

# Polymerization of Ethylene: Some Aspects of Metallocene Catalyst Stabilization Under Homogeneous and Heterogeneous Reaction Conditions

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**ABSTRACT:** The development of metallocene-based catalysts is an important advance on the study of polyolefinic materials. However, due to the rather different conditions that are established in actual applications, only around 3% of these polymers are obtained from metallocene technology. In view of this, novel strategies must be developed to produce metallocene-based catalysts that are more thermally stable, which is a fundamental requirement to establish metallocene technologies. Homogeneous and heterogeneous polymerizations of ethylene were compared, using the  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{MAO}$  system. Homogeneous polymerizations were more active than the corresponding supported reactions. At low ethylene pressure, the addition of 1-hexene increases the activity under homogeneous conditions. Nevertheless, this is not observed on the respective supported systems. At higher pressure conditions, all polymerizations attained higher yields. However, when the reaction tempera-

ture increases the activity significantly decreases under homogeneous conditions. Furthermore, when the polymerization was performed under heterogeneous conditions the deactivation was lower. The homogeneous and supported catalytic systems show different characteristics and, in all attempted reactions, immobilization of the molecular catalyst reduces the activity. However, the deactivation ratio was lower when the polymerization was performed under heterogeneous conditions. This means that immobilization of  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  on silica can improve the thermal stability of the catalytic species. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3051–3057, 2011

**Key words:** olefin polymerization; metallocene; thermostability of metallocene catalyst; high temperature olefin polymerization; homogeneous versus heterogeneous olefin polymerization

## INTRODUCTION

Over the last 20 years, metallocene-based catalysts for olefin polymerization have been considered one of the most important scientific and technological advances on the development of new polyolefinic materials.<sup>1–7</sup> These catalytic systems are significantly different from previous generations of Ziegler-Natta catalysts. Metallocene catalysts can be tailored to produce polyolefins with unique stereoregularities, degrees of tacticity, and monomer incorporation. Part of this progress is due to the efforts of organometallic chemists to validate olefin polymerization mechanisms, and comprehend electronic and steric factors that modulate catalytic species.<sup>8–17</sup> For that reason, we have now at our disposal quite a few

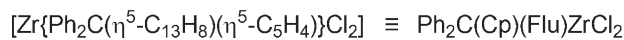
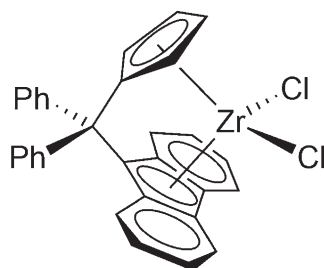
molecular catalytic systems that generate a wide range of polyolefinic materials.<sup>18,19</sup>

Metallocene-based polymers, varying from crystalline to elastomeric materials,<sup>20</sup> have been commercially available since 1991.<sup>21</sup> However, until now, less than 3% of the polyolefin produced are obtained from metallocene technology.<sup>22</sup> The polymers prepared from this technology have been driven to be used on specific markets in which value-added and higher priced polymers can compete.<sup>23</sup> Impact strength and toughness, better melt characteristics, and improved clarity in films are some of their properties.<sup>24,25</sup> This restricted use of metallocene-based polymers are mostly due to the fact that those polymers are obtained under mild polymerization reaction conditions, with temperatures normally around 40–80°C, since higher reaction temperatures lead to catalyst decomposition and/or lower molecular weight polymers.<sup>26–28</sup> Indeed, most of the technology developed for polyolefin production, based on classic Ziegler-Natta catalysts, is held on processes which normally operate at more severe polymerization reaction conditions (higher temperatures and pressures).<sup>29</sup> Briefly, there are two major

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**Figure 1** Molecular structure of the precatalyst employed.

