

# Effect of Cocatalysts on Ethylene Polymerization with Fluorinated Bisphenoxyimine Titanium as a Catalyst

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**ABSTRACT:** In this study, we examined various alkylaluminums, including triethylaluminum (TEA), triisobutylaluminum (TIBA), and diethylaluminum chloride (DEAC), as cocatalysts for the activation of ethylene polymerizations in the presence of a fluorinated Fujita group invented titanium (FI-Ti) catalyst, bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato] titanium(IV) dichloride (complex **1**). DEAC, because of the strong Lewis acidity, was an efficient cocatalyst for activating complex **1** for the ethylene polymerizations, whereas TEA and TIBA as cocatalysts could hardly polymerize ethylene. The effects of the polymerization temperature and Al/Ti molar ratio on the formation of active species, properties, and molecular weight of the

resulting polyethylene were investigated. In the complex **1**/DEAC catalyst system, the oxidation states of Ti active species were determined by electron paramagnetic resonance. The results demonstrated that Ti(IV) active species were inclined to polymerize ethylene and yielded high-molecular-weight polyethylene. Comparatively, Ti(III) active species resulted from the reduction of Ti(IV) by DEAC and afforded oligomers. Moreover, the bigger steric bulk for the cocatalysts was necessary to achieve ethylene living polymerization with the fluorinated FI-Ti catalyst. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 572–576, 2011

**Key words:** ESR/EPR; oligomers; polyethylene (PE)

## INTRODUCTION

Significant time and effort have been dedicated to exploring for ethylene polymerization well-defined Ti(IV) complexes, such as titanocenes, half-titanocenes,<sup>1–18</sup> and posttitanocenes bearing two phenoxyimine chelate ligands, called *Fujita group invented titanium (FI-Ti) catalysts*.<sup>s19–45</sup> In principle, suitable cocatalysts are required for the conversion of Ti(IV) complexes into highly active ethylene polymerization species. To clarify the effects of cocatalysts on titanocenes, especially half-titanocenes, intensive investigations have been conducted.<sup>1–4,7–10,15,16</sup> Because of the stronger Lewis acidity, bigger steric bulk, and weaker reduction ability, methylaluminoxane (MAO) and/or modified methylaluminoxane (MMAO) are preferred cocatalysts to the common alkylaluminum [trimethylaluminum, triethylaluminum (TEA), triisobutylaluminum (TIBA), and diethylaluminum chloride (DEAC)] counterparts for the formation of stable cationic Ti(IV) active species. With regard to titanocenes and half-

titanocenes, especially the latter, Ti(IV) active species can be reduced by MAO/MMAO; therefore, Ti species in different oxidation states probably coexist in the catalyst systems.<sup>15,17,18</sup> Only Ti(IV) active species display high ethylene polymerization activity in MAO-activated titanocene or half-titanocene catalysts systems.<sup>3,4,8</sup>

Because MAO and borate cocatalysts were originally developed to activate metallocenes,<sup>3,8,15,16</sup> these cocatalysts have been shown to be the most efficient cocatalysts for Fujita group invented (FI) catalysts.<sup>19–34,49–51</sup> Remarkably, MAO-activated FI catalysts achieved highly active living ethylene polymerization at ambient temperature or higher.<sup>24–28</sup> However, the widely application of MAO or/and borate is constrained because of their high cost. In addition, MAO has to be used in large excess to achieve the optimum ethylene polymerization activity. The uncertain structure and properties of MAO are dependent on the commercial supplier and synthetic method. Consequently, it is necessary to find suitable alternatives to replace MAO and borate.

On the basis of the phenoxyimine ligands of FI complexes containing electron-rich heteroatoms (O and N) that potentially interact with cocatalysts, Fujita and coworkers<sup>52,53</sup> discovered that MgCl<sub>2</sub>-based compounds were also good cocatalysts for FI catalysts. For this study, we selected a fluorinated FI-Ti catalyst: bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato] titanium(IV) dichloride (complex **1**; Fig. 1), which is an effective living ethylene

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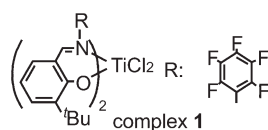


Figure 1 Complex 1.

polymerization catalyst in the presence of MAO,<sup>24–28</sup> to investigate the influences of such alkylaluminum cocatalysts as TEA, TIBA, and DEAC on both the formation and oxidation states of active Ti species in ethylene polymerizations.

