

System Dynamics Applied to Analysis Modeling and Simulation of Chain Growth Polymerization Process.

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Abstract

The problem to be addressed is the dynamics of the chain growth polymerization process via free radicals. This process consists in a series of chemical reactions by which a macromolecule is formed by the addition of many structural units called mers. The reactions taking place are initiation, propagation and termination of the growing macromolecule or molecular chain.

The problem was focused under the General Theory of Systems and the methodology of System Dynamics. This work is an example of interdisciplinary interaction between Chemical Engineering and Systems Engineering through the System Dynamics methodology.

The modeling of polymerization processes is an up to date topic of both scientific and industrial practice importance. The developed model is based on the species balance equations and also on an isomorphism with population models.

The model is composed of a set of only sixteen, but very complex non-linear differential equations, whose solution is very restrictive with respect to the simulation time interval used, due to the great differences in order of magnitude of the characteristic time of occurrence of the various events taking place in the process. In this particular, the authors consider to have made a contribution to establish criteria to quantify what is called in the literature as the appropriate simulation time interval.

The proposed model is ahead of the traditional models of polymerization, in as much as the second ones predict only the behavior of the stable species and the chain length average, whereas the proposed model includes besides the dynamics of the unstable species. On the other hand, the proposed model excludes the pseudo-stationary assumption, on which the traditional models are based on, and which, according to our results, is not completely valid. As a general conclusion, the Dynamics System methodology appears to be an effective problem-solving tool in interdisciplinary environments.

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INTRODUCTION

This paper deals with the mathematical modeling and simulation of a chain growth polymerization process via free radicals, using the systemic approach and the system dynamics methodology.

Polymerization is a widely known process in the chemical industry. Kinetics and mathematical models to simulate the process have been known for decades (Flory 1953). The traditional models make use of an assumption called the pseudo stationary state (sss) condition, by which the mathematical difficulties vanish, and the solution of the model leads to results that predict fairly well laboratory data, but with the drawback of preventing the prediction of the dynamics of the unstable species present in the reaction mass, which in turn may be valuable to explain and control other phenomena of industrial importance, such as the so called autoacceleration of the process.

Since it is known that the system dynamics methodology is a powerful tool to model, simulate and analyse processes in interdisciplinary environments, it appeared worthwhile to model and simulate the referred process without any assumption. Some of the results are presented here. The qualitative validation of the proposed model was confronted against the traditional model. Experimental validation is under course and will be reported later.

System dynamics applied to the complete kinetics model, lead to the prediction of the dynamics of all of the variables in the process and also allowed to discuss the validity of the sss assumption.

This case may be another example of the synergism of system dynamics with other disciplines as chemical engineering to solve problems of interest. (Andrade and Gómez 1990)

THE PHENOMENON

A polymer is a molecular chain consisting of several structural units bound together by covalent bonds. The structural units, mers, are formed from small molecules of chemical compounds known as monomers. When these mers join together by a process similar to the threading of beads, polymers are formed. The average number of structural units forming the molecular chains is an important variable in determining the end use properties of the polymer material, and is called the degree of polymerization.

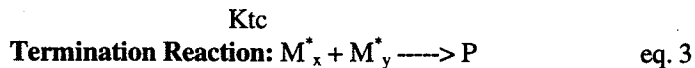
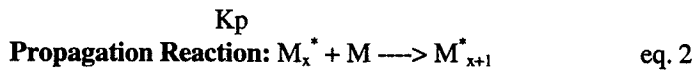
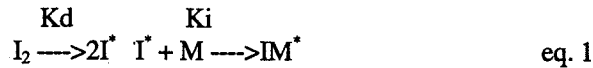
For certain type of monomers (styrene, ethylene, methyl methacrylate and many others), polymerization takes place in the presence of small amounts of compounds called initiators. The initiator continually decomposes and generates growth centers (free radicals in the case under study) in the reaction mass. This radical species is chemically very active and react rapidly with a monomer molecule forming a growing radical. These two reactions are called the initiation of the polymerization. (See equation 1). Thus there are two types of radicals in the reaction mass: primary radicals generated by the initiator molecules (I^*) and growing radicals (M^*) generated by the reaction between primary radicals and monomer molecules (M).