limitations that often prevent access of metallocene-base catalysts to be applied on high temperature reaction conditions: (i) the catalyst efficiency and (ii) the molecular weight of the obtained polymers. Both of these factors decrease as a function of rising temperature.<sup>27,30</sup> Thus, to extend the use of metallocene catalyst technology, it is important to prepare catalysts that are able to produce high molecular weight polymers at more severe polymerization reaction conditions, with very high catalytic activities and short residence times.<sup>30,31</sup>

Different research groups<sup>32–34</sup> carried out a series of systematic studies on copolymerization of ethylene and  $\alpha$ -olefins to discover suitable metallocene-based catalysts that can be employed under more severe polymerization reaction conditions. They verified that some of the most thermally stable metallocene catalysts are ansa-metallocene derivatives, bearing fluorenyl fragments, and containing phenyl groups at the bridged carbon.<sup>35,36</sup> To bring more light to this subject, we have recently carried out a systematic investigation on ethylene homopolymerization at high temperatures and pressures, using metallocene catalysts under ternary system conditions,  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{PhNHMe}_2\cdot\text{B}(\text{C}_6\text{F}_5)_4/(i\text{-Bu})_3\text{Al}$ .<sup>37</sup> These observations rationally lead to selection of  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  as a good catalyst candidate to be explored in depth. Figure 1 displays the molecular structure of the precatalyst, employed on this work.

Anchoring metallocene complexes on suitable supports is also one good strategy to reach more thermally stable metallocene-type catalyst systems.<sup>38,39</sup> The immobilization, for example, decreases the probability of forming bimolecular complexes,<sup>40</sup> which are dormant or inactive catalytic species. Thus, the immobilization of metallocene catalysts on a carrier suppresses any interactions of the polymerizing sites, reducing the deactivation rate of the catalytic system.<sup>7,34,41</sup> Furthermore, the immobilization of molecular catalysts, like metallocenes, give convenient consequences that are normally required for indus-

trial scale polymerization processes, for example, avoidance of reactor fouling, less cocatalyst requirement, good and uniform polymer morphology, high polymer density, etc.<sup>42–44</sup> For this purpose, several classes of single-center metallocene and nonmetallocene catalysts have been immobilized on supports, and their performance have been investigated in olefin polymerization.<sup>42,43,45</sup>

One of the earliest works related to the immobilization of metallocene catalysts for olefin polymerization was presented by Chien in 1976, using  $\text{Mg}(\text{OH})\text{Cl}$  as support, and  $\text{AlEt}_2\text{Cl}$  as cocatalyst.<sup>44</sup> Since then, different support materials have been investigated, but amorphous silica is the most required support for metallocene immobilization.<sup>42,46,47</sup> Silica, due to its unique surface chemistry, enables the immobilization of reagents, and provides good control of the morphological features of the obtained polymer particles.<sup>45,48,49</sup> It is important to remark that, regardless of the immobilization processes, the advantages of the corresponding homogeneous system (high catalytic activity, stereochemical control, ability to produce copolymers with statistical comonomer distribution, etc.) must be kept after immobilization, while providing reduction of the cocatalyst amount required, and improving the morphological characteristics of the polymers, as well as the thermal stability of the catalytic system.<sup>31,45,42,50–53</sup>

In this article, we report our results on the homo- and copolymerization of ethylene at different reaction temperatures, employing  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  as precatalyst and methylalumoxane, MAO, as cocatalyst under homogeneous and heterogeneous conditions.

## EXPERIMENTAL

### Materials

All chemicals were analytical reagent grade and were manipulated under inert atmosphere using standard Schlenk techniques. Dichloromethane (Dinâmica) was dried over  $\text{P}_2\text{O}_5$  and distilled just before use. Hexane (Dinâmica) was dried with  $\text{Na}/\text{benzophenone}$ , distilled, and stored under argon. The complex  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  was prepared according to literature procedures.<sup>54,55</sup> Silica Grace 948 ( $255 \text{ m}^2 \text{ g}^{-1}$ ; pore size: 248 Å) was activated under vacuum ( $P < 10^{-4} \text{ mbar}$ ) for 16 h at  $100^\circ\text{C}$  before use. Ethylene and argon (from White Martins/Praxair) were passed through molecular sieve columns. MAO (Witco, 10.0 wt % toluene solution) was used without further purification. The 1-hexene (Acros Organics) was dried with  $\text{Na}$ , distilled, and stored under argon before use.

