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Optical Properties Of Doped Polyaniline

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ABSTRACT

Comparison of electrical conductivity and optical absorption spectrum of undoped PANI(polyaniline) and PANI doped with cobalt chloride, ferric chloride, copper chloride, hydrochloric acid is made. Absorption line shape is best fitted with Gaussian oscillators with different resonance frequencies, damping factors and relative oscillator strengths. copper chloride doped PANI is promising material for electronic application.

KEYWORDS

Optical absorption;
Oscillator strengths;
Damping factor;
Localized;
Delocalized carriers.

INTRODUCTION

Conducting polymer with polyaromatic backbone including polypyrrole, polythiophene, polyaniline etc has received a great deal of attention in the last two decades. Polyaniline has attracted attention because of its electronic, electrochemical and optical properties, environmental and thermal stability[1-5]. Polyaniline, however, is severely limited in view of its insolubility in common organic solvents making its characterization rather intricate. Recently, synthesis of some substituted polyanilines which are soluble in organic solvents as well as in water beside being thermally and environmentally stable have been achieved[6-8]. In order to obtain materials with superior electrical and optical properties we have synthesized polyaniline(PANI) doped with different dopants like cobalt chloride($CoCl_2$),copper chloride ($CuCl_2$), ferric chloride($FeCl_3$) and hydrochloric acid (HCl) and characterized by their electrical conductivities in solid form, UV-vis optical absorbance spectrum in dimethyl sulphoxide as a solvent (DMSO) and Fourier transform infra-red spectrum.

EXPERIMENTAL

Aniline(Merck) was double distilled under vacuum and 0.1(N) solution of different dopants were prepared. Ten ml aniline mixed with 40ml double distilled water. 50ml 0.1(N) of dopant solutions mixed with aniline water mixture with continuous magnetic stirring. 25gm of solid ammonium persulphate added to the mixture kept at 0^0C with continuous stirring for 2 hours and left at rest to polymerize for 24 hours. The doped PANI precipitate was collected on a filter and dried in an oven overnight at 30^0C.

The green coloured powdered samples were made into pellets by a pressure of 10 tons/cm^2 and D.C conductivity was measured by standard four-probe method using silver paste at room temperature.

The UV-vis absorption spectra of the samples were taken by a double beam spectrophotometer (Systronics) 2101 model using dimethyl sulphoxide as a solvent. The samples marked as A, B, C, D and E are undoped PANI, $CoCl_2$, $CuCl_2$, $FeCl_3$, and HCl doped PANI respectively.

The infrared spectra of the doped and undoped PANI samples were taken in KBr pellets using a Matsonn 1000 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the UV-vis absorption spectra of different samples in solution. The spectrum of the polymers mainly consists of three absorption bands at 298-308nm, 335-390nm and 558-616nm respectively. The first band is due to π-π^* transition in the benzoid rings and the other two bands are due to exciton absorption of the quinoid rings respectively[9]. Figure 2 shows the Fourier transform I.R.spectra of undoped PANI and chemically doped PANI with cobalt chloride($CoCl_2$), copper chloride ($CuCl_2$), Ferric chloride($FeCl_3$), hydrochloric acid(HCl). The bands observed at 1590 and 1500cm^{-1} for undoped PANI show a shift in doped PANI. The observed shift is likely due to quinoid rngs in PANI being converted into benzenoid rings[11]. The broad and intense band observed at 1100cm^{-1} in the doped form is also characteristic for conductive PANI and is due to charge delocalization on the polymer backbone[12]. The intensity of this peak is a measure of the delocalization of the electrons or the conductivity[13].

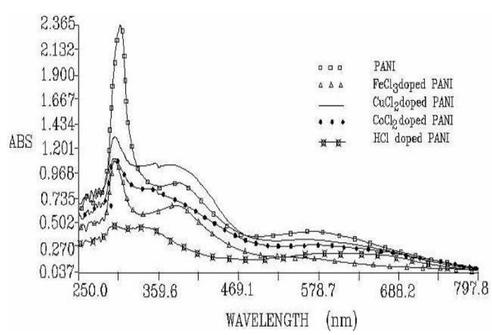

Figure 1 : UV-vis spectrum of PANI and different doped PANI

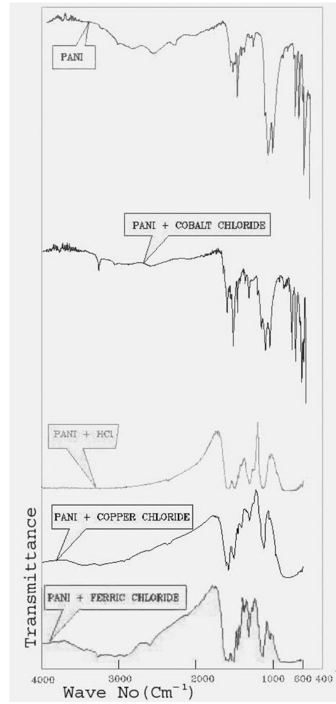

Figure 2 : FTIR spectrum of PANI and doped PANI.

The shape of the curve depends on carrier concentration, their life time and transition energy. Due to doppler homogeneous broadening the line shape function will be Lorentzian and inhomogeneous broadening mechanism will result in a Gaussian line shape. The shapes of the absorption spectra were best fitted to Gaussian oscillators with resonance frequencies, damping factors and relative oscillator strengths. The parameters for these oscillators are given in TABLE 1. The absorbance A is given by

$$A=\sum A_n \exp\text{-}\{(E-E_n)/\beta_n\}^2$$

Where E is the photon energy in ev. Near the resonance $E=E_n$, the absorption coefficient becomes very large and the medium is essentially opaque to the electromagnetic wave at $E=E_n$. The peak corresponding to large damping factor is related to large absorption i.e., in the neighbourhood of absorption the refractive index decreases with increasing frequency. In HCl doped PANI oscillator strength is

TABLE 1 : Gaussian oscillators with different parameters and electrical conductivities of different doped polyanilines

Sample	Oscillator	Resonance energy (E_n) in ev	Strength A_n (Arbitrary unit)	Damping factor(β_n) in ev	Electrical conductivity(σ) in S/cm
A	1	4.036	1.618	24.8	0.370
	2	2.824	0.558	α	
	3	2.170	0.396	17.53	
B	1	4.155	0.961	12.4	0.240
	3	2.218	0.326	α	
C	1	4.22	0.844	12.4	0.117
	2	2.985	0.579	12.4	
	3	2.215	0.283	12.4	
D	1	4.392	0.606	17.53	0.310
	2	2.823	0.369	α	
	3	2.751	0.320	α	
E	1	4.415	0.373	α	0.210
	2	3.216	0.299	α	
	3	2.303	0.272	α	

almost constant for all the peaks. All the curves are similar except for $CoCl_2$ doped PANI, which may be due to degenerate ground state of Co^{++}-ion. Broad and narrow peaks are contributions from delocalized and localized charge carriers[10]. The electrical conductivities of the samples are shown in TABLE 1. The electrical conductivity in undoped sample is more than doped one due to more mobility of carriers. In $CuCl_2$ doped PANI damping factor is constant which can be used as potential electronic material for composite purposes.

CONCLUSION

Depending upon dopant and inhomogeneity of the sample and ratio of localized and delocalized carriers different absorption as well as line widths are obtained. $CuCl_2$ doped PANI is the promising electronic material, due to constant damping factor in different electromagnetic regions.

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