Modification in polyaniline oxidation state as a consequence of anthracene doping

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ABSTRACT

The modification in oxidation state of polyaniline when it was doped with anthracene was studied through UV-VIS Absorption studies and FTIR measurements. UV-VIS absorption studies indicated that with increasing dopant concentration the intensity of absorption at 600 nm increases. This is attributed to the change in population of quinoid imine units in the polymer backbone. Two significant changes were observed in the FTIR spectrum of bare and doped polyaniline. First is appearance of a peak at 1140.0 cm^{-1} in doped compounds, attributed to vibration of the $-NH^+=$ structure. It suggests increase in number of quinoid imine units in doped polymer. And second is decrease in intensity in the peak at 1294.8 cm^{-1} in doped polyaniline, which is attributed to decrease in л electron delocalization across the polymer backbone. The change in intensity of absorption at 600 nm depicts modification in oxidation state of polyaniline. This structural modification in polyaniline is assigned to the anthracene doping in it, which may also lead to corresponding changes in its properties. This binary system can be explored for the study of mutual interaction of anthracene and polyaniline.

Keywords: Organic compounds, chemical synthesis, FTIR, electrical conductivity.

INTRODUCTION

Scientific interest in polyaniline originates from the fact that this conjugated polymer can be doped either by charge transfer or by the acid/base (protonation) reaction that converts the semiconducting emeraldine base form to the conducting emeraldine salt[1]. The excellent environmental and thermal stability in the conducting form and the potential for relatively low cost make polyaniline an attractive material for applications in batteries[2,3,] light-emitting diodes[4], and anti-static packaging and coatings[5]. Chang Ryoo and Eun Jeon et. al.[6], performed photoconductivity experiments on polyaniline in its all

three oxidation states with a view to evaluate its energy band structure and to find out corresponding band gap energies. The oxidation state of polyaniline determines its energy band structure in the sense that, change in oxidation state implies change in structure of polymer chain. There are three basic oxidation states of polyaniline. They are 1) leucoemeraldine base 2) emeraldine base and 3) pernigraniline base. This classification is based on the number of quinoid imine segments in the polyaniline backbone[7]. It was observed that these oxidation states are vulnerable to the exposure to chemical and/or physical reactions and environmental conditions such as moisture; light etc. the interconversion of all three oxidation states is therefore possible. For ex. photoexcitation and exposure to moisture etc. leads to the oxidation (reduction) of polyaniline by removing (introducing) electrons from this polymer, which causes its aging. The photo-oxidation converts polyaniline into its completely oxidized state, namely pernigraniline salt[8]. Another consequence of photo-oxidation is low photoconductivity of polyaniline. According to Epstein *et al.*[9] exposure to light induces formation of excitons into polyaniline. Some of these excitons dissociate into polarons. These photoexcited polarons have a low mobility leading to low photoconductivity of polyaniline. Therefore it is evident that interconversion of polyaniline oxidation states does not only change its structure but also induce change in its properties. Therefore in order to achieve a structural tunability for desired applications, the process of modification in oxidation state must be evaluated. If polyaniline can be doped with a material that can induce charge transfer process into it then a structural modification can be expected and it can be studied through relevant characterization techniques. Anthracene is one such material that is known due to its ability to induce PET (photoinduced electron transfer) processes[10] and it is one of the most employed chromophores. A considerable number of papers have focussed on the use of anthracene containing compounds as protein photo cleavers[11], organic light-emitting diodes and materials[12-15], crystal engineering[16], molecular imprinted polymers[17], sensors and chemosensors[18-20]. It has been reported to exhibit two kinds of photoconductivity, namely, bulk and surface[21]. Anthracene is thus reported to be electroactive in UV region[22, 23] and polyaniline on the other hand in Vis/IR region and hence a composite of these two would exhibit good photoconductivity in entire UV-VIS-IR region. Rukenstein *et al.*[24] have developed emulsion polymerization pathway for the preparation of conductive polyaniline composite using the stabilization of emulsion by surfactant. He reported this method to produce PANI/PMMA[25], PANI/PS[26] and PANI/SBS rubber[27] composite. The present paper reports the synthesis of polyaniline/anthracene doped system by emulsion polymerization pathway and the study of effect of varying the concentrations of anthracene on polyaniline oxidation state.

