

Results Coming from Homogeneous and Supported Metallocene Catalysts in the Homo- and Copolymerization of Olefins

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Summary: Ethylene, propylene and α -olefins were homo- and copolymerized in the presence of a series of homogeneous catalytic systems consisting of methylaluminoxane (MAO) and group IV metallocenes such as $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (I), $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ (II), $\text{Et}(2\text{-Me-Ind})_2\text{ZrCl}_2$ (III), $\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$ (IV). It was found that the catalytic activity, the incorporation of comonomer in the case of copolymers, and the microstructure of the polymers depend on the catalyst's structure. For heterogeneous catalysts, several supports based on metal oxide compounds have been investigated, with special emphasis in those obtained by the sol-gel preparation technique. The homo- and copolymerization of the monomers in the homogeneous systems studied where also investigated using the same catalyst system, but in a heterogeneous medium. Comparative results from the homogeneous and heterogeneous systems are presented and discussed.

Introduction

Homopolymers and copolymers of ethylene and/or propylene with long-chain α -olefins obtained via catalysis are important commercial materials, since their development for different applications has been characterised by their major production and consumption in the last few years, and consequently great efforts have been made to find new and more efficient catalysts to produce these polymers^[1].

Advances in the design of single site catalysts are providing an ever-growing menu of metal-ligand combinations suitable for catalysing the polymerization of olefins^[2]. These catalysts enable control over the polymerization reaction and therefore of important bulk properties of the resulting polymer^[3]. An excellent body of mechanistic work also exists that provides insight into how the active site technology is making a considerable impact on the commercial processes that produce these commodity products^[4-5].

The use of metallocene catalysts has allowed a very rapid development in the field of polyolefins. These catalysts present single-site characteristics (and very high activities), and thus all the sites produce nearly the same chain architecture, leading to polymers with a narrow molecular weight distribution. In the case of copolymers with α -olefins, the side branches are randomly distributed in the polymer backbone.^[6-8]

Considering the extensive experience acquired by our group in the study of the homo- and copolymerization of ethylene with several α -olefins using metallocene catalysts, we have found it convenient to study the coordinating action of different pairs of catalysts for making polyethylene copolymers from a single readily available monomer, and to explore the possibility of producing these materials with elastomeric properties. The homo- and copolymerization of propylene with α -olefins, and the preparation of heterogeneous catalysts based on metallocene compounds were also studied.

In order to study the effect of the metallocene structures on the polymerization of olefins we chose four metallocenes (Figure 1): $\text{Et(Ind)}_2\text{ZrCl}_2$ (I), $\text{Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$ (II), $\text{Et(2-Me-Ind)}_2\text{ZrCl}_2$ (III), $\text{Ph}_2\text{C(Flu)(Cp)ZrCl}_2$ (IV).

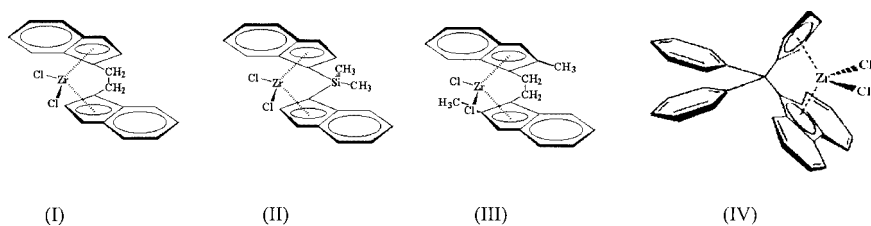


Figure 1: Metallocene catalysts

With these catalyst systems it is possible to analyse the influence of the different types of interannular bridges ($-\text{CH}_2-\text{CH}_2-$; $(\text{CH}_3)_2\text{Si}$), the presence of substituents in the aromatic ring (catalysts I and III), and finally the type of stereoselectivity that the catalyst has on the microstructure and properties of the resulting polymer.

Homogeneous Catalysts

Our earlier studies^[9-13] showed that several metallocene catalysts promote the copolymerization of ethylene with α -olefins. Copolymers of ethylene-1-hexene and ethylene-1-octadecene with highly elastomeric properties were obtained. Activities

around 50,000 [kg polymer/ mol h bar] for the homopolymerization of ethylene and 100,000 [kg polymer/ mol h bar] for copolymerization were obtained (Figure 2) and incorporation values of up to 18 mol-% for the 1-hexene comonomer (Figure 3).

