

PAPER • OPEN ACCESS

Creating molecular weight distribution of butadiene rubber on neodymium-based catalytic system

To cite this article: G V Manuyko *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **734** 012066

View the [article online](#) for updates and enhancements.

Creating molecular weight distribution of butadiene rubber on neodymium-based catalytic system

G V Manuyko¹, D V Bashkirov², V V Bronskaya², T V Ignashina², O S Kharitonova³ and G A Aminova¹

¹Department of Technology of Engineering Materials, Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation

²Department of Chemical Process Engineering, Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation

³Department of Chemical Technology of Petroleum and Gas Processing, Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation

E-mail: olga.220499@mail.ru

Abstract. The method of calculation of the molecular weight distribution (MWD) of rubber SDRN synthesized in the cascade of reactors with a continuous mixer in the presence of chain transfer to the polymer (by direct numerical solution system of equations arising from the kinetic scheme of polymerization with special selection of boundary conditions, maximum length of macromolecules and calculation step value). Numerical solution of mathematical model that is systems of differential equations for concentrations of monomer, co-catalyst and macromolecules of polymer together with thermal balance is obtained. The influence of regime parameters on MWD and molecular mass characteristics of the final product obtained using molecular weight distribution are analyzed.

The most important characteristic of the molecular structure of polymers, determining their rheological and physical and mechanical properties, is the molecular weight distribution (MWD) by the number of monomeric links [1-3]. A lot of methods of modeling with the aim of exhaustive description of process including creating neural network model [4]. Information on the influence of polymerization conditions and catalyst composition on the polymer MWD allows to find out the mechanism of polymerization reaction, the nature of active centers, as well as formulate approaches for obtaining of a wide range of polymers with specified properties [5,6]. That's why defining MWD and searching methods of its task-oriented regulation are an important task of scientific and technical research in the catalytic polymerization.

There are a number of unresolved problems (overgrowing by the polymer of the first reactor, quality mismatch of rubber to international standards), which can be solved by technological methods, for the industrial process of synthesis of butadiene rubber on the neodymium-based catalytic system (SDRN) [7-14].

Molecular-mass characteristics of rubber vary in wide range and depend on the ratio of components of the catalytic system, concentrations of catalyst and monomer, process design. The influence of the



temperature regime on polymerization processes is also an important factor determining the quantitative and qualitative characteristics of the obtained products[15-24].

Therefore, the study of the joint processes of heat transfer and chemical transformation on the polymer MWD together with modeling of the branching (branching process) of macromolecules will allow to more clearly control the properties of rubber.

SDRN rubber is obtained by the method of coordinated ionic polymerization of butadiene in the “nephras” solution under the action of a neodymium-based catalytic system: neodymium versatate /diisobutylaluminium hydride/ethylaluminium sesquichloride. The butadiene polymerization process in the “nephras” solvent in the presence of a catalyst is carried out continuously in 2-4 polymerizers in a cascade. Each polymerizer is a machine equipped with a helicoidal mixer and a jacket for cooling. The temperature in the last reactor can reach 110°C (figure 1).

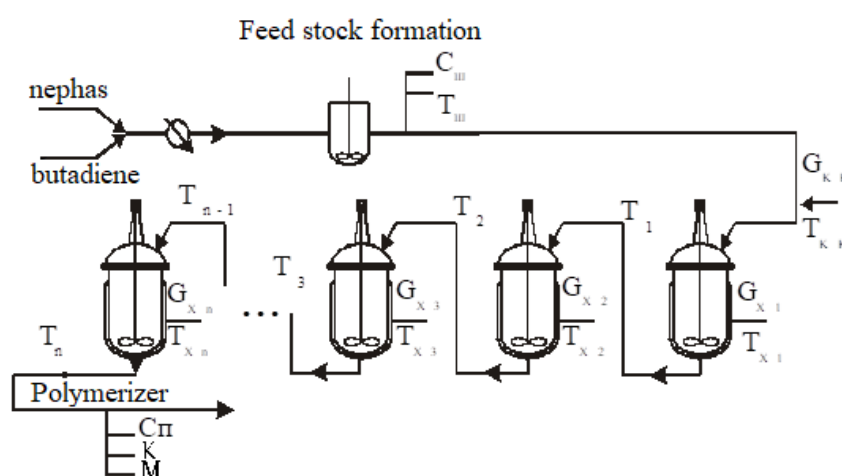


Figure 1. Technological scheme of the process of solution polymerization of butadiene on a neodymium containing catalyst.

