

Modification of polyethylene polydispersity by blending a Ziegler-Natta catalyst with a group of IV-half metallocene or scorpionate complexes

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Abstract

Polymerization of ethylene catalyzed by a blend of INPETUS[®], a Ziegler-Natta catalyst, with some half metallocenes such as CpTiCl₃ (1), Cp^{*}MCl₃ (M = Ti, Hf) (2,3) and IndZrCl₃ (4) or with tris(pyrazolyl)borate complexes like TpTiCl₃ (5) and Tp^{*}TiCl₃ (6) in the presence of MAO, was carried out in a single reactor. Activities of the mixtures using the half metallocenes (2) and (3) were higher than those obtained with (1) and (4). On the other hand, the blends with tris(pyrazolyl)borate complexes (5) and (6) showed the lowest activities of both types of complexes used. Molecular weight of polyethylene (PE) obtained from the mixture with Cp^{*}TiCl₃ (2) was slightly higher than that of PE obtained with INPETUS[®] and the complex (6) and higher than those of the blends studied in this work. Molecular weight distribution (MWD) of the PE from INPETUS[®]/IndZrCl₃ (4), produced at very mild reaction conditions, was considerably similar to a type of PE obtained in industrial plants under more severe reaction conditions. The polymers resulting from these blends showed melting temperatures characteristic of HDPE. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The possibility of increasing polymer property profile constitutes a permanent research area aimed at producing more attractive materials [1]. Specially for polyethylene (PE), control of the molecular weight (M_w) and molecular weight distribution (MWD) is

of fundamental significance in product performance. Thus, blending of PE with different M_w and MWD helps to improve processability and mechanical properties of final products, allowing to extend their industrial applications.

This fact suggests that tuning the MWD of the polymer as far as a bimodal distribution, which is considered an ideal situation, leads to reach polymers with double MWD, condition that is responsible for better mechanical and rheological properties of the final polymer [2].

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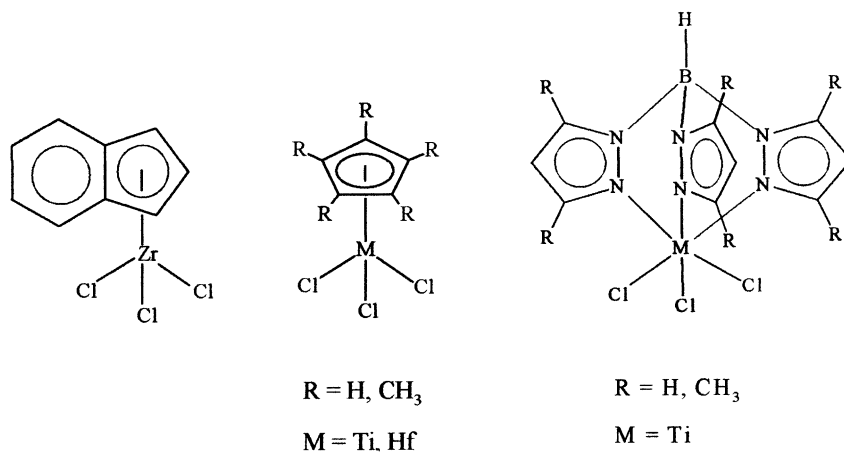


Fig. 1. Metallocene and Scorpionate complexes used in the blends with INPETUS[®].

With a view to obtain different commercial PEs (LDPE, LLDPE, HDPE) several process types, such as high pressure, solution, slurry and gas phase, have been used in industrial plants. Some of them involve high pressures, high temperatures and addition of hydrogen to the industrial process. Through combination of different reactors and modification of operational conditions the desired products can be obtained. However, these are operational strategies and require significant investments [3–5].

Several patents to broaden MWD polymers have been registered to minimize operational and inversion cost and produce improved PEs by using single reactors. Some of them consist of the use of two metallocenes activated with MAO as co-catalyst [6,7]. Another one involves the use of a mixture of a Ziegler-Natta catalyst (Z-N catalyst) and a metallocene [8–11]. Recently, the combination of early-late transition metal catalyst as a method to broaden the MWD in PE was reported [12]. In all cases, the strategy consisted of modifying the catalyst and co-catalyst charge to the reactor. The generation of two catalytic sites, which have different kinetic responses, such as different propagation and termination rate constants for ethylene polymerization, was assumed to be responsible for the MWD broadening.

