

SYNTHESIS AND CHARACTERISATION OF POLY-O-ANISIDINE - A CONDUCTING POLYMER.

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Poly-o-anisidine was prepared by electrochemical and chemical methods in H_2SO_4 and $HClO_4$ media. The electro-deposition of poly-o-anisidine and its electrochemical behaviour were studied by cyclic voltammetry. The polymer samples obtained were characterised by IR and GPC analysis.

Key words: Conducting polymer, poly-o-anisidine, cyclic voltammetry.

INTRODUCTION

During recent years considerable interest has developed on the polymerisation of aniline and its evaluation for different applications [1, 2]. The investigation of polymer films on electrode surface is one of the most active research area in the field of electrochemistry [3-8].

In the search for new conducting polymers of the aniline type, investigations have been directed towards aniline modified by substituents in the ring [9-12].

In the present paper, the preparation and characterisation of poly-o-anisidine are reported. The effect of o-methoxy group present in o-anisidine on the oxidation potential and the electrical conductivity are also discussed.

EXPERIMENTAL

o-Anisidine and other chemicals were of Analytical grade and used without purification for all the experiments except for voltammetric studies. For cyclic voltammetric experiments o-anisidine was vacuum distilled and then used. Cyclic voltammetric experiments were carried out in a divided three electrode cell. The glassy carbon disc (0.1963 cm^2) mirror finished with graded energy (1/0-4/0) was used as the working electrode. Platinum foil and saturated calomel electrode were used as the counter and reference electrodes respectively.

Preparative electrolysis was carried out in an undivided cell galvanostatically in 1M acid (H_2SO_4 or $HClO_4$). 0.1M o-anisidine was used for getting reasonable polymer growth. Stainless steel plates of $4 \times 2.5 \text{ cm}^2$ were used both as anode and cathode. All the electrochemical experiments were carried out under nitrogen atmosphere and at room temperature.

Poly-o-anisidine was chemically prepared from 0.1M solution in 1M H_2SO_4 by using ammonium per sulphate as the oxidising agent [13] at temperature below 278K and under nitrogen atmosphere. The resulting polymer products were washed repeatedly with dil. H_2SO_4 and dried under vacuum.

The voltammetric apparatus includes the Wenking potentiostat (model LB 75M) modulated by Wenking voltage scan generator (model VSG 72) coupled with Rikadenki X-Y-t recorder.

The IR spectra of the polymer sample were taken on a Perkin-Elmer model 783 Spectrophotometer in KBr.

The polymer samples were neutralised with NH_4OH and washed with water and dried under vacuum. The resulting polymer was dissolved in tetrahydro furan and its molecular weight was determined on a Shimadzu Gel Permeation Chromatograph

(GPC/LC-6A) equipped with two STYRAGEL columns and with a differential refractometer detector.

The electrical resistivity of the polymer samples were measured at room temperature on compressed pellets using the conventional four-probe technique [14].

RESULTS AND DISCUSSIONS

Cyclic Voltammetry

The cyclic voltammetry of o-anisidine shows an oxidative irreversible peak at 0.8V (Fig. 1a) and on the reverse and subsequent sweep a redox couple at 0.33V appeared in addition to the irreversible peak. The oxidation potential (0.8V) is 0.2V less anodic than for aniline [15] which may be due to the presence of electron releasing methoxy group in the ortho position.

If the potential is reversed before peak potential 0.7V (Fig. 1b) peak current does not change on continuous cycling but the peak current value decrease continuously on crossing the peak potential (Fig. 1a). This can be attributed to the progressive degradation of the polymer at higher anodic potential. The redox cycle at 0.33V may be due to the formation of the oligomeric intermediate formed during oxidation of o-anisidine.

In the blank solution (without monomer) the polymer film electrode shows cycle at 0.33V, which may be due to the incorporated oligomer (dimer or trimer) in the film. The variation peak current of the redox cycle with sweep rate is shown in Fig. 2. The i_p values varies linearly with $\nu^{1/2}$ (Fig. 3). Thus the redox process is a diffusion controlled process.

Electrochemical Polymerisation

The electropolymerisation of o-anisidine in 1M H_2SO_4 and 1M $HClO_4$ resulted in homogeneous coating on the electrode surface. At low current density (10 mA.cm^{-2}) an oily coating was obtained. This oily layer was dissolved in tetrahydrofuran and analysed by GPC. The GPC analysis indicates that molecular weight is in the order of oligomeric products. The formation of oligomeric products in low current densities can be attributed to the tail-to-tail coupling during the polymerisation of o-anisidine. When the current density was raised to 50 mA.cm^{-2} the coating was uniform. Then the polymer coating formed in the electrode surface was scrapped and analysed further.

