

# Particle Control of Ziegler–Natta Catalysts Based on $\text{TiCl}_3$ for Propylene Polymerization. Effect of Prepolymerization

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## SYNOPSIS

Prepolymerizations employing an extremely high stereospecific and high active catalyst based on  $\text{TiCl}_3$  modified by di-*n*-butyl ether (DBE) were carried out with different monomers (styrene, propylene, hexene-1, cyclopentadiene). The influence of prepolymerization on the morphology of polypropylene obtained with  $\text{TiCl}_3$  catalyst was investigated. The catalyst was synthesized by  $\text{TiCl}_4$  reduction in toluene solution with  $\text{AlEt}_3 \cdot \text{DBE}$  complex. The polymer morphology was evaluated through optical and scanning electron microscopies and polymer bulk density and particle size distribution. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The morphological control of Ziegler–Natta catalysts may result in many advantages concerning the polymerization process and product. There is a new family of high-yield catalysts that is not only very simple to prepare but also produces polymers of controlled particle size. These catalysts show high yield, high isotactic index, and excellent powder morphology (narrow distribution of the particle diameter, high bulk density, high flowability, very low content of fines, etc.).

Many theoretical models have been presented to explain the replication process of the growing polymer particle desired from the Ziegler–Natta catalyst. In the solid core model,<sup>1</sup> a spherical catalyst grain is surrounded by a spherical shell of polymer that has been growing around it. The reactions occur only on the surface of the catalyst granule. The radius of the spherical polymer shell grows with the reaction time.<sup>2</sup> The polymeric core model describes the growing particle as catalyst sites embedded in the polymer. In this model, active centers are set in the solid polymer–catalyst matrix and an outer polymeric coat grows around the inner sphere. This model assumes the flow of catalyst sites with an inner polymeric

core of fixed site concentration and an outer layer with a radial velocity for the growth of the polymer granule.

Catalysts used in industrial production for polyethylene and polypropylene are frequently preactivated by polymerization of a small amount of olefin in the presence of an alkylaluminum compound.<sup>3</sup> As it claimed in some patents,<sup>4,5</sup> such prepolymerization may reduce the catalyst fragmentation and hence improve the polymer morphology. The true nature and mechanism of the prepolymerization step is still not very well elucidated and requires further attention.

The catalyst used in this work was prepared with di-*n*-butyl ether as the internal base. Hence, its solid structure is very porous and consequently breakable.<sup>6</sup> A distinct characteristic of the olefin polymerization process is the rupture of the initial catalyst structure into small fragments. The fragmentation process occurs particularly in the first stages of  $\alpha$ -olefin polymerization because too-fast growth may cause the catalyst “explosion” and prevent a regular replication. The microparticles of catalyst formed by fragmentation become independent grains and this is the main cause of fines formation at the end of the polymerization process. Prepolymerization is normally used in order to grant mechanical stability and to maintain the morphology of catalyst grains. A possible explanation is the prevention of catalyst

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rupture due to a rubber coat shell formed at mild reaction conditions. In addition, the growth of prepolymer can expose occluded catalyst centers, enhancing the catalyst activity.

During the last 4 years, we have been interested in  $\text{TiCl}_3$  catalysts. We have already developed a highly active and stereospecific one for propylene polymerization. It is now our aim to control the morphology of catalyst particles. This article deals with the effects of prepolymerization using different monomers on the propylene polymerization.

## EXPERIMENTAL

The procedures and catalyst synthesis were already reported in an earlier article.<sup>6</sup>

### Prepolymerization

Prepolymerizations were carried out in iso-octane suspension (500 mL) employing 20 mmol of Ti,  $\text{AlEt}_3/\text{Ti}$  mole ratio = 0.2 and different styrene (St)/Ti or cyclopentadiene (Cp)/Ti mole ratios at 30°C for 15 min. The prepolymerization with propylene was carried out at 0.013 bar for 15 min. The prepolymerized catalysts were washed thoroughly with iso-octane and Ti content was determined by colorimetric method. Polymerizations with prepolymerized catalysts with hexene-1 were carried out *in situ*, that is, as soon as the prepolymerization was finished in the same medium.

### Polymerization

All propylene polymerizations were carried out in iso-octane suspension (500 mL) and propylene was continuously supplied under a pressure of 0.133 bar for 1 h at 50°C. At the stated time the monomer feeding was stopped, the polymer slurry degassed to remove unreacted propylene, and the polymer was washed thoroughly with *n*-hexane and dried at 80°C.

