Obtaining medium molecular characteristics of cation copolymerization of isobutylene and isoprene

R R Dmitricheva, I O Antonova, G V Manuyko, G A Aminova, V V Bronskaya, R S Shaikhetdinova, D S Balzamov and O S Kharitonova

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

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

Department of Power Supply of Enterprises and Energy Resource Saving Technologies, Kazan State Power Engineering University, Krasnoselskaya St., 51, Kazan 420066, Russian Federation

Department 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. Synthetic rubber has been interesting since the first days of research. Commercial isobutylene polymers are homopolymers and copolymers containing a small amount of isoprene. Isoprene has the great technical importance in connection with the production of synthetic rubbers that are close in structure and properties to natural rubber. These days, chlorinated and brominated butyl rubber derivatives have the highest sales volume. Butyl rubber is one of the synthetic rubber which is produced in quite large quantities on the world market. Commercial butyl rubber that is a copolymer of isobutylene and ~1.5 %mol isoprene, is produced by carbocationic methods. There is a mathematical model of periodic isothermal process of copolymerization of isobutylene and isoprene using AlCl3 catalyst in the solution of CH3Cl in a periodic reactor consisting of four reactions, that are chain growth, two chain transfer reactions to solvent and reinitiation, in this article. Nowadays, the cation polymerization for the synthesis of new materials of commercial interest rapidly develop and have the widespread use. One of such materials is butyl rubber, which is produced at -98°C in an inert methylchloride diluent in the presence of the AlCl3 initiator.

Isobutylene was first polymerized in 1837 and a high molecular product was not produced. Later it was found that when the temperature of polymerization decreases, molecular weight increases. Butyl rubber was synthesized in 1937 in “Standard Oil Development Co.” by scientists Thomas and Sparks. When polymerizing the first samples, 1,3-butadiene was used as a comonomer. However, it has been found that isoprene was a more suitable comonomer. The industrial production of butyl rubber in 1943 was a huge scientific and technological achievement, taken into account the complexity of this technology.

Due to the fact that cation copolymerization process at fairly low temperatures is very sensitive to the presence of various impurities, it is necessary to monitor their initial quantity in monomers,
solution and catalyst. Therefore, the raw products are thoroughly dried and cleaned. If the reaction norms are not observed, the polymerization reaction is slowed down, resulting in reducing molecular weight and yield butyl rubber.

![Diagram](image_url)

**Figure 1.** Scheme of production of butyl rubber in methyl chloride: 1 is a container for batch preparation; 2, 3, 8, 9 are pumps; 4, 5, 10, 11 are condensers; 6 is a polymerizer; 7 is a degasifier; 11 is a vacuum pump; 12 is a separator; 13 is a heater; I is isobutylene; II is isoprene; III is recycled methyl chloride; IV is liquid propane; V is liquid ethylene; VI is stopper; VII is anti-agglomerator; VIII is hydrocarbons for compression; IV is cooled catalyst solution; X is steam.

The burden materials are prepared by mixing isobutylene, which is purified from impurities by rectification, isopropene, drained with azeotropic drying, and recycled metal chloride in the container 1 by the circulation pump 2 (Figure 1). Chromatographs are installed on the finished product line. According to chromatographic analysis, the composition of the burden materials is adjusted depending on the brand of the produced rubber.

Using pump 3 the finished burden materials are fed into propane 4 and ethylene 5 condensers, which are cooled to operating temperature (about -95°C) during the evaporation of propane (at -41°C) and ethylene (at -110°C).

Copolymerization of isobutylene with isoprene proceeds in tubular-type reactor 6 (polymerizer), where a temperature about -100°C is maintained using liquid ethylene. The burden materials and catalyst solution are fed to the bottom part of the reactor, mixed by an axial circulation pump and the reaction mass is fed through the central transfer pipe to the top part of the polymerizer, where the peripheral circulation tubes washed by liquid ethylene are returned to the bottom part. The resulting copolymer is not soluble in methyl chloride. The dispersion of butyl rubber containing 8-12% polymer, 6-10% monomers and methyl chloride is replaced by the supplied burden materials and removed from the polymerizer through the discharge pipe into the aqueous degasifier 7. To deactivate the catalyst, isopropyl alcohol is fed into the discharge pipe.

