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Research Article

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# Synthesis and characterization of conducting poly N-ethyl aniline doped with organic acids

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## ABSTRACT

*A substituted polyaniline, Poly (N-ethyl aniline) (PNEA), doped with different organic acids like acetic acid, oxalic acid and propionic acid has been synthesized by chemical polymerization method, using ammonium persulphate as an oxidizing agent. Characterization has been carried out by UV-Vis spectroscopy, FTIR spectroscopy, and conductivity measurements. The polymer, poly (N-ethyl aniline) doped with oxalic acid has been found to be highly soluble in common organic solvents. FTIR studies have revealed that oxalic acid doped poly (N-ethyl aniline) shows a broad and intense band at 3732.38cm$^{-1}$ and 1000-1087 cm$^{-1,}$ accounting for a higher degree of doping.*

**Keywords:** Conducting polymer; Dopant; Polyaniline; UV-Vis; FTIR

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## INTRODUCTION

Among the available synthetic macromolecules, conducting polymers have been extensively studied over the last few decades and have become polymers of great scientific and industrial importance [1–3]. One such conducting polymer Polyaniline (PANI) and its derivatives are an emerging subject of interest due to their wide range of conductivity and their use in insulating to metallic engines, unique redox properties, good environmental stability[3], ability to dope with protonic acids [4], ease of synthesis and practical applications in various fields including, photovoltaic cells, light weight batteries, flexible LED, electromagnetic interference (EMI) shielding, electronic display boards, anticorrosion coatings and sensors for ammonia, alcohols, ethers etc [4–6]. The commercial applications however are based on the ease of solubility and processability.

Like most conjugated polymers PNEA (Poly N-ethyl aniline), a subject of interest in this research, is insoluble in common solvents, difficult to process and infusible [4-6], because of strong interchain interactions. Therefore this has lead to intensive researches in order to enhance the properties like solubility, processability and conductivity.

Organic acids are known to improve the solubility and the processability of PANI [7-9] and its conjugated polymers like PNEA. Soluble and conductive organic acid doped PNEA has been synthesized in laboratory using acids like acetic acid, oxalic acid and propionic acid which provide an increased conductivity and solubility of the polymer in common organic solvents [10].

PNEA synthesized by Kulkarni et.al in 2007 using camphor sulphonic acid and p-TSA has been investigated as humidity sensor [11]. In addition to this PANI has also been synthesized in 2010 by the chemical oxidative polymerization method using organic acids like acetic, citric, oxalic and tartaric acid as dopants, where the effect of dopant ions on the polymer properties were discussed [12].

The aim of the present research was to carry out chemical oxidative synthesis of organic acid doped PNEA using acetic acid, oxalic acid and propionic acid , thereby improving the conductivity and solubility of the polymer in common organic solvents, such as m-cresol, benzyl alcohol and NMP(N-methyl pyrrolidinone) etc. The physicochemical properties of doped PNEA prepared have been compared using various analytical techniques such as UV-Vis, FTIR spectroscopy and conductivity measurements.

## EXPERIMENTAL SECTION

Polymerization of N-ethyl aniline monomer (Qualigen, A.R. grade) (Fig.1) was carried out by oxidative polymerization method [12-14] using ammonium per sulphate (Loba) as an oxidant and aqueous conducting media containing organic acids (acetic acid, oxalic acid and propionic acid (Qualigen)). All the chemicals used were A.R. grade and purified by distillation before use.

The synthesis was carried out taking 1.2ml the monomer solution and 2M acetic acid and stirred continuously at low temperature (0-4$^0$C) for 30 minutes in a three necked flask. The oxidizing agent, ammonium persulphate was then added drop wise after complete addition of which the reaction mixture was kept under constant stirring for 24 hr. A dark green precipitate of the polymer formed was isolated by filtration followed by drying in an oven at 60-70$^0$C for 24hr. Similar procedure was adopted with the change of the organic acid for oxalic acid and propionic acid.

