

More on the electropolymerization of styrene

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The cathodic reduction of styrene in acetonitrile and tetra-*n*-butylammonium tetrafluoroborate is discussed. A well defined voltammetric wave was obtained at $E_p = -2.8$ V and its study reveals irreversible electron transfer as the first step in the electrochemical reaction. The polystyrene forms on the platinum electrode surface (with a molecular weight of 10^6) and it was possible to find conditions (galvanostatic electrolysis in $\text{CHCl}_3/\text{n-Bu}_4\text{NBF}_4$) where its production rate was increased more than 70 times compared with the first potentiostatic electrolyses.

(Keywords: styrene; electropolymerization; cathodic reduction; electrochemical reduction; cathodic electropolymerization; electrochemical polymerization)

INTRODUCTION

Electrically initiated anionic polymerization of several monomers has been studied and evidence for both polymer formation on the electrode surface¹⁻⁴ and in the bulk of the electrolytic solution⁵⁻⁸ has been obtained. In polar organic solvents, such as dimethyl formamide, polymerization occurs in the homogeneous phase, though the initiating species are formed by heterogeneous electron transfer reactions at the electrodes. In these cases, no living carbanions were formed and polymerization did not continue after cessation of the current. Most of the studies reporting living anion formation have been done in tetrahydrofuran solutions and the concentration of living polyanions has been controlled by the current and by reversal of electrolytic polarity⁸. The effect of electrode material, electric field, voltage, current density, electrolytic medium and other variables when polymerization occurs on the electrode surface have also been previously considered⁹⁻¹¹. The factors controlling the coating thickness, the morphology of the polymer deposit and the adhesion of the polymer formed on the metal substrate were considered by Subramanian⁴.

In this paper, voltammetric and synthetic results for the cathodic reduction of styrene in acetonitrile and tetrabutylammonium tetrafluoroborate on a platinum electrode are reported. The aim of this work was to obtain information about the route followed by polymerization under these conditions and to seek conditions where the polymer production rate was high.

EXPERIMENTAL

Instrumentation

All the electrochemical experiments were carried out with a PAR 173 potentiostat/galvanostat coupled to a PAR 175 universal programmer and an HP7044A X-Y recorder. For electrolyses, an HP6186C d.c. current source and a Fluka 8000A ammeter were used.

Analysis of products used a Perkin-Elmer 72713 i.r. spectrophotometer and a Varian T60A spectrometer.

Characterization of the polymer was performed using a Waters Associates Inc. 200 g.p.c. instrument.

Cells and electrodes

All experiments were carried out in three electrode cells. For voltammetric experiments, the styrene concentration ranged from 5×10^{-3} to 10^{-1} M and the working (5×10^{-2} cm²) and secondary electrodes were platinum wire and helicoidal gauze, respectively. The reference electrode was always Ag/AgNO₃ (0.01 M) in the same electrolytic medium, and it was separated from the working electrode by a Luggin capillary.

For preparative electrolyses, 10 vol% styrene solutions were utilized and the electrodes were 1 cm² platinum gauzes separated by a large-area glass sinter. The catholyte was stirred with a magnetic stirrer and a stream of argon, and it was also protected from the air.

Chemicals

Solutions were prepared from purified acetonitrile (Fluka AG)¹², tetrahydrofuran (Aldrich)¹³, styrene (Aldrich)¹⁴, tetra-*n*-butylammonium perchlorate (Pfaltz)¹³ and distilled water. Tetra-*n*-butylammonium tetrafluoroborate was prepared from tetra-*n*-butylammonium bromide and sodium tetrafluoroborate, and then purified¹⁴.

Analysis

After completion of the electrolysis, the catholyte was reduced in volume and the polymer precipitated from methanol. It was filtered off and purified by dissolution in chloroform and further precipitation with methanol.

The n.m.r. and i.r. analyses confirmed the polystyrene formation and dissolved samples in chloroform were injected into the gel permeation chromatograph using a column temperature of 40°C and an internal pressure of 148 psi.

RESULTS

Cyclic voltammograms were recorded for styrene on platinum electrode in the potential range from 2.5 V to -3.5 V. Figure 1 shows a typical voltammogram of

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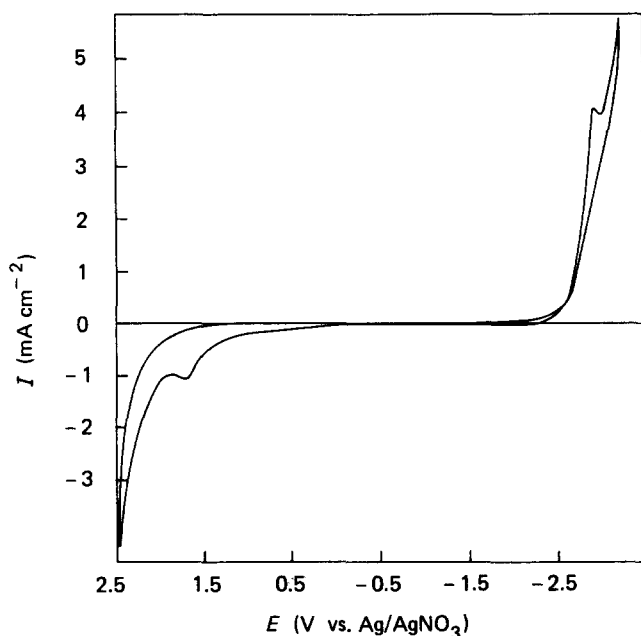


