# Supporting Information

## Polymer-supported metal catalysts for the heterogeneous

## polymerisation of lactones

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### **1.** Materials

Reagents and solvents were purchased from commercial suppliers and used without further modification unless specified. *L*-LA was recrystallised in dry toluene three times and stored under argon prior to use. 4-methylbenzyl alcohol was recrystallised in diethyl ether and stored under argon. All dry solvents were used directly from an MBraun solvent purification system and dried further over molecular sieves (3 Å).

<sup>1</sup>H NMR spectra were collected using a Bruker Avance 400 or 500 Hz spectrometer. Chemical shifts ( $\delta$ ) are expressed in parts per million (ppm) and relative to residual protonated solvent. Coupling constants are expressed in Hertz (Hz). Notation of signals are as follows: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Attenuated total reflectance infra-red (ATR-IR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. CHN microanalysis was carried out at the Science Centre at the London Metropolitan University by Mr. Stephen Boyer. Inductively coupled plasma-Optical Emission Spectrometry (ICP-OES) was conducted by Exeter Analytical.

Scanning Electron microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis were performed on a JEOL JSM-6480LV SEM spectrometer, with an Oxford INCA X-ray analyser. A low vacuum mode was applied to the samples for EDX, using a back scattered electron (BSE) detector. The samples were gold coated (70 nm) prior to SEM imaging in high vacuum mode, using a secondary electron detector.

Thermogravimetric analysis (TGA) was performed on a Setaram Setys Evolution TGA 16/18 between 30 and 600 °C (10 °C/min) under a flow of argon.

Differential Scanning Calorimetry (DSC) analysis was conducted using a TA Instruments DSC Q20 instrument. After holding at 40 °C, the polymer sample was heated to 200 °C at a heating rate of 10 °C/min. The sample was held at 200 °C for 1 minute then cooled to 40 °C once more at 10 °C/min, where it was held for a further minute. A second heating

cycle was performed, heating the sample at 5 °C/min to 200 °C. The  $T_m$  value was obtained from the second cycle.

Size exclusion chromatography (SEC) data was collected using an Agilent 1260 Infinity Gel Permeation Chromatography (GPC) instrument equipped with PLgel 5  $\mu$ m MIXED-D column (300 × 7.5 mm) at 1  $\mu$ l min<sup>-1</sup> flow rate at 35 °C, using the desired sample dissolved in THF (1 mg ml<sup>-1</sup>).  $M_n$  and  $M_w$  data was calculated using refractive index (RI) methods against polystyrene standards, and the values were corrected by multiplying by 0.58 and 0.56 to account for PLA and PCL, respectively.<sup>1,2</sup> Molecular weights for PDL were reported relative to polystyrene standards. Matrix-assisted laser-desorption time-of-flight (MALDI-ToF) analysis was performed using a Bruker Autoflex speed instrument using a DCTB matrix (trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile) and NaTFA to ionise the sample. Attenuated-Total-Reflection-Fourier-Transform-Infra-Red (ATR-FT-IR) monitored ROP of *L*-LA with immobilised catalysts was carried out using a model IN350-T IR probe, connected to a Bruker Matrix-MF spectrometer. Data was processed using Opus 7.5 software (Bruker), with further processing performed in Microsoft Excel.

### 2. Synthesis of complexes



#### 2.1 Synthesis of immobilised metal Schiff-base complexes

Scheme S1. Synthetic route to the immobilised ligands on (chloromethyl)polystyrene (PS) resin.

Following the literature procedures: In a typical PS functionalisation, a commercially available (chloromethyl)polystyrene resin, crosslinked with 5.5% DVB (divinylbenzene) (Merrifield's resin, 5.5 mmol  $g^{-1}$ , 11 mmol), and NaHCO<sub>3</sub> (11 mmol) were stirred in DMSO (20 mL) at 155 °C for 6 hours. The solvent was removed by vacuum filtration, and light-yellow PS-CHO beads were washed with DMSO until the filtrate ran clear. The PS-CHO beads were dried *in vacuo* at 100 °C for two hours.

PS-CH<sub>2</sub>Cl starting material IR (ATR, cm<sup>-1</sup>) 2919 *v*(C-H), 1604 *v*(C=C),1264 *v*(C-Cl), 825 *v*(C=C), 673 *v*(C-Cl).

PS-CHO IR (ATR, cm<sup>-1</sup>) 2918 v(C-H), 2746 v(C-H, aldehyde), 1697 v(C=O), 826 v(C=C). PS-CHO (29.02 g/mol): calcd. C 83.10, H 6.99, N 0.00, O 9.91; found C 56.46, H 6.16, N 0.00. Loading: calcd. 6.20 mmol/g; found 6.20 mmol/g. 100% yield.

PS-CHO (5.5 mmol) was then stirred with the appropriate amine (5.5 mmol) in ethanol at reflux for 6 hours, to produce ligand **PS-HL<sup>H</sup>**. The orange product was collected by vacuum filtration, washed with ethanol until the filtrate ran clear, then dried *in vacuo* at 50 °C for two hours.

**PS-HL<sup>H</sup>** IR (ATR, cm<sup>-1</sup>) 3381 v(O-H), 2920 v(C-H), 1698 v(C=O), 1623 v(C=N), 1598 v(C=C), 1285 vC-N), 1247 v(C-O), 827 v(C=C). PS-C<sub>7</sub>H<sub>6</sub>NO (120.13 g/mol): calcd. C 81.65, H 6.47, N 5.55, O 6.33; found C 76.36, H 6.43, N 2.28. Loading: calcd. 3.96 mmol/g; found 4.24 mmol/g. >100% yield (note that yields greater than 100% indicate residual salts or impurities on the catalyst surface).

**PS-HL**<sup>tBu</sup> IR (ATR, cm<sup>-1</sup>) 3675 v(O-H), 2952 v(C-H), 1699 v(C=O), 1624 v(C=N), 1605 v(C=C), 1267 v(C-N), 1247 v (C-O), 825 v(C=C). PS-C<sub>15</sub>H<sub>22</sub>NO (232.37 g/mol): calcd. C 84.74, H 8.68, N 3.07, O 3.51; found C 80.70, H 7.23, N 2.63. Loading: calcd. 6.20 mmol/g; found 1.88 mmol/g. 77% yield.