Chemical polymerisation

In H_2SO_4 and $HClO_4$ media poly-o-anisidine was obtained as dark green powder. The yield of polymer increases on increasing the concentration of oxidising agent (Table I). This may be due to

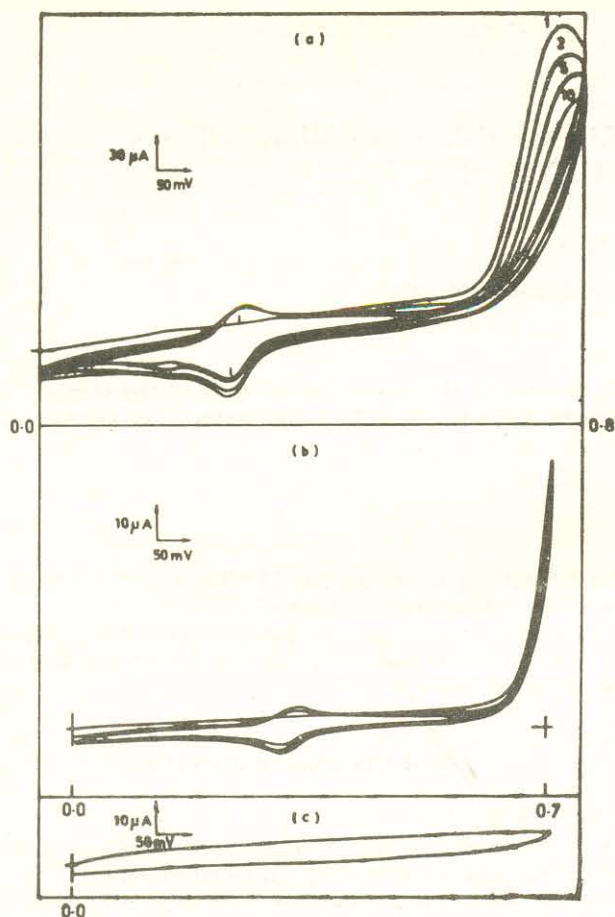


Fig. 1: Cyclic voltammogram of *o*-Anisidine oxidation in 1 MH_2SO_4 on GCE. Sweep rate: $20\text{ mV}\cdot\text{s}^{-1}$. (a) 0.1M, 0-0.7V, (b) 0.01M *o*-Anisidine 0-0.7V and (c) 1M H_2SO_4 .

the generation of more initiating species at higher concentration of oxidising agent.

IR Spectral studies

IR Spectra of the samples prepared by chemical and electrochemical methods were similar. The I.R.Spectra of the polymer sample is shown in Fig. 4. The IR Spectrum in the C-H bending region shows two bands at 800 and 850 cm^{-1} . Thus IR spectral studies confirm the head-to-tail coupling during polymerization reaction (i.e. 1,2,4-trisubstitution).

GPC analysis

Gel Permeation Chromatograph of the polymer sample is shown in Fig. 5. The polymer molecular weight was found to be around 3000 with respect to the standard poly-styrene.

Conductivity

The conductivity of the polymer samples are in the order $10^{-3}\text{ cm}^{-1}\cdot\text{ohm}^{-1}$. The conductivity of poly-*o*-anisidine is three orders of magnitude lower than the polyaniline [16]. The decrease in conductivity of the polymers may be due to the presence electron releasing -OMe group in the ortho position which reduces the stability of intermediate oxidation state. Thus the decrease in conductivity can be attributed to the increased distortion of polymeric chain.