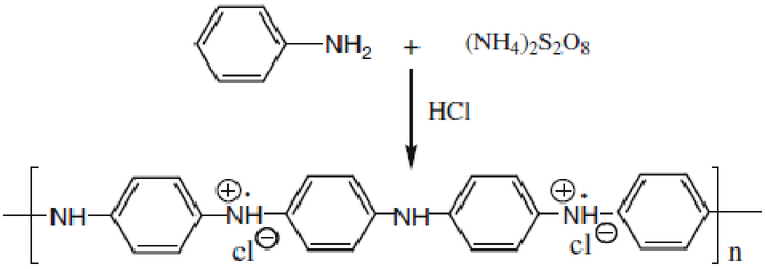

**Figure 1. Chemical polymerization of Polyaniline**

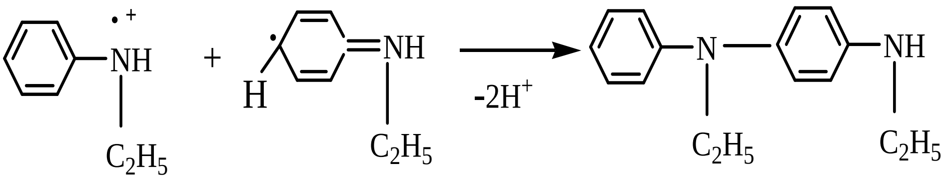

**Figure 2. Polymerization mechanism of Poly N-ethyl aniline**

The UV-Vis spectra of the polymers prepared were recorded in NMP, by using UV-Visible double beam spectrophotometer (Model Hitachi 2000) in the range of 200-1000nm. Similarly the IR spectrum of PNEA was taken on Perkin Elmer spectrum 2000 FTIR spectrophotometer in the range of 400-4000cm$^{-1}$. For conductivity measurements polymer pellets of about 0.2cm thickness and 1cm diameter were prepared in a stainless steel die and conductivity was measured with the help of a two probe technique [14].

## RESULTS AND DISCUSSION

### 3.1. UV-Vis spectra

The UV-VIS spectra of PNEA (Fig.3) doped with acetic acid, oxalic acid and propionic acid was recorded in NMP solvent, which showed different absorption at different wavelength. The spectra revealed the enhanced solubility of

PNEA synthesized in the presence of oxalic acid as compared to acetic acid and propionic acid. This can be attributed to the presence of a greater charge on the polymer chain in the organic acid oxalic acid doped polymer leading to a higher degree of solvation of the polymer due to hydrogen bonding between the solvent and polymer chains [15].

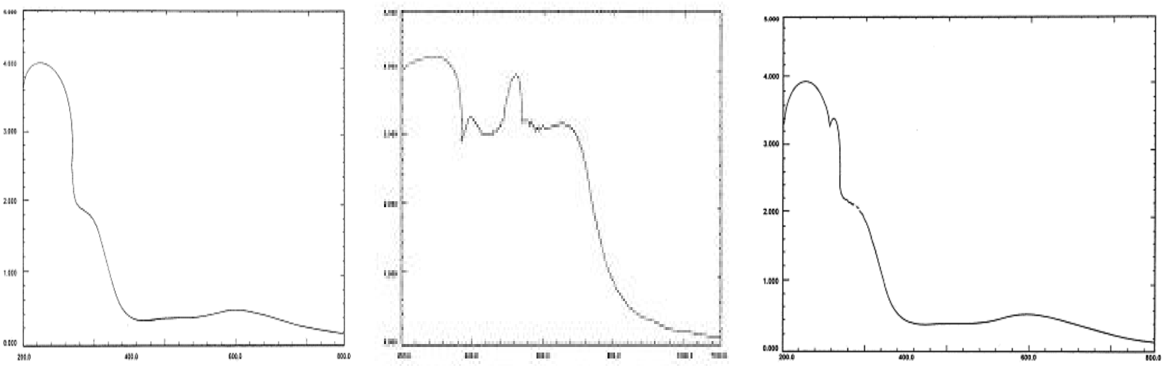

**Figure 3. UV Spectra of PNEA taken in NMP a) doped with acetic acid, b) doped with oxalic acidic, d) doped with propionic acid**

Optical properties of conducting polymers are important for the development and understanding of basic structure of the material [17]. Conjugation existing in the polymers is characterized by their electronic spectra. PNEA showed a maximum absorption of 3.0679 at a wavelength of 675nm when oxalic acid was used. High absorption and relatively sharp peaks in oxalic acid doped PNEA in UV spectra indicated the higher degree of solubility [17, 18].

### 3.2. FTIR Spectra

IR (Infra Red) spectroscopy is a very powerful tool to detect the structure of synthesized molecules and the changes taking place after a treatment [17-19]. The IR spectra of the pure polymer showed absorption frequency and position of the peak different from that of the doped product. The prepared polymer samples were tested for their response for ammonia. PNEA showed sensitivity when exposed to ammonia [19]. When the polymer was exposed to ammonia vapor it depicted differences in specific bands, which were more significant in oxalic acid and acetic acid doped polymers as compared to propionic acid doped polymer. When the polymer was exposed to ammonia a slight increase in stretching frequency was observed. The IR spectra for acetic acid, oxalic acid and propionic acid doped polymer have been shown in Fig. 4. Characteristic peak locations were related to the corresponding chemical bonds (Table 1).

