

## Supporting information for

# [(Salen\*)Co(OAc)] as robust initiator for the immortal bulk ring-opening (co)polymerization of L-lactide and $\epsilon$ -caprolactone

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Table S1. Results of the bulk ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) at 120 °C initiated by complex **1**.

Entry	[CL] <sub>0</sub> /[ <b>1</b> ]	[MeOH]/[ <b>1</b> ]	Time (h)	Conv. <sup>a</sup> (%)	$M_{n,theo}$ <sup>b</sup> (g/mol)	$M_{n,corr}$ <sup>c</sup> (g/mol)	$\bar{D}$ <sup>d</sup>
1	500	0	24	2.5	1400	1600	1.04
2	500	0	48	3	1700	1700	1.04
3	500	0	96	4	2300	2500	1.03
4	500	0	120	9	5100	4600	1.04
5	500	0	168	60	34200	9300	1.20
6	500	2	21.5	6	1150	1700	1.02
7	500	2	48	11	2100	2200	1.10
8	500	2	72	17	3200	3100	1.07
9	500	2	96	27	5300	5200	1.09
10	500	5	21.5	8	800	800	1.20
11	500	5	48	17	1600	1900	1.10
12	500	5	72	23	2200	2300	1.08
13	500	5	96	43	4200	4500	1.09

<sup>a</sup> Determined by gravimetry and/or from <sup>1</sup>H NMR analysis. <sup>b</sup> Calculated according to  $M_{n,theo} = ([CL]_0/[1]) \times (1/([1]+[MeOH])) \times M_{CL} \times \text{conversion}$ , where  $M_{CL} = 114.14$  g/mol. The molecular weights of both the  $\alpha$ - (initiating group(s)) and  $\omega$ -chain (H) end were not taking into account due to their negligible masses.

<sup>c</sup> Determined by gel permeation chromatography (GPC), using polystyrene (PS) standards and applying the correction factor of 0.56. <sup>d</sup> Determined by GPC.

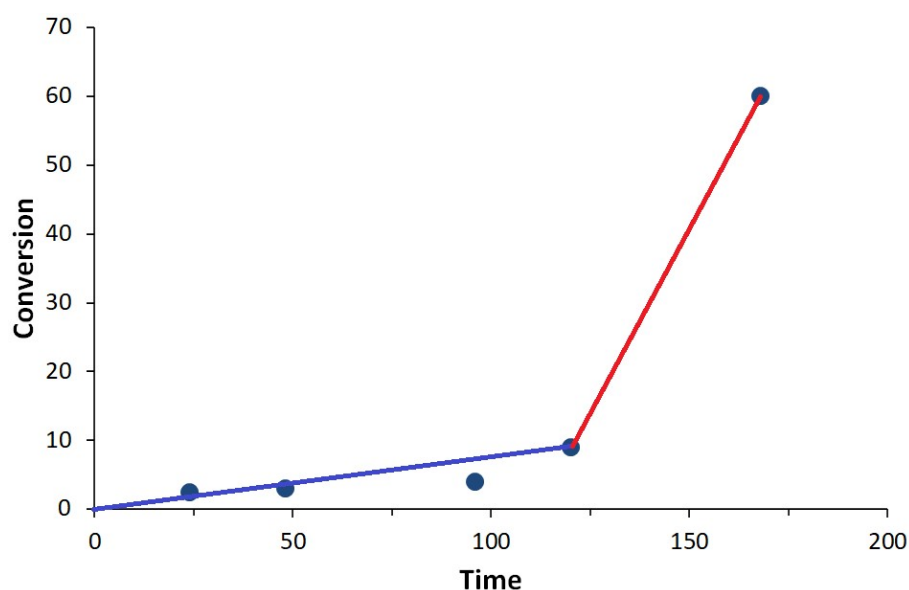


Figure S1. Plot of the conversion as a function of time for the bulk ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) at 120 °C initiated by complex **1** (initial ratio:  $[\text{CL}]/[\mathbf{1}] = 500$ ). Two ROP regimes can be observed, an initially slow ROP until 120 h (blue line).

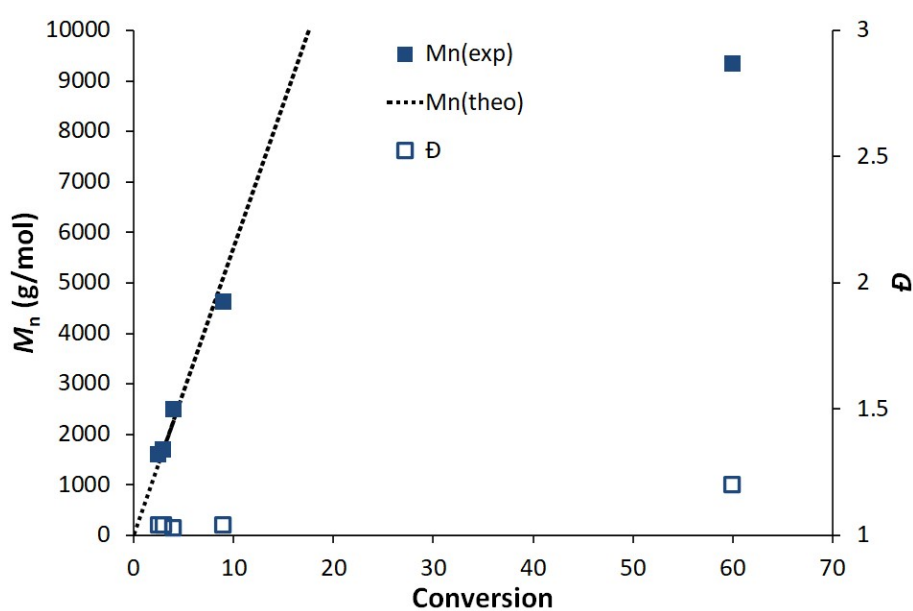


Figure S2. Dependence of the PCL molar masses ( $M_{n,\text{corr}}$ , solid symbols) and dispersity indexes ( $\bar{D}$ , empty symbols) on the CL conversion for the bulk ROP of CL at 120 °C initiated by complex **1** (initial ratio:  $[\text{CL}]/[\mathbf{1}] = 500$ ). The dotted black line represents the theoretical  $M_n$  values.

