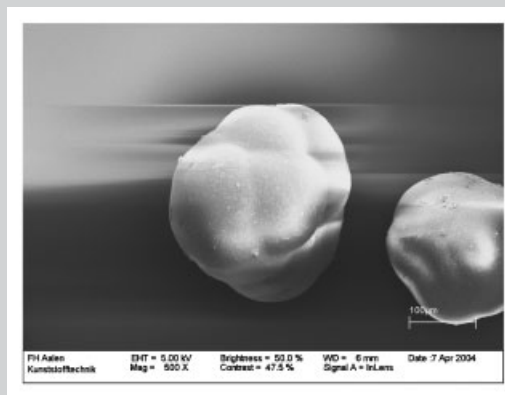


Summary: A comparison of PP qualities, which are produced with two different polymerization techniques—gas phase (GP) and liquid pool (LP)—under precise control of the polymerization temperature (70 °C) and pressure (GP = 25 bar, LP < 60 bar) using identical Ziegler-Natta catalyst (TiCl₄/phthalate/MgCl₂ + TEA/silane), is presented. A series of homopolymer PP in a wide MW range from 100 000 to 1 600 000 g · mol⁻¹ was polymerized. During polymerization all samples were characterized exactly by their Rp-profil. The effect of hydrogen on the initial reaction rate and on MW and MWD was analyzed on the basis of this so-called kinetic fingerprint. The results showed that the polymerization rate reached a maximum for LP, of about 150 kg · g_{cat}⁻¹ · h⁻¹, in contrast to GP with a maximum of R_{p,0} = 45 kg · g_{cat}⁻¹ · h⁻¹. Analysis was carried out by means of GPC, SEM, DSC, platte-platte rheometer, and WAXS. The results first showed that the MWD of LP PP is narrower (PD ~ 6.8) than for the GP PP (PD ~ 8), polymerized in two steps. An SEM study of the powder particle shows the typical dent surface morphology of polymers using Ziegler-Natta catalysts for polymerization. WAXS and DSC analysis demonstrated that almost only the α-modification of crystalline structure exists and that the crystallinity becomes considerably higher after solidification from melt. Further-

more, it was found that the crystallite size distribution depends on the polymerization technique. Rheological studies indicate that GP PP behaves more elastically. To summarize, it is shown that PP produced with the LP polymerization technique is more homogenous and of high quality.



Particle geometry of gas phase and liquid pool polymerized PP powder observed by SEM (PP-L0).

Comparison of Gas and Liquid Propylene Polymerization Technique – Hydrogen Effect on Thermal, Rheological, and Morphological Properties of PP

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Introduction

Poly(propylene)s are commercially produced using different polymerization processes; the main ones are the gas phase (GP) processes with a fluidized bed reactor and liquid bulk processes with a bulk loop reactor.^[1–3] In leading polymerization technologies, such as Spheripol and

Spherizone (both Basell), Unipol (Dow), Innovene (BP) and Borstar (Borealis), both methods come in use, and are even coupled in some cases. However, the liquid pool (LP) process is increasingly gaining importance. Here, it should be noted that the so-called slurry process is in a liquid phase as well, but in this process the liquid propylene is dissolved and polymerized in a solution (e.g., hexane or

heptane). By contrast, the LP process uses pure liquid propylene monomer itself as a reaction medium. In comparison with the GP process, this results in two advantages: a higher polymerization rate due to higher monomer concentration and no eliminating of additional components. This leads to a reduction in operation costs and consequently, to efficient production of poly(propylene) (PP).

In the past, many endeavors have been made to achieve a continuous improvement in reactor operability and better control of the polymer properties. In particular, a lot of kinetic and morphological analyses form the basis of these endeavors, which is supported by numerous publications.^[4–31] Furthermore, there are many articles discussing the final properties of plastic parts influenced by structural changes and processing conditions.^[32–36] However, these papers contain hardly any information about the “kinetic history” of synthesized polymers and moreover, there are no studies which compare PP quality obtained from experiments carried out in gaseous and liquid propylene and using identical modern Ziegler-Natta (ZN) catalysts.

Furthermore, the knowledge about the effect of the polymerization technique on the polymerization kinetics and the characteristics of synthesized polymer is very important for fundamental understanding of the relationship between the catalysts behavior, polymerization process, chain structure, processing behavior, and end-use properties. Gahleitner^[37] has announced this knowledge, reaching from the production of polymers to their final properties, as the so-called “chain of knowledge,” which is an important tool in speeding up market-oriented product development.

On this basis, this article focuses on the comparison of the structure and characteristic properties of synthesized PP, using gas phase and liquid pool polymerization processes with identical highly active Ziegler-Natta (ZN) catalyst and also takes polymerization kinetics into consideration. Of primary interest is the comparative study of the influence of hydrogen on the thermal, rheological, and structural properties of gas phase and liquid pool PP.

Experimental Part

A series of gas phase (GP) and liquid pool (LP) polymerization experiments of propylene, with highly active Ziegler-Natta catalyst, was carried out under industrial reaction conditions. The hydrogen concentration was varied from 0 to 1 500 mg H₂ in a 5 L volume reactor, to achieve a wide average molecular weight (MW) range from 100 000 to 1 600 000 g · mol⁻¹. The modern catalyst used, was an MgCl₂/TiCl₄ catalyst in conjunction with triethyl aluminum (TEA) as co-catalyst, an internal phthalate donor, and an external silane donor, which is suitable for GP and LP propylene polymerization. The catalyst was activated in a glove box in nitrogen atmosphere. The external silane donor, TEA and hexane were mixed together in a vial. The contact time of 30 min of the components leads to

complexation of the silane and the TEA at room temperature. In a second vial the catalyst was diluted in hexane. 10 min after the mixture of the external donor and TEA was injected, the diluted catalyst was injected too.

Additionally, two commercially available industrial samples—one synthesized in GP and one in liquid phase, were comparatively studied.

Polymerization

The polymerization of propylene in GP and LP was carried out in a 5 L stainless steel autoclave reactor. This reactor is equipped with a PID temperature control system to control the water cooling system for maintaining quasi isothermal conditions. For all tests the reaction rate is measured using a calorimetric principle. Under isothermal bulk conditions and assuring a constant heat transfer coefficient from reactor to jacket, the temperature difference between reactor and jacket is a measure for the reaction rate. The experimental setup and data analysis has been described in detail by Al-haj Ali^[11] and van Putten.^[12]

For liquid pool polymerization, the reactor was first filled with liquid propylene at room temperature, which reached a pressure of about 35 bar. Before filling hydrogen, the reactor was successively heated up to the polymerization temperature of 70 °C, whilst, simultaneously the rising pressure was reduced by flushing the system, always ensuring that the reactor was completely filled with liquid propylene. After this the reactor was enriched with the required hydrogen to a total pressure of maximum 60 bar. Then the polymerization reaction was started by injection of the scavenger and the catalyst in succession. Approximately between 30 and 60 min the polymerization reaction was terminated by injection of methanol. The reactor was exhausted and cooled down and afterwards flushed several times with nitrogen to remove the last monomer. The powder was finally taken from the reactor and dried for 4 h in a vacuum oven at a temperature of 50 °C.