More recently, we reported the use of INPETUS[®], a Z-N catalyst, with different metallocenes activated only with MAO [13]. The study showed that the catalyst system works without addition of an extra

activator and hydrogen. Thus, different MWD were obtained; in particular a bimodal one was observed by using CpZrCl₃ as a metallocene. As an extension of our previous work, the results of ethylene polymerization by using a blend of INPETUS[®] with different half metallocenes and its tris(pyrazolyl)borate analogue complexes (Fig. 1) are reported. Also, 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 a solvent was dried over sodium and deoxygenated prior to use. The INPETUS[®], TpTiCl₃ and Tp*TiCl₃ catalysts were prepared according to the published procedure [14–16]. CpTiCl₃, Cp*MCl₃ (Ti, Hf) and IndZrCl₃ (STREM) were used as received. MAO (12.2 wt.% Al, Akzo Nobel, USA) was used as a co-catalyst. 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 M_w and MWD were determined by means of gel permeation chromatography (GPC)

(Waters 150-CV) with *o*-dichlorobenzene stabilized with 0.25 g/l of Irganox 1076 as a solvent at 135 °C. 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 were introduced under argon atmosphere at 70 °C; then, the mixture of INPETUS[®] (1.5×10^{-5} mol Ti) with metal complexes (1.7×10^{-5} mol metal) and MAO (1.7×10^{-2} mol Al) as co-catalyst was added. The reaction started by the admission of 5 atm of ethylene at 80 °C under stirring (600 rpm). After 1 h, the reaction was quenched with ethanol (2 ml), ethylene excess was vented, and the resulting polymer was stirred with a hydrochloric acid/water/ethanol mixture (5/85/10), neutralized with NaHCO₃ solution and finally vacuum dried at 60 °C.

3. Results and discussion

As previously reported, the blending of INPETUS[®] and metallocenes activated only with MAO produced PE with a bimodal distribution when CpZrCl₃ was employed [13]. Our curiosity prompted us to study further the geometric and electronic properties of half-sandwich or scorpionate complexes to find any correlation between the metallocene structure and their influence on the MWD of the PE. Also, there exists interest in finding out if other complexes like poly(pyrazolyl)borates, which are isolobal with the Cp ligand [17,18], may contribute to increase MWD

when they are used as a blend with INPETUS[®] in the same way that metallocene does.

First, all metal complexes were tested for ethylene polymerization without INPETUS[®] in order to determine their catalytic activity performance and to know their MWD profile before the blend condition. The results obtained are summarized in Table 1.

As shown in Table 1, the metallocene complexes in all cases were more active than the Tps analogue under the polymerization conditions. Regarding the MWD, all values were narrow characteristic of a common SSC [7,19]. Moreover, for the Tps complexes, the MWD was not determined, however the literature reports that those complexes produce PE with broad MWD under mild reaction conditions [20]. In the case of INPETUS[®], its MWD was slightly broad as expected for a improved Z-N catalyst.

Once the behavior of each complexes was obtained, a number of experiments were carried out with mixtures of INPETUS[®] and half metallocenes such as CpTiCl₃ (1), Cp*TiCl₃ (2), Cp*HfCl₃ (3), IndZrCl₃ (4) or with tris(pyrazolyl)borate complexes like TpTiCl₃ (5) and Tp*TiCl₃ (6) in a ratio INPETUS[®]/metal complexes close to 1. The experimental results are shown in Table 2.

With the exceptions of IndZrCl₃ and Cp*TiCl₃, in general, catalytic blends reported in the Table 2 showed higher activities than the complexes (Table 1) used in the present work. Particularly, the INPETUS[®]/Cp*TiCl₃ catalyst system (2) showed more than twice the activity in comparison with its normal Cp catalyst system (1) (entry 2 versus 1). In the case of the Cp* ligand substitution by an indenyl ligand, the activity of the resulting catalytic system

Table 1
Ethylene polymerization initiated by INPETUS[®] and complexes 1–6 activated with MAO^a

Entry	Complexes	Activity (kg PE/mol Mh)	M_w (10^4)	M_w/M_n	T_m (°C)	T_c (°C)
7	INPETUS [®]	300	26	3.3	140.4	117.7
8	CpTiCl ₃ (1)	180	30	2.1	144.2	116.9
9	Cp*TiCl ₃ (2)	150	4.6	2.2	136.2	116.1
10	Cp*HfCl ₃ (3)	190	7.6	2.3	137.2	116.4
11	IndZrCl ₃ (4)	290	3.9	2.3	133.4	116.0
12	TpTiCl ₃ (5)	20	4.5 ^b		134.8	117.6
13	Tp*TiCl ₃ (6)	24	6.8 ^b		132.3	116.4

^a Conditions: [Al]/[M] = 1000, $T = 80$ °C, $P = 5$ atm, $t = 1$ h.