### Polymer Characterization

The polymer melting point was determined from the peak of the differential scanning calorimetry (DSC) curve, measured with a Perkin-Elmer (mod. DSC-2) apparatus. DSC measurements were made at a heating rate of 10°C/min. The samples were melted at 205°C. The crystallinity of the polymer was calculated from the heat of fusion values, using the following relation:

$$\text{crystallinity (\%)} = \frac{\Delta H_f \cdot 100}{\Delta H_f^0}$$

where  $\Delta H_f$  is the heat of fusion of the sample, as determined from the DSC curve, and  $\Delta H_f^0$  is the heat of fusion of folded-chain polyolefin crystals (49.8 cal/g for polypropylene).<sup>7</sup>

The morphologies of polypropylene were examined in a scanning electron microscope (SEM) and in an optical one. SEM measurements were scanned with a JEOL apparatus at vacuum of  $10^{-5}$  mmHg and at an accelerating voltage of 25 kV. The samples were prepared by coating with gold. The technique is close to that generally employed in SEM work. A certain number of flakes were deposited on a metallic sample holder. The samples were metal-coated prior to SEM examination. Polymeric particles must be stuck on the sample holder by means of double-sided adhesive tape. Such sample preparation is considered good if polymer flakes are arranged into a monolayer on the surface of the sample holder. One should not try to separate them systematically from one another, which is a very difficult task due to the tendency to agglomeration caused by electrostatic forces.

The particle size distribution was determined by laser diffraction technique (Particle sizer 3600 E type, Malvern Instruments) and by sieving.

## RESULTS AND DISCUSSION

We observed that it is possible to obtain at suitable conditions a catalyst with controlled morphology (spherical shape). The  $\text{TiCl}_3$  catalyst prepared through  $\text{TiCl}_4 \cdot \text{DBE}$  complex in toluene solution was selected due to its better morphology (spherical) for studying the effects of prepolymerization upon it.<sup>6</sup> For a better understanding of the growth mechanism and the morphological control of the polymer obtained with this system, it is important to clarify the influence of monomer type and reaction conditions during the prepolymerization. Therefore, in this work we studied the propylene polymerization using the prepolymerized catalysts and investigated the effects of prepolymerization conditions on polypropylene morphological control. Table I shows the synthesis parameters of prepolymerization and some properties of catalyst and polymers obtained therefrom. In a general way, the prepolymerization modified the polypropylene bulk density, diminishing it. Probably the prepolymerized catalyst grains became more porous than the original one and hence the final polymer particles presented lower bulk density ( $\rho_a$ ). As it noted in Table I, the prepolymerized catalyst with St at monomer/Ti mole ratio of 1.0 produced a polypropylene with the highest bulk density

**Table I** Synthesis Parameters and Characteristics of Polypropylene

Catalyst Number	Monomer <sup>a</sup>	Monomer/Ti Mole Ratio	Ti Content <sup>b</sup>	Bulk Density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	Crystallinity <sup>c</sup> (%)
1	—	—	5.53	0.41	157	32
2	St	1	4.37	0.45	156	33
3	St	10	2.12	0.41	157	33
4	He	0.25	— <sup>d</sup>	0.35	154	21
5	He	0.50	— <sup>d</sup>	0.33	154	23
6	He	2.00	— <sup>e</sup>	0.21	156	14
7	Cp	1.00	5.12	0.34	154	24
8	Cp	2.00	4.75	0.34	156	17
9	Pr	— <sup>f</sup>	4.47	0.36	154	18

<sup>a</sup> Monomer used in the prepolymerization: Cp, cyclopentadiene; He, hexene-1; Pr, propylene; St, styrene.

<sup>b</sup> Determined by calorimetry (mmol Ti/g of catalyst).

<sup>c</sup> Calculated from folded chain polypropylene crystal.

<sup>d</sup> It was not determined that the Ti content and the prepolymerized catalyst was used *in situ*.

