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# The influence of some synthesis parameters on Ziegler-Natta catalyst performance

## 2. Effect on polypropylene morphology

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## ABSTRACT

Catalysts based on $TiCl_3$ modified by di-n-butyl ether (DBE) as internal base were synthesized with the aim to obtain polypropylene particles of controlled morphology. Two routes were used to synthesize the catalysts (System A and System B). In System A, DBE employed as internal base was complexed with $TiCl_4$ and diethylaluminum chloride (DEAC) in iso-octane solution and in System B, DBE was complexed with triethylaluminum (TEA) and $TiCl_4$ in toluene solution. The catalysts were evaluated in propylene polymerization and the polymer morphology was characterized by optical and scanning electron microscopies, bulk density and particle size distribution.

## INTRODUCTION

There is a strong relation between the morphology of polyolefins and the morphology of the Ziegler-Natta catalyst used to produce them since the polymer replicates the catalyst particle (1). Polymer particles with uniform and high standard morphology are requested because they readily fluidize in the reactor and the pelletizing step can be eliminated from the industrial process. In addition, controlling the polymer particle size is important since finely grained or coarsely may be desired depending on the application.

During the formation of the polymer, the $TiCl_3$ particle becomes dispersed throughout the polymer particle (2). The architecture of the $TiCl_3$ particle is largely determined by the method used for its synthesis (3). Secondary $TiCl_3$ particles formed by reaction of $TiCl_4$ with aluminum alkyls can be very large (20 to 40 μm) but they are in fact comprised of many smaller primary particles, about 0.01 to 0.1 μm diameters (2,4).

A peculiar characteristic of the olefin polymerization process is the fracture of the initial catalyst particles into small fragments, with dimensions thousands of times smaller than the initial size. This process is particularly critical in the first stages of α-olefin polymerization because a too-fast growth particles could cause the catalyst "explosion" and hence prevent regular replication (5-7).
Process conditions have an specially important effect on particle

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morphology during the initial stages of polymerization. The polymer bulk density decreases with increasing of operating temperature. The combination of high temperature and low pressure results in lower polymer bulk density (8). Kim and Woo (9) have observed no change in the shape of particle size distributions with temperature although a decrease in bulk density with increasing temperature was observed. It was suggested that the decrease in bulk density was provoked by the increase of voids within the particles.

Under appropriate conditions of catalyst preparation and polymerization, uniformly sized, compact polymer particles can be obtained, having the desired size and shape, since they reproduce the original shape of the catalyst particle.

During the last three years, we have been interested in $TiCl_3$ catalysts. In a previous paper (10), the role of di-n-butyl ether (DBE) and the type of solvent employed in catalyst synthesis for propylene polymerization was studied. It was observed that the polymer morphology and catalyst activity was strongly influenced by the chosen system. In this paper, the polymer morphology and particle size distribution for the same systems (A and B) are reported.

## EXPERIMENTAL PART

### Catalyst synthesis

The details of synthesis were described in previous papers (10,11).

**System A**
Catalyst was prepared by the $TiCl_4$. DBE complex reduction with $AlClEt_2$ at 5°C in iso-octane solution.

**System B**
Catalyst were prepared by the $TiCl_4$ reduction with $AlEt_3$. DBE complex at -10°C in toluene solution.

### Propylene polymerization

All propylene polymerizations were carried out in iso-octane syspension (500 ml) and propylene was continuously supplied under a pressure of 100 mmHg for one hour 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.

The morphologies of polypropylene were examined by scanning electron microscopy (SEM) and by optical microscopy. SEM measurements were scanned with a Jeol apparatus at $10^{-5}$ mmHg and at an accelerating voltage of 25 kV. The samples were prepared by coating with gold. This technique is similar to that generally used in SEM work. A certain number of flakes was deposited on a metallic sample holder. The whole preparation was metal-coated prior to introduction into the SEM. Polymeric particles must be placed on the sample holder by means of double-sided adhesive tape. Sample preparation was considered satisfactory when the polymer flakes were arranged into a monolayer on the surface of the sample holder. The flakes should not be separated manually because of agglomeration caused by electrostatic forces.

The particle size distribution was determined through laser diffraction by employing Particle sizer 3600 E type - Malvern Instruments and by sieving.

