High-temperature and high-pressure ethylene polymerization using a cationic activated metallocene catalytic system

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Abstract

BACKGROUND: Normally, olefin polymerization via metallocene-based catalysis occurs under mild conditions. However, most technology developed for polyolefin production is designed for more severe temperature and pressure processes. Attaining more thermally stable metallocene systems for industrial applications is an important challenge for researchers.

RESULTS: A systematic study of ethylene homopolymerization at higher temperatures and pressures, employing the ternary system $Ph_2C(Cp)(Flu)ZrCl_2/PhNHMe_2B(C_6F_5)_4/(i-Bu)_3Al$, is presented The optimal activity for this system is achieved with a Zr/B/Al molar ratio of 1/6/250 and a temperatures of around 130 °C. However, the amount of activator strongly affects the molecular weight and the polydispersity of the polymers produced. Polyethylene produced with Zr/B/Al molar ratios between 1/2/250 and 1/6/250 show no significant difference in their temperature of fusion (T_m) and their crystallinity (X_c). In contrast, in the presence of activator amounts higher than 1/6/250, both the temperature of fusion and polymer crystallinity undergo a steep decrease. All polymers presented lamellar morphology when the activator was present, and an amorphous aspect when the activator was not employed.

CONCLUSION: The presence of the activator is essential for thermal stabilization of the catalytic system. Variation of the Zr/B/Al ratio leads to modifications of the catalytic activity as well as to the properties of the polymers synthesized.
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Keywords: polyolefins; metallocene; homogeneous catalysis; high-temperature olefin polymerization; high-pressure olefin polymerization

INTRODUCTION

Over the last 20 years, metallocene-based catalysts for olefin polymerization have been considered as one of the most important scientific and technological developments on polyolefinic materials. Part of this development has been due to the efforts of synthetic organometallic chemists to understand and validate olefin polymerization mechanisms. For this reason, we have now at our disposal quite a few molecular catalytic systems, based on active sites which can exhibit different steric and electronic properties, allowing access to tailor-made polyolefinic materials.[1,2]

In spite of this, there are only a few examples of industrial processes for olefin polymerization founded on metallocene-based technology.[3] They are usually used to supply specific markets.[4,5] In general, olefin polymerization via metallocene catalysts occurs under very mild conditions of temperature, i.e. around 40–80 °C.[6] This statement is frequently mentioned because most metallocene active species are very sensitive to higher reaction temperatures, therefore leading to polymers with shorter chains, and lower polymer yields.[7,8] Indeed, most of the technology developed for polyolefin production is designed for processes which normally apply at more severe temperatures and pressures.[9] In view of this, academic and industrial research groups are interested in developing new catalytic systems based on single-centre catalysts, which can effectively work at higher temperatures and pressures and short residence time.

To achieve tailor-made polyolefins, a series of systematic and catalyst design studies were carried

out. As a result, polymers with high levels of stereo-regularity in the main chain, homogeneous comonomer distribution and controlled molecular weight distribution can be obtained.[1,2] For thermally stable metallocene catalysts, the same strategy must be applied. It is known[10] that precursors must have certain characteristics. (i) The presence of fluorenyl fragments seems to be important to obtain high molecular weight polyolefins. The bulky nature of fluorenyl ligands suppresses β-H elimination, thus resulting in a decrease of the probability of chain-termination reactions occurring. It is important to keep in mind that fluorenyl ligands are more suitable to undergo haptotropic rearrangement and ring-slippage reactions.[11,12] However the isomerization fluorenyl fragments can be hindered via *ansa*-metallocene derivatives. (ii) The presence of phenyl groups at the bridged carbon increases the pentahapto character of the fluorenyl moiety. These observations rationally considered the metallocene complex $Ph_2C(Cp)(Flu)ZrCl_2$ as a good candidate as a catalyst precursor for olefin polymerization at higher temperatures.

Yano and co-workers[13,14] carried out a series of systematic studies on copolymerization of ethylene and α-olefins in order to find out suitable metallocene-based catalytic systems for high-yield production of polyolefins with high molecular weights under severe reaction polymerization conditions. They showed that the ternary system $Ph_2C(Cp)(Flu)ZrCl_2/PhNHMe_2.B(C_6F_5)_4/(i\text{-}Bu)_3Al$ (precatalyst/activator/cocatalyst) is able to produce high molecular weight polyethylene with reasonable yields under high temperatures and pressures (170 °C and 2 MPa). Nevertheless, the activity of this catalytic system is not very high at standard polymerization reaction temperatures for metallocenic systems, i.e. at high temperatures the polymerization behaviour changes.

