

## THERMAL PROPERTIES OF PHENYLENEDIAMINE AND ITS APPLICATION OF SEMICONDUCTING PROPERTIES

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### ABSTRACT

Poly orthophenylenediamine were synthesized by via chemical oxidative polymerization method by using two different oxidizing agent are potassium dichromate and potassium per sulfate. Polymers using the spectral techniques like FTIR and the morphology have been carried on SEM. The stability was analyzed by using TGA and DSC was found to have high thermal stability. Electrical conductivity as a function of room temperature has been measured by four point probe method. The analysis method of dielectric constant ( $\epsilon'$ ), dielectric loss ( $\epsilon''$ ), tangent loss ( $\delta$ ) and reactive part of the impedance analysis ( $Z'$  and  $Z''$ ) at room temperature were studies.

**KEYWORDS:** Poly orthophenylenediamine, thermal stability, dielectric, electrical conductivity.

### INTRODUCTION

Polymers have traditionally been considered as a good electrical insulators and a variety of their applications have relied on their insulating property.<sup>[1]</sup> Conducting polymers have become the foci of much research in material science and among all; polyaniline and polypyrrole have received greater attraction due to their favorable economics, easy synthesis, environmental stability, and unique chemistry.<sup>[2]</sup> Electronically conducting polymers have been used as artificial metals because they can act as substitutes for metals and semiconductors in electrical and electronic devices and at the same possessing the mechanical properties of polymers.<sup>[3]</sup> The widely exploited properties of conducting polymers in technological and commercial applications are their thermally withstanding capacity, bio-compatibility, electrical conductivity, switching capability between conducting-oxidized and insulating-reduced state.<sup>[4]</sup>

Among the family of conducting polymers, Polyaniline is one of the most promising polymer because of its unique electrical properties, easy polymerization, low cost of monomers, high environmental stability and its wide applications in microelectronic devices, light weight batteries, sensors, super capacitors, microwave absorption and corrosion inhibition.<sup>[5,6]</sup>

PANI is a typical phenylene-based polymer having a chemically flexible-NH group flanked on either side by phenylene rings. The protonation and deprotonation and various other physico-chemical properties of PANI can be related to the presence of the -NH- group.<sup>[7]</sup>

Phenylenediamines belong to aniline derivatives and Poly (ophenylenediamine) shows different properties when compared to polyaniline. The derivatives of Polyaniline (PANI) are found applications in different fields like removal of heavy metals from the industrial effluents, anticorrosive agents, sensor studies, microelectronic devices, electromagnetic shielding and in optics. The synthesized poly phenylenediamine (PPD) by chemical oxidation method has been formed by dication units in its Pernigraniline base form and radical cations in its Emeraldine salt form.<sup>[8]</sup>

### EXPERIMENTAL

#### MATERIAL AND METHOD

All the chemicals used were Analytical grade (AR). The monomer orthophenylenediamine, potassium dichromate, potassium persulfate, hydrochloric acid was purchased as an analytical grade and were used as received. Synthesis of polyorthophenylenediamine has been carried out by via chemical oxidative polymerization method. 0.5 mol of orthophenylenediamine is dissolved in 1M HCl to form orthophenylenediamine hydrochloride. The reaction mixture with vigorous stirring in order to keep the orthophenylenediamine hydrochloride suspended in the solution. The reaction mixture 0.5M of potassium dichromate/ potassium persulfate (A & B) its act an oxidant was added drop wise slowly with continuous stirring for 2-3 hours at room temperature to polymerize. The precipitate was filtered and washed with double distilled water. Finally the resulting precipitate was collected by filtration and washed several times with double distilled water. The resultant precipitate was dried at room temperature for 48 hours.

The detail of characterization techniques were examined FTIR on a ABB-MB-3000 spectrometer. The UV-Vis spectra of the synthesized polymers and their nanocomposites were measured using Perkin-Elmer Lambda spectrophotometer by dissolving the polymers in DMSO solvent. TGA were recorded using Perkin Elmer Diamond under a nitrogen atmosphere up to 700°C using the heating rate of 10°C/min and The Differential scanning calorimetry were measured using Mettler Toledo DSC 822e instrument from room temperature to 500°C for the synthesized polymers SEM morphology was studied using a Model Jeol 6390 LV. Electrical conductivities of the isomers of poly ortho phenylenediamine were recorded at room temperature by the four-point probe technique using LCR meter HP484A..

