MATHEMATICAL SIMULATION STUDY OF COPOLYMER COMPOSITION AND COMPOSITIONAL HETEROGENEITY DURING THE SYNTHESIS OF EMULSION-TYPE BUTADIENE-STYRENE RUBBER

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ABSTRACT

At the moment, synthetic rubbers range is wide enough. The most common are the rubbers received through the mechanism of free-radical copolymerization of butadiene with styrene in the emulsion. Procedure of monomer addition to the polymer chain determines the properties of rubber. Production of styrene-butadiene rubber is a complex process, which simplifies the study of the construction of mathematical model. In turn, it allows to understand course of the process, perform its optimization and predict characteristics of the final product.

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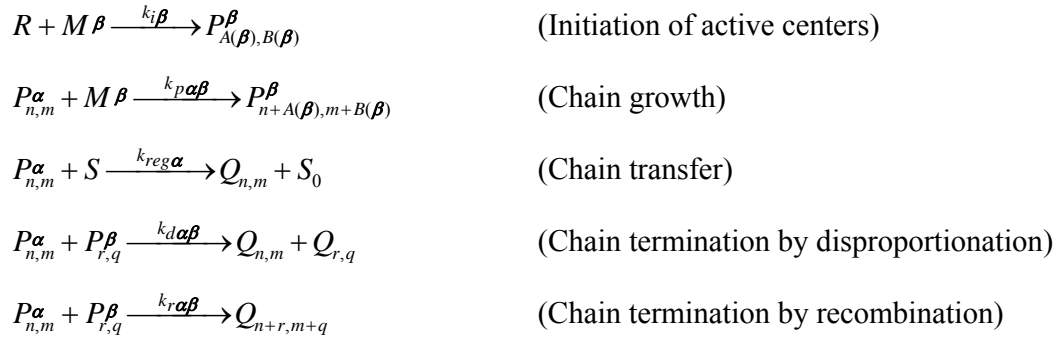
INTRODUCTION

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, it has been assumed 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:

$$I \xrightarrow{k_d} 2R \qquad \text{(Initiator decay)}$$
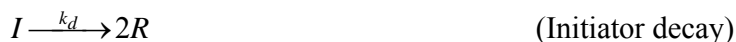
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$$R + M^\beta \xrightarrow{\;k_i\beta\;} P^\beta_{A(\beta),B(\beta)} \qquad \text{(Initiation of active centers)}$$

$$P^\alpha_{n,m} + M^\beta \xrightarrow{\;k_p\alpha\beta\;} P^\beta_{n+A(\beta),m+B(\beta)} \qquad \text{(Chain growth)}$$

$$P^\alpha_{n,m} + S \xrightarrow{\;k_{reg}\alpha\;} Q_{n,m} + S_0 \qquad \text{(Chain transfer)}$$

$$P^\alpha_{n,m} + P^\beta_{r,q} \xrightarrow{\;k_d\alpha\beta\;} Q_{n,m} + Q_{r,q} \qquad \text{(Chain termination by disproportionation)}$$

$$P^\alpha_{n,m} + P^\beta_{r,q} \xrightarrow{\;k_r\alpha\beta\;} Q_{n+r,m+q} \qquad \text{(Chain termination by recombination)}$$

Where $\alpha, \beta = \overline{1,2}$; 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 $n + m$ comprising n units of the M^1 monomer and m 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; $A(\beta) = \{1 \text{ if } \beta = 1, \text{ else } 0\}$; $B(\beta) = \{1 \text{ if } \beta = 2, \text{ else } 0\}$. Mathematical model of butadiene-styrene copolymerization can be represented as a system of non-linear differential equations[6]:

$$
\left\{
\begin{aligned}
&\frac{dI}{dt} = -k_i I, \\[4pt]
&\frac{dM^1}{dt} = -k_{p11}M^1\sum_{n,m=0}^{\infty}P^1_{n,m} - k_{p21}M^1\sum_{n,m=0}^{\infty}P^2_{n,m}, \\[4pt]
&\frac{dM^2}{dt} = -k_{p12}M^2\sum_{n,m=0}^{\infty}P^1_{n,m} - k_{p22}M^2\sum_{n,m=0}^{\infty}P^2_{n,m}, \\[4pt]
&\frac{dS}{dt} = -k_{reg1}S\sum_{n,m=0}^{\infty}P^1_{n,m} - k_{reg2}S\sum_{n,m=0}^{\infty}P^2_{n,m}, \\[4pt]
&\frac{dP^1_{n,m}}{dt} = (k_{p11}M^1 + k_{p12}M^2)P^1_{n,m} - (k_{p11}P^1_{n-1,m} + k_{p21}P^2_{n-1,m})M^1 + \\[4pt]
&\quad + (k_{r11}P^1_{n,m} + k_{d11}P^1_{n,m})\sum_{n,m=0}^{\infty}P^1_{n,m} + (k_{r12}P^1_{n,m} + k_{d12}P^1_{n,m})\sum_{n,m=0}^{\infty}P^2_{n,m} + k_{reg1}SP^1_{n,m}, \\[4pt]
&\frac{dP^2_{n,m}}{dt} = (k_{p22}M^2 + k_{p21}M^1)P^2_{n,m} - (k_{p12}P^1_{n,m-1} + k_{p22}P^2_{n,m-1})M^2 + \\[4pt]
&\quad + (k_{r22}P^2_{n,m} + k_{d22}P^2_{n,m})\sum_{n,m=0}^{\infty}P^2_{n,m} + (k_{r21}P^2_{n,m} + k_{d21}P^2_{n,m})\sum_{n,m=0}^{\infty}P^1_{n,m} + k_{reg2}SP^2_{n,m}, \\[4pt]
&\frac{dQ_{n,m}}{dt} = (k_{d11}P^1_{n,m} + k_{d21}P^2_{n,m})\sum_{r,q=0}^{\infty}P^1_{r,q} + (k_{d12}P^1_{n,m} + k_{d22}P^2_{n,m})\sum_{r,q=0}^{\infty}P^2_{r,q} + \\[4pt]
&\quad + \frac{k_{r11}}{2}\sum_{r,q=0}^{\infty}P^1_{r,q}P^1_{n-r,m-q} + \frac{k_{r12}}{2}\sum_{r,q=0}^{\infty}P^1_{r,q}P^2_{n-r,m-q} + \frac{k_{r21}}{2}\sum_{r,q=0}^{\infty}P^2_{r,q}P^1_{n-r,m-q} + \\[4pt]
&\quad + \frac{k_{r22}}{2}\sum_{r,q=0}^{\infty}P^2_{r,q}P^2_{n-r,m-q} + k_{reg1}SP^1_{n,m} + k_{reg2}SP^2_{n,m}.
\end{aligned}
\right.
\qquad \text{…(1)}
$$

EXPERIMENTAL

The direct problem is solved using a whole set of kinetic parameters that characterize the rates of the corresponding steps. However, not all the values were found to match the conditions and mechanism of the emulsion copolymerization process at a given temperature. Therefore, to refine some kinetic parameters (namely, the reaction rate constants of chain termination by the recombination and disproportionation mechanisms), the inverse problem was solved[4]. If the working model of the copolymerization process is available, it is most convenient to solve the inverse problem of copolymerization kinetics using the "direct problem method". The approach consists of the following: the molecular characteristics for the assumed kinetic scheme of the process are calculated by solving the direct problem and the results are compared to the corresponding experimental data.

The match between the calculated values of inherent viscosity and conversion, i.e., with those process characteristics and polymer properties that can be satisfactorily described by the working model, with the corresponding experimental data is used as the source for solving the inverse problem. The problem is reduced to find the minimum of functional of match between the model and experimental values and is solved in three stages.

