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A systematic study of the kinetics of polymerisation of ethylene using supported metallocene catalysts

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ABSTRACT

A factorial design was used to understand how reaction parameters such as the monomer concentration, temperature, alkyl aluminium concentration, etc. influence the reaction rate and the polymer properties on two types of metallocene catalyst systems. The polymerisation kinetics and molecular weight distribution (MWD) obtained using a novel system (catalyst supported on an activated silica) were to those obtained with the reference system (same catalyst and silica but activated with MAO). As expected, the reaction temperature and the monomer concentration are the most important factors influencing the polymerisation rate, and this is independent of the catalytic system. Otherwise, the statistical approach allowed us to identify useful levels of MAO and comonomer at which to run in order to maximise the reaction rate.

1. Introduction

One of the main reasons for the interest in metallocene catalysis is the potential for unprecedented control over the polymer microstructure, the generation of new polymer architectures, and the development of new polymer reactions [1–3]. The main difference between metallocenes and catalysts such as Ziegler–Natta (ZN) and Phillips catalysts (chromium oxides) is that – in principle – one and only one configuration is obtained during the activation of these sterically hindered molecules, and consequently only one type of active site can be formed. With ZN or Phillips catalyst it is thought that the active sites can have many different configurations, each of which can produce different molecular weights and have different copolymerisation rates as well. For this reason, metallocenes are often referred to as "single-site" catalysts, and they offer us the possibility of tailoring the molecular weight and molecular weight distribution, as well as rates of comonomer incorporation by varying the nature of the ligand at the active centre. As we will see below, well-defined metallocene complexes do not necessarily lead to single-site catalysts especially in the case of supported catalysts. Nevertheless, even if the act of supporting a metallocene can produce changes that lead to "multiple site behaviour", they still give us much finer control over molecular structure than is possible with other types of catalysts.

The discovery of metallocenes themselves dates back to the early 1950s, when Kealy and Pauson [4] first synthesised bis(cylopentadienyl)iron (Cp_2Fe, or ferrocene). However, these original metallocenes had low activities (<100 $g_{polymer}/mol_{metal}/h$), poor stability during the polymerisation of ethylene, and produced only low molecular weight polymers. Additionally, they were not active in propylene polymerisation [5]. Later it was found that activators, such as diethylaluminium chloride (DEAC) improved the rates of polymerisation [6]. It was observed that the activity was function of the purity of the ethylene. In fact, when the quantity of oxygen present in the ethylene varied from 0.003 to 0.025 mol%, the activity was approximately multiplied by ten (activity varied from 2600 $g_{polymer}/mol_{Ti}/h$ to 35,000 $g_{polymer}/mol_{Ti}/h$). Later, Reichert and Meyer [7] proved that the polymerisation rate could be enhanced by adding a small quantity of water to a titanocene/alkyl aluminium chloride system. This observation was totally unexpected because in the case of Ziegler–Natta or Phillips catalysts, water acts as a poison. In 1976, Sinn and Kaminsky [1] demonstrated that the metallocene complex: Cp_2TiMe_2 was very active when contacted with trimethylaluminium (TMA) that had initially been precontacted with water. This relatively high activity was attributed to the reaction of water and alkyl aluminium to form aluminoxane, in this case methylaluminoxane (MAO). The polyethylene obtained with this catalytic systems had different properties than the one obtained with Ziegler–Natta catalysts, and in particular the molecular weight distribution was very narrow

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with a polydispersity index (PDI) was around 2. This low value of polydispersity index indicates that only one type of active site is present. Metallocenes reached commercially viable rates when Sinn et al. [2] independently synthesised MAO and used it as cocatalyst with a zirconocene complex. These new catalytic systems were at least ten times more active than the best Ziegler–Natta catalysts at equal quantity of metal.

These initial studies on metallocenes were performed using a homogeneous catalyst. These homogeneous systems present certain disadvantages, in particular they required a very large amount of MAO to achieve the maximum polymerisation reaction rate (MAO is an expensive, unstable, and self-igniting compound). While solution, or homogeneous, processes are becoming commercially important, heterogeneous (i.e. on supported catalysts) slurry or gas phase processes remain the predominant means for making polyethylene. Therefore, the development of effective techniques for the immobilisation of homogeneous single site catalyst on a suitable support material has become an essential step for the widespread implementation of the metallocene catalysts in polyolefin production. The objective of supporting a catalyst is to immobilize it and to preserve the advantages of the homogeneous form in terms of high activity and control of the polymer microstructure, and at the same time to provide acceptable polymer particle morphology, high bulk density, and to prevent reactor fouling and fines productions.

Consequently, it is crucial to understand the impact of the physical and chemical properties of the catalyst support on the polymer produced. The role of the physical properties (particle size, porosity, etc.) will be discussed in a separate publication from our group [8]. In this paper, we will concentrate on understanding the role of the activation system on catalyst performance. MAO appears to be the most common cocatalyst used in industrial situations, but we will also discuss new types of activation systems that are being developed.

During the immobilisation stage, MAO is assumed to chemically bond to the silica support, and that the activated metallocene cation is fixed to the supported MAO by electrostatic interactions. The interaction between the catalytic complex and the support is essential since this will strongly influence the possibility of leaching [9]. Partial absence of the catalyst components metallocene/MAO on the porous supporting material might, in certain cases, cause an incomplete fragmentation of the silica gel, which in turn leads to larger silica fragments within the final polymer particle [10]. This is detrimental to certain end-use applications. Therefore, it is important to choose the right combination of conditions for the supporting procedure. Three main processes for the immobilisation of the catalytic system on the silica support are described in the literature [11]:

1. Anchoring the MAO cocatalyst with the hydroxyl groups present on the silica surface, followed by impregnation with the metallocene. A modified version of this method can be found in the literature and implies the use of alkyl aluminium to replace the MAO.
2. Anchoring the metallocene to the silica support (modified with a previous treatment or not) and then reacting the MAO solution. The reaction conditions can be either mild or more drastic, i.e. high temperature or long contact time. This route was the first one to be applied.
3. One step impregnation with a preactivated complex MAO/metallocene.

For all the immobilisation techniques described, the mixing time and temperature are important parameters since they seem to influence both the catalytic performance and the final properties of the polymer [11,12]. The different methods are difficult to compare in the sense that the nature of silica, metallocene, etc. varies from study to study. However, the impregnation of MAO in toluene at temperatures around 60–100 °C, followed by washing in warm toluene and drying under vacuum seems to be an effective technique. In most industrial processes, the MAO is synthesised separately and afterwards contacted with the support. No real evidence of the localisation of the MAO was found in the literature, but it seems to be generally admitted that MAO encapsulates the silica particles [12].

