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MATHEMATICAL MODELLING OF THE COPOLYMERIZATION OF STYRENE WITH MALEIC ANHYDRIDE IN A HOMOGENEOUS ENVIRONMENT

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ABSTRACT

In this paper, a mathematical model based on the kinetic scheme of the copolymerization of styrene and maleic anhydride was built. The mathematical model is a system of ordinary differential equations whose dimension tends to infinity, because of the infinite number of the reaction components. Applying the method of statistical moments, infinite system of ordinary differential equations is reduced to a system with a finite number of equations and becomes solvable. Numerical solution of the target system to determine the average molecular properties such as number average and weight average molecular weights and polydispersity index.

Key words: Copolymerization, Kinetic scheme, Mathematical model, Polymerization process, Styrene, Maleic anhydride, Stiromal, The method of moments, The molecular weight distribution.

INTRODUCTION

In the modern industrial production methods are increasingly used mathematical modeling of technological processes, allowing to solve problems of prediction and optimization of production. Currently, one of the most urgent problems in conducting experimental studies is the problem of extracting the maximum amount of useful information on the investigational process at minimal cost[1,2]. In solving production problems and insufficient knowledge of the mechanisms of the processes is not always possible to perform a sufficient number of required experiments[3]. In this regard, the development of a mathematical model is an actual job.

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The paper presents a mathematical model of the process of obtaining styrene and maleic anhydride.

Copolymers of styrene with maleic anhydride are important commercial products and used in various industries: in oil - a part of the drilling fluid, in paint - as a film former, in the foundry industry - for the preparation of core mixtures, as a stabilizer in the production of polymers, as flocculant in the treatment of industrial waste water and also used as a binder in coatings or as a feedstock for the production of photo-polymer binders and radiation-curable coatings, etc.

EXPERIMENTAL

Kinetic method for modeling polymerization processes is the generation and numerical solution of kinetic equations for the concentrations of all types of particles participating in the process (molecules, free radicals, macromolecules, macromolecular free radicals). The kinetic scheme of polymerization of styrene with maleic anhydride comprises the following elementary steps:

- Initiator decomposition $I \xrightarrow{k_i} 2R$,
- Chain growth $R + M \xrightarrow{k_{i1}} P_1$,
- The continuation chain $P_i + M \xrightarrow{k_p} P_{i+1}, i \geq 1$.
- Chain termination as a result of interaction with the radical $P_n + R \xrightarrow{k_r} Q_n$,
- Chain termination by recombination $P_n + P_m \xrightarrow{k_{rec}} Q_{n+m}$,
- Chain termination disproportionation $P_n + P_m \xrightarrow{k_{dis}} Q_n + Q_m$,

where M – monomer, R – free radical, I – initiator, P_n, Q_n – active ("growing") and inactive ("dead") the chain length of the copolymer, respectively containing n links M monomer, k_i, k_{i1}, k_p, k_r, k_{rec}, k_{dis} – constants of elementary stages of initiation, growth stages and open circuit, respectively.

The regular alternation of links due to the influence of polarity and steric effects of acceptor-donor functional groups with opposing interfacing with double bonds. In the copolymerization of maleic anhydride and styrene considering mesomeric structure in the

transition state. The determining factor in this alternation are polar resonance forms in transition, which are similar to a molecular complex. Therefore, the link of "styrene + maleic anhydride" in the description of the mathematical model was made for a single monomer.

Making up the matrix of stoichiometric coefficients and multiplying it on the column vector of reaction velocities, obtain the infinite system of ordinary nonlinear differential equations describing the copolymerization of styrene with maleic anhydride. Next, using the method of moments, infinite system of differential equations reduced to the target system relative to distribution of moments, used in statistics and probability theory to estimate the distribution of the random variables. Moments of order j of the active and inactive polymer chains, calculated by the formulas[4,5]:

$$\mu_j = \sum_{i=2}^{\infty} i^j [P_i], \quad \eta_j = \sum_{i=2}^{\infty} i^j [Q_i] \qquad \ldots(1)$$

To calculate the average molecular weight of the copolymer is necessary to know moments up to second order. Then the system of differential equations for moments the molecular weight distribution (MWD) of the polymer by means of (1) takes the form:

$$\frac{d[I]}{dt} = -k_i [I],$$

$$\frac{d[R]}{dt} = 2 k_i f [I] - k_{i1} [M] [R] - k_r [P_1] [R],$$

$$\frac{d[M]}{dt} = -[M] k_p \mu_0 - [M] k_{i1} [R],$$

$$\frac{d[P_1]}{dt} = k_{i1} [M] [R] - k_p [M] [P_1] - k_r [R] [P_1] - (k_{rec} + k_{dis}) [P_1]^2 \mu_0,$$

$$\frac{d[Q_1]}{dt} = k_r [R] [P_1] + \frac{1}{2} k_{rec} [P_1] [R] + k_{dis} [P_1]^2 \mu_0,$$

$$\frac{d\mu_0}{dt} = k_p [M] [P_1] - k_r [R] \mu_0 - (k_{rec} + k_{dis}) [P_1] \mu_0^2, \qquad \ldots(2)$$

$$\frac{d\mu_1}{dt} = k_p [M] [P_1] + k_p [M] [P_1] \mu_0 - k_r [R] \mu_1 - (k_{rec} + k_{dis}) [P_1] \mu_1 \mu_0,$$

