Modeling of a continuous process of isoprene polymerization in the presence of titanium-based catalyst systems under polycentric conditions

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Abstract. In the research is represented the mathematical model of the periodic process of isoprene polymerization in the presence of titanium-containing catalyst systems. By the process of constructing of the mathematical model was taken into account the polycentric nature of the applied catalytic system. On purpose of organization of the possibility to describe a continuous process in a cascade of ideal mixing reactors, the mathematical model was supplemented by the corresponding hydrodynamic mechanism. For the resulting system of differential equations, a numerical solution method was programmatically implemented and was conducted a computational experiment to predict the main molecular characteristics of the resulting product.

1. Introduction
The synthetic rubber industry is one of the important sectors of the domestic petrochemical industry. Isoprene-based rubber, whose chemical composition is identical to natural, is very popular in the market for polymer products. The main part of the obtained polyisoprene is the product of isoprene solution polymerization in the presence of microheterogeneous titanium Ziegler-Natta catalyst systems characterized by high stereospecificity and the ability to produce SKI-3 rubber with a complex of necessary consumer properties. Previous studies [1] showed that the successful modification of catalytic systems is possible through the use of a tubular turbulent apparatus in the technology of the production process at the stages of catalyst formation. This approach to improve molecular characteristics allows to obtain polyisoprene with a narrow molecular weight distribution and reduce catalyst consumption. The construction of a mathematical model that takes into account such technological changes allows not only to predict the properties of the resulting product, but also to optimize the further production process.

2. Materials and methods
The polymerization process in the production of rubber of the SKI-3 brand is produced in a continuous way in a battery of connected to each other polymerizers in series (figure 1), by way of which are used as cylindrical vertical apparatuses with a volume of 16.6 m³, equipped with four-tier two-blade mixing devices. The power of the electric motor of mixing device is 30 kW, what ensures a mixing speed of 20 ÷ 40 rpm. The coolant is not supplied in the polymerizer, and the temperature of the reaction mixture is controlled by the temperature of the incoming monomer solution and the dosage of the catalyst.

At the stage of preparation of the catalytic complex is installed, a small-sized tubular turbulent apparatus of a diffuser-confuser structure (figure 2) with the following technological parameters: diffuser
diameter 65 mm; confuser diameter 35 mm; diffuser-confuser section length 190 mm; number of sections – 7.

Figure 1. Scheme of continuous production of polyisoprene.
Figure 2. Principal technological scheme of the stage of preparation of the isopropanol complex of titanium chloride in the form of a suspension in liquid paraffin. 1 – volumetric apparatus with a stirrer, 2 – centrifugal pump; 3 – tubular turbulent apparatus; 4 – selection of a suspension for the preparation of the catalyst and polymerization.

The construction of a system for modeling the structure of a block reproducing a reactor model will be carried out according to the modular principle [2]: the kinetic module constructed at the first level will be supplemented with a macrokinetic module that takes into account hydrodynamic and energy mechanisms. Then, quality indicators will be monitored to assess the adequacy of the constructed mathematical model.

2.1. Construction of a kinetic model of a periodic process
The results of the experiment and the solution of the inverse problem of the formation of the molecular mass distribution of polyisoprene allows us to conclude that two types of active centres are possible during polymerization on TiCl₄·nIPA-TIBA-PP catalyst system [3]. In addition, we take into account the fact that the initiation stage is not limiting and the initiation itself is instantaneous. Then the kinetic scheme of the process will take the following form:

1) Chain growth

\[ P_i^j + M \xrightarrow{k_{p,i}^j} P_{i+1}^j, \]

2) Chain transfer to monomer

\[ P_i^j + M \xrightarrow{k_{m,i}^j} Q_i + P_i^{j+1}, \]

3) Chain transfer to organoaluminum compound (OAC)

\[ P_i^j + A \xrightarrow{k_{a,i}^j} Q_i + P_i^j, \]

4) The downfall of active centers

\[ P_i^j \xrightarrow{k_{d,i}^j} Q_i, \]

5) Transition of active centers to each other

\[ P_i^j \xrightarrow{k_{12,i}^j} P_i^{j+1}, \]

\[ P_i^j \xrightarrow{k_{31,i}^j} P_{i+1}^j, \]

where \( M \) is the monomer, \( A \) is the concentration of OAC, characterizes the type of active center \( P_i^j \), is the active ("growing") polymer chain length \( i \) on the \( j \) type of active centers; \( Q_i \) – inactive ("dead") chain.
of the copolymer long \( i \), \( k_i^1, k_i^2, k_i^3, k_i^4, k_i^5 \) are constants characterizing the reaction rate of chain growth, transfer to the monomer, transfer to the organoaluminum compound (OAC), the downfall of active centers and the transition of active centers to each other, respectively.

