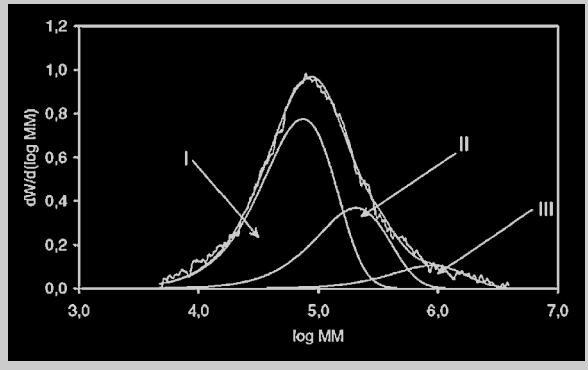
Summary: $Me_2Si(Ind)_2ZrCl_2$ was in situ immobilized onto SMAO and used for ethylene and propylene polymerization in the presence of TEA or TIBA as cocatalyst. The catalytic system $Me_2Si(Ind)_2ZrCl_2$/SMAO exhibited different behavior depending on the amount and nature of the alkylaluminum employed and on the monomer type. The catalyst activity was nearly 0.4 kg polymer $\cdot$ g cat^{-1} $\cdot$ h^{-1} with both cocatalysts for propylene polymerization. Similar activities were observed for ethylene polymerization in the presence of TIBA. When ethylene was polymerized using TEA at an Al/Zr molar ratio of 250, the activity was 10 times higher. Polyethylenes made by in situ supported or homogeneous catalyst systems had practically the same melting point (T_m). On the other hand, poly(propylenes) made using in situ supported catalyst systems had a slightly lower T_m than poly(propylenes) made using homogeneous catalyst systems. The nature and amount of the alkylaluminum also influenced the molar mass. The poly(propylene) molar mass was higher when TIBA was the cocatalyst. The opposite behavior was observed for the polyethylenes. Concerning the alkylaluminum concentration, the molar mass of the polymers decreased as the amount of TEA increased. In the presence of TIBA, the polyethylene's molar mass was almost the same, independent of the alkylaluminum concentration, and the poly(propylene) molar mass increased with increasing amounts of cocatalyst. The deconvolution of the GPC curves showed 2 peaks for the homogeneous system and 3 peaks for the heterogeneous in situ supported system. The only exception was observed when TEA was used at an Al/Zr molar ratio of 500, where the best fit was obtained with 2 peaks. Based on the GPC deconvolution results and on the theoretical modeling, a proposal for the active site structure was made.



Molar mass distribution deconvolution of polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TIBA with 500 mol/mol of alkylaluminum as cocatalyst.

Ethylene and Propylene Polymerization Using In Situ Supported $Me_2Si(Ind)_2ZrCl_2$ Catalyst: Experimental and Theoretical Study

Fernando C. Franceschini,[1] Tatiana T. da R. Tavares,[1] João H. Z. dos Santos,[2] Maria L. Ferreira,[3] João B. P. Soares[4]*

[1] Ipiranga Petroquímica S.A., Divisão de Desenvolvimento e Especialidades, Departamento de Desenvolvimento de Produto, Pólo Petroquímico do Sul, BR 386 Rodovia Tabaí Canoas, km 419, Caixa Postal 08, CEP 95853–000, Triunfo, Brazil
Fax: + 55 51 3457 1070; E-mail: fernando@ipiranga.com.br
[2] Instituto de Química da UFRGS, Av. Bento Gonçalves, 9500, CEP 91501-970, Porto Alegre, Brazil
[3] PLAPIQUI-UNS-CONICET, Camino La Carrindanga, km 7, CC717-8000, Bahía Blanca, Argentina
[4] Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

Received: October 26, 2005; Revised: January 3, 2006; Accepted: January 4, 2006; DOI: 10.1002/mame.200500360

Keywords: GPC deconvolution; in situ immobilization; metallocene catalysts; modeling

Introduction

In situ immobilization of metallocenes is a simple procedure for a catalyst supported directly in the polymerization reactor. A homogeneous metallocene catalyst solution, a MAO-modified silica support (SMAO) and an alkylaluminum are simultaneously added to the reactor, followed by monomer addition. No other preparation steps are involved and no pre-contacting of catalyst, cocatalyst and support is required. This procedure was first described some years ago, and has been used in ethylene homopolymerization and copolymerization with the catalysts

Cp_2ZrCl_2, Cp_2HfCl_2, $Et(Ind)_2ZrCl_2$, $Et(Ind)_2ZrMe_2$, $[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$ (CGC catalyst from Dow) and $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, a bridged binuclear catalyst.[1–8]

In our previous publications we have shown that in situ supported metallocenes can also be used to polymerize propylene with $Me_2Si(Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$, with common alkylaluminum as cocatalysts, and SMAO as the support. The maximum catalyst load onto the support, the influence of the nature and concentration of the alkylaluminum on the catalyst activity and on the polymer properties, the polymer morphology and an investigation of the number and types of active sites present on the catalyst based on the deconvolution of the molar mass distribution curves measured by gel permeation chromatography (GPC) have been described.[9–11]

In the present investigation, we compare the behavior of $Me_2Si(Ind)_2ZrCl_2$/SMAO (in situ immobilized) for the polymerization of ethylene and propylene in the presence of TEA or TIBA as cocatalyst. The catalyst activity and the polymer properties were correlated to the type and amount of alkylaluminum present in the reactor. Based on deconvolution results of the GPC curves, possible structures for the active sites were proposed using theoretical modeling.