The gas phase experiments were performed in a sequence of pre-polymerization to prevent thermal runaway of the growing particle in the initial stage and gas phase main polymerization. First pre-polymerization was carried out in liquid pool almost similarly to liquid pool polymerization described above. Pre-polymerization was performed at a moderate temperature of 40 °C and started with the injection of scavenger and catalyst. The scavenger was injected 5 min prior to the catalyst. After successful pre-polymerization (about 20 g pre-polymer has been prepared), the reactor was flushed at 60 °C and filled with gaseous propylene and subsequently hydrogen. During the gas phase polymerization process, the pressure was kept constant at 25 bar by adding gaseous propylene through an automated mass flow controller. To end the experiment the reactor was flushed off and the powder was taken from the reactor and dried for 4 h in a vacuum oven at 50 °C.

The specific properties of the synthesized PP powder, polymerized in GP and LP, and the industrial PP samples are listed in Table 1. The PP samples polymerized in the laboratory exist in the form of powder as opposed to the industrial samples, which are available in form of granules. That means, the PP

Table 1. Polymerization conditions and related molecular properties of poly(propylene) samples.

Sample ^{a)}	H ₂	H ₂	$\bar{M}_w \times 10^{-3}$	Polydispersity (PD)
	mg	mol-%		
PP-L0	0	0	1 600 ^{b)}	na ^{c)}
PP-L25	25	0.02	1 120	6.4
PP-L50	50	0.05	833	6.6
PP-L150	150	0.15	462	7.2
PP-L250	250	0.26	320	6.8
PP-L500	500	0.51	244	7.3
PP-L1000	1 000	1.00	153	7.3
PP-L1500	1 500	1.56	101 ^{b)}	na
PP-LI	na	na	265	5.7
PP-G0	0	0	1 120	9.4
PP-G25	25	0.18	1 150	8.0
PP-G50	50	0.37	877	7.9
PP-G100	100	0.73	444	7.1
PP-G150	150	1.09	417	7.4
PP-G1500	1 500	9.92	157	9.1
PP-GI	na	na	395	4.9

^{a)} L indicates liquid phase PP; G indicates gas phase PP; I indicates industrial PP.

^{b)} Evaluated from rheological data.

^{c)} na, not analyzed.

samples from the industry passed a further processing step. Furthermore, it has to be considered, that the industrial samples were polymerized using different catalysts, and that unknown additives were already added.

Polymer Properties

To avoid any degradation of the polymer during the tests, 1% stabilizer IRGANOX B215 from CIBA, which stabilized the polymer against oxidative and thermally induced degradation during melt processing, was added to the PP powder.

The structural data [average MW and molecular weight distribution (MWD)], were analyzed by GPC at an external institution.

The rheological investigations were carried out using a plate-plate rheometer Gemini 200 from Bohlin Instruments. The shear dependent viscosity (shear thinning behavior) was analyzed in rotation at 200 °C, whereby, the shear rate logarithmically varied from 0.001 to 100 s⁻¹. The shear modulus of polymer melt and its dependency on angular frequency was obtained by oscillation measurements. At a temperature of 200 °C, a sinusoidal strain with constant amplitude of 1%, was applied and the angular frequency was subsequently varied from 0.01 to 100 Hz. For both methods in rheological testing the gap between both plates was 0.5 mm and the measuring system was flushed with nitrogen to avoid any sample degradation.

The thermal investigations by differential scanning calorimetry (DSC) were carried out at a temperature range of 30–280 °C, using a Mettler-Toledo DSC type 821^c. A sample mass of 5.6 mg accurate within a tolerance of ±0.1 mg of PP powder,

was placed in a 20 µl aluminum crucible and was measured in nitrogen atmosphere at a heating rate of 20 K · min⁻¹.

For wide-angle X-ray scanning (WAXS) experiments, the Rigaku Geigerflex was used to measure diffraction intensity versus 2Θ. The measurements were performed within a diffraction angle range of between 10 and 40°. The SEM used for morphological observation was type Gemini from LEO, which operated with an acceleration voltage of 10 kV. Samples were pre-treated by sputtering the surface with Au/Pd.

Results and Discussion

Polymerization Kinetics

The kinetics of GP and LP polymerization, with heterogeneous catalysts, is described using a kinetic model of the first order, which is based on the following assumptions:^[13,14]

- Reaction rate is proportional to the total concentration of active centers in catalysts.
- Activation is completed during pre-contacting.
- Deactivation is first order.
- Use of an active reactivity for the multi-site catalysts.

For isothermal conditions the reaction rate R_p can be described as a function of time according to the following equation:

$$R_p = R_{p,0} e^{-k_d t} \quad (1)$$

with

$$k_d = k_{d,0} e^{-\frac{E_{a,d}}{RT}} \quad (2)$$

Here, $R_{p,0}$ is the initial reaction rate, k_d the deactivation constant, $E_{a,d}$ the activation energy for the lumped deactivation reaction, and T indicates the temperature.

Experimentally, the reaction rate of the LP polymerization, was measured by means of a calorimetric method, which is described by Samson et al.^[13,14] and Pater et al.^[15,16] in more detail. For gas phase polymerization, the reaction rate can be estimated by continuously measuring the pressure inside the reactor and neglecting no sorption of the monomer in the amorphous part of the polymer.^[17,18]

For comparing the polymerization kinetics of GP and LP polymerization processes the initial reaction rate $R_{p,0}$ was mathematically calculated by linearizing the reaction rate-time (R_p - t) curve to the maximum reaction rate and subsequent extrapolation to $t=0$. Figure 1 shows the measured reaction rate as a function of the time for the LP experiments, and the modeled R_p - t curve for PP-L50 (dashed line indicates the fitted and extrapolated R_p - t curve) as an example.