For processes proceeding by the polymerization mechanism, a difference in the resulting macromolecules in length is characteristically. In this connection, instead of a product with a fixed molecular weight, a certain molecular mass distribution of the polymer (MMD) is obtained, for the analysis of which the concepts of the moments of active and inactive chains differing in the type of active center at its end are introduced [2].

\[
\mu^1_j = \sum_{i=2}^{+\infty} i^j P_i^1, \quad \eta^1_j = \sum_{i=2}^{+\infty} i^j Q_i^1, \\
\mu^2_j = \sum_{i=2}^{+\infty} i^j P_i^2, \quad \eta^2_j = \sum_{i=2}^{+\infty} i^j Q_i^2.
\]

In addition, it is necessary to determine the derivatives of the moments of active and inactive chains with respect to the staying time:

\[
\begin{align*}
\frac{d\mu^1_j}{dt} &= \sum_{i=2}^{+\infty} i^j \frac{dP_i^1}{dt}, \\
\frac{d\eta^1_j}{dt} &= \sum_{i=2}^{+\infty} i^j \frac{dQ_i^1}{dt}, \\
\frac{d\mu^2_j}{dt} &= \sum_{i=2}^{+\infty} i^j \frac{dP_i^2}{dt}, \\
\frac{d\eta^2_j}{dt} &= \sum_{i=2}^{+\infty} i^j \frac{dQ_i^2}{dt}.
\end{align*}
\]

Based on the described kinetic scheme using the law of the acting masses, we write the system of differential equations describing the change in the concentrations of all components of the polymerization mass:

\[
\begin{align*}
\frac{dM}{dt} &= -M \left( \sum_{i=0}^{+\infty} P_i^1 (k_p^1 + k_m^1) + \sum_{i=0}^{+\infty} P_i^2 (k_p^2 + k_m^2) \right), \\
\frac{dA}{dt} &= -A \left( k_d^1 \sum_{i=0}^{+\infty} P_i^1 + k_d^2 \sum_{i=0}^{+\infty} P_i^2 \right), \\
\frac{dP_i^1}{dt} &= -k_p^1 M P_i^1 \left( k_p^1 M + k_d^1 A \right) \sum_{i=2}^{+\infty} P_i^1 - k_d^1 P_i^1 + k_c^1 P_i^2 - k_c^2 P_i^1, \\
\frac{dP_i^2}{dt} &= -k_p^2 M P_i^2 \left( k_p^2 M + k_d^2 A \right) \sum_{i=2}^{+\infty} P_i^2 - k_d^2 P_i^2 + k_c^2 P_i^1 - k_c^1 P_i^2, \\
\frac{dQ_i^1}{dt} &= k_m^1 M P_i^1 + k_a^1 A P_i^1 + k_d^1 P_i^1, \\
\frac{dQ_i^2}{dt} &= k_m^2 M P_i^2 + k_a^2 A P_i^2 + k_d^2 P_i^2, \\
\frac{dP_i}{dt} &= k_p^1 \left( P_{i-1}^1 - P_i^1 \right) - k_m^1 M P_i^1 - k_a^1 A P_i^1 - k_d^1 P_i^1 - k_c^2 P_i^1 + k_c^1 P_i^2.
\end{align*}
\]
The constructed system of differential equations (4) with initial conditions (5) is a mathematical model of the periodic process of polymerization of isoprene on a titanium-containing catalyst system in a few of the dynamic of active centers.

The initial conditions for system (4) are of the form:
\[
M(0) = M_0, A(0) = A_0,
\]
\[
P^i_j(0) = P^j_0, Q(0) = 0,
\]
\[
\mu^i_j(0) = \mu^j^{\mu}(0) = \eta^i_j(0) = \eta^{\eta}(0) = 0,
\]
\[
i, s, m = 0..3, \quad j, r = 1..2.
\]

The constructed system of differential equations (4) with initial conditions (5) is a mathematical model of the periodic process of polymerization of isoprene on a titanium-containing catalyst system in a few of the dynamic of active centers.

