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Estimation of the Polymerization Rate of Liquid Propylene Using Adiabatic Reaction Calorimetry and Reaction Dilatometry

Mohammad Al-haj Ali,* Ben Betlem, Brian Roffel, Günter Weickert

The use of pressure-drop and constant-pressure dilatometry for obtaining rate data for liquid propylene polymerization in filled batch reactors was examined. The first method uses reaction temperature and pressure as well as the compressibility of the reactor contents to calculate the polymerization rate; in the second, the polymerization rate is calculated from the monomer feed rate to the reactor. Estimated polymerization rates compare well to those obtained using the well-developed isoperibolic calorimetry technique, besides pressure-drop dilatometry provides more kinetic information during the initial stages of the polymerization than the other methods.

Introduction

In polymerization reactions, the rate of reaction has a major impact on polymer morphology and polymer molecular properties, such as molecular weight distribution (MWD) and chemical composition distribution (CCD). In addition, the rate of reaction is a critical issue in safety studies, since it is directly related to the amount of heat produced during the reaction.

Generally, the polymerization rate can be determined experimentally by measuring the change in any property

during the course of the polymerization such as solubility, refractive index and density.^[1] However, the measurement of these properties is not a simple task during the polymerization reaction because sensors in the reaction mixture are easily fouled by the sticky polymer. Furthermore, sensor technology for on-line monitoring is still in its infancy.^[2,3] Fortunately, the situation is better when dealing with sensors that monitor reactor operation, since temperature, pressure and flows can be measured easily. Thus, different techniques, which are based on these measurements, were developed to estimate the polymerization rate: (i) the flow rate technique, (ii) the calorimetric approach, and (iii) the dilatometry method.

Flow Rate Technique

The flow rate technique is the simplest approach among the three techniques. It is based on continuous compensation of monomer consumption such that the pressure in the system is kept constant. This technique is usually used in gas phase or slurry polymerization reactions.

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However, in the case of isothermal liquid-pool polymerization in partially-filled reactors, this method is not applicable, since the reactor pressure is determined by the vapor pressure of the system and does not change with conversion, as long as liquid monomer is present in the reactor.

Calorimetry

The principles of the calorimetric method were developed a long time ago. However, only in the last thirty years have intensive developments and applications of calorimeters been reported in the literature. Calorimeters are used for many purposes such as:

1. Determination of the reaction conversion.^[4,5]
2. Estimation of the overall heat transfer coefficients in reactors.^[6]
3. Control of the molecular weight distribution.^[7]
4. Determination of kinetic constants.^[8–10]
5. Establishing safety limits for batch, semi-batch and continuous chemical reactions.^[11]

The basis of a calorimetric measurement is the heat balance of a stirred-tank reactor. For this purpose the heat flux produced by the chemical reaction and power added by the stirrer are compared to the heat removal by accumulation, convection, conduction, and heat loss to the surrounding in a macroscopic heat balance. The reaction mass is regarded as perfectly mixed, and changes in both kinetic and potential energies as well as heats of mixing and solution are neglected.

Generally, the calorimeters are subdivided according to their operation mode into^[11,12] one of the following types:

1. Adiabatic calorimetry.
2. Isoperibolic calorimetry.
3. Isothermal calorimetry.

According to Moritz,^[11] adiabatic reaction calorimeters are dangerous for use in highly exothermic reactions. Moreover, the large changes in temperature affects the reactions in terms of undesired side reactions such as catalyst deactivation and mass transfer of different components between phases. Thus, adiabatic calorimeters are not suitable for the investigation of polymerization reactions.^a Accordingly, isothermal and isoperibolic reaction calorimeters, with small temperature changes, are suitable for monitoring such reactions. In this contribution isothermal calorimetry will not be considered, a detailed

^aInvestigation of runaway behavior is an exception.

description of this technique for liquid propylene polymerization can be found in ref.^[13–15]

