

Supporting Information

Synthesis of Ultrahigh-Molecular-Weight Ethylene/1-Octene Copolymers with Salalen Titanium (IV) Complexes Activated by Methyaluminoxane

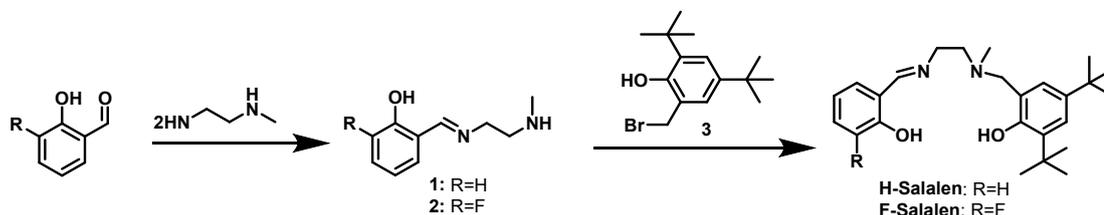
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1. Synthesis of Salalen titanium complexes

The related ligands and final complexes were synthesized by the following synthetic routes¹:



1.1 Synthesis of 2-(((methylamino)ethylimino)methyl)-phenol

N-Methylethylenediamine (1.12g, 15.2 mmol) was added to the toluene solution (30ml) of salicylaldehyde (1.8g, 15.2 mmol), followed by refluxing for 120 minutes. Then the toluene was removed by evaporation under vacuum to obtain a yellow oil for direct use, with a yield of 97 %. ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 3H, CH₃), 2.83 (t, 2H, CH₂), 3.62 (t, 2H, CH₂), 6.75 - 6.89 (m, 2H, ArH), 7.13-7.22 (m, 2H, ArH), 8.28 (s, 1H, N=CH). ¹³C NMR (125 MHz, CDCl₃) δ 36.3 (CH₃), 51.9, 59.6 (CH₂), 117.2, 118.5, 131.4, 132.4, (Ar-CH), 138.5 (Ar-C), 161.4 (Ar-O), 166.1 (CH). Anal. Calcd for C₁₀H₁₄N₂O: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.43; H, 7.95; N, 15.78.

1.2 Synthesis of 2-(((methylamino)ethylimino)methyl)-6-fluorinephenol

N-Methylethylenediamine (1.12g, 15.2 mmol) was added to the toluene solution (30ml) of 3-fluoro-2-hydroxybenzaldehyde (2.1g, 15.2 mmol), followed refluxing for 120 minutes. Then the toluene was removed by evaporation under vacuum to obtain a brown oil for direct use, with a yield of 93 %. ¹H NMR (500 MHz, CDCl₃) δ 2.46 (s, 3H, CH₃), 2.93 (t, 2H, CH₂), 3.74 (t, 2H, CH₂), 6.86 (t, 1H, ArH), 6.94 (d, 1H, ArH), 7.28 (d, 1H, ArH), 8.39 (s, 1H, N=CH). ¹³C NMR (125 MHz, CDCl₃) δ 36.3 (CH₃), 48.9, 51.5 (CH₂), 117.5, 125.6, 128.8, 130.2 (Ar-C), 151.1 (Ar-O), 154.3 (Ar-F), 161.2 (CH). Anal. Calcd for C₁₀H₁₃FN₂O: C, 61.21; H, 6.68; N, 9.68. Found: C, 61.25; H, 6.62; N, 9.62

