



SOLVING THE DIRECT PROBLEM OF BUTADIENE-STYRENE COPOLYMERIZATION

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ABSTRACT

The production of polymeric materials occupies one of the leading positions in today's chemical industry. The production of polymeric products relies on the process of repeated addition of monomer molecules to the active sites of a growing chain. If two or more monomers are used as starting compounds, the process is referred to as copolymerization. In particular, synthetic rubber is produced by this mechanism. In view of the fast development of computers and extensive industrial use of polymerization processes, the issues of their mathematical simulation are of current interest. Building a mathematical model allows one not only to predict the properties of a product but also optimize the production process.

Key words: Modeling and simulation, Copolymerization, Kinetic scheme, Synthetic rubber.

INTRODUCTION

Copolymerization in the production of synthetic rubber is carried out by a continuous method in a chain of sequential polymerization reactors at 5°C¹. A scheme of the production process is shown in Fig. 1. A concentrated aqueous phase including a solution of a basic emulsifier, electrolyte, dispersant, and activator is prepared in a vessel by mixing the components in predefined amounts and then diluted with water in a stream. The ready-made aqueous phase is passed through a cooler with brine as the coolant and then fed to an orifice mixer for mixing with monomers that represent a hydrocarbon phase. The hydrocarbon phase (blend) is prepared by continuous mixing of butadiene and styrene fed in a predefined ratio into an orifice mixer, undergoes alkaline aqueous washing, and is mixed with the aqueous phase first in an orifice mixer and then in a bulk mixer. The mixture is pumped to the first reactor in a chain of sequential polymerization reactors usually comprising 12

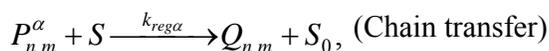
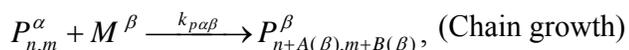
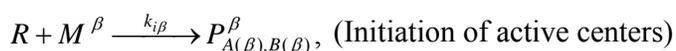
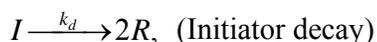
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standard reactors, 12 or 20 cubic meters in volume. The chain transfer agent is injected at two points: at the beginning of the process as a 5% solution (90% of the total amount), while the remaining amount (10%) is injected as a 1% emulsion in water at a second point in one of the polymerization reactors, namely, the 5th, 6th, 7th, or 8th one in the sequence.

Pinane hydroperoxide is used as the copolymerization initiator. The molecular mass is controlled using tert-dodecylmercaptane. The copolymerization process is terminated at 70% monomer conversion by introducing a special stopper reagent, namely, diethylhydroxylamine.

EXPERIMENTAL

The kinetic method for the simulation of polymerization processes involves composing and numerical solution of kinetic equations for the concentrations of all types of particles involved in the process. To build a model of butadiene-styrene copolymerization, let us assume that the reactivity of the active center at the end of a growing chain is determined by the nature of the terminal unit. Then the kinetic scheme of butadiene-styrene copolymerization can be described by the following steps:



Here $\alpha, \beta = 1, 2$; M^1 and M^2 are the monomers of the first and second type; $P_{n,m}$ and $Q_{n,m}$ are the active and inactive polymer chains with length $m + n$ comprising m units of the M^1 monomer and n units of the M^2 monomer, respectively; $k_i, k_p, k_{reg}, k_d,$ and k_r are the reaction rate constants of initiation, growth, chain propagation, disproportionation, and recombination elementary stages, respectively; $A(\beta) = \{1 \text{ if } \beta = 1, \text{ else } 0\}$; $B(\beta) = \{1 \text{ if } \beta = 2, \text{ else } 0\}$.

A principal difference of polymerization processes from any other chemical processes is that, instead of a product with a constant molecular mass, some molecular-mass distribution (MMD) of the polymer is formed. The statistic polymerization theory relies on

the possibility of MMD analysis based on specific mean molecular masses \bar{M}_w and \bar{M}_n referred to as mass-average and number-average masses². To perform analysis, the concept of moments is introduced for active chains:

$$\psi_k^{M^1} = \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} (nw_a + mw_b)^k P_{n,m}^1,$$

$$\psi_k^{M^2} = \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} (nw_a + mw_b)^k P_{n,m}^2,$$

and for inactive chains:

$$\psi_k^Q = \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} (nw_a + mw_b)^k Q_{n,m},$$

Where $k = 0, 1, \dots, \infty$.

