UNIVERSITY OF THE WESTERN CAPE

DEPARTMENT OF CHEMISTRY

MASTER OF SCIENCE (CHEMISTRY)

ELECTROCHEMICAL EVALUATION OF CHEMICALLY MODIFIED MICROELECTRODES

By

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BY

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Dissertation presented in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at the University of the Western Cape.

Year : 2001

DECLARATION BY THE CANDIDATE

I, **Johanna Mpharu Moeletsi** , hereby declare that this thesis is my own work and has not been submitted at another University

……………………………………

ACKNOWLEDGEMENTS

I wish to acknowledge most sincerely to everyone who contributed in one way or the other to the completion of this research. In particular I wish to record my deepest thanks to :

- **Jehovah Almighty** for the leading power and strength he gave all of us who contributed to this work, by putting all our thoughts together to accomplish our goals of this project.
- **Professor Andrew Crouch,** for his patience during my dissertation and for his guidance and continuous encouragement given throughout the project. His professionalism , enthusiasm and moral support has been inspirational.
- **Dr Michael Polhuis, Prof IR Green, Prof S Mapolie** for their capable assistance in characterization of the compounds.
- **Danie Klopper** (Head of Scientific Services Department -CMC) for allowing me to utilize all facilities needed for this dissertation.
- My colleagues, **Khwezi Mpumlwana, Mjikisile Vulindlu, Desiree Damon, Roland Moollan, Nkosinathi Tshabalala, Zinhle Buthelezi, David Dookoo, CMC Trade Waste staff and UWC Chemistry staff** for their support and motivation and believing in me.
- To my family and friends for their love, patience and understanding.
- Lastly, to my **mother Maidi** , **brother Lebogang, grandmother Mateme and my late grandfather Shikwane**, for the courage and sense of humour which made things easier in many cases.

ABBREVIATIONS

CV	Cyclic Voltammetry
ASV	Anodic Stripping Voltammetry
TBT	Time Base Technique
PANI	polyaniline
PANMet	poly-N-n-methylaniline
PANEt	poly-N-n-ethylaniline
PANBut	poly-N-n-butylaniline
PANOct	poly-N-n-octylaniline
PANBenz	poly-N-n-benzylaniline

ABSTRACT

Aniline and N-alkylated substituted anilines have been polymerized by chemical and electrochemical methods. The chemically synthesized polymers indicated that N-alkylation improves solubility remarkably in common organic solvents. The compounds were characterized by FTIR, ^{1}H NMR, TGA and also studied by cyclic voltammetry on glassy carbon macroelectrodes for comparison with electrochemical synthesized polymers.

Aniline and its derivatives were also electrochemically polymerized on a glassy carbon electrodes. These modified electrodes were used in the presence of ions (Cl^-, SO_4^{2-}, NO_3^-, ClO_4^-, PO_4^{3-}) to study the electronic and ionic effects. The ionic trends observed were PANI : $H_2SO_4 \gg HCl \gg HNO_3 \gg HClO_4 \gg H_3PO_4$, PANMet : $HClO_4 \approx H_2SO_4 \gg HCl \gg HNO_3 \gg H_3PO_4$, PANEt : $H_2SO_4 \gg HClO_4 \gg HNO_3 \gg H_3PO_4 \gg HCl$, PANBut : $HNO_3 \gg H_2SO_4 \gg HClO_4 \gg HCl \gg H_3PO_4$, and PANBenzyl $HClO_4 \gg HCl \gg H_2SO_4 \gg H_3PO_4$.

The modified electrodes were further utilized to detect heavy metals (Pb, Zn, Cd and Cu) utilizing both macroelectrodes and microelectrodes. It was found that the polyaniline surface is more selective towards copper detection on a macroelectrodes compared to microelectrodes.

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CHAPTER 1

MOTIVATION AND GOALS

1.1 PROJECT MOTIVATION

The main focus of this project is to exploit the advantages of microelectrodes and modify them with conductive polymers for development of sensors for metallic detection. Much of the interest in microelectrodes is due to Wightman and his co-workers, and their interest in applying microelectrodes in the detection of neurotransmitter concentration in mammalian brains [1].

Modification of electrodes with conductive polymers on macroelectrodes (2.5 – 3.0 mm) is well established and influenced the basis of the current work. The modifications of polymers were employed on working electrodes such as glassy carbon, Pt, and Au [2]. Studies have been performed by voltammetric techniques. Applying similar techniques on microelectrodes will necessitate improved modifications of the polymers due to the advantages of microelectrodes.

Microelectrodes of diameter (1μm-100μm) have shown great promise over conventional electrodes. The features associated with microelectrodes are its fast response due to small size, small sample volume required, no deoxygenation of solutions, and improved detection limits. It lends itself easily to miniturization [3].

The polymer that has been most extensively studied on modified electrodes is Polyaniline [4]. It is a conductive polymer with many commercial and technological applications such as electrochromic devices, secondary batteries, electromagnetic interference shielding, and corrosion protection [4-15].

Exploiting the fact that it is conductive and environmentally stable [16] makes it an ideal candidate to be used as a modified surface in the detection of trace metals. Its chemical structure also predicts that it is a ligand that can interact within metallic species. An intensive study of polyaniline is important, since the structure has nitrogen lone pairs with conductive binding sites and five oxidation states due to resonance effects. It is insoluble in many organic solvents and has a complex mechanism [17]. The chemical synthesis and characterization of polyaniline is well established and well documented.

The review of modification of polyaniline on macroelectrodes will enable us to compare it with microelectrodes, and eventually use these electrodes as a sensor for trace metal analysis. It is also important to study the substituted polyaniline in order to determine the influence of steric hindrance and the initiation process of the monomers.

Only isolated cases of synthesis and the use of N-derivatised polyanilines are reported in the literature [18-20]. An objective of this work is to chemically synthesis a range of Poly-N-n-alkylanilines for use as modifiers on glassy carbon electrodes. Eventually, polyaniline and poly-N-n-alkylaniline surfaces are used as a sensors for metallic detection.

1.2 AIMS AND OBJECTIVES OF THE STUDY

The principal objective of this study is to chemically modify microelectrodes with different conductive polymers for detection of metallic species. The focus is on the investigation of polyaniline and its derivatives (poly-alkylanilines) such as poly-N-n-methylaniline, poly-N-n-ethylaniline, poly-N-n-butylaniline, poly-N-n-octylaniline, and poly-N-n-benzylaniline.

Initially the study will include a comparison between macroelectrodes and microelectrodes, and familiarization with voltammetric techniques used in microelectrochemistry. The approach will be to synthesize polyaniline and N-derivatized polyanilines chemically and complete characterization by FTIR, NMR, Thermal analysis will take place. The modification and metallic detection studies of the polymers will be determined by cyclic and stripping voltammetry respectively. To optimize the rate of polymerization the effect of electrolytes (NO_3^-, SO_4^{2-} Cl^-, ClO_4^-, PO_4^{3-}) need to be determined. The electrochemical effect due to N-derivatization will then be studied.

CHAPTER 2

CHEMICAL SYNTHESIS OF POLYANILINE AND POLYALKYLANILINE DERAVITIVES

Summary : *Polyaniline and poly-N-n-alkylanilines were chemically synthesized by strong oxidizing agents and further characterized by FTIR, NMR, TGA, and DSC. The polymers were dissolved in different solvents and used to modify glassy carbon electrodes for use in voltammtery.*

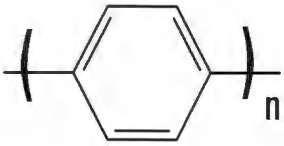
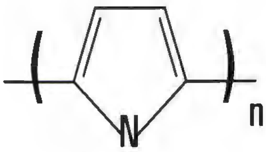
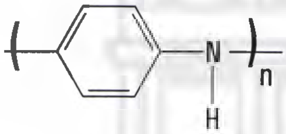
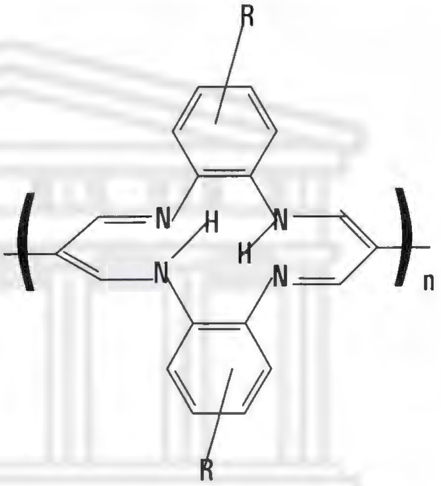
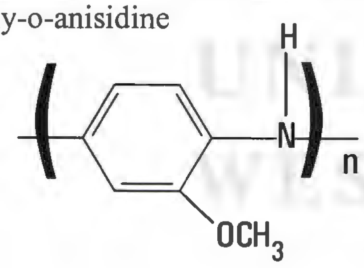
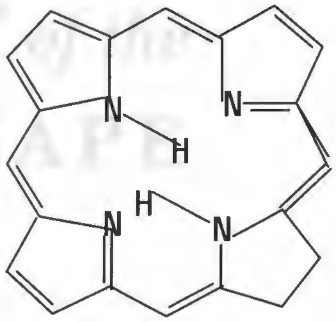
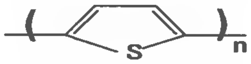
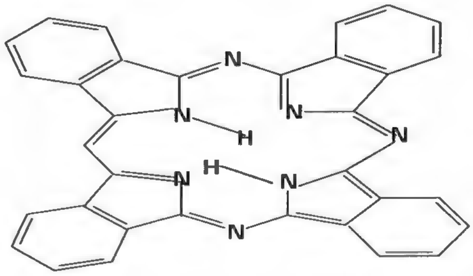
THEORY

2.1. CONDUCTIVE POLYMERS

Conductive polymers have received considerable attention in the past decades. A tremendous amount of interest has developed in of polymer films, which can be switched into a conductive state. It is the electroactivity, the property of these materials to switch between two states, coupled with fact that the two states have widely differing conductivities which make conductive polymers attractive for many technological applications [21]. This is also the characteristic that makes this area of science and technology particularly suited for the electrochemist. There has been a great deal of interest in the modification of electrode surfaces with polymeric materials. This was mainly to impart such properties as resistance to corrosion, resistance to fouling by reaction products, and better interaction between solution species and electrode surface [22].

Beside the conductive properties, these materials are also electrochromic and can be structurally modified to be non susceptible to photo corrosion. These are important considerations which should not be overlooked when pursuing the development of a technology based on these materials. Other consideration such as cost and stability may often favour the use of material. Some of the polymers which have been used to modified the electrodes [22] are shown in Table 2.1.

Table 2.1 Structures of some conductive polymers used as electrodes

Polyparaphenylene 	Polypyrrole 
Polyaniline 	Substituted dibenzotetraaza[14]annulenes 
Poly-o-anisidine 	Substituted porphyrins 
Polythiophene 	Substituted phthalocyanides 

2.2 RESEARCH AND DEVELOPMENT OF CONDUCTIVE POLYMERS

The pioneering work of Diaz *et al.* [23] on electrochemically prepared conducting polypyrrole has triggered a new era of research for both polymer chemist and material scientist. As a consequence, many reports dealing with electrochemical preparation and characteristics of conducting polyheterocycles (particularly polypyrrole and polythiophene) has been published [24]. In order to get a fairly detailed account of R & D activities in this field, one can always refer to some of the available reviews. For example the work on electrochemical preparation of polypyrrole up to 1983 has been reviewed by Daiz and Kanazawa [25]. The results on electrochemically prepared polythiophene and polyisothionapthalene have been reported by Wudl and his co-workers [26]. Malhotra *et al* [27] have published a comprehensive review on the studies of electrochemically synthesized polyheterocycles.

Most of the researchers in this field have emphasized the immediate application of electrochemically synthesized conducting polymers, particularly polypyrrole and polythiophene in battery technology and possible applications in electronic optoelectronic devices like solar cells [28] photoconductors[29, 30], electrochromic display [31], etc. At present all the efforts in the field of conductive polymers is due to the fact that the π-electron conjugation along the back bone of the polymer chain is one of the criteria for the polymer to exhibit good electrical (conducting and semiconducting) behaviour.

2.3 SYNTHESIS OF CONDUCTIVE POLYMERS

Conducting polymer films have been prepared on electrode surface by a number of different routes. The route most often chosen is electrochemical polymerization from a solution on the order of 0.01-0.1M in monomer or oligomer. Nonaqueous solvents such as acetonitrile, methylene chloride, or in some cases propylene carbonate are used for the synrthesis of polythiophene, poly-p-phenylene, and polypyrrole, whereas polyaniline can be prepared in either nonaqueous or in acidic aqueous media. A more exotic example is that of the electro-oxidation of benzene in $AlCl_3$/ N-butylpyridium chloride [22] to produce poly-p-phenylene. Monomer or oligomer concentration and solvent are not the only variable to be optimized for electrosynthesis of polymer films. Other parameters include the background electrolyte, temperature, and mode of oxidation (coulostatic, potentiostatic voltage pulse, or sawtooth wave). This last parameter has been shown to have a profound effect on the morphology of the polymer film [22].

2.4. POLYANILINE AS A CONDUCTIVE POLYMER

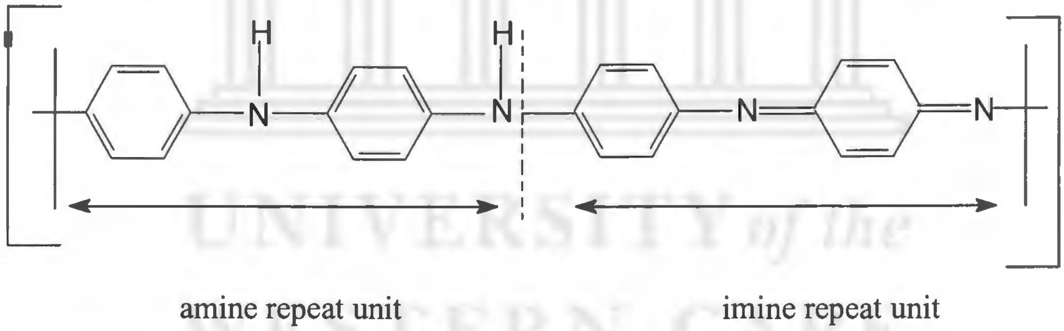
Polyaniline (PANI) is the oldest organic polymer ever synthesized. It has recently aroused great scientific and commercial interest due to its various technological applications. It is an environmentally and thermally stable conductive polymer with excellent electrical, magnetic and optical properties. The potential application of polyaniline includes secondary batteries, electromagnetic interference shielding, molecular sensor, and non-linear optical devices [32].

First reported in 1862, polyaniline[33] was described in 1910 –1912 as existing in four different oxidation states, each of which was an octomer[34,35]. A few scattered papers appeared in the 1950s and 1960s on polyaniline oligomers[36] and the electrochemical and $FeCl_3$ oxidation of aniline[37,38]. Of particular importance was a study of the emeraldine form of the material involving the effect of acids on conductivity, its basic electrochemical characteristics and its possible use in aqueous electrolyte rechargeable batteries [23].

There are still many unresolved problems concerning the structure and properties such as electrical conductivity and the mechanism. The complexities are in the molecular structure and its poor solubility in water and in most organic solvents. In general the polymer is synthesized chemically and electrochemically in acidic media. It is also different from other conductive polymers in that it can be doped to a conductive form without changing the number of π electrons through protonation by exposure to an appropriate protonic acid / aqueous solution [49].

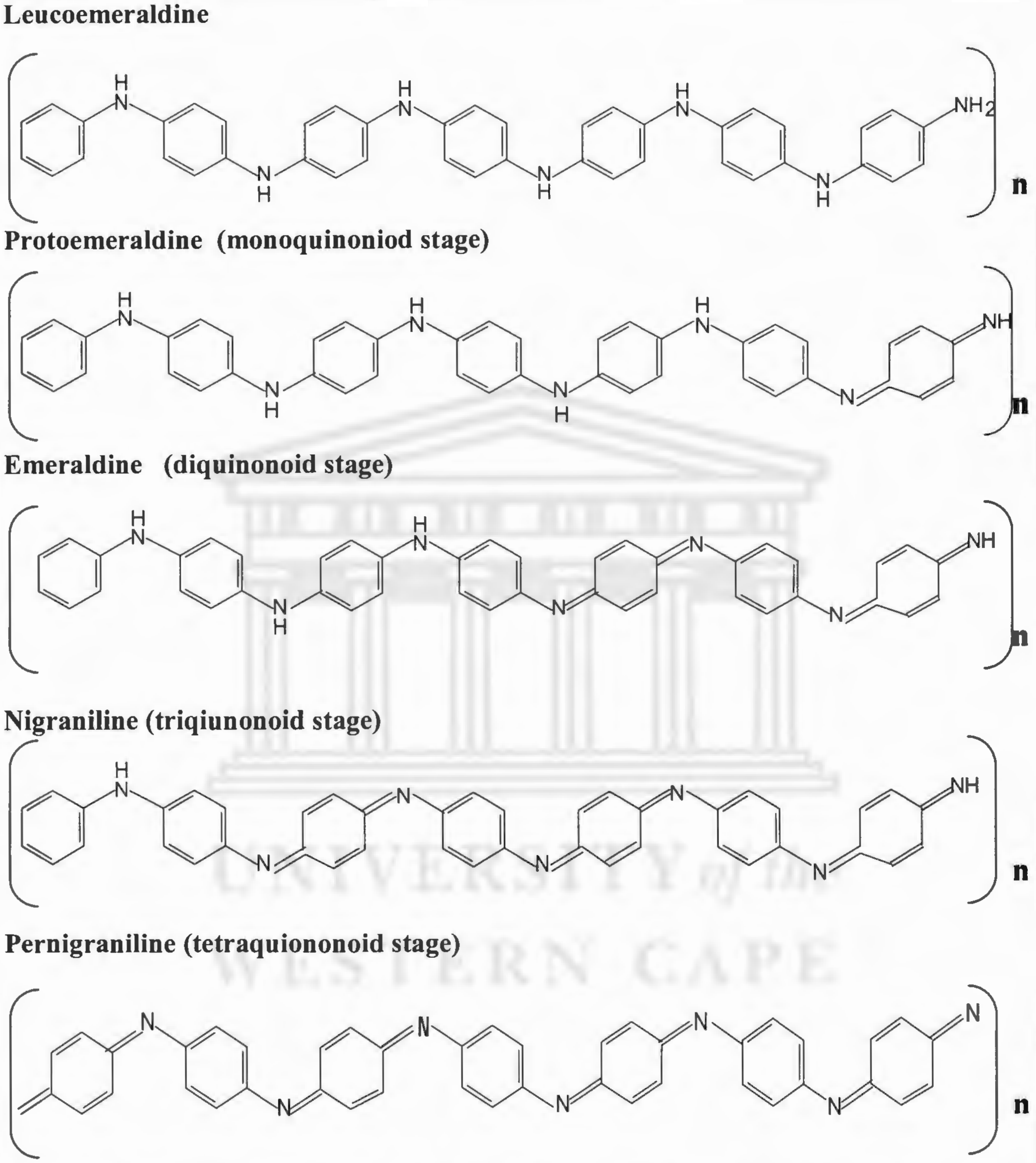
2.4.1 STRUCTURES OF POLYANILINE

PANI is a simple 1,4 coupling product of the monomeric aniline molecule. It contains alternating aniline and imine repeat units. The base form has been generalised as the composition of alternating reduced amine repeat units and oxidized imine repeat units as in Scheme 1. [40,41].



Scheme 1

In both cases, either one or both of the nitrogen atoms in a repeat unit may be protonated , depending on the pH of the solution to which the polymer has been exposed. Proto-emeraldine, emeraldine and nigraniline are the intermediate oxidation states of the above mentioned forms of PANI. Many investigation carried out on synthesis has shown that polyaniline has five oxidation states [42] as in (Scheme 2). Leucoemeraldine is the completely reduced form of polyaniline was first synthesized in 1910. It can be prepared as an analytically pure, off white powder by the reduction of emeraldine base, the most commonly used reducing agents being phenyl hydrazine or hydrazine. ^{13}C n.m.r. studies show that the bulk of the blue material is still in the leucoemeraldine oxidation state.

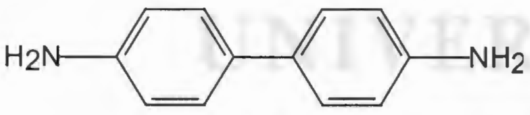


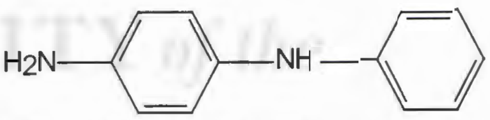
Scheme 2 : Represent five oxidation forms of polyaniline. *(A A Syed and M K Dinesan, Talanta, 38, 8, 1991, 815)* .

Pure pernigraniline, the completely oxidized form of polyaniline, has recently been synthesis for the first time [42]. It was reported in 1910 to be formed in an impure state by the oxidation of emeraldine base, but it was unstable and rapidly disproportionated, especially when wet. The most obvious problem with respect to PANI is related to the colour of the synthesized powder. This is the basis for the question about how the polymerization of aniline to form oligomers and / or polymers proceeds and what the by-products of the reaction should be [40]. Different laboratories has yielded different colours of PANI, the colour ranging from voilet to deep blue for undoped powders.

2.4.2 SYNTHESIS AND MECHANISM OF POLYANILINE FORMATION

PANI is prepared initially by the oxidation of the aniline monomer and its growth chain is via the electrophilic substitution reaction. Glarum and Marshall [43] carried out spectroscopic studies of aniline and found that oxidation takes place before the electrochemical peak potential at Pt electrode. It is believe to proceed via a radical cation (ϕ- $NH_2^{+)}$ coupling with either another radical or parent molecule. The product have been proposed to be the tail to tail dimer i.e. benzidine, and head to tail dimer N-phenyl-p-phenylene diamine.





Stilwell and Park found that the growth mechanism to be follows.

$$(PANI)^{sem} \rightarrow (PANI)^{ox} + xe^-$$

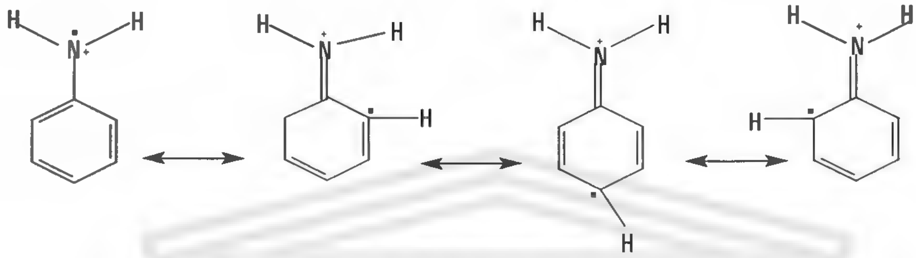
$$(PANI)^{ox} + An \rightarrow\rightarrow\rightarrow (PANI)_{x-1}{}^{ox} - An_2{}^{red}$$

where An is aniline $(PANI)^{sem}$ is the partially oxidised PANI with radical cation present, and $(PANI)^{ox}$ the dication. When this process is cycled once, a total of three electrons are removed from each aniline molecule, x become x-1 and the highest oxidation state is retained.

PANI is a precipitation product from an aqueous solution containing ammonium peroxydisulphate acids like hydrochloric, sulphuric, nitric or perchloric, and aniline. This direct route represents the classical approach to polyaniline synthesis in which aniline the monomer is converted directly to a conjugated polymer by a condensation process. It is not possible to polymerize the ortho- and meta–substituted aniline derivatives, due to the steric and weak inductive effects of the substituents[42]. The para –position should be kept free for radical coupling. There are four major parameters affect the course of the reaction and the nature of the final product. These are nature of the medium, the concentration of the oxidant, duration of the reaction and the temperature of the medium.

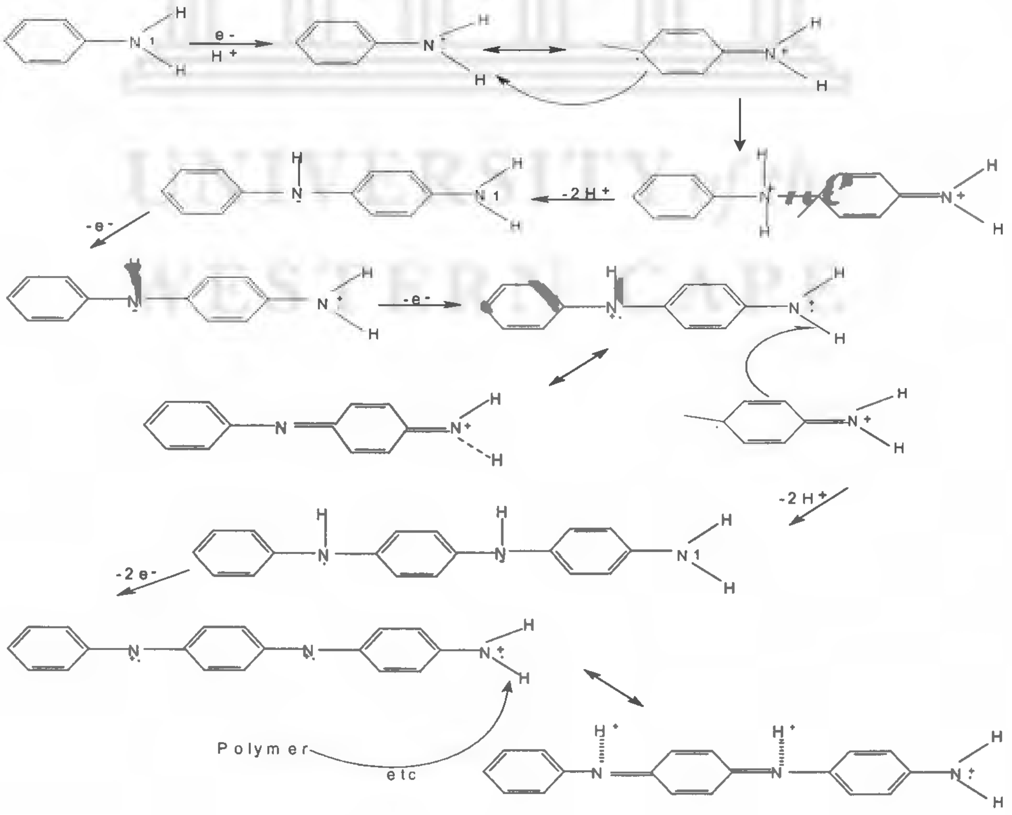
The numerous methods employed to synthesize PANI have produced several products [42] which differ in their nature and properties and must represent the results of a multitude of polymerization mechanisms of aniline. In general, polymerization proceed via the radical cation of monomer, which then reacts with a second radical cation of the monomer to give a dimer by eliminating two protons. At the potential required to oxidize the monomer, the dimer or higher oligomer would also be oxidized. This could react further with the radical cation of the monomer to build up the aniline chain.

Mohilner *et al.*[37], Breitenbach and Heckner [44], Hand and Nelson, [45] and Genies and co-workers[46] have proposed mechanisms for the electropolymerization of aniline. The point of agreement in the proposed mechanism is the first step of the oxidation of aniline, i.e. the formation of the radical cation. This radical cation gives three different resonance forms as shown in Scheme 3. There are two mechanisms for anodic oxidation of aniline in acidic and alkaline media have been reported. The mechanism in acidic media was proposed by Mohilner *et al* [37]. based upon the measurement of the kinetic parameters of the initial charge transfer step, and upon direct comparison of the properties, including infrared studies of the precipitate formed on the anode. On the basis of the experimental evidence, it was suggested that *p*-aminodiphenylamine is one of the intermediates in the electrochemical oxidation of aniline. They also demonstrated that *p*-aminodiphenylamine undergoing electrochemical oxidation with greater facility than aniline.