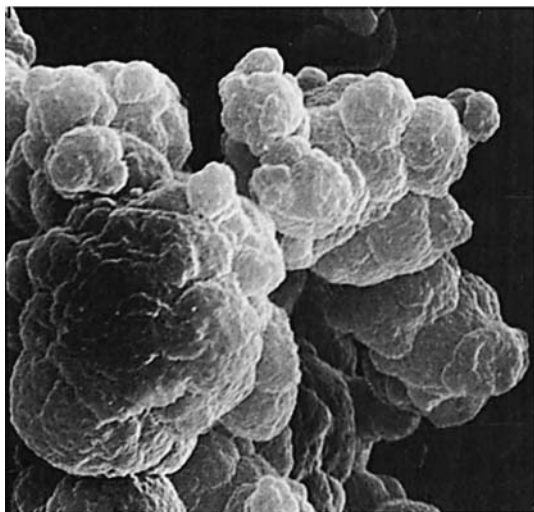
<sup>e</sup> Prepolymer was soluble in iso-octane.

<sup>f</sup> Propylene pressure during the prepolymerization, 0.013 bar.

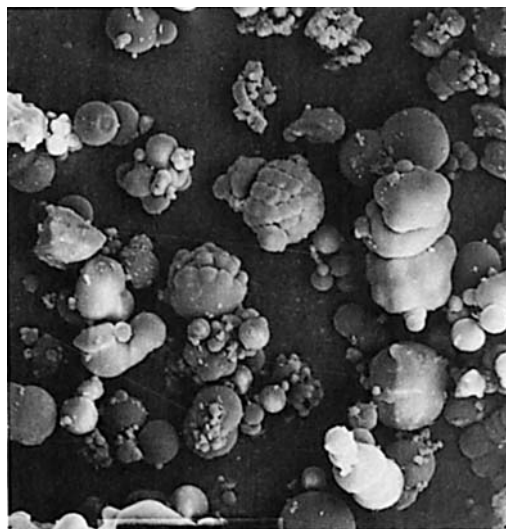
(catalyst #3;  $\rho_a = 0.45 \text{ g/cm}^3$ ). This prepolymer was able to maintain the catalyst structure. Probably the prepolymerized catalysts with hexene (He), Cp, or propylene (Pr) exhibited lower bulk densities due to a higher amorphous phase content. The crystallinities and the melting temperatures of polypropylene obtained from prepolymerized catalysts confirm this assumption. The crystallinity and the melting temperatures of polymers obtained from prepolymerized catalysts with Cp, Pr, or He showed the lowest bulk density values compared to the polymers produced with the nonprepolymerized catalyst and with those prepolymerized with St

(Table I). With the aim of obtaining more information about the change in polymer morphology, SEM was taken on typical polymers (catalysts #1 and #2). The results shown in Figures 1 and 2 indicate the change of the polymer morphology by using prepolymerization. It is possible to observe that the polymer obtained with the prepolymerized catalyst presented agglomerates under the same particle (Fig. 1). Probably the catalyst particles became more porous, enhancing the available catalyst centers.

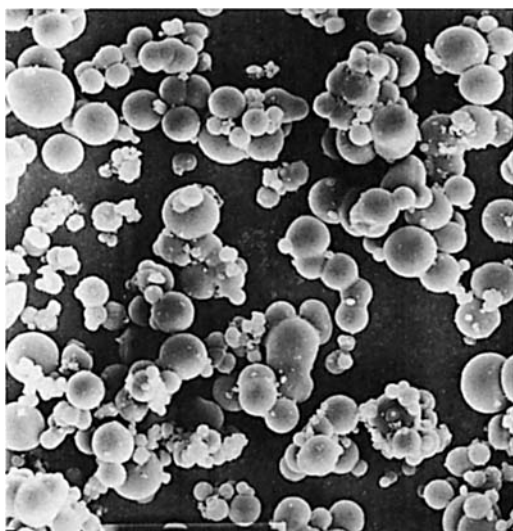
The Ti content decreased when the monomer/Ti mole ratio was increased, indicating the higher



**Figure 1** SEM micrograph of polypropylene particles obtained from nonprepolymerized catalyst prepared at DBE/TiCl<sub>4</sub> mole ratio of 1.50 (4000× magnification).



