

Electrical and optical properties of poly(aniline-co-8-anilino-1-naphthalene sulphonic acid) — A material for ESD applications

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The homopolymer of aniline (An) and its copolymer with 8-anilino-1-naphthalene sulphonic acid (8-ANSA) was synthesized by chemical oxidative as well as electrochemical polymerization process in the presence of *para*-toluene sulphonic acid (PTSA) as a dopant. The spectral, thermal, morphological and electrochemical properties of PTSA doped polyaniline and its copolymer (An-co-8-ANSA) were studied and compared to elucidate the effect of the inclusion of 8-ANSA in the copolymer feed. The resultant copolymer showed better solubility and processability but this approach usually results in the lowering of conductivity, hence the ratio of aniline and 8-ANSA in the copolymer feed was selected to 80:20. The room temperature conductivity of the PTSA doped polyaniline (PANI-PTS) and poly(An-co-8-ANSA) in 80:20 was found to be in the order of 1.74 S/cm to 9.77×10^{-1} S/cm, respectively. Conductivity mechanism of charge transport has been investigated in the range 30-300K. In the temperature range 30-70 K, copolymer showed tunneling mechanism. However, above 70 K conductivity attributes to Mott's variable range hopping (VRH) mechanism. The electrochemical behaviour of the polymers was studied by cyclic voltametry. The structure of the copolymer is characterized by ¹H NMR spectroscopy, UV-visible and FTIR spectroscopy. Electrostatic charge dissipation (ESD) of the conducting copolymer blend was also studied by blending of 1% of PTSA doped polyaniline and poly(aniline-co-8-ANSA) with LDPE which shows a static decay time of 0.1 to 0.25 sec on dissipating the charge from 5000 to 500 V.

Keywords: Conducting polymer, Polyaniline, Poly(aniline-co-8-anilino-1-naphthalenesulphonic acid), Conductivity, Electrostatic charge dissipation

1 Introduction

Conducting polymers have become very popular in the field of material science due to their promising and novel electrical properties. Electrically conducting polymers represents an important class of materials with potential applications in number of devices like electrode materials in energy storage devices¹⁻³, sensors⁴⁻⁵, shielding of equipments from electromagnetic interference⁶⁻⁹, electrostatic charge dissipation¹⁰⁻¹², organic light emitting diodes¹³⁻¹⁶, anticorrosive materials¹⁷⁻²⁰ etc. Among conducting polymers, polyaniline²¹⁻²⁵ has a special representation due to easy synthesis, environmental stability, simple non-redox doping by protonic acids. Also chemical doping and undoping can reversibly control the electrical conductivity of the polymers and that is the reason for its extensive use as sensor material for toxic gases and hazardous vapours. However, the commercial exploitation of most of the applications based on polyaniline is closely linked to the ease of its processability. Various attempts have been made to improve its processability. Copolymerization of aniline with alkyl substituted aniline and

N-substituted aniline is one of conventional methods to enhance the processability and solubility of conducting polymers²⁶⁻³¹. Polyaniline is one of the oldest of conducting polymers. Its copolymerization with alkyl and N-substituted anilines have been extensively studied³²⁻³⁴. Copolymerization of aniline and its doping with functionalized dopants like PTSA, DBSA, lignosulphonic acid and naphthalene sulphonic acid etc. are one of the conventional methods to acquire the desirable properties of polyaniline³⁵. Polymerization of aniline in the presence of naphthalene sulphonic acid has been extensively studied³⁶⁻³⁷.

In this work, copolymerization of aniline with novel N-substituted aniline like 8-anilino-1-naphthalene sulphonic acid (8-ANSA) was carried out by electrochemical as well as chemical oxidative polymerization method. In this case, comonomer (8-ANSA) has N-substituted aniline ring and naphthalene sulphonic acid unit attached to aniline as N-substituent. The existence of naphthalene sulphonic group as a substituent in the polymer chain played an important role in improving the solubility and

processability of polyaniline. The low loading level (1%) of this copolymer in LDPE were used as electrostatic charge dissipative material. The properties of resultant copolymers were determined by XRD, UV-visible spectroscopy, FTIR and conductivity measurement. The electrochemical behaviour of copolymer film was characterized by cyclic voltametric techniques.