Polymerization occurs by a rapid sequential addition of monomer molecules to the growing centers. Growing chain radicals keep on adding monomer molecules sequentially through a reaction known as propagation. (See equation 2). It should be noticed that in the propagation reaction, the active center (free radical) appears again in the extreme of the growing polymeric chain.

Reaction between two growing radicals would make both species unreactive by destroying the active free radicals. This is known as the termination reaction. (See equation 3). (There are some other types of termination reactions not considered here). (Ramírez 1987).

The sequence of the reactions can be represented with the following equations:

Initiation Reaction:



Meaning of the symbols:

- I_2 : Initiator concentration.
- I^* : Primary radicals concentration.
- M : Monomer concentration.
- M_x^* : Concentration of growing radicals of x-mers.
- P : Polymer concentration.

There are thus five kinds of species in the reaction mass at any time.

Primary radicals and growing radicals are unstable species. It is known that their concentration is very low. The sss assumption establishes that their concentration is constant, thus their net rate of production (flow rate) would be zero.

Each of the reactions described is considered an elementary reaction, meaning that their rate equations can be deduced straightforward: the net rate of change of concentration of a particular species is equal to the rate of generation minus the rate of consumption of that particular species. Therefore:

Rate of initiator decomposition:

$$r_I(t) = d[I_2]/dt = (-2) \cdot f \cdot K_d \cdot [I_2] \quad \text{eq. 4}$$

f is the fraction of free radicals formed that effectively is available for the next reaction.

Net rate of change of primary radicals:

$$r_{I^*}(t) = d[I^*]/dt = 2 \cdot f \cdot K_d \cdot [I_2] - K_i \cdot [I^*] \cdot [M] \quad \text{eq. 5}$$

Net rate of change of growing radicals:

$$r_{M^*}(t) = d[M^*]/dt = K_i \cdot [I^*] \cdot [M] - 2 \cdot K_t \cdot [M^*] \cdot [M^*] \quad \text{eq. 6}$$

Polymerization reaction rate:

$$r_p(t) = d[M]/dt = -K_p \cdot [M^*] \cdot [M] - K_i \cdot [I^*] \cdot [M] \quad \text{eq. 7}$$

Termination reaction rate:

$$r_t(t) = d[P]/dt = K_t \cdot [M^*] \cdot [M^*] \quad \text{eq. 8}$$

The specific reaction rate (rate for unitary concentration of reactive species) is represented by the K values for each reaction. Values of these parameters are shown in Table 1 for the case of styrene as the monomer and AIBN as the initiator. These values are reported elsewhere (Brandrup and Immergut 1966). Notice that K values are temperature dependent.

Table 1. Specific reaction rates at two different temperatures for the case of styrene and AIBN.	
T=60°C	T=90°C
Kd=8,5*10 ⁻⁶ s ⁻¹	Kd=3,38*10 ⁻⁴ s ⁻¹
Kp=145 l/mol*s	Kp=361 l/mol*s
Kt=2,9*10 ⁷ l/mol*s	Kt=3,67*10 ⁷ l/mol*s

SYSTEM DYNAMICS MODELING

Elements of the model

The state variables (stock variables) are the concentration of the five species present in the reaction mass. The flow variables are the rate of the reactions taking place. The set of constants and parameters is conformed by the specific rate constants, the K values, and the f factor. The auxiliary variables are the instantaneous and the average degree of polymerization and the fraction of monomer consumed to form the polymer molecular chains:

Xi : Instantaneous degree of polymerization

Xa : Average degree of polymerization

Pc : Fraction of monomer consumption or monomer conversion.

Feedback diagram

Figure 1 shows the feedback loop diagram (Aracil 1992). It is interesting to note the interaction between a positive loop with two negative loops. That interaction and the difference in orders of magnitude of the specific reaction constants, characterize the dynamics of the process.

Forrester diagram

Figure 2 shows the Forrester or stock and flows diagram. Two additional flows are added, namely the prime initiator and the prime polymer flow, due to the fact that in the initiation reaction, one molecule decomposes

in two primary radical molecules, and in the termination reaction, two growing radicals form one polymer molecule.

