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Building a model of the isoprene polymerization process in the presence of microheterogeneous neodymium catalytic systems

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Abstract. In the research is built the mathematical model of the isoprene polymerization process in the presence of microheterogeneous neodymium catalytic systems. The direct problem is solved and is analyzed the molecular-mass distribution of the polymer. An algorithm of solving the inverse problem for search and elaboration of the kinetic parameters of the research process is developed.

1. Introduction

Production of polymer materials takes one of the leading places in the modern chemical and petrochemical industry. A significant share in it brings the production of synthetic polyisoprene, which accounts for more than 700 thousand tons of the product in year. Polyisoprene is a product of solution polymerization of isoprene in the presence of microheterogeneous titanium and neodymium catalytic system type Ziegler-Natta, characterized by high stereo specificity and the possibility of obtaining rubber of stamps SKI-3 and SKI-5 with a complex of necessary consumer properties. Earlier made studies [1] have shown, it's possible to impact on the dispersion of microheterogeneous catalytic system of the Ziegler-Natta due to local hydrodynamic influence on the reaction mixture by changing the technological scheme of the preparation of the titanium catalyst. Building of the mathematical model taking into account these changes allows not only to predict the properties of the product, but also to optimize the production process.

2. The technology of the production process

The process of isoprene polymerization in rubber production is carried out in a continuous method in a battery of sequentially interconnected polymerizers, by way of which are used the vertical cylindrical apparatus with a volume of 16.6 m³, equipped with four-tier two-vane mixing devices. The power of the electric motor of the mixing device is 30 kW, what provides a mixing speed of 20÷40 rpm. The delivery of the heat carrier to the polymerizers is not carried out, and the temperature of the reaction mixture is regulated by the temperature of the incoming monomer solution and the dosage of the catalyst.

Particularly the polymerization of isoprene in the presence of a neodymium catalyst in industrial production is carried out using a cascade of three bulk reactors. The initial temperature of the isoprene solution in isopentane is 0-minus 5⁰C, the mass flow rate is 20 t/h. The consumption of neodymium catalyst is 1 mol. NdCl₃/10000 mol. isoprene. In order to



regulate the molecular weight of the polymer, into the process line is continuously supplied the diisobutylaluminium hydride (DIBAH). The scheme of the production process is shown in Fig.1

3. A kinetic scheme of the polymerization process

The kinetic method of modeling polymerization processes is the compilation and numerical solution of kinetic equations for the concentration of all types of particles involved in the process [3]. The construction of a mathematical model is complicated by the kinetic heterogeneity of the neodymium catalyst, which, alongside with other factors, is determined by the amount of isopropyl alcohol (IPA) included in the complex. The results of the experiments and the solution of the inverse problem of the formation of the molecular mass distribution of polyisoprene allows to judge that in the process of polymerization of isoprene on the catalytic system $\text{NdCl}_3\text{-nIPA-TIBA}$ (triisobutylaluminium)-PP is possible the existence of two types of active centers (AC). This leads to a twofold increase of number of considered reactions, which are complicated by the search of kinetic parameters [4,5] characterizing the rate of one or the other reaction. However, the hydrodynamic effect on the reaction mixture of synthesis $\text{NdCl}_3\text{-nIPA}$ synthesis (method 2) leads to an increase in the content in structure of the complex IPA and the formation of a monocenter catalyst, which greatly simplifies the search for kinetic constants.