Aniline (Loba Chemie, India) and 8-anilino-1-naphthalene sulphonic acid (8-ANSA) (Sigma Aldrich, USA), were used as monomers. *Para* toluene sulphonic acid (Merck, India) was used as synthesizing medium. Aqueous solutions were prepared from the double distilled water having specific resistivity of 1Mohm-cm.

2 Experimental Details

The PTSA doped polyaniline, poly(An-co-8-ANSA) were chemically prepared by free radical oxidative polymerization route. The concentration of aniline and 8-ANSA was 0.1 mole and that of PTSA was 1.0 mole. For the preparation of copolymers, aniline and 8-ANSA were mixed in 80:20 molar ratios in the presence of PTSA medium. Polymerization was initiated by the drop wise addition of ammonium persulphate solution (0.1 mole, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in distilled water). The polymerization was carried out in the temperature range 0-3°C for a period of 4-6 h. The synthesized polymer was isolated from reaction mixture by filtration and washed with distilled water to remove oxidant and oligomers. Polymers were collected by filtration followed by drying under vacuum oven at 50°C.

Copolymer of 8-ANSA and aniline of varying composition (i.e. by varying the comonomers feed compositions in the initial feed) were synthesized by electrochemical polymerization of aniline with (8-ANSA) on platinum electrode (working electrode) versus saturated calomel electrode (SCE) (reference electrode) and Pt as counter electrode. The polymer films were grown on the platinum (working) electrode in PTSA medium of monomers and co-monomers with various feed ratio at room temperature using cyclic potential sweep techniques. For synthesis of their copolymers, the concentration of both comonomers was 0.1 M and that of PTSA was 1.0 M. The potentials were swept continuously in the range -0.2-0.90 V versus SCE at a scan rate³⁸ of 20 mV/s. Peak potential values of the corresponding polymers and copolymers were recorded in PTSA medium. The copolymer film was deposited on the electrode which

was collected followed by filtration and washed with distilled water followed by drying under vacuum oven at 50°C.

The UV-visible spectra of the samples (using DMSO as solvent) were recorded using Shimadzu UV-1601 spectrophotometer. NICOLET 5700 FTIR spectrophotometer was used for the structural characterization of polymers. Spectra were recorded in KBr pellets in the range 400-4000 cm^{-1} . TGA (Mettler Toledo TGA/SDTA 851^e) was used to investigate the thermal stability of polymers in nitrogen atmosphere. A heating rate of 10°C/min in nitrogen atmosphere was used for carrying out these experiments. XRD of the powder samples were recorded on D8 Advance Bruker AXS X-ray diffractometer from $2\theta = 10^\circ$ to 70° at a scan rate of 0.0250 s^{-1} . ¹H NMR spectra of samples were recorded in DMSO-*d*₆ solvent on high resolution Bruker 300 MHz NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Micromorphology of the synthesized polymers was observed using SEM (Leo)

For the conductivity measurements, pellets of dimensions (length 13 mm, width 7 mm, thickness 1-2 mm) were prepared and the resistivities were measured by four-point probe technique using (Keithley 220 Programmable Current Source and 181 Nanovoltmeter). The conductivity at low temperature has been measured with the help, 6221DC current source of Keithley and 331 Lake Shore temperature controller connected through a PC. The measurement of antistatic decay time of the copolymer sheet was carried out on Static Decay Meter; model 406 D, Electro-tech System, Inc, USA (ETS).

