

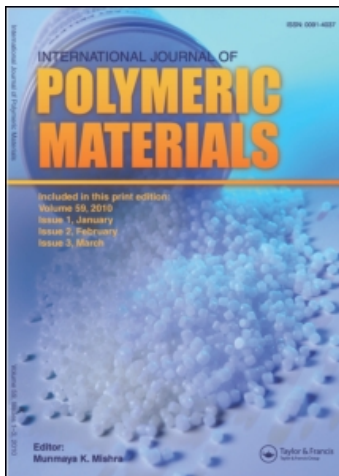
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A. R. Nabiullin<sup>a</sup>; S. M. Usmanov<sup>a</sup>; Yu. I. Puzin<sup>b</sup>; R. Kh. Yumagulova<sup>c</sup>; Yu. B. Monakov<sup>c</sup>

<sup>a</sup> Birk's State Pedagogical Institute, Birk <sup>b</sup> Ufa' State Oil Technological University, Ufa, Kosmonavtov <sup>c</sup> Institute of Organic Chemistry of Ufa' Research Center of RAS, Ufa, Prospekt Oktyabrya

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# Radical Polymerization of Methyl Methacrylate in Presence of Ferrocene. Monte Carlo Simulation

A. R. NABIULLIN<sup>a</sup>, S. M. USMANOV<sup>a</sup>, Yu. I. PUZIN<sup>b</sup>,  
R. KH. YUMAGULOVA<sup>c</sup> and Yu. B. MONAKOV<sup>c,\*</sup>

<sup>a</sup>*Birsk' State Pedagogical Institute, 452320, Birsk, Internatsionalnaya, 10;*

<sup>b</sup>*Ufa' State Oil Technological University, 450062, Ufa, Kosmonavtov, 1;*

<sup>c</sup>*Institute of Organic Chemistry of Ufa' Research Center of RAS, 450054 Ufa, Prospekt Oktyabrya, 69*

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Monte-Carlo technique is used for the numerical simulation of radical polymerization kinetics of methyl methacrylate in the presence or absence of ferrocene and exposition of molecular-weight distribution during the process. The peculiarities of polymeric radical concentration changes at the initial stage of polymerization are shown. Satisfactory correspondence between calculated and experimental data is obtained. The data of numerical experiment have allowed to evaluate the influence of ferrocene on kinetic parameters of polymerization.

**Keywords:** Radical polymerization; Methyl methacrylate; Ferrocene; Monte-Carlo; Simulation; Molecular-weight distribution; Polymerization rate

## 1. INTRODUCTION

The process of radical polymerization is described by a system of differential equations [1, 2]. However, its analytical solution is practically impossible. Therefore, analysis of the radical polymerization kinetic is carried out using a pseudo-steady approximation of

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\*Corresponding author.

polymer radical concentration [3] that substantially simplifies the system of differential equations.

In the present article the Monte-Carlo method is used for the mathematical description of radical polymerization process. The application of the method is based on the independence of elementary reactions caused by a random process during the polymerization, and the Monte-Carlo method allows to simulate these reactions with definite probability. Thus, the model offered by us enables the use of differential equation system of elementary reactions more generally, and not to use pseudo-steady approximation.

The method of Monte-Carlo is used by us for the kinetic analysis of the initial stage of radical polymerization. Radical polymerization of vinyl compounds was studied most [4, 5]. The kinetic model of this process was worked out in detail and confirmed experimentally. Therefore, comparative analysis of the experimental and computational kinetic characteristics obtained by the Monte-Carlo method allows to calibrate the model used by us.

The analysis of the polymerization kinetic by the application of the Monte-Carlo method enables to observe changes of monomer concentration. These data allows to obtain additional information on changes of free radical concentration and on the nature of changes in the molecular-weight distribution (MWD) at the initial polymerization stage.

The study of the influences of various compounds on the process of polymerization is of special practical interest. In this article the results of simulation of methyl methacrylate (MMA) polymerization kinetics in the presence of ferrocene are described.