### Catalyst preparation

Complex  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  was directly immobilized on preactivated silica (1.00 g) using dried  $\text{CH}_2\text{Cl}_2$  as solvent, corresponding to a 0.50 wt % Zr/ $\text{SiO}_2$ . The mixture was stirred for 2 h at 0°C. The solid was recuperated by filtration, and washed with  $6 \times 5.0$  mL of dried  $\text{CH}_2\text{Cl}_2$ . The salmon red solid was finally dried under vacuum for 4 h.

### Characterization of the support and the supported catalyst

DRIFTS measurements were made in an ABB-BOMEM FTLA 2000-100 FT-IR spectrophotometer at 298 K, using a DRIFT accessory equipped with a chamber for air-sensitive samples.

Zirconium loadings in catalysts were determined by Rutherford Backscattering Spectrometry (RBS) using a  $\text{He}^+$  beam of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. This method is based on the determination of the number and the energy of the detected particles, which are elastically scattered in the Coulombic field of the atomic nuclei of the target.<sup>56</sup> In this study, the Zr/Si atomic ratio was determined from the heights of the signals corresponding to each of the elements in the spectra and then converted to wt % Zr/ $\text{SiO}_2$ .

### Polymer characterization

Polymer melting points ( $T_m$ ) and crystallinities ( $\chi_c$ ) were determined on a Perkin-Elmer DSC-4 differential scanning calorimeter connected to a thermal analyst 5000 integrator and calibrated with indium, using a heating rate of  $10^\circ\text{C min}^{-1}$  in the temperature range of 40–160°C. The heating cycle was performed twice, but only the results of the second scan are reported.

### Polymerization reactions

Ethylene polymerizations were conducted using both homogeneous (Zr) and supported (Zr/ $\text{SiO}_2$ ) catalyst in the presence of MAO as cocatalyst. Two polymerization processes were employed in this study, low (1.6 bar), and higher (5.0 bar) ethylene reaction pressures. Just before polymerizations, both reactors were treated with triethylaluminum (150 mL, 10 wt % of TMA in toluene) for 30 min under argon. Acidified (HCl) ethanol was used to quench all polymerization processes, and the reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at 60°C overnight.

### Low pressure polymerizations

The polymerizations were performed in 150 mL of dried toluene in a 300-mL Pyrex glass reactor connected to a constant temperature circulator and equipped with magnetic stirring and inlets for argon and ethylene. MAO was used as cocatalyst. For each experiment, a mass of catalyst, corresponding to  $10^{-5}$  mol  $\text{L}^{-1}$  of Zr, was transferred under argon into the reactor together with 2 mL of dry toluene. In this reactor, all homo- and copolymerization reactions were performed with 1.6 bar of absolute pressure of ethylene for 30 min at 60°C. The copolymerizations were carried out with comonomer concentrations of 0.25 or 0.50 mol  $\text{L}^{-1}$  of 1-hexene in the reaction medium.

### High pressure polymerizations

The polymerizations were performed in 300 mL of dried toluene in a 1.1-L Büchiglasuster reactor connected to a constant temperature circulator and equipped with magnetic stirring and inlets for argon and ethylene. Again, MAO was used as cocatalyst. The mass of catalyst corresponded to  $10^{-5}$  mol  $\text{L}^{-1}$  of Zr, which was transferred under argon into the reactor together with 2 mL of dry toluene. With this reactor, all homo- and copolymerization reactions were performed at 5.0 bar of absolute ethylene pressure for 30 min at 60°C. The copolymerizations were carried out with comonomer concentrations of 0.25 or 0.50 mol  $\text{L}^{-1}$  of 1-hexene in the reaction medium.

