Ethylene polymerization activity under practical conditions displayed by zirconium complexes having two phenoxy-imine chelate ligands

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Abstract

Ethylene polymerization using zirconium complexes having two phenoxy-imine chelate ligands was investigated at 50 and 75°C at 0.9 MPa ethylene pressure. The activity of the proto-catalyst, *N*-[(3-*t*-butylsalicylidene)anilinato]zirconium(IV)-dichloride (**1**), decreased by increasing the polymerization temperature (50°C: 1192 kg-PE/mmol-Zr·h, 75°C: 209 kg-PE/mmol-Zr·h). The introduction of an electron donating group, such as an *n*-hexyl and a methoxy group, on the imine nitrogen or at the *para*-position of phenoxy oxygen in a benzene ring suppressed the activity decrease, however, the activity at 75°C was still lower than that at 50°C. The combination of an *n*-hexyl or a cyclohexyl group on the imine nitrogen and a methoxy group at the *para*-position of the phenoxy oxygen enhanced activity at 75°C. Thus, *N*-[(3-*t*-butyl-5-methoxysalicylidene)-*n*-hexylaminato]zirconium(IV)dichloride (**5**) and *N*-[(3-*t*-butyl-5-methoxysalicylidene)cyclohexylaminato]zirconium(IV)dichloride (**6**) displayed activities of greater than 1000 kg-PE/mmol-Zr h. Moreover, the introduction of an adamantyl or a cumyl group at the position adjacent to the phenoxy oxygen further increased the activity. *N*-[(3-Adamantyl-5-methoxysalicylidene)cyclohexylaminato]zirconium(IV)dichloride (**7**), *N*-[(3-cumyl-5-methoxysalicylidene)-*n*-hexylaminato]zirconium(IV)dichloride (**8**), and *N*-[(3-cumyl-5-methoxysalicylidene)cyclohexylaminato]zirconium(IV)dichloride (**9**) displayed exceptionally high activity (**7**: 3052 kg-PE/mmol-Zr·h, **8**: 7078 kg-PE/mmol-Zr·h, **9**: 7224 kg-PE/mmol-Zr·h). © 2001 Published by Elsevier Science B.V.

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1. Introduction

The research and development of highly active olefin polymerization catalysts has significantly contributed to not only academic fields but also to the industrial domain [1–5]. In particular, historically, the development of highly active catalysts at high temperatures has led to industrially useful technologies since industrial olefin polymerization is conducted at high temperatures, generally higher than 70°C, in the light of chemical engineering requirements.

A recent example is the development of the group 4 metallocenes, which produce a variety of polyolefins with novel properties, displaying high activity at high polymerization temperatures [4–11]. Based on the metallocene catalysts, the industrial production of linear low-density polyethylene, isotactic

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polypropylene, syndiotactic polypropylene, and syndiotactic polystyrene, etc. has been commercially successful. Therefore, much effort has been devoted to the research and development of transition metal complexes with a view to creating new industrially available olefin polymerization catalysts other than the metallocene catalysts. As a result, recently, a certain number of high performance new olefin polymerization catalysts have been discovered [12,13]. Some of them display a sufficiently high ethylene polymerization activity for the industrial production at high polymerization temperatures [14–16].

Recently, we have acquired new zirconium complexes having two phenoxy-imine chelate ligands, named FI Catalysts, which display a very high ethylene polymerization activity using MAO as a co-catalyst at ambient polymerization temperatures under atmospheric pressure [17,18]. In addition, we have revealed that the zirconium complexes are capable of producing polyethylene of low to exceptionally high molecular weight by selecting the co-catalyst as well as by changing the ligand structure [19,20]. As a continuation of this work, we have investigated ethylene polymerization using the zirconium complexes at high temperatures, aimed at developing industrially available new olefin polymerization catalysts.

