Int. J. Chem. Sci.: 14(4), 2016, 2860-2866
ISSN 0972-768X
www.sadgurupublications.com

MODELING OF RADICAL COPOLYMERIZATION PROCESSES ON THE BASIS OF THE MOMENTS METHOD

IGOR GRIGORYEV[*], TATIANA MIKHAILOVA and SVETLANA MUSTAFINA

Deparment of Physics and Mathematics, Bashkir State University, Sterlitamak City, Lenin Avenue, 37;
Postal Index – 453103 REPUBLIC OF BASHKORTOSTAN, RUSSIAN FEDERATION

ABSTRACT

The mechanism of radical copolymerization of styrene and maleic anhydride in a homogeneous medium has been studied in the paper. A mathematical model has been built on the basis of the radical copolymerization mechanism of styrene and maleic anhydride. The mathematical model is a system of ordinary differential equations. A numerical solution of the target system enables to determine the average molecular properties such as average number and average weight molecular weights. The calculations based on the model correspond to the experimental data.

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

INTRODUCTION

In modern industrial production, there are increasingly used the methods of mathematical modeling of technological processes, enabling to solve the problems of the production prediction and optimization[1]. Currently, one of the most topical problems in conducting experimental research is the problem of extracting the maximum amount of useful information on the process under study at a minimum cost[2]. It is not always possible to carry out a sufficient number of the experiments in the process of solving some industrial problems and with insufficient knowledge of the mechanisms of processes. Therefore, it is appropriate to construct mathematical models with the method of experiment design. In this regard, the development of a mathematical model of radical copolymerization is of great importance.

---

[*] Author for correspondence; E-mail: grigoryevigor@mail.ru, T.A.Mihailova@yandex.ru, Mustafina_SA@mail.ru, Ph.: +79870562312, +79610479799, +79174044558

Cospolymers of styrene and maleic anhydride are important commercial products and are used in industry, for example, as binding elements in coatings or as a feedstock for the production of photo-polymer binders and radiation-curable coatings.

EXPERIMENTAL

The kinetic scheme of polymerization of styrene with maleic anhydride comprises the following elementary steps:

1. Initiator decomposition $\mathrm{I} \xrightarrow{\mathrm{k_i}} 2\mathrm{R}$,
2. Chain growth $R + M \xrightarrow{k_{i1}} P_1$,
3. The continuation chain $P_i + M \xrightarrow{k_p} P_{i+1}, i \geq 1$.
4. Chain termination as a result of interaction with the radical $P_n + R \xrightarrow{k_r} Q_n$,
5. Chain termination by recombination $P_n + P_m \xrightarrow{k_{rec}} Q_{n+m}$,
6. 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.

Regular alternation of units take place due to the influence of polarity, steric and acceptor-donor effects of functional groups based on opposing interfaces with double bonds. In the copolymerization of maleic anhydride and styrene, there are considered mesomeric structures in a transitional state. The determining factor of the alternation is polar resonance forms in the transitional state, which are similar to molecular complexes. Therefore, the unit of «styrene + maleic anhydride» in the description of the mathematical model has been taken as a single monomer.

Making up a matrix of stoichiometric coefficients and multiplying it on the column vector of velocities reaction, we obtain the system of ordinary nonlinear differential equations describing the process of copolymerization of styrene with maleic anhydride[3]. As the formation of polymer macromolecules is an unlimited process and the number of the reaction components of the process is infinite, the model system is –

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

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

$$\frac{d[M]}{dt} = -[M]k_p\sum_{i=1}^{\infty}[P_i] - [M]k_{i1}[R], \qquad \ldots(1)$$

$$\frac{d[P_i]}{dt} = k_p[M][P_{i-1}] - k_p[M][P_i] - k_r[R][P_i] - k_{rec}[P_i]\sum_{j=1}^{\infty}[P_j] - k_{dis}[P_i]\sum_{j=1}^{\infty}[P_j],\ 2 \le i \le \infty,$$

$$\frac{d[Q_i]}{dt} = k_r[R][P_i] + \frac{1}{2}k_{rec}\sum_{j=1}^{i-1}[P_j][P_{i-j}] + k_{dis}[P_i]\sum_{j=1}^{\infty}[P_j],\ 2 \le i \le \infty,$$

where $[\ldots]$ – concentration of the relevant substances.

Initial data for the system (1) can be represented as –

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

$$\left[Q_1^{(0)}\right] = 0,\ \left[P_i^{(0)}\right] = 0,\ \left[Q_i^{(0)}\right] = 0,\ \ i \ge 2 \qquad \ldots(2)$$

To find the solution of system (1) with the initial conditions (2), you must convert it to its final form.

