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Microkinetic Videomicroscopic Analysis of the Olefin-Copolymerization with Heterogeneous Catalysts

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Summary: Videomicroscopy as a tool for investigating olefin gas phase co-polymerization is presented in this paper. This technique enables the simultaneous detection of the individual growth of a large number of catalyst particles. The focus is to study the kinetic behaviour of different types of Ziegler- and metallocene catalysts and to demonstrate that videomicroscopy can help to assign a given catalyst system to the appropriate model. Further, the density problem, the estimation of activation energies of single grains, the particle volume enlargement of amorphous copolymers and the comonomer effect are adressed.

Keywords: comonomer effect; copolymerization; heterogeneous catalysis; single grain kinetics; video microscopy

Introduction

In industrial practice ethylene and propylene are polymerized predominantly by slurry, bulk, and gase phase processes with heterogeneous catalysts. The catalyst is typically supported on and in a porous microsphere on and in which the polymer grows. In this way the original form of the catalyst particle is used to control the morphology of the final product (catalyst grain - polymer grain replica). Because of the hydraulic forces due to the growing polymer, the catalyst particle breaks into nanometer-sized fragments. This fragmentation process is a decisive step in the determination of the final particle morphology and was investigated with increased endeavor in the recent time [1–14]. According to the "polymer growth and particle expansion model" [2–5], the polymerization process e.g. for a heterogeneous metallocene/MAO/SiO_2 catalyst can be summarized as follows. In the initial prepolymerization phase a thin shell of polymer is formed on the particle at the beginning of the polymerization process. This is followed by a phase of reduced activity, caused by the diffusion-limiting effect due to the crystalline polymer layer. After this "diffusion phase" the active centers in the inner part of the particle are also provided more and more with monomer. Because of the hydraulic forces from the growing polymer, fragmentation of the SiO_2 support from the surface to the interior occurs. Consequently new active centers are released and the overall polymerization rate increases. These different stages of the starting catalyst and the subsequent polymerization process are demonstrated in Figure 1. Especially Figure 1 right, the expansion phase exhibits clearly how the SiO_2 support material, which was initially composed of particles 30–60 μm in size, now corresponds to the primary particles 10–20 nm in size within the polymer matrix.

$MgCl_2$, as a support for polymerization catalysts fragments much more extensively at low polymer yields, since it consists of agglomerations of small crystalline subparticles, which are more loosely aggregated than in the case of SiO_2. Hence, high polymerization rates are reached immediately (multigrain model [15], polymeric flow model [16,17]).

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The main parameters influencing the catalyst fragmentation include the nature of the support material and the distribution of the active species therein, the polymerization rate especially in the early stages, the mass and heat transfer in dependence on particle porosity, crystalline and amorphous compartments of the polymer and finally monomer concentration and reaction temperature. X. Zheng and J. Loos have recently summarized up [Lit. 2005] that there are only two kinds of fragmentation behaviour, which can come forward with the different supports: i) the catalyst fragments layer by layer, gradually from the outer surface to the center of the particle, or ii) at the beginning of the polymerization there is an instantaneously break up into a large amount of sub-particles.

During the last ten years, videomicroscopy has been introduced as tool for investigating the kinetics of growing particles [18,19,14,8–10] [20, 21 and 22 with experimental detail]. This technique enables the simultaneous detection of the individual growth of a large number of catalyst particles. In addition to visualizing polymer growth and the replication of catalyst morphology it is able to obtain detailed information about the polymerization kinetics of numerous catalyst particles, which act as discrete microreactors in the industrial process. In this paper, the application of videomicroscopy for the investigation of α-olefin copolymerization is presented. The purpose is to study the kinetic behaviour of different types of Ziegler- and metallocene catalyst systems during gas phase copolymerization and also to demonstrate that videomicroscopy can help to assign a given experimental catalyst system to the appropriate model. Together with ^{13}C NMR analysis it was possible to explain certain aspects of copolymer growth and the comonomer effect.

