

Ethylene Homo- and Copolymerization Over MgCl₂-TiCl₄ Catalysts: Polymerization Kinetics and Polymer Particle Morphology

Mehdi Hassan Nejad,¹ Paolo Ferrari,² Gianni Pennini,² Giuliano Cecchin²

¹National Petrochemical Company, R&T, 14358 Tehran, Iran

²Basell Polyolefins, "G. Natta" Research Center, 44100 Ferrara, Italy

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ABSTRACT: Three procatalysts of the MgCl₂/TiCl₄ type, differing mainly in their morphological characteristics, were investigated in ethylene polymerization and ethylene-1-butene copolymerization. Apparently, hydrogen has an intrinsic and general deactivating effect but it can also play an activating effect in homopolymerization. This peculiarity was found to be related to a catastrophic breakage of the polymer/catalyst particles during growth and thus to the exposure of new active centers. In this case the kinetic profiles are irregular and characterized by one or more secondary peaks which reflect the moment when this morphology-driven rate-enhancement effect takes place. In general, the prepolymerization of the procatalysts with propylene tends to slightly enhance homopolymerization

rate, to slow down copolymerization rate and to stabilize the morphology of the growing polymer particles, thus preventing the occurrence of the irregular kinetic profiles observed during homopolymerization in the presence of hydrogen. The behavior of the procatalysts investigated was found to depend on the distribution of their pore size rather than the absolute values of their porosity. Likely this is due to an easier diffusion of the monomer and a more regular and homogeneous growth of the polymer within larger as opposed to smaller pores. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3388–3402, 2008

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INTRODUCTION

It is known that the homopolymerization and copolymerization of ethylene with heterogeneous Ziegler-Natta catalysts is characterized by many peculiarities^{1–13}:

In homopolymerization, ethylene appears to be less reactive than expected based on its intrinsic reactivity.

The presence of a higher 1-olefin as comonomer usually brings about a marked increase of the polymerization rate with respect to the homopolymerization. This is in contrast with the copolymerization theory, which predicts a decrease of polymerization rate due to the lower intrinsic reactivity of the higher 1-olefin with respect to ethylene.

The kinetics of homopolymerization are often characterized by a build-up type profile, frequently preceded by an induction period, whereas the copolymerization is usually charac-

terized by a fast and strong initial peak, followed by a decay-type profile.

Catalyst prepolymerization either with propylene or higher alpha olefins has a substantial rate-enhancing effect in ethylene homopolymerization.

Both pure chemical or physical phenomena have been invoked to explain these kinetic features. The chemical factors include, e.g.: displacement of adsorbed or complexed molecules, formation of new active centers or activation of dormant centers by higher α -olefin monomers. For instance, according to Kissin and coworkers,^{11,12} the above peculiarities, and other features of ethylene polymerization, can be explained based on the multicenter nature of the active species, coupled with the hypothesis that the presence of the Ti—C₂H₅ bond in active centers strongly decreases their reactivity because of stabilization by an agostic interaction between the hydrogen of the methyl group and the titanium atom. The insertion of a higher olefin in the Ti—polymer bonds prevents the formation of such "dormant" centers and thus accelerates the reaction rate.

The physical factors include in turn pure diffusivity phenomena like, e.g., easier access for the monomer to the active centers due to the reduced crystallinity of the surrounding polymer layer brought

Correspondence to: G. Pennini (gianni.pennini@lyondellbasell.com).

about by the incorporation of the monomer,^{3,7,8,11} or diffusivity plus mechanical phenomena involving the fragmentation of the growing catalyst-polymer particle. In this connection, it is worth mentioning the extensive studies carried out by Tait et al.^{4,6,10} on the homo and copolymerization of ethylene with higher alpha olefins, including prepolymerization. The authors conclude that the disintegration of the catalyst particles is the major cause of the activating effect of higher 1-olefins in ethylene copolymerization, or homopolymerization following higher 1-olefins prepolymerization. This brings about an increase of the effective working surface of the catalyst and thus also in the number of active centers.

In addition, the diffusion of the cocatalyst, especially when bulky enough, has been proposed to play a role in ethylene polymerization with heterogeneous Ziegler-Natta catalysts.¹⁴

In the presence of diffusion limitations for both monomer and/or cocatalyst, it is clear that both the nature (e.g., the degree of crystallinity) of the nascent polymer and the porosity and friability of the catalyst particle can play a fundamental role. In particular, the progressive fragmentation of the catalyst particle resulting from the hydraulic forces generated by the growing polymer can expose new catalyst centers that would be otherwise not available to the monomer.

Control and fine tuning of polymer particle morphology is particularly important for industry. In general, polymer particles having spherical shape, tuned size, and narrow size distribution with no broken particles or "fines" are most desired since these properties are key to maximize plant productivity, optimize reactor operability, and guarantee product consistency.

In this connection, it has long been recognized that the pretreatment of the catalyst particle with small amounts of propylene under mild conditions (prepolymerization), frequently used in industrial operations, not only prevents an uncontrolled breakage of the polyethylene particle during the "main" polymerization stage but also can enhance the reaction rate in ethylene homopolymerization. This is due to the fact that the presence of even small amounts of polypropylene causes a preexpansion of the catalyst particle, its controlled fragmentation into its primary particles, without loss of its "macro" integrity, and thus the exposure of all the available active centers to the ethylene monomer since the beginning of the reaction.

In general, polyethylene particle growth over a heterogeneous catalyst looks more complicated than that of propylene and is far from being clearly understood. Thus, the morphology of the nascent polyethylene particles is characterized by many structural peculiarities like the presence of threads,

cobwebs, onion textures etc.¹⁵ The occurrence of this latter morphological feature, first experimentally reported by Galli et al.,^{16,17} and usually combined with an acceleration-type kinetic profile, indicates that the growth of the polyethylene particle can occur step-by-step, or layer-by-layer, according to the mechanism proposed by Chiovetta's¹⁸⁻²⁰ and Fink's groups²¹⁻²³: at the beginning only the catalyst surface shell is available for polymerization, then the hydraulic stresses generated by the growing polymer are able to expose a new catalyst shell, and so on. Thus, after a rapid initial peak, the rate drops and, following an induction period, tends to increase as the reaction goes on, to reach a maximum value when the fragmentation process has gone to completion. In the absence of catalyst deactivation, this upper limit corresponds to a stationary state. These features depend both on the nature of the catalyst particle and on the polymerization conditions and thus cannot be easily generalized. Additional kinetic complications arise from the fact that heterogeneous Ziegler-Natta catalysts generally bear active species that differ in both intrinsic reactivity and stability in time.

From the above considerations, it is clear that both kinetic and morphological studies are necessary to clarify the complex features of ethylene polymerization over heterogeneous Ziegler-Natta systems. As already mentioned, many publications have dealt with this subject and both unsupported catalysts and systems based on TiCl_4 supported on MgCl_2 or its precursors have been investigated. For instance, Tait et al.⁴ have compared the behavior of TiCl_3 with two $\text{MgCl}_2/\text{TiCl}_4$ catalysts containing either ethylbenzoate or diisobutylphthalate as internal donors. On the other hand, no systematic and comparative investigations have been reported so far focusing on the physical nature rather than on the chemical nature of the catalyst particle.

Based on the above considerations, this is one of the most important factors that should affect both polymerization kinetics and polymer morphology in general and in particular for ethylene, due to the high reactivity to diffusivity ratio of the monomer. To this end, we have selected three spherical $\text{MgCl}_2/\text{TiCl}_4$ catalysts having similar chemical composition but differing in their main morphological properties like size, porosity, and pore distribution. Each catalyst has been tested, either as neat or after prepolymerization, in both ethylene homopolymerization and ethylene-1-butene copolymerization, both in the presence or absence of hydrogen. In this article, we would like to show how the kinetic profiles and the morphology of the resulting polymer particles can have a strong and mutual influence, depending on both catalyst nature and polymerization conditions. In particular, we would like to pin-

point some kinetic peculiarities that, at least to the best of our knowledge, have never been experimentally observed before.

EXPERIMENTAL

Materials

The procatalysts used were spherical, $MgCl_2$ -supported systems having the general formula $MgCl_2/ TiCl_4/ID$, where the internal donor ID is diisobutylphthalate (DIBP). They mainly differ in their morphological properties (see Table I and Diagram 1). During (co)polymerization they were used in combination with triethylaluminum (TEA) as cocatalyst, used as a 10% (wt/vol) solution in hexane and with cyclohexyl-methyl-dimethoxysilane (CHMMS) as external donor (ED), used as a 6% (wt/vol) in hexane. Ethylene purity was 99.8% min, 1-butene 99.3% min, and propane 99.6% min. Ethylene was purified by passing through three columns containing, respectively, CuO (for CO removal), molecular sieves MS 3A (for water removal), and a SELEXSORB system from Alcoa (for the removal of CO_2 , COS, alcohols and oxygenated compounds, AsH_3 and PH_3). Propane was purified by passing through a column containing molecular sieves MS 3A and then a column containing SELEXSORB. Before use, all gases were checked by standard polymerization tests.

