Assessing the Hydrodynamic Effect on the Molecular Parameters of the Isoprene Polymerization Product in the Presence of a Neodymium-Based Catalytic System

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ABSTRACT: The paper presents findings on the kinetic regularities of polyisoprene production in the presence of neodymium-based catalytic systems for large-scale production processes. A mathematical model has been developed for batch and continuous isoprene polymerization. The study identified dependences of changes in the number-average and mass-average molecular weight of the resulting product on the length of the applied reactor cascade under continuous static operation. The description of the continuous production mode leads to the necessity of analyzing the structure of the flows by means of the distribution functions of the residence time in the reactor, which is the basis for the formation of a block of modules of the hydrodynamic level. A change in the length of the reactor cascade leads to a change in the residence time of particles in the reactor and, consequently, to a change in the hydrodynamic regime. With the help of mathematical modeling tools, the influence of the hydrodynamic regime in the reaction zone on the molecular weight distribution of the resulting product is revealed.

1. INTRODUCTION

Extensive research of lanthanide-containing catalytic systems1,2 promoted their implementation into synthetic isoprene rubber production. Previous studies have found a distinct advantage of this type of catalyst in producing cis-1,4 polymers that make them highly popular. Industrial isoprene polymerization based on lanthanide catalytic systems can include neodymium chloride3 and gadolinium.4 The gadolinium catalyst based polyisoprene production was initiated at the turn of 2017–2018. Meanwhile, much experimental evidence has been accumulated for neodymium chloride polyisoprenes produced both periodically and continuously. The continuous production for this type of catalytic system made it possible to produce polyisoprene of consumer properties very close to natural rubber. In Russia, the product based on neodymium-containing catalytic systems is known under the SKI-5 and SKI-5PM trademarks. SKI-5PM is commonly used in the food industry and medicine. The continuous production of SKI-5PM does not differ from the SKI-5 production and has similar structural and technological aspects.

Operating conditions in any continuous production are focused on producing a product with certain physicochemical properties. SKI-5 is made under Russian state standard GOST and technical specifications TU 2294–015–73776139–2009. Since the main physical–mechanical properties of finished products (Mooney viscosity, Karrer plasticity, elasticity, inherent viscosity) are closely related to molecular weight distribution (MWD), the study employs the basic MWD parameters: $M_w$, $M_n$, and their ratio, called the molecular-weight dispersity $M_w/M_n$.

One of the core features of isoprene polymerization in the presence of microheterogenic catalytic systems is the high-molecular-weight dispersity (up to $4\sim5$) of the resulting product, which is explained by the presence of kinetically nonequivalent active centers forming macromolecules of different molecular weights in the polymerization system. The kinetic heterogeneity of neodymium catalysts in the production of 1,4-cis-polyisoprene can explain the initiation of multimodal MWD, and, accordingly, it is taken into account when constructing models. Previous research5 showed that besides modifying the catalytic system by using different additives, the catalyst preparation in turbulent flows depends on a hydrodynamic effect of a tubular turbulent apparatus.6,7

At the same time, it is of great interest to evaluate macrokinetic patterns of the hydrodynamic regime in the
reaction zone in conditions of continuous industrial production. When traditional methods can no longer have the necessary effect on the molecular parameters of the resulting product, a different operation condition of continuous production can provide a product with the desired consumer properties. Thus, studies of the physicochemical regularities of isoprene polymerization for different operation conditions of continuous production and the influence of the hydrodynamic regime on the resulting product’s molecular weight distribution are essential for a deeper understanding of isoprene production processes.

This paper aims to assess the hydrodynamic effect on the molecular parameters of the resulting product using mathematical modeling on the example of a continuous isoprene polymerization in a cascade of reactors in the presence of neodymium-based catalytic systems.

2. DATA AND METHODOLOGY

Experimental and theoretical studies were conducted using the NdCl₃–nIPA-TIBA-PP catalytic system, based on the suspension of neodymium chloride NdCl₃–nIPA, where n = 2.8–3.0 in liquid paraffin fraction C14–C17, obtained from the neodymium oxide with Nd₂O₃/TREO = 99.90 wt. % (TREO is the sum of the rare earth oxides; i-C₃H₇OH, the Russian state standard GOST 9805–84, “dehydrated,” the weight fraction of the basic substance is not less than 99.7%; i-C₃H₇OH, the Russian specifications TU 38.10330–83, amm. 1–3, P-1, the weight fraction of the basic substance is not less than 97% technical mixture of cis- and trans-isomers at the ratio 35:65.)

