# A highly active and site selective indium catalyst for lactide polymerization

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### A. Experimental section

General considerations. Unless otherwise indicated, all air- and/or water-sensitive reactions were carried out under dry nitrogen using either an MBraun glove box or standard Schlenk line techniques. NMR spectra were recorded on a Bruker Avance 400 MHz and 600 MHz spectrometer. <sup>1</sup>H NMR chemical shifts are reported in ppm versus residual protons in deuterated chloroform;  $\delta$  7.27 CDCl<sub>3</sub>. <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are reported in ppm versus residual  ${}^{13}C$  in the solvent;  $\delta$  77.2 CDCl<sub>3</sub>. Diffraction measurements for X-ray crystallography were made on a Bruker X8 APEX II diffraction with graphite monochromated Mo-Ka radiation. The structures (Table S2) were solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software of Bruker-AXS. Unless specified, all non-hydrogens were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined. Elemental C, H, N analysis was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of unknown samples was determined by using a calibration factor. The calibration factor was determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition. Molecular weights were determined by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Water 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm) HR5E, HR4 and HR2, Water 2410 differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min<sup>-1</sup> was used and samples were dissolved in THF (2 mg mL<sup>-1</sup>). Narrow molecular weight polystyrene standards were used for calibration purposes. The molar mass was calculated with ASTRA© 5 software using the Mark-Houwink parameters<sup>1</sup> ( $K=1.832 \times 10^4$  dL/g, a= 0.69), laser light scattering detector data, and concentration detector. Distribution and moment procedures of ASTRA© 5 was used calculate molar mass moments M<sub>n</sub> M<sub>w</sub> and M<sub>z</sub>.

*Materials*. Solvents (Tetrahydrofuran, toluene, hexanes and diethyl ether) were collected from an MBraun Solvent Purification System whose columns are packed with activated alumina.  $CH_2Cl_2$  was purified followed by the literature procedures to remove any impurities, dried over  $CaH_2$  and degassed through a series of freeze-pump-thaw cycles.  $CD_2Cl_2$ ,  $CDCl_3$  and cyclohexane were dried over  $CaH_2$ , and degassed through a series of freeze-pump-thaw cycles. *rac*-LA was a gift from PURAC America Inc. and recrystallized twice from hot dried toluene. 1,3,5-trimethoxybenzene was purchased from Aldrich and used as received. (rac)- and (*R*,*R*)-H<sub>2</sub>(ONNO) and KCH<sub>2</sub>Ph were synthesized according to previously reported procedures.<sup>2, 3</sup>

### (*R*,*R*)-(ONNO)InCl complex (*R*,*R*-1)

A solution of (R,R)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine  $(R,R-H_2(ONNO))$ (0.725 g, 1.33 mmol) in toluene was added to a stirring slurry of KCH<sub>2</sub>Ph (0.345 g, 2.65 mmol) in toluene (25 mL, room temperature). The resulting mixture was stirred at room temperature for 24 h. The solvent was subsequently evaporated under vacuum and the resulting solid was washed with cold hexanes and dried under vacuum to afford a yellow solid (0.781 g). This was added as a solution in THF to a stirring slurry of InCl<sub>3</sub> (0.278 g, 1.26 mmol) in THF (total volume 25 mL, room temperature). The resulting mixture was stirred at room temperature for 16 h. The mixture was filtered and the solution was dried under vacuum to afford a solid which was washed with cold hexanes and dried to yield (*R*,*R*)-1 as a yellow solid (0.763 g, 83%). <sup>1</sup>H NMR (400.19 MHz, CDCl<sub>3</sub>):  $\delta$  8.42 (1H, s, N=CH), 8.21 (1H, s, N=CH), 7.51-7.50 (2H, m, ArH), 6.99 (1H, s, ArH) 6.95 (1H, s, ArH) 3.71-3.64(1H, m, -CH- of DACH) 3.253.17(1H, m, -C*H*- of DACH), 2.68-2.64(1H, m, -C*H*<sub>2</sub>- of DACH), 2.48-24.5 (1H, m, -C*H*<sub>2</sub>- of DACH), 2.11-2.08 (2H, m, -C*H*<sub>2</sub>- of DACH), 1.53-1.43 (4H, m, -C*H*<sub>2</sub>- of DACH) 1.50 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>), 1.49 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>), 1.31 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>), 1.30 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>):  $\delta$  170.99, 167.75, 167.03, 142.64, 142.57, 137.73, 137.62, 130.62, 129.49, 117.50, 117.30, 65.05, 63.55, 35.68, 33.97, 31.35, 29.51, 28.63, 26.86, 24.21, 23.70. Anal. calcd (found) for C<sub>36</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>InCl: C 62.21 (62.36), H 7.54 (7.45), N 4.03 (4.04).

