Synthesis of Novel Salicylaldimine Titanium Complexes and Their Catalytic Activity in Ethylene Polymerization (Postprint)

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Abstract

Using inexpensive salicylaldehyde and TiCl4 as the main raw materials, four salicylaldimine ligands (5-8) and titanium complexes containing bis(phenoxyimine) ligands [O-C6H4-ortho-CH=N-2, 6-(i-Pr)2-C6H3]2TiCl2(13), [O-(5-NO2)-C6H3-ortho-CH=N-2, 6-(i-Pr)2-C6H3]2TiCl2(14), [O-(3, 5-di-Br)-C6H2-ortho-CH=N-2, 6-(i-Pr)2-C6H3]2TiCl2(15), and [O-(3, 5-di-C(CH3)3)-C6H2-ortho-CH= N-2, 6-(i-Pr)2-C6H3]2TiCl2 (16) were synthesized. The molecular structures of ligands 5-8 were characterized by MS, 1H- NMR, and elemental analysis, while the molecular structures of complexes 13-16 were characterized by 1H-NMR and elemental analysis. After activation by MAO (methylaluminoxane), titanium complexes (13-16) could effectively catalyze ethylene polymerization in toluene solvent. Under the conditions of 60°C, 2.0 MPa, and a cocatalyst to main catalyst molar ratio of n(MAO)/n(cat) = 1500 1, the ethylene polymerization activities of titanium complexes (14-16) were 1022.73-1302.27 g · PE/(mmol · Ti · h · MPa), which were much higher than that of the unsubstituted salicylaldimine titanium complex (13). The viscosity-average molecular weight of the obtained polyethylene (determined by viscometry) was 19266-44754, and the molecular weight distribution Mw /Mn determined by GPC was 1.88-2.12. The polymer sample obtained from ethylene polymerization catalyzed by the most active catalyst 15 was characterized by 13C-NMR and DSC, and the results indicated it was linear crystalline polyethylene.

Full Text

Preamble

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Synthesis of Novel Titanium Complexes with Salicylaldimine Ligands and Their Catalytic Performance for Ethylene Polymerization

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Abstract

Four salicylaldimine ligands (5-8) and their titanium complexes containing bis(phenoxy-imine) ligands—[O-C_6H_4-ortho-CH=N-2,6-(i-Pr)$_2$-C_6H_3]$_2$$TiCl_2$ (13), [O-(5-NO_2)-C_6H_3-ortho-CH=N-2,6-(i-Pr)$_2$-C_6H_3]$_2$$TiCl_2$ (14), [O-(3,5-di-Br)-C_6H_2-ortho-CH=N-2,6-(i-Pr)$_2$-C_6H_3]$_2$$TiCl_2$ (15), and [O-(3,5-di-C(CH_3)$_3$)-C_6H_2-ortho-CH=N-2,6-(i-Pr)$_2$-C_6H_3]$_2$$TiCl_2$ (16)—were synthesized using inexpensive salicylaldehyde and $TiCl_4$ as raw materials. The molecular structures of ligands 5-8 were characterized by MS, ^{1}H-NMR, and elemental analysis, while complexes 13-16 were characterized by ^{1}H-NMR and elemental analysis. After activation with MAO (methylaluminoxane), titanium complexes 13-16 effectively catalyzed ethylene polymerization in toluene. Under conditions of 60°C, 2.0 MPa, and a molar ratio of cocatalyst to catalyst n(MAO)/n(cat) = 1500:1, the catalytic activities of complexes 14-16 reached 1022.73–1302.27 g · PE/(mmol · Ti · h · MPa), significantly higher than that of the unsubstituted salicylaldimine titanium complex (13). The resulting polyethylene exhibited viscosity-average molecular weights (measured by viscometry) of 19,266–44,754 and molecular weight distributions Mw/Mn of 1.88–2.12 (determined by GPC). The polymer sample obtained with the most active catalyst 15

was characterized by ^{13}C-NMR and DSC, confirming it as linear crystalline polyethylene.

