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Propylene Polymerization in Liquid Monomer with a Ziegler-Natta Catalyst in Bench Scale Reactors. Kinetics and Model to Predict Reaction Yields

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Summary: The study of new catalytic systems is critical in order to develop improved and cost effective polymerization processes. One of the methods to evaluate the performance of a catalytic system is by means of bench scale reactors. Despite its difference in size with large scale industrial plants, bench scale reactors have proved to be a valuable tool to understand the behavior of the catalytic system during the polymerization. In this work, a method to estimate the kinetic parameters of propylene polymerization over a conventional Ziegler Natta catalyst is evaluated. Thus, it was possible to set up a semi-empirical model to correlate the reaction yield with the polymerization time, the hydrogen content in the reactor and the reaction temperature. This model proves to be useful to evaluate the performance of a catalytic system within the range of normal operating conditions. A brief study on the particle size distribution of the products is also carried out.

Keywords: kinetics (polym.); poly(propylene) (PP); Ziegler-Natta polymerization

Introduction

Since their discovery in the early 1950s, Ziegler-Natta catalysts have centered an intense research activity because of their role in olefin polymerization.[1] Even if these catalysts have been deeply studied over the past decades and that some basic polymerization principles are widely accepted, no unequivocal polymerization mechanism has yet been devised to fully describe their behavior.[2] This is due to the complexity of the catalyst systems employed. Nevertheless, an approach of the kinetic aspects of the polymerization reaction is suitable in order to predict the evolution of the reactive system. It is also important to consider the

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polymerization kinetics when trying to understand the chemicals processes, either at laboratory scale or large-industrial scale.

There are several ways to evaluate the behavior of a Ziegler-Natta catalytic system during the polymerization process. One of them is by means of small bench scale reactors (1 to 5 liter reactors, so called autoclaves). Because of their size and cost, they are more accessible for research laboratories. Even if they work in a discontinuous way and need special operation and care to provide just a few grams of polymer per batch, bench scale reactors are a very effective tool when trying study the impact of process conditions on the performance of a catalytic system.

Downscaling the process has often been considered to be a difficulty. This is due to the polymerization itself and to its related process conditions. Because of the high exothermicity of the reaction, the equipments need a good temperature regulation system. Because of the extreme sensibility of the catalyst to traces of impurities (such as H_2O, O_2, etc.) any experimental study must be carried out with hermetic inert systems, in order to maintain the high activity of the catalyst. Nevertheless, if used accurately, they prove to be extremely effective and coherent tools for catalyst evaluation.

In this work a bench scale reactor is used to study the behavior of a $MgCl_2$ supported Ziegler-Natta catalyst. Based on the polymerization kinetics, the experimental results lead to the development of a semi-empirical predictive model that correlates the polymerization yield with some basic process conditions: Polymerization time, Temperature, and Hydrogen content in the reactor. A brief study on the particle size distribution of the products is also carried out.

Fundamentals

Polymerization Kinetics

Many authors have studied the kinetic behavior of the Ziegler Natta catalysts during olefin polymerization.[3] Previous works report kinetic models based upon the reaction mechanisms.[4] It must be reminded that the polymerization kinetics of propylene by means of Ziegler Natta catalysts are complex. The activation mechanisms of the catalytic centers by the cocatalyst, and its complexation with internal and external electron donors are still not fully clarified.[5] The presence of multiple catalytic sites must be taken into account, each site having its own propagation rate constant and chain transfer constant.[6] Further more, the catalytic active centers decrease in number during decay because of chemical deactivation.[7] Nevertheless, it is possible to have an approach to the overall kinetic rate by making some assumptions, taking only into account the determining steps of the polymerization.[8] Even if the reaction kinetics are complex, they are limited by the polymer propagation, and the catalyst decay. This last one takes into account the decrease of the number of active sites during the reaction. Thus, through this simplification, it is possible to consider that these two steps describe most of the system kinetics.

Table 1. Kinetic Models as a function of the decay order.

