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Monte Carlo Simulation of Photo-initiated Bulk Polymerization of Furfuryl Methacrylate

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ABSTRACT

A robust Monte Carlo simulation as a stochastic random-based method was employed to study the bulk photopolymerization of furfuryl methacrylate (FM) at various temperatures. An appropriate mechanism of polymerization considering a vast variety of reactions was selected and therefore, a reliable algorithm was designed. In addition, experimental results were used to evaluate the simulation procedure and algorithm and consequently, confirm the simulation results. The concentration profiles of different species with respect to irradiation time were obtained by this simulation method. In addition, the effect of temperature variation on the concentration of species has been evaluated. At higher temperatures, an increase in the rate of FM consumption was revealed which is because of an increment in the propagation rate constants of acrylic macroradicals. At 40°C of the early stages of the photopolymerization, M_1^* concentration increases rapidly with respect to irradiation time; this is on account of the superior primary initiation constants compared to other temperatures. However, due to the acrylic macroradicals termination, intermolecular degradative transfer, allylic-acrylic termination and acrylic primary termination, M_1^* concentration reaches a plateau. Moreover, the highest concentration of M_1^* was achieved at 0°C. A data analysis based on the least square method was performed to evaluate the FM concentration and consequently, a reliable agreement between the experimental data and the Monte Carlo simulation results were obtained at different temperatures.

Key Words:

Monte Carlo simulation;
photopolymerization;
furfuryl methacrylate;
radical polymerization;
mechanism.

INTRODUCTION

Photopolymerization is a light induced polymerization system which is employed to synthesize various polymer structures [1,2]. In comparison with the conventional radical polymerization systems, photopolymerization instead of heat-induced polymerization has the advantage of successful application in solvent-free formulations. Light could be easily turned on and off; therefore, a precise spatial control of the reaction can be obtained [3]. In addition, photopolymerization can be initiated even at low energy inputs, which can lead to extreme reaction rates [4].

Photopolymerization systems are mainly used to synthesize acrylic biomaterials. Due to rapid gelation in photopolymerization, this process is employed in the formulation of dental and orthopedic acrylic products [1]. For these numerous applications, this technology has gained a great deal

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of attention in the past few years. Additionally, the theoretical interests in their mechanism and simulation are rapidly growing [5].

Furfuryl methacrylate (FM) is a class of acrylofuranic monomers that is mainly used in biomedical applications [6,7]. FM is usually used as liquid in biomaterial application [8] and on account of its low shrinkage after polymerization; this monomer is preferred to other methacrylic monomers such as methyl methacrylate [9]. Even at low conversions, homopolymerization of FM results in an insoluble cross-linked polymer. Hindered free radicals of the allylic type, generated from the furan moiety of FM, would subsequently retard the polymerization process [9]. A review of related literature gives an indication that a few mathematical models have been applied to simulate the bulk photopolymerization of FM. Lange et al. employed the non-linear ordinary differential equation system (ODEs) to model photopolymerization of FM [7]. They also studied formation of networks in the photopolymerization of FM by using Tobita method at low conversions [10]. Simulation of this process using CORUB model has been investigated by Corzo et al. [6].

Statistical nature of chain growth and termination reactions serves probability theory methods (especially Monte Carlo simulation) as powerful tools in the simulation of polymerization reactions. By storage of the whole information on chain reactions, Monte Carlo simulation methods can assess the distributions of the chain lengths and its mean values. Moreover, Monte Carlo simulation method just needs reaction rate constants to simulate polymerization reactions. Furthermore, Monte Carlo methods are capable of estimating the composition drift and azeotropic properties of copolymers which are in agreement with the experimental and analytical methods. In addition, because of the statistical nature of (co)polymerization reactions, Monte Carlo methods have been used as powerful tools to simulate numerous (co)polymerization reactions [11-15].

Monte Carlo method has not yet been applied to simulate the bulk photopolymerization of FM. Thus, in this work, photopolymerization of FM is studied using the Monte Carlo simulation method and the results are compared with available experimental data from the literature.