Statistical theory of polymerization is based on the assumption of the possibility of analyzing the molecular weight distribution (MWD) according to the average molecular weights $M_n,\ M_\omega$. To analyze them there are used the concepts of moments, which are commonly applied in statistics and the theory of probability to estimate the distribution of random variables[4]. For the moments of any order, basically, we have: $m_j = \mu_j + \eta_j$, where η_j, μ_j is j - th moments of active and inactive polymer chains calculated in accord with the following formulas:

$$\mu_j = \sum_{i=2}^{\infty} i^j [P_i],\ \ \eta_j = \sum_{i=2}^{\infty} i^j [Q_i] \qquad \ldots(3)$$

Let's rewrite the previously obtained system (1) as a system of differential equations regarding the distribution of moments μ_j and η_j. To do this it is required to find the values $\mu_0(t), \mu_1(t), \mu_2(t)$. From (3) we obtain the expressions for the moments in the following form:

$$\frac{d\mu_0}{dt} = k_p[M]\sum_{i=2}^{\infty}[P_{i-1}] - k_p[M]\sum_{i=2}^{\infty}[P_i] - k_r[R]\sum_{i=2}^{\infty}[P_i] - k_{rec}\sum_{i=2}^{\infty}[P_i]\sum_{j=1}^{\infty}[P_j]$$

$$- k_{dis}\sum_{i=2}^{\infty}[P_i]\sum_{j=1}^{\infty}[P_j] \qquad \ldots(4)$$

$$\frac{d\mu_1}{dt} = k_p[M]\sum_{i=2}^{\infty}i[P_{i-1}] - k_p[M]\sum_{i=2}^{\infty}i[P_i] - k_r[R]\sum_{i=2}^{\infty}i[P_i] - k_{rec}\sum_{i=2}^{\infty}i[P_i]\sum_{j=1}^{\infty}[P_j]$$

$$- k_{dis}\sum_{i=2}^{\infty}i[P_i]\sum_{j=1}^{\infty}[P_j] \qquad \ldots(5)$$

$$\frac{d\mu_2}{dt} = k_p[M]\sum_{i=2}^{\infty}i^2[P_{i-1}] - k_p[M]\sum_{i=2}^{\infty}i^2[P_i] - k_r[R]\sum_{i=2}^{\infty}i^2[P_i] -$$

$$- k_{rec}\sum_{i=2}^{\infty}i^2[P_i]\sum_{j=1}^{\infty}[P_j] - k_{dis}\sum_{i=2}^{\infty}i^2[P_i]\sum_{j=1}^{\infty}[P_j] \qquad \ldots(6)$$

Let’s simplify the first component in the right side of (5):

$$k_p[M]\sum_{i=2}^{\infty}i[P_{i-1}] = k_p[M]\sum_{i=2}^{\infty}(i-1+1)[P_{i-1}] \qquad \ldots(7)$$

Let’s divide the sum of the row in the right side of (7) into two sums:

$$k_p[M]\sum_{i=2}^{\infty}(i-1+1)[P_{i-1}] = k_p[M]\sum_{i=2}^{\infty}(i-1)[P_{i-1}] + k_p[M]\sum_{i=2}^{\infty}[P_{i-1}] \qquad \ldots(8)$$

Let’s change the index of the first sum in the right side (8):

$$k_p[M]\sum_{i=2}^{\infty}(i-1)[P_{i-1}] + k_p[M]\sum_{i=2}^{\infty}[P_{i-1}] = k_p[M]\sum_{i=1}^{\infty}i[P_i] + k_p[M][P_1]\mu_0 \qquad \ldots(9)$$

Similarly, let’s transform the first component in equation (6):

$$k_p[M]\sum_{i=2}^{\infty}i^2[P_{i-1}] = k_p[M][P_1]\mu_2 + 2k_p[M][P_1]\mu_1 + k_p[M][P_1]\mu_0 \qquad \ldots(10)$$

Similarly, we obtain expressions for the moments $\eta_0(t), \eta_1(t), \eta_2(t),$ from formula (3) in the following form:

$$\frac{d\eta_0}{dt} = k_r[R]\sum_{i=2}^{\infty}[P_i] + \frac{1}{2}k_{rec}\sum_{i=2}^{\infty}\sum_{j=1}^{i-1}[P_j][P_{i-j}] + +k_{dis}\sum_{i=2}^{\infty}[P_i]\sum_{j=1}^{\infty}[P_j] \qquad \ldots(11)$$

$$\frac{d\eta_1}{dt} = k_r[R]\sum_{i=2}^{\infty}i[P_i] + \frac{1}{2}k_{rec}\sum_{i=2}^{\infty}\sum_{j=1}^{i-1}i[P_j][P_{i-j}] + k_{dis}\sum_{i=2}^{\infty}i[P_i]\sum_{j=1}^{\infty}[P_j] \qquad \ldots(12)$$

$$\frac{d\eta_2}{dt} = k_r[R]\sum_{i=2}^{\infty}i^2[P_i] + \frac{1}{2}k_{rec}\sum_{i=2}^{\infty}\sum_{j=1}^{i-1}i^2[P_j][P_{i-j}] + k_{dis}\sum_{i=2}^{\infty}i^2[P_i]\sum_{j=1}^{\infty}[P_j] \qquad \ldots(13)$$

