

# Self-Immobilization of Methylaluminoxane in Metallocene-Induced Olefin Polymerization Reactions

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**ABSTRACT:** Metallocene complexes carrying one or two  $\omega$ -alkenyl ligands were activated with methylaluminoxane (MAO) to give homogeneous catalyst solutions. The reaction with ethylene formed heterogeneous catalysts by self-immobilization. In the activation step, the  $\omega$ -alkenyl groups were transferred from the metal of the metallocene complex to the

activating MAO agent and then underwent copolymerization reactions with ethylene induced by other active sites. This method is a universal approach to the heterogenization of homogeneous catalysts by copolymerization with  $\omega$ -alkenyl functionalized cocatalysts. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3379–3382, 2003

## INTRODUCTION

The industrial application of homogeneous metallocene complexes in the slurry loop process requires the heterogenization of such catalysts. The conventional method for this heterogenization is the application of organic or inorganic materials as support<sup>1–6</sup> to prepare so-called drop-in catalysts.

A more elegant method avoids the use of any support materials: the catalyst precursors are functionalized with an  $\omega$ -alkenyl substituent on the ligand framework and can then be copolymerized with ethylene in a homogeneous solution after their activation with methylaluminoxane (MAO).<sup>7–9</sup> Such a prepolymerized heterogeneous catalyst prevents any reactor fouling and can be stored for years without losing its original activity.

Another very effective approach is the application of heterogenized cocatalysts, such as partially hydrolyzed trimethylaluminum, on various support materials.<sup>10–12</sup> These have the unique potential to be used for all different kinds of homogeneous catalyst precursors.

In this article, we report the self-immobilization of commercially available MAO by functionalization of the active species with an  $\omega$ -alkenyl substituent in the activation process.

## EXPERIMENTAL

### NMR spectroscopy

A Bruker NMR instrument (ARX 250) was used to record the NMR spectra. The organometallic samples

were placed in NMR tubes under argon and measured at 25°C. The chemical shifts in <sup>1</sup>H-NMR spectra were referred to the residual proton signal of the solvent ( $\delta$  = 7.15 ppm for benzene) and in <sup>13</sup>C-NMR spectra to the solvent signal ( $\delta$  = 128.0 ppm for benzene-*d*<sub>6</sub>).

### General synthesis procedure for Grignard reagents

To a mixture of 0.02 g of Mg (0.82 mmol) in 80 mL of ether, the corresponding bromide was added dropwise. The residue of Mg was filtered, and the solution was used for further reactions.

### Synthesis of complexes 2–4

Cp<sub>2</sub>ZrBr<sub>2</sub> (1 g, 3.4 mmol) was dissolved in 50 mL of toluene. The corresponding bromide Grignard (3.4 mmol) was added, and the solution was stirred for 5 h. The solution was filtered over sodium sulfate, and the solvent was evaporated. The residue was washed twice with 50 mL of pentane and dried *in vacuo*. The yields were 35–50%.

### Synthesis of complexes 5–7

Cp<sub>2</sub>ZrCl<sub>2</sub> (1 g, 3.4 mmol) was dissolved in 50 mL of toluene. The corresponding bromide Grignard (6.8 mmol) was added and stirred over night. After filtration of the solution over sodium sulfate, the solvent was evaporated. The residue was washed with 100 mL of pentane, and the solvent was evaporated. The yields were 30–40%.

### Homopolymerization of ethylene

*n*-Pentane (500 mL) was placed in a 1-L Büchi laboratory autoclave (Eislinger, Germany) and mixed with

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TABLE I  
NMR Characterization of Complexes 2-7

Complex	<sup>1</sup> H-NMR <sup>a</sup>	<sup>13</sup> C-NMR <sup>b</sup>
2	5.92 (m, 1H), 5.79 (s, 10H), 5.00 (m, 2H), 2.47 (m, 2H)	141.2 (=CH), 112.7 (CH), 104.6 (=CH <sub>2</sub> ), 57.2 (CH <sub>2</sub> )
3	5.88 (m, 1H), 5.75 (s, 10H), 5.00 (m, 2H), 2.35 (m, 2H), 1.08 (m, 2H)	138.9 (=CH), 112.6 (CH), 103.2 (=CH <sub>2</sub> ), 56.9 (CH <sub>2</sub> ), 38.5 (CH <sub>2</sub> )
4	6.13 (s, 10H), 5.85 (m, 1H), 5.20 (m, 2H), 3.89 (m, 2H), 2.05 (m, 2H), 1.51 (m, 2H)	139.6 (=CH), 114.8 (=CH <sub>2</sub> ), 114.2 (CH), 56.9 (CH <sub>2</sub> ), 40.6 (CH <sub>2</sub> ), 33.9 (CH <sub>2</sub> )
5	5.90 (m, 2H), 5.76 (s, 10H), 4.86 (m, 4H), 2.36 (m, 4H)	139.8 (=CH), 112.4 (CH), 102.9 (=CH <sub>2</sub> ), 2.22 (CH <sub>2</sub> )
6	5.78 (m, 2H), 5.72 (s, 10H), 4.89 (m, 4H), 2.21 (m, 4H), 0.89 (m, 4H)	137.9 (=CH), 11.9 (CH), 101.9 (=CH <sub>2</sub> ), 53.2 (CH <sub>2</sub> ), 36.4 (CH <sub>2</sub> )
7	6.02 (s, 10H), 5.76 (m, 2H), 5.08 (m, 4H), 3.69 (m, 4H), 1.87 (m, 4H), 1.39 (m, 4H)	138.2 (=CH), 113.2 (=CH <sub>2</sub> ), 113.6 (CH), 53.8 (CH <sub>2</sub> ), 38.7 (CH <sub>2</sub> ), 31.9 (CH <sub>2</sub> )