Mechanism

The mechanism of the photopolymerization of FM initiated by AIBN is as follows [7]:

Photo-induced primary radical production:

$$I_a \xrightarrow{\varphi} 2R^* \quad (1)$$

Primary initiation:

$$R^* + FM \xrightarrow{k_i} \left(M_1^*\right)_1 \quad (2)$$

Acrylic macroradical propagation:

$$\left(M_1^*\right)_n + FM \xrightarrow{k_p} \left(M_1^*\right)_{n+1} \quad (3)$$

Acrylic macroradical termination:

$$\left(M_1^*\right)_n + \left(M_1^*\right)_m \xrightarrow{k_t} P_{n+m} \quad (4)$$

Intermolecular degradative transfer:

$$\left(M_1^*\right)_n + FM \xrightarrow{k_{trd1}} P_n + \left(M_2^*\right)_1 \quad (5)$$

Re-initiation:

$$\left(M_2^*\right)_1 + FM \xrightarrow{k_{is}} \left(M_1^*\right)_2 \quad (6)$$

Allylic-acrylic termination:

$$\left(M_2^*\right)_1 + \left(M_1^*\right)_m \xrightarrow{k_{tc}} P_{1+m} \quad (7)$$

Allylic primary termination:

$$\left(M_2^*\right)_1 + R^* \xrightarrow{k_{tp2}} P_1 \quad (8)$$

Acrylic primary termination:

$$\left(M_1^*\right)_n + R^* \xrightarrow{k_{tp1}} P_n \quad (9)$$

Primary degradative transfer:

$$FM + R^* \xrightarrow{k_{ptrd}} \left(M_2^*\right)_1 \quad (10)$$

Monomer transfer:

$$\left(M_1^*\right)_n + FM \xrightarrow{k_{trm}} P_n + \left(M_1^*\right)_1 \quad (11)$$

Table 1. Kinetic parameters employed in the simulation at different temperatures [7].

Parameter	Unit	Temperature (°C)			
		40	30	10	0
k_p	$L.mol^{-1}.s^{-1}$	2837	2060	1915	725.7
k_i	$L.mol^{-1}.s^{-1}$	995.1	946.3	841.6	802.6
φ	adimensional	0.3133	0.1097	0.1131	0.4868
I_a	Einstein. $L^{-1}.s^{-1}$	2.29×10^{-6}	1.41×10^{-6}	1.91×10^{-6}	1.92×10^{-6}
[I]	mol/L	1.5×10^{-2}	1.5×10^{-2}	1.5×10^{-2}	1.5×10^{-2}
k_t	$L.mol^{-1}.s^{-1}$	1.25×10^{6}	1.05×10^{6}	6.3×10^{5}	6×10^{5}
k_{tp1}	$L.mol^{-1}.s^{-1}$	2.2×10^{6}	1.7×10^{6}	1.14×10^{6}	7×10^{5}
k_{trd1}	$L.mol^{-1}.s^{-1}$	1991	1302	1132	621.8
k_{tp2}	$L.mol^{-1}.s^{-1}$	1.4×10^{5}	7.73×10^{4}	2.36×10^{4}	10^{4}
k_{ptrd}	$L.mol^{-1}.s^{-1}$	8970	5456	1781	998.8
k_{is}	$L.mol^{-1}.s^{-1}$	0.5825	0.563	0.197	3.97×10^{-2}
k_{tc}	$L.mol^{-1}.s^{-1}$	9.13×10^{4}	3.123×10^{4}	1.657×10^{4}	1.001×10^{4}
k_{trm}	$L.mol^{-1}.s^{-1}$	12.71	9.298	9.00	1.00