Dornik and co-workers[15] carried out similar work with a series of metallocene/methylaluminoxane (MAO)-based systems. They observed that the half-lives of these systems are higher than those observed for ternary ones. However, for future industrial applications, ternary systems are much more attractive, since the amount of MAO normally required in the reaction mixture is very high. Thus, to increase knowledge in this area, we present in this paper a systematic study of ethylene homopolymerization at high temperatures and pressures, using the ternary system $Ph_2C(Cp)(Flu)ZrCl_2/PhNHMe_2B(C_6F_5)_4/(i\text{-}Bu)_3Al$. The effects of catalytic activity and properties of the polymers obtained, modifying the molar ratio of Zr/B/Al in the reactor and the temperature of reaction, were evaluated.

EXPERIMENTAL
Materials
All experiments with air-sensitive materials were carried out under argon atmosphere, using standard Schlenk techniques. Toluene and cyclohexane were dried over Na/benzophenone. All solvents were distilled and stored under argon before use. Triisobutylaluminium (TIBA), 4.5 wt% Al in hexane, was commercially obtained from Akzo Nobel (Netherlands) and used as received. The precatalyst $Ph_2C(Cp)(Flu)ZrCl_2$ and the activator $[PhNHMe_2][B(C_6F_5)_4]$ were commercially obtained from Boulder Scientific (Germany) and used without purification.

Polymerization procedure
All reagents were handled under nitrogen atmosphere. Polymerization reactions were carried out in a 300 mL Parr reactor (Parr, USA) equipped with a mechanic stirrer, a Parr thermocouple, pressure-measuring systems and various inlets. The reactor was flushed several times with nitrogen, and filled with cyclohexane (70 mL). The mechanic stirrer was set at 650 rpm, the temperature was adjusted to the desired value and the reactor was pressurized with ethylene at 2 MPa. The solutions of the catalyst components were prepared in a way to ensure that the total amount for each solution was 10 mL. The solutions of TIBA, metallocene and borate were prepared using cyclohexane and added, in this order, through a syringe-type pump. The polymerization was started after adding all catalyst components. Ethylene was continuously supplied from a storage vessel to maintain the pressure constant. The reactor was depressurized, and the polymerization reaction was quenched by adding ethanol. The synthesized polymers were washed with ethanol and dried under reduced pressure at 50 °C until constant weight.

Characterization of the polymers
SEM analysis
The surface morphology of the polymeric samples was investigated using an SS-550 scanning electron microscope from Shimadzu (Japan). The samples were coated with gold (20 nm), using an IC-50 metallizor from Shimadzu.

DSC analysis
The values of melting points (T_m) of all polymers were determined using a model TA-50 differential scanning calorimeter from Shimadzu (Japan), applying a heating rate of 10 °C min^{-1}, from 40 to 200 °C, under nitrogen atmosphere (50 mL min^{-1}). The degree of crystallinity determined from the fusion enthalpy of the polymers obtained was based on the melting heat of 100% crystalline polyethylene ($X_c = 290$ kJ g^{-1}).[16]

SEC analysis
The values of the weight-average molecular weight (M_w) and M_w/M_n were determined using a model

PL-GPC 200 SEC instrument from Polymers Laboratories (USA), operating at $130\,^{\circ}C$, equipped with a refractive index detector, and three PLGel MIXED columns of 5, 10 and $20\,\mu m$, with a limit of 1.0×10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, employing a flow rate of $1.0\,mL\,min^{-1}$.

RESULTS AND DISCUSSION
Catalytic activity
The ternary system, based on $Ph_2C(Cp)(Flu)ZrCl_2$, TIBA and $[PhNHMe_2][B(C_6F_5)_4]$, was employed to catalyse ethylene polymerization under high-pressure and high-temperature conditions. The system was evaluated in terms of reactivity, using different Zr/B/Al molar ratios and temperatures, as well as some of the physicochemical properties of the polymers obtained.

