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Mathematical Simulation of the Synthesis of *cis*-1,4-Polybutadiene on a Cobalt-Containing Catalyst in the Presence of Ethylene

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Abstract—Based on an analysis of experimental results and published data, the main elementary steps of the anionic coordination polymerization of butadiene rubber on a cobalt-containing catalyst in the presence of ethylene were found, and a mathematical model of the periodic process at an optimum water content was developed. The molecular-weight characteristics of the process depending on ethylene concentration were studied with the use of this model.

INTRODUCTION

The possibility of preparing *cis*-1,4-polybutadiene in the presence of cobalt-containing catalysts was demonstrated more than 40 years ago [1]. Later, researchers' interest in catalytic systems based on cobalt compounds in combination with alkylaluminum halides somewhat decreased because of the high sensitivity of the reaction to the slightest changes in the composition of the system and the occurrence of secondary cationic processes. The current intensification of studies in polybutadiene production in the presence of cobalt-containing catalytic systems is due to a number of advantages over traditional catalysts based on titanium halides: the low concentration of the catalyst in use, the high molecular weight of the resulting polymer, weak branching, and the cost efficiency of the process.

The question of the structure of a catalytic complex is still an open question. A study of reasons for the generation of several types of active sites in the Ziegler–Natta catalytic systems resulted in the conclusion that the concentration of water and its dual nature have the greatest effect on the inhomogeneity of the catalytic system. The ability of water to exhibit both electron-acceptor and proton-donor properties is of common knowledge. The dissolution of water in toluene at low temperatures shifts the equilibrium to the formation of H_3O^+ ions, the occurrence of which in the system results in an increase in the positive charge on a metal.

It is well known that a high stereospecificity of the catalytic system, a maximum steady-state rate of the process, and a high molecular weight of the polymer are observed at an optimum water content. The effect of water concentration on the formation of active centers has been reported [2, 3]; it was noted that at an optimum water content, active centers responsible for the anionic mechanism of polymerization are formed (in these centers, the metal ion occurs in a high oxidation state). These are the so-called active centers of the first type. The formation of active centers that result in secondary cationic processes does not occur at an optimum concentration of water and on freezing to –20°C. Therefore, in the polymerization of butadiene, the following stages of complex formation are performed to provide the formation of active centers of the same type:

—moisture formation in toluene with the monomer added;

—preparation of an inactive complex at –10 to –20°C;

—preparation of an active complex by heating the inactive complex for 0.5–1.0 h at 20–25°C;

—moisture formation in the mixture at –20°C for 0.5–1.0 h before the polymerization process.

Because only one-type active centers occur at an optimum concentration of water, the concentration of active centers in the system remains almost unchanged in the course of the reaction.

In the development of a mathematical model for the synthesis of synthetic butadiene rubber on a cobalt-containing catalyst, a molecular-kinetic scheme of the process is required, which would take into account the main reactions that occur in the system. Based on various experimental relationships published [4–10], a mechanism for the polymerization process can be proposed, and its main elementary steps can be identified, although the structure of active centers in cobalt-containing catalytic systems and the reactivity of these systems are still unclear.

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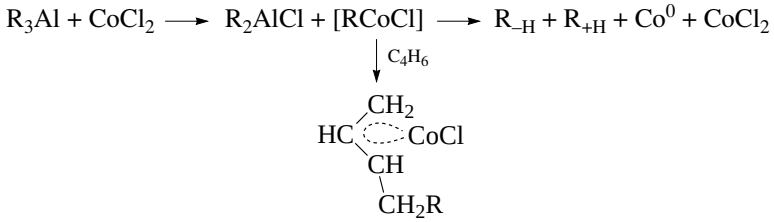
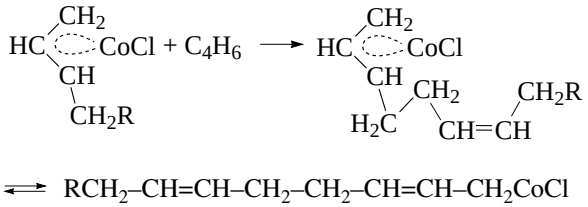
The process of butadiene polymerization consists of several steps. At the first step (initiation), the formation of a catalytic complex (active centers) takes place; in the presence of the monomer, a π-allyl complex of the transition metal is formed, whereas cobalt metal is formed in the absence of the monomer [11]:



(I)

Because the reaction of initiation is performed in the presence of a diene, the organometallic compound does not decompose to form cobalt metal.

