

Reaction calorimetric investigation of 1-olefin homo- and copolymerization using homogeneous metallocene catalysts

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Abstract

A polymerization reactor system was designed to monitor simultaneously total and individual polymerization rates of liquid and gaseous 1-olefin monomers. Key element of this system is the combination of mass-flow meters and heat flow calorimetry. Polymerization kinetics of propene- and 1-octene-homo- and copolymerizations using the homogeneous methylalumoxane-activated Cp_2ZrCl_2 were investigated. Monomer reactivity ratios and rate constants were determined from calorimetric data.

Keywords: Calorimetry; Copolymerization; Cyclopentadienyl derivatives; Homogeneous catalysis; Kinetics; Polymerization; MAO; Mass flow measurement; Metallocene; Monomer reactivity ratios; 1-Octene; Propene; Ziegler–Natta catalysts; Zirconium

1. Introduction

Modern generations of metallocene-based Ziegler–Natta catalysts consist of essentially one type of catalytically active center which produces 1-olefin-homo- and copolymers with narrow molecular weight distributions and uniform comonomer distributions [1–3]. The development of such single-site catalysts greatly facilitates the elucidation of elementary reactions in transition-metal catalysed polyinsertion and stimulates the production of novel polyolefin materials [4–6]. Objective of our research is to understand polymerization kinetics of the metallocene-catalyzed homo- and copolymerization of 1-olefins. Here we report a new reactor system, combining feed control and reaction calorimetry, to simultaneously monitor total polymerization rate and individual

polymerization rates of gaseous and liquid 1-olefins. The homogeneous Cp_2ZrCl_2 catalyst activated with methylalumoxane (MAO) [7,8] has been used to prepare propene and 1-octene homo- and copolymers.

2. Apparatus

The calorimeter RM-2S with a 200 ml/100 atm stainless-steel reactor and the VRC-IN interface were supplied by ChemiSens AB (S-223 78 Lund, Sweden). This reactor system is a combined heat flow and heat balance calorimeter. The calorimeter was equipped with a personal computer and software for graphic display and data storage. As is apparent in Fig. 1, a mass flow meter (F-111C, Bronkhorst, NL-7261 AK Ruurlo, Netherlands) and a pressure gage were connected to the VRC-

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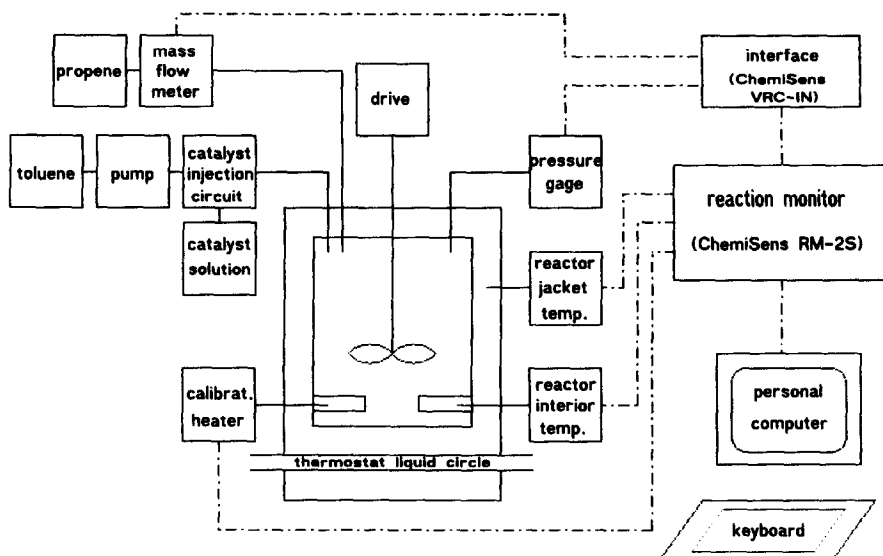


Fig. 1. Scheme of the reaction calorimeter combined with mass flow meter for gaseous monomers, catalyst and solvent feed, and pressure and temperature control.

IN interface. A HPLC injection circuit and a high pressure pump were used for the injection of the catalyst solution. With this reactor system it was possible to measure reactor temperature, reactor pressure, heat flow, heat balance, and mass flow and control pressure and temperature independently.