## **2. APPLYING OF MONTE-CARLO METHOD FOR THE DESCRIPTION OF RADICAL POLYMERIZATION**

The method of Monte-Carlo has broad applications, first of all, in the simulation of physical processes in polymers. In particular, the dynamic Monte-Carlo method is utilised for simulation of molecular motion on a computer [6, 7]. Thus the motion of a polymer chain is estimated as a pseudo-steady process consisting of successive changes

of chain conformation by a given rule. Monte-Carlo method was applied to the simulation of radical polymerization only in recent years [9–11]. The complexity of the depicted process and the necessity of a large RAM of computer are the primary reasons for it.

### 3. MONTE-CARLO MATHEMATICAL MODEL OF RADICAL POLYMERIZATION

Polymerization was modelled on a cubic lattice by dimension  $100 \times 100 \times 100$ . We considered that the clusters of the grid are occupied by polymer and the monomer is between clusters of the grating. The clusters of grating become occurred at the moment of its addition to growing chain.

Each simulation consisted of a successive series of monomer molecule additions to growing chains and the radical was displaced to one of adjacent clusters of the grid as a result of each of these acts. In other words, the polymer chain was placed on the grid and its length was equal to the number of the occurred clusters of grid.

The process of polymerization contains elements of chance which are described by the rules of probability. Therefore, the application of Monte-Carlo method for simulation of polymerization is initially justified. The essence of the Monte-Carlo method consists in generation beforehand of the given probabilities of the various random events. Random events are in our model:

- (1) Selection of the polymer radical  $R_i$  which should connect to itself the monomer molecule at the given moment, where  $i$  is one of randomly selected numbers uniformly distributed on an interval  $[1, \dots, R]$ ,  $R$  is the quantity of polymer radicals to be in the system at this moment.
- (2) Selection of the growth direction ( $j$ ) of a radical which occurred in one of the possible directions of travel on the grid (the return was eliminated), where  $j$  is randomly selected from an interval  $[1, \dots, 5]$ .
- (3) Selection of a termination reaction (recombination or disproportionation) on the random number  $\xi \in (0; 1)$  and on the relation between the termination rate constants carried out by different

mechanisms ( $r_0$ ), *i.e.*,

if  $\xi < \frac{1}{r_0 + 1}$  then recombination;

if  $\xi \geq \frac{1}{r_0 + 1}$  then disproportionation.

- (4) Choice between the reactions of propagation and transfer on the monomer with calculations of these reaction probabilities:

$$p_p = p_2 = \frac{V_p}{V} \quad (1)$$

$$p_{ct} = p_1 = \frac{V_{ct}}{V} \quad (2)$$

where  $V = V_{ct} + V_p$  and  $p_1$  or  $p_2$  are the probability of transfer and growth reactions, respectively.

The normalization condition is satisfied for the probabilities of propagation and transfer reactions by:

$$p_1 + p_2 = 1 \quad (3)$$

From the knowledge of  $p_1$  and  $p_2$  probabilities, it is possible to determine the type of reaction that will take place at the given stage of simulation.

It is necessary in this method of simulation, as compared with a method based on the solution of differential equation systems, to deal with separate molecules instead of with concentrations. Therefore, some transformations were made to link the quantity of molecules of reactants to the rates of the applicable reactions.

For this purpose we proceeded as follows:

- (1) Set quantity of the initiator molecules  $I_0$ .
- (2) Calculated the volume ( $v_0$ ) which they can occupy at a given concentration  $[I]_0$ :

$$v_0 = \frac{I_0}{[I]_0}$$

Otherwise, volume  $v_0$  is the molar volume of the reactor.

- (3) Take into consideration the relationship between concentration and quantity of reagent molecules under the following scheme:

$$V = k \prod_{i=1}^n [C]_i = k \frac{\prod_{i=1}^n C_i}{v_0^n} = k^* \prod_{i=1}^n C_i \quad (4)$$

where  $C_i$  and  $[C]_i$  are the quantity of molecules and concentration of  $i$ -compound respectively;  $k^*$  is a reduced constant,  $n$ -reaction order.