Scheme 3 : Resonance forms of aniline radical cation

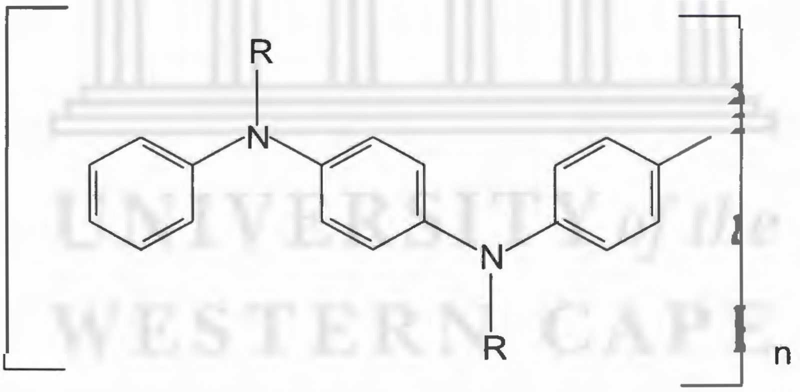
2.4.3. PROPOSED MECHANISM BY *GENIES AND CO -WORKERS*



2.4.4 THE STUDY OF POLYANILINE DERIVATIVES

Polyaniline has a difficult mechanism to follow since it has five oxidation states. Each state from *Scheme 2* has different colour. The polymer is also difficult to process due to lack of solubility in many organic solvents. This is due to the stiffness of polymer backbone and the hydrogen binding between adjacent polymeric chains [43]. The poor solubility limits not only the industrial applications, but also the complete investigation and understanding of the polymeric structure.

Recently, much research has been devoted to studies on the solubility of polyaniline in common solvents [47,48]. According to Levon *et al* [49], replacing the N-Hydrogen with an N-alkyl group could improve the solubility of PANI in other organic solvents.



Poly-N-n-alkylanilines derivatives: R= H, $-CH_3$, $-C_2H_5$, C_4H_9, Benzyl

In our case the investigation of the substitution of N-alkyl group to the polymer backbone will give clarification on the route of mechanism and the polymerization rate. Alkyl group acts as donor group to the nitrogen, therefore the deprotonation process become easier for the formation of the polymer. It will also be interesting to evaluate the steric and the ionic effects of these polymers.

2.5. EXPERIMENTAL PROCEDURES

2.5.1 CHEMICAL SYNTHESIS OF POLYANILINE AND DERAVITIVES

Polyaniline was synthesised by chemical oxidation of monomer aniline (20ml) (Aldrich reagent grade) and Potassium dichromate (12g) (NT Laboratory supplies, AR grade) were dissolved separately in 188 ml of 1.5 M HCl aqueous solution [32]. $K_2Cr_2O_7$ solution was added dropwise to the stirred solution of aniline hydrochloride. After reacting for 1 hr the black precipitate was filtrated, washed with 1M HCl until the filtrate was clear, and dried under vacuum for 48 hrs. The product obtained was a HCl doped polyaniline. It was undoped with an excess amount of 1M $NH_3.H_2O$ aqueous solution and washed with excess water to obtain the intrinsic form of polyaniline labelled as PANI. The substituted aniline monomers (N-n-methylaniline, N-n-ethylaniline, N-n-butylaniline, and N-n-benzylaniline) were prepared similarly.

2.5.2 CHEMICAL SYNTHESIS OF POLY-N-n-OCTYLANILINE

The dried emeraldine base form of polyaniline (PANI 7.27 g) was reacted with excess NaH in dried dimethylsulphoxide (DMSO) at about 45 ^{0}C under a dried nitrogen atmosphere for 6 hrs. The colour of the solution changed from dark blue to green black. The solution was subsequently reacted with excess octylbromide for 16 hrs at room temperature to give blue-black solution. The resulting solution was precipitated with 1M HCl aqueous solution, and the green precipitate was washed by a large amount of water and dried under dynamic vacuum. Then PANOct was obtained then washed with a large amount of n-hexane and then dried under dynamic vacuum pumping for 48 hrs [50].

2.5.3. CHARACTERISATION OF POLYMERS

An FTIR spectrophotometer (Perkin–Elmer paragon 1000 model) was used to identify chemical structures of polymers, Solid specimen of PANI and Pan-N-alkyl derivatives bases in both the neutral and acid-doped states were prepared by mixing their powders with KBr [50]. The thermal stability of polymers was investigated by both TGA and DSC in the temperature range of 50 ^{0}C – 900 ^{0}C under nitrogen. The programmed heating rate was 20^0 C/min. ^{1}H NMR spectra of the polymer in deuterated chloroform were recorded with a 200 MHz NMR spectrometer.

2.6 RESULTS AND DISCUSSIONS

2.6.1. FTIR spectroscopy of Polyaniline and derivatives

The FTIR spectra of PANI, PANEt and PANBut in the 4000 – 500 cm^{-1} region are shown in Fig 2.1(a),(b), and (c) respectively. All N-alkylated aniline bases exhibit similar IR spectral patterns.

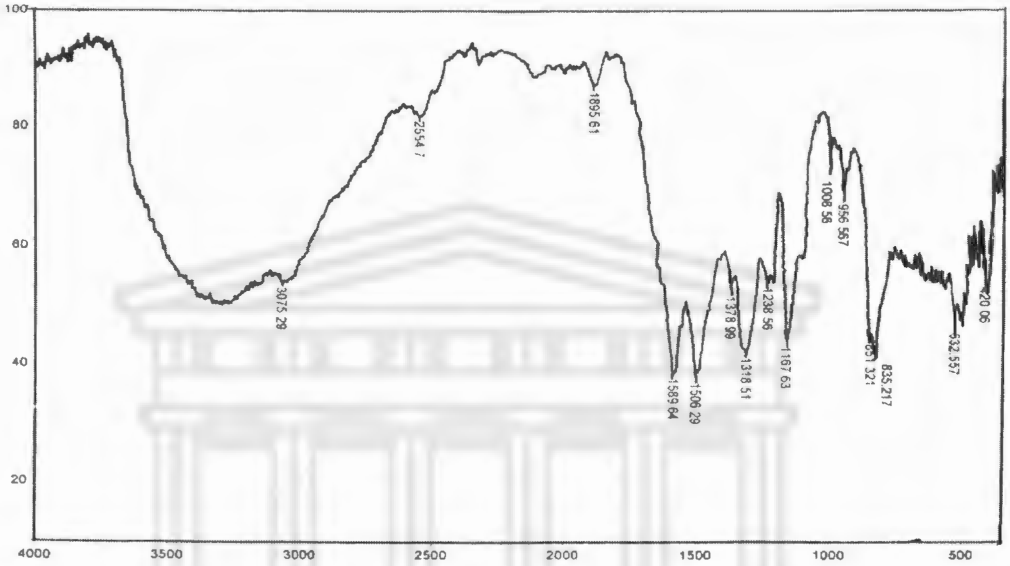


Fig 2.1 (a) FTIR spectra of PANI (KBr powder)

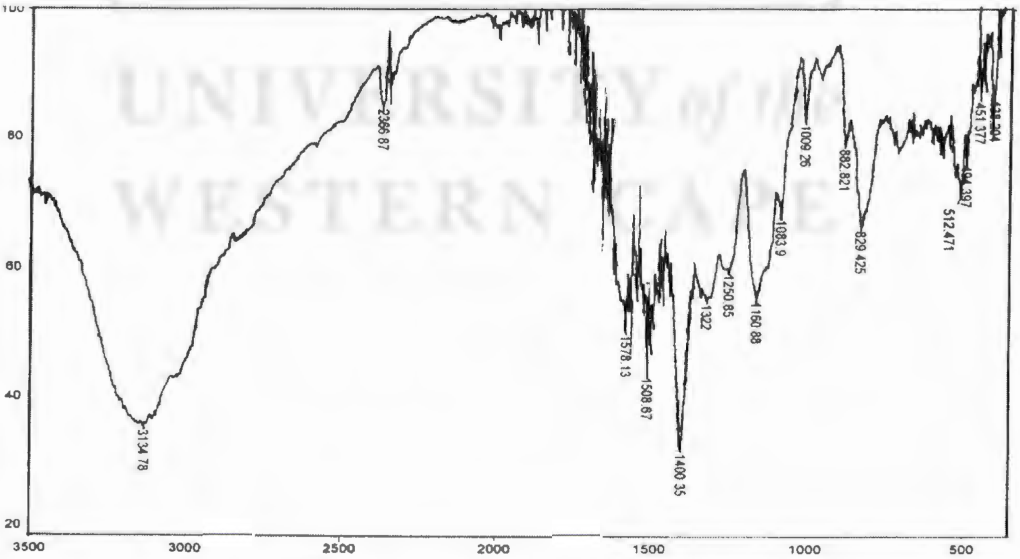


Fig 2.1 (b) FTIR spectra of PANEt (KBr powder)

The ring stretching of quinoid and benzenoid forms is observed between 1506 and 1596 cm^{-1} respectively [50,51].The ratios of the absorption intensities at 1506 and 1596 cm^{-1}

are slightly lower than in emeraldine bases before converting to N-alkylated emeraldine bases. The $C_{aromatic} - N$ stretching band of an aromatic amine appears at 1306 cm^{-1}

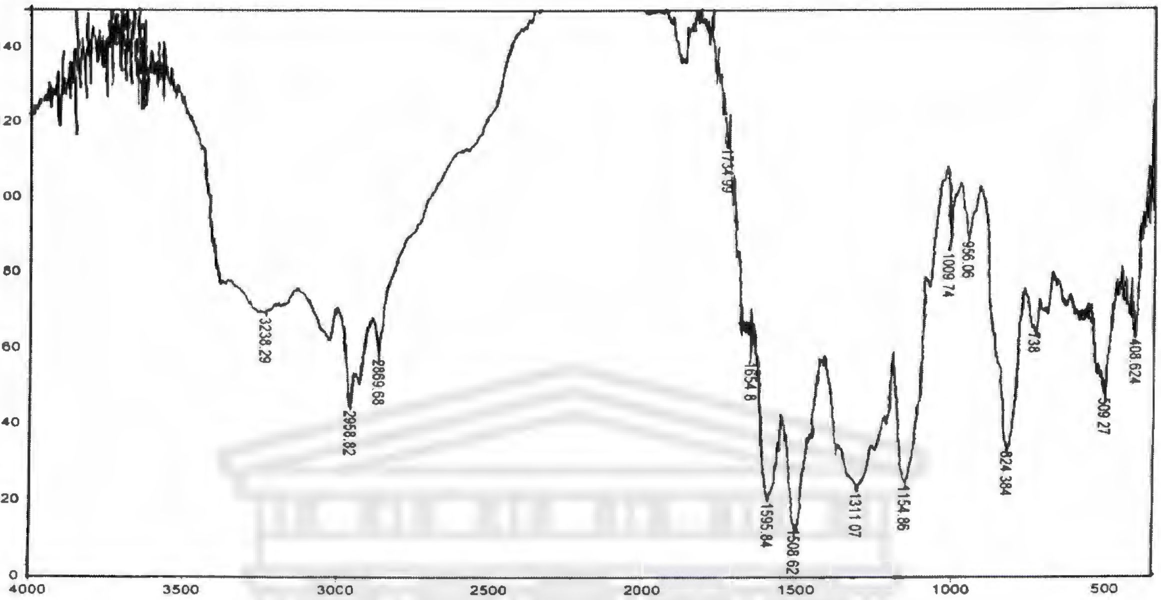


Fig 2.1 (c) FTIR spectra of PANBut (KBr powder)

The absorption peak 1165 cm^{-1} is characteristic of the N=Q=N vibration (where Q denotes the quinoid ring [52]. The presence of the absorption peaks at 2922 and 2852cm^{-1}, characteristic of asymmetry and symmetric aliphatic C-H stretching vibration, respectively [53], indicates the existence of the alkyl substituents.

The presence of the absorption peak at 8299 cm^{-1} (as emeraldine base) is characteristic of the out of plane bending vibration of the 1,4 disubstituted benzene ring [50], together with absence of a splitting of this peak into two peaks 820 and 870 cm^{-1}, shows that no ring substitution occurs in the present PANI derivatives, while the presence of the absorption peaks at 1252 cm, characteristic of the $C_{aliphatic}$ –N stretching [53] indicates that the alkyl substituents are linked to the amine nitrogens.

The following table is a summary of the IR data for the different polymers. It follows the same trend as was described earlier.

Table 2.1 : IR Data of poly(N-n-alkylaniles)

Vibration Mode	**PANI (cm^{-1})**	**PanN1 (cm^{-1})**	**PanN2 (cm^{-1})**	**PanN4 (cm^{-1})**	**PanN8 (cm^{-1})**	**PanBenzyl (cm^{-1})**
$-CH_2$ stretch	-	2871	3134	2958	2955	-
C-H stretch	3076	2805	2867	2869	2853	-
Quinoid	1589	1596	1578	1596	1598	1591
Benzoid	1506	1506	1509	1509	1510	1507
C-N bond	1318	1454	1400	1311	1455	1314
=N- vib	1168	1169	1161	1154	1150	1148
$-CH_2$ rock	730-900	730-900	730-882	738	700	702
C-H bond	1234	1250	1251	1154	1017	1247
C-H o.o.p.	851	823	829	824	829	828

2.6.2 SOLUBILITY OF POLYANILINES AND DERIVATIVES.

Improvement of the solubility of stiff polymers by incorporation of the alkyl side chain in the polymers has been reported extensively [54,55]. The qualitative solubility values are summarised in table 2. Polyaniline is slightly soluble in many solvents (unlike the substituted N-alkylanilines polymers). It agrees with the concept that the side chains acts as "bound solvents" in the class of rigid polymers with flexible side chains. In addition increasing in solubility may be owing to a lowering of the stiffness of polymeric chains[26,28].

Table 2.3 : **Solubility of N-alkylated Polyanilines in various solvents.**

Polymer	DMSO	THF	$CHCl_3$	CH_2Cl_2
PANI	++	+	+	-
PANMet	+	+	+	+
PANEt	+	+	+	+
PANBut	-	+	+	+
PANOct	-	++	++	++
PANBenz	++	++	++	++

++ very soluble , + partially soluble, insoluble.

Molecular Weight Distribution (MWD) of the polymers was measured to identify possible chain branching, polymerization process is classified as a step growth type [37]. Due to lack of solubility of the polymers the results were inconclusive.

2.6.3 THERMOGRAVIMETRIC ANALYSIS

The results of TGA are shown in fig 2 (a) (b) and (c) for the PANMet, PANOct, and PANBenz. The first weight loss at lower temperature results from moisture of unknown molecules (mainly solvent). The second weight loss at the higher temperature indicates a structural decomposition of the polymer [56]. Polymethylaniline started to degrade at 300^0 C and was completely decomposed at 600^0 C. An endothermic heat flow accompanied by ≈ 38 % weight loss is observed. All poly- N-alkylanilines shows weight loss starting from 250^0 C and majority weight loss at 600^0 C. The weight loss at 300 °C is due to the elimination of alkyl chain side group as indicated by Hwang et al [50] and Haba et al [57]. Thermal analysis has been reported in many literature reviews [57-59]. Table 3 summarises the TGA weight loss of other polymers.

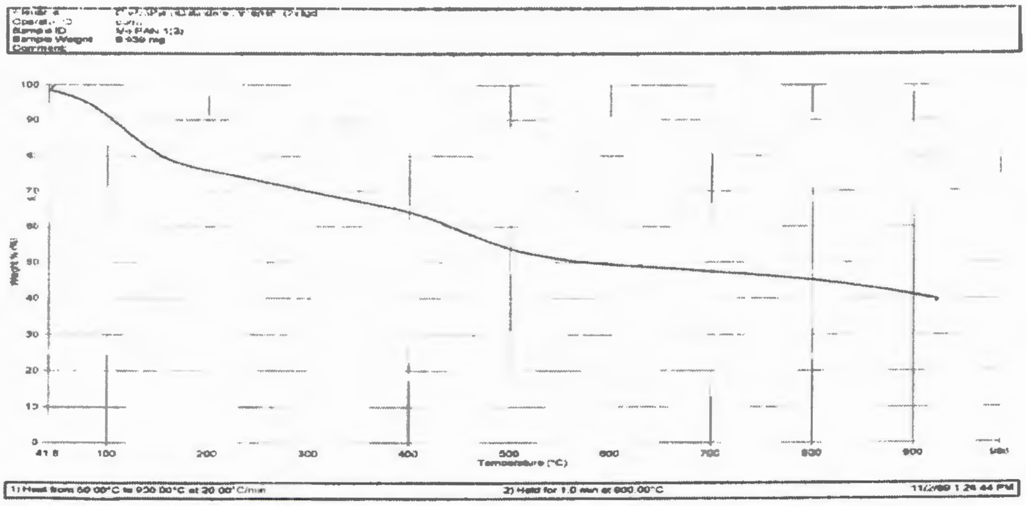


Fig2.2 (a) : A TGA thermogram of PANMet (20^0C/min)

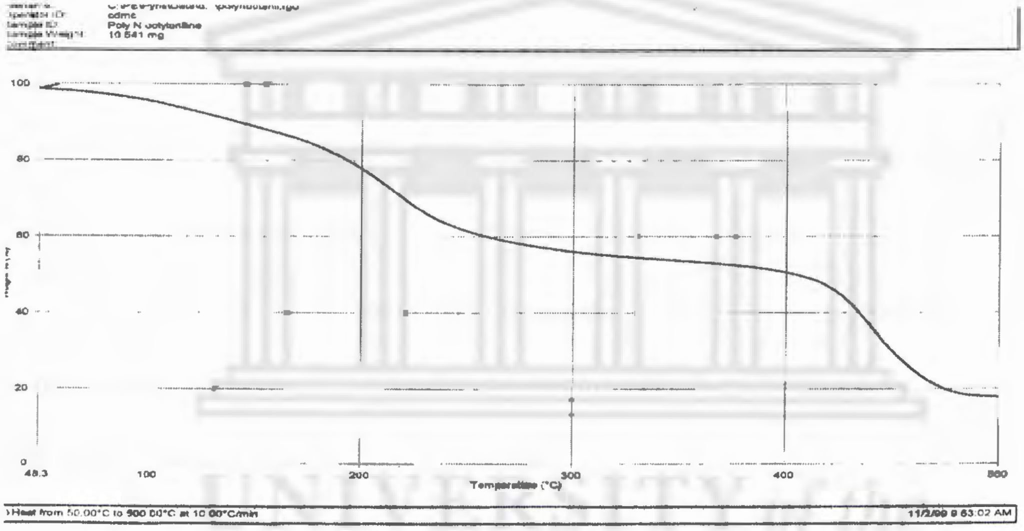


Fig2.2 (b) : A TGA thermogram of PANOct (20^0C/min)

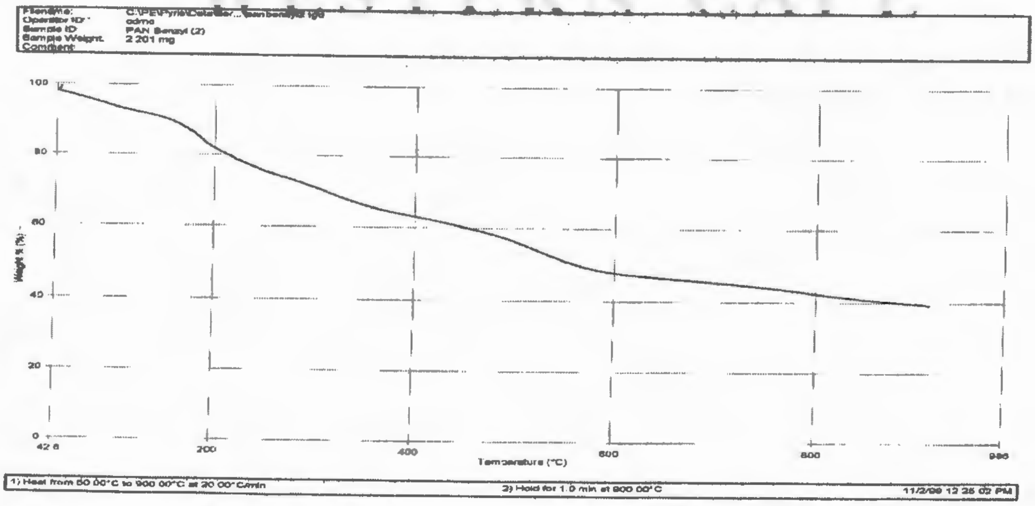


Fig2.2 (c) : A TGA thermogram of PANBenz (20^0C/min)

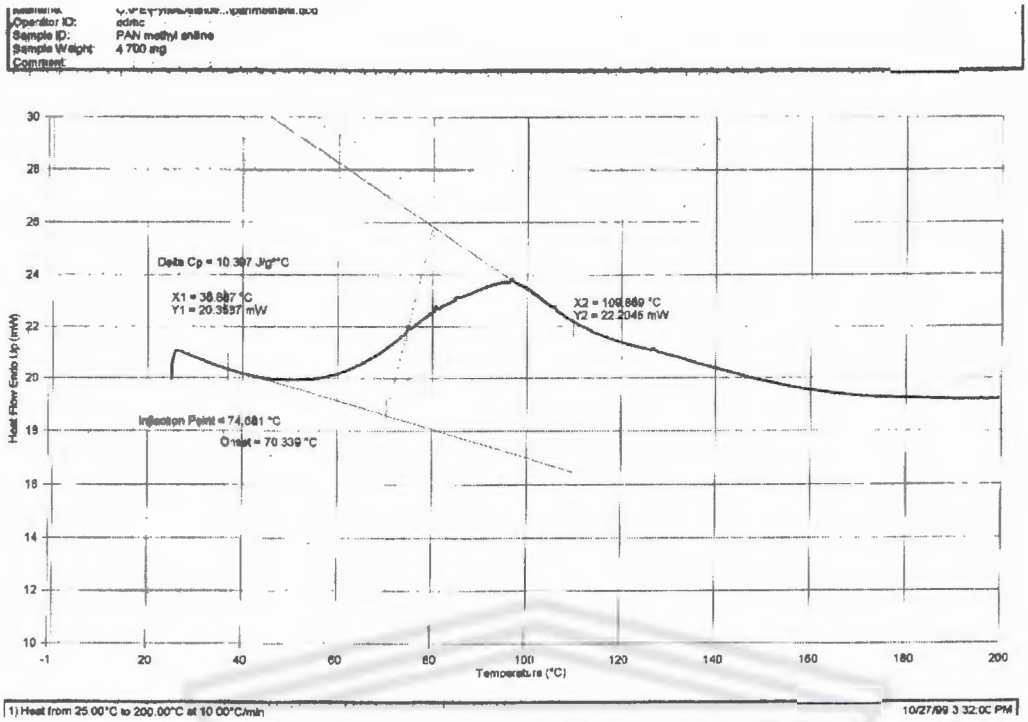
Table 2.4 : Thermogravimetric analysis of polymers.

POLYMER	% Weight loss	Temperature range
PANI	14 %	370^0 C – 600°C
PANMet	20 %	350^0 C – 550°C
PANEt	45 %	350^0 C – 600°C
PANOct	38 %	350^0 C – 600°C
PAN Benz	22 %	270^0 C – 600°C

2.6.4 DIFFERENTIAL THERMAL ANALYSIS

Differential Scanning Calorimeter (DSC) is most commonly used to determine thermal transition such as glass transitions, melting, cross-linking reactions, and decomposition. However, it measures only the total heat flow and the sum of all thermal transitions in the sample. The glass transition temperarure T_g is the characteristic temperature at which glassy amorphous polymers become flexible or rubber like because of the onset of the concerted motion of large segments of the polymer molecules [60-62].

Fig 2.3 (a), represent the DSC thermogram of poly-N-methylaniline under N_2 atmosphere. An endothermic peak between 37 ^{0}C –70^0C and exothermic peak between 75^0C-109 ^{0}C were observed. The endothermic peaks are most likely attributed to the removable water, which was consistent with TGA results [63]. The chemical process associated with exothermic peak may be related to a recrystallization [64] or cross-linking reaction[65,66] but not decomposition since there was no weight loss during this temperature range as determined by TGA. Fig 2.3 (b) represent the DSC thermogram of poly-N-benzylaniline and follows different trend to the alkyl group because of the phenol group both endothermic and exothermic peaks are higher.



Operator ID: edmc
Sample ID: PAN methyl aniline
Sample Weight: 4.700 mg
Comment:

1) Heat from 25.00°C to 200.00°C at 10.00°C/min
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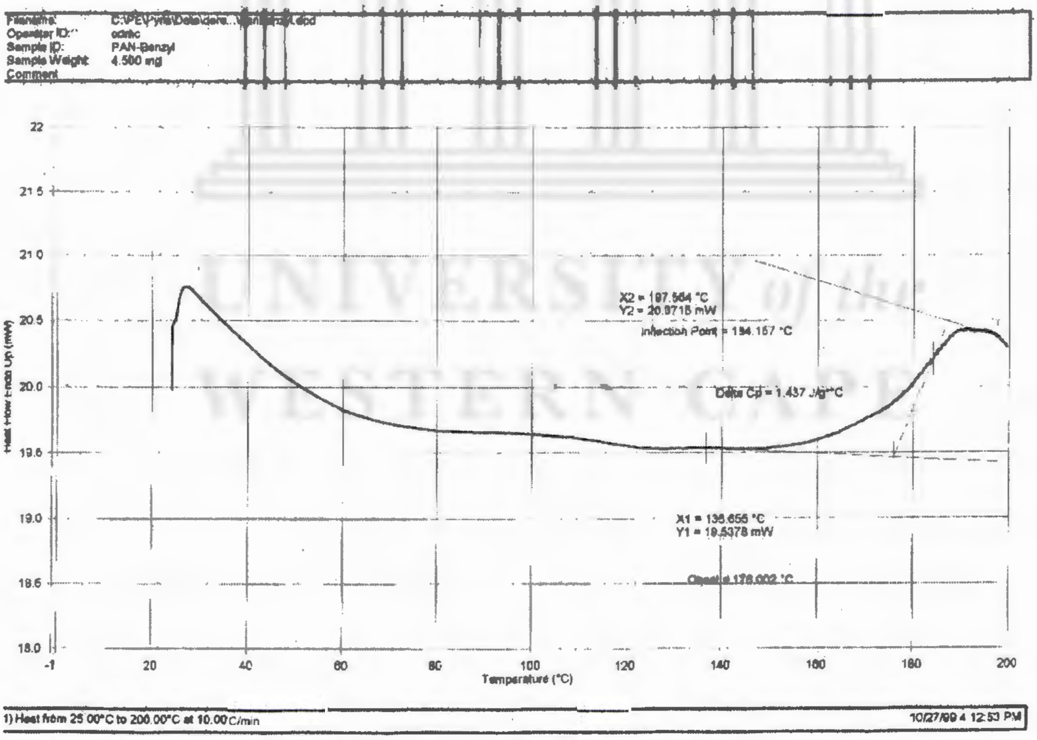
Fig 2.3 (a) DSC of PANMet at 10 ^{0}C/min.



Filename: C:\PE\Pyris\Data\dera...\panbenzyl.dsd
Operator ID: edmc
Sample ID: PAN-Benzyl
Sample Weight: 4.500 mg
Comment

1) Heat from 25.00°C to 200.00°C at 10.00°C/min
10/27/99 4:12:53 PM

Fig 2.3 (b) DSC of PANBenz at 10 ^{0}C/min.

Table 2.5 shows that for polymers with short side chain, such as PANMet –PANOctyl, two thermal transitions are observed between endothermic and exothermic. The transition at 75 ^{0}C for exhibit second order shapes with additional endothermal relaxation [49]. In the subsequent heating, only the second order upshift in heat capacity are seen. The transitions are assigned to be glass transition temperatures. The observed endothermic heat in the first heating run at the end of the glass transition can be defined as the enthalpic relaxation process of the annealed glass state [67]. The T_g temperature observed in the below table shows that the effect of alkyl chain substituent increases with the decrease in temparature on DSC endothermic regions. The same observations were also obtained for other conjugated polymers for instance (polyalkylthiophene) bearing short chains. PANBenz displayed different endothermic tempeture due to its different properties as compared to the alkyl substituent.