2. Experimental

2.1. General

Dried solvents (tetrahydrofuran (THF), dichloromethane) used for complex syntheses were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. *n*-Heptane (Wako Pure Chemical Industries, Ltd.) used as a polymerization solvent was dried over Al_2O_3 and degassed by the bubbling of nitrogen gas. Cp_2ZrCl_2 (Wako Pure Chemical Industries, Ltd.) was used without further purification. Ethylene was purchased from Sumitomo Seika Co., Ltd. The co-catalyst, methylalmoxane (MAO) was purchased from Albemarle as a 1.2 M toluene solution, and the remaining trimethylaluminum was evaporated in vacuo prior to use.

2.1.1. Ligand and complex analyses
NMR spectra were recorded on a JEOL270 spectrometer at ambient temperatures. Chemical shifts for the ^{1}H NMR were referenced to an internal solvent resonance and reported relative to tetramethylsilane (TMS). Elemental analysis for CHN was carried out by the CHNO type from the Helaus Co. The elemental analysis for Zr was carried out using the ICP method by a SHIMADZU ICPS-8000 after dry ashing and dilute nitric acid dissolution. The FD–MS spectra were recorded on a SX-102A from Japan Electron Optics Laboratory Co., Ltd.

2.1.2. Polymer characterization
The intrinsic viscosity [η] was measured in decalin at 135°C using an Ubbelohde viscometer. The viscosity average molecular weight (M_v) values of polyethylene were calculated using the following equation: $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$ [21].

2.2. General complex synthesis procedure

2.2.1. Ligand Syntheses
Ligand syntheses were carried out under nitrogen using oven-dried glassware. Treatment of an *ortho*-substituted phenol compound with *para*-formaldehyde in the presence of ethylmagnesiumbromide and triethylamine produced a salicylaldehyde compound in 60–80% yield [17,22]. This compound reacted with a primary amine compound via Schiff base condensation in ethanol to afford the corresponding phenoxy-imine ligand in approximately 80–100% yield [17].

2.2.2. Complex Syntheses
All complex synthesis manipulations were performed with the exclusion of oxygen and moisture under argon using standard Schlenk techniques. A typical procedure for a complexation is as follows: to a stirred solution of a phenoxy-imine ligand (10.0 mmol) in THF (100 ml) at −78°C, an *n*-butyllithium hexane solution (10.5 mmol) was added dropwise over a 5 min period. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting solution was added dropwise over a 30 min period to a stirred solution of $ZrCl_4(THF)_2$ (5.0 mmol) in THF (100 ml) at −78°C. The mixture was allowed to warm to room temperature and stirred for 15 h. The resulting mixture was concentrated in vacuo to give a solid to which dichloromethane (60 ml) was added, and the mixture stirred for 5 min. The resulting mixture

was filtered, and then the residue was washed with dichloromethane. The combined organic filtrates were concentrated in vacuo to afford the crude complex. The crude complex was recrystallized from solution to give a zirconium complex.

2.3. Bis[N-(3-t-butylsalicylidene)anilinato]-zirconium(IV)dichloride (*1*)

Fluorescent yellow single crystals (52% yield). ^{1}H NMR (CDCl$_3$): δ. 1.33–1.59 (m, 18H, *t*-Bu), 6.78–7.42 (m, 16H, aromatic-H), 8.12 (s, 2H, CH=N). Et$_2$O of crystallization: [1.20 (t, 6H, $J = 5.2$ Hz, CH$_3$), 3.48 (q, 4H, $J = 5.2$ Hz, CH$_2$)]. Anal. found: C, 60.86; H, 5.36; N, 3.67; Zr, 12.70%. Calculated for ZrC$_{34}$H$_{36}$N$_2$O$_2$Cl$_2$ + Et$_2$O: C, 61.60; H, 6.26; N, 3.78; Zr, 12.31%. FD–MS, 664 (M$^+$) (see [18])

2.4. Bis[N-(3-t-butylsalicylidene)-n-hexylaminato]-zirconium(IV)dichloride (*2*)

Yellow crystals (35% yield). ^{1}H NMR (CDCl$_3$): δ. 0.90–1.54 (m, 40H, CH$_2$, CH$_3$, *t*-Bu), 3.40–3.55 (m, 4H, N–CH$_2$), 6.81–7.55 (m, 6H, aromatic-H), 8.08 (s, 2H, CH=N). Anal. found: C, 59.86; H, 7.56; N, 4.22; Zr, 13.25%. Calculated for ZrC$_{34}$H$_{52}$N$_2$O$_2$Cl$_2$: C, 59.80; H, 7.67; N, 4.10; Zr, 13.36%. FD–MS, 680 (M$^+$).

