

## CATIONIC POLYMERIZATION OF STYRENE WITH ELECTROCHEMICALLY GENERATED PERCHLORIC ACID—II

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(Received 30 May 1973)

**Abstract**—The electroinitiated polymerization of styrene in  $\text{LiClO}_4$ -PC solutions has a living character due to the absence of termination. Marked side reactions were observed, limiting the yields. These reactions are mainly due to monomer oxidation by  $\text{HClO}_4$  and polymer degradation at the anode. They can be minimized by increasing the monomer concentration. Conversion vs time curves show an induction period, an ascending linear portion and a descending portion. Kinetic treatment limited to the ascending portions shows that the polymerization is first-order with respect to monomer and  $\text{HClO}_4$  concentrations.  $K_p$  values are considerably lower than those found in  $\text{HClO}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  and in  $\text{HClO}_4$ - $\text{CH}_2\text{Cl}_2$ , thus confirming that the influence of the solvent in these processes is not merely electrostatic.

### INTRODUCTION

The concept of living polymers has been usually associated with anionic polymerization but living cationic polymerizations have been reported by Szwarc [1], Pepper [2], Mengoli [3] and Funt [4]. In particular, Pepper [2] interprets the polymerization of styrene in  $\text{HClO}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  as a transfer dominated living polymerization, characterized by fast initiation and no termination. As a consequence of this characteristic, the catalyst is not consumed and can polymerize further doses of monomer.\*

Living polymerizations carried out by carbonium ions have been observed when using styrene as monomer [2, 3, 4]. This is probably related to the stability of polystyrylcarbonium ions, which is the optimum for such polymerizations. More reactive monomers, such as the ethers, do not give under the same conditions cationic polymerizations having a living character [5].

Part I reported some features of the polymerization of styrene initiated by electrochemically generated  $\text{HClO}_4$  in propylene carbonate (PC). The influence of factors such as temperature, current, monomer and electrolyte concentrations, and changes in the dielectric constant of the medium have been described. Some features of this polymerization are very peculiar; the most striking is degradation of the polymer chains, seeming to occur in spite of the experimental conditions. Kinetic curves have now been examined in order to elucidate this phenomenon.

\* The definition of living polymerization here used is that one given by Pepper [2] and not the more rigorous one given by Szwarc [1], who excludes both transfer and termination reactions in living-polymerizations.

### EXPERIMENTAL

#### Materials

Tetrabutylammonium perchlorate ( $\text{TBAClO}_4$ ) was prepared from tetrabutylammonium hydroxide (40 per cent aqueous solution, Fluka) and perchloric acid (70 per cent aqueous solution, Merck) by the method described by Boden [6].

For other materials, see Part I.

#### Apparatus and technique

The electrolytic cell and other experimental details are reported in Part I. Yields as a function of time were determined by stopping the electrolyses and adding excess methanol. For electrolyses at 20 mA, the residual monomer was also determined by gas chromatography (GLC), diluting with methanol the electrolysed solutions. In this way, polystyrene was separated from the solution, so that the analysis of styrene was performed in a virtually homogeneous solution.

The operating conditions for GLC were as follows: column, 2 m stainless steel; packing, 15 per cent Apiezon L on Chromosorb P 80-100 mesh; temperature, 120°; carrier gas, nitrogen (38 ml/min); thermal conductivity detector; *m*-xylene as a reference standard. The temperature was raised to 200° and the flow rate to 45 ml/min when trying to detect styrene oligomers.

When electrolysing  $\text{TBAClO}_4$ -styrene-PC solutions, marked diffusion of the solution from anolyte to catholyte was observed. To avoid this shortcoming, the catholyte was filled with a saturated  $\text{LiClO}_4$ -PC solution.

