Influence of Porosity on the Fragmentation of Ziegler-Natta Catalyst in the Early Stages of Propylene Polymerization

Xuejing Zheng,^{1,2#} Makarand S. Pimplapure,^{2,3} Günter Weickert^{2,3} Joachim Loos^{1,2*}

¹ Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600MB Eindhoven, The Netherlands; Fax number +31 40 2436999; j.loos@tue.nl

² Dutch Polymer Institute, P.O. Box 902, 5600AX Eindhoven, The Netherlands

³ Faculty of Chemical Engineering, Process Technology Institute Twente, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

Current address: College of Materials Engineering, Zhengzhou University, P. R. China, 450052

(Received: 15 December, 2005; published: 10 June, 2006)

Abstract: Catalyst fragmentation and polymer growth in the early stages of propylene polymerization has been investigated using different Ziegler-Natta catalysts. Polymerization was carried out in slurry under mild conditions and stopped at low yield. Scanning electron microscopy (SEM) has been used to characterize the surface and cross sectional morphology of polymer particles at different stages of particle growth. Different fragmentation behavior is observed, and it is found that the way that catalyst fragments in the early stages of polymerization is greatly influenced by the porosity of the catalyst. When a less porous catalyst was used, the resulting mass diffusion limitation causes layer-by-layer fragmentation, starting at the outer surface of the catalyst particle to the center. In contrast, for highly porous catalyst, monomer can easily penetrate into the pores of the catalyst / polymer particle. The polymer growing throughout the particle results in a coarse and instantaneous fragmentation.

Introduction

Through several generations, heterogeneous Ziegler-Natta catalysts for the synthesis of polyolefins have been markedly improved to increase, e.g., their activity as well as their stereospecificity [1-4]. Over the years, significant progress has been made in understanding how the catalyst activity, stereoselectivity, hydrogen response etc. can be finely tuned by operating at the active centre level, mainly acting on the nature of electron donors. With increased catalyst activity, the problem of polymer particle production with uncontrolled morphology is becoming notable. The high activity catalyst can generate hot spots in the polymer particles or produce polymer fines, which will easily cause reactor fouling. Many attempts have been made in the past to get a balance between high catalyst activity and good polymer particle morphology control. However, the results are not very satisfying because there are still too many open parameters that have to be considered. Good morphology for polymer particle usually means spherical shape, narrow particle size distribution, high bulk density, controlled degree of porosity, controlled internal composition and high process flowability [1, 5]. When using titanium based catalysts supported on magnesium chloride, a prepolymerization step is often used, which is essentially a polymerization step performed under mild conditions and at low reaction rates. It is well accepted

that the particle fragmentation process during prepolymerization is a decisive step in the determination of the final particle morphology [5-9].

Ferrero, Chiovetta, Noristi, Weickert, Fink, Cecchin and others have contributed to a great extent to the understanding of catalyst fragmentation and polyolefin particle growth using supported catalysts [5, 6, 10-22]. Studies in the area of nascent, as-polymerized morphology of polyolefin particles indicate two different catalyst fragmentation behaviours. Ferrero, Chiovetta and Fink [11-19] used electron microscopy technique to study the parameters that affect the way the catalyst breaks up in MgCl_2 supported Ziegler-Natta catalysts and silica supported metallocene catalysts. The fragmentation of catalysts in their work was described as “layer-by-layer”, which means that the catalyst particle breaks up from the external surface gradually to the center of the macroparticle until the whole catalyst particle is fragmented. However, a different particle growth mechanism has been reported in the work of Pater and Weickert [5]. They showed a rapid fragmentation of the catalyst into a large number of small sub-particles in a low rate polypropylene polymerization. It was reported that the whole catalyst particle breaks up into a large amount of sub-particles at the beginning of the polymerization. Each fragment acts as a nucleus around which further polymer growth occurs. The fragments remain entrapped and dispersed in the growing polymer mass and move outward in proportion to the local volumetric expansion due to the polymerization.

In the present work, propylene polymerization was carried out in hexane slurry under very mild conditions using MgCl_2 supported Ziegler-Natta catalysts. The polymerization was stopped at low yield, expressed as grams of polymer per gram catalyst. The surface and cross sectional morphology of the catalyst and polymer particles was characterized by scanning electron microscopy, enabling us to monitor the support fragmentation behavior and polymer particle growth in the very early stages of the polymerization.

