

Influence of water upon the rate of cationic polymerization of styrene. III.*

Inhibition and induction periods, non-stationarity

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Both inhibition and induction periods of the tin tetrachloride-catalyzed styrene polymerization increase monotonously with the increasing concentration of water in the system. The overall polymerization rate proceeds, under these conditions, through a maximum. If the concentration of water in the nonpolar medium is less than equimolar with regard to the initiator, then the conversion curve assumes the form of several waves. Each wave resembles an independent polymerization process with its inhibition and induction period. The length of waves and both periods is a function of identical factors. Neither tin tetrachloride monohydrate nor dihydrate can be an initiating centre. The concentration of active centres slowly decreases even during the main stage of polymerization.

The interpretation of inhibition and induction periods as well as the explanation of the wave formation on conversion curves is inevitable for understanding of the tin tetrachloride-catalyzed polymerization of styrene. These phenomena have already been observed by *Colclough* and *Dainton* [1] during the polymerization carried out in tetrachloromethane. They define the inhibition period as the time during which hydrogen chloride (formed through the hydrolysis of tin tetrachloride) reacts with styrene forming an efficient transferring agent — 1-chloroethylbenzene. This compound reacts with the growing end during the induction period. By this process species are formed which must again proceed through the initiation cycle to form an active centre. The transfer process is so fast that no high polymer can be formed in the presence of 1-chloroethylbenzene. The authors, however, were unable to account for the periodic hydrogen chloride formation.

The stationarity of the process of styrene polymerization is strongly dependent on the type of the initiating acid. Both non-stationary [2, 3] and stationary [4] polymerizations have been described. The mechanism of the termination reactions is not, in fact, clearly understood. The formation of waves on conversion curves is a special case of a non-stationary system where both the disappearance and the regeneration of active centres are controlled by some spontaneous pulses.

In this work we would like to contribute to the elucidation of stationarity problem of the tin tetrachloride-catalyzed polymerization of styrene.

* For Part I and II see Ref. [5].

Experimental

Chemicals, their preparation and purification together with apparatus and working procedure have already been described in our previous communications [5]. The inhibition period was defined as the time period elapsed between the mixing of reactants and the first movement of a meniscus in the dilatometer; the induction period is then the time interval between this point and the inflexion of the contraction curve.

The decrease in the concentration of active centres during the main polymerization step was evaluated from the reaction rate decrease. A given amount of reactants containing double concentration of the initiator was transferred into a dilatometer bulb of a corresponding volume. The same amount of reactants but without the initiator was added to this mixture after 24, 48, and 97 hours, respectively. The observed reaction rate was expressed in percents of the rate measured during the blank experiment (without "ageing" of the reactants). The polymerizations were reproducible within less than $\pm 5\%$ of conversion. Other procedures or modifications will be mentioned in the text.

Results and discussion

Typical contraction curves obtained during the polymerization in toluene demonstrating the influence of water on the induction and inhibition period as well as on the rate of conversion of monomer to polymer are shown in Fig. 1. Contraction curves corresponding to the same system but with 1,1,2,2-tetrachloroethane as solvent are without waves. The dependence of the length of the inhibition and induction period respectively upon the water concentration at constant temperature is shown in Fig. 2, the temperature dependence is depicted in Fig. 3, and the dependence on the tin tetrachloride concentration is seen in Fig. 4.

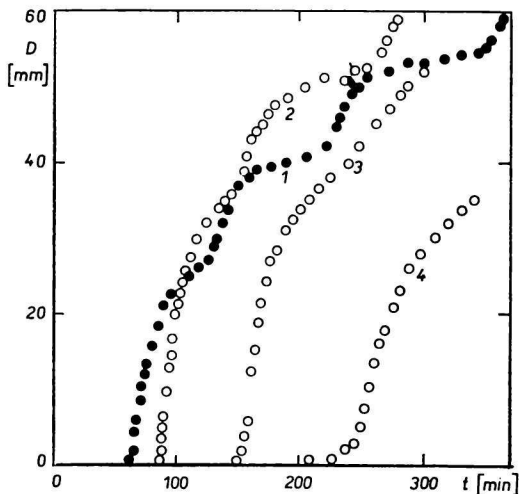


Fig. 1. Contraction curves of styrene polymerization in toluene. Temperature 35°C ; styrene concentration 1.50 mol kg^{-1} ; tin tetrachloride concentration 6.6 mmol kg^{-1} ; water concentration (mmol kg^{-1}).
1. 0.7; 2. 4.6; 3. 8.6; 4. 11.6.

