Supporting information for

Magnesium complexes supported by salan-like ligands: synthesis, characterization and application in the ring-opening polymerization of *rac*-lactide

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Contents:

Table S1. Crystallographic data of complexes **1**, **1'**, **2**, **3**

	1	**1'**	**2**	**3**
Empirical formula	$C_{33}H_{59}MgN_3O_2Si_2$	$C_{31}H_{55}MgN_3O_2Si_2$	$C_{45.50}H_{69}MgN_3O_2Si_2$	$C_{25}H_{41}C_{l2}MgN_3O_2Si_2$
Formula weight	610.32	582.27	770.53	567.00
Temp (K)	293(2) K	293(2) K	296(2) K	293(2) K
Crystal size (mm)	0.40 × 0.20 × 0.18	0.268 × 0.213 × 0.169	0.10 × 0.06 × 0.05	0.200 × 0.150 × 0.140
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	C2/c	$P2_1/c$
a (Å)	9.423(4)	14.9422(11)	18.031(3)	11.650(5)
b (Å)	27.293(10)	17.3627(13)	12.120(2)	14.321(6)
c (Å)	15.241(6)	14.9983(12)	44.305(8)	18.739(7)
α (°)	90	90	90	90
β (°)	101.172(5)	114.3660(10)	98.088(3)	97.448(5)
γ (°)	90	90	90°	90
Volume(Å ^{3})	3846(2)	3544.5(5)	9586(3)	3100(2)
Z	4	4	8	4
$Density_{calc}$ (mg/m^3)	1.054	1.091	1.062	1.215
Abs coeff. (mm^{-1})	0.138	0.147	0.123	0.333
F (000)	1336	1272	3352	1208
θ range (°)	1.492 to 25.009	1.62 to 26.00	0.93 to 25.00	1.763 to 26.010
Data collected (hkl)	–11 to 11, –28 to 32, –18 to 11	–11 to 18, –21 to 20, –18 to 16	–21 to 20, –13 to 14, –51 to 52	–14 to 12, –14 to 17, –23 to 23
Reflns collected/unique	15806 / 6765	19159 / 6957	27785 / 8417	13710 / 6095
R(int)	0.0562	0.0461	0.0388	0.0558
Max. and min. transmn.	0.821 and 0.648	1.00000 and 0.47141	0.9939 and 0.9878	0.9549 and 0.9365
Data / restrains / para	6765 / 0 / 385	6957 / 42 / 403	8417 / 0 / 483	6095 / 0 / 325
Goodness-of-fit on F^2	0.993	0.983	1.063	0.928
Final R_1 ,wR_2 [$I > 2\sigma(I)$]	0.0617, 0.1683	0.0531, 0.1254	0.0673, 0.1881	0.0498, 0.1125
R_1 , wR_2 (all data)	0.1024, 0.1929	0.1084, 0.1510	0.0915, 0.2076	0.0974, 0.1344
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.373 and –0.263	0.342 and –0.252	0.329 and –0.268	0.270 and –0.199

Table S2. The selected bond lengths (Å) and bond angles (°) in **1**, **1'**, **2**, **3**

