JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Propylene–ethylene copolymers by one-monomer metallocene catalyzed polymerization

Marcos L. Dias [a,*], Daniela E.B. Lopes [a], Andrei V. Grafov [b,1]

[a] *Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro,*
CP 68525, 21945-970 Rio de Janeiro, RJ, Brazil
[b] *V.I. Vernadskii Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine,*
Prospekt Palladina 32/34, UA-03142 Kiev, Ukraine

Abstract

Propylene polymerization with $Ind_2Zr(OFl)Cl$, where Ind = indenyl and OFl = deprotonized moiety of fenchyl alcohol (1,3,3-trimethyl bicyclo[2.2.1]heptan-2-ol) was investigated. The catalyst is capable to polymerize the monomer producing elastomeric propylene–ethylene copolymers containing blocks of ethylene units and atactic propylene sequences. The amount of ethylene units is controlled by the reaction conditions and up to 35.4 mol% ethylene could be obtained. The copolymers with high ethylene sequences content crystallizes resulting in melting transitions in the range of 120 °C. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Propylene; Copolymer; Metallocene; σ-Ligand; 1,3-Insertion

1. Introduction

In the last 15 years, the research activities in the field of olefin polymerization has been directed towards metallocene catalysts [1–4]. Although the search on new metallocene catalysts has mainly been focused on changes within η^5-bonded aromatic rings [5,6], a substitution of the chloro-ligands for other σ-bonded groups at the central metal represents another interesting approach which can result in catalysts either with better performance or capable to produce polymers with new microstructures.

Earlier, some examples of the influence of the σ-ligand in metallocene core on the performance of the catalyst were reported [7–12]. First, the differences in polymerization rate were shown comparing the behaviour of dimethylzirconocene and zirconocene dichloride [7]. The substitution of chloro-ligands by alcoholato-moieties also had a positive influence in the case of styrene polymerization with half-metallocenes activated by methylaluminoxane (MAO). For instance, when $CpTiCl_2(OR)$/MAO (R = Me, Et, iPr) was used as the catalytic system, an increase was observed both in the catalyst's activity and in the syndiospecificity, when compared with the trichloride analogue [8,9]. Another example is the zirconocene binaphtholate that produces a significant fraction of non-cycled units in cyclopolymerization of 1,5-hexadiene [10,11]. Finally, fluorinated half-sandwich complexes were reported to be more active than the chloro-analogues

* Corresponding author. Tel.: +55-21-2562-7221;
fax: +55-21-2270-1317.
E-mail addresses: mldias@ima.ufrj.br (M.L. Dias),
a_grafov@ionc.kar.net (A.V. Grafov).
[1] Tel.: +380-44-444-3270; fax: +380-44-444-3070.

[12]. However, until now electronic and steric effects arising from the η^5-ligand system are considered to be the main factors influencing the performance of the catalyst, while the influence of different σ-ligands on monomer co-ordination, the rate of chain propagation and chain termination reactions was still underestimated.

From this point of view, group 4 metallocene complexes with sterically hindered σ-bonded ligands represent a particular interest. In recent years, series of such metallocene alcoholates containing bridged alicyclic moieties (bicyclo[3.1.1]heptane, bicyclo[2.2.1]heptane or adamantane) were synthesized and characterized comprehensively [13–16]. Previously, we have shown that the presence of voluminous σ-bonded ligand(s) in the molecule of the co-ordination compound, as well as peculiar structure of the ligand possessing indifferent sterically hindered hydrocarbon periphery, influence the performance of the catalyst in homogeneous metallocene-MAO system and characteristics of the obtained polymers [17–19]. Independently, Benetollo et al. [20] also arrived to support similar conclusions.

2. Experimental

2.1. Materials

Polymerization grade propylene was kindly donated by Polibrasil and purified by passing through columns of molecular sieves 3 Å. Indene, pentane, THF, toluene and benzene were purified according to conventional procedures. MAO (30 wt.% toluene solution) kindly supplied by Witco, butyllithium and fenchyl alcohol (1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol) (Aldrich) were used without further purification. Nitrogen and argon were used after passing through columns with molecular sieves 3 Å and copper catalyst.

