DOI: 10.1002/masy.200751333

Kinetic Study of the Copolymerisation of Ethylene with a Single Site Catalyst in Propane Slurry Polymerisation

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Summary: The kinetic behaviour of a supported metallocene catalyst in slurry polymerisation of ethylene with 1-hexene under industrially relevant reaction conditions has been studied.Polymerisation experiments were carried out in a 5-litre stirred tank reactor in a temperature range from 60 to 80 °C and ethylene partial pressures from 5 to 15 bar. Comonomer and hydrogen amounts were varied as well. The catalyst showed pronounced activation and slow deactivation during runtimes of about 1 hour. Strong influences of 1-hexene ("hexene effect") and hydrogen ("hydrogen effect") on the activity profiles were observed.Based on the experimental results, a kinetic model has been derived in order to describe and predict important polymerisation data such as activity profile, comonomer content and molecular weight distributions with respect to the reaction conditions.The presented kinetic model is able to describe the observed effects of 1-hexene and hydrogen on the activity profiles, as well as the comonomer incorporation across a broad range of polymerisation conditions. The molecular weight distributions can be simulated with good qualitative agreement to the experimental data.

Keywords: copolymerisation; kinetics; metallocene; modelling; polyethylene (PE)

Introduction

The development of metallocene single site catalysts in the past decades led to a vast variety of catalysts and catalyst classes as described by many authors previously (e.g. Tuchbreiter and Mülhaupt[1] or Severn et al.[2]). The demand of single site produced polyolefins with tailored molecular weight distributions is increasing due to their unique properties. A detailed understanding of catalyst behaviour under different process conditions in terms of kinetics and polymer properties is important in order to secure safe and efficient operation and faster scale-up to pilot and full-scale production. Lab scale polymerisations at industrially relevant conditions are a cheap possibility of testing a catalyst's behaviour which can be carried out with very small quantities of catalyst. The analysing of the experimental data in the form of a mathematical model makes the handling of the generated data easier and allows a better implementation to process and reactor modelling.

In this study, a silica supported single site catalyst of Borealis was used in the copolymerisation of ethylene with 1-hexene in a propane slurry.

Supported catalysts in slurry polymerisation often show an increase of the activity in time, which is then followed by a deactivation period. Activity profiles in PE-homopolymerisations with metallocene catalysts can often be described by reaction

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schemes containing an activation and deactivation step along with a propagation reaction. This approach was used for instance by Xu, Chakravati and Ray.[3] Wang et al.[4] used an extended scheme by adding a reactivation step for active sites and transfer reactions in order to describe molecular weight distributions. Slurry and gas phase homopolymerisation of ethylene was compared by Bergstra and Weickert[5] in a kinetic study at industrially relevant conditions. Effective reaction orders between one and two with respect to bulk phase concentrations of ethylene can be described by a kinetic model with reversible activation step of pre-active sites with monomer.

In order to describe copolymerisations, one needs at least two propagation reactions. Commonly accepted schemes are the 0th, 1st and 2nd order Markov models, describing the propagation reactions of copolymerisations. The 0th order model, meaning no influence of the last inserted monomer on the next propagation step, can be used to describe overall copolymer composition. In order to describe polymer micro structure, higher order approaches are needed. In higher order Markov models, the rate of monomer insertion depends on the type of the previously inserted monomers. Examples of the use of Markov models are the publications of Wall[6] (0th order), Mayo and Lewis[7] (1st order) and Fink and Richter[8] (2nd order).

In literature it is well known that the addition of 1-hexene can dramatically increase the polymerisation activity. Since comonomer incorporation is slower compared to ethylene, this effect cannot be described by Markov models with feasible parameters; as such it requires additional efforts. Detailed studies of rate enhancement effects caused by 1-hexene were performed by Jaber and Ray[9] for a Ziegler-Natta catalyst. Karol, Kao and Cann[10] found a decreasing rate enhancement effect with increasing length of the α-olefin comonomer for different titanium and vanadium catalysts. The suggested explanation is a reversible coordination of ligands to the active sites. Kissin[11] used a similar approach to describe activity influences of 1-hexene and hydrogen in Zigler-Natta gas phase polymerisations. A model based on the complexation of reactants at the active sites, changing their reactivity and copolymerisation behaviour was suggested by Shimizu[12] and adapted to metallocene gas phase copolymerisation of ethylene with 1-hexene by Bergstra.[13]

Another explanation of rate enhancement can be concluded from Tait and Berry,[14] which showed an increased number of active sites taking part in a Ziegler-Natta copolymerisation of ethylene with 4-methyl-1-pentene (4 to 6%) compared to its PE-homopolymerisation (0.4%). Similarities might be expected for heterogeneous metallocene polymerisations. Physical influences as reduced crystallinity due to comonomer incorporation, better catalyst break-up or swelling and co-sorption effects in gas-phase polymerisations are discussed as well (e.g. McAuley et al.[15]).

