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# DETERMINATION OF THE OPTIMUM CONDITIONS FOR SYNTHESIS OF A DIENE RUBBER BASED ON A NEODYMIUM-CONTAINING CATALYTIC SYSTEM WITH DEFINITE BRANCHING CHARACTERISTICS

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*A mathematical simulation of the concurrent processes of heat exchange and chemical transformation in the synthesis of a diene rubber based on a neodymium-containing catalytic system (CDNR) in a cascade of continuous reactors has been carried out. A model is proposed for investigating the branching of the CDNR. The problem of optimization of the polymerization of a butadiene rubber based on a neodymium-containing catalyst was solved for the case of an increasing number of reactors in a cascade.*

At present, the possibility of use of compounds of 4*f*-elements for polymerization of linked dienes is being intensively investigated. The prospects and advisability of the use of lanthanoid catalytic systems for the synthesis of a butadiene rubber are determined first of all by the useful properties of the polymer obtained: large molecular mass, stereoregularity (the content of 1,4-cis-links reaches 99%), and absence of a gel. An important property of lanthanoids is their nontoxicity, which makes it possible to use them widely in pharmacology and medicine. Polymers obtained with these catalysts demonstrate a high efficiency as well as excellent physical, mechanical, and technological characteristics.

However, a butadiene rubber obtained on the basis of a neodymium catalyst has, along with advantages, certain disadvantages associated with a cold flow, a narrow molecular-mass distribution, and the absence of branched molecules. In this case, a small cross-linking of chains can prevent a cold flow. Modern methods of polymerization allow one to attain this result via the formation of a small number of branchings. When ethyl aluminum sesquichloride is used instead of diisobutyl aluminum chloride, the content of chloride ions in the catalytic system is increased, and an additional halogenation of the active centers makes it possible to a decrease the cold flow.

The activity of catalytic systems containing halogenides of lanthanoids depends on the nature of the halogen. For example, the ultimate production of a polymer based on a neodymium-containing catalytic system in the presence of a chlorine-containing component is larger as compared to other halogens [1]. In this case, the hydride complex $HNdCl_2$ adds to the growing chain with the formation of an additional active center, which leads to polymer transfer.

Thus, an increase in the content of the chlorine-containing compound in the molar ratio [Cl/Nd] to 2–2.5 increases the branching of the polymer, which influences the plastoelastic properties of the rubber. In this case, the cold flow of the rubber decreases and its polydispersity increases; however, the microstructure of the rubber (the content of 1,4-cis-links) remains unchanged. Moreover, it was established that the branching of the rubber and, accordingly, its cold flow depend on the temperature at which it is synthesized [2, 3].

In the present work, a mathematical simulation of the polymerization of a butadiene rubber on the basis of a neodymium catalyst in a cascade of well-stirred continuous reactors of volume $V$ has been carried out. It was assumed that the volumetric rate of flow $V_{\text{mix}}$ of the monomer and the initiator fed into the first reactor is constant and that their average residence time $\tau$ in the reactor of volume $V$ is equal to $V/V_{\text{mix}}$. The concentrations of the monomer and the initiator in the incoming flow are $M_0$ and $I_0$ respectively.

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Analysis of the mechanism of the process being investigated has shown that this process proceeds by the following kinetic scheme:

| | |
|---|---|
| Initiation | $I_0 + M \xrightarrow{k_i} R(1, 1)$ |
| Chain propagation | $R(i, l) + M \xrightarrow{k_r} R(i, l+1)$ |
| Chain transfer to the organoaluminum compound | $R(i, l) + [\mathrm{Al}] \xrightarrow{k_{\mathrm{t.Al}}} R(i-1, l) + R(1, 1)$ |
| Inherent chain transfer | $R(i, l) + \mathrm{M} \xrightarrow{k_{\mathrm{t.m}}} R(i-1, l) + R(1, l)$ |
| Spontaneous chain transfer realized in two stages | (a) chain transfer itself $R(i, l) \xrightarrow{k_{\mathrm{sp}}} R(i-1, l) + S^*$<br>(b) reinitiation $S^* + M \xrightarrow{k_{\mathrm{ri}}} R(1, l)$ |
| Polymer transfer | $R(i, l) + R(i', l') \rightarrow \xrightarrow{k_{\mathrm{t.p}}\, i'\, l} R(i+1, l) + R(i'-1, l')$<br>$\xrightarrow{k_{\mathrm{t.p}}\, i'\, l} R(i-1, l) + R(i'+1, l')$ |
| Deactivation | $R(i, l) \xrightarrow{k_d} R(i-1, l)$ |

