Kinetic scheme of the synthesis of butadiene rubber on a modified lithium catalytic system taking into account its polycentricity

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Abstract. A mathematical simulation of the synthesis of butadiene rubber in a batch reactor under the action of an organolithium catalytic system in the presence of a modifier and with the addition of toluene to a solvent is carried out. A kinetic scheme of the process is proposed and the velocity constants of the elementary stages are determined on the basis of the developed model.

1. Introducing
One of the most characteristic differences between the processes of anionic and radical polymerization is that even when using initiators that seem to be individual (i.e. formally consisting of a single chemical substance), several forms of active centers (associated and non-associated molecules, solvates of ion pairs of different compositions, free ions, etc.), differing in their reactivity, can simultaneously be present in systems. This circumstance has a significant impact on the kinetics of polymerization processes and the molecular mass characteristics of the resulting polymers.
2. Materials and methods
The influence of various forms of active centers becomes the more significant if we take into account that recently in laboratory and industrial practice, along with individual initiators of polymerization, mixed ones consisting of two or more components are used.

According to modern ideas about the structure and mechanism of the formation of active centers of an organolithium catalytic system in the presence of a modifier and toluene, the process of the exchange of the activity can be represented as follows (figure 1):

\[
\text{BuLi} + \text{R'}\text{ONa} \rightleftharpoons \text{Bu} \quad \text{Li} \quad \text{Na} \quad \text{O} \quad \text{R'} \rightleftharpoons \text{BuNa} + \text{R'}\text{OLi}
\]

**Figure 1.** The process of the exchange of the activity (R’ONa, R’OLi are sodium and lithium alkoxides, respectively).

Further, Li and Na (or a bimetallic complex) are designated-M_t

In the presence of a modifier, the polymerization of butadiene on an organolithium catalytic system is characterized by the first order of reaction according to the concentrations of the monomer and the catalyst and it proceeds without an induction period, so the initiation will be assumed to be instantaneous.

Calculations of molecular mass characteristics and subsequent comparison of the calculated curves with experimental data allow to identify the true mechanism of chain growth, in particular, to establish whether the process takes place at one or several types of active centres, to determine the role of exchange reactions and to estimate kinetic constants.

The next stage of the polymerization is the chain growth reaction (figure 2):

\[
P_n \sim \text{CH}_2-\text{CH} = \text{CH} - \text{CH}_2 \sim \text{Mt}^+ \rightleftharpoons \text{P}_{n+1} \sim \text{CH}_2-\text{CH} = \text{CH} - \text{CH}_2 \sim \text{Mt}^+ \quad \text{CH}_2
\]

\[
\text{CH}_4 \quad \text{C}_4\text{H}_6 \quad \text{k}_p \quad \text{C}_4\text{H}_6 \quad \text{k}_p
\]

**Figure 2.** The chain growth reaction.

An increase in the content of side vinyl groups in the polymer chain leads to the fact that the probability of transfer of chain to the polymer increases significantly. This leads to the formation of branched macromolecules, which has a positive effect on the physical and mechanical characteristics of the resulting rubber, such as viscosity and cold flowability, so it is important to include the chain transfer reaction to the polymer in the kinetic scheme (figure 3).
Toluene is introduced into the polymerization system to prevent gel formation. When toluene interacts with a "living" polymer chain in the presence of a modifier, a chain transfer reaction to toluene occurs:

A) the actual transfer:
\[
P \sim \text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \sim \text{Mt}^+ + \text{CH}_3 \xrightarrow{k_{tr}} \text{P} \sim \text{CH}_2\text{CH}_2\text{CH} = \text{CH}_3 + \text{CH}_2\text{Mt}^+
\]

B) the reinitiation:
\[
\text{CH}_2\text{Mt}^+ + \text{C}_6\text{H}_6 \xrightarrow{k_{\text{rei}}} \text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \sim \text{Mt}^+
\]

Also, to describe the process of polymerization of butadiene under the action of an organolithium catalytic system in the presence of a modifier, the transfer of a chain to a monomer was considered (figure 4).

\[
P \sim \text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \sim \text{Mt}^+ + \text{CH}_3\text{C} = \text{CH} - \text{CH}_2 \xrightarrow{k_{\text{im}}} \text{P} \sim \text{CH} = \text{CH} - \text{CH} = \text{CH}_2 + \text{CH}_3\text{C} = \text{CH} - \text{CH}_2\text{CH}_2 \sim \text{Mt}^+
\]

Figure 3. The chain transfer reaction to the polymer.

