Kinetic scheme of the SDRC rubber synthesis process

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Abstract. The research of the chemical kinetics of the SDRC rubber synthesis is performed under the optimal water content in the conditions of the chain transfer and cross-growth reactions. The main reactions of the butadiene polymerization mechanism on a cobalt-containing catalytic system that are a chain growth, a chain transfer to monomer, a chain transfer to polymer, spontaneous chain transfer, a chain cross growth reaction are presented. The main assumptions of the presented kinetic scheme are that active centres of one type are formed at the optimum water concentration, the total concentration of active centres is constant and equal to the initiator concentration, at the optimum water concentration the process is considered “uninterrupted” (there is no deactivation). The article presents the theoretical foundations of chemical kinetics of the SDRC rubber synthesis. The cross-growth reaction of polybutadiene macromolecules is possible only through conjugated double bonds, the number of which in the macromolecule is limited. Therefore, this reaction can carry out without gelation to large monomer conversion values. In this regard, the mechanism of the butadiene polymerization reaction on a cobalt catalyst based on the cross growth reaction of “living” macromolecules with “living” and “dead” macromolecules was also considered.

The reaction, leading to the chain branching, effects on the most important effect on molecular weight characteristics and properties of butadiene rubber on a cobalt catalyst [1-7]. Nowadays, the reaction of chain transfer is quite well investigated. The cross-growth reaction is researched only by type “live” with “dead”. There is no mathematical description of the cross-growth reaction by type “live” with “live” for anionic polymerization due to insufficient description of the mechanism of this reaction and significant complication of the solution of the system of kinetic equations. Therefore, it is very important to study the cooperative effect of reactions of chain transfer and cross-growth of macromolecules to establish the mechanism of the polymerization process initiated by cobalt-containing catalytic system and to choose between possible process mechanisms. Numerical experiments make it possible to
consider the influence of different reactions of transfer and cross-growth of macromolecules on the polymerization process in a wide range of input parameters, to calculate the conditions of production of rubber with defined branching and molecular mass characteristics, which is a topical problem for science and chemical industry [8-21].

Several different mechanisms of polymerization are assumed on the basis of the analysis of literature and experimental data.

The butadiene polymerization process involves the following stages. The first one is the stage of initiation (figure 1), where the catalytic complex that is active centres is formed i.e. an allylic complex of transition metal is formed in the presence of the monomer, a metal cobalt is formed in the absence of a monomer:

\[
R_3\text{Al} + \text{CoCl}_2 \rightarrow R_2\text{AlCl} + [\text{RCocl}] \rightarrow H_2C\left(\begin{array}{c}
\text{C} \\
\text{CH} \\
\text{CH}_2 \\
\text{R}
\end{array}\right) \text{Co} \left(\begin{array}{c}
\text{X} \\
\text{Al} \\
\text{X} \\
\text{X}
\end{array}\right) X
\]

**Figure 1.** The initiation reaction.

Whereas the initiation reaction is carried out in the presence of the diene, the decay of the organometallic compound with the formation of metallic cobalt does not occur.

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

\[
H_2C\left(\begin{array}{c}
\text{C} \\
\text{CH} \\
\text{CH}_2 \\
\text{R}
\end{array}\right) \text{Co} \left(\begin{array}{c}
\text{X} \\
\text{Al} \\
\text{X} \\
\text{X}
\end{array}\right) X \rightarrow R-CH_2 \quad H_2C-CH_2
\]

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

It is believed that the chain transfer reaction to the monomer is a consequent spontaneous processing of two reactions:

Reaction 1 is the breakdown of the active centre and the formation of the hydride complex (conjugated double bonds formed at the ends of the chain (figure 3)):

\[
H_2C\left(\begin{array}{c}
\text{C} \\
\text{CH} \\
\text{CH}_2 \\
\text{R}
\end{array}\right) \text{Co} \left(\begin{array}{c}
\text{X} \\
\text{Al} \\
\text{X} \\
\text{X}
\end{array}\right) X \rightarrow R-CH=CH \quad CH=CH_2 + H\text{CoX} + \text{AlX}_3
\]