The most relevant results are displayed in Table 1. The effects of the activator amount on the catalytic activity are summarized in Fig. 1. The data were evaluated from tests performed at a polymerization temperature of $150\,^{\circ}C$, with Zr and Al concentrations of 87×10^{-3} and $22\,mmol\,L^{-1}$, respectively. The results indicate that optimal activity is achieved with a Zr/B/Al molar ration of 1/6/250. Lower activator amounts do not really affect the catalytic activity under these reaction conditions; however, their presence is fundamental to ascertain significant polymer productivity, as seen in entry 1 of Table 1. It is known[14] that counterions like $B(C_6F_5)_4^-$ promote higher thermostability of metallocene cationic active species. Nevertheless, a higher amount of activator reduces the catalytic activity. This can be related to the formation of a critical concentration of free amine in the reaction medium, leading to deactivation of the catalyst via coordination at the active species locus.

Another remark is related to the increment of the cocatalyst (TIBA) concentration (see entries 2 and 6 in Table 1). It was verified that the catalytic activity was not notably changed when the amount of cocatalyst was altered in this range. This suggests that when the amount of TIBA is high enough to alkylate and clean up the reaction medium, the catalytic activity is not
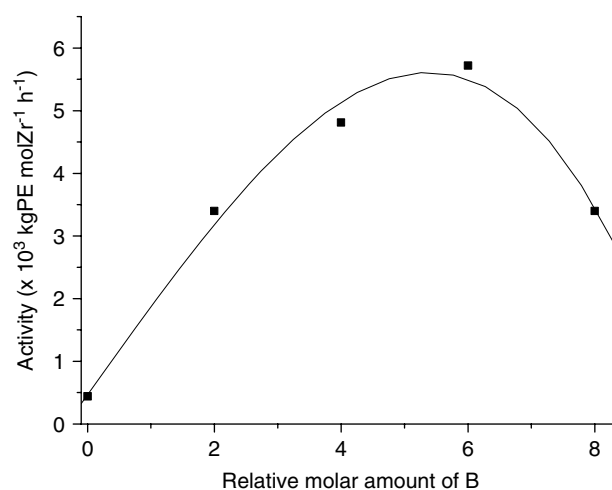

Figure 1. Effect of activator concentration on the catalytic activity at Zr/B/Al molar ratio of 1/B/250 (entries 1–5 in Table 1).

significantly modified. However, it was reported, for a related system, that for very high Al concentrations the productivity decreases.[17] This is a very positive feature of this catalytic system when compared with its analogous one, activated in the presence of MAO, which normally requires higher ratio of Al/Zr.[18]

The influence of the polymerization temperature on the ethylene polymerization yield is remarkable. Akimoto and Yano[13] demonstrated that the ternary system consisting of $Ph_2C(Cp)(Flu)ZrCl_2$, $PhNHMe_2 \cdot B(C_6F_5)_4$ and $(i\text{-}Bu)_3Al$ studied here displays very low activity at reaction temperatures between 40 and $80\,^{\circ}C$. This temperature range is normally employed with metallocene-based catalysis.[19] They also show that at higher temperatures this catalytic system is more active.[20] In fact, we carried out polymerization tests at temperatures between 130 and $170\,^{\circ}C$, for short periods of time (5 min). We observed lower polymer productivity at reaction temperatures higher than $130\,^{\circ}C$, as seen in Table 1 (entries 4, 7 and 8) and Fig. 2. This feature is probably due to the thermodynamic and kinetic instability of the system under these extreme reaction conditions. However, reaction temperatures around $130\,^{\circ}C$ allow for high

Table 1. Ethylene homopolymerization with $Ph_2(Cp)(Flu)ZrCl_2$-based catalyst at high temperature/high pressure[a]

Entry	Zr/B/Al[b]	Temperature[c] ($^{\circ}C$)	Activity ($\times 10^3\,kgPE\,mol\,Zr^{-1}\,h^{-1}$)	M_w ($\times 10^3\,g\,mol^{-1}$)	M_w/M_n	T_m ($^{\circ}C$)	X_c (%)
1	1/0/250	150	0.44	–	–	131	31
2	1/2/250	150	3.40	54.5	4.0	129	66
3	1/4/250	150	4.61	17.1	2.9	129	67
4	1/6/250	150	5.72	22.0	3.2	128	60
5	1/8/250	150	3.40	9.5	2.1	122	19
6	1/2/500	150	3.86	92.7	12	128	79
7	1/6/250	170	1.14	58.5	35	125	39
8	1/6/250	130	13.2	12.0	2.9	130	62
9	1/6/250	100	11.7				