The next step of polymerization is the reaction of chain propagation:



(II)

The chain-propagation reaction has a number of special features [12]:

—first order with respect to monomer concentration;

—first order with respect to catalyst (cobalt) concentration;

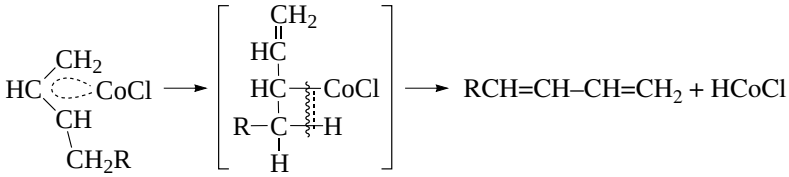
—total activation energy of 8.2 kcal/mol;

—one active center (on a cobalt basis) results in the formation of a considerable number of molecules due to chain-transfer reactions.

The reactions of chain transfer to the monomer, ethylene, and a polymer; spontaneous transfer; and polymer crosslinking occur simultaneously with chain propagation.

There is an opinion [13–18] that the reaction of chain transfer to the monomer consists of two consecutive steps:

(1) The decomposition of the active center and the formation of a hydride complex:



(III)

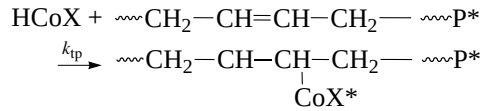
In this case, conjugated double bonds are formed at the ends of the chain [18].

(2) The regeneration of the active center; that is, the growth of a new polymer chain

$$HCoCl + C_4H_6 \longrightarrow \pi\text{-}C_4H_7CoCl. \qquad \text{(IV)}$$

In essence, reactions (III) and (IV) are the consecutive steps of spontaneous chain transfer rather than the reaction of chain transfer to the monomer. In spite of this fact, chain transfer to the monomer will also be considered for generality.

The same hydride complex can add to a growing chain with the formation of an additional active center on it; this results in chain branching, that is, chain transfer to the polymer



(V)

Moreover, B.A. Dolgoplosk suggested that conjugated double bonds are also formed as a result of the migration of double bonds

$$\sim CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\sim$$
$$\xrightarrow{H^+} \sim CH_2CH_2\overset{(+)}{C}HCH_2CH_2CH{=}CHCH_2\sim$$
$$\xrightarrow{-H^+} \sim CH_2CH_2CH{=}CH{-}CH_2{-}CH{=}CHCH_2\sim \qquad \text{(VI)}$$
$$\xrightarrow{H^+} \sim CH_2CH_2CH_2\overset{(+)}{C}HCH_2CH{=}CHCH_2\sim$$
$$\xrightarrow{-H^+} \sim CH_2CH_2CH_2CH{=}CH{-}CH{=}CHCH_2\sim$$

Conjugated double bonds allow macromolecules to enter, while slowly, crosslinking reactions in the interaction with the active center of another macromolecule:

$$R{-}CH{=}CH{-}CH{=}CH{-}R^* + HCoXR \longrightarrow R{-}CH_2{-}CH{-}CH{-}CH_2{-}R^*$$
$$\text{(VII)}$$

This leads to the formation of various branched polymer structures. The rate of growth of the macromolecule increases with the increasing number of active centers in it; in turn, the number of active centers increases with the increasing size of this macromolecule [19].

Moreover, the appearance of branched molecules is a necessary but insufficient condition for gel formation. A situation can occur in which the total monomer in the system undergoes polymerization before a macroscopic three-dimensional polymer network has a chance to form. Gel formation is associated with a sharp inhomogeneity in the growth of various polymer chains; because of this, individual highly branched molecules can grow to macroscopic sizes even at low degrees of conversion. To determine the conditions of gel formation, the change in the statistical characteristics of the molecular-weight distribution of polymer chains with time should be studied. The crosslinking reaction of polymer chains was described in the literature [19] for radical polymerization, whereas a particular case of the crosslinking of "living" and "dead" macromolecules was considered for anionic polymerization [20].

Therefore, we consider one more reaction: the branching (crosslinking)

$$R(i, l) + R(j, n) \xrightarrow{k_c(in + jl)} R(i + j, l + n), \qquad \text{(VIII)}$$

where $R(i, l)$ and $R(j, n)$ are the concentrations of macromolecules with i and j active centers and l and n monomer units.