A remarkable difference was observed in the IR spectra in terms of specific bands and shifts in three polymers. The peaks obtained in oxalic acid doped polymer were broad and intense, especially the ones obtained at 3732.38cm$^{-1}$ and 1000-1087 cm$^{-1}$, which accounted for a higher degree of protonation of amine and imine. However the peaks observed in the case of acetic acid and propionic acid were comparatively sharp and narrow, indicating a lower degree of protonation and doping [17-19]. The bands observed in acetic acid ,oxalic acid and propionic acid doped PNEA at 3034.13, 3732.38, 2972 cm$^{-1}$ respectively were due to N-H stretching whereas the bands at 2332.02, 2357.09, 2337 cm$^{-1}$ were due to C-H stretching. The C-N stretching of aromatic amines was evident from the peaks obtained at 1255.70, 1259.56, and 1251 cm$^{-1}$ in acetic acid, oxalic acid and propionic acid doped PNEA. The intense peak observed at 1500-1 510 cm$^{-1}$ in acetic acid and oxalic acid doped polymer indicated quinoid ring stretching frequency. While the peaks observed at 1373.36, 1375.29 cm$^{-1}$ indicated benzenoid ring units [20].

### 3.3. Conductivity

During in situ synthesis of PNEA, the organic acids get added to the polymer chains as dopants. The conductivity of PNEA doped with oxalic acid showed highest conductivity. This occurs because the oxidation and doping degree of the PNEA doped with oxalic acid is greater than that of that doped with acetic and propionic acid. The conductivity of the samples increased upon exposure to ammonia vapours, which was attributed to the presence of a high concentration of COO- ions serving as dopant along with a few oxalic acid doped sites and trapped COOH molecules present in polymer matrix.

During exposure to ammonia, some molecules of ammonia were adsorbed while other interacted with the anions present in the polymer form $NH_4^+$ anions salt. This lead to loss of anions together with the charge imbalance caused over the polymer chain. These effects are neutralized by the trapped COOH molecules, which may occupy the free dopant sites thereby increasing the carrier concentration and hence the conductivity. The polymer showed a change in resistance under exposure to ammonia vapor, suggesting the applicability of these polymeric materials as ammonia sensors [21].

