Electronic Supplementary Information for Dalton Transactions

(Electronic Supporting Information)

Versatile Catalytic Systems Based on Complexes of Zinc, Magnesium and Calcium Supported by a Bulky Bis(Morpholinomethyl)Phenoxy Ligand for the Large-Scale Immortal Ring-Opening Polymerisation of Cyclic Esters

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Table S1. Polymerisation data using zinc complexes ($ZnEt_2$, **3** or **4**) / ROH binary catalytic systems.[a]

Entry	Monomer	Initiator	ROH	$[M]_0/[Zn]_0/[ROH]_0$	$[M]_0$ ($mol \cdot L^{-1}$)	Time (h)	Yield[b] (%)	TOF[c] (h^{-1})	$M_{n,calc}$[d] ($g \cdot mol^{-1}$)	$M_{n,SEC}$[e] ($g \cdot mol^{-1}$)	M_w/M_n[e]	P_r[f]
1	L-LA	[LO[1]]H	^{i}PrOH	1 000/-/10	2.0	1	0	0	N/A	N/A	N/A	
2	L-LA	**3**	^{i}PrOH	1 000/1/0	2.0	1	18	180	26 000	10 300	2.24	
3	L-LA	**3**	^{i}PrOH	1 000/1/10	2.0	1	97	970	14 000	15 100	1.10	1.00
4	L-LA	**3**	^{i}PrOH	5 000/1/25	4.0	1	71	3 550	20 500	20 600	1.09	
5	L-LA	**3**	^{i}PrOH	5 000/1/25	4.0	1.5	94	3 130	27 100	26 200	1.16	
6	L-LA	$ZnEt_2$	^{i}PrOH	20 000/1/250	6.0	1.33	11	1 650	1 300	1 600	1.09	
7	L-LA	**4**	^{i}PrOH	20 000/1/250	6.0	1.33	65	9 770	7 500	6 700	1.10	
8	L-LA	**3**	^{i}PrOH	20 000/1/250	6.0	1.33	74	11 130	8 600	8 900	1.16	
9	L-LA	**3**	^{i}PrOH	20 000/1/100	6.0	3	95	6 330	27 400	26 800	1.28	
10	L-LA	**3**	^{i}PrOH	20 000/1/175	6.0	3	98	6 530	16 200	16 100	1.20	
11	L-LA	**3**	^{i}PrOH	20 000/1/250	6.0	3	98	6 530	11 300	11 600	1.26	
12	L-LA	**3**	^{i}PrOH	20 000/1/500	6.0	3	97	6 470	5 600	5 400	1.32	
13	L-LA	**3**	^{i}PrOH	20 000/1/750	6.0	3	94	6 270	3 600	3 000	1.46	
14	L-LA	**3**	^{i}PrOH	20 000/1/1 000	6.0	3	99	6 600	2 900	2 400	1.33	1.00
15	L-LA	**3**	^{i}PrOH	50 000/1/500	6.0	16	100	3 125	14 500	13 500	1.60	
16	*rac*-LA	**3**	^{i}PrOH	1 000/1/10	2.0	1	95	950	14 000	13 000	1.10	0.50
17[g]	*rac*-LA	**3**	^{i}PrOH	1 000/1/10	2.0	1	68	680	13 000	12 700	1.19	0.45
18	BBL	**3**	^{i}PrOH	500/1/10	Bulk	3	95	158	4 100	4 300	1.07	0.50

[a] Polymerisations performed in toluene at 60 °C. [b] Isolated yield of polymer. [c] Non-optimized turnover frequency ($mol(L\text{-}LA) \cdot mol(Zn)^{-1} \cdot h^{-1}$) calculated over the whole reaction time. [d] Calculated from $[L\text{-}LA]_0/[^iPrOH]_0 \times$ monomer conversion $\times M_{L\text{-}LA} + M_{iPrOH}$, with $M_{L\text{-}LA} = 144\ g \cdot mol^{-1}$ and $M_{iPrOH} = 60\ g \cdot mol^{-1}$. [e] Determined by size exclusion chromatography *vs.* polystyrene standards and corrected by a factor of 0.58. [f] Probability of a *meso* linkage between two repetitive units as determined by examination of the methine region of the ^1H homonuclear decoupled NMR spectrum of the polymers. [g] Polymerisation carried out in THF.

