

Copolymerization of Ethylene and 1-Octene by Homogeneous and Different Supported Metallocenic Catalysts

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ABSTRACT: In this work, the performance of the homogeneous catalyst system based on $\text{Et}(\text{Flu})_2\text{ZrCl}_2/\text{MAO}$ was evaluated on the copolymerization of ethylene and 1-octene. Characteristics of some of the produced polymers were also investigated. A study was performed to compare this system with that of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$. The influence of different support materials for the Cp_2ZrCl_2 was also evaluated, using silica, MgCl_2 , and the zeolite sodic mordenite NaM. An increase in activity was observed in relation to the comonomer addition for the two homogeneous catalysts. The copolymers produced by the $\text{Et}(\text{Flu})_2\text{ZrCl}_2/\text{MAO}$ system showed higher molecular weight and narrower molecular weight distribution. We verified that the catalyst supported on SiO_2 was the most active one, although the copolymers produced with the catalyst supported on NaM showed higher molecular weight and lower molecular weight distribution. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 724–730, 2001

Key words: ethylene/1-octene copolymer; metallocene catalyst; supported catalyst; silica; zeolite sodic mordenite

INTRODUCTION

The copolymerization of ethylene and 1-octene produces a polyethylene with linear C6 branches distributed along the polymer chain (LLDPE), decreasing the density and the crystallinity of the final product, improving its processability and optical properties. With the development of the Ziegler–Natta catalysts, these copolymers started being produced on a commercial scale. LLDPE is a very important class of resins for the blown and cast film industry and in the areas of food packaging, nonfood packaging, and also nonpackaging.^{1–4}

It is known that the development of metallocene catalysts activated by methylaluminoxane affords a high catalyst activity, excellent stereoregularity, and comonomer distribution, leading to polyolefins that are inaccessible through conventional heterogeneous Ziegler–Natta catalysts.⁵

Nevertheless, the homogeneous catalyst systems based on metallocenes require high aluminum-to-transition metal molar ratios and an extensive polymer washing, so as to remove residual aluminum, and also are not suitable for industrial applications such as gas-phase and slurry polymerization processes. To overcome these disadvantages, metallocene compounds have been supported mainly on inorganic carriers.^{6,7}

Thus, the objective of this work was to investigate the influence of different inorganic materials

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used as support for the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system, evaluating them in the homopolymerization and copolymerization of ethylene and 1-octene. A comparative study of these catalyst systems with the homogeneous $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ and $\text{Et}(\text{Flu})_2\text{ZrCl}_2/\text{MAO}$ was also done.

EXPERIMENTAL

General Procedures

All operations were performed under nitrogen by using conventional Schlenk techniques. MAO 10 wt % toluene solution was kindly supplied by Witco (Germany) and used without purification. Research-grade ethylene supplied by White Martins S.A. (Brazil) and nitrogen were treated through columns of a 3-Å molecular sieve and copper catalyst. Toluene and 1-octene were distilled over sodium/benzophenone under nitrogen.

Synthesis of Catalysts

The complex ethylidene-bis(fluorenyl) zirconocene $[\text{Et}(\text{Flu})_2\text{ZrCl}_2]$ was synthesized by conventional techniques described in the literature,^{8–10} and bis(cyclopentadienyl) zirconocene (Cp_2ZrCl_2) was supplied by Witco Co. (Germany) and used as received.

Preparation of the Supported Catalyst

SiO_2 and ball milling-activated MgCl_2 were pretreated with MAO (2.5 mmol/g support) in a toluene solution and then impregnated with 0.05 mmol $\text{Cp}_2\text{ZrCl}_2/\text{g}$ support. NaM was directly treated with the metallocene. The experimental conditions were chosen based on earlier studies.^{11–13}

Polymerization

Polymerization experiments were carried out in a 0.5-L Buchi glass autoclave (solution polymerization with 100 mL of toluene and continuous olefin feed) at constant pressure (2 bar) for 0.5 h. 1-Octene was charged to the monomer/solvent/MAO mixture. The polymerization were quenched with HCl/5% ethanol solution. The polymers were separated by filtration, washed, and dried under reduced pressure at 50°C to a constant weight.

