

RE-BUILDING KNOWLEDGE BY ASSUMPTION OF COMPLEXITY WITH SYSTEM DYNAMICS. A CASE EXAMPLE IN POLYMERIZATION PROCESS ENGINEERING.

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Introduction

This paper is a continuation of one presented in the 1994 International Conference on System Dynamics [1]. That was an opportunity to discuss about the industrial importance of chain polymerization process; to present a model of the reactions taking place and the dynamics of molecular species calculated by a corresponding mathematical model using SD methodology. This paper presents a more complete model of the reactions occurring in the process, the corresponding mathematical model and a comparison of results: those calculated with a traditional, non SD approach, ours using SD and those gathered experimentally[2].

In performing this research work, it has been found fruitful to reflect on two concepts: **rebuilding of knowledge** and, **model construction and simulation step by step in increasing complexity**, both using Systemic Thinking, ST, and in particular SD.

Rebuilding knowledge stands for a process of doing again the construction of concepts and models, making clear consciousness about how were constructed before and, from that experience and the same interpretation context, to propose new ways, new points of view, new set of conditions, by taking advantage of ST, SD and now available relative powerful computer machines and software, with the aim of getting a better understanding and prediction of the phenomenon under consideration.

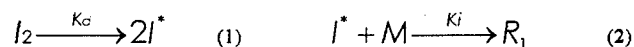
Model construction and simulation step by step in increasing complexity stands for the process of proposing a series of models beginning from simplified ones and removing simplifications step by step, keeping track of changes in simulation difficulties in face of model improvement in degree of correspondence with the phenomena under consideration and, in prediction of experimental results. Each model describes a more complete dynamics; the new contains the old; the cost may be higher mathematical difficulties, the revenue may be a better model. Complexity is a result of considering realistic models.

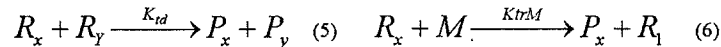
SD appears to be a very convenient tool to perform those processes referred before, inasmuch as since the very beginning, SD provides a systemic, integral approach, appropriate to a dynamic phenomenon, and also because SD has a "natural" flexibility for adding or taking away model components to vary the completeness of pre-existing models.

Traditional Model

Chain polymerization process has been simulated by decades [3] making use of different mathematical tools but always based on a basic and so called **quasi-steady-state assumption**:

Model of reactions





The initiator I_2 is decomposed into two active primary radicals I^* , a fraction of which reacts with monomer, M , to form a growing radical R . A molecular chain is formed because a growing radical reacts and adds each time a new monomer molecule. In general a growing radical of x -mers (x units of monomer joint by chemical bounds), reacts with a monomer molecule to give a growing radical of $x+1$ mers.

The growing reaction is stopped if the growing radical loses its free radicals. This event can occur by way of several reactions: combination, when two growing chains react to form a new polymer chain with coupled radicals. Disproportionation, when a growing radical receives one free radical of another growing chain given place to two different polymer chains, one with a more stable double bound. Transfer reaction, when a growing chain transfers its free radical to any other species present in the reaction system such as monomer, polymer, solvent and so on.

Mathematical model

$$\frac{dI_2(t)}{dt} = -K_d \times I_2(t) \quad (7)$$

$$\frac{dM(t)}{dt} = -K_p \times M(t) \times R(t) \quad (8)$$

$$\frac{dR(t)}{dt} = -K_{tc} \times [R(t)]^2 - K_{td} \times [R(t)]^2 \quad (9)$$

$$R(t) = \sqrt{\frac{2 \times f \times K_d \times I_2(t)}{K_{tc} + K_{td}}} \quad (10)$$

$$\frac{dM(t)}{dt} = -(K_p) \times \sqrt{\frac{2 \times f \times K_d \times I_2(t)}{K_{tc} + K_{td}}} \times M(t) \quad (11)$$

The first two reaction (equations 1 and 2) are regarded as initiation. The kinetics of initiation is taking to be equation 7. Notice that the second reaction (equation 2) is not considered to affect the kinetics of the initiation. The reason is that these two reactions occur in series and the velocity of series is that of the slower event, which happens to be the decomposition of initiator.

The kinetics of the polymerization reaction is considered to be equation 8. Notice that in this equation, monomer spent in the formation of growing radical is not considered (equation 2).

The kinetic of the different termination reactions is represented by equation 9.

In order to solve this complex equation system, a quasi-steady-state assumption is formulated: initiation rate is equal to termination rate, which implies that the dynamics of the concentration of R becomes stable: $dR/dt=0$; then R is calculated by equation 10.

Observe that equation 10 predicts a non constant R since initiator concentration changes by consumption. That prediction is in contradiction with the quasi-steady-state assumption. In the case of non isothermal process, R also may change significantly due to the effect of temperature on specific rate K_d , K_{tc} , and K_{td} .

The importance of this assumption is that allow to re-write the polymerization reaction rate in terms of initially known and measurable conditions (equation 11).