Results and discussion

Fig. 1 shows the surface morphology of catalyst-I particles and the polymer particles at the yield of 2.2 g/g, 7.2 g/g and 28.0 g/g, respectively. Catalyst-I is about 50 μm in diameter. The catalyst particles appear to be composed of many small spherical sub-particles, with diameters of about 5 μm . The polymer particles reflect the dual morphological hierarchy of the initial catalyst particles producing polymer around each catalyst fragment to form polymer sub-particles, which stick together to form polymer particles. As the consequence, cauliflower morphology is observed. As widely accepted in literature, the polymerization shows high degree of replication, which means that the shape of the originally used carrier material is maintained during the polymerization.

Fig. 2 shows the surface morphology of catalyst-II particles and the polymer particles at the yield of 0.8 g/g, 1.4 g/g and 20.0 g/g, respectively. Catalyst-II particles are spherical in shape, with diameter of about 50-100 μm . The surface of the catalyst particle is smooth and no aggregation of sub-particles is observed. The shapes of the polymer particles are spherical, also showing good morphological replication. The surface of the polymer particles becomes rough, due to the polymer accumulation.

Fig. 1. LVSEM images of surface morphology at different magnifications of a) catalyst-I) and polymer particles at the yield of b) 2.2 g/g, c) 7.2 g/g and d) 28.0 g/g, respectively.

Fig. 2. LVSEM images of surface morphology at different magnifications of a) catalyst-II and polymer particles over catalyst-II at the yield of b) 0.8 g/g, c) 1.4 g/g and d) 20.0 g/g, respectively.

The SEM images in Fig. 3 show the cross-sectional morphology of the polymer particles based on catalyst-I at the same yields as in Fig. 1: 2.2 g/g, 7.2 g/g and 28.0 g/g, respectively. The bright phase is the catalyst particle, and the dark phase belongs to the freshly formed polymer phase, as indicated in Figs. 3a and 3b. In Fig. 3a it is seen that, at yield of 2.2 g/g, an unfragmented catalyst particle remains in the center of the polymer particle. Close to the surface of this big catalyst particle, some small sized catalyst sub-particles are visible; and close to the surface of the catalyst sub-particles, some tiny catalyst microparticles with the diameter in the order of 1-2 μm can be clearly recognized (Fig. 3b). EDX was used to detect the elemental composition of the microparticle marked in the Fig. 3b at high magnification.

Fig. 3. LVSEM images of cross sectional morphology of PP particles at different yield polymerized from catalyst-I. The rectangles mark the area of the corresponding higher magnification images. The circle in 3b marks the area analyzed by EDX in Fig. 4.

The energy dispersive X-ray spectrum of Fig. 4 shows that there are five main elements detected in the chosen area: carbon (C), oxygen (O), magnesium (Mg),

aluminum (Al) and chlorine (Cl). Carbon may result from the polypropylene formed and also from cocatalyst and donors present in the catalyst system. A small peak of aluminum detected is from cocatalyst AlEt_3 , and for this kind of samples oxygen is always present. There are obvious magnesium and chlorine peaks in the spectrum, which result from the catalyst. Therefore, it can be confirmed that these microparticles in Fig. 3b are the catalyst fragments. With a weight percentage of about 2%, the titanium (Ti) concentration in the catalyst, however, is low so that its detection is difficult by EDX. The cross section of a polymer particle at yield of 7.2 g/g shows that there are still relatively big catalyst sub-particles in the centre of the polymer particle, with a diameter of about 20 μm , as shown in Fig. 3c. Taking each of the catalyst sub-particles as nucleus, polymer has formed at the surface and links the fragments. While near the surface of each sub-particle, the catalyst breaks up into many microparticles. After further polymerization, leading to a yield of 28.0 g/g, the cross sectional morphology in Figs. 3e and 3f shows that the catalyst particle fragments completely. A very compact polymer phase is formed. The original support is so finely divided that it is hard to detect residues within the polymer particle by SEM. One should realize that – under “industrial” polymerization conditions – this critical yield can be reached within one second. The cross sectional morphologies in Fig. 3 very well elucidate how the catalyst fragmentation starts at the outer surface of the particle and break-up gradually continues to the centre. The way that catalyst-I fragments can be described as “layer-by-layer” fragmentation, as indicated in the literature. It can be envisioned that the polymerization starts at the active sites, which are originally located within the pores of the support, at the surface of the catalyst particle. With polymer growth, the polymer formed in the pores of the MgCl_2 support creates hydraulic forces and mechanically breaks up the support. Once the outer layer of the catalyst particle is fragmented, a new set of fresh pores within the particle is exposed to the arriving monomer. The active centres, which are unavailable to monomer before fragmentation, are now located in the exterior of the recently formed fragments and remain active, maintaining polymer production.