1.3 Synthesis of 2-(bromomethyl)-4,6-di-tert-butylphenol

2,4-di-tert-butylpheno (1.7 g, 42.2 mmol) of was added to 25 ml glacial acetic acid, and stirred to sufficiently dissolved. Then paraformaldehyde (1.4g, 46.7mmol) was added to the solution and continued to stir at room temperature for 120 minutes. HBr solution in acetic acid (45 ml, 33 wt %) was added dropwise to the formed suspension, followed by stirring for 30 minutes. Finally orange oil was obtained by removing residual HBr and acetic acid, using n-hexene as a recrystallization solvent to produce orange crystalline, with a yield of 91 %. ¹H NMR (500 MHz, CDCl₃) δ 1.29 (s, 9H, C(CH₃)₃), 1.43 (s, 9H, C(CH₃)₃), 4.58 (s, 2H, CH₂Br), 5.28 (s, 1H, OH), 7.10 (d, 1H, ArH), 7.33 (d, 1H, ArH). ¹³C NMR (125 MHz, CDCl₃) δ 32.23, 34.14, 35.46, 37.00, 37.59, 125.93, 127.55, 128.48, 139.20, 145.91, 154.48. Calcd for C₁₁H₁₅BrO: C, 54.34; H, 6.22. Found: C, 54,.39; H, 6.34.

1.4 Synthesis of H-Salalen ligand

THF solution of 2-(((methylamino)ethylimino)methyl]-phenol (2.44 g, 13.7 mmol) and 9 ml Triethylamine was added into 30ml THF solution of 2-(bromomethyl)-4,6-di-tert-butylphenol (4.1g, 13.7mmol), and then stirred at room temperature for 120 minutes, followed by filtration and removing solvent under vacuum. Finally, methanol was used as a recrystallization solvent to obtain yellow crystalline, with a yield of 82 %. ¹H NMR (500 MHz, CDCl₃) δ 1.27 (s, 9H, C(CH₃)₃), 1.36 (s, 9H, C(CH₃)₃), 2.39 (s, 3H, CH₃) 2.84 (t, 2H, CH₂), 3.74 (s, 2H, CH₂), 3.78 (t, 2H, CH₂), 6.82 (s, 1H, ArH), 6.88 (t, 1H, ArH), 6.96 (d, 1H, ArH), 7.17-7.35 (m, 3H, ArH), 8.37 (s, 1H, N=CH). ¹³C NMR (125 MHz, CDCl₃) δ 29.6, 31.7, 34.2, 34.8, 42.1, 57.0, 57.6, 62.3, 117.0, 118.7, 118.8, 121.0, 123.0, 131.4, 132.4, 135.9, 140.6, 154.3, 161.0, 166.3. Anal. Calcd for C₂₅H₃₆N₂O₂: C, 75.72; H, 9.15; N, 7.06. Found: C, 75.75; H, 9.16; N, 7.05. HRMS (ESI) *m/z*: [M⁺H]⁺ calcd for C₂₅H₃₇N₂O₂, 397.2855, found, 397.2842.

1.5 Synthesis of F-Salalen ligand

THF solution of 2-(((methylamino)ethylimino)methyl]-6-fluorinephenol (1.96 g, 10 mmol) and 9 ml Triethylamine was added into 30ml THF solution of 2-(bromomethyl)-4,6-di-tert-butylphenol (3.29 g, 11 mmol), and then stirred at room

temperature for 120 minutes, followed by filtration and removing solvent under vacuum. Finally, methanol was used as a recrystallization solvent to obtain yellow crystalline, with a yield of 76 %. ^1H NMR (500 MHz, CDCl_3) δ 1.27 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.35 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.39 (s, 3H, CH_3) 2.85 (t, 2H, CH_2), 3.74 (s, 2H, CH_2), 3.80 (t, 2H, CH_2), 6.74-6.84 (m, 2H), 7.03 (dd, 1H, ArH), 7.13 (td, 1H, ArH), 7.20 (dd, 1H, ArH), 8.37 (s, 1H, N=CH). ^{13}C NMR (125 MHz, CDCl_3) δ 29.5, 31.7, 34.1, 34.8, 42.1, 56.8, 57.2, 62.1, 117.7, 118.5, 120.8, 123.0, 126.4, 135.6, 140.6, 149.9, 150.4, 152.3, 154.1, 166.0. ^{19}F NMR (470 MHz, CDCl_3) δ -138.1. Calcd for $\text{C}_{25}\text{H}_{35}\text{FN}_2\text{O}_2$: C, 72.43; H, 8.51; N, 6.76. Found: C, 72.50; H, 8.55; N, 6.83. HRMS (ESI) m/z : $[\text{M}^+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{36}\text{FN}_2\text{O}_2$, 415.2761, found, 415.2755.