The polymer-transfer reaction does not changes the number-averaged degree of polymerization $P_n$; however, it serves to form a branched polymer and not a linear one as in the case of spontaneous chain transfer and inherent chain transfer. Because of this, it is necessary to introduce one more parameter characterizing the number of branchings of a macromolecule $b$. Using the laws of polymerization kinetics, we will pass from the kinetic scheme to a system consisting of an infinite number of differential equations:

$$\frac{dM_k}{dt} = \frac{M_{k-1} - M_k}{\tau} - k_{rk} M_k I_0 , \quad \frac{d\,[\mathrm{Al}]_k}{dt} = \frac{[\mathrm{Al}]_{k-1} - [\mathrm{Al}]_k}{\tau} - k_{\mathrm{t.Al}k}\,[\mathrm{Al}]_k I_0 ,$$

$$\begin{aligned} \frac{\partial R_k(b, i, l)}{\partial t} &= \frac{R_{k-1}(b, i, l) - r_k(b, i, l)}{\tau} - i k_{rk} M_k \frac{\partial R_k(b, i, l)}{\partial l} + \\ &+ k_{\mathrm{t.p}k} l I_0 \Big[ R_k(b-1, i-1, l) - R_k(b, i, l) \Big] + \\ &+ \Big( k_{\mathrm{t.p}k} M_0 x_k + k_{\mathrm{sp}k} + k_{\mathrm{t.m}k} M_k + k_{\mathrm{t.Al}k}\,[\mathrm{Al}]_k \Big) \Big[ (i+1)\, R_k(b, i+1, l) - i R_k(b, i, l) \Big] + \\ &+ \frac{I_0}{\tau} \delta_{k,1} \delta_{b,0} \delta_{i,1} \delta(l) + \Big( k_{\mathrm{sp}k} + k_{\mathrm{t.m}k} M_k + k_{\mathrm{t.Al}k}\,[\mathrm{Al}]_k \Big) I_0 \delta_{i,1} \delta_{b,0} \delta(l) . \end{aligned} \tag{1}$$

According to the kinetic scheme, the system of equations (1) defines the time change in the concentrations of the monomer, the organoaluminum compound, and the growing chains in the $k$th reactor of the cascade. The first terms of Eqs. (1) characterize the supply of the substance to the reactor and the removal of it from the reactor.

We now determine the ratio between the average lengths of the main chain $L_m$ and the side branches $L_b$. Let us denote the concentrations of macromolecules with an active main chain and a cold main chain of length $l$ by $N_{ak}$ and $N_{ck}$ respectively. The average length of the main chain is determined as

$$L_{mk} = \frac{\int\limits_0^\infty l\,(N_{ak} + N_{ck})\, dl}{\int\limits_0^\infty (N_{ak} + N_{ck})\, dl} .$$

