About building a basis surface in inverse kinetic problems for non-break processes of diene polymerization

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Abstract. The work contains a mathematical description of diene polymerization with a neodym-based Ziegler-Natta catalysts. The resulting system of differential equations was reduced from infinite to finite by the method of moments. For this, the basis of nonlinear parametric functions was searched with a method allowing obtain expressions that reflect the kinetics of the polymerization process. The obtained basis of two functions enables us to construct a surface containing local regions of the minimum of the objective function which define the starting points for search of optimum kinetic constant values.

1. Introduction

The investigation of complex multistage processes such as polymerization processes combines both experimental analysis [1,2] and the theoretical grounds of the molecular characteristics obtained [3-5], the latter being inalienable from mathematical modelling that permits to adequately describe the process kinetics [6-10] and objectively evaluate the regular kinetic patterns being defined [1,11,12]. The techniques used must both permit to build mathematical models of polymerization processes and make computational experiments possible [3,11]. It is due to them that the researcher is able to carry out preliminary analysis of regular kinetic patterns [5,7] and evaluate the behavior of a series of kinetic parameters [9-12]. One may list among them the kinetic constants of the process unit step rates [1-4], as these values are not defined experimentally but are nevertheless basic to any process kinetics description.

The kinetic constant values are found both by statistical [8,9] and kinetic methods [1,11,12]. Incorrect search conditions lead to non-unique solutions of inverse kinetic problems and, as a matter of fact, to multiple sets of optimum values that describe the process adequately. In this case, the statement of search for a global optimum renders it impossible to find due to the equal influence the kinetic parameters have on the process. It therefore seems more reasonable to define the constant uncertainty range where the behavior and values of experimental data lie within acceptable limits [1,3].

2. Mathematical description of polymerization process

The basis is searched using a model of butadiene polymerization over a neodymium ZN catalyst, the process including three unit steps, namely propagation, chain transfer to monomer and chain transfer to an organoaluminium compound (OAC) [1]. The kinetic scheme is shown below:

\[
\begin{align*}
\text{R}_i + M \xrightarrow{k_p} \text{R}_i^+ + M \\
\text{R}_i^+ + M \xrightarrow{k_M} \text{R}_i^+ + P_i \\
\text{R}_i + A \xrightarrow{k_A} \text{R}_i^+ + P_i
\end{align*}
\]

where \(\text{R}_i\) and \(P_i\) are, respectively, active and inactive polymer chains having length \(i\); \(k_p\), \(k_M\), \(k_A\) are the rate constants of propagation reaction, chain transfer to monomer reaction and chain transfer to OAC reaction, respectively; \(M\) is monomer; and \(A\) is OAC.

In the mathematical modelling of the process using the laws of chemical kinetics, a system of infinitely many ordinary differential equations is proposed for consideration, where each equation characterizes the rate of chemical change over time.

\[
\begin{align*}
\frac{dM}{dt} &= -M(k_p + k_M)k_p \sum_{i=1}^{\infty} \text{R}_i^+ \\
\frac{dA}{dt} &= -Ak_A \sum_{i=1}^{\infty} \text{R}_i^+ \\
\frac{d\text{R}_i}{dt} &= -k_p MR_i + (k_M M + k_A A) \sum_{i=2}^{\infty} \text{R}_i \\
\frac{dP_i}{dt} &= (k_M M + k_A A) \text{R}_i \\
\frac{d\text{R}_i}{dt} &= k_p M(R_{i-1} - \text{R}_i) - (k_M M + k_A A) \text{R}_i, i \geq 2 \\
\frac{dP_i}{dt} &= (k_M M + k_A A) \text{R}_i, i \geq 2
\end{align*}
\]

with initial data

\[
M^{(0)} = M(0), A^{(0)} = A(0), C_{AC} = R^{(0)}_{AC} = R_i(0), P_i(0) = 0, R^{(0)}_i = P^{(0)}_i = 0, i \geq 2
\]

