



Reaction Calorimetry for Studying Kinetics in Bulk Phase Polymerization of Propene

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Dedicated to Prof. Joao Soares on the occasion of his 60th birthday

Polypropylene is one of the commercially most important polymers and is produced via coordinative polymerization with supported metal-organic catalysts in different processes. While kinetic measurements for slurry and gas-phase polymerization of propene are well-established, for bulk phase polymerization of propene, often the only kinetic information obtained from an experiment is the yield. In this paper, two calorimetric methods and their application for measurement of kinetics of bulk phase polymerization of propene are discussed. On the one hand a special calibration-free heat flow calorimeter and on the other hand power compensation calorimetry coupled with a software sensor for online baseline correction.

2. Kinetic Measurements of Olefin Polymerization

In gas-phase or slurry polymerizations, a measuring principle often applied is based on the pressure drop due to the consumption of (gaseous) monomer via the formation of (solid) polymer. The kinetic information is accessible by semi-batch experiments, where monomer is fed to the reactor in order to maintain constant pressure, controlled by a pressure control loop. At isothermal conditions, the fed amount of monomer into the reactor corresponds to the monomer consumption

and is proportional to the gross reaction rate of the polymerization reaction. The consumed monomer is related to the catalyst amount initially injected into the reactor and, thus, the current activity of the catalyst can be determined at any reaction time leading to the catalyst specific activity-time profiles.

The described method is well established for investigating the reaction kinetics of coordination catalysts under gas-phase polymerization conditions. Kinetic investigations of Ziegler-Natta catalysts in gas-phase polymerization of propene were carried out, e.g., by Choi and Ray,^[2] Soares and Hamielec,^[3] Samson et al.,^[4] Meier, Weickert and van Swaaij,^[5] and Kettner.^[6] Kinetic studies of Metallocene catalysts in gas-phase polymerization are described by Meier, Weickert and van Swaaij,^[7] and by Piduhn.^[8] Kröner^[9] investigated the kinetic of heterophasic copolymerization of propene with ethene using the same measuring approach. Furthermore, kinetics of coordination catalysts for olefin polymerization in slurry can be investigated based on the same measuring principle as for gas-phase polymerizations. Examples can be found in the investigations of Keii,^[10] Kahrmann^[11] and Kröner.^[12]

In bulk polymerization processes, the polymerization is carried out in liquid monomer. Therein, the overall reactor pressure nearly corresponds to the vapor pressure of the liquid. Hence, the above described approach of the semi-batch monomer feed according to the pressure drop is not applicable. In industrial practice, often the only kinetic information available from lab-scale bulk phase polymerization experiments is the yield at the end of the polymerization reaction.^[13,14] For this “off-line” method, many experiments and a good reproducibility are required in order to determine a detailed kinetic profile.

Despite the commercial importance of bulk phase polymerization of propene, surprisingly little information about online-measurements of the reaction rate in bulk phase polymerization of propene is available in open literature. The available

1. Introduction

Polypropylene belongs with a global production of 68 million tons in 2017^[1] to one of the most important polymers with manifold applications in everyday life. Polypropylene is industrially exclusively produced by coordinative polymerization with the help of metal-organic coordination catalysts. In coordinative polymerization, polymerization kinetics are dependent on the catalyst that means, for each new catalyst evolving, kinetic measurements are required.

Catalytic olefin polymerization reactions can be carried out in gas-phase, in slurry phase using an inert diluent or under bulk conditions in liquid monomer, or combinations thereof. Depending on the polymerization conditions, specific measuring principles have to be applied in order to determine the polymerization kinetics.

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papers on online-measurement of polymerization rate in bulk phase polymerization either used dilatometric or calorimetric measurement principles.

Al-haj Ali et al.^[15] investigated the kinetics of Ziegler-Natta catalysts in bulk phase polymerization using dilatometry in a fully filled reactor. In order to estimate the reaction rate, they implemented a functional equation, which uses the compressibility and volume expansivity of the reaction mixture as a function of pressure and temperature. With the developed method, comparable results as with calorimetric measurements were derived.

Patzlaff^[16] described a dilatometric method in partially filled reactors and investigated kinetics of different Ziegler-Natta catalysts in bulk phase polymerization. The catalyst was injected together with pentane. During polymerization, with consumption of the monomer, the composition of the liquid monomer-pentane mixture changed, which resulted in a significant effect on the vapor pressure. From the measured pressure drop, the polymerization rate was determined taking into account the vapor-liquid equilibrium of the reaction mixture.

In case of reaction calorimetry, the heat generated by the exothermal polymerization reaction is measured as signal to determine the kinetics of the polymerization reaction.

Calorimetry is widely used for determination of polymerization kinetics. Calorimetric methods can be classified according to, first, their principle of heat measurement (e.g., heat flow, heat balance or power compensation calorimetry) and, second, the applied temperature control mode (isothermal, adiabatic, isoperibolic). A detailed description of the several calorimetric principles applicable for kinetic investigations of chemical reactions is given in the review article of Zogg et al.^[17]

In general, the heat released from the exothermal polymerization reaction is proportional to the rate of polymerization according to Equation (1)

$$\dot{Q}_{\text{Chem}} = R_p \cdot V_R \cdot (-\Delta H_R) \quad (1)$$

With \dot{Q}_{Chem} (W) as released heat by the chemical reaction, R_p (mol L⁻¹ s⁻¹) as overall reaction rate of polymerization, V_R (l) as reaction volume and ΔH_R (J mol⁻¹) as reaction enthalpy, which is negative for exothermal reactions.

For kinetic investigations of polymerization reactions, a method often applied is heat flow calorimetry. The basic principle is that the heat flow (generated by the exothermal polymerization reaction) from the reactor content through the reactor walls into the surrounding thermostatic liquid is determined by measuring the temperature difference between reactor and thermostating liquid. The heat flow is calculated according to the heat transfer equation (Equation (2))

$$\dot{Q}_{\text{jacket}} = k_L \cdot A \cdot (T_R - T_J) \quad (2)$$

Wherein \dot{Q}_{jacket} (W) is the removed heat flow, k_L (W m⁻² K⁻¹) is the overall heat transfer coefficient, A (m²) is the overall heat transfer area, T_R is the reactor temperature and T_J is the mean jacket temperature (K).

Kinetic studies of Ziegler-Natta catalysts under propene bulk polymerization conditions using isothermal heat flow

calorimetry were carried out by Meier et al.,^[7] Pater et al.^[18–20] as well as Samson et al.^[21] Korber et al.^[22,23] studied the kinetics of a silica supported metallocene/MAO catalyst in propene bulk phase as well as in propene slurry polymerization using the commercial RC1 reaction calorimeter, which works according to the heat flow technology. Al-haj Ali et al.^[15] used isoperibolic heat flow calorimetry for the determination of kinetics of Ziegler-Natta catalysts under bulk polymerization conditions in comparison with the dilatometric method.