2.2. Synthesis of chloro-fencholato-bis(indenyl)-zirconium

All manipulations with air-sensitive materials were carried out using glove-box and Schlenk techniques. Ind_2ZrCl_2 was synthesized according to [21]

and identified spectroscopically. The synthesis of mixed-ligand bis(indenyl)-zirconium derivative was realized by a modification of our previously described procedure [13,14], applying an inverse addition order of the reagents. A stoichiometric quantity of lithium fencholate solution in benzene/THF 3:1 solvent mixture was added dropwise to a suspension of the metallocene dichloride. The monoalcoholate of bis(indenyl)-zirconium chloride was isolated and purified by our previously described procedures [14] using benzene as the solvent. The $Ind_2Zr(OFl)Cl$ complex was obtained as almost white powder (Yield: 55.4%; Zr content: calculated 17.88%, found 17.12%), its structure was confirmed by FT-IR, ^1H and ^{13}C NMR-spectroscopies.

2.3. Polymerization

Propylene polymerizations were performed in a 250 ml glass reactor equipped with mechanical stirrer (Büchi). Toluene (100 ml) and a prescribed amount of MAO were injected to the reactor under nitrogen atmosphere. Subsequently, the monomer was fed and a toluene solution containing a specified amount of the metallocene was added. Then, the monomer was continuously fed to maintain a constant polymerization pressure (0.01–3 bar) for 1 h at the reaction temperature. The polymerization was terminated by adding a dilute solution of hydrochloric acid in methanol. The polymer was washed with a plenty of methanol and vacuum dried.

2.4. Polymer characterization

Molecular weights and polydispersity indices were determined by gel permeation chromatography (GPC) using a Waters 150 CV instrument at 135 °C, 1,2,4-trichlorobenzene as eluent and a calibration curve prepared with monodisperse polystyrene standards. ^{13}C NMR measurements were carried out on Varian Mercury 300 instrument. The copolymers were dissolved in dichlorobenzene/benzene-D_6 = 9/1 and quantitatively analyzed at 80 °C. Ethylene content in the copolymer was determined according to [22]. Differential scanning calorimetry (DSC) measurements were made on Perkin-Elmer DSC-7 instrument applying a heating rate of 10 °C/min.
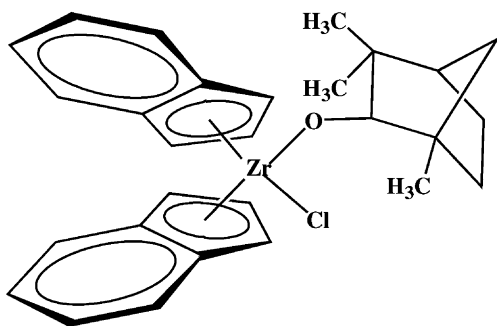
Fig. 1. Molecular structure of Ind$_2$Zr(OFl)Cl.

3. Results and discussion

In this communication, we report another interesting effect arising from application of metallocenes with sterically hindered σ-ligands to propylene polymerization. It is a well-known fact that catalytic system based on dichloride of bis-(indenyl)-zirconium and MAO polymerizes propylene producing atactic polymer [23]. Unexpectedly, new non-bridged monochloro-fencholato-bis-(indenyl)-zirconium gave rise to propylene–ethylene copolymers by one-monomer polymerization process.

The complex in question of the formula Ind$_2$Zr-(OFl)Cl (where Ind = indenyl; OFl = OC$_{10}$H$_{17}$—a deprotonated moiety of fenchyl alcohol) has a geometry shown in the Fig. 1.