Order (n)	$-\frac{dV}{dt}$	V(t)	Y(t)
1.0	K_dV	$V = V_o e^{-K_d \cdot t}$	$Y = \frac{V_o}{K_d}(1 - e^{-K_d \cdot t})$
1.5	$K_dV^{1.5}$	$V = \frac{V_o}{(1 + \frac{V_o^{1/2} \cdot K_d}{2} \cdot t)^2}$	$Y = \frac{V_o \cdot t}{(1 + \frac{V_o^{1/2} \cdot K_d}{2} \cdot t)}$
2.0	K_dV^2	$V = \frac{V_o}{(1 + V_o \cdot K_d \cdot t)}$	$Y = \frac{1}{K_d}\ln(1 + V_o K_d t)$
n	K_dV^n	$V = \left[V_o^{1-n} + K_d(1-n) \cdot t\right]^{\frac{1}{1-n}}$	$Y = \frac{1}{K_d(n-2)}\left[\left(V_o^{1-n} + K(n-1)t\right)^{\frac{2-n}{1-n}} - V_o^{2-n}\right]$

The single propagation rates of the multiple sites are gathered into a single propagation rate. The overall kinetic rate (V) is then given by the following expression:

$$V = k_p[C_m].[C^*] \qquad (1)$$

Where k_p is the overall propagation constant, C_m is the concentration of monomer and C^* that of the active sites. Many studies have confirmed that the polymerization rate has a 1st order dependence in respect to the monomer concentration.[8-9-10-11-12]

In the same way, it may be considered that the catalyst decay through different chemical mechanisms is summed up by a single deactivation rate. By this way the decay of the catalyst is described by a decreasing number of active sites with time, according to the following expression.[8-9-10-11-12]:

$$-\frac{dC^*}{dt} = K_D \cdot (C^*)^n \quad (2)$$

The combination of equations (1) and (2) gives a general expression that takes into account the decay of the catalytic reaction with time:

$$V' = \frac{dV}{dt} = K_d \cdot V^n \qquad (3)$$

Where K_d is defined as follows:

$$K_d = \frac{K_D}{K_p^{n-1}} \qquad (4)$$

In these expressions, K_D is the deactivation constant and n is the catalytic decay order, V' is decay rate (g PP /g cat.min^2) and V is the polymerization rate (g PP/g cat.min).

Integration of (3) leads to the expression for the polymerization rate (V) against time (t), where V_0 is the initial rate for undecayed catalyst. A second integration leads to the expression of the reaction yield (Y) as a function of polymerization time. The mathematical form of these models changes in relation with the value of the decay order (n), and the results are summarized in Table 1.

The results of the polymerization essays as a function of time are the clue to determine which model fits best to real experience, and thus find out which is the decay order of the catalyst.

Experimental

The polymerization essays were carried out in an autoclave system (Figure 1). The equipment is composed of three sections. The first one corresponds to the raw materials storage and to the purification systems for the streams going to the reactor. The second section includes the measurement vessels and accessories that are used to introduce the catalyst into the reactor. The third section is the reactor itself. With a volume of 4 liters, the reactor is surrounded by a jacket that helps to maintain a constant reaction temperature by means of a cooling control system.

Before beginning the essays, a large amount of the same batch of propylene (polymer grade) and catalyst is stored in order to ensure a constant quality of the raw materials during the hole experimental set up. The raw materials are purified as they are forced to go through molecular sieves and alumina that remove traces of catalyst poisons (such as O_2, CO, H_2O, etc...).