At the beginning of the reaction an obvious rise of the polymerization rate is visible. This effect is caused by the kinetic measurement method and is not valid, due to the fact

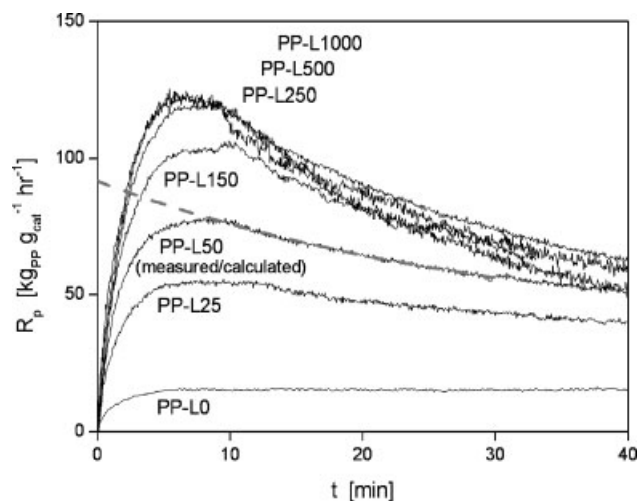


Figure 1. Time dependent reaction rate for liquid pool experiments with different hydrogen amounts.

of the quasi steady state assumption. After the reaction rate passes a maximum, the deactivation of the catalyst is recognizable by a continuous decay of the reaction rate after a polymerization time of about 10 min. There the deactivation process of the active sites on the catalyst depends strongly on the initial activity. For example, the activity of PP-L1000 drops of about 60% from a maximum activity of $R_{p,10} = 120 \text{ kg}_{\text{PP}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ to an activity of $R_{p,60} = 70 \text{ kg}_{\text{PP}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ within 50 min, contrary to almost constant activity of $20 \text{ kg}_{\text{PP}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ in the case of PP-L0.

In fact, the time dependent reaction rate profile (measured at the University of Twente for the first time 1996) reflects characteristically, the polymerization run for each experiment and therefore, it can be considered as a kinetic fingerprint for the respective polymer produced.

Figure 2 shows the calculated initial reaction rate as a function of the hydrogen concentration for GP and LP

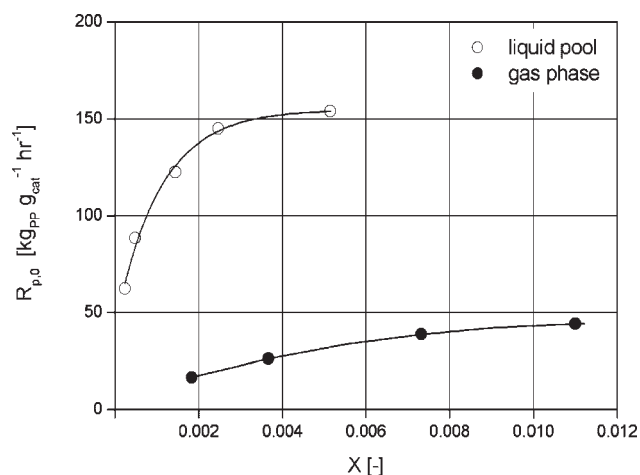


Figure 2. Initial reaction rate in gas and liquid pool as a function of the molar ratio (hydrogen concentration in proportion to the monomer concentration).

polymerization. As mentioned before, the presence of hydrogen increases the initial polymerization rate significantly. It is well known that the hydrogen influences the activity of the catalysts, but the mechanism of the activation process by hydrogen is still discussed controversially.^[13–27] Although different theories exist, the majority of opinion is that deactivated sides (so called dormant or sleeping sides), caused by irregular 2,1 insertion of the monomer, will be reactivated by hydrogen and with that the total activity of the catalyst increases.

For LP, the initial polymerization rate reaches a maximum of about 150 and $45 \text{ kg}_{\text{PP}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ in GP. This difference between the maximum initial polymerization rates can be explained by a higher monomer concentration near the active center in LP polymerization as reported by Meier.^[18]

Natta et al. [1959], were the first to study the hydrogen response on MW of olefin polymerization using $\alpha\text{-TiCl}_3$ catalysts. They found that the experimental data fitted well using Equation (3), where the reciprocal MW is a root function of the partial hydrogen pressure.

$$\frac{1}{\bar{M}_w} = K_1 + K_2 \sqrt{p_{\text{H}_2}} \quad (3)$$

When using the molar ratio instead of pressure, Equation (3) can be rewritten as follows:

$$p_{\text{H}_2} \sim \frac{\text{H}_2}{M} = X \quad (4)$$

$$\frac{1}{\bar{M}_w} = K_1 + K_2 \sqrt{X} \quad (5)$$

where K_1 and K_2 are structural constants and X the molar ratio [hydrogen concentration (H_2) in proportion to the monomer concentration (M)].

Transforming Equation (3)–(5), this function can be easily used for comparing the hydrogen response of GP and LP polymerization. Figure 3 shows that the measurement points for both GP and LP, fit well by using Equation (4). Contrary to the first results of Natta et al., but in accordance with numerous other investigation using modern ZN catalysts, the MW decreases as the hydrogen amount increases even at very high hydrogen concentration, due to an increase in the chain transfer reaction of hydrogen.^[13–27]

By contrast, hydrogen does not influence the polydispersity (PD) of the molecular weight distribution (MWD) significantly. Only negligible changes occur using different amounts of hydrogen for propylene polymerization. The monomodal PD, measured by GPC, varies for LP PP between 6.4 and 7.3. In contrast to this, the PP produced in GP, yields noticeably with a broad MWD of about 8. These are typical values for PP polymerized with a multi-site ZN catalyst of the 4th generation. In the meantime, modern ZN catalysts are capable of producing PP with a PD of about 3,

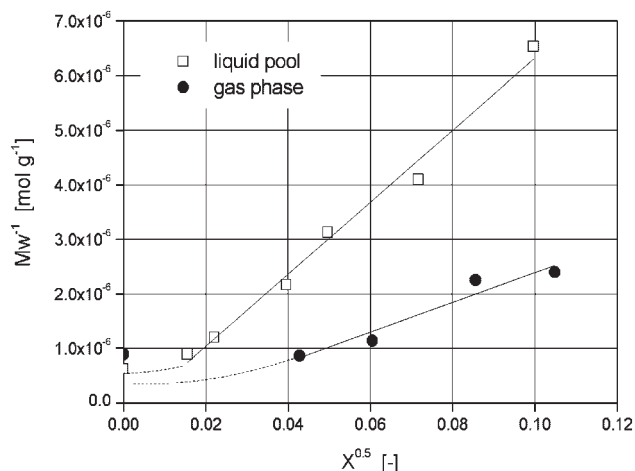


Figure 3. Reciprocal average molecular weight as a function of mole fraction hydrogen for gas phase and liquid pool polymerization.

and with single-site catalysts (e.g., metallocene) it is even possible to achieve polymers with a considerably narrow MWD of about PD = 2.

The MWD can be modeled on the basis of the measured polymerization kinetics. Weickert^[38] [2004] presents a four-site model, which permits the prediction of MWD for LP PP. Figure 4 demonstrates the fitting of the experimental GPC curve with the modeled MWD as example for PP-L50 (solid line indicates the model); as well as for the measured GPC results the model also shows that the PD is not influenced by the hydrogen fundamentally. Here, the PD is little, but not significantly, affected by the polymerization technique used. The PD of GL PP is slightly higher than that of LP PP, because of the mixture of the pre-polymer and the proper polymer, in the case of the two step GP polymerization.

