A dynamical system to describe the cationic photopolymerization of tetrahydrofuran initiated by systems sensitizer-sulfonium salt

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Abstract

Most studies in theoretical chemistry are interest to model microscopic properties of atoms and molecules that participate of some experiment. In many cases these approaches leading them to a very complex construction and using, in general, stochastic processes to describe the behavior of the system. In this paper we considered a mathematical approach to describe the behavior (variation in time) of chemicals concentration upon the photoinitiated polymerization of the terahydrofuran by systems sensitizer-sulfonium salt. The mathematical approach is based in an ordinary differential equation where the parameters are time-dependent functions, which were solved numerically by Euler Numerical Method, first order. The main properties of the chemicals involved in this reaction were responsible to generate three assumptions used as a basis to construct the present approach. We argue that these assumptions are responsible to model completely the system. This verified in the theoretical results. The ideas presented her can be easily modified to any system where the chemicals that interact with the experimental environment follow the same patterns of behavior. Results showed that these assumptions combined with the correct mathematical procedures resulted in a set of patterns observed experimentally.
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1. Introduction

The research in Polymer Photochemistry has been expanded in different fields and subjects. For example, free radicals and cationic photoinitiated polymerizations are experimentally tested, even in studies of kinetics mechanisms as in fundamental aspects described by those reactions. Moreover, there are current and real potential applications in photocuring, including coatings, paints, adhesives, graphic arts, microelectronics, optics, medicine, stereolithography and laser writing [1]. The design of new reactive monomers and oligomers, improved photoinitiators and more efficient photosensitizers would be following presumably accompany market growth [2].

Photoinduced polymerization is usually considered as a chain reaction where the initiation step is produced by a photochemical event. Accordingly, the liquid monomer formulation exposed to UV or visible light is converted into a solid polymer [3].

Particularly, the study of the cationic polymerizations initiated by visible light is important due to the large variety of monomers that can be polymerized by cationic photo-initiation, but not by radical processes, as for example several vinyl and cyclic monomers, like alkyl vinyl ethers and industrially important epoxides [4]. Some works that use the initiator onium salt (triphenylsulfonium hexafluor-oarsenate, S^+) had been sensitized by Perylene (Pery) [5], Phenothiazine (Phe) [6] or Thioxanthone (TX) [7] promoting the photoinitiated polymerization of tetrahydrofuran (THF).

Works in photoinitiated polymerizations by free radical [8–11] and cationic [5–7,12] process relate the deduction of the involved photochemistry mechanism [5–11], and evaluate the kinetics parameters by precise methods of analyzes [12]. Nevertheless, mathematical approaches to describe these systems are not found frequently at the literature.

Historically, mathematical methods to describe chemical

reactions have been introduced in science with a considerable success [13–15]. In a more specific context, we can cite the use of these tools in reactions of polymerization photoinitiated as the study, by Runge-Kutta methods, of thermosetting plastic material produced by UV radiation [16]; the development of a mathematical model that describes photocure and photopolymerization kinetics [17]; a mathematical description of various temporal parameters related with the light intensity made by Terrones and Pearlstein and Ivanov and Decker [18]; the study of the photopolymerization of furfuryl methacrylate under the point of view of kinetics modelling of the crosslinking [19] and of the stochastic model named CORUB used to do a phenomenological description of this reaction [20]; and the study by isothermal photocalorimetry of kinetic of photo-initiated polymerization of a dimethacrylate oligomer using a mechanistic model in order to determine the different kinetic rate constants of the system [21].

In this paper, we propose a mathematical approach to give an overview about the behavior (variation in time) of the concentration of the chemicals upon the photoinitiated polymerization process. More specifically, we are interested to predict the concentration variation through time increment for these chemicals. For this, it was constructed a set of equations, time-dependent, that describe patterns of variation in time of the tetrahydrofuran polymerization photo-initiated by systems sensitizer-sulfonium salt and their main chemicals components. Nevertheless, this specificity can be migrated to systems of polymerization photoiniated where the interacting chemicals follow the same qualitative behavior.

