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# Ethylene and propylene polymerization behavior of a series of bis(phenoxy–imine)titanium complexes

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**Abstract**

This contribution reports ethylene and propylene polymerization behavior of a series of Ti complexes bearing a pair of phenoxy–imine chelate ligands. The bis(phenoxy–imine)Ti complexes in conjunction with methylalumoxane (MAO) can be active catalysts for the polymerization of ethylene. Unexpectedly, this $C_2$ symmetric catalyst produces syndiotactic polypropylene. $^{13}$C NMR spectroscopy has revealed that the syndiotacticity arises from a chain-end control mechanism. Substitutions on the phenoxy–imine ligands have substantial effects on both ethylene and propylene polymerization behavior of the complexes. In particular, the steric bulk of the substituent *ortho* to the phenoxy–oxygen is fundamental to obtaining high activity and high molecular weight for ethylene polymerization and high syndioselectivity for the chain-end controlled propylene polymerization. The highest ethylene polymerization activity, 3240 kg/mol-cat h, exhibited by a complex having a *t*-butyl group *ortho* to the phenoxy–oxygen, represents one of the highest reported to date for Ti-based non-metallocene catalysts. Additionally, the polypropylene produced exhibits a $T_m$, 140 °C, and syndioselectivity, *rrrr* 83.7% (achieved by a complex bearing a trimethylsilyl group *ortho* to the phenoxy–oxygen) that are among the highest for polypropylenes produced via a chain-end control mechanism. Hence, the bis(phenoxy–imine)Ti complexes are rare examples of non-metallocene catalysts that are useful for the polymerization of not only ethylene but also propylene.
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*Keywords:* Olefin polymerization catalyst; Non-metallocene; Phenoxy–imine ligand; Titanium; FI Catalysts

## 1. Introduction

Over the past two decades, highly-active well-defined transition metal complex catalysts have been developed, and they have become important single-site alternatives to the heterogeneous Ziegler-Natta catalysts. This is because these single-site catalysts possess an advantage of control over polymer molecular weight and molecular weight distribution, uniform comonomer incorporation, and precise control of polymer stereoregularity due to their well-defined active sites. In fact, the development of such catalysts has enabled the synthesis of polyolefinic materials with a wide range of well-defined microstructures and related properties. Although metallocene catalysts [1] and constrained-geometry catalysts (CGC) [2] have been in the forefront of these developments, recent work focused on the search for non-metallocene catalysts [3–26] has led to the discovery of catalysts capable of producing unique polymers that are difficult or impossible to prepare using metallocene catalysts and CGC.

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We believe that among catalyst components ligands play the most important role in polymerization. During our ligand-oriented catalyst design program [27,28] we discovered new families of transition metal complexes containing non-symmetric bidentate phenoxy–imine [29–52], pyrrolide–imine [53–55], indolide–imine [56,57], phenoxy–pyridine [58], phenoxy–ether [59], or imine–pyridine [27] chelate ligands. These complexes show excellent performance for olefin polymerization including the living polymerization or copolymerization of ethylene, ethylene–propylene, propylene, and ethylene–norbornene leading to a variety of unique polymers, some of which are unavailable with conventional catalysts. Recently, much effort has been directed towards the development of catalysts based on phenoxy–imine ligated early transition metal complexes for olefin polymerization [60–73].

As part of our ongoing investigations with respect to the structure–catalytic performance relationships of bis(phenoxy–imine) group 4 transition metal complexes (originally developed at Mitsui and named FI Catalysts), we report herein catalytic performance of a series of bis(phenoxy–imine)Ti complexes, Ti-FI Catalysts, for the polymerization of ethylene or propylene. Some of the results described herein have been disclosed previously in the form of patents [74–76].

## 2. Experimental

### 2.1. General

#### 2.1.1. Materials

Dried solvents (diethyl ether, dichloromethane, ethanol, and *n*-hexane) used for ligand and complex syntheses were purchased from Wako Pure Chemical Industries Ltd., and used without further purification. Toluene employed as a polymerization solvent (Wako Pure Chemical Industries Ltd.) was dried over $Al_2O_3$ and degassed by the bubbling with dried nitrogen gas. Phenol compounds and aniline compounds for ligand syntheses were obtained from Aldrich, Wako Pure Chemical Industries Ltd., Acros Organics, Kanto Chemical Co. Inc., or Tokyo Kasei Kogyo Co. Ltd. Chlorotrimethylsilane (Wako Pure Chemical Industries Ltd.), a 1.0 M boron trichloride $CH_2Cl_2$ solution (Aldrich), and a 1.0 M $TiCl_4$ toluene solution (Aldrich) were used as received. Ethylene and propylene were obtained from Sumitomo Seika Co. and Mitsui Chemicals Inc., respectively. Methylalumoxane (MAO) for ethylene polymerization was purchased from Albemarle Corporation as a 1.2 M of a toluene solution, and the remaining trimethylaluminum was evaporated in vacuo prior to use (dried MAO, DMAO). MAO for propylene polymerization was purchased from Witco Co. and used as received. All other chemicals were obtained commercially and used as received.

#### 2.1.2. Ligand and complex analyses

$^1$H NMR spectra were recorded on a JEOL270 spectrometer (270 MHz) in $CDCl_3$ at ambient temperatures. Chemical shifts for $^1$H NMR were referenced to an internal solvent resonance and reported relative to tetramethylsilane. FD-MS spectra were recorded on an SX-102A instrument from Japan Electron Optics Laboratory Co. Ltd. Elemental analyses for CHN were carried out by a CHNO type analyzer from Helaus Co.

#### 2.1.3. Polymer characterization

$^{13}$C NMR spectra of polypropylenes were recorded on an ECP500 spectrometer (125 MHz) from Japan Electron Optics Laboratory Co. Ltd., using *o*-dichlorobenzene with 20% benzene-$d_6$ as a solvent at 120 °C. Molecular weights ($M_w$ and $M_n$) and molecular weight distributions ($M_w/M_n$) of polyethylenes and polypropylenes were determined using a Waters GPC2000 gel permeation chromatograph equipped with four TSKgel columns (two sets of TSKgelGMH$_6$HT and two sets of TSKgelGMH$_6$-HTL) at 140 °C using polystyrene calibration. *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 ml/min. Transition melting temperatures ($T_m$) of the polypropylenes were determined by DSC with a Shimadzu DSC-60 differential scanning calorimeter, measured upon reheating the polymer sample to 200 °C at a heating rate of 10 °C/min.

### 2.2. Ligand and complex syntheses

Ligand syntheses were carried out under nitrogen using oven-dried glassware. All manipulations of complex syntheses were performed with exclusion of oxygen and moisture under argon using standard Schlenk and cannula techniques using oven-dried glassware.