Experimental Part

Materials

All the experiments were performed under an inert atmosphere using Schlenk techniques. The catalyst *rac*-dimethylsilylenebis(indenyl)zirconium dichloride ($Me_2Si(Ind)_2ZrCl_2$) (Crompton), the support MAO-modified silica (SMAO, 23 wt.-% Al, Crompton) and the cocatalysts MAO (10 wt.-% in toluene, Crompton), triethylaluminum (TEA) and triisobutylaluminum (TIBA) (both from Akzo) were used without purification. Ethylene and propylene were used as received from the cracker (Copesul, Triunfo, RS, Brazil), without any further purification. Toluene and hexane were purified through refluxing over sodium followed by distillation. Hexane was degassed by bubbling nitrogen before each reaction.

Polymerization

Polymerizations were done in a 1.5 L stainless steel reactor equipped with a mechanical stirrer, an electrical temperature controller and inlets for nitrogen and ethylene or propylene. The reactor was filled with SMAO ($Al_{SMAO}/Zr = 500$ mol/mol), 0.75 L of hexane, 10 mL of catalyst solution (10^{-5} mol catalyst in toluene) and alkylaluminum. When the mixture reached 60 °C, the stirring rate was set at 750 rpm and the reactor was pressurized with ethylene or propylene up to 6.0 bar (partial pressure) for 60 min. Acidified ethanol was used to quench the process. The polymer product was filtered, washed with distilled water and ethanol and dried at 80 °C under a vacuum. The mass of dry polymer was measured to determine product yield. Each polymerization was repeated at least twice. All results discussed in this paper are the average of these duplicate runs. The homogeneous polymerizations were carried out in the same way, but only MAO ($Al_{MAO}/Zr = 500$ mol/mol) was added to the reactor with the catalyst.

Polymer Characterization

Melting temperatures (T_m) were determined using a TA Instruments 2920 differential scanning calorimeter (DSC), according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan are reported here. The heating rate was $10\,^{\circ}C \cdot min^{-1}$ in the temperature range 30–200 °C under a nitrogen atmosphere. Molar mass distributions were determined by high temperature gel permeation chromatography (GPC) using a 150C Waters instrument equipped with four GMHXL-HT (TosoHaas) columns at 138 °C. 1,2,4-Trichlorobenzene was used as the mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards. The deconvolution of the polymer molar mass distribution was performed using an Excel spreadsheet. To obtain the best fit between the measured GPC curve and the fitted GPC curve (sum of the deconvoluted curves), Excel's Solver routine was used to minimize the sum of the squares of the differences between the measured and the fitted GPC curves ($\Sigma\Delta^2$). For each GPC curve, the deconvolution process was carried out considering 1, 2, 3 or 4 curves or peaks. In all results presented in this work the parameter $\Sigma\Delta^2$ had the lowest possible value, without overlapping of curves or peaks.[12]

Theoretical Method

The MM2 calculations to obtain the steric energies were done using the MOPAC section of Chem3D from Cambridge Soft, version 5, taking into consideration the steric energies for different arrangements of SMAO and the catalyst. Since the main interest was to evaluate steric interactions, the electronic structure was not explicitly considered. The distances Zr-indenyl were fixed considering the published literature dealing with structural facts on zirconocenes. The model of SMAO included 1 Al and 2 Si atoms. The Al atoms were saturated with O and the Si atoms with OH, according to previously published works.[13–18]

The zirconocenes were modeled with all their atoms, considering the structural information available, using the method developed by Ferreira et al.[13]. This approach has produced manuscripts describing zirconocene adsorption on SiO_2,[14] MAO adsorption on SiO_2,[15] zirconocene reaction with MAO or SiO_2[16,17] and the presentation of a new model of active site for olefin polymerization.[18,19]

Results and Discussion

Experimental Data

Table 1 shows the catalytic activity and the average polymer properties for the polymerizations carried out in this investigation. Data from homogeneous polymerizations with both monomers using MAO ($Al_{MAO}/Zr = 500$ mol/mol) as cocatalyst were also included for comparison.

Table 1. Catalytic activity of the system $Me_2Si(Ind)_2ZrCl_2$/SMAO in the presence of TEA or TIBA as cocatalyst, and properties of the polymers obtained with homogeneous and in situ polymerization of ethylene and propylene.

Alkylaluminum		Activity	T_m	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Type	Concentration[a] mol/mol	kg polymer · g cat^{-1} · h^{-1}	°C	kg · mol^{-1}	kg · mol^{-1}	
Polyethylene						
Homogeneous polymerization[b]		5.1	133	67	166	2.5
TEA	70	1.3	132	75	191	2.5
	250	4.0	132	66	154	2.3
	500	3.2	132	65	143	2.2
TIBA	70	0.6	133	53	184	3.5
	250	0.5	132	51	164	3.2
	500	0.3	132	53	185	3.5
Poly(propylene)						
Homogeneous polymerization[b]		4.6	142	16	34	2.1
TEA	70	0.3	142	22	45	2.1
	250	0.4	141	20	42	2.1
	500	0.3	140	16	30	1.9
TIBA	70	0.5	139	24	53	2.2
	250	0.6	141	30	63	2.1
	500	0.2	140	33	68	2.1

[a] $Al_{alkylaluminum}/Zr$ ratio.
[b] $Al_{MAO}/Zr = 500$ mol/mol. Without external alkylaluminum as R_3Al, only MAO.