**PS-HL**<sup>CI</sup> IR (ATR, cm<sup>-1</sup>) 3378 v (O-H), 2921 v(C-H), 1698 v(C=O), 1604 v(C=N), 1573 v(C=C), 1269 v(C-N), 1269 v(C-O), 1168 v(C-O, 3° alcohol), 842 (C-Cl), 827 v(C=C). PS-C<sub>7</sub>H<sub>4</sub>Cl<sub>2</sub>NO (189.01 g/mol): calcd. C 64.13, H 4.45, N 4.36, O 4.97, Cl 22.09; found C 74.29, H 6.30, N 1.16. Loading: calcd. 3.11 mmol/g; found 0.84 mmol/g. 16% yield.



**Scheme S2.** Synthetic route to the immobilised complexes on (chloromethyl)polystyrene (PS) resin.

**PS-HL<sup>H</sup>** (1.7 mmol) was stirred with a metal carboxylate source (1.7 mmol) in methanol (15 mL) under reflux for 6 hours. The complex was collected by vacuum filtration and washed with methanol until the filtrate ran clear, then dried *in vacuo* at 50 °C for two hours.

**PS-L<sup>H</sup>ZnOAc** IR (ATR, cm<sup>-1</sup>) 2920 *v*(C-H), 1698 *v*(C=O), 1604 *v*(br, C=N), 1574 *v*(complexed COO<sup>-</sup>), 1453 *v*(C-H, methyl), 1282 *v*(C-N), 1259 *v*(C-O). PS-C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub>Zn (243.56 g/mol): calcd. C 59.80, H 4.75, N 3.90, O 13.35, Zn 18.21; found C 68.14, H 6.37, N 1.36. Loading: calcd. 2.78 mmol/g; found 1.68 mmol/g. 50% yield.

**PS-L<sup>H</sup>MgOAc** IR (ATR, cm<sup>-1</sup>) 2922 v(C-H), 1698 v(C=O), 1604 v(C=N), 1576 v(complexed COO<sup>-</sup>), 1286 v(C-N), 1248 v(C-O). PS-C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub>Mg (202. 46 g/mol): calcd. C 68.75, H 5.48, N 4.18, O 14.33, Mg 7.26; found C 77.37, H 6.35, N 1.54. Loading: calcd. 2.78 mmol/g; found 0.99 mmol/g. 27% yield.

**PS-L<sup>H</sup>CuOAc** IR (ATR, cm<sup>-1</sup>) 2920 v(C-H), 1697 v(C=O), 1603 v(br, C=N), 1574 v(complexed COO<sup>-</sup>), 1453 v(C-H, methyl), 1286 v(C-N), 1245 v(C-O). PS-C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub>Cu

(241.70 g/mol): calcd. C 61.54, H 4.91, N 3.75, O 12.82, Cu 16.99; found C 71.34, H 5.73, N 1.41. Loading: calcd. 2.78 mmol/g; found 1.26 mmol/g. 38% yield.

**PS-L<sup>H</sup>NiOAc** IR (ATR, cm<sup>-1</sup>) 2919 *v*(C-H), 2158-1974 *v*(C-H), 1698 *v*(C =O), 1604 *v*(C=N), 1572 *v*(complexed COO<sup>-</sup>), 1451 *v*(C-H, methyl), 1289 *v*(C-N), 1251 *v*(C-O). PS-C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub>Ni (236.84 g/mol): calcd. C 62.35, H 4.97, N 3.79, O 12.99, Ni 15.90; found C 72.32, H 5.80, N 1.41. Loading: calcd. 2.71 mmol/g; found 1.21 mmol/g. 36% yield.

**PS-L<sup>H</sup>SnOAc** IR (ATR, cm<sup>-1</sup>) 2921 *v*(C-H), 1698 *v*(C=O), 1603 *v*(C=N), 1574 *v*(complexed COO<sup>-</sup>), 1452 *v*(C-H, methyl), 1287 *v*(C-N), 1259 *v*(C-O). PS-C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub>Sn (296.86 g/mol): calcd. C 53.63, H 4.27, N 3.26, O 11.18, Sn 27.65; found C 69.66, H 5.45, N 1.74. Loading: calcd. 2.33 mmol/g; found 1.08 mmol/g. 34% yield.

**PS-L<sup>H</sup>CaOAc** IR (ATR, cm<sup>-1</sup>) 3373 v(O-H), 2921 v(C-H), 1697 v(C=O), 1602 v(C=N), 1573 v(br, complexed COO<sup>-</sup>), 1451 v(C-H, methyl), 1287 v(C-N), 1248 v(C-O). PS-C<sub>9</sub>H<sub>8</sub>NO<sub>3</sub>Ca (218.23 g/mol): calcd. C 65.66, H 5.23, N 4.00, O 13.68, Ca 11.43; found C 73.06, H 6.07, N 1.69. Loading: calcd. 2.71 mmol/g; found 0.92 mmol/g. 26% yield.

**PS-L<sup>H</sup>SnOct** IR (ATR, cm<sup>-1</sup>) 2926-2859 v(C-H), 1699 v(C=O), 1623 v(br, uncomplexed C=N), 1599 v(C=C), 1583 v(complexed COO<sup>-</sup>), 1453 v(C-H, methyl), 1290 v(C-N), 1251 v(C-O). PS-C<sub>15</sub>H<sub>20</sub>NO<sub>3</sub>Sn (381.04 g/mol): calcd. C 58.87, H 5.93, N 2.73, O 9.34, Sn 23.12; found C 69.66, H 5.45, N 1.74. Loading: calcd. 1.95 mmol/g; found 1.03 mmol/g. 35% yield.

The same procedure was used to complex  $Zn(OAc)_2.2H_2O$  and  $Sn(Oct)_2$  to ligand **PS-HL**<sup>tBu</sup>, and **PS-HL**<sup>CI</sup>.

**PS-L<sup>tBu</sup>ZnOAc** IR (ATR, cm<sup>-1</sup>) 2952 *v*(C-H), 1702 *v*(remaining C=O), 1604 *v*(C=N), 1576 *v*(complexed COO<sup>-</sup>), 1267 *v*(C-N), 1248 *v*(C-O). PS-C<sub>17</sub>H<sub>24</sub>NO<sub>3</sub>Zn (355.80 g/mol): calcd. C 59.25, H 6.86, N 3.73, O 12.76, Zn 17.40; found C 80.95, H 7.15, N 1.15. Loading: calcd. 2.71 mmol/g; found 2.36 mmol/g. 84% yield.

