

Effect of Dopant Ions on the Electrical Conductivity and Microstructure of Polyaniline (Emeraldine Salt)

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ABSTRACT

Samples of polyaniline (emeraldine salt) were prepared with different protonic acid dopants, namely, hydrochloric acid (HCl), nitric acid (HNO₃), perchloric acid (HClO₄), sulfuric acid (H₂SO₄), and hydroiodic acid (HI). Using the two-point probe method, it was found that the samples had ohmic behaviors in which high linear coefficients were found in the range 0.9686–0.9997. On the other hand, the electrical conductivities were measured using the Van der Pauw method. The undoped sample had a conductivity of 5×10^{-4} S/cm. The highest conductivity of 109.04 S/cm was observed for the HClO₄-doped sample, while the lowest value (0.02 S/cm) was obtained for the HI-doped sample. These conductivities were compared with the computed energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) where it was found that they are inversely proportional to each other. Scanning electron microscopy revealed significant differences among the samples in terms of shapes and morphologies.

INTRODUCTION

Conducting organic polymers are highly conjugated *p*-electron systems that display unusual electronic properties such as low ionization potentials and high electron affinities; they are also called “synthetic metals.” Many researches are now focused on studying conducting polymers such as polyacetylene, polythiophene, polypyrrole, and polyaniline among others (Kroschwitz, 1998).

Polyaniline (PAni) exists in a variety of forms that differ in chemical and physical properties. The most common

protonated emeraldine has a conductivity at the semiconductor level of the order of 100 S cm^{-1} , which is many orders of magnitude higher than that of common polymers ($<10^{-9} \text{ S cm}^{-1}$) but lower than that of typical metals ($>10^4 \text{ S cm}^{-1}$) (Stetjskal et al., 1996; Stetjskal & Gilbert, 2002). The various electron states in conducting polymers are in terms of the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) or the HOMO-LUMO gap, energy gap (Vardeny & Wei, 1998).

As shown in Fig. 1, the emeraldine base (PAni-EB) can be made conducting by adding a protonic acid dopant. After protonation, there will be dissociation of bipolaron to form two polarons, where a bipolaron form will be achieved. It is believed that for the

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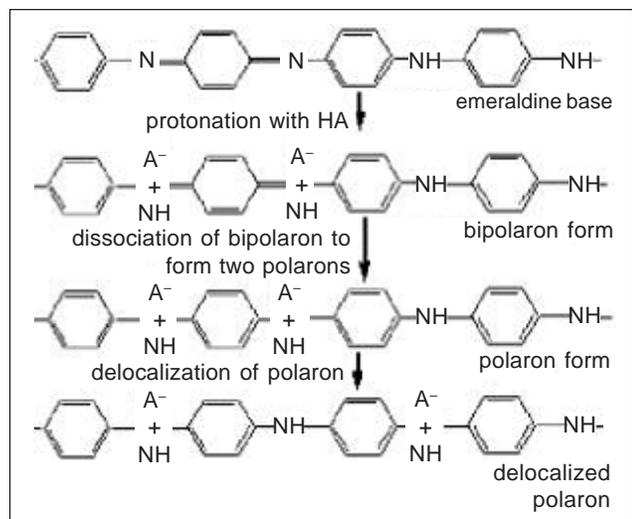


Fig. 1. Protonic acid doping of polyaniline (emeraldine base) (Trchova et al., 1998).

nondegenerate conducting polymers, the bipolarons are the charge carriers. In the polaron form, there will be delocalization of polarons after which polarons will be delocalized yielding a green conducting emeraldine salt (PAni-ES) (Stetjskal & Gibert, 2002; Gorman & Grubbs, 1991; Trchova et al., 1998). Polyaniline is not charge-conjugation symmetric, where the valence band and conduction bands are asymmetric to a great extent (Ghos et al., 2001).

The efficient polymerization of aniline is achieved only in acidic medium, where aniline exists as anilinium cation. A variety of inorganic and organic acids at different concentrations have been used in the syntheses of PAni; the resulting PAni-ES, protonated with various acids, differs in solubility, conductivity, and stability (Trivedi, 1997).

