Synthesis and Characterization of Polyaniline Doped with Cu-Salts and Cu-Complexes

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ABSTRACT

In this work, we have synthesized polyaniline doped with Cu (II) salts and coordination complexes in presence of Aniline was polymerized in presence ammonium persulphate (APS). We varied the concentration of APS and also that of Cu (II) salts and complexes to see the effect of these on the properties of polyaniline. We investigated the effect of the dopant and ligand around Cu (II) ion on the morphology, crystallinity and conductivity of the resultant polyaniline. The products were characterized by UV-Vis, FT-IR spectroscopy, while the morphology and crystallinity were investigated by scanning electron microscopy, and X-ray diffraction studies respectively. Results show that the morphology, crystallinity and conductivity of the doped polyanilines are found to be influenced by nature of ligand.

KEYWORDS: *Conducting polymer, polyaniline, Cu-salts and Cu-complexes, dopant*

1. INTRODUCTION

Among the family of intrinsically conducting polymers, polyaniline (PANI) has been most actively investigated due to its unique doping/dedoping behavior, facile synthesis and good environmental stability [1]. The beauty of this class of material is that the conductive properties could be tuned by doping. Polyaniline (PANI) is unique among the family of conjugated polymers since its doping level could be readily controlled through an acid doping and base dedoping process [2].

Besides the use of different protic acids as dopants [3], Lewis acids and transition metal ions [4-7] have also been used as dopants in polyaniline synthesis. Over the past years, there has been a growing interest in the research on polyaniline (PANI)/metal systems [8-10]. This is because of their potential practical applications, as redox-active catalyst [11], corrosion inhibitor [6] and organic electronic [12] and electroluminescent devices [13]. Transition metal ions can act as oxidizing agents as well. which can act as oxidizing agent, According to O.P Dimitriev [10] doping occur through a two-step redox process. At first, the metal ions oxidize EB-PANI amine nitrogen atoms; afterwards, the reduced metal ions coordinate to imine nitrogen and finally, the reduced cations are oxidized by the imine groups, resulting in radical cation segments (ES-PANI) and the corresponding oxidized metal ions [10]. O.P Dimitriev [10] reported that the formation of complex of transition metal and PANI are dependent on both the cation and anion of the inorganic salt used, as well as on the solvent. In some cases, formation of the complex occurred in the form of a precipitate directly in the solution. Change of anion with same metal cation produced different results. He observed that the addition of the LaNO$_3$ to the dimethyl form amide (DMF) solution of EB-PANI did not result in formation of any precipitate, whereas use of the LaCI$_3$, yielded a dark-green precipitate in a few minutes. It has also been reported that the conductivity of films doped by nitrates of transition metals was usually 1 or 2 orders of magnitude smaller as compared to films doped by chlorides [4].

In the present work, our objective is to study the effect of the various ligands around the Cu^{+2} ion used as dopants on the properties of polyaniline and reported the effect of the size of ligands around the Cu^{+2} ions on the properties of Cu^{+2} doped polyaniline.

2. EXPERIMENTAL
2.1. Materials
Aniline was distilled under reduced pressure before use. Copper sulphate ($CuSO_4.5H_2O$), hydrochloric acid (HCl), ammonia, ethylene diamine, ammonium persulphate (APS), acetone and methanol were analytical grade chemicals of MERCK-India and they were used as received without further purification.