Experimental Part

The experiments were carried out at the Borealis Research Centre in Porvoo, Finland. Propane was used as suspension media, ethylene as monomer, 1-hexene as comonomer and hydrogen was used as chain transfer agent. All educts were dried and traces of impurities were removed by a series of purification columns.

The slurry polymerisations were performed in a 5-litre stirred tank reactor, pressure rated up to 100 bar. Feeding to the reactor was controlled by a set of thermal mass flow controllers. Both batch and continuous feeding could be realised during the reaction (Figure 1). The reactor temperature was controlled via a cascaded control. The catalyst powder was injected in the reactor by overpressure.

Polymerisation Procedure

Prior to the reaction the whole reactor system and tubing were inertised. After

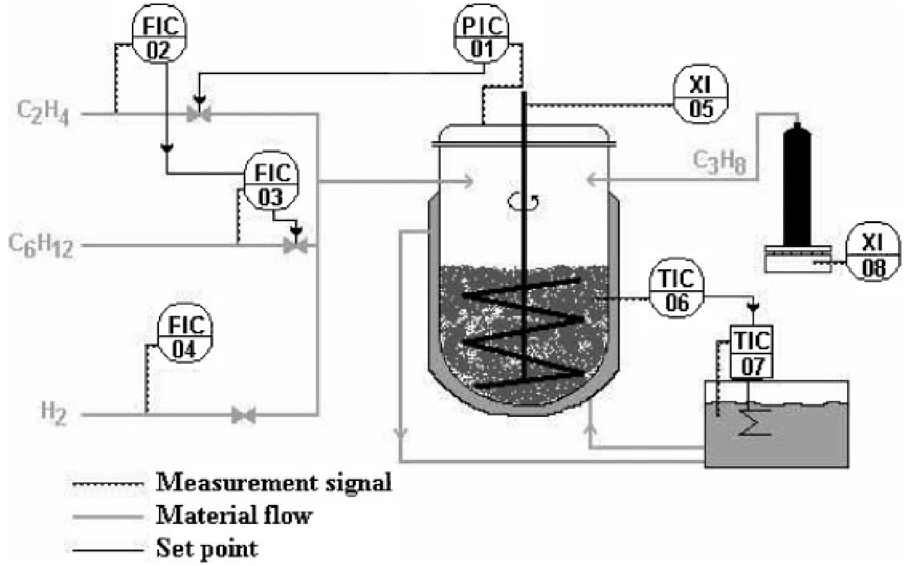

Figure 1.
Schematical reactor setup and control loops.

inertisation, the reactor was filled with 1.2 kg of propane as well as an initial amount of 1-hexene. The system was heated up to reaction temperature and then pressurised with ethylene and hydrogen until the set ethylene partial pressure was reached. The reaction was started by injection of the catalyst into the reactor. The experiments were carried out under isothermal conditions. Ethylene feed was regulated by a pressure control loop in order to maintain a constant pressure. Hydrogen and 1-hexene were fed with a constant ratio to ethylene (slave factor). All feeds, pressure and temperature were monitored and logged to a data acquisition system.

Typical polymerisation times were around 40 minutes to 1 hour. Afterwards the reactor was slowly vented, the polymer was removed and degassed for at least one day in a fume hood.

Pre-Study Results

Prior to the kinetic study, tests concerning mass transfer limitations, catalyst poisoning and reproducibility were performed. A typical temperature, activity and pressure profile of one experiment is plotted in Figure 2.

In order to obtain reliable kinetic data, one has to ensure that the activity profiles are independent of the catalyst amount. Changing activity profiles with catalyst amount can be caused by significant catalyst poisoning or mass transfer limitations at reactor scale. Different amounts of catalyst (200, 300, 400 mg) were used in a series of experiments. Because all experiments showed the same activity profiles, it is possible to conclude that catalyst poisoning is negligible for the tested range.