Figure 4. The reaction of the transfer of a chain to a monomer.

3. Results
The following kinetic scheme is proposed for the mechanism of the polymerization of butadiene on an organolithium catalyst in the presence of a modifier:
**Table 1.** The kinetic scheme of the mechanism of the polymerization of butadiene on an organolithium catalyst in the presence of a modifier. I is the – initiator concentration, M is the –monomer concentration, S is the toluene concentration, k is the rate constants of the corresponding reactions, R(i, j, l) – is the concentration of macromolecules with i-active centers of the first type, j-active centers of the second type and l –monomeric links.

| Stages                              | Reactions                                                                 |
|-------------------------------------|---------------------------------------------------------------------------|
| the initiation                       | on the centers of the first type                                          |
|                                     | \[ I + M \xrightarrow{k_{i,1}} R(1,0,1) \]                               |
|                                     | on the centers of the second type                                         |
|                                     | \[ I + M \xrightarrow{k_{i,2}} R(0,1,1) \]                               |
| the chain growth                    | \[ R(i, j, l) + M \xrightarrow{k_{j,1}} R(i, j, l + 1) \]                 |
|                                     | \[ R(i, j, l) + M \xrightarrow{k_{j,2}} R(i, j, l + 1) \]                 |
| the chain transfer to toluene        | \[ R(i, j, l) + S \xrightarrow{k_{i,2}} R(i, j - 1, l) + S_2^* \]       |
| (a) the actual transfer that occurs  |                                                                           |
| on the centers of the first type     |                                                                           |
| (b) the reinitiation                |                                                                           |
|                                     | \[ S_1^* + M \xrightarrow{k_{m,1}} R(1,0,1) \]                           |
|                                     | \[ S_2^* + M \xrightarrow{k_{m,2}} R(0,1,1) \]                           |
| the chain transfer to the monomer    | \[ R(i, j, l) + M \xrightarrow{k_{m,1}} R(i - 1, j, l) + R(1,0,1) \]     |
|                                     | \[ R(i, j, l) + M \xrightarrow{k_{m,2}} R(i - 1, j, l) + R(0,1,1) \]     |
| the chain transfer to the polymer    | \[ R(i, j, l) + R(i', j', l') \xrightarrow{k_{p,1,1'}} R(i + 1, j, l) + R(i'-1, j', l') \] |
|                                     | \[ R(i, j, l) + R(i', j', l') \xrightarrow{k_{p,2,1'}} R(i - 1, j, l) + R(i'+1, j', l') \] |
|                                     | \[ R(i, j, l) + R(i', j', l') \xrightarrow{k_{p,2,1'}} R(i, j - 1, l) + R(i', j' - 1, l') \] |
| the exchange of active centers       | \[ R(i, j, l) \xrightleftharpoons{\alpha}^\pm \ R(i - 1, j, l + 1) \]    |

For the first time, the kinetic scheme of butadiene polymerization on a modified lithium-containing catalytic system includes chain transfer reactions to a monomer and a polymer.