After transformation of the equations for rates of change initiation  $V_i$  or propagation  $V_p$  and termination  $V_t$  we obtain:

$$V_i = 2f k_d^* I \quad (5)$$

$$V_p = k_p^* M M \quad (6)$$

$$V_t = k_t^* M^2 \quad (7)$$

where  $M$  is the number of monomer molecules;  $M \cdot$  is the number of polymer radicals;  $I$  is the number of the initiator molecules.

The procedure of simulation consists of the following steps:

*Step 1 Initiation* The unit on the grid was randomly selected where the initiated monomer molecule was placed. It was considered that each initiator molecule yields one primary radical on the average, in other words, efficiency of initiation ( $f$ ) is equal 0.5. The number  $i$  was assigned to each radical formed and the variable  $R(i)$ , in which the length of a radical will be stored, equated to 1. In variables  $x(i)$ ,  $y(i)$ ,  $z(i)$  there were stored the co-ordinates of a radical ( $x$ ,  $y$ ,  $z$ ) on the grid.

*Step 2* Calculation of initiation and growth reaction rates. We set a small time period  $\Delta t$  and quantities of the acts of growth and initiation calculated for this time:

$$N_p = V_p \cdot v_0 \cdot \Delta t \quad (8)$$

$$N_i = V_i \cdot v_0 \cdot \Delta t \quad (9)$$

where  $v_0$  is molar volume of the reactor.

As a rule,  $N_p$  and  $N_i$  are not integers. Therefore it is necessary to round off to the proximate integer. Thus the round-off error in each step is randomly distributed to range  $\pm 0.5$  and the mean statistical error of the simulation is equal to zero as a whole.

*Step 3 Chain propagation* At present, a single  $i$ -radical from all of "living" radicals is selected randomly. The direction of its subsequent movement on the grid is determined by random rule for this radical (*i.e.*, growth carries out) then the value  $R(i)$  increases per volume unit. The applicable co-ordinate of the radical changes also depending on the direction of travel and the number of monomer molecules decreased per volume unit.

*Step 4 Chain transfer on a monomer* At present, a single  $i$ -radical from all of "living" radicals is selected randomly. The presence in an adjacent volume unit of the monomer molecule on which the reaction of chain transfer will be implemented determines by random process. Thereof the polymer chain  $P(i) = R(i)$  is formed, and a new radical  $R(R + 1)$  with chain length equal 1 will be generated. The number of monomer molecules decreased per unit volume and the number of polymer radicals remains invariable.

*Step 5 Chain termination* The analysis of the radical environment is carried out in the presence at adjacent clusters of other radical for termination to occur after each act of growth or initiation. If the radical is in one of the proximate adjacent clusters of the grid, the termination reaction is carried out, but a kind of reaction (disproportionation or recombination) must be previously defined. If  $i$  and  $j$  polymer radicals react it is considered that the recombination will derive a polymer chain  $P(i) = R(i) + R(j)$  after termination. In case of disproportionation two polymer chains formed  $P(i) = R(i)$  and  $P(j) = R(j)$ . Total amount of radicals  $R$  decreases by 2 in both cases.

*Step 6* Completion of experiment is carried out:

- (1) After achievement of given conversion;
- (2) Upon the expiration of a given time;
- (3) At the request of the experimenter.

After the completion of the simulation we calculated the polymerization degree and length of each polymer chain.

### 3.1. The Input Data for Numerical Experiment

The following parameters were set for the simulation:

- (1) Constant of propagation rate ( $k_p$ );
- (2) Constant of initiator decomposition rate ( $k_d$ );
- (3) Initial concentration of the initiator  $[I]_0$ ;
- (4) Initial concentration of monomer  $[M]_0$ ;
- (5) Time of polymerization ( $T_p$ ) or conversion expected ( $U$ , %).

During MMA radical polymerization the benzoyl peroxide (BP) was used as the initiator, the temperature was taken to equal 60°C, and the constant of propagation rate is equal  $k_p = 705$  (l/(mol · min)) [5].