## EXPERIMENTAL

### General methods

All manipulations involving air-sensitive materials were carried out with standard Schlenk techniques under an atmosphere of extrapure-grade nitrogen. Dichloromethane was distilled from P<sub>2</sub>O<sub>5</sub>, and toluene was refluxed over sodium for 48 h and distilled under a nitrogen atmosphere before use. GPC of the polymers was performed on a Waters 150C at 135 °C with 1,2,4-trichlorobenzene as the solvent. The columns were calibrated with narrow-molecular-weight-distribution polystyrene standards. The <sup>13</sup>C-NMR spectra of the polyethylene (PE) samples were recorded at 120 °C in a 10-mm tube with an Inova 500-MHz spectrometer. The samples were dissolved in *o*-dichlorobenzene/benzene-*d*<sub>6</sub> to form a 15 wt % solution. The chemical shift value (30.00 ppm) of the main backbone methylene was used as an internal standard. The electron paramagnetic resonance (EPR) measurements were recorded in the X-band at room temperature on a Bruker ESP200-E spectrometer with the field centered at 3360G. The signals of *g*<sub>3</sub> and *g*<sub>4</sub> of Mn<sup>2+</sup> in MnO powder were used as the standard sample. The oligomers were detected on a Voyage gas chromatograph/mass spectrometer with *n*-C<sub>8</sub>H<sub>10</sub> as the internal standard.

### Synthesis of the ligand and complex 1

The preparation of the ligand, *N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato, and the corresponding complex (complex 1) followed the procedure described by Fujita et al.<sup>24</sup>

ANAL. Calcd for C<sub>17</sub>H<sub>14</sub>NOF<sub>5</sub>: C, 59.48%; H, 4.11%; N, 4.08%. Found: C, 59.08%; H, 3.93%; N, 3.82%. Calcd for TiC<sub>34</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>F<sub>10</sub>Cl<sub>2</sub>: C, 50.38%; H, 3.26%; N, 3.49%. Found: C, 50.25%; H, 3.16%; N, 3.33%.

### Ethylene polymerization

The polymerization runs were carried out under an extrapure-grade nitrogen atmosphere in 100-mL glass flasks equipped with magnetic stirrers. Toluene

and MAO or DEAC, TEA, or TIBA were introduced into the reactor and then saturated with 0.15 MPa of ethylene; last, the toluene solution of complex 1 was added. After the required time, the polymerizations were terminated by the addition of excess acidic methanol (5 wt % HCl). The polymers were washed with ethanol and dried *in vacuo* at 60 °C to a constant weight.

### EPR samples

The samples were prepared according to the following general procedure. Complex 1 (3.5 mg) was weighed in a glass vial, which was sealed with a rubber septum in a dry box. Toluene was introduced into the vial by a syringe to dissolve the sample, and finally, the solution of the organometallic precursor and the proper cocatalyst was mixed in a Schlenk tube to prepare a solution of the catalytic system with a predetermined concentration (1.2 μmol/mL). The solution was transferred into the EPR tube by a syringe and analyzed under the experimental conditions described in the previous text.

## RESULTS AND DISCUSSION

The results of the ethylene polymerizations catalyzed by complex 1 in the presence of TEA, DEAC, TIBA, or MAO (activated) are summarized in Table I. Complex 1/MAO displayed the highest ethylene polymerization activity at Al/Ti = 1000 and 25 °C. With the nature of the strong Lewis acidity of MAO, cationic Ti(VI) active species could easily form and further promote highly active ethylene polymerizations. As shown in the EPR diagram [Fig. 2(a)], the indicator of the oxidation state of Ti implied that Ti(VI) active species were not reduced by MAO. Moreover, DEAC was also an effective cocatalyst in activating the resulting fluorinated FI-Ti catalyst for the ethylene polymerization at Al/Ti = 300 and 25 °C. However, TEA or TIBA as a cocatalyst could hardly activate the ethylene polymerization under any of the tried experimental conditions. As is well known, the Lewis acidity of DEAC is stronger than those of TEA and TIBA, which was beneficial for the formation of cationic Ti active species for complex 1. Moreover, there was some evidence for the formation of bimetallic Ti–Mg species bridged by chlorine.<sup>52,53</sup> It was hypothesized that the phenoxyimine ligand donors tended to interact with DEAC. In consequence, DEAC enriched around the electron-deficient Ti centers, and the formation of bimetallic Ti–Al species bridged by the chlorine atom was facilitated. Through the cleavage of the chlorine linkage, cationic Ti(VI) active species evolved from the bimetallic species eventually. Likewise, the EPR

TABLE I  
Ethylene Polymerizations with Complex 1 Activated by Various Cocatalysts