The system is rearranged to its final form by the method of moments [1]:
\[
\frac{dM}{dt} = -M(R_1 + \mu_0)(k_p + k_M)
\]
\[
\frac{dA}{dt} = -Ak_A(R_1 + \mu_0)
\]
\[
\frac{dR_1}{dt} = -k_pMR_1 + k_MM\mu_0 + k_AA\mu_0
\]
\[
\frac{d\lambda_0}{dt} = k_pMR_0 - k_MM\mu_0 - k_AA\mu_0
\]
\[
\frac{d\lambda_1}{dt} = k_M\mu_0 + k_AA\mu_0
\]
\[
\frac{d\lambda_2}{dt} = 2k_pMR_1 + k_pM\mu_0 - (k_M + k_A)\mu_1
\]
\[
\frac{d\lambda_3}{dt} = (k_M + k_A)\mu_2
\]
\[
\frac{d\lambda_4}{dt} = 4k_pMR_1 + k_pM\mu_0 + 2k_pM\mu_1 - (k_M + k_A)\mu_2
\]

The initial data are as follows:

\[M^{(0)} = M(0), \quad A^{(0)} = A(0), \quad C_{AC} = R_1^{(0)} = R_1(0), \quad \lambda_k^{(0)} = \mu_k^{(0)} = 0, \quad k = 0.2\]

3. Basis search method

Some tentative assumptions have to be made for the search of basis.

Due to the mutual opposition of differential equations \(\frac{dR_1}{dt}\) and \(\frac{d\mu_0}{dt}\), the total concentration of \(R_1\) and additive component \(\mu_0\) remains a constant in polymerization. Assuming that they are actually of radical nature, both of them may be accepted as intermediate substances, subsequently,

\[
\frac{dR_1}{dt} \geq 0
\]
\[
\frac{d\mu_0}{dt} \geq 0
\]

The latter (3) can be used to obtain another material balance equation from the third equation of system (1):

\[k_pMR_1 = k_M\mu_0 + k_AA\mu_0\]

Expression (4) demonstrates the relation between initial components \(M, A, R_1\). However, the concentration of chemical \(R_1\) is conditionally initial, as it is determined from a ratio

\[\alpha = k_p \cdot R_1(0)\]

where \(\alpha\) is the system kinetic activity and \(R_1(0)\) is a function of propagation rate constant \(k_p\).
Assumptions (3) to (4) are defining for this approach. An assumption of change is applied to \( M \) and \( A \), since they are initial substances:

\[
M' = M(1 + \varepsilon_1) \\
A' = A(1 + \varepsilon_2)
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) is the amount of change of concentrations of chemicals \( M \) and \( A \) relative to initial.

By inserting (6) into system (1) and leaving only moments of zeroth order, the system rearranges to (7):

\[
\begin{align*}
\frac{dM'}{dt} &= -M'(R_1 + \mu_0)(k_p + k_M) \\
\frac{dA'}{dt} &= -A'k_A(R_1 + \mu_0) \\
\frac{dR_1}{dt} &= -k_pM'R_1 + k_MM'\mu_0 + k_AA'\mu_0 \\
\frac{d\mu_0}{dt} &= k_pM'R_1 - k_MM'\mu_0 - k_AA'\mu_0 \\
\frac{d\lambda}{dt} &= k_MM'(\mu_0 + R_1) + k_AA'(\mu_0 + R_1)
\end{align*}
\]

with initial data:

\[
M^{(0)} = M'(0), A^{(0)} = A'(0), R_1^{(0)} = R_1(0), \lambda^{(0)} = \mu_0^{(0)} = 0
\]

Where \( \lambda \) stands for the zero moment of inactive chains calculated with the following formula:

\[
\lambda(t) = \lambda_0(t) + P(t) = \sum_{i=2}^{\infty} P_i(t) + P_1(t) = \sum_{i=1}^{\infty} P_i(t)
\]

The functions and the constant vector are determined in line with the applied approach [8,9]:

\[
f_1 = (M', A', \lambda), f_2 = (R_1, \mu_0) = y \\
k' = (k_p, k_M, k_A, \varepsilon_1, \varepsilon_2)
\]

