Morphology Evolution in the Early Stages of Olefin Polymerization

Xuejing Zheng,[1,2] *Joachim Loos*[1]

Summary: The olefin polymerizations were carried out by using silica supported metallocene/MAO catalysts and $MgCl_2$ supported Ziegler-Natta catalysts under mild reaction conditions and stopped at very low yield. The surface and cross sectional morphology of the polymer particles were characterized by using scanning electron microscopy (SEM). A homogeneous distribution of (co)catalyst on the support material is a prerequisite condition to get a homogeneous fragmentation and uniform polymer particle morphology. In the present work the catalysts show two different fragmentation behaviors. They can gradually fragment from the outer to the inner surface of the catalyst particle, or instantaneously break up into a large amount of small sub-particles at the beginning of the polymerization. The incorporation of comonomer does not change the general catalyst fragmentation scheme but delays the catalysts break-up progress.

Keywords: catalysts; fragmentation; morphology; olefin; polymerization

1. Introduction

The properties of olefin polymers, e.g. molecular weight and molecular weight distribution, chain length distribution, comonomer content and composition, greatly depend on the molecular microstructure of polyolefin. The control of the molecular microstructure has been an important task in olefin polymerization. Significant progress has been made in understanding how catalyst activity, stereoselectivity, hydrogen response, etc., can be finely tuned by operating at the active center level.[1–4] In olefin polymerization, the single polymer particle can be viewed as a microreactor, characterized by its own kinetics and balances of mass and energy.[1,3,5] Apart from the nature of the active species, the microstructure of the final polymer is greatly affected by mass and heat transfer during the polymerization, especially in the early stages of polymerization. When monomer contacts the active sites on the surface of the catalyst, polymer production takes place and the fast-forming polymer will deposit on the catalyst surface and pores. Therefore, the monomer must diffuse through the boundary layer around the catalyst particle, through the thin polymer layer and through the pores of the supported catalyst to reach the active sites, where polymerization takes place. It can be understood that, for a given reactor system, the morphology of the polymer/catalyst particle, e.g., the pore size, pore size distribution, pore structure, the crystallinity of polymer formed, is the decisive factor to determine the mass and heat transport. Therefore, a good control of particle morphology is of great importance to get a good control of microstructure and macrostructure of the final polymer.

It has been generally accepted that the shape and morphology of a polymer particle are determined by the shape and

---

[1] Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600MB Eindhoven, The Netherlands;
Fax number +31 40 2436999;
E-mail: j.loos@tue.nl, and
Dutch Polymer Institute, P.O. Box 902, 5600AX Eindhoven, The Netherlands
[2] Current Address: College of Materials Engineering, Zhengzhou University, P. R. China, 450052

initial morphology of the original supported catalyst as well as by the way the catalyst particle break up.[3,4,6] In industry, prepolymerization with a highly active catalyst, which is essentially a polymerization step performed under mild conditions and at low reaction rates, is often employed to get a gentle break-up and controlled particle morphology. The low reaction rates allow full activation of the catalyst and lead to a controlled fragmentation of the supported catalyst. The understanding of the fragmentation behavior, especially in the early stages of olefin polymerization, represents an important research task, aiming at a good polymer particle morphology control without a prepolymerization procedure. Many attempts have been made in the past to get a balance between high catalyst activity and good polymer particle morphology, which usually means spherical shape, narrow particle size distribution, high bulk density, controlled degree of porosity, controlled internal composition and high process flowability.[1] The results are still not very satisfying because there are too many open parameters that must be considered.

This paper focusses on the key parameters that affect the catalyst fragmentation and polymer particle morphology. Olefin homo- and copolymerizations were carried out in slurry by using $MgCl_2$ supported Ziegler-Natta catalysts or silica supported metallocene/MAO catalysts under mild conditions and stopped at low yield. The surface and cross sectional morphology of the catalyst and polymer particles were characterized by using microscopic techniques, enabling us to monitor the support fragmentation and polymer particle growth in the very early stages of the polymerization.

2. Experimental

2.1 Polymerization Procedure

Olefin homo- and copolymerizations were carried out in slurry using $MgCl_2$-supported Ziegler-Natta catalysts and silica-supported metallocene/MAO catalysts under mild conditions and stopped at low yield. Detailed information about the used materials and the polymerization procedures can be found in references 7–11.