In a study of the effect of ^{14}C-labeled ethylene on the molecular weight of polybutadiene, it was found that ethylene was a constituent of the chain [21]. It was also found that a decrease in the molecular weight of the polymer was related to an increase in the rate of chain transfer on going to a π-allyl state to the σ bond $\sim CH_2{-}CoX$ in accordance with the reaction scheme

$$\text{(IX)}$$

Chain transfer in the presence of ethylene results in the formation of the nonconjugated system of double bonds $\sim CH_2CH{=}CHCH_2CH{=}CH_2$. Previously, the occurrence of a reaction of this kind was experimentally established using the interaction of $(\pi\text{-}C_4H_7NiCl)_2$ with ethylene in a benzene solution as an example [21]. The reaction products at 20°C were a mixture of hexanes and nonconjugated hexadiene. Direct experimental evidence was obtained in a study of the concentration of conjugated double bonds in polybutadiene formed under the action of the nickel oleate–diisobutylaluminum chloride–water system at a 1 : 150 : 21 molar ratio between components. The system used resulted in the formation of low-molecular-weight polymers; this seemed necessary for the quantitative evaluation of the concentration of conjugated double bonds.

The formation of five conjugated systems of double bonds in the absence of ethylene can be due to only the migration of double bonds in a polymer chain. Under certain conditions, this migration occurs under the action of catalyst components.

In the presence of ethylene, the molecular weight of the polymer decreases symbatically with an increase in the concentration of ethylene; in this case, the concentration of conjugated double bonds decreases.

Based on the above considerations, we can propose the following kinetic scheme for polymerization on a cobalt-containing catalyst in the presence of ethylene:

Initiation	$I + M \xrightarrow{k_i} R(1,1),$
Chain growth	$R(i, l) + M \xrightarrow{k_p} R(i, l + 1),$
Spontaneous chain transfer, which occurs in two steps	
(a) chain transfer	$R(i, l) \xrightarrow{k_{sp}} R(i - 1, l) + S^*,$
(b) reinitiation	$S^* + M \xrightarrow{k_{ri}} R(1, 1),$
Chain transfer to the monomer	$R(i, l) + M \xrightarrow{k_{tm}} R(i - 1, l) + R(1, 1),$
Chain transfer to the polymer	$R(i, l) + R(j, n) \xrightarrow{\substack{k_{tp}jl \\ k_{tp}in}} \begin{matrix} R(i + 1, l) + R(j - 1, n) \\ R(i - 1, l) + R(j + 1, n), \end{matrix}$
Polymer crosslinking reaction	$R(i, l) + R(j, n) \xrightarrow{k_c(in + jl)} R(i + j, l + n),$
Chain transfer to ethylene	$R(i, l) + E \xrightarrow{k_{te}} R(i - 1, l) + R(1, 1).$

Here, I is the concentration of an initiator; M is the concentration of the monomer; S^* is the concentration of transient species resulting from chain transfer (probably HCoCl); E is the concentration of ethylene; and k are the rate constants of the corresponding reactions. The rate of macromolecule crosslinking is proportional to $k_c(in + jl)$; that is, it depends on the number of active centers in the interacting molecules and on their lengths; $R(i, l)$ is the concentration of macromolecules with i active centers and l monomer units.

In the development of a mathematical model for the polymerization of synthetic butadiene rubber on a cobalt-containing catalyst at an optimum concentration of water in the presence of ethylene, a number of assumptions were made:

(1) One type of active center is formed at an optimum concentration of water.

(2) The total concentration of active centers is constant and equal to the concentration of an initiator.

(3) The process is considered as "unterminated" (without deactivation) at the optimum water content of the system.

According to the kinetic scheme, the set of equations that describes changes in the concentrations of the monomer, ethylene, and growing chains with time for a periodic process has the form

$$\frac{dM}{dt} = -k_p MR, \quad \text{at} \quad M|_{t=0} = M_0, \tag{1}$$

$$\frac{dE}{dt} = -k_{te} ER, \quad \text{at} \quad E|_{t=0} = E_0, \tag{2}$$

$$\frac{\partial R(i, l)}{\partial t} = -ik_p \frac{\partial R(i, l)}{\partial \lambda}$$

