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REPORT

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CYCLIC VOLTAMMETRY OF POLYSULFIDE (THIOKOL) PREPOLYMERS AND RELATED COMPOUNDS

Waldemar Mazurek

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POSTAL ADDRESS: Director, Materials Research Laboratories
P.O. Box 50, Ascot Vale, Victoria 3032, Australia

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AUTHOR(S)	CORPORATE AUTHOR
MAZUREK, Waldemar	Materials Research Laboratories P.O. Box 50, Ascot Vale, Victoria 3032

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The cyclic voltammetry of polysulfide prepolymers and related monomeric sulfur compounds has been examined at a gold wire electrode. Electrode processes have been assigned to the polysulfide prepolymers on the basis of those occurring in the model compounds. It has been shown that the technique may be used in the quantitative determination of sulfur or in the determination of prepolymer content in a commercial formulation.

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CONTENTS

CYCLIC VOLTAMMETRY OF POLYSULFIDE (THIOKOL) PREPOLYMERS AND RELATED COMPOUNDS

1. INTRODUCTION

Polysulfide polymers form durable, flexible sealants which are resistant to fuels. They have found widespread application in the marine and construction industries [1,2] and they are considered essential materials for use in all types of military aircraft.

The prepolymers have the general formula:

$$H[S.CH_2.CH_2.O.CH_2.O.CH_2.CH_2.S]_nH$$

with average molecular weights in the range of 1000 to 8000 [1,2]. Crosslinking agents are also incorporated to impart solvent resistance. Polymerization of the prepolymer is usually accomplished through oxidation of the terminal thiol groups to form disulfides. In some cases these oxidations reactions are known to involve the formation of intermediate compounds [1,3] but few have been documented. Thus a knowledge of the various redox reactions which occur in such oxidation processes is necessary to understand the chemistry of the curing mechanism.

In addition, associated with the use of the polysulfide sealants by the RAAF is the problem of long term storage of the formulated prepolymers which over a period of time become very viscous and hence unusable. Characterisation of the reactions typical of the prepolymer functional groups is consequently very relevant to this problem. Because redox reactions are fundamental to the behaviour of thiols/disulfides, electrochemical techniques are most appropriate to these compounds.

Although the electrochemistry of low molecular weight, monomeric thiols and disulfides has been extensively reported, only one polarographic study has been reported for polysulfides [4]. In the present work, the cyclic voltammetry of thiols, disulfides and a trisulfide is examined at a gold electrode and comparisons are made with polysulfide (Thiokol) prepolymers. Although the polysulfide prepolymers contain essentially disulfide and thiol functional groups, trisulfides are generated as intermediates in the manufacturing process [1]. The purpose of including a trisulfide in the present work is to determine whether it can be electrochemically distinguished from disulfides, and if so, whether such compounds can be detected in polysulfide prepolymers.

Earlier studies on the electrochemistry of thiols and disulfides were carried out at a mercury electrode on cysteine and cystine. The reduction of the cystine disulfide bond, in aqueous solution, was found to be electrochemically irreversible [5-8] with the overall reaction being:

$$\mathrm{RSSR + 2e + 2H^+ \rightarrow 2RSH} \qquad (1)$$

The data supports evidence for a reaction with the electrode:

$$\mathrm{RSSR + Hg \rightleftharpoons Hg(RS)_2} \qquad (2)$$

$$\mathrm{Hg(RS)_2 + 2e + 2H^+ \rightleftharpoons Hg + 2RSH} \qquad (3)$$

For the case of cystine both reactions (2) and (3) are reversible and are manifested as a kinetically controlled prewave. At more negative potentials, process (1) is observed as an irreversible main wave [7].

Similar behaviour is observed in the electrochemistry of thiols at a mercury electrode [9]:

$$\mathrm{RSH + Hg \rightleftharpoons HgRS + H^+ + e} \qquad (4)$$

$$\mathrm{2HgRS \overset{fast}{\rightleftharpoons} Hg(RS)_2 + Hg} \qquad (5)$$

Chemical reactions of this nature are not apparent at the platinum or gold electrodes. However, other reactions have been suggested as taking place in the case of cysteine, in an aqueous medium [10,11]:

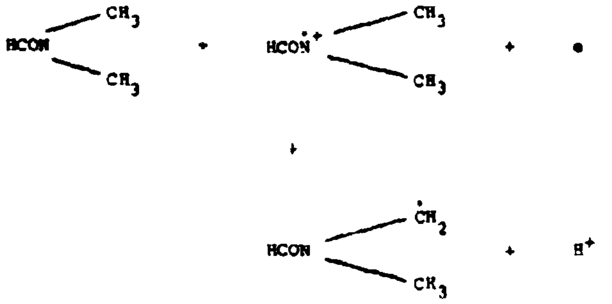
$$\left.\begin{array}{l}\mathrm{RSH \rightarrow RS\cdot + H^+ + e}\\ \mathrm{RS\cdot + 3H_2O \rightarrow RSO_3H + 5e + 5H^+}\\ \mathrm{Pt + H_2O \rightarrow PtO + 2H^+ + 2e}\end{array}\right\} \qquad (6)$$

Platinum and gold electrodes, in contrast to mercury, afford a wide range of usable working potentials. Consequently both the reduction and oxidation processes of thiols become accessible. Of the two solid electrodes, gold has a high oxidation potential and the absorption of hydrogen appears to be less apparent [11,12]. The low popularity of this electrode is due to the difficulty in forming a seal with glass.