## 4. RESULTS OF NUMERICAL MODELLING OF RADICAL POLYMERIZATION

### 4.1. Calculation of the Termination Constant Rate $k_t$

Plots of polymer radical concentration  $[M]$  experimentally obtained and dependent on formula (10) *versus* time are shown in Figure 1 at different initial concentrations of the initiator  $[I]_0$ .

$$\frac{d[M]}{dt} = V_i - k_t[M]^2 \quad (10)$$

As is obvious from Figure 1, all relations  $[M] = \varphi(t)$  reach an equilibrium state with time. The time of the approach of relation  $[M] = \varphi(t)$  to the plateau is determined in each concrete case from formula (11). If the initiator concentration increases the time of stationary state decreases and the applicable value of  $[M]$  increases.

$$[M] = \sqrt{\frac{V_i}{k_t}} \cdot \text{th} \left( \sqrt{k_t V_i} \cdot t \right) \quad (11)$$

The points in the Figure 1 are the results of numerical experiment. They are described by Eq. (10) with inaccuracy of no more than 5%.



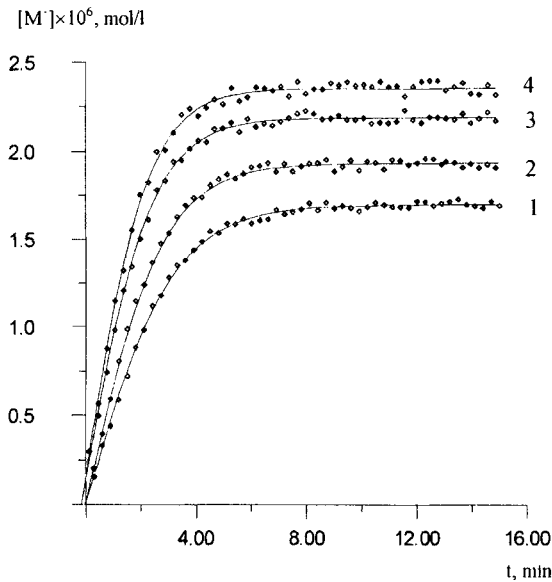


FIGURE 1 Plots of polymer radical concentrations vs. time. Initiator concentration  $[I]_0$  are: 1– $1 \cdot 10^{-3}$ ; 2– $1,5 \cdot 10^{-3}$ ; 3– $2 \cdot 10^{-3}$ ; 4– $2,7 \cdot 10^{-3}$  mol/l. The continuous lines are determined according to Eq. (10).

TABLE I Some kinetic parameters of MMA polymerization at 60°C

$NN$	$[I]_0 \cdot 10^3, (mol/l)$	$t_{st}, min$	$[M]_{st} \cdot 10^6, (mol/l)$	$k_t \cdot 10^{-5}, (l/(mol \cdot min))$
1	1	10,5	1,69	1,81
2	1,5	8,4	1,92	1,87
3	2	7,8	2,18	1,91
4	2,7	9,0	2,35	1,93
average value $\langle k_t \rangle$				1,88

The applicable termination rate constant  $k_t$  was determined by the optimization method [12]. The design  $k_t$  values are shown in Table I and their average value  $\langle k_t \rangle$  agrees with  $k_t$  calculated by the Arrhenius equation [13]:

$$k_t = 1,09 \cdot 10^6 \exp\left(-\frac{5000}{RT}\right) = 1,79 \cdot 10^5, \left(\frac{1}{mol \cdot min}\right)$$

where  $T = 333$  K is the temperature of MMA polymerization.

We will also use the value retrieved by us for the termination rate constant  $k_t = 1,88 \cdot 10^5$  (l/(mol · min)) in further calculations.

#### 4.2. Calculation of Polymerization Rate

The dependence on time of the concentration of monomer being polymerized and counted by Monte-Carlo method is shown in Figure 2. Thus, the termination rate constant  $k_t$  obtained from the results of numerical experiment was utilised for calculation of relation  $[M]^* = f(t)$ . The MMA polymerization velocity is obtained from the tangent of the straight line angle approximating the applicable design points (Fig. 2), and the calculations being made after an equilibrium state was achieved by the reaction system.