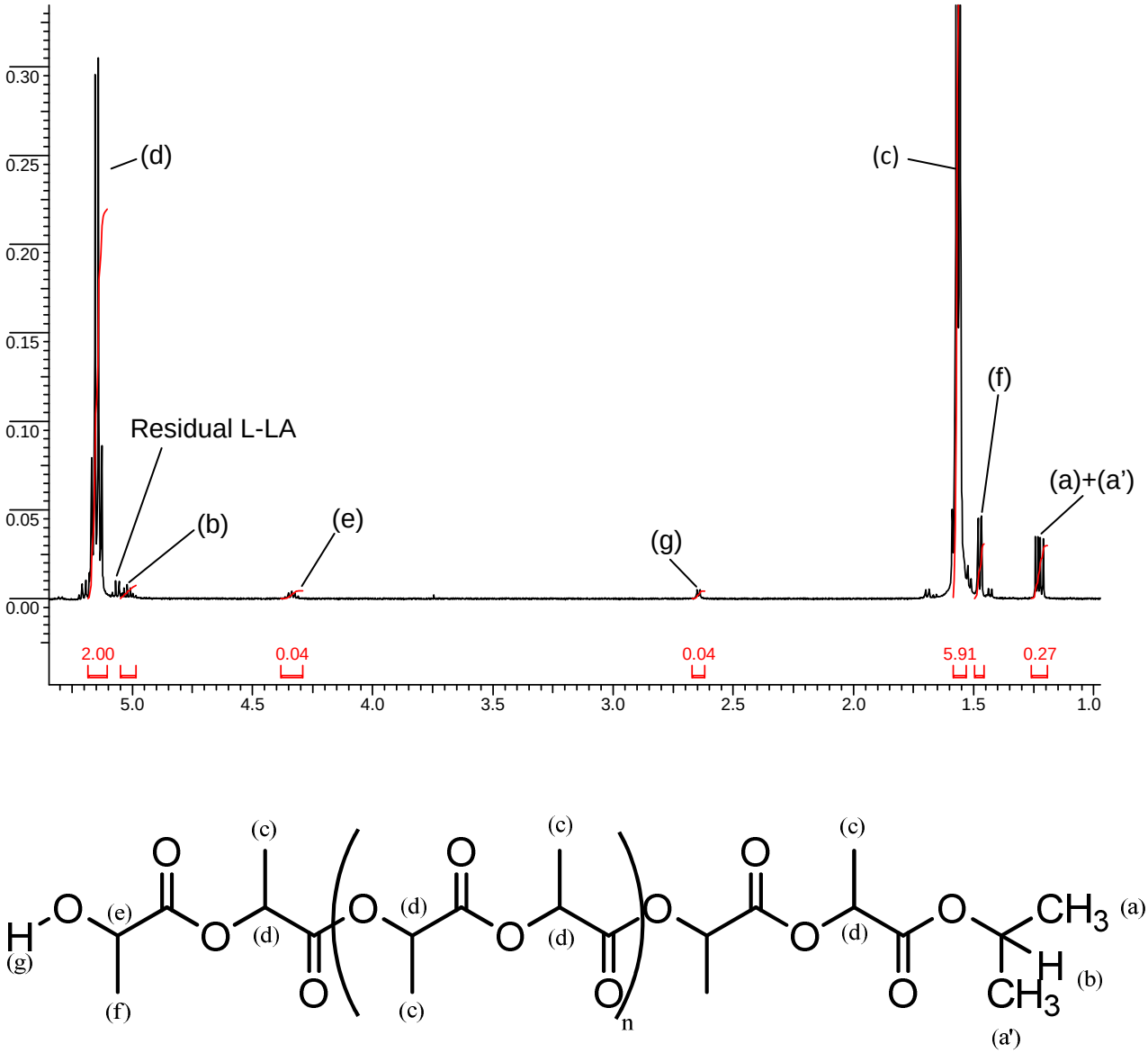

Figure S1: ^{1}H NMR spectrum of a low molecular weight PLLA prepared with L-LA/**2**/^{i}PrOH in relative amounts of 500/1/25 (500.13 MHz, $CDCl_3$, 25 °C, 64 scans, D1 = 0.50 sec).

