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MATHEMATICAL MODELING OF THE PROCESS OF POLYMERIZATION OF BUTADIENE ON A COBALT CATALYST IN THE PERIODIC REGIME

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The mechanism of the process of polymerization of butadiene on a cobalt catalyst is investigated by comparing two mathematical models. Experimental data and results of calculations according to the proposed kinetic schemes of the process are compared.

Butadiene rubber on a cobalt-containing catalyst (SKDK) is produced by the method of ionic polymerization of butadiene in a nephras solution. A special technology of manufacturing a catalyst complex which ensures the formation of active centers of the same type is used. As the experience of bringing this process to a commercial level shows, the polymerization rate and the molecular-weight characteristics and accordingly the properties of polymers in wide intervals depend on many factors, especially on the batching of the catalyst system, the proportion of the components, the temperature, etc. On the other hand, the behavior of the catalyst system is obviously not clearly understood. Therefore, to reveal the true mechanism of the polymerization reaction in producing SKDK rubber and to subsequently optimize industrial production it is expedient to carry out mathematical modeling of this process.

Despite the significant difficulties in conducting the experiments and scanty information on the structure of the catalyst and the mechanism of the polymerization reaction, data on investigating the kinetics of a wide range of Ziegler–Natt catalyst systems have appeared in the press [1]. However the monitoring of the process and the development of the model are described in a relatively small part of the literature sources [2]. For example, although a number of models of the reaction have been presented for such olefins as ethylene and propylene [3–9] the diversity of the processes and catalyst systems of polymerization has been shown only in some publications [10–15].

An analogous situation occurs in the field of polymerization of butadiene. In [16], to study solution polymerization of butadiene in a batch reactor with the use of cobalt octoate/diethylaluminum chloride/water as a catalyst the concept of a fractional factorial experiment of two levels has been used. Honig et al. established the importance of the branching reaction, which is in essence the reaction of cross-linking of two polymer molecules. However, in actual fact, cross-linking of only the "dead" chain and the "living" chain was realized in this model, which considerably distorts the picture of the process. Furthermore, the z-mean molecular weight of the polymer was not obtained and too many identification parameters were introduced, because of which the coefficients became fitting in character.

In the investigation proposed, the modeling is carried out based on different versions of kinetic schemes of the process. The first scheme involves, in addition to the main stages of the process of polymerization, i.e., initiation, growth of the chain, transfer of it to a monomer and a polymer, and termination of the chain, also the stage of spontaneous chain transfer. The other kinetic scheme describes the mechanism of the reaction of cross-linking of molecules under the action of migration of double bonds. The true mechanism of the process is established by comparing experimental data and results of calculations according to the proposed kinetic schemes of the process.

Theory. *Polymerization Mechanism.* Two different mechanisms of polymerization are assumed based on an analysis of literature and experimental data.

In the opinion of Azizov et al. [17], the side reactions involve the decomposition of the active center with the formation of the intermediate state HCo*X*, where *X* is the set of ligands at the cobalt center:

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$$\sim\sim\sim P^*\ ,\ \mathrm{Co}X \xrightarrow{k_{\mathrm{d}}} \sim\sim\sim P + \mathrm{HCo}X^*\ . \tag{1}$$

Such reactions with the formation of hybrid complexes represent the ordinary way of decomposition of the organic complexes of transition metals (β elimination) [18, 19]. Depending on the nature of the formed compound $\mathrm{HCo}X^*$ it can partially be irreversibly deactivated, which leads to an incomplete yield of the polymer

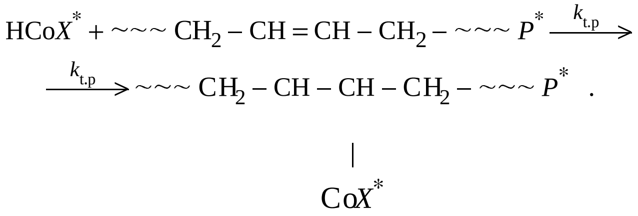
$$\mathrm{HCo}X^* \xrightarrow{k_{\mathrm{d}}} \text{inactive product}; \tag{2}$$

and also activate the growth of a new polymer chain

$$\mathrm{HCo}X^* + M \xrightarrow{k_{\mathrm{p}}} P^*(1, 1)\ . \tag{3}$$

Reactions (1) and (3) are in essence the successive stages of the reaction of spontaneous chain transfer and not the reaction of chain transfer to a monomer (inherent chain transfer), as has been said in [20]. Despite this fact, the reaction of chain transfer to a monomer will also be considered for generality.

