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Polyethylenes produced with zirconocene immobilized on MAO-modified silicas

Daniela Bianchini[a], Kátia Messias Bichinho[b], João Henrique Zimnoch dos Santos[a,*]

[a]Departamento de Química Inorganica, Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, 91509-900 Porto Alegre, RS, Brazil

[b]CIENTEC, Fundação de Ciência e Tecnologia, Rua Washington Luiz 675, 90010-460 Porto Alegre, RS, Brazil

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Abstract

The effect of Al content on MAO-modified silicas was evaluated on catalyst activity, on polymer properties and on residual metal content in the resulting polyethylenes. MAO-modified silicas were prepared by impregnating MAO toluene solutions in concentration range between 0.5 and 20.0 wt% Al/SiO_2. Commercial MAO-modified silica (Witco) containing 24.4 wt% Al/SiO_2 was used for comparative reasons. The resulting modified-silicas were employed as supports for grafting $(n\text{BuCp})_2\text{ZrCl}_2$. Using external MAO as cocatalyst (Al/Zr = 2000) no difference in catalyst activity was observed. Nevertheless, for Al/Zr = 500, catalyst activities were shown to be higher for supported zirconocene systems containing 0.0–2.0 wt% Al/SiO_2 range. According to DSC analysis, one T_m peak was detected for polymer obtained with catalyst prepared with 0.5 wt% Al/SiO_2 (135 °C), but two T_m peaks were observed for polymers obtained with catalysts prepared with 10.0 wt% Al/SiO_2 (136 and 141 °C) and 20.0 wt% Al/SiO_2 (133 and 141 °C). © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Zirconocene; Silica-supported metallocenes; Ethylene polymerization

1. Introduction

Metallocene catalysts have become increasingly important as potential new generation Ziegler–Natta catalysts. Metallocene/methylaluminoxane (MAO) systems combine high activity with the possibility of tailoring polymer properties such as molecular weight and molecular weight distribution as well as stereochemical structure through a suitable ligand design at the metal center. Nevertheless, the commercial success of metallocene catalysts for olefin polymerization partially depends on their compatibility with current polymerization plants, which run slurry or gas-phase process using heterogeneous Ziegler–Natta catalysts. Metallocene catalysts are soluble and have to be adapted for production of polyolefins on an industrial scale. The immobilization of metallocene catalysts on supports, such as silica, is an alternative approach for utilization of these catalysts in industrial plants [1]. Metallocene catalyst can be anchoring upon supports or modified supports, containing MAO or organosilanes. Many synthetic routes have been proposed in the literature [2–4].

MAO is an oligomer obtained from the controlled hydrolysis of trimethylaluminum (TMA) with hydrated solids. The exact structure is not completely elucidated yet, but recent works have demonstrated that MAO is constituted of coordinated molecules of hexa-methyl-tetra-aluminoxane [5]. NMR data shows that all aluminum atoms in MAO solutions are four-coordinated and all oxygen atoms are three-coordinated. These data suggest a very strong degree of inter- and intramolecular association in MAO molecules. MAO has many functions in the polymerization such as to remove impurities (scavenger), to alkylate the metal center, to abstract methyl of alkylated complex, to produce and to stabilize active species [6–9].

An increasing number of papers dealing with the interaction of MAO (TMA) and silica are reported in the literature. Soga and Kaminaka [10] studied the impregnation step of metallocenes on silica, and they pointed out the possibility of reacting OH from silica surface and MAO/TMA quantitatively. Zakharov et al. [11] reported infrared studies on TMA/silica and MAO-TMA/silica interaction, proposing that TMA react with silica terminal OH groups via protolysis reaction, yielding methane. Bartram and Rogers [12], based on Si-methyl and Al-methyl population ratios, supports a chemisorption model, in which a monomethylaluminum surface complex and methyl groups bonded to silicon are proposed as the majority species on the surface

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* Corresponding author. Tel.: +55-5133167238; fax: +55-5133167304.
E-mail address: jhzds@if.ufrgs.br (J.H. Zimnoch dos Santos).

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at 300 K. We have previously determined the MAO and TMA adsorption isotherms on silica, which was shown to be about 8.0–10.0 wt% Al/SiO_2 and 3.0 wt% Al/SiO_2, respectively [13]. Besides, we have monitored the reaction by in situ infrared (FT-IR) [14] and diffuse reflectance infrared (DRIFTS) [15] techniques, and observed that in fact MAO plays a steric role during the surface reaction, preventing non-consumed OH groups to react further.