According to the kinetic scheme, the system of equations describing the time change in the concentrations of monomer, toluene and growing chains, as well as the exchange of active centers for a periodic isothermal process will be as follows:

\[
\frac{dM}{dt} = -(k_{p,1}\sigma + k_{p,2}(1-\sigma))MI_0, \quad M_{\mid t=0} = M_0
\]

(1)

\[
\frac{dS}{dt} = -(k_{T,1}\sigma + k_{T,2}(1-\sigma))SI_0, \quad S_{\mid t=0} = S_0
\]

(2)
\[
\frac{\partial R(i, j, l)}{\partial t} = -i k_{p,1} M \frac{\partial R(i, j, l)}{\partial l} - j k_{p,2} M \frac{\partial R(i, j, l)}{\partial l} + \\
+ l k_{p,1} \sigma I_0 [R(i-1, j, l) - R(i, j, l)] + l k_{p,2} (1 - \sigma) I_0 [R(i, j-1, l) - R(i, j, l)] + \\
+ (k_{p,1}(M_0 - M) + k_{m,1} M + k_{T,1} S)[(i+1)R(i+1, j, l) - iR(i, j, l)] + \\
+ (k_{p,2}(M_0 - M) + k_{m,2} M + k_{T,2} S)[(j+1)R(i, j+1, l) - jR(i, j, l)] + \\
+ (k_{m,1} M + k_{T,1} S) \sigma \delta_{i,1} \delta_{j,0} \delta(\ell) + \\
+ (k_{m,2} M + k_{T,2} S)(1 - \sigma) I_0 \delta_{i,0} \delta_{j,1} \delta(\ell) + \\
+ k_b [(i+1)R(i-1, j+1, l) - jR(i, j, l)] + k_a [(i+1)R(i+1, j-1, l) - iR(i, j, l)] \\
i, j = 0, 1, 2, \ldots, \quad 0 \leq l < \infty \quad R(i, j, \ell)|_{\ell=0} = (\sigma \delta_{i,1} \delta_{j,0} + (1 - \sigma) I_0 \delta_{i,0} \delta_{j,1}) \delta(\ell)
\]

where $\sigma$ is the molar fraction of active centers of the first type.

Equation (1) describes the change in the concentration of the monomer over time. Since, $\frac{k_{m,1}}{k_{p,1}}, \frac{k_{m,2}}{k_{p,2}}$ are much less than one, the consumption of the monomer for the chain transfer reaction and reinitiation in (1) can be neglected. Equation (2) describes the change in the toluene concentration over time. Toluene is consumed in the process of transfer of the chain to toluene. Equation (3) describes the change in the concentration of growing polymer macromolecules. In equation (3) the first two terms on the right side describe the change in $R(i, j, \ell)$ as a result of growth, the following four – change $R(i, j, \ell)$ in the reactions of chain transfer, the next two terms describe the emergence of new short growing chains in reinitiation and, finally, the last two terms describe the reaction of the exchange activity. Equation (3) is written in the approximation of long chains.

Using the generating function

\[
F(s, q, p, x) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \int_{0}^{\infty} \exp(-pz)r_{i,j}(z)dz,
\]

the system of equations (3) can be reduced to a single equation with respect to the function $F$.

\[
\frac{\partial F}{\partial x} = \frac{\partial}{\partial s} \left( s F + \lambda q \frac{\partial F}{\partial q} \right) + \frac{\tilde{\gamma}_{p,1} \sigma}{1-x} (1-s) \frac{\partial F}{\partial p} + \frac{\tilde{\gamma}_{p,2} (1-\sigma)}{1-x} (1-q) \frac{\partial F}{\partial p} + \\
+ \left( \frac{\tilde{\gamma}_{p,1} X}{1-x} + \tilde{\gamma}_{m,1} + \tilde{\gamma}_{T,1} (1-x) \right) (1-s) \frac{\partial F}{\partial s} + \\
+ \left( \frac{\tilde{\gamma}_{p,2} X}{1-x} + \tilde{\gamma}_{m,2} + \tilde{\gamma}_{T,2} (1-x) \right) (1-q) \frac{\partial F}{\partial q} + \\
+ \left( \tilde{\gamma}_{m,1} + \tilde{\gamma}_{T,1} (1-x) \right) \sigma q + \left( \tilde{\gamma}_{m,2} + \tilde{\gamma}_{T,2} (1-x) \right) (1-\sigma) q + \\
+ \frac{A \varepsilon}{1-x} (s-q) \frac{\partial F}{\partial q} + \frac{B \varepsilon}{1-x} (q-s) \frac{\partial F}{\partial s}
\]

\[\text{(4)}\]
where $\tilde{g} = \frac{1}{\sigma + (1 - \sigma) \lambda}$, $\tilde{k}_p = k_{p,1} \sigma + k_{p,2} (1 - \sigma)$, $S = S_0 (1 - x)^{\gamma_{T,0}}$, $\Theta = \frac{S_0}{I_0}$ is the molar ratio of the toluene concentration to the initiator concentration at the initial time, $\lambda = \frac{k_{p,2}}{k_{p,1}}$, $\gamma_{m,1} = \frac{\beta k_{m,1}}{k_{p,1}}$.