*2.2.1. Preparation of bis[N-(3-methylsalicylidene)-anilinato]titanium(IV)dichloride (**2**)*

*2.2.1.1. Synthesis of 3-methylsalicylaldehyde.* To a stirred 3.0 M ethylmagnesium bromide diethyl ether solution (10 ml, 30.0 mmol), a solution of *o*-cresol (3.00 g, 27.7 mmol) in THF (40 ml) was added dropwise over a 10 min period at 0 °C. After the mixture was stirred for 4 h at room temperature, dried toluene (100 ml) and then a mixture of triethylamine (5.80 ml, 41.6 mmol) and paraformaldehyde (2.82 g, 94% purity, 93.9 mmol) were added to the resulting mixture. The mixture was stirred at 60 °C for 2 h, and to the resulting mixture, a 6 N HCl (20 ml) was added at 0 °C. The organic phase was washed with saturated $NaHCO_3$ (aq.) (50 ml) and then with brine (50 ml). The organic phase was dried over $MgSO_4$, and concentrated in vacuo to afford a yellow oil, which was purified by column chromatography on silica gel using hexane/ethyl acetate (20/1) as eluent to give 3-methylsalicylaldehyde (2.07 g, 15.2 mmol) as a yellow oil in 55% yield. $^1$H NMR ($CDCl_3$) $\delta$ 2.25 (s, 3H, Me), 6.90 (t, $J = 7.6$ Hz, 1H, aromatic-H), 7.35 (s, 1H, aromatic-H), 7.38 (s, 1H, aromatic-H), 9.84 (s, 1H, CHO), 11.25 (s, 1H, OH).

*2.2.1.2. Synthesis of N-(3-metylsalicylidene)aniline (**b**).* To a stirred mixture of 3-methylsalicylaldehyde (4.90 g, 36.0 mmol) in ethanol (160 ml), a solution of aniline (3.35 g, 36.0 mmol) in ethanol (20 ml) was added dropwise over a 5 min period at room temperature. The mixture was stirred for 23 h and then concentrated in vacuo to yield a crude imine compound as a reddish brown oil. Purification by column chromatography on silica gel using hexane/ethyl acetate (100/2) as eluent gave *N*-(3-methylsalicylidene)aniline (4.71 g, 22.3 mmol) as pale orange crystals in 59% yield. $^1$H NMR ($CDCl_3$) $\delta$ 2.69 (s, 3H, Me), 7.60–7.81 (m, 8H, aromatic-H), 8.66 (s, 1H, CH=N), 13.59 (s, 1H, OH).

*2.2.1.3. Synthesis of bis[N-(3-methylsalicylidene)anilinato]titanium(IV)dichloride (**2**).* To a stirred solution of *N*-(3-methylsalicylidene)aniline (**b**) (1.00 g, 4.73 mmol) in dried diethyl ether (20 ml) at −78 °C, a 1.55 M *n*-butyllithium *n*-hexane solution (3.21 ml, 4.97 mmol) was added dropwise over a 5 min period. The mixture was allowed to warm to room temperature and stirred for 6 h. The resulting mixture was added dropwise over a 20 min period to a 0.5 M heptane solution of $TiCl_4$ (4.73 ml, 2.37 mmol) in dried diethyl ether (30 ml) at −78 °C with stirring. The mixture was allowed to warm to room temperature and stirred for 17 h. Concentration of the resulting mixture in vacuo gave a crude product. Dried $CH_2Cl_2$ (100 ml) was added to the crude product, and the mixture was stirred for 15 min and then filtered. The resulting solid was washed with dried *n*-hexane (10 ml × 2). The combined organic filtrates were concentrated in vacuo to afford a brown solid. Dried *n*-hexane (30 ml) was added to the solid and stirred for 5 min, and then filtered. The resulting solid was dried in vacuo to give complex **2** (0.96 g, 1.78 mmol) as pale brown crystals in 75% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.90–2.37 (s, 6H, Me), 6.50–7.30 (m, 16H, aromatic-H), 7.90–8.12 (m, 2H, CH=N); FD-MS, 538 ($M^+$). Anal. Found: C, 62.75; H, 4.45; N, 5.09. Calcd. for $TiC_{28}H_{24}N_2O_2Cl_2$: C, 62.36; H, 4.49; N, 5.19.

Complexes **1**, and **4**–**8** and their ligands were prepared by an analogous route to that outlined for complex **2** or ligand (**b**).

*2.2.2. bis[N-(Salicylidene)anilinato]titanium(IV)-dichloride (**1**)*

Ligand **a**, *N*-(salicylidene)aniline, as orange crystals in 94% yield: $^1$H NMR ($CDCl_3$) $\delta$ 6.82–7.48 (m, 9H, aromatic-H), 8.62 (s, 1H, CH=N), 13.24 (s, 1H, OH).

Complex **1**, as brown crystals in 66% yield: $^1$H NMR($CDCl_3$) $\delta$ 6.21–7.65 (m, 18H, aromatic-H), 7.90–8.13 (m, 2H, CH=N); FD-MS, 510 ($M^+$). Anal. found: C, 61.11; H, 3.95; N, 5.67. Calcd. for $TiC_{26}H_{20}N_2O_2Cl_2$: C, 61.08; H, 3.94; N, 5.48.

*2.2.3. bis[N-(3-Trimethylsilylsalicylidene)anilinato]-titanium(IV)dichloride (**4**)*

Ligand **d**, *N*-(3-trimethylsilylsalicylidene)aniline, as yellow crystals in 88% yield: $^1$H NMR ($CDCl_3$) $\delta$ 0.36 (s, 9H, Me), 6.90–7.50 (m, 8H, aromatic-H), 8.62 (s, 1H, CH=N), 13.42 (s, 1H, OH).

Complex **4**, as brown crystals in 54% yield: $^1$H NMR ($CDCl_3$) $\delta$ 0.38–0.55 (m, 18H, Me), 7.00–7.19 (m, 16H, aromatic-H), 8.03 (s, 2H, CH=N); FD-MS, 654 ($M^+$). Anal. found: C, 58.76; H, 5.21; N, 4.30. Calcd. for $TiC_{32}H_{36}N_2O_2Si_2Cl_2$: C, 58.63; H, 5.53; N, 4.27.

*2.2.4. bis[N-(3-tert-Butylsalicylidene)-2′-methylanilinato]titanium(IV)dichloride (**5**)*

Ligand **e**, *N*-(3-*tert*-butylsalicylidene)-2′-methylaniline, as an orange oil in 87% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.48 (s, 9H, $^t$Bu), 2.41 (s, 3H, Me), 6.83–7.40 (m, 7H, aromatic-H), 8.54 (s, 1H, CH=N), 13.94 (s, 1H, OH).

