Mechanism of Butadiene Polymerization on Cobalt-Containing Catalyst


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Abstract—Based on experimental results and reference data, the main elementary stages of butadiene polymerization on a cobalt-containing catalyst were determined and a mathematical model of the polymerization was developed. The following characteristics of the process were studied using this model: number-average, weight-average, and sedimentation-average degrees of polymerization and branching factor.

SKDK rubber is 1,4-cis-polybutadiene prepared with a cobalt-containing catalyst. This rubber, along with titanium (SKD) and rare-earth (SV-22, SV-23) rubbers, is used in production of tires, industrial rubber, industrial asbestos ware, shock-resistant polyvinyl chloride, and other items.

To develop a mathematical model of SKDK synthesis, the molecular-kinetic scheme considering the main reactions in the system is required. The synthesis mechanism can be formulated, and its main elementary stages determined, on the basis of reference data and various experimental dependences [1–6], although the structure of active centers of cobalt-containing catalytic systems and their reactivity are not yet clearly understood.

Butadiene polymerization includes some stages. The first of them is initiation, when a catalytic complex with active centers is formed: in the presence of a monomer, it is a \( \pi \)-allyl complex of the transition metal, and in the absence of the monomer, cobalt is reduced to metal [1]:

\[
R_3Al + CoCl_2 \rightarrow R_2AlCl + [RCoCl] \rightarrow R_4H \\
\downarrow \quad C_4H_6 \\
\begin{array}{c}
\text{CH}_2 \\
\text{HC} \\
\text{CH} \\
\text{CH}_2R
\end{array}
\]

\[
+ \quad R_4H + Co_0 + CoCl_2.
\]

The next stage is chain propagation.
where \( R \) is the concentration of macromolecules with \( i \) active centers and \( l \) monomeric units, \( R(i, n) \) is the concentration of macromolecules with \( j \) active centers and \( n \) monomeric units, and \( k_c \) is the rate constant of macromolecule cross-linking.

The double and conjugated double bonds present in diene polymers can enter into secondary reactions under the action of the components of catalytic systems and catalytic complexes themselves.

\[
R(i, l) + R(j, n) \xrightarrow{k_c (i + j)} R(i + j, l + n),
\]

where \( R(i, l) \) is the concentration of macromolecules with \( i \) active centers and \( l \) monomeric units, \( R(j, n) \) is the concentration of macromolecules with \( j \) active centers and \( n \) monomeric units, and \( k_c \) is the rate constant of macromolecule cross-linking.

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\[
\rightarrow \text{RCH=CH-CH}= \text{CH}_2 + \text{HCoX}.
\]

In the process, conjugated double bonds are formed on chain ends [8]. The same bonds are formed by migration of double bonds within molecular chain.

(2) Regeneration of active center, i.e., propagation of a new polymer chain:

\[
\text{HCoCl} + \text{C}_6\text{H}_6 \rightarrow \pi-\text{C}_4\text{H}_2\text{CoCl}.
\]

In the process, the hydride complex can be deactivated. The same hydride complex can add to a propagating chain with formation of an additional active center, which results in chain branching. Molecules slowly cross-link by reaction of conjugated double bonds with active centers of another molecule. This gives branched polymeric species of various structures. The propagation rate grows with increasing number of active centers in the macromolecule. In turn, the number of centers increases with growth of the macromolecule [8].

In addition, appearance of branched macromolecules is the necessary but insufficient condition for gelation. It is also probable that all monomer molecules polymerize before the formation of macroscopic polymeric three-dimensional network. Gelation is caused by pronounced nonuniformity in the growth of various polymeric chains. As a result, separate strongly branched molecules can grow to macroscopic di- or even at a low conversion. To determine the gelation conditions, it is necessary to monitor how statistical characteristics of the molecular-mass distribution (MMD) of polymeric chains vary over time. The mechanism of cross-linking of polymeric chains for the case of radical polymerization is described [8]. For anionic polymerization, a particular case of cross-linking of “living” and “dead” macromolecules was considered [9]. Let us consider additionally branching (cross-linking):

\[
\text{RCoX}_2 \cdot \text{H}_2\text{O}-\text{R}_2\text{AlCl} \text{ system contains the components R}_2\text{AlCl-H}_2\text{O and RAICl}_2-\text{H}_2\text{O capable to initiate cationic polymerization. In addition to the above catalysts, hydrogen chloride can be formed in the system as a result of catalyst hydrolysis with a water impurity. For instance, high-molecular-weight cis-polybutadiene is comparatively rapidly converted into a gel under the action of RAICl}_2 \cdot \text{H}_2\text{O. The contribution of the intermolecular reaction will strongly increase with increasing polymer concentration. Organometallic complexes can react with both conjugated and olefin bonds of the polymeric chains. Taking the above into consideration, we can suggest the following kinetic scheme of polymerization on the cobalt-containing catalyst:}
\]

initiation

\[
I + M \xrightarrow{k_i} R(1,1);
\]

chain propagation

\[
R(i, l) + M \xrightarrow{k_p} R(i, l + 1);
\]

spontaneous chain transfer (in two stages)

(a) transfer proper

\[
R(i, l) \xrightarrow{k_{sp}} R(i - 1, l) + S^*;
\]

(b) reinitiation

\[
S^* + M \xrightarrow{k_{ini}} R(1,1);
\]

chain transfer to monomer

\[
R(i, l) + M \xrightarrow{k_{tm}} R(i - 1, l) + R(1,1);
\]

chain transfer to polymer

\[
R(i, l) + R(i', l') \rightarrow R(i + 1, l) + R(i' - 1, l'),
\]

polymer cross-linking

\[
R(i, l) + R(i', l') \rightarrow R(i - 1, l) + R(i' + 1, l');
\]

chain termination

\[
R(i, l) \xrightarrow{k_t} R(i - 1, l);
\]