Monte Carlo method for modelling the copolymerization of isobutylene and isoprene

I O Antonova\(^1\), R R Dmitrieveva\(^1\), V V Bronskaya\(^2\), G V Manuyko\(^1\), O S Kharitonova\(^3,5\) and D S Balzamov\(^4\)

\(^1\)Department of Technology of Engineering Materials, Kazan National Research Technological University, Kazan, Russian Federation
\(^2\)Department of Chemical Process Engineering, Kazan National Research Technological University, Kazan, Russian Federation
\(^3\)Department of Chemical Technology of Petroleum and Gas Processing, Kazan National Research Technological University, Kazan, Russian Federation
\(^4\)Department of Power Supply of Enterprises and Energy Resource Saving Technologies, Kazan State Power Engineering University, Kazan, Russian Federation

\(^5\)E-mail: oharitonova36@gmail.com

Abstract. There is the algorithm of modelling the copolymerization of isobutylene and isoprene in the medium of methyl chloride. This algorithm is based on the Monte Carlo method. The algorithm allows to perform simulations with a large value of the statistical ensemble at a saleable using of computer time. Whereby, the following reactions are modelled: initiation, chain growth and chain transfer to the monomer. In the process of work, the program calculates the dependence of the concentrations of all reagents on the polymerization time: active centres, monomers and chain transfer agents. The result of the calculation is the molecular-weight distribution curve.

The kinetics of polymerization is the important part of the development of polymerization, which describes changes in the polymerization activity and properties of the polymer depending on the polymerization time. In addition, the polymerization kinetics can be described using model equations. There are three leading modelling methods: the statistical modelling method, the empirical modelling method and the kinetic method [1-4].

The computer simulation of polymerization processes using the Monte Carlo method is used when the kinetic mechanism is very complex. The important advantage of the kinetic modelling of the polymerization reactions using the Monte Carlo method is that detailed information about the microstructure of polymers is available, which allows to track the time dynamics of changes in the concentrations of the system components and build the molecular weight distribution of the process.

The Monte Carlo method has attracted a lot of attention in the field of the polymerization kinetics with the development of computer technology and mathematically based algorithm.

The ability of the Monte Carlo method to model the whole polymerization process facilitates a more thorough study of whether the proposed kinetic mechanism and coefficients provide a relevant representation of the polymerization.
To date, many articles about the kinetics of polymerization have been published. However, the research at the microscale level is infrequent. There is even less research on the microscale polymerization kinetics based on the Monte Carlo method.

The dynamic Monte Carlo model was developed by Simon and other [5-8] to describe the distribution of the chain length of polyolefins that was obtained using the coordination catalysts, depending on the polymerization time. Their model showed favorable flexibility compared to the GPC curves that was obtained in the experiments, but there were no microscale kinetic data for the active center type.

Most models of the polymerization of olefin proposed using the Monte Carlo method suggest that there is a type with a single active center in the polymerization system. Practically, the conclusions about the existence of several types of active centers in the process of polymerization of butyl rubber that was catalyzed by Lewis acids were confirmed [9-14].

Therefore, it is important to study the microscale kinetics of the butyl rubber polymerization system, including several types of active centers. Special attention is paid to the description of the dynamic evolution of active centers and their influence on the polymerization kinetics using the Monte Carlo method.

The following reactions were included in the kinetic scheme of the cationic copolymerization of isobutylene with isoprene:

**Initiation:**
\[
M_1 + I \xrightarrow{k_{a1}} R_1(1,0) \\
M_2 + I \xrightarrow{k_{a2}} R_2(0,1)
\]

**Chain growth:**
\[
R_1(l_1, l_2) + M_1 \xrightarrow{k_{p11}} R_1(l_1 + 1, l_2) \\
R_2(l_1, l_2) + M_1 \xrightarrow{k_{p12}} R_2(l_1 + 1, l_2) \\
R_1(l_1, l_2) + M_2 \xrightarrow{k_{p11}} R_1(l_1, l_2 + 1) \\
R_2(l_1, l_2) + M_2 \xrightarrow{k_{p12}} R_2(l_1, l_2 + 1)
\]

**Chain transfer to monomer:**
\[
R_1(l_1, l_2) + M_1 \xrightarrow{k_{tr11}} P_1(l_1, l_2) + R_1(1,0) \\
R_2(l_1, l_2) + M_1 \xrightarrow{k_{tr12}} P_2(l_1, l_2) + R_1(1,0) \\
R_1(l_1, l_2) + M_2 \xrightarrow{k_{tr12}} P_1(l_1, l_2) + R_2(0,1) \\
R_2(n, m) + M_2 \xrightarrow{k_{tr22}} P_2(n, m) + R_2(0,1)
\]

In the scheme above, the following designations were used: \( I \) is the initiator; \( M_1, M_2 \) are isobutylene and isoprene monomers, respectively; \( R_1(1,0), R_2(0,1) \) are the active chain with one isobutylene and isoprene link, respectively; \( R_1(l_1, l_2), R_2(l_1, l_2) \) is the active polymer chains with isoprene and isobutylene link at the end, respectively; \( k_{a1}, k_{p11}, k_{tr11} \) are the constants of initiation, chain growth, transfer to the monomer, respectively \((i = 1, 2)\).