Keywords: organic polymer materials, titanium complex, catalyst, ethylene polymerization, phenoxy-imine ligands, activity

1. Introduction

In recent years, the synthesis of high-performance polyolefin catalysts using phenoxy-imine ligands has become a research hotspot in olefin coordination polymerization [**?**]. Structural modification of ligands by introducing substituent groups with specific steric hindrance or electronic effects enables tailoring of catalyst molecular structures to produce polymeric materials with unique structures and properties [**?**]. Liu et al. [**?**] investigated titanium catalysts containing such ligands, which, when combined with $ZnEt_2$, catalyzed the synthesis of bimodal polyethylene with controllable molecular weight and exhibited high activity. Matoishi et al. [**?**] examined the ethylene polymerization activity of 16 such catalysts and catalyzed the synthesis of novel PE/PEG materials with good performance. Damavandi et al. [**?**] synthesized two new zirconium-based FI-type catalysts by altering the ligand structure on the salicylaldimine group, finding that replacing the monoaryl ring on the imine nitrogen with an aromatic fused ring increased steric hindrance and reduced catalytic activity, but increased the molecular weight of the resulting polyethylene. Many late-transition non-metallocene complexes with phenoxy-imine ligands exhibit high activity for ethylene coordination polymerization comparable to early-transition metal complexes such as metallocene chromium, zirconium, and titanium [**?**, **?**].

Studies by Younkin et al. [**?**], Connor et al. [**?**], and Bansleben et al. [**?**] on nickel compounds containing such ligands for ethylene polymerization demonstrated that introducing bulky substituents at the ortho and para positions of the salicylaldehyde oxygen significantly enhanced ethylene polymerization activity. Suzuki et al. [**?**] introduced strong electron-withdrawing groups into the ligands to improve the polymerization performance of Group IVB complexes for ethylene and pioneered the use of salicylaldimine early-transition metal complexes (known as FI catalysts) for ethylene polymerization, discovering they exhibited higher catalytic activity than metallocene compounds Cp_2TiCl_2 and Cp_2ZrCl_2. Although many zirconium-based FI catalysts synthesized by Fujita' s group showed high activity, conventional titanium-based FI catalysts generally exhibited relatively low activity [**?**]. After introducing strongly electron-withdrawing fluorine groups F(s) onto the phenoxy-imine ligands, such titanium-based FI catalysts demonstrated extremely high activity for ethylene and propylene polymerization under mild conditions [**?**, **?**]. However, these fluorine-containing FI-type titanium catalysts are not readily accessible, resulting in high preparation costs that hinder industrialization. Jin et al. [**?**] synthesized allyl Schiff base titanium metal complexes that, in the presence of cocatalyst (MMAO), also showed high

catalytic activity for ethylene polymerization. The synthesized bidentate titanium olefin polymerization catalyst $[C_3H_6(N{=}CH\text{-}Ar\text{-}O)_2]TiCl_2$ [**?**] exhibited not only high catalytic activity but also mild polymerization conditions and could produce polyethylene with different molecular weights. To obtain efficient FI catalysts with high industrial potential, this work uses inexpensive and readily available salicylaldehyde as the starting material to prepare four substituted salicylaldehydes through high-yield reactions such as bromination and nitration. Condensation with 2,6-diisopropylaniline followed by coordination with $TiCl_4$ yields FI-type titanium catalysts for ethylene polymerization.

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2. Experimental

2.1 Materials and Reagents

Reagent-grade materials included 2,6-diisopropylaniline and methylaluminoxane (MAO) as a 1.25 mol/L toluene solution. Solvents such as tetrahydrofuran (THF), toluene, and petroleum ether were first dried over NaOH(s) for several days, then refluxed with benzophenone and sodium until turning purple, and distilled under argon protection.

2.2 Synthesis of Ligands and Complexes

The synthetic routes for ligands 5-8 are shown in [Figure 1: see original paper].

(1) Synthesis of 5-nitrosalicylaldehyde
5-nitrosalicylaldehyde was synthesized following the method in reference [**?**]. The product was obtained as light yellow crystals with a yield of 56.00% and melting point of 125–127°C (literature value 125–126°C). GC-MS analysis showed a purity of 97.60%, with the remainder being 3-nitrosalicylaldehyde. Major mass fragments (m/z): 167 (M^+, 100), 151, 137, 120, 109, 75, 65, 53, 39.

