# STRUCTURAL ANALYSIS OF POLYANILINE-POLYPYRROLE COPOLYMERS VIA PYROLYSIS MASS SPECTROMETRY

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

FERİDE TEZAL

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMISTRY

FEBRUARY 2007

Approval of the Graduate School of Natural and Applied Sciences.

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Ahmet Önal
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Jale Hacaloğlu
Co-Supervisor

Prof. Dr. Zuhal Küçükyavuz
Supervisor

Examining Committee Members

Prof. Dr. Duygu Kısakürek (METU, CHEM)

Prof. Dr. Zuhal Küçükyavuz (METU, CHEM)

Prof. Dr. Jale Hacaloğlu (METU, CHEM)

Prof. Dr. Ali Usanmaz (METU, CHEM)

Assist. Prof. Dr. Mehmet Sankır (TOBB ETU)

**“I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.”**

**Name, Last name : Feride TEZAL**

**Signature :**

# ABSTRACT

## STRUCTURAL ANALYSIS OF POLYANILINE-POLYPYRROLE COPOLYMERS VIA PYROLYSIS MASS SPECTROMETRY

TEZAL, Feride
MS., Department of Chemistry
Supervisor: Prof. Dr. Zuhal Küçükyavuz
Co-Supervisor: Prof. Dr. Jale Hacaloğlu

February 2007, 88 pages.

This thesis describes recent progress in electrochemical preparation of several conducting polymers. In particular, the synthesis and characterizations of pure polyaniline, pure polypyrrole, polyaniline/polypyrrole and polypyrrole/polyaniline copolymers and polyaniline-polypyrrole physical blends were studied. The focus has included firstly synthesis of these electrically conductive polymers.

Secondly, thermal characteristics of electrochemically synthesized homopolymers, copolymers and their physical blends were investigated by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and direct pyrolysis mass spectrometry (DIP-MS) techniques. In general, TGA analysis showed three-step thermal degradation. The first, at 100$^o$C, was attributed to water, and unreacted monomers. The second weight losses observed at around 150 $^o$C was because of evolution of water and/or acid. Finally, the removal of the dopant ion and low molecular weight species from the matrix were observed for pure PANI and pure PPy at 230 and 280 $^o$C, respectively. PANI/PPy films and PPy/PANI films have decomposition temperatures at 272$^o$C because of the loss of the dopant ion. It was also observed that pure PPy was thermally more resistant than pure PANI.

Thirdly, thermal characteristics, and degradation products of electrochemically prepared PANI/PPy and PPy/PANI films in solutions containing variable dopant (${SO_4}^{2-}$) concentrations were analyzed and compared with pyrolysis mass spectrometry. Similar to TGA study, there were three main thermal degradation steps namely, evolution of low molecular weight species, dopant based products and degradation products of polymers. The dopant concentration was monitored to optimize the degradation behavior. Pyrolysis mass spectrometry data showed that the degree of degradation of the polymer already coated on the electrode enhanced as the dopant concentration used in synthesis increased.

Keywords: polyaniline, polypyrrole, PANI/PPy film, PPy/PANI film, direct pyrolysis mass spectrometry

# ÖZ

## POLİANİLİN-POLİPİROL KOPOLİMERLERİNİN PİROLİZ KÜTLE SPEKTROMETRİ YÖNTEMİYLE YAPISAL ANALİZİ

TEZAL, Feride
MS., Kimya
Tez Yöneticisi: Prof. Dr. Zuhal Küçükyavuz
Ortak Tez Yöneticisi: Prof. Dr. Jale Hacaloğlu

Şubat 2007, 88 sayfa.

Bu çalışmanın ilk kısmında saf polianilin (PANI), saf polipirol (PPy), polianilin/polipirol ve polipirol/polianilin filmleri ile polianilin-polipirol fiziksel fiziksel karışımı elektrokimyasal yöntemle sentezlendi.

Çalışmanın ikinci kısmında, elektrokimyasal yöntemle sentezlenen homopolimerler, kopolimerler ve onların fiziksel karışımlarının termal karakterizasyonları TGA, DSC ve direkt piroliz kütle spektrometrisi yöntemleri kullanılarak yapıldı. Genel olarak TGA analizlerinde üç basamakta kütle kaybı olduğu gözlendi. Bunlardan ilki 100 $^oC$ ye kadar su kaybından dolayı gözlenirken ikinci basamaktaki kütle kaybı 150 $^oC$ civarında yine su kaybı ve/veya asit kaybından dolayı gözlendi. Son olarak üçüncü basamak kütle kaybının saf PANI için 230 $^oC$ ve saf PPy için 280 $^oC$ civarında, dopant ve düşük molekül kütleli türlerin matristen çıkışı neticesinde gerçekleştiği gözlendi. Özellikle dopant iyonunun kaybına bağlı olarak PANI/PPy ve PPy/PANI filmlerinin bozunum sıcaklığı 272 $^oC$ civarında gerçekleşti. Ayrıca yüksek sıcaklıklarda saf PPy'nin PANI'ye göre ısıya karsı daha dirençli olduğu gözlendi.

Farklı dopant ($SO_4^{2-}$) konsantrasyonlarında elektrokimyasal olarak sentezlenen PANI/PPy ve PPY/PANI filmlerinin ısıl karakterizasyonları ve bozunum ürünleri piroliz kütle spektrometri yöntemiyle analiz edilip, karşılaştırıldı. Íncelenen tüm maddeler için, düşük molekül kütleli türlerin çıkışı, dopant tabanlı ürünlerin çıkışı ve polimerlerin bozunum ürünlerinin çıkışına bağlı olarak üç temel ısıl bozunum basamağı kaydedildi. Ayrıca dopant konsantrasyonu artarken, sentez esnasında elektrot yüzeyine önce kaplanan polimerin bozunum miktarının arttığı saptandı.

Anahtar Kelimeler: polianilin, polipirol, PANI/PPy film, PPy/PANI film, direkt piroliz kütle spektometrisi

# ACKNOWLEDGMENTS

I would like to express my appreciation to my supervisor Prof. Dr. Zuhal Küçükyavuz for her guidance, patience and advice throughout this work. Then, I would like to express my sincere gratitude to my co-supervisor Prof.Dr. Jale Hacaloğlu. Without her advice, encouragements, technical and moral supports this thesis would never have been written.

My very special thanks goes to my friend Faris Abu-Hasan for his endless helps, encouragements, technical and moral support.I saw that there is still a man who helps people without response in the world.

I wish to thank to my friends Çetin Börüban ,Yasin Kanbur and Yusuf Nur for their help and friendship.

I would like to thank to my family for their patience and moral support. Without their love and affection, I have never completed this study.

I also wish to express my thanks to Mehmet Göregen for his trust and moral support.

TO THE MEMORY OF MY FATHER

# TABLE OF CONTENTS

# LIST OF TABLES

**TABLE**

# LIST OF FIGURES

**FIGURE**

# CHAPTER 1

# INTRODUCTION

## 1.1 Conducting Polymers

### 1.1.1 Conduction in Polymers

For most of the history of polymer technology one of the most valuable properties of synthetic polymers has been their ability to act as excellent insulators. For that reason they are widely used in electrical engineering. In spite of this there has been great interest for many years in the possibility of producing electrically conducting polymers. The obvious attraction is to combine the electrical properties and high added value applications of a semiconductor or a metal with the advantages of a polymer in one material. Polymers attract electrical and electronics industries because of the ease and low cost of their preparation and fabrication, as compared to semiconductors and metals, and because of their mechanical properties.

Certain types of polymers display conductivity lying between the conductivities of insulators and of metals. The term "conductive polymer" has two different meanings. The first definition encompasses polymers filled with conductive materials such as carbon black, metal flakes of fibers. The major function of the polymer is to serve as a glue to hold the conductive elements together in a solid entity. The second term applies to polymers whose backbones are responsible for the generation and propagation of charge carriers. The conductivities of selected materials are given in Figure 1.1.

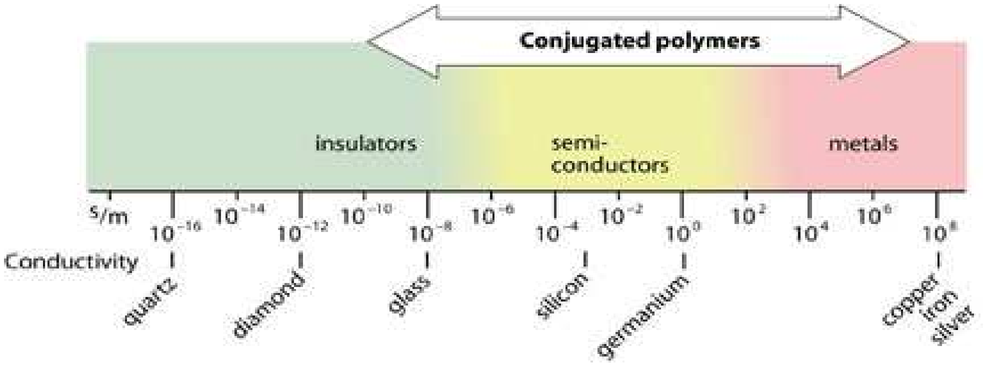


Figure 1.1: Conductivities of selected materials

Although polymers are known as good insulators, it is not new that the organic compounds act as conducting materials. The study of conductivity of organic compounds goes back to the beginning of this century. The existence of a small but measurable dark conductivity in anthracene as well as photo conductivity was reported in 1906 [1]. The interest in the field of organic semiconductors was considered in 1941 when Szent-Györgi suggested that the transfer of $\pi$ electrons from molecule to molecule may play an important role in physical processes of living organisms [2].

Since the resistivity of anthracene is in the order of $10^{14}$-$10^{15}$ ohm.cm, it should be classified as a good insulator. In spite of this classification, in 1960 Kallman and Pape [3], for the first time, showed the passage of electric current across the interface between substances which had been previously regarded as highly nonconducting. Thus, a piece of anthracene in solution can act as an electrode and exchange charges with ions in the surrounding solution. Later on, it was concluded that the electrochemical reactions would take place at the anthracene-aqueous solution interface. The compounds which are present in solution were able to inject holes into the valence band or receive electrons from conduction band.

During the last 30 years, many attempts have been made to produce polymers with high electrical conductivity and much effort has been directed towards the synthesis of polyacetylene . 1970s Shrikawa and Ikeda [4,5] demonstrated the possibility of preparing self supporting films of polyacetylene by direct polymerization of acetylene. The polymer produced was a poor semiconductor. In 1977 MacDiarmid et al. [6] treated polyacetylene with Lewis acids or bases, as a result conductivity increased by up to 13 orders of magnitude. After this publication there has been an explosive growth of research into the whole range of conjugated polymer structures.

This great increase on the study of polymers may be due to the uses of them. They can be used in prevention of dust collecting electrostatic charges, as conductive surfaces for electroplating nonconductors or for printed circuit boards.

Nowadays, they are used in extremely large areas, such as sensors, batteries, photovoltaics, ion gates, time release electrodes for chemicals.

### 1.1.2 Conduction Mechanism

#### 1.1.2.1 Band Theory

Solids can be classified as conductors, insulators and semiconductors with respect to their conductivities.