In the present paper we report some results concerning the effect of variation of Al content in MAO-modified silicas, on the catalyst activity, on polymer properties and on residual metal content in the polymers. Supported catalysts were prepared by impregnating silica with MAO solution in concentration range between 0.5 and 20.0 wt% Al/SiO_2, followed by $(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$ grafting. Ethylene polymerization reactions were performed using external MAO and MMAO-7 as cocatalysts and the resulting polymers were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and X-ray fluorescence spectroscopy (XRF).

2. Experimental

2.1. Materials

Silica Grace 948 (255 $m^2 g^{-1}$) was activated under vacuum ($P < 10^{-4}$ mbar) for 16 h at 450 °C. The support was then cooled to room temperature under dynamic vacuum and stored under dried argon. MAO (generously supplied by Witco, 10.0 wt% toluene solution, MMAO-7 (*modified methylaluminoxane*, type-7) (generously supplied by Akzo Nobel, 12.89 wt% isopar-E solution), Commercial MAO-modified silica (Witco), bis(*n*-butylcyclopentadienyl) zirconium dichloride ($(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$) (Witco) were used without further purification. Ethylene, provided by COPESUL Co., and argon were deoxygenated and dried through columns of BTS (generously supplied by BASF) and activated molecular sieve (13 Å) prior to use. Purum grade toluene was deoxygenated and dried by standard techniques before use.

2.2. Preparation of supported catalysts

All grafting experiments were performed under inert atmosphere using the Schlenk technique. MAO-modified silicas were prepared by impregnating 1.0 g of thermally treated silica Grace 948 with a MAO toluene solution, in concentration range corresponding from 0.5 to 20.0 wt% Al/SiO_2, at room temperature for 1 h. Commercial MAO-modified silica (Witco) containing 24.4 wt% Al/SiO_2 was used for comparative reasons. The solvent was removed by vacuum and then ($(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$) toluene solution corresponding to 1.5 wt% Zr/SiO_2 was added and stirred for 30 min at 60 °C. The slurry was then filtered through a fritted disk. The resulting solids were washed with 10×2.0 cm^3 of toluene and dried under vacuum for 4 h. Metal content was determined by Rutherford backscattering spectrometry (RBS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) according to protocol reported elsewhere [16–18].

2.3. Polymerization reactions

Ethylene homopolymerizations were performed in 0.25 dm^3 of toluene in a 1.00 dm^3 Pyrex glass reactor connected to a constant temperature circulator and equipped with mechanical stirring and inlets for argon and the monomer. MAO and MMAO-7 were used as cocatalyst in an Al/Zr = 500 (MMAO-7 and MAO) or Al/Zr = 2000 (MAO). For each experiment, a mass of catalyst system corresponding to 10^{-5} mol l^{-1} of Zr was suspended in 0.01 dm^3 of toluene and transferred into the reactor under argon. The polymerizations were performed at atmospheric pressure of ethylene at 60 °C temperature for 30 min. Acidified (HCl) ethanol was used to quench the processes, and reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at room temperature.

2.4. Polyethylene characterization

Molar masses and molar mass distributions were investigated with a Waters CV plus 150C high-temperature GPC instrument, equipped with viscometrical detector, optic differential refractometer, and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limit 1×10^7 for polystyrene. 1,2,4-trichlorobenzene was used as solvent, at a flow rate of 1 $cm^3 min^{-1}$. The analyses were performed at 140 °C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low-density polyethylenes and polypropylenes.

Polymer melting points (T_m) and crystallinities (χ_c) were determined on a Polymer Laboratories DSC differential scanning calorimeter calibrated with Indium, using a heating rate of 10 °C min^{-1} in the temperature range 30–150 °C. The heating cycle was performed twice, but only the results of the second scan are reported, because the former is influenced by the mechanical and thermal history of the samples.

Residual metal content was determined by X-ray fluorescence (XRF) spectroscopy, using Rigaku (RIX 3100) wavelength dispersive X-ray fluorescence spectrometer, with a rhodium tube operated at 50 kV and 70 mA, a LiF 200 crystal, and a scintillation counter. Samples were pressed as homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems.