Building a matrix of stoichiometric coefficients and multiplying it by the column-vector of reaction rates results in an infinite (*ca.* 10^6) system of non-linear differential equations describing the butadiene-styrene copolymerization process:

$$\left\{ \begin{array}{l} \frac{dI}{dt} = -k_i I, \\ \frac{dM^1}{dt} = -k_{p11} M^1 \sum_{n,m=0}^{\infty} P_{n,m}^1 - k_{p21} M^1 \sum_{n,m=0}^{\infty} P_{n,m}^2, \\ \frac{dM^2}{dt} = -k_{p12} M^2 \sum_{n,m=0}^{\infty} P_{n,m}^1 - k_{p22} M^2 \sum_{n,m=0}^{\infty} P_{n,m}^2, \\ \frac{dS}{dt} = -k_{reg1} S \sum_{n,m=0}^{\infty} P_{n,m}^1 - k_{reg2} S \sum_{n,m=0}^{\infty} P_{n,m}^2, \\ \frac{dP_{n,m}^1}{dt} = (k_{p11} M^1 + k_{p12} M^2) P_{n,m}^1 - (k_{p11} P_{n-1,m}^1 + k_{p21} P_{n-1,m}^2) M^1 + \\ + (k_{r11} P_{n,m}^1 + k_{d11} P_{n,m}^1) \sum_{n,m=0}^{\infty} P_{n,m}^1 + (k_{r12} P_{n,m}^1 + k_{d12} P_{n,m}^1) \sum_{n,m=0}^{\infty} P_{n,m}^2 + k_{reg1} S P_{n,m}^1, \\ \frac{dP_{n,m}^2}{dt} = (k_{p22} M^2 + k_{p21} M^1) P_{n,m}^2 - (k_{p12} P_{n,m-1}^1 + k_{p22} P_{n,m-1}^2) M^2 + \\ + (k_{r22} P_{n,m}^2 + k_{d22} P_{n,m}^2) \sum_{n,m=0}^{\infty} P_{n,m}^2 + (k_{r21} P_{n,m}^2 + k_{d21} P_{n,m}^2) \sum_{n,m=0}^{\infty} P_{n,m}^1 + k_{reg2} S P_{n,m}^2, \\ \frac{dQ_{n,m}}{dt} = (k_{d11} P_{n,m}^1 + k_{d21} P_{n,m}^2) \sum_{r,q=0}^{\infty} P_{r,q}^1 + (k_{d12} P_{n,m}^1 + k_{d22} P_{n,m}^2) \sum_{r,q=0}^{\infty} P_{r,q}^2 + \\ + \frac{k_{r11}}{2} \sum_{r,q=0}^{\infty} P_{r,q}^1 P_{n-r,m-q}^1 + \frac{k_{r12}}{2} \sum_{r,q=0}^{\infty} P_{r,q}^1 P_{n-r,m-q}^2 + \frac{k_{r21}}{2} \sum_{r,q=0}^{\infty} P_{r,q}^2 P_{n-r,m-q}^1 + \\ + \frac{k_{r22}}{2} \sum_{r,q=0}^{\infty} P_{r,q}^2 P_{n-r,m-q}^2 + k_{reg1} S P_{n,m}^1 + k_{reg2} S P_{n,m}^2. \end{array} \right. \dots (1)$$

Let us simplify the system based on the following assumptions: 1) the rates of variation of radical concentrations in the system are much smaller than the rates of their formation and decay, *i.e.*, a quasi-steady state with respect to radicals is established in the polymerization system³; 2) the reactivity of a macroradical does not depend on its length.