Obviously, to create equations that reproduce experimental results without any supposition is an easy task. Therefore, to create equations that connect characteristics of the chemicals with the experimental measures is not a trivial task. As motivation for this question, we constructed a set of coupled equations, differential ordinary equations, solved numerically. In these equations we suppose that the chemical variables follow specific patterns of time variation. They were modeled mathematically using a 'picture' of the quantitative behavior of the macroscopic interactions, when the system is initialized by light. This system of equations explains the mechanistic behavior of the concentrations through time variation in the process of photo-polymerization. This theoretical approach is a deterministic[1] and depends only from an initial condition to start the simulation.

Results have shown that the mathematical suppositions to model the system are sufficient to achieve results that reproduce the experimental data. Our main motivation behind the model is show that: starting with appropriated

assumptions it is possible generate quantitative tools that reproduce satisfactorily the real system. In cationic systems, determine equations that explain the rate of polymerization using the assumption of steady state is a procedure with considerable difficult. For this reason determine equations that explain cationic polymerization through their main variables, in terms of values of concentration, is important for a better understanding about these type of systems.
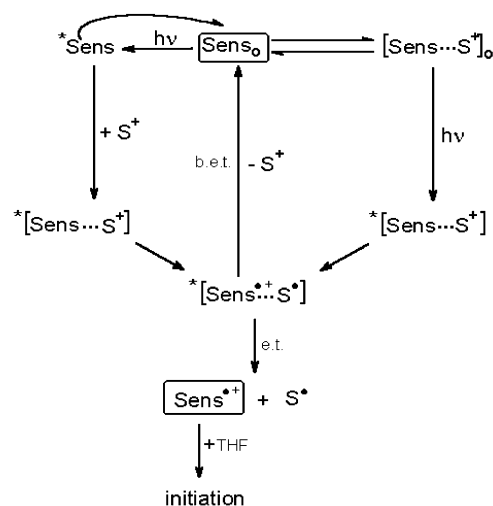
2. Methods

2.1. Polymerization mechanism

In any photoinitiated polymerizations, the initiation mechanism considered must be based in the results of the photophysical and photochemical behavior of sensitizer (Sens) in presence of the initiator and the monomer. For cationic photoinitiated polymerizations also it is thus.

The elemental reactions involved in the initiation process must be evaluated independently in order to be able to propose a mechanism leading to the formation of the initiating cation radicals. Mechanistic studies were reported for the cationic photopolymerization of THF by sulphonium salts sensitized by Pery, TX and Phe. In simplified way, the sensitized photolysis of onium salts can occur by transference of energy or electron. However, based in experimental photophysical/photochemical data for systems of cationic photoinitiated polymerization [5–7], already mentioned, a more complete and general mechanism can be considered (Scheme 1).

This mechanism only considers the interactions that can lead to the formation of the cation radical ($Sens^{+\cdot}$), the true initiators of the polymerization. $Sens_o$, $*Sens$ and $Sens^{+\cdot}$ indicate the fundamental, excited (singlet and/or triplet) states of the sensitizer (Sens) and cation radical, respectively. The associations $[Sens\ S^+]_o$ and $*[Sens\cdot S^+]$

Scheme 1.

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correspond to the complex formed between Sens and S^+ in the ground state and to the complex of excited encounter, which may lead to the exciplex *[Sens$^{+\cdot}\cdot$S$^\cdot$] after electron transfer. After the interaction between THF and Sens$^{+\cdot}$ that marks the start of the polymerization, where part it is regenerated to Sens through time increment.

Obviously, associations formed between Sens and THF in the ground and excited states also are possible but they do not lead to the formation of species capable to initiate the polymerization [5–7] and therefore is not considered here. For the Pery, no chemistry or any other evidence of the participation of the triplet state of the sensitizer was found [5].

After the formation of Sens$^{+\cdot}$, this interacts with the monomer (THF) and initiates a sequence of three events that lead to polymerization: initiation, propagation and termination. The equations below follow this sequence to cationic polymerization in the general way. The initiation process can be generalized as,

$$C^+N^- + M \xrightarrow{k_i} CM^+N^- \tag{1}$$

where C^+, N^- and M represent a generic cationic species, negative counter ion and monomer, respectively. Note that the C^+ species can remain attached or not to polymer chain in growing, depending on the system.

