

## Modelling of Polymerization Reactions

### 2. Computer Simulation of Iodine Initiated Polymerization of Styrene

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#### Summary

The paper reports the development of a mathematical model which has been applied to the polymerization of styrene initiated by iodine in ethylene dichloride solution. Our previous work on the system concluded for a pseudocationic mechanism based on the admission of non-ionic propagating species.

The computer analysis performed using the mathematical model allowed us to derive theoretical conversion- and conductivity-time curves which perfectly reproduce the experimental shapes under different conditions. The agreement between the theoretical and experimental results demonstrates that the reaction mechanism previously formulated and the mathematical treatment proposed are correct.

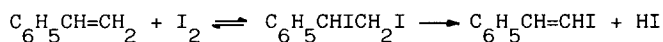
#### Introduction

During the last fifteen years our group investigated thoroughly the polymerization of vinyl monomers initiated by iodine in chlorinated solvents.

In different papers the mechanistic aspects of styrene (GIUSTI 1966; GIUSTI ANDRUZZI 1966), acenaphthylene (GIUSTI et al. 1966; CERRAI et al. 1968), anethole (ANDRUZZI et al. 1970a; ANDRUZZI et al. 1970b), isobutyl- and cyclohexyl-vinylether (CERRAI et al. 1974) were discussed on the basis of kinetic experiments both in the absence and in the presence of d.c. electric fields. Following the kinetics of polymerization and the electrical conductivity of the solutions under different experimental conditions by an high vacuum technique, it was possible to conclude that the prevailing nature of these polymerizations is "pseudocationic", i.e. the chain carriers are non-ionic species formed by interaction between monomer and iodine.

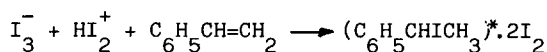
The general mechanism may be so summarized:

- monomer (i.e. styrene) reacts with iodine giving the corresponding diiodide, which in turn generates hydrogen iodide:



- hydrogen iodide through an equilibrium reaction with free iodine gives  $\text{I}_3^-$  and  $\text{HI}_2^+$ ,
- the latter species add onto monomer to give the non-ionic propagating

species activated by coordination with free iodine:



The application of d.c. electric fields together with experiments carried out with added  $I_3^-$  as ionic counterion (GUERRA et al.1973) permitted to distinguish between the different monomers studied, so to conclude that at least in anethole and vinyl ethers polymerization "ionic" chain carriers must also be present. The above mentioned work has been clearly and thoroughly resumed in two very recent reviews (GANDINI, CHERADAME 1980; KENNEDY, MARECHAL 1982), where it is discussed also by comparison with the work of other Authors (PARNELL 1969; LEDWITH, SHERRINGTON 1971; JANJUA 1973).

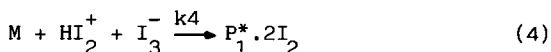
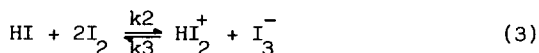
In order to confirm the validity of the reaction mechanism and of the kinetic models evaluated for the systems so far studied, the aim of this paper and the followings in the series is the development of mathematical models which permit to reproduce the experimental results. In particular this paper wish to report a mathematical model especially derived for the iodine initiated polymerization of styrene in ethylene dichloride solution so to obtain through a computer analysis the theoretical conversion- and conductivity-time curves for different initial iodine and monomer concentrations. A similar procedure has been recently applied by us to a different system in the first paper of this series (MASCHIO et al., in press).

#### Model development

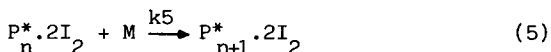
The iodine initiated polymerization of styrene is characterized by S-shaped conversion-time curves with an acceleration period decreasing with an increase in initial iodine concentration. The conductivity-time curves show three different stages in each run: a) an initial increase of conductivity corresponding to the acceleration period; b) a second period during which the conductivity remains fairly constant; c) a final conductivity increase which starts at the end of the polymerization when the residual monomer concentration is very low.