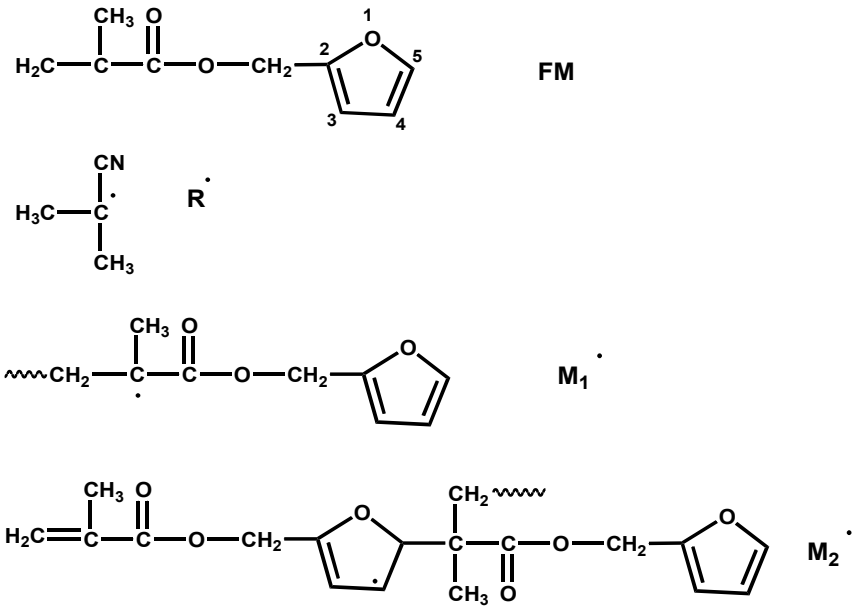
where, P_n represents dead polymer chains. I_a denotes the concentration of initiator species which is as follows:

$$I_a = I_0(1-\exp\{-\varepsilon[I]l\}) \quad (12)$$

where, φ is initiation quantum yield, I_a is intensity of light absorbed by photoinitiator AIBN (Einstein. $L^{-1}.s^{-1}$), I_0 is incident light intensity (Einstein. $L^{-1}.s^{-1}$), ε is molar absorption coefficient of the photoinitiator AIBN ($L.mol^{-1}.cm^{-1}$), [I] is photoinitiator concentration ($mol.L^{-1}$), and l is optical path length (cm). The values of I_a, φ and other parameters are indicated in Table 1. Scheme I depicts the various species involved in the mechanism.

Monte Carlo Simulation Method

Although in using the Monte Carlo method one can simulate polymerization on a molecular scale and to



Scheme I. Structure of the species involved in the mechanism of the photopolymerization of furfuryl methacrylate [7].

avoid the huge amount of computation, this method is better to be employed for small scale reaction volumes. In other words, the simulation volume has been chosen just enough to reduce the simulation time to a reasonable value; however, the reaction volume needs to be large enough to meet the statistical criteria. Therefore, a simulation volume which consists of 10^9 FM molecules has been applied for computer operation. Subsequently, the number of other components is calculated based on FM molecules:

$$V = \frac{N_M}{[M]N_{av}} \tag{13}$$

$$N_X = [X]N_{av}V \tag{14}$$

where, V is simulation volume, N_M denotes the number of monomers, [M] is monomer concentration, N_{av} is Avogadro's number, N_x represents the number of X molecules and [X] is the concentration of X species. In addition, because the Monte Carlo simulation method deals with a number of molecules (instead of concentration); stochastic reaction rates need to be replaced by the macroscopic ones. Provided that there are L reactions in the simulation, the probability of incidence of reaction l (P_l) is given by eqn (15) [16-21]:

$$P_l = \frac{a_l}{\sum_{l=1}^{l=L} a_l} \tag{15}$$

where, a_l is the stochastic reaction rate for reaction l and it is defined by eqn (16):

$$a = h \times c \tag{16}$$

In this equation, h represents the number of reactants and c stands for the stochastic rate constants and correlates with ordinary reaction rates:
First-order reactions:

$$c = k \tag{17}$$

Second-order reactions:

$$c = \frac{k}{VN_{av}} \tag{18}$$

Regarding r_1 as a random number which is generated during the simulation, based on the following criteria, a reaction is assumed feasible:

$$0 < r_1 \le P_1 \quad \Rightarrow \quad reaction\ 1 \tag{19}$$

$$P_{l-1} < r_1 \le P_l \quad \Rightarrow \quad reaction\ l \tag{20}$$

In the course of the reaction, to select a polymer chain for reaction, first all chains of the same active centres are considered as a group. Then, the probability of the reaction of this group is calculated by dividing the number of chains in the group by all the chains which is available in the reaction medium. Afterwards, the reactions are selected according to the relations 19 and 20 to start randomly. Finally, another random number is generated to compute the reaction time intervals (eqn 21):