(2) Synthesis of 3,5-dibromosalicylaldehyde
3,5-dibromosalicylaldehyde was synthesized following the method in reference [**?**]. The product was obtained as light yellow needle crystals with a yield of 83.00% and melting point of 85–86°C (literature value 84–86°C). GC-MS analysis showed a purity of 98.71%. Major mass fragments (m/z): 280 (M, 100%), 262, 252, 234, 223, 170, 155, 143, 119, 91, 74, 63.

(3) Synthesis of 3,5-di-tert-butylsalicylaldehyde
3,5-di-tert-butylsalicylaldehyde was synthesized following the method in reference [**?**]. The product was obtained as light yellow crystals with a yield of 76.60% and melting point of 58–59°C (literature value 58–60°C). Major mass fragments (m/z): 234 (M^+, 28%), 219 (M^+-CH_3, 100%), 191, 163, 135, 57. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.65 (s, 1H, OH), 9.86 (s, 1H, CHO), 7.59 (d, J_{HH} = 1H, Ar-H), 7.35 (d, J_{HH} = 1H, Ar-H), 1.43 (s, 9H, -$C(CH_3)_3$), 1.33 (s, 9H, -$C(CH_3)_3$).

(4) Synthesis of Ligands 5, 6, 7, and 8

Four salicylaldimine ligands were synthesized following the method in reference [**?**]. Using 30.0 mL ethanol as solvent, 50.00 mmol of the synthesized substituted salicylaldehyde and 8.90 g of 2,6-diisopropylaniline were added with 0.5 mL formic acid. After stirring at room temperature for 10 h, a large amount of yellow powder formed. The mixture was cooled, filtered, washed with cold anhydrous ethanol, and recrystallized from anhydrous ethanol to obtain yellow needle crystals 5-8. The yields were 91.21%, 90.80%, 90.92%, and 92.50%, with purities of 98.81%, 98.44%, 99.13%, and 96.97%, respectively.

Ligand 5: ^{1}H-NMR: δ = 1.18 (d, J_{HH} = 4.8 Hz, 12H, CH_3), 3.04 (m, 2H, i-Pr-CH), 6.93 (d, J_{HH} = 4.8 Hz, 1H, Ar-H), 7.09 (d, J_{HH} = 3.6 Hz, 1H, Ar-H), 7.18 (s, 3H, Ar-H), 7.35 (d, J_{HH} = 3.6 Hz, 1H, Ar-H), 7.42 (d, J_{HH} = 3.6 Hz, 1H, Ar-H), 8.30 (s, 1H, CH=N), 14.98 (s, 1H, OH). Elemental analysis ($C_{19}H_{23}ON$, 281.40): found (calcd) (%): C 81.34 (81.10), H 8.36 (8.24), N 4.80 (4.98).

Ligand 6: Major MS fragments: m/z = 326 (M^+, 83%), 311 (M^+-CH_3, 75%), 269, 252, 22, 188, 174, 146, 132, 117, 91, 77. IR (cm^{-1}): 3410, 3076, 1622, 1500, 1330, 1180, 826. ^{1}H-NMR: δ = 1.32 (d, J_{HH} = 4 Hz, 12H, CH_3), 3.15 (m, 2H, i-Pr-CH), 7.23–7.42 (m, 3H, Ar-H), 8.39–8.49 (m, 3H, Ar-H), 8.59 (s, 1H, CH=N), 14.28 (s, 1H, OH). Elemental analysis ($C_{19}H_{22}O_3N_2$, 326.39): found (calcd) (%): C 69.71 (69.92), H 6.86 (6.79), N 8.52 (8.58).

Ligand 7: Major MS fragments: m/z = 439 (M^+, 85%), 424 (M^+-CH_3, 88%), 382 (100%), 367, 301, 265, 220, 204, 188, 174, 160, 146, 132, 117, 104, 91, 77, 63, 41. ^{1}H-NMR: δ = 1.29 (d, J_{HH} = 2 Hz, 12H, CH_3), 3.13 (m, 2H, i-Pr-CH), 7.28 (s, 3H, Ar-H), 7.51 (s, 1H, Ar-H), 7.98 (s, 1H, Ar-H), 8.45 (s, 1H, CH=N), 14.11 (s, 1H, OH). Elemental analysis ($C_{19}H_{21}Br_2ON$, 439.19): found (calcd) (%): C 52.09 (51.96), H 4.65 (4.82), N 3.13 (3.19).

