Journal of Engineering Physics and Thermophysics, Vol. 75, No. 4, 2002

METHOD OF SOLUTION OF A SYSTEM OF EQUATIONS DESCRIBING THE CONTINUOUS PROCESS OF POLYMERIZATION UNDER CONDITIONS OF A POLYADDITION REACTION

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UDC 66.021.3.06

A method of solution of a system of equations which describe the continuous process of polymerization of butadiene on a cobalt catalyst accompanied by the polyaddition reaction is proposed. The moments of second and third orders as functions of the distribution of macromolecules by the degree of polymerization and the number of active centers in each reactor are compared. The values of the conversion of a monomer for which the moments go to infinity (which means gelation in the reactor) are determined. The solution is based on the replacement of variables which made it possible to reduce the equation of the fourth degree for the moments to a quadratic equation and to single out the branch corresponding to the actual process. The algebraic transformations and calculation were carried out with the use of the Matematika 3.0 package.

The process of polymerization of rubber is often accompanied by reactions resulting in a branched polymer, which can be both the aim of the process and an undesirable side phenomenon. The branching of macromolecules influences their molecular-weight distribution and largely determines the physicomechanical properties of a polymer and thus the field of its industrial use.

Furthermore, the appearance of branched macromolecules can be responsible for the formation of a gel. However, there can be a situation where 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 a sharp nonuniformity of the growth of different polymer chains because of which individual strongly branched molecules can increase to a macroscopic size even for low conversions of the monomer. To determine the conditions of occurrence of a gel one must investigate the time variation of the statistical characteristics of the molecular-weight distribution of polymer chains. In the literature sources, there is a mathematical description of the reaction of polyaddition (cross-linking of macromolecules) of polymer chains for the process of radical polymerization [1], and the particular case of polyaddition of "living" macromolecules to "dead" ones is considered for the process of anionic polymerization [2].

Below, we propose a method of solution of a system of equations which describe the continuous process of polymerization of butadiene on a cobalt catalyst accompanied by the reaction of polyaddition of macromolecules.

In the case where the growth of macromolecules, transfer to a monomer, a polymer, and an impurity, spontaneous transfer, and the reaction of polyaddition of macromolecules are possible, the corresponding equations of consumption of the monomer, exhaustion of the impurity, and formation of polymerization products in the kth reactor of the cascade have the form [1]

$$\frac{dM_k}{dt} = \frac{M_{k-1} - M_k}{\tau} - k_{\mathrm{p},k} M_k I_0 \,; \tag{1}$$

$$\frac{\partial R_k (i, l)}{\partial t} = \frac{R_{k-1} (i, l) - R_k (i, l)}{\tau} - i k_{\mathrm{p},k} M_k \frac{\partial R_k (i, l)}{\partial l} +$$

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$$+ (k_{\text{sp},k} + k_{\text{t.m},k} M_k + k_{\text{t.p},k} (M_0 - M_k) + k_{\text{t.e}} E_k) \, [(i+1) \, R_k (i+1, l) - i R_k (i, l)] +$$

$$+ k_{\text{t.p},k} l I_0 \, [R_k (i-1, l) - R_k (i, l)] + \frac{k_{\text{c},k}}{2} \sum_{j=0}^{i} \int_0^l [j (l-n) + n (i-j)] \, R_k (j, n) \, R_k (i-j, l-n) \, dn -$$

$$- k_{\text{c},k} R_k (i, l) \sum_{j=0}^{\infty} \int_0^{\infty} (in + jl) \, R (j, n) \, dn + (k_{\text{sp},k} + K_{\text{t.m},k} M_k + k_{\text{t.e},k} E_k) \, I_0 \delta_{i,1} \delta (l) +$$

$$+ \frac{I_0}{\tau} \delta_{k,1} \delta_{i,1} \delta (l) \, , \quad i = 1, 2, \ldots \, , \quad k = 1, 2, \ldots \, , \quad 0 \le l < \infty \, ; \tag{2}$$

$$\frac{dE_k}{dt} = \frac{E_{k-1} - E_k}{\tau} - k_{\text{t.e},k} E_k I_0 \, . \tag{3}$$

In deriving Eqs. (1)–(3), it has been assumed that a change in the volume of the system in polymerization can be disregarded. The first term on the right-hand side of (2) describes a variation in the concentration $R_k(i, l)$ as a result of the entry and exit of the polymer from the kth reactor, the second term describes this variation as a result of the growth of macromolecules, the other four terms describe a variation in the concentration because of the reactions of chain transfer and polyaddition, and the last two terms describe the formation of short chains in the case of instantaneous initiation and transfer of a chain. Equation (2) is written in the approximation of long chains.

