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MATHEMATICAL STUDY OF THE BUTADIENE-STYRENE COPOLYMERIZATION PRODUCT BY THE MONTE CARLO METHOD

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ABSTRACT

Statistical approach to the description of mathematical model of butadiene-styrene copolymerization process has been considered in this paper. The approach is based on the Monte Carlo method. The mathematical model allows researching properties of the product of copolymerization and predicting values of molecular characteristics depending on conversion and carrying out the calculation of copolymer's molecular weight distribution.

Key words: Copolymerization, Butadiene, Styrene, Statistical approach, Monte Carlo method, Molecular weight distribution.

INTRODUCTION

At the present time, the range of synthetic rubbers which are made at the domestic industrial enterprises, are rather wide. This is due to labor input of receiving and low quality indicators of plant rubber. Basis of synthetic rubbers production (butadiene, butadiene-styrene, isoprene, butadiene-nitrile, etc.) are polymerization processes. Rubbers, which represent a product of radical copolymerization of butadiene with styrene in an emulsion are the most widespread, as they are used for obtaining rubber materials for various purposes. The combination of monomers in a chain of successive reactions of connection with each other influences qualitatively important properties of rubbers. But their production

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represents difficult technological process, which studying becomes simpler at building of mathematical model. Simulation allows one not only to predict the properties of a product but also optimize the production process[1]. Therefore, the important task is studying and modification of copolymerization product's quality indicators by methods of mathematical modelling.

EXPERIMENTAL

In describing the mathematical model of the copolymerization processes there are two approaches: kinetic and statistical. Kinetic approach is classical in solving problems of chemical kinetics and has successfully established itself not only in the study of physical and chemical phenomena, but also in the optimization of technological processes in the chemical industry. This 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. These equations are derived from the conditions of the material balance for each component reactions involving the law of mass action, which determines the rate of formation and disappearance of this component[2]. As the number of monomer molecules can reach tens of thousands, the kinetic scheme, which includes all the main reaction occurring in the system is reduced to an almost infinite system of differential equations. Directly to solve such a system is not possible, so at writing the model equations, it is converted to moments of the molecular weight distribution[3]. Using such a simplification of the system allows us to calculate the average molecular characteristics of the resulting product, as well as under conditions of uncertainty of the rate constants of some elementary reactions successfully formulate and solve the inverse problem[4]. However, to get the picture changes the molecular weight distribution and study the composition of the product obtained in this approach is no longer possible.

When using statistical approach the polymer chain's simulation is carried out by means of random variables. The basis of this approach is the simulation of the each polymer molecule's propagation. Each link of the growing polymeric chain is considered as concrete random process of the conditional motion along the polymer molecule, and the probability of random processes realization is considered to an equal portion of the molecules corresponding to it among all others in a reaction system. The major advantage of a statistical method is that it allows to exhaustingly describe detailed structure of macromolecules in terms of several probability parameters[5]. This approach to the simulation of polymerization processes bears in itself the Monte Carlo method, which represents a numerical method of mathematical tasks solution by means of modelling of random values. As the method works at the level of particles, it gives the chance to accumulate information

on structure and length of the formed polymer chains and to receive molecular characteristics of polymerization's product at any moment.

For realization a statistical approach to the simulation of copolymerization process, we apply the method proposed in 1977 by the American physicist Gillespie[6]. Describe the algorithm of the following sequence of steps.

(i) For 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:

Initiator decomposition

$$I \xrightarrow{k_d} 2R$$

Initiation of active centers

$$R + M^{\beta} \xrightarrow{k_{i\beta}} P^{\beta}_{A(\beta),\,B(\beta)}$$

Chain propagation

$$P^{\alpha}_{n,m} + M^{\beta} \xrightarrow{k_{p\alpha\beta}} P^{\beta}_{n+A(\beta),\ m+B(\beta)}$$

Chain transfer

$$P^{\alpha}_{n,m} + S \xrightarrow{k_{reg\,\alpha}} Q_{n,m} + S_0$$

Chain termination by disproportionation

$$P^{\alpha}_{n,m} + P^{\beta}_{r,q} \xrightarrow{k_{d\alpha\beta}} Q_{n,m} + Q_{r,q}$$

Chain termination by recombination

$$P^{\alpha}_{n,m} + P^{\beta}_{r,q} \xrightarrow{k_{r\alpha\beta}} Q_{n+r,m+q}$$

where $\alpha, \beta = \overline{1,2}$; M^1, 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, k_r are the reaction

rate constants of initiation, growth, chain propagation, disproportionation, and recombination elementary stages, respectively; A(β) = {1, if β = 1; else 0}; B(β) = {1, if β = 2; else 0}[2].

(ii) Transform the experimental rate constant of elementary reactions to stochastic rate constants according to the following equations:

$\tilde{k} = k$ for first order reactions;

$\tilde{k} = \frac{k}{V.N_A}$ for bimolecular reactions between different species (V is the reaction volume, N_A is the Avogadro's number).