Table 1 Sample Coding and the Conductivity values

Dopant Name	Dopant Conc. (M)	Sample code	Conductivity (Scm^{-1})
No Dopant	Nil	EB-PANI	1.2×10^{-9}
HCl	0.01	HCl-PANI	3.845
$CuSO_4.5H_2O$	0.002	A	0.477
	0.006	B	0.556
	0.02	C	0.667
	0.04	D	0.778
	0.08	E	0.899
$[Cu(NH_3)_4]SO_4$	0.002	A1	0.367
	0.006	B1	0.389
	0.02	C1	0.423
	0.04	D1	0.451
	0.08	E1	0.487
$[Cu(en)_2]SO_4$	0.002	A2	0.321
	0.006	B2	0.345
	0.02	C2	0.365
	0.04	D2	0.388
	0.08	E2	0.422
$[Cu(en)_3]SO_4$	002	A3	0.167
	0.006	B3	0.189
	0.02	C3	0.246
	0.04	D3	0.271
	0.08	E3	0.295

2.2. Preparation of $[Cu(en)_2]SO_4$ and $[Cu(en)_3]SO_4$
Bis-ethylenediamine Copper (II) sulphate was prepared by the reaction of anhydrous copper (II) sulphate with ethylenediamine in a molar ratio of 1:1 in distilled water [15]. Dark blue prismatic crystals were obtained by slow evaporation of the solvent used. Tris-ethylenediamine copper (II) sulphate was prepared by mixing hydrated copper (II) sulphate and large excess of ethylenediamine and then recrystallising it from water [16].

2.3. Synthesis of Polyaniline Hydrochloride (HCl-PANI)
Polyaniline Hydrochloride (HCl-PANI) was synthesized by the procedure of MacDiarmid *et al.*[17]. 1.82 mL (0.04 mol) of distilled aniline was dissolved in 100 mL 1M HCl solution and cooled to 0-5°C. To this, 20 mL cold ammoniumpersulphate (APS) solution containing 4.56 g (0.04 mol) APS was added very slowly in a dropwise manner. The reaction mixture was then agitated for 3 h. Polyaniline hydrochloride thus formed was filtered under suction, washed with dilute HCl, water and methanol and dried under vacuum. It was labeled as HCl-PANI

2.4. Preparation of Emeraldine base form of Polyaniline (EB-PANI)
The dried emeraldine salt form of polyaniline (ES-PANI) was grounded to fine powder. The powdered HCl-PANI was then agitated with 0.1 M NH_4OH solution (P^H 9) for 6 h to form emeraldine base of polyaniline (EB-PANI). It was then filtered under vacuum, washed with water and dried. It was labeled EB-PANI.

2.5. Preparation of polyaniline doped with $CuSO_4.5H_2O$, $[Cu(NH_3)_4]SO_4$, $[Cu(en)_2]SO_4$ and $[Cu(en)_3]SO_4$
Aniline (1.82 ml 0.04 mol) was added to 100 mL water containing requisite amount of copper (II) compound or complex (table 1). The reaction mixture was stirred for 2 h and 4.56 g (0.04 mol) $(NH_4)_2S_2O_8$ dissolved in 20 mL water was added drop wise over a period of 30 minutes. The reaction temperature was maintained at 0-5°C. It was kept undisturbed for 24 h for the reaction to complete. The resultant polyaniline was filtered, washed with rectified spirit and acetone and then vacuum dried at 60°C for 5 h.

3. CHARACTERIZATION
The FTIR spectra of all samples were recorded in a SHIMADZU IR Affinity-1 spectrophotometer as KBr pellet at room temperature in the range of 4000-400 cm^{-1}. The UV-Vis absorption spectra were recorded in the 300-900 nm range in a SHIMADZU UV-1800 spectrophotometer using 1-methyl 2-pyrrolidone (NMP) as solvent. The phase identification of finely powdered samples were performed with an X'Pert Pro X-ray diffractometer, Phillips with nickel-filtered Cu kα radiation (wavelength = 1.5414 Å) in the 2θ range of 5-40˚. Thermo gravimetric analysis (TGA) of the samples was carried out in a Perkin Elmer Pyris 1 TGA instrument at a heating rate of 10°C/min under N_2 atmosphere over a temperature range of 30-800°C. SEM-micrographs were obtained in a JSM-6360 (JEOL) scanning electron microscope at an accelerating voltage of 20 kV. The electrical

conductivities of the samples were measured at room temperature with dry pressed pellets by standard four probe technique.

