Supporting Information belonging to

N-heterocyclic iron complexes catalyze the ring-opening polymerization of lactide

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Content

1. TGA of complex 1

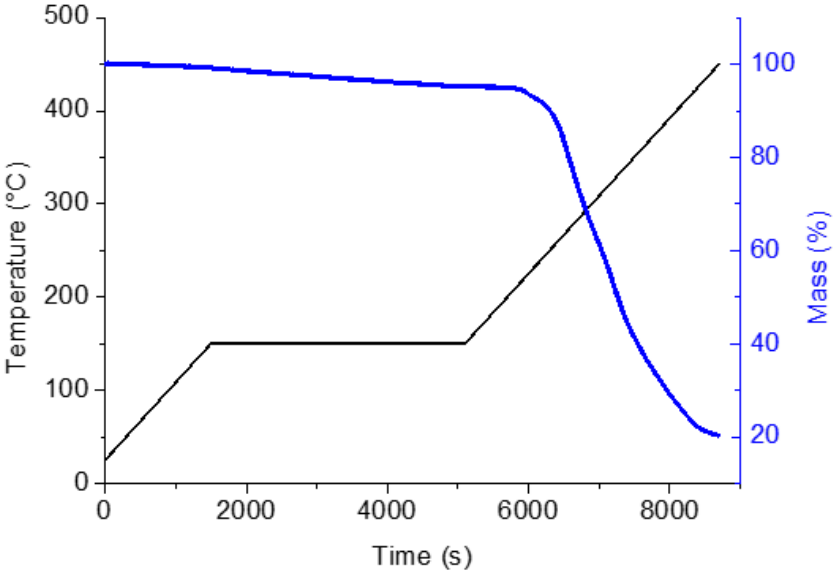

Figure S1. *TGA trace of complex **1**. The plot shows the mass of the complex (%) over time (blue line) and the change of temperature over time (black line).*

2. Polymerization data

Table S1. *Polymerization data of technical grade rac-LA with compound **1*** [a]

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
1	21	8500	30266	0.28	11000	1.29
2	33	20400	47562	0.42	33300	1.63
3	47	28500	67739	0.42	44800	1.58
5	67	35000	96564	0.36	61200	1.75
7	71	40100	102329	0.39	68800	1.72
10	75	37300	108095	0.34	62800	1.68
15	79	38800	113860	0.34	67000	1.73
30	82	34000	118183	0.29	61300	1.80
60	84	33000	121066	0.27	61100	1.86
120	91	27100	131155	0.21	52600	1.94

[a] *Conditions: bulk polymerization of rac-LA at 150 °C, [LA]/[**1**] = 1000, m(LA) = 1.6 g.* [b] *The theoretical number-average molecular weight was calculated from the monomer to catalyst ratio and the conversion of the reaction on the assumption that the catalyst initiates the polymerization.*

Table S2. *Polymerization data of technical grade rac-LA with compound* ***1*** *[a]*

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
2	12	19000	86476	0.21	30400	1.60
6	23	33100	165745	0.19	50400	1.52
10	28	45000	201776	0.22	67900	1.51
30	48	54800	345902	0.16	87400	1.60
60	54	57600	389140	0.15	88900	1.54
90	57	64900	410759	0.16	101500	1.56
120	57	55200	410759	0.13	89900	1.63
150	69	59300	497235	0.12	94700	1.60
24h	86	31900	619742	0.05	54700	1.72

*[a] Conditions: bulk polymerization of rac-LA at 150 °C, [LA]/[**1**] = 5000, m(LA) = 4.8 g. [b] The theoretical number-average molecular weight was calculated from the monomer to catalyst ratio and the conversion of the reaction on the assumption that the catalyst initiates the polymerization.*

Table S3. *Polymerization data of recrystallized rac-LA with compound* ***1****, without initiator* *[a]*

Run #1

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
1	14	15600	20177	0.77	23200	1.49
3	34	18500	49001	0.38	26700	1.45
5	40	42900	57648	0.74	64300	1.50
7	47	38800	67736	0.57	63700	1.64
10	53	44000	76384	0.58	71200	1.62
15	55	36800	79266	0.46	62000	1.68
30	66	47300	95119	0.50	79100	1.67
60	74	10400	106649	0.10	23000	2.21
120	80	19100	115296	0.17	38600	2.02

Run #2

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
1	16	21300	23059	0.92	30900	1.45
3	20	24800	28824	0.86	39800	1.61
5	25	27000	36030	0.75	42300	1.56
7	31	32100	44677	0.72	46500	1.45
10	32	33700	46118	0.73	49200	1.46
15	38	31000	54766	0.57	47900	1.54
30	49	37800	70619	0.54	56700	1.50
60	60	29400	86472	0.34	56600	1.92
120	65	22900	93678	0.24	44000	1.92

*[a] Conditions: bulk polymerization of recryst-LA at 150 °C, [LA]/[**1**] = 1000, m(LA) = 1.6 g. [b] The theoretical number-average molecular weight was calculated from the monomer to catalyst ratio and the conversion of the reaction on the assumption that the catalyst initiates the polymerization.*

Table S4. *Polymerization data of recrystallized rac-LA with compound* ***1****, with BnOH as initiator*[a]

Run #1

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
1	13	6600	18736	0.35	7400	1.12
3	36	22700	51883	0.44	30200	1.33
5	50	29000	72060	0.40	41900	1.45
7	57	32700	82148	0.40	50100	1.53
10	63	35500	90796	0.39	55500	1.56
15	69	37900	99443	0.38	62600	1.65
30	77	25700	110972	0.23	47500	1.85
60	81	29100	116737	0.25	55900	1.92
120	87	23700	125384	0.19	46200	1.95

Run #2

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
1	20	117000	28824	0.41	13500	1.16
3	53	30300	76384	0.40	44100	1.46
5	65	28100	93678	0.30	49500	1.76
7	68	30900	98002	0.29	49700	1.61
10	71	27400	102325	0.27	48400	1.77
15	72	24600	103766	0.24	44900	1.82
30	78	24200	112414	0.22	43600	1.80
60	87	28700	125384	0.23	52100	1.81
120	89	24300	128267	0.19	47000	1.93