**PS-L**<sup>tBu</sup>**SnOct** IR (ATR, cm<sup>-1</sup>) 2952 *v*(C-H), 1697 *v*(remaining C=O), 1604 *v*(C=N), 1605 *v*(C=C), 1573 *v*(complexed COO<sup>-</sup>), 1265 *v*(C-N), 1247 *v*(C-O). PS-C<sub>23</sub>H<sub>37</sub>NO<sub>3</sub>Sn (494.29 g/mol): calcd. C 57.31, H 7.57, N 2.72, O 9.32, Sn 23.08; found C 78.07, H 6.95, N 1.19. Loading: calcd. 1.94 mol/g; found 1.94 mmol/g. 100% yield.

**PS-L<sup>CI</sup>ZnOAc** IR (ATR, cm<sup>-1</sup>) 2921 *v*(C-H), 1698 *v*(remaining C=O), 1602 *v*(C=N), 1571 *v*(complexed COO<sup>-</sup>), 1454 *v*(C-H, methyl), 1260 *v*(C-N), 1213 *v*(C-O), 842 *v*(C-Cl), 826 *v*(C=C). PS-C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>NO<sub>3</sub>Zn (312.43 g/mol): calcd. C 79.83, H 6.87, N 0.74, O 2.53, Cl 3.75, Zn 6.27; found C 72.66, H 6.20, N 0.93. Loading: calcd. 0.76 mmol/g; found 0.43 mmol/g. 54% yield.

**PS-L<sup>CI</sup>SnOAc** IR (ATR, cm<sup>-1</sup>) 2921 *v*(C-H), 1698 *v*(remaining C=O), 1602 *v*(C=N), 1571 *v*(complexed COO<sup>-</sup>), 1264 *v*(C-N), 1213 *v*(C-O), 1448 *v*(C-H, methyl), 842 *v*(C-Cl), 826 *v*(C=C). PS-C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>NO<sub>3</sub>Sn (365.76 g/mol): calcd. C 53.91, H 5.03, N 2.29, O 7.83, Cl 11.58, Sn 19.37; found C 68.34, H 5.80, N 0.94. Loading: calcd. 2.01 mol/g; found 1.94 mmol/g. >100% yield.

**PS-L<sup>CI</sup>SnOct** IR (ATR, cm<sup>-1</sup>) 2923 *v*(C-H), 1697 *v*(remaining C=O), 1602 *v*(C=N), 1571 *v*(complexed COO<sup>-</sup>), 1450 *v*(C-H, methyl), 1266 *v*(C-N), 1213 *v*(C-O), 842 *v*(C-Cl), 826 *v*(C=C). PS-C<sub>15</sub>H<sub>8</sub>Cl<sub>2</sub>NO<sub>3</sub>Sn (450.02 g/mol): calcd. C 51.90, H 4.89, N 2.41, O 8.24, Cl 12.19, Sn 20.38; found C 66.70, H 5.92, N 0.95. Loading: calcd. 1.72 mol/g; found 2.99 mmol/g. >100% yield.

**S**8

#### 2.2 Synthesis of immobilised amine complexes



Scheme S3. Synthetic route to immobilising the amine (reduced) analogue ligands.

The immobilised amine ligands were synthesised as follows: Aminomethyl(polystyrene) (1 g, 4 mmol/g, 4 mmol) was stirred with the appropriate catechol (4 mmol) in CH<sub>3</sub>CN (10 mL) at reflux for one hour. The mixture was then cooled to room temperature and stirred for a further three hours. The resulting product **PS-HL**<sup>H</sup><sub>red</sub> was a green powder, characterised by IR.

**PS-HL<sup>H</sup>**<sub>red</sub> IR (ATR, cm<sup>-1</sup>) 3358 v(O-H), 3023 v(N-H), 2922 v(C-H), 1596 v(C=C), 1484 v(C=C), 1254 v(C-N), 1028 v (C-O). PS-C<sub>7</sub>H<sub>8</sub>NO (122.15 g/mol): calcd. C 83.88, H 7.35, N 4.10, O 4.67; found C 81.59, H 7.12, N 4.11. Loading: calcd. 2.92 mmol/g; found 2.89 mmol/g. 99% yield.

**PS-HL**<sup>tBu</sup><sub>red</sub> IR (ATR, cm<sup>-1</sup>) 3350 v(O-H), 3024 v(N-H), 2950-2863 v(C-H), 1599 v(C=C), 1492 v(C=C), 1251 v(C-N), 1225 v(C-N), 1018 v(C-O). PS-C<sub>15</sub>H<sub>24</sub>NO (234.39 g/mol): calcd. C 84.31, H 9.09, N 3.08, O 3.52; found C 87.21, H 8.36, N 3.56. Loading: calcd. 2.20 mmol/g; found 1.79 mmol/g. 70% yield.



Scheme S4. Synthetic route to complexing the amine (reduced) ligands.

Complexation of the amine tethered ligands were achieved as with the Schiff-base complexes.

**PS-L<sup>H</sup>**<sub>red</sub>**ZnOAc** IR (ATR, cm<sup>-1</sup>) 2952 v(C-H), 1552 v(complexed COO<sup>-</sup>), 1489 v(C-N), 1441 v(C-H, methyl), 1256 v(C-N), 1018 v(C-O). PS-C<sub>9</sub>H<sub>10</sub>NO<sub>3</sub> Zn (245.58 g/mol): calcd. C 67.01, H 5.85, N 2.98, O 10.22, Zn 13.93; found C 58.81, H 5.52, N 2.88. Loading: calcd. 2.34 mmol/g; found 1.79 mmol/g. >100% yield.

**PS-L<sup>H</sup>**<sub>red</sub>**SnOct** IR (ATR, cm<sup>-1</sup>) 2922 *v*(C-H), 1580 *v*(complexed COO<sup>-</sup>), 1475 *v*(C-N), 1450 *v*(C-H), 1241 *v*(C-N). PS-C<sub>15</sub>H<sub>22</sub>NO<sub>3</sub>Sn (383.06 g/mol): calcd. C 63.59, H 6.52, N 2.32, O 7.93, Sn 19.64; found C 70.18, H 6.35, N 3.28. Loading: calcd. 2.34 mmol/g; found 1.12 mmol/g. 54% yield.

**PS-L**<sup>tBu</sup><sub>red</sub>**ZnOAc** IR (ATR, cm<sup>-1</sup>) 3024 v(N-H), 2924 v(C-H), 1601 v(C=C), 1566 v(complexed COO<sup>-</sup>), 1450 v(C-H, methyl), 1305 v(C-N), 1026 v(C-O). PS-C<sub>17</sub>H<sub>26</sub>NO<sub>3</sub>Zn (357.82 g/mol): calcd. C 73.79, H 7.54, N 2.05, O 7.03, Zn 9.59; found C 82.14, H 6.94, N 3.02. Loading: calcd. 1.47 mmol/g; found 0.45 mmol/g. 26% yield.

