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Priority Communication

New olefin polymerization catalyst systems comprised of bis(phenoxy-imine) titanium complexes and $MgCl_2$-based activators

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Abstract

$MgCl_2/i$-butylaluminum 2-ethyl-1-hexoxide, $i\text{-Bu}_m\text{Al(OR)}_n$, prepared by the dealcoholysis of the $MgCl_2$/2-ethyl-1-hexanol adduct with $i\text{-Bu}_3\text{Al}$, was investigated as an activator for bis(phenoxy-imine)Ti complexes. The complexes with $MgCl_2/i\text{-Bu}_m\text{Al(OR)}_n$ displayed very high ethylene polymerization activities comparable to those obtained with methylalumoxane (MAO) activation. In addition, the activities obtained were comparable to or exceeded that found for the Cp_2TiCl_2/MAO catalyst system under identical conditions. Moreover, the catalyst systems produced narrow molecular weight distribution polyethylenes displaying good morphology. These are the first examples of MAO- or borate-free, highly active, single-site catalysts based on a transition metal complex and a $MgCl_2$-based activator.

Keywords: Catalysis; Polymerization; Activator; Magnesium dichloride; Alkylaluminum; Transition metal complex; FI catalysts

1. Introduction

The development of $MgCl_2$-supported titanium catalysts, beginning in the late 1960s, has had an enormous impact on the polyolefin industry [1,2]. These catalysts have contributed to the tremendous growth of polyolefin production and are still the pillars of the polyolefin industry. Although the catalytic efficiency is high, rational catalyst design for well-defined polyolefins is difficult because of the heterogeneous and multi-site nature of these catalysts. The mode and mechanism of action of these catalysts is still a topic of current research. It is known from kinetic studies that $MgCl_2$, originally used as a support, increases both the concentration of active species and the chain propagation rate constant [3]. It is believed that $MgCl_2$ functions as an activator [4–6] for titanium chloride species as well as a support [7–9]. Up to now, several highly active transition metal complexes including metallocenes with $MgCl_2$-based activator catalyst systems, often introduced as $MgCl_2$-supported catalyst systems, have been reported [10–15]. These catalyst systems normally give polymers with broad molecular weight distributions. Recently, Kissin et al. have reported that a mixture of Et_2AlCl or Me_2AlCl with Bu_2Mg, resulting in the formation of $MgCl_2$, effectively activates metallocenes to generate single-site catalysts, though lower activities relative to MAO activation [16] are observed. There is, however, no report regarding highly active, single-site catalysts based on transition metal complexes with $MgCl_2$-based activators which provide narrow molecular weight distribution polymers with narrow chemical homogeneity in comonomer distributions.

Recently, as a result of ligand-oriented catalyst design research [17–19], we have developed bis(phenoxy-imine)Ti group 4 transition metal complexes, named FI catalysts, for olefin polymerization [20–26]. These complexes displayed very high ethylene polymerization activities with MAO activator. We postulated that $MgCl_2$ may work as an activator for the bis(phenoxy-imine)Ti complexes since these complexes possess O and N heteroatoms in the ligands, which are capable of electronically interacting with $MgCl_2$. Thus, we decided to investigate $MgCl_2$ as an activator for the bis(phenoxy-imine)Ti complexes in the hope of developing high-performance catalysts based on these complexes. In this communication, we describe new catalyst systems comprised of bis(phenoxy-imine) titanium complexes and $MgCl_2$-based activators, which produce narrow molecular weight distribution polyethylenes with very high activities,

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comparable to those found for MAO activator systems. This represents the first examples of MAO- or borate-free, highly active, single-site catalysts based on $MgCl_2$-based activator systems.

2. Experimental

2.1. General procedures and materials

All manipulations of air- and/or water-sensitive compounds were performed under a dry nitrogen atmosphere using standard Schlenk flask techniques or in a dry nitrogen glovebox. n-Decane (Mitsui Chemicals, Inc.) and toluene (Wako Pure Chemical Industries, Ltd.) were dried over Al_2O_3. 2-Ethyl-1-hexanol (Wako Pure Chemical Industries, Ltd.) was dried by bubbling through highly pure dry N_2. Anhydrous $MgCl_2$ was purchased from Toho Catalyst Co., Ltd., and was used as received. Cp_2TiCl_2 (Wako Pure Chemical Industries, Ltd.) and i-Bu_3Al (Tosoh-Akzo Co., Ltd.) were used without further purification. Methylalumoxane (MAO) was purchased from Albemarle as a 1.2 M toluene solution and used as received. Ethylene and propylene were obtained from Sumitomo Seika Co., Ltd., and Mitsui Chemicals, Inc., respectively.

