

Prepolymerization of Ethylene with a Ziegler–Natta Catalyst

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Received 4 April 2006; accepted 5 February 2007

DOI 10.1002/app.26354

Published online 14 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The slurry prepolymerization of ethylene using $\text{TiCl}_4/\text{MgCl}_2$ as a catalyst was investigated. A 2³-factorial experimental design method was employed to study the effects of the temperature, hydrogen, and active cocatalyst-to-catalyst molar ratio (Al/Ti) on the catalyst activity, prepolymer melt flow index, and powder bulk density. All dependent variables increased when the active Al/Ti ratio increased from 1 to 2. The hydrogen–Al/Ti interaction had a significant effect on the prepolymer melt flow index and catalyst activity. The hydrogen (partial pressure ranging from 0.5 to 1.5 bar) and temperature (ranging from 60 to 80°C) variables as well as the hydrogen–temperature and hydrogen–temperature–Al/Ti interactions increased the prepolymer powder bulk density, which ranged from 0.11 to 0.373 g/cc. To find the

reason for the prepolymer powder bulk density variation with the operating conditions, the particle size distribution and crystallinity of the prepolymers were determined. The increasing catalyst activity, ranging from 132 to 660 g of polyethylene/mmol of Ti, enhanced the weight percentage of fines, which ranged from 3 to 60, and decreased the average particle size, which ranged from 562 to 120 μm . This was the reason for the increasing prepolymer powder bulk density and could be due to the breakup of the prepolymer particles during prepolymerization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2703–2711, 2007

Key words: morphology; polyethylene (PE); Ziegler–Natta polymerization

INTRODUCTION

The gas-phase polymerization of olefins using highly active Ziegler–Natta (Z–N) catalysts is one of the most important methods of polyolefin production used in the polymer industry.^{1,2} Using highly active Z–N catalysts in gas-phase reactors causes difficulties in the operation of these types of reactors, so a prepolymerization step of Z–N catalysts in a slurry phase is often mandatory to control and reduce the activity of the catalyst and thus polymer particle overheating in gas-phase polymerization.^{3–9}

The prepolymerization, which is a preliminary step, is carried out under mild operating conditions (low temperature and monomer concentration/pressure) and has significant effects on the main polymerization step. This issue has been reported in the literature. For instance, the effect of prepolymerization on the microstructure of ethylene/1-hexene copolymers made with an MgCl_2 -supported TiCl_3 catalysts was investigated by Chu et al.³ They

observed that prepolymerization increased the polymerization rate as well as the reactivity of 1-hexene and changed the short chain branch distribution of the produced polymer but did not alter its molecular weight distribution. Yiagopoulos et al.⁴ developed a comprehensive mathematical particle growth model accounting for external and internal mass-transfer limitations appearing during the growth of highly active Z–N catalysts in gas-phase olefin polymerization and showed that by the proper selection of the prepolymerization temperature and time, particle overheating can be significantly reduced, whereas the polymerization rate is enhanced. Also, Pater et al.,^{5–7} by applying a new method of prepolymerization, so-called nonisothermal prepolymerization, studied experimentally the effects of prepolymerization and reaction conditions on the polymerization of liquid propylene with a Z–N catalyst and revealed that when prepolymerization was used, thermal runaway on the particle scale was avoided.

The prepolymerization process can industrially be a semibatch or continuous process. In a semibatch process, the produced prepolymer at the end of the prepolymerization is dried by a hot nitrogen gas flow. Then, the dried prepolymer powder is stored under nitrogen blanketing and fed to the main gas-

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Contract grant sponsor: R&T National Petrochemical Co. (Iran).

phase polymerization reactor (e.g., BP Chemical).^{10–13} In the continuous process, which often is carried out in a loop reactor, the produced prepolymer is fed to the main polymerization reactor directly (e.g., the Spherilene process).^{14,15}

In the semibatch prepolymerization process, the properties of the produced prepolymer powder, such as the prepolymer yield, melt flow index (MFI), and powder bulk density, because of their importance, are measured and controlled before it is fed into the main gas-phase reactor. The prepolymer yield, which is affected by the catalyst activity in the prepolymerization step, can be related to the prepolymer activity in the main gas-phase polymerization and in turn can influence the operation of the gas-phase reactor. The powder bulk density of the prepolymer can influence the storage and handling of the prepolymer powder from storage vessels to the gas-phase reactor. These properties are affected by the prepolymerization operating conditions, that is, the temperature, hydrogen, and cocatalyst-to-catalyst molar ratio (Al/Ti).

As stated previously, the effect of prepolymerization on the main polymerization step has been frequently investigated in the literature; however, the effects of the prepolymerization conditions and their interactions on the prepolymer properties have not been reported in the open literature.