(iii) Then calculate the reaction rate for every reaction according to the equation:

$$R_i = \tilde{k}_i.X_A.X_B$$

where $\tilde{k}_i$ – is the rate constant of the i-th reaction in which reagents A and B participate; X_A, X_B are the numbers of reagent's molecules.

The total reaction rate is then calculated as the summation of the individual reaction rates:

$$R_{sum} = R_1 + R_2 + \ldots + R_n$$

Where n – is the number of elementary reactions forming kinetic scheme of the copolymerization process.

(iv) Then the probability of any reaction taking place at a given time is calculated by the following equation:

$$p_i = \frac{R_i}{R_{sum}}, i = 1..n$$

It is apparent that $p_1 + p_2 + \ldots + p_n = 1$.

(v) Generate a random number r uniformly distributed between 0 and 1 and pick up such value k that the inequality took place:

$$\sum_{i=1}^{k-1} p_i < r < \sum_{i=1}^{k} p_i .$$

Consequently, reaction under an index k has to result from an imitating choice.

(vi) Continuing reasoning similarly, we will build all scheme of carrying out reaction[7].

RESULTS AND DISCUSSION

On the basis of the developed algorithm the program complex was created in the integrated development programming environment Visual Studio in the C# language[8]. It allowing carrying out calculation of process of emulsion-type butadiene-styrene copolymerization in the reactor on the basis of mathematical model. To illustrate the operation of the program complex computational experiment has been performed to study the process brought to the 70% monomer conversion. The following compounding of process was used: polymerizer volume – 10.8 m^3, the total weight of the monomer mixture – 3 t., dosage of butadiene – 70 weight parts, styrene – 30 weight parts, initiator (pinane hydroperoxide) – 0.048 weight parts, chain-transfer agent (tertiary dodecyl mercaptan) – 0.28 weight parts.

The constructed model allows to investigate properties of copolymerization product and to predict values of molecular characteristics of copolymer. Fig. 1 and Fig. 2 shows the dependences of values of number-average and weight-average molecular masses on conversion of monomers, which represents the share of transformation of the sum of both monomers to copolymer.

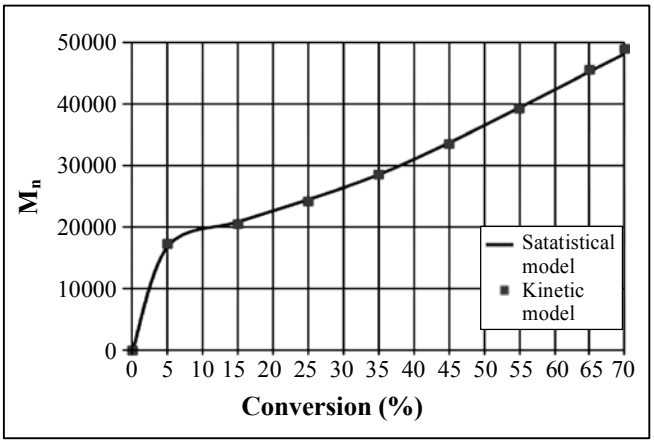

Fig. 1: Dependence of number-average molecular mass values of copolymer on conversion

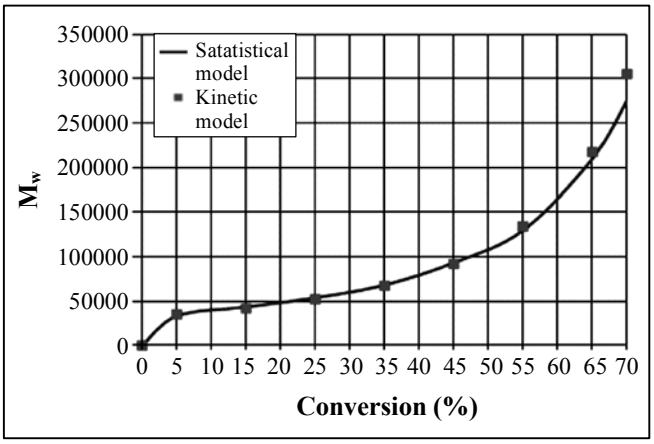

Fig. 2: Dependence of weight-average molecular mass values of copolymer on conversion

One of the most important characteristics of copolymerization's product is intrinsic viscosity [η]. For its definition the following dependence was used[9]:

$$[\eta] = 5.4 \times 10^{-4} M_{\eta}^{0.66}$$

where M_{η} – viscosity-average molecular weight.