Ligand 8: Major MS fragments: m/z = 393 (M^+, 100%), 378, 362, 350, 336, 320, 203, 188, 174, 162, 146, 132, 119, 105, 91, 77, 57, 41. ^{1}H-NMR: δ = 1.23 (d, J_{HH} = 3.6 Hz, 12H, i-Pr-CH_3), 1.35 (s, 18H, $C(CH_3)_3$), 3.07 (m, 2H, i-Pr-CH), 7.22 (s, 3H, Ar-H), 7.49 (s, 1H, Ar-H), 7.91 (s, 1H, Ar-H), 8.53 (s, 1H, CH=N), 14.23 (s, 1H, OH). Elemental analysis ($C_{27}H_{39}ON$, 393.61): found (calcd) (%): C 82.56 (82.39), H 9.76 (9.99), N 3.68 (3.56).

2.3 Synthesis of Complexes

Using standard Schlenk techniques, four FI-type titanium catalysts 13-16 were synthesized following the routes shown in [Figure 2: see original paper].

(1) Synthesis of Complex 13

First, 1.48 g (5.27 mmol) of ligand 5 was dissolved in 20.0 mL dichloromethane. This solution was added dropwise to a 150 mL Schlenk flask containing 5.00 g (2.64 mmol) $TiCl_4$ and 30.0 mL dichloromethane. The mixture gradually turned deep purple and was stirred at room temperature for 2 h. After removing the

solvent under reduced pressure, the residue was washed twice with pentane (10.0 mL) and dried under vacuum to obtain ligand 9. The obtained ligand 9 was dissolved in 50.0 mL dichloromethane, and 0.41 g (4.00 mmol) NEt_3 was added. The mixture was stirred at room temperature for 4 h. After removing the solvent under reduced pressure, 100.0 mL tetrahydrofuran was added. NH_4Cl was removed by filtration, and the filtrate was concentrated under reduced pressure. The remaining solid was washed twice with pentane (10.0 mL) to yield 1.13 g (1.67 mmol) of an orange solid, with a yield of 63.38%.

(2) Synthesis of Complex 14

In a 150 mL Schlenk flask that had been evacuated and purged with Ar, 0.02 mol NaH and 50.0 mL THF were added, followed by 3.26 g (10.00 mmol) of ligand 6. The reaction proceeded for 3 h. Unreacted NaH was removed by filtration to obtain the THF solution of ligand sodium salt 10. This solution was added dropwise at -78°C under vigorous stirring to a solution containing 1.70 g (5.00 mmol) $TiCl_4 \cdot 2THF$ and 50.0 mL THF. After addition, the mixture was gradually warmed to room temperature and stirred for 18 h. The solvent was removed under reduced pressure, and 40.0 mL dichloromethane was added with stirring for 15 min. After filtration, the filter cake was washed with dichloromethane (10.0 mL × 2). The combined filtrate was concentrated under reduced pressure to obtain a red solid. The solid was stirred with 20.0 mL diethyl ether and 40.0 mL petroleum ether for 30 min. After filtration, the filter cake was washed twice with petroleum ether (15.0 mL × 2) and dried under vacuum to yield 2.29 g (2.98 mmol) of reddish-brown complex 14, with a yield of 59.60%.

(3) Synthesis of Complex 15

In a 150 mL Schlenk flask that had been evacuated and purged with Ar, 2.31 g (5.27 mmol) of ligand 7 and 20.0 mL dichloromethane were added. A solution containing 0.50 g (2.64 mmol) freshly distilled $TiCl_4$ and 30.0 mL dichloromethane was added dropwise at room temperature. The resulting light red solution was stirred at room temperature for 2 h, then 735.0 L NEt_3 (534.00 mg, 5.27 mmol) was added. The mixture was stirred for an additional 2 h. After removing the solvent under reduced pressure, 80.0 mL toluene was added with stirring for 30 min. The mixture was filtered to remove NH_4Cl, and the clear solution was concentrated to 20.0 mL and placed in a -20°C refrigerator. Red crystals precipitated, and after removing the solvent, the product was washed twice with petroleum ether (15.0 mL × 2). Drying under vacuum yielded 1.89 g (1.90 mmol) of red complex 15, with a yield of 72.11%.