[a] *Conditions: bulk polymerization of recryst-LA at 150 °C, [LA]/[**1**]/[BnOH] = 1000:1:1, m(LA) = 1.6 g.* [b] *The theoretical number-average molecular weight was calculated from the monomer to catalyst ratio and the conversion of the reaction on the assumption that the catalyst initiates the polymerization.*

Table S5. *Polymerization data of complexes* ***2–4*** *for the determination of* k_{app}[a]

Complex **2**	**[LA]:[cat] = 5000:1**, 3.5 mmol LA, 0.0022 mmol **2**			
Reaction time (min)	Conversion (%)	Ln($[LA]_0/[LA]_t$)	Conversion (%)	Ln($[LA]_0/[LA]_t$)
0	0	0	1	0.01005
1	1	0.01005	2	0.02020
2	2	0.02020	4	0.04082
3	3	0.03046	7	0.07257
4	4	0.04082	8	0.08338
6	6	0.06188	9	0.09431
8	8	0.08338	10	0.10536
10	n.d.	n.d.	14	0.15082
15	15	0.16252	19	0.21072
20	21	0.23572	20	0.22314
30	27	0.31471	23	0.26136
60	42	0.54473	31	0.37106
120	58	0.86750	41	0.52763

Complex **3**	**[LA]:[cat] = 5000:1**, 3.5 mmol LA, 0.0022 mmol **3**			
Reaction time (min)	Conversion (%)	Ln($[LA]_0/[LA]_t$)	Conversion (%)	Ln($[LA]_0/[LA]_t$)
0	0	0	0	0
1	2	0.02020	0	0
2	5	0.05129	4	0.04082
3	9	0.09431	9	0.09431
4	13	0.13926	13	0.13926
6	16	0.17435	18	0.19845
8	19	0.21072	23	0.26136
10	21	0.23572	29	0.34249
15	26	0.30111	35	0.43078
20	29	0.34249	40	0.51083
30	35	0.43078	46	0.61619
60	43	0.56212	54	0.77653
120	55	0.79851	64	1.02165

Complex **4**	**[LA]:[cat] = 5000:1**, 3.5 mmol LA, 0.0022 mmol **4**			
Reaction time (min)	Conversion (%)	Ln($[LA]_0/[LA]_t$)	Conversion (%)	Ln($[LA]_0/[LA]_t$)
0	0	0	0	0
1	5	0.05129	3	0.03046
2	11	0.11653	10	0.10536
3	16	0.17435	12	0.12783
4	18	0.19845	16	0.17435
6	25	0.28768	21	0.23572
8	27	0.31471	27	0.31471
10	29	0.34249	28	0.32850
15	35	0.43078	36	0.44629
20	38	0.47804	38	0.47804
30	44	0.57982	46	0.61619
60	54	0.77653	58	0.86750
120	65	1.04982	68	1.13943

[a] *general conditions: rac-LA, n(LA) = 11. 1 mmol, 150 ˚C, neat, [LA]/[cat], 500 rpm, n.d. = not determined.*

Table S6. *Polymerization data of technical grade rac-LA with compound **2*** [a]

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
15	15	29600	108094	0.27	45300	1.53
20	21	38700	151332	0.26	63500	1.64
30	27	45100	194570	0.23	74900	1.66
60	42	47200	302665	0.16	84100	1.78
120	58	45100	417965	0.11	83700	1.86

[a] *Conditions: bulk polymerization of rac-LA at 150 ˚C, [LA]/[**2**] = 5000, m(LA) = 1.6 g.* [b] *The theoretical number-average molecular weight was calculated from the monomer to catalyst ratio and the conversion of the reaction on the assumption that the catalyst initiates the polymerization.*

Table S7. *Polymerization data of technical grade rac-LA with compound* ***4*** [a]

Time (min)	Conversion (%)	obs M_n [g mol^{-1}]	theor M_n [b] [g mol^{-1}]	obs M_n/ theor M_n	M_w [g mol^{-1}]	$Đ$
6	25	18700	180158	0.09	26235	1.40
10	29	26100	208983	0.12	40032	1.53
15	35	27200	252221	0.11	43770	1.61
20	38	32800	273839	0.12	52430	1.60
30	44	33700	317077	0.11	54851	1.63
60	54	45000	389140	0.12	73851	1.64
120	65	43900	468410	0.09	71999	1.64

[a] *Conditions: bulk polymerization of rac-LA at 150 ˚C, [LA]/[****4****] = 5000, m(LA) = 1.6 g.* [b] *The theoretical number-average molecular weight was calculated from the monomer to catalyst ratio and the conversion of the reaction on the assumption that the catalyst initiates the polymerization.*

Table S8. *Polymerization data of complex* ***1*** *under different [LA]:[cat] ratios*

	Run #1		*Run #2*	
1	**[LA]:[cat] = 500:1**, 3.5 mmol LA, 0.007 mmol **1**			
Reaction time (min)	Conversion (%) [b]	Ln([LA]$_0$/[LA]$_t$)	Conversion (%)	Ln([LA]$_0$/[LA]$_t$)
0	0	0	0	
30	15	0.16252	5	0.05129
60	38	0.47804	24	0.27444
90	53	0.75502	39	0.49430
120	60	0.91629	51	0.71335
180	82	1.71480	69	1.17118
240	87	2.04022	77	1.46968
300	89	2.20727	83	1.77196

	[LA]:[cat] = 5000:1			
	30 mmol LA, 0.006 mmol **1**		33.3mmol LA, 0.0067 mmol **1**	
Reaction time (min)	Conversion (%)	Ln([LA]$_0$/[LA]$_t$)	Conversion (%)	Ln([LA]$_0$/[LA]$_t$)
0	5	0.05129	0	0
10	25	0.28768	28	0.32850
30	37	0.46204	48	0.65393
45	47	0.63488	n.d.	n.d.
60	48	0.65393	54	0.77653
135	63	0.99425	n.d.	n.d.
150	n.d.	n.d.	69	1.17118
180	63	0.99425	n.d.	n.d.