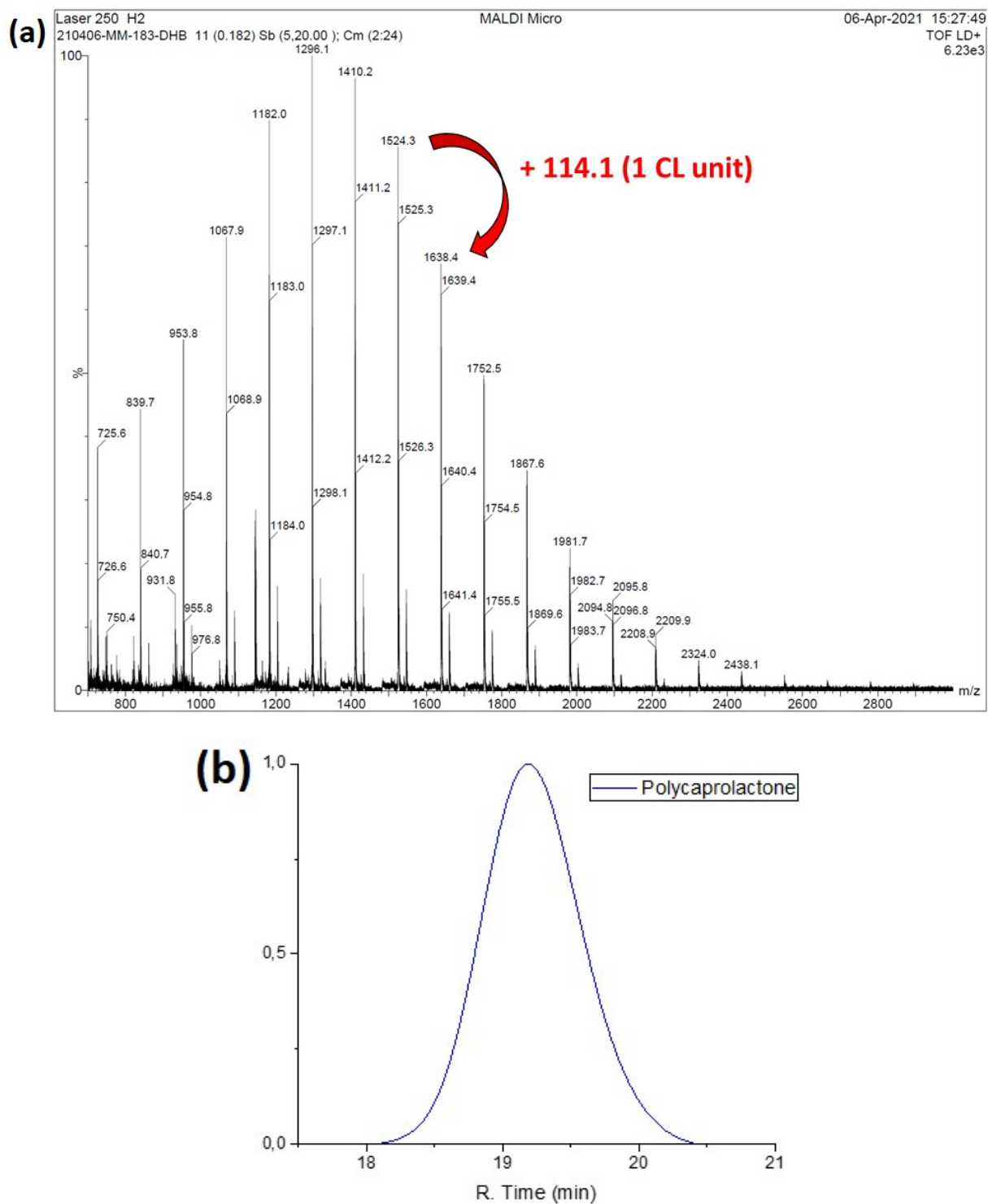


Figure S3. Analyses of the low molar-mass PCL prepared by ROP of CL mediated by **1**. Conditions: CL/**1** = 200/1, bulk, 100 °C, 70 h, 18% conversion. (a) MALDI-ToF mass spectrum (matrix: polymer/DHB/NaI 1:3:1); (b) GPC trace ( $M_{n,corr}$  = 1600 g/mol,  $\bar{D}$  = 1.07).

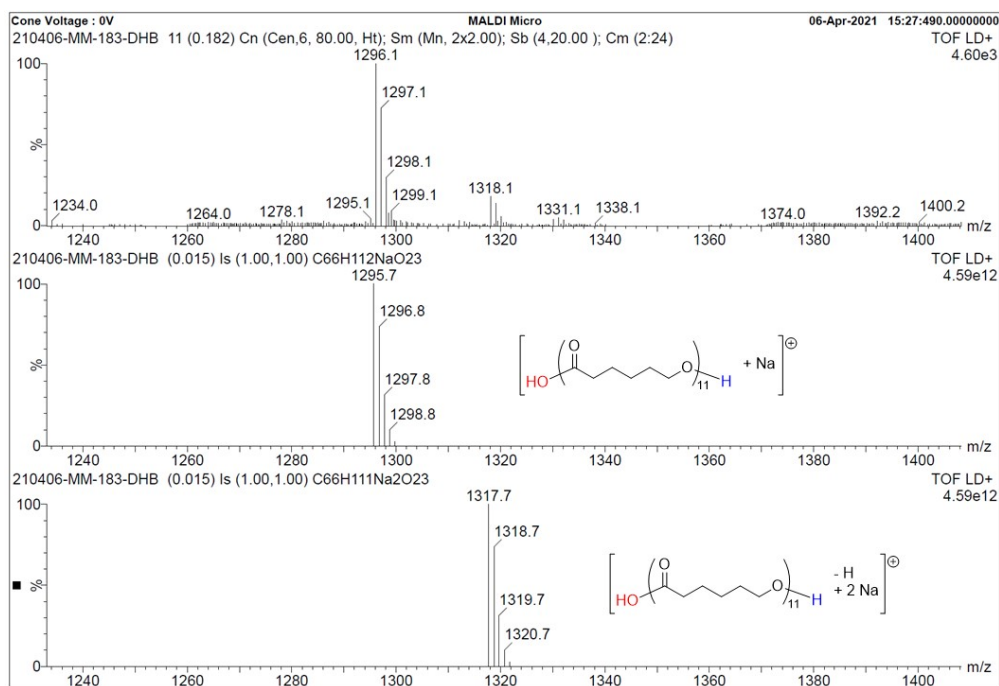


Figure S4. Expanded region of the MALDI-ToF spectrum in Figure S3 highlighting the isotopic envelopes with main peaks at 1296.1 and 1317.7 a.u. (top) and simulated isotopic distributions for two proposed formulas for 11 CL units (middle and bottom).

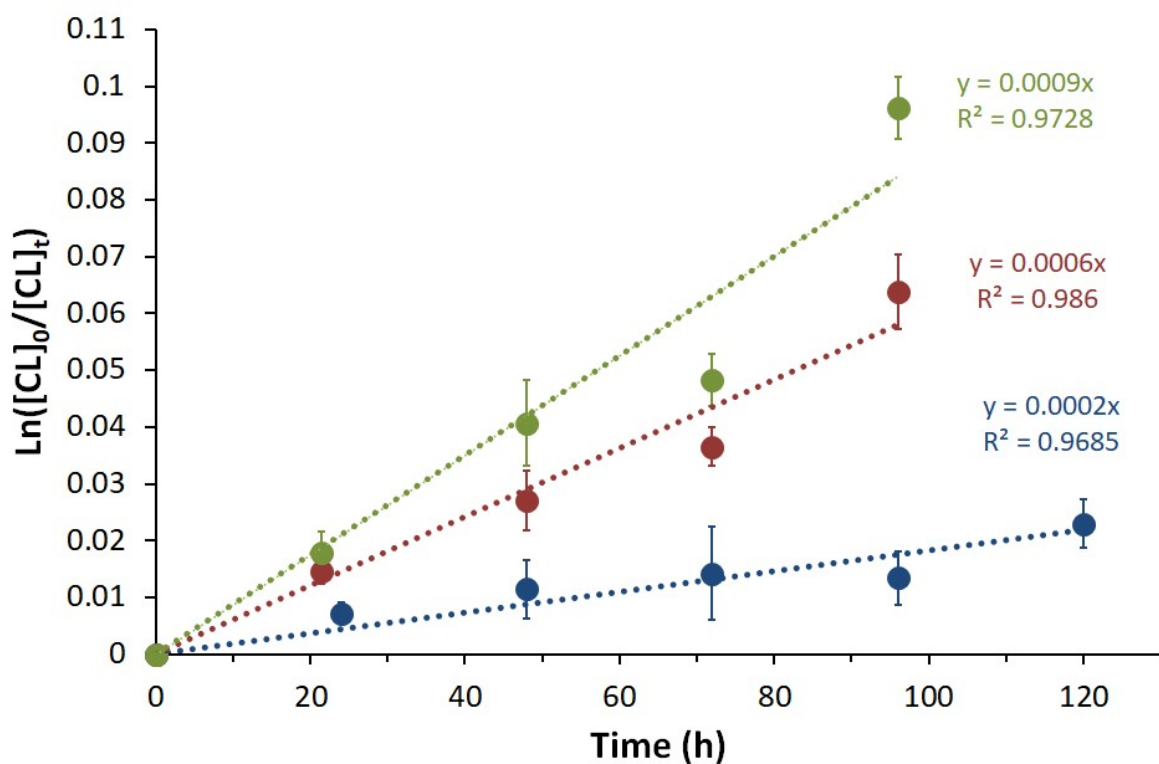


Figure S5. Pseudo-first-order kinetic data for the bulk ROP of CL at 120 °C initiated by complex 1 in the absence or presence of MeOH (initial ratio [CL]/[1]/[MeOH] = 500:1:0 (blue), 2 (red), 5 (green)). Each data point represents the average of three independent experiments and error bars correspond to the standard deviation. The linear fits are shown as visual guides.