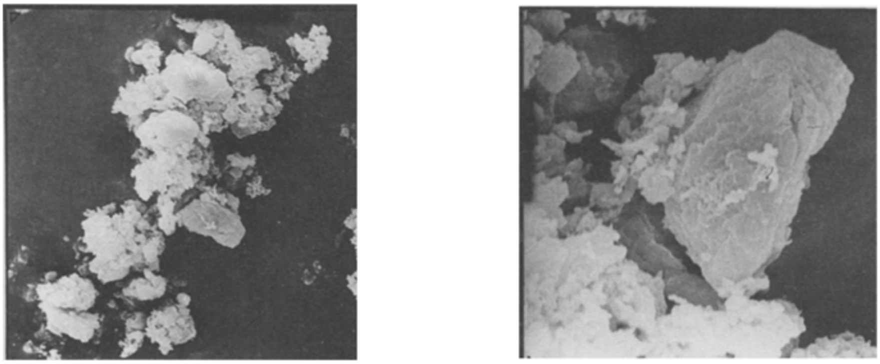
## RESULTS AND DISCUSSION

It is well known that the use of electron-donors in $TiCl_3$ catalyst synthesis promotes the formation of porous structures and defective crystals. This way $\delta$-$TiCl_3$ crystals that exhibit better catalyst performance can be produced than the other forms of $TiCl_3$ ($\alpha$-, $\beta$-, and $\gamma$-$TiCl_3$) (11).

A porous structure yields more active centers enhancing catalyst activity, however, the catalyst particles become fragile. Friability of catalyst grains is responsible for uncontrolled fragmentation and hence, for fines and heterogeneous particles at the end of the polymerization (7). We have noted that the use of DBE and the choice of the solvent used in catalyst synthesis have a strong influence on the catalyst structure and performance. This paper deals with the effects of these chemicals on polymer morphology obtained from $TiCl_3$-based catalysts. The following results of catalyst performance were used together with previously reported results for a comprehensive discussion of the differences between the two systems (A and B) (11-13).

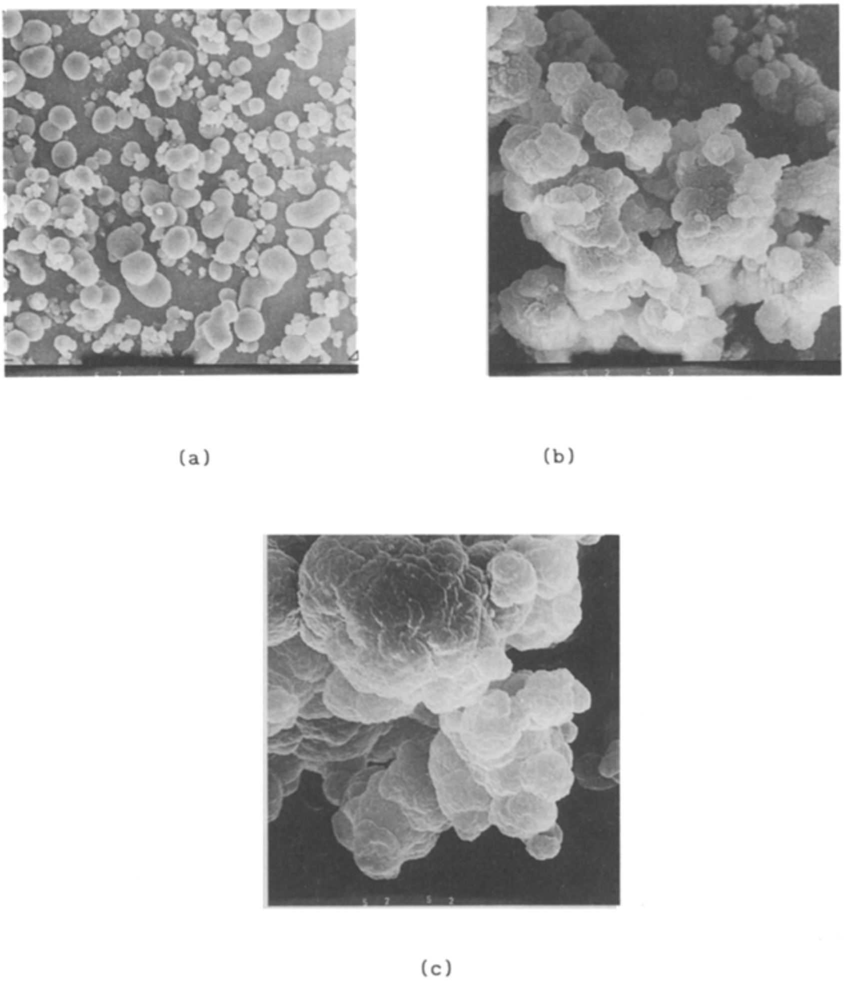
The difference on polymer morphologies due to the use of system A or B cannot be due to the employ of different cocatalyst (DEAC and TEA respectively) since TEA as a cocatalyst with system A did not change the polymer morphology.

