

## **Electrochemically controlled molecular weight of polystyrene production**

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### SUMMARY

It is well known that physical properties such as mechanical and thermal characteristics of a polymer are highly dependent on its molecular weight and molecular weight distribution (MWD). This feature encourages our interest for finding suitable conditions that allow us to control the molecular weight of the formed polymer, by controlling the experimental parameters. We are reporting some results about the electropolymerization of styrene in tetrahydrofuran with tetrabutylammonium tetrafluoroborate and sodium tetraphenylboron as supporting electrolytes. From the electrolyses using tetrabutylammonium tetrafluoroborate two molecular weight distribution curves, showing weight average molecular weight values ( $M_w$ ) of  $3.6 \times 10^5$  -  $1.7 \times 10^6$  for the first and  $5 \times 10^3$  for the second one were observed. When using sodium tetraphenylboron a unique distribution curve was displayed suggesting that the weight average molecular weight of the polystyrene, increases by increasing the current density; the observed MWD being rather low.

### INTRODUCTION

Electropolymerization of styrene has been widely studied (1-7) and the present results indicate that, depending upon the system under study, different mechanistic routes can take place. The electrochemical route of polymerization has the additional advantage of producing a "cleaner" reaction and allowing simplicity in the separation of the products. Furthermore, it has been recognized that the electroinitiated polymerization permits the control of the reaction rates in some cases and molecular weights in others. B.Funt et al. (2) have reported the molecular weight control of polystyrene and poly( $\alpha$ -methylstyrene), at low temperatures.

In the present work the results of the electropolymerization of styrene in tetrahydrofuran in the presence of sodium tetraphenyl boron and tetrabutylammonium tetrafluoroborate at room temperature and different current densities are discussed.

### EXPERIMENTAL

Cyclic voltammetry and polarization experiments were performed using a PAR 173 Potentiostat/Galvanostat coupled to a PAR 175 Universal programmer and an HP 7044A x-y recorder. The electrolyses were carried out with an HP 6186C DC current source, a LRG16FM DC Power Supply and an HP 34750A digital multimeter.

For the analysis of products and characterization of the polymer, a Perkin-Elmer 72713 IR Spectrometer, a Varian T60A NMR Spectrometer and a Waters Associates 200 GPC instrument were used. The GPC was operated

at 40°C and equipped with four columns connected in series and packed with "Styragel"  $10^3$ ,  $10^4$ ,  $10^5$ ,  $10^6$  Å. Chloroform was used as solvent and calibration was made with standard polystyrenes of known molecular weight.

The voltammetric cell was used for both, cyclic voltammetry and polarization experiments. The working electrode was a  $5 \times 10^{-2}$  cm<sup>2</sup> platinum wire surrounded by a 200 mesh platinum gauze counter electrode. All measurements were made against a Ag/AgNO<sub>3</sub> (0.01M) reference electrode.

For preparative electrolyses 10% styrene solutions in THF/supporting electrolyte (0.1M) were used. Two 9 cm<sup>2</sup> parallel platinum gauzes placed in a two compartment cell were the working and secondary electrodes. The catholyte was magnetically stirred and an inert atmosphere was kept during the experiment.

All the experiments were run at room temperature and the concentration of supporting electrolyte was always 0.1M.

Except for the sodium tetraphenyl boron (BDH R.G.) which was used from the bottle and vacuum dried during 24 hours at 80°C, all the other reagents were purified according to the cited references: styrene (8) (MERCK 99%), tetrahydrofuran (9) (MERCK 99%), tetrabutylammonium tetrafluoroborate (10) (SIGMA P.G.), chloroform (11) (MERCK A.G.) and methanol (11) (BDH 99%).

Cyclic voltammograms were monitored within the potential range 0.000-3.500 V, scanning from 50 to 300 mV.s<sup>-1</sup>

Polarization curves of 10% w/v styrene solution and its background were constructed using a point by point procedure between 0.000 V and 250 V.

For controlled current electrolyses in both systems the current densities used were within the range 10-30 mA.cm<sup>-2</sup>, according to the polarization curves.

After completion of each electrolysis the working electrode was washed with chloroform, the resulting solution was poured into the catholyte and then evaporated to a lower volume. The polymer was precipitated from methanol, filtered and purified (12). IR, NMR and GPC analyses were then carried out.