## (rac)-(ONNO)InCl complex (rac-1)

The racemic complex was prepared and purified in an analogous manner to (R,R)-1 from (rac)-H<sub>2</sub>(ONNO) (1.05 g, 1.92 mmol) to yield (rac)-1 (1.134 g, yield 85 %) Suitable crystals for X-ray diffraction were grown by slow diffusion Yellow coloured X-ray quality crystals were obtained by crystalizing in diethyl ether for four days at -30 °C. The complex has an identical NMR signature to that of (*R*,*R*)-1. Anal. calcd (found) for C<sub>36</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>InCl: C 62.21 (62.19), H 7.54 (7.50), N 4.03 (4.06).

## (*R*,*R*)-(ONNO)InOEt(*R*,*R*-2)

Complex (*R*,*R*)-1(0.763 g, 1.10 mmol) was dissolved in toluene and added to a slurry of NaOEt (0.075 g, 1.10 mmol) in toluene. The mixture was stirred at room temperature for 48 h. The resulting mixture was filtered and the solution evaporated under vacuum to afford a solid which was washed with cold hexanes and dried to obtain (*R*,*R*)-2 as a yellow solid (0.639 g, 82%). <sup>1</sup>H NMR (400.19 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (1H, s, N=C*H*), 8.04 (1H, s, N=C*H*), 7.40-7.39 (1H, s, Ar*H*), 7.38-7.37 (1H, s, Ar*H*), 6.91-6.90 (1H, s, Ar*H*), 6.77-6.76 (1H, s, Ar*H*), 3.90-3.86 (1H, m, -C*H*- of DACH), 3.61-3.40 (2H, m, -C*H*<sub>2</sub>- of  $-OCH_2CH_3$ ), 3.76-3.72(1H, m, -C*H*- of DACH), 2.31-2.26 (1H, m, -C*H*<sub>2</sub>- of DACH), 2.07-2.03 (1H, m, -C*H*<sub>2</sub>- of DACH), 2.00-1.94 (1H, m, -C*H*<sub>2</sub>- of DACH), 1.85-1.82 (1H, m, -C*H*<sub>2</sub>- of DACH), 1.63-1.16 (4H, m, -*CH*<sub>2</sub>- of DACH) 1.49 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>), 1.30 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>), 1.29 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>), 1.27 (9H, s, Ar-C(*CH*<sub>3</sub>)<sub>3</sub>), 1.07 (3H, t, -*CH*<sub>3</sub> of  $-OCH_2CH_3$ ) <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>):  $\delta$  170.53, 168.55, 168.23, 162.72, 141.99, 141.86, 135.18, 134.64, 129.27, 128.98, 128.26, 118.06, 117.52, 68.47, 62.77, 59.05, 35.78, 35.53, 33.83, 31.38, 30.67, 29.95, 29.69, 27.26, 24.78, 24.42, 20.88. Anal. calcd (found) for C<sub>38</sub>H<sub>57</sub>N<sub>2</sub>O<sub>3</sub>In: C 64.77 (64.92), H 8.15 (7.98), N 3.98 (4.09).

## rac-(ONNO)InOEt (rac-2)

The racemic complex was prepared and purified in an analogous manner (R,R)-**2** from rac-**1** (1.134 g, 1.63 mmol) to yield rac-**2** (0.932g, yield 81% with respect to rac-**1**) Suitable crystals for X-ray diffraction were grown by crystalizing in cyclohexane for three days at -30 °C. The complex has an identical NMR signature to that of (R,R)-**2**. Anal. calcd (found) for C<sub>38</sub>H<sub>57</sub>N<sub>2</sub>O<sub>3</sub>In: C 64.77 (64.85), H 8.15 (8.08), N 3.98 (4.02).

