Polymer Bulletin 10, 321-327 (1983)

Polymer Bulletin

Modelling of Polymerization Reactions

3. Computer Simulation of Iodine Initiated Polymerization of Styrene: Effect of Temperature, Solvent and Hydrogen Iodide Cocatalysis

G. Maschio, P. Cerrai and P. Giusti

Centro di Studi dei Processi Ionici di Polymerizzazione e delle Proprietà
Fisiche e Tecnologiche di Sistemi Macromolecolari del C.N.R.,
c/o Dipartimento di Ingegneria Chimica, Università di Pisa, via Diotisalvi 2, I-56100 Pisa, Italy

Summary

The paper deals with the effect of the reaction temperature, the solvent polarity and the hydrogen iodide cocatalysis on the iodine initiated polymerization of styrene. Through a computer simulation based on a mathematical model previously proposed, different theoretical curves have been obtained which are in agreement with the experimental features of the system.

Introduction

In the previous paper of the series we reported on a mathematical model especially developed for simulating the iodine initiated pseudo-cationic polymerization of styrene in ethylene dichloride solution at 30°C (MASCHIO et al. 1982). In order to reproduce the experimental data concerning the effect of temperature and solvent on the system, new rate constant values of the different polymerization steps have been derived. Concerning the hydrogen iodide cocatalysis, the effect of the acid concentration both on the conversion-time, conductivity-time curves and on the molecular weight of polymers has been demonstrated to agree with the experimental findings.

Modelling of the system

The reaction mechanism we proposed as operating in the absence of added hydrogen iodide is the following:

-initiation:

$$I_2 + M \overset{K}{\rightleftharpoons} MI_2 \qquad (1)$$

$$MI_2 \xrightarrow{k1} MI + HI \qquad (2)$$

$$HI + 2I_2 \underset{k3}{\overset{k2}{\rightleftharpoons}} HI_2^+ + I_3^- \qquad (3)$$

$$M + HI_2^+ + I_3^- \xrightarrow{k4} P_1^*\cdot 2I_2 \qquad (4)$$

- propagation:

$$P_n^*\cdot 2I_2 + M \xrightarrow{k5} P_{n+1}^*\cdot 2I_2 \qquad (5)$$

- chain breaking:

$$P_n^*\cdot 2I_2 \xrightarrow{k6} M_n + HI + 2I_2 \qquad (6)$$

The relatively slow formation of hydrogen iodide in the initiation process eq.(2), was likely suggested as responsible of the S-shaped conversion-time curves and of the initial increase in conductivity. The complete course of conversion and conductivity throughout the polymerization was then reproduced by assuming a special set of equations, eqs. (7) to (15) in the previous paper, to represent a material balance of each component of the system.

That mathematical model has been now modified in order to account both for the influence of temperature and solvent on the kinetics and to evaluate the molecular weight of polymers. The experimental rate of monomer consumption measured at different temperatures between 10° and 30°C per mits to calculate an activation energy value of 7,600 cal/mole (GIUSTI 1966). This value can be attributed to the propagation step, eq.(5), by admitting that the monomer consumption occurs almost completely into this step of the polymerization. As far as the activation energies of the other steps of the whole process, values in agreement with relevant literature data (KUNITAKE,TAKARABE 1979; HAYES,PEPPER 1961) have been assumed. On the basis of these assumption the following kinetic constants for the whole process in the form of Arrhenius relationships have been derived:

$$\begin{aligned} k1 &= 5.33\cdot 10^{5}\ \exp(-8000/RT) & k2 &= 3.40\cdot 10^{6}\ \exp(-8000/RT) \\ k3 &= 8.18\cdot 10^{4}\ \exp(-8000/RT) & k4 &= 5.09\cdot 10^{5}\ \exp(-8000/RT) \qquad (7) \\ k5 &= 4.29\cdot 10^{6}\ \exp(-7600/RT) & k6 &= 5.08\cdot 10^{2}\ \exp(-5000/RT) \end{aligned}$$

Concerning the molecular weight of polymers, the value of the polymerization degree has been determined by means of a general probabilistic method recently discussed (GIUSTI,MASCHIO 1982).