General (co)polymerization procedure

Most of the ethylene polymerization experiments were performed in propane slurry using a 4-L stainless steel reactor equipped with a magnetically driven stirrer (impeller) rotating at 560 rpm, and provided with temperature control ($\pm 0.1^\circ C$), pressure control (± 0.1 bar) and flowmeter (max flow rate 680 g/h, max error $\pm 4\%$). Ethylene and propane are introduced from connection lines into the reactor through FRCs (flow record and control device).

Unless otherwise specified, the general (co)polymerization procedure was as follows:

The catalytic system is prepared as hexane slurry, premixing in a glass flask for 5 min the procatalyst (about 15 mg) with the cocatalyst (TEA) and the external donor (CHMMS). The amount

TABLE I
Characterization of Studied Ziegler-Natta Catalysts

	A	B	C
Ti wt %	2.2	2.6	3.3
Mg wt %	19.1	18.8	18.0
Cl wt %	58.4	58.7	58.8
P50 (μm)	59.7	62	45.5
Porosity (cm^3/g)	0.519	0.646	0.313

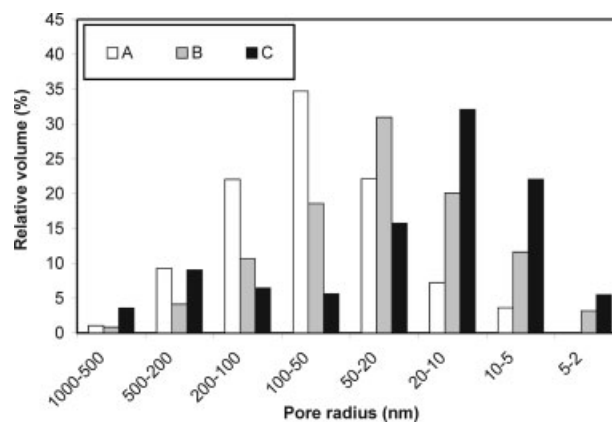


Diagram 1 Pore size distributions of the investigated procatalysts.

of TEA is generally 0.982 g and the TEA/CHMMS molar ratio is 15.

The reactor is dried/cleaned via repeated flushing (three times) with propane at $60-70^\circ C$ and then the temperature is brought to $30^\circ C$. At this temperature, propane (1600 mL), the desired amount of comonomer (generally 200 g when used), and of hydrogen (generally 7.8N liters) are introduced into the reactor. The temperature of the autoclave is then raised to $75^\circ C$ and a proper amount of ethylene is fed so as to reach the desired monomer overpressure, generally 7 bar. Once temperature and pressure have been stabilized, the catalytic mixture is fed into the reactor from a bomb by nitrogen overpressure. The (co)polymerization is generally conducted at $75^\circ C$ and at a total pressure of about 35 barg, usually for 2 h. Some trials have been carried out for longer time or introducing the catalyst mixture at $30^\circ C$ and atmospheric pressure; in this latter case propane is fed, the temperature is raised to $75^\circ C$, 200 g comonomer and, finally, ethylene up to the desired pressure (in about 5 min) are added.

The reactor temperature and pressure as well as the consumption of ethylene in time (flow rate) are monitored and recorded via a YOKOGAWA distributed control system.

After each polymerization test a file containing all the information necessary to draw the related ethylene consumption curve over time (i.e., the kinetic curve) is available.

Please note that ethylene consumption is recorded automatically in a continuous way and that the symbols reported in the figures only serve as indicators to discriminate the various runs.

Consumption of 1-butene during the copolymerization is kept below 10% of the initial amount fed into the reactor.

At the end of the reaction, the gases are stripped-off, first venting the reactor, then purging it

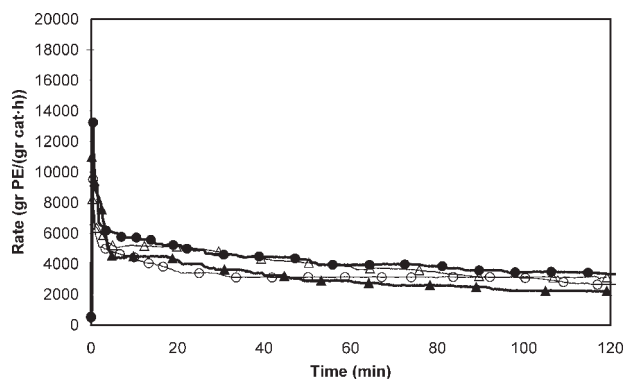


Figure 1 Rate-time profiles of ethylene homopolymerization with catalyst A, (Δ) neat procatalyst with hydrogen, (\circ) neat procatalyst without hydrogen, (\blacktriangle) prepolymerized procatalyst with hydrogen, (\bullet) prepolymerized procatalyst without hydrogen.

with nitrogen at 60°C for 30 min; the polymer is recovered and dried at 70°C.

Some polymerizations were carried out in a 40-L stainless steel reactor, using the same procedure described above.

The catalyst prepolymerizations were conducted *in situ* (directly in the reactor), feeding the monomer (propylene) at 30°C and in propane for the time necessary to polymerize, i.e., about 100 g of monomer per gram of procatalyst in 30 min.

Catalyst and polymer characterization

The catalyst porosity measurements were performed with a mercury porosimeter Pascal 240 from Thermoelectron using the Washburn equation.

The Hg pressure adopted was in the range from 7 to 2000 bar; with this method pore radii in the range 4–75,000 nm can be determined.

The morphology of the polymer particles and of their sections was observed via optical microscopy using a Leica optical microscope equipped with video camera.

RESULTS

Three catalyst systems of the type $\text{MgCl}_2/\text{ID-AlEt}_3/\text{ED}$, where the internal donor (ID) is diisobutylphthalate and the external donor (ED) is cyclohexyl (methyl)dimethoxysilane were tested in ethylene homo- and ethylene-1-butene copolymerization, both in the absence and in the presence of hydrogen. Some of them were also tested both in the neat form and after prepolymerization with propylene. All (co)polymerization experiments were conducted premixing the procatalyst with the cocatalyst mixture to avoid any possible diffusion limitations connected with transport of the aluminum alkyl to the active centers.¹⁴

The melt indices (ISO 1133 method, condition E) of the (co)polymers, as well as homopolymers, are in the 0–3 dg/min range.

The procatalysts used, indicated as A, B, and C, have similar chemical characteristics, have spherical shape, and narrow particle size distribution but differ in their morphological properties (see Table I and Diagram 1). In particular, catalysts A and B have similar degrees of porosity but different pore size distributions (pore radii centered around 50–100 and 20–50 nm, respectively), whereas catalyst C has both a lower degree of porosity and smaller pore size (pore radius centered around 10–20 nm) with respect to catalysts A and B.

Procatalyst A

Kinetics

The ethylene consumption rate versus time curves are reported separately, for homopolymerization and copolymerization experiments, in Figures 1 and 2, respectively. In general, both homo- and copolymerization tests show qualitatively the same kinetic profile, characterized by an initial peak followed by a fast decay and then by a relatively long pseudostationary period. However the absolute rate can be substantially affected by the status of the procatalyst (neat or prepolymerized), by the presence of the comonomer as well as by the presence of hydrogen.

Figure 1, that shows the effects of both prepolymerization and of the presence of hydrogen in ethylene homopolymerization, indicates that both factors have only a moderate effect on polymerization kinetics. In particular, the presence of hydrogen has a marginal rate-enhancement effect for the neat procatalyst and a marginal rate-depression effect for the prepolymerized procatalyst; the use of polypropylene as prepolymer slightly enhances the polymerization

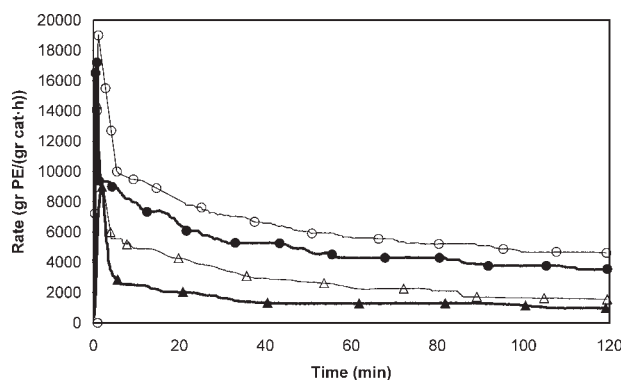


Figure 2 Rate-time profiles of ethylene-1-butene copolymerization with catalyst A, (Δ) neat procatalyst with hydrogen, (\circ) neat procatalyst without hydrogen, (\blacktriangle) prepolymerized procatalyst with hydrogen, (\bullet) prepolymerized procatalyst without hydrogen.