Polymer Characterization

Polymer average molecular weight and molecular weight distribution were investigated by size-ex-

clusion chromatography (SEC) with a Waters 150 CV Instrument (Waters Instruments, Rochester, MN) at 135°C, using 1,2,4-trichlorobenzene as eluent, and a calibration curve was prepared with monodisperse polystyrene standards.

The 1-octene molar percentage in the polymer chain was obtained by nuclear magnetic resonance ^{13}C -NMR. The spectra were recorded and measured on a Varian model Mercury spectrometer (Varian Associates, Palo Alto, CA) operating at 300 MHz. The method was based on the analysis of ethylene copolymers with 1-octene as described by De Pooter et al.¹⁴ Although this method is valid for products containing 1–10% of the second alkene, we considered it to estimate the 1-octene mol % values. This investigation includes the chemical shift assignments (relative to that of the isolated methylene carbons at 30.0 ppm) and a set of experimental conditions for the quantitative analysis of branching. Figure 1 shows the ethylene–octene-1 copolymer obtained at 70°C with 3.6 g of 1-octene in the charge for the homogeneous polymerization with $\text{Et}(\text{Flu})_2\text{ZrCl}_2$, and Table I shows the range of chemical shift used for quantitative analysis. Equations (1) to (5) are used to obtain the mol % octene-1.

$$\text{O1} = (\text{A} + 2\text{C} + 2\text{D})/2 \quad (1)$$

$$\text{O2} = [1.5\text{A} + 2\text{B} + (\text{D} + \text{E}) - \text{D}]/3 \quad (2)$$

$$\text{O}' = (\text{O1} + \text{O2})/2 \quad (3)$$

$$\text{E}' = [(\text{F} + \text{G} + \text{H}) - (3\text{A} + 3\text{B} + \text{H} + \text{P} + \text{I})]/2 + \text{O}' \quad (4)$$

$$\text{Mol \% octene-1} = [(100)\text{O}']/(\text{O}' + \text{E}') \quad (5)$$

Differential scanning calorimetry (DSC) analyses were determined on a Perkin–Elmer Differential Scanning Calorimeter DSC 7 (Perkin Elmer Cetus Instruments, Norwalk, CT), using a heating rate of 20°C/min in the temperature range of 30–220°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

Tables II and III show the results of weight-average molecular weight and molecular weight distribution for the produced polymers, as well as catalyst activity and molar percentage of octene-1