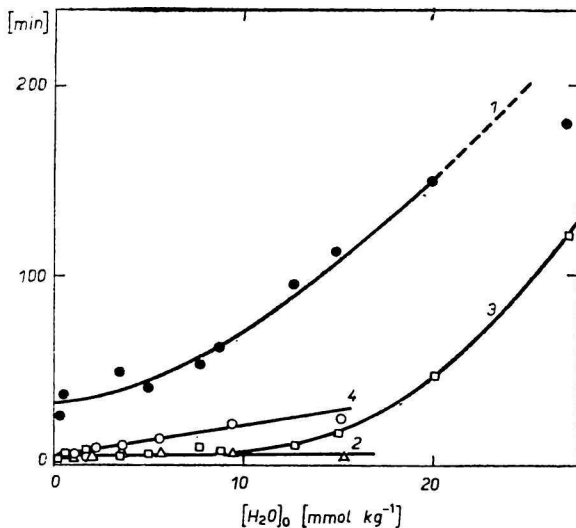


Fig. 2. The dependence of inhibition (curve 1, 2) and induction (curve 3, 4) periods on the water concentration. Temperature 35°C; tin tetrachloride concentration 6.6 mmol kg⁻¹; styrene concentration in toluene (mol kg⁻¹). 1. and 3. 2.98; concentration in 1,1,2,2-tetrachloroethane (mol kg⁻¹): 2. and 4. 1.90.

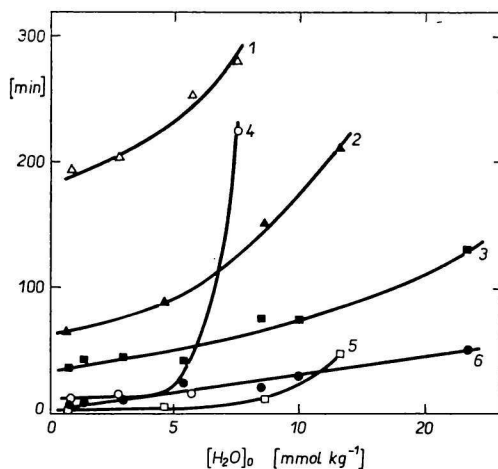


Fig. 3. The dependence of inhibition and induction period on the water concentration at various temperatures.

Styrene concentration 1.50 mol kg⁻¹ in toluene; tin tetrachloride concentration 6.6 mmol kg⁻¹; t [°C] — inhibition period.

1. 20; 2. 35; 3. 50; induction period: 4. 20; 5. 35; 6. 50.

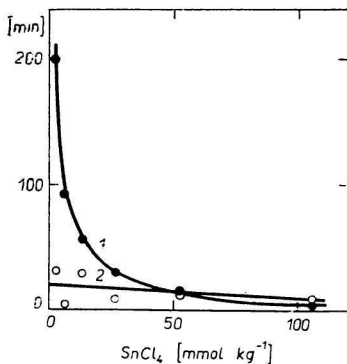


Fig. 4. The dependence of inhibition and induction period on tin tetrachloride concentration.

Temperature 20°C; styrene concentration in toluene 2.98 mol kg⁻¹; initial concentration of water 2.1–3.5 mmol kg⁻¹.

1. inhibition period; 2. induction period.

The inhibition period does not change whereas the induction period increases with the increasing concentration of water during the polymerization in 1,1,2,2-tetrachloroethane. When the polymerization is carried out in nonpolar toluene, the inhibition period increases with the increasing water concentration, the induction period remaining constant. Colclough and Dainton [6] have observed neither inhibition nor induction period in 1,2-dichloroethane, whereas the results of their experiments carried out in nonpolar tetrachloromethane correspond qualitatively to our observations in the case of 1,1,2,2-tetrachloroethane.

It again suggests that the influence of solvents is a complex function which cannot be sufficiently expressed only on the basis of dielectric constant. Szwarc [7] has already pointed out that the increase of the dipole moment of 1,2-dichloroethane may be due to the electric field in the close vicinity of ions and ion pairs respectively, by preferring more polar gauche conformation. Colclough and Dainton, when polymerizing in tetrachloromethane, used an initiator concentration higher by order than that employed by us during the polymerization of styrene in equally nonpolar toluene. The observed differences in lengths of both inhibition and induction periods could be partially accounted for by mentioned factors.