The initiator ion pair produced in the initiation step proceeds to propagate by successive additions of monomer molecules;
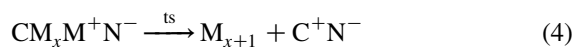
$$CM_x^+N^- + M \xrightarrow{k_P} CM_xM^+N^- \tag{2}$$
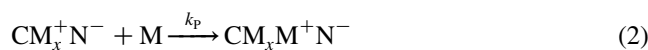
Many reactions lead the termination of chain growth in cationic polymerization, as

(a) Chain transfer to monomer:

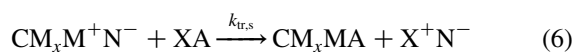$$CM_xM^+N^- + M \xrightarrow{k_{tr,M}} M_{x+1} + CM^+N^- \tag{3}$$
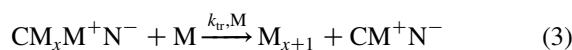
(b) Spontaneous termination:

$$CM_xM^+N^- \xrightarrow{ts} M_{x+1} + C^+N^- \tag{4}$$

(c) Combination with counter ion:

$$CM_xM^+N^- \xrightarrow{t} CM_xMN \tag{5}$$

(d) Termination by transfer agents (XA, solvent, impurity, etc) by transfer of a negative fragment A^-:

$$CM_xM^+N^- + XA \xrightarrow{k_{tr,s}} CM_xMA + X^+N^- \tag{6}$$

The starting point for the mathematical approach is the variation of concentration of cation radical (Sens$^{+\cdot}$) formed in time and consequently, the chemicals variables related with this process, which are: salt and monomer concentration, the proportionality of conversion monomer to polymer[2], where their values are time-dependent. From this, we suppose that the rate of monomer disappearance is related with the initial conversion, salt concentration and the initial value of the monomer concentration or

$$\frac{-d[M]}{dt} = kf_{conversion}[S^+][M] \tag{7}$$

where k is a constant and $f_{conversion}$, $[S^+]$, $[M]$ are the proportionality of conversion, salt concentration and monomer concentration, respectively. Solving this equation we found the Eq. (10) for a generic time variation. This supposition will be explained in the next section.

2.2. The mathematical approach

In Chemistry, mathematical and statistical the methods are useful to describe since microscopic phenomenon as macroscopic patterns. Most of them are based in differential methods added with statistical ideas, known as Statistical Mechanics [22]. These methods considered a less number of variables when compared with deterministic methods. They are imprecise but many results show large possibilities of applications. In spite of this, deterministic methods are difficult to implement or compute owing to the number of variables and assumptions that must be considered. Nevertheless, they lead better-structured concepts, results and assumptions explaining clearly the considered phenomenon. Deterministic methods, usually based in systems of differential equations, lead the study to a level where the results are predictable even if the system is complex.

For the cationic photoinitiated polymerization here reported, was used a set of equations that describe the proportionality of conversion, through variation of time for the three different systems of Sens-salt in diverse concentrations. The follow equations are the first step of this mathematical approach used. To construct these equations were made a group of assumptions about the behavior of the macroscopic system. All variables are interconnected by their chemical properties. Actually, for this approach, the main variable observed is the concentration of the involved chemicals in the system.

We are interested in modelling parameters of the polymerization and, consequently, the proportionality of conversion, represented by the function. This function is dependent of a group of chemical variables: the concentration of cation radical [Sens$^{+\cdot}$], the concentration of monomer [M], the concentration of salt [S+] and the quantum yield of polymerization. Now, we present the structure of the mathematical ideas generated to reproduce the experimental data initiating with the three assumptions that are the basis of our results. These assumptions are based

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[2] The word proportionality is used as synonymous of the word the conversion to differentiate the theoretical from the experimental results.

empirically in the Scheme 1 that shows, as important result, the interaction between the chemicals.

2.2.1. Assumption (1)

The polymerization reaction is initiated when the interaction between $Sens^{+\cdot}$ species and the monomer THF starts, which causes a decreasing of cation radical concentration $[Sens^{+\cdot}]$, given in $(mol\,L^{-1})$. This cation radical is produced by the interaction between Sens and light. More than this, the variables $[Sens^{+\cdot}]$ and $f_{conversion}$ are connect when the process begin. In other words, when the process of polymerization start both the $[Sens^{+\cdot}]$ and the $f_{conversion}$ determine the values of each other as showed in Eq. (8).

$$[Sens^{+\cdot}]_{t+1} = [Sens^{+\cdot}]_t f_{conversion} \times e^{(-t\rho)}, \tag{8}$$

where ρ is a positive parameter of adjust and the function $f_{conversion}$ (mol/l) is the function given by the proportion of conversion monomer–polymer.