Let us excerpt the variation rates of radical concentrations $\frac{dP_{n,m}^1}{dt}$ and $\frac{dP_{n,m}^2}{dt}$ from system (1), which are equal to zero according to the first assumption. Then, using the designations:

$$C_{M^1} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} P_{n,m}^1, \quad C_{M^2} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} P_{n,m}^2, \quad \dots(2)$$

we obtain the following system:

$$\begin{aligned} & (k_{p11}M^1 + k_{p12}M^2 + k_{reg1}S + (k_{r11} + k_{d11})C_{M^1} + (k_{r12} + k_{d12})C_{M^2})P_{n,m}^1 = \\ & = M^1 (k_{p11}P_{n-1,m}^1 + k_{p21}P_{n-1,m}^2), \\ & (k_{p22}M^2 + k_{p21}M^1 + k_{reg2}S + (k_{r21} + k_{d21})C_{M^1} + (k_{r22} + k_{d22})C_{M^2})P_{n,m}^2 = \\ & = M^2 (k_{p12}P_{n-1,m}^1 + k_{p22}P_{n-1,m}^2), \quad n, m > 1. \end{aligned} \quad \dots(3)$$

We'll solve it using generating functions in the form:

$$\begin{aligned} G(s, u) &= \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} s^{n+m} u^{nw_a + mw_b} P_{n,m}^1, \\ F(s, u) &= \sum_{n=0}^{+\infty} \sum_{m=0}^{+\infty} s^{n+m} u^{nw_a + mw_b} P_{n,m}^2. \end{aligned} \quad \dots(4)$$

By multiplying the left and right parts of equation (3) by $S^{n+m}u^{nw_a + mw_b}$ and summing the resulting expressions by n, m , we obtain the system of equations from which we will express $G(s, u)$ and $F(s, u)$.

We will use the expressions for $G(s, u)$ and $F(s, u)$ obtained in this way to calculate the MMD moments of the active copolymer chains⁴:

$$\begin{aligned} \psi_k^{M^1} &= \left. \frac{d^k G(s, u)}{du^k} \right|_{s=u=1}, \\ \psi_k^{M^2} &= \left. \frac{d^k F(s, u)}{du^k} \right|_{s=u=1}, \end{aligned} \quad \dots(5)$$

Where $\psi_k^{M^1}$, $\psi_k^{M^2}$ are the k-th order moments of active copolymer chains differing in the nature of the terminal unit; w_a , w_b are the molecular masses of the M^1 and M^2 monomers, respectively.

The formulas for calculation of MMD moments for inactive polymer chains are obtained by multiplying the expression for $\frac{dQ_{n,m}}{dt}$ from system (1) by $(nw_a + mw_b)^k$ and summing the resulting expressions by n, m.

To calculate the mean molecular masses, we need to know the moments up to the 2nd order, inclusive, then the system of differential equations with respect to the MMD moments of the copolymer takes the form:

$$\left\{ \begin{array}{l} \frac{dI}{dt} = -k_i I, \\ \frac{dM^1}{dt} = -k_{p11} M^1 C_{M^1} - k_{p21} M^1 C_{M^2}, \\ \frac{dM^2}{dt} = -k_{p12} M^2 C_{M^1} - k_{p22} M^2 C_{M^2}, \\ \frac{dS}{dt} = -k_{reg1} S C_{M^1} - k_{reg2} S C_{M^2}, \\ \frac{d\psi_0^Q}{dt} = \frac{k_{r11}}{2} (\psi_0^{M^1})^2 + k_{r12} \psi_0^{M^1} \psi_0^{M^2} + \frac{k_{r22}}{2} (\psi_0^{M^2})^2 + \\ + (k_{reg1} S + k_{d11} C_{M^1} + k_{d12} C_{M^2}) \psi_0^{M^1} + (k_{reg2} S + k_{d21} C_{M^1} + k_{d22} C_{M^2}) \psi_0^{M^2}, \\ \frac{d\psi_1^Q}{dt} = k_{r11} \psi_0^{M^1} \psi_1^{M^1} + k_{r22} \psi_0^{M^2} \psi_1^{M^2} + k_{r12} (\psi_0^{M^1} \psi_1^{M^2} + \psi_1^{M^1} \psi_0^{M^2}) + \\ + (k_{reg1} S + k_{d11} C_{M^1} + k_{d12} C_{M^2}) \psi_1^{M^1} + (k_{reg2} S + k_{d21} C_{M^1} + k_{d22} C_{M^2}) \psi_1^{M^2}, \\ \frac{d\psi_2^Q}{dt} = k_{r11} \left((\psi_1^{M^1})^2 + \psi_0^{M^1} \psi_2^{M^1} \right) + k_{r22} \left((\psi_1^{M^2})^2 + \psi_0^{M^2} \psi_2^{M^2} \right) + \\ + (k_{reg1} S + k_{d11} C_{M^1} + k_{d12} C_{M^2}) \psi_2^{M^1} + (k_{reg2} S + k_{d21} C_{M^1} + k_{d22} C_{M^2}) \psi_2^{M^2} + \\ + k_{r12} (\psi_0^{M^1} \psi_2^{M^2} + 2\psi_1^{M^1} \psi_1^{M^2} + \psi_2^{M^1} \psi_0^{M^2}). \end{array} \right. \dots(6)$$