**Figure 3.** The reaction of conjugated double bonds formation.
Reaction 2 is the regeneration of the active centre (figure 4), i.e. the growth of a new polymer chain:

\[ \text{HCoX} + \text{C}_4\text{H}_6 \rightarrow \text{C}_4\text{H}_7\text{CoX} \]

**Figure 4.** The reaction of the active centre regeneration.

Reactions 1 and 2 are consequent stages of the reaction of spontaneous chain transfer and not the reaction of chain transfer to the monomer. Despite this, the chain transfer reaction to the monomer is considered for generality. The same hydride complex can join a growing chain to form an additional active centre on it, resulting in the transfer of the chain to the polymer:

\[ \text{HCoX} + \text{R} - \text{CH}_2 - \text{CH} \equiv \text{CH} - \text{CH}_2 - \text{R}^* \rightarrow \]

\[ \rightarrow \text{R} - \text{CH}_2 - \text{CH} \equiv \text{CH} - \text{CH}_2 - \text{R}^* \]

\[ \rightarrow \text{R} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{R}^* \]

**Figure 5.** The chain transfer reaction to the polymer.

A distinctive feature of the structure of polybutadiene chains obtained on cobalt-containing catalytic systems is the presence of conjugated double bonds formed at the end of the chain as a result of chain transfer reaction to monomer or spontaneous transfer (figure 6):

\[ \text{R} - \text{CH}_2 - \text{CH} \equiv \text{CH} - \text{CH}_2 \text{-----CoX} + \text{C}_4\text{H}_6 \rightarrow \]

\[ \text{C}_4\text{H}_7\text{CoX} + \text{R} - \text{CH} \equiv \text{CH} - \text{CH} \equiv \text{CH}_2 \]

**Figure 6.** The chain transfer reaction to the monomer.

When studying the kinetics and mechanism of the reaction of migration of double bonds under the influence of complex cobalt compounds used for stereospecific polymerization of dienes, it was found that the reactions of migration and isomerization of double bonds proceeds through the stage of formation of \( \text{NCoX} \) leading to a chain process. Consecutive addition and detachment of \( \text{NCoX} \) leads to the formation of a conjugated double bond (figure 7):
Figure 7. The reaction of a conjugated double bond formation.

The conjugated double bonds allow macromolecules slowly to react to cross-growth reaction when interacting with the active centre of another macromolecule (figure 8):

\[
\begin{align*}
R-\text{CH}_2\text{CH} & \rightarrow \text{CHCH}_2\text{CH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{H}^+ \\
R-\text{CH}_2\text{CH}_2 \rightarrow \text{CHCH}_2\text{CH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{H}^+ \\
R-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} & \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{H}^+ \\
R-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} & \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{H}^+ \\
R-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} & \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{H}^+ \\
R-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} & \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{CHCH}_2\text{CH} \rightarrow \text{H}^+ \\
\end{align*}
\]

Figure 8. The cross-growth reaction.

This leads to the formation of branched polymer structures of different configurations. The growth rate of the macromolecule increases with increase in the number of active centres in it and the number of the active centres increases with the increase in the size of the macromolecule.

It should be noted that the cross-growth reaction of polybutadiene macromolecules is possible only by conjugated double bonds, the number of which in the macromolecule is limited, so this reaction can flow without gel formation to large monomer conversion values. The mechanism for the butadiene polymerization reaction on a cobalt catalyst based on the reaction of cross-growth of “live” macromolecules with “live” and “dead” macromolecules is considered.

The analysis of literature sources showed that simultaneous reactions of cross-growth of polymeric chains and reactions of transfer of the chain to the polymer are possible during the polymerization of butadiene with cobalt-containing catalytic systems. It proposes the existence of a mechanism of the polymerization process, which includes both the chain transfer reaction to the polymer and the reaction of the cross-growth of macromolecules.

The most difficult is to construct and identify a mathematical model of the polymerization process, when neither the mechanism nor the constants of elementary reactions are known, but the use of mathematical methods has made it possible to speed up the decision process. The evaluation criterion in this situation is statistical: most correct mechanisms will be the one that provides minimum dispersion.