Complex **5**, as reddish brown crystals in 58% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.14–1.23 (m, 18H, $^t$Bu), 2.40 (s, 6H, Me), 6.44–7.80 (m, 14H, aromatic-H), 8.19 (s, 2H, CH=N); FD-MS, 650 ($M^+$). Anal. found: C, 65.81; H, 6.29; N, 4.12. Calcd. for $TiC_{36}H_{40}N_2O_2Cl_2$: C, 66.37; H, 6.19; N, 4.30.

*2.2.5. bis[N-(3-tert-Butylsalicylidene)-2′-isopropylanilinato]titanium(IV)dichloride (**6**)*

Ligand **f**, *N*-(3-*tert*-butylsalicylidene)-2′-*iso*-propylaniline, as a yellow oil in 97% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.21 (s, 6H, Me), 1.49 (s, 9H, $^t$Bu), 3.49 (m, 1H, CH), 6.88–7.43 (m, 7H, aromatic-H), 8.57 (s, 1H, CH=N), 13.79 (s, 1H, OH).

Complex **6**, as ocher crystals in 71% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.13 (s, 18H, $^t$Bu), 1.23 (d, $J$ = 13.2 Hz, 6H, Me), 1.25 (d, $J$ = 14.3 Hz, 6H, Me), 3.28 (m, 2H,CH), 6.46–7.49 (m, 14H, aromatic-H), 8.22 (s, 2H, CH=N); FD-MS, 706 ($M^+$). Anal. found: C, 67.72; H, 7.03; N, 3.90. Calcd. for $TiC_{40}H_{48}N_2O_2Cl_2$: C, 67.90; H, 6.84; N, 3.96.

*2.2.6. bis[N-(3-tert-Butyl-5-methylsalicylidene)anilinato]titanium(IV)dichloride (**7**)*

Ligand **g**, *N*-(3-*tert*-butyl-5-methylsalicylidene)aniline, as an orange oil in 97% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.46 (s, 9H, $^t$Bu), 2.30 (s, 3H, Me), 7.03–7.43 (m, 7H, aromatic-H), 8.56 (s, 1H, CH=N), 13.65 (s, 1H, OH).

Complex **7**, as reddish brown crystals in 52% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.31 (s, 18H, $^t$Bu), 2.27 (s, 6H, Me), 6.72–7.42 (m, 14H, aromatic-H), 8.02 (s, 2H, CH=N); FD-MS, 650 ($M^+$). Anal. found: C, 65.95; H, 6.12; N, 4.10. Calcd. for $TiC_{36}H_{40}N_2O_2Cl_2$: C, 66.37; H, 6.19; N, 4.30.

*2.2.7. bis[N-(3,5-di-tert-Butylsalicylidene)anilinato]titanium(IV)dichloride (**8**)*

Ligand **h**, *N*-(3,5-di-*tert*-butylsalicylidene)aniline, as yellow crystals in 93% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.37 (s, 9H, *t*-Bu), 1.51 (s, 9H, *t*-Bu), 7.22–7.46 (m, 7H, aromatic-H), 8.66 (s, 1H, CH=N), 13.69 (s, 1H, OH).

Complex **8**, as brown crystals in 65% yield: $^1$H NMR($CDCl_3$) $\delta$ 1.27 (s, 18H, $^t$Bu), 1.34 (s, 18H, $^t$Bu), 6.87–7.66 (m, 14H, aromatic-H), 8.06 (s, 2H, CH=N); FD-MS, 734 ($M^+$). Anal. found: C, 67.78; H, 7.03; N, 3.70. Calcd. for $TiC_{42}H_{52}N_2O_2Si_2Cl_2$: C, 68.57; H, 7.12; N, 3.81.

*2.3. Polymerization procedure*

*2.3.1. Ethylene polymerization*

Ethylene polymerization was carried out under atmospheric pressure in toluene in a 500 ml glass reactor equipped with a propeller-like stirrer. Toluene (250 ml) was introduced into the nitrogen-purged reactor and stirred (600 rpm). Toluene was kept at 25 °C, and then the ethylene gas feed (100 l/h) was started. After 10 min, polymerization was initiated by adding a toluene solution of DMAO (1.0 M, 1.25 ml) and then an 0.005 mM solution of a complex in toluene (1 ml, 5 μmol) into the reactor. After 30 min, *sec*-butyl alcohol (10 ml) was added to terminate the polymerization. The resulting mixture was added to acidified methanol (1000 ml containing 2 ml of concentrated HCl). The polymer was recovered by filtration, washed with methanol (200 ml) and dried in a vacuum oven at 80 °C for 10 h.

*2.3.2. Propylene polymerization*

Propylene polymerization was carried out in a 1000 ml stainless steel reactor equipped with a propeller-like stirrer. Toluene (350 ml) was introduced into the reactor under propylene atmospheric pressure at 0 °C. Propylene gas was pumped into the reactor up to 0.37 MPa propylene pressure with stirring (350 rpm) at 1 °C. Polymerization was initiated by adding a 1.5 M MAO solution in toluene (10 ml, 15 mmol) and then an 0.00833 M complex solution in toluene (12 ml, 0.1 mmol) into the reactor. After 6 h, the polymerization was terminated by the addition of methanol (5 ml). The reactor was vented and the resulting mixture was added to acidified methanol (1500 ml containing 5 ml of concentrated HCl). The polymer was recovered by filtration, washed with methanol (200 ml × 2), and dried in a vacuum oven at 80 °C for 10 h.

## 3. Results and discussion

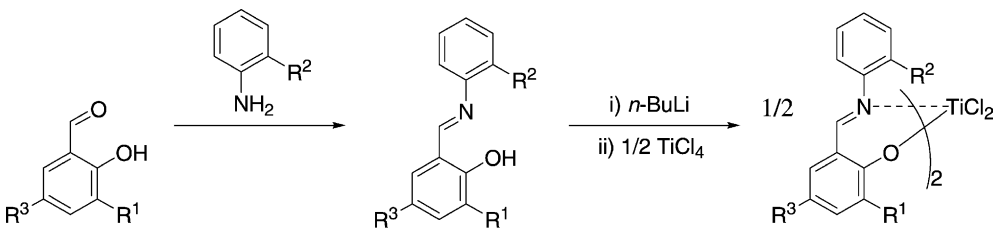
### 3.1. Syntheses of ligands and complexes

The syntheses of phenoxy–imine ligand (**c**) and complex **3** were previously reported [29,39,74]. Phenoxy–imine ligands (**a**), (**b**), and (**d**)–(**h**) were conveniently prepared in high yields (59–97%) by the Schiff base condensation of the appropriate aniline and salicylaldehyde derivatives. Bis(phenoxy–imine)Ti complexes **1** [60], **2** and **4**–**8** were readily synthesized in good yields (52–75%) by treating $TiCl_4$ with the lithium salt of the corresponding phenoxy–imine ligand according to Scheme 1. The complexes **1**–**8** have potentially five configurations as a consequence of different binding geometries of the two non-symmetric bidentate phenoxy–imine ligands. However, considering simple valence shell electrons repulsion concepts, it is reasonable that the complexes are assumed to have a configuration with a *trans*-O, *cis*-N, and *cis*-Cl arrangement. X-ray crystallographic analyses [29,39,60,74] revealed that complexes **1** and **3** contain approximately octahedrally coordinated metal centers with mutually *cis* imine-nitrogens, *trans* phenoxy–oxygens, and *cis* chlorines. Therefore, the complexes **1** and **3** have $C_2$ symmetry. Complexes **2** and **4**–**8** are presumed to take the same configurations as complexes **1** and **3**. An important feature of these complexes is that the chlorines occupy mutually *cis* coordination sites. This is potentially significant for generating efficient polymerization active centers since a crucial requirement for a highly-active catalyst is to have a pair of *cis* located sites for olefin polymerization.