2.2 Evaluation of Particle Morphology

The surface and cross sectional morphologies of the samples were investigated using a Philips environmental scanning electron microscope XL-30 ESEM FEG (Philips, The Netherlands, now Fei Co.) equipped with a filed emission gun and operated in low voltage mode (LVSEM) or controlled atmosphere mode. Polymers are generally susceptible to beam-induced radiation damage and, as insulators, they charge heavily under electron beam.[12] To prevent both, the morphological characterization in the present work is performed at low acceleration voltages of 1–1.2 kV, which still offers high resolution, but results 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 N_2 atmosphere at an accelerating voltage of 20 kV in controlled atmosphere operation mode. No additional coating of the sample surface was done because charging is not an issue for the chosen imaging conditions.

For the investigation of cross sections, the catalyst and polymer particles were embedded in SPURR low viscosity epoxy resin (SPI Supplies) and cut with a razor blade. For $MgCl_2$-supported Ziegler-Natta catalysts, the samples for surface and cross sectional characterization have to be transferred into the SEM chamber as quickly as possible so as to minimize the contact with moisture and oxygen of the atmosphere.

The porosity (surface area, pore volume and average pore size) of the catalysts was measured by BET 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 Table 1.

Table 1.
Characteristics of catalysts applied.

	Catalyst-I	Catalyst-II
Ti (%)	2.5	2.0
Cocatalyst	$AlEt_3$	$AlEt_3$
Internal donor	dibutylphthalate	diisobutyl phthalate
External donor	diisopropyl dimethoxy silane	dicyclopentyl di-methoxy silane
Surface area (m^2/g)	106	212
Average pore diameter (Å)	60	97
Pore volume (cm^3/g)	0.16	0.51

3. Results and Discussion

3.1 Effect of Catalyst Preparation on Polymer Particle Morphology

A precondition to get a good polymer particle morphology is a firm and homogeneous distribution of (co)catalyst on the support material. Numerous techniques have been disclosed for supporting and finishing the catalyst in order to optimize catalyst activity, particle morphology, and particle bulk density without seriously affecting polymer properties. $MgCl_2$ has been found to be the best support material for Ziegler-Natta catalysts due to similarities in atomic size, shape and coordination number between Mg and Ti. For metallocene/MAO catalysts, the most common route to immobilized metallocenes consists of physisorbing the catalyst precursor onto an MAO-pretreated silica support or treating silica with a metallocene/MAO mixture. The active sites should be firmly anchored on the surface of the support, to avoid problems such as catalyst leaching. Leaching of the active sites will result in poor polymer morphology, very small particles (fines), and, eventually, in reactor fouling (Figure 1).

For heterogeneous catalysts, the preparation procedure of immobilizating the (co)catalyst on support material should be carefully selected to guarantee a homogeneous distribution of (co)catalyst. Improper impregnation conditions will result in a heterogeneous distribution of (co)catalyst on support particles, which will finally bring about polymer particle with poor morphology. The EDX mappings in Figure 2 reveal that the silica calcined at 250 °C gave a core-shell distribution of aluminum element, indicating a relatively high concentration of MAO at and close to the particle surface, but very little MAO in the particle interior. Due to the absence of active sites in the center of the catalyst particle, the polymerization can only take place on the outer layer of the catalyst particle and even after long polymerization times the center of the support remains non-fragmented and covered by the formed polymer (Figure 2). The produced polymer particle is of inferior quality and cannot be used for further processing. This is evidently not desirable and therefore should be avoided in industrial processes for olefin polymerization.

If (co)catalyst is distributed throughout the support particle, while close to the outer surface the (co)catalyst has higher concentration than that in the center, the catalyst particle can break up completely, but with a very rough surface morphology, as shown in Figure 3. As indicated in the literature, a very useful refinement of the supporting technique is recommended to solve this problem, called as "incipient wetness" method, in which the pore volume of the

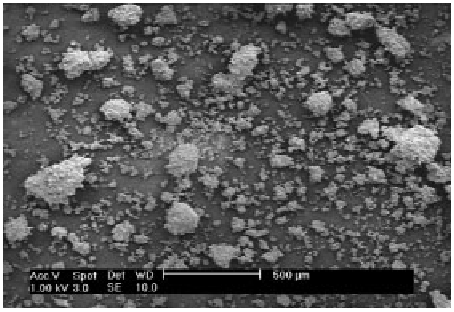

Figure 1.
Undesired poly(propylene) particle morphology due to the leaching of active sites from support.