The first part of this research was the use of a 2³-factorial experiment design method to investigate the effects of the temperature, hydrogen, and Al/Ti ratio and their interactions in the slurry prepolymerization of ethylene with TiCl₄/MgCl₂ as a catalyst and tri-*n*-octyl aluminum (TnOA) as a cocatalyst on the prepolymer MFI and powder bulk density as well as the catalyst activity. Then, the particle size distribution (PSD), crystallinity, and scanning electron microscopy (SEM) of the prepolymer particles were determined to interpret the effects of the prepolymerization operating conditions on the prepolymer powder bulk density.

EXPERIMENTAL

Materials

MgCl₂-supported TiCl₄ catalyst solution in *n*-hexane having 150 mmol/L of Ti and a TnOA cocatalyst solution in *n*-hexane having 810 mmol/L of Al were used as received. Ethylene, hydrogen, and nitrogen gases (99.99%) were supplied by Messer Co. (Krefeld, Germany) and Roham Gas Co., (Tehran, Iran) respectively. All gases were further purified with filled columns of molecular sieves that absorbed the humidity, CO₂, and sulfur compounds. Acridine (98%) and 1-butanol (99.9%) were applied as received from Merck (Darmstadt, Germany).

Prepolymerization procedure

The prepolymerization procedure used in this research was based on a method commonly used in industrial processes.^{10–13} In this process, after the successive addition of the solvent, cocatalyst, catalyst, and hydrogen to the reactor, ethylene is continuously fed at a constant flow rate to obtain a prepolymer yield of approximately 35–40 g of polyethylene/mM Ti. In the course of the reaction, the reactor pressure gradually increases because of the deactivation of the catalyst along with a pressure buildup of about 1–2 bar. However, in our experiments, because of the different compositions applied to study their effects on the prepolymer properties in comparison with the unique compositions used in industry, we let the reaction proceed until 4 bar of pressure buildup in the reactor.

The typical procedure in this research was as follows. The slurry prepolymerization reactions of ethylene were performed in a 1-L jacketed, round-bottom, stainless steel reactor equipped with a mechanical spiral stirrer and an oil-circulating temperature control system. After the reactor was purged by nitrogen for 2 h at 60°C, about 400 mL of *n*-hexane was transferred to the reactor under nitrogen blanketing. Then, a 2-mL TnOA solution was added by a gas-tight syringe under a nitrogen atmosphere to scavenge trapped oxygen and remove impurities in the reactor. Before the feeding of the catalyst, to determine the remaining amount of active TnOA in the reactor, a sample of a known volume was taken, and the acridin reagent was added to it. The remaining active TnOA was measured by the titration of the sample with a 1-butanol solution with a given concentration. Then, the catalyst and cocatalyst in appropriate amounts were injected into the reactor by a gas-tight syringe under a nitrogen atmosphere to obtain the required active molar ratio of Al to Ti (1, 1.5, or 2). After the temperature was increased to the desired reaction temperature, hydrogen was fed up to a specific pressure, and ethylene was continuously fed at a constant flow rate to the reactor. The flow rate of ethylene was almost constant in the course of the prepolymerization; however, because the supplied ethylene pressure was fixed at 4 bar, the ethylene flow was reduced during the last minutes of the reaction as the reactor pressure was increased. Whenever the catalyst activity was high, the period of pressurizing the reactor and the prepolymerization time were long. Therefore, according to the catalyst activity, the reaction times were different. Finally, the reaction was stopped by the evacuation of hydrogen and ethylene gases from the reactor, and the produced prepolymer slurry was drained and dried. The prepolymer yield was determined by the weight of the dried prepolymer at the end of the reaction. Because the reaction times of the

experiments were different, the catalyst activity was calculated as the weight of the produced prepolymer in 10 min of the reaction, which was common in all the experiments as follows:

$$\begin{aligned} \text{Catalyst activity (g of polyethylene/mM Ti h)} \\ = \text{Total prepolymer yield (g of polyethylene} \\ \text{/mM Ti)/(10/60)h} \quad (1) \end{aligned}$$

Characterization

The MFI and powder bulk density of the produced prepolymer were determined by ASTM D 1238 and D 1895B, respectively. The PSD of the prepolymer powders was measured by the sieve method. The differential scanning calorimetry (DSC) method was used to determine the crystallinity of the nascent prepolymers in the reactor with a DSC polymer labs machine in a temperature range of 30–200°C. About 2–5 mg of the prepolymer powder with 2% accuracy was heated from the ambient temperature to 200°C at a rate of 10°C/min. From the resultant endothermic curve, the heat of fusion (ΔH_f) was obtained, and the crystallinity percentage of the nascent prepolymer was calculated with the following relation:

$$\text{Crystallinity (\%)} = (\Delta H_f / \Delta H_f^*) \times 100 \quad (2)$$

where ΔH_f^* is the heat of fusion of completely crystalline polyethylene samples (i.e., 69 cal/g).