Stage 1: Approximation of the conversion plot. Conversion is calculated using the equations characterizing the rate of concentration changes for the M^1 and M^2 monomers

$$\frac{dM^1}{dt} = -k_{p11}M^1\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P^1_{n,m} - k_{p21}M^1\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P^2_{n,m},$$

$$\frac{dM^2}{dt} = -k_{p12}M^2\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P^1_{n,m} - k_{p22}M^2\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P^2_{n,m} \qquad \ldots(2)$$

where the concentrations of active chains are calculated applying the quasi-steady-state hypothesis

$$\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P^1_{n,m} = \sqrt{\frac{2k_d I}{(k_{r11}+k_{d11})+2\beta(k_{r12}+k_{d12})+\beta^2(k_{r12}+k_{d12})}} \qquad \ldots(3)$$

$$\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P^2_{n,m} = \beta\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P^1_{n,m} \qquad \ldots(4)$$

Then, identification of unknown kinetic parameters in the form of the ratio $2k_d I / ((k_{r11}+k_{d11})+2\beta(k_{r12}+k_{d12})+\beta^2(k_{r12}+k_{d12}))$ is carried out by minimizing the following functional:

$$H(z) = \sum_{j=1}^{p} (K_j^{\exp} - K_j^{calc})^2 \qquad \ldots(5)$$

$$z = \frac{2k_d I}{(k_{r11} + k_{d11}) + 2\beta(k_{r12} + k_{d12}) + \beta^2(k_{r12} + k_{d12})} \qquad \ldots(6)$$

where $K_j^{\exp}$ are the conversion values determined during the experiment and K_j^{calc} are the calculated conversion values.

Stage 2: Approximation of intrinsic viscosity values. By approximation of the conversion plot, the following ratio was found:

$$\frac{k_d}{(k_{r11} + k_{d11}) + 2\beta(k_{r12} + k_{d12}) + \beta^2(k_{r12} + k_{d12})}$$

which was recorded and used in subsequent calculations. The intrinsic viscosity values were calculated using following relationship[1]:

$$[\eta] = 5.4 \times 10^{-4} M_\eta^{Q^{0.66}} \qquad \ldots(7)$$

Approximation of intrinsic viscosity values involves minimization of the functional:

$$H(z) = \sum_{j=1}^{p} ([\eta]_j^{\exp} - [\eta]_j^{calc})^2, z = (k_r, k_d) \qquad \ldots(8)$$

where $[\eta]_j^{\exp}$ are the intrinsic viscosity values determined during the experiment and $[\eta]_j^{calc}$ are the calculated intrinsic viscosity values.

Refining the kinetic parameters by minimization of functionals (5) and (8) was carried out using the Hooke-Jeeves numeric algorithm of the configuration method.

Stage 3: The second stage of solving the inverse problem does not allow a unique solution to be obtained. Additional analysis of the molecular mass distribution (MMD) was performed in order to choose an adequate set of kinetic parameters from among the set of solutions obtained. The MMD was built using the model Schulz-Flory distribution that considers the possibility of chain transfer by interaction with the chain transfer agent. In such case, the mass distribution is determined by the following relationship:

$$q_w(M) = \frac{p\lambda^2}{2-p} M e^{-\lambda M} + \frac{(1-p)\lambda^3}{2-p} M^2 e^{-\lambda M} \qquad \ldots (9)$$

where λ is a statistical MMD parameter expressed as the ratio of the chain termination rate to the chain growth rate; P is the fraction of polymer radicals that decay by the disproportionation mechanism.

Table 1 lists the values of kinetic parameters that give the best approximation of the calculated MMD curve to the experimental points (Fig. 1).
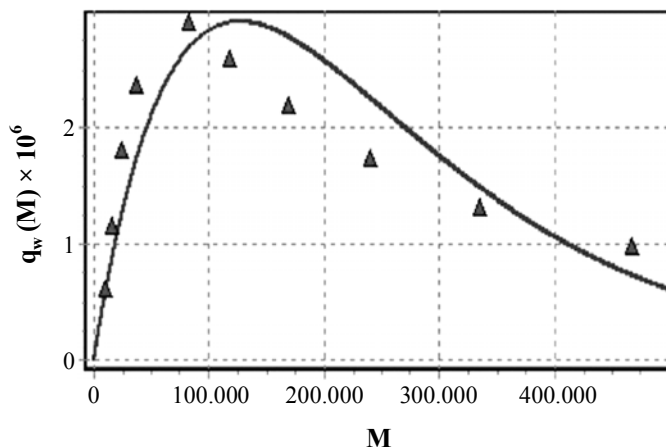
Fig. 1: Plots of experimental (▲) and calculated values (solid line) of molecular mass distribution on molecular mass

Table 1: Values of kinetic parameters obtained during solution of the inverse problem

k_{r11}	20-30 l/(mol·s)	k_{d11}	0-10 l/(mol·s)
$k_{r12} = k_{r21}$	0-10 l/(mol·s)	$k_{d12} = k_{d21}$	0-10 l/(mol·s)
k_{r22}	0-10 l/(mol·s)	k_{d22}	0-10 l/(mol·s)

The calculated kinetic parameters were used to obtain the relationships of averaged molecular characteristics, conversion and characteristic viscosity on the number of the polymerization reactor (Fig. 2)[5].