Based on the proposed kinetic scheme, the system of differential equations describing the instantaneous rates of change in the concentrations of the system components was obtained:
\[
\frac{d[I]}{dt} = -(k_{a1}[M_1] + k_{a2}[M_2])[I],
\]
The simulation of the process of the copolymerization of isobutylene with isoprene in a batch reactor was considered in this paper [19-23]. The kinetic model with several active centers is proposed using the Monte Carlo method. The obtained model of the cationic copolymerization kinetics of isobutylene with isoprene, which includes the reactions of initiation, chain growth and transfer to the monomer, makes it possible to accumulate the information about the length and composition of the chains of the resulting copolymer and track this process in dynamics.

\[
\frac{d[M_1]}{dt} = -[M_1](k_{a1}[I] + J_{100}(k_{p11} + k_{tr11}) + J_{200}(k_{p21} + k_{tr21})),
\]

\[
\frac{d[M_2]}{dt} = -[M_2](k_{a2}[I] + J_{100}(k_{p12} + k_{tr12}) + J_{200}(k_{p22} + k_{tr22})),
\]

\[
\frac{d[R_1(1,0)]}{dt} = k_{a1}[M_1][I] - (k_{p11} + k_{tr11})[M_1][R_1(1,0)] - (k_{p12} + k_{tr12})[M_2][R_1(1,0)] + (k_{tr11}J_{100} + k_{tr21}J_{200})[M_1],
\]

\[
\frac{d[R_2(1,0)]}{dt} = k_{a2}[M_2][I] - (k_{p22} + k_{tr22})[M_2][R_1(1,0)] - (k_{p21} + k_{tr21})[M_2][R_1(1,0)] + (k_{tr22}J_{100} + k_{tr21}J_{200})[M_2],
\]

\[
\frac{dJ_{100}}{dt} = k_{p21}[M_1]J_{200} - ((k_{p12} + k_{tr12})[M_2] + k_{tr11}[M_1])J_{100},
\]

\[
\frac{dJ_{200}}{dt} = k_{p12}[M_2]J_{100} - ((k_{p21} + k_{tr21})[M_1] + k_{tr22}[M_2])J_{200},
\]

\[
\frac{dJ_{300}}{dt} = J_{100}(k_{tr11}[M_1] + k_{tr12}[M_2]),
\]

\[
\frac{dJ_{400}}{dt} = J_{200}(k_{tr22}[M_2] + k_{tr21}[M_1]).
\]

In this system $J_{100}$ is the total concentration of living chains with isobutylene links at the ends, $J_{200}$ is the total concentration of living chains of isoprene links at the ends, $J_{300}$ is the total concentration of "dead" chains with isobutylene links at the ends, $J_{400}$ is the total concentration of "dead" chains of isoprene units on the ends.

It should be noted that due to the low reactivity of isoprene and a small concentration of isoprene in the reaction mass, the value of the constant $k_{ip}$ can be set to zero, the values of the elementary reaction rates $k_{p11}, k_{p21}, k_{p12}, k_{p22}, k_{tr11}, k_{tr21}, k_{tr12}, k_{tr22}$ were taken from [15-18].

The resulting system was solved using the Monte Carlo method in the Wolfram Mathematica computer programming environment. When composing the program code, the if, While, and For loop statements, as well as the Join, Table, Append, Insert and Delete standard system functions were used. They allowed to update the data arrays that stored information about the ongoing copolymerization process. The dynamic data arrays were separately filled for chains with isoprene and isobutylene links at the ends and the array for "dead" polymer chains was formed. At each time step, the number of reactions considered in the kinetic scheme was determined and the chain number on which the selected reaction took place was randomly generated.

The calculation algorithm is a flow chart of the following type (figure 1).