2.5. Bis[N-(3-t-butylsalicylidene)cyclohexylaminato]-zirconium(IV)dichloride (*3*)

Yellow powder (43% yield). ^{1}H NMR (CDCl$_3$): δ. 1.55 (s, 18H, *t*-Bu), 0.80–2.40 (m, 20H, CH$_2$), 3.80–4.00 (m, 2H, CH), 6.79–7.64 (m, 6H, aromatic-H), 8.31 (s, 2H, CH=N). Anal. found: C, 60.04; H, 7.44; N, 4.42; Zr, 13.28%. Calculated for ZrC$_{34}$H$_{48}$N$_2$O$_2$Cl$_2$: C, 60.15; H, 7.13; N, 4.13; Zr, 13.44%. FD–MS, 678 (M$^+$).

2.6. Bis[N-(3-t-butyl-5-methoxysalicylidene)anilinato]zirconium(IV)dichloride (*4*)

Yellow crystals (68% yield). ^{1}H NMR (CDCl$_3$): δ. 1.19–1.70 (m, 18H, *t*-Bu), 3.78 (brs, 6H, OMe), 6.47–7.35 (m, 14H, aromatic-H), 7.90–8.15 (m, 2H, CH=N). Anal. found: C, 59.09; H, 5.61; N, 3.67; Zr,

12.42%. Calculated for ZrC$_{36}$H$_{40}$N$_2$O$_4$Cl$_2$: C, 59.49; H, 5.55; N, 3.85; Zr, 12.55%. FD–MS, 726 (M$^+$).

2.7. Bis[N-(3-t-butyl-5-methoxysalicylidene)-n-hexylaminato]zirconium(IV)dichloride (*5*)

Yellow powder (22% yield). ^{1}H NMR (CDCl$_3$): δ. 0.80–1.75 (m, 22H, CH$_2$, CH$_3$), 1.58 (s, 18H, *t*-Bu), 3.41–3.69 (m, 4H, N–CH$_2$), 3.83 (s, 6H, OMe), 6.69 (s, 2H, aromatic-H), 7.20 (s, 2H, aromatic-H), 8.14 (s, 2H, CH=N). Anal. found: C, 57.98; H, 7.66; N, 3.66; Zr, 12.40%. Calculated for ZrC$_{36}$H$_{56}$N$_2$O$_4$Cl$_2$: C, 58.20; H, 7.60; N, 3.77; Zr, 12.28%. FD–MS, 742 (M$^+$).

2.8. Bis[N-(3-t-butyl-5-methoxysalicylidene)cyclohexylaminato]zirconium(IV)dichloride (*6*)

Yellow powder (74% yield). ^{1}H NMR (CDCl$_3$): δ. 1.58 (s, 18H, *t*-Bu), 1.16–2.11 (m, 20H, CH$_2$), 3.75–3.95 (m, 2H, CH), 3.80 (s, 6H, OMe), 6.64 (s, 2H, aromatic-H), 7.21 (s, 2H, aromatic-H), 8.19 (s, 2H, CH=N). Anal. found: C, 58.85; H, 7.35; N, 3.59; Zr, 12.56%. Calculated for ZrC$_{36}$H$_{52}$N$_2$O$_4$Cl$_2$: C, 58.51; H, 7.09; N, 3.79; Zr, 12.35%. FD–MS, 738 (M$^+$).

