

Research Letter

Dynamical Model to Describe the Interactions between the Chemical Components in Environment of Photopolymerization of MMA by Dye/Amine Systems

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This work discusses the model that explains the aspects of photopolymerization of methyl methacrylate initiated by dye/amine systems. This model is based on a simulation that uses differential equations. A similar model following the hypothesis presented here was used with success in a preliminary work, by Magini and Rodrigues (2005), to describe the cationic photopolymerization of THF in the presence of sensitizers/sulfonium salt systems. Using the same structure was possible to generate a straight correlation between experimental and theoretical results for this system, free radically initiated, opening an important theoretical understanding about the photopolymerization systems and their chemical relations during the reaction.

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1. Introduction

Polymer science has been the subject of many investigations [1, 2]. This occurs owing to the potential applications of these materials, from basic research to applicable context. The applications commonly appear in industry of biomaterials and manufactured products [3, 4]. On the other hand, basic studies such as polymer formation, theoretical and experimental, or studies around the physical chemistry properties of polymers can be cited [5–16].

Theoretical studies about process of photopolymerization are described by statistical methods [17–19], analysis by interpolation, or similar methods [20, 21]. However, these works do not present evidences of predictability. In statistical mechanics, the results are focused in the dynamical formation of the polymer and simulated by numerical methods like Monte Carlo [18, 22]. The second approach, curves analysis, has a more straight connection with the experimental behavior of the polymerization, but the character of prediction is not considered. Normally, the prediction is a consequence of the model that uses differential equations to determine the behavior of parameters and chemicals involved [23–26].

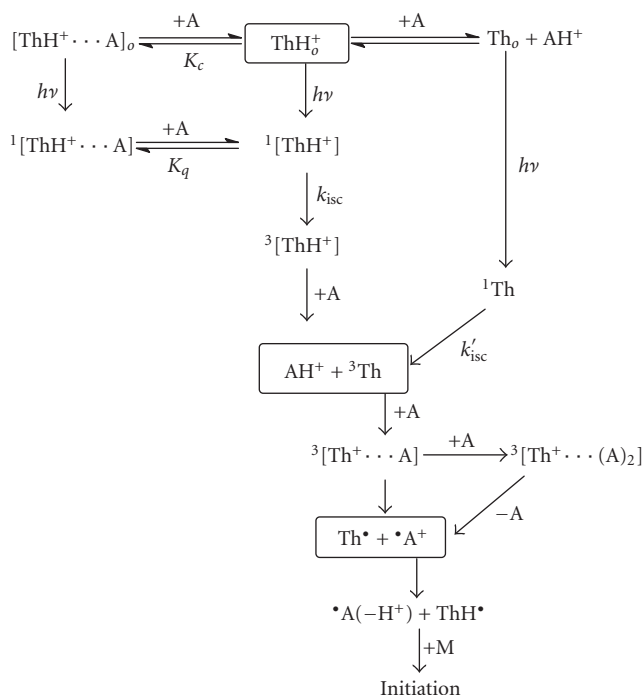
This work presents a set of mathematical supposition that determines how the different chemicals react in a photopolymerization process in the presence of sensitizers. These hypotheses and models were demonstrated in a preliminary work [27] for a specific problem: the cationic photopolymerization of tetrahydrofuran initiated by systems sensitizer-sulfonium salt. The present work shows that the first model can be applied with the same success for dye/amine systems. Moreover, new experimental results about these systems are showed.

2. Methodology

Measurements were performed according to previous descriptions [10, 12] and R_p , the rate of polymerization, was calculated using the standard expression below [10, 12]:

$$R_p = \frac{h}{F \cdot t \cdot f} [M] \text{ (mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}\text{)}, \quad (1)$$

where h is the contraction in volume in the capillary at time t (s), $F = (100 \cdot (dp - dm)/dp)$ relates the volume contraction with the molar densities of the polymer and the monomer in



SCHEME 1

solution, [M], is the concentration of monomer, and f is the volume fraction of monomer in the solution.