The changes in physicochemical properties of PAni that occur in response to various external stimuli are useful for various applications (Levi, 2000). Many of these applications are based on the electroactive properties of PAni such as bioelectronics, polymer-modified electrodes, and polymer-based amperometric biosensors (Lyons, 1994). The combination of electrical properties typical of semiconductors with parameters characteristic of polymers have resulted in the development of “plastic” microelectronics (Hamers, 2001), electrochromic devices (Rosseinsky & Mortimer, 2001), tailor-made composite systems

(Prokes et al., 2000), and “smart” fabrics (El-Sherif et al., 2000). The choice of physical properties of PAni suitable for specific applications is thus of fundamental importance (Stetjskal & Gilbert, 2002).

The main objective of the present study is to determine the effects of dopant ions on the conductivity and microstructure of PAni-ES.

METHODOLOGY

Chemical synthesis of polyaniline (emeraldine salt)

The PAni-ES samples were chemically synthesized using reagent-grade aniline, ammonium peroxydisulfate (APS), and the appropriate dopant (HCl, HNO₃, HClO₄, H₂SO₄, or HI). The standard procedure for the polymerization of aniline was followed (Stetjskal & Gilbert, 2002). A 0.25 M aqueous solution of APS was mixed with 0.2 M of aniline in 1 M of the acid dopant. The mixture was stirred and maintained at 4°C in an ice bath. The green precipitate formed was filtered, washed with distilled water and acetone, and dried in a vacuum oven for 3 h at 40°C.

Characterization of polyaniline

Before characterization, the samples were pelletized at 7 tons for 10 min using a Carver hydraulic press. Sufficiently thin samples of ~1 mm were derived.

All the prepared polyaniline samples were characterized in terms of electrical conductivity and microstructure using a scanning electron microscope (SEM).

For conductivity and electrical properties, silver paste was used to attach the gold wires as contacts. Then, current-voltage (*I-V*) measurements were done using the two-point probe method and resistivity measurements were derived using the Van der Pauw method in an in-line configuration (Ghos et al., 2001).

Before taking the SEM images, the samples were coated with gold for 5 min for usually sufficient coating using an ion sputtering system to increase the source of electrons (Ordillas). SEM images of the polymeric

samples were taken using Philips XI30 SEM (Hussain & Kumar, 2003). The samples were studied at different magnifications for topographic comparisons.

RESULTS AND DISCUSSION

Electrical properties

The polyaniline samples were synthesized using different dopants. The final product was a green conducting emeraldine salt Pani-ES (Stetjskal & Gilbert, 2002; Trivedi, 1997). The current-voltage (I - V) curves of the undoped and HClO_4 -doped samples are shown in Figs. 2 and 3, respectively, which show ohmic behavior from -1.0 to 1.0 mA. This range of current was used to check the symmetry of the curves. These were derived using a two-point probe I - V measurement with gold wires attached by silver paste as contacts. Inconsistent readings of the voltage near zero current was due to the difficulty of measuring small voltages.

Conductors generally show ohmic behavior wherein the voltage across the material varies linearly with the current and the I - V plot has a constant slope, which is the resistance of a material. This means that the current density linearly increases with the applied electric field.

Shown also in the graph are the correlations of current with voltage. It can be observed that the slope of the

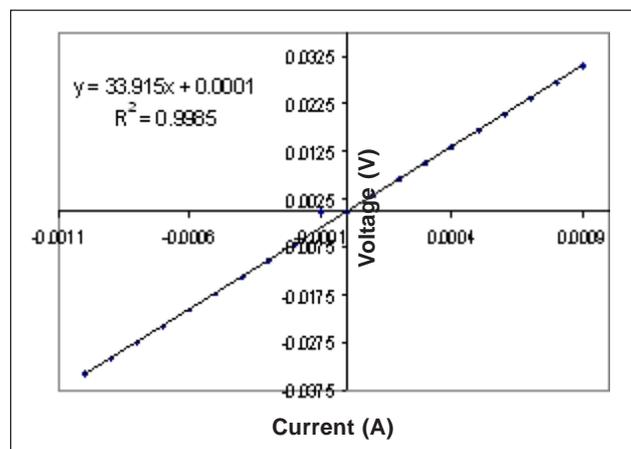


Fig. 2. I - V curve of PANi-ES with HClO_4 dopant showing symmetry from -1 to 1 mA.

