A Single Catalyst for Promoting Reverse Processes: Synthesis and Chemical Degradation of Polylactide

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Synthesis and characterization of the ligand L1

Scheme 1. Synthesis of ligand L1.

The ligand was synthetized by condensation of the 2-(2-pyridyl) ethylamine (660 mg, 5.40 mmol) with the salicyl aldehyde (660 mg, 5.40 mmol). The reaction was performed in reflux of ethanol (40 mL) overnight. The solvent was removed under vacuum, forming an orange oil in high yields (81%).

The success of performed reaction was confirmed by $^1$H NMR experiment, which spectrum is illustrated in the following figure:

Figure S1. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of ligand L1.

$^1$H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 13.6 (s, 1H, -OH), 8.46 (d, J = 4.1 Hz, 1H, Py-H), 7.67 (s, 1H, CH=N), 7.08 (d, J = 8.2 Hz, 1H, Ph-H), 7.02 (dt, J$_1$ = 7.2 Hz, J$_2$ = 1.5 Hz, 1H, Ph-H), 6.96 (dt, J$_1$ = 7.5 Hz, J$_2$ = 1.7 Hz, 1H, Py-H), 6.79 (d, J = 7.6 Hz, 1H, Ph-H), 6.69 (d, J = 7.6 Hz, 1H, Py-H), 6.63 (dt, J$_1$ = 7.2 Hz, J$_2$ = 1.1 Hz, 1H, Ph-H), 6.56 (d, J = 7.2 Hz, 1H, Py-H), 3.68 (t, J = 6.9 Hz, 2H, CH$_2$), 2.86 (t, J = 6.9 Hz, 2H, CH$_3$).
Synthesis and characterization of the complex 1

Scheme 2. Synthesis of complex 1.

To a stirred solution containing Zinc bis(bis(trimethylsilyl)amide) (773 mg, 2.0 mmol) in dry benzene (4.0mL) was added dropwise a solution of the ligand precursor L1 (453 mg, 2.0 mmol) in dry benzene (2.0mL). The solution was stirred for 3h at room temperature. The solvent was removed under vacuum, forming a red solid. Yield: 80%. The formation of the desired species was confirmed by NMR and elemental analysis. Elemental Analysis calculated for: C20H31N3OSi2Zn (%): C, 53.26; H, 6.93; N, 9.32; Found: C, 52.98; H, 7.02; N, 9.47.

Figure S2. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of complex 1.

$^1$H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 8.31 (d, J = 5.2Hz, 1H, Ha), 7.36 (d, J = 8.6Hz, 1H, Hb), 7.25 (m, 1H, Hc), 7.22 (s, 1H, Hd), 6.80 (m, 2H, Hm–Hf), 6.53 (t, J = 7.8Hz, 1H, He), 6.40 (d, J = 7.8Hz, 1H, Hf), 6.31 (t, J = 6.5Hz, 1H, Hg), 3.22 (m, 2H, Hh). 3.01 (m, 2H, Hg), 0.47 (s, 18H, -SiMe$_3$).
Figure S3. $^{13}$C NMR spectrum (100 MHz, $C_6D_6$, 298 K) of complex 1.

$^{13}$C NMR (100 MHz, $C_6D_6$, 298 K): $\delta$ 171.6 (Cq), 169.5 (Cg), 157.8 (Cq), 149.1 (Ca), 138.7 (Cm), 135.2 (Cc), 135.0 (Cl), 124.6 (Ce), 124.4 (Ch), 122.8 (Cb), 119.0 (Cq), 113.6 (Cl), 55.4 (Cl), 35.4 (Ce), 6.12 ($-SiMe_3$). Cq means quaternary carbon.

Figure S4. Aromatic region of COSY NMR spectrum (400 MHz, $C_6D_6$, 298 K) of complex 1.
Figure S5. NOESY NMR spectrum (600 MHz, C6D6, 298 K) of complex 1.

Figure S6. Aromatic region of HSQC NMR spectrum (600 MHz, C6D6, 298 K) of complex 1.
**Figure S7.** Aliphatic region of HSQC NMR spectrum (600 MHz, C₆D₆, 298 K) of complex 1.

**Figure S8.** DOSY NMR spectrum (400 MHz, C₆D₆, 298 K) of complex 1 (D = 7.73 × 10⁻¹⁰ m²/s) in the presence of tetrakis(trimethylsilyl)silane TMSS as standard (D = 9.59 × 10⁻¹⁰ m²/s).
Figure S9. $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex 1.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): δ 8.49 (d, J = 5.2Hz, 1H, Ha), 7.84 (m, 2H, Hg-c), 7.41 (d, J = 7.8Hz, 1H, Hd), 7.35 (t, J = 6.5Hz, 1H, Hb), 7.18 (t, J = 8.7Hz, 1H, Hl), 6.94 (dd, J$_1$ = 7.8Hz, J$_2$ = 1.7Hz, 1H, Hn), 6.76 (d, J = 8.6Hz, 1H, Hm), 6.44 (t, J = 7.8Hz, 1H, Hf), 3.93 (m, 2H, Hf). 3.49 (m, 2H, Hf), -0.0336 (s, 18H, -SiMe$_3$).
Figure S10. $^{13}$C NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex 1.
$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 170.4, 169.6, 158.1, 149.0, 139.9, 135.1, 134.5, 125.6, 123.4, 123.3, 119.1, 113.6, 55.9, 35.7, 5.40.

