DOI: 10.1002/masy.200951112

Heterogeneous Copolymerization of Ethylene and α-olefins Using Aluminohydride-Zirconocene/SiO$_2$/MAO by High-Throughput Screening

Rogelio Charles,[1] *Alba Nidia Estrada,*[2] *Luis Lugo,*[1] *Javier Revilla,**[1]
Maricela García,[2] *Odilia Pérez**[2]

Summary: Copolymerizations of ethylene and α-olefins (1-hexene and 1-octene) using a supported catalyst derived from the activation of a zirconocene aluminohydride complex with PMAO and MMAO are reported. The supported (nBu-Cp$_2$ZrH$_3$AlH$_2$)/SiO$_2$/MAO system was evaluated by high-throughput techniques, in order to find approaches to the optimal copolymerization conditions. The polymerization reactions were carried out in a parallel polymerization reactors system (PPR) by Symyx Technologies, Inc. The screening of the activity of the supported system and the molecular weight (MW) of the polymers and copolymers obtained in the PPR, allowed us to optimize copolymerization conditions, like hydrogen (H$_2$) addition to control MW and molecular weight distribution (MWD), polymerization temperature, co-catalyst ratio, and solvent type. The copolymerization reactions were scaled-up in order to validate the performance of the catalytic system at higher polymerization scales, according to the results obtained in the combinatorial phase. The scaled-up copolymerizations of ethylene with 1-hexene and 1-octene, showed high activities and MW, and low comonomer incorporation (from 0.3 to 1.3 mol-%, determined by ^{13}C NMR). However, the crystallinity (X_c), thermal properties (T_c and T_m) and densities of the polyethylenes obtained with the supported (nBu-Cp$_2$ZrH$_3$AlH$_2$)/SiO$_2$/MAO system, were significantly modified, approaching those of metallocene linear low-density polyethylenes (mLLDPE).

Keywords: heterogeneous ethylene copolymerization; high-throughput polymer synthesis; metallocene catalyst; scaled-up polymerizations

Introduction

High throughput synthesis and activity screening of new metallocene systems have led to rapid identification of potential polymerization catalysts.[1] Advancements in olefin catalysis using single-site catalysts (SSC) have produced many grades of polyolefins with precise control of their microstructures, molecular weights (MW) and molecular weight distributions (MWD).[2] The copolymerization of ethylene and α-olefins using metallocene catalysts generates higher levels of comonomer incorporation, and better comonomer distribution in polyethylene than Ziegler-Natta (ZN) catalysts.[2] In addition, branchings in the main backbone of the polyolefins, are reduced using metallocene catalysts compared to those polyolefins produced with ZN catalysts. These homogeneous microstructures result in linear low-density polyethylene (LLDPE) with improved physical and mechanical properties, and processability.[3]

According to comonomer content, different grades of LLDPE can be obtained,

---

[1] Centro de Investigación y Desarrollo Tecnológico, Ave. de los Sauces No. 87, Parque Industrial Lerma, Edo. de México, C.P. 52000
E-mail: javier.revilla@desc.com.mx
[2] Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna 140 Saltillo, Coah. México C.P. 25253
E-mail: odilia@ciqa.mx

by controlling the copolymerization conditions (temperature, pressure, comonomer concentration, etc.). The main processing properties are related to their lower melting temperatures, lower melt viscosities and smaller crystallite size, providing prominent sealing properties to be used for film and packing applications.[4]

In order to be used in industrial slurry or gas phase processes, metallocene catalysts have been heterogenized in different kinds of inorganic supports by means of several methods reported in the literature.[5] The most applied method for supporting metallocenes involves the use of modified silica previously treated with MAO (SiO_2/MAO) according to the route reported by Ribeiro et al.[5a]

Recently, we reported the use of a new metallocene system, based in zirconocene aluminohydride complexes, activated with Lewis acids such as $B(C_6F_5)_3$ as well as with MAO in homogeneous phase, for ethylene polymerization.[6] The structure and features of this kind of complexes, like thermal stability and different state of aggregation, has been studied since 1990 by several research groups, and this was taken into account in further studies on polymerization catalysis.[7]

The activity of the zirconocene aluminohydride system was 30%–40% higher than that showed by the analogous zirconocene dichloride, when activated with MAO and probed under the same polymerization conditions.[6] The higher activities showed by the zirconocene aluminohydrides could be attributed to the presence of terminal and bridging zirconium hydride bonds (Zr-H and Zr-H-Al), which confers instability to the complexes, making them more active to polymerize olefins. After supporting on modified silica (SiO_2/MAO), these zirconocene aluminohydrides have increased stability, likely because the silica support prevents their aggregation and/or destruction of the zirconium-hydride bonds. The nBu-$Cp_2ZrHAlH_4$ complex supported on MAO-modified silica was the first zirconocene aluminohydride derivative studied for ethylene homopolymerization and compared with the analogous zirconocene dichloride (nBu-Cp_2ZrCl_2), a commercial catalyst for ethylene polymerizations.[8]

In this context, we report herein ethylene/1-hexene and ethylene/1-octene copolymerization experiments with the zirconocene aluminohydride complex (nBu-$Cp_2ZrH_3AlH_2$), supported on modified silica (SiO_2/MAO) and activated with MAO or MMAO. The ethylene homopolymerization was also studied under the same conditions, in order to compare with the copolymerization experiments. The addition of molecular hydrogen (H_2) as chain transfer agent to control MW and MWD was also considered in these studies.

