Linear low-density polyethylene synthesis promoted by homogeneous and supported catalysts

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Abstract: Linear low-density polyethylenes (LLDPEs) were obtained through the copolymerization of ethylene with 1-hexene using $(nBuCp)_2ZrCl_2$ co-catalyzed by methylaluminoxane (MAO). For comparative reasons, the same metallocene was supported on silica ($0.85\,wt\%Zr/SiO_2$) by grafting. The copolymerizations were performed in toluene, at 1.6 bar of ethylene, 60 °C and in an Al/Zr molar ratio of 2500. The 1-hexene concentration varied from 0 to $0.50\,mol\,L^{-1}$. The resulting copolymers were characterized by GPC, DSC and ^{13}C NMR.

The catalytic activities remained close to 2×10^7 and 7×10^6 $(g\,pol)\,mol\,Zr^{-1}\,bar^{-1}\,h^{-1}$ for the homogeneous and supported systems, respectively. For the homogeneous system, the catalytic activity and the comonomer incorporation increased with the 1-hexene concentration up to $0.30\,mol\,l^{-1}$. Higher comonomer concentrations led to a decrease in catalytic activity in the case of the homogeneous system. The highest comonomer incorporation (6.3 mol%) was achieved with $0.50\,mol\,l^{-1}$ of 1-hexene in the reaction medium. The supported system afforded lower comonomer incorporations (maximum 4.0 mol%). The effect of the 1-hexene incorporation can also be evaluated through the polymer properties, namely, crystallinity, melting temperature, molecular weight and polydispersity.
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Keywords: linear low-density polyethylene; LLDPE; copolymerization; metallocene catalyst; 1-hexene; supported catalyst

INTRODUCTION

The development of metallocene catalysts activated by methylaluminoxane (MAO) afford a combination of high activity with excellent stereoregularity and comonomer distribution producing polyolefins which are inaccessible through heterogeneous Ziegler–Natta catalysts.[1] Moreover, metallocenes permit the copolymerization of ethylene with α-olefins, forming linear low-density polyethylenes (LLDPEs), which, because of the short branching from the incorporated α-olefins, present lower melting points, lower crystallinities and lower densities, making films formed from these materials more flexible and better processable.[2] These copolymers have a great industrial interest and can find applications in packing, in shrink films, in cable coatings, just to mention a few.

Nevertheless, these soluble catalysts are unsuitable for industrial applications, where heterogeneous catalyst systems are required for gas-phase and slurry polymerization processes or for large-scale polymer production. One approach to overcome this problem consists of the heterogenization of such catalysts, by supporting them on inorganic carriers. Several routes, employing different supports, are described in the scientific and patent literature (see, for example, refs 3–6). The majority of these preparations have involved silica supports.

Among the metallocene complexes, some patents report the properties of supported $(nBuCp)_2ZrCl_2$ in ethylene homo- and copolymerization. Properties such as high melt tension polyethylene[7] or reduction of fouling and sheeting in the reactor during ethylene homopolymerization[8] are claimed with supported $(nBuCp)_2ZrCl_2$ on modified silicas. Concerning copolymerizations, for instance, linear ethylene-1-hexene copolymer, the applicability of which was tested in retort containers for medical and food packaging purposes because their melting point (T_m) is higher than the sterilization temperature, was obtained with a catalyst resulting from the mixture of silica support, $(nBuCp)_2ZrCl_2$, MAO and alkylaluminium compounds.[9] Bimodal molecular weight

distribution ethylene-1-hexene copolymers were obtained with solid catalysts prepared from the combination of dibutylmagnesium, titanium dichloride, MAO and $(n\text{BuCp})_2\text{ZrCl}_2$.[10] Ethylene-1-butene copolymers were also produced from MAO-modified silica impregnated with $(n\text{BuCp})_2\text{ZrCl}_2$, co-catalyzed by isoBu$_3$Al.[11]

In previous works,[12,13] we studied the influence of several parameters in the immobilization of $(n\text{BuCp})_2\text{ZrCl}_2$ on silica, taking into account the grafted metal content, together with the ethylene polymerization activity. Based on a series of results we were able to develop an optimized $(n\text{BuCp})_2\text{ZrCl}_2$ supported catalyst. In other studies,[14–19] we investigated some experimental aspects dealing with ethylene-α-olefin copolymerizations, employing soluble metallocene catalysts activated by MAO.

