Investigations of the Initial State Polymerization of Propylene with Ziegler–Natta Catalysts in Slurry

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ABSTRACT: The initial state polymerization of propylene with Ziegler–Natta catalysts has been investigated and discussed at very low polymerization yields under adiabatic industrial prepolymerization conditions in diluted slurry regarding the effects of significant process parameters like monomer pressure, aluminum alkyl, and donor kind and concentration including the morphology of the catalyst/polymer particles formed. A sharp temperature increase in the first minutes of the initial state polymerization is followed by a temperature maximum and a slow decrease. With cocatalyst triethyl aluminum (TEAL), high prepolymerization yields were already achieved at a molar ratio TEAL/Ti of 3.0, remaining about constant until ratios of at least 300. The external donor dicyclopentyl dimethoxy silane leads to higher polymerization yields than the donor cyclohexyl dimethoxymethyl silane in the initial state polymerization too; however, both show a remarkable decreasing effect on polymerization yield above a specific molar ratio donor/Ti obviously correlated with the bulkiness of the alkyl groups. The particle size of the catalyst and the catalyst/prepolymer particles is increasing with polymerization yield until about 22 g PP/g Cat with particles almost perfectly spherical. The particle size distribution is rather broad at lower prepolymerization stages but unifying with lower polymerization rates at higher polymerization times. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 354–359, 2007

Key words: Ziegler–Natta polymerization; catalysts; poly(propylene); morphology; adiabatic initial state polymerization

INTRODUCTION

Despite an outstanding effort in scientific and technological development of propylene polymerization processes based on metallocenes of group 4 transition metals as catalysts in coordination polymerization in the last decades, conventional slurry polymerization processes based on magnesium chloride supported titanium tetrachloride as Ziegler–Natta catalysts have maintained a strong position in commercial processes for standard polypropylene grades.[1,2] One reason for this position is the advantageously defined catalyst/polymer particle formation and the subsequent defined fragmentation and growth of these particles in the heterogeneous polymerization reaction.

Since the first catalyst/polymer particle fragmentation, predetermining the morphology of the resulting polymer powder essential for the following processing of the low density powder to higher density polypropylene pellets by extrusion, is already completed in the initial state of the polymerization reaction at polymerization yields lower than about 20–30 g polypropylene/gram of catalyst, much attention has been paid to this initial state polymerization or prepolymerization phase recently. To ensure thermally controlled initial state polymerizations, the effect of the ultra low-yield slurry prepolymerization of hexene followed by a liquid propylene polymerization by Ziegler–Natta catalysts on kinetics and morphology has been investigated.[3] Observing the fragmentation process in the initial slurry polymerization of propylene in hexane by Ziegler–Natta catalysts it was found that this process is controlled by the formation of a protective polymer layer around the fragmented catalyst particles preventing these particles from disintegrating. During the formation of this polymer layer the polymerization rate is high, decreases and reaches a constant activity at low polymerization yields of 2–3 g polypropylene/gram of catalyst at its completion, probably controlled by the monomer diffusion rate through the polymer layer.[4] The incorporation of the comonomer ethylene does not change the general catalyst fragmentation process, but slows it down, which is probably the result of a higher mobility of the propylene-ethylene copolymer molecules at the active polymerization sites.[5]

However, because the effects of significant process parameters like monomer pressure, aluminum alkyl, and donor kind and concentration have not been investigated on the initial state polymerization of

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propylene with Ziegler–Natta catalysts at low polymerization yields under adiabatic industrial prepolymerization conditions in slurry in detail yet, this has been performed in this study, including the morphology of the catalyst/polymer particles formed.

EXPERIMENTAL

Materials

Triethyl aluminum (TEAL) solution in hexane as a cocatalyst was purchased from Akzo Nobel Corporation and propylene as the monomer from Linde AG. Hexane obtained from Merck KgaA was used after additional drying over molecular sieves.

The catalyst used was a commercially available magnesium chloride supported titanium tetrachloride Ziegler–Natta catalyst with a titanium content of 2.3 wt %, a magnesium content of 21.0 wt % and an average particle size of 65.6 μm with di-iso-butylphthalate as internal donor. Dicyclopentyl dimethoxy silane was used as an external donor.