[a] Polymerization conditions: pressure of 2 MPa; 5 min reaction time; 5.6 mg of catalyst.
[b] Molar ratio.
[c] Temperature of the polymerization reaction. In all reactions the reaction temperature increased by up to $5 \pm 2\,^{\circ}C$.
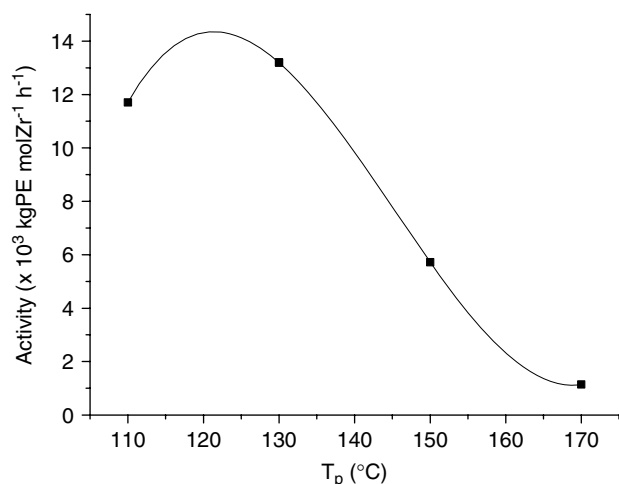
Figure 2. Polymerization temperature effects on catalytic activity (entries 4, 7–9 in Table 1).
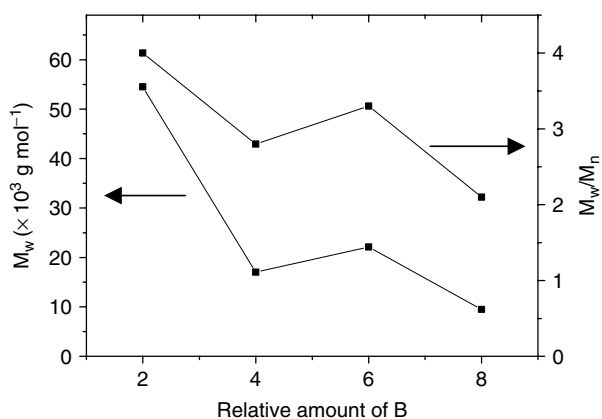

Figure 3. Influence of the relative amount of activator on M_w and M_w/M_n of polyethylene (entries 2–5 in Table 1).

Figure 4. Influence of the relative amount of activator in the reaction medium on T_m and X_c of polyethylene (entries 2–5 in Table 1).

rates of polymerization with reasonable lifetime of the active species.[6,21]

Properties of the synthesized polymers

The molecular weights and polydispersities of the polymers obtained are influenced by the boron ratio used. As shown in Fig. 3, polyethylene produced with the lowest ratio of activator (Zr/B/Al = 1/2/250) has M_w of 54 500 g mol^{-1}. However, increasing the activator amount in the reactor induces a decreasing trend of M_w of the polyethylene. The same tendency is verified in relation to the polydispersity of the polymers, i.e. as the amount of activator increases, a decrease of the M_w/M_n ratio is observed, as depicted in Fig. 3. The decrease of the polydispersity when the amount of activator increases can be explained by the fact that higher amounts of activator in the reaction medium provide fewer conditions to achieve other active species in equilibrium, which leads to the formation of polymer chains with different molecular weights.[22] Here it is important to remark that active species for olefin polymerization are formed even without the presence of activator.[23] The molecular weight is also affected by the content of activator in
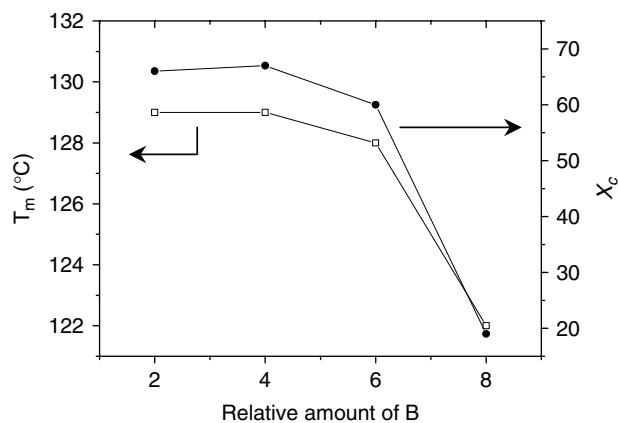
the reaction medium. However, the explanation of this effect requires further investigations, but we suggest that the borate can act as a chain transfer agent, reducing M_w.[14,24]

The temperature of fusion and crystallinity of the polymers obtained were also evaluated in terms of the amount of activator in the reactor. As depicted in Fig. 4, polyethylene samples produced with Zr/B/Al molar ratios between 1/2/250 and 1/6/250 show no significant difference in T_m and X_c, remaining nearly constant with values around 129 °C and 64%, respectively. However, in the presence of an activator amount higher than 1/6/250, both temperature of fusion and polymer crystallinity undergo a steep decrease. With a molar ratio of Zr/B/Al = 1/8/250, T_m and X_c decrease to 122 °C and 19%, respectively.