### RESULTS AND DISCUSSION

#### Living character

The living character of the polymerization of styrene in  $\text{LiClO}_4$ -PC solutions was inferred from the following observations:

(1) A  $\text{LiClO}_4$  0.1 M-styrene 1.0 M-PC solution was

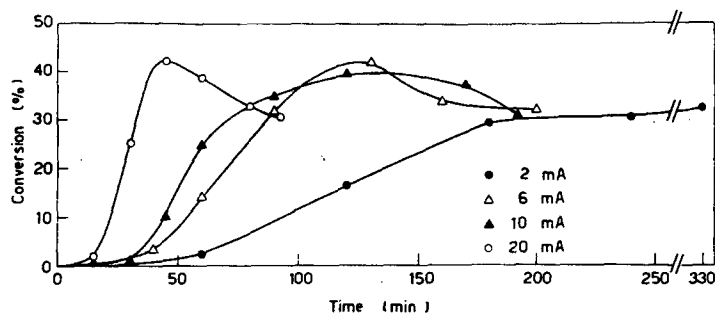


Fig. 1. Kinetic curves at various currents.  $\text{LiClO}_4$  0.1 M, styrene 1.0 M,  $25^\circ$ .

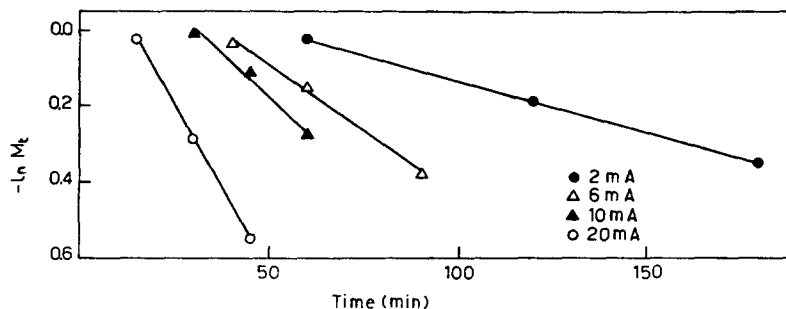


Fig. 2. First-order plots at various currents.

electrolysed at 25 mA for 1 hr (i.e. until all styrene had reacted); adding more monomer, after interrupting the current, a new fast polymerization occurred. This behaviour is connected with the recovery of  $\text{HClO}_4$ . However, the molecular weight remained constant (ca. 2700), thus indicating that the second dose of monomer did not add to the chains previously formed.

(2) Interrupting the current, the polymerization proceeded spontaneously. When this was done in a polymerization at 20 mA after 20 min, the conversion increased from 7.5 to 25.7 per cent after 40 min and to 39.6 per cent after 260 min. Since the catalyst is not consumed in termination reactions, the relatively low conversions, also observed during continuous electrolyses, seem to indicate the presence of side reactions (see below).

#### Kinetic curves

Conversion vs time curves at various currents in 1 M styrene solutions are reported in Fig. 1. It should be noted that: (a) conversions are never complete, their maximum being ca. 42 per cent; (b) curves made at 6, 10 and 20 mA exhibit a decrease in conversion with time; (c) there is an induction period decreasing with current.

This behaviour is quite different from that found in  $\text{HClO}_4\text{-C}_2\text{H}_4\text{Cl}_2$  [2] and  $\text{HClO}_4\text{-CH}_2\text{Cl}_2$  [7], as well as in the electroinitiated polymerizations of styrene in  $\text{TBAClO}_4\text{-C}_6\text{H}_5\text{NO}_2$  [3] and  $\text{TBAClO}_4\text{-CH}_2\text{Cl}_2$  [4].

To find a reliable order of reaction, the first-order

kinetic equation was applied only to the points in the ascending portions of the curves of Fig. 1, after the induction period. The results are shown in Fig. 2. Straight lines corresponding to the equation:

$$-\ln M_t = k_1 t$$

were found. As expected, the curves do not pass through the origin; the different extrapolation values give the amount of current corresponding to the induction period. The slopes of the straight lines give the first-order rate constants,  $k_1$ , which are linearly dependent on the electrolysis current, as shown in Fig. 3. As previously found [8], the concentration of  $\text{HClO}_4$  is proportional to the current, so that the relation:

$$k_1 = k_p [\text{HClO}_4] \quad (1)$$

may be derived,  $k_p$  being the propagation rate constant. The same relation between  $k_1$  and  $k_p$  was derived

