

# Toward the bimodality of polyethylene, initiated with a mixture of a Ziegler–Natta and a metallocene/MAO catalyst system

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## Abstract

Polymerization of ethylene catalyzed by a mixture of a Ziegler–Natta (Z–N) and a metallocene system cocatalyzed with methylaluminumoxane (MAO) were carried out in a single reactor. The Z–N catalyst can be activated in the presence of MAO, without any addition of a conventional Z–N activator. The activities of the mixture Z–N with  $Cp_2MCl_2$  ( $M = Ti, Zr, Hf$ ) (**1,2,3**) or  $CpZrCl_3$  (**4**) were lower than the obtained with the mixture Z–N and  $en(Ind)_2ZrCl_2$  (**5**). The weight-average molecular weight (Mw) of the polyethylene (PE) obtained with the mixture Z–N with  $Cp_2MCl_2$  ( $M = Ti, Zr, Hf$ ) or  $en(Ind)_2ZrCl_2$  was lower than the PE obtained with Z–N and  $CpZrCl_3$ . For the binary mixture of Z–N with  $CpZrCl_3$  (**4**), the PE obtained showed a bimodal molecular weight distribution (MWD) for an appropriate composition of the mixed catalyst in the absence of hydrogen in the reaction medium. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Ethylene; Polyethylene; MAO; Ziegler–Natta catalyst; Metallocene; Bimodal

## 1. Introduction

It has been said that bimodality has become an additional degree of freedom in tailoring polyethylene (PE) [1]. In addition, the prevailing industrial method up to now for making bimodal PEs uses multi-stage reactors. However, according to some authors, this method of

multi-stage reactors is expensive [2–4], cumbersome and time-consuming [4,5]. Therefore, it is desirable to produce bimodal PEs in one step and in one reactor.

One way of producing a bimodal PE is by using two metallocenes with methylaluminumoxane (MAO). This method has been reported in several instances before [2,3,6,7]. Another similar method involves the use of a mixture of a Ziegler–Natta (Z–N) catalyst and a metallocene [8–11]. Both of these methods are based on the generation of two catalytic sites that have different kinetic responses, such as different propaga-

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tion and termination rate constants for ethylene polymerization. Thus, the whole catalytic system would produce a blend of polymeric chains with two predominant molecular masses.

When running a mixture of a Z–N and a metallocene catalyst for olefin polymerization, commonly it is necessary the use of a combination of a conventional Z–N activator and MAO [4,12], and the polymer would exhibit various types of molecular weight distribution (MWD) in accordance with the experimental conditions used. The possibility of producing bimodal PE, with this approach, but only using MAO as activator in a single reactor, represents an attractive strategy to be applied in current PE plants [13].

In this paper, preliminary results of ethylene polymerizations using a Z–N catalyst developed in our group [14] with different metallocenes are shown and the properties of the polymers obtained are discussed.

## 2. Experimental

### 2.1. Experimental procedure

All reactions and manipulations were carried out under argon atmosphere. Toluene as solvent was dried over sodium and it was deoxygenated prior to use. The Z–N catalyst INPETUS<sup>®</sup> was prepared according to the published procedure [14]. Cp<sub>2</sub>MCl<sub>2</sub> (M = Ti, Zr, Hf) CpZrCl<sub>3</sub> and en(Ind)<sub>2</sub>ZrCl<sub>2</sub> (en = ethylene, Ind = indenyl) were used as received. MAO (12.2 wt.% Al, Akzo Nobel, USA) was used as a cocatalyst.

The polymerization reactions were performed in a stainless steel 300 ml Parr reactor provided with a temperature control unit. Melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) of the obtained polymers, were measured by differential scanning calorimetry (DSC) (DSC30 Mettler) at 10°C/min. Weight-average molecular weight (Mw) and MWD, were determined by means of gel permeation chromatography (GPC) (Waters 150-CV) with *o*-di-chlorobenzene stabilized with 0.25 g/l of Irganox 1076 as a solvent at 135°C and the results were analyzed using universal calibration curves based on polystyrene standards.

### 2.2. Polymerization runs

In a 300-ml stainless steel Parr autoclave, 100 ml of toluene was introduced under argon atmosphere at 70°C; then, the mixture of Z–N/metallocene catalyst ( $3.5 \times 10^{-6}$  M) and MAO ( $1.6 \times 10^{-3}$  M) as cocatalyst were added. The reaction started by the admission of 5 atm of ethylene at 80°C with stirring (600 rpm). After 1 h, the reaction was quenched with ethanol (2 ml), excess ethylene was vented, and the resulting polymer was stirred with hydrochloric acid/water/ethanol mixture (5:85:10), neutralized with NaHCO<sub>3</sub> solution and finally vacuum dried at 60°C.

## 3. Results and discussion

In order to get information about the activity of the Z–N catalyst (INPETUS<sup>®</sup>) activated only

Table 1  
Ethylene polymerization with Z–N catalyst activated with MAO

Catalyst	Al/Ti	Activity <sup>a</sup>	Mw <sup>b</sup> (g/mol)	Mw/Mn <sup>c</sup> (g/mol)	T <sub>m</sub> (°C) <sup>d</sup>	T <sub>c</sub> (°C) <sup>e</sup>
INPETUS <sup>™</sup>	1020	462	259,600	3.1	140.4	117.7

Conditions: [Ti] =  $8.2 \times 10^{-5}$  M, MAO =  $8.8 \times 10^{-4}$  M, toluene = 100 ml,  $T = 80^\circ\text{C}$ , PC<sub>2</sub>H<sub>4</sub> = 5 atm,  $t = 1$  h.

<sup>a</sup> KgPE/mol metal h.

<sup>b</sup> Mw: weight-average molecular weight.