The function $f_{conversion}$ has been modeled to give an asymptotic fit i.e., for high values of time the function has a smooth behavior. Obviously, this assumption is beyond of any intuition. The concentrations values for the chemicals involved in this process have fixes values; they are not increasing in time, which leads the conversion to a limit value (saturation). All equations were based in the behavior empirically expected for the $[Sens^{+\cdot}]$, $[S^+]$ and $[M]$ during the polymerization.

2.2.2. Assumption (2)

The salt concentration $[S^+]$ can be considered the main variable for the process of $Sens^{+\cdot}\cdot S^{\cdot}$ and production. Since this process begins the values of $[S^+]$ decreasing in the same rate of $[Sens^{+\cdot}]$. This supposition is represented by Eq. (9).

$$[S^+]_{t+1} = [S^+]_t e^{(-t\beta)}. \tag{9}$$

For the present system $[S^+]_t$ for $t=0$ is the initial concentration of salt.

2.2.3. Assumption (3)

We argue that the monomer concentration, THF $[M]$, decreases exponentially with the increase of $f_{conversion}$ and $[S^+]_t$. Thus the equation that determines the variation of the monomer concentration, (mol/L) we solved the Eq. (7) in a range of time t and $t+1$ resulting in Eq. (10).

$$[M]_{t+1} = [M]_t \exp(-f_{conversion} \times [S^+]_t \times \delta), \tag{10}$$

where δ is a parameter of adjust. Where $[M]_t$ is the value of monomer concentration when the process of polymerization is started. This assumption is strongly connected with the macroscopic interactions in the chemical environment of the system: when the function $f_{conversion}$ grows, the monomer and the salt are consumed. When the values of $f_{conversion}$ and $[S^+]_t$ are maximum the $[M]_t$ value achieve its minimum

value. The parameter d is resulted from the solution of Eq. (7) and its related with the initial values of salt concentration and $f_{conversion}$. The same occurs with t ρ and β parameters, they are resulted from solution of each differential ordinary equation that model the variation of species $[Sens^{+\cdot}]$ and $[S^+]$ respectively.

The final form proposed to determine the proportionality of conversion or, percentage of conversion, in time is given by the Eq. (11).

$$\frac{df_{conversion}}{dt} = ([Sens^{+\cdot}]_t + \alpha\Phi_m + [M]_t$$
$$+ f_{conversion})^{1/2} \times ([S^+]_t)^{1/2} \tag{11}$$

Notice that the units are given in $(mol\,L^{-1})$ this fact is observed by the multiplication between the terms $[Sens^{+\cdot}]_t + \alpha\Phi_m + [M] + f)^{1/2}$ and $([S^+]_t)^{1/2}$. This equation is the simplest form that we can assume to explain the proportionality of conversion. Mathematically, the direct sum of the terms $[Sens^{+\cdot}], \alpha\Phi_m[M]_t$, and f is the most basic construction for the Eq. (11). The multiplication by the term $[S^+]_t$ is a condition imposed: when salt concentration is zero $f_{conversion}$ has to be null. The constant α has dimension of mol-second per Einsteins and Φ_m is called quantum yield of polymerization that will be discuss in next sentence. The quantum yield incorporates the effects of the light intensity, as showed in Eq. (12).

The constant α can be interpreted as the number of mols that absorbs radiation in time. The form proposed for the Eq. (4) reveals an important characteristic of the macroscopic system: the salt concentration is the initiator of the entire process consequently its value is directly connected with the initial value of $f_{conversion}$. For $t=0$, $[S^+]_t=0$, as result the value of $f_{conversion}$ is null.