The cross-sectional morphology of polymer particles formed with catalyst-II is shown in Fig. 5. Although polymerization conditions, such as monomer pressure and polymerization temperature, are the same as for polymerization with catalyst-I, catalyst-II presents a very different fragmentation behavior. Figs. 5a and 5b show the cross sectional morphology of polymer particles at very low yield of 0.8 g/g. It is seen that just such little amount of polymer is sufficient to break the whole catalyst particle into a large amount of small sub-particles, with the diameter ranging from 1 to 10 μm . The broken catalyst particles do not lose overall integrity because the individual fragments are held together by the polymer formed. The cross sectional morphology of polymer from catalyst-II at the yield of 1.4 g/g is shown in Figs. 5c and 5d. The polymer particle presents a very porous structure. Because of the different textures embedding resin, polymer formed and the catalyst fragments can be assigned as indicated in Figs. 5c and 5d: the bright phase is the highly porous polymer, and only few small catalyst fragments with even brighter appearance can be found in Fig. 5d. It is seen that with higher polymer yield the catalyst sub-particles break up further to form small and hardly to detect fragments. Only near the outer surface of the particle are catalyst fragments with a diameter of less than 1 μm visible, as shown in Fig. 5d. At the yield of 20.0 g/g, more polymers are formed and the particle presents a spherical but very porous morphology, as shown in Figs. 5e and 5f. The catalyst has been fragmented so intensively that it is not possible to detect any fragments by using SEM. The fragmentation behaviour of catalyst-II can be described as instantaneous break-up, as introduced in Pater's work [5]. It should be noted that the

fragmentation behaviour of the two catalysts is reproducible as known from repeating the polymerization procedure several times.

Fig. 4. EDX spectrum of the microparticle as marked by a circle in Fig. 3b.

It is well accepted that the fragmentation of a catalyst is governed by the competition between the build up and relaxation of stresses in the particle due to the production of polymer at the active sites. Several parameters mainly influence the catalyst fragmentation in the early stages of the polymerization, e.g. the nature of the catalyst (the physical properties of the support material and the active sites distribution), the polymerization rate (related to the catalyst activity and the polymerization conditions applied), mass and heat transportation (related to the reactor design, the porosity of the particle, the crystallinity of polymer formed, the monomer pressure and reaction temperature), etc. As for the physical properties of the catalyst particle, the pore size and surface area are important characteristics that strongly determine the performance of catalysts. From BET measurements, the average pore diameters of catalyst-I and catalyst-II are 60 Å and 97 Å, respectively; the surface areas are 106 m²/g and 212 m²/g; and the pore volumes are 0.16 cm³/g and 0.51 cm³/g, respectively (Table 1). The data show that catalyst-II has larger pores and at the same time has larger surface area than catalyst-I. The influence of the catalyst porosity on its fragmentation behaviour and the polymer growth can now be discussed.

When monomer diffuses into the pores of the catalyst particle and reaches the active sites, polymerization happens immediately. When a thin polymer skin forms on the catalyst particle, monomer has to diffuse through this polymer layer to reach the active sites in the pores of the support material. If the pores are small and the formed polymer layer is compact and dense, monomer diffusion limitation becomes notable. The polymerization tends to take place at and close to the particle surface. If enough polymers are formed and the hydraulic pressure reaches a critical value, the external layer of the particle breaks up and a layer-by-layer fragmentation is observed. In contrast, the highly porous structures of catalyst-II and the porous or open polymer formed permit the monomer to penetrate easily through the pores and reach the active sites not only on the outer surface but also in the centre of the catalyst particle. Polymer chains grow and fill the pores throughout the particle. The hydraulic pressure build-up causes a coarse break-up of the whole catalyst particle and, therefore, results in an instantaneous fragmentation. It is seen that in the present case the catalyst fragmentation behaviour is a complicated result of monomer diffusion rate and the polymerization rate.

Fig. 5. LVSEM images of the cross section morphology of PP particles at different yield polymerized from catalyst-II. The rectangles mark the area of the corresponding higher magnification images.