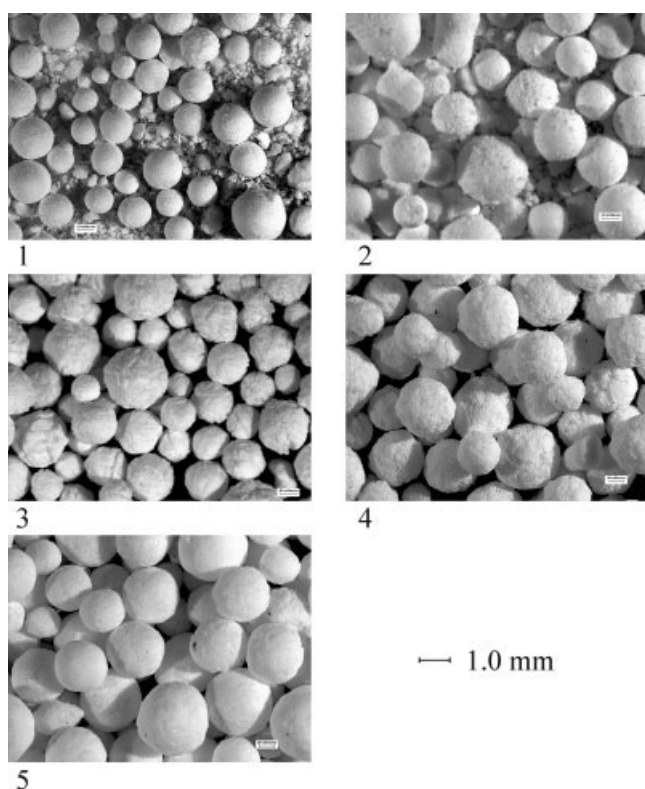


Figure 3 Morphology of the homopolymer particles obtained using catalyst A, 1. neat procatalyst with hydrogen, 2. neat procatalyst without hydrogen, 3. prepolymerized procatalyst with hydrogen, 4. prepolymerized procatalyst without hydrogen, 5. ethylene prepolymerized procatalyst without hydrogen.

rate in the absence of hydrogen but slightly depresses polymerization rate in the presence of hydrogen. The situation is somewhat different for the ethylene-1-butene copolymerization experiments (Fig. 2). Actually, in this case, the presence of hydrogen brings about a substantial rate depression effect for both the neat and the prepolymerized procatalyst versions. A significant rate depression effect is also brought about by prepolymerization, both in the presence and absence of hydrogen. As for the comparison between homo- and copolymerization, it can be observed (compare Fig. 1 with Fig. 2) that copolymerization rates can reach absolute values that are considerably higher than those of homopolymerization; on the other hand, in some instances, copolymerization rate can even be lower than homopolymerization rate. In any case the rate enhancement effects due to the presence of comonomer are not so spectacular as those often reported in the literature.¹⁰⁻¹³ During our experimentation, we have observed, in agreement with Tait,¹⁰ that copolymerization rate tends first to increase and then to decrease again as 1-butene concentration increases. The kinetic profiles reported in Figure 2 are relevant to copolymerization experiments performed with the most effective concentration of comonomer.

Polymer particle morphology

The morphology of the homopolymer particles is affected by both hydrogen and prepolymerization (Fig. 3). In the absence of both hydrogen and prepolymerization, the polymer particles show a fairly good spherical shape but also some broken fragments and fines. The presence of hydrogen tends to further deteriorate the morphology of the growing particles, as indicated by the occurrence of relatively larger amounts of fines. Prepolymerization leads to a substantial improvement in the polymer particle morphology and, actually, they exhibit an almost perfect spherical shape, with no fines, both in the presence and in the absence of hydrogen. As for the morphology of copolymer particles, it can be observed (Fig. 4) that in general they are spherical in shape: in the presence of hydrogen and without prepolymerization, they show only a very limited amount of fines, which disappear completely either in the absence of hydrogen or in the presence of hydrogen with prepolymerization.

It is interesting to note that, in any of the conditions investigated, the sections of the homopolymer particles reveal the frequent presence of a central void surrounded by a compact crown in homopolymers, whereas the copolymer particles appear generally more homogeneous (Fig. 5).

Procatalyst B

The rate-time curves relevant to homo- and copolymerization experiments performed with catalyst B are reported in Figures 6 and 7, respectively. As can be seen, the kinetic profiles obtained with the pro-

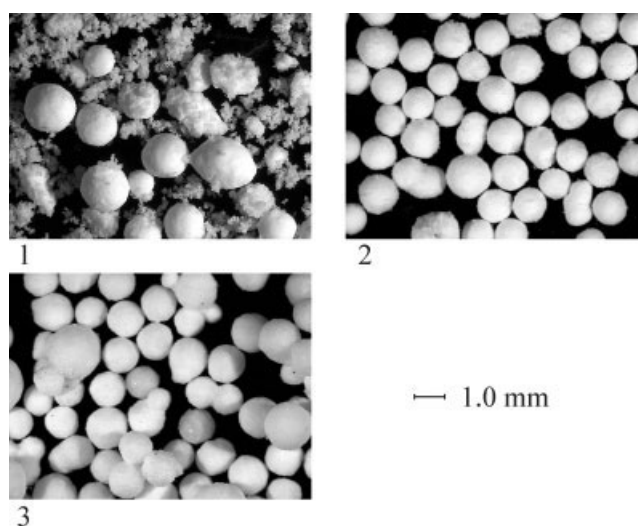


Figure 4 Morphology of the copolymer particles obtained using catalyst A, 1. neat procatalyst with hydrogen, 2. neat procatalyst without hydrogen, 3. prepolymerized procatalyst with hydrogen.

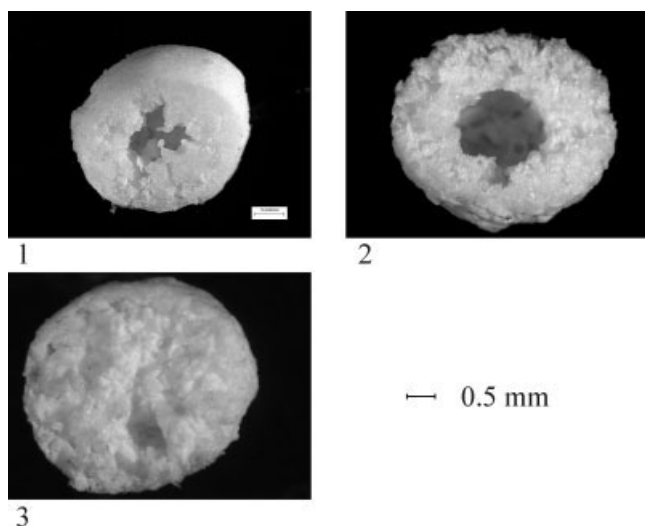


Figure 5 Typical sections of polymer particles obtained using catalyst A, 1. homopolymer with neat catalyst without hydrogen, 2. homopolymer with prepolymerized catalyst with hydrogen, 3. copolymer with neat catalyst without hydrogen.

catalyst B exhibit some distinct peculiarities with respect to catalyst A. Since in this case the mutual influence of polymerization kinetics and polymer particle morphology appears to be specially important, the two aspects have been treated together along the paragraph.

With both catalysts A and B, the copolymerization runs show qualitatively the same behavior: an initial peak followed by a relatively slow decay period. However, in the case of homopolymerization, the kinetic profiles look more complicated for catalyst B (this is the reason why homopolymerization runs have been prolonged for 7 h) and, in particular, are strongly affected by hydrogen. Actually, in the presence of hydrogen, ethylene homopolymerization is characterized by a peculiar path: an initial peak fol-

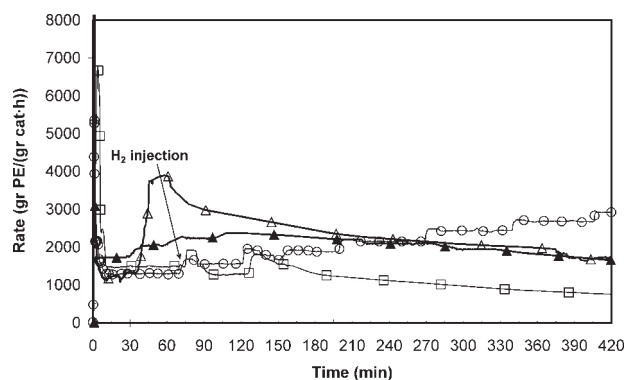


Figure 6 Rate-time profiles of homopolymerization with catalyst B, (Δ) neat procatalyst with hydrogen, (\circ) neat procatalyst without hydrogen, (\blacktriangle) prepolymerized procatalyst with hydrogen, (\square) neat procatalyst without hydrogen and hydrogen injection after 70 min.