The degasifier 7 maintains a constant water level at a temperature of 70°C with the bulk of the monomers and methyl chloride evaporating, which are sent for compression and processing after the
condensers 10 and 11. To prevent the agglutination of rubber crumbs, an anti-agglomerator that is calcium stearate (up to 1.5% of the rubber mass) is supplied in the degasifier. Using the pump 8 the rubber suspension in the water is fed from the degasifier 7 to the vacuum degasifier 9, where the residues of monomers and methyl chloride are removed. From vacuum degasifier 9 rubber with water is sent to extracting, drying and packaging.

Butyl rubber polymerizer is a vertical cylindrical reactor with six-tier mixing device. Nowadays, reactors of this type are used for industrial synthesis of butyl rubber (volume of 16 or 24 m³), as they are able to almost provide the hydrodynamic mode of perfect mixing.

Polymer producers often face the problem of reducing production costs and improving polymer quality. To achieve these goals, it needs to develop complex mathematical models allowing to predict molecular properties according to reactor configuration and operating conditions.

Having reviewed the scientific literature [1-6] for the mechanism of cation copolymerization of isobutylene and isoprene using AlCl₃ catalyst in the solution of CH₃Cl in reactor of periodic action, the kinetic process scheme is proposed. It includes several elementary reactions:

Chain growth:

\[ R_1(\ell_1, \ell_2) + M_1 \xrightarrow{k_{11}} R_i(\ell_1 + 1, \ell_2) \]  \hspace{1cm} (1)

\[ R_1(\ell_1, \ell_2) + M_2 \xrightarrow{k_{12}} R_i(\ell_1, \ell_2 + 1) \]  \hspace{1cm} (2)

\[ R_2(\ell_1, \ell_2) + M_1 \xrightarrow{k_{21}} R_i(\ell_1, \ell_2 + 1) \]  \hspace{1cm} (3)

\[ R_2(\ell_1, \ell_2) + M_2 \xrightarrow{k_{22}} R_i(\ell_1, \ell_2 + 1) \]  \hspace{1cm} (4)

Chain transfer to the monomer:

\[ R_i(\ell_1, \ell_2) + M_1 \xrightarrow{k_{31}} P_1(\ell_1, \ell_2) + R_i(\ell_1, \ell_2) \]  \hspace{1cm} (5)

\[ R_i(\ell_1, \ell_2) + M_2 \xrightarrow{k_{32}} P_1(\ell_1, \ell_2) + R_i(\ell_1, \ell_2) \]  \hspace{1cm} (6)
\[ R_2(\ell_1, \ell_2) + M_1 \xrightarrow{k_211} P_2(\ell_1, \ell_2) + R_2(\ell_1, \ell_2) \]  
(7)

\[ R_2(\ell_1, \ell_2) + M_2 \xrightarrow{k_222} P_2(\ell_1, \ell_2) + R_2(\ell_1, \ell_2) \]  
(8)

Chain transfer to solvent:

\[ R_i(l_1, l_2) + S \xrightarrow{k_{li1}} P(l_1, l_2) + S' \]  
(9)

\[ R_i(l_1, l_2) + S \xrightarrow{k_{li2}} P(l_1, l_2) + S' \]  
(10)

Reinitiation:

\[ S' + M_1 \xrightarrow{k_{i1}} R_1(1, 0) \]  
(11)

\[ S' + M_2 \xrightarrow{k_{i2}} R_0(0, 1) \]  
(12)

where \( M_i \) is a monomer of \( i \)-th type, \( i = 1, 2 \); \( R_i(l_1, l_2) \) is a growing polymeric chain with the end link of the \( i \)-th type containing \( l_1 \) monomeric links of the 1st type and \( l_2 \) monomeric links of 2nd type; \( P(l_1, l_2) \) is a dead polymer chain; \( S \) is a solvent; \( S' \) is an intermediate active particle. Initiation was assumed to be instantaneous.