Isoperibolic Calorimetry

By means of isoperibolic calorimetry, the jacket temperature is kept constant during the experiment. As shown in Figure 1, after catalyst injection, the reactor temperature increases slightly reaching a quasi-steady state value after few minutes. As in isothermal operation, the temperature difference between the cooling jacket and the reaction mass corresponds to the polymerization rate. Assuming isothermal conditions, which is reasonable as about 0.5 K is sufficient to measure the entire rate profile accurately,^[14] the reaction rate is calculated from:^[16,17]

$$R_p \approx C \cdot (\Delta T - \Delta T_{BL}) \quad (1)$$

where ΔT_{BL} , the so-called *baseline* temperature difference, is the temperature difference between the reactor temperature and the average temperature of the cooling jacket of the reactor when no reaction takes place. C is defined as:

$$C = \frac{\bar{U} \cdot A_{wall}}{m_c \cdot \Delta H_r} \quad (2)$$

C is assumed to be constant during the polymerization reaction.

It should be emphasized that this technique only works as long as the increase in reaction temperature is small, since the kinetic constants should be related to a constant reaction temperature. To overcome this problem, the amount of catalyst added should be reduced; unfortunately, this increases the probability of catalyst poisoning.

Previous Work

Reaction calorimetry has been implemented in the field of polymerization, different publications show its applicability to free radical polymerization,^[18] and emulsion polymerization.^[4,19,20] However, because of the sensitivity

Figure 1. Temperature profile for isoperibolic calorimetry during propylene polymerization.

for impurities in the ppm range and the danger associated with explosive liquids and gases, this method did not find application in catalytic olefin polymerization until 1994.

In 1994, at the University of Twente, polymerization rate profiles based on isothermal calorimetry were measured^[8] for the first time. Considering an energy balance around the reactor, the authors derived an equation to calculate the polymerization rate assuming that the heat transfer through the reactor wall can be calculated using an average heat transfer coefficient. This method was improved to be used as an isoperibolic calorimeter. Pater^[21] and Shimizu et al.^[9] used this slightly improved calorimetric method to study the kinetics of liquid-pool propylene polymerization with highly active Ziegler-Natta catalysts.

Finally, Korber et al.^[22] studied the kinetics of liquid-pool polymerization of propylene with a silica-supported metallocenes/MAO catalyst, implementing a commercial isothermal calorimeter, at different polymerization conditions.

It should be noted that a key aspect of the calorimetric techniques, both isothermal and isoperibolic, is that there is a loss in kinetic information during the first few minutes which are required to reach the thermal quasi-steady state equilibrium.

Another key aspect of the calorimetric measurements is that the reaction heat flow is measured relative to a baseline, as mentioned earlier. The baseline may drift due to changes in the system and variations in the heat transfer coefficient. This implies that significant error may arise if an incorrect choice of baseline form is made, particularly if there is a large shift in baseline over the course of the reaction.^b

Dilatometry

In industrial applications, poly(propylene) is usually produced in loop reactors, which are operated fully filled with liquid monomer. The production of poly(propylene) results in a shrinkage of the reactor's content because of the large difference in polymer and monomer density. This shrinkage phenomenon is a kinetic signal and the experimental technique is known as *dilatometry*. It is an accurate method for polymerization reactions with a large difference in density between monomer and polymer^[1] as long as the volume shrinkage can be related to the reaction kinetics. Thus, this technique is widely used in the study of emulsion polymerization kinetics.

Since the polymerization reactor is operated filled with liquid monomer, volume shrinkage will lead to a sensitive

decrease in the reactor pressure. This can be used to develop a new dilatometric strategy to measure reaction rate profiles in liquid propylene polymerization.^[14]

The purpose of this research is twofold. The first objective is to use the dilatometric technique in studying the kinetics of liquid propylene polymerization. This strategy will be implemented in two ways:

1. Pressure-drop dilatometry: the reaction rate is calculated using the pressure drop recorded during the polymerization reaction.
2. Compensation dilatometry: in this approach the reactor pressure is kept constant through continuous compensation of the monomer consumption. The reaction rate is calculated using the amount of monomer fed to the reactor.

The second objective of this paper is to extend the verification of the dilatometric technique by a detailed comparison of reaction rates measured by both this technique and isoperibolic calorimetry.

