Trade Science Inc.

Magnetic, optical and electrical properties of zirconium doped polyaniline

K.Gupta[1]*, P.C.Jana[2]

[1]**Mahisila Govt. Colony High School, Mahisila, PO-Asansol, Dist-Burdwan, State-West Bengal-713303, (INDIA)**
[2]**Department of Chemistry, BBCollege, Asansol-713303, West Bengal, (INDIA)**
Tel : +919434592968
E-mail : kajal_pchem@yahoo.co.in, kajalgupta.env@gmail.com
Received: 20th September, 2007 ; Accepted: 25th September, 2007

ABSTRACT

Comparison of optical absorption spectrum and magnetic field dependent susceptibility of Polyaniline (PANI) and Zirconium doped polyaniline is made. The effect of doping agents on polyaniline backbone with electrical conductivity and magnetic susceptibility is discussed. Doping by Zirconium compound may alter the magnetic property and electrical conductivity of polyaniline. Zirconium doped PANI is promising material for technological applications.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Conducting polymers have emerged as a very important class of materials because of their unique electrical, magnetic, optical and chemical properties leading to the wide range of technological applications. This class of materials provides tremendous scope for tuning of their electrical conductivity by way of doping[1,2]. Among different conducting polymers, Polyanilines (PANI) are the most extensively studied materials due to the ease of synthesis, better environmental, thermal stabilities and greater scope of playing with chemistry to tailor their properties[3-7]. However, when they are taken in the composite form their electrical, magnetic properties and others are altered from those of the basic materials. In order to obtain materials with superior electrical, optical and magnetic properties we have synthesized polyaniline(PANI) doped with Zirconyl nitrate and characterized by their electrical conductivities in solid form, UV-vis optical absorbance spectrum in Dim-

ethyl sulphoxide as a solvent(DMSO) and Fourier transform infra-red spectrum and magnetic susceptibility (Gouys method).

Sample preparation

Aniline(E.Merck, India) was double distilled. Hydrochloric acid(HCl) (E.Merck, India) and Ammonium persulphate(E.Merck, India) and Zirconyl nitrate were used in as received state.

The synthesis of polymer was carried out in a three-necked round-bottom flask that was kept at constant temperature ($\sim0^0$C). 100ml HCl acid solution of aniline (prepared in the ratio aniline: HCl=1:5) was taken in the flask. Ammonium persulphate solution (0.5M) of required quantity was added very slowly with the help of specially designed system with rigorous stirring using magnetic stirrer. Ammonium persulphate was used in the mole-ratio[Aniline]/[Ammonium persulphate]of 0.5. The reaction mixture was stirred for five hours. The precipitated green polyaniline salt was filtered, and then

Full Paper

A:Undoped PANI

B:Zr doped PANI
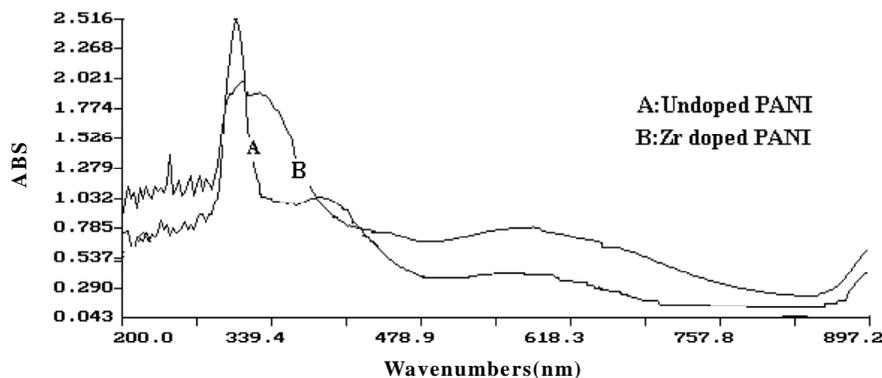
Figure 1: UV-vis spectrum of polyaniline & doped polyaniline

washed with distilled water(ice-cold) until the washing liquid was completely colourless. The material was dried at room temperature for forty-eight hours under dynamic vacuum.

