Supporting Information

Complexities in the Ring-Opening Polymerization of Lactide by Chiral Salen Aluminum Initiators

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Table S1 Crystallographic details for (*R*,*R*-salen)AlOCH$_2$C(*S*)HMeCl and (*S*,*S*-salen)AlOCH$_2$C(*S*)HMeCl.

	(*R*,*R*)-*S*	(*S*,*S*)-*S*
Empirical formula	$C_{39}H_{58}AlClN_2O_3$	$C_{39}H_{58}AlClN_2O_3$
Formular weight	665.30	665.30
Temperature (K)	200	150
Wavelenghth (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
Unit cell dimensions		
a (Å)	14.923(1)	14.927(1)
b (Å)	11.021(1)	10.941(1)
c (Å)	23.440(1)	23.393(1)
ß (^{o})	93.397(1)	93.69(1)
V (Å^3)	3848.6(7)	3812.5(7)
Z	4	4
D_{calc} (mg m^{-3})	1.148	1.159
Absorption coefficient (mm^{-1})	0.159	0.160
F(000)	1440	1440
Crystal size (mm^{-3})	0.38x0.19x0.15	0.38x0.31x0.27
Theta range for data collection (^{o})	1.58-22.99	1.57-25.03
Index ranges	$-16\leq h\leq 16$, $-12\leq k\leq 12$, $-25\leq l\leq 25$	$-17\leq h\leq 17$, $-13\leq k\leq 12$, $-27\leq l\leq 27$
Reflections collected	60183	60079
Independent reflections	10692[R_{int}=0.073]	13387[R_{int}=0.058]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10692/1/886	13387/1/826
Flack parameter	0.00(9)	0.00(8)
Goodness-of-fit on F^2	1.021	1.020
Final R indices [I>2σ(I)]	R_1=0.0508, wR_2=0.1237	R_1=0.0555, wR_2=0.1321
R indices (all data)	R_1=0.0749, wR_2=0.1364	R_1=0.0852, wR_2=0.1467
Largest difference peak and hole (e/Å^3)	0.412 and -0.506	0.565 and -0.371

Table S2 Selected bond distances (Å) and angles (deg) for (*R*,*R*-salen)AlOCH$_2$C(*S*)HMeCl and (*S*,*S*-salen)AlOCH$_2$C(*S*)HMeCl. (The atom numbers are corresponding to Fig. 1)

(*R*,*R*)-*S*		(*S*,*S*)-*S*	
Al1─O1	1.797(3)	Al2─O5	1.798(3)
Al1─O2	1.804(3)	Al2─O6	1.820(3)
Al1─O3	1.746(3)	Al2─O4	1.748(3)
Al1─N1	2.021(3)	Al2─N3	2.004(3)
Al1─N2	1.999(3)	Al2─N4	2.010(3)
O3─C38	1.377(6)	O4─C76	1.401(5)
C38─C39	1.501(7)	C76─C77	1.488(6)
C39─C40	1.497(7)	C77─C78	1.504(7)
Cl1─C39	1.809(5)	Cl2─C77	1.811(4)
O3─Al1─O1	109.7(1)	O4─Al2─O5	111.0(1)
O3─Al1─O2	107.2(1)	O4─Al2─O6	106.5(1)
O3─Al1─N1	96.5(1)	O4─Al2─N3	97.0(1)
O3─Al1─N2	104.3(1)	O4─Al2─N4	103.2(1)
O1─Al1─O2	89.8(1)	O5─Al2─O6	89.8(1)
O1─Al1─N1	88.8(1)	O5─Al2─N3	88.8(1)
O1─Al1─N2	144.9(2)	O5─Al2─N4	144.9(1)
O2─Al1─N2	88.2(1)	O6─Al2─N4	88.2(1)
O2─Al1─N1	155.2(1)	O6─Al2─N3	155.3(1)
N1─Al1─N2	78.9(1)	N3─Al2─N4	79.0(1)
C38─O3─Al1	127.3(3)	C76─O4─Al2	124.4(3)
O3─C38─C39	113.6(4)	O4─C76─C77	113.0(4)
C38─C39─C40	112.6(5)	C76─C77─C78	112.0(4)
C38─C39─Cl1	110.2(3)	C76─C77─Cl2	111.0(3)
C40─C39─Cl1	111.5(4)	C78─C77─Cl2	111.4(3)