Propylene polymerizations were carried out in toluene at 0.01 and 3 bar with the above organozirconium compound activated by MAO using 5 μmol of the complex and Al/Zr ratio = 2000. Table 1 shows the results obtained by 1 h polymerizations at temperatures between 0 and 25 °C. Data obtained with the initial non-bridged bis-(indenyl)-zirconium

dichloride (Ind$_2$ZrCl$_2$) and with ansa-zirconocene: ethylene-bis(indenyl)-zirconium dichloride (EtInd$_2$ss ZrCl$_2$) are also presented in the Table 1 for comparison.

Bridged and non-bridged bis-(indenyl)-zirconium dichlorides were more active with respect to mono-alcoholate compound. Nevertheless, the latter showed a completely different behaviour as propylene polymerization catalyst. During the reaction with the mono-alcoholato complex, the polymerization medium was homogeneous, indicating complete solubility of the formed polymer, as expected. After precipitation, the polymers revealed a rubber-like appearance. The solid rubber-like polymer obtained at 0 °C was completely transparent, while those synthesized at 20 and 25 °C showed white heterogeneities, suggesting a presence of domains with different morphology.

The activity of the catalyst decreased 10 times with the decrease of the polymerization temperature from 20 to 0 °C. Curiously, the heating curve of the DSC analysis showed a transition associated with melting of crystalline domains at 100–120 °C for the polymers prepared at temperatures near 20 °C. A corresponding crystallization peak was observed at 80 °C on the cooling curve. The sample prepared at 0 °C did not show any similar behaviour.

^{13}C NMR spectra of the polymers obtained at 0 and 20 °C (at 3 bar) are shown in Figs. 2 and 3. In addition to characteristic ^{13}C resonances of polypropylene (methyl carbons at 20.0–22.5 ppm, methyne carbons at 28.0–29.5 ppm and methylene carbons at 45.5–48.5 ppm), typical signals of longer methylene sequences at 30.0–31.5 ppm, as well as those of branched polyethylenes at 38–40, 33.5–35.5 ppm, 27.5–28.0 and 24.5–25.5 ppm are present in both spectra. These resonances clearly indicate a formation of

Table 1
Propylene polymerization with indenyl-zirconocenes

Catalyst	P (bar)	T_p (°C)	Activity (kgPol/molZr h)	M_w	M_w/M_n	T_m (°C)	Ethylene (mol%)	PP type
Et(Ind)$_2$ZrCl$_2$	0.01	25	3080	32800	2.0	133	–	Isotactic
Ind$_2$ZrCl$_2$	0.01	25	334	12100	2.0	–	–	Atactic
	0.01	25	6	310000	2.9	127	–	Atactic
Ind$_2$Zr(OFl)Cl	3	0	70	108000	2.4	–	7.0	Atactic
	3	20	700	170000	3.9	116	35.4	Atactic