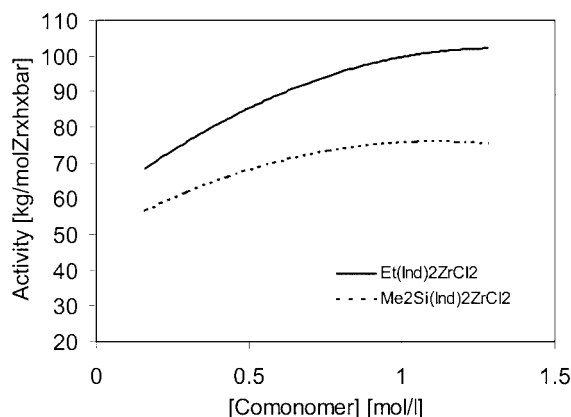


Figure 2: Influence of 1-hexene concentration on catalytic activity for two different metallocene systems.

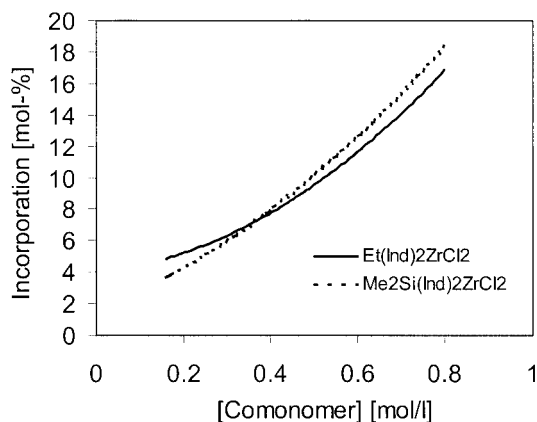


Figure 3: Influence of 1-hexene concentration on comonomer incorporation for two different metallocene systems.

The $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalytic system in both cases (homo- and copolymerization) showed the highest catalytic activity (Figures 2 and 4). The $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ (II) system, however, reaches a large comonomer incorporation in the copolymerization of ethylene with α -olefins (Figures 3 and 5), especially with long-chain olefins like 1-octadecene,^[9-10] as shown in Figure 5.

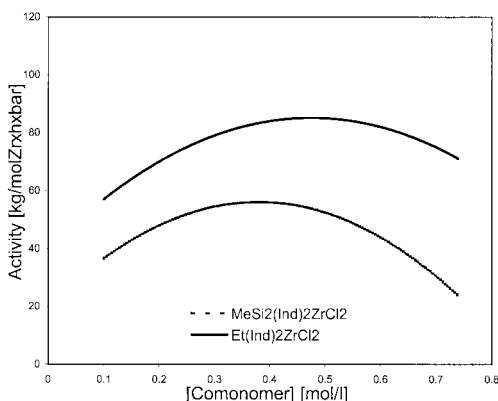


Figure 4: Influence of 1-octadecene concentration on catalytic activity for two different metallocene systems.

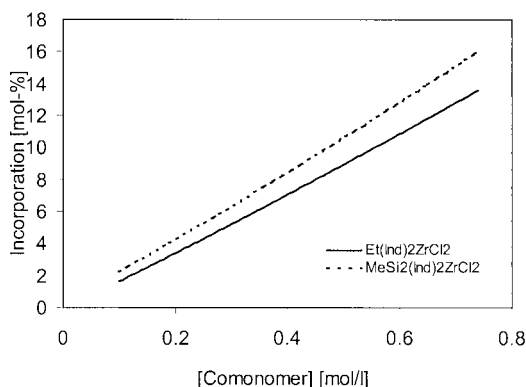


Figure 5: Influence of 1-octadecene concentration on comonomer incorporation for two different metallocene systems.