Run	Cocatalyst	Polymerization temperature (°C)	Al/Ti (mol/mol)	Polymerization time (min)	Activity $\times 10^{-5}$ [g of PE (mol of Ti) $^{-1}$ h $^{-1}$ ] <sup>a</sup>	$M_w \times 10^{-4b}$	$M_w/M_n$ <sup>b</sup>
1	DEAC	25	200	10	1.26	4.97	1.28
2	DEAC	25	300	10	2.39	4.79	1.44
3	DEAC	25	800	10	0.61 + oligomer	2.43	1.45
4	DEAC	25	1000	10	0.36 + oligomer	1.93	1.51
5	DEAC	25	1200	10	Oligomer	—	—
6	DEAC	0	800	10	1.22	4.53	1.26
7	DEAC	0	1000	10	1.86	3.37	1.29
8 <sup>c</sup>	DEAC	0	800	10	1.03 + oligomer	ND	ND
9	DEAC	35	800	10	0.43 + oligomer	ND	ND
10	DEAC	50	800	10	0.19 + oligomer	ND	ND
11	DEAC	25	300	2	5.82	3.61	1.26
12	DEAC	25	300	4	5.81	4.48	1.11
13	DEAC	25	300	6	3.87	4.65	1.37
14	MAO	25	1000	10	4.87	7.28	1.12
15	TEA	25	300	10	Trace	—	—
16	TEA	0	300	10	Trace	—	—
17	TEA	50	300	10	Trace	—	—
18	TIBA	25	300	10	Trace	—	—
19	TIBA	0	300	10	Trace	—	—
20	TIBA	50	300	10	Trace	—	—

The polymerization conditions were as follows: the Ti concentration was  $3 \times 10^{-5}$  mol/L, the C<sub>2</sub>H<sub>4</sub> pressure was 0.15 MPa, and toluene was used as the solvent.  $M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight; ND = not determined.

<sup>a</sup> The catalytic activity was contributed by Ti(VI) active species, which produced high-molecular-weight PE.

<sup>b</sup> Determined by GPC.

<sup>c</sup> Ethylene polymerization proceeded at 0°C in the presence of the preactivated catalyst system (complex 1/DECA; [Al]/[Ti] = 800) at 25°C.

diagram [Fig. 2(b)] indicates no DEAC-reduced Ti(III) active species at Al/Ti = 300 and 25°C.

It is now widely accepted that living olefin polymerization activated by fluorine FI-Ti/MAO originates from the key attractive interaction between *ortho*-fluorine of the phenoxyimine ligand and a  $\beta$ -hydrogen on the growing PE chain.<sup>24</sup> The strong  $\beta$ -hydrogen agostic interaction prevents both  $\beta$ -hydrogen elimination and  $\beta$ -hydrogen transfer to the monomer.<sup>24–28</sup> In terms of living polymerization, the growing PE chain transfer to MAO is certainly suppressed.

Actually, as displayed in Table I, the molecular weight and molecular weight distribution of the PE obtained by complex 1/DEAC depended on the polymerization time, temperature, and Al/Ti molar ratio; this suggested that the growing PE chains could transfer to Al species. In the early stage of the ethylene polymerization (polymerization time  $\leq 4$  min, run 10), the performance proceeded analogously to living polymerization. However, the decay of polymerization activity was observed from the middle to the late polymerization stage. An increasing deviation between the GPC-determined molecular weight of PE and the linear-time-predicted molecular weight of PE was evident (Table I, run 11 and run 2). The broadened molecular weight distributions approached around 1.5 (run 2). When the ratio of

Al/Ti increased from 300 to 1000, the molecular weight of PE decreased from  $4.79 \times 10^4$  to  $1.93 \times 10^4$  (Table I, runs 2 and 4). In addition, the characteristic shifts of PE (Al/Ti = 1000 at 25°C) displayed in the <sup>13</sup>C-NMR spectrum (Fig. 3) could only be attributed to methyl termini and the methylene carbons in backbone chain. No shifts corresponding to olefinic termini derived from  $\beta$ -hydrogen elimination were

