

# A Supported Titanium Postmetallocene Catalyst: Effect of Selected Conditions on Ethylene Polymerization

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**ABSTRACT:** Ethylene polymerization with a titanium complex [*N,N*-ethylenebis(3-methoxysalicylideneiminato)titanium dichloride] immobilized on the magnesium support with the formula  $\text{MgCl}_2(\text{THF})_{0.32}(\text{Et}_2\text{AlCl})_{0.36}$  was studied. In particular, the effects of polymerization temperature, monomer pressure, and polymerization time on the activity of the catalyst and on the polyethylene properties (molecular weight and its distribution, melting point, crystallinity, and bulk density) were evaluated. The findings of investigations prove that the studied supported titanium catalyst is highly active in ethylene

polymerization, and its activity increases with increasing temperature and monomer pressure. Moreover, stability of the catalytic systems is dependent on the activator type used.  $\text{Me}_3\text{Al}$ , when employed as an activator, makes the catalytic system undergo no deactivation in practice. The catalyst coupled with MAO turned out less stable. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1848–1852, 2012

**Key words:** polyethylene; molecular weight distribution; melting point; catalysts; supports

## INTRODUCTION

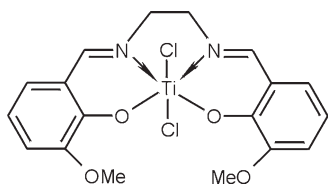
Postmetallocene catalysts have attracted much interest recently because of their various chemical structures and thus possible formation of polymer products with diversified properties. For example, bis(phenoxy-imine) early transition metal complexes are able to produce vinyl—and Al-terminated polyethylenes (PEs), highly isotactic and syndiotactic polypropylenes, high molecular weight atactic poly(1-hexene)s, bi- and trimodal PEs and polyolefinic block copolymers.<sup>1</sup> And with the other complexes—diimine late transition metal complexes—is possible to obtain ethylene homopolymer, whose structure varies from highly branched to linear.<sup>2</sup> It should be stressed, however, that these are primarily homogeneous systems,<sup>3,4</sup> although a few attempts were made lately to immobilize them on a carrier.<sup>5–7</sup> Our group also studied the effect of anchoring postmetallocene catalysts, vanadium and titanium ones, and the magnesium compounds were used as a support.<sup>8–10</sup> Magnesium chloride has so far been considered the best support for Ziegler-Natta catalysts and it is commonly employed to immobilize them.<sup>11</sup> That type of support, i.e., highly dispersed  $\text{MgCl}_2$ , was used to immobilize  $\text{TiCl}_4$  and a catalytic system was obtained

which was highly active both in ethylene polymerization and copolymerization.<sup>12</sup> In other studies,  $\text{TiCl}_4$  was fixed to the magnesium support in the form of magnesium chloride complex with tetrahydrofuran modified with diethyl aluminum chloride.<sup>13</sup> That catalyst not only offered high activity but also it turned out stable in ethylene polymerization, and the polymer product was characterized by good morphology. A somewhat different type of support, and namely spherical  $\text{MgCl}_2 \cdot n\text{EtOH}$  dealcoholated by heating, was used in.<sup>14</sup> When  $\text{TiCl}_4$  was immobilized on that support, the resultant catalyst had high specific surface area (184.4  $\text{m}^2/\text{g}$ ) and high activity in ethylene polymerization [20.23 kg PE/(mmol Ti·h)].

As regards another generation of ethylene polymerization organometallic catalysts, i.e., metallocene catalysts, silica was a dominating support for those systems initially.<sup>15–18</sup> Effective immobilization of such systems on a magnesium support became possible much later. A very active catalyst for ethylene polymerization was for example obtained by immobilization of  $(n\text{-PrCp})_2\text{ZrCl}_2$  on magnesium support of type  $\text{MgCl}_2 \cdot 1.1\text{EtOH}/\text{AlEt}_3$ .<sup>19</sup> Its activity results from the presence of the support sites with high Lewis acidity. A similar type of the magnesium support, i.e.,  $\text{MgCl}_2 \cdot n(\text{alcohol})$  (for  $\text{C}_2\text{H}_5\text{OH}$   $n = 3.33$  and for  $\text{CH}_3\text{OH}$   $n = 4$ ) modified with an organoaluminum compound (triisobutylaluminum being the best in that group) was also used to immobilize other metallocenes,  $\text{Cp}_2\text{ZrCl}_2$  and *rac*-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub>, which were then utilized in ethylene copolymerization with 1-hexene.<sup>20</sup>

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**Scheme 1** The structure of titanium complex.