In addition, by the formulation of the reaction scheme, it was assumed that the rate of the initiation reaction is much greater than the rate of the chain growth reaction, and the initiation reaction is not limiting. Then the kinetic scheme of the isoprene polymerization process in the presence of neodymium-containing catalytic systems can be described as the following stages:

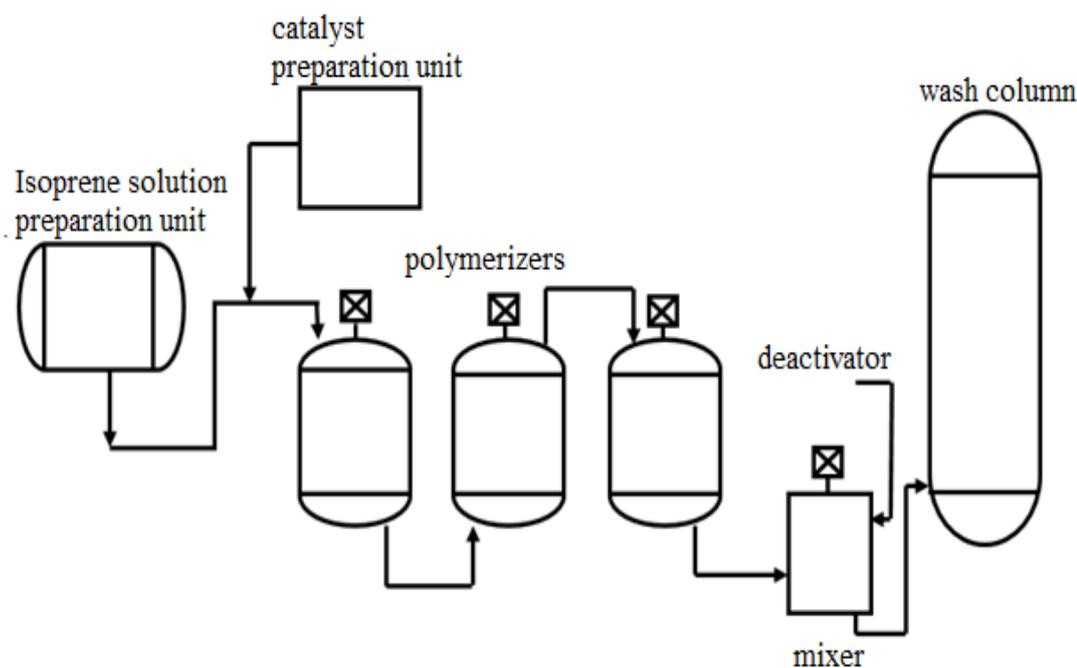
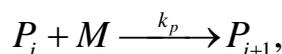
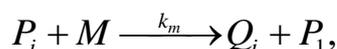


Fig.1. Scheme of the continuous production of rubber SKI-3

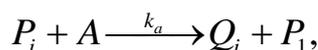
1. Chain growth



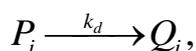
2. Chain transfer to monomer



3. Chain transfer to organoaluminum connection (OAC)



4. Death of active centers



where M – is the monomer, A – the concentration of OAC, P_i – the active chain of the polymer length i ; Q_i – inactive chain of the polymer length i , k_p, k_m, k_a, k_d – the rate constants of the reaction of chain growth, transfer to monomer, to the OAC and the death of active centers respectively.

4. The construction of the mathematical model and the solution of the direct problem

The principal difference between polymerization processes from all other chemical processes is that instead of a product with a fixed molecular weight is obtained a certain molecular weight distribution of the polymer (MWD). The static theory of polymerization is based on the possibility of MWD analysis by a special kind average molecular masses $\overline{M}_w, \overline{M}_n$, called the average mass and the average count [6]. For the analysis of MWD are entered concepts of moments of active and inactive chains:

$$\begin{aligned} \mu_j &= \sum_{i=2}^{+\infty} i^j P_i, \\ \eta_j &= \sum_{i=2}^{+\infty} i^j Q_i. \end{aligned} \quad (1)$$

In addition, it is necessary to find derivative moments of active and inactive chains by the location time

$$\begin{aligned} \frac{d\mu_j}{dt} &= \sum_{i=2}^{+\infty} i^j \frac{dP_i}{dt}, \\ \frac{d\eta_j}{dt} &= \sum_{i=2}^{+\infty} i^j \frac{dQ_i}{dt}. \end{aligned} \quad (2)$$