$$+ (k_{sp} + k_{tm} M + k_{te} E)[(i + 1)R(i + 1, l) - iR(i, l)]$$

$$+ \frac{k_c}{2} \sum_{j=0}^{i} \int_0^l [j(l - n) + n(i - j)]R(j, n)$$

$$\times R(i - j, l - n)dn - k_c R(i, l)$$

$$\times \sum_{j=0}^{\infty} \int_0^{\infty} (in + jl)R(j, n)dn \tag{3}$$

$$+ k_{tp} \sum_{j=0}^{\infty} lj \int_0^{\infty} R(j, n)dn[R(i - 1, l) - R(i, l)]$$

$$+ k_{tp} \sum_{j=0}^{\infty} \int_0^{\infty} nR(j, n)dn[(i + 1)R(i + 1, l) - iR(i, l)]$$

$$+ (k_{sp} + k_{tm} M + k_{te} E)I_0 \delta_{i,1} \delta(l),$$

$$0 \le l < \infty, \quad i = 1, 2, \ldots .$$

Because k_{tm}/k_p and k_{sp}/k_p are always lower than unity, the monomer consumptions in chain-transfer and reinitiation reactions in Eq. (1) can be neglected. The first term in the right-hand side of Eq. (3) describes the change in $R(i, l)$ as a result of growth; the following five terms describe the changes in $R(i, l)$ as a result of chain-transfer, crosslinking, and termination reactions; the last term describes the appearance of new short macromolecules in reinitiation.

The results of a study of cobalt-containing catalysts demonstrated that polymerization usually occurs with no induction period. Therefore, we assume that initiation is instantaneous. By this is meant that the following initial conditions are considered: $M = M_0$ and $R(i, l) = I_0 \delta_{l,1} \delta_{i,1}$, where $\delta_{i,j} = \begin{cases} 1, & i = j \\ 0, & i \ne j \end{cases}$. In the absence of termination, the condition of instantaneous initiation implies that the total concentration of active centers $R + S^*$ is constant and equal to the initiator concentration I_0.

It is believed that the initiation reactions occur at least as quickly as the reaction of chain transfer (otherwise, it would be more likely a termination reaction). In this case, the concentration of transient species S^* is

found from the quasi-steady-state relationship, which corresponds to the kinetic scheme,

$$\frac{dS^*}{dt} = k_{sp}R - \left(k_{ri}M + k_t + k_{tp}\sum_{i,l} lR(i,l)\right)S^* \approx 0.$$

Therefore, $S^* = \dfrac{k_{sp}R}{k_{ri}M + k_t + k_{tp}P}$ ($R = \sum_{i,l}^{\infty} lR(i,l)$ is the total concentration of growing chains, and $P = \sum_{i,l} lR(i,l) = M_0x$ is the total concentration of the monomer in the system). Because $S^* \le \dfrac{k_{sp}R}{k_{ri}M} < \dfrac{k_{sp}}{k_pM}$, and the ratio $\alpha = \dfrac{k_{sp}}{k_pM_0}$, which characterizes the intensity of spontaneous transfer, is very low ($\alpha \ll 1$; otherwise, an oligomer rather than polymer would be formed), $S^* \ll R$ and active centers mainly occur on growing chains.

Equation (3) was written in the approximation of long chains. Integrating Eq. (1) and using the definition of conversion $x = 1 - \dfrac{M}{M_0}$, we obtain the time dependence of monomer conversion

$$x = 1 - e^{-k_pI_0t}. \quad (4)$$

Equation (2) can also be easily integrated:

$$E = E_0(1-x)^{k_{te}/k_p}. \quad (5)$$

With the use of the definition of conversion and the time dependence of monomer conversion, we turn from the time dependence to the conversion dependence in Eqs. (3).

Then, Eqs. (3) can be written in the form

$$k_pI_0(1-x)\frac{\partial R(i,l)}{\partial x} = -ik_pM_0(1-x)\frac{\partial R(i,l)}{\partial l}$$
$$+ (k_{sp} + k_{tm}M + k_{te}E)[(i+1)R(i+1,l) - iR(i,l)]$$
$$+ \frac{k_c}{2}\sum_{j=0}^{i}\int_0^l [j(l-n) + n(i-j)]R(j,n)R(i-j,l-n)dn$$
$$- k_ciR(i,l)M_0x - k_clR(i,l)I_0 \quad (6)$$
$$+ \left(k_{sp} + k_{tm}M_0(1-x) + k_{te}E_0(1-x)\frac{k_{te}}{k_p}\right)I_0\delta_{i,1}\delta(l)$$
$$+ k_{tp}lI_0[R(i-1,l) - iR(i,l)]$$
$$+ k_{tp}M_0x[(i+1)R(i+1,l) - iR(i,l)].$$

