Polymer Bulletin 34, 199–202 (1995)

Polymer Bulletin

Mono-aryloxy or mono-alkoxy zirconium complexes/methylaluminoxane catalyst system in ethylene polymerization

Makoto Mitani [1], **Kunihiro Oouchi** [1], **Michiya Hayakawa** [1], **Tohru Yamada** [1], **Teruaki Mukaiyama** [2]

[1] Basic Research Laboratories for Polymer Chemistry, Mitsui Petrochemical Industries, Ltd., Nagaura, Sodegaura-shi, Chiba 299-02 Japan
[2] Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162 Japan

Received: 20 September 1994/Revised version: 7 November 1994/Accepted: 18 November 1994

Summary

Mono-aryloxy zirconium complexes **1-6** or mono-alkoxy zirconium complexes **7-10** were prepared and the ethylene polymerization was carried out in the presence of these complexes / methylaluminoxane. Steric factor of the aryloxy and alkoxy ligands in the complexes remarkably influenced on activity of ethylene polymerization.

Introduction

After a catalyst systems composed of group 4 metallocenes and methylaluminoxane (MAO) were discovered, they attracted much attention as a new class of olefin polymerization catalyst from both academic and industrial points of view (1). Therefore, a number of metallocene complexes have been synthesized and some of them exhibit high catalytic activities.

Little attention has been paid to group 4 metal alkoxide complexes as polymerization catalyst because these complexes show very low activities. Recently, it has been reported that some of phenoxy titanium complexes are useful catalysts to effectively produce polystyrene (2) and ethylene-styrene copolymer (3). Concerning zirconium or hafnium catalysts, di- or tri- phenoxy complexes appeared in patent (4) and were employed for ethylene polymerization in the coexistence of MAO. Since a wide variety of aryloxy and alkoxy zirconium complexes are easily synthesized, they offer promising prospect of developing a specific and versatile catalyst for olefin polymerization.

In order to elucidate electronic and steric effects of the phenoxy or alkoxy ligands, the use of mono- phenoxy or alkoxy zirconium catalyst systems, which were expected to clarify the ligand effects distinctly but were little studied as polymerization catalyst, were investigated. We would like to report here the preparation of various mono- phenoxy or alkoxy zirconium complexes and the examination of the ligand effect on activities of ethylene polymerization.

Experimental

General: ^{1}H-NMR measurements of complexes were performed on a JEOL Model FX-270 spectrometer. Molecular masses were determined by gel permeation chromatography (GPC) on a WATERS 150-C instrument at 140 °C. All operations were carried out under dry nitrogen or argon atmosphere.
Material: $ZrCl_4$ (Rare Metallic Co., Ltd.) and polymerization grade ethylene (Sumitomo Seika Co., Ltd.) were used without further purification. n-Butyllithium (n-hexane solution, Kanto Chemical Co. Inc.) and MAO (10 wt% in toluene, Schering AG) were employed. Phenols such as phenol, 4-fluorophenol, 3,5-dimethylphenol, 2,6-dimethylphenol (Tokyo Kasei Kogyo Co., Ltd.), 3,4,5-trimethoxyphenol and 2,6-diphenylphenol (Aldrich Chemical Company, Inc.) or alcohols such as 2,6-

dimethylcyclohexanol, 1-adamantanol, (*1S*)-*end*-(-)-borneol (Tokyo Kasei Kogyo Co., Ltd.), and (*1R*)-*end*-(+)-fencyl alcohol (Aldrich Chemical Company, Inc.) were used without further purification.

Preparation of catalyst; General procedure

One equivalent of n-butyllithium (1.6 M solution in hexane) was added at room temperature to a solution of phenol or alcohol in THF and stirred at room temperature for 2 hr. This solution was added dropwise to a solution of anhydrous zirconium(IV) chloride in THF at -78 °C and warmed up to room temperature. After 4 hr, the solvent was removed *in vacuo*. The residue was extracted with benzene and filtered over a G-4 Schlenk flit. The filtrate was concentrated and dried *in vacuo* at room temperature to afford mono- phenoxy or alkoxy zirconium complexes.