On the basis of the described kinetic scheme using the law of active masses, we write a system of differential equations describing the change in the concentrations of all components of the polymerization mass:

$$\left\{ \begin{aligned} \frac{dM}{dt} &= -M \sum_{i=0}^{\infty} P_i (k_p + k_m), \\ \frac{dA}{dt} &= -k_a A \sum_{i=0}^{\infty} P_i, \\ \frac{dP_1}{dt} &= -k_p M P_1 + (k_m M + k_a A) \sum_{i=2}^{\infty} P_i, \\ \frac{dQ_1}{dt} &= k_m M P_1 + k_a A P_1, \\ \frac{dP_i}{dt} &= k_p M (P_{i-1} - P_i) - k_m M P_i - k_a A P_i - k_d P_i, \\ \frac{dQ_i}{dt} &= k_m M P_i + k_a A P_i + k_d P_i. \end{aligned} \right. \quad (3)$$

The derived system of equations containing infinite sums we transform by the method of moments to a system of differential equations for statistical moments of the molecular mass distribution of polyisoprene (4), where μ_i, η_i - moments of molecular mass distribution of active and inactive chains respectively.

$$\left\{ \begin{aligned} \frac{dM}{dt} &= -M P_1 (k_p + k_m) - M \mu_0 (k_p + k_m), \\ \frac{dA}{dt} &= -k_a A P_1 - k_a A \mu_0, \\ \frac{dP_1}{dt} &= -k_p M P_1 + (k_m M + k_a A) \mu_0, \\ \frac{dQ_1}{dt} &= k_m M P_1 + k_a A P_1, \\ \frac{d\mu_0}{dt} &= k_p M P_1 - (k_m M + k_a A + k_d) \mu_0, \\ \frac{d\eta_0}{dt} &= (k_m M + k_a A + k_d) \mu_0, \\ \frac{d\mu_1}{dt} &= 2k_p M P_1 + k_p M \mu_0 - (k_m M + k_a A + k_d) \mu_1, \\ \frac{d\eta_1}{dt} &= (k_m M + k_a A + k_d) \mu_1, \\ \frac{d\mu_2}{dt} &= 4k_p M P_1 + k_p M \mu_0 + 2k_p M \mu_1 - (k_m M + k_a A + k_d) \mu_2, \\ \frac{d\eta_2}{dt} &= (k_m M + k_a A + k_d) \mu_2, \\ \frac{d\mu_3}{dt} &= 8k_p M P_1 + 3k_p M (\mu_2 + \mu_1) + k_p M \mu_0 - (k_m M + k_a A + k_d) \mu_3, \\ \frac{d\eta_3}{dt} &= (k_m M + k_a A + k_d) \mu_3, \end{aligned} \right. \quad (4)$$

The initial conditions for the system (4) are as follows:

$$\begin{aligned} M(0) &= M_0, A(0) = A_0, \\ P_1(0) &= P_0, Q(0) = 0, \\ \mu_i(0) &= \eta_i(0) = 0, i = 0 \dots 3. \end{aligned} \quad (5)$$

The calculation of the average count (M_n) and average mass (M_w) molecular masses will be produced on the basis of the obtained values of the moments of active and inactive chains:

$$\begin{aligned} M_n &= m_0 \frac{\mu_2 + \eta_2}{\mu_1 + \eta_1}, \\ M_w &= m_0 \frac{\mu_3 + \eta_3}{\mu_2 + \eta_2}, \end{aligned} \quad (6)$$

where m_0 – is the molar mass of isoprene ($m_0 = 68.119$ g/mol.).

For further calculation of averaged molecular characteristics it is necessary to know the values of all rate constants of elementary reactions of the kinetic scheme of the process. It should be taken into account that the required values of constants in the case of isoprene polymerization on catalytic systems with different mole content of IPA have a different in size character. To find kinetic constants, the inverse problem was solved [7].

5. Solution of the inverse problem

The strategy of finding the kinetic parameters of polymerization consist in search of the minimum matching function of the experimentally determined parameters and calculated on the basis of a mathematical model describing the polymerization process.

