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Olefin polymerization catalyzed by homo- or heterobimetallic zirconocene complex/methylaluminoxane system

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Summary

Polymerization of ethylene and copolymerization of ethylene-propylene proceeded smoothly by using homometallic binuclear zirconium complex **1** or heterometallic binuclear zirconium-titanium complex 2/methylaluminoxane catalyst system. The molecular weight distributions of polymers obtained by the binuclear zirconium complexes were broader than that produced by mononuclear zirconium complex.

Introduction

Homo- and heterometallic binuclear complexes are expected to exhibit novel reactivities which are not shown by mononuclear complexes. Numerous binuclear complexes have been synthesized and examined with respect to their catalytic activities in various chemical reactions (1). Group 4 metallocenes/methylaluminoxane(MAO) systems are actively studied as useful homogeneous catalysts in Ziegler-Natta olefin polymerization (2). Therefore, the bimetallic group 4 metallocenes would offer the possibilities of specific polymerization catalyst by cooperative effects between two metal centers. Bridged bis(cyclopentadienyl) ligand systems containing two metal centers are appropriate to examine these cooperative effects because both metal sites are held in close proximity during the polymerization. Concerning the syntheses of these bimetallic group 4 metallocenes, several examples were already reported by Petersen (3), Nifant'ef (4), Green (5), and others (6). However, few were reported to employ these binuclear complexes as catalysts in olefin polymerization (7) and detailed studies on their polymerization behavior or the influences on the properties of polymer products are not yet appeared.

In this communication, we would like to report preparations of homo- and heterobimetallic zirconocene complexes having bridged bis(cyclopentadienyl) ligand and behavior of these binuclear complex catalysts in olefin polymerization.

Experimental

General: ^{1}H-NMR spectra of complexes were measured by JEOL Model FX-270 spectrometer. Molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) on a WATERS 150-C instrument at 140 °C in 1,2,4-trichlorobenzene. The propylene contents of the copolymers were measured by IR method (8). Solvents were dried over Na/benzophenone and all operations were carried out under dry nitrogen or argon atmosphere.

Material: $CpZrCl_3$, $CpTiCl_3$ (Strem Chemicals, Inc.) and polymerization grade ethylene (Sumitomo Seika Co., Ltd.) were used without further purification. MAO (10 wt% in toluene, Schering AG) was employed. $[Me_2SiCp_2]Li_2$ and complex **1** were prepared by literature procedures (3).

Preparation of complex 2

A solution of $CpZrCl_3$(2.18g, 8.30mmol) in 55ml of THF was added to a solution of $[Me_2SiCp_2]Li_2$(1.66g, 8.30mmol) in THF(80ml) at -78 °C and stirred for 1 hr. After warming up to room temperature, the mixture was stirred for another 1 hr and cooled to -78 °C. A solution of $CpTiCl_3$(1.82g, 8.30mmol) in 40ml of THF was added to the mixture and stirred for 1 hr. The mixture was warmed up to room temperature and stirred for 12 hr. After the solvent was removed *in vacuo*, the residue was extracted with $CHCl_3$ and filtered over a G-4 Schlenk filter. Concentration of the filtrate and recrystallization from toluene yielded 0.53g of the complex **2** as red solid.

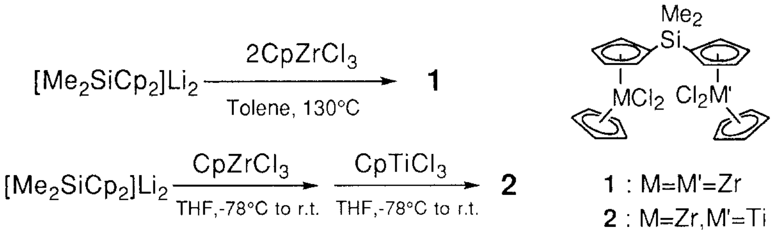
^{1}H-NMR (270 MHz, THF-d_8) : δ = 6.82(2H, t), 6.75(2H, t), 6.65(2H, t), 6.62(2H, t), 6.48(5H, s), 6.43(5H, s), 0.65(6H, s).

Polymerization

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 ethylene or mixed ethylene/propylene gas was introduced into the flask at temperatures as shown in Table 1 or Table 3. A prescribed amount of MAO was added to the solution and a solution of the catalyst in toluene was successively added. The polymerization was quenched by adding methanol/HCl and the resulting solution was poured into a large amount of methanol. The resulting polymer was isolated by filtration and dried *in vacuo*.