The copolymerization conditions of the supported pre-catalyst (nBu-$Cp_2ZrHAlH_4$)/SiO_2/MAO, were first screened in a combinatorial equipment, using a parallel polymerization reactor from Symyx Technologies^{TM}, in order to optimize copolymerization parameters (such as H_2 pressure, catalyst concentration, polymerization temperature, solvent type, and cocatalyst/catalyst (Al/Zr) ratio) that could be used to successfully scale up the polymerization and copolymerization reactions.[9] The copolymerization conditions obtained from the PPR were then scaled-up to the pilot plant level in order to validate the performance of the supported zirconocene aluminohydride catalytic system.

Experimental Part

Materials

nBu-Cp_2ZrCl_2 (98%, Strem), $LiAlH_4$ (1M solution in diethyl ether, Aldrich), methylaluminoxane (PMAO, 10 wt.-% solution in toluene, Aldrich), modified methylaluminoxane (MMAO-7, 13 wt.-% in isopar-E, Akzo Nobel Chemicals Inc.), ethylene (99.8%, Infra, Air Products), were used as received.

Comonomers, 1-hexene (99%, Aldrich) and 1-octene (98%, Aldrich), were distilled under atmospherical pressure before using.

Solvents, diethyl ether, toluene, isooctane and hexane, were reagent grade

(Aldrich) distilled from the appropriate drying agents under Ar atmosphere. Hexane (Conoco-Phillips) was used for the 5 gal reactions, as received.

Polymer Characterization

Molecular weight and polydispersity were measured by gel permeation chromatography (GPC) in a Gel Alliance GPV 2000 instrument at 140 °C. The equipment used three styragel columns, and was coupled to a refractive index (IR) detector (480 nm) and to a multi-angle light scattering (LS) detector (690 nm). 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1 mL/min. The columns were calibrated with narrow molar distribution polyethylene standards.

Differential scanning calorimetry analyses were performed on a modulated TA Instrument 2920, at a heating rate of 10 °C/min on a temperature range from 50 to 160 °C. Through a second heating cycle the thermal and mechanical history of the samples was eliminated.

Percent of crystallinity (% X_c) was determined by wide-angle X-ray diffraction in a diffractometer Siemens D 5000 at 25 mV and 35 Kv, relating amorphous and crystalline areas.

The density of the samples was determined by column gradient method according to the ASTM-D-1505-03 norm.

Comonomer incorporation was determined by ^{13}C NMR spectroscopy in a JEOL Eclipse 300. The ^{13}C NMR spectra were obtained at 100 °C in the equipment operating at 75 MHz. Sample solutions of polymers and copolymers were prepared in tetrachloroethylene using deutered benzene as external reference.

Synthesis of nBu-$Cp_2ZrH_3AlH_2$

All the operations were carried out on a standard high-vacuum line or in a dry-box under inert atmosphere.

The nBu-$Cp_2ZrH_3AlH_2$ was synthesized as reported in a previous work, based on the zirconocene aluminohydrides syntheses reported by Stephan and co-workers.[7] A solution of nBu-Cp_2ZrCl_2 (3.2×10^{-3} mol) in diethyl ether (20 mL) was stirred at 0 °C and 2.2 equiv of $LiAlH_4$ (7.07×10^{-3} mol) in diethyl ether was dropped during 10 min. The formation of a fine white powder was observed when the mixture was allowed to warm to room temperature (30 min) and the solution was filtered. The diethyl ether was evaporated to provide the corresponding zirconocene aluminohydride in quantitative yield, which was dissolved in tolulene (30 mL).

Supporting of the pre-catalyst (nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO)

The supported pre-catalyst was prepared according to the method reported for metallocene complexes.[5]

15 mL of a10 wt.-% solution of PMAO (without TMA) in toluene was added to a suspension of SiO_2 (1 g SiO_2/20 mL of toluene), previously dehydrated for 6 h at 800 °C. The addition of the PMAO solution was carried out at 0 °C, and then the mixture was allowed to warm to room temperature for 1 h. Then, suspension was heated at 50 °C for 2 h. The slurry was filtered and washed twice with toluene to obtain the modified silica (SiO_2/MAO).