## RESULT AND DISCUSSION

### FTIR spectroscopy

FTIR spectrum of POPDA (Figure 1) measurement was carried out the molecular bonding of POPDA/K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. For the POPDA (Figure 1A) the important characteristic peak appear at 1509.10 cm<sup>-1</sup> due to C=C stretching of quinoid rings 1484.22 cm<sup>-1</sup> due to benzenoid ring which conforms the formation of polymer.

In the FTIR spectrum of POPDA/ K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Figure 1B) some important peaks are observed such as 3449 cm<sup>-1</sup> and 2917.72 cm<sup>-1</sup> due to N-H bending 2487.72 cm<sup>-1</sup> due to C-H stretching due to CH<sub>2</sub> bending and 643.04 cm<sup>-1</sup>. By comparing the spectra of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> it observed in the different oxidant the characteristic stretching frequency are shifted towards lower frequency side which may be due to vander waal's interaction between K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and POPDA chain and thus spectra conform the formation of polymer.

### UV-Vis spectroscopy

The UV-vis absorption spectra of the polymer were measured as shown in fig 2(A and B). The UV region is two absorption peaks at 370nm and 390nm is due to HCl. These absorption bands increases with increasing the result is in agreement with the study for polymer synthesized by Hcl doping dispersed in PoPDA where the characterized absorption peaks are 200-800nm wavelength [9]. The absorption bands around at 420 and 440nm that is attributed to the π-π\* transition of the benzenoid ring and n-π\* transition of the benenoid to quinoid. Furthermore by the addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> intensityb of the peak increased due to intraction between the polymer and the oxidant.

### Thermogravimetric analysis

The thermogram of PoPDA form shows a weight loss of 10-12% upto 100°C, a weight loss of 25% from 100-470°C and a weight loss of 40% from 470-800°C. When the polymer mixed with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in different oxidant as shown in fig 3, Thermogram suggest mainly two weight loss they are first weight loss correspond to the loss of water molecules, slowly removal of oligomer

and the loss of impurities upto 130°C. The second weight loss corresponds to the degradation of polymeric backbone and the PoPDA in the range of 200-450°C. The thermal stability of the polymer depends upon the oxidant, which is turn is governed by the competition between benzenoid and quinoid of the N-H group of the phenylenediamine in ortho position.<sup>[10]</sup>

### Differential Scanning calorimetry

The DSC is used to obtain the thermal critical points like melting temperature (T<sub>m</sub>), enthalpy specific heat or glass transition temperature (T<sub>g</sub>) of the substance. DSC spectra of PoPDA synthesized at the different oxidant are given in figure 4. The endothermic peak observed for the PoPDA at the initial temperature of 30°C causes bond scissoring followed by bond formation that are involved when the polymers are heated and the bond scissoring is endothermic, which is compensated by the heat generated due to the bond formation as shown by an exothermic peak from 100-120°C. The PoPDA shows an endothermic peak at 105.29°C which is due to the glass transtition temperature (T<sub>g</sub>). The polymer starts to melt above 300°C which is characteristic of melting temperature(T<sub>m</sub>).<sup>[11]</sup>

### Scanning Electron Microscope

Scanning electron microscopy of the polymer provides a clear morphology. Two different morphologies obtained for polymers with different magnification are presented in fig 5 (a&b). Morphology of the PoPDA results reveals that the polymer exists in granular morphology reported for the PoPDA with different oxidant. This figure reveals crystalline as well as amorphous morphology with non-uniformity in the surface. The extension of the polymer chain with alternative PoPDA moiety produces less regular and amorphous structure.<sup>[12]</sup>

### Electrical conductivity

Electrical conductivity shows conductivity over a wide range from 10<sup>-11</sup> to 10<sup>-2</sup> S/cm whereas semiconducting polymer in the region 10<sup>-6</sup> to 10<sup>-11</sup> S/cm.<sup>[13]</sup> The electrical conductivity of the PoPDA prepared was studied by four point probe method at room temperature. Conductivity increased significantly from the 4.23x10-8 to 3.18x10-7 semiconducting nature. The increased in conductivity may be due to increases of efficiency of charge transfer between backbone of polymer chains and the oxidant.

