Synthesis and Characterisation of Polyaniline Using Picric Acid as an Organic Dopant

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ABSTRACT The organic conducting polymers also called as "synthetic metals" have received considerable attraction among chemists. Polyaniline holds a special position amongst conducting polymers due to its low cost, easy synthesis and processibility. Its conductivity and chemical properties can be modified by doping with suitable dopants. The present paper deals with the synthesis of polyaniline by chemical oxidative polymerization using picric acid as the dopant. Characterisation of Polyaniline picrate (PANIPI) is carried out using UV-Visible, FT-IR, 1HNMR, mass and elemental analysis. The electrical conductivity of pressed pellet is 1.5 Scm-1. The effect of thermal treatment on PANIPI is investigated using four probe conductivity and TGA technique. SEM, PXRD and particle size analysis have been used to reveal its size and structural morphology.

Introduction

Organic polymers that possess electrical, electronic, magnetic and optical properties of a metal besides retaining the mechanical properties, processibility etc., are termed[1] as intrinsically conducting polymers or "synthetic metals." Polyanilines (PANI) doped with acids are widely used in microelectronics[2] owing to its switching ability between insulating and conductive states by simple doping[3,4] Highly conducting doped forms are obtained by two completely different process- protonic acid doping (Scheme 1) and oxidative doping (Scheme 2).
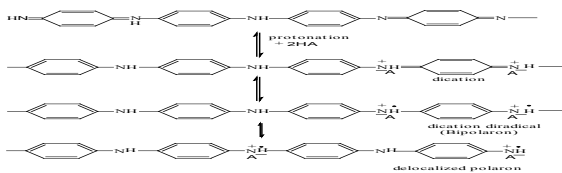
Scheme 1 Protonic acid doping

Doping of PANI has been attempted using various inorganic acids,[5-9] organic acids[10-14] and other compounds such as C60, phosphoric acid diesters etc.[15-17] Generally organic acids are known to improve the processibility of PANI.[18,19] When picric acid and emeraldine base are mixed and processed in the solid state[20] and solution[21-23] the conductivity of the PANIPI increases from 10^{-9} to 0.1 Scm[-1]. The chemical oxidative method (scheme 2) yields a pristine polymer of higher conductivity. Although a large amount of research is devoted to characterize emeraldine salts from inorganic acids, there are very few reports on organic acid dopants. Hence in this paper, the emeraldine picrate(PANIPI) is prepared by chemical oxidative polymerization of aniline and picric acid and the resulting polymer is characterized through various methods.

Experimental

Aniline (BDH) was doubly distilled under vacuum prior to use. All other chemicals were analytical grade reagents and used as received. Doubly distilled water was used for preparing the solutions. Solvents were purified and dried according to standard procedures.

Spectral measurements

The electronic spectra were recorded in the wavelength range 190-1200 nm using a Lambda 25 Perkin Elmer UV-Visible spectrophotometer. Infra red measurements in the range 400-4000 cm^{-1} were obtained on a Perkin Elmer RXI FT-IR spectrometer as KBr pellets. The ^{1}H NMR spectrum was recorded using a Bruker DRX - 400 spectrophotometer in DMSO-d$_6$ with tetramethyl silane as the internal standard. The mass spectra of the polymer were recorded on a Jeol-Accu TOF JMS-T100LC mass spectrometer having a Dart source (Direct Analysis in Real Time). Dry Helium was used with 4 LPM flow rate for ionization at 350°C. The orifice was set at 28 V and the spectra were collected as an average of 6-8 scans.

Structural characterisation

Elemental analysis was performed on a CHNSO Elemental analyser Vario EL- III. The DC conductivity of PANIPI was measured in the pellet form with size of 12 mm in diameter and 2.75 mm in thickness was determined using a four probe technique. Four pellets were tested and the conductivity of each pellet was measured several times at different positions of the pellet. The average of all the measurements was taken as the conductivity of the sample. Thermal stability of PANIPI was studied using SDT Q600 V20.9 Build 20 between 20°C-1000°C with the heating rate of 10°C/min in Nitrogen atmosphere. The density of the pellet was evaluated by Archimedes method by weighing the pellet in air and in liquid paraffin. Size measurements of PANIPI in aqueous solution were determined by Bluewave Mictrotrac Flex 10.5.4 particle size analyser. X-ray diffraction measurements were made with a Rigaku Ultima III X-ray diffractometer using CuKα target (λ = 1.5418 A°). SEM micrograph was recorded using JEOL JSM-5600LV Scanning Electron Microscope.