Conditions: reaction time, 1h; Al/Zr ratio, 2000; catalyst concentration, 5×10^{-5} M; solvent volume, 100 ml.
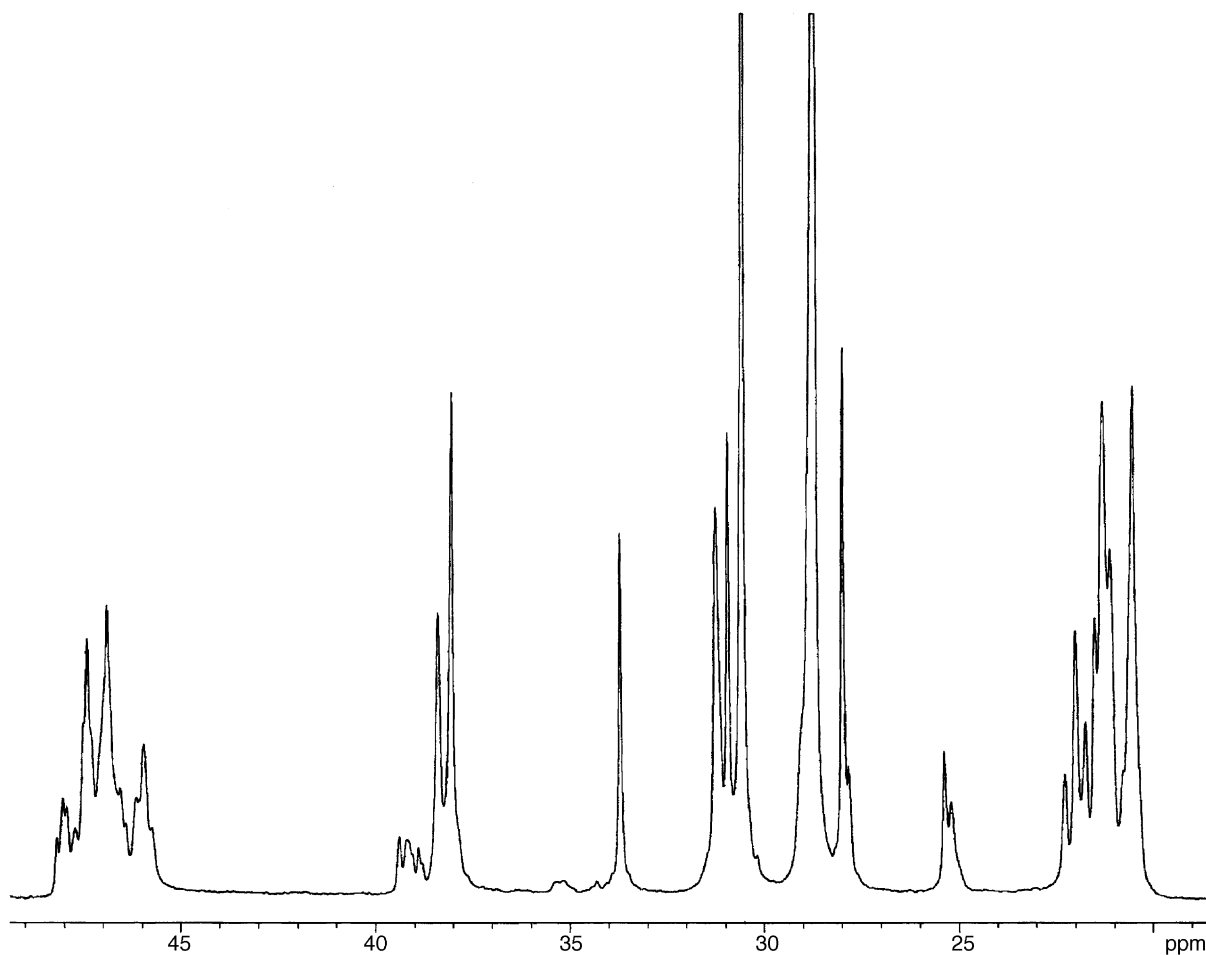
Fig. 2. ^{13}C NMR spectrum of the propylene polymer obtained with Ind$_2$Zr(OFl)Cl/MAO at 20 °C.

propylene–ethylene copolymer [22] from propylene used as a single monomer. Integration of the above resonances gave a result of 35.4 mol% of ethylene units that could be considered as very high. Thus, we report here the first obtaining of propylene–ethylene copolymer with so high content of ethylene units generated by a single-monomer propylene polymerization.

We would like to point out a possibility to control the amount of ethylene, and consequently, the copolymer properties by the polymerization conditions, such as temperature, pressure and monomer concentration. Only 7 mol% ethylene are present in the copolymer obtained at 0 °C, while high ethylene unit content was attained at 20 °C.

