

Electrochemical ring-opening polymerization of ethylene sulphide by cathodic polarization

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Poly(ethylene sulphide) (PES) films adherent to platinum surfaces are obtained by cathodic polarization in organic media (acetonitrile, dimethylformamide or tetrahydrofuran) with $N(\text{Bu})_4\text{ClO}_4$ as background electrolyte in the presence of 0.13 M ethylene sulphide (ES). Two types of polymer are obtained depending on the medium and the polarization conditions: (a) thin 1–2 μm elastomer films in tetrahydrofuran, and in the two other solvents at moderately negative potentials; (b) powdery deposits on the elastomer film (10–20 μm thickness) in acetonitrile and dimethylformamide at high negative potentials ($-3.5 \text{ V} < E < -2.5 \text{ V}$). Unlike the polymer films prepared by anodic polarization, which are partially oxidized ($\text{S}^{\delta+}$) and doped by ClO_4^- ions, these polymer films are devoid of any doping and do not contain positively charged sulphur atoms.

(Keywords: electropolymerization; thin film; poly(ethylene sulphide); crystalline; X-ray diffraction)

INTRODUCTION

Ethylene sulphide (ES) easily undergoes ionic polymerization in the presence of acid or basic catalysts; the latter lead to higher reaction rates and yield polymers with higher molecular weight¹.

Several anionic initiators such as naphthalene-sodium and sodium hydroxide at low concentrations^{2–4}, tertiary amines, oxides, carbonates, sulphides and miscellaneous metal salts, particularly of zinc and cadmium^{5,6}, lead to the formation of partially crystalline poly(ethylene sulphide).

Ring-opening polymerizations may also be electrochemically initiated. Previous work from this laboratory has shown that poly(tetramethylene oxide) films are formed on anodically polarized Pt electrodes in tetrahydrofuran (THF)⁷. More recently, three of the present authors showed that crystalline poly(ethylene sulphide) (PES) doped with anions may be obtained by electrochemical oxidation of ethylene sulphide, which results in the opening of the episulphide bond⁸.

In the present work, a new type of partially crystallized PES is obtained by electrochemical reduction of ethylene sulphide.

RESULTS AND DISCUSSION

The PES films are formed on the surface of platinum by electrochemical reduction of ES dissolved in organic solvents (dimethylformamide (DMF), acetonitrile and THF), either at room temperature or at -30°C , with 0.1 M tetrabutylammonium perchlorate (TBAP) as background electrolyte. The platinum electrode is either polarized at a constant potential value, or submitted to a cyclic voltage.

Potentiodynamic electroreduction of ethylene sulphide

The electrochemical reduction of TBAP on a platinum microelectrode in acetonitrile with water concentrations

ranging from $5 \times 10^{-3} \text{ M}$ to 10^{-2} M begins at ca. -2 V . When 10^{-2} M or 10^{-1} M ES is added, the electrochemical curve displays no change irrespective of water concentration. This shows that ES is not directly reduced in such conditions. Film formation occurs only for ES concentrations greater than $5 \times 10^{-2} \text{ M}$.

In all cases an attempt was made to detect the intermediate species formed in the course of the polymerization process by performing cyclic potential sweeps at 0.5 V s^{-1} . No signal was detected, which indicates that the initiation is indirect.

In the case of a platinum plate, the polymer film is obtained by submitting the platinum electrode to several potential cycles between 0 V and a negative potential value, E_1 .

When $E_1 = -2.5 \text{ V}$, a very thin, transparent, slightly brown elastomer-like deposit forms on the electrode surface. Films that display the same characteristics were obtained in the three solvents at both temperatures. The platinum electrode was passivated owing to film formation after three potential cycles.

When the potential cycles were carried out beyond -2.8 V ($E_1 \leq -2.8 \text{ V}$), other experimental conditions being similar, a bilayered film was obtained in DMF or acetonitrile. The lower layer was transparent and elastomer-like, whereas the upper layer consisted of a white powder. A white solid with the same chemical composition as the upper layer was precipitated simultaneously from the solution. In THF under such conditions a film similar to that obtained with $E_1 = -2.5 \text{ V}$ was formed. In the three solvents at both temperatures, the platinum electrode was totally passivated after 4 potential cycles.