Since the process in question is a copolymerization process involving two monomers (butadiene and styrene), it is also required that the model predict the copolymer composition and distribution of units in the chain. This is due to the fact that the properties of copolymers

are largely determined by the polymer composition and distribution of units of particular monomers, *i.e.*, compositional heterogeneity (CH). The CH is considerably affected by the activity of the monomers and by various physical factors.
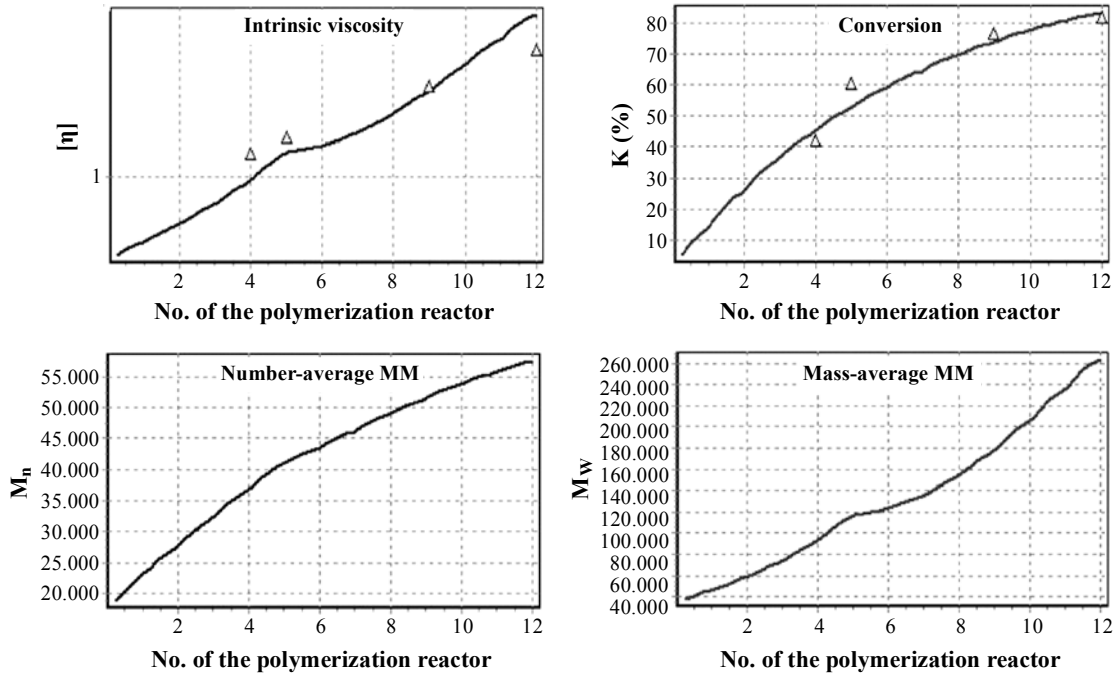
Fig. 2: Plots of experimental (▲) and calculated (solid lines) values of conversion, intrinsic viscosity, number-average and mass-average molecular masses versus time

If we take an arbitrary copolymer molecule, it can be characterized by the numbers m and n of the M^1 and M^2 monomer units. These numbers are considered as the components of some vector I characterizing the molecule chemical size $l = m + n$ and composition $\zeta_1 = \dfrac{m}{l}$, $\zeta_2 = \dfrac{m}{l}$.

