

## Short Communication

## Tandem catalysis of iron and titanium non-metallocene catalysts for the production of branched polyethylene

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## ABSTRACT

Branched polyethylene was successfully produced with ethylene as the sole monomer stock by a novel binary tandem catalyst system composed of 2,6-bis(imino)pyridyl iron complex (**1**) and mono  $\beta$ -diiminato titanium complex (**2**) activated only by MMAO, in which the complex **2** was the first non-metallocene titanium complex used as copolymerization catalyst. The copolymerization activity can reach up to  $10^6$  g/mol Ti $\cdot$ h $\cdot$ atm. And by simple adjustment of the catalyst molar ratios and polymerization conditions, polymers with various branches including ethyl, butyl and long branches and varying branching degrees (from 0 to 10.7/1000 C) can be efficiently produced.

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## 1. Introduction

Branched polyethylene such as linear low-density polyethylene (LLDPE), produced commonly by copolymerization of ethylene with  $\alpha$ -olefin comonomers such as 1-butene, 1-hexene, and 1-octene with conventional Ziegler–Natta catalysts or recently developed single-site metallocene catalysts, has extensive commodity applications due to the presence of short-chain branches that can enhance processability and the mechanical performance of polyethylene products, such as the stiffness, stress-crack resistance, tensile strength. However, one of the most important limitations of the current processes is the high cost of  $\alpha$ -olefin that comes from ethylene oligomerization. Recently, considerable efforts have been made to search for alternative processes that promote the synthesis of branched polyethylene from ethylene directly. These single-step processes have obvious advantages over traditionally used two-stage process in the costs of plant investment and operation.

Compared with the commonly used two-stage process, tandem catalysis is preferred to prepare branched polyethylene, which is also called *in-situ* copolymerization and was firstly reported by Beach and Kissin in the 1980s [1,2]. After that, a wide variety of promising tandem catalytic systems involving

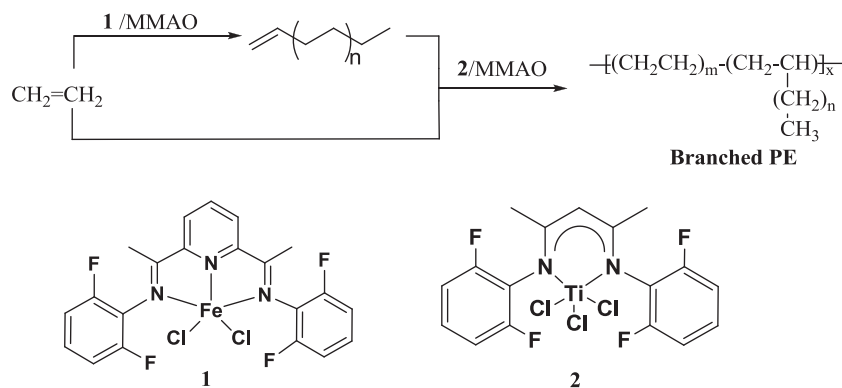
two different Ziegler–Natta catalysts [1–4], Ziegler–Natta catalyst/homogeneous catalyst [5,6], and two or three different homogeneous catalysts [7–22] have been developed to prepare branched polyethylene *in situ*. At these binary tandem catalytic systems, the copolymerization catalysts are always Ziegler–Natta or metallocene catalysts.

In recent years, the group 4 non-metallocene catalysts have attracted great attention due to their good catalytic performances for the controlled synthesis of polyolefin products [23–26]. Recently we have been committed to find some novel early and late transition non-metallocene catalysts with excellent catalytic performances by regulating the coordination environments of central metal with electronic effects or synergistic steric and electronic effect of substituents on ligands [27–29], and found that the mono  $\beta$ -diiminato titanium complexes bearing fluoro substituents exhibited superb activities not only for ethylene polymerization but also for copolymerization of ethylene and  $\alpha$ -olefin. Qian et al. also reported that the 2,6-bis(imino)pyridyl iron complexes with two fluoro substituents could oligomerize ethylene to  $\alpha$ -olefin with high activity and selectivity [30–32]. To investigate the compatibility and matching of the tandem catalysis of iron and titanium non-metallocene catalysts, we designed the binary tandem catalytic system with iron complex **1** as oligomerization catalyst and titanium complex **2** as copolymerization catalyst and tested their catalytic behaviors, which was shown in Scheme 1. To the best of our knowledge, this is the first example of effective tandem catalytic systems with non-metallocene titanium complex as copolymerization catalyst.

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**Scheme 1.** Preparation of branched polyethylene by tandem catalysis of iron and titanium non-metallocene catalysts.

## 2. Experimental

### 2.1. Materials

All work involving air- and/or moisture-sensitive compounds were carried out with standard Schlenk techniques. MMAO (7% aluminum in a heptane solution) was purchased from Akzo Nobel Chemical, Inc. Iron complex **1** and titanium complex **2** were prepared according to literature [30,31] and our previous works [27].