A Philips XL30 scanning electronic microscopy (Eindhoven, The Netherlands) was used to study the surface morphology of the prepolymer particles. The samples were previously deposited on SEM stubs, which were coated with a gold film to avoid electrostatic discharges during observation.

RESULTS AND DISCUSSION

Study of the effect of the operating conditions with a 2³-factorial design method on the catalyst activity, prepolymer MFI, and powder bulk density

The prepolymerization experiments were designed by a 2³-factorial experimental design method with one replication to study the effects of the operating conditions as independent variables and their interactions on the prepolymer MFI and powder bulk density as well as the catalyst activity as dependent variables. The considered operating conditions were the temperature, hydrogen pressure, and cocatalyst-to-catalyst ratio (Al/Ti). The levels of these variables (shown in Table I) were selected on the basis of values commonly used in industry.

Table II shows the experimental conditions for the prepolymerization of ethylene and the results,

TABLE I
Factor Levels of the Independent Variables for Ethylene Prepolymerization

Independent variable	Low level (-1)	Midpoint (0)	High level (+1)
Temperature (°C)	60	70	80
Hydrogen pressure (bar)	0.5	1.0	1.5
Al/Ti molar ratio	1.0	1.5	2.0

including the prepolymer MFI (g/10 min), powder bulk density(g/cc), catalyst activity (g of polyethylene/mmol of Ti h), time length of the prepolymerization, prepolymer yield (g of polyethylene/mmol of Ti), and catalyst activity decay characteristic (bar/min).

An analysis of variance (ANOVA) was applied to analyze the results to explore the effect and significance of the independent parameters and their interactions on the dependent variables. The significance probability (*p* value) was calculated to evaluate the significance of the effects. If the calculated value is higher than a certain significance level, usually set to 0.05, an effect is considered statistically relevant.^{16,17} Furthermore, the ANOVA was used to plot surface responses to show the variations of the dependent variables as functions of the independent variables.

Table III shows the results of the ANOVA for the prepolymerization experiments.

These results show that the effect of the Al/Ti ratio on the catalyst activity was highly significant and that the temperature had a moderate effect; however, the hydrogen pressure had no significant effect on the catalyst activity. Furthermore, the effects of H₂ pressure–temperature, temperature–Al/Ti, and H₂ pressure–temperature–Al/Ti interactions were not significant on the catalyst activity, and the H₂ pressure–Al/Ti interaction had little pertinent effect.

Figure 1 illustrates surface plots of the catalyst activity in the prepolymerization as a function of the temperature and Al/Ti ratio, the hydrogen and temperature, and the hydrogen and Al/Ti ratio. In Figure 1, the third independent variable, which has not been mentioned, is assumed to be constant in its high value. For instance, in Figure 1(a), the hydrogen value is constant at 1.5 bar. The same assumption is made for the results shown in Figures 2 and 3.

As can be seen in Table II and Figure 1, the catalyst activity was significantly enhanced with the increase in the Al/Ti ratio from 1 to 2. This can be related to more activation of dormant sites in the catalyst by an increase in the Al/Ti molar ratio, which influences directly the reaction rate and catalyst activity.^{18,19} Nevertheless, increasing the reaction temperature from 60 to 80°C decreased the catalyst activity in our experiments, and this can be related to the ethylene content in the slurry reaction media at

TABLE II
Conditions and Results for the Ethylene Prepolymerization Experiments Using a Z–N Catalyst

Independent variables				Results					
H ₂ (bar)	Temperature (°C)	Al/Ti	Catalyst activity (g of polyethylene/mmole Ti h)	Prepolymer MFI (g/10 min)	Powder bulk density (g/cc)	Time (min)	Yield (g of polyethylene/mmole Ti)	Catalyst activity decay characteristic (bar/min) ^a	
1	0.5	60	1	216	0.06	0.112	43	36	0.081
2	0.5	60	1	198	0.04	0.122	41	33	0.085
3	1.5	60	1	240	0.30	0.130	40	40	0.063
4	1.5	60	1	288	0.38	0.138	43	48	0.058
5	0.5	80	1	162	0.009	0.110	36	27	0.097
6	0.5	80	1	132	0.005	0.124	34	22	0.103
7	1.5	80	1	180	0	0.155	32	30	0.078
8	1.5	80	1	192	0	0.135	34	32	0.074
9	0.5	60	2	576	1.1	0.19	118	96	0.030
10	0.5	60	2	660	1.7	0.27	125	110	0.028
11	1.5	60	2	576	1.9	0.228	118	96	0.021
12	1.5	60	2	630	2.15	0.240	122	105	0.021
13	0.5	80	2	528	0.7	0.202	98	88	0.036
14	0.5	80	2	570	0.76	0.224	100	95	0.035
15	1.5	80	2	468	1.5	0.337	80	78	0.031
16	1.5	80	2	510	1.8	0.373	86	85	0.029
17	1.0	70	1.5	288	1.2	0.162	58	48	0.052
18	1.0	70	1.5	210	0.8	0.186	50	35	0.060