The same complex $\mathrm{HCo}X^*$ can add to the growing chain with the formation of an additional active center on it:



$$\mathrm{HCo}X^* + \sim\sim\sim \mathrm{CH_2 - CH = CH - CH_2} - \sim\sim\sim P^* \xrightarrow{k_{\mathrm{t.p}}}$$
$$\xrightarrow{k_{\mathrm{t.p}}} \sim\sim\sim \mathrm{CH_2 - CH -} \underset{\substack{|\\ \mathrm{Co}X^*}}{\mathrm{CH}} \mathrm{- CH_2} - \sim\sim\sim P^*\ . \tag{4}$$

Reactions (1) and (4) together represent the reaction of chain transfer to a polymer, which leads to an additional extension of the molecular-weight distribution of the polymer.

Then, based on what has been stated above, we can assume the following kinetic scheme of the process of polymerization on a cobalt-containing catalyst:

1) initiation: $I + M = \xrightarrow{k_{\mathrm{i}}} R(1, 1)$,

2) growth of the chain: $R(i, l) + M \xrightarrow{k_{\mathrm{p}}} R(i, l + 1)$,

3) spontaneous chain transfer: $R(i, l) \xrightarrow{k_{\mathrm{sp}}} R(i - 1, l) + S^*$ and $S^* + M \xrightarrow{k_{\mathrm{ri}}} R(1, 1)$,

4) chain transfer to a monomer: $R(i, l) + M \xrightarrow{k_{\mathrm{t.m}}} R(i - 1, l) + R(1, 1)$,

5) chain transfer to a polymer: $R(i, l) + R(i', l') \longrightarrow \begin{cases} \xrightarrow{k_{\mathrm{t.p}i'l}} R(i + 1, l) + R(i' - 1, l'), \\ \xrightarrow{k_{\mathrm{t.p}il'}} R(i - 1, l) + R(i' + 1, l'), \end{cases}$

6) termination of the chain: $R(i, l) \xrightarrow{k_{\mathrm{d}}} R(i - 1, l)$, where k with a subscript is the rate constant of the corresponding reaction.

A distinguishing feature of the chain structure of polybutadiene produced with cobalt catalyst systems is the presence of conjugated double bonds which are formed at the end of the chain by the reaction of chain transfer to a monomer or the reaction of spontaneous transfer:

$$P - \mathrm{CH_2 - CH = CH - CH_2 - Co}X^* + \mathrm{C_4H_6} \xrightarrow{k_{\mathrm{t.m}}} \pi\,\mathrm{C_4H_3Co}X + P - \mathrm{CH = CH - CH = CH_2}\ .$$

Furthermore, it has been assumed in [18] that conjugated double bonds are formed by migration of any double bonds. In studying the kinetics and mechanism of the reaction of migration of double bonds under the influence of complex cobalt compounds used for stereoscopic polymerization of dienes, it has been established that the reactions of migration and isomerization of double bonds experience the stage of formation of HMeX leading to a chain process. Successive attachment and detachment of HMeX cause the formation of a conjugated double bond.

The conjugated double bonds enable macromolecules, even if slowly, to enter into the cross-linking reaction in interaction of them with the active center of another macromolecule. This leads to the formation of branched polymer structures of different configurations. The rate of growth of a macromolecule increases with increase in the number of active centers in it, while the number of the latter increases in turn with increase in the size of this macromolecule.

It should be noted that polybutadiene macromolecules can be cross-linked to only conjugated double bonds and not to any double bonds, as is indicated in [16, 23]. The number of conjugated double bonds is very limited in a polybutadiene macromolecule; therefore, this reaction can occur without gelation to high values of the conversion of the monomer.