## RESULTS AND DISCUSSION

Previous studies have demonstrated that  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  is a good molecular pattern for the development of more thermally stable metallocene complex catalysts.<sup>32–34,37</sup> Its immobilization on suitable supports can be an option to further increase its thermal stability, leading to catalytic systems that can work at higher polymerization reaction temperatures.<sup>57</sup>

Among the several methods to prepare immobilized metallocene-based catalyst systems,<sup>48,58–60</sup> we adopted the direct heterogenization of the metallocene on preactivated silica. The grafting process was monitored by DRIFTS. Thermal-treated silica is characterized by a strong band at  $3747\text{ cm}^{-1}$  attributed to  $\nu_{(\text{O}-\text{H})}$  from isolated silanol groups.<sup>61</sup> After grafting the metallocene the intensity of this band is reduced and new bands appear between 2987 and  $2885\text{ cm}^{-1}$ , attributed to  $\nu_{(\text{C}-\text{H})}$  of the organic fragment of the complex.<sup>62</sup> The quantification of the Zr content at the resulting grafted systems was measured by RBS and results indicated that 0.22 wt %

**TABLE I**  
**Results of the Ethylene Polymerization Under Homo- and Heterogeneous Conditions, Using Ph<sub>2</sub>C(Cp)(Flu)ZrCl<sub>2</sub> as Precatalyst Species**

Entry	Cat.	$P_E$ (bar)	Al/Zr	$T$ (°C)	1-Hex. (mol L <sup>-1</sup> )	$T_m$ (°C)	$\chi_c$ (%)	Yield (g)	Activity (kgPE mol <sup>-1</sup> Zr <sup>-1</sup> h <sup>-1</sup> bar <sup>-1</sup> )
1	Zr	1.6	500	60	–	–	–		n.d.
2	Zr/SiO <sub>2</sub>	1.6	500	60	–	–	–		n.d.
3	Zr	1.6	1000	60	–	129	16	0.075	62
4	Zr/SiO <sub>2</sub>	1.6	1000	60	–	128	7.0	0.015	12
5	Zr	1.6	2000	60	–	132	37	0.682	569
6	Zr/SiO <sub>2</sub>	1.6	2000	60	–	130	10	0.337	281
7	Zr	1.6	3000	60	–	131	43	0.075	62
8	Zr/SiO <sub>2</sub>	1.6	3000	60	–	133	40	0.052	44
9	Zr	1.6	2000	60	0.25	106	2.9	4.95	4120
10	Zr/SiO <sub>2</sub>	1.6	2000	60	0.25	n.d.	n.d.	0.382	319
11	Zr	1.6	2000	60	0.50	n.d.	n.d.	6.30	5250
12	Zr/SiO <sub>2</sub>	1.6	2000	60	0.50	128	2.6	0.007	6
13	Zr	5.0	2000	120	–	126	44	8.40	1120
14	Zr/SiO <sub>2</sub>	5.0	2000	120	–	130	48	1.95	260
15	Zr	5.0	2000	160	–	125	39	3.37	450
16	Zr/SiO <sub>2</sub>	5.0	2000	160	–	130	12	1.80	240
17	Zr	5.0	3000	120	–	128	50	9.30	1240
18	Zr/SiO <sub>2</sub>	5.0	3000	120	–	131	34	4.65	620
19	Zr	5.0	2000	120	0.25	114	32	10.2	1360
20	Zr/SiO <sub>2</sub>	5.0	2000	120	0.25	125	24	2.40	320
21	Zr	5.0	2000	120	0.50	105	4.5	12.4	1660
22	Zr/SiO <sub>2</sub>	5.0	2000	120	0.50	127	4.9	0.150	20

Reaction conditions. [Zr] = 10<sup>-5</sup> mol L<sup>-1</sup>;  $t$  = 30 min;  $V$  = 0.150 L of toluene for polymerization at 1.6 bar;  $V$  = 0.300 L of toluene for polymerization at 5.0 bar. n.d. = not determined.