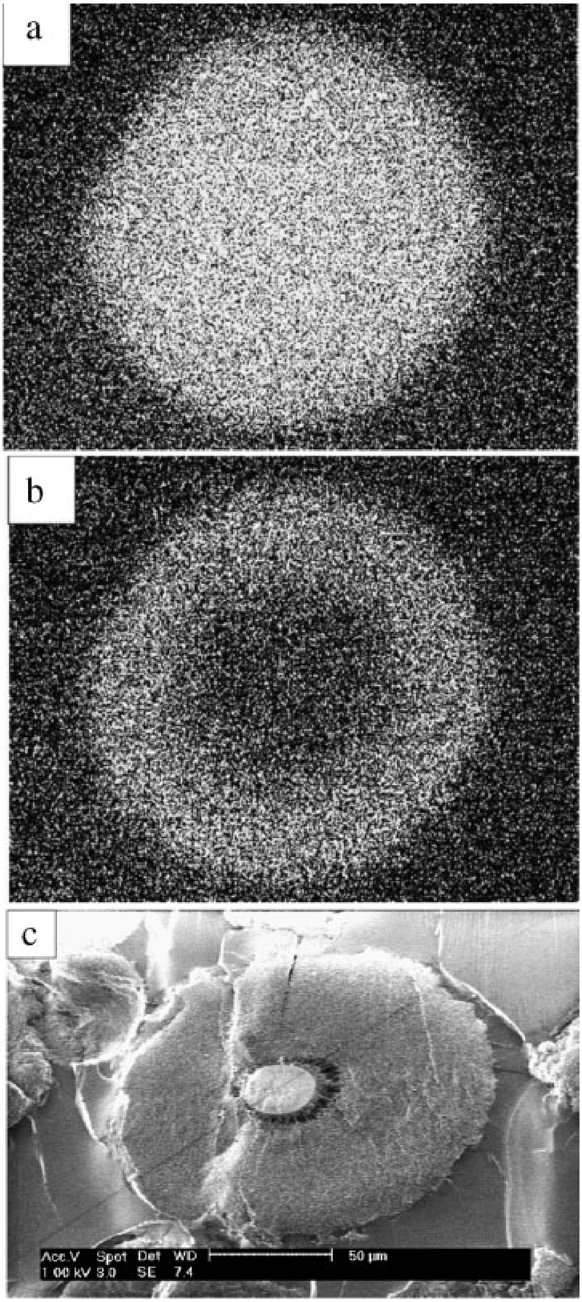

Figure 2.
a) silica mapping, and b) aluminum mapping of catalyst particle cross section; c) cross sectional morphology of a poly(propylene) particle.

support is measured and a volume of catalyst solution is added which only just fills the pores of the support. The solution is added to the support held under low pressure in order to improve penetration into the pores of the support. One advantage to this method is that the catalyst occupies the pores of the support and less of