[(**L**^{1})MgN(SiMe$_3$)$_2$] (**1**)			
Mg1-O1	1.917(2)	Mg1-N2	2.333(3)
Mg1-N3	2.033(3)	Mg1···Si1	3.1934(16)
Mg1-O2	2.206(2)	Si1-N3	1.690(3)
Mg1-N1	2.227(3)	Si2-N3	1.702(3)
O1-Mg1-N3	119.36(11)	N1-Mg1-N2	77.89(12)
O1-Mg1-O2	88.80(8)	O1-Mg1-N2	98.82(9)
N3-Mg1-O2	94.45(9)	N3-Mg1-N2	141.69(10)
O1-Mg1-N1	90.82(9)	O2-Mg1-N2	82.65(9)
N3-Mg1-N1	102.90(11)	Si1-N3-Si2	119.80(14)
O2-Mg1-N1	160.24(11)		
[(**L**^{1})MgN(SiHMe$_2$)$_2$] (**1'**)			
Mg1-O2	1.9145(19)	Mg1-O1	2.2605(18)
Mg1-N3	2.012(2)	Mg1···Si1	3.1063(12)
Mg1-N2	2.231(2)	Mg1···Si2	3.1860(11)
Mg1-N1	2.246(2)	Si1-N3	1.679(2)
O2-Mg1-N3	120.04(9)	O2-Mg1-O1	87.98(7)
O2-Mg1-N2	91.78(8)	N3-Mg1-O1	93.24(8)
N3-Mg1-N2	103.65(9)	N2-Mg1-O1	160.53(8)
O2-Mg1-N1	107.99(8)	N1-Mg1-O1	83.18(7)
N3-Mg1-N1	131.70(9)	Si2-N3-Si1	126.34(12)
N2-Mg1-N1	78.38(8)		
[(**L**^{2})MgN(SiMe$_3$)$_2$] (**2**)			
Mg1-O2	1.928(2)	Mg1-N1	2.324(3)
Mg1-N3	2.062(3)	Si1-N3	1.703(3)
Mg1-O1	2.201(2)	Si2-N3	1.698(3)
Mg1-N2	2.228(3)	O1-Mg1-N2	161.09(10)
O2-Mg1-N3	118.09(11)	O2-Mg1-N1	97.81(9)
O2-Mg1-O1	89.54(9)	N3-Mg1-N1	144.03(11)
N3-Mg1-O1	93.93(10)	O1-Mg1-N1	83.71(9)
O2-Mg1-N2	91.16(9)	N2-Mg1-N1	77.48(10)
N3-Mg1-N2	102.36(11)	Si2-N3-Si1	119.92(15)
[(**L**^{3})MgN(SiMe$_3$)$_2$] (**3**)			
Mg1-O1	1.929(2)	Mg1-N2	2.308(3)
Mg1-N3	2.036(2)	Mg1···Si1	3.1783(14)
Mg1-O2	2.173(2)	N3-Si2	1.698(2)
Mg1-N1	2.247(2)	N3-Si1	1.700(2)

O1-Mg1-N3	115.72(9)	O1-Mg1-N2	98.43(8)
O1-Mg1-O2	88.38(9)	N3-Mg1-N2	145.72(9)
N3-Mg1-O2	94.41(9)	O2-Mg1-N2	83.18(8)
O1-Mg1-N1	90.61(9)	N1-Mg1-N2	78.25(9)
N3-Mg1-N1	103.04(10)	Si2-N3-Si1	120.07(12)
O2-Mg1-N1	161.06(10)		

Table S3. ROP of *rac*-LA initiated by magnesium silylamido complexes.

Run	Cat.	$[LA]_0/[Mg]_0/[^iPrOH]$ [a]	Solv.	t (min)	Conv. [b] (%)	$M_{n,calcd.}$ [c] (10^4)	M_n [d] (10^4)	PDI [d]	P_m
1	**1**	200:1:0	Tol.	20	80	2.31	--[i]	--[i]	
2		200:1:0	Tol.	25	97	2.78	3.85	2.10	0.68
3		200:1:1	Tol.	8	93	2.68	--[i]	--[i]	
4		200:1:1	Tol.	10	99	2.86	2.46	1.88	0.70
5		200:1:0	THF	3	64	1.84	--[i]	--[i]	
6		200:1:0	THF	5	84	2.42	4.51	2.17	0.44
7		200:1:1	THF	1	96	2.77	2.77	1.35	0.45
8	**1'**	200:1:0	Tol.	10	73	2.10	--[i]	--[i]	
9		200:1:0	Tol.	15	80	2.30	5.31	1.69	0.66
10		200:1:1	Tol.	3	88	2.54	--[i]	--[i]	
11		200:1:1	Tol.	5	96	2.77	1.02	2.21	0.59
12	**2**	200:1:0	Tol.	20	98	2.82	3.01	2.08	0.67
13		200:1:1	Tol.	5	99	2.86	2.50	1.64	0.69
14		200:1:1[f]	Tol.	300	98	2.82	--[i]	--[i]	0.65
15		200:1:1[g]	Tol.	1440	87	2.51	--[i]	--[i]	0.66
16		200:1:1[h]	Tol.	1440	63	1.82	--[i]	--[i]	0.65
17		200:1:0	THF	3	61	1.76	--[i]	--[i]	
18		200:1:0	THF	5	84	2.42	3.54	1.87	0.52
19		200:1:1	THF	1	96	2.77	1.22	1.59	0.50
20	**3**	200:1:0	Tol.	75	84	2.42	2.85	1.80	0.62
21		200:1:0	Tol.	90	91	2.62	--[i]	--[i]	
22		200:1:0	Tol.	105	96	2.77	2.69	1.66	0.65
23		200:1:1	Tol.	15	98	2.83	1.65	1.46	0.62
24		200:1:0	THF	20	86	2.48	--[i]	--[i]	
25		200:1:0	THF	30	91	2.62	3.86	1.66	0.38
26		200:1:1	THF	10	58	1.68	1.49	1.28	0.41
27	**4**	200:1:0	Tol.	1800	75	2.16	--[i]	--[i]	
28		200:1:0	Tol.	2190	84	2.42	0.97	2.03	0.61
29		200:1:1	Tol.	20	96	2.77	1.84	2.03	0.67
30		200:1:0	THF	30	72	2.07	4.36	1.88	0.39
31		200:1:0	THF	60	85	2.45	0.92	3.00	0.39
32		200:1:1	THF	5	97	2.80	2.79	1.57	0.40

