ELECTROCHEMICAL STUDY OF POLYANILINE POWDER AND ITS CHARACTERIZATION

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ABSTRACT

Polyaniline powder has been successfully synthesized which has received great attention due to its stable environment and possessing excellent electrical, optical and an electrochemical properties. Synthesizing polyaniline powder was conducted to estimate the electrochemical and it's characteristic. Here polyaniline powder was synthesized by oxidative polymerization with Ammonium Persulphate used as oxidant. The blue color polyaniline powder was further characterized using Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), X-Ray Diffraction (XRD), and Cyclic Volatmmetry (CV). The FTIR spectrum shows the presence of benzoid and quinoid ring observed at 1500 cm^{-1} and 1600 cm^{-1}. A shark peak centered around 25.3° and 14.7°. Thermogram of polyaniline powder shows three step of weight loss ranging from 0°C to 600°C, 15 % for the first step and 13 % for the second step. The capacitance of polyaniline powder 8 F/g was obtained. The Nquist plots shows a semicircle indicating low resistivity.

ABSTRAK

Polianilin serbuk yang telah berjaya disintesis telah mendapat perhatian yang meluas kerana kestabilan persekitaran dan memiliki sifat-sifat elektrik, optik dan ciri-ciri elektrokimia yang bagus. Sintesis polianilin serbuk dijalankan untuk mangangarkan elektrokimia serta ciri-cirinya. Polianilin serbuk telah disintesis melalui oksidatif pempolimeran dengan mengunakan ammonium persulfate sebagai oksidan. Polianilin serbuk yang berwarna biru telah dikaji ciri-cirinya dengan mengunakan FTIR, TGA, XRD dan CV. Spektrum FTIR menunjukkan kehadiran gelang benzoid dan quinoid yang diperhatikan pada 1500 cm^{-1} dan 1600 cm^{-1}. Puncak tajam yang berpusat di sekitar $25.3°$ dan $14.7°$. Thermogram polianilin serbuk menunjukkan tiga peringkat penurunan kehilangan berat antara 0 °C hingga 600 °C, dimana 15 % pada peringat pertama manakala 13 % pada peringkat kedua. Kapasitan yang diperolehi oleh polianilin serbuk adalah 8 F/g. Bagi plot 'Nyquist' telah menunjukkan satu bulatan separuh membuktikan rintangan yang rendah bagi polianilin serbuk.

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LIST OF SYMBOLS

=	Double Bond
°C	Degree Celsius
C	Carbon
d	Distance
E_{pc}	Reduction peak
E_{pu}	Oxidation peak
i_{pc}	Reduction
i_{pu}	Oxidation
N	Nitrogen
O	Oxygen
ʎ	Wavelength
θ	Theta

LIST OF ABBREVIATIONS

APS	Ammonium Persulphate
CV	Cyclic Voltammetry
DSC	Differential Scanning Calorimetry
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
PANI	Polyaniline
TGA	Thermal Gravimetric Analysis
WAXD	Wide Angle X-Ray Diffraction
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1   BACKGROUND INFORMATION

Today our modern life style is dependent, the large extent, on the usage of organic polymers. Thermal and electrical insulators specifically plastics may be a surprised to hear specifically plastics being used as conductors of electricity. Hence, demonstrating the versatility of polymers, with higher electrical conductivity will lead to development of new materials which are unavailable for construction (Raymond et al., 1981).

In the modern world, plastic and electrical devices are always integrated together. However, in 1977 an electrically conductive, quasi one dimensional organic polymer, polyacetylene was discovered by Chiang et al. (1977). Hence for the last 20 years, various conducting polymers were developed as reported by Skotheim et al. (1986). The excitement about these polymeric materials is evidenced by the fact that the fields of conducting polymers have currently attracted scientists from diverse areas of interest such as synthetic chemistry, electrochemistry, solid state physics, materials science, polymer science, electronics and electrical engineering (Yilmaz et al., 2007).

Among the various conducting polymers available like polythiophene, poly pyrroles and polyaniline. Polyaniline is emerging as the material of choice for various applications. The interest in this conducting polymer stems from the fact that many different ring and nitrogen-substituted derivatives can be readily synthesized and each of the derivatives can exist in different oxidation states which in principle

can be "doped" with various dopants either by non-redox processes or by partial chemical or electrochemical oxidation process. These properties, when combined together performs higher electrical conductivity on doping, ease of synthesizing and processing, environmentally stable and relatively low cost of the starting material strongly suggests their significant potential technological applicability as reported by Yilmaz et al. (2007).