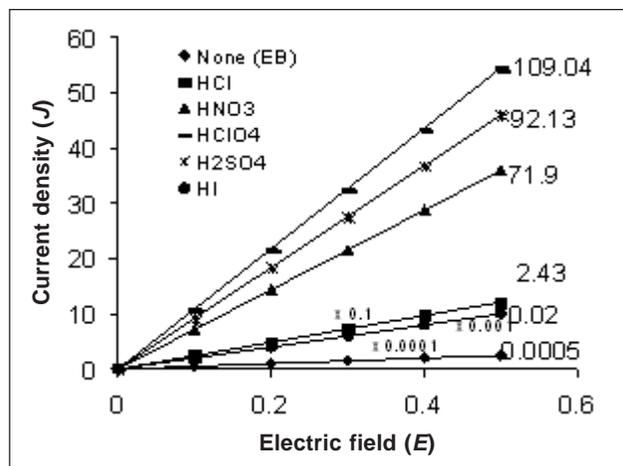


Fig. 3. Scaled plots of current density versus electric field for PANi-ES with different dopants showing the slopes as the conductivity in S/cm.

graph is the resistance of the samples since the y axis is the voltage (V) and the x axis is the current (I).

Inconsistent portions in some of the I - V plots, e.g., undoped and HCl -doped PANi-ES, may be due to the irregular structures of the samples. It is therefore necessary to ensure good pelletization in order to have good measurements from these synthesized materials. This is consistent with the observation that the electrical properties of conducting polymers are strongly influenced by the effect of disorder, since conducting polymers are partially crystalline and partially amorphous (Long et al., 2003).

Very high correlation coefficients in the range of 0.9686 – 0.9997 were observed for the I - V plots of the PANi samples. This indicates that all samples behave as ohmic conductors. Shown in Table 1 are values of the electrical conductivity of undoped and doped polyaniline samples. The differences in conductivity values are due to the effect of dopant ions. As can be seen, the undoped sample has conductivities in the range of 10^{-4} , which makes the sample highly insulating typical of a normal polymer. The highest conductivity (109.04 S/cm) was obtained for the HClO_4 -doped sample; the lowest conductivity (0.08 S/cm) was exhibited by the HI -doped sample. These experimental values fit within in the range of conductivity for PANi specified (Trchova et al., 1998).

Table 1. Conductivity and computed energy gap of the undoped and doped polyaniline samples.

Dopant	Conductivity (S/cm)	HOMO-LUMO Energy gap ^{a,b} , (eV)
None (EB)	5.00×10^{-4}	2.61
H+	2.43	2.44 ^c
HCl	71.90	3.37
HNO ₃	109.04	2.79
HClO ₄	92.13	2.45
H ₂ SO ₄	0.02	2.65 ^d
HI		3.02

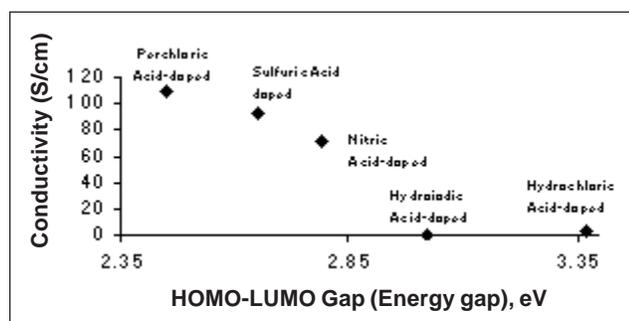
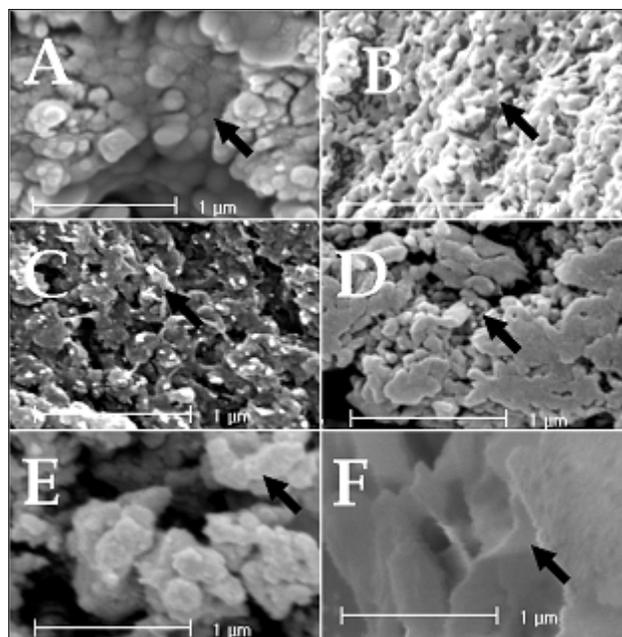
^aFor beta orbital.^bAtienza et al., 2004.^cPascual, 2003.^dBased on HSO₄⁻ as dopant ion.