(4) Synthesis of Complex 16

In a 150 mL Schlenk flask that had been evacuated and purged with Ar, 3.92 g (10.00 mmol) of ligand 8, 50.0 mL THF, and 0.02 mol NaH were reacted at room temperature for 3 h. Unreacted NaH was removed by filtration to obtain the THF solution of ligand sodium salt 12. This sodium salt solution was added dropwise at -78°C under stirring to a mixed solution containing 50.0 mL THF and 1.70 g (5.00 mmol) $TiCl_4 \cdot 2THF$. The mixture was slowly warmed to room temperature and stirred for 18 h. After completion, the solvent

was removed under reduced pressure, and 40.0 mL dichloromethane was added. The mixture was stirred, filtered, and the filter cake was washed with 20.0 mL dichloromethane. The filtrate was concentrated under reduced pressure to obtain a red solid. The solid was stirred with 40.0 mL petroleum ether and 20.0 mL diethyl ether for 15 min. After filtration, the filter cake was washed twice with 30.0 mL petroleum ether. Drying under reduced pressure yielded 2.49 g (2.75 mmol) of complex 16, with a yield of 55.00%.

2.4 Ethylene Polymerization Reaction

Ethylene polymerization under pressure was conducted in a 100 mL stainless steel autoclave equipped with a 500 r/min stirrer, feed tube, and gas inlet, as shown in [Figure 3: see original paper]. The reaction temperature was controlled by a temperature control system, and the ethylene pressure was controlled by a pressure valve. Before polymerization, the autoclave was dried, and the autoclave and connected system were evacuated to remove oxygen, then purged three times with ethylene gas. Under ethylene protection, a mixture of catalyst and MAO in toluene solution (total volume 30.0 mL) was added through the feed port in one batch. After feeding, the feed valve was immediately closed and ethylene was introduced to control the reaction temperature and pressure. After the reaction, the system was vented and discharged. The reaction was terminated with ethanol solution containing 10% hydrochloric acid. The obtained polymer was filtered and washed multiple times with ethanol and pure water, then dried under vacuum at 60°C to constant weight for catalyst activity calculation.

Polyethylene molecular weight was determined by viscometry and gel permeation chromatography (GPC). For viscometry, decalin was used as solvent at (135$±$0.1)°C with an Ubbelohde viscometer to measure [ ], and the viscosity-average molecular weight M was calculated using the formula] = 6.77 × 10. For GPC, measurements were performed at 135°C using 1,2,4-trichlorobenzene as mobile phase on a Waters-150-C-ALC/GPC instrument. Polymer melting points were measured using a Perkin Elmer DSC-7 differential scanning calorimeter at a scanning rate of 10°C/min over a range of 50–160°C.

2.5 Analysis and Testing

Elemental analysis was performed on a Perkin-Elmer 240 elemental analyzer using quantitative oxygen combustion and a thermal conductivity detector. FT-IR spectra of ligands and complexes were recorded on a VERTEX 70 spectrometer (KBr pellets). ^{1}H-NMR spectra were recorded on a Bruker Avance DMX500 spectrometer using TMS as internal standard and $CDCl_3$ as solvent. Gas chromatography was performed on an HP6890 instrument with an SE-30 capillary column (50 m × 0.2 × 0.5 m) and FID detector. Mass spectrometry was conducted on an HP6890/5973 GC-MS system using electron impact ionization at 70 eV over a temperature range of 50–300°C.

3. Results and Discussion

3.1 Synthesis and Characterization of Catalysts

Four different methods were employed to coordinate ligands 5-8 with titanium chlorides. Ligands 5 and 7 coordinated with $TiCl_4$ to form intermediate complexes 9 and 11, which then reacted with NEt_3 to form final complexes 13 and 15. In contrast, ligands 6 and 8 formed sodium salts 10 and 12 with NaH, which then coordinated with $TiCl_4 \cdot 2THF$ to form final complexes 14 and 16.

