

## Ethylene polymerization with novel silicon bridged homo-dinuclear cyanoethyl cyclopentadienyl complexes of titanium and zirconium\*

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**Abstract:** Novel homo-dinuclear silicon bridged cyanoethyl cyclopentadienyl complexes of titanium and zirconium  $(\text{CH}_3)_2\text{Si}((\eta^5 - \text{C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CN})(\text{C}_5\text{H}_5)\text{MCl}_2)_2$  ( $\text{M} = \text{Ti}(1), \text{Zr}(2)$ ) were synthesized and developed for the polymerization of ethylene. Compared with their corresponding mononuclear complexes  $(\eta^5 - \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CN})(\text{C}_5\text{H}_5)\text{MCl}_2$  ( $\text{M} = \text{Ti}(3), \text{Zr}(4)$ ), the dinuclear complexes had higher catalytic activity. And the polyethylene produced had a higher molecular weight than that obtained with mononuclear catalysts. Effects of conditions on the ethylene polymerization catalyzed by (2)/MAO (methylaluminoxane) were studied in detail. The catalyst showed a very high activity ( $> 10^6$  g PE/mol Zr·h) under low catalyst concentration and high molar ratio of Al/Zr.

**Key words:** Homo-dinuclear catalyst, Titanocene, Zirconocene, Polyethylene, Chemical engineering

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(Mitani et al., 1996; Donald et al., 2001).

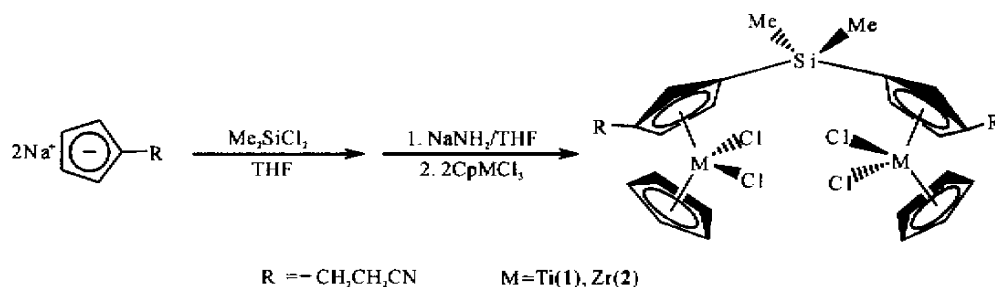
## INTRODUCTION

Metallocene catalyst based on single site active center is currently an important research field due to its highly catalytic activity, narrow molecular weight distribution (MWD) and tailored polymer micro-structure (Brintzinger et al., 1995; Kaminsky, 2001). However, on the other hand, the narrow MWD of the resulting polyethylene has brought some processing problems arising from the high shear viscosity and low melt extensional viscosity of the product. In order to improve the processability of polyolefin, some mixed metallocene catalysts and multinuclear metallocene catalysts were used to initiate the polymerization of olefins (Soga et al., 1998; Albers et al., 1988). The results showed that the MWD of polyolefins produced by the above mentioned catalysts became broader

## METHOD

All operations were carried out under argon atmosphere using standard Schlenk techniques. Solvents were distilled under argon from sodium-potassium alloy before use. MAO was purchased from Albemarle. Polymerizations of ethylene were run in 100 ml Schlenk flask equipped with a magnetic stirrer. The pressure was maintained at 0.11 MPa. MAO was used as co-catalyst to activate the polymerization. Molecular weight of polyethylene was determined by viscosity method (Francis et al., 1958).

The homodinuclear silicon bridged cyanoethyl cyclopentadienyl titanium and zirconium complexes  $(\text{CH}_3)_2\text{Si}((\eta^5 - \text{C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CN})(\text{C}_5\text{H}_5)\text{MCl}_2)_2$  ( $\text{M} = \text{Ti}(1), \text{Zr}(2)$ ) were synthesized as shown in Fig. 1.