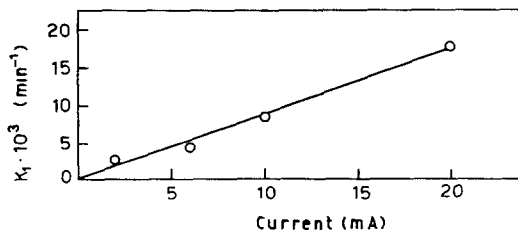


Fig. 3. Dependence of the experimental rate constant on the current of electrolysis.

by Pepper [2] and Plesch [7]. Thus, over the ranges examined, the relation:

$$-dM/dt = k_p [\text{HClO}_4] \cdot [\text{M}]$$

holds true. Due to the conditions of continuous electrolysis, Eqn. (1) cannot be used to derive  $k_p$  values.

To provide a more complete view of this polymerization, the concentration of unreacted styrene was determined with GLC for the polymerization at 20 mA (Fig. 4). The result was quite surprising, because the styrene was seen to have reacted almost completely. The curves have the sigmoidal shape typical of non-terminating polymerizations in which the concentration of active centres increases continuously, so that steady-state conditions are not attained. This would indicate at first sight that styrene disappears only through a polymerization process, which is living in character.

The kinetic equation developed by Funt [4] for continuous electrolysis, on the basis of the conventional polymerization of styrene described by Pepper [2], was applied to the curves of Fig. 4. A certain departure from the linearity expected for the curves  $\ln M_0/M_t$  vs  $t^2$  was observed; in particular, the first four points of the curves show a definite concave up trend.

Limiting the application of Funt's equation to the points of Fig. 2, better straight lines were obtained. Still, there is some scatter, which is greater than that expected from experimental errors. From the slope of the straight lines, the  $k_p$  values reported in Table 1 are derived. An increasing trend with current was found; this result, together with the GLC results, suggest that there is not a strict proportionality between number of active centres and amount of current passed, i.e. side reactions occur which do not lead to polymer.

On the other hand, direct side reactions of the monomer with  $\text{HClO}_4$ , such as protonation or formation of oligomers, may take place only with an excess of acid over styrene [9, 10]. Working at 20 mA, an excess of acid is attained only after 60 min

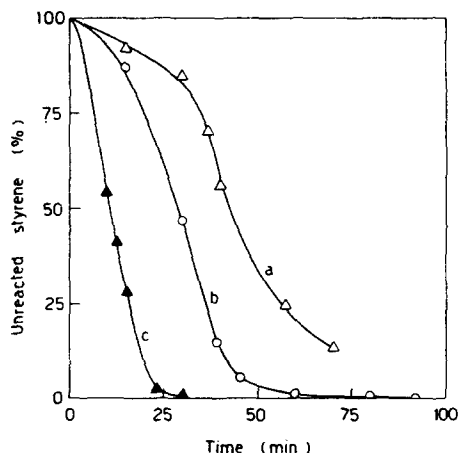


Fig. 4. Gas chromatographic analysis for unreacted styrene. A, 0°; b, 25°; c, 40°.  $\text{LiClO}_4$  0.1 M, styrene 1.0 M, 20 mA, 25°.

Table 1.

Current (mA)	$k_1 \times 10^3$ ( $\text{min}^{-1}$ )	$k_p$ ( $\text{l/mol sec}$ )
2	2.7	0.30
6	6.9	0.45
10	8.4	0.55
20	17.7	0.80

( $m_{\text{HClO}_4}/m_{\text{styr.}} = 9.4$ ), when almost all styrene has reacted.

There is some evidence that the main side reaction is an oxidation of the monomer due to the decomposition of  $\text{HClO}_4$ .  $\text{HClO}_4$ -PC solutions have indeed a yellow-red colour which becomes deeper with time and their capacity of polymerizing styrene decrease on standing. This means that the acid decomposes giving  $\text{O}_2$  which can oxidize the monomer. Repeating at time intervals GLC experiments on a given  $\text{LiClO}_4$ -styrene-PC solution after electrolysis, the styrene peak was seen to disappear progressively.