One challenge of the heat flow measurement in polymerization reactions is that the heat transfer coefficient k_L and the active heat transfer area (A) are often not constant during the course of the polymerization reaction (e.g., due to increasing viscosity of the reaction mixture, changing composition of the reaction mixture, filling level or fouling at the reactor walls). And, thus, a complex calibration of the heat transfer coefficient is often required.

In this article, two further calorimetric methods and their application for kinetic studies of coordination catalysts in propene bulk phase polymerization are presented—the application of a special, calibration-free heat flow calorimeter and power compensation calorimetry coupled with a software sensor for online baseline correction.

3. Calibration-Free Heat Flow Reaction Calorimeter

In order to overcome the challenge of estimating the heat transfer coefficient, we here report kinetic measurements for bulk phase polymerization of propene using a special type of calibration-free heat flow calorimeter. Core of the setup is the commercially available reaction calorimeter CPA202 provided by ChemiSens. The working principle of the calorimeter is based on heat flow calorimetry, wherein the heat flow is measured via heat conductivity in the reactor base.^[24]

3.1. Working Principle

A scheme of the reaction calorimeter and the basic working principle is shown in **Figure 1**. The reactor (autoclave, hastelloy, 0.25 L) is placed in a thermostating bath. The calorimeter is operated under isothermal conditions keeping reactor and bath temperature constant. In order to avoid any internal heat flux, the

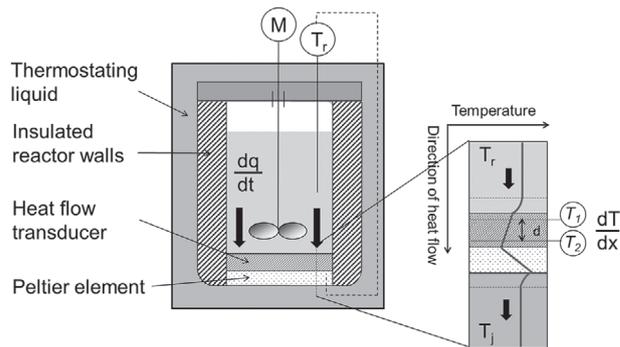


Figure 1. Measuring principle of reaction calorimeter CPA202^[24,25] ChemiSens.

temperature of the surrounding thermostating liquid is always kept 0.2 °C higher than the reactor temperature. The reactor bottom consists of a steel plate equipped with temperature sensors and a Peltier element. The Peltier element acts as reversible heat pump creating the necessary temperature difference between reactor inlet and surrounding thermostating liquid in order to drive the heat flow out of the reactor. The temperature difference is measured by temperature sensors (heat flow transducers), which are placed in a defined distance in the steel plate.

The total heat balance of the reaction calorimeter is given in Equation (3). Therein, the chemical heat produced by the polymerization (\dot{Q}_{chem}) is equal to the measured heat flow through the reactor base (\dot{Q}_{HF}) minus the stirring power (P_{Stirr}) introduced by the stirrer plus the accumulated heat in the reactor ($\dot{Q}_{\text{accumulation}}$). Heat losses to the surrounding thermostating liquid can be neglected due to the active insulation.^[25]

$$\dot{Q}_{\text{chem}} = \dot{Q}_{\text{HF}} - P_{\text{Stirr}} + \dot{Q}_{\text{accumulation}} \quad (3)$$

The energy introduced into the system by the stirrer is measured via a torque transducer. Once the reactor operates at isothermal conditions, the accumulation term disappears and the overall heat balance simplifies to Equation (4)

$$\dot{Q}_{\text{chem}} = \dot{Q}_{\text{HF}} - P_{\text{Stirr}} \quad (4)$$

Finally, the heat flow generated by the exothermal polymerization reaction is calculated via the heat conductivity according to Equation (5).

$$\dot{Q}_{\text{HF}} = \lambda \cdot \frac{A}{d} (T_1 - T_2) \quad (5)$$

With λ ($\text{W m}^{-1} \text{K}^{-1}$) as specific heat conductivity coefficient of steel, A (m^2) as defined area of the reactor base, d (m) is the distance between the temperature sensors and $T_1 - T_2$ (K) is the measured temperature difference in the reactor base.

The main advantage of this type of reaction calorimeter is that the heat flow measurement is independent of the heat transfer conditions in the reactor. Changes of the reactor content (e.g., increased viscosity of the reaction mixture, changing composition of the reaction mixture or fouling at the reactor walls) or variations in the filling level do not affect the measurement as the heat flow is measured by heat conductivity in the reactor bottom, independent of heat transfer conditions in the reactor. Thus, no complex calibration of heat transfer coefficients like for conventional heat flow calorimetry is needed.

The calorimeter is delivered calibrated by the manufacturer over the entire operating temperature range. However, there is a calibration heater included in the setup in order to test the calibration validity and system performance. In a non-reacting system, this calibration heater is used to generate a specific thermal power inside the reactor and, thus, heat flow measurements can be validated.

3.2. Kinetic Study of a Supported Metallocene Catalyst in Propene Bulk Polymerization Conditions Using the Calibration-Free Heat Flow Reaction Calorimeter

The described calibration-free heat flow reaction calorimeter was employed to study the kinetics of a supported metallocene catalyst. The polymerizations were carried out in liquid propene under industrially relevant conditions. In particular, the effect of reaction temperature and hydrogen concentration on the kinetic behavior of the catalyst (catalyst activity over reaction time) was studied. Moreover, the effect of prepolymerization degree on the resulting catalyst activity was investigated using the reaction calorimeter.^[6,28]

3.2.1. Experimental Conditions

The reaction conditions of the polymerization are summarized in Table 1. Liquid propene (purity 2.5, Linde, Air Liquide), which was further purified in a separate raw material purification system described elsewhere,^[6] and hydrogen (purity 6.0, Linde), which was used as chain transfer agent, were added batch-wise into the inertized reactor. Triisobutylaluminum (1.0 M solution in hexane, Sigma-Aldrich) was used as scavenger in order to remove last impurities in the reactor.

3.2.2. External Prepolymerization Procedure

Prepolymerization is a method to avoid or reduce catalyst overheating at the beginning of the polymerization.^[18–21,26] In low rate conditions (typically low temperature), without overheating, the reaction is started and, by a moderate particle growth, heat transfer area for the subsequent main-stage polymerization is generated.

Prepolymerization experiments were carried out in the outlined calibration-free heat flow calorimeter. After cleaning and inertizing the reactor, hydrogen, propene and scavenger were

Table 1. Reaction conditions for the bulk polymerization of propene with metallocene catalyst.

