



STUDY OF THE STYRENE AND MALEIC ANHYDRIDE COPOLYMERIZATION PROCESS BY MATHEMATICAL MODELING METHODS

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ABSTRACT

The mechanism of radical copolymerization of styrene and maleic anhydride in a homogeneous medium has been studied in the paper. There have been selected the conditions of styrene and maleic anhydride copolymerization. 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.

Keywords: copolymerization, kinetic scheme, mathematical model, polymerization process, styrene, maleic anhydride, stiromal, moments, the molecular weight distribution.

1. 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]-[4]. 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.

Copolymers 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.

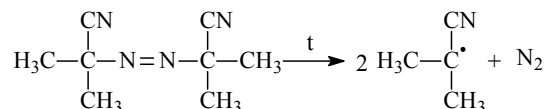
There is known a way to obtain styrene-maleic anhydride copolymers by a radical copolymerization of styrene and maleic anhydride in cyclohexanone solution at 140-150 °C over 3 wt. % (Poroform CHHK-57). Also there have been known a method where acetone can be used as one of the solvents. The initial ratio of monomers (mol) Styrene: Maleic anhydride - 1: 1, the ratio of monomers to the solvent (module) - 1: 4. Porophore is used as an initiator. In the current technology the process of obtaining stiromal is carried out in a heterogeneous aromatic solvent environment. The copolymer obtained by this method is released in the form of extremely fine dispersion which increases a fire and explosion hazard process. Furthermore, this method is characterized by a low productivity and high flow of deficient aromatic solvents.

Hence, it is quite important to work out a new technology of the process of styrene copolymerization with maleic anhydride in a homogeneous environment. It can significantly reduce solvent losses and the time of copolymerization.

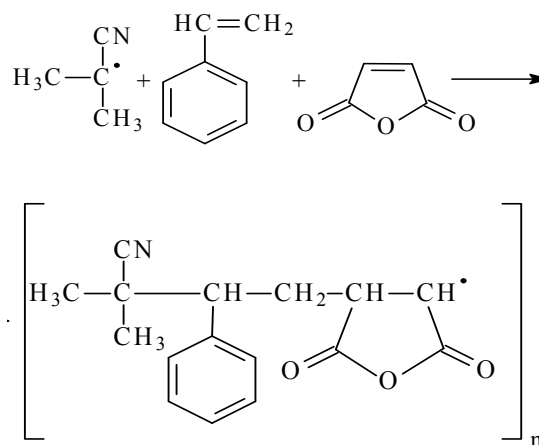
2. EXPERIMENTAL

The process of copolymerization of styrene with maleic anhydride through the following stages:

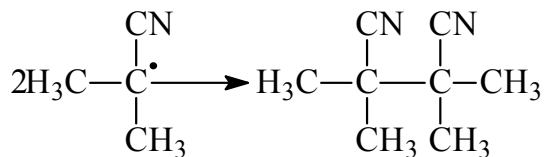
a) The disintegration of initiator (formation of radicals that initiate copolymerization)



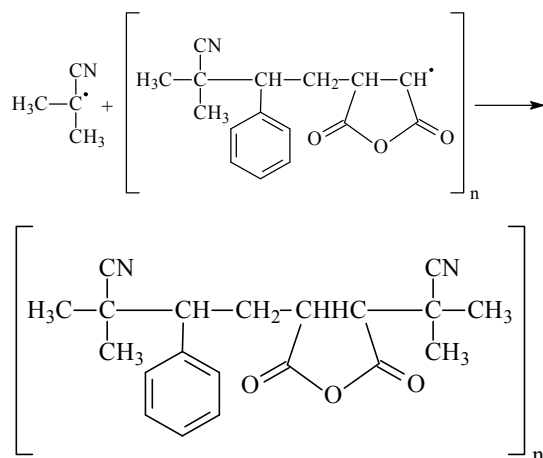
b) Chain growth



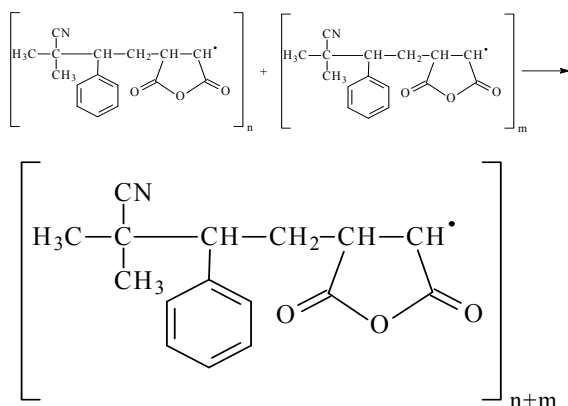
where n and m are degrees of copolymerization. For stiromal n = m.