A toluene solution of nBu-$Cp_2ZrH_3AlH_2$ (3.2×10^{-3} mol/30 mL toluene) was dropped to 1 g of modified silica (SiO_2/MAO) suspended in 30 mL of toluene, using Al:Zr molar ratio (10:1), according to formulations reported in the literature for highly active supported metallocenes.[10] The addition was carried out at 0 °C an then the mixture was stirred for 12 h at room temperature. The slurry was filtered, washed twice with toluene and dried in vacuum for 6 h. The content of Zr (1.97 wt.-%) was determined by atomic absorption (AA), and the supported pre-catalyst nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO was storaged in a glove box.

High-Throughput Polymerizations

The automated parallel synthesizer from Symyx Technologies allows from 6 to 48 reactions to be performed in parallel, depending on the reaction vessel used (4–6 mL). Each reaction vessel can be heated or cooled through a jacketed oil bath. Before each reaction, the vessels were heated for 1.5 h at 85 °C with 0.2 M TIBAL/toluene to remove all moisture traces.

Polymerizations conditions were screened at different temperatures (50, 70 and 90 °C), catalyst concentrations ($[Zr] = 4 \times 10^{-2}$, 4×10^{-3}, and 4×10^{-5}M), two kinds of polymerization solvents (hexane and isooctane), three MAO/Zr ratios (10,000, 5,000, and 2,500), and two ethylene/hydrogen ratios ($C_2/H_2 = 120/30$ and 120/15 psig/psig).

Stock solutions of the pre-catalyst and cocatalyst were prepared to be used for each set of reactions. A mass of 0.002 g of the supported pre-catalyst (nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO) was suspended in 20 mL of solvent (isooctane or hexane) to prepare a 1 mg/mL solution. A 0.5 M solution in toluene of PMAO was prepared to be used as the cocatalyst.

The vessels were loaded inside a glovebox utilizing a 3-axis liquid handling robot. The corresponding solvent was added automatically with a syringe, and then the PMAO and comonomer solutions. The vessels were heated to the corresponding temperature, and the pressure of each reaction vessel was controlled and monitored at 120 psig of ethylene, or ethylene/hydrogen (C_2/H_2, 120/15 psig/psig). The corresponding volume of suspended pre-catalyst was added to start the polymerization, and the reaction vessels were mechanically stirred with Teflon-coated stirring blades, by vortexing (600 rpm), for 15 minutes. After this time, ethylene feed was stopped, and the vessels were cooled to 30 °C. The catalytic system was quenched adding 2 mL of acidified methanol (10 wt.-% HCl) to each reaction vessel, after cooling to 30^o C. The polyethylenes were filtered, washed with methanol and dried in a vacuum oven for 1 h.

Polymerization and Copolymerization Scale-Up

The polymerization and copolymerization reactions were scaled-up to a 5 gal Parr reactor equipped with a mass flow meter, a temperature controller, Ar, ethylene and solvent inlets. Before each polymerization, the reactor was heated under vacuum for 1 h at 100 °C and purged with Ar several times.

The reactor was charged successively with hexane (Conoco-Phillips, 7 L), the cocatalyst solution (MMAO-7, 13 wt.-% in isopar-E, Akzo Nobel Chemicals Inc. 46.5 mL), and the corresponding amount of comonomer (1-hexene or 1-octene). The mixture was allowed to react as ‘‘scavenger’’ for 30 min, and the pre-catalyst (nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO) suspended in hexane inside a stainless steel cylinder was finally added to the reactor. The polymerization started by addition of ethylene or the mixture (C_2/H_2, 1200/150 psig/psig). Polymerization and copolymerization conditions for all the runs were as follows: ethylene or C_2/H_2 pressure of 120 psig, 7 L of hexane, polymerization temperature of 70 °C, comonomer addition 1-hexene or 1-octene (10 and 20 wt.- %), and polymerization time of 1 h.

The polymerization was stopped by rapid depressurization of the reactor, the polymer was washed one time with methanol, and dried in a vacuum oven for 4 h.

Results and Discussions

In this work we have evaluated the copolymerization activity of the zirconocene aluminohydride system (nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO) in heterogeneous phase for ethylene and α-olefins (1-hexene and 1-octene), using high throughput techniques, [9] in order to approach to the main optimal parameters of copolymerization. The statistical data treatment was accomplished through the mining data software (Spot Fire).