Pressure-Drop Dilatometry

Temperature and Pressure Profiles in a Fully Filled Reactor

Before describing pressure-drop dilatometry, it is worth taking a closer look at the pressure, reactor temperature, and inlet and outlet jacket temperature profiles. Figure 2 shows these profiles for a typical propylene polymerization experiment. Before catalyst injection, the reactor temperature and pressure are 70 °C and 48 bar, respectively. When the catalyst is injected, point A, system pressure and temperature increase immediately. Since the reactor is operated in isoperibolic mode, the outlet jacket temperature increases due to the heat production during the polymerization reactions. After a short time, at point B, the pressure reaches its maximum value (49 bar) and starts decreasing, while the reaction temperature still increases. During this period, two factors affect the

Figure 2. Temperature and pressure profiles during a typical propylene polymerization experiment in a filled batch reactor.

^bIn liquid propylene slurry, this effect can be neglected up to about 25% solid content.

pressure: (i) temperature increase, and (ii) polymer production. The increase in temperature has a more pronounced effect which leads to a pressure increase. When the system reaches point B, the second factor becomes dominant and the pressure starts decreasing. At point C, the polymerization temperature reaches its maximum value (72.8 °C), and starts decreasing until the end of the experiment.

Calculation of the Polymerization Rate R_p

Using the pressure-drop dilatometry technique, the reaction rate can be calculated from the pressure drop recorded during the polymerization reaction. Because of the change in reactor temperature during the polymerization reaction, the change in monomer volume depends not only on the reaction pressure, P , but also on the reaction temperature, T .

This method is based on the compressibility behavior of the monomer inside the reactor. The polymerization reactor usually contains not only monomer but also amorphous and crystalline polymer and hexane that are used to inject the catalyst. The presence of such a mixture affects the compressibility of the monomer; consequently an average compressibility should be used instead of the value for pure monomer.

It can be shown that a relationship between P , T and monomer density, ρ_m , can be expressed by the functional equation:

$$-\left(\frac{1}{\rho_{m,0}}\right) \cdot \frac{d\rho_m}{dt} = -\bar{\kappa} \cdot \frac{dP}{dt} + \bar{\beta} \cdot \frac{dT}{dt} \quad (3)$$

where $\rho_{m,0}$ is the initial monomer density, and the average volume expansivity, $\bar{\beta}$, and the average isothermal compressibility, $\bar{\kappa}$, are defined as follows:

$$\bar{\beta} = \frac{\beta_m \cdot \nu_{0,m} + \beta_p \cdot \nu_{0,p}}{\nu_{0,m} + \nu_{0,p}} \quad (4)$$

$$\bar{\kappa} = \frac{\kappa_m \cdot \nu_{0,m} + \kappa_p \cdot \nu_{0,p}}{\nu_{0,m} + \nu_{0,p}} \quad (5)$$

here $\nu_{0,m}$ and $\nu_{0,p}$ are the original specific volumes for the monomer and polymer, respectively. We assume that the effect of hydrogen on the average compressibility is negligible.

Note that at $t = t_p$, in Figure 2, $dP/dt = 0$ and consequently

$$-\left(\frac{1}{\rho_{m,0}}\right) \cdot \frac{d\rho_m}{dt} = \bar{\beta} \cdot \frac{dT}{dt} \quad (6)$$

Similarly, at $t = t_r$, $dT/dt = 0$, it holds that:

$$-\left(\frac{1}{\rho_{m,0}}\right) \cdot \frac{d\rho_m}{dt} = -\bar{\kappa} \cdot \frac{dP}{dt} \quad (7)$$

Equation (6) and (7) can be used to give approximate values of $\bar{\beta}$ and $\bar{\kappa}$.