The temperature treatment of the support will be governed by several factors such as the polymerisation process, cocatalyst, target properties of the polymer, etc. It is the parameter that exerts the greatest influence on the immobilisation of the active species because it regulates the concentration of the OH groups on the surface of the support [13–17]. For instance, it has been found that the number of hydroxyl groups present on the surface of the silica at 250 °C was two times higher than at 600 °C [17,18]. Consequently, the chemical fixation of MAO on the silica calcinated at 250 °C will be higher and the diffusion of MAO throughout the particle will be slower.

In order to form active systems, catalyst precursors must be transformed into active catalysts by appropriate and effective activating species. The cocatalyst is a vital part of a catalytic active cation–anion ion pair, and may significantly influence polymerisation characteristics and polymer properties. There appears to be a consensus in the literature that methylaluminoxane (MAO) is to be more effective as cocatalyst than the other aluminoxanes such as ethylaluminoxane (EAO) and isobutylaluminoxane (IBAO) [19]. Consequently, we will concentrate on MAO for our aluminoxane activator. It should be pointed out that although extensive research has been carried out in both academia and industry, the exact composition and structure of MAO are still not entirely clear [20,21].

However MAO is not necessarily the last word in metallocene activation. For instance several research groups, e.g. [22–25] worked on the use of boranes and borates to activate different types of metallocene, i.e. di- or mono-alkyl metallocene. These and other studies have been reviewed by Severn et al. [12]. The general conclusion is that these interesting products because they generate catalytic systems with activity comparable to that obtained with MAO, and the polymer properties are unchanged or improved. However the active species are associated to the surface support only by electrostatic or van der Walls interactions, so the polarity of the solvent medium during the polymerisation has a great importance [26]. Other groups therefore investigated the possibility of directly modifying the surface of the support in order to create species which can react and activate a metallocene complex. Soga and co-workers [27–29] demonstrated that the activation of a metallocene was possible by using a support having a sufficient Lewis acidity in combination with an alkyl aluminium. However, the activities in polymerisation obtained with this type of activated support are low compared to those obtained with a metallocene supported on a support treated with MAO. In order to overcome this limitation, one can also consider the modification of the surface in order to create a sufficient Lewis acidity. Based on the fact that the support needs to have a sufficient Lewis acidity [16,27], Saudemont et al. patented a method to create a Lewis acidity on the surface of the silica [30]. One of the claims of the patent in question is the synthesis of a new type of metallocene-supported catalyst. This catalytic system can be used in slurry, gas or bulk-phase polymerisations of at least one olefin, such as ethylene, propylene, 1-hexene, etc. A subsequent patent was filed on an activating support having acid sites based on alumina and fluor, in which the fluor is directly linked to the alumina [31]. This patent teaches there is no need of an activating agent such as MAO.

While supported metallocene catalysts offer great possibilities in terms of tailoring polymer properties, but some improvements

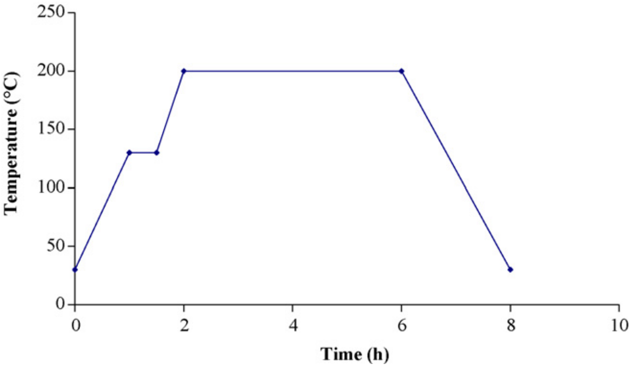

Fig. 1. Temperature programme for the thermal treatment of silica.

have to be performed to widespread their use industrially. It appears that extensive research is currently underway in order to find the best combination cocatalyst/metallocene complex/support because the best cocatalyst available at this time, MAO, has two main disadvantages: its price and instability. The discovery of an activated support, i.e. silica treated with alumina and fluorine seems to be good alternative.

The main objectives of this investigation are therefore to understand how reaction parameters such as the monomer concentration, temperature, alkyl aluminium concentration, etc. influence the reaction rate and the polymer properties on two types of metallocene catalyst systems. We will compare the polymerisation kinetics and molecular weight distribution (MWD) obtained using a novel system (catalyst supported on an activated silica) to those obtained with the reference system (same catalyst and silica but activated with MAO). For this study, a factorial approach will be performed to reduce the number of experiments and to detect the main parameters as well as the eventual existing interactions.

2. Experimental

Two types of catalyst supports were investigated in the current paper. The same metallocene complex, ethylenebis(indenyl)zirconium dichloride ($EtInd_2ZrCl_2$) and the same silica was used in both cases, but the support differ in terms of silica treatment. The first catalyst is based on silica treated with methylaluminoxane (MAO), whereas the second consists of silica treated with aluminium and fluorine as described in the patent WO 2005/075525 [31]. The MAO was supplied by Albemarle (solution 30 wt% in toluene) and used without further analysis. For the sake of simplicity, the first support will be called SMAO and the second, activated support. It should also be noted that in the case of SMAO, a dry catalyst is obtained whereas when using the activated support, the support and a solution of the metallocene complex in toluene are contacted just before their introduction into the reactor. In this section, the synthesis and the characteristics of these both systems will be investigated.

2.1. Synthesis of the SMAO catalyst

The most common technique reported in the literature is to anchor the MAO on dehydroxylated silica and afterwards to tether the metallocene complex [2]. 5 g of silica are introduced in a Schlenk-tube and calcinated under dynamic vacuum ($\cong 10^{-7}$ bar) using the temperature program represented in Fig. 1. This program was based on the one used in Ref. [31]. The maximum temperature was optimised as discussed below. Note that the short plateau at 130 °C is necessary to remove any absorbed water.

After this treatment, the concentration of the hydroxyl groups (OH groups) on the surface of silica was found to be around 4 OH/nm^2 by titration with triethylaluminium.

The dehydroxylated silica was suspended in toluene. A commercial MAO from Albermarle (solution at 30 wt% in toluene) was added to the suspension in sufficient quantity to fix 15 wt% of aluminium on the silica. The mixture was gently stirred for 1 h at 85 °C. After the reaction, silica was washed three times with toluene at 85 °C and dried under static vacuum. The solid SMAO obtained is a white, free-flowing powder.