2.9. Bis[N-(3-adamantyl-5-methoxysalicylidene)-cyclohexylaminato]zirconium(IV)dichloride (*7*)

Yellow powder (13% yield). ^{1}H NMR (CDCl$_3$): δ. 0.87–2.49 (m, 50H, adamantyl-H, cyclohexyl–CH$_2$), 3.79 (s, 6H, OMe), 3.74–4.00 (m, 2H, N–CH), 6.66 (s, 2H, aromatic-H), 7.13 (s, 2H, aromatic-H), 8.19 (s, 2H, CH=N). Anal. found: C, 64.58; H, 7.19; N, 3.49; Zr, 9.99%. Calculated for ZrC$_{48}$H$_{64}$N$_2$O$_4$Cl$_2$: C, 64.40; H, 7.21; N, 3.13; Zr, 10.19%. FD–MS, 894 (M$^+$).

2.10. Bis[N-(3-cumyl-5-methoxysalicylidene)-n-hexylaminato]zirconium(IV)dichloride (*8*)

Yellow powder (32% yield). ^{1}H NMR (CDCl$_3$): δ. 0.50–2.02 (m, 34H, CH$_2$), 2.38–2.82 (m, 4H, N–CH$_2$), 3.78 (s, 3H, OMe), 3.83 (s, 3H, OMe), 6.37–7.51 (m, 14H, aromatic-H), 7.85 (s, 2H, CH=N). Anal. found: C, 63.89; H, 7.19; N, 3.77; Zr, 10.22%. Calculated for ZrC$_{46}$H$_{60}$N$_2$O$_4$Cl$_2$: C, 63.72; H, 6.97; N, 3.23; Zr, 10.52%. FD–MS, 866 (M$^+$).

2.11. Bis[N-(3-cumyl-5-methoxysalicylidene)-cyclohexylaminato]zirconium(IV)dichloride (9)

Yellow powder (52% yield). ^{1}H NMR (CDCl$_3$): δ. 0.81–2.12 (m, 20H, CH$_2$), 1.84 (s, 6H, Me), 1.98 (s, 6H, Me), 3.54–3.75 (m, 2H, N–CH), 3.84 (s, 3H, OMe), 3.75 (s, 3H, OMe), 6.60–6.73 (m, 2H, aromatic-H), 7.08–7.45 (m, 12H, aromatic-H), 8.11 (s, 2H, CH=N). Anal. found: C, 64.44; H, 6.41; N, 3.59; Zr, 10.49%. Calculated for ZrC$_{46}$H$_{56}$N$_2$O$_4$Cl$_2$: C, 64.01; H, 6.54; N, 3.25; Zr, 10.57%. FD–MS, 863 (M$^+$).

2.12. Ethylene polymerization

Ethylene polymerization was carried out under 0.9 MPa ethylene pressure in n-heptane in a 1000 ml stainless steel reactor equipped with a propeller-like stirrer. n-Heptane (500 ml) was introduced into the reactor under ethylene atmospheric pressure, and the n-heptane was thermostated to a prescribed polymerization temperature with stirring (150 rpm). A toluene solution of MAO (1.25 M), and then a toluene solution of the complex were added to the reactor. For initiating polymerization, the ethylene gas feed immediately pumped into the reactor up to 0.9 MPa ethylene pressure with vigorous stirring (350 rpm), and the ethylene pressure was maintained at 0.9 MPa by continuous ethylene feed. After 15 min, the ethylene gas feed was ceased to terminate the polymerization. The resulting mixture was cooled to room temperature and carefully degassed. Methanol (1000 ml) and concentrated HCl (5 ml) were added to quench the catalyst and solubilize the catalyst residue into the acidic methanol. The resulting precipitate was collected by filtration, washed with methanol (500 ml), and dried in vacuo at 80°C for 10 h to give polyethylene.