### 2.2. Characterization

The  $^{13}\text{C}$  NMR data of the ethylene/ $\alpha$ -olefin copolymers were obtained on a Varian XL 300 MHz spectrometer at 120 °C with *o*- $\text{C}_6\text{D}_4\text{Cl}_2$  as the solvent. The chemical shift value (30.00 ppm) of the main backbone methylene was used as an internal standard. Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. The differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter. Each sample was heated from 30 to 200 °C at a heating rate of 10 °C/min and reheated at the same rate. The  $M_n$  and  $M_w/M_n$  of the polymers were determined at 150 °C with a PL-GPC 220 high-temperature chromatograph using a polystyrene calibration. 1,2,4-Trichlorobenzene was employed as the solvent at a flow rate of 1.0 mL/min.

### 2.3. General procedure of *in-situ* copolymerization

The procedure of *in-situ* copolymerization was referred to literature [27].

## 3. Results and discussion

Both the bisiminoipyridyl iron complex (**1**) and non-metallocene titanium complex (**2**) are highly active catalysts for ethylene oligomerization or polymerization in the presence of MMAO [27,30]. Moreover, **2**/MMAO can also copolymerize ethylene and  $\alpha$ -olefin with high activity and comonomer incorporation. Based on these observations, we prepared branched polyethylene by tandem catalysis with bisiminoipyridyl iron complex (**1**) and non-metallocene titanium complex (**2**) as dual-functional catalysts using ethylene as the sole stock. The reaction conditions such as the polymerization temperature, Fe/Ti and Al/(Fe + Ti) molar ratios can influence the copolymerization activities and properties of the copolymers. The branching degrees, molecular weights and melting temperatures are measured by  $^{13}\text{C}$  NMR, GPC and DSC, respectively. The results are summarized in Table 1.

A clear trend was that the activity as calculated for Ti complex increased distinctively from  $1.45 \times 10^6$  to  $5.23 \times 10^6$  g/mol Ti·h·atm

when the Fe/Ti molar ratio increased from 0:1 to 4:1 (samples 1–6 of Table 1). These results may be explained by a positive comonomer effect, *i.e.*, more  $\alpha$ -olefins would be produced with more oligomerization catalyst added, thus leads to higher calculated activities for Ti complex.

As the most effective tool, the high temperature  $^{13}\text{C}$  NMR spectrum can directly prove the existence of branching structures and be used to calculate the branching degrees as well as the proportion of different branches. The  $^{13}\text{C}$  NMR spectra of polymers catalyzed by **2**/MMAO and **1**/**2**/MMAO were shown in Fig. 1. The polymer produced by **2**/MMAO proved to be moderate-molecular-weight linear polyethylene with methyl and isobutyl chain ends and with no unsaturated groups [33–35], probably due to chain transfer to aluminum which would result in almost completely saturated polymer chains. Besides the main peak at 30 ppm, the peaks at 13.98, 22.71, 32.18 and 29.57 ppm are due to the 1C, 2C, 3C and 4C in chain ends, respectively, and the other peaks are attributable to the carbon of isobutyl chain derived from isobutyl modified methylaluminoxane. Compared with the  $^{13}\text{C}$  NMR spectrum of polymer catalyzed by **2**/MMAO, several extra peaks at 11.19, 23.37, 26.87, 27.40, 34.21, 34.71, 38.36, and 39.86 ppm appeared for the polymer produced by **1**/**2**/MMAO, which can be attributed to the ethyl, butyl, and longer branches. Moreover, the  $^{13}\text{C}$  NMR spectrum of the moderate-molecular-weight copolymer is different in part from high-molecular-weight branched polyethylene or mixtures of branched polyethylene and unreacted  $\alpha$ -olefin reported in literatures [33]. For example, the peaks at 27.63, 28.27, and 39.51 ppm which attributed to isobutyl carbon in chain ends did not appear in the  $^{13}\text{C}$  NMR spectra of

**Table 1**  
Tandem catalysis of Fe (**1**) and Ti (**2**) catalysts.<sup>a</sup>

Sample	Ti ( $\mu\text{mol}$ )	Fe/Ti <sup>b</sup>	Al/(Ti + Fe)	Temp (°C)	$M_w$	$M_w/M_n$	Act. <sup>c</sup>	$T_m$ <sup>d</sup> (°C)	$N^e$
1	0	0	1500	25	6103	2.44	1.45	130.3	0
2	4	1/2	1500	25	3776	2.21	1.93	119.1	6.9
3	2	1/1	1500	25	6138	2.29	3.47	119.6	7.4
4	2	2/1	1500	25	6803	2.31	4.53	118.9	7.9
5	1	3/1	1500	25	6941	2.18	4.87	118.9	
6	1	4/1	1500	25	6805	2.10	5.23	117.3	10.7
7	1	1/1	500	25	6617	2.25	1.21	132.0	
8	2	1/1	1000	25	6423	2.33	1.52	126.5	
9	2	1/1	2000	25	6157	2.41	2.42	125.5	3.3
10	2	1/1	1500	0	6385	2.12	0.55	133.3	
11	2	1/1	1500	50	7689	2.26	2.09	125.5	0

<sup>a</sup> 50 ml toluene, 30 min, 1 atm pressure.

<sup>b</sup> Molar ratios.

<sup>c</sup> Calculated as titanium complexes,  $10^6$  g mol Ti<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>.

<sup>d</sup> Measured by DSC.

<sup>e</sup> Measured by  $^{13}\text{C}$ NMR, Branches/1000 C.

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