



Real-time monitoring of ethene/1-hexene copolymerizations: determination of catalyst activity, copolymer composition and copolymerization parameters

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Abstract

High-throughput development of catalysts, initiators, and polymeric materials combines automated parallel catalyst synthesis and automated polymerization reactors. The reactors can be additionally equipped with on-line monitoring (ReactIR from Mettler) based on ATR-FT-IR technique. This powerful tool has proven to be a very valuable probe for high-throughput experiments. During copolymerizations of ethene and 1-hexene monomers, the ReactIR was used to monitor the 1-hexene conversion as well as polymer formation, polymer concentration, and polymer composition. This gives access to information on catalyst activity, activation and deactivation times of the catalyst, polymerization kinetics, copolymerization parameters, and the degree of homogeneity of the resulting copolymers. The technology is especially useful for solution copolymerization. The spectrometer can be applied in the lab as well as in pilot plants and production facilities where rapid on-line analyses are useful for product quality control.

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1. Introduction

Due to the applications of new synthesis techniques called ‘high-throughput screening’ or ‘combinatorial chemistry’ the search for new or improved catalysts and the improvement of their property profiles and processing has increased dramatically [1–6]. Key instruments to this advanced research technology are laboratory robotic systems, rapid analyses and on-line reaction monitoring [7–9]. Applying such high-throughput chemistry, reaction data can be obtained fast without delay typical for many conventional time-consuming analytical tools such as NMR spectroscopy and conventional size exclusion chromatography. In this field, real-time monitoring of polymerizations has been proven to be a very useful tool for understanding

the chemistry of the reaction from both the point of basic science and industry. Since the development of a new generation of well defined single-site catalysts during the 1950’s and metallocene-based catalysts in the 1980’s, improved tailor-made linear low density polyethylene (LLDPE) with low, medium and high 1-olefin content have become available and received significant attention [10–12]. These dramatic advances have impacted the polyolefin industry and meantime, polyolefins such as Engage[®] from DuPont elastomers, Affinity[®] from Dow Plastics or Lupolex[®] and Lufflexen[®] from Basell, all ethene/1-olefin copolymers, have become important commercial products. There is a still continuing interest in advancing processes and in finding new catalytic systems for olefin copolymerizations with non-polar as well as polar comonomers. Combining laboratory automation engineering with fast measuring techniques, such as ReactIR, offer very good prospects to push the development in this field. The ReactIR technique has already been successfully applied to follow

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monomer conversion on-line while homo- and copolymerizations, such as radical polymerizations [13–19], living anionic polymerizations [20], cationic polymerizations [21–23], polycondensation [24] and polyinsertion [25,26]. To the best of our knowledge, this is the first successful attempt to exploit real-time ReactIR-based on-line monitoring in high-throughput experiments to determine catalyst activity, catalyst activation and deactivation, polymerization kinetics, copolymerization parameters, and the degree of homogeneity of the resulting copolymers. This paper reports on the development of the ReactIR on-line monitoring system and its application in catalytic solution copolymerization of olefins to monitor the conversion of the monomers, the formation of the polymer and the study of kinetic phenomena of the chemical reactions.

2. Experimental

2.1. Materials

Rac-Me₂Si(2-Me-4-PhenInd)₂ZrCl₂ (MPI), *rac*-Me₂-Si(Ind)₂-ZrCl₂ (MI), *rac*-Me₂Si(Ind)₂-ZrCl₂ (I) were obtained from BASF AG, 1-hexene from Merck, MAO from Crompton Germany, toluene from Roth GmbH, ethene from Gerling Holz u. Co, Handels-GmbH, Hamburg. Toluene was refluxed and distilled over Na/K alloy and 1-hexene was distilled over CaH₂ prior to use. MPI, MI, I, ethene and MAO were used without further purification. All

catalyst components, including toluene solvent and monomers, were handled and stored under a dry argon atmosphere. All manipulations of compounds were carried out by standard Schlenk, vacuum and glove box techniques.