Polymerization procedure

In general, a slurry of 0.05 g of the catalyst in 5 mL of hexane was precontacted in a glove box with a premix of 2.0 g of a 1M solution of TEAL in hexane and 0.03 g of the external donor in a 25 mL septumcapped, crimp-sealed glass vial for 5 min at ambient temperature.

To run the polymerization trials, the glass vial was then put in a shaker gently moving and the monomer was added as a gas through a syringe needle and kept at a constant pressure in the vial for the fixed period of time. During this time the temperature was exactly recorded by a thermocouple within the vial, but no effort was made to keep the temperature constant in the vial. In all cases a fast temperature rise was observed upon monomer addition. At the end, the monomer feed was discontinued, the vial was opened in the glove box again and the prepolymerized catalyst was dried and weighed back to determine the yield of the prepolymerization, also confirmed by monomer consumption measurements. Shaking has been selected to avoid destruction of the catalyst/polymer particles in the initial state as observed by using a magnetic stirrer, whereas no shaking led to diffusion controlled reactions observable in polymerization yields of only 5.77 g PP/g Cat at polymerization times of 15 min in comparison to 20.54 g PP/g Cat by shaking (initial temperature 23°C).

Morphology characterization

The morphology of the polymers was characterized by Scanning electron microscopy by micrographs of prepolymers at different prepolymerization stages as well as by micrographs of cross-sections from the prepolymer particles.

RESULTS AND DISCUSSION

Since the polymerization rates at the initial states of industrial propylene polymerization processes are high and can not easily be followed by conventional methods, these polymerizations were performed in a diluted stage at lower temperatures near room temperature and at industrial conditions of an adiabatic temperature profile. Therefore, the temperature profile has also been monitored as a sensitive method for the indication of the polymerization rate,[4] besides gravimetric analysis and measurements of the monomer flow.

Effect of process parameters on prepolymerization

A general profile of the temperature within the vial with increasing polymerization time is shown in Figure 1. A sharp temperature increase is observed in the first minutes of the experiment followed by a slow decrease during most of the time range until 30 min. Within the first minute a polymerization yield of already 5.3 g polypropylene/gram of catalyst (g PP/g Cat) is achieved, increasing to 17.3 g PP/g Cat beyond the temperature maximum after 10 min, and only slowly increasing to 33.4 g PP/g Cat at 30 min of polymerization. A more detailed investigation of the first period of the very rapid temperature increase suggesting high initial reaction rates until the temperature maximum is given in Figure 2. As shown, the rapid temperature increase is caused by a very high polymerization rate at the beginning of 5.33 g PP/(g Cat × min) at 1 min, significantly
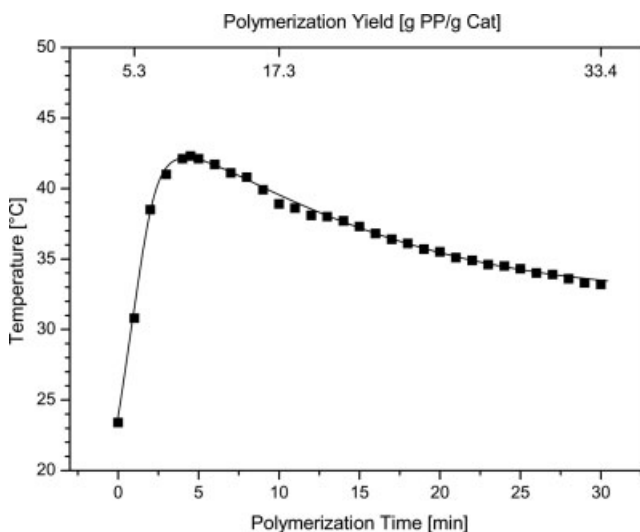
Figure 1 General temperature profile of polymerization within the glass vial during the initial state of polymerization and correlation to polymerization yield (propylene pressure 1 bar; initial temperature 23.4°C; external donor dicyclopentyl dimethoxy silane; vial volume 20 mL).

decreasing with polymerization time to 2.81 g PP/(g Cat × min) at 2.5 min and slowly diminishing to 1.61 g PP/(g Cat × min) after 6 min. During the temperature change, an opposite effect of increasing polymerization rate by a temperature increase and decreasing monomer concentration by a lower propylene solubility in hexane at the same partial pressure with increasing temperature is taking place, both outside of reaching a steady state at lower polymerization times.