#### ROP of lactide: In situ studies

All samples for NMR scale polymerization were prepared in Teflon sealed NMR tubes under an N<sub>2</sub> atmosphere. The NMR tube was charged with a stock solution of catalyst ([(ONNO)In(OEt)]<sub>2</sub>) in CD<sub>2</sub>Cl<sub>2</sub> (0.25 mL, 0.0011 mmol) and frozen. Then a 0.25 mL of CD<sub>2</sub>Cl<sub>2</sub> was added and frozen to create a buffer between the catalyst and the lactide monomer. Finally the stock solution with rac-lactide (0.50 mL, 0.45 mmol) and the internal standard 1,3,5-trimethoxybenzene (5 mg, 0.03 mmol per 0.50 mL) was added and frozen. The sealed and evacuated NMR tube was immediately taken to the NMR spectrometer (400 MHz Avance Bruker Spectrometer) to monitor the polymerization at 25 °C.

## ROP of lactide: Large scale samples for GPC and <sup>1</sup>H{<sup>1</sup>H} NMR studies

In a 20 mL scintillation vial, rac-2 (5 mg, 0.035 mmol) was dissolved in 1 mL of  $CH_2Cl_2$  and *rac*-lactide (0.205 g, 1.42 mmol) in 1.5 mL of  $CH_2Cl_2$  was added and the total volume made to 3 mL. The reaction was allowed to proceed for 4 h after which time the reaction was quenched with a few drops of HCl in ether. A 0.5 mL sample of the reaction mixture was evaporated under vacuum for 3 hours and was dissolved in  $CDCl_3$ . <sup>1</sup>H{<sup>1</sup>H} NMR spectrum of the methine region was obtained on a Bruker 600 MHz spectrometer. A analogous procedure was followed for the polymerization of rac-lactide with (*R*,*R*)-2. Thereafter the mixture was evaporated under vacuum and the polymer was isolated by washing 3 times with cold methanol. The isolated polymer was subsequently dried under vacuum for 4 h prior to GPC analysis.

#### **ROP** of lactide: In the melt polymerization

In a Schlenk flask, (R,R)-2 (5 mg, 0.035 mmol) and *rac*-lactide (0.202 g, 1.40 mmol) were added and mixed to homogenize the mixture. This was subsequently heated to 130 °C, to obtain slurry which allowed to react for 10 minutes. The reaction was subsequently quenched with a few drops of HCl in ether.

#### Determination of melting point $(T_m)$ and $(T_g)$ values

The  $T_m$  and  $T_g$  values of the polymers were obtained using a TA differential scanning calorimeter (DSC) Q 1000. Approximately 2–3 mg of the samples were weighed and sealed in an aluminum pan. The experiments were carried out under a nitrogen atmosphere. The samples were heated at a rate of 10 °C/min from 40 to 200 °C and then held isothermally for 5 min to destroy any residual nuclei before cooling at 5 °C /min. The transition and melting temperatures were obtained from a second heating sequence, performed at 10 °C /min.

**B.** Characterization of complexes in solution



Figure S1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of rac-(ONNO)InCl (rac-1).



Figure S2. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C) spectrum of rac-(ONNO)InCl (rac-1).



Figure S3. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of (R,R)-(ONNO)InCl((R,R)-1)



Figure S4. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C) spectrum of (R,R)-(ONNO)InCl ((R,R)-1).



Figure S5. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of rac-(ONNO)InOEt (rac-2).



Figure S6.  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>, 25 °C) spectrum of rac-(ONNO)InOEt (rac-2).



Figure S7. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of (R,R)-(ONNO)InOEt ((R,R)-2).



Figure S8. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C) spectrum of (R,R)-(ONNO)InOEt ((R,R)-2).



#### Pulsed gradient spin-echo (PGSE) spectroscopy data of the pro-ligand and complexes

**Figure S9.** Plot of  $\ln(I/I_0)$  vs.  $\gamma^2 \delta^2 G^2 [\Delta - (\delta/3)] \times 10^{-10}$  (m<sup>2</sup> s) from PGSE experiments for the internal standard tetrakis(trimethylsilyl)silane (TMSS) in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C. The slopes from the trend line for each trial were averaged to obtain the translational diffusion coefficient (D<sub>t</sub>). I = observed spin echo intensity, I<sub>0</sub> = intensity in the absence of a gradient, G = gradient strength,  $\gamma$  = gyromagnetic ratio,  $\delta$  = length of gradient pulse,  $\Delta$  = delay between gradient midpoints.