Usually, the monomer diffusion rate is mainly determined by the porosity of the particle and the crystallinity of the polymer formed. The polymerization rate is dramatically affected by the catalyst activity and the polymerization conditions applied. It can then be deduced that even for one given catalyst system, polymerization with different monomers may result in different catalyst fragmentation behaviour. For example, it is known that, under proper polymerization conditions, a catalyst breaking up instantaneously for propylene polymerization may break up layer-by-layer for ethylene polymerization, since the difference between propagation rate and diffusion rate is greater in the case of ethylene polymerization [3]. Further experimental work is in progress dealing with this feature and the influence of copolymerization on the fragmentation behaviour.

Conclusions

Propylene polymerization was carried out in slurry under mild polymerization conditions by using different Ziegler-Natta catalysts. The characterization of the cross

sectional morphology of the polymer particles at low yields was demonstrated to be a very useful method to study the catalyst fragmentation. The catalysts studied show different fragmentation behaviours: they gradually fragment from outer surface to the center of the catalyst particle, or instantaneously break up into a large amount of small sub-particles at the beginning of the polymerization. In the present study it is believed that the different fragmentation behaviour is related to the different particle porosity. The polymerization with less porous particles tends to take place first only at the exterior of a particle due to the monomer diffusion limitation. In contrast, the highly porous catalyst particles have larger pores, therefore, less monomer diffusion limitation. Monomer can easily diffuse into the pores of the catalyst / polymer particles and polymerization happens not only on the outer surface but also in the centre of the catalyst particle. The hydraulic pressure build-up throughout the whole catalyst results in an instantaneous fragmentation.

Experimental part

Materials and polymerization procedure

Two industrial MgCl_2 -supported Ziegler-Natta catalysts, were used in our study, denoted as catalyst-I and catalyst-II. The description and typical properties of the two catalysts can be found in Table 1.

The catalyst components were prepared in a glove box under nitrogen atmosphere. "Pro Analysi" quality hexane (Merck) was used to suspend the catalyst. Propylene was obtained from Indugas with a purity > 99.5 %, with propane as main impurity. The catalysts were suspended in a mineral oil and weighed in a vial and diluted with hexane. The aluminum alkyl and the donor are weighed in separate vials, and both diluted with hexane.

Polymerizations were carried out in a 1-liter jacketed glass reactor. Pater et al. have described the complete experimental set up [5]. For the present studies, the reactor was provided with a magnetic stirrer in place of a membrane pump, in order to ensure the same degree of stirring even with a relatively high amount of polymer in the slurry towards the end of the reaction. After heating overnight at 120 °C, the reactor was evacuated for 5 min and flushed with nitrogen at 90 °C. The reactor was tested for gas leakage and then charged with 150 mL of hexane at 20 °C. The reactor pressure was adjusted to 0.8 bar by either adding nitrogen or applying vacuum. Then monomer was fed to the reactor till the pressure reached 1.25 bar and catalyst system was then injected. As soon as catalyst came in contact with monomer, polymerization started consuming monomer and the pressure was maintained by supplying fresh monomer via mass flow meter. The reactor was purged when desired yield was reached. More detailed information on polymerization procedures applied can be found in reference 8.

Particle morphology characterization

The catalyst particles for SEM surface observations were prepared in a glove box under N_2 atmosphere, and then transferred into the microscope chamber as quickly as possible so as to minimize the contact with moisture and oxygen of the atmosphere. For the investigation of polymer particle cross sections, the particles were embedded in SPURR low viscosity epoxy resin (SPI Supplies) and cut with a razor blade. The cross-sectioned samples were then placed on the sample mount and transferred into the SEM chamber quickly. Morphological investigation was

performed with a scanning electron microscope XL-30 ESEM FEG (Philips, now Fei Co., The Netherlands) equipped with a field emission gun and operated in low voltage mode (LVSEM) or controlled atmosphere mode. Polymers are generally susceptible to beam-induced radiation damage and, as non-conductors, they charge heavily under electron beam [23]. To prevent both, the morphological characterization in this work was performed at low acceleration voltages of 1-2 kV, which still offers high resolution, but resulted in negligible beam damage of the samples and reduced sample charging. No further sample treatment such as etching or coating with conductive thin film was done.

To detect the elemental distribution, energy dispersive X-Ray analysis (EDX) was performed under controlled N₂ atmosphere at an accelerating voltage of 20 kV in controlled atmosphere operation mode. Again, no additional coating of the sample surface was done because charging is not an issue for the chosen conditions.