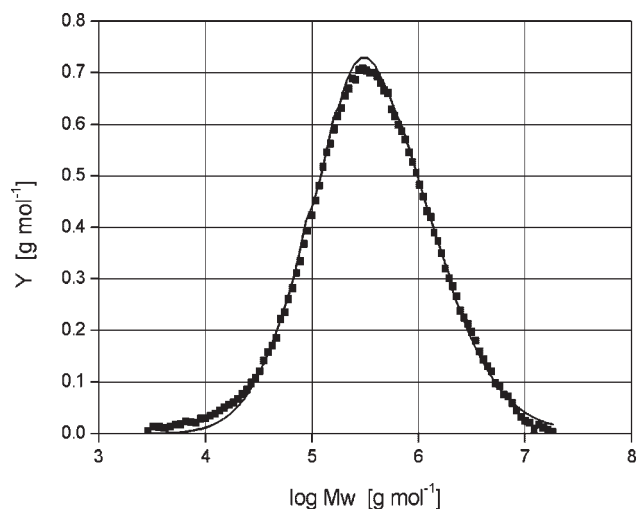


Figure 4. Fitting of experimental GPC curve with a modeled MWD for PP-L50.^[38]

Rheological Properties

By rheological measurements, it is possible to analyze the shear dependent flowing behavior and therefore to characterize the pseudo plasticity of polymer melts, which means its shear thinning behavior, and the zero viscosity.

Figure 5 shows the results of the rheological measurement of LP PP, possessing different average MW according to the concentration of hydrogen during polymerization.

It is obvious that the viscosity of PP polymers, drops as the shear rate increases. At low shear rates, which characterize the Newtonian plateau, the zero viscosity depends on the molecular weight and decreases as the hydrogen concentration increases and therefore as the average molecular weight is lowered. At a higher frequency, the slope of the viscosity curve, representing the pseudo plasticity, varies, depending on the average molecular weight. The slope becomes flatter along with a rise in hydrogen concentration and a lower average molecular weight, respectively.

At low shear rates, molten polymers have a constant viscosity, the so-called Newtonian plateau, which is equivalent to the zero viscosity η_0 and strongly affected by the molecular weight of the sample. It is well known, that above a critical molecular weight M_c , the zero viscosity η_0 relates to the average molecular weight \bar{M}_w according to Equation (6).

$$\eta_0 \approx k \cdot \bar{M}_w^1 \quad (6)$$

The zero viscosity of linear polymers with narrow molecular weight distribution, varies by about (3.4)th power of the weight average molecular weight. In the case of PP, values from 2.9 to 3.8 are presented in the literature.^[37,39–42] However, there are no details about the polymer synthesis (catalysts, polymerization technique, polymerization temperature, etc.) or about additives, such as anti-oxidants or lubricants, which possibly influence these results.

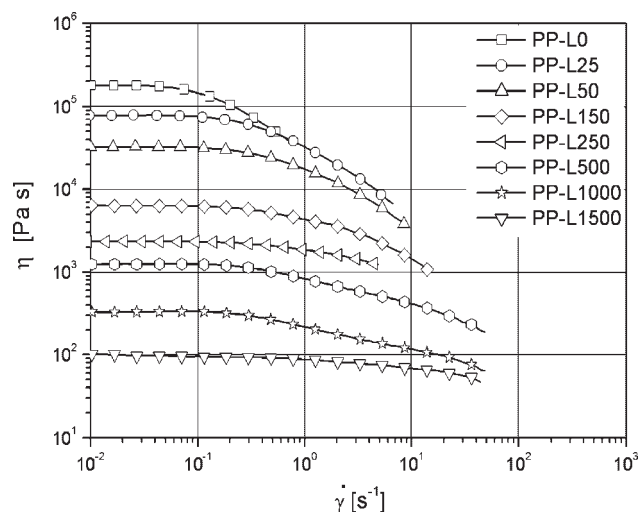


Figure 5. Shear thinning behavior of liquid pool PP series.

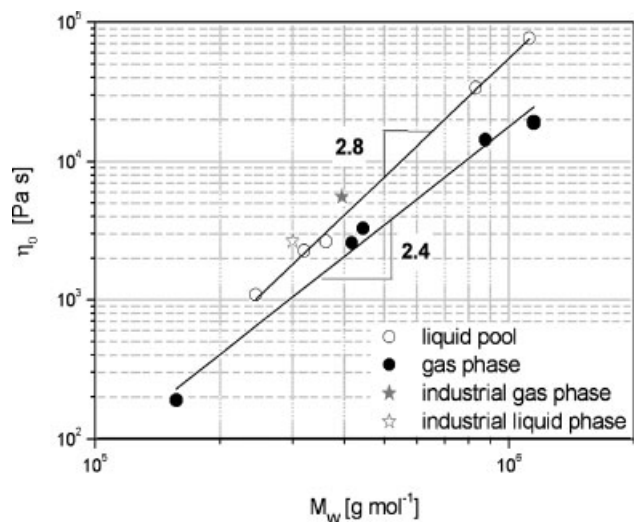


Figure 6. Zero viscosity versus average molecular weight of gas phase and liquid pool PP.

The relationship between the zero viscosity and the average molecular weight of gas and LP PP, is presented in Figure 6. LP PP shows a linear relation with a slope of 2.8, for the mathematical fit of the logarithmic curve. As opposed to experiments in LP, a slope of 2.4 on logarithmic coordinates is found for GP PP. The industrial PP, synthesized in gas and liquid phase, respectively, shows almost the same values than the LP PP.

On the basis of this linear relationship, the average molecular weight for two LP PP samples (PP-L0 and PP-L1500), can be estimated at $1\,600\,000\text{ g}\cdot\text{mol}^{-1}$ for PP-L0 and $101\,000\text{ g}\cdot\text{mol}^{-1}$ for PP-L1500, respectively. The higher molecular weight sample PP-L0 could not be analyzed by GPC due to less solubility in THF. Therefore, investigation of the zero viscosity is an advantage, especially for extremely high molecular weight samples, in order to determine the average molecular weight of these chromatographically undetectable PP samples.

Beside this, the comparison of the gas and LP PP shows lower zero viscosity for GP PP, at the same average molecular weight. This is due to different molecular weight distribution. In the case of broad molecular weight distribution, a countable fraction of short polymer chains exist; these act as lubricants and improve the flow behavior of long polymer chains. Consequently, the broader molecular weight distribution of the GP PP of about $PD = 8$ leads to lower zero viscosity in comparison to LP PP, with an average PD of 6.8. Note, the PD of the industrial GP sample is notably narrower than the PD of the GP PP samples, which were polymerized in the University laboratory.