1.2   PROBLEM STATEMENT

Polyaniline has attracted considerable attention due to its low cost, simple synthesis, good electrical and optical properties with excellent environmental stability. It has a potential application towards electronic and optical devices. Often polyaniline is synthesized from aniline based on an oxidative polymerization of aniline using an oxidant in presence of a strong acid dopant. Ammonium persulphate (APS) is the most commonly well known oxidant used. Polyaniline powder has possesses higher crystalinity and electrical conductivity. Hence, demonstrating the versatility of polymers, with higher electrical conductivity will lead to development of new materials which are unavailable for construction. The actual objective of my current work is to study the capacitance of the polyaniline/graphene fiber by electrospinning method. But due to the break down of electrospinning machine we unable to study, we changed our study on polyaniline/graphene composites. The result for polyaniline/graphene was insufficient to explore more. The initial study on polyaniline powder has been explored which still needs to explored.

1.3   OBJECTIVE OF THE STUDY

The current objective of the project is to study the electrochemical behavior of polyaniline powder synthesized.

1.4 SCOPE OF WORK

The scope of research work is:

(i)   To synthesize polyaniline powder.

(ii) To physically and chemically characterize polyaniline powder and to measure its capacitance by electrochemical measurements.

CHAPTER 2

LITERATURE REVIEW

2.1 CONDUCTING POLYMERS

In the past, it was believed that organic polymers are excellent insulators which provide significant advantage for various application as reported (Kanatzidis et al., 1990). However this concept was first challenged when reports of conducting or semiconducting polymeric materials such as polyacetylene and polyaniline began to appear in the literature (Chiang et al., 1977). It was only then the doping of polyacetylene succeeded. During this period of time appeared new concepts of physics to be realized. Organic polymers when doped forms conducting polymers, with remarkable ability to conduct electrical conductivity which began to promote technological and scientific interest.

In semiconductor physics, undoped semiconductors are said to be intrinsically conducting, while doped semiconductors are extrinsically conducting. In order, doped polymers are often referred as "intrinsically conducting polymers" (ICPs).

The ICPs are more commonly known as "synthetic metals" referring to the class of organic polymers possessing not only better mechanical properties and processibility, but even possess unique electrical, magnetic, and optical properties of metals. Thus, due to presence of the fundamental properties of these conducting polymers provide electrical conductivity to achieved charge carrier (electron or hole) through a π conjugated polymer backbone.

On discovery made by MacDiarmid and his coworkers (1987) reported, polyacetylene, (CH)x, now commonly known as the prototype conducting polymer, can be either be chemically or electrochemically, p- or n-doped, to become conducting. Hence, then onwards the development of the conducting polymer field is continued to be of interest at a rapid rate. The rapid growth rate has stimulated both in the field's of fundamental synthetic novelty and in cross-disciplinary sections such as – chemist, electrochemists, physicists and electronic and electrical engineers – but to its actual potential technological applications.