On the basis of these experimental findings the reaction mechanism proposed for the polymerization of styrene initiated by iodine is the following:

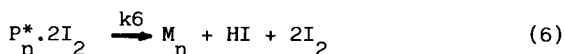
- initiation:



- propagation:



- chain breaking:



where M is the styrene,  $MI_2$  is the styrene diiodide,  $P_n^*$  is the growing polymer chain and  $M_n$  is the dead polymer chain. Assuming very fast the diiodide formation from iodine and monomer (1), from the whole mechanism the material balance for each component can be written as follows:

$$[MI_2] = K[I_2][M] \quad (7)$$

$$d[I_2]/dt = 2(k_6[P_n^*] - k_2[HI][I_2]^2 + k_3[HI_2^+][I_3^-]) \quad (8)$$

$$d[HI]/dt = k_1[MI_2] + k_6[P_n^*] - k_2[HI][I_2]^2 + k_3[HI_2^+][I_3^-] \quad (9)$$

$$d[M]/dt = -(k_4[HI_2^+][I_3^-] + k_5[P_n^*])[M] \quad (10)$$

$$d[HI_2^+]/dt = d[I_3^-]/dt = k_2[HI][I_2]^2 - k_4[M][HI_2^+][I_3^-] - k_3[HI_2^+][I_3^-] \quad (11)$$

$$d[P_n^*]/dt = k_4[M][HI_2^+][I_3^-] - k_6[P_n^*] \quad (12)$$

$$d[M_n]/dt = k_6[P_n^*] \quad (13)$$

This set of ordinary differential equations constitutes the mathematical model used for the simulation of the polymerization system studied. By solving the set of equations under different initial conditions is possible to obtain the concentration-time course of each chemical species of the polymerizing system. From the data obtained is then possible to derive the plots of the conversion and the conductivity vs. time.

For the conversion-time curve it was used the obvious relationship:

$$C = [M]_0(1 - [M]/[M]_0) = [M]_0 - [M] \quad (14)$$

For the conductivity-time curve it was applied the following equation:

$$\lambda = a[I_2] + b([HI_2^+] + [I_3^-]) - c([HI_2^+] + [I_3^-])^2 + d/[M] + e \quad (15)$$

The a, b, c and e numerical coefficients have been determined by a numerical regression analysis from the conductometric data previously obtained (GIUSTI 1966) in experiments with different initial iodine concentration. The term  $d/[M]$  has been introduced in order to account for the increase of conductivity with the decrease of monomer concentration at the end of the polymerization.

The values of kinetic constants have been especially chosen on the basis both of our experimental data and of corresponding values obtained by other Authors for similar systems.

The numerical values of coefficients and kinetic constants used in applying the mathematical model have been:

$$a = 12.0 \quad b = 80.0 \quad c = 800$$

$$d = 0.1 \quad e = 0.1$$

$$k_1 = 0.7 \text{ min}^{-1}$$

$$k_3 = 0.1 \text{ l.mole}^{-1}.\text{min}^{-1}$$

$$k_5 = 10.0 \text{ l.mole}^{-1}.\text{min}^{-1}$$

$$K = 0.5$$

$$k_2 = 4.0 \text{ l}^2.\text{mole}^{-2}.\text{min}^{-1}$$

$$k_4 = 0.6 \text{ l}^2.\text{mole}^{-2}.\text{min}^{-1}$$

$$k_6 = 0.1 \text{ min}^{-1}$$

### Results and discussion

Several simulation runs have been carried out with different initial concentration conditions. Conversion- and conductivity-time curves obtained through the proposed mathematical model have been compared with the experimental curves, as shown in Fig. 1, 2 and 3.

The almost perfect agreement between the theoretical and experimental curve suggests that the reaction mechanism proposed and the mathematical model derived are quite correct.

In particular the theoretical curves in Fig. 1 and 2 confirm the acceleration period present in the conversion-time curves of experiments with different initial iodine or monomer concentration.