If the conditions of computer experiment are  $T_p = 60^\circ\text{C}$ ,  $[I]_0 = 1 \cdot 10^{-3}$  mol/l,  $k_t = 1,88 \cdot 10^5$  (l/(mol · min)) the obtained MMA polymerization velocity equals  $6,2 \cdot 10^{-3}$  (mol/(l · min)). This value coincides with accuracy 3% to the applicable values of MMA

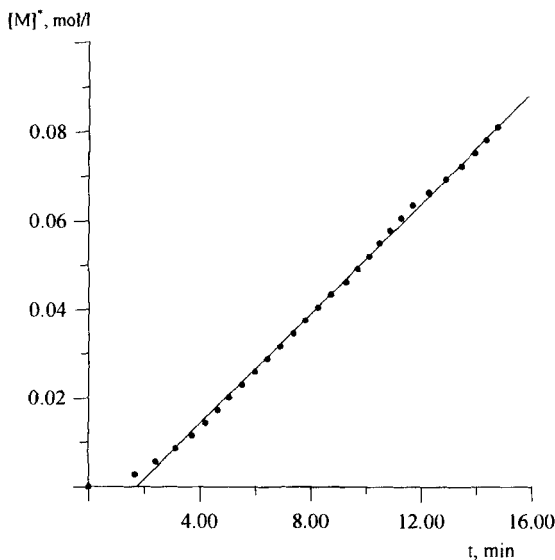


FIGURE 2 Concentration of monomer polymerized during polymerization. Initiator concentration  $[I]_0$  is  $1 \cdot 10^{-3}$  mol/l,  $k_t = 1,88 \cdot 10^5$  (l/(mol · min)).

polymerization velocity obtained during chemical experiment [13] conducted under the same conditions.

### 4.3. Simulation of Polymerization in Presence of Ferrocene

A considerable growth of the initial polymerization velocity is observed in the presence of ferrocene (Fc), accompanied by a considerable decrease of polymerization degree of the obtained polymer [13]. The presence of Fc in the reaction system influences on the initiation parameters, first of all, therefore it is taken into account in the considered model as [11]:

$$V_i = 2k_d[I]^m[Fc]^n \quad (12)$$

where  $m$  and  $n$  are orders of initiation of the polymerization initiator and Fc accordingly. Experimental data [11, 13] and the results of numerical experiment have shown that  $m \approx 1$ . The computational relations of polymer radical concentrations *versus* time are shown in Figure 3 for various concentrations of Fc. It is seen from the figure,

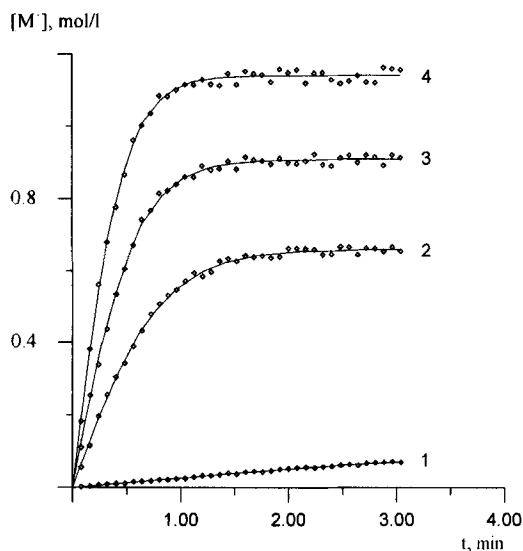


FIGURE 3 Plots of polymer radical concentrations *vs.* time in the presence of various concentrations of ferrocene.  $[Fc]_0$  are: 1-0; 2- $0,2 \cdot 10^{-3}$ ; 3- $0,5 \cdot 10^{-3}$ ; 4- $1 \times 10^{-3}$  mol/l. Initiator concentration  $[I]_0$  is  $1 \cdot 10^{-3}$  mol/l. The continuous lines are determined according to Eq. (10).

that the minor rise of Fc concentration results in strong increase of MMA polymerization rate. In fact, the sharp increase of polymer radical concentration  $[M]$  is the result of Fc presence in the reaction system at the initial polymerization stage. The higher the Fc concentration the faster the applicable equilibrium value  $[M]$  is reached (Fig. 2). The values of rate and degree of polymerization are shown in Table II.