Components	Amount	Comment	Reaction conditions	Range	Comment
Propene	75 g	≈150 mL at 23 °C	Prepolymerization temperature	25 °C	
Hydrogen	0–0.14 mol%	Feed concentration, corresponds to mol H ₂ per total moles H ₂ +C ₃	Prepolymerization time	15–60 min	According prepoly degree
Catalyst	1 mg	Dry or dispersed in 1 mL heptane	Polymerization temperature	55–80 °C	
TIBA	0.8 mmol	1 M solution in hexane	Polymerization time	60 min	
			Stirrer speed	350 rpm	

added into the evacuated reactor at low temperature of 10 °C, which was then heated up to reaction temperature. About 20 to 25 mg of pure supported metallocene catalyst, dispersed in 1 mL heptane, were injected with liquid propene into the reactor. The prepolymerization was carried out at 25 °C, at total reactor pressure of 12 bar, while monitoring the reaction rate until the desired degree of prepolymerization (DP) was reached. The prepolymerization was stopped by releasing the monomer and flushing several times with nitrogen in order to remove all remaining monomer. The reactor pressurized with nitrogen was then dried for several hours in an oven at 40 °C in order to remove any water from the outer reactor surface. Afterward, the reactor was inserted into the glove box, where the prepolymerized catalyst was recovered under inert conditions and weighted out. The exact degree of prepolymerization was calculated from the weighed amount of produced prepolymer per initial amount of catalyst. More details on the procedure are described elsewhere.^[6] Prepolymers with a degree of prepolymerization between 50 to 200 mg_{PP}/mg_{Cat} were produced.

3.2.3. Main-Stage Bulk Phase Polymerization Procedure

In a second step, the prepolymerized catalyst was injected into the reactor directly at reaction conditions. Therein, an appropriate amount of dry, prepolymerized catalyst of specific prepolymerization degree corresponding to 1 mg pure catalyst was injected with high-pressure nitrogen ($\Delta p \approx 2\text{--}5$ bar) into the prepared reactor. For the evaluated temperature range from 55 to 80 °C, the total reactor pressure was 26–39 bar. The polymerization was carried out for 1 h and was stopped by flushing off the monomer. The catalyst was further deactivated using compressed air.

With this method, a fast access to the kinetic information, directly after catalyst injection, could be achieved. Furthermore, prepolymer with a defined prepolymerization degree could be tested (no undefined heating up periods as for in-situ prepolymerization). For a detailed description of the method development as well as the comparison with the in-situ prepolymerization method it is referred to Kettner.^[6,28]

3.2.4. Experimental Data from Calorimetric Measurements and Calculation of Activity

For the kinetic measurements, the calorimeter was operated at isothermal conditions. The power input by the magnetic coupled stirrer was measured via a torque transducer. The gained experimental data are shown in **Figure 2** exemplary for a bulk polymerization carried out at 70 °C using a prepolymerized metallocene catalyst.

With the calorimeter, a good temperature control of the polymerization reaction with the high active metallocene catalyst could be achieved. There is only a small temperature increase of typically below 1 °C after catalyst injection, isothermal conditions are reached fast. This allows a fast access to the kinetic information. The energy input by the stirrer is nearly zero and remains constant during reaction

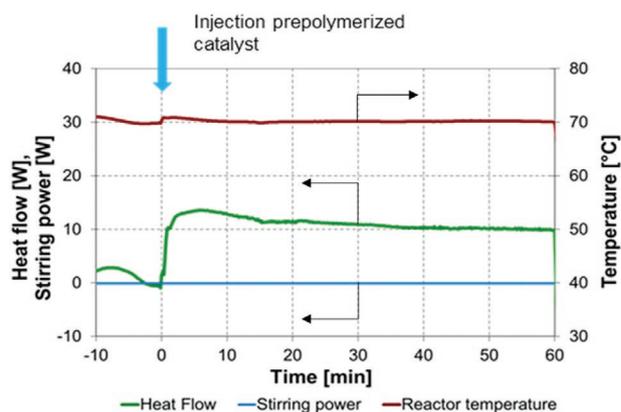


Figure 2. Recorded experimental data from calorimetric measurements (example polymerization at 70 °C, prepolymerized metallocene catalyst, DP = 100 mg_{PP}/mg_{Cat}).

time, as for polymer dispersions, the increase in viscosity with the polymer content is much less compared to polymer solutions.

At isothermal conditions, the measured heat flow corresponds to the released heat of the polymerization reaction, which is proportional to the current overall polymerization rate (Equation (1)). Based on the heat balance of the calorimeter (Equations (3) and (4)), the reaction rate can be determined according to Equation (6)

$$\dot{Q}_{\text{chem}} = \dot{Q}_{\text{HF}} - P_{\text{stirr}} = V_R \cdot R_P \cdot (-\Delta H_R) \quad (6)$$

The current catalyst activity, which is defined as amount of produced polymer per amount of catalyst and polymerization time, can be calculated at any time using Equation (7)

$$A = \frac{m_{\text{PP}}}{m_{\text{Cat}} \cdot t} = \frac{V_R \cdot R_P \cdot M_{\text{C}_3}}{m_{\text{Cat}}} \cdot 3600 \frac{\text{s}}{\text{h}} = \frac{\dot{Q}_{\text{chem}} \cdot M_{\text{C}_3}}{m_{\text{Cat}} \cdot (-\Delta H_R)} \cdot 3600 \frac{\text{s}}{\text{h}} \quad (7)$$

Wherein A (kg_{PP} g_{Cat}⁻¹ h⁻¹) is the current catalyst activity, m_{PP} (kg) is the amount of polypropylene, m_{Cat} (g) is the amount of catalyst, t (h) is the polymerization time. R_P (mol L⁻¹ s⁻¹) is the overall reaction rate of polymerization, V_R (l) is the reaction volume, \dot{Q}_{chem} (W) is the chemical heat produced by the polymerization and M_{C_3} (g mol⁻¹) is the molecular weight of propene. For the reaction enthalpy ΔH_R of polymerization of liquid propene to solid polypropylene, a literature value of $\Delta H_R = -83$ kJ mol⁻¹ is used.^[27]

The average activity \bar{A} , defined as total amount of produced polymer related to catalyst amount and 1 h polymerization time, can be determined by integrating the measured heat flow curve over reaction time (Equations (8) and (9))

$$\bar{A} = \frac{m_{\text{PP, total}}}{m_{\text{Cat}} \cdot t_{\text{total}}} \quad (8)$$

$$m_{\text{PP, total}} = \frac{\int_0^t \dot{Q}_{\text{chem}} dt \cdot M_{\text{C}_3}}{(-\Delta_R H)} \quad (9)$$

3.2.5. Validation of the Calorimetric Measurements

For validation of the calorimetric measurements, the average catalyst activity derived from the calorimetric measurements was compared with the experimentally determined average activity (derived from weighted polymer yield after 1 h polymerization time), **Figure 3**.