If ε is the probability of chain propagation and $(1 - \varepsilon)$ the probability of spontaneous chain breaking, the instantaneous value of ε is given by:

$$\varepsilon = \frac{Rp}{Rp + Rt} = \frac{k5[M][P_n^*]}{k5[M][P_n^*] + k6\ [P_n^*]} = \frac{k5[M]}{k5[M] + k6} \qquad (8)$$

and the instantaneous value of the frequency function is:

$$F(r) = \varepsilon^{(r-1)}\cdot(1-\varepsilon) \qquad (9)$$

By integrating versus time in order to obtain the integral probability up to a generic reaction time $\bar{t}$, it follows:

$$\bar{\varepsilon} = \frac{1}{\bar{t}} \int_0^{\bar{t}} \varepsilon\, dt = \frac{1}{\bar{t}} \int_0^{\bar{t}} k5\ \frac{[M]}{[M] + (k6/k5)}\ dt \qquad (10)$$

In the model development the eq.(10) has been solved by the Cavalieri-Simpson method. The number average degree of polymerization can be then calculated as follows:

$$\overline{DP}_n = 1/(1-\bar{\varepsilon}) \qquad (11)$$

No particular modification to the mathematical model reported in the previous paper has been introduced in order to simulate the effect of added hydrogen iodide on the kinetics of the system. Conversion- and conductivity-time curves as well as molecular weight of polymers at different initial concentration of acid have been reproduced by applying the sets of equations, eqs.(7) to (15) in the previous paper, and kinetic constants previously established, so confirming the correctness of the reaction mechanism proposed, eqs.(1) to (6).

Results and discussion

The influence of the temperature on the kinetics of the system has been simulated on the basis of the set of kinetic constants formulated in the previous section (eqs.7). In Fig. 1 the predicted and experimental conversion-time curves for runs at a constant initial concentration of monomer and iodine but at different temperatures between 10° and 30°C are compared. The good agreement obtained indicates that the values derived for the activation energy and the elementary rate constants are quite correct in the temperature range examined.

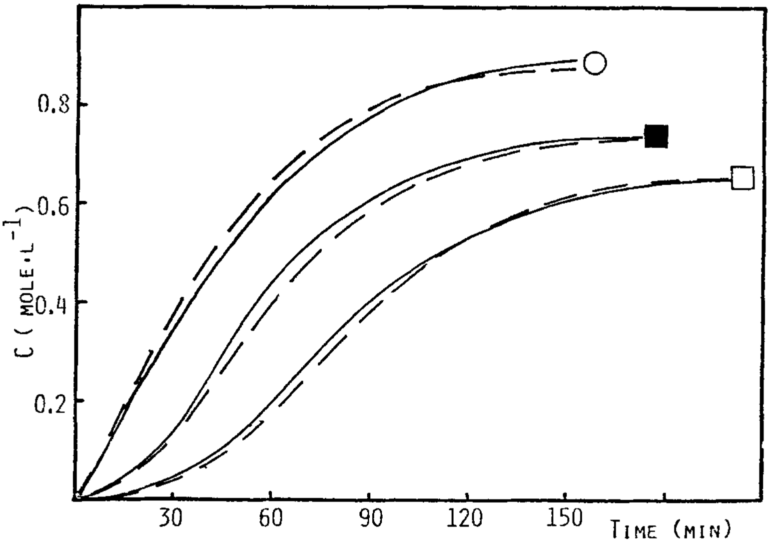

Fig. 1 - Theoretical (———) and experimental (- - - -) conversion-time curves for runs at different temperatures. Solvent: $C_2H_4Cl_2$; $[M]_0$= 0.87 mole.l^{-1}; $[I_2]_0$ = 0.120 mole.l^{-1}; (○): 30°C, (■): 20°C, (□): 10°C.

The cocatalytic role of hydrogen iodide on the system has been confirmed by reproducing previous experimental results obtained in experiments with different initial concentration of added acid. (GIUSTI, ANDRUZZI 1968) It must be emphasized that the computer simulation has been accomplished without any correction to the balance equations and kinetic constants valid for polymerizations initiated by iodine alone, but simply giving as input of the computer simulation initial conditions equal to those of the experimental runs.

In Figs. 2a and 2b the theoretical and experimental conversion- and conductivity-time curves are shown. Fig. 2a demonstrates a perfect reproduction throughout the whole polymerization of the conversion-time curves obtained in the presence of different acid concentrations.