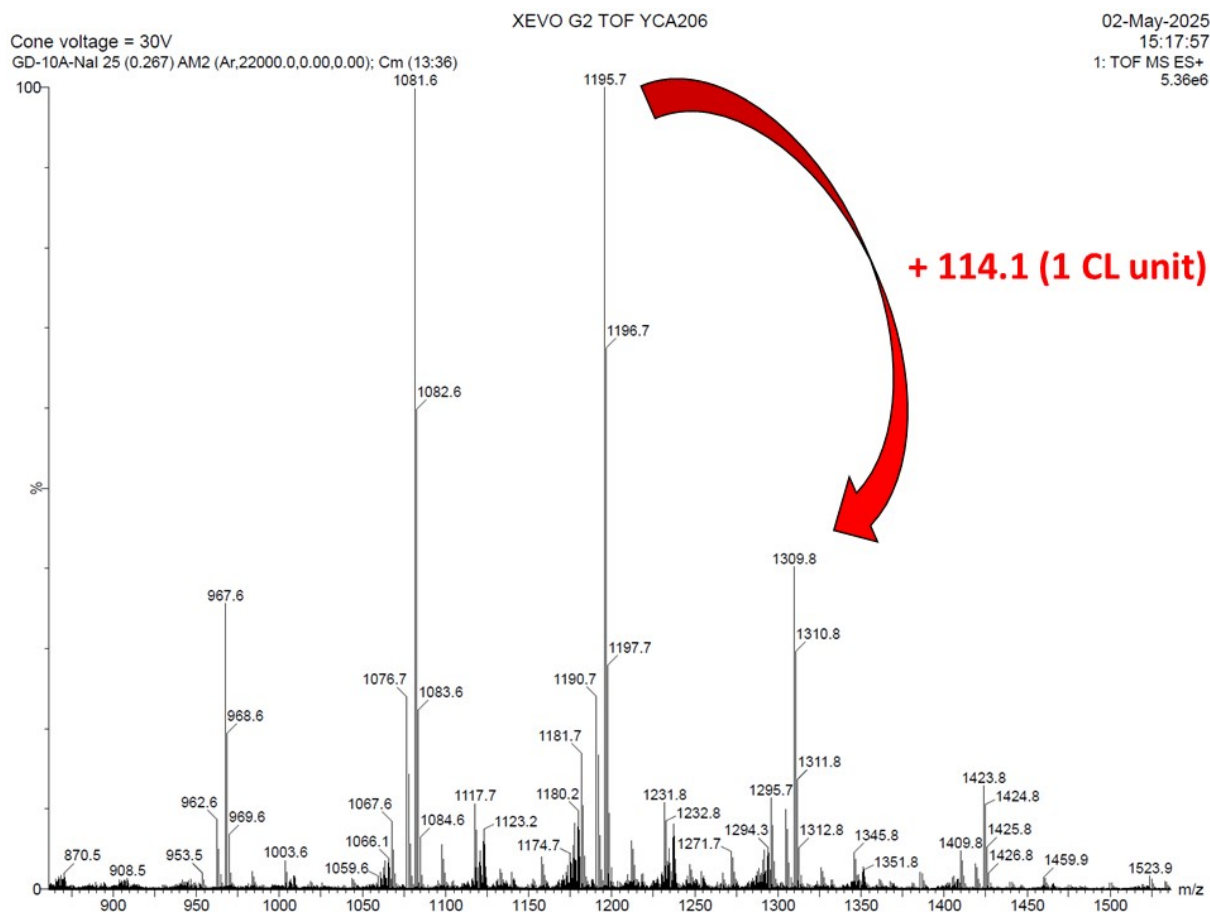


Figure S6. ESI-MS spectrum (with addition of NaI) of the low molar-mass PCL prepared by immortal ROP of CL mediated by **1**. Conditions: CL/**1**/MeOH = 500/1/2, bulk, 120 °C, 21.5 h, 6% conversion,  $M_{n,corr}$  = 1700 g/mol,  $D$  = 1.02 (Table S1, Entry 6).



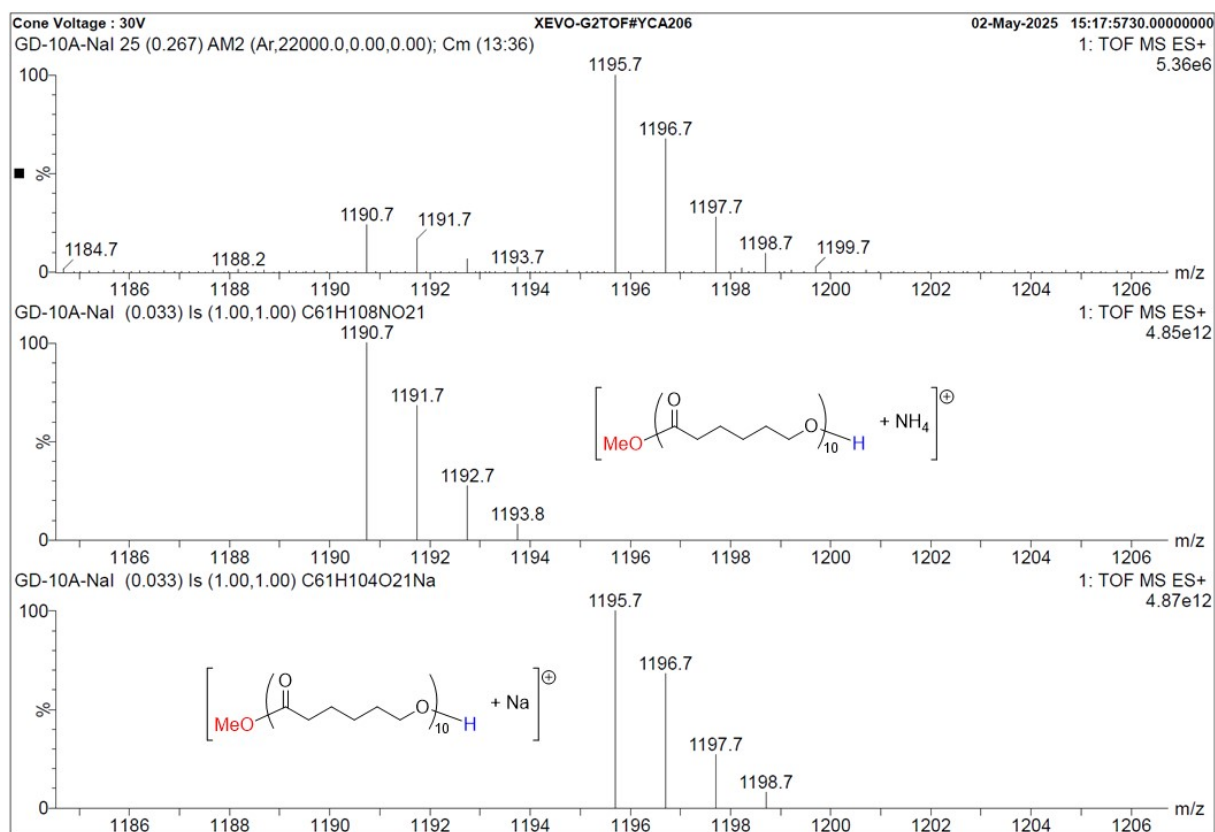


Figure S7. Expanded region of the ESI-MS spectrum in Figure S5 highlighting the isotopic envelopes with peaks at 1190.7 and 1195.7 a.u. (top) and simulated isotopic distributions for two proposed formulas for 10 CL units (middle and bottom).

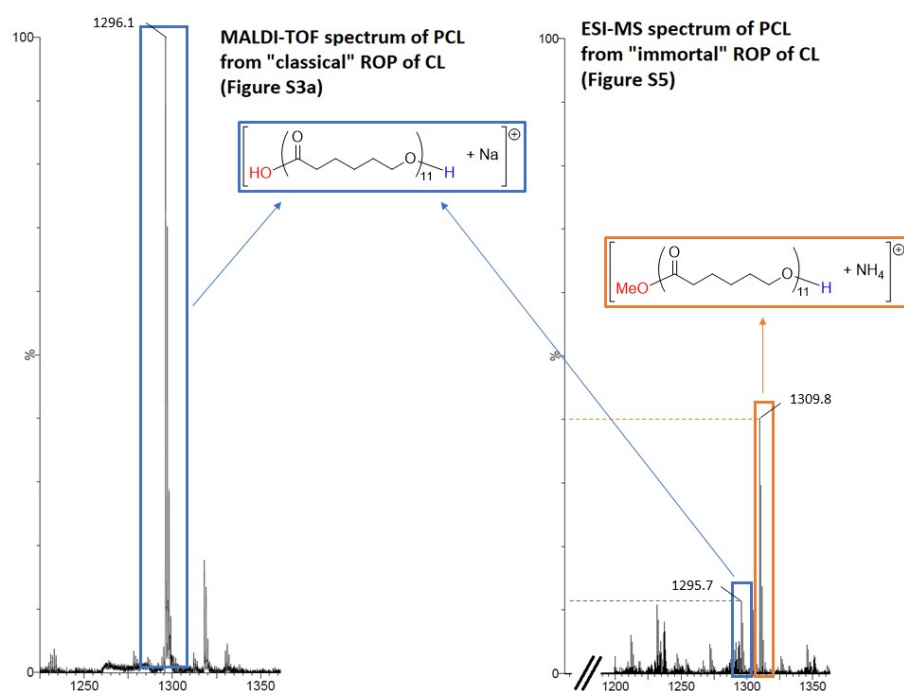


Figure S8. Expanded regions of the MALDI-ToF spectra in Figure S3a and ESI-MS spectrum in Figure S5 highlighting the presence of the isotopic envelope corresponding to PCL initiated by the OAc group (blue boxes) in both spectra.