The approach is implemented by way of matrix search:

\[
\frac{\partial f_1}{\partial k'}, \frac{\partial f_1}{\partial y}, \frac{\partial f_2}{\partial k'}, \frac{\partial f_2}{\partial y}
\]

and searching matrix \( U \):

\[
U = \frac{\partial f_1}{\partial k'} \frac{\partial f_1}{\partial y} \left[ \frac{\partial f_2}{\partial y} \right]^{-1} \frac{\partial f_2}{\partial k'}
\]

4. Results

All required elements (10) to (11) were found, as were the basis functions for the process:

\[
\rho_1(k') = k_A(1 + \varepsilon_2) \\
\rho_2(k') = k_p(1 + \varepsilon_1)k_M(1 + \varepsilon_1)
\]
They demonstrate that the influence of the growing chain transfer to OAC stage increases throughout the process and that the faster the OAC is consumed, the more significant the contribution of this reaction rate becomes to the general process rate. At the same time, constants $k_p$ and $k_M$ are quite strongly interconnected, while each of them is in turn connected to monomer $M$.

The findings derived from analytical inferences are completely congruent with the physical and chemical feature of the process under study, specifically, that the higher the monomer conversion, the more the influence of the chain transfer step on polymer product formation. Functions (12) to (13), are, in their turn, the basis of the space which could be built on the respective vectors.

Given that the values of the unit step rate constants are solutions of the inverse kinetic problem obtained in study [1,3,4] for butadiene polymerization initiated by the NdCl₃-3TBP-TOA catalytic system. Table 1 below shows the constant values obtained by way of calculations and experimentally.

| Table 1. Kinetic parameters of butadiene polymerization obtained by calculation. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $C_{AC} \times 10^4$ (mol/litre) | $k_p$ (litre/mol·min) | $k_M \times 10^2$ (litre/mol·min) | $k_A$ (litre/mol·min) | $\alpha \times 10^3$ (min⁻¹) |
| Calculate | 5.7 | 20.1 | 3.8 | 2.1 | 11.5 |
| Experiment | 6.5 | 17.4 | 2.4 | 1.5 | 11.3 |

The inverse kinetic problem solving process suggested two steps, the first involving determination of the kinetic activity of system (5), where the uncertainty interval does not exceed 2%.

The second step involved functional minimization by number average molecular weight:

$$Z(k_p,k_M,k_A) = (M_{N}^{calc}(t_i) - M_{N}^{exp}(t_i))^2$$

At the second step of solving the inverse kinetic problem, the search for three rate constants $k_p$, $k_M$ and $k_A$, the simultaneously carried out, then the domain of uncertainty in the values of the constants $k_M$ and $k_A$ are significantly increased in comparison with the interval of uncertainty in the value of the kinetic activity system $\alpha$.

The following table 2 shows the calculated values of the determination errors and the corresponding uncertainty intervals for the values of the kinetic constants.

| Table 2. The calculated values of the errors and uncertainty intervals for kinetic constants. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $C_{AC} \times 10^4$ (mol/litre) | $k_p$ (litre/mol·min) | $k_M \times 10^2$ (litre/mol·min) | $k_A$ (litre/mol·min) | $\alpha \times 10^3$ (min⁻¹) |
| Uncertainty intervals | (4.9;6.5) | (17.3;22.9) | (2.1;5.5) | (1.3;2.9) | (11.3;11.7) |
| Error (%) | 14 | 14 | 46 | 40 | 2 |

However, the value of the number average molecular weight is proportional to the value of the number average degree of polymerization; therefore, $M_N$ can be "replaced" by $P_N$, calculated as the ratio of the growth rate to the total break rate:
\[ P_N = \frac{W_P}{W_M^0 + W_A^0} \]  

(15)

In this case, the functional (14) will be calculated as (16)

\[ Z_2(k_p^j, k_M^j, k_A^j) = \left( \frac{W_P(t_k) - P_N(t_k)}{W_M^0(t_k) + W_A^0(t_k)} \right)^2 \]  

(16)

The function \( Z_2 \) can be represented as a surface in the region of definition \( \{k_p \times k_M\} \) or \( \{k_p \times k_A\} \), or \( \{k_M \times k_A\} \), in each case one of the constants remains at a fixed value. The figures below show the change in the \( Z_2 \) function in two different projections.