**PS-L<sup>tBu</sup>**<sub>red</sub>**SnOct** IR (ATR, cm<sup>-1</sup>) 3024 v(N-H), 2922 v(C-H), 1603 v(C=C), 1480 v(C=C), 1245 v(C-H), 1305 v(C-N), 1016 v(C-O). PS-C<sub>23</sub>H<sub>38</sub>NO<sub>3</sub>Sn (495.30 g/mol): calcd. C 70.20, H 7.75, N 1.71, O 5.85, Sn 14.48; found C 82.14, H 6.94, N 3.02. Loading: calcd. 1.22 mmol/g; found 0.29 mmol/g. 17% yield.

#### 2.3 Synthesis of 2,4-di-*tert*-butyl-6-aminophenol



Aqueous ammonia (3.61 mL, 32.8 mmol) was added dropwise to a dark yellow solution of 3,5-di-*tert*-butyl-o-benzoquinone (1 g, 4.6 mmol) in methanol (12 mL), and the reaction was left to stir at room temperature for 15 minutes. The reaction turned dark red, and on addition

of NaBH<sub>4</sub> (0.1717 g, 4.6 mmol) the reaction instantly turned a light orange colour. The mixture was stirred for 10 minutes, after which the reaction was quenched with DI water and a light yellow/green product precipitated out. The product was separated out between diethyl ether and DI water, and the combined organic phases were dried with Mg<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* to give a yellow/orange crude product which was washed with pentane to dissolve out any impurities. The product was dried under vacuum for 1 hour (54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.92 (d, J<sub>HH</sub> = 2.3 Hz, 1H, Ar), 6.82 (d, J<sub>HH</sub> = 2.3 Hz, 1H, Ar), 5.67 (s, 1H, OH), 3.15 (s, 2H, NH), 1.41 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (s, 2 H, C(CH<sub>3</sub>)<sub>3</sub>).

#### 2.4 Synthesis of 2,4-dichloro-6-aminophenol



2,4-dichloro-6-nitrophenol (1g, 5 mmol, 1 equiv.) was stirred under reflux in ethanol (20 mL) with SnCl<sub>2</sub>.2H<sub>2</sub>O (5.42 g, 25 mmol, 5 equiv.) for 30 minutes. The solution was then cooled to room temperature, then poured into ice (50 mL). NaHCO<sub>3</sub> was added to neutralise the mixture. The residual white solid was removed by vacuum filtration, and the filtrate was washed with ethyl acetate (3×30 mL) to extract the organic phase. The combined organic phases were washed with brine (3×20 mL), then dried with MgSO<sub>4</sub>. The latter was removed by gravity filtration, and the solvent was removed *in vacuo* to produce an off-white solid (35%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  6.72 (s, 1H, Ar-<u>H</u>), 6.61 (s, 1H, Ar-<u>H</u>), 5.36 (s, 1H, O<u>H</u>), 3.75 (s, 2H, N<u>H</u><sub>2</sub>); MS (ESI+): [C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>NO]<sup>+</sup> Theoretical: 176.97, Found: 177.98; IR (ATR, cm<sup>-1</sup>) 3397  $\nu$ (N-H), 3310  $\nu$ (N-H), 2925  $\nu$ (br, O-H), 1584  $\nu$ (C=C), 1477  $\nu$ (N-H), 1320  $\nu$ (C-N), 1227  $\nu$ (C-N), 1162  $\nu$ (C-O), 834  $\nu$ (C=C), 708  $\nu$ (C=C).

### 3. Ring-opening Polymerisation (ROP) procedures

#### 3.1 Melt ROP of *L*-lactide (*L*-LA) with immobilised catalysts

A 50:1:1 ratio of L-Lactide (1 g, 6.9 mmol), 4-methylbenzyl alcohol and the catalyst were added to a Schlenk flask and stirred at 130 °C for the required reaction time. Once complete, the polymerisation was quenched with technical grade *n*-hexane (1 mL) to precipitate the polymer, and the reaction was dissolved in dichloromethane (DCM, 10 mL). The heterogeneous catalysts were recovered from the solubilised polymer via vacuum filtration, then dried and characterised by IR (ATR, cm<sup>-1</sup>) once recovered. The solvent was removed from the reaction mixture *in vacuo*, yielding the crude polymer. Purification of PLA was achieved by dissolving the crude polymer in the minimum amount of DCM. Dropwise addition of the sample to a stirred solution of technical grade *n*-hexane (ten times the amount of DCM) precipitated out the polymer. The latter was collected by vacuum filtration and dried *in vacuo*. Analysis of the methine region of the crude polymer by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) gave the conversion (the -CHCH<sub>3</sub> proton in the monomer: 5.05 ppm, polymer: ca. 5.16 ppm). GPC (1-2 mg sample dissolved in 1 mL THF; analysis by refractive index and corrected by a factor of 0.58 for PLA, 0.56 for PCL)<sup>1,2</sup> was used to determine  $M_n$ ,  $M_w$  and  $D_M$ , and was compared to the theoretical value (Equation 1). The  $M_{n,NMR}$  was calculated from the aromatic proton signal of the 4-MeBnO<sup>-</sup> end group at 7.18 ppm. MALDI-ToF (using NaTFA and a DCTB matrix in THF) enabled determination of end groups.

Expected 
$$M_n = [LA] \times \left(\frac{\text{NMR Conv.}}{100}\right) \times 144.13 \text{ g mol}^{-1}$$
 Eq. 1

## 3.2 In-situ Attenuated Total Reflection-Fourier Transform-Infrared (ATR-FT-IR) monitored ROP of L-LA

A J. Young's flask was charged with L-LA (3 g, 20.8 mmol, 1 equiv.), immobilised catalyst (0.1 mmol, 0.005 equiv.), 4-methylbenzyl alcohol (50.9 mg, 0.4 mmol, 0.02 equiv.) and a magnetic stirrer in the glovebox, in a LA:Cat:I ratio of 200:1:4. The flask was sealed and removed from the glovebox. Under a flow of argon, the stopper was removed and replaced by an ATR-FT-IR probe (model IN350-T, connected to a Bruker Matrix-MF spectrometer). A background spectrum was obtained prior to positioning the probe into the reaction mixture so that the mechanical stirrer did not interfere with the probe. The flask, equipped with the probe, was placed into a pre-heated oil bath set to 130 °C to melt the L-LA, upon which real-time ATR-FT-IR data collection on the Opus 7.5 software (Bruker) began. Kinetic information was collected by integrating the L-LA and PLA peaks at 1160-1200 cm<sup>-1</sup> and 1203-1265 cm<sup>-1</sup> respectively, in the absorption spectrum, then plotting the natural logarithm of [LA]<sub>t</sub> against time (t), to obtain a linear, first order reaction with respect to monomer. Conversion was obtained using a calibration of the IR signals at 174 °C. Measurements were obtained of samples of varying PLA:LA mol% ratios, then the peak areas of each of LA and PLA were plotted against concentration to find a relationship in the form of y = mx + c (Figure S1, Figure S2).