Mathematical model

With the help of the feedback and Forrester diagrams, and considering that the concentration of a species at a given time is equal to the concentration of the same species in the preceeding time interval, plus the net change of concentration in that time interval, the mathematical model can be formulated:

$$\begin{aligned}
 I(t + \Delta t) &= I(t) + r_I(t) * \Delta t && \text{eq. 9} \\
 r_I(t) &= d[I_2]/dt = (-2) * f * K_d * [I_2] && \text{eq. 4} \\
 I^*(t + \Delta t) &= I^*(t) + r_{I^*}(t) * \Delta t && \text{eq. 10} \\
 r_{I^*}(t) &= d[I^*]/dt = 2 * f * K_d * [I_2] - K_i * [I^*] * [M] && \text{eq. 5} \\
 M(t + \Delta t) &= M(t) + r_p(t) * \Delta t && \text{eq. 11} \\
 r_p(t) &= d[M]/dt = - K_p * [M^*] * [M] - K_i * [I^*] * [M] && \text{eq. 7} \\
 M^*(t + \Delta t) &= M^*(t) + r_{M^*}(t) * \Delta t && \text{eq. 12} \\
 r_{M^*}(t) &= d[M^*]/dt = K_i * [I^*] * [M] - 2 * K_t * [M^*] * [M^*] && \text{eq. 6} \\
 P(t + \Delta t) &= P(t) + r_t(t) * \Delta t && \text{eq. 13} \\
 r_t(t) &= d[P]/dt = K_t * [M^*] * [M^*] && \text{eq. 8} \\
 X_i &= (K_i * [I^*] * [M] + K_p * [M^*] * [M]) / (K_t * [M^*] * [M^*]) && \text{eq. 14} \\
 X_a &= ([M(t=0)] - [M(t)]) / [P(t)] && \text{eq. 15} \\
 P_c &= ([M(t=0)] - [M(t)]) / [M(t=0)] && \text{eq. 16}
 \end{aligned}$$

SIMULATION

The proposed model was simulated using a home made software called EVOLUTION, for two state conditions, differing in temperature, which is reflected in the different values of the K parameters.(See Table 2).

Table 2. State conditions used to simulate the polymerization process.	
T=60°C	T=90°C
M=8,64 mol/l	M=8,64 mol/l
I ₂ =0,01 mol/l	I ₂ =0,01 mol/l
K _d =8,5*10 ⁻⁶ s ⁻¹	K _d =3,38*10 ⁻⁴ s ⁻¹
K _p =145 l/mol*s	K _p =361 l/mol*s
K _t =2,9*10 ⁷ l/mol*s	K _t =3,67*10 ⁷ l/mol*s

It is important to notice that the specific propagation reaction rate,(Kp), for the case of 60°C, is around six orders of magnitud higher than the specific initiator decomposition reaction rate (Kd), and five orders of magnitud lower than the specific termination reaction rate (Kt). Such big differences in the order of magnitud of the different reactions taking place simultaneously in the polymerization process, makes very crucial the choosing of the simulation time interval. It is usually stated that for simulation purposes, a convenient time interval should be choosen. It happened that for state conditios at 60°C, the appropriate time interval could not be higher than 7.9*10⁻⁵ second, for the program to run. In searching for that value, it was necessary to make clear a criterion to estimate the "convenient" simulation time interval. That is, that the simulation time interval should be less or equal to the characteristic time of the

most rapid event in the process, which in turns is related with the expected life time of the species taking place in that event. In analogy with the population models, that life time was calculated as the concentration of the species divided by its rate of disappearance. For the case under study, the shortest life time corresponds to the growing radical and is in the order of $8 \cdot 10^{-5}$ second.

It is also important to notice that temperature affects differently to each one of the specific rate constants and as a consequence, the dynamics of the process may be completely changed. That was the case presented here. At 90°C the most drastic change occurs in the value of K_d (two orders of magnitude according with Table 2). As a consequence, the shortest life time is not any more the growing radical, but the primary radical with a value of $3.2 \cdot 10^{-4}$ second.

RESULTS

Figure 3 and Figure 4 show the predicted dynamics of the concentration of initiator (a), primary radical (b) monomer (c), growing radical (d), polymer (e). Also it is shown the dynamics of the instantaneous degree of polymerization (f) and the average degree of polymerization (g). There is a general qualitative and quantitative agreement with results predicted by the traditional model with respects to the dynamics of the concentration of monomer, initiator, polymer and also on the degree of polymerization.