2. RESULTS AND DISCUSSION

Many reports on the electrochemistry of the thiol group have concentrated on aqueous solutions. However, the solubilities of the polysulfide prepolymers, aliphatic thiols and disulfides are limited to non-aqueous solvents. Of the solvents which suit the requirements of solubility and potential range, dimethylformamide (DMF) is most suitable due to its ability to dissolve most compounds, low volatility and wide temperature range which allows measurements from -61° to 155°C. However, this solvent is susceptible to degradation, even at room temperature, with the formation of dimethylamine and carbon monoxide [13].

The anodic limiting reaction of DMF in the presence of a perchlorate supporting electrolyte is oxidation by removal of an electron from the amide nitrogen followed by the loss of a proton, resulting in formation of $HCON(CH_3)\dot{C}H_2$ which may participate in electrode reactions [13,14].



(7)

Because of their solubility in a wide range of solvents, tetraalkylammonium salts are most commonly used as supporting electrolytes. Limiting reduction potentials of up to -2.85V vs. the SCE (saturated calomel electrode) at a mercury working electrode have been reported with tetrabutylammonium perchlorate in DMF, while tetraethylammonium perchlorate is limited to -2.7V [15].

Associated with the use of nonaqueous solvents in electrochemical studies is the problem of junction potentials when aqueous reference electrodes, such as SCE, are used. This decreases the reliability of the reference potential. The low conductivity of nonaqueous solutions increases the internal resistance of the electrochemical cell (ohmic drop) compared with that of an aqueous medium.

The use of the ferrocenium/ferrocene couple (Fc^+/Fc) as an internal reference can minimise these problems [16]. The potential of the couple remains constant and independent of the solvent [17] provided that no reaction occurs with the contents of the electrochemical cell. Under these circumstances the couple is observed at +0.400V vs. NHE (normal hydrogen electrode).

As the couple is electrochemically reversible, the difference between the anodic and cathodic peak potentials (ΔE) should be equal to 60mV [18]. A higher value indicates an ohmic drop in the cell circuit arising from the resistance of the solvent [19]. For a given solvent/electrolyte system with a reversible couple, variations in ΔE are usually due to the distance of the working electrode from the reference electrode.

Subsequent to each experiment, the reference electrode was calibrated against the Fc^+/Fc couple. Using this technique, a series of thiols, disulfides, polysulfide prepolymers and a trisulfide were examined by cyclic voltammetry at a gold wire electrode, in the range -2.73V to +1.23V (vs. Fc^+/Fc).

(a) <u>Thiols</u>

The cyclic voltammogram of 1-butanethiol (Fig. 1) shows a broad reduction peak (1) at -2.38V, on the initial scan and at -2.30V on subsequent scans at $100mVs^{-1}$ scan rate. The reduction process is electrochemically irreversible. On the reverse scan an oxidation peak (2) at -0.64V is generated from the products arising from (1). A principal oxidation peak (3) is observed at +0.85V. On the second scan a reduction peak (4) appears at -1.16V which was not present during the initial scan.

Studies of aliphatic and aromatic thiols in acetonitrile (gold electrode) [20] and DMF (platinum electrode) [21] suggest that the electrode processes may be assigned as follows:

$2RSH + 2e \rightarrow 2RS^- + H_2$, peak (1), -2.38V (8)

$2RS^- \rightarrow RSSR + 2e$, peak (2), -0.64V (9)

$2RSH \rightarrow RSSR + 2e + 2H^+$, peak (3), +0.85V (10)

$2H^+ + 2e \rightarrow H_2$, peak (4), -1.16V (11)

$$\left.\begin{array}{l} RSSR + 2e \rightarrow 2RS^- \\ 2RSH + 2e \rightarrow 2RS^- + H_2 \end{array}\right\} \quad \text{peak (1'), -2.30V} \qquad (12)$$

The reoxidation of the thiolate anion of the thiol:

$$2RS^- + H_2 \rightarrow 2RSH + 2e \qquad (13)$$

is not apparent under the experimental conditions reported in this work although it has been observed in the case of thiophenol in DMF at a platinum electrode (-0.56V) [21]. The thiol is, however, regenerated as indicated by the constant height of peak (3) with continuous scanning.