<sup>c</sup> Mw/Mn: polydispersity.

<sup>d</sup> T<sub>m</sub>: peak melting temperature of PE.

<sup>e</sup> T<sub>c</sub>: peak crystallization temperature of PE.

with MAO, a comparative polymerization run was carried out under standard conditions. The INPETUS<sup>®</sup> comprises a magnesium chloride supported TiCl<sub>4</sub> catalyst in which the propriety combination of matched additives increases the activity of the catalyst and improves the properties of the resulted PE [14]. As can be seen in Table 1, the Z–N catalyst was activated by using MAO. Under this relatively highly reducing condition, the Z–N catalyst polymerized ethylene with a lower activity than when a common activator such as triethyl aluminum (TEA) is used for ethylene polymerization. Similarly, the Mw resulted reduced when compared with the obtained with TEA [14]. On the other hand, polydispersity (Mw/Mn) was typical of a Z–N catalyst.

A number of experiments were carried out with the mixture of the Z–N catalyst INPETUS<sup>®</sup> with five different metallocenes such as Cp<sub>2</sub>TiCl<sub>2</sub> (**1**), Cp<sub>2</sub>ZrCl<sub>2</sub> (**2**), Cp<sub>2</sub>HfCl<sub>2</sub> (**3**), CpZrCl<sub>3</sub> (**4**) and en(ind)<sub>2</sub>ZrCl<sub>2</sub> (**5**). The experimental results are shown in Table 2.

The mixture of the *ansa* metallocene **5** with the Z–N catalyst, showed the highest activity of all the metallocene tested in this work. The polydispersity of the polymers obtained with the mixture of INPETUS<sup>™</sup> and the metallocene **1**, **2**, **3** and **5** were narrow, which is characteristic of polymers obtained by using a single site catalysts (SSC) [7]. The above result suggests that the MWD be strongly influenced by the

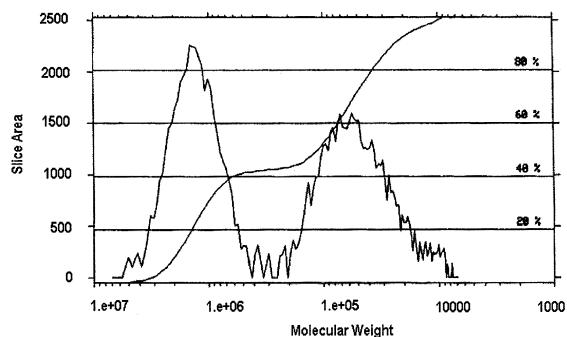


Fig. 1. GPC of the PE obtained with the mixture CpZrCl<sub>3</sub>/INPETUS<sup>®</sup>.

metallocene contribution. However, for the mixture of INPETUS<sup>®</sup> with the metallocene **4**, the polydispersity of the polymer increased up to 11 and PE with a bimodal MWD was obtained as can be seen in Fig. 1.

In addition, no hydrogen was used in this work in order to facilitate the broadness of the molecular weight, strategy usually employed for the preparation of bimodal polymers [15]. The *T<sub>m</sub>* and *T<sub>c</sub>* of PEs prepared with the mixed catalyst were independent of the catalytic system and the value was founded in the region commonly for HDPE [16].

More detailed experiments for the polymerization of ethylene initiated with a Z–N catalyst in conjunction with other metallocenes are in progress and the results will be published in a future communication.

Table 2

Polymerization of ethylene initiated with a mixture of a Z–N and a metallocene catalyst activated with MAO. Properties of the PEs obtained

Metallocene	Activity <sup>a</sup>	Mw (g/mol) <sup>b</sup>	Mw/Mn <sup>c</sup> (g/mol)	<i>T<sub>m</sub></i> (°C) <sup>d</sup>	<i>T<sub>c</sub></i> (°C) <sup>e</sup>
Cp <sub>2</sub> TiCl <sub>2</sub> ( <b>1</b> )	608	110,500	2.6	130.1	119.8
Cp <sub>2</sub> ZrCl <sub>2</sub> ( <b>2</b> )	530	132,500	2.9	134.0	121.3
Cp <sub>2</sub> HfCl <sub>2</sub> ( <b>3</b> )	290	99,900	2.6	135.2	119.8
CpZrCl <sub>3</sub> ( <b>4</b> )	447	697,000	11.2	138.5	118.9
en(ind) <sub>2</sub> ZrCl <sub>2</sub> ( <b>5</b> )	1090	99,600	2.7	133.7	119.2

Conditions: [Al]/[Ti] = 1050, [Al]/[M] = 2800, *T* = 80°C, PC<sub>2</sub>H<sub>4</sub> = 5 atm, *t* = 1 h.

<sup>a</sup> KgPE/mol metal h.

<sup>b</sup> Mw: weight-average molecular weight.

<sup>c</sup> Mw/Mn: polydispersity.

<sup>d</sup> *T<sub>m</sub>*: peak melting temperature.

<sup>e</sup> *T<sub>c</sub>*: peak crystallization temperature.

#### 4. Conclusions

The mixture of a Z–N catalyst INPETUS<sup>®</sup> with different metallocenes activated with MAO, can polymerize ethylene in a single reactor, without any extra activator and in the absence of hydrogen with moderate activity. The PE obtained showed narrow MWD when Cp<sub>2</sub>TiCl<sub>2</sub> (**1**), Cp<sub>2</sub>ZrCl<sub>2</sub> (**2**), Cp<sub>2</sub>HfCl<sub>2</sub> (**3**), and en(ind)<sub>2</sub>ZrCl<sub>2</sub> (**5**) were used as metallocenes; however, when CpZrCl<sub>3</sub> (**4**) was used with INPETUS<sup>®</sup>, a bimodal PE was produced.

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