Synthesis of PANIPI

An aqueous solution of ammonium peroxydisulphate (0.1M) was added drop wise to a stirred solution of aniline (0.1 M) and aqueous picric acid (0.05 M) at ambient temperature. The stirring was continued for 2 hrs to ensure completion of the reaction. The colour of the solution changed from yellow, purple, blue and green in the end. The precipitated green emeraldine salt is filtered and washed repeatedly with distilled water. Traces of unreacted oligomers were removed by repeated washing with ethanol and acetone. The green powder obtained was ultrasonically stirred in diethylether and hexane until a free flowing powder was obtained. The

doped pristine polymer was filtered and dried under dynamic vacuum at 313 K for 24 hrs.

Results and Discussion

Chemical oxidative polymerization of aniline in the presence of picric acid proceeds as in scheme 2.

$$4n\ (C_6H_5N.\ HA) + 5n\ (NH_4)_2S_2O_8 \longrightarrow (C_{24}H_{18}N_4.2HA) + 5n(NH_4)_2S_2O_8 + 2nHA + 5nH_2SO_4$$

Scheme 2 oxidative doping

The absorption spectra of polyanilines generally depend on the level of doping, extent of conjugation, nature of the polymer and solvent[24]. In the UV-Visible spectra of NMP and DMF solutions of PANIPI (Figure 1), two bands around (360 nm) ~3.4 eV and 620 nm (~2 eV) are observed. The band around 3.4 eV is due to the π-π^* transitions in benzenoid rings and at 2 eV is due to transitions in the imino-quinone moieties in the PANIPI matrix.[25,26] The intensity ratio of these two bands (Q/B) is found to be 0.39 and 0.25 in NMP and DMF respectively. In DMSO as solvent, besides these two peaks a free electron absorption tail is observed in the region of 800-1100 nm indicative of emeraldine salt formation.[24]
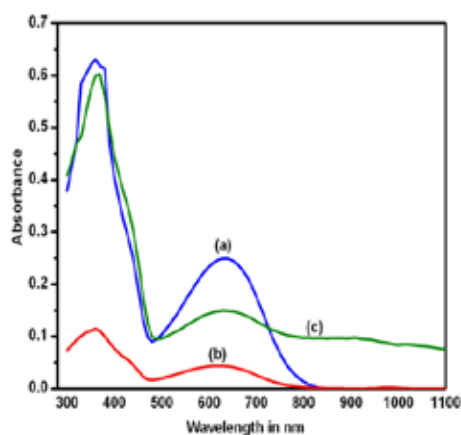

Figure 1 UV-Visible spectra of PANIPI in three different aprotic solvents (a)-NMP (b)-DMF (c)-DMSO

In the FT-IR spectrum, the large descending base line in the spectral region 4000-2000 cm^{-1} has been attributed to free-electron conduction in the doped polymer.[27] The characteristic peaks observed at 1588 and 1491 cm^{-1} are due to quinoid and benzenoid ring stretching frequencies respectively.[28,29] The band at 1300 cm^{-1} is attributed to the C-N stretching frequency for the doped PANI[30,31] and the C-NO$_2$ group of picric acid. A strong absorption at 1137 cm^{-1} is characteristic of protonated state of polyaniline.[32] The C-H out of plane bending vibration of 1,4-disubstituted ring is found at 797 cm^{-1}.
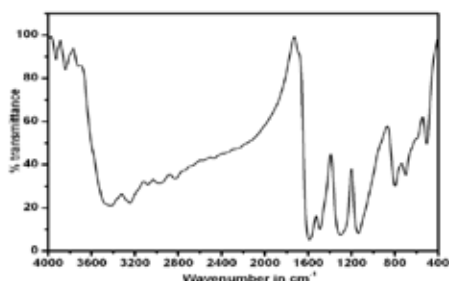