In batch reactors, the relationship between reaction rate and density profile can be described by Equation (8), assuming a constant volume system:

$$-\frac{d\rho_m}{dt} = R_p \cdot \left[\frac{m_c}{V}\right] \quad (8)$$

where R_p (in $\text{kg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$) is the polymerization rate, m_c is the catalyst mass, and V is the volume of the reactor. Substituting Equation (8) into Equation (3), the reaction rate can be expressed as a function of both temperature and pressure profiles:

$$R_p = M_1 \cdot \frac{dP}{dt} + M_2 \cdot \frac{dT}{dt} \quad (9)$$

with

$$M_1 = -\left[\frac{\bar{\kappa} \cdot \rho_0 \cdot V}{m_c}\right] \quad (10)$$

$$M_2 = \left[\frac{\bar{\beta} \cdot \rho_0 \cdot V}{m_c}\right] \quad (11)$$

It is well-known that the volume expansivity and isothermal compressibility are functions of system temperature and pressure; however, the variations in $\bar{\kappa}$ and $\bar{\beta}$ can be neglected because the changes in reaction temperature and pressure are limited.

The yield can be calculated by integrating the rate, Equation (9), over the reaction time:

$$\text{Yield}_{\text{calc}} = \int_0^t R_p \cdot dt \quad (12)$$

The measured yield can be determined by weighing the dry product from the polymerization. The calculated yield should be equal to the measured yield. This fact is used to determine the values of M_1 and M_2 using fitting techniques.

Compensation Dilatometry

In this approach the reactor pressure is kept constant through the continuous compensation of monomer consumption. The reaction rate is calculated from the

amount of monomer fed to the reactor. Alladyshev et al.^[23] studied liquid propylene polymerization in fully-filled reactors. These authors determined the polymerization rate using the amount of propylene charged into the reactor in order to keep reactor pressure constant.

Similar to the previous dilatometric technique, the reactor dilatometer has been developed especially for kinetic studies of liquid propylene polymerization. However, the dilatometer in this approach is somewhat more complex because of the implementation of a pump, propylene storage vessel and balance.

The first few minutes of the polymerization reaction in this dilatometer are similar to that in the pressure-drop dilatometer and isoperibolic calorimeter. After catalyst injection, system pressure increases until it reaches its maximum value, after which it reaches the equilibrium state. As soon as the reaction pressure starts decreasing, the pump starts adding monomer until the reactor pressure returns back to its maximum value, then the pump stops. This procedure continues during the polymerization reaction such that $P_{\text{reactor}} = P_{\text{maximum}} \pm 0.2$ bar in this investigation. This pressure fluctuation is relatively much smaller than the reactor pressure drop, approximately 15 bar, which has to be compensated.

Calculation of the Polymerization Rate

Starting with a reactor that is totally filled with liquid propylene; let V_L be the volume of the monomer that has reacted within certain period of time Δt , and the volume of the produced polymer within the same period is V_p , then the reduction in the volume of the reactor content, ΔV , due to the polymerization reaction will be equal to:

$$\Delta V = V_L - V_p \quad (13)$$

To keep the pressure in the reactor constant, monomer should be fed with a volume ΔV . This term can be measured as a function of the pumped propylene mass:

$$\Delta V = \frac{\Delta m_{\text{pump}}}{\rho_m} \quad (14)$$

where ρ_m is the density of liquid monomer. The right-hand side in Equation ((13) can also be rewritten in terms of the mass of reacted monomer, Δm_{prod} , and the densities of the polymer and the monomer:

$$V_L - V_p = \Delta m_{\text{prod}} \cdot \left[\frac{1}{\rho_m} - \frac{1}{\rho_p} \right] \quad (15)$$

Combining and rearranging Equation (14) and (15) results in the final equation that is used to calculate the

mass of polymer produced at different reaction times:

$$\Delta m_{\text{prod}}(t) = \frac{\Delta m_{\text{pump}}(t)}{\rho_m \cdot \left[\frac{1}{\rho_m} - \frac{1}{\rho_p} \right]} \quad (16)$$

