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INVESTIGATION OF SIMULTANEOUS CHEMICAL-TRANSFORMATION AND HEAT-EXCHANGE PROCESS OCCURRING IN THE PROCESS OF SYNTHESIS OF DIVINYL RUBBER ON THE BASIS OF A COBALTOUS CATALYST IN A CASCADE OF TWO CONTINUOUS-OPERATION REACTORS

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A mathematical model of polymerization of butadiene based on a cobaltous catalyst in a cascade of two continuous-operation reactors has been developed. The simultaneous processes of chemical transformations and heat exchange occurring in this case were described by a system of equations for heat balance and initial times of molecular-mass distribution in a steady-state regime. The model developed was used for investigating the dependence of the molecular-mass characteristics of the polymerization process studied and the temperature in the cascade of reactors on the monomer and initiator concentrations as well as for determining the optimum regimes of the polymerization process.

The course of chemical-technological processes and, especially, chemical reactions is mainly determined by their temperature. Therefore, apparatus, particularly chemical reactors in which chemical processes and reactions are conducted should be designed with account for such thermal effects as the liberation, absorption, and transfer of heat occurring in these processes and the influence of temperature on them.

In the general case, an exothermic reaction occurring in a reactor can has at least two important consequences for the reactor and the products obtained. First, in the case of an exothermic reaction, heat is removed incompletely from the reactor, which leads to its thermal self-excited acceleration and unstable operation. Second, variations in the temperature of the polymerization process influence such important parameters of a polymer as the mean molecular mass and the molecular-mass distribution because all kinetic constants are temperature-dependent.

A polymerizer used for obtaining a synthetic divinyl rubber on the basis of a cobaltous catalyst (SDRC) is equipped with a helicoidal mixer with scrapers. Under the action of the mixer, the mixture in this apparatus circulates up along the belt and down along the axis of the apparatus (or the other way round). The circulation loop and local vortices formed near the belt make it possible to obtain homogeneous temperature and concentration fields in the apparatus. The heat exchange in such an apparatus was analyzed in [1, 2]. It has been established that the heat exchange in it can be described in the first approximation with the use of an ideal-mixing model.

The heat-balance equation for a constant volume of different substances in an ideal mixing reactor is written as [3, 4]

$$\tau \frac{dT}{dt} \sum_{j=1}^{\infty} c_j C_j = \sum_{j=1}^{\infty} c_j C_j \left(T^{\text{in}} - T\right) + \tau \sum_{i=1}^{s} \left(-\Delta H_i\right) r_i - \frac{Q_{\text{a}}}{V_{\text{mix}}} . \tag{1}$$

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If the dependence of the heat capacity of a reaction-mixture unit volume $c = \sum_{j=1}^{\infty} c_j C_j$ on the temperature and pressure is neglected, the first term on the right side of Eq. (1) will be equal to $c(T^{\text{in}} - T)$ and the equation for the kth reactor will take the form

$$\tau \frac{dT_k}{dt} = (T_{k-1} - T_k) + \tau \sum_{i=1}^{s} \frac{(-\Delta H_{i,k})}{c_k} r_{i,k} - \frac{Q_{\text{a}k}}{V_{\text{mix}} c_k}\,. \tag{2}$$

In the reactor considered, heat is removed through a jacket with the use of a cooling agent. The form of $Q_{\text{a}k}$ depends on the type of heat-removal system; however, the value of this quantity is always proportional to the difference $\Delta T = T_k - T_{\text{a}}^{\text{in}}$.

In the case of ideal mixing in the reactor jacket [3–5],

$$Q_{\text{a}} = \frac{K_{\text{h}} F V_{\text{a}} c_{\text{a}}}{K_{\text{h}} F + c_{\text{a}} V_{\text{a}}} (T - T_{\text{a}}^{\text{in}})\,. \tag{3}$$

This expression was obtained starting from the following reasonings. If the rate of circulation of a heat-transfer agent is so high that its temperature in the jacket T_{a} is constant, $Q_{\text{a}} = K_{\text{h}} F (T - T_{\text{a}})$. The heat flow removed through the jacket is equal to $Q_{\text{a}} = V_{\text{a}} c_{\text{a}} (T_{\text{a}} - T_{\text{a}}^{\text{in}})$. Eliminating T_{a} from these equations, we obtain dependence (3).

