

Synthesis and characterization of polyaniline salts with phenoxy acetic acids by emulsion polymerization

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Polyaniline salts have been synthesized by chemical oxidative polymerization of aniline in the presence of phenoxy acetic acid and its two derivatives using emulsion method at room temperature and characterized by different techniques such as infrared, ^1H and ^{13}C NMR, UV-visible spectroscopy, SEM, wide angle X-ray diffractograms and conductivity measurements. These polyaniline salts have the desirable property of high solubility for processability in solvents such as DMF, DMSO and a mixture of CHCl_3 and acetone and they exhibit fairly good conductivity of $\sim 3.0 \times 10^{-3} \text{ S cm}^{-1}$. The variations in solubility, conductivity and morphology with the protonating strength of the dopants are examined.

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Among electrically conducting organic polymers, which have attracted much attention, polyaniline (PANI) is one of the most widely studied material. A wide range of technological applications have been associated with polyaniline, for example, in electrostatic dissipation, anticorrosion coatings, in various optoelectronic devices¹ and as an antistatic material². However, the poor processability of polyaniline, which is true of the other conducting polymers as well, has limited its applications. Synthesis of polyaniline salts with various dopants is of fundamental importance in exploiting its solubility in common organic solvents for improved processability. Various types of acids have been used in the protonation of polyaniline. These are introduced either directly during the polymerization of aniline or they are reacted a priori with polyaniline base. Inorganic acids³⁻⁶ such as hydrochloric and sulphuric acids are the most common. Organic acids⁷⁻¹¹ such as camphorsulfonic and dodecylbenzenesulfonic acids have also been used for protonation. Carboxylic acids like formic¹², maleic¹³ and tartaric acids¹⁴ have also been employed in limited number of studies. However, these polyaniline salts possess limited solubility.

Weak acids with higher pK_a values offer additional information with respect to the doping property of PANI. Phenoxy acetic acids present a combination of hydrogen bonding and phenyl stacking^{10,11} for the protonation of PANI. In this paper, we describe the synthesis of protonated polyaniline with phenoxy

acetic acid (PAA) and two of its derivatives by the emulsion polymerization of aniline using ammonium persulphate as the oxidant. In recent years emulsion polymerization has come to the forefront^{15,16}. The emulsion process has the distinct advantage that the polymerization is carried out in a heterogeneous system in which the reaction takes place in a large number of loci dispersed in a continuous external phase. Thermal and viscosity problems are much less significant here than in bulk polymerization. Polymers of high molecular weight can be obtained. The PAA dopants are introduced during the polymerization of aniline by emulsion procedure using ammonium persulphate as the oxidising agent. The polyaniline salts synthesized have been subjected to spectral, electrical and morphological studies.

Materials and Methods

Reagent grade aniline and phenol were used after the usual purification. Chloroacetic acid, sodium hydroxide and sodium lauryl sulphate were used as received.

Synthesis

Phenoxy acetic acid and its two derivatives were synthesized following the literature method¹⁷. A mixture of phenol (or 2-chlorophenol or 3,4-dimethylphenol) (1.0 mol) and sodium hydroxide solution (1.0 mol) was taken in a round bottomed flask. An aqueous solution of monochloroacetic acid (1.0 mol) was added to this mixture. Sufficient

amount of water to dissolve the sodium salt of phenol was added. The reaction mixture was heated gently on a boiling water bath for about 4 h. After cooling, it was acidified with hydrochloric acid. The precipitated phenoxyacetic acid was filtered, dried and recrystallized from hot water.

A typical procedure for the preparation of the polyaniline salt is as follows.

Phenoxy acetic acid (or its derivative) was dissolved in 100 ml of chloroform. The emulsifier, i.e. sodium lauryl sulfate (2.25 g) in 50 ml of distilled water was added to it under constant stirring to obtain a milky white emulsion. Aniline (2.6 ml) was then added to it followed by the dropwise addition of an aqueous solution of 0.1 M ammonium persulphate as the oxidant (5.7 g) when a greenish colouration develops indicating the onset of polymerization. The reaction mixture was continuously stirred for about 24 h at room temperature. The organic phase was then separated and washed with distilled water. It was added to 600 ml of acetone to break the emulsion and precipitate out the polyaniline salt. After 10 h, the precipitate was filtered, washed with water followed by acetone and dried under vacuum.