2.2. Polymerization

The copolymerization process of ethene/1-hexene was carried out in an automated 0.6 l Büchi glass double jacket reactor which was developed together with Labeq AG (<http://www.swissreactor.com>). (Fig. 1) Important parameters like reactor temperature, jacket temperature, stirrer rotation speed and pressure were controlled and recorded by a computer. The reactor was filled with toluene and temperature control was started at a user-defined setpoint (25 °C). After thermal equilibration, a specified amount of toluene MAO solution (10 wt%) and a specified amount of 1-hexene was added before the reactor system was flushed with ethene until the system was saturated. The polymerization was started by adding the calculated amount of catalyst MPI (9, 4.5 μmol/l), MI (9, 4.5 μmol/l) or I (9, 4.5 μmol/l) dissolved in 10 ml of toluene. The ethene pressure was kept constant at 2 bar and 4 bar respectively during the polymerization by means of a mass flow meter. The total volume of the reaction mixture was 200 ml. The copolymer formed was precipitated in 1 l of methanol acidified with 30 ml of 10 wt% aqueous HCl, filtered, and dried at 60 °C under vacuum.

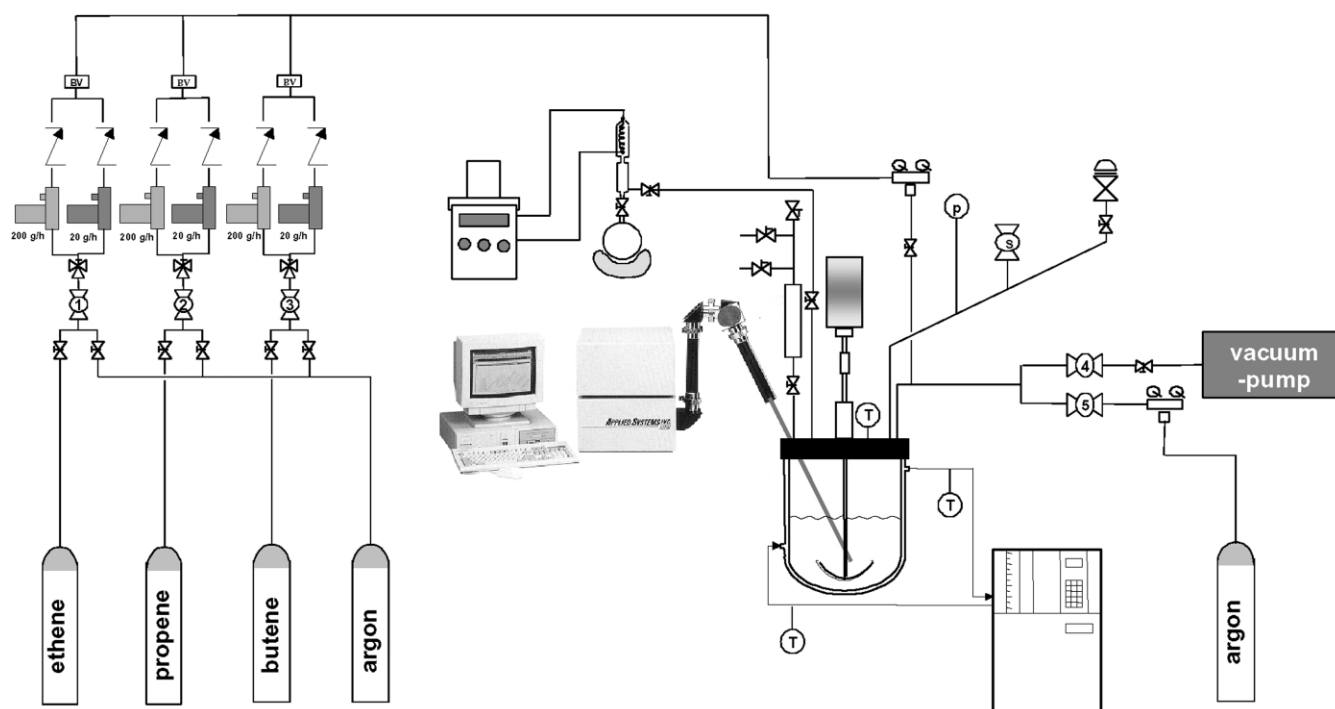


Fig. 1. Polymerization reactor system with ReactIR.