In addition to the MMD considered above, an important role for copolymers is played by the size-composition distribution (SCD)[2], both numeric and mass-based. The numeric SCD $f_N(I)$ equals the fraction of molecules in a sample of a polymer characterized by vector I. The mass-based SCD $f_W(I)$ equals the fraction of all units in these molecules. The latter is determined by the ratio:

$$f_W(I) = f_W(l)W(l|\zeta) \qquad\qquad …(10)$$

where $f_W(l)$ is the size distribution and $W(l|\zeta)$ is the fractional composition distribution.

To obtain the SCD of the copolymerization products present in the reaction mixture at a given conversion p, one should average the instantaneous SCD values over p:

$$\langle f_W(l, \zeta) \rangle = \frac{1}{p} \int_0^p f_W(l, p') W(l|\zeta; p') dp' \qquad \ldots(11)$$

Since the molecular mass of the copolymerization product is rather high, the majority of monomer units will be involved in rather long chains. Within this approximation, the instantaneous component of composition distribution is neglected in comparison with its conversion component, and SCD is factored as a product of distributions by size and by composition:

$$\langle f_W(l, \zeta) \rangle = f_W(l; p') W(l|\zeta; p') \qquad \ldots(12)$$

The first of them is described by the following expression:

$$f_W(l) = \left[\frac{(1-\lambda)l}{2} \theta + \lambda \right] \theta^2 l e^{-\theta l} \qquad \ldots(13)$$

where λ is the fraction of radicals that decay by the disproportionation mechanism,

$$\theta = \frac{k_i I}{k_{p11} C_{M1} M^1 + k_{p12} C_{M1} M^2 + k_{p21} C_{M2} M^1 + k_{p22} C_{M2} M^2}$$

and the parameters are taken at the conversion value where the instantaneous copolymer composition X equals ζ. The second distribution has the form:

$$\langle f_W(l; p') \rangle = \frac{1}{p} \left| \frac{dX}{dp} \right|^{-1}_{X=\zeta} \qquad \ldots(14)$$

The latter distribution is built using the dependence of instantaneous copolymer composition X on conversion p in parametric form:

$$X = X(x), x = x(p) \qquad \ldots(15)$$

where x is the molar fraction of monomers.

The SCD of the copolymerization products was obtained by means of a software complex used to solve the direct and inverse problems but expanded to enable numeric calculations of the distributions specified above. Distribution (14) that was found for a conversion of 70% has the form shown in Fig. 3.
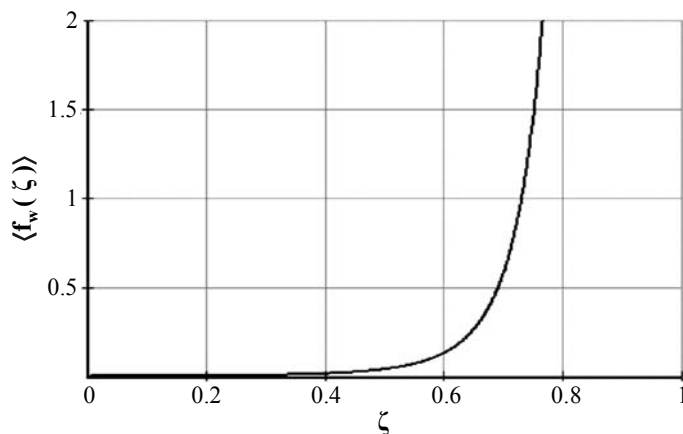
Fig. 3: Composition distribution curve for products of binary butadiene-styrene copolymerization obtained at a conversion of 70%