The polyaniline salt synthesized was converted into the free emeraldine base. For this purpose, 1 g of the polyaniline salt was finely powdered and suspended in 250 ml of 0.05 M NaOH solution and stirred for 12 h. The mixture was filtered, washed with 250 ml of 0.05 M NaOH solution and dried in vacuum for 36 h.

Physical measurements

The UV-visible absorption spectra were recorded using a Hitachi U-3400 spectrophotometer using DMSO as the solvent. FT-IR spectra were recorded using a Bruker-IFS 55 spectrometer by the KBr pellet technique. The ^1H and ^{13}C NMR spectra were obtained in $\text{DMSO}-d_6$ with a Bruker AMX 400 MHz spectrometer using tetramethylsilane as the internal reference. Conductivity measurements were made at room temperature using the four-probe technique on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. Thermogravimetric (TGA) measurements were performed using a Mettler Toledo Star System at a heating rate of $20^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Scanning electron microscopic (SEM) measurements were carried out with a JEOL JSM 5600L scanning electron microscope. Wide angle X-ray diffractograms were recorded for the powdered materials using a Siemens D5005 X-ray powder diffractometer.

The solubility of the polymer was evaluated by the following method: About 10 mg of the powdered sample was added to 1 ml of the solvent at 25°C and dispersed thoroughly. After the mixture was stirred for 2 h and the procedure was repeated by adding 0.5 mL of the solvent each time till the compound dissolves.

Results and Discussion

PAA and its two derivatives form salts with PANI and yield conducting green protonated PANI salts. The yield of the polyaniline salt calculated on the basis of the aniline monomer taken varies from 20-43% as seen from Table 1. The variation in the yield of the PANI PAA derivatives can be understood in terms of the stereoelectronic effects of the substituents on the phenyl ring of the PAA. The Cl substituent is electron withdrawing while the CH_3 group is electron donating. The two CH_3 groups in the DMPAA may offer increased steric hindrance than Cl in CIPAA.

Polyaniline has been categorized as an intractable material which is neither soluble nor fusible under normal conditions. The interest in polyaniline as a most suitable conducting polymer has stemmed several strategies to induce solubility and processability in polyaniline. One method is to utilize appropriate organic acids to modify the processability of polyaniline as noted in the introduction. The organic acids influence the solubility of polyaniline through their dipole properties and their tendency to form hydrogen bonds¹⁸. The solubility of the PANI salts was determined in different solvents. It was found that the PANI salts are completely soluble in polar solvents such as DMF, DMSO and a mixture of CHCl_3 and acetone. They are partially soluble in CHCl_3 . One of the aims of the present study of the synthesis of the PANI salt with PAA and its derivatives was to enhance its processability in solution. It is satisfying to note that PANI DMPAA salt shows the best solubility. It is soluble to the extent of 10 g/lit in DMSO as well as in CHCl_3 and acetone mixture (1:3 by volume). The other salts are comparatively somewhat less soluble (3-5 g/lit).

Absorption spectra

Table 1 shows the absorption spectral data of the polyaniline salt as well as its base in DMSO. The spectrum of the PANI base exhibits only two bands at 330 and 636 nm, whereas the polyaniline salts show four absorption bands at 330-335, 427-435, 614-636 and 914-960 nm (see Table 1). The 335 nm

Table I—Yield, absorption bands and conductivity data for the polyaniline salts and the base

Sample	Yield(%)	Absorption maxima (nm)				Conductivity (S cm ⁻¹)
PANI-PAA	43	330	—	636	960	3.22×10^{-3}
PANI-Cl PAA	25	335	435	614	930	3.72×10^{-3}
PANI-DMPAA	20	333	427	633	914	1.54×10^{-3}
PANI-base	60	330	—	636	—	$<10^{-8}$