<sup>a</sup> 25°C in benzene-d<sub>6</sub>, δ (ppm) relative to benzene (7.15).

<sup>b</sup> 25°C in benzene-d<sub>6</sub>, δ (ppm) relative to benzene (128.0)

the catalyst solution. The autoclave was thermostated at 60°C. An ethylene pressure of 10 bar was applied. The mixture was stirred for 1 h at 60°C, and the reaction was terminated by the release of the pressure in the reactor. The obtained polymer was dried *in vacuo*.

#### Heteropolymerization of ethylene

To the activated catalyst precursor solution, 1 g of silica/μmol of catalyst precursor was added and placed in a 1-L Büchi laboratory autoclave with 500 mL of *n*-pentane. The autoclave was thermostated at 60°C, and an ethylene pressure of 10 bar was applied. After being stirred for 1 h at 60°C, the reaction was terminated by the release of the pressure in the reactor. The obtained polymer was dried *in vacuo*.

#### Prepolymerization of catalyst precursors 2-7

The catalyst precursor (10 mg) was dissolved in 30 mL of toluene and activated with MAO (Zr/Al 1:1000). An

ethylene pressure of 1.5 bar was applied, and the solution was stirred for 20 min at room temperature. After filtration of the solution, the polymer residue was dried *in vacuo*. The prepolymerized catalyst precursor was placed in 500 mL of pentane in a 1-L Büchi laboratory autoclave. The mixture was thermostated at 60°C, and an ethylene pressure of 10 bar was applied. After being stirred for 1 h at 60°C, the reaction was terminated by the release of the pressure in the reactor. The obtained polymer was dried *in vacuo*.

## RESULTS AND DISCUSSION

### Synthesis and characterization of metallocene complexes with ω-alkenyl ligands

The reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> (1) in diethyl ether with various Grignard reagents containing ω-alkenyl groups gave the corresponding monosubstituted and disubstituted complexes, depending on the stoichiometry of the reactants:

TABLE II  
Polymerization Data

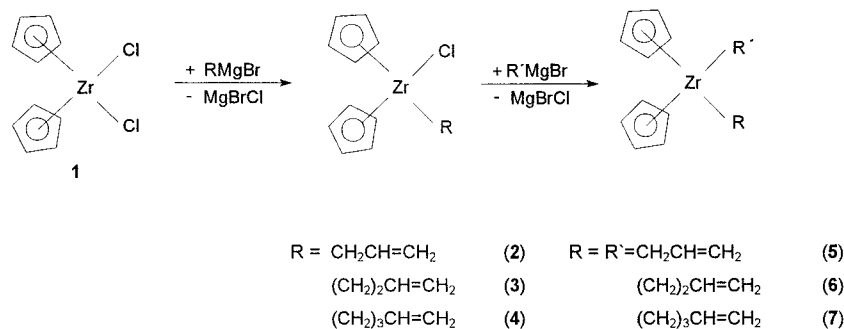
Catalyst precursor	Homogeneous catalysis <sup>a</sup>			Heterogeneous catalysis <sup>b</sup>		
	Activity [kg of PE/g of Zr h]	$M_w$ [g/mol]	$D$ [ $M_w/M_n$ ]	Activity [kg of PE/g of Zr · h]	$M_w$ [g/mol]	$D$ [ $M_w/M_n$ ]
1	150	290,000	n.d.	75	270,000	n.d.
2	400	359,000	4.023	120	332,000	3.922
3	320	358,000	4.163	90	333,000	4.166
4	285	333,000	5.069	75	362,000	4.378
5	350	241,000	3.926	205	228,000	3.789
6	300	249,000	3.904	138	231,000	3.921
7	245	263,000	4.203	105	243,000	4.067

$M_w$  = weight-average molecular weights;  $M_n$  = number average molecular weight

$T_p$  = polymerization temperature; PE = poly ethylene

<sup>a</sup>  $T_p$  = 60°C; solvent, 500 ml pentane, 10 bar ethylene pressure; [Zr]/[Al] = 1:2500.

