Synthesis and characterization of $FeCl_4^-$-doped polyaniline

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(Received 22 May 1991; revised 25 June 1991; accepted 24 July 1991)

A new tetrachloroferrate-doped ($FeCl_4^-$) salt of emeraldine (polyaniline) has been obtained in a non-aqueous medium. From elemental analysis and Mössbauer studies, the salt has been identified to contain iron exclusively in the +3 oxidation state. Data on temperature-dependent d.c. conductivity and dielectric constant measurements on the doped polyaniline salt in the X-band of the microwave region are also discussed.

(Keywords: conducting polymers; polyaniline; Mössbauer studies; synthesis; characterization)

INTRODUCTION

Conducting polymers in general and the polyaniline family of polymers in particular have created intense scientific and technological interest[1,2]. Polyaniline or the better known emeraldine base (EB) form of the polymer differs substantially[3] from various polyheterocyclics, i.e. polypyrrole, polythiophene, etc., polyaromatics and polyacetylenes in several respects. This polymer is not charge-conjugation symmetric because neither Fermi level nor band gap are formed in the centre of the pi band, thus making the valence and conduction bands asymmetric. Secondly, both carbon rings and nitrogen atoms are within the conjugation path, forming a generalized 'A–B' polymer. Thirdly, emeraldine base forms an insulating–metallic state if protons are added to the –N= sites while the number of electrons in the chain is held constant.

A number of recent studies have shown that emeraldine base can be chemically doped to the metallic conducting regime by aqueous protonic acids[4,5]. On the other hand, treatment of leuco-emeraldine with oxidizing agents[6] such as Cl_2, $NOPF_6$, $FeCl_3$, etc., gives the emeraldine salts of polyaniline. It was further shown that the electrical properties of polyaniline salts are strongly dependent on the preparation method, the various oxidation states, the doping level and the conformation of the molecules in the product. The influence of ring[7] as well as N-substitution[8,9] in the aniline molecule on the conductivity and solubility of polyanilines has been the subject of recent investigations.

Since the first report on iron-doped polyacetylene and poly(*p*-phenylene) by Pron *et al.*[10] in 1981, there have been consistent efforts to make a variety of metal-halide-doped conducting polymers[11–15]. Recently, in our laboratories iron-chloride-doped conducting polymers/copolymers derived from (i) pyrrole, (ii) pyrrole plus phenylene oxide, (iii) thiophene and (iv) thiophene plus methylthiophene were synthesized by an electrochemical method. All the materials were found to have iron in mixed oxidation states as evident from Mössbauer studies[16]. In the case of polyaniline, though $FeCl_3$ has been used to oxidize the leuco-emeraldine to a conducting polyaniline salt[17], very little is known about the exact nature of the dopant. The present report is an attempt to show that polyaniline can be doped with $FeCl_4^-$ ions in a well defined way by using the method of protonic doping in a non-aqueous medium. Further, some of the physical properties such as d.c. electrical conductivity, dielectric constant and Mössbauer parameters are also discussed.

EXPERIMENTAL

Polymerization of aniline

Aniline was polymerized using $(NH_4)_2S_2O_8$ in 1 M HCl in air using the detailed method described elsewhere[18].

Synthesis of emeraldine base

Emeraldine hydrochloride prepared as described above was deprotonated in air to emeraldine base using 0.1 M NH_4OH as described elsewhere[18].

Synthesis of $FeCl_4^-$-doped polyaniline

First, 11.0 g anhydrous $FeCl_3$ was dissolved in 100 ml concentrated HCl (10 M) to give a 0.68 M solution of $FeCl_3$ in HCl. The solution was shaken with 250 ml diethyl ether to extract $HFeCl_4$ (ref. 19). The ethereal layer was separated with the help of a separating funnel and to it was added 10 g of emeraldine base. The reaction mixture was stirred for 1 h until the colour of the polymer changed from reddish brown to deep blue. It was filtered and washed with four portions of diethyl ether and dried in air. Total weight of the product obtained was 15.5 g. Analysis: iron 10.1%, chlorine 25.2%.

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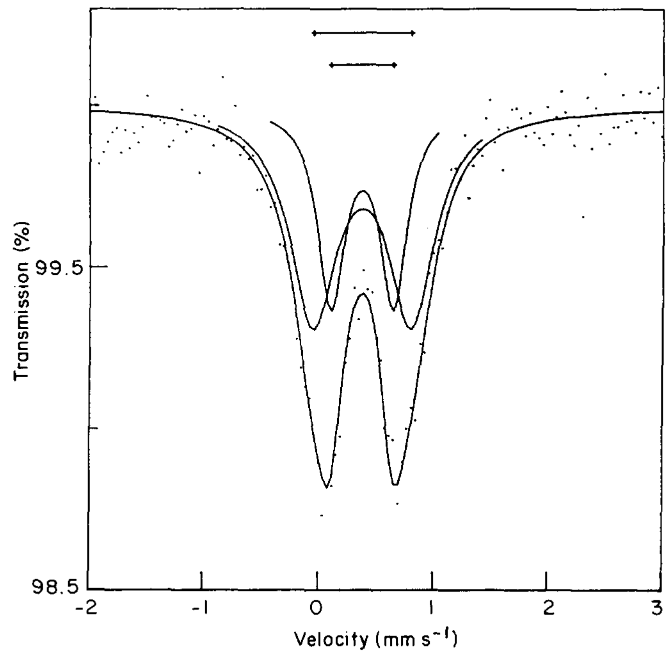