	[LA]:[cat] = 1000:1, 3.5 mmol LA, 0.011 mmol **1**			
Reaction time (min)	Conversion (%)	Ln([LA]$_0$/[LA]$_t$)	Conversion (%)	Ln([LA]$_0$/[LA]$_t$)
0	0	0	0	0
1	20	0.22314	24	0.27444
2	38	0.47804	50	0.69315

3	54	0.77653	70	1.20397
4	63	0.99425	77	1.46968
5	n.d.	n.d.	79	1.56065
7	n.d.	n.d.	81	1.66073
8	71	1.23787	n.d.	n.d.
10	n.d.	n.d.	83	1.77196
15	78	1.51413	87	2.04022
20	79	1.56065	n.d.	n.d.
25	79	1.56065	n.d.	n.d.
30	81	1.66073	n.d.	n.d.
60	87	2.04022	88	2.12026
120	91	2.40795	91	2.40795

	[LA]:[cat] = 1500:1, 3.5 mmol LA, 0.0074 mmol **1**			
Reaction time (min)	Conversion (%)	Ln($[LA]_0/[LA]_t$)	Conversion (%)	Ln($[LA]_0/[LA]_t$)
0	4	0.04082	0	0
1	22	0.24846	15	0.16252
2	32	0.38566	33	0.40048
3	44	0.57982	46	0.61619
4	48	0.65393	55	0.79851
6	58	0.86750	64	1.02165
8	61	0.94161	67	1.10866
10	67	1.10866	n.d.	n.d.
16	n.d.	n.d.	72	1.27297
20	72	1.27297	n.d.	n.d.
30	75	1.38629	75	1.38629
60	78	1.51413	78	1.51413
120	86	1.96611	85	1.89712

	[LA]:[cat] = 2775:1, 3.5 mmol LA, 0.004 mmol **1**			
Reaction time (min)	Conversion (%)	Ln($[LA]_0/[LA]_t$)	Conversion (%)	Ln($[LA]_0/[LA]_t$)
0	0	0	0	0
1	9	0.09431	7	0.07257
2	16	0.17435	12	0.12783
3	22	0.24846	19	0.21072
4	25	0.28768	20	0.22314
6	n.d.	n.d.	24	0.27444
8	36	0.44629	28	0.32850
10	39	0.49430	29	0.34249
12	40	0.51083	32	0.38566
15	45	0.59784	39	0.49430
20	51	0.71335	n.d.	n.d.
55	61	0.94161	n.d.	n.d.
70	67	1.10866	n.d.	n.d.
120	76	1.42712	60	0.91629

	[LA]:[cat] = 5000:1, 3.5 mmol LA, 0.0022 mmol **1**			
Reaction time (min)	Conversion (%)	Ln($[LA]_0/[LA]_t$)	Conversion (%)	Ln($[LA]_0/[LA]_t$)
0	0	0	0	0
1	2	0.02020	6	0.06188
2	n.d.	n.d.	11	0.11653
3	13	0.13926	16	0.17435
4	14	0.15082	22	0.24846
5	n.d.	n.d.	25	0.28768
6	23	0.26137	29	0.34249
8	28	0.32850	32	0.38566
10	32	0.38566	n.d.	n.d.
15	38	0.47804	53	0.75502
20	46	0.61619	55	0.79851
25	52	0.73397	n.d.	n.d.
30	59	0.89160	62	0.96758
40	62	0.96758	n.d.	n.d.
55	68	1.13943	n.d.	n.d.
63	n.d.	n.d.	65	1.04982
70	74	1.34707	n.d.	n.d.
98	77	1.46968	n.d.	n.d.
120	82	1.71480	82	1.71480

	[LA]:[cat] = 10,000:1, 3.5 mmol LA, 0.0011 mmol **1**			
Reaction time (min)	Conversion (%)	Ln($[LA]_0/[LA]_t$)	Conversion (%)	Ln($[LA]_0/[LA]_t$)
0	0	0	0	0
3	1	0.01005	4	0.04082
8	9	0.09431	7	0.07257
20	16	0.17435	12	0.12783
45	25	0.28768	22	0.24846
105	38	0.47804	25	0.28768
120	56	0.82098	28	0.32850
24 h	80	1.60944	n.d.	n.d.

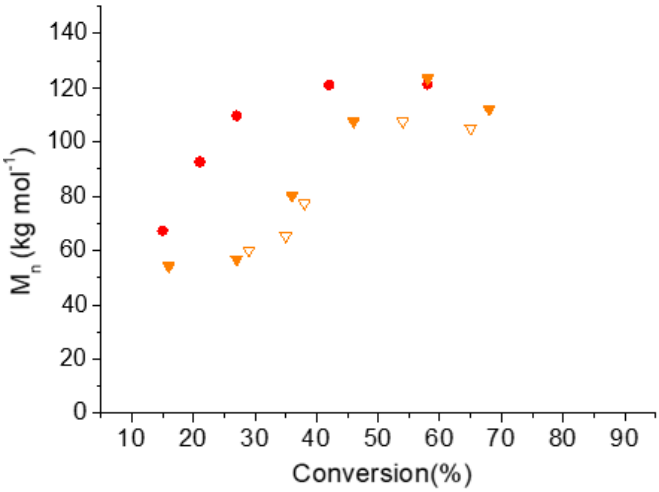

Figure S2. *Plots of the number-average molecular weight (M_n,) of PLA prepared by the bulk polymerization of rac-LA at 150 °C catalyzed by complex **2** and **4** vs conversion. Red circles are for [LA]/[**2**] = 1000:1 (m(LA) = 1.6 g) and orange triangles are for [LA]/[**4**] = 5000:1 (m(LA) = 1.6 g, open and closed triangles represent two parallel runs).*