**Figure S1.** Calibration curve at 174 °C to correlate the ATR-FT-IR integrated peak area of lactide (at 1240 cm<sup>-1</sup>) to the concentration.<sup>3</sup>



**Figure S2.** Calibration curve at 174 °C to correlate the ATR-FT-IR integrated peak area of PLA (at 1185 cm<sup>-1</sup>) to the concentration.<sup>3</sup>

#### 3.3 Solution phase ROP of L-LA with immobilised catalysts

A 50:1:1 ratio of *L*-Lactide (1 g, 6.9 mmol, 0.69 M), 4-methylbenzyl alcohol and the catalyst were added to a Schlenk flask and stirred at 80 °C in dry toluene or tetrahydrofuran (THF, 10 mL) for the required reaction time. Once complete, the polymerisation was quenched with analytical grade *n*-hexane (1 mL), and the immobilised catalysts were recovered *via* vacuum filtration. The solvent was removed *in vacuo*, yielding the crude polymer. Analysis of the crude polymer by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) gave the conversion of monomer to polymer.

#### **3.4 Sheldon test for heterogeneity**

A 50:1:1 ratio of *L*-Lactide (1g, 6.9 mmol), 4-methylbenzylalcohol and PS-LHSnOct was stirred at 130 °C under an argon atmosphere for 30 minutes. The reaction was removed from the heat and brought into an argon filled glovebox, by which time the monomer/polymer mixture had crystallised out. Some of the mixture was transferred to a second Schlenk flask, taking care to avoid transfer of the catalyst over. A <sup>1</sup>H NMR in CDCl<sub>3</sub> was obtained at this point. The two batches of reaction mixture (one with catalyst and one without) were then allowed to react for a further two hours until the full reaction time had elapsed. The reactions were quenched with technical grade *n*-hexane (~0.5 mL) and a work-up was carried out as described in section 3.1.

### 4. Calculation of loading and elemental % composition

a. Starting from 1 g PS-CH<sub>2</sub>Cl resin (5.5 mmol/g), the weight of PS in the resin must be calculated:

5.5 *mmol* amine × 49.48  $g mol^{-1}$  CH<sub>2</sub>Cl = 272.14 mg of CH<sub>2</sub>Cl in resin

$$1000 mg resin - 272.14 mg = 727.86 mg PS$$

b. Calculation of the weight remaining CH<sub>2</sub>Cl when conversion = X %; assume X = 50%:

 $50 \% \times 5.5 \text{ mmol CH}_2$ Cl = 2.75 mmol CH<sub>2</sub>Cl remaining

 $2.75 \text{ mmol CH}_2\text{Cl} \times 49.48 \text{ mg CH}_2\text{Cl}$  remaining

c. Calculation of the weight of CHO (product) groups when X = 50%, 2.75 mmol CHO have formed:

2.75 mmol CHO  $\times$  29.02 g mol<sup>-1</sup> CHO = 79.805 mg of CHO groups in resin

d. Calculation of the total (new) weight of the resin:

$$\sum mg_{PS} + mg_{CH_2Cl\,remaining} + mg_{CHO} = 943.74\,mg\,resin\,(total)$$

e. Calculation of TU loading from conversion (where X = 50%)

$$mmol \ g^{-1}$$
 CHO loading =  $\frac{\text{weight CHO at X\%} \div \text{Total resin weight}}{Mr_{CHO}}$ 

 $mmol \ g^{-1} \ \text{CHO} \ \text{loading} = \frac{79.805 \ mg \ \text{CHO} \ \text{at} \ 50\% \ \div \ 1542.36 \ mg \ \text{resin total}}{29.02 \ g \ mol^{-1} \ \text{CHO}} \times 10^3$ 

$$mmol \ g^{-1}$$
CHO loading = 2.91  $mmol \ g^{-1}$ 

f. Calculation of mass % of each component within the resin (e.g. mass % PS):

mass % PS = 
$$\frac{879 mg PS}{943.74 mg resin total} \times 100 = 77.13\%$$

Complete for the CH<sub>2</sub>Cl and CHO, using values from (b) and (c).

g. Calculation of the % composition of elements in each of the three components (e.g. carbon):

• PS chemical formula (repeat unit): C<sub>8</sub>H<sub>8</sub>

%C in PS = 
$$\frac{Mr_C \times \text{ratio}}{\sum Mr_{\text{All Elements}} \times \text{ratio element}}$$
%C in PS = 
$$\frac{12.01 \text{ g mol}^{-1} \times 8}{104.16 \text{ g mol}^{-1}} = 92.24\%$$

• CH<sub>2</sub>Cl chemical formula: CH<sub>2</sub>Cl

%C in CH<sub>2</sub>Cl = 
$$\frac{12.01 \ g \ mol^{-1} \times 1}{49.48 \ g \ mol^{-1}} = 24.27\%$$

• CHO chemical formula: CHO

%C in CHO = 
$$\frac{12.01 \ g \ mol^{-1} \times 1}{29.01 \ g \ mol^{-1}} = 41.40\%$$

h. Final resin composition (e.g. total % C in resin):

%C (total) = (%C in PS × mass % PS) + (%C in  $CH_2Cl \times mass % CH_2Cl$ )

+ (%C in CHO × mass % CHO)

Steps (6)-(8) should be completed for each element present in the different components of the resin.

## 5. Energy Dispersive X-ray (EDX) spectra



**Figure S3.** EDX spectrum of **PS-L<sup>H</sup>ZnOAc**, showing the lack of Cl in the complex, and presence of Zn and O, indicating successful immobilisation of the complex.



**Figure S4.** EDX spectrum of **PS-L<sup>H</sup>SnOct**, showing the lack of Cl in the complex, and presence of Sn and O, indicating successful immobilisation of the complex.