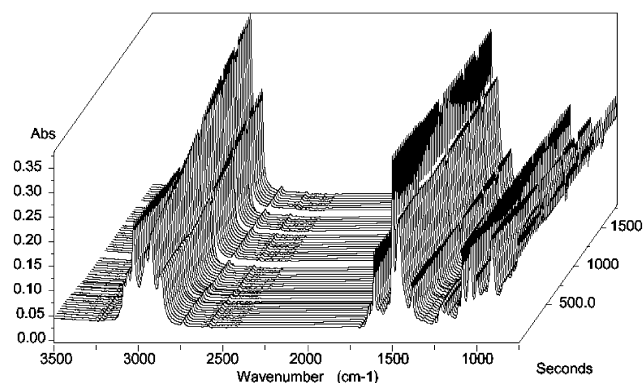


Fig. 2. 3D representation of time-resolved spectral data (I, 80 mol% 1-hexene, 2 bar).

2.3. Analytics

A ReactIR™ 1000 reaction analysis system from Mettler equipped with a DiComp ATR (diamond-composite attenuated total reflection) probe optimized for maximum sensitivity was used to monitor real-time mid FTIR-spectra from 4000 to 600 cm^{-1} continuously at 30 s time intervals during the polymerization. Kinetic data were extracted from the reaction spectra as described below. Fig. 1 shows the polymerization reactor system equipped with ReactIR. Fig. 2 shows the time-dependent spectral data in the range [3500–800 cm^{-1}] for a single experiment.

The relative ethene and comonomer incorporation as well as the dyad distribution was determined by ^{13}C NMR-Spectroscopy according to literature procedures [27]. ^{13}C NMR-spectra were recorded from solutions of 40–60 mg of polymer in 0.5 ml of $\text{C}_2\text{D}_2\text{Cl}_4$ at 400 K by a Bruker ARX 300 at 75.4 MHz, with a 90° pulse angle, inverse gated decoupling, 5 s delay and at least 5000 scans. These signals were referenced to $\text{C}_2\text{D}_2\text{Cl}_4$ ($\delta = 74.06$ ppm).

3. Data analysis

3.1. Extraction of reaction profiles

The extraction of the reaction profiles from the time-resolved spectral data depends on the details of the experiment. The methods described below apply to a semi batch copolymerization of ethene with 1-hexene as comonomer where the reactor is initially charged with catalyst, cocatalyst and comonomer and ethene is fed permanently into the system. However, the adaptation to other reaction schemes is straightforward.

3.1.1. Calibration of 1-hexene concentration

The estimation of the 1-hexene concentration in solution is done with an inverse least square model (ILS) [28]. We take into account two spectral regions which are sensitive

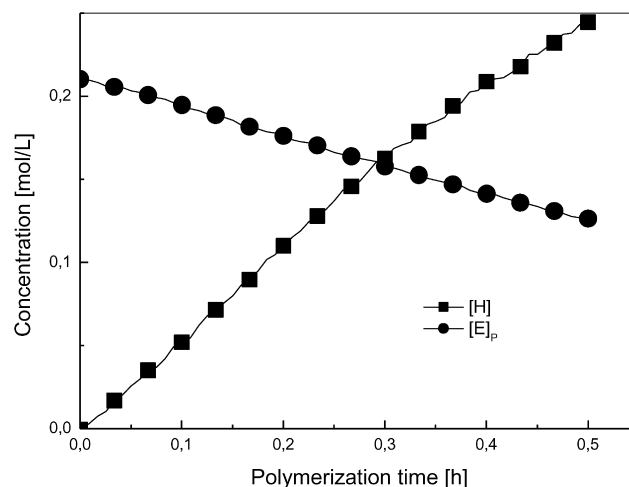


Fig. 3. Time evolution of the 1-hexene concentration [H] and the concentration of ethene [E]_p incorporated into polymer computed from the spectral data shown in Fig. 2 (I, 80 mol% 1-hexene, 2 bar).

towards $\text{C}=\text{CH}_2$ vibrations, namely [1655–1630 cm^{-1}] and [1015–975 cm^{-1}] [29]. The intensity in these bands is exclusively caused by the 1-hexene concentration in solution and therefore, the corresponding integrals are correlated to this quantity. The ILS-model is based on a linear model for the relation between the concentration and the band intensities of the form

$$[\text{H}] = a_1 I_1 + a_2 I_2 + b,$$

where [H] denotes the concentration of 1-hexene in solution, and I_1 and I_2 the integrals over region 1 and 2, respectively. In the training step, the unknown parameters a_1 , a_2 , and b are estimated by least square regression using the initial spectra, since for these spectra the 1-hexene concentration is known.