The initial conditions for system (6) have the form:

$$\begin{aligned}
 I(0) &= I_0, \quad M^1(0) = M_0^1, \quad M^2(0) = M_0^2, \\
 S(0) &= S_0, \quad \psi_i^Q(0) = \psi_i^{M^1}(0) = \psi_i^{M^2}(0) = 0, \\
 i &= 0,1,2.
 \end{aligned}
 \quad \dots(7)$$

Let us substitute the calculated values of molecular-mass distribution moments of the copolymer into the formulas for the number-average (M_n^Q) and mass-average (M_w^Q) molecular masses:

$$M_n^Q = \frac{\psi_1^Q}{\psi_0^Q}, \quad M_w^Q = \frac{\psi_2^Q}{\psi_1^Q}. \quad \dots(8)$$

An equally important indicator of the copolymerization product quality is given by characteristic viscosity $[\eta]$, which we'll calculate using the relationship described in⁵:

$$[\eta] = 5.4 \times 10^{-4} M_n^{Q0.66}. \quad \dots(9)$$

Application of 4th order Adams-Moulton implicit method for numeric solution of the stiff system of differential equations (6)-(7) and use of formulas (8)-(9) allows an unambiguous determination of the relationship of M_w^Q , M_n^Q and $[\eta]$ on copolymerization time to be obtained⁶.

When switching to continuous flow industrial reactor systems, one should consider the effect of hydrodynamic stage, which is described by analyzing the structure of flows based on distribution functions of residence times in a reactor. This allows one to distinguish groups of module types for reactors: ideal displacement, ideal mixing, and intermediate type.

The existing production reactors belong to the ideal mixing type. Since a continuous process is referred to, the reactors in question are best characterized as ideal mixing reactors of continuous action, i.e., reagents are continuously fed into a reactor, while the reaction mixture containing products and original compounds is vigorously stirred and continuously withdrawn from the reactor. The mean time of residence in such a reactor equals V/W , where V is the reactor volume and W is the total volume feed rate of all the reagents.

Convenient recurrent relationships between MMD moments exist for ideal mixing reactors:

$$\theta \frac{dm_j^{(k)}}{dt} = m_j^{(k-1)} - m_j^{(k)} + \theta \left(\frac{dm_j^*}{dt} \right)^{(k)} \quad \dots(8)$$

Using the kinetic modules obtained above, we obtain the following expression for continuous polymerization processes in the k -th reactor of the cascade

$$\theta^{(k)} \frac{d\bar{Y}^{(k)}}{dt} = \bar{Y}^{(k-1)} - \bar{Y}^{(k)} + \theta^{(k)} \bar{R}_y^{(k)}, \quad \dots(9)$$

where $\theta^{(k)}$ is the residence time of the reaction mixture in the k -th reactor of the cascade; the form of $\bar{R}_y^{(k)}$ is determined by the kinetic module used.

Taking (9) into account, the system of differential equations describing the butadiene-styrene continuous copolymerization process in a cascade of reactors will assume the form:

$$\left\{ \begin{aligned} \frac{dI}{dt} &= \frac{\bar{I}^{(k-1)} - \bar{I}^{(k)}}{\theta^{(k)}} - k_i I, \\ \frac{dM^{1(k)}}{dt} &= \frac{\bar{M}^{1(k-1)} - \bar{M}^{1(k)}}{\theta^{(k)}} - k_{p11} M^{1(k)} C_{M^1} - k_{p21} M^{1(k)} C_{M^2}, \\ \frac{dM^{2(k)}}{dt} &= \frac{\bar{M}^{2(k-1)} - \bar{M}^{2(k)}}{\theta^{(k)}} - k_{p12} M^{2(k)} C_{M^1} - k_{p22} M^{2(k)} C_{M^2}, \\ \frac{dS^{(k)}}{dt} &= \frac{\bar{S}^{(k-1)} - \bar{S}^{(k)}}{\theta^{(k)}} - k_{reg1} S^{(k)} \sum_{n,m=0}^{\infty} P_{n,m}^1 - k_{reg2} S^{(k)} \sum_{n,m=0}^{\infty} P_{n,m}^2, \\ \frac{d\psi_0^{Q(k)}}{dt} &= \frac{\bar{\psi}_0^{Q(k-1)} - \bar{\psi}_0^{Q(k)}}{\theta^{(k)}} + \left(\frac{1}{2} k_{r11} + k_{d11} \right) \left(\psi_0^{M^1(k)} \right)^2 + \\ &+ (k_{r12} + 2k_{d12}) \psi_0^{M^1(k)} \psi_0^{M^2(k)} + \left(\frac{1}{2} k_{r22} + k_{d22} \right) \left(\psi_0^{M^2(k)} \right)^2 + \\ &+ k_{reg1} S \psi_0^{M^1(k)} + k_{reg2} S \psi_0^{M^2(k)}, \\ \frac{d\psi_1^{Q(k)}}{dt} &= \frac{\bar{\psi}_1^{Q(k-1)} - \bar{\psi}_1^{Q(k)}}{\theta^{(k)}} + (k_{r11} + k_{d11}) \psi_0^{M^1(k)} \psi_1^{M^1(k)} + \\ &+ (k_{r12} + k_{d12}) \left(\psi_0^{M^1(k)} \psi_1^{M^2(k)} + \psi_1^{M^1(k)} \psi_0^{M^2(k)} \right) + \\ &+ (k_{r22} + k_{d22}) \psi_0^{M^2(k)} \psi_1^{M^2(k)} + k_{reg1} S \psi_1^{M^1(k)} + k_{reg2} S \psi_1^{M^2(k)}, \\ \frac{d\psi_2^{Q(k)}}{dt} &= \frac{\bar{\psi}_2^{Q(k-1)} - \bar{\psi}_2^{Q(k)}}{\theta^{(k)}} + (k_{r11} + k_{d11}) \psi_0^{M^1(k)} \psi_2^{M^1(k)} + k_{r11} \left(\psi_1^{M^1(k)} \right)^2 + \\ &+ (k_{r12} + k_{d12}) \left(\psi_0^{M^1(k)} \psi_2^{M^2(k)} + \psi_2^{M^1(k)} \psi_0^{M^2(k)} \right) + 2k_{r12} \psi_1^{M^1(k)} \psi_1^{M^2(k)} + \\ &+ (k_{r22} + k_{d22}) \psi_0^{M^2(k)} \psi_2^{M^2(k)} + k_{reg1} S \psi_2^{M^1(k)} + k_{reg2} S \psi_2^{M^2(k)}. \end{aligned} \right. \quad \dots(10)$$

The initial conditions for system (10) will assume the form:

$$I^{(0)}(0) = I_0, M^{1(0)}(0) = M_0^1, M^{2(0)}(0) = M_0^2, S^{(0)}(0) = S_0, \\ \psi_i^{Q(0)}(0) = \psi_i^{M^1(0)}(0) = \psi_i^{M^2(0)}(0) = 0, i = 0,1,2, \dots(11)$$

where I_0 is the initial concentration of the initiator; M_0^1 and M_0^2 are the initial concentrations of butadiene and styrene, respectively; and S_0 is the initial concentration of the chain transfer agent.

RESULTS AND DISCUSSION

Solving the system of differential equations (10)-(11) allows one to calculate the characteristics of the copolymer product formed as a function of the number of the polymerizer⁷, calculate the molecular mass distribution, obtain plots of reagent consumption, conversion, and polydispersity versus time.

ACKNOWLEDGEMENT

Research work was supported by the Ministry of Education and Science of the Russian Federation as a part of the base portion of the state task in the field of scientific activity.

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Accepted : 16.03.2014