Table 2.5 : DSC endothermic and exothermic peaks of polymers

Polymer	**DSC endothermic**	**DSC exothermic**
PANI	30^{0}C – 72 ^{0}C	77^{0}C – 120 ^{0}C
PANMet	37 ^{0}C –70 ^{0}C	75^{0}C – 109 ^{0}C
PANEt	35 ^{0}C – 71 ^{0}C	75^{0}C – 104 ^{0}C
PANOct	44 ^{0}C – 65 ^{0}C	75 ^{0}C –103 ^{0}C
PANBenz	136^{0}C – 176 ^{0}C	184 ^{0}C – 197^0 C

2.6.5 NMR SPECTROSCOPY OF POLYANILINE DERAVITIVES

Additional information about polymers structure could be readily obtained from ^{1}H NMR spectroscopy. ^{1}H NMR spectrum of poly-N-butylaniline is shown in Fig 2.4 (a). This polymer was chosen for its good solubility due to its relatively long alkyl chain. The polymer was run in deuterated chloroform. The deuterated chloroform served as internal reference at 7.25 ppm. The aromatic protons gives a broad peak around 6.8 ppm, the proton of the methylene bonded to the nitrogen (C1) of the butyl group appear as a small peak at 3.07 ppm , and protons of the other methylene groups (C1-C2) appear at 1.64 and 1.37 ppm respectively and the terminal methyl group (C4) at 0.95 ppm [50].

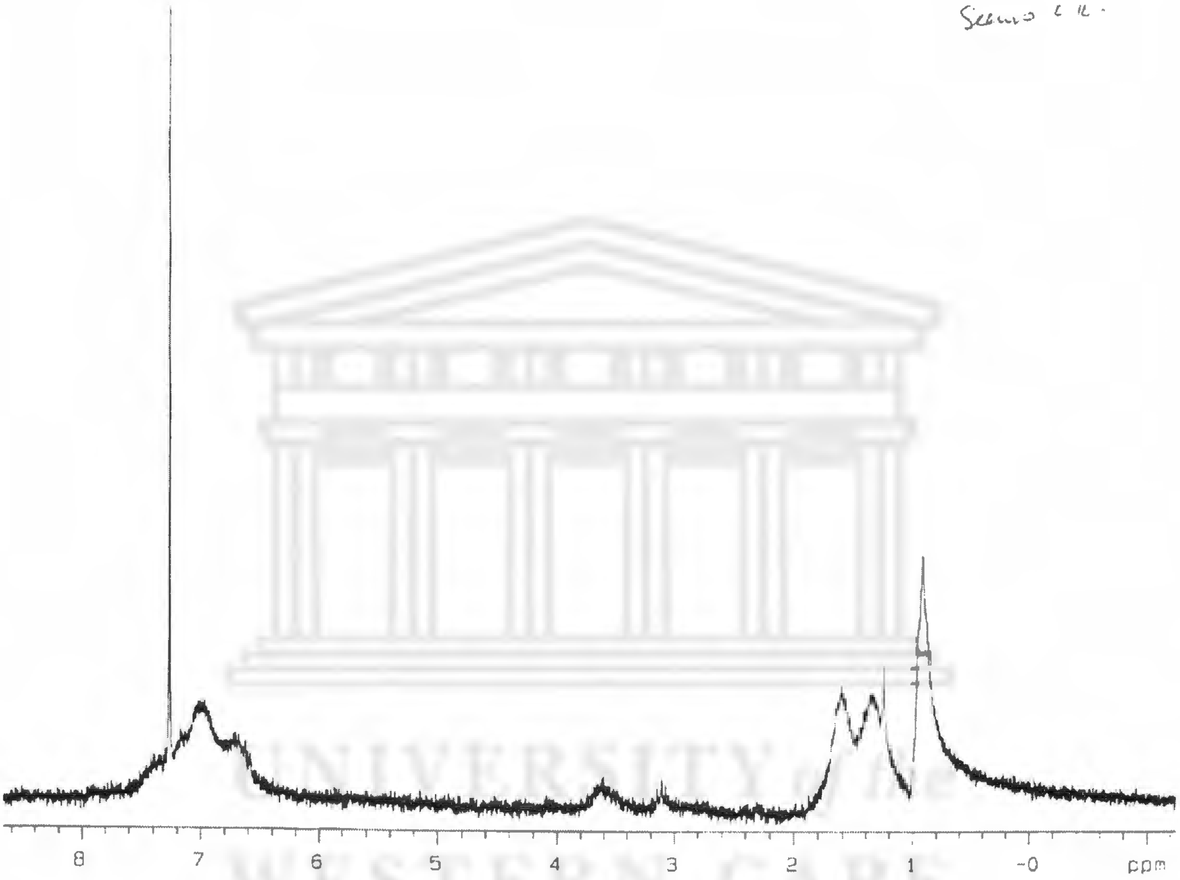


Fig 2.4 (a) ^{1}H NMR spectrum ($CDCl_3$) of chemically synthesised PANButylaniline.

Another example is shown on Fig 2.4 (b) ^{1}H NMR spectrum ($CDCl_3$) of chemically synthesised poly-N-methylaniline at 6.73 ppm peak is assigned for aromatic protons while peak 3.07 correspond to C_1 of the alkyl chain . At 0.96 ppm is the peak correlating to C_1.The proton at $C_1 \approx 3.5$ ppm is consider to be N-H bond. Polyaniline as the main compound is insoluble in many common organic compounds and it was complex to run NMR studies. Many researchers tried to dope PANI with methane sulphonic acid and other dopants [50] and investigated NMR studies.

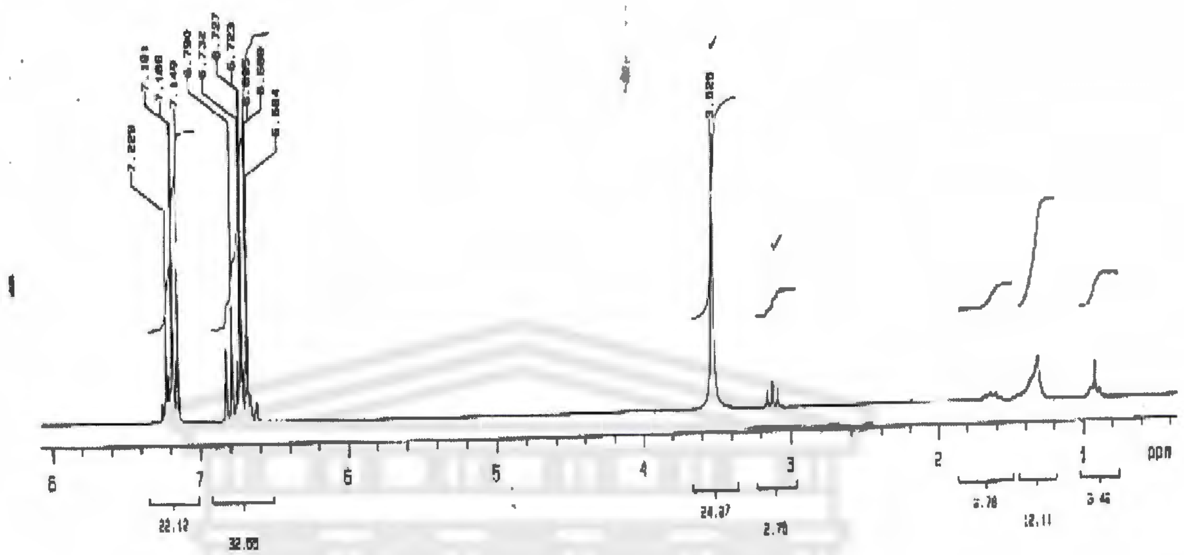


Fig 2.4 (b). ^{1}H NMR spectrum ($CDCl_3$) of chemically synthesised Poly-N-n-methylaniline

2.7 CONCLUSIONS

Chemical synthesis of polyaniline and poly-N-n-alkylanilines was successfully achieved. Most of the results were reproducible and compares competently with the literature. Poly-N-n-alkylanilines are soluble in most organic solvents than polyaniline. The characterization of these polymers was also successfully achieved. FTIR data has shown the Benzenoid and quinoid peak at 1506 cm^{-1} and 1596 cm^{-1} respectively and agrees with the literature. Thermal analysis gave a good study on the decomposition of the polymers and finally proton NMR indicated the expected structures of the polymers.

CHAPTER 3

ELECTROPOLYMERIZATION ON GLASSY CARBON MICROELECTRODES AND MODIFICATION BY POLYANILINE AND POLY-N-n-ALKYLANILINES

Summary : *Polyaniline and poly-N-n-alkylaniline derivatives were employed to electropolymerise glassy carbon microelectrodes by cyclic voltammetry to study the influence of polymerization rates. The ionic and steric effects of the polymers were also investigated in the presence of various anions.*

3.1 THEORY

3.1.1. VOLTAMMETRY AN ANALYTICAL OR CHARACTERISATION TOOL

Voltammetry is a technique that is used to study the solution composition via the current-potential relationships in an electrochemical cell by studying the current-time response of a working electrode at a controlled potential. Heyrovsky initiated the development of polarography (the name applied to direct current dc voltammetry when a dropping mercury microelectrode is used), in 1922. It marked a significant advance in electrochemical methodology. It is widely used by inorganic, physical and biological chemists for non-analytical purposes of adsorption processes on surfaces and for electron-transfer mechanisms [68].

The procedure normally involves the use of a cell with an assembly of three electrodes: working electrode at which the electrolysis under investigation takes place, a reference electrode which is used to measure the potential of the working electrode and an auxiliary electrode which together with the working electrode carries the electrolysis current. The electrochemical methods most commonly used in research and routine chemical analysis are cyclic and stripping voltammetry.

3.1.2 CYCLIC VOLTAMMETRY

In the last fifteen years Cyclic voltammetry (CV) has become a popular tool for studying electrochemical reactions. Organic chemists have applied the technique to the study of biosynthetic reaction pathways and to studies of electrochemically generated free radicals. An increasing number of inorganic chemists have been using CV to evaluate the effects of ligands on the oxidation/reduction potential of the central metal ion in complexes and multinuclear clusters.

Cyclic voltammetry consists of the cyclic variation of the potential of an electrode that is immersed in an unstirred solution and measuring the resulting current. The potential of this working electrode is controlled versus a reference electrode such as a saturated calomel electrode (SCE) or Ag/AgCl electrode. The excitation signal for CV is a linear potential scan with a triangular wave form. This triangular potential excitation signal sweeps the potential of the electrode between the two values called the switching potential. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered to be a response signal to the potential excitation. CV has been used to characterise the redox behaviour of compounds and to elucidate the kinetics of electrode reactions. Ingeniously designed cells permit us to measure optical and magnetic resonance spectra of some intermediates, thereby helping to establish structures. It is also used to determine the stability constants of metal complexes [69].

3.1.3. MICROELECTRODES IN CHEMISTRY

In the early 1970s a number of research groups exploited the advantage of microelectrodes, because in every area of analytical chemistry it seemed that smaller is better. The development and use of voltammetric microelectrodes is greatly extending the scope of electrochemical investigation. These electrodes are of a micrometer dimension (0.5-50mm). The interest in microelectrodes is due to the work of Wightman and co-workers [1]. He noted several advantageous properties compared to conventional electrodes: small size, time independent current response at long time, and a more rapid time response.

The primary application of microelectrodes was on neurotransmitter concentration in mammalian brains. These neurotransmitters, mainly dopamine, serotonin, etc. are easily oxidised by carbon electrodes and as such in *vivo* voltammetry provided a unique way to monitor chemical changes arising from neuronal actions [1]. Recently, the emphasis has been on utilising these microelectrodes as biosensors [3]. Much if this interest has come from clinical research where the small size of the electrode has encouraged its use for in-vivo studies.

There are a variety of materials, shapes and sizes of electrode reported where carbon, gold, platinum, mercury and copper are the most commonly used materials. The most extensively used microelectrodes have been disk shaped with a diameter of 10mm. Glassy-like carbon and carbon paste are most frequently encountered but increasing interest has been shown in the use of carbon fibre as an electrode material. Some work has been done on utilising carbon fibre microelectrodes as substrates for mercury films [3]. They are formed from high temperature pyrolysis of materials such as polyacronitrile.

The fibre is sealed with an epoxy in a glass capillary. The electrode probe, the diffusion layer and the diffusion profile was measured with a 2mm resolution normal to the conventional electrode. Carbon fibre electrode are useful in anodic stripping applications [70].

3.1.4. GENERAL CHARACTERISTICS OF MICROELECTRODES

Wightman *et al* [1] have noted several advantageous properties of microelectrodes. They have found that microelectrodes fit into small places, small current as low as 10-17A can be measured with ease, hey are useful in resistive non-aqueous media because of less iR drop. They have rapid voltage scan because of small double layer capacitance and this allow short-lived species to be studied. The rate of mass transport to and from the electrode increases as the electrode size decreases.

3.1.5. APPLICATIONS OF MICROELECTRODES

The most widely used application of microelectrode is for the in vivo voltammetric determination of neurotransmitters in mammalian brain [1]. There are other applications that take advantage of the total small size of the electrode used over the conventional electrode. The small active areas of microelectrodes offer unique studies in the areas of electrodeposition and electrodissolution (corrosion). Other area of use of microelectrodes includes, metal recovery, determination of thermodynamic and kinetic information, spectroelectrochemistry and electrosynthesis.

Several of the potential analytical applications of microelectrodes arise because of the larger ratio of Faradaic to residual current. This advantage occurs because of the predominance of non-planar diffusion. In voltammetry, microelectrodes has shown very low detection limits [3]. Microelectrodes can be used for modification purpose and also be utilized for the determination of trace metals. The properties of microelectrodes have lead to simplifications of the instrumentation and expanded the number of chemical system amenable to electrochemical analysis [3].

3.1.6. MODIFIED MICROELECTRODES

Modified microelectrodes are electrochemical sensors, which consist of a transducer; which transform the response into a signal that can be detected at a chemically selective layer. The transducer may be optical (e.g. a fiber optic cable sensor, electrical, potentiometric, amperometric, thermal and etc). The modified microelectrode can be prepared by several different methods and are therefore often referred to as polymer coated, functionalised electrostatically bound electrodes [1].

3.1.7. TECHNIQUES USED TO MODIFY ELECTRODES

This includes :

(i) **Strong Chemisorption**: Species that attached themselves easily to the electrode than the bulk solution, e.g. organic compounds.

(ii) **Covalent attachment**: chemicals reaction forms bonds between the substrate and the molecule of interest.

(iii) **Polymer Layers**: Dipping the electrode into solution containing a dissolved polymer and allowing the solvent to evaporate to form a thin film surface [71].

In this work PANI and its derivatives are used for modifying microelectrodes by the covalent attachment. The monomer aniline will be electrosynthesize in an acid media to effect polymerization. Chemically synthesis of PANI and its derivatives (*Chapter 2)* are also used to modify the electrodes.

3.1.8. FACTORS AFFECTING THE GROWTH OF POLYANILINE

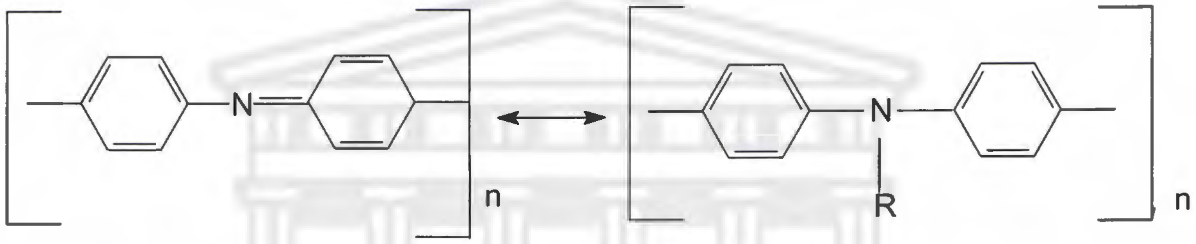
Several factors have been examined that influence the growth of film of PANI. Such factors are the solution composition, scan rate, ion effect etc. Most authors have performed cyclic voltammetry of polyaniline in acidic media i.e. H_2SO_4. They have also studied the size effect of anions. Larger anions seem to have lower mobility in the polymer films and consequently decrease the speed of electrochemical response of polyaniline during successive potential cycling. The participation of anions and cations in the redox-induced processes of intrinsically conducting polymers has become evident since the first investigation. Unfortunately the complex interaction between the ions and the charge carries in polymers is still obscure. The most widely accepted model to explain the behaviour of anions/cation was proposed by Huang *et al* [72]. They suggested that during electrochemical doping egress and anion ingress take place to an extent which is dependent upon the degree of profanation of the polyaniline sample examined and upon the nature of the anion incorporated.

Lapkowski and Genies [73] reported an anion effect on the ESR signal of doped PANI. Particularly interesting is the conclusion that the sulphate ion tends to interact more strongly than perchlorate ion with the positive charge on the polymer chain.

3.1.9. ELECTROCHEMICAL SYNTHESIS OF POLY- N-n-ALKYLANILINES

The study of poly-N-n-alkylanilines was established in this project to compare their properties with polyaniline. Polyaniline is difficult to process because its insolubility in common organic solvents. It is because of the stiffness of its backbone that results from delocalized electronic structure. It is also unstable at melting processing temperature, thereby limits its applications [49,50].

Several ring and N-substituted Polyaniline soluble in common organic solvents have been prepared directly from polymerization of the corresponding aniline monomers [49,50, 74]. The incorporation of the side groups into polyaniline has enhanced its solubility and processability and changed its properties. The electrochemical synthesis of poly-N-n-aniline is essential by taking advantage of the fact that alkyl groups are electron-donating groups, which augment the π - electron density along the conjugated polymeric chain.



R = H, CH_3, CH_3CH_2, C_4H_9 and Benzyl

The purpose of this work is to prepare N-n-alkyl substituted Polyaniline by electrochemical oxidation to examine the influence of the donating groups (R) and steric interactions at the nitrogen. Secondly optimization of the polymerization process with different electrolytes will develop certain electrochemical properties. As to N-alkylation, Levon *et al* [49] incorporated flexible long alkyl chains into Polyaniline via an N-alkylation reaction of the leucemeraldine form, which improved the solubility of PANI in different electrolytes and have found that H_2SO_4 was the best electrolyte. The same behaviour will be examined.

3.2. EXPERIMENTAL PROCEDURE

3.2.1. (a) CHEMICALS AND SOLUTIONS

All chemicals used were reagent grade or better and were used as received. Stock solutions of 100mM aniline, N-methylaniline, N-ethylaniline, N-n-butylaniline, N-benzylaniline were prepared in different electrolytes, i.e. 1M H_2SO_4, 1M HNO_3, 1M HCl prepared with ultra pure distilled water which was a Milli Q-water purification unit.

3.2.1. (b) PRACTICAL CONSIDERATION AND APPLICATIONS

Reference electrode

When making any measurement in analytical chemistry it is important to minimize the variables, therefore the primary requirement of a reference electrode is that it provides a contact potential and it is independent of the composition of the sample solution. Absolute electrode potential need not be measured, instead, relative potential are recorded. The reference electrode must satisfy the following criteria:

1) It must have a potential, constant with respect to the SHE and independent of the solution into which it is immersed.
2) The filling solution in the electrode must not react with the analyte.
3) The filling solution should have ion of equal conductance to minimize the formation of any potential at the liquid junction [75].

Auxiliary Electrodes

The function of the auxiliary electrode is to complete the circuit, allowing charge to flow through the cell. Auxiliary electrodes are usually platinum wires, foils or mesh, most commercial system supply platinum wire electrodes. Mercury pools and graphite rods are sometimes used, but are not common for analytical measurements [75].

Carbon Electrodes

Carbon electrodes include vitrous carbon, and carbon paste electrodes. The glassy carbon is the most commonly used in electroanalytical applications. The usual electrode construction is a rod of glassy carbon, sealed into an inert electrode body, a disc of the electrode material is exposed to the solution. The cleaning of these electrode chemical or chemical treatment of the electrodes surface is required, Carbon electrode are particularly useful for anodic studies, modified electrodes and also for stripping analysis [75].

3.2.2. TYPES OF ELECTRODES AND MAINTANANCE

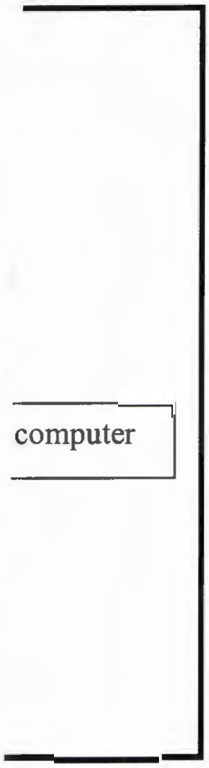
The working electrodes used were project was glassy carbon electrode, i.e. 4mm macroelectrode and 1.0μm microelectrode. The reference electrode was Ag/AgCl saturated KCl electrode and the counterelectrode was Pt wire. The working electrode was cleaned by first polishing with 1.0μm and 0.3μm alumina polish. The electrodes were electrochemically cleaned by Single Potential Time Base Technique (TBT) process between 0.00mV-1500mV in 1M H_2SO_4 at 100mV/s. Background scans of glassy carbon electrode in aniline free solution were taken before each experiment to ensure a clean unmodified surface.

3.2.3. INSTRUMENTATION

BAS-100B (Bioanalytical System, Inc) performed Cyclic and Stripping Voltammetry and also Time Base Technique for electrode cleaning. CV was for electrosynthesis of polyaniline (PANI) and Stripping for metal species detection.

3.2.4. MODIFICATION OF POLYMERS BY CYCLIC VOLTAMMETRY

Cyclic voltammetric set-up was used to polymerize aniline and alkylaniline as in the schematic diagram in Fig 3.1. 10ml of the solution of 100mM aniline and alkyl derivatives in 1M H_2SO_4 was each pipetted in BAS glass container in three electrodes system. The Ag/AgCl **(C)** electrode acted as reference electrode, micro glassy carbon **(A)** electrode as the working electrode and Pt **(B)** wire as the counterelectrode. The potential sweep operated at the scan rate of 50 mV/s with 100 scans. The system was compared with the macroelectrodes set up in order to establish the basis of the current work. The



·alkylaniline.

3.2.6. GENERAL PARAMETERS OF CYCLIC VOLTAMMETRY

Table 3.1 : General parameters applied for polymerization of aniline and N-alkylaniline in different electrolytes

Initial potential	(mV)	:	-200
High potential	(mV)	:	800
Low Potential	(mV)	:	-200
Initial P/N		:	P
Scan speed	(mV/s)	:	100
Sweep segment		:	15
Quite time	(s)	:	10
Sensitivity	A/V	:	1E-6

The above parameters were used for all practical purpose for the electrosynthesis of the polymers.

3.2.7. CLEANING OF MICROELECTRODES BY TIME BASE TECHNIQUES

The maintenance of the microelectrode is essential for each modification, since polyaniline films are not easily degraded due to its stability at the applied potential [42]. It is important that the conditions are such that the microelectrode is pure and polished for every run to avoid contamination. Oxidative degradation of polyaniline was observed between 1300 mV/s and 1500 mV/s. The Time Base Technique (TBT) was therefore the method used to clean the electrode at the potentials exceeding 1500mV/s. The cleaning of the microelectrode was confirmed by running a cyclic voltammogram of 1M H_2SO_4 as the background.

3.2.8. GENERAL PARAMETERS TBT METHOD

Table 3.2 : General parameters employed for purification of the glassy carbon microelectrode

Initial Potential	(mV)	: 1500
Sample Interval	(ms)	: 500
Sample Time	(s)	: 600
Precond E	(mV)	: 0
Precond Time	(s)	: 0
Quiet Time	(s)	: 0
Sensitivity	(A/V)	: 1E-6

3.2.9. ELECTROCHEMISTRY OF CHEMICALLY SYNTHESIS POLYMERS

Electrochemistry of the polymers was done in three electrode cell as in the experimental set-up *Fig 3.1* with 1mm glassy carbon macroelectrode as a working electrode, Ag/AgCl as reference electrode, and Pt as the counterelectrode. The potential applied was between 0.2 V and 0.8V at a scan rate of 50mV/s with two cyclic scans. The polymers were dissolved in DMSO, THF, CH_2Cl_2, $CHCl_3$ and the film were pasted on the working electrode and dried in the oven at temperature of 50 ^{0} C. Each electrode was dipped on 1M H_2SO_4, HNO_3, $HClO_4$, HCl to study the trend of polymerization [76]. This was done for the comparison of the main electrosynthesis of PANI and derivatives.

3.3. RESULTS AND DISCUSSIONS

3.3.1. MODIFICATION OF MACRO/MICROELECTRODES

Cyclic voltammograms of PANI are shown in Fig 3.2 (a) and (a) on macroelectrodes and microelectrodes respectively. Aniline was electrodeposited between – 0.2 V to 0.8 V vs Ag/AgCl reference electrode with similar conditions throughout the experiments. The growth of the polymer in Fig 3.2 (a) shown redox peaks A/A' at ≈ 0.10 V- 0.23 V while Fig 3. 2 (b) has three redox pairs peak A/A', C/C' and the middle peaks B/B'.

The peak A/A' in Fig 3.2(a) shows a rapid growth rate in polymerization of aniline even if similar condition were applied as in the microelectrode. The deposition rate is accelerated as polymerization proceeds, and the currents of all peaks increase with increasing number of potential cycles. In other words deposited PANI exert an autocatalytic activity on the electrodes [77,78]. Polymerization of aniline on the macroelectrode has shown the average of the two redox peaks pairs as in Fig 3.2 (a). The comparison of the two profiles reflects the difference in the polymerization mechanism. The surface of the electrodes after film polymerization is attributed to the leucoemeraldine form of polyaniline[79].

Kobayashi *et al* [79] have done UV studies to verify the change in redox peaks identified above. They have found that there was a green colour change at ≈ -0.2 V and a dark blue change at ≈ 0.5 V. These colour changes were associated leucoemeraldine and pernigraniline respectively. Although in the above instances the conditions were similar, it is clear the difference was due to the size of the electrode. The rate at which electrons are transferred between the electrode surface and molecules in the interfacial region is influenced by the relative values of the applied potential [80]; however, once the molecules in the interfacial region have been electrolyzed, molecules need to be transported from the bulk solution in order to maintain electrolysis. Hence the current also depends critically on the rate of mass transport between the interfacial region and the bulk solution.