Additionally, the evaluation of the loss and storage modulus is helpful in gaining useful molecular information. An representation of the storage and loss modulus of the LP PP versus frequency, for three different hydrogen concentrations (changing average molecular weight) is shown in

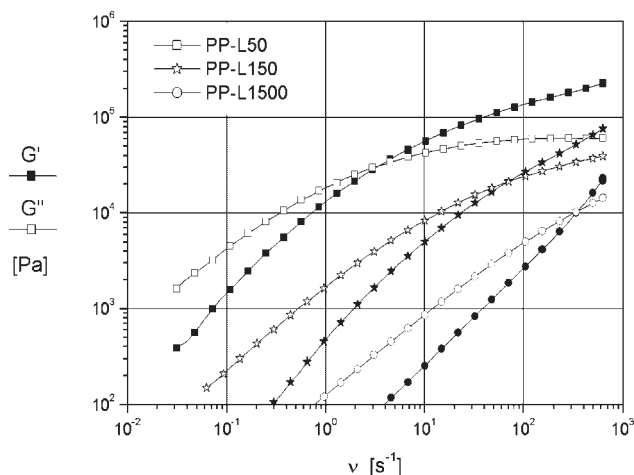


Figure 7. Storage and loss modulus versus frequency of liquid pool PP at $200\text{ }^{\circ}\text{C}$.

Figure 7. In all cases at low frequency the loss modulus (G'') (characterizing the plastic behavior) is higher than the storage modulus (G') (characterizing the elastic behavior). The polymer chains have sufficient time for molecular displacement; this is why they follow the oscillating excitation by rheometer. At higher frequencies the relaxation time of the polymer chains becomes too small in comparison to the input frequency; therefore, the molecular chains lack mobility and flow with less viscosity. In consequence, the storage modulus becomes higher than the loss modulus.

The frequency at which the storage modulus G' crosses the loss modulus G'' is the so-called cross-over frequency. This point depends strongly on the average molecular weight and the molecular weight distribution as shown in Figure 8.

The slight difference in slope between the GP and LP PP, as well as the values of the industrial PP samples, can be explained by the different molecular weight distribution,

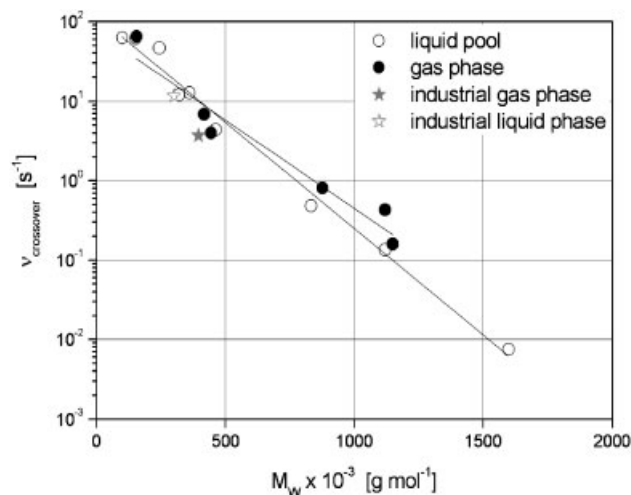


Figure 8. Cross-over frequency, measured by rheometer versus average molecular weight of gas phase and liquid pool PP.

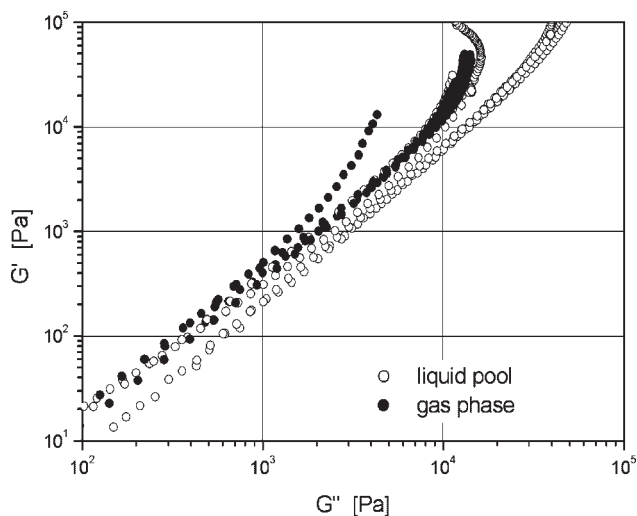


Figure 9. Storage modulus (G') versus loss modulus (G''), measured by rheometer of gas phase and liquid pool PP samples at 200 °C.

just as mentioned above, and is also reported by other authors.^[42,43]

Furthermore, the effect of the molecular weight distribution on the viscoelastic behavior of the polymer melt, can be characterized using a $\log G' - \log G''$ plot, as shown in Figure 9. It was found^[44–47] that such a plot is sensitive to the structural state of polymer and can be used to evaluate the relative intensity of elasticity to viscosity. Harrell and Nakajima^[46] established that G' at a constant G'' , is higher for ethylene-propylene copolymer samples with broader molecular weight distribution. Fujiyama et al.,^[47] verified these results for homopolymer PP samples.

Figure 9 shows the $\log G' - \log G''$ plot for GP PP and LP PP. The measured data of both polymerization experiments are scattered around a straight line. However, the comparison of the storage modulus, at the same loss modulus of GP and LP, shows a higher storage modulus for the GP PP samples. Therefore, GP PP behaves more elastically than LP PP. This can be put down to the narrow molecular weight distribution in the case of LP PP and is in full agreement with the results of Fujiyama et al.^[47]

Thermal Properties

DSC measurements were carried out on different PP materials to study the melt enthalpy, representing the crystallinity of each sample, and its crystallite size distributions. The first heating scans for the series of LP experiments are shown in Figure 10. The dashed line is an assistant line to highlight the variation in the peak maximum location of the melting range with molecular weight. The melting peak of the lower molecular weight PP samples (adding high hydrogen concentration during polymerization) shift to a lower temperature, except for the melting peak of the PP sample PP-L0 where no hydrogen was added during its

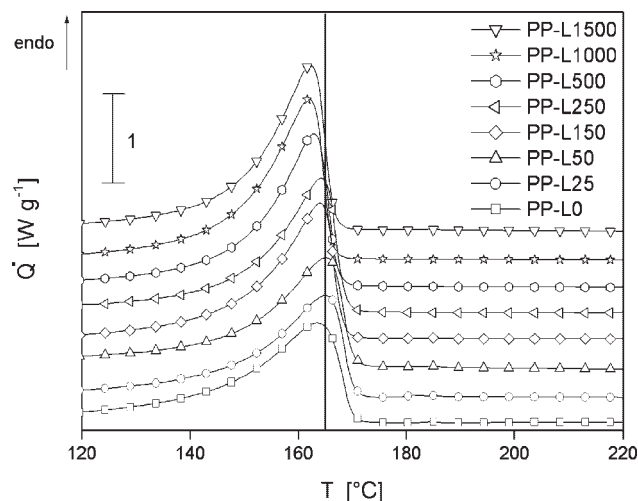


Figure 10. DSC scan for liquid pool PP powder (1st heating, heating rate: 20 K · min⁻¹, N₂ atmosphere).

LP polymerization. This sample takes a special position, although it is scattered around the maximum peak temperature of 165 °C as well as the other samples. The melting point of 165 °C is typical for endothermic melting of the α -phase.^[48–52]

Moreover, it is remarkable that the melting endotherms of the lower molecular weight PP samples, become higher and narrower compared to higher molecular weight materials. This result will be separately discussed in Figure 12.

