Numerical study of polymerization processes on various catalytic systems

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Abstract. A set of algorithms for determining the averaged molecular characteristics of the polymer and finding the optimal initial concentrations was built on the basis of the mathematical software for solving rigid and non-rigid systems of ordinary differential equations describing various polymerization processes. With the help of the developed mathematical and software computational experiments were carried out for various technological parameters and production recipes for the considered processes. The dependencies of the molecular mass characteristics of the copolymer on the time of polymerization or conversion of monomers were built, which showed agreement with the data obtained as a result of experiments in the central factory laboratory of Synthez-Kauchuk OJSC (Sterlitamak, Republic of Bashkortostan) and the laboratory of physico-chemical studies of polymers of BashSU.

1. Introduction

Polymerization processes are the most popular research processes due to their widespread use and great opportunities. The use of synthetic rubbers has found itself in various branches of science of technology: they are not limited to the tire industry, they are used in medicine, and in the production of household appliances, and in other areas. One of the most important and urgent tasks of studying polymerization processes is the study of the kinetics of the process, the relationships between the reagents, and their influence on each other. Knowledge of these mechanisms allows you to build models of processes and further determine process parameters [1].

The basis of the formation of the polymer chain is the active center involved in the growth stages of the kinetic and molecular chains. Depending on the nature of the active center, radical, anionic, cationic, and coordination polymerization processes are distinguished [2]. In the industrial production of synthetic rubbers, methods of mathematical modeling of technological processes are increasingly being used to solve problems of forecasting and optimizing production. Then the constructed mathematical model will characterize the changes occurring within the system. Since these changes are reflected in the form of differential equations, then in the aggregate the whole process is represented by a system of differential equations [3]. It should be noted that the resulting systems have a large dimension, which must be limited.

The fundamentals of modeling polymerization processes are given by foreign researchers by Goldfinger G. and Alfrey T. [4], as well as Lewis F. and Mayo F.[5] who proposed independently from each other the simplest model of a limit link. The study of kinetic schemes continued in the works of foreign researchers Mertz E., Willing C and...
domestic scientists Semchikova Yu., Berlin A. A., Wolfson S. A. [6]. The modular principle for constructing a mathematical model is proposed in the works of Podvalniy S. L. and Kafarov V.V.[7], according to which the kinetic description of the process should be supplemented with a macrokinetic module that will take into account the hydrodynamic and energy patterns of the process under consideration. The study of processes and devices on the scale and conditions of industrial production is complex and time-consuming, therefore, the task of automating the sequence of stages of constructing a model becomes more urgent. More precisely, we are talking about creating automated programs for modeling processes and reactors, which would have great flexibility and versatility and could be used with minimal revision to study complex chemical-technological processes.

2. Methods

Radical polymerization is one of the main industrial methods that receive more than half of the polymers produced in the world: a number of synthetic rubbers, polyethylene, polyvinyl chloride, polyacrylates, water-soluble carbochain polyelectrolytes, polystyrene and many others.

Radical polymerization involves several stages: initiation stage, chain growth, price transfer, and chain termination stage [8].

The initiation of radical polymerization consists in the nucleation of free radicals in the reaction systems, which are capable of starting reaction chains. This stage occurs due to the thermal decomposition into two fragments of the initiator molecules; each fragment in turn is the primary free radical and can initiate the growth of the polymer chain:

$$I \rightarrow 2R,$$

where $k_i$ – the rate constant of the initiator decay, characteristic of this type of initiator, $R$ – free radical, $I$ – initiator.

Then the primary radical attaches to a molecule of the monomer:

$$R + M \rightarrow P_1,$$

where $k_i$ – initiation rate constant, $R$ – free radical, $P_1$ – an active (“growing”) polymer chain of a length equal to one, containing one $M$ monomer unit.

Chain growth consists in the sequential attachment of monomer molecules to a growing radical. Chain growth occurs by the scheme:

$$P_n + M \rightarrow P_{n+1},$$

where $k_{p1}, k_{p2}, \ldots, k_{pn}$ – chain growth rate constants, $P_n$ – active polymer chains of length $n$ containing $n$ monomer $M$ links.

It is usually assumed that the reaction rate constants for active polymerization chains with an arbitrary length of units are constant, i.e. $k_{p1} = k_{p2} = \ldots = k_{pn} = k$.