Fig. 4. Conductivity versus HOMO-LUMO gap plot of the PANi-ES samples with different dopants.

Figure 4 is the plot of current density versus electric field of the samples. The figures were scaled to fit the slopes of different samples which are the conductivity values. The higher the slope, the higher the conductivity. From Figs. 2 and 3, it is manifested that the current density linearly increases with the applied electric field. The conductivities are presented in Table 1 together with computed HOMO-LUMO energy gap data.

As shown in Table 1, the experimental values of conductivity were found to exhibit roughly an inverse correlation with the computed values of the energy gap between the HOMO and LUMO; these values have been reported by other researchers (Atienza et al., 2004; Pascual, 2003). A plot of the conductivity versus HOMO-LUMO gap is shown in Fig. 4.

Thus, the smallest HOMO-LUMO gap was observed for the HClO₄-doped sample, while the biggest energy gaps were obtained for HCl- and HI-doped samples.

Fig. 5. SEM images at ~26000x magnification of (A) undoped PANi, (B) HCl-doped, (C) HNO₃-doped, (D) HClO₄-doped, (E) H₂SO₄-doped, and (F) HI-doped polyaniline samples showing distinct structures pointed by arrows.

The HOMO-LUMO gap is the molecular counterpart of the band gap for the macroscopic polymeric solid.

Microstructure of polyaniline

As shown in the SEM images of Fig. 5 the PANi-ES samples with varying dopants exhibit varying microstructures. Variation in microstructure leads to different conductivities of the samples. The addition of acid dopants alters the polymer lattice, which leads to the ionization of sites in the chains. The defects in the chain due to the dopant ions provide the mobility of the charge carriers on which conduction depends (Kroschwitz, 1988). The conductivity is also dependent on the number of charge carriers.

The undoped sample in Fig. 5(a) displays globular but irregular morphology. Figure 5(b) shows the HCl-doped PANi showing fine threadlike structures fused together. The HNO₃-doped sample has a fine and grainy structure fused together but with void spaces [Fig. 5(c)], while the HClO₄-doped sample [Fig. 5(d)] has corallike structures with elongated bodies. Figure 5(e) shows a porous pattern of globular microstructures for the H₂SO₄-doped sample. Lastly, Fig. 5(f) shows the loose

flaky structures of the HI-doped sample. The low conductivity of the HI-doped sample may be due to these loose flaky structures and air spaces that are present. The orientation of structures and morphology of samples at the macroscopic level affects the mobility of charge carriers and, thus, influences conductivity (Kroschwitz, 1988).

CONCLUSION

Polyaniline salts (PAni-ES) were found to exhibit varying electrical conductivities. All prepared samples showed ohmic behavior. The doped PAni samples showed a dramatic increase in conductivities compared with undoped PAni. The HClO₄-doped sample gave the highest conductivity (109.04 S/cm) which is 2x10⁵ times greater than that of the undoped sample, while HI-doped PAni gave a conductivity of 0.02 S/cm. The experimental conductivity values generally showed an inverse correlation with the computed values of the HOMO-LUMO energy gap reported by other researchers (Atienza et al., 2004; Pascual, 2003). The scanning electron microscope (SEM) pictures of the doped PAni samples showed varying microstructures, e.g., the HClO₄-doped sample exhibited a corallike structure, while HI-doped PAni showed a loose flaky structure. Further investigation of the morphology of samples will give a better understanding of bulk conductivity.

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