The dependence of the polymerization rate on the monomer concentration indicated by the propylene pressure at the initial state of polymerization is demonstrated in Figure 3 until polymerization times of 3 min. The highest polymerization rates can be observed at the initial polymerization states within about 1 min at all monomer pressures, vigorously decreasing with time and only slowly dropping off at higher polymerization times until 3 min. In general, the polymerization rate also increases with increasing propylene concentration during the initial state polymerization. Since the dependence of the polymerization rate on propylene concentration is linear at low polymerization times of 1 and 2 min, this indicates that monomer diffusion and mass transfer between gas phase and liquid phase at different monomer pressures seems to be negligible regarding rate determining factors in initial state polymerizations under these conditions.

The influence of the cocatalyst TEAL on the prepolymerization activity is shown in Figure 4 at a constant polymerization time of 15 min. Already very low concentrations of TEAL cause a significant increase of the activity of the supported Ziegler–Natta catalyst visible in polymerization yield reaching a plateau value at about 6.5 g PP/g Cat and maintaining it until at least molar ratios TEAL/Ti of 300. The lowest amount of TEAL about leading to
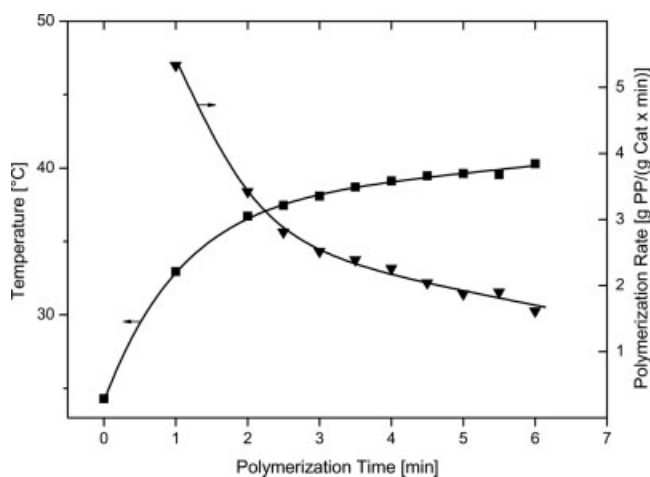
Figure 3 Effect of monomer pressure on polymerization rate in dependence on polymerization time for the initial state polymerization (initial temperature 24.3°C).

the high prepolymerization yields is 0.05 mL corresponding to a molar ratio TEAL/Ti of 3.0, which is a very low amount of an aluminum alkyl to activate a Ziegler–Natta catalyst.

The effect of the concentration of the external donor dicyclopentyl dimethoxy silane on the polymerization yield of the adiabatic prepolymerization is summarized in Figure 5 at a polymerization time of 10 min. Whereas the polymerization yield increases with an increasing molar ratio of donor/Ti at low donor concentrations, it drops down after reaching a molar ratio of donor/Ti of 4 and remains constant at higher molar ratios until at least 18. A decrease of the polymerization yield with increasing amount of external donor has also been observed at the very