## RESULTS

Cyclic voltammetry of styrene in THF/NaBØ<sub>4</sub> at 200 mV.s<sup>-1</sup> shows in Fig. 1, an irreversible reduction peak at -2.500 V. The voltammetric data for the system THF/n-Bu<sub>4</sub>NBF<sub>4</sub> has been reported (13).

Polarization curves for the reduction of styrene in n-Bu<sub>4</sub>NF<sub>4</sub> predict an increase of the current density (Fig. 2b) compared with its background (Fig. 2a), whilst the styrene, in the presence of NaBØ<sub>4</sub>, tends to depress slightly the background curve (Figs. 3a and 3b).

Electrolyses, followed at different current densities, produce the data shown in Tables I and II.

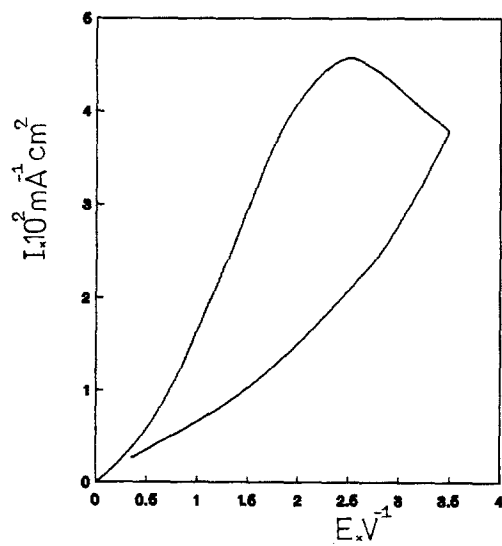


Fig. 1. Cyclic voltammogram of  
2mM Styrene in THF/NaBF<sub>4</sub>  
 $\nu = 200 \text{ mV} \cdot \text{s}^{-1}$

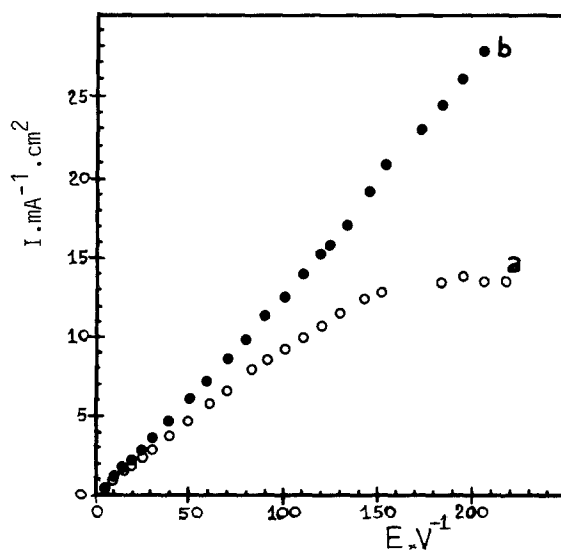


Fig. 2. Polarization curves of :  
○ THF/n-Bu<sub>4</sub>NBF<sub>4</sub> (0.1M)  
● 10% Styrene in THF/n-Bu<sub>4</sub>NBF<sub>4</sub> (0.1M)

Table I. Electrolysis results. 10% Styrene in THF/ $n\text{-Bu}_4\text{NBF}_4$  (0.1M).

EXPERIMENT	CURRENT DENSITY $\text{mA}\cdot\text{cm}^{-2}$	POLYMER OBTAINED (mg)	CONVERSION %	$\bar{M}_n$ $\times 10^{-3}$	$\bar{M}_w$ $\times 10^{-3}$	MWD
1	11.10	20.33	1.12	180	362	2.01
2	13.30	23.40	1.29	219	1,566	7.16
3	20.00	26.72	1.47	158	313	1.98
4	24.40	29.34	1.61	113	336	2.93
5	28.90	32.01	1.76	271	1,808	6.66

Table II. Electrolysis results. 10% Styrene in THF/ $\text{NaB}\bar{O}_4$ (0.1M).