Chain termination occurs as a result of deactivation of active particles. There are three options for termination the chain, the first two of which are the most likely:

1) by recombination

$$P_n + P_m \rightarrow Q_{n+m},$$

2) by disproportionation

$$P_n + P_m \rightarrow Q_n + Q_m,$$
where \( k_{rec}, k_{dis}, k_{sp} \) – chain termination rate constants by recombination, disproportionation, and spontaneous path, respectively, \( P_n, Q_n \) – active and inactive polymer chains of length \( n \), respectively, containing \( n \) units of monomer \( M \).

The stage of chain transfer is that the regulator that is introduced into the system breaks off the growing chain, but at the same time the regulator itself becomes a free radical and starts a new kinetic chain of polymerization. Chain transfer can occur on the following agents:

- to the solvent
  \[
P_n + S \rightarrow Q_n + P_1^0,
  \]
- to the monomer
  \[
P_n + M \rightarrow Q_n + P_1,
  \]
- to the polymer
  \[
P_n + Q_m \rightarrow Q_{n+m} + M - 1 + P_1,
  \]

where \( k_{js}, k_{jm}, k_{jp} \) – the transmission constants of the chains respectively, \( S \) – agent, \( P_n, Q_n \) – active and inactive polymer chains of length \( n \), respectively, containing \( n \) units of monomer \( M \).

Thus, the generalized kinetic radical polymerization scheme comprises the following elementary steps:

1. Initiator decomposition
   \[
   I \rightarrow 2R,
   \]
2. Chain growth
   \[
   R + M \rightarrow P_1,
   \]
3. Continuation of the chain
   \[
   P_1 + M \rightarrow P_2, P_1 + M \rightarrow P_{1,2},
   \]
4. Death of active centers
   \[
   P_n \rightarrow Q_n,
   \]
5. Recombination of active chains
   \[
   P_n + P_m \rightarrow Q_{n+m},
   \]
6. Disproportioning of active circuits
   \[
   P_n + P_m \rightarrow Q_n + Q_m,
   \]

where \( I \) – initiator, \( R \) – free radical, \( M \) – monomer, \( P_n, Q_n \) – active (“growing”) and inactive (“dead”) chain lengths of the copolymer, respectively, containing \( n \) links with monomer \( M \), \( k_i, k_{i1}, k_p, k_r, k_{rec}, k_{dis} \) – constants of elementary stages of initiation, growth, and chain termination stages respectively.

To describe the kinetics of the mechanism, it suffices to write out the velocity equations for the elementary stages of the process. They will determine the behavior of the catalytic system itself.
Thus, the speed of the chain growth stage will be the product of the concentrations of monomer and active centers, taken with a coefficient in the form of the rate constant of the same stage:

\[ W_p = k_p C_a M. \quad (10) \]

The speed of the growth stage will be determined by the monomer concentration, which decreases with time, since the concentration of active centers remains constant during the process. However, the rate of decrease in monomer concentration decreases with increasing process time. This means that with deep degrees of conversion the values of growth rates will be close to each other. This fact testifies to the so-called conversion "plateau", i.e. reaching a certain degree of conversion, the monomer in the system is practically not spent.

The total chain transfer rate can be written by combining two types of chain transfer stages present in the kinetic scheme:

\[ W_o = k_M MC_a + k_A AC_a. \quad (11) \]

The same formula can be rewritten as:

\[ W_o = W_M + W_A. \quad (12) \]

Analysis of the dependence (11) suggests that the speed of chain transmissions decreases with the process time. This behavior of the velocity affects the values of the average numerical molecular characteristics of the polymer, which, like the conversion curve, are characterized by the appearance of a "plateau" at deep conversion degrees.

Making a matrix of the stoichiometric coefficients of reactions of the general kinetic scheme, having performed the operations of transposition and multiplication by a column vector of reaction rates, we obtain a system of differential equations for the concentrations of substances:

\[
\begin{align*}
\frac{d[I]}{dt} &= -k_i[I] \\
\frac{d[R]}{dt} &= 2k_i[I] - k_{\text{i,n}}[M][R] - k_i[P_i][R] \\
\frac{d[M]}{dt} &= -[M]k_i \sum_{j=1}^{\infty} [P_j] - [M]k_i[R] \\
\frac{d[P_i]}{dt} &= k_i[M][R] - k_i[M][P_i] - k_i[R][P_i] - k_{\text{rec}}[P_i] \sum_{j=1}^{\infty} [P_j] - k_{\text{dis}}[P_i] \sum_{j=1}^{\infty} [P_j] \\
\frac{d[Q_i]}{dt} &= k_i[R][P_i] + \frac{1}{2}k_{\text{rec}}[P_i][R] + \sum_{j=1}^{\infty} [P_j] \\
\frac{d[P_{i-1}]}{dt} &= k_p[M][P_{i-1}] - k_p[M][P_i] - k_p[R][P_i] - k_{\text{rec}}[P_i] \sum_{j=1}^{\infty} [P_j] - \\
&- k_{\text{dis}}[P_i] \sum_{j=1}^{\infty} [P_j], 2 \leq i \leq \infty, \\
\frac{d[Q_j]}{dt} &= k_r[R][P_j] + \frac{1}{2}k_{\text{rec}} \sum_{j=1}^{\infty} [P_j][P_{i-j}] + k_{\text{dis}}[P_i] \sum_{j=1}^{\infty} [P_j], 2 \leq i \leq \infty,
\end{align*}
\]

where \([..]\) – concentration of the relevant substances (\([I]\) – initiator, \([R]\) – free radical, \([M]\) – monomer, \([P_i],[Q_j]\) – active (“growing”) and inactive (“dead”) chain lengths of the copolymer, respectively, containing \(n\) links with monomer \(M\)), \(f\) – efficiency of initiation,
$k_i, k_{i1}, k_p, k_r, k_{rec}, k_{dis}$ — constants of elementary stages of initiation, growth, and chain termination stages respectively.

The resulting system of differential equations (13) for a generalized kinetic scheme allows us to formulate the problem of determining its solution based on the initial data:

\[
I^{(0)} = I(0), \quad M^{(0)} = M(0), \\
R^{(0)} = 0, \quad P_i^{(0)} = 0, \quad Q_i^{(0)} = 0, \\
P_i^{(0)} = 0, \quad Q_i^{(0)} = 0, \quad i \geq 2.
\] (14)

Thus, system (13) is a mathematical model of the process, where concentrations of reagents play the role of functions. It is seen that system (13) is autonomous. As can be seen from system (13), it is infinite, since it is assumed that the process goes on until the monomer is completely exhausted, which may mean the formation of polymer chains of a sufficiently long length. Therefore, generalizing the assumption made, system (13) has an infinite number of equations. Each of them is an ordinary differential equation of the first order. Analysis of the right sides of the equations shows that the maximum degree of the addendum does not exceed two. This characterizes the molecular nature of the reaction, since according to the general kinetic scheme; most of the reactions are bimolecular. It can also be seen that the monomer participates in the corresponding reactions as the initial substance no more than twice, which indicates the first order of the rate of reactions according to the monomer.

Solving the direct kinetic problem means finding a solution to the system of ordinary differential equations (13) under the given conditions (14) and the known values of the kinetic rate constants of elementary reactions. If it is required to find a set of kinetic constants such that the behavior of a number of functions of system (13) is known in advance, this leads to finding the solution of the inverse kinetic problem.

Analyzing the general kinetic scheme, it can be noted that disproportionation and recombination reactions are included in it as chain termination reactions, which belong to the class of bimolecular chain termination reactions. The change of the right parts of the equations is a distinctive feature of the system of ordinary differential equations characterizing the processes of continuous polymerization. The inclusion of these stages of breakage affects the behavior of inactive polymer chains, that is, we can say that the likelihood of the appearance of such chains increases. In other words, the number of stages in which these chains may appear actually increases.

3. Results and discussion
One of the most important processes in the industrial production of synthetic rubber is the process of isoprene polymerization. The kinetic scheme of polymerization of isoprene comprises the following elementary steps:
1. Initiator decomposition:
   \[ I \rightarrow P_0. \]
2. Chain growth:
   \[ P_i + M \rightarrow P_{i+1}, \quad 0 \leq i \leq \infty. \]
3. Chain transfer to the monomer M:
   \[ P_i + M \rightarrow Q_i + P_i, \quad 2 \leq i \leq \infty. \]
4. Transfer of the chain to an organoaluminum compound A:
   \[ P_i + A \rightarrow Q_i + P_i, \quad 2 \leq i \leq \infty. \]
5. Death of active centers:

\[ P_i \rightarrow Q_i, \quad 2 \leq i \leq \infty, \]

where \( M \) – monomer, \( A \) – organoaluminum compound, \( I \) – initiator, \( P_m, Q_n \) – active (“growing”) and inactive (“dead”) chain lengths of the copolymer, respectively, containing \( n \) links with monomer \( k_i, k_p, k_m, k_o, k_d \) – constants of elementary stages of initiation, growth, transfer to monomer, organoaluminum compound and deactivation of active centers, respectively.