Figure 2 Dependence of temperature and polymerization rate on time until the temperature maximum of the initial state polymerization (propylene pressure 1 bar; vial volume 25 mL).
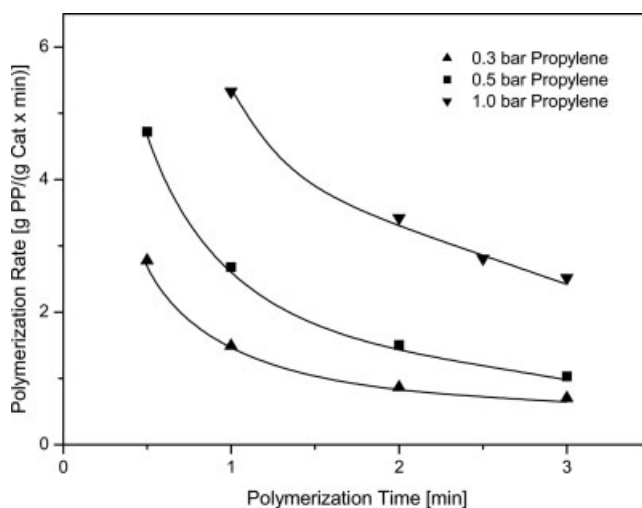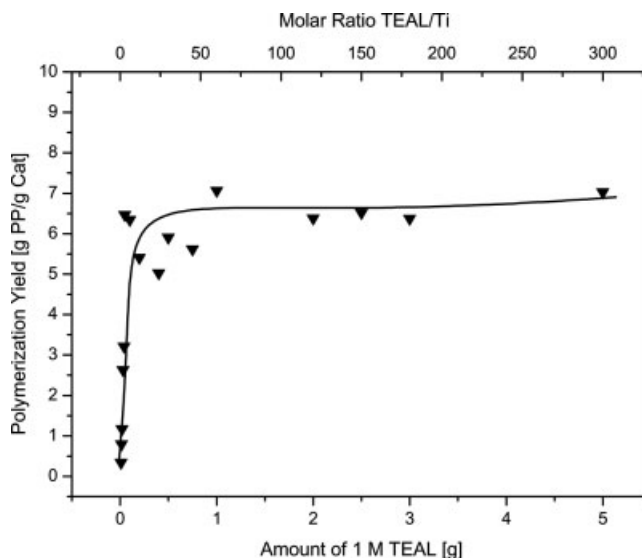
Figure 4 Influence of the cocatalyst triethyl aluminum on the prepolymerization activity (propylene pressure 0.5 bar; initial temperature 24.4°C).
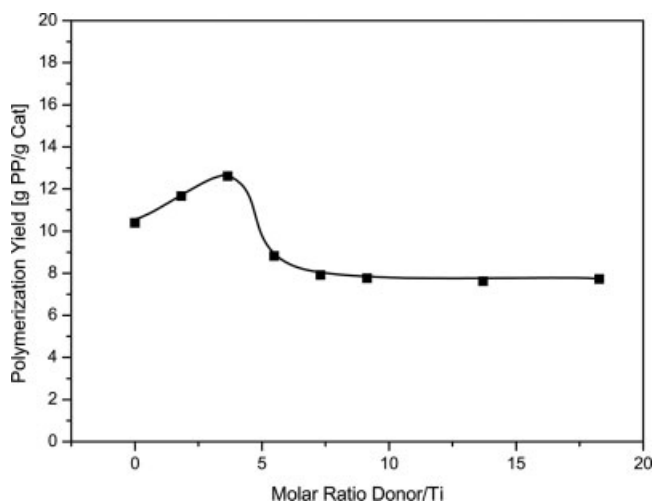
Figure 5 Effect of the concentration of the external donor dicyclopentyl dimethoxy silane on the polymerization yield (initial temperature 24°C, polymerization time 10 min).

high productivities of conventional propylene polymerizations with $MgCl_2$ supported $TiCl_4$ Ziegler–Natta catalysts and different silanes as external donors.[6,7] However, the reason for the stepwise decrease of the polymerization yield, which has also been observed with the donor cyclohexyl dimethoxymethyl silane but at a higher molar ratio donor/Ti of above 9, is not clear yet. Obviously, one reason for this behavior might be rearrangement steps of the different donors within the $MgCl_2$ lattice accompanied by a decrease of the number of the active polymerization sites of different stereospecificity or of a decrease of the activity of these sites. Here, an external donor with two bulky substituents as in the case of dicyclopentyl dimethoxy silane might be
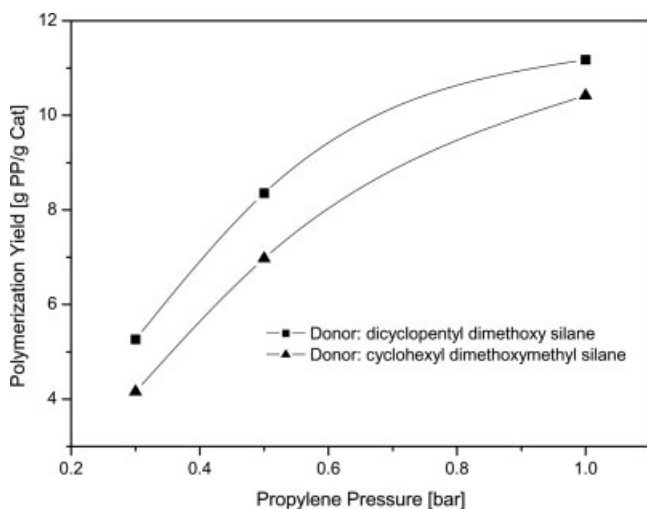
more efficient than a donor with only one bulky substituent in cyclohexyl dimethoxymethyl silane.