The porosity (surface area, pore volume and average pore size) of the catalysts was measured by Brunauer-Emmet-Teller (BET) method using nitrogen physisorption (Quantachrome Autosorb-6) at liquid nitrogen temperature. Before measurements the catalysts were degassed for 2 h at 250 °C. The results are listed in Tab. 1.

Tab. 1. Characteristics of catalysts applied.

	Catalyst-I	Catalyst-II
Ti (%)	2.5	2.0
Cocatalyst	AlEt ₃	AlEt ₃
Internal donor	Dibutylphthalate	Diisobutylphthalate
External donor	diisopropyldimethoxysilane	di-cyclopentyldi-methoxysilane
Surface area (m ² /g)	106	212
Average pore diameter (Å)	60	97
Pore volume (cm ³ /g)	0.16	0.51

Acknowledgements

The authors gratefully acknowledge support from *Dutch Polymer Institute* for Projects #331 and #118. The authors wish to thank *Dr. John C. Chadwick* for stimulating discussions.

References

- [1] Galli, P.; Vecellio, G.; *Prog. Polym. Sci.* **2001**, 26,1287.
- [2] Soga, K.; Shiono, T.; *Prog. Polym. Sci.* **1997**, 22, 1503.
- [3] Cecchin, G.; Morini, G.; Piemontesi, F.; Kirk-Othmer Encyclopedia of Chemical Technology. Published by John Wiley & Sons Inc., **2003**
- [4] Cecchin, G.; Morini, G.; Pelliconi, A.; *Macromol. Symp.* **2001**, 173,195.
- [5] Pater, J. T. M.; Weickert, G.; Loos, J.; van Swaaij, W. P. M.; *Chem. Eng. Sci.* **2001**, 56, 4107.

- [6] Weickert, G.; Meier, G. B.; Pater, J. T. M.; Westerterp, K. P.; Chem. Eng. Sci. **1999**, *54*, 3291.
- [7] Kittilsen, P.; Svendsen, H. F.; AIChE J. **2003**, *49*, 1495.
- [8] Pimplapure, M. S.; Zheng, X.; Loos, J.; Weickert, G.; Macromol. Rapid. Commun. **2005**, *26*, 1155.
- [9] Zheng, X.; Pimplapure, M. S.; Weickert, G.; Loos, J.; Macromol. Rapid. Commun. **2006**, *27*, 15.
- [10] Noristi, L.; Marchetti, E.; Baruzzi, G.; Sgarzi, P. J.; Polym. Sci. Part A: Polym. Chem. **1994**, *32*, 3047.
- [11] Ferrero, M. A.; Chiovetta, M. G.; Polym. Eng. Sci. **1987**, *27*, 1436.
- [12] Ferrero, M. A.; Chiovetta, M. G.; Polym. Eng. Sci. **1987**, *27*, 1448.
- [13] Ferrero, M. A.; Chiovetta, M. G.; Polym. Eng. Sci. **1991**, *31*, 886.
- [14] Ferrero, M. A.; Chiovetta, M. G.; Polym. Eng. Sci. **1991**, *31*, 904.
- [15] Bonini, F.; Fraaije, V.; Fink, G.; J. Polym. Sci. Part A: Polym. Chem. **1995**, *33*, 2393.
- [16] Zechlin, J.; Steinmetz, B.; Tesche, B.; Fink, G.; Macromol. Chem. Phys. **2000**, *201*, 515.
- [17] Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B.; Chem. Rev. **2000**, *100*, 1377.
- [18] Knoke, S.; Korber, F.; Fink, G.; Tesche, B.; Macromol. Chem. Phys. **2003**, *204*, 607.
- [19] Steinmetz, B.; Tesche, B.; Przybyla, C.; Zechlin, J.; Fink, G.; Acta. Polymer. **1997**, *48*, 392.
- [20] Cecchin, G.; Marchetti, E.; Baruzzi, G.; Macromol. Chem. Phys. **2001**, *202*, 1987.
- [21] Kittilsen, P.; McKenna, T. F.; Svendsen, H.; Jakobsen, H. A.; Fredriksen, S. B.; Chem. Eng. Sci. **2001**, *56*, 4015.
- [22] Zheng, X.; Smit, M.; Chadwick, J. C.; Loos, J.; Macromolecules **2005**, *38*, 4673.
- [23] Butler, J. H.; Joy, D. C.; Bradley, G. F.; Krause, S. J.; Polymer **1995**, *36*, 1781.