A comparison of the molecular structure of the complex **3** with that of its Zr congener demonstrated that Ti metal in the complex **3** is more shielded and sterically hindered by the ligands compared to the Zr congener as shown by the considerably shorter Ti–O, Ti–N and Ti–Cl bond distances, and the larger O–Ti–O bond angle due to the smaller ionic radius of $Ti^{4+}$ (0.68 Å) relative to $Zr^{4+}$ (0.86 Å) though the two complexes possess the same configurations. These structural differences between the two complexes are thought to be common to bis(phenoxy–imine)Ti and Zr complexes having the same ligands.

### 3.2. Ethylene polymerization results

Bis(phenoxy–imine)Ti complexes **1**–**8**, in combination with DMAO as a cocatalyst, were evaluated as catalysts for the polymerization of ethylene in




**a–h** **1–8**

| ligand | complex | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|---|
| **a** | **1** | H | H | H |
| **b** | **2** | Me | H | H |
| **c** | **3** | $^t$Bu | H | H |
| **d** | **4** | $SiMe_3$ | H | H |
| **e** | **5** | $^t$Bu | Me | H |
| **f** | **6** | $^t$Bu | $^i$Pr | H |
| **g** | **7** | $^t$Bu | H | Me |
| **h** | **8** | $^t$Bu | H | $^t$Bu |

Scheme 1. Synthetic route to titanium complexes.

Table 1
Ethylene polymerization with complexes **1**–**8**/DMAO[a]

| Entry | Complex | Yield (g) | Activity (kg-PE/mol-Ti h) | $M_w$ ($\times 10^3$) | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | **1** | 0.095 | 38 | 66 | 3.13 |
| 2 | **2** | 0.615 | 246 | 402 | 1.54 |
| 3 | **3** | 8.100 | 3240 | 1281 | 2.55 |
| 4 | **4** | 6.665 | 2666 | 1105 | 2.51 |
| 5 | **5** | 0.753 | 301 | 355 | 2.14 |
| 6 | **6** | 0.466 | 186 | 296 | 1.29 |
| 7 | **7** | 4.275 | 1710 | 1096 | 2.35 |
| 8 | **8** | 6.171 | 2468 | 1133 | 2.35 |

[a] Polymerization conditions: solvent, toluene, 250 ml, complex 5 μmol, DMAO, 1.25 mmol; ethylene, atmospheric pressure 100 l/h; polymerization time, 30 min; polymerization temperature, 25 °C.

toluene solvent at 25 °C for 30 min under atmospheric pressure. All the complexes are active ethylene polymerization catalysts under the given conditions, and produced highly-linear polyethylenes (branching less than 1 per 1000 carbon atoms; based on IR analysis). The polymerization results are collected in Table 1. The data demonstrated that the steric bulk of the $R^1$ substituent significantly affects both catalytic activity and product molecular weight. Complex **1** bearing a hydrogen at the $R^1$ position ($R^2 = R^3 = H$) gave polyethylene with an $M_w$ of 66,000, displaying a moderate activity of 38 kg-PE/mol-cat h under these conditions. Complex **2** having a sterically bulkier substituent, a methyl, at the $R^1$ position yielded much higher molecular weight polyethylene ($M_w$ 402,000) with a considerably enhanced activity of 246 kg-PE/mol-cat h compared with the complex **1** ($R^1 = H$). Thus, the attachment of the methyl increased catalytic activity and product molecular weight by a factor of ca. 6 versus complex **1**. The effects of the steric bulk of the $R^1$ substituent were more pronounced for complexes **3** and **4**, possessing a *t*-butyl and a trimethylsilyl, respectively. Complex **3** ($R^1 = t$-butyl) displayed a still higher activity of 3240 kg-PE/mol-cat h and provided polyethylene with a further enhanced molecular weight ($M_w$ 1,281,000). Likewise, complex **4** ($R^1$ = trimethylsilyl) showed a very high activity of 2666 kg-PE/mol-cat h and furnished high molecular weight polyethylene ($M_w$ 1,105,000). Therefore, the increase in the steric bulk of the $R^1$ substituent resulted in the marked enhancement in both the catalytic activity and the product molecular weight. The activity obtained with complex **3**, 3240 kg-PE/mol-cat h, represents one of the highest reported for Ti complexes with no Cp ligand(s) under the same or similar conditions. Similar effects of the $R^1$ substituent were observed for the corresponding bis(phenoxy–imine)Zr complexes, as reported previously [31,33,74]. The increase in the catalytic activity as a result of introducing sterically-hindered substituent at the $R^1$ position may be attributed to the fact that the steric bulk of the $R^1$ substituent plays an essential role in the ion separation between the cationic active species and the anionic cocatalyst. The effective ion separation will provide more space for polymerization and, in addition, enhances the degree of unsaturation associated with the catalytically active cationic species. On the other hand, the increase in the product molecular weight may be ascribed to the fact that the steric congestion exerted by the $R^1$ substituent diminishes the rate of chain termination.