^b M_v .

Table 2

Ethylene polymerization initiated by a blend of INPETUS[®] and complexes 1–6 activated with MAO^a

Entry	Complexes/INPETUS [®]	Activity (kg PE/mol Mh)	M_w (10^4)	M_w/M_n	T_m (°C)	T_c (°C)
1	CpTiCl ₃ (1)	108	28	4.2	136.6	116.8
2	Cp*TiCl ₃ (2)	290	42	2.9	137.7	114.5
3	Cp*HfCl ₃ (3)	300	16	2.0	139.1	120.6
4	IndZrCl ₃ (4)	205	10	2.4	136.2	117.8
5	TpTiCl ₃ (5)	74	21	4.1	136.7	119.4
6	Tp*TiCl ₃ (6)	70	35	4.7	135.4	118.2

^a Conditions: [Al]/[Ti] = 1130, [Al]/[M] = 1000, $T = 80$ °C, $P = 5$ atm, $t = 1$ h.

(**4**) moderately decreases (entries 2, 3 versus 4). Furthermore, when the cyclopentadienyls were replaced by stronger electron-donors and more sterically hindered analogues, such as tris(pyrazolyl)borates, the activity of both catalytic systems (**5**) and (**6**) dramatically decreases; more marked in the case of the Tp* ligand (Table 2, entry 2 versus 6).

The results suggest that the presence of the methyl groups in each kind of ligand may operate in different ways during blending with the Z-N catalyst. In one case, for instance, in the Cp ring, methyl groups will produce better active species for INPETUS[®]/metallocene systems during polymerization; in consequence, a good catalytic activity is observed. On the other hand, for the Tp ligand, the presence of methyl groups in the pyrazolyl rings does not contribute to the activity of the resulting catalytic system (Table 2, entry 2 versus 6) as the Cp* ligand does. The results above point out that apart from the fact that the Tp ligand is isolobal with the Cp, our results showed that different interactions between the Z-N and those complexes are operating. This fact means considerable consequences in the activity of the resulting systems. Thus, the catalytic tendencies observed can be considered as a result of the synergistic effect of the active species of the complex, formed in the middle of the reaction, and the heterogeneous Z-N catalyst active sites.

The fact that the tris(pyrazolyl)borates cause a drop in the activity of the resulted blend can be modified probably by using a milder reaction conditions, for example, a low reaction temperature. The Tp complexes are known because they have better activities in the ethylene polymerization at temperatures below 80 °C [20,21]. However, for the purpose of this work, in

order to compare these complexes with the metallocenes and employ the industrial polymerization conditions used by INPETUS[®] [13] we decided not to carry out polymerization reactions at low temperatures.

Another interesting fact is shown in Table 2, when nature of the metal is studied. When the titanium complex (**1**) is compared with the analogous zirconium complex, CpZrCl₃ (activity = 427 kg PE/mol Zr h; under the same conditions [13]), a dramatic activity reduction is observed (entry 1). However, it was moderate when the titanium center is combined with Cp* ligand (entry 2). Furthermore, when the titanium metal center was changed by hafnium (**3**) (entry 2 versus 3), the catalytic activity of the blends was almost the same. The above results suggest that the types of complexes and the metal centers have a strong influence on the activity of the resulting catalytic blend system.

The analysis of the polydispersity of the polymers obtained with the mixture of INPETUS[®] with half metallocenes displayed in Table 2 showed that they were slightly influenced by the type of metallocene used. For systems comprising metallocenes (**2**), (**3**) and (**4**), the resulting MWDs were narrow, which is characteristic of polymers obtained by means of single site catalysts (SSC) [7,19]. For the catalytic systems (**1**), (**5**) and (**6**), the MWDs obtained were slightly broader.