3. Polymerization procedure

Cp_2ZrCl_2 and 1-octene were obtained from Aldrich Co., MAO (10 wt%, $M_n = 1000$ g/mol) from Witco GmbH (former Schering AG), toluene from Roth GmbH, and propene (polymerization grade) from the BASF AG. Toluene solvent was rectified over LiAlH_4 , refluxed and distilled over Na/K alloy prior to use. 1-Octene was distilled over CaH_2 . Cp_2ZrCl_2 , propene, and MAO were used without further purification. All substances were handled under dry and oxygen-free argon atmosphere.

The stainless-steel reactor was rinsed with 150 ml of a 0.03 mol/l $\text{Al}(\text{CH}(\text{CH}_3)_2)_3$ solution in toluene prior to use. Toluene, 1-octene (0–0.82 mol/l), and MAO (50 mmol/l) were pumped into the stainless-steel reactor. The total volume of the reaction mixture was 100 ml and the polym-

erization temperature was 40°C. After the calibration of the calorimeter propene (0–0.82 mol/l, equal to 0–2 atm at 40°C) was added and heat flow (\dot{Q}_{sat}) and mass flow (\dot{M}_{sat}) of the saturation of propene in toluene were measured for the calculation of the heat of solution ($Q_{\text{P,sol}}$) of propene in toluene (1).

$$Q_{\text{P,sol}} = M_{\text{P}} * \sum_{t=t_0}^{t_1} \dot{Q}_{\text{sat}} / \sum_{t=t_0}^{t_1} \dot{M}_{\text{sat}} \quad (1)$$

where M_{P} = molecular weight of propene, t_0 = start of saturation, t_1 = end of saturation.

The total concentration of the monomers (propene and 1-octene) was 0.82 mol/l in all runs. After saturating toluene with propene, 2 ml of Cp_2ZrCl_2 solution in toluene (1.46 mg Cp_2ZrCl_2 equivalent to 50 $\mu\text{mol/l}$ and $\text{Al/Zr} = 1000$) was added to start the polymerization. The pressure of propene was kept constant during the polymerization. After 1 h the calorimeter was calibrated again (postcalibration), before quenching the polymerization with 10 ml methanol.

4. Determination of the individual copolymerization heat flow components

The total heat flow observed (\dot{Q}_{tot}) is the sum

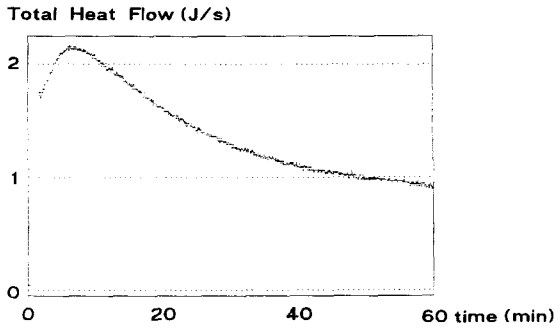


Fig. 2. Total heat flow (\dot{Q}_{tot}) of propene/1-octene (1 mol/l mol) copolymerization as a function of time (Polymerization conditions: 0.41 mol/l propene, 0.41 mol/l 1-octene, 50 $\mu\text{mol/l}$ Cp_2ZrCl_2 , 50 mmol/l MAO (Al/Zr = 1000), solvent: toluene, total volume of the reaction mixture: 100 ml, polymerization temperature: 40°C.).

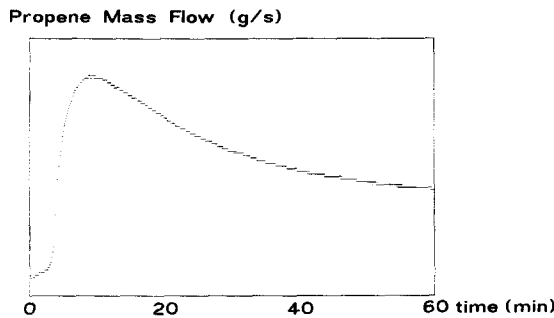


Fig. 3. Propene mass flow (\dot{M}_p) as a function of time (Polymerization conditions: 0.41 mol/l propene, 0.41 mol/l 1-octene, 50 $\mu\text{mol/l}$ Cp_2ZrCl_2 , 50 mmol/l MAO (Al/Zr = 1000), solvent: toluene, total volume of the reaction mixture: 100 ml, polymerization temperature: 40°C.).