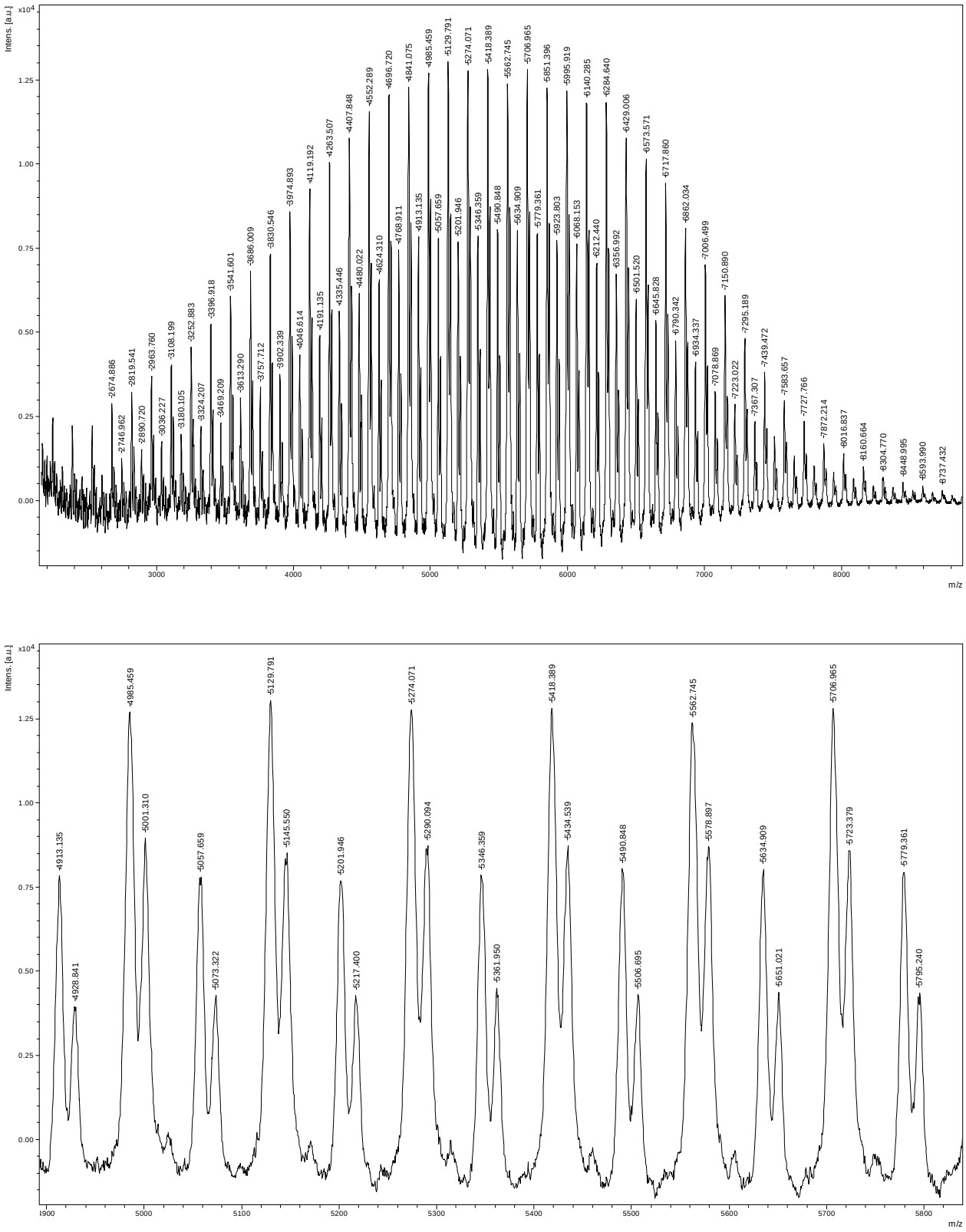

Figure S2: MALDI-TOF mass spectrum (main population: Na^+; minor population: K^+) of a low molecular weight PLLA having a number average molecular weight $\overline{Mn}_{SEC}$ of 4 600 g·mol^{-1}, prepared with L-LA/**1**/^{i}PrOH in relative amounts of 5 000/1/100 (71% conversion).