The distribution of copolymerization products by size and composition is shown in Fig. 4. The composition of the copolymer mixture for this state is as follows: the content of butadiene is 68.8% and that of styrene is 31.2%.
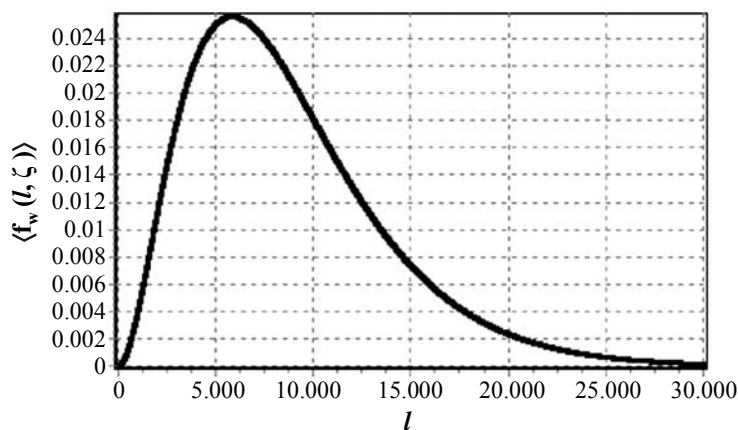
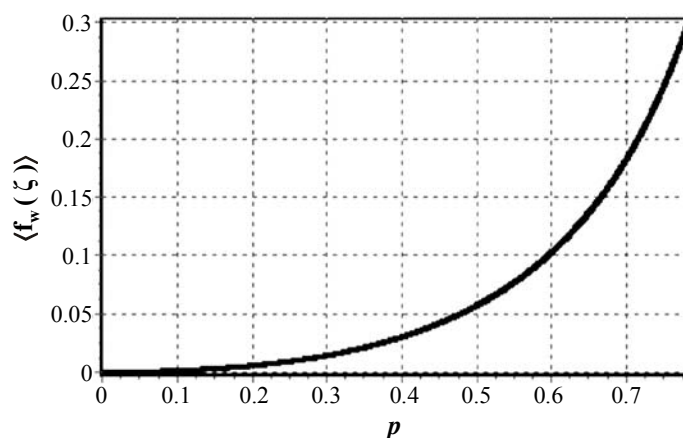**Fig. 4: Distribution of copolymerization products by size and composition at a conversion of 70%**

To improve the quality of the copolymerization product, it is important to know the copolymerization conditions where products with inhomogeneous composition can be formed, in order to avoid undesirable composition heterogeneity of the copolymerization products. This heterogeneity is quantitatively characterized by the dispersion of composition distribution (CD):

$$\left\langle \sigma^2 \right\rangle = \frac{1}{p} \int_0^p \sigma^2(p')\,dp' = \left\langle X^2 \right\rangle - \left\langle X \right\rangle^2 \qquad \ldots(25)$$

Where $\langle X \rangle$ is the average composition obtained by averaging its instantaneous value X over all degrees of conversion p' smaller than p:

$$\left\langle X \right\rangle = \frac{1}{p} \int_0^p X\,dp' \qquad \ldots(26)$$

The values of CD expressed as a difference of the two integrals were calculated using the Runge-Kutta numerical method. The conversion plot obtained by this method is shown in Fig.5.

Fig. 5: Conversion plot of the dispersion of composition distribution of butadiene-styrene copolymerization products

RESULTS AND DISCUSSION

A mathematical model of butadiene-styrene copolymerization has been built. The model makes it possible to calculate the molecular weight distribution, obtain plots of

reagent consumption, conversion, and polydispersity versus time, analyze the chemical size and composition of macromolecules, as well as composition heterogeneity.

REFERENCES

1.   C. Booth, L. R. Beason and J. T. Bailey, J. Appl. Polymer Sci., **13**, 116-123 (1961).

2.   A. R. Khokhlov and S. I. Kuchanov, Lectures on the Physical Chemistry of Polymers, Mir, Moscow (2000).

3.   P. A. Kirpichnikov, V. V. Beresnev and L. M. Popova, Album of Process Schemes of the Main Production Units in Synthetic Rubber Industry, Khimiya, Leningrad (1986).

4.   E. N. Miftakhov and S. A. Mustafina, Simulation and Theoretical Studies of Continuous Emulsion Copolymerization Process, Vestnik UGATU, 15, **5(45)**, 98-104 (2011).

5.   E. N. Miftakhov, S. A. Mustafina and I. Sh. Nasyrov, Simulation of Butadiene-Styrene Free Radical Copolymerization Process in the Production of Emulsion Type Rubbers, Vestnik KGTU, **24**, 78-82 (2012).

6.   S. A. Mustafina, E. N. Miftakhov and T. A. Mikhailova, Solving the Direct Problem of Butaiene-Styrene Copolymerization, Int. J. Chem. Sci., **12-2**, 564-572 (2014).