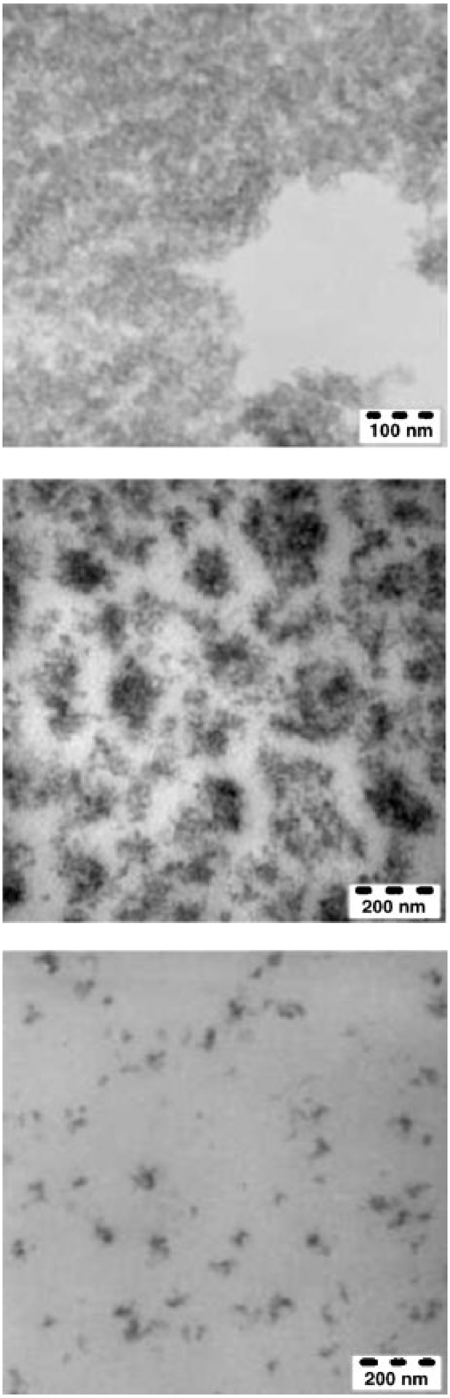


Figure 1.
TEM images of ultrathin sections of a metallocene/MAO/silica catalyst particle (top), of a polymer particle during the fragmentation phase (middle) and of a polymer particle during the expansion phase (bottom).

Results and Discussion

Video microscopy (see Figure 2) consists of a combination of a 50 ml gas phase reactor

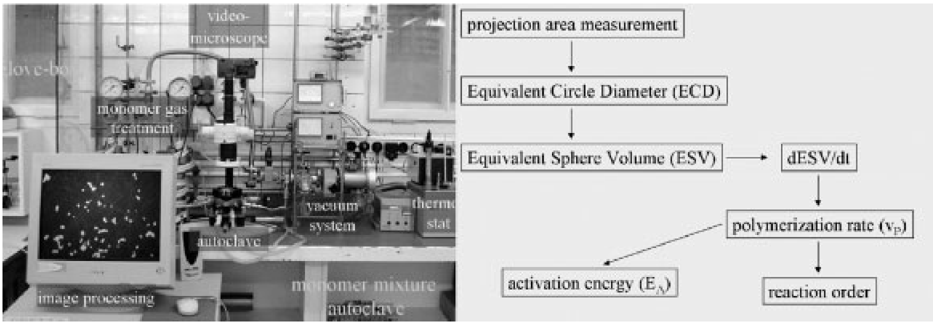


Figure 2.
Video microscopy equipment (left) and particle growth evaluation (right).

with a microscope connected to a digital camera that allows the observation of single catalyst grains during the whole polymerization. The collected images are processed to determine the projection area of each catalyst particle. Although the projection area of the particles is the primary quantity measured, it is easier to comprehend the size of the particles in terms of their diameter and volume (see Figure 2 right). The projection area can be used to estimate the diameter of a circle of equivalent area (equivalent circle diameter, ECD) or from that the volume of a sphere having an equivalent projection area (equivalent sphere volume, ESV).