Taking into account that $\gamma_m = (\beta k_{tm})/k_p$ is the intensity of chain transfer to the monomer, $\gamma_{sp} = k_{sp}/(k_pI_0)$ is the intensity of spontaneous transfer, $\gamma_p = (\beta k_{tp})/k_p$ is the intensity of chain transfer to the polymer, $\gamma_c = k_c/I_0k_p$ is the intensity of the crosslinking reaction of macromolecules, and $\gamma_e = k_{te}E_0/(k_pI_0)$ is the reaction intensity of transfer to ethylene, Eq. (6) takes the form

$$\frac{\partial R(i,l)}{\partial x} = -i\beta\frac{\partial R(i,l)}{\partial l} + \left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\varepsilon\beta}}}\right)[(i+1)R(i+1,l) - iR(i,l)]$$
$$+ \frac{\gamma_c}{2(1-x)}\sum_{j=0}^{i}\int_0^l [j(l-n)$$
$$+ n(i-j)]R(j,n)R(i-j,l-n)dn$$
$$- \frac{\gamma_c}{(1-x)}(iR(i,l)M_0x - lR(i,l)I_0) \quad (7)$$
$$+ \left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\varepsilon\beta}}}\right)I_0\delta_{i,1}\delta(l)$$
$$+ \frac{\gamma_p l}{\beta(1-x)}[R(i-1,l) - iR(i,l)]$$
$$+ \frac{\gamma_p x}{1-x}[(i+1)R(i+1,l) - iR(i,l)], \quad i = 1, 2, 3\ldots,$$

where $\varepsilon = \dfrac{E_0}{M_0}$ is the mole fraction of ethylene.

With the use of the function $f = \sum_{i=0}^{\infty} s^i \int_0^{\infty} e^{-pl} R(i,l)dl$, which is usually termed a generating function, the set of Eqs. (7) can be reduced to the following single equation:

$$\frac{\partial f}{x} = -\beta\rho\frac{\partial f}{\partial s} + \left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\varepsilon\beta}}}\right)(1-s)\frac{\partial f}{\partial s}$$
$$- \frac{\gamma_c}{1-x}s\frac{\partial f}{\partial s}\frac{\partial f}{\partial p} - \frac{\gamma_c}{1-x}\left(M_0xs\frac{\partial f}{\partial s} - I_0\frac{\partial f}{\partial p}\right)$$
$$+ \left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\varepsilon\beta}}}\right)I_0s \quad (8)$$
$$+ \frac{\gamma_p}{\beta(1-x)}(1-s)\frac{\partial f}{\partial p} + \frac{x\gamma_p}{(1-x)}(1-s)\frac{\partial f}{\partial s}.$$

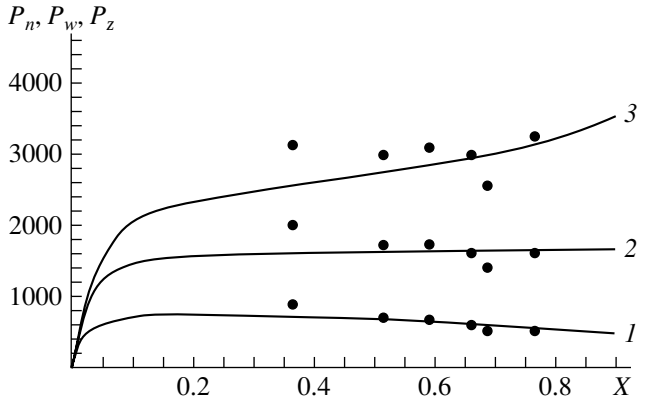


Fig. 1. Comparison between experimental data and calculated conversion dependence of the degrees of polymerization: (*1*) number-average $\bar{P}_n$, (*2*) weight-average $\bar{P}_w$, and (*3*) *z*-average $\bar{P}_z$ degrees of polymerization. Points and lines indicate experimental data and calculated curves, respectively. k_{sp} = 0.69 min^{-1}; k_c = 0.02 min^{-1}; k_{tm} = 0.45 l mol^{-1} min^{-1}; k_p = 788 l mol^{-1} min^{-1}; k_{tp} = 0.34 l mol^{-1} min^{-1}; k_{te} = 0.6 l mol^{-1} min^{-1}; I_0 = 0.0000562 mol/l; M_0 = 1.48 mol/l; ethylene content $\tilde{\varepsilon}$ = 2.1 mol %.

