CATIONIC POLYMERIZATION OF STYRENE WITH ELECTROCHEMICALLY GENERATED PERCHLORIC ACID—I

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Abstract—The electroinitiated polymerization of styrene in $LiClO_4$–propylene carbonate solutions leads to polystyrene at the anode through the formation of $HClO_4$. The influences on this polymerization of factors such as temperature, current, monomer and electrolyte concentrations, and dielectric constant of the medium, have been examined. The trends of the yields as functions of these factors show some anomalies. In particular, there is a maximum in the yield vs current curve. The molecular weights are relatively low, due to transfer processes, both spontaneous and involving monomer. The propagation proceeds by a cationic mechanism. in which free ions are in equilibrium with ion pairs.

INTRODUCTION

It is generally recognized that electroinitiated polymerization allows control of the rates of the reactions, thus giving the possibility of describing precisely their kinetic behaviour. This holds true particularly when the monomer is not activated by a direct electrode reaction, i.e. when some catalytic species are electrolytically formed (indirect initiation). In this way, the concentration of the catalyst and the reaction rate can be regulated by simply varying the current imposed upon the system.

In the field of cationic polymerizations, Mengoli and Vidotto recently described the possibility of performing a controlled polymerization of butylvinylethers using $NaB(Ph)_4$ as electrolyte which, due to its low oxidation potential, prevents the direct monomer oxidation [1,2]. The same authors described the formation of 9–10 diphenylanthracene radical cations [3] and the subsequent controlled polymerization of n-butylvinylether.

In the first paper of this series [4], the electroinitiated polymerization of styrene in $LiClO_4$–propylene carbonate (PC) solutions has been reported to occur through the anodic formation of $HClO_4$, which is responsible for the initiation. Pepper [5] and Plesch [6] pointed out the reproducibility and the simple kinetics of this polymerization in $C_2H_4Cl_2$ and CH_2Cl_2, respectively. The long dispute between these authors on the mechanism of the process is well known. Pepper favours cationic propagation; Plesch claims that the polymerization proceeds through ester formation, i.e. that the mechanism is pseudocationic. Also in PC the $HClO_4$-initiated polymerization of styrene shows some obscure features; nevertheless, the propagation mechanism has been sufficiently elucidated as well as the influence of some parameters on the process.

This is the first example of an acid-catalysed polymerization made through an electrochemical process. In principle, one can generate similarly protonic acids other than $HClO_4$ as well as Lewis acids, using convenient electrolytes and electrodic substrates. This may result in a useful tool for controlling the reaction rate of cationic polymerizations catalyzed by these substances.

EXPERIMENTAL

Materials

Styrene (Merck) was stored over CaH_2 and distilled under reduced pressure immediately before use. PC (anhydrous, Fluka) was distilled under reduced pressure without additives [7]. "Anhydrous" commercial $LiClO_4$ was freed from water (ca. 1·2 per cent) by melting under vacuum at 250°. This treatment was effective in reducing the water content of $LiClO_4$–PC solutions to about 5 p.p.m., as seen with a Karl Fischer apparatus. Ethylene carbonate (EC) (Merck) was distilled under vacuum over CaO.

Apparatus and technique

Constant current electrolyses (2–30 mA) were performed with a stabilized high voltage power supply (45 mA, 450 V). A two-compartment cell having a low porosity sintered glass disk (in order to minimize diffusion phenomena) and platinum foil electrodes (area 1 cm^2) were employed. Eight cm^3 of solution were put in each compartment and kept under purified nitrogen throughout the electrolysis.

Yields were determined by precipitation with excess methanol. Four redissolutions with CCl_4 and reprecipitations with CH_3OH were needed to obtain a white polymer free from PC.