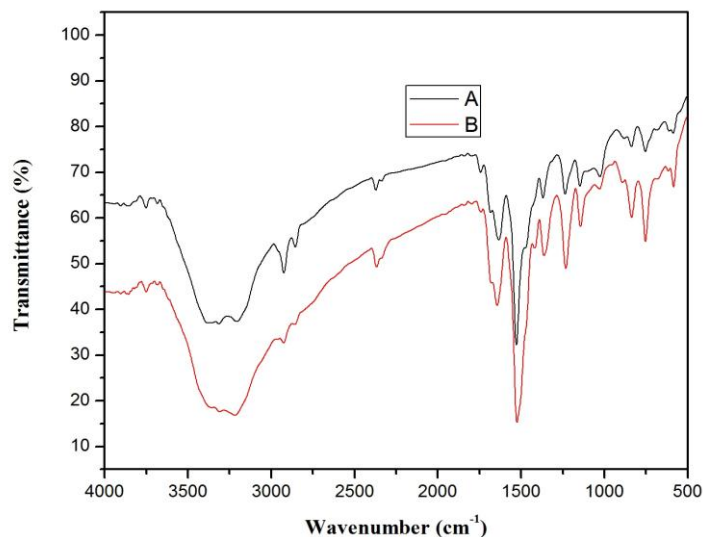


Figure 1: FT-IR Spectra of PoPDA and its different oxidant (A)  $K_2Cr_2O_7$  (B)  $K_2S_2O_8$ .

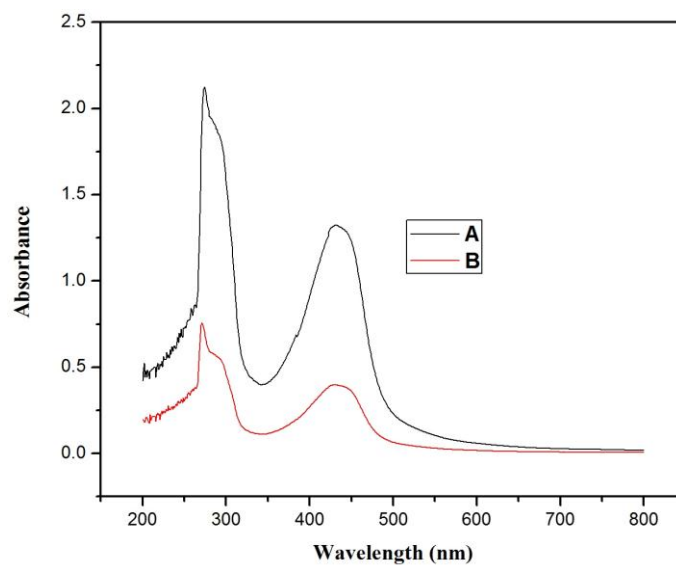


Figure 2: UV spectra of PoPDA and its different oxidant (A)  $K_2Cr_2O_7$  (B)  $K_2S_2O_8$ .

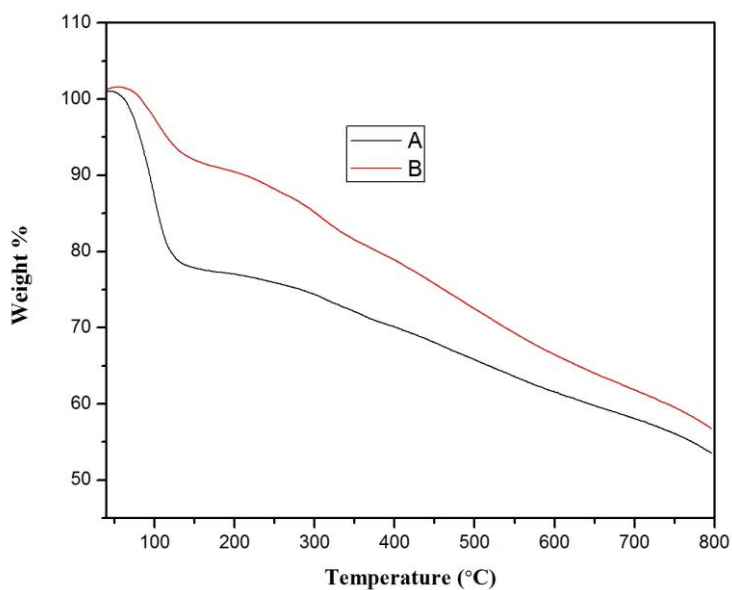


Figure 3: TGA of PoPDA and its different oxidant (A)  $K_2Cr_2O_7$  (B)  $K_2S_2O_8$ .