4. RESULTS AND DISCUSSION
4.1. UV-VISIBLE SPECTRAL STUDIES

The UV-Vis spectra of EB-PANI, HCl-PANI and PANI doped with Cu^{+2} ion with different ligands are presented in figure 1. The benzenoid to quinoid excitation transition (BQET) was observed at 634 nm for the undoped PANI. For HCl doped PANI this peak disappeared. But on being doped by Cu^{+2} ion this peak undergoes a blue shift to the range of 533-573 nm from 634 nm. Similar blue shift was also reported by Chen et al. [18] when they used a number of transition metal ions including Cu^{+2} to dope PANI. Hirao et al. [19] ascribed such a blue shift to the complexation of the Cu^{+2} ion with polyaniline and Chen et al. [18] also attributed this shift to the interaction of transition metal ions with polyaniline molecular chains. The observed blue shift may be due to complexation of the Cu^{+2} ion with the polyaniline as well as due to partial oxidation of polymer backbone [20]. Further it was observed that this shift was dependent on the size or bulkiness of the ligands around Cu^{+2} ion. It is evident from figure 1 that larger the size of the ligands smaller is the blue shift. This is due to less efficient complexation of Cu^{+2} ion with polyaniline caused by the bulkiness of the ligands around the Cu^{+2} ion. Concentration of the dopant also has an influence on the extent of such a blue shift [21]. It was observed that for the same ligand higher the concentration of the dopant larger was the blue shift. This is evident from figure 2, figure 3, figure 4 and figure 5 where the concentration of the dopants was varied for the same ligand. When the dopant concentration was high, the extent of doping became more efficient showing a larger blue shift.
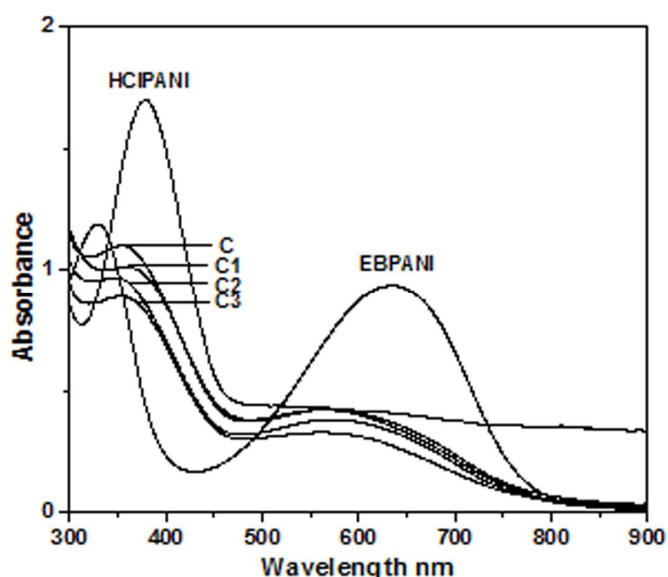

