Anodic and cathodic electrochemical 'ring-opening' polymerization of styrene sulphide in organic media

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(Received 19 April 1988; revised 22 July 1988; accepted 4 November 1988)

Poly(styrene sulphide) (PStS) films or soluble polymers were obtained by ring-opening electropolymerization of styrene sulphide (StS) submitted to either a cathodic or an anodic polarization on different metallic electrodes (Pt, Fe, Ni, Al). Linear PStS chains were formed in both cases, and they were made up of about 280 and 170 monomer units respectively. The films obtained by oxidation in CH_3CN on Pt were transparent, plastic and amorphous, whereas those formed by reduction on Fe, Ni or Pt were powdered and amorphous. The conductivity of these films ranged between 10^{-10} and 10^{-11} S cm^{-1}. Their structure was characterized by infra-red, nuclear magnetic resonance and X-ray photoelectron spectroscopy, gel permeation chromatography and X-ray diffraction. Only soluble polymers were synthesized by reduction of StS in dimethylsulphoxide and dimethylformamide.

(Keywords: styrene sulphide polymer; electrochemistry; thin films; ^{13}C nuclear magnetic resonance)

INTRODUCTION

Recently, we have shown that adherent poly(ethylene sulphide) (PES) films could be deposited on a metallic surface either by electrochemical reduction or by electrochemical oxidation of episulphides[1,2]. Semiconductive films were obtained in acetonitrile medium by electro-oxidation of ethylene sulphide (ES) or propylene sulphide (PS)[2]. Similar poly(ethylene sulphide) films were formed also by electro-reduction of ES in dimethylformamide (DMF), dimethylsulphoxide (DMSO), tetrahydrofuran (THF) and acetonitrile (AcN) media[1]. However, in the latter case, we found that the properties of these films were highly dependent on the medium, and furthermore their conductivity and crystallinity were weaker than those observed with polymers obtained by oxidation.

In this work we propose to extend the ring-opening polymerization technique to styrene sulphide in several organic solvents. Similarly to previous results on alkyl episulphides[1,2] we found that two different electrochemical routes (reduction or oxidation) can be used to carry out the electropolymerization of styrene sulphide.

RESULTS AND DISCUSSION

Anodic electropolymerization of styrene sulphide (StS)

Electro-oxidation of 0.1 M StS was carried out on Pt in 50 cm^3 of 0.1 M tetra-n-butylammonium tetrafluoroborate ($TBABF_4$) AcN solution. The oxidation was started at 1.6 V, far below the oxidation of the supporting electrolyte which occurred at about 2.2 V. A transparent, plastic, adherent and homogeneous film was formed after several cycles performed between 0 and 2.5 V (*Figure 1*).

Cathodic electropolymerization of StS

The electro-reduction of StS was carried out on different electrodes (Pt, Fe, Ni and Al) in various solvents DMSO, AcN and DMF containing 0.1 M $TBABF_4$. For all solvents, the reduction of the monomer started on platinum and iron electrodes at about −2.3 V, very close to the salt reduction (−2.2 V). By applying several cyclic polymerization scans at the electrode between 0 and −2.5 V, film formation was only observed with platinum, iron and nickel electrodes in AcN. In DMF or DMSO, no film formation was detected independently of electrode (Pt, Fe, Ni or Al), but a soluble polymer was obtained (*Table 1*).

Physicochemical properties of PStS films

The films formed by anodic polymerization (O-films)

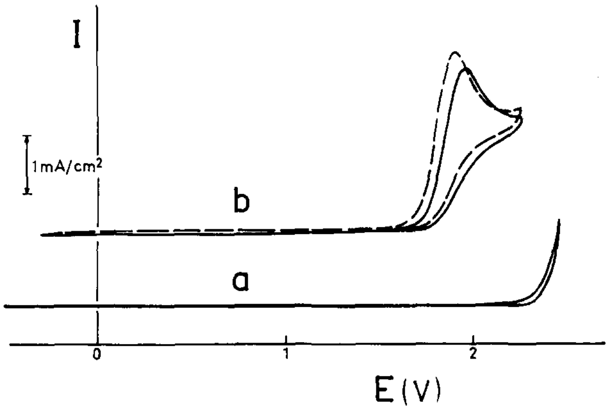

Figure 1 Cyclic voltammograms at a Pt electrode (diam. 2 mm) recorded at 50 mV S^{-1}: (a) in 0.1 M $TBAClO_4$ CH_3CN medium; (b) in 0.1 M $TBAClO_4$ + 0.1 M styrene sulphide CH_3CN medium (--- first scan, —— fifth scan)