The influence of the kind of external donor on polymerization behavior at prepolymerization is shown in Figure 6 at different monomer concentrations at a constant polymerization time of 15 min. It is evident, that the donor dicyclopentyl dimethoxy silane leads to higher polymerization yields than the donor cyclohexyl dimethoxymethyl silane at all propylene pressures investigated on a weight as well as on a molar basis. This confirms, that external donors which are sterically more bulky in the two alkyl groups of the silane, besides the two methoxy groups, are more effective for the catalyst performance also in the propylene initial state polymerization.[8] Furthermore, the dependence of the polymerization yield on propylene pressure in Figure 6 is not linear in comparison to the linear relationship at low polymerization times of 1 and 2 min mentioned for Figure 3. This indicates that additional processes of monomer diffusion and mass transfer between gas phase and liquid phase up to the active polymerization site of the catalyst/polymer particle are getting more important as rate determining steps with increasing polymerization times during the initial state polymerization.

These findings were confirmed by investigations on the role of the solvent. If the low viscosity solvent hexane was substituted by the same amount of a paraffine oil of much higher viscosity under comparable conditions (propylene pressure 1 bar, initial temperature 24.3°C) with the external donor dicyclopentyl dimethoxy silane, the polymerization yield after a polymerization time of 15 min dropped down significantly from 15.8 to 4.2 g PP/g Cat caused by different monomer solubilities and by diffusion control by solvent viscosity.
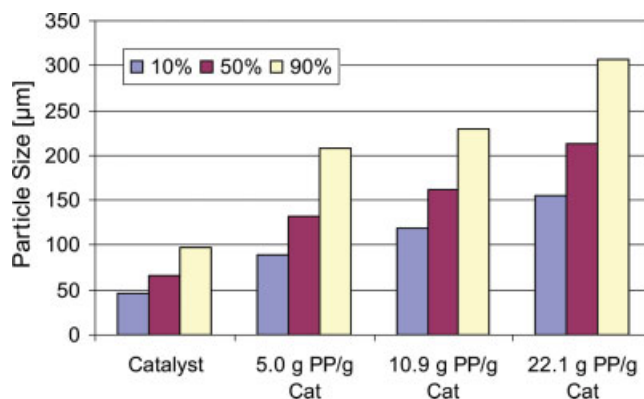

Figure 6 Influence of the kind of the external donor on prepolymerization behavior at different propylene pressures (initial temperature 24°C; polymerization time 15 min; molar ratios donor/Ti: 5.5-dicyclopentyl dimethoxy silane, 6.7-cyclohexyl dimethoxymethyl silane).

Figure 7 Particle size of the catalyst/prepolymer particles depending on polymerization yield (initial temperature 24°C; propylene pressures of 0.3, 0.5, and 1.0 bar; polymerization time 15 min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Morphology in prepolymerization

Because the initial state polymerization has a significant impact on the subsequent main polymerization to extremely high polymerization conversions and obviously on shape and size of the polymer particles formed, the morphology of prepolymerization particles was investigated in more detail.

At first, the particle size of the catalyst and the catalyst/prepolymer particles was measured with increasing polymerization yield until about 22 g PP/g Cat using a laser scattering device in an experiment at different propylene pressures of 0.3, 0.5, and 1.0 bar at the same polymerization time of 15 min (Fig. 7). With increasing polymerization yield, the average particle size of the catalyst/prepolymer particles is steadily increasing starting at the particle size of the catalyst of 65.6 μm until 213.8 μm at the highest polymerization yield of 22.1 g PP/g Cat.

Scanning electron micrographs of catalyst/prepolymer particles at different stages of polymerization yields adjusted by the polymerization time (according to the conditions of Fig. 2) are shown in Figure 8 at several magnifications. Although the par-

ticle size distribution of the supported catalyst itself is rather narrow, it is interesting to note that the particle size distribution of the catalyst/polymer particles is rather broad at the lower prepolymerization stages of 2.5 and 5.3 g PP/g Cat. At higher polymerization yields of 12.2 and 20.4 g PP/g Cat, the particle size distribution narrows again. This suggests that the individual catalyst/polymer particles quickly grow to a certain size only slowly growing furthermore until all other particles have reached about the same size. This is in agreement with the high polymerization rates at very low polymerization times and with the significantly lower rates at higher polymerization times (Fig. 2) leading to an unification of the particle size. The shape of the catalyst/polymer particles is almost perfectly spherical.