2.2. Preparation of an $MgCl_2/2$-ethyl-1-hexanol adduct solution

Anhydrous $MgCl_2$ (9.52 g, 100 mmol) was added portionwise to a stirred solution of 2-ethyl-1-hexanol (39.07 g, 300 mmol) in decane (48.5 ml) at room temperature. The resultant mixture was heated at 140 °C for 4 h with stirring, which gave a clear solution. After cooling to room temperature, the resulting solution was added to a dissolved solution of 2-ethyl-1-hexanol (39.07 g, 300 mmol) in toluene (853.1 ml) at room temperature to give a 0.10 M $MgCl_2/2$-ethyl-1-hexanol adduct solution.

2.3. Ethylene polymerization

Ethylene polymerization was carried out in a 1000-ml stainless steel reactor equipped with a propeller-like stirrer at 50 °C under 0.9 MPa ethylene pressure in toluene. Toluene (500 ml) was introduced into the reactor under ethylene atmospheric pressure, and the toluene was thermostated to 50 °C with stirring (150 rpm). A 1.00 M i-Bu_3Al solution in toluene (2.40 ml, 2.40 mmol) and a 0.10 M $MgCl_2/2$-ethyl-1-hexanol adduct solution (4.00 ml, 0.40 mmol as Mg) were added, respectively, to the reactor and stirred for 3 min to give $MgCl_2/i\text{-}Bu_mAl(OR)_n$. Subsequently, a 0.0005 M toluene solution of a complex (1.00 ml, 0.5 µmol) was added to the reactor. Ethylene was pumped into the reactor up to 0.9 MPa pressure with vigorous stirring (350 rpm) to initiate polymerization. Ethylene pressure was maintained at 0.9 MPa by a continuous ethylene feed. After 30 min, the polymerization was quenched by an injection of methanol (5 ml). The reactor was vented and the resulting mixture was added to acidified methanol (1000 ml containing 5 ml of conc. HCl). The polymer was isolated by filtration, washed with methanol (200 ml × 2), and dried overnight in a vacuum oven at 80 °C to constant weight.

2.4. Ethylene–propylene copolymerization

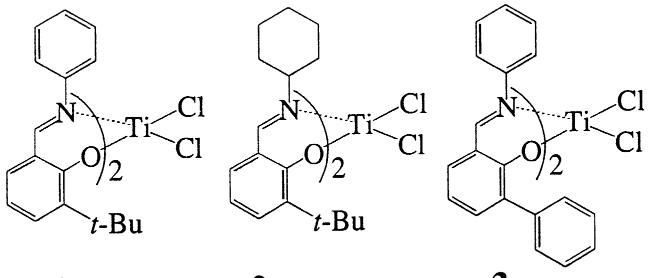
Ethylene–propylene copolymerization was carried out in a 1000-ml stainless steel reactor equipped with two propeller-like stirrers at 50 °C under 0.9 MPa ethylene/propylene total pressure. Toluene (400 ml) was introduced into the reactor under ethylene at atmospheric pressure at room temperature. Propylene (40 l) was pumped into the reactor with the aid of a gas flow meter (4.1 l/min, 9.75 min) with vigorous stirring (800 rpm). After the solution was thermostated to 50 °C, ethylene was pumped into the reactor with a total pressure of up to 0.9 MPa. A 1.00 M i-Bu_3Al solution in toluene (4.80 ml, 4.80 mmol) and a 0.10 M $MgCl_2/2$-ethyl-1-hexanol adduct solution (8.00 ml, 0.80 mmol as Mg) were added to the reactor and stirred for 3 min to give $MgCl_2/i\text{-}Bu_mAl(OR)_n$. Polymerization was started by adding a 0.001 M toluene solution of complex **3** (1.00 ml, 1.0 µmol) to the reactor. Total pressure was maintained at 0.9 MPa by a continuous ethylene feed. After 30 min, the polymerization was quenched by the injection of methanol (5 ml). The reactor was vented and the resulting mixture was added to acidified methanol (1500 ml containing 5 ml of conc. HCl). The polymer was isolated by filtration, washed with methanol (200 ml × 2), and dried overnight in a vacuum oven at 130 °C to a constant weight.