The concentrations of the monomer, the initiator, and the impurity in the entrance flow are, respectively, equal to M_0, I_0, and E_0 $(E_0/M_0 = \varepsilon)$.

Equation (1) is written without account taken of the consumption of the monomer by the reactions of chain transfer and reinitiation, since the rate of these reactions is much lower than the rate of growth of the chain. In the general case, the temperature in different reactors can be dissimilar; therefore, the rate constants have the subscript k. For the steady-state isothermal process in a cascade of identical reactors the system of equations (1)–(3) is simplified. For such a regime the increase in the conversion of the monomer in passage from reactor to reactor is described by the expression

$$x_k = 1 - (1 + \varphi)^{-k} \, , \quad \varphi = k_\text{p} I_0 \tau \, .$$

By employing the auxiliary function

$$F_k = \sum_{i=0}^{\infty} s^i \int_0^{\infty} \exp(-pz) \, r_k (i, z) \, dz$$

$(r_k(i, z) = \beta R_k(i, l)/I_0, \; z = l/\beta)$, we obtain a system of algebraic equations relative to $J_{ij,k} = \left. \dfrac{\partial^{i+j} F_k}{\partial s^i \partial p^j} \right|_{\substack{s=1 \\ p=0}}$, which are necessary to calculate the number-mean, weighted-mean, and z-mean degrees of polymerization $P_{\text{n},k}$, $P_{\text{w},k}$, and $P_{\text{z},k}$:

$$J_{00,k} = J_{00,k-1} + \delta_{k,1} + \left[\gamma_\text{sp} + \frac{\gamma_\text{t.e}}{\left(1 + \varphi \dfrac{\gamma_\text{t.e}}{\beta\varepsilon} \right)^k} + \gamma_\text{t.m} (1 - x_k) \right] \varphi - \varphi \tilde{\gamma}_\text{c} x_k \, ,$$

$$J_{01,k} = - x_k \, , \; J_{02,k} = \frac{J_{02,k-1} - 2\varphi (1 - x_k) \, J_{11,k}}{1 + 2\varphi \tilde{\gamma}_\text{c} J_{11,k}} \, ,$$

$$J_{11,k} = \frac{J_{11,k-1} - \varphi\,(1 - x_k)\,(1 + J_{20,k}) - \varphi\tilde{\gamma}_{\text{c}} J_{02,k}\,(1 + J_{20,k}) - \varphi\gamma_{\text{t.p}} J_{02,k}}{1 + \varphi\gamma_{\text{sp}} + \varphi\gamma_{\text{t.m}}\,(1 - x_k) + \varphi\gamma_{\text{t.p}} x_k + \dfrac{\varphi\gamma_{\text{t.e}}}{\left(1 + \varphi\,\dfrac{\gamma_{\text{t.e}}}{\beta\varepsilon}\right)^k} + J_{11,k}\varphi\tilde{\gamma}_{\text{c}}},$$

$$J_{20,k} = \frac{J_{20,k-1} - 2\varphi\tilde{\gamma}_{\text{c}} J_{11,k} - 2\varphi\gamma_{\text{t.p}} J_{11,k}}{1 + 2\varphi\gamma_{\text{sp}} + 2\varphi\gamma_{\text{t.m}}\,(1 - x_k) + 2\varphi\tilde{\gamma}_{\text{c}} J_{11,k} + 2\varphi\gamma_{\text{t.p}} x_k + \dfrac{2\varphi\gamma_{\text{t.e}}}{\left(1 + \varphi\,\dfrac{\gamma_{\text{t.e}}}{\beta\varepsilon}\right)^k}},$$