The  $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$  support was described in Refs. <sup>5</sup> and <sup>6</sup> to be used for immobilization of not only metallocene but also nonmetallocene titanium catalysts. Those supported catalysts were found to be much more active than their homogeneous equivalents, and immobilization additionally eliminated MAO and borate activators. Moreover, catalysts immobilized on such type of carrier demonstrated high stability during the polymerization process. In another report,<sup>7</sup> bis(phenoxy-imine)zirconium catalyst was impregnated onto the MAO-modified spherical  $\text{MgCl}_2$  support. The obtained catalyst showed not only high activity in ethylene polymerization but also it produced spherical polymers with high bulk density.

Two types of magnesium supports:  $\text{MgCl}_2(\text{EtOH})_{3,4}$ <sup>8</sup> and  $\text{MgCl}_2(\text{THF})_2$ <sup>9,10</sup> were used to immobilize salen complexes of transition metals in our earlier studies, both of them modified with organoaluminum compound. A carrier with the formula  $\text{MgCl}_2(\text{THF})_{0.32}(\text{Et}_2\text{AlCl})_{0.36}$ , obtained as a result of modification of  $\text{MgCl}_2(\text{THF})_2$  by diethylaluminum chloride, was found superior within the supports tested. This report presents the results from the successive stage of our research program on supported postmetallocene catalysts, i.e., optimization of ethylene polymerization conditions which involve the use of *N,N*-ethylenebis(3-methoxysalicylideneimine) titanium dichloride complex, Scheme 1, supported on  $\text{MgCl}_2(\text{THF})_{0.32}(\text{Et}_2\text{AlCl})_{0.36}$ . Stability of that catalytic system in the ethylene polymerization process was additionally verified.

## EXPERIMENTAL

### Materials

Ethylene (3.0 grade, Linde Gas) and nitrogen (Messer) were purified by passing it over a column of sodium metal supported on  $\text{Al}_2\text{O}_3$ . Hexane was distilled from sodium/benzophenone. MAO (Witco, 10.0 wt %),  $\text{Me}_3\text{Al}$  (Witco, 2M), argon (5.0 grade, Linde Gas) were used as received.

### General methods

All handling operations were performed under inert atmosphere (nitrogen or argon), with the use of the standard Schlenk and glove box techniques. Differential scanning calorimetry (DSC) analyses were carried

out with the 2010 DSC calorimeter (TA Instruments). The second heating cycle was used for collecting DSC thermogram data, at a rate of 10 K/min. The percent crystallinity was calculated from the equation:  $\chi_c = \Delta H_f (100/290)$ .<sup>21</sup> The numbers of branches in PEs were determined by FTIR method, using the Nicole Nexus 2002 FTIR spectrometer. The samples were used in the form of polymer powder pills with KBr. Average molecular weight ( $M_w$ ) and molecular weight distributions ( $M_w/M_n$ ) of PE were determined by gel permeation chromatography using Alliance 135 GPCV 2000 apparatus equipped with three columns: HT3, HT4, HT6E, at 135°C using polystyrene calibration (Shodex Standards Type SM-105,  $M_w$  range 1200–3800000). 1,2,4-Trichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min. The particle size distribution was analyzed with the use of the vibratory sieve shaker from Fritsch. Every polymer sample was shaken over 20 min using the set of sieves with the mesh size within 1.6–0.063 mm.