Dependence on Temperature

For example, Figure 3 shows the ECD versus time curves of a silica supported metallocene/MAO catalyst system. The additional interesting parameter here is the dependence on the temperature. Looking at the shape of the curves, at low temperature (13 °C) we are in the phase of low activity, which is the diffusion phase. With increasing temperature this phase is shortened more and more and the steep and steeper curve

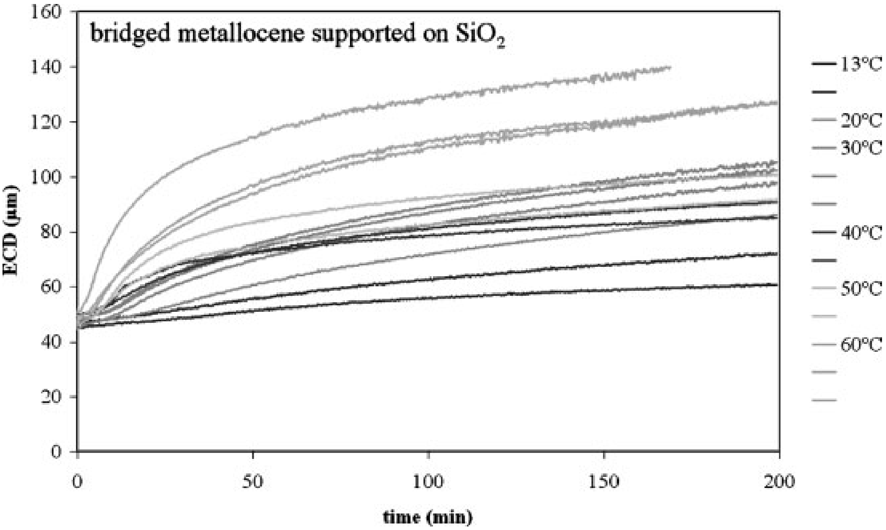


Figure 3.
ECD versus time curves for a bridged metallocene/MAO catalyst supported on SiO_2 in dependence on temperature (2 bar ethylene).

segments of the particle fragmentation phase appear earlier and earlier, followed then by the particle expansion phase. This behaviour clearly assigns this silica supported catalyst system to the ‘‘polymer growth and particle expanding model’’and illustrates impressive the potential of the videomicroscopy. Please realize, every temperature in Figure 3 represents separate experiments and the curves with the same temperature represent different single catalyst grains of comparable diameter. Hence, the question arises: can we compare grains with grains from different experiments? Our experimental results prove: the more homogeneous the distribution of the catalyst components in the support volume the more correct is the comparison. Figure 4 shows the activation energies calculated from the curves from Figure 3 by means of two ways. Similar E_A-values (35 kJ/mol and 37 kJ/mol respectively) obtained are the proof that the Al- and the Zr-compound are homogeneously distributed in all grains of this catalyst charge and additionaly, that no deactivation of active centers on the surface has taken place during these experiments because of impurities.

Density Problem

For the calculation of the polymerization rate v_p the ECD curves were converted into the ESV curves and from these the derivation dESV / dt formed (Figure 5 top). In the formula for v_p a decisive problem appears: that is in the nominator the term d_{PE}, the density of the growing catalyst-polyethylene-grain, which is changed during the polymerization. We describe this fact with the terminus ‘‘density problematic situation’’, which is an unsolved question in the literature. In order to investigate this fact we measured in experimental series the density in dependence of time. A result is shown in Figure 5 bottom and indeed, starting with the density of a SiO_2 supported catalyst system the density of the growing and expanding particle is decreased considerably. With the program ‘‘OriginPro7’’ a ‘‘Fit-Function’’ was generated, which describes the course of the density versus polymerization time exactly. This ‘‘Fit-Function’’ is also used to convert the ESV into the activity of a single particle in g_{PE} / mol_{Zr} h, which is important for industrial application.