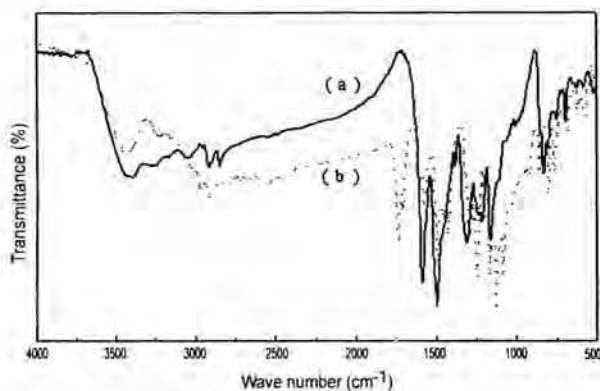


Fig. 1—FT-IR spectra of (a) PANI-base and (b) PANI-DMPAA.

absorption band of the base/salt could be assigned to the π - π^* transition of the benzenoid ring and the ~ 635 nm band has been identified as due to the charge transfer transition (n - π^*) from the HOMO of the benzenoid ring (non-bonded nitrogen lone pair) to the LUMO (π^*) of the quinoid ring. The bands near 435 nm in the spectra of the salts are assigned as due to the polaron transitions. Polaron transitions are found only in the spectrum of the polyaniline salt. Interestingly the longest wavelength band is found at significantly higher wavelengths than that observed in other PANI salts. This suggests the formation of polyaniline of higher molecular weight.

A correlation between the conductivity of the polyaniline salt and the intensity of the longest wavelength band was noticed. The 930 nm band is due to the $-\text{NH}_2^+$ species which is generated on protonation of polyaniline and its intensity is a measure of doping. Continued oxidation of the polymer would lead to the conversion of the $-\text{NH}_2^+$ to NH^+ group, consequently resulting in a decrease in the intensity of the 930 nm band and also a decrease in the conductivity of the polyaniline salts.

FTIR spectroscopy

The FT-IR spectrum of PANI base is compared with that of PANI DMPAA in Fig. 1. A more direct evidence for the protonation of polyaniline is obtained from the FT IR spectra of PANI-PAA salts. The spectra of PAA and its two derivatives show a strong

broad band at 3630 – 3660 cm^{-1} due to OH stretching and a strong doublet at 1750 , 1720 cm^{-1} , which corresponds to C=O stretching vibration. The -OH stretching frequency decreases to about 3400 – 3420 cm^{-1} and the C=O stretching band by 10 to 15 cm^{-1} showing clearly hydrogen bonding type of interactions between PANI and PAA compounds. The NH stretching in PANI salts is observed at 3240 – 3260 cm^{-1} showing a small dependence on doping anion.

The chief bands at 1580 and 1500 cm^{-1} in the polyaniline salts correspond to the stretching vibrations of the quinonoid and benzenoid rings respectively¹⁹. The latter band is more intense than the former. The ratio of the infrared band intensity at ~ 1500 and 1590 cm^{-1} is directly related to the oxidation state of the polymer. In the case of PANI-PAA salts more benzenoid units exist in the polymer than the quinonoid units i.e. PANI is less oxidized. Consistent with this finding the band characteristic of the PANI base is found at 1375 cm^{-1} in all the FT-IR spectra demonstrating that doping is partial. The band arising from C-N stretching adjacent to the quinonoid ring is found at 1420 cm^{-1} , while the band due to C-N stretching of the secondary aromatic amine occurs near 1296 cm^{-1} . In the 1010 – 1170 cm^{-1} region, the aromatic C-H inplane bending modes are observed. The characteristic out of plane C-H deformations of 1,4-disubstituted benzene ring of PANI are found at 800 and 860 cm^{-1} .