The SMAO was once again suspended in toluene and a known quantity of metallocene complex, in our case $EtInd_2ZrCl_2$, was added in order to tether 2 wt% on the silica. The mixture was stirred at low stirrer speed during 1 h at 30 °C. Afterwards, the solid was washed three times with heptane and dried under static vacuum. The solid catalyst obtained, $EtInd_2ZrCl_2$ supported on SMAO, was an orange free-flowing powder.

2.2. Synthesis of the activated support

The synthesis of the activated support was performed as described in [31]. According to this invention, the following steps can describe the preparation of the support:

- Dehydroxylation of silica.
- Formation of fluorinated acid sites.
- Thermal treatments in a fluidised bed in order to generate a support having a sufficient level of acidity to activate the metallocene complex.

Note that the SMAO and activated supports were made from the similar silicas in order to facilitate the comparison of the 2. However, we verified that the different activation routes did not adversely influence the porosity and particle size distribution of the final catalysts. For reasons of brevity, the results of this preliminary study will not be presented here. The overall conclusion is that all of the catalysts had very similar particle size distributions and initial porosity. The different treatments did not change this [32]. Finally, it should also be noted that the active site concentration is 0.4% in the case of $EtInd_2ZrCl_2$ supported on the activated silica vs 2% in the case of SMAO – this will obviously have a potential impact on the observed reaction rates.

2.3. Polymerisation reaction and polymer characterisations

In this following section, a description of the reaction procedure as well as the different analytical techniques employed for the characterisation of the polymer is performed.

The reactor was first cleaned stirring with a solution of triethylaluminum (TEA) in heptane at 90 °C for 10 min to remove any impurities that might be present. The reactor was then purified at 90 °C under vacuum for at least 30 min. All glassware was filled with argon and emptied by vacuum three times in order to remove all possible traces of water and air. 500 ml of solvent (heptane) was mixed with 0.2 ml of pure triisobutylaluminium (TiBA) and a known quantity of comonomer (in our case 1-hexene). This mixture is introduced into the reactor, which then is brought to the desired reaction temperature and pressure. The catalyst support is suspended in 15 ml of heptane, a known quantity of TiBA (acting as an activator) and, in the case of the activated support, a known quantity of catalytic solution at 0.4 wt% in toluene with respect to the support (the sites are already present on the support in the case of the SMAO) are successively added before the introduction in the reactor. The catalyst mixture is injected into the reactor via an injection cartridge using an overpressure of ethylene. When the reaction is finished, the contents are rapidly degassed and the temperature is decreased in order to stop the reaction. The final polymer powder is filtered and dried under vacuum at 100 °C for 2 h.

2.4. Polymer characterisation

SEM was used for the visual study of the external surface of the polymer or catalyst particles. Two different apparatus were used to perform SEM depending where the experiments were carried out a microscope JSM6400 from Jeol or a Hitachi S800.

The bulk density or apparent density is the weight per unit volume of a material including voids in the tested material. The bulk density was measured as described in the norm ASTM D 1895.

A DSC using a Pyris I from PerkinElmer was used to measure polymer crystallinity and melting temperature. The polymer sample (about 10 mg) is first heated to 190 °C at a rate of 5 °C/min to remove its thermal history. It is then cooled down to 40 °C at 5 °C/min. A second heating cycle at the scanning rate of 5 °C/min is carried out to acquire the DSC thermogram. The polymer melt temperature was taken at the peak temperature, i.e. at the value where all the polymer chains have melted. The crystallinity is calculated as the enthalpy change of the sample divided by the enthalpy of pure polyethylene, where the enthalpy of crystallisation of pure polyethylene is taken to be equal to 269.69 J/gPE [3].

The particle size distribution was evaluated by sieving as described by the norm ASTM D 1921-89. The size of the sieves used will vary with the type of material to analyse and the precision desired for the results. In our case, the sizes of the different sieves used were: 1000, 500, 400, 325, 250, 200, 160, 125, 100, 80, 63, 45 and 36 μm.

SEC (size exclusion chromatography, also called gel permeation chromatography; GPC) was used for the determination of the molecular weight distribution (MWD) and the average molecular weights (M_n and M_w). The analysis was performed at a temperature of 150 °C and with a flow rate of TCB (trichlorobenzene) of 0.92 ml/min using a Waters Alliance 2000 GPC. Molecular weights and molecular weight distribution were determined using the universal calibration curves obtained from narrow polystyrene standards.

In order to get an approximate notion of the influence that the different supporting and/or activation treatments used here influence the structure of the active sites, the MWD thus obtained were deconvoluted using the method proposed by Soares and Hamielec [33]. They deconvoluted the experimental MWD into a certain number of Flory distributions (each of which is associated with a given type of site) by minimising the difference between the experimental distribution and the estimated one via the sum of Flory's distribution. This algorithm provides us the minimum number of active sites needed to successfully model the MWD of homo- or copolymers for a given set of reaction conditions (T, [C_2], [TiBA], etc.). However, it is important to note that while the information that we get is useful, there is no guarantee that this is exactly the number of family of active sites present on the catalyst. Nevertheless, this technique is interesting to understand how the different families of active sites are influenced by the reaction parameters.

3. Results and discussion

For each catalytic system, four reaction parameters were investigated in order to characterise their effect on ethylene/1-hexene copolymerisation kinetics and copolymer properties (molecular weight, bulk density, etc.):

- Concentration of the alkylating agent: [TiBA].
- Contact time between support and alkylating agent: contact time.
- Temperature of polymerisation: T.
- Ethylene concentration: [C_2].

Table 1
Experimental conditions of the random sampling model for the SMAO catalyst.

[TiBA] (mmol/l)	Time (min)	T (°C)	[C_2] (mol/l)
0.5	0	65	0.2
4	0	65	0.2
0.5	20	65	0.2
4	20	65	0.2
0.5	0	85	0.2
4	0	85	0.2
0.5	20	85	0.2
4	20	85	0.2
0.5	0	65	1
4	0	65	1
0.5	20	65	1
4	20	65	1
0.5	0	85	1
4	0	85	1
0.5	20	85	1
4	20	85	1
2.25	10	75	0.6
2.25	10	75	0.6
2.25	10	75	0.6

By definition the contact time represents the contact time between the catalyst and the alkylating agent in the case of the SMAO support and the contact between the suspension (activated support/alkylating agent) and the catalytic solution in the case of the activated support. The 1-hexene concentration was kept constant in all runs. In addition, as one of the performance characteristics that we will consider is comonomer uptake, a preliminary study was run to consider whether or not composition drift was important in this reactor, and to determine whether or not the way in which the comonomer (here hexene) was added had an impact on the reaction rate and polymer properties. The results of this preliminary study not detailed here for reasons of brevity [32] showed that there no visible effects on the kinetic profile and polymer properties were noted when 1-hexene was added at different times, and this is the case for both of the catalysts considered. Consequently, there appears to be no real problem of composition drift in our batch reactor. In the reminder of this work, in the copolymerisation reaction the comonomer will be introduced in one shot at the beginning of the reaction.