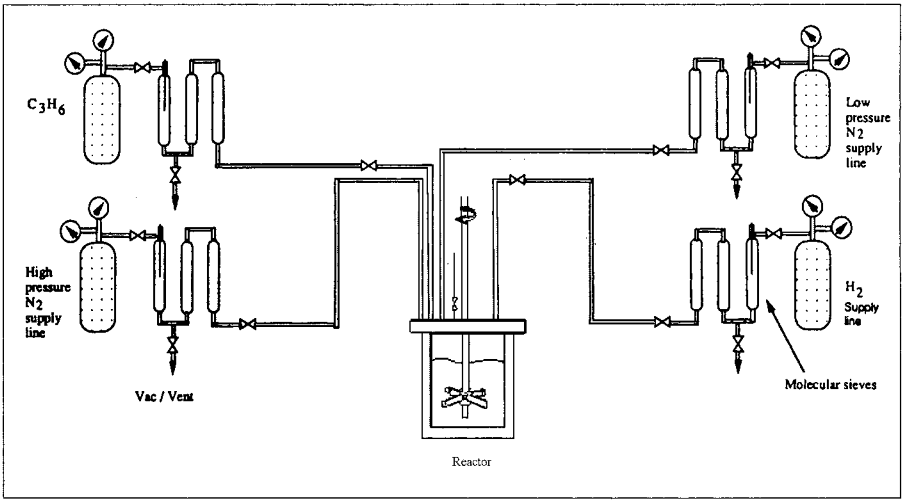

Figure 1. Autoclave system for propylene polymerization.

The propylene polymerization essays were carried out in a liquid propylene (pool) medium. The catalytic system was a conventional Ziegler-Natta catalyst, based on $TiCl_4$ and an internal donor, supported on $MgCl_2$. The use of triethyl-aluminium (TEA) as the catalyst activator, and of an external electron donor to control the polymer stereoregularity, is needed.

Because of the extreme sensibility of the catalyst system to a large range of impurities (poisons), all the operations are done under an inert atmosphere of nitrogen. The reaction operations are performed in successive stages.

At first, fixed amounts of TEA, external donor and catalyst are introduced in an appropriate vessel, in the presence of small amounts of an organic solvent. A precise amount of minutes is then given to the compounds to let them interact and to form the catalytic complex.

There after, the catalytic complex is introduced into the reactor altogether with the amounts of hydrogen and propylene required for the reaction Then the temperature and the pressure are risen until the reaction conditions are reached. The elapsed time of the temperature rise is controlled, and always lasts the same amount of time. The reaction is then maintained during a carefully controlled lapse of time, and it is stopped by turning the temperature down and flashing out the unreacted monomer. The polymer is then recovered from the reactor, dried in an oven and weighed to calculate the amount of polymer produced per gram of catalyst (reaction yield).

During the first part of this work, a set of essays was carried out in order to set the most suitable working conditions. Based on these preliminary results, the most appropriate TEA/Catalyst, TEA/Donor and Catalyst/Donor ratios were used during the rest of the experimental setup. In the second series of essays, the influence of three basic operation variables on the polymerization yield was evaluated, carrying out the essays within a range of the reaction time (from 30 to 120 min), a range of hydrogen content in the reactor (from 0 to 9.5 bars) and a range of temperature (from 50 °C to 80 °C).

Results

Setting the operation conditions

In the first series of essays, a set of reactions were carried out to determine the most suitable conditions for the polymerization reaction. The overall results are shown in Table 2.

Table 2. Operating Conditions (Standard Values).

Bench Reactor Volume	4 liters
Catalyst	20 mg.
Al / Ti molar ratio	1000
Al / External Donor molar ratio	12
Stirring Speed	550r.p.m.
Reaction Time	120 min.
Reaction Temperature	70 °C
Hydrogen Partial Pressure	3,5 bar

Stirring Speed

Because of the nature of the reactive system, based upon polymerization in liquid propylene, problems related to external diffusion of the monomer towards the catalyst active sites are not expected. Nevertheless, the stirring speed in the reactor has been evaluated in order to select a value that ensures a correct dispersion of the catalyst in the reactor, avoiding high shear values that could affect the polymer particle distribution. Three essays were carried out with different stirring speeds (Figure 2). For low speed values, the low polymer yield might be due to a bad dispersion of the catalyst in the reactor. For high speed values, the yield is almost unchanged. In order to avoid fragmentation of the resulting polymer particles due to shear stress at high speed values, the value 550 rpm is selected as a standard for all the essays to be done further on.