Table S2. Results of the bulk ROP of *L*-lactide (LLA) at 120 °C initiated by complex **1**.

Entry	[LLA] <sub>0</sub> /[ <b>1</b> ]	[BnOH]/[ <b>1</b> ]	Time (h)	Conv. <sup>a</sup> (%)	<i>M</i> <sub>n,theo</sub> <sup>b</sup> (g/mol)	<i>M</i> <sub>n,corr</sub> <sup>c</sup> (g/mol)	<i>Đ</i> <sup>d</sup>
1	500	0	9	3	2200	700	1.03
2	500	0	24	6	4300	1900	1.34
3	500	0	35	11	7900	7600	1.13
4	500	0	48	16	11500	10800	1.34
5	500	0	96	33	23800	14100	1.30
6	500	2	21.5	11.5	2900	1700	1.20
7	500	2	48	28.5	7000	3800	1.33
8	500	2	72	36	8800	4800	1.31
9	500	2	96	45	10900	5700	1.36
10	500	5	21.5	23	2900	2000	1.25
11	500	5	46	36	4400	5300	1.19
12	500	5	72	45	5500	6200	1.29

<sup>a</sup> Determined by gravimetry and/or from <sup>1</sup>H NMR analysis. <sup>b</sup> Calculated according to  $M_{n,theo} = ([LLA]_0/[1]) \times (1/([1]+[MeOH])) \times M_{LLA} \times \text{conversion}$ , where [init] = 1, 3 or 6 for [BnOH]/[**1**] = 0, 2, 5, respectively, and  $M_{LLA} = 144.13$  g/mol. The molecular weights of both the α- (initiating group(s)) and ω-chain (H) end were not taking into account due to their negligible masses. <sup>c</sup> Determined by GPC using polystyrene standards and applying the correction factor of 0.58. <sup>d</sup> Determined by GPC.

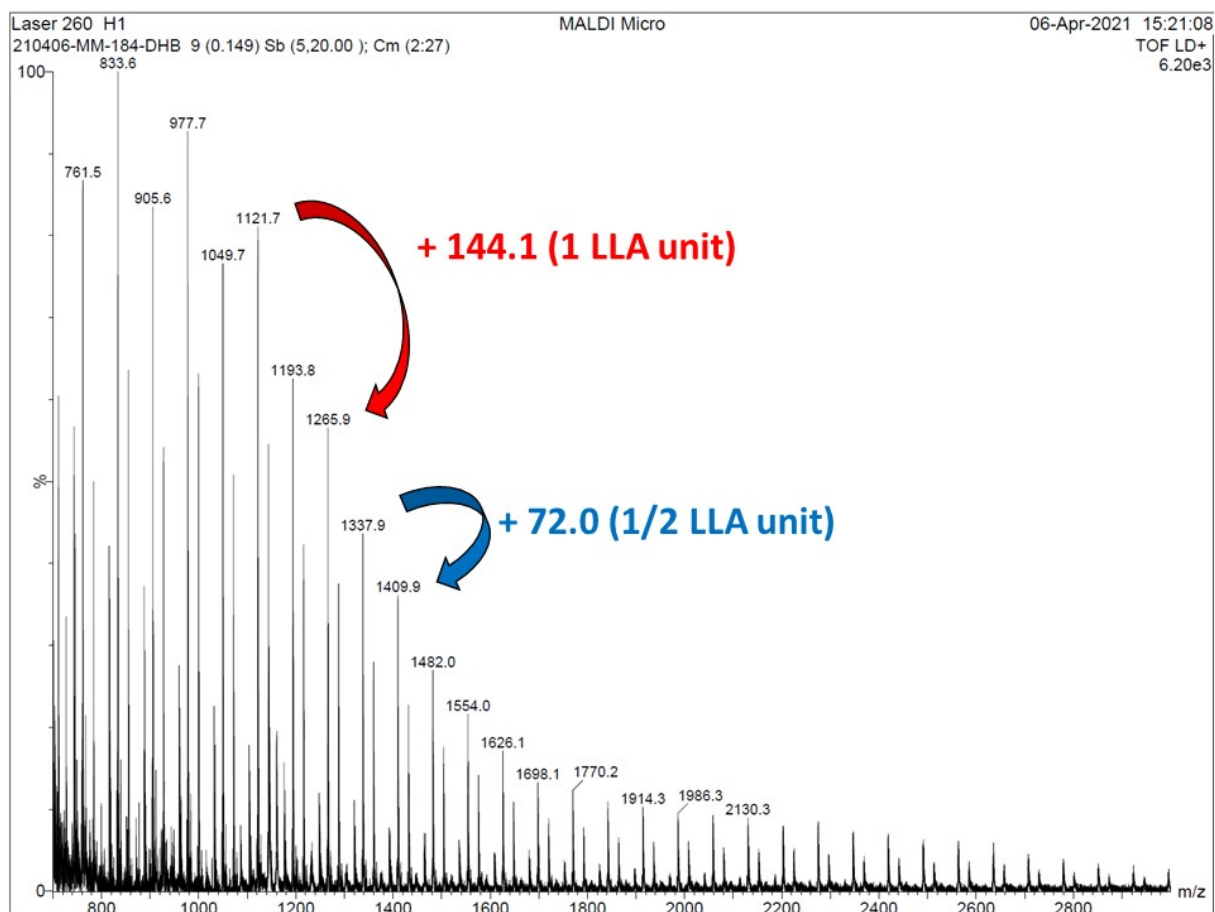


Figure S9. MALDI-ToF mass spectrum (matrix: polymer/DHB/NaI 1:3:1) of the low molar-mass PLLA prepared by ROP of LLA mediated by **1**. Conditions: LLA/**1** = 500/1, bulk, 120 °C, 24 h, 6% conversion,  $M_{n,corr}$  = 1900 g/mol,  $\bar{D}$  = 1.14 (Table S2 – Entry 2).