NdCl₃–nIPA suspension undergoes a hydrodynamic effect in a tubular turbulent apparatus of a diffuser–confuser design. The ratio of the components used is NdCl₃/Al(i-C₃H₇)₂NdCl₃/Al(i-C₃H₇)₂/piperylene = 1/12/2 mol.

The initial temperature of the isoprene solution in isopentane was 0 °C. The flow rate is 20 t/h. The load on the battery by monomers will be taken as 4.2 t/h. The isoprene concentration in isopentane is 15 wt. %.

Continuous industrial production enables up to 9 cascade reactors of up to 16.6 m³. All the polymerizers used can be attributed to the ideal mixing reactors by their design features. The loading rate characterizes each step of isoprene polymerization, the above mechanism can be used to write down a system of ordinary differential eqs 1 characterizing the change in the material balance for each component of the reactions. The constructed system is a kinetic model of the process.¹⁰ The numerical solution of the system (eq 1) provides a forecast of the main molecular characteristics and reagent consumption rates for the entire polymerization period:

2. Inherent chain transfer

\[ P_i + M \xrightarrow{k_i} Q_i + P_i \]

3. Chain transfer to the organoaluminum (triisobutylaluminum)

\[ P_i + A_{TIBA} \xrightarrow{k_{ad}} Q_i + P_i \]

4. Chain transfer to the organoaluminum (diisobutylaluminum hydride)

\[ P_i + A_{DIBAH} \xrightarrow{k_{ad}} Q_i + P_i \]

5. Decay of active centers

\[ P_i \xrightarrow{k_i} Q_i \]

where M is the monomer concentration, \( A_{TIBA} \) and \( A_{DIBAH} \) are the concentrations of organoaluminum (triisobutylaluminum and diisobutylaluminum hydride, respectively), \( P_i \) is an active (“growing”) polymer chain; \( Q_i \) is an inactive (“dead”) polymer chain; \( k_{ad} \), \( k_{at} \), \( k_{nr} \), \( k_{d} \) are constants of the chain growth reaction rates, transfer to the monomer, organoaluminum compounds (triisobutylaluminum and diisobutylaluminum hydride), and the decay of active centers, respectively.

The kinetic mechanism of isoprene polymerization can be presented in terms of the formal language as the following stages:

1. Chain growth

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

\[
\begin{align*}
\frac{dM}{dt} &= -M \sum_{i=0}^{\infty} P_i (k_p + k_m) \\
\frac{dA_{TIBA}}{dt} &= -k_{nr} A_{TIBA} \sum_{i=0}^{\infty} P_i \\
\frac{dA_{DIBAH}}{dt} &= -k_{nr} A_{DIBAH} \sum_{i=0}^{\infty} P_i \\
\frac{dP_i}{dt} &= -k_p M P_i + (k_m M + k_{nr} A_{TIBA} + k_{nr} A_{DIBAH}) \sum_{i=2}^{\infty} P_i \\
\frac{dQ_i}{dt} &= k_{nr} M P_i + k_{nr} A_{TIBA} P_i + k_{nr} A_{DIBAH} P_i \\
\frac{dP}{dt} &= k_{nr} M (P_{i-1} - P_i) - k_m M P_i - k_{nr} A_{TIBA} P_i \\
&- k_{nr} A_{DIBAH} P_i - k_d P_i \\
\frac{dQ}{dt} &= k_{nr} M P_i + k_{nr} A_{TIBA} P_i + k_{nr} A_{DIBAH} P_i + k_d P_i
\end{align*}
\]
To analyze the molecular weight distribution of the resulting product, the concepts of active and inactive chain moments are used:\(^{(13)}\)

\[\mu_j = \sum_{i=2}^{\infty} i!P_i, \quad \eta_j = \sum_{i=2}^{\infty} i!Q_i\]  
(2)

The moments of active \(\mu_j\) and inactive chains \(\eta_j\) are used to calculate the averaged molecular characteristics:

\[M_n = m_0\mu_1 + \eta_1, \quad \bar{M}_n = m_0\mu_2 + \eta_2\]  
(3)

where \(m_0\) is the molecular weight of isoprene, \(M_n\) and \(\bar{M}_n\) are the number-average and mass-average molecular weight, respectively. The resulting values of the number-average and mass-average molecular weights can be used to find the molecular-weight dispersity value \(D_M\) as the ratio \(D_M = \bar{M}_n/M_n\). Molecular-weight dispersity characterizes the width of the molecular weight distribution of the resulting polymer and is used to estimate the heterogeneity of the resulting polymer product numerically.