Various of polymers undergo redox doping process other than cis- and trans-polyacetylene, (CH)x as reported by Skotheim et al. (1986). Polymers such as polyparaphenylene (Elsenbaumer et al., 1086), poly(phenyllenevinyllene) (Elsenbaumer et al., 1986), polypyrrole (Street et al., 1986), polythiophene (G. Tourillon et al., 1986), polyfuran (Kossmekl et al., 1986) etc., and their ring and N-substituted derivatives undergo redox p-doping and/or n-doping as shown in Figure 2.2. Moreover, the synthesis of new polymers systems such as poly(heterocycle)vinylenes, where Y=NH, NR, S and O, have attracted considerable attention due their unique combination of physical properties, solution processibility and environmental stability in the doped form (T. A. Skotheim et al., 1986).
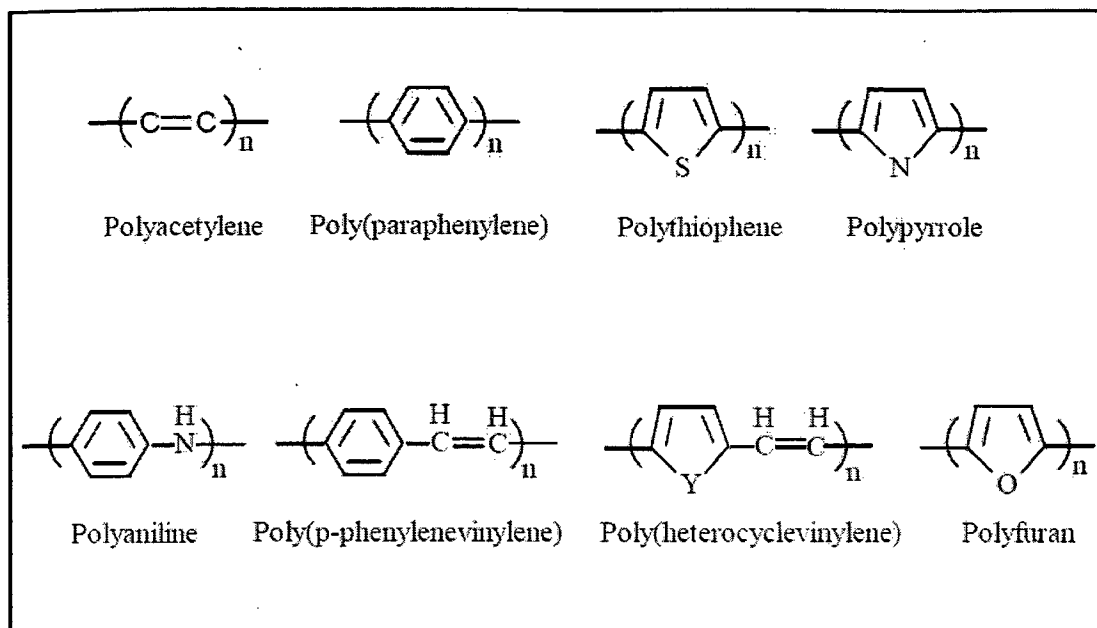
Figure 2.1: Selected examples of intrinsically conducting polymers

2.2 POLYANILINE (PANI)

Electrically conducting polymers in their pristine and doped state have been the materials of great interest for their applications in modern technologies. Among the conducting polymers known polyaniline (PANI) has special representation, characteristic properties due to use for advanced applications in several fields of technology are required. The first report on the production of "aniline black" dated back in 1862 where Letheby used a platinum electrode. During anodic oxidation of aniline containing sulfuric acid solution obtained a dark-green precipitate as reported by Trivedi et al. (1997). This green powdery material soon turned as 'aniline black'. Thus interest in this material was retained almost for more than a century since "aniline black" was a powder, intracting material, a mixture of several products which is quite difficult to investigate. Greena and Woodhead performed the first organic synthesis and classified intermediate products in the "aniline black" formation. Five different aniline octamers were identified which was named as leucormeraldine base, protoemeraldine, emeraldine,

nigraniline and pernigraniline. These names are still in use, indicating various oxidation states of PANI (Figure 2.1).
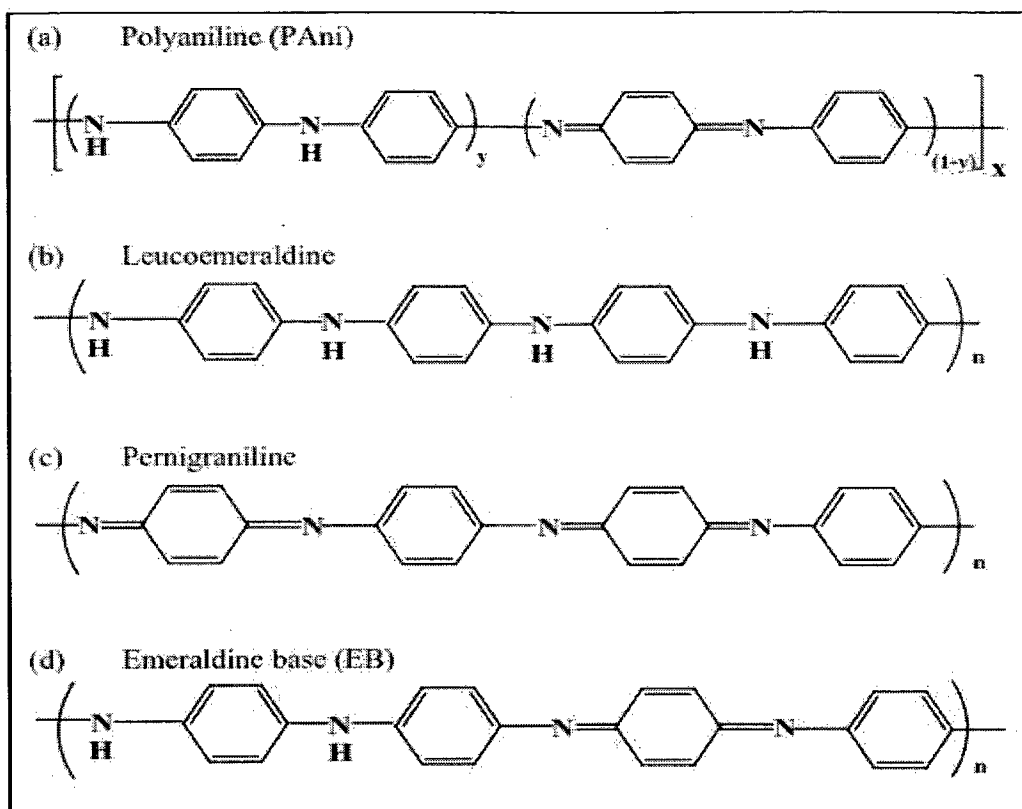