Figure 1 Room-temperature ^{57}Fe Mössbauer spectrum of $FeCl_4^-$-doped polyaniline

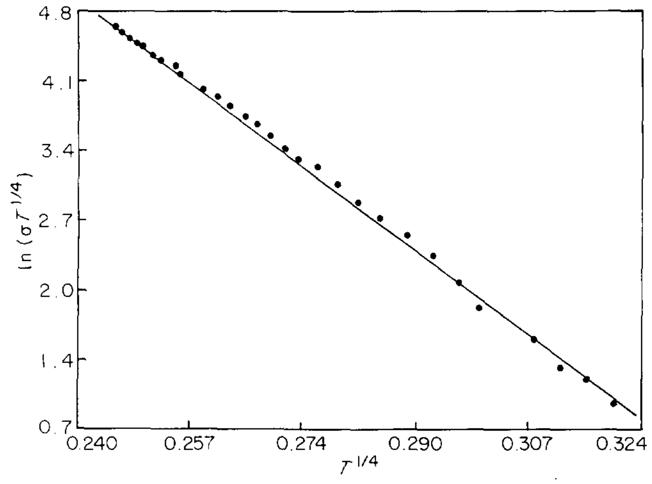

Figure 2 Variable-range hopping plot for $FeCl_4^-$-doped polyaniline

Physical measurements

D.c. electrical conductivity was measured from 77 to 300 K by using the standard four-probe technique. Microwave measurements were done by using the standing-wave method using a waveguide in the X-band (8–12 GHz) with an HP 8350 sweep oscillator as the source of microwave frequencies. Magnetic susceptibility measurements were done by using a vibrating sample magnetometer. Mössbauer studies were done in standard transmission geometry using a Wissel spectrometer in constant-acceleration mode with a Canberra series 35 plus multichannel analyser. The spectral data were fitted by the method of least squares by using a computer program[20].

RESULTS AND DISCUSSION

Doping of $FeCl_4^-$ ions

The elemental analysis for iron and chlorine clearly indicates that (i) iron and chlorine are in the ratio of 1:4, i.e. in the form of $FeCl_4^-$ ions and (ii) the dopant concentration in the polymer is 25%. Thus it is established that protonation of emeraldine base has taken place in the non-aqueous medium giving $FeCl_4^-$ ions as the dopants.

Mössbauer studies

^{57}Fe Mössbauer studies, besides confirming the doping of $FeCl_4^-$, also suggest the presence of two different environments around Fe^{3+} sites as shown in *Figure 1*. The isomer shift values for both sites are equal (0.37 mm s^{-1}), indicating the equal values of s-electron densities around iron at the two sites. However, the two different values of quadrupole splitting, i.e. 0.54 and 0.85 mm s^{-1}, are rather high and suggest different degrees of distortion of $FeCl_4^-$ tetrahedra[21], depending on their locations in the polymeric lattice. Broadly speaking, one such location may be a terminal position while the other may be in the bulk. Furthermore, the higher linewidth (0.49 mm s^{-1}) of the doublet with quadrupole splitting of 0.85 mm s^{-1} suggests inequivalent iron sites in the molecule[22].

D.c. electrical conductivity

A plot of $T^{1/4}$ *versus* $\log \sigma T^{1/2}$ gives a straight line (*Figure 2*) and follows the variable-range hopping (VRH) model according to Mott's formula[23]:

$$\sigma_{dc} = \frac{9e^2\nu_0}{64\alpha^2}\left(\frac{T_0}{T}\right)^{1/2} N(E_F)\, exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right]$$

By using the above equation we have calculated the parameters as given in *Table 1* by taking the value of delocalization length α^{-1} to be equal to 9 Å (two rings)[24].

Microwave measurements

The measured value of the dielectric constant in the X-band (8–12 GHz) region was found to be constant and equal to 70. This value is quite comparable with those of the other salts of emeraldine reported earlier[25,26].

CONCLUSIONS

From the above studies we conclude that (i) protonation of emeraldine base with $HFeCl_4$ is possible in a non-aqueous medium to give $FeCl_4^-$-doped emeraldine salt in which the iron is present exclusively in the +3 oxidation state as is evident from Mössbauer studies, and (ii) the high value of attempt frequency ν_0 along with the appearance of broad Mössbauer spectral lines suggest a low crystallinity in the present polymer.

Table 1 Parameters calculated from VRH plot for $FeCl_4^-$-doped polyaniline

Characteristic temp., T_0 (K)	5.75 × 10^6
Density of states at Fermi level, $N(E_F)$ (eV^{-1} cm^{-3})	4.963 × 10^{20}
Attempt frequency, ν_0 (s^{-1})	4.92 × 10^{36}
Hopping distance,	
$R_{300 K}$ (Å)	39.88
$R_{100 K}$ (Å)	52.45
Activation energy, E (eV)	0.1
Barrier height, W_D (eV)	7.4

ACKNOWLEDGEMENTS

The authors are grateful to Shri J. V. Ramana Rao, Director, and Dr A. R. Reddy, Joint Director, Defence Laboratory, Jodhpur, for their keen interest in the present work.

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