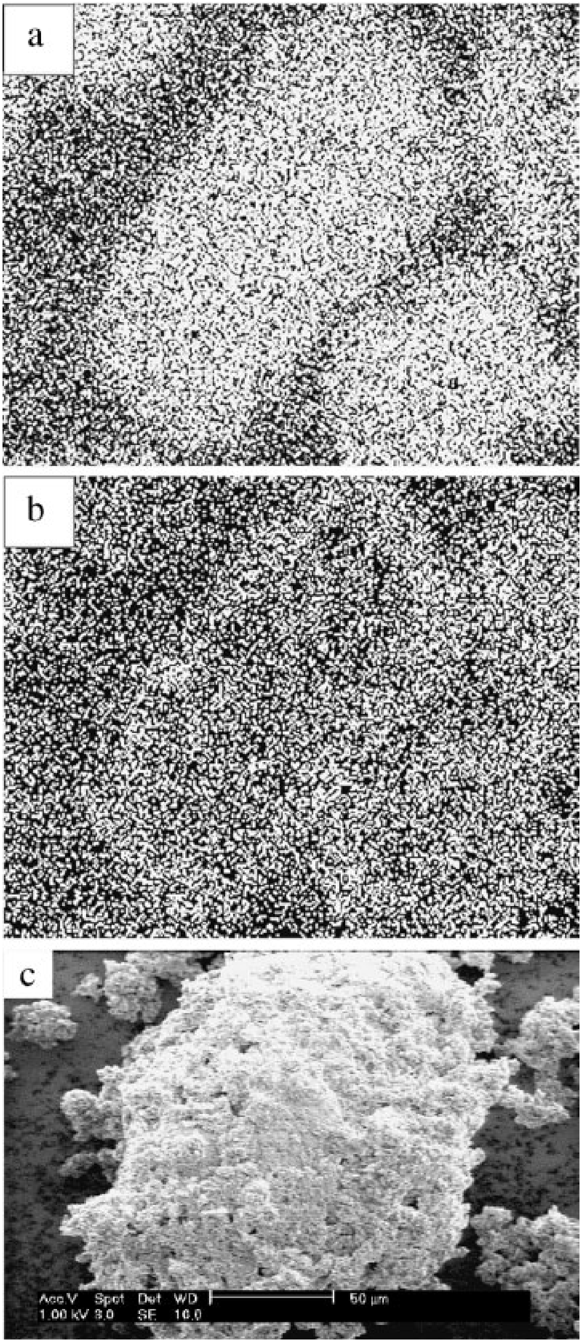

Figure 3.
a) silica mapping, and b) aluminium mapping of catalyst particle cross section; c) surface morphology of a poly(propylene) particle.

the surface, leading to improved particle morphology.[13–15]

3.2 The Fragmentation Process During Polymerization

For olefin polymerizations catalyzed by heterogeneous supported catalysts, one of the most unique features is the breakup of the solid catalyst particles, so that active catalytic sites, which are mostly located in the inner pore surface, would be exposed to the bulk fluid by the disintegration of the original catalyst, and keep the polymerization continue. To investigate the fragmentation process at the beginning of the polymerization, propylene polymerization was carried out in heptane slurry at 50 °C and under a monomer pressure of 4 bar using a silica supported metallocene catalyst (*rac*-Et(Ind)$_2$ZrCl$_2$) with very low activity. The surface images of a polymer particle are shown in Figure 4. It should be noted that the yield of polymer is about 1.7 g/g (polymer/ catalyst); however, the yield of every single polymer particle can be different because of the polydispersity. At the beginning of the polymerization, a small amount of already produced polymer breaks up the catalyst particle, as the cracks can be observed (Figure 4b). At high magnification, it shows that polymer formed on the surface of the catalyst particle is in the shape of flake (Figure 4c). With increasing polymer-production, hydraulic force is built up increasingly and results in further fragmentation (Figure 4d). The catalyst particle breaks into irregular sub-particles with the diameter ranging from 5 to 20 μm. The individual catalyst fragments are held together by the polymer formed. Figure 4 shows that the fragmentation takes place at the very beginning of the propylene polymerization and illustrates how the hydraulic force of the polymer formed in the pores of the support breaks up the catalyst particle.

3.3 Different Fragmentation Behavior

Over the years many attempts have been made to understand the catalyst fragmenta-

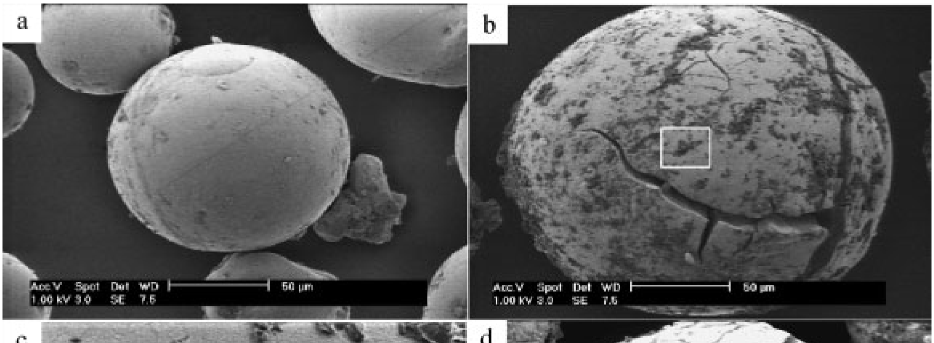

Figure 4.