Results obtained from the stress-strain behaviour of some ethylene-1-octadecene copolymers, obtained and quenched from the melt, are shown in Figure 6. It is clear that the effect of the incorporated comonomer changes the mechanical behaviour of the curve, going from a rigid material as PE to one elastomeric type material in the case of C4 (highest incorporation).^[11]

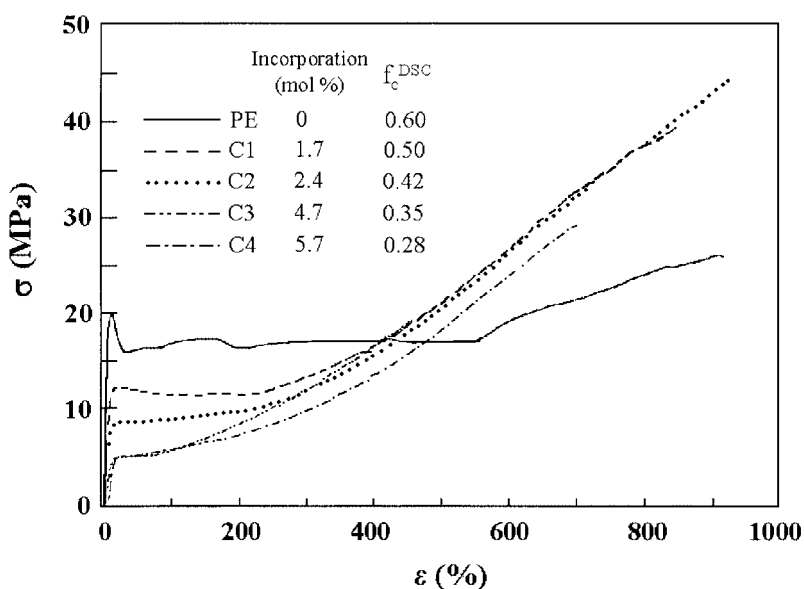


Figure 6: Stress-strain curves for different samples at room temperature

For the homopolymerization of propylene, the trends found are the same as for ethylene, which mean that the highest activity values were found with the $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ (I) catalytic system^[12].

For the copolymerization of propylene with different comonomers, the results obtained with catalytic system I show high catalytic activities. Figure 7 shows the results of these studies. An increase in activity is seen for all the comonomers.

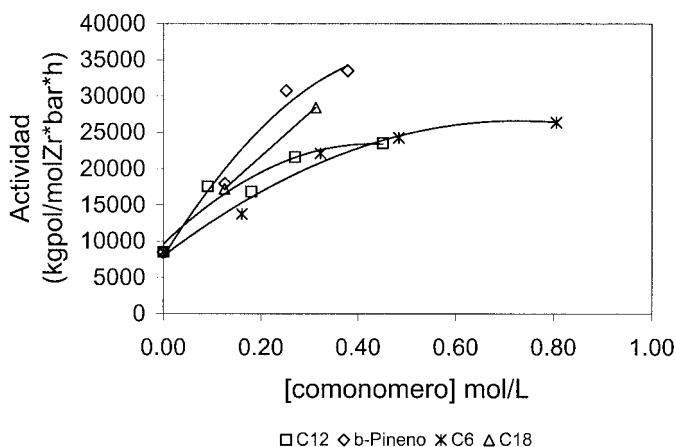


Figure 7: Influence of comonomer concentration on catalytic activity for propylene copolymerization.

The study related to the homopolymerization of long-chain α -olefins is also quite useful, since very valuable information can be obtained that makes it possible to understand more completely the behavior of α -olefins when used as comonomers in copolymerization reactions with other olefins^[13-14]. The homopolymerization of 1-octadecene by using $\text{rac-Et(Ind)}_2\text{ZrCl}_2/\text{MAO}$ (I) and $\text{rac-Me}_2\text{Si(Ind)}_2\text{ZrCl}_2/\text{MAO}$ (II) as catalyst systems has already been reported by our research group. Table 1 shows the main results.

Table 1: Influence of temperature and catalytic system on activity and molecular weight in the homopolymerization of 1-octadecene.

Catalyst	Temperature	Conversion	Activity	Mw	Mw/Mn
	°C	%	[kg Pol / mol Zr bar]	[g/mol]	
I	70	77	1200	6326	1.6
	30	28	470	22647	1.8
II	70	33	530	9943	1.5
	30	25	400	25044	1.7
III	70	63	1000	5473	1.6
	30	25	400	22055	1.7
IV	70	47	730	19056	1.6
	30	7	110	37676	2.2

The results show that the catalytic activity of system III is similar to that obtained for system I, where the methyl group does not have any effect. The catalytic activity of system II was found to be the lowest of all the catalyst systems studied. This behavior is possibly associated with charge effects on the metallic center, and may also be due to the opening of the angle between the indenyl rings which leads to a change in the bridge.