Complex 13: ^{1}H-NMR: δ = 1.13 (d, J_{HH} = 2.8 Hz, 24H, i-Pr-CH_3), 3.55-3.67 (m, 4H, i-Pr-CH), 6.76 (d, J_{HH} = 4.8 Hz, 2H, Ar-H), 7.13 (d, J_{HH} = 2.8 Hz, 2H, Ar-H), 7.21 (d, J_{HH} = 3.6 Hz, 2H, Ar-H), 7.25 (d, J_{HH} = 3.6 Hz, 2H, Ar-H), 7.31 (d, J_{HH} = 4.4 Hz, 2H, Ar-H), 7.61 (d, J_{HH} = 3.2 Hz, 2H, Ar-H), 7.67 (d, J_{HH} = 4.4 Hz, 2H, Ar-H), 8.43 (m, 2H, CH=N). Elemental analysis ($C_{38}H_{44}O_2N_2TiCl_2$, 679.56): found (calcd) (%): C 67.42 (67.16), H 6.41 (6.53), N 4.32 (4.12).

Complex 14: The ^{1}H-NMR spectrum is shown in [Figure 4: see original paper]. The data indicate: δ = 1.15 (d, J_{HH} = 4 Hz, 24H, i-Pr-CH_3), 2.92-2.95 (m, 2H, i-Pr-CH), 3.15 (m, 2H, i-Pr-CH), 6.81-7.18 (m, 12H, Ar-H), 8.35-8.37 (m, 2H, CH=N). Elemental analysis ($C_{38}H_{42}O_6N_4TiCl_2$, 769.56): found (calcd) (%): C 59.64 (59.31), H 5.36 (5.50), N 7.42 (7.28). IR analysis (cm^{-1}): 3078, 1602, 1058, 1336, 1134, 826, 620, 490. Comparison of IR spectra between ligand 6 and complex 14 revealed significant differences: the C=N stretching vibration of the complex appeared at 1602 cm^{-1}, shifting 20 cm^{-1} lower than the corresponding ligand peak at 1622 cm^{-1}, indicating nitrogen atom participation in coordination. The disappearance of the -OH characteristic absorption peak also confirmed deprotonation of the hydroxyl group during complex synthesis.

Complex 15: The ^{1}H-NMR characterization is shown in [Figure 5: see original paper]. The data indicate: δ = 1.17 (d, J_{HH} = 4 Hz, 24H, i-Pr-CH_3), 2.92 (m, 4H, i-Pr-CH), 7.20 (s, 6H, Ar-H), 7.44 (s, 2H, Ar-H), 7.80 (s, 2H, Ar-H), 8.20 (s, 2H, CH=N). Elemental analysis ($C_{38}H_{40}Br_4O_2N_2TiCl_2$, 995.15): found (calcd) (%): C 45.97 (45.86), H 4.22 (4.05), N 2.63 (2.81).

Complex 16: ^{1}H-NMR: δ = 1.22 (d, J_{HH} = 4.8 Hz, 24H, i-Pr-CH_3), 1.31 (s, 18H, -C(CH_3)$_3$), 1.35 (s, 18H, -C(CH_3)$_3$), 2.98-3.29 (m, 4H, i-Pr-CH), 7.11-7.42 (m, 10H, Ar-H), 8.15 (s, 2H, CH=N). Elemental analysis ($C_{54}H_{76}O_2N_2TiCl_2$, 903.99): found (calcd) (%): C 71.98 (71.75), H 8.53 (8.47), N 3.02 (3.10).

Comparing the ^{1}H-NMR data of 5 vs. 13, 6 vs. 14, 7 vs. 15, and 8 vs. 16, the -OH peaks disappeared in complexes 13, 14, 15, and 16. Additionally, hydrogens near the coordinating O and N atoms showed chemical shifts (i-Pr-CH, Ar-CH=N- shifted downfield) [**?**, **?**], confirming that ligands 5, 6, 7, and 8 formed complexes 13, 14, 15, and 16 with titanium compounds, respectively. Elemental analysis results confirmed the composition of the target compounds.