The infrared band at 1308 cm^{-1} is strengthened on protonation and the intensity of the band characteristic of the conducting protonated form at about 1246 cm^{-1} increases. The latter band is attributed as due to C-N⁺ stretching mode in the polaron structure¹⁸. A band corresponding to the bending mode of $-\text{NH}^+=$ occurs at 1128 cm^{-1} on protonation. It indicates the presence of positive charges in the chain and the distribution of the dihedral angle between the quinonoid and benzenoid rings.

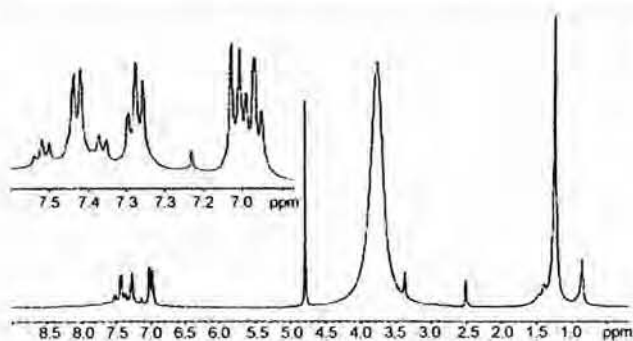
NMR spectra

Figure 2 shows the ^1H NMR spectrum of PANI-CIPAA salt. The ^1H and ^{13}C chemical shifts of the

Table 2— ^1H and ^{13}C chemical shifts in δ ppm for PANI salts*

Assignment	PANI -PAA	PANI -Cl PAA	PANI -DMPAA
^1H NMR signals			
Quinoid ring	7.29	7.30	7.26
Benzenoid ring	6.9 (6.6-7.33)	6.94 (6.9,7.0,7.25,7.4)	6.6 (6.66, 6.73)
-NH	3.7	3.9	3.6
-O-CH ₂ -	(--) 4.7 (4.5)	(--) 4.8 (4.8)	(--) 4.6 (4.63)
-CH ₃	-	-	2.1 & 2.2 (2.2, 2.25)
^{13}C NMR signals			
-CH (Quinoid ring)	134.69	130.03	135.38
-CH (Benzenoid ring)	126.2, 119.7 (124, 130)	128.0, 121.87 (114,124,127,130,153)	133.74, 121 (116,130,138,155)
-O-CH ₂ -	69.79 (67.0)	71.4 (66.00)	69.82 (65.11)
-COOH	172.75 (171.22)	-- (172.09)	175.52 (172.75)
-CH ₃	-	-	23.62 & 24.83 (18.84, 20.04)

*Values in the parenthesis are the corresponding chemical shifts of the dopants

Fig. 2— ^1H NMR spectra of PANI-Cl PAA.

PANI-salts are listed in Table 2. The spectrum of the PANI PAA salt exhibits a sharp singlet at δ 4.7 ppm, which is characteristic of the dopant arising from the -OCH₂ group. The signals due to the aromatic protons of the quinonoid ring (doped state) and the benzenoid protons of PANI in the region of 6.6-7.3 ppm overlaps with the aromatic protons of the dopant and are not much useful. The downfield shift of the signal corresponding to the aromatic and N-H protons is attributed to the conversion of some of the -NH groups into -NH₂⁺ on protonation of PANI by PAA. The characteristic methyl resonance peak of DMPAA is observed as two sharp intense singlets at δ 2.13 and 2.18 ppm. The results demonstrate the occurrence of PAA and its derivatives in the PANI salts.

As in the ^1H NMR, there is extensive overlapping between the ^{13}C signals of PANI and PAA

compounds in the spectra of PANI salts in the aromatic region, rendering it difficult to draw unambiguous conclusions. However, the ^{13}C resonance signals of the OCH₂ group of PAA and its derivatives shift by 3-5 ppm in the spectra of the PANI salts. Similarly the carboxylate carbon of PAA and its derivatives also shifts by 2-3 ppm in the PANI salts. The methyl resonance peak of DMPAA shifts by 4 to 5 ppm in the PANI-DMPAA salts. These shifts clearly demonstrate the chemical interaction between PANI and PAA and its derivatives.