The comparison shows that the calculated average activities from the calorimetric measurements are in a good agreement with the experimental average activities within a 10% error range.

Furthermore, as shown in **Figure 4**, repeating experiments at same reaction conditions reveal a very good reproducibility of the kinetic measurements in terms of obtained activity profiles of the metallocene catalyst.

3.2.6. Influence of Degree of Prepolymerization on Reaction Rate at Main-Stage Bulk Phase Polymerization

In order to optimize the degree of prepolymerization, main-stage test polymerizations at 70 °C and 0.05 mol% hydrogen (corresponds to initial hydrogen feed concentration into reactor, given as mol fraction of mol hydrogen per total moles of hydrogen and propene) have been carried out with the different prepolymers prepared according to Section 3.2.2.

Figure 5 shows the resulting average bulk activities for prepolymerized metallocene catalyst of different prepolymerization degree.

Depending on the degree of prepolymerization, different average activities for the same metallocene catalyst were obtained. A maximum activity in main-stage polymerization was reached when prepolymer with a degree of prepolymerization of $\approx 160 \text{ mg}_{\text{PP}}/\text{mg}_{\text{Cat}}$ was used. Hence, for all further studies, prepolymers with the optimized degree of prepolymerization of $160 \text{ mg}_{\text{PP}}/\text{mg}_{\text{Cat}}$ were used.

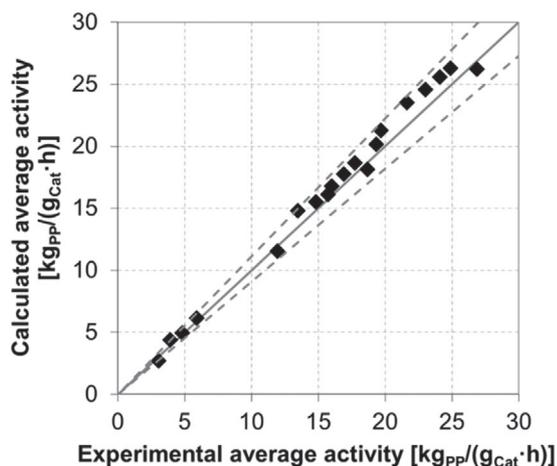


Figure 3. Validation calorimetric measurements—Comparison experimental and calculated average activities (metallocene bulk phase polymerizations, $T = 55\text{--}80 \text{ }^\circ\text{C}$, $c_{\text{H}_2, \text{feed}} = 0\text{--}0.11 \text{ mol}\%$), dotted lines represent a 10% error range.

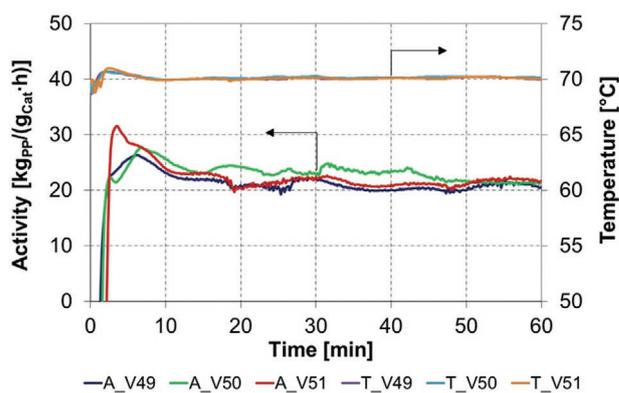


Figure 4. Reproducibility—Activity profiles of prepolymerized metallocene catalyst in propene bulk polymerization ($T = 70 \text{ }^\circ\text{C}$, $c_{\text{H}_2, \text{feed}} = 0.05 \text{ mol}\%$, $\text{PD} = 100 \text{ mg}_{\text{PP}}/\text{mg}_{\text{Cat}}$).

3.2.7. Influence of Reaction Temperature and Hydrogen Concentration on Catalyst Activity and Kinetic Profile

The kinetics of the metallocene catalyst was studied at different reaction conditions, e.g., reaction temperatures ranging from 55 to 80 °C and different hydrogen feed concentrations ranging from 0 to 0.14 mol% (corresponds to initial hydrogen feed concentration into the reactor, given as mol hydrogen per total moles hydrogen and propene). Please note that the actual hydrogen concentration in liquid propene depends also on filling degree and temperature and is typically significantly lower compared to the feed concentration.

For the kinetic investigations, prepolymerized metallocene catalyst ($\text{DP} = 160 \text{ mg}_{\text{PP}}/\text{mg}_{\text{Cat}}$) was injected directly at main polymerization temperature. **Figure 6** shows the effect of reaction temperature on the activity profiles as well as on obtained average catalyst activities.

The average catalyst activity increases with increasing reaction temperature from 55 to 70 °C, where a maximum activity is reached. A further increase above 70 °C leads to a drop in the average catalyst activity.

The same trends can be seen in the kinetic profiles from the calorimetric measurements but more detailed information

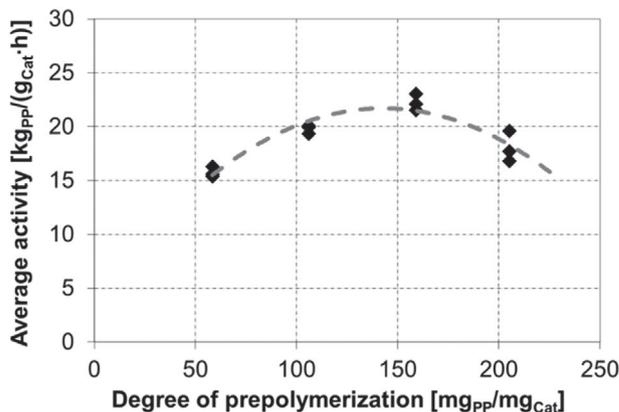


Figure 5. Influence prepolymerization degree on resulting average bulk phase polymerization activity ($T_{\text{poly}} = 70 \text{ }^\circ\text{C}$, $c_{\text{H}_2, \text{feed}} = 0.05 \text{ mol}\%$).