^a The catalyst activity decay characteristic was measured by the pressure buildup divided by the time length of the reaction. The pressure buildup was the ultimate pressure (4 bar) minus the initial pressure in the reactor, which was different with respect to the hydrogen pressure applied in each experiment (0.5, 1.0, or 1.5 bar).

different temperatures. Indeed, the reactor consists of slurry and vapor phases, and the increase in the reaction temperature decreases the slurry phase fraction in the reactor; this leads to the decrease in the ethylene content in the reaction mixture. This decrease and the lower ethylene solubility at higher temperatures lead to the decrease in the ethylene amount in the slurry phase, whereas the catalyst amount remains unchanged, and as a result, the catalyst activity is reduced. This observation was quantitatively revealed by the calculation of the vapor and liquid fractions in the reactor as well as the molar fractions of the components in each phase

with the Peng–Robinson equation of state. It seems that the effect of lowering the ethylene amount in the slurry phase suppressed the effect of increasing the temperature on the kinetic constants, and the overall reaction rate decreased with an increasing reaction temperature in the experiments.

The results of the ANOVA for the MFI, presented in Table III, show that all the variables had significant effects on the prepolymer MFI, but the Al/Ti effect was the most relevant effect, being even more important than the hydrogen pressure. The H₂ pressure–Al/Ti interaction had a significant effect, but the other interactions did not. Figure 2 shows

TABLE III
Significance of the Effects of Independent Variables and Their Interactions on the Prepolymer MFIs, Powder Bulk Densities, and Catalyst Activities

Independent variable	Dependent variables					
	Catalyst activity		MFI		Powder bulk density	
	<i>p</i>	Significance	<i>p</i>	Significance	<i>p</i>	Significance
H ₂ pressure	0.757	Not significant	0.001	Significant	0.004	Significant
Temperature	0.001	Significant	0.004	Significant	0.042	Significant
Al/Ti	0.000	Highly significant	0.000	Highly significant	0.000	Highly significant
H ₂ pressure–temperature	0.364	Not significant	0.996	Not significant	0.014	Significant
H ₂ pressure–Al/Ti	0.031	Significant	0.008	Significant	0.066	Not significant
Temperature–Al/Ti	0.512	Not significant	0.104	Not significant	0.086	Not significant
H ₂ pressure–temperature–Al/Ti	0.691	Not significant	0.14	Not significant	0.029	Significant

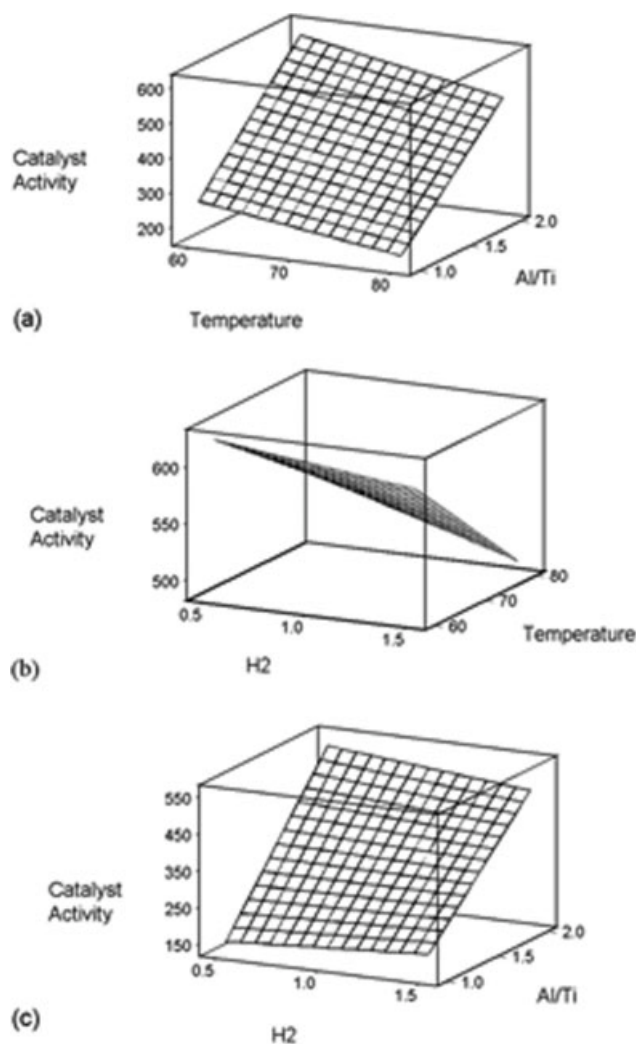


Figure 1 Response surface plots for the catalyst activity variation versus independent variables: (a) the temperature versus the Al/Ti ratio with the hydrogen pressure constant at 1.5 bar, (b) H₂ versus the temperature with the Al/Ti ratio constant at 2, and (c) H₂ versus the Al/Ti ratio with the temperature constant at 80°C.

surface plots for the prepolymer MFI as a function of the temperature and Al/Ti ratio, the hydrogen and temperature, and the hydrogen and Al/Ti ratio.