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0032-3861/89/040752-04$03.00

Table 1 Anodic electrochemical polymerization of 0.1 M StS+0.1 M TBAClO$_4$ in different solvents

Solvent	Electrode	Film formation	Film aspect	Observations
AcN	Pt	Yes	White powdery deposit	A white powdery polymer precipitate was also formed in the solution
	Fe	Yes		
	Ni	Yes		
	Al	No	–	Only a white powdery polymer precipitated in the medium
DMF	Pt	No	–	Formation of a soluble PStS polymer
	Fe	No	–	
DMSO	Ni	No	–	
	Al	No	–	

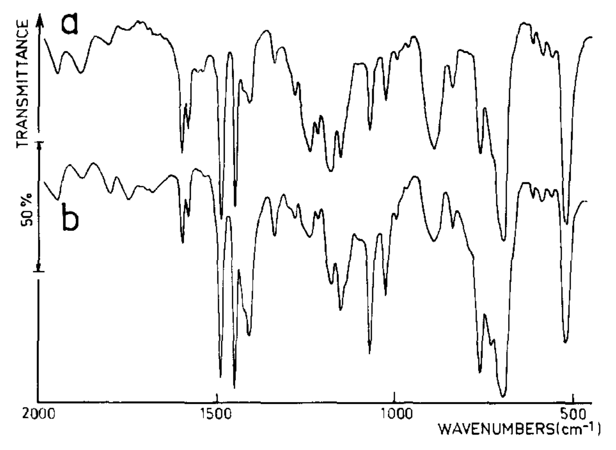


Figure 2 Multiple-reflection infra-red spectra of poly(styrene sulphide) films obtained in 0.1 M TBAClO$_4$+0.1 M StS CH$_3$CN medium: (a) by anodic polymerization; (b) by cathodic polymerization

are transparent, homogeneous, stable and plastic-like. In contrast, the deposits obtained by cathodic polymerization (R-films) are constituted by homogeneous, stable and white powders. These films are soluble in most organic solvents (DMF, THF, DMSO, CH$_3$Cl, CH$_2$Cl$_2$, CCl$_4$,...) but are insoluble in acetone, methanol or AcN. The melting points of O-films range from 240 to 250°C, while R-films melt between 210 and 220°C. The soluble polymers formed in DMF or DMSO media are characterized by intermediate values ranging between 220 and 230°C.

The thicknesses of the O-films are around 8–10 μm and their conductivity is about 10^{-10} S cm^{-1}. The thicknesses of R-films are smaller (2–4 μm) and their conductivity values are about 10^{-11} S cm^{-1}. It is worth while to note that rubber-like films can also be obtained by dissolving O-films in CHCl$_3$ and allowing the solution to evaporate slowly on the platinum surface. A similar result was obtained by Noshay from 'chemical' poly(styrene sulphide) in benzene solution[3].

Film analysis

I.r. spectroscopy. I.r. spectra of O-films and R-films performed on platinum and iron electrodes are shown in *Figure 2* and they are identical to those given by Noshay[3]. No band characteristic of BF$_4$ anion could be detected in O-films, indicating the absence of doping of the film.

X-ray photoelectron spectroscopy (x.p.s.). O-films and R-films have practically the same characteristics, with only one neutral sulphur peak (S 2p$^{3/2}$ binding energy at 163.4 eV) and one C 1S peak at 285 eV. The C/S atomic ratio is close to 8, and no trace of N, B and F could be detected, confirming the i.r. spectra results.

Table 2 Molecular weights of O- and R-films (PStS) determined by g.p.c.