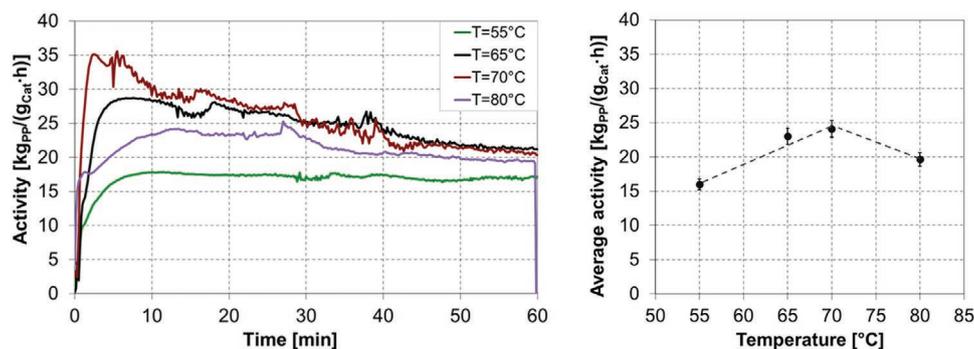


Figure 6. Influence of reaction temperature on: left) activity profile, right) average activity ($T = 55\text{--}80\text{ }^{\circ}\text{C}$, $c_{\text{H}_2, \text{feed}} = 0.11\text{ mol}\%$, $\text{PD} = 160\text{ mg}_{\text{PP}}/\text{mg}_{\text{Cat}}$).

of the course of activity over reaction time can be gained. At low reaction temperature of 55 °C, low initial catalyst activity and a flat kinetic profile over reaction time is detected. With increasing reaction temperature up to 70 °C, higher initial catalyst activities and a clear activity decay over reaction time is visible. High temperatures of 80 °C lead to a drop in the catalyst activity and the kinetic profile is on a lower level again.

Figure 7 shows the influence of hydrogen on the average activity and on the kinetic profile of the metallocene catalyst.

With increasing hydrogen feed concentration up to 0.05 mol%, the average catalyst activity increases, where an activity plateau is reached. A further increase in H₂ does not lead to higher average activities. The same trend is visible in the kinetic profiles. At higher concentrations, identical kinetic profiles are obtained. Interestingly, without H₂, the current catalyst activity in the beginning is low and increases with increasing reaction time. Whereas at high reaction temperatures, a high initial catalyst activity and a clear activity decay over reaction time can be observed.

Based on the experimentally derived kinetic profiles from calorimetric measurements, a kinetic model for the studied catalyst was developed, which is described elsewhere.^[6,29] Kinetic models can be further used, e.g., for simulation and optimization of the polymerization process, prediction of product properties, e.g., molecular weight and molecular weight distribution, or for safety calculations such as thermal runaway scenarios or design of safety equipment.

4. Power Compensation Calorimetry

4.1. Principle of Power Compensation Calorimetry

A power compensation calorimetry setup consists of an internal electrical heater submerged in the contents of a partially filled reactor (in this case liquid propene) paired with an external cooler (Figure 8).

The jacket temperature is always kept at a constant temperature, a few degrees below the reactor temperature. Hence, there is a heat flow from the reactor to the jacket. If no reaction takes place, this heat flow to the jacket is compensated by the power dissipated from the electrical heating element in order to keep the reactor in thermal equilibrium. If now an exothermal reaction takes place, less electrical power is needed in order to keep the reactor in thermal equilibrium. The heat flow released by the exothermal chemical reaction is basically accessible by the difference of the compensation power needed with and without chemical reaction.

The energy balance at isothermal conditions can be written as the following (Equation (10))^[30,31]

$$P + \dot{Q}_{\text{chem}} + P_{\text{stirr}} = \dot{Q}_{\text{jacket}} + \dot{Q}_{\text{loss}} \quad (10)$$

Where \dot{Q}_{chem} represents the heat released by the polymerization reaction, P is the energy provided by the electrical heater, P_{stirr}

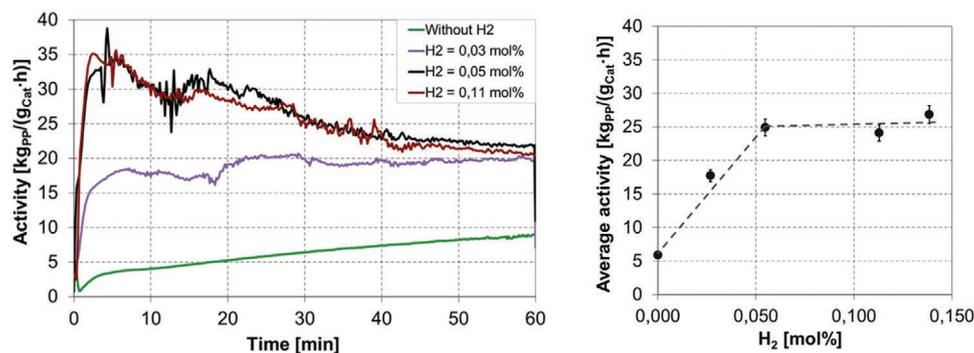


Figure 7. Influence of hydrogen concentration on: left) activity profile, right) average activity ($T = 70\text{ }^{\circ}\text{C}$, $c_{\text{H}_2, \text{feed}} = 0\text{--}0.14\text{ mol}\%$, $\text{PD} = 160\text{ mg}_{\text{PP}}/\text{mg}_{\text{Cat}}$).

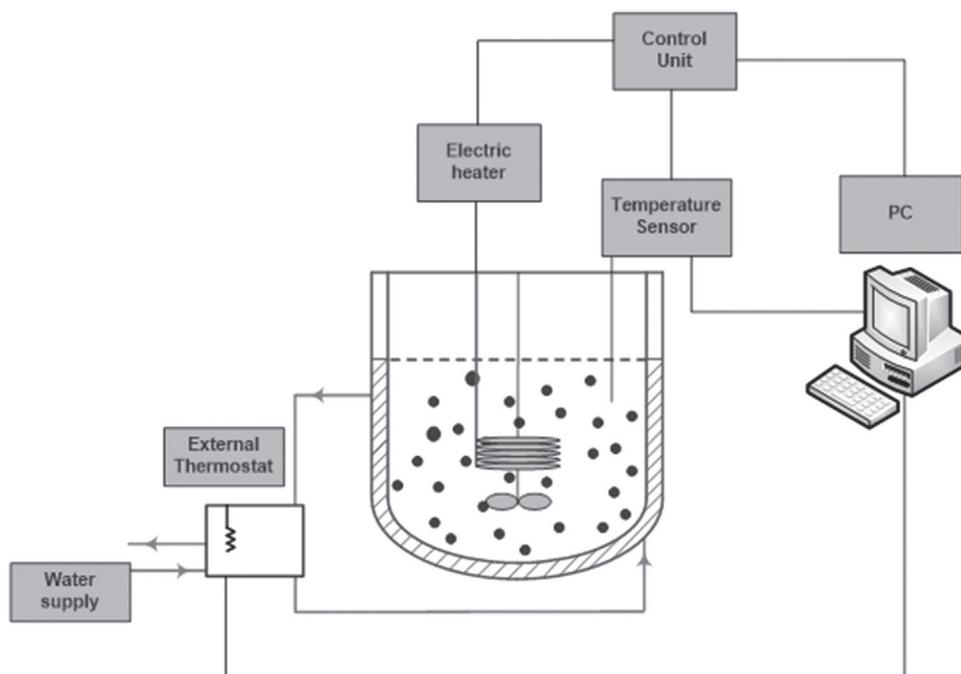


Figure 8. Power compensation reaction calorimeter setup.

is the energy dissipated by the stirrer, \dot{Q}_{jacket} is the heat flow to the jacket and \dot{Q}_{loss} are the energy losses to the environment.