In the case of nonideal mixing in the reactor jacket,

$$Q_{\text{a}} = V_{\text{a}} c_{\text{a}} \left[1 - \exp\left(-\frac{K_{\text{h}} F}{c_{\text{a}} V_{\text{a}}} \right) \right] (T - T_{\text{a}}^{\text{in}})\,. \tag{4}$$

Expression (4) was obtained starting from the following reasonings. If the temperature of the heat-transfer agent in the jacket changes from T_{a}^{in} to $T_{\text{a}}^{\text{out}}$ and it is equal to T in the ideal-mixing reactor,

$$Q_{\text{a}} = K_{\text{h}} F \Delta T_{\text{av}}\,,$$

where

$$\Delta T_{\text{av}} = \frac{(T - T_{\text{a}}^{\text{in}}) - (T - T_{\text{a}}^{\text{out}})}{\ln \left(\dfrac{T - T_{\text{a}}^{\text{in}}}{T - T_{\text{a}}^{\text{out}}} \right)}$$

is the average driving force of heat transfer. In this case, $Q_{\text{a}} = V_{\text{a}} c_{\text{a}} (T_{\text{a}}^{\text{out}} - T_{\text{a}}^{\text{in}})$. Eliminating $T_{\text{a}}^{\text{out}}$ from the last two relations, we obtain Eq. (4), which will be used in the further calculations.

Thermal models of polymerization processes differ mainly in the second term of the right side of Eq. (2). If we restrict ourselves to the consideration of the total heat released at the three main stages of polymerization (chain initiation, chain propagation, and chain transfer), the heat release will be equal to

$$\sum_{j=1}^{s} (-\Delta H_j) = -\Delta H_{\text{i}} r_{\text{i}} - \Delta H_{\text{p}} r_{\text{p}} - \Delta H_{\text{t}} r_{\text{t}}\,.$$

Equations for the total rates of reactions at the stages of chain initiation r_{i}, chain propagation r_{p}, and chain transfer r_{t} were obtained from the kinetic equations. The first two rates are usually equal for all models: $r_{\text{i}} = k_{\text{i}} M$ and

$r_{\mathrm{p}} = k_{\mathrm{p}} M \sum\limits_{i=1}^{\infty} \sum\limits_{l=1}^{\infty} R\,(i,\, l)$. The equations for the chain-propagation rate will be different for different models. They have the following form, depending on the type of model:

$$r_{\mathrm{t}} = \begin{cases} k_{\mathrm{sp}} \sum\limits_{i=1}^{\infty} \sum\limits_{l=1}^{\infty} R\,(i,\, l) \text{ — for spontaneous chain transfer ;} \\ k_{\mathrm{t.m}} \sum\limits_{i=1}^{\infty} \sum\limits_{l=1}^{\infty} R\,(i,\, l) \text{ — for inherent chain transfer etc.} \end{cases}$$

The constants of the elementary stages usually represent Arrhenius temperature functions:

$$k_{\mathrm{p}} = k_{\mathrm{p}}^{0} \exp\left(-\frac{E_{\mathrm{p}}}{RT}\right) = k_{\mathrm{p}}\,(T)\,,$$

$$k_{\mathrm{sp}} = k_{\mathrm{sp}}^{0} \exp\left(-\frac{E_{\mathrm{sp}}}{RT}\right) = k_{\mathrm{sp}}\,(T)\,,$$

$$k_{\mathrm{t.p}} = k_{\mathrm{t.p}}^{0} \exp\left(-\frac{E_{\mathrm{t.p}}}{RT}\right) = k_{\mathrm{t.p}}\,(T)\,,$$

$$k_{\mathrm{t.m}} = k_{\mathrm{t.m}}^{0} \exp\left(-\frac{E_{\mathrm{t.m}}}{RT}\right) = k_{\mathrm{t.m}}\,(T)\,.$$

Using the mathematical model of kinetics of continuous polymerization of butadiene on the basis of a cobaltous catalyst [6, 7], we obtained a system of differential equations for material and heat balance and initial times of the molecular-mass distribution in a steady-state regime:

$$\frac{T_{k-1} - T_k}{\tau} + \frac{(-\Delta H)\, m}{c_{\mathrm{mix}k}\rho_{\mathrm{mix}k}}\, k_{\mathrm{p}k}^{0} \exp\left(-\frac{E_k}{RT_k}\right) I_0 M_0\,(1 - x_k) - \frac{G_{\mathrm{a}} c_{\mathrm{a}}}{G_{\mathrm{mix}} c_{\mathrm{mix}k} \tau}\left[1 - \exp\left(-\frac{K_{\mathrm{h}k} F}{G_{\mathrm{a}} c_{\mathrm{a}}}\right)\right](T_k - T_{\mathrm{a}}^{\mathrm{in}}) = 0\,,$$