This also shows that the catalytic activities of all the catalyst systems decreased when the polymerizations were performed at 30° C, giving similar activity values for catalyst systems I, II and III. Catalyst system IV showed the lowest catalytic activity at 30° C. The catalytic activity of system IV was 6.5 times lower for polymerizations carried out at 30° C as compared with those performed at 70° C^[15].

Finally, we have looked into the importance of the copolymers of ethylene with α -olefins. In this context we have also studied this copolymerization producing the comonomer in situ via oligomerization of ethylene with an iron catalyst $[(2\text{-ArN-C(Me)}_2\text{C}_5\text{H}_3)\text{FeCl}_2]$ (V). The polymers obtained with this system have different branch lengths incorporated in the main polymer chain, as shown in Figure 8.^[16]

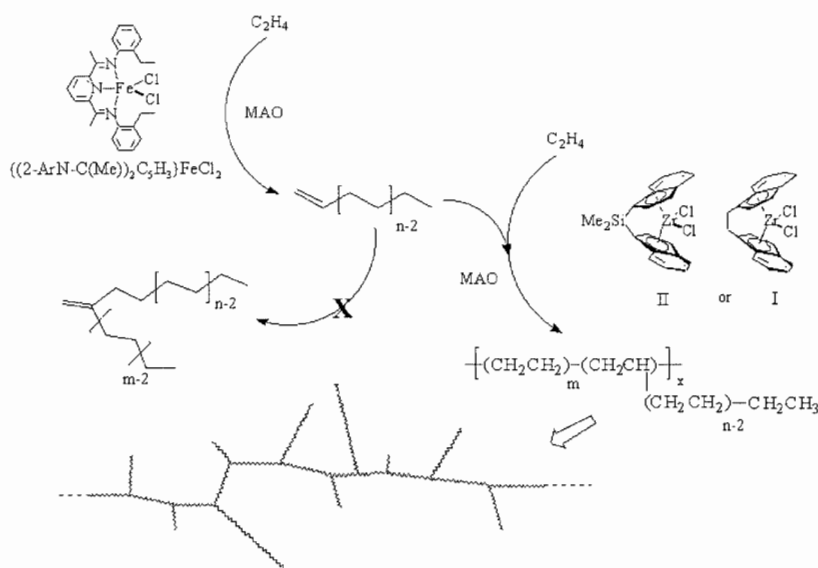


Figure 8: Simultaneous oligomerization and polymerization of ethylene with iron and zirconium catalysts.

Table 2: Ethylene copolymerization by producing the comonomer in situ: Fe/EtInd₂ZrCl₂/MAO catalytic system^(a).

Entry	Fe/Zr	Activity ^(b)	T_m (°C) ^(c)	$M_w \times 10^{-3}$	M_w/M_n	Incorporation mol % ^(d)
1	4.6	34,060	124	81.2	1.68	2
2	9.3	16,850	112	65.1	1.65	2.8
3	1.9	27,884	119	74.6	1.56	1.8
4	3.1	18,259	119	81.8	1.61	2.2
5	4.7	16,180	117	68.7	1.68	2.5
6	2	20,850	121	81.1	1.91	1.8

Table 3: Ethylene copolymerization by producing the comonomer in situ: Fe/Me₂Si(Ind)₂ZrCl₂/MAO catalytic system^(a).

Entry	Fe/Zr	Activity ^(b)	T_m (°C) ^(c)	$M_w \times 10^{-3}$	M_w/M_n	Incorporation mol % ^(d)
1	4.5	20,933	123	55.9	16.1	2.4
2	10	9,850	125	29.9	13.2	3
3	2.9	19,455	121	83.9	15.6	2.9
4	4.5	12,090	124	57.3	15.2	4
5	2	12,675	120	80.5	9.1	2.3

For both tables:

(a) **Reaction Conditions:** Solvent, toluene; polymerization time, 0.5 h.; stirrer speed, 500 rpm; pressure, 2 bar; temperature, 60 °C; Al/Fe, 2000; Al/Zr, 2000-15000. (b) kg polymer/(molZr+molFe)(h)(bar). (c) Melting Point determined by DSC. (d) Moles of branching per 100 ethylene units.