Figure 2.2: Various states of oxidation and protonation of polyaniline

Source: Epstein et al. (1999); Bredas et al. (1997)

Polyaniline is a typical phenylene-based polymer having a chemically flexible - NH – group in a polymer chain flanked either side by a phenylene ring. It is an unique polymer because it can exist in a various structures depending on the value of (1-y) in the general formula of the polymer shown in Figure 2.2 (a) (Epstein et al., 1999; Bredas et al., 1997). The electronic properties of PANI is visualized as a mixed oxidation state polymer composed of reduced {-NH-B-NH-} and

oxidized {-N=Q=N-} of repeated units where –B- and =Q= denotes a benzenoid and a quinoid unit respectively to form the polymer chain (Figure 2.1 (a)), the average oxidation state is given by 1-y. depending upon the oxidation state of nitrogen atoms which exist as amine or imine configuration. PANI can adopt various structures in several oxidation states, ranging from the completely reduced leucomerladine base state (LEB) (Figure 2,1 (b)), y-1 = 0, to the fully oxidized Pernigraniline Base State (PNB) (Figure 2.1 (c)), where 1-y = 1. The "half" oxidized (1-y = 0.5) where emeraldine base state (EB) (figure 2.1 (d)) is a semiconductor and is composed of an alternating sequence of two benzenoid and a quinoid unit. While the protonated form is the conducting emeraldine salt (ES).

PANI owns advantages over other conducting polymers owing to its moderate synthesis route, superior environmental stability and undergoing simple doping by protonating acid protonating easily.

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

Aniline (99.5 %, ChemAR) as the monomer was used. Ammonium persulphate APS [(NH$_3$)$_2$S$_2$O$_8$] from R & M Marketing, Essex, U.K.. The hydrochloric acid (37 %, HCl) used from Sigma Aldrich Chemicals Co..

3.2 EXPERIMENTAL

3.2.1 Preparation of Polyaniline Powder

Polyaniline powder were synthesized by a rapid mixing reaction. The purified aniline (0.3 g, 3.2 mmol) was dissolved in 10 mL of 1 M HCl aqueous solution while maintaining out vigorous stirring at room temperature. Ammonium persulfate (0.18 g, 0.8 mmol) in 10 mL of 1 M HCl aqueous solution was rapidly poured into the aniline solution. Polymerization took place in about 5 mins showing the characteristic green color of polyaniline emeraldine salt to be appeared. The mixture was allowed to stir at room temperature (RT) for overnight. The mixture was then diluted with 100 mL of water. The precipitated polymer was then collected by filtration and repetitively washed with water, ethanol, and hexane until the filtrate became colorless. The samples were then kept for drying. On drying the sample coloured was deep blue color powder representing PANI powder.

3.3 CHARACTERIZATION OF POLYANILINE POWDER.

The samples on preparation were characterized various using the instruments as listed below.

3.3.1 Fourier Transform Infrared Spectroscopy Analysis (FTIR)

Vibrational spectras of the samples were recorded using Perkin Elmer Spectrum 100 FT-IR Spectrometer in the range of $400 - 4000$ cm^{-1} with 4 cm^{-1} resolution. The PANI powdered mixed with KBr powder to form PANI KBr pellets. The interactions of PANI was examined.