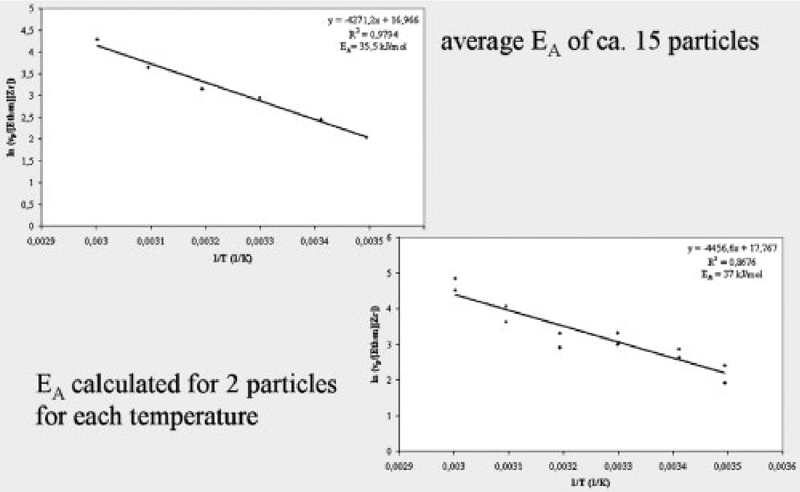


Figure 4.
Estimation of the activation energies from the single grain kinetic curves of Figure 3. Arrhenius plot of ln v_p, the polymerization rate normalized on the Zr- compound concentration and on the ethylene concentration, versus reciprocal tem-perature in K.

$$v_{P_{MAX}} = \frac{dESV/dt_{MAX} \cdot d_{PE}}{V_R \cdot MG_E \cdot 60}$$

v_p: polymerization rate [mol_E/l s]
$dESV/dt_{max}$: maximum of the differentiated ESV-profiles [cm^3/min]
d_{PE}: PE density [g/cm^3]
MW_E: ethylene molecular weight [g/mol]
V_R: reactor volume [l]

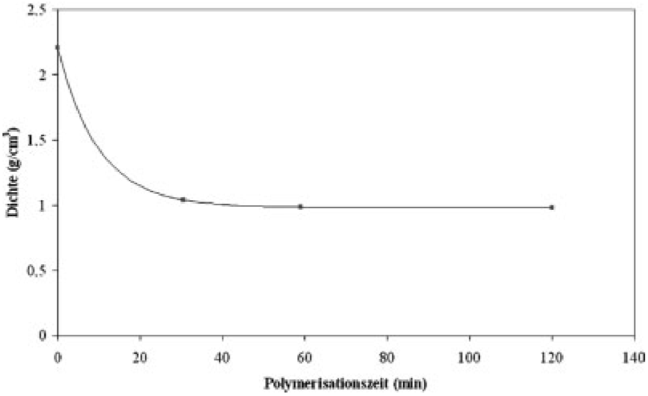
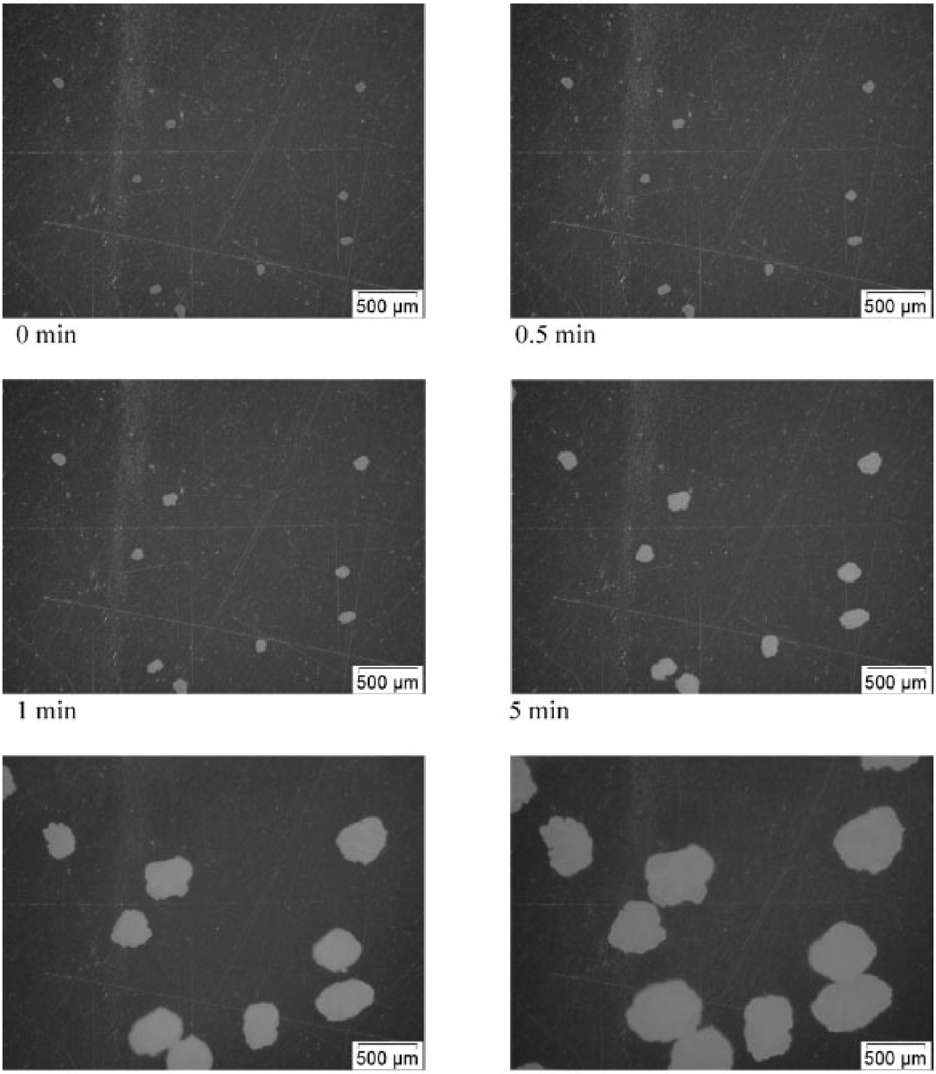