3. Results and discussion

Silica surface is covered with silanol groups (Si–OH) and adsorbed H_2O molecules. When silica is submitted to thermal treatment, H_2O molecules are removed and silanol

Table 1
Zr content immobilized on MAO-modified silicas (nd: not determined)

Initial impregnated MAO (wt% Al/SiO_2)	Immobilized $(nBuCp)_2ZrCl_2$	
	(wt% Zr/SiO_2)[b]	(wt% Al/SiO_2)[c]
0.0	0.4	0.0
0.5	1.0	0.5
2.0	1.5	1.8
4.0	1.5	3.9
8.0	1.2	nd
10.0	1.2	9.8
15.0	1.1	nd
20.0	0.6	nd
24.4[a]	1.0	17.8

[a] WITCO: MAO-commercial silica;
[b] determined by RBS;
[c] determined by ICP-OES.

groups density is decreased by intermolecular reaction. After treatment at higher temperatures (450 °C) the silica surface presents mainly isolated and, to a lesser extent, geminal hydroxyl groups and surface siloxane bridges [19]. Zirconocene reacts with silica surface through the silanol groups. Isolated hydroxyl groups generate active species, while geminal hydroxyl groups bidentate species, which are inactive for polymerization. Similar reactions take place when MAO is reacted with thermally or chemically pretreated silica, evolving methane. The chemically modified support is then suitable to subsequent addition of the metallocene catalyst precursor in a second step [20]. It is worth mentioning recent works from Duchateau et al. [21,22] who has employed cuboctametric silsesquioxane mono(silanol) to mimic the surface of partially dehydroxylated silica and to model the surface reaction between metallocene and silica, as well as reactivation of mono- and bidentate Si–O–Zr species by MAO.

Table 1 reports the resulting zirconocene content determined by RBS expressed in terms of wt% Zr/SiO_2. Metal content remained comprised between 0.4 and 1.5 wt% Zr/SiO_2, being the highest value reached in the 2.0–4.0 wt% Al/SiO_2 range. Since Si and Al cannot be resolved by RBS, Al content was determined by ICP-OES after sample acid digestion. Roughly no Al leaching reaction seems to be significant after zirconocene grafting under our experimental conditions for supports containing up to 10.0 wt% Al/SiO_2. In the case of commercial MAO-modified silica we observed a reduction of ca. 25% of the initial Al content.

Fig. 1 shows the catalyst activity of $(nBuCp)_2ZrCl_2$ supported on MAO-modified silicas, containing 0.5–20.0 wt% Al/SiO_2. For comparative reasons, data concerning the immobilization of the metallocene on bare silica (0.0 wt% Al/SiO_2) were also included. All the systems were shown to be active in ethylene polymerization using external MAO as cocatalyst. For Al/Zr = 2000, the catalyst activity was roughly higher for all catalyst using MAO-modified silicas in comparison to that employing bare silica as support. Besides, catalyst activity remained constant through the studied range.

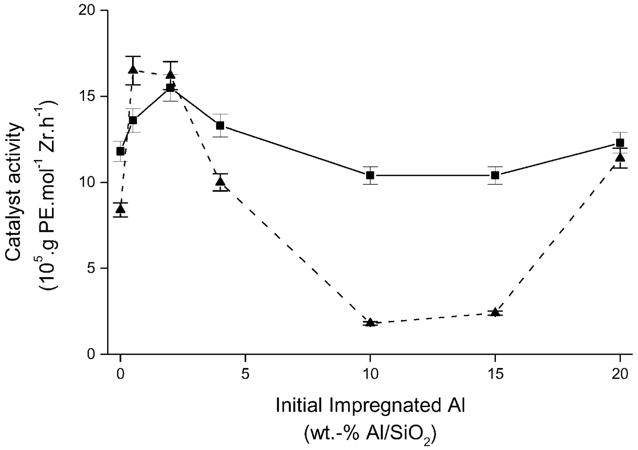

Fig. 1. Influence of the initial impregnated Al on ethylene homopolymerization activity using supported $(nBuCp)_2ZrCl_2$. Polymerization reactions were performed in toluene under 1 atm of ethylene pressure at 60 °C with $[Zr] = 10^{-5}$ mol l^{-1}. Al/Zr (▲) 500 and (■) 2000 (external MAO).