As shown in Table II and Figure 2, the hydrogen and Al/Ti ratio increased the prepolymer MFI. The increase in the hydrogen pressure and Al/Ti ratio in the reactor enhanced the chain-transfer reactions to hydrogen and to alkyl aluminum, respectively.^{20–22} This led to the decrease in the molecular weight and the increase in the prepolymer MFI. On the other hand, the results showed that the reaction temperature decreased the prepolymer MFI. This MFI drop can mainly be attributed to the decreasing slurry phase fraction in the reactor, as explained earlier, and, consequently, the decreasing amount of hydrogen in the slurry phase.

Furthermore, the ANOVA results in Table III for the prepolymer powder bulk density show that the hydrogen, temperature, and Al/Ti variables as well as the H₂ pressure–temperature and H₂ pressure–temperature–Al/Ti interactions had important effects. However, the most relevant effect was related to the Al/Ti variable. In addition, surface plots for the powder bulk density as a function of the temperature and Al/Ti ratio, the hydrogen and temperature, and the hydrogen and Al/Ti ratio are illustrated in Figure 3.

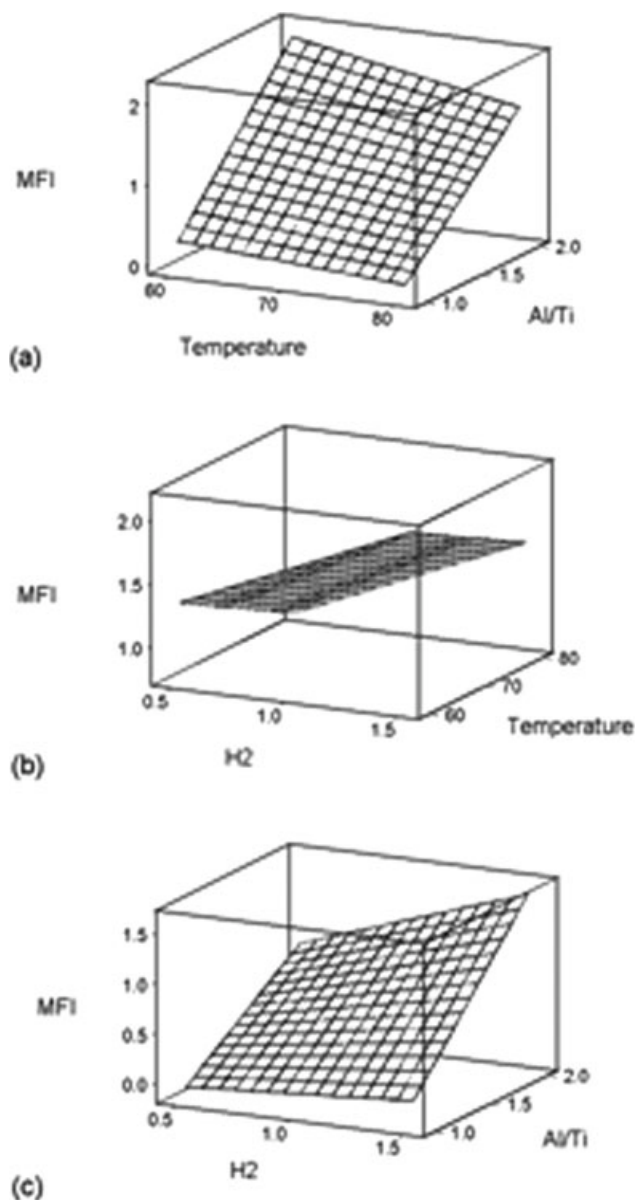


Figure 2 Response surface plots for the prepolymer MFI variation versus independent variables: (a) the temperature versus the Al/Ti ratio with the hydrogen pressure constant at 1.5 bar, (b) H₂ versus the temperature with the Al/Ti ratio constant at 2, and (c) H₂ versus the Al/Ti ratio with the temperature constant at 80°C.