LVSEM images of the surface morphology of a) catalyst particle, b) poly(propylene) on catalyst particle at very low yield. c) high magnification of marked area in b, and d) poly(propylene) on catalyst particle at higher yield.

tion and polyolefin particle growth using supported catalysts.[5–11,16–27] Two catalyst fragmentation behaviors are reported in these studies. Ferrero, Chiovetta and Fink [18–26] used electron microscopy technique to investigate the key parameters that affect the catalyst fragmentation 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 indicates that the catalyst particle breaks up from the external surface to the center of the particle until the whole catalyst particle is fragmented. However, a different particle growth mechanism has been reported in the work of Pater and Weickert.[16] They showed a rapid fragmentation of the catalyst into a large number of small subparticles in a low rate poly(propylene) polymerization. It was reported that the whole catalyst particle breaks up into a lot of small pieces at the beginning of the polymerization. The fragments remain entrapped and dispersed in the growing polymer mass and move outward in proportion to the local volumetric expansion due to polymerization. In this section, propylene homopolymerization and propylene-ethylene copolymerization were carried out using $MgCl_2$-supported Ziegler-Natta catalysts in heptane slurry at 25 °C under the monomer pressure of 1.25 bar and stopped at different polymerization time to get different yield. Two different Ziegler-Natta catalysts were applied, denoted as catalyst-I and catalyst-II. The characteristics of the catalysts are listed in Table 1.

The SEM images in Figure 5 show the cross-sectional morphology of the poly(propylene) particles prepared from catalyst-I at the yield of 2.2 g/g and 7.2 g/g. The bright phase is the catalyst particle, and the dark phase belongs to the freshly formed polymer phase. The cross sectional morphology of the polymer particle shows that, at the yield of 2.2 g/g, the polymer

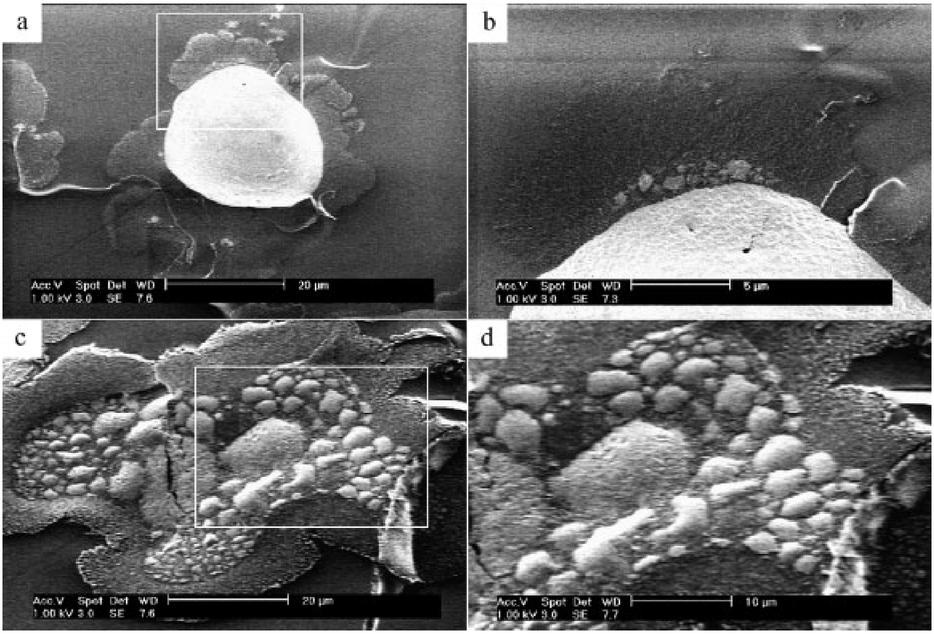

Figure 5.
LVSEM images of cross sectional morphology of poly(propylene) particles polymerized from catalyst-I at the yield of a) 2.2 g/g, and b) 7.2 g/g. The rectangles mark the area of the corresponding higher magnification images.

grows on the surface of the particle, and the catalyst particle remains unfragmented in the center of the particle. At higher magnification and close to the surface of the catalyst in the center, the catalyst microparticles with the diameter in the order of 1–2 μm can be clearly recognized (Fig. 5b). It shows that the polymer growth takes place on the surface and the hydraulic force can only break the external layer of the catalyst particle. With polymer growth the catalyst breaks intensively (Figs. 5c and 5d). Not only the catalyst close to the outer surface breaks up into a large amount of sub-particles, but also the catalyst in the center starts to fragment. The polymer phase formed is very compact. The catalyst break-up in propylene homopolymerization from catalyst-I shows a typical layer-by-layer fragmentation, because the catalyst fragmentation starts at the outer surface of the particle and break-up gradually continues to the center.