Since in bulk phase polymerization of propene the viscosity of the resulting polymer dispersion is low, also the dissipated stirrer power is low and is neglected in the following.

The heat flow to the jacket is proportional to the heat transfer coefficient k_L , the heat transfer area A and the temperature difference ΔT , as described already in Equation (2).

4.2. Experimental Setup

In this work, addition of power compensation calorimetry to an existing 5 L stainless steel reactor setup for bulk and gas-phase polymerization of propene (Power compensation calorimetry is only used during bulk polymerization stage) is reported.

The compensation heater was purchased from Polymer Reactor Technology GmbH, Ahaus / Germany, and has a maximum power of 700 W. It is controlled by a PID-controller and a safety temperature limiter (both Eurotherm).

A matching double ribbon helical stirrer was designed by our group and manufactured in a mechanical workshop (Figure 9). The jacket temperature is controlled by a thermostat (Single Temperiertechnik GmbH, STW 1-6-50-K3D), the reactor is equipped with PT100 temperature measurements and a pressure gauge (Rosemount GmbH, model 2088).

The setup can operate in a pressure range between vacuum up to 40 bars and at temperatures ranging from 10 to 90 °C.

For illustration, an example of a bulk phase polymerization run with a Ziegler-Natta catalyst at 75 °C in the outlined setup using power compensation calorimetry is depicted in Figure 10.

The heater power before injection of the catalyst is shown as P_0 in Figure 10 and equals to about 295 W. As polymerization

begins with injection of the catalyst, a sharp drop in power provided by the electrical heater is observed. This can be attributed to the heat released by the polymerization reaction. Please note



Figure 9. 5 L bulk-gas-phase reactor with power compensation heater and double helical ribbon stirrer.

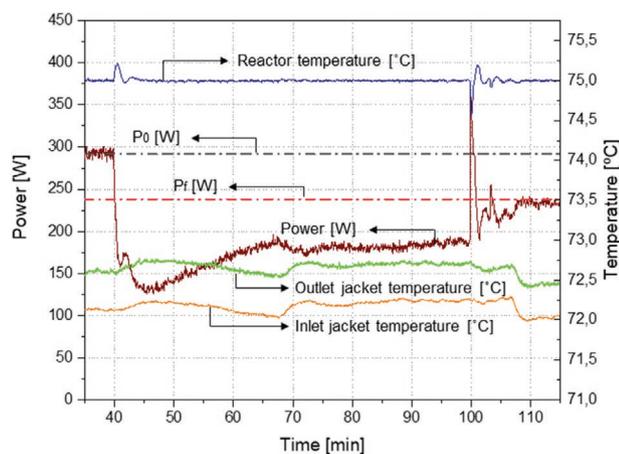


Figure 10. Example compensation heater power and reactor temperature in bulk phase polymerization run.

the excellent temperature control of the reactor system, as the reactor temperature at injection of the catalyst only increases about 0.2 °C for about 2 min. After 1 h of polymerization, the reaction is quenched by injecting ethanol into the reactor. The heat flow to the jacket after the end of the reaction, noted as P_f in Figure 10, is about 240 W. The observed change in heat flow to the jacket is due to changes in the heat transfer area during polymerization and has to be taken into account for further analysis of the calorimetry experiments.

4.3. Heat Transfer to the Jacket

A challenge in application of power compensation calorimetry for bulk phase polymerization of propene is the change of filling level. In a batch bulk phase polymerization process, due to the much higher density of polypropylene compared to liquid propene, the liquid volume level in the reactor is decreasing. Thus, also the heat transfer area decreases with conversion (Figure 11). In order to determine and quantify the change of the heat transfer conditions, calibration experiments with different filling levels and temperature differences have been carried out. Therein, the heat flow to the jacket for different filling levels is measured in absence of any chemical reaction, which means the term \dot{Q}_{chem} is equal to zero.

The resulting heat balance of the reactor during the calibration experiments is as follows (Equation (11))

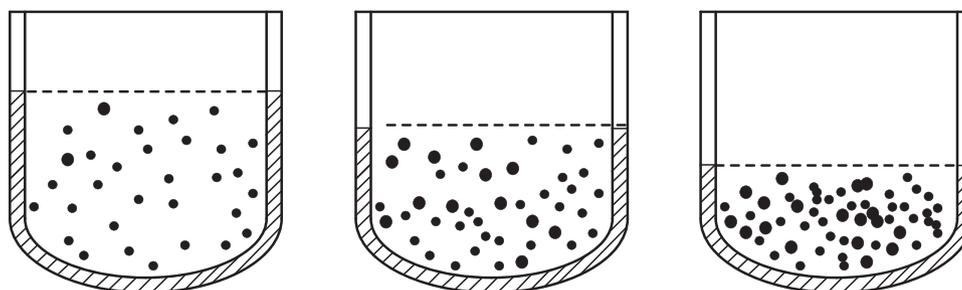


Figure 11. Change of filling level during batch-wise bulk phase polymerization of propene (schematic).

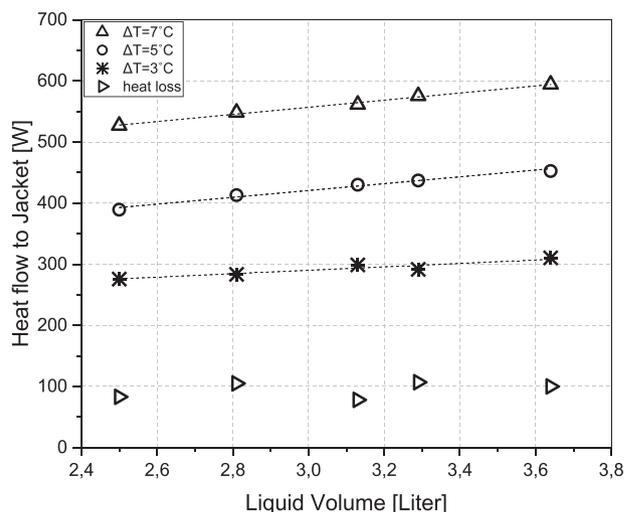


Figure 12. Heat flow to jacket versus filling volume and temperature difference.

$$P = \dot{Q}_{jacket} + \dot{Q}_{loss} = k_L \cdot A \cdot \Delta T + \dot{Q}_{loss} \quad (11)$$

The obtained data of the heat flow to the jacket depending on filling level and temperature difference are shown in Figure 12.