	Oxidation (O-film)	Reduction (R-film)
$\bar{M}_w$	29 086	17 418
$\bar{M}_n$	12 038	5 326
$I = M_w/M_n$	2.4	3.2

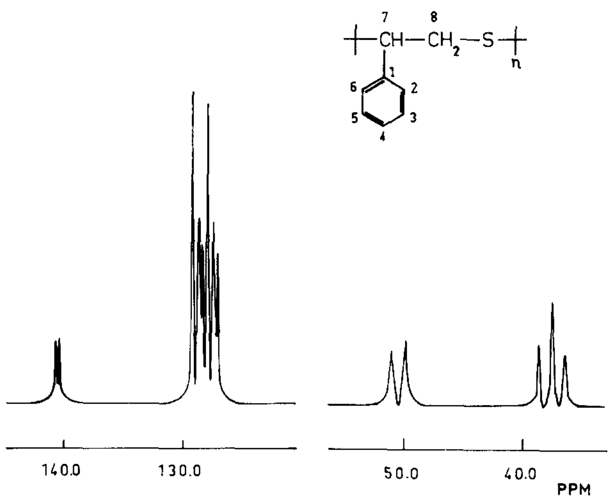


Figure 3 500 MHz ^{13}C n.m.r. spectra of the poly(styrene sulphide)

Gel permeation chromatography (g.p.c.). Number ($\bar{M}_n$) and weight- ($\bar{M}_w$) average molecular weights were determined by g.p.c. in THF solvent as an eluent. The g.p.c. curves were calibrated with standard-mass polystyrene solution. The results concerning polymers obtained by oxidation or reduction of 0.1 M StS in 0.1 M TBABF$_4$ AcN solutions are reported in *Table 2*. It indicates that the O-film chains are constituted of about 280 monomer units, whereas the R-film chains would be shorter with only 167 monomer units. The polydispersity indexes are also greater for the R-film ($I = 3.2$) than for the O-film ($I = 2.4$).

N.m.r. analysis. The ^{13}C n.m.r. spectrum (*Figure 3*) of the polymer synthesized by oxidation of StS in CH$_3$CN medium was carried out at 500 MHz in CDCl$_3$. The same results were found with O- and R-films formed in CH$_3$CN

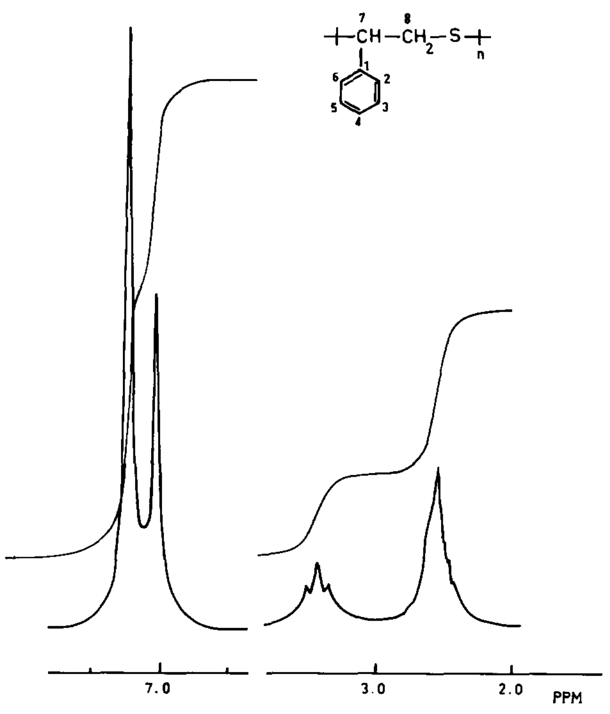
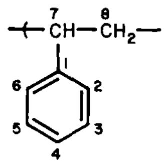


Figure 4 500 MHz ^1H n.m.r. spectra of the poly(styrene sulphide)

and with soluble polymers obtained in DMSO and DMF. The n.m.r. data are in agreement with a polymeric linear structure:



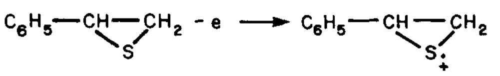
Aromatic carbons are characterized by four doublets centred at 140.5, 128.51, 128.0 and 127.68 ppm corresponding to C1 ($J_{C1-C7H}=30$ Hz), C3 and C5 ($J_{C3-H}=J_{C5-H}=158$ Hz), C2 and C6 ($J_{C2-H}=J_{C6-H}=158$ Hz) and C4 ($J_{C4-H}=160$ Hz), respectively. One doublet and a triplet centred at 50.37 and 37.8 ppm are attributed to C7 ($J_{C7-H}=144$ Hz) and C8 ($J_{C8-H}=141$ Hz), respectively.

The proton n.m.r. spectrum (*Figure 4*) is characterized by two distinct peaks at 7.21 and 7.01 ppm with an intensity ratio of 3/2 corresponding to *meta-para* and *ortho* protons respectively. A similar splitting of the H aromatic signal was also observed by Sigwalt *et al.*[4] for polystyrene (PSt) with degree of polymerization exceeding 23 repeat units. It is worth noting that the same splitting effect is also observed with PStS, which confirms the high degree of polymerization of our polymers.