Charge may be carried by ions or by electrons. Depending on the charge carriers involved, conductivity may be classified as ionic or electronic. Ionic conductivity involves positively (cations) or negatively (anions) charged ions.

Energy level diagrams for conductors, insulators and semiconductors are shown in Figure 1.2.

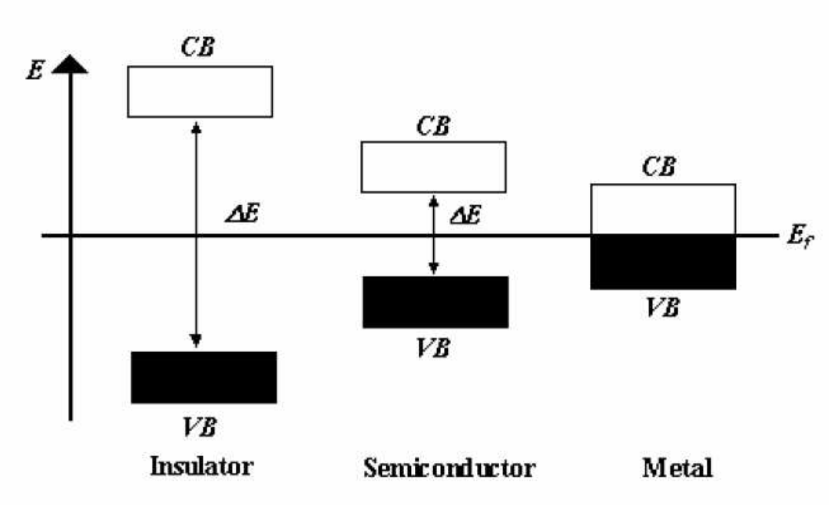


Figure 1.2: Energy level diagrams for three types of solids

In metals, the electrons are assumed to be free to move throughout the volume of the metal. In a molecular solid, It may be considered that the valance electrons are not completely localized at the particular atom or molecule from which they come. The solid may be regarded as a giant molecule with the assembly of valence electrons ranging over the whole solid.

The delocalized molecular orbitals formed in case of metals should not be classified as bonding or antibonding as is done for molecular orbitals in diatomic molecules; they are called energy levels which are not degenerate, taken together as a band. The highest energy band that is filled with electrons is called the valence band, and the next band is the conduction band.

The separation between these two bands is referred as the energy gap. each band consists of many individual levels as seen in Figure 1.2. In case of conductors, the valence band is overlapped by an empty conduction band. These two bands are separated from an empty upper conduction band by a forbidden energy zone. Electrical conductivity takes place by means of the motion of electrons within the lower conduction band. There is no need to supply the energy required to bridge the forbidden zone and the upper conduction band (Figure 1.2.a).

In an insulator, the valence band is full, the conduction band is empty and is widely separated from conduction band. Electron motion is only possible if energy is provided to promote electrons across the comparatively large forbidden zone to the conduction band. For that reason the conductivities of insulators are very low.

In a semiconductors, similar to that of an insulator, the valence band is full, the conduction band is empty. But, there is some means by which excess electrons or holes have been added to the crystal to populate conduction band which results in conductivity. There are two categories of semiconductors, namely intrinsic and extrinsic semiconductors.

#### 1.1.2.2 Intrinsic Semiconductors

In this case, thermal excitation of interatomic bond create conduction electrons or holes. The temperature necessary for this excitation is related to and determined by the forbidden gap. For a semiconductor the forbidden zone is sufficiently narrow that electrons can be promoted from the valence band to the conduction band. After the removal of electrons from the valence band the vacancies are left. For this reason, remaining electrons in the valence band move under the influence of an electric field. Carriers can be two types, which are the electrons carrying negative charge (n-type) and holes carrying positive charge (p-type). In intrinsic semiconductors, the excitation of an electron to conduction band leaves a hole in the valence band; both species involved in conduction process. The total conductivity results from the movement of both kinds of carriers. For an intrinsic semiconductor, the conductivity $\sigma$ is given by Equation (1.1), e is the electronic charge, n and p are electron and hole concentrations, respectively, and $\mu_n$ and $\mu_p$ their respective mobilities.

$$\sigma = n\ e\ \mu_n + p\ e\ \mu_p \tag{1.1}$$

#### 1.1.2.3 Extrinsic Semiconductors

In most cases electron-donating or electron-accepting impurities participate in the generation of charge carriers. In this cases either holes or electrons play the dominant role in the transport. These are the extrinsic semiconductors and are termed as p-type or n-type semiconductors according to the charge carriers (holes or electrons respectively). For example, III-A elements such as Al, Ga or In can be added in small amounts to pure silicon to produce p-type semiconductors. Each Si atom has 4 valence electrons that are used in the bonding of the network lattice. A boron atom has three valence electrons. Hence a boron atom that assumes a position of a silicon atom in the crystal lattice can form only 3 of the 4 bonds required for a perfect lattice, and an electron vacancy is introduced. An electron from a nearby bond can move into this vacancy, thus completing the 4 bonds on the boron atom but, at the same time, leaving a vacancy at the original site of the electron. In this way electrons move through the structure.

Other type of impurity is donor impurity. This may be achieved by adding species such as antimony to silicon. This type of extrinsic semiconductor is known as n-type.

### 1.1.3 Electrical Conductivity in Polymers

A type of conducting polymer which has attracted researchers for twenty years fits neither the intrinsic nor the additive conductor classification. These newer materials are generally known as insulators or poor conductors in their pristine state. However, later on it was investigated that upon exposure to oxidizing or reducing agents their conductivity increases. Thus, an insulating material can progressively be oxidized or reduced. By this way the conductivity may range from semiconductor to metallic regime. The residue from the oxidizing or reducing agent becomes part of the new material which has different structure and properties from the starting material. The overall process is often referred as doping. In this process once the polymer is electronically charged, counter ions from solution enter the polymer fibrils to produce electrostatic neutrality. However, this type of doping seen in polymer is not same as the semiconductor doping which is done by impurities such as silicon.

The semiconductivity in organic compounds was first observed in certain polymer hydrocarbons and dyes. The analysis and observations have identified conducting polymers as possessing fully conjugated backbones which are capable of undergoing charge transfer in associated with appropriate electron acceptors or donors. As a result a conjugated backbone is the prerequisite for a polymer to become conductive.

### 1.1.4 Electrical Conductivity in Conjugated Polymers

Polyacetylene is the first organic conducting material. It has been the most extensively studied of all the conducting polymer systems. The basic concepts involving polyacetylene $(\mathrm{CH})_x$ can be also applied to other polymers such as poly(p-phenylene), polythiophene, polypyrrole and polyaniline. For that reason, it is better to deal with polyacetylene in the area related with the conductivity.

The origin of the conductivity in the polymers arises from the state of relative oxidation or reduction [7,8]. In these cases the polymer loses or gains electrons. It is possible to change the magnitude of conductivity of a semiconductor such a value that may exceed that of metals. This was the first conducting organic polymer.

Until 1970 the polymer obtained from acetylene was a black unprocessable powder resembling to carbon black. Polyacetylene has three of the four valence of the carbon atom $sp^2$ hybridized orbitals, two of them forming sigma bonds and the 3rd forming the pendant bond with the H atom. The remaining pi electrons are involved in forming the extended conjugated structure which is prerequisite of organic conductivity [9-12].

### 1.1.5 Conducting Polymer Synthesis

The major techniques used to synthesize conducting polymers with conjugated backbones are four types:

1- Pyrolysis

2- Ziegler Natta Catalysis

3- Electrochemical Polymerization

4- Condensation Polymerization

5- Microwave Assisted Polymerization.

The electrochemical reactions which produce conducting polymers may be illustrated in the following steps. These are shown as following:

$$HMH \longrightarrow HM^{+}H + e^{-}$$

$$2HM^{+}H \longrightarrow HM^{+}HHM^{+}H \longrightarrow HMMH + 2H^{+}$$

$$xHMH \longrightarrow HM_{x}H + (2x-2)H^{+} + (2x-2)e^{-}$$

$$HM_{x}H \longrightarrow (HM_{x}H)^{+y} + ye^{-}$$

In the first step, a monomer M is oxidized at the electrode surface, thereby giving an electron forming a radical cation, $M^{+}$ is formed. The second step involves the coupling of two radical cations to produce a dimer. Then this immediately releases two protons. Street et al [13] found that a decrease in pH during electrochemical polymerization is consistent with the elimination of protons. Repeating steps 1 and 2, continually increased the length of the growing oligomer chain. The next reaction can be represented by equation shown in step 3. Here x represents a large number that shows the number of monomeric units which interact to form a polymer, $HM_{x}H$. In this step (2x-2) protons and an equal number of electrons are released. In the final step 4, the polymer $HM_{x}H$ is oxidized. Here y electrons are released and the oxidized polymer $H(M_{x})^{+y}H$ is formed. The degree of polymerization x is not known precisely. However an estimation may be done by tritium labeling studies carried out on poly-3,4-dimethylpyrrole perchlorate [14]. Electrochemical polymerization of the 2,5-tritiated monomer leads to elimination of all the tritium except those found at chain ends. Comparision of the radioactivity of the monomer to that or the polymer showed that x value was about 750.

The electrochemical doping process proceeds much the same as with chemical doping. However, in case of electrochemical doping the energy for the oxidation (acceptor doping) or reduction (donor doping) is provided by an external voltage source (or by the chemical potential of the counter electrode) and the counter ion for the resulting ionized polymer is supplied from the supporting electrolyte.

There are several advantages of the electrochemical polymerization of conducting polymers such as:

i- Reactions are carried out at room temperature.

ii- Thicknesses of the films can be controlled by varying either the potential or the current with time.

iii- Polymer films are directly formed at the electrode surface.

iv- It is possible to produce homogeneous films.

v- Doping of the polymer can be achieved with the desired ion simultaneously.

vi- It is possible to obtain copolymers and graft polymers.

### 1.1.6 Conducting Polymer Blends

Various aromatic compounds can be polymerized by electrochemical oxidation in a solution containing supporting electrolyte. By electrochemical oxidation hydrogen is subtracted from the monomer and fully conjugated aromatic polymers are formed. The highest conductivity of electrochemically produced conducting polymers is about 500 S/cm, for poly(3-methylthiophene) [15]. Polypyrrole and polyaniline also show high conductivity and good stability in ambient conditions [16]. However, several drawbacks limit the application of polypyrrole and polyaniline for practical uses as a conducting polymers. These films are very hard, deeply black in color and hard to be produced with a controlled conductivity. They are hard and brittle, a free standing films of these polymers is difficult to handle. In order to get rid of these drawbacks and improve the quality, several studies were done. It was thought that the quality may be enhanced by blending it with a second polymer. The process of blending has been performed in several ways, such as by mechanical mixture of the molten polymers or by the radiation induced polymerization of monomer sorbed into the host polymer [17]. Conductive composite films can be prepared electrochemically [18,19]. The electrochemical preparation has several advantages. The properties of the film obtained can be changed simply by varying the electrolysis conditions. Also, it eliminates the need of strong oxidizing agents and hazardous dopants. Electrochemical blending is extensively studied by several authors[18,20-23]. In the case of electrochemical polymerization, the electrode is coated with an electrochemically inactive insulating polymer film. In this case, the monomer molecules and the electrolyte anions can diffuse into the polymer films, when the electrolyte solution is adjusted according to the kind of the polymer used. The polymerization starts around the interface between the electrode surface and the polymer film. The resultant polyaniline film grows through the the matrix polymer, forming a novel electrically conducting polymer alloy film.