## 6. Thermogravimetric analysis (TGA)



**Figure S5.** Thermogravimetric analysis (TGA) of ligand **PS-HL**<sup>H</sup> (grey) and its metal complex, **PS-L**<sup>H</sup>**ZnOAc** (red), and their first derivative traces.

Table S1. TGA mass loss list for PS-HL<sup>H</sup> and PS-L<sup>H</sup>ZnOAc.

Sample	Mass loss event	Δm (mg)	Δm (%)	Time (min)	Temp (°C)	mg PS in sample (% of resin)	mg Ligand in sample (% of resin)	mg M- OR in sample (% of resin)
PS-HL <sup>H</sup>	1	4.168	34.45	24-37	332	-	5.76 (47.6)	-
	2	7.497	61.96	37-57	509	6.3 (52.4)	-	-

	1	0.246	3.28	11-21	174	-	-	3.82 (51.09)
PS- L <sup>H</sup> ZnOAc	2	2.112	28.23	27-37	370	-	2.59 (34.6)	-
	3	4.550	60.82	37-57	427	2.41 (32.21)	-	-
	1	0.507	4.61	22-29	280	-	-	5.60 (50.82)
PS- L <sup>H</sup> SnOct	2	3.664	33.31	29-44	388	-	2.55 (23.20)	-
	3	4.678	42.53	44-57	562	2.86 (25.98)	-	-

## 7. Differential Scanning Calorimetry (DSC)



**Figure S6.** DSC trace of PLA formed by **PS-L<sup>H</sup>SnOct** (90%,  $M_n$  35250 Da,  $D_M$  1.27,  $T_m$  175 °C). Conditions: [LA]:[Cat]:[I] = 400:1:1, 24 hours in the melt at 130 °C.



**Figure S7.** DSC trace of PLA formed by  $Sn(Oct)_2$  (90%,  $M_n$  24000 Da,  $D_M$  1.88,  $T_m$  171 °C). Conditions: [LA]:[Cat]:[I] = 400:1:1, 24 hours in the melt at 130 °C.

## 8. <sup>1</sup>H Nuclear Magnetic Resonance (NMR) spectra



5.24 5.22 5.22 5.12 5.19 5.18 5.17 5.16 5.15 5.14 5.13 5.12 5.11 5.10 5.09 5.08 5.07 5.06 5.05 5.04 5.03 5.02 5.01 9.09 4.98 4.97 5.28 5.26 5.24 5.22 5.20 5.18 5.16 5.14 5.12 5.10 5.08 5.04 5.02 5.00 4.98 4.96

**Figure S8.** Methine region of PLA (ca. 5.19 ppm) and lactide (5.05 ppm) in the <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of the crude PLA formed with (A) **PS-L<sup>tBu</sup>SnOct** and (B) a 4-dimethylaminopiperidine (DMAP) catalyst immobilised onto PS (PS-DMAP) which participates in epimerisation. The scrambled quartet at 5.19 and 5.05 ppm in (B) shows that the strength of the base resulted in a high degree of epimerisation of the lactide.



**Figure S9.** Example of PLA produced by the **PS-L<sup>H</sup>SnOct** catalysed ROP of *rac*-LA. (A) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of the crude polymer, (B) Homonuclear Decoupled <sup>1</sup>H{<sup>1</sup>H} NMR (500 MHz, CDCl<sub>3</sub>). Conditions: [LA]:[Cat]:[I] = 50:1:1, 2.5 h in the melt at 130 °C. Probability of heterotactic enchainment calculated by  $P_r = \sqrt{2 \times isi}$ .<sup>4</sup>

Entry	Catalyst	Pr
1	PS-L <sup>H</sup> ZnOAc	0.53
2	PS-L <sup>H</sup> SnOct	0.59
3	Sn(Oct) <sub>2</sub>	0.61
4	Zn(OAc) <sub>2</sub> .2H <sub>2</sub> O	0.51

Table S2. Homonuclear Decoupled <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of PLA produced by PS-L<sup>H</sup>SnOct.

Conditions: [LA]:[Cat]:[I] = 50:1:1, 2.5 h in the melt at 130 °C. Probability of heterotactic enchainment calculated by  $P_r = \sqrt{2 \times isi}$ .<sup>4</sup>

## 9. Polymerisation data



**Figure S10.** Sheldon test for heterogeneity: The catalyst was removed after 45 minutes (62% conversion, [LA]:[Cat]:[I] = 50:1:1 in the melt at 130 °C for 2.5 hours) and the batch without catalyst led to low conversion (72%), whilst the remaining batch reached 94% conversion ( $M_n$  6750 Da,  $D_M$  1.13).

**Table S3.** Polymerisation data from the ROP of *L*-LA with **PS-L<sup>R</sup>MOR'** and **PS-L<sup>R</sup><sub>red</sub>MOR'** catalysts (R = H, 'Bu, Cl, R' = OAc, Oct) and control reactions, using [LA]:[Cat]:[I] = 50:1:1 in the melt at 130 °C for 24 hours.

Entry	Catalyst	Conv. (%) <sup>a</sup>	$M_{ m n,Theo}{}^{ m b}$	$M_{ m n,NMR}{}^{ m a}$	<i>M</i> n <sup>c</sup>	M <sub>w</sub> c	${oldsymbol{\mathcal{D}}}_{\mathrm{M}}^{c}$
1	PS-L <sup>tBu</sup> ZnOAc	23	1650	850	1000	1200	1.16
2	PS-L <sup>CI</sup> ZnOAc	87	6300	4300	4550	6100	1.33
3	PS-L <sup>H</sup> <sub>red</sub> ZnOAc	75	5400	3850	5100	7850	1.53
4	PS-L <sup>tBu</sup> redZnOAc	45	3250	1100	3200	4000	1.24

5	PS-L <sup>CI</sup> SnOAc	96	6900	5100	6271	9200	1.47
6	PS-L <sup>tBu</sup> SnOct	69	4950	1400	6200	7050	1.48
<b>7</b> <sup>d</sup>	PS-L <sup>CI</sup> SnOct	94	6750	1350	5700	6550	1.15
8	PS-L <sup>H</sup> redSnOct	22	1600	900	550	650	1.14
9	PS-L <sup>tBu</sup> redSnOct	21	1500	850	500	550	1.08

<sup>a</sup>Determined from the <sup>1</sup>H NMR spectrum. <sup>b</sup>Theoretical  $M_n = (144 \times \text{equiv. LA}) \times (\frac{\text{Conv.}}{100})$ . <sup>c</sup>As determined by SEC (THF) using RI methods, relative to polystyrene standards (multiplied by a factor of 0.58, rounded to the nearest 50).<sup>1</sup> <sup>d</sup>Result obtained after 2.5 hours.