This scheme differs from the previous one in that it lacks the chain termination stages by recombination and disproportionation.

Similarly, we obtain an infinite system of ordinary differential equations for the concentrations of substances:

\[
\begin{align*}
\frac{d[I]}{dt} &= -k_i[I] \\
\frac{d[P_i]}{dt} &= f_i[P_i] - k_r[M][P_i] \\
\frac{d[P_i]}{dt} &= -k_r[M][P_i] + k_m[M] \sum_{j=1}^{\infty} [P_j] + k_s[A] \sum_{j=1}^{\infty} [P_j] - k_d[P_i] \\
\frac{d[M]}{dt} &= -k_r + k_m[M] \sum_{j=1}^{\infty} [P_j] \\
\frac{d[Q_i]}{dt} &= k_m[M][P_i] + k_s[A][P_i] + k_d[P_i] \\
\frac{d[A]}{dt} &= -k_s[A] \sum_{j=1}^{\infty} [P_j] \\
\frac{d[P_i]}{dt} &= k_r[M][P_{i-1}] - k_r[M][P_i] - k_m[M][P_i] - k_s[A][P_i] - k_d[P_i] ; \quad 2 \leq i \leq \infty, \\
\frac{d[Q_i]}{dt} &= k_m[M][P_i] + k_s[A][P_i] + k_d[P_i], \quad 2 \leq i \leq \infty, \\
\end{align*}
\]

where \([..]\) – concentration of the relevant substances (\([M]\) – monomer, \([A]\) – organoaluminum compound, \([R]\) – free radical, \([I]\) – initiator, \([P_n], [Q_n]\) – active (“growing”) and inactive (“dead”) chain lengths of the copolymer, respectively, containing \( n \) links with monomer \( k_i, k_p, k_m, k_o, k_d \) – constants of elementary stages of initiation, growth, transfer to monomer, organoaluminum compound and deactivation of active centers, respectively.

Initial data in this case can be represented as:

\[
\begin{align*}
[I^{(0)}] &= [I(0)], [M^{(0)}] = [M(0)], \\
[R^{(0)}] &= 0, [P_1^{(0)}] = 0, [O^{(0)}] = 0, \\
[P_i^{(0)}] &= 0, [Q_i^{(0)}] = 0, \quad i \geq 2.
\end{align*}
\]

The resulting system (14) with the initial conditions (15) contains an infinite number of differential equations, since the formation of polymer macromolecules goes to infinite chain length.

There are a large number of methods that allow finding a numerical solution of systems of differential equations of this type. The application of some is based on the principle of quasistationary of Semenov-Bodenstein. This principle is that the rate of change in the concentration of radicals is too small compared to the rate of change in the concentration of monomer. This assumption greatly simplifies the calculations, since allows you to equate to zero the kinetic equations for the concentrations of “short-lived” components, as well as being
one of the possible methods for solving rigid systems of differential equations. But the application of these methods is limited only by the initial stage, when polymers have a short chain length.

In this work, the so-called method of moments was used. The application of the method of moments is justified in cases when it is necessary to determine the quantitative characteristics of the polymer and on the basis of them to build the molecular mass distribution. The law of its description may be different: the distribution of Beasley, the distribution of Flory and several others. Another advantage of the method is to convert the source system to the final form without imposing additional restrictions [9].

The construction of mathematical models in the framework of the method is based on the expression of the moments of the distribution of active and inactive circuits. The statistical theory of polymerization is based on the assumption of the possibility of analyzing molecular mass distributions (MWD) by average molecular masses $M_n$, $M_w$ and polydispersity coefficient $K_D$. The concepts of moments are used for their analysis, which are used in statistics and probability theory to estimate the distribution of random variables.