**Fig. 1**  $(\text{CH}_3)_2\text{Si}((\eta^5 - \text{C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CN})(\text{C}_5\text{H}_5)\text{MCl}_2)_2$  (M = Ti(1), Zr(2)) synthetic scheme

## RESULTS AND DISCUSSION

### 1. Comparison of the dinuclear and mononuclear complexes in ethylene polymerization

The polymerization characters of the homodinuclear catalysts 1, 2 and their corresponding mononuclear catalysts ( $\eta^5 -$

$\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CN})(\text{C}_5\text{H}_5)\text{MCl}_2$  (M = Ti(3), Zr(4)) (Liang et al., 2001) are shown in Table 1.

The activity of the dinuclear catalysts was somewhat higher than that of their corresponding mononuclear catalysts. And the polyethylene produced had a higher molecular weight than that synthesized with mononuclear catalysts.

**Table 1** Comparison of the dinuclear and mononuclear complexes on ethylene polymerization

Catalyst	Activity $\times 10^{-5}$ (g PE/mol M·h)	Molecular weight ( $M_w \times 10^{-4}$ )
<b>1</b> <sup>a</sup>	0.42	9.86
<b>2</b> <sup>a</sup>	3.08	11.7
<b>3</b> <sup>b</sup>	0.37	2.21
<b>4</b> <sup>b</sup>	1.31	4.21

<sup>a</sup> Polymerization condition:  $[\text{M}] = 4 \times 10^{-4}$  mol/L;  $[\text{Al}]/[\text{M}] = 1000$ ; Temperature 60°C; Time 30 min.

<sup>b</sup> Polymerization condition:  $[\text{M}] = 4 \times 10^{-4}$  mol/L;  $[\text{Al}]/[\text{M}] = 1000$ ; Temperature 60°C; Time 60 min.

### 2. Effects of conditions on the ethylene polymerization catalyzed by (2)/MAO

Effects of conditions on the ethylene polymerization catalyzed by (2)/MAO were studied in detail (see Table 2). The catalyst exhibited very high activity ( $> 10^6$ ) under low catalyst concentration and high molar ratio of

Al/Zr. The activity and molecular weight increased with temperature from 30°C to 60°C, but decreased rapidly when the temperature rose to 80°C because of the exacerbation of chain transfer reaction. The small effect of polymerization time on the activity and molecular weight revealed that the active center was quite steady and had a long life.

**Table 2** Results of ethylene polymerization with  $(\text{CH}_3)_2\text{Si}((\eta^5 - \text{C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CN})(\text{C}_5\text{H}_5)\text{ZrCl}_2)_2/\text{MAO}$

Run	$[\text{cat}] \times 10^5$ mol/L	Al/Zr	$T_p$ (°C)	$t_p$ (min)	Activity $\times 10^{-5}$ (g PE/mol Zr·h)	Molecular weight ( $M_w \times 10^{-5}$ )
1	1	2000	60	30	0.12	—
2	1	10000	60	30	25.06	2.09
3	2	2000	60	30	2.22	0.509
4	4	2000	60	30	7.44	2.39
5	6	2000	60	30	6.42	1.50

(continued in next page)

Run	[cat] × 10 <sup>5</sup> (mol/L)	Al/Zr	T <sub>p</sub> (°C)	t <sub>p</sub> (min)	Activity × 10 <sup>-5</sup> (g PE/mol Zr•h)	Molecular weight (M <sub>w</sub> × 10 <sup>-5</sup> )
6	8	2000	60	30	5.66	1.13
7	20	1000	60	30	3.08	1.17
8	4	1000	60	30	0.12	0.548
9	4	3000	60	30	9.66	1.84
10	4	4000	60	30	10.26	1.73
11	4	2000	30	30	1.02	1.28
12	4	2000	45	30	2.22	1.51
13	4	2000	80	30	2.22	0.198
14	4	2000	60	15	6.90	1.58
15	4	2000	60	45	5.70	1.67
16	4	2000	60	60	5.42	1.45

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