**Figure S11.** Polymers made using (A) **PS-L<sup>H</sup>ZnOAc** (6450 Da, [LA]:[Cat]:[I]=50:1:1), (B) **PS-L<sup>H</sup>SnOct** (5900 Da, [LA]:[Cat]:[I]=50:1:1), (C) **PS-L<sup>H</sup>SnOct** (35250 Da, [LA]:[Cat]:[I]=200:1:4) and (D) Sn(Oct)<sub>2</sub> (24000 Da, [LA]:[Cat]:[I]=200:1:4).

## 10. Kinetic data from *in-situ* ATR-FT-IR



**Figure S12.** Ether stretch of the lactide (left,  $1240 \text{ cm}^{-1}$ ) and PLA (right,  $1185 \text{ cm}^{-1}$ ) in the *In-Situ* Attenuated Total Reflectance Infra-Red (ATR-FT-IR) spectrum. Collated spectra collected from the ROP of *L*-LA using Sn(Oct)<sub>2</sub>. Conditions: [LA]:[Cat]:[I] = 200:1:4. 130 °C, 55 minutes.



**Figure S13.** (A) Conversion of lactide to PLA over time for **PS-L<sup>H</sup>ZnOAc**, 6 hours in the melt, [LA]:[Cat]:[I] = 200:1:4, 130 °C (89%,  $M_n$  6100,  $D_M$  1.15). (B) Semi-logarithmic plot of the concentration of lactide, [LA], monitored by *in-situ* ATR-FT-IR using **PS-L<sup>H</sup>ZnOAc**.



**Figure S14.** Semi-logarithmic plot of the concentration of lactide, [LA], monitored by *in-situ* ATR-FT-IR using a new batch of **PS-L<sup>H</sup>SnOct**. Conditions: 130 °C in the melt. Red trace: [LA]:[Cat]:[I] = 200:1:4,  $k_{obs}$  6.10×10<sup>-4</sup> s<sup>-1</sup> (90%,  $M_n$  6700 Da,  $D_M$  1.08). Grey trace: 400:1:8,  $k_{obs}$  3.49×10<sup>-4</sup> s<sup>-1</sup> (87%,  $M_n$  6800 Da,  $D_M$  1.07).

# 11. Matrix Assisted Laser Desorption Time-of-Flight (MALDI-ToF)



**Figure S15.** MALDI-ToF spectrum of PLA from **PS-L<sup>H</sup>ZnOAc**. Conditions: [LA]:[Cat]:[I] = 50:1:1, 24 hours in the melt at 130 °C (84%,  $M_n$  6450,  $D_M$  1.23, major series: degree of polymerisation (DP) = 39).



**Figure S16.** MALDI-ToF spectrum of PLA from **PS-L<sup>H</sup>SnOct** after (A) 2.5 h (87%,  $M_n$  6300,  $\mathcal{D}_M$  1.17, major series: DP = 40) and (B) 24 h (93%,  $M_n$  6000,  $\mathcal{D}_M$  1.49, major series: DP = 24). Conditions: [LA]:[Cat]:[I] = 50:1:1, in the melt at 130 °C.



Figure S17. MALDI-ToF spectrum of PLA from PS-L<sup>tBu</sup>SnOct. Conditions: [LA]:[Cat]:[I] = 50:1:1, 24 hours in the melt at 130 °C (69%,  $M_n$  6250,  $D_M$  1.48, major series: DP = 29).



**Figure S18.** MALDI-ToF spectrum of PLA from **PS-L**<sup>CI</sup>**SnOct**. Conditions: [LA]:[Cat]:[I] = 200:1:4, 55 minutes in the melt at 130 °C (83%,  $M_n$  6000,  $\mathcal{D}_M$  1.05, major series: DP = 35).

## 12. Size Exclusion Chromatography (SEC) traces



**Figure S19.** SEC dispersity trace of PLA produced with **PS-L<sup>H</sup>SnOct** in the melt (130 °C) after (A) 2.5 h ([LA]:[Cat]:[I] = 200:1:4, 87%,  $M_n$  6300,  $D_M$  1.17), and (B) 24 h ([LA]:[Cat]:[I] = 50:1:1, 93%,  $M_n$  6000,  $D_M$  1.49).



**Figure S20.** Size exclusion chromatography (SEC) trace of PLA produced by **PS-L<sup>H</sup>SnOct**. Conditions: [LA]:[Cat]:[I] = 200:1:4, 2.5 h in the melt at 130 °C (87%,  $M_n$  6300,  $D_M$  1.17).

## 13. Polymerisation data from reuse study



**Figure S21.** Recycling study of **PS-L<sup>H</sup>MOR'**, where M = Zn, Mg, Ca and Sn and R' = OAc or Oct. Conditions: [LA]:[Cat]:[I] = 50:1:1, 24 hours in the melt at 130 °C.

**Table S4.** Polymerisation data from the recycling study of **PS-L<sup>H</sup>MOR'** (M = Zn, Mg, Ca and Sn and R' = OAc or Oct) in the ROP of *L*-LA. Conditions: [LA]:[Cat]:[I] = 50:1:1 in the melt at 130 °C for 24 hours.

Entry	Catalyst	<b>Conv.</b> (%) <sup>a</sup>	Mn,Theo <sup>b</sup>	M <sub>n,NMR</sub> <sup>a</sup>	<i>M</i> <sub>n</sub> <sup>c</sup>	$\boldsymbol{D}_{\mathrm{M}}^{\mathbf{c}}$
1	PS-L <sup>H</sup> ZnOAc	84	6050	5800	4650	1.23
2	PS-L <sup>H</sup> ZnOAc Reused	33	2400	2150	2750	1.25
3	PS-L <sup>H</sup> MgOAc	30	3150	1350	1150	1.05
4	PS-L <sup>H</sup> MgOAc Reused	4	300	-	-	1.05
5	PS-L <sup>H</sup> CaOAc	30	2150	950	1750	1.11
6	PS-L <sup>H</sup> CaOAc Reused	18	1300	1000	-	-
7	PS-L <sup>H</sup> SnOct	93	6700	3150	5900	1.49
8	PS-SnL <sup>H</sup> Oct Reused	82	5900	3000	9750	1.51

<sup>a</sup>Determined from the <sup>1</sup>H NMR spectrum. <sup>b</sup>Theoretical  $M_n = (144 \times \text{equiv. LA}) \times \left(\frac{\text{Conv.}}{100}\right)$ . <sup>c</sup>As determined by SEC (THF) using RI methods, relative to polystyrene standards (multiplied by a factor of 0.58, rounded to the nearest 50).<sup>1</sup>



**Figure S22.** Methine region in the <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of crude PLA after 6 reuse cycles using **PS-L<sup>H</sup>SnOct** (Conditions: [LA]:[Cat]:[I] = 50:1:1, 2.5 hours in the melt at 130 °C).