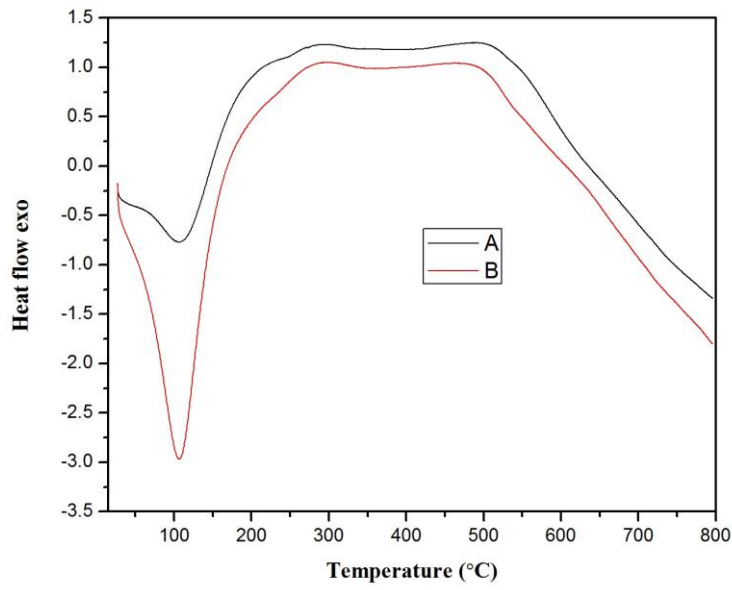


Figure 4: DSC OF PoPDA and its different oxidant (A)  $K_2Cr_2O_7$  (B)  $K_2S_2O_8$ .