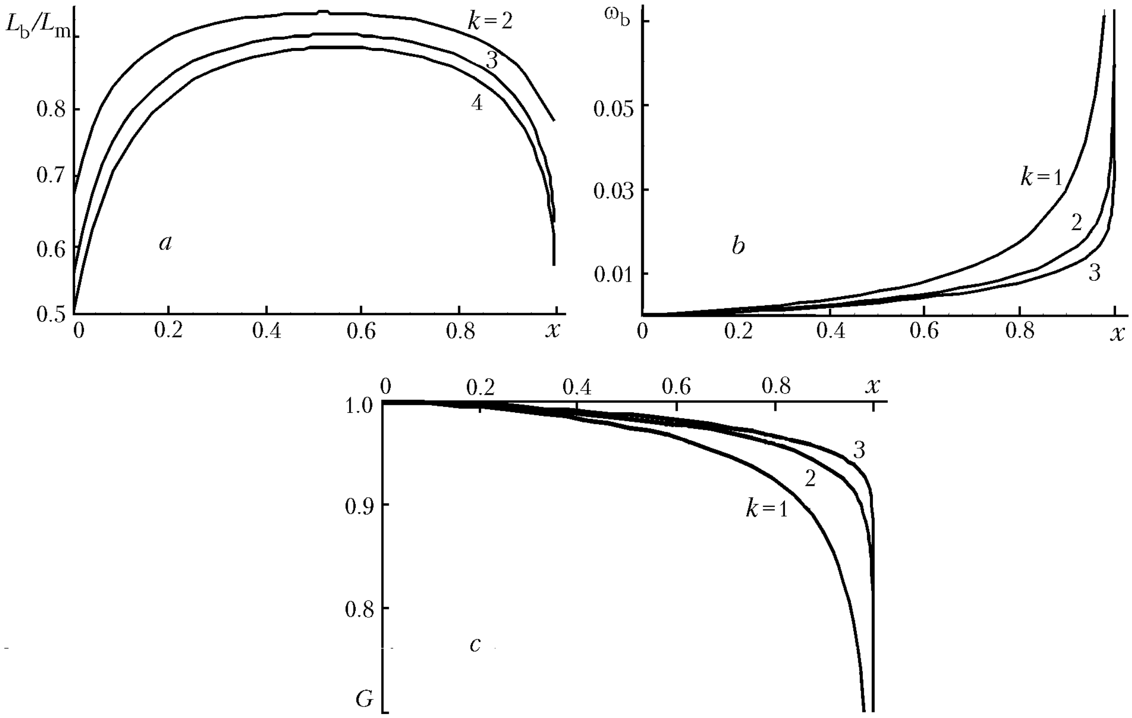

Fig. 1. Dependence of the ratio between the length of the side branches $L_b$ and the length of the main chain $L_m$ (a), the weight fraction of the polymer in the side branches (b), and the $G$-factor (c) on the conversion for the cases of different numbers of reactors in a cascade (isothermic regime).

The stationary system of equations for $N_{ak}$ and $N_{ck}$ has the form

$$\frac{\partial N_{ak}(l)}{\partial t} = \frac{N_{ak-1} - N_{ak}}{\tau} - k_{rk} M_k \frac{\partial N_{ak}}{\partial l} - k_{t.pk} M_0 x_k N_{ak} - k_{spk} N_{ak} - k_{t.mk} M_k N_{ak} -$$

$$- k_{t.Alk}\,[\mathrm{Al}]_k N_{ak} + \left(\frac{I_0}{\tau}\,\delta_{k,1} + k_{spk} I_0 + k_{t.mk} M_k I_0 + k_{t.Alk}\,[\mathrm{Al}]_k I_0\right) \delta\,(l) = 0\,, \tag{2}$$

$$\frac{\partial N_{ck}(l)}{\partial t} = \frac{N_{ck-1} - N_{ck}}{\tau} + k_{t.pk} M_0 x_k N_{ak} + k_{spk} N_{ak} + k_{t.mk} M_k N_{ak} + k_{t.Alk}\,[\mathrm{Al}]_k N_{ak} = 0\,.$$

From system (2), we find an expression for $L_{m,1}$ in the first reactor

$$L_{m,1} = \frac{\int\limits_0^\infty l\,(N_{a,1} + N_{c,1})\,dl}{\int\limits_0^\infty (N_{a,1} + N_{c,1})\,dl} = \frac{\beta x_1}{1 + \varphi_1 \left(\gamma_{t.p,1} x_1 + \gamma_{sp,1} + \gamma_{t.m,1}(1 - x_1) + \dfrac{\gamma_{t.Al,1}}{1 + \dfrac{\gamma_{t.Al,1}\varphi_1}{\varepsilon}}\right)}\,. \tag{3}$$

The average length of the side branches can be determined from the relation

$$L_{bk} = \frac{W_{bk}}{N_{bk}} = \frac{M_0 x_k - W_{mk}}{N_{mk}\rho_{bk}}\,,$$

where $W_{bk}$ and $W_{mk}$ are the weights of the polymer in the side and main chains respectively. It follows herefrom that

$$L_{b,1} = \frac{\beta x_1}{1 + \varphi_1 \left( \gamma_{t.p,1} x_1 + \gamma_{sp,1} + \gamma_{t.m,1} (1 - x_1) + \dfrac{\gamma_{t.Al,1}}{1 + \dfrac{\gamma_{t.Al,1}\varphi_1}{\varepsilon}} \right)},$$

i.e., $L_{m,1} = L_{b,1}$ in the first reactor. This is explained by the fact that, in a well-stirred reactor, all the active centers in both the main chain and the side branches have equal probabilities for growth. The formulas for the second and third reactors were obtained analogously. They show that the ratio $L_b/L_m$ decreases when the number of reactors in a cascade increases (Fig. 1a). Relatively long side chains practically cease to form at a conversion of 0.7. The branches formed at a stronger conversion do not influence the properties of the polymer.