3. Results and discussion

A zirconium complex having two phenoxy-imine chelate ligands, N-[(3-t-butylsalicylidene)anilinato]-zirconium(IV)dichloride (1), was investigated for ethylene polymerization using MAO as a cocatalyst under 0.9 MPa ethylene pressure. At 50°C, complex 1 displayed a very high activity of 1192 kg-PE/mmol-Zr·h. However, at 75°C, the activity decreased to 209 kg-PE/mmol-Zr·h. We assume that the activity decrease was due to the low thermal stability of the active species derived from complex 1, namely the decomposition of the active species at a high temperature. Hence, in order to suppress the decomposition of the active species caused by the high temperature, we modified the electronic character of the ligand by introducing electron-donating group(s) at the R^1 and/or R^2 positions, since the introduction of electron donating group(s) is (are) expected to strengthen the bonds between the zirconium metal and the ligands, thus, improving the thermal stability of the active species.
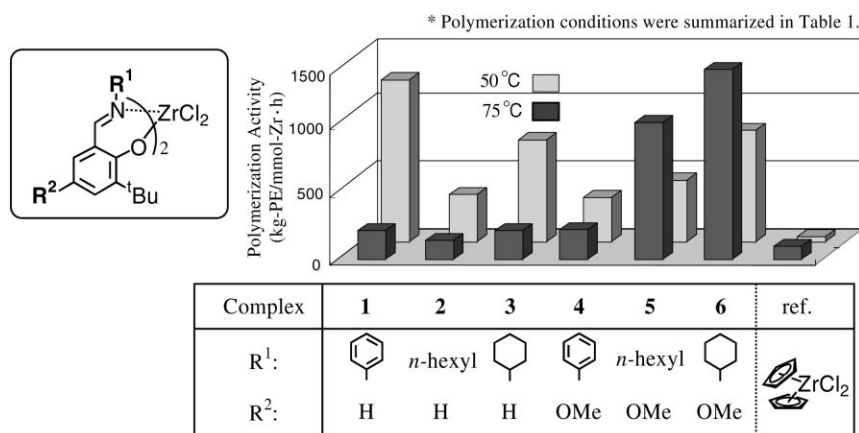

Fig. 1. Ethylene polymerization activities at 50 and 75°C displayed by complexes 1–6.

Table 1
Ethylene polymerization results using complexes **1–6**[a]

Entry	Complex	Amount of complex (μmol)	Temperature (°C)	Yield (g)	Activity (kg-PE/mmol-Zr·h)	$M_v/10^4$
1	**1**	0.05	50	14.90	1192	4.7
2	**1**	0.05	75	2.61	209	10.0
3	**2**	0.2	50	17.30	346	1.1
4	**2**	0.2	75	6.99	140	2.0
5	**3**	0.1	50	18.78	751	1.5
6	**3**	0.1	75	5.27	211	3.0
7	**4**	0.1	50	8.19	328	36.3
8	**4**	0.1	75	5.51	220	22.7
9	**5**	0.05	50	5.67	454	9.9
10	**5**	0.05	75	12.59	1008	3.8
11	**6**	0.05	50	10.22	818	16.8
12	**6**	0.05	75	18.28	1462	5.4
13	Cp_2ZrCl_2	0.2	50	1.92	38	43.1
14	Cp_2ZrCl_2	0.2	75	4.86	97	19.6

[a] Conditions: 0.9 MPa ethylene pressure, MAO (Al); 1.25 mmol, *n*-heptane, 500 ml; polymerization time, 15 min.

The introduction of an *n*-hexyl or a cyclohexyl group instead of the phenyl group at the R^1 position, complexes **2** (R^1 = *n*-hexyl) and **3** (R^1 = cyclohexyl), resulted in mitigating the activity decrease, based on a comparison of the activities at 50 and 75°C.

Alternatively, the introduction of a methoxy group at the R^2 position, complex **4**, also resulted in suppressing the activity decrease. Although the activity decrease for complexes **2–4** was mitigated compared to that for complex **1**, the absolute activity values displayed by complexes **2–4** at 75°C were nearly equal to or less than that exhibited by complex **1**.

Surprisingly, a combination of an *n*-hexyl or a cyclohexyl group at the R^1 position and a methoxy group at the R^2 position was very effective in enhancing the activity at 75°C. Complexes **5** (R^1 = *n*-hexyl, R^2 = OMe) and **6** (R^1 = cyclohexyl, R^2 = OMe) displayed activities of 1008 and 1462 kg-PE/mmol-Zr·h at 75°C, respectively. These activity values were 5–7 times higher than that displayed by complex **1** at 75°C, and moreover, far superior to that of Cp_2ZrCl_2 (Fig. 1 and Table 1).

