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Lactide Polymerization Catalyzed by Manganese Complexes

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Supporting Information

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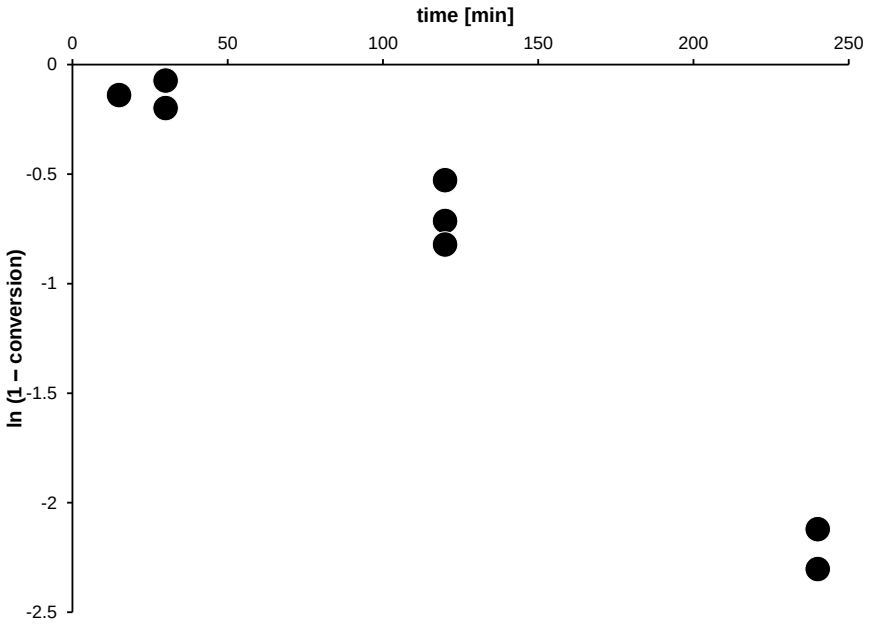

Figure S1. Linearized plot (assuming a reaction 1st order in lactide) for polymerizations with **5a**·MeOH.

Table S1. Conversions of all *rac*-lactide polymerization experiments [a]

Catalyst	Alcohol added	Reaction time [min]	Conversion [%] run 1	run 2	run 3	run 4
3a		120	49 [c]	53 [d]		
3a		240	52 [c]	43 [d]		
3a		360	91 [c]	47 [c]	56 [d]	51 [d]
3b		240	38	71 [c]		
3b		360	48	81 [c]		
4a·MeOH		15	8	7		
4a·MeOH		30	*56* [b]	7	5	10
4a·MeOH		60	6			
4a·MeOH		120	7			
4a·MeOH	1 MeOH	15	7	4	18	
4a·MeOH	1 MeOH	30	5	0	0	8
4a·MeOH	2 MeOH	5	4			
4a·MeOH	2 MeOH	15	49	18	4	8
4a·MeOH	2 MeOH	30	47	14		
4a·MeOH	2 MeOH	60	48	17	61	
4a·MeOH	2 MeOH	90	17	27		
4a·MeOH	2 MeOH	120	39	88		
4a·MeOH	2 MeOH	240	30			
4a·MeOH	5 BnOH	60	16	22		
4a·MeOH	5 BnOH	120	32			
4a·MeOH	5 BnOH	240	43			
4a·MeOH	15 BnOH	30	65	37		
4a·MeOH	35 BnOH	30	89	59		
4a·MeOH	95 BnOH	30	97	90		
4a·MeOH	1 NaOMe	60	27			
4a·MeOH	1 NaOMe	120	13			
4b·MeOH	2 MeOH	5	3			
4b·MeOH	2 MeOH	15	4	5		
4b·MeOH	2 MeOH	30	5	4	4	
4b·MeOH	2 MeOH	60	3	7	4	
4b·MeOH	1 NaOMe	120	1			
5a·MeOH		15	13			
5a·MeOH		30	18	7		
5a·MeOH		120	51	41 [c]	56 [d]	
5a·MeOH		240	88	90 [c]	88 [d]	70 [e]
5a·MeOH	5 BnOH	30	17			
5a·MeOH	5 BnOH	60	19	27		
5a·MeOH	5 BnOH	120	30			
5a·MeOH	5 BnOH	240	95			
NaOMe		360	29	38		

[a] Conditions: *rac*-lactide : catalyst = 200:1, sealed tube under N_2, neat monomer, 130 °C. [b] Outlier, not reported in the main text. [c] *rac*-lactide : catalyst = 100:1. [d] *rac*-lactide : catalyst = 300:1. [e] *rac*-lactide : catalyst = 1000:1.