It was shown that as polyaniline starts to grow from the film side attached to the ITO electrode surface, only the electrode side of the film becomes conductive in the early stages of the polymerization [22]. The surface side contacted with the polymer solution is insulating at first and shows no conductivity. The alloy films are layered in structure as shown in Figure 1.3. The structure of the

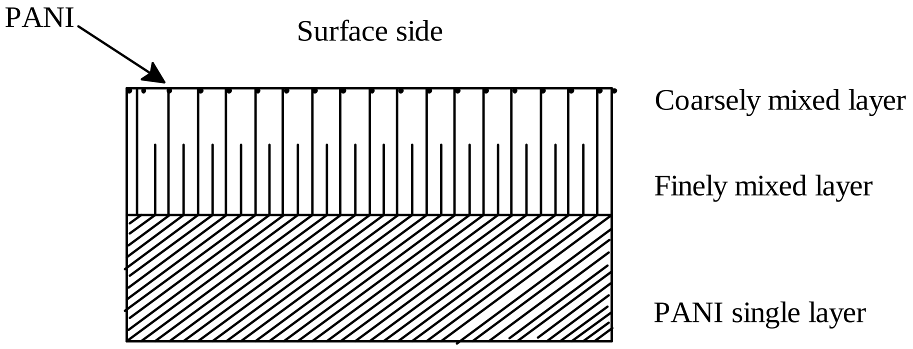


Figure 1.3: Structural model of polyaniline based alloy film

electrode side of the film indicated that a thin and pure polyaniline layer forms on the electrode side of the film. The second layer is a thick and fine mixture of the base film and the polyaniline chains. The third layer is mainly an insulating base polymer, where polyaniline chains grew coarsely on the film surface forming projections.

### 1.1.7 Application of Conducting Polymers

In recent decades, conducting polymers gained great interest because of their high-tech applications in electronics, optoelectronics, sensors and energy storage devices. However, poor processibility and stability of conducting polymers have limited their practical applications. Conducting polymers are usually brittle materials. Hence, many studies were conducted to improve their mechanical properties. Environmental stability, mechanical and physical properties can be additionally improved through preparation of composites and blends [24]. Conducting polymers possess the electronic, electrical and optical properties of a metal while retaining the processability and mechanical properties usually associated with a conventional polymer [25].

The application area of polymers is already wide and it has a visible tendency to grow wider. As an outcome of the developments in polymer technology, conductive polymers can form substitutes for naturally conductive materials. Conductive polymers are being used commonly for various purposes including rechargeable batteries, condensers, chemical transistors, production of semiconductor photoanodes, and electrochemical displays, restoration of data, indicators of gasometers and biochemical analysis [26].

## 1.2 Polyaniline and Polypyrrole

### 1.2.1 Properties of Polyaniline

Polyaniline (PANI) was first synthesized in 1862 and its properties as a conducting polymer have been extensively studied. Figure 1.4. summarizes the repeat unit for the various forms The excellent environmental and thermal stability in the conducting form and the potential for relatively low cost make PANI an attractive material for applications in batteries, light-emitting diodes, and anti-static packaging and coatings. PANI has been considered an intractable material; it decomposes before melting and is insoluble in common solvents. In recent years, however, three solvents have been reported to dissolve PANI: N-methylpyrrolidinone (NMP), specific amines and concentrated acids [27].

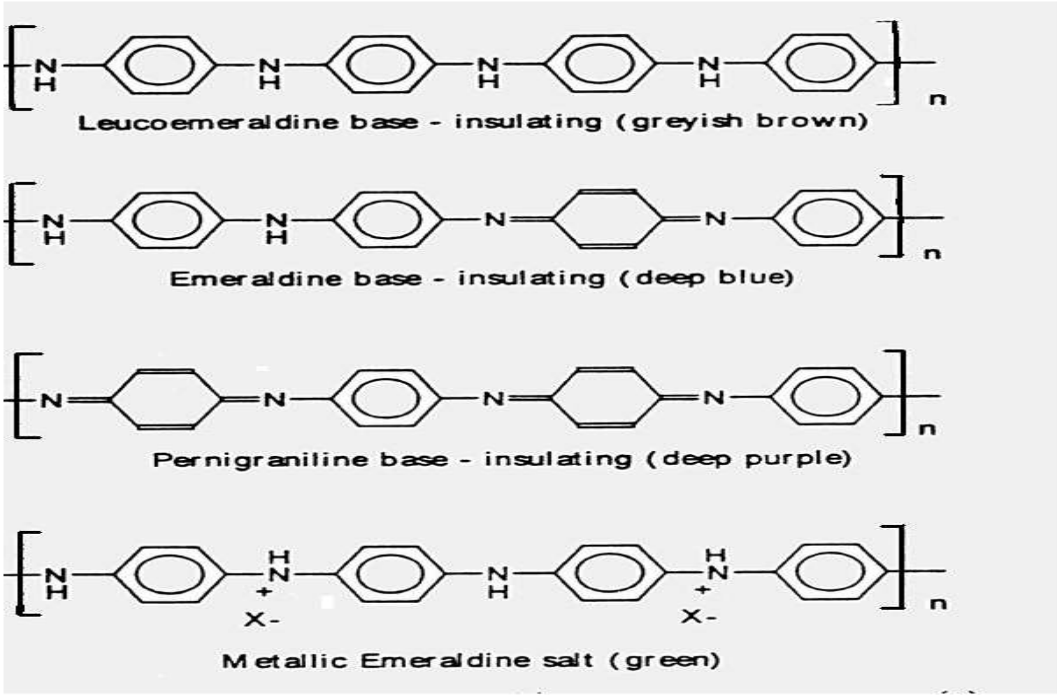


Figure 1.4: Repeat units for the various forms of polyaniline

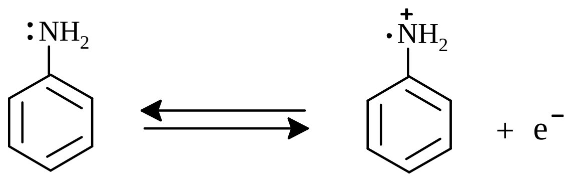
Conductive PANI can easily be obtained by electrochemical or chemical methods. However the electrochemical method has an advantage as the resulting polymer does not contain contaminants from the oxidative agents [28]. The chemical technique gives a powder product while it is possible to obtain a conductive polymer film form by the electrochemical method. The electrochemical polymerization of PANI is generally carried out on noble metal electrodes such as Pt/Au in acidic media by continuous scan, or constant potential electrolysis [29] . High quality PANI films were synthesized by Diaz and Logan [30]. They performed electrochemical polymerization of aniline in an aqueous solution of 0.1 M $H_2SO_4$ and growing of free-standing PANI film on a platinum electrode was achieved by continuously sweeping the potential between -0.2 and + 0.8 V versus SCE

[30]. The synthesis and characterization of PANI doped with different anions is critical, since many properties of the final polymer are influenced by the nature of the dopant anion. For instance, the solubility of PANI, which is an important criterion or processibility and characterization, can be improved by doping it with big anions such as camphor sulphonic acid and 5-sulphosalicylic acid. It was reported that the dopant anions which improve PANIs solubility generally contain carboxylic groups. The conductivity of PANI synthesized electrochemically was depend on the redox state of the polymer, the solution pH, water content and, to a lesser extent, the type of dopant anions. The type of dopant anions also affects the stability of the conductivity in PANI at different atmospheres and temperatures [31].

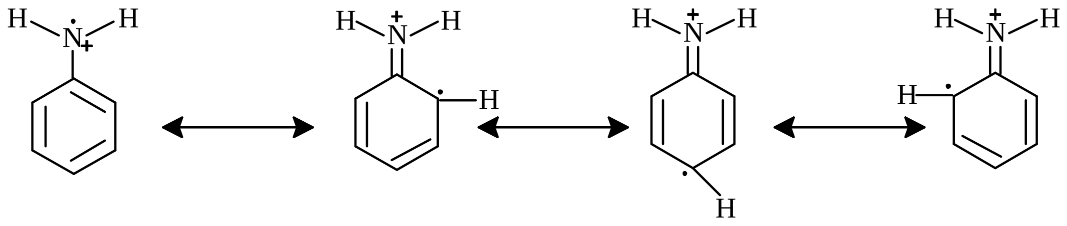
### 1.2.2 Mechanisms of Polyaniline Formation

The numerous methods employed to synthesize PANI have been proposed several products which differ in their nature and properties and must represent the results of a multitude of polymerization mechanisms of aniline. In general, polymerization proceeds via the radical cation of the 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 oligomers could also be oxidized, and thus could react further with the radical cation of the monomer to build up the aniline chain.

Mohilner et al., [32], Breitenbach and Heckner, [33-35], Hand and Nelson,[36,37] and Genies and co-workers [38,39] have proposed mechanisms for electropolymerization of aniline. The point of agreement in the proposed mechanisms is the first step of oxidation of aniline, i.e., formation of the radical cation. This radical cation gives three different resonance forms as shown in Figure 1.5.



Formation of aniline radical cation



Resonance forms of aniline radical cation

Figure 1.5: Formation of aniline radical cation and resonance forms of aniline radical cation

Two different mechanisms for the anodic oxidation of aniline in acidic and alkaline media have been reported [32,33-35]. The mechanism in acidic media was proposed by Mohilner et al. [32] based upon measurement of the kinetic parameters for 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 their 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. The mechanism of polymerization of aniline in a basic medium, like acetonitrile-pyridine, proceeds in a way essentially similar to that proposed earlier in the acid medium.

The anodic oxidation of aniline stipulates only the dimerization process [36,37]. The formation of oligomers with the n value $>2$ is ruled out in case the resulting product is a linear chain. Furthermore, it was concluded that the electrolysis product of aniline earlier characterized as "aniline black", emeraldine, etc., is largely, if not completely, composed of quinone-hydroquinone mixtures with a small amount of benzidine salt, and composition contingent upon the parent molecule. This is contradictory to our present understanding where the n value determined by gel studies is shown to be greater than 800 repeat units [38].

The mechanism proposed by Genies and co-workers [38,39] for electropolymerization of aniline in acidic media is based on detailed studies [40-42]. Nevertheless, the results concerning the chronoamperometric plots during potential scanning, and potential step methods of electrodeposition of PANI have been taken into account [38,43]. The mechanism is displayed in Figure 1.6.