The kinetic scheme of the polymerization process of butadiene on the neodymium-based catalytic system was developed on the basis of the analysis of the process mechanism by literature sources and experimental data. Moving from a kinetic scheme to a system consisting of large number of differential equations describing the process butadiene polymerization on a neodymium catalyst in a cascade of continuous reactors is occurred based on the laws of kinetics of polymerization processes.

$$\begin{aligned}
 \frac{dM_k}{dt} &= \frac{M_{k-1} - M_k}{\tau} - k_{p,k} M_k I_0, \\
 \frac{dAl_k}{dt} &= \frac{Al_{k-1} - Al_k}{\tau} - k_{tAl,k} Al_k I_0, \\
 \frac{\partial R_k(b, i, \ell)}{\partial t} &= \frac{R_{k-1}(b, i, \ell) - R_k(b, i, \ell)}{\tau} - ik_{p,k} M_k \frac{\partial R_k(b, i, \ell)}{\partial \ell} + \\
 &\quad + k_{tp,k} \ell I_0 (R_k(b-1, i-1, \ell) - R_k(b, i, \ell)) + \\
 &\quad + (k_{tp,k} M_0 x_k + k_{sp,k} + k_{tm,k} M_k + k_{tAl,k} Al_k) ((i+1)R_k(b, i+1, \ell) - iR_k(b, i, \ell)) + \\
 &\quad + \frac{I_0}{\tau} \delta_{k,1} \delta_{b,0} \delta_{i,1} \delta(\ell) + (k_{sp,k} + k_{tm,k} M_k + k_{tAl,k} Al_k) I_0 \delta_{i,1} \delta_{b,0} \delta(\ell).
 \end{aligned} \tag{1}$$

$$k = 1, 2, \dots; \quad i, b = 0, 1, 2, \dots; \quad 0 \leq \ell < \infty$$

where $R_k(b, i, l)$ is the concentration of macromolecules with the number of branches b , i active centres and l monomeric links in the k -th cascade reactor, $k_{p, k}$, $k_{tm, k}$, $k_{tAl, k}$, $k_{ip, k}$, $k_{sp, k}$ are constants of growth rate, chain transfer to monomer, organic-aluminum-compound, polymer and spontaneous chain transfer in k -th reactor, respectively; δ_{ij} is Kronecker symbol, $\delta(l)$ is a generalized Dirac function.

Differential equations (1) for the concentration of macromolecules $R_k(b, i, l)$ in the k -th reactor of cascade contain members describing the increase in the length of macromolecules as a result of growth, the change in the number of active centers owned by these macromolecules due to chain transfer reactions, short chain formation during transmission and instantaneous reinitiation, as well as input and output flows. Equations (1) are written in the approximation of long chains used for high molecular weight polymers.

This system of equations (1) together with the equations of thermal balance is a mathematical model of the considered process and is solved directly numerically.

The MWD function calculation is carried out. Molecular weight distributions of the polymer obtained in the cascade of perfect mixing reactors are constructed on the basis of a mathematical model. The influence of transfer reaction and polymerization conditions on the change of molecular weight distribution (MWD) of polymerization products is theoretically researched.