$$\frac{d\mu_2}{dt} = k_p[M]\left([P_1]\mu_2 + 2[P_1]\mu_1 + [P_1]\mu_0 - \mu_2\right) - k_r[R]\mu_2 - \left(k_{rec} + k_{dis}\right)[P_1]\mu_2\mu_0,$$

$$\frac{d\eta_0}{dt} = k_r[R]\mu_0 + k_{rec}[P_1]^2\mu_0^2 + k_{dis}[P_1]\mu_0^2,$$

$$\frac{d\eta_1}{dt} = k_r[R]\mu_1 + k_{rec}[P_1]^2\mu_1\mu_0 + k_{dis}[P_1]\mu_1\mu_0,$$

$$\frac{d\eta_2}{dt} = k_r[R]\mu_2 + k_{rec}[P_1]^2\left(\mu_2\mu_0 + \mu_1^2\right) + k_{dis}[P_1]\mu_2\mu_0.$$

where $[\ldots]$ – concentration of the relevant substances [M] – monomer, [R] – free radical, [I] – initiator, $[P_n]$ $[Q_n]$ – active ("growing") and inactive ("dead") the chain length of the copolymer, respectively containing n links M monomer), f – efficiency of initiation.

Initial data in this case can be represented as:

$$\left[I^{(0)}\right] = [I(0)],\ \left[M^{(0)}\right] = [M(0)],\ \left[R^{(0)}\right] = 0,\ \left[P_1^{(0)}\right] = 0,\ \left[Q_1^{(0)}\right] = 0 \qquad \ldots(3)$$

$$\mu_k(0) = 0,\ \eta_k(0) = 0,\quad k = 0, 1, 2.$$

The obtained values moments are substituted into the formula for finding the average molecular weight M_n, M_ω and polydispersity index K_D.[6]

The value M_n determines the average length of the polymer macromolecules called average molecular weight. It is calculated by the following formula:

$$M_n(t) = m\ \frac{\mu_1(t) + \eta_1(t)}{\mu_0(t) + \eta_0(t)}$$

where m is the molecular weight of the monomer.

If this parameter M_n is characterized, as a rule, low molecular weight part of the MWD, then the parameter M_ω is the average of the distribution of molecular weight and is calculated by the formula: $M_w(t) = m\dfrac{\mu_2(t) + \eta_2(t)}{\mu_1(t) + \eta_1(t)}$.

To estimate the width of the MWD is generally used parameter called the polydispersity index. Polydispersity index is close in meaning to the dispersion (scatter) the molecular weight and is calculated using the following formula: $K_D = \frac{M_\omega}{M_n}$.

RESULTS AND DISCUSSION

The constructed model was tested on experimental data obtained in a scientific laboratory of polymer chemistry of the Bashkir state University.The experiment was conducted on the next boot of the reagents: solvent (acetone) 400 mL, the monomers in the ratio 1:1, maleic anhydride 55 g., styrene 55 g., the initiator (porofor) 0.5 g.

Applying the Runge-Kutta method to solve the system (2) with initial conditions (3) have been identified depending on the concentration of the initiator I of the monomer M on the contact time, and found the calculated values for average M_n and weight average M_ω molecular weight.

The results of computational experiments revealed that there is a range of values of number average molecular weight M_n of the copolymer from 202.3 to 203.4. In this case, the breach polymerization ratio at 0.54% due to the presence of a small amount of water in the solvent, whereby a partial deactivation of maleic anhydride.

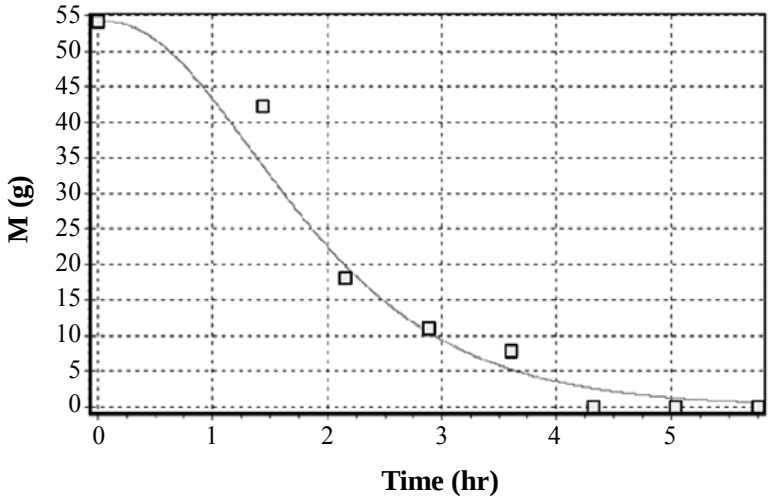

Fig. 1: The dependence of the experimental (points) and calculated according to the mathematical model (solid line) concentrations of monomer (maleic anhydride) from time

CONCLUSION

Thus, for the polymerization process was built the mathematical model presented in the form of a system of ordinary differential equations. Using the method of statistical moments, the system was converted to a closed type. With the help of this model were obtained the expressions for the averaged molecular characteristics. Method of moments applicable for any type of polymerization, because the definition of MWD and its parameters M_n, M_ω, K_D, the process is straightforward.

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