The anomalous presence of ethylene sequences in a polymer derived from propylene polymerization can be only explained by occurrence of 1,3-insertion [24,25]. This type of insertion was first reported for the polymerization of propylene with Pd(CN)$_2$ [26]. According to Busico et al. [27], propylene isotactic polymerization with group 4 metallocenes of C$_2$-symmetry generates stereoregular polymers typically containing up to 1.5 mol% of regioirregularities including 2,1-inserted units. This amount of regioirregularities is rather high with respect to those produced with a majority of heterogeneous catalysts, i.e. below 0.1 mol%. The content of 1,3-insertion and relative proportion regarding to 2,1-insertion
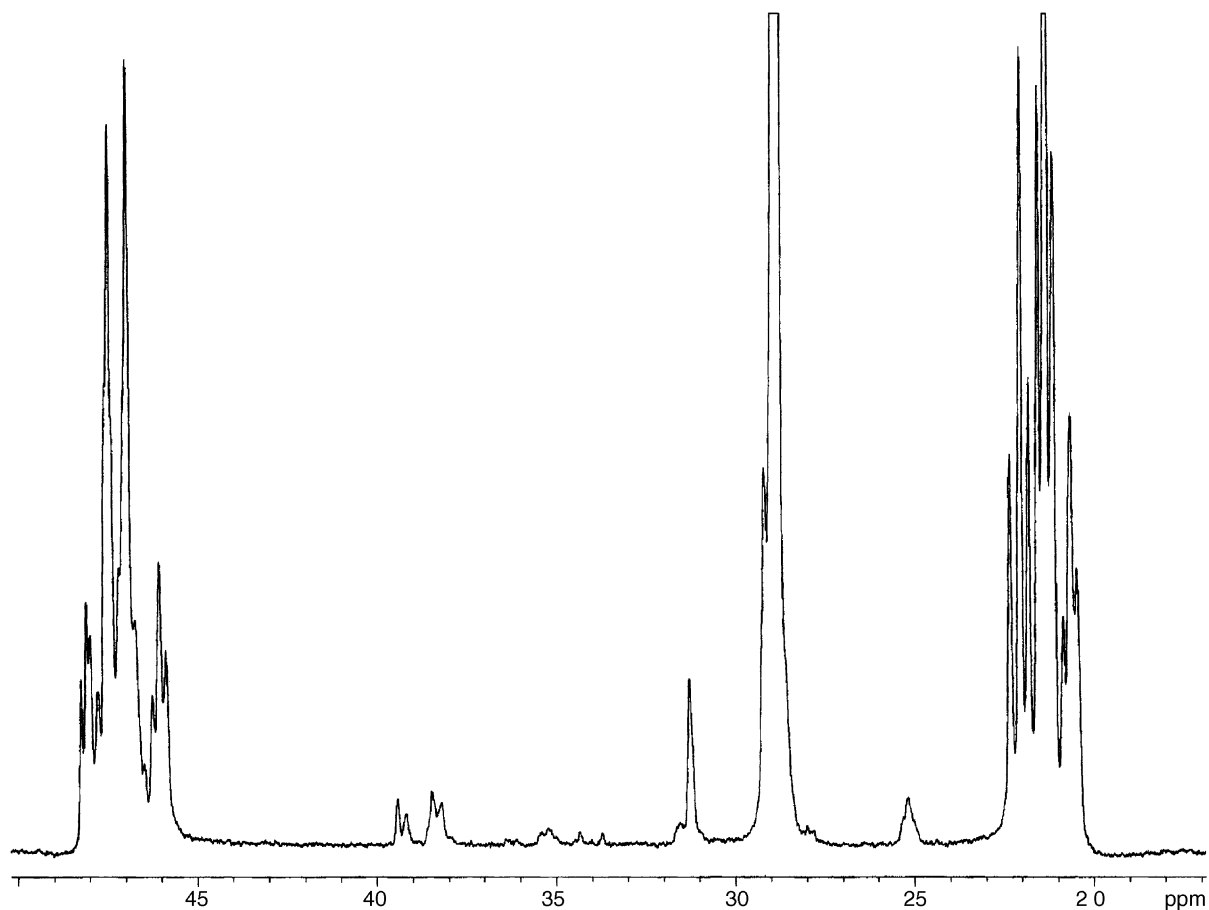
Fig. 3. ^{13}C NMR spectrum of the propylene polymer obtained with Ind$_2$Zr(OFl)Cl/MAO at 0 °C.