Figure 2 UV-Vis spectra of PANI doped with $CuSO_4.5H_2O$
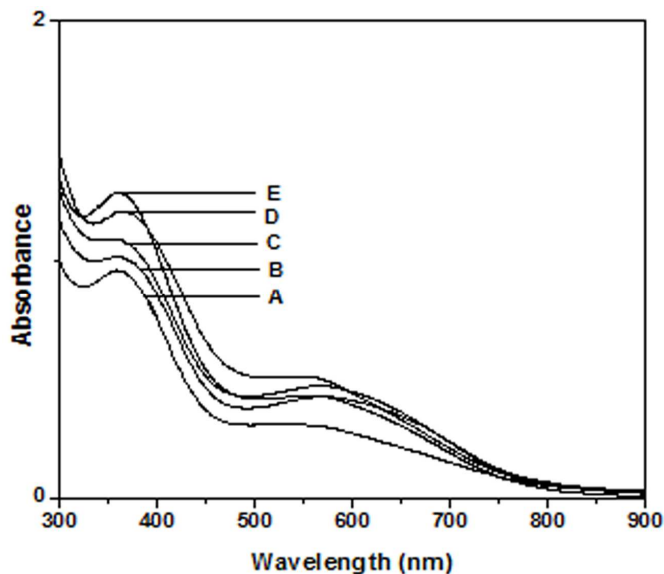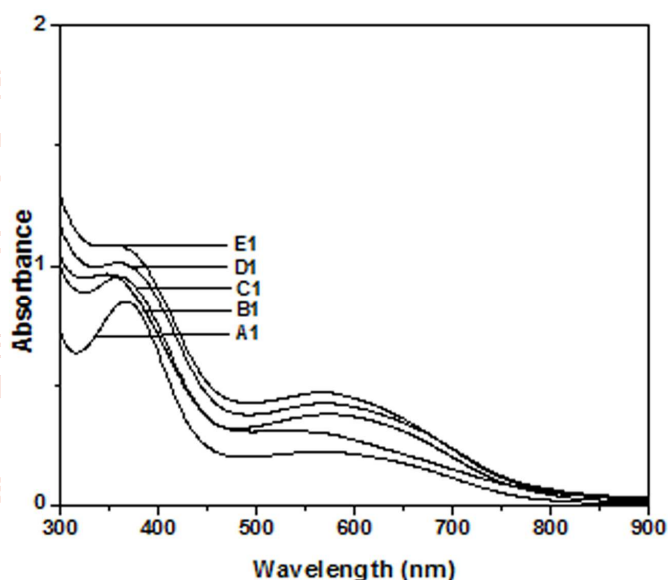

Figure 3 UV-Vis spectra of PANI doped with $[Cu(NH_3)_4]SO_4$

Figure 1 UV-Vis spectra of EB-PANI, HCl-PANI C C1, C2 and C3
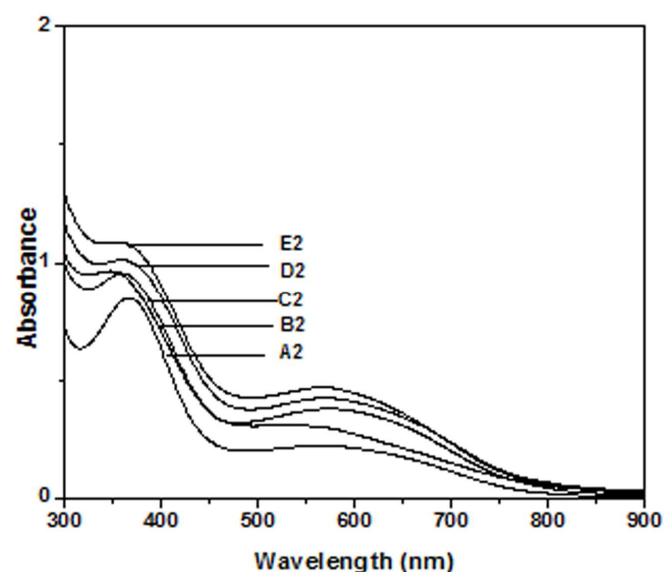
Figure 4 UV-Vis spectra of PANI doped with $[Cu(en)_2]SO_4$

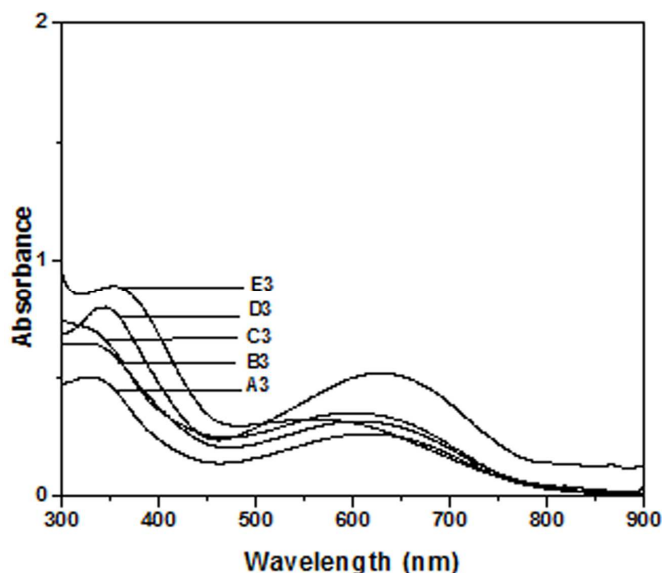**Figure 5 UV-Vis spectra of PANI doped with [Cu)en)$_3$]SO$_4$**