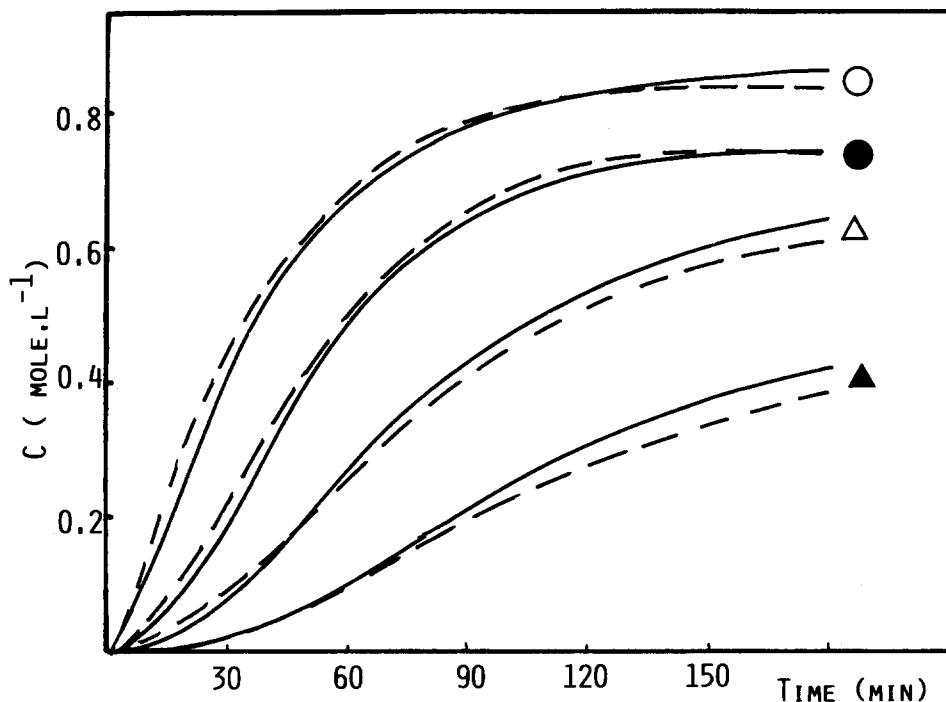


Fig. 1 - Theoretical (—) and experimental (---) conversion-time curves for runs with different initial iodine concentration.  $[M]_0 = 0.87 \text{ mole.l}^{-1}$ ;  $[I_2]_0 = (\blacktriangle): 0.060 \text{ mole.l}^{-1}, (\triangle): 0.080 \text{ mole.l}^{-1}, (\bullet): 0.105 \text{ mole.l}^{-1}, (\circ): 0.120 \text{ mole.l}^{-1}$

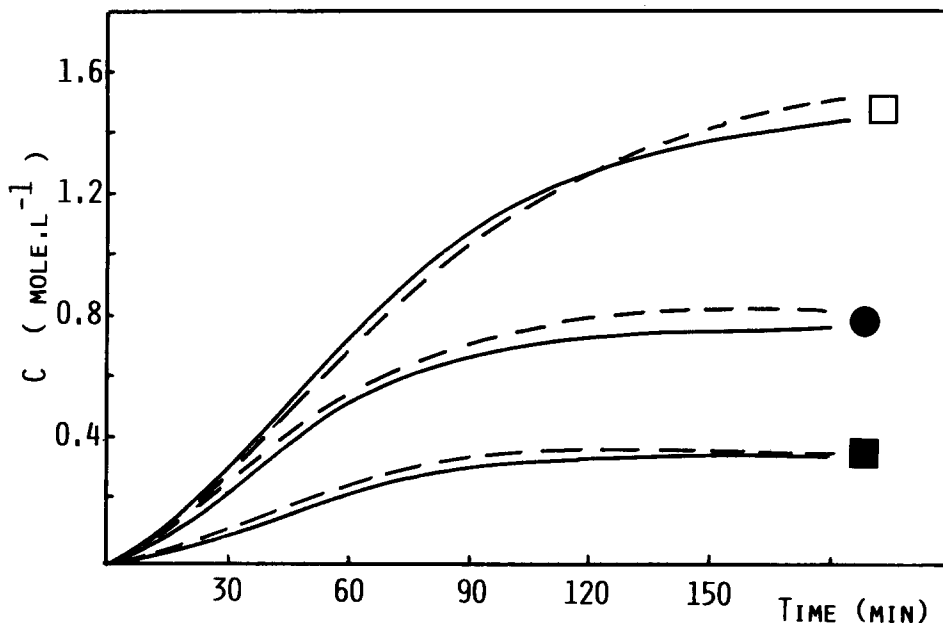


Fig. 2 - Theoretical (—) and experimental (---) conversion-time curves for runs with different initial styrene concentration.  $[I_2]_0 = 0.105 \text{ mole.l}^{-1}$ ;  $[M] = (\blacksquare): 0.4 \text{ mole.l}^{-1}, (\bullet): 0.87 \text{ mole.l}^{-1}, (\square): 1.74 \text{ mole.l}^{-1}$

The obtaining of the shape up to the inflection point of the curves is strictly connected with the assumption of equations (1) to (4) for the initiation process which results so confirmed together with the good reliability of the kinetic constants used in the mathematical treatment. The portion of curve after the inflection point was reproduced by admission of the propagation and termination processes in equations (5) and (6) where the propagating species is the iodine activated polystyryl iodide, which expels hydrogen iodide giving dead polymer molecules.