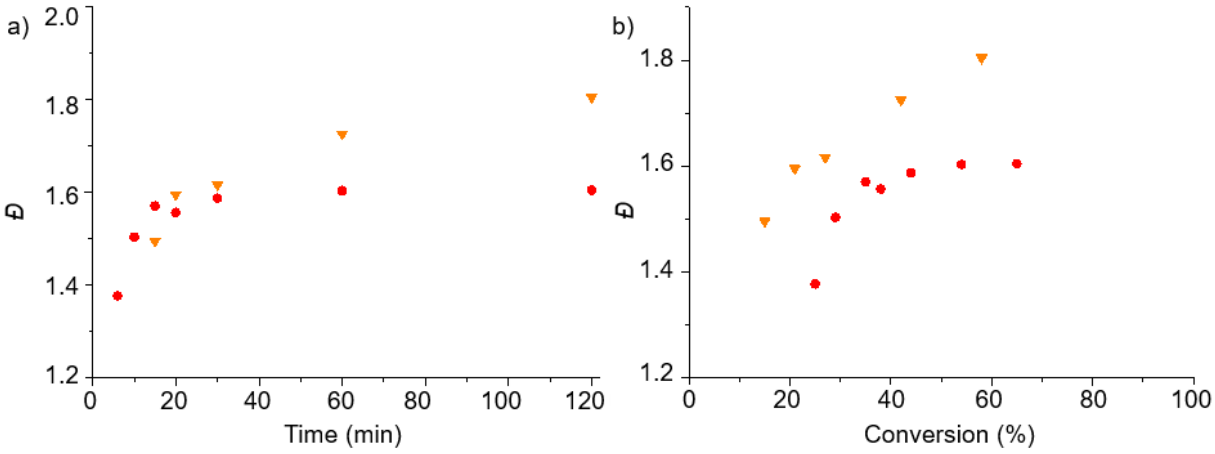

Figure S3. *Plots of the dispersity a) vs time and b) conversion of PLA prepared by the bulk polymerization of rac-LA at 150 °C catalyzed by complex **2** and **4**.* Red circles *are for [LA]/[**2**] = 1000:1 (m(LA) = 1.6 g) and orange triangles are for [LA]/[4] = 5000:1 (m(LA) =* 1.6 *g).*

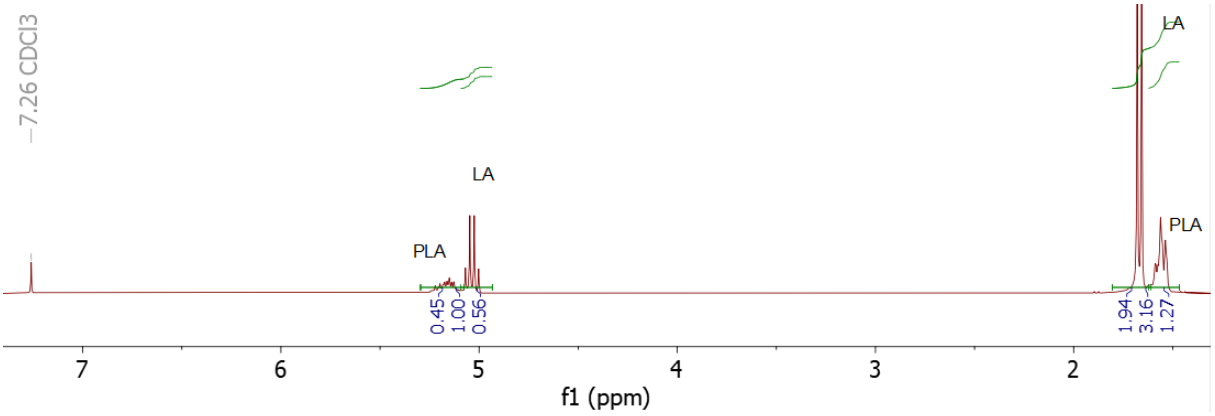

Figure S4. *Representative ^{1}H NMR spectrum that illustrates how the monomer conversion was determined by ^{1}H NMR spectroscopy, 60 min sample from the bulk polymerization of rac-LA at 150 °C catalyzed by complex* ***1****, [LA]/[****1****] = 5000:1 (m(LA) = 1.6 g.*

3. Polymer analysis

3.1 MALDI-ToF MS data

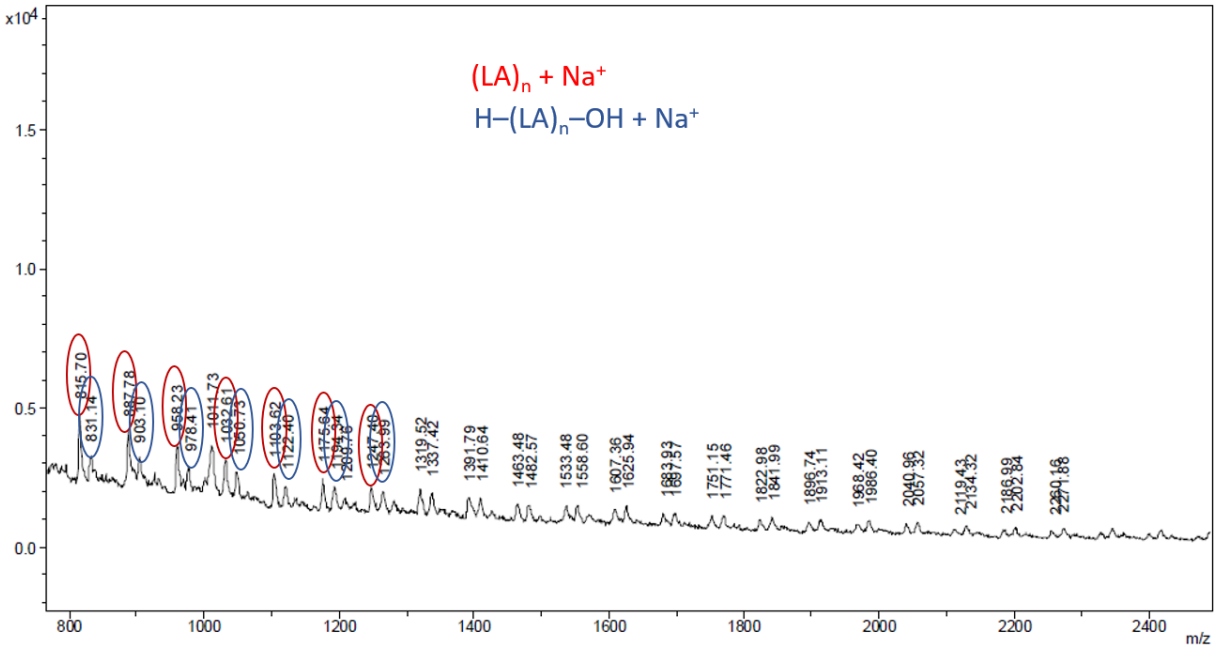

Figure S5. *MALDI-TOF spectrum of PLA prepared by the bulk polymerization of recrystallized rac-LA at 150 °C, 1 min, catalyzed by complex* ***1*** *[LA]/[****1****] = 50:1.*