[a] [*rac*-LA]$_0$ = 1.0 M, [Mg]$_0$ = 0.005 M, T = 25 ± 1 °C; [b] Determined by ^{1}H NMR spectroscopy; [c] $M_{n,calcd}$ = ([LA]$_0$/[Mg]$_0$) × 144.13 × conv.%; [d] Determined by GPC, Waters M515 pump, 25 °C, 1 mL min^{-1}, PS as standards.; [e] P_m is the probability of forming a new *m*- dyad, determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled ^{1}H NMR spectrum. [f] Conducted under 5 ºC; [g] Conducted under -20 ºC; [h] Conducted under -39 ºC. [i] not detected.

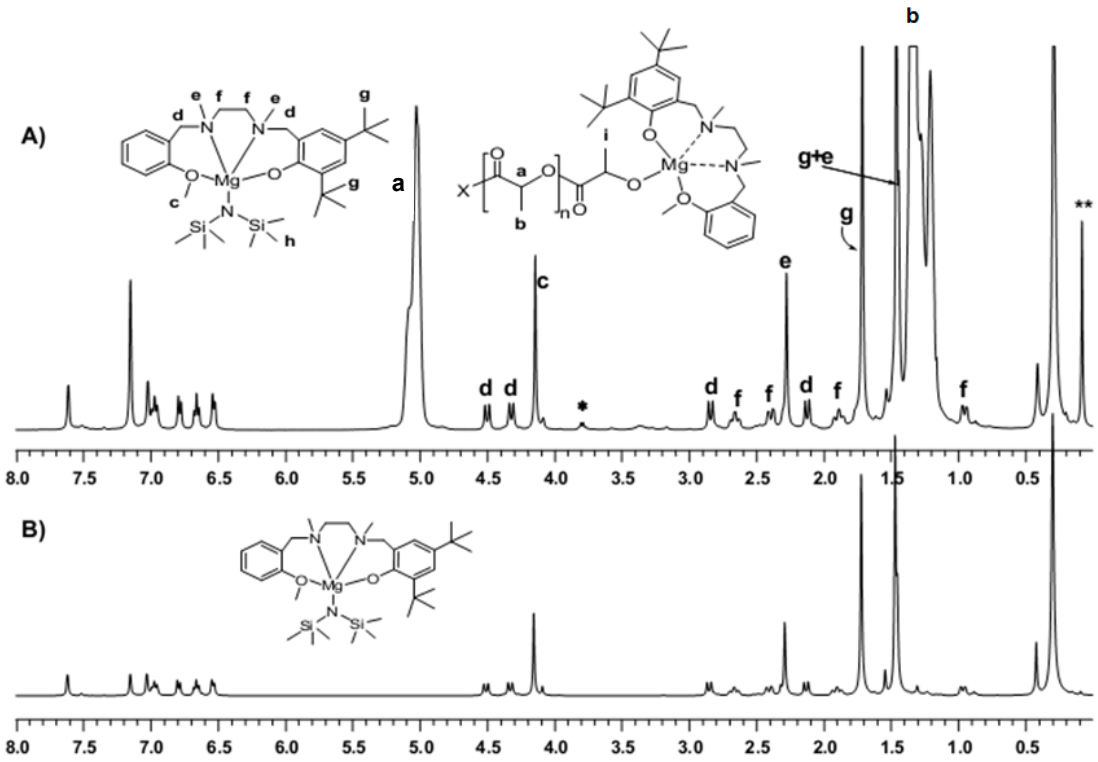


Fig. S1 ^{1}H NMR spectra of A) active *rac*-lactide oligomer by **1**; B) complex **1** (400 MHz, C_6D_6; *, monomer; **, free $HN(SiMe_3)_2$; $[rac\text{-LA}]_0$:$[Mg]_0$ = 20:1, at 20 ºC.)