$$x_k = \frac{x_{k-1} + \varphi_k}{1 + \varphi_k}\,,$$

$$J_{00,k} = J_{00,k-1} + \delta_{k,1} + [\gamma_{\mathrm{sp}k} + \gamma_{\mathrm{t.m}k}\,(1 - x_k)]\,\varphi_k - \varphi_k \tilde{\gamma}_{\mathrm{c}k} x_k\,,$$

$$J_{01,k} = -\,x_k\,,$$

$$J_{02,k} = \frac{J_{02,k-1} - 2\varphi_k\,(1 - x_k)\, J_{11,k}}{1 + 2\varphi_k \tilde{\gamma}_{\mathrm{c}k} J_{11,k}}\,,$$

$$J_{11,k}\,[1 + \varphi_k \gamma_{\mathrm{sp}k} + \varphi_k \gamma_{\mathrm{t.m}k}\,(1 - x_k) + \varphi_k \gamma_{\mathrm{t.p}k} x_k] + J_{11,k}^{2} \varphi_k \tilde{\gamma}_{\mathrm{c}k} =$$

$$= J_{11,k-1} - \varphi_k\,(1 - x_k)\,(1 + J_{20,k}) - \varphi_k \tilde{\gamma}_{\mathrm{c}k} J_{02,k}\,(1 + J_{20,k}) - \varphi_k \gamma_{\mathrm{t.p}k} J_{02,k}\,,$$

$$J_{20,k}\,[1 + 2\varphi_k \gamma_{\mathrm{sp}k} + 2\varphi_k \gamma_{\mathrm{t.m}k}\,(1 - x_k) + 2\varphi_k\, \tilde{\gamma}_{\mathrm{c}k} J_{11,k} + 2\varphi_k \gamma_{\mathrm{t.p}k} x_k] =$$

$$= J_{20,k-1} - 2\varphi_k \tilde{\gamma}_{\mathrm{c}k} J_{11,k} - 2\varphi_k \gamma_{\mathrm{t.p}k} J_{11,k}\,, \tag{5}$$

$$J_{03,k} = \frac{J_{03,k-1} - 3\varphi_k J_{12,k}\,(1 - x_k + \tilde{\gamma}_{ck} J_{02,k})}{1 + 3\varphi_k \tilde{\gamma}_{ck} J_{11,k}}\,,$$

$$J_{30,k} = \frac{J_{30,k-1} - 3\varphi_k\,[\tilde{\gamma}_{ck} J_{20,k}\,(2J_{11,k} + J_{21,2}) + J_{21,k}\,(\tilde{\gamma}_{ck} + \gamma_{\mathrm{t.p}k})]}{1 + 3\varphi_k\,(\gamma_{\mathrm{sp}k} + \gamma_{\mathrm{t.m}k}\,(1 - x_k) + \tilde{\gamma}_{ck} J_{11,k} + \gamma_{\mathrm{t.p}k} x_k)}\,,$$

$$J_{21,k} = \Big\{J_{21,k-1} - \varphi_k\,[(1 - x_k)\,(2J_{20,k} + J_{30,k}) + 2\tilde{\gamma}_{ck} J_{20,k}\,(J_{02,k} + J_{12,k}) + 2J_{12,k}\,(\tilde{\gamma}_{ck} + \gamma_{\mathrm{t.p}k}) +$$

$$+ \tilde{\gamma}_{ck}\,(2J_{11,k}^2 + J_{30,k} J_{02,k})]\Big\} / [1 + 2\varphi_k\,(\gamma_{\mathrm{sp}k} + \gamma_{\mathrm{t.m}k}\,(1 - x_k)) + 3\varphi_k \tilde{\gamma}_{ck} J_{11,k} + 2\varphi_k \gamma_{\mathrm{t.p}k} x_k]\,,$$

$$J_{12,k} = \Big\{J_{12,k-1} - 2\varphi_k\,[(1 - x_k)\,(J_{11,k} + J_{21,k}) + 2\tilde{\gamma}_{ck} J_{02,k}\,(J_{11,k} + J_{21,k}) +$$

$$+ \tilde{\gamma}_{ck} J_{03,k}\,(1 + J_{20,k}) + J_{03,k} \gamma_{\mathrm{t.p}k}]\Big\} / [1 + \varphi_k\,(\gamma_{\mathrm{sp}k} + \gamma_{\mathrm{t.m}k}\,(1 - x_k)) + 3\tilde{\gamma}_{ck} J_{11,k} + \gamma_{\mathrm{t.p}k} x_k]\,.$$

The terms on the left side of the first equation of system (5) define the changes in the temperature in the kth reactor of the cascade of reactors, caused by the incoming and outward flows (first term), the heat release as a result of the polymerization reaction (second term), and the heat removal through the jacket (third term).