This parasitic reaction may explain the gap between styrene concentration found gravimetrically and gas-chromatographically. However, as shown by the decreases observed in the yields (Fig. 1), another important process occurs in solution, i.e. degradation of the polymer chains. This phenomenon, which is still obscure, is certainly influenced by the current, as demonstrated by interrupting the electrolysis after 45 min at 20 mA and observing no decrease in conversion. It seems to occur when almost all styrene has reacted (see GLC and gravimetric curves at 20 mA and 25°), but one cannot exclude its influence also in the previous stages of the polymerization.

It is quite difficult to state whether this degradation may be regarded as a true depropagation, i.e. its final product is the monomer again. In fact, any compound formed during the degradation is oxidized by the oxygen developed by  $\text{HClO}_4$  (the concentration and decomposition of which are obviously greater in the latest stages of the electrolysis).

From GLC it can be seen: (a) at low retention times (before the styrene peak), a long-tailed peak which is absent in solutions not containing styrene; this peak may possibly account for the oxidation product(s); (b) at high retention times, a low peak, the intensity of which increases with electrolysis time, probably due to an oligomer of styrene [11]; however, its maximum concentration is very low compared to that of initial styrene (about 2 per cent).

Determinations of the molecular weights for the polymer obtained at 20 mA, in the range 23–93 min, showed that the number average molecular weight remained constant at the mean value of 2550. Thus, the degradation does not form an appreciable amount of polymeric fragments capable of affecting the average degree of polymerization. From Fig. 3 of Part I, it can be seen that as conversions decrease (with current), molecular weights slightly increase. This possibly

means that the degradation mainly involves chains of lower molecular weight, so that the residual polymer has a little higher molecular weight in the range 20–30 mA.

The influence of the concentration of  $\text{LiClO}_4$  on the degradation is shown in Fig. 5 (the electrolyses were continued to complete lithium electrodeposition). The curves confirm the electrochemical nature of the phenomenon which is considerably affected by the ionic strength of the solution. Titration of  $\text{ClO}_4^-$  in the cathodic compartment, after prolonged electrolysis of a  $\text{LiClO}_4$ -PC solution, revealed that most of the anion had diffused into the anodic compartment so further increasing the ionic strength of the anolyte.

Figure 6 shows the kinetic curves obtained using  $\text{TBAClO}_4$  instead of  $\text{LiClO}_4$  and increasing the monomer concentration to 4.0 M. The change of the cation does not significantly modify the curve, simply making the maximum flatter and shifted to longer times. An increased monomer concentration results in a higher conversion, as was expected (see Part I). The side reactions, therefore, seem to be reduced mainly by increases in monomer concentration. Indeed, this increases the rate of propagation and decreases the ratio  $[\text{HClO}_4]/[\text{styr.}]$ , thus limiting the monomer oxidation. The lower extent of the polymer degradation in the solution containing more styrene may possibly be due to the presence of longer chains. In fact, the molecular weight increases from 2700 for 1 M styrene solutions to 3600 for 4 M styrene solutions. This may be sufficient to increase the resistance of the polymer to degradation (or, possibly, depropagation).

Table 1 shows that the  $k_p$  values depend to some extent on the amount of current passed, i.e. they are somewhat affected by the side reactions. However, their mean value ( $k_p = 0.5$  l/mol sec) may still be considered as representative of the velocity of propagation. In  $\text{C}_2\text{H}_4\text{Cl}_2$ ,  $k_p$  is 17.0 l/mol sec at 25° [2] and in  $\text{CH}_2\text{Cl}_2$  is 10.6 l/mol sec at 19° [7]. As noted also by Pepper [2], the  $k_p$  values do not correlate with dielectric constants; therefore, the influence of the solvent on  $k_p$  is more complicated. A contribution to the lower value found in PC may arise from the relatively high  $\text{LiClO}_4$  concentration used, which decreases the percentage of free ions, thus decreasing the propagation

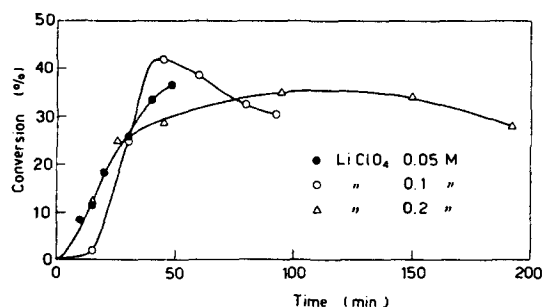


Fig. 5. Kinetic curves as a function of  $\text{LiClO}_4$  concentration. Styrene 1.0 M, 20 mA, 25°.