2.1. Model Development

2.1.1. Radical Chain Polymerization Mechanism

For radical chain polymerization, the initiation mechanism is based on results of photophysical and photochemical behaviors of the initiator. The dye absorbs light in the visible region or UV in the presence of the coinitiator and monomer. In this way, the elemental reactions involved at the initiation process must be evaluated independently.

Many mechanistic studies were reported for radical chain polymerization of MMA by thionine dye (ThH⁺) in the presence of an amine A (triethanolamine, TO, or triethylamine, TE) [10–12]. A complete and general mechanism for these systems has been described (Scheme 1) [10–12].

[ThH⁺·A] and [Th⁺...A] refer to dye-amine complexes which may be formed in the ground state, or in the excited states as singlet and triplet exciplexes. An alternative pathway including a triplex [ThH...A]₂ (intermediate present in this kind of reactions due to the high concentration of amine present) is also introduced in the scheme [12]. In most studies, the radicals originated from amines have been proved to be responsible for the chain initiation in many photoinitiated polymerizations. Also, the interaction between the singlet state of ThH⁺ and MMA does not lead to polymerization and the decrease of the polymerization rates, as well as that of the dye semireduced radical yield, observed at high amine concentrations, indicates that excited

dye molecules will be increasingly quenched by the amine, precluding their conversion to triplets which originate the active radicals leading to polymerization. Due to multiplicity restrictions, singlet exciplexes are not supposed to lead to separated radicals. The semithionine species (ThH[•]) appears in the reaction scheme after both the proton and electron transfer stages which generate the amine radical [•]A(-H⁺) by deprotonation of the cation radical of the amines, A^{•+} [11, 12].

Similarly to preliminary work [27], the starting point for the mathematical approach is the variation of amine radical concentration ([•]A(-H⁺)) in time, which interacts with the monomer (MMA) and initiates a sequence of events leading to polymerization. Consequently, the values of chemical variables related with this process time dependent are as follows: amine and monomer concentrations, the conversion of monomer to polymer. From this point, it was supposed that the reduction of rate of the monomer concentration is related with the initial value of conversion, of the amine concentration, and of the monomer in accordance with

$$-\frac{d[M]}{dt} = \delta f c[A][M], \quad (2)$$

where δ is a nondimensional constant, resulted from the solution of the differential equation, $f c$, [A] and [M] are conversion function amine concentration and monomer concentration, respectively. The conversion function can be interpreted as the behavior of the polymerization or the proportionality of conversion that determines how the monomer is increased or decreased. Solving this equation leads to (5). This supposition will be explained in the next section.

3. The Modeling

The chemical assumptions of the model presented here follow the same mathematical structure of the dynamical model proposed by Magini and Rodrigues [27] and use the same equations for radical chain photopolymerization systems. The intention of this study is to achieve a global approach for photopolymerization systems and understand how the interaction between the chemical variables is.

To explain the radical chain photopolymerization, here reported, a set of equations that describes the conversion function, through variation of time for two different systems of dye-amine in diverse concentrations, was used.

Assumption 1. The polymerization reaction is initiated from interaction between [•]A(-H⁺) species and the monomer MMA (M), which causes a decreasing of amine radical concentration. This species is produced by the interaction between ThH⁺, light, and amine. Independently of amine (A) and thionine (ThH⁺) initial concentrations, in the final portion of process and immediately before the interaction of [•]A(-H⁺) with monomer (Scheme 1), the concentrations of ThH[•] and [•]A(-H⁺) are numerically equal. The process of polymerization is connected with [[•]A(-H⁺)] and $f c$. Equation (3) comes from the information above:

$$[\text{ThH}^{\bullet}]_{t+1} = [\text{ThH}^{\bullet}]_t f c \times \exp(-\rho t). \quad (3)$$