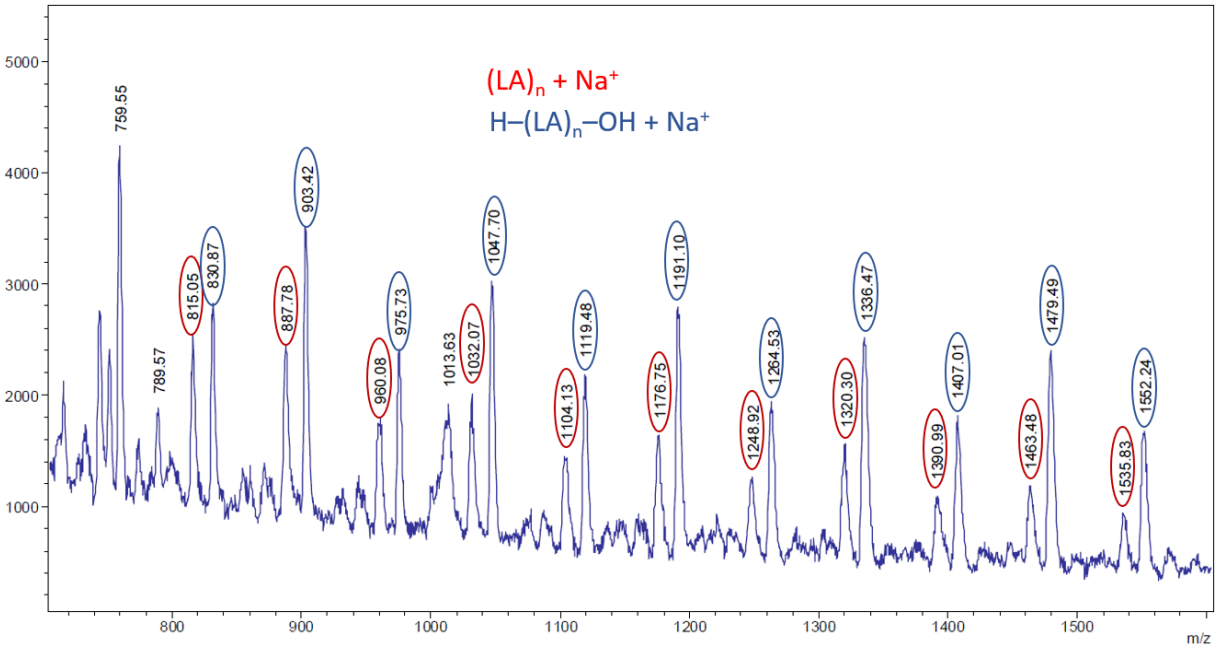

Figure S6. *MALDI-TOF spectrum of PLA prepared by the bulk polymerization of recrystallized rac-LA at 150 °C, 1 min, catalyzed by complex* ***1*** *[LA]/[**1**] = 1000:1.*

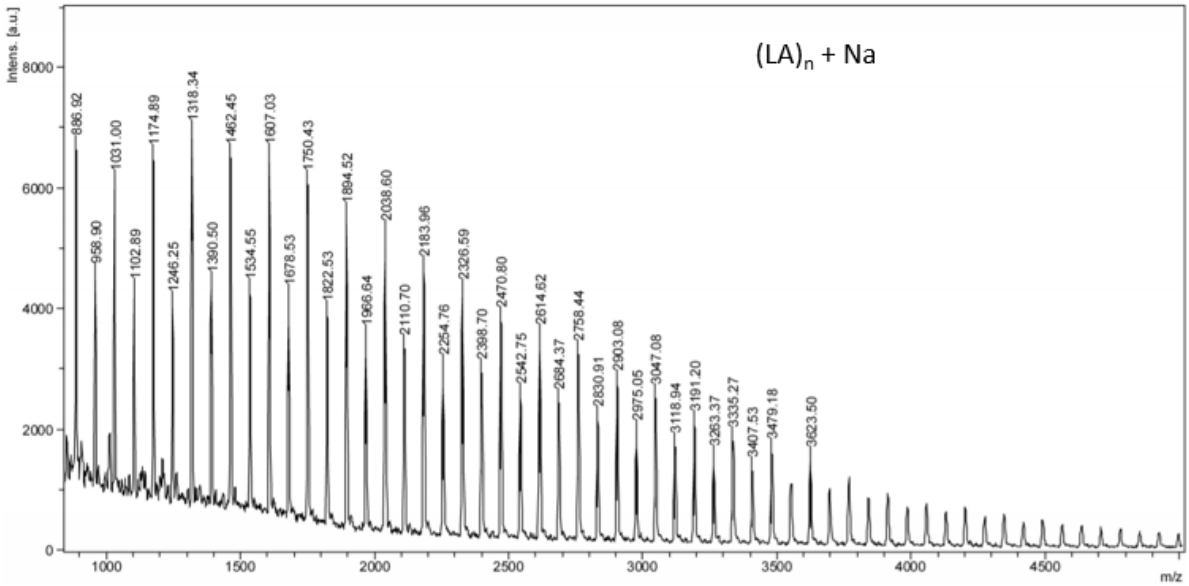

Figure S7. *MALDI-TOF spectrum of PLA prepared by the bulk polymerization of rac-LA at 150 °C, 60 min, catalyzed by complex* ***1*** *[LA]/[**1**] = 1000:1. Dissolved in CH_2Cl_2 and precipitated in Et_2O twice.*