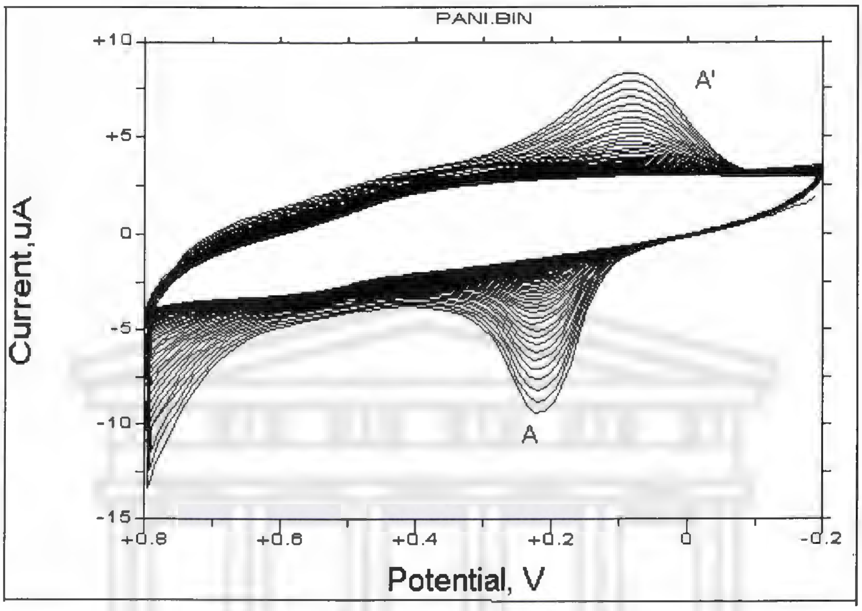


Fig 3.2(a) : Represent a cyclic voltammogram of polyaniline at glassy macroelectrode at the scan rate of 50 mV/s

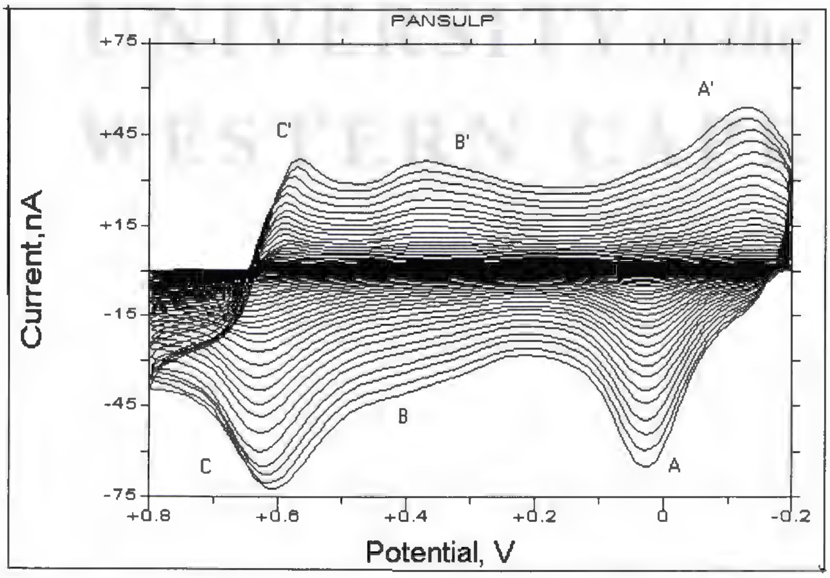
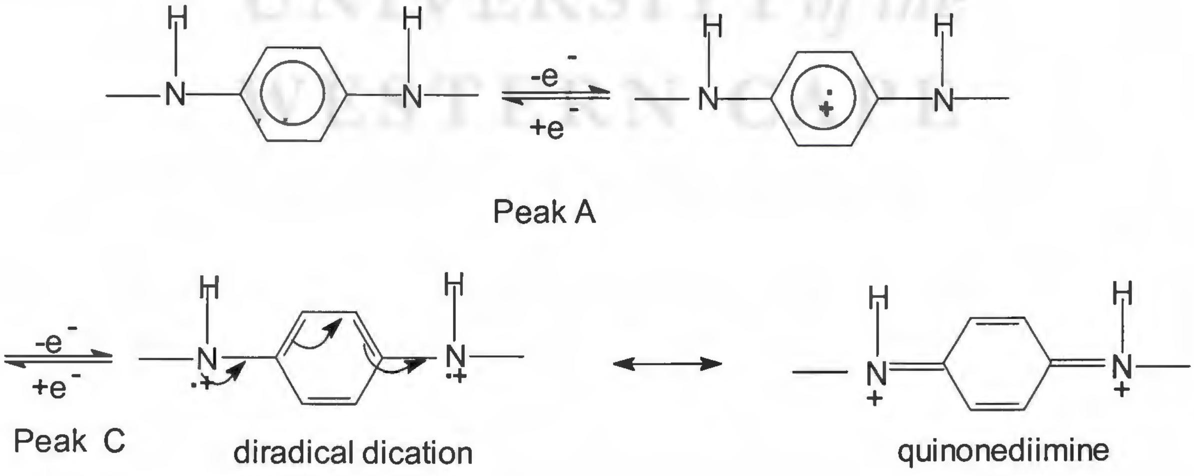


Fig 3.2(b) : Represent a cyclic voltammogram of polyaniline at glassy] microelectrode at the scan rate of 50 mV/s.

Steady state behaviour requires that the rate of charge tranfer, the electrode surface and the rate of mass transport to the electrode surface be identical. The conditions of diffusion, convection and migration gradients must be accomplished. It can be concluded that microelectrode are more sensitive than macroelectrodes because the rate of mass transport to the electrode increases as the electrode size decreases.

Many researchers [79-93] of PANI electrosynthesis have found similar features as in Fig 3.2 (b). Experiments were performed by electrodeposition of aniline on different electrodes, and CV technique was applied to understand the mechanism of PANI. The peak A/A' is well known as radical cation (leucoemeraldine / emeraldine) and peak C/C' is due to the diradical dication (emeraldine / perniganiline) transformations. Peak A identified as radical cation was generated upon oxidation which persist in the film until the potential reaches values designated as peak C. At peak C, the diradical dication is generated which establishes the equilibrium with the resonance form[77] :

REACTION 1



It was concluded [77] that CV peaks A and C are relevant to the redox chemistry of PANI. When the potential becomes more positive than C, diradical dication are generated, which allows a further PANI growth if aniline is present in solution. For the growth of PANI the radical cation generated upon oxidation forms a bond with another radical, as a results the diradical dication produced becomes reduced. The process is called the catalytic mechanism [77]. It is shown that the oxidation of this particular surface species into the diradical or dication was crucial for the growth to occur. Peak C is associated with the highly oxidised state of the oligomer[85]. The anodic peak A is regarded as the appearance of the "polaron state", which is transformed into "bipolaron" at the potential of peak C.

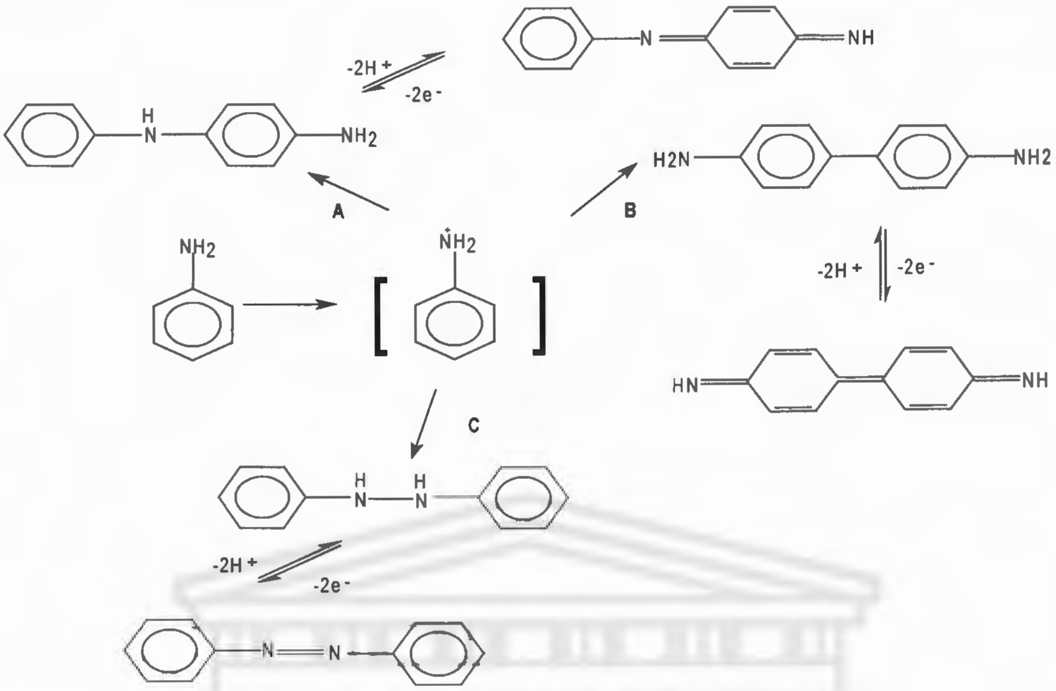
The cyclic voltammogram in Fig.3.2 (b) has a more pronounced peak and consists of the middle peaks B/B'. There has been some controversy over the middle peaks B/B' in the cyclic voltammograms. Stillwell and Park [77] assigned the B/B' as the benzo/hydroquinone (BQ/HQ) couple. The benzoquinone was produced via a hydrolysis reaction. Species like benzindine, p-aminophenol, and benzoquinoiimine dimer were possible products during the reaction. There could also be carbozole formation, cross-linking structures and by-products of hydrolysis reactions.

Kitani *et al* [89] interpreted these peaks as resulting from the redox reaction of benzoquinone. The identification of the middle peaks depends upon many factors such as scan rate, concentration, solubility and the type of electrolyte. Genies *et al* [90] have suggested that B/B' is related to phenazine rings resulting from the formation of cross-linked PANI chains by direct reaction of the aniline nitrenium cation in another PANI chain. Mailhe Randolph and Desilvestro suggested that the middle peak may be attributed to the crosslinking site induced by PPDA [91].

Yang and Bard [85] interpreted the middle peaks as the results of the redox reaction of p-hydrodiphenylamine and ADPA in the early stages, but benzoqiunone and p-aminophenol later. Alternatively, at the fast scan rate oxidative hydrolysis is suppressed and the middle peak is the results of the redox reaction of ADPA. When a lower concentration is used only ADPA is the dominant intermediate with the fastest reaction kinetics. Ansari *et al* [82] related the middle peaks as the formation of quinone as a consequence of a hydrolysis reaction based on positive potential. Wu and Yang related middle peaks as Benzoquinone/Hydroquinone (BQ/HQ) couple[81]. At earlier electrolysis times benzidine is produced in large amount, whereas at later times the predominant dimer formed is N-phenyl-p-phenylene diamine (PPD) molecule [86].

Mandic and Kovac [84] assumed peak B/B' to represent the dimer or dimer hydrolysis product. In their electrosynthesis of PANI they decreased the aniline concentration from 10^{-1} to 10^{-3} M and found that peak A/A' and C/C' were decreased and the middle peaks were well developed. These results suggested that polyaniline prevails from solutions of higher aniline concentration and that by decreasing the monomer concentration the product recorded as the middle peak is favoured. In general most authors agree that the are intermediate reaction occuring during polymerization. Thus the electrooxidation mechanism are envisaged to occur via the formation of aniline radical cations, which can then couple to form ring dimers by the three parallel pathways of reaction 2. The proportion of the three products N-phenyl-p-phenylenediamine (PPDA), Benzindine and hydrazobenzene is known to be pH dependent [93].

REACTION 2



3.3.2. EFFECT OF ELECTROLYTES ON POLYANILINE

The structure and properties of PANI depends upon the type of electrolytes in solution. Different electrolytes were employed to study the proposed mechanism of PANI.

Fig 3.3 (a) indicates a cyclic voltammogram of polyaniline in 1M HCl, (b) indicates cyclic voltammogram of polyaniline in 1M HNO_3, (c) indicates cyclic voltammogram of polyaniline in 1M $HClO_4$, (d) indicates cyclic voltammogram of polyaniline in 1M H_3PO_4.

Fig 3.3 (a) have three redox peaks. Peak A/A' is related to the radical cation and peak C/C' is the diradical dication. The observation is that the radical cation predominates, this is influence by the size of Cl^- ions during electropolymerization. It indicates that the radical cation is the rate determining step in the mechanism of PANI. The Cl^- ions stabilize the cation (polaron) the polymer backbone and this reduces the growth rate as the diradical dication rate step is lowered. Dimerisation is observed at the peak B/B' and can be related to benzoquinone/hydroquinone couple [77,85,86,91-,93].

The redox pairs in Fig. 3.3 (b), peak A is due to the radical cation and peak B is due to diradical dication. The NO_3^- allows the mechanism to give the average of both redox peaks as observed by peaks A'+ B'. Fig 3.3 (c) also shows the same trend as the electropolymerization of aniline in Fig 3.3 (b). Fig 3.3 (d) indicates polymerization of PANI in PO_4^{3-} ions. The diradical dication predominates.

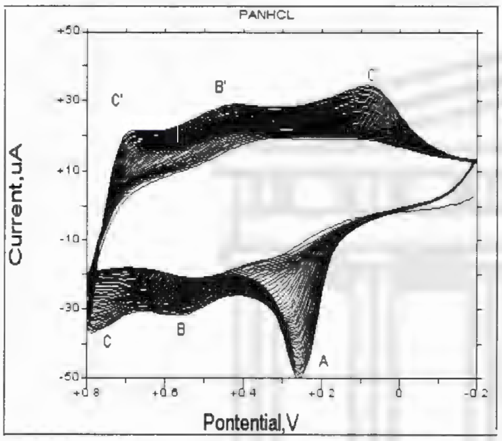


Fig 3.3 (a) CV of PANI in 1M HCl

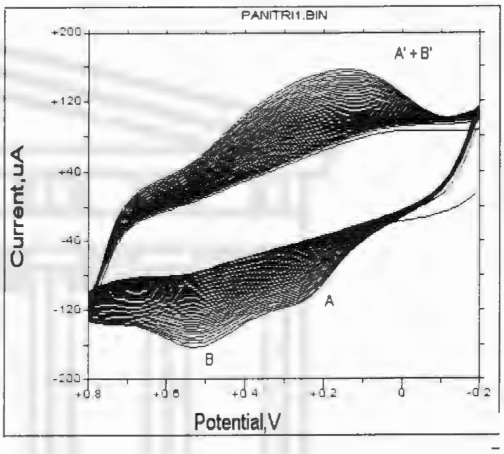
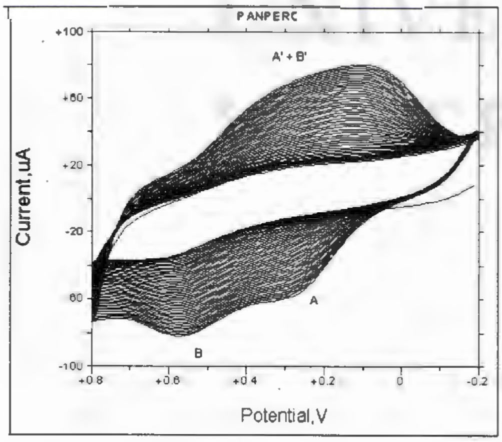


Fig 3.3 (b) CV of PANI in 1M HNO_3



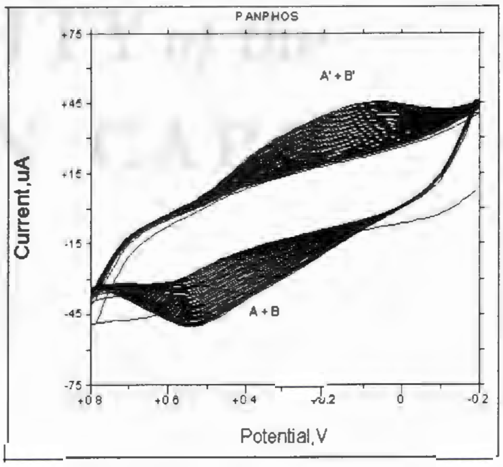


Fig 3.3 (c) CV of PANI in 1M $HClO_4$

Fig 3.3 (d) CV of PANI in 1M H_3PO_4

The comparison of the PANI polymerization in different electrolytes shows that sulphuric acid is the most suitable electrolyte. If the scan rate is lowered the mechanism would have followed the same trend as in PANI. The growth of PANI as observed in Fig 3.4 follows a trend that has been reported in the literature: H_2SO_4 >> HCl >> HNO_3 >> $HClO_4$ >> H_3PO_4 [94].

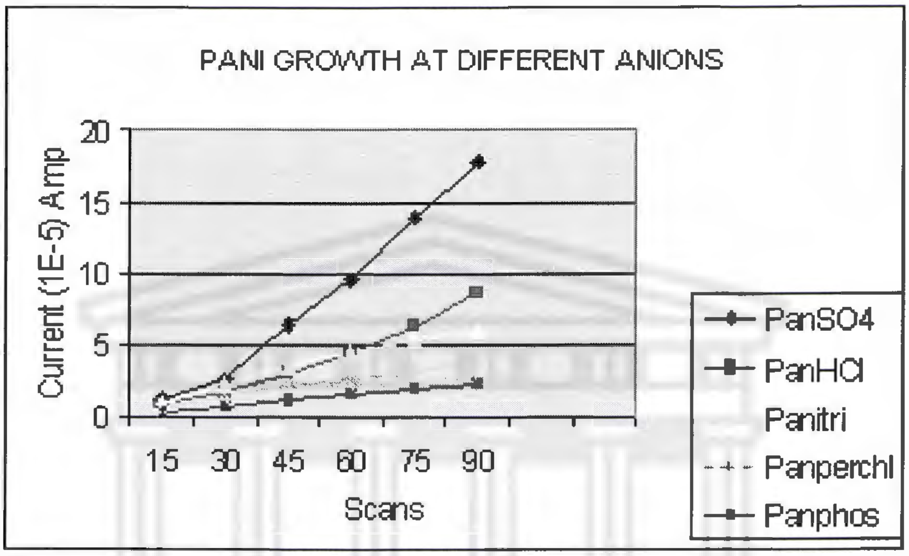
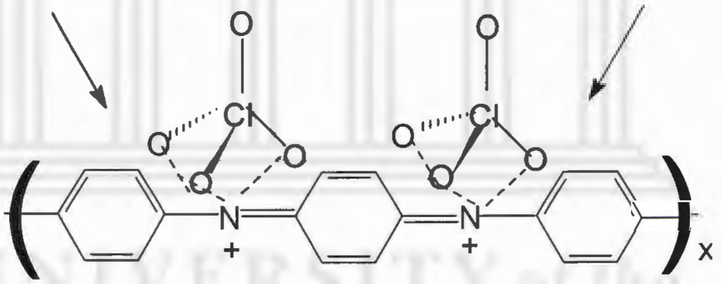


Fig 3.4: Variation of peak height in different electrolytes (1.0 M) solution, 0.1 M aniline at the scan rate 50mV/s.

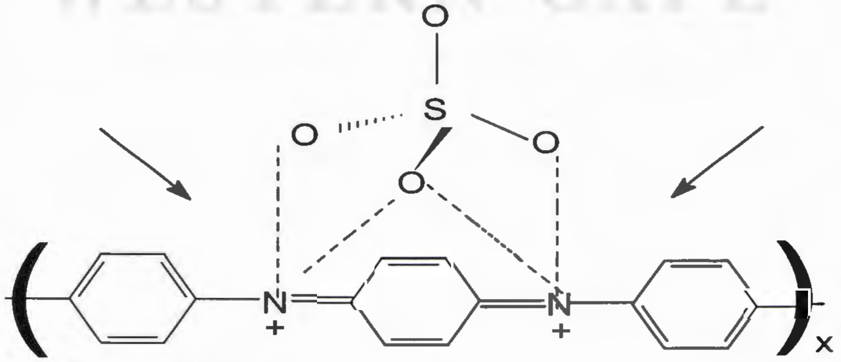
The growth rate of PANI films is apparently dependent on the type of anion. Except for the finding of Wang *et al* (H_2SO_4 > H_3PO_4 > $HClO_4$ > HCl) [95], an almost similar order has been reported, such as (H_2SO_4 > HCl > HNO_3 >$HClO_4$ > HBF_4 > CF_3CO_2H). The anions can be grouped into two types, i.e. class 1 (BF_4^-, ClO_4^- and CF_3COO^-) and class 2 (SO_4^{2-}, NO_3^- and Cl^-). Class 1 anions promoted a compact structure (with a fibre structure) while class 2 anions resulted in an open structure (structure a granular structure) [96,97].

The rate of the increase of the new peaks is also strongly influenced by the anion present. It is shown in Fig 3. 4 that with continuous applied potential cycles, the value of the resulting peak currents differs significantly, depending on the acid in the solution (i.e. on the anion present). It also means that the amount of charge corresponding to the redox process of deposited PANI differs. The order above shows that growth of PANI films is greatly dependent upon anion present, which suggest that different nucleation mechanism might be involved in the PANI deposit growth [94]. The influence of anions is explained by different degree of the specific adsorption of anions which, being available at the electrode surface, instantaneously get incorporated into resulting PANI deposit, promoting further polymerization reaction [98].

Lippe and Holze [99] have indicated that the nature of the anions incorporated in the positively charged polymer seem to have an effect on the mobility in the polymer films and consequently decrease the speed of electrochemical response of polyaniline during successive potential cyclic. It was evidently shown by the "shielding effect" model [99].



(a) perchlorate ions shielding effect



(b) sulphate ions shielding effect

Fig 3.5 : Illustration of the shielding effect of different anions can have on the nucleophilic attack of ions at bipolaron sites of polyaniline chain.

According the Lippe and Holze the ClO_4^- ions stabilise the cation (polaron) very rapid during the electrodeposition of aniline. This reduces polymerization and the current is lowered as seen in Fig 3.5 (a) for perchlorate ions. The sulphate ion stabilises the bipolaron (diradical dication). This is then the source of continuous polymerization. The diradical dications are shielded by the sulphate ion and this is called the "doubling effect", and hence H_2SO_4 have been found to be the most suitable for electrochemical polymerization of polyaniline.

3.3.3. POLYMERIZATION OF SUBSTITUTED N-n-ALKYLANILINE

Polyaniline is insoluble in many organic solvents due to the stiffness of the backbone and the hydrogen interaction between adjacent chains limits [49]. This can be overcome by chemical modification with alkyl polyanilines. The study conducted on polymers in this case was to study the effect of ions and also establish whether steric hindrance plays a role during the electropolymerization of N-n-alkylanilines.

Polymerization of aniline derivatives in H_2SO_4 was studied to evaluate the growth of the polymers. The general trend in Fig 3.6 (b), (c), and (d) show that the growth is towards the redox reaction between emeraldine /pernigraniline (bipolaron state) domination [100]. In the other hand Fig 3.6 (a) shows the average of the two peaks that are identified due to leucoemeraldine/emeraldine (polaron state). If the scan rate was lowered to at least 20mV/s the two peaks could have been identified as in the cyclic voltammogram of polyaniline in microelectrodes.

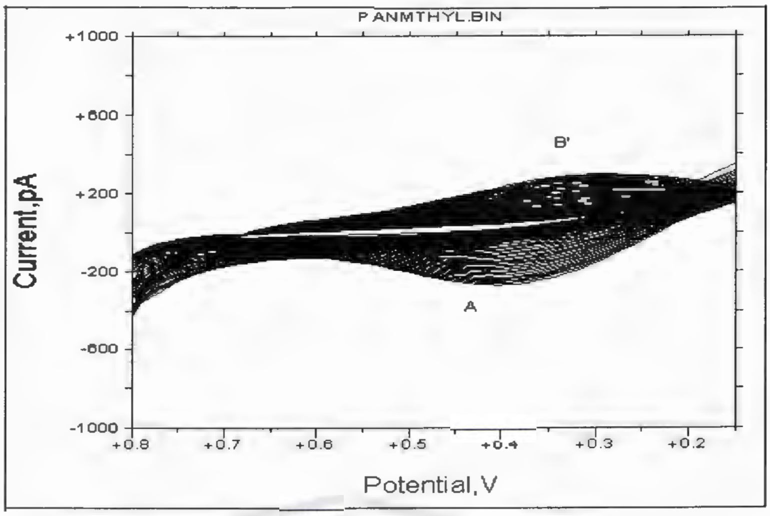


Fig 3.6 (a): represent CV of poly-N-methylaniline in 1M H_2SO_4.

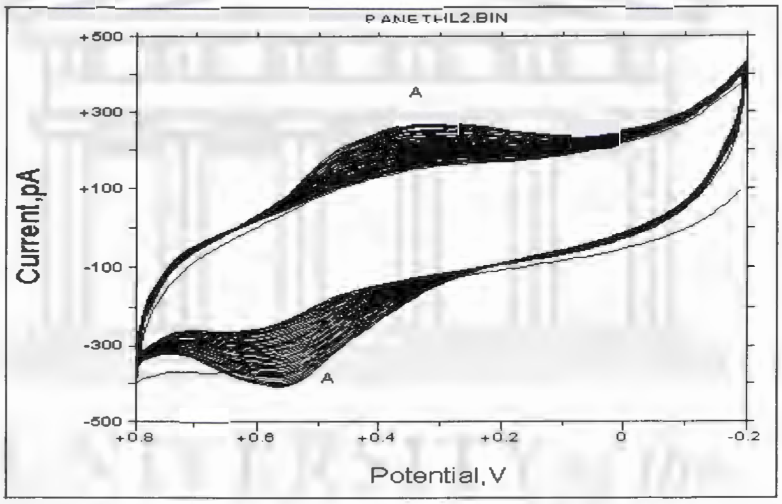


Fig 3.6 (b) : represent CV of poly-N-n-ethylaniline in 1M H_2SO_4.

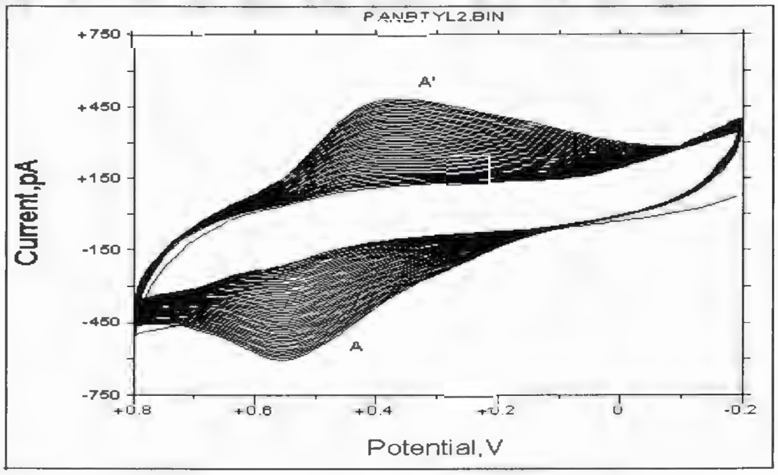


Fig 3.6 (c) : represent CV of poly-N-butylaniline in 1M H_2SO_4.

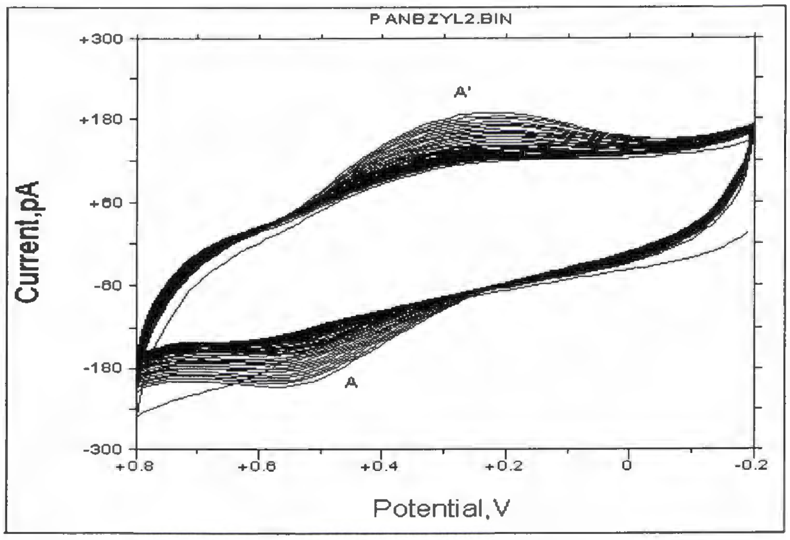


Fig 3.6 (d): represent CV of poly-N-n-benzylaniline in H_2SO_4.

The growth rates of the polymers in 1M H_2SO_4 are illustrated in Fig 3.7. It was expected that poly–N-n-butylaniline growth will deteriorate because of steric hindrance. Fig 3.7 illustrates that the growth rate is more improved with N-n-butylaniline and steric hindrance does not play a role during polymerization. Poly-N-n-benzylaniline growth is lower in this case due to steric hindrance. Although alkylaniline polymerization was examined, it is clear that aniline polymerization is more pronounced in H_2SO_4. Comparison of the cyclic voltammograms of N-alkylaniline and aniline show that PANI in Fig 3.2 (b) is electrochemical stable because there is no deprotonation process involved [100].

Conductivities of poly- N-n-alkylaniline were found to be low [21] as compared to PANI, but Fig 3.7 indicates that the electronic properties (donor / acceptor character) of N-substitution of the polyaniline considerably affects the conductivity. Electron donating groups increase the polymer conductivity [22]. The alkyl groups are electron-donating which augment the π-electron density along the conjugated polymeric chain [22]. In this regard the nitrogen play a role in the electronic transportation, in which the molecular orbital and lone pairs are involved.