depend on π-ligands type of the metallocene core, polymerization temperature and monomer concentration [28]. Isomerization of secondary Zr-alkyl units derived from 2,1-insertion to primary Zr-alkyl ones before the next monomer insertion was suggested for 1,3-units formation [27–29]. A propylene–ethylene pseudo-copolymer was produced by liquid propylene homopolymerization with the rigid C$_2$-symmetric ethylene-bis(4,7-dimethyl-tetrahydroindenyl)-zirconium dichloride at 70 °C [28]. The presence of methyl groups at positions 4 and 7 of the hydrogenated ring enhanced 1,3-enchainment to 23.6 mol%, when compared to 0.2 mol% obtained with the non-substituted ethylene-bis(tetrahydroindenyl)-zirconium dichloride. Nevertheless, the amount of 1,3-inserted units reported in this communication is the highest one ever

known. The present paper shows the first example of a capability of non-bridged bis(indenyl)-zirconium derivative to produce a high content of ethylene crystallizable blocks during propylene homopolymerization.

It is also interesting to note a predominance of mrrr pentad at 20.51 ppm, shown in the expanded ^{13}C NMR spectra of methyl region (see Fig. 4a) of the polymer obtained at 20 °C, although propylene sequences are atactic in nature. The above indicates the increase in syndiotactic diad sequences, when compared with the copolymer prepared at 0 °C where the methyl pentad distribution really corresponds to atactic polymer.

The mono-alcoholate complex was active in ethylene polymerization, but the activity was lower than that of the corresponding dichloride [30,31]. It could
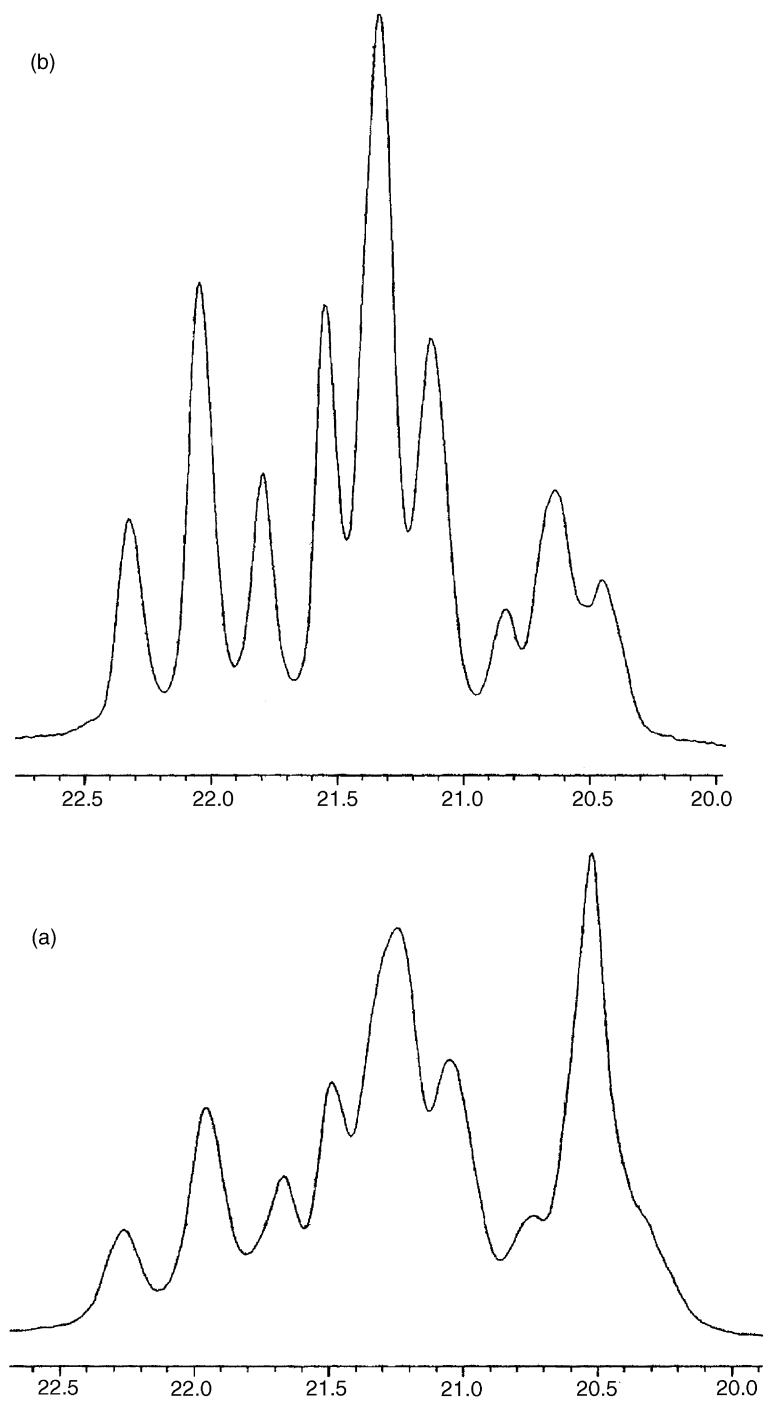
Fig. 4. Expanded ^{13}C NMR spectra of the methyl region of propylene–ethylene copolymer obtained at (a) 20 °C and (b) 0 °C.