Modifying the resulting system of differential eqs 1 taking into account eq 2 results in a system of finite dimension eqs 4:

\[
\begin{align*}
\frac{dM}{dt} &= -k_MR_j + k_u\rho_j - M\eta_j(k_j + k_u) \\
\frac{dA_{\text{TIBA}}}{dt} &= -k_uA_{\text{TIBA}}P_1 - k_uA_{\text{TIBA}}\eta_0 \\
\frac{dA_{\text{DIBAH}}}{dt} &= -k_uA_{\text{DIBAH}}P_1 - k_uA_{\text{DIBAH}}\eta_0 \\
\frac{dP}{dt} &= -k_Mk_R + (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}})\eta_1 \\
\frac{dQ}{dt} &= k_uM + (k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}})\eta_1 \\
\frac{d\eta_0}{dt} &= k_Mk_R - (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}})\rho_j - k_u\rho_j(k_j + k_u) \mu_0 \\
\frac{d\eta_1}{dt} &= (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}} + k_1)\eta_0 \\
\frac{d\eta_2}{dt} &= 2k_Mk_R + k_u\rho_j - (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}} + k_2)\mu_0 \\
\frac{d\eta_1}{dt} &= (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}} + k_1)\eta_1 \\
\frac{d\eta_2}{dt} &= 4k_Mk_R + 2k_u\rho_j + 2k_M\rho_1 - (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}} + k_2)\mu_0 \\
\frac{d\mu_0}{dt} &= 4k_Mk_R + k_u\rho_j + 2k_M\rho_1 - (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}} + k_2)\mu_0 \\
\frac{d\mu_1}{dt} &= (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}} + k_1)\eta_2 \\
\frac{d\mu_2}{dt} &= (k_uM + k_uA_{\text{TIBA}} + k_uA_{\text{DIBAH}} + k_2)\eta_2
\end{align*}
\]

(4)

The initial conditions for system 4 are given as follows:

\[M(0) = M_0, \quad A_{\text{TIBA}}(0) = A_{\text{TIBA}(0)} \]
\[A_{\text{DIBAH}}(0) = A_{\text{DIBAH}(0)}, \quad R(0) = P_0, \quad Q(0) = 0 \]
\[\mu_j(0) = \eta_j(0) = 0, \quad i = 0, \ldots, 2\]  
(5)

The developed system of differential eqs 4 with initial conditions 5 is a mathematical model of the isoprene polymerization process for a modified catalytic system. To assess the hydrodynamic effect of a continuous process in a cascade of reactors, it is necessary to supplement this kinetic model with a macrokinetic module that considers the corresponding regularities.\(^{(13)}\) Currently, the continuous industrial production in Russia is based on a cascade of ideal mixing reactors. Reagents are constantly fed, intensively mixed, and removed from the reactor. The average residence time in such a reactor can be calculated as \(V/W\), where \(V\) is the volume of the reactor, and \(W\) is the total volumetric feed rate of all reagents. Given that continuous operation is characterized by a high mixing rate, it is assumed that there are no reagent concentration gradients in the reactor at any given time.

The moments of molecular weight distribution for ideal mixing reactors can be expressed in terms of recurrent relations:\(^{(13)}\)

\[
\frac{d\bar{Y}^k(i)}{dt} = \left(\frac{\bar{Y}^k(i-1) - \bar{Y}^k(i)}{\theta^k}\right) + \bar{R}^k(i)
\]  
(6)