**Figure S10.** Plot of  $\ln(I/I_0)$  vs.  $\gamma^2 \delta^2 G^2 [\Delta - (\delta/3)] \times 10^{-10}$  (m<sup>2</sup> s) from PGSE experiment for rac-(ONNO)H<sub>2</sub> proligand (2 mM) in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C. Intensities of four well separated peaks were individually plotted to obtain the above trend lines. The slopes from the trend line for each peak were averaged to obtain the translational diffusion coefficient (D<sub>t</sub>). I = observed spin echo intensity, I<sub>0</sub> = intensity in the absence of a gradient, G = gradient strength,  $\gamma$  = gyromagnetic ratio,  $\delta$  = length of gradient pulse,  $\Delta$  = delay between gradient midpoints.



**Figure S11.** Plot of  $\ln(I/I_0)$  vs.  $\gamma^2 \delta^2 G^2 [\Delta - (\delta/3)] \times 10^{-10}$  (m<sup>2</sup> s) from PGSE experiment for rac-1(2 mM) in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C. Intensities of four well separated peaks were individually plotted to obtain the above trend lines. The slopes from the trend line for each peak were averaged to obtain the translational diffusion coefficient (D<sub>t</sub>). I = observed spin echo intensity, I<sub>0</sub> = intensity in the absence of a gradient, G = gradient strength,  $\gamma$  = gyromagnetic ratio,  $\delta$  = length of gradient pulse,  $\Delta$  = delay between gradient midpoints.



**Figure S12.** Plot of  $\ln(I/I_0)$  vs.  $\gamma^2 \delta^2 G^2[\Delta - (\delta/3)] \times 10^{-10}$  (m<sup>2</sup> s) from PGSE experiment for rac-2 (2 mM) in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C. Intensities of four well separated peaks were individually plotted to obtain the above trend lines. The slopes from the trend line for each peak were averaged to obtain the translational diffusion coefficient (D<sub>t</sub>). I = observed spin echo intensity, I<sub>0</sub> = intensity in the absence of a gradient, G = gradient strength,  $\gamma$  = gyromagnetic ratio,  $\delta$  = length of gradient pulse,  $\Delta$  = delay between gradient midpoints.

	$D_t(\times 10^{-10}\mathrm{m}^2\mathrm{s}^{-2})$	$r_{\rm H}({ m \hat{A}})$	$r_{X-ray}(\hat{A})$
H <sub>2</sub> (ONNO)	9.5(0.3)	5.6(0.2)	5.9
(ONNO)InCl	9.1(0.2)	6.0(0.1)	5.9
$(ONNO)In(\mu-0Et)_2$	6.5(0.5)	7.6(0.6)	6.6

**Table S1:** Translational diffusion coefficients ( $D_t$ ), hydrodynamic radii ( $r_H$ ), X-ray crystallographic radii ( $r_{x-ray}$ ) for the ligand and complexes. Hydrodynamic Radii ( $r_H$ ) were calculated from translational diffusion coefficients ( $D_t$ ) obtained from PGSE. X-ray crystallographic data of ligand,<sup>4</sup> rac-1 and rac-2 was used to calculate  $r_{x-ray}$  using the equation  $r_{x-ray} = ((3/4)\pi V)^{\frac{1}{3}}$  where V is a volume of a unit cell.

The translational diffusion coefficients  $(D_t)$  were calculated from the plots of  $\ln(I/I_0)$  vs.  $\gamma^2 \delta^2 G^2[\Delta - (\delta/3)] \times 10^{-10}$  (m<sup>2</sup> s) as indicated above. A modified Stokes-Einstein equation (1) was used to calculate the  $c^{sa} r_H^{sa}$  value.<sup>5</sup> Equation **2** was used to determine  $f_s$ . A plot of  $c^{sa} r_H^{sa}$  vs.  $r_H^{sa}$  based equation **3** reported by Chen *et al.* was used to  $r_H^{sa \cdot 6}$ .

$$c^{sa}r_{H}^{sa} = \frac{D_{t}^{st}c^{st}f_{s}^{st}r_{H}^{st}}{D_{t}^{sa}f_{s}^{sa}}$$
(1)

 $D_t^{st}$  = translational diffusion coefficient of internal standard (TMSS,  $D_t^{st} \approx 14.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)