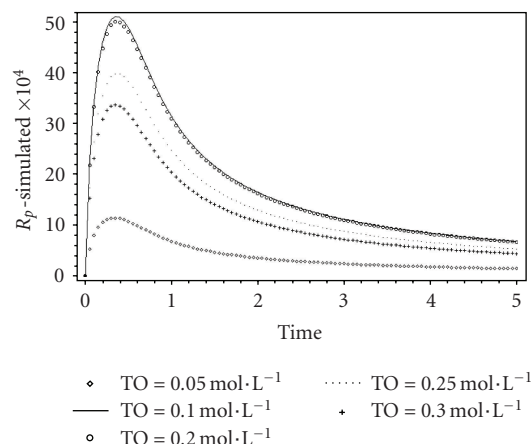


FIGURE 1: Simulated values for velocity of polymerization of MMA, R_p , using data of Table 1 for different concentrations of TO.

It has been assumed that ThH^\bullet species concentration has an exponential variation (directly dependent of the initial value of the conversion function, represented here by fc) with a scale parameter ρ , which determines how fast is the variation of $[\text{ThH}^\bullet]$ in time. Notice that this variable is consumed when time (t) is increasing. The term fc provides a smooth decreasing of $[\text{ThH}^\bullet]$. This variable is analogous to the $[\text{Sens}^{**}]$ introduced in the work of Magini and Rodrigues [27].

Assumption 2. Amine is the chemical variable that determines the efficiency of the photopolymerization processes. By analyzing the value of $[A]$ and its influence on the polymerization induced by light, it can be concluded that when $[A]$ assumes null value for $t = 0$, the photopolymerization processes do not occur, mathematically represented in (4). This hypothesis results in the final form of the conversion function given by (6), where the term $([A]_t)^{1/2}$ multiplies all terms. If the value of $[A]$ is null for $t = 0$, (4) assumes the value zero and (5) assumes a constant value:

$$[A]_{t+1} = [A]_t \times \exp(-\beta t). \quad (4)$$

Assumption 3. The variation of monomer concentration has exponential dependency with the values of $[A]$, the variable that limits this reaction, and fc . This equation is consequence of the solution of (1) for a range of time values $t < t' < t + 1$:

$$[M]_{t+1} = [M]_t \times \exp(-fc[A]_t\delta), \quad (5)$$

where δ is a parameter of adjustmentⁱⁱ, and $[M]_t$ is the value of monomer concentration when the process of polymerization is started. This supposition is correlated with the complexity of the mechanism of photopolymerization, Scheme 1, and with the work proposed by Magini and Rodrigues [27] that follows the same complexity; when the function fc grows, the monomer and the amine are consumed; when the values of fc and $[A]_t$ are maximum, the $[M]_t$ value achieves its minimum value.

The values of ρ and β parameters are resulted from solution of each differential ordinary equation that models

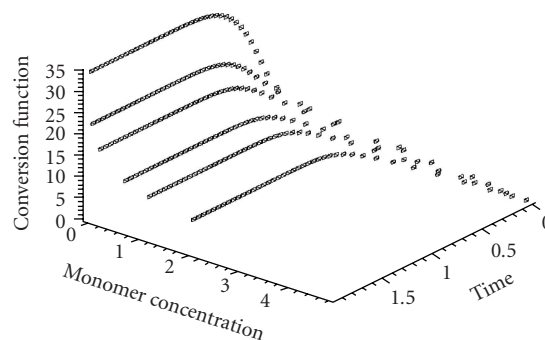


FIGURE 2: Theoretical results for the fc of MMA at different concentrations of TO and quantum yields Φ_m where $\Phi_1 < \Phi_2 < \dots < \Phi_6$.