Under influence of the light, the efficiency of a system of polymerization can be described by the rate of initiation, represented by R_i, and by the rate of polymerization, R_p, which depends on the experimental conditions. This last one is related with the quantum yield of polymerization, Φ_m, which is defined as the number of monomer units polymerized per absorbed photon and mathematically represented in Eq. (13) [23]:

$$\Phi_m = \frac{R_p}{I_a}, \tag{12}$$

where I_a is the intensity of absorbed light in mols of light quanta (called Einsteins in photochemistry) per liter-second. As the notation of rate of polymerization, R_p, is mol per liter-second, the quantum yield of polymerization, Φ_m, is mol per Einsteins.

The main equation has a strong connection with the chemical ideas [5–7]: when more salt we have, more is the percentage of conversion. Therefore, the salt concentration is responsible to determine the conversion in time. Nevertheless, this dependency is limited by the monomers concentration and by the conversion in itself. The term

$([S^+]_t)^{1/2}$ promotes a smooth increase of the function $f_{conversion}$, more than this, he define the values of the conversion rate. In other words, the quantity of (mol/L) converted in polymer through time increment. For each value of time the equation give one value of conversion in mol/L.

All parameters determine the relations with the experimental values, where the percentage of conversion was calculated using:

$$\% = \frac{h}{Ff}[THF] \quad (mol/L) \tag{13}$$

where h is the contraction in volume in the capillary of the dilatometer (measured with a cathetometer) at time t; f is the volume fraction of monomer THF in the solution; F is the volume contraction related to the densities of polymer and monomer in solution and [THF] the monomer molar concentration.

These systems have a non-linear behavior, i.e., a small variation of any chemical variable is responsible to considerable differences in the final result. Moreover, the $\alpha\Phi_m$ value has an important contribution for the final result. It makes sense since that the numbers of monomer-units polymerized per light photon absorbed by the Sens defines the quantum yield of polymerization Φ_m, and α is an numerical adjust parameter denoted by the intensity of absorbed light per liter of solution.

3. Results and discussions

The results were obtained solving the equations numerically by Euler, first order, for different sensitizers. These data were plotted together with the experimental considering the variables in each axis: variation of both proportionality of conversion and THF concentration [M](y-axis) in time (x-axis), and variation of the cation radical concentration [Sens$^{+\cdot}$](y-axis) for different salt concentrations [S$^+$](x-axis). The equation has a strong dynamical feature; the values in Eqs. (8)–(11) are changed simultaneously when the time is increased. This kind of system is called coupling system. The main aspect of a coupling system is its numerical instability, generating the necessity of considerable attention when the computational procedure is executed.

In accordance with the Scheme 1 the cation radical Sens$^{+\cdot}$ appears of the interaction of Sens with S$^+$ and the increase of its concentration in time is the responsible for the increase of conversion monomer to polymer. This fact was used as basis to formulate of Eqs. (9)–(12). Therefore, it is expected from a chemical and mathematical view that: the increase of [Sens$^{+\cdot}$] is fundamentally connected with the increase of $f_{conversion}$, when more sensitizers are available in the system better are the interactions between monomer and salt, consequently, better is the conversion rate.
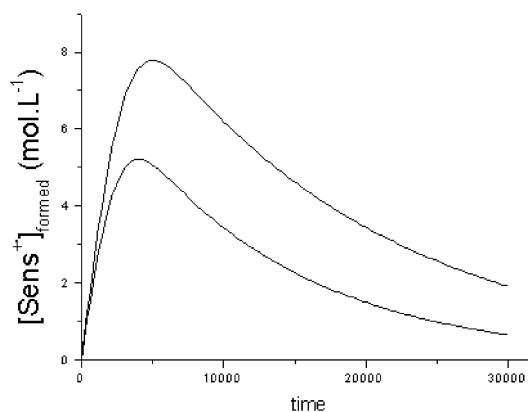

Fig. 1. Mathematical approach fit for concentration of cation radical (Sens$^{+\cdot}$) formed as a function of time and varying [S$^+$]: 1.0×10^{-4} and 3.0×10^{-4} mol L^{-1}, from bottom to top.

The Fig. 1 shows the behavior of [Sens$^{+\cdot}$] in time, exemplified for the Phe. In this figure is plotted the numerical results obtained from the theoretical solutions of Eq. (8)–(11). Notice that, for values of time bigger than $t\cong5000$ the [Sens$^{+\cdot}$] decreasing exponentially. This is in according with the chemical description of the Scheme 1. Another important fact, verifying Fig. 1, is the linear growing of [Sens$^{+\cdot}$] up to the time when the polymerization achieves its maximum value, as shown in Fig. 2 at $t\cong5000\ s$, correlated to the value $t\cong5000$ in Fig. 1 where the [Sens$^{+\cdot}$] is maximum.