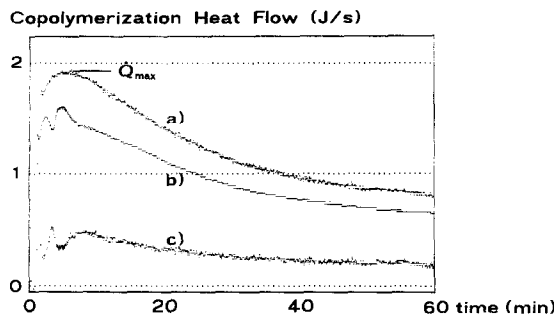


Fig. 4. a) Copolymerization heat flow ($\dot{Q}_{\text{OP, pol}}$) as a function of time (The maximum heat flow (\dot{Q}_{max}) is marked), b) propene polymerization heat flow ($\dot{Q}_{\text{P, pol}}$) as a function of time, c) 1-octene polymerization heat flow ($\dot{Q}_{\text{O, pol}}$) as a function of time. (Polymerization conditions: 0.41 mol/l propene, 0.41 mol/l 1-octene, 50 $\mu\text{mol/l}$ Cp_2ZrCl_2 , 50 mmol/l MAO (Al/Zr = 1000), solvent: toluene, total volume of the reaction mixture: 100 ml, polymerization temperature: 40°C.).

of three components: the heat flow of heat of solution of propene in toluene ($\dot{Q}_{\text{P, sol}}$), the heat flow resulting from propene polymerization ($\dot{Q}_{\text{P, pol}}$),

and the heat flow resulting from 1-octene polymerization ($\dot{Q}_{\text{O, pol}}$) (see (2) and Fig. 2).

$$\dot{Q}_{\text{tot}} = \dot{Q}_{\text{P, sol}} + \dot{Q}_{\text{P, pol}} + \dot{Q}_{\text{O, pol}} \quad (2)$$

Thus the heat flow of the copolymerization reaction ($\dot{Q}_{\text{PO, pol}}$) is measured as reduced total heat flow by subtracting the heat flow of the solution heat of propene in toluene ($\dot{Q}_{\text{P, sol}}$) from the total heat flow (\dot{Q}_{tot}) (3).

$$\dot{Q}_{\text{PO, pol}} = \dot{Q}_{\text{P, pol}} + \dot{Q}_{\text{O, pol}} = \dot{Q}_{\text{tot}} - \dot{Q}_{\text{P, sol}} \quad (3)$$

As depicted in Fig. 3, the mass flow of propene (\dot{M}_p) which is required to maintain constant reactor pressure, was measured using the mass flow meter. The heat flow of solution heat of propene ($\dot{Q}_{\text{P, sol}}$) in toluene can be calculated using Eq. (4).

$$\dot{Q}_{\text{P, sol}} = \dot{Q}_{\text{P, sol}} * \dot{M}_p / M_p \quad (4)$$

The calculated heat flow of the copolymerization ($\dot{Q}_{\text{PO, pol}}$) is shown in Fig. 4 as a function of time.

The heat flow of the propene polymerization ($\dot{Q}_{\text{P, pol}}$) can be calculated using the mass flow of propene into the reactor (\dot{M}_p) and the heat of propene homopolymerization ($Q_{\text{P, pol}}$) (5). The heat of propene homopolymerization ($Q_{\text{P, pol}}$) was determined from a propene homopolymerization experiment.

$$\dot{Q}_{\text{P, pol}} = Q_{\text{P, pol}} * \dot{M}_p / M_p \quad (5)$$

As the solubility of propene in toluene depends strongly on temperature and pressure, even small changes of the reaction conditions, especially at the start of polymerization, have to be taken into account.

The calculated heat flow of propene polymerization ($\dot{Q}_{\text{P, pol}}$) is shown in Fig. 4. As can be seen, these changes of the polymerization conditions at the beginning of the polymerization were not completely compensated.