The manipulations of all anhydrous products and cell filling were initially performed in a dry-box, thus avoiding atmospheric moisture contamination. Subsequently, the insensitivity of the system to water traces was shown and open air manipulative methods were employed.
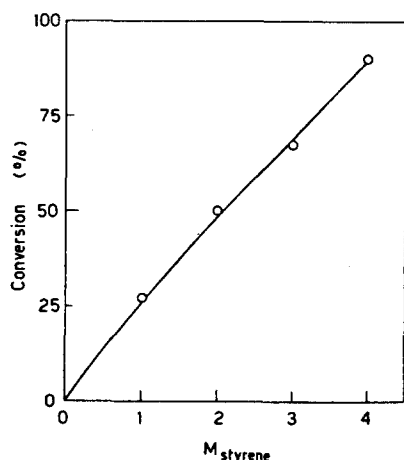
Fig. 1. Formation of polystyrene at various monomer concentrations. Conditions of the electrolyses: $LiClO_4$ 0·1 M, 25 mA, 25°, 1 hr.

Molecular weights were obtained by vapour pressure osmometry.

RESULTS AND DISCUSSION

$LiClO_4$–PC solutions are completely stable in the absence of current, but their electrolysis gives rise to yellow–red oxidation products. As previously reported [4], $HClO_4$ is formed as a consequence of this process. After 1 hr of electrolysis at 25 mA (90 Q), an almost quantitative formation of $HClO_4$ was observed in the anodic compartment of the cell (0·90 m-equiv of H^+ compared with the expected 0·93 m-equiv). The resulting polymer, obtained by adding styrene to the electrolysed $LiClO_4$–PC solution or by adding the monomer to the solution to be electrolysed, was mostly insoluble in PC, thus giving rise to a heterogeneous polymerization. The influences of temperature, current, and monomer and electrolyte concentrations have been examined; the results are reported below. To study the influence of the dielectric constant of the medium, PC–EC solutions have been used.

Influence of monomer concentration

The monomer–polymer conversion is strongly dependent on the styrene concentration (Fig. 1); a four-fold increase in concentration results in an almost corresponding increase in yield, i.e. the reaction rate seems to be linearly dependent on concentration, as found in several cationic polymerizations.

Molecular weights increase slightly with monomer concentration and their values are very low (2700–3600 in the range 1·0–4·0 M), suggesting that they are mainly governed by transfer processes. The number average degree of polymerization is related to the rate of the processes occurring during polymerization by the Mayo's relation:

$$1/\overline{DP} = R_t/R_p + C_M + C_E + C_S[S]/[M],$$

where R_t and R_p are the rate transfer constants for ter-

mination and propagation, C_M, C_E and C_S are the transfer constants to monomer, electrolyte and solvent, respectively. C_E is negligible because the electrolyte does not affect the molecular weights, as seen by varying the concentration of $LiClO_4$. Electrolyses at 10 mA of 0·2 M $LiClO_4$–PC solutions at various styrene concentrations (limiting conversions to 10 per cent), followed by molecular weight determinations, led to Fig. 2. The slope gives directly the transfer constant to solvent, $8·7 \times 10^{-4}$. The intercept ($2·9 \times 10^{-2}$) gives $R_t/R_p + C_M$. It will be later pointed out that the system has no true termination, therefore the value of the intercept gives C_M. The value is quite high, as found in several cationic polymerizations, and accounts for the low molecular weights observed. This transfer process, however, as suggested by Pepper [5] and verified in this work, must be associated with spontaneous transfer, which is independent of monomer concentration and gives rise to terminal double bonds and regeneration of $HClO_4$.

It should be noted that the variation in the dielectric constant (D) caused by the addition of styrene to PC can, to some extent, affect the molecular weight, due to its influence on the association of the growing cations with their counterions. However, Mengoli and Vidotto [1] have demonstrated that this influence does not greatly affect C_M in CH_3CN–$C_6H_5NO_2$ mixtures. Molecular weight measurements in PC–EC solutions (see below) confirm that the degree of polymerization is slightly affected by significant variations of D. Therefore, although the value $C_M = 2·9 \times 10^{-2}$ must be taken with some care, it describes well the importance of transfer to monomer.