(b) Disulfides

The cyclic voltammogram of dibutyl disulfide at 200mVs^{-1} scan rate, shows a reduction peak (1) at -2.28V (Fig. 2). The principal reduction process being:

$$RSSR + 2e \rightarrow 2RS^-, \quad \text{peak (1), -2.28V} \qquad (14)$$

An oxidation peak (2) is apparent at -0.61V which arises from the oxidation of the thiolate:

$$2RS^- \rightarrow RSSR + 2e, \quad \text{peak (2), -0.61V} \qquad (15)$$

The appearance of this peak is dependent on process (14) and its intensity is kinetically controlled in the range 20 to 500mVs^{-1}. At low scan rates (< 50mVs^{-1}) it is barely evident against the solvent background current. This behaviour is indicative of a competing reaction:

$$RS^- + \underset{\text{(solvent, electrolyte)}}{\text{reactants}} \rightarrow \text{product (electroinactive)} \qquad (16)$$

Peak (3) is independent of process (14) and consequently it does not arise from the reaction product of this process. Studies of diphenyl disulfide in acetonitrile using $LiClO_4$ as the supporting electrolyte, have indicated the formation of benzenesulfonate at highly positive potentials [22]. A similar process may be responsible for peak (3):

$$RSSR \rightarrow [RSSR]^+ + e \xrightarrow{ClO_4^-} RSO_3^-, \quad \text{peak (3), +0.78V} \qquad (17)$$

The cyclic voltammetry of diphenyl disulfide shows that it is more easily reduced than either dipentyl disulfide or dibutyl disulfide. Process (14) occurs at -1.888V (at 50mVs^{-1}, scan rate) and consequently it is easily discerned in the presence of the aliphatic analogues. Process (15) also occurs at a less negative potential (-0.470V at 50mVs^{-1}, scan rate) and shows a lower dependency on scan rate in the range 20 to 1000 mVs^{-1}. This is indicative of a slower competing reaction than that observed for the aliphatic disulfides (16).

$$PhS^- + \underset{\text{(solvent, supporting electrolyte)}}{\text{reactants}} \xrightarrow{\text{slow}} \underset{\text{(electroinactive)}}{\text{product}} \qquad (18)$$

(c) Dibutyl Trisulfide

The cyclic voltammetry of dibutyl trisulfide is far more complex than that of the corresponding disulfide. Differences are most apparent in both the reduction processes and in the oxidation of the resultant products (Fig. 3). Two reduction peaks (1,1') are evident (-2.079V and -2.347V) at a scan rate of 50mVs^{-1}.

The paucity of published data on the electrochemistry of trisulfides prevents definitive assignments of the redox processes, however the principal reduction processes may be envisaged as follows:

$$BuSSSBu + 2e \rightarrow BuSS^- + BuS^-, \qquad \text{peak (1), -2.079V} \qquad (19)$$

$$BuSS^- + 2e \rightarrow BuS^- + S^{2-}, \qquad \text{peak (1'), -2.347V} \qquad (20)$$

although chemical reactions may be involved.

A group of three oxidation peaks (2), centred at -0.733V, arises from the reduction products (process 1 and 1') in a similar way to that observed in the thiols and disulfides. At a scan rate of 200mVs^{-1} they are more prominent and occur in the range -0.883 to -0.573V. These oxidation processes begin at more negative potentials than those of the corresponding thiol and disulfide and consequently some are thermodynamically more favourable. The oxidation processes could include the following reactions:

$$BuSS^- + BuS^- \rightarrow BuSSSBu + 2e \qquad (21)$$

$$BuS^- + S^{2-} \rightarrow BuSS^- + 2e \qquad (22)$$

$$2BuS^- \rightarrow BuSSBu + 2e \qquad (23)$$

As in the case of the thiols and disulfides, competing chemical reactions in fact occur as indicated by the scan rate dependence.

The oxidation of BuSSSBu, peak (3), occurs at +0.837V at $50 mVs^{-1}$ scan rate and intensifies on scanning through peaks (1,1'). It is probable that electroactive products from the previous processes (22,23) also contribute to this oxidation peak:

BuSSSBu + product(s) + ne, peak (3), 0.837V (24)

$BuSS^-$ + " "

BuSSBu + " "

At more rapid scan rates (> $100 mVs^{-1}$) additional reduction peaks (4,5) are observed subsequent to peak (3) (Fig. 4). Thus additional electroactive species (say A and B) are generated by the processes contributing to peak (3):

BuSSSBu + A + B + ne, peak (3), +0.879V ($200 mVs^{-1}$) (25)

$A + ne + A^{n-}$, peak (4), -0.913V ($200 mVs^{-1}$)

$B + ne + B^{n-}$, peak (5), -1.853V ($200 mVs^{-1}$)

The nature of the products A and B is unknown but they are unlikely to be disulfides as the reduction potentials are too positive. The absence of peaks (4) and (5) at low scan rates suggests that A and B are unstable and undergo chemical reactions on the cyclic voltammetry time scale.