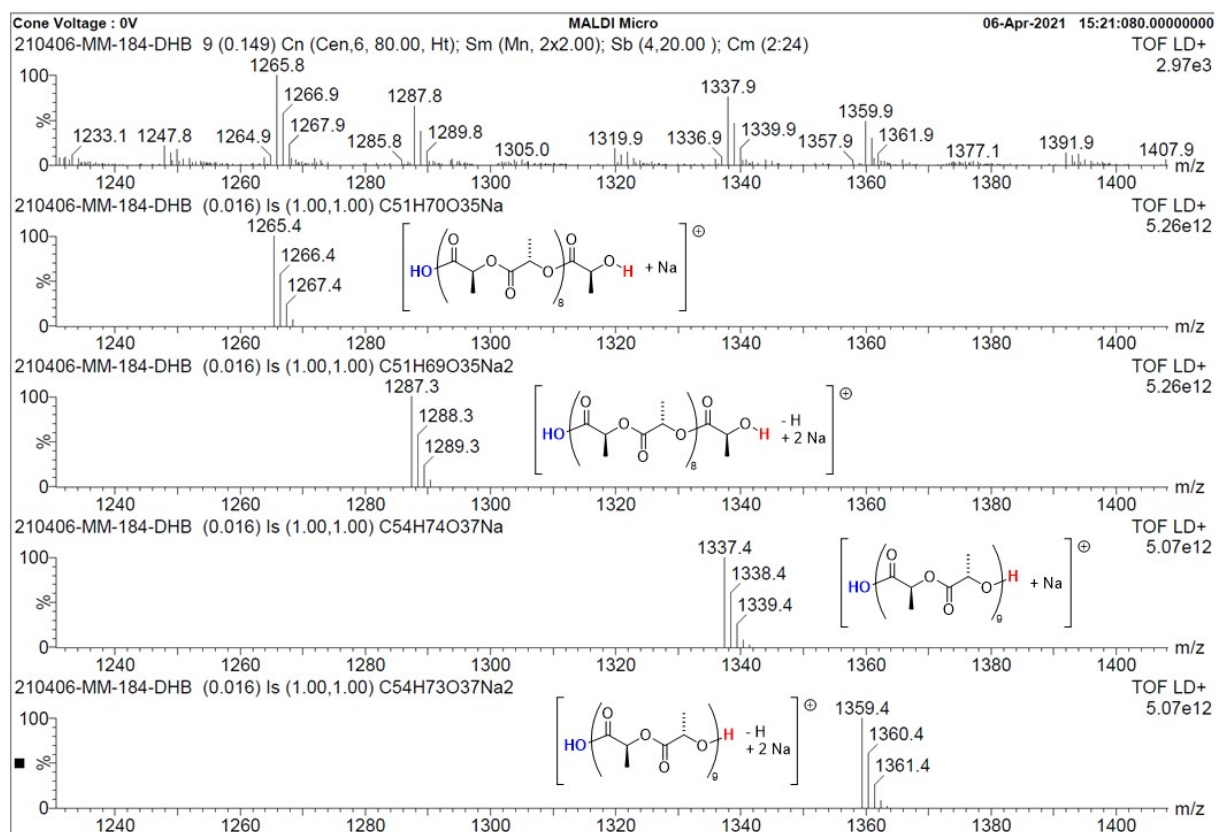


Figure S10. Expanded region of the ESI-MS spectrum in Figure S7 highlighting different isotopic envelopes in the region 1265.8-1359.4 a.u. (1<sup>st</sup> line) and simulated isotopic distributions for four proposed formulas for 8 LLA units (2<sup>nd</sup> and 3<sup>rd</sup> lines) and 9 LLA units (4<sup>th</sup> and 5<sup>th</sup> lines).

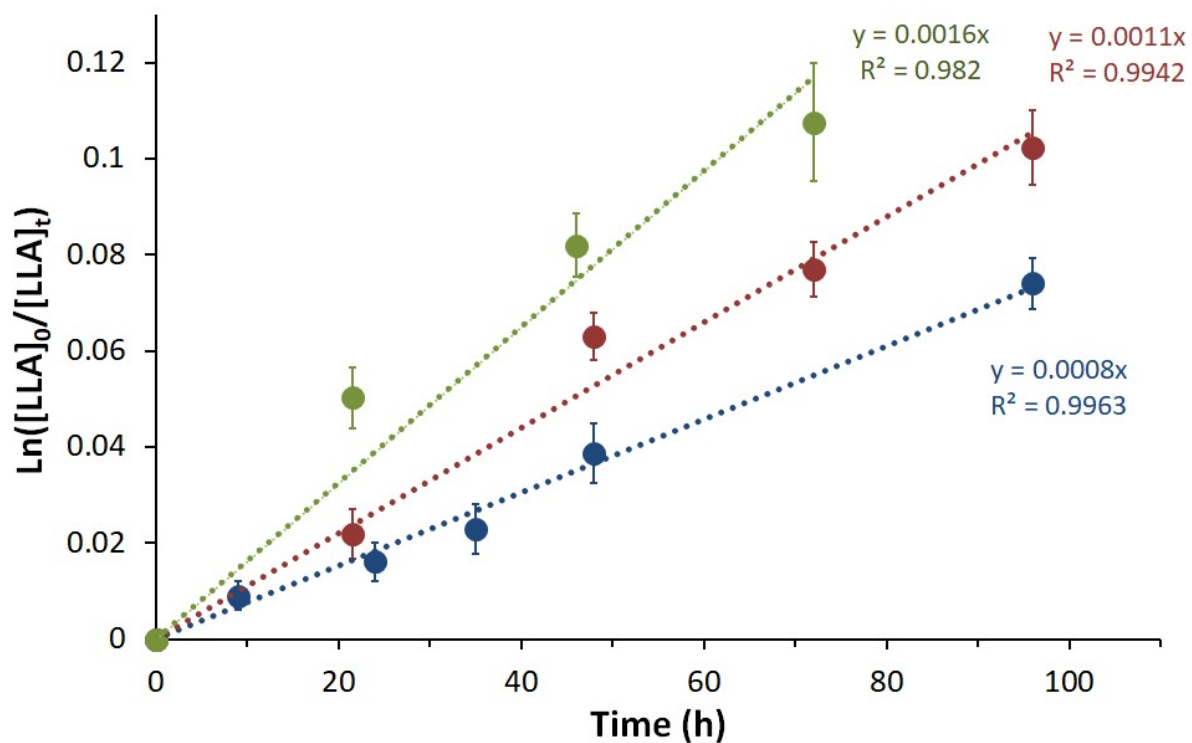


Figure S11. Pseudo-first-order kinetic data for the bulk ROP of LLA at 120 °C initiated by complex **1** in the absence or presence of MeOH (initial ratio [LLA]/[**1**]/[MeOH] = 500:1:0 (blue), 2 (red), 5 (green)). Each data point represents the average of three independent experiments and error bars correspond to the standard deviation. The linear fits are shown as visual guides.

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Baseline subtraction width 500.0 Da

CFL-2025-07-03-B.txt RT: 0.00 Spectrum: 1 691886 Points

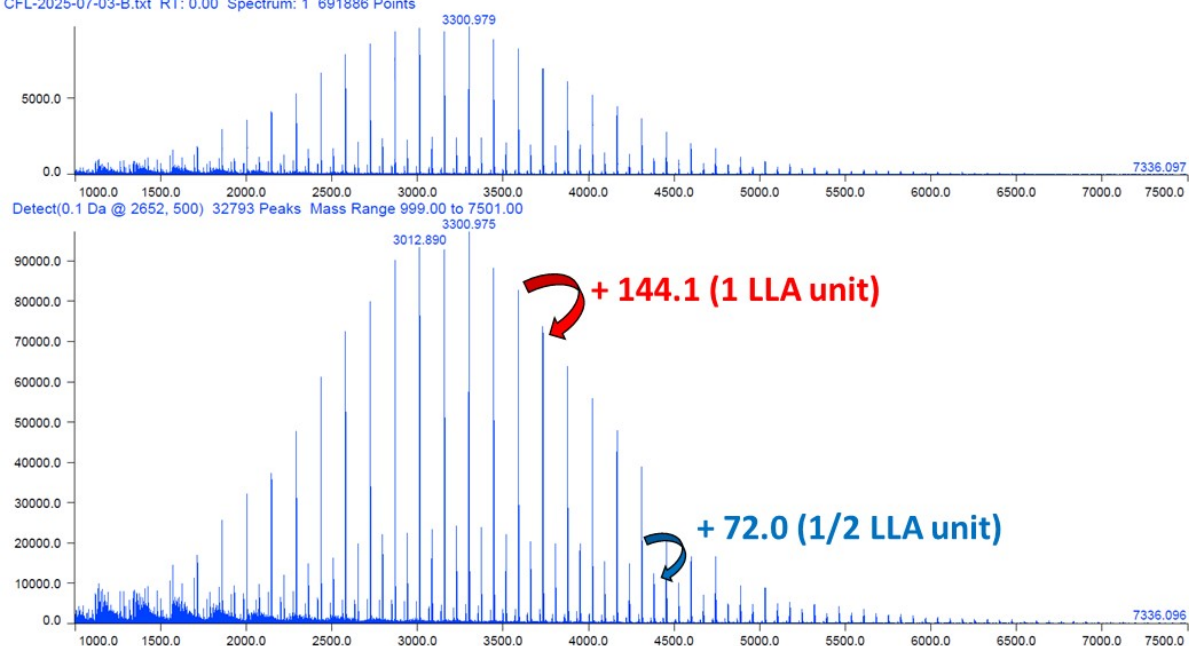


Figure S12. MALDI-ToF mass spectrum (matrix: polymer/DHB/NaI 1:3:1) of the low molar-mass PLLA prepared by immortal ROP of LLA mediated by **1**. Conditions: LLA/**1** = 500/5, bulk, 120 °C, 24 h, 29% conversion,  $M_{n,corr}$  = 3300 g/mol,  $\bar{D}$  = 1.16.