In the present work, we have investigated the catalytic activity of soluble and silica-supported $(n\text{BuCp})_2\text{ZrCl}_2$ in the ethylene-1-hexene copolymerization using the optimized conditions previously studied. These studies permitted the production of copolymers with better incorporations of 1-hexene than the copolymerizations described before with this catalyst.[26] The resulting copolymers were characterized by gel permeation chromatography (GPC), carbon 13 nuclear magnetic resonance (^{13}C NMR) and differential scanning calorimetric (DSC) analysis.

EXPERIMENTAL
Materials (chemicals)
Grace 948 silica ($255\,\text{m}^2\text{g}^{-1}$) was activated under vacuum ($<10^{-4}$ mbar) for 16 h at 450 °C. The support was then cooled at room temperature under dynamic vacuum and stored under dried argon. MAO (kindly supplied by Witco, 10.0 wt% toluene solution, 1.7 Al as TMA, average molar mass $900\,\text{g mol}^{-1}$) and $(n\text{BuCp})_2\text{ZrCl}_2$ (Witco) were used without further purification. Ethylene (Copesul Co) and argon were deoxygenated and dried through columns of activated molecular sieve (13 Å) before use. Toluene (purum grade) and 1-hexene (Aldrich) were deoxygenated and dried by standard techniques before use.

Preparation of supported catalysts
All experiments were performed under inert atmosphere using the Schlenk technique. A toluene solution of $(n\text{BuCp})_2\text{ZrCl}_2$ was added to 1.0 g of pretreated silica (Grace 948), in a concentration corresponding to 1.5 wt% Zr/SiO$_2$, and the mixture was stirred for 1 h at 80 °C. The slurry was filtered through a sinter using a vacuum and argon line. The resulting solid was washed with 12×2.0 mL of toluene and dried under vacuum for 4 h. The resultant catalysts contained 0.85 wt% Zr/SiO$_2$ determined by Rutherford backscattering spectrometry.[12,13]

Polymerization
Ethylene copolymerizations were performed in 0.3 L

of toluene in a 1.0 L Pyrex glass reactor connected to a constant temperature circulator, equipped with a mechanical stirrer, and inlets for argon and the monomer. MAO was used as co-catalyst in an Al/Zr molar ratio of 2500. For each experiment 2×10^{-6} mol of Zr was suspended in toluene and transferred into the reactor under argon. The polymerizations were performed at 1.6 bar pressure of ethylene at 60 °C for 30 min. The reagents were introduced into the reactor in the following order: toluene, MAO, comonomer, monomer and catalyst. 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.

Polymer characterization
Polymer melting points (T_m) were determined on a TA 2100 Thermal Analyst differential scanning calorimeter calibrated with indium, using a heating rate of $10\,°\text{C min}^{-1}$ in the temperature range 30–160 °C. The heating cycle was performed twice, but only the results of the second scan are reported. Molar masses and molar mass distributions were investigated with a Waters high-temperature GPC instrument, CV plus system, Model 150C, equipped with viscosimetric detector, optic differential refractometer and three Styragel HT type columns (HT3, HT4 and HT6) with an exclusion limit of 1×10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of $1\,\text{mL min}^{-1}$. The analyses were performed at 140 °C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and then universally with linear low density polyethylenes and polypropylenes. ^{13}C NMR was employed to determine the composition and sequence distribution of the copolymers according to the literature procedures.[20] The ^{13}C NMR spectra were recorded between 80 and 90 °C using a Varian 300 spectrometer operating at 75 MHz. Sample solutions of the copolymer were prepared in *o*-dichlorobenzene and benzene-d_6 (20 v/v). Spectra were taken with a 74 ° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. In these conditions the spectra are 90% quantitative if only carbon atoms that have a relaxation time (T_1) inferior to 2.0 s are taken into account.[21]