As the four parameters studied can vary over a wide range, we decided to use a statistical approach to experimental design in order to obtain a maximum of information from the minimum number of experiments necessary. In this study, the range of each parameters as well as the number of levels possible in this range were defined based on the conditions typically used for copolymerisation in a commercial context:

- [TiBA] from 0.5 to 4 mmol/l with 8 levels.
- Contact time from 0 to 20 min with 5 levels.
- T from 65 to 85 °C with 3 levels.
- [C_2] from 0.2 to 1 mol/l with 5 levels.

If we wanted to test all of the possible permutations, we would need to do 600 experiments (without accounting for any replicate experiments). It is therefore more practical to use a random sampling model.

A factorial matrix of experiments allowed us to use only the lower and upper limits of each variable (cf. Table 1). For statistical evaluation, three tests in the middle of the range (of each parameter) were also carried out. This will allow us to validate the limit of our experimental parameters, and depending on the results, the experimental domain can be extended out of the ranges or detailed in the ranges defined before.

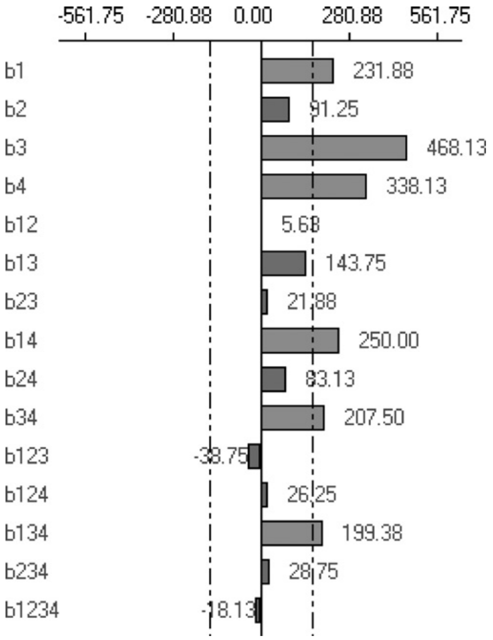

Fig. 2. Coefficients for the average activity with $EtInd_2ZrCl_2$/SMAO. The dashed lines are the 95% confidence interval. 1 = [TiBA], 2 = contact time, 3 = T and 4 = $[C_2]$.

The experimental results were analysed using a commercial software package, NemrodW^{TM} that allows us to construct an empirical model based on Eq. (1) that correlates a measured output (e.g. average activity, molecular weight, etc.) to the different parameters and their possible interactions.

$$\text{Output} = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{\substack{i,j=1\\ i\neq j}}^{4} b_{ij} X_i X_j + \sum_{\substack{i,j,k=1\\ i\neq j\neq k}}^{4} b_{ijk} X_i X_j X_k + \sum_{\substack{i,j,k,l=1\\ i\neq j\neq k\neq l}}^{4} b_{ijkl} X_i X_j X_k X_l \qquad (1)$$

where b_i represents the coefficients of the model relative to the different parameters X_i. By definition, X_1 = [TiBA], X_2 = contact time, $X_3 = T$, and $X_4 = [C_2]$. In the case where only two parameters are studied, Eq. (1) can be reduced to:

$$\text{Output} = b_0 + \sum_{i=1}^{2} b_i X_i + \sum_{i=1}^{2} b_{ii} X_i X_i + \sum_{\substack{i,j=1\\ i\neq j}}^{2} b_{ij} X_i X_j \qquad (2)$$

where b_i represents the coefficients of the model and X_i the different parameters. By definition, X_1 = [TiBA], $X_2 = [C_2]$. Each parameters b_i or b_{ij} can have a positive or a negative effect on the analysed output.

3.1. Effect on the average activity

3.1.1. SMAO support

The experiments defined in Table 1 were carried out randomly and the comonomer content was fixed at 2.44 wt% in heptane for all the reactions using the SMAO system. The coefficients of Eq. (1) and the 95% CI are shown in Fig. 2 for the SMAO supported catalyst. Three of the four parameters seem to have a significant effect at 95% confidence: the quantity of TiBA, temperature, and monomer concentration. They all have a positive effect, which means that an increase of the concerned parameters will induce an increase of the average activity. Concerning the interactions of the first order, only the one existing between the significant parameters are important. Unexpectedly, there is no interaction between the quantity of alkyl aluminium and the temperature (b_{13}) even though both of these factors are significant on an individual level. The strong interaction between TiBA concentration and monomer concentration (b_{14}) is probably due to the scavenging effect of the alkyl aluminium. In fact, increasing the quantity of monomer will increase the concentration of impurities, thus an increase of TiBA will be favourable to clean the reaction medium. Finally, the only second order interactions that are significant at this level are those between the three principal parameters.

Table 2
Extended random sampling model for SMAO support.

[TiBA] (mmol/l)	Time (min)	T (°C)	$[C_2]$ (mol/l)
6	10	85	1
4	10	85	1
5.5	10	85	1.2
4.5	10	85	0.8
5.5	10	85	0.8
4.5	10	85	1.2
5	10	85	1
5	10	85	1
5	10	85	1

Since the contact time between the catalyst and TiBA does not appear to have a significant influence on the average activity, the contact time was set at 10 min for the subsequent experiments. In addition, as all the other parameters have a positive effect, it was decided to extend the experimental matrix above the upper limits of each one. The new extended random sampling model is described in Table 2. The concentration of the alkylating agent was varied between 4 and 6 mmol/l, and the monomer concentration between 1 and 1.2 mol/l. For experimental reasons (limitation due to the ethylene storage tank), we could not increase the monomer concentration further, and the temperature could not be greater than 85 °C. This new set of experiments will allow us to determine the range of conditions of monomer and TiBA concentration for which we can expect the highest possible activities.

