Supporting Information

Group 4 initiators for the stereoselective ROP of rac-β-butyrolactone and its copolymerization with rac-lactide

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1.1 Polymerization procedure

For solution polymerizations of rac-lactide the monomer:initiator ratio employed was 100:1 at a temperature of 80 °C, in all cases the solvent was toluene and 0.7 g of rac-lactide was used. After the reaction time, methanol was added to quench the reaction and any resulting solid dissolved in dichloromethane. The solvents were removed in-vacuo and the resulting solid was washed with copious amounts of methanol to remove any unreacted monomer. ¹H NMR spectroscopy (CDCl₃) and GPC (THF) were used to determine tacticity and molecular weights ($M_n$ and $M_w$) of the polymers produced; $P_t$ (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ¹H NMR spectra.

1.2 Kinetics procedure

A 0.6 ml solution of rac-lactide in d₄-toluene was prepared with an initial concentration of 0.578 mol dm⁻³ based on 0.05 g of rac-lactide in a monomer to initiator ratio of 100:1 using {Hf(2)O'Pr}₂, {Hf(4)O'Pr}₂, {Zr(2)O'Pr}₂, {Zr(4)O'Pr}₂, as the initiators. The ¹H NMR spectra of the sample was obtained at 80 °C over a period of 13 hours at 15 minute intervals. The relative concentrations of the monomer and polymer were determined from analysis of the ¹H NMR spectra and ln[A₀]/[Aₜ] vs time plotted.

1.3 Butyrolactone Polymerization

*General Procedure for BBL polymerization 300:1*

BBL (1.0 g, 11.6 mmol) and {Hf(2)O'Pr}₂ catalyst (30 mg, 38 µmol) were dissolved in toluene (1.0 ml) and heated in a sealed vessel at 80 °C for 24 hours. The reaction was cooled to RT and quenched with MeOH (~1 ml) and CH₂Cl₂ (~5 ml). Solvent was removed and resulting solid dried under vacuum. The solid was dissolved in minimal CH₂Cl₂ and precipitated with MeOH. The precipitate was filtered and dried under vacuum.

![Figure 1: ¹H NMR (300MHz, CDCl₃) of PHB from {Hf(2)O'Pr}₂ at 80 °C](image-url)
General Procedure for copolymerization of BBL:LA 150:150:1

BBL (0.37 g, 4.3 mmol), rac-LA (625 mg, 4.3 mmol) and \( \text{Hf}^2\text{OiPr}_2 \) catalyst (22 mg, 28 µmol) were dissolved in toluene (1.0 ml) and heated in a sealed vessel at 80 °C for 24 hours. The reaction was cooled to RT and quenched with MeOH (~1 ml) and CH\(_2\)Cl\(_2\) (~5 ml). Solvent was removed and resulting solid dried under vacuum. The solid was dissolved in minimal CH\(_2\)Cl\(_2\) and precipitated with MeOH. The precipitate was filtered and dried under vacuum.

![NMR spectrum](image)

**Figure 2** \(^1\text{H} \text{NMR (300MHz, CDCl}_3\) of PHB-\(b\)-PLA from \( \text{Hf}^2\text{OiPr}_2 \) at 80 °C

**Determination of Tacticity**

The tacticity was determined by deconvolution of carbonyl signal of the \(^{13}\text{C} \{^1\text{H}\} \text{NMR spectrum (300 MHz in CDCl}_3\).
Figure 3 $^{13}$C-$^1$H NMR (300MHz, CDCl$_3$) of PHB from {Hf(2)OiPr$_2$} at 40 °C
Figure 4 $^{13}$C-$^1$H and $^1$H NMR (500MHz, CDCl$_3$) for PLA-b-PHB
1.4 GPC

Figure 5 \{\text{Hf(2)OPr}_2\} solution polymerisation for 24 hours at 80 °C
1.5 Ligand and Complex Synthesis:

2-hydroxyaniline (1 g, 9.16 mmol) was dissolved in THF (20 cm³), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (5.49 g, 18.35 mmol) in THF (20 cm³) was added. Triethylamine (1.86 g, 3 ml, 18.35 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated via flash chromatography (CH₂Cl₂) to obtain the product (3.82 g, 76 %). ¹H NMR (CDCl₃) 1.28 (18H, s, C(CH₃)₃), 1.40 (18H, s, C(CH₃)₃), 4.14 (4H, s, CH₂), 6.82 – 6.87 (2H, m, Ar-H), 6.97 (3H, d J = 2.5 Hz, Ar-H), 7.20 (2H, d J = 2.5 Hz, Ar-H) and 7.24 (1H, d J = 1.5 Hz, Ar-H)