From Eqs. (1) it follows that the average number of branchings of individual macromolecules in the *k*th reactor is equal to

$$\rho_{bk} = \frac{\int\limits_0^\infty \sum\limits_{b,l} bR_k (b, i, l)\, dl}{\int\limits_0^\infty \sum\limits_{b,l} R_k (b, i, l)\, dl} = \frac{\sum\limits_k \gamma_{t.pk} \varphi_k x_k}{1 + \sum\limits_k \varphi_k \left( \gamma_{spk} + \gamma_{t.mk} (1 - x_k) + \gamma_{t.Alk} \Big/ \left( 1 + \dfrac{\gamma_{t.Alk}\varphi_k}{\varepsilon} \right)^{k} \right)}.$$

And in the first reactor, the weight fraction of the polymer in the side branches $\omega_{bk} = W_{bk}/(M_0 x_k)$ is equal to

$$\omega_{b,1} = \frac{M_0 x_1 - L_{m,1} N_1}{M_0 x_1} = \frac{\gamma_{t.p,1} \varphi_1 x_1}{1 + \varphi_1 \left( \gamma_{t.p,1} x_1 + \gamma_{sp,1} + \gamma_{t.m,1} (1 - x_1) + \gamma_{t.Al,1} \Big/ \left( 1 + \dfrac{\gamma_{t.Al,1}\varphi_1}{\varepsilon} \right) \right)}.$$

When the number of reactors increases, the number of branchings of individual macromolecules and, accordingly, the weight fraction of the polymer in the side branches substantially decreases at a strong conversion (Fig. 1b).

The influence of the branching of polymers on their hydrodynamic properties can be estimated using the *G*-factor. In the case that is most closest to the case being considered (branches of different sizes are statistically distributed between the macromolecules), the ratio between the undisturbed mean-square radii of a branched polymer $\langle S^2 \rangle_b$ and a linear $\langle S^2 \rangle_{lin}$ polymer is determined by the formula

$$g \equiv \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_{lin}} = 1 - \omega_b - \frac{3\omega_b^2}{r_b} + \frac{\omega_b^3}{r_b^2}.$$

We will determine the *G*-factor as the ratio between the characteristic viscosities of these polymers:

$$G \equiv \frac{[\eta]_b}{[\eta]_{lin}} = g^{1.5 - \omega_b},$$

where $[\eta]_{lin}$ and $[\eta]_b$ are the characteristic viscosities of the linear and branched polymers respectively. It is seen that the *G*-factor increases with increase in the number of reactors in the cascade and, accordingly, the branching of the polymer decreases (Fig. 1c).

We have carried out numerical experiments for an actual production process of synthesis of a CDNR. The corresponding heat-balance equation for the *k*th reactor of the cascade has the form