In the case of Al/Zr = 500, catalysts were shown to be more sensible to the external MAO amount. Catalysts prepared with supports containing up to 2.0 wt% Al/SiO_2 presented increasing catalyst activity, being comparable to that observed in the case of Al/Zr = 2000. In other words, for such systems, the Al/Zr ratio is reduced significantly, keeping high activity. For supported catalyst systems, this behavior has been attributed to steric effect played by silica surface which partially or completely inhibit bimolecular deactivation processes [23]. However, it decreased for systems containing up to 15.0 wt% Al/SiO_2. Surprisingly, catalysts prepared with 20.0 wt% Al/SiO_2 presented high activity. It is worth noting that commercial MAO contains ca. 20.0 wt% of Al content as TMA; i.e. using 20.0 wt% of Al of the MAO, ca. of 4.0 wt% Al/SiO_2 corresponds to TMA species. It was already reported that the supported MAO activator can also to be prepared by in situ hydrolysis of TMA with hydrated silicas containing between 10 and 50 wt% absorbed water [24,25]. Therefore, it is likely that under such conditions different surface species might be generated involving in situ MAO formation and TMA reaction with silanol groups. Besides, we cannot neglect the possibility of leaching under such conditions, where the extremely high amount of MAO on the surface might lead to loose surface species. In solution, these species would act as homogeneous catalyst. Nevertheless, the exhibited activities were shown to be very lower in comparison to those of the homogeneous system [26]. Under the same experimental conditions $(nBuCp)_2ZrCl_2$ in Al/Zr = 2000 produced 73.4×10^5 g PE mol^{-1} Zr h^{-1}. Comparatively, in the case of homogeneous metallocene, the reaction was practically instantaneous, while in the supported ones, there was roughly 10 min of induction time. In homogeneous systems, every site is potentially active, while in supported systems some surface generated species are inactive. Besides silica

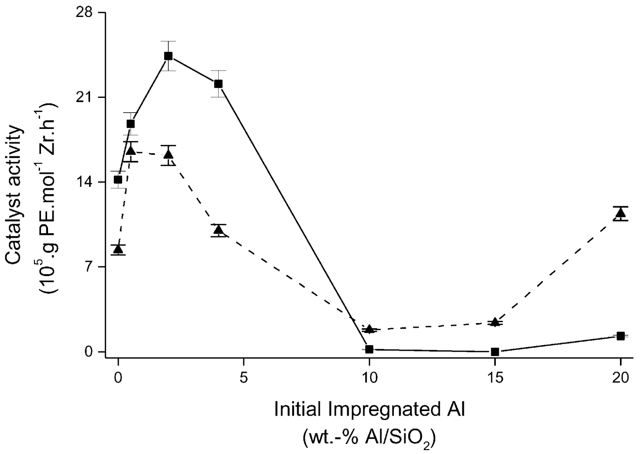

Fig. 2. Influence of the initial impregnated Al on ethylene homopolymerization activity using supported $(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$. Polymerization reactions were performed in toluene under 1 atm of ethylene pressure at 60 °C with $[\mathrm{Zr}] = 10^{-5}$ mol l^{-1}. (▲) MAO and (■) MMAO cocatalyst were used ($\mathrm{Al/Zr} = 500$).

surface plays the role of a huge ligand which renders difficult the access of the monomer to the active site.

The immobilization of zirconocene on MAO-modified silicas with different Al content seems to generate different active species for polymerization reactions. Species generated in Al content below the saturation level (8–10 wt% Al/SiO$_2$) [13] present a different behavior than those generated in Al content above the saturation level. As already mentioned, external MAO has cocatalyst and scavenger functions in polymerization [6–9]. In reactions performed with $\mathrm{Al/Zr} = 2000$, it seems that the amount of MAO is enough to stabilize active sites and to remove impurities. The catalyst activity remained almost roughly constant for all systems. This behavior was not observed when the polymerization was carried on with $\mathrm{Al/Zr} = 500$. The catalyst activity for Al content below the saturation level is higher than that above the saturation level, except for 20.0 wt% Al/SiO$_2$ system. It is possible that unstable Al surface species are generated for Al content above the saturation level and this Al/Zr ratio is not enough to stabilize them.