The heat flow of the 1-octene polymerization ($\dot{Q}_{\text{O, pol}}$) can be calculated by subtracting the heat flow of the propene polymerization ($\dot{Q}_{\text{P, pol}}$) from the heat flow of the copolymerization reaction ($\dot{Q}_{\text{PO, pol}}$) (see (6) and Fig. 4).

$$\dot{Q}_{\text{O, pol}} = \dot{Q}_{\text{PO, pol}} - \dot{Q}_{\text{P, pol}} \quad (6)$$

5. Calculation of the monomer reactivity ratios

For the calculation of the monomer reactivity ratios the equations of the Mayo/Lewis model [9] were used. As a consequence of the first-order Markoffian statistics, the total polymerization rate (R_{tot}) depends on the number of active sites ($[M_O^*]$, $[M_P^*]$), the monomer concentrations ($[M_O]$, $[M_P]$), and the rate constants (k_{OO} , k_{OP} , k_{PO} , k_{PP}) (7).

$$\begin{aligned} R_{\text{tot}} &= R_{OO} + R_{OP} + R_{PO} + R_{PP} \\ &= k_{OO}[M_O^*][M_O] + k_{OP}[M_O^*][M_P] \\ &\quad + k_{PO}[M_P^*][M_O] + k_{PP}[M_P^*][M_P] \end{aligned} \quad (7)$$

At the beginning of the polymerization reaction the number of active sites is assumed to be the same in the performed experiments, since the same amount of the catalyst is used (8).

$$[M_O^*] + [M_P^*] = \text{const.} \quad (8)$$

The heat flow of the copolymerization ($\dot{Q}_{OP,\text{pol}}$) depends on the polymerization rates and the polymerization heat of the monomers 1-octene and propene ($Q_{O,\text{pol}}$, $Q_{P,\text{pol}}$) (9).

$$\begin{aligned} \dot{Q}_{OP,\text{pol}} &= (R_{OO} + R_{PO}) * Q_{O,\text{pol}} \\ &\quad + (R_{OP} + R_{PP}) * Q_{P,\text{pol}} \end{aligned} \quad (9)$$

$Q_{O,\text{pol}}$ and $Q_{P,\text{pol}}$ are determined from the corresponding homopolymerizations and found to be equivalent within limits of errors. Thus Eq. (9) leads to the simple correlation where the heat flow of the copolymerization ($\dot{Q}_{OP,\text{pol}}$) is proportional to the total polymerization rate (R_{tot}) (10).

$$\begin{aligned} Q_{P,\text{pol}} &= Q_{O,\text{pol}} \Rightarrow \\ \dot{Q}_{OP,\text{pol}} &= (R_{OO} + R_{PO} + R_{OP} + R_{PP}) * Q_{P,\text{pol}} \\ &= R_{\text{tot}} * Q_{P,\text{pol}} \end{aligned} \quad (10)$$

Because of the deactivation of the catalyst with time, the maximum heat flow of the total polymerization reaction (\dot{Q}_{max} , see Fig. 4) is used for calculating the total polymerization rate (R_{tot}).

The homopolymerization rate constants (k_{OO} , k_{PP}) are calculated from the homopolymerizations

of the monomers. The use of Eqs. (11), (12), and (13) leads to Eq. (14).

$$\begin{aligned} R_{OP} &= R_{PO} \Rightarrow \\ [M_O^*]/[M_P^*] &= k_{PO}[M_O]/k_{OP}[M_P] \end{aligned} \quad (11)$$

$$r_O = k_{OO}/k_{OP} \quad (12)$$

$$r_P = k_{PP}/k_{PO} \quad (13)$$

$$\begin{aligned} R_{\text{tot}}k_{PP}[M_O] - k_{OO}k_{PP}[M_O]^2 r_O \\ + (R_{\text{tot}}k_{OO}[M_P] - k_{PP}k_{OO}[M_P]^2)r_P \\ = 2k_{OO}k_{PP}[M_O][M_P] \end{aligned} \quad (14)$$

Abbreviation of Eq. (14): $a * r_O + b * r_P = c$

Eq. (14) contains two undefined constants: r_O and r_P . These constants can be evaluated using the data of two copolymerizations 1 and 2 ((15) and (16)).