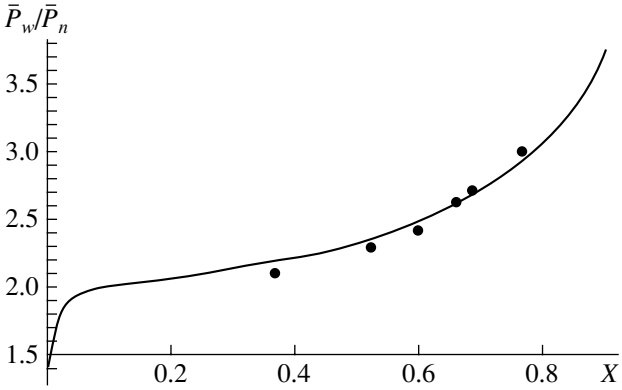


Fig. 2. Comparison between experimental data and the calculated conversion dependence of the polydispersity index ($\bar{P}_w/\bar{P}_n$). $\tilde{\varepsilon}$ = 2.1 mol %. Points and line indicate experimental data and the calculated curve, respectively.

Repeatedly differentiating Eq. (8) with respect to *s* and *p*, we can obtain relationships for calculating the macromolecule statistical moments of polymerization degree (*l*) and active center number (*i*) distributions.

We introduce the following notation: $J_{ij} = \left.\frac{\partial^{i+j} f}{\partial s^i \partial p^j}\right|_{\substack{s=1\\p=0}}$; by the definition of the moments of the molecular-weight distribution (MWD), $J_{00} = f|_{\substack{s=1\\p=0}} = \mu_0$ is the total concentration (number) of polymer chains at a point *t* in time; $J_{10} = \left.\frac{\partial f}{\partial s}\right|_{\substack{s=1\\p=0}} = I_0$ is the total concentration (number) of active centers at a point *t* in time; $J_{01} = \left.\frac{\partial f}{\partial p}\right|_{\substack{s=1\\p=0}} = -\mu_1 = -M_0 x$ is the concentration of polymer formed by a point *t* in time (of the opposite sign); $J_{02} = \left.\frac{\partial^2 f}{\partial p^2}\right|_{\substack{s=1\\p=0}} = \mu_2$ and $J_{03} = \left.\frac{\partial^3 f}{\partial p^3}\right|_{\substack{s=1\\p=0}} = -\mu_3$ are the second and third moments, respectively. The set of equations for calculating MWD moments has the form

$$\frac{dJ_{00}}{dx} = \left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\beta\varepsilon}}}\right) I_0 - \frac{\gamma_c M_0 x}{1-x} I_0,$$

$$\frac{dJ_{02}}{dx} = -2\beta J_{11} - \frac{2\gamma_c}{(1-x)} J_{11} J_{02},$$

$$\frac{dJ_{03}}{dx} = -3\beta J_{12} - 3\frac{\gamma_c}{(1-x)} J_{02} J_{12} - 3\frac{\gamma_c}{1-x} J_{11} J_{03},$$

$$\frac{dJ_{12}}{dx} = -2\beta(J_{11} - J_{21})$$

$$-\left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\beta\varepsilon}}}\right) J_{12}$$

$$-\frac{\gamma_c}{(1-x)}(J_{12}J_{11} + 2J_{11}J_{02})$$

$$-\frac{\gamma_c}{1-x}(2J_{21}J_{02} + 2J_{11}J_{12} + J_{10}J_{03} + J_{20}J_{03})$$

$$-\frac{\gamma_p}{1-x}\left(\frac{J_{03}}{\beta} - xJ_{12}\right),$$

$$\frac{dJ_{11}}{dx} = -\beta I_0 - \beta J_{20} - \left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\beta\varepsilon}}}\right) J_{11}$$

$$-\frac{\gamma_c}{(1-x)}(J_{11}^2 + J_{20}J_{02} + I_0 J_{02}) - \frac{\gamma_p}{1-x}\left(\frac{J_{02}}{\beta} + xJ_{11}\right), \quad (9)$$

$$\frac{dJ_{20}}{dx} = -2\left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\beta\varepsilon}}}\right) J_{20}$$

$$-\frac{2\gamma_c}{(1-x)}[I_0 J_{11} + J_{20}J_{11}] - \frac{2\gamma_p}{1-x}\left[\frac{1}{\beta}J_{11} - xJ_{20}\right],$$