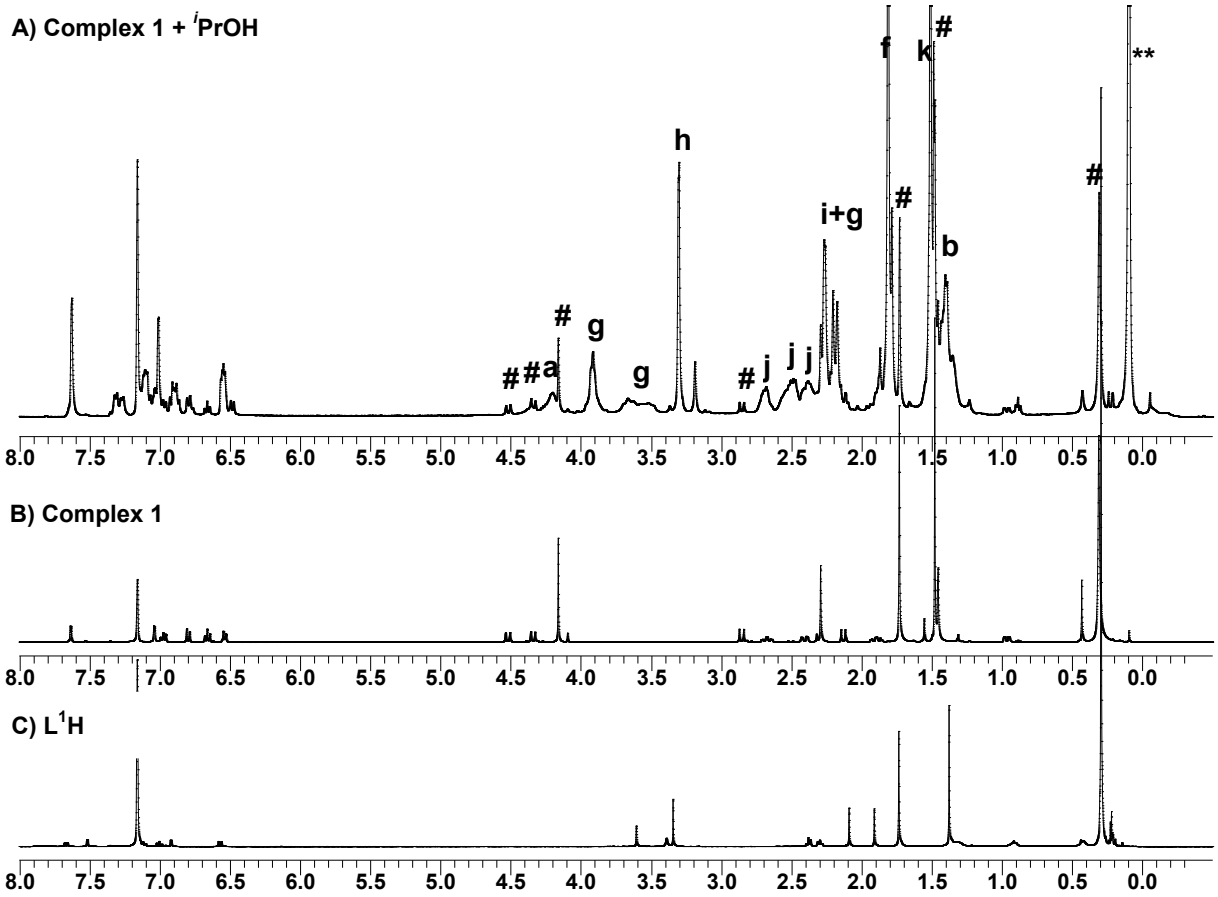


Fig. S2 ^{1}H NMR spectra of A) the NMR-scale reaction of complex **1** with ^{i}PrOH; B) complex **1**; C) proligand $\mathbf{L^{1}H}$ (C_6D_6, 400 M Hz; $[Mg]_0$:$[^{i}PrOH]_0$ > 1:1; at 25 ºC, #, signals of complex **1**; **, free $HN(SiMe_2)_2$).

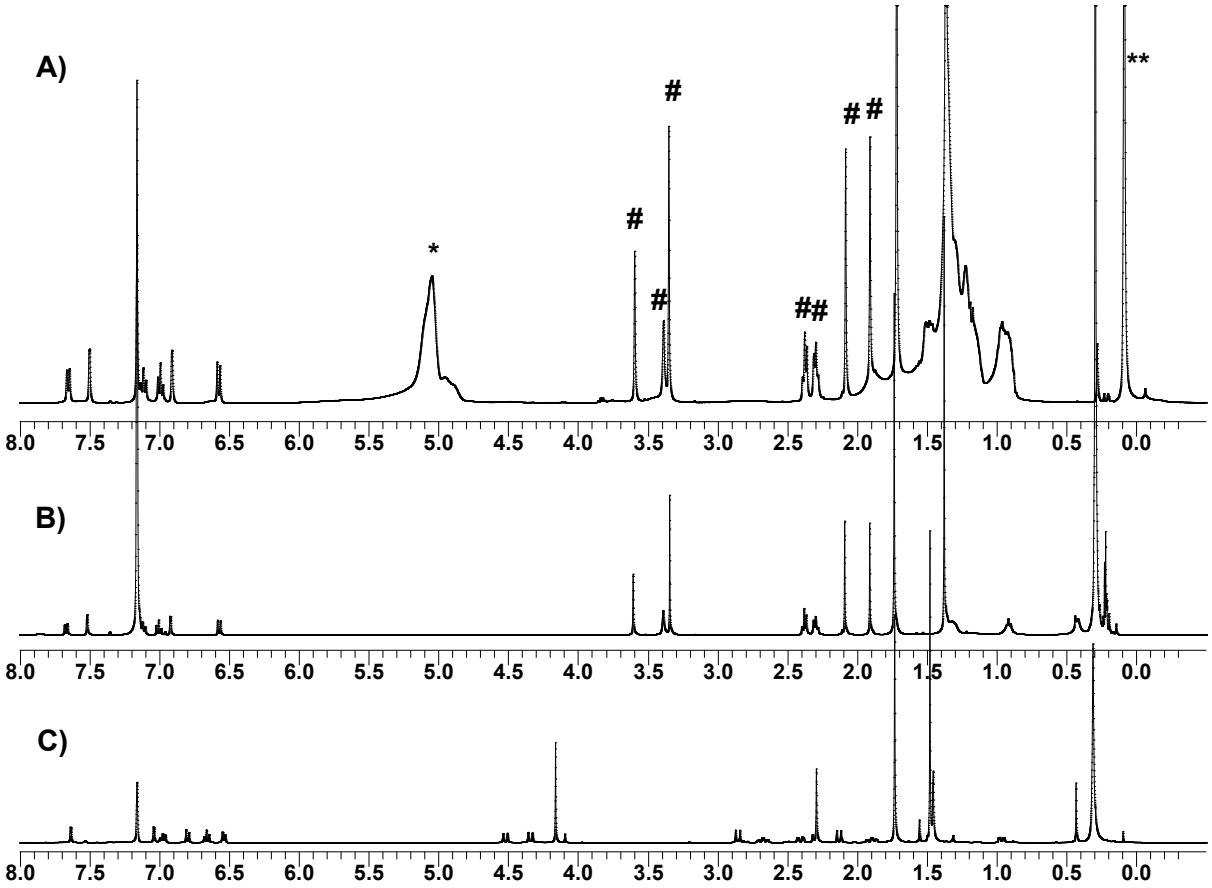


Fig. S3 ^{1}H NMR spectra of A) the NMR-scale polymerization of *rac*-lactide by complex **1** and 2 equiv. of ^{i}PrOH; B) proligand $\mathbf{L^{1}H}$; C) complex **1** (C_6D_6, 400 MHz; [*rac*-LA]:$[Mg]_0$:[^{i}PrOH]$_0$ = 20:1:2; at 25 ºC, #, signals of proligand $\mathbf{L^{1}H}$; *signal of polymer; **, free $HN(SiMe_2)_2$).