The steric bulk of the $R^2$ substituent also has a significant influence on the catalytic performance of the complexes but differently compared with the $R^1$ substituent. Complex **5** bearing a methyl at the $R^2$ position demonstrated an activity of 301 kg-PE/mol-cat h and gave polyethylene with an $M_w$ of 355,000. The activity and molecular weight values obtained with complex **5** are much lower than complex **3** ($R^2 = H$). In addition, complex **6** with an *i*-propyl at the $R^2$ position exhibited more reduced activity (186 kg-PE/mol-cat h) and furnished polyethylene with further decreased molecular weight ($M_w$ 296,000). Therefore, the increase in the steric bulk of the $R^2$ substituent resulted in the quite deleterious effects on the catalytic activity and the product molecular weight. The decrease in the catalytic activity as a result of introducing the alkyl group into the $R^2$ position seems reasonable and is probably attributed to the increased steric congestion in close proximity to the active site, which reduces the catalytic activity by hindering access of ethylene to the active site and/or growth of the polymer chain. However, the decrease in the product molecular weight was rather unexpected since for the Zr congeners the attachment of the methyl or the *i*-propyl to the $R^2$ position greatly enhances the product molecular weight [31,33,74]. Considering that a molecular weight is determined by the relative rate of chain propagation and chain termination, these results indicated that the introduction of the methyl or the *i*-propyl to the $R^2$ position reduces

Table 2
Propylene polymerization with complexes **1**–**8**/MAO[a]

| Entry | Complex | Yield (g) | Activity (kg-PP/mol-Ti h) | $M_w$ ($\times 10^3$) | $M_w/M_n$ | $T_m$ (°C) | rrrr (%) |
|---|---|---|---|---|---|---|---|
| 1 | **1** | 0.239 | 0.40 | 735/15 | 2.93/1.51 | n.d. | – |
| 2 | **2** | 4.021 | 6.70 | 101 | 1.47 | n.d. | – |
| 3 | **3** | 0.570 | 0.95 | 6 | 1.38 | 97 | 62.9 |
| 4 | **4** | 0.960 | 1.60 | 14 | 1.73 | 140 | 83.7 |
| 5 | **5** | 0.006 | 0.01 | – | – | – | – |
| 6 | **6** | 0.041 | 0.07 | 4014 | 120.78 | n.d. | – |
| 7 | **7** | 0.561 | 0.94 | 7 | 1.39 | 101 | 66.4 |
| 8 | **8** | 1.265 | 2.11 | 11 | 1.55 | 107 | 68.8 |

[a] Polymerization conditions: solvent, toluene, 350 ml, complex 0.1 mmol, MAO, 15 mmol; propylene 0.37 MPa; polymerization time, 6 h; polymerization temperature, 1 °C.

the rate of chain propagation relative to that of chain termination, which may be ascribed to the fact that bis(phenoxy–imine)Ti complexes have more packed and shielded structures than their Zr counterparts.

Alternatively, the $R^3$ substituent had an effect on the catalytic activity but very little influence on the product molecular weight. Thus, complexes **7** ($R^3$ = methyl) and **8** ($R^3$ = *t*-butyl) displayed activities of 1710 kg-PE/mol-cat h (complex **7**) and 2468 kg-PE/mol-cat h (complex **8**), being fairly different from that obtained with complex **3** (3240 kg-PE/mol-cat h) and produced polyethylenes having molecular weights of 1,096,000 (complex **7**) and 1,133,000 (complex **8**), being almost the same as that for the complex **3** ($R^3$ = H). There is no clear relationship between the catalytic activity and the steric bulk of the $R^3$ substituent (activity order: H > *t*-Bu > Me). This is presumably due to the difference of electronic structure between the complexes considering that the $R^3$ position is located far from the active site.

Molecular weight distribution ($M_w/M_n$) data based on GPC analyses showed that complexes **1**–**8** afforded polyethylenes with narrow $M_w/M_n$ values in the range of 1.29–3.13, indicating normal single-site behavior under the conditions summarized in Table 1.

### 3.3. Propylene polymerization results

Results from the X-ray analyses of complexes **1** [60] and **3** [29,39,74], the complexes examined are thought to possess $C_2$ symmetry, as discussed. Consequently, the Ti complexes were initially targeted as viable catalysts that produce isotactic polymers via a site-control mechanism. Complexes **1**–**8** were investigated as propylene polymerization catalysts at 1 °C under 0.37 MPa of propylene using MAO[1] as a cocatalyst for 6 h. The relevant results are collected in Table 2. The effects of the substituents **1**–**3** on the catalytic performance of the complexes are rather different from those observed for ethylene polymerization, but again steric bulk in the *ortho* position of the phenoxy–oxygen ($R^1$ substituent) is revealed to be of critical importance in achieving high catalytic performance. Complex **1** ($R^1$ = H) had a very low activity of 0.40 kg-PP/mol-cat h and provided bimodal polypropylene with maxima at $M_w$ 15,000 ($M_w/M_n$ = 1.51) and $M_w$ 735,000 ($M_w/M_n$ = 2.93). The bimodal behavior of complex **1** may be ascribed to the catalyst decay because of the long polymerization time of 6 h, as well as the extremely reduced steric bulk of the $R^1$ substituent ($R^1$ = H) which provides steric protection to the phenoxy–oxygen from the cocatalyst MAO. However, the possibility cannot be ruled out that the bimodal polypropylene originates from structural isomers which arise from different modes of ligand coordination. Com-

[1] Although for ethylene polymerization with the Ti complexes the MAO used has no significant influence on catalytic properties, for propylene polymerization it has a profound influence on both the catalytic activity and syndiospecificity of the catalyst system; for example, complexes **3** and **8** with DMAO (dried MAO from which most of the $AlMe_3$ is removed; MAO was purchased from Albemarle) demonstrated higher activities compared with the MAO (standard MAO which contains about 10 wt.% $AlMe_3$; purchased from Witco Co.) cocatalyst system and formed substantially atactic polypropylenes [37]. The reason for the great difference in catalyst performance as a result of using DMAO and MAO as cocatalysts for the polymerization of propylene is unclear at the present time and is a focus of our current work.

plex **2** having a sterically-hindered substituent, a methyl, at the $R^1$ position showed a higher activity of 6.70 kg-PP/mol-cat h compared with complex **1** ($R^1$ = H) and produced polypropylene possessing $M_w$ of 101,000. However, further increase in the size of the $R^1$ substituent resulted in diminished activities and product molecular weights. Complex **3** ($R^1$ = *t*-butyl) exhibited a lower activity of 0.95 kg-PP/mol-cat h, by a factor of ca. 1/7, and generated polypropylene having $M_w$ of 6000, by a factor of ca. 1/17. Moreover, complex **4** ($R^1$ = trimethylsilyl) displayed a still decreased activity of 1.60 kg-PP/mol-cat h and formed polypropylene with an $M_w$ of 14,000. It is clear that steric effects of the $R^1$ substituent significantly influence the activity of the complexes, and a moderate degree of steric crowding seems to be optimal for propylene polymerization. The observations with respect to catalytic activity probably originate from the fact that the introduction of steric bulk into the $R^1$ position can have two competing effects: (1) activity increase due to an effective ion separation (the pro effect); (2) activity decrease because of an introduced steric obstacle (the con effect).

The introduction of a methyl or an *i*-propyl group into the $R^2$ position resulted in practically inactive catalysts for the polymerization of propylene, probably due to steric hindrance, as expected by the results obtained from ethylene polymerization.