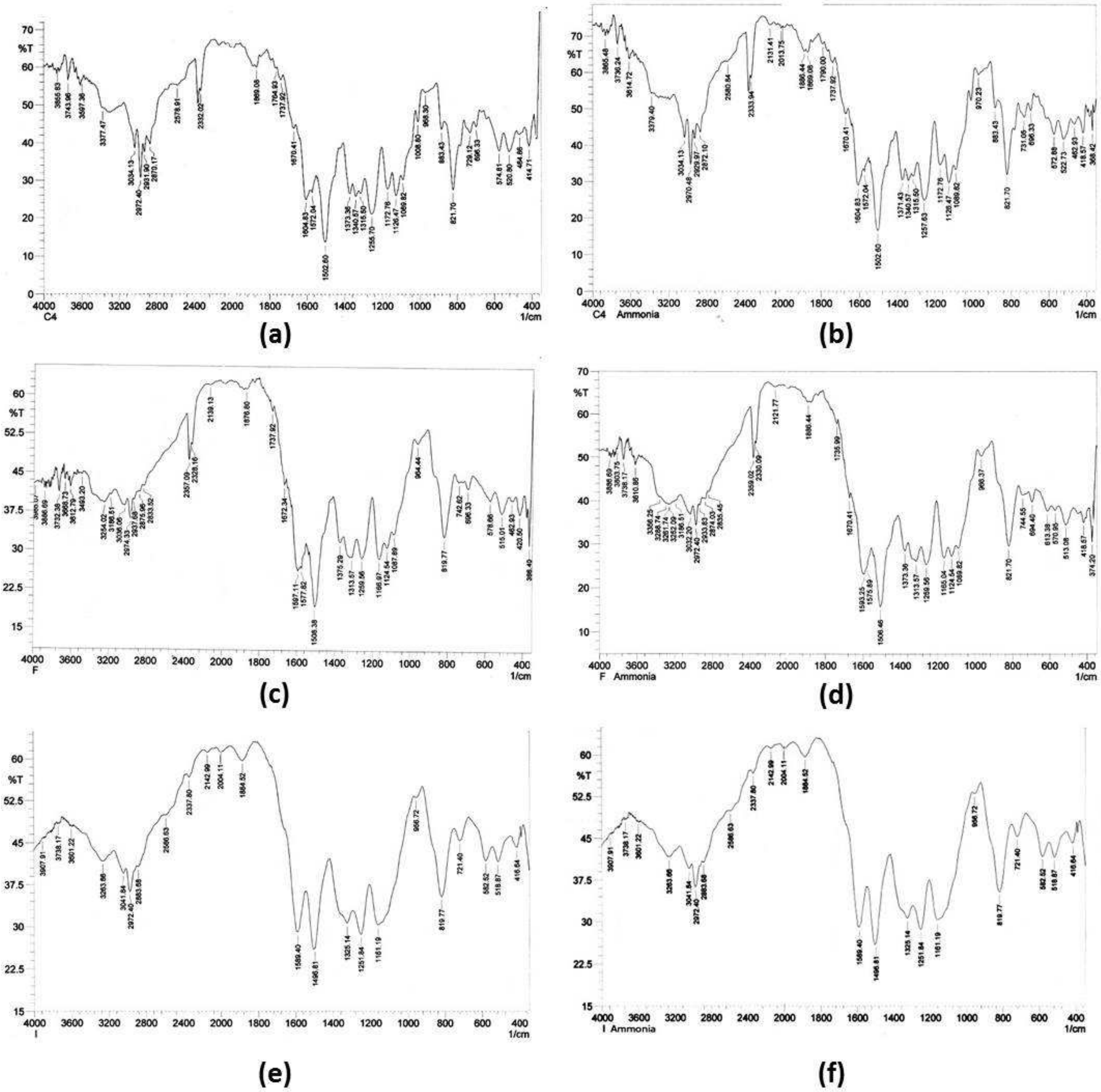

**Figure 4. FTIR absorption spectra of acetic acid, oxalic acid and propionic acid doped PNEA: acetic acid doped PNEA (a); acetic acid doped PNEA expose to ammonia (b); oxalic acid doped PNEA (c) oxalic acid doped PNEA expose to ammonia (d) propionic acid doped PNEA (e) propionic acid doped PNEA expose to ammonia (f)**

**Table 1. FT-IR bands (cm$^{-1}$) for acetic acid, oxalic acid and propionic acid doped PNEA**

| Acetic acid doped PNEA ( cm$^{-1}$) | Oxalic acid doped PNEA (cm$^{-1}$) | Prop-ionic acid doped PNEA (cm-1) | Peak assignment |
|---|---|---|---|
| 610-729.12 | 610-742 | 610-721 | Out of plane C–H bending vibration |
| 821.7 | 819.77 | 819.77 | *Para* di-substituted benzene ring |
| 968 | 1000-1087 | 956 | Vibration band of dopant anion |
| 1126.47 | 1124.54 | 1161 | Secondary (C–N) stretching band |
| 1255.7 | 1259.56 | 1251 | Aromatic C–N stretching band |
| 1373.36 | 1375.29 | 1325 | Benzenoid ring stretching band |
| 1502.6 | 1508.38 | 1496 | Quinoid ring stretching band |
| 1572.04 | 1597.11 | 1589 | Carbonyl (C=O) stretching band |
| 1670.41 | 1672.34 | ------ | $(NH_2)$+ saturated amine |
| 1869.08 | 1737 | 1884 | Aliphatic C-H stretching freq. |
| 2332.02 | 2357.09 | 2337 | C–H aromatic stretching band |
| 3034.13 | 3732.38 | 2972 | N–H stretching band |

The conductivity order of acid doped PNEA were found to be Oxalic acid doped PNEA> Propionic acid doped PNEA > Acetic acid doped PNEA (Table 2).

**Table 2. Conductivity of organic acid doped polyaniline**

| Sample | Conductivity before exposure to ammonia vapors ( S cm$^{-1}$) | Conductivity after exposure to ammonia vapors (S cm$^{-1}$) |
|---|---|---|
| Acetic acid doped PNEA | $0.5\times10^{-4}$ | $0.7\times10^{-3}$ |
| Oxalic acid doped PNEA | $1.6\times10^{-2}$ | $3.2\times10^{-1}$ |
| Propionic acid doped PNEA | $0.4\times10^{-3}$ | $4.2\times10^{-2}$ |

## CONCLUSION

PNEA salts were synthesized by chemical oxidative method in different protonation media. During PNEA synthesis different organic acids were added to the polymer chains as dopants. In comparison to the acetic acid and propionic acid doped polymer, oxalic acid doped polymer was found to have a greater solubility in organic solvents. The conductivity of samples exposed to ammonia was higher than those without exposure, which suggested theses samples to be superior materials as sensors for ammonia vapors.

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