Figure 11 shows the measured melt enthalpy against the average molecular weight from the first and second heating scan of GP and LP PP samples. The melt enthalpy was integrated in the temperature range from 90 to 190 °C using a linear baseline. As expected, as shown in Figure 11, the melt enthalpy decreases as the average molecular weight

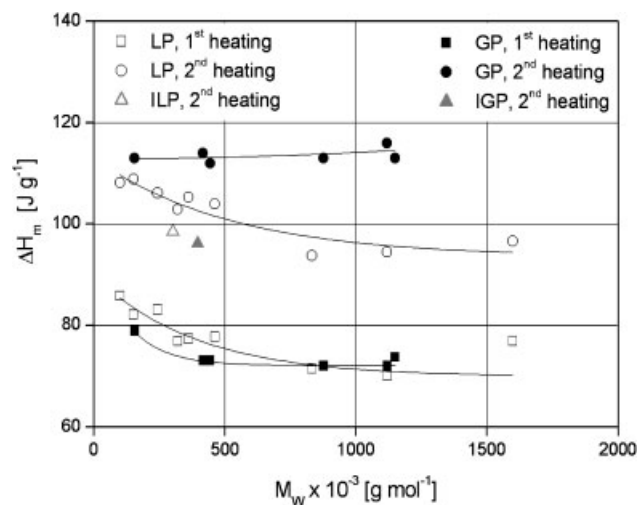


Figure 11. Melt enthalpy versus molecular weight of gas phase and liquid pool PP, determined by DSC.

increases to a minimum melt enthalpy in the first heating scan of about $70 \text{ J} \cdot \text{g}^{-1}$ for both gas and LP PP. This effect occurs because the higher molecular weight polymer hinders the crystallization process, which leads to lower crystalline fraction.

Furthermore, it is apparent that the melt enthalpy of all PP samples, at the second heating, is higher than at the first heating. However, the PP powders were degassed after polymerization and annealed during the drying procedure; this should usually increase the crystallinity. Obviously the folding of the polymer chains to crystallites inside the reactor is not as good as in the melt state.

Moreover, the melt enthalpy from the second heating scan is higher in the case of the GP PP series than that of the LP PP one. This result can be explained in reference to the rheological analysis. It was found that the GP PP shows lower zero viscosity in comparison to LP samples. Consequently, the higher flowability of the GP PP polymers causes improved crystallization capability.

From the industrial PP samples (gas and liquid phase PP samples) only the melt enthalpy of the second heating is demonstrated in Figure 11 because of the fact that these samples contain unknown additives, which can affect their behaviors; and additionally, the samples were melting processed after their polymerization and therefore the thermal history is changed. For these reasons, only the second heating can be discussed with the other PP samples. The melt enthalpy, analyzed in the second heating, of the industrial PP samples is slightly lower than of the PP samples polymerized in the laboratory.

Figure 12 shows the height/width ratio of the melting peak as a function of average molecular weight for both gas and LP PP samples. The height/width ratio describes the crystallite size distribution of a semi-crystalline material;

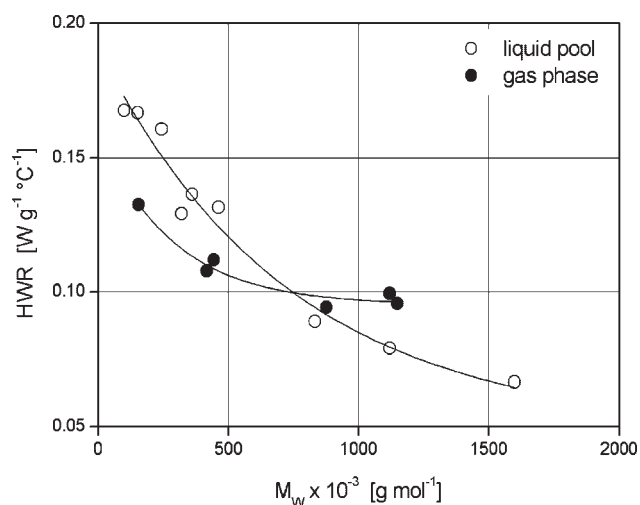


Figure 12. Height/width ratio of melting peak, measured by DSC versus average molecular weight of gas phase and liquid pool PP (1st heating, heating rate: $20 \text{ K} \cdot \text{min}^{-1}$, N_2 atmosphere).

the higher ratio shows the narrow crystallite size distribution and therefore more homogenous crystallinity.

The LP PP samples show a considerable decrease in height/width ratio as the average molecular weight increases. Therefore, the crystallite size distribution becomes broader as the average molecular weight increases. In the case of GP PP, the trend between the structural properties and the average molecular weight is also visible, but not so distinctive. This is presumably, caused by the relatively broad molecular weight distribution of the GP samples; PD of GP PP samples is about 8 and for LP PP samples is less than 7.3.

Morphology

Wide-angle X-ray diffraction was performed to characterize the crystal structure of some representative PP samples. Therefore, the WAXS diagram (intensity versus 2Θ) of PP-L0, PP-L25, and PP-L1500 is shown in Figure 13. As expected, because of DSC results, the α -phase of crystallinity exists for the majority. Additionally, a small diffraction peak at about $20^\circ 2\Theta$ can be noticed for the PP-L1500 sample, which Marigo et al.^[53] and de Rosa et al.^[54] have found for the reflex of the existence of a γ -polymorphous structure in *i*-PP. Consequently, this observed (117) peak identifies the γ -modification of the crystalline structure, although, it could not be analyzed by DSC due to low accuracy of such calorimetric measurements. Campbell et al.,^[55] have reported that the γ -phase is developed preferably on PP samples with low molecular weight and high pressure, during the solidification process. Therefore, it seems the γ -modification of the crystalline structure is created in the case of the low molecular weight PP sample PP-L1500, because of the existing high pressure up to 60 bar in the polymerization reactor.

Figure 14 shows the shape of PP particles, obtained after polymerization in GP and LP, which were detected by the

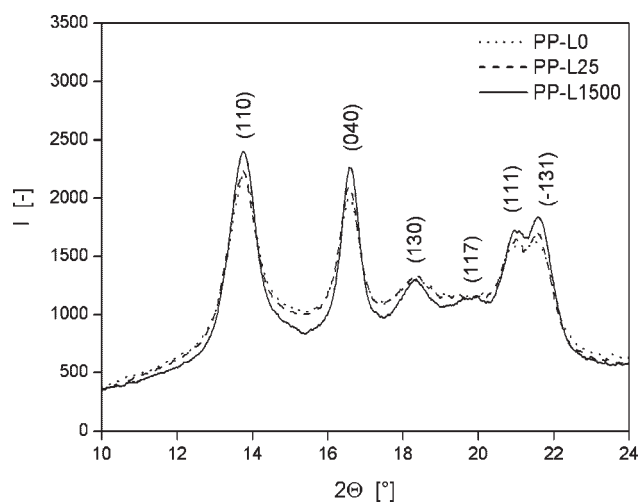


Figure 13. WAXS scans of liquid pool PP samples.