A summary of the results obtained for the different Fe/EtInd₂ZrCl₂/MAO/C₂H₄ and Fe/Me₂Si(Ind)₂ZrCl₂/MAO/C₂H₄ combinations are given in Tables 2 and 3, respectively. Analysing Table 2, it was found that for a given concentration of Zr, increasing the Fe/Zr ratio leads to a reduction in the activity. Relative to Fe/Me₂Si(Ind)₂ZrCl₂/MAO/C₂H₄ combinations, the same trend was observed for this system with respect to the catalyst content, which means that the increase in the Fe/Zr ratio decreases the activity, and when the total metal concentration is raised, a lower activity is observed. On the other hand, a larger amount of ethylene was consumed by the Fe/EtInd₂ZrCl₂/MAO/C₂H₄ catalyst system. It was also observed that for a constant Fe/Zr ratio the activity decreases at a higher total metal concentration (see entries 1 and 5 in Table 2). ¹³C NMR data for the polymers obtained are consistent with a branched structure. For this combination, the percentage branching increases with the Fe/Zr ratio. The last columns of Tables 2 and 3 contain the percentage of branching calculated by using a published method.^[17]

The polymers produced by Fe/Me₂Si(Ind)₂ZrCl₂/MAO/C₂H₄ combinations are characterized by a broad and bimodal molecular weight distribution. The low molecular weight fraction becomes more pronounced as the Fe/Zr ratio increases, giving compositions similar to those of the product obtained with the Fe catalyst. Compared with the product obtained using Fe/EtInd₂ZrCl₂/MAO/C₂H₄ systems, the latter are characterized by presenting a monomodal narrow molecular weight. The branching backbone, which increases with increasing concentration of the iron catalyst, and the monomodal weight distribution strongly support the formation of branched polyethylene and an efficient conversion of the monomer to polymeric material.

Heterogeneous Catalysts

In order to turn metallocene catalysts into a morphological control tool, a good method is to heterogenize the catalysts. Although a decrease in catalytic activity with respect to the homogenous systems is expected, the morphology of the polymer and the temperature control of the reaction can be improved. Also, fouling of the reactor, the amount of co-catalyst used, and the cost of the process can be reduced^[18-21].

These catalytic systems are based on the immobilization of the metallocene complex on an inert medium (support), without loss of properties and with enhanced physico-chemical characteristics. The basis for these heterogeneous catalysts is to find new supports. These are obtained by preparing different types of oxides like SiO₂, MgO, TiO₂, SiO₂-TiO₂ using sol-gel techniques, leading to more efficient interactions with the metallocene complexes. With this technique it is possible to obtain supports having specific surface area, pore volume and diameter, particle size, and controlled morphology.

Support Preparation

Table 4 summarizes the results of the physical characterization of different silica samples prepared from xerogels via the sol-gel technique. These xerogels were prepared with siloxane sols formed under linear polymerization conditions and by varying the amount of chitosan (CHI) incorporated in them.

Table 4: Effect of precursor xerogel composition, obtained by solvent extraction, on the surface characteristics of silica after calcination for 2 hours at 550 °C.

<i>Sample</i>	<i>Precursor</i>	<i>Molar Ratio</i>	<i>S_{BET}</i>	<i>Pore Diameter</i>	<i>Pore Volume</i>	<i>Obs.</i>
	<i>Type</i>	<i>CHI/SiO₂</i>	<i>m²/g</i>	<i>Å</i>	<i>cm³/g</i>	
S ₀	Formic Ac	0	45	493	0	Blank
S ₆	Si sol with chitosan	0.06	323	14	0.156	Microporous
S ₅	Si sol with chitosan	0.1	327	15	0.16	Microporous
S ₄	Si sol with chitosan	0.2	503	30	0.221	Microporous
S ₃	Si sol with chitosan	0.5	632	31	0.41	Mesoporous

S_{BET}: Specific surface area.

In sample S₀ the silica obtained from a precursor gel without CHI shows a low specific surface area and is non-porous in the measured range. Here, the siloxane sol was mixed with HCOOH which had been used as the solvent for CHI, in order to use the resulting silica as a blank which shows that formic acid does not affect sample porosity. The result is in agreement with the formation of non-porous films in the samples obtained from linear sols.