 $c^{st}$  = internal standard size correction factor (TMSS,  $c^{st}$  = 5.1)

 $f_s^{st}$  = internal standard size and shape correction factor (TMSS,  $f_s^{st}$  = 1)

- $r_{H}^{st}$  = internal standard hydrodynamic radius (TMSS, 4.51 Å)
- $D_t^{sa}$  = translational diffusion coefficient of sample (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)
- $c^{sa}$  = sample size correction factor
- $f_s^{sa}$  = sample size and shape correction factor calculated from eq (2)
- $r_H^{sa}$  = sample hydrodynamic radius

$$f_s = \frac{\sqrt{1 - \left(\frac{b}{a}\right)^2}}{\left(\frac{b}{a}\right)^2 \ln \frac{1 + \sqrt{1 - \left(\frac{b}{a}\right)^2}}{\left(\frac{b}{a}\right)}}$$
(2)

a = major semiaxes of a prolate ellipsoid estimated from X-ray crystal structure b = minor semiaxes of a prolate ellipsoid estimated from X-ray crystal structure

$$cr_{H} = \frac{6r_{H}}{1 + 0.695 \left(\frac{r_{solv}}{r_{H}}\right)^{2.234}}$$
(3)

 $r_{solv}$  = hydrodynamic radius of the solvent (CH<sub>2</sub>Cl<sub>2</sub> = 2.49 Å)

 $r_H$  = hydrodynamic radius of sample

#### C. Characterization of complexes in the solid state



**Figure S13.** Molecular structures of rac-1 (left) and rac-2 (right) depicted with ellipsoids at 50% probability (H atoms and solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (°) for rac-1: In1-Cl1 2.371(2), In1-O1 2.050(6), In1-O2 2.044(6), In1-N1 2.171(7), In1-N2 2.207(7), O1-In1-Cl1 116.72(19), O2-In1-Cl1 106.86(19), N1-In1-Cl1 101.2(2), N2-In1-Cl1 113.40(19), O2-In1-O1 90.0(2), O2-In1-N1 150.9(3), O1-In1-N1 84.3(3), O2-In1-N2 85.8(2), O1-In1-N2 128.6(3), N1-In1-N2 75.8(3). Selected bond lengths (Å) and angles (°) for rac-2: O1-In1 2.080(5), O2-In1 2.128(5), O3-In1 2.121(5), N1-In1 2.259(6), N2-In1 2.206(6), O1-In1-O3 109.79(19), O1-In1-O2 88.6(2), O3-In1-O2 93.08(19), O1-In1-N2 151.6(2), O3-In1-N2 97.1(2), O2-In1-N2 80.9(2), O1-In1-N1 84.8(2), O3-In1-N1 156.4(2), O2-In1-N1 106.1(2), N2-In1-N1 73.1(2).



Figure S14. Atom connectivity for (R, R/S, S) dimer of complex rac-2.

	rac-1	rac <b>-2</b>		
empirical formula	C <sub>36</sub> H <sub>52</sub> N <sub>2</sub> O <sub>2</sub> InCl	C <sub>100</sub> H <sub>162</sub> N <sub>4</sub> O <sub>6</sub> In <sub>2</sub>		
Fw	695.07	1745.98		
T (K)	90	100		
a (Å)	12.805(3)	29.058(1)		
b (Å)	26.307(6)	17.6316(9)		
c (Å)	10.923(3)	20.292(1)		
a (deg)	90	90		
b (deg)	108.242(4)	110.009(3)		
g (deg)	90	90		
volume (Å <sup>3</sup> )	3495(2)	9768.8(9)		
Ζ	4	8		
crystal system	monoclinic	Monoclinic		
space group	$P 2_1/c$ (#14)	C 2/c (#15)		
$d_{calc}$ (g/cm <sup>3</sup> )	1.321	1.187		
$\mu$ (MoK $\alpha$ ) (cm <sup>-1</sup> )	7.85	5.23		
2qmax (deg)	45.1	45		
absorption correction $(T_{min}, T_{max})$	0.498, 0.984	0.374, 0.990		
total no. of reflections	23431	68784		
no. of indep reflections (R <sub>int</sub> )	4571 (0.102)	6435, (0.141)		
residuals (refined on $F^2$ , all data):				
$R_1; wR_2$	0.094; 0.161	0.094; 0.180		
GOF	1.03	1.11		
no. observations $[I > 2s(I)]$	3314	4925		
residuals (refined on $F^2$ ): $R_1^a$ ; $wR_2^b$	0.059; 0.141	0.063; 0.146		
<sup>a</sup> R1 = $\Sigma$   Fo  -  Fc   / $\Sigma$  Fo ; <sup>b</sup> wR <sub>2</sub> = [ $\Sigma$ (w(F <sub>o</sub> <sup>2</sup> - F <sub>c</sub> <sup>2</sup> ) <sup>2</sup> )/ $\Sigma$ w(F <sub>o</sub> <sup>2</sup> ) <sup>2</sup> ] <sup>1/2</sup> .				