We have recently reported that changing the *t*-butyl group at the R^3 position to an adamantyl or a cumyl

Table 2
Ethylene polymerization results using complexes **7–9**[a]
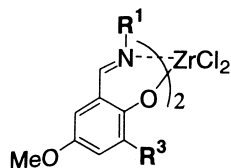
Entry	Complex	R^1	R^3	Amount of complex (μmol)	Temperature (°C)	Yield (g)	Activity (kg-PE/mmol-Zr·h)	$M_v/10^4$
1	**7**	Cyclohexyl	Adamantyl	0.02	50	9.49	1898	32.8
2	**7**	Cyclohexyl	Adamantyl	0.02	75	15.26	3052	9.5
3	**8**	*n*-Hexyl	Cumyl	0.01	50	8.12	3250	13.4
4	**8**	*n*-Hexyl	Cumyl	0.01	75	17.70	7078	3.9
5	**9**	Cyclohexyl	Cumyl	0.01	50	9.16	3665	17.2
6	**9**	Cyclohexyl	Cumyl	0.005	75	9.06	7224	10.4

[a] Conditions: 0.9 MPa ethylene pressure, MAO (M); 1.25 mmol, *n*-heptane, 500 ml; polymerization time, 15 mm.

group, sterically larger than the *t*-butyl group, enhanced the polymerization activity at 25°C under ethylene at atmospheric pressure [19,20]. Therefore, we prepared complexes **7** (R^1 = cyclohexyl, R^2 = OMe, R^3 = adamantyl), **8** (R^1 = *n*-hexyl, R^2 = OMe, R^3 = cumyl) and **9** (R^1 = cyclohexyl, R^2 = OMe, R^3 = cumyl), and investigated the complexes for ethylene polymerization at 0.9 MPa ethylene pressure at 50 and 75°C (Table 2).

As expected, complexes **7**–**9** displayed much higher activities at 50 and 75°C compared to the corresponding complexes having the *t*-butyl group at the R^3 position. Namely, complex **7**, having an adamantyl group at the R^3 position, exhibited ethylene polymerization activities of 1898 and 3052 kg-PE/mmol-Zr·h at 50 and 75°C, respectively. Furthermore, complexes **8** and **9**, both having a cumyl group at the R^3 position, exhibited exceptionally high ethylene polymerization activities of 3250 and 3665 kg-PE/mmol-Zr·h at 50°C, respectively. Moreover, these complexes displayed higher activities at 75°C (**8**: 7078 kg-PE/mmol-Zr·h and **9**: 7224 kg-PE/mmol-Zr·h) than those at 50°C. As far as we are aware, the activities displayed by complexes **8** and **9** at 75°C under 0.9 MPa ethylene pressure, more than 7000 kg-PE/mmol-Zr·h, are some of the highest values exhibited by olefin polymerization catalysts under the same or similar polymerization conditions.

4. Conclusion

In this study, we demonstrated that zirconium complexes bearing two phenoxy-imine chelate ligands, FI Catalysts, displayed very high ethylene polymerization activities at 75°C under 0.9 MPa ethylene pressure as a result of a suitable catalyst design. Although the proto-catalyst **1** displayed decreased activity at 75°C compared to that at 50°C, introducing electron-donating groups at the R^1 and R^2 positions increased the activity at 75°C. Moreover, further improvement in the activity at 75°C is achieved by the introduction of an adamantyl or a cumyl group at the R^3 position. Thus, exceptionally high activity, more than 7000 kg-PE/mmol-Zr h, is attained using **8** and **9**, both having a cumyl group at the R^3 position. These results clearly indicate that zirconium complexes having two phenoxy-imine ligands have not only potential capacity but also practical use, and therefore, these complexes possess great potential as new olefin polymerization catalysts.

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