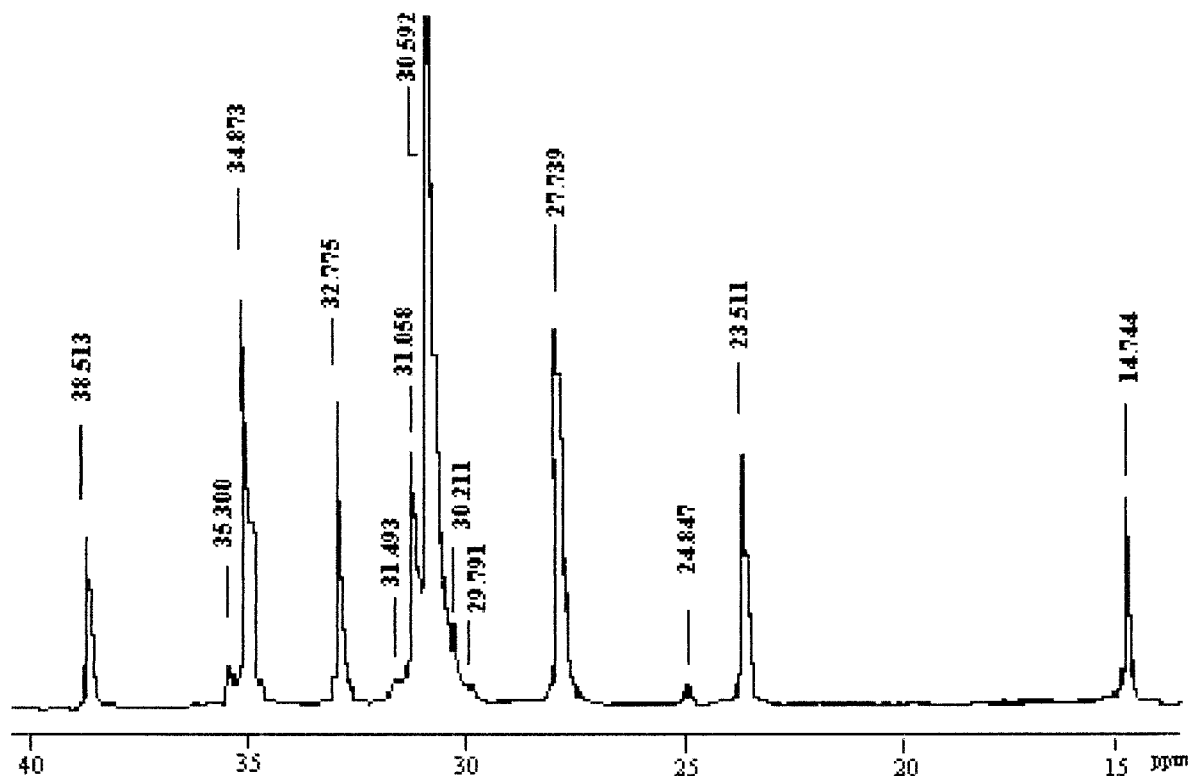


Figure 1 ^{13}C -NMR spectrum of an obtained ethylene/octene-1 copolymer (experiment 4A).

incorporated in the polymer chain for the homogeneous systems used.

Considering the ethylene homopolymerization, an increase in the catalyst activity was observed, whereas the molecular weight had sharply decreased at higher polymerization temperature for both systems. This observation indicates the thermal stability of such a bulky ligand with fluorenyl rings, despite its mobility and fluxion. It is also

Table I Integration Limits for Ethylene/Octene-1 Copolymers^a

Area	Region (ppm)
A	41.5 to 40.5
B	40.5 to 39.5
C	39.5 to 37.0
D	Peak at 35.8
D + E	36.8 to 33.2
F + G + H	33.2 to 25.5
H	28.5 to 26.5
I	25.0 to 24.0
P	24.0 to 22.0

^a From De Pooter et al.¹⁴

notable that, at 50°C, the $\text{Et}(\text{Flu})_2\text{ZrCl}_2$ system produced polyethylene with a slightly larger polydispersity compared to that of the Cp_2ZrCl_2 system, and according to the studies for $\text{Et}(\text{Flu})(\text{Cp})\text{ZrCl}_2$,¹⁵ the reason is supposed to be attributed to the activity of two slightly different coordination sites as a result of the conformation metallocene isomers.¹⁵ The ligand structure is flexible and the two carbon atoms in the ethylene bridge can form two different arrangements. At 70°C the polydispersity increased sharply for the Cp_2ZrCl_2 system but not for the $\text{Et}(\text{Flu})_2\text{ZrCl}_2$ system because the interconversion between the two conformers becomes more rapid, there becomes only one active species, and the polydispersity tends to decrease, counterbalancing the transfer reaction rate.

For both catalysts used, a significant improvement was also verified in the activity with the comonomer addition in the reaction medium, with a decrease in the molecular weight, mainly in the case of the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system, caused by the beta hydrogen chain transference, which occurs more rapidly by the introduction of octene-1. The increase in catalyst activity by the addition of a

Table II Copolymerization of Ethylene and 1-Octene with Et(Flu)₂ZrCl₂/MAO (A) Homogeneous Catalytic System^a

Experiment	1-Octene Charge (g)	Polymerization Temperature (°C)	Yield (g)	Activity (ton Pol mol Zr ⁻¹ h ⁻¹)	M_w ($\times 10^{-5}$)	M_w/M_n	1-Octene (mol %)	Conversion (%)
1A	0	50	3.50	1.4	6.64	2.4	—	—
2A	0	70	7.20	2.8	1.52	2.4	—	—
3A	3.6	50	9.28	3.7	3.40	2.3	10.34	81
4A	3.6	70	8.50	3.4	2.02	2.3	8.60	64
5A	14.3	50	8.78	3.5	1.23	1.8	23.27	34
6A	14.3	70	11.23	4.5	1.30	1.9	27.26	47