where \(\theta^k\) stands for the residence time of the reaction mixture in the \(k\)th cascade reactor and the form \(\bar{R}^k(i)\) is determined by the adopted kinetic module, vector \(Y\) is determined by the dimension of the system of eqs 4, and therefore, \(Y = (M, A_{\text{TIBA}}, A_{\text{DIBAH}}, P, Q, \mu_0, \eta_0, \mu_1, \eta_1, \mu_2, \eta_2)\). It must be noted that the model recurrence of the initial moments of non-normalized distributions complies with the vector \(Y\) components,\(^{(13)}\) whereas building models based on \(dM_\mu/dt\), \(dM_\eta/dt\), and \(dK/dt\) can result in more complicated equations not convenient for modeling and subsequent analysis. Equation 6 provides the comprehensive system of differential eqs 4—5 by the macrokinetic module of the isoprene polymerization. A computational experiment using a system of differential eqs 4—5, and eq 6 can identify patterns of changes in product characteristics in starting (dynamic) modes, taking place rarely in industrial production (reactor start-up, shutdown, removal from service). Previously, such calculations were made for the isoprene polymerization based on neodymium catalytic systems with modifying additives TEA or TGA\(^{(14)}\) and a titanium catalytic system.\(^{(15)}\) This paper focuses on the stationary (static) operation characterized by no changes in the reagent concentrations and working conditions for a sufficiently long period. Since the product characteristics and concentrations of the starting substances within one polymerizer do not alter, the operation process can be called steady (static). To calculate static modes of continuous production, the left part of eq 6 must be zeroed, and a system of differential equations must be changed to a system of nonlinear algebraic equations, each derived from the relation

\[
\left(\frac{\bar{Y}^k(i-1) - \bar{Y}^k(i)}{\theta^k}\right) + \bar{R}^k(i) = 0
\]  
(7)

Before modeling and making corresponding recommendations for industrial production, it is necessary to perform a brief preliminary analysis. It must be stressed that rubber is mainly produced in a cascade of reactors: several series-connected reactors (from 3 to 16) make up a cascade (the so-called battery), depending on the required operating rate, up to 4—5 batteries work in parallel. The required number of reactors in the cascade varies depending on the type of product (monomer, catalytic system). Since the polymer produced in a batch operation is ideal, the large-scale continuous production must be aimed at manufacturing products with similar molecular characteristics. As a rule, the more reactors in the cascade, the closer the continuous production is to the batch operation.\(^{(13)}\) While a monomer conversion (equivalent to
the operation rate) requires a lower number of reactors, making molecular characteristics close to those resulting from the batch operation requires a higher number of reactors. Thus, the necessary conversion in simulating isoprene polymerization based on neodymium catalytic systems with modifying additives is achieved with three continuous production reactors, while there must be ten reactors to get the required averaged molecular characteristics. Therefore, industrial production requires the solution of some compromise problem. A monomer—catalyst system gets its own results on the number of reactors in each case. In previous studies, butadiene polymerization in a cascade of reactors using neodymium catalysts was examined by modeling changes in MWD using a cascade of 4 reactors, taking into account chain transfer and other characteristics of the reaction system. The isoprene polymerization has not been paid much attention. This study seeks to address this research gap.

The calculated data were obtained by the numerical method of the Levenberg–Marquardt solution and the author’s software package and used to interpret the findings graphically.

3. RESULTS AND DISCUSSION

This paper investigates the hydrodynamic effect on the molecular characteristics of the resulting product by conducting a series of computational experiments with different numbers of reactors. The study is based on the following assumptions:

- there are no more than nine reactors used in the cascade (a larger number is impossible due to the technological design of industrial production)
- temperature changes insignificantly, which makes it possible to ignore its effect on the kinetic parameters of the polymerization process
- the acceptable conversion at the output of the first reactor does not exceed 50%, since a higher conversion value results in a significant heat release and consequently a change in the kinetic parameters of the reactions
- the polymerization process is performed until the conversion is 75%
- the residence time of the reaction mixture in each polymerizer is constant and calculated based on the number of cascade reactors. To set different residence times of the mixture in conditions of industrial production is operationally impossible

Under the conditions described in the Data and Methodology, the molar ratios of substances were calculated: isoprene 1.39 mol/L, diisobutylaluminum hydride 0.000177 mol/L, active centers 0.00014 mol/L, triisobutylaluminum 0.00168 mol/L. The reagent concentration values are necessary to set the initial conditions of the system of differential eqs 4–5, taking into account eq 6. The following kinetic parameters were used to make calculations: $k_p = 48 \ l/(mol\cdot s)$, $k_{cat} = 8.16 \ l/(mol\cdot s)$, $k_{cat} = 0.96 \ l/(mol\cdot s)$, $k_{cat} = 0.0048 \ l/(mol\cdot s)$, $k_d = 0 \ s^{-1}$