Conductivity

The protonation is well documented by the conductivity measurements. The conductivity of PANI base is less than $10^{-8} \text{ S cm}^{-1}$. It increases after protonation by phenoxy acetic acids to 1.5×10^{-3} to $3.7 \times 10^{-3} \text{ S cm}^{-1}$ (Table 1) i.e. by over six orders of magnitude. This is a level of conductivity that may be of interest for some applications². Interestingly, PANI ClPAA salt exhibits slightly higher conductivity than PANI-PAA salt. The electron withdrawing nature of the chlorine substituent renders the -COOH proton more acidic thus facilitating the protonation. This interpretation seems to get support from the slightly lower conductivity observed for PANI DMPAA, where the weakly electron donating methyl groups render the carboxylic hydrogen less acidic.

Table 3—Position of Bragg's peaks for polyaniline salts (2θ (d(Å))^a)

Sample	2θ (d(Å)) ^a					
PANI-PAA			25.3 (3.51)	24.76 (3.59)	20.00 (4.43)	12.46 (7.09)
PANI-Cl PAA	27.86 (3.19)	26.78 (3.32)	25.00 (3.55)	24.02 (3.70)	19.68 (4.50)	16.38 (5.40)
PANI-DMPAA		26.06 (3.41)			18.6 (4.76)	14.38 (6.15)
						8.12 (10.84)

The value in the parenthesis is the Bragg's distance d in Å

Thermogravimetric analysis

The thermogravimetry (TGA) and differential thermal analysis (DTA) of the samples were recorded from 20 to 600°C at a heating rate of 20°C min⁻¹ in static air. The thermogram shows a three step weight loss behaviour. The weight loss in the first step up to about 100-140°C is due to the loss of moisture. In the second step (up to 300-350°C), the weight loss is due to the loss of the dopant. A slow and gradual weight loss profile was noticed for PANI salts after 400°C, due to their decomposition. The thermograms showed the PANI ClPAA salt to be thermally more stable than PANI-HCl salt.

The DTA and DTG curves of the PANI-PAA salts show an endothermic peak around 100-120°C and two exothermic peaks, a broad peak due to the loss of dopant (200-250°C) and another around 450-500°C due to the complete decomposition. As noted from the DTA studies, the polyaniline base seems to be slightly more stable than the salt.

Morphology and X-ray diffraction

The scanning electron micrographs reveal a granular morphology for the PANI-PAA salt, which is similar to that reported for the PANI salts with other dopants²⁰. Figure 3 shows the SEM picture of PANI ClPAA salt. It reveals crystalline as well as amorphous morphology in contrast to the PANI base. The positions of the Bragg's peaks along with their d spacing obtained from the wide angle X-ray powder diffractograms are given in Table 3. The PANI base and its salts exhibit their strongest peak at $2\theta = 9-10^\circ$, their second strongest peak at $23-26^\circ$, a medium intensity peak at $19-22^\circ$ and a weak peak at $14-16^\circ$. The number of sharp peaks in the diffractogram is the highest in the PANI ClPAA salt showing its more crystalline nature and is the least in PANI-DMPAA salt. The X-ray powder diffractograms of the PANI salts are consistent with the results of the SEM studies.

Pouget *et al.*^{21,22} have carried out comprehensive X-ray diffraction studies on polyaniline emeraldine

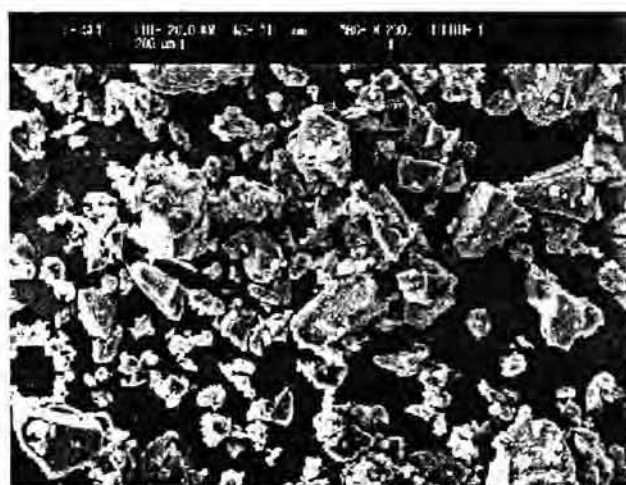


Fig. 3—SEM of PANI Cl PAA salt.