System (5) was solved by the method of changing variables [7] with the use of a Mathematica 4.0 package of applied computer programs. The conversion of the monomer at the output of the first and second reactors is exactly calculated in the following way. The main stage of calculation of the reactor is solution of the stationary equations for a definite initial mixture of reaction products in a definite state [3]. We now consider the heat-balance equation for an ideal-mixing reactor:

$$T_k - T_{k-1} + \frac{G_\mathrm{a} c_\mathrm{a}}{G_\mathrm{mix} c_{\mathrm{mix}k}} \left(1 - \exp\left(-\frac{K_{\mathrm{h}k} F}{G_\mathrm{a} c_\mathrm{a}}\right)\right)(T_k - T_\mathrm{a}^\mathrm{in}) = \frac{(-\Delta H)\,m}{c_{\mathrm{mix}k} \rho_{\mathrm{mix}k}}\, I_0 M_0\,(1 - x_k)\,\tau k_{\mathrm{p}k}^0 \exp\left(-\frac{E_k}{RT_k}\right). \tag{6}$$

Let us denote the right side of the equation, characterizing the increase in the temperature in the reactor as a result of the exothermic polymerization reaction, by U_1, and the left side of this equation, describing the change in the temperature in the reactor caused by the incoming and outward reaction-mixture flows and the heat-exchange in the jacket, by U_2.

For the first reactor, we obtained the following simplified expressions for U_1 since $x_1 = \dfrac{k_{\mathrm{p}1}^0 \exp(-E/RT)\, I_0 \tau}{1 + k_{\mathrm{p}1}^0 \exp(-E/RT_1)\, I_0 \tau}$ in accordance with the kinetics of the process and for U_2:

$$U_1 = \frac{(-\Delta H)\,m}{c_{\mathrm{mix}1} \rho_{\mathrm{mix}1}}\, M_0\, \frac{k_{\mathrm{p}1}^0 \exp\left(-\dfrac{E}{RT_1}\right) I_0 \tau}{1 + k_{\mathrm{p}1}^0 \exp\left(-\dfrac{E}{RT_1}\right) I_0 \tau}\,,$$

$$U_2 = T_1 - T^\mathrm{in} + \frac{G_\mathrm{a} c_\mathrm{a}}{G_\mathrm{mix} c_{\mathrm{mix}1}} \left(1 - \exp\left(-\frac{K_{\mathrm{h}1} F}{G_\mathrm{a} c_\mathrm{a}}\right)\right)(T_1 - T_\mathrm{a}^\mathrm{in})\,.$$

Solution of Eq. (6) at $k = 1$ gives the temperature in the first reactor T_1 on condition that the other parameters are fixed (plant data). At $I_0 = 0.00002$ kmole/m^3 and $M_0 = 1.22$ kmole/m^3, $T_1 = 282.04$ K (Fig. 1a).

If T_1 is known, the monomer conversion in the first reactor x_1 can be calculated in the following way:

$$x_1 = 1 - \frac{c_{\mathrm{mix}1} \rho_{\mathrm{mix}1}}{(-\Delta H)\, m M_0 I_0 \tau k_{\mathrm{p}1}^0 \exp\left(-\dfrac{E_k}{RT_1}\right)} \left[T_1 - T_\mathrm{in} + \frac{G_\mathrm{a} c_\mathrm{a}}{G_\mathrm{mix} c_{\mathrm{mix}1}} \left(1 - \exp\left(-\frac{K_{\mathrm{h}1} F}{G_\mathrm{a} c_\mathrm{a}}\right)\right)(T_1 - T_\mathrm{a}^\mathrm{in})\right].$$

