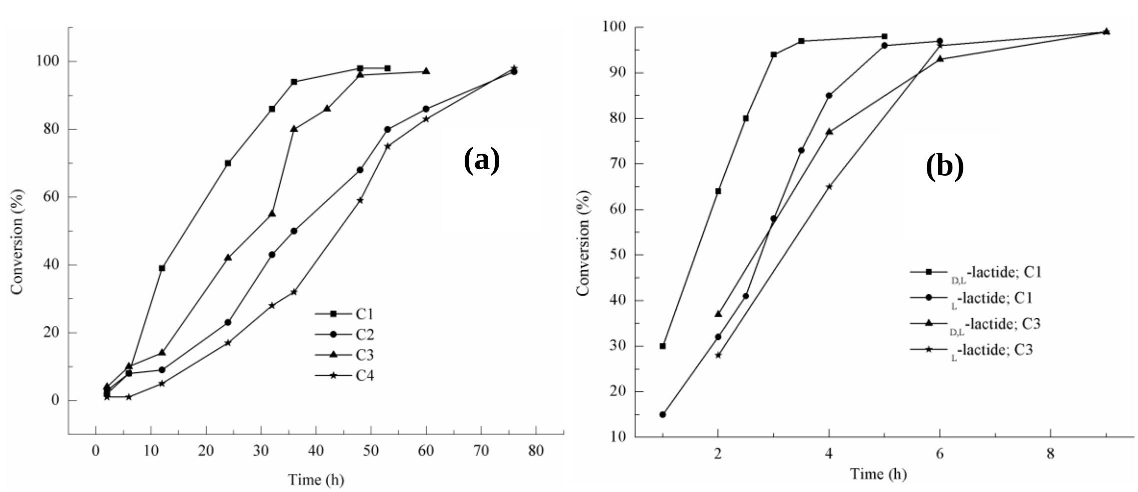


Figure S9. (a) Bulk polymerization of ε-CL to PCL with time for complexes **1**–**4** at 110 °C, M/I = 200, $[CL]_o$ = 0.01 mol and [1] = 0.00005 mol and (b) Polymerization of $_{D,L}$-lactide and $_L$-lactide to polylactides using complexes **1** and **3** in toluene at 110 °C, $[CL]_o/[I]$ = 200.

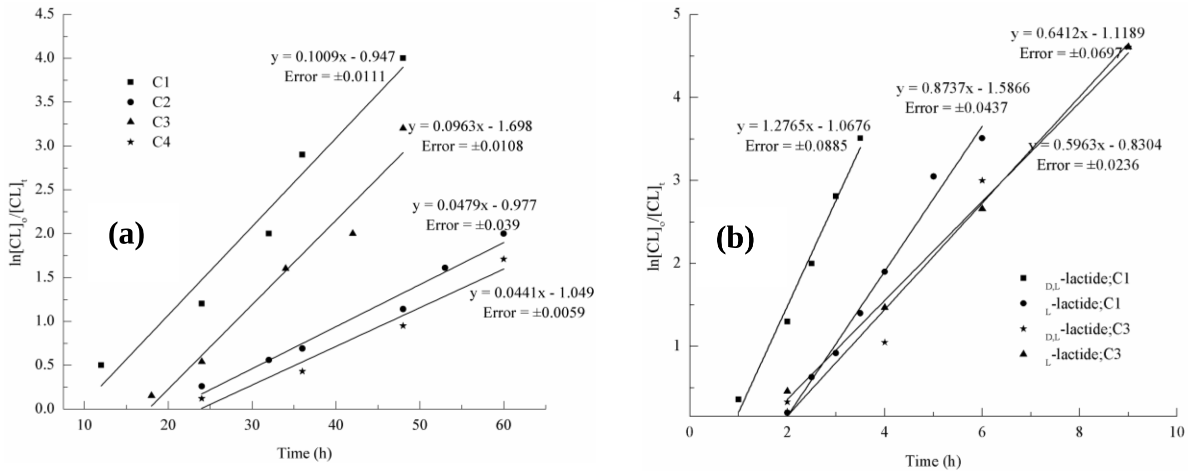


Figure S10. (a) First order kinetic plots of $\ln[CL]_o/[CL]_t$ *vs*. time for complexes **1**–**4** in the bulk polymerization of ε-CL at 110 ^oC, $[CL]_o/[I] = 200$. (b) First order kinetic plots of $\ln[CL]_o/[CL]_t$ *vs*. time for complexes **1** and **3** in the polymerization of $_{D,L}$-lactide and $_L$-lactide to polylactides in toluene at 110 ^oC, $[CL]_o/[I] = 200$.