The supported metallocene complexes had lower activities than the corresponding homogeneous metallocene catalysts, as expected and already observed using the in situ immobilization procedure.[5,6] Among the possible reasons for this poor catalytic activity of the supported systems are the significant steric hindrance around the active site caused by the support surface, the deactivation of catalytic sites and the inefficient production of active sites during the immobilization process,[5] generating nearly 1% of total Zr active species after the catalyst immobilization procedure.[20]

In the range of alkylaluminum concentrations ($Al_{alkylaluminum}/Zr = 70-500$ mol/mol) studied, the catalyst activity was almost the same for propylene polymerization using TEA and TIBA (≈0.4 kg polymer · g cat^{-1} · h^{-1}). Similar results were also observed for ethylene polymerization using TIBA as cocatalyst. On the other hand, in the ethylene polymerizations carried out with $Me_2Si(Ind)_2ZrCl_2$/SMAO in the presence of TEA, the catalyst activity was substantially higher. When a molar ratio of Al_{TEA}/Zr of 250 was used, the catalyst activity was 4.0 kg PE · g cat^{-1} · h^{-1}, almost 80% of the activity observed for the equivalent homogeneous ethylene polymerization.

In the copolymerization of ethylene and 1-hexene with $Et(Ind)_2ZrCl_2$ in situ immobilized onto SMAO, higher activities were observed using TMA as cocatalyst than with TEA or TIBA.[4] It was speculated that this decrease in activity could be linked to the reduction ability of the cocatalysts or to steric hindrance. Due to the increasing bulkiness of the alkylaluminums TEA and TIBA, it is possible that the access to the catalyst molecules on the support is limited, reducing the number of active sites and, as a consequence, reducing the activity of the catalyst.

A similar phenomenon might explain the lower activity of the $Me_2Si(Ind)_2ZrCl_2$/SMAO for the ethylene polymerization using TIBA, since TIBA is bulkier than TEA. On the other hand, catalyst activity for propylene polymerization was independent of alkylaluminum type. Thus, one can speculate that, in the presence of propylene, the difference in molecular sizes between TEA and TIBA is not so relevant.

While the polyethylenes had almost the same melting temperature (T_m), all poly(propylenes) produced with the in situ supported catalyst showed lower T_ms than the polymer synthesized in homogeneous conditions. This may be due to the formation of regioirregularities during the growth of the poly(propylene) chain on the supported catalyst such as 1,3- and/or 2,1-misinsertions.[20] Besides, it demonstrates that the support plays a significant role on propylene insertion.

All polyethylenes had higher molar masses than the poly(propylenes). According to Brintzinger et al., isospecific metallocene catalysts usually polymerize ethylene at rates four to five times faster than those for propylene.[21] This increase in polymerization rate will be reflected in a higher molar mass, provided that the chain transfer rates do not increase at the same rate. The polydispersity of the polyethylenes was higher than that of the poly(propylenes).

In the range of alkylaluminum concentrations evaluated, the effect of the nature of the cocatalyst type on the

polydispersity of the polymers was different depending on the monomer. As can be seen in Table 1, the polyethylenes produced with TIBA had higher polydispersities than those obtained using TEA, while all poly(propylenes) had basically the same polydispersity.

The type and the concentration of the alkylaluminum influenced the molar mass of the polymers in different ways. Poly(propylenes) prepared with the in situ supported catalyst had a higher molar mass when TIBA was used. It has been suggested that alkylaluminums having bulkier ligands may have a lower rate of chain transfer to cocatalyst, resulting in polymers with higher molar masses.[22] Nevertheless, polyethylenes had exactly the opposite behavior: resins made with TEA had higher molar masses than those made with TIBA.

The molar mass of poly(propylenes) increased as the concentration of TIBA increased, while in the case of the polyethylenes, the molar mass was essentially independent of the concentration of TIBA in the reactor. Interestingly, the molar masses of polyethylene and poly(propylene) always decreased with increasing concentration of TEA.

In order to estimate the number of active site types present in the catalytic system, the GPC curves were deconvoluted into Flory's most probable distributions,[12,23] and the results are shown in Table 2. Although the polydispersity of the polyethylenes produced in the presence of TEA and with the homogeneous system, as well as of the poly(propylenes), was almost the same, the result of the mathematical deconvolution was not the same for all polymers. The GPC curves of the polymers produced with the homogeneous (unsupported) catalyst were deconvoluted into only two peaks, indicating the presence of two active site types. The GPC curves of almost all polymers prepared via in situ immobilization of the catalyst were best fitted into three peaks, indicating the presence of three kinds of active sites. The only exceptions were the polymers produced with Al/Zr = 500 mol/mol of TEA, in which the best fit was obtained with two peaks. Up to now it is not clear why in the presence of a high amount of TEA (Al/Zr = 500 mol/mol) active sites 3 do not generate polymer, while using TIBA at the same concentration 3 peaks are obtained in the GPC deconvolution, i.e., sites 3 are still active. It should be speculated that under this condition active sites 3 are completely deactivated due to the higher alkylation power of TEA in comparison to TIBA. Besides, as shown in our previous work, it should also be mentioned that in the polymerization of propylene using Al_{TEA}/Zr = 1 000 mol/mol, the best fit was also achieved with only 2 peaks. Nevertheless, with Al_{TIBA}/Zr = 1 000 mol/mol 3 peaks are still obtained in the mathematical deconvolution of the GPC curve.[11] Figure 1 to 6 show examples of GPC deconvolution curves.