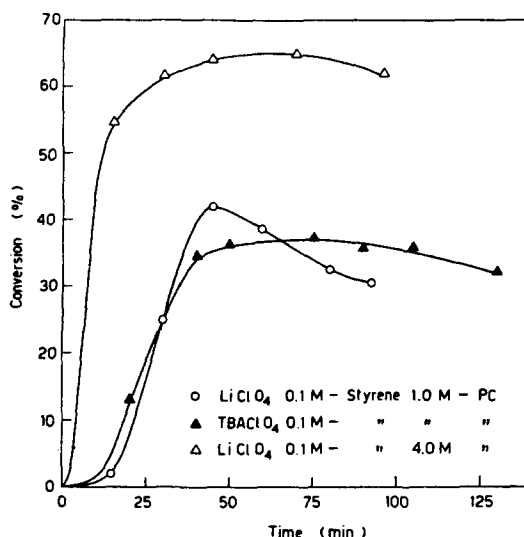


Fig. 6. Influence of the support electrolyte and of monomer concentration on conversions as a function of time.

rate constant. This effect is counterbalanced by the good dielectric properties of PC.

#### Current efficiency

Figures 7 and 8 show the current efficiencies, expressed in moles of polymer per Faraday, as a function of the factors influencing the polymerization. The efficiencies are always less than unity and tend to approach this value only at high monomer concentrations. The existence of marked transfer processes (Part I) should lead to higher efficiencies [12]. Some current may be consumed by impurities and decomposition of solvent, but these effects certainly become of little importance at high currents and monomer concentrations, as shown by the short induction periods observed under these conditions. It is more probable that the side reactions of both monomer and polymer are the main cause of the low efficiencies. These reactions become more important on increasing the temperature, the current and the concentration of  $\text{LiClO}_4$ . On the basis of the efficiencies, the conditions for

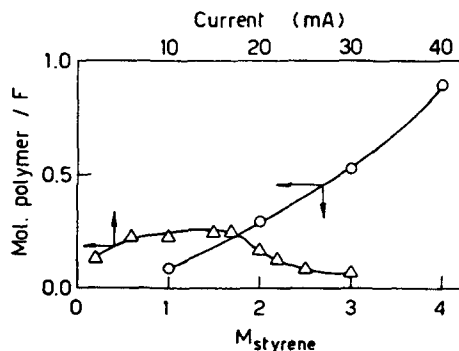


Fig. 7. Current efficiency as a function of monomer concentration and current.

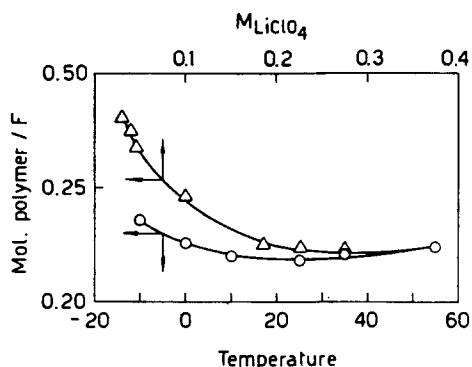


Fig. 8. Current efficiency as a function of temperature and electrolyte concentration.

obtaining the higher styrene conversion seem to be (limiting this assessment to the data reported in this work):  $\text{LiClO}_4$  0.03 M, styrene 4.0 M, 18 mA,  $-10^\circ$ .

#### CONCLUSION

The electroinitiated polymerization of styrene in  $\text{LiClO}_4$ -PC solutions has no termination, since the catalyst is recovered, so that, supposing a very fast initiation step [2], the propagation is rate determining.

The polymerization may be regarded as living, characterized by marked transfer processes and important side reactions of both monomer and polymer.