A very different type of fragmentation was observed in propylene polymerization by using catalyst-II (Figure 6). Although polymerization conditions, such as monomer pressure and polymerization temperature, are the same as for polymerization with catalyst-I, catalyst-II shows a very rough and instantaneous fragmentation. Figures 6a and 6b show the cross sectional morphology of polymer particles at the yield of 0.8 g/g. It is seen that just a little amount of already produced polymer breaks the whole catalyst particle into a large amount of small sub-particles, with the diameter up to 10 μm. The cross sectional morphology of polymer from catalyst-II at the yield of 1.4 g/g is shown in Figures 6c and 6d. The polymer particle presents a very porous structure. The catalyst particles have been broken up intensively and it is hard to detect the catalyst fragments. The fragmentation behavior of catalyst-II is similar to the report in Pater's work.[16]

From the morphological investigation of propylene homopolymerization in Figures 5 and 6 it is seen that the catalysts can break up in different ways. It can fragment layer-by-layer, from the outer surface gradually to the center of the catalyst particle, or it can break up instantaneously at the beginning of the polymerization. The different fragmentation behavior observed is believed to be the result of different particle porosity. The BET measurements show that catalyst-II has larger pores (Table 1) and at the same time a larger surface area than catalyst-I. It can be deduced that polymerization with less porous particles tends to take place only at the exterior and close to the catalyst/polymer particle surface due to the monomer diffusion limitation. In contrast, the highly porous catalyst particles have large 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 at the center of the catalyst particle. The hydraulic pressure build-up throughout the whole particle generates an instantaneous fragmentation.

Propylene-ethylene copolymerization were carried out by using the two catalysts to investigate the influence of the comonomer incorporation on the catalyst fragmentation. The cross sectional morphology of the copolymer particles is shown in Figure 7. Comparing the morphology of copolymer (Figure 7) and homopolymer particles (Figures 5 and 6), it is seen that the incorporation of ethylene delayed the catalysts break-up progress, as it is seen that copolymer particles at higher yield show a similar fragmentation degree as the corresponding propylene homopolymer particles at lower yield. This is believed to be the result of the high mobility of copolymer molecular chains. In propylene-ethylene copolymerization, the comonomer incorporation disrupts the polymer crystallization ability and results in a copolymer with low crystallinity. Furthermore, the polymerization temperature (60 °C) is much higher than the glass transition temperature of the copolymer (below 0 °C). As in rubbery state, the copolymer molecules have good mobility. When the copolymer grows around the active sites