On the other hand, surface area, as well as pore volume and average pore size, increases with the amount of CHI in the precursor solution up to a CHI/SiO₂ molar ratio of 0.5. The pore size distribution is narrow and monomodal, which could be explained on the basis of an homogeneous distribution of the growing polymer domains inside the inorganic network. By studying hybrid CHI/SiO₂ films with molar ratios 0.5-0.6 (1:1 by weight), we found that a hybrid complex with a nanocomposite is formed.^[22]

The increase of initial amount of chitosan (sample S₆), the differential plot for pore volume shows a multimodal and broad distribution of pore size. We think that an excess over the molar composition of the complex should induce phase separation and formation of heterogeneous domains in the composite sample. As expected, after elimination of the organic part the size of the pores should be related to the size of the polymer domains present in the precursor xerogel.

In conclusion, we have shown that the porosity of the silica can be tailored by varying the composition of the hybrid precursor. Moreover, the morphology of the hybrid xerogel and of the final silica after the elimination of the organic residue depends on the method of preparation.^[23]

Catalyst Preparation

When the goal is to obtain supports for olefin polymerization, the most important parameters to control are the physicochemical characteristics of the support. Figure 9 shows catalyst preparation with the supports obtained by the sol-gel technique, and Table 5 shows the results of the preparation of the different supports.

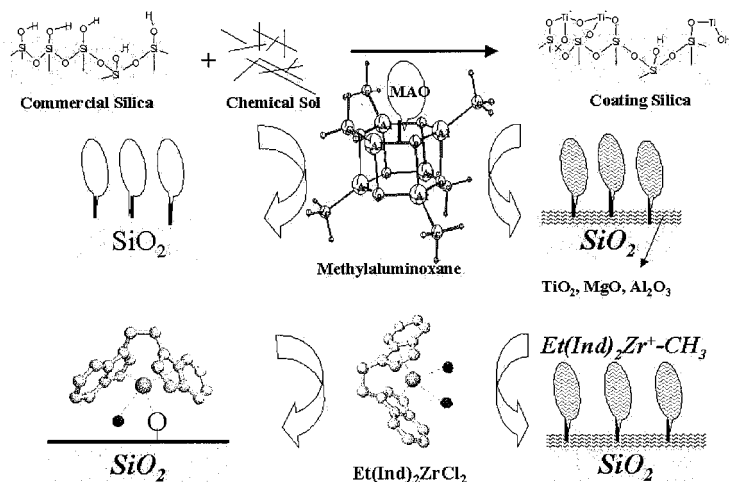


Figure 9: Catalyst preparation.

Table 5 shows the change in the values of the BET area and of the volume and size of the porous supports, by coating commercial silica (ES70) particles with different oxides, and particularly after modification with MAO. This last step, modification with methylaluminoxane, shows the most remarkable changes in the properties of the particles.

The supports presented below had high activities with the Et(Ind)₂ZrCl₂ (I) catalyst and MAO as a co-catalyst in ethylene polymerization. These catalytic systems reach catalytic activities comparable to that of the commercial silica (SiO₂MAO), but require less methylaluminoxane in the modification step (see Table 5). Table 6 summarizes the results of ethylene polymerization with these types of catalysts.

Table 5: Surface modification of silica (ES70) by the sol-gel technique: change in specific surface area, porosity and chemical composition of the supports.

<i>ES70 Coating</i> %	<i>S_{BET}</i> <i>m²/g</i>	<i>Pore</i> <i>Volume</i> <i>cm³/g</i>	<i>Pore</i> <i>Diameter</i> <i>Å</i>	<i>Modified</i> <i>Support</i>	<i>S_{BET}</i> <i>m²/g</i>	<i>Pore</i> <i>Volume</i> <i>m³/g</i>	<i>Pore</i> <i>Diameter</i> <i>Å</i>	<i>Al</i> %-pp	<i>Ti</i> %-pp
-	255	1,34	171	<i>ES70M</i>	206	1,02	156	10,5	-
<i>Al₂O₃-100</i>	236	1,42	194	<i>ES70AlM</i>	184	0,96	164	-	-
<i>TiO₂-50</i>	226	1,35	187	<i>ES70Ti5M</i>	193	0,87	143	12,8	2,0
<i>TiO₂-100</i>	236	1,38	189	<i>ES70TiM</i>	216	-	-	10,2	4,2
<i>SiO₂-TiO₂-100</i>	249	1,48	191	<i>ES70SiTiM</i>	210	-	-	13,9	1,9
<i>MgO-100</i>	241	1,47	181	<i>ES70MgM</i>	229	0,96	139	-	-
<i>MgO-50</i>	247	1,49	187	<i>ES70Mg5M</i>	-	-	-	-	-
-	-	-	-	<i>SiO₂MAO*</i>	328	0,51	75	22	-
-	-	-	-	<i>TiO₂M**</i>	80	0,15	65	10	-

ES70: Commercial Silica; M: modification with MAO.