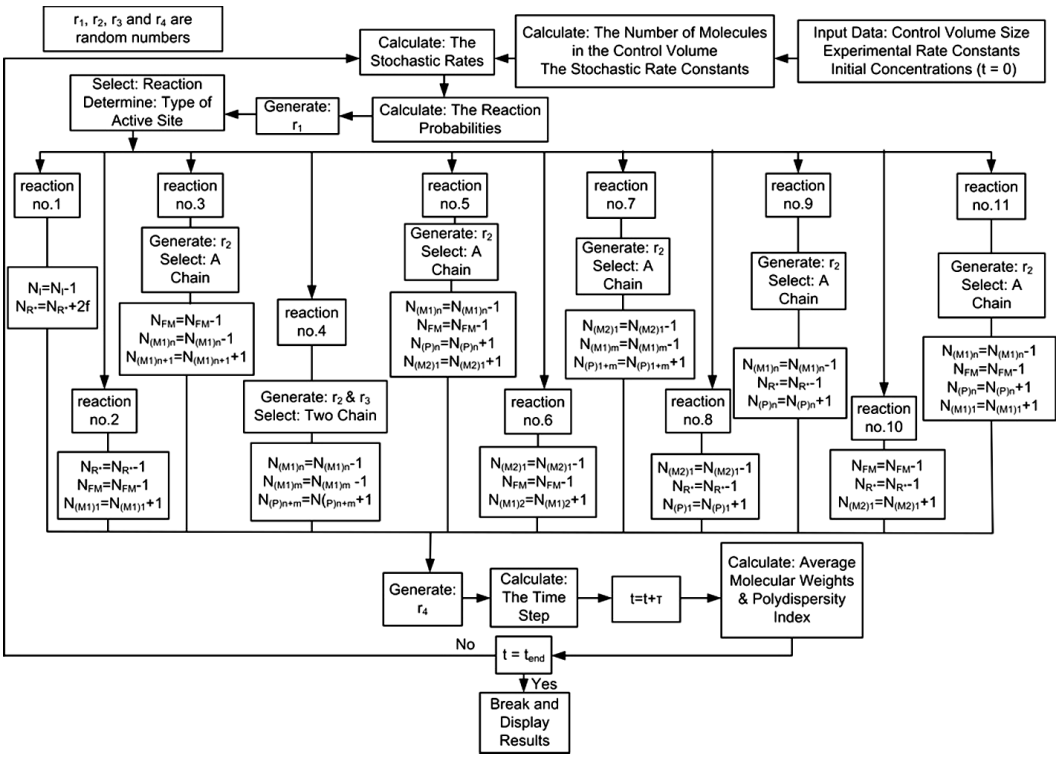
$$\tau = \frac{1}{\sum_1^L a_l} \ln\left(\frac{1}{r_3}\right) \tag{21}$$

Random numbers have been widely employed in the Monte Carlo methods [11]. Considering that the most random numbers used in Monte Carlo methods are pseudo-random, they need to meet some criteria required for uniformity and sequential correlations [12].

Therefore, improved Mersenne twister random number generator [13], which has a cycle length of 2^{19937}-1 and satisfies the tests of uniformity and serial correlation [14,15], has been considered in this work. The simulation programme was written in C++ and executed on a four-processor (Pentium Intel Xeon (4×2.3 GHz)) hp server running SuSE Linux as its operating system. Schematic representation of the Monte Carlo method algorithm which is used in the current study is illustrated in Scheme II.

Simulation Results

Variation of the FM concentration versus irradiation time in various temperatures is presented in Figure 1. As expected, polymerization rate increases by temperature which is on account of an increase in the propagation constant of acrylic macroradicals. According to the results, there is a relatively



Scheme II. Monte Carlo simulation algorithm for furfuryl methacrylate photopolymerization.

appropriate correlation between the experimental and simulation data which more confirms the validity of the simulation algorithm. Data analysis results are shown in Table 2.

Figure 2 shows the change in M_1^* concentration with irradiation time at various temperatures. At 40°C, in the first stages of the irradiation, due to higher value of k_i (primary initiation) in comparison with the other temperatures, M_1^* concentration increases rapidly.