1.6 Synthesis of H-Salalen titanium complex

A Schlenk flask was cooled to 0 °C after heating in vacuum and nitrogen replacement for three times, then added H-Salalen ligand (0.5797 g, 1.51 mmol) and 30 ml anhydrous ether. *n*-BuLi (2.5 M in hexane, 3.2 mmol) was added dropwise into the solution slowly and stirred for 60 minutes. Then, TiCl_4 (1 M in toluene, 1.6 mmol) and 30 ml toluene was added to the formed solution at -78 °C, and the mixture was stirred for 60 minutes. The solution was then gradually allowed to warm to room temperature and reacted for another 120 minutes. The insoluble inorganic salts were then filtered under nitrogen atmosphere. The filtrate was evaporated in vacuum to remove solvent, and the residual solid was washed with hexane three times and dried in vacuum to give a dark red powder. Recrystallization in cold toluene gave deep red crystals with a yield of 56 %. ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 1.09 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{A}}$), 1.29 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{A}}$), 1.33 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{B}}$), 1.56 (s, 9H, $\text{C}(\text{CH}_3)_3^{\text{B}}$), 2.67 (d, 1H, CH_2^{A}), 2.70 (s, 3H, CH_3^{B}), 2.75 (d, 1H, CH_2^{B}), 3.00 (t, 1H, CH_2^{A}), 3.05 (s, 3H, CH_3^{A}) 3.50 (d, 1H, CH_2^{B}), 3.58 (d, 1H, CH_2^{A}), 3.62 (d, 1H, CH_2^{A}), 3.86–3.98 (m, 2H, CH_2^{B}), 4.42 (t, 1H, CH_2^{A}), 4.45 (t, 1H, CH_2^{B}), 5.04 (d, 1H, CH_2^{A}), 5.36 (d, 1H, CH_2^{B}), 6.91 (d, 1 H, Ar- H^{A}), 7.00 (s, 1H, Ar- H^{A}), 7.06 (t, 1H, Ar- H^{A}) 7.19 (s, 1H, Ar- H^{A}), 7.27 (t, 1H, Ar- H^{B}), 7.33 (m, 1H, Ar- H^{B}), 7.41 (d, 1H, Ar- H^{A}), 7.48-7.53 (m, 1H, Ar- H^{B}), 7.56 (t, 1H, Ar- H^{B}), 7.61 (t, 1H, Ar- H^{A}), 8.18 (s, 1H, CH^{A}), 8.32 (s, 1H, CH^{B}). ^{13}C NMR (125 MHz,

$C_2D_2Cl_4$) δ 30.6, 31.6, 32.7, 35.6, 35.7, 54.0, 57.7, 59.6, 67.5, 116.9, 123.1, 124.4, 124.7, 125.2, 127.3, 129.4, 130.2, 134.9, 136.9, 137.6, 136.9, 160.1, 163.2, 163.4. Calcd for $C_{25}H_{34}Cl_2N_2O_2Ti$: C, 58.50; H, 6.68; N, 5.46. Found: C, 58.49; H, 6.62; N, 5.48.