* Witco commercial silica treated with MAO.

** TiO₂, obtained by sol-gel techniques with chitosan.

Table 6: Effect of type of support on catalytic activity in the polymerization of ethylene (Et(Ind)₂ZrCl₂/MAO).

Catalyst	% Zr	Al/Zr	[Zr] Moles	Activity [Kg PE/ mol h bar]	Bulk Density [g/mL]
SiO ₂ MMEt	0.2	2500	6.E-06	2258	0.22
	0.19	2400	6.E-06	2569	0.24
ESSiTiMMEt	0.18	3000	4.E-06	2919	0.42
	0.22	2500	6.E-06	2342	-
ESTiMMEt	0.2	2400	6.E-06	2150	0.23
	0.2	2400	6.E-06	2036	0.13
ESMgMMEt	0.15	3600	4.E-06	3901	0.40
	0.27	2400	6.E-06	2349	0.18
ESMg5MMEt	0.17	3100	5.E-06	2354	0.22
ESSiTiMMEt 20/80	0.11	3100	5.E-06	3247	-
MgOMMEt	0.2	2500	6.E-06	4032	0.16
S ₀ MMEt*	0.12	2500	6.E-06	3465	0.28
	0.12	2500	6.E-06	3904	0.30

* Correspond to a silica from table 4.

Catalyst SiO₂MMEt is well known and is taken as a reference. In general, all the systems studied had similar activities, and many of them had higher activities, as commented above, particularly those catalysts obtained from ESMgMMEt, MgOMMEt and S₀MMEt, the latter supported on silica obtained by the sol-gel technique.

The use of these heterogeneous systems has improved polymer morphology because the polymer grows around the support and takes its particle shape. So, we can have a

polymer with a spherical shape and a controlled morphology depending on the final use of this material.

In general, the trend in the copolymerization of ethylene with 1-hexene and 1-octadecene in heterogeneous systems is the same for the homogeneous system (see Figure 10). This means that the olefin with the longer chain (1-octadecene) shows the highest activity for both systems, however the catalytic activity values are as expected lower for the heterogeneous systems.

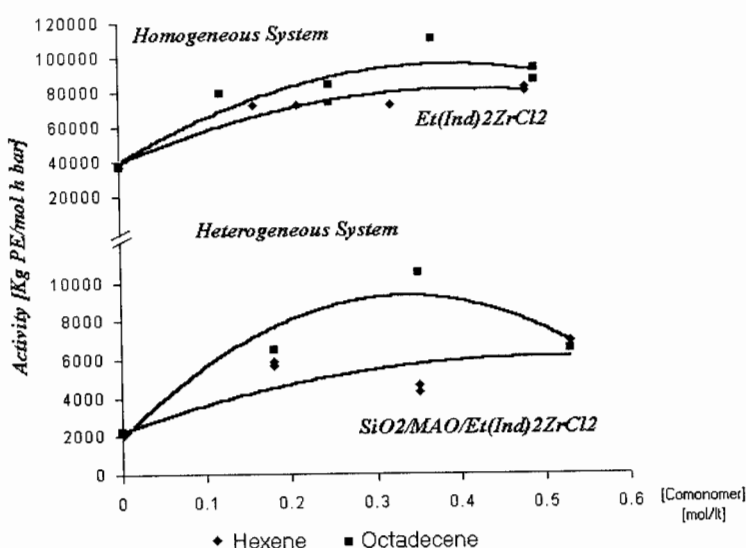


Figure 10: Comparative results between homogeneous and heterogeneous system for the copolymerization of ethylene with 1-hexene and 1-octadecene.