RESULTS
Figure 1 shows the activity of $(n\text{BuCp})_2\text{ZrCl}_2$, homogeneous and supported on silica. By comparing both sets of each system, we can observe that the catalytic activities were higher in the case of the homogeneous catalytic system. Moreover, in both homogeneous and supported systems, the ethylene-1-hexene copolymerizations presented higher catalytic activities than the ethylene homopolymerization. This behaviour is known as the comonomer effect, which is typical for Ziegler–Natta catalysts, and has been also previously
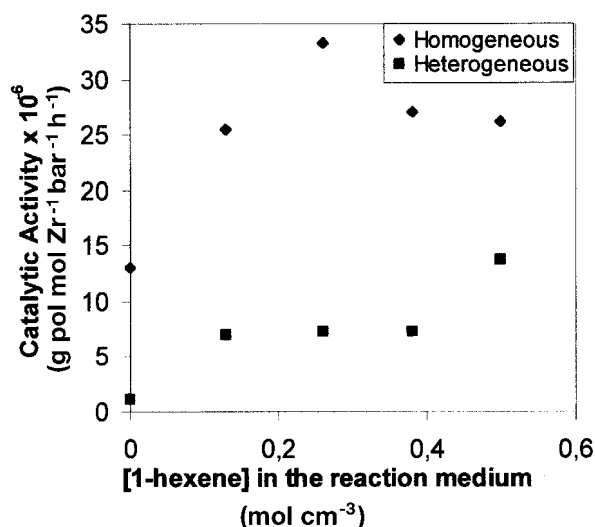
Figure 1. Trends of homo-polymerization and copolymerization activity of(*n*BuCp)₂ZrCl₂, homogeneous and supported systems, obtained with different 1-hexene concentrations.
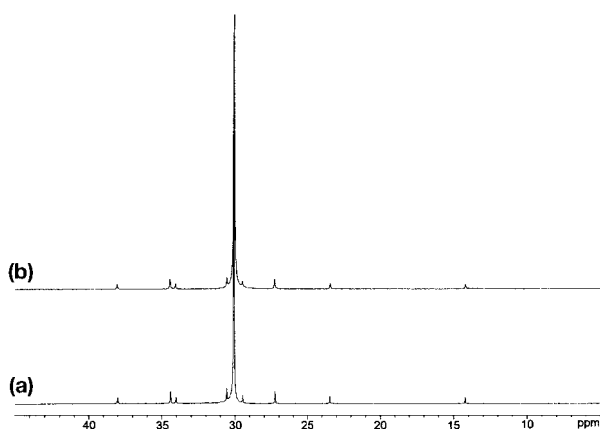

Figure 2. ¹³C NMR spectra of ethylene-1-hexene copolymer obtained with homogeneous (*n*BuCp)₂ZrCl₂ (curve a) and (*n*BuCp)₂ZrCl₂/SiO₂ (curve b). Initial comonomer concentration 0.26 mol L⁻¹.

reported for other MAO-activated zirconocenes.[14,16,18,19,22–25]

The increase of comonomer concentration in the reaction medium seems not to influence greatly the copolymerization catalytic activity for the lower 1-hexene concentrations. However, concentrations higher than $0.38\,\mathrm{mol\,L^{-1}}$ seem to lower the catalyst activity in the case of homogeneous systems. Different behaviour can be noted for the supported systems, where higher comonomer concentration leads to an increase in the activity.

The comonomer composition was obtained by ¹³C NMR spectroscopy. Figure 2 shows a typical ¹³C NMR spectrum for copolymer produced by homogeneous (Fig 2, curve a) and supported (Fig 2, curve b) catalyst systems, using the same initial comonomer concentration $(0.26\,\mathrm{mol\,L^{-1}})$ present in the reaction medium.

Table 1 shows the triad distributions, and the copolymer 1-hexene and ethylene contents for each 1-hexene concentration used in the reaction medium. Also shown is the ethylene (n_E) and 1-hexene (n_H) average sequence length and the ethylene (r_E) and 1-hexene (r_H) reactivity ratios calculated from ¹³C NMR sequence data.[17] These results show that, (a) the soluble catalytic system results in higher incorporation than the heterogeneous one; (b) the 1-hexene content in the copolymer increases with higher concentrations of comonomer in the reaction medium, contrary to the results presented in the literature.[26] However, for the supported system this trend is less accentuated. An augmentation of four times in 1-hexene concentration in the reaction medium (from 0.13 to $0.50\,\mathrm{mol\,L^{-1}}$) leads to an increase of the comonomer incorporation of almost three times in the soluble system, and of about two times in the heterogeneous system.