A more detailed examination is currently being undertaken into these electrode processes but the present preliminary study is sufficient for meaningful comparisons with polysulfide prepolymers.

(d) Polysulfide Prepolymers (Thiokols)

Having studied the cyclic voltammetry of some thiols, disulfides and a trisulfide, it is now possible to examine the cyclic voltammetry of commercial polysulfide prepolymers and to assign electrode reactions by analogy. Neglecting the small differences in crosslinking and molecular weight, the various polysulfide prepolymers differ mainly in the ratio of thiol to disulfide [1,2]. LP-3 has the highest thiol content of the Thiokol prepolymers currently available [2].

The cyclic voltammetry of LP-3 (Fig. 5) is similar to that expected for a mixture of a thiol and a disulfide. Some features of the electrochemical behaviour of the prepolymer are immediately apparent. The $-OCH_2O-$ moiety appears to be electroinactive and there appear to be no processes which may be construed as being due to the presence of a trisulfide. Consequently, the peaks may be attributed to the following processes (at $100mVs^{-1}$):

$$\left.\begin{array}{l} RSSR + 2e \rightarrow 2RS^- \\ \\ 2RSH + 2e \rightarrow 2RS^- \end{array}\right\} \quad \text{peak (1), } -2.31V \qquad (26)$$

$$2RS^- \rightarrow RSSR + 2e, \quad \text{peak (2), } -0.65V$$

$$\left.\begin{array}{l} RSSR \rightarrow [RSSR]^+ + e \\ \\ 2RSH \rightarrow RSSR + 2H^+ + 2e \end{array}\right\} \quad \text{peak (3), } +0.890V \qquad (27)$$

The peak potentials of LP-3 are in good agreement with those of the aliphatic sulfur analogues. Peak (4) which was observed with the thiols, is not evident in the cyclic voltammetry of LP-3. This is due to the low concentration of thiol in the prepolymer.

Analysis of peaks (1), (2) and (3) by examination of the variation in peak current with scan rate, shows that only process (1) is diffusion controlled (Table 1). A plot of peak current versus concentration of LP-3 gives a straight line for peaks (1) and (3) but not for peak (2) (Figs. 6-8). This is consistent with the reactions associated with this peak as previously discussed. Thus peaks (1) and (3), preferably the former, may be used for quantitative analysis of sulfur groups.

The cyclic voltammetry of LP-2, which contains 1.5-2.5 percent thiol, is very similar to that of LP-3. The low concentration of thiol is reflected the low intensities of peaks (2) and (3) (Fig. 9). Again, peak (4) is not observed for the same reason. Analysis of these peaks (Table 2) similarly shows that only peak (1) is diffusion controlled. The variation of peak current with concentration is linear for only this peak (Figs. 10-12).

Thus cyclic voltammetry at a gold electrode offers the possibility of a quantitative determination of sulfur in polysulfide prepolymers. It also enables a facile determination of the prepolymer content (for known commercial prepolymers) in a commercial formulation. This technique is far less time consuming than the traditional method of disulfide determination by reduction with zinc amalgam followed by the determination of the thiol with silver nitrate [23]. The thiol content may also be determined electrochemically but with a lower degree of reliability, particularly at low concentrations (2 percent). Further quantitative work is currently being undertaken using a rotating disc electrode.

3. EXPERIMENTAL

The thiols and ferrocene were purchased from Aldrich Chemical Co. Butanethiol was distilled under nitrogen prior to use. Dipentyl disulfide and dibutyl disulfide were prepared from the corresponding thiols by oxidation with hydrogen peroxide [24] and dibutyl trisulfide was synthesised by reaction of sulfur dichloride with 1-butanethiol [25]. Analytical grade (Univar) N,N-dimethylformamide was obtained from Ajax Chemicals and was used without further purification. Tetraethylammonium perchlorate (Fluka) was recrystallised twice from hot water and dried at 60°C. Thiokol LP-3 and LP-2 were used as supplied by Thiokol Corporation, USA.

The cyclic voltammetry measurements were carried out under argon in a 1[illegible] cm^3 Princeton Applied Research electrochemical cell using a gold wire working electrode and a platinum wire counter electrode. A reference electrode (aqueous saturated calomel electrode) was maintained in electrical contact with the cell solution via a Luggin tube containing a glass frit (porosity 3) and filled with solution containing the supporting electrolyte (0.1M). The test compounds were present at a concentration of 0.002M unless otherwise indicated. A Utah Electronics model 0152 potentiostat was used together with a model 0151 sweep generator. The voltammograms were recorded on a Rikadenki model RW-101 X-Y recorder. All potentials quoted in this work are referenced to the Fc$^+$/Fc couple (+0.400V vs. NHE) unless otherwise stated.