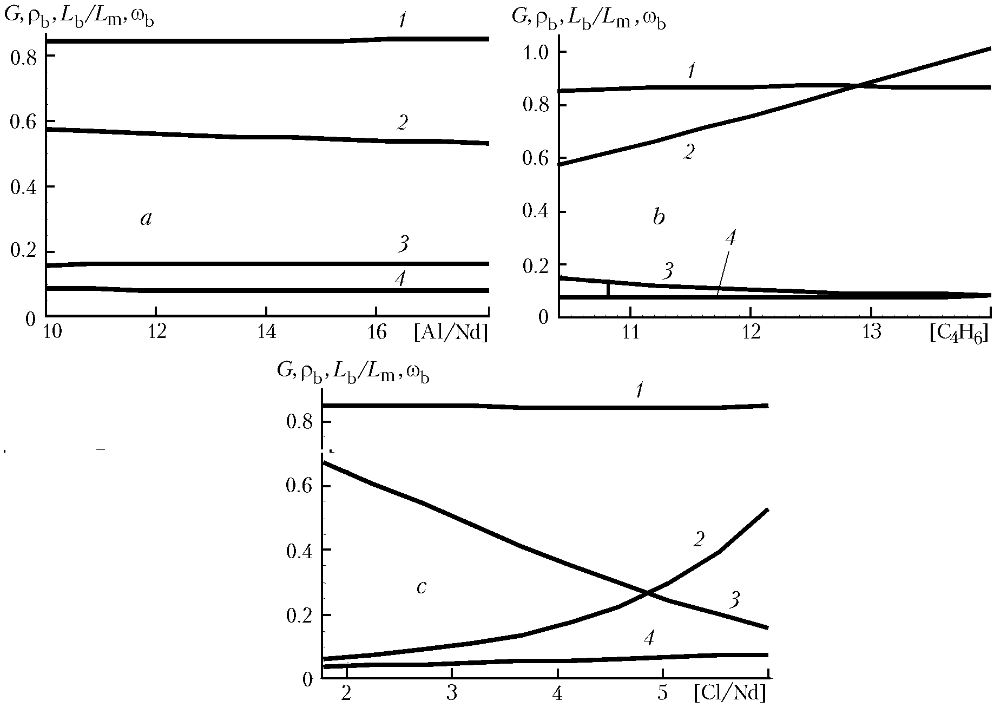

Fig. 2. Dependence of the $G$-factor (1), the average number of branchings of individual macromolecules $\rho_b$ (2), the ratio between the length of the side branches and the length of the main chain $L_b/L_m$ (3), and the weight fraction of the polymer in the side branches $\omega_b$ (4) on the aluminum concentration [Al/Nd] (a), monomer concentration [$C_4H_6$] (b), and the chlorine concentration [Cl/Nd] (c). $G_{mix}$ = 50 tons/h. $\rho_b$, kg/m$^3$; [Al/Nd], [Cl/Nd], mole %; [$C_4H_6$], weight %.

$$(T_k - T_{k-1}) + \frac{G_{c.a}c_{c.a}}{G_{mix}c_{mixk}}\left(1 - \exp\left[-\frac{K_{h.tk}F}{G_{c.a}c_{c.a}}\right]\right)\left(T_k - T^{in}_{c.a}\right) =$$

$$= \frac{(-\Delta H)\, m}{c_{mixk}\,\rho_{mixk}} I_0 M_0 (1 - x_k)\, \tau k^0_{rk} \exp\left[-\frac{E_k}{RT_k}\right].$$

The concurrent processes of heat transfer and chemical transformation were calculated by the methods and algorithms presented in [4]. Unlike the optimization of the process of synthesis of the CDNR, the optimum conditions for the synthesis of a butadiene rubber based on a neodymium-containing catalyst were determined for the case of increasing number of reactors in a cascade; therefore, it may be inferred that the production of the polymer increases with increase in the number of reactors in a cascade.

The conditions of synthesis of the polymer being investigated were optimized on the basis of the kinetic model of the process developed by us, which defines the change in the rate of the polymerization reaction and in the structure of the polymer with time and space depending on the temperature, the concentration of reagents, and other factors. As a criterion of optimum conditions of the polymerization process, the maximum productive capacity of a cascade of polymerization reactors was used. As the optimization parameters, we used the concentrations of the monomer [$C_4H_6$], neodymium [Nd], and the organoaluminum compound $[Al]_0$ as well as the temperature $T^{in}$ and the flow rate $G_{mix}$ of the reaction mixture at the input of the first reactor of the cascade. The limits set on the productive capacity of the polymerizers correspond to the conditions necessary for the obtaining a synthetic rubber of certain quality:

1) the number-averaged molecular mass of the polymer $M_n \leq$ 150 ths units;