The density of liquid propylene can be estimated in simple ways using either the well-known temperature correlations, see for example Rowley et al.,^[24] or different equation of states. However, this is not the case with the determination of the in situ polymer density, ρ_p . This difficulty results from the fact that ρ_p varies with polymerization time and conditions. In addition, measuring this variable on-line is still not a simple task. An average value for ρ_p can be estimated using the yield of the produced polymer and the total mass of the pumped monomer, in addition to using Equation (15). The polymerization rate, R_p , can be estimated by dividing Δm_{prod} by the corresponding time span:

$$R_p = \frac{\Delta m_{\text{prod}}}{\Delta t \cdot m_c} \quad (17)$$

Experimental Part

Materials

Propylene used in the experiments was “polymerization grade” and obtained from Indugas. The purity was more than 99.5%, with propane as a main impurity. Hydrogen used had a purity higher than 99.999%; it was further purified by passing it over a reduced BTS copper catalyst, obtained from BASF, and subsequently passing through three different beds of molecular sieves, with pore sizes of 13, 4 and 3 Å, respectively. Propylene was purified in the same way; additionally it was passed over a bed of oxidized BTS catalyst to remove CO. TiCl_4 supported on MgCl_2 with phthalate as internal donor and an external silane donor was used as a catalyst with TEA as a cocatalyst and scavenger.

Reactor System

A 5 L stainless steel jacketed batch reactor (Büchi BEP 280) with a separately heated cover plate was used; it is described elsewhere.^[9,10,17,25] For intensive mixing, the reactor was equipped with a turbine stirrer operated at 2000 rpm. The pneumatic injection system allows the introduction of liquids and slurries into the reactor, even at high reactor pressures. The cooling medium temperature is kept constant within ± 0.01 K during isoperibolic experiments.

The reactor is connected to an HPLC pump, which is connected to a 1 L propylene storage vessel. The vessel is set on a balance. This configuration is used to keep the pressure constant inside the reactor when compensation dilatometry technique is used for estimating the polymerization rate.

Experimental Procedure

The reactor was flushed with nitrogen gas five times at 90 °C and purged with propylene gas at the beginning of the experiment, then filled with liquid propylene and heated up to the reaction temperature. When the temperature reached the set point, hydrogen was injected. The reactor temperature and pressure were monitored as a function of time. As soon as both became stable for an interval of 3 min, the reaction was started by injecting the prepared catalyst into the reactor.

The experiments were executed under isoperibolic conditions. Thus, just after the catalyst injection, the temperature control system becomes active in trying to keep the jacket temperature constant, the reaction temperature increases slightly reaching a quasi-steady-state after about 1.5 min in the case that a fully pre-activated catalyst is used. The heat of polymerization was measured under quasi-steady state conditions. Data were collected every 3 s. The polymerization reaction was finally terminated by rapidly flushing the unreacted propylene. After each experiment, the resulting polymer was dried under vacuum at 50 °C for 4 h.

Results and Discussion

A number of polymerization tests were carried out; the recipes and the polymerization yields are shown in Table 1. The reactions were carried out at constant temperature, cocatalyst concentration and donor concentration. The main difference between these experiments is the hydrogen concentration and the technique implemented in calculating the polymerization profile.

Reproducibility

The reproducibility has been tested by repeating a standard experiment. The experimental results show excellent reproducibility in polymerization rate profiles.^[17]

Experimental Results

Pressure-Drop Dilatometry

In Figure 3a–c the time versus polymerization rate plots are shown for Runs 1, 2 and 4. From these plots, different facts can be observed. First, the curves resulting from dilatometric and the corresponding calorimetric data are almost similar; only in the initial stages is there a discrepancy. In isoperibolic calorimetry, the quasi-steady state heat balance is used to estimate the polymerization rate; thus, calculating the polymerization rate during the first few minutes is not possible. The dilatometric approach includes the dynamics of both reaction pressure and temperature which are measured fast with a short time lag (≈ 3.0 s) from the early beginning of the polymerization reaction; this results in more accurate estimations of polymerization rate particularly at the beginning. Note that the oscillations, in the initial period, are attributed to the differential approach used to estimate the time derivatives of pressure and temperature.