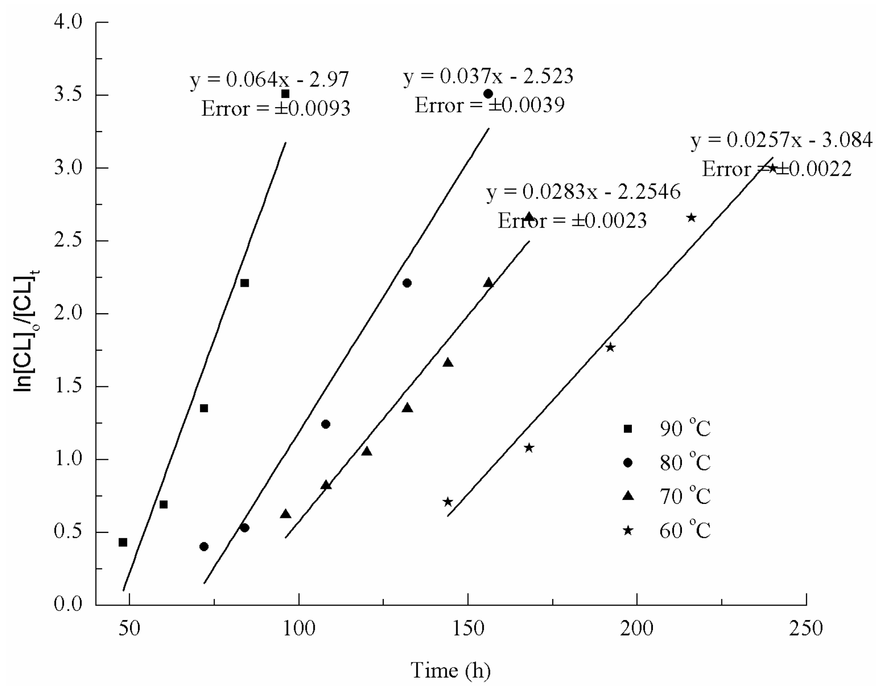


Figure S11. Semi-logarithmic kinetic plots for ε-CL polymerization catalyzed by complex **3** at various temperatures

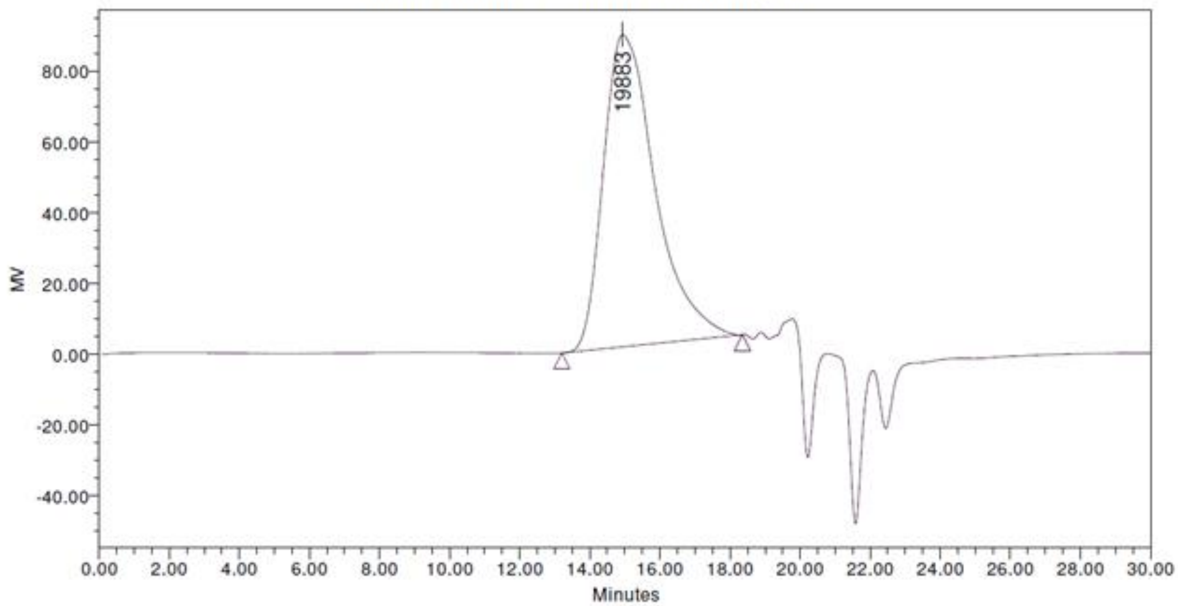
Stellenbosch University

Project Name: GPC2006
Reported by User: System

SAMPLE INFORMATION

Sample Name:	ED003	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	2014/12/03 07:25:32 PM
Vial:	3	Acq. Method:	GPC_im_UV254_320
Injection #:	1	Date Processed:	2014/12/04 08:23:02 AM
Injection Volume:	100.00 ul	Channel Name:	410
Run Time:	30.00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name	20141203pm