3.3.2 Thermogravimetry Analysis (TGA)

Thermogravimetry analysis of PANI was investigated by using TGA/DSC 1 STAR System using nitrogen as a purged gas. The rate heating was 10 °C/min in the ranging 20 °C to 600 °C.

3.3.3 X-ray Diffraction (XRD)

The X-ray diffraction of syntesized PANI in powder form were obtained using Rigaku Miniflex X-ray Diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 30 mA. The scan range from 5 - 60° with a step size of 0.04 ° s^{-1}. The samples were loaded in powder form on glass substrates for XRD measuremnet.

3.3.4 Cyclic Voltammetry (CV)

Cyclic voltammograms of PANI powder were recorded by where Ag/AgCl electrode was used as the reference electrode. 0.05 g PANI powders were mixed with 1 mL ethanol which was sonicated for time 1 h. The cyclic voltammograms was obtained at room temperature. [PANI powder-ethanol] solution was used scanning between -0.03 and 0.6 V with a scan rate of 10 mV/s. All electrochemical measurements were conducted in a three electrode cell, where gold was used as working electrode. Platinum sheet as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The electrolyte used in the current work was 0.01 M KCl solution.

3.3.5 Impedance Spectroscopy (EIS)

Impedance measurements were performed for PANI powder taken in 1 M KCl aqueous electrolyte solution suing electrochemical impedance spectroscopy (EIS). From impedance measurements one can study redox resistance reaction and equivalent resistance. EIS were collected with a frequency range of 0.1 Hz – 10 kHz with a DC bias of 10 V. The EIS data were analyzed using Nyquist plots showing the frequency response of the electrode/electrolyte system and are a plot of the imaginary components (Z'') of the impedance against the real components (Z').

CHAPTER 4.

RESULTS & DISCUSSION

4.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY ANALYSIS

Infrared absorption spectra are long known and well established in characterizing the chain structure of polymers. This includes the configurationally and conformational structure of the chains and the identification of defect structures and end groups. The infrared spectrum of polyaniline powder obtained from this study is shown in Figure 4.1.

The bands related to N-H stretching of an aromatic amine (>NH stretching) normally appear in the region between 3100 cm^{-1} and 3500 cm^{-1} reported by Ray et al. (2000). Due to the presence of moisture in the samples, we see a broad band near 3400 cm^{-1} with medium intensity. The bands could be assigned to the asymmetric modes of $-NH_2^+$ group, reported earlier by Rao et al. (2002). Whereas the band around 2922 cm^{-1} is due to the aromatic C-H stretching.

The two bands observed between 1440 – 1600 cm^{-1} region is related to the stretching of the C-N bonds of the benzenic and quinonic rings, respectively and are present due to the conducting state of the polymer as reported by Paul et al. (2000). The intensity of these bands illustrates an idea of the oxidation state of polyaniline powder is in the emeraldine base form reported by Campos et al. (1999). The bands corresponding to quinoid (N-Q-N) and benzenoid (N-B-N) ring stretching modes is observed at 1600 cm^{-1} and 1500 cm^{-1}, respectively.