The heat loss of the reactor setup to the environment (\dot{Q}_{loss}) were determined to be around 100 W, independent of filling level. As expected, the heat flow to the jacket is increasing both with filling level and with temperature difference.

The liquid volumes were calculated from the fed amounts using flash calculations. The heat transfer area at a given filling level was extracted from the design of the used autoclave (possible vortexes due to stirring were neglected). The reproducibility of the calibration experiments has been checked by repeating the measurements throughout this work. The heat flow to the jacket, as illustrated in Figure 12, are estimated to have an error range of $\pm 4\%$.

By combining Equations (2) and (11), the heat transfer coefficient k_L can be calculated. k_L depends strongly on properties of the reaction mixture^[32] (such as temperature, density, viscosity) and stirring conditions.^[30,33,34]

For the given reactor setup at 75 °C with a helical stirrer at 100 rpm stirring speed, the heat removal can be characterized by a heat transfer coefficient k_L of about

$$k_L = 700 \pm 8\% \frac{\text{W}}{\text{m}^2 \cdot \text{K}}$$

4.4. Software Sensor for Online Baseline-Correction

Since the heat transfer area is changing during a batch-wise bulk polymerization reaction, the heat flow to the jacket is changing during polymerization reaction as well.

For a corresponding baseline correction, a software sensor has been developed, which couples the power compensation calorimetry data with a material balance for propene and flash calculations in order to determine filling level and heat flow to the jacket online during a polymerization run.

A flowsheet of the software sensor is depicted in **Figure 13**.

At start of an experiment, first the initial amount of propene, the amount of catalyst and the temperature difference between reactor and jacket have to be provided. In the software sensor, for the current amount of liquid propene in the reactor, a flash-calculation is performed in order to determine the vapor and liquid fraction of propene and, thus, the liquid filling level in the reactor. With the filling level and the temperature difference between reactor and jacket, the heat flow to the jacket \dot{Q}_{jacket} is estimated based on the calibration measurements described in Section 4.3.

With the help of \dot{Q}_{jacket} and the measured compensation power P , the chemical heat flow \dot{Q}_{chem} is calculated. From the chemical heat flow, the rate of propene consumption can be concluded and both the propene material balance and the filling volume can be updated. The program continues in this order until the last data point is obtained.

The software sensor is programmed in separate Matlab-procedure, which is called from the data acquisition-software.

The online software sensor provides a non-linear baseline correction for the heat flow to the jacket based on the kinetics of the corresponding experiment. An example can be seen in **Figure 14**. The activity of the catalyst at any given time of the reaction can be calculated according to Equation (7).

4.5. Validation

The accuracy of the data obtained by the calorimeter can be checked by comparison of the predicted yield based on calorimetric measurements, with the actual weighed yield at the end of the polymerization. In **Figure 15**, such a comparison is performed in the form of a parity diagram. As can be seen, the error is typically well below 10%.

4.6. Application Example—Catalyst Kinetics in Bulk Phase Polymerization

4.6.1. Experimental Conditions

1500 g liquid propene (purity 2.5, Linde, Air Liquide), which was further purified in a separate raw material purification system was fed into the inertized reactor. 0.58 mol% hydrogen (purity 6.0, Linde), was used as chain transfer agent in the

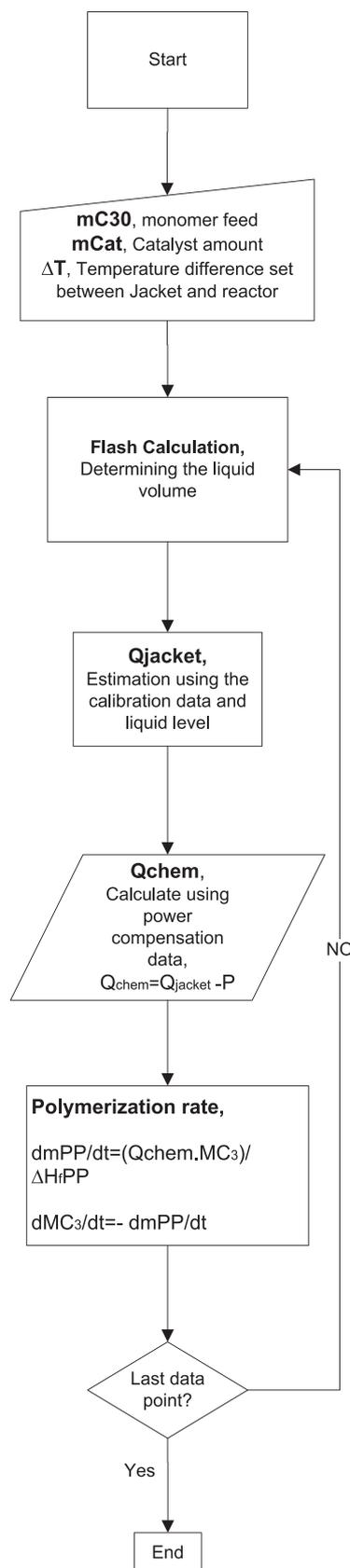


Figure 13. Flow-sheet software sensor for online-baseline correction.

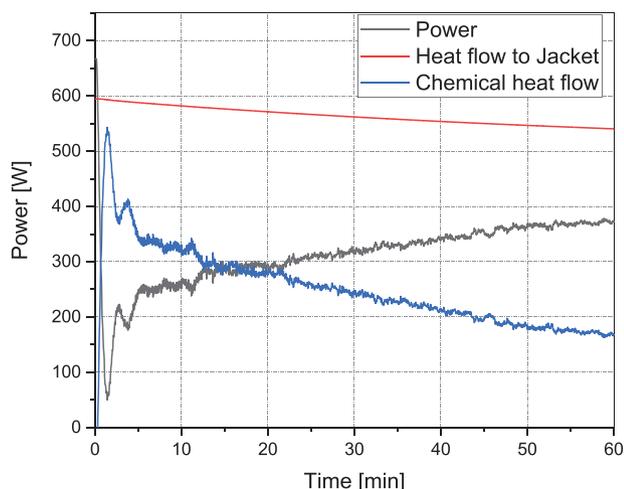


Figure 14. Example non-linear baseline correction computed by online-software sensor.

feed. Triethylaluminum (1.0 M solution in hexane, Sigma-Aldrich) was used as cocatalyst and scavenger. Cyclohexyltrimethoxysilane (1.0 M solution in hexane, Sigma-Aldrich) was used as external electron donor. Two industrial Ziegler-Natta catalysts A and B were tested. About 10 mg of catalyst was injected into the reactor at mild conditions (25 °C). After an in situ prepolymerization step, reactor temperature was raised up to 75 °C, where the main polymerization took place for 1 h. Experimental conditions are summarized in Table 2.