^a [Zr] = 0.005 mmol; [Al]/[Zr] = 2000.

bulkier α -olefin comonomer is often observed, called the “comonomer effect,” which is usually explained as simply the result of decreased mass-transfer limitation. Polymer solubility is increased in the case of copolymers, and the apparent increase in the polymerization rate may be a result of the higher ethylene concentration in the reaction medium attributed to the faster ethylene diffusion.

Although we observed an extremely high conversion of 1-octene, showing that the ethylene/1-octene ratio may be changed significantly during the polymerization, we can make some interesting observations.

Significantly, for the Et(Flu)₂ZrCl₂ system, the polydispersity was narrower with the introduction of the comonomer, despite its conversion was found to be so high. This might indicate that at a higher polymerization rate, there is virtually only one type of active center.

The copolymers obtained from the Et(Flu)₂ZrCl₂/MAO system showed higher average molecular weight, compared with that produced by

Cp₂ZrCl₂/MAO, because of the extremely congested environment of the fluorenyl rings surrounding the transition metal, which hinders the beta hydrogen interaction, and therefore, the chain transference. Moreover, the copolymers obtained with the bisfluorenyl system showed clearly narrower MWD than that obtained by Cp₂ZrCl₂, despite the higher comonomer conversion for all polymerizations, which might cause some variation in monomer ratio during the reaction time (compare reactions with similar conversion magnitude, such as reactions 4A and 4B, 6A and 6B).

The calorimetric analysis showed no melting temperature for the synthesized copolymers with the two homogeneous catalyst systems, even for those with the lowest comonomer concentration in the reaction medium, and also with the heterogeneous systems (the results of which will be discussed afterward), indicating a uniform comonomer addition in the polymer chain.

It was observed that the amount of 1-octene in the produced copolymers showed extremely high

Table III Copolymerization of Ethylene and 1-Octene with Cp₂ZrCl₂/MAO (B) Homogeneous Catalytic System^a

Experiment	1-Octene Charge (g)	Polymerization Temperature (°C)	Yield (g)	Activity (ton Pol mol Zr ⁻¹ h ⁻¹)	M_w ($\times 10^{-5}$)	M_w/M_n	1-Octene (mol %)	Conversion (%)
1B	0	50	4.26	1.7	1.40	2.2	—	—
2B	0	70	13.78	5.5	0.86	2.8	—	—
3B	3.6	50	25.72	10.3	0.41	3.7	7.22	100
4B	3.6	70	16.52	6.6	0.22	3.5	4.42	72
5B	14.3	50	37.87	15.1	0.14	3.6	8.84	74
6B	14.3	70	26.25	10.5	0.07	3.2	7.11	43

^a [Zr] = 0.005 mmol; [Al]/[Zr] = 2000.

Table IV Copolymerization of Ethylene and 1-Octene with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ Heterogeneous Catalytic System

Kind of Support ^a	1-Octene Charge (g)	Yield ^b (g)	Activity (ton Pol mol Zr ⁻¹ h ⁻¹)	M_w ($\times 10^{-5}$)	M_w/M_n	1-Octene (mol %)	Conversion (%)
SiO ₂	0	7.38	2.9	8.93	2.3	—	—
MgCl ₂	0	3.65	1.4	7.25	2.7	—	—
NaM	0	2.30	0.9	8.82	2.1	—	—
SiO ₂	14.3	8.89	3.5	0.60	2.3	11.42	21
MgCl ₂	14.3	3.21	1.3	0.79	2.3	5.62	4
NaM	14.3	0.53	0.2	1.62	1.8	5.85	1

^a At 100 mg supported catalyst/100 mL toluene; 50°C.