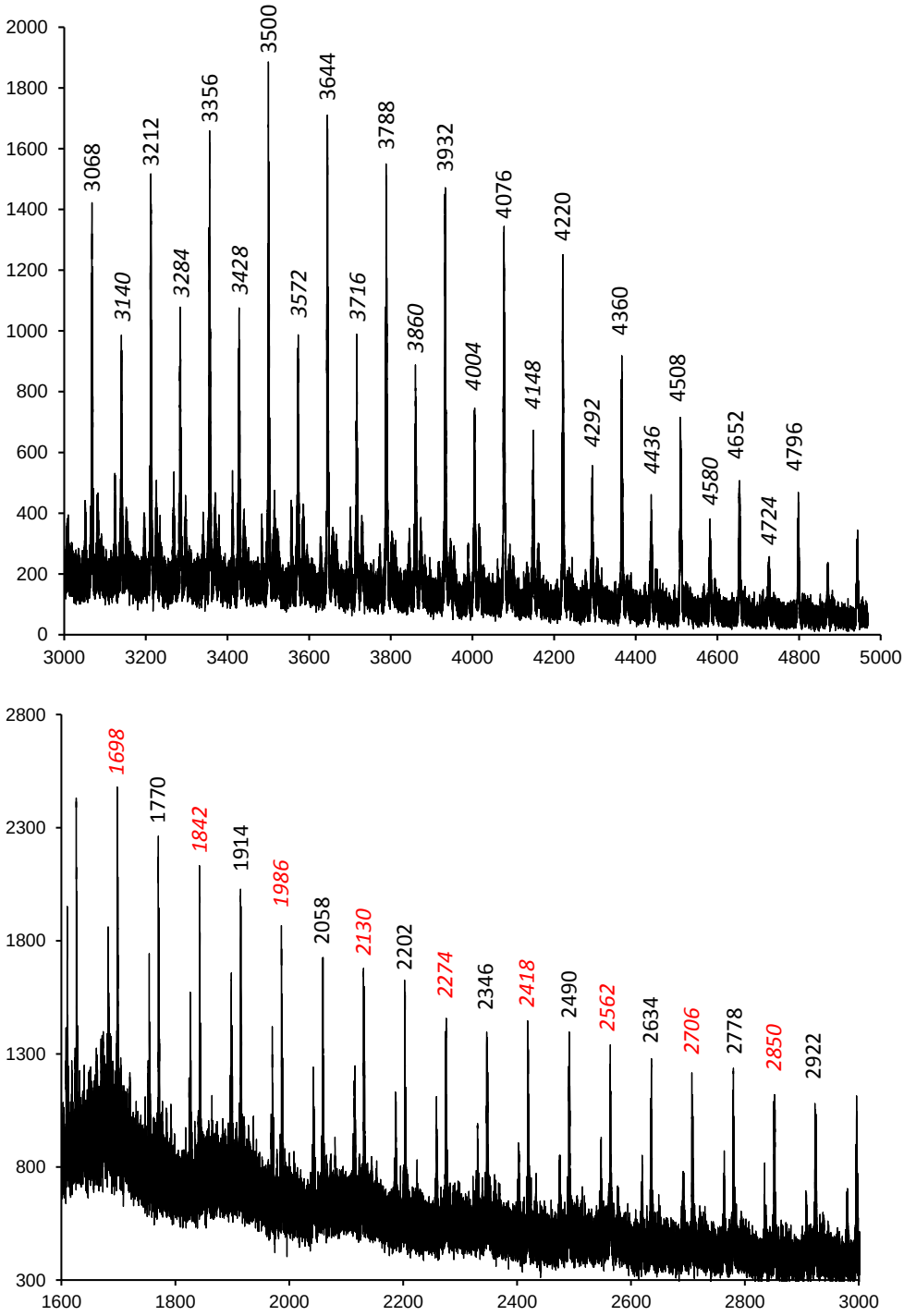

Figure S2. MALDI spectra of polymerizations with **5a**·MeOH, lactide:catalyst = 100. Top: after 2 h, bottom: after 4 h. Numbers in italics correspond to m/z = (n+0.5)·M(lactide), thus polymer resulting from transesterification reactions. Na^+ was added to the matrix and incorporated in the polymer ion. A second small series with Δm/z = –16 was attributed to polymer containing Li^+ instead of Na^+.

Table S2. Comparison of calculated elemental analyses from X-ray structural analysis and combustion analyses after drying. Most data indicate partial or total loss of co-crystallized solvent on drying.

Compound	Formula according to X-ray structure	Proposed formula after drying	Combustion analysis
3a	$C_{35}H_{57}MnN_2O_3 \cdot MeOH$	$C_{35}H_{57}MnN_2O_3 \cdot MeOH$	
	C, 67.47; H, 9.60; N, 4.37	C, 67.47; H, 9.60; N, 4.37	C, 67.00; H, 9.26; N, 4.44
3b		$C_{19}H_{21}Cl_4MnN_2O_3$	
		C, 43.71; H, 4.05; N, 5.37.	C, 43.35; H, 3.67; N, 5.38
4a·MeOH	$C_{36}H_{50}ClMnN_2O_2(MeOH) \cdot H_2O$	$C_{36}H_{50}ClMnN_2O_2(MeOH)_{0.5}$	
	C, 65.04; H, 8.26; N, 4.10	C, 67.53; H, 8.07; N, 4.31.	C, 67.72; H, 8.14; N, 4.29
4b·MeOH	$C_{21}H_{18}Cl_5MnN_2O_3 \cdot 2$ MeOH	$C_{21}H_{18}Cl_5MnN_2O_3$	
	C, 42.99; H, 4.08; N, 4.36	C, 43.60; H, 3.14; N, 4.84	C, 43.49; H, 2.95; N, 4.62
5a·MeOH	$C_{38}H_{57}MnN_2O_4 \cdot MeOH$	$C_{38}H_{57}MnN_2O_4$	
	C, 67.61; H, 8.87; N, 4.04	C, 69.07; H, 8.69; N, 4.24	C, 69.10; H, 8.58; N, 4.34