Figure S11. Aromatic region of COSY NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex 1.
Figure S12. TGA measurement of the complex 1 at 150°C.
General procedure for the polymerization of lactide at room temperature

The polymerization was carried out under inert conditions. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with lactide. The metal-complex and iPrOH (0.1 M solution of iPrOH in dichloromethane) were added in a 4 mL vial and mixture was stirred for 5’ then added dichloromethane and transferred in the monomer. The reaction mixture was stirred at room temperature. During the reaction, small aliquots of the reaction mixture were sampled, dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy. At the end of the polymerization the product was precipitated in hexane then filtered and dried in a vacuum oven.

General procedure for the polymerization of lactide at high temperature

The polymerization was carried out under inert conditions. In a Braun Labmaster glovebox, a magnetically stirred reactor flask (50 mL) was charged with lactide. The metal-complex and 1 equivalent of BzOH (0.1 M solution of BzOH in toluene) were added in a 2 mL vial and the mixture was stirred for 5’ then transferred in the monomer and, finally, mixed to more equivalents of BzOH. The reaction mixture was stirred at 150°C. During the reaction, small aliquots of the reaction mixture were sampled, dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy. At the end of the polymerization the product was precipitated in hexane then filtered and dried in a vacuum oven.

Figure S13. MALDI-TOF of P(rac-LA) sample run 2 Table 1.
Figure S14. MALDI-TOF of P(L-LA) sample run 11 Table 1.

Figure S15. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of a P(rac-LA) sample Table S1.
Figure S16. GPC analysis of sample 12 Table 1.
Figure S17. Methine region of the homonuclear decoupled $^1$H NMR spectrum (CDCl$_3$, RT, 400MHz) of a P(L-LA) sample run 12 Table 1.

Figure S18. Methine region of the homonuclear decoupled $^1$H NMR spectrum (CDCl$_3$, RT, 400MHz) of a P(D,L-LA) sample run 2 Table 1.
Figure S19. DSC measurement of a P(L-LA) sample run 10 Table 1.

Table S1. Polymerization of lactides promoted by 1.

| Run | Mon  | [LA]/[Zn]/[ROH] | T  | Time | Conv | TOF (h⁻¹) |
|-----|------|-----------------|----|------|------|-----------|
| 1   | rac-LA | 100/1/0        | 25 | 8    | 61   | 457       |
| 2   | rac-LA | 100/1/1        | 25 | 0.5  | 22   | 2640      |
| 3   | rac-LA | 400/1/1        | 25 | 0.5  | 59   | 28320     |
| 4   | L-LA  | 400/1/1        | 25 | 0.5  | 54   | 25920     |
| 5   | L-LA  | 400/1/40       | 25 | 0.5  | 31   | 14880     |
| 6   | L-LA  | 400/1/100      | 25 | 2    | 67   | 8040      |
| 7*  | L-LA  | 1000/1/2       | 25 | 2    | 56   | 16800     |
| 8*  | L-LA  | 1000/1/2       | 25 | 2    | 56   | 16800     |
| 9*  | L-LA  | 1000/1/0       | 150| 4    | 23   | 3450      |
| 10* | L-LA  | 1000/1/10      | 150| 1    | 100  | 60000     |
| 11* | L-LA  | 1000/1/50      | 150| 0.5  | 100  | 120000    |
| 12* | L-LA  | 5000/1/50      | 150| 5    | 82   | 49200     |
| 13* | L-LA  | 400/1/1        | 25 | 0.5  | 0.5  | 12000     |
All reactions were carried out by using 10 µmol of Zn catalyst at 25 °C in CH$_2$Cl$_2$ (2 mL), ROH was iPrOH for runs at 25 °C and BzOH for runs at 150 °C. Experimental $M_n$ (corrected using factor of 0.58) and $D$ values were determined by GPC analysis in THF using polystyrene standards. Calculated $M^\text{th}(\text{KDa})$ = 144.14 x ([LA]/[ROH]) x conversion of LA. LA purified by a single crystallization unpurified LA. Technical grade purity LA, solvent free. Reaction performed in THF.