The other absorption peak observed for undoped PANI was at 329 nm which is attributed to π-π* transition in the benzenoid rings [22-25]. On being doped, the π-π* peak undergoes a red shift to the polaronic range of 348-377 nm. This peak is related to the doping level and the formation of polaron [26]. For HCl-PANI, the intensity of this peak is maximum, which means a high degree of doping. The intensity of the polaronic peak decreases with increase in bulkiness of the ligands around Cu^{+2} ions. This is evident from plots C, C1, C2 and C3 of figure 1 with CuSO$_4$.5H$_2$O, [Cu(NH$_3$)$_4$]SO$_4$, [Cu(en)$_2$]SO$_4$ and [Cu(en)$_3$]SO$_4$ as dopants respectively. Larger the ligand size, greater was the steric hindrance and lesser was the degree of doping. Increase in intensity of the polaronic peak after doping EB-PANI with CuCl$_2$ had also been observed by Nikolaidis *et al.* [25] from EPR studies. The polaronic peak for HCl-PANI is at 377 nm while for samples C, C1, C2 and C3 they are at 359 nm, 355 nm 354 nm and 348 nm respectively showing that larger the ligand size lesser was the shift towards polaronic range. That the peak in the range 348-377 nm was related to the doping level was further evident from figure 2, 3 & 4 where CuSO$_4$.5H$_2$O, [Cu(en)$_2$]SO$_4$ and [Cu(en)$_3$]SO$_4$ were used as dopants. It was observed that the intensity of this peak increased with the rise in concentration of the dopant. The increased concentration of the dopant increased the doping level. The rise in the intensity of the polaron peak went parallel to the rise in the conductivity values.

4.2. FTIR SPECTROSCOPIC STUDIES

The FT-IR spectra of all the samples are presented in figure 6. The FTIR spectrum of EB-PANI shows characteristic peaks at 1597, 1487, 1346, 1149, and 810 cm^{-1}. The peaks at 1597 cm^{-1} is attributed to C=C stretching mode of vibration for quinoid rings [4] and