All the above results confirm that the alkylaluminum is not just acting as a scavenger. In fact, it should be playing a significant role with the catalyst, affecting the activity of the system and the properties of the polymers.

Theoretical Modeling

Figure 7 shows the proposed structures for the active sites on the homogeneous $Me_2Si(Ind)_2ZrCl_2$/MAO system, following the ideas previously presented by Ferreira

Table 2. GPC curves deconvolution. Molar mass ($\bar{M}_n$) and fraction of the polymer generated by each active site type using TEA or TIBA as cocatalyst.

Alkylaluminum		Peak/active site 1		Peak/active site 2		Peak/active site 3	
Type	Concentration[a)]	$\bar{M}_n$	Fraction	$\bar{M}_n$	Fraction	$\bar{M}_n$	Fraction
	mol/mol	kg · mol^{-1}	%	kg · mol^{-1}	%	kg · mol^{-1}	%
Polyethylene							
Homogeneous polymerization[b)]		57	70	159	30	–	–
TEA	70	46	58	126	33	287	9
	250	41	57	89	30	191	13
	500	42	59	109	41	–	–
TIBA	70	37	57	89	33	360	10
	250	36	55	89	37	370	8
	500	37	62	103	30	445	8
Poly(propylene)							
Homogeneous polymerization[b)]		8.1	23	19	77	–	–
TEA	70	8.6	16	23	78	57	6
	250	7.4	18	21	69	41	13
	500	9.7	44	20	56	–	–
TIBA	70	9.6	19	23	52	42	29
	250	5.7	4	18	29	38	67
	500	9.8	11	32	63	47	26

a) $Al_{alkylaluminum}$/Zr ratio.
b) Al_{MAO}/Zr = 500 mol/mol. Without external alkylaluminum as R_3Al, only MAO.

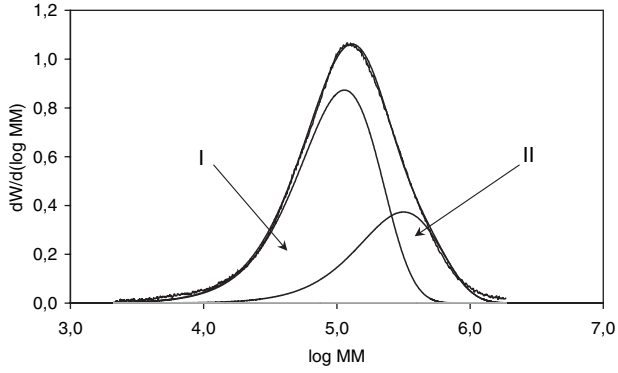


Figure 1. Molar mass distribution deconvolution of the polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/MAO.

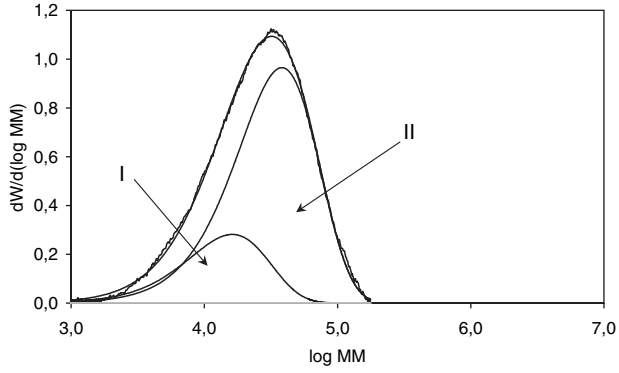


Figure 4. Molar mass distribution deconvolution of the poly(propylene) prepared with the system $Me_2Si(Ind)_2ZrCl_2$/MAO.

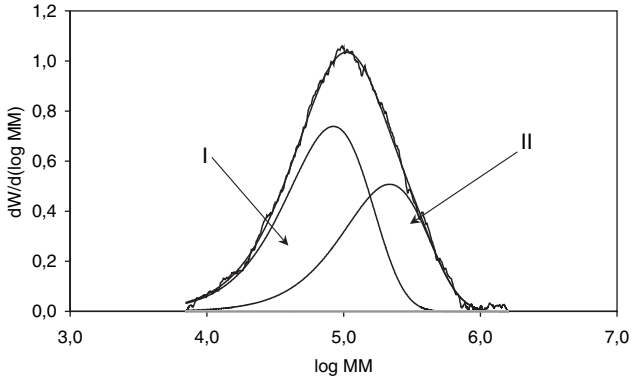


Figure 2. Molar mass distribution deconvolution of the polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TEA with 500 mol/mol of alkylaluminum as cocatalyst.

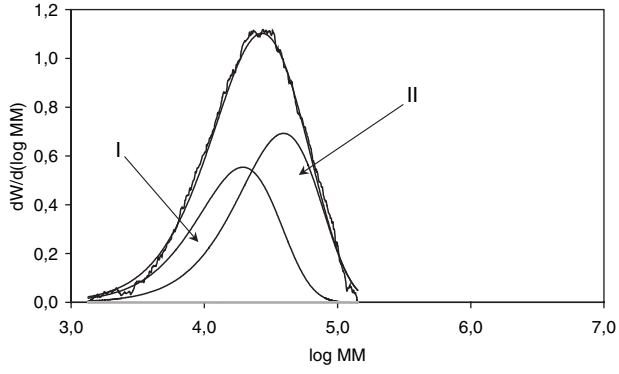


Figure 5. Molar mass distribution deconvolution of the poly(propylene) prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TEA with 500 mol/mol of alkylaluminum as cocatalyst.

et al.[18,19]. The monomer used was ethylene, but the proposal is also valid for propylene. Several facts are relevant when the structures of Figure 7 are analyzed. Two active site types are proposed and:

(a) Structures 7(a) and 7(b) are equivalent, as well as structures 7(c) and 7(d).