Furthermore, the appearance of branched macromolecules is a necessary but insufficient condition of formation of a gel. The situation is also possible in which the entire monomer available in the system is polymerized before a macroscopic three-dimensional polymer network is formed. The formation of a gel is related to the strong nonuniformity of the growth of different polymer chains because of which individual strongly branched molecules can attain a macroscopic size already with low degrees of conversion. To determine the conditions of occurrence of a gel one must investigate a change in the statistical characteristics of the molecular-weight distributions of polymer chains with time. In the literature sources, there is a description of the reaction of cross-linking of polymer chains for the process of radical polymerization [23], and a particular case of cross-linking of "living" macromolecules and "dead" macromolecules is considered for the process of anionic polymerization [16].

Therefore, we consider another kinetic scheme of the reaction of polymerization of butadiene on a cobalt catalyst which is based on the reaction of cross-linking of "living" macromolecules with "living" and "dead" macromolecules for the process of anionic polymerization of butadiene. The macromolecules add only to conjugated double bonds and not to double bonds, as is indicated in [16]. The scheme differs from the first one in that the reaction of transfer to a polymer is replaced by the reaction of branching (cross-linking):

$$R\,(i,\,l) + R\,(j,\,n) \xrightarrow{k_{\mathrm{c}}(in+jl)} R\,(i+j,\,l+n)\,. \tag{5}$$

Mathematical Modeling. Taking account of spontaneous chain transfer and chain transfer to a polymer. According to the first kinetic scheme, the system of equations describing the time change of the concentrations of the monomer and of growing and dead chains has, for the periodic process, the form

$$\frac{dM}{dt} = -\,k_{\mathrm{p}}MR - k_{\mathrm{sp}}R - k_{\mathrm{t.m}}MR\,, \quad M\big|_{t=0} = M_0\,, \tag{6}$$

$$\frac{dR}{dt} = -\,k_{\mathrm{d}}R\,, \quad R\big|_{t=0} = I_0\,, \tag{7}$$

$$\frac{dR\,(i,\,l)}{dt} = -\,ik_{\mathrm{p}}M\,[R\,(i,\,l) - R\,(i,\,l-1)] + lk_{\mathrm{t.p}}R\,[R\,(i-1,\,l) - R\,(i,\,l)] +$$

$$+\,(k_{\mathrm{t.p}}\,(M_0 - M) + k_{\mathrm{sp}} + k_{\mathrm{t.m}}M + k_{\mathrm{d}})\,[(i+1)\,R\,(i+1,\,l) - iR\,(i,\,l)] +$$

$$+\,(k_{\mathrm{sp}} + k_{\mathrm{t.m}}M)\,I_0\delta_{i,1}\delta_{l,1}\,, \quad i = 0,\,1,\,2,\,\ldots\,, \quad l = 1,\,2,\,\ldots\,. \tag{8}$$

Since $k_{\mathrm{t.m}}/k_{\mathrm{p}}$ and $k_{\mathrm{sp}}/k_{\mathrm{p}}$ are always much less than unity, the consumption of the monomer by the chain-transfer reactions and reinitiation in (6) can be disregarded. The first term on the right-hand side in Eq. (8) describes the change in the concentration $R(i,\,l)$ as a result of the chain growth, the subsequent two terms describe the change in $R(i,\,l)$ as a result of the reactions of transfer and termination, and finally the last term describes the occurrence of new short macromolecules in reinitiation.

Equation (7) characterizes the rate of disappearance of the total concentration of the active centers $R = \sum_{i,l}^{\infty} iR(i, l)$. We decided to disregard deactivation in the first approximation.

Using the method of statistical moments, from Eqs. (6) and (8) we obtain the following expression for the dependence of the number-mean degree of polymerization on the conversion:

$$P_{\mathrm{n}} = \frac{\beta x}{1 + \gamma_{\mathrm{t.m}} x - \gamma_{\mathrm{sp}} \ln \left(\dfrac{1 - x + \alpha}{1 + \alpha} \right)},$$

where the conversion of the monomer is $x = (M_0 - M)/M_0$, the conversion equation is $x = (1 + \alpha)\,[1 - \exp(-k_{\mathrm{p}} I_0 t)]$, the parameter $\gamma_{\mathrm{sp}} = k_{\mathrm{sp}}/(k_{\mathrm{p}} I_0)$ characterizes the intensity of spontaneous transfer, and $\alpha = k_{\mathrm{sp}}/(k_{\mathrm{p}} M_0)$.