Potentiostatic polymerization of ethylene sulphide

In this case the platinum electrode was maintained at -2.8 V for a few minutes with the same solvents and at the same temperatures as previously.

The polymer films obtained in DMF or acetonitrile at both temperatures were similar to those formed in potentiodynamic experiments. In both solvents precipitation of a white powder occurred simultaneously with film formation. The current density decreased very rapidly and became negligible within a few seconds.

In THF the potentiostatic polarization led to the same results as potential sweeps between 0 and -2.8 V (elastomeric films).

Physicochemical properties of PES films (Table 1)

All films obtained at both temperatures with potential cycles between 0 and -2.5 V in DMF, acetonitrile or THF were transparent elastomers. Their melting point ($190 \pm 2^\circ\text{C}$) was similar to that of poly(ethylene sulphide) prepared by chemical polymerization with initiators such as RNH_2 , NaOH or NaOC_2H_5 (ref. 1). They are quite adherent to platinum even after ultrasonic rinsing in acetone.

The white powdery deposit formed in potential cycles with $E_1 \leq -2.8$ V, or with a constant polarization at -2.8 V in DMF or acetonitrile did not adhere to platinum. Ultrasonic rinsing in acetone resulted in this case in film detachment. The melting point of this deposit ($220 \pm 2^\circ\text{C}$) corresponded to that of chemically polymerized PES with a tertiary amine as initiator⁶.

In THF under these conditions, the films were elastomers with melting point $200 \pm 2^\circ\text{C}$, and adhered to platinum even when submitted to ultrasonic rinsing in acetone.

All these compounds were stable when exposed to air and insoluble in usual organic solvents. The resistivity of the elastomeric films as well as that of the powdery deposits was of the order of $5 \times 10^9 \Omega \text{ cm}$. The thickness of the films was $1-2 \mu\text{m}$ whereas that of the powdery deposits varied between $10-20 \mu\text{m}$. The films obtained by electrochemical oxidation⁸ had thickness of $0.5-2 \mu\text{m}$ and resistivity of $\sim 5 \times 10^8 \Omega \text{ cm}$.

Analysis of the polymers

Infra-red spectroscopy. The i.r. spectra of the polymers formed by electroreduction of ES (Figure 1a) were identical to that of chemically prepared PES⁹ but differed from those of polymers obtained by anodic polymerization (Figure 1b).

The bands located at $1200-1100 \text{ cm}^{-1}$ and $700-600 \text{ cm}^{-1}$ are distinctive of C-S bond valence vibrations. The strong and wide bands due to the perchlorate anion at 1090 and 620 cm^{-1} that were observed with the anodically polymerized films (Figure 1b) were not

Table 1 Characteristics of PES films synthesized in different organic solvents at -30°C and 25°C

Polarization mode	Solvent		
	DMF	Acetonitrile	THF
Potential sweeps 0 to -2.5 V	Elastomer (m.p. 190°C)	Elastomer (m.p. 190°C)	Elastomer (m.p. 190°C)
Potential sweeps 0 to -3.0 V	Elastomer + powder (m.p. 220°C)	Elastomer + powder (m.p. 220°C)	Elastomer (m.p. 200°C)
Constant potential	Elastomer + powder (m.p. 220°C)	Elastomer + powder (m.p. 220°C)	Elastomer (m.p. 200°C)