Even if both of these parameters have a positive effect (Fig. 3(a)) on the average copolymerisation activity, their influence is very different. The monomer concentration is the only statistically significant parameter (cf. Fig. 3(b)). An increase of the concentration of TiBA from 4 to 6 mmol/l has only a small effect on the average activity whereas an increase of the monomer concentration from 0.8 to 1.2 mol/l allows us to multiply the activity by 1.5. This result was expected as the reaction rate is proportional to the monomer concentration with a reaction order around 1. At the higher levels of these two parameters, it appears that the interaction between them is also insignificant at a confidence level of 95%.

To conclude the reaction conditions that allow us to obtain the highest copolymerisation average activity with the $EtInd_2ZrCl_2$/SMAO catalyst are: temperature: 85 °C, $[C_2]$ = 1.2 mol/l, [TiBA] = 4 mmol/l, contact time: 10 min. It is important to note that these values are valid only in the range of variation of the parameters defined above.

3.1.2. Activated support

As the aim is to compare both catalytic systems, the same reaction parameters were studied. However, in the case of the $EtInd_2ZrCl_2$/activated support catalyst, the range of some parameters, particularly the lower limit, had to be modified. The random sampling model defined above was applied, but with a lower limit of 1.5 mmol/l for the concentration of TiBA and 2 min for the contact

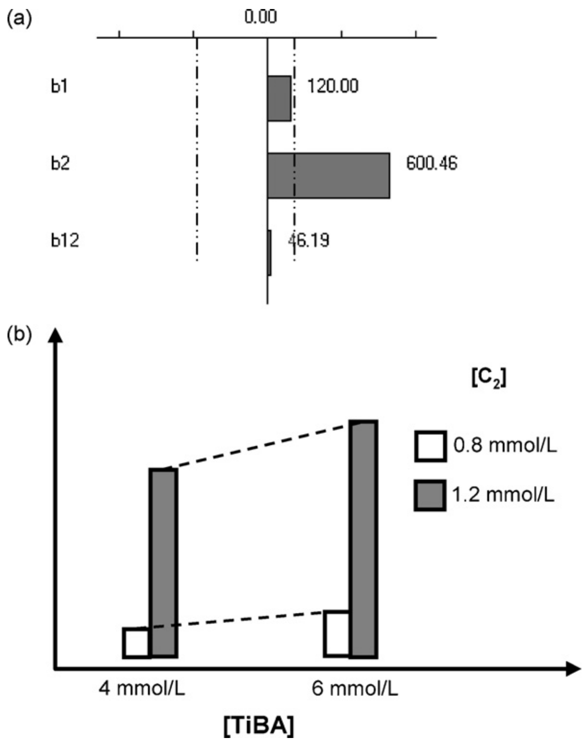

Fig. 3. (a) Coefficients for the average activity with $EtInd_2ZrCl_2$/SMAO. (b) Graphic representation of the effects of the different parameters on the average activity. 1 = [TiBA] and 2 = [C_2].

time. With this catalytic system, if the support and the alkylating agent are not contacted before introduction into the reactor, no polymerisation activity is observed. In addition, if the alkylating agent concentration is too low, some soluble polymer will be formed (i.e. the heptane after the reaction is not transparent). As previously, all the experiments were carried randomly and the comonomer content was fixed to 2.44 wt% in all reactions. The same objectives were fixed for the analysis of the results.

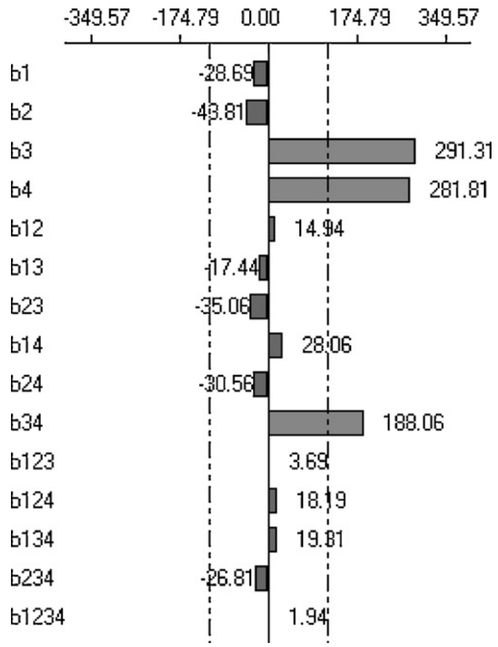

Fig. 4. Coefficients for the average activity with $EtInd_2ZrCl_2$/activated support.

Table 3
Refined random sampling model for activated support.

[TiBA] (mmol/l)	Time (min)	T (°C)	[C_2] (mol/l)
4	11	85	1
1.5	11	85	1
3.375	19	85	1
2.125	3	85	1
3.375	3	85	1
2.125	19	85	1
2.75	11	85	1
2.75	11	85	1

As can be seen in Fig. 4, only two parameters have a significant positive effect on the average activity: the reaction temperature and the monomer concentration. However it is possible that the two dominant ones hide the effects of the two other parameters. Consequently, the random sampling model was refined as shown in Table 3 in order to study more in details the effect of the alkylating agent concentration and contact time. The two other parameters were set up at their upper limit, i.e. $T = 85\,^\circ\mathrm{C}$ and [C_2] = 1.2 mol/l.

The results of the refined random model are represented in Fig. 5. Both parameters have an effect, but one is positive and the other negative. The representation in Fig. 5(b) clearly demonstrates that the optimal path is a compromise between the quantity of alkyl aluminium and the contact time. If the TiBA concentration is high, the contact time should be low (and vice versa).

To conclude, the reaction conditions that allow us to obtain the highest copolymerisation average activity with the $EtInd_2ZrCl_2$/activated support catalyst are: temperature: 85 °C, [C_2]: 1.2 mol/l, [TiBA]: 2.5 mmol/l, contact time: 10 min. Once again, these values are valid only in the range of variation of the parameters.

Reaction curves for the two catalyst systems are shown in Fig. 6 for the same conditions. It should be noted here that although the reaction rate with the SMAO support appears to be higher, the rate of polymerisation per potential site is actually higher in

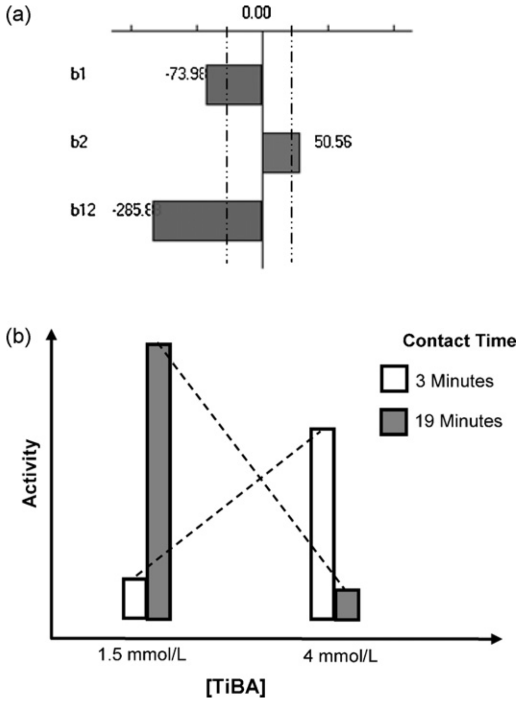

Fig. 5. (a) Coefficients for the average activity with $EtInd_2ZrCl_2$/activted support. (b) Graphic representation of the effects of the different parameters on the average activity.