Transfer to a polymer exerts no influence on the number-mean degree of polymerization, since the number of chains remains constant in this reaction. However, transfer to a polymer leads to the formation of a branched polymer, thus extending the molecular weight distribution. The influence of this reaction on the molecular-weight distribution has been investigated theoretically in [21, 22] in detail.

To calculate the weighted-mean and z-mean degree of polymerization we consider the system of equations (8) for the distribution of macromolecules by length and by the number of active centers. Having passed from the time dependence to a conversion one, with account for $\frac{dR(i, l)}{dt} = k_{\mathrm{p}} I_0 (1 + \alpha - 1) \frac{dR(i, l)}{dx} \xrightarrow{\qquad} d/dt =$ $= [k_{\mathrm{p}} I_0 (1 + \alpha - x)]\, d/dx\}$ upon introduction of the dimensionless concentrations of the chains $r_i(z) = \beta R(i, l)/I_0$ $(z = l/\beta)$ from (8) we obtain the equation

$$(1 - x + \alpha) \frac{\partial r_i}{\partial x} = - i\,(1 - x) \frac{\partial r_i}{\partial z} + \gamma_{\mathrm{t.p}} z\,(r_{i-1} - r_i) + (\gamma_{\mathrm{t.p}} x + \gamma_{\mathrm{sp}})\,((i + 1)\, r_{i+1} - i r_i) + \gamma_{\mathrm{sp}} \delta_{i,1} \delta(z)\,,$$

$$i = 0, 1, 2, \ldots\,. \tag{9}$$

In deriving Eq. (9), we have used the approximation of long chains; $\beta = M_0/I_0$ is the theoretical degree of polymerization and the parameter $\gamma_{\mathrm{t.p}} = \beta k_{\mathrm{t.p}}/k_{\mathrm{p}}$ characterizes the intensity of the transfer to a polymer.

To solve (9) we introduce the function

$$F(s, p, x) = \sum_{i=0}^{\infty} s^i \int_0^{\infty} \exp(-pz)\, r_i(z)\, dz\,,$$

which is the analog of the generating distribution function.

We obtain the equation for the function F by multiplying each term of Eqs. (9) by $s^i \exp(-pz)$, summing up with respect to i, and integrating with respect to z:

$$(1 - x + \alpha) \frac{\partial F}{\partial x} + (1 - x)\, sp \frac{\partial F}{\partial s} + (\gamma_{\mathrm{sp}} + \gamma_{\mathrm{t.p}} x) \frac{\partial F}{\partial s} (s - 1) + \gamma_{\mathrm{t.p}} \frac{\partial F}{\partial s} (s - 1) = \gamma_{\mathrm{sp}} s\,. \tag{10}$$

From the initial condition for $R(i, l)$ we find the initial condition $F(s, p, x = 0) = s$.

The arbitrary statistical moment of the molecular-weight distribution μ_k is related to F by the relation

$$\mu_k \equiv \sum_i \int l^k R(i, l) = (-1)^k I_0 \beta^k \left. \frac{\partial^k F}{\partial p^k} \right|_{s=1,\, p=0}.$$

We introduce the following notation: $J_{ij} = \left.\dfrac{\partial^{i+j}F}{\partial s^i \partial p^j}\right|_{s=1,p=0}$ is the derivative of F of order $(i+j)$. By definition of the moments of the molecular-weight distribution $\mu_k = (-1)^k I_0 \beta^k J_{0k}$. For the derivatives of zero order and first order we have the obvious relations determined by their physical meaning:

$J_{00} - 1 - \gamma_{\text{sp}} \ln \dfrac{1 - x + \alpha}{1 + \alpha}$ is the total number of chains (it is referred to I_0),

$J_{01} = -x$ is the amount of the polymer formed (referred to M_0),

and $J_{10} = 1$ is the total concentration of the active centers (it is referred to I_0).

The equations for the derivatives of higher order are obtained in differentiating (10) with respect to s and p as many times as necessary.

