Computer modelling of radiation-induced in-source solid state polymerizations

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An algorithmic model of polymerization at the source of radiation is described. The macromolecules are simulated by means of random walks generated by the Monte Carlo method. It was found that the model results agree well with the experimental data as well as with the mathematical description of the model.

INTRODUCTION

Radiation polymerization of a monomer sample in the solid state, placed in a radiation source is a highly complex phenomenon. It is the result of numerous sometimes competing, processes. To observe each of these processes separately and to determine its influence on the final polymerization effect is difficult.

These obstacles may be overcome by using the technique of algorithmic modelling. The algorithm we have derived is based on methods of constructing random walks in spacial lattices both known from the literature[1,2] as well as our original ones, used in the modelling of polymer chains. The modelling algorithm embraces several steps in the polymerization process, e.g. initiation, chain growth and chain termination by deactivation or trapping within the polymer mass. It should be stressed, however, that the model can be complicated by introducing additional assumptions, but this has not been the aim of the present paper.

Using a computational model it is possible to observe the influence of some initial parameters on the final polymerization effect and also to check the course of the process during the experiment.

DESCRIPTION OF THE METHOD

The computation process studied has a pseudostochastic character due to the use of a pseudorandom number generator with a uniform distribution in the finite interval. All points with integer values for their coordinates and which belong to a cubic unit of space measuring 60 by 60 by 60 units represent a single monomer crystal. It is assumed that one monomer molecule is located at every point of this kind. Any of these molecules may become the origin of a polymer chain if it is excited by an appropriately high energy radiation quantum. The radiaiton process is modelled by a random choice of lattice points throughout the process of polymerization. The relative frequency of choices is regarded as a magnitude equivalent to the radiation dose power, I. Any of the chosen active molecules may adjoin neighbouring ones, thus forming a polymer chain. The direction of chain growth is also determined by a pseudorandom choice, taking into consideration the prohibition of mutual intersection of chains (i.e. double occupation of the same point of lattice). The termination of chain growth may be caused either by deactivation of a macroradical, occurring with a definite probability K_t, or by the active end becoming trapped in the polymer mass.

The algorithm contains time as a parameter; this makes it possible to formulate kinetic dependences. The conventional time unit is terminated at the moment of having made one attempt at addition of a subsequent link to every growing chain. The conversion of a monomer into polymer is expressed by the ratio of a sum of length of all random walks to the number of points in the cube. The process continues until the conversion ratio approaches 0.5.

It should also be stressed that in the algorithm under discussion, the lengthening of any random walk by one link requires a check-up whether or not the new point is one of some hundred thousand points already occupied by the polymer. If we take into consideration that several hundred chains are growing simultaneously, then the impracticability of generating unlimited random walks becomes obvious[2]. We have applied a highly effective method of coding[5], which enabled us to build up a programme, whose working period is 10–20 min on a fast digital computer. The capacity of the FORTRAN program is 20–40 thousand words.

DISCUSSION

The properties of the algorithm under discussion have been investigated at four sets of initial data corresponding to various powers of radiation dose at a fixed constant period of chain termination. After the lapse of equal time periods the values of conversion, number of growing macroradicals and total number of all chains contained in the sample at the given moment of the process were derived using the computer. *Figure 1* shows the dependence of conversion on time at the following dose powers: 0.01, 0.02, 0.03 and 0.04; the value of the rate constant of the chain-terminating reaction is equal to 0.0001. All values of rate constants for the reaction are determined by the choice of time unit which is quite arbitrary. *Figure 2* shows the dependence of the total number of all chains (upper curves) and the number of active chains (lower curves) on time. The flat areas
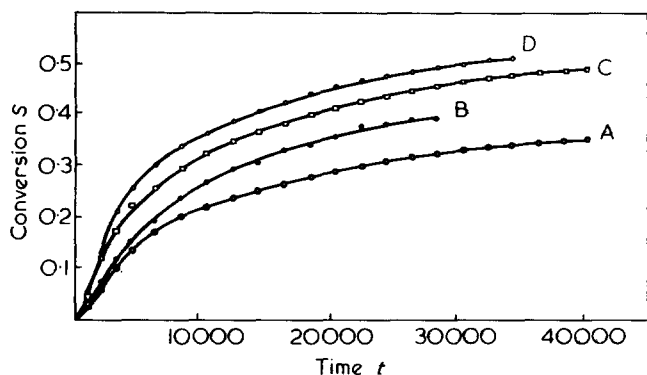
Figure 1 Dependence of conversion (S) on time. Dose power I = 0.01 (A); 0.02 (B); 0.03 (C) and 0.04 (D)

of the lower curves correspond to approximately stationary conditions. As is seen in the Figure, the stationary state is reached after a comparatively long period of polymerization which corresponds to the conversion of 0.2–0.4 order. Hence the process cannot be investigated if an assumption of a stationary state is made as a basis of the studies[4].