These results showed that the mixture of a Z-N (INPETUS[®]) and metallocenes or tris(pyrazolyl) borate complexes (entries 1–6) did not produce that MWD as was previously obtained with INPETUS[®]/CpZrCl₃ catalyst system under the same conditions [13]. The result hints that the ligands bonded to the metal center play an important role because they can modify the kinetic responses of the active species.

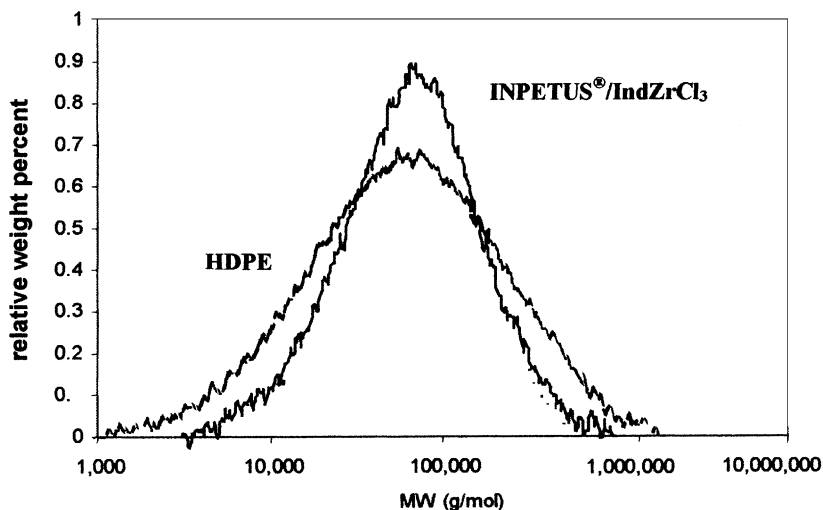


Fig. 2. MWD profile of the PE obtained from INPETUS[®]/IndZrCl₃ vs. HDPE obtained from a Z-N catalyst and hydrogen at bench scale.

Also, it confirms that in order to obtain bimodal MWD it is necessary to combine two different metal centers, for example, zirconium (CpZrCl₃) and titanium (INPETUS[®]) whose kinetic responses are modulated by the ligands around Cp.

Different commercial PE grades can be achieved by means of the addition of hydrogen to the industrial reactor. In any catalytic system used in this work hy-

drogen was used in order to modify Mw and MWD. However, the analysis of the GPC obtained by the blend of INPETUS[®] and the IndZrCl₃ complex (4) produced an interesting result.

The MWD profile (Fig. 2) of the polymer obtained with this catalytic system is very close to the MWD profile of a PE class produced by a common Z-N catalyst and hydrogen addition at pilot plant scale. Also,

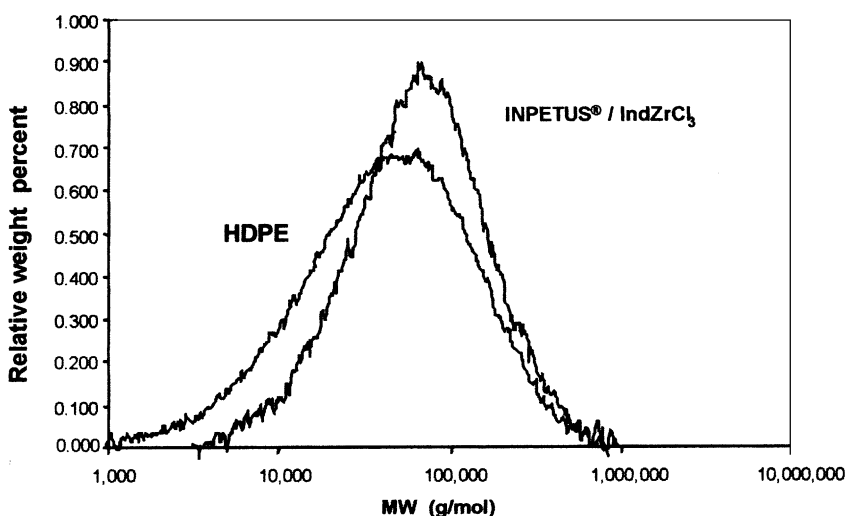


Fig. 3. MWD of the PE obtained with the blend of INPETUS[®]/IndZrCl₃ vs. HDPE obtained from an industrial scale process.

the MWD of polymer obtained is very similar to a class of PE produced by industrial plants, using a common Z-N catalyst under severe reaction conditions (200 °C, 600 psig). Fig. 3 displays the resulting MWD profiles.

