Application of the Monte Carlo method in modeling the isoprene polymerization process in the presence of the polycentric titanium-containing catalytic system

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Abstract. The article proposes an approach to modeling the periodic process of polymerization under conditions of polycentricity of the catalytic system, based on the Monte Carlo method, as well as the foundations of its software implementation. The solution polymerization process of isoprene is based on the industrial production of isoprene rubber. The isoprene polymerization process considered in the paper proceeds in a batch mode. The algorithm is based on simulating the growth of each polymer model and tracking the processes occurring with it. The results of testing the algorithm for the isoprene polymerization process on the assumption of a titanium-containing catalytic system are demonstrated. The constructed model makes it possible to study the molecular weight characteristics of the polymer depending on the conversion of the monomer, to calculate the molecular weight distribution of the resulting product at any time, to carry out the process of each type of active site, and the total distribution. The article presents the results of a computational experiment, the initial data of which correspond to laboratory studies. The results of the computational experiment showed good agreement with laboratory data.

1. Introduction

Currently, the range of synthetic rubbers is quite wide. This range of rubbers is due to the fact that natural rubber has low quality indicators, suitable for the creation of rubber products. In this regard, studies of polymerization processes are of great interest for both modern science and the world production of synthetic rubber. This area of research provides the best opportunities for studying statistical features and factors affecting polymerization processes, and allows you to describe physical processes with high accuracy [1-3].

The production of synthetic rubbers (isoprene, butadiene, styrene butadiene, nitrile butadiene, etc.) is based on the processes of polymerization and polycondensation. One of the most common industrial polymeric materials is isoprene-based rubber. But its production is a complex technological process carried out in the presence of catalysts of the Ziegler-Natta type.

As part of this work, we will consider the process of solution polymerization of isoprene on the TiCl₄-nIPA-TIBA-PP catalytic system (IPA is isopropyl alcohol, TIBA is triisobutylaluminum, PP is
piperylene). The investigated process is carried out in a periodic mode. The industrial production of polyisoprene involves a preliminary hydrodynamic effect on the catalytic complex using a tubular turbulent apparatus. The result of this influence more often than others is a change in the nature of polycentricity [4-5]. In particular, in the case under consideration, two types of active centers are revealed.

Since the study of the process and characteristics of the resulting product in an industrial environment is labor intensive, methods of mathematical modeling are used to solve such a problem. Modeling allows not only to predict the characteristics of the final product depending on the recipe and process conditions, but also to optimize it. Consequently, an important task today is the study and modification of the qualitative indicators of polymerization products using mathematical modeling methods.

2. Materials and methods
In the mathematical description of polymerization processes, the kinetic and statistical approaches are conventionally distinguished. The kinetic approach consists in compiling and solving material balance equations for the concentrations of all types of molecules involved in the polymerization process [6]. The resulting system of differential equations has almost infinite dimension and is solved using various simplifying methods, such as the method of moments and the method of generating functions [7-9]. This approach can be successfully used to calculate the average molecular characteristics of a polymer.

When using the statistical approach, the growing polymer chain is simulated using random variables. This approach is based on the imitation of the growth of each polymer molecule: each link of the growing polymer chain is considered as a specific random process of conditional motion along the polymer molecule, and the probability of the implementation of a random process is considered equal to the fraction of the corresponding molecules among all others in the reaction system.

The advantage of the kinetic approach is the high speed of calculations, which makes it possible to use it in the control of the polymerization process for solving problems of experiment’s planning. However, when modeling and analyzing the properties of the polymerization product using the kinetic approach, difficulties arise. Due to the use of simplifying methods when solving a system of differential equations, it allows calculating only the averaged characteristics of the final polymerization product, and to construct the molecular weight distribution, it is necessary to use model functions.