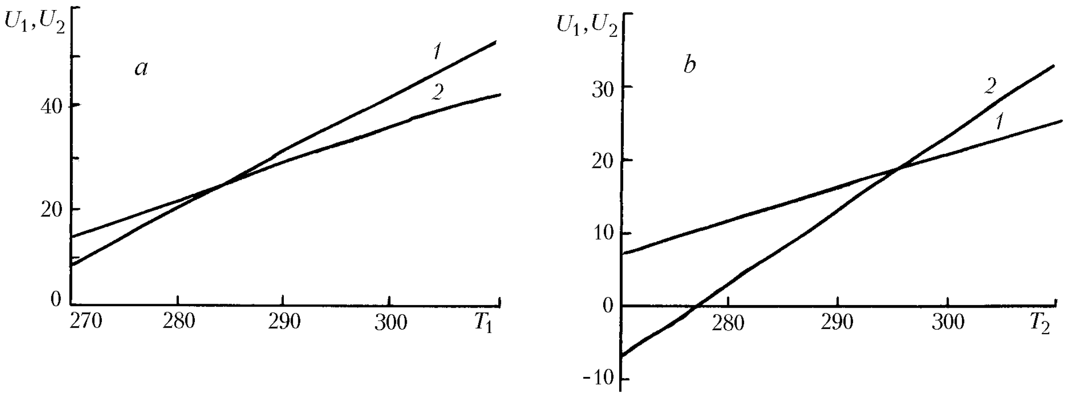

Fig. 1. Temperature dependences of the heat release U_1 (1) and heat removal U_2 (2) in the first (a) and second (b) reactors at $T^{\text{in}} = -10^{\circ}\text{C}$, $T_a^{\text{in}} = -10^{\circ}\text{C}$, $G_a = 1000$ kg/h, $G_{\text{mix}} = 8000$ kg/h, $F = 36\ \text{m}^2$; $E_k = 8.2$ kcal/kmole, $\Delta H = -1508$ kJ/kg. T_1, T_2, K.

We obtained $x_1 = 0.367$.

We calculated the mean-number, mean-weight, and mean-sedimentation degrees of polymerization at the output of the first reactor: $P_n = 1297.63$, $P_w = 3033.34$, and $P_z = 5622.84$.

The parameters of the second reactor were calculated analogously:

$$U_1 = \frac{(-\Delta H)\, m}{c_{\text{mix}2}\rho_{\text{mix}2}} M_0 \frac{k_{\text{p}2}^0 \exp\left(-\dfrac{E_k}{RT_2}\right) I_0 \tau}{\left(1 + k_{\text{p}2}^0 \exp\left(-\dfrac{E_k}{RT_2}\right) I_0 \tau\right)\left(1 + k_{\text{p}1}^0 \exp\left(-\dfrac{E_k}{RT_1}\right) I_0 \tau\right)},$$

$$x_2 = \frac{x_1 + k_{\text{p}2}^0 \exp\left(-\dfrac{E_k}{RT_2}\right) I_0 \tau}{1 + k_{\text{p}2}^0 \exp\left(-\dfrac{E_k}{RT_2}\right) I_0 \tau},$$

$$U_2 = T_2 - T_1 + \frac{G_a c_a}{G_{\text{mix}} c_{\text{mix}2}} \left(1 - \exp\left(-\frac{K_{\text{h}2} F}{G_a c_a}\right)\right)(T_2 - T_a^{\text{in}}).$$

Solving Eq. (6) at $k = 2$, we determined the temperature in the second reactor T_2 on condition that the other parameters were fixed (plant data). At $I_0 = 0.00002$ kmole/m^3 and $M_0 = 1.22$ kmole/m^3, $T_2 = 296.3$ K (Fig. 1b).

If T_2 is known, the monomer conversion in the second reactor is defined as

$$x_2 = 1 - \frac{c_{\text{mix}2}\rho_{\text{mix}2}}{(-\Delta H)\, m M_0 I_0 \tau k_{\text{p}2}^0 \exp\left(-\dfrac{E_k}{RT_2}\right)} \left[T_2 - T_1 + \frac{G_a c_a}{G_{\text{mix}} c_{\text{mix}2}} \left(1 - \exp\left(-\frac{K_{\text{h}2} F}{G_a c_a}\right)\right)(T_2 - T_a^{\text{in}})\right],$$

We obtained $x_2 = 0.65$. The mean-number, mean-weight, and mean-sedimentation degrees of polymerization at the output of the second reactor were equal to $P_n = 910.009$, $P_w = 2715.53$, and $P_z = 6256.44$.

We calculated the temperature in the first reactor at different values of the initiator concentration I_0 and monomer concentration M_0 in the incoming flow (Fig. 2). The calculations have shown that both an increase in the initiator concentration and an increase in the monomer concentration lead to a significant increase in the temperature in the first reactor T_1; in this case, the temperature in the second reactor T_2 is much higher than the permissible temperature. The temperature of the incoming flow also significantly influences T_1 and the monomer conversion in the