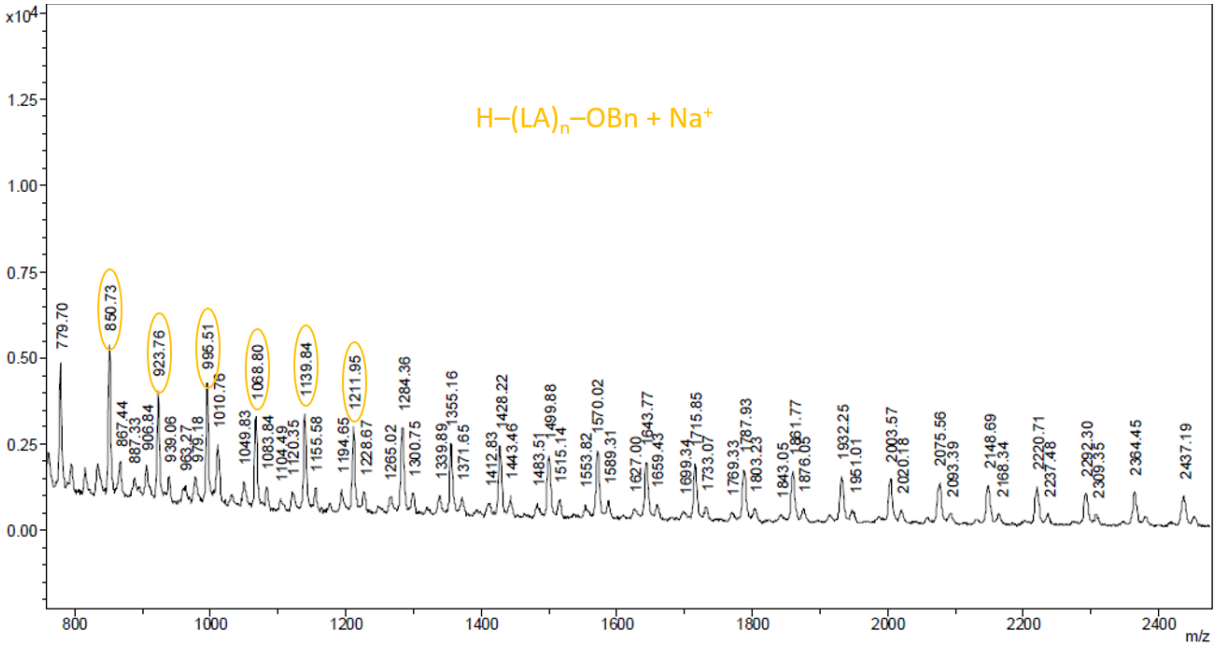

Figure S8. *MALDI-TOF spectrum of PLA prepared by the bulk polymerization of recrystallized rac-LA at 150 °C, 1 min, catalyzed by complex* ***1*** *[LA]/[**1**]/[BnOH] = 50:1:1.*

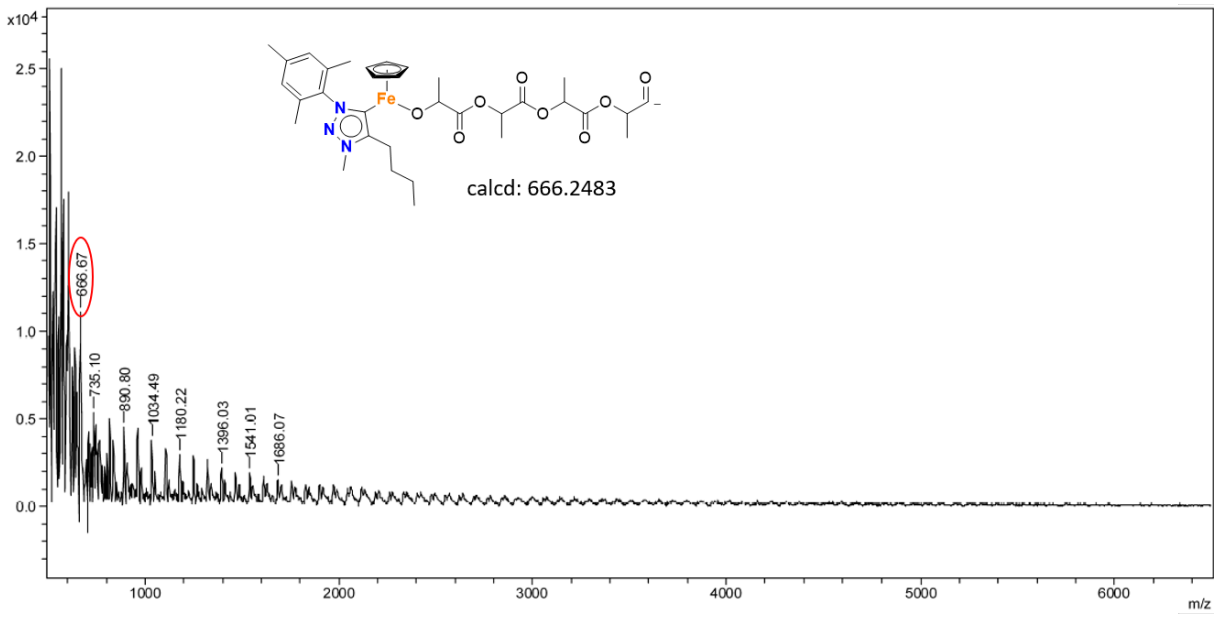

Figure S9. *MALDI-TOF spectrum of PLA prepared by the bulk polymerization of rac-LA at 150 °C, 45 min, catalyzed by complex* ***1*** *[LA]/[**1**] = 50:1.*