2.2. Building of a mathematical model of a continuous process

In the transition to continuous industrial reactor systems it is necessary to supplement the model with a macrokinetic description of the process, taking into account energy and hydrodynamic mechanisms. The basis for the formation of a block of hydrodynamic level is the analysis of the flux structure by the distribution functions of the staying time in the reactor. Such an analysis allows us to identify groups of typical modules for reactors: ideal displacement, ideal mixing and intermediate type. In the existing production polymerizers belong to ideal mixing reactors. Since this is a continuous process, the reactors under consideration can be more correctly characterized as ideal mixing reactors of continuous process[2,6]. Previously a similar approach was used to passage to a continuous process for the production of styrene-butadiene rubber [4].

For ideal mixing reactors, recurrence relations are introduced that allow modifying the previously obtained mathematical model of production
\[
\frac{d\bar{Y}^{(k)}}{dt} = \frac{\left(\bar{Y}^{(k-1)} - \bar{Y}^{(k)}\right)}{\theta^{(k)}} + \bar{R}_y^{(k)},
\]

where \( \theta^{(k)} \) is the staying time of the reaction mixture in the \( k \)-th reactor of the cascade, and the form \( \bar{R}_y^{(k)} \) is determined by the adopted kinetic module.

Taking into account the equation (6) the system of differential equations describing the process of polymerization of isoprene in reactors cascade by the continuous way will take form:

\[
\begin{align*}
\frac{dM^{(k)}}{dt} &= \frac{M^{(k-1)} - M^{(k)}}{\theta^{(k)}} - M^{(k)}P_1^{(k)}\left(k_1^1 + k_1^m\right) - M^{(k)}P_2^{(k)}\left(k_2^1 + k_2^m\right) - M^{(k)}P_0^{(k)}\left(k_0^1 + k_0^m\right)

M^{(k)} = \left(k_0^1 + k_0^m\right),

\frac{dA^{(k)}}{dt} &= A^{(k-1)} - \left(k_a^1 A^{(k)}P_1^{(k)} - k_a^2 A^{(k)}P_2^{(k)} - k_a^1 A^{(k)}P_0^{(k)} - k_a^2 A^{(k)}P_0^{(k)}\right),

\frac{dP_1^{(k)}}{dt} &= \frac{P_1^{(k-1)} - P_1^{(k)}}{\theta^{(k)}} - k_p^1 M^{(k)}P_1^{(k)} + \mu_0^{(k)}\left(k_m^1 M^{(k)} + k_a^1 A^{(k)}\right) - k_d^1 P_1^{(k)} +

\left(1 - j\right)^2 k_c^1 P_1^{(k)} + \left(1 + j\right)^2 k_c^1 P_1^{(k)},

\frac{dQ_1^{(k)}}{dt} &= Q_1^{(k-1)} - Q_1^{(k)} + k_m^1 M^{(k)}P_1^{(k)} + k_a^1 A^{(k)}P_1^{(k)} + k_d^1 P_1^{(k)} +

\frac{dQ_2^{(k)}}{dt} &= Q_2^{(k-1)} - Q_2^{(k)} + k_m^1 M^{(k)}P_1^{(k)} + k_a^1 A^{(k)}P_1^{(k)} +

\frac{d\mu_s^{(k)}}{dt} &= \mu_s^{(k-1)} - \mu_s^{(k)} + \Psi_s^{(k)}(k_p, k_m, k_a, k_d, k_c, M^{(k)}, A^{(k)}, P_1^{(k)}, P_2^{(k)}) +

\frac{d\eta_s^{(k)}}{dt} &= \eta_s^{(k-1)} - \eta_s^{(k)} + \Psi_s^{(k)}(k_p, k_m, k_a, k_d, k_c, M^{(k)}, A^{(k)}, P_1^{(k)}, P_2^{(k)}).
\end{align*}
\]

Initial conditions for the system (7) are:

\[
M^{(0)}(0) = M_0^{(0)}, \quad A^{(0)}(0) = A_0^{(0)},

P_1^{(0)}(0) = P_0^{(0)}, \quad Q_1^{(0)}(0) = 0,

\mu_s^{(0)}(0) = \eta_s^{(0)}(0) = 0,

i, s, m = 0..3, \quad j, r = 1.2.
\]

3. Results and Discussion

To control the adequacy of the build mathematical model was conducted the solving of a direct problem[8].