^b Number considering 0.05 mmol Zr/g of support surface.

values. Moreover, the copolymers obtained through the $\text{Et}(\text{Flu})_2\text{ZrCl}_2$ catalyst system had higher comonomer incorporation, under the same polymerization conditions, compared with that obtained through the Cp_2ZrCl_2 catalyst, especially at greater amounts of comonomer in the reaction medium, in spite of the much higher volume of fluorenyl ligands. In the case of this latter catalyst system, the amount of 1-octene did not significantly vary at different synthesis conditions, even in reaction 6B, with the lower comonomer conversion. Besides, for both systems, in general, the enhancement of the reaction temperature caused lower comonomer incorporation, as expected, because the ethylene insertion ratio increased more significantly.

Table IV shows the results of the effect of

comonomer addition and the type of support on the Cp_2ZrCl_2 catalyst activity and polymer characteristics.

$\text{Et}(\text{Flu})_2\text{ZrCl}_2$ was also impregnated in these supports under the same conditions as those of Cp_2ZrCl_2 , and this catalyst was tested for polymerization, although no product was obtained. The high bulkiness of this metallocene molecule causes a weak interaction with the support surface, which is easily washable, especially in toluene.

The supported catalyst performance was compared with that of the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ homogeneous system, under the same experimental conditions.

The supported catalyst activities were high for ethylene homopolymerizations compared with that of the homogeneous system, as shown in

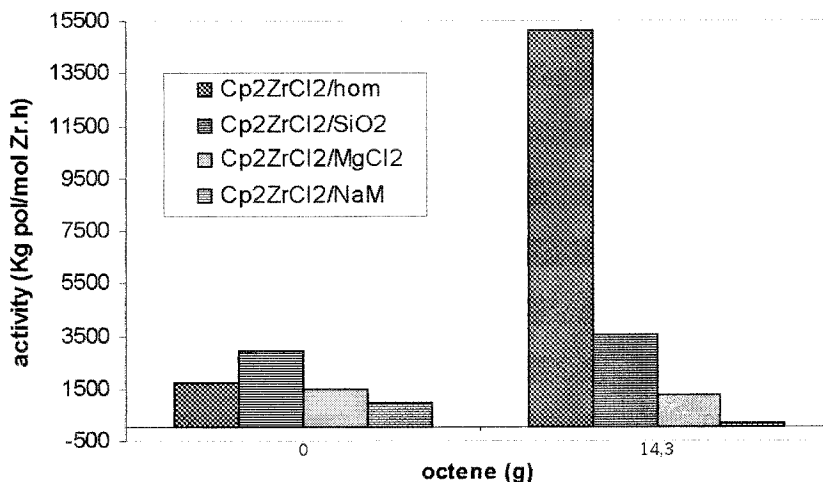


Figure 2 Influence of the support type and comonomer amount on the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst activity.

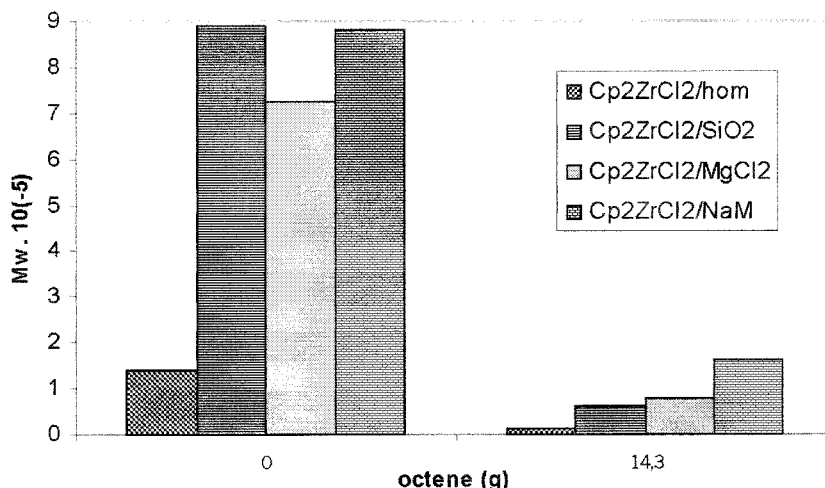


Figure 3 Influence of the support type and comonomer amount on the polymer molecular weight.