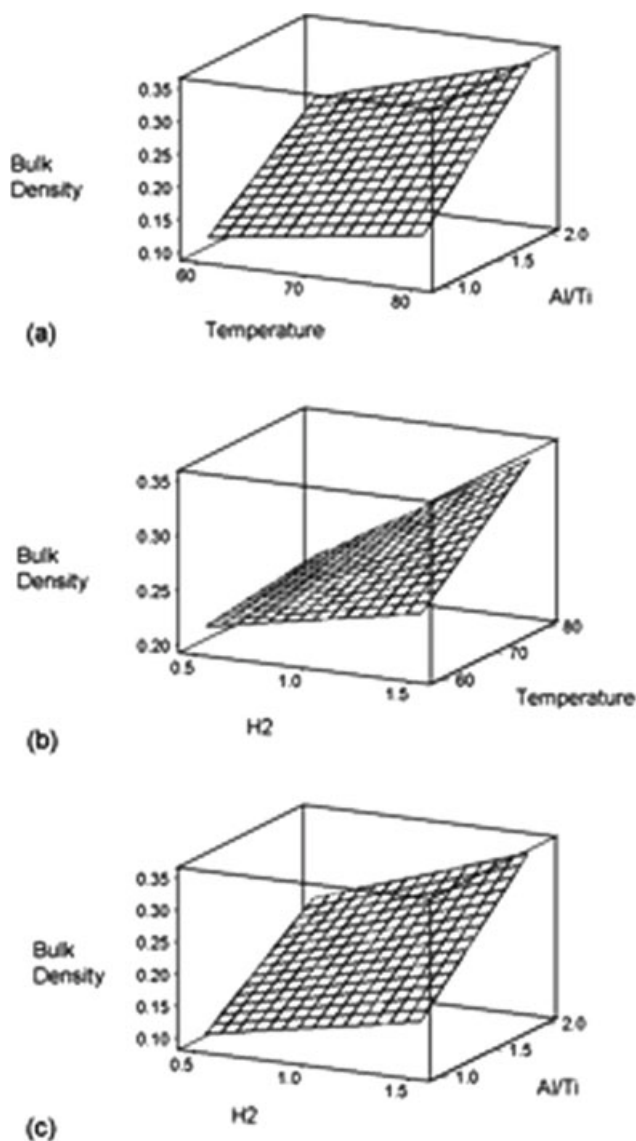


Figure 3 Response surface plots for the prepolymer powder bulk density variation versus independent variables: (a) the temperature versus the Al/Ti ratio with the hydrogen pressure constant at 1.5 bar, (b) H_2 versus the temperature with the Al/Ti ratio constant at 2, and (c) H_2 versus the Al/Ti ratio with the temperature constant at 80°C .

This figure and the data in Table II illustrate that all the variables increased the prepolymer powder bulk density under the experimental conditions. The interpretation of these observations needs more data, which are presented in the next section.

Figures 1–3 were achieved under the assumption of a linear dependence between the independent and dependent variables. This assumption was examined with two replicate experiments in center points of a 2^3 -factorial experiment design and with an F test. It was recognized that the effects of the independent variables on the MFI and powder bulk density of the prepolymer were linear, whereas these effects on the catalyst activity were not linear. There-

fore, some quadratic curvature should be considered for the catalyst activity. Indeed, a new method for the design of experiments such as composite design should be applied to realize quadratic curvatures for the dependence of the catalyst activity on the studied independent variables. This was not included in this research, but we will accomplish it in future research.

Study of the effect of the operating conditions on the prepolymer powder bulk density

As a matter of fact, the powder bulk density of the polymer/prepolymer particles is affected by many factors, such as the PSD, morphology, and crystallinity. For this reason, and to interpret and explore in more detail the effects of the operating conditions on the prepolymer powder bulk density presented in the preceding section, the PSD, crystallinity, and SEM of some samples were determined.

The volume-average particle diameter (APS) and weight percentage of particles smaller than $125\ \mu$ (fines) of the prepolymer particles were calculated with the results of PSD measurements by the sieve method. Table IV presents the APS and weight percentage of the fines of the prepolymer particles along with their crystallinity, powder bulk density, and catalyst activity under different experiment conditions.

The variations of the catalyst activity versus the APS and weight percentage of fines as well as the catalyst activity versus the powder bulk density are shown in Figures 4 and 5, respectively. Figure 4 shows that there are two completely distinct regions. In region 1, the produced prepolymers with an Al/Ti ratio of 1 had a lower catalyst activity, larger APS, and less fines than the prepolymers in region 2 with an Al/Ti ratio of 2. This can be attributed to the increase in nonuniform fragmentation and breakup of the catalyst/prepolymer particles during prepolymerization with increasing catalyst activity. In the same manner, Figure 5 shows that there are two different regions with low and high catalyst activity and low and high powder bulk density of the prepolymer, respectively. Therefore, the increase in the powder bulk density can be related to the decrease in APS and the generation of more fines with higher catalyst activity.

In addition, as shown in Figure 3, the powder bulk density of the prepolymer increased with increasing hydrogen pressure in the reactor. The crystallinity percentages of the prepolymer particles, presented in Table IV, show that in cases with the same reaction temperature and Al/Ti ratio, when the hydrogen pressure in the reactor increased, the crystallinity degree rose, and this might have led to the increase in the prepolymer powder bulk density.