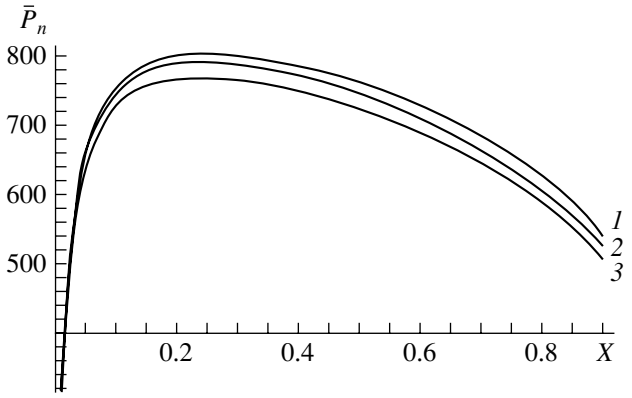


Fig. 3. Dependence of the number-average degree of polymerization (P_n) on conversion at different ethylene contents: $\tilde{\varepsilon}$ = (*1*) 1, (*2*) 3, or (*3*) 6 mol %.

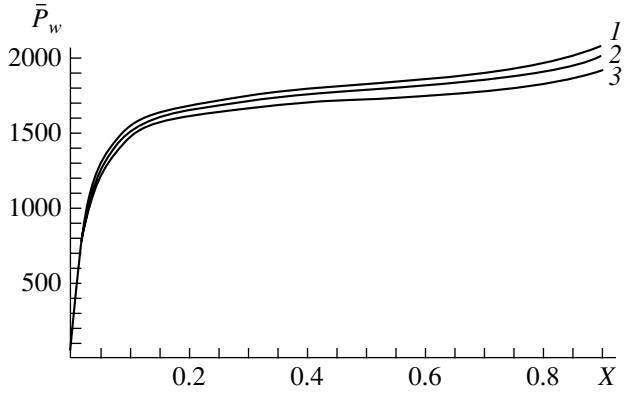


Fig. 4. Dependence of the weight-average degree of polymerization (P_w) on conversion at different ethylene contents: $\tilde{\varepsilon}$ = (*1*) 1, (*2*) 3, or (*3*) 6 mol %.

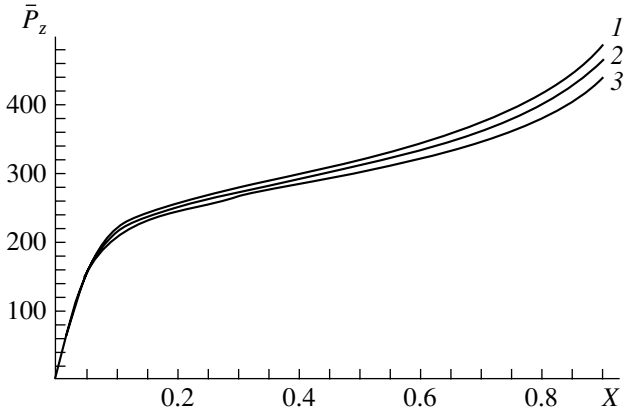


Fig. 5. Dependence of the *z*-average degree of polymerization (P_z) on conversion at different ethylene contents: $\tilde{\varepsilon}$ = (*1*) 1, (*2*) 3, or (*3*) 6 mol %.

$$\frac{dJ_{30}}{dx} = -3\left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\beta\varepsilon}}}\right)J_{30}$$

$$-3\frac{\gamma_c}{(1-x)}(2J_{20}J_{11} + I_0J_{21} + J_{30}J_{11} + J_{20}J_{21})$$

$$-\frac{\gamma_p}{1-x}\left(\frac{J_{21}}{\beta} - xJ_{30}\right),$$

$$\frac{dJ_{21}}{dx} = -\beta J_{30} - 2\beta J_{20}$$

$$-2\left(\frac{\gamma_{sp}}{1-x} + \gamma_m + \frac{\gamma_e}{(1-x)^{1-\frac{\gamma_e}{\beta\varepsilon}}}\right)J_{21}$$

$$-\frac{\gamma_c}{(1-x)}(2J_{20}J_{02} + 2J_{11}^2 + 2I_0J_{12} + J_{30}J_{02}$$

$$+ 2J_{20}J_{12} + 3J_{21}J_{11}) - 2\frac{\gamma_p}{1-x}\left(\frac{J_{12}}{\beta} - xJ_{21}\right).$$

Initial conditions: at $x = 0$ $\mu_0 = I_0$, $\mu_1 = \mu_2 = \mu_3 = J_{11} = J_{12} = J_{20} = J_{21} = J_{30} = 0$.

$$\bar{P}_n = \mu_1/\mu_0,\ \bar{P}_w = \mu_2/\mu_1,\ \bar{P}_z = \mu_3/\mu_2.$$

The results of calculations from the set of Eqs. (9) with the use of the Mathematica 4.1 package and experimental data are compared in Figs. 1 and 2.