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TABLE 1

ANALYSIS OF PEAKS (1), (2) AND (3) IN THE CYCLIC VOLTAMMOGRAM OF LP-3

Peak (1)			
Scan Rate (ν) mVs^{-1}	E_{pc}[a] (vs. Fc$^+$/Fc) V	i_{pc}[b] μA	$i_{pc}\cdot\nu^{-1/2}$ μAmV$^{-1/2}$s$^{1/2}$
500	-2.355	272.5	12.2
200	-2.330	182.5	12.9
100	-2.310	122	12.2
50	-2.335	87	12.3
20	-2.260	57.5	12.9
Peak (2)			
Scan Rate mVs^{-1}	E_{pa}[c] (vs. Fc$^+$/Fc) V	i_{pa}[d] μA	$i_{pa}\cdot\nu^{-1/2}$ μAmV$^{-1/2}$s$^{1/2}$
500	-0.600	45	2.01
200	-0.620	25	1.77
100	-0.670	8	0.80
50	-0.715	4.5	0.61
20	-0.780	1	0.22
Peak (3)			
500	+0.930	100	4.5
200	+0.900	47.5	3.4
100	+0.890	42	4.2
50	+0.870	14	2.0
20	+0.850	5	1.1

[a] Cathodic peak potential

[b] Cathodic peak current

[c] Anodic peak potential

[d] Anodic peak current

TABLE 2

ANALYSIS OF PEAKS (1), (2) AND (3) IN THE CYCLIC VOLTAMMOGRAM OF LP-2

Peak (1)

Scan Rate (ν) mVs^{-1}	E_{pc}^{a}(vs. Fc^{+}/Fc) V	i_{pc}^{b} µA	$i_{pc}\cdot\nu^{-1/2}$ µAmV$^{-1/2}$s$^{1/2}$
1000	-2.319	162.0	4.74
500	-2.299	110.4	4.85
200	-2.299	66.0	4.67
100	-2.299	48.5	4.94
50	-2.311	33.5	5.12

Peak (2)

Scan Rate mVs^{-1}	E_{pa}^{c}(vs. Fc^{+}/Fc) V	i_{pa}^{d} µA	$i_{pa}\cdot\nu^{-1/2}$ µAmV$^{-1/2}$s$^{1/2}$
1000	-0.605	32.0	1.01
500	-0.625	21.0	0.94
200	-0.665	10.5	0.74
100	-0.725	4.0	0.40
50	-	-	-

Peak (3)

1000	+0.935	68.0	2.15
500	+0.915	40.0	1.78
200	+0.905	17.0	1.20
100	+0.865	9.0	0.90
50	+0.845	5.0	0.22

a Cathodic peak potential

b Cathodic peak current

c Anodic peak potential

d Anodic peak current

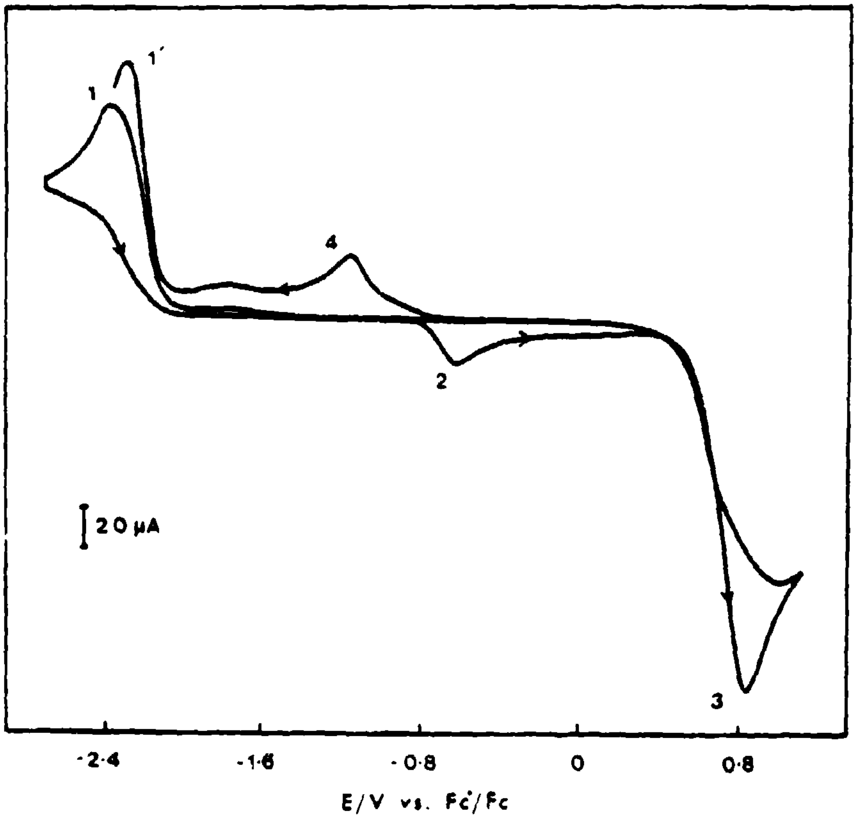

FIGURE 1. - Cyclic voltammogram (current vs. potential) of butanethiol in 0.1M Et_4NClO_4/DMF at a gold electrode and 100mVs^{-1} scan rate.