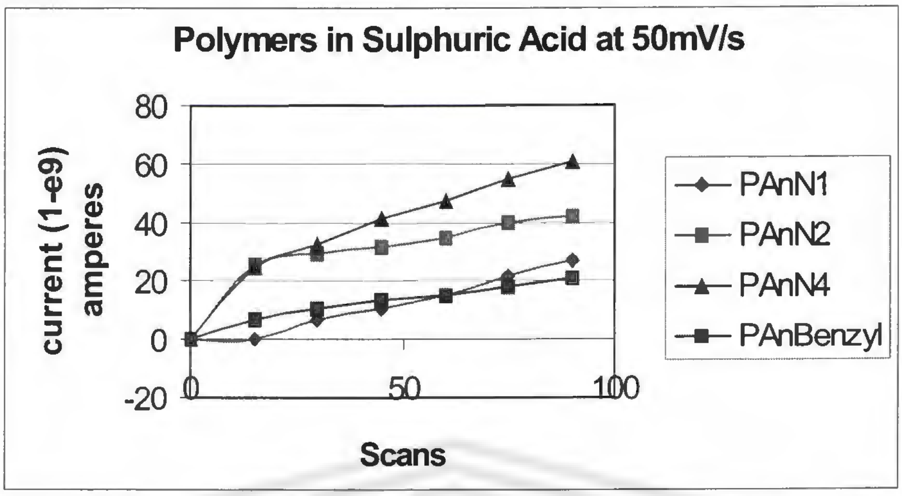


Fig 3.7 : Illustration of the growth rate of polymers in 1M H_2SO_4. PanN1 (poly-N-methylaniline), PanN2 (poly-N-ethylaniline), PanN4 (poly-N-butylaniline)

The two effects, steric and electronic, may be regarded as being responsible for the decrease in the conductivies and the decrease in the basicity of the imine nitrogen [17]. In this case it is observed that throughout the electrochemical synthesis, both steric and electronic effects have a lesser effect on the conductivity of poly-N-n-alkylaniline. Polymerization occurs despite these effects, thus to reach the optimum level where steric hindrance take place, there must be an increase in chain length. Poly-N-n-benzylaniline was the only polymer, which showed the property of steric hindrance while the poly-N-n-butylaniline growth rate increased. Further N-alkylation from (N-n-hexylaniline to N-n-dodecyl) will decrease the growth rate due to steric effects [100].

3.3.4. EFFECT OF ELECTROLYTES ON POLY-N-n-METHYLANILINE

The effect of different electrolytes was studied in the polymerization of N-n-methylaniline as in Fig 3.8. The figures illustrate common trends amongst the CV's. The redox peaks observed in (b), (c), and (d) are the average of the two redox peaks A + B of the radical cation and diradical dication. The current is lowered due to polymerization of PANMet in HCl, HNO_3, H_3PO_4. In $HClO_4$ Fig 3.8 (a) both the redox peak are similar as in the CV of PANI at microelectrodes *Fig 3.2 (b)*.

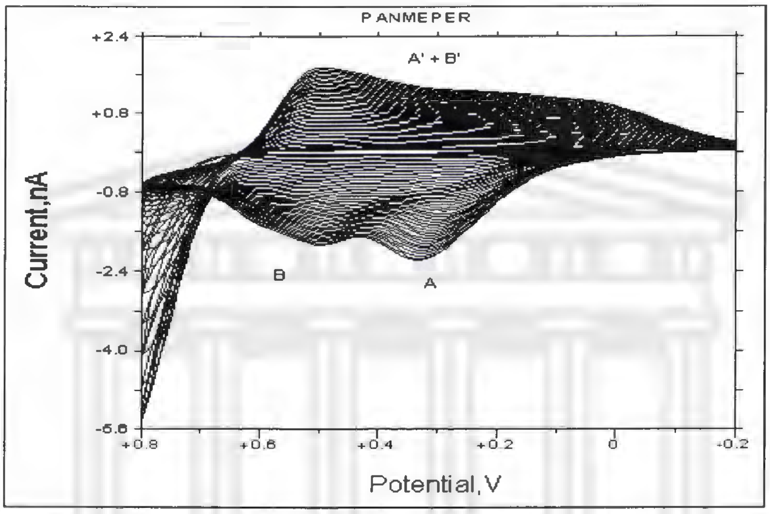


Fig 3. 8 (a) : Represent CV of poly-N-methylaniline in perchloric acid.

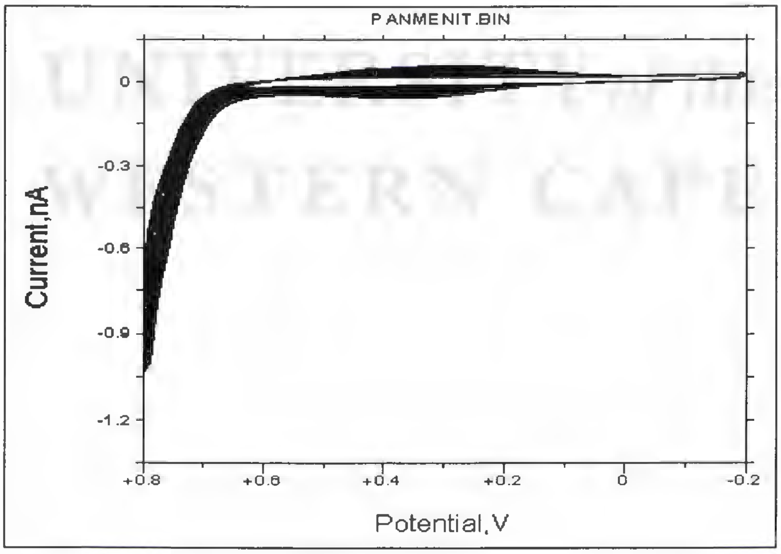


Fig 3.8 (b) : Represent CV of poly-N-methylaniline in nitric acid.

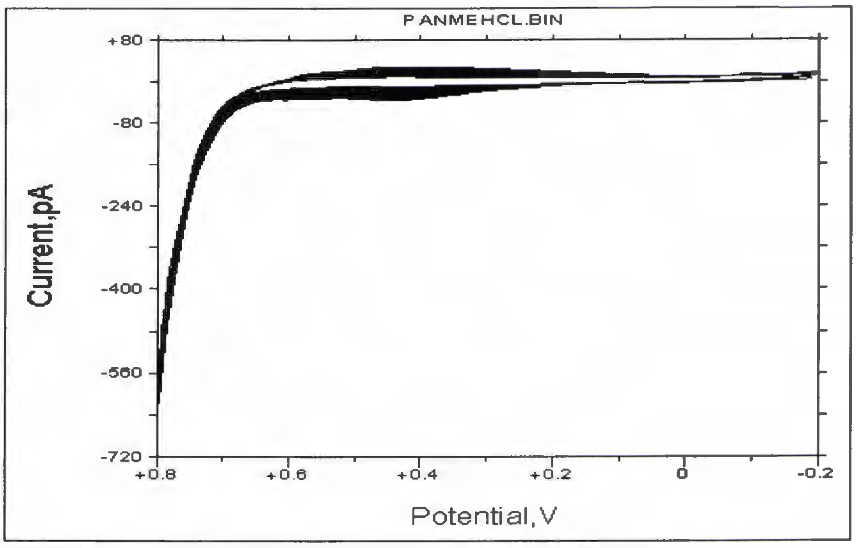


Fig 3.8 (c) : Represent CV of poly-N-methylaniline in hydrochloric acid.

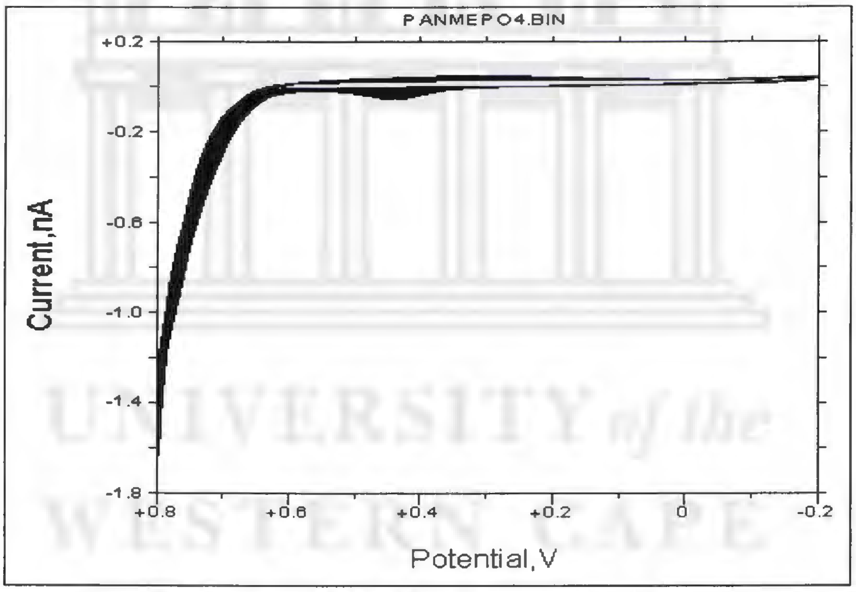


Fig 3.8 (d) Represent V of poly-N-methylaniline in phosphoric acid.

The interesting aspect observed in Fig 3.8 (a) is that $HClO_4$ seems to favour the same type of the mechanism as aniline polymerised in H_2SO_4.This can be explained by the Lippe and Holze model of the shielding effect in Fig 3.9. Perchlorates ions have the highest donating capacity and the highest pKa value of the inorganic acids used. The ions allow the backbone structure to partially act as a bipolaron because the methyl group is bulky. This causes the reaction to be slow and the growth becomes improved. This shows that the mechanism favoured is similar to that of aniline polymerization. The methyl group attached to the nitrogen is an electron donating towards the ring. The inductive effect plays a role in such that it increases the electron density towards the ring.

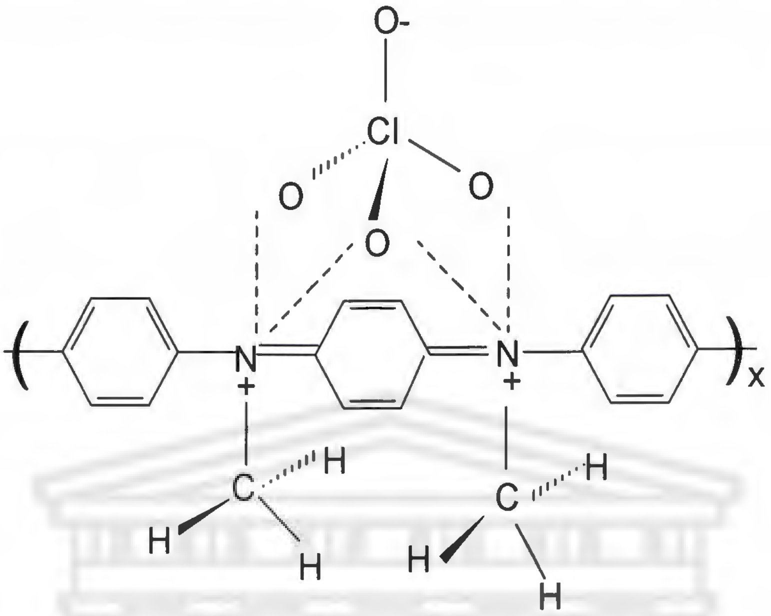


Fig 3.9: Illustration of the shielding effect that different anions can have on the nucleophilic attack of ions at bipolaron sites of poly-N-n-methylaniline chain.

The curves of polymerization growth are seen in Fig 3.10 (a) and (b). The observation in the Fig 3.10 (a) and (b) indicate that the growth rate in sulphuric acid is similar to that of perchlorate acid. The perchloric ions bind in such a way that they allow a double shielding effect on the nitrogen [99]. The order of the electrolytes for the PANMet is $HClO_4 \approx H_2SO_4$ >> HCl >> HNO_3 >> H_3PO_4. The pH also has the influence on the observed order.

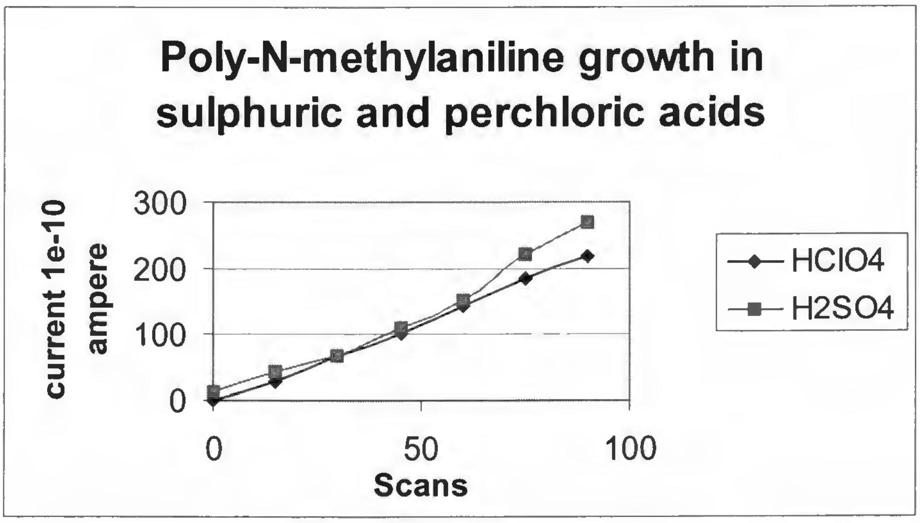


Fig 3.10 (a): Indicates the growth rate of Poly-N-methylaniline in 1M H_2SO_4 and 1M $HClO_4$.

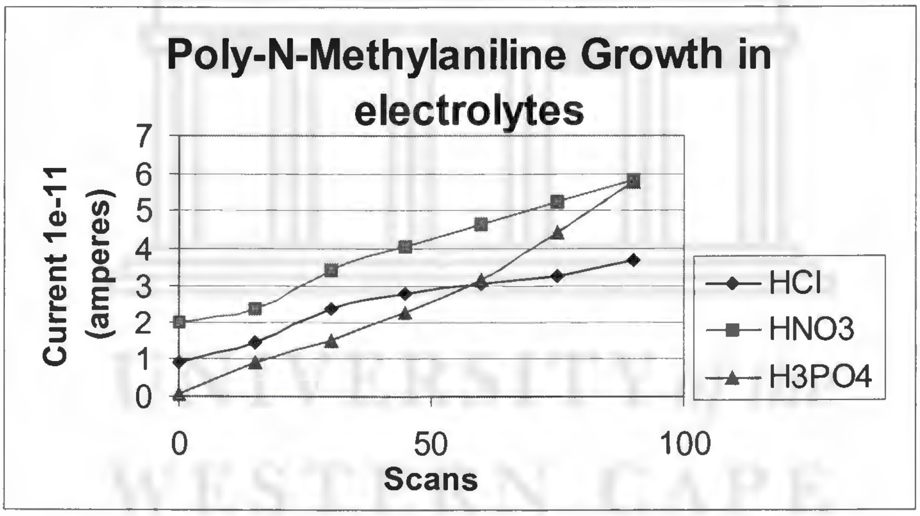


Fig 10 (b): Indicates the growth rate of Poly-N-methylaniline in 1M HCl, HNO_3, H_3PO_4.

3.3.5. EFFECT OF ELECTROLYTES ON POLY-N-n-ETHYLANILINE.

The CV's of Poly-N-n-ethylaniline) are represented Fig 3.11 (a), (b), (c) and (d). HNO_3, H_3PO_4 and HCl are weaker electrolytes as compared to H_2SO_4 and $HClO_4$. Polymerization of PANet in H_2SO_4 shows that the diradical cation (bipolaron) mechanism

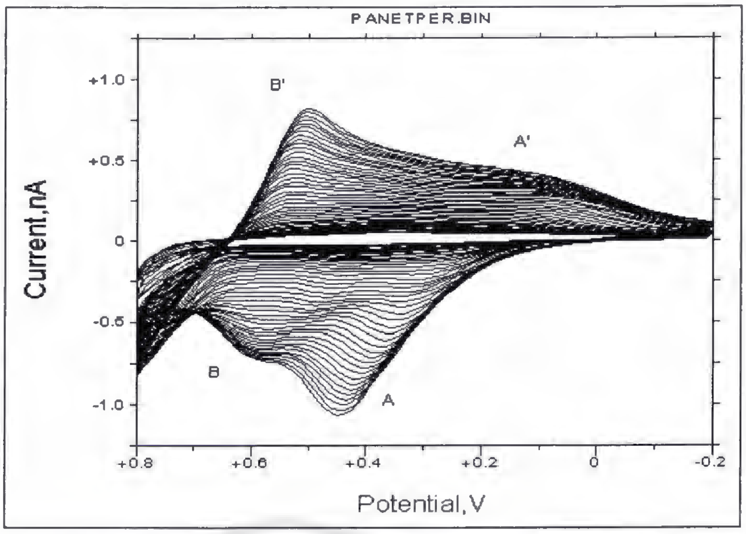


Fig 3.11 (a) Represent CV of poly-N-ethylaniline in perchloric acid.

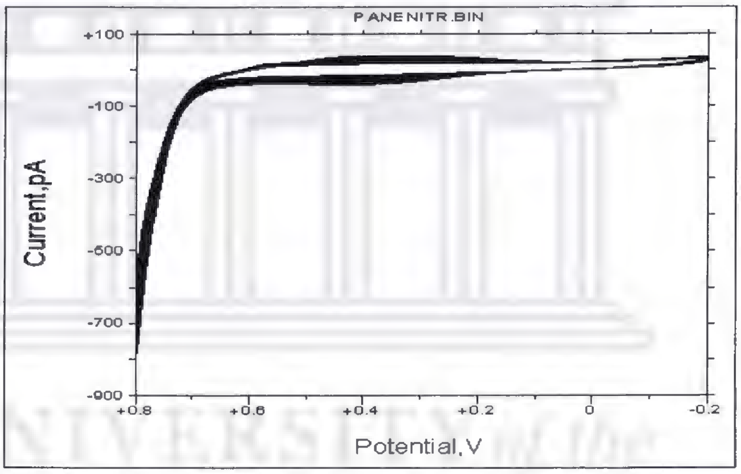


Fig 3.11(b) Represent CV of poly-N-ethylaniline in nitric acid.

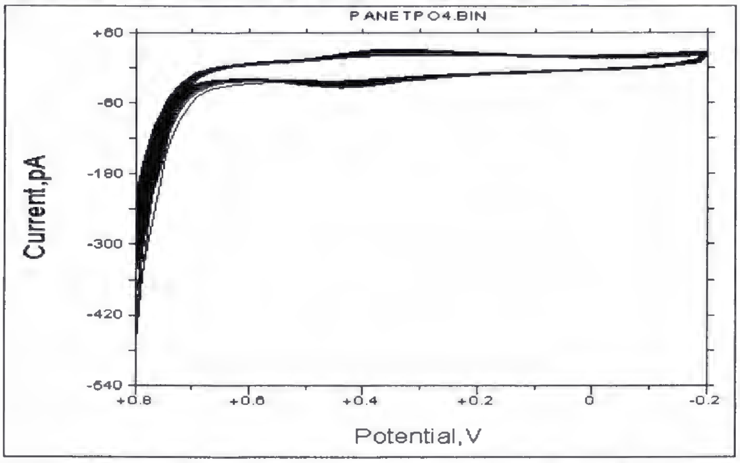


Fig 3.11 (c) : Represent CV of poly-N-ethylaniline in phosphoric acid.

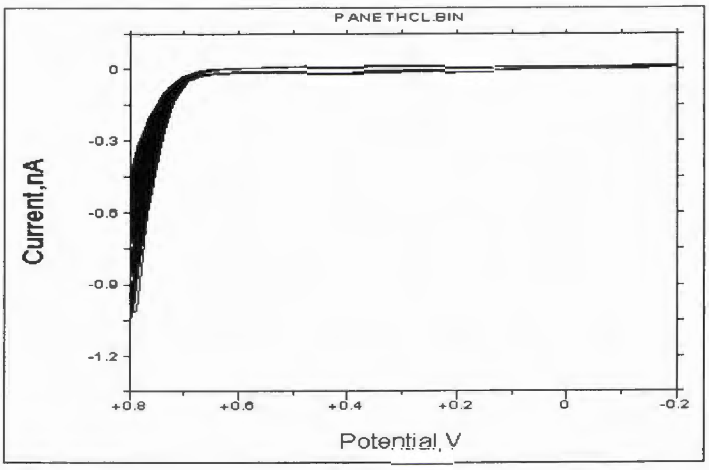


Fig 3.11 (d) Represent CV of poly-N-ethylaniline in hydrochloric acid.

predominates whiles in $HClO_4$ both the radical (polaron) and diradical ions (bipolaron) are the rate-determining step in the mechanism. Previously it was shown that PANMet growth was improved in $HClO_4$ due to the shielding effect. Ethyl group contributes more to the basicity of Nitrogen than the methyl group.

The other aspect to take into consideration is the effect of steric interactions of the alkyl group with respect to ClO_4^- and SO_4^{2-} ions with reference to the shielding effect model [99]. The inductive effect increase as the alkyl chain increases. PANet follows the same mechanism trend of PANMet in ClO_4^- ions. The ethyl group favours to polymerize in SO_4^{2-} ions than ClO_4^- ions. The bulky group promotes the SO_4^{2-} ions to have double shielding effect in the polymer backbone as in Fig 3.12.

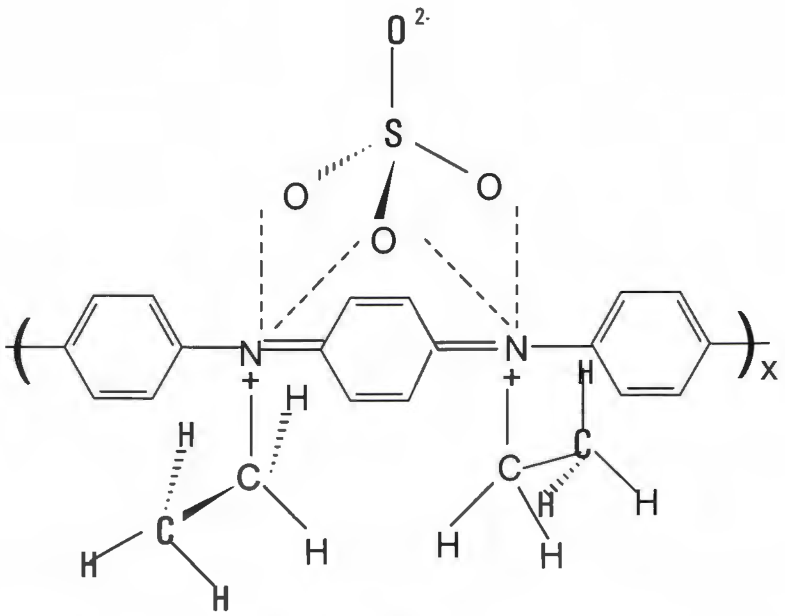


Fig 3.12 : Illustration of the shielding effect that different anions can have on the nucleophilic attack of ions at bipolaron sites of poly-N-ethylaniline chain.

The order of the electrolytes for the PANet electrosynthesis is H_2SO_4>> $HClO_4$ >> HNO_3 >> H_3PO_4 >>HCl. The sulphate ions have more influence on the polymerization of PANet. The bipolaron mechanism predominates with the least influence observed in chloride ions. The size of the ions influences the rate of polymerization. If the scan rate of PANet is lowered using sulphate ions as an electrolyte, it would be possible to observe a similar cyclic voltammogram than the one of PANI.

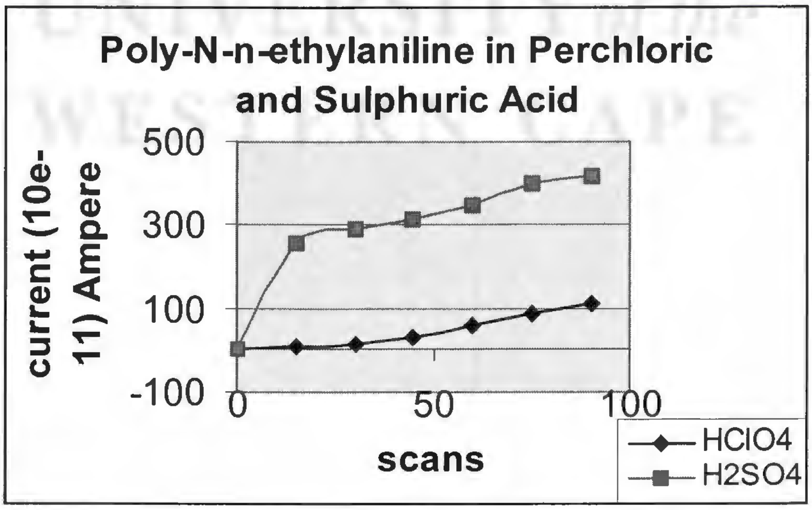


Fig 3.13 (a): Indicates the growth rate of Poly-N-n-ethylaniline in 1M H_2SO_4 AND 1M $HClO_4$

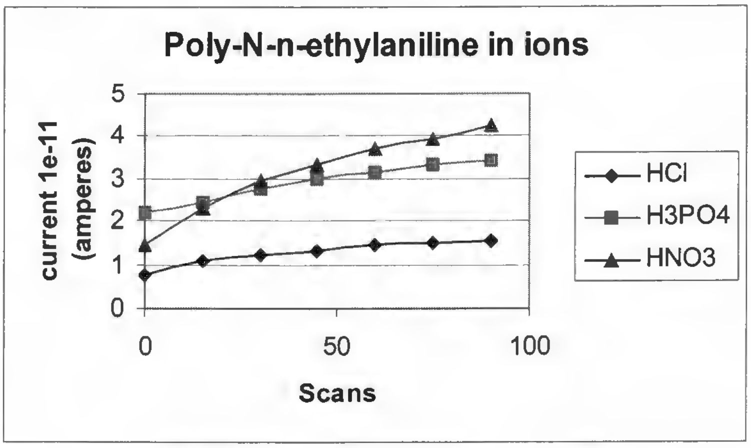


Fig 3.13 (b): Indicates the growth rate of Poly-N-n-ethylaniline in 1M HCl, HNO_3, H_3PO_4.

3.3.6. EFFECT OF ELECTROLYTES ON POLY-N-n-BUTYLANILINE

The cyclic voltammetry shown in Fig 3.12 (a)-(d) indicates the electrosynthesis of poly-N-n-butylaniline (PANBut) in different electrolytes. Previously, it was shown in Fig 3.2 (b) that PANI have two pairs of redox peaks that are due to polarons and bipolarons. PANBut in Fig 3.12 (a)-(d) exhibit the bipolaron mechanism in all cases. Dao *et al* [100] represented that the behaviour noticed in PANBut was due to the electrochemical stability.

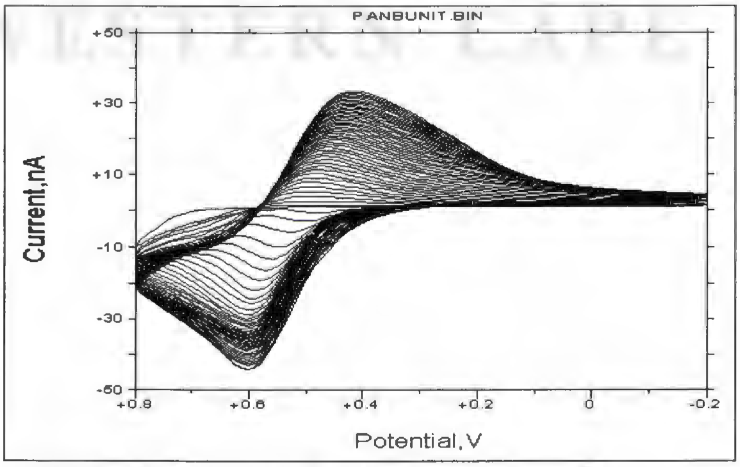


Fig 3.14 (a) : Represent CV of poly-N-butylaniline in nitric acid.