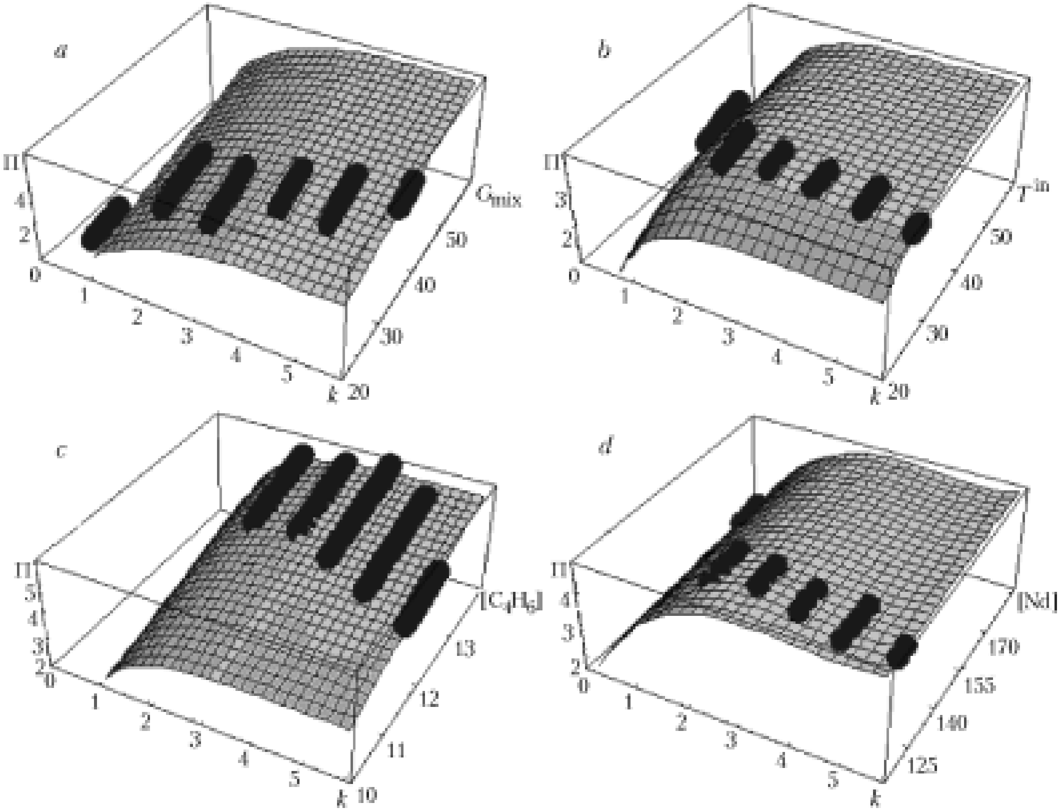

Fig. 3. Dependence of the productive capacity of a cascade of reactors on the number of reactors and the flow rate of the mixture (a) ([Nd] = 0.00009 mole/liter), the temperature at the input (b) ([Nd] = 130 kg/h, $G_{mix}$ = 35 tons/h), the monomer concentration (c) ([Nd] = 130 kg/h, $G_{mix}$ = 40 tons/h), neodymium concentration (d) ($G_{mix}$ = 40 tons/h): a, b, d) $T^{in}$ = 30°C; a, c, d) $[C_4H_6]$ = 12 wt. %; a–d) [Al/Nd] = 18 mole %. Π, tons/h; $G_{mix}$, tons/h; $T^{in}$, °C; $[C_4H_6]$, wt. %; [Nd], kg/h.

2) the polydispersity coefficient $M_w/M_n$ is no more than 3.0;

3) the medium-sedimentation mass of the polymer $M_z \leq 1$ mln units.

The neodymium concentration [Nd] was varied within the range 0.000018–0.00008 mole/liter, the concentration of the monomer $[C_4H_6]$ was varied within the limits 10–15 wt.%, the flow rate of the reaction mixture $G_{mix}$ was changed from 30 to 50 tons/h, and the input temperature $T^{in}$ was varied within the range 20–40°C.

We investigated the influence of the indicated parameters of the polymer being considered on the characteristics of its branching. The results of numerical experiments show that an increase in the concentration of the organoaluminum compound leads to an insignificant decrease in this characteristics and practically has no influence on the branching (Fig. 2a). On the contrary, an increase in the concentration of the monomer decreases the branching, even though the average number of branchings of individual macromolecules increases in this case. This is explained by the fact that the length of the side branches decreases when the concentration of the monomer increases, i.e., highly branched chains with short side branches are formed. Slightly branched chains with long side branches are formed at a low monomer concentration because the weight fraction of the side branches is also very large (Fig. 2c).