Table 2
Catalyst activity using hexane as solvent and MMAO-7 as cocatalyst (polymerization conditions: $T = 60$ °C; $[\mathrm{Zr}] = 10^{-5}$ mol l^{-1}; cocatalyst: MMAO-7; $\mathrm{Al/Zr} = 2000$; solvent: hexane; ethylene pressure: 1 atm; reaction time: 30 min)

Initial impregnated Al (wt% Al/SiO$_2$)	Catalyst activity (10^5 g PE mol^{-1} Zr h^{-1})
0.5	3.8
2.0	4.8
4.0	0.6
10.0	Traces
20.0	Traces

Catalyst activity was also evaluated for $\mathrm{Al/Zr} = 500$ using MMAO-7 as cocatalyst. MMAO-7 is soluble in aliphatic solvent and ca. of 20% of the R–Al groups are not methyl-aluminum groups [27]. Fig. 2 shows the results for ethylene polymerization. For comparative reasons, data concerning MAO as cocatalysts were also included. For both cocatalysts, catalyst activity was shown to obey roughly the same trend. As in the previous case the catalyst activity was shown to be higher for systems containing Al content below saturation level than that containing Al content above the saturation level. For Al contents lower than saturation level, the resulting supported catalysts were shown to be more active when MMAO-7 was employed as cocatalyst. On the other hand, for Al content higher than 10.0 wt% Al/SiO$_2$, MAO was shown to exhibit a better performance as cocatalyst. Table 2 shows the catalyst activity using hexane as solvent and MMAO-7 as cocatalyst. Catalyst activity for systems with Al content below the saturation level is higher than that with Al content above saturation level, where only traces were obtained. Comparing data of Table 2 to those of Fig. 2, in spite of both different Al/Zr ratios (500 × 2000) and polymerization solvent (hexane × toluene), we observe the same trend in both cases. Although MMAO-7 being more soluble in hexane than that in toluene, the catalyst activity in hexane was shown to be lower than in toluene, even if Al/Zr is different.

The resulting polymers were characterized by GPC, DSC, and XRF measurements. Table 3 reports on properties of polymers produced with different catalyst systems, characterized by GPC and DSC.

We observe that for polymers obtained with external MAO ($\mathrm{Al/Zr} = 2000$), the molecular weight remained roughly constant for all MAO-modified silicas with different Al contents. But the molecular weight for polymers obtained in the $\mathrm{Al/Zr} = 500$ is higher than that using $\mathrm{Al/Zr} = 2000$. These results might suggest that MAO can act as a chain transfer agent, as already reported in the literature [28]. The molecular weight of polymers obtained with external MMAO-7 is higher than that in the case of external MAO, keeping the same Al/Zr molar ratio. These results suggest that MMAO-7 might be a poorer chain transfer agent than MAO. For $\mathrm{Al/Zr} = 500$, the resulting polymer molecular weight produced with MAO-modified silicas with Al content above the saturation level is higher than that produced with Al content below the saturation level. It seems that Al content on surface influences on polymer molecular weight when lower amount of external MAO ($\mathrm{Al/Zr} = 500$) is employed. Thus, catalyst sites generated below and above saturation level produce polymers with different molecular weight. Comparing heterogeneous and homogeneous systems in $\mathrm{Al/Zr} = 2000$, we can observe that the polymer obtained with homogeneous system has lower molecular weight than those obtained with heterogeneous systems. This fact could be attributed to the blocking of one of the sides of the active site by the support, hindering the deactivation step. In other words, the β-elimination transfer reaction between two metallocene centers is hindered, resulting in a larger growth of the polymer chain, and therefore in a higher molecular weight [29].

Table 3
Effect of the impregnated Al on the properties of polyethylenes (polymerization conditions: $T = 60$ °C; $[Zr] = 10^{-5}$ mol l^{-1} (toluene); ethylene pressure: 1 atm; reaction time: 30 min)

Initial	M_w (10^5 g mol^{-1})			M_w/M_n			T_m (°C)			Crystallinity (%)		
Impregnated Al (wt% Al/SiO$_2$)	MAO 2000	MAO 500	MMAO 500	MAO 2000	MAO 500	MMAO 500	MAO 2000	MAO 500	MMAO 500	MAO 2000	MAO 500	MAO 500
(nBuCp)$_2$ZrCl$_2$	0.9	–	–	2.5	–	–	135	–	–	48	–	–
0.0	1.2	2.1	2.6	2.5	2.2	2.1	137	134	134	63	20	46
0.5	1.4	1.3	2.2	2.6	2.4	2.1	139	135	134	61	46	48
2.0	1.2	1.8	2.7	3.5	2.1	2.0	134	135 141	134	65	40	46
4.0	1.1	1.6	2.2	2.8	2.4	3.0	135	136 141	134	65	44	42
10.0	1.9	2.1	3.6	2.0	2.1	3.4	133	136 141	136	54	35	34
15.0	1.5	2.1	–	2.5	2.0	–	137	135 139	–	58	61	–
20.0	1.2	2.0	3.2	2.7	2.1	3.2	138	133 141	135	61	28	33
24.4[a]	1.4	2.4	3.6	2.3	2.2	2.7	134	137 141	136	56	32	45

[a] WITCO: MAO-commercial silica.