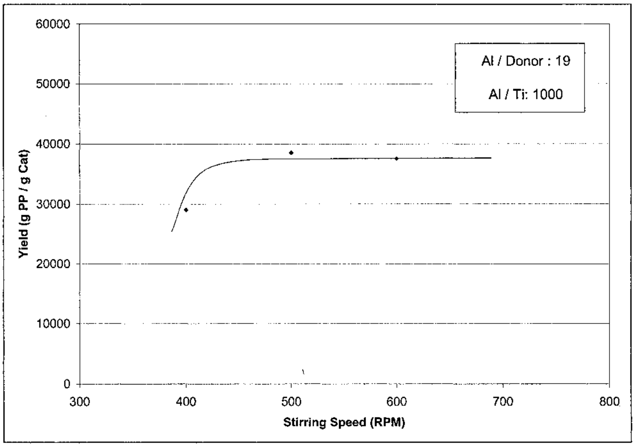

Figure 2. Influence of the stirring speed.

Catalyst content

The amount of catalyst fed into the reactor is limited by the volume of the reactor. It is possible to produce just a few grams of polymer in order to avoid build up and homogeneity problems during the reaction. The essays carried out to determine the amount of polymer to be fed into the reactor (Figure 3) shows that 12 mg is the most suitable quantity of catalyst to be fed into the reactor.

Al/Ti Ratio

TEA has an important effect over the polymerization kinetics. TEA is not only believed to act as the catalyst activator, but also as a scavenger, reducing the impact of the presence impurities that would poison the catalyst. A series of essays were carried out using Al/Ti ratios from 450 to 1200 (Figure 4). From the results, it can be seen that the polymerization yield reaches a maximum when the Al/Ti molar ratio ranges values close to 900. This value is selected as standard for all the essays to be done further on.

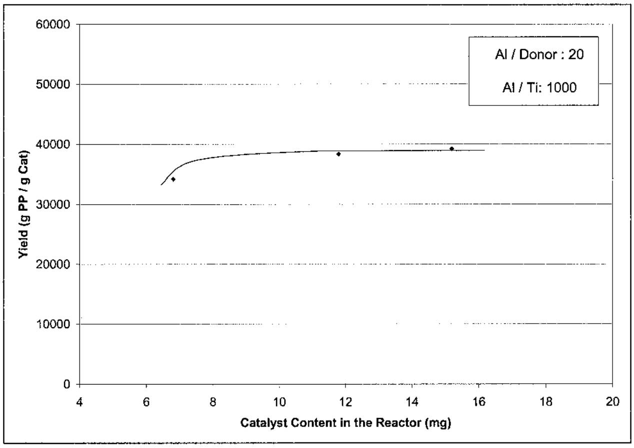

Figure 3. Influence of the catalyst content.

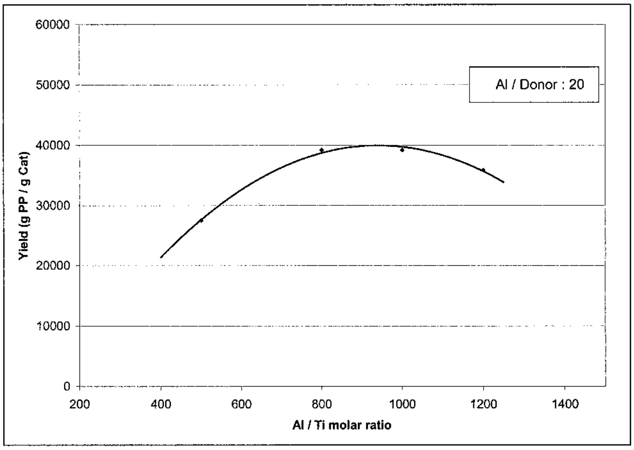

Figure 4. Influence of Al/Ti molar ratio.

Al/External Donor Ratio

During the olefin polymerization with Ziegler Natta catalysts, external donors are generally employed. These are believed to react with non-stereospecific sites, and deactivating them.

By this way, the presence of an external donor within the catalytic system increases the stereospecificity of the reaction and affects the polymerization kinetics. Thus, as the donor content increases the polymer isotacticity increases too, but the catalyst activity decreases. As it can be seen in figure 5, the catalyst yield increases with increasing Al/Donor ratios. From these results, the value 20 is selected as a standard condition for the Al/Donor molar ratio.