Transfer of monomers to the active sites can be hindered either by transport resistances at reactor level, such as transport from the vapour to the liquid phase, within the liquid phase and through the particle boundary layer or by diffusion within the particle. Diffusion within the particles cannot be affected by the operation conditions of the reactor. On the other hand, transport limitations at the reactor scale can be minimised by intensive stirring.

In order to exclude significant transport resistances, the stirring speed during one experiment was varied between 300 to

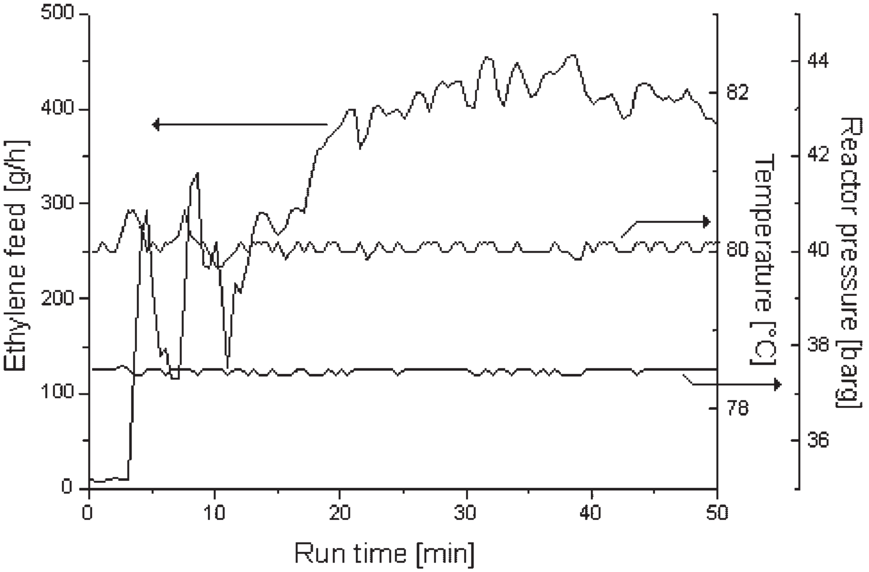

Figure 2.
Typical profiles of activity, reactor temperature and pressure.

525 rpm. The presence of notable transport resistances would then be indicated by a stepwise increase in activity at higher stirring speeds and vice versa. A good stirring speed was found to be 450 rpm. Due to the pressure control and the absence of transport limitations on reactor level, one can roughly assume constant ethylene concentrations in the reactor. This means that the amount of continuously fed ethylene equals its consumption due to reaction. Ethylene consumption in relation to catalyst amount is called ''activity'' in the frame of this publication. Reproducibility of the activity profiles was constantly verified.

Reaction Conditions

The following operation parameters were varied in the kinetic study:

Reaction temperature: 60 and 80 °C -
1-hexene feed ratio: 0 to 15 mmol/mol
Ethylene partial pressure: 5 to 15 bar -
Hydrogen feed ratio: 0 to 3 mmol/mol

Polymerisation experiments were carried out at 80 °C and 60 °C. For each temperature an experimental plan was designed to cover a set of high and low values of the operation conditions around a defined centre point (Figure 3). The initial batch feeds of 1-hexene and hydrogen were chosen carefully in order to minimize concentration drifts in time and achieve constant reaction conditions.

For clear identification of the influences of each operation parameter, it was decided to change the value of only one parameter for each experiment (Figure 3). In addition, a few experiments deviating from this scheme were conducted in order to confirm some conclusions.

The centre point is defined by 10 bar ethylene partial pressure, 7.5 mmol/mol 1-hexene feed ratio and 1.5 mmol/mol hydrogen feed ratio for each temperature.