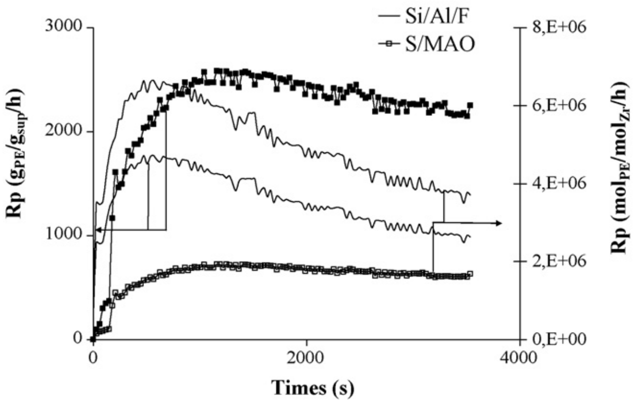

Fig. 6. Comparison of the activity profile for both catalytic systems. Conditions: $T = 85\,^{\circ}C$, $[C_2] = 1.2$ mol/l, [1-hexene] = 2.44 wt%, [TiBA] = 4 mmol/l, contact time = 10 min.

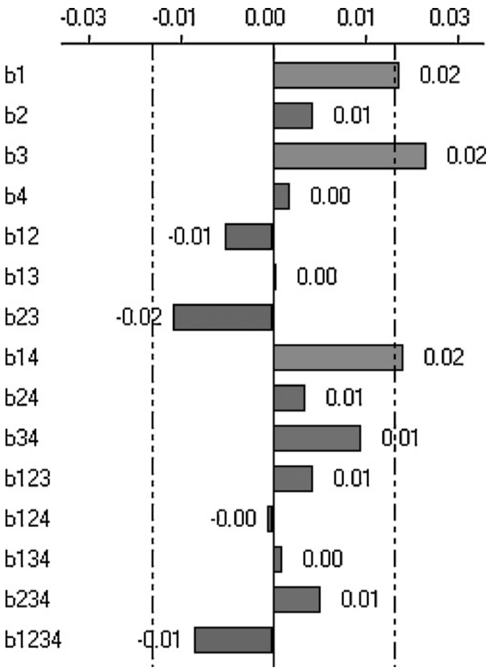

Fig. 7. Coefficients for the bulk density with $EtInd_2ZrCl_2$/SMAO. The dashed lines are the 95% confidence interval.

the case of the activated support since the concentration of metallocene is five times lower in the latter case. Although a value of [TiBA] = 2.5 mmol/l is preferred for the activated support, this figure shows experiments run under identical conditions (optimal for the SMAO support) in order to compare them on an equal footing. It can be seen that the activated support has lower peak and average activities (although these are still in a commercially viable range).

3.2. Effect on the polymer properties

The same type of statistical study was performed on different polymer properties such as bulk density, crystallinity and molecular weight.

3.2.1. Bulk density

The coefficients of Eq. (1) with the bulk density as the output are represented in Fig. 7 for the SMAO supported catalyst (no data is available for the activated support). The concentrations of alkyl aluminium and reaction temperature have a positive effect, and the interaction of TiBA-monomer also seems to be significant at 95% confidence. It is not clear why this is. The relationship between reaction rate and morphology (the bulk density is obviously related to the shape and porosity of the polymer particles) is a complex one, to say the least [34].

3.2.2. Melting temperature

The coefficients of Eq. (1) with melt temperature as the output are represented in Fig. 8. Once again, only two parameters have a significant influence for the SMAO system: the temperature and the monomer concentration, with the latter being more significant. The effect of monomer was predictable because as the experiments were carried out with the same concentration of comonomer (2.44 wt%), the ratio ethylene/1-hexene increases when the ethylene concentration increases and thus the polymer formed will be more crystalline. In addition, no interactions are observed to be significant for the SMAO system.

As can be seen in Fig. 8(b) the results for the activated support are slightly different. In addition to the temperature and monomer concentrations showing a similar influence as we saw above, the alkyl concentration is also significant. Furthermore, the 1–4 interaction (alkyl and monomer concentration) is significant, but unexpectedly negative (unexpected since the impact of these two parameters individually is positive as one would think). A much more in-depth treatment of this aspect is needed in order to fully comprehend the reasons for this. Suffice to say that this demonstrates that there is a noticeable impact of how the catalyst is supported, not just on the activity but also on the polymer properties.

The melting temperature varies from 121 °C for the less crystalline up to 131 °C for the copolymer obtained with 1 mol/l of ethylene for both the SMAO and activated supports.

3.2.3. Molecular weight

The average molecular weights (M_n and M_W) and the molecular weight distribution (MWD) are very important in terms of end-use properties. In fact depending on the M_W, the processability will not be the same. In this part, we will first study the influence of the reaction parameters on the average molecular weight using a statistical approach and we will also deconvolute the MWD in order to determine the effects of these reactions parameters on each family of active sites.

3.2.3.1. Effect on the average molecular weights. The coefficients of Eq. (1) are represented in Fig. 9 for the SMAO system. Only two parameters have statistically significant influence on M_n and M_W: as expected, the temperature has a negative effect and the monomer concentration has a positive effect. The increase of the molecular weight with the monomer pressure was also observed by Soares and Penlidis [35] and indicates that the chain termination mechanism is controlled by β-hybride elimination or transfer to the cocatalyst. No significant interactions between the parameters are observable. While these two parameters have an influence on the average molecular weights, it can be noted that the variation of the molecular weight is not particularly significant with M_n varying from 28,000 to 35,000 and M_W varying from 120,000 to 150,000.