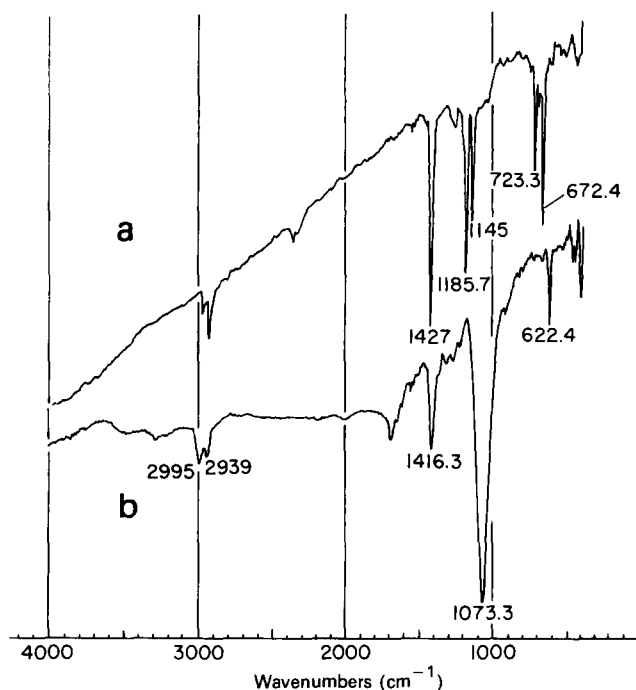


Figure 1 Multiple reflection i.r. spectra of PES films obtained by polarization of a platinum electrode in $\text{CH}_3\text{CN} + (0.1 \text{ M}) \text{N}(\text{Bu})_4\text{ClO}_4 + (0.13 \text{ M}) \text{ES}$. (a) Cathodic polarization ($E = -2.8$ V); (b) anodic polarization ($E = +2.8$ V)

observed in the case of the cathodically prepared polymers.

X-ray photoelectron spectroscopy. The XPS spectra of the polymers (Figure 2) show that the C/S atomic ratio is close to 2. No nitrogen and no chlorine were detected; traces of oxygen (about 1 oxygen atom per 100 carbon atoms) were observed in each experiment. It is difficult to assign oxygen at this low concentration either to atmospheric contamination or to OH end groups incorporated in the polymer chain.

The spectra reveal the presence of only one type of sulphur atoms (neutral sulphur; S 2p binding energy 163.4 eV) whereas in anodically prepared polymers two forms of sulphur are present (neutral sulphur and positively charged sulphur at 167.4 eV compensated by perchlorate anions that have entered the polymer matrix).

The i.r. and XPS analyses clearly show that no such doping occurs when the polymerization is effected by electroreduction.

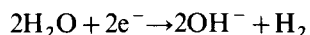
X-ray diffraction. The X-ray diffraction diagram of films obtained in DMF and acetonitrile displays strong peaks at 10.7 , 4.53 and 4.25 \AA and less intense peaks at 3.62 , 2.67 and 2.3 \AA (Figure 3), which indicates that the polymers are microcrystalline compounds. Similar results were reported by Sigwalt *et al.*² for this type of polymer prepared by anionic polymerization. The insolubility of these compounds in usual solvents is probably due to their crystallinity².

Polymerization mechanism

The fact that two different types of PES film (elastomer and powder) are obtained depending on the solvent and the applied potential may be accounted for by the existence of two different initiation processes.

When the potential is between -2.5 and -3 V in an organic solvent containing tetrabutylammonium per-

chlorate and traces of water, two electrochemical reactions may occur:



or

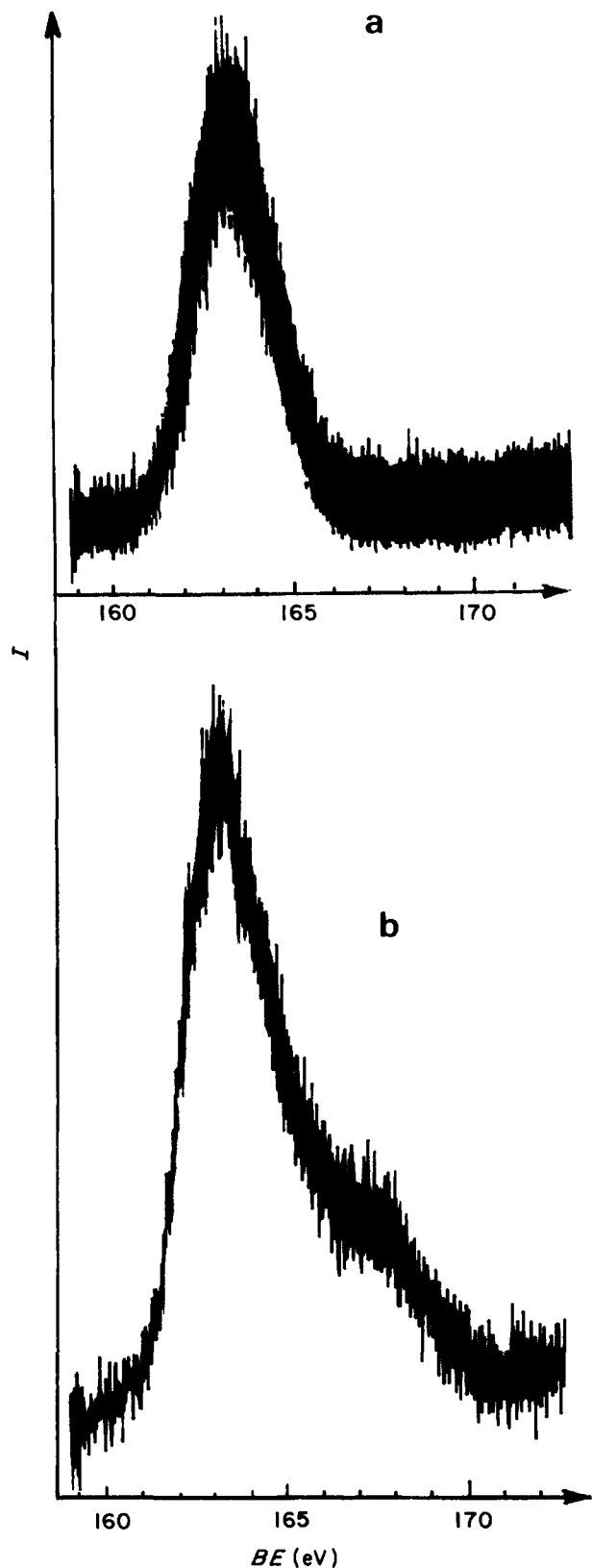
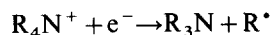


Figure 2 XPS spectra of PES films obtained under the same conditions as in Figure 1. (a) Cathodic polarization (S(0)); (b) anodic polarization (S(0) + S⁴⁺)

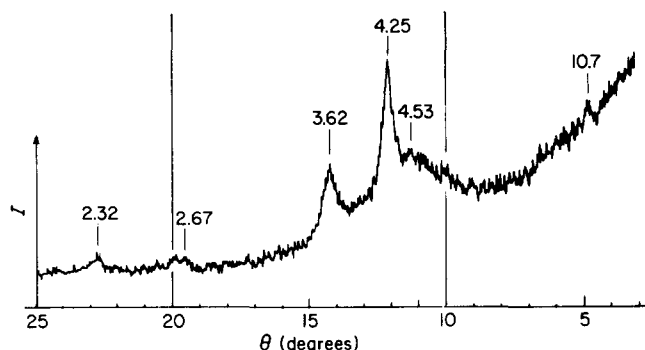


Figure 3 X-ray diffraction pattern obtained from a powdery PES deposit on platinum surface (same electrochemical conditions as in Figure 1a)

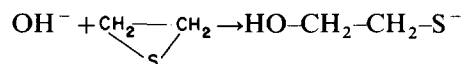
leading to the formation of OH⁻ and R₃N (ref. 10). At moderately negative potential, water reduction is predominant, whereas at lower potential ammonium reduction occurs.

Tertiary amines and OH⁻ may initiate ES polymerization: however, the former are efficient only in polar media such as DMF or acetonitrile, and not in THF, which is insufficiently polar³.