Influence of current

The conversion increases linearly with the current flowing through the cell up to about 18 mA (Fig. 3) and then decreases considerably. This is unusual behaviour because the current efficiency (moles of polymer formed per Faraday) is shown to increase with current in other electroinitiated polymerizations. As will be stressed in Part II of this work, side reactions of both monomer and polymer may be responsible for this
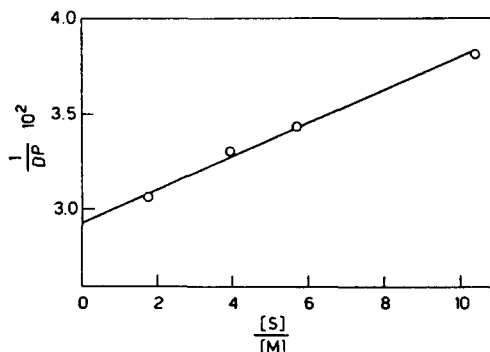

Fig. 2. Dependence of the degree of polymerization on the monomer concentration. $LiClO_4$ 0·2 M, 10 mA, 25°, 10 per cent conversion.
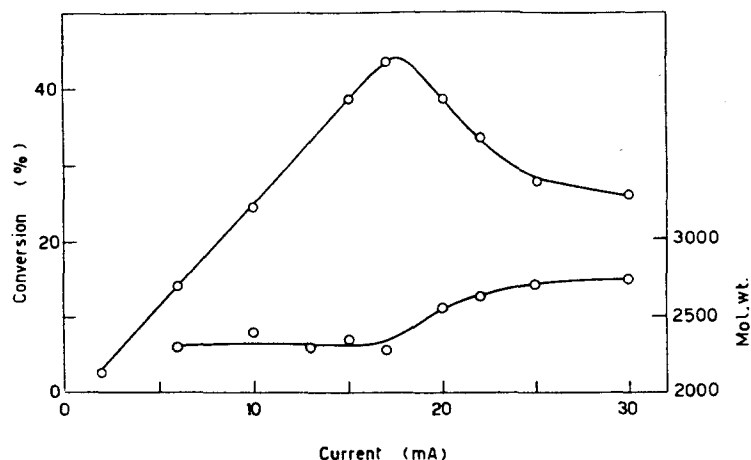
Fig. 3. Formation of polystyrene (ordinate left) and molecular weights (ordinate right) at various currents.
Conditions of the electrolyses: $LiClO_4$ 0·1 M, styrene 1·0 M, 25°, 1 hr.

trend. Also, diffusion phenomena may contribute to decrease the yields. In fact, layers of polymer tend to precipitate on the electrode and thickness increases with current. This may limit the diffusion of the electrolyte towards the electrode to form $HClO_4$ and the diffusion of the latter into the bulk of the solution to initiate the polymerization. However, increases in monomer concentration also increase the thickness of the polymer layers, but this does not affect the conversion (Fig. 1). Therefore, this effect cannot be very important.

Molecular weights also exhibit an anomalous trend with current (Fig. 3). A higher current density should increase the concentration of active centres and this should result in a higher number of chains and, consequently, in lower molecular weights. In this case, too, transfer processes seem to overwhelm any other factor, thus determining the values observed. The values in the range 6–17 mA are slightly lower. This may be due to limitation of the length of some chains by impurities present in solution.

Influence of the electrolyte concentration

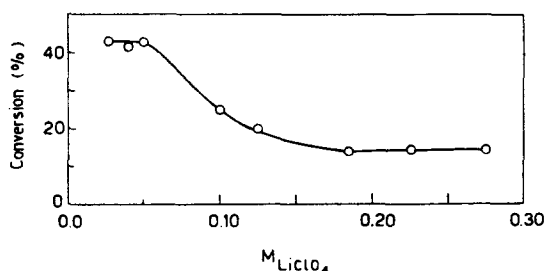The $LiClO_4$ concentration has been varied between 0·03 and 0·275 M (Fig. 4). The conversion was almost