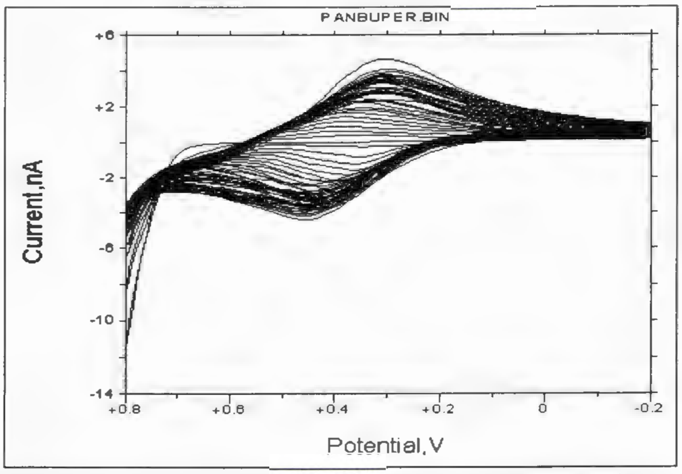


Fig 3.14 (b) : Represent CV of poly-N-butylaniline in perchloric acid.

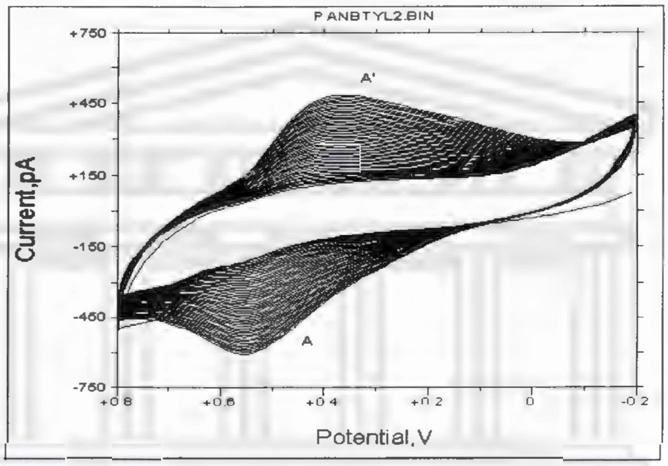


Fig 3.14 (c) : Represent CV of poly-N-butylaniline in sulphuric acid.

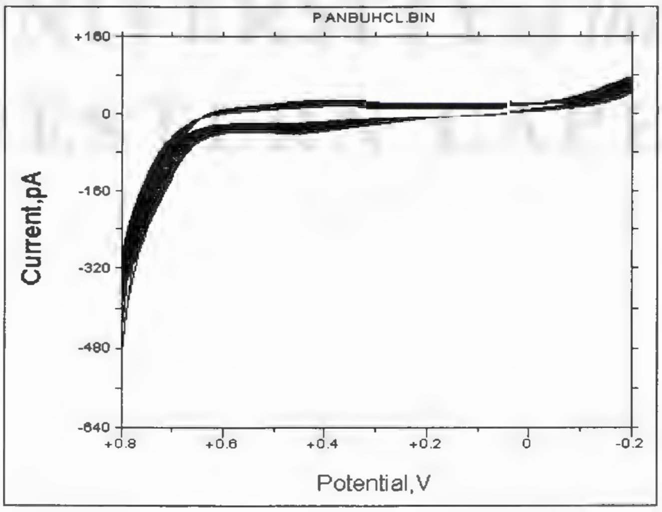


Fig 3.14 (d) : Represent CV of poly-N-butylaniline in hydrochloric acid.

The growth of PANBut is favoured more in the HNO_3 than in H_2SO_4. On average the mechanism of polymerization of the polymer HNO_3, H_2SO_4, and $HClO_4$ follows the diradical dication (emeraldine / perniganiline).

The Lewis structure given above indicates that the double bond may be in any three locations to give the structure to have identical energies. Therefore all three structures contribute equally to the resonance hybrid [102]. In the synthesis of PANBut the alkyl group acts as an activating group, which make the reactivity of the ring to increase due the electronegativity. The contribution of NO^{3-} acts as a good oxidising agent with equal resonance hybrid, and similar size. This influences the reaction to occur via the mechanism of diradical dication. The steric effects play no role in the growth of PANBut. There is no deprotonation in the N-alkyl substitute, and this increases the reactivity of the polymer backbone due to eletron affinity. The shielding effect model favours the polymer below.

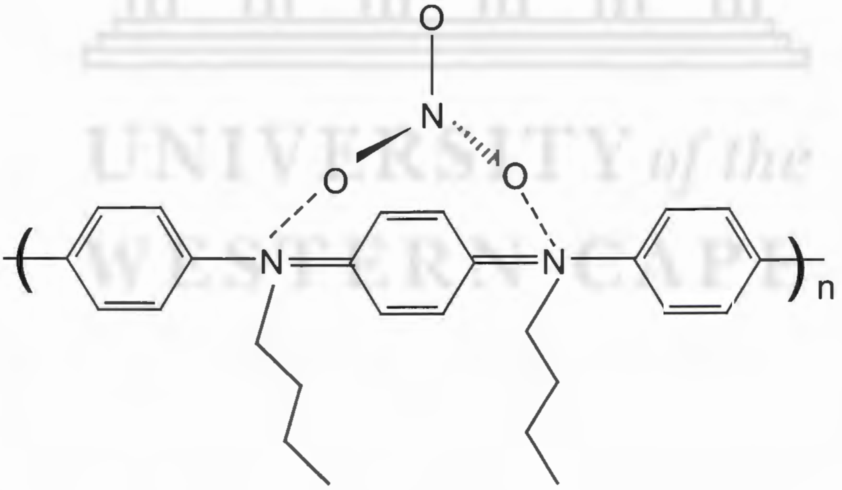


Fig 3. 15 : Illustration of the shielding effect that different anions can have on the nucleophilicattack of ions at bipolaron sites of poly-N-n-butylaniline chain.

The order of the electrolytes for the PANBut electrosynthesis is HNO_3 >> H_2SO_4>> $HClO_4$ >> HCl >>H_3PO_4. The following graphs illustrate the behaviour.

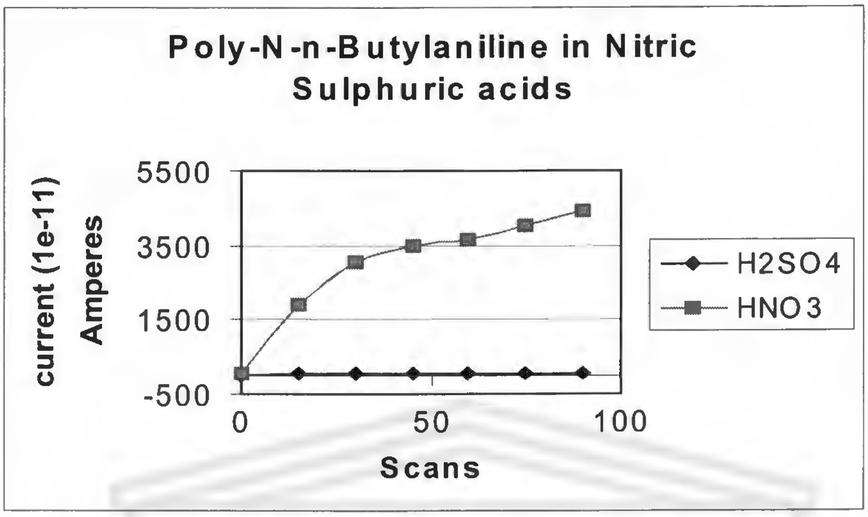


Fig 3.16(a) : Indicates the growth rate of Poly-N-n-butylaniline in 1M HNO_3, 1M H_2SO_4 and 1M $HClO_4$.

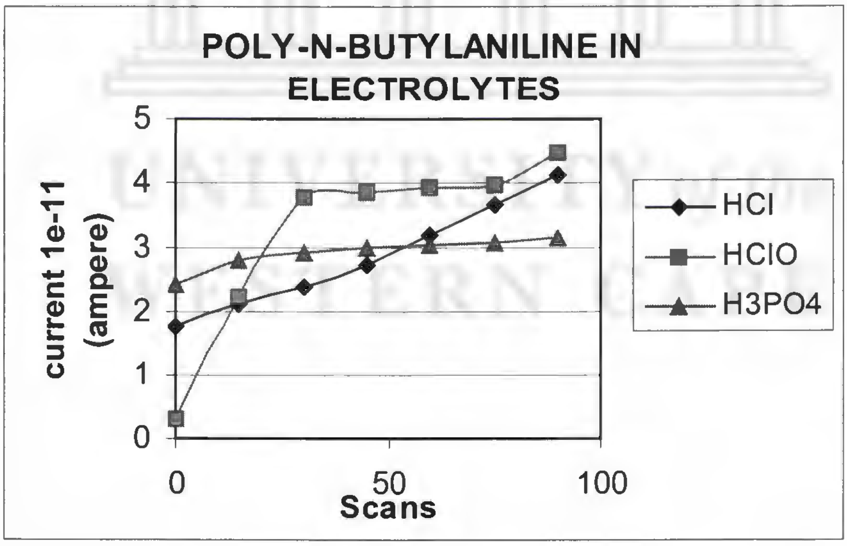


Fig 3.16 (b) : Indicates the growth rate of Poly-N-n-butylaniline in 1M HCl and 1M H_3PO_4.

3.3.7.EFFECT OF ELECTROLYTES ON POLY-N-n-BENZYLANILINE

Fig 3.15 (a) represent cyclic voltammogram of poly-N-n-benzylaniline in HCl. There are two redox peaks that have been identified in the previous polymers. The peak A/A' is well known as the radical cation (polaron) and peak C/C' is due to diradical dication transformation. The middle peak B/B' are interpreted as dimer or hydrolysis products and are related to benzoquinone/hydroquinone (BQ/HQ) couple.

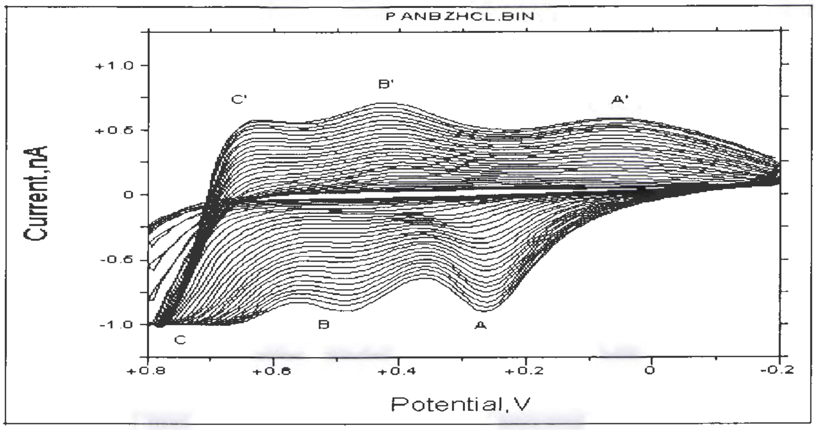


Fig 3.17 (a) : Represent CV of poly-N-benzylaniline in 1M HCl.

Another interesting observation on the electrosynthesis of PANBenz is that the diradical dication (bipolaron) predominates as shown by Fig 14 (b)-(d). This implies that the favoured mechanism is the bipolaronic form in $HClO_4$, H_2SO_4, and H_3PO_4. PANBenz was insoluble in HNO_3 unlike PANBut where this acid acted as a strong oxidising agent..

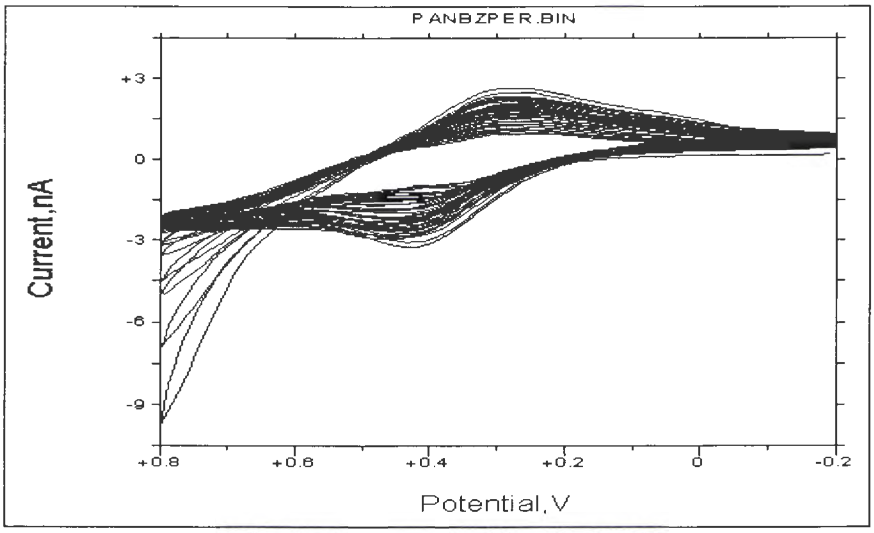


Fig 3.17 (b) : Represent CV of poly-N-benzylaniline in 1M $HClO_4$.

The order of the growth rate is $HClO_4$ >> HCl >>H_2SO_4>> H_3PO_4 as shown by the Fig 3.16 (a) and (b) below. It was impossible to study due to the fact that N-n-benzylaniline is insoluble in HNO_3.

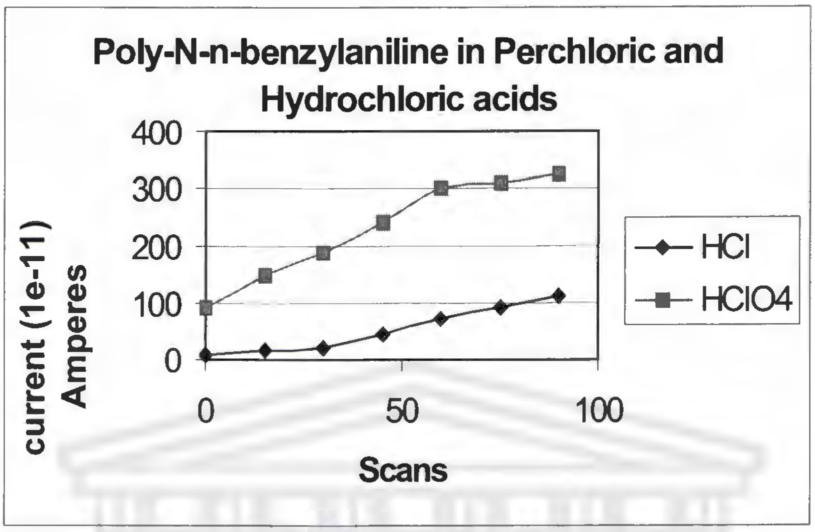


Fig 3.18 (a): Indicates the growth rate of Poly-N-n-Benzylaniline in 1M HCl (b) and 1M $HClO_4$

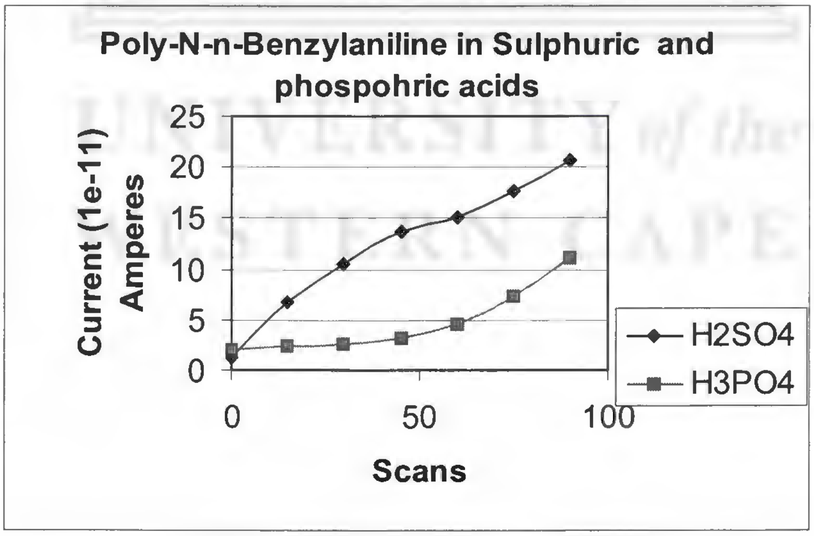
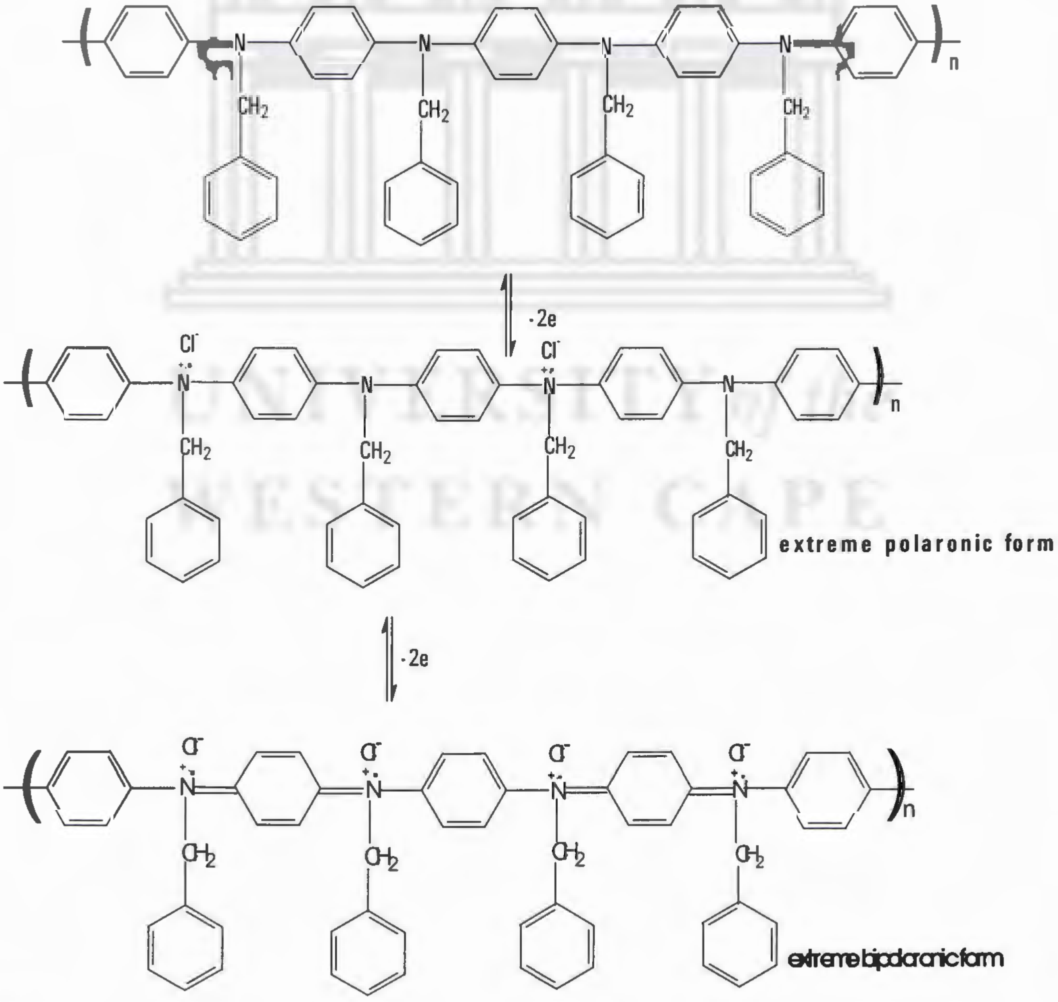


Fig 3.18 (b): Indicates the growth rate of Poly-N-n-Benzylaniline in 1M H_2SO_4 and 1M H_3PO_4.

The cyclic voltammogram of PANBenz shows interesting redox peaks, which were also identified by Stillwell and Park[77]. The electrosynthesis only differs in that the electrolyte used in PANBenz is HCl while for PANI it is H_2SO_4. Comparing the two polymers, it is clear that PANBenz favours the same mechanism as that of PANI[77]. The effect of the electrolytes on PANBenz is influenced by the size of the anion. Cl ions are small in size and there are lesser interactions, thus allowing the bulky phenol group to influence the rate of the mechanism. The bulky benzyl group has more electron density and steers the reaction via the mechanism of polaronic and bipolaronic forms as in scheme 3 below. The rate of the reaction in this case is influenced by the steric effect and not the ionic effect although the ionic strength of the electrolytes is identical.



Scheme 3

3.3.8. CYCLIC VOLTAMMETRY OF CHEMICALLY SYNTHESIZED POLYMERS

The chemical synthesized polymers were compared with electrochemical synthesized polymers. They were evaluated in term of the mechanism they followed. The figures below are the cyclic voltammograms of polymers that were scanned in nitric and hydrochloric acids as the supporting electrolytes. Cyclic voltammetry curves of poly(N-alkylaniline) were recorded at 50 mV/s scan rates between – 0.2 V and 0 .8 V vs Ag/AgCl . The polymers show that they are electroactive and no significant differences were observed as seen from table3.3. The general observations of the CV's indicates that their reactions either favours the radical cation or diradical dication mechanism [76,100].

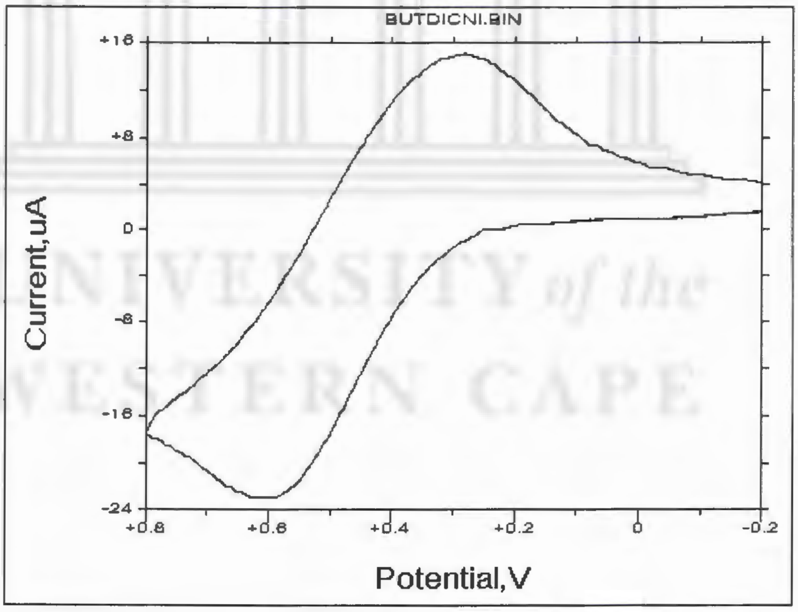


Fig 3.19.(a) Represent CV of polybutylaniline in 1M HNO_3

The above figure shows the cyclic voltammogram of electrochemical synthesized poly-N-butylaniline. Similar patterns of CV were observed and confirmed that the mechanism favours the bipolaron state.

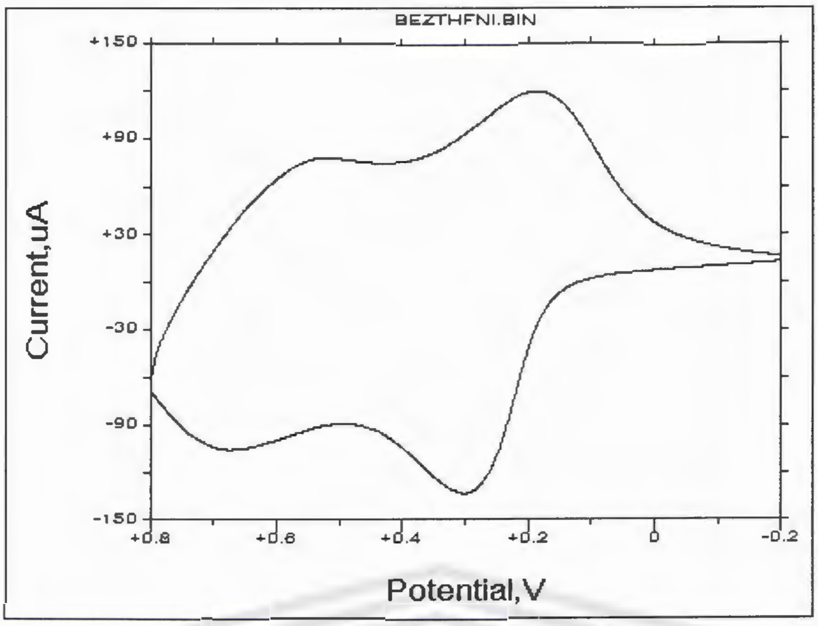


Figure 3.19(b) : Represent CV of poly-N-benzylaniline in 1M $HClO_4$

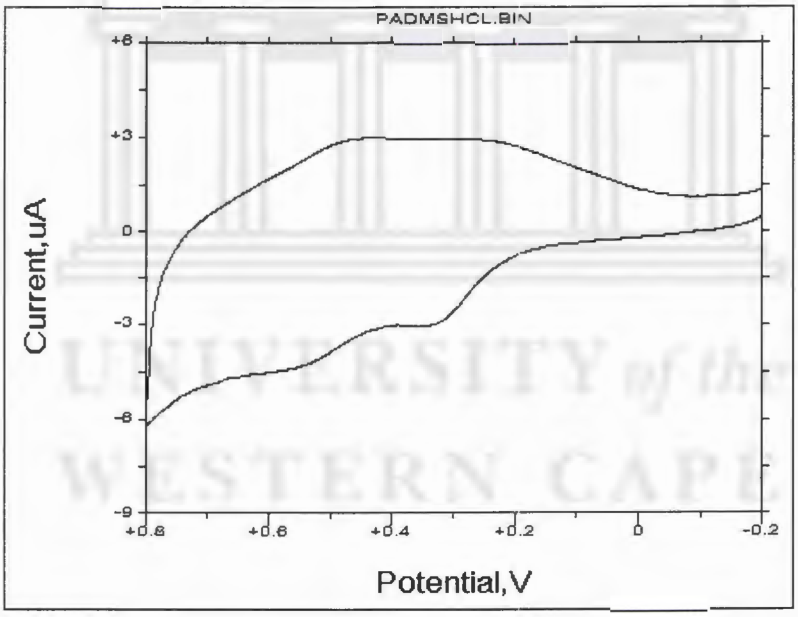


Figure 3.19(c) : Represent CV of polyaniline in 1M HCl

Figure 3.19 (b) and (c) represent CV's of poly-N-benzylaniline and polyaniline in different electrolytes respectively. The peak observed for poly-N-benzylaniline at 0.3 V is the average between the polaron and bipolaron states. The CV of polyaniline indicates that both polaron and bipolaron state mechanism is favoured. It compares well with the electrochemically synthesized polyaniline as in Fig 3.2 (b).

Table 3.3 : Redox potential peaks of polyaniline and derivatives.

ELECTROLYTE	**SOLVENT**	**PANI (V)**	**PANMet (V)**	**PANEt (V)**	**PANBut (V)**	**PANOct (V)**	**PANBenz (V)**
1M HCl	THF	0.30	0.48	0.62	0.62	-	0.31
	DMSO	0.32 0.55	0.45	0.55	0.35 0.55	-	0.34 0.55
	CH2Cl2	0.36 0.62	0.42	0.63	0.61	-	0.31
	CHCl3	0.60	0.43	0.65	0.60	-	0.34
1M HNO_3	THF	0.35 0.58	0.45	0.65	0.60	-	0.30
	DMSO	0.30 0.55	0.32 0.55	0.55	0.32 0.52	-	-
	CH2Cl2	0.60	0.45 0.65	0.65	0.60	0.61	0.34
	CHCl3	0.60	0.47	0.62	0.51	0.62	0.30

3.4. CONCLUSIONS

The modification of polyaniline (PANI) on glassy carbon electrodes were more pronounced on microelectrodes than macroelectrodes. H_2SO_4 was shown to the best electrolyte for the electrosynthesis of PANI. H_2SO_4 promotes the chain growth through a bipolaron mechanism. This is in good agreement with previously reported results [91-99]. The effect of electrolytes was to promote the growth rate. Larger anions seem to have a lower mobility in the polymer film, and consequently decrease the speed of electrochemical response of PANI during the successive potentials. This was clearly explained by Lippe and Holze [99] in the shielding effect model. The SO_4^{2-} ions tends to have a double shielding effect and increase polymerization while the ClO_4^- has a single shielding effect and reduce polymerization. The two redox pairs are associated with the leucoemraldine/pernigraniline transformations and the "middle peaks" (associated with carbozole formation, cross-linking, hydrolysis and by-products) are due to Benzoquinone/Hydroquinone transformations.