SYNTHESIS AND CHARACTERIZATION

Anthracene, aniline, ammonium peroxydisulphate, sodium dodecylsulphate, methanol, hydrochloric acid, N, N-dimethyl formamide, acetone and chloroform were all purchased from Merck India Pvt. Ltd. and used as received without further purification. Ammonium peroxy-disulphate $[(NH_4)_2S_2O_8]$ is a strong oxidizing agent which is used to catalyze polymerization[28]. Sodium dodecylsulphate [SDS - $C_{12}H_{25}SO_4Na$] is used

to maintain the acidic nature of the reaction mixture. In a typical experiment, (as shown in the flow chart of *Fig.1*) the aqueous solution of SDS was used as emulsion medium. A solution of aniline and the host anthracene was prepared in chloroform in dispersed phase. The aniline was polymerized by emulsion polymerization by introducing APS as oxidizing agent. Keeping the amount of all the reactants to be constant, the anthracene concentration was varied between 0.25 wt% to 0.5 wt%. Commencement of polymerization was marked by a gradual change in colour of the solution from pale white to dark green in a reaction that continued till four hours as reported in[29]. The reaction mixture was then allowed to stand under ambient conditions for 12 hrs and then filtered. The as obtained dark green filtrate was washed repeatedly with distilled water and methanol to remove the unreacted oligomers and traces of anionic surfactant etc. Final product was dried in ambient conditions for well over three days and stored in polyethylene vials for further characterizations. *Table 1* depicts the nomenclature maintained for these compounds and the corresponding wt% of anthracene in them.   These compounds were subjected to optical absorption studies in the wavelength range 200-1200 nm using UV–VIS spectrophotometer (UVPC 1601, Shimadzu Corp. Japan). Infrared spectra of KBr pellets of samples were recorded (4 scans per spectrum at 2 cm^{-1} resolution) with a Perkin–Elmer Spectrum RX – I FTIR spectrometer in the range of 400–4000 cm^{-1}.

RESULTS AND DISCUSSION

1. UV-VIS Absorption Measurements

　　　　The doped and undoped compounds were dissolved in DMF solvent and UV–Vis absorption spectra recorded in the wavelength range 200-1200 nm. The optical absorption peak of weakly doped polyaniline and composite powder is shown in *Fig.3*. From this figure, it is seen that there are only two peaks; one at 320 nm assigned for the π- π* transition within the benzenoid ring[30] and another at 600 nm in the spectra of S-1 along with an additional peak below 300 nm. During the study of different oxidation states of polyaniline, Albuquerque *et.al.*[31] explained the appearance of 320 nm peak both in emeraldine and pernigraniline forms of polyaniline, while the peak at 600 nm was categorically assigned to completely oxidized pernigraniline form only. Its appearance in the emeraldine base form of polyaniline was assigned to the molecular exciton associated with the quinone-imine structure. We however have a reason to believe that it belongs to as prepared weakly doped polyaniline samples. As has already been stated the emeraldine base polyaniline contains non conducting regions made of quinoid-imine structures, and depending upon the degree of oxidation of polyaniline, its optical absorption intensity and the peak position too varies. So when polyaniline is in leucoemeraldine oxidation state which is its completely reduced form, theoretically there are no quinoid-imine segments across the chain and hence no or very low optical absorption is found at 600 nm[32]. Which is why it is assigned degree of oxidation, 1-y = 0 [32]. Whereas, the pernigraniline oxidation state of polyaniline which is its completely oxidised form shows a very intense optical absorption band at 600 nm, and it is assigned with 1-y = 1. The degree of oxidation of emeraldine base form of polyaniline is thus assigned an intermediate value of 1-y = 0.5, suggesting that there are as many quinoid-imine units in the backbone as there are benzenoid-amine units. Hence low intensity of optical absorption band appearing at 600 nm in the spectra of S-1 in *Fig.2* is prompting us to declare it being only weakly

protonated. Therefore a detailed study for the identification of exact oxidation state of polyaniline was carried out. ***Table 1*** depicts the value of oxidation state of polyaniline with respect to the dopant concentration. It was calculated by the method reported by Albuquerqy *et. Al.*[31]. Both FTIR spectra and UV-Via absorption studies are in well agreement with those already reported for weakly protonated polyaniline[33, 34, 35]. When anthracene was doped in polyaniline, the 600 nm peak underwent a remarkable change. As we can see in ***Fig.2*** the intensity of this peak is increasing with the increasing dopant concentration. The rise or fall in the intensity of this peak has been taken to represent the increasing and/or decreasing concentration of quinoid-imine structures in the backbone of polyaniline[31, 36]. This increase in intensity of absorption might indicate a possible charge transfer interaction between dopant and host molecules because of which a modification in oxidation state of polyaniline may happen. As shown in ***Table 1*** the oxidation state of polyaniline is shifted towards value of pernigraniline state. So it can be said that anthracene doping in polyaniline makes it loose its electrons to anthracene and converts the benzenoid units in its backbone to the quinoid units. This results in increased intensity of absorption at 600 nm after doping.