Another focus of this work was to investigate the morphological characteristics of the polymers obtained just after their isolation by quenching the polymerization. The morphology of the polymers was thus characterized using SEM analysis. A strong effect was observed in the morphology of the polymer due to the presence of the activator. All polymers presented a lamellar morphology when the activator was present, independently of its amount in the reaction medium. However, an amorphous polymer was obtained when the activator was not employed (Fig. 5(B)). Indeed, this observation corroborates the polymer properties discussed above. The crystallinity of the polymer obtained without the presence of activator is very low (Table 1, entry 1).

The same tendency is observed when one compares polymers obtained under the same conditions but at different reaction temperatures, namely 150 and 170 °C. It was verified that the morphological aspect of the polymers obtained at higher temperature are more amorphous (Fig. 6(B)).

CONCLUSIONS

The ternary catalytic system Ph$_2$C(Cp)(Flu)ZrCl$_2$/PhNMe$_2$HB(C$_6$F$_5$)$_4$/(i-Bu)$_3$Al is very active for ethylene homopolymerization under high temperatures
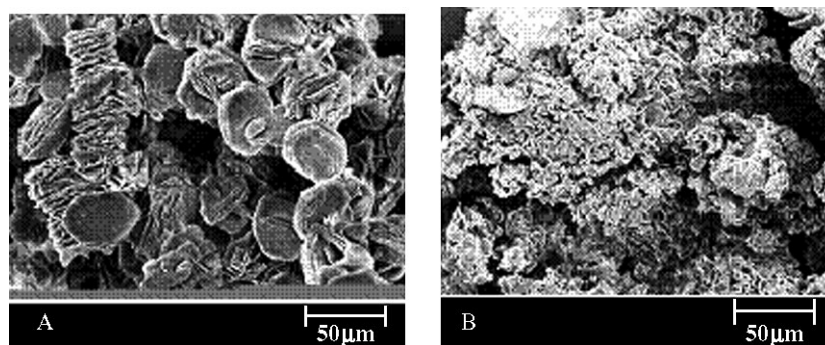
Figure 5. SEM micrographs (×300) of polymers obtained at Zr/B/Al molar ratios equal to (A) 1/6/250 and (B) 1/0/250 (entries 4 and 5 in Table 1, respectively).

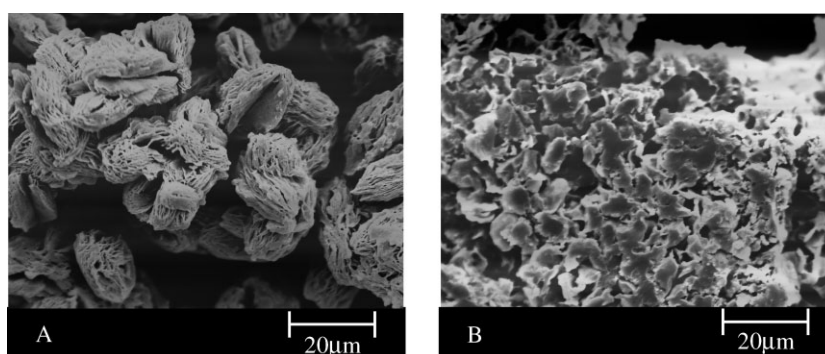**Figure 6.** SEM micrographs (×600) of polymers obtained at temperatures of (A) 130 °C and (B) 170 °C (entries 8 and 7 in Table 1, respectively).

and pressures. The presence of the activator is essential for thermal stabilization of the catalytic system. Variation at the Zr/B/Al ratio leads to modification of the activity of the system as well as of the properties of the polymers synthesized. Morphological analysis of the polymers obtained just after their isolation (quenching the polymerization reactions) can be a qualitative parameter to evaluate the crystallinity of the polymers obtained.

ACKNOWLEDGEMENTS

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