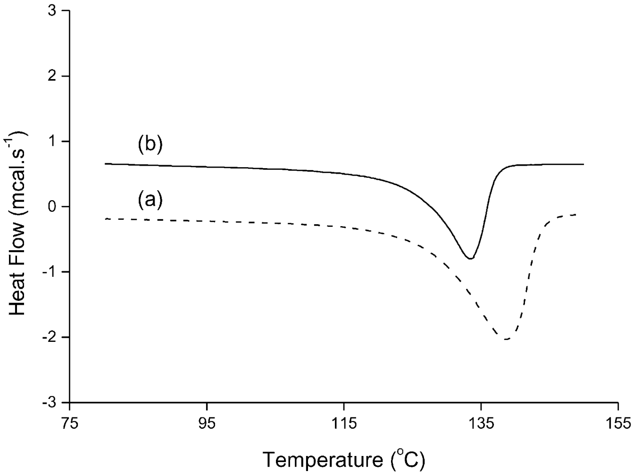

Fig. 3. DSC melting curves of ethylene polymers produced with supported $(n\text{BuCp})_2\text{ZrCl}_2$ on MAO-modified silicas containing (a) 0.5 wt% Al/SiO_2 and (b) 10.0 wt% Al/SiO_2. MAO cocatalyst was used (Al/Zr = 2000).

The molecular weight distribution remained between 2.0 and 3.5. For systems containing aluminum content higher than 4.0 wt% Al/SiO_2, molecular weight distribution is higher for polymers obtained with external MMAO-7, suggesting a more heterogeneous nature of the catalyst sites.

Concerning DSC analysis, polymers obtained with external MAO in Al/Zr = 2000 presented only one melting point peak. Fig. 3 shows T_m measured for polymers obtained with supported metallocene presenting Al content below and above saturation level. For polymers obtained with catalyst using 0.5 wt% Al/SiO_2 support, T_m is 139 °C and for those obtained with 10.0 wt% Al/SiO_2 one, T_m is 133 °C.

Polymers obtained with Al/Zr = 500 present different behavior. Fig. 4 shows T_m measured for polymers obtained with Al content below and above saturation level. We observe that the T_m of the polymer obtained with 0.5 wt% Al/SiO_2 support is 135 °C. Under same polymerization and characterization conditions we observe that there are two peaks for the polymers produced with 10.0 wt% Al/SiO_2 (136 and 141 °C) and 20.0 wt% Al/SiO_2 (133 and 141 °C). It seems that the zirconocene species generated with MAO-modified silicas, containing Al content below and above the saturation level, produce different polymeric species. Although resulting polymers show different melting point, their molecular weight is quite similar (Table 3), showing no evidence of bimodality. Nevertheless we cannot neglect the possibility of nucleation effects. In fact, X-ray photoelectronic spectroscopy (XPS) measurements showed the presence of two aluminum species for contents higher than 10.0 wt% Al/SiO_2 [30] which could partially explain the existence of these two peaks. Anyway if these two signals in the thermograms are arising from different surface species, these might be sensible to the external MAO concentration. The possibility of branching are also under investigation.

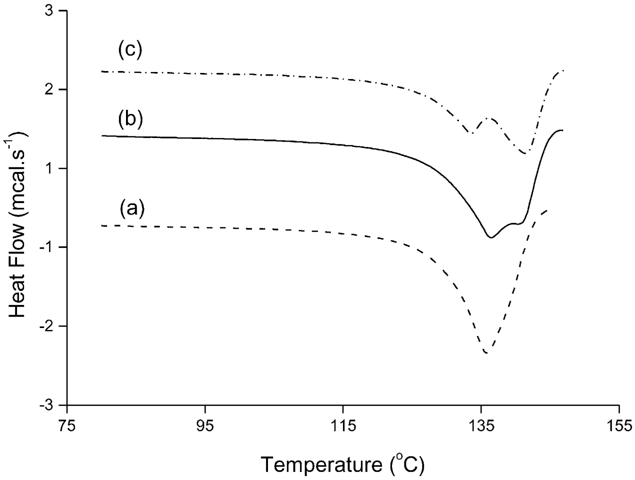

Fig. 4. DSC melting curves of ethylene polymers produced with supported $(n\text{BuCp})_2\text{ZrCl}_2$ on MAO-modified silicas containing (a) 0.5 wt% Al/SiO_2 (b) 10.0 wt% Al/SiO_2 and (c) 20.0 wt% Al/SiO_2. MAO cocatalyst was used (Al/Zr = 500).