The complexes **1**-**10** have been characterized by ^{1}H-NMR spectroscopy. ^{1}H-NMR (270 MHz, $CDCl_3$) : Complex **1** ; δ = 2.06(8H, br s), 4.47(8H, br s), 6.98(1H, t), 7.13(2H, d), 7.27(2H, t). Complex **2** ; δ = 2.06(8H, br s), 3.79(3H, s), 3.84(3H, s), 4.49(8H, br s), 6.42(2H, t). Complex **3** ; δ = 1.62(8H, br s), 3.43(8H, br s), 6.81-7.01(4H, m), 7.01-7.18(4H, m). Complex **4** ; δ = 2.02(8H, br s), 2.27(6H, s), 4.32(8H, br s), 6.63(1H, s), 6.78(2H, s). Complex **5** ; δ = 1.28(12H, br s), 2.49(6H, s), 3.90(8H, br s), 6.80(1H, m), 6.97(2H, m). Complex **6** ; δ = 1.68(4H, br s), 3.87(4H, br s), 7.10-7.80(13H, m). Complex **7** ; δ = 1.60(1H, t), 2.02(10H, br s), 2.14(3H, br s), 4.34(8H, br s). Complex **8** ; δ = 0.81(3H, s), 0.85(3H, s), 1.00(3H, s), 1.20-1.85(7H, m), 2.02(8H, br s), 4.33(8H, br s), 4.71(1H, m). Complex **9** ; δ = 1.21(6H, s), 1.20-1.90(8H, m), 2.05(8H, br s), 3.38(1H, s), 4.39(8H, br s) cis, trans mixture. Complex **10** ; δ = 1.04(3H, s), 1.10(3H, s), 1.30(3H, s), 1.00-1.85(7H, m), 2.02(8H, br s), 4.09(1H, s), 4.35(8H, br s).

Ethylene polymerization:

Method A: A three-necked flask (50 mL) equipped with gas inlet and outlet tubes was flushed with dry nitrogen, and dry toluene (20 mL) was placed in the flask. Toluene was saturated with ethylene at room temperature and a prescribed amount of MAO was added. A solution of 0.02 mmol of the catalyst **1**-**10** in toluene was added successively, then the feed of ethylene was stopped and the reaction system was closed immediately. After one and three minutes, each internal pressure of the reactor was measured by manometer.

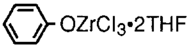
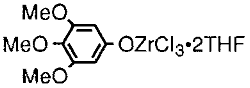
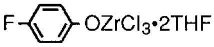
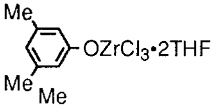
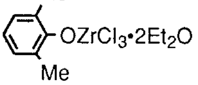
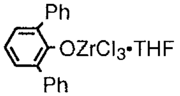
Method B: A five-necked flask (500 mL) equipped with a thermometer, gas inlet and outlet tubes, and an agitator was flushed with dry nitrogen. Dry toluene (200 mL) was placed in the flask and saturated with ethylene at temperature as shown in Table 3. A prescribed amount of MAO was added to the solution and a solution of 0.01 mmol of the catalyst **10** in toluene was added successively. During the polymerization, ethylene was continuously fed and the polymerization was quenched by adding methanol / HCl. The resulting solution was poured into a large amount of methanol. The obtained polymer was isolated by filtration and dried *in vacuo*.

Results and discussion

Aryloxy or alkoxy zirconium complexes **1**-**10** were prepared from zirconium tetrachloride and the corresponding phenols or alcohols according to the reported method (3b), and a typical preparative procedure was described in Experimental. The zirconium complex catalyzed ethylene polymerization were performed with MAO as co-catalyst in the closed reactor connected with a manometer, by which the internal pressure were measured (*Method A*). The catalytic activities of the complexes were estimated by ethylene consumption, which is corresponding to decrease of the internal pressure at one and three minutes, indicated as ΔP_1 and ΔP_3, respectively.

First, a wide variety of mono-phenoxy zirconium complex catalysts were examined in ethylene polymerization using MAO as co-catalyst. By using phenoxy zirconium complexes containing an electron-withdrawing or electron-donating substituents, such as fluoro, methoxy or methyl (Entries 2, 3 or 4 in Table 1), in the aromatic ligand, no electronic effect was observed concerning the catalytic activities. On the contrary, it was found that 2,6-di-substituted phenoxy ligand improved the activity of ethylene polymerization; that is, by using 2,6-dimethylphenoxy zirconium complex as the catalyst, the absorption of ethylene reached 130 torr after three minutes (Entry 5), while 75 torr in the presence of complex **1** (Entry 1). The more bulky phenoxy ligand having two phenyl groups at 2,6-positions was remarkably effective to increase the catalytic activity (Entry 6).