where $k_p$, $k_{cat}$, $k_{cat}$, $k_{cat}$ and $k_d$ are constants characterizing the chain propagation rate, chain transfer to diisobutyl aluminum hydride, triisobutyl aluminum, monomer, and decay of active centers, respectively. Figure 1 shows the change in the molecular averages $M_n$ and $M_w$ in the last reactor depending on the number of cascade reactors used (from 2 to 9). The polymerization reactions in all the studied conditions took place at conversion up to 75%. The product characteristics were read at the outlet of the last polymerizer. The residence time in the polymerizer for each series of calculations was different. Thus, the residence time of the reaction mixture for a cascade of two polymerizers was 49 min in each of them, while the residence time for a cascade of nine polymerizers was just over 8 min. The remaining values of the residence time are shown in the table. The computational experiments suggest that a higher length of the reactor cascade results in a steady increase in the average molecular weights. The number-average molecular weight $M_n$ of the product produced in a cascade of two polymerizers at 75% conversion is $317 \times 10^3$, while it equals $355 \times 10^3$ for a cascade of nine polymerizers at the same conversion. The mass-average molecular weight $M_w$ similarly changes the value of $647 \times 10^3$ for two polymerizers to $728 \times 10^3$ for a cascade of nine polymerizers (Table 1).

A more detailed analysis of changes in the molecular characteristics of the resulting product was made by developing the dependence of the change in the width of the molecular weight distribution expressed by the molecular-weight dispersity of the polymer product. The results of the computational experiment are shown in Figure 2. The width of the resulting product’s molecular weight distribution does not change significantly and remains 2 to 2.1.

Due to technical limitations, conducting computational experiments for a longer reactor cascade length does not make sense. However, the research findings indicate that at the higher length of the cascade, $N \gg 1$, $M_n$ and $M_w$ values will approximate the average molecular weights characteristic for batch polymerization ($M_n = 365 \times 10^3$, $M_w = 748 \times 10^3$ obtained by calculation for the same experimental conditions).

The computational results obtained are in line with the expectations and are relevant to the emerging issues of industrial process control in the synthesis of polymer products. This parameter change can be used to get a product with a...
larger molecular weight and the preserved width of the molecular weight distribution. The resulting dependences demonstrate a significant influence of hydrodynamic characteristics on the molecular weight distribution of the polymer product. The nonlinear pattern of the change makes it possible to use this effect as a tool for influencing the molecular and consumer properties of polyisoprene, especially in conditions when other ways are limited.

The approach used to determine static modes of continuous polymerization makes it easy to find the values at the output of each polymerizer, regardless of the cascade length. The change in molecular characteristics in each polymerizer, starting with the loading of the reaction mixture, is also of great interest. Figures 3 and 4 show the computational experiment results for nine cascade polymerizers in the system.

### Table 1. Residence Time in the Polymerizer Depending on the Cascade Length

| number of cascade reactors | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------------------------|---|---|---|---|---|---|---|---|
| Residence time, min        | 49.5 | 29 | 20.5 | 15.8 | 12.8 | 10.8 | 9.4 | 8.2 |

### Figures

#### Figure 2. Molecular-weight dispersity dependence on the \( N \) number of cascade reactors at 75% conversion.

#### Figure 3. Dependence of (a) the number-average molecular weight; (b) the mass-average molecular weight of polyisoprene from the number of polymerizers for a cascade of 9 reactors.

#### Figure 4. Dependence of the polyisoprene conversion values on the polymerizer number for a cascade of 9 reactors.

### 4. CONCLUSION

This study applied mathematical modeling tools and computational experiments to calculate the molecular parameters of polyisoprene in the presence of a modified catalytic system based on neodymium chloride for continuous static production. The resulting dependences have indicated the nonlinear change in the averaged molecular characteristics and, consequently, the strong impact of the reactor cascade length on the molecular weight distribution of the product. Overall, it emphasizes the hydrodynamic effect of continuous production as a factor that can be used for controlling industrial polymerization processes and formulating optimal control objectives in the future.

The problem considered in this paper is the basis for further optimization formulation. Its success depends on a good initial approximation for convergence and stability of the optimization procedure, especially when some variables are discrete (the number of reactors in the cascade, the number of parallel batteries). At the same time, others are continuous (temperature profile, catalyst concentration, etc.) with many restrictions.

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Notes
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