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

$$J_{30,k} = \frac{J_{30,k-1} - 3\varphi\,(\tilde{\gamma}_{\text{c}} J_{20,k}\,(2J_{11,k} + J_{21,k}) + J_{21,k}\,(\tilde{\gamma}_{\text{c}} + \gamma_{\text{t.p}}))}{1 + 3\varphi\left(\gamma_{\text{sp}} + \dfrac{\gamma_{\text{t.e}}}{\left(1 + \varphi\,\dfrac{\gamma_{\text{t.e}}}{\beta\varepsilon}\right)^k} + \gamma_{\text{t.m}}\,(1 - x_k) + \tilde{\gamma}_{\text{c}} J_{11,k} + \gamma_{\text{t.p}} x_k\right)},$$

$$J_{21,k} = (J_{21,k-1} - \varphi\,((1 - x_k)\,(2J_{20,k} + J_{30,k}) + 2\tilde{\gamma}_{\text{c}} J_{20,k}\,(J_{02,k} + J_{12,k}) + 2J_{12,k}\,(\tilde{\gamma}_{\text{c}} + \gamma_{\text{t.p}}) +$$

$$+ \tilde{\gamma}_{\text{c}}\,(2J_{11,k}^2 + J_{30,k} J_{02,k}))) \Bigg/ \left(1 + 2\varphi\left(\gamma_{\text{sp}} + \frac{\gamma_{\text{t.e}}}{\left(1 + \varphi\,\dfrac{\gamma_{\text{t.e}}}{\beta\varepsilon}\right)^k} + \gamma_{\text{t.m}}\,(1 - x_k)\right) + 3\varphi\tilde{\gamma}_{\text{c}} J_{11,k} + 2\varphi\gamma_{\text{t.p}} x_k\right),$$

$$J_{12,k} = (J_{12,k-1} - 2\varphi\,((1 - x_k)\,(J_{11,k} + J_{21,k}) + 2\tilde{\gamma}_{\text{c}} J_{02,k}\,(J_{11,k} + J_{21,k}) +$$

$$+ \tilde{\gamma}_{\text{c}} J_{03,k}\,(1 + J_{20,k}) + J_{03,k}\gamma_{\text{t.p}})) \Bigg/ \left(1 + \varphi\left(\gamma_{\text{sp}} + \frac{\gamma_{\text{t.e}}}{\left(1 + \varphi\,\dfrac{\gamma_{\text{t.e}}}{\beta\varepsilon}\right)^k} + \gamma_{\text{t.m}}\,(1 - x_k)\right) + 3\tilde{\gamma}_{\text{c}} J_{11,k} + \gamma_{\text{t.p}} x_k\right),$$

$$P_{\text{n},k} = \beta\,\frac{x_k}{J_{00,k}}, \quad P_{\text{w},k} = \beta\,\frac{J_{02,k}}{x_k}, \quad P_{\text{z},k} = -\,\beta\,\frac{J_{03,k}}{J_{02,k}}. \tag{4}$$

Here

$$\gamma_{\text{t.m},k} = \frac{\beta k_{\text{t.m},k}}{k_{\text{p},k}},\ \gamma_{\text{sp},k} = \frac{k_{\text{sp},k}}{k_{\text{p},k} I_0},\ \gamma_{\text{t.p},k} = \frac{\beta k_{\text{t.p},k}}{k_{\text{p},k}},\ \tilde{\gamma}_{\text{c},k} = \frac{\beta k_{\text{c},k}}{k_{\text{p},k}},\ \gamma_{\text{t.e},k} = \frac{\beta\varepsilon k_{\text{t.e},k}}{k_{\text{p},k}}\ .$$

When $\tilde{\gamma}_{\text{c}} = 0$ the system of equations (4) is solved by the ordinary tools of the Matematika 3.0 package. If $\tilde{\gamma}_{\text{c}} > 0$ (i.e., the reaction of polyaddition of macromolecules is carried out in the course of polymerization), in transforming system (4), one obtains an equation of the fourth degree relative to the moments $J_{ij,k}$, which is impossible to solve by the ordinary tools of the Matematika 3.0 package. For this case, we propose the following method of solution of the system of equations (4).