Broad Unknown Relative Chromatogram



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		8631	18468	19883	28657	38314	2.139812	1.551756	2.074657

Figure S12. GPC traces of PCL obtained from catalyst **3**, M/I = 200, time 53 h, 110 °C.

Stellenbosch University

Project Name: GPC2006

Reported by User: System

SAMPLE INFORMATION

Sample Name:	ED013	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	2014/12/04 12:45:57 AM
Vial:	13	Acq. Method:	GPC_im_UV254_320
Injection #:	1	Date Processed:	2014/12/04 08:23:02 AM
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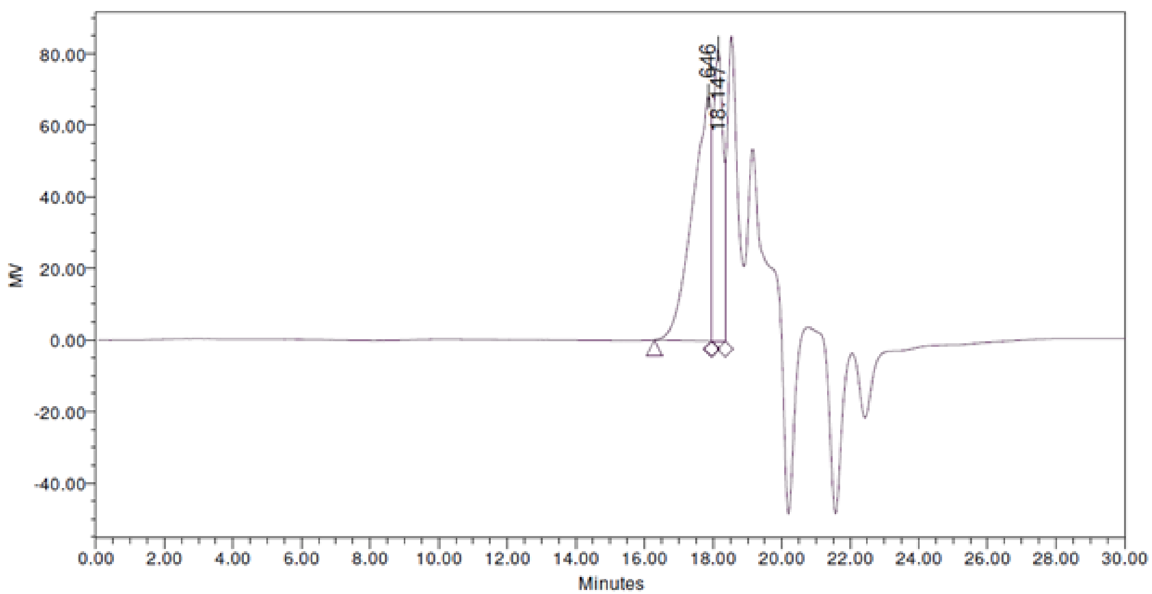
Run Time:	30.00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name	20141203pm