Re-building the model

Considering the same model of reactions, the authors of this paper have proposed a model based on SD methodology in which all reactions are considered and the quasi-steady-state assumption is removed:

$$\frac{dNI_2(t)}{dt} = -K_d \times NI_2(t) \quad (12)$$

$$\frac{dNI^*(t)}{dt} = 2 \times f \times K_d \times NI_2(t) - K_i \times \frac{NI(t) \times NM(t)}{V(t)} \quad (13)$$

$$\frac{dNM(t)}{dt} = -K_i \times \frac{NI^*(t) \times NM(t)}{V(t)} - K_p \times \frac{NM(t) \times NR(t)}{V(t)} - K_{trM} \times \frac{NM(t) \times NR(t)}{V(t)} \quad (14)$$

$$\frac{dNR(t)}{dt} = -K_i \times \frac{NI^*(t) \times NM(t)}{V(t)} - (K_{tc} + K_{td}) \frac{NR(t)^2}{V(t)} \quad (15)$$

$$\frac{dNP(t)}{dt} = \frac{1}{2} \times K_{tc} \times \frac{NR(t)^2}{V(t)} + K_{td} \times \frac{NR(t)^2}{V(t)} + K_{trM} \times \frac{NM(t) \times NR(t)}{V(t)} + K_{trX} \times \frac{NX(t) \times NR(t)}{V(t)} \quad (16)$$

(In this set of equations, the letter N before the species, indicates "number of moles". Letter V indicates reaction volume).

Values of specific reaction K_d , K_p , K_{tc} , K_{trM} and K_{td} are reported in the literature. No value for K_i is reported since this equation is not considered in the traditional model. However, it may be considered that K_i should be of the same order of K_p , since in both cases a radical reacts with a monomer molecule.

Trying to solve this mathematical model, it was found that a very low time step integration was required, in the order of 10^{-4} seconds. This difficulty did not appear when solving the traditional model. The reason is that the time step integration should be lower than the characteristic time of the slowest event. Using isomorphism with population dynamics, the characteristic time of a species can be calculated as its concentration divided by the rate of consumption. It was found that primary radical has the lowest characteristic time, which varies as is shown in figure 1. In order to get a relative convenient time of computer machine, the software was adjusted to calculate the characteristic time for each iteration and to use this value as the corresponding time step of integration.

Results

Figure 2 and 3 shows the results of the dynamic of monomer consumption and number average molecular weight. Comparison can be made of experimental results with the predicted values using

the traditional model and ours. Notice that both models make a good prediction of monomer consumption. However, our model makes a better prediction of the dynamics of number average molecular weight.

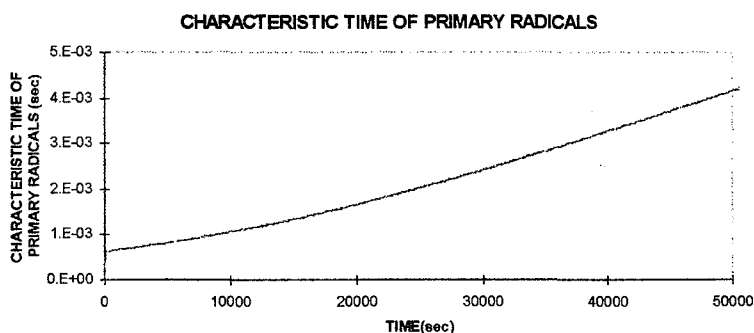


Figure 1. Characteristic Time of Primary Radicals.

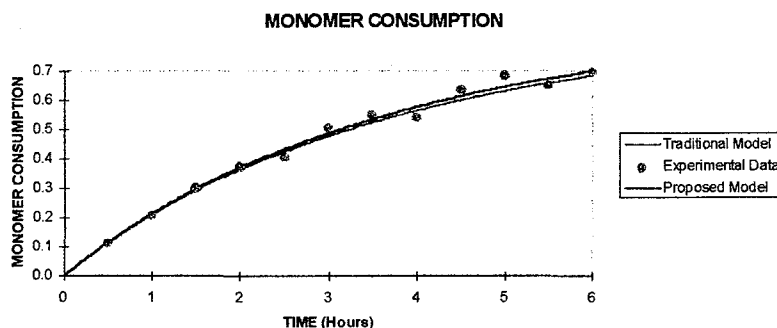


Figure 2. Monomer Consumption.

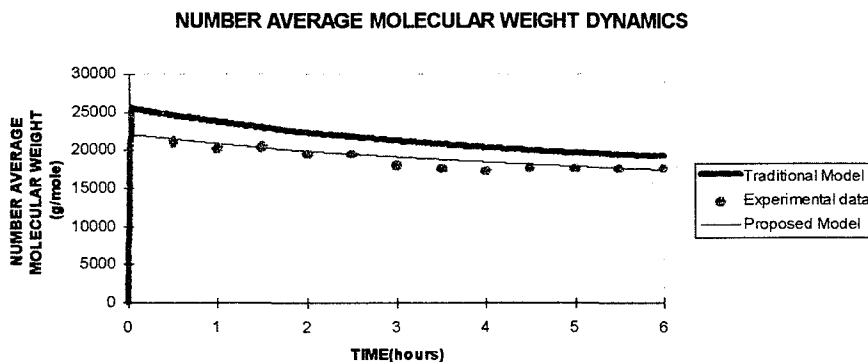


Figure 3. Number Average Molecular Weight Dynamics..

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