Zr/SiO<sub>2</sub> (0.024 mmol Zr g<sup>-1</sup> support) is effectively supported, e.g., around 44% of the Zr initial content.

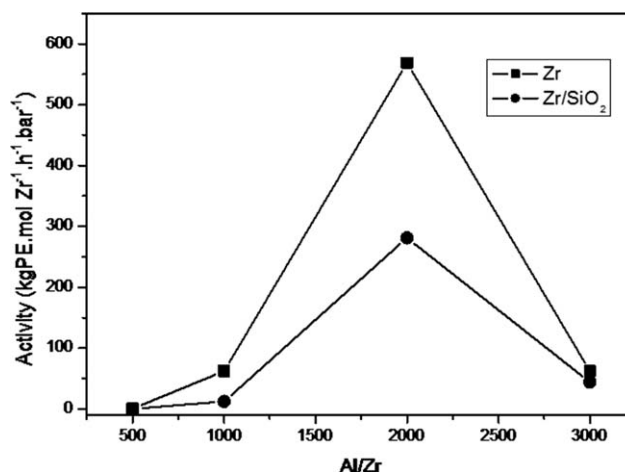
The ethylene (co)polymerizations were conducted under homogeneous and heterogeneous conditions, using MAO as cocatalyst, and the complex Ph<sub>2</sub>C(Cp)(Flu)ZrCl<sub>2</sub> as precatalyst. All results are summarized in Table I.

Our first polymerization set of tests were performed at low temperature (60°C) and ethylene pressure (1.6 bar), see Entries 1–12 in Table I. We have carried out an ethylene polymerization comparative study between reactions performed under homogeneous conditions, with the corresponding attempts under heterogeneous conditions. As expected, it was observed that the homogeneous reactions are more active in comparison with the corresponding supported systems, since there is a decrease in the concentration of active species when molecular metallocene compounds are immobilized.<sup>51</sup> Furthermore, the support itself (silica surface) may act as a huge ligand, hindering the access of the monomer to the active sites.

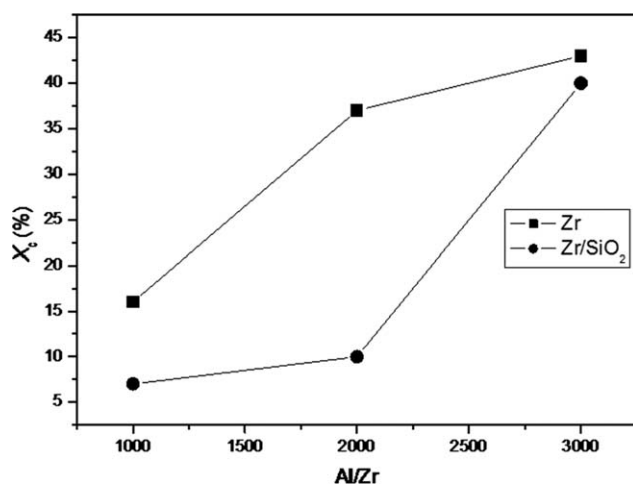
Figure 2 displays the dependence of the Al/Zr molar ratio on the catalytic activity of ethylene homopolymerization, using both catalytic systems (see Entries 1–8 in Table I). It is clear that, at these reaction conditions, the systems present the same profile, and one could suppose that all reactions in fact occurred under homogeneous conditions.

Nevertheless, the polymers obtained presented different physicochemical characteristics, which mean that the catalysts in each system are, indeed, different. Of course, we cannot neglect the possibility of leaching of some supported metallocene to the solution.<sup>53</sup>

On this first set of reactions, maximum catalytic activity occurs at Al/Zr = 2000 (see Entries 5 and 6 in Table I). At Al/Zr = 500, both systems present no



**Figure 2** Effect of Al/Zr molar ratio on the catalytic activity of homogeneous and supported conditions of molecular system (Entries 1–8 on Table I).