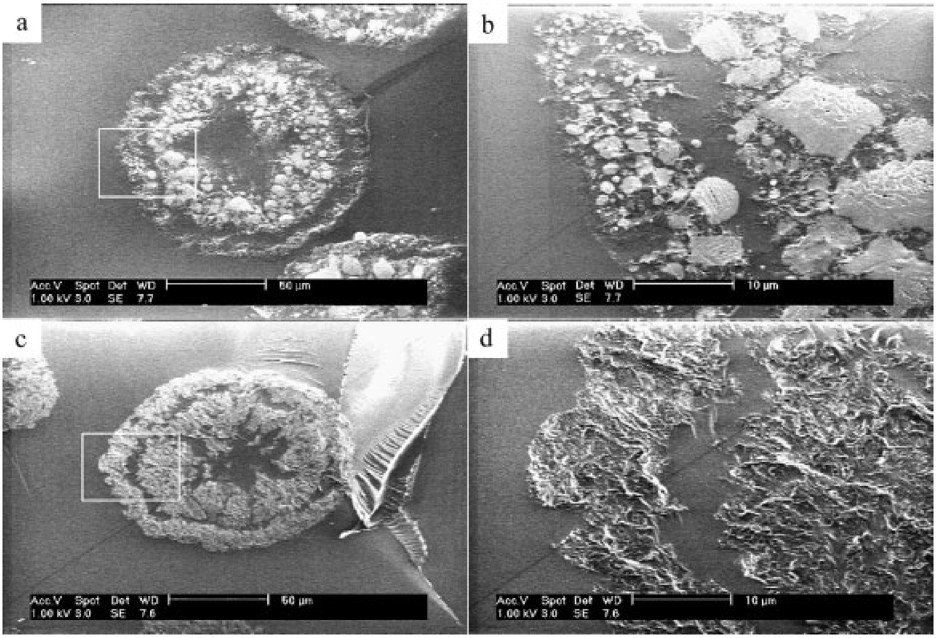

Figure 6.
LVSEM images of cross sectional morphology of poly(propylene) particles polymerized from catalyst-II at the yield of a, b) 0.8 g/g, and c, d) 1.4 g/g. The rectangles mark the area of the corresponding higher magnification images.

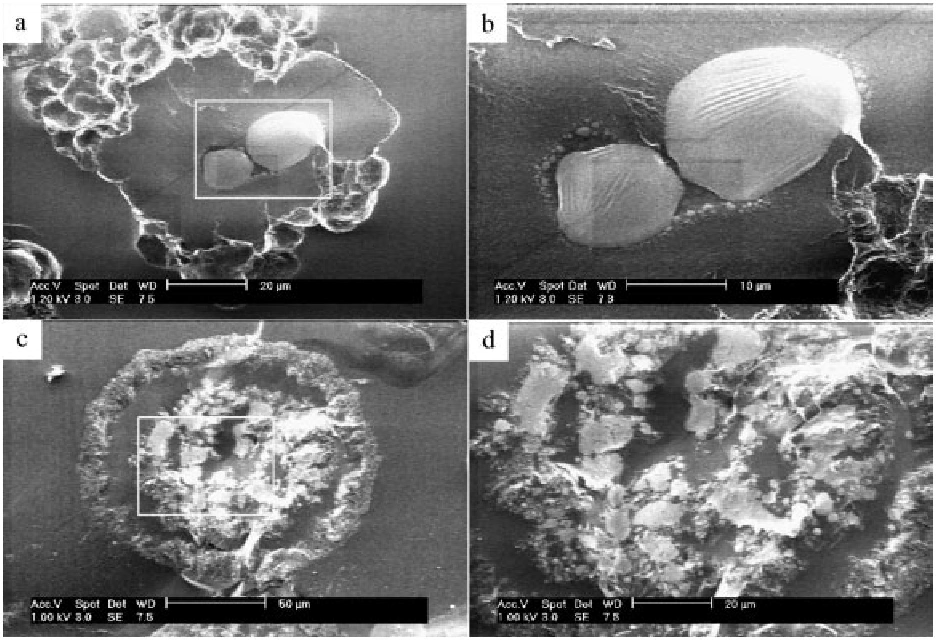

Figure 7.
LVSEM images of cross sectional morphology of propylene-ethylene copolymer particles a, b) from catalyst-I at the yield of 7.0 g/g, and c, d) from catalyst-II at the yield of 1.4 g/g. The rectangles mark the area of the corresponding higher magnification images.

and accumulates in the pores of the support, the hydraulic pressure builds up. Under stress, the copolymer can deform or even flow away from where it forms. The hydraulic pressure is therefore released. Only when more copolymer is formed in the pore and the hydraulic pressure is increasingly built up, the catalyst eventually can break up. Therefore, the catalysts used in copolymerization show a delayed fragmentation.

Conclusion

The fragmentation of the catalyst and the growth of the polymer particle are governed by the competition between the buildup and relaxation of stresses in the catalyst particle. In the present work several parameters are discussed influencing the catalyst fragmentation in the early stages of the polymerization. The active sites distribution on the catalyst particle is a prerequisite condition for a homogeneous fragmentation and good polymer particle morphology. For similar polymerization conditions, the porosity of the catalyst and polymer particle influence the way the catalysts fragment because of different mass transport capabilities. Polymerization with less porous particles tends to take place only at the exterior of a particle due to the monomer diffusion limitation. In contrast, the highly porous catalyst particles have large pores, therefore, less monomer diffusion limitation. The monomer diffuses easily into the pores of the catalyst/polymer particles and polymerization happens at the entire supported catalyst particle. The hydraulic pressure build-up throughout the whole catalyst results in instantaneous fragmentation. The catalyst's break-up progress is retarded in copolymerization, as the result of the high mobility of copolymer molecules.