This pristine polyaniline salt was deprotonated to convert it into the emeraldine base by treatment of 3% ammonium hydroxide solution for four hours. The base was then washed with distilled water(ice cold) and dried at room temperature for forty-eight hours under dynamic vacuum. The composites were prepared by thorough mixing of Zirconyl nitrate with emeraldine base by mechanically grinding them in a pestle mortar.

Measurements

The green coloured powdered samples were made into pellets by a pressure of 5 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 infrared spectra of the doped and undoped PANI samples were taken in KBr pellets using a Matsonn 1000 FTIR spectrophotometer.

A glass test tube filled up to a certain height(18cm) with the sample is suspended from an arm of a sensitive balance(Gouys method) such that the bottom part of the sample is in a strong magnetic field and the top part is no vibrational and air disturbance. Usually an electromagnet giving a constant magnetic field(H) in the rage of 1000 to 5000 gauss is used. The Force experienced by the sample is measured by the change in weight. Thus the susceptibility per gm is calculated by the equation

$X_g = 2l \times \Delta m \times g/mH^2$

Where m and l represent the mass and the length of the sample, Δm=change in mass due to the imposition of the magnetic field. X_m(molar susceptibility) for two rings of doped PANI were determined after diamagnetic correction of glass. The samples marked as A, and B are undoped PANI, Zirconyl nitrate doped-PANI respectively.

RESULTS AND DISCUSSION

UV-vis absorption spectra

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 295-340nm, 390-405nm and 590-610nm 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[8]. It is observed that absorbance of polyaniline lowers by the doping of the zirconyl nitrate with polyaniline. It is because π-π* transition in the benzenoid rings lowers with the doping by the rare earth materials. This may be the reason for the decrease in electrical conductivity with doping (TABLE 1).

FTIR studies

Figure 2 shows the fourier transform i.r.spectra of undoped PANI and Zirconyl nitrate doped PANI. The bands observed at 1550 and 1530cm^{-1} for undoped PANI show a shift in doped PANI. The observed shift is likely due to quinoid rings in PANI being converted into benzenoid rings[9]. The broad and intense band observed at 1100cm^{-1} in the doped form is also char-

Full Paper
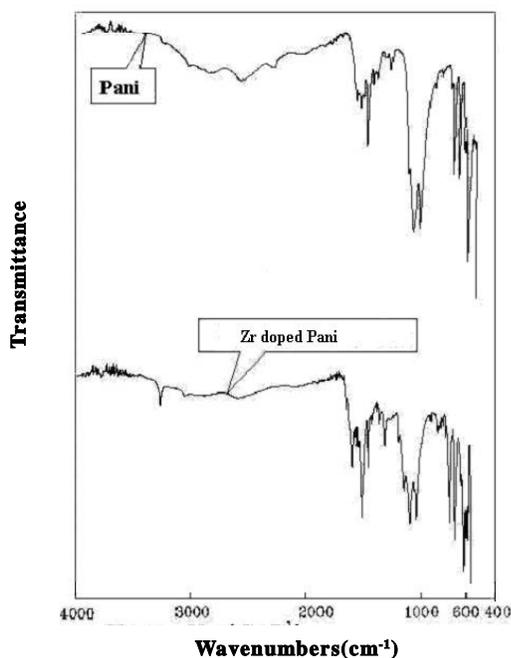
Figure 2 : FTIR spectrum of undoped and doped polyaniline
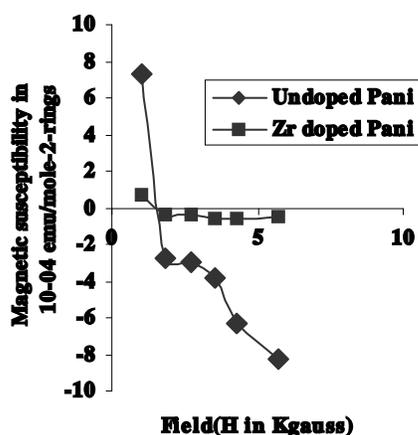
Figure 3 : Field dependence of magnetic susceptibilities(χ) of doped and undoped polyaniline

acteristic for conductive PANI and is due to charge delocalization on the polymer backbone[10]. The intensity of this peak is a measure of the delocalization of the electrons or the conductivity[11]. The band at 3447.68cm^{-1} is the characteristic N-H stretching vibrations.