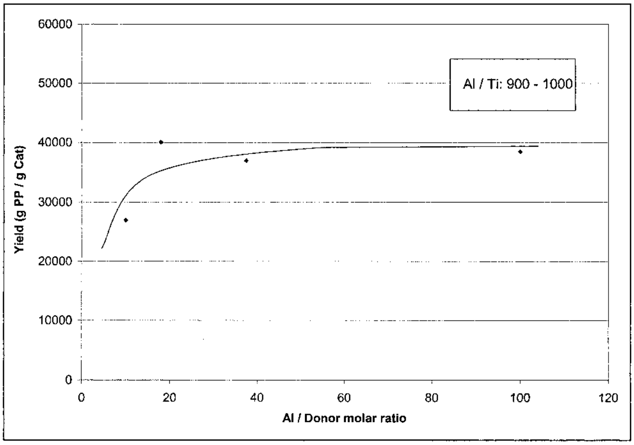

Figure 5. Influence of Al / Donor molar ratio.

Influence of the polymerization conditions

In order to evaluate the influence of the operation conditions on the reaction yield, during the second series of essays, the operating variables are studied one by one within a certain range as the rest of conditions are set to the values of the standard conditions shown in Table 2.

Influence of the reaction time

Several polymerizations were carried out, measuring the reaction yield for a set of reaction times. The experimental results show how the reaction yield increases as the polymerization rate decays with reaction time. The essays were repeated under the same conditions for several hydrogen contents in the reactor. By means of statistical correlations, it was possible to determine that the experimental results fit the best to the non-linear function of the reaction yield with a decay order n=1. This conclusion is coherent for all the results, for the whole range of hydrogen contents in the reactor. The correlation factor (R2>0.9950) gives an estimate of how good the adjustments are. Figure 6 shows the plot of the reaction yield against time for the experimental data and for the mathematical model. The percentage deviations of the experimental points with the mathematical model are in this case below 5%.

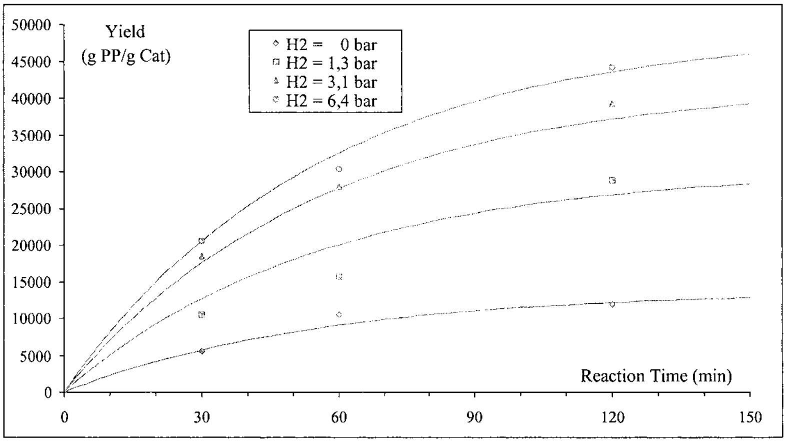

Figure 6. Experimental Results (Yield vs. Time).

These results are also in accordance with the results of previous works.[8-9-10-11-12] Obviously, the decay order for the Ziegler Natta catalysts has been a subject of debate for quite a long time. Even if some authors report that the reaction yield model fits properly to a decay order n=2 or even n=1.5 for reaction times above 2 or 3 hours, from the present results it is possible to see that the decay order n=1 fits properly when the reaction times are below 120 minutes. Here, it is necessary to point out that the decay of the catalyst is an overall parameter that expresses the interaction of several elementary reactions. By that way the value of the decay order does not reveal the basic mechanisms of the catalyst decay.