2.5. Polymer characterization

Polymer molecular weights (M_w) and molecular weight distributions (M_w/M_n) were determined using a Waters 150-C gel permeation chromatograph at 145 °C with polyethylene calibration and equipped with three TSKgel columns (two sets of TSKgelGMH$_{HR}$-H(S)HT and TSKgel GMH$_6$-HTL). GPC-IR spectrum was obtained on a Nicolet Magna560 FT-IR, using a Millipore GPC-150 gel permeation chromatograph at 140 °C equipped with two Plgel-MIXED-A (polyethylene calibration). The propylene content of the ethylene/propylene copolymer was determined by means of IR analysis using an FT/IR-350 from JASCO Co.

3. Results and discussion

The $MgCl_2$-based activator used in this study was prepared by the dealcoholysis of a $MgCl_2$/alcohol adduct with i-Bu_3Al since this method produces highly porous small $MgCl_2$ particles, which should be suitable as an activator. Treatment of $MgCl_2$ with 6.0 eq of 2-ethyl-1-hexanol in decane at 140 °C formed a $MgCl_2/2$-ethyl-1-



1 **2** **3**

Scheme 1. Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]titanium(IV) dichloride (**1**), Bis[*N*-(3-*tert*-butylsalicylidene)cyclohexylaminato]titanium(IV) dichloride (**2**), Bis[*N*-(3-phenylsalicylidene)anilinato]titanium(IV) dichloride (**3**).

hexanol adduct solution, and subsequent dealcoholysis with 6.0 eq of i-Bu$_3$Al to MgCl$_2$ at 50 °C yielded a mixture of MgCl$_2$ and i-butylaluminum 2-ethyl-1-hexoxide, i-Bu$_m$Al(OR)$_n$, which was used as an activator. X-ray analysis indicated the formation of MgCl$_2$ having a crystallite size of 28 Å determined by the (110) reflection [27]. Bis(phenoxy-imine)Ti complexes **1**–**3** were obtained by the reaction of TiCl$_4$ with 2.0 eq of the lithium salt of the corresponding phenoxy-imine ligands using the previously described method (Scheme 1) [21,23].

Ethylene polymerization with complexes **1**–**3** were conducted under ethylene (0.9 MPa pressure) at 50 °C for 30 min using the above mentioned MgCl$_2$/i-Bu$_m$Al(OR)$_n$ as an activator. i-Butylaluminum 2-ethyl-1-hexoxide, i-Bu$_m$Al(OR)$_n$, such as i-Bu$_2$Al(2-ethyl-1-hexoxide), are expected to work as in situ alkylating reagents for the Ti complexes as well as scavengers in a polymerization sysytem, and MgCl$_2$ may function as a Lewis acid to generate a cationic active species from an alkylated complex [28]. For comparison, i-Bu$_m$Al(OR)$_n$ prepared from 2-ethyl-1-hexanol and i-Bu$_3$Al, i-Bu$_3$Al and MAO were evaluated as activators in addition to MgCl$_2$/i-Bu$_m$Al(OR)$_n$. The polymerization results are collected in Table 1. The complexes with MgCl$_2$/i-Bu$_m$Al(OR)$_n$ activator systems displayed high activities in the range of 20.8–36.3 kg-PE/mmol-cat · h, with a steady uptake of ethylene over the 30-min duration of the run. These are rare examples of MAO- or borate-free highly active catalysts for ethylene polymerization based on group 4 metals. It is of great significance that the activities obtained using MgCl$_2$/i-Bu$_m$Al(OR)$_n$ as the activator are comparable to those seen with the MAO activator system. Notably, the activities obtained with complexes/MgCl$_2$/i-Bu$_m$Al(OR)$_n$ are comparable to or exceed that found for the Cp$_2$TiCl$_2$/MAO catalyst system under the same conditions. Alternatively, complexes **1**–**3** combined with i-Bu$_m$Al(OR)$_n$ or i-Bu$_3$Al exhibited practically no activities under identical polymerization conditions. These results demonstrated that MgCl$_2$/i-Bu$_m$Al(OR)$_n$ is an effective activator for bis(phenoxy-imine)Ti complexes, and MgCl$_2$ is a pivotal component of the activator. A typical metallocene, Cp$_2$TiCl$_2$, combined with MgCl$_2$/i-Bu$_m$Al(OR)$_n$ displayed a low activity of 2.3 kg-PE/mmol-cat · h, which is substantially lower than that obtained with MAO activator by a factor of ca. 1/10, under the same conditions. The high performance exhibited by MgCl$_2$/i-Bu$_m$Al(OR)$_n$ as the activator towards the bis(phenoxy-imine)Ti complexes **1**–**3** compared with Cp$_2$TiCl$_2$ may be related to the fact that the bis(phenoxy-imine) complexes possess O and N heteroatoms in the ligand, which are capable of electronically interacting with MgCl$_2$.