EXPERIMENT	CURRENT DENSITY $\text{mA}\cdot\text{cm}^{-2}$	POLYMER OBTAINED (mg)	CONVERSION %	$\bar{M}_n$ $\times 10^{-3}$	$\bar{M}_w$ $\times 10^{-3}$	MWD
1	10.70	25.60	1.41	2.95	5.60	1.90
2	11.90	28.10	1.55	3.24	6.33	1.96
3	14.10	28.95	1.60	143.00	352.00	2.47
4	15.40	29.40	1.62	271.00	825.00	3.05
5	16.10	31.14	1.72	382.00	951.00	2.49

When the  $n\text{-Bu}_4\text{NBF}_4$  is used as supporting electrolyte the polymer grows to approximately  $\bar{M}_w = 3.6 \times 10^5$  in some cases and  $\bar{M}_w = 1.7 \times 10^6$  in others. Fig. 4 shows the gel permeation chromatograms for several values of current densities and a second distribution curve ( $\bar{M}_w = 5 \times 10^3$ ) is observed at lower current densities. When the Styrene is reduced in the presence of  $\text{NaB}\bar{O}_4$

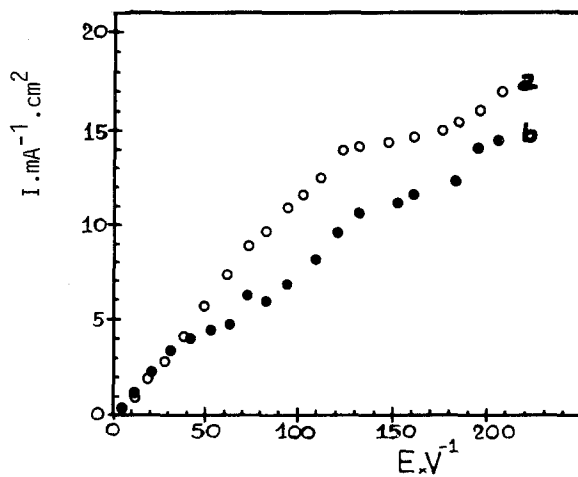


Fig. 3. Polarization curves of:  
 ○ THF /  $NaB_4$  (0.1M)  
 ● 10% Styrene in THF /  $NaB_4$  (0.1M)

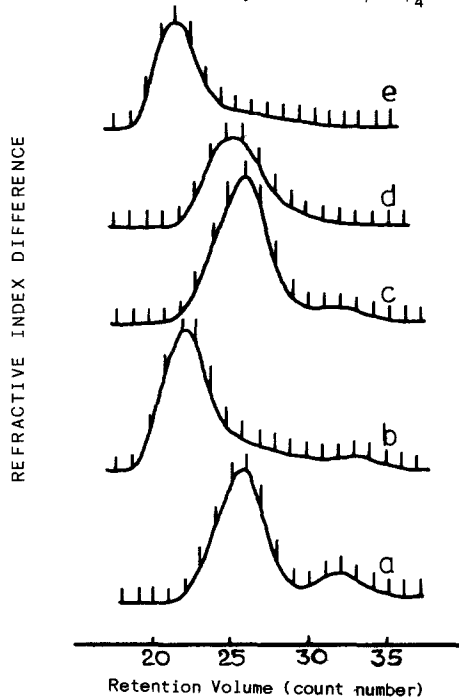


Fig. 4. GPC of the electrolysis product.  
 Styrene-THF/ $n-Bu_4NBF_4$ ,  $I, mA^{-1} \times Cm^2$ ;  
 (a) 11.1; (b) 13.3; (c) 20.0;  
 (d) 24.4; (e) 28.9

a direct proportionality is found between  $\overline{M}_w$  and the current density (Fig. 5), and a single distribution curve is observed.

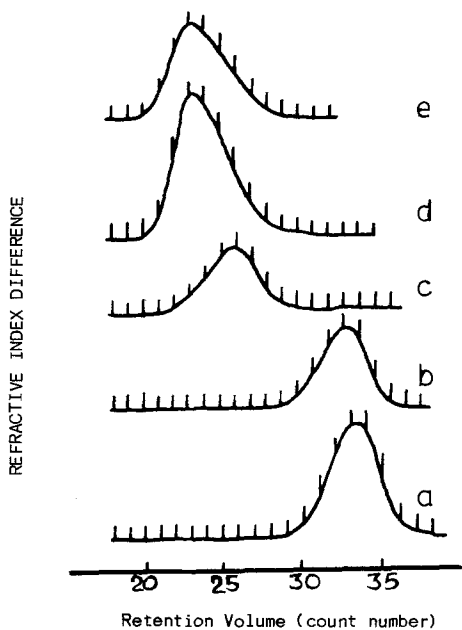
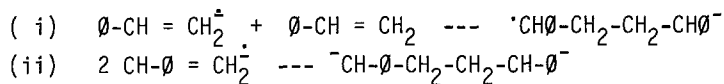