For the derivatives of second order and third order for $s = 1$ and $p = 0$ the corresponding equations have the form

$$(1 - x + \alpha)\frac{dJ_{20}}{dx} + 2\,(\gamma_{\text{t.p}}x + \gamma_{\text{sp}})\,J_{20} + 2\gamma_{\text{t.p}}\,J_{11} = 0\,,$$

$$(1 - x + \alpha)\frac{dJ_{11}}{dx} + (\gamma_{\text{t.p}}x + \gamma_{\text{sp}})\,J_{11} + (1 - x)\,(J_{20} + 1) + \gamma_{\text{t.p}}\,J_{02} = 0\,,$$

$$(1 - x + \alpha)\frac{dJ_{02}}{dx} + 2\,(1 - x)\,J_{11} = 0\,,$$

$$(1 - x + \alpha)\frac{dJ_{03}}{dx} + 3\,(1 - x)\,J_{12} = 0\,,$$

$$(1 - x + \alpha)\frac{dJ_{12}}{dlx} + 2\,(1 - x)\,J_{11} + 2\,(1 - x)\,J_{21} + (\gamma_{\text{t.p}}x + \gamma_{\text{sp}})\,J_{12} + 3\gamma_{\text{t.p}}\,J_{03} = 0\,, \tag{11}$$

$$(1 - x + \alpha)\frac{dJ_{21}}{dx} + 2\,(1 - x)\,J_{20} + 2\,(\gamma_{\text{sp}} + \gamma_{\text{t.p}}x)\,J_{21} + (1 - x)\,J_{30} + 2\gamma_{\text{t.p}}\,J_{12} = 0\,,$$

$$(1 - x + \alpha)\frac{dJ_{30}}{dx} + 3(\gamma_{\text{t.p}}x + \gamma_{\text{sp}})\,J_{30} + 2\gamma_{\text{t.p}}\,J_{21} = 0\,.$$

When $x = 0$, $J_{11} = J_{20} = J_{02} = J_{03} = J_{12} = J_{21} = J_{30} = 0$.

The relations for the derivatives of second order and third order are necessary to calculate the weighted-mean and z-mean degrees of polymerization:

$$\mu_1 = -\,I_0\,\beta J_{01} = I_0\,\beta x\,,\quad \mu_2 = I_0\,\beta^2 J_{02}\,,\quad \mu_3 = -\,I_0\,\beta^3 J_{03}\,,\quad P_{\text{w}} = \frac{\mu_2}{\mu_1} = \frac{\beta J_{02}}{x}\,,\quad P_{\text{z}} = \frac{\mu_3}{\mu_2} = -\,\beta\,\frac{J_{03}}{J_{02}}\,.$$

The polydispersity coefficients are computed from the formulas

$$k_{\text{w/n}} = \frac{P_{\text{w}}}{P_{\text{n}}} = \frac{J_{02}\left(1 + \gamma_{\text{t.m}}x - \gamma_{\text{sp}}\ln\left(\dfrac{1 - x + \alpha}{1 + \alpha}\right)\right)}{x^2}\,,\quad k_{\text{z/w}} = \frac{P_{\text{z}}}{P_{\text{w}}} = -\,\frac{xJ_{03}}{J_{02}^2}\,.$$

System (11) has an analytical solution which, however, is rather cumbersome and is expressed in terms of exponential integral functions inconvenient for use; therefore, it is more expedient to analyze the dependence of the mean degrees of polymerization on the parameters of the intensities of chain transfer $\gamma_{\text{t.p}}$ and γ_{sp} using numerical integration of system (11).