Influence of the hydrogen content in the reactor

It is well known that the catalyst activity increases with higher hydrogen content in the polymerization reactor.[13] From the experimental runs (Figures 7 and 8), it was possible to determine that the value of the deactivation constant is not significantly affected by the level of hydrogen content in the reactor. This result confirms an assumption undertaken in a previous work.[14] that the hydrogen content in the reactor had little influence on the deactivation constant. On the contrary, the initial polymerization rate grows with the hydrogen content in the reactor, until an upper limit is reached for values above 6 bar (Figure 7). This might be attributed to a reactivation of dormant sites by hydrogen. This is reflected in the previous model by an increase of the initial polymerization rate with higher hydrogen contents, which may be introduced by the following empirical expression:

$$Vo = A\left(1 - Be^{-C \cdot P_{H_2}}\right) \qquad (5)$$

Where $\mathbf{P_{H_2}}$ is the hydrogen content in the reactor (bar) and A, B, and C are specific constants. The non-linear correlation of the model with the results gives the values of the model parameters, while the correlation factor allow us to estimate the accuracy of the model (R2>0.997).

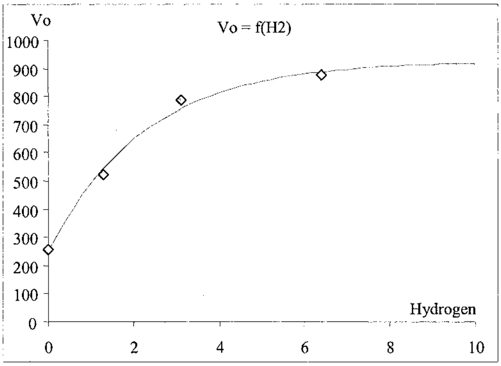

Figure 7. Initial polymerization rate vs. Hydrogen content.

Influence of the reaction temperature on the polymerization yield

From the experimental essays, it can be seen how the catalyst activity increases with increasing values of the reaction temperature (Figure 8).

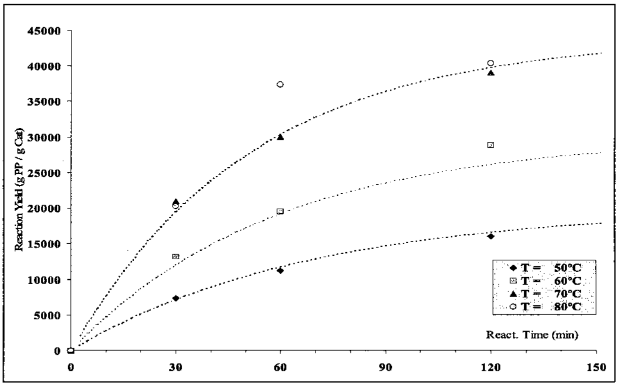

Figure 8. Influence of the Reaction Temperature.

The reaction temperature is assumed to affect both kinetic terms, the initial polymerization rate and the deactivation constant (Vo and K_d), according to the Arrhenius laws:

$$Vo = A_o e^{\frac{-E_a}{RT}} \qquad (6)$$

$$K_d = A'_o e^{\frac{-E'_a}{RT}} \qquad (7)$$

Where Ea and Ea' are the activation energies for each the kinetic parameters.

Figure 9 shows the plot of ln(V) versus the inverse values of the absolute reaction temperature. On the same way, Figure 10 shows the plot of $\ln(K_d)$ versus the inverse values of the absolute reaction temperature. In both cases, the values fall nearly on a straight line for reaction temperatures below 75 °C. But in both cases, the values for the reaction temperature of 80 °C are slightly off the Arrhenius plot. This behavior might be due to increasing diffusional effects at the highest temperatures.

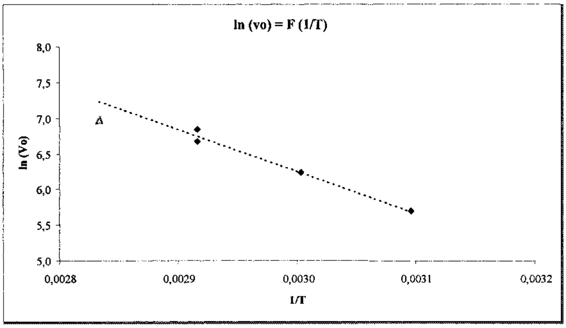

Figure 9. Arrhenius plot of Vo vs. 1/T.