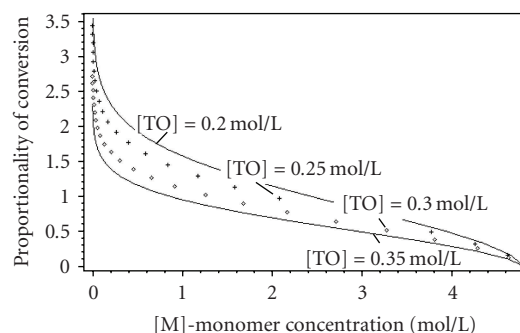


FIGURE 3: Values of fc through the decreasing of monomer concentration. Different values of $[TO]$ are plotted.

the variation of species $[\text{ThH}^\bullet]$ and $[A]$. The result from (1) is related with the initial values of amine concentration and fc . The differential equation below is the final form proposed to determine the conversion function, in time, give in $\text{mol} \cdot \text{L}^{-1}$:

$$\frac{d fc}{dt} = ([\text{ThH}^\bullet]_t + \alpha \Phi_m + [M]_t + fc)^{1/2} ([A]_t)^{1/2}. \quad (6)$$

The constant α has dimension of mol-second per Einstein and can be interpreted as the number of mol that absorbs radiation in time. The term Φ_m (Einstein per liter-second), called quantum yield of polymerization, is defined as the number of monomer units polymerized per absorbed photon and incorporates the effects of the light intensity in (6). This equation is the simplest form assumed to explain the conversion function. The direct sum of the terms can be considered the most basic construction for (6) and the multiplication by the term $[A]_t$ reveals that fc has to be null when amine concentration is zero. The amine concentration is the precursor of the entire process, and consequently its value is directly connected with the initial value of fc . For $t = 0$, $[A]_t = 0$, and as a result the value of fc is null.

The results obtained here allow generalizing the model for two distinct systems: cationic and free radical. This is a new way to see these systems, and the comments about this correlation will be done in the discussions. Values of $[M]$, $[A]$, and $[\text{ThH}^\bullet]$ were computed simultaneously with the result given by the solution of the differential equation (6).

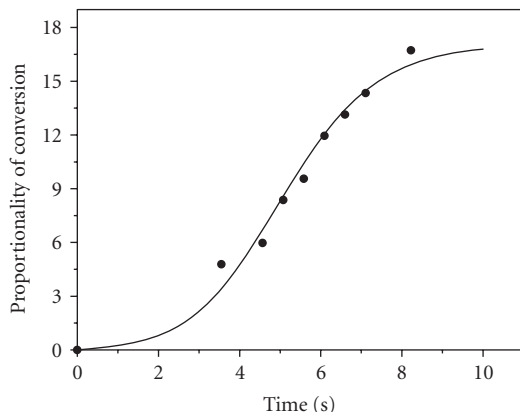


FIGURE 4: fc of MMA photopolymerization in the presence of ThH^+ ($0.8 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) and TE ($0.1 \text{ mol}\cdot\text{L}^{-1}$) systems. Experimental data is represented by the symbol (\bullet) and the numerical by the continuous line.

4. Results and Discussions

Table 1 lists the polymerization rate (R_p), the polymerization quantum yield (Φ_m), and the monomer conversions for the photopolymerization of MMA obtained at different TO concentrations. Values were obtained as previously described [12].

It can be seen that the polymerization rate increases and reaches a maximum value when TO concentrations are $0.10 \text{ mol}\cdot\text{L}^{-1}$ and $0.20 \text{ mol}\cdot\text{L}^{-1}$, decreasing afterward. This decrease is ascribed mainly to the quenching of the ThH^+ singlet excited state, which decreases the amount of triplets produced by intersystem crossing and, therefore, the yield of initiating radicals. The same behavior has been described for various monomer/initiator/amine systems [10–12, 28, 29] and it suggests that the polymerization is originated from the interaction of the amine with the triplet excited state of the dye. The amine radical $\cdot\text{A}(-\text{H}^+)$, resulted from the chain initiation, comes from bleaching of the dye during the photoinitiated polymerization and it originates from reactions of the semithionine species (ThH^*) after both the proton and electron transfer stages.