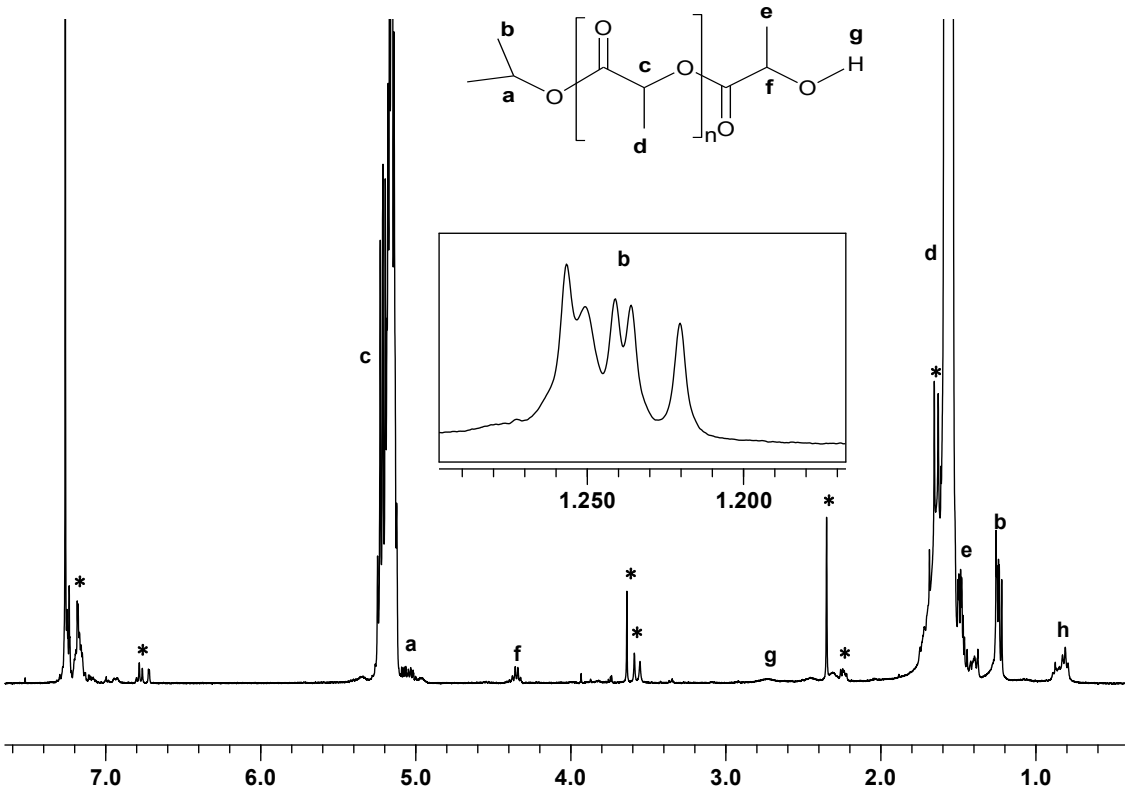
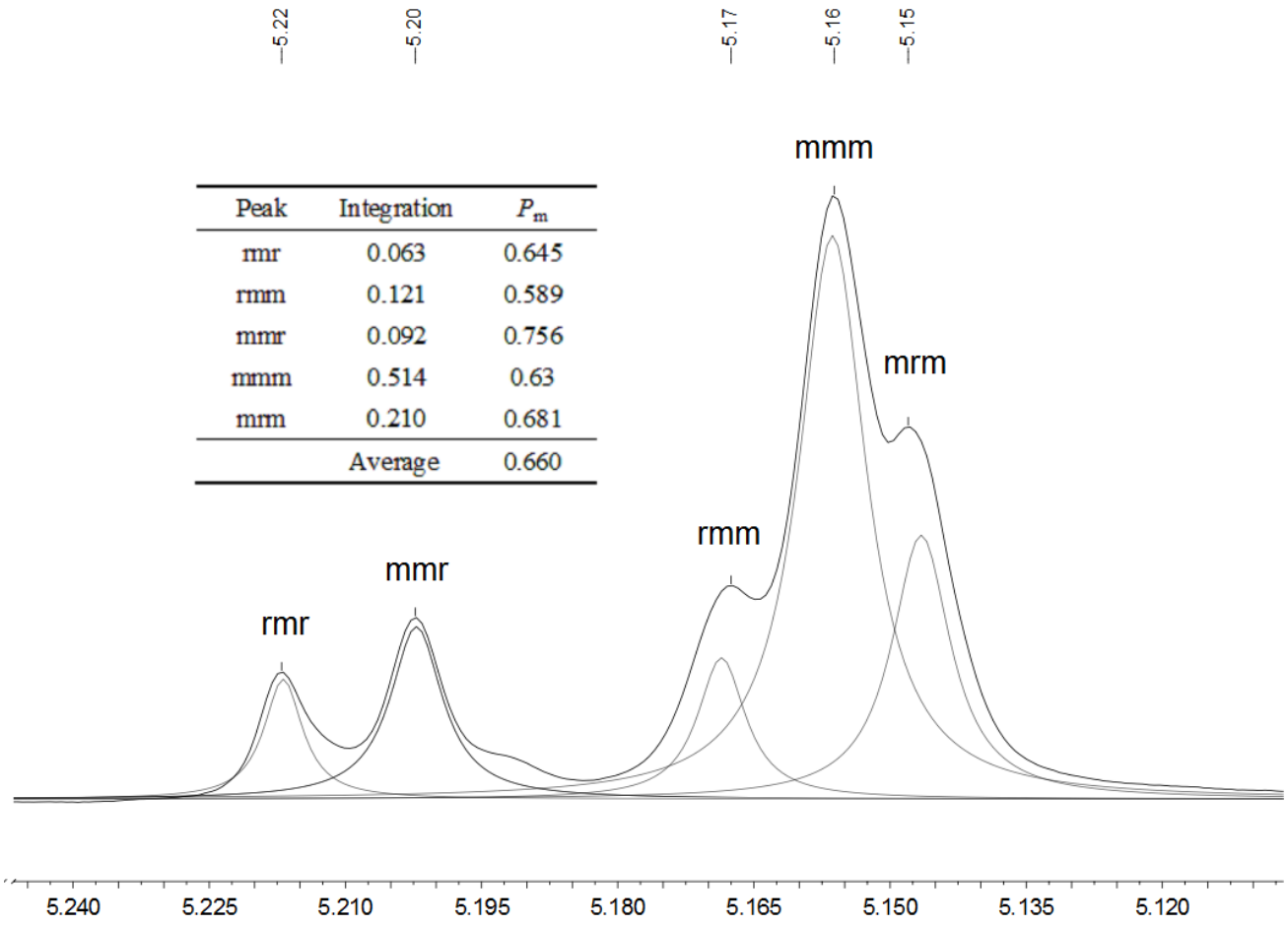