TABLE IV
PSDs, Powder Bulk Densities, and Crystallinity Measurements of the Prepolymer Samples Along with the Catalyst Activities Under Different Prepolymerization Conditions

	Independent variables			Results				
	H ₂ (bar)	Temperature (°C)	Al/Ti	Catalyst activity (g of polyethylene/ mM Ti h)	Bulk density (g/cc)	APS (μ)	Fines (wt %) ^a	Crystallinity (%)
1	0.5	60	1	216	0.112	320	8	35
2	1.5	60	1	240	0.130	442	6	54
3	0.5	80	1	162	0.110	562	5	31
4	1.5	80	1	180	0.155	450	3	50
5	0.5	60	2	576	0.190	196	30	47
6	1.5	60	2	576	0.228	147	55	55
7	0.5	80	2	528	0.202	171	36	44
8	1.5	80	2	468	0.337	120	60	57

^a Less than 125 μ.

Furthermore, it was observed that, even though the temperature had the lowest significant effect on the powder bulk density statistically (cf. respective *p* values in Table III), its increase led to the increase in the powder bulk density of the prepolymer. As explained in the preceding section, increasing the temperature led to the lowering of the reaction rate in the experiments. According to the results illustrated in Table IV for cases in which the hydrogen and Al/Ti ratio were constant, the elevation of the temperature from 60 to 80°C resulted in a decrease in APS and the generation of more fines, whereas the catalyst activity was lowered and the crystallinity of the prepolymer particles was not changed to a great extent. This could mean that with increasing temperature, despite decreasing catalyst activity, the fragmentation process, leading to the breakup of the prepolymer particles and generation of fines, increased. This might be related to the microstructure and mechanical strength of the catalyst and its career as well as the response to the temperature increase. This temperature response, as explained by Grof et al.,²³ can also be related to the higher mass-transfer resistance in the growing prepolymer particles

at higher temperatures, which leads to uneven growth of the particles and even the formation of fines.

These results might seem to be different from the results reported in the literature. Pater et al.⁷ investigated the influence of the temperature, hydrogen, and monomer concentration on the morphology of polypropylene powder in the polymerization of liquid propylene with a fourth-generation Z-N catalyst. They concluded that the initial reaction rate is the crucial factor in the development of the shape of the polymer particle, and when the initial polymerization rate is high, the particle will not be able to replicate the shape of the catalyst particle, will form irregularly shaped surface structures, will have high porosity, and will show low values for bulk densities. Yu et al.²⁴ also studied the effects of the temperature, Al/Ti ratio, and external donor on the morphology and PSD of polypropylene in solution propylene polymerization with a spherical Z-N catalyst. They concluded that these parameters have no significant effect on the morphology of polypropyl-

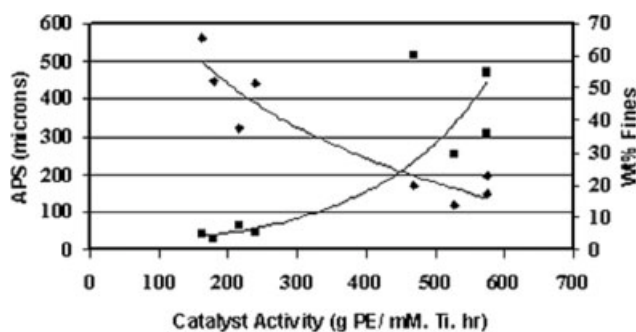


Figure 4 (◆) APS variations and (■) weight percentage variations of fines for the prepolymer powders versus the catalyst activity.

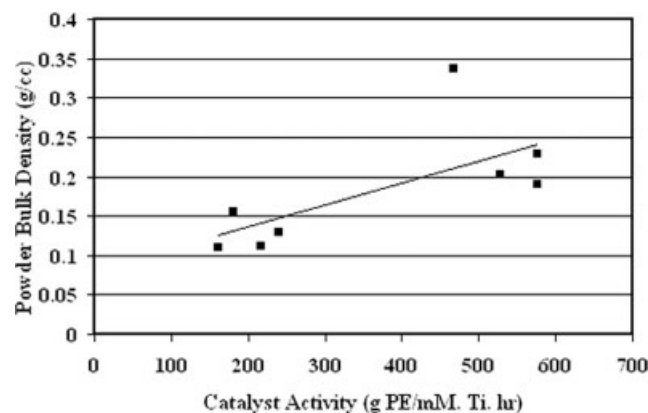


Figure 5 Powder bulk density of the prepolymer versus the catalyst activity.

ene particles. However, they changed the catalyst activity so that the volumetric PSD increased with the increase in the catalyst activity.