The relationship between the contraction and conversion found experimentally was strictly linear. This fact indirectly signifies that the average degree of polymerization of polystyrene formed during the induction period will not be markedly different from that of a polymer formed in more advanced stages of polymerization. The contraction observed during the dimerization is only one fifth of that during the formation of a dekamer or higher polymer [8, 9]. Trimer and other oligomers will also have lower density than the dekamer.

The induction periods in our system are thus not caused by the formation of oligomers during the initial stage of polymerization but they are due to genuine kinetic factors. During this stage the concentration of active centres is increasing. This statement can be further corroborated. The ratio of the slope of contraction curve at the inflexion to the slope at the onset of the induction period could be 5 at most if the process is stationary; the observed values are (especially in the presence of higher concentrations of water) much greater.

The length of the inhibition period is influenced even by such a subtle factor as the concentration of the stock solution of the initiator. Adequate volumes of this solution were taken for polymerization (Fig. 5).

We attempted to verify the hypothesis of Colclough by carrying out the polymerization

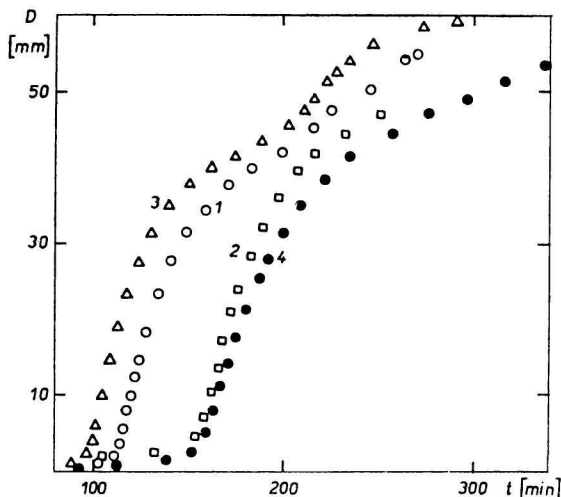


Fig. 5. Contraction curves of styrene polymerization initiated by tin tetrachloride taken from stock solution of different concentration.

Styrene concentration 1.50 mol kg^{-1} in toluene; initial concentration of water 3.5 mmol kg^{-1} ; temperature 35°C . Stock solution concentration equals Y . This solution was transferred to a dilatometer to give 6.6 mmol kg^{-1} . Polymerization was carried out immediately after the preparation of the stock solution:

1. $Y = 5\%$ volume; 2. $Y = 0.1\%$ volume. Polymerization carried out after 48 hours after the preparation of the stock solution: 3. $Y = 5\%$ volume; 4. $Y = 0.1\%$ volume.

in the presence of hydrogen chloride. The addition of HCl increases the inhibition period similarly as the same amount of water. It is not possible that the addition of water in the low concentration region could cause the evolution of equimolar quantity of hydrogen chloride through the hydrolysis of tin tetrachloride. There is no reason for a given amount of water and tin tetrachloride taken from solutions of different concentration to give varying amount of hydrogen chloride. No cause is known which would account for periodic evolution of hydrogen chloride. These reasons are sufficient for expressing doubts about the validity of hypothesis of Colclough.

The height and length of waves on the contraction curves depend on the concentration of water, monomer (Fig. 1) and temperature; the higher the concentration of the initiator the more pronounced are the waves. It suggests a close relationship between the formation of waves and the inhibition and induction periods, respectively. The occurrence of waves in homogeneous system supports the hypothesis according to which the active centres are formed from tin tetrachloride precursor *via* an intermediate stage of some "sleeping centres". The sleeping centres can be formed not only from the precursor but also from the growing active centres after transfer — the polymerization is stopped. Transformation of the sleeping centres into active ones proceeds in pulses; polymerization starts and ceases again. It is probably quite different case of non-stationarity than that described by Pepper [2, 10]. The character of sleeping centres is not quite understood.