3.2 Ethylene Polymerization Catalysis

Ethylene polymerization was catalyzed by complexes 13, 14, 15, and 16 under reaction conditions of 60°C, 2.0 MPa pressure, and 1 h reaction time. Catalyst activities were calculated based on the dried polymer yield, and polyethylene molecular weights were determined by viscometry. The results calculated according to formula (1) are listed in .

Comparison of entries 1 and 3, 1 and 5, 1 and 7, and 1 and 9 in shows that the cocatalyst alone has no catalytic activity for ethylene polymerization in the absence of the main catalyst. Comparison of entries 6 and 7, which show the highest activity, reveals that the main catalyst alone has no catalytic activity for ethylene polymerization in the absence of cocatalyst, a pattern applicable to complexes 13, 14, and 16. When the catalytic system composed of main catalyst and cocatalyst at a certain ratio catalyzes ethylene polymerization, high activity is observed, primarily because: (1) cocatalyst MAO can remove harmful impurities from the polymerization system; and (2) MAO alkylates the halogenated metal complex and forms the true active center with the main catalyst (halogenated metal complex), maintaining the stability of the active center [**?**].

The results in show that under identical reaction conditions, the ethylene polymerization activities of substituted phenoxy-imine titanium complexes 14-16 follow the order: $15 > 14 > 16$, all significantly higher than that of unsubstituted phenoxy-imine titanium complex 13 ($120.45\ g \cdot PE/(mmol \cdot Ti \cdot h \cdot MPa)$). A possible explanation is that the introduction of electron-withdrawing substituents such as nitro and halogen groups leads to a substantial increase in the number of active polymerization centers [**?**]. Specifically, electron-withdrawing substituents on the ligand increase the number of metal-carbon cationic active centers, reducing the activation energy for ethylene insertion, with stronger electron-withdrawing ability correlating with higher catalytic activity [**?**, **?**]. Introducing bulky substituents such as tert-butyl groups (complex 16) into the phenoxy structure also significantly enhances catalytic activity compared to the unsubstituted complex. However, synthesis of such tert-butyl-substituted complexes is considerably more difficult than bromo- or nitro-substituted complexes. Therefore, coordination catalyst 15 has greater development potential and offers significant cost advantages compared to Mitsui Chemicals' Fujita catalysts [**?**, **?**] that introduce strongly electron-withdrawing fluorine groups F(s) and trifluoromethyl groups CF_3(s) onto the phenoxy-imine ligands.

3.3 Effect of Reaction Time on Ethylene Polymerization

To investigate the active lifetime of the complexes for ethylene polymerization, polymerization reactions catalyzed by complexes 13-16 were terminated at 15, 30, 45, 60, 75, 90, 105, and 120 min, and the polymer yields were measured.

As shown in , when the weighed polymer yield was divided by catalyst moles, reaction time, and polymerization pressure, catalyst activity initially increased

then decreased with prolonged reaction time, reaching maximum activity at approximately 60–75 min. At 120 min, the catalysts were essentially deactivated. This indicates that the active lifetime of these catalysts is less than 2 h. The main reasons are: (1) at the beginning of polymerization, the catalysts can be fully activated by MAO, showing high activity; (2) as polymerization time extends, polymer yield continuously increases, and more catalyst particles become encapsulated by polyethylene product, losing contact with ethylene monomer; and (3) increased polymer viscosity in the later stages of reaction also reduces sufficient contact between active centers and ethylene monomer, significantly diminishing chain propagation after a certain time [**?**, **?**].

Comparison of the effects of various complexes on ethylene polymerization reveals the activity order: complex 15 > complex 14 > complex 16 > complex 13.