The statistical approach allows an exhaustive description of the detailed structure of macromolecules in terms of several probabilistic parameters [10-12]. This approach to modeling polymerization processes is the basis of the Monte Carlo simulation method. In this case, the mathematical model is a set of particles corresponding to individual molecules and macromolecules, which makes it possible to accumulate information on the number and length of the resulting polymer macromolecules and to obtain the actual values of the molecular characteristics of the polymerization product at any time, which makes it possible to observe the course of the process in dynamics.

We use the statistical approach to modeling the batch process of isoprene solution polymerization. First, it is necessary to write out the kinetic scheme of isoprene polymerization in the presence of a polycentric catalytic system [13]:

1. Chain growth:

\[ P_i^j + M \xrightarrow{k_i^j} P_{i+1}^j \]

2. Chain transfer to monomer:

\[ P_i^j + M \xrightarrow{k_i^j} Q_i + P_1^j \]

3. Chain transfer to organoaluminum compound (OAC):

\[ P_i^j + A \xrightarrow{k_i^j} Q_i + P_1^j \]

4. Death of active sites:
5. Transition of active sites into each other:

\[ P_i^j \xrightarrow{k_{ij}} Q_i \]

where \( M \) – monomer, \( A \) – organoaluminum compound’s concentration, \( j, l = 1, 2 \) – characterizes the type of active site, \( P_i^j \) – active ("growing") polymer chain with length \( i \) on the \( j \) type of active site; \( Q_i \) – inactive ("dead") polymer chain with length \( i \), \( k_{p}^j, k_{m}^j, k_{d}^j, k_x^j \) – constants characterizing the reaction rate of chain growth, transfer to monomer, transfer to organoaluminum compound (OAC), death of active sites and transition of active sites to each other, respectively.

In an earlier work [14], an algorithm was presented for modeling the periodic process of styrene-butadiene copolymerization by the Monte Carlo method, the implementation of which is based on the method proposed in 1977 by the physicist D. Gillespie [15] for modeling oscillatory processes. The using of the algorithm assumes a preliminary transformation of the rate constants of elementary reactions for second-order reactions according to the formula:

\[
\tilde{k} = \frac{k}{V \cdot N_A},
\]

where \( V \) – reactor volume, \( N_A \) – Avogadro's number. The rate constants of first-order reactions do not change.

The main stages of the proposed algorithm are:
1) calculating the rate of each reaction – the calculation is carried out according to the law of mass action, the number of particles of the substance in the system is used as the concentrations of the monomer and the organoaluminum compound, and for active and inactive polymer macromolecules, the concentration is the number of chains of a given type in the system;
2) calculating the probabilities of each reaction at a given time;
3) generating a uniformly distributed random number on the interval from 0 to 1 and determining the type of the played reaction – the probabilities are sequentially located on the segment from 0 to 1, filling it completely, then a random number is generated and the part of the segment into which the number falls is determined; the selected segment corresponds to the reaction to be imitated;
4) imitating a generated reaction.

This process is repeated cyclically until the required monomer conversion value is reached.

Simulation of a performed reaction is based on a change in the total number of molecules involved in the reaction of reagents. It should be noted that the molecules of the monomer and the organoaluminum compound will be characterized only by their quantity, and the macromolecules of the polymer – by the number that reflects the number of links in the chain. The software implementation of the algorithm implies that it is advisable to store all macromolecules in a dynamic array, and since the process under study is characterized by the presence of several types of active centers, this requires its own dynamic array for each type [16]. The described structure allows one to obtain the following information: the total number of polymer chains, the length of each chain, the number average and weight average molecular weights of the polymer, molecular weight distribution, and other characteristics.

Let us describe how reactions are simulated using the example of individual stages:
1. Chain growth:
   • decrease in the number of monomer molecules per unit;
• selection of a random chain in the array of active chains corresponding to the j-th type of active site;
• increase in the length of the selected polymer chain per unit.

2. Chain transfer to monomer:
• decrease in the number of monomer molecules per unit;
• selection of a random chain in the array of active chains corresponding to the j-th type of active site;
• adding the selected chain to the array of inactive chains;
• removal of the selected chain from the array of active chains corresponding to the j-th type of active site;
• adding a chain of unit length to the array of active chains corresponding to the j-th type of active site.