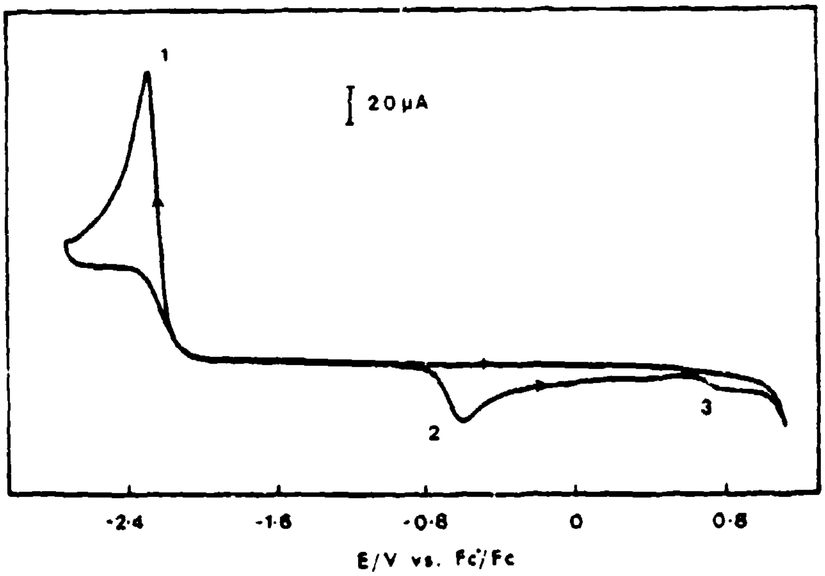

FIGURE 2 - Cyclic voltammogram (current vs. potential) of dibutyl disulfide in 0.1M Et_4NClO_4/DMF at gold electrode and 200mVs^{-1} scan rate.

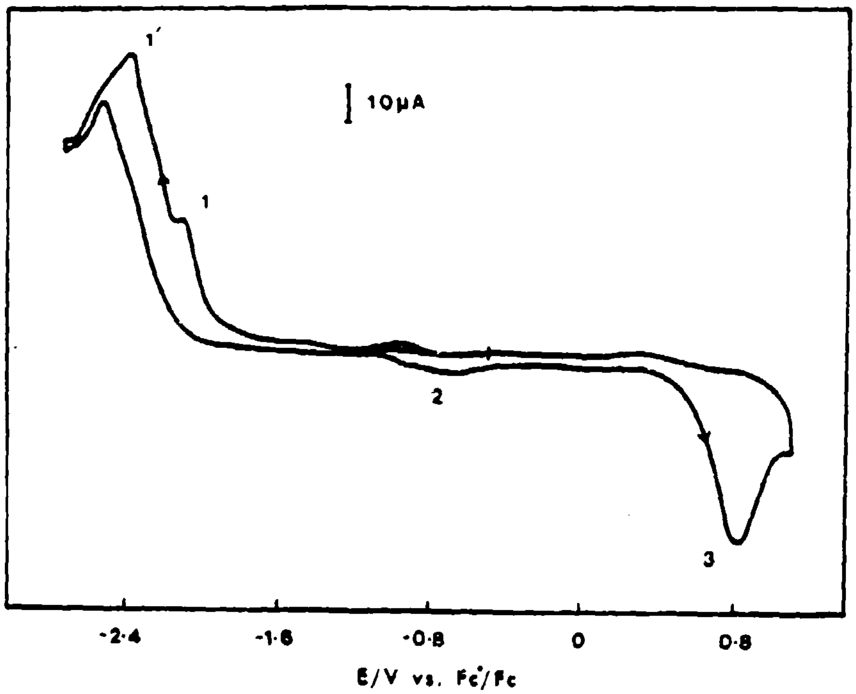

FIGURE 3 - Cyclic voltammogram (current vs. potential) of dibutyl trisulfide in 0.1M Et_4NClO_4/DMF at gold electrode and $50mVs^{-1}$ scan rate.