Kinetic Study Results

The following figures show the experimentally obtained activity profiles (as well as the simulated curves, see modelling section). As one would expect, activity rises with ethylene partial pressure (Figure 4 and 5), but in a non-linear way. The maximum activity

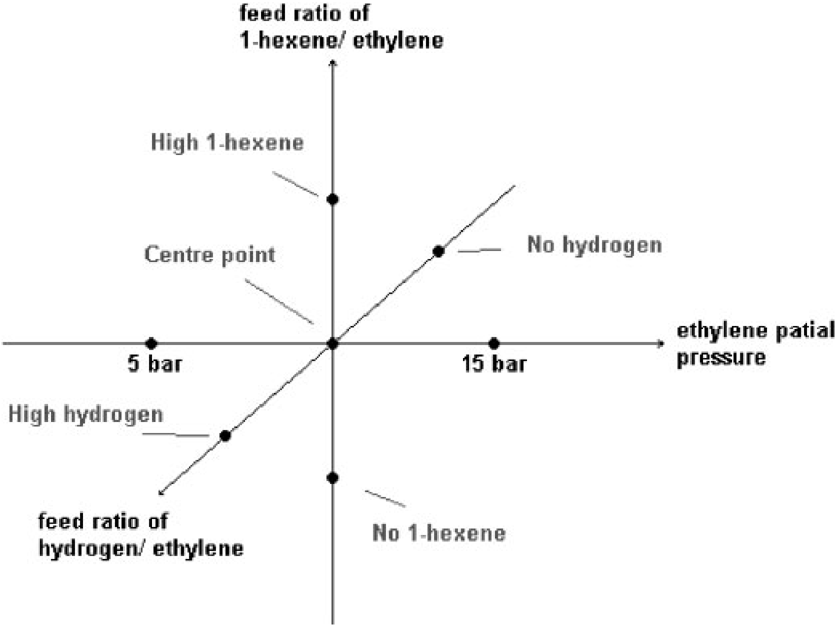

Figure 3.
Experimental design plan.

peak is shifted to earlier times with higher ethylene pressures as well.

At 80 °C there is a pronounced effect of 1-hexene on activity (Figure 6). The peak activity rises to roughly 300% of the homopolymerisation. Surprisingly the effect of 1-hexene is less important at 60 °C (Figure 7). The increase of peak activity seems to be limited to 50% only and seems to decrease for too high 1-hexene amounts. However, these activity changes are not significant compared to experimental deviations.

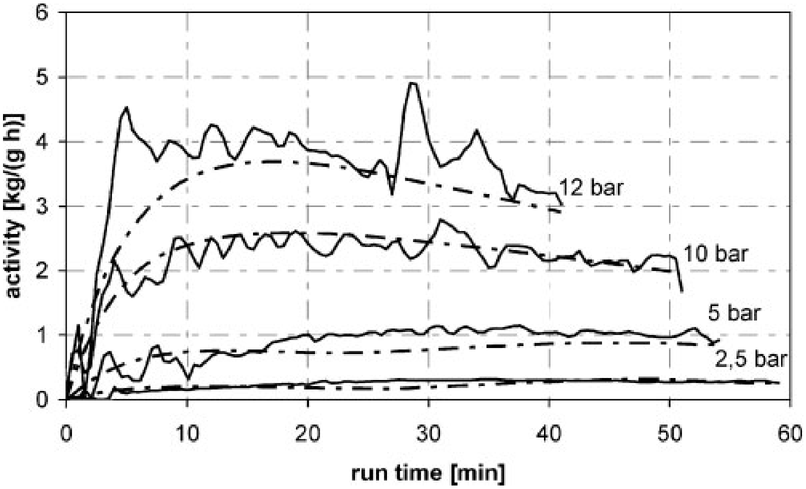

Figure 4.
Variation of ethylene partial pressure at 80 °C.

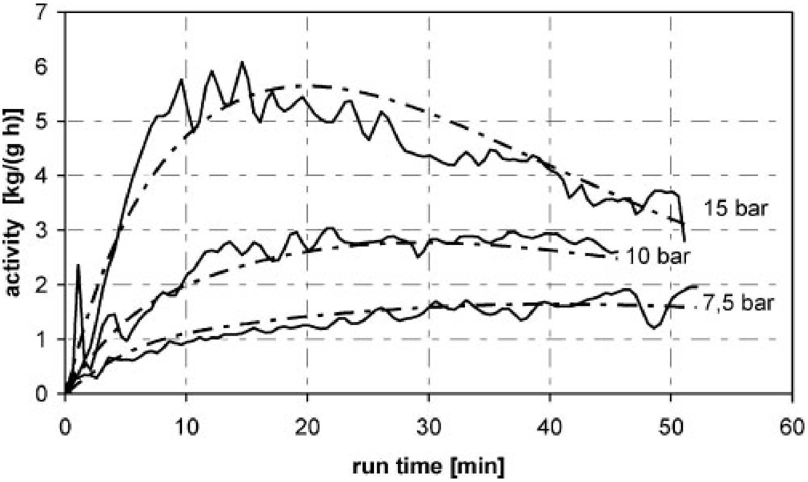

Figure 5.
Variation of ethylene partial pressure at 60 °C.