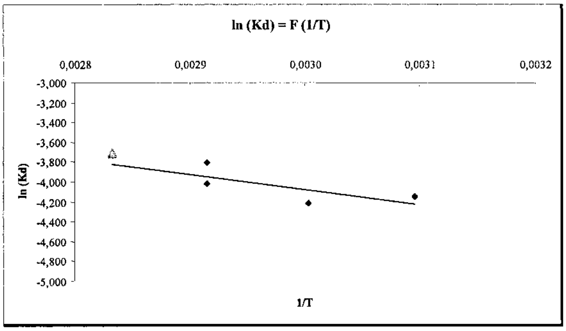

Figure 10. Arrhenius plot of K_d vs 1/T.

As a global result, the polymerization yield is then given by the following expression

$$Y = A\left(1 - Be^{-C[H_2]}\right)\frac{\left(1 - e^{-K_d \cdot t}\right)}{K_d} \qquad (8)$$

Where A, B, C are specific constants, $\mathbf{P_{H_2}}$ is the hydrogen content in the reactor (bar), $\mathbf{K_d}$ the deactivation constant of the catalytic system and **t** the reaction time (min).

In Figure 11, the plot of the experimental Yields is given in relation to the ones estimated by the model for all of the series of essays. As it can be seen, the model fits to the experimental results with high accuracy, with percentage deviations below 10%.

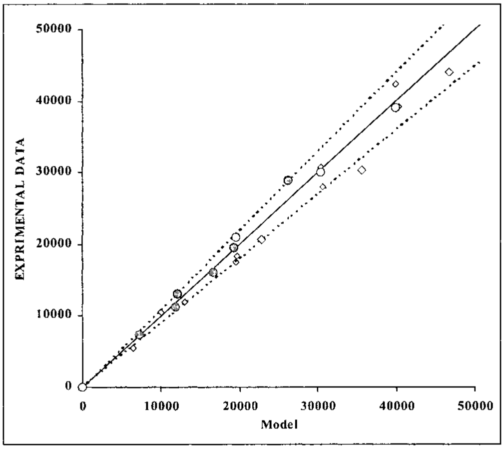

Figure 11. Correlation model vs. experimental results.

Replication phenomenon

Since the first industrial developments, several theories have been established in order to explain the morphology of the Ziegler Natta catalysts and its reaction products.[15-16] As a matter of fact, the final shape and size of the polymer powder depends on how it expands around the catalyst grain: as the reaction proceeds, the polymer particle grows and replicates the physical characteristics of the catalyst particle at a larger scale (shape, texture, particle size distribution, etc.). This is known as the replication phenomenon. Even if the particle growth mechanisms are complex, experimental evidence demonstrates that, during the first polymerization steps, the catalyst particles disrupt into a larger number of small fragments. Even though they are segregated, the catalyst fragments are hold together by the growing polymer that acts as a binder, while being uniformly dispersed inside the polymer particle. As a consequence, as the polymer particle grows around the catalyst particle, the fragments expand outwards, maintaining the same physical shape and characteristics of the initial catalyst particle (Figure 12).

The polymer particle size depends on the initial catalyst particle size, the reaction yield (i.e. the quantity of polymer formed), and the catalyst geometric parameters (volumetric factors).

The very first seconds of the polymerization are critical on what concerns the replication phenomenon. In this phase the catalyst particles are broken apart, and the polymer is formed around them. If the heat that the reaction generates is not properly evacuated and the catalyst activity and mass flow at the particle level are not carefully controlled during these first steps, the polymer fragments are more likely to break, and the replication phenomenon does not occur. Thus, if the prepolymerization conditions are severe, the catalyst particles might segregate in independent particles and not be bounded. In order to observe the replication phenomenon, a prepolymerization should be carried out under mild conditions.

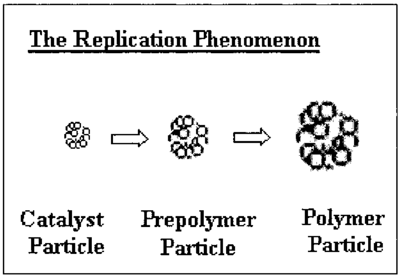

Figure 12. The replication phenomenon.