As a result of modelling, the following graphs of the molecular weight distribution of the copolymer are obtained (figure 2, figure 3). For comparison, the distribution graphs for different values of the statistical ensemble $N=10^3$ and $N=10^9$ are shown below.
As a result of the research, the graphs of the dependence of the molecular weight on the mass fractions of the copolymer are presented.
References

[1] Markina E A 2010 Synthesis of butyl rubber using a modified catalytic system based on the aluminium chloride (dissertation) 19 pages

[2] Sangalov Yu A 2001 Polymers and copolymers of isobutylene: Fundamental problems and applied aspects ed Y A Sangalov and K S Minsker (Ufa: Gilem) 384 p

[3] Dmitriicheva R R, Antonova I O, Manuyko G V, Aminova G A, Bronskaya V V, Shaikhetdinova R S, Balzamov D S and Kharitonova O S 2020 Obtaining medium molecular characteristics of cation copolymerization of isobutylene and isoprene IOP Conf. Ser. Mater. Sci. Eng. 862 062045

[4] Freitas M F and Pinto J C 1996 J. Appl. Polym. Sci. 60 1109-26

[5] Zhang X, Lu C and Liang M 2009 J. Polymer Res. 16 411

[6] Kharitonova O S, Bronskaya V V, Ignashina T V, Al-Muntaser A A and Khairullina L E 2008 Modeling of absorption process using neural networks IOP Conference Series: Earth and Environmental Science 315 032025

[7] Honig A J, Cloor P E, MacCredon J F and Hamieles A E 1987 J. Appl. Polym. Sci. 3 829-41

[8] Epple U, Schneider H A and Percec V 1986 Copolymerization Polymer Bulletin 16 137-42

[9] Aminova G A, Manuiko G V, Bronskaya V V, Ignashina T V, D’yakonov G S, Bashkirov D V and Demidova È V 2008 Influence of chain-transfer reactions on the molecular-weight-distribution function of diene rubber on a neodymium-containing catalyst system Journal of Engineering Physics and Thermophysics 81 1247-51

[10] Manuiko G V, Aminova G A, Bronskaya V V., Ignashina T V, D’Yakonov G S and Bashkirov D 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

[11] Aminova G A, Manuiko G V, Litvinenko G I, D’Yakonov G S, Zolotarev V L, Filipova A G, Ignashina T V, Davydova V V and Antonova O V 2002 Mechanism of butadiene polymerization on cobalt-containing catalyst Russian Journal of Applied Chemistry 75 1146-50

[12] Manuyko G V, Bashkirov D V, Bronskaya V V, Ignashina T V, Kharitonova O S and Aminova G A 2020 Creating molecular weight distribution of butadiene rubber on neodymium-based catalytic system IOP Conference Series: Materials Science and Engineering 734 012066

[13] Tsapaev A A, Gumerov F M, Mazanov S V, Kharitonova O S and Bronskaya V V 2019 Neural network model of the process of supercritical water oxidation of utilization of industrial effluent water J. Phys.: Conf. Ser. 1399 033119

[14] Aminiva G A, Manuiko G V, Bronskaya V V, Ignashina T V, D’yakonov G S and Bashkirov D V 2009 Controlling the characteristics of butadiene rubber on the basis of molecular weight distribution Theoretical Foundations of Chemical Engineering 43 206-11

[15] Yoon W J, Kim Y S, Kim I S and Choi K Y 2004 Recent Advances in Polymer Reaction Engineering: Modeling and Control of Polymer Properties Korean J. Chem. Eng. 21 147

[16] Arest-Jakubovich A A and Litvinenko G I 1996 Chain Transfer Reactions in Anionic Polymerization of Nonpolar Monomers Prog. Polym. Sci. 21 335

[17] Robert N W, Timothy D S and Tsou A H 2003 Encyclopedia of Polymer Science and Technology 5 356-81

[18] Grigoryeva O, Fainleib A, Tolstov A et al 2005 J. Appl. Polym. Sci. 95 659

[19] Karger-Kocsis J, Meszaros L and Barany T 2013 J. Mater. Sci. 48 1-5

[20] Cohen P, Abadie M J M, Schue F and Richards D H 1982 Block copolymerization by a cation to anion transformation process: 2. Polymerization of styrene by polyTHF possessing terminal secondary nitranions Polymer 23 1105-7

[21] Worsfold D J and Bywater S 1964 Anionic polymerization of isoprene Canadian Journal of Chemistry 42 2884-92

[22] Chang C C, Halasa A F and Miller J W 1993 The reaction engineering of the anionic
polymerization of isoprene \textit{J. Appl. Polym. Sci.} \textbf{47} 1589-99

[23] Chang C C, Halasa A F, Miller J W and Hsu L 1994 Modelling studies of the controlled anionic copolymerization of butadiene and styrene \textit{Polym. Int.} \textbf{33} 151-9