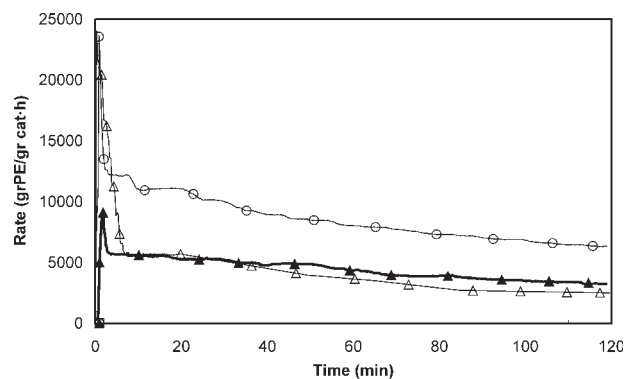


Figure 7 Rate-time profiles of copolymerization with catalyst B, (Δ) neat procatalyst with hydrogen, (\circ) neat procatalyst without hydrogen, (\blacktriangle) prepolymerized procatalyst with hydrogen.

lowed by a rapid decay, then by a relatively short pseudostationary state followed by a sudden increase in the reaction rate and, finally, by a long and slow decay period.

This striking, "irregular" kinetic profile has been experimentally observed and reproduced, at least qualitatively, many times and thus can hardly be considered an artifact. On the other hand, the phenomenon is less reproducible from the quantitative standpoint. The occurrence of a secondary peak in the kinetic profile would suggest that some sort of "catastrophic" and somewhat "random" change in the nature of the growing polymer particles occurs during the reaction. To check this hypothesis, some polymer particles have been collected during the course of polymerization. The morphological inspection of the growing polymer particles reveals that,

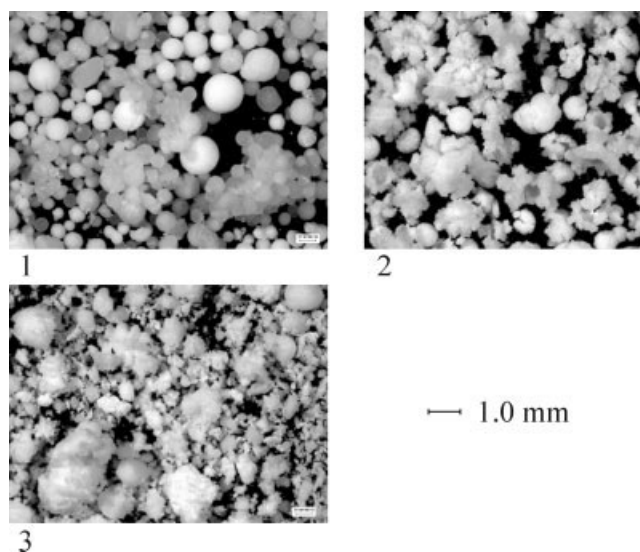


Figure 8 Morphology of the homopolymer particles obtained with catalyst B (neat catalyst with hydrogen) at increasing polymerization times, 1. after 20 min, 2. after 50 min, 3. after 120 min.

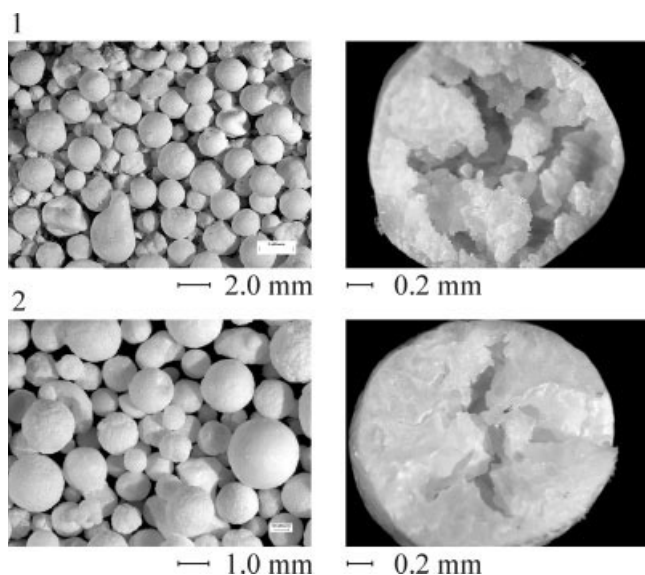


Figure 9 Morphology (surfaces and sections) of the homopolymer particles obtained with catalyst B, 1. neat catalyst without hydrogen, 2. prepolymerized catalyst with hydrogen.

while before the rate-enhancement step they maintain their integrity, many of them are indeed broken after this step. Actually, after 50-min polymerization, the initial spherical polymer shape is completely lost with the formation of broken particles and fines (Fig. 8). It is interesting to note that the same catalyst B prepolymerized with propylene and polymerized with ethylene in the presence of hydrogen does not show these peculiarities. Actually in this case, contrary to what happens with the neat catalyst, the kinetic profile is "normal" with no sudden rate enhancements effects (Fig. 6), and the polymer particles preserve their integrity until the end of polymerization (Fig. 9). Quite interestingly, while the experiments performed with the neat procatalyst in the presence of hydrogen reveal the appearance of a secondary peak, the experiments performed in the absence of hydrogen show an intriguing behavior and, in particular, a build-up profile consisting of regular steps that continues at least for 7 h (Fig. 6). This profile cannot be considered an artifact since it has been repeatedly reproduced, both qualitatively and quantitatively, and even at larger scale using a 40-L reactor. It is interesting to note that, in contrast to what happens with the neat catalyst in the presence of hydrogen, in both cases, either using the neat or the prepolymerized catalyst, the growing polymer particle shows an almost perfect spherical shape until the end of polymerization, even though the presence of an external shell and internal cracks can generally be observed (Fig. 9). To check the consistency of these kinetic features with a stepwise

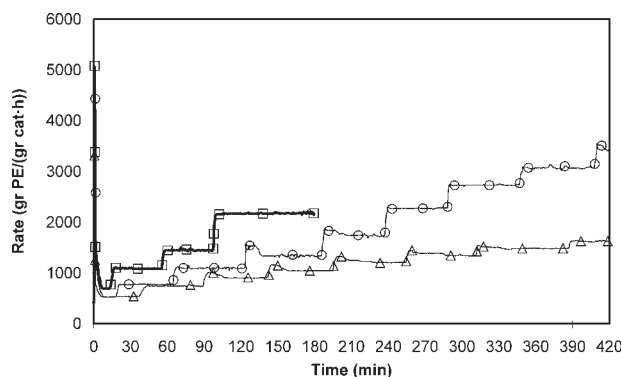


Figure 10 Rate-time profiles of homopolymerization with catalyst B (neat catalyst without hydrogen) at different conditions, (Δ) ethylene partial pressure 7 bar, (\circ) ethylene partial pressure 10 bar, (\square) ethylene partial pressure 10 bar without external donor.

mechanism of polymer growth (see discussion), we performed additional experiments in which an increase of the overall polymerization rate was promoted either by increasing the ethylene partial pressure or by removing the external donor from the catalyst mixture. In both cases the steps increase in height and are observed at shorter times compared with the standard polymerization procedure (Fig. 10). To gain additional information about the hydrogen effect, a run was performed starting the polymerization in the absence of hydrogen and then feeding the standard amount of hydrogen after 70 min: a decay in the polymerization rate took place after hydrogen injection (Fig. 6). The morphology of the resulting polymer particles is similar to that obtained in the absence of hydrogen.

It is worth noting that the same catalyst used in propylene polymerization (no hydrogen fed in the reactor) follows the usual kinetic path, e.g., a fast initial peak with no induction time, followed by a strong and fast deactivation in time. The morphology of the resulting polymer particles is quite regular (Fig. 11).