c) Chain termination, $n = \overline{1, \infty}$ 

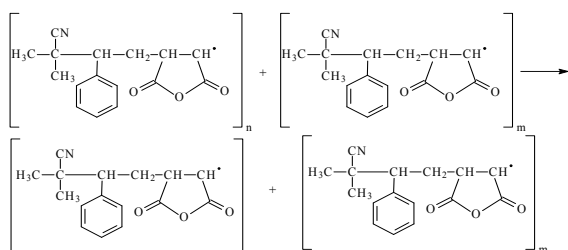
Chain termination as a result of interaction with the radical:



Chain termination by recombination:

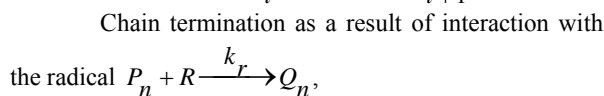
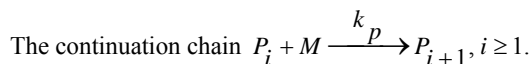
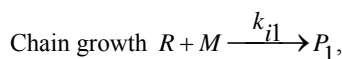
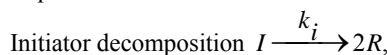


Chain termination disproportionation:

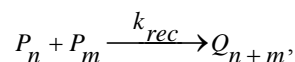


Regular alternations of units take place due to the influence of polarity, steric and acceptor-donor effects of functional groups based on opposing interfaces with double bonds. In the copolymerization of maleic anhydride and styrene, there are considered mesomeric structures in a transitional state. 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.

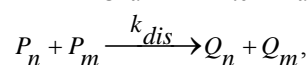
A kinetic method for modeling copolymerization processes consists in a generation and numerical solution of kinetic equations for the concentrations of all types of particles participating in the process (molecules, free radicals, macromolecules, macromolecular free radicals). The kinetic scheme of copolymerization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



Chain termination by recombination



Chain termination disproportionation



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.

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. 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:

$$\begin{aligned} \frac{d[I]}{dt} &= -k_i[I], \\ \frac{d[R]}{dt} &= 2k_i[I] - k_{i1}[M][R] - k_r[P_1][R], \\ \frac{d[M]}{dt} &= -[M]k_p \sum_{i=1}^{\infty} [P_i] - [M]k_{i1}[R], \end{aligned} \quad (1)$$



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

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

where [...] – concentration of the relevant substances.

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

$$\begin{aligned} [I^{(0)}] &= [I(0)], [M^{(0)}] = [M(0)], [R^{(0)}] = 0, [P_1^{(0)}] = 0, \\ [Q_1^{(0)}] &= 0, [P_i^{(0)}] = 0, [Q_i^{(0)}] = 0, \quad i \geq 2. \end{aligned} \quad (2)$$

To find the solution of system (1) with the initial conditions (2), you must convert it to its final form. Statistical theory of copolymerization is based on the assumption of the possibility of analyzing the molecular weight distribution (MWD) according to the average molecular weights M_n , M_w . 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. 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 [5]:

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

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:

$$\frac{d\mu_0}{dt} = k_p[M] \sum_{i=2}^{\infty} [P_{i-1}] - k_p[M] \sum_{i=2}^{\infty} [P_i] - k_r[R] \sum_{i=2}^{\infty} [P_i] - k_{rec} \sum_{i=2}^{\infty} [P_i] \sum_{j=1}^{\infty} [P_j] - k_{dis} \sum_{i=2}^{\infty} [P_i] \sum_{j=1}^{\infty} [P_j] \quad (4)$$

$$\frac{d\mu_1}{dt} = k_p[M] \sum_{i=2}^{\infty} i [P_{i-1}] - k_p[M] \sum_{i=2}^{\infty} i [P_i] - k_r[R] \sum_{i=2}^{\infty} i [P_i] - k_{rec} \sum_{i=2}^{\infty} i [P_i] \sum_{j=1}^{\infty} [P_j] - k_{dis} \sum_{i=2}^{\infty} i [P_i] \sum_{j=1}^{\infty} [P_j] \quad (5)$$