the one at 1487 cm^{-1} is attributed to C=C stretching mode of vibration for benzenoid rings [4] and ring stretching due to C-C and C-H. The peak at 1346 cm^{-1} is due to C-N stretching, C=-N$^+$ stretching and C-H bending mode benzenoid units. The band at 1149 cm^{-1} is the characteristic mode of N=Q=N and the one at 810 cm^{-1} is due to C-H out of plane bending of 1,4 disubstituted benzene [19]. FTIR spectrum of HCl doped PANI shows vibration bands at 1584, 1502, 1352, 1114 and 804 cm^{-1}. On being doped with HCl, there is a red shift of the quinoid peak while a blue shift is observed for the benzenoid peak. Similar behavior is observed on being doped with dopants based on Cu^{+2} ions viz. CuSO$_4$.5H$_2$O, [Cu(NH$_3$)$_4$]SO$_4$, [Cu(en)$_2$]SO$_4$ and [Cu(en)$_3$]SO$_4$. It is seen that the band at 1597 cm^{-1} is red shifted to 1584 cm^{-1} while the band at 1487 cm^{-1} is blue shifted to 1502 cm^{-1} with much increase in intensity of the peak. The characteristic mode of N=Q=N which appeared at 1149 cm^{-1} for EB-PANI is now red shifted to 1114 cm^{-1} for HCl-PANI again with a considerable increase in intensity of the peak. The C-H out of plane bending of 1,4 disubstituted benzene is slightly red shifted in HCl-PANI compared to EB-PANI. After doping with CuSO$_4$.5H$_2$O, [Cu(NH$_3$)$_4$]SO$_4$, [Cu(en)$_2$]SO$_4$ and [Cu(en)$_3$]SO$_4$ the peak at 1597 cm^{-1} (EB-PANI) is red shifted to the range of 1585-1592 cm^{-1} with increase in peak intensity. The position of this red shift is found to be slightly dependent on the size of the ligands. Sample C3 with [Cu(en)$_3$]SO$_4$ as the dopant shows the peak at 1592 cm^{-1} and sample C2 with [Cu(en)$_2$]SO$_4$ as dopant shows it at 1589 cm^{-1} and while the dopant is CuSO$_4$.5H$_2$O the peak position is at 1586 cm^{-1}.
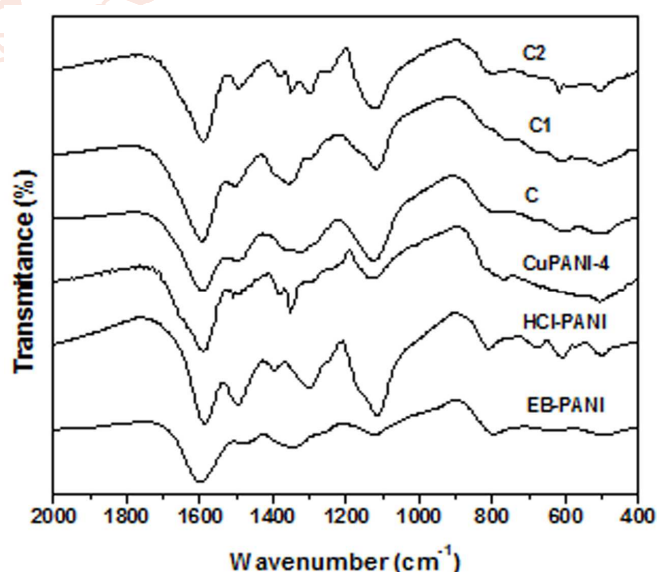

Figure 6 FTIR spectra of EB-PANI, HCl-PANI, C, C1, C2 and C3

The position of this band can be taken as indicative of the degree of oxidation of the polymer backbone. This red shifted band indicates the increase in the

relative number of quinoid groups in the polymer [8]. Another important change that observed with the Cu^{+2} ion doped PANI is that the weak peak at 1449 cm^{-1}(EB-PANI) is blue shifted to 1502 cm^{-1} and becomes sharp. The sharpness is maximum in HCl-PANI and minimum in sample C3 with $[Cu(en)_3]SO_4$ as dopant indicating the influence of the ligand bulkiness. Similar red shift was observed with the peak at 1149 cm^{-1} after doping with Cu^{+2} salt and complexes. The peak at 1149 cm^{-1} which is a measure of electron delocalization in PANI [26] was shifted to 1110-1114 cm^{-1} in $CuSO_4.5H_2O$, $[Cu(NH_3)_4]SO_4$, $[Cu(en)_2]SO_4$ and $[Cu(en)_3]SO_4$ doped PANI and apparently becomes broader than in EB-PANI. Intensity of this peak increased with decrease in ligand size (figure 6). FTIR spectra indicates the complexation between the polyaniline and Cu^{+2} ion and the degree of complexation is influenced by the size of the ligands