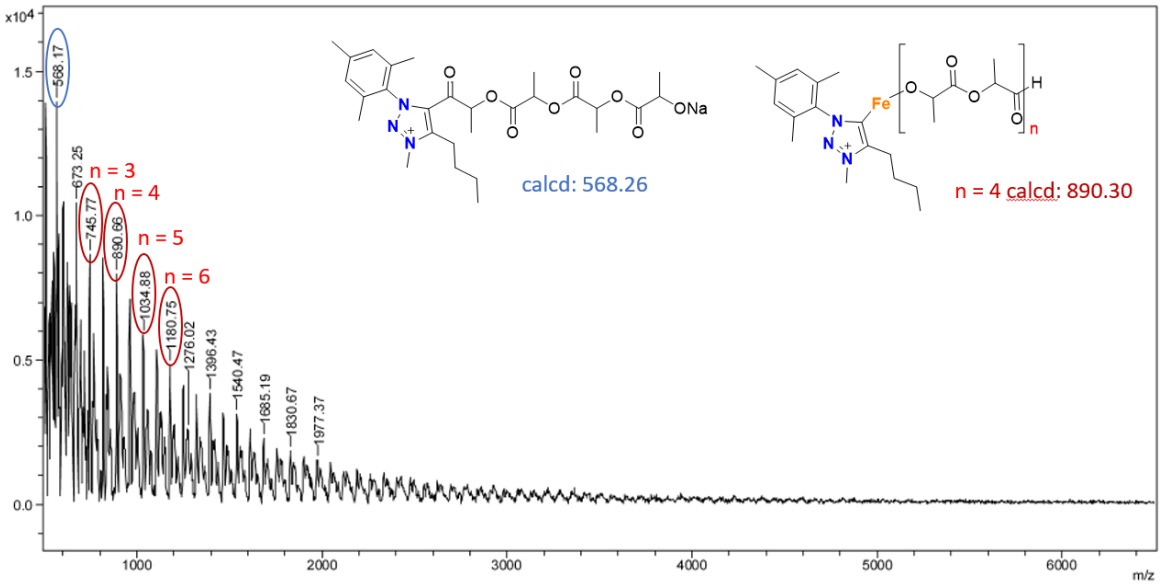

Figure S10. *MALDI-TOF spectrum of PLA prepared by the bulk polymerization of rac-LA at 150 °C, 10 min, catalyzed by complex* ***1*** *[LA]/[**1**] = 50:1.*

3.2 TGA and DSC data

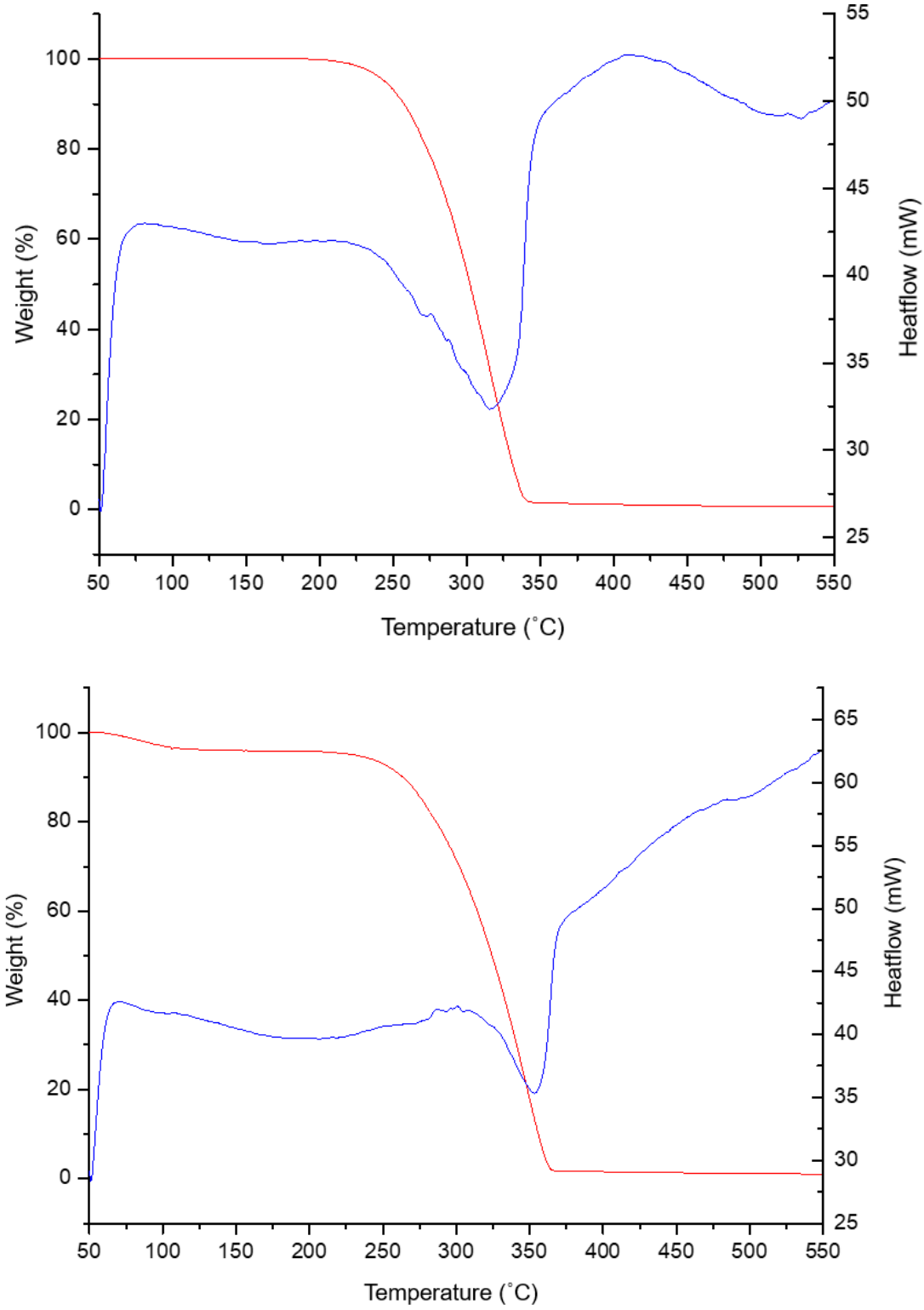

Figure S11. *Representative result of a TGA sample, mass loss (weight-%) and heat flow of precipitated polymers. Catalyzed by: top $FeCp(CO)_2I$ (entry 3 Table 1), bottom* ***1*** *(entry 3 Table 3).*