A detailed view of a part of a catalyst/polymer particle prepolymerized with 2.5 g PP/g Cat is given in Figure 8. A polypropylene shell of 3–5 μm thickness is clearly visible at the outside of the particle (Fig. 9). This polymer layer is formed at the earliest stages of the initial state polymerization of propylene and seems to be complete at polymer loadings of
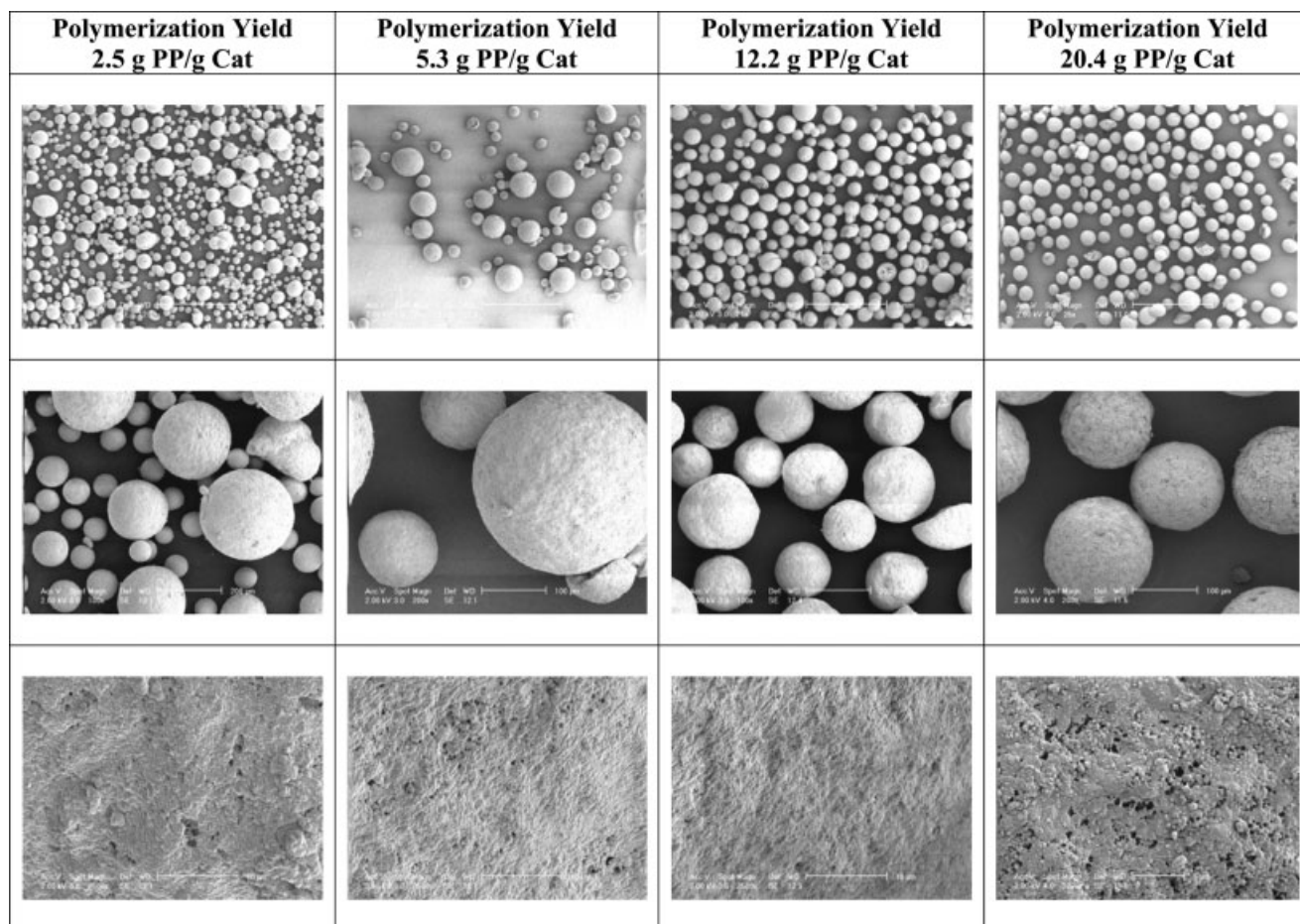