Taking account of the cross-linking of polymer macromolecules. In this case, the system of kinetic equations for polymerization products has the form

$$\frac{dM}{dt} = -k_{\text{p}} M I_0\,, \quad R = \sum_{i=0}^{\infty} i \int_0^{\infty} R(i, l)\, dl = I_0\,,$$

$$\frac{\partial R(i, l)}{\partial t} = -ik_{\text{p}} M \frac{\partial R(i, l)}{\partial l} + (k_{\text{sp}} + k_{\text{t.m}} M)\,[(i+1)\, R(i+1, l) - iR(i, l)] + (k_{\text{sp}} + k_{\text{t.m}} M)\, I_0 \delta_{i,1} \delta(l) +$$

$$+ \frac{k_{\text{c}}}{2} \sum_{j=0}^{i} \int_0^{l} [j(l-n) + n(i-j)]\, R(j, n)\, R(i-j, l-n)\, dn - k_{\text{c}} R(i, l) \sum_{j=0}^{\infty} \int_0^{\infty} (in + jl) \times \qquad (12)$$

$$\times R(j, n)\, dn\,, \quad i = 0, 1, 2, \ldots\,.$$

The rate of the reaction of cross-linking of the macromolecules is in proportion to $k_{\text{c}}(in + jl)$, i.e., depends on the number of active centers of the interacting molecules and on their lengths.

For the auxiliary function $f = \sum_{i=0}^{\infty} s \int_0^{\infty} \exp(-pl)\, R(i, l)\, dl$, from (12) we obtain the equation

$$\frac{\partial f}{\partial x} = -\beta sp \frac{\partial f}{\partial s} + \left(\frac{\gamma_{\text{sp}}}{1-x} + \gamma_{\text{t.m}}\right)(s-1) \frac{\partial f}{\partial s} + \left(\frac{\gamma_{\text{sp}}}{1-x} + \gamma_{\text{t.m}}\right) I_0 s - \frac{\gamma_{\text{c}}}{1-x} s \frac{\partial f}{\partial s} \frac{\partial f}{\partial p} - \frac{\gamma_{\text{c}}}{1-x} \left(\mu_1 s \frac{\partial f}{\partial s} - I_0 \frac{\partial f}{\partial p}\right), \qquad (13)$$

where the parameter $\gamma_{\text{c}} = k_{\text{c}}/(k_{\text{p}} I_0)$ characterizes the intensity of cross-linking of the polymer molecules.

By differentiating Eq. (13) with respect to s and p as many times as necessary, we obtain the system of equations to compute the statistical moments of the molecular-weight distribution

$$\frac{d\mu_0}{dx} = \left(\frac{\gamma_{\text{sp}}}{1-x} + \gamma_{\text{t.m}}\right) I_0 - \frac{\gamma_{\text{c}}}{1-x} I_0 \mu_1\,,$$

$$\mu_1 = M_0 x\,,$$

$$\frac{d\mu_2}{dx} = -2\beta J_{11} - 2 \frac{\gamma_{\text{c}}}{1-x} \mu_2 J_{11}\,,$$

$$\frac{dJ_{11}}{dx} = -\beta I_0 - \beta J_{20} - \left(\frac{\gamma_{\text{sp}}}{1-x} + \gamma_{\text{t.m}}\right) J_{11} + \frac{\gamma_{\text{c}}}{1-x} (I_0 \mu_2 + J_{11}^2 + J_{20} \mu_2)\,,$$

$$\frac{dJ_{20}}{dx} = -2 \left(\frac{\gamma_{\text{sp}}}{1-x} + \gamma_{\text{t.m}}\right) J_{20} + 2 \frac{\gamma_{\text{c}}}{1-x} (I_0 J_{11} + J_{20} J_{11})\,,$$

$$\frac{d\mu_3}{dx} = -3\beta J_{12} - \frac{\gamma_{\text{c}}}{1-x} (3\mu_2 J_{11} - 3\mu_3 J_{11})\,,$$

$$\frac{dJ_{12}}{dx} = -2\beta (I_{11} + J_{21}) - \left(\frac{\gamma_{\text{sp}}}{1-x} + \gamma_{\text{t.m}}\right) J_{12} - \frac{\gamma_{\text{c}}}{1-x} (2J_{11} \mu_2 - I_0 \mu_3) - \frac{\gamma_{\text{c}}}{1-x} (2J_{21} \mu_2 + 3J_{11} J_{12} - J_{20} \mu_3)\,,$$