Interestingly, the polyethylenes formed with the complexes **1**–**3**/MgCl$_2$/i-Bu$_m$Al(OR)$_n$ systems show the morphology of well-defined particles, whereas those with the MAO activator system display ill-defined polymer morphology (Fig. 1). These facts indicate that the complex exists on the surface of a solid MgCl$_2$/i-Bu$_m$Al(OR)$_n$ activator, and the polymerization occurred on the surface. Therefore, the complexes with MgCl$_2$/i-Bu$_m$Al(OR)$_n$ activator systems were shown to be MgCl$_2$-supported catalyst systems, indicating that the systems have the potential for control of polymer morphology.

Remarkably, the molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$) values of the polyethylenes arising from complexes **1**–**3**/

Table 1
Ethylene polymerization results with complexes **1**–**3** or Cp$_2$TiCl$_2$ using MgCl$_2$/i-Bu$_m$Al(OR)$_n$, i-Bu$_m$Al(OR)$_n$, i-Bu$_3$Al or MAO as an activator[a]

Complex	Activator	Amount of activator (mmol)		Yield	Activity[b]	M_w[c]	$M_\mathrm{w}/M_\mathrm{n}$[c]
		Mg	Al	(g)		$\times 10^{-4}$	
1	MgCl$_2$/i-Bu$_m$Al(OR)$_n$	0.40	2.40	9.07	36.3	50.9	2.66
2	MgCl$_2$/i-Bu$_m$Al(OR)$_n$	0.40	2.40	5.21	20.8	59.6	2.67
3	MgCl$_2$/i-Bu$_m$Al(OR)$_n$	0.40	2.40	9.01	36.0	23.1	2.40
Cp$_2$TiCl$_2$	MgCl$_2$/i-Bu$_m$Al(OR)$_n$	0.40	2.40	0.57	2.3	81.3	5.74
1	i-Bu$_m$Al(OR)$_n$	0	2.40	trace	–	–	–
1	i-Bu$_3$Al	0	2.40	trace	–	–	–
1	MAO		1.25	11.16	44.6	46.4	2.38
2	MAO		1.25	5.35	21.4	62.5	2.74
3	MAO		1.25	24.77	99.1	22.9	2.07
Cp$_2$TiCl$_2$	MAO		1.25	6.01	24.0	110.5	4.42

[a] Conditions: 50 °C, 0.9 MPa ethylene pressure; solvent, toluene 500 ml; polymerization time, 30 min; complex amount 0.5 µmol.

[b] Activity: kg of polymer/mmol of cat · h.

[c] Determined by GPC.