A factorial experimental design was performed to study ethylene-1-hexene and ethylene-1-octene copolymerizations, in the combinatorial equipment, to determine the statistical effects of catalyst concentration, temperature, solvent type, MAO/Zr ratio, and comonomer concentration,

Table 1.
Preliminary screen of ethylene polymerization and ethylene-1-hexene copolymerization reactions with the system nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO

T (°C)	1-hexene (%)	Activity 10^6 g PE/(molZr*hr)] isooctane	Activity 10^6 g PE/(molZr*hr)] hexane
50	0	15.46	9.81
50	5	16.1	11.14
50	10	19.55	13.97
70	0	16.34	15.01
70	5	17.9	16.91
70	10	22.7	21.27
90	0	14.66	10.94
90	5	15.6	13.92

T = 70 °C, $Pc_2 = 120$ psig, [cat] $= 4 \times 10^{-5}$ mol/L, MAO/Zr = 2500, t = 15 min, 600 rpm

where two or three levels of each variable were defined.

The performance of the aluminohydride zirconocene metallocene was first evaluated in the ethylene-1-hexene coplymerizations using MAO as co-catalyst at Al/Zr ratio of 2500, and ethylene pressure of 120 psig. The levels of the independent variables were chosen based on ethylene homopolymerization preliminary results with the aluminohydride zirconocene catalyst. The first set of experiments included 9 reactions, where two or three levels were employed to study the following parameters: solvent type (isooctane or hexane), polymerization temperature (50, 70 and 90 °C), and addition (5 and 10 wt-%). Results of this preliminary screening are collected in Table 1. The experiments were replicated twice to obtain an average polymerization activity. A high reproducibility of the results on activity were observed in the most of the experiments and these data were focused to select the best polymerization conditions for scaling up the reactions.

Polymerization conditions that led to best catalyst activity were obtained at 70 °C using isooctane as solvent and 10 wt-% of comonomer (Figure 1).

At 70 °C, the catalytic activity decreased by only 3% using hexane as solvent when compared to the activity in isooctane, which can be considered within the interval of variation of experimental errors in this kind of reactions. At 50 °C the effect of the solvent was higher than at 70 °C probably due to the lower polarity of the hexane whereas the catalytic contact ion-pair could prevalence over the solvent-separated ion-pair which can diminish the activity of the active specie[11]. At different temperatures, the comonomer effect was evident since

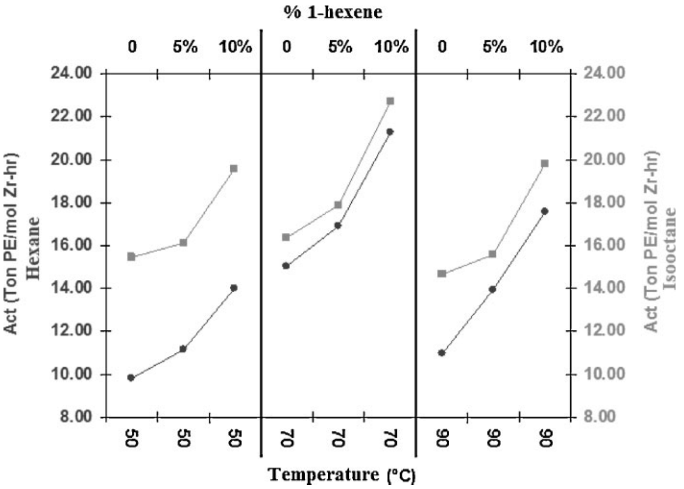

Figure 1.
Catalytic activity of the nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO at different polymerization and copolymerization conditions of ethylene and ethylene-1-hexene respectively.

Table 2.
Ethylene polymerization and ethylene-1-hexene copolymerization results obtained with the system nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO

Solvent	1-hexene (%)	Activity (10^6 g PE/mol Zr-hr)	Mw (10^3 g/mol)	I (Mw/Mn)	T_m (°C)	T_c (°C)
Isooctane	0	23.07	63.4	2.7	131.27	121.04
	5	30.30	52.8	2.1	128.17	118.56
	10	37.29	46.3	2.4	126.37	115.01
Hexane	0	23.46	41.3	1.7	131.8	121.56
	5	31.80	25.8	1.7	129.24	118.42
	10	32.76	14.7	1.9	120.48	111.91

$T = 70°C$, 500 rpm, $[Cat] = 7.3 \times 10^{-5}$ mol, MMAO/Zr = 2500, $Pc_2 = 120$ psig, $C_2/H_2 = 1200/150$ psig

the polymerization rate increased steadily with increasing 1-hexene concentration in both solvents. The lowest activities were observed at 90 °C, both for homopolymerization and copolymerizations with different comonomer concentration, and can be attributed to the thermal instability of the catalytic system.

The characterization by GPC of the copolymers obtained in this set of experiments showed high weight average molecular weights (M_w) around 900,000 g/mol. As is well known in this kind of polymerization reactions, the addition of a chain transfer agent like molecular hydrogen (H_2) is frequently used in order to control the molecular weight and molecular weight distributions.

The effect of the hydrogen addition on the Mw and activity in the copolymerization reactions was also studied in this work, and after some preliminary test on the hydrogen addition, a new set of experiments was carried out adding an initial charge of 15 psig of H_2 to the PPR reactors.