In the prediction step, the linear model is then used to estimate the 1-hexene-concentration for the spectra for $t > 0$ by computing the integrals and applying the model. Fig. 3 shows an example of the extracted profile for a single reaction. The total amount of 1-hexene consumed during the reaction is obtained by subtracting the final 1-hexene-concentration from its initial value.

3.1.2. Calibration of ethene consumption

The calibration of the ethene consumption is not as straightforward as the calibration of the 1-hexene concentration. This has two reasons: First, ethene in solution does not show a significant absorption in the IR-range and therefore the concentration in solution can not be observed. Second, the ethene concentration in solution is kept constant in our experiments by permanently feeding ethene into the reactor and therefore, even if it would be observable, it would not be related to ethene consumption.

In order to calibrate the ethene consumption we use a different scheme. First, we compute the total amount of

ethene which was consumed during the reaction. This quantity can be obtained from the total amount of 1-hexene consumed in the reaction and the composition of the product which has been measured using ^{13}C NMR.

In a second step—the training step—these data are used to perform a partial least squares (PLS) calibration which correlates the difference-spectra between the final and initial spectra to the total amount of ethene consumed. This PLS-model takes into account the two regions $[3200\text{--}2700\text{ cm}^{-1}]$ and $[1700\text{--}1300\text{ cm}^{-1}]$ which are sensitive for C–H vibrations.

In the final step—the prediction step—we estimate the amount of ethene consumed up to a given time t by subtracting the initial spectrum from the spectrum at time t and applying the PLS model [30]. Fig. 3 shows an example of the extracted profile.

3.1.3. Catalyst activity

From the concentration of 1-hexene in solution and the amount of consumed ethene we can compute the molar

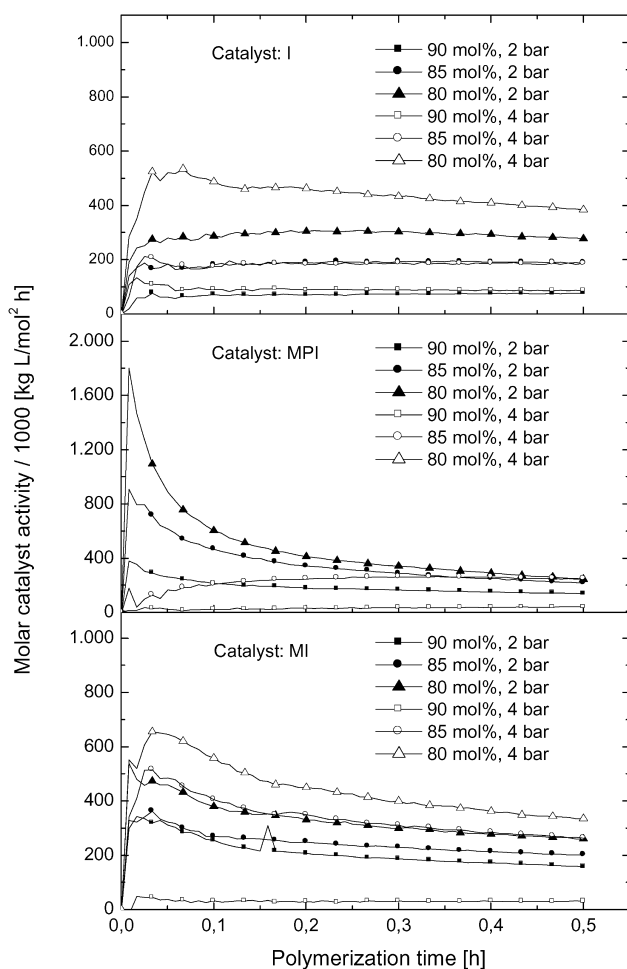


Fig. 4. Molar catalyst activity for three different catalyst systems at different reaction conditions (initial amount of hexene in mol% and ethene pressure in bar).

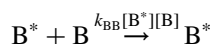
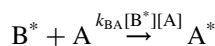
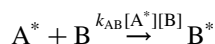
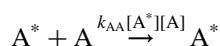
catalyst activity A which is defined as

$$A = \frac{\sum n_i}{\sum [M_i] n_{\text{cat}} t}$$

In this relation, n_i is the amount of monomer i incorporated into polymer, $[M_i]$ is the initial concentration of monomer i in solution, n_{cat} is the amount of catalyst and t is the polymerization time (Fig. 4).