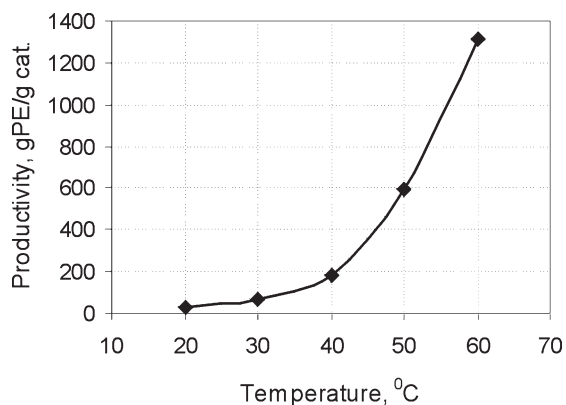
### Catalyst synthesis

Salen complex of titanium (*N,N*-ethylenebis(3-methoxysalicylideneimine)titanium dichloride) was prepared by reaction of  $\text{TiCl}_4$  and salen ligand in  $\text{CH}_2\text{Cl}_2$ , overnight, at room temperature. The details of the procedure are presented in ref. <sup>22</sup> The supported precatalyst (**Cat-1**) was synthesized according to the procedure described in Ref. <sup>9</sup>. First the magnesium complex  $\text{MgCl}_2(\text{THF})_2$  was modified with the  $\text{Et}_2\text{AlCl}$  ( $\text{Mg}/\text{Al} = 1/2$  mol/mol) in hexane, during 1.5 h, at room temperature, and then the so-prepared carrier material (2.19 g) and salen complex (0.1028 g, 0.2309 mmol) were comilled in hexane/toluene at room temperature overnight. The resulting solid was separated, washed several times with toluene and hexane, and dried until free-flowing.

Synthesized precatalyst contained 5.67 mg of Ti per gram of catalyst and 31 mg of Al per g of catalyst (measured by AAS method). Its specific surface area (obtained from the standard BET method) was 14.9  $\text{m}^2/\text{g}$ , pore volume 0.06  $\text{cm}^3/\text{g}$  and pore diameter 21.9 nm (calculated following the BJH method).<sup>10</sup> The precatalyst (**Cat-2**) was synthesized using the same procedure.

### Ethylene polymerization

The ethylene polymerization was carried out in a 1 L Büchi autoclave equipped with an anchor stirrer and a jacket for temperature control. The autoclave was charged with 0.15 L of hexane, the cocatalyst and precatalyst, in that order, at the desired temperature. Then the ethylene gas feed was started. The polymerization was continued for prescribed time at 250 rpm and after a reactor was depressurized and



**Figure 1** Effect of polymerization temperature on activity of **Cat-1**/ $\text{Me}_3\text{Al}$ . Polymerization conditions: reaction time 30 min, monomer pressure 5 atm, 8 mmol of activator, 0.01 g of catalyst.

cooled down, and resulting mixture was poured into acidified methanol. The polymer was filtered off, washed several times with methanol and dried *in vacuo*. Ethylene polymerization kinetics were measured with the use of a mass flowmeter.

## RESULTS AND DISCUSSION

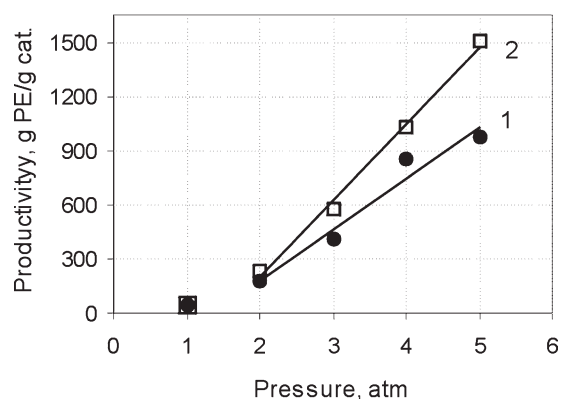
Supported titanium catalysts, obtained by immobilization of *N,N*-ethylenebis(3-methoxysalicylideneiminato)titanium dichloride or *N,N*-ethylenebis(salicylidene-iminato)titanium dichloride on the magnesium support  $\text{MgCl}_2(\text{THF})_{0.32}(\text{Et}_2\text{AlCl})_{0.36}$  (**Cat-1** and **Cat-2**, respectively), were initially characterized within our earlier study.<sup>10</sup> Those catalysts, after activation with the use of various organoaluminium compounds, proved high activity in polymerization of ethylene, and MAO and  $\text{Me}_3\text{Al}$  were found to be most effective activators. It is well known that the composition of a catalytic system and polymerization conditions can essentially affect, but differently for different systems, the polymerization yield and product properties. Within our research, we then optimized the process conditions for ethylene polymerization with the use of the catalyst **Cat-1**, i.e., we selected the most favorable temperature and monomer pressure for the reaction. In addition, stability of the tested catalytic system was verified over the course of the process.