TABLE II Polymerization of MMA in presence of ferrocene at 60°C  $[BP]_0 = 1 \cdot 10^3$  (mol/l)

$[Fc]_0 \cdot 10^3$ (mol/l)	Polymerization rate $W_p \cdot 10^3$ (mol/(l·min))	Polymerization degree $P \cdot 10^{-4}$
0	6,20	2,05
0,2	35,14	0,38
0,5	46,39	0,27
1,0	58,58	0,21

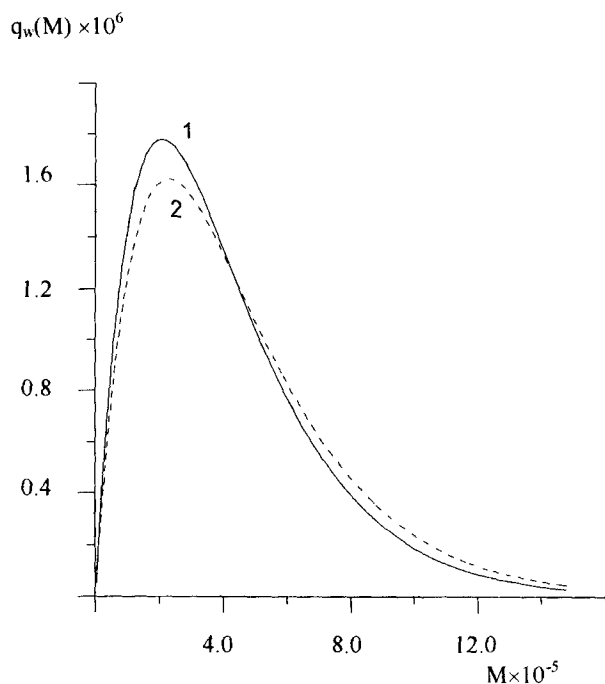


FIGURE 4 Molecular-weight distribution of polymer obtained. Parameters of process are:  $[I]_0 = 1 \cdot 10^{-3}$  mol/l;  $k_t = 1,88 \cdot 10^5$  (l/(mol·min)). Polymerization conversion is: 1-1%; 2-3%.

#### 4.4. The Calculation of Molecular-weight Distribution

Use of the Monte-Carlo method for simulation of radical polymerization process allows to observe the MWD change during the reaction. In fact [1–5, 14], the calculation of MWD curve from the kinetic data and its comparison to an experimental curve is very interesting. Thus, the computational problem is the calculation of the cumulative distribution function of polymer of a molecular mass based on known mechanism of fundamental reactions and kinetic constants.

Having theoretical MWD it is possible to compare it to an experimental curve. Such a comparison yields valuable information on the validity of selected model of polymerization process and allows to update values for various kinetic constants.

The MWD curves of poly(methyl methacrylate) of the initial stage of reaction without the component Fc (Fig. 4) and in presence of Fc (Fig. 5) are satisfactorily described by linear combination of Schulz'

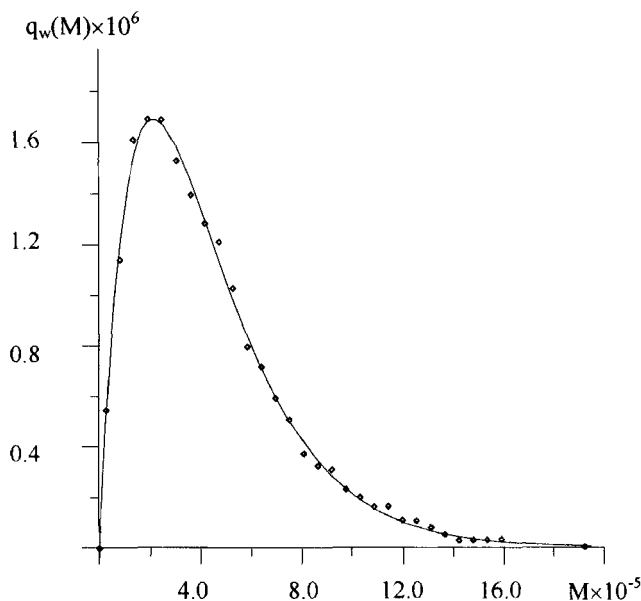


FIGURE 5 Molecular-weight distribution of polymer obtained in presence of ferrocene. Parameters of process are:  $[Fc]_0 = 1 \times 10^{-3}$  mol/l;  $[I]_0 = 1 \cdot 10^{-3}$  mol/l;  $k_t = 1,88 \cdot 10^5$  l/(mol · min)). The continuous lines are determined according to Eq. (13).