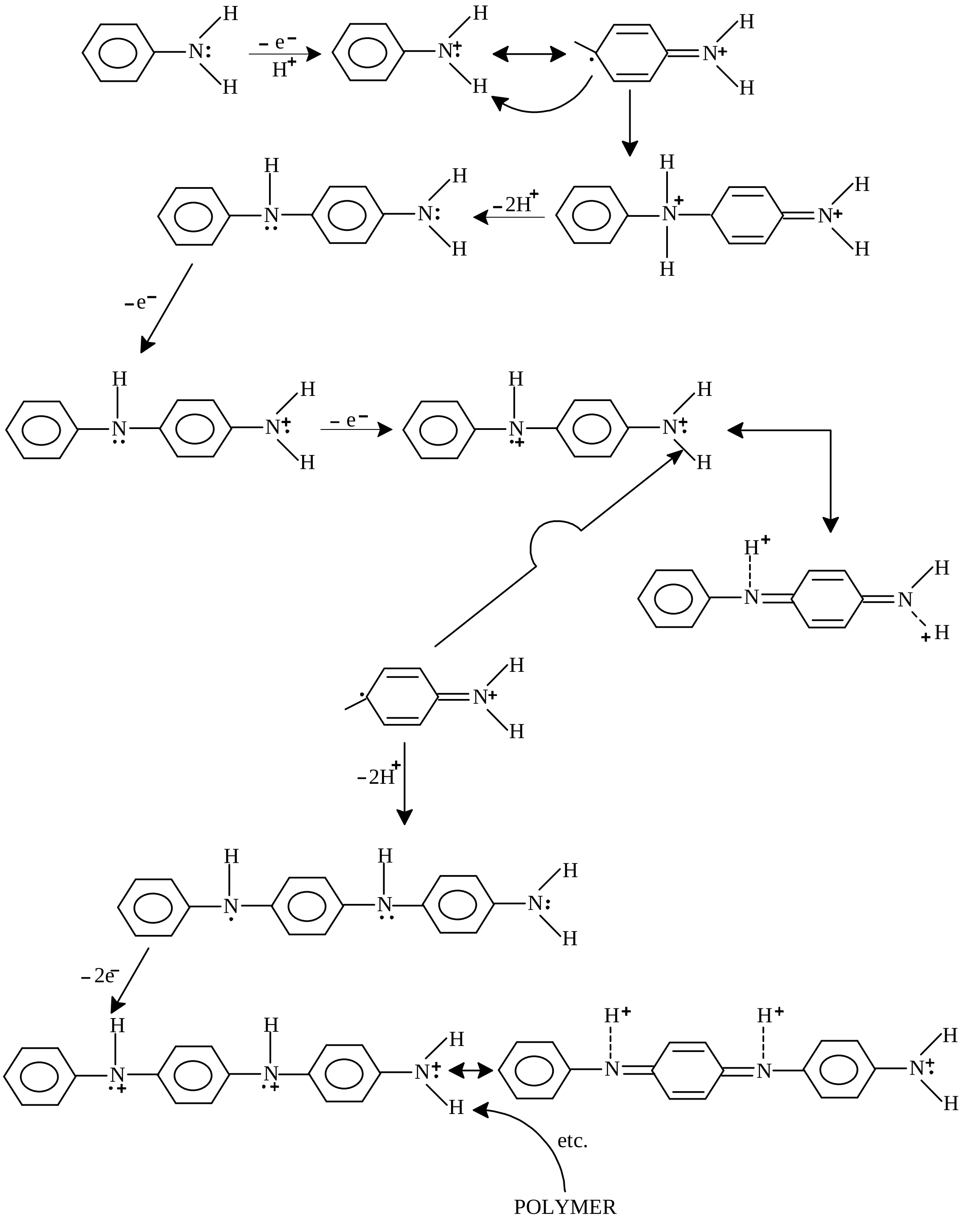


Figure 1.6: Mechanism of formation of conducting polyaniline

### 1.2.3 Properties of Polypyrrole

Pyrrole was known to form a conductive “pyrrole black” [44] via spontaneous polymerization, and its history can be dated back in 1916 [45]. In 1968 [46], it was noted that pyrrole could be electrochemically polymerized using a variety of oxidation agents to give a black conducting powder. It can be synthesized both aqueous and non-aqueous solution during electrochemical polymerization. Among all known conducting polymers, polypyrrole (Ppy) stands out as an excellent one because of its good environmental stability, high conductivity, and ease of synthesis. It is stable in a wild range of potential, during thousands of charge-discharge cycles, and under properly selected conditions its response is fast. In contrast to polyaniline it can operate both in acidic and neutral solutions, which makes the polypyrrole electrode attractive for use as sensors material in the bioelectroanalytical chemistry. Polypyrrole is a relatively air stable organic conducting polymer, which suffers from poor processability. The use of new tailor made reactive statistical copolymers for the synthesis of sterically stabilized polypyrrole colloids is described [47]. Moreover, compared to other heterocycles its oxidation potential is low. For all of these reasons, polypyrrole has been an interesting material to study. Polypyrrole can be prepared in various forms, depending on the method used and on the preparation conditions. A general difficulty of the reproducible polypyrrole preparation arises from its complexity. The structure and hence the properties of the resulting polypyrrole are strongly influenced by a number of variables (e.g., the oxidation potential, the monomer concentration, the preparation temperature) that are not perfectly controlled. Therefore, the results on polypyrrole vary widely. Two basic methods are used for the preparation of polypyrrole: chemical and electrochemical synthesis [48,49].

The chemical synthesis of polypyrrole produces easily arbitrary amounts of polypyrrole in various forms, but its producibility is poor. The electrochemical synthesis of polypyrrole can be conveniently carried out. An advantage of the electrochemical methods is that the preparation process can be simply controlled through the current or the applied potential and the charge consumed. A disadvantage is that polypyrrole can be prepared only in the form of a relatively thin film deposited on the surface of a conducting material. In the last few years, the goal of researchers has been to improve physical properties of Ppy- like processibility and mechanical integrity. To achieve this goal, composites and copolymers of Ppy with insulating thermoplastic were synthesized. In preparation of conducting composites, the electrochemical method is preferred because it is easy, clean and selective [25].

### 1.2.4 Electrochemical Polymerization of Pyrrole

The electrochemical polymerization of pyrrole was one of the first experiments to produce a conductive polymeric material. Dall'olio et al.[50], in 1968, obtained a powdery precipitate on platinum electrode by oxidizing pyrrole in aqueous $H_2SO_4$. It was known as pyrrole black and the conductivity was 8 $\mathrm{Scm}^{-1}$ and possessed a large number of free spins.

In 1979 Diaz et al.[51] produced coherent films of polypyrrole which could be peeled off from the platinum electrode.

The structure of polypyrrole is believed to be pyrrole units coupled through their 2-and 5-positions which are known to be the most reactive toward addition and substitution reactions. However the exact chemical configuration is not known.

The mechanism of the electrochemical polymerization of pyrrole is believed to proceed via the radical cation of the monomer. This can be represented in Figure 1.7. First, the initial oxidation step produces a radical cation which can either react with another radical cation to produce a dimer or undergo an electrophilic attack with a neutral monomer. The electrochemical polymerization reaction occurs only when the applied potential is sufficient to oxidize the monomer.At the applied potentials, the coupling of two radicals is more likely because the number of neutral species at the electrode surface will be essentially zero at these potentials. The charge consumed during polymer formation has a linear time dependence (at least initially) and is independent of pyrrole concentration. If there are no nucleophiles in the system which are thought to be capable of reacting with the radical cations, they will give a dimer cation which readily eliminates $2H^+$.

The chain growth is the terminated either when the radical cation of the growing chain becomes too unreactive or, more likely, when the reactive end of the chain becomes sterically blocked for further reaction. Polymer chain bears a charge of unity for every three to four pyrrole rings. The level of oxidation is an intrinsic characteristic of the polymer and is not sensitive to the nature of the anion. However, the anion not only influence the structural properties and the electroactivies of the films, but also the mechanical properties of the films.

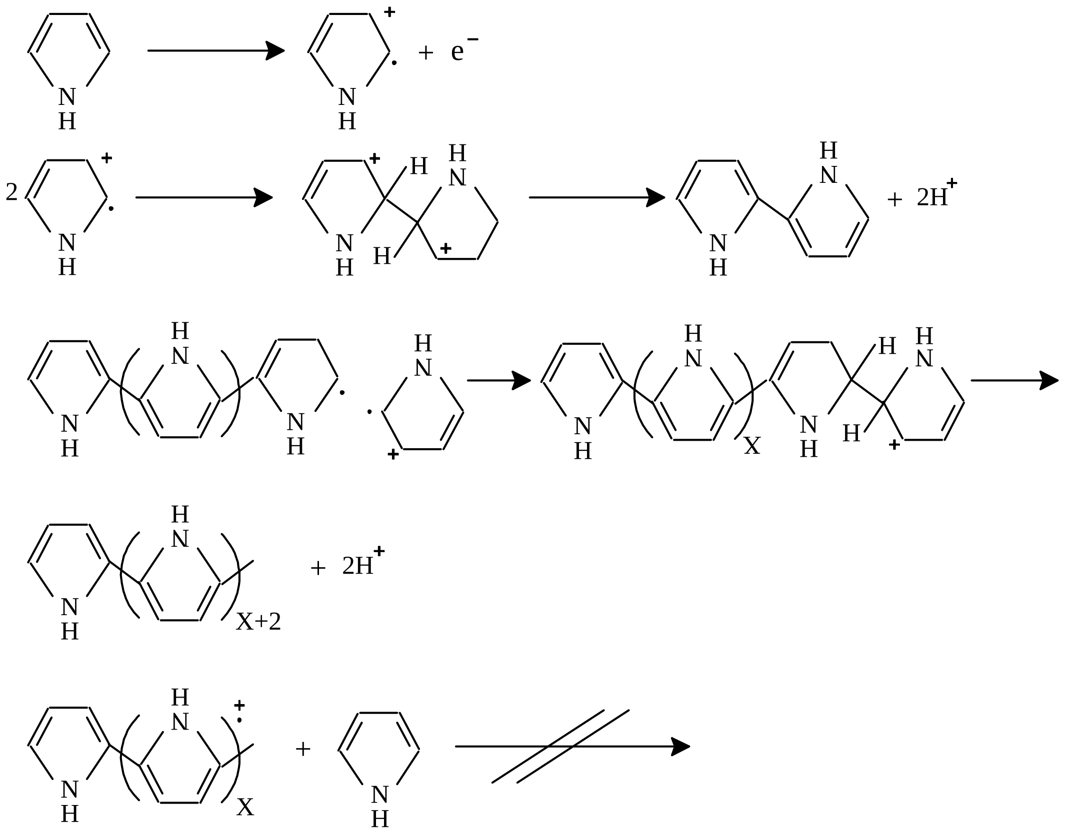


Figure 1.7: The electrochemical polymerization of pyrrole

## 1.3 Pyrolysis Mass Spectrometry

Pyrolysis is the thermal degradation of a material in an inert atmosphere or in vacuum. It causes molecules to cleave at their weakest points to produce smaller, volatile fragments called pyrolysate. Pyrolysis products can be identified by mass spectrometry (MS), gas chromatography (GC) and infrared spectroscopy (IR). The major advantage of pyrolysis techniques compared to other techniques is the simple sample preparation.

Pyrolysis techniques coupled to mass spectrometers to separate and identify pyrolysis products by ionizing, separating and measuring ions according to their mass-to- charge ratio (m/z). The combined technique is known as pyrolysis mass spectrometry (Py-MS).