However, two observations should be made: first, the dynamics of the two types of radicals is predicted with the proposed model, and could not be predicted with the traditional model. Second, the concentration of unstable species is not constant as it is assumed by applying the sss condition.

Comparing Figures 3 and 4, it is clear the quantitative effect of a temperature change in the polymerization system. At higher temperature the depletion of initiator and of monomer is much faster due to the higher rate of production of primary radicals. The striking difference occurs with the dynamics of the degree of polymerization: decreases with reaction time at 60°C whereas increases at 90°C .

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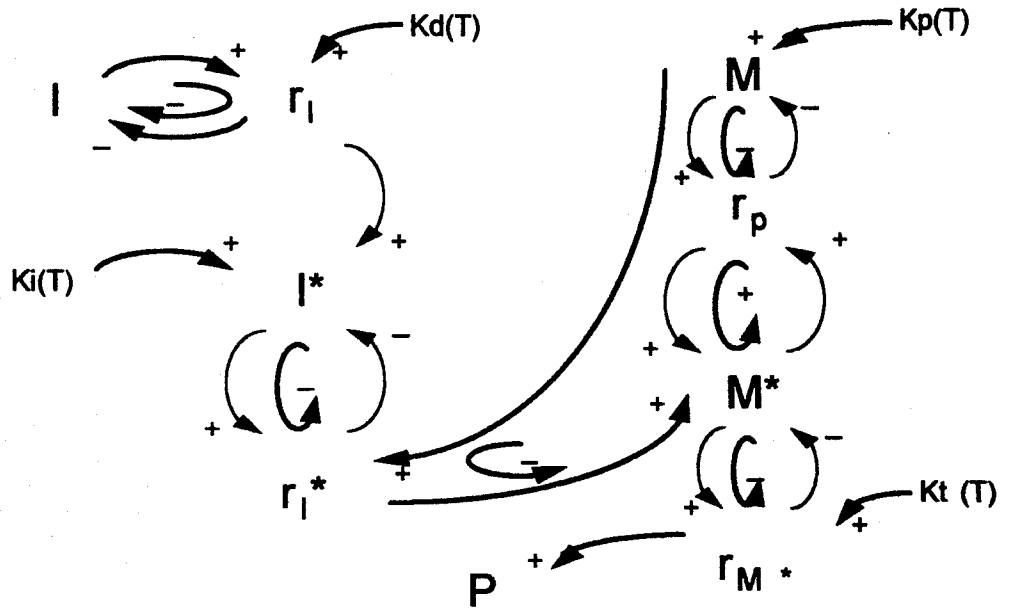