Figure 2 FTIR spectrum of PANIPI

In the ^{1}H NMR spectrum, the signal at 9.3 ppm is due to the ring protons of the picric acid and a broad peak centered around 8.2 ppm may be assigned to hydrogen bonding be-tween N-H of PANI and O-H of picric acid. The benzenoid ring protons are found at 7.4 ppm and 7.3 ppm as multiplets.[33,34] The quinoid ring protons are centered at 7.2 ppm. The two singlets at 7.08 ppm and 6.95 ppm are assigned to two picrate ions present on the imino nitrogens. The free N-H group exhibits signal at 1.2 ppm while N-H$^+$ peaks are found at 1.18 ppm as triplet[35]. The presence of interstitial water molecules are substantiated by a sharp signal at 5.78 ppm with an intensity ratio corresponding to two water molecules.[36] The results of CHNSO analysis also correspond to two water molecules when different values are assigned to n from 0.1 to 4 (Table1).

In the mass spectra (Figure 3a – ESI[-] mode) the picrate ion moiety is found at m/z = 228. The molecular ion (M+1) peak at m/z =366 present in the positive DART mass spectrum (Figure 3b) corresponds to 4 aniline units.[37] The m/z peak at 345 correspond to the removal of interstitial water molecules as H$_3$O$^+$. The intense m/z peak at 291 is attributed to 3 aniline units and a water molecule. The m/z peaks at 61, 89 and 99 account for the positive ions that have fragmented from picric acid.[22]
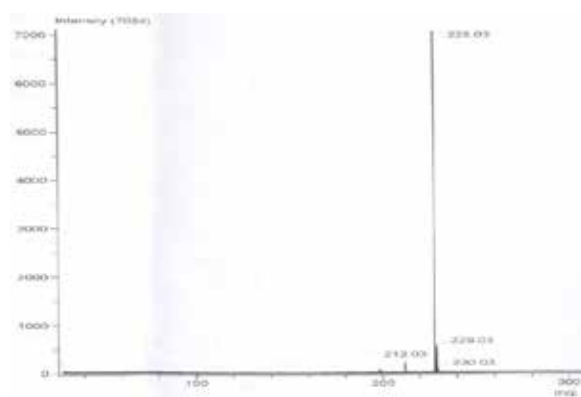

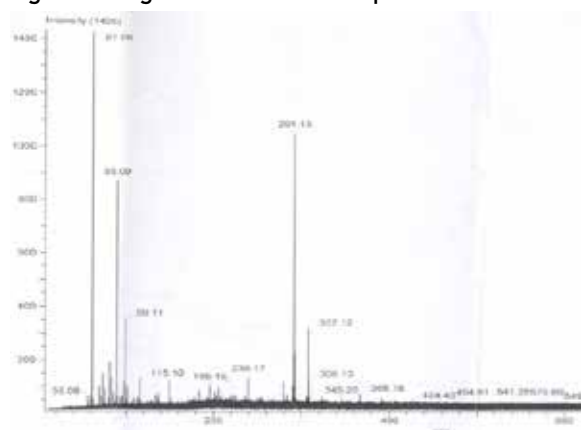**Figure 3a Negative ion DART mass spectrum**

Figure 3b Positive ion DART mass spectrum

The chemical composition (C, H, N, S and O) of PANIPI corresponds to the empirical formula $C_{24}H_{18}N_4$. $(C_6H_3N_3O_7)_{1.4}$ .2H$_2$O. Percentages of C, H and N are calculated theoretically by varying the values of n as described by Palaniappan etal.[38] At a particular value of n the calculated and experimental values are in close agreement and it corresponds to 1.4 picric acid molecule and 2 water molecules. Thus the monomeric unit weight can be considered as 672 g mol^{-1}. The doping percentage of picric acid present in PANIPI is 36.7%. This doping level is found to be in agreement with the emeraldine picrate obtained by the protonation of emeraldine base (39%).