Pyrolysis mass spectrometry is an important technique in understanding structure and thermal behavior of polymers. Pyrolysis mass spectrometry can also be used to study the stereoregularity of homopolymer through tetrameres or higher oligomers.

Pyrolysis mass spectrometry is a very sensitive technique applied for structural characterization of inorganic, organic, and bioorganic compounds. Molecules have distinctive fragmentation patterns that provide structural information to identify structural components. Pyrolysis mass spectrometry can be utilized for investigating thermal stability, thermal degradation mechanisms and decomposition products of polymers [52].

### 1.3.1 Pyrolysis Techniques With Mass Spectrometry System

For the pyrolysis analysis with mass spectrometry indirect (evolved gas analysis), direct, flash (rapid), curie point and laser pyrolysis techniques are used. Using these techniques, the total ion chromatograms and mass spectra of the decomposition products can be analyzed by recording mass spectra continuously during pyrolysis [53].

#### 1.3.1.1 Indirect (Evolved Gas) Pyrolysis Techniques

The nature and amount of evolved gaseous products from a sample heated using a controlled temperature program can be determined by evolved gas analysis. In this technique, as heating occurs in a closed chamber connected to the MS, only gaseous volatile and low molecular weight products enter into MS system and can then be analyzed [54,55].

#### 1.3.1.2 Direct Insertion Probe Pyrolysis Mass Spectrometry

Mass spectrometry only separates and detects gas phase ions. Usually, ionization occurs in the gas phase. Therefore, a sample that is a solid, liquid or part of a solution, should be converted into the gas phase before subjecting analysis by spectrometry. For solids, sample volatilization is achieved by using a Direct Insertion Probe. It is a simple and quick method for structural and thermal characterization of the polymers [56,57]. Pyrolysis is achieved inside the mass spectrometer (MS) under high vacuum conditions of the MS. Both low molecular weight products and relatively high molecular weight fragments can be detected as condensation is prevented. Since pyrolysis mass spectrometry techniques are carried out under high vacuum conditions, the possibility of secondary reactions is minimized. For this reason, possibility of the secondary reactions is prevented and primarily thermal degradation products can be analyzed. The temperature is increased gradually and the degradation products as a function of temperature can be detected continuously during the process.

## 1.4 Aim of the Study

The purpose of this study is to investigate the thermal characteristics, decomposition products and thermal degradation behavior of electrochemically synthesized pure PANI, pure PPy, PANI/PPy films, PPy/PANI films and PANI-PPy physical blend via thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and direct pyrolysis mass spectrometry techniques. Different dopant concentrations were used to determine the effects of increasing dopant concentrations on electrochemically synthesized PANI/PPy and PPy/PANI films for comparison purposes.

# CHAPTER 2

# EXPERIMENTAL

## 2.1 Raw Materials

Following chemicals were used for experimental process

- Aniline: Reagent quality aniline (Merck) was used without purification.
- Pyrrole: Reagent quality pyrrole( Merck) was used without purification.
- Sulfuric acid: Fluka, was used without purification.

## 2.2 Instrumentation

### 2.2.1 Potentiostat

Electrolysis was performed by Entek PS95D model potentiostat. This device was used for the supply of a constant potential during the electrochemical polymerization. A potentiostat requires an electrochemical cell with three electrodes called working, reference and counter electrodes. Electrochemical reactions studied occur at the working electrode.

The reference electrode is used in measuring the working electrode potential. A reference electrode should have a constant electrochemical potential as long as no current flows through it. Potentiostat is used to maintain the voltage difference between the working and reference electrodes at a constant desired value during the electrolysis.

### 2.2.2 Electrolysis Cell

Constant potential electrolysis (CPE) was carried out in a electrolysis cell with three electrode system namely working, counter and reference electrodes. The cell for controlled potential electrolysis system is shown in Figure 2.1. The working and the counter electrodes were platinum foils with an area of 3 $cm^2$. The total volume was 50 ml and the counter and the working electrode compartments were separated by porosity sintered glass disc. The reference electrode was $Ag/Ag^+$. The electrolysis cell was made capable of passing $N_2$ gas through and/or above the solution by providing suitable gas inlets.

### 2.2.3 Differential Scanning Calorimeter (DSC)

Many of the physical (e.g., evaporation) or chemical (e.g., decomposition) transformation are associated with heat absorption (endothermic) or heat liberation (exothermic) [58]. DSC measures the differential heat between an inert reference and the sample upon heating or cooling at a particular rate or under

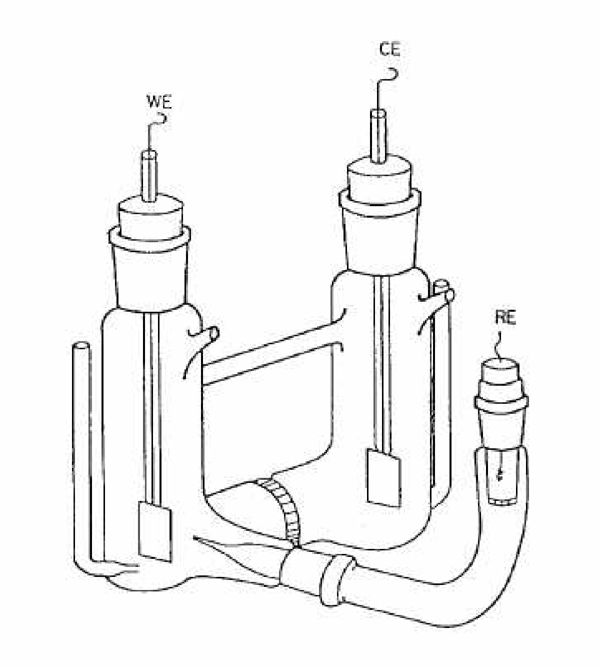


Figure 2.1: Electrolysis Cell

isothermal conditions. If a particular material shows a different thermal characteristic, differential heat flow will exist and DSC will register a signal.

DSC has found applications in almost every class of materials. Examples include evaluation of phase transformation (glass transition, melting, solidification, etc.), decomposition, polymerization, gelation, and curing; evaluation of processing, thermal, and mechanical histories and process modeling.

In this work, DSC experiments were carried out on a DuPont 2100 thermal analyzer system equipped with appropriate modules and interface.

### 2.2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique that permits the continuous weighing of a sample as a function of temperature and/or as a function of time at a desired temperature [58].

In TGA, the sample is heated from room temperature up to 1700$^o$C. The experiments involve several combinations of programmed and isothermal steps.TGA experiments can be conducted in various atmospheres, e.g., vacuum or static flowing inert gases. Modern instruments coupled with mass spectrometry (TGA/MS) offer the possibility for identifying the nature of the weight changes revealed by TGA.

In this work, TGA was used to determine the weight change of the polymer powder with respect to applied temperature. The instruments used were either a Perkin Elmer Pyris1 Thermal Gravimetric Analyzer system equipped with a computer or a DuPont 2100 thermal analyzer system. All experiments were performed in a inert static flowing gas such as argon or nitrogen gases. The temperature was increased at a rate of 10$^o$C/min from room temperature to 1000$^o$C.

## 2.3 Mass Spectrometer

Hawlett-Packard 5973 quadruple mass spectrometry system coupled with a JHP SIS direct insertion probe pyrolysis system was used in this study. There are three main components of mass spectrometry system:

- an ion source which produce ions from the sample to be analyzed
- an analyzer that separetes these ions according to their mass to charge ratios
- and a detector which detects the ions emerging from the analyzer and measure their mass and abundance In addition, a sample introduction system is necessary to introduce the samples to be analyzed to the ion source while providing the high vacuum requirements ($\sim 10^{-6}$ to $10^{-8}$ mbar ). A computer is used to process the data and control the instrument through feedback. Figure 2.2. shows the main components of the mass spectrometer.

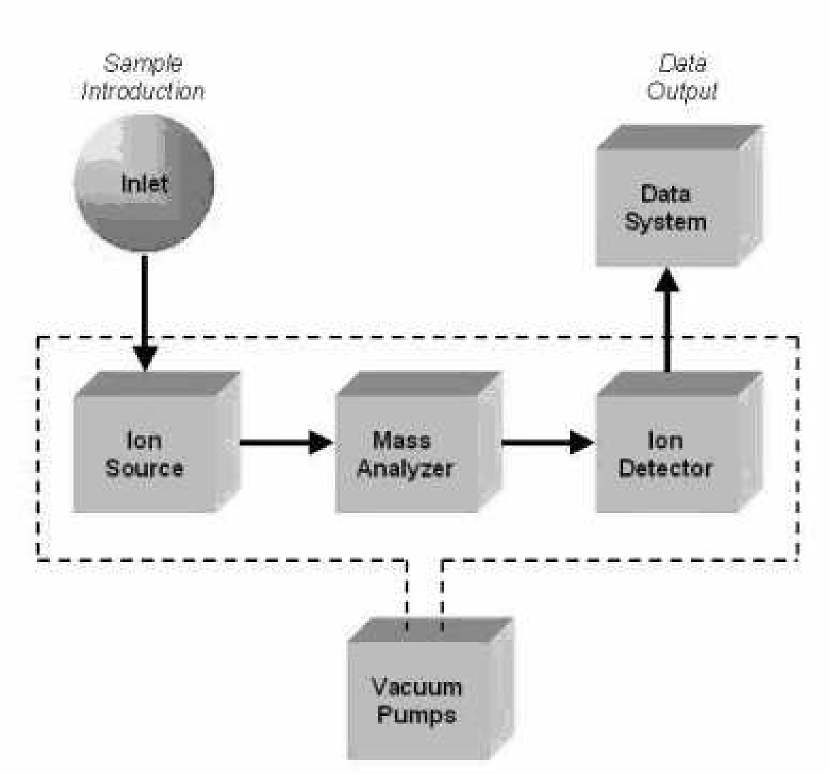


Figure 2.2: Block diagram of mass spectrometer

### 2.3.1 Sample Inlet

5973 HP quadruple mass spectrometry system was coupled to JHP SIS direct insertion probe pyrolysis system, which provides flexibility, direct heating of the sample and fast ramp rates. The heater is positioned at the tip of the probe where it is in direct contact with flared sample vial which is strong and easy to use. Analysis were performed by inserting very small amount (0.01 mg) of sample into the sample vials. By probe software, it is possible to programme heating rates. The temperature increased at a rate of $10^{o}$C/min and kept constant for 10 min at $445^{o}$C

### 2.3.2 Ion Source

The traditional method of ion production in mass spectrometry is electron impact or electron ionization (EI). In electron impact ionization, gaseous sample molecules are bombarded with a stream of high energy electrons, and then positive ions are produced. The sample is ionized and/or fragmented, as represented by the following equation:

$$AB + e^- \longrightarrow A^+ + B + 2e^-$$

In this study, electron impact ion source was used. The experiments were carried out using 70 and 19 eV electrons to control and minimize dissociation of thermal decomposition products.