 Table S2. Selected crystallographic parameters

D. ROP of LA with rac- or (R,R)-2

## a) ROP plots of 200 equiv of [LA] vs. [initiator (R,R)-2]



**Figure S15.** The ROP plots of 200 equiv of [LA] vs. [initiator]. All reactions were carried out in  $CD_2Cl_2$  at 25 °C and followed to 90% conversion by <sup>1</sup>H NMR spectroscopy. [catalyst] = 0.0011 M, [LA] = 0.45 M. The value of  $k_{obs}$  was determined from the slope of the plots of ln([LA]/[TMB]) vs. time.

b) ROP plots of 200 equiv of [LA] vs. [initiator rac-2]



**Figure S16.** The ROP plots of 200 equiv of [LA] vs. [initiator]. All reactions were carried out in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C and followed to 90% conversion by <sup>1</sup>H NMR spectroscopy. [[(ONNO)In(OEt)]<sub>2</sub>] = 0.0011 M, [LA] = 0.45 M. The value of  $k_{obs}$  was determined from the slope of the plots of ln([LA]/[TMB]) vs. time

# E. <sup>1</sup>H{<sup>1</sup>H} NMR analysis of polymers

All homonuclear decoupled <sup>1</sup>H NMR spectra were performed on a Bruker Avance 600 MHz spectrometer with a cryoprobe. The  $P_m$  and  $P_r$  values were calculated from the following formulas which are based on tetrad probabilities in the polymerization of *rac*-lactide as calculated from Bernoullian statistics.<sup>7</sup> The assignment for each tetrad's chemical shift is based on the generally accepted values.<sup>8</sup>



**Figure S17.** <sup>1</sup>H{<sup>1</sup>H} NMR spectra (CDCl<sub>3</sub>, 25 °C) of methine regions for ROP of *rac*-LA with (left) *rac*-**2** at 97% conversion and (right) (R,R)-**2** at 96% conversion at 25 °C in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S18.** <sup>1</sup>H{<sup>1</sup>H} NMR spectra of (CDCl<sub>3</sub>, 25 °C) the methine region for ROP of *rac*-LA with (*R*,*R*)-2 after (a) 11% (b) 24% (c) 37% (d) 47% (e) 60% (f) 81% (g) 97% conversion at 25 °C in CH<sub>2</sub>Cl<sub>2</sub>.

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**Figure S19.** <sup>1</sup>H{<sup>1</sup>H} NMR spectra of (CDCl<sub>3</sub>, 25 °C) the methine region for ROP of *rac*-LA with rac-**2** after (a) 11% (b) 24% (c) 37% (d) 47% (e) 60% (f) 81% (g) 97% conversion at 25 °C in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S20.** <sup>1</sup>H{<sup>1</sup>H} NMR spectra of (CDCl<sub>3</sub>, 25 °C) the methine region for ROP of *rac*-LA with rac-2 after >98% conversion at 25 °C in a) THF b) Benzene c) Toluene.

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#### F. DSC measurement of polymers



**Figure S21.** Heat flow vs. temperature curve for PLA formed polymerizing *rac*-LA with (*R*,*R*)-2 at a monomer : initiator ratio of 500 at 25 °C in  $CH_2Cl_2$  ( $P_m = 0.77$ ). The curve shows a glass transition temperature of 59 °C and a melting point of 140 °C.

#### G. Plots of P<sub>m</sub> vs. conversion



**Figure S22.** Plot of  $P_m$  vs. conversion for polymerization of rac-LA with a: (left) (*R*,*R*)-2; b: (right) (rac)-2. Depicted with 5% error bars.

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