base and (hydrochloric acid and camphor sulfonic acid) salts, as powders as well as stretched and unstretched films. They have investigated the effect of repeated doping and dedoping processes on these materials. They conclude that polyaniline contains both crystalline and amorphous regions consistent with the findings of the present work.

Conclusions

Protonated electrically conducting polyaniline salts with phenoxy acetic acid and its two derivatives are highly soluble in solvents such as DMF, DMSO and a mixture of CHCl₃ and acetone and hence possess the desirable property for processability. The emulsion method of oxidative polymerization of aniline gives moderate yields of the product. These polyaniline salts possess moderate conductivity. The proton interaction is dominating but the nature of the anion too plays an important role in establishing the redox state of the polymer.

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References

- 1 Andre J M & Delahalle J J, *Chem Rev*, 91 (1991) 843.
- 2 Trivedi D C & Dhawan S K, *Synth Met*, 58 (1993) 309.
- 3 Paul E M, Ricco A J & Wrighton M S, *J Phys Chem*, 89 (1985) 1441.
- 4 Wan M & Yang J, *J Appl Poly Sci*, 55 (1995) 399.
- 5 Sandi G & Vanysek P, *Synth Met*, 64 (1994) 1.
- 6 Torresi R M, Cordoba de Torresi S I, Gabrielli C, Keddani M & Takenouti H, *Synth Met*, 61 (1993) 291.
- 7 Tzou K & Gregory R V, *Synth Met*, 53 (1993) 365.
- 8 Cao Y & Heeger A J, *Synth Met*, 52 (1993) 193.
- 9 Cao Y & Smith P, *Polymer*, 34 (1993) 3139.
- 10 Stejskal J, Sapurina I, Trchova M, Proes J, Krivka I & Tobolkova E, *Macromolecules*, 31 (1998) 2218.
- 11 Trznadel M & Rannou P, *Synth Met*, 101 (1999) 842.
- 12 Hatchett D W, Josowicz M & Janata J, *J Phys Chem B*, 103 (1999) 10992.
- 13 Samui A B, Patankar A S, Satpute R S & Deb P C, *Synth Met*, 125 (2002) 423.
- 14 Palaniappan S, *Eur Polym J*, 37 (2001) 975.
- 15 Osterholm J E, Cao Y, Klavetter F & Smith P, *Polymer*, 35 (1994) 2902.
- 16 Kinlen P J, Liu J, Ding Y, Graham C R & Remsen E E, *Macromolecules*, 31 (1998) 1735.
- 17 Furniss B S, Hannaford A J, Smith P W G & Tatchell A R, *Vogel's text book of practical organic chemistry* (ELBS, Longman, London), 1984; p 754.
- 18 Trivedi D C, *Hand book of organic conductive molecules and polymers*, edited by H S Nalwa, Vol. 2 (Wiley, Chichester) 1997, p 528, 532.
- 19 Quillard S, Louran G, Buisson J P, Boyer M, Lapkowski M, Pron A & Lefrant S, *Synth Met*, 84 (1997) 805.
- 20 Palle Swapna Rao, Sathyanarayana D N & Palaniappan S, *Macromolecules*, 35 (2002) 4988.
- 21 Pouget J P, Oblakowski Z, Nagami Y, Albouy P A, Laridjani M, Oh E J, Min Y, MacDiarmid A G, Tsukamoto J, Ishiguro T & Epstein A J, *Synth Met*, 65 (1994) 131.
- 22 Pouget J P, Jozefowicz M E, Epstein, A J, Tang X & MacDiarmid, A G, *Macromolecules*, 24 (1991) 779.