The simulations of the polymerization rate (R_p) for TO using the experimental values for concentration and polymerization quantum yield, Table 1, are shown in Figure 1, where R_p reproduced by the approach follows an approximated pattern when compared with the experimental results. Similarly, in Figure 1, it is possible to see an optimum value of the concentration of TO and quantum yield to achieve higher values for these measures.

In Figure 1, the R_p values were calibrated to accept the numerical discrepancy between the values of R_p , conversion, and time. The R_p is resulted from the rate between the conversion function and the monomer concentration. The results show the behavior through the time variation. The results presented in Figure 1 confirm the coherence of this approach to classify and determine the general behavior of chemical variables, which are directly influenced by the photopolymerization processes.

TABLE 1: Experimental data for polymerization of MMA ($4.8 \text{ mol}\cdot\text{L}^{-1}$) in methanol (1:1) at 30°C photoinitiated by ThH^+ ($0.8 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$)/TO.

TO ($\text{mol}\cdot\text{L}^{-1}$)	R_p ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$) $\times 10^5$	Φ_m	Conversion
0.050	2.14	66	0.013
0.10	3.02	140	0.039
0.20	3.82	146	0.043
0.25	3.28	126	0.037
0.30	2.33	90	0.025
0.35	1.63	70	0.016

Numerical tests were realized for TO with different values of polymerization quantum yield. In Figure 2, the theoretical behaviors of the conversion function for different values of quantum yields and time are showed. The starting values of monomer concentration for all curves were the same, $4.8 \text{ mol}\cdot\text{L}^{-1}$ (experimental value). This initial value was fixed to study the influence of monomer variation under of the quantum yield. It is possible to see the relation between high values of fc directly related with the high values of quantum yield, which is experimentally expected.

Figure 3 describes the conversion function versus the variation of monomer concentration for different values of [TO], which is fixed for each curve. The results showed are in a straight accordance with the experimental data, Table 1. The maximum value of the conversion function is obtained when the $[\text{TO}] = 0.20 \text{ mol}\cdot\text{L}^{-1}$. For values bigger than $0.20 \text{ mol}\cdot\text{L}^{-1}$, the value of fc decay. In Table 1, this fact is verified, for $[\text{TO}] = 0.20 \text{ mol}\cdot\text{L}^{-1}$, the conversion is 0.043 (maximum), for $[\text{TO}] = 0.25 \text{ mol}\cdot\text{L}^{-1}$, $[\text{TO}] = 0.30 \text{ mol}\cdot\text{L}^{-1}$, and $[\text{TO}] = 0.35 \text{ mol}\cdot\text{L}^{-1}$, the values of conversion are 0.037, 0.025, and 0.016, respectively. The curve in Figure 3 follows the same pattern.

The previous experimental results obtained to polymerization of MMA photoinitiated by ThH^+ /TE [12] are here comparing with theoretical behavior. The initial study was completed generating a set of theoretical tests that show the relation between values of amine concentration, polymerization quantum yield and monomer starting values. Figure 4 shows that theoretical and experimental values for $0.1 \text{ mol}\cdot\text{L}^{-1}$ of TE are well correlated.

5. Conclusions

Both experimental and simulated data were compared, and the correlation between their values was verified (Figures 1, 2, and 4). The R_p was theoretically calculated, and its value is in accordance with the experimental results proving the capacity of adaptation of this simulation for these systems (free radical). The same occurs for the conversion function at different values of [TO], where the theoretical fit reproduces the behavior of the experimental data, as shown in Table 1. α , ρ , δ , and β are adjust parameters, related the initial concentration of chemicals. The chemical parameters were completely described in this dynamical approach, as the results show. The assumptions show clearly how the concentrations vary through the time.

As in the previous work [27], an only function describes the system, and in a deeper view was proved that it is possible to establish a theoretical adjust with two systems of polymerization: cationic and free radical. The mechanism logic that induces the polymerization process follows similar patterns for these two systems. As a consequence, the model constructed for cationic systems can be adjusted for free radical systems.

Acknowledgment

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