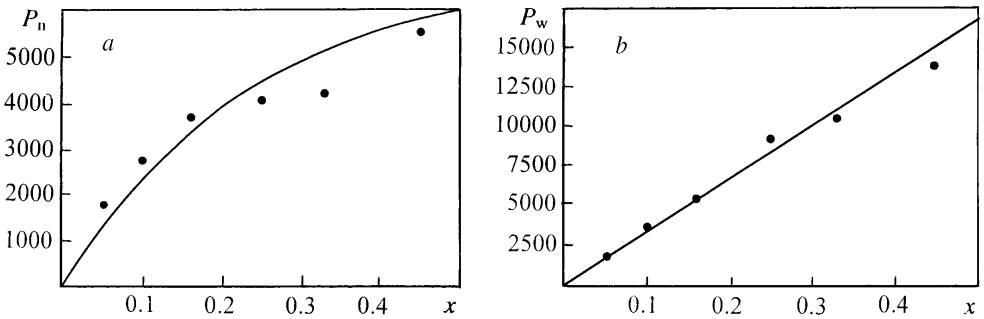


Fig. 1. Change in the number-mean (a) and weighted-mean (b) degree of polymerization as compared to experimental data with account for the transfer to a polymer ($k_{t.p} = 0.6$, $k_p = 297.2$, $k_{t.m} = 0.012$, $k_c = 0$, $k_{sp} = 0.03$, $I_0 = 0.00006$ mole/liter, and $M_0 = 1.85$ mole/liter): points, experiment; curve, calculation.

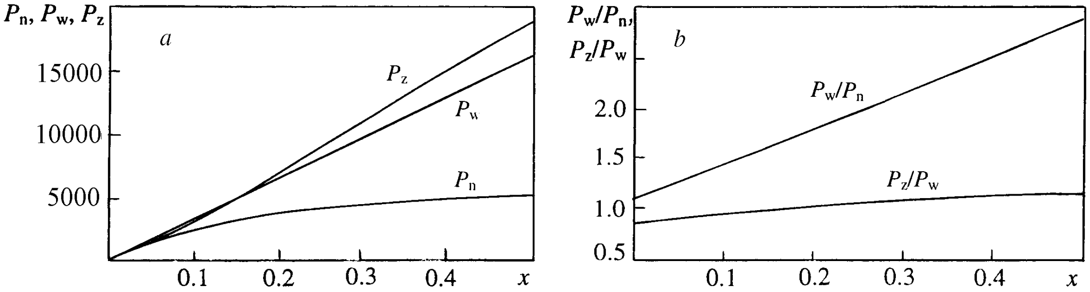


Fig. 2. Change in the number-mean, weighted-mean, and sedimentation-mean degree of polymerization (a) and in the polydispersity coefficients P_w/P_n and P_z/P_w (b) with account for the transfer of a chain to a polymer for the parameters indicated in Fig. 1.

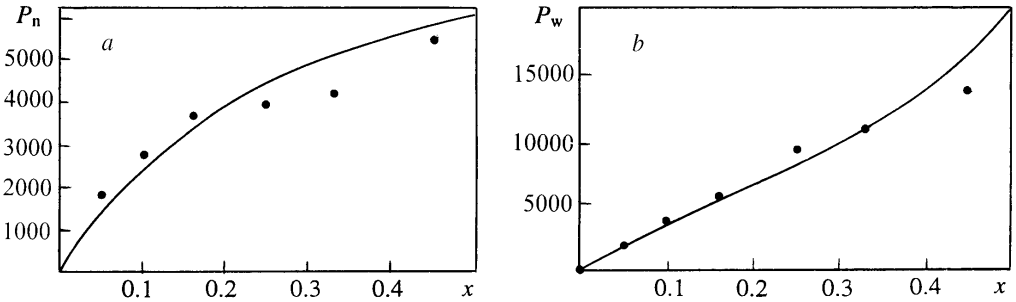


Fig. 3. Change in the number-mean (a) and weighted-mean (b) degree of polymerization as compared to experimental data with account for cross-linking ($k_{t.p} = 0$, $k_p = 297.2$, $k_{t.m} = 0.004$, $k_c = 0.008$, $k_{sp} = 0.0395$, $I_0 = 0.00006$ mole/liter, and $M_0 = 1.85$ mole/liter): points, experiment; curve, calculation.