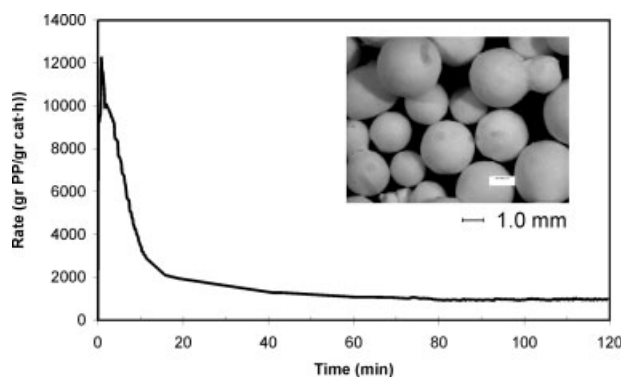


Figure 11 Rate-time profile of propylene polymerization with catalyst B (hexane slurry, 7 bar without hydrogen).

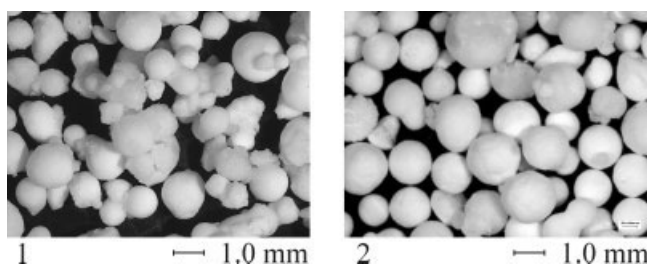


Figure 12 Morphology of the copolymer particles obtained with catalyst B, 1. neat catalyst with hydrogen, 2. prepolymerized catalyst with hydrogen.

Coming back to copolymerization runs, they confirm, as in the case of procatalyst A, that the presence of hydrogen brings about a considerable decrease in polymerization rate, while prepolymerization also tends to decrease the rate, even though only limited to the initial peak (Fig. 7). Finally, it is worth noting that copolymerization rate tends to be generally higher (considerably higher in the absence of hydrogen) than homopolymerization rate so that the difference between the copolymerization and homopolymerization rates tends to be higher than with catalyst A (compare Figs. 6 and 7 and note the different scale of the figures). As for the morphological aspects, the copolymer particles exhibit in any case a perfect spherical shape (Fig. 12).

Procatalyst C

The kinetic profiles relevant to homo- and copolymerization experiments are reported in Figures 13 and 14, respectively.

Using procatalyst C, similar kinetic features as using catalyst B have been observed: significant difference in co- and homopolymerization rates in the absence of hydrogen, "normal" kinetic profile and

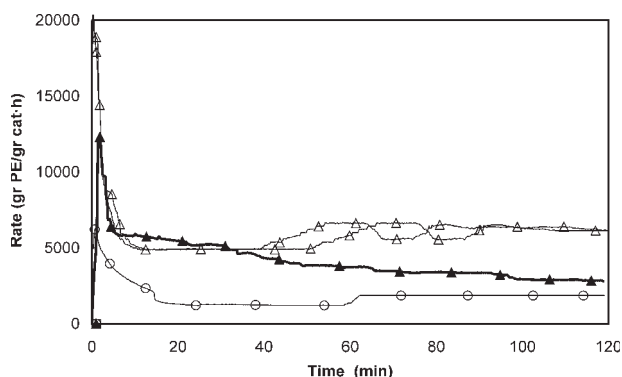


Figure 13 Rate-time profiles of homopolymerization with catalyst C; (Δ) neat procatalyst with hydrogen, (\circ) neat procatalyst without hydrogen, (\blacktriangle) prepolymerized procatalyst with hydrogen.

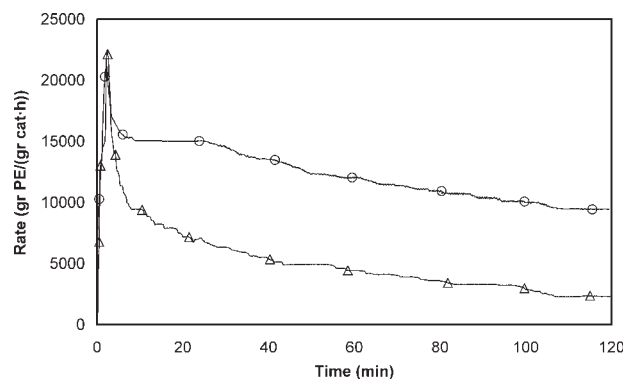


Figure 14 Rate-time profiles of copolymerization with catalyst C, (Δ) neat procatalyst with hydrogen, (\circ) neat procatalyst without hydrogen.

strong deactivating effect of hydrogen for ethylene-1-butene copolymerization and "unusual" and "irregular" kinetic profile, once again repeatedly rechecked and reproduced, for ethylene homopolymerization in the presence of hydrogen. Actually, in comparison with catalyst B, the kinetic profile in the presence of hydrogen is even more peculiar in that, after the initial sharp decay and the first stationary period, the polymerization rate suddenly increases then decreases and increases again, in a sort of "random" multistep mechanism resulting in multiple secondary peaks (Fig. 13). Also in this case the phenomenon is quantitatively poorly reproducible and is related to a "catastrophic" change in the nature of the growing polymer particles. In fact, the polymer particle morphology changes from almost spherical before the first peak to partially exploded

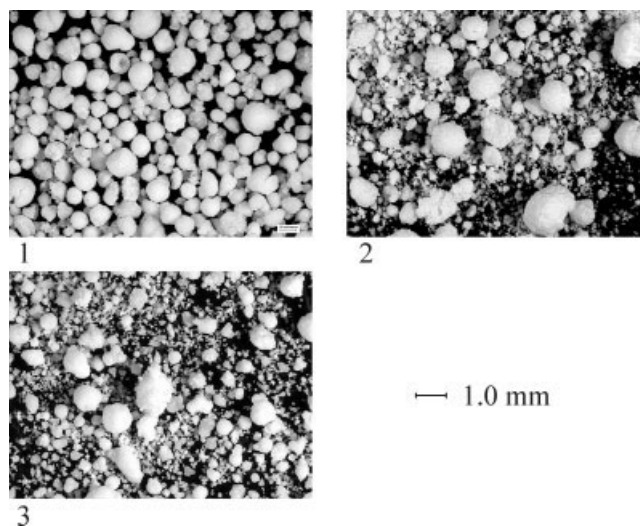


Figure 15 Morphology of the homopolymer particles obtained with catalyst C (neat catalyst with hydrogen) at increasing polymerization times, 1. after 50 min, 2. after 80 min, 3. after 120 min.

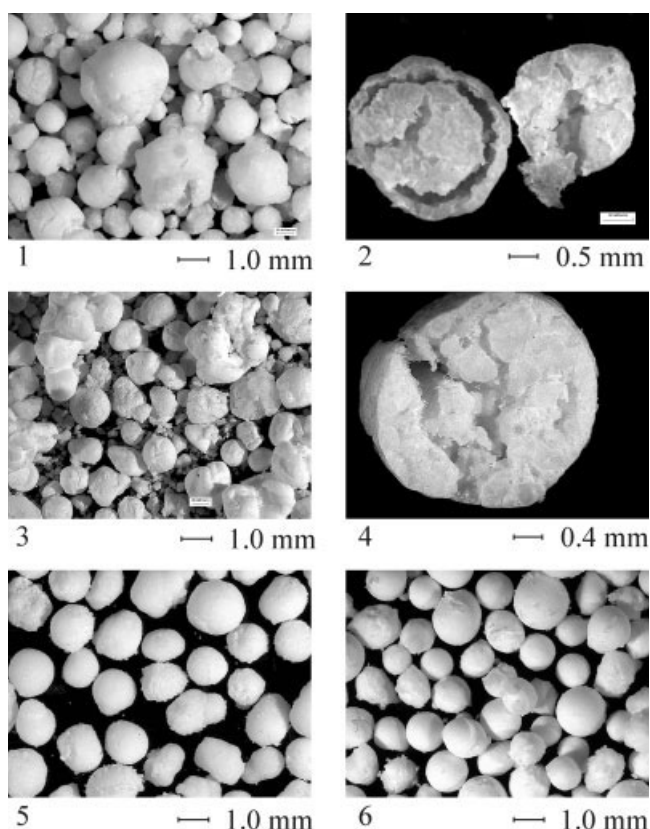


Figure 16 Morphology of homopolymer and copolymer particles obtained with catalyst C, 1. homopolymer surface, neat catalyst without hydrogen, 2. homopolymer section, as above, 3. homopolymer surface, neat catalyst without hydrogen and hydrogen injection after 20 min, 4. homopolymer section, as above, 5. homopolymer surface, prepolymerized catalyst with hydrogen, 6. copolymer surface, neat catalyst with hydrogen.

after the first peak and to completely disintegrated after the second peak (Fig. 15). Thus, at the end of the polymerization, the polymer consists of both exploded grains and fine fragments, with the absence of any spherical particles. In the absence of hydrogen the polymerization rate is substantially lower and the relevant kinetic profile looks more regular. On the other hand, also in this case a sudden rise in polymerization rate can be observed (Fig. 13). It is important to point out that with catalyst C the morphology of the polymer particles obtained in the absence of hydrogen is less regular than that obtained with catalyst B under the same conditions and, in particular, often shows the presence of broken particles and a distinct crust at their surface (Fig. 16). Homopolymerization experiments performed in the presence of hydrogen following procatalyst prepolymerization with propylene, show a decrease in polymerization rate with respect to the plain procatalyst; this is mainly due to the absence of the secondary peaks observed in the corresponding runs performed with the neat catalyst (Fig. 13). The morphology of the resulting polymer particles is

substantially better even than that obtained with the neat catalyst in the absence of hydrogen (Fig. 16).