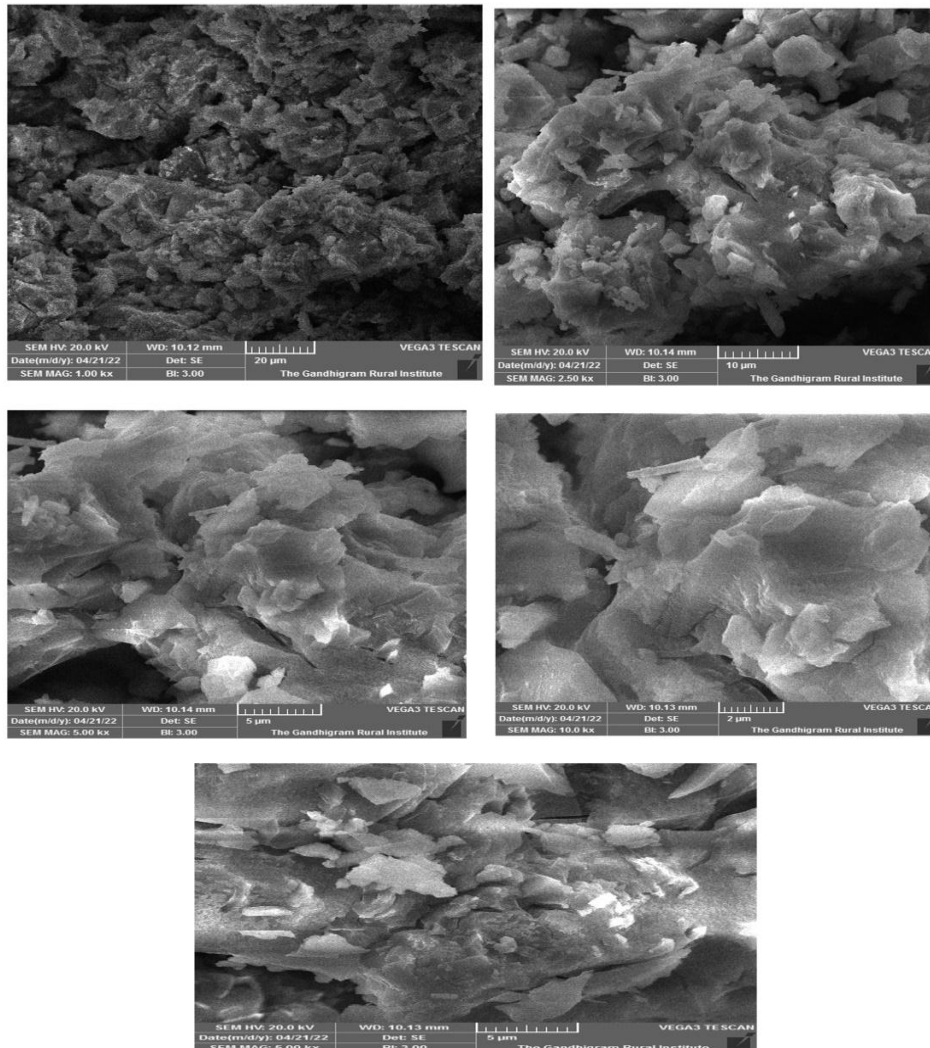


Figure 5: SEM image of PoPDA and its different oxidant AS  $K_2Cr_2O_7$  AND  $K_2S_2O_8$ .

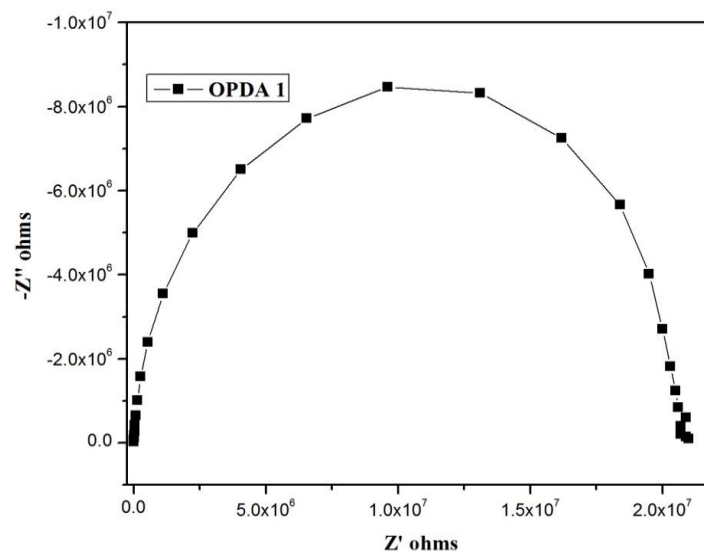


Figure 6A: Electrical conductivity of PoPDA and its oxidant of  $K_2Cr_2O_7$ .

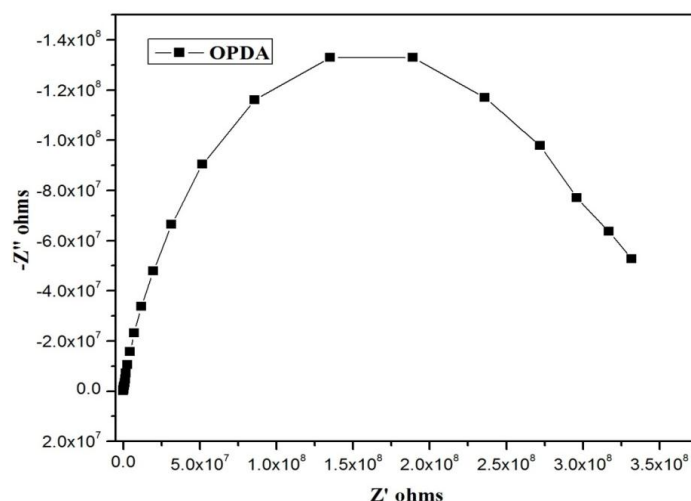


Figure 6B: Electrical conductivity of PoPDA and its oxidant of  $K_2S_2O_8$ .

## CONCLUSION

Polymer was prepared successfully by chemical polymerization method. The popda were prepared and the characterized using FT-IR and UV-Vis spectroscopy. Polymer synthesized with different oxidant like  $K_2S_2O_8$  and  $K_2Cr_2O_7$ . SEM images showed morphology with different oxidant shows granular and rod like structure. The electrical conductivity measured shows thermally activated exponential behavior. It was found that there was an enhancement of  $10^{-8}$  to  $10^{-7}$  shows increased conductivity at room temperature.

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