**Figure 3** Effect of Al/Zr molar ratio on the crystallinity of the obtained polymers prepared under homogeneous and heterogeneous conditions (Entries 1–8 on Table I).

activity, indicating that a minimum Al/Zr ratio is required for both systems to become active. This result is in agreement with the usual trend observed on a number of metallocene catalytic systems, in which it is necessary to add a minimum amount of MAO to clean up the reaction medium and obtain the active form of the catalyst.<sup>61</sup> An increase of Al/Zr ratio to 3000 leads to a decrease of the catalytic activity. At this level of Al concentration, low active metallocene species are formed.<sup>63,64</sup> It is worth mentioning that metallocene-supported catalysts achieve higher activities at lower levels of Al/Zr molar ratios when compared to reaction carried out under homogeneous conditions.<sup>38</sup> With our supported catalytic systems, we believed also that part of the MAO added is consumed due to the presence of silanol groups on the silica surface, which explain, in this case, the requirement of higher concentration of MAO into the reaction medium,<sup>65,66</sup> and, for this reason, both systems present the same profile of activity in relation to the Al/Zr molar ratio.

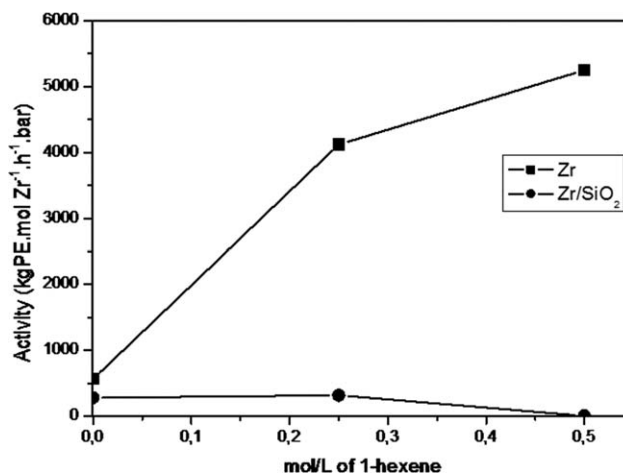
It is also worth mentioning that the  $T_m$  and  $\chi_c$  of the obtained polymers increased with the Al/Zr ratio (see Runs 3–8). The polymers obtained with the supported catalyst present lower crystallinity than those obtained from homogeneous conditions. But when a Al/Zr ratio of 3000 is reached (see Entries 7 and 8) both catalytic systems reach practically the same values (see Fig. 3). These results are not completely well understood until now, but we suppose that it must be related to the influence of MAO concentration on the polymerization rate constants of chain propagation versus chain termination.<sup>63,64</sup> At mild conditions of pressure and temperature for example, when high Al/Zr molar ratio are ascertain, the environmental differences around the active species in polymerization reactions, at homogeneous or

heterogeneous conditions, are minimized, which can explain the similarities of obtained polymer properties.