Table 2 shows the results of the polymerization and copolymerization reactions carried out in the presence of hydrogen, in order to decrease the molecular weight of the copolymers. The experiments were carried out at 70 °C in isooctane and hexane as solvents.

The activity increased about 30–40% using H_2 as chain transfer agent in both solvents, as shown in Figure 2.

The positive effect of the H_2 addition on the activity of ethylene polymerization has also been observed at high temperatures for other Ziegler-Natta heterogeneous systems, where has been proposed an increase of the propagation rate constant, formation of new active sites, or the reactivation of

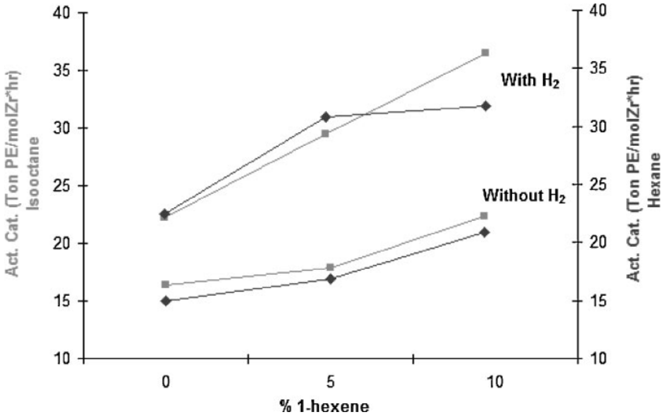

Figure 2.
Hydrogen effect (15 psig) on the polymerization and co-polymerization activities of ethylene and ethylene-1-hexene respectively.

dead sites in the catalytic system, as an explanation for this acceleration effect caused by H_2 additon[12]. The comonomer effect was also observed in these experiments, leading to higher activities as the concentration of comonomer increased in the presence of H_2 (Figure 2).

Molecular weight in the polymers and copolymers obtained with H_2 addition decreased more than one order of magnitude in comparison with the polymers made without H_2 (Table 2). The trend to reduction in the molecular weight is more evident at higher concentrations of comonomer, as observed in Figure 3, where chain transfer reactions to the comonomer can also be carried out in the copolymerizations.

Polymers with lower molecular weights were obtained in hexane compared to isooctane (Table 2), probably related to the lower activity showed in this solvent[11a], and polydispersities decreased by approximately 20% in hexane (less polar solvent), where more homogeneous active sites could be generated than in isooctane (more polar solvent).

Thermal analysis by DSC showed a decrease in the T_m and T_c values of the polymers and copolymers obtained in both solvents (Figure 4) where the lowest crystallization and melting temperatures were observed for the copolymers synthesized in hexane. This fact seems to indicate a higher level of comonomer incorporation when the copolymerization reactions are carried out in hexane.

The different polymerization behaviors in the two solvents may be attributed to the changes in polarity, related to their dielectric constants, where isooctane (1.94) is slightly more polar than hexane (1.88). Changes in the medium polarity can induce a better incorporation of the comonomer in the polyethylene chains, as well as to generate more chain transfer reactions to the comonomer, when comonomer concentration in the reactor increases[11].

The effect of the cocatalyst on the activity of polymerization and copolymerization was also studied at various MAO/Zr ratios (10,000, 5000, and 2500). Figure 5 compares the activities obtained in these experiments. The effect of the cocatalyst on single-site polymerizations is well known. Usually, the activity increases when the cocatalyst ratio is increased, until a certain value, and after that, becomes a constant.[13] For the interval of MAO/Zr ratio of 2,500 to 10,000 evaluated in these experiments, the catalyst activity remains almost constant. Therefore the polymerizations were carried out at MAO/Zr ratios of 2,500 or lower.

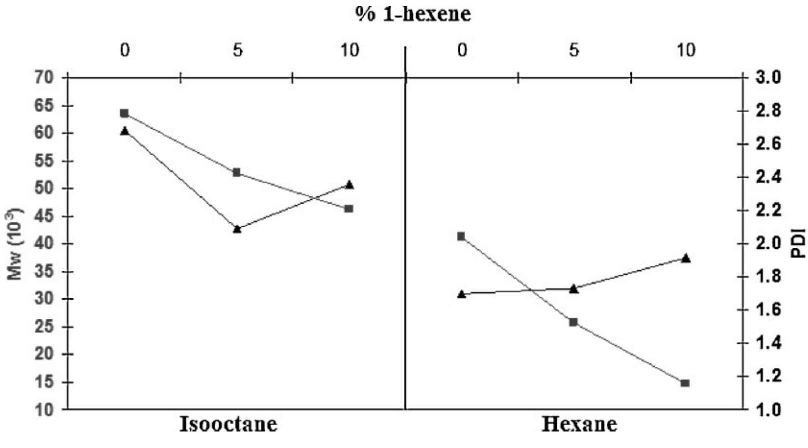

Figure 3.
Molecular weight (Mw) and polydispersity (I) for ethylene polymers and ethylene-1-hexene copolymers synthesized with the nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO system in hexane and isooctane.