The points calculated by Euler Method from Eq. (11) are plotted in Fig. 2 together with the experimental data for the proportionality of conversion of THF as a function of the time for two different concentrations of sulfonium salt S$^+$. The results show that the points calculated with the mathematical approach proposed, Eqs. (8)–(11) follow the same general trend as the measured values. The difference between the values for different sensitizers was generated, basically, by the distinct values of Φ_m.

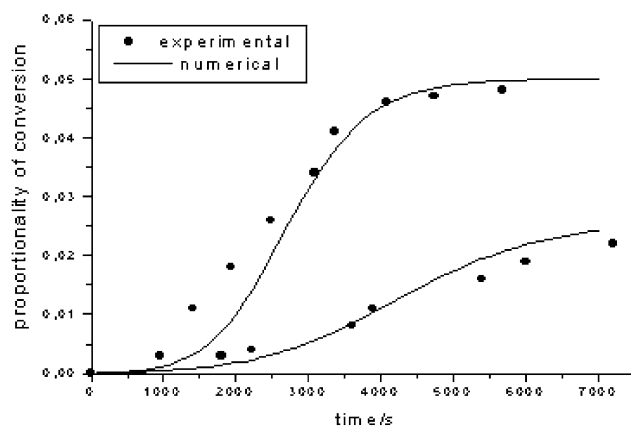The same numerical tests were improved for the Pery and

Fig. 2. Proportionality of conversion of the photopolymerization of THF in the presence of system Phe (7.0×10^{-4} mol L^{-1}) and [S$^+$]: 1.0×10^{-4} and 3.0×10^{-4} mol L^{-1}, from bottom to top. Experimental data is represented by the symbol ($\bullet$) and the numerical by the continuous line.
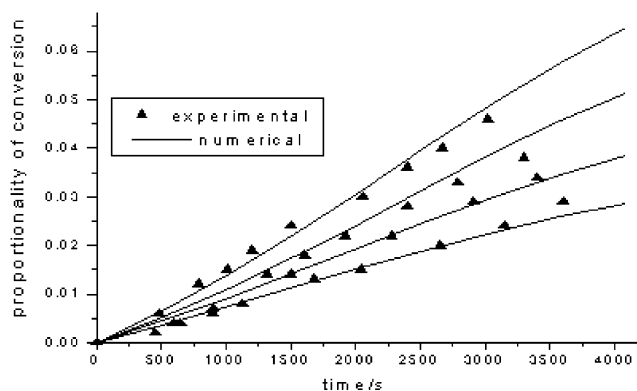
Fig. 3. Proportionality of conversion of the photopolymerization of THF in the presence of system Pery (2.0×10^{-4} mol L^{-1}) and [S$^+$]: 1.4×10^{-4}, 1.8×10^{-4}, 2.85×10^{-4}, and 4.0×10^{-4} mol L^{-1}, from bottom to top. Experimental data is represented by the symbol (▲) and mathematical approach by the continuous line.

Tx, similar graphs are gotten, Figs. 3 and 4, in total agreement with the assumptions formulated. More specifically, two distinct behaviors can be observed when these figures are compared. In Fig. 3 the proportionality of conversion has a linear increase. In Figs. 4 and 2 the experimental fit is S-type. Both cases, linear and S-type are completely described by the equations proposed and explained by the chemical process that lead to initiation of the polymerization [6,7]. The approach for each system considers the same initial condition despite the salt concentration.