be attributed to more difficult alkylation of the transition metal core due to a presence of the voluminous sterically shielding bridged alicyclic ligand. However, as our previous results show, several sterically hindered zirconocene dialcoholates possess a comparable or higher activities in ethylene polymerization at elevated temperatures and pressures (90 °C, 15 bar) with respect to dichloride analogues [18]. The observed behaviour suggests that higher temperatures promote easier M–O bond cleavage necessary to form the active species. Better results observed at higher temperatures also suggests that active species derived from the alcoholates of metallocenes are more stable even at unusually high polymerization temperatures with respect to traditional metallocenes.

Actually accepted mechanism for olefin polymerization catalyzed by metallocene assumes that the σ-ligands are removed from the metallocene coordination node by the MAO molecule upon formation of the cationic active species. On the other hand, the nature of the counter-ion can influence the catalyst activity [32,33]. Nevertheless, the leaving σ-ligands (typically Cl^- or lower alkyl- or alkoxy-moieties) have always been beyond the attention. Typically, they are called "spectator" ligands. These ligands of small dimensions does not influence significantly the growing polymer chain. However, the bridged alicyclic alcoholato-ligand used by us has comparable dimensions with the remaining part of the transition metal complex molecule. As one may suppose, due to sterical hindrance of the fencholato-moiety the alkylation of the co-ordination centre does not necessarily proceed to formation of dialkylated species. An intermediate complex $Ind_2ZrMe(OFl)$ generated at the first alkylation step could then react with MAO to produce an ion-pair like $[Ind_2ZrMe]^+[MAO–OFl]^-$ with the bridged alicyclic σ-ligand being re-coordinated to the MAO counter-ion. To our minds, the presence of this sterical obstacle in a heteronuclear active centre of the metallocene-MAO catalyst, provides a reasonable explanation for observed changes in the polymerization behaviour, when the contribution of 1,3-insertions became more significant. The presence of the bulky moiety in the metallocene complex is also responsible for the decrease in the catalytic activity due to lower activation rate provoked by sterical hindrance.

Finally, our empirically derived conclusions about the role of sterically demanding σ-ligands meets a support and are in a good agreement with the modern theoretical studies. Quantum chemical calculations by density functional theory (DFT) and quadratic configuration interaction with singles and doubles (QCISD) methods demonstrate: as the polymer chain propagates, "the steric effect of the spectator ligands significantly affects the polymerization rate and selectivity" [34].

Acknowledgements

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