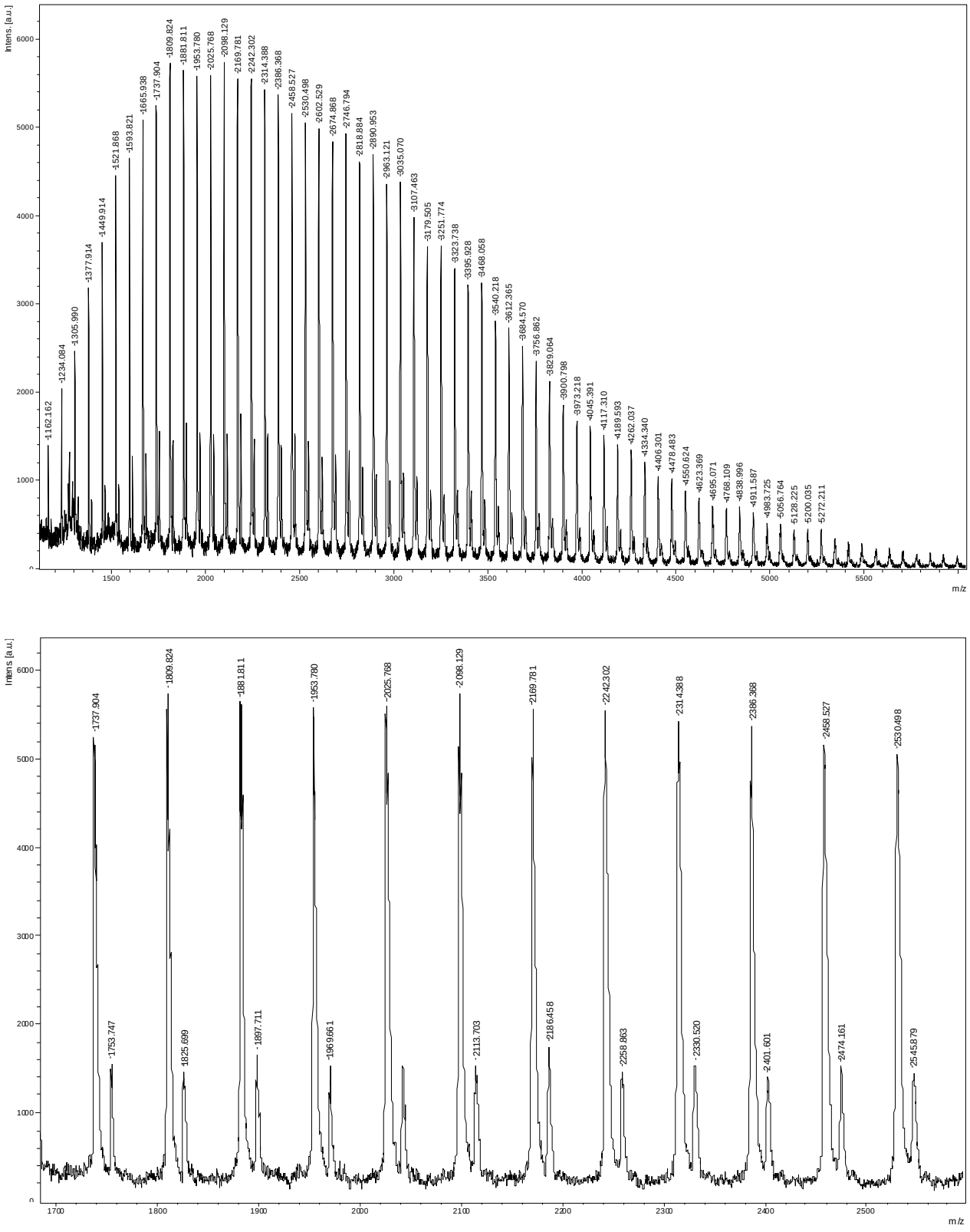

Figure S3: MALDI-TOF mass spectrum (main population: Na^+; minor population: K^+) of a low molecular weight PLLA having a number average molecular weight $\overline{Mn}_{SEC}$ of 3 000 g·mol^{-1}, prepared with L-LA/**2**/^{i}PrOH in relative amounts of 500/1/25 (86% conversion).