3 Results and Discussion

The homopolymerization of aniline and its copolymerization with 8-ANSA proceed through the formation of a radical cation by an internal redox reaction, which causes the reorganization of electronic structure, to give two semi-quinone radical cations. These radical cations through the coupling reaction lead to the formation of stable electrically conducting polymer. 8-ANSA is N-substituted aniline having naphthalene sulphonic acid as a substituent in the amine ring. Copolymerization of 8-ANSA with aniline in acidic medium (PTSA), polymerization occurred selectively via the -NH group. Sulphonic group did not eliminate during the copolymerization. Moreover, the -SO₃H group of 8-ANSA unit in the copolymer chain takes part in improving the

processibility and solubility of the copolymer which leads to the formation of highly processable, soluble and stable electrically conducting polymer. During the copolymerization of aniline with 8-ANSA in tosylate medium, it has been observed that the dopant (PTSA) as well as naphthalene sulphonic acid unit attached to the copolymer chain offer steric-hindrance affecting the copolymer alignment, resulting in the formation of flexible and soluble conducting copolymers³⁹.

The electrochemical polymerization of aniline and its copolymers with 8-anilino-1-naphthalene-sulphonic acid in PTSA medium was done by sweeping the potential in the potential range -0.2 - 0.9 V versus SCE on platinum electrode at a scan rate of 20 mV/s. On comparing the electrochemical growth behaviour of aniline and its copolymer, it has been observed that the cyclic voltammogram of aniline growth in PTSA medium differs from the growth behaviour observed for its copolymer as shown in Fig. 1. The growth curves reveal that the peak current values increase with the increase in the cycling behaviour indicating that the radical cations generated at the electrode surface undergo further reaction to dimer, trimer etc. that are more readily oxidized leading to shift in electrode peak potential values and also an indication of polymer growth. The comparison of peak potential data indicates that the first redox value of polyaniline in PTSA medium lies at 0.188 V versus saturated calomel electrode (SCE), whereas the first peak potential value of its copolymer with 8-ANSA in 80:20 molar ratio lies at 0.287 V as shown in Fig. 2. On increasing the molar ratio of 8-ANSA in the copolymer composition, the peak potential shifted to positive direction. Copolymer of aniline with 8-ANSA in 50:50 molar ratio showed the

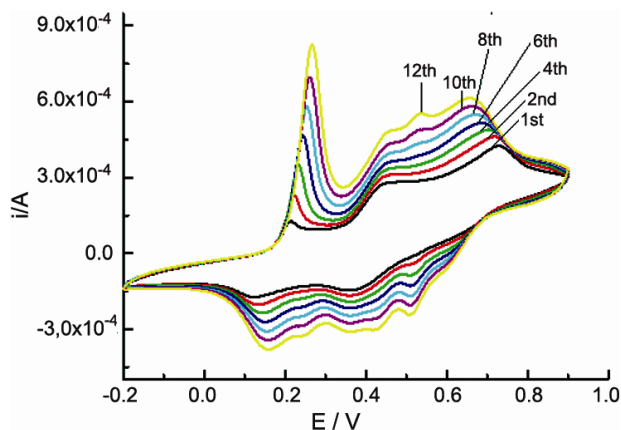


Fig. 1 — Electrochemical growth behaviour of comonomer of aniline and 8-ANSA in 50: 50 molar ratios in 1.0 M PTSA medium on platinum electrode versus SCE at the scan rate of 20 mV/s, with no of different cycles

first peak potential value lies at 0.462 V. While in the case of homopolymer of 8-ANSA in PTSA medium (Fig. 2), the first peak potential value shifts to the higher potential at 0.532 V. This implies that the copolymerization leads to larger peak potential shift, associated with electron transfer which indicates the presence of 8-anilino-1-naphthalenesulphonic acid, due to the steric and inductive effect of naphthalene sulphonic acid group which is attached to the copolymers chain in the form of pendant side chain, induce some non-planar configurations that decrease the conjugation along the polymer backbone which is responsible for the positive shift in the oxidation potential.