Alternatively, the substituent at the $R^3$ position exercised an effect on both the catalytic activity and the product molecular weight but not significantly, presumably because of the location of the $R^3$ position being far from the polymerization center. Complexes **7** ($R^3$ = methyl) and **8** ($R^3$ = *t*-butyl) displayed decreased activities of 0.94 kg-PP/mol-cat h and 2.11 kg-PP/mol-cat h, and afforded polypropylenes having reduced $M_w$ of 7000 and 11,000, respectively.

The molecular weight distribution ($M_w/M_n$) values of the polypropylenes formed using complexes **2**, **3**, **4**, **7** and **8** are in the range of 1.39–1.73, indicating that the polymers are produced by single-site catalysts.[2] On the other hand, though complex **6** produced narrow molecular weight distribution polyethylene ($M_w/M_n$ = 1.29) the same complex provided exceptionally broad molecular weight distribution polypropylene ($M_w/M_n$ 120.78), suggesting a loss of active site uniformity under the given conditions. The reason for this observation is unclear at present.

The semicrystalline and crystalline polymers arising from complexes **3**, **4**, **7** and **8** exhibit peak melting temperatures ($T_m$'s) ranging from 97 to 140 °C, indicative of the formation of stereoregular polymers. Surprisingly, microstructural analyses using $^{13}C$ NMR spectroscopy revealed that the polymers are syndiotactic polypropylenes containing *rrrr* pentads in the range of 62.9–83.7%. The unexpected formation of syndiotactic polypropylenes suggests that catalyst symmetry is not a rigid requirement for determining polymer stereochemistry though a predictable relationship between catalyst symmetry and polymer tacticity has been practically established vis-à-vis metallocene catalysts. The syndiotactic polypropylenes formed from complexes **3**, **4**, **7** and **8** involve isolated *m*-dyad errors (*rrrm* and *rmrr*; a stereochemical error is propagated) in the methyl pentad region (Fig. 1), showing that the polymer-chain-end controls the syndiospecificity of propylene insertion (chain-end control mechanism). With combinatorial approach, Tian and Coates [63] have successfully obtained complex **8**, which gave syndiotactic polypropylene containing 71.6% *rrrr* pentads (20 °C) via a chain-end control mechanism. Assuming that an active species originating from complexes **3**, **4**, **7** and **8** adopts an octahedral coordination geometry with a *trans*-O and *cis*-N disposition, a chain-end control mechanism overrides the $C_2$ symmetry of the bis(phenoxy–imine)Ti complexes. Recently, Lambetrti et al. [70] have reported the results of chain-end controlled propylene polymerization using complexes **3** and **8**, and described that the solvent employed affects the syndiospecificity of the complex **3**. The high syndioregularity (62.9–83.7% rrrr pentads) obtained with the bis(phenoxy–imine)Ti complexes by chain-end control is unusual because chain-end control operates well at very low to sub-

[2] Interestingly, under limited conditions bis(phenoxy-imine)Ti complexes possess some characteristics of living ethylene polymerization. For example, complex **3** at 25 °C for 1 min produced narrow molecular weight distribution polyethylene ($M_w/M_n$ 1.12). Similarly, these complexes have some characteristics of the living polymerization of propylene, as indicated by the narrow $M_w/M_n$ values listed in Table 2. As reported, fluorinated versions of the complexes are capable of inducing highly-controlled, thermally robust living propylene [36–38,42,76] as well as ethylene polymerization [35,41,76] by the unprecedented interaction of the fluorine in the ligand and a β-hydrogen of a growing polymer chain.

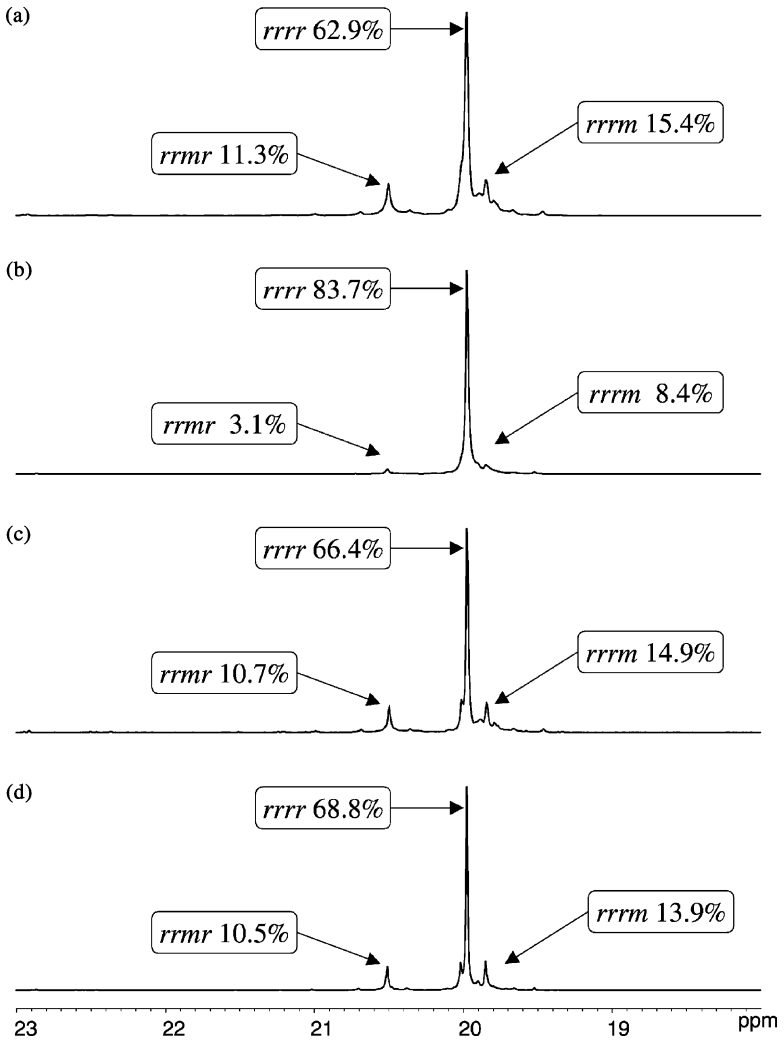



Fig. 1. $^{13}$C NMR spectra of methyl pentad regions of polypropylenes with (a) complex **3**, (b) complex **4**, (c) complex **7**, and (d) complex **8**/MAO.

ambient temperatures and loses its stereoregulating capability at elevated temperatures. To the best of our knowledge, the pentad value obtained with complex **4**, 83.7% *rrrr*, is one of the highest reported to date for syndiotactic polypropylenes produced via a chain-end control mechanism.[3] A striking feature observed in the data is that the $R^1$ substituent plays a decisive role in the achievement of the syndiospecific polymerization. Thus, complexes **3**, **4**, **7** and **8**, having a *t*-butyl or a trimethylsilyl at the $R^1$ position, all formed syndiotactic polypropylenes whereas complexes **1** and **2**, bearing less sterically-encumbered substituent, a methyl or a hydrogen, at the $R^1$ position produced practically atactic polypropylenes. Similar effects were observed for bis(phenoxy–imine)Ti complexes having perfluoroaryl substutients [42]. Therefore, the generality of the importance of the steric bulk of the $R^1$ substituent to syndiospecific propylene polymerization has been confirmed. These facts suggested that the $R^1$ sub-