$$\frac{dJ_{21}}{dx} = -2J_{20} - J_{30} - 2\left(\frac{\gamma_{sp}}{1-x} + \gamma_{t.m}\right)J_{21} - \frac{\gamma_c}{1-x}\left(2J_{20}\,\mu_2 + 2J_{12}I_0 + J_{30}\,\mu_2 + 2J_{11}^2 + J_{30}\,\mu_2 + 3J_{21}J_{11} + J_{20}J_{12}\right),$$

$$\frac{dJ_{30}}{dx} = -3\left(\frac{\gamma_{sp}}{1-x} + \gamma_{t.m}\right)J_{30} - \frac{\gamma_c}{1-x}\left(6J_{20}J_{11} + 3J_{21}I_0 + 3J_{30}J_{11} + 3J_{20}J_{21}\right). \tag{14}$$

The initial conditions are as follows: when $x = 0$, $\mu_0 = I_0$ and $\mu_1 = \mu_2 = \mu_3 = J_{11} = J_{20} = J_{12} = J_{21} = J_{30} = 0$.

Results. The adequacy of the models was checked against the experimental data of the literature source [16]. The results of the calculations according to two different kinetic schemes are presented in Figs. 1–4. The error of the

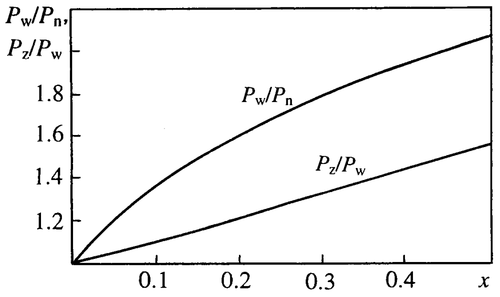


Fig. 4. Change in the polydispersity coefficients P_w/P_n and P_z/P_w with account for cross-linking for the parameters indicated in Fig. 3.

computations according to the scheme with account for the transfer to a polymer amounted to 26.3%, while the error of the computations according to the scheme with account for the cross-linking reaction amounted to 20.1%. Consequently, we can tentatively infer that the second kinetic scheme describes the process more adequately, i.e., polymerization occurs predominantly by means of conjugate double bonds through cross-linking of the macromolecules. The mathematical model presented can be used as the basis for optimization of the process of synthesis of SKDK rubber.

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NOTATION

P^*, active polymer chain; P, "dead" polymer chain; HCoX^*, active cobalt complex; $R(i', l')$, concentration of growing chains with the number of active centers i' and chain length l'; i, number of active centers in the macromolecule; k_i, initiation rate constant; $k_{t.m}$, rate constant of chain transfer to a monomer; k_p, growth rate constant; k_{sp}, rate constant of spontaneous chain transfer; $k_{t.p}$, rate constant of chain transfer to a polymer; k_{ri}, reinitiation rate constant; k_c, cross-linking rate constant; k_d, deactivation rate constant; l, number of monomer links in the macromolecule; t, time; $\delta_{i,j}$, Kronecker function; i, concentration of the initiator; I_0, initial content of the initiator; M, concentration of the monomer; M_0, initial concentration of the monomer; S^*, concentration of the intermediate active particles; $R(i, l)$, macromolecule with i active centers and l monomer links; P_n, number-mean degree of polymerization; P_w, weighted-mean degree of polymerization; P_z, z-mean degree of polymerization; α, parameter characterizing the rate of spontaneous transfer; β, degree of polymerization of the polymer in the case of total conversion; $\gamma_{t.m}$, intensity of transfer of a chain to a monomer; γ_{sp}, intensity of spontaneous chain transfer; $\gamma_{t.p}$, intensity of transfer of a chain to a polymer; γ_c, intensity of cross-linking of polymer molecules; μ_k, statistical moment of the molecular-weight distribution of kth order; z, s, and p, auxiliary variables; $k_{w/n}$ and $k_{z/w}$, polydispersity coefficients; SKDK, synthetic divinyl rubber on a cobalt catalyst. Subscripts: i, initiation; t.m, transfer to a monomer; p, growth of the chain; sp, spontaneous chain transfer; t.p, transfer to a polymer, ri, reinitiation; c, cross-linking; d, deactivation; n, number; w, weight; *, "living" chain.

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