The properties of the polymers obtained by the two sets of catalytic systems are shown in Table 2. The increase of the 1-hexene incorporation in the polymer chain leads to a reduction in the crystallinity (X_c). Even a small amount of comonomer incorporation

Table 1. Triad distribution, comonomer average sequence length, reactivity ratios and copolymer 1-hexene and ethylene contents for each 1-hexene concentration used in the reaction medium

[H] in the medium (mol L⁻¹)	[HHH] (%)	[EHH] (%)	[EHE] (%)	[EEE] (%)	[HEH] (%)	[HEE] (%)	[H] (%)	[E] (%)	n_E	n_H	r_E	r_H
Homogeneous catalytic system												
0.13	0	0	2.3	93.0	0	4.7	2.3	97.7	42	1	48	≈0
0.26	0	0	3.0	91.0	0	6.0	3.0	97.0	32	1	73	≈0
0.38	0	0	4.5	86.4	0	9.0	4.5	95.5	21	1	70	≈0
0.50	0	0	6.3	80.9	0, 2	12.6	6.3	93.7	15	1	62	≈0
Supported catalytic system												
0.13	0	0	2.1	93.7	0	4.2	2.1	97.9	47	1	54	≈0
0.26	0	0	2.4	92.7	0	4.9	2.4	97.6	40	1	92	≈0
0.38	0	0	3.6	89.1	0	7.2	3.6	96.4	27	1	89	≈0
0.50	0	0.2	3.8	88.2	0.30	7.6	4.0	96.0	24	1	105	0.002

Table 2. Properties of the polymers obtained by the two sets of catalytic systems, homogeneous and supported

[H] (%)	Melting point (°C)	Crystallinity (%)	M_w ($gmol^{-1}$)	$M_w M_n$
Homogeneous catalytic system				
0	137.6	53	159 000	2.4
2.3	118.8	34	120 000	2.8
3.0	115.1	33	127 000	3.0
4.5	104.5	32	47 200	2.5
6.3	96.0	9	27 700	1.9
Supported catalytic system				
0	139.5	58	381 800	2.6
2.1	118.9	40	203 000	2.3
2.4	112.7	32	150 000	2.3
3.6	108.8	30	130 000	2.2
3.8	106.8	25	73 000	1.8

cause a noticeable reduction in crystallinity as we can observe when comparing the ethylene homopolymer (53%) to the resulting copolymer containing 2.3 mol% of 1-hexene, for instance where X_c is reduced considerably (34%).

A similar trend can be observed in the melting point (T_m) of the copolymers. As the 1-hexene incorporation rises, the loss of crystallinity causes a reduction of the melting temperature of the material. It is worth mentioning that these reductions are less important in the set of supported systems because of the lower comonomer incorporation in this case.

Regarding the molecular weight, according to Table 2 the copolymers, together with the case of polyethylene, obtained with the supported catalyst present higher molecular weight. In both cases the molecular weight decreases abruptly above 4.0% of 1-hexene incorporated. According to Table 2, the polydispersity of the copolymers remained close to 2.0 which is typical for single site catalysts. As was shown in previous work,[15] the polydispersity becomes narrower with increasing amounts of comonomer incorporated.

DISCUSSION

The immobilization of (nBuCp)$_2$ZrCl$_2$ on silica lead to a less active catalytic system. According to Fig 1, the activity of (nBuCp)$_2$ZrCl$_2$/SiO$_2$ is almost four times lower when compared to the homogenous system. This has already been discussed in the literature[27] and can be explained taking into account that in the supported catalyst preparation, during the grafting reaction, different adsorptions might take place, leading to different sites on the surface, some of which are inactive for polymerization. Therefore not all the Zr present in the catalyst is necessarily an active species. It is worth mentioning that completely different active species are generated when the metallocene is directly grafted on the silica, compared to those formed in the case of MAO-modified silicas. The former species are rather active in ethylene

polymerization, and such systems exhibit a catalytic activity, which is nearly half that obtained with MAO-mediated supported catalysts.[28] Chien and He[29] reported that [Ind]$_2$ZrCl$_2$ was not retained directly on the silica surface, leading consequently to no activity in ethylene–propylene copolymerization, while it could be grafted onto an MAO/SiO$_2$ support. In previous work,[12,13] we have already verified that grafting (nBuCp)$_2$ZrCl$_2$ on dehydroxylated silica afforded supported catalyst systems which were active in ethylene homopoymerization. In the present work, we have verified that such a catalytic system is also active in ethylene and 1-hexene copolymerization, producing LLDPE having a narrow molecular weight distribution (1.8–2.6), indicating /homogeneity in the nature of the surface active species.