Experimental data for identification of the process mechanism are taken from a literature source, where the concept of a fractional factor experiment of two levels was used for the study of solution polymerization of butadiene in a reactor of periodic action with application of cobalt octanoate/diethylaluminyl chloride/water as a catalyst.

As a result of process identification, mechanism kinetic scheme of polymerization process on cobalt-containing catalyst has the following form:
Table 1. The kinetic scheme of polymerization process on cobalt-containing catalyst.

| Stages                              | Reactions                                                                 |
|-------------------------------------|---------------------------------------------------------------------------|
| initiation                          | \( I + M \xrightarrow{k_i} R(1,1) \)                                    |
| chain growth                        | \( R(i, \ell) + M \xrightarrow{k_{pe}} R(i, \ell + 1) \)                 |
| spontaneous chain transfer taking   |                                                                           |
| place in two stages                 |                                                                           |
| a) transfer                         | \( R(i, \ell) \xrightarrow{k_p} R(i-1, \ell) + S^* \)                    |
| b) reinitiation                     | \( S^* + M \xrightarrow{k_{in}} R(1,1) \)                                |
| transfer of the chain to the monomer| \( R(i, \ell) + M \xrightarrow{k_{m}} R(i-1, \ell) + R(1,1) \)          |
| transfer of the chain to the polymer | \( R(i, \ell) + R(j, n) \xrightarrow{k_{pe}} R(i+1, \ell) + R(j-1, n) \) |
| reaction of cross-growth            | \( R(i, \ell) + R(j, n) \xrightarrow{k_{pe}} R(i+j, \ell + n) \)        |
| desactivation                       | \( R(i, \ell) \xrightarrow{k_{i}} R(i-1, \ell) \)                      |

where \( I \) is the initiator concentration, \( M \) is the monomer concentration \( S^* \), the concentration of intermediate particles resulting from transfer (possibly HSOX), \( k \) is the speed constants of corresponding reactions. The rate of reaction of the cross growth of macromolecules \( R(i, \ell) \) is proportional to \( k_{i}(m+n+j \ell) \), that is depends on the number of active centres of the interacting molecules and their length, is the concentration of macromolecules with \( i \) that is active centres and \( \ell \) that is monomeric links.

Spontaneous chain transmission and the reaction of cross growth of macromolecules by type “live” with “live” or “dead” are included into the molecular kinetic scheme besides the usual reaction of initiation, chain growth, transfer of chain to monomer and polymer. Previously, spontaneous chain transfer and the reaction of the cross-growth of macromolecules by the type “live” with “live” or “dead” were not included into the molecular kinetic scheme of the polymerization process butadiene. The reaction of cross-growth of macromolecules by the type “living” with “dead” was considered in some works. Analysis of experimental data showed that the transfer of the chain to solvent and aluminium-organic compound is not in this polymerization system.

The analysis of existing theories about the mechanism of formation and action of active centres of cobalt-containing catalytic system is carried out. A distinctive feature of the structure of polybutadiene chains obtained on cobalt-containing catalytic systems is the presence of conjugated double bonds formed at the end of the chain as a result of chain transfer reaction to monomer or spontaneous transfer. Conjugated double bonds are formed by the migration of double bonds, which allow macromolecules to react to cross growth when interacting with active centre of another macromolecule. The reaction of cross-growth of polybutadiene macromolecules is possible only by the conjugated double bonds, the number of which in the macromolecule is limited, so this reaction can occur without gels formation up to large values of monomer conversion. Previously, spontaneous chain transfer and the reaction of the cross-growth of macromolecules by the type “live” with “live” or “dead” were not included into the molecular kinetic scheme of the polymerization process butadiene. Analysis of experimental data showed that the transfer of the chain to solvent and aluminium-organic compound is not in this polymerization system.

The particularity of the mathematical model for the periodic regime is accounting the reaction of the cross-growth of macromolecules by the type “live” with “live”. The solution of the system of equations was carried out on the basis of the method of statistical moments and the producing function. As a result, the ratios for calculating the statistical moments of macromolecules distribution by the polymerization degree and the number of active centres were obtained.
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