1.7 Synthesis of F-Salalen titanium complex

A Schlenk flask was cooled to 0 °C after heating in vacuum and nitrogen replacement for three times, then added F-Salalen ligand (0.5662 g, 1.366 mmol) and 30 ml anhydrous ether. n-BuLi (2.5 M in hexane, 2.5 mmol) was added dropwise into the solution slowly and stirred for 60 minutes. Then, $TiCl_4$ (1 M in toluene, 1.2 mmol) and 30 ml toluene was added to the formed solution at -78 °C, and the mixture was stirred for 60 minutes. The solution was then gradually allowed to warm to room temperature and reacted for another 120 minutes. The insoluble inorganic salts were then filtered under nitrogen atmosphere. The filtrate was evaporated in vacuum to remove solvent, and the residual solid was washed with hexane three times and dried in vacuum to give a dark red powder. Recrystallization in cold toluene gave red crystals with a yield of 64 %. 1H NMR (500 MHz, $C_2D_2Cl_4$) δ 1.08 (s, 9H, $C(CH_3)_3^A$), 1.29 (s, 9H, $C(CH_3)_3^A$), 1.33 (s, 9H, $C(CH_3)_3^B$), 1.55 (s, 9H, $C(CH_3)_3^B$), 2.69 (d, 1H, CH_2^A), 2.71 (s, 3H, CH_3^B), 2.80 (dd, 1H, CH_2^B), 3.00 (t, 1H, CH_2^A), 3.23 (s, 3H, CH_3^A) 3.51 (d, 1H, CH_2^B), 3.57 (d, 1H, CH_2^A), 3.65 (d, 1H, CH_2^A), 3.85–4.01 (m, 2H, CH_2^B), 4.43 (t, 1H, CH_2^A), 4.47 (t, 1H, CH_2^B), 5.02 (d, 1H, CH_2^A), 5.34 (d, 1H, CH_2^B), 6.95-7.04 (m, 2H, Ar- H^A), 7.06 (s, 1H, Ar- H^B), 7.16-7.23 (m, 2H, Ar- H^A), 7.24-7.36 (m, 4H, Ar- H^B), 7.39 (t, 1H, Ar- H^A), 8.21 (s, 1H, CH^A), 8.35 (s, 1H, CH^B). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 30.6, 31.6, 32.6, 35.6, 35.7, 54.3, 57.8, 59.7, 67.7, 122.5, 123.3, 123.5, 124.7, 124.7, 125.3, 126.2, 127.4, 129.8, 136.9, 147.3, 148.6, 160.1, 162.7, 162.8. ^{19}F NMR (470 MHz, $C_2D_2Cl_4$) δ -129.9 (Ar- F^A), -129.0 (Ar- F^B). Calcd for $C_{25}H_{33}Cl_2FN_2O_2Ti$: C, 56.52; H, 6.26; N, 5.27. Found: C, 56.49; H, 6.29; N, 5.29.