Further studies of poly-N-n-alkylaniline derivatives were conducted to investigate the electronic and steric effects towards the mechanism. The comparison of these polymers with PANI shows that the majority favoured the extreme bipolaronic (diradical dication) forms as indicated in the Table 3.4.1. Alkyl group acted as an activating group and increased the reactivity of the ring because there is no deprotonation in the initial step of polymerization. The reason for the diradical dication to predominate is that the polymers are more stable than polyaniline [100]. The choice of the electrosynthesis of the polymers depends on the type of electrolyte and the alkyl chain length with lesser interactions.

Table 3.4. Polymers synthesis in acids and their general mechanism

POLYMER	BEST ELECTROLYTE	MECHANISM
PANI	H_2SO_4	Polaron / bipolaron
PANMet	$HClO_4$	Bipolaron
PANEt	H_2SO_4	Bipolaron
PANBut	HNO_3	Bipolaron
PANBenz	HCl	Polaron / bipolaron

Table 3.4. is a summary of the best electrolyte for polymer polymerization, as well as the mechanism which best fit the propagation of polymerization.

CHAPTER 4

ANALYTICAL DETECTION OF HEAVY METALS BY CHEMICALLY MODIFIED MACRO/MICROELECTRODES

Summary : *Polyaniline and the derivatives of poly-N-n-alkylaniline were electrochemically synthesised and used as sensors for the detection of Zinc* (Zn^{2+})*, Cadmuin* (Cd^{2+})*, Copper* (Cu^{2+}) *and Lead* (Pb^{2+}) *by stripping voltammetry.*

4.1. STRIPPING VOLTAMMETRY

Stripping voltammetry is an electrochemical process whereby the analyte is firstly deposited on the microelectrode usually from a stirred solution. After an accurately measured period the electrolysis is discontinued, the stirring is stopped and the deposited analyte is determined voltammetrically. This first step is referred to as pre concentration. Secondly the analyte is redissolved or stripped from the microelectrode. Stripping methods are of prime importance in trace metal work because the concentrating aspects of the electrolysis permit the determination of minute amounts of an analyte with reasonable accuracy. Analysis of solutions ranging from 10^{-6} to 10^{-9} M becomes feasible. The method is also simple and rapid [75].

There are two types of stripping analysis, mainly anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV). In ASV, the microelectrode behaves as the cathode during the deposition step and the anode during the stripping step, with the analyte being oxidised back to the original form. In CSV the microelectrode behaves as an anode during the deposition step and the cathode during the stripping. ASV has been resurgent in interest due to the ease and sensitivity for heavy metal determination. CSV has proven to be a sensitive and a reliable technique for determination of many organic and pharmaceutical compounds. These are more sensitive to voltammetric and atomic absorption spectrometry methods [68].

4.2. METALS AND THE ENVIRONMENT

The term 'heavy metal' is frequently encountered in the environmental literature and is usually used to designate metals that are the cause of adverse biological reaction. Originally, the expression had scientifically a legitimate origin as it referred to metals such as lead and mercury. Heavy metals have gained great significance in the chemical toxicological studies of the environment. In contrast to most of the numerous other environmentally important chemicals, metals have particular property of not being biological degradable.

In all types of natural waters, the toxic heavy metals levels remain in the trace or even ultra trace range. The typical range goes from several 100 μg/l in highly polluted rivers to 0.0001 μg/l in unpolluted open ocean waters, depending again on the particular metal. Rain in slightly heavily polluted regions usually contains heavy metal levels between 0.1 and 1000 μg/l depending again on the particular metal. Despite their occurrence at only trace levels, these toxic heavy metals constitute a group of prime significance among the chemical of environment importance in natural waters [103].

Among the most hazardous heavy metals are Cd, Pb, and Hg. These three metals are toxic at all concentrations and have no known biological function. In humans toxic metals can cause brain damage, kidney and liver disorder and bone damage. Inhalation of fumes or dusts containing cadmium compounds that produces symptoms suggestive of food poisoning microbial in of origin.

Although at present numerous trace element are known to be essential for animals and humans (As, Cr, Co, Cu, F, I, Fe, Mn, Ni, Se, SI, Sn, V, and Zn) under conditions of excessive dietary or environmental exposure, they are all capable of becoming toxic and impairing their respective biological function, resulting in poor health status[5]. In general the toxicity of the metals stems from the fact that they are biological non-degradable and have a tendency to accumulate in vital organs e.g. brain, liver, or bones of humans and their accumulation becomes progressively more toxic [104].

4.3. ASPECTS OF TRACE METALS

Instrumental methods of determination are needed which combine high sensitivity with high accuracy i.e. small risk of systematic errors, and satisfactory precision. Reasonable rates of determination, convenience in operation, compactness of instrumentation and reasonable cost for the necessary instrumentation are further important features of any really useful method. In recent years, the emphasis of trace metals analysis techniques was diverted from determination of total concentrations towards the measurement of elemental speciation. In general, the choice of analytical method for making trace metals depends on the following aspects:

Trace analysis requires the successful solution of three problems.

1). Achieving sufficient sensitivity of the i.e. a sufficiently high signal-to-noise ratio.

2). Achieving the selectivity required to determine trace components of the systems in the presence of other substances at concentration several orders of magnitude higher. This problem usually requires preliminary separation method.

3). Obtaining sufficient pure chemicals and mastering the work with very dilute solution in which the amount of the substance dissolve, diminished through adsorption on the walls of the vessels, hydrolysis etc.

Although numerous instrumental methods of determination are now available, all above mention methods satisfy the general requirements outlined above. Among the most suitable methods for the determination of heavy metals, advance voltammetry, usually in the differential-pulse or sometimes the square-wave mode is very attractive. Voltammetry can be extremely sensitive and provides inherently high precision and potentialities for simultaneous determination of various heavy metals. Moreover voltammetry has the particular advantage of being, in principle, a species sensitive method, not just an element sensitive method, providing very significant and versatile opportunities for studies of heavy metals speciation in natural waters [104].

These potentialities, stemming fundamentally from the fact that voltammetry is based on Faraday's laws, have made the voltammetric approach a choice for trace analysis and studies of trace metals in all types of water [104]. This together with the low detection limits and wide range of application make voltammetric techniques the preferred choice.

4.4. EXPERIMENTAL PROCEDURE

4.4.1. DETECTION OF HEAVY METALS BY STRIPPING VOLTAMMETRY

Sample solutions

1) 0.015 M Hg^{2+} stock solution : Triple distilled mercury (0.3 g) was dissolved with several drops of concentrated nitric acid and was diluted to 100 ml with distilled water.
2) 1 x 10^{-4} M Hg^{2+} / 0.1 M KNO_3 solution : Dilute 6.7 ml of stock Hg^{2+} solution with 900ml of water and 10.1 g KNO_3 was added and to dilute to 1000 ml.
3) 25 ppm standard Pb^{2+} solution : Dilute 2.5 ml of Fisher standard Pb^{2+} solution (1000 ppm) to 100 ml with 0.0010 M HNO_3 solution. 25 ppm standard Cu^{2+} solution

was prepared in a similar way.

4) A series (600-50 ppm) of solutions of Pb^{2+}/Cd^{2+} and Cu^{2+}/Zn^{2+} were prepared by diluting 25ppm Pb^{2+} and 25ppm Cd^{2+} to 25ml with 1×10^{-4}M Hg/KNO_3. Cu^{2+} and Zn^{2+} were done in a similar manner.

5) The sample solution of each Cd^{2+}/Pb^{2+} was placed and stirred in the glass cell mounted onto the C-113 cell stand. Place all the three electrodes as **section 3.4.3** set-up. The solution was degassed for 10min. Preconcentration or deposition time was 60(s), and the quite time 10(s). After obtaining the equilibrium the analyte was stripped off in order to detect the metallic species. This was conducted on unmodified macroelectrode and PANI modified macroelectrode. Furthermore the detection of metallic species was applied on microelectrodes.

4.4.2. STRIPPING VOLTAMMETRY GENERAL PARAMETERS

Table 4.1 General parameters of stripping voltammetry applied for metallic detection

Mode		**: Differential Pulse Stripping**
Initial Potential	(mV)	:-1000
Final Potential	(mV)	: 200
Scan Speed	(mV/s)	: 20
Sample Width	(ms)	: 17
Pulse Amp	(mV)	: 50
Pulse Width	(ms)	: 50
Pulse Period	(ms)	: 200
Quiet Time	(s)	: 10
Deposition Time	(s)	: 60
Sensitivity	(A/V)	: 1E-6

The above parameters were used for all practical purpose.

4.5. RESULTS AND DISCUSSION

DETECTION OF HEAVY METALS ON UNMODIFIED AND MODIFIED MACROELECTRODES USING STRIPPING VOLTAMMETRY.

4.5.1. DETECTION OF LEAD AND CADMIUM ON UN/MODIFIED MACROELECTRODE

Detection of metal species Pb^{2+} and Cd^{2+} KNO_3 solution were conducted by stripping voltammetry using a glassy carbon electrode as described in Sec 4.4.1.This procedure was followed to evaluate the behaviour of the electrode towards the sensitivity and selectivity. Fig 4.1 (a) illustrates an anodic stripping voltammogram of Pb^{2+} and Cd^{2+} at an unmodified (glassy carbon) macroelectrode. The detection of Pb^{2+} and Cd^{2+} were found at the potentials of 0.40V and 0.60V respectively. The Cd^{2+} potential peak was lower than the Pb^{2+} potential peak due to their different electrochemical responses. Cd^{2+} forms intermetallic reactions more readily than Pb^{2+}. These voltammetric patterns are characteristic of those published widely in the literature.

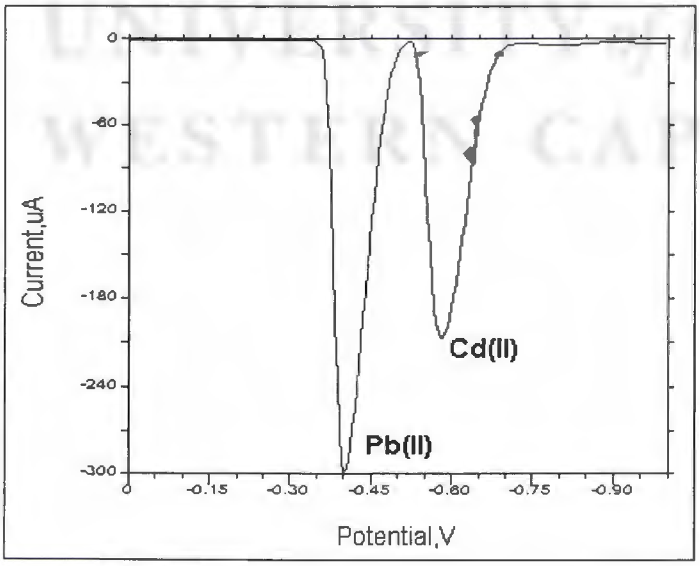


Fig 4.1(a) Representative anodic stripping voltammogram of Cd^{2+} and Pb^{2+} detected on the glassy carbon macroelectrode.

Fig 4.1.(b) below represent an anodic stripping voltammogram of the detection of Cd^{2+} and Pb^{2+} at a modified glassy carbon macroelectrode. The electrode was modified by electropolymerizing aniline at a potential between - 0.2 V to 0.8 V. The electrochemical response of Pb^{2+} and Cd^{2+} at this PANI modified electrode is lower than that on the unmodified glassy carbon macroelectrode. However, the peaks appear at the same potentials, indicating that the modified surface could potentially be utilized for detection of Pb^{2+} and Cd^{2+}. It is also important to establish the effect of pre-concentration of Pb^{2+} and Cd^{2+} on the modified electrode to investigate any possibility of intermetallic reaction with the modified surface.

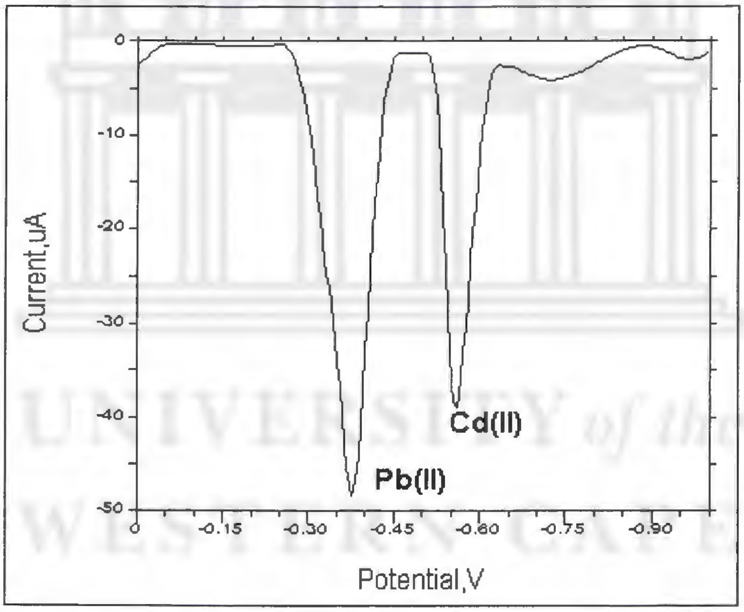


Fig 4.1.(b) Representative anodic stripping voltammogram of Cd^{2+} and Pb^{2+} detected on a PANI surface on glassy carbon macroelectrode.

Fig 4.2. shows a plot of current vs. deposition time for the two metals in question. The maximum deposition time for Pb^{2+} on the modified surface is ≈ 200 sec and and for Cd^{2+} is ≈ 300 sec. This indicates that a saturation of this surface takes place after these times. It is clearly observed by the plateau that is reached beyond these maximum times.

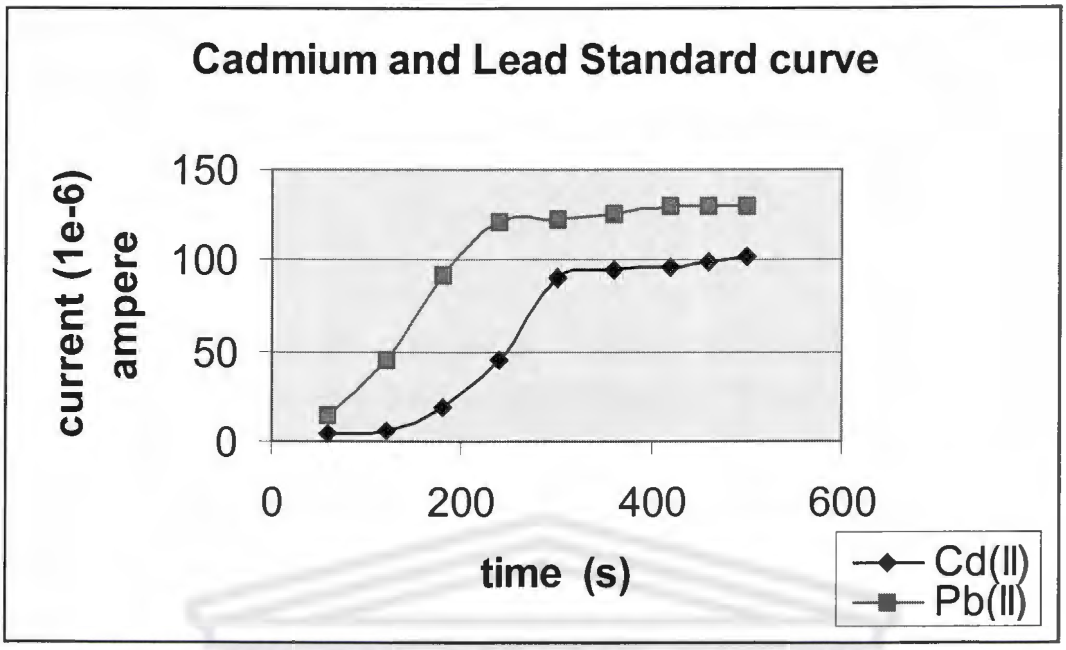


Fig 4.2 Indicates the deposition time of polyaniline on the detection of Cadmium and Lead.

After establishing the deposition maxima the minimum detection limits had to be determined. This was done by determining the peak current of solutions of different concentrations of respective metals. Fig 4.3 (a) and (b) are the curves of the unmodified and modified macroelectrode response for Cd^{2+} and Pb^{2+} respectively. These curves show that the unmodified electrode gives a linear response whilst the modified gives a non linear response over the concentration range 0 to 600 ppb. The response of the detection of Pb^{2+} shows that the current initially rises fast for the unmodified surface, reaching a maximum at ≈ 100 ppb solution. The modified surface shows a lower response that is linear over the concentration range of 0 – 500 ppb.

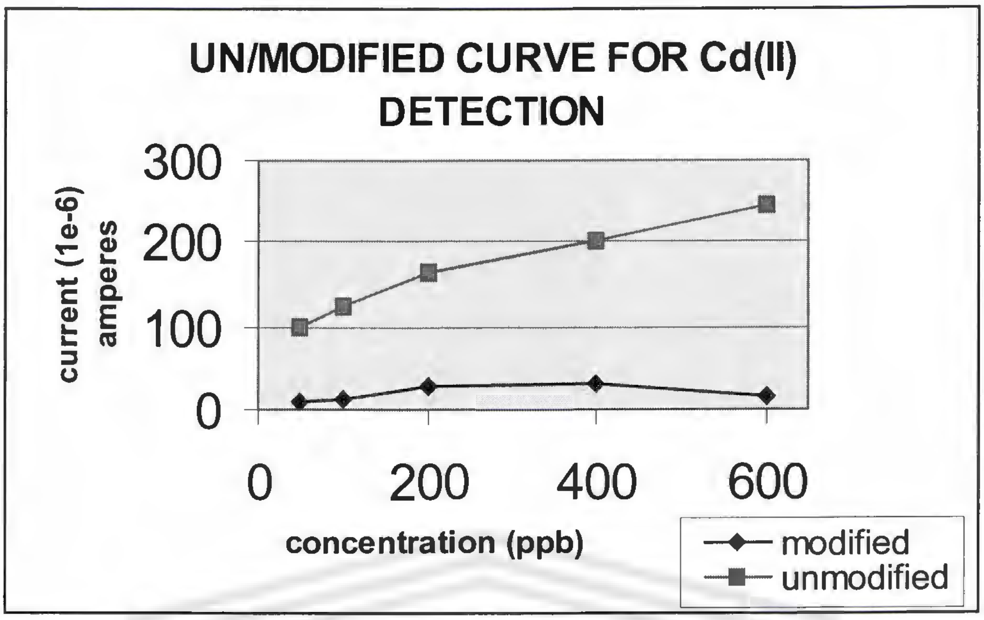


Fig 4.3. (a) Indicates the comparison of modified (PANI) and unmodified (glassy carbon) for Cadmium detection.

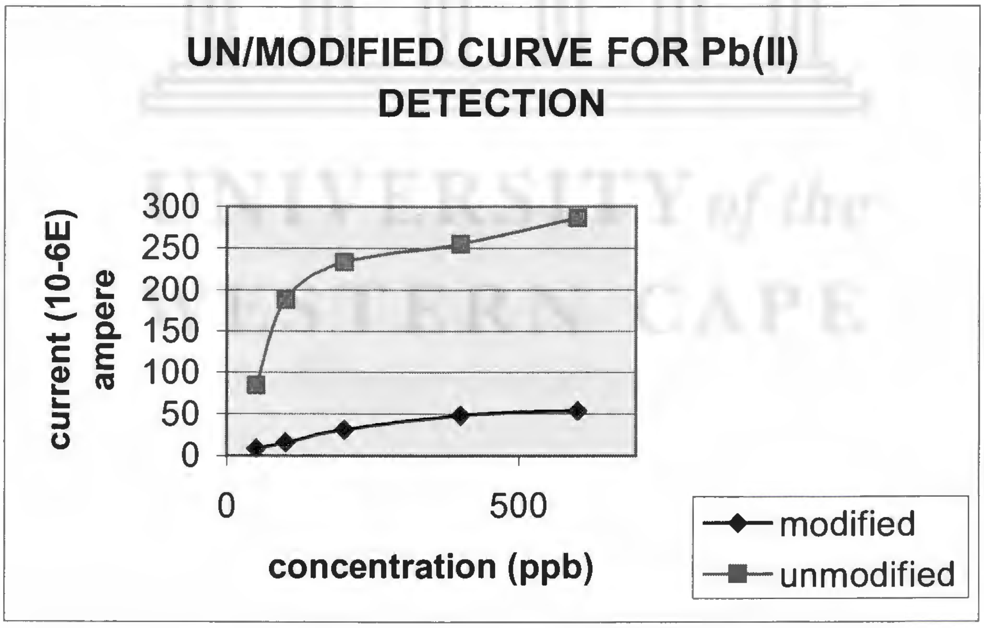


Fig 4.3(b) Indicates the comparison of modified (PANI) and un/modified (glassy carbon) for Lead detection.

4.5.2. DETECTION OF ZINC AND COPPER ON UN/MODIFIED MACROELECTRODE

Stripping voltammetry of Zn^{2+} and Cu^{2+} was performed in a similar manner to Cd^{2+} and Pb^{2+}. Fig 4.4 (a) shows an anodic stripping voltammogram of Zn^{2+} and Cu^{2+} at an unmodified (glassy carbon) macroelectrode. The detection of Zn^{2+} and Cu^{2+} were found at –1.1 V and 0.1 V respectively. The Cu^{2+} shows higher potential peak than Zn^{2+} and this is due to their different electrochemical responses. Intermetallic interactions also transpire readily towards copper detection. These voltammetric patterns are similar to those found in the literature.

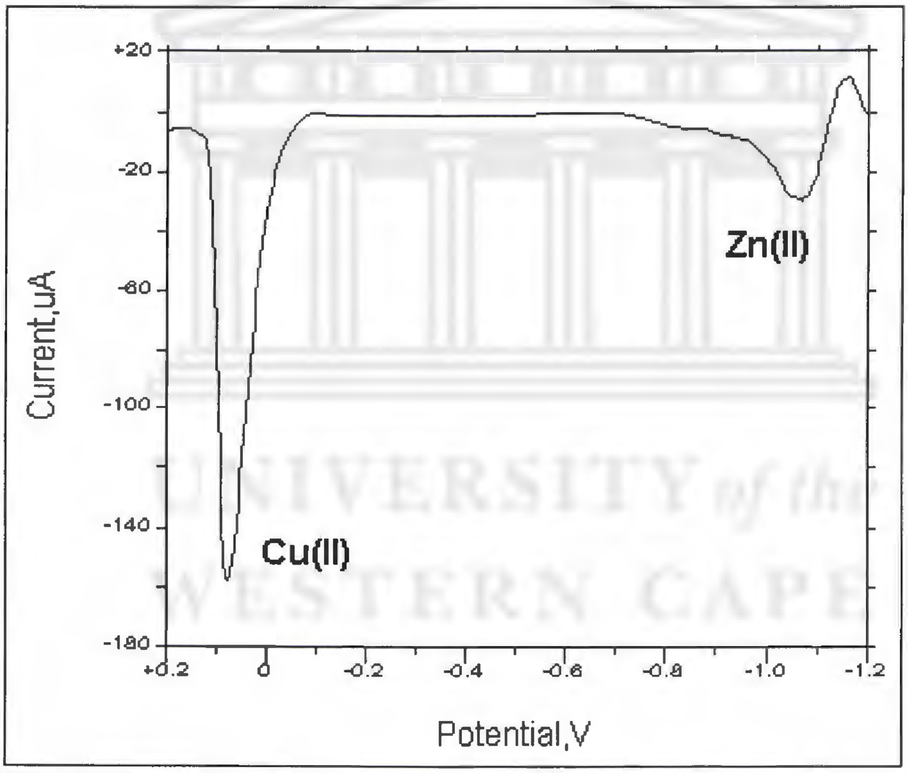


Fig 4.4 (a) Represent anodic stripping voltammogram of Zn^{2+} and Cu^{2+} detection on the glassy carbon macroelectrode.

Fig 4.4 (b) below illustrates an anodic stripping voltammogram of Zn^{2+} and Cu^{2+} at a modified glassy carbon macroelectrode. The electrode was modified by electropolymerizing aniline at the potential between - 0.2 V to 0.8 V. The electrochemical response of Cu^{2+} and Zn^{2+} at this PANI modified electrode is lower than that of the unmodified glassy carbon macroelectrode. This was previously observed with cadmium and lead detection. The effect of pre-concentration of Cu^{2+} and Zn^{2+} on the modified electrode was important to investigate any possibility of intermetallic reaction with the modified surface.

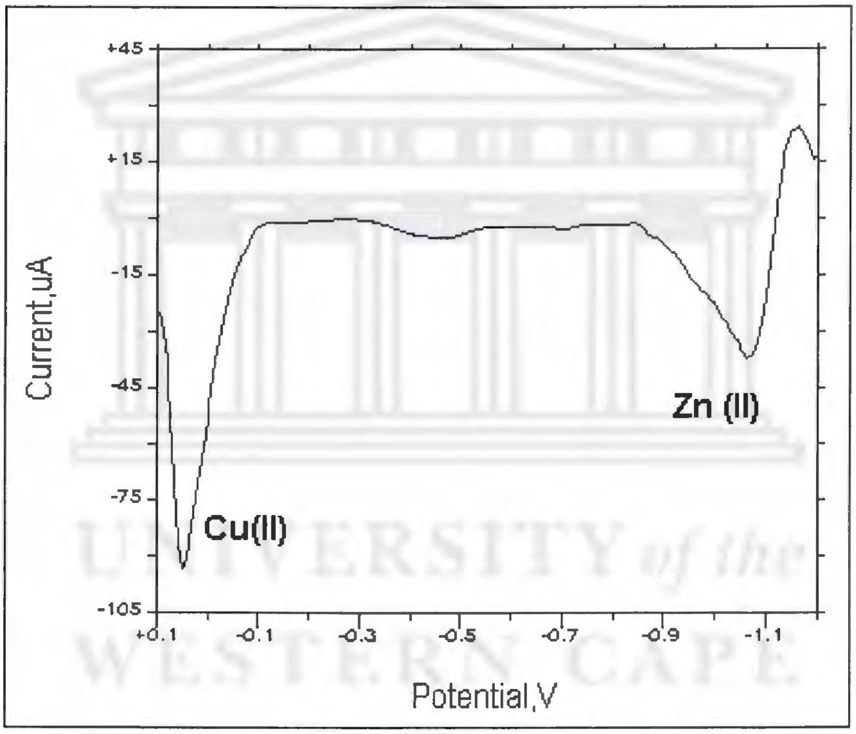


Fig 4.4 (b): Representative anodic stripping voltammogram of Zn^{2+} and Cu^{2+} detection on the glassy carbon macroelectrode.

Fig 4.5 (a) shows a plot of current vs. deposition time for the Zn^{2+}. The maximum deposition time for Zn^{2+} on the modified surface is ≈ 340 sec. Fig 4.5 (b) shows a plot for Cu^{2+} is ≈ 180 sec. This indicates that a saturation of this surface takes place after these times. It is clearly observed by the plateau, which is reached beyond these maximum times. Zn detection is not clearly defined. Interactions might take place at the electrode surface.