It can be seen that from Fig. 10 that once again three of the four parameters have an influence on the average molecular weight for the activated support. The concentrations of TiBA and monomer have a positive effect whereas the temperature has a negative impact. In addition, interactions between the main parameters are observable, and in particular those involving the TiBA and monomer concentration, and the temperature and monomer concentration. Since the 1–4 interaction is important in the melting temperature, it is not necessarily unexpected that it has a similar impact on the average molecular weights since the two proper-

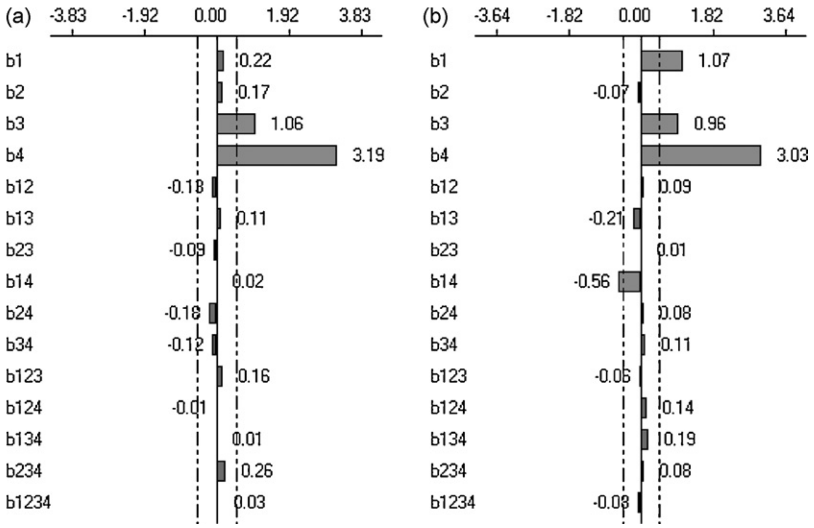

Fig. 8. Coefficients for the melting temperature with (a) $EtInd_2ZrCl_2$/SMAO and (b) activated support. The dashed lines are the 95% confidence interval.

ties will be related. Finally, it can be noted that the variation of the molecular weight is slightly more significant than with the previous catalyst, with M_n varying from 20,000 to 35,000, and M_W from 100,000 to 160,000. The PDI remained in the range 3–4.

3.2.3.2. Effect on the different family of active sites. Deconvolution of the molecular weight distribution allows us to quantify the heterogeneity of the active sites on the support. Ideally, a single type of active site will produce a Flory-distributed polymer – i.e. one with a polydispersity index of 2. If the PDI is greater than 2, this implies that there might be more than one type of site on the support (if we discount mass transfer resistance). The deconvolutions were performed using the method presented by Soares and Hamielec [33], where we iterate on the number of families of sites until the residual error between the measured and predicted MWD is less than some specific value. In this work, the tolerance of the residual error (χ^2) was set to 0.01.

It was found that in all cases, three families of active sites were sufficient to model the MWD for both activation systems. We will arbitrarily define family 1 as having the lowest molecular weight, and 3 the highest. The weight fractions of each of these sites, as well as the average molecular weight produced at each can theoretically vary from run to run. However, it turns out that the relative mass fractions of each type of site do not appear to vary in a significant manner (results not shown). For the SMAO activated system, the breakdown is as follows: 37% for family 1, 40% for family 2 and 23% for family 3 with an error of ±3% for each. For the activated support, it is 40% for family 1, 40% for family 2 and 20% for family 3 with an error of ±3% for each – essentially the same as for the other activation system.

The influence on the average molecular weight for each type of site did change. As shown in Fig. 11, the temperature and monomer concentration have a similar impact on the average molecular weight for each type of site (as expected) for the SMAO activated system. Some interactions between the most significant parameters are observed, in particular there is a negative interaction between the quantity of alkyl aluminium and the contact time. Similarly, increasing both the alkyl and the monomer concentrations has a negative impact on the molecular weights of families 1 and 2 (but not 3). This might be due to the modification of the active sites when the contact time is too long. It is also interesting to note that a

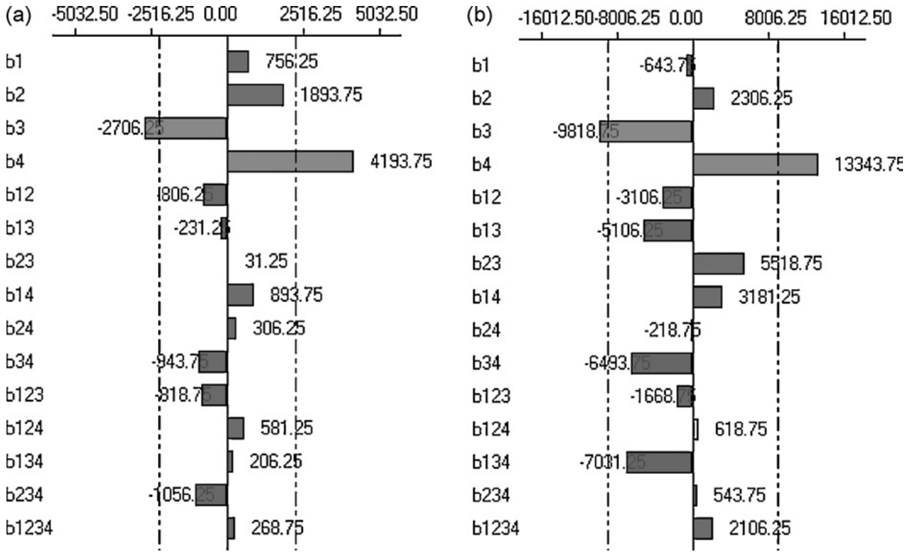

Fig. 9. Coefficients for the molecular weight with $EtInd_2ZrCl_2$/SMAO: (a) for M_n and (b) for M_W.