### 2.3.3 Analyzer

A mass analyzer is used to separate the ions formed in the ion source according to their mass-to-charge ratio. There are number of different mass analyzers such as time-of-flight, quadrupole, magnetic sector and fourier transform analyzers. A quadrupole mass analyzer is a device which uses the stability of trajectories to separate ions according to their m/z ratio. A quadrupole consist of four rods arranged in parallel where those opposite to another are electrically connected. A quadrupole has a number of advantages including the low cost construction, their compact size, and fast scanning capability. The 5973 HP system used works with a quadrupole mass analyzer with a range 1.6-800 amu (atomic mass units).

### 2.3.4 Detector

The ion beam passes through the mass analyzer and is then detected and transformed into a usable signal by a detector. In the present work the detector is a high energy conversion dynode (HED) coupled to an electron multiplier (EM). The detector is located at the exit and of the quadrupole mass filter.

## 2.4 Procedure

### 2.4.1 Electrochemical Polymerization of Aniline

Polyaniline was prepared by electrochemical polymerization of 0.1 M aniline at +0.8V for 30 minutes in 0.5 M aqueous $H_2SO_4$ solution. Nitrogen gas was purged from the system prior to the electrolysis. The electrode was then washed with distilled water to remove the supporting electrolyte and dried at $60^o$C for 3 hours.Polyaniline was obtained in powder form.

### 2.4.2 Electrochemical Polymerization of Pyrrole

Polypyrrole was prepared by electrochemical polymerization of 0.02 M pyrrole +1.0 V for 30 minutes in 0.5 M aqueous $H_2SO_4$ solution. Nitrogen gas was purged from the system prior to the electrolysis.Electrode was then washed with distilled water to remove the supporting electrolyte and dried at $60^o$C for 3 hours.Polypyrrole was obtained in the form of freestanding films and peeled off from the electrode

### 2.4.3 Synthesis of PANI/PPy Films

0.1 M aniline monomer was polymerized electrochemically in 0.25 M $H_2SO_4$ aqueous solution for 30 minutes at +0.8V under inert atmosphere.Electrode was then washed with distilled water to remove the supporting electrolyte and dried at $60^o$C for 1 hour. The Polyaniline coated platinum electrode was then used as working electrode for electropolymerization of 0.02 M pyrrole monomer in 0.25 M $H_2SO_4$ aqueous solution for 30 minutes at +1.0V under inert atmosphere. The Electrode was then washed with distilled water to remove the supporting electrolyte after the synthesis and dried at $60^o$C for 3 hours. This procedure was repeated using 0.50 M $H_2SO_4$ and 1.0 M $H_2SO_4$ electrolyte/solvent system.

### 2.4.4 Synthesis of PPy/PANI Films

0.02 M pyrrole monomer was polymerized electrochemically in 0.25 M $H_2SO_4$ for 30 minutes at +1.0 V under inert atmosphere. The electrode was then washed with distilled water to remove the supporting electrolyte and dried at 60$^o$C for 1 hour. The Polypyrrole coated platinum electrode was then used as working electrode for electropolymerization of 0.1 M aniline in 0.25 M $H_2SO_4$aqueous solution for 30 minutes at +0.8 V under inert atmosphere. The electrode was then washed with distilled water to remove the supporting electrolyte and dried at 60$^o$C for 3 hours. This procedure was repeated using 0.50 M $H_2SO_4$ and 1.0 M $H_2SO_4$ electrolyte/solvent system.

### 2.4.5 Preparation of PANI/PPy Physical Blend

0.1 M aniline was polymerized electrochemically in 0.50 M $H_2SO_4$ aqueous solution for 30 minutes at +0.8 V under inert atmosphere. The electrode was then washed with distilled water to remove the supporting electrolyte and dried at 60$^o$C for 3 hour. 0.02 M pyrrole monomer was polymerized electrochemically in 0.50 M $H_2SO_4$ aqueous solution for 30 minutes at +1.0 V under inert atmosphere.Electrode was then washed with distilled water to remove the supporting electrolyte and dried at 60$^o$C for 3 hours. Then electrochemically synthesized homopolymers, PANI and PPy, were mixed physically.

# CHAPTER 3

# RESULTS AND DISCUSSIONS

## 3.1 Thermal Analysis

In any application knowledge of the stability and degradation is of primary importance and several studies have appeared in the literature on stability of polyaniline. Thermal stability of PANI was mainly investigated by means of thermogravimetric analysis [59-73]. In some of these studies data from other characterization techniques such as elemental analysis, differential scanning calorimetry, x-ray photoelectron spectroscopy, infrared spectroscopy, UV-visible spectroscopy, and conductivity measurements have been reported. The conductivity was clearly shown to decrease with time, with a rate depending on the nature of the dopant as well on the morphology of the material.

It has been determined that undoped polyaniline (polyemeraldine base form) does not show any significant decomposition below 700 K [68, 69]. The lowered thermal stability of the conducting form is mainly attributed to the decomposition of the counterion. In general, three stages of thermal degradation, the first being due to removal of dopants, the second due to loss of low molecular weight oligomers or side products and the final due to the degradation of backbone units of PANI were detected. It has been noticed that the thermostability of protonated PANI is the same as for the dopants stability [64]. Among the several studies on thermal degradation of PANI, only few were concentrated on identification of thermal degradation products. In a recent work, direct insertion probe pyrolysis mass spectrometry technique was applied to investigate the thermal and the structural characteristics of electrochemically prepared HCl and $HNO_3$ doped polyaniline (PANI) films [74]. It has been determined that the thermal degradation of both of the samples showed three main thermal degradation stages. The first was associated with evolution of solvent and low molecular weight species adsorbed on the polymer, the second was attributed to evolution of dopant based products and the final degradation stage at moderate and elevated temperatures was associated with evolution of degradation products of the polymer. Chlorination and nitrolysis of aniline during the electrochemical polymerization was detected. It has been further determined that as the electrolysis period was increased, the extent of substitution increased. In addition, for the $HNO_3$ doped PANI evolution of $CO_2$ at elevated temperatures confirmed oxidation of the polymer film during the electrolysis.

Pyrolysis mass spectrometry analysis of $BF_4^-$ and p-toluene sulfonic acid doped polypyrrole showed that pyrolysis of doped polypyrrole mainly occurs in three regions as in the case of PANI [75-77]. The low temperature peaks were associated with adsorbed water, the solvent and the unreacted pyrrole. The dopant peaks were recorded around 250$^o$C. In the last stage of pyrolysis decomposition products of PPy were observed. In general, only very low yield for monomer and oligomers was detected due to the crosslinked structure which caused decomposition of the pyrrole ring. It has been noted that at high $BF_4{}^-$ concentrations, aromatic structure was enhanced contrary to what was observed for p-toluene sulfonic acid doped polypyrrole samples, most probably due to higher extent of oxidation. It has been determined that although counterion dependence of structure was noted, considering the results obtained in previous studies it may be proposed that thermal stability of both of the polypyrrole forms are independent of the type of the dopants involved and doping levels studied.

In this work, the thermal degradation behavior of pure PANI, pure PPy homopolymers, PANI-PPy physical blend, PANI/PPy, PPy/PANI films and the effect of dopant concentration on structural and thermal characteristics are discussed using TGA, DSC and pyrolysis mass spectrometry techniques.

### 3.1.1 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis measurements were done from room temperature to 1000$^o$C at a heating rate of 10$^o$C/min under $N_2$ atmosphere. In Figures 3.1-3.4, our discussion is aimed to show the amount of weight loss with respect to temperature in electrochemically synthesized pure polyaniline, pure polypyrrole, PANI/PPy Film, PPy/PANI film in 0.5 M $H_2SO_4$ respectively.

Table 3.1: TGA results of electrochemically synthesized pure PANI, pure PPy, PANI/PPy film, PPy/PANI film in 0.50 M $H_2SO_4$

| POLYMER | Decomposition Temperature ($^oC$) | % weight loss at Decomposition Temperature | % weight loss at 430$^o$C | % weight loss at 830$^o$C |
|---|---|---|---|---|
| Pure PANI | 230 | 33 | 62 | 98 |
| Pure PPy | 280 | 32 | 47 | 95 |
| PANI/Ppy | 272 | 43 | 54 | 97 |
| PPy/PANI | 272 | 22 | 37 | 98 |

All these Figures, mentioned above, have the similar behavior. They showed nearly the same stability. They had three step weight loss behavior with different percentages. The first weight loss has been seen at temperatures up to 100$^o$C. This can be attributed to loss of water molecules from the polymer matrix. The second weight loss started at around 150$^o$C which is due to co-evolution of water and/or evolution of acid. Finally, the third step starting at around 250$^o$C has been seen. It indicates oxidative degradation of the polymer backbone.

#### 3.1.1.1 Thermal Gravimetric Analysis (TGA) of Pure PANI and Pure PPy

Table 3.1 shows maximum decomposition temperatures and remaining percent weight of pure PANI and pure PPy, synthesized in aqueous $H_2SO_4$, at specific temperatures. The transitions for pure PANI at 230$^o$C and for pure PPy at 280$^o$C are due to the removal of the dopant ion and low molecular weight species from the matrix. If we compare thermal behaviors of these pure polymers, PANI has a lower decomposition temperature than PPy and but it has nearly the same transition showing %33 weight loss at 230$^o$C (Figure 3.1). However, Ppy has a higher decomposition temperature at 280$^o$C with a %32 weight loss (Figure 3.2). PPy had a slightly smaller weight loss than PANI at their decomposition temperatures. Also, TGA of pure PPy indicated at 830$^o$C %5 of weight remains, but for pure PANI at the same temperature only %3 of the weight remained. Hence, we can conclude that pure PPy is slightly more resistant to heat than pure PANI.