2. Characterization of Poly(ethylene-*co*-1-octene) by ^{13}C NMR

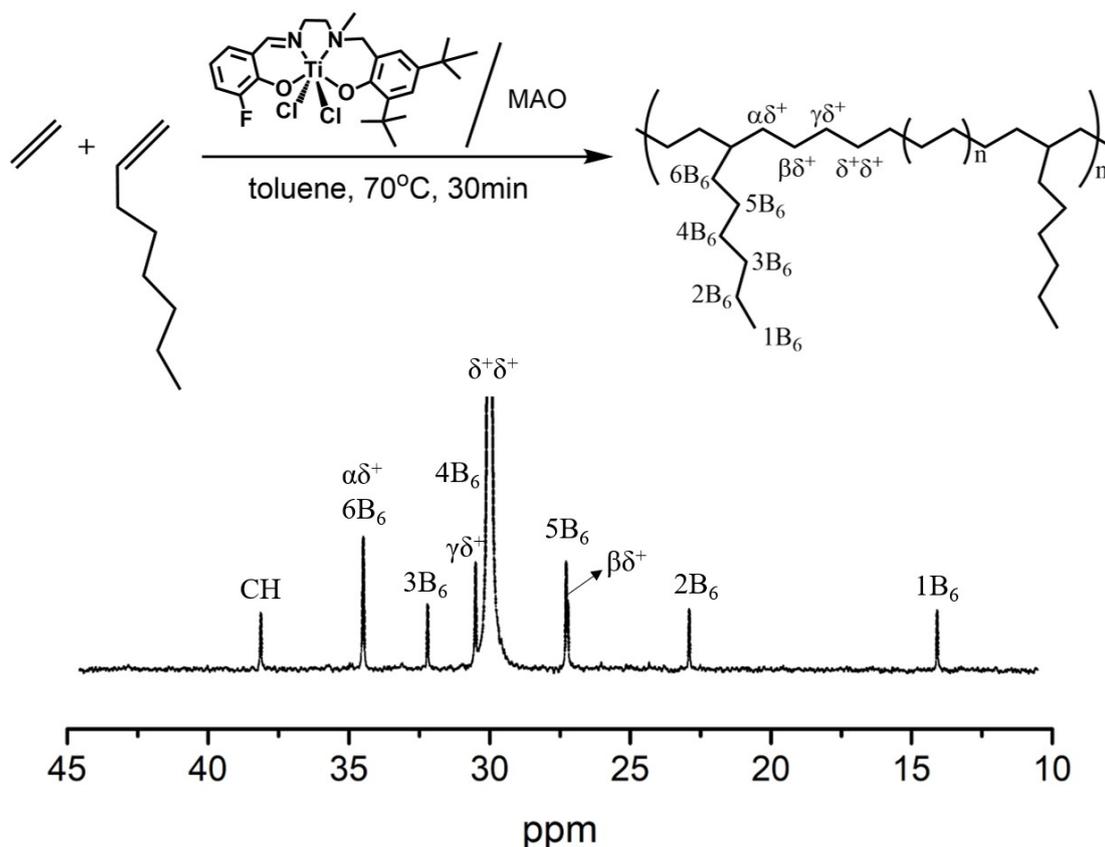


Figure 1. ^{13}C NMR spectrum of poly(ethylene-*co*-1-octene) obtained using the (F-salalen)TiCl₂/MAO (entry 6 in Table 2).

Table 1. Chemical shift calculated and observed and assignments of poly(ethylene-*co*-1-octene) in ^{13}C NMR spectrum.

Carbon assignments	chemical shift (ppm)		Sequence assignment
	previous works ^{2,3}	experimental	
1B ₆	14.02, 14.07	14.01	EOE, EOO, OOE, OOO
2B ₆	22.84, 22.88	22.90	EOE, EOO, OOE, OOO
βδ ⁺	27.33	27.22	EOE
5B ₆	27.33	27.29	EOEE, EEOE
δ ⁺ δ ⁺	29.536	29.97	(EEE) _n
γδ ⁺	30.476	30.50	OEEE, EEEO
3B ₆	32.18, 32.2	32.20	EOE
αδ ⁺ , 6B ₆	34.61, 34.70	34.48	EOEE, EEOE
CH	38.23, 38.24	38.13	EOE

Table 2 The triad and diad distributions for poly(ethylene-*co*-1-octene):E = ethylene, O= 1-octene.^{4,6}

[EEE]	[EEO] +[OEE]	[EOE]	[OEO]	[OOE] +[EOO]	[OOO]	[EE]	[EO] +[OE]	[OO]	r_E	r_O	$r_E r_O$
82.6	11.2	3.8	1.3	1.0	0.1	88.2	11.2	0.6	11.25	0.15	1.69

The “E” average sequence length was calculated by ¹³C NMR triad distribution.⁴

“E” average sequence length = $[EEE + (EEO + OEE) + OEO] / [OEO + 1/2(OEE + EEO)] = 13.8$

3. Analysis of Wide Angle X-ray Diffraction (WAXD)

The crystal size and % crystallinity from XRD were calculated by MDI Jade.⁷⁻⁹

Table 3. The crystal parameters of entry 1, 11, 12, 13, 5, 14 calculated from XRD.

entry	1	11	12	13	5	14
X_c (%)	72.7	68.7	50.1	43.7	28.4	23.4
D_{110} (nm)	26.4	25.3	26.6	20.2	21.3	26.2
D_{200} (nm)	22.3	21.9	21.7	19.5	18.4	23.1