3. Chain transfer to organoaluminum compound:
• decrease in the number of organoaluminum compound molecules per unit;
• selection of a random chain in the array of active chains corresponding to the j-th type of active site;
• adding the selected chain to the array of inactive chains;
• removal of the selected chain from the array of active chains corresponding to the j-th type of active site;
• adding a chain of unit length to the array of active chains corresponding to the j-th type of active site.

4. Death of active sites:
• selection of a random chain in the array of active chains corresponding to the j-th type of active site;
• adding the selected chain to the array of inactive chains;
• removal of the selected chain from the array of active chains corresponding to the j-th type of active site.

5. Transition of active sites into each other:
• selection of a random chain in the array of active chains corresponding to the first (second) type of active site;
• adding the selected chain to the array of active chains corresponding to the second (first) type of active site;
• deleting the selected chain from the array of active chains corresponding to the first (second) type of active site.

3. Results and discussion
The authors of the article have developed an algorithm for the numerical study of the periodic process of isoprene polymerization in the presence of the polycentric titanium-based catalytic system. The algorithm is implemented in the Visual C++ programming language and can be used to simulate polymerization processes in the presence of catalytic systems containing up to 4 types of active sites.

To illustrate the operation of the program, based on the proposed algorithm, the computational experiment was carried out to study the process of isoprene polymerization in the presence of the titanium-containing catalytic system. In this case, the conditions of the process were used, corresponding to the laboratory ones (table 1) [13].

Based on the experimental conditions, the molar concentrations of the reagents were obtained:
– isoprene molar concentration – 1.388 mol/L;
– molar concentration of organoaluminum compound – 0.0014 mol/L;
– molar concentration of catalyst – 0.0014 mol/L.
Table 1. Conditions for conducting the isoprene polymerization process.

| Condition                                      | Value                          |
|------------------------------------------------|--------------------------------|
| Catalyst concentration (by $TiCl_4$)          | 0.0375 g/ml                    |
| Ratio $TiCl_4$ / TIBA / piperylene / DFO in the catalyst | 1 mol / 1 mol / 0.2 mol / 0.15 mol |
| Catalyst dosage                               | 1 mol $TiCl_4$ / 980 mol of isoprene |
| Concentration of isoamylenes in the original mixture | 0% weight.                    |
| Isoprene concentration in the initial mixture | 15.0% weight.                  |
| Polymerization temperature                     | 20ºC                           |

It should be noted that the concentration of active sites was set in an amount of 2.2% of the added volume of the catalyst in a molar ratio with the predominant functioning of active sites of the second type, the fraction of which is 0.92.

The constructed model makes it possible to predict the values of the molecular characteristics of the polymer. Earlier, a similar computational experiment was carried out on the basis of simulation using the kinetic approach [13]. The simulation results are shown in figures 1-3, namely, the dependence of the values of the number-average molecular weight, the weight-average molecular weight and the coefficient of polydispersity of the polymer on the conversion of monomers (the proportion of conversion of monomer into polymer), respectively.

![Figure 1. Dependence of the values of the weight-average molecular weight of the polymer on the conversion of monomers (line – the results of the statistical approach, the dotted line – the results of the kinetic approach).](attachment:figure1.png)
Figure 2. Dependence of the values of the weight-average molecular weight of the polymer on the conversion of monomers (line – the results of the statistical approach, the dotted line – the results of the kinetic approach).