The immobilization of $(n\text{BuCp})_2\text{ZrCl}_2$ catalyst on silica seems to influence polymer crystallinity, since polymer obtained with homogeneous system presents lower crystallinity than those obtained with heterogeneous systems (Al/Zr = 2000). For both external MAO and MMAO-7, the crystallinity of the polymers obtained in Al/Zr = 500 is higher than that obtained with external MAO in Al/Zr = 2000. It seems that the cocatalyst amount influences the crystallinity of the polymers.

Residual metal content in polymers produced by metallocene catalysts were already determined by RBS [31] and XPS [32]. In the present study, we performed elementary analysis using XRF spectroscopy. Fig. 5 shows a typical XRF spectrum of these polymers. Residual Zr content was lower than the limit detection level for this element in this technique. Nevertheless, Al content could be measured. Table 4 reports the residual Al content for two polymer produced under different Al/Zr ratio. We observe that

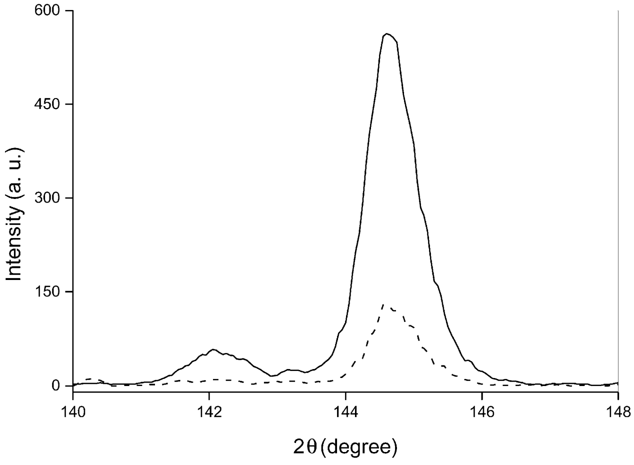

Fig. 5. XRF spectrum for polymers obtained with different Al/Zr ratio: (- - -) Al/Zr = 500 and (—) Al/Zr = 2000.

Table 4
Residual Al content in the polymers obtained with external MAO as cocatalyst (polymerization conditions: catalyst containing 0.5 wt% Al/SiO_2; $T = 60\,°C$; $[Zr] = 10^{-5}\ mol\ l^{-1}$ (toluene); ethylene pressure: 1 atm; reaction time: 30 min)

Al/Zr	Al (ppm)	Catalyst activity (10^5 g PE mol^{-1} Zr h^{-1})
500	1150	16.5
2000	6320	13.6

residual Al content for polymers obtained with Al/Zr = 2000 is higher than that obtained with Al/Zr = 500. We cannot neglect the fact that the catalyst activity was shown to be lower, which can lead to higher residual metal content.

4. Conclusion

MAO-modified silicas containing different amounts of Al afford different catalyst surface species by zirconocene grafting. Active sites with different stability are generated for Al content below and above the saturation level (7.0–8.0 wt% Al/SiO_2). The nature and Al/Zr ratio of cocatalyst used on the polymerization reaction influences on catalyst activity.

Polymers produced with Al/Zr = 500 presented higher molecular weight than those produced with Al/Zr = 2000. The molecular weight for polymers produced with MMAO-7 is higher than those obtained with MAO. It seems that MMAO-7 is a poorer chain transfer agent than MAO.

Molecular weight distributions remain between 2.0 and 3.5. In general, molecular weight distribution for MMAO-7 is higher than for MAO. It indicates that the nature of the catalyst species is slightly more heterogeneous than in the case of MAO.

Two melting points are observed for polymers produced with MAO-modified silicas with Al content higher than 2.0 wt% Al/SiO_2 and Al/Zr = 500 (MAO).