Figure 1. Feedback Diagram

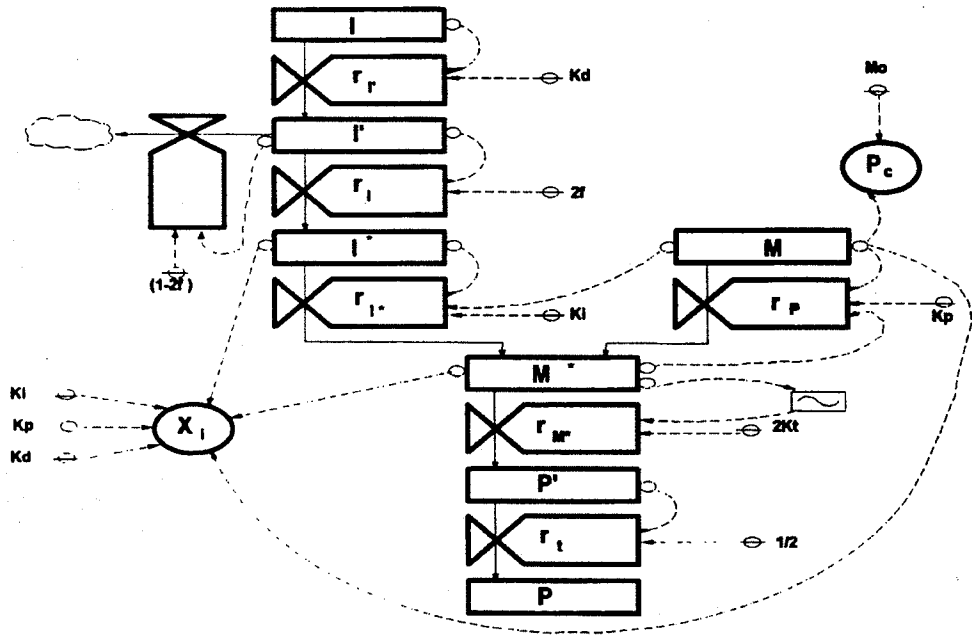


Figure 2. Forrester Diagram

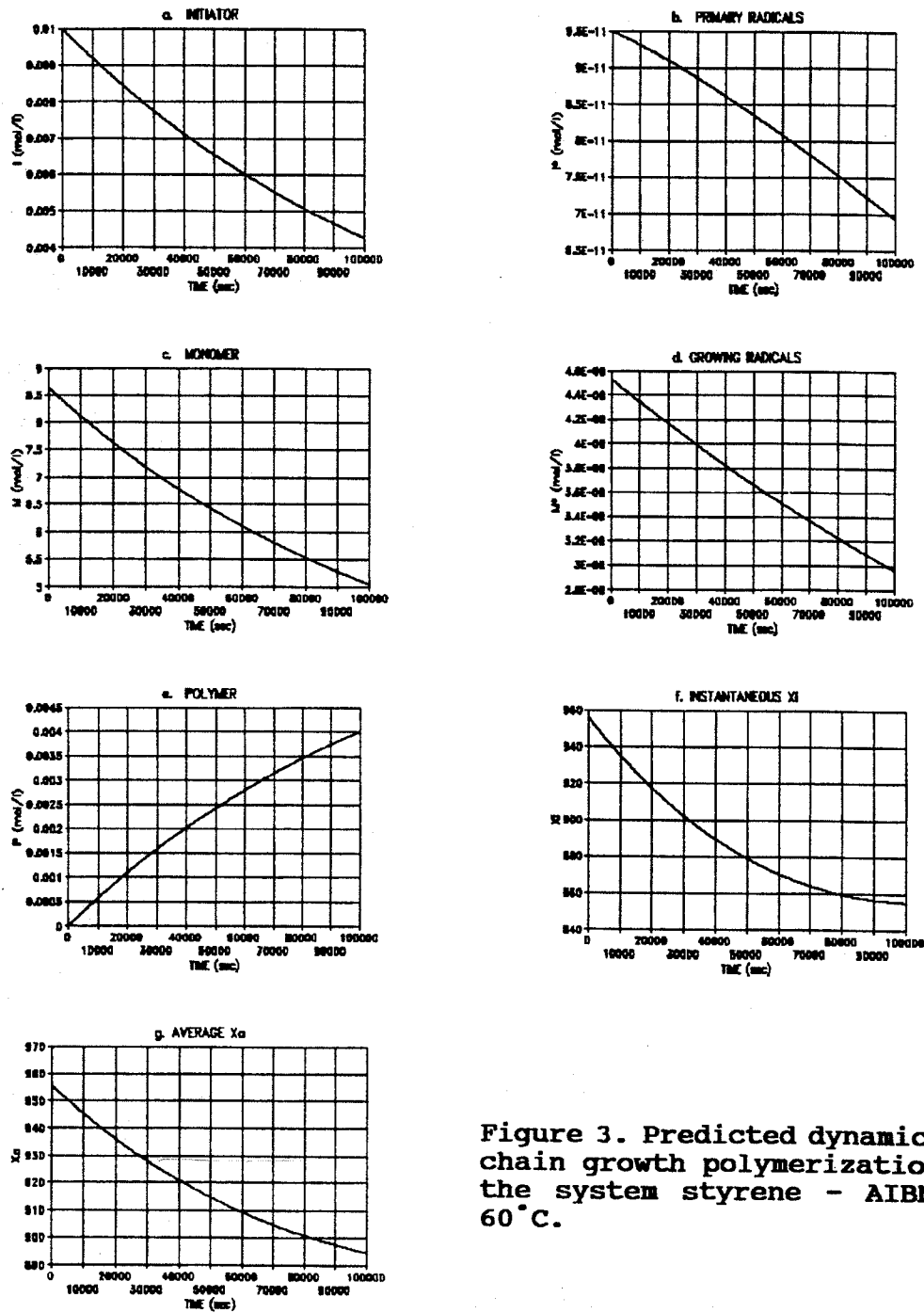


Figure 3. Predicted dynamics of chain growth polymerization of the system styrene - AIBN at 60°C.