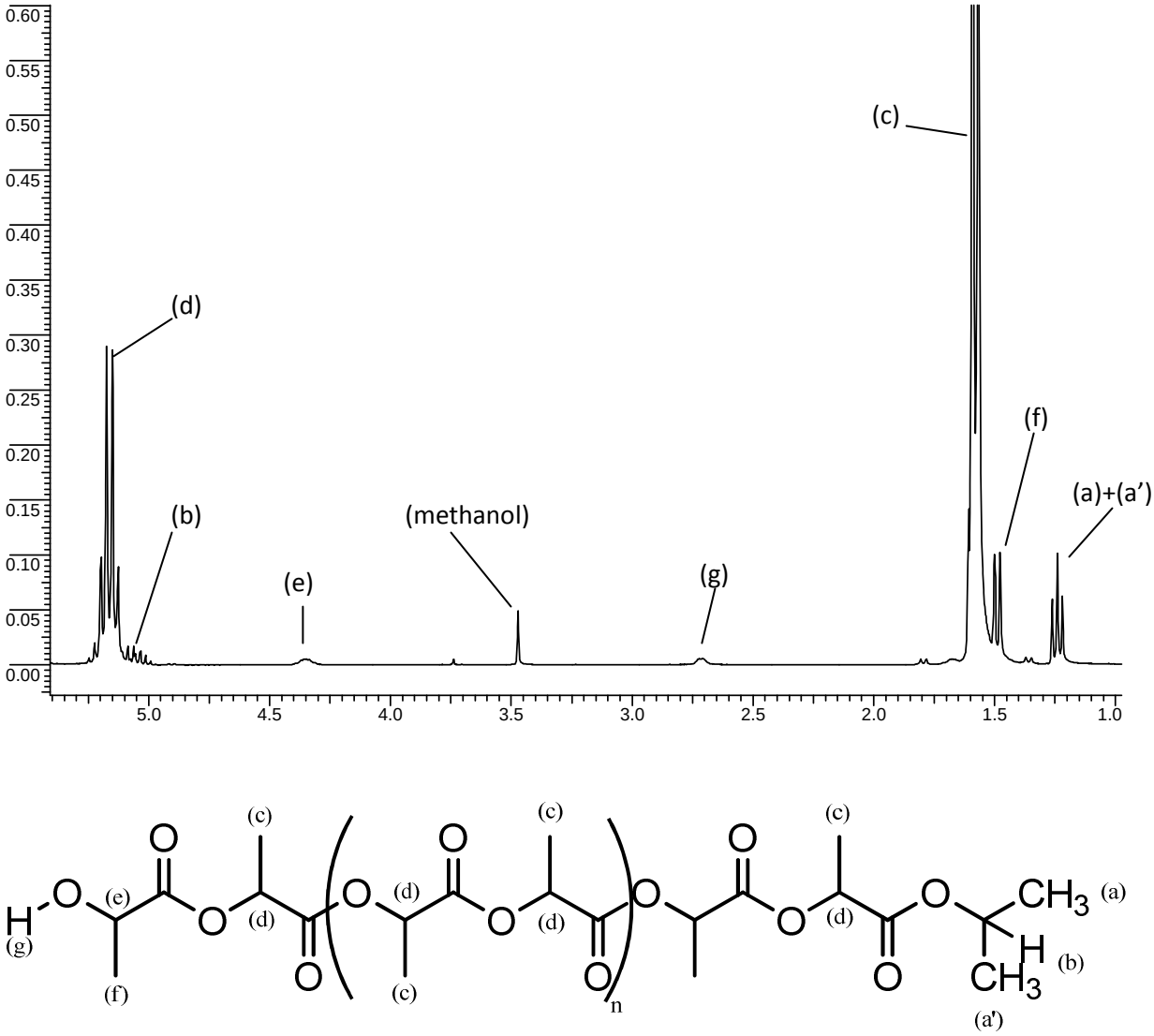

Figure S4: ^{1}H NMR spectrum of a low molecular weight PLLA prepared with L-LA/**3**/^{i}PrOH in relative amounts of 100/1/10 (500.13 MHz, $CDCl_3$, 25 °C, 16 scans, D1 = 0.50 sec).