[3] The corresponding complex having a perfluorophenyl group on the imine-nitrogen exhibited higher syndiospecificity, rrrr 87.4%, probably due to an attractive interaction between the fluorine *ortho* to the imine-nitrogen and a growing polymer chain [36].

stituent is situated in close proximity to the active site, and that the $R^1$ substituent can have steric repulsion against the methyl of the reacting propylene leading to isospecific polymerization. Though the exact cause for this unexpected syndiospecificity displayed by bis(phenoxy–imine)Ti complexes with $C_2$ symmetry warrants further investigation, the syndiospecificity can be explained by a rapid site-inversion relative to chain propagation [70] if a catalytically active species possesses an octahedral geometry with a *trans*-O and *cis*-N arrangement. This site-inversion model was originally proposed for syndiospecific propylene polymerization using V-based catalysts [77]. Recently, based on a QM/MM theoretical study Cavallo and co-workers [71,72] have proposed a site-inversion mechanism that can explain the unexpected syndiospecificity exhibited by the bis(phenoxy–imine)Ti complexes with $C_2$ symmetry. Additionally, their proposal can also explain that the steric bulk of the substituent *ortho* to the phenoxy–oxygen in bis(phenoxy–imine)Ti complexes plays a crucial role in determining the syndiospecificity of the polymerization. Regarding the regiochemistry of the propylene insertion, we postulated that the high level of chain-end controlled syndiospecific polymerization results from a 2,1-insertion of propylene. This is because chain-end control is enhanced by 2,1-insertion due to steric requirements compared to 1,2-insertion and complex **3**/$Ph_3CB(C_6F_5)_4$/$^{i}Bu_3Al$ favors 2,1-insertion of 1-hexene and forms poly(1-hexene)s with ca. 50 mol% regioirregular units [32]. Mechanistic studies of propylene polymerization with bis(phenoxy–imine)Ti complexes using both experimental and theoretical approaches have been reported by Lambetrti et al. [70], Hustad et al. [65], Talarico et al. [73], and Saito et al. [37]; all demonstrating that 2,1-insertion is predominant for chain propagation, as postulated. The results described herein with propylene polymerization as well as our previous reports indicated that bis(phenoxy–imine)Ti complexes have opened a new field of highly-stereoselective chain-end controlled propylene polymerization at elevated temperatures. The principal behavior of the bis(phenoxy–imine)Ti complexes for propylene polymerization (chain-end controlled syndiospecific polymerization via a 2,1-insertion) is the same as that of V-based catalysts though the V-based catalysts suffer from low stereoselectivity. The results obtained suggest that phenoxy–imine ligands can play a vital role in the polymerization of both ethylene and propylene, and these ligands change central Ti metal to V metal vis-à-vis stereochemical features of propylene polymerization.

## 4. Conclusion

In conclusion, we have demonstrated that bis(phenoxy–imine)Ti complexes, Ti-FI Catalysts, can be activated with MAO to give high-performance catalysts for the polymerization of not only ethylene but also propylene. Ti-FI Catalysts are capable of producing high molecular weight polyethylenes with high activities and highly-syndiotactic polypropylenes via a chain-end-control mechanism. The phenoxy–imine-ligand structures greatly influence the catalytic properties of the complexes. The catalytic performance of the complexes having a sterically bulky substituent *ortho* to the phenoxy–oxygen is outstanding for Ti-based non-metallocene catalysts. The results introduced herein together with our previous reports indicate that the FI Catalyst family represents a significant addition to the list of high-performance catalysts for olefin polymerization.

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## References

[1] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. 34 (1995) 1143.
[2] A.L. Mcknight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.
[3] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 428.
[4] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
[5] T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, Makromol. Chem., Rapid Commun. 10 (1989) 349.
[6] H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake, N. Kibino, Macromolecules 25 (1992) 5115.
[7] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.