The catalyst and polymer particles in the course of polymerization, depending on the microstructure of the catalyst itself and its support (mechanical strength, porosity, etc.) and polymerization conditions (temperature, monomer concentration, etc.), may fragment and deform in different ways. Merquior et al.²⁵ classified particle fragmentation into four categories: (1) uniform particle fragmentation resulting in the morphological replication of catalyst particles to polymer particles, (2) nonuniform fragmentation causing the deformation of final polymer particles, (3) breakup of polymer particles and production of fines, and (4) melting of particles and formation of large agglomerations leading to the interruption of the reactor operation.

From this classification and the results reported in Figures 4 and 5, it can be concluded that the fragmentation in the prepolymerization experiments could be classified as the third type of fragmentation. However,

the fragmentation reported by Pater et al.⁷ and Yu et al.²⁴ can be considered the first and second types of fragmentation classified by Merquior et al.²⁵

The surface morphology of the prepolymer particles was also examined with SEM. The surface of the prepolymer particles synthesized with lower catalyst activity was smoother than the surface of the particles with higher catalyst activity. The SEM pictures of the prepolymer particles synthesized under operating conditions with low and high catalyst activities, that is, entries 2 and 8 in Table IV, are shown in Figure 6(a,b), respectively. This is in agreement with what was concluded by Kim and Woo.²⁶ The exterior surface of the polymer sample obtained at a lower catalyst efficiency was covered by globules, as shown in Figure 6(a), whereas the polymer samples obtained at a higher catalyst efficiency had a wormlike texture, almost the same as what is shown in Figure 6(b).

CONCLUSIONS

Ethylene prepolymerization experiments using $\text{TiCl}_4/\text{MgCl}_2$ as a catalyst and TnOA as a cocatalyst were carried out to study the effects of the prepolymerization conditions, that is, the hydrogen, temperature, and Al/Ti molar ratio and their interactions, on the prepolymer MFI and powder bulk density as well as the catalyst activity.

Using a factorial experiment design method, we concluded that all the independent variables had a significant effect on the prepolymer MFI and powder bulk density. The H_2 pressure–Al/Ti interaction was the only interaction that had a significant effect on the MFI, whereas the effects of the H_2 pressure–temperature and H_2 pressure–temperature–Al/Ti interactions on the powder bulk density of the prepolymer were important. The catalyst activity was also significantly affected by the temperature and Al/Ti variables as well as the H_2 pressure–Al/Ti interaction. Furthermore, the Al/Ti ratio was the most important variable for changing or controlling all dependent variables.

From the measurement of the PSD of the prepolymer particles, it was found that at higher Al/Ti values (i.e., higher catalyst activity) and to a lesser extent at higher temperatures, the production of fines increased through the nonuniform fragmentation and breakup of the prepolymer particles during prepolymerization.

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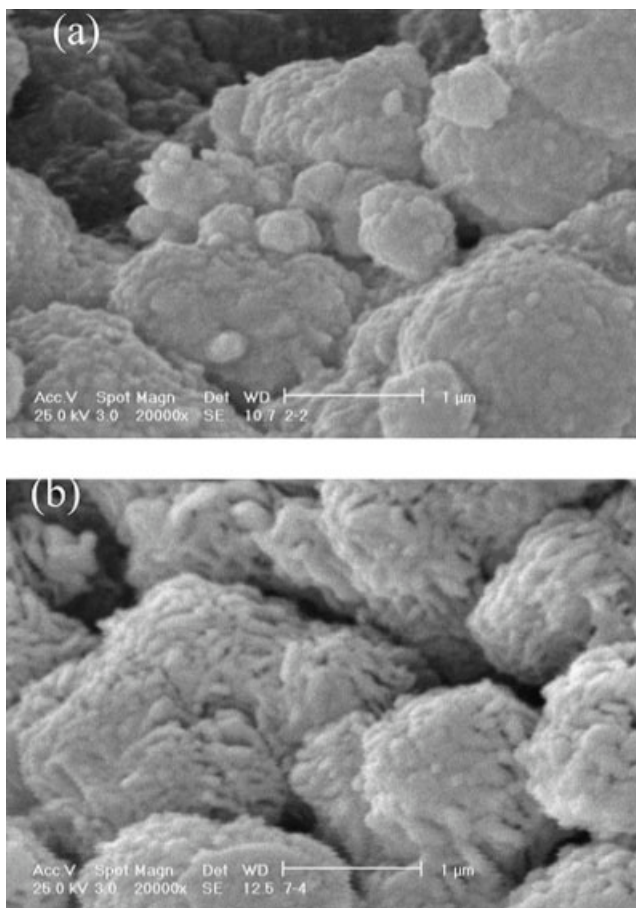


Figure 6 SEM pictures of two samples of prepolymer powders with (a) low catalyst activity (for the experimental conditions, see entry 2 in Table IV) and (b) high catalyst activity (for the experimental conditions, see entry 8 in Table IV).

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