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References

- [1] VK. Gupta In: Cheremisinoff NP, editor. Handbook of Engineering Polymeric Material, New York: Marcel Dekker, **1997**,155-65
- [2] (a) W. Kaminsky, H. Sim, Eds.; Springer-Verlag; Berlin. **1988** (b) G. Fink, R. Mülhaupt, H.H. Brintzinger, Eds.; Springer-Verlag; Berlin. **1995** (c) A. Togm, R.L. Halterman, Eds.; Wiley-VCH: New York **1998**. (d) G.J.P. Britovack, V.C. Gibson, D.F. Wass, Angew Chem.; Int. Ed. Ed.Engl. **1999**. 429. (e) M.J. Bochmann, Chem. Soc. Dalton trans. **1996**.
- [3] (a) D. Rotman, chem. Week **1996**, 158 (36), 37. (b) M. Paige, M. Chem. Eng. News **1998**, 76, 6(49), 25.
- [4] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, M. Angew. Chem. Int. Ed. Engl. **1995**, 34, 1143a) B. L. Small, M. Brookhart, A. Bennett, J. Am. Chem. Soc. **1998**, 120, 4049. b) R. W. Barnhart, G. C. Bazan, J. Am. Chem Soc. **1998**, 120, 1082. c) W. Kaminsky, R. Engeausen, K. Zoumis, W. Spaleck, J. Rohrmann, Makromol. Chem. **1992**, 193, 1643.
- [5] L. Resconi, A. Fait, F. Piemontesi, M. Colonna, H. Rychlicki, R. Zeigler, Macromolecules **1995**, 28, 6667-6676.
- [6] (a) J. Ewen, J. Am. Chem. Soc. **1984**, 106, 6355. (b) J. Ewen, U.S. Patent **1985**, 4,522, 982 to Exxon. (c) J. Ewen, L. Haspeslagh, J. Atwood, H. Zhang, J. Am. Chem. Soc. **1987**, 109, 6544.
- [7] W. Kaminsky, K. Külper, H. H. Brintzinger, F. Wild, Angew. Chem. Int. Ed. Engl. **1985**, 24, 507.
- [8] V. Busico, R. Cipullo, Prog Polym. Sci., **2001**, 26, 443.
- [9] R. Quijada, G. Galland, R.S. Mauler, Macromol Chem Physics **1996**,197, 3091-8.
- [10] R. Quijada, A. Narváez, R. Rojas, F.M. Rabagliati, G.B. Galland, R.S. Mauler, R. Benavente, E. Pérez, J. Pereña, A. Bello, Macromol. Chem. Phys. **1999**, 200, 1306.
- [11] R. Benavente, E. Pérez, R. Quijada, J Polym Sci B: Polym Phys **2001**,39, 277-285.
- [12] J.L. Guevara, R. Quijada, P. Saavedra, H. Palza, G. Galland, submitted to Bol. Soc. Chil. Quím. **2001**.
- [13] R. Quijada, J. Dupont, M. Lacerda, R. Scipioni, G. Galland, Macromol. Chem. Phys. **1995**, 196, 3991.
- [14] J.L. Guevara, R. Rojas, A. Narvaez, R. Quijada, Bol. Soc. Chil. Quím. **1999**, 44, 497.

- [15] J.L. Guevara, M. Yazdani-Pedram, G. Galland, D. Ribeiro, *Journal of Polymer Science, Part A: Polymer Chemistry*, Submitted March, **2002**.
- [16] R. Quijada, R. Rojas, G. Bazan, Z. Komon, R. Mauler, G.B. Galland, *Macromolecules*, **2001**,34, 2411-2417.
- [17] G.B. Galland, R. F. de Souza, R.S. Mauler, F. F. Nunes, *Macromolecules*, **1999**,32, 1620.
- [18] T. Kamfjord, T.S. Wester, E. Rytter, *Macromol. Rapid Commun.* **1998**,19, 505-509.
- [19] M.R. Ribeiro, A. Deffieux, M. Portela, *Ind. Eng. Chem. Res.* **1997**, 36, 1224-1237.
- [20] J. Tudor, D. O'Hare, *Chem. Commun.* **1997**,6, 603.
- [21] K. Soga, T. Arai, H. Nozawa, T. Uozomi, *Macromol. Symp.* **1995**, 97, 53.
- [22] J. Retuert, A. Nuñez, M. Yazdani-Pedram, F. Martínez, *Macromol. Rapid Commun.* **1997**,18,163.
- [23] J. Retuert, M. Yazdani-Pedram, V. Arias, R. Quijada, *Chemistry Materials*, Submitted Nov., **2001**.