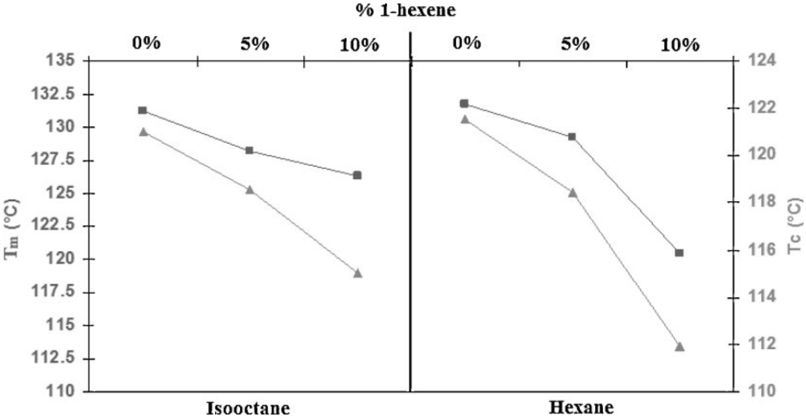

Figure 4.

DSC results for ethylene polymer and ethylene-1-hexene copolymers obtained with the nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO system in hexane and isooctane.

According to the results obtained from the high throughput screening, we could establish the main parameter conditions for scaling up the copolymerization reactions to validate the reliability of the results obtained in the PPR.

The polymerization and copolymerization reactions were further carried out in a 5 gallon stainless steel calorimetric reactor, at polymerization temperature of 70 °C, ethylene pressure of 120 psig, using hexane as solvent, and ethylene/hydrogen ratio of 1200/150 psig, as established in the combinatorial equipment. It was also necessary to change the cocatalyst to modified MAO (MMAO) from Akzo Nobel Co., instead of PMAO (Sigma-Aldrich) used in the PPR, as well as the MAO/Zr ratio (MAO/Zr = 1000), due to the larger amounts of cocatalyst required in the 5 gal reactor. The polymerization solvent (hexane) was also selected between hexane and isooctane, since the activity for ethylene-1-hexene copolymerizations at 70 °C, was only 3% lower than the corresponding catalytic activities obtained in isooctane. The experiments were also carried out with 1-octene at 10 wt-% and at higher concentrations of

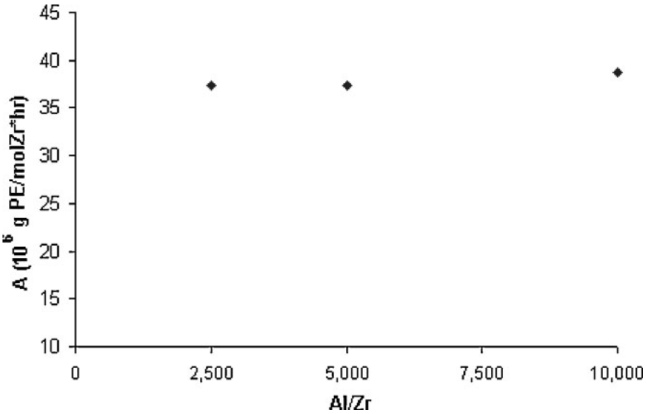

Figure 5.

Activity of the nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO in ethylene-1-hexene (10 wt-%) copolymerizations at different MAO/Zr ratios.

Table 3.
Ethylene polymerization and ethylene-α-olefins copolymerizations (5 Gallon reactor) using the (nBu-$Cp_2ZrHAlH_4$)/SiO_2/MAO catalytic system.

Entry	Sample	Comonomer (wt- %)	A (10^6 gPE/molZr-hr)	Mw (g/mol)	I (Mn/Mw)	Tc (°C)	Tm (°C)	ΔH°m (J/g)	Xc (%)	d (g/ml)
1	HDPE	0	5.12	99,162	2.78	117.0	134.31	193.5	77.1	0.956
2	C_2/C_6	10	4.69	94,809	3.06	113.8	126.1	160.0	67.7	0.951
3	C_2/C_6	20	8.30	86,151	3.05	108.0	119.0	146.4	65.8	0.949
4	C_2/C_8	10	13.47	94,775	2.85	115.5	130.84	172.4	68.6	0.944
5	C_2/C_8	20	14.58	87,979	3.09	114.48	130.08	154.9	63.6	0.943

Hexane, $T = 70\,°C$, 500 rpm, $[Cat] = 7.33 \times 10^{-5}$ mol, MMAO/Zr = 1000, $Pc_2 = 120$ psig, $C_2/H_2 = 1200/150$ psig.

comonomer (20 wt-%). Table 3 shows the results of the ethylene homopolymerization and ethylene-α-olefin copolymerizations, carried out in these experiments.