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

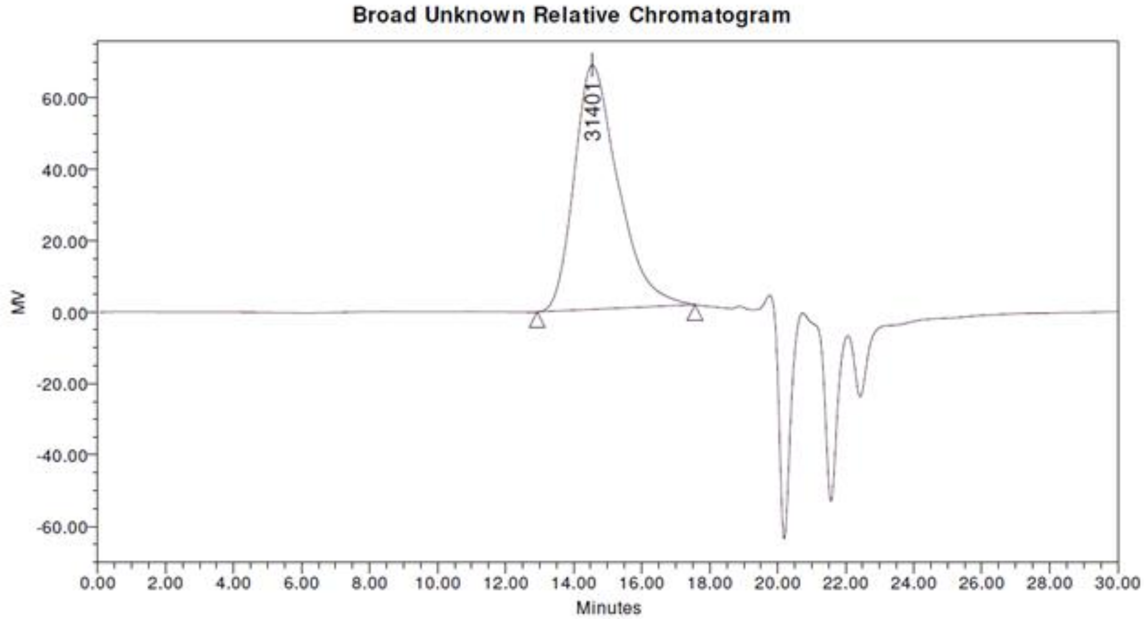
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		898	1006	646	1164	1381	1.120301	1.157019	1.372802

Figure S13. GPC traces of PCL obtained from catalyst **3**, M/I = 200, in methanol, time 180 mins, 110 °C.

Stellenbosch University
Project Name: GPC2006
Reported by User: System

SAMPLE INFORMATION

Sample Name:	ED016	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	2014/12/04 02:22:02 AM
Vial:	16	Acq. Method:	GPC_im_UV254_320
Injection #:	1	Date Processed:	2014/12/04 08:23:02 AM
Injection Volume:	100.00 ul	Channel Name:	410
Run Time:	30.00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name	20141203pm



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		16866	31127	31401	45986	61134	1.845614	1.477348	1.963994

Figure S14. GPC traces of PLA obtained from catalyst **3**, M/I = 200, in toluene, time 9 h, 110 °C.

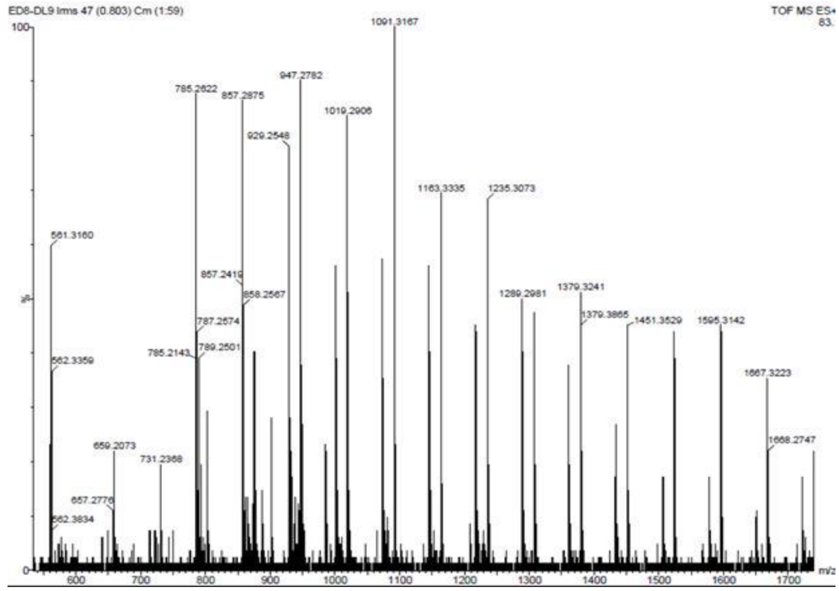


Figure S15. ES-MS of the crude PLA (from $_{D,L}$-lactide) from catalyst **3**, $[CL]_o/[\mathbf{3}] = 200$, 9 h, showing distribution of two structural components.