3.2. Statistical Copolymerization

We consider the situation where a copolymer is formed by the reaction of two monomer species A and B. The dynamics of this reaction is described by the model of statistical copolymerization. Within the first order Markov-approximation, the probability for the incorporation of a molecule of species A or B at the end of the chain only depends on the type of the latest insertion, i.e. if the last molecule inserted in the chain is of type A or B, and on the concentration of the monomer. Thus, the state of a single polymer chain is completely described by the type of the most recent insertion and we denote by A^* and B^* chains ending with A and B, respectively. Within this model four different reactions are taken into account:



The rates for the individual reactions are marked on top of the arrows. They depend on the actual concentration of the species in solution which is denoted by a quantity in squared brackets.

3.2.1. Batch polymerization

In a batch reaction, the reactor is charged with catalyst, cocatalyst, monomer and comonomer at the beginning of the reaction. Monomer and comonomer are consumed during the reaction and therefore, the ratio between these is in general not constant in time. The differential equations for the educt and product concentrations can be derived from the reaction scheme above

$$\frac{d}{dt}[A] = -k_{AA}[A^*][A] - k_{BA}[B^*][A]$$

$$\frac{d}{dt}[B] = -k_{AB}[A^*][B] - k_{BB}[B^*][B]$$

$$\frac{d}{dt}[A^*] = -k_{AB}[A^*][B] + k_{BA}[B^*][A]$$

$$\frac{d}{dt}[B^*] = k_{AB}[A^*][B] - k_{BA}[B^*][A]$$

This system can be simplified by noting that the sum of $[A^*]$

and $[B^*]$ is constant in time since

$$\frac{d}{dt}([A^*] + [B^*]) = 0,$$

i.e. $[A^*] + [B^*] = [C]$.

Defining the new variable

$$z = \frac{[A^*]}{[A^*] + [B^*]} = [A^*]/[C]$$

which describes the fraction of polymer chains where the latest incorporated monomer is of type A, the dynamical system can then be written as

$$\frac{d}{dt}[A] = -[C][A]\{k_{AA}z + k_{BA}(1 - z)\}$$

$$\frac{d}{dt}[B] = -[C][B]\{k_{AB}z + k_{BB}(1 - z)\}$$

$$\frac{d}{dt}z = -k_{AB}z[B] + k_{BA}(1 - z)[A]$$

The constant $[C]$, which is the sum of the concentrations of the active centers, is of the order of the concentration of the activated catalyst. This quantity is in general however small compared to the monomer concentrations $[A]$ and $[B]$. Therefore, the relaxation of z to its equilibrium value is fast compared to the time evolution of $[A]$ and $[B]$ which allows the adiabatic elimination of z . In the dynamical system we can therefore replace z by its quasi stationary value

$$z = \frac{k_{BA}[A]}{k_{BA}[A] + k_{AB}[B]},$$

which depends on the actual concentrations of the monomers A and B and the copolymerization parameters. This yields the non-linear system of two coupled differential equations

$$\frac{d}{dt}[A] = -k_{AB}k_{BA}[C][A] \frac{r_A[A] + [B]}{k_{BA}[A] + k_{AB}[B]}$$

$$\frac{d}{dt}[B] = -k_{AB}k_{BA}[C][B] \frac{r_B[B] + [A]}{k_{BA}[A] + k_{AB}[B]}$$

Note, that according to standard notations, we have defined the dimensionless r -parameters $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$, which specify the ratio of the reactivity rates for homo and cross growth.

3.2.2. Catalyst activation and deactivation

The model sketched above still contains some simplification of the real situation, since the overall kinetics is also determined by further factors: The reaction must be initiated by activating the catalyst, and it slows down due to deactivation of the catalyst. These effects can be accounted for by introducing a phenomenological weight function $w(t)$

for the reaction rates, i.e.

$$k \rightarrow w(t)k,$$

which models the kinetics of the catalyst. For the function $w(t)$ we make a biexponential parametric model of the form

$$w(t) = e^{-\alpha t} - e^{-\beta t}.$$

The time constant $1/\beta$ is the activation time of the catalyst and $1/\alpha$ is a time scale for the deactivation. Using this model, the final dynamical system for batch reaction reads

$$\frac{d}{dt}[A] = -k_{AB}k_{BA}[C][A] \frac{r_A[A] + [B]}{k_{BA}[A] + k_{AB}[B]} (e^{-\alpha t} - e^{-\beta t})$$

$$\frac{d}{dt}[B] = -k_{AB}k_{BA}[C][B] \frac{r_B[B] + [A]}{k_{BA}[A] + k_{AB}[B]} (e^{-\alpha t} - e^{-\beta t})$$