3.4 High-Temperature GPC Characterization of Polyethylene

lists the polyethylene molecular weights and distributions determined by gel permeation chromatography (GPC). In the table, Mw is weight-average molecular weight, Mv is viscosity-average molecular weight, Mp is peak molecular weight, Mn is number-average molecular weight, Mz is z-average molecular weight, and Mw/Mn is molecular weight distribution. The results show that polyethylene obtained from the three substituted salicylaldimine titanium compounds 14/MAO, 15/MAO, and 16/MAO systems has higher molecular weight than that from unsubstituted compound 13/MAO, with narrower molecular weight distributions characteristic of single active-center catalysts. The main reason is that the complex forms a metal active center $M[^{+}]L[^{-}]$ under the action of cocatalyst, initiating ethylene polymerization. Ethylene monomer inserts between M-L to complete chain initiation, generating $MCH_2CH_2[^{+}]L[^{-}]$. The chain propagation rate $Rp = \{MCH_2CH_2L\} \cdot \{CH_2{=}CH_2\}$. When both the chain initiation segment concentration and ethylene monomer concentration are relatively high, the chain propagation rate is faster, forming long polyethylene chains. The presence of electron-withdrawing nitro or bromo groups on ligand L increases the positive charge of the active center, promoting chain initiation and increasing Rp, thereby increasing polymer chain length. Additionally, the steric effect of bulky substituents (tert-butyl) at the ortho position of phenoxy can prevent the active center from binding with components other than monomer, allowing the catalytic system formed by complex 16 to maintain activity longer under polymerization conditions than the unsubstituted complex 13/MAO system. Consequently, the catalyzed polyethylene has higher molecular weight and slightly broader distribution [**?**].

Although electronic and steric effects enable catalytic systems 14-16 to produce polyethylene with higher molecular weight, catalyst deactivation (including coupling reactions between active chain molecules and intermolecular coupling at high active species concentrations) and chain transfer reactions (including transfer to solvent, impurities, etc.) cause some polymer chains to terminate before

forming large molecular weights, resulting in relatively broad molecular weight distributions. Further modification of ligand molecular structure, such as introducing strong electron-withdrawing groups at the para position of phenoxy and bulky substituents at the ortho position to prevent deactivation and chain transfer, may enable further control of polymer molecular weight and distribution.

3.5 DSC Testing of Polyethylene

DSC test results for polyethylene samples are shown in [Figure 6: see original paper]. The DSC curves for four PE samples (labeled 13#, 14#, 15#, 16#) show that the melting peaks of 14#, 15#, and 16# polyethylene are similar, with high melting points (greater than 130°C). Sample 15# exhibits a melting point as high as 132.6°C, consistent with the thermal properties of crystalline polyethylene. Sample 13# has a slightly lower melting point, and its processing temperature is lower than other samples.

3.6 ^{13}C-NMR Characterization of Polyethylene

Under identical conditions, catalyst 15 showed the highest activity for ethylene polymerization, reaching 1302.27 g · PE/(mmol · Ti · h · MPa). The polyethylene sample obtained from catalyst 15 was characterized by ^{13}C-NMR, with results shown in [Figure 7: see original paper].

In [Figure 7: see original paper], the three peaks at chemical shifts of 128–133 ppm correspond to the three types of carbon (1,1-position carbon; 2,2-position carbon; and 3,3-position carbon) from the o-dichlorobenzene-d_4 solvent used to dissolve PE. The peak at 30 ppm corresponds to the carbon signal of linear polyethylene chain segments -[CH_2]n- [**?**, **?**]. The ^{13}C-NMR characterization of the polyethylene sample indicates that the polyethylene obtained with catalyst 15 has saturated chain ends, due to high molecular weight and restricted β-H transfer reactions [**?**]. Furthermore, the ^{13}C-NMR and DSC characterization results demonstrate that the polyethylene obtained with catalyst 15 is linear crystalline polyethylene [**?**].

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4. Conclusion

Under conditions of relatively high temperature and low MAO/cat molar ratio, substituted salicylaldimine titanium catalysts 14-16 effectively catalyze ethylene polymerization. At process conditions of 2.0 MPa, 60°C, and n_{Al}/n_{Ti} = 1500:1, polymerization activities reach 1022.73–1302.27 g · PE/(mmol · Ti · h · MPa), all significantly higher than that of unsubstituted salicylaldimine titanium dichloride 13. Introduction of strongly electron-withdrawing nitro and halogen groups into the ligand substantially enhances ethylene polymerization activity. Ethylene homopolymerization catalyzed by titanium complex 15 in MAO-activated toluene solution yields high molecular weight linear crystalline

polyethylene. The strongly electron-withdrawing salicylaldimine titanium complexes 14 and 15 offer advantages of low cost, high synthesis yield, high catalytic activity, and high polymer molecular weight, demonstrating significant potential for industrial development.

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