**Scheme S5.** Coordination-Insertion mechanism for the ROP of *L*-LA, showing the dynamic exchange between the coordinated and free PLA. The exchange can be promoted by any protonating quenching agent, such as 2-ethylhexanoic acid (HOct).



**Figure S23.** <sup>119</sup>Sn NMR (187 MHz, CDCl<sub>3</sub>) spectra of a PLA sample produced with Sn(Oct)<sub>2</sub>. (A) 0 to -1000 ppm (780 scans), (B) -1000 to -2000 ppm (512 scans), (C) 900 to -100 ppm (599 scans) and (D) 1800 to 800 pm (1847 scans).

**Table S5.** Mass balance of **PS-L<sup>H</sup>SnOct** over the 7 reuse cycles. Initial mass of catalyst: 71.2 mg.<sup>a</sup>

Use #	Mass of recovered catalyst (mg)
1	71.8
2	99.5
3	99.8
4	100.2
5	96.9
6	92.8
7	78.4

<sup>a</sup>Conditions: [LA]:[Cat]:[I] = 50:1:1 in the melt at 130 °C, 1g lactide scale. Decrease in mass during the last two measurements was due to loss of the catalyst during transfers between vessels, due to the catalyst breaking up during ROP.



**Figure S24.** SEM images of (A) Fresh **PS-L<sup>H</sup>SnOct**, (B) recovered **PS-L<sup>H</sup>SnOct** post-ROP, at ×100 (left), ×1000 (centre) and ×2000 (right) magnification.



**Figure S25.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of residual PLA collected after attempting to regenerate the catalyst by stirring the latter in DCM and acetic acid for 72 hours. Depolymerisation is evidenced by the generation of a lactic acid quartet at 4.36 ppm arising from the methine hydrogen.

### 14. Catalyst Scope

**Table S6.** Polymerisation data from the solution phase ROP of *L*-LA with **PS-L<sup>H</sup>MOR'** catalysts ( $\mathbf{R'} = \mathbf{OAc}$  or Oct) and control reactions over 24 hours, using [LA]:[Cat]:[I] = 50:1:1 ([LA] = 0.69 mol L<sup>-1</sup>).

Entry	Catalyst	Solvent	Temp. (°C)	Conv. (%) <sup>a</sup>	<i>M</i> n, Theo <sup>b</sup>	M <sub>n</sub> c	M <sub>w</sub> c	$\boldsymbol{H}_{M}^{c}$
1	PS-L <sup>H</sup> SnOct	THF	rt	3	200	-	-	-
2	PS- L <sup>H</sup> ZnOAc	THF	rt	0	0	-	-	-
3	PS-L <sup>H</sup> SnOct	Toluene	80	77	5550	4400	4800	1.09
4	PS- L <sup>H</sup> ZnOAc	Toluene	80	19	1350	2000	2100	1.07
5	Sn(Oct) <sub>2</sub>	Toluene	80	93	6700	5200	6050	1.16

<sup>a</sup>Determined from the <sup>1</sup>H NMR spectrum. <sup>b</sup>Theoretical  $M_n = (144 \times \text{equiv. LA}) \times (\frac{\text{Conv.}}{100})$ . <sup>c</sup>As determined by SEC (THF) using RI methods, relative to polystyrene standards (multiplied by a factor of 0.58, rounded to the nearest 50).<sup>1</sup>

Table S7. Polymerisation data from the ROP of *L*-LA with **PS-L<sup>H</sup>SnOct** over 24 hours, using

[LA]:[I] = 400:1.

Entry	[LA]:[Cat]	ppm	Temp. (°C)	Conv. (%) <sup>a</sup>	<i>M</i> n, Theo <sup>b</sup>	<i>M</i> <sub>n</sub> <sup>c</sup>	$M_{ m w}{}^{ m c}$	$\boldsymbol{B}_{\mathrm{M}}^{\mathrm{c}}$	TON	TOF (h <sup>-1</sup> )
1	400:6×10 <sup>-3</sup>	15	130	0	0	-	-	-	-	-
2	400:6×10 <sup>-3</sup>	15	180	41	23650	17750	18900	1.07	19451	810.4
3	400:0.25	625	130	52	39800	15950	18750	1.18	841	35.0
4	400:0.5	1250	130	69	30000	31350	39800	1.13	558	23.3

<sup>a</sup>Determined from the <sup>1</sup>H NMR spectrum. <sup>b</sup>Theoretical  $M_n = (144 \times \text{equiv. LA}) \times (\frac{\text{Conv.}}{100})$ . <sup>c</sup>As determined by SEC (THF) using RI methods, relative to polystyrene standards (multiplied by a factor of 0.58, rounded to the nearest 50).<sup>1</sup>



**Figure S26.** (A) Semi-logarithmic plot of the concentration of lactide, [LA], monitored by *insitu* ATR-FT-IR using **PS-L<sup>H</sup>SnOct** ( $k_{obs}$  1.25×10<sup>-3</sup> s<sup>-1</sup>). (B) Conversion of lactide to PLA over time for **PS-L<sup>H</sup>SnOct**, 20 minutes in the melt, [LA]:[Cat]:[I] = 200:1:4, 180 °C (89%,  $M_n$ 7500,  $M_n$ , Theo 6400,  $D_M$  1.25).



**Figure S27.** (A) Semi-logarithmic plot of the concentration of lactide, [LA], monitored by *insitu* ATR-FT-IR using Sn(Oct)<sub>2</sub> ( $k_{obs}$  6.67×10<sup>-3</sup> s<sup>-1</sup>). (B) Conversion of lactide to PLA over time for Sn(Oct)<sub>2</sub>, 3 minutes in the melt, [LA]:[Cat]:[I] = 200:1:4, 180 °C (96%,  $M_n$  8250,  $M_n$ , <sub>Theo</sub> 6900,  $D_M$  1.53).

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