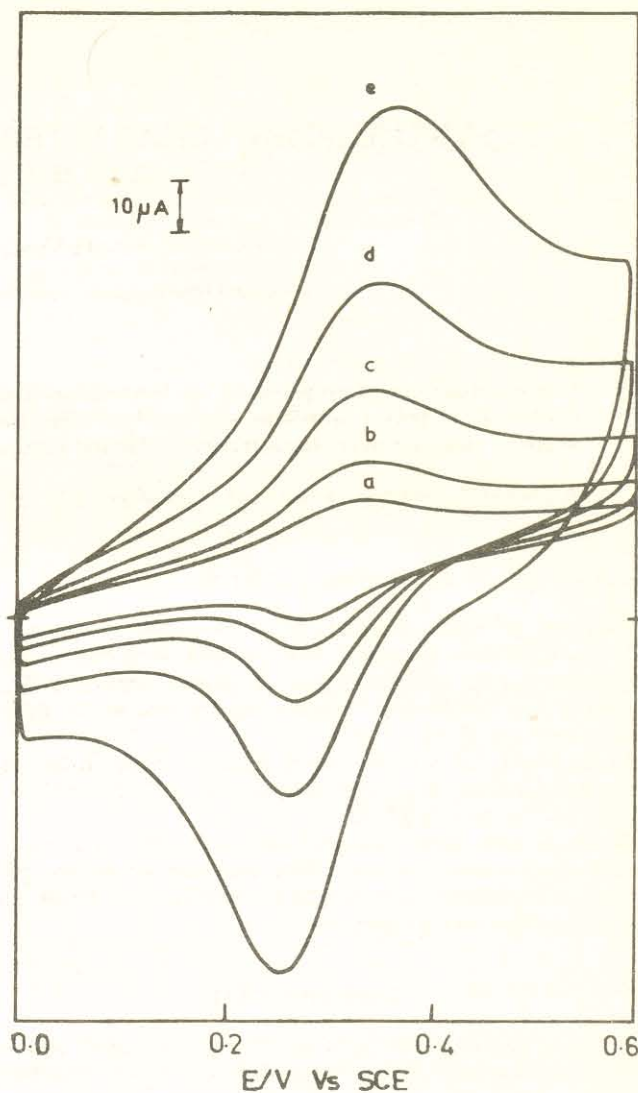


Fig. 2: Cyclic voltammogram of Poly-*o*-Anisidine in 1M H_2SO_4 on GCE. Sweep rate: (a) $20\text{ mV}\cdot\text{s}^{-1}$; (b) $40\text{ mV}\cdot\text{s}^{-1}$; (c) $80\text{ mV}\cdot\text{s}^{-1}$; (d) $160\text{ mV}\cdot\text{s}^{-1}$ and (e) $320\text{ mV}\cdot\text{s}^{-1}$

CONCLUSION

The presence of electron releasing -OMe group in ortho position favours the electropolymerisation of *o*-anisidine and the oxidation potential of the same is lowered by 0.2V compared to that of aniline. The electrical conductivity of poly-*o*-anisidine is lower by three orders of magnitude than poly-*o*-aniline due to the presence of electron releasing -OMe group, which reduces stability of intermediate oxidation state.

TABLE-I: Effect of concentration of oxidising agent in $HClO_4$ medium

$[(NH_4)_2S_2O_8]$ (M)	Yield of polymer (%)
0.1	38
0.2	55
0.3	68
0.4	82

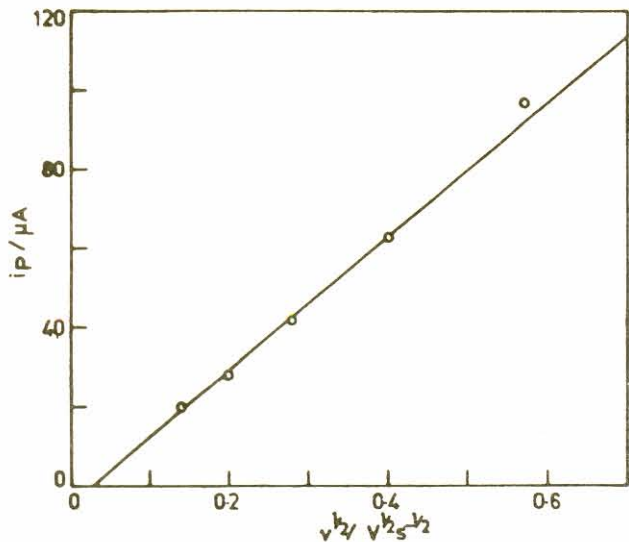


Fig. 3: Variation of peak current with sweep rate

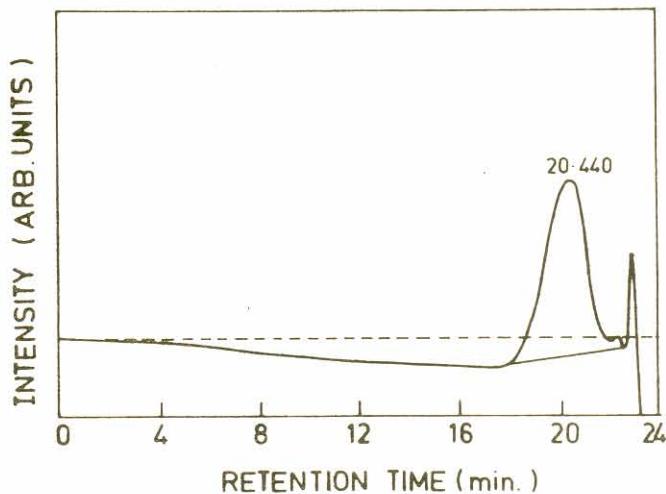


Fig. 5: Gel Permeation Chromatograph of poly-o-Anisidine in THF, flow rate of the polymer solution is $1 \text{ mL} \cdot \text{min}^{-1}$.

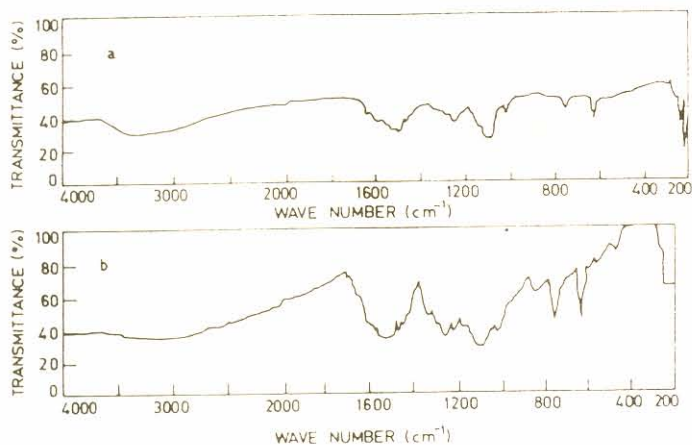


Fig. 4: IR spectra of poly-o-Anisidine in KBr (a) Chemically prepared and (b) Electrochemically prepared.

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