As mentioned previously, in assumption 3, the monomer concentration THF is connected with the salt concentration and also of the concentration of Sens, as discussed before. In Fig. 5 is observed the decreasing of monomer concentration THF at the same time that the polymer is formed, around $t\cong5000$. This result obtained by the approach is in according with the chemical idea of the behavior for these systems.
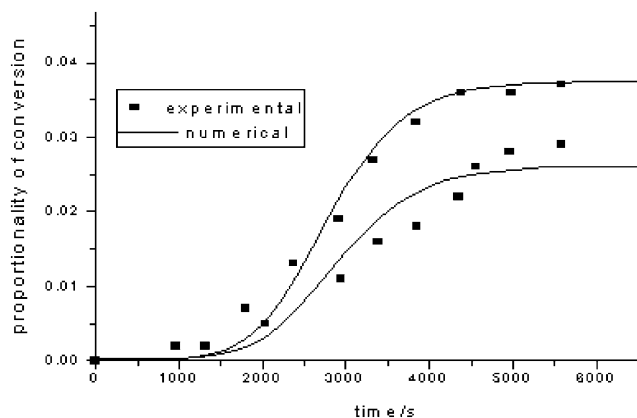

Fig. 4. Proportionality of conversion of the photopolymerization of THF in the presence of system TX (2.0×10^{-4} mol L^{-1}) and [S$^+$]: 9.0×10^{-4}, and 1.2×10^{-3} mol L^{-1}, from bottom to top. Experimental data is represented by the symbol (■) and the continuous line represents the theoretical results.
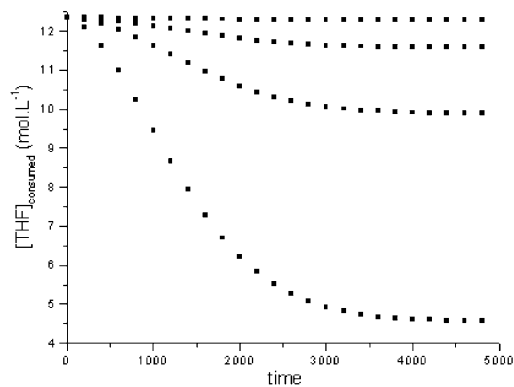

Fig. 5. THF concentration consumed as a function of time (both in arbitrary units) in the presence of the system Phe (7.0×10^{-4} mol L^{-1}) and S$^+$ ([S$^+$]=1.0×10^{-4}, 3.0×10^{-4}, 5.0×10^{-4} and 1.0×10^{-3} mol L^{-1}, from bottom to top).

The result show that when bigger is the value of [S$^+$] more monomer THF is used. The curve on bottom is resulted from a higher concentration of salt, 1.0×10^{-3} mol L^{-1} and obviously higher consume of the monomer. Nevertheless, when the time is increased the monomer concentration achieves a constant value. In spite of this fact, part of the monomer still remains in the solution without reacting. This fact is resulted from assumption 3 that consider the influence of the system environment in the monomer concentration through time variation.

4. Conclusions

The equations proposals to model the polymerization photoinitiated of the THF by systems of sensitizer-sulfonium salt showed fidelity when compared with the experimental results. Moreover, the results were extrapolated to different sensitizers with a good theoretical approximation. It was describe various aspects of these systems where the variables involved were modeled by equations time-dependent. In fact, the temporal variation of the proportionally of conversion, monomer and salt concentration, and consumption of Sens$^{+\cdot}$ and of THF were completely describe in this dynamical approach. The theoretical results show one pattern in this kind of system: the curves are substantially S-type, with different angular coefficients. The angular coefficients are connected with the initial values of the concentrations and the value of $\varPhi_m$. Only in the case of the polymerization of THF in presence of Pery with different salt concentration the curve is not a S-type. Nevertheless, the theoretical results for this case follow the same pattern of fit. Note that, this model is useful to represent curves with completely different patterns only by changing the initial values of the equations without change their form.

An important result is the different curves obtained for different concentration and systems. The adjust parameters α, ρ, δ and β received similar values because they are

resulted from initial values of concentrations for the salt, sensitizers, etc…. Most of curves presented a good adjust with the experimental data. A weak point to be pointed in this present work is the absence of an analytical solution for the set of equations, in other words, one function (unique) that describe the system. The main difficult was to compute the values of $[M]$, $[Sens^{+\cdot}]$ and $[S^{+}]$ simultaneously with the result given by the solution of the differential Eq. (11). The temporal relations associated with these chemical, assumptions (1), (2) and (3), that related clearly how the concentrations vary through the time. This is the focus of the present paper, understand the macroscopic behavior of the concentrations through the time variation and represent them theoretically. The consistence between the theoretical results and experimental data were an important contribution to understand the relations between the chemical in these kind of experimental environment in a macroscopic view.

Acknowledgements

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