The function of molecular weight distribution is defined as follows:

$$f_W(\ell) \equiv \ell \frac{\sum_i \sum_b R(b, i, \ell)}{\int_0^\infty \sum_i \sum_b R(b, i, \ell) d\ell}$$

It is known that numerical methods for solving the system of differential equations are approximate. To ensure that the solutions of the system of differential equations for the concentration of macromolecules $R_{i, k}(l)$ were obtained with acceptable accuracy, the relative error was determined:

$$\Delta_k = \left| \mu_{1k} - M_0 x_k \right| / (M_0 x_k), \text{ where } \mu_{1k} = \int_0^{N_\ell} \left(\sum_{b=0}^{N_b} \sum_{i=0}^{N_i} R(b, i, \ell) \right) \ell d\ell$$

This check is based on the fact that the first moment of the MWD μ_{1k} is equal to the concentration of formed polymer: $\mu_{1k} = M_0 x_k$. The correct choice of chain length N_i and the value of the calculation step allows to ensure the necessary accuracy of calculations $\Delta_k < \varepsilon$. In addition, the program for constructing distribution functions $R_{i, k}(l)$ has been probed in specific cases where only one of the intensity of spontaneous chain transfer or chain transfer to monomer, for which analytical solutions of equations (1) are obtained, is different from zero. The distribution functions constructed numerically and by analytical formulas practically coincide ($\varepsilon \leq 0.02$).

An important task is to establish the relation between the properties of polymers and the regime parameters of process. This problem can be solved by using a mathematical model that takes into account the main characteristics of the process and the MWD of the resulting product. In this regard, numerical experiments on the developed mathematical model were carried out, the influence of technological parameters on the polymer MWD and, as a result, on molecular-mass characteristics was researched.

Increasing the input temperature leads to an increase in the intensity of the chain transfer resulting in an increase in the proportion of low-polymeric fraction and the polydispersity index (figure 2).

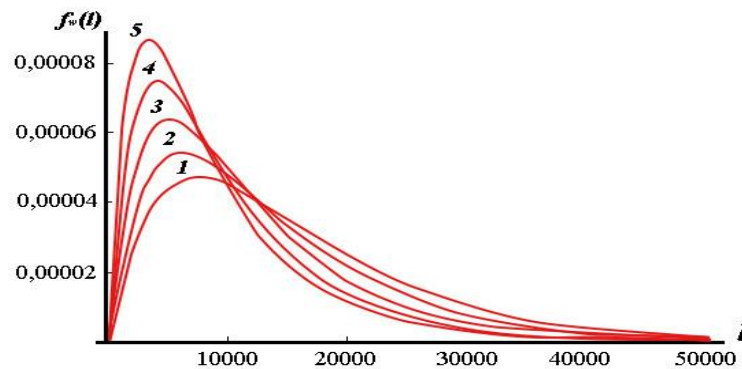


Figure 2. MWD at the output from the third reactor of cascade at different input temperature; curve 1 — $T^{\text{input}} = 20\text{ }^{\circ}\text{C}$, 2 — $30\text{ }^{\circ}\text{C}$, 3 — $40\text{ }^{\circ}\text{C}$, 4 — $50\text{ }^{\circ}\text{C}$, 5 — $60\text{ }^{\circ}\text{C}$.

Increasing the initiator concentration leads to the increase of low-polymeric fractions and the decrease of high-polymeric fractions. Consequently, the MWD shifts to the left, the polydispersity index increases. At the same time, the characteristic viscosity of the polymerizate grows.

Enlarging the monomer concentration leads to a slight growth in the polydispersity index. The MWD is expanding: the proportion of high-polymeric fraction increases, the low-polymeric fraction decreases.

The polydispersion index and the cold flow of polymer are in a certain dependence. It is important that the polydispersion slightly change under reducing cold flow. This problem in production is solved purely mechanically: the final product (polymer) coming from different batteries (with different number of reactors) is simply mixed, thereby averaging molecular mass characteristics.

Numerical experiments were carried out to add the MWD functions of polymers obtained under different process modes and, consequently, by different characteristics, which confirmed the tendency to averaging the molecular mass characteristics of the final (total) product in relation to the components, as shown by MWD diagrams for batteries with different input temperatures and initial monomer concentrations.