Figure 1 Cyclic voltammetry of 5.2×10^{-3} M styrene in $\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NBF}_4$ (0.1 M) on platinum electrode; $\nu = 0.02 \text{ V s}^{-1}$

5.2×10^{-3} M styrene in $\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NBF}_4$. The oxidation peak potential appeared at +1.7 V and a reduction peak potential was observed at -2.8 V. The peak current for the reduction process is proportional to the square root of the potential scan rate, indicating that the reaction is diffusion-controlled; however, it remains totally irreversible even at the highest sweep rates. The results also showed electron transfer with $n = 1$ (calculated from the cyclic voltammetry) and first order in the monomer ($d \log I_d/d \log c = 1$) as the first step in the reduction process. The I_p current decreased when using repetitive sweeps.

Samples of the product formed in different electrolyses were analysed by n.m.r. and i.r. and the spectra compared well with those of polystyrene standard; n.m.r. bands at 7.0, 6.5 and 1.6 ppm, and i.r. bands at 3120, 3070, 2950, 2900, 1600, 780 and 720 cm^{-1} were observed. Figure 2 reports the gel permeation chromatographs of a further series of electrolyses at various potentials. The molecular weight was found to be high and of the same order of magnitude. Close dispersion values were obtained as can be seen in Table 1.

A series of controlled potential electrolyses were carried out to determine the rate of polymer production and the effect on it of various parameters. The electrolysis potential was fixed at the plateau region and during the electrolysis the visual observation of polymer threads growing on the electrode surface was possible. When the current had decayed to a low value, the catholyte solution was isolated and worked up. The electrode coverage by the polymer formed led to the design of experiments in order to reach conditions where the electrode surface remains active, in order to complete the reaction. Table 2 summarizes the experiments and compares the production rates in the various cases.

Electrolyses at constant potential and constant current showed low values of the polymer production rate. Indeed, the electrolysis current decayed rapidly to a low value and polymer formation stopped. When 'minielectrolyses' (sets of short-time electrolyses, after

each of which the product formed is separated) were performed, and the polymer was recovered after each experiment from the electrode surface, the amount produced increased. The same effect was observed when pulse potential electrolyses were carried out. The highest value for the estimated formation rate (Table 3) corresponds to the constant current electrolyses with chloroform and $n\text{-Bu}_4\text{NBF}_4$ (0.2 M). Under these conditions, a value of $0.13 \text{ mg min}^{-1} \text{ cm}^{-2}$ polymer formation rate with a molecular weight of 10^6 was obtained.

DISCUSSION

Many authors have discussed the mechanism of the electrochemical reduction of the styrene monomer, and it has been found that, depending upon the electrochemical system, the electrochemical reaction can follow one of several mechanisms. The CV results reveal that, under the conditions of this study, the reduction occurs irreversibly at -2.8 V by direct electron transfer to the monomeric species. The reaction order with respect to the styrene concentration was determined to be unity, and from the first voltammetric sweep at high sweep rates a value of unity for overall electron transfer was also obtained. The polymer grows at one of its ends on the electrode surface, as suggested by the decreasing current when using repetitive scans and the visual observation of polymer threads growing on it. The results also reveal that the

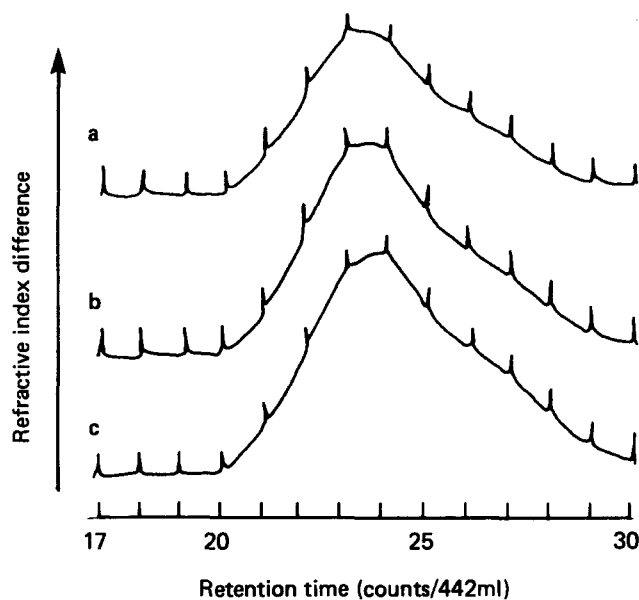


Figure 2 Gel permeation chromatograms of the electrolysis product: (a) potentiostatic electrolysis; (b) pulse potential electrolysis (see Table 2); (c) galvanostatic electrolysis