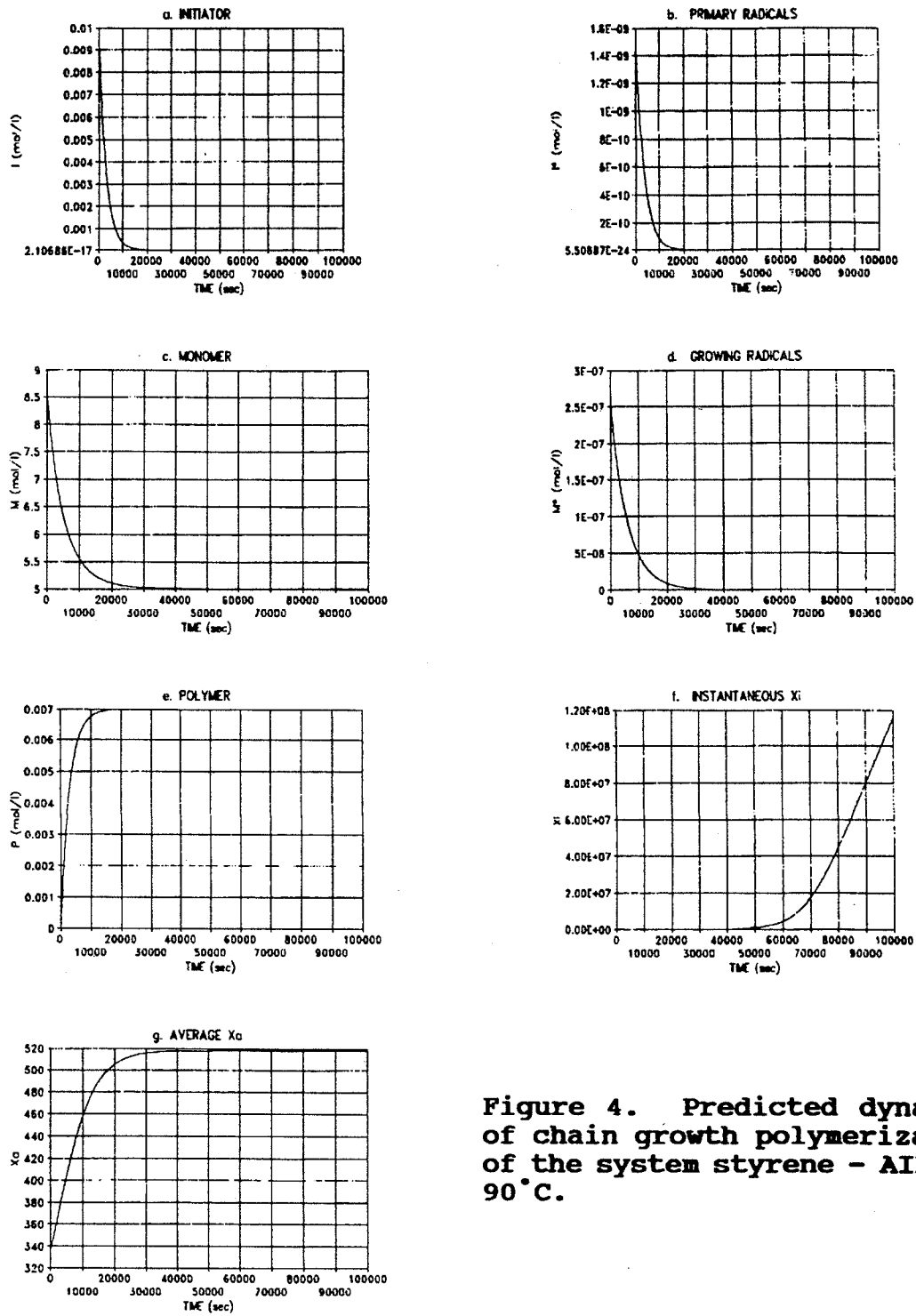


Figure 4. Predicted dynamics of chain growth polymerization of the system styrene - AIBN at 90°C.