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### Homopolymer Results Summary

Series	Label	Mv	Ms	PD	DPn	DPw	DPz	Percent Series	Percent Spectrum
Total/Average	3302.221	3561.809	3812.322	1.080	44.350	47.955	51.433	100.00	49.32
S1	3376.866	3613.847	3844.120	1.070	45.375	48.577	51.475	88.50	43.85
S2	2710.950	3145.058	3557.660	1.260	36.141	42.168	47.897	11.10	5.47

Series	Label	Alpha	Omega
Series	End Group	Repeat	End Group
Total/Average	C7H70	C3H402	H
S1	C7H70	C3H402	H
S2	C7H70	C3H402	H

Series	Label	Charge State	Adduct	Adduct Charge	Loss	Series Formula
Total/Average	1	Na	1			
S1	1	Na	1			C7H70 [C3H402] n H + Na
S2	1	Na	1	H2O		C7H70 [C3H402] n H + Na - H2O

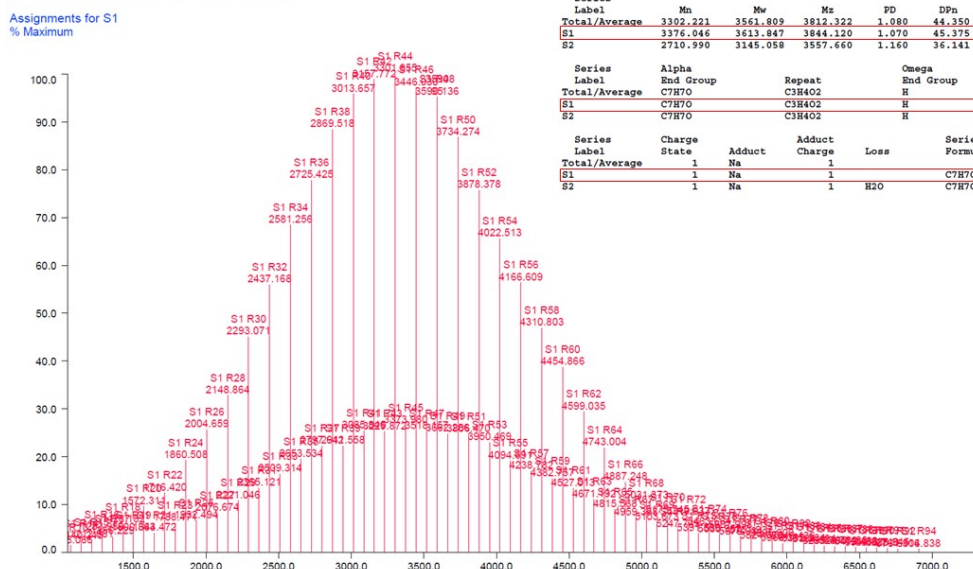


Figure S13a. Most abundant homopolymer identified using the Polymerix software, from the MALDI-ToF mass spectrum in Figure S9.

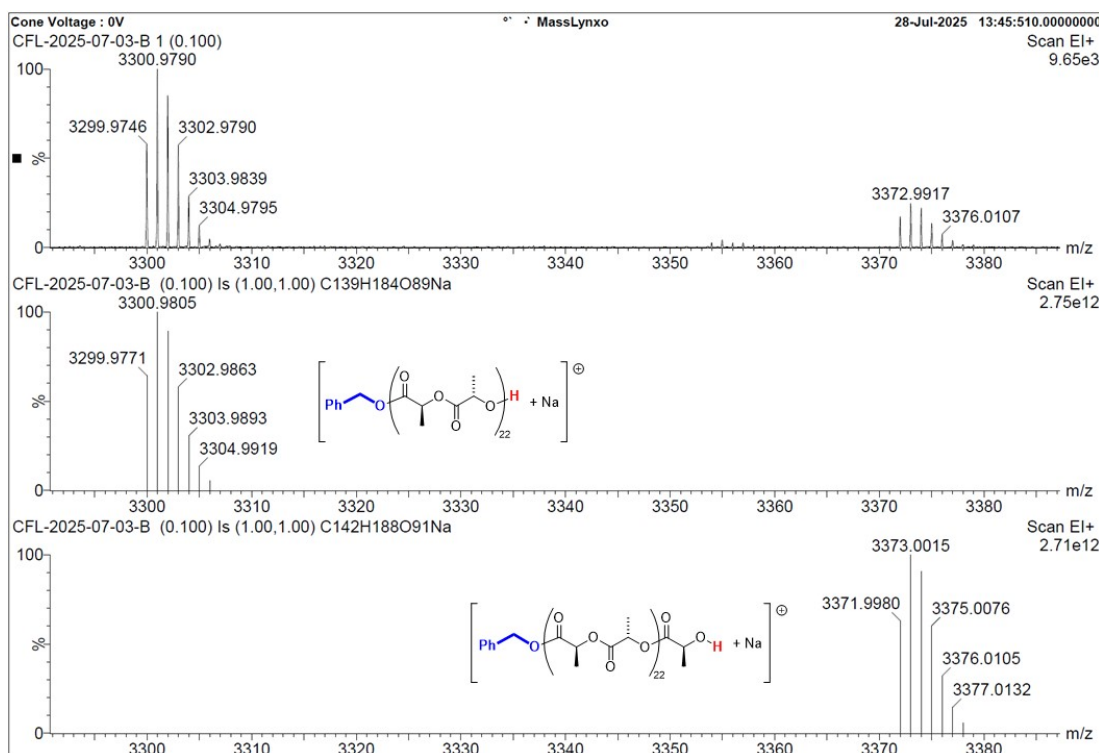


Figure S13b. Expanded region of the MALDI-ToF spectrum in Figure S9 highlighting the isotopic envelopes with main peaks at 3300.9 and 3372.9 a.u. (top) and simulated isotopic distributions for two proposed formulas for 22 LLA units (middle and bottom).



Assignments for S2  
% Maximum

### Homopolymer Results Summary

Series								Percent	Percent
Label	Mn	Mw	Mz	PD	DPn	DPw	DPz	Series	Spectrum
Total/Average	3302.221	3561.809	3912.322	1.080	44.350	47.955	51.433	100.00	49.32
S1	3374.65	3613.847	3844.120	1.075	45.575	48.577	51.875	88.90	43.85
S2	2710.990	3145.058	3557.660	1.160	36.141	42.168	47.897	11.10	5.47
Series	Alpha			Omega					
Label	Rnd Group	Repeat			Rnd Group				
Total/Average	C7H7O	C3H4O2			H				
S1	C7H7O	C3H4O2			H				
S2	C7H7O	C3H4O2			H				
Series	Charge	Adduct			Series	Formula			
Label	State	Adduct	Charge	Loss					
Total/Average	1	Na	1		C7H7O	[C3H4O2]n H + Na			
S1	1	Na	1		C7H7O	[C3H4O2]n H + Na			
S2	1	Na	2	H2O	C7H7O	[C3H4O2]n H + Na - H2O			

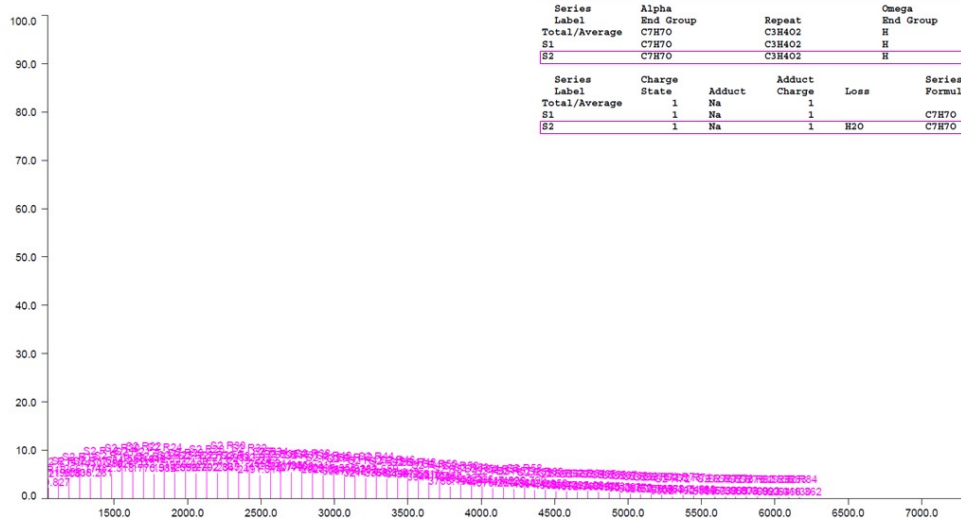


Figure S14a. Lowest abundant homopolymer identified using the Polymerix software, from the MALDI-ToF mass spectrum in Figure S9.