Figures 1 and 2 depict polypropylene morphologies obtained with system A and B respectively. The SEM micrography of polypropylene particles obtained with system A presents particles of more irregular shape and with more fines then those obtained with system B. Polymer particles obtained with system B are almost spherical and present less fines. Furthermore, the size distribution for the particles produced by system B is narrower. Micrographs 1b and 2c show the peculiar polymer layers which probably are due to replication of the $TiCl_3$ catalyst structures (1) of systems A and B.



(a) (b)

Figure 1 - SEM micrographs of polypropylene particles obtained with catalyst prepared at $DBE/TiCl_4$ mole ratio = 0.67 in iso-octane solution. Polymerization time: 10 min. ($AlClEt$ cocatalyst) Magnification: 1000X (a) and 4000X (b)



(a) (b)

(c)

Figure 2 - SEM micrographs of polypropylene particles obtained with catalyst prepared in toluene solution: (a) DBE/$TiCl_4$ = 0.8; catalyst activity = 572 gPP/gTi.h; magnification = 200X; (b) DBE/$TiCl_4$ = 0.3; catalyst activity = 157 gPP/gTi.h; magnification = 1000X; (c) DBE/$TiCl_4$ = 1.5; catalyst activity = 377 gPP/gTi.h; magnification = 4000X. For all polymerizations: time = one hour and cocatalyst = $AlEt_3$

The particle size distribution is very difficult to determine due to the tendency of the particles to agglomerate because of electrostatic forces. In this work, the flake agglomeration was diminished by the use of ethanol as dispersive liquid. The agglomeration of polypropylene particles was reduced to a minimum when ultrasound and ethanol were used during the determination of the size distribution by laser diffraction. Figure 3 shows that the particle size distribution of the polymer obtained by system A was wider than that from system B. The more regular forms of polymer particles obtained from system B may be attributed to the more homogeneous catalyst particles formed during catalyst synthesis. It is well known that ethers with short chains such as di-n-butyl ether, are more soluble in aromatic solvents than in aliphatic ones. Thus, because toluene was employed in system B, it formed a more homogeneous system during catalyst synthesis.

The overall morphology of polymer particles including average diameter, size distribution, fine content, shape, bulk density, surface roughness, and porosity is affected by the polymerization rate and rate profile (9). For system B, the size of polymer particles increases slightly with increasing catalytic activity (Figure 3).

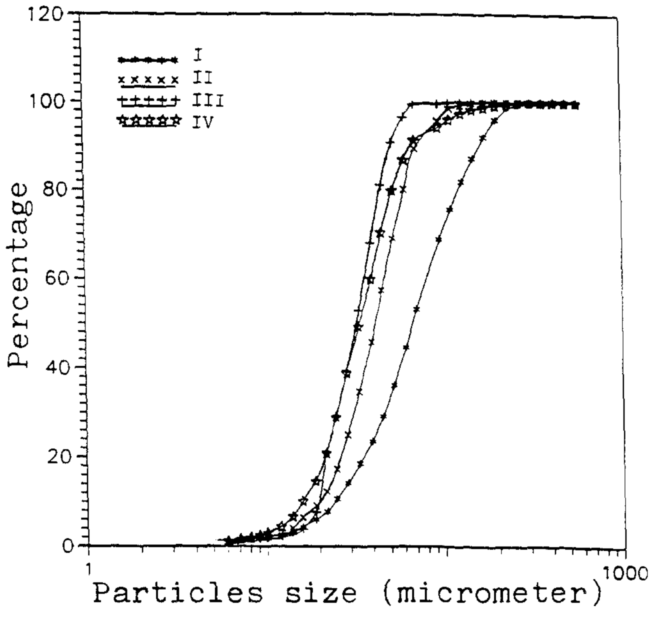


Figure 3 - Particle size distribution curves obtained by laser diffraction. Polypropylene particles obtained with catalyst prepared at DBE/$TiCl_4$ mole ratio = 0.67 in iso-octane; catalyst activity = 137 gPP/gTi.h (I); DBE/$TiCl_4$ mole ratio = 0.8 in toluene, catalyst activity = 572 gPP/gTi.h (II); DBE/$TiCl_4$ mole ratio = 0.4 in toluene, catalyst activity = 201 gPP/gTi.h (III); DBE/$TiCl_4$ mole ratio = 1.5 in toluene, catalyst activity = 377 gPP/gTi.h (IV).

In general, the results of sieving for the determination of particle size distribution are intermediate between the values obtained from laser diffraction without ultrasound and with it. These results show that shaking during sieving was insufficient to separate the agglomerated particles.

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