A rigorous description of the kinetics of the modelled process is given by the set of equations:

$$\frac{dR}{dt} = I(1 - S) - K_t R$$

$$\frac{dS}{dt} = K(1 - S)R \tag{1}$$

where S is the conversion of monomer into polymer, R is the number of active chains in the modelled system, K is the propagation constant of the polymer chains, and t is time. Applying boundary conditions:

$$R_{t=0} = 0$$

$$S_{t=0} = 0 \tag{2}$$

a set equivalent to equations (1) is obtained:

$$u' = -u + v$$

$$v' = -u \cdot v$$

$$u(0) = 0 \tag{3}$$

$$v(0) = \alpha$$

where

$$\alpha = \frac{I \cdot K}{K_t^2}$$

The equivalence of these two sets follows from equations (4):

$$R(t) = \frac{K_t}{K} u(K_t \cdot t)$$

$$y(t) = \frac{K_t^2}{I \cdot K} v(K_t \cdot t) \tag{4}$$

where $y = 1 - S$.

By substitution of equation (5):

$$w(t) = \ln[v(t)] \qquad t > 0$$

$$w(0) = \ln \alpha = \beta \tag{5}$$

We obtain equation (6):

$$u' = -u + e^w$$

$$w' = -u \tag{6}$$

Consequently, set (1) is reduced to equation (7):

$$w'' + w' + e^w = 0 \tag{7}$$

with boundary conditions (8):

$$w(0) = \beta$$

$$w'(0) = 0 \tag{8}$$

A strict analytical solution of an equation of this type consists in finding the limit at $i \to \infty$ of the sequence of solutions of equation (9) which, for a general case, is not possible:

$$w_i'' + w_i' + \left(1 + \frac{w_i}{i}\right)^i = 0; \qquad i = 1,2,\ldots \tag{9}$$

Consequently, any deviation from the stationary state theory, even for a description of kinetics of a simple model of polymerization leads to a set of non-linear differential equations, the analytical solution of which encounters serious difficulties. On the other hand, the curves obtained as a result of computational experiment with the application of the modelling algorithm described above, satisfies the set of equations (1) in its difference form. This is a consequence of the modelling algorithm having been derived on the basis of a definite physical model of a real process of polymerization. Hence, the curves in *Figure 1* are the solutions of the set of equations (1). It follows that algorithms of the type discussed here can also be regarded as a method of stochastic integration of sets of highly complicated kinetic equations.
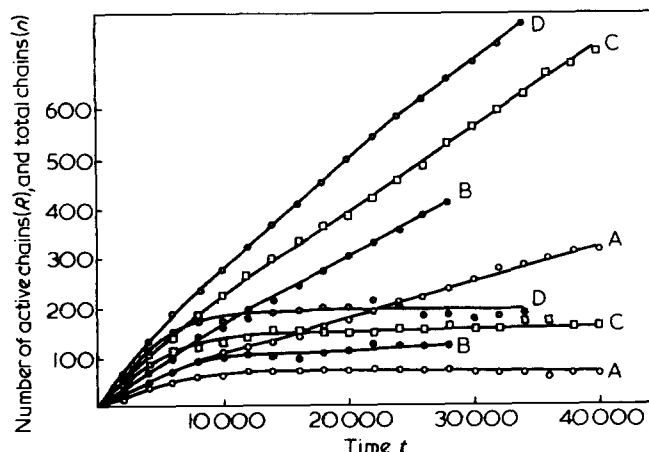

Figure 2 Dependence of the number of active chains (R) (bottom curves) and total number of all chains (n) (upper curves) on time. Dose power I as in *Figure 1*
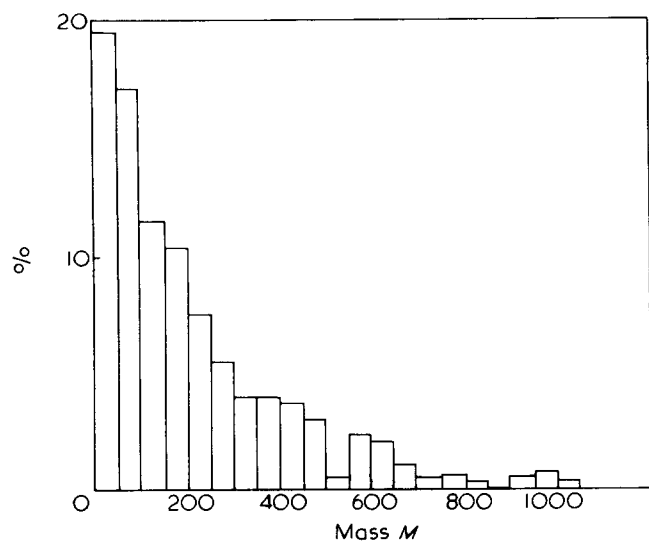
Figure 3 Distribution of polymer masses (*M*)

The method of algorithmic modelling has enabled us to investigate parameters, the determination of which, in the case of a real chemical experiment, may be extraordinarily difficult, e.g. the distribution of polymer masses. An experimental determination of real mass distribution, strictly corresponding to the final moment of polymerizing a solid sample in the radiation source, has not yet been practically feasible. The mass distribution calculated for the process modelled is shown in *Figure 3*, using the initial assumptions indicated above.

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