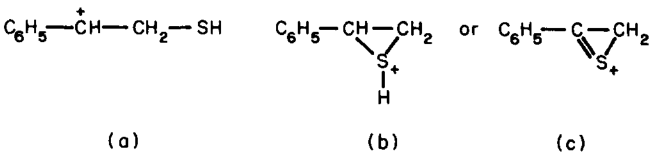
A triplet at 2.02 ppm due to CH and an ill-resolved peak at 2.53 ppm attributed to CH_2 are also found, in agreement with the linear structure of PStS.

Mechanism

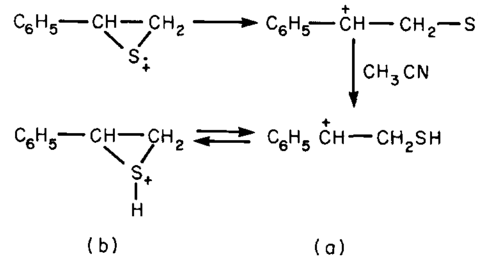
Oxidation. From the voltammetric curves it appears that the monomer is oxidized at a lower potential than that of the oxidation of the electrolyte. We can postulate that in a first step an unstable radical cation is formed, according to:



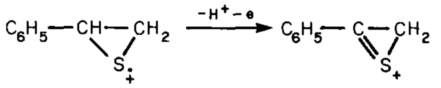
This intermediate undergoes rapid successive reactions (chemically or electrochemically) leading to an irreversible wave, which might involve the formation of different initiating cationic species, such as:



Species (a) and (b) might result from H-atom abstraction from the solvent, which behaves as a hydrogen donor[5] according to the scheme:

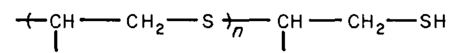


Species (c) is known to be a strong cationic initiator[6], and could be formed after a second electronic transfer, by the reaction:



Then, the ring-opening polymerization occurs following a cationic process, similar to the one proposed for ethylene sulphide[2].

X.p.s. analysis indicates that all S atoms are neutral (S 2p$^{3/2}$ at 163.4 eV), which precludes any doping process. In contrast with ethylene sulphide[2], the termination reaction would be linear and not cyclic, which would correspond to the structure:



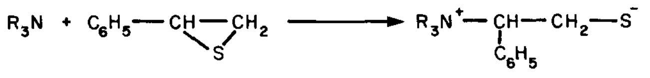
$$\left[\underset{C_6H_5}{\underset{|}{CH}}-CH_2-S\right]_n \underset{C_6H_5}{\underset{|}{CH}}-CH_2-SH$$

An additional proof favouring this cationic polymerization process is given by the absence of e.p.r. signal in the films under study.

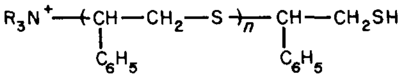
Reduction. When the reduction is carried out in 0.1 M $TBAClO_4$ AcN, DMF or DMSO media, a cathodic barrier occurs at −2.2 V. It is due to the reduction of the ammonium cation, which leads to the formation of a tertiary amine, and of a mixture of alkane and alkene[7] according to the scheme:

$$\overset{+}{N}R_4 + e \rightarrow NR_3 + R^{\cdot}$$
$$2R^{\cdot} \rightarrow RH_{-1} + RH$$

When monomer is added the onset of the reduction wave is virtually unchanged (−2.3 V), and therefore in DMF, DMSO and CH_3CN we can predict a nucleophilic addition of the tertiary amine to the monomer[1,8,9] according to the reaction:



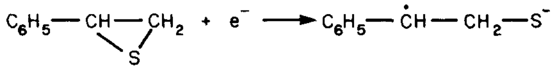
In this case, the polymerization would follow an anionic process, leading to the linear structure:



$$R_3N^+\text{—}(\underset{C_6H_5}{CH}\text{—}CH_2\text{—}S)_n\text{—}\underset{C_6H_5}{CH}\text{—}CH_2SH$$

As the molecular weight of this polymer is very high, this might explain why no x.p.s. signal was observed.