$\gamma_{m,2} = \frac{\beta k_{m,2}}{k_{p,1}}$, $\gamma_{p,1} = \frac{\beta k_{p,1}}{k_{p,1}}$, $\gamma_{p,2} = \frac{\beta k_{p,2}}{k_{p,1}}$, $\gamma_{T,1} = \frac{k_{T,1} \Theta}{k_{p,1}}$, $\gamma_{T,2} = \frac{k_{T,2} \Theta}{k_{p,2}}$ – is the intensity of chain transfers to the monomer, polymer and toluene at the centres of each type, respectively, $\bar{A} = \frac{\tilde{g}}{I_0}$, $\bar{B} = \frac{k_0 \tilde{g}}{k_1 I_0}$, $\mathcal{E} = \frac{k_1}{k_{p,1}}$, $\bar{\gamma}_{p,1} = \tilde{g} \gamma_{p,1}$, $\bar{\gamma}_{p,2} = \lambda \tilde{g} \gamma_{p,2}$, $\bar{\gamma}_{m,1} = \tilde{g} \gamma_{m,1}$, $\bar{\gamma}_{m,2} = \lambda \tilde{g} \gamma_{m,2}$, $\bar{\gamma}_{T,1} = \tilde{g} \gamma_{T,1}$, $\bar{\gamma}_{T,2} = \lambda \tilde{g} \gamma_{T,2}$, $\bar{\gamma}_{T} = \bar{\gamma}_{T,0} + \bar{\gamma}_{T,2} (1 - \sigma)$, $\beta = \frac{M_0}{I_0}$, $r_j(z) = \frac{\beta R(i, j, 1)}{I_0}$, $z = \frac{1}{\beta}$.

By differentiating equation (4) the corresponding number of times in $s, q$ and $p$ relations are obtained for calculating the statistical moments of the distribution of macromolecules according to the degree of polymerization $\ell$ and the number of active centres of each type. The derivative $F$ of order $(i + j + n)$ for $s = I$, $q = 1$, $p = \theta$ is found as follows (5):

$$J_{yn} = \left. \frac{\partial^{i+j+n} F}{\partial s^i \partial q^j \partial p^n} \right|_{s=1, q=1, p=0}$$

(5)

Moreover, the system becomes more complicated, since the distribution of macromolecules is no longer made up by the number of one type of active centres, as was done in previous works of our scientific group, but by the number of both types of active centres.

By determining the moments of molecular mass distribution $\mu_n = (-1)^n I^p J_{00n}$, in particular, $\mu_0 = I_0 J_{000}$ is the number of polymer chains per unit volume of the reaction mixture, $\mu_1 = -I_0 B J_{001} = M_0 x$ is the amount of polymer formed per unit volume of the reaction mixture, $J_{100} = \sigma$ is the molar fraction of active centres of the first type, $J_{010} = 1 - \sigma$ is the molar fraction of active centres of the second type.

The dependences of the average molecular weights on the concentration of the monomer are determined by the formulas (6):

$$\bar{M}_n(x) = m_0 \frac{\beta J}{J_{000}(x)} \cdot \bar{M}_m(x) = m_0 \frac{\beta J_{002}(x)}{x}, \bar{M}_c(x) = -m_0 \frac{\beta J_{003}(x)}{J_{002}(x)}$$

(6)

Where $m_0$ is the molecular weight of the monomer link.