A comparison of the MWD function calculated according to the proposed model and measured by gel permeation chromatography was also carried out. As a result, it was found out that the calculation function of the MWD describes experimental data. The relative error did not exceed 15% (figure 3).

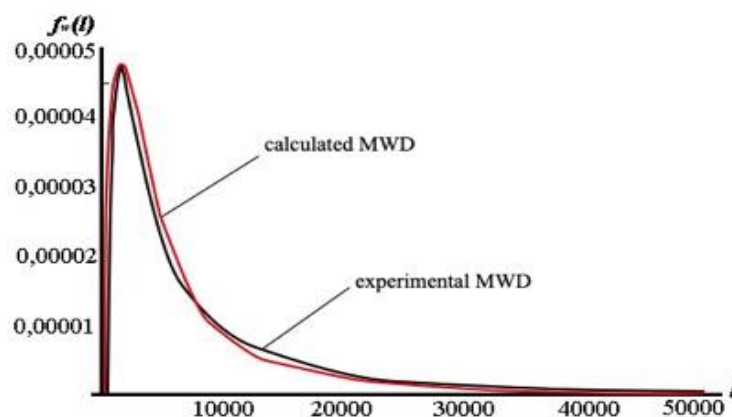


Figure 3. Comparison of experimental and calculated MWD functions.

In addition, this comparison was made for experimental data obtained after mixing rubber at the output of 7 batteries with different modes. Mathematical models were developed and mathematical

modeling of polybutadiene synthesis process on the catalytic system of neodymium versatate/diisobutylaluminium hydride/ethylaluminium sesquichloride in the cascade of continuous action reactors taking into account the branching was carried out. Numerical solution of mathematical model, that is systems of differential equations for concentrations of monomer, co-catalyst and polymer together with thermal balance, relatively to concentrations of macromolecules in the reaction system was obtained. A method for calculating the molecular weight distribution function was developed. The influence of regime parameters on MWD and molecular-mass characteristics of the final product obtained using MWD was analyzed.

References

- [1] Aminova G A , Manuiko G V, Bronskaya V V, Ismagilova A I and D'yakonov G S 2004 Mathematical simulation of the synthesis of cis-1,4-polybutadiene on a cobalt-containing catalyst in the presence of ethylene *Kinetics and Catalysis* **45** 288-96
- [2] Aminova G A , Manuiko G V, Bronskaya V V, Ismagilova A I and D'Yakonov G S 2006 Mathematical modeling of butadiene rubber synthesis process on neodymium-containing catalyst system *Polymer Science - Series A* **48** 881-6
- [3] Aminova G A, Manuiko G V, Ignashina T V, Bronskaya V V, Kharitonova N E, D'Yakonov G S and Arkhireev V P 2006 Optimal parameters of butadiene polymerization in the synthesis of rubber on a neodymium-containing catalytic system *Theoretical Foundations of Chemical Engineering* **40** 59-67
- [4] Kharitonova O S, Bronskaya V V, Ignashina T V, Al-Muntaser A A and Khairullina L E 2019 Modeling of absorption process using neural networks *IOP Conf. Ser.: Earth Environ. Sci.* **315** 032025
- [5] Manuiko G V, Aminova G A, Bronskaya V V, D'Yakonov G S and Bashkirov D V 2008 Calculation of the molecular weight distribution of the polymer produced in a cascade of reactors with allowance for chain transfer to the polymer *Theoretical Foundations of Chemical Engineering* **42** 336-9
- [6] Aminova G A, Manuiko G V, Bronskaya V V, Ignashina T V, Litvinenko G I, D'yakonov G S, Bashkirov D V and Demidova E V 2008 Effect of the operating conditions of synthesizing diene rubber with a neodymium-based catalytic system on its branching characteristics *Theoretical Foundations of Chemical Engineering* **42** 60-6
- [7] Manuiko G V, Aminova G A, Bronskaya V V, Ignashina T V, D'Yakonov G S and Bashkirov D V 2008 Calculation of the molecular weight distribution of the polymer produced in a cascade of reactors with allowance for chain transfer to the polymer *Theoretical Foundations of Chemical Engineering* **42** 336-9
- [8] Aminova G A, Bronshtejn M D, Manuiko G V, Ignashina T V, Davydova V V, Antonova O V, D'yakonov G S, Reshetova I G and Kharitonova N E 2002 Method of solution of a system of equations describing the continuous process of polymerization under conditions of a polyaddition reaction *Inzhenerno-Fizicheskii Zhurnal* **75** 165-9
- [9] Hsieh H L 1965 Molecular weight and molecular weight distribution of polymers prepared from butyllithiums *J. Polym. Sci.* **3** 163.
- [10] Roovers J E L and Bywater S 1975 The reaction of tert-butyllithium with styrene and isoprene. A comparison of chain initiation with the isomers of butyllithium *Macromolecules* **8** 251-4
- [11] Lewis H L and Brown T L 1970 Association of Alkylolithium Compounds in Hydrocarbon Media Alkylolithium-Base Interactions *J. Am. Chem. Soc.* **92** 4664-70
- [12] Worsfold D J and Bywater S 1964 Anionic polymerization of isoprene *Canadian Journal of Chemistry* **42** 2884-92
- [13] Chang C C, Halasa A F and Miller J W 1993 The reaction engineering of the anionic polymerization of isoprene *J. Appl. Polym. Sci.* **47** 1589-99
- [14] Chang C C, Halasa A F, Miller J W and Hsu L 1994 Modelling studies of the controlled anionic copolymerization of butadiene and styrene. *Polym. Int.* **33** 151-9