<sup>b</sup>  $T_p$  = 60°C; solvent, 500 ml pentane, 10 bar ethylene pressure; [Zr]/[Al] = 1:1500; 1g silica/μmol, Zr. n.d. = not determined.



Complexes 2–7 were purified by filtration of the reaction solutions over  $\text{Na}_2\text{SO}_4$ . The NMR spectroscopic characterization (Table I) indicates the purity of the complexes.

### Heterogenization of MAO

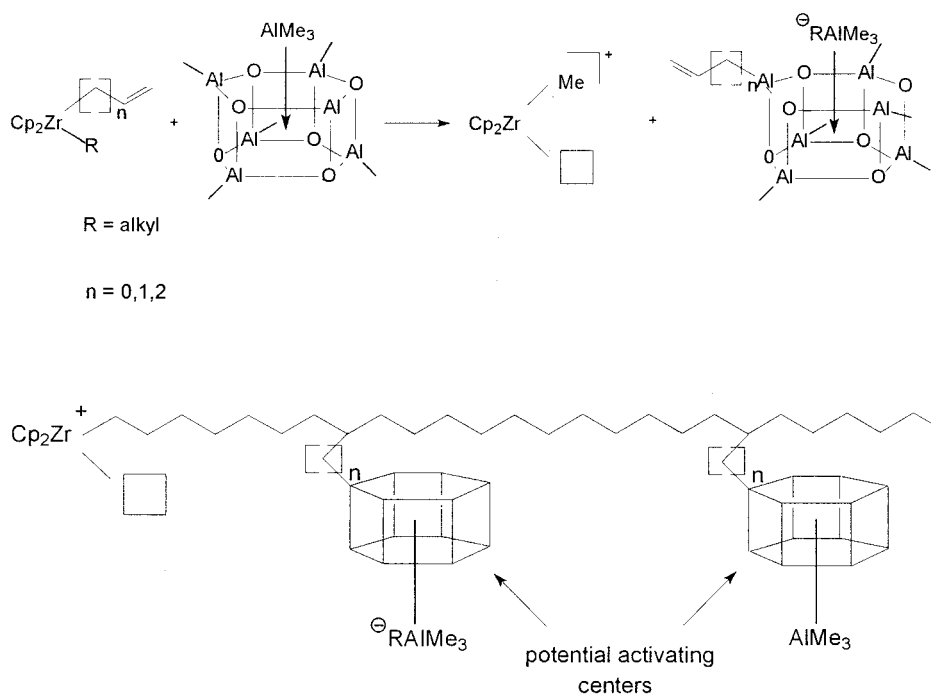
Complexes 2–7 obtained  $\omega$ -alkenyl ligands. The activation of these complexes with MAO resulted in colored homogeneous solutions. As soon as ethylene was bubbled through these solutions, a colored precipitate was formed. After filtration and washing with toluene, this solid could be used for heterogeneous ethylene polymerization without the application of any support material (Table II).

The polymerization results depended on the kind of polymerization: the best activities were achieved when the homogeneous catalyst solution was used

directly for ethylene polymerization without the isolation of any prepolymerized catalyst. A slightly lower activity was observed when the homogeneous catalyst was supported on silica. When the prepolymerized catalyst was isolated from the reaction mixture and applied as a solid, the activities dropped considerably (see Table III).

However, no fouling of the reactor was observed in any of the cases.

We interpret these results in the following manner. The active species of the cocatalyst MAO is supposed to be a cage-type compound containing monomeric  $\text{AlMe}_3$  units.<sup>13–19</sup> In the activation process, the  $\omega$ -alkenyl group was transferred from the metal to the MAO cage. Then, the  $\omega$ -alkenyl functionalized MAO cage participated in a copolymerization reaction with ethylene and was thus incorporated into the polymer chain:



**TABLE III**  
**Polymerization Data of the Self-Immobilized Catalyst**  
**Precursors 2-7**

Prepolymerized catalysts <sup>a</sup>	
Complex	Activity [kg of PE/g of Zrh]
2	25
3	15
4	10
5	31
6	28
7	17

<sup>a</sup>  $T_p = 60^\circ\text{C}$ ; solvent: 500 ml pentane; 10 bar ethylene pressure;  $[\text{Zr}]/[\text{Al}] = 1:1000$ .

The methylation step in this process was accomplished by a monomeric trimethylaluminum group that was located in the cage. Due to dynamic equilibria and the fact that a bulky  $\omega$ -alkenyl group does not fit into the inside of an MAO cage, a rapid methyl/ $\omega$ -alkenyl exchange transferred the  $\omega$ -alkenyl group to the outer sphere of MAO where it was available for copolymerization with ethylene.

The activity of such isolated solid prepolymerized catalysts was lower than for the homogeneous or heterogeneous cases. This may have been due to the fact that there were no longer sufficient MAO cages available for the formation of cationic centers.

Experiments to synthesize a self-immobilizing MAO by the reaction of  $\omega$ -alkenyl Grignard reagents with commercial MAO did not give satisfying results.

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