4. Successive Self-nucleation And Annealing (SSA) test

Successive self-nucleation and annealing (SSA) analysis was carried out at the heating and cooling rates of 10 °C/min⁻¹. Samples were first heated to 180 °C, maintained for 10 min, and cooled down to 40 °C. After 1min at 40 °C, samples were heated to the first self-nucleation temperature (T1), maintained for 10 min then cooled down to 40 °C. Successive self-nucleation was achieved by repeatedly heating to the next self-nucleation temperatures and cooling down to 40 °C. After covering the temperature range between 130 and 40 °C, the final heating ramp from 40 up to 200 °C was applied to collect all melting endotherms.¹⁰

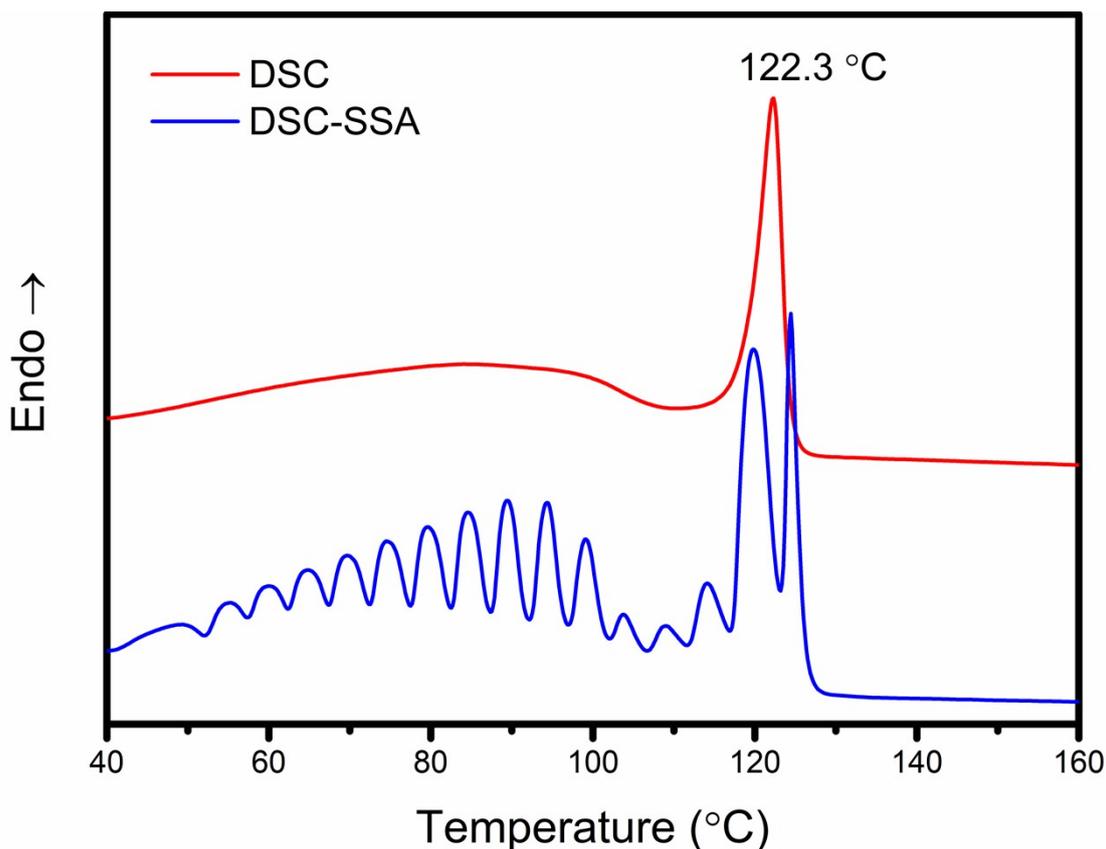


Figure 2. The DSC-SSA thermogram of entry 13.

4. References

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