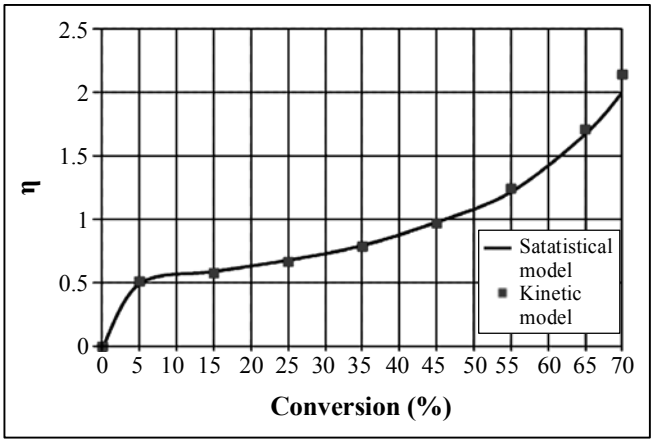

Fig. 3: Dependence of intrinsic viscosity values of copolymer on conversion

Earlier in work[10], calculation of copolymerization process on the basis of kinetic approach to modelling was carried out. Results of statistical approach show satisfactory

coordination with results of kinetic model. The relative difference between values for number-average molecular mass makes no more than 2.43%, for weight-average molecular mass – no more than 9.64%, for intrinsic viscosity – no more than 6.47% (the maximal values correspond to conversion of 70%).

For an assessment of quality of the received product the absolute importance is made by molecular weight distribution as at any sample of polymer there are macromolecules of the different sizes. It shows a ratio of quantities of macromolecules of different molecular masses. Fig. 4 shows the plot of copolymer's molecular weight distribution at 70% conversion, which represents the dependence between molecular weight and polymer mass fractions. Molecular-weight distribution is narrow, that is in copolymer prevails the fraction with a certain molecular weight and the part of fractions with smaller or larger values of molecular weights is much lower. In this example, there is predominance of fractions having a molecular weight about $5 \cdot 10^4 - 6 \cdot 10^4$. The peak of a curve corresponds to value of number-average molecular mass of copolymer.

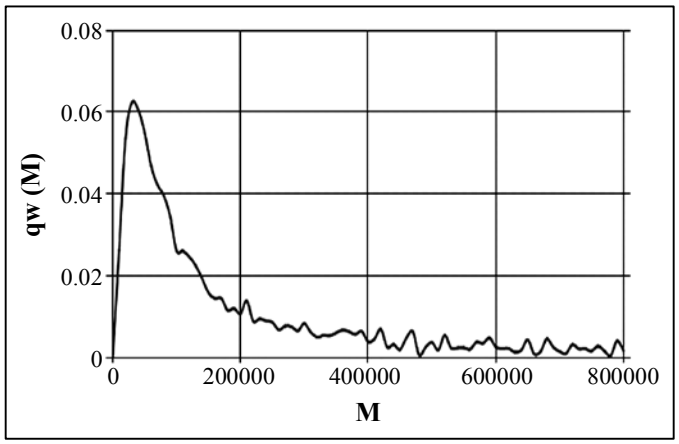

Fig. 4: Molecular weight distribution of copolymer at 70% conversion

CONCLUSION

The statistical approach considered in this paper allows studying properties of the product of emulsion-type butadiene-styrene copolymerization. As simulation of each macromolecule's growth and tracing of the processes happening to it is the basis of this approach, it allows accumulating information on composition and length of the formed copolymer chains. On the basis of this information carrying out the calculation of molecular weight distribution and prediction dependences of change of the main copolymer's molecular characteristics on conversion is possible at any moment.

REFERENCES

1. S. L. Podval'nyi, Simulation of Industrial Polymerization Processes, Moscow: Khimiya (Chemistry, in Rus.) Publishing House (1979) p. 256.

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

3. 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, Herald KTU, Kazan, **24** (2012) pp. 78-82.

4. E. N. Miftakhov, I. Sh. Nasyrov and S. A. Mustafina, Simulation of Butadiene-Styrene Emulsion Copolymerization Process, Bashkir Chem. J. Ufa, **18(1)**, 21-24 (2011).

5. A. R. Khokhlov and S. I. Kuchanov, Lectures on the Physical Chemistry of Polymers, Moscow: Mir (World, in Rus) (2000) p. 193.

6. D. Gillespie, Exact Stochastic Simulation of Coupled Chemical Reactions, J. Phys. Chem., **81(25)**, 2340-2361 (1977).

7. D. V. Berzina, T. A. Mikhailova, E. N. Miftakhov and S. A. Mustafina, Simulation Approach to the Analysis of Copolymerization Processes, European J. Nat. History, **6**, 28-29 (2013).

8. T. A. Mikhailova, E. N. Miftakhov and S. A. Mustafina, Computer Modelling of the Emulsion-type Copolymerization Process on the Basis of the Monte Carlo Method, Control Systems and Informational Technologies, **3.2(57)**, 250-254 (2014).

9. C. Booth, L. R. Beason and J. T. Bailey, Incremental Modification of Styrene-Butadiene Rubber with Tert-dodecyl Mercaptan, J. Appl. Polymer Sci., **13**, 116-123 (1961).

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

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