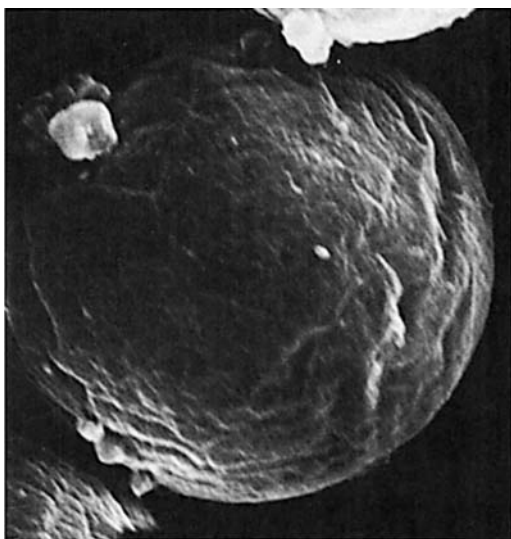
**Figure 2** SEM micrograph of polypropylene particles obtained from prepolymerized catalyst with styrene at monomer/Ti mole ratio of 1.00 (300× magnification).



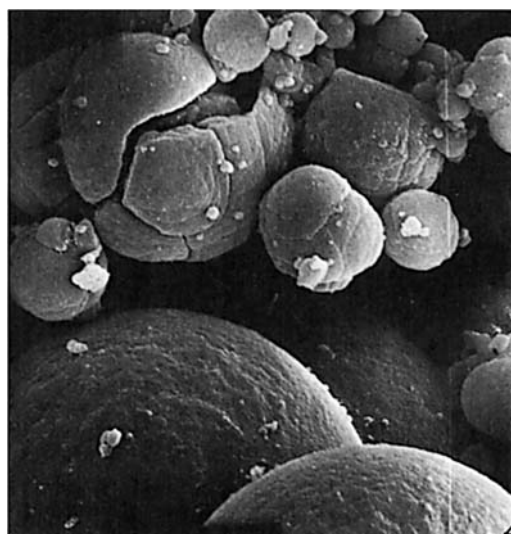
**Figure 3** SEM micrograph of polypropylene particles obtained from prepolymerized catalyst with cyclopentadiene at monomer/Ti mole ratio of 2.00 (200 $\times$  magnification).

monomer incorporation into the prepolymerized catalyst. The Ti contents of the prepolymerized catalysts were lower than the nonprepolymerized one (Table I).

In a general way, the preliminary observations in optical microscopy have shown that the polypropylene obtained with prepolymerized catalysts presented spherical shape. Figure 3 shows an SEM

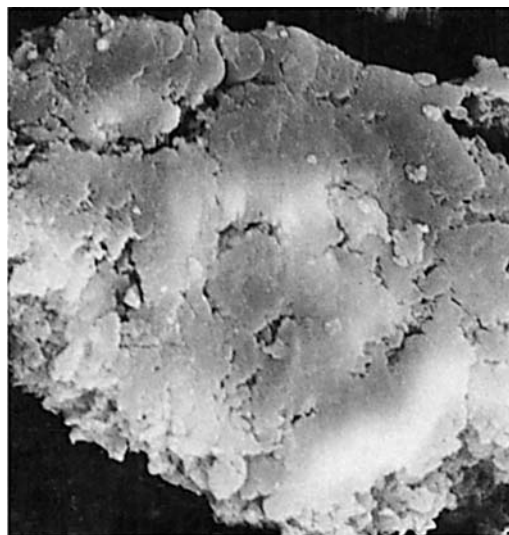


**Figure 4** SEM micrograph of polypropylene particles obtained from prepolymerized catalyst with cyclopentadiene at monomer/Ti mole ratio of 1.00 (2500 $\times$  magnification).



**Figure 5** SEM micrograph of polypropylene particles obtained from prepolymerized catalyst with hexene-1 at monomer/Ti mole ratio of 0.50 (1000 $\times$  magnification).

(140 $\times$  magnification) of the polypropylene grains obtained with prepolymerized catalyst with cyclopentadiene at Cp/Ti mole ratio of 2.0. It can be noted that the polymer particles presented a spherical shape with some particle agglomerations. As it can be seen in Figures 4 and 5, the polymer particles exhibited uniform shapes (spherical) and in some cases the particle fragmentation was observed. It has long been understood that the so-called prepolymerization actually consists of polymerizing a



**Figure 6** SEM micrograph of polypropylene particles obtained from prepolymerized catalyst with hexene-1 at monomer/Ti mole ratio of 2.00 (1000 $\times$  magnification).