The mechanism proposed and the validity of the mathematical model applied are confirmed by the perfect reproduction of the indeed complex conductivity-time curves, as shown in Fig. 3 for experiments with different initial iodine concentration.

The initial increase in conductivity, strictly corresponding to the acceleration period in Fig. 1, can be ascribed to the relatively slow production of hydrogen iodide in the initiation process.

The conductivity remains then constant during the steady state because the new hydrogen iodide formed both in (2) and in (6) reaction generates a corresponding concentration of non-conducting propagating species.

At the end of the polymerization the conductivity increases again as hydrogen iodide in the absence of residual monomer reacts with free iodine according to the equilibrium (3).

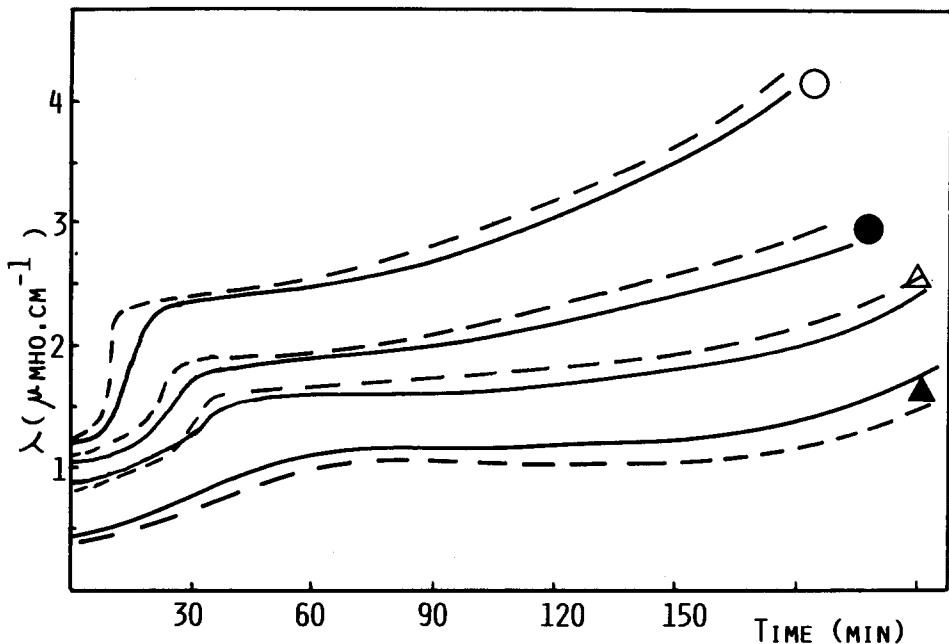


Fig. 3 - Theoretical (—) and experimental (---) conductivity-time curves for runs with different initial iodine concentration.  $[M]_0 = 0.87 \text{ mole.l}^{-1}$ ;  $[I_2]_0 = (\blacktriangle): 0.060 \text{ mole.l}^{-1}, (\triangle): 0.080 \text{ mole.l}^{-1}, (\bullet): 0.105 \text{ mole.l}^{-1}, (\circ): 0.120 \text{ mole.l}^{-1}$

Through a similar mathematical approach a future paper in the series will report the results obtained by a computer simulation concerning the role of hydrogen iodide concentration added as cocatalyst, the solvent polarity, the reaction temperature and the molecular weight of polymers obtained.

#### List of symbols

- M	monomer (styrene)
- MI	unsaturated side product
- MI <sub>2</sub>	styrene diiodide
- M <sub>n</sub> <sup>2</sup>	dead polymer chains
- P <sub>n</sub> <sup>*</sup>	growing polymer chains
- k <sub>1</sub> , k <sub>2</sub> , k <sub>3</sub> , k <sub>4</sub>	initiation rate constants
- k <sub>5</sub>	propagation rate constant
- k <sub>6</sub>	chain breaking rate constant
- K	equilibrium constant
- C	conversion
- a, b, c, d, e	conductivity coefficients
- λ	specific conductivity
- t	time

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