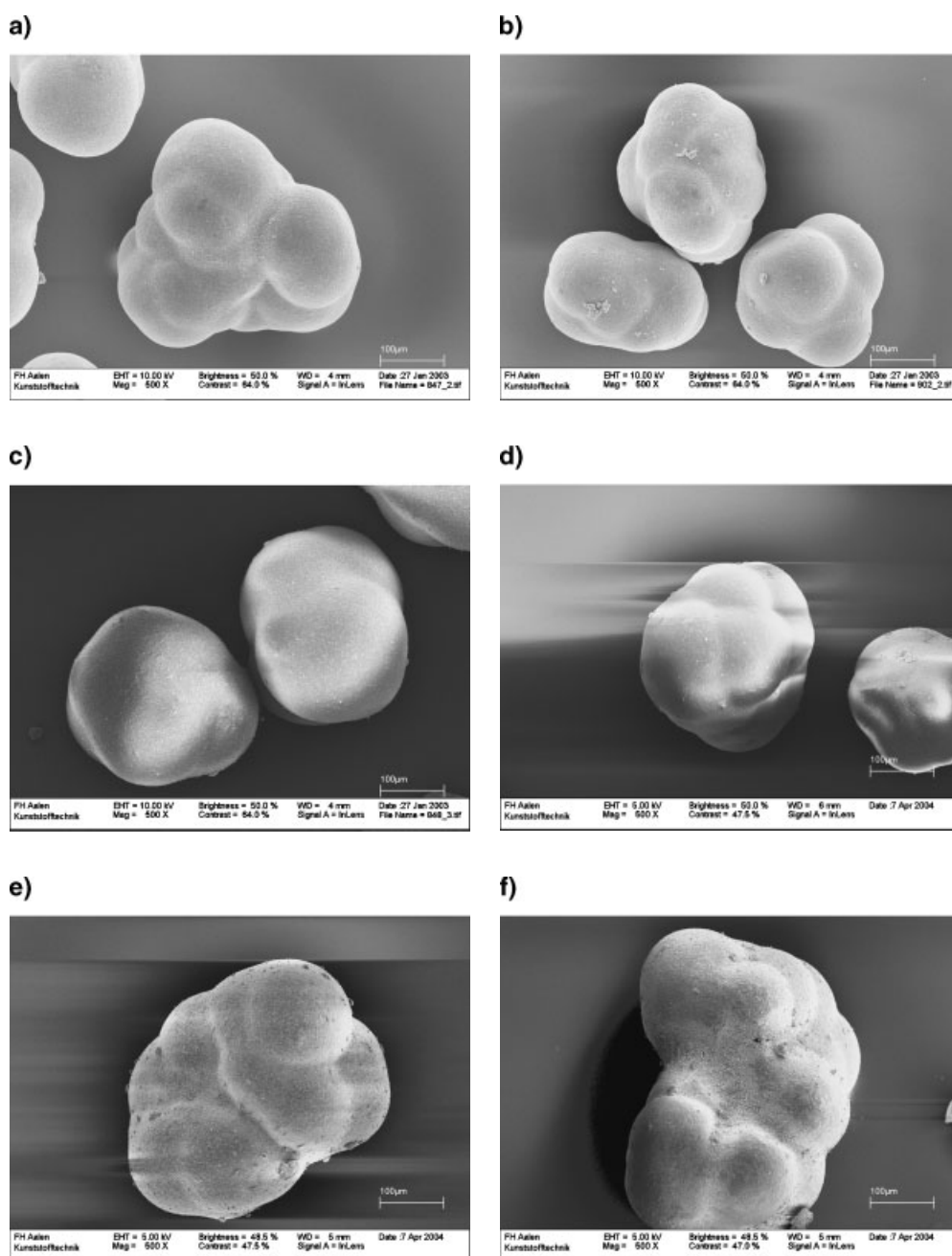


Figure 14. Particle geometry of gas phase and liquid pool polymerized PP powder observed by SEM. (a) PP-G0, (b) PP-G50, (c) PP-G1500, (d) PP-L0, (e) PP-L50, and (f) PP-L1500.

SEM investigation. Representative for both polymerization processes are particles shown which were polymerized without hydrogen and with 50 and 1500 mg hydrogen. As expected, the pictures show the typical dent but smooth surface morphology for particles, which were polymerized with Ziegler-Natta catalysts. It was found that the polymer tends to replicate the shape and texture of the catalyst.^[56–58] When polymerization starts, the support material (here MgCl_2) begins to fragment and the polymer grows to a particle around each fragment.

In spite of the different polymerization processes, no significant differences in morphology can be recognized between GP and LP particles. This could be a result of the two-step polymerization of GP process. The morphological structure which forms during the pre-polymerization process in LP dominates for the final GP particle structure.

Figure 15 shows the cross-section of particles from some LP experiments. As a result, different porosity of the particles can be observed. Besides PP-L1500, all other samples show similar less porosity. Strong porosity with