2. FTIR Spectroscopy

FTIR spectroscopy is a powerful tool to monitor the changes in the molecular structure. ***Fig.3*** shows the FTIR spectra of anthracene, undoped and doped compounds. In polyaniline polarons are responsible for the broad absorption band at wavenumbers above 2000 cm^{-1} namely 3445.8 cm^{-1}, 2921.2 cm^{-1} and 2363.9 cm^{-1} [33, 38, 39]. The main peaks consistent with quinone and benzene ring deformations are observed at 1559.1 cm^{-1} and

1472.3 cm^{-1}. The absorption band at 1294.8 cm^{-1} is due to C–N stretching of secondary aromatic amine which represents л electron delocalization induced in the polymer by protonation[33]. The band characteristic of the conducting protonated form is observed at about 1235.3 cm^{-1} which has been interpreted as C-N$^{+\bullet}$ stretching vibration in the polaron structure[40]. The region 900–700 cm^{-1} corresponds to aromatic ring and out-of-plane C–H deformation vibrations. Their frequencies are mainly determined by the number of adjacent hydrogen atoms in the ring[41]. The characteristic peaks of anthracene as shown in ***Fig.3*** are found at 3046.4 cm^{-1}, 881.2 cm^{-1}, 725.5 cm^{-1} and 470.6 cm^{-1} in S-2, and at 3040.2 cm^{-1}, 878.7 cm^{-1}, 721.4 cm^{-1} and 473.3 cm^{-1} in S-3[42]. The fact that thus formed polyaniline is only weakly doped is emphasized by the absence of a peak at 1140 cm^{-1} both in the spectra of polyaniline and the composites. This peak represents the vibration mode of the – NH$^+$= structure, which is formed during protonation[43]. Chiang and MacDiarmid *et.al* [43] used it as a measure of the extent of electron delocalization in the polymer. The intensity of this peak can therefore be considered as a measure of the degree of doping of the polymer backbone[43]. ***Fig. 3*** depicts a substantial drop with a slight red shift in the intensity of both of the broad band's above 2000 cm^{-1} namely 3445.8 cm^{-1} and 2921.2 cm^{-1}, suggesting the absence of polaronic transitions in the doped compounds however behaviour of the band at 2363.9 cm^{-1} could not be verified. Similarly the absorption band at 1294.8 cm^{-1} which signifies л electron delocalization can be seen to have undergone a blue shift and also visibly reduced in intensity in the doped compounds. A major change can also be observed in the signature peak of conducting protonated form of polyaniline

which is at 1235.3 cm^{-1} [43]. It is decreasing in intensity with increasing dopant concentration, so much so that in S-3 it's absolutely vanished. This means that the deprotonation is more pronounced in doped compounds. But deprotonation in polyaniline is not only manifested through hampering the л electron delocalization and/or through removal of counter ions. A structural change in polyaniline chain also accompanies the deprotonation i.e. the benzenoid units get changed into quinoid units which is manifested by a substantial blue shift in peaks at 1559.1 cm^{-1} and 1472.3 cm^{-1} respectively[33]. This however is not the case here for only those peaks that signify л electron delocalization and protonation of polyaniline have undergone changes whereas the peak at 1559.1 cm^{-1} is only slightly blue shifted.   Another major aspect synonymous with substantial deprotonation is appearance of a band at 1374 cm^{-1} in the neighbourhood of quinoid ring that is associated with complete deprotonation of polyaniline doped with HCl[33, 34]. It signifies C–N stretching vibration. But it never appeared in spectra of doped compounds even when the concentration of anthracene was maximum (S-3). It may mean that polyaniline macromolecules persistently retain small conducting segments in all the doped compounds irrespective of the concentration of anthracene. Anthracene should be either helping in building up of non conducting segments around the polymer chain or forming charge transfer complexes with polyaniline macromolecules. So that in any of the two ways it would hamper the charge delocalization without inducing deprotonation. Width of the peaks at 3046.4 cm^{-1} in S-2 and at 3040.2 cm^{-1} in S-3 is actually prompting us to accredit anthracene for increasing nonconducting segments and modifying the oxidation state of polyaniline. FTIR spectra of

both the samples depict that these peaks are broader than they are in pure anthracene's spectra. According to G.Madhurambal *et. al.*[42] when hydrogen atoms in the anthracene ring are not exerting any bonding interaction with molecules then this peak appears sharper. So it may be that the hydrogen atoms in the anthracene ring may be bonding with polyaniline chain. Using the UV-Vis data and value of oxidation state of doped polyaniline given in *Table 1*, it can be postulated that the anthracene molecules tend to oxidise the polyaniline macromolecules. When such an oxidation of polyaniline happens then the population of quinoid imine segments increases as the FTIR spectra of the doped compounds depicted.

