

## SOLUBLE CONDUCTING POLYMERS

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Electrochemically as well as chemically processible conductive polymers from the substituted aromatic compounds such as aniline have been synthesized. The characterisation of this polymer has been carried out by U. V. visible spectroscopy. These may find usefulness in high energy density polymer batteries.

**Key words:** Conducting polymer, spectra and absorbance

### INTRODUCTION

Recently electrically conductive polymers have attracted considerable attention, owing to various properties such as electrochromism and energy storage [1-4]. The characterization and processing of conducting polymers are important from scientific and industrial point of view. Difficulties arise from the infusibility and insolubility of the conducting polymers because of the stiffness of the main chains consisting of conjugate double bonds.

The electroactivity of polyaniline (PA) and particularly of electrochemically synthesised polyanilines has been widely explored in aqueous electrolytes [2-5]. In this communication we are presenting our results on chemically and electrochemically synthesised polyaniline in nonaqueous medium.

It is envisaged that these soluble polymers may find application as a conducting ink in electronic industries as well as for casting thin film electrodes for low weight high energy density organic batteries.

### EXPERIMENTAL

The polyaniline was synthesised chemically in the nonaqueous medium such as *t*-butyl alcohol (tBuA) by adding  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  to a solution of aniline containing 1%  $\text{H}_2\text{SO}_4$  with continuous stirring for 4 hours. The polymer so obtained was washed with t-BuA and water and dried under dynamic vacuum.

Anodic polymerisation studies were carried out in solutions containing either  $1 \times 10^{-1}\text{M}$   $\text{LiClO}_4$  or tetrabutyl ammonium fluoroborate in acetonitrile or MeOH containing 0.5m aniline. At potential 1.20V vs SCE, the surface becomes covered by dark brown adherent deposit and the solution turns to dark brown.

The slow evaporation of the electrolyte after removing all the insoluble polymers gives a conducting film, the conductivity of which has been found to be lower than the polymer deposited on the anode surface. The UV-visible spectra of PA in DMSO, DMF, MeOH and  $\text{CHCl}_3$  were taken on a Hitachi Spectrophotometer. The results are recorded in Table II.

### RESULTS AND DISCUSSION

Generally, polyaniline is obtained chemically in aqueous solution [2]. But it has been observed that on preparing PA chemically in

nonaqueous medium, a soluble polymer of PA is obtained having maximum solubility in DMSO and DMF and least solubility in  $\text{CHCl}_3$  and  $\text{CH}_3\text{OH}$ .

The U.V. visible spectral data of PA in different solvents is recorded in Table I.

TABLE I: Spectra of polyaniline

Solvent	Dielectric Constant	$\lambda_{\text{max}}$ , nm
$\text{CHCl}_3$	4.10	560, 385, 269
$\text{CH}_3\text{OH}$	32.70	558, 362, 251
DMF	36.71	582, 326.7, 275
DMSO	46.60	571.4, 317.5, 268.9

There is considerable effect of dielectric constant on the structure of the polymer. As can be seen, highest absorbance for any given peak is observed in  $\text{CHCl}_3$  whose dielectric constant is 4.1, and least absorbance observed in DMSO medium. This behaviour suggests that the polymer is in ionic form since in a solvent with less dielectric constant, a large aggregate of polymeric ionic species will form, which will give rise to high absorbance, and in DMSO where the species are more ionic due to more solvation the polymer remains less aggregated. The interesting observation is that in aprotic solvents like  $\text{CHCl}_3$  and DMSO, the highest absorbance was found at 385 and 317.5nm. This peak has a blue shift in protic solvents like DMF and  $\text{CH}_3\text{OH}$  where it occurs at 326.7 and 362.0 nm respectively. This observation suggests that the end of polymer chain has a free hydrogen which therefore, due to H-bonding gives rise to the shift. Hence due to the blue shift with  $\lambda_{\text{max}}$  with the polarity of the solvent, we assign this band as  $\pi \rightarrow \pi^*$  transition.

The U.V. visible spectra of the polymer obtained electrochemically is recorded in Table II.

TABLE-II: Spectra of electrochemical polyaniline

Electrolyte	Solvent	$\lambda_{\text{max}}$ , nm
TBAPF <sub>4</sub>	$\text{CH}_3\text{CN}$	525(br), 374.2, 310.3
$\text{LiClO}_4$	$\text{CH}_3\text{CN}$	541.6(br), 344.4, 310.3

Table II reveals interesting observations. With the change in electrolyte by keeping the solvent constant like  $\text{CH}_3\text{CN}$ , one finds that in presence of  $\text{BF}_4^-$  anion, the absorbance bands are observed at 525 nm (br), 374.2 nm and 310.3 nm. The absorbance band at 525 nm has a red shift and gets shifted to 541.6 nm in  $\text{ClO}_4^-$  ion. This band may therefore be due to  $n \rightarrow \pi^*$  transition. The other band at 374.2 nm ( $\text{BF}_4^-$  ion) has a blue shift to 344.4 nm ( $\text{ClO}_4^-$  ion). We feel that these bands are associated with the formation of adducts due to the presence of anions.

However the interesting feature of the spectra is that in both the anions, the band appears at 310.3 nm but it is more intense in case of  $\text{BF}_4^-$  ion than  $\text{ClO}_4^-$  ion. We assign this band as due to  $\pi \rightarrow \pi^*$  transition. This observation confirms our conductivity measurement studies by 4-probe method where we get a higher conductive value when the polymer is synthesised in presence of  $\text{BF}_4^-$  ion.

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