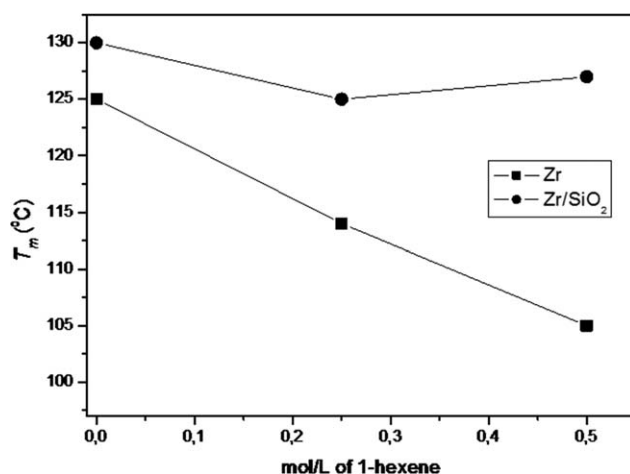
In the case of copolymerization, at low ethylene pressure (1.6 bar), the addition of a suitable concentration of 1-hexene increases considerably the activity of the homogeneous catalytic system (compare Entry 5 with 9 and 11). This behavior resides in the so-called comonomer effect,<sup>67</sup> which, in fact, can be related to the activation of dormant sites due to the presence of higher  $\alpha$ -olefins in the reaction medium, or to the easier access of the monomers to the catalyst site, since, for the last, the reduction in polymer crystallinity render the diffusion of the monomer less difficult. Nevertheless, this trend is not observed for polymerization reactions run with the supported catalyst. A concentration of  $0.25 \text{ mol L}^{-1}$  of 1-hexene does not affect significantly the activity of the systems (see Fig. 4), but higher concentrations of the comonomer cause reduction (compare Entry 6 with 10 and 12). Here, we have to remind that silica surface plays the role of a huge ligand which impairs the access of relatively bulky monomers to the active site.<sup>68</sup>

At more severe reaction conditions of pressure (5.0 bar) and temperatures (120 and  $160^\circ\text{C}$ ), all (co)polymerizations attained higher yields in comparison with those performed at 1.6 bar and  $60^\circ\text{C}$ . At more severe reaction conditions it seems that higher activities are obtained at higher Al/Zr molar ratios, from 2000 to 3000 (compare Entries 13 with 17, and 14 with 18). The increment of Al/Zr molar ratio at higher temperatures is necessary to achieve higher catalytic activity, since higher Al/Zr molar ratios assist an increase of the concentration of active species at more severe reaction conditions.

It is important to remark that an increase of the reaction temperature from 120 to  $160^\circ\text{C}$  leads to a



**Figure 4** Effect of the addition of comonomer (1-hexene) on the catalytic activity of homogeneous and supported molecular systems (Entries 5–6 and 9–12 on Table I).



**Figure 5** Effect of the addition of comonomer (1-hexene) on the melting point of the polymers obtained at homogeneous and supported conditions (Entries 15–16 and 19–22 on Table I).

decrease,  $\sim 50\%$ , of the activity under homogeneous conditions (see Entries 13 and 15). However, when the polymerization was performed under heterogeneous conditions the deactivation was lower. This means that immobilization of  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  on silica improves the thermal stability of the catalytic species (see Entries 14 and 16).

At a certain level, under more severe reaction conditions, all polymers obtained from the heterogeneous catalytic system present higher  $T_m$  than the polymers obtained from the corresponding homogeneous one (see Fig. 5). This observation indicates that at higher pressures the probability of comonomer incorporation decreases.

The copolymerization performed at higher temperatures and pressures displays the same tendency in terms of catalytic activity that was verified for the corresponding reactions at mild conditions, i.e., the addition of 1-hexene increases the catalytic activity of the homogeneous system (compare Entries 15 and 19), but at higher concentrations of the comonomer in the reaction medium a significant reduction of the activity is observed in the case of the supported system.

It is also worth commenting, that all polymers isolated present no specific morphologies. Granular features were observed for all homopolymers, and more relative rubbery aspects for the copolymers. As expected, the copolymers obtained from supported catalysts presented less rubbery aspect than that produced from their analogous homogeneous systems.

## CONCLUSIONS

The homogeneous and supported catalytic systems show different characteristics. Independently of the reaction conditions employed, the immobilization of

the molecular catalyst reduces the activity. Also, the addition of 1-hexene increases the catalytic activity of the homogeneous system, but at higher concentrations of comonomer in the reaction medium and when supported systems are used a significant reduction of the activity is detected. At more severe reaction conditions, an increase in the reaction temperature leads to a significant reduction of the activity under homogeneous conditions. However, when the polymerization was performed under heterogeneous conditions the deactivation ratio was lower. This means that immobilization of  $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  on silica improves the thermal stability of the catalytic species.

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