We attempted to answer the question whether the main stage of the polymerization process is accompanied by the decrease of active centres concentration or the sum of active and sleeping centres when the polymerization is carried out in a medium facilitating

the formation of waves. We followed the polymerization rate of a standard system where the active centres could be altered (see Experimental). It could be calculated from the results obtained at various concentrations of water, in various solvents and for

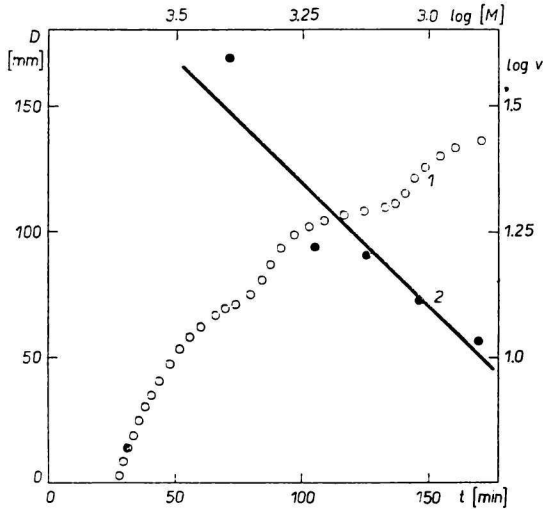


Fig. 6. Styrene polymerization in toluene at 35°C.
Styrene concentration 2.98 mol kg⁻¹; tin tetrachloride concentration 6.6 mmol kg⁻¹;
initial concentration of water < 0.3 mmol kg⁻¹.
1. contraction curve; 2. the plot of log rate vs. log $[M]$.

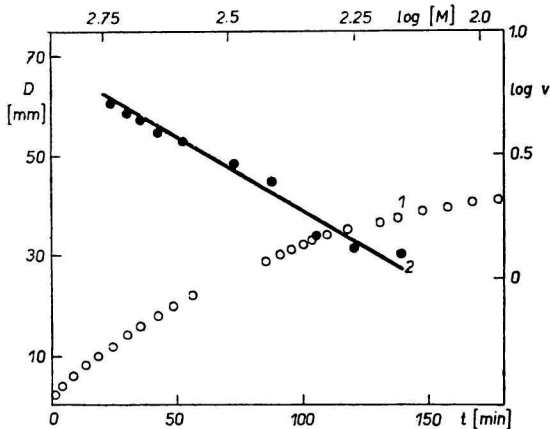


Fig. 7. Styrene polymerization in tetrachloroethane at 35°C.
Styrene concentration 0.43 mol kg⁻¹; tin tetrachloride concentration 12.9 mmol kg⁻¹;
initial water concentration 23.8 mmol kg⁻¹.
1. contraction curve; 2. log rate vs. log $[M]$ plot.

different time that the half-life period of the reaction leading to the disappearance of active centres is *ca.* 10 hours. In the first approximation the polymerizations lasting *ca.* 90 minutes without the inhibition period can be regarded as stationary (the disappearance of centres is, under these circumstances, less than 10%). The agreement between this conclusion and the results of experiments can be seen in Figs. 6 and 7. Lines 2 shown in the figures were calculated from the relationship

$$-\frac{d[M]}{dt} = k[\text{SnCl}_4]^z [M] = k_0[M],$$

where $[M]$ = monomer concentration, z = reaction order with regard to SnCl_4 , k_0 being the effective rate constant including SnCl_4 concentration; $k_0 = 1.6 \times 10^{-2} \text{ min}^{-1}$ (Fig. 6) and $1 \times 10^{-2} \text{ min}^{-1}$ (Fig. 7).

References

1. Colclough, R. O. and Dainton, F. S., *Trans. Faraday Soc.* **54**, 886 (1958).
2. Hayes, M. J. and Pepper, D. C., *Proc. Roy. Soc. (London)* **A263**, 63 (1961).
3. Overberger, C. G., Ehrig, R. J., and Marcus, R. A., *J. Amer. Chem. Soc.* **80**, 2456 (1958).
4. Pepper, D. C. and Reilly, P. J., *J. Polym. Sci.* **58**, 639 (1962).
5. Kučera, M., Švábík, J., and Majerová, K., *Collect. Czech. Chem. Commun.* **37**, 2004, 2708 (1972).
6. Colclough, R. O. and Dainton, F. S., *Trans. Faraday Soc.* **54**, 894 (1958).
7. Szwarc, M., *Carbanions, Living Polymers and Electron-Transfer Processes*, p. 238. Interscience-Wiley, New York, 1968.
8. Rubens, L. C. and Skochdopole, R. E., *J. Appl. Polym. Sci.* **9**, 1487 (1965).
9. Fox, T. G. and Flory, P. J., *J. Polym. Sci.* **14**, 315 (1954).
10. Burton, R. E. and Pepper, D. C., *Proc. Roy. Soc. (London)* **A263**, 58 (1961).

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