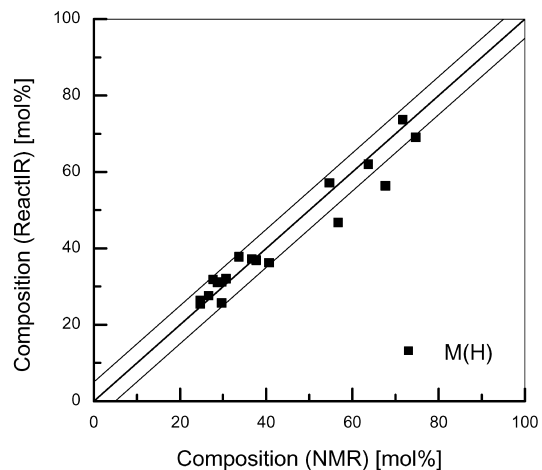
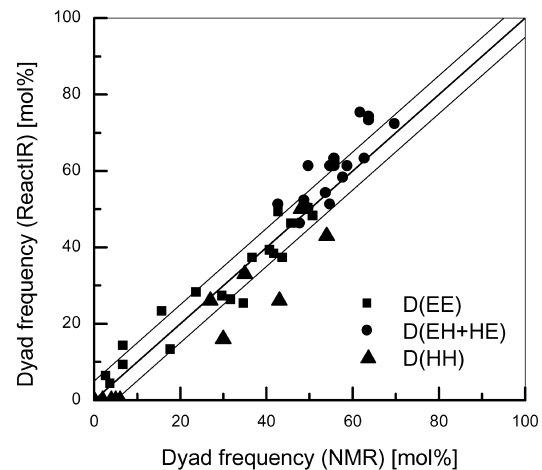


Fig. 6. Dyad and monad distribution determined by NMR versus the computed distributions based on the copolymerization parameters estimated using the ReactIR. The lines denote the 1- σ -intervals.

The original equations can be recovered in the limit $\alpha \rightarrow 0$, $\beta \rightarrow \infty$.

3.2.3. Dyad-distributions

From the statistical model described above, we can also derive the dynamic equations for further observables such as the concentration of dyads AA, AB + BA, and BB in polymer:

$$\frac{d}{dt}[\text{AA}]_P = k_{\text{AB}}k_{\text{BA}}[\text{C}] \frac{r_{\text{A}}[\text{A}]^2}{k_{\text{BA}}[\text{A}] + k_{\text{AB}}[\text{B}]} (e^{-\alpha t} - e^{-\beta t})$$

$$\frac{d}{dt}[\text{AB} + \text{BA}]_P = 2k_{\text{AB}}k_{\text{BA}}[\text{C}] \frac{[\text{A}][\text{B}]}{k_{\text{BA}}[\text{A}] + k_{\text{AB}}[\text{B}]} (e^{-\alpha t} - e^{-\beta t})$$

$$\frac{d}{dt}[\text{BB}]_P = k_{\text{AB}}k_{\text{BA}}[\text{C}] \frac{r_{\text{B}}[\text{B}]^2}{k_{\text{BA}}[\text{A}] + k_{\text{AB}}[\text{B}]} (e^{-\alpha t} - e^{-\beta t})$$

Together with the initial condition $[\text{AA}](0) = [\text{AB} + \text{BA}](0) = [\text{BB}](0) = 0$, these equations can be solved simultaneously with the dynamic equations for $[\text{A}]$ and $[\text{B}]$. The final values for the dyad concentrations can be used to compute a theoretical dyad distribution as it is observable e.g. by ^{13}C NMR (Fig. 6).

3.2.4. Semi-batch-polymerization

In a semi-batch experiment, the reactor is first charged with catalyst, cocatalyst and comonomer at predefined concentrations. Then the monomer gas (ethene in our experiments) is supplied to keep the pressure constant, i.e. the consumed monomer gas is permanently fed back into the system, whereas the comonomer concentration decreases. Therefore, in this situation the concentration of species A is not a dynamic variable but a parameter of the system.