An increased activity comparable to the "hexene effect" was observed at 60 °C (Figure 9) for increasing hydrogen feeds. The "hydrogen effect" was also observed for homopolymerisation with comparable magnitude (not plotted in the figures). Hence the dormant site theory[16,17] cannot be applied for the explanation of the hydrogen effect, because miss-insertions are not possible for ethylene homopolymerisations. At 80 °C hydrogen did not alter the activity level (Figure 8).

Besides the activity profiles, average comonomer content in the final polymer (analysed by Fourier transformation infrared spectroscopy) as well as its molecular weight distribution (analysed by size exclusion chromatography) were determined.

The strong temperature dependency of the polymersation rate enhancing effects of

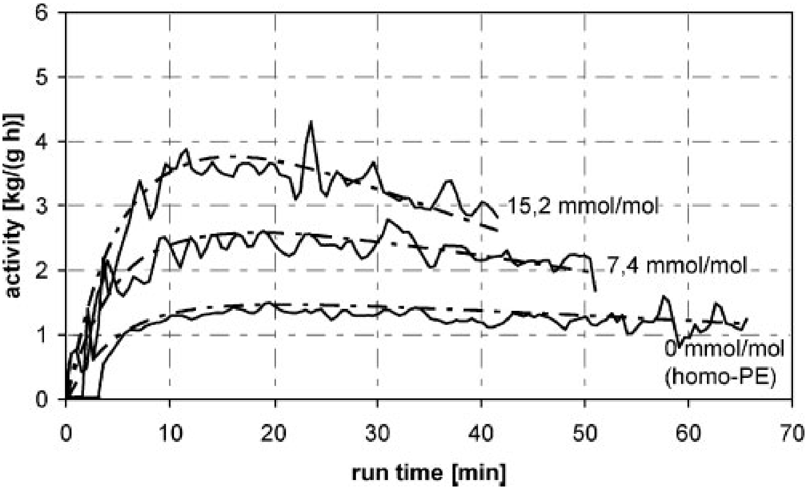

Figure 6.
Variation of molar 1-hexene to ethylene feeding ratios at 80 °C.

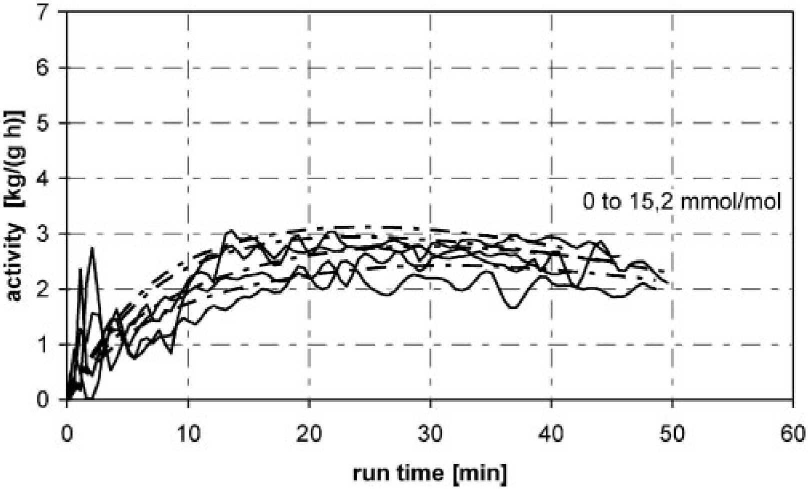

Figure 7.
Variation of molar 1-hexene to ethylene feeding ratios at 60 °C.

1-hexene (strong at 80 °C, minor at 60 °C) resp. hydrogen (strong at 60 °C, not present at 80 °C) is a surprising, unexpected, but experimentally clearly proven result.

The produced polymers contain up to 4%(wt) of 1-hexene, corresponding to a density range from 925 to 970 kg/m^3. Molecular weights obtained were in between 7 and 130 kg/mol (number average molecular weight). As expected, molecular weight was mainly regulated by the addition of hydrogen, as Figure 10 shows.