Results and discussion

Synthetic procedures of complexes are given in Scheme 1. Homometallic binuclear zirconium complex **1** was prepared from $[Me_2SiCp_2]Li_2$ and two equivalents of monocyclopentadienylzirconium trichloride according to the reported method (3). Heterometallic binuclear zirconium-titanium complex **2** was prepared by stepwise treatments of $[Me_2SiCp_2]Li_2$ with monocyclopentadienylzirconium trichloride and monocyclopentadienyltitanium trichloride. The detailed preparative procedure was described in Experimental. The analytically pure samples of complex **1** and **2** were obtained as white solid and red solid, respectively. The ^{1}H-NMR spectra of complex **1** was in agreement with the reported data (3). The complex **2**, which was recrystallized from toluene, was confirmed by ^{1}H-NMR (4) to be pure without any by-products such as **1**, titanium-titanium complex and others (9).



Scheme 1

Ethylene polymerization catalyzed by homo- and heterobinuclear zirconium complexes were carried out by using MAO as co-catalyst. The productivities of complex **1** and complex **2** at 60°C were 9800 and 7300 g-PE/mmol Cat.•h•atm, respectively (Entries 2 and 5 in Table 1). As a result of polymerization at various temperatures, it was found that binuclear complexes showed the highest productivity at 60 °C. The productivities of binuclear complexes were somewhat lower and the polymerization behavior was similar to that of mononuclear Cp_2ZrCl_2 complex.

Table1. Ethylene Polymerization[1] Catalyzed by Binuclear Zirconium Complexes/MAO

Entry	Complex	Temp. (°C)	Time (min)	Polymer yield(g)	Productivity[2]
1	**1**	30	15	1.03	4100
2	**1**	60	5	0.82	9800
3	**1**	90	20	1.33	4000
4	**2**	30	15	0.75	3000
5	**2**	60	10	1.21	7300
6	**2**	90	30	1.28	2600
7	Cp_2ZrCl_2	30	5	0.80	19200
8	Cp_2ZrCl_2	60	5	1.86	44700
9	Cp_2ZrCl_2	90	10	2.15	25800

1) Polymerization conditions: Toluene 200ml, $P(C_2H_4)$ 1atm, Catalyst 1.0μmol(Entry1-6), 0.5μmol(Entry7-9), [Al]/[Cat.]=750.

2) g-PE/mmol Cat. •h•atm.

The molecular weights and molecular weight distributions of thus obtained polyethylene were measured by GPC (Table 2). It is well known that mononuclear metallocene/MAO systems usually produce narrow polydispersity polyethylene (Mw/Mn = 2.0-2.5) (2). On the contrary, by using homo- and heterobinuclear zirconium complexes, the obtained polyethylene showed broad molecular weight distribution at 60 °C (Entries 1 and 3). At higher polymerization temperature, the Mw/Mn values of the polymer increased to 3.40 by using complex **1** and 5.42 by using complex **2** (Entries 2 and 4). These results indicate that the heterobinuclear complex **2** has more remarkable influence on properties of polymer products.

The molecular weight distribution curves of obtained polyethylene are shown in Figure 1. The curve (a) by complex **2** appeared unimodal and broadened toward both high and low molecular weight sides compared with the curve (b) by Cp_2ZrCl_2. Concerning the catalytic activity and polydispersity of the polymer, 1:1 mixture of Cp_2ZrCl_2 and Cp_2TiCl_2 afforded almost the same results obtained by Cp_2ZrCl_2 alone probably because of much less activity of titanium complex than zirconium complex (10). Therefore, these effects on molecular weight distributions could be regard as specific behavior of the binuclear complexes in ethylene polymerization.

Table 2. Molecular Weights and Molecular Weight Distributions[1] of Obtained Polyethylene

Entry	Complex	Pol.Temp (°C)	Mw ($\times 10^4$)	Mw/Mn
1	**1**	60	30.9	3.22
2	**1**	90	5.1	3.40
3	**2**	60	40.7	3.80
4	**2**	90	7.1	5.42
5	Cp_2ZrCl_2	60	40.1	2.03
6	Cp_2ZrCl_2	90	7.2	2.05

1) Determined by GPC.

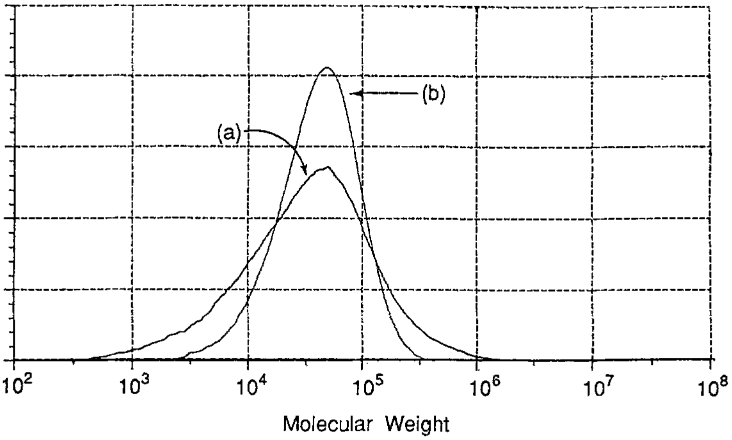


Fig 1. GPC Curves of the Polyethylene obtained by Complex 2 / MAO (a) and Cp_2ZrCl_2 / MAO (b) at 90°C