¹³C{¹H} NMR (CDCl₃) 29.8, 31.6 (C(CH₃)₃), 34.1, 34.6 (C(CH₃)₃), 56.4 (CH₂), 114.7, 116.1, 120.6 (Ar-CH), 121.8 (Ar-C), 122.1, 123.5, 125.8 (Ar-CH), 135.5, 135.6, 141.7 (Ar-C), 151.3, 152.1 (Ar-O). m/z calc. C₃₆H₅₁NO₃ 546.3947, found 546.3985

2-amino-p-cresol (1 g, 8.12 mmol) was dissolved in THF (20 cm³), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (4.84 g, 16.17 mmol) in THF (20 cm³) was added. Triethylamine (1.64 g, 2.5 ml, 16.17 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated via flash chromatography (CH₂Cl₂) to obtain the product (3.46 g, 76 %). ¹H NMR (CDCl₃) 1.29 (18H, s, C(CH₃)₃), 1.40 (18H, s, C(CH₃)₃), 2.23 (3H, s, CH₃), 4.13 (4H, s, CH₂), 6.74 (2H, dd J = 4.5 Hz, 1.5 Hz, Ar-H), 7.00 (2H, d J = 2.5 Hz, Ar-H), 7.04 (1H, d J = 1.5 Hz, Ar-H) and 7.20 (2H, d J = 2.5 Hz, Ar-H).

¹³C{¹H} NMR (CDCl₃) 20.7 (CH₃), 29.7, 31.6 (C(CH₃)₃), 34.1, 34.6 (C(CH₃)₃), 56.3 (CH₂), 114.6, 115.7, 120.7 (Ar-CH), 121.7 (Ar-C), 123.4, 125.8 (Ar-CH), 129.8, 135.2, 135.6, 141.5 (Ar-C), 148.6, 152.2 (Ar-O). m/z calc. C₃₇H₅₃NO₃Na 582.3923, found 582.3913.
2-amino-4-tert-butylphenol (1 g, 8.12 mmol) was dissolved in THF (20 cm³), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (3.62 g, 12.10 mmol) in THF (20 cm³) was added. Triethylamine (1.23 g, 2.0 ml, 12.10 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated via flash chromatography (CH₂Cl₂) to obtain the product (2.12 g, 58 %). ¹H NMR (CDCl₃) 1.28 (9H, s, C(CH₃)₃), 1.30 (18H, s, C(CH₃)₃), 1.42 (18H, s, C(CH₃)₃), 4.19 (4H, s, CH₂), 6.79 (1H, d J = 8.5 Hz, Ar-H), 6.99 (1H, d J = 8.5 Hz, Ar-H), 7.03 (2H, d J = 1.5 Hz, Ar-H), 7.22 (2H, d J = 1.5 Hz, Ar-H), 7.31 (1H, s, Ar-H). ¹³C{¹H} NMR (CDCl₃) 29.8, 31.5, 31.6 (C(CH₃)₃), 34.1, 34.3, 34.6 (C(CH₃)₃), 56.4 (CH₂), 115.3, 119.2, (Ar-CH), 121.8 (Ar-C), 122.2, 123.5, 125.6 (Ar-CH), 134.7, 135.6, 141.5, 143.3 (Ar-C), 148.5, 152.2 (Ar-O). m/z calc. C₄₀H₅₉NO₃⁺ = 602.4573, found 602.4620

2-amino-4-chlorophenol (1 g, 6.97 mmol) was dissolved in THF (20 cm³), to which a solution of 3,5-di-tert-2-hydroxybenzyl bromide (4.17 g, 13.94 mmol) in THF (20 cm³) was added. Triethylamine (1.41 g, 2.0 ml, 13.94 mmol) was added and the mixture stirred at 80 °C for three hours. The precipitate was filtered and the solvent removed under reduced pressure. The product was isolated via flash chromatography (CH₂Cl₂) to obtain the product (2.30 g, 57 %). ¹H NMR (CDCl₃) 1.30 (18H, s, C(CH₃)₃), 1.41 (18H, s, C(CH₃)₃), 4.12 (4H, s, CH₂), 6.76 (1H, d J = 8.5 Hz, Ar-H), 6.91 (1H, dd J = 8.5 Hz, 2.5 Hz, Ar-H), 7.01 (2H, d J = 2.5 Hz, Ar-H), 7.20 (1H, d J = 2.5 Hz, Ar-H), 7.22 (2H, d J = 2.5 Hz, Ar-H). ¹³C{¹H} NMR (CDCl₃) 29.7, 31.6 (C(CH₃)₃), 34.1, 34.6 (C(CH₃)₃), 56.1 (CH₂), 116.8, (Ar-CH), 121.4 (Ar-C), 122.7, 123.6 (Ar-CH), 124.9 (Ar-C), 125.3, 126.0 (Ar-CH) 135.6, 136.6, 141.8 (Ar-C), 150.0, 152.0 (Ar-O). m/z calc. C₃₆H₴₇NO₃Cl⁺ = 580.3557, found 580.3523.