Let for an arbitrary (kth) reactor $x = x_k$ be the conversion at the exit from the kth reactor, $\{J_{20},\ J_{11},\ J_{02}\}$ and $\{J_{30},\ J_{21},\ J_{12},\ J_{03}\}$ be the moments of second and third order which are considered as functions of x, and $\{\text{in}_{20},\ \text{in}_{11},\ \text{in}_{02},\ \text{in}_{30},\ \text{in}_{21},\ \text{in}_{12},\ \text{in}_{30}\}$ be the moments at the entrance to the kth reactor, i.e., the corresponding moments at the exit of the $(k - 1)$th reactor considered as functions of the conversion in the kth reactor. For example, $\text{in}_{30}[x_k] = J_{30(k-1)}[x_{k-1}]$.

Since we are considering the steady-state isothermal process in the cascade of identical reactors, the relation

$$(1 - x_{k-1})^{1/(k-1)} = (1 - x_k)^{1/k} = 1/(1 + \varphi) \tag{5}$$

holds.

Computation of the moments of third order in terms of x and the moments of second order, cumbersome as it is, presents no problem since $\{J_{30},\ J_{21},\ J_{12},\ J_{03}\}$ satisfy the following system of linear equations:

$$\begin{gathered}
J_{03} = \frac{\mathrm{in}_{03} - 3\varphi J_{12}\,(1 - x + \tilde{\gamma}_{\mathrm{c}} J_{02})}{1 + 3\varphi\tilde{\gamma}_{\mathrm{c}} J_{11}}\,, \\[2ex]
J_{30} = \frac{\mathrm{in}_{30} - 3\varphi\,((\tilde{\gamma}_{\mathrm{c}} + \gamma_{\mathrm{t.p}})\,J_{12} + \tilde{\gamma}_{\mathrm{c}} J_{20}\,(2J_{11} + J_{21}))}{1 + 3\varphi\,(\mathrm{etn} + \gamma_{\mathrm{sp}} + \tilde{\gamma}_{\mathrm{c}} J_{11} + \gamma_{\mathrm{t.m}}\,(1 - x) + \gamma_{\mathrm{t.p}} x)}\,, \\[2ex]
J_{21} = \frac{\mathrm{in}_{21} - \varphi\,((1 - x)\,(2J_{02} + J_{12}) + 2J_{12}\,(\tilde{\gamma}_{\mathrm{c}} + \gamma_{\mathrm{t.p}}) + \gamma_{\mathrm{c}}\,(2J_{11}J_{11} + J_{30}J_{02}))}{1 + \varphi\,(2\,(\gamma_{\mathrm{sp}} + \gamma_{\mathrm{t.m}}\,(1 - x) + \mathrm{etn}) + 3\tilde{\gamma}_{\mathrm{c}} J_{11} + 2\gamma_{\mathrm{t.p}} x)}\,, \\[2ex]
J_{12} = \frac{\mathrm{in}_{12} - \varphi\,(2\,(1 - x)\,(J_{11} + J_{21}) + 2\tilde{\gamma}_{\mathrm{c}} J_{02}\,(J_{11} + J_{21}) + \tilde{\gamma}_{\mathrm{c}} J_{03}\,(1 + J_{20}) + \gamma_{\mathrm{t.p}} J_{03})}{1 + \varphi\,(\gamma_{\mathrm{sp}} + \gamma_{\mathrm{t.m}}\,(1 - x) + \mathrm{etn} + 3\tilde{\gamma}_{\mathrm{c}} J_{11} + 2\gamma_{\mathrm{t.p}} x)}\,,
\end{gathered} \tag{6}$$

where $\mathrm{etn} = \gamma_{\mathrm{t.e}}/(1 + \varphi\gamma_{\mathrm{t.e}}/(\beta\varepsilon))^n$.