The binuclear zirconium complexes/MAO systems were also effective in ethylene-propylene copolymerization (see Table 3). The copolymers containing about 20mol% propylene have broader polydispersity than polyethylene homopolymer. As the result of measurement of propylene content vs. molecular weight by GPC-IR (Figure 2), it was found that the propylene content in the copolymer was higher at low molecular weight region and decreased with increasing the molecular weight when complex **2** was used (11). In contrast, by using Cp_2ZrCl_2, the propylene content of the copolymer was almost constant from low molecular weight region to high molecular weight region owing to the homogeneity of active species.

These results suggest that multiple active sites with different catalytic characters coexist in homometallic zirconium-zirconium complex and heterometallic zirconium-titanium complex/MAO systems. It is reasonable to consider that the distinctions between mononuclear complex and binuclear complexes were caused by cooperative effect of two center metals in the complexes. In order to support these hypothesis, further studies on the synthesis of various heterobimetallic zirconium complexes which have bridged bis(cyclopentadienyl) ligand and investigation of polymerization behavior are under way.

Table 3. Ethylene-propylene Copolymerization[1] Catalyzed by Binuclear Zirconium Complexes/MAO

Entry	Complex	Propylene[2] Content(mol%)	Mw[3] ($\times 10^4$)	Mw/Mn[3]
1	**1**	18.8	14.3	5.14
2	**2**	22.2	18.7	6.33
3	Cp_2ZrCl_2	20.0	4.6	2.09

1) Polymerization conditions: Toluene 200ml, 30°C, [Al]/[Cat.]=750, Ethylene/Propyrene Feed Ratio 50/50(Entry 1, 2), 70/30(Entry 3).

2) Determined by IR. 3) Determined by GPC.

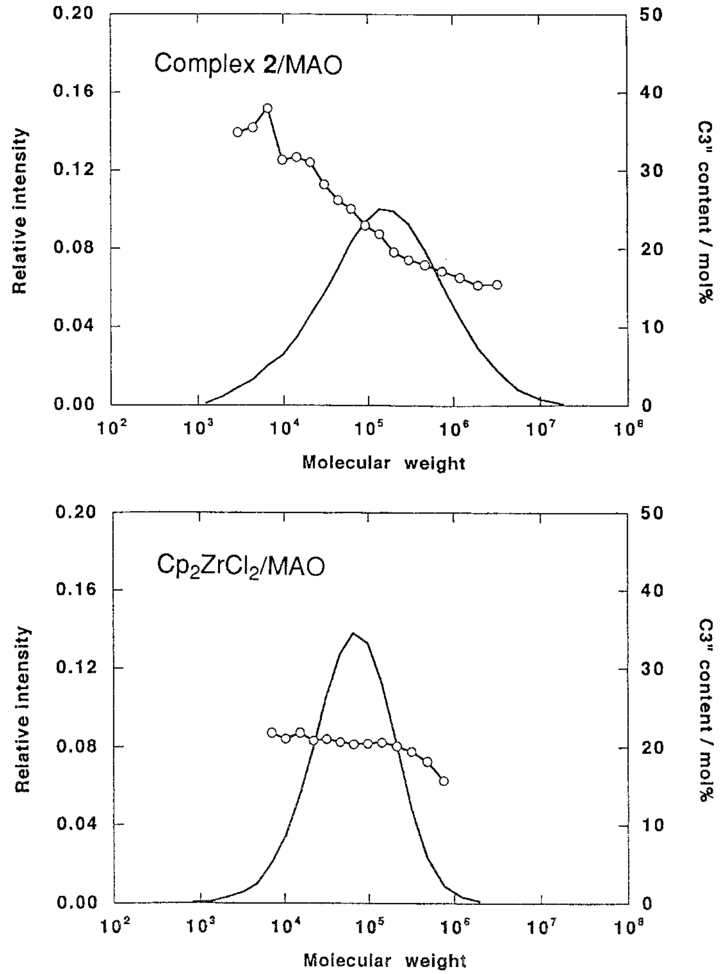


Fig 2. GPC Curves and Propylene Contents of the Ethylene-propylene Copolymer Obtained by Complex **2**/MAO and Cp_2ZrCl_2/MAO

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9. The complex **2**, complex **1** and Ti-Ti complex are easily distinguishable each other by ^{1}H-NMR analysis. See Ref. 3 and 4.
10. As it is difficult to form di-cation in one molecule, it should be reasonable to assume only one zirconium center in the binuclear complexes **1** and **2** was active site for polymerization. See Ref. 7a.
11. By using homometallic binuclear complex **1**, similar results were obtained concerning propylene content of the copolymer.