During the identification, the objective function was selected: $f(k_{p,1}, k_{p,2}, k_{T,1}, k_{m,2}, k_{p,2}, k_1) = \sum_{j=1}^{n} \sum_{i=1}^{m} \left| y_j^p(t_j) - y_j^p(t_j) \right|$, where $i$ is the number of the observed indicator, $j$ is the measurement number, $t_1, t_2, t_3, \ldots$ – are the time points at which the concentration values were measured $y_i^{\lambda}(t)$, $y_i^{\rho}(t)$ – are calculated kinetic curves for the values of constants $k_{p,1}, k_{p,2}, k_{T,1}, k_{m,2}, k_{p,2}, k_1$. The relative deviations of the experimental parameters $y^\varepsilon$ were estimated.
from the calculated y \(^p\), where the parameters are \(k_{p,1}, k_{p,2}, k_{RT,2}, k_{m,r,2}, k_{q,2}, k_i\) determined from the minimum condition of the objective function. When finding unknown parameters for a batch reactor, the following set of experimental data was used: \(\{x_{\sigma_1}, x_{\sigma_0,1}, M_n^2, M_w^2, M_z^2, g \text{- factor}^3\}\).

The difficulty of identification was that for a two-center system, it was already necessary to determine the velocity constants for both types of active centers. This problem was solved as follows: the effective growth constant \(\tilde{k}_p\) was determined from the dependence of the conversion on time with the working ratio BuLi : Mod = 1: 0.1. The growth constant of the second type of centers \(k_{p2}\) was obtained from the conversion curve during the polymerization under the conditions of BuLi : Md = 1: 1. It was assumed that the proportion of active centers of the first type \(\sigma\) did not change during the polymerization and that there is an exchange of active centres between macromolecules. The growth constant for the active centres of the first type \(k_{p1}\) was determined from the ratio \(\tilde{k}_p = \sigma k_{p1} + (1-\sigma)k_{p2}\).

As a result of identification and in accordance with the literature data, it turned out that the chain growth reaction mainly occurs at the active centres of the first type. The reactions of chain growth, chain transfer to toluene, monomer and polymer are carried out on the active centres of the second type. Exchange reactions occur between the active centres.

The results of the studies of a process are presented in Figure 4-6.

Figure 1 shows the dependence of the conversion on time at different temperatures. There is a regular increase in the slope of the conversion curve with an increase in the temperature of the experiment, which indicates a symmetric dependence of the effective growth constant on temperature.

The following figures show the dependence of the molecular weight characteristics on the conversion, calculated for a single-centre and two-centre model. As a result of the numerical experiment, it was obtained that the two-centre model most adequately describes the process under study in the presence of toluene and a modifier in a batch reactor. For calculations based on the single-center model, a software package was used that was previously developed to describe the process of synthesis of SRDN and SRDC, which took into account the chain transfers to the monomer and polymer.

\[\text{Figure 5. The dependence of the conversion on the time when } M_0 = 1.3 \text{ kmol/m}^3, I_0 = 0.00021 \times 0.8 \text{ kmol/m}^3: 1-t = 90^\circ \text{C ( } \tilde{k}_p = 6952 \text{ m}^3/\text{kmol}*\text{min}); 2-t = 70^\circ \text{C ( } \tilde{k}_p = 583.8 \text{ m}^3/\text{kmol}*\text{min}); 3-t = 50^\circ \text{C ( } \tilde{k}_p = 78 \text{ m}^3/\text{kmol}*\text{min}); 4-t = 30^\circ \text{C ( } \tilde{k}_p = 11.47 \text{ m}^3/\text{kmol}*\text{min}). \bullet - \text{experimental points, } - - \text{calculated lines.}\]
4. Conclusion

A two-center mathematical model of the synthesis of butadiene rubber in a batch reactor in the presence of a modified organolithium catalytic system, complicated by chain transfer reactions and exchange reactions between active centers, has been developed. A kinetic scheme of the process is proposed and, based on the developed two-center model, the velocity constants of elementary stages for each type of active centers are determined. Using the method of the generating function, relations were obtained for calculating the moments of the molecular mass distribution of macromolecules by the degree of polymerization and by the number of active centers of each type.

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