

Synthesis of conductive polyaniline in sulphamic acid medium

Sundeep Kumar Dhawan and Dinesh Chandra Trivedi

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

This study reports the oxidative polymerization of aniline in presence of sulphamic acid to yield a DMSO - DMF soluble polymer.

Key words: Conducting polymers, polyaniline, sulphamic acid

INTRODUCTION

The polyaniline family of polymers are known for nearly eighty years [1]. There are various methods available for the preparation of polyaniline (PAn) but almost all the methods yield untraceable and insoluble polymer [2]. Recently it has been reported that PAn can be made soluble in 80% acetic acid [3] and also in 98% H_2SO_4 [4]. However, these PAn solutions may prove to be of little utility. However, this solubilizing phenomenon of PAn gives the clue that solute-solvent interaction is possible perhaps by H-bonding to cause charge induced dipole polarization in macromolecular system to give soluble polymer [5,6]. It is thought that if such is the case, then some acids which are known to have hydrophilic tendency must also yield the soluble polymer. Keeping this theme in mind, electrochemical and chemical polymerization of aniline was carried out in presence of sulphamic acid, which is a $-NH_2$ substituted sulphuric acid, whose PKa in water is 1.04.

EXPERIMENTAL

The chemical polymerization was carried out by using aqueous persulphate solution (0.3 mole). The electrochemical polymerization was carried out at 0.72V vs SCE at Pt, ITO and stainless steel anodes using 0.1M aniline in 1M aqueous sulphamic acid solution. The $10\mu m$ thick polymer thus obtained had a conductivity of 0.2 S/cm.

RESULTS AND DISCUSSION

The cyclic voltammogram recorded during electropolymerization from $-0.2V$ to $0.8V$ vs SCE gave three peaks in both forward and backward sweeps. The data are given in Table I. These observations reveal that the middle peak corresponding to $C_6H_5NH^+$ cation is generated at 340 mV in the present case whereas in H_2SO_4 medium, middle peak occurs at 290 mV. These findings indicate that sulphamic acid adduct of aniline is taking part in the polymerization reaction. This assumption of ours gets support from FTIR spectrum where a band at 1046 and 1021 cm^{-1} due

to $-SO_3$ stretching of sulphamate anion is observed. The other bands observed are: 3149 , 2924 and 2854 cm^{-1} due to $-NH$ protonation, 1571 and 1483 cm^{-1} due to quinoid and benzoid structure. The very strong band at 1111 cm^{-1} with a shoulder at 1144 cm^{-1} has been assigned due to the charge on polymer backbone. This band vanishes on neutralisation of charge (Fig. 1).

TABLE-I

PAn medium	1st peak		2nd peak		3rd peak	
	$E_{p\text{ ox}}$ (mV)	ΔE_p (mV)	$E_{p\text{ ox}}$ (mV)	ΔE_p (mV)	$E_{p\text{ ox}}$ (mV)	ΔE_p (mV)
Sulphamic acid	120	210	340	90	600	110
Sulphuric acid	130	210	290	70	530	100

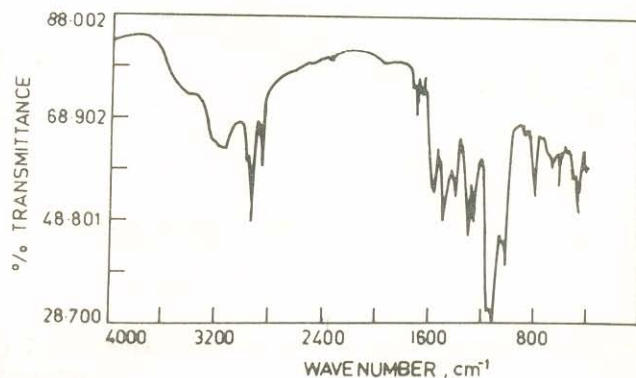


Fig. 1: F.T.I.R. spectra of polyaniline

The diffuse reflectance spectra on Pt substrate gave a well defined band at 419 nm and a very broad band at 682 nm (inset Fig. 2). The neutralized polymer gave a featureless spectra where λ_{max} lies at 528 nm . The polymer synthesised in presence of H_2SO_4 gave the bands at 320 , 420 and 800 nm . This shows that the orientation of film in the present case is different.

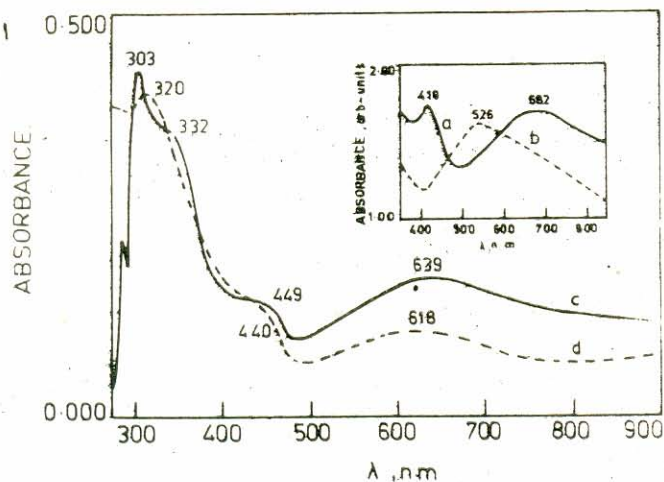


Fig. 2: Electronic spectra of PAN
c,d - in DMSO solution
a,b (insert) on Pt substrate

As indicated earlier, this methodology should yield soluble polymer. It has been found that the polymer prepared by this method is 4% soluble in DMSO and DMF at 300K. The electronic spectra of this solution

gave absorption bands at 303, 332, 448 and 639 nm. This blue shift in solution absorption spectra indicates that during solubilization the polymer collapses to give short chain polymer, nevertheless, on evaporation of solution the original behaviour can be seen.

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