Fig.5. GPC of the electrolyses product, Styrene-THF/ $\text{NaB}^{\ominus}$   
 $I \times \text{mA}^{-1} \times \text{Cm}^2$  : (a) 10.7; (b) 11.9; (c) 14.1; (d) 15.4 (e) 16.1

## DISCUSSION

As it is well known, the electroinitiated polymerization of styrene at a cathode occurs by formation of the ion radical, which undergoes a further reaction to the dianion:



depending on the rate of the heterogeneous initiation and the monomer concentration (1). The presence of proton in the medium inhibits the growth of the polymer chain by destruction of the radical anion and the polyanion formed during the propagation step.

Electrolysis of styrene in THF and  $n\text{-Bu}_4\text{NBF}_4$  results in the depletion of two distribution curves in the GPC when working at low current densities and room temperature. The low molecular weight distribution curve which could be attributable to the destruction of the growing polymer chain by the proton (from the weak supporting electrolyte acid in a very strong basic medium), is less significant as the current density increases. A unique distribution curve is indeed observed at high current densities (over  $25 \text{ mA}\cdot\text{cm}^{-2}$ ) with a  $\bar{M}_w$  ranging from  $3 \times 10^5$  to  $2 \times 10^6$ . From these and previous results (7), it seems that when working in an aprotic medium in the presence of the salt  $n\text{-Bu}_4\text{NBF}_4$  and high current densities, a unique distribution curve is obtained for the electrochemical polymerization of styrene, with a constant value of  $\bar{M}_w$  with a confidence limit of about  $\pm 10\%$ .

When solutions of styrene containing sodium tetraphenyl boron were electrolyzed at various current densities, the GPC showed a proportional variation of the  $\bar{M}_w$  of the polymer with the applied current density (Fig. 6). A single distribution curve was found in the range of current densities studied. Under the working conditions employed we were able to perform electrolyses at current densities ranging from 10 to  $16 \text{ mA}\cdot\text{cm}^{-2}$ . Such values led to molecular weights such as  $5.75 \times 10^3$  and  $9.16 \times 10^5$  at room temperature.

The dispersities were relatively narrow and the polymerization stopped after the cessation of the applied current. These interesting results suggests that further studies have to be done to increase the conversion and the current efficiency. In agreement with the literature (14) NMR analysis of the polymer formed shows that it is atactic.

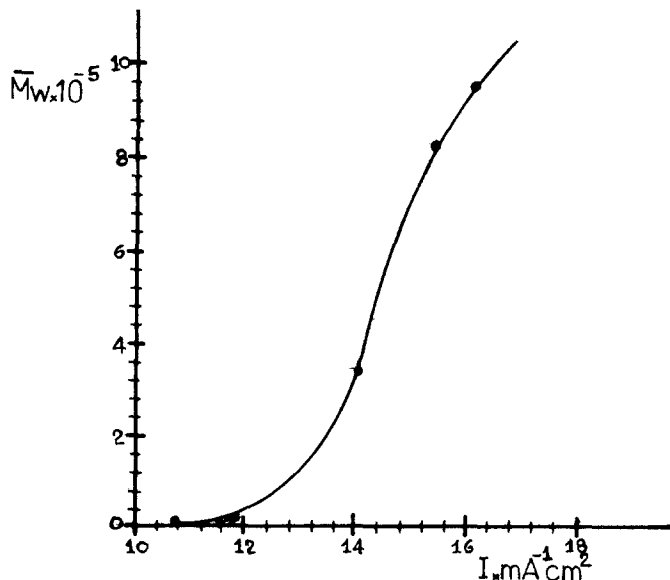


Fig. 6.  $\bar{M}_w$  of the polymer formed vs current density. Styrene-THF- $\text{NaBPh}_4$

**ACKNOWLEDGMENTS**

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