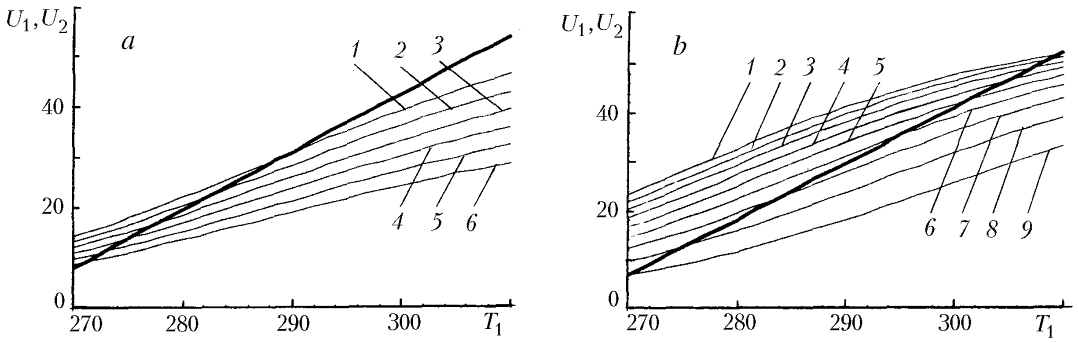

Fig. 2. Temperature dependences of the heat release U_1 at different values of M_0 [M_0 = 1.3 (1), 1.2 (2), 1.1 (3), 1.0 (4), 0.9 (5), and 0.8 kmole/m^3 (6)] and I_0 [I_0 = 0.05 (1), 0.045 (2), 0.04 (3), 0.035 (4), 0.03 (5), 0.025 (6), 0.02 (7), 0.015 (8), and 0.01 mole/m^3 (9)]; the semiboldface line denotes the heat removal U_2. T_1, K.

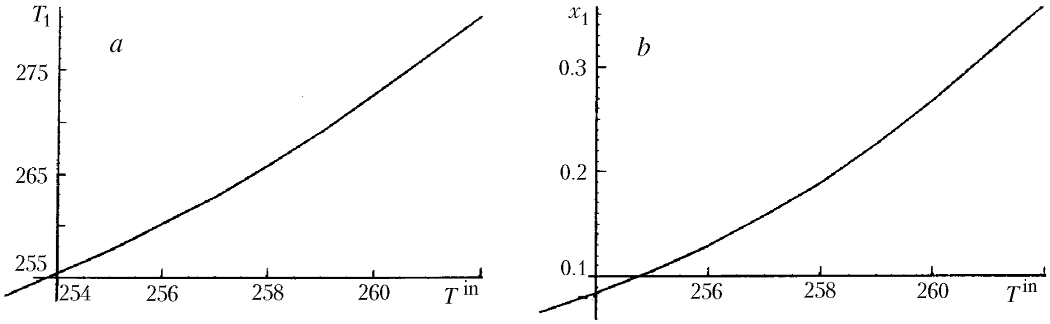

Fig. 3. Dependence of the temperature T_1 (a) and the conversion x_1 (b) in the first reactor on the temperature of the reagents at the input of the reactor. T_1, T^{in}, K.

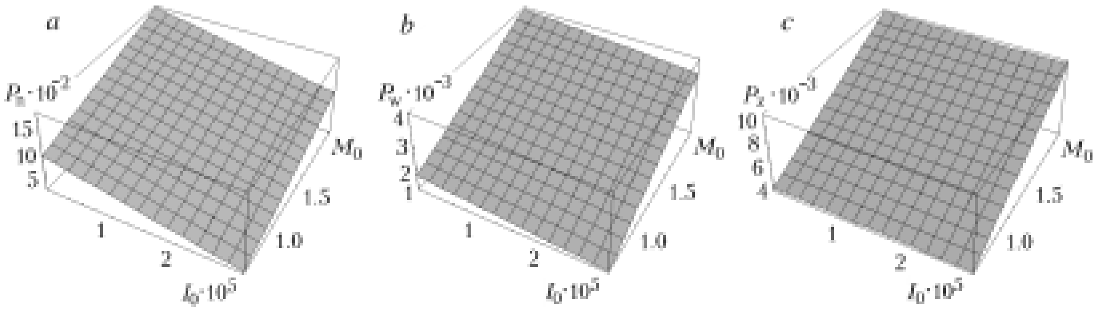

Fig. 4. Dependence of the mean-number (a), mean-weight (b), and mean-sedimentation (c) degree of polymerization on the concentration of the initiator I_0 and monomer M_0 in the incoming flow at k_p = 23.22 liters/(mole·sec), k_{sp} = 0.0079 sec^{-1}, k_c = 0.0003 liter/(mole·sec), $k_{t.m}$ = 0.0026 liter/(mole·sec), and $k_{t.p}$ = 0.002 liter/(mole·sec). I_0, M_0, mole/liter.

first reactor x_1 (Fig. 3). The temperature in the reactor and the conversion temperature increase with increase in the temperature of the mixture.