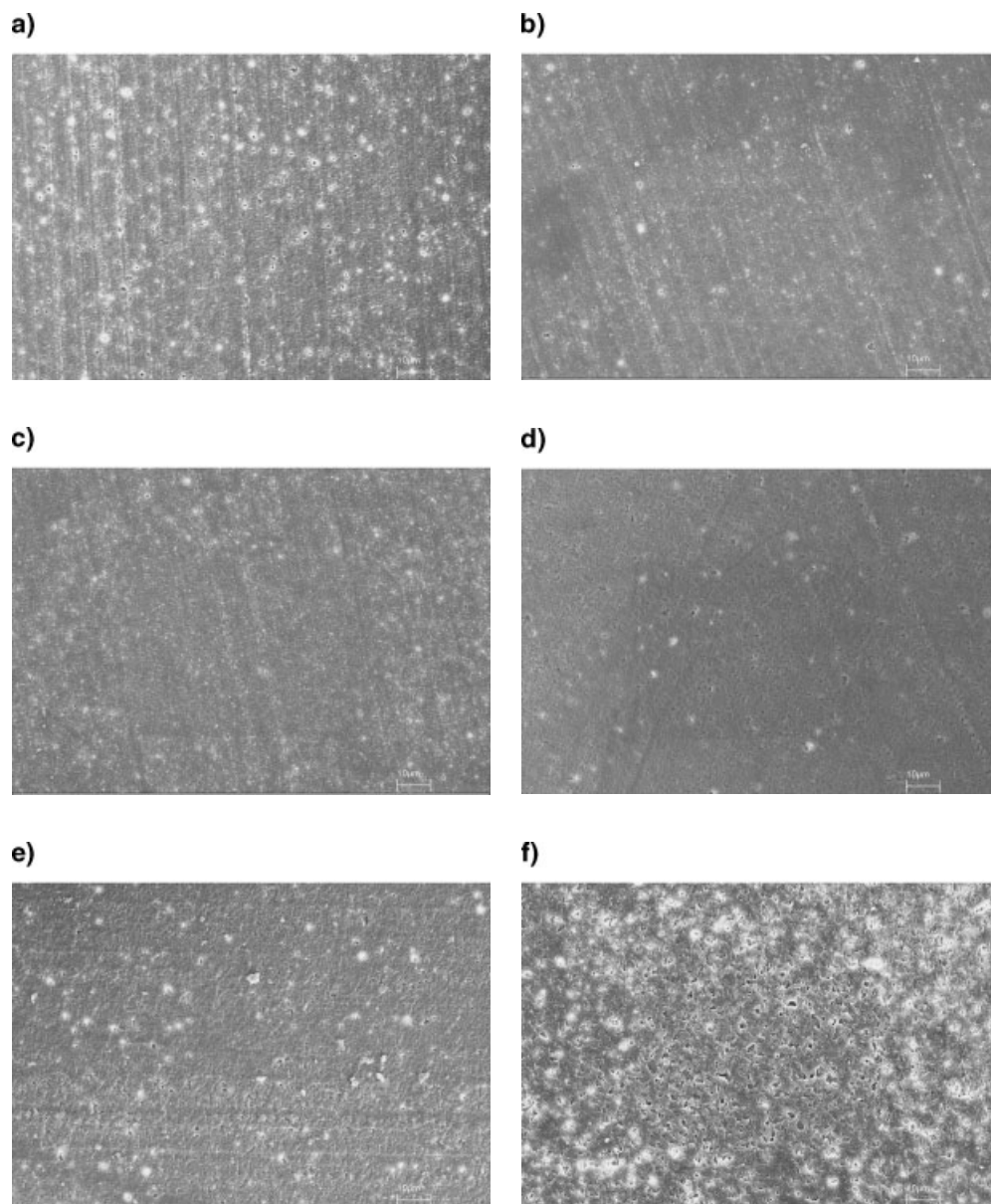


Figure 15. Cross-section morphology of liquid pool particles observed by SEM. (a) PP-L0, (b) PP-L25, (c) PP-L50, (d) PP-L150, (e) PP-L250, and (f) PP-L1500.

large pores is only given for the particle polymerized at high polymerization rate.^[15]

Conclusion

In consideration of the known kinetic fingerprint, the quality of the polymers achieved from the main polymerization processes for PP synthesis (a GP and LP polymerization technique) was compared. In particular, the effect of hydrogen on the polymerization kinetics and subsequently on the structural, rheological, thermal, and morphological properties of poly(propylene) was investigated.

A series of PP samples with different average molecular weight up to $1\,600\,000\text{ g}\cdot\text{mol}^{-1}$ in GP and LP were synthesized, using hydrogen as molecular weight modifier.

Differences between the GP and LP polymerization could be detected in the polymerization kinetics and also in rheological and thermal properties. For example, the initial polymerization rate reaches a maximum for LP of about $150\text{ kg}_{\text{PP}}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ in contrast to the GP initial polymerization rate, which is only about $45\text{ kg}_{\text{PP}}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$. This difference is caused by the higher monomer concentration on the catalysts' active sides in the case of liquid propylene polymerization.

Furthermore, the rheological investigations have shown that the zero viscosity of GP PP is less than that of LP PP,

measured with the same molecular weight. The difference could be explained by the various PD of gas and LP PP. This fact seems to be also the reason for the higher elasticity of GP PP.

Studies on the thermal properties have imposed the effect of the polymerization technique on the crystallite distribution. LP PP with low molecular weight have shown narrow crystallite size distribution; particularly the PP sample PP-L1500 shows considerable and highly homogenous crystallinity. Additionally, it has been found that the crystalline fraction of all PP samples rises after solidification from the melt. Consequently, the folding ability of the polymer chains to crystallites inside the reactor is not as good as in the melt state.

From morphological investigations, it could be recognized that beside the α -form majority, a small fraction of γ -modification on the crystalline structure exists in PP with low molecular weight.

In fact, the industrial PP samples, polymerized in gas and liquid phase, show similar properties than the PP samples, which were synthesized in the laboratory.

Finally, LP polymerization gains more homogenous PP material with improved properties, compared to GP polymerization using the same Ziegler-Natta catalyst and polymerization conditions.

Notation

a	Exponent [–]
C*	Number of active sites [$\text{mol} \cdot \text{g}_{\text{cat}}^{-1}$]
C_m	Monomer concentration [$\text{kg} \cdot \text{m}^{-3}$]
E_a	Activation energy [$\text{kJ} \cdot \text{mol}^{-1}$]
G'	Storage modulus [Pa]
G''	Loss modulus [Pa]
ΔH_m	Melt enthalpy [$\text{J} \cdot \text{g}^{-1}$]
HWR	Height/width-ratio [$\text{W} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$]
I	Intensity [a.u.]
k	Constant [$\text{Pa} \cdot \text{s} (\text{mol} \cdot \text{g}^{-1})^a$]
K_1	Constant [–]
K_2	Constant [–]
k_d	Deactivation rate constant [h^{-1}]
k_p	Propagation rate constant [$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$]
M	Monomer concentration [$\text{mol} \cdot \text{L}^{-1}$]
M_c	Critical molecular weight [$\text{g} \cdot \text{mol}^{-1}$]
\bar{M}_n	Number average molecular weight [$\text{g} \cdot \text{mol}^{-1}$]
\bar{M}_w	Weight average molecular weight [$\text{g} \cdot \text{mol}^{-1}$]
MWD	Molecular weight distribution [–]
p_{H_2}	Partial pressure of hydrogen [bar]
PD	Polydispersity [–]
Q	Heat flow [$\text{W} \cdot \text{g}^{-1}$]
R	Gas constant [$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$]
R_p	Polymerization rate [$\text{kg}_{\text{PP}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$]

$R_{p,0}$	Initial polymerization rate [$\text{kg}_{\text{PP}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$]
t	Time [h^{-1}]
T	Temperature [K]
X	Molar ratio (H_2/M) [$\text{mol} \cdot \text{mol}^{-1}$]
Y	Standard format for GPC curve ($Y_j^d M_{mj}$) [$\text{g} \cdot \text{mol}^{-1}$]
γ	Shear rate [s^{-1}]
η_0	Zero viscosity [$\text{Pa} \cdot \text{s}$]
ν	Frequency [s^{-1}]
$\nu_{\text{cross-over}}$	Cross-over frequency ($G' = G''$) [s^{-1}]
DSC	Differential scanning calorimetry
GP	Gas phase
I	Industrial
LP	Liquid pool
PP	Poly(propylene)
SEM	Scanning electron microscopy
WAXS	Wide-angle X-ray scanning diffractometry

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