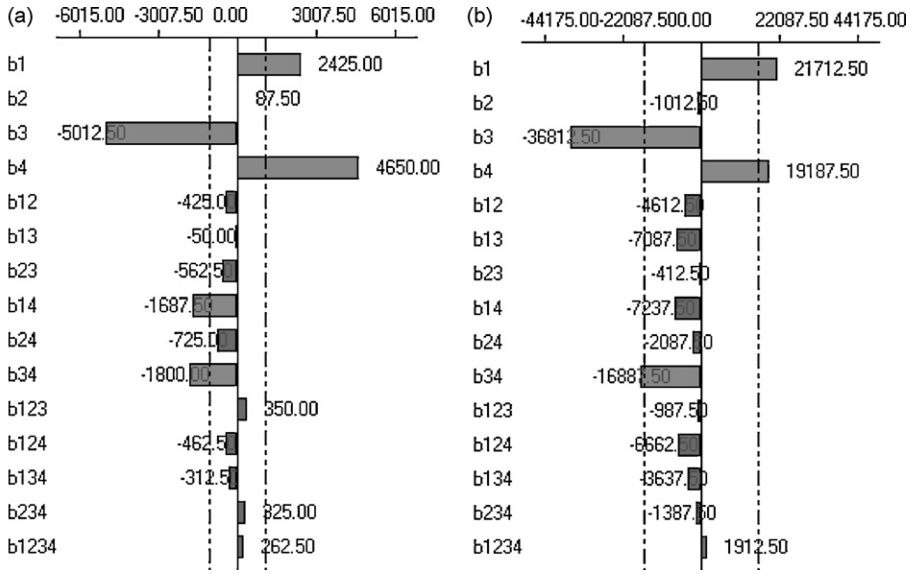

Fig. 10. Coefficients for the molecular weight with activated support: (a) for M_n and (b) for M_W.

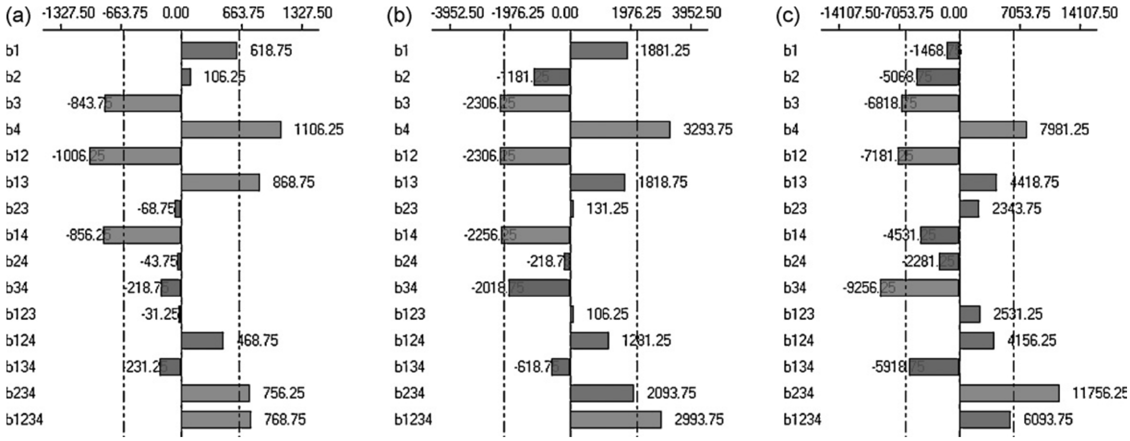

Fig. 11. Coefficients for the molecular weight with $EtInd_2ZrCl_2$/SMAO: (a) M_{W1}, (b) M_{W2}, and (c) M_{W3}.

concurrent increase in temperature and in the ethylene concentration leads to a decrease in the average molecular weight, but only for family 3 with the highest molecular weights. Why this should be is not clear at the present time.

The same set of results for the activated support is shown in Fig. 12. It can be seen that, on the whole, the different parameters influence the molecular weights at each type of site in a similar way. The only major difference is that there does not appear to be a 1–2

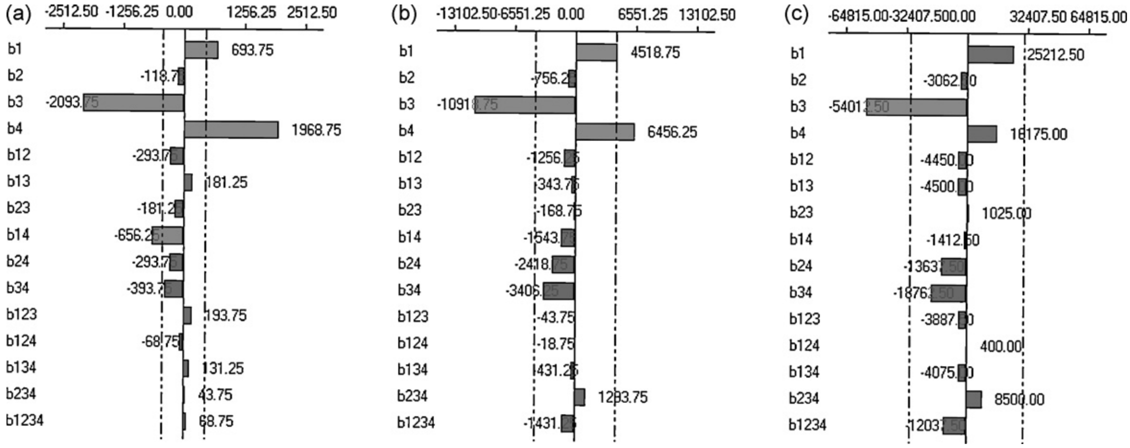

Fig. 12. Coefficients for the molecular weight with $EtInd_2ZrCl_2$/activated support: (a) M_{W1}, (b) M_{W2}, and (c) M_{W3}.

interaction for the activated support, whereas this is significant at 9% for the SMAO activation.

4. Conclusions

The statistical approach allowed us to determine the main parameters having an influence on the kinetics and polymer properties. As one would probably expect, the reaction temperature and the monomer concentration are the most important factors influencing the polymerisation rate, and this is independent of the catalytic system. Concerning the concentration of alkyl aluminium, we showed that a high concentration could lead to a decrease of the activity for the catalyst supported on the activated support. However, we have to keep in mind that these conclusions are only valid in the experimental range defined.

Concerning the polymer properties, we can remark that similar products are obtained with both catalytic systems in terms of molecular weight, melting point and PDI, but that the second order interactions involving the alkyl aluminium appear to play a greater role for the activated support than for the SMAO support. However, when comparing the activity profile obtained with the two systems (under the same experimental conditions), we can remark that the catalyst supported on silica treated with SMAO has a stable activity, whereas the activated support exhibits a certain amount of deactivation under the conditions studied here. In addition, when comparing the activity in terms of $g_{PE}/g_{support}/h$ the average activity is higher for the SMAO than for the activated support but in terms of $mol_{PE}/mol_{Zr}/h$, the inverse is observed.

This preliminary approach allowed us to identify the parameters most likely to influence the reaction rates and basic molecular properties of the polymer of interest. It should be pointed out that this type of study is useful from an operational point of view, and in particular in identifying the most promising or important areas of study for a comparative look at the underlying fundamental chemistries proper to each of the supports. However it is clear that if one is to better understand the kinetic mechanisms coming into play, a much more detailed study would be required.

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