As the initial rate constants of a continuous process, we used the rate constants of a periodic process occurring at the same ratios between the initial reagents. The model obtained was used for optimization of the technological regimes of SDRC synthesis. The maximum output of the cascade of polymerizers was used as an optimization criterion:

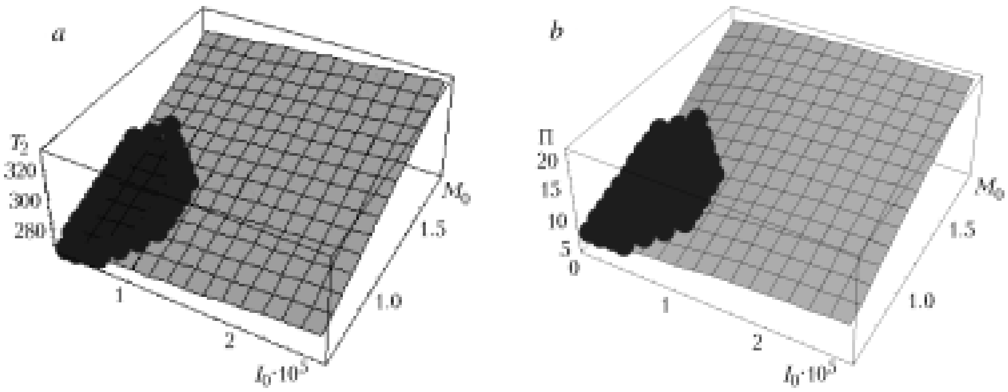

Fig. 5. Dependence of the temperature in the second reactor (a) and the capacity of the cascade of reactors (b) on the concentration of the initiator I_0 and monomer M_0 in the incoming flow at k_p = 23.22 liters/(mole·sec), k_{sp} = 0.0079 sec^{-1}, k_c = 0.0003 liter/(mole·sec), $k_{t.m}$ = 0.0026 liter/(mole·sec), $k_{t.p}$ = 0.002 liter/(mole·sec). I_0, M_0, mole/liter; T_2, K; P, mole/h.

TABLE 1. Recommended Technological Regimes at Different Temperatures of Cooling of Initial Components

Parameters	T_{mix}, °C						
	–5	–8	–10	–12	–16	–20	–25
I_0, 10^4 moles/liter	0.26	0.26	0.32	0.36	0.38	0.4	0.38
M_0, mole/liter	1.12	1.22	1.22	1.22	1.348	1.348	1.47
mass %	9	10	10	10	11	11	12
t, h	1.096	1.097	1.097	1.097	1.098	1.22	1.57
V_{mix}, *kg/h*	10 000	10 000	10 000	10 000	10 000	9000	7000
At the output of the first reactor							
T_1, °C	11.4	9.97	9.6	8.6	5.7	0.73	–0.82
x_1	0.34	0.33	0.35	0.37	0.34	0.32	0.34
P_{n1}	1253.03	1378.01	1369.4	1348.13	1492.4	1523.1	1631.9
P_{w1}	2812.6	3120.3	3098.14	3067.7	3390.3	3428.9	3738.5
P_{z1}	4903.7	5511.7	5471.3	5467.4	6032.3	6023.7	6739.5
P_{w1}/P_{n1}	2.24	2.26	2.26	2.28	2.27	2.25	2.29
P_{z1}/P_{w1}	1.74	1.77	1.77	1.78	1.78	1.76	1.8
At the output of the second reactor							
T_2, °C	23.99	25.3	25.5	24.99	24.4	20.7	22.7
x_2^{out}	0.63	0.63	0.67	0.69	0.68	0.67	0.73
P_{n2}	907.5	969.4	960.9	929.7	1009.7	1046.7	1009.04
P_{w2}	2476.8	2754.3	2738.7	2711.8	3012.3	30446.7	3328.6
P_{z2}	5273.8	6091.5	6078.02	6128.3	6986.5	6931.6	8455.3
P_{w2}/P_{n2}	2.73	2.84	2.85	2.91	2.98	2.91	3.298
P_{z2}/P_{w2}	2.13	2.21	2.22	2.26	2.32	2.28	2.54
Π, kmole/h	10.49	11.73	13.43	12.83	14.05	12.29	11.31

$$\Pi = V_{\mathrm{mix}} M_0 x \to \max .$$

The optimization parameters were the initial monomer content in the mixture M_0, the initiator concentration I_0, and the temperature and time of stay in the apparatus of the cascade.

The efficiency of polymerizers was determined for the following parameters of the synthetic rubber:

(1) the mean-number mass of the polymer M_{n} = 50,000–60,000 units;

(2) the polydispersity coefficient $M_{\mathrm{w}}/M_{\mathrm{n}}$ is no more than 3.0–3.5;

(3) the relation between the mean-sedimentation and mean-weight masses of the polymer $M_{\mathrm{z}}/M_{\mathrm{w}}$ is no more than 2.5–2.8.