Figure 1 shows \( Z_2 \) in projection \( \{k_M \times k_A\} \).

![Figure 1](image1.png)

**Figure 1.** Mesh function \( Z_2 \) in the region:
\[ k_p = 17.3, \quad k_M \in [0.017; 0.0299], \quad k_A \in [1.3; 2.9]. \]

Figure 2 shows \( Z_2 \) in projection \( \{k_p \times k_A\} \).

![Figure 2](image2.png)

**Figure 2.** Mesh function \( Z_2 \) in the region:
\[ k_p \in [17.3; 22.9], \quad k_M = 0.0204, \quad k_A \in [1.3; 2.9]. \]

Note, the figures 1 and 2 do not give a visual representation of the change \( Z_2 \) due to the fixation of one of the constants. The question about its adequate representation becomes no less important than the search for its local or global optima.
To solve this question, one should use expressions for the basis functions (12) and (13). Further, by constructing a mesh two-dimensional domain \((k_p \cdot k_M) \times k_A\), which can be taken as the definition domain, the basis surface of the function \(Z_2\) is obtained. Its minimum domains show the maximum approximations of the calculated values of the number-average degree of polymerization to the experimental values, which allows one to determine the corresponding optimal sets of kinetic constants \(k_p\), \(k_M\), \(k_A\).

Software to calculate the function (16) was created. It allows to calculate the domain \((k_p \cdot k_M) \times k_A\) and values of the function \(Z_2\), as well as output the resulting data to file and build surface drawings using existing software products.

Using the created software and the available software for constructing 3D surfaces, figure 3, showing the variation of the grid function over a given domain.

![Figure 3. Mesh function \(Z_2\) obtained in the region \(([10;30] \cdot [0.014;0.038]) \times [1.0;2.1])\].](image)

Systematical appearance of break points indicates that the same value of the product \((k_p \cdot k_M)\) but with different mixes of \(k_p\) and \(k_M\) leads both to the minimum and maximum of function \(Z_2\), and that admissibility of kinetic constant values for the actual process is of importance here.

Analyzing figure 3, there is a possibility that the areas of sharp drops in the values of the function \(Z_2\) from small values to very large ones are potential areas of local minima. In addition, it can be seen that at the minimum value \(k_A\), the amplitude of the change in the \(Z_2\) values is higher than at the maximum \(k_A\). Perhaps this is due to the fact that the sets of constants at \(k_A = 1\) are not optimal. Therefore, optimal sets of constants are found for large values \(k_A\). If you smooth this surface, you can get a different picture of the representation of the function \(Z_2\).
Figure 4. Smoothed mesh function $Z_2$ obtained in the region $([-10;30] \times [0.014;0.038]) \times [1.0;2.1]$.

The figure 4 shows the surface is smoother, but it also gives an approximate behavior of the function $Z_2$ in the specified area.

Sometimes a 3D-image of a surface does not give clear and descriptive characteristics, therefore, in parallel with a three-dimensional image, often the picture is presented in the form of a contour graph with isolines uniting areas of the same value of the function under consideration. This helps to trace the uniformity or relief of the function image. The figures 5 and 6 show the surface, but with a boundary along the upper limit of the function change.

Figure 5. Mesh function $Z_2$ limited by upper limit of $6 \times 10^4$.

The figure 6 shows that some of the $Z_2$ function values have been lost, but local minimum areas have appeared and could be used as starting sets for next computational experiments.
The red rectangle in figure 6 characterized the area of variation function $Z_2$ which obtained earlier as solution of inverse kinetic problem for minimization (14) at the second step. It is shows that the left of the red area are found sets of constants which decrease functional (14) in comparison with the value in the selected area. There is the quality of finding solutions.

5. Conclusions
Using of the approach described in the research may serve as a preliminary step in solving inverse problems of kinetic process rate constant search. Frequently, the basic method used is the method of repetitive direct kinetic problem solving using numerical methods of direct search of optimum values. Both collection of statistics and definition of starting points for the search are essential. Exactly this good definition of a starting point that comes forward as the principal criterion for an adequate optimum, and, therefore, for revealing the real mechanisms of the actual process.

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