Looking more closely at the discrepancies during the initial stages the following should be stressed. The information during this period given by dilatometry is consistent with the present state of knowledge concerning this type of polymerization process. This issue is discussed in more detail in Al-haj Ali et al.^[26]

Second, since the difference between the estimated polymerization rates using both techniques is small, the assumption of constant fitting parameters, M_1 and M_2 in Equation (9), seems acceptable; consequently β and $\bar{\kappa}$ could be assumed constant since other parameters in Equation (10) and (11) are independent of the specific experiment. Table 2 gives the M_1 and M_2 values for the experiments. The results show that M_2 does not change with changing hydrogen concentration in the system, for hydrogen additions up to 250 mg. The situation is different for M_1 ; the compressibility changes when adding small

Table 1. Recipes used in the polymerization experiment. Reaction: $T = 70$ °C, catalyst = 3.78 mg, TEA = 1 040 mg, and donor = 50 mg.

Run	H ₂ added	Yield	Technique
	mg	kg · g _{cat} ⁻¹ · h ⁻¹	
1	0	14.5	Pressure-drop dilatometry ^{c)}
2	50	57.1	Pressure-drop dilatometry ^{c)}
3	150	82.5	Pressure-drop dilatometry ^{c)}
4	250	83	Pressure-drop dilatometry ^{c)}
5 ^{b)}	1 000	78.2	Pressure-drop dilatometry ^{c)}
6	150	79.9	Constant-pressure dilatometry

^{a)}Reaction conditions: $T = 70$ °C, catalyst = 1.58 mg, TEA = 1 040 mg, and donor = 50 mg; ^{b)}Polymerization rate is calculated also using isoperibolic calorimetry.

Figure 3. Dilatometry versus isoperibolic calorimetry for propylene polymerization with: (a) 0.0, (b) 50, (c) 250, and (d) 150 mg H₂.

amounts of hydrogen; however, this parameter is constant at high hydrogen concentrations.

The predictability of this approach is examined by fixing the values M_1 and M_2 to be 1.6 and 2.0 respectively and

Table 2. Fitting parameters for Equation (9).

Run	1	2	4	5
M_1	1.85	1.57	1.62	3.10
M_2	2.01	1.99	2.05	4.8
M_2/M_1	1.09	1.27	1.27	1.55

estimating the polymerization rate when 150 mg H₂ is added (Run 3). The results, Figure 3d, show satisfactory agreement with the calorimetric method. The predictability of this technique is examined further by considering the polymerization experiment using an extremely high hydrogen concentration (Run 5). For this experiment, catalyst mass and $\rho_{m,0}$ are 1.58 mg and 355 kg·m⁻³, respectively, compared to 3.78 mg and 425 kg·m⁻³ for the others. M_1 and M_2 for Run 5 are estimated by two approaches: (i) using the fixed values for these parameters that are obtained for the previous experiments, this approach gives 3.2 and 4 respectively, and (ii) fitting these parameters, this method gives 3.1 and 4.8 respectively. Figure 4 illustrates the results for both approaches; the former approach shows a good agreement with the calorimetric method with a maximum error of 20%. The latter approach gives better agreement with 5% maximum error. The obtained polymerization profiles are further used to estimate the reaction yield. The second method gives a yield of 85 g compared to 90.4 g obtained experimentally. Interestingly, the difference between the two methods is not high, even though the fitting parameters, for the first approach, are obtained at hydrogen concentrations far below that for the considered experiment.

The comparison between the fitted and the estimated model parameters (Run 5) gives a clear indication that the volume expansivity term, M_2 , is the reason for the difference in the obtained fits. A possible reason for this difference in M_2 values could be that increasing hydrogen concentration has a pronounced effect on β ; however, this would need experimental verification.

Based on these results, it can be stated that for a specific reactor system, pressure-drop parameters can be taken as constants within certain operating conditions and this method can be used to predict the polymerization rate even when the polymerization reaction takes place; that is, the method can be used on-line.

Figure 4. Dilatometry versus isoperibolic calorimetry for propylene polymerization with 1000 mg H₂: (a) isoperibolic calorimetry, (b) dilatometry model with optimal fitted parameters, and (c) dilatometry model with fitted parameters which is estimated using polymerization experiments with different H₂ concentration.