Increasing temperature over the studied range, i.e., from 20 to 60°C, was found (Fig. 1) to significantly modify activity of the catalytic system under investigation. As can be seen, the higher temperature the more PE is produced, and that is an exponential relation. At the highest temperature covered by the study, activity of the **Cat-1**/ $\text{Me}_3\text{Al}$  system reaches 1.31 kg/(g cat·0.5h), which corresponds to 290.04 kg PE/(g Ti 0.5 h). A similar relation was obtained earlier for another salen complex:  $\text{Ti}(\text{salen})\text{Cl}_2$ , which was immobilized on the same support.<sup>10</sup> Hence, the supported

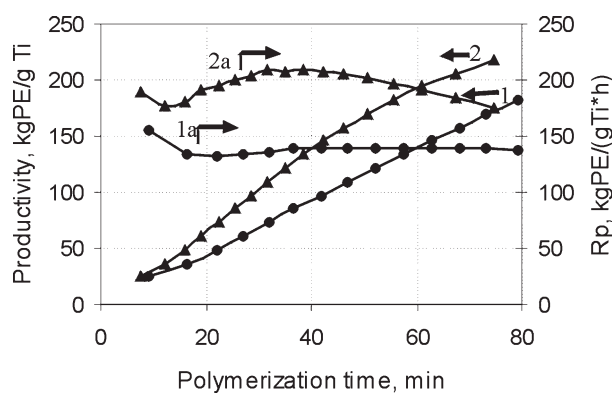
catalysts as developed by us, which contain type [O,N,N,O] complexes, offer high thermal stability. The effective activation energy ( $E_a$ ) of ethylene polymerization over that catalyst, calculated from the data presented in Figure 1, is 19.6 kcal/mol. That value is comparable with the value of  $E_a$  as calculated for a similar catalyst, i.e., for the salen-type titanium complex immobilized on the magnesium support  $\text{MgCl}_2 \cdot 3.4\text{EtOH}/\text{Et}_2\text{AlCl}$  and activated with the use of  $\text{Et}_3\text{Al}$ ,<sup>23</sup> which energy value amounts to 22 kcal/mol.

Pressure of ethylene feed made another factor which was verified for its effect on the activity of the investigated supported catalyst. Increasing monomer pressure within 1–5 atm turned out to cause a considerable growth in the catalyst productivity, but the growth was not linear. The linear relation was found within the pressure range of 2–5 atm (Fig. 2, curve 1). To check whether this relation of productivity changes versus pressure is typical for the developed supported catalysts which contain salen complexes of titanium, tests were repeated for another catalyst of the same type, i.e., **Cat-2**. The situation was similar to that for the previous system: the increasing pressure in the ethylene polymerization process with the use of **Cat-2** resulted in nonlinear rise in the reaction yield (over the whole pressure range), while linear growth was observed within 2–5 atm. Similar relations were also noted for polymerization with the use of other supported catalytic systems. It was reported in Ref. 24 that the activity of the supported catalyst [2,6-bis(imino)pyridyl iron dichloride/magnesium dichloride], after activation with  $\text{AlR}_3$ , was not directly proportional to the monomer pressure over the whole range (1.5, 3, 5, and 10 bar), but only within 3–10 bars. The exponential response of activity to increasing pressure was observed in<sup>25</sup> for the Ziegler Natta catalyst  $\text{TiCl}_4/\text{MgCl}_2$  (ethoxide type).