Figure 2. For the copolymerizations with 1-octene, it was possible to observe an increase in the SiO_2 supported catalyst activity and a decrease in the NaM-supported catalyst activity with the comonomer addition.

For all the experimental conditions employed in the homo- and copolymerizations we observed a higher weight-average molecular weight and lower molecular weight distribution for the polymers produced by the supported catalysts, compared with that of the homogeneous system, as can be seen in Figures 3 and 4.

It was also verified that the most active catalyst was the one supported on SiO_2 , whereas the zeolite sodic mordenite support resulted in a

catalyst that produced copolymer with higher molecular weight and narrower molecular weight distribution. The special property of this zeolite support was already discussed in previous studies.¹¹

Considering the comonomer incorporation, we can postulate that the kind of support influences the 1-octene percentage in the copolymer, where silica showed a higher value than that of the homogeneous catalyst system, whereas MgCl_2 and NaM supports presented equally lower 1-octene percentages (Fig. 5). More evidence of the nature of active sites is required to explain the observed differences in the comonomer incorporation abilities.

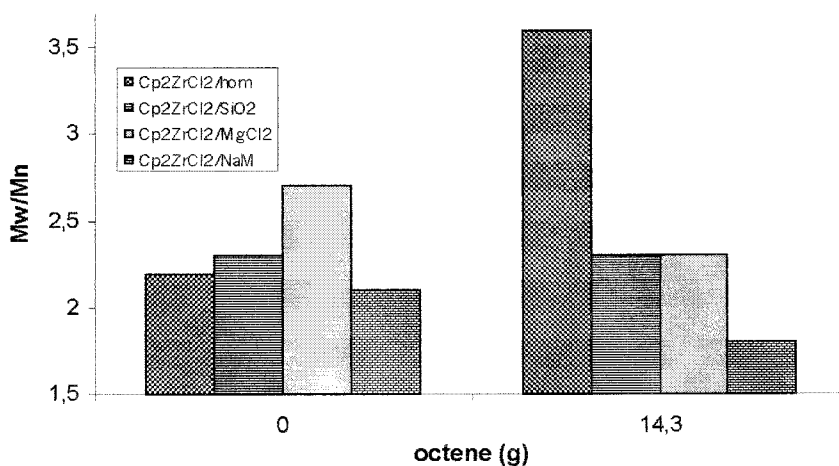


Figure 4 Influence of the support type and comonomer amount on the polymer molecular weight distribution.

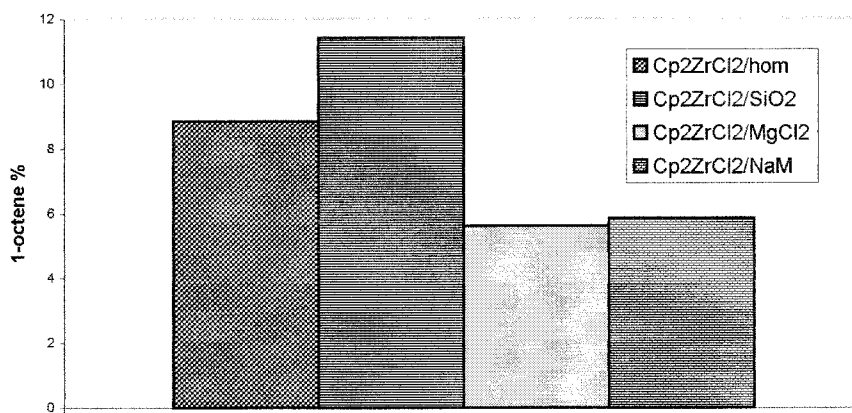


Figure 5 Influence of the support type and comonomer amount on the copolymer 1-octene percentage.

CONCLUSIONS

Both homogeneous catalytic systems showed the comonomer effect, considering that a significant increase was observed in the activity with the addition of a larger comonomer in the reaction medium. This effect was also verified for the catalyst supported on SiO₂. Only for the mordenite-supported catalyst did the activity decrease with the comonomer addition, although the produced polymer presented the highest molecular weight.

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