The moments of second order satisfy the system of equations

$$J_{02} = \frac{\mathrm{in}_{02} - 2\varphi\,(1 - x) + J_{11}}{1 + 2\varphi\tilde{\gamma}_{\mathrm{c}} J_{11}}\,,$$

$$J_{20} = \frac{\mathrm{in}_{20} - 2\varphi J_{11}\,(\tilde{\gamma}_{\mathrm{c}} + \gamma_{\mathrm{t.p}})}{1 + 2\varphi\,(\gamma_{\mathrm{sp}} + \gamma_{\mathrm{t.m}}\,(1 - x) + \tilde{\gamma}_{\mathrm{c}} J_{11} + \gamma_{\mathrm{t.p}} x + \mathrm{etn})}\,,$$

$$\begin{gathered}
-\,\mathrm{in}_{11} + J_{11}\,(1 + \varphi\,(\gamma_{\mathrm{sp}} + \gamma_{\mathrm{t.m}}\,(1 - x) + \gamma_{\mathrm{t.p}} x + \mathrm{etn})) + J_{11}J_{11}\varphi\tilde{\gamma}_{\mathrm{c}} + \\
+\,\varphi\,((1 - x)\,(1 + J_{20}) + \gamma_{\mathrm{t.p}} J_{02} + \tilde{\gamma}_{\mathrm{c}} J_{02}\,(1 + J_{20})) = 0\,,
\end{gathered}$$

whose solution is reduced to the equation of the fourth degree relative to J_{11}

$$a\,[4]\cdot(J_{11})^4 + a\,[3]\cdot(J_{11})^3 + a\,[2]\cdot(J_{11})^2 + a\,[1]\cdot(J_{11}) + a\,[0] = 0\,, \tag{7}$$

where

$$\begin{gathered}
a\,[0] = -\,\mathrm{in}_{11} + 2\varphi^2\,(1 + (\tilde{\gamma}_{\mathrm{c}} + \gamma_{\mathrm{t.p}})\,\mathrm{in}_{02} - x)\,(\mathrm{etn} + \gamma_{\mathrm{t.m}} + \gamma_{\mathrm{sp}} - \gamma_{\mathrm{t.m}} x) + \\
+\,\varphi\,(1 + \mathrm{in}_{20} + \mathrm{in}_{02}\,(\tilde{\gamma}_{\mathrm{c}} + \gamma_{\mathrm{t.p}} + \tilde{\gamma}_{\mathrm{c}}\mathrm{in}_{20}) - x - (2\gamma_{\mathrm{t.p}}\mathrm{in}_{11} + \mathrm{in}_{20})\,x - 2\,\mathrm{in}_{11}\,(\mathrm{etn} + \gamma_{\mathrm{t.m}} + \gamma_{\mathrm{sp}} - \gamma_{\mathrm{t.m}} x))\,, \\
a\,[1] = (1 + \varphi\,(\mathrm{etn} + \gamma_{\mathrm{t.m}} + \gamma_{\mathrm{sp}} - \gamma_{\mathrm{t.m}} x + \gamma_{\mathrm{t.p}} x))\,(1 + 2\varphi\,(\mathrm{etn} + \gamma_{\mathrm{t.m}} + \gamma_{\mathrm{sp}} - 2\tilde{\gamma}_{\mathrm{c}}\mathrm{in}_{11} - \\
-\,\gamma_{\mathrm{t.m}} x + \gamma_{\mathrm{t.p}}\,(2\varphi\,(-\,1 + x) + x)))\,, \\
a\,[2] = \varphi\tilde{\gamma}_{\mathrm{c}}\,(5 + 2\varphi\,(2\,\mathrm{etn}^2\,\varphi + 5\,(\gamma_{\mathrm{t.m}} + \gamma_{\mathrm{t.p}})\,x + 2\varphi\,(-\,\gamma_{\mathrm{t.p}} + \gamma_{\mathrm{t.m}}^2\,(-\,1 + x)^2 +
\end{gathered}$$

$$+\gamma_{\mathrm{t.p}}x-2\gamma_{\mathrm{t.m}}\,(-1+x)\,(\gamma_{\mathrm{sp}}+\gamma_{\mathrm{t.p}}x)+(\gamma_{\mathrm{sp}}+\gamma_{\mathrm{t.p}}x)^2)+$$