Figure 5.
Formula for the experimental estimation of the polymerization rate of single grains (top); density measurements after different polymerization times (0, 30, 60 and 120 minutes at 50 °C and 2 bar ethylene) and mathematical construction of the "Density-Fit-Function" (bottom).

Ethylene-Propylene Copolymerization with a $MgCl_2$ supported Ziegler-Catalyst

Figure 6 demonstrates a sequence of snapshots of growing particles during the ethylene-propylene copolymerization after 0, 0.5, 1, 5, 30 and 165 minutes of polymerization with an industrial Ziegler-Catalyst. This catalyst consists of $TiCl_4$ on $MgCl_2$, is activated with TEA and an external donor and was originally optimized for propylene gas phase polymerization. Contrary to silica supported systems the $MgCl_2$ support particles of this system have a brown color because of the $TiCl_4$ compound. Already after 30 seconds a growth of the catalyst grains can be observed and after 1 minute because of the increasing polymer amount the color of the particles begins to change from brown towards white. Moreover in the first 30 minutes the particle expansion augments very fast, all particles expand equable and the initial round (spherical) form of the catalyst grains remains preserved during the whole polymerization. In other words, this system shows a very good catalyst grain polymer grain replica and is best appropriate for the videomicroscopic kinetic investigation. This is also proved in Figure 7, in which again the ECD curves are plotted versus the polymerization time. The copolymerization rate and therefore also the particle expansion starts immediately and accelerates very strong



0 min 0.5 min

1 min 5 min

30 min 165 min

Figure 6.
Snapshots of the growing particles during ethylene-propylene copolymerization (feed ratio P:E 0.67) with a $MgCl_2$ supported Ziegler-Catalyst at 50 °C and 2 bar. Initial diameter of the grains ca 90 μm.

until to the flattening of the curves due to the longer diffusion paths of the monomer through the polymer.

This is the reason that no comonomer effect can be observed with this high active catalyst system. According to the shape of the single particle curves, this catalyst system can be descibed with the "multi grain model".