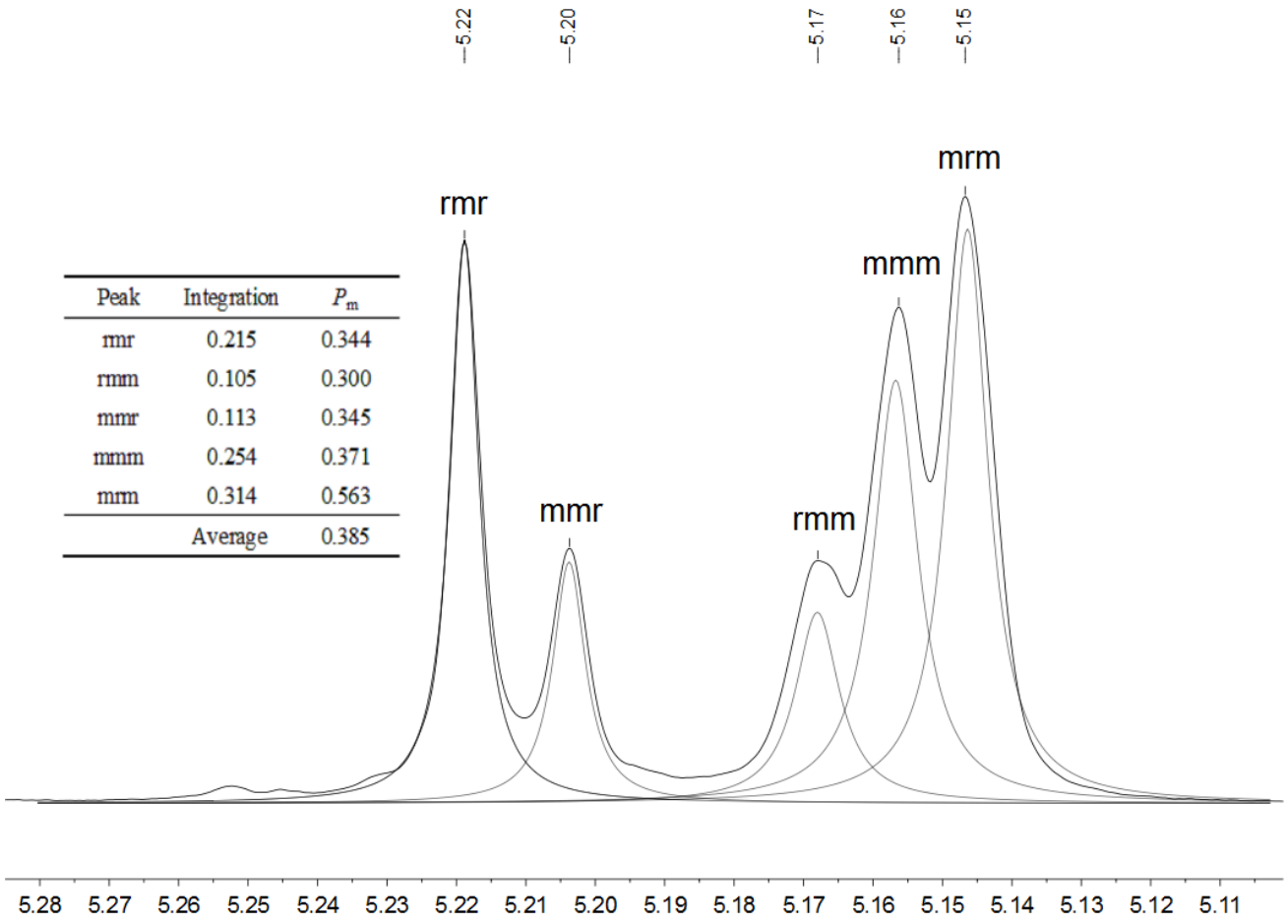