- [15] Beckelmann D and Bandermann F 1999 Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements *J. Appl. Polym. Sci.* **73** 1533.
- [16] Richards D H 1977 The polymerization and copolymerization of butadiene *Chem. Soc. Rev.* **6** 235-60
- [17] Milner R, Young R N and Luxton A R 1983 A viscometric study of the interaction of polybutadienyllithium with N, N, N', N'-tetramethylethylenediamine in benzene *Polymer* **24** 543-46
- [18] Quirk R P and McFay D 1981 Solvation of polymeric organolithium compounds. Stoichiometry and heats of interaction of N,N,N',N'-tetramethylethylenediamine (TMEDA) with poly(styryl)lithium and poly(isoprenyl)lithium *J. Polym. Sci.: Polym. Chem. Ed* **19** 1445-9
- [19] Bruzzone M, Corradini G and Amato F 1966 Technological characteristics of polyisoprenes with different 1,4-cis contents *Rubber Chemistry and Technology* **39** 1593-607
- [20] Kent E G and Swinney F B 1966 Properties and applications of trans-1,4 polyisoprene *Ind. Eng. Chem. Prod. Res. Develop* **5** 134-8
- [21] Bywater S, Firat Y and Black P E 1984 Microstructures of polybutadienes prepared by anionic polymerization in polar solvents. Ion-pair and solvent effects *J. Polym. Sci.: Polym. Chem. Ed.* **22** 669-72
- [22] Tenorio-Lopez J A, Benvenuta-Tapia J J, Vivaldo-Lima E, Rios-Enriquez M A and de Nieto-Pena M L 2012 Modeling of polymerization rate and microstructure in the anionic polymerization of isoprene using n-butyl lithium and N,N,N',N'-tetramethylethylenediamine considering different reactivities of the structural units *J. Polym. Res.*
- [23] Benvenuta-Tapia J J, Tenorio-Lopez J A, Montiel C and Rios-Guerrero L 2008 Kinetics of the anionic polymerization of buta-1,3-diene considering different reactivities of the cis, trans and vinyl structural units *Macromol. React. Eng.* **22** 436-51
- [24] Halasa A F and Hsu W L 2002 Synthesis of high vinyl elastomers via mixed organolithium and sodium alkoxide in the presence of polar modifier *Polymer* **43** 7111-8