For the moments of any order, basically, we have [10]:

$$m_j = \mu_j + \eta_j,$$

where $\eta_j, \mu_j$ is $j$-th moments of active and inactive polymer chains calculated in accord with the following formulas:

$$\mu_j = \sum_{i=2}^{\infty} i^j [P_i],$$

$$\eta_j = \sum_{i=2}^{\infty} i^j [Q_i].$$

For the substitution of moments in system (15), in addition to the expressions (18) - (19) themselves, it is necessary to define derivatives $\mu_j$ and $\eta_j$ with respect to time, which can be found by the following rule

$$\frac{d\mu_j}{dt} = \sum_{i=2}^{\infty} i^j \frac{d[P_i]}{dt},$$

$$\frac{d\eta_j}{dt} = \sum_{i=2}^{\infty} i^j \frac{d[Q_i]}{dt}.$$  

The found moment values are substituted into the formula for the average molecular weight $M_n$, $M_w$ and the polydispersity index $K_D$ (22) - (23).

The value of $M_n$ determines the average weight of the polymer macromolecules called average molecular weight. It is calculated by the following formula [11]:

$$M_n(t) = m \frac{\mu_0(t) + \eta_0(t)}{\mu_1(t) + \eta_1(t)},$$

where $m$ is the molecular weight of the monomer.

If parameter $M_n$ is characterized as a low molecular weight part of the MWD, then parameter $M_w$ is the average of the distribution of molecular weight and is calculated by the formula [12]:

$$M_w(t) = m \frac{\mu_2(t) + \eta_2(t)}{\mu_1(t) + \eta_1(t)}.$$
where \( m \) is the molecular weight of the monomer.
To estimate the width of the MMD, a parameter called the polydispersity coefficient is usually used. The coefficient of polydispersity is close in meaning to the dispersion (spread) of molecular weight and is calculated by the following formula:

\[
K_D = \frac{M_w}{M_n}.
\]

Let’s perform the necessary replacements and substitutes, and system (15) can be written in the closed form. This system has a finite number of equations and is soluble in regard with the following moments[13]:

\[
\begin{align*}
\frac{d[I]}{dt} &= -k_1[I], \\
\frac{d[P_n]}{dt} &= f_k[P_0] - k_p[M]P_1, \\
\frac{d[P_1]}{dt} &= -k_p[M]P_1 + k_m[M]u_0 + k_a[A]u_0 - k_d[P_1], \\
\frac{d[M]}{dt} &= -(k_p + k_m[M]P_1 - (k_p + k_m[M])u_0, \\
\frac{d[Q_1]}{dt} &= k_w[M]P_1 + k_a[A]P_1 + k_d[P_1], \\
\frac{d[A]}{dt} &= -k_a[A]P_1 - k_a[A]u_0.
\end{align*}
\]

(25)

Initial data in this case can be represented as:

\[
[I^{(0)}] = [I(0)], [M^{(0)}] = [M(0)], [K^{(0)}] = 0, [P_1^{(0)}] = 0, [Q_1^{(0)}] = 0, \\
\mu_0 = 0, \eta_1(0) = 0, k = 0.1, 2.
\]

(26)

The result of solving the direct kinetic problem (25) - (26) is the dependence of the change in the molecular characteristics of the resulting polymer on the polymerization time: the average \( M_w \) and weight average \( M_n \) molecular weights [14].

The constructed model was tested on experimental data obtained in the factory laboratory.

4. Summary

For the catalytic system VOCl3-Al(i-C4H9)3 in the laboratory, an experiment was carried out with the following conditions: \( T = 25^\circ C, C_M^{(0)} = 1 \text{ mol / l}, C_V^{(0)} = 5 \cdot 10^{-3} \text{ mol / l}, C_A^{(0)} = 10.8 \cdot 10^{-5} \text{ mol / l}. \)
Pic. 1 and pic. 2 show that average $M_n$ and weight-average $M_w$ molecular weights are increasing functions versus time. We note that after 60 minutes of polymerization both characteristics take a constant value.

![Pic.1 The average molecular weight $M_n$ versus time.](image1)

![Pic.2 The average of the distribution of molecular weight $M_w$ versus time.](image2)

Pic.3 The dependence of monomer conversion $U$ of the duration of the polymerization.

5. Conclusions
Thus, the polymerization conditions have been selected in the work. On the basis of the mathematical model, the values of the monomer concentrations versus the polymerization time have been constructed, and the values of number average and weight average molecular weights have been found. The simulation and experimental results show a satisfactory agreement.

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