Acknowledgements

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References

[1] Hlatky GG. In: Scheirs J, Kaminsky W, editors. Metallocene-based polyolefins, West Sussex: Wiley, vol. 1. 2000. p. 201–18.
[2] Hlatky GG. Chem Rev 2000;100:1347–76.
[3] Ban HT, Arai T, Ahn C-H, Uozumi T, Soga K. Curr Trends Polym Sci 1999;4:47–60.
[4] Ribeiro MR, Deffieux A, Portela MF. Ind Engng Chem Res 1997;36:1224–8.
[5] Sinn H, Schimel I, Ott M, Thienen N, von Harder A, Hagendorf W, Heitmann B, Haupt E. In: Kaminsky W, editor. Metalorganic catalysts for synthesis and polymerization. Heidelberg: Springer, 1999. p. 105–22.
[6] Babushkin DE, Semikolenova NV, Panchenko VN, Sobolev AP, Zakharov VA, Talsi EP. Macromol Chem Phys 1997;198:3845–54.
[7] Tritto I, Méalares C, Sacchi MC, Locatelli P. Macromol Chem Phys 1997;198:3963–77.
[8] Chien JCW, Sugimoto R. J Polym Sci A, Polym Chem 1991;29:549–57.
[9] Sinn H, Kaminsky W, Vomman H-J, Woldt R. Angew Chem, Int Ed Engl 1980;19:390.
[10] Soga K, Kaminaka M. Makromol Chem 1993;194:1745–53.
[11] Panchenko VN, Semikolenova NV, Danilova IG, Paukshtis EA, Zakharov VA. J Mol Catal A: Chem 1999;142:27–37.
[12] Bartram ME, Michalske TA, Rogers Jr. JW. J Phys Chem 1991;95:4453–63.
[13] Dos Santos JHZ, Dorneles S, Stedile FC, Dupont J, Forte MMC, Baumvol IJR. Macromol Chem Phys 1997;198:3529–37.
[14] Dos Santos JHZ, Krug C, Rosa MB, Stedile FC, Dupont J, Forte MC. J Mol Catal A: Chem 1999;139:199–207.
[15] Haag MC, Krug C, Dupont J, Galland GB, Dos Santos JHZ, Uozumi T, Sano T, Soga K. J Mol Catal A: Chem 2001;169:275–87.
[16] Stedile FC, Dos Santos JHZ. Nucl Instrum Meth B 1998;136-139:1259.
[17] Stedile FC, Dos Santos JHZ. Phys Status Solidi 1999;173:123.
[18] Dos Santos JHZ, Ban TH, Teranishi T, Uozumi T, Sano T, Soga K. J Mol Catal A: Chem 2000;158:541–57.
[19] Vansant EF, van der Voort P, Vrancken KC. Stud Surf Sci 1995;93: Chapter 3.
[20] Chen Y-X, Marks TJ. Chem Rev 2000;100:1391–434.
[21] Duchateau R, Abbenhuis HCL, Van Santen RA, Theile SK-H, van Tol MFH. Organometallics 1998;17:5222.
[22] Skowronska-Ptasinska MD, Duchateau R, van Santen RA, Yap GPA. Organometallics 2001;20:3519–30.
[23] Chen Y-X, Rausch MD, Chien JCW. J Polym Sci Part A, Polym Chem 1995;33:2093–108.
[24] Chang M. US Patent (Exxon Chemicals Co) 5,008,228, 1991; 4,935,397; 4,914,253; 4,912,075, 1990.
[25] Hermann H-F, Backmann B, Spaleck W. US Patent (Hoechst AG) 5,578,537, 1996.
[26] Dos Santos JHZ, Rosa MB, Krug C, Stedile FC, Haag MC, Dupont J, Forte MC. J Polym Sci, Part A: Polym Chem 1999;37:1987–96.
[27] Procedures of the Akzo Bulletin, February 1997.
[28] Byun D-J, Shin D-K, Kim SY. Macromol Rapid Commun 1999;20:419–22.
[29] Kaminsky W, Renner F. Makromol Chem, Rapid Commun 1993;14:239–43.
[30] Bianchini D, Dos Santos JHZ, Uozumi T, Sano T, Soga K. Submitted for publication.
[31] Haag MC, Dos Santos JHZ, Stedile FC, Dupont J. J Appl Polym Sci 1999;74:1997–2003.
[32] Dos Santos JHZ, Uozumi T, Teranishi T, Sano T, Soga K. Polymer 2001;42:4517–25.