Figure 8 Scanning electron micrographs of catalyst/prepolymer particles at different stages of polymerization yields (bar scale: top 1 mm, middle 250 μm, bottom 10 μm; conditions comparable to Fig. 2).
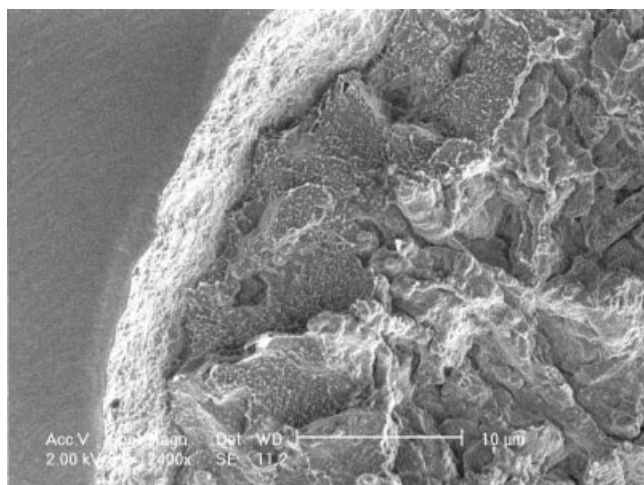
Figure 9 Catalyst/polymer particle prepolymerized with 2.5 g PP/g Cat of Figure 8 showing a polypropylene shell of 3–5 µm thickness.

about 3–6 g PP/g Cat. Once this polymer layer is completing, the polymerization rate decreases due to the hindered diffusion of the propylene monomer through this layer. This is confirmed by the linear relationship between polymerization rate and propylene pressure at very low polymerization times of 1 and 2 min (Fig. 3) not indicating significant hindrance of monomer diffusion, and by the significant influence of diffusion shown at long polymerization times of 15 min in Figure 6.

Furthermore, the polymer layer also protects the catalyst/polymer particle from being disintegrated and is responsible for maintaining of a good polymer powder morphology without fines during further polymerizations. This has experimentally been demonstrated by using a prepolymer of a polymerization yield of 6 g PP/g Cat in a separate propylene batch polymerization process at a mileage of 11 kg PP/g Cat resulting in a polymer with an average particle size of 1660 µm and only 0.1 % of fines lower than 250 µm in contradiction to a polymer of an average particle size of 1700 µm, but with 3.0 % of fines lower than 250 µm and without a defined separate prepolymerization reaction. Therefore, the best polymer morphology is obtained if the first contact between monomer and catalyst takes place under controlled conditions such as low monomer concentration and low shear loads allowing a controlled fragmentation and perfect replication process of the catalyst particles.

CONCLUSIONS

This study has shown that the initial state polymerization of propylene with Ziegler–Natta catalysts can successfully be investigated at very low polymerization yields under adiabatic industrial prepolymeriza-

tion conditions in a diluted slurry. The effects regarding significant process parameters like monomer pressure, aluminum alkyl, and donor kind and concentration including the morphology of the catalyst/polymer particles formed can adequately be examined and were discussed in detail.

In the prepolymerization reaction it has been shown, that a sharp temperature increase in the first minutes of the initial state polymerization is followed by a temperature maximum and a slow decrease during the following time caused by a high polymerization rate at the beginning significantly decreasing with time. This is also observable at increasing monomer concentrations resulting in higher polymerization rates. With cocatalyst TEAL, high prepolymerization yields were already achieved at a molar ratio TEAL/Ti of 3.0, remaining about constant until molar ratios of at least 300. The external donor dicyclopentyl dimethoxy silane leads to higher polymerization yields than the donor cyclohexyl dimethoxymethyl silane in the initial state polymerization too; however, both show a remarkable decreasing effect on polymerization yield above a specific molar ratio donor/Ti obviously correlated with the bulkiness of the alkyl groups.

Regarding the morphology development, the particle size of the catalyst and the catalyst/prepolymer particles is increasing with polymerization yield until about 22 g PP/g Cat with particles almost perfectly spherical. However, the particle size distribution is rather broad at lower prepolymerization stages but unifying with lower polymerization rates at higher polymerization times. A polypropylene shell of 3–5 µm thickness is already observable on the catalyst/polymer particle prepolymerized with 2.5 g PP/g Cat.

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