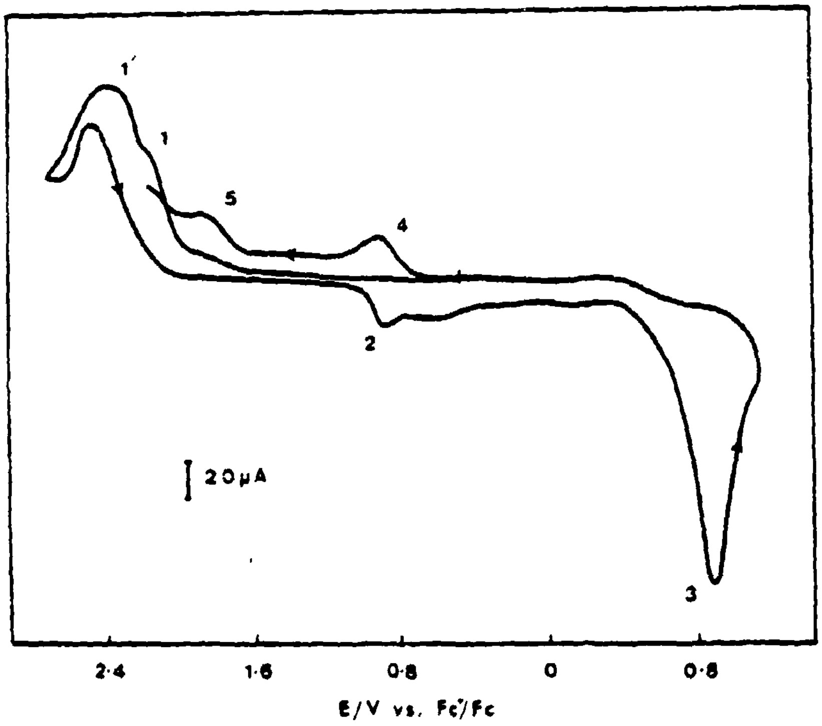

FIGURE 4 - Cyclic voltammogram (current vs. potential) of dibutyl trisulfide in 0.1M Et_4NClO_4/DMF at gold electrode and $200 mVs^{-1}$ scan rate.

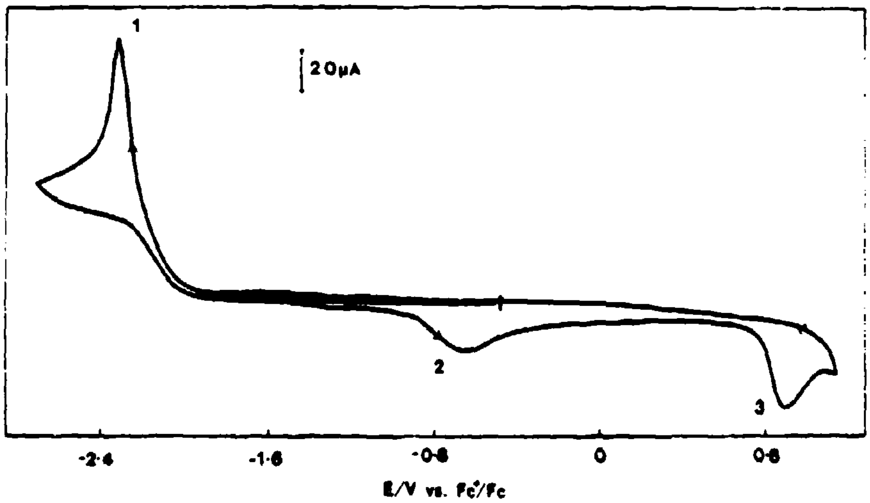

FIGURE 5 - Cyclic voltammogram (current vs. potential) of LP-3 polysulfide prepolymer in 0.1M Et_4NClO_4/DMF at gold electrode and 100mVs^{-1} scan rate.

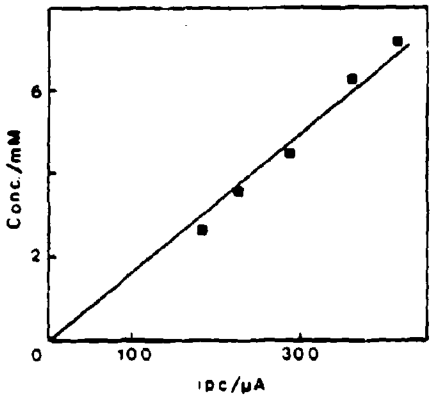

FIGURE 6 - Variation of peak (1) current with concentration (based on the monomer unit) of LP-3 at 100mVs^{-1} scan rate.

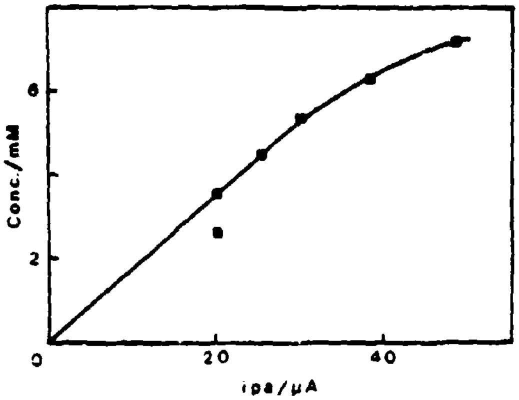

FIGURE 7 - Variation of peak (2) current with concentration (based on the monomer unit) of LP-3 at 100mVs^{-1} scan rate.