The solvent greatly influences the polymerization. Indeed, its anodic decomposition creates the catalyst; its high dielectric constant favours monomer transfer

and affects the propagation rate through the formation of some free ions; it determines the instability of  $\text{HClO}_4$  (which is stable in chlorinated solvents at comparable concentrations [2]) and thus favours the parasitic oxidation reaction.

Obviously, further investigation is needed with this solvent and with others having high dielectric constants, since most of the ionic polymerizations studied so far have been carried out in solvents of low or medium D.

**Acknowledgement**—The work was carried out with the financial support of the Consiglio Nazionale delle Ricerche (C.N.R.) of Italy.

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**Résumé**—La polymérisation électrochimique du styrène dans des solutions de  $\text{LiClO}_4$ -PC donne naissance à un polymère vivant à cause de l'absence de terminaison. On observe des réactions latérales importantes, ce qui limite le rendement. Ces réactions sont principalement dues à l'oxydation du monomère par  $\text{HClO}_4$  et à la dégradation du polymère à l'anode. Ceci peut être diminué en augmentant la concentration du monomère. Les courbes de conversion en fonction du temps présentent une période d'induction, une partie linéaire croissante et une partie décroissante. Le traitement cinétique limité à la partie croissante montre que la polymérisation est du premier ordre par rapport aux concentrations en monomère et en  $\text{HClO}_4$ . Les valeurs de  $K_p$  sont considérablement plus faibles que celles trouvées avec  $\text{HClO}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  et  $\text{HClO}_4$ - $\text{CH}_2\text{Cl}_2$ , confirmant ainsi que l'influence du solvant sur ces processus n'est pas simplement électrostatique.

**Sommario**—La polimerizzazione elettroiniziata dello stirene in soluzioni  $\text{LiClO}_4$ -PC ha un carattere vivente, in quanto non presenta evidenza di reazioni di terminazione. Essa presenta condiderevoli reazioni collaterali che limitano le rese. Queste reazioni sono principalmente dovute alla ossidazione del monomero da parte di  $\text{HClO}_4$  ed alla degradazione anodica del polimero. Esse possono essere limitate aumentando la concentrazione del monomero. Le curve conversione/tempo sono formate essenzialmente da un periodo d'induzione, da un tratto crescente lineare e da un tratto decrescente. Dal trattamento cinetico limitato ai tratti crescenti delle curve si rileva che la polimerizzazione è del primo ordine rispetto alla concentrazione di  $\text{HClO}_4$  e del monomero. I valori di  $k_p$  sono notevolmente inferiori a quelli trovati in  $\text{HClO}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  e in  $\text{HClO}_4$ - $\text{CH}_2\text{Cl}_2$ . Questo conferma che l'influenza del solvente su questi processi non è puramente elettrostatica.

**Zusammenfassung**—Die elektroinitiierte Polymerisation von Styrol in  $\text{LiClO}_4$ -Propylencarbonat-Lösungen verläuft nach einem "lebenden" Mechanismus; Abbruchreaktionen treten nicht auf. Jedoch werden Nebenreaktionen beobachtet, die die Ausbeute an Polymerem herabsetzen. Diese Nebenreaktionen sind hauptsächlich Oxidation des Monomeren durch  $\text{HClO}_4$  und Abbau des Polymeren an der Anode. Durch Erhöhung der Monomerkonzentration können diese Nebenreaktionen klein gehalten werden. Zeit-Umsatz-Kurven zeigen eine Induktionsperiode, einen linearen aufsteigenden Teil und einen abfallenden Teil. Im aufsteigenden Teil gehorcht die Polymerisation der 1. Ordnung bezüglich Monomer- und  $\text{HClO}_4$ -Konzentration.  $K_p$ -Werte liegen beträchtlich tiefer als in den Systemen  $\text{HClO}_4$ - $\text{C}_2\text{H}_4\text{Cl}_2$  und in  $\text{HClO}_4$ - $\text{CH}_2\text{Cl}_2$ . Das zeigt, daß der Lösungsmiteleinfluß bei diesen Prozessen nicht nur elektrostatischer Art ist.