Ethylene-1-Butene Copolymerization with the $MgCl_2$ supported Ziegler-Catalyst

As mentioned above, also the sructure and the morpholgy of the polymer coming into existence influence the kinetic of the growing polymer particles. In the case of the ethylene-propylene copolymerization a solid partially crystalline copolymer resulted. In the case of the ethylene-1-butene

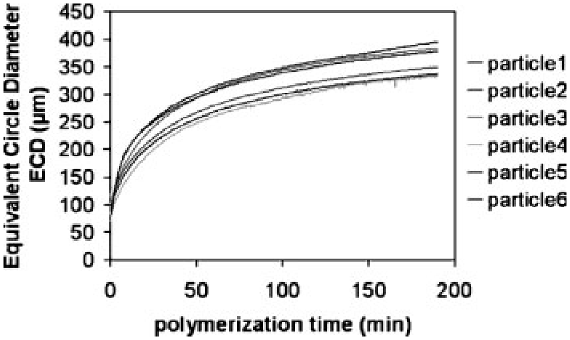


Figure 7.
ECD curves versus time for the ethylene-propylene copolymerization with a $MgCl_2$ supported Ziegler catalyst activated with TEA and an external donor (2 bar monomer mixture and 50 °C).

copolymerization an amorphous rubber like voluminous copolymer is formed. This amorphous copolymer has a much lower density than a polymer with many crystalline compartments; hence, in other words, the volume of an amorphous polymer is larger than the volume of a comparable crystalline polymer. The sequence of Figure 8 demonstrates snapshuts of growing particles during the ethylene-1.butene copoly-merization after 0, 1, 5, 30, 60 and 165 minutes of polymerization with the highly active Ziegler-Catalyst. Again within the first 30 minutes the particle growth augments very fast, all particles expand equable and maintain theire spherical form and the system shows an excellent catalyst grain polymer grain replica. But the new interesting aspect now is the particle volume enlargement due to the lower density of the formed amorphous copolymer.

This volume enlargement effect additionally is reflected in the shape of the ECD versus time curves in Figure 9. Again the copolymerization and the particle expansion start immediately and accelerate very strong; but the impression arises that there is a stronger particle expansion and hence a faster copolymerization rate. In this context one compare the copolymer particle end-diameters from Figure 7 with ca 350 µm and from Figure 9 with ca 500 µm.

Ethylene-1-Butene Copolymerization with an unbridged Metallocene/MAO Catalyst supported on SiO_2

The catalyst used in this investigations which try to clarify the comonomer effect consists of the metallocene $[(R)\ Cp]_2ZrCl_2$ supported on MAO/silica and is industrially used for the copo-lymerization of ethylene with small amounts of higher α-olefines. A paper in detail about our investigations, results and explanation concerning the comonomer effect is published recently [21]. Hence, we can shorter treat this theme in this last section.

Figure 10 shows the ECD plots versus time derived from the particle projection areas of the corresponding ethylene-1-butene copolymerization snap shut sequences for different 1-butene to ethylene ratios in the feed gas.The general growth profile for the copolymerization with different feed gas ratios (Figure 10((b)–(d))) is characterized by an initial low activity (induction period, diffusion phase), followed by a steep increase of the ECD curves (fragmentation phase) and a consequent milder slope (expansion phase). These different stages are more prominent with increasing particle size, as the number of active sites is greater.Similar to the results for the ethylene-propylene copolymerization [21], the induction period becomes more pronounced with increasing 1-butene concentration in the feed gas