Let's perform the necessary replacements and substitutes, and system (1) can be written in the closed form. This system has a finite number of equations and is soluble in regard with the following moments:

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

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

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

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

$$\frac{d\mu_1}{dt} = k_p[M][P_1] + k_p[M][P_1]\mu_0 - k_r[R]\mu_1 - (k_{rec} + k_{dis})[P_1]\mu_1\mu_0 \qquad \ldots(14)$$

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

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

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

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

where [...]– 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 –

$$\left[I^{(0)}\right]=\left[I(0)\right],\ \left[M^{(0)}\right]=\left[M(0)\right],\ \left[R^{(0)}\right]=0,\ \left[P_1^{(0)}\right]=0,\ \left[Q_1^{(0)}\right]=0, \qquad \ldots(15)$$

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

The obtained values of the moments are used to find the average molecular weights M_n, M_w:

$$M_n(t)=m\frac{\mu_1(t)+\eta_1(t)}{\mu_0(t)+\eta_0(t)},\ M_w(t)=m\frac{\mu_2(t)+\eta_2(t)}{\mu_1(t)+\eta_1(t)} \qquad \ldots(16)$$

where *m*- the molecular weight of the monomer.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the calculated values of average number and average weight molecular weights according to the time of copolymerization of styrene with maleic anhydride, obtained on the basis of mathematical model (3) - (4) and formulas (5) - (6) to calculate M_n, and M_w.

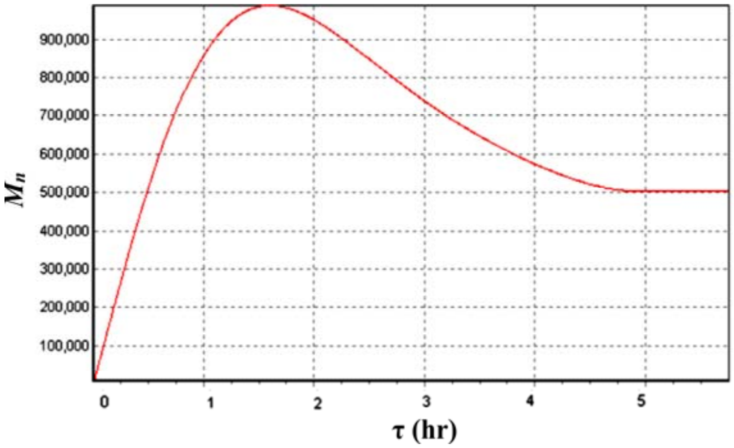

Fig. 1: Dependency of calculated values of average molecular wights on time

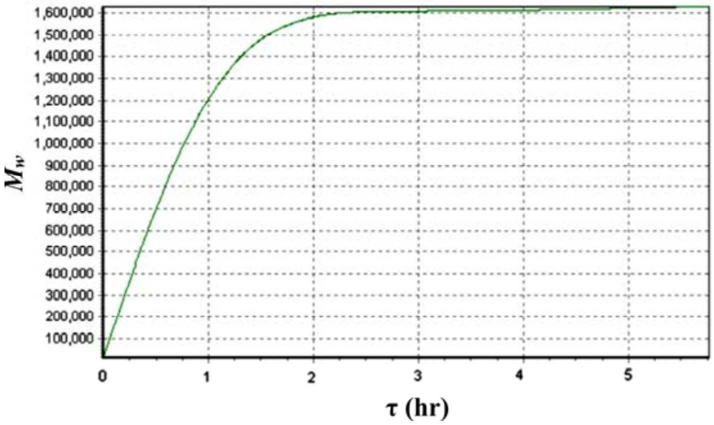

Fig. 2: Dependency of calculated values of average weight molecular weights on time

CONCLUSION

Thus, the mathematical models of copolymerization of styrene with maleic anhydride have been demonstrated in the paper. With the method of statistical moments, the obtained system has been converted into a closed type. On the basis of the model there have been found the values of average molecular numbers and average weight molecular weights. One of the disadvantages of the method is that it does not give explicit dependencies for the values of polymer concentrations.

REFERENCES

1. S. Mustafina, E. Miftakhov and T. Mikhailova, Solving the Direct Problem of Butadiene-Styrene Copolymerization, Int. J. Chem. Sci., **12(2)**, 564-572 (2014).
2. I. Grigoryev, E. Miftakhov and Svetlana Mustafina, Mathematical Modelling of the Copolymerization of Styrene with Maleic Anhydride in a Homogeneous Environment, Int. J. Chem. Sci., **14(1)**, 381-386 (2016).
3. I. Grigoryev and Svetlana Mustafina, Global Optimization of Functions of Several Variables using Parallel Technologies, Int. J. Pure Appl. Math., **106(1)**, 301-306 (2016).
4. G. Shangareeva, I. Grigoryev and Svetlana Mustafina, Comparative Analysis of Numerical Solution of Optimal Control Problems, Int. J. Pure Appl. Math., **110(4)**, 645-649 (2016).

Revised : 22.11.2016 *Accepted : 25.11.2016*