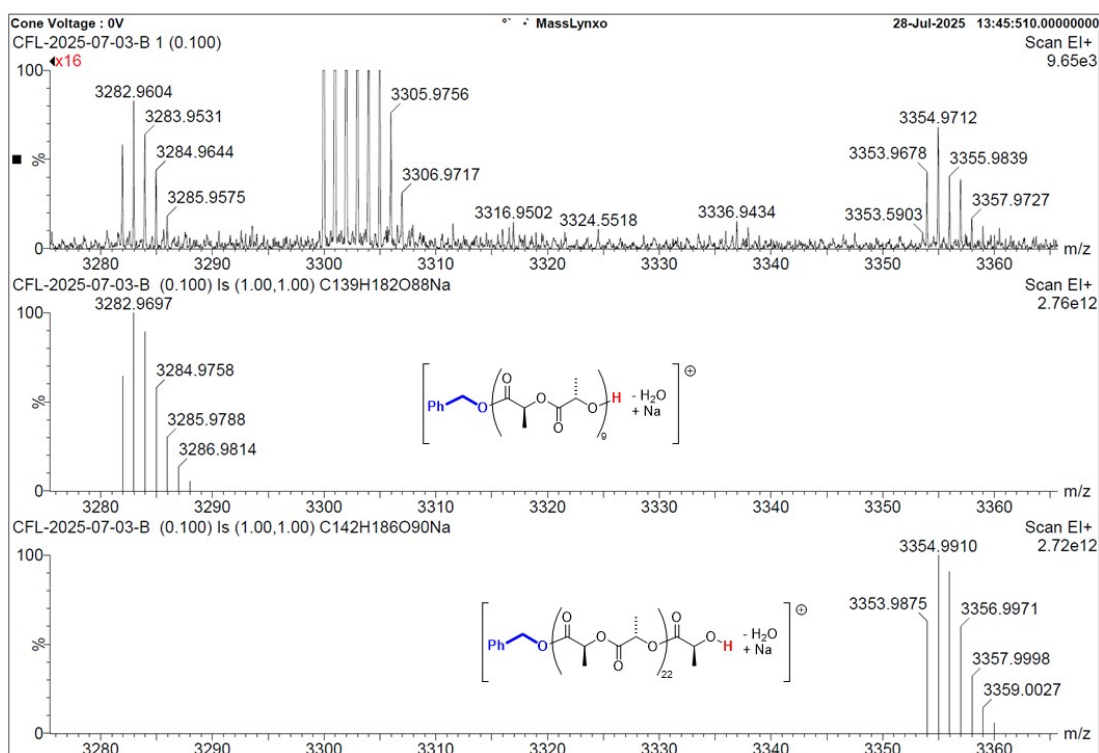


Figure S14b. Expanded region of the MALDI-ToF spectrum in Figure S9 (zoom x16) highlighting the isotopic envelopes with main peaks at 3282.9 and 3354.9 a.u. (top) and simulated isotopic distributions for two proposed formulas for 22 LLA units (middle and bottom).

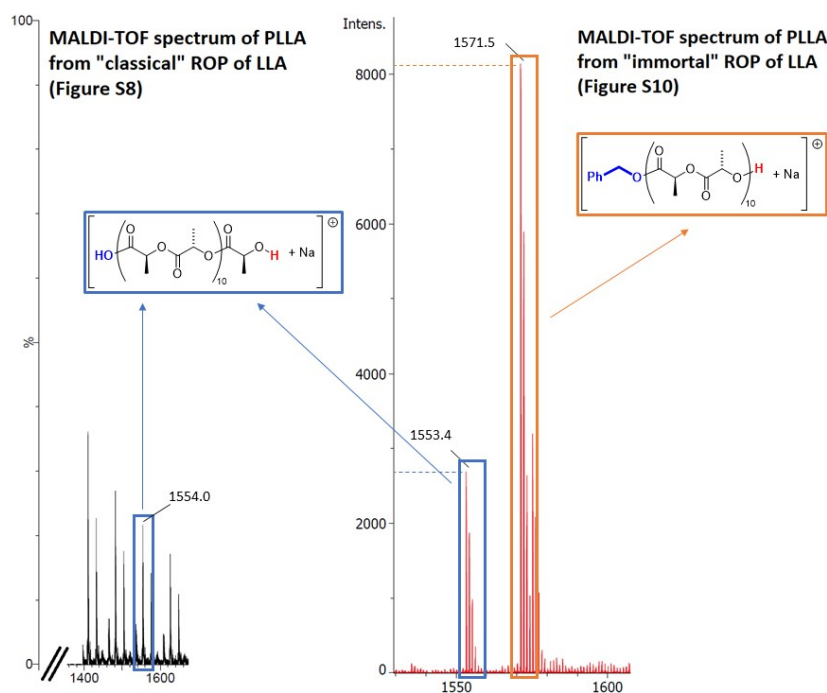


Figure S15. Expanded regions of the MALDI-ToF spectra in Figure S8 and Figure S10 highlighting the presence of the isotopic envelope corresponding to PLLA initiated by the OAc group (blue boxes) in both spectra.

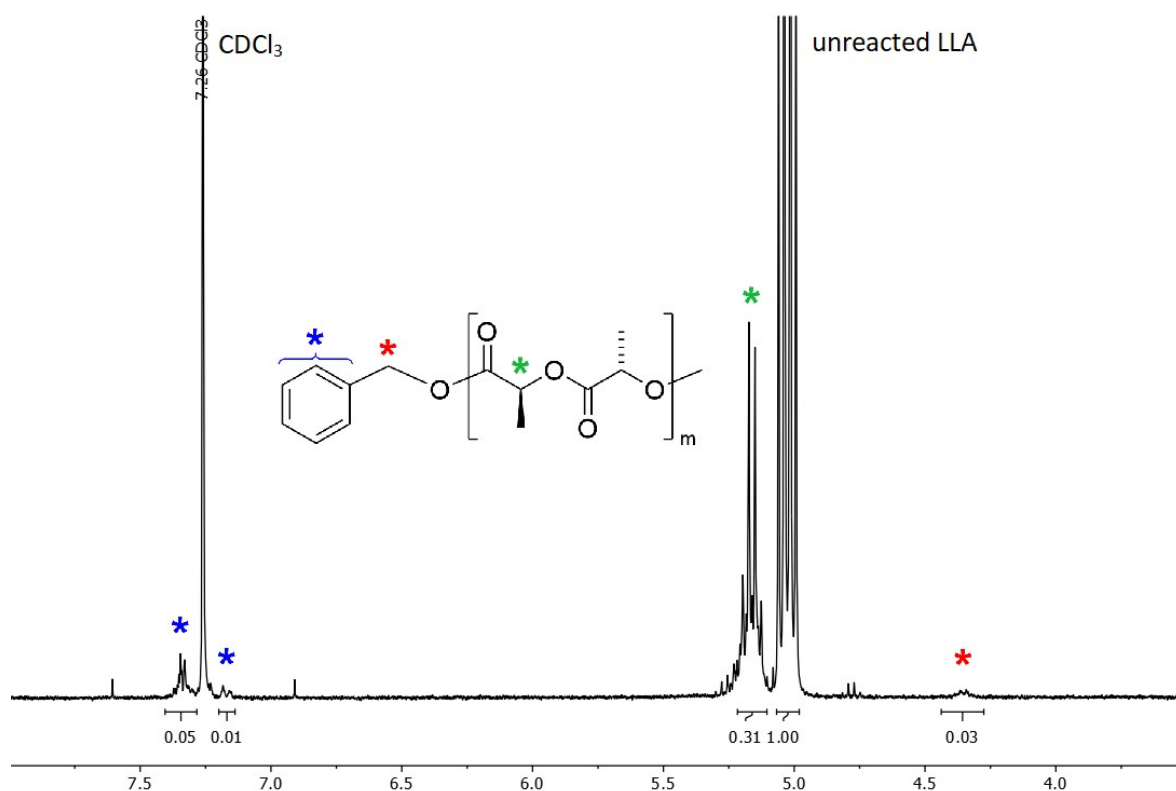


Figure S16. <sup>1</sup>H NMR spectrum (expansion of the 3.5-8 ppm region, CDCl<sub>3</sub>) of the PLLA prepared by immortal ROP of LLA mediated by **1**, showing the signals of the terminal PLLA-OCH<sub>2</sub>Ph group. Conditions: LLA/**1**/BnOH = 500/1/5, bulk, 120 °C, 21.5 h, 23% conversion, *M*<sub>n,corr</sub> = 1700 g/mol, *D* = 1.02 (Table S1- Entry 10).