The conducting copolymer film of aniline and 8-ANSA on electrode surface exhibits multiple colour change on switching the potential from -0.2 to 0.9 V

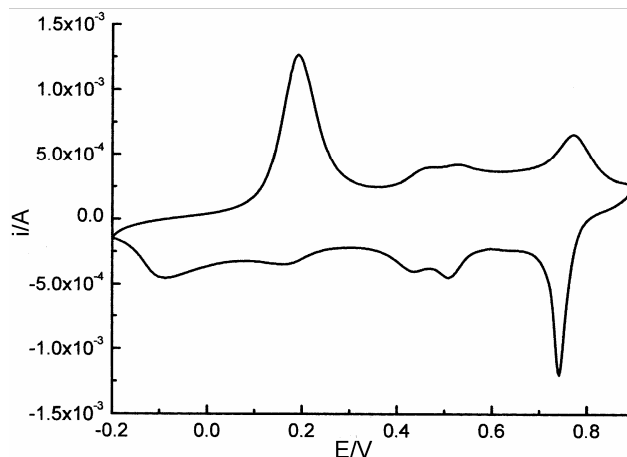


Fig. 2(a) — Cyclic voltammograms of PANI-PTSA on platinum electrode vs SCE at the scan rate of 20 mV/s

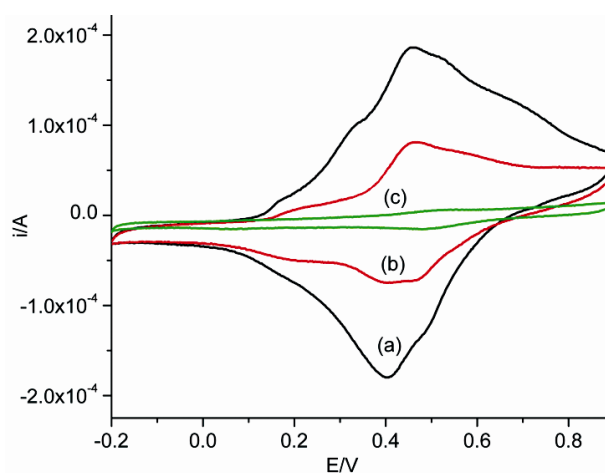


Fig. 2(b) — Cyclic voltammograms of poly(An-co-8-ANSA) film in (a) 80:20, (b) 50:50 and (c) homopolymer of 8-ANSA in 1.0 M PTSA medium on Platinum electrode vs SCE at the scan rate of 20 mV/s

versus SCE. These changes correspond to different colour oxidation state that appears on varying the potential. The chronoamperometric response of poly (An-co-8-ANSA) film in PTSA medium is shown in the Fig. 3. The repetitive switching test to estimate the cyclic life of the electro chromic copolymer film shows good stability.

Figure 4 shows the ^1H NMR spectra of the PTSA doped homopolymer of aniline and its copolymer with 8-ANSA in $\text{DMSO}-d_6$ solvent. The ^1H NMR spectra of the PTSA doped polyaniline are characterized by the four signals. The signals in the region of 7.8-6.3 ppm are assigned to the aromatic protons and another weak signal at 4.4 ppm is due to the N-H protons. A sharp peak at $\delta = 1.3$ ppm which is due to the $-\text{CH}_3$ protons of PTSA unit and other highly deshielded and weak peak has been observed at

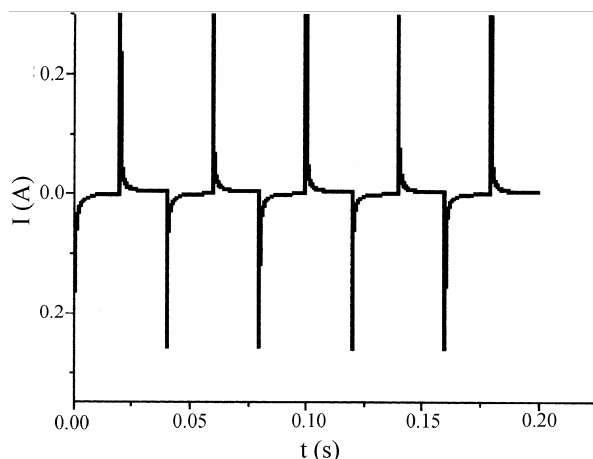


Fig. 3 — Chronoamperometric response of poly(aniline-co-8-ANSA) film in PTSA medium