As for the differences in copolymerization and homopolymerization, it can be observed that, in the absence of hydrogen, copolymerization rate is considerably higher than homopolymerization rate. In the presence of hydrogen, homopolymerization rate can exceed copolymerization rate, especially during the pseudostationary state (compare Figs. 13 and 14). The morphology of copolymer particles looks quite regular even in the presence of hydrogen (Fig. 16).

DISCUSSION

It is known that homo and copolymerization of ethylene over both unsupported and $MgCl_2$ -supported catalysts, like those we have used throughout our experimentation, is rather complex because of the concurrence and superimposition of several chemical and physical phenomena. These include, e.g., the plurality of active centers and their evolution, usually deactivation, in time; the nature of the growing polymer (crystallinity, permeability etc.) and, finally, the nature of the solid catalyst component (porosity, friability etc.) and of the cocatalyst (reducing power, diffusivity etc.). In particular, polymerization kinetics can result from the competition between the chemical deactivation and the physical activation of the active species. Usually, in the absence of mass transfer limitations the kinetic profiles are characterized by a decay-type profile that reflects the intrinsic instability of the active centers. The kinetic profiles tend to switch from a decay-type (usually found in copolymerization) to a build-up type (usually found in homopolymerization) as the mass transfer phenomena become more and more important. In general, our copolymerization experiments, using 1-butene as comonomer, are in agreement with the results and conclusions reported in the literature: copolymerization rate is considerably higher (in the absence of hydrogen) than homopolymerization rate and the relevant kinetic profiles are characterized by a very rapid build-up followed by a decay period (Figs. 1, 2, 6, 7, 13, 14). These kinetic features are not unexpected and have already been reported and rationalized by many authors.¹⁻¹³ For instance, according to Ray's simulations,²⁴ the reduction in polymer crystallinity brought about by the incorporation of the monomer can increase both microparticle diffusivity (by an order of magnitude) and monomer solubility (by a factor of 4). For the typical experiments reported in this work, the crystallinity (DSC) of the nascent polymer particles drops from 72 to 47% passing from homopolymers to copolymers. Thus, in this case ethylene, due to the reduced crystallinity of the nascent polymer, has easy and

almost immediate access even to the innermost active centers. In addition, Tait's results¹⁰ demonstrate that the increase of copolymerization versus homopolymerization rate is due to an increase of the concentration of active centers. Thus the entire potential working surface of the procatalyst is active since the beginning of the polymerization and the relevant kinetic profile is dominated by the intrinsic instability of the active centers. Also, the polymer particles grow in spherical shape with no internal voids. All these experimental evidences indicate that in our case copolymerization is not limited by mass transfer limitations, the procatalyst is fully accessible to the monomer and the relevant polymer particles likely grow according to the "multigrain" mechanism proposed by Harmon Ray et al.²⁵ (with the proviso that the polymer particle can be made of subglobules that in turn consist of microglobular clusters). Evidence of diffusion limitation in copolymerization has been reported, however, in ethylene/1-hexene copolymerizations carried out with silica supported metallocenes.^{26,27}

Again in agreement with Tait¹⁰ we found that the copolymerization rate versus comonomer concentration tends first to increase and then to decrease. This would indicate that the physically driven rate enhancing effect resulting from the comonomer incorporation and thus the increase of polymer permeability tends to be counterbalanced by the reduced intrinsic insertion rate of the comonomer in the growing chain.

It is known that prepolymerization of the procatalyst with propylene or higher olefin has usually a considerable rate enhancement effect in ethylene homopolymerization.^{9,10} The rate enhancement effects brought about by alpha olefin-based prepolymers have been investigated in depth by Tait et al.¹⁰ with both TiCl_3 and $\text{MgCl}_2/\text{TiCl}_4$ catalyst systems. Based on experimental evidence including both kinetic profiles and determination of the concentration of active centers, the authors conclude that, among the possible effects, physical disintegration of the catalyst particles plays the major role and is the major cause for the rate enhancement phenomenon.

With the catalyst we have investigated, it is interesting to note that prepolymerization with propylene generally tends to slow down copolymerization rate, whereas it can either enhance or decrease homopolymerization rate (see below). In any case, prepolymerization leads to a considerable improvement of the morphology of the growing polymer particles. This can be rationalized assuming the following main roles for the prepolymer:

Formation of a thin polymer shell around the microparticles that make up the procatalyst,

thus preventing its catastrophic breakage, and at the same time promoting its controlled disintegration and thus the exposure of new active centers. It is worth noting that when the prepolymer is isotactic polypropylene, the prepolymer cage is generally more crystalline than a typical ethylene-1-butene copolymer. Following these assumptions and based on our experimental results, we can conclude that, whereas in any case prepolymerization with polypropylene has a beneficial effect on the morphological stability of the growing particles, it can have, exactly for the same reason, a rate-decreasing effect on polymerization rate. In the case of copolymerization, prepolymerization with propylene generally causes a decrease in polymerization rate (Figs. 2 and 7). This indicates that the predisintegration based rate enhancing effect is not operative: the possible diffusion limitations have been already *solved* by the reduced copolymer crystallinity, there is no need to prefragment the procatalyst particle since it is already fully accessible to the monomers. On the other hand the propylene prepolymer forms around the active centers a sort of barrier which is more crystalline and thus less permeable than the shell formed by the copolymer. As a consequence, prepolymerization with propylene has the net effect of causing some diffusion limitations for the monomers and thus decreasing the polymerization rate. As we will see later on, the effect of prepolymerization is more complex when the polymerization is severely controlled by mass transfer limitations and other physical complications, as is the case of homopolymerization, especially with catalysts B and C.

In short, copolymerization experiments show little novelty with respect to what already reported in the literature.

More peculiar and intriguing are the homopolymerization experiments, in particular those performed with catalysts B and C.

Generally in these cases homopolymerization is controlled by mass transfer limitations and seems to take place according to the stepwise polymer particle growth mechanism proposed by Chiovetta's¹⁸⁻²⁰ and Fink's groups.²¹⁻²³ A first indication of this mode of growth is represented by the presence of internal voids and, in some instances, surface shells in the polymer particles (Figs. 5, 9, and 16). This is still in agreement with what is described in the literature but we have observed some intriguing phenomena that have never been reported before, at least to the best of our knowledge. These include both peculiarities in kinetic profiles as well as striking morpholog-

ical and kinetic effects brought about by the presence of hydrogen.

Whereas with catalyst A the homopolymerization kinetics are similar to those usually reported in the literature, and the relevant profile is only slightly affected by hydrogen (Fig. 1), with catalysts B and C the homopolymerization rates are peculiar in that the relevant profiles exhibit some distinct features that in turn are strongly affected by the presence or absence of hydrogen. It is interesting to note that the presence of hydrogen tends to increase the homopolymerization rate, especially during the pseudostationary period, with all the neat versions of the procatalysts we have studied, but in this case both catalysts B and C exhibit a quite irregular kinetic profile, characterized by the occurrence of one (catalyst B) or more (catalyst C) secondary peaks as polymerization proceeds (Figs. 6 and 13, respectively). The presence of a secondary peak after the main initial peak was already observed by Han-Adebekun et al.²⁸ during ethylene polymerization with $\text{MgCl}_2/\text{TiCl}_4$ catalysts and was attributed to a change of the oxidation state of titanium atoms. Also, whereas the macromorphology of the growing particles obtained with catalyst A is only slightly worsened by hydrogen (Fig. 3), using catalysts B and C it deteriorates (Figs. 8 and 15, respectively) concurrently with peaks in the polymerization rate. Again, we found that the addition of hydrogen tends to deactivate the polymerization, also when the hydrogen injection is performed during the course of polymerization, in all cases where the morphology of the growing particles is preserved. This means that with the catalysts we have used, in the absence of any morphological factors, hydrogen has an intrinsic and general deactivating effect, likely chemical in nature, even though the relevant mechanism is unknown. Actually, in contrast with propylene polymerization over $\text{MgCl}_2/\text{TiCl}_4$ systems, where the effects and activating effect of hydrogen (reactivation of dormant centers derived from 2,1 monomer insertion) are well documented and understood,^{29–32} in ethylene polymerization both the effects and mechanism of action of hydrogen are still controversial and unclear.³³ In fact, hydrogen can have either negligible effect, or can increase or decrease the polymerization rate of ethylene with catalysts based on Ti-halides supported on MgCl_2 or its precursors. With the same catalyst, hydrogen can also slightly increase and then decrease polymerization rate. The hydrogen effect has been explained taking into account both chemical and physical factors. Among the chemical factors one can cite^{9,33} are slow addition of the monomer to the Ti—H bond, competition with the monomer for adsorption at the active centers or, according to Kissin, formation of dormant β -agostic stabilized Ti—CH₂—CH₃ species upon addition of the first ethylene unit to the Ti—H