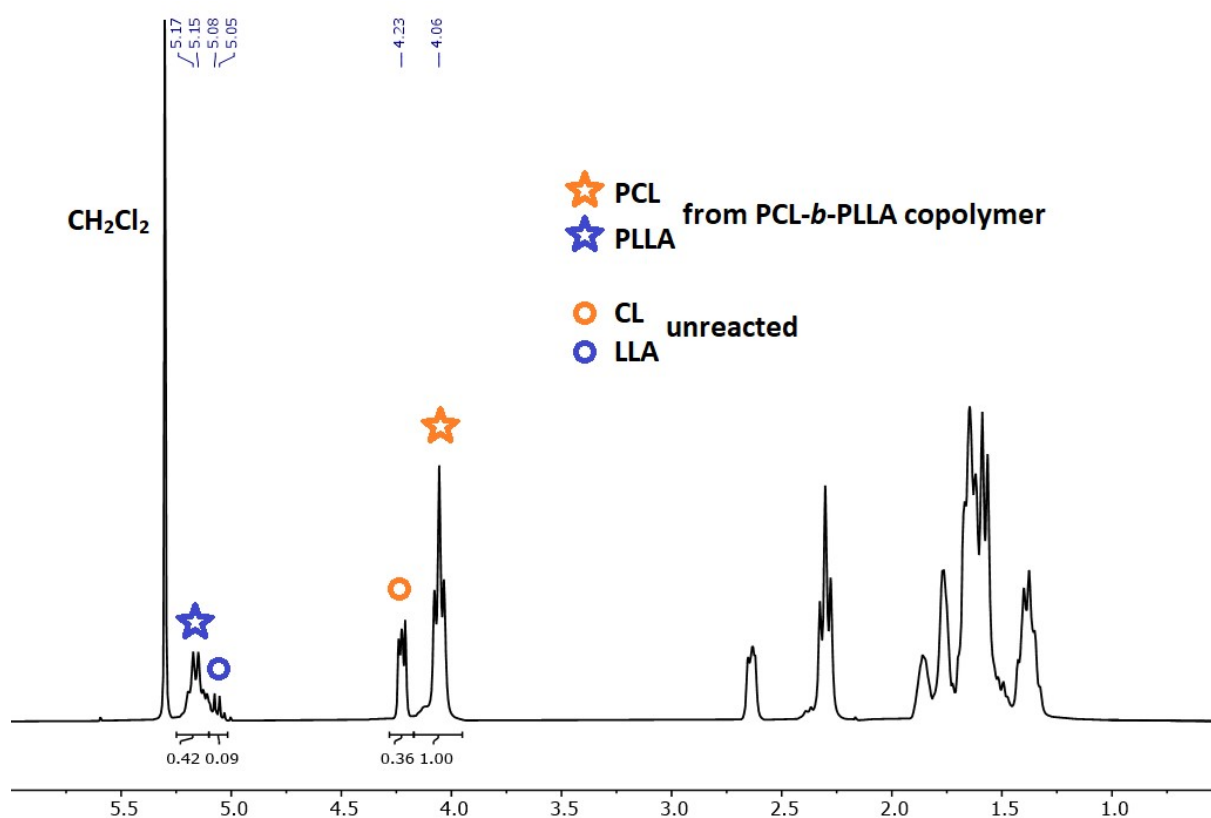


Figure S17. <sup>1</sup>H NMR spectrum (expansion of the 0.5-6 ppm region, CDCl<sub>3</sub>) of the reaction medium (diluted in CH<sub>2</sub>Cl<sub>2</sub>) of the sequential bulk copolymerization of CL and LLA catalysed by complex **1** under immortal conditions. Conditions: Co/CL/LLA/BnOH = 1/500/500/10, bulk, 120 °C, 108 + 48 h, 73% and 82% conversion of CL and LLA, respectively.

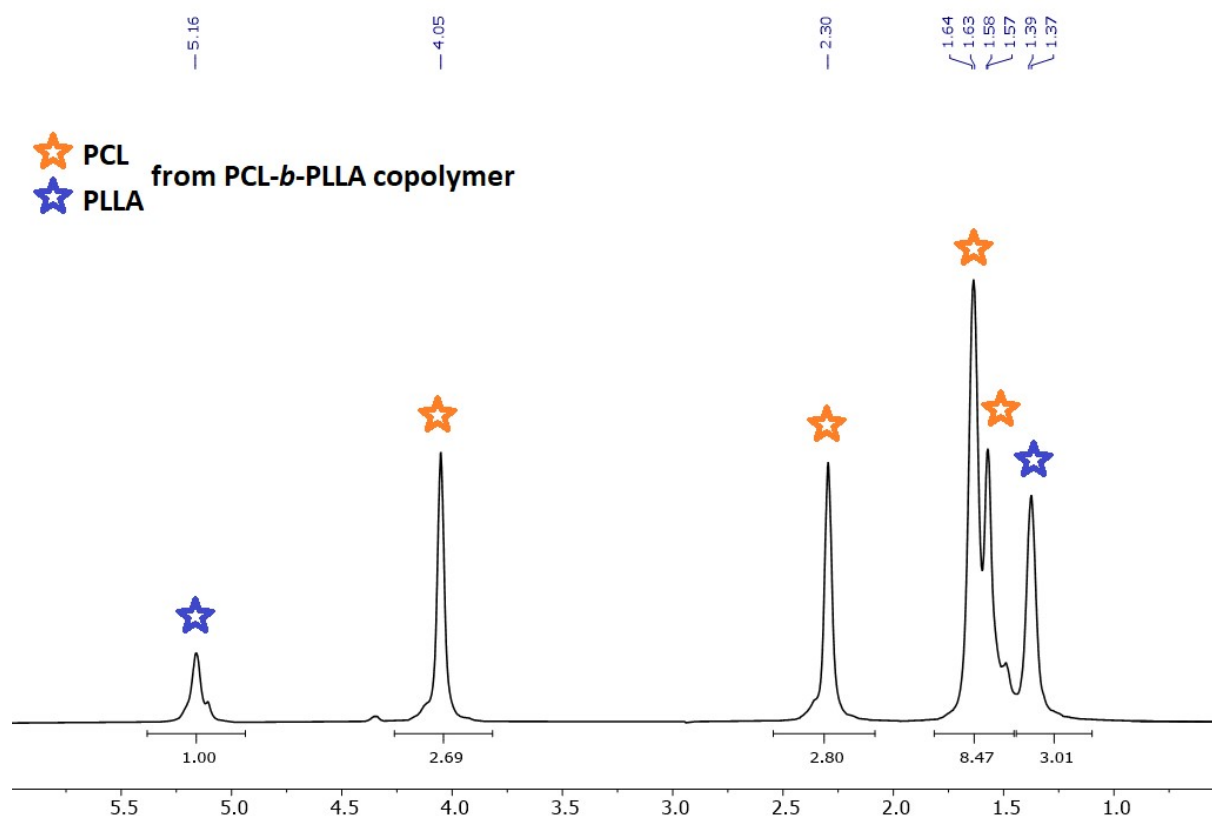


Figure S18.  $^1\text{H}$  NMR spectrum (expansion of the 0.5–6 ppm region,  $\text{CDCl}_3$ ) of the isolated PCL-*b*-PLLA block copolymer synthesized by sequential bulk copolymerization of CL and LLA catalysed by complex **1** under immortal conditions. Conditions: Co/CL/LLA/BnOH = 1/500/500/10, bulk, 120 °C, 108 + 48 h, 73% and 82% conversion of CL and LLA, respectively.