It should be emphasized that the variation of $\bar{\beta}$ and $\bar{\kappa}$ with operating conditions might be complicated and a separate study would be required to obtain accurate information; however, this is beyond the scope of this study. Instead, a brief study was done to estimate the ratio of $\bar{\beta}$ to $\bar{\kappa}$ at three hydrogen concentrations: 0, 100 and 1000 mg. The measurements were performed in a system without reaction so that $R_p = 0$; subsequently, Equation (9) can be rewritten as:

$$\left(\frac{\Delta P/\Delta t}{\Delta T/\Delta t}\right)_V = \frac{\bar{\beta}}{\bar{\kappa}} \quad (18)$$

In this study, the reactor is filled totally with liquid propylene at 30 °C, and left until reactor pressure and temperature stabilize. In the three experiments, reactor temperature is increased from 30 to 80 °C; when the target temperature is reached the system is left again until it

Figure 5. Estimation of β/κ at different hydrogen concentrations: (a) 0.0, (b) 100, and (c) 1000 mg.

Figure 6. Pressure and monomer feed during propylene polymerization rate in a constant pressure dilatometer.

reaches the quasi-equilibrium state. Figure 5 shows the profiles for the ratio of $\bar{\beta}$ to $\bar{\kappa}$ and reactor pressure at different hydrogen concentrations. At equilibrium, this ratio has values of 0.48, 0.45 and 0.49 at hydrogen amounts of 0, 100 and 1000 mg respectively. This gives a clear indication that the addition of hydrogen does not affect the ratio itself; subsequently, $\bar{\beta}$ and $\bar{\kappa}$ respond similarly to the changes in hydrogen concentration.

These findings may not be applicable if polymerization is performed because the reaction results in a complex mixture of polymer, monomer and hydrogen. This applicability is checked by estimating this ratio (M_2/M_1) using the data in Table 2, which results in different values. The reason for the discrepancy is not fully clear; more research is required to gain a deeper understanding of the results and to improve the dilatometric approach.

Compensation Dilatometry

Constant-pressure dilatometry is implemented in calculating the polymerization rate at 70 °C and an added hydrogen amount of 150 mg (Run 6). Figure 6 shows the pressure profile and the decrease in monomer inside the storage vessel for this run. Table 3 shows the measured yield and the amount of monomer added to keep the dilatometer pressure constant; these values with monomer density are used to estimate the value of in situ ρ_p . The resulted value is comparable to the known value of poly(propylene) density. This gives a clear indication that measured parameters are accurate enough to be used in polymerization rate calculations.

Table 3. Polymerization parameters used in polymerization rate calculations (Run 6).

Polymerization Yield	Propylene Pumped	ρ_m	ρ_p
g	g	kg · m ⁻³	kg · m ⁻³
112.7	64.8	415.6	978

Figure 7. Isoperibolic calorimetry versus constant-pressure dilatometry.

Figure 7 shows the polymerization profiles that are estimated by compensation dilatometry and isoperibolic calorimetry. The polymerization experiments were performed using similar experimental conditions which are given in Table 1. Within the experimental reproducibility, both approaches give comparable kinetic information: the decay rate of the polymerization profiles is almost equal; in addition, extrapolating these profiles to $t=0$ gives comparable values for the initial polymerization rate.

The dilatometric method could not be implemented before the reactor pressure starts decreasing and the pump starts running, this requires about 5.0 min for the studied

Figure 8. Comparison between temperature profiles for constant-pressure dilatometry and isoperibolic calorimetry.

experiment. The kinetic information within this time interval is therefore not available. Thus, compared to the calorimetric method, this technique does not give more insight into the early stage of the polymerization reaction.

Note that the addition of liquid monomer during the polymerization reaction has almost no effect on the temperature profile, Figure 8, although the monomer temperature is lower than the temperature of reactor contents. This is attributed to the fact that the reaction is highly exothermic with a uniform distribution of the produced heat due to good mixing of reactor contents. In addition, the mass of monomer fed to the reactor (70 g) is

Table 4. Comparison between isoperibolic calorimetry and dilatometric techniques.