The above results suggest that the blend of INPETUS[®]/half metallocene can be used to tune the MWD for the production of a different degree of polymer and to simulate the production of polymers obtained from industrial plants under more severe reaction conditions.

Finally the melting (T_m) and crystallinity (T_c) temperatures of PEs prepared with the blends of INPETUS[®]/complexes 1–6 were independent of the catalytic system and the values (Table 2) are characteristic for high-density polyethylene (HDPE) [22].

4. Conclusions

The blends of INPETUS[®] with different half metallocene or tris(pyrazolyl)borate complexes activated with MAO can polymerize ethylene in a single reactor, without any extra activator and in the absence of hydrogen, with moderate activity. The nature of the metallocene and metal center has an effect on the activity of the catalytic system. The MWD of the PE obtained is slightly affected by the type of metallocene or tris(pyrazolyl)borate complexes used. The INPETUS[®]/IndZrCl₃ catalytic system shows that is possible to use this type of strategy for the production of different degree of PEs for industrial application.

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References

- [1] L.A. Utracki, *Polymer Alloys and Blends*, Hanser, Munich, 1989.
- [2] J.P. Thiersault, D.M. Rondelez, *PRI Polyethylene—The 1990s and Beyond*, London, May 1992.
- [3] P.M. Stricklen, Phillip Petroleum Co., US Patent 4939217, (1990) [3a] Chem. Abstr. 113 (1990) 116088 r.
- [4] P.M. Stricklen, Phillip Petroleum Co., US Patent 5064797, (1991).
- [5] F.Y. Lo, T.E. Nowlin, P.P. Shirodkar, Mobil Oil Corporation, US Patent 5032562, (1991), Chem. Abstr. 115 (1991) 160025h.
- [6] J.A. Ewen, H.C. Welborn Jr, Exxon Research and Engineering Co., Eur. Patent EP 0128045, (1984), US Patent US 4,530,914, (1985).
- [7] A. Ahlers, W. Kaminsky, *Makromol. Chem. Rapid Commun.* 9 (1988) 457.
- [8] W.M. Coleman, G.F. Schmidt, R.E. Campbell Jr., M.S. Delaney, The Dow Chemical Co., US Patent 4,659,685, (1987).
- [9] T.M. Pettijohn, Phillips Petroleum Co., US Patent 5,182,244, (1993).
- [10] H.C. Welborn Jr., Exxon Chemical Patents Inc., US Patent 4,701,432, (1987).
- [11] S. Williams, P.J. Maddox, C. Chabrand, P.S. Hope, in: *Proceedings of the Fourth International Business Forum on Specialty Polyolefins SPO'94*, Houston, Texas, September 1994, pp. 277–286.
- [12] S. Mocking, *Macromol. Rapid Commun.* 20 (1999) 139.
- [13] F. López-Linares, A. Díaz, H. Ortega, J. Matos, P. Joskowicz, G. Agrifoglio, *J. Mol. Catal.* 159 (2000) 269.
- [14] A. Díaz, J. Liscano, M. Trujillo, G. Agrifoglio, J. Matos, INTEVEP, S.A., US Patent 5,767,034, (1998).
- [15] P. Burchill, M.G.H. Wallbridge, *Inorg. Nucl. Chem. Lett.* 12 (1976) 93.
- [16] J.K. Kouba, S.S. Wreford, *Inorg. Chem.* 15 (1976) 93.
- [17] S. Trofimenko, *Chem. Rev.* 93 (1993) 943.
- [18] N. Kitajima, W.B. Tolman, *Prog. Inorg. Chem.* 43 (1995) 419.
- [19] W. Kaminsky, *Catal. Today* 20 (1994) 257.
- [20] H. Nakazawa, S. Ikai, K. Imaoka, Y. Kai, T. Yano, *J. Mol. Catal.* 132 (1998) 33.
- [21] A. Karam, M. Jimeno, J. Lezama, E. Catarí, A. Figueroa, B. R. De Gascue, *J. Mol. Catal.* 3254 (2001) 1–8.
- [22] J.G. Fatou, *Handbook of Polyolefins, Synthesis and Properties*, Marcel Dekker, New York, 1993, 235.