$$r_O = (b_2 * c_1 - b_1 * c_2) / (a_1 * b_2 - a_2 * b_1) \quad (15)$$

$$r_P = (a_1 * c_2 - c_1 * a_2) / (a_1 * b_2 - a_2 * b_1) \quad (16)$$

6. Results

The $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system was selected as model catalyst because both catalyst and homo-or copolymers, respectively, remain in solution during the polymerization. The use of Eqs. (15) and (16) in connection with the data of the experiments (see Table 1) leads to $r_O = 0.69$ and $r_P = 4.8$. The monomer reactivity ratios determined by ^{13}C -NMR are $r_O = 0.61$ and $r_P = 5.0$. The accordance of the calculated r_O and r_P determined by the maximum heat flow (\dot{Q}_{max}) with the r_O and r_P determined by NMR is shown in Fig. 5. The upper curve represents the maximum heat flow as

Table 1
Experimental maximum heat flows

1-Octene [mol%]	Propene [mol%]	Max. heat flow (\dot{Q}_{max}) [J/s]
100	0	0.57 ± 0.05
75	25	0.90 ± 0.05
50	50	1.78 ± 0.05
25	75	3.03 ± 0.05
0	100	5.18 ± 0.05

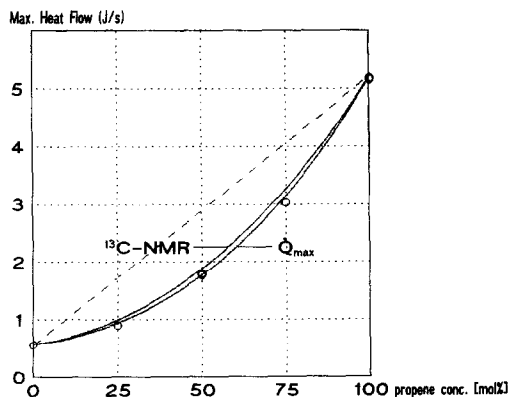


Fig. 5. Maximum heat flow (Q_{\max}) as a function of propene concentration (0 mol% propene is equal to 100 mol% 1-octene, polymerization conditions: 0–0.82 mol/l propene, 0–0.82 mol/l 1-octene (total concentration of the monomers: 0.82 mol/l in all runs), 50 $\mu\text{mol/l}$ Cp_2ZrCl_2 , 50 mmol/l MAO (Al/Zr = 1000), solvent: toluene, total volume of the reaction mixture: 100 ml, polymerization temperature: 40°C.).

Table 2
Relative copolymerization rate constants

Rate constant	Value [$\text{l mol}^{-1} \text{s}^{-1}$]
k_{PP}	1.68
k_{PO}	0.34 ^a /0.35 ^b
k_{OP}	0.30 ^a /0.27 ^b
k_{OO}	0.19

^a Using r_{O} and r_{P} determined by ^{13}C -NMR.

^b Using r_{O} and r_{P} determined by Q_{\max} .

a function of the propene content of in the polymerization mixture using the r_{O} and r_{P} determined by NMR. The lower curve is calculated with the r_{O} and r_{P} determined by the Eqs. (15) and (16).

As indicated in Table 2, the four relative rate constants of the copolymerization reaction can be calculated using the homopolymerization rate constants k_{OO} and k_{PP} and the monomer reactivity ratios r_{O} and r_{P} .

The relative values of the rate constants can be explained on the basis of steric interactions when the monomer complexes at the vacant coordination site and inserts into the zirconium alkyl bond. The less sterically hindered propene inserts faster when compared to 1-octene insertion ($k_{\text{PP}} > k_{\text{OO}}$). Interestingly, the last monomeric unit appears to influence the insertion of the 1-olefin monomers. In comparison to polymers where a propene unit is attached to the active center, the presence of a

1-octene unit adjacent to the active center accounts for lower rate constants ($k_{\text{PP}} > k_{\text{OP}}$ and $k_{\text{PO}} > k_{\text{OO}}$).

7. Conclusions

The reaction calorimeter equipped with a mass flow meter monitors simultaneously the total and individual kinetics of the copolymerization of liquid and gaseous monomers. The equations of the kinetics of free radical copolymerization (first-order Markoffian statistics) are valid within limits of errors for the 1-olefin copolymerization with the single site catalyst Cp_2ZrCl_2 activated with MAO. When two homo- and two (or more) copolymerization experiments are performed, it is possible to determine the monomer reactivity ratios as well as the four propagation rate constants. This provides the basis for a better understanding of the chain propagation process and the parameters governing the incorporation of the comonomers of the active sites. This insight into elementary reactions offers interesting potential in controlling 1-olefin copolymerizations with single site metallocene catalysts.

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