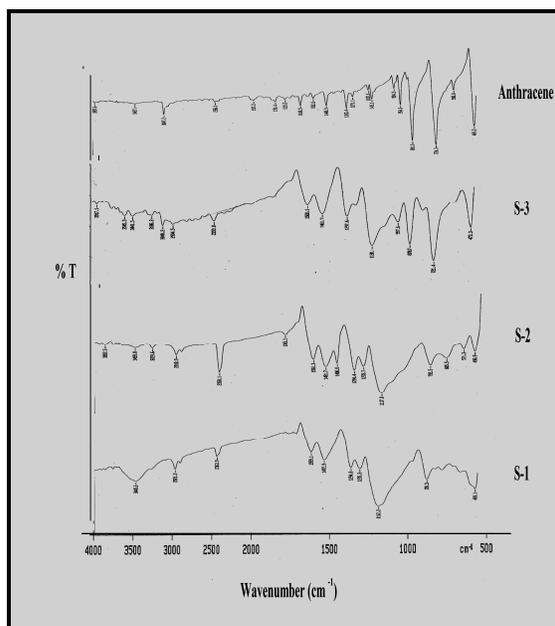*Table 1*:   Sample codes, oxidation state and corresponding wt% of anthracene polyaniline.

Sample Code	wt% of Anthracene	Polyaniline oxidation state
S – 1	00	0.57
S – 2	0.25	0.58
S – 3	0.5	0.68
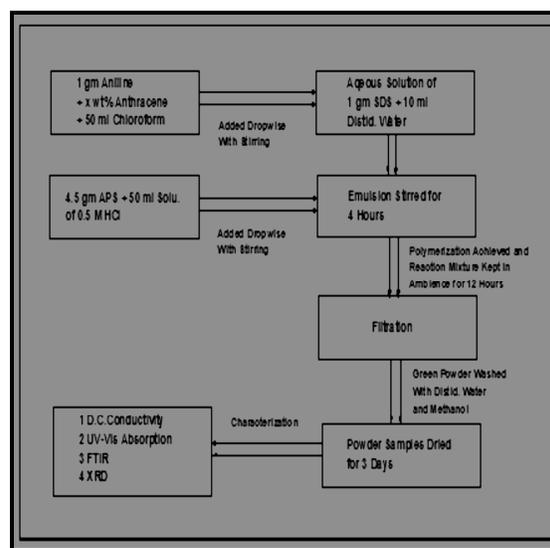
Fig.1: **Flow chart for synthesis of anthracene doped polyaniline.**
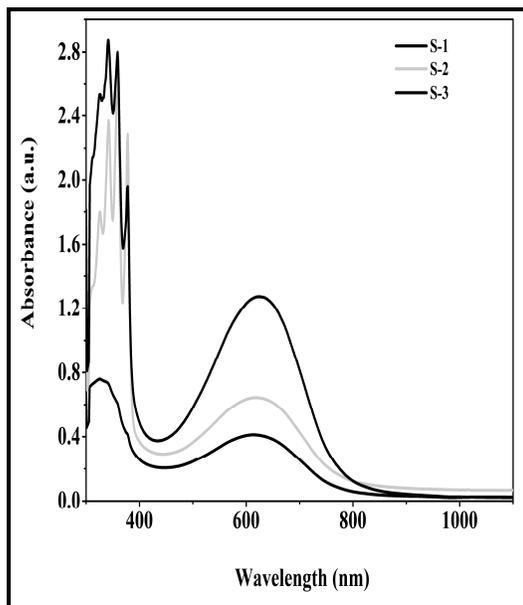
Fig.2:   UV-Vis absorption spectra of doped and undoped compounds

Fig.3:   FTIR spectra of doped and undoped compounds.

CONCLUSIONS

Polyaniline was doped with anthracene emulsion polymerization method. Change in oxidation state of polyaniline was studied with respect to anthracene concentration. The anthracene doping may give rise to mainly two possibilities, 1) Segregation of anthracene molecules as non conducting regions around polyaniline macromolecules without interacting with them, or 2) oxidation of polyaniline macromolecules by anthracene, through the formation of charge transfer complexes. Although the formation of anticipated charge transfer complex between dopant and host molecules was not clear still it was observed from UV-Vis and FTIR studies that after doping the oxidation state of polyaniline shifts towards higher values. The higher value of oxidation state of polyaniline indicates the formation of quinoid units across its backbone. These compounds also resulted in better solubility in common organic solvents such as DMF, which is an added advantage as compared to the pure polyaniline synthesized through the same method. These compounds are expected to be photosensitive and UV active and could be tested for photoconductive applications.

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