Experiments were performed to identify the kinetic constants of the model of polymerization. The relative deviations of the experimental characteristics $y^{(expt)}$ from the calculated characteristics $y^{(calcd)}$: $\sum_i \left|\frac{y_i^{(calcd)} - y_i^{(expt)}}{y_i^{(expt)}}\right| \longrightarrow \min$, where i is the characteristic number, were evaluated. In this case, the experimental data set $\left\{x^{(expt)},\ \bar{P}_n^{(expt)},\ \bar{P}_w^{(expt)},\ \bar{P}_z^{(expt)},\ \frac{\bar{P}_w^{(expt)}}{\bar{P}_n^{(expt)}}\right\}$ was used. The model was identified by varying the parameters k_{tm}, k_{tp}, k_{sp}, k_c, and k_{te}.

The maximum difference between the experimental and calculated data was 18.6%; this provides support for the validity of the mechanism proposed for butadiene polymerization on a cobalt-containing catalyst.

The conversion dependence of the number-average, weight-average, and *z*-average degrees of polymerization (Figs. 3–5) indicates that the addition of ethylene to the system decreased the molecular weight of the polymer symbatically with an increase in the concentration of ethylene.

The incorporation of branching reactions (transfer to the polymer and crosslinking) into the polymerization model resulted in a good agreement between the calculated and experimental data. It can be seen in Fig. 2 how branching changes with conversion: the polydispersity index $\bar{P}_w/\bar{P}_n$ approximately changed from 2.5 to 3.6; this is indicative of considerable branching at monomer conversions higher than 40%.

CONCLUSIONS

(1) Based on published and experimental data, a kinetic scheme and a mathematical model were developed for the polymerization of butadiene rubber on a cobalt-containing catalyst in the presence of ethylene for a batch process.

(2) The addition of ethylene to the system decreased the molecular weight of the polymer symbatically with an increase in the concentration of ethylene. In this case, the concentration of conjugated double bonds decreased.

(3) An important role of branching reactions (chain transfer to the polymer and the crosslinking of macromolecules) was found. Simulation was performed for living-to-living macromolecule crosslinking.

(4) The mathematical model presented can form a basis for recommendations concerning changes in the process conditions of butadiene polymerization and for the optimization of the properties of synthetic rubber.

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APPENDIX

Symbols:

k_i is the rate constant of initiation;

k_{tm} is the rate constant of chain transfer to the monomer;

k_p is the rate constant of propagation;

k_{sp} is the rate constant of spontaneous chain transfer;

k_{tp} is the rate constant of chain transfer to the polymer;

k_{ri} is the rate constant of reinitiation;

k_e is the rate constant of transfer to ethylene;

k_c is the rate constant of molecule crosslinking;

$x = \dfrac{M_0 - M}{M_0}$ is the conversion of the monomer;

I_0 is the concentration of an initiator;

M is the concentration of the monomer;

M_0 is the initial concentration of the monomer;

$R(i, l)$ is the concentration of macromolecules with i active centers and l monomer units;

$\bar{P}_n$ is the number-average degree of polymerization;

$\bar{P}_w$ is the weight-average degree of polymerization;

$\bar{P}_z$ is the z-average degree of polymerization;

$\beta = M_0/I_0$ is the theoretical degree of polymerization of a living polymer at full conversion;

$\gamma_m = (\beta k_{tm})/k_p$ is the intensity of chain transfer to the monomer;

$\gamma_s = k_{sp}/(k_p I_0)$ is the intensity of spontaneous chain transfer;

$\gamma_p = (\beta k_{tp})/k_p$ is the intensity of chain transfer to the polymer;

$\gamma_c = k_c/I_0 k_p$ is the reaction intensity of molecule crosslinking;

$\gamma_e = k_{te}E_0/(k_p I_0)$ is the reaction intensity of transfer to ethylene;

$\varepsilon = \dfrac{E_0}{M_0}$ is the mole fraction of ethylene.

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