To improve the cold-flow value of a rubber, it is necessary to increase its branching. For this purpose, a chlorine-containing component is introduced into the composition of a catalytic complex in the process of the production synthesis. Therefore, we investigated the influence of the concentration of the chlorine-containing component on the main characteristics of the branching of the polymer being investigated. It is seen from Fig. 2c that, when the chlorine concentration increases, the number of branchings increases, the length of the main branch decreases, and the length of

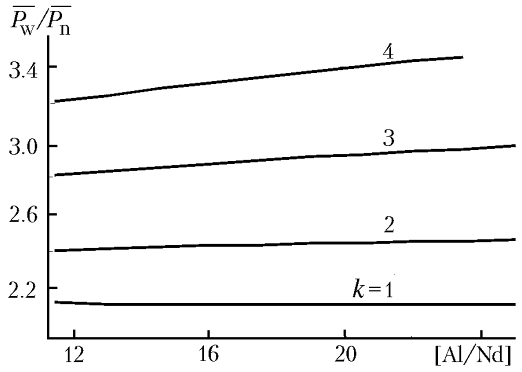

Fig. 4. Dependence of the polydispersity coefficient of the polymer $\overline{P}_w/\overline{P}_n$ on the concentration of the organoaluminum compound for different numbers of reactors. [Al/Nd], wt. %.

the side branch decreases sharply. Thus, the polymer macromolecules become very branched and have very short side branches. Our analysis has shown that an increase in the number of reactors leads to a decrease in the molecular-mass characteristics and widens the molecular-mass distribution.

The production of a polymer depends mainly on the concentration of the monomer as well as the flow rate and the input temperature of the reaction mixture. Figure 3 shows the range of operating parameters at which a rubber of necessary quality is synthesized. It is seen that, when the number of reactors increases, the range of optimum parameters of the process shifts toward the region of increased flow rates of the reaction mixture and decreased input temperatures and concentrations of the monomer and neodymium.

When the neodymium concentration increases in the reaction mixture, the molecular-mass values of the polymer decrease regularly and its polydispersity increases smoothly. The latter also takes place when the concentration of the organoaluminum compound increases; this effect is enhanced with increase in the number of reactors in a cascade (Fig. 4). However, as compared to the periodic process, the influence of the concentration of the organoaluminum compound on the molecular mass and the molecular-mass distribution of the polybutadiene formed is not so significant.

The mathematical model proposed is universal because, depending on the production and customers requirements, it makes it possible to calculate additional characteristics of the polymer obtained with the use of additional mathematical models. Unlike the existing mathematical models, the model proposed can be used for a very wide range of input parameters of the polymerization process because it accounts for the concurrent processes of heat exchange and chemical transformation occurring in this process.

## CONCLUSIONS

1. Relations for calculating the average number of branchings of individual macromolecules of a polymer, the average lengths of its main chain and side branches, the weight fraction of the polymer in the side branches, and the *G*-factor have been derived.

2. The problem on optimization of the conditions for polymerization of butadiene on the basis of a neodymium-containing catalyst in the case of an increasing number of reactors in a cascade has been solved.

3. The influence of the number of reactors in a cascade on the main branching characteristics of the polymer being considered has been analyzed.

4. The optimum conditions of the polymerization process that provide a high-quality polymer with definite molecular-mass characteristics at a maximum productive capacity of a cascade of reactors have been determined.

5. The results of this work can be used as a scientific base for the development of recommendations on the conduction of a production process of synthesis of a butadiene rubber on the basis of a neodymium-containing catalytic system.