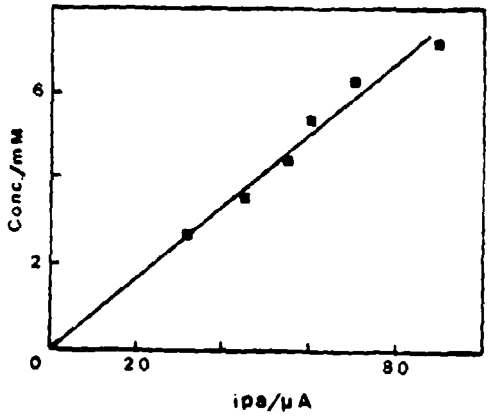

FIGURE 8 - Variation of peak (3) current with concentration (based on the monomer unit) of LP-3 at 100mVs^{-1} scan rate.

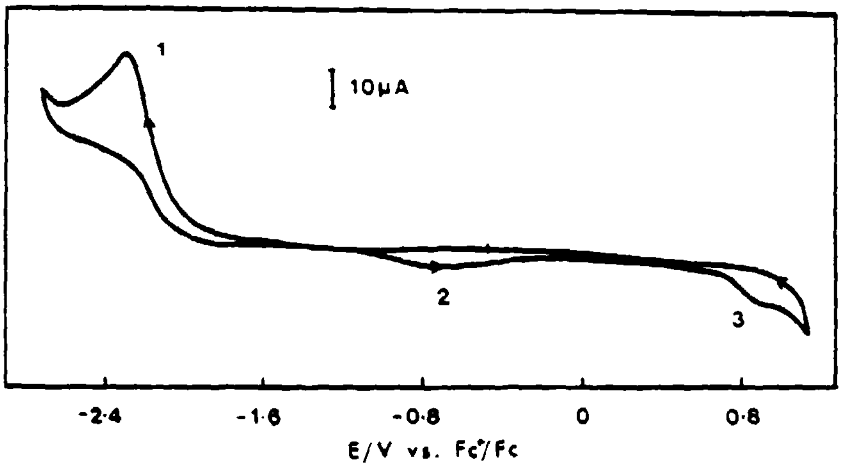

FIGURE 9 - Cyclic voltammogram of (current vs. potential) LP-2 polysulfide in 0.1M Et_4NClO_4/DMF at a gold electrode.

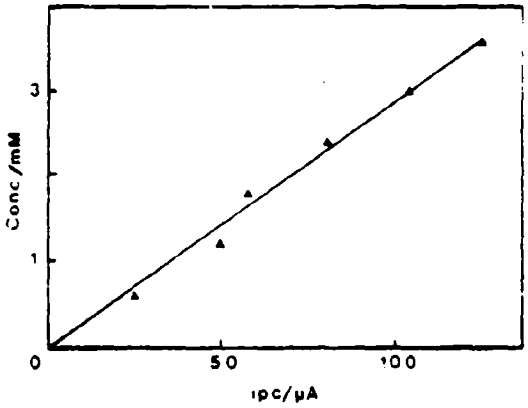

FIGURE 10 - Variation of peak (1) current with concentration (based on the monomer unit) of LP-2 at 200mVs^{-1} scan rate.

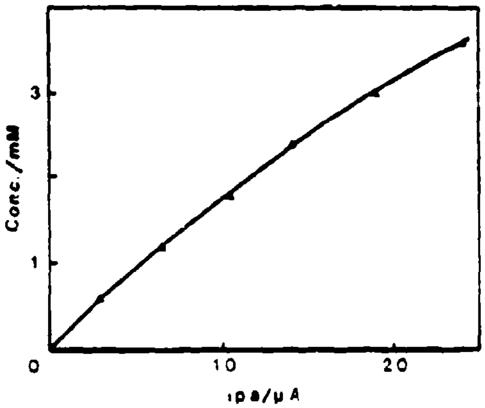

FIGURE 11 - Variation of peak (2) current with concentration (based on the monomer unit) of LP-2 at 200mVs^{-1} scan rate.

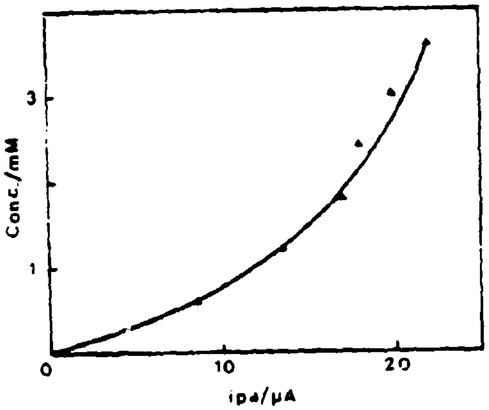

FIGURE 12 - Variation of peak (3) current with concentration (based on the monomer unit) of LP-2 at 200mVs^{-1} scan rate.

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