However, we cannot rule out the possibility of monomer reduction, which would yield a powerful nucleophilic species as well, according to:

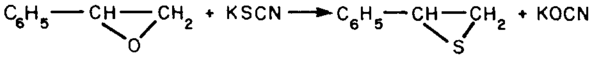


This intermediate would initiate the polymerization process in the same way as previously, and would yield polymer chains without nitrogen.

EXPERIMENTAL

Reagents

Styrene sulphide was prepared from styrene oxide and potassium thiocyanate[10], according to the scheme:



The product distilled at 49–50°C under reduced pressure (0.4 torr). Its purity was tested by g.p.c., using a capillary column (Intersmat IGC 121 FL). Dimethylformamide (DMF), acetonitrile (AcN) and dimethylsulphoxide (DMSO) were purified as previously[1]. Tetra-n-butylammonium tetrafluoroborate ($TBABF_4$) (Fluka) was dried under vacuum at room temperature.

Apparatus and electropolymerization

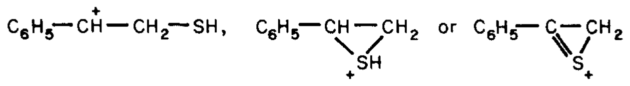
The electrochemical cell was made of a classical three-electrode mounting, connected to a PAR model 173 potentiostat, driven by PAR model 175 pilot. A Sefram model TGM 164 *XY* recorder was utilized. To carry out the electropolymerization we used a platinum working electrode made of a rectangular glass slide (10 x 25 mm) coated with a thin platinum layer (500 nm); the nickel, iron and aluminium working electrodes were made of massive metal plates (35 x 17 mm). The counter-electrode was a platinum wire placed inside a sintered glass tube dipping into the solution, and the reference electrode was a silver wire in contact with a saturated silver chloride solution, separated from the electrolysis solution by a sintered glass.

Analysis techniques

X.p.s., X-ray diffraction and resistivity measurements were performed as previously described[1]. Infra-red spectra were performed with a Nicolet model 60 SX *FT*i.r. spectrometer. ^{13}C and ^1H n.m.r. spectra were recorded with a 500 MHz Brucker apparatus, using $CDCl_3$ and tetramethylsilane (TMS) as internal references. Molecular-weight distributions were determined by g.p.c. in THF on a Waters Associates instrument fitted with μ-Styragel columns (10^5, 10^4, 10^3, 500 and 100 Å) calibrated with polystyrene standards.

CONCLUSIONS

In this study we have shown that styrene sulphide could be polymerized by either an anodic or a cathodic process. The molecular weights of polymers obtained by anodic polarization are higher than those from polymers formed by reduction, but in both cases all spectroscopic data confirm that the poly(styrene sulphide) chains are linear. By oxidation, the polymerization is triggered by cationic species which could be:



The cathodic process, which might involve reduction of both the ammonium salt and monomer, would yield two possible nucleophilic reagents such as:

$$N(Bu)_3 \quad \text{or} \quad C_6H_5\text{-}\dot{C}H\text{-}CH_2\text{-}S^-$$

which could initiate the polymerization. Work is currently in progress to identify the nature of these intermediates.

ACKNOWLEDGEMENT

We gratefully thank Professor J. P. Vairon, Université Paris 6, for carrying out g.p.c. measurements on our polymers.

REFERENCES

1 Aeiyach, S., Delamar, M., Dubois, J. E. and Lacaze, P. C. *Polymer* 1986, **27**, 1273

2 Aeiyach, S., Dubois, J. E. and Lacaze, P. C. *J. Electroanal. Chem.* 1986, **207**, 117

3 Noshay, A. and Price, C. C. *J. Polym. Sci.* 1961, **54**, 533

4 Benaboura, A., Deffieuxanel, A. and Sigwalt, P. *Makromol. Chem.* 1987, **188**, 21

5 Bridger, R. F. and Russel, G. A. *J. Am. Chem. Soc.* 1963, **85**, 3754

6 Lautenschlaeger, F. *J. Macromol. Sci. Chem.* (*A*), 1972, **6**, 1089

7 Dubois, J. E., Desbène-Monvernay, A. and Lacaze, P. C. *J. Electroanal. Chem.* 1976, **72**, 353

8 Nicco, A. and Boucherou, B. *Eur. Polym. J.* 1970, **6**, 1477

9 Cooper, W. *Br. Polym. J.* 1971, **3**, 28

10 Steward, J. *J. Org. Chem.* 1963, **28**, 596