**Table II Morphological Parameters of Polypropylene Obtained From Prepolymerized Catalyst**

Sample Number	Prepolymerization Monomer	Monomer/Ti Mole Ratio	Average Particle Size <sup>a</sup> ( $\mu\text{m}$ )	Average Particle Size <sup>b</sup> ( $\mu\text{m}$ )	Average Particle Size <sup>c</sup> ( $\mu\text{m}$ )
1	—	—	63	63	48
2	St	1	54	48	43
3	St	10	59	> 150	41
4	He	0.25	—	—	—
5	He	0.50	92	85	46
6	He	2.00	79	72	38
7	Cp	1.00	73	65	53
8	Cp	2.00	72	70	52
9	Pr	— <sup>d</sup>	105	88	59

<sup>a</sup> Obtained from Malvern apparatus without ultrasound.

<sup>b</sup> Obtained from sieving.

<sup>c</sup> Obtained from Malvern apparatus with ultrasound.

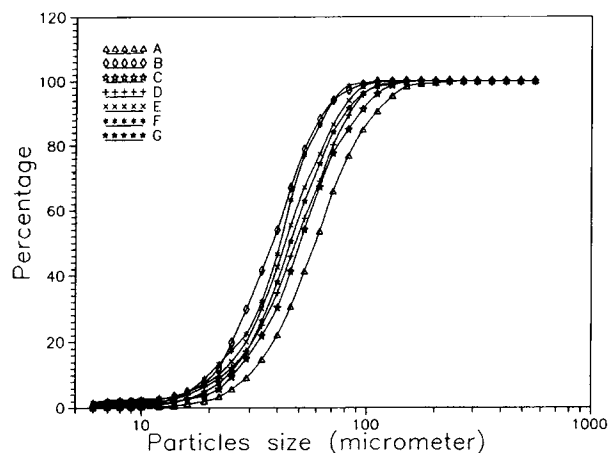
<sup>d</sup> Propylene pressure during the prepolymerization, 0.013 bar.

monomer onto the surface of the catalyst at mild reaction conditions. Employing He as the prepolymerization monomer, which could produce a soluble polymer in hydrocarbons (like iso-octane used as diluent in the prepolymerization), it was observed that a thin red-violet dispersion was formed soon after the introduction of  $\text{TiCl}_3$  catalyst and He. It was also observed that this dispersion was stable and did not separate into solid and liquid phases. Thus, contacting the  $\text{TiCl}_3/\text{AlEt}_3$  system with a small amount of He, a stable catalyst was obtained for using *in situ*. Figure 6 shows an SEM picture of polypropylene flake produced by the prepolymerized catalyst with He at a monomer/Ti mole ratio of 2.0. It was observed that the particle presented irregular form with many fragments and pores. This result can be attributed to the higher reactivity of He compared to Cp or St.

The analysis of polymer particle size was carried out by two methods: sieving and laser diffraction techniques (using Malvern apparatus). Because the particle size distribution is very difficult to determine because of the tendency of the flakes to agglomerate by the electrostatic forces, two methods of analysis were employed in order to permit a better understanding of the results. Table II shows that the results of sieving for average particle size are intermediate between the values obtained from the Malvern equipment with and without employing ultrasound. These results reveal that the shaking speed employed during the sieving was not enough to separate the agglomerated particles. The results from laser diffraction show that the values of average particle size obtained from the Malvern apparatus

employing ultrasound were lower than those obtained without it. The ultrasound was able to better separate the agglomerated flakes. The suitable dispersive liquid used in the Malvern equipment was verified to be ethanol.

Figure 7 shows that the particle size distribution of the polymers obtained by prepolymerized catalysts did not change significantly. Taking these results into consideration, such a decrease of particle fragmentation may be attributed to the prepolymer coat on the catalyst particles. It seems that the prepolymer coat (amorphous phase) improved the catalyst mechanical stability. Indeed, this coat probably prevented the catalyst rupture during the Pr polymerization. In some cases, the activity of prepolymerized catalyst in Pr polymerization was higher



**Figure 7** Particle size distribution curves obtained through Malvern apparatus.

than that of the nonprepolymerized one (catalyst #2, #5, and #9). In those examples, it seems that the prepolymerization was able to expose more active centers on the catalysts.

## CONCLUSIONS

The assumption of the solid core model, which considers that the number of active sites is fixed, was not verified. Some evidences of the enhancement of catalyst activity pointed out this fact. The prepolymer coat appears to expose the occluded catalyst centers. The morphology of polymer particles was maintained and the fragmentation phenomenon was reduced by the use of prepolymerization. The differences in catalyst morphologies and their performances among the prepolymerized catalysts were attributed to the differences on the prepolymerization monomer reactivities.

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