As expected, for polymerizations carried out with modified MAO (MMAO), and lower MAO/Zr ratios, the polymerization and copolymerization activities were decreased by approximately 60%, as compared with the results obtained using hexane as solvent in the PPR (Table 1, entries 4–6). There are three different causes related to the large decrease observed in the activity when using MMAO in the scaled up polymerization reactions. For one side, is well known the complex mixture contained in the MMAO (tri-isobutyl aluminoxane and methyl alumonoxane), the lower MAO/Zr = 1000 used for scaling up polymerizations, and on the other hand the higher level of impurities more difficult to control in this system.

In spite of the lower activities obtained in these polymerizations, the comonomer effect is also evident at this scale, as shown in Table 3 (entries 3 and 5): the polymerization activity increases at higher comonomer concentrations, as observed at the combinatorial level. In these experiments, the monomer type effect is also observed: copolymerizations with 1-octene had the higher catalytic activities than those with 1-hexene.

Table 3 also shows that the polyolefins made in the 5 gal reactor had higher molecular weights. Polidispersities (I) were also larger than those of copolymers made in the PPR. This fact can be related to the use of MMAO as co-catalyst, which could generates in situ, different types of catalytic species, since is known that MMAO contains a mix of ligands (methyl and isobutyl).

Crystallization (T_c) and melting (T_m) temperatures, crystallinity (X_c), density (d) and heat of fusion (ΔH_f) tend to decrease as the comonomer size and concentration increase, which indicates increasing comonomer incorporation in the polyethylene chains. Crystallinity (X_c) decreases to approximately 12–20% with the addition of either kind of comonomer, which is according to the observed for the thermal analyses of the materials.

Figure 6 compares the thermograms of the ethylene-1-hexene copolymers with the corresponding thermogram of HDPE. The copolymers DSC curves (10 and 20 wt-%) were shifted to lower temperatures. Also can be observed in Figure 6 that copolymer curves are broader than that of the HDPE, which indicates lower crystallinity, due to the presence of short chain branching from comonomer insertions.

The copolymers were characterized by ^{13}C NMR, in order to probe the presence of the comonomer incorporation, and also to obtain an approach of the incorporation grade in mol percent (mol-%) of 1-hexene and 1-octene, through the integration of the CH_2 backbone signal, related to one CH_2 signal from branching.

The incorporation of comonomer were calculated between 0.3 to 1.3%, showing higher incorporation levels, using 1-hexene as comonomer. Table 4 shows results of the copolymers composition, calculated from the ^{13}C NMR spectra integration.

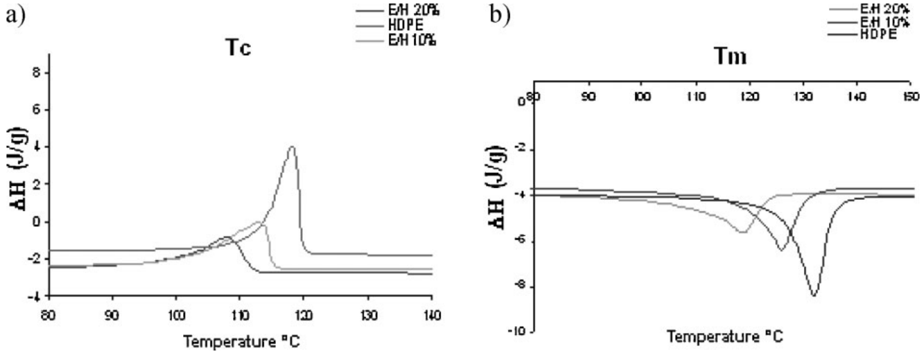

Figure 6.
Thermograms a) Crystallization temperatures (Tm) and b) Melting temperatures (Tm) of the ethylene-1-hexene copolymers at 10 and 20 wt.-% of co-monomer addition, compared with the HDPE obtained under the same polymerization conditions. E/H (ethylene-1-hexene).

Table 4.
Co-monomers content of the copolymers ethylene-1-hexene (C_2/C_6) and ethylene-1-octene (C_2/C_8).

Sample	Comonomer Addition (wt-%)	Comonomer Content* (mol-%)
C_2/C_6	10	0.3
C_2/C_6	20	1.3
C_2/C_8	10	0.7
C_2/C_8	20	1.0

*calculated by ^{13}C NMR

Conclusions

The supported nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO system evaluated in the copolymerization of ethylene and α-olefins, showed high activities, and high molecular weights (Mw) in the copolymers obtained, at low ratios of co-catalyst (MAO/Zr = 2,500 and 1,000).