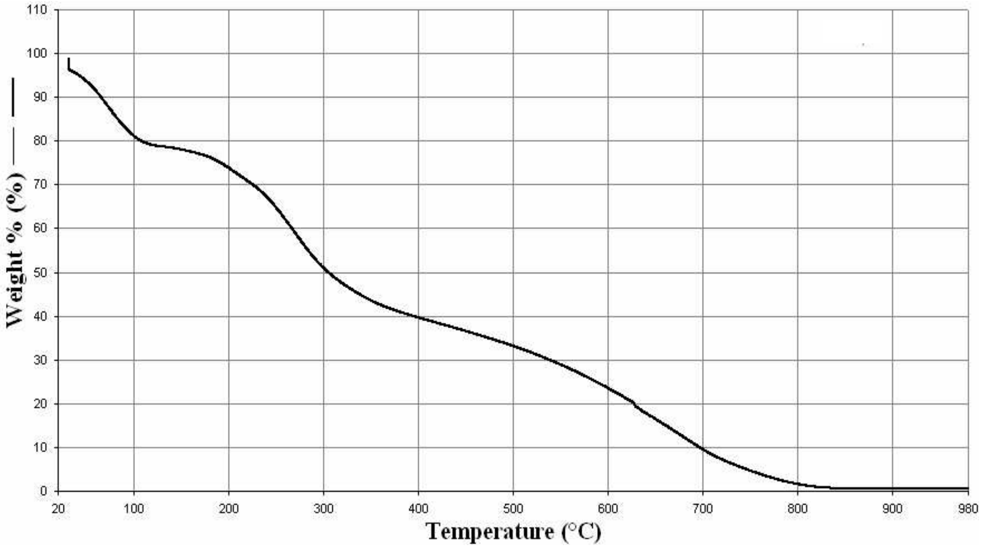


Figure 3.1: TGA of pure PANI

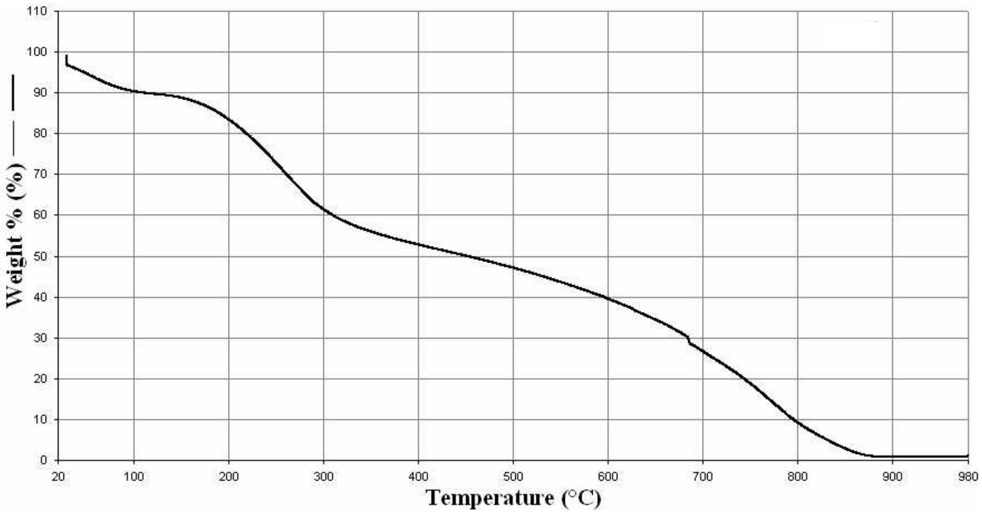


Figure 3.2: TGA of pure PPy

#### 3.1.1.2 Thermal Gravimetric Analysis (TGA) of PANI/PPy and PPy/PANI Films

Table 3.1 shows maximum decomposition temperatures and remaining percent weight of PANI/PPy and PPy/PANI films, synthesized in aqueous $H_2SO_4$, at specific temperatures.

PANI/Ppy film has a decomposition temperature at 272$^o$C. % 43 weight losses were observed at this temperature and % 3 is left when heated up to 830$^o$C (Figure 3.4). From these data we can say that PANI/Ppy film showed less resistance to heat than its pure components at its decomposition temperature. But the value of its remaining weight at 830$^o$C was between that of its pure components.

PPy/PANI film showed completely different behavior than PANI/PPy film. PPy/PANI film has a decomposition temperature at 272$^o$C. % 22 weight losses were observed at this temperature and % 2 is left when heated up to 830$^o$C (Figure

3.3). In contrast to PANI/Ppy film, PPy /PANI film showed more resistance to heat than its pure components at its decomposition temperature. It has been observed that % 2 of its weight remained after the heating up to 830$^o$C which has the same value as in the pure PANI.

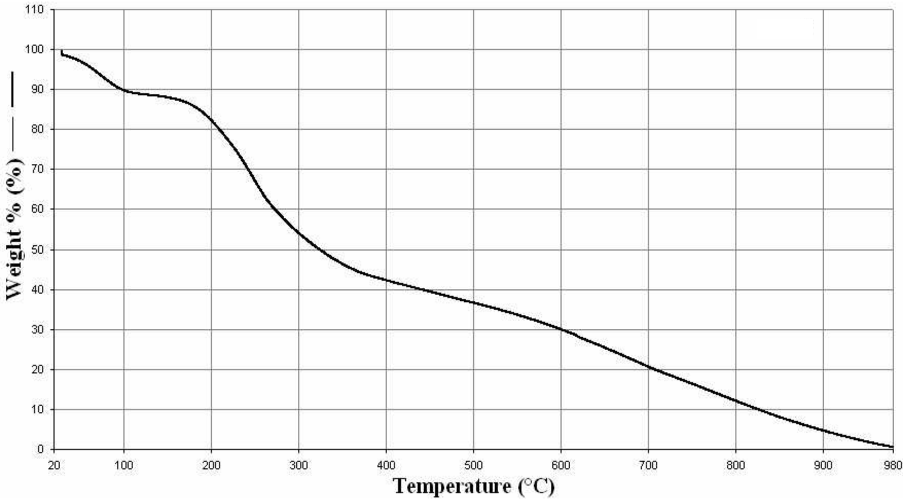


Figure 3.3: TGA of PPy/PANI film in 0.50 M $H_2SO_4$

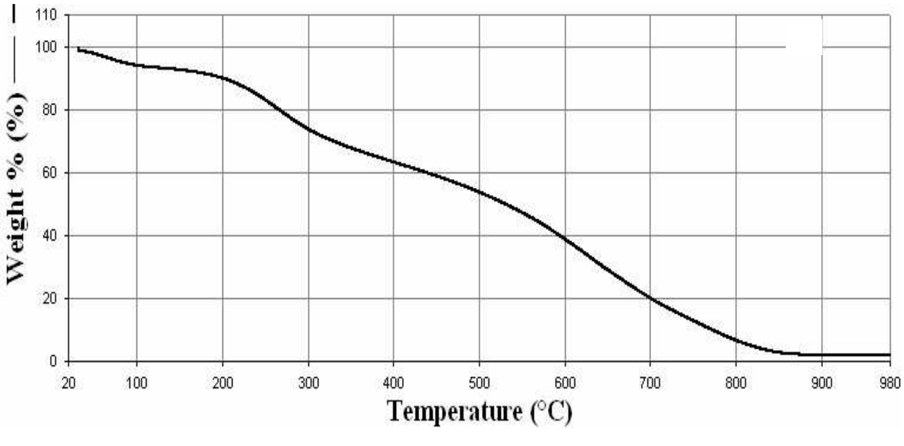


Figure 3.4: TGA of PANI/PPy film in 0.50 M $H_2SO_4$

### 3.1.2 Differential Scanning Calorimetry Analysis (DSC)

Figures 3.5-3.8 shows DSC behavior of electrochemically synthesized pure polyaniline, pure polypyrrole, PANI/PPy Film, PPy/PANI film in 0.5 M $H_2SO_4$ respectively. In all of these figures, only endothermic peaks could be observed at different temperatures according to synthesis conditions.

These endothermic peaks were most likely due to the vaporization of water, which was proofed by TGA results mentioned before. The chemical process related to the exothermic peaks, which indicate crosslinking reactions were not observed in any of these DSC Figures.

Figure 3.5. and 3.6. demonstrates The DSC thermogram of pure PANI and pure PPy synthesized in 0.5 M $H_2SO_4$. Pure PANI showed two endothermic transitions at around 140 $^{o}$C and 275 $^{o}$C. Pure PPy exhibited endothermic transitions at around 100 $^{o}$C and 280 $^{o}$C. The first transitions occurred due to the evolution of low molecular weight fragments. Second transitions have been seen due to the loss of dopant ion. Hence, PPy has slightly higher decomposition temperature than PANI which is also confirmed with TGA results.

Figure 3.7. demonstrates the DSC thermogram of PANI/PPy film which exhibited endothermic transitions at around 90$^{o}$C and 250 $^{o}$C. Figure 3.8. shows the DSC thermogram of PPy/PANI film which exhibited endothermic transitions at around 110C and 270 $^{o}$C. These transitions have been seen again due to the evolution of low molecular fragments and dopant ion respectively.