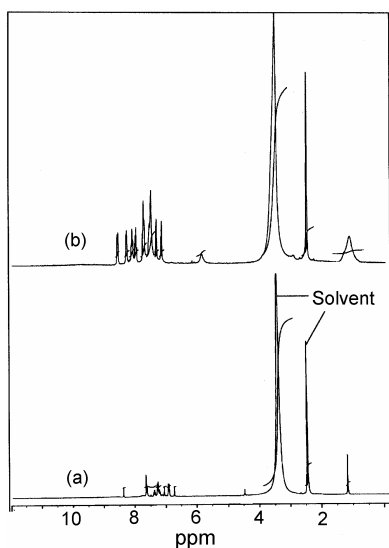


Fig. 4 — ^1H NMR spectra of the PTSA doped (a) polyaniline and (b) poly(An-co-8-ANSA) in $\text{DMSO}-d_6$

$\delta = 8.3$ ppm owing to the single proton attached to the $-\text{SO}_3\text{H}$ group of dopant. Poly(An-co-8-ANSA) exhibited the signals around $\delta \sim 6.9$ to 8.1 ppm which are assigned to aromatic protons attached to the aniline and naphthalene unit. The shifting of the peaks of the aromatic protons to downfield region in case of poly (An-co-8-ANSA) attributed to the aromatic protons attached to the naphthalene unit which exhibited the signals near $\delta = 7.8$ to 8.1 ppm. While the aromatic protons of aniline unit present in the copolymer showed the signals at around $\delta = 6.6$ to 7.8 ppm. The PMR spectrum of the copolymer further showed a highly deshielded protons attached to sulphonic group of naphthalene unit of the copolymer at around $\delta = 8.5$ ppm. Moreover, a weak signal at around $\delta = 8.1$ ppm has been observed in the case of copolymer which attributed to the proton attached to the sulphonic group of the dopant (PTSA). In case of aniline, the signal for amino protons was observed at 3.3 to 4.2 ppm. PANI-PTSA system exhibited the weak signal at $\delta = 4.4$ ppm which are assigned to -N-H protons. When aniline is copolymerized with 8-ANSA in acidic medium in the presence of PTSA, -NH proton in the copolymer chain were found to be highly deshielded and the resultant copolymer showed the signal for -NH proton in the region of 5.1 to 5.8 ppm indicating the presence of aniline as well as 8-anilino-1-naphthalene sulphonic acid units in the copolymer chain. Moreover, the presence of a sharp singlet at $\delta = 1.2$ ppm due to methyl proton in PTSA doped poly(An-co-8-ANSA) is also indicating the influence of the dopant (PTSA) in the copolymer chain.

FTIR spectra of PTSA doped polyaniline and poly(An-co-8-ANSA) is shown in Fig. 5. PANI-PTSA showed the characteristic bands at around 814 cm^{-1} due to the out- of- plane C-H bending vibrations and is indicative of the *para* coupling i.e.

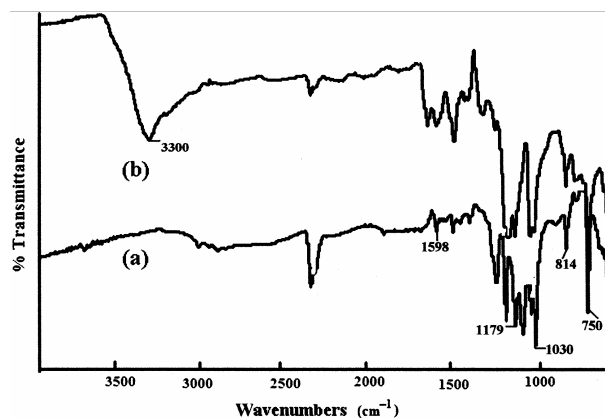


Fig. 5 — FTIR spectra of PTSA doped polymers (a) polyaniline, (b) poly(An-co-8-ANSA)