An approach to the optimal copolymerization conditions was obtained, using a combinatorial equipment (PPR), where the ratio ethylene/hydrogen (C_2/H_2) was determined as 1200/150 psig, in order to produce Mw around 100,000- 80,000 g/mol.

The supported catalytic system worked for scaling up the copolymerization reactions (5 gal reactor), according to the main copolymerization parameters founded in the PPR.

Although the supported nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO showed low incorporation of α-olefins, the copolymers exhibit significant modification in their crystallinity degree and thermal properties.

According to the above results obtained for ethylene-1-hexene and ethylene-1-octene copolymers, and taking into account their density values, we can consider that the supported nBu-$Cp_2ZrH_3AlH_2/SiO_2$/MAO system produce medium density polyethylene.

Acknowledgements: The authors thank to CONACYT México for financial support (Project No. 022059). Also thank the technical support to Javier Borjas and Luis Enrique Reyes for AA analyses, Aída Hernández for GPC and DSC analyses and Víctor Eduardo Comparán for technical support at the pilot plant.

[1] [1a] H. Zhang, R. Hoogenboom, M. A. R. Meier, U. S. Schubert, *Meas. Sci. Technol.* **2005**, 203–211; [6b] D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, A. J. P. White, D. J. Williams, *J. Am Chem. Soc.* **2005**, *127*, 11037.

[2] [2a] F. J. Zhang, M. Song, T. J. Lu, J. P. Liu, T. B. He, *Polymer* **2002**, *43*, 1453; [2b] S. Rylhoff, W. Kaminsky, *Macromol. Chem. Phys.* **2006**, *207*, 1450.

[3] [3a] K. Jokela, A. Vaananen, M. Torkkeli, P. Stara, R. Serimaa, B. Lofgren, *J. Polym. Sci. Part B: Polym. Phys.* **2001**, *39*, 1860; [3b] N. Hadjichristidis, M. Xenidou, H. Iatrou, M. Pitskalis, Y. Poulos, A. Avgeropoulos, S. Sioula, S. Paraskeva, G. Velis, D. J. Lohse, D. N. Schulz, L. J. Fetters, P. J. Wright, R. A. Mendelson, C. A. García-Franco, T. Sun, C. J. Ruff, *Macromolecules*, **2000**, *33*, 2424.

[4] [4a] A. J. Peacock, "*Handbook of Polyethylene, Structures, Properties, and Applications*", 1st edition,

Marcel Dekker Inc., **2000**, p. 2–35; [4b] P. Meka, J. M. Farley, *J. Appl. Polym. Sci.* **1994**, *51*, 121; [4c] P. Starck, A. Malmberg, B. Löfgren, *J. Appl. Polym. Sci.* **2002**, *83*, 1140.

[5] [5a] M. R. Ribeiro, A. Deffieux, M. F. Portela, *Ind. Eng. Chem. Res.* **1997**, *36*, 1224; [5b] D. Lee, S. Shin, *Macromol. Symp.* **1995**, *97*, 195.

[6] R. González, J. Chai, R. Charles, O. Pérez-Camacho, S. Kniajanski, S. Collins, *Organometallics*, **2006**, *25*, 5366.

[7] [7a] B. M. Bulychev, *Polyhedron*, **1990**, *9*, 387; [7b] N. Etkin, D. W. Stephan, *Organometallics*, **1998**, *17*, 763; [7c] K. Khan, C. L. Raston, J. E. McGrady, B. W. Skelton, A. H. White, *Organometallics*, **1997**, *16*, 3252.

[8] H. F. Mark, ''*Encyclopedia of Polymer Science and Technology*'', 3er edition, Wiley-Interscience, **2000**, *52*, p. 459.

[9] H. Zhang, R. Hoogenboom, M. A. R. Meier, U. S. Schubert, *Meas. Sci. and Technol.* **2005**, *16*, 203.

[10] G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347–1376.

[11] [11a] F. Forlini, E. Princi, I. Tritto, M. C. Sacchi, F. Piemontesi, *Macromol. Chem. Phys.* **2002**, *203*, 645–652; [11b] F. Forlini, Z.-Q. Fan, I. Tritto, P. Locatelli, M. C. Sacchi, *Macromol. Chem. Phys.* **1997**, *198*, 2397–2408.

[12] [12a] A. D. Martino, G. Weickert, T. F. L. McKenna, *Macromol. React. Eng.* **2007**, *1*, 229–242; [12b] I. Kouzai, B. Liu, T. Wada, M. Terano, *Macromol. React. Eng.* **2007**, *1*, 160–164; [12c] K.-J-. Chu, J. B. P. Soares, A. Pendilis, *Macromol. Chem. Phys* **2000**, *201*, 552–557.

[13] M. M. de Camargo, F. O. Vieira da Cunha, J. H. Z. dos Santos, J. J. Zacca, *Polymer*, **2003**, *44*, 1377.