centers.^{12,13} Among the physical factors, only the activating role of hydrogen is taken into consideration and, according to Marques et al.,⁶ it might be due to the lowering of polymer molecular weight resulting thus in a better access of the monomer to the active centers. We have no elements to discuss the mechanism by which hydrogen slows down polymerization rate but would like to propose an alternative mechanism which explains and is consistent with both the activating effect of hydrogen and the presence of one or more secondary peaks in the irregular kinetic profiles obtained with catalysts B and C. The experimental evidence achieved with catalysts B and C favors a morphology-driven activating mechanism by hydrogen. In particular, the presence of hydrogen brings about a disintegration of the growing polymer particles and thus the exposition of additional active centers. The phenomenon is similar to that promoted by an effective prepolymerization but with a substantial difference: it takes place via a random and catastrophic breakage instead of a controlled disintegration of the polymer particles so that they lose their integrity and original spherical shape (incidentally, this accounts for the fact that the relevant kinetic profiles are not so well reproducible from the quantitative standpoint). Also the slight rate-enhancement effect of hydrogen with catalyst A can be explained based on the same principle: slight worsening of polymer particle morphology with the presence of more fines than without hydrogen. When the morphology of the growing particles is preserved, as is the case of copolymerization in general and of homopolymerization with prepolymerized procatalysts in particular, the deactivating effect of hydrogen prevails. Only when the morphology of the growing polymer particles is sufficiently deteriorated does the physically-driven activating effect of hydrogen exceed its chemically-driven deactivating effect. This rate-enhancing phenomenon apparently reflects the degree to which the particle morphology is deteriorated: only slightly with catalyst A but considerably with both catalysts B and C. This also explains why, in the presence of hydrogen, prepolymerization with propylene can decrease homopolymerization rate. It is true that prepolymerization promotes the controlled disintegration of the procatalyst but it is also true that it prevents the catastrophic breakage of the growing polymer/procatalyst particles and thus also the associated rate enhancing effects. Apparently, the prepolymerization conditions we have used are not able to expose all the available active centers of our procatalysts, thus the physically-driven rate enhancement brought about by the prepolymer is far less spectacular than that observed, e.g., by Tait¹⁰ or Soares⁹ and is less effective than the catastrophic breakage of the particles during polymer growth. On the other hand,

there is no doubt that, when an activation of the catalyst occurs, it takes place via a physically driven mechanism.

Before discussing the possible mechanism by which hydrogen promotes, in some instances, an uncontrolled and catastrophic breakage of the polymer particle, it is worth commenting on the homopolymerization experiments performed without hydrogen and, in particular, the kinetic profiles observed using catalyst B. As already mentioned they are fairly reproducible and, after a very rapid initial peak, invariably assume a quite regular staircase-like pattern which lasts for several hours (Fig. 6); in addition the resulting polymer particles maintain their original shape during the whole course of polymerization, even though they show the presence of internal cracks and surface shells (Fig. 9). This behavior is consistent with, and strongly supports, a layer-by-layer mode of polymer particle growth which is in agreement with the mechanisms proposed by Chiovetta's and Fink's groups: at the very beginning of the reaction, the monomer reacts at the available catalyst surface forming a thin, highly crystalline polymer layer which acts as a diffusion barrier for the monomer. The very fast initial peak is thus followed by an induction period of relatively low activity. As the reaction goes on, the hydraulic forces generated by the growing polymer are able to fragment the first shell and, once a critical volume is reached, the next shell is made available to the monomer, and so on. This occurs in the correspondence with a critical volume per each shell and is associated with a critical time. Each shell contributes to the reaction independently, but only from the moment of its activation. Thus, the whole kinetic profile results from the cumulative contribution of each shell involved. As a result, the reaction rate reaches a maximum value when all shells are available, e.g., when the growing particle is completely fragmented so that all its active centers are exposed to the monomer. In the absence of catalyst deactivation, this corresponds to a stationary polymerization regime. This hypothesis is supported by the experimental evidence that, by increasing the absolute polymerization rate, either via increase of the monomer partial pressure or via removal of the external donor, the steps in the kinetic profile appear earlier as polymerization rate increases (Fig. 10). This indicates that the key factor for the occurrence of these steps is hardly represented by chemical reasons, as suggested by Han-Adebekun et al.²⁸ to explain the emergence of secondary peaks during ethylene homopolymerization with $\text{MgCl}_2/\text{TiCl}_4$ catalysts. In particular, in order for a given particle shell to become active it is necessary that the preceding shell reaches a given critical volume, e.g., a critical mileage in terms of mass of polymer per mass of cata-

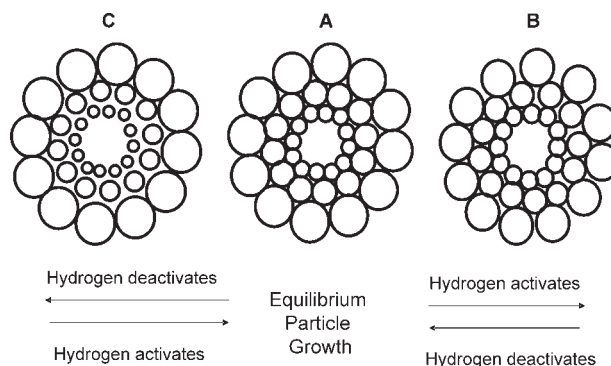


Figure 17 Schematic model of layer-by-layer polymer growth and possible hydrogen effect, A. equilibrium growth of polymer shells, B. the most internal shell grows faster than its equilibrium value, C. the most internal shell grows slower than its equilibrium value.

lyst, so as to generate hydraulic forces sufficiently high to fragment the relevant procatalyst substrate. It is clear that the time to reach this critical volume decreases with increasing polymerization rate. As a result, the critical parameter which dominates this phenomenon is not polymerization time but rather the cumulative catalyst productivity. Also, the height of the steps increases with polymerization rate and once again this is in agreement with the proposed mechanism. Actually, if we assume that the height of a given step reflects the rate R contributed by the relevant catalyst shell via the well known equation $R = K_p C_p [M]$, it is clear that it should increase either as monomer concentration $[M]$ increases (experiment with increased monomer pressure) or the number of active centers C_p increases (experiment without external donor), as experimentally found.

It is interesting to note that the theoretical treatment by Fink et al.²² concerning their stepwise fragmentation model requires the presence of steps in the "numerical" kinetic profiles, even though having different shape with respect to our experimental steps. In addition, in our case the controlled catalyst fragmentation and thus the build-up period is a relatively slow process that continues for several hours.

To the best of our knowledge, the kinetic profiles we have observed constitute the first experimental kinetic evidence for the stepwise mechanism of polymer growth with shell-by-shell fragmentation.

As for the mechanism by which the presence of hydrogen can affect the morphology of the growing polymer catalyst particles, we can reason as follows:

Suppose that the polymerization suffers from mass transfer limitations and the polymer particle growth occurs layer-by-layer according to the following limiting and schematic cases (Fig. 17):

- A. Equilibrium concerted growth of the various polymer shells

- B. Growth of the inner shells faster than the equilibrium condition leading, e.g., to the formation of surface threads or cracks.
- C. Growth of the inner shells slower than the equilibrium conditions, leading to the formation of onion-like morphologies and/or internal void/cracks.