[8] L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267.
[9] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
[10] A.V. der Linden, C.J. Schaverien, N. Meijboom, C.J. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008.
[11] J.D. Scollard, D.H. McConville, J.J. Vittal, N.C. Payne, J. Mol. Catal. A, Chem. 128 (1998) 201.
[12] R. Baumann, W.M. Davis, R.R. Schrock, J. Am. Chem. Soc. 119 (1997) 3830.
[13] K. Hakala, B. Lofgren, M. Polamo, M. Leskela, Macromol. Rapid Commun. 18 (1997) 635.
[14] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.
[15] T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460.
[16] Y.-M. Jeon, S.J. Park, J. Heo, K. Kim, Organometallics 17 (1998) 3161.
[17] K. Nomura, N. Naga, K. Takaoki, Organometallics 31 (1998) 8009.
[18] K. Nomura, A. Sagara, Y. Imanishi, Macromolecules 35 (2002) 1583.
[19] C. Averbuj, E. Tish, M.S. Eisen, J. Am. Chem. Soc. 120 (1998) 8640.
[20] D.W. Stephan, F. Guerin, R.E.v.H. Spence, L. Koch, X. Gao, S.J. Brown, J.W. Swabey, Q. Wang, W. Xu, P. Zoricak, D.G. Harrison, Organometallics 18 (1999) 2046.
[21] E.Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, Chem. Commun. (2000) 379.
[22] E.Y. Tshuva, I. Goldberg, M. Kol, J. Am. Chem. Soc. 122 (2000) 10706.
[23] Y. Matsuo, K. Mashima, K. Tani, Chem. Lett. (2000) 1114.
[24] S. Murtuza, O.L. Casagrande Jr., R.F. Jordan, Organometallics 21 (2002) 1882.
[25] H. Hagimoto, T. Shiono, T. Ikeda, Macromol. Rapid Commun. 23 (2002) 73.
[26] H. Hagimoto, T. Shiono, T. Ikeda, Macromolecules 35 (2002) 5744.
[27] S. Matsui, T. Fujita, Catal. Today 66 (2001) 61.
[28] H. Makio, N. Kashiwa, T. Fujita, Adv. Synth. Catal. 344 (2002) 477.
[29] S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, T. Fujita, Chem. Lett. (1999) 1065.
[30] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, T. Fujita, Chem. Lett. (1999) 1163.
[31] S. Matsui, M. Mitani, J. Saito, N. Matsukawa, H. Tanaka, T. Nakano, T. Fujita, Chem. Lett. (2000) 554.
[32] J. Saito, M. Mitani, S. Matsui, N. Kashiwa, T. Fujita, Macromol. Rapid Commun. 21 (2000) 1333.
[33] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 123 (2001) 6847.
[34] N. Matsukawa, S. Matsui, M. Mitani, J. Saito, K. Tsuru, N. Kashiwa, T. Fujita, J. Mol. Catal. A, Chem. 169 (2001) 99.
[35] J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa, T. Fujita, Angew. Chem. Int. Ed. 40 (2001) 2918.
[36] J. Saito, M. Mitani, J. Mohri, S. Ishii, Y. Yoshida, T. Matsugi, S. Kojoh, N. Kashiwa, T. Fujita, Chem. Lett. (2001) 576.
[37] J. Saito, M. Mitani, M. Onda, J. Mohri, S. Ishii, Y. Yoshida, T. Nakano, H. Tanaka, T. Matsugi, S. Kojoh, N. Kashiwa, T. Fujita, Macromol. Rapid Commun. 22 (2001) 1072.
[38] S. Kojoh, T. Matsugi, J. Saito, M. Mitani, T. Fujita, N. Kashiwa, Chem. Lett. (2001) 822.
[39] J. Saito, M. Mitani, S. Matsui, Y. Tohi, H. Makio, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, Macromol. Chem. Phys. 203 (2002) 59.
[40] S. Ishii, J. Saito, M. Mitani, J. Mohri, N. Matsukawa, N. Kashiwa, T. Fujita, J. Mol. Catal. A, Chem. 179 (2002) 11.
[41] M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 3327.
[42] M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 7888.
[43] S. Ishii, M. Mitani, J. Saito, S. Matsuura, S. Kojoh, N. Kashiwa, T. Fujita, Chem. Lett. (2002) 740.
[44] S. Ishii, J. Saito, M. Matsuura, M. Mitani, N. Kashiwa, T. Fujita, Macromol. Rapid Commun. 23 (2002) 693.
[45] J. Saito, M. Onda, S. Matsui, M. Mitani, R. Furuyama, H. Tanaka, T. Fujita, Macromol. Rapid Commun. 23 (2002) 1118.
[46] Y. Tohi, H. Makio, S. Matsui, M. Onda, T. Fujta, Macromolecules 36 (2003) 523.
[47] J. Saito, Y. Suzuki, T. Fujita, Chem. Lett., in press.
[48] Y. Nakayama, H. Bando, Y. Sonobe, H. Kaneko, N. Kashiwa, T. Fujita, J. Catal., in press.
[49] M. Mitani, R. Furuyama, J. Mohri, J. Saito, Y. Yoshida, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc., in press.
[50] M. Mitani, T. Nakano, T. Fujita, Chem. Eur. J., in press.
[51] M. Mitani, J. Mohri, R. Furuyama, S. Ishii, T. Fujita, Chem. Lett. 32 (2003) 238.
[52] Y. Suzuki, N. Kashiwa, T. Fujita, Chem. Lett. (2002) 358.
[53] Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, M. Nitabaru, T. Nakano, H. Tanaka, T. Fujita, Chem. Lett. (2000) 1270.
[54] Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, Organometallics 20 (2001) 4793.
[55] Y. Yoshida, J. Saito, M. Mitani, Y. Takagi, S. Matsui, S. Ishii, T. Nakano, N. Kashiwa, T. Fujita, Chem. Commun. (2002) 1298.
[56] T. Matsugi, S. Matsui, S. Kojoh, Y. Takagi, Y. Inoue, T. Fujita, N. Kashiwa, Chem. Lett. (2001) 566.
[57] T. Matsugi, S. Matsui, S. Kojoh, Y. Takagi, Y. Inoue, T. Nakano, T. Fujita, N. Kashiwa, Macromolecules 35 (2002) 4880.
[58] Y. Inoue, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, Chem. Lett. (2001) 1060.
[59] Y. Suzuki, Y. Inoue, H. Tanaka, N. Kashiwa, T. Fujita, in: Proceedings of the Meeting of the 90th Catalyst Society of Japan, Hamamatsu, 2002, p. 167.

[60] J. Strauch, T.H. Warren, G. Erker, R. Fröhlich, P. Saarenketo, Inorg. Chim. Acta 300–302 (2000) 810.
[61] V.C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2000) 1969.
[62] D.J. Jones, V.C. Gibson, S.M. Green, P.J. Maddox, Chem. Commun. (2002) 1038.
[63] J. Tian, G.W. Coates, Angew. Chem. Int. Ed. 39 (2000) 3626.
[64] P.D. Hustad, J. Tian, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 5134.
[65] P.D. Hustad, J. Tian, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 3614.
[66] P.B. Mackenzie, L.S. Moody, C.M. Killian, J.A. Ponasik, G.G. Lavoie, J.C. Pearson, T.W. Smith, L.A. Tucker, M. Moore, A. Farthing, G. King, M. Meadows, C. Sass, E. Savitiski, Polym. Mater. Sci. Eng. 84 (2001) 326.
[67] P.D. Knight, A.J. Clarke, B.S. Kimberley, R.A. Jackson, P. Scott, Chem. Commun. (2002) 352.
[68] D.J.H. Emslie, W.E. Piers, R. McDonald, J. Chem. Soc., Dalton Trans. (2002) 293.
[69] J. Huang, B. Lian, Y. Qian, W. Zhou, W. Chen, G. Zheng, Macromolecules 35 (2002) 4871.
[70] M. Lambetrti, D. Pappalardo, A. Zambelli, C. Pellecchia, Macromolecules 35 (2002) 658.
[71] L. Cavallo, G. Talarico, in: Proceedings of the 2nd JAIST/JLPO Workshop on Ziegler-Natta Catalysts, Sorrento, 20–21 June 2002.
[72] G. Milano, L. Cavallo, G. Guerra, J. Am. Chem. Soc. 124 (2002) 13368.
[73] G. Talarico, V. Busico, R. Cipullo, L. Cavallo, in: Proceedings of the 1st Blue Sky Conference on Catalytic Olefin Polymerization, Sorrento, 17–20 June 2002.
[74] T. Fujita, Y. Tohi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio, T. Tsutsui, Eur. Patent 0874005 (1998), filing date April 25, 1997, Chem. Abstr. 129 (1998) 331166.
[75] K. Tsuru, M. Mitani, Y. Takagi, T. Fujita, JP Patent 119316 (2000), filing date October 20, 1998.
[76] M. Mitani, Y. Yoshida, J. Mohri, K. Tsuru, S. Ishii, S. Kojoh, T. Matsugi, J. Saito, N. Matsukawa, S. Matsui, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, WO Patent 01/55231 A1 (2001), filing date January 26, 2000, Chem. Abstr. 135 (2001) 137852.
[77] P. Corradini, G. Guerra, R. Pucciariello, Macromolecules 18 (1985) 2030.