Property	Calorimetry ^{a)}	Compensation dilatometry	Pressure-drop dilatometry
Measurements needed	Polymerization temperature	The amount of monomer pumped	Polymerization temperature ^{b)} and pressure
Calculations required	Energy balance equation and polymerization yield	Polymerization yield and equation that describes the volume change due to polymer formation	Yield and compressibility
Accuracy	Heat transfer coefficient should be constant, which is usually achievable	Depends on the accuracy of the in situ polymer density.	As long as the fluctuations in $\bar{\kappa}$ and $\bar{\beta}$ are limited.
Results		Comparable with rate profiles obtained by isoperibolic calorimetry	
Kinetics not available	First 1.5 min	Until maximum pressure is reached	None
Simplicity ^{c)}	difficult	simple	difficult
On-line implementation	Not applicable	Limited applicability	Limited applicability
Conditions	Partially and fully-filled reactors	Filled reactors only	

^{a)}Isoperibolic calorimetry; ^{b)}If the reaction performed isothermally, no temperature measurements are required.

small compared to the mass of propylene inside the reactor (2 000 g).

Table 4 shows a comparison between isoperibolic calorimetry and the dilatometric techniques.

Conclusion

The polymerization rate of liquid propylene was calculated using the dilatometric technique and compared to the value obtained from the isoperibolic calorimetry approach. Dilatometry was applied in two scenarios: (i) pressure-drop approach and (ii) constant pressure approach. In pressure-drop dilatometry, reactor pressure is allowed to vary. The polymerization rate is estimated using the compressibility of reactor contents and reaction temperature and pressure.

Using the constant-pressure method, reactor pressure is kept constant through the continuous compensation of monomer consumption. Monomer feed rate is used to estimate the polymerization rate.

The applicability of these methods to calculate the polymerization rates and the verification of the resulted kinetic data were demonstrated using several polymerization runs. The simultaneous use of isoperibolic calorimetry to measure the reaction rate showed that the polymerization rate profiles which are obtained by both techniques are comparable. Contrary to the isoperibolic calorimetry method, the pressure-drop dilatometry method allows estimation of the polymerization rate at the initial stages of the polymerization reaction. However, this is not possible when constant-pressure dilatometry is used. This is due to the fact that monomer is not fed to the reactor before reactor pressure starts decreasing, which requires a few minutes after catalyst injection.

Similar to the isoperibolic calorimetry method, dilatometric methods depend on a few parameters which are not known accurately. Yet, the estimated parameters can be used to calculate the polymerization rate at other reaction conditions; subsequently, the dilatometric techniques can be used to estimate the polymerization rate on-line. This is applicable within a predefined range of operating conditions relatively close to the operating point at which the parameters were found. Understanding the effect of hydrogen on these parameters, especially $\bar{\beta}$, requires additional research.

Nomenclature

A_w	average wall area inside the reactor available for heat transfer m^2
ΔH_r	heat of polymerization reaction $kJ \cdot kg^{-1}$

m_c	mass of catalyst injected mg
M_1	fitting parameter $kg \cdot g_{cat}^{-1} \cdot bar^{-1}$
M_2	fitting parameter $kg \cdot g_{cat}^{-1} \cdot ^\circ C^{-1}$
P	reaction pressure bar
R_p	rate of polymerization $kg \cdot g_{cat}^{-1} \cdot h^{-1}$
T	reaction temperature $^\circ C$
ΔT_{BL}	difference between reactor temperature and average jacket temperature before starting reaction $^\circ C$
t	time h
$\bar{U}$	average heat transfer coefficient $W \cdot m^{-2} \cdot ^\circ C^{-1}$
V_r	reactor volume m^3
V_L	volume of the reacted monomer m^3
V_p	volume of the produced polymer m^3

Greek Letters

β	isothermal compressibility $^\circ C^{-1}$
κ	volume expansivity bar^{-1}
ρ_m	monomer density $Kg \cdot m^{-3}$
ρ_p	polymer density $Kg \cdot m^{-3}$
v_m	specific volume of the monomer $Mol \cdot m^{-3}$
v_p	specific volume of the polymer $mol \cdot m^{-3}$

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