4.6.2. Catalyst Activities

By using the outlined power compensation calorimetry method, homo-polymerization kinetics of propene at 75 °C for two different Ziegler-Natta type catalysts were studied.

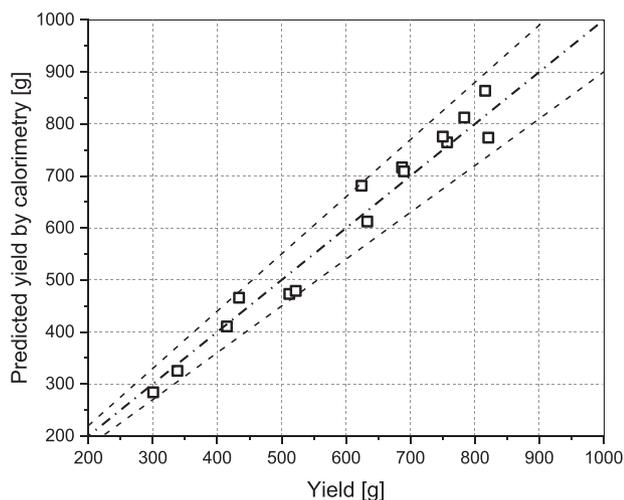


Figure 15. Parity diagram for predicted yield versus actual yield, the dotted lines represent a 10% error range.

Table 2. Reaction conditions for the bulk polymerization of propene with Ziegler-Natta catalyst.

Components	Amount	Comment	Reaction conditions	Range
Propene	1500 g	Fed at 25 °C	Prepolymerization temperature	25 °C
Hydrogen	0.58 mol%	Feed concentration, corresponds to mol H ₂ per total moles H ₂ +C ₃	Prepolymerization time	10 min
Catalyst	≈10 mg	Dispersed in 1 mL hexane	Polymerization temperature	75 °C
TEA	1 mmol	1 M solution in hexane	Polymerization time	60 min
C-Donor	0.05 mmol	1 M solution in hexane	Stirrer speed	100 rpm

Reproduced activity profiles for these catalysts at 75 °C and 0.58 mol% hydrogen in the feed are presented in Figure 16.

The calorimetric measurements show a good reproducibility and give detailed insights in the activation and deactivation behavior of the studied catalysts.

4.7. Multi-Stage polymerization of High Impact Polypropylene

One important class of polypropylene materials are hetero-phasic copolymers. These materials consist of a matrix-material (either propylene homopolymer or random-copolymer) and an elastomeric ethylene-rich copolymer, which is not miscible with the matrix material and acts as impact modifier. In some processes (as, e.g., the Spheripol process by LyondellBasell), the matrix material is produced in bulk phase polymerization, while the elastomeric copolymer is produced in a subsequent gas-phase polymerization stage. One important parameter of these kind of products is the

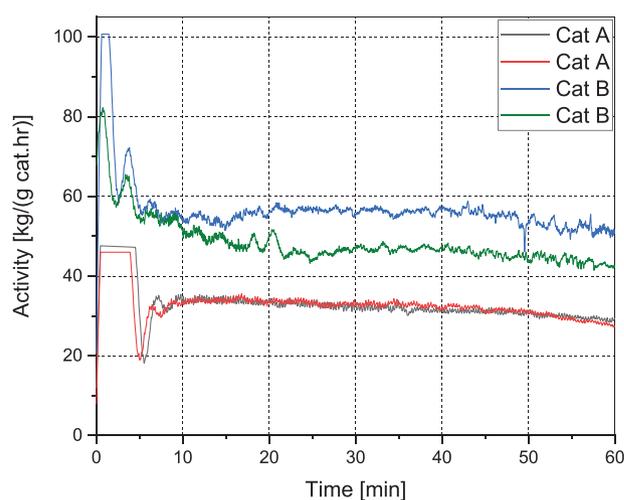


Figure 16. Activity versus time at 75 °C in bulk phase polymerization of propene for two industrial Ziegler-Natta catalysts.

rubber content that means the amount of elastomeric ethylene-propylene copolymer related to the amount of matrix polymer.

In typical lab-setups, without calorimetric measurement, the amount of matrix material after bulk polymerization, before gas-phase copolymerization is not known. It either has to be determined by separate experiments without copolymerization, which is additional effort and requires very good reproducibility from run to run, or it can only be assessed afterward by analytic means. A direct control of rubber content is not possible in this case.

Power compensation calorimetry enables to online determine and control the amount of matrix polymer made and, thus, enables to precisely adjust the rubber content in the subsequent gas-phase polymerization and, hence, provides a valuable tool for product development.

5. Summary and Conclusions

Reaction calorimetry is a powerful tool to increase the information content obtained from bulk phase polymerization experiments significantly.

Two calorimetric approaches and setups have been introduced in this paper.

The calibration-free heat flow calorimeter has the advantage that the measurement of the heat flow is independent of any heat transfer conditions in the reactor. Therefore, no calibration measurements are required. The sensitivity of the calorimeter is high and, due to the small reactor size, it can be easily introduced into the glove box. Hence, this calorimeter is also well suited for prepolymerization studies. For high-rate experiments with high-active catalysts, the small reactor size might lead to practical issues with feeding of very small amounts of pure catalyst.

Power compensation calorimetry is a possibility to add calorimetric measurements to existing setups at relatively low costs. Here, the addition of power compensation calorimetry to an existing 5 liter setup for multi-stage polymerization (bulk/ gas-phase) was demonstrated. The power compensation method offers excellent temperature control throughout the reaction. For correct interpretation of the measured data, changes in the heat flow to the jacket due to changes in the filling level have to be taken into account. For this purpose, an online software sensor for baseline correction was developed, which combines the calorimetric measurement with a material balance for propene and flash-calculations in order to estimate the filling level and heat flow to the jacket during the course of polymerization.

Application of the outlined techniques were demonstrated with measurements of the polymerization rate of a supported metallocene catalyst in propene bulk phase polymerization, a prepoly study with the same metallocene catalyst and assessment of the polymerization rate of supported Ziegler-Natta catalysts in propene bulk phase polymerization conditions.

The gained polymerization data can be used, e.g., for development of kinetic models as well as for target-oriented product development, e.g., the polymerization of heterophasic copolymers with controlled rubber content.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bulk phase polymerization, kinetics, polypropylene, reaction calorimetry

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