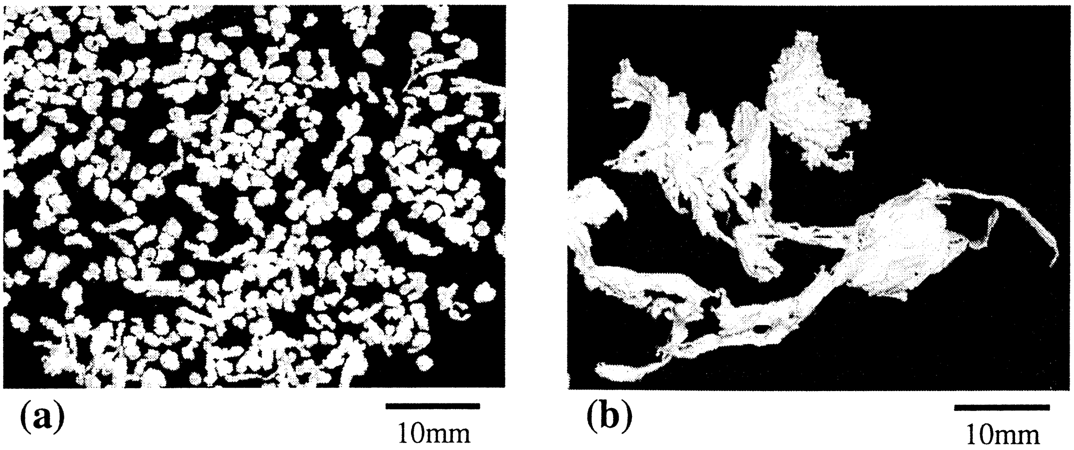


Fig. 1. Photographs of the polyethylenes formed with complex **1** using (a) $MgCl_2/i\text{-}Bu_mAl(OR)_n$ or (b) MAO as an activator.

$MgCl_2/i\text{-}Bu_mAl(OR)_n$ systems lie in the range of 2.40–2.67 (MAO activation; 2.07–2.74), suggesting that the polymers are produced by single active species. To our knowledge, these are the first examples of single-site catalysts based on nonmetallocene complexes and $MgCl_2$-based activators.

To further confirm single-site catalysis of $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activator systems, copolymerization of ethylene with propylene was performed at 50 °C for 30 min under 0.9 MPa total pressure and the comonomer composition distribution of the resulting copolymer was investigated. Complex **3** with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activator system produced copolymer having a propylene content of 29.3 mol% (based on IR analysis) with a narrow M_w/M_n of 1.70, displaying a high activity of 28.2 kg-polymer/mmol-cat · h. Notably, GPC-IR analysis revealed that the copolymer possesses extremely narrow propylene distribution (Fig. 2), confirming the chemically homogeneous catalysis of the system. As far as we are aware, this is the first example of a transition metal complex with a $MgCl_2$-based activator which produces a polymer with narrow distributions of molecular weight and chemical composition.

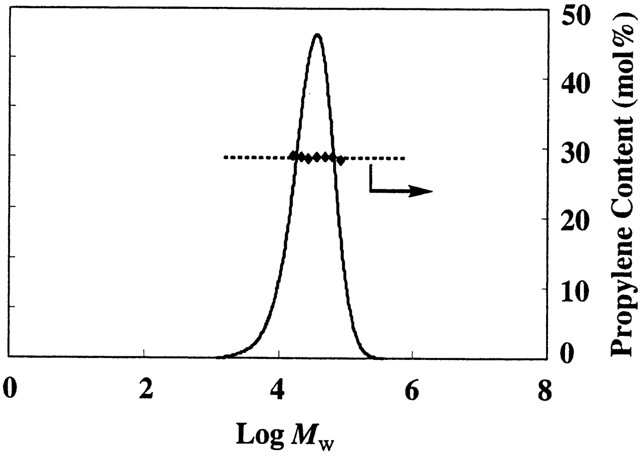


Fig. 2. GPC-IR chart of the ethylene–propylene copolymer arising from complex **3** using $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activator.

In summary, new olefin polymerization catalyst systems comprised of bis(phenoxy-imine)Ti complexes and $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activators have been introduced. The systems display very high ethylene polymerization activities comparable to those with MAO activator systems and produce narrow molecular weight distribution polymers. The results described herein represent the first examples of MAO- and borate-free, highly active single-site catalyst systems, which potentially possess a technological advantage of the control over polymer morphology. Investigations aimed at better understanding the mechanism for $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activation is underway and will be reported in due course.

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