Nevertheless, it remains approximately constant after a while which is because of the acrylic macroradical termination, intermolecular degradative transfer, allylic-acrylic termination, and acrylic

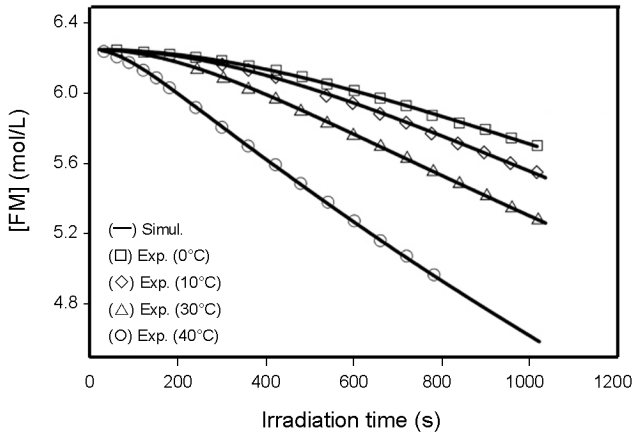


Figure 1. Furfuryl methacrylate concentration vs. irradiation time at different temperatures.

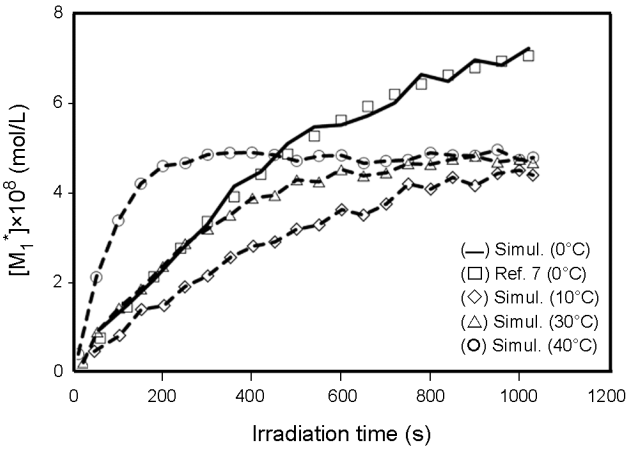


Figure 2. M_1^* concentration versus irradiation time at different temperatures.

Table 2. Data analysis results for comparing simulation and experimental results based on least square method.

Temperature (°C)	Number of data	R^2
0	17	0.9999
10	16	0.9998
30	14	0.9997
40	16	0.9999

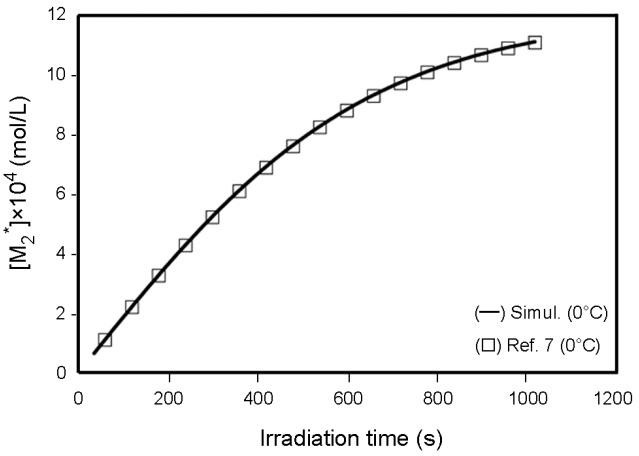


Figure 3. M_2^* concentration versus irradiation time at 0°C.

primary termination. At 0°C, M_1^* has the highest concentration at the end of the irradiation compared with the other temperatures. This is due to the lowest amount of k_t, k_{trd1}, k_{tc} and k_{tp1}. Also, as presented in Figure 3, the simulation results are in agreement with ref. 7 for M_2^* concentration in 0°C.

CONCLUSION

Photopolymerization of furfuryl methacrylate using Monte Carlo simulation method was studied accurately. Subsequently, experimental results were employed to evaluate the simulation data and confirm the validity of the simulation procedure. The rate of the FM concentration variation versus irradiation time increases at higher temperatures. Experimental data and simulated results for the change of FM concentration with irradiation time are in good agreement. At the starting time of irradiation, M_1^* increases rapidly at 40°C and after a while it remains constant. At 0°C, towards the end of the irradiation, the highest amount of concentration of M_2^* is obtained compared with other temperatures. However, at 30°C and 40°C, M_2^* remains constant after a while. At 40°C, before 400 s of irradiation, M_2^* exceeds that of condition of 10°C.

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