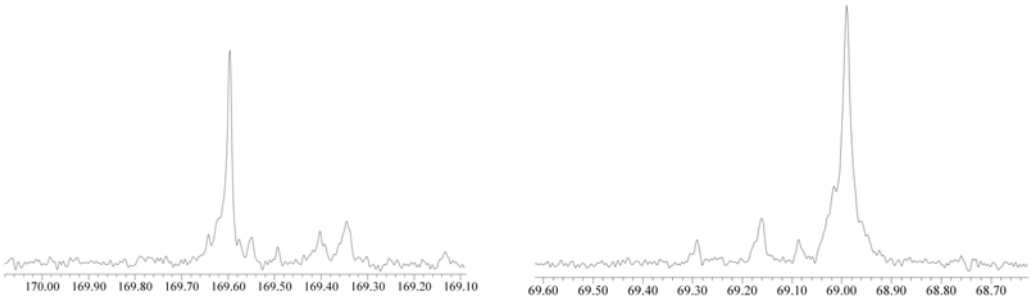

Figure S1. ^{13}C NMR of the PLA formed in the polymerization reaction of 70:30 *L*:*D* lactide by (*S*,*S*)-**2** initiator.

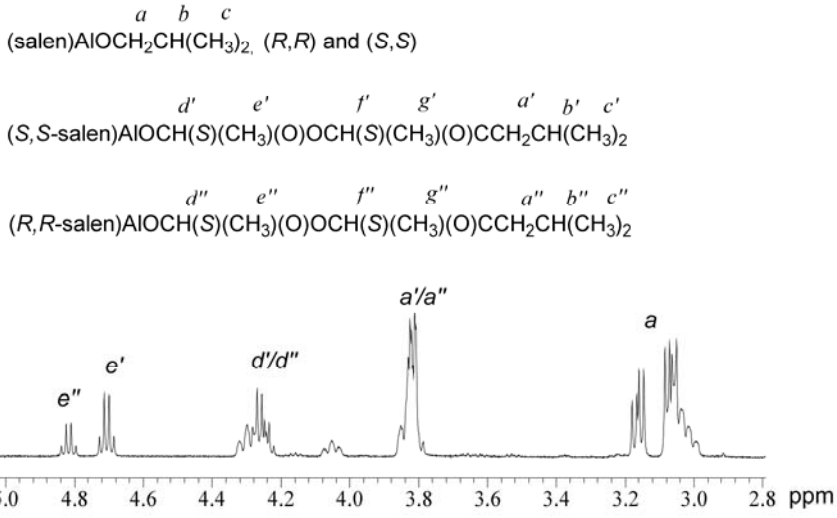

Figure S2. ^{1}H NMR of the reaction mixture of (*rac*-salen)AlOCH$_2$CHMe$_2$ and L-lactide.

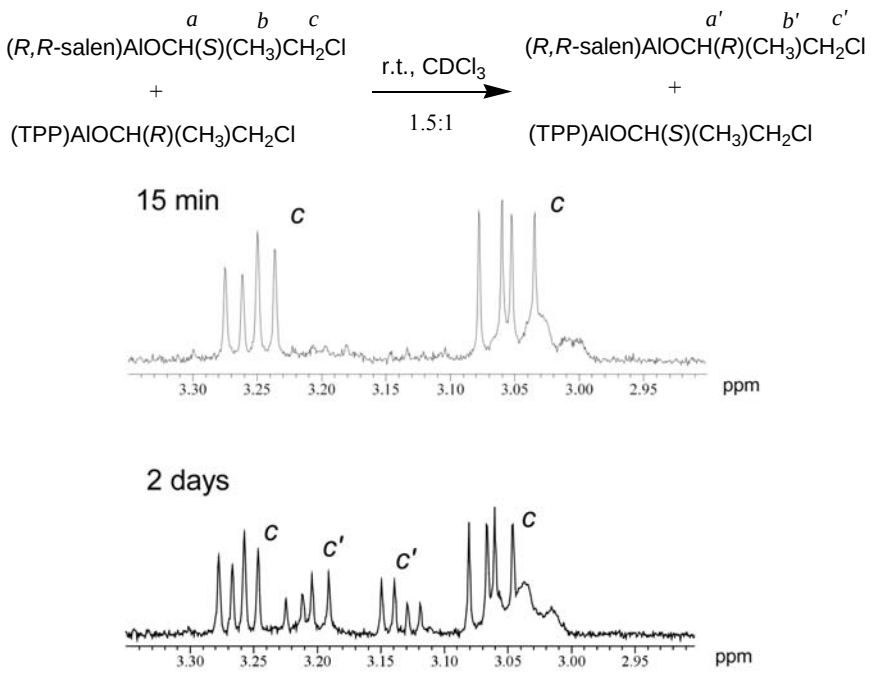

Figure S3. ^{1}H NMR showing the exchange reaction between (TPP)AlOR and (salen)AlOR. (The preparation of complexes and ^{1}H NMR assignments can be found in reference, Chisholm, M. H.; Zhou, Z. *J. Am. Chem. Soc*., **2004**, 126, 11030-11039.)