For the numerical solve of the obtained system of differential equations (7) with initial conditions (8) was used the algorithm of Adam-Bashforts method[8].

The process of polymerization of isoprene on the catalytic system TiCl₄-nPA-TIBA-PP was carried out by the following conditions:

- Catalytic system TiCl₄-TIBA-piperylene-DFO
- Ratio TiCl₄/Al(i-C₃H₇OH)₃/piperylene / DFO = 1/1/0.2/0.15 mol
- The number of reactors in the cascade = 2.
- Type of reactor – ideal mixing reactor.
- The working volume of the reactor – 16.6 m³.
- The initial temperature of the solution of isoprene in isopentane was -50°C.
- Mass consumption 19 t / h.
- The battery load on the monomers is 5.4 t / h.
- The concentration of isoprene in isopentane – 15% wt.
- The consumption of the titanium catalyst was 1 mol TiCl₄/980 mol of isoprene.
- Diisobutylaluminum hydride supply is absent.
The constants characterizing the rates of elementary stages were taken from the literature [9] and are shown in table 1. The concentration of active centers was set in the amount of 2.2% of the initial volume of the catalyst with the predominant functioning of the active centers of the second type [3], the proportion of which is 0.92.

|                  | 1 type of active center | 2 type of active center |
|------------------|-------------------------|-------------------------|
| $k_p$, [1/(mol·min)] | 1200                    | 2230                    |
| $k_a$, [1/(mol·min)] | 5                       | 5                       |
| $k_m$, [1/(mol·min)] | 1.35                    | 0.34                    |
| $k_c$, [1/min]    | 0                       | 0                       |
| $k_d$, [1/min]    | 0.01                    | 0.026                   |

The values of the moments obtained from the solution of the system of differential equations (7)-(8) were used to determine the dependences of the conversion, averaged molecular masses, and polydispersity on time in the context of each polymerizer (figures 3-6).

**Figure 3.** The dependence of the experimental (points) and calculated (solid line) conversion values on time for each polymerizer.

**Figure 4.** The dependence of the experimental (points) and calculated (solid line) values of the number average molecular weight on time for each polymerizer.
Figure 5. The dependence of the experimental (points) and calculated (solid line) values of the mass-average molecular weight on time for each polymerizer.

Figure 6. The dependence of the experimental (points) and calculated (solid line) values of polydispersity on time for each polymerizer.

Since the constructed mathematical model (7)-(8) takes into account the nature of polycentricity, it is possible to obtain the dependences of the averaged molecular characteristics for each type of active centers separately[10]. Figures 7-8 shows the behavior of the mass-average molecular weight for each type of active center in the context of each polymerizer.

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4. Conclusion

In this work was constructed a mathematical model that describes the continuous process for producing polyisoprene on the TiCl4-TIBA-piperylene-DFO catalytic system. The modification of the preparation stage of the catalytic complex using in the scheme a tubular turbulent apparatus made it possible to reduce the system to a practically monocenter one (the proportion of active centers of the first type was 0.08, of the second type – 0.92). The nature of polycentricity is reflected in the kinetic scheme of the process and as a consequence in the mathematical model of the process represented by a system of differential equations. To summary the almost infinite system of differential equations to the final form, was
successfully applied the method of moments, which allows to predict the average molecular characteristics of the product during the numerical solution.

![Figure 7](image1.png)

**Figure 7.** The dependence of the experimental (points) and calculated (solid line) values of the mass-average molecular weight on time for each polymerizer for active centers of the first type.

![Figure 8](image2.png)

**Figure 8.** The dependence of the experimental (points) and calculated (solid line) values of the mass-average molecular weight on time for each polymerizer for active centers of the second type.

Since large-scale production assumes a continuous mode of conducting the process, the mathematical model was supplemented by the corresponding recurrence relations characteristic for the cascade of reactors of ideal mixing. For the resulting system of differential equations, a computational experiment was conducted to determine the dependence of conversion, number average and mass average molecular weights. The obtained results showed good agreement with the experimental results. The principles of constructing of this mathematical model can be applied to isoprene polymerization processes in the presence of other catalytic systems, for example, based on neodymium, in the production of synthetic rubber brand SKI-5. For the case when the catalyst will be characterized by the presence of only one type of active centres, it is possible to set the fraction of the second type equal to zero, what will allow using the already constructed mathematical model.

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