**General procedure for the depolymerization of polylactide in solution**

The depolymerization reaction was carried out under an inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with polylactide and MeOH. In a vial (4mL) the metal-complex was dissolved in THF and added to the polymer. The reaction mixture was stirred at room temperature. At desired times, small aliquots of the reaction mixture were sampled, dissolved in CDCl$_3$ or CD$_2$Cl$_2$ and analyzed by 1H NMR spectroscopy. At the end of the depolymerization the reaction was stopped with CH$_2$Cl$_2$ and dried under vacuum.

| PLA sample | Mn (KDa) | $D$  | $T_f$ (°C) |
|------------|---------|-----|----------|
| P(L-LA) 1  | 160     | 1.2 | 179      |
| P(D,L-LA)  | 13      | 1.1 |          |
| P(L-LA) 2  | 30      | 1.1 | 171      |
| P(L-LA) 3  | 48      | 1.8 | 170      |
| P(L-LA) 4  | 92      | 1.5 | 178      |
| P(L-LA) cup| 58      | 1.9 | 150      |
| P(L-LA) filament | 20     | 2.9 | 168      |

Table S2. Number average molecular weight (Mn), dispersity ($D$) and $T_f$ of PLA samples used for depolymerization reactions.
Figure S20. $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) depolymerized PLLA.

Figure S21. Kinetic profile for degradation of a poly (rac-LA) sample ([PLA]$0 = 0.44$ M; [polyester linkages]$0/[Zn]0 = 60$; CH$_2$Cl$_2$ (0.45 mL) as solvent; MeOH 0.05mL).
Figure S22. Pseudofirst-order kinetic plot for degradation of poly(rac) lactide ([PLA]₀ = 0.44 M; [polyester linkages]₀/[Zn]₀ = 60; CH₂Cl₂ (0.45 mL) as solvent; MeOH 0.05mL). Pseudofirst-order rate is = 1.50 h⁻¹ at 25°C (R² = 0.9962).

General procedure for the depolymerization of polylactide solvent free

The depolymerization reaction was carried out under an inert atmosphere. In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with polylactide. In a vial (4mL) the metal-complex was dissolved in MeOH or EtOH and added to the polymer. The reaction mixture was stirred at room temperature. At desired times, small aliquots of the reaction mixture were sampled, dissolved in CDCl₃ or C₆D₆ and analyzed by ¹H NMR spectroscopy. At the end of the depolymerization the reaction was stopped with CH₂Cl₂ and dried under vacuum.
Figure S23. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of methyl-lactide (Me-La).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ 4.27 (q, J = 6.7Hz, 1H, H$_b$), 3.77 (s, 3H, H$_a$), 2.95 (br, 1H, -OH), 1.40 (d, J = 6.8Hz, 3H, H$_c$).
Figure S24. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of ethyl-lactide (Et-La).

$^1$H NMR (400 MHz, C$_6$D$_6$, 298 K): $\delta$ 4.04 (q, $J = 6.9$Hz, 1H, H$_b$), 3.82 (q, $J = 7.2$Hz, 2H, H$_c$), 2.76 (br, 1H, -OH), 1.23 (d, $J = 6.9$Hz, 3H, H$_a$), 0.82 (t, $J = 7.1$Hz, 3H, H$_d$).
**Table S3.** Methanolysis of PLAs performed in THF solution.\(^a\)

| Run | Sample     | Mn\(^b\) (KDa) | Time (h) | \(^d\)XInt | \(^c\)Sme-La | \(^c\)YMe-La |
|-----|------------|----------------|----------|-------------|--------------|--------------|
| 1   | P(L-LA)    | 30             | 1        | 100         | 61           | 61           |
|     |            |                | 1.5      | 100         | 100          | 100          |
| 2   | P(L-LA)    | 48             | 1        | 100         | 74           | 74           |
|     |            |                | 1.5      | 100         | 100          | 100          |
| 3   | P(L-LA)    | 92             | 1        | 100         | 77           | 77           |
|     |            |                | 1.5      | 100         | 100          | 100          |
| 4   | P(L-LA)    | 14             | 0.5      | 94          | 74           | 70           |
|     |            |                | 1        | 97          | 95           | 92           |
| 5   | P(D,L-LA)  | 13             | 0.5      | 55          | 27           | 15           |
|     |            |                | 1        | 55          | 48           | 27           |
| 6   | P(D,L-LA)  | 44             | 1        | 75          | 69           | 52           |
|     |            |                | 2        | 88          | 89           | 78           |
| 7\(^d\) | P(L-LA) | 30             | 2        | 89          | 38           | 34           |
|     |            |                | 4.5      | 97          | 61           | 60           |
|     |            |                |          | 24          | 100          | 100          |
| 8\(^d\) | PLA cup | 58             | 2        | 100         | 47           | 47           |
|     |            |                | 4.5      | 100         | 100          | 100          |
| 9\(^d\) | PLA filament | 20         | 2        | 84          | 26           | 22           |
|     |            |                | 4.5      | 100         | 62           | 62           |

\(^a\)All reactions were carried out by using 5 µmol of Zn catalyst (0.6 mol % relative to ester linkages) in 1.8 mL of THF, with 0.2 mL of MeOH. \(^b\)M\(_n\) = the experimental (GPC) values of the recorded molecular weight of the polymer. \(^c\)Determinated by \(^1\)H NMR; \(^d\)reaction performed in air.