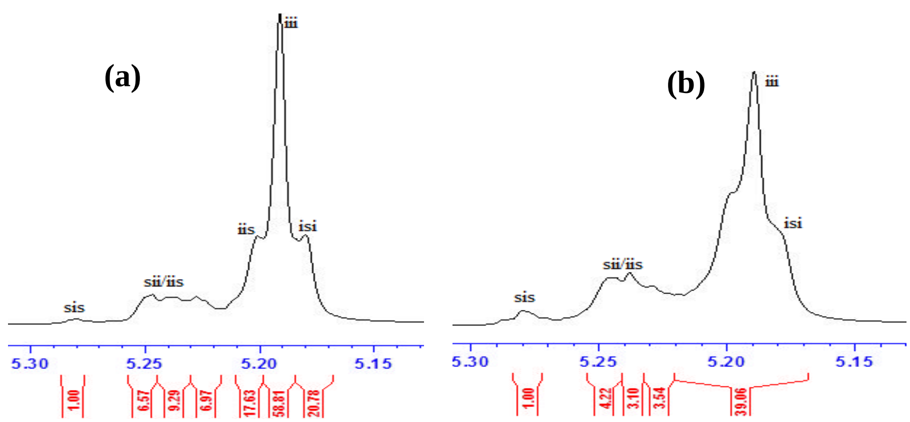


Figure S16. ^{1}H homonuclear decoupled NMR of the methine region of poly($_{L}$-LA) formed with (a) complex **1** and (b) complex **3**, respectively.

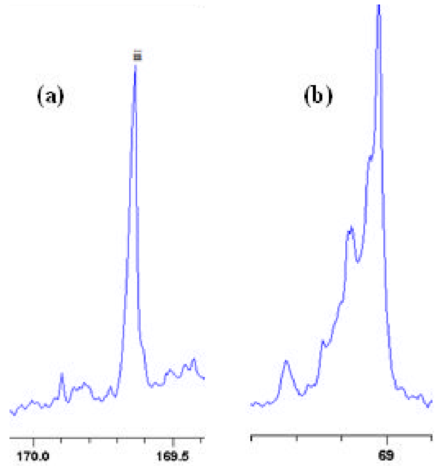


Figure S17. (a) ^{13}C NMR spectra carbonyl region and (b) ^{13}C NMR methine region of poly($_{L}$-LA).

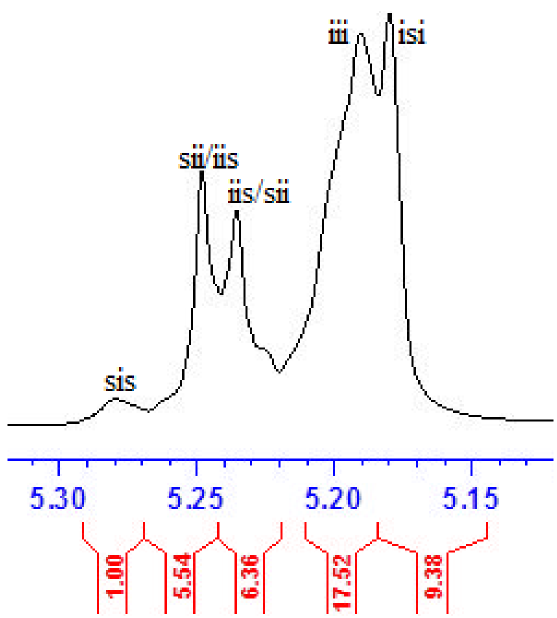


Figure S18. ^{1}H homonuclear decoupled NMR of the methine region of poly($_{D,L}$-LA).