That relation between changing process pressure and changing activity for supported catalysts is likely



**Figure 2** Effect of monomer pressure on activity of supported titanium catalyst activated by MAO. Polymerization conditions: 0.01 g of catalyst, 8 mmol of activator, temperature 60°C, time 30 min; (1) **Cat-1**, (2) **Cat-2**.



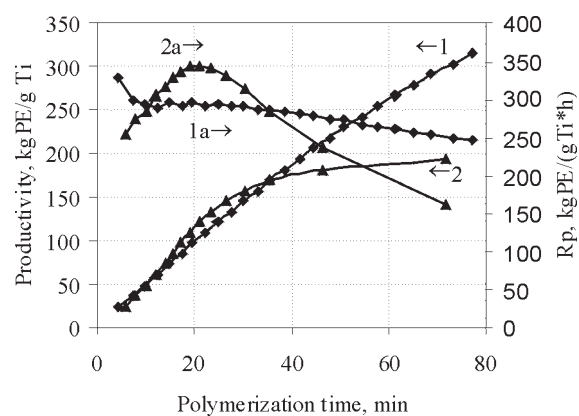
**Figure 3** Comparison of kinetic profiles of ethylene polymerization at 50°C using **Cat-1**/ $\text{Me}_3\text{Al}$  (1 and 1a) and **Cat-1**/MAO (2 and 2a).

to result from the induction period at low pressure values, due to slow disintegration of the catalyst and initiation of polymerization on newly uncovered areas under low monomer pressure.<sup>26</sup> The process is faster at higher ethylene pressures. One may arrive at such conclusions on the basis of the observations presented in Ref.<sup>26</sup> where polymerization with the use of the titanium catalyst (immobilized on silica gel) was studied, and where the induction period was observed at low monomer pressure values, while it was absent at higher values.

### Catalyst deactivation

It is very important for the industrial polymerization processes that the catalytic system offers constant activity over time. Having that in mind, we verified changes in polymerization rate and in productivity of the studied catalyst **Cat-1** at various temperatures and for various activators.

The profiles for productivity of **Cat-1** (and for polymerization rate) versus time are different for different reaction temperatures and different activators used. At 50°C and for  $\text{Me}_3\text{Al}$ , the catalytic sys-



**Figure 4** Comparison of kinetic profiles of ethylene polymerization at 60°C using **Cat-1**/ $\text{Me}_3\text{Al}$  (1 and 1a) and **Cat-1**/MAO (2 and 2a).

tem underwent no deactivation in practice over the studied span of time, i.e., up to 80 min. (Fig. 3). Under the same conditions, on the other hand, but with the use of MAO as an activator, the ethylene polymerization rate reached its maximum after 30 min., and then the catalytic system suffered some deactivation, although that decline was not considerable (Fig. 3, curve 2a). At a higher temperature of 60°C, however, activity of that catalytic system started going noticeably down as quickly as after about 20 min (Fig. 4, curve 2a). The **Cat-1**/ $\text{Me}_3\text{Al}$  system turned out clearly more stable, also at higher temperatures; some slight deactivation appeared after 30 min (Fig. 5, curve 1a). Hence, there is no need to employ MAO for activation of the studied supported salen-type catalyst since a simple alkyl aluminum compound ( $\text{Me}_3\text{Al}$ ) makes a definitely more advantageous activator—it assures stable polymerization kinetics and high activity of the catalyst.