From the series of essays carried out to study the influence of the polymerization time, the initial catalyst particle size distribution, and the final polymer size distribution were evaluated. As it can be seen from Figure 13, the polymer particle size grows with the increase of the polymerization time. This is due to the increase of the reaction yield with the reaction time, reaching an upper limit value for the largest polymerization times. This behavior is in accordance with the model developed when the decay order is n=1.

It is thus possible to develop a method to asses the final particle size as a function of the initial catalyst size distribution, the reaction parameters and the catalyst physical characteristics. On the same way, it is possible to determine the prepolymer size distribution when the final polymer particle size distribution and the other reaction parameters are known.

In Figure 13, the experimental results correspond to the catalyst size distribution and to the final polymer particle size distribution. By means of a mathematical model, the prepolymer size distribution can be calculated from the final polymer size distribution. As it can be seen in the figure, the prepolymer particle size distribution is the same for all of the essays, meaning that the replication phenomenon takes place, all the products being a replica of the same prepolymer. Nevertheless, the prepolymer particle distribution does not match the one of the catalyst. This is likely to be due to fragmentation during the initial polymerization steps. As mentioned before during the experimental set up, the polymerization begins directly with a controlled increase of the temperature from 25 °C to 70 °C. In order to obtain a more accurate catalyst replication, the initial prepolymerization step should be studied, employing milder conditions.

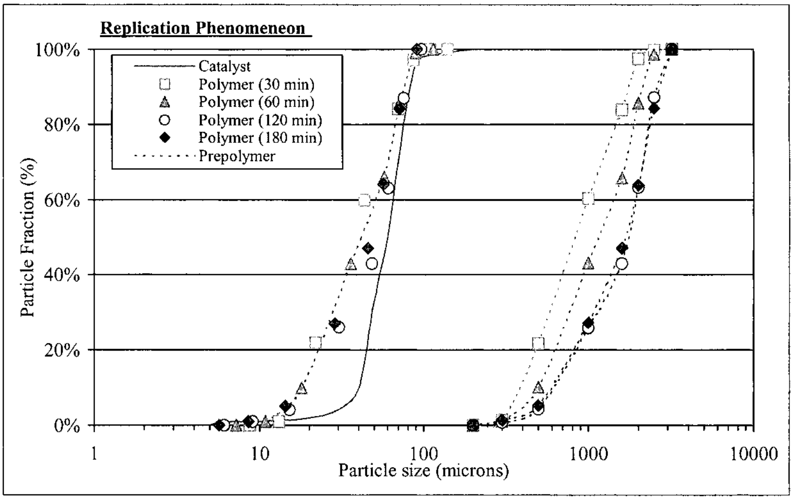

Figure 13. The replication phenomenon.

Conclusions

This work allowed us to prove the suitability of liquid pool propylene polymerization in bench scale reactors to investigate the reaction kinetics. After selecting a set of optimum reaction conditions, and evaluating the impact of the Al/Ti and the Al/Donor molar ratios on the reaction yield, it was possible to model the kinetic behavior of a highly active $TiCl_4/MgCl_2$ catalyst with an expression where the initial reaction rate and the deactivation constant are the key variables. From the evaluation, it was possible to determine that the reaction yield increases as the polymerization rate decays with reaction time, a behavior is typical from many Ziegler Natta catalysts. Within the range of time considered, the experimental results fit properly to a kinetic model where the overall deactivation order is n=1. It was also possible to see that the initial polymerization rate grows with the hydrogen content in the reactor, until an upper limit is reached for values above 6 bar. The presence of hydrogen strongly increases the initial activity of the catalyst, by increasing the initial polymerization rate. Within the range of polymerization conditions, the reaction yield may be then given by the following expression:

$$Y = A\left(1 - Be^{-C \cdot P_{H_2}}\right)\frac{\left(1 - e^{-K_d \cdot t}\right)}{K_d}$$

The model predicts the reaction yield as a function of three basic operating conditions: the reaction time, the hydrogen content in the reactor, and the reaction temperature.

In this work it was also possible to study the catalyst replication phenomenon and see that the polymer particles not only replicate the shape and texture of the initial catalyst, but also its particle size distribution.

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