$$\frac{d\mu_2}{dt} = k_p[M] \sum_{i=2}^{\infty} i^2 [P_{i-1}] - k_p[M] \sum_{i=2}^{\infty} i^2 [P_i] - k_r[R] \sum_{i=2}^{\infty} i^2 [P_i] - k_{rec} \sum_{i=2}^{\infty} i^2 [P_i] \sum_{j=1}^{\infty} [P_j] - k_{dis} \sum_{i=2}^{\infty} i^2 [P_i] \sum_{j=1}^{\infty} [P_j]; \quad (6)$$

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

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

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

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

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

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

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



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

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

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

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

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

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:

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

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

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

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

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

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

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

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

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:

$$\begin{aligned} [I^{(0)}] &= [I(0)], [M^{(0)}] = [M(0)], [R^{(0)}] = 0, [P_1^{(0)}] = 0, \\ [Q_1^{(0)}] &= 0, \mu_k(0) = 0, \eta_k(0) = 0, k = 0, 1, 2. \end{aligned} \quad (15)$$

The obtained values of the moments are used to find the average molecular weights M_n, M_w [6]:

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

where m – the molecular weight of the monomer.

4. RESULTS AND DISCUSSIONS

The developed model was tested on the experimental data obtained in the scientific laboratory of polymer chemistry of the Bashkir State University. The experiment was carried out under the following reagents loading: solvent (acetone) 400 ml, the monomers in the ratio 1:1, maleic anhydride 55 g., styrene 55 g., the initiator (porophore) 0.5 g.

When applying the Runge-Kutta method to solve systems (14) with initial conditions (15) there have been identified dependences of the concentration of the initiator I , of the monomer M on the contact time, and have been found the calculated values for average M_n and weight average M_w molecular weights.

Figure-1 show the variation of the experimental (points) values and values of concentrations of monomer (maleic anhydride) with time calculated according to the mathematical model (solid line) Figure-2, Figure-3 show the calculated values of average number and average weight molecular wights according to the time of



copolymerization of styrene with maleic anhydride, obtained on the basis of mathematical model (14) - (15)

and formulas (16) to calculate M_n and M_w .

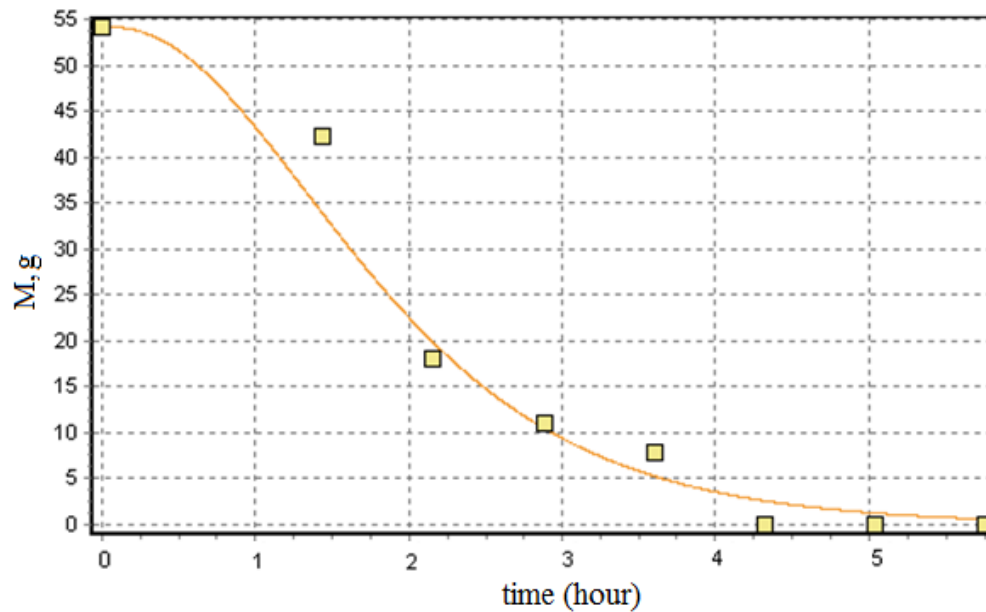


Figure-1. The variation of the experimental (points) values and values of concentrations of monomer (maleic anhydride) with time calculated according to the mathematical model (solid line).