Development of the Kinetic Model

The investigated three-phase system and the reaction kinetics of coordinative polymerisations lead to a complex process behaviour. The aim of the model is to

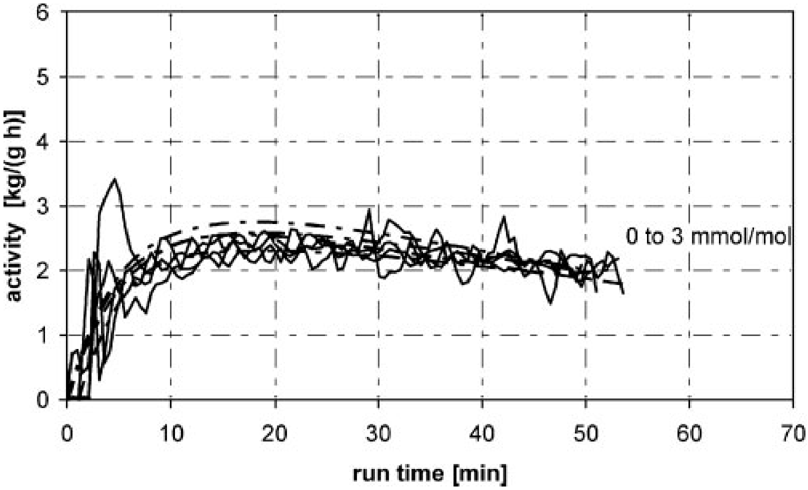

Figure 8.
Variation of hydrogen to ethylene feeding ratios at 80 °C.

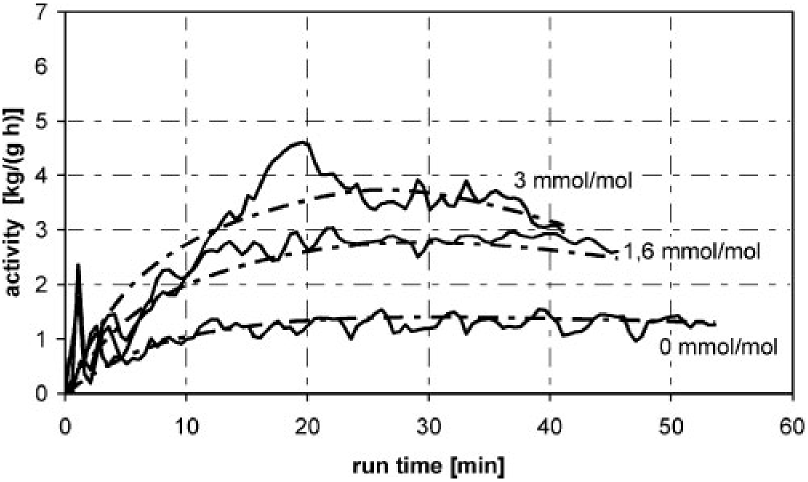

Figure 9.
Variation of hydrogen to ethylene feeding ratios at 60 °C.

describe the measured experimental data, with focus on the

- activity-time profile,
- comonomer content,
- molecular weight distribution of the polymer products

depending on the process conditions temperature, ethylene partial pressure, hydrogen and 1-hexene amounts with a theoretically justified model.

The following approach is used:

According to the reaction temperature and the initial batch-fed amounts in each experiment, the initial liquid phase concentrations of the reaction partners and the liquid phase volume are estimated by vapour-liquid-equilibrium calculations using the Peng-Robinson method (calculated with Aspen Plus®). The concentrations of the reaction partners in the polymer phase are assumed to be equal to their concentrations in the liquid phase. The concentrations of catalyst, active sites and growing chains are balanced in the polymer phase. Mass and heat transfer effects are neglected in this study.

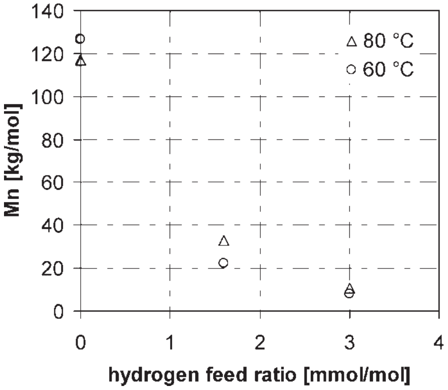

Figure 10.
Hydrogen response of the catalyst at 10 bar ethylene pressure (copolymerisation).