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## NOTATION

$[\mathrm{Al}]_0$, initial concentration of the organoaluminum compound (OAC); $[\mathrm{Al}]_k$, current concentration of the OAC; $c_{\mathrm{mix}k}$, specific heat of the mixture in the $k$th reactor; $c_{\mathrm{c.a}}$, specific heat of a unit volume of a cooling agent; $E_k$, total activation energy for the $k$th reactor; $F$, heat-transfer surface; $G_{\mathrm{mix}}$ and $G_{\mathrm{c.a}}$, mass flows of the mixture and the cooling agent in an apparatus; $I_0$, initial concentration of an initiator; $K_{\mathrm{h.t}}$, heat-transfer coefficient; $k$, number of a reactor in a cascade of reactors; $k_{\mathrm{i}}$, $k_{\mathrm{r}}$, $k_{\mathrm{tAl}}$, $k_{\mathrm{t.m}}$, $k_{\mathrm{sp}}$, $k_{\mathrm{ri}}$, $k_{\mathrm{t.p}}$, $k_{\mathrm{d}}$, constants of the rates of initiation, growth, chain transfer to the OAC, inherent chain transfer, spontaneous chain transfer, reinitiation, polymer transfer, and deactivation respectively; $L_{\mathrm{m}}$ and $L_{\mathrm{b}}$, average lengths of the main and side branches; $M_0$, initial concentration of a monomer; $M_k$, current concentration of the monomer; $m$, molecular mass of the monomer; $N_{\mathrm{a}}$ and $N_{\mathrm{c}}$, concentrations of macromolecules with an active and a cold main chain; $N_{\mathrm{b}}$ and $N_{\mathrm{m}}$, concentrations of macromolecules in the side and main chains; $R(b, i, l)$, concentration of macromolecules ($b$, number of branchings; $i$, number of active centers; $l$, length of the chain); $R$, universal gas constant; $P_{\mathrm{n}}$, $P_{\mathrm{w}}$, and $P_{\mathrm{z}}$, number-averaged, weight-averaged, and medium-sedimentation degrees of polymerization; $P_{\mathrm{w}}/P_{\mathrm{n}}$, polydispersity coefficient; $T^{\mathrm{in}}$, temperature of the incoming flow; $T$, average temperature in the reactor; $T^{\mathrm{in}}_{\mathrm{c.a}}$, temperature of the cooling agent at the inlet of the jacket; $t$, current time; $V_{\mathrm{mix}}$ and $V_{\mathrm{c.a}}$, volumetric rate of flow of the reaction mixture and the cooling agent; $W_{\mathrm{b}}$ and $W_{\mathrm{m}}$, weight of the polymer in the side and main branches; $x_k$, conversion of the monomer in the $k$th reactor; $\beta = M_0/I_0$, degree of polymerization of the living polymer in the case of complete conversion; $\delta(l) = \begin{cases} \infty, & l = 0 \\ 0, & l \neq 0 \end{cases}$, Dirac function; $\delta_{\mathrm{i},j}$, Kronecker function; $\varepsilon = [\mathrm{Al}]_0/I_0$, molar ratio between the organoaluminum compound and neodymium; $\Delta H$, heat effect of the polymerization reaction; $\Pi$, productive capacity of the cascade of reactors; $\varphi_k = k_{\mathrm{r}k}I_0\tau$, effective parameter characterizing a well-stirred reactor; $\gamma_{\mathrm{t.m}} = \beta k_{\mathrm{t.m}}/k_{\mathrm{r}}$, $\gamma_{\mathrm{t.p}} = \beta k_{\mathrm{t.p}}/k_{\mathrm{r}}$, $\gamma_{\mathrm{t.Al}} = \varepsilon k_{\mathrm{t.Al}}/k_{\mathrm{r}}$, $\gamma_{\mathrm{sp}} = k_{\mathrm{sp}}/(k_{\mathrm{r}}I_0)$, intensities of the inherent chain transfer, polymer transfer, chain transfer to the OAC, and the spontaneous chain transfer respectively; $\rho_{\mathrm{mix}k}$, density of the mixture in the $k$th reactor; $\rho_{\mathrm{b}}$, average number of branchings of individual macromolecules; $\tau = V/V_{\mathrm{mix}}$, average residence time of the reaction mixture in the reactor; $\omega_{\mathrm{b}}$, weight fraction of the polymer in the side branches. Subscripts: a, active chain; b, side branch; d, deactivation; i, initiation; c, cold chain; n, numerical; ri, reinitiation; sp, spontaneous chain transfer; t, chain transfer; t.m, monomer chain transfer; t.p, polymer chain transfer; w, weight; z, sedimentation; in, input; out, output; h.t, heat transfer; m, main branch; r, chain-propagation reaction; mix, reaction mixture; c.a, cooling agent; 0, initial moment of time; lin, linear polymer.

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