4.3. MORPHOLOGY STUDIES

Figure 7 shows the SEM images of EB-PANI and PANI doped with $CuSO_4.5H_2O$, $[Cu(NH)_3]SO_4$, $[Cu(en)_2]SO_4$ and $[Cu(en)_3]SO_4$. EB-PANI shows a regular scaly structure in its SEM micrograph as seen in the figure. When PANI is doped with Cu^{+2} ions the
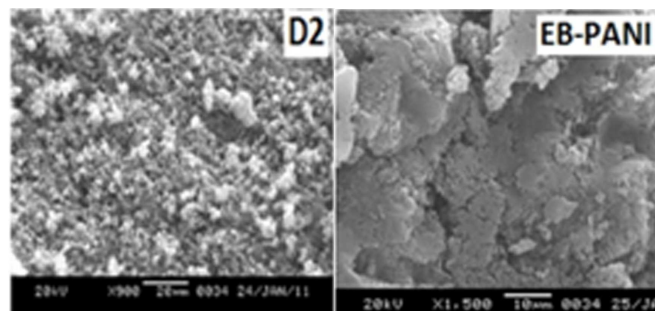

Figure 7 SEM images of EB-PANI and PANI doped with CuSO₄.5H₂O, [Cu(NH)₃]SO₄, [Cu(en)₂]SO₄ and [Cu(en)₃]SO₄

Morphology becomes irregular, granular and agglomerated. The particles are randomly aggregated and rough surfaces appeared. Doping with Cu^{+2} ion results in an aggregation and networking of polyaniline molecular chains. This is because transition metal ions such as Cu^{+2} may bind to several nitrogen sites in the polyaniline chain or may form inter-chain linkages among several adjacent polyaniline chains by coordination [27-28]. Looking into the SEM images of C, C1, C2 and C3 it is observed that the size of the ligands around Cu^{+2} ion has an effect on the morphology. The size of the granules increases with increase in ligand size. Similar morphology of transition metal ion doped PANI was also observed by Chen *et al*. [18]

4.4. XRD STUDIES

In addition to the polaronic species formed due to doping the electrical conductivity of doped PANI is also influenced by the crystalline domain formation [29]. Figure 8 shows the XRD patterns of EB-PANI, HCl-PANI, and PANI doped with $CuSO_4.5H_2O$ (C), $[Cu(NH_3)_4]SO_4$ (C1), $[Cu(en)_2]SO_4$ (C2), and $[Cu(en)_3]SO_4$ (C3). EB-PANI shows a very broad peak at $2\theta = 12°$ and another one low intensity peak at $2\theta = 24°$. HCl-PANI show a broad peak at $2\theta = 25°$, another broad peak at around $2\theta = 20°$ and also a sharp peak at around $2\theta = 6.4°$. XRD plot of EB-PANI shows its amorphous nature [30].
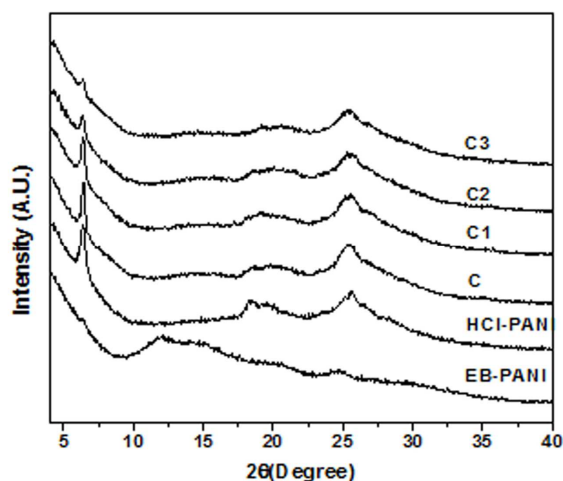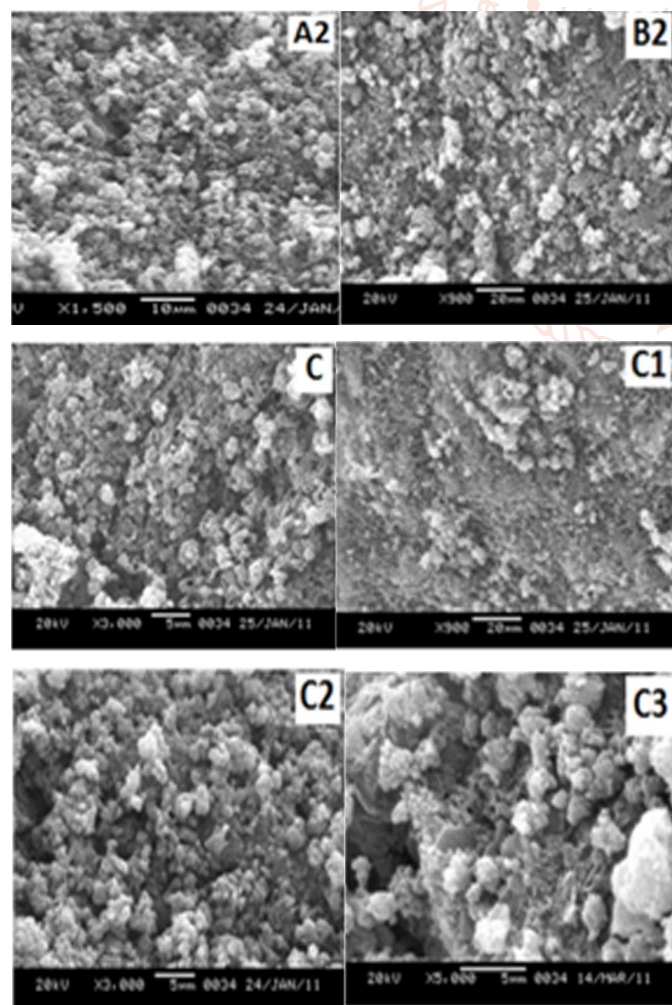