The catalytic activity was shown to be sensitive to the comonomer concentration. For both systems, the copolymerization catalytic activity is much higher than that for homopolymerization. This could be attributed to the higher solubility of the copolymer in the reaction medium which might allow higher diffusion rates of the monomers onto the active sites, therefore enhancing the copolymerization activity.[30] However, the lower activity presented by the homogeneous system at 1-hexene concentrations higher than 0.38 mol l^{-1} might be associated with an increase of comonomer in the polymeric growing chain, which in turn leads to a reduction in activity because of a decrease in the propagation rate with the comonomer incorporation. This activity behaviour is not observed for the supported catalyst, because of the lower 1-hexene incorporation for the 1-hexene concentrations in the reaction medium studied. For such a system, we could observe an increase in activity as the comonomer concentration is enhanced in the medium. Soga and Kaminaka[31] also reported an apparent polymerization activity increase with increasing 1-hexene concentration in the case of an Et[Ind]$_2$ZrCl$_2$/MAO/SiO$_2$ system activated by triisobutylaluminium.

Comparing the results of catalytic activity and incorporation obtained with the (nBuCp)$_2$ZrCl$_2$ homogeneous catalytic system with those concerning other metallocenes in exactly the same experimental conditions[14] it can be said that: (a) this system was the most active of the ethylene-1-hexene copolymerization systems which followed the order (nBuCp)$_2$ZrCl$_2$ > C$_2$H$_4$(Ind)$_2$ZrCl$_2$ ≈ (CH$_3$)SiCp$_2$ZrCl$_2$ ≈ Cp$_2$ZrCl$_2$ > Ind$_2$ZrCl$_2$; (b) the behaviour concerning 1-hexene incorporation is similar to the non-bridged catalysts (Cp$_2$ZrCl$_2$ and Ind$_2$ZrCl$_2$) that show half of the incorporation of the bridged catalysts (C$_2$H$_4$(Ind)$_2$ZrCl$_2$ and (CH$_3$)SiCp$_2$ZrCl$_2$). This may indicate that α-olefin insertion is controlled only by the coordination angle of the ligands in the catalyst and that the bulky n-butyl substituents in the cyclopentadienyl moiety do not influence this insertion.

The low comonomer incorporation of the (nBuCp)$_2$ZrCl$_2$ supported system can be attributed to a steric effect played by the silica surface, blocking

one of the metallocene faces, therefore reducing the accessibility of the comonomer onto the active sites.

The triad sequence distributions and the average length of the 1-hexene sequences show that for this 1-hexene incorporation, the α-olefin is mainly isolated between ethylene units. The average length of ethylene sequences n_E is indicative of an almost random comonomer incorporation (n_E is close to $100/c$ where c is the comonomer concentration in the copolymer). The higher ethylene reactivity ratio (r_E) presented for polymerization in the case of the supported catalyst indicates a higher facility for homopolymerization than for copolymerization, compared to polymerization with soluble catalyst. The copolymers obtained with the supported systems had higher molecular weights when compared to those obtained with the homogenous systems. This behaviour has already been mentioned in the literature,[25] and is attributed to immobilized metallocene on a surface hindering the bimolecular reaction between two catalytic centres, which might lead to β-hydrogen transfer. Therefore, this enables longer growth of the polymer chain, resulting in polymer with higher molecular weights.

The decrease of molecular weight with comonomer incorporation was previously studied by us through chain-end analysis by NMR,[32] which showed that the terminal double bonds formed by hydride β-elimination are mainly between comonomer units. This trend suggests that 1-hexene incorporation favours chain termination reactions, consequently leading to lower molecular weight copolymers.

CONCLUSIONS

The production of LLDPE can be achieved with $(nBuCp)_2ZrCl_2$, with a very high catalytic activity. This activity is higher in the homogeneous catalytic system than in the supported one. The maximum comonomer incorporation (6.3 mol%) was achieved using $0.50\,mol\,L^{-1}$ of 1-hexene in the reaction medium. The immobilization of such a metallocene on silica produced a catalytic system which lead to a small amount of comonomer incorporation (maximum 4.0 mol%), probably due to a steric effect of the silica surface. Comonomer incorporation on the supported system is still higher than the levels mentioned in the literature for the soluble catalyst.

The supported catalytic system leads to polymers with higher molecular weights and narrow molecular weight distribution than the homogeneous one. The polydispersity is close to two for the soluble and supported systems, suggesting that in both cases we are in the presence of only one kind of catalytic site.

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