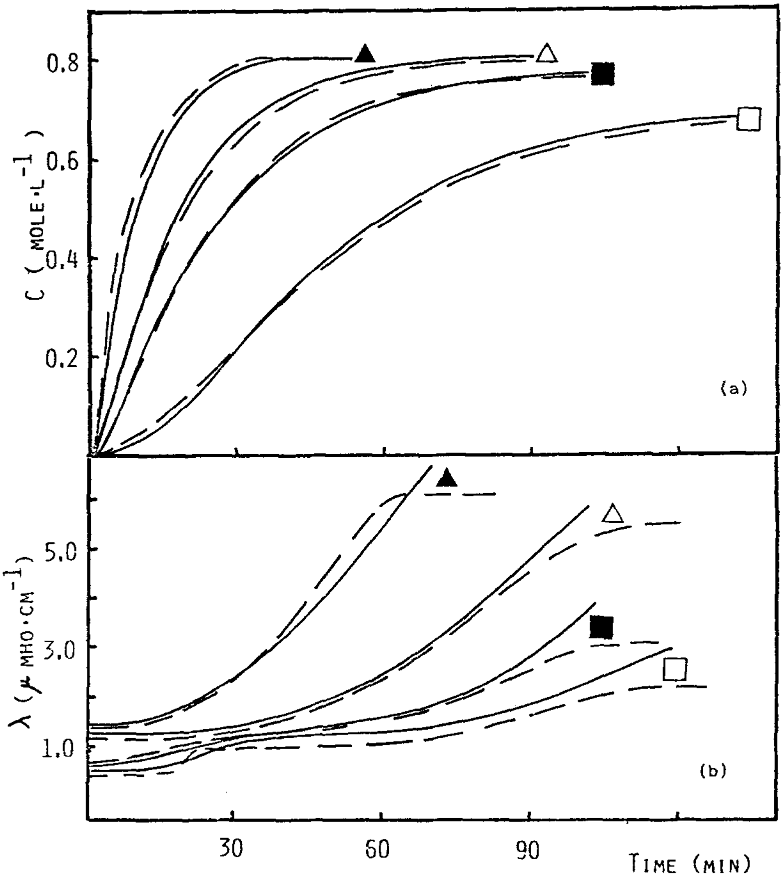

Fig. 2 - Theoretical (——) and experimental (- - -) conversion-time (a) and conductivity-time (b) curves for runs with different initial hydrogen iodide concentration. Solvent: $C_2H_4Cl_2$; $[M]_0$=0.8 mole.l^{-1}; $[I_2]_0$ = 0.100 mole.l^{-1}; $[HI]_0$ = (□): no acid, (■): 0.050 mole.l^{-1}; (△): 0.100 mole.l^{-1}, (▲): 0.150 mole.l^{-1}; Temp.: 30°C.

Increasing concentrations of hydrogen iodide give rise to an increase of the polymerization rate and a progressive decrease of the acceleration period which tends to vanish for the higher acid concentration, so indicating the step (2) of the mechanism proposed to be prevailingly the rate controlling one, even if some minor influence on the apparent rate must be abscribed to the formation of active centers in the step (4).

Concerning the conductivity during the polymerization, Fig. 2b shows that the experimental shape is reproduced by the model used at least up to the complete conversion. The experimental plateau of the conductivity attained after the end of the reaction as a consequence of the combined establishment of steps (6) and (3) is not reproduced by the model since it was especially derived to simulate the process during the polymerization reaction.

The above described eqs.(8) to (11) have been applied to obtain the molecular weight of polymers from experiments with different initial concentration of hydrogen iodide; the results obtained are shown in Fig. 3.

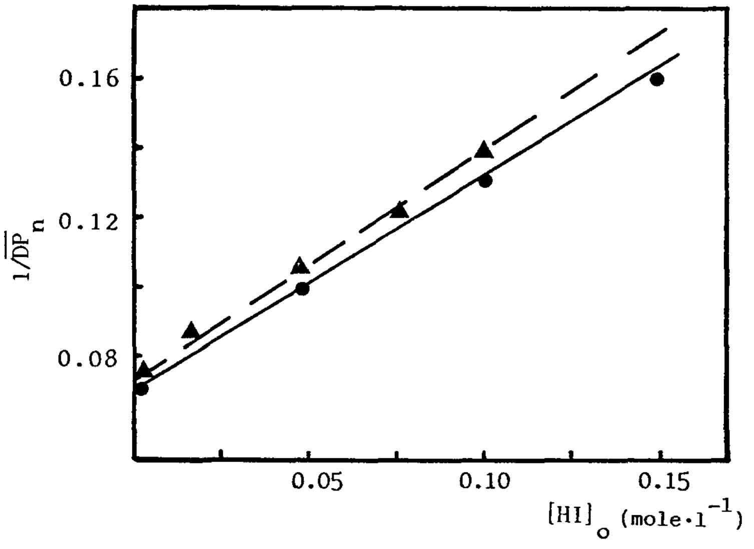

Fig. 3 - Effect of hydrogen iodide concentration on the molecular weight of polymer: theoretical (●) and experimental (▲) values. Solvent: $C_2H_4Cl_2$; $[M]_o = 0.87$ mole.l-1; $[I_2]_o = 0.147$ mole.l^{-1}; Temp.: 30°C.

According to the model proposed, the degree of polymerization decreases by increasing the added acid due to the higher concentration of active centres formed by the steps (3) and (4).