Figure 8 XRD Plots of EB-PANI, HCl-PANI, C, C1, C2 and C3

The presence of peak at $2\theta = 6.4°$ for HCl-PANI implies the development of partial crystallinity in its structure.[31] Similar peak is also observed for samples C, C1, C2 and C3 although with decreased intensity of the peak. This is indicative of the presence of low crystalline order in Cu^{+2} ion doped PANI in comparison to HCl doped PANI. Further the sharpness of the peak at $2\theta = 6.4°$ decreases slightly with increase in ligand size which again reflects the effect of ligand size on the development of crystalline domains.

4.5. CONDUCTIVITY STUDIES

The conductivity measurements were carried out at room temperature in a four-probe electrode arrangement apparatus. The samples used were in pressed pellet forms. The results of conductivity studies are presented in table 1. The conductivity studies broadly revealed two facts: Firstly, the conductivity increased with the rise in concentration of Cu^{+2} ion with a particular ligand and secondly the conductivity decreased with the rise in the bulkiness of the ligand around the Cu^{+2} ion for the same concentration of Cu^{+2} ion.

We have observed that the conductivity is influenced by the nature of the groups or ligands around the dopant Cu^{+2} ion. The conductivity decreases with the rise in the steric crowding around the Cu^{+2} ion. (Table1). Steric crowding around Cu^{+2} ion hinders the chain alignment and causes the conductivity to decrease. Also, steric crowding reduces the accessibility of Cu^{+2} ion to the polymer backbone and this is responsible for the decreased conductivity with increase in ligand size.

5. CONCLUSIONS

It is found that better the coordination higher the conductivity of the doped polyaniline [31] That is, by manipulating the extent of coordination between the Cu^{+2} and polyaniline it is possible to modulate the electrical conductivity of polyaniline. From our studies it was observed that by changing the nature and size of ligands around the Cu^{+2} ion, the electrical conductivity could be modulated. This was due to variation in the extent of interaction between the Cu^{+2} ion and polyaniline as a result of interference from the ligands. Further, this also resulted in difference in morphology as well as crystallinity of the doped polyaniline.

6. ACKNOWLEDGEMENTS

7. REFERENCES

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