distributions of the second and third orders [3]:

$$q_w(M) = wM\alpha^2 \exp(-\alpha M) + (1 - w)M^2\alpha^3 \exp(-\alpha M) \quad (13)$$

where  $\alpha = 1/M_n$ ,  $M_n$  is the number-average molecular mass,  $w$ —probability of termination by disproportionation.

It is obvious from a Figure 5 that a good conformity to relation (13) is observed with points obtained from numerical experiment. It is confirmed also by calculations of dependence of the average weight characteristic on the parameter  $M_w/M_n$  where  $M_w$  is weight-average molecular mass. At the initial stage of MMA polymerization the  $M_w/M_n$  equals approximately 2, with accuracy of 4%.

In Figure 4 the MW distribution of poly(methyl methacrylate)  $q_w(M)$  is indicated at different conversions of monomer. It is seen that the MWD curves are similar at the initial stage of MMA

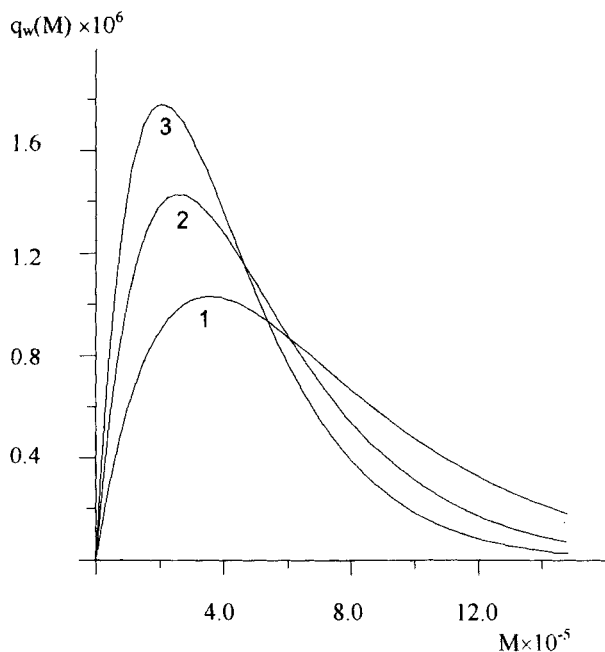


FIGURE 6 Molecular-weight distribution of polymer obtained in the presence of ferrocene. Parameters of process are:  $[Fc]_0 = 1-0,2 \cdot 10^{-3}$ ;  $2-0,5 \cdot 10^{-3}$ ;  $3-10^{-3}$  mol/l.  $[I]_0$  is  $1 \cdot 10^{-3}$  mol/l;  $k_t = 1,88 \cdot 10^5$  (l/(mol · min)).

polymerization (conversion up to 3%), and the small displacement of  $M_w$  is only observed in the area of large polymer molecules.

In Figure 6 the MWD curves of PMMA calculated at different Fc concentrations are shown. It is seen that when the Fc concentrations in the reaction system increase, the polymer molecules become more polydisperse, and both the  $M_n$  and  $M_w$  characteristics also grow.

## 5. CONCLUSION

The Monte-Carlo method and mathematical model offered by us provide sufficient detail to consider the features of MMA radical polymerization. During the calculation, the principle of stationarity was not specially used but the numerical experiment has shown that the system reaches an equilibrium (pseudo-steady) condition dependent on radical concentrations. The model enables to calculate a transition time of a system in a quasi-stationary state. A distinctive feature of this model is that it allows to calculate the MWD curve for any stage of MMA polymerization. The computational relations obtained by the use of classic model of radical polymerization, with Monte-Carlo method, and in chemical experiment all well conformed with each other.

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