The system, consisting of an infinite number of differential equations, which was solved using the method of producing function, is obtained based on the laws of kinetics:

\[ \frac{dM}{dt} = k_{p,11}M_1J_1 + k_{p,12}M_2J_1 + k_{p,21}M_1J_2 + k_{p,22}M_2J_2 + k_{s,3}S'I_1 + k_{s,2}S'I_2 + \]

\[ + k_{m,11}M_1J_1 + k_{m,21}M_1J_2 + k_{m,12}M_2J_1 + k_{m,22}M_2J_2, \]  
(13)

\[ \frac{dR_i(\ell_1, \ell_2)}{dt} = k_{l,11}M_i[ R_i(\ell_1 - 1, \ell_2) - R_i(\ell_1, \ell_2)] - k_{l,12}M_iR_i(\ell_1, \ell_2) + k_{l,21}M_iR_i(\ell_1 - 1, \ell_2) - k_{o,1}SR_i(\ell_1, \ell_2) + \]

\[ + k_{s,1}S'M_i\delta_{\ell_1,0}\delta_{\ell_2,0} - k_{m,11}M_iR_i(\ell_1, \ell_2) - k_{m,12}M_iR_i(\ell_1, \ell_2) + k_{m,11}M_i\delta_{\ell_1,0}\delta_{\ell_2,0} + k_{m,22}M_i\delta_{\ell_1,0}\delta_{\ell_2,0}, \]  
(14)

\[ \frac{dR_i(\ell_1, \ell_2)}{dt} = k_{l,22}M_i[ R_i(\ell_1, \ell_2 - 1) - R_i(\ell_1, \ell_2)] + k_{l,12}M_iR_i(\ell_1, \ell_2 - 1) - k_{p,21}M_iR_i(\ell_1, \ell_2) - k_{o,2}SR_i(\ell_1, \ell_2) + \]

\[ + k_{s,2}S'M_i\delta_{\ell_1,0}\delta_{\ell_2,0} - k_{m,21}M_iR_i(\ell_1, \ell_2) - k_{m,22}M_iR_i(\ell_1, \ell_2) + k_{m,21}M_i\delta_{\ell_1,0}\delta_{\ell_2,0} + k_{m,22}M_i\delta_{\ell_1,0}\delta_{\ell_2,0}, \]  
(15)

\[ \frac{dP(\ell_1, \ell_2)}{dt} = k_{o,1}SR_1(\ell_1, \ell_2) + k_{o,2}SR_2(\ell_1, \ell_2) + k_{m,11}M_1R_1(\ell_1, \ell_2) + k_{m,21}M_1R_2(\ell_1, \ell_2) + \]

\[ + k_{m,12}M_2R_1(\ell_1, \ell_2) + k_{m,22}M_2R_2(\ell_1, \ell_2) \]  
(16)
As a result of the numerical experiment, the dependence on conversion for the number-average molecular weight $M_n$, the mass-average molecular weight $M_w$ and the coefficient of polydispersion $K_D$ was obtained under initial conditions: monomer concentration $M_0$ is equal to 4.9 mol/m$^3$, initiator concentration $I_0$ equals $1.08 \times 10^{-5}$ mol/m$^3$, temperature $T_0$ is 173 K (figure 3-5):

![Figure 5. Dependence $K_D$ on monomer conversion.](image)

Product quality is a much more complex issue in polymerization processes than in simple short chain reactions, due to the molecular properties of the polymer product, which significantly affect the chemical, physical, rheological, thermal, mechanical properties, as well as the final use of the polymer. Therefore, the development of complex mathematical models for predicting polymer quality and operating conditions are the key to efficient production of high quality and improvement efficiency and economy.

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