Fig. 4. Formation of polystyrene at various electrolyte concentrations. Conditions of the electrolyses: styrene 1·0 M, 10 mA, 25°, 1 hr.

constant over the range 0·03–0·05 M and then markedly decreased to a value of about 15 per cent which remained constant for concentrations exceeding 0·15 M. This behaviour seems to suggest the hypothesis of propagation through free carbonium ions in equilibrium with their ion pairs:

$$—R^+.ClO_4^- \rightleftharpoons —R^+ + ClO_4^-. \qquad (1)$$
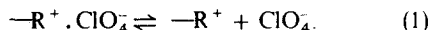
It is evident that an increase in ClO_4^- concentration shifts the equilibrium (1) towards ion pair formation, thus making slower the propagation, which is rate determining in $HClO_4$-catalysed polymerizations [5,6].

Other evidence confirms the cationic mechanism: (a) p-benzoquinone has no great effect on the polymerization [4]; (b) a yellow–red colour developed from the beginning in the anolyte and its intensity increased with time; (c) attempts to copolymerize anodically styrene and acrylonitrile led to polystyrene only; (d) changes in the dielectric constant (obtained adding EC to PC) resulted in a marked variation in the yields.

The last piece of evidence seems to confirm that free carbonium ions propagate in equilibrium with their ion pairs. The high dielectric constant of PC (64·4 at 25°) tends to shift equilibrium (1) to the right, and indeed $LiClO_4$ and $TBAClO_4$ are reported to be completely dissociated in PC [8]. On the other hand, the relatively high $LiClO_4$ concentration, needed to perform continuous electrolyses, tends to shift the equilibrium to left.

It is necessary to comment on the fact that a cationic propagation is not affected by water traces which are certainly present in solution and should immediately kill carbonium ions. The insensitivity of the system to water was taken by Plesch [6] as support for the pseudo-cationic mechanism in chlorinated solvents. Pepper [5] pointed out that this insensitivity implies either a faster initiation compared with monomer protonation by H_2O or, alternatively, that initiation is not rate

determining and, even when reduced by water, remains much faster than propagation. Pepper's considerations seem reasonably applicable to this system. It must be noted, furthermore, that: (a) water traces in electroinitiated polymerizations may be electrolysed in the first stages of the reaction, and (b) Butler [9] pointed out that, in $LiClO_4$-PC solutions, the water is to a large extent in the solvation shell of lithium ions and the remainder is hydrogen bonded to the oxygen of PC.

Molecular weights are fairly constant, within experimental error, with $LiClO_4$ concentration (mean value 2500). This indicates the absence of transfer to the electrolyte and of a limiting effect of ClO_4^- on the chain lengths through ester formation. As pointed out by Pepper [6] and Funt [10], the poor nucleophilicity of ClO_4^- makes very unlikely a termination process based on ester formation.

Influence of temperature

Figure 5 shows the trend of the conversion over the range -10 to $55°$. The marked decrease on increasing the temperature seems to agree with the trend frequently observed in cationic polymerizations [11, 12]. However, Pepper [5] and Plesch [6] report values increasing with temperature for the propagation constant k_p and a faster consumption of styrene with temperature was observed in this system (Part II). Thus, yields increasing with temperature are expected mainly because a temperature increase tends to shift equilibrium (1) towards free ion formation. The decrease shown in Fig. 5 may possibly be explained on the basis of side reactions, their extent increasing with temperature. These reactions will be more extensively studied in Part II.