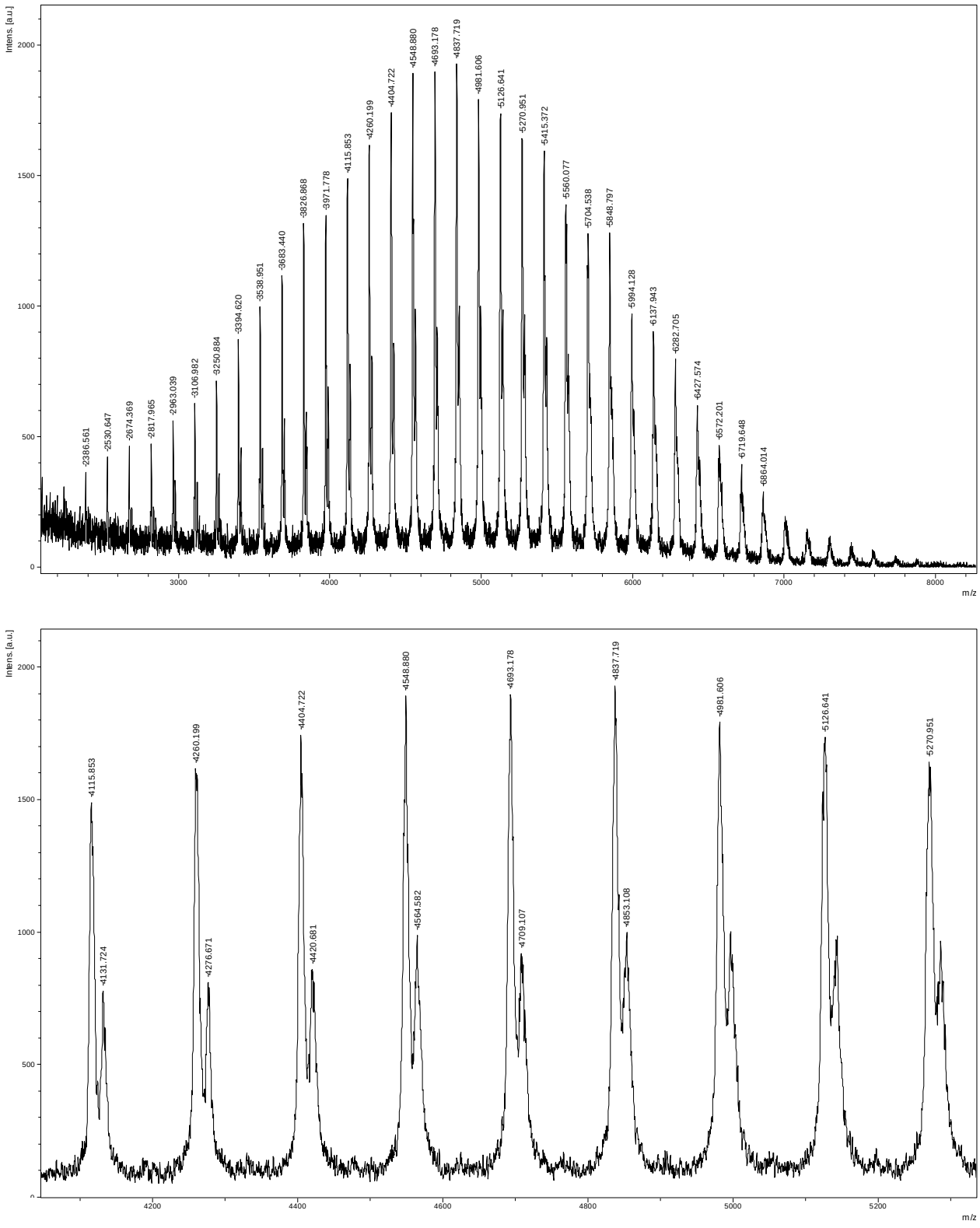

Figure S5: MALDI-TOF mass spectrum (main population: Na^+; minor population: K^+) of a low molecular weight PLLA having a number average molecular weight $\overline{Mn}_{SEC}$ of 4 700 g·mol^{-1}, prepared with L-LA/**3**/^{i}PrOH in relative amounts of 1 000/1/10 (20% conversion).