Electrical conductivity

The shape of the curve depends on carrier concentration, their lifetime and transition energy. Broad and narrow peaks are contributions from delocalized and localized charge carriers[12]. The electrical conductivity

TABLE 1: different peaks, the corresponding absorbance and electrical conductivity (σ)

Samples	Peaks (λ nm)	Absorbance (arbitrary units)	Electrical conductivity(σ) S/cm
A	330.0	2.516	
	390.0	1.030	0.370
	602.2	0.290	
B	300.4	2.021	
	340.0	1.774	0.212
	610.0	0.785	

TABLE 2: Field (H) dependence of magnetic susceptibility (χ) of the samples

Field (H in Kgauss)	X_M in 10^{-04}emu/mole-2-rings	
	A	B
1.000	7.28	0.658
1.850	-2.76	-0.384
2.750	-2.97	-0.348
3.150	-3.82	-0.614
4.280	-6.32	-0.592
5.720	-8.30	-0.500

A: undoped PANI, B: Zirconyl nitrate-doped PANI

in undoped polyaniline is more than zirconyl nitrate doped polyaniline. The electrical conductivity of the polyaniline decreases with the doping by the zirconyl nitrate. This is due to the localization of the charge carriers with doping and hence decreases the mobility of the charge carriers. The electrical conductivities of the samples are shown in TABLE 1.

Magnetic property studies

Figure 3 shows that with increase of the magnetic field the magnetic susceptibility decreases for both the undoped and doped PANI. Field dependent magnetic susceptibility of the samples are shown in TABLE 2. It is interesting that the magnetic susceptibility decreases more for the undoped PANI than the doped PANI with increase in the magnetic field. With the decrease in the magnetic field susceptibility of undoped PANI increases more than that of Zirconyl nitrate doped PANI. At high magnetic fields the localization of the charge carriers of Zirconyl nitrate doped PANI occurs more than undoped PANI but at low magnetic field the localization of undoped PANI occurs more than that of doped PANI.

CONCLUSION

The magnetic susceptibility of the polyaniline and zirconyl nitrate doped polyaniline is field dependent. The unusual magnetic field dependent susceptibilities are very

Full Paper

interesting in these doped polyaniline. The ratio of the localized and the delocalized carrier changes by the doping with the zirconyl nitrate and this can also control the unusual field dependence. We can use zirconyl nitrate doped PANI as the promising material for technological applications by controlling magnetic and electrical property.

ACKNOWLEDGMENT

REFERENCES

[1] H.C.Pant, M.K.Patra, S.C.Negi, A.Bhatia, S.R. Vadera, N.Kumar; Indian Aca of Sci., **29**, 379-384 **(2006)**.

[2] A.G.Mac Diarmid, J.C.Chiang, A.J.Epstein; Chem. Soc., **88**, 317 **(1989)**.

[3] T.E.Olinga, J.Frayssc, J.P.Travers, A.Dufreanc, A. Pron; Macromolecules, **33**, 2107 **(2000)**.

[4] E.M.Genics, A.Boyle, M.Lapkowski, C.Tsintaris; Synth.Met., **36**, 139 **(1990)**.

[5] E.Ruckenstein, W.Yin; Macromolecules, **33**, 1129 **(2000)**.

[6] T.A.Stotheim; 'Handbook of Conducting Polymers New York: Marcel Dekker, **1**, **(1987)**.

[7] K.Gupta, P.C.Jana; Macromolecules, An Indian Journal

[8] C.M.Gupta, S.S.Umare; Macromolecules, **25**, 138 **(1992)**.

[9] D.C.Trivedi, S.K.Dhawan; Ibid., **58**, 309 **(1993)**.

[10] Y.H.Kim, C.Foster, J.Chiang, A.J.Heeger; Ibid., **26**, 49 **(1988)**.

[11] J.Tang, X.Jing, B.Wang, F.Wang; Ibid., **24**, 231 **(1988)**.

[12] K.Mizoguchi; Synth.Met., **35**, 119 **(2001)**.