Figure 3. Dependence of the values of the polymer polydispersity index on the conversion of monomers (line – the results of the statistical approach, the dotted line – the results of the kinetic approach).
The polydispersity of a polymer is expressed as the ratio of the weight average molecular weight of the polymer to the average molecular weight and makes it possible to characterize the width of the molecular weight distribution of the resulting product. The results of the statistical approach show satisfactory agreement with the results of the kinetic approach. The relative difference between the calculated values for the number-average molecular weight of the polymer is no more than 17% (the maximum value corresponds to a conversion of 20%), and at the end of the process the relative difference is 3% (at a conversion of 65%). The relative difference between the calculated values for the weight-average molecular weight of the polymer is no more than 11% (the maximum value corresponds to a conversion of 20%), and at the end of the process the relative difference is 7% (at a conversion of 65%). The relative difference between the calculated values for the polydispersity of the polymer is no more than 18% (the maximum value corresponds to a conversion of 10%), and at the end of the process the relative difference is 4% (at a conversion of 65%).

Any polymer sample is characterized by the presence of macromolecules of various sizes; therefore, the picture of the molecular weight distribution is important for assessing the quality of the resulting product. The molecular weight distribution shows the ratio of the amounts of macromolecules of different molecular weights, and the polydispersity coefficient makes it possible to characterize the width of the molecular weight distribution. Since the process considered in the framework of the computational experiment proceeds under polycentricity conditions, the overall molecular weight distribution of the polymer was constructed (figure 4), as well as the molecular weight distribution separately for each type of active site (figures 5-6).

![Figure 4. Differential curve of the molecular weight distribution of the polymer (the line is the result of the statistical approach, the dotted line is the model distribution).](image)
Figure 5. Molecular weight distribution of polymer macromolecules corresponding to the first type active sites (line – results of a statistical approach, dotted line – model distribution).

Figure 6. Molecular weight distribution of polymer macromolecules corresponding to the second type active sites (line – results of a statistical approach, dotted line – model distribution).
The figures show a comparison of the curves of the molecular weight distribution of polyisoprene, for the construction of which both the kinetic approach (dashed line - the model distribution was used in conjunction with the solution of the direct problem) and the statistical approach, which is based on the Monte Carlo method, were used. In contrast to the kinetic approach, which works only with the use of model distribution functions, the statistical approach allows the most accurate construction of the molecular distribution. To construct a molecular weight distribution, it is required to fractionate the inactive macromolecules of the obtained polymer by their weight - partitioning into fractions, each of which covers a certain range of molecular weight).

For example, for fractions with a step of 1000: 0-1000, 1000-2000, 2000-3000, etc. (including the right border in the interval). Further, it is necessary to distribute inactive macromolecules with the corresponding molecular weight into fractions. After that, for each fraction, the mass fraction of the fraction is calculated – the ratio of the total mass of inactive macromolecules of the fraction to the total mass of all inactive macromolecules of the polymer. In order to normalize the data, each found mass fraction is additionally divided by a fractionation step. The resulting dependence of the normalized mass fraction of the fraction on the molecular weight (or the logarithm of the molecular weight) is a differential molecular weight distribution curve. But since the calculation of the mass fraction can be performed both separately for each type of active center, and in total for both types, then, accordingly, the molecular weight distribution can be constructed both total and separately for each type of active site.

Analysis of the curves in figures 4-6 allows us to identify a pronounced correspondence of the constructed distributions. The present fluctuations and noises for the molecular weight distribution curve constructed by Monte Carlo simulation are explained by the peculiarities of the method and the value of the volume of macromolecules taken for the calculation.

4. Conclusion

Thus, the approach presented in this work for modeling polymerization processes under polycentricity by the Monte Carlo method and the developed software product make it possible to study the properties of the isoprene polymerization product proceeding in a batch mode in the presence of the polycentric titanium-containing catalytic system. Since this approach is based on the imitation of the growth of each macromolecule and tracking the processes occurring with it, this makes it possible to accumulate information on the length of the resulting polymer chains. Based on this information, it is possible to predict the dependences of the change in the main molecular characteristics of the polymer on the conversion of monomers at any time during the process – the number average and weight average molecular weights, the polymer polydispersity index, and it is also possible to plot the molecular weight distribution of the resulting product for each type of active center, as well as total.

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