The aim is to develop a kinetic model capable of describing the experimental results with a minimum number of parameters. Since the focus of this study is not on copolymer microstructure, the copolymerisation kinetics were described by a 0^{th} order Markov model, meaning that the type of the last inserted monomer has no effect on the rate of the next propagation step. The challenge is to include the observed effects of 1-hexene and hydrogen on the activity-time profiles.

In this case, physical effects such as increased crystallinity or co-sorption effects could not explain the observed experimental results; hence we focused on kinetic approaches. Basically the increased activities can be described by increased reactivity of each active site (e.g. reversible complexation) or by a higher number of active sites taking part in the reaction. Since complexation models basically lead to at least two different types of active sites that exist parallel to each other, which contrasts with the definition of single site catalysts and which require more kinetic parameters, we decided to describe the increased activities by an increased number of active sites. We postulate additional activation reactions with ethylene, 1-hexene and hydrogen in order to alter the number of active sites taking part in the reaction. In order to describe the experimentally observed strong temperature dependency of the rate enhancing effects of 1-hexene and hydrogen, it can be anticipated that these phenomenological activation reactions will have strong temperature dependencies.

$$
\begin{array}{lll}
\textit{Activation} & \textit{Transfer} & C_2 \ldots \textit{ethylene} \\
Me + C_2 \xrightarrow{kiA} Me_0^* & Me_j^* + C_2 \xrightarrow{ktA} Me_0^* + D_j & C_6 \ldots 1 - \textit{hexene} \\
Me + C_6 \xrightarrow{kiB} Me_0^* & Me_j^* + C_6 \xrightarrow{ktB} Me_0^* + D_j & H_2 \ldots \textit{hydrogen} \\
Me + H_2 \xrightarrow{kiH2} Me_0^* & Me_j^* + H_2 \xrightarrow{ktH2} Me_0^* + D_j & \\
\textit{Propagation} & \textit{Deactivation} & \\
Me_j^* + C_2 \xrightarrow{kpA} Me_{j+1}^* & Me_j^* \xrightarrow{kd} Me^{deactivated} + D_j & \\
Me_j^* + C_6 \xrightarrow{kpB} Me_{j+1}^* & &
\end{array}
$$

We call this approach the "Markov 0th order model with extended activation scheme". Another attempt involved a single activation step with a set of preceding equilibrium reactions all forming the same kind of pre-active sites.[18] The preceding equilibrium model did not improve simulation results significantly and will not be presented in this publication.

The mass balance equations for each component were integrated over time, yielding concentration profiles and activity profiles as well as comonomer contents in the final polymer. In order to calculate molecular weight distributions, we used the most probable Schulz-Flory distribution[19] with a PDI of two for the instantaneously produced polymer (single site character). Time integration of the instantaneous distributions leads to the molecular weight distribution of the final polymer product.

The kinetic parameters for each temperature were fitted separately (Table 1).

Activation energies have been calculated, however these have been determined only from two temperatures, hence the activation energies have large uncertainties and should only be applied with great care. Furthermore, it has to taken into account, that the kinetics are formulated with respect to liquid phase concentrations, whereas the polymerisation takes place in the polymer particles formed. Hence the kinetic parameters determined are a superposition of intrinsic reaction kinetics and phase equilibria between polymer and liquid phase.

The activation energy for the ethylene propagation reaction is with 46 kJ in the

Table 1.
Kinetic parameters "Markov 0th order model with extended activation scheme"

	k_{iA} [l/(mol s)]	k_{Ib} [l/(mol s)]	k_{iH2} [l/(mol s)]	k_{pA} [l/(mol s)]	k_{pB} [l/(mol s)]	K_d [s^{-1}]	k_{tH2} [l/(mol s)]	k_{tA} [l/(mol s)]	k_{tB} [l/(mol s)]
60 °C	$5.9\ 10^{-5}$	$1.6\ 10^{-3}$	$1.1\ 10^{-1}$	6943	616	$1.8\ 10^{-3}$	5094	0.72	34
80 °C	$1.0\ 10^{-4}$	$8.0\ 10^{-3}$	$9.3\ 10^{-3}$	17876	6827	$3.1\ 10^{-3}$	5090	1.70	175
E_A [kJ/mol]	25.8	77.6	−122.5	46.1	117.3	25.6	0	42	80