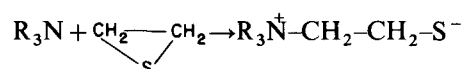
Elastomer films were obtained at moderate potentials in DMF and acetonitrile, and in THF in all the conditions studied, which suggests that the elastomer films result from OH⁻ initiation, whereas R₃N initiation yields powder deposits.

Reductions performed in the presence of high water concentrations (~0.1 M) indeed show that only the elastomeric film is formed in such conditions. If the concentration of water is greater than 0.1 M (~0.2 M) the polymerization no longer occurs: in such a case water is an inhibitor.

Thus the two initiation reactions are probably the following⁶:



for elastomer films, and:



for the powder deposits.

The molecular weights of these polymers are probably high because the melting point is 220°C. As a consequence, the bulk concentration of nitrogen is low: this accounts for the fact that i.r. spectroscopy gives no evidence of C-N bonds and that no N1s XPS signal is observed with the powdery polymers.

EXPERIMENTAL

The electropolymerization cell was made of a classical three electrodes mounting, connected to a PAR model 173 potentiostat driven by a PAR model 175 pilot, and to a Sefram model TGM 164 XY-recorder.

For i.r., XPS, X-ray diffraction and resistivity measurements, the working electrode was made of a rectangular glass slide (10 × 25 mm). One of its faces was coated with a thin (about 500 nm) platinum layer deposited by cathodic sputtering, using a Balzers-Sputron II with a platinum target (Balzers, purity 99.9%).

For electrochemical measurements, a platinum micro disc electrode was used (2 mm diameter, Tacussel EDI); the platinum disc was polished with diamond paste before each experiment and rinsed in acetone (Prolabo Rectapur) with ultrasonic stirring.

The counter electrode was a platinum wire (0.8 mm diameter, 40–50 mm length), placed inside a sintered glass tube dipping into the solution. For each solvent, the reference electrode consisted of a silver wire dipping into a saturated silver chloride solution containing the supporting electrolyte and placed inside a sintered glass tube in contact with the electrolysis solution.

Before each experiment, the solution was deaerated by flushing with dry argon and then was maintained under low argon over-pressure.

XPS analysis was carried out with a VG Escalab MKI spectrometer (MgK α source, 50 eV energy, under pressures in the 10⁻⁹ mbar range). X-ray diffraction spectra were obtained by the Debye-Scherrer method using a Philips diffractometer and the CoK α emission ray. Resistivity and thickness of the films were evaluated by measuring the R and C parallel components of a platinum/film/mercury sandwich. A Wayne Kerr Bridge (Autobalance Universal Bridge B 642) was used and a mean value of $\epsilon = 8$ was assumed¹¹.

Ethylene sulphide (Fluka) was dried over calcium hydride, and then distilled in nitrogen atmosphere before each experiment.

Acetonitrile (RP Prolabo), dried on silicagel for several days, was distilled a first time on P₂O₅ under a nitrogen current and then a second time over calcium hydride. DMF (Prolabo) was dried over phosphorus(V) oxide, then treated with potassium hydroxide and distilled over calcium hydride under low pressure of argon. THF (Merck-Schuchardt) was treated with potassium hydroxide pellets for several days, refluxed over calcium hydride for 24 h and finally distilled under nitrogen.

Tetra-n-butylammonium perchlorate and tetra-n-

ethylammonium perchlorate (Fluka) were dried under vacuum and at room temperature before use.

The water concentration was measured by Karl Fischer titration.

CONCLUSION

The polymerization of ethylene sulphide can be electrochemically induced in aprotic media by anionic initiators resulting from reduction reaction such as OH⁻ from residual water or R₃N from ammonium ions.

The polymeric deposits thus obtained differ from those obtained by anodic polarization: they contain no positive charges on sulphur atoms and, consequently, are not doped with perchlorate anions. They are also less crystalline and display a slightly higher resistivity. The experimental conditions seem to have a greater influence on the polymer structure for cathodic than for anodic polarization.

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