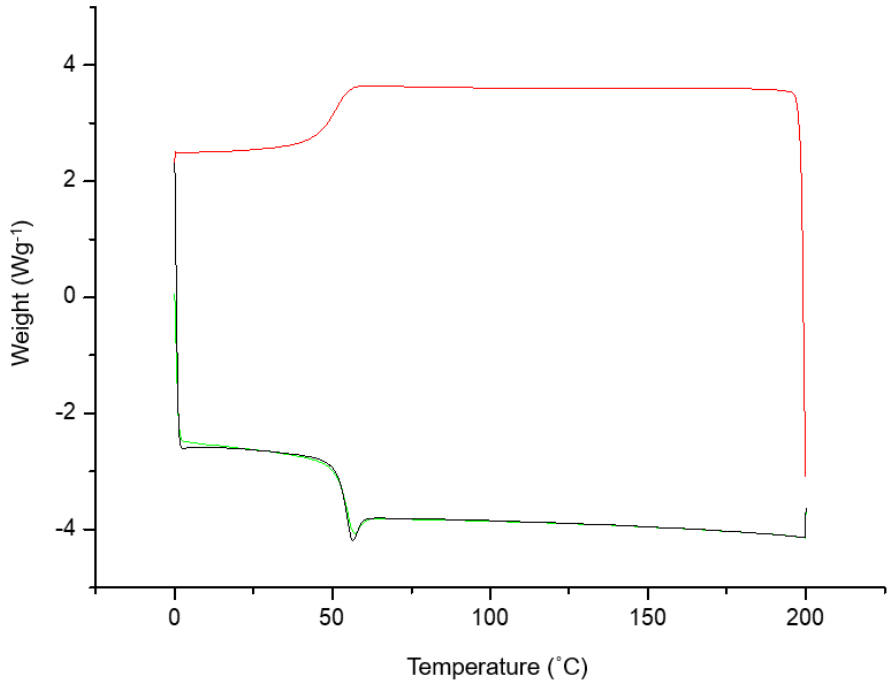

Figure S12. *DSC of a representative polymer sample obtained from* ***1****-catalysed LA polymerization (entry 3 of Table 3).*

3.3 SEC analyses

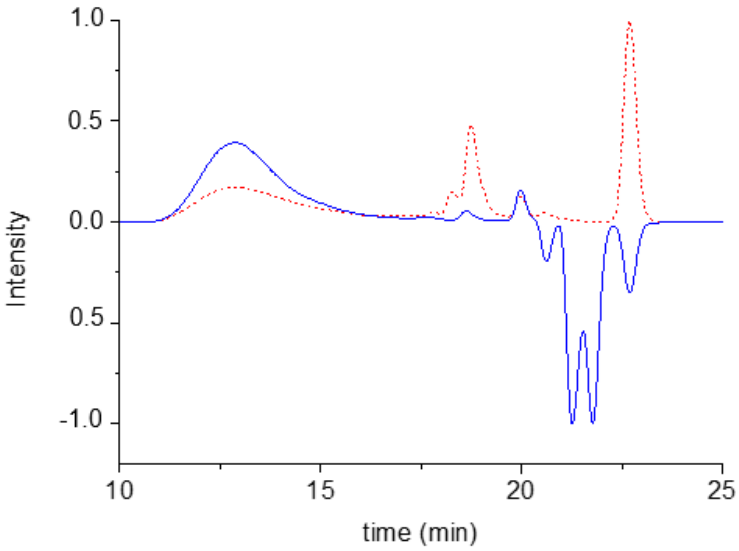

Figure S13. *SEC analysis of precipitated polymer obtained from the following reaction conditions: [rac-LA]/[****1****] = 5000:1, 150 ˚C, 500 rpm, m(LA) = 1.6 mg. Refractive index (blue line) UV absorbance (red dashed line)*

3.4 Visual analysis

Figure S14. *Photographs of PLA prepared by the bulk polymerization of rac-LA at 150 °C, 30 min, catalyzed by complex* ***1*** *[LA]/[**1**] = 250:1.: Left before precipitation, middle after precipitation in EtOH. Right photograph of film prepared by weighing 250 g PLA, prepared from ([LA]/[**1**] = 1000:1), dissolving it in CD_2Cl_2, casting on petri dish and drying under vacuum for 7 days.*

4. Equations and constants for rate determinations

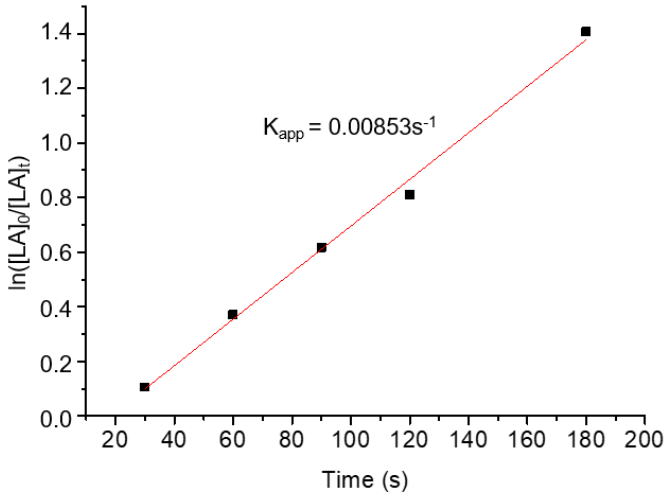

Figure S15. *Plot of the $ln([LA)_0/[LA]_t)$ values measured for the reaction reported in Table S5 vs time. Conditions: rac-LA (500 mg, 3.5 mmol),* ***1*** *(6.9 µmol) [LA]/[**1**] = 500:1, 150 °C, 500 rpm. The slope of the linear regressions yields k_{app} of complexes* ***1****, (R^2 >0.98).*

Table S9. *Apparent polymerization rate constants k_{app} for all experiments obtained via linear regression*

Complex	[*rac*-LA]/[cat]	k_{app} (h^{-1})	k_{app} 10^{-4} (s^{-1})	R^2
1	5000:1	3.06	8.5±0.6	0.9814
2	5000:1	0.90	2.5±0.2	0.9821
3	5000:1	2.63	7.3±0.3	0.9949
4	5000:1	2.88	8.0±0.6	0.9810
1	500:1	30.7	85.3±3.3	0.9940
1	1000:1	19.4	53.9±4.1	0.9861
1	1500:1	11.9	33.0±0.4	0.9996
1	2775:1	4.43	12.3±0.4	0.9974
1	5000:1	3.06	8.5±0.6	0.9932
1	10,000:1	0.33	0.9±0.1	0.9871

*The rate constant of propagation was calculated from least square regression of $k_{app} = k_p$**[1]** from the values of Table S5, which yields $k_p = 0.6986\ s^{-1}$ –a ($R^2 = 0.9870$).*