Acknowledgement: The authors wish to thank *Dr. John C. Chadwick, Dr. Madri Smit, Dr. Makarand S. Pimplapure* and *Dr. Günter Weickert* for providing interesting samples and for stimulating discussion. The authors gratefully acknowledge support from *Dutch Polymer Institute* for Projects #331.

[1] P. Galli, G. Vecellio, *Prog. Polym. Sci.* **2001**, *26*, 1287.
[2] K. Soga, T. Shiono, *Prog. Polym. Sci.* **1997**, *22*, 1503.
[3] G. Cecchin, G. Morini, F. Piemontesi, in: "*Kirk-Othmer Encyclopedia of Chemical Technology*", John Wiley & Sons Inc., New York 2003.
[4] G. Cecchin, G. Morini, A. Pelliconi, *Macromol. Symp.* **2001**, *173*, 195.
[5] G. Weickert, G. B. Meier, J. T. M. Pater, K. R. Westerterp, *Chem. Eng. Sci.* **1999**, *54*, 3291.
[6] G. Cecchin, E. Marchetti, G. Baruzzi, *Macromol. Chem. Phys.* **2001**, *202*, 1987.
[7] X. Zheng, M. S. Pimplapure, G. Weickert, J. Loos, *e-polymer*, submitted.
[8] X. Zheng, M. S. Pimplapure, G. Weickert, J. Loos, *Macromol. Rapid. Commun.* 2006, in press.
[9] M. S. Pimplapure, X. Zheng, J. Loos, G. Weickert, *Macromol. Rapid. Commun.* **2005**, *26*, 1155.
[10] X. Zheng, M. Smit, J. C. Chadwick, J. Loos, *Macromolecules* **2005**, *38*, 4673.
[11] M. Smit, X. Zheng, J. Loos, J. C. Chadwick, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2743.
[12] J. H. Butler, D. C. Joy, G. F. Bradley, S. J. Krause, *Polymer* **1995**, *36*, 1781.
[13] G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347.
[14] T. E. Nowlin, F. Y. Lo, R. S. Shinomoto, P. P. Shirodkar, *U.S. Patent* 5, 332, 706, 1994; *Chem. Abstr.* **1995**, *123*, 11238.
[15] K. Kallio, O. Andell, H. Knuuttila, U. Palmqvist, *PCT Int. Appl.* 95/12622, 1995; *Chem. Abstr.* **1995**, *123*, 257800.
[16] J. T. M. Pater, G. Weickert, J. Loos, W. P. M. van Swaaij, *Chem. Eng. Sci.* **2001**, *56*, 4107.
[17] L. Noristi, E. Marchetti, G. Baruzzi, P. J. Sgarzi, *Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 3047.
[18] M. A. Ferrero, M. G. Chiovetta, *Polym. Eng. Sci.* **1987**, *27*, 1436.
[19] M. A. Ferrero, M. G. Chiovetta, *Polym. Eng. Sci.* **1987**, *27*, 1448.
[20] M. A. Ferrero, M. G. Chiovetta, *Polym. Eng. Sci.* **1991**, *31*, 886.
[21] M. A. Ferrero, M. G. Chiovetta, *Polym. Eng. Sci.* **1991**, *31*, 904.
[22] F. Bonini, V. Fraaije, G. Fink, *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 2393.
[23] J. Zechlin, B. Steinmetz, B. Tesche, G. Fink, *Macromol. Chem. Phys.* **2000**, *201*, 515.
[24] G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla, B. Tesche, *Chem. Rev.* **2000**, *100*, 1377.
[25] S. Knoke, F. Korber, G. Fink, B. Tesche, *Macromol. Chem. Phys.* **2003**, *204*, 607.
[26] B. Steinmetz, B. Tesche, C. Przybyla, J. Zechlin, G. Fink, *Acta. Polymer.* **1997**, *48*, 392.
[27] W. D. Niegisch, S. T. Crisafulli, T. S. Nagel, B. E. Wagner, *Macromolecules* **1992**, *25*, 3910.