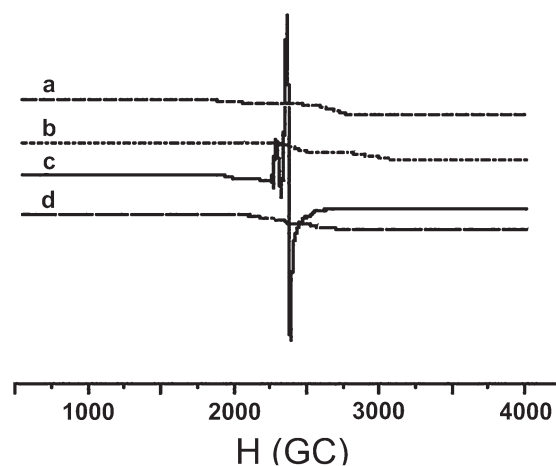


Figure 2 EPR spectra of the mixtures at 25°C: (a) MAO/complex 1 (Al/Ti = 1000), (b) DEAC/complex 1 (Al/Ti = 300), (c) DEAC/complex 1 (Al/Ti = 800), and (d) TIBA/complex 1 (Al/Ti = 800)

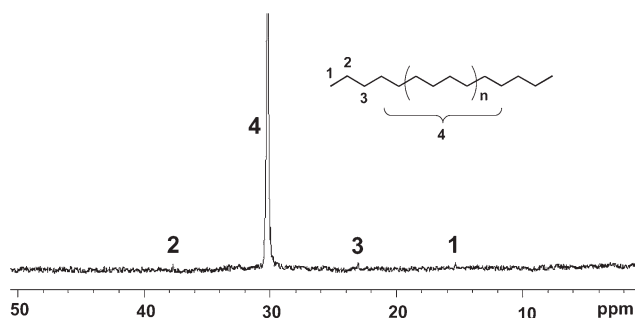


Figure 3  $^{13}\text{C}$ -NMR spectrum of PE (run 4 in Table I).

observed. All of these results suggested that the steric bulk of the counterion was also an underlying precondition for the achievement of living ethylene polymerization in the presence of the fluorinated FI-Ti catalyst.

To activate complex **1** to form Ti(IV) active species and scavenge impurities, an appropriate amount of DECA was required. With increasing ratio of Al/Ti from 200 to 300 (25°C), the catalytic activity monotonically increased to  $2.39 \times 10^5$  g of PE (mol of Ti) $^{-1}$  h $^{-1}$  (Table I). However, the activity decreased with the further increasing ratio of Al to Ti. Oligomers were originally observed at Al/Ti = 800. When the ratio of Al/Ti was up to 1200, all of the afforded products were oligomers. In the meanwhile, EPR analyses [Fig. 2(c)] disclosed the existence of Ti(III) active species derived from the DEAC-reduced Ti(IV) species at Al/Ti = 800 and 25°C. On the basis of these experimental results, we propose that oligomers originated from the enchainment PE chains on either the Ti(IV) or Ti(III) active species. Two verified ethylene polymerizations were conducted. One polymerization was carried out at 0°C by the introduction of the preactivated complex **1** (complex **1**/DECA, Al/Ti = 800, 25°C; Table I, run 8). Both PEs and oligomers were yielded. The other ethylene polymerization was carried out with all of the procedures at 0°C (complex **1**/DECA, Al/Ti = 800; Table I, run 6). They all yielded PEs. Therefore, it was reasonable to conclude that the Ti(III) active species was the oligomerization species. The obtained oligomers (run 3) were determined to be saturated linear alkanes, C $_{18}$ H $_{38}$ , C $_{20}$ H $_{42}$ , C $_{22}$ H $_{46}$ , and C $_{24}$ H $_{50}$ , by gas chromatography/mass spectrometry. The suppressed  $\beta$ -hydrogen elimination on Ti(III) active species was likely to be a direct result of strong  $\beta$ -hydrogen agostic interaction.

With increasing polymerization temperature, complex **1**/DEAC exhibited decreased activity (Table I). This was possibly due to the sped up reduction of Ti(IV) into Ti(III) active species and the decreased ethylene concentration in toluene at higher temperatures. Furthermore, the faster chain transfer to DEAC at higher temperatures resulted in the

decreased molecular weight of PE and a broadened molecular weight distribution.

## CONCLUSIONS

Under appropriate conditions, a fluorinated FI-Ti catalyst (complex **1**) displayed comparable activity for ethylene polymerization in the presence of DEAC as MAO, whereas TEA and TIBA, used as cocatalysts, could hardly polymerize ethylene. Cationic Ti(IV) active species, necessary for ethylene polymerization to produce high-molecular-weight PE, could be formed in terms of strong Lewis acidity and alkylation ability of DEAC. However, as the Al/Ti molar ratio and polymerization temperature increased, DEAC reduced the Ti(IV) active species to Ti(III) ones; this only yielded ethylene oligomers. The steric bulkiness of the counterion, which contributed to restrain the chain transfer and chain termination, was also a premise for achieving ethylene living polymerization for fluorinated FI-Ti catalysts.

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