(b) The difference between structures 7(a)–7(b) and 7(c)–7(d) is the distribution of the ligands around the Zr, i.e., the MAO position related to the bis-indenyl rings. The MAO and bis-indenyl rings are in the same plane in structure 7(c) and 7(d) and in different planes in structures 7(a) and 7(b).

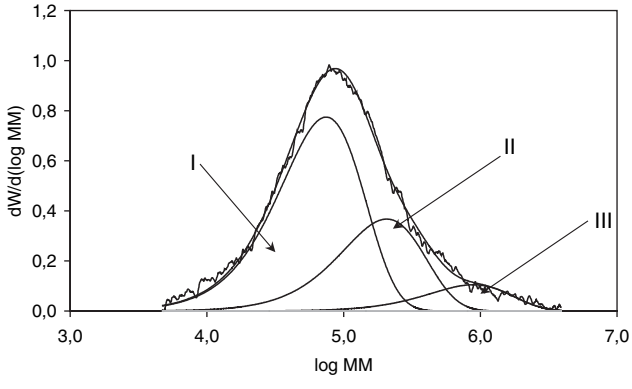


Figure 3. Molar mass distribution deconvolution of the polyethylene prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TIBA with 500 mol/mol of alkylaluminum as cocatalyst.

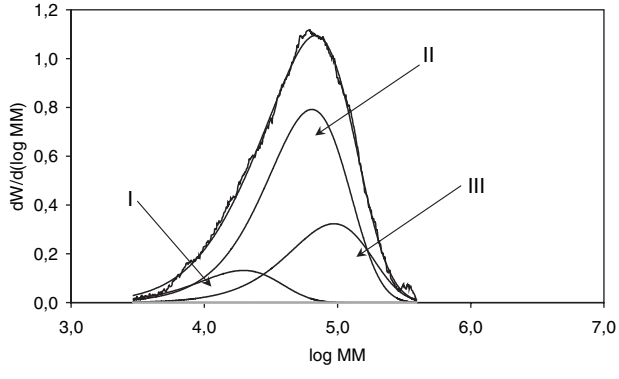


Figure 6. Molar mass distribution deconvolution of the poly(propylene) prepared with the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/TIBA with 500 mol/mol of alkylaluminum as cocatalyst.

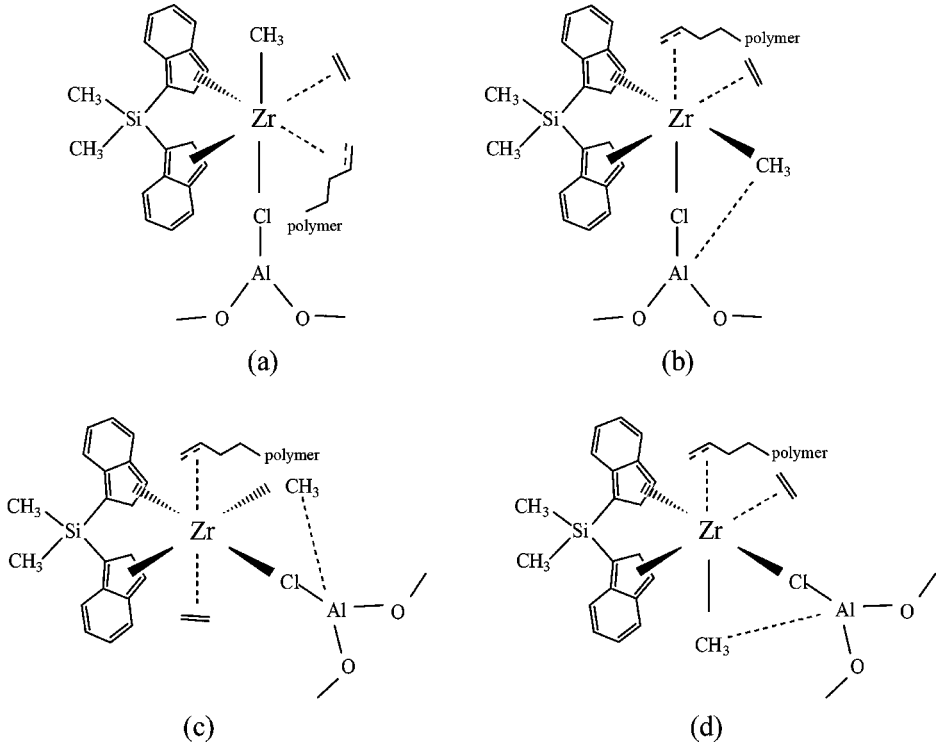


Figure 7. Proposed structures for the active site types in the system $Me_2Si(Ind)_2ZrCl_2$/MAO: (a) and (b) active site 1; (c) and (d) active site 2.

(c) The position occupied by the coordinated olefin could be taken by another MAO molecule without important changes in the electronics because the new coordinating MAO would act as a Lewis base.
(d) The structures that include the interaction of MAO and methyl groups (7(b), 7(c) and 7(d)) are favored.
(e) The active sites for ethylene and propylene polymerization are the same, although with different k_p (chain propagation rate constant) and k_{ter} (chain termination rate constant) values.