As a consequence, we can consider the concentration $[\text{A}]_P$ of monomer A incorporated in the product polymer as a further observable of the system. For a semi-batch reaction the derivation sketched above thus leads to the following

differential equations for the concentrations:

$$\frac{d}{dt}[\text{A}]_P = k_{\text{AB}}k_{\text{BA}}[\text{C}][\text{A}] \frac{r_{\text{A}}[\text{A}] + [\text{B}]}{k_{\text{BA}}[\text{A}] + k_{\text{AB}}[\text{B}]} (e^{-\alpha t} - e^{-\beta t})$$

$$\frac{d}{dt}[\text{B}] = -k_{\text{AB}}k_{\text{BA}}[\text{C}][\text{B}] \frac{r_{\text{B}}[\text{B}] + [\text{A}]}{k_{\text{BA}}[\text{A}] + k_{\text{AB}}[\text{B}]} (e^{-\alpha t} - e^{-\beta t})$$

Note, that in this case the dynamics of the comonomer concentration $[\text{B}]$ is independent of the concentration of monomer A in polymer—it only depends on the concentration of monomer A in solution which is constant in time.

3.3. Estimation of copolymerization parameters

Using the measured time-dependent concentrations $[\text{A}]_P$ and $[\text{B}]$, a maximum likelihood approach is used to estimate the copolymerization parameters [31]. Since the analytical solution of the above ordinary differential equation describing the time evolution of the observed concentrations is not available, the copolymerization parameters can not be estimated directly.

Hence, the differential equation presented above has to be solved repeatedly in order to minimize the residual sum of squares

$$\chi^2(\theta) = \sum_i \left[\frac{y^{\text{D}}(t_i) - y^{\text{M}}(t_i, \theta)}{\sigma_i} \right]^2,$$

where $y^{\text{D}}(t_i)$ denotes the measurement vector at time t_i and $y^{\text{M}}(t_i, \theta)$ is the prediction from the model, based on a parameter vector θ containing the copolymerization parameters and the initial conditions. By minimizing $\chi^2(\theta)$ with respect to θ one obtains a maximum likelihood estimate of the copolymerization parameters (Table 1). The corresponding confidence intervals have been determined by fitting the model to only five of out six of the experiments and repeating the procedure until every experiment has been left out.

4. Results and discussion

We have investigated three different catalyst systems (namely MPI, MI and I) and performed six ethene/1-hexene copolymerizations for each under different process conditions. The molar catalyst activity for the individual reactions has been computed from the reaction profiles and is depicted in Fig. 4.

Kinetic parameters of each catalyst system (such as the copolymerization parameters) are obtained by fitting the observed data to the model of statistical copolymerization as discussed above. In our experiments, we have performed a simultaneous fit of the parameters r_{E} and r_{H} for each catalyst (i.e. the fit is based on six experiments) and the parameters α

Table 1

r -Parameter as determined by fitting a statistical model to the data obtained by ReactIR and r -Parameter as determined by using a simplified model and the dyad distribution determined by ^{13}C NMR

Catalyst	MPI	MI	I
r_{E} (ReactIR) ^a	2.0 ± 1.6	7.4 ± 1.0	6.2 ± 0.3
r_{E} (NMR) ^b	1.8 ± 0.5	7.4 ± 1.0	8.4 ± 0.4
r_{H} (ReactIR) ^a	0.3 ± 0.1	0.01 ± 0.01	0.0 ± 0.003
r_{H} (NMR) ^b	0.3 ± 0.04	0.01 ± 0.01	0.1 ± 0.1

^a The mean and error have been determined by fitting the model to only five of out six of the experiments and repeating the procedure until every experiment has been left out.

^b The mean and error have been determined by averaging the r -parameters for all six experiments.