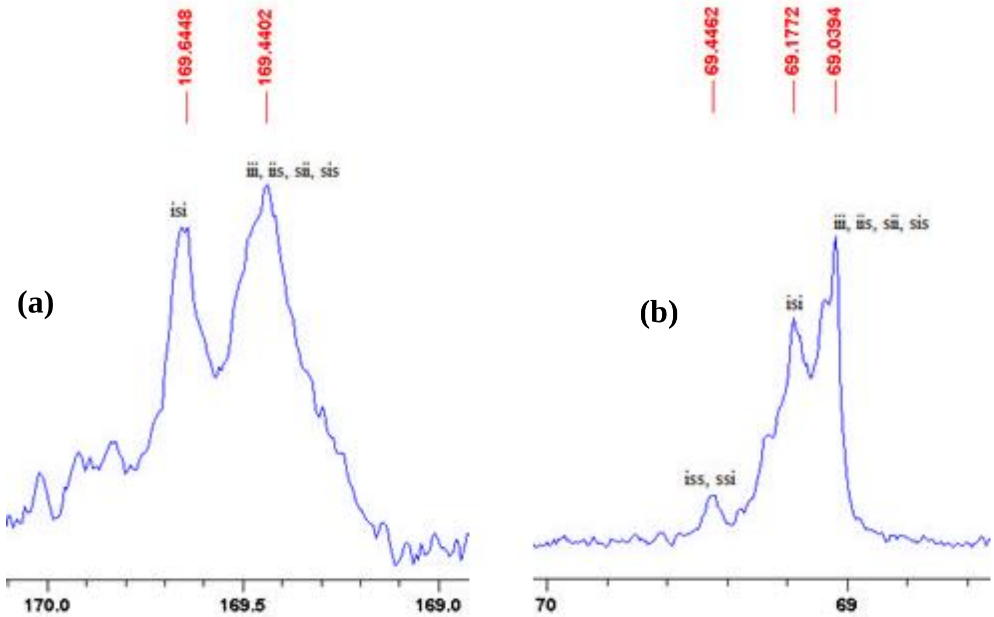


Figure S19. (a) ^{13}C NMR spectra carbonyl region and (b) ^{13}C NMR methine region of poly($_{D,L}$-LA)

Table S1. Crystal data collection and structural refinement parameters for complexes **1–4**

	1	**2**	**3**	**4**
Empirical formula	$C_{46}H_{58}N_4O_{12}Zn_3$	$C_{58}H_{84}N_4O_8Zn_2$	$C_{46}H_{60}N_4O_8Zn_2$	$C_{58}H_{84}Cu_2N_4O_8$
Formula weight	1055.07	1096.03	927.72	1092.37
Temperature (K)	173(2)	173(2)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	*P*-1	*P*-1	$P2_1/c$
a/Å	9.5958(6)	13.9570(3)	9.4219(7)	15.4331(10)
b/Å	15.6026(9)	21.3908(4)	12.1061(9)	12.4453(9)
c/Å	16.4916(10)	21.4967(5)	20.8673(18)	16.2537(11)
α	90°	94.542(10)°	85.831(5)°	90°
β	103.752(2)°	108.766(10)°	85.579(5)°	104.965(3)°
γ	90°	100.316(10)°	77.657(4)°	90°
Volume ($Å^3$)	2398.3(3)	5913.6(2)	2314.4(3)	3016.0(4)
Z	2	4	2	2
Density (calculated)	1.461 Mg/m^3	1.231 Mg/m^3	1.331 Mg/m^3	1.203 Mg/m^3
Absorption coefficient	1.552 mm^{-1}	0.864 mm^{-1}	1.091 mm^{-1}	0.757 mm^{-1}
F(000)	1096	2336	976	1164
Crystal size	0.41 x 0.36 x 0.32 mm^3	0.36 x 0.33 x 0.29 mm^3	0.18 x 0.15 x 0.12 mm^3	0.36 x 0.34 x 0.34 mm^3
Theta range for data collection	1.82 to 28.59°	0.978 to 28.433°	0.980 to 27.917°	1.366 to 25.493°
Index ranges	$-12 \le h \le 12$, $-20 \le k \le 20$, $-21 \le l \le 22$	$-17 \le h \le 18$, $-27 \le k \le 28$, $-27 \le l \le 28$	$-12 \le h \le 12$, $-15 \le k \le 14$, $-26 \le l \le 26$	$-18 \le h \le 18$, $-15 \le k \le 15$, $-19 \le l \le 19$
Reflections collected	53536	133169	36720	57141
Independent reflections	6033 [R(int) = 0.0176]	28279 [R(int) = 0.0230]	10307 [R(int) = 0.0342]	5593 [R(int) = 0.0338]
Completeness to theta = 28.59°	100%	100.0%	98.10%	100.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.609 and 0.524	0.791 and 0.683	0.877 and 0.822	0.773 and 0.769
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6032 / 0 / 302	28279 / 2 / 1348	10307 / 5 / 567	5593 / 0 / 325
Goodness-of-fit on F^2	1.059	1.041	1.135	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0273, wR_2 = 0.0715	R1 = 0.0338, wR_2 = 0.0815	R1 = 0.0510, wR_2 = 0.1165	R1 = 0.0312, wR_2 = 0.0841
R indices (all data)	R1 = 0.0287, wR_2 = 0.0725	R1 = 0.0475, wR_2 = 0.0910	R1 = 0.0633, wR_2 = 0.1237	R1 = 0.0361, wR_2 = 0.0875
Largest diff. peak and hole	0.949 and -0.742 e.$Å^{-3}$	0.745 and -0.480 e.$Å^{-3}$	0.740 and -0.555 e.$Å^{-3}$	0.351 and -0.361 e.$Å^{-3}$