Table 1 Molecular weight and dispersion values of polystyrene formed under different electrolysis conditions

Electrolyses	Time (h)	Molecular weight		Dispersion, D
		\bar{M}_w	\bar{M}_n	
Constant potential minielectrolyses	6.0	1.79×10^6	526.8×10^3	3.4
Pulse potential	4.8	1.68×10^6	395×10^3	4.3
Galvanostatic minielectrolyses	4.7	1.59×10^6	322.9×10^3	4.9

Table 2 Formation rate values of polystyrene under different electrolysis conditions

Type	Potential (V)	Current (μA)	Duration (h)	Pulse duration (s)		Minielectrolyses Duration (min)	Polymer weight (mg)	Estimated formation rate ($\text{mg min}^{-1} \text{cm}^{-2}$)
				Cathode	Anode			
Potentiostatic	-3.2	-	8.0	-	-	continuous	0.9	-
Potentiostatic	-3.2	-	8.3	-	-	10	32.0	0.064
Pulse	(0.0; -3.2)	-	10.0	2.0	2.0	non-interrupted	-	-
Pulse	(0.0; -3.2)	-	2.3	2.0	2.0	10	5.4	0.039
Pulse	(1.6; -3.2)	-	4.8	1.0	1.0	10	8.9	0.031
Pulse	(1.6; -3.2)	-	6.9	720.0	360.0	18	14.9	0.036
Galvanostatic	-	25.0	7.4	-	-	non-interrupted	3.8	0.009
Galvanostatic	-	25.0	4.7	-	-	10	12.0	0.042
Galvanostatic in chloroform	-	84.0	8.0	-	-	non-interrupted	64.2	0.134

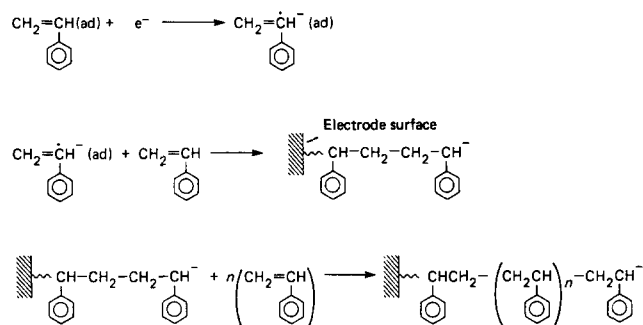
Table 3 Relative increase in the formation rate of polystyrene

Electrolyses	Electrolytic media	Formation rate, V_f ($\text{mg min}^{-1} \text{cm}^{-2}$)	Increase in V_f of the polymer
Continuous potentiostatic (-3.2 V)	$\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NBF}_4$	0.0025	1.0
Potentiostatic minielectrolyses (-3.2 V)	$\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NBF}_4$	0.0640	33.7
Pulses (-3.2 V; 1.6 V)	$\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NBF}_4$	0.0360	18.9
Pulses (-3.2 V; 0.0 V)	$\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NBF}_4$	0.0390	20.5
Galvanostatic minielectrolyses (25 μA)	$\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NBF}_4$	0.0420	22.1
Galvanostatic (84.0 μA)	$\text{CHCl}_3/n\text{-Bu}_4\text{NBF}_4$	0.1340	70.5

reaction is diffusion-controlled (I_p vs. $\delta^{1/2}$ is linear with zero intercept) under the conditions of this study.

All these results are compatible with the sequence shown in Scheme I. It could also be observed that only a few growing nuclei were formed. The termination step was not considered in this study.

Scheme I



Polystyrene was identified as the reaction product and from the first potentiostatic electrolyses only small amounts of the polymer were obtained because of the existence of few growing nuclei and their adsorption onto the electrode surface. Electrolysis using a strongly stirred medium, sets of minielectrolyses, pulse electrolysis, galvanostatic electrolysis and electrolyses using different electrolytic media were performed to increase the polymer production rate. The constant current experiments with $\text{CHCl}_3/n\text{-Bu}_4\text{NBF}_4$ as electrolytic medium showed the

highest value, and it is believed that this is because of the high solubility of the polymer in such a medium, which restores the surface for more monomer to continue polymerizing. After so doing, its production rate increases more than 70 times (Table 3) compared to the initial potential constant electrolyses, in experiments using low currents and low monomer concentrations. Surprisingly, the molecular weight of the polymer formed remains constant (10^6) in all cases.

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