The influence of the polymerization medium has been examined on the basis of the different results obtained in ethylene dichloride or methylene chloride solution. In the latter solvent maximum rates of polymerization three to four times lower were obtained together with proportionally longer acceleration periods (GIUSTI 1966). Owing to the close polarity of two solvents, we can reasonably hypothesize that the change in medium does not influence the reaction mechanism but only the elementary kinetic constants for which we assumed the following values at 30°C, when methylene chloride is used as solvent:

$$\begin{array}{ll} k1 = 0.4\ \mathrm{min}^{-1} & k2 = 2.2\ \mathrm{l}^{2}\cdot\mathrm{mole}^{-2}\cdot\mathrm{min}^{-1} \\ k3 = 0.05\ \mathrm{l.mole}^{-1}.\mathrm{min}^{-1} & k4 = 0.45\ \mathrm{l}^{2}.\mathrm{mole}^{-2}.\mathrm{min}^{-1} \\ k5 = 7.0\ \mathrm{l.mole}^{-1}.\mathrm{min}^{-1} & k6 = 0.09\ \mathrm{min}^{-1} \end{array} \qquad (12)$$

With respect to the corresponding values stated in the previous paper for polymerizations in ethylene dichloride solution (MASCHIO et al. 1982), we have clearly diminished the kinetic constants related to the initiation step (k1 to k4), while a slight correction has been introduced in the values referring to the propagation and chain breaking steps (k5 and k6). The good agreement between the theoretical and experimental conversion-time curves shown in Fig.4 demonstrates the validity of the rate constants used.

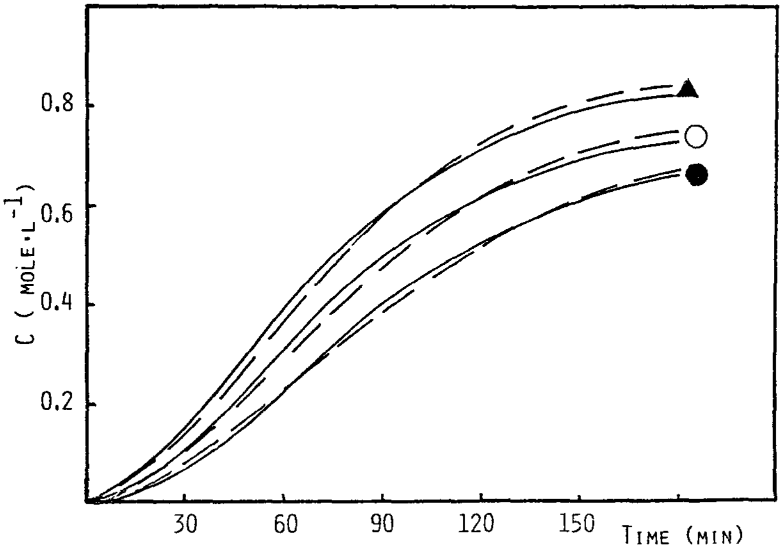

Fig. 4 - Theoretical (———) and experimental (– – – –) conversion-time curves for runs with different initial iodine concentration. Solvent : CH_2Cl_2; $[M]_0$= 0.87 mole·l^{-1}; $[I_2]_0$= (●): 0.124 mole·l^{-1}, (○): 0.134 mole.l^{-1},(▲): 0.144 mole·l^{-1}; Temp.= 30°C.

In conclusion the results obtained by the computer simulation of the polymerization of styrene by iodine under different experimental conditions fully confirm the pseudocationic nature of the system and the role played by the hydrogen iodide in the whole reaction mechanism. Similar theoretical models will be developed in future papers of the series in order to simulate or reinvestigate polymerization systems having a different ionic character with the aim to confirm reaction mechanisms previously formulated and to assign reliable values to the kinetic constants of the different steps.

References

GIUSTI, P.: Chim. e Ind.(Milan) 48, 435 (1966)
GIUSTI, P. and ANDRUZZI, F.: Chim. e Ind.(Milan) 48, 442 (1966)
GIUSTI, P. and ANDRUZZI, F.: J.Polym.Sci.,C-16, 3797 (1968)
GIUSTI, P. and MASCHIO, G.: Chim. e Ind. (Milan) 64, 492 (1982)
HAYES, M.J. and PEPPER, D.C.: Proc.R.Soc.London, Ser.A, 263, 63 (1961)
KUNITAKE, T. and TAKARABE, K.: Macromolecules, 12,1061 (1979)
MASCHIO, G.,CERRAI, P. and GIUSTI, P.: Polymer Bull., 8, 147 (1982)

Acknowledgement

This work has been partly financially supported by the Special Project " Chimica Fine e Secondaria " of Italian C.N.R.

Accepted June 24, 1983 C