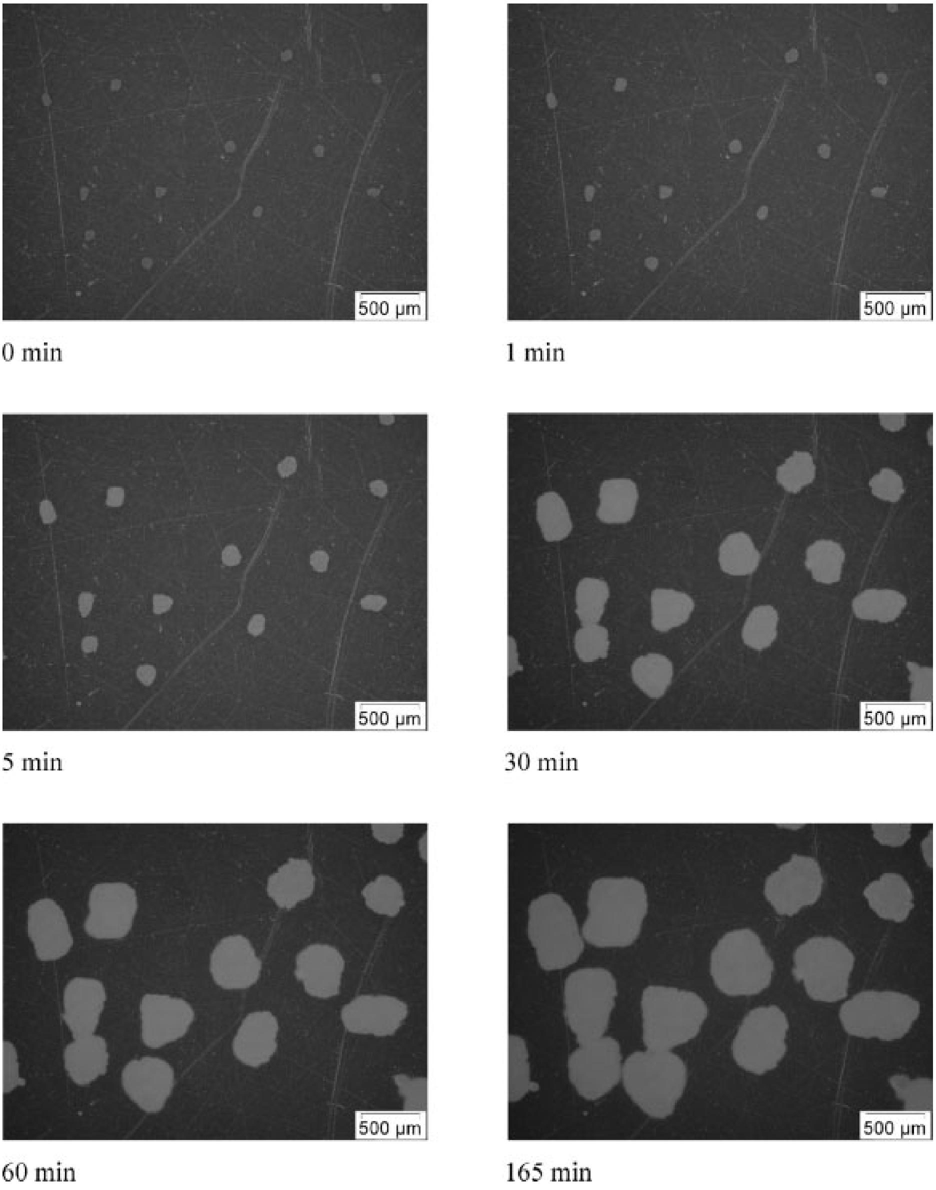


Figure 8.
Snapshuts of the growing particles during ethylene-1-butene copolymerization (feed ratio B:E 0.40) with a $MgCl_2$ supported Ziegler-Catalyst at 50 °C and 2 bar monomer mixture. Initial diameter of the grains ca 90 µm.

(Figure 10(a)–(d)). This in turn shows that the early stages of the copolymerization proceed more slowly with increasing 1-butene content in the feed gas. Additionally, the simultaneously measured overall gas consumption increased upon addition of small amounts of 1-butene in the feed gas to reach a maximum at a 1-butene to ethylene ratio of 0.10 (Figure 10(b)) and then decreased again. In this way the so called “comonomer effect” could bedetected directly and assigned to the relevant comonomer concentration. These informations led finally to adapting