We carried out numerical experiments for a continuous process. The initiator concentration was varied from 0.0002 to 0.00004 mole/liter and the monomer concentration accounted for 5–15% of the reaction-mixture amount. The calculation data obtained are presented in Fig. 4. It is seen from the figures that the molecular-mass parameters increase significantly with increase in the monomer concentration. At the same time, these parameters decrease with increase in the initiator concentration in the system. The dark regions in Fig. 5 correspond to the regimes of synthesis of SDRC that are optimum for obtaining the molecular-mass parameters providing a desired quality of this synthetic rubber at a maximum output of the cascade of reactors and an optimum temperature in the second reactor.

We also investigated the influence of a change in the time of stay of mixture reagents in the polymerizer and the temperature of the mixture on the output of the cascade. The recommended optimum regimes of SDRC polymerization are presented in Table 1. We varied the concentration M_0 in the incoming flow, I_0, and the time of stay of the reaction mixture in the reactors of the cascade. A regime was considered as optimum when SDRC of desired quality was obtained at a maximum output.

The heat-transfer and polymerization processes occurring at a time in a cascade of two continuous-operation reactors have been investigated. The optimum regimes of SDRC synthesis have been determined. The data obtained form a theoretical basis for controlled synthesis of a synthetic rubber with definite molecular-mass parameters.

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NOTATION

C_j, concentration of the jth component of a mixture; c_j, heat capacity of the jth component of a mixture; $c_{\mathrm{mix}.k}$, heat capacity of the mixture in the kth reactor; c_{a}, heat capacity of a unit volume of the cooling agent; E_k, total activation energy of the kth reactor; F, heat-transfer surface; G_{mix} and G_{a}, weight rate of the mixture and coolant flows in the apparatus; I_0, concentration of the initiating agent; $J_{i,j}$, moments of the molecular-mass distribution of macromolecules in the polymerization system; K_{h}, heat-transfer coefficient; k, constants of elementary stages; m, molecular mass of the monomer; M, current concentration of the monomer; M_0, monomer concentration; Q_{a}, heat removed through the cooling system; $R(i, l)$, concentration of macromolecules with a number of active centers i and a length of the chain l; R, universal gas constant; r_i, rate of the ith stage of the reaction; P_{n}, P_{w}, and P_{z}, mean-number, mean-weight, and mean-sedimentation degrees of polymerization; s, number of elementary stages of the polymerization process; t, time of stay of the reaction mixture in the reactor, h; T^{in}, temperature of the incoming flow; T, mean temperature in the reactor; $T_{\mathrm{a}}^{\mathrm{in}}$, temperature of the cooling agent at the input of the jacket; V_{mix}, volumetric rate of the reaction mixture; V, volume of the reactor; V_{a}, volumetric rate of the cooling agent; x_k, monomer conversion in the kth reactor; $\beta = M_0/l_0$, degree of polymerization of the living polymer in the case of complete transformation; $\delta_{i,j}$, Kronecker symbol; ΔH_i, thermal effect at the ith stage of the reaction; Π, output of the reactor cascade, kmole/h; $\varphi_k = k_{\mathrm{p}k} I_o \tau$, effective parameter characterizing an ideal-mixing reactor; $\gamma_{\mathrm{t.m}} = \beta k_{\mathrm{t.m}}/k_{\mathrm{p}}$, $\gamma_{\mathrm{t.p}} = \beta k_{\mathrm{t.p}}/k_{\mathrm{p}}$, $\gamma_{\mathrm{sp}} = k_{\mathrm{sp}}/(k_{\mathrm{p}} I_0)$, and $\tilde{\gamma}_{\mathrm{c}} = \beta k_{\mathrm{c}}/k_{\mathrm{p}}$, rates of inherent chain transfer, polymer transfer, spontaneous transfer, and cross-linking of macromolecules; $\rho_{\mathrm{mix}.k}$, density of the mixture in the kth reactor; $\tau = V/V_{\mathrm{mix}}$, mean time of stay of the mixture in the reactor. Subscripts: p, chain-propagation reaction; c, reaction of cross-linking of chains; mix, reaction mixture; h, heat transfer; a, cooling agent; i, initiation; j, number of a mixture component; k, number of a reaction; n, numerical; sp, spontaneous chain transfer; t.m, inherent chain transfer; t.p, polymer transfer; w, weight; z, sedimentation; in, input; out, output; av, average; t, chain transfer.

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