{Hf(2)(OiPr)₃}₂ Hf(OiPr)₄ PrOH (0.5 g, 1.05 mmol) was dissolved in toluene (20 cm³) to which 2H₃ (0.57 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed in-vacuo and the product was recrystallised in hexane. After 4 days at -20 °C a crop of crystals were obtained which were filtered and dried. ¹H (d₈-THF) 1.20 (36H, s, C(CH₃)₃), 1.38 (12H, d J = 6 Hz, CH₃ isopropoxide), 1.48 (36H, s, C(CH₃)₃), 3.82 (4H, br s, CH₂), 4.12 (4H, d J = 12.5 Hz, CH₂), 4.67 (2H, sept J = 6 Hz, CH isopropoxide), 6.33 (2H, dd J = 1.5 Hz, 8.0 Hz, Ar-H), 6.62 (2H, dd J = 1.5 Hz, 8.0 Hz, Ar-H), 6.84 (4H, td J = 1.5 Hz, 8.0 Hz, Ar-H), 7.13 – 7.19 (6H, m, Ar-H), 7.47 (2H, dd J = 1.5 Hz, 8.0 Hz, Ar-H). ¹³C{¹H} (d₈-THF) 28.3 (CH₃ isopropoxide), 32.2 (C(CH₃)₃), 34.7, 35.7 (C(CH₃)₃), 60.0 (CH₂), 72.4 (CH isopropoxide), 118.2, 119.0, 123.9 (Ar-CH), 125.1 (Ar-C), 126.3,
129.1, 129.7 (Ar-CH), 131.7, 140.2, 140.4 (Ar-C), 132.8, 163.0 (Ar-O). Anal: Calc for C_{39}H_{55}NO_{4}Hf C, 60.03; H, 7.10; N, 1.79. Found: C, 60.7; H, 7.41; N, 1.69.

\{\text{Hf(3)OiPr}_{2} \text{Hf(OiPr)}_{4} \text{iPrOH}\} (0.5 \text{ g}, 1.05 \text{ mmol}) was dissolved in toluene (20 cm^3) to which 3H\text{I} (0.59 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed \textit{in-vacuo} and the product was recrystallised in hexane. After 7 days at -20 °C a crop of crystals were obtained which were filtered and dried. \textsuperscript{1}H \{(d\text{e}-THF) 1.20 (36H, s, C(CH\text{H}_3)_2), 1.37 (12H, d J = 6 Hz, CH\text{H}_3 isopropoxide), 1.48 (36H, s, C(CH\text{H}_3)_2), 2.23 (3H, s, CH\text{H}_2), 3.84 (4H, br s, CH\text{H}_2), 4.10 (4H, d J = 12.5 Hz, CH\text{H}_2), 4.66 (2H, sept J = 6.0 Hz, CH isopropoxide), 6.21 (2H, d J = 8.0 Hz, Ar-H), 6.62 (2H, dd J = 2.0 Hz, 8.5 Hz, Ar-H), 6.77 – 6.95 (4H, m, Ar-H), 7.14 – 7.23 (4H, m, Ar-H), 7.28 (2H, d J = 2.0 Hz, Ar-H). \textsuperscript{13}C \{(d\text{e}-THF) 20.9 (CH\text{H}_3), 29.4 (CH\text{H}_3 isopropoxide), 32.3 (C(CH\text{H}_3)_2), 34.8, 35.8 (C(CH\text{H}_3)_2), 63.8 (CH\text{H}_2), 72.4 (CH isopropoxide), 118.6, 123.9, 124.2 (Ar-CH), 125.3 (Ar-C), 126.4, 129.7 (Ar-CH), 137.2, 139.9, 140.2 (Ar-C), 158.6, 160.7 (Ar-O). Anal: Calc for C_{40}H_{57}NO_{4}Hf C, 60.48; H, 7.23; N, 1.76. Found: C, 59.4; H, 7.17; N, 1.74.