Molecular weights decrease, as expected, with temperature (Fig. 5) but the variation is not great (2850–1950), thus indicating only a slight effect of temperature on transfer processes. However, the step observed between 25 and 35° is noteworthy; in this range, the activation energy of propagation seems to increase
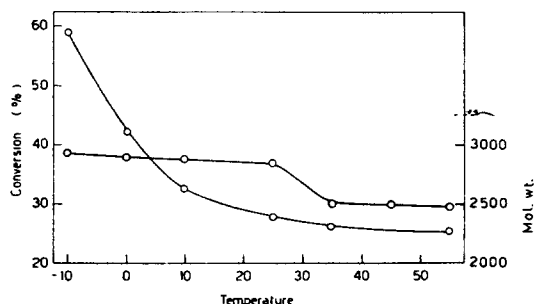

Fig. 5. Formation of polystyrene (ordinate left) and molecular weights (ordinate right) at various temperatures. Conditions of the electrolyses: 25 mA, 1 hr, $LiClO_4$ 0·1 M, styrene 1·0 M.
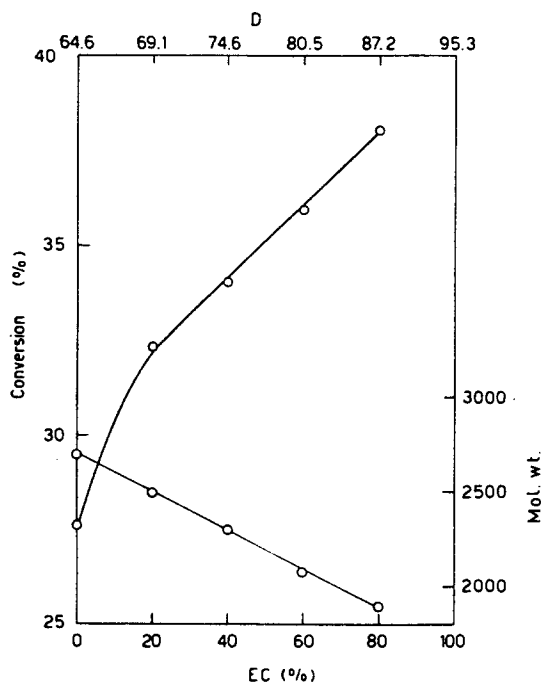

Fig. 6. Formation of polystyrene (ordinate left) and molecular weights (ordinate right) at different dielectric constants. Conditions of the electrolyses: $LiClO_4$ 0·1 M, styrene 1·0 M, 25 mA, 25°, 1 hr.

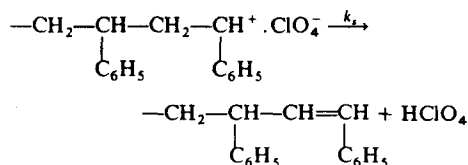appreciably compared with that of the transfer processes.

Influence of dielectric constant

Figure 6 shows the variations of yields and molecular weights caused by varying the dielectric constant of the medium from 64·4 to 87·2 by addition of EC to PC. The values of D for each mixture have been derived from the data of Seward [13]. The increase in conversion is expected, as reported above, due to the favourable influence of an increase of D on the dissociation of ion pairs and on the propagation rate. The initial increase in conversion obtained by adding 20 per cent EC to PC should be noted. This is possibly due to the decrease in viscosity [14] which gives rise to an increase in the conductivities and in the velocities of diffusion.
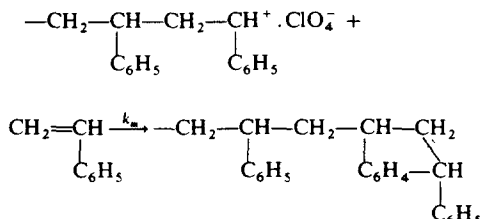
The linear decrease of molecular weight with D can be predicted. Pepper [5] observed that, for these temperatures, the transfer processes to monomer are enhanced by the more polar solvents. Indeed, an increase in D results in an increase of the percentage of free ions and this makes more probable the transfer of the positive charge (less shielded by the counterion) to a monomer.

As previously stated, the polymerization is characterized by two transfer processes, viz. spontaneous and to monomer.