CONCLUSIONS

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. The method of moments can be applied for any type of copolymerization because the definition of MWD and its parameters M_n , M_w , K_D is at unambiguous process.

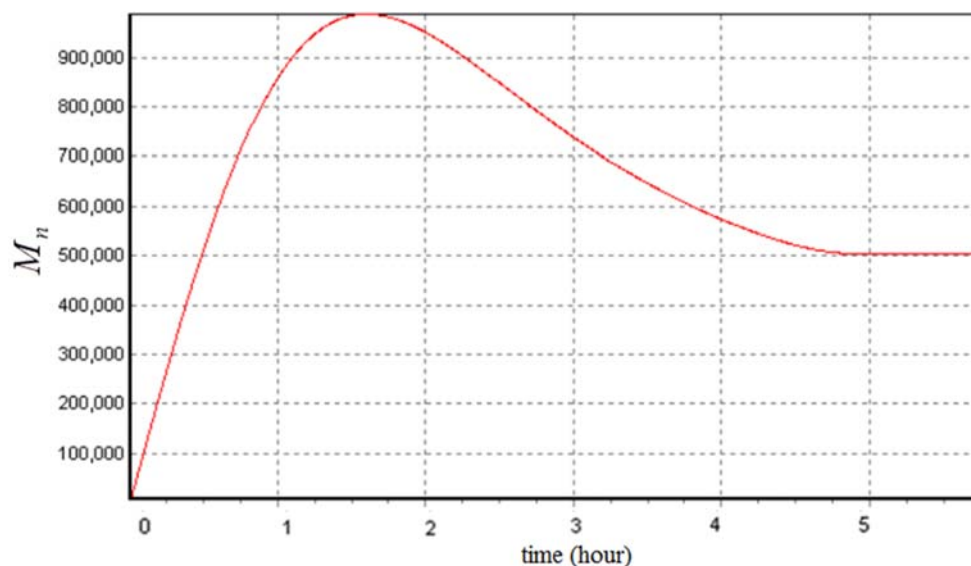


Figure-2. Dependency of calculated values of average molecular weights on time.

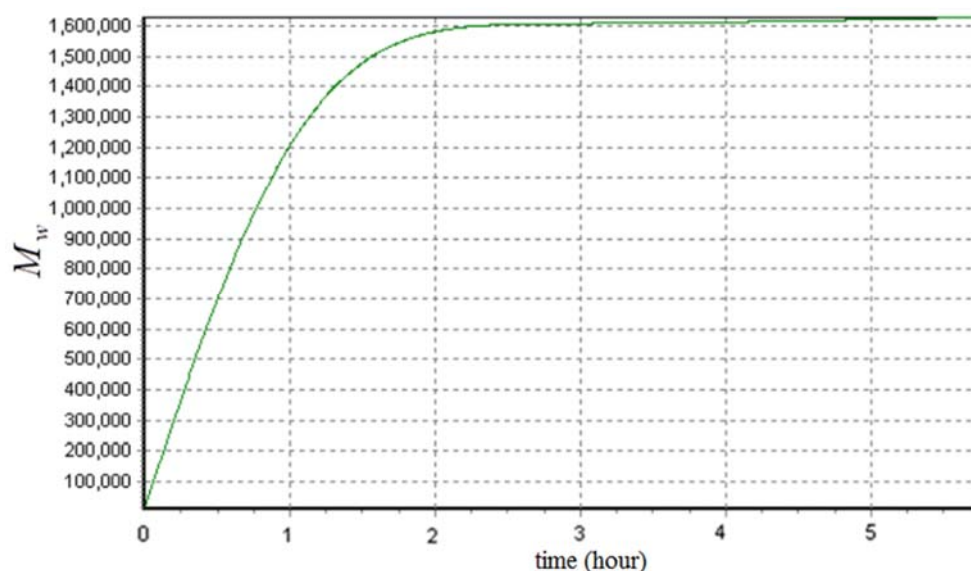


Figure-3. Dependency of calculated values of of average weight molecular wights on time.

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