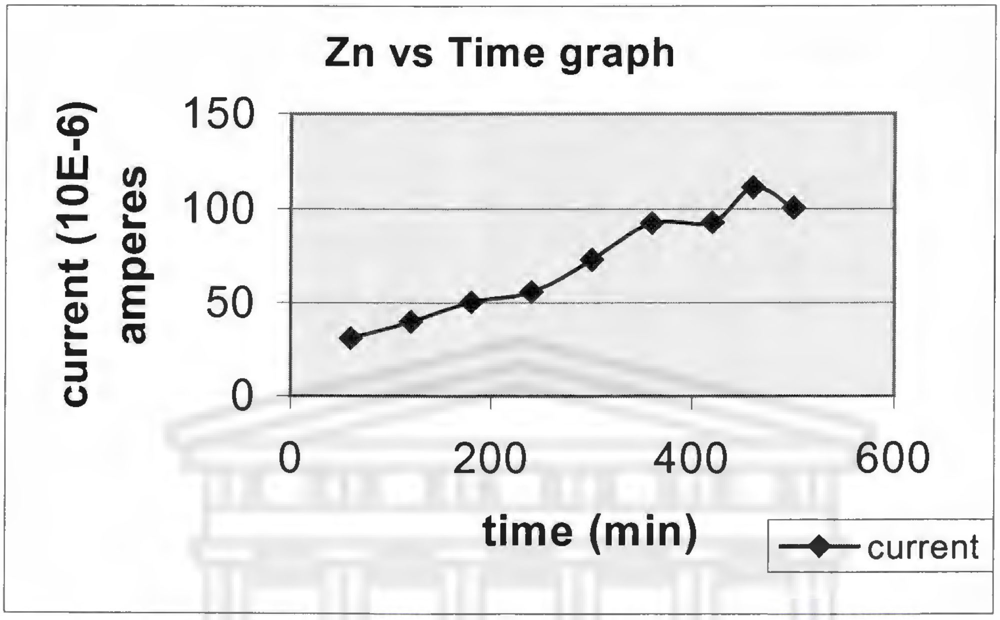


Fig 4.5 (a). Indicates the deposition time of polyaniline on the detection of Zn.

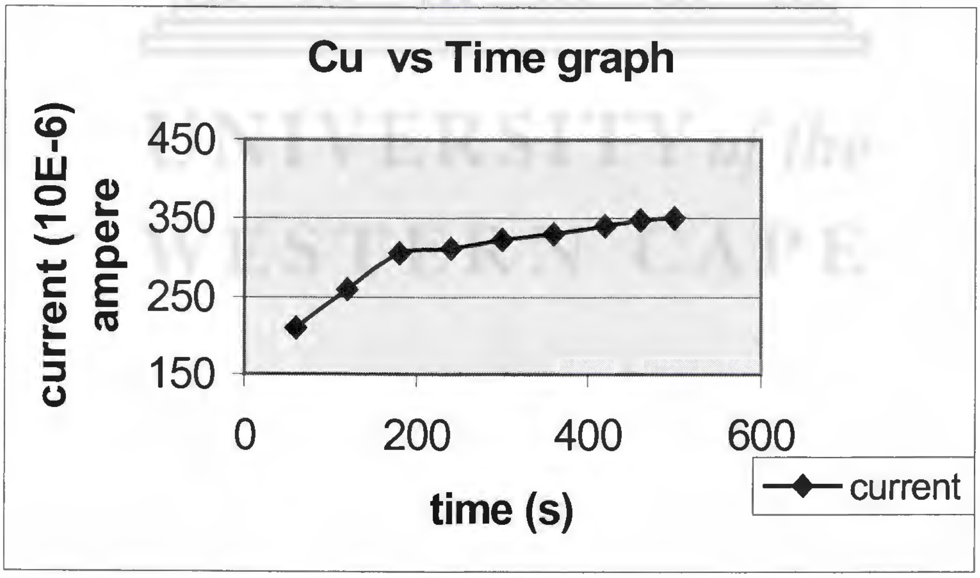


Fig 4.5 (b). Indicates the deposition time of polyaniline on the detection of Copper.

The minimum detection limits had to be determined after the establishment of maximum deposition time. This was done by determining the peak current of solutions of different concentrations of the respective metals. Fig 4.6 (a) and (b) are the curves of the unmodified and modified macroelectrode response for Cu^{2+} and Zn^{2+} respectively. These curves show that the unmodified electrode gives a linear response whilst the modified electrode gives a non linear response over the concentration range of 0 to 600 ppb for copper detection. The response of the detection of Cu^{2+} shows that the current grows steadily for the unmodified surface, reaching a maximum at ≈ 200 ppb solution. The modified surface shows a lower response which is linear over the concentration range of 0 – 600 ppb.

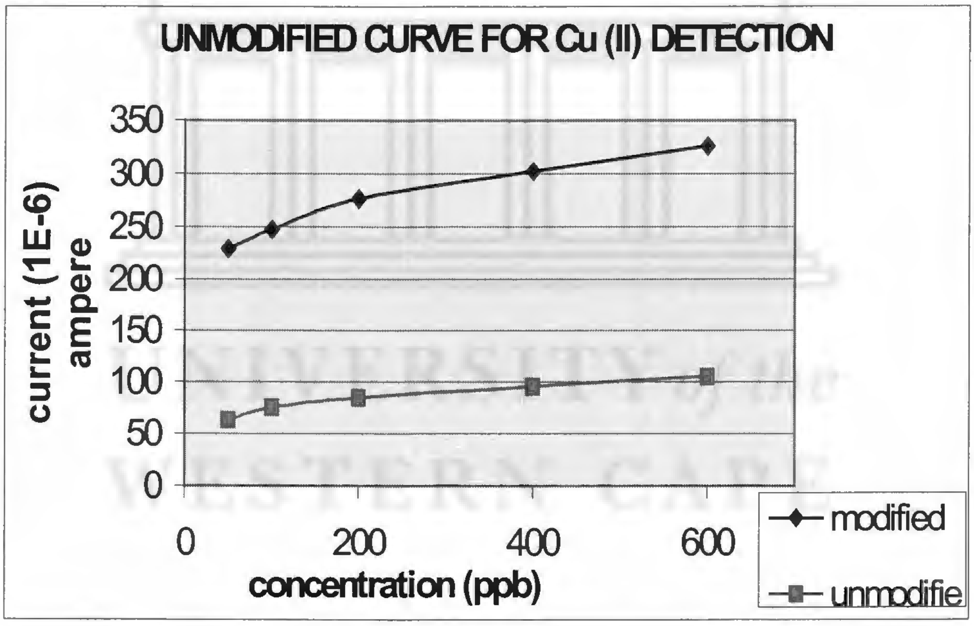


Fig 4.6 (a) Indicates the comparison of modified (PANI) and unmodified (glassy carbon) for Copper detection.

The response of the detection of Zn^{2+} shows that the current initially rises fast for the unmodified surface, reaching a maximum at ≈ 200 ppb solution. The modified surface shows a lower response which is linear over the concentration range of 0 – 200 ppb.

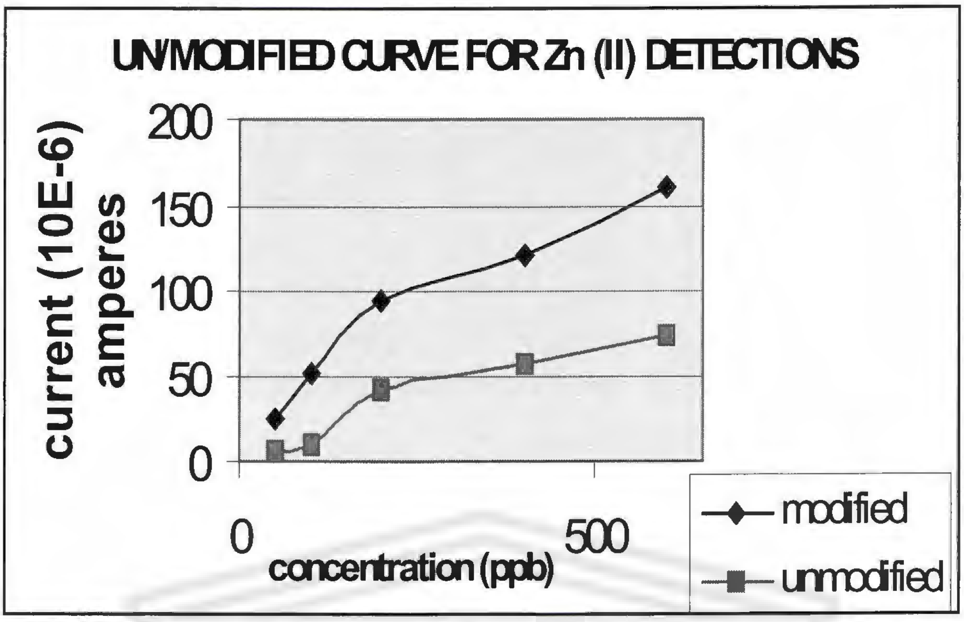


Fig 4.6. (b) Indicates the comparison of modified (PANI) and unmodified (glassy carbon) for Zinc detection.

4.5.3. STRIPPING VOLTAMMETRY OF UN/MODIFIED MICROELECTRODE ON COPPER AND LEAD.

Modification of microelectrode with the polyaniline was performed by cyclic voltammetry as described in Sec 3.2.4. Subsequently stripping voltammetry was used to detect Cu^{2+} and Pb^{2+} under same conditions as was used for the macroelectrode as described in Sec 4.4.1. Fig 4.7 (a) represent the anodic stripping voltammogram of a glassy carbon microelectrode in contact with Pb^{2+} and Cu^{2+}. Fig 4.7. (b) represents anodic the stripping voltammetry of the same metals on a PANI modified microelectrode. The potentials of Pb^{2+} and Cu^{2+} are observed at -0.65V and -0.12V respectively on the glassy carbon microelectrode. The voltammogram on the PANI modified electrode shows a pronounced broad peak for Cu^{2+} at the potential of 0.25 V. The response of the microelectrode differ from that of the macroelectrode in the sense that lower currents are detected for the metals. The peak current for Cu^{2+} shows a significant increase when the modified glassy carbon microelectrode was used. No peak was observed for Pb^{2+}, showing that Cu^{2+} could be selectively detected in the presence of other metals.

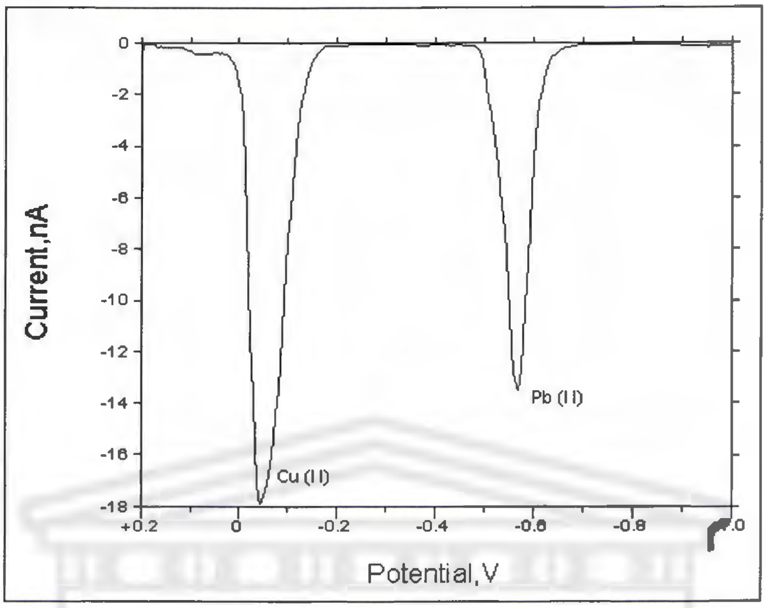


Fig 4.7(a) Representative anodic stripping voltammogram of glassy carbon microelectrode.

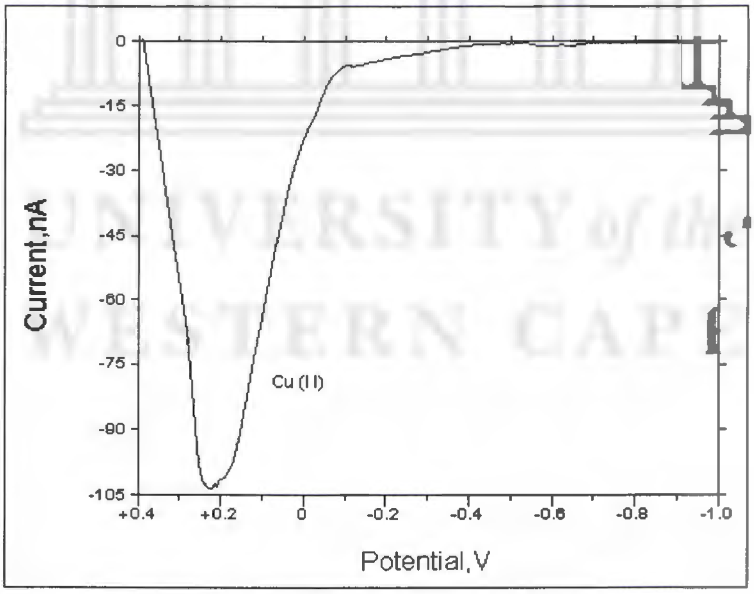


Fig 4.7(a) Representative of anodic stripping voltammogram of PANI microelectrode for copper and lead detection.

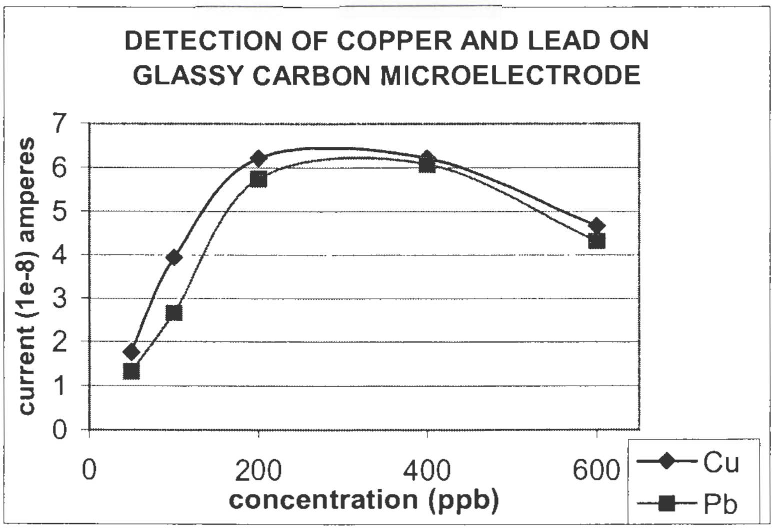


Fig 4. 8 (a) Detection of Copper and Lead on glassy carbon microelectrode

The unmodified microelectrode study was conducted to establish the behaviour of the electrode. Fig 4.8 (a) shows that there is a rapid growth in peak current until it reaches concentrations of 200 ppb in both lead and copper solutions. As the concentration increases the glassy carbon microelectrode becomes saturated. The behaviour of the modified microelectrode as a function of concentration was studied as displayed in Fig 4.8 (b). It indicates that strong adsorption takes place at lower concentrations hence high peak currents are observed for modified electrodes.

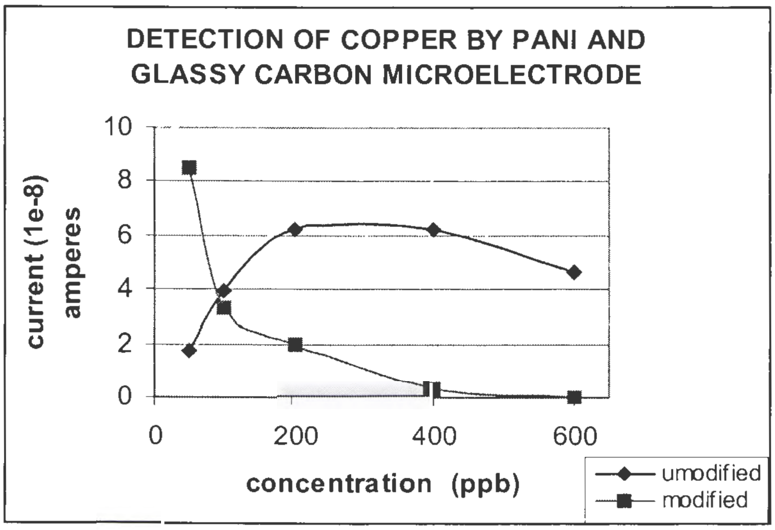
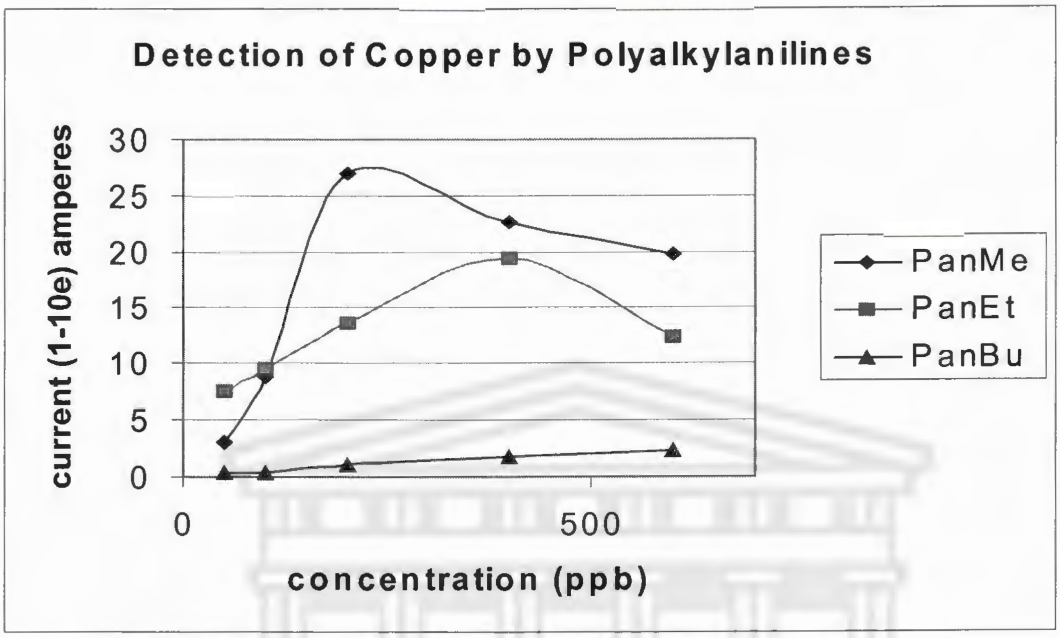


Fig 4.8 (b) Detection of Copper and Lead on glassy carbon and PANI microelectrode

4.5.4 DETECTION OF OTHER METALLIC SPECIES WITH POLY-N-N-ALKYLANILINES



4.8 (c) **Detection of copper on poly-N-n-alkylaniline microelectrode**

Fig 4.8 (c) represents anodic stripping voltammograms of the detection of copper on poly-N-n-alkylaniline derivatives modified microelectrodes. The detection of copper shows that there is a rapid growth in concentration until it reaches 200 ppb and 400ppb by PANMet and PANEt modified microelectrode respectively. PANBut shows steady growth for copper detection. As the concentration increases the modified polyaniline derivatives microelectrode becomes saturated. No discernable detection was observed with other metals.

4.6 CONCLUSIONS

Chemically modified macroelectrodes were reasonably successfully used to detect heavy metals in particular Cu, Pb, Cd and Zn. It was found that macroelectrodes have lower detection limits for various metals. Microelectrodes detection has shown to be sensitive towards copper when polyanilines and its derivatives were used for modification of the electrodes.

TABLE 4.2.

Comparison of modified macroelctrode and microelectrode on metallic detection

Subject	**Macroelectrode**	**Microelectrode**
Surface	$\approx 12\ mm^2$	$3.89\ x10^2\ \mu m$
Current limitations	100 (μA/V)	100 (nA/V)
Response	Slow	Fast
Sensitivity	less sensitive	more sensitive
Selectivity	non selective	Selective
Specificity	non specific	Specific
Metallic interactions	usually transpires	Inconclusive

Table 4.2 summarizes the responses of the different modified surfaces for metallic species.

CHAPTER 5

GENERAL CONCLUSIONS

Summary : *The chapter summarises the overall conclusions of the objectives of the project on chemical and electrochemical evaluation of modified microelectrodes*

5.1. INTRODUCTION

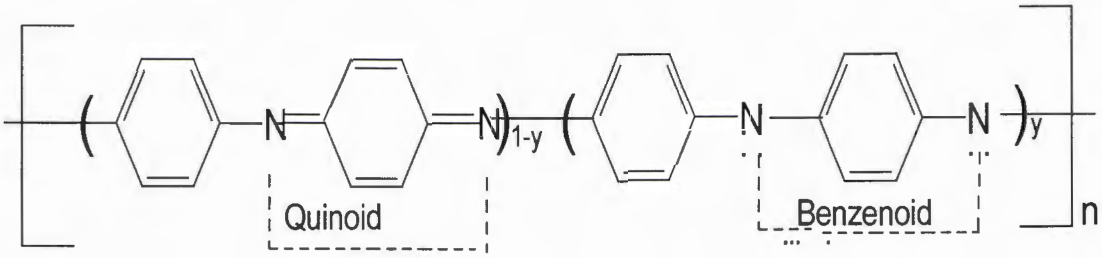
The main goals of the project were to evaluate chemically modified macroelectrodes and microelectrodes with conductive polymers and used them as sensors to detect heavy metals (Cr, Cu, Pb, Zn). There were three approaches taken for the principal objective of the project: Chemical synthesis of polyaniline and Poly-N-n-alkylaniline *(chapter 2)* Familiarisation of voltammetric techniques such as cyclic voltammetry for polymerization (*chapter 3)* and metallic detection by stripping voltammetry (*Chapter 4*).

The approaches were clearly defined in *(chapter 1 Sec 1.2).* Polyaniline (conductive polymer) and microelectrode voltammetry were the key components of the study. Polyaniline and its N-alkyl derivatives are conductive polymers that are environmentally stable. This led to the need to explore this as a typical sensor for metallic detection. These can only be done by studying the chemistry of polyaniline, and later use this for the proposed application.

Considering the attention given to conductive polymers, and the role they played in a variety of applications, the purpose of this project was to synthesize polyaniline and eventually compare the chemically and electrochemical synthesised *(chapter 3)* films. Polyaniline synthesis was successfully achieved and observed as a green emeraldine base. The Poly-N-n-alkylanilines synthesis were successfully achieved and characterised by ^{1}H NMR, FTIR, TGA, and DSC. These were also electrochemically evaluated on glassy carbon macroelectrodes *(Chapter 3).*

The mechanisms of PANI formation were not well defined and there were also problems experienced with solubility. The polymers were insoluble in many common organic solvents. Substituted N-alkylated anilines were introduced to increase the solubility of the parent PANI. The solubility of Poly-N-n-alkylanilines (N-methyl, N-ethyl, N-butyl, N-octylaniline, N-Benzylaniline) differ in the degree of solubility (*refer table* 2.3). An increase in the alkyl chain to six or seven carbon increases the solubility in most organic solvents (such as tetrahydrofuran, dichloromethane, and chloroform). The incorporation of flexible chains on polyaniline through an N-alkylation method at the emeraldine base provides a remarkably improved solubility.

FTIR spectroscopy shows that the spectra obtained were identical to that obtained in the literature. All Poly-N-n-alkylanilines presented similar FTIR patterns. The most important vibration modes of the different polymers are summarized in *(chapter 2 Table 1).* The important absorption intensities peaks were the quinoid and benzenoid forms at 1506 cm^{-1} and 1596 cm^{-1}. Chevalier et al [19] observed intensity ratio of the bands of the quinoid and benzenoid forms which were characteristic of moderately oxidized polymers. The scheme 1 represent quinoid and benzenoid forms during polyaniline formation.



Scheme 1

The same observations were made with PANI in *Fig 2.1 (a)* where the absorption intensity ratio of (Q/B) are equal while PANBut *Fig 2.1 (c)* shows high intensity of the benzenoid peak. The benzenoid peak predominates for PANBut. This was also seen in the electrochemical polymerization of both PANI and PANBut in H_2SO_4 (*Fig 3.1 and Fig 3.2)*. This confirms the general conclusion on the mechanism of polymerization of PANI, which is via polaron and bipolaron. PANBut favours the bipolaron mechanism. The difference in the shift of absorption bands of aromatic vibrations indicates structural and geometrical features that were dramatically affected by N-substitution.

Cyclic voltammetry curves of PANI and its derivatives were recorded between –0.2 V to 0.8 V at the scan rate of 50 mV/s. Most of the redox behaviour followed the radical cation (polaron) and the diradical dication (bipolaron) mechanism as explained in *chapter 3.* Identical peaks were observed irrespective of the type of solvent. The type of electrolyte for electrochemical synthesis played an important role in the mechanism. Steric and electronic effects play a role in this respect. In conclusion most of the results on the synthesis of PANI and its N-alkyl derivatives agrees with the existing literature.

Modification of electrodes with polyaniline has been done by many authors in macroelectrodes in H_2SO_4 media. The main objective in this case was to compare the response of macroelectrodes and microelectrodes by PANI polymerization. It was found that *(section 3.3 Fig 3.1 and 3.2)* the cyclic voltammetry of PANI follows different routes because of the electrode surface. On macroelectrodes the mechanism of the radical cation prevails whiles on microelectrodes the mechanistic pathway of radical cation and diradical dication prevails. The difference between the electrode sensitivity is due to factors such as mass transport. The general results have indicated that the microelectrrodes were best for polymerization and mechanistic studies.

The success of polymerization of aniline and N-alkylanilnes by the cyclic voltammetry method depended on many factors such as the type of solution, ionic strength, steric effects, scan rates and electrode size. It was important to investigate those aspects in order to give a clear understanding of the polymerization mechanism *(chapter 3 reaction 1).*

(a) The effect of electrolytes of the polymers

The polymers and their suitable electrolytes are summarised in *(Chapter 3 Table 3.4.1).* For example the most effective growth pattern for PANI was found in H_2SO_4 and the least in H_3PO_4. PANI derivatives responded differently in the different electrolytes. This was clearly explained by Lippe and Holze by using a shielding effect model. The focus was more on the orientation of the anion to shield the nitrogen in the polymer backbone. The order of electrolytes are summarised in the table that follows:

Table 5.1. Ionic orders of polymers

POLYMER	**IONIC ORDER**
Polyaniline	H_2SO_4 >> HCl >> HNO_3 >> $HClO_4$ >> H_3PO_4
Poly-N-methylaniline	$HClO_4 \approx H_2SO_4$ >> HCl >> HNO_3 >> H_3PO_4
Poly-N-ethylaniline	H_2SO_4 >> $HClO_4$ >> HNO_3 >> H_3PO_4 >> HCl
Poly-N-butylaniline	HNO_3 >> H_2SO_4 >> $HClO_4$ >> HCl >> H_3PO_4
Poly-N-benzylaniline	$HClO_4$ >> HCl >> H_2SO_4 >> H_3PO_4 *HNO_3

* Insoluble in the polymer

(b) Influence of the steric effect

Many researchers performed the chemical synthesis of N-alkylanilines in order to improve the solubility of PANI. The route taken for electrosynthesis of N-alkylaniline was to take advantage of the electron donating ability of the alkyl group, which augment the π electrons density along the conjugated polymeric chain. The alkyl group acts as an activating group towards the mechanism. Deprotonation of the starting monomer becomes easier during the initiation process. The other aspect was to monitor the steric effect.

All the N-alkylaniline derivatives show that the polymer growth was influenced by an increase in alkyl chain. Predomination of a diradical dication mechanism was observed by alkylaniline derivatives *(Table 3.4.1)*. It shows that the polymers were more stable than polyaniline.

The modification of electrodes is explained in *chapter3*. The purpose of *chapter 4* was to utilize the same modified electrode for metallic detection. The study of evaluating the performance of macroelectrodes and microelectrodes towards metal detection was stimulated by the conductance of the polymer. These electrodes can act as sensors for environment analysis of heavy metals. The detection of heavy metals was done by anodic stripping voltammetry on modified macro and microelectrodes respectively. The metals of study were (Cr, Cu, Pb, Zn) on macroelectrodes. The investigation of modified macroelectrode detection was the basis of further study of microelectrode detection.

Metal species Pb^{2+},Cd^{2+} ,Cu^{2+} and Zn^{2+} in HNO_3 solution were detected by the anodic stripping voltammetry technique. It was found that on modified macroelectrodes the response of metals towards the electrode surface suffered from intermetallic interactions (*Fig 4.1(b).*). The effect of deposition time was used to clarify the optimum time to strip the metal on the electrode surface *(Fig 4.2)*

Polyaniline and Poly-N-n-alkylaniline were modified on glassy carbon microelectrode and used as detectors of heavy metals. Polyaniline and its derivatives reacted poorly towards Lead detection. Microelectrodes detection has shown to be sensitive towards copper when polyanilines and its derivatives were used for modification of the electrodes.

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