Table 1. Ethylene Polymerization[a] with Mono-phenoxy Zr Complexes / MAO

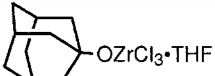
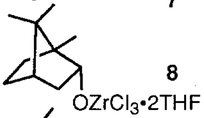
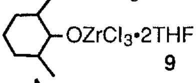
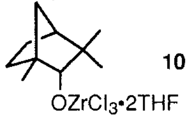
Entry	Complex		Ethylene Absorption[b]	
			ΔP_1(torr)	ΔP_3(torr)
1		**1**	31	75
2		**2**	14	37
3		**3**	29	64
4		**4**	27	66
5		**5**	48	130
6		**6**	200	392

a) Polymerization conditions: [Zr]=1.0 x 10^{-3} mol/L, [Al]/[Zr]=100, in toluene, at room temperature.
b) ΔP_1 and ΔP_3 are decrease of internal pressure after 1min and 3min, respectively.

Few were reported on alkoxy zirconium complexes catalyzed ethylene polymerization. It was found that mono-alkoxy zirconium complexes **7-10** also have catalytic activities for ethylene polymerization (Table 2). The similar steric effect on the activity was observed expectedly; that is, the complex less hindered around the central zirconium metal (**7**, Entry 1) showed low activity, whereas the notable improvement was achieved by using the alkoxy complex containing the hindered ligand, such as borneol and 2,6-dimethylcyclohexanol derivatives (Entries 2 and 3), and the best result was obtained by using complex **10** derived from fenchyl alcohol (Entry 4).

The behavior of complex **10** in ethylene polymerization was examined in detail according to the method B described in Experimental. The productivity was calculated based on the weight of obtained polymer (Table 3). As a result of optimization of polymerization conditions using complex **10** , the highest productivity corresponding to 1547 kg/mol Zr•hr was observed at 30 °C (5) .

Table2. Ethylene Polymerization[a] with Mono-alkoxy Zr Complexes / MAO

Entry	Complex	Ethylene Absorption[b]	
		ΔP_1(torr)	ΔP_3(torr)
1	 **7**	48	88
2	 **8**	106	217
3	 **9**	284	443
4	 **10**	389	519

a) Polymerization conditions: [Zr]=1.0 x 10^{-3} mol/L, [Al]/[Zr]=100, in toluene, at room temperature.
b) ΔP_1 and ΔP_3 are decrease of internal pressure after 1min and 3min, respectively.

Table3. Ethylene Polymerization[a] with Complex **10** / MAO

Entry	T_p(°C)	Time (min)	Polymer Yield (g)	Productivity (KgPE /molZr•hr)	10^{-3}Mw
1	60	5	0.366	439	4.21
2	30	8	2.062	1547	5.88
3	0	10	0.774	464	8.40

a) Polymerization conditions: [Zr]= 5.0 x 10^{-5} mol/L, [Al]/[Zr]=100, toluene =200 mL
$P(C_2H_4)$ =1atm

It was also confirmed in ethylene polymerization catalyzed by alkoxy zirconium complex that the bulkiness around the zirconium atom in complex is significant to achieve high activity of polymerization (6) . It is reasonable to consider that the bulky substituent in these ligands effectively shield the central metal and avoid the undesirable decomposition of complex during the polymerization.

In conclusion, it was found that the alkoxy zirconium complex having new class of bulky cycloalkanol ligand, such as fenchyl alcohol, showed higher activity in ethylene polymerization compared with phenoxy zirconium complexes .

References

1. Kaminsky, W.; Clapper, K.; Brintzinger, K. K.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, *7*, 2375. Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255.
2. Zambelli, A.; Oliva, L.; Pellechia, C. *Macromolecules* **1989**, *22*, 2129.
3. a) Miyatake, T.; Mizunuma, K.; Kakugo, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 203. b) Aaltonen, P.; Seppälä, J.; Matilainen, L.; Leskelä, M. *Macromolecules* **1994**, *27*, 3136.
4. Canich, J. U.S. Patent 5,079,205, **1992**.
5. Under the same condition, the productivity of phenoxy zirconium complex **6** was 268 kg/mol Zr•hr.
6. Similar steric effect was reported in ring-opening metathesis polymerization catalyzed by group 6 metal alkoxide. Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20* , 1169. Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.