Fig. S4 ^{1}H NMR spectrum of *rac*-lactide oligomer obtained by **1**/^{i}PrOH after termination with wet petroleum ether ($CDCl_3$, 400 MHz; h, signals of PE; *, signals of proligand; $[rac\text{-LA}]_0$:$[Mg]_0$:$[^{i}PrOH]_0$ = 20:1:1, in toluene).



Peak	Integration	P_m
rmr	0.063	0.645
rmm	0.121	0.589
mmr	0.092	0.756
mmm	0.514	0.63
mrm	0.210	0.681
	Average	0.660

Fig. S5 The methine region of homonuclear decoupled ^{1}H NMR spectrum of PLA produced from *rac*-LA initiated by **1'** in toluene ($CDCl_3$, 400 MHz, $[rac\text{-LA}]_0$:$[Mg]_0$ = 200:1, in toluene).



Peak	Integration	P_m
rmr	0.215	0.344
rmm	0.105	0.300
mmr	0.113	0.345
mmm	0.254	0.371
mrm	0.314	0.563
	Average	0.385

Fig. S6 The methine region of homonuclear decoupled ^{1}H NMR spectrum of PLA produced from *rac*-LA initiated by **4** in THF ($CDCl_3$, 400 MHz, $[rac\text{-LA}]_0$:$[Mg]_0$ = 200:1, in THF).