typical range between 20 and 60 kJ/mol as can be found in literature.[13,20–24] Ethylene incorporation is from 2.5 (60 °C) to 10 times faster compared to 1-hexene incorporation. The activation energy for the deactivation reaction is with 25.6 kJ/mol also in a typical range. The activation energies for the activation reactions are model-specific and in general difficult to compare. For the activation with ethylene and 1-hexene again activation energies in the typical ranges have been determined (25 resp. 77 kJ/mol). The activation energy for activation with hydrogen is with −122 kJ/mol very unusual. This value results from the strong difference in the effect of hydrogen on activity between 60 and 80 °C. The activation energy for transfer to hydrogen is close to zero, which is unusual. This can possibly be explained by the overlay of reaction kinetics and sorption equilibria, it is well known that solubility of hydrogen in hydrocarbons shows some anomalies compared to other compounds.

For better data on activation energies, more experimental data at different temperatures is required.

The simulated activity profiles correspond quite well with the experimental data (Figure 4 to 9). Measured and simulated comonomer contents are plotted in the parity diagram (Figure 11). Figure 12 displays the number average molecular weight in a parity diagram. In some experiments polydispersities up to 3.9 were measured. Even though the presented model takes into account for temporal changes in bulk concentrations, the predicted polydispersities differ only slightly from two. The highest experimental polydispersities were observed for high hydrogen concentrations. One possible explanation could be the occurrence of mass-transfers restrictions for hydrogen on particle level and as a consequence a broadening of the MWD. Another explanation in opposite direction could be ethylene conversion leading to enrichment of hydrogen over the particle radius, however this is also speculative.

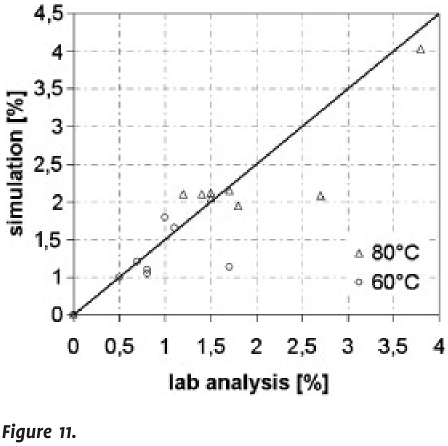

Figure 11.
Parity diagram of comonomer content.

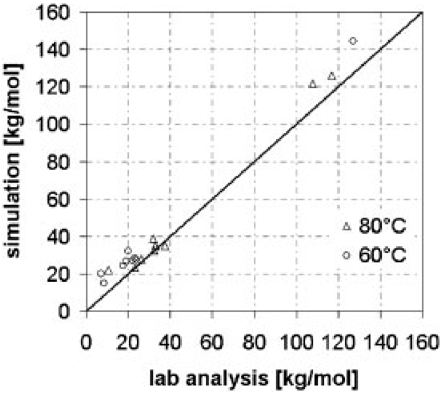

Figure 12.
Parity diagram of number average molecular weights.

Conclusion

The studied catalyst showed pronounced activation and slow deactivation during runtimes of about 1 hour. As expected, the molecular weight of the formed polymer is mainly affected by hydrogen. Chain transfers to ethylene or 1-hexene are only of minor importance.

Strong influences of 1-hexene ("hexene effect") and hydrogen ("hydrogen effect") on the activity profiles were observed. Surprisingly, both effects depend strongly on polymerisation temperature. At 60 °C nearly no 1-hexene effect, but a pronounced effect of hydrogen (also in homopolymerisations) on polymerisation activity could be detected. At 80 °C, a pronounced effect of 1-hexene on polymerisation activity was observed, but no effect of hydrogen on catalyst activity.

The root cause for this behaviour is not explicitly clarified yet. However, the polymerisation behaviour of the catalyst could be described by a kinetic model with a simple copolymerisation scheme (0^{th} Markov model) and additional activation reactions with the reaction partners. The presented kinetic model is able to describe the observed effects of 1-hexene and hydrogen on the activity profiles, as well as the comonomer incorporation and the molecular weight over a broad range of polymerisation conditions.

Acknowledgements: We would like to thank Borealis Polymers Oy, Finland, for hosting and financing this graduate research.

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