Of course, in both cases (B) and (C) the morphology of the growing polymer spheres is less perfect than in case (A) and they are prone to the formation of broken particles or fines due to spontaneous explosion or implosion or via collisions with themselves and the reactor walls. In the presence of hydrogen, due to its higher diffusivity with respect to the monomer, it is reasonable to assume that the hydrogen to ethylene ratio is higher in the bulk than at the surface of the growing particle. If hydrogen plays no other kinetic effect than its chain transfer role, its presence has no impact on polymer particle morphology. In contrast, when hydrogen has either an activating effect or a deactivating effect, its presence can either worsen or alleviate the situation from the morphology standpoint, depending on the specific modes of polymer growth. When this takes place according to mode (A), hydrogen will in any case tend to deteriorate the particle morphology, leading to cases (B) or (C) when it activates or deactivates the reaction, respectively. On the other hand, starting from cases (B) or (C), hydrogen tends to alleviate the situation when it has a deactivating effect or an activating effect, respectively, since both polymer growth modes tend to approach the equilibrium situation. Needless to say, the polymer particle morphology will be further worsened when, starting from the mentioned cases, hydrogen behaves in the opposite way.

Our experimental results demonstrate that hydrogen can have two effects that are in competition with each other: a chemical deactivating effect and a physical activating effect. The former is always present whereas the latter is only and always associated with a catastrophic breakage of the growing particles. Based on the morphology of the resulting homopolymer particles, the three procatalysts tested likely behave as follows: in the absence of hydrogen, procatalysts A and B promote a polymer particle growth according to the models (A) (compact particles with the presence of internal voids) and (C) (presence of both a surface crust and internal voids/cracks) of Figure 17, respectively, (Figs. 5 and 9). Thus, the presence of hydrogen leads only to a slight worsening of particle morphology for procatalyst A (Fig. 3), whereas it brings about a considerable morphological deterioration for procatalyst B, with the formation of broken spheres and fines (Fig. 8). As for catalyst C, even in the absence of hydrogen the morphology of the resulting polymer particles is

considerably deteriorated, with the presence of broken particles which, in addition, show the presence of distinct surface crust (Fig. 16). Thus, in this case polymer particle growth apparently occurs according to a sort of scheme (C) worse and it only remains for hydrogen to worsen an already very bad morphological situation. In summary, the rate-enhancement effect of hydrogen, when operative, occurs via a physical and indirect way: first it leads to a deterioration of the morphology of the growing particles, resulting in their catastrophic breakage, either spontaneous or via collisions with themselves and with the reactor walls; then, the new active centers exposed by this phenomenon promote a sudden and significant increase of the polymerization rate.

Based on the morphological characteristics of the procatalysts tested (Table 1 and Diagram 1), we must conclude that their kinetic features and the morphology of the resulting polymer particles are more dominated by the distribution of the size of pores rather than the absolute values of their porosity. Within the ranges investigated and at the same level of porosity (about $0.55 \text{ cm}^3/\text{g}$), pores having radii centered around 50–100 nm (catalyst A) are apparently more effective in providing the morphological stability of the growing particles than pores having radii centered in the 20–50 nm range (catalysts B). The morphological situation is even worse in the presence of both lower porosity values ($0.3 \text{ cm}^3/\text{g}$) and pore radii (centered in the 10–20 nm range), as is the case of procatalyst C. This is likely due to an easier and more regular access of the monomer to the catalyst surface through larger pores than through smaller pores. This results in a more homogeneous polymer growth inside the catalyst particle, an easier and more regular fragmentation of the procatalyst during polymer growth, which also means better polymer particle morphology and minimization of those kinetic complications associated to its deterioration with time or, better, productivity. This also accounts well for the fact that, in the absence of the complications brought about by hydrogen and prepolymerization, the differences between co- and homopolymerization rates, both in terms of absolute values and kinetic profiles, are less evident for catalyst A than for catalysts B and C. This means that homopolymerization over procatalyst A is relatively more close to kinetic-control than over procatalysts B and C thanks to a relatively easier fragmentation during polymer growth.

It is worth noting that the above-mentioned staircase profile observed for catalyst B turns into a normal decay profile when, using the same catalyst system, propylene is substituted for ethylene (Figure 11). Likely in this case polymer growth and replication occur under kinetic control without large diffusion limitations and the polymerization profile is

dominated by the intrinsic stability or, better, instability of the active centers. This indicates that, the catalyst nature being the same, the monomer nature (diffusivity to reactivity ratio) can play a key role in defining the polymerization mechanism and the relevant kinetic profile.

CONCLUSIONS

Homo and copolymerization of ethylene with MgCl_2 -supported Ziegler-Natta catalyst systems is really complex because of the occurrence of both chemical and physical factors. This paper likely adds further complications to those already reported and commented in the literature.

Whereas copolymerization kinetics over the catalyst we have investigated follow the normal behavior, homopolymerization kinetics are characterized by a number of peculiarities that, at least to the best of our knowledge, have never reported before. These include some apparently controversial effects connected with both the prepolymerization and the presence of hydrogen, and the irregular or the staircase kinetic profiles observed with some catalysts. In particular, we observed that both prepolymerization and the presence of hydrogen can either increase or decrease polymerization rate.

Based on the experimental evidence, all these phenomena can be rationalized by assuming, as generally accepted, that ethylene homopolymerization is dominated by mass transfer limitations and that polymer particle growth occurs according to a step-by-step mechanism. The presence of hydrogen apparently tends to perturb the regular growth of the particles and thus promotes their catastrophic breakage, with the formation of particle fragments and fines. This accounts well for the irregular kinetic profiles, with the presence of one or more secondary peaks, observed with some catalysts. On the other hand, prepolymerization with propylene promotes a more or less effective and complete controlled disintegration of the procatalyst but tends to preserve the integrity of the growing polymer/catalyst particles. Now, any kind of factor that brings about a disintegration, either controlled or catastrophic of the growing polymer/procatalyst particles is also able to increase the effective working surface of the system and thus to increase the number of the active centers. Our experimental results indicate that prepolymerization is generally effective in enhancing the initial homopolymerization (not copolymerization) rate, but in the presence of hydrogen it also tends to decrease or, better, not to increase the pseudostationary rate just because it prevents the catastrophic breakage of the polymer particles during growth. On the other hand, the activating effect of hydrogen is only and always associated with a catastrophic breakage of the growing particles

(when the particle morphology is preserved or already deteriorated it has a deactivating effect). Thus, the two morphology-related rate enhancing factors can be in competition with each other: apparently when both are operative, the catastrophic breakage effect prevails over the controlled disintegration effect. The fact that prepolymerization tends to slow down the copolymerization rate can be explained by assuming that, in this case, the mass transfer limitations for the monomer to the active centers have been resolved by the reduced crystallinity and increased permeability of the copolymer, and there is no need of catalyst predisintegration. Thus, the only effect of the prepolymer (isotactic polypropylene) is that of forming a thin crystalline polymer layer around the active centers which serves as diffusion barrier for the monomer.

As for the mentioned peculiarities in the kinetics of homopolymerization, the irregular profiles have been already explained in terms of a random breakage of the growing particles brought about by the presence of hydrogen. The regular staircase profile observed in the absence of hydrogen with one of the catalysts investigated is in turn a clear indication of a polymer particle growth layer-by-layer according to the well known Laurence-Chiovetta's model and, indeed, represent the first experimental kinetic evidence of the relevant mechanism, at least to the best of our knowledge.

Another important aspect of this investigation is the dependence of the morphological stability of the growing polymer particles on the nature of the parent procatalyst. Both copolymerization and homopolymerization preceded by prepolymerization lead in any case to polymer particles that replicate the spherical shape of the original catalyst particles. However, in the absence of prepolymerization, the morphological stability of the polymer particles as well as polymerization kinetics is largely dominated by the morphological features of the procatalyst. With catalyst A, the polymer particles tend to replicate the spherical shape of the procatalyst both in the absence and presence of hydrogen, with catalyst B the spherical shape is only preserved in the absence of hydrogen and, finally, with catalyst C, the morphology is substantially deteriorated in both cases. Based on the characteristics of the procatalysts investigated, we must conclude that these phenomena are more related to differences in the distribution of the size of pores than to differences in the absolute porosity values of the original procatalyst particles. It is worth noting that, using the same procatalyst B, the polymerization reaction switches from mass transfer control to kinetic control when ethylene is replaced with a monomer having lower reactivity to diffusivity ratio, like propylene.

In summary, polymerization kinetics and polymer particle morphology are strongly affected by the na-

ture of the monomer, the nature of the polymer and the nature of the catalyst: whereas copolymerization kinetics are mainly dominated by the intrinsic stability of active centers, homopolymerization kinetics, due to the high reactivity to diffusivity ratio of ethylene, is also controlled by mass transfer limitations and thus complicated by physical factors like crystallinity of the growing polymer particles and the mechanical features (mainly friability) of the procatalyst particles. In this respect, our results indicate that, at the same degree of porosity, the presence of pores having relatively large size guarantees a more regular fragmentation of the procatalyst particle during polymer particle growth and thus a better polymer particle morphology.

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