$$+\,\mathrm{etn}\,(5+4\varphi\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x)))),$$

$$a\,[3]=8\varphi^2\tilde{\gamma}_{\mathrm{c}}^2\,(1+\varphi\,(\mathrm{etn}+\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x)),$$

$$a\,[4]=4\varphi^3\tilde{\gamma}_{\mathrm{c}}^3\,.$$

Physically meaningful are just the roots of Eq. (7) which are continuous in x. To find them we introduce the new variable

$$g=(J_{11}+1/(2\varphi\tilde{\gamma}_{\mathrm{c}})+(\mathrm{etn}+\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x)/(2\tilde{\gamma}_{\mathrm{c}}))^2\,.$$

Then

$$J_{11}=\pm\sqrt{g}-(1/(2\varphi\tilde{\gamma}_{\mathrm{c}})+(\mathrm{etn}+\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x)/(2\tilde{\gamma}_{\mathrm{c}}))\,. \tag{8}$$

But a minus sign in front of the radical would not do, since in this case J_{11} would tend to infinity for $x\to 0$ (we recall that φ satisfies Eq. (5), $x>0$, and $\tilde{\gamma}_{\mathrm{c}}>0$). Equation (8) is quadratic relative to the variable g: $d\cdot g^2+b\cdot g+c=0$, where the coefficients d, b, and c are determined by the equalities

$$d=4\varphi^2\tilde{\gamma}_{\mathrm{c}}^3\,,$$

$$b=-\gamma_{\mathrm{c}}\,(1+2\varphi\,(\mathrm{etn}^2\,\varphi+\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}+2\tilde{\gamma}_{\mathrm{c}}\,\mathrm{in}_{11}+(-\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{t.p}})\,x+$$

$$+\,\varphi\,(2\gamma_{\mathrm{t.p}}+(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}})^2-2\,(\gamma_{\mathrm{t.p}}+(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{t.p}})\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}))\,x+$$

$$+\,(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{t.p}})^2\,x^2)+\mathrm{etn}\,(1+2\varphi\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x)))),$$

$$c=\frac{1}{4\tilde{\gamma}_{\mathrm{c}}}\,(\mathrm{etn}^4\,\varphi^2+(4\gamma_{\mathrm{t.p}}+\gamma_{\mathrm{t.m}}^2\,(-1+x)^2-4\gamma_{\mathrm{t.p}}x-2\gamma_{\mathrm{t.m}}\,(-1+x)\,(\gamma_{\mathrm{sp}}+\gamma_{\mathrm{t.p}}x)+$$

$$+\,(\gamma_{\mathrm{sp}}+\gamma_{\mathrm{t.p}}x)^2)\,(1+\varphi\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x))^2+2\,\mathrm{etn}^3\,\varphi\,(1+2\varphi\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x))+$$

$$+\,4\tilde{\gamma}_{\mathrm{c}}^2\,\mathrm{in}_{02}\,(1+\mathrm{in}_{20}+2\varphi\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x))+$$

$$+\,\mathrm{etn}^2\,(1+\varphi\,(6\gamma_{\mathrm{sp}}+4\tilde{\gamma}_{\mathrm{c}}\,\mathrm{in}_{11}-6\gamma_{\mathrm{t.m}}\,(-1+x)+6\gamma_{\mathrm{t.p}}x^2)+2\varphi^2\,(2\gamma_{\mathrm{t.p}}+3\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}})^2-$$

$$-\,2\,(\gamma_{\mathrm{t.p}}+3\,(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{t.p}})\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}))\,x+3\,(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{t.p}})^2\,x^2))+$$

$$+\,2\,\mathrm{etn}\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}-\gamma_{\mathrm{t.m}}x+\gamma_{\mathrm{t.p}}x-2\varphi^2\,(-\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{sp}}+\gamma_{\mathrm{t.m}}x-\gamma_{\mathrm{t.p}}x)\times$$