Table 1. Theoretical and Experimental Chemical composition of PANIPI

	C (%)	H (%)	N (%)	S *(%)	O (%)	N
Theoretical	55.65	3.80	15.81	-	24.73	1.4
experimental	55.43	3.84	15.65	0.509	24.57	

* sulphur from oxidant and acid (scheme 2)

The conductivity (σ Scm^{-1}) of the sample is measured by the four probe method and calculated using the formula (1),

$$\sigma = (V/I \times \prod/\ln2 \times t)^{-1} \qquad (1)$$

I = the current applied in amperes, V = voltage measured in volts, t = thickness in mm respectively. Electrical conductivity of the polyaniline is strongly sensitive to most synthetic variables and post treatments.[40] However, it has been found that the nature of anion can have a profound effect on the properties and molecular structure of the polymer.[40] The conductivity of the PANIPI obtained in the present work is 1.5 Scm^{-1}. The reprotonated polymer prepared by Stejskal et al[19,20] exhibited a conductivity of 9.6×10^{-3} Scm^{-1} while the solid state protonation resulted in a conductivity of only 0.12 Scm^{-1}. The ohmic behaviour (Figure 4a) and high conductivity observed in the present work at ambient temperatures indicates that PANIPI prepared by chemical oxidative method falls in the "metallic regime". The conductivity of the sample followed Arrhenius type equation (2) as the temperature is increased.

$$\log \sigma = \log \sigma_0 - E_a/RT \qquad (2)$$

Eventhough linearity [41] is found upto 373 K ($E_a = 8.92 \times 10^{-4}$ Kcal mol^{-1}), at higher temperature a decrease in conductivity with a break is observed. This pattern is due to loss of water molecules (T =373K) (Figure 4c) and subsequent loss of picric acid (T = 415K) as the temperature is increased from 373K – 430K. This behaviour corroborates the findings from (Figure 5) elemental and thermal analysis done at higher temperatures. The chemical oxidative method results in the creation of intermediate states connected with increased conductivity and low activation energy. The oxidation creates a positive charge defect as a result of which the electron assumes a polaron state, the energy of which lies in the optical band gap energy 1-3 eV. Charge hopping among the polymer chains is believed to be the dominant conduction mechanism in almost all conducting polymers.[42] Further, the presence of interstitial water molecules of the PANIPI may be another reason for higher conductivity at ambient temperature. Density of PANIPI is found to be 1.4 g cm^{-3} similar to earlier results with picric acid as dopant.[19,20]
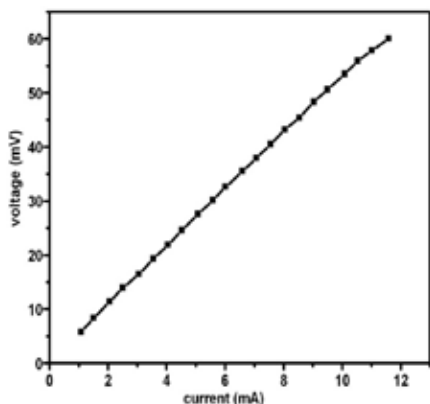

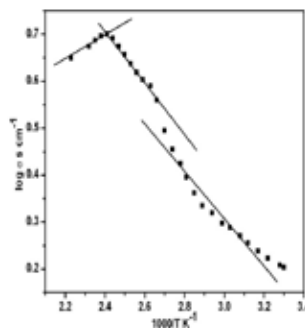Figure 4a Variation of current with voltage

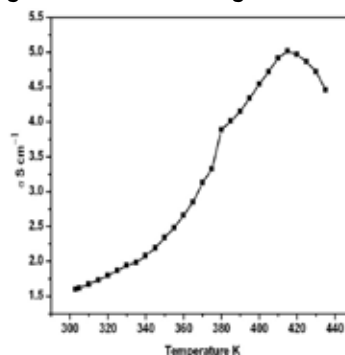**Figure 4b Variation of log σ with T^{-1}**