\{\text{Hf(4)OiPr}_{2} \text{Hf(OiPr)}_{4} \text{iPrOH}\} (0.5 \text{ g}, 1.05 \text{ mmol}) was dissolved in toluene (20 cm^3) to which 4H\text{I} (0.63 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed \textit{in-vacuo} and the product was recrystallised in hexane. After 2 days at -20 °C a crop of crystals were obtained which were filtered and dried. \textsuperscript{1}H \{(d\text{e}-THF) 1.20 (18H, s, C(CH\text{H}_3)_2), 1.30 (36H, s, C(CH\text{H}_3)_2), 1.37 (12H, d J = 6 Hz, CH\text{H}_3 isopropoxide), 1.47 (36H, s, C(CH\text{H}_3)_2), 3.90 (4H, br s, CH\text{H}_2), 4.11 (4H, d J = 12.5 Hz, CH\text{H}_2), 4.66 (2H, sept J = 6.0 Hz, CH isopropoxide), 6.26 (2H, d J = 8.5 Hz, Ar-H), 6.90 (4H, dd J = 2.0 Hz, 8.5 Hz, Ar-H), 7.04 – 7.29 (6H, m, Ar-H), 7.46 (2H, d J = 2.0 Hz, Ar-H). \textsuperscript{13}C \{(d\text{e}-THF) 26.1 (CH\text{H}_3 isopropoxide), 32.3, 32.4 (C(CH\text{H}_3)_2), 34.8, 35.0, 35.8 (C(CH\text{H}_3)_2), 64.6 (CH\text{H}_2), 72.4 (CH isopropoxide), 118.2, 120.5, 124.0 (Ar-CH), 125.3 (Ar-C), 125.9, 126.3 (Ar-CH), 135.0, 137.2, 139.5, 141.1 (Ar-C), 158.7, 160.6 (Ar-O). Anal: Calc for C_{43}H_{61}NO_{4}Hf C, 61.74; H, 7.59; N, 1.67. Found: C, 60.3; H, 7.83; N, 1.52.

\{\text{Hf(5)OiPr}_{2} \text{Hf(OiPr)}_{4} \text{iPrOH}\} (0.5 \text{ g}, 1.05 \text{ mmol}) was dissolved in toluene (20 cm^3) to which 5H\text{I} (0.61 g, 1.05 mmol) was added. The solution was stirred for 2 hours, after which time the solvent was removed \textit{in-vacuo} and the product was recrystallised in hexane. After 20 days at -20 °C a crop of crystals were obtained which were filtered and dried. \textsuperscript{1}H \{(d\text{e}-THF) 1.08 (12H, d J = 6 Hz, CH\text{H}_3 isopropoxide), 1.21 (36H, s, C(CH\text{H}_3)_2), 1.37 (12H, d J = 6 Hz, CH\text{H}_3 isopropoxide), 1.47 (36H, s, C(CH\text{H}_3)_2), 3.84 (4H, br s, CH\text{H}_2), 4.11 (4H, dd J = 6.5 Hz, 12.5 Hz, CH\text{H}_2), 4.65 (2H, sept J = 6.0 Hz, CH isopropoxide), 6.28 (2H, dd J = 2.5 Hz, 8.5 Hz, Ar-H), 6.84 (4H, td J = 2.5 Hz, 8.5 Hz, Ar-H), 7.15 – 7.23 (4H, m, Ar-H), 7.53 (2H, d J = 2.5 Hz, Ar-H), 7.59 (2H, d J = 2.5 Hz, Ar-H). \textsuperscript{13}C \{(d\text{e}-THF) 26.1 (CH\text{H}_3 isopropoxide), 28.2, 30.8 (C(CH\text{H}_3)_2), 32.2, 32.3 (C(CH\text{H}_3)_2), 34.8, 35.8 (C(CH\text{H}_3)_2), 61.9 (CH\text{H}_2), 72.6 (CH isopropoxide), 119.9 (Ar-CH), 122.5, 123.0 (Ar-C), 124.1, 124.9 (Ar-CH), 125.0 (Ar-C), 126.5, 129.1 (Ar-CH), 137.4, 140.5 (Ar-C), 162.1, 162.3 (Ar-O). Anal: Calc for C_{39}H_{54}NO_{3}Cl\text{Hf C, 57.49; H, 6.67; N, 1.72. Found: C, 57.6; H, 6.77; N, 1.70.
1.6 NMR of complexes

**Figure 6**: $^1$H NMR of {Hf(2)O\textit{Pr})$_2$ at room temperature in d$_8$-THF showing fluxionality

**Figure 7**: $^1$H NMR of {Hf(2)O\textit{Pr})$_2$ at 230 K in d$_8$-THF showing that the complex has been isolated in its monomeric form at low temperature with the possibility of a THF molecule coordinated to the metal centre differentiating all protons of the CH$_2$ groups to be in equivalent.

The investigation of variable temperature shows that with the bulkier ligand with a 'Bu at the para position to the oxygen on the amine phenyl ring differentiates all protons into 4 doublets at 233 K indicating the all the protons are in different environments. However, with the less steric bulky ligand with a H at the para position to the oxygen on the amine phenyl ring, at low temperature, two protons are still seen as equivalent, and the other two are inequivalent shown by a singlet and two doublets.