The band characteristic of the conducting polymer due to the delocalization of electrical changes reported by Campos et al. (1999) as a sharp and strong band at region around 1150 cm^{-1}.
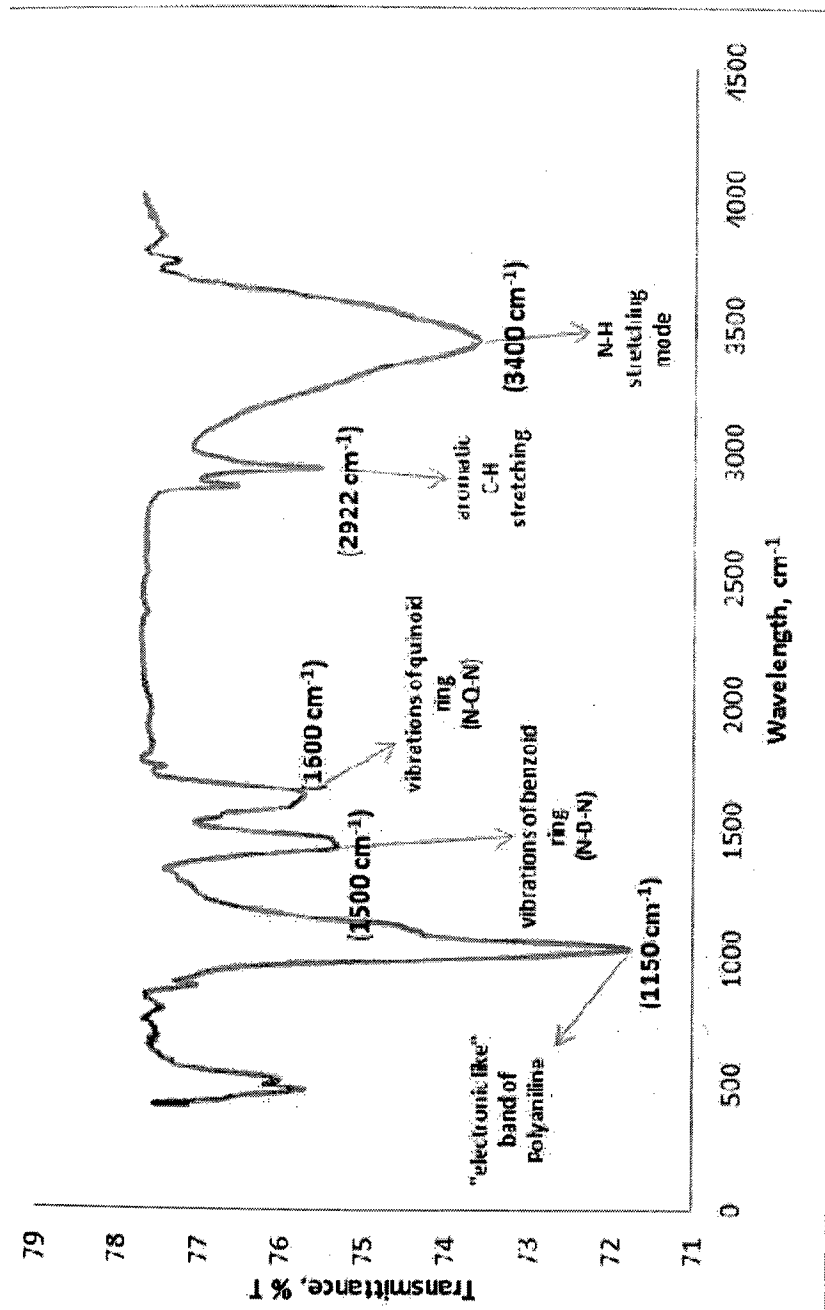
Figure 4.1: FTIR spectra of Polyaniline powder

4.2 X-RAY DIFFRACTION POWDER ANALYSIS

Many materials, especially polymers, have a substantial volume fraction without crystalline order. Though these regions are often termed amorphous, they frequently have specific local order. Structural information and crystallinity of the polyaniline powder are very important in order to understand the interchain interaction that could affect the electrical conductivity of the polymer matrices. The respective diffraction patterns of polyaniline powder are shown in Figure 4.2 with diffraction data are tabulated in Table 4.1.

Just like regular rigid polymers that own lots of benzene rings, the XRD pattern of polyaniline powder obtained is similar to previous reports reported made by Zhang et al. (2004) where the orientation of the polymer has been taken on the basis of a pseudo orthorhombic cell reported by Djurado et al. (1997). As reported in most literature, most of the forms of polyaniline powder essentially amorphous and show the presence of broad high-angle asymmetric scattering peaks stretching from 2θ between 15 - 25°. The main peaks of the synthesized polyaniline powder itself seems to comprise at least three broad separate peaks situated at approximately at 14.6°, 20.41° and 25.39°, corresponding to d-spacing of 6.06 x 10^{-10}, 4.35 x 10^{-10}, and 3.50 x 10^{-10} Å indicating a low degree of crystallinity of the polymer and consistent with those as reported by Djurado et al. (1997) and Laridjani et al. (1992).

Table 4.1: Peaks position of polyaniline powder for XRD analysis

PANI powder	2θ (°)	d-spacing (Å)
d-spacing (Å)		
when 2θ = 14.6	14.6	6.06 x 10^{-10}
$d = n\lambda / 2\sin\theta$	20.45	4.35 x 10^{-10}
$= \dfrac{(1)(1.54 \times 10^{-10})}{2\sin(14.6/2)}$	25.34	3.50 x 10^{-10}