### Polymer properties

The ethylene polymerization process, in which the investigated supported precatalyst is employed,

**TABLE I**  
Properties of Polyethylene Obtained with **Cat-1**

Entry	$T$ (°C)	Activator	Bulk density (g/dm <sup>3</sup> )	nCH <sub>3</sub> /100°C	$T_m$ (°C)	C (%)	$M_w$ (kg/mol)	$M_w/M_n$
1	20	$\text{Me}_3\text{Al}^a$	–	2.01	136.3	49.3	2429	5.60
2	30		–	0	136.7	48.1	2162	7.77
3	40		157	0	137.2	52.7	1262	10.89
4	50		164	0	139.3	50.4	1166	8.67
5	60		180	0.07	138.1	57.6	1005	9.34
6	40	$\text{MAO}^b$	267	1.31	137.6	53.6	2214	6.05
7	50		248	0.87	137.8	56.0	2100	6.80
8	60		288	0.09	138.7	62.7	2076	12.02
9	50	$\text{Me}_3\text{Al}^b$	275	1.44	138.1	53.4	1852	7.84
10	60		300	1.49	138.5	58.6	1802	9.51

<sup>a</sup> Polymerization time 30 min.

<sup>b</sup> Polymerization time 90 min.

Polymerization conditions: 0.015 g of catalyst, 8 mmol of activator, ethylene pressure 5 atm.

always yields linear PE with high melting point (over 136°C) and high molecular weight (Table I). It can be seen that the values of molecular weights clearly depends on both the reaction conditions and activator type. Increasing polymerization temperature from 20 to 60°C results in successive decreasing of  $M_w$  of PEs from 2400 kg/mol to 1000 kg/mol (Table I, entry 1-5). Moreover, we can see that longer polymerization time (at the same others polymerization conditions and activator type) leads to higher molecular weight of polymer product (Table I, entry 5 and 10 or 4 and 9). All produced polymers are characterized by broad molecular weight distribution in the range of 5.60–12.02 and higher values of  $M_w/M_n$  possess PEs obtained at higher temperature.

Moreover, the obtained polymers are characterized by good morphological properties, including *inter alia* advantageously high bulk density, up to 300 g/dm<sup>3</sup>. That value, however, is much dependent on the reaction conditions. That is to say that increased reaction temperatures, and first of all longer reaction times, result in the higher bulk density values for the obtained products, which is favorable. When Me<sub>3</sub>Al was used as an activator in polymerization, bulk density of the polymer produced after a 30-min. reaction was within 157–180 g/dm<sup>3</sup> depending on the process temperature. However, when the reaction time was extended to 90 min, polymers with much higher bulk densities were obtained, i.e., 275 and 300 g/dm<sup>3</sup> for 50°C and 60°C, respectively. One of the reasons of higher bulk density after longer polymerization time can be mechanical grinding. So we analyzed the particle size distribution of polymer obtained after 30 and 90 min at 50 and 60°C. We found that, independently on polymerization temperature in the polymers obtained after longer polymerization time are not present fractions with the lowest particle size, i.e., with average particle size 0.2; 0.15; 0.1; 0.08 mm. These fractions together in the polymers obtained after 30 min at 60°C and 50°C amounts to 19.22% and 6.76%, respectively. So the higher bulk density after longer polymerization time rather is not caused by mechanical grinding.

High bulk density values were obtained too in polymerization which took 90 min and which involved MAO as an activator. Those values were contained within 267–288 g/dm<sup>3</sup> depending on the process temperature, so they were slightly below those for the polymers produced with the use of Me<sub>3</sub>Al as an activator.

## CONCLUSIONS

The titanium complex, *N,N*-ethylenebis(3-methoxysilylideneiminato)titanium dichloride, immobilized on the magnesium support with the formula MgCl<sub>2</sub>(THF)<sub>0.32</sub>(Et<sub>2</sub>AlCl)<sub>0.36</sub> exhibited high catalytic

activity for ethylene polymerization; its activity was dependent to a considerable degree on reaction conditions, and it was growing both for higher polymerization temperatures and for higher monomer pressures. Moreover, the obtained types of the kinetic profiles show that the stability of investigated catalytic systems depends on temperature and on the activator type. **Cat-1/Me<sub>3</sub>Al** in practice did not decay over the studied span of time at 50°C. In addition, the polymerization conditions were found to have no significant influence on the properties of the obtained products, apart from bulk density which grows significantly with increasing polymerization time and temperature.

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