Figure 4c Variation of σ with T

PANIPI follows a typical three step decomposition pattern. First stage is the loss of water molecules (< 10 wt%) below 110°C, second stage between 130-250°C (25 wt%) is due to the loss of the dopant picric acid. Degradation of polymer backbone (45 wt%) occurs between 300-900°C. The thermogravimetric decomposition of PANIPI also supports its conducting behavior as reported in many polyaniline salts.[43,44]
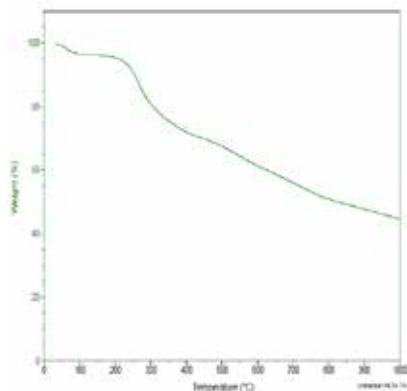

Figure 5 Thermogram of PANIPI

Morphology and crystallinity
PXRD pattern of PANIPI is shown in the (Figure 6) The crystalline domain size (L) of PANIPI is calculated using Scherrer's formula(3), is found to be 2-9 nm

$$L= 0.9\lambda / \beta\cos\theta \qquad (3)$$

Where L= coherence length, λ = wavelength of CuKα radiation, β= full width at half maximum of peak with maximum intensity. The PANIPI exhibits high degree of crystallinity as evidenced by the sharpening of the peaks centered at lower 2θ values at 30° (d ~ 2.90A°). Generally conductivity is directly related to crystallinity in protonated PANI systems.[32] The increased crystallinity may be the reason for the higher conductivity of PANIPI prepared by chemical oxidative polymerization compared to protonation methods.
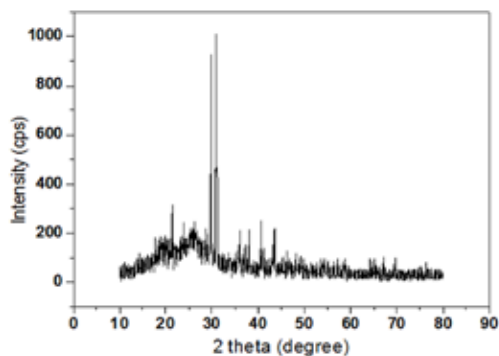
Figure 6 PXRD pattern of PANIPI

The SEM micrograph of PANIPI (Figure 7) shows better cohesion and higher aggregation[32] along with a granular morphology due to the presence of picrate anion.
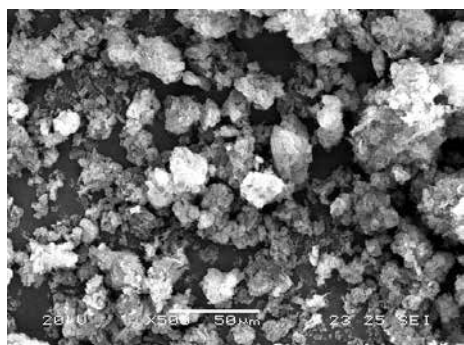

Figure 7 Scanning electron micrograph of PANIPI

The particle size analysis of PANIPI prepared by chemical oxidative polymerization in aqueous solution reveals that the particles have a diameter of 6.28 μm and a width of 4.02 μm. PANIPI can be considered to be cluster of micro crystallites.[45]

Conclusion

PANIPI synthesized by chemical oxidative polymerization resulted in a pristine polymer with superior conductivity compared to the polymers prepared by protonation method. UV-Visible data recorded in DMSO showed the formation of emeraldine salt. PXRD and SEM indicate the presence of cluster of crystallites. The IR, ^{1}HNMR and mass spectra confirmed the presence of picrate moiety in the polymer matrix. The loss of dopant on thermal treatment is evinced from the decrease in conductivity and TGA thermogram. The morphology studies clearly depicts that PANIPI is a cluster of micro crystallites.

Acknowledgement

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