The solution of the inverse problem for this process was carried out in two stages. At the first stage, on the basis of experimental data on the conversion change, was carried out the search of constants of chain growth rates and chain transfer to the monomer by the way of minimizing of the functional following type:

$$H(z) = \sum_{i=1}^p (K_i^{\text{exp.}} - K_i^{\text{calc.}})^2, \vec{z} = (k_p, k_m), \quad (7)$$

where $K_j^{\text{exp.}}$ – value of conversion defined in the course of the experiment, $K_j^{\text{calc.}}$ – the calculated values of conversion.

At the second stage, on the basis of experimental data on the change of the average count and average mass molecular masses of polyisoprene was carried out the search for the constants of the chain transfer rates to the OAC and the reaction of the death AC by the way of minimizing two functional types simultaneously:

$$\begin{aligned} F(w) &= \sum_{i=1}^p (M_n^{\text{exp.}} - M_n^{\text{calc.}})^2, \vec{w} = (k_a, k_d), \\ G(w) &= \sum_{i=1}^p (M_w^{\text{exp.}} - M_w^{\text{calc.}})^2, \vec{w} = (k_a, k_d). \end{aligned} \quad (8)$$

For the refinement of the kinetic parameters by the way of minimizing the functional (7)–(8) was used the numerical method of multidimensional minimization-the method of configurations (Hook - Jeeves) [8].

The results of the calculations for the solution of the inverse problem: the rate constant for the reaction of chain growth $k_p = 481 / (\text{mol} \cdot \text{s})$, the rate constant for the reaction of chain transfer to the OAC $k_a = 2401 / (\text{mol} \cdot \text{s})$, the rate constant for the reaction of chain transfer to the monomer and the rate constant for the reaction of the death of AC k_d got value close to 0.

6. Computational experiment

To check the adequacy of the constructed mathematical model and the calculated values of the kinetic parameters was carried out the solution of the direct problem. For the numerical solution of the obtained system of differential equations was used an implicit Adams-Moulton method of the 4th order [9].

The process of isoprene polymerization on $\text{NdCl}_3 \cdot n\text{IPA-TIBA-PP}$ catalytic system was carried out under the following conditions:

- concentration of chloride neodymium in toluene solution-0.035 mol/l;
- ratio $\text{NdCl}_3/\text{Al}(\text{i-C}_4\text{H}_9)_3 / \text{piperylene} = 1/12/2$ mol.
- consumption of neodymium catalyst - 1 mol $\text{NdCl}_3 / 10000$ mol isoprene;
- isoprene concentration in isopentane is 15% by weight.
- the temperature of the process 20°C .

The moment values obtained from the solution of the system (4)-(5) were used to determine the dependence M_n, M_w and conversion of the polymerization time (Fig. 2). From the given dependences it can be seen that the values of conversion and averaged molecular masses satisfactorily describe the data of the results of the experiment conducted in the laboratory, what confirms the adequacy of the model we use.

7. Results

The built mathematical model of the process of polymerization of isoprene in the catalytic system $\text{NdCl}_3 \cdot n\text{IPA-TIBA-PP}$ allows to make calculations of average molecular characteristics, to obtain the dependence of the consumption of reagents, conversion dependence and polydispersity with time. From the obtained graphs it is seen that the conversion of 70% is achieved in one hour of the process, and the polydispersity of the resulting product after an hour is at the level of 4.2-4.3, which corresponds to the experimental data.

By solving the inverse problem was carried out the identification of unknown kinetic parameters. Analyzing the results of the numerical experiment it can be noted that the reaction of the chain transfer to the monomer and the reaction of the decay of the active centers have less influence on the MMP of the product and its conversion dependence in the case of a controlled polymerization process. Computational experiment for industrially significant process shows satisfactory agreement with the experimental data obtained in the laboratory.