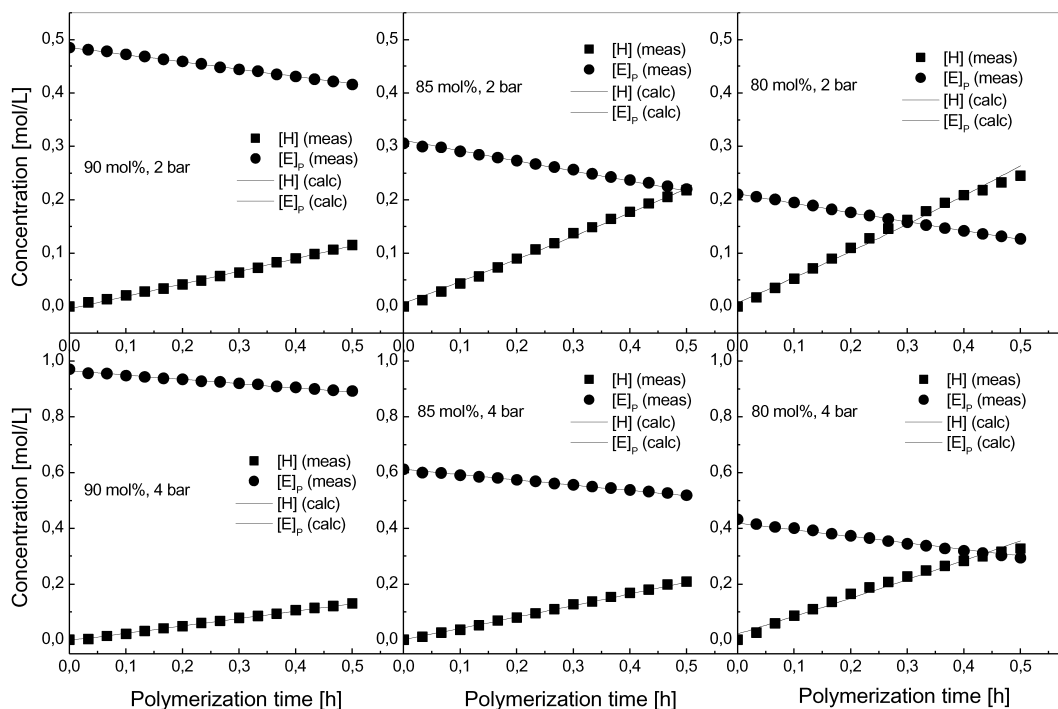


Fig. 5. Measured and calculated time evolution of the 1-hexene concentration [H] and ethene concentration [E]_p incorporated into polymer for catalyst I at different reaction conditions (initial amount of 1-hexene in mol% and pressure in bar).

and β are fitted individually to each experiment. The parameters [C], k_{EH} and k_{HE} can only be identified up to a common factor due to a symmetry in the differential equations.

The results of the fits are summarized in Table 1 and compared to r -parameters which can be calculated by fitting a simplified model to the dyad distribution obtained by ¹³C NMR [31]. Fig. 5 shows the calculated time evolution of [E]_p and [H] using the estimated parameters against the measured profiles which reveals a very good agreement. Thus, the model and the fitted parameters are capable of explaining the observed dynamics.

As an independent test of the model and the parameter fit, we have also computed the dyad distribution for each experiment using the model and the fitted parameters and compared it to the actual dyad distribution (Fig. 6). This comparison revealed a standard error of prediction for the dyads of approximately 5% and a standard error for the monads of approximately 4% which is (taking into account the experimental limitations) a very satisfactory result.

5. Summary

In this article, we have demonstrated that ReactIR spectroscopy provides a very efficient and reliable spectroscopic technique for fast polymer analysis by means of in situ monitoring of the kinetics of the copolymerization of polyolefines. Employing multivariate calibration models,

we have extracted information about the dynamics of the reaction from the observed spectra. This data can for example be used to determine the time dependence of the molar catalyst activity or to investigate composition drifts.

Employing the model of statistical copolymerization, we can additionally obtain important kinetic parameters of the catalyst systems under considerations. The model and the estimated parameters are validated twofold: first, we compared the observed reaction dynamics with the calculated by using the estimated parameters, and second by evaluating the dyad distribution from the model and comparing it to values obtained by ¹³C NMR. Both tests showed a very good agreement. Since the on-line monitoring also provides information on the polymer concentration the resulting solutions can be injected into a size exclusion chromatography. In conclusion, the automated on-line monitoring of olefin solution copolymerization provides an effective new tool for high throughput solution polymerization screening and the real time determination of catalyst activity, catalyst deactivation, comonomer incorporation and copolymer sequence distribution as well as copolymer molecular weights and molecular weight distributions. Since a few minutes holdup time is sufficient to examine different catalysts or to vary a polymerization parameter, respectively, more than one hundred runs can be performed during 24 h operation of this reactor system equipped with on-line monitoring. Evaluation of catalyst decay and polymerization kinetics can be used to identify living polymerization reactions.

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