(A) Spontaneous:

$$-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-\underset{\underset{C_6H_5}{|}}{\overset{+}{CH}}.ClO_4^- \xrightarrow{k_s}$$

$$-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-\underset{\underset{C_6H_5}{|}}{CH}=CH + HClO_4$$

(B) To monomer:

$$-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-\underset{\underset{C_6H_5}{|}}{\overset{+}{CH}}.ClO_4^- +$$

$$CH_2=\underset{\underset{C_6H_5}{|}}{CH} \xrightarrow{k_m} -CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-\underset{\underset{C_6H_4-\underset{\underset{C_6H_5}{|}}{CH}}{|}}{CH}-CH_2$$

The first process leads to the formation of terminal double bonds and to the recovery of $HClO_4$. Double bonds were seen by NMR analysis and the regeneration of the catalyst was indicated by adding more monomer, after consumption of the first dose and interruption of the current, and observing the polymerization to continue. The second process gives rise to chains with indanyl end groups.

CONCLUSION

The electrolytic formation of $HClO_4$ in $LiClO_4$–styrene–PC solutions gives rise to a polymerization having several features in common with the conventional polymerization catalysed by $HClO_4$ in $C_2H_4Cl_2$ [5] and CH_2Cl_2 [6]. In particular, the molecular weights are mainly controlled by marked transfer processes (both spontaneous and to monomer). The possibility of recovering the catalyst makes the system non-terminating, i.e. the polymerization seems to have a living character.

Several pieces of evidence suggest that propagation proceeds through a real cationic mechanism in which free ions are in equilibrium with their ion pairs. This equilibrium may be influenced by changing the dielectric constant of the medium and ClO_4^- concentration.

Some features are quite peculiar, such as the maximum in the yields as a function of the current and the considerable decrease of the yields with temperature. These patterns are explicable on the basis of side reactions to be more extensively examined in Part II.

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Résumé—Lors de l'amorçage électrochimique de la polymérisation du styrène dans les solutions de $LiClO_4$–carbonate on observe la formation de $HClO_4$ puis le dépôt du polystyrène sur l'anode. On a examiné l'influence sur cette polymérisation de facteurs tels que la température, le courant les concentrations en monomère et en électrolyte, et la constante diélectrique du milieu. Les rendements en fonction de ces facteurs presentent quelques anomalies. En particulier, il y a un maximum sur la courbe du rendement en fonction du courant. Les masses moléculaires sont relativement faibles, ce qui est dû à un processus de transfert à la fois spontané et impliquant le monomère. La propagation procède par un mécanisme cationique où les ions libres sont en équilibre avec les paires ioniques.

Sommario—La polimerizzazione elettroiniziata dello stirene in $LiClO_4$–propilencarbonato porta ad ottenere polistirene all'anodo attraverso la formazione di $HClO_4$. E' stata esaminata l'influenza su questa polimerizzazione di fattori come la temperatura, la corrente, la concentrazione del monomero e dell'elettrolita, la costante dielettrica del mezzo. Gli andamenti delle rese in funzione di questi fattori presentano alcune anomalie. I pesi molecolari hanno valori generalmente bassi e ciò viene spiegato sulla base di fenomeni di trasferimento di catena, sia spontanei che al monomero. La propagazione avviene tramite un meccanismo cationico, nel quale ioni liberi sono in equilibrio con le rispettive coppie di ioni.

Zusammenfassung—Bei der elektroinitiierten Polymerisation von Styrol in LiClO$_4$-Propylencarbonat Lösungen entsteht Polystyrol an der Anode durch die Bildung von HClO$_4$. Für diese Polymerisation wurde der Einfluß von Temperatur, Stromstärke, Monomer- und Elektrolytkonzentration und Dielektrizitätskonstante des Reaktionsmediums untersucht. Dabei zeigen die Ausbeutetrends als Funktion dieser Faktoren einige Anomalien. So tritt ein Maximum auf bei der Auftragung von Ausbeute gegen Stromstärke. Die Molekulargewichte sind infolge Übertragungsreaktionen relativ niedrig. Diese Übertragungsreaktionen treten spontan auf und Umfassen auch das Monomere. Kettenwachstum verläuft nach einem kationischen Mechanismus, bei dem freie Ionen im Gleichgewicht mit den Ionenpaaren stehen.