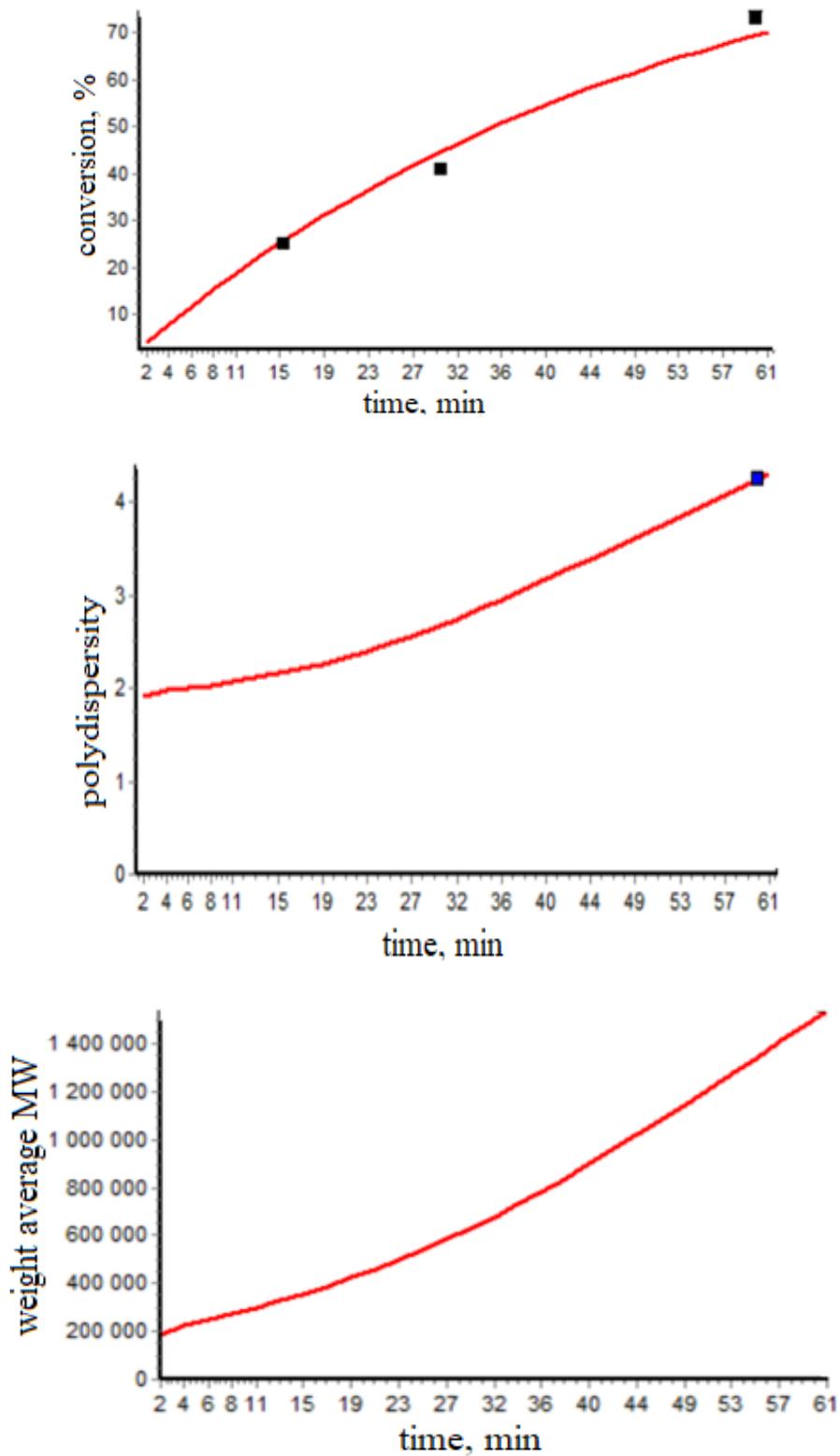


Fig. 2. Dependence of experimental (points) and calculated (solid line) values of conversion, polydispersity and average mass molecular weight on time.

8. Acknowledgement

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