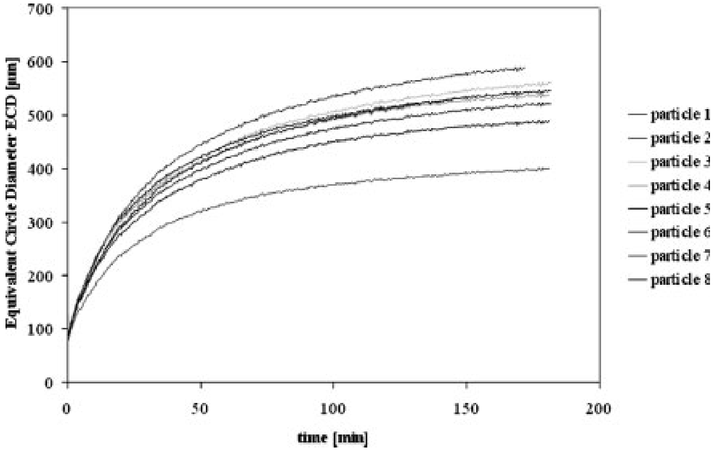


Figure 9.
ECD curves versus time for the ethylene-1-butene copolymerization with a $MgCl_2$ supported Ziegler catalyst activated with TEA and an external donor (B:E 0.40, 2 bar monomer mixture and 50 °C).

the ''polymer growth and particle expansion model'' to the copolymerization of ethylene with propylene or 1-butene as follows. At the beginning of the copolymerization a thin layer of copolymer rich in ethylene and thus crystalline is formed and hinders monomer, especially the α-olefin, diffusion through the layer to the inner active centers, resulting in a decreased catalytic activity. At this point, a higher α-olefin concentration produces greater comonomer diffusion through the

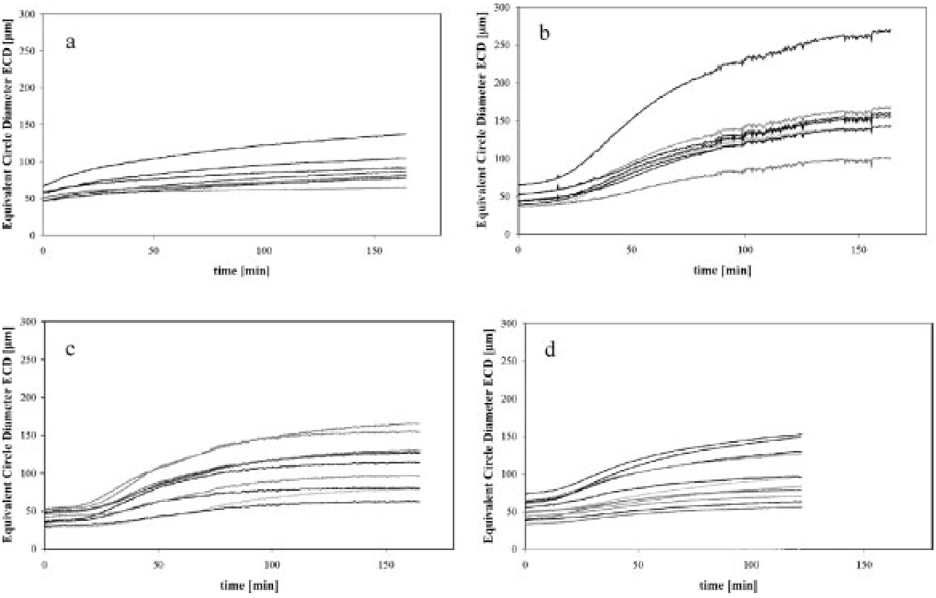


Figure 10.
ECD curves versus time for the ethylene-1-butene copolymerization with an unbridged metallocene/MAO catalyst supported on silica at 30 °C and 2 bar. B:E in the feed gas: (a) 0, (b) 0.10, (c) 0.11 and (d) 0.25. The curves in (a)–(d) represent particles with different size.

polymer layer that results, after a comparable diffusion time, in a greater occurrence of the comonomer effect. This gives rise to particle fragmentation by which new active centers are released which become accessible to propylene or 1-butene as well. In this way particle expansion occurs and the copolymer becomes richer and richer in α-olefin leading to a more amorphous copolymer that shows a grater final particle volume.

By closer observation of the Figure 10(d) it can be notized that the image processing was only possible for the first 122 minutes. As described previously [20] a high contrast is re-quired to allow digital evaluation, which was not more obtained after 122 minutes of copolymerization because the particles became transparent. A reasonable explanation for this phenomenon is that at higher 1-butene concentrations the the molecular weight decreases since the β-hydrogen elimination reaction is more favored and the copolymer becomes amorphous.

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