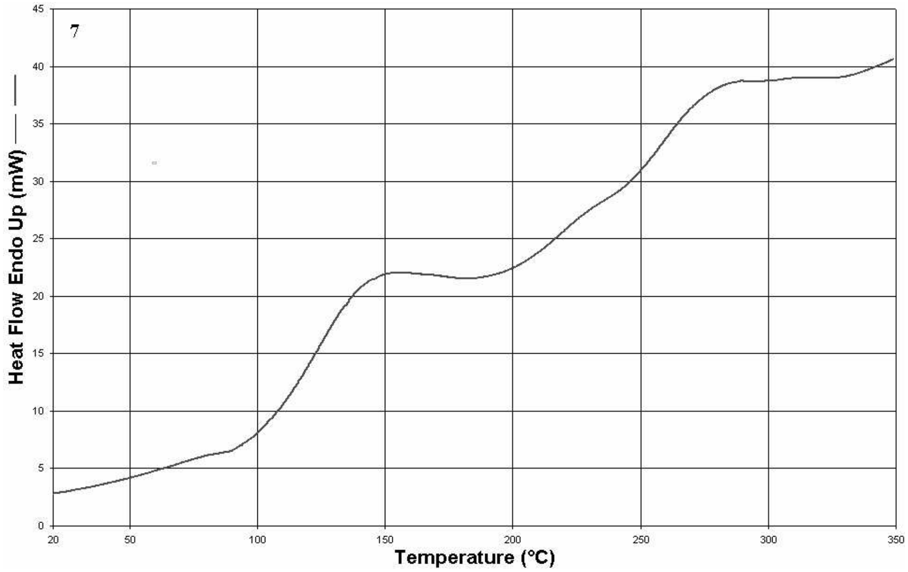


Figure 3.5: DSC of pure PANI

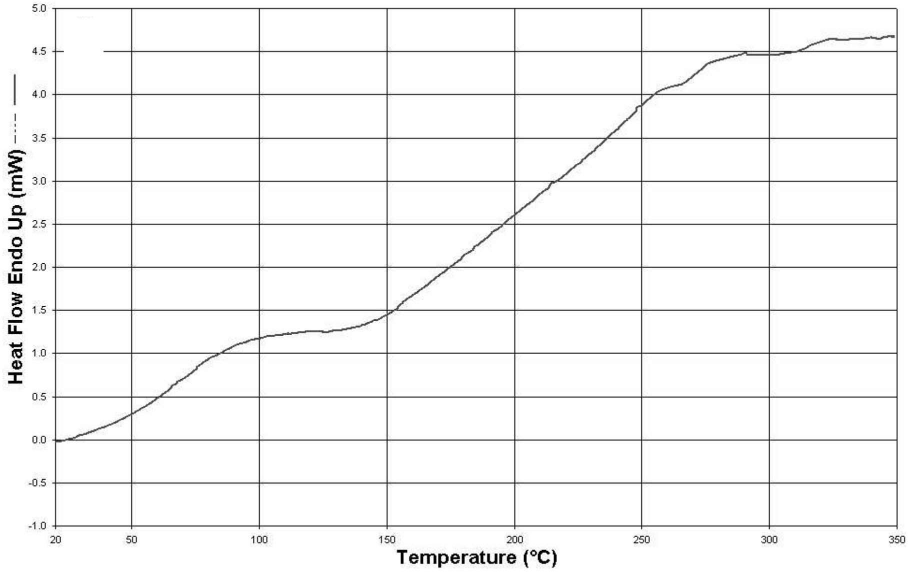


Figure 3.6: DSC of pure PPy

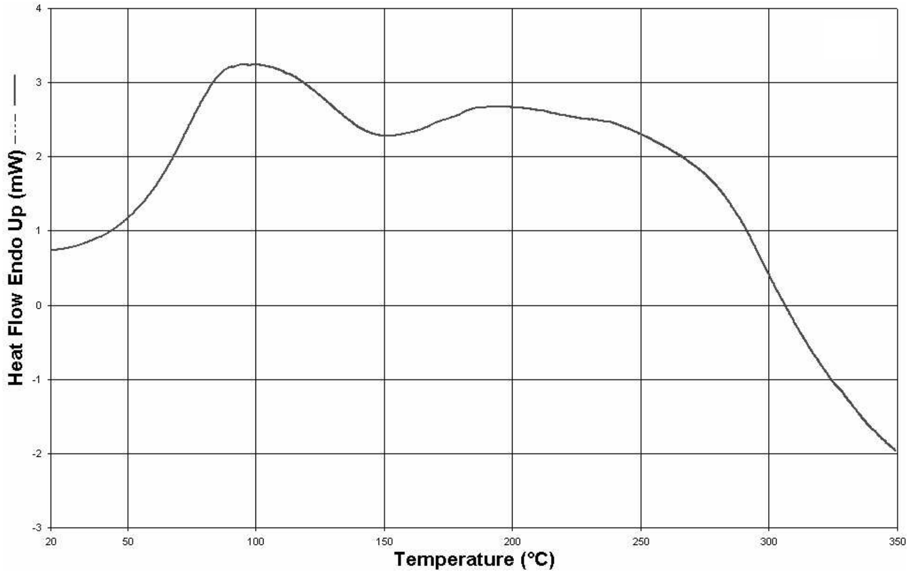


Figure 3.7: DSC of PANI/PPy film in 0.50 M $H_2SO_4$

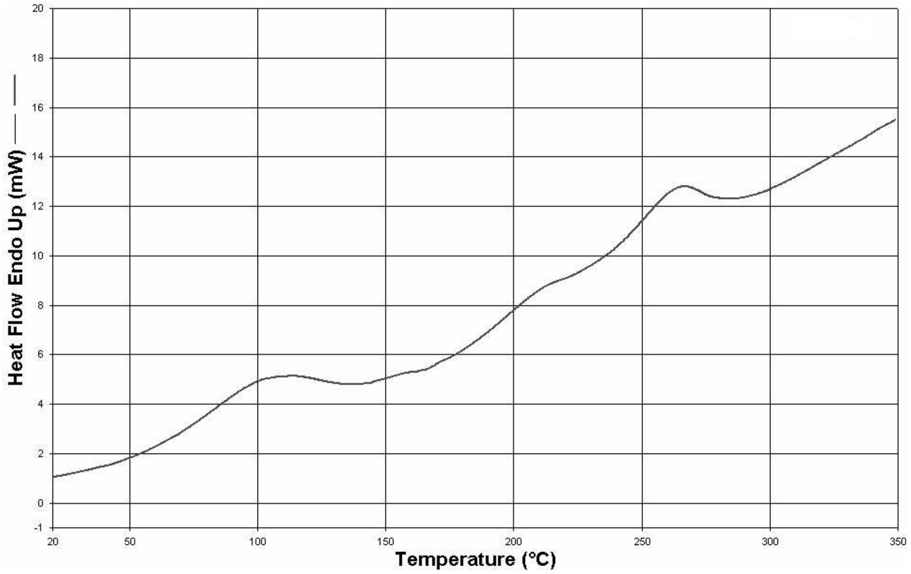


Figure 3.8: DSC of PPy/PANI film in 0.50 M $H_2SO_4$

### 3.1.3 Mass Spectrometry Analysis

#### 3.1.3.1 Electrochemically Prepared Pure PANI Film in 0.50 M $H_2SO_4$

The total ion current (TIC) curve recorded during the pyrolysis of 0.50M $H_2SO_4$ doped pure PANI is shown in Figure 3.9. together with the mass spectra recorded at the maxima of the TIC curve. The mass spectral data are summarized in Table 3.2.

At moderate and high temperatures, presence of $H_2O$ (m/z=17 and 18 Da) peaks has been observed. As the temperature increased, relative intensity of water increased. Evolution of water at low temperatures showed the presence of water adsorbed on the sample. On the other hand, its evolution at high temperatures indicated genenaration of water during the decomposition of the polymer pointing out oxidation of the polymer.

Dopant based peaks such as SO ( m/z=48 Da) and $SO_2$ ( m/z=64 Da) were more intense than those based to degradation products of PANI

Evolution profiles of some characteristic products, namely $CO_2$ (m/z =44 Da), $H_2SO_2$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO (m/z = 48 Da), $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z =93 Da) are shown in Figure 3.10.

It could be concluded that at elevated temperatures, relative yield of monomer namely $C_6H_5NH_2$ (m/z= 93) was quite high indicating the decomposition of polyaniline homopolymer. Evolution of polyaniline dimer (m/z =184 Da) and diphenylamine $C_6H_5NHC_6H_5$ (m/z =169 Da) at high temperatures showed similar trends with the monomer. But it was noticed that the relative yield of polyaniline dimer and diphenylamine were much lower.

Evolution of $SO_2$, $CO_2$ and CO at high temperatures indicated that the polymers exposed to oxidation in the $H_2SO_4$ medium during the synthesis or storage conditions. It was also noted that as the temperature increased the evolution of $CO_2$ increased as can be observed from the data given in Table 3.2.

Table 3.2: The characteristic and/ or intense peaks present in the pyrolysis mass spectra at the maxima of the TIC curves of O.5M $H_2SO_4$ doped Pure PANI, Pure PPy, PANI/PPy phys.blend

| | Pure PANI Relative Yield | | Pure PPy Relative Yield | | PANI/PPy phys. blend Relative Yield | | Assignment |
|---|---|---|---|---|---|---|---|
| m/z | 270$^o$C | 445$^o$C | 265$^o$C | 445$^o$C | 265$^o$C | 445$^o$C | |
| 18 | 207 | 409 | 207 | 846 | 026 | 355 | $H_2O$ |
| 26 | 1 | 6 | 01 | 18 | 00 | 12 | $C_2H_2$, CN |
| 44 | 039 | 124 | 0205 | 1000 | 138 | 553 | $CO_2$ |
| 48 | 478 | 438 | 457 | 081 | 444 | 426 | SO |
| 64 | 1000 | 1000 | 1000 | 0179 | 1000 | 1000 | $SO_2$ |
| 65 | 74 | 56 | 10 | 09 | 42 | 53 | $C_5H_5$ |
| 66 | 109 | 127 | 52 | 16 | 058 | 107 | $C_4H_4N$ or $H_2SO_2$ |
| 67 | 09 | 17 | 04 | 20 | 01 | 12 | $C_4H_4NH$ (monomer) |
| 80 | 102 | 025 | 00 | 00 | 15 | 00 | $C_5H_6N$ or $SO_3$ |
| 93 | 152 | 253 | 01 | 15 | 064 | 183 | $C_6H_5NH_2$ (monomer) |
| 132 | 00 | 00 | 00 | 00 | 00 | 00 | Pyrrole dimer |
| 169 | 00 | 19 | 00 | 03 | 00 | 02 | $C_6H_5NHC_6H_5$ |
| 184 | 01 | 16 | 00 | 00 | 00 | 01 | aniline dimer |

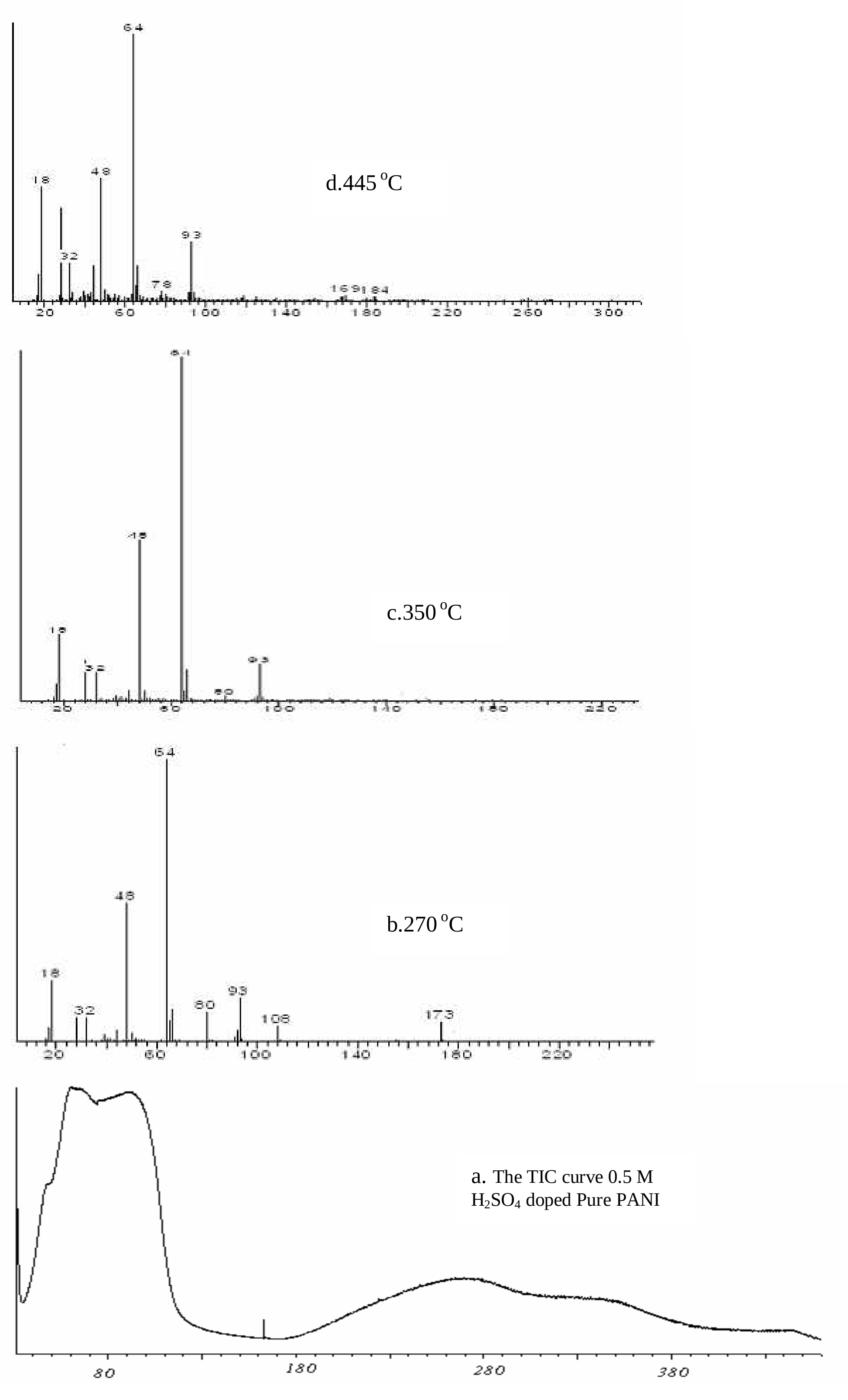


Figure 3.9: Total ion current curve of a. 0.5 M $H_2SO_4$ doped Pure PANI and the mass spectra recorded at b.270$^o$C, c. 350$^o$C, d.445$^o$C.