Catalyst activities might be similar in ethylene and propylene polymerization with the homogeneous system because no steric and/or electronic effects are expected for both monomers. This can be assumed because there is no substitution in the indenyl ligands of the catalyst. The molar mass of the poly(propylene) samples is far lower than those of the polyethylenes produced and the amount of polymer produced by each site type is different, showing that the propagation reactions and the concentration of each site type are different depending on the monomer. For propylene, the polymer produced in the major percentage is the one with the highest molar mass. The opposite is observed in the case of ethylene, i.e., a higher amount of polymer with low molar mass is formed.

As can be seen in Figure 7(a) and 7(b), active sites 1 have the growing chain and the coordinated olefin placed side by side. Due to this proximity, it might be supposed that active sites 1 are more prone to producing low molar mass fractions than active sites 2, since chain transfer to monomer could take place more easily. Figure 7(c) and 7(d) show that in active sites 2 the coordinated olefin is not as available to chain transfer reactions as in active sites 1, and it can be expected that active sites 2 will produce polymer with higher molar mass.

For each active site type, the reciprocal of the number average molar mass of the polymer chains can be related to the parameter τ in Flory's distribution:[24]

$$\frac{1}{M_n} = \tau = \frac{k_m}{k_p} + \frac{k_\beta}{k_p[M]} + \frac{k_{MAO}[MAO]}{k_p[M]} + \frac{k_{H_2}[H_2]}{k_p[M]} \qquad (1)$$

where k_m is the chain transfer to monomer rate constant, k_β is the β-hydride elimination rate constant, k_{MAO} is the chain transfer to MAO rate constant, k_{H_2} is the chain transfer to hydrogen rate constant, k_p is the chain propagation rate constant, $[M]$ is the monomer concentration, $[MAO]$ is the MAO concentration and $[H_2]$ is the hydrogen concentration.

As it is supposed that the polymer produced in active sites 1 is more influenced by the transfer reaction to monomer, one might assume that

$$\frac{1}{M_n} = \tau \cong \frac{k_m}{k_p} \gg \frac{k_\beta}{k_p[M]} + \frac{k_{MAO}[MAO]}{k_p[M]} + \frac{k_{H_2}[H_2]}{k_p[M]} \qquad (2)$$

Thus, when carrying out polymerizations with different monomer partial pressures, it is expected that the molar

Table 3. GPC curve deconvolution: Molar mass ($\bar{M}_n$) and fraction of the polyethylene generated by each active site type in homogeneous conditions.

Ethylene pressure	Peak/active site 1		Peak/active site 2	
	$\bar{M}_n$	Fraction	$\bar{M}_n$	Fraction
bar	$kg \cdot mol^{-1}$	%	$kg \cdot mol^{-1}$	%
5.0	54	56	155	44
7.0	47	64	120	35

mass of the polymer produced by active sites 1 will either not change or will show a lower change compared to the polymer made by active sites 2. The deconvolution results of the GPC curves of polyethylenes produced under homogeneous conditions with ethylene partial pressures varying between 5.0 and 7.0 bar are shown in Table 3. The molar mass of the polyethylene produced with active sites 1 decreased by 13% while that of the polymer made with active sites 2 decreased by 23% when the ethylene partial pressure was changed from 5.0 to 7.0 bar, confirming the previous assumptions. It should be emphasized that, according to Equation (1), an increase in the molar mass of the polymer made by active sites 2 was expected with increasing ethylene pressure. Nevertheless, similar results have already been described for ethylene polymerization carried out using $Et(Ind)_2ZrCl_2$ in the absence of hydrogen and for low hydrogen concentrations.[25] This result is yet to be explained.

Figure 8 shows the proposed structures for the supported system $Me_2Si(Ind)_2ZrCl_2$/SMAO. As mentioned for Figure 7, the monomer used was ethylene, but the proposal is also valid for propylene. Considering the same ideas previously discussed for the homogeneous system, four different structures, sites 1 through 4, are proposed. Two of the four structures (active sites 1 and 2 - Figure 8(a) to 8(d)) are similar to those proposed to the homogenous system, but the presence of the support and the possibility of TEA or TIBA coordination, replacing the monomer, makes the overall electronics on Zr different. The alkylaluminum probably decreases the electrophilicity of the metal because of the strength of the coordination, and the MAO at the SiO_2 surface is not the same compared to that of the homogeneous system, $Me_2Si(Ind)_2ZrCl_2$/MAO.

Active sites 3 and 4 are supposed to coordinate the alkylaluminum, i.e., it is assumed that the alkylaluminum is chemically bonded to the Zr. As the homogeneous polymerizations were carried out using no external alkylaluminum such as TEA or TIBA, but MAO, active sites 3 and 4 are not present in the homogeneous system.

As the deconvolution of the GPC curves of the polymers produced using the heterogeneous catalyst showed 3 peaks (except for the polymers prepared in the presence of TEA with Al/Zr = 500 mol/mol) it might be supposed that one of the structures proposed in Figure 8(e) and 8(f) does not generate an active site for polymerization. Due to the bulkiness of the support, of the bis-indenyl rings and of the group AlR_2 present in both structures, it might be assumed that structure 8(f) shows higher steric hindrance than structure 8(e) and therefore it is probably inactive for ethylene and propylene polymerization.

Table 4. Steric energy of the proposed active site types.

Catalytic system	Figure	Steric energy
		$kcal \cdot mol^{-1}$
Homogeneous	7(a)	−145.3
$Me_2Si(Ind)_2ZrCl_2$/MAO	7(b)	−142.6
	7(c)	−136.9
	7(d)	−138.2
Heterogeneous	8(a)	−142.2
$Me_2Si(Ind)_2ZrCl_2$/SMAO/AlR_3	8(b)	−143.0
	8(c)	−142.8
	8(d)	−138.9
	8(e)	−121.8
	8(f)	−141.8

Table 4 shows the steric energy calculated for each structure in Figure 7 and 8. Although structure 8(f) (site type 4) has smaller steric energy than structure 8(e) (site type 3), i.e., −141.8 against −121.8 $kcal \cdot mol^{-1}$, the site type represented by structure 8(f) does not polymerize due to the higher steric hindrance. It must be emphasized that the more stable structures during the coordination step are not always the ones with the lowest activation energy for the insertion step.[26] Taking into account the steric hindrance and the step of olefin coordination, it can be speculated that the most probable structures should be 8(a)–8(b) (site type 1), 8(c)–8(d) (site type 2) and 8(e) (site type 3).

Conclusion

The in situ immobilized system $Me_2Si(Ind)_2ZrCl_2$/SMAO showed lower activity for propylene polymerization in the presence of TEA or TIBA, and for ethylene polymerization in the presence of TIBA than the homogeneous system $Me_2Si(Ind)_2ZrCl_2$/MAO. However, when ethylene was polymerized using $Me_2Si(Ind)_2ZrCl_2$/SMAO with TEA as cocatalyst, almost 80% of the homogeneous system activity was reached.

The poly(propylenes) prepared using the in situ supported catalyst system had a slightly lower melting point than the poly(propylenes) made using the homogeneous catalyst system. On the other hand, the polyethylenes made using in situ supported catalyst and by homogeneous catalyst systems showed practically the same melting point.

The nature and the amount of the alkylaluminum used as cocatalyst influenced the molar mass of the polymers prepared when using the in situ immobilization of the metallocene catalyst onto SMAO. The poly(propylene) molar mass was higher when TIBA was used as the

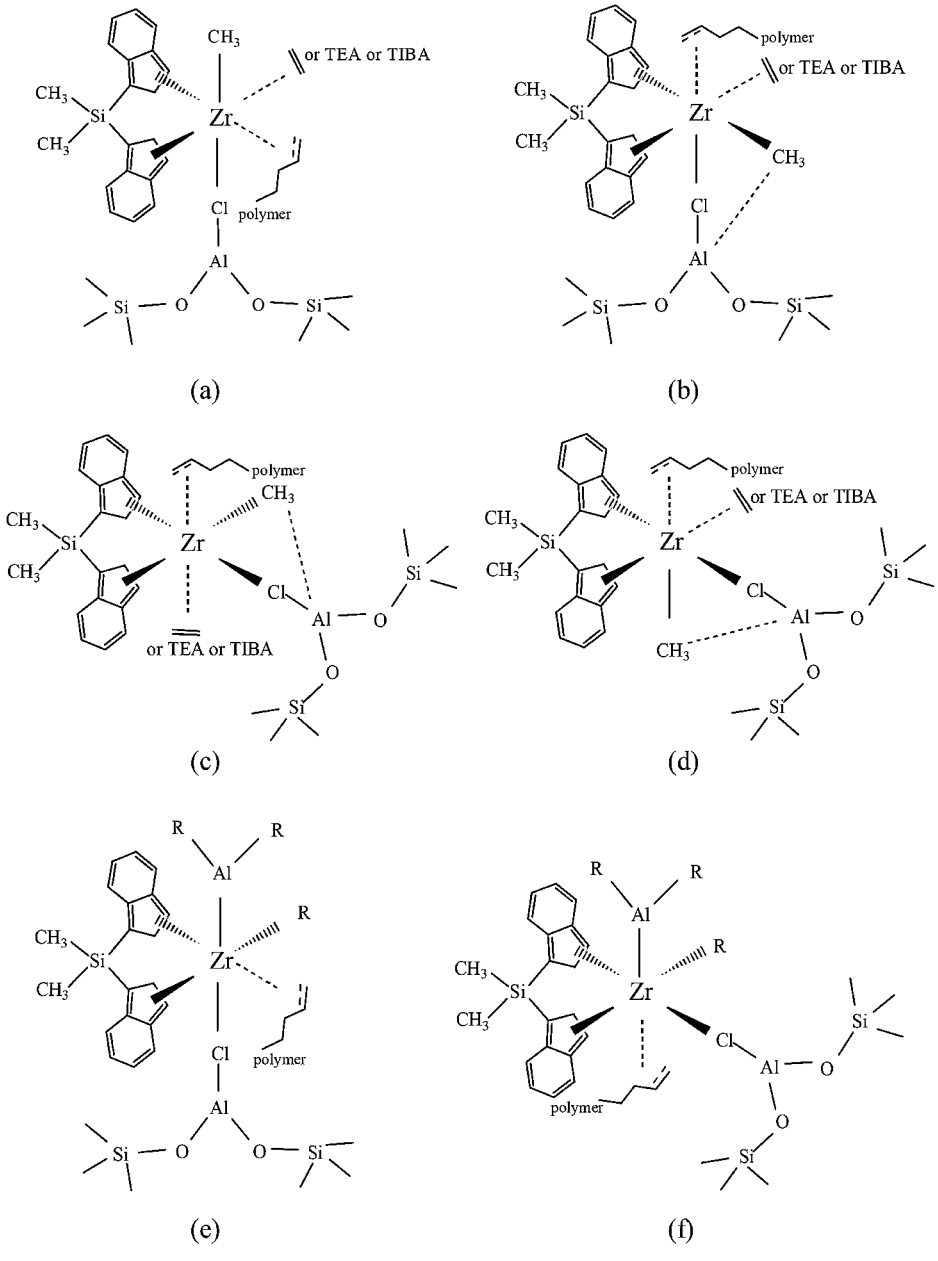


Figure 8. Proposed structures for the active site types in the system $Me_2Si(Ind)_2ZrCl_2$/SMAO/AlR_3: (a) and (b) active site 1; (c) and (d) active site 2; (e) active site 3; (f) active site 4.

cocatalyst, but the opposite behavior was observed for the polyethylenes. As the amount of TEA increased, the molar mass of the polymers decreased. In the presence of TIBA, the polyethylene molar mass was almost the same, independent of the alkylaluminum concentration, and the poly(propylene) molar mass increased with increasing amounts of cocatalyst. The polyethylenes had a higher polydispersity when TIBA was used as a cocatalyst. These results confirm that the cocatalyst acts not just as a scavenger, but also plays an important role on the catalyst.

The GPC curve deconvolution showed 2 peaks for the homogeneous systems and 3 peaks for almost all heterogeneous in situ systems, indicating the presence of 2 and 3 different types of active sites, respectively. The only exception was observed when TEA was used at an Al/Zr molar ratio of 500, where the best fit was obtained with 2 peaks. Based on these results and on theoretical modeling, it was possible to propose the structure of the active sites.

The results presented in this paper confirm the importance of the alkylaluminum used as a cocatalyst in the generation of a different type of active sites when SMAO is used as support, and the role of the olefin in the generation and stabilization of the active sites.

Acknowledgements: The authors would like to thank *CNPq-RHAE, FAPERGS* (F. C. Franceschini., T. T. da R. Tavares, J. H. Z. dos Santos) and *CONICET* (M. L. Ferreira) for financial support.

[1] K. J. Chu, C. L. P. Shan, J. B. P. Soares, A. Penlidis, *Macromol. Chem. Phys.* **1999**, *200*, 2372.
[2] K. J. Chu, J. B. P. Soares, A. Penlidis, *Macromol. Chem. Phys.* **2000**, *201*, 340.
[3] K. J. Chu, J. B. P. Soares, A. Penlidis, *Macromol. Chem. Phys.* **2000**, *201*, 552.
[4] C. L. P. Shan, K. J. Chu, J. B. P. Soares, A. Penlidis, *Macromol. Chem. Phys.* **2000**, *201*, 2195.
[5] K. J. Chu, J. B. P. Soares, A. Penlidis, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 462.
[6] K. J. Chu, J. B. P. Soares, A. Penlidis, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1803.
[7] H. W. Lee, Y. H. Park, *Catal. Today* **2002**, *64*, 309.
[8] H. W. Lee, S. H. Ahn, Y. H. Park, *J. Mol. Catal. A: Chem.* **2003**, *194*, 19.
[9] F. C. Franceschini, T. T. da R. Tavares, P. P. Greco, D. Bianchini, F. C. Stedile, G. B. Galland, J. H. Z. Dos Santos, J. B. P. Soares, *J. Mol. Catal. A: Chem.* **2003**, *202*, 127.
[10] F. C. Franceschini, T. T. da R. Tavares, J. H. Z. dos Santos, J. B. P. Soares, *Macromol. Chem. Phys.* **2004**, *205*, 1525.
[11] F. C. Franceschini, T. T. da R. Tavares, P. P. Greco, G. B. Galland, J. H. Z. Dos Santos, J. B. P. Soares, *J. Appl. Polym. Sci.* **2005**, *95*, 1050.
[12] J. B. P. Soares, A. E. Hamilec, *Polymer* **2257**, *36*, 2257.
[13] M. L. Ferreira, A. Juan, D. E. Damiani, *React. Kinet. Catal. Lett.* **1998**, *64*, 139.
[14] M. L. Ferreira, P. G. Belelli, A. Juan, D. E. Damiani, *Macromol. Chem. Phys.* **2000**, *202*, 1334.
[15] M. L. Ferreira, P. G. Belelli, D. E. Damiani, *Macromol. Chem. Phys.* **2001**, *202*, 495.
[16] P. Belelli, A. M. Eberhardt, M. L. Ferreira, J. H. Z. Dos Santos, D. E. Damiani, *Recent Res. Dev. Polym. Sci.* **2003**, *7*, 223.
[17] M. L. Ferreira, P. Greco, J. H. Z. dos Santos, D. E. Damiani, *J. Mol. Catal. A: Chem.* **2001**, *172*, 97.
[18] M. L. Ferreira, *Macromol. Theor. Simul.* **2002**, *11*, 250.
[19] M. L. Ferreira, *Macromol. Theor. Simul.* **2002**, *11*, 267.
[20] G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347.
[21] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143.
[22] W. Michiels, A. Muñoz-Escalona, *Macromol. Symp.* **1995**, *97*, 171.
[23] Y. V. Kissin, *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 227.
[24] J. B. P. Soares, *Polym. React. Eng.* **1998**, *6*, 225.
[25] J. D. Kim, J. B. P. Soares, G. L. Rempel, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 331.
[26] M. H. Prosend, F. Schaper, H. H. Brintzinger, "*Metalorganic Catalysts for Synthesis and Polymerization*", W. Kaminsky, Ed., Springer, Berlin 1999, p. 223.