$$\times\,(2\gamma_{\mathrm{t.p}}+(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}})^2-2\,(\gamma_{\mathrm{t.p}}\,(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{sp}})\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}}))\,x+(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{t.p}})^2\,x^2)+$$

$$+\,\varphi\,(4\gamma_{\mathrm{t.p}}+3\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}})^2+4\tilde{\gamma}_{\mathrm{c}}\,(1+(\tilde{\gamma}_{\mathrm{c}}+\gamma_{\mathrm{t.p}})\,\mathrm{in}_{02}+(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}})\,\mathrm{in}_{11}-$$

$$-\,2\,(2\gamma_{\mathrm{t.p}}+3\,(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{t.p}})\,(\gamma_{\mathrm{t.m}}+\gamma_{\mathrm{sp}})+2\gamma_{\mathrm{c}}\,(1+\gamma_{\mathrm{t.m}}\,\mathrm{in}_{11}-\gamma_{\mathrm{t.p}}\,\mathrm{in}_{11}))\,x+3\,(\gamma_{\mathrm{t.m}}-\gamma_{\mathrm{t.p}})^2\,x^2))+$$

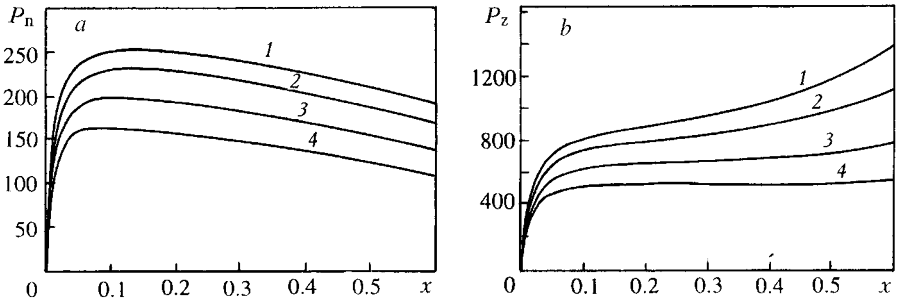

Fig. 1. Change in the number-mean (a) and sedimentation-mean (b) degrees of polymerization of the polymer for a cascade of two reactors at the exit from the second reactor with conversion of the monomer for different contents of ethylene in the system ($M_0 = 1.85$ mole/liter; $I_0 = 0.00006$ mole/liter, $k_p = 297.2$, $k_{t.e} = 0$, $k_c = 0.01$, $k_{t.m} = 0.5$, $k_{t.p} = 0.5$, $k_{sp} = 1$): 1, 2, 3, and 4) concentration of ethylene is 0, 1, 3, and 6% respectively.

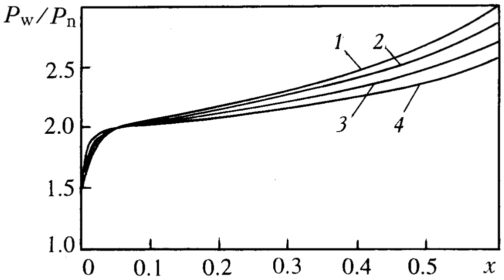

Fig. 2. Polydispersivity coefficient P_w/P_n of the polymer for a cascade of two reactors at the exit from the second reactor vs. conversion of the monomer for different contents of ethylene (see the caption to Fig. 1 for the value of the parameters): 1–4) notation is the same as in Fig. 1.

$$+ 4\tilde{\gamma}_c (1 + \gamma_{t.p}\, in_{02} + in_{20} - x - in_{20}x + \varphi (- \gamma_{t.m} - \gamma_{sp} + \gamma_{t.m}x - \gamma_{t.p}x) \times$$

$$\times (- 2 - \gamma_{sp}\, in_{11} + \gamma_{t.m}\, in_{11} (- 1 + x) + 2x - \gamma_{t.p} (2\, in_{02} + in_{11}\, x)))) \, .$$

Of the two roots of this equation, only one satisfies the condition of boundedness of J_{11} for $x \to 0$: $g = (-b + \sqrt{b^2 - 4dc})/(2d)$. We note that for J_{11} corresponding to this root for all the positive values of the parameter $\tilde{\gamma}_c$ and any values of the parameters $\gamma_{t.e}$, γ_{sp}, and $\gamma_{t.p}$ the equality

$$J_{11}[x] = - x + o(x^2)$$

holds.

Thus, we have proposed an original method of solution of a system of equations which describe the process of polymerization with account taken of the reaction of polyaddition (cross-linking of macromolecules) following the pattern "living" with "living" and "dead" for a continuous process of polymerization. Formula (8) makes it possible to find the moments of second and third orders as continuously differentiable functions of conversion and to investigate the dependence of the basic molecular-weight characteristics on different parameters.

This method was employed to study the influence of the reaction of polyaddition of macromolecules on the process of polymerization in producing synthetic rubber on a cobalt catalyst in a cascade of two continuous reactors with introduction of ethylene into the system. Figures 1 and 2 show that the increase in the concentration of ethylene leads to a significant decrease in the molecular-weight characteristics. As the content of ethylene is increased to 6%, one is able to avoid gelation and attain acceptable values of the polydispersity parameter of the rubber.

This work was carried out with support from the Russian Foundation for Basic Research, grant No. 00-15-99438.

NOTATION

i, number of active centers in the macromolecule; l, number of monomer links in the macromolecule; $x_k = (M_0 - M_k)/M_0$, conversion in the kth reactor of the cascade; I_0, concentration of the initiator at the extrance to the first reactor; M_k, concentration of the monomer in the kth reactor; M_0, initial concentration of the monomer (at the entrance to the first reactor); E_0, initial concentration of the impurity (ethylene); $R_k(i, l)$, concentration of macromolecules with i active centers and l monomer links in the kth reactor; $P_{\mathrm{n},k}$, number-mean degree of polymerization in the kth reactor; $P_{\mathrm{w},k}$, weighted-mean degree of polymerization in the kth reactor; $P_{\mathrm{z},k}$, sedimentation-mean, or z-mean, degree of polymerization in the kth reactor; $P_{\mathrm{w},k}/P_{\mathrm{n},k}$, polydispersity coefficient; $\beta = M_0/I_0$, degree of polymerization of a "living" polymer in the case of total conversion; $k_{\mathrm{c},k}$, rate constant of polyaddition of macromolecules in the kth reactor; $k_{\mathrm{t.m},k}$, rate constant of the chain transfer to a monomer in the kth reactor; $k_{\mathrm{p},k}$, growth rate constant in the kth reactor; $k_{\mathrm{sp},k}$, rate constant of spontaneous chain transfer in the kth reactor; $k_{\mathrm{t.e},k}$, rate constant of chain transfer to an impurity (ethylene) in the kth reactor; $\gamma_{\mathrm{t.m},k}$, intensity of chain transfer to a monomer in the kth reactor; $\gamma_{\mathrm{sp},k}$, intensity of spontaneous chain transfer in the kth reactor; $\gamma_{\mathrm{t.p},k}$, intensity of chain transfer to a polymer in the kth reactor; $\tilde{\gamma}_{\mathrm{c},k}$, intensity of the reaction of cross-linking of macromolecules of the kth reactor; $\gamma_{\mathrm{t.e},k}$, intensity of the reaction of transfer of a chain to an impurity (ethylene) in the kth reactor; φ, effective parameter determining conversion in the mixing reactor; τ, average time of stay in one reactor of the cascade; t, running polymerization time; F_k, generating function; s, p, and z, auxiliary variables; $r_k(i, z)$, dimensionless concentration of polymer chains; $J_{ij,k}$, derivative of F_k of the order $(i + j)$, or moment of $(i + j)$th order, for the kth reactor; $\mathrm{in}_{ij}[x_k]$, moment of $(i + j)$th order at the entrance to the kth reactor; etn, auxiliary variable dependent on the intensity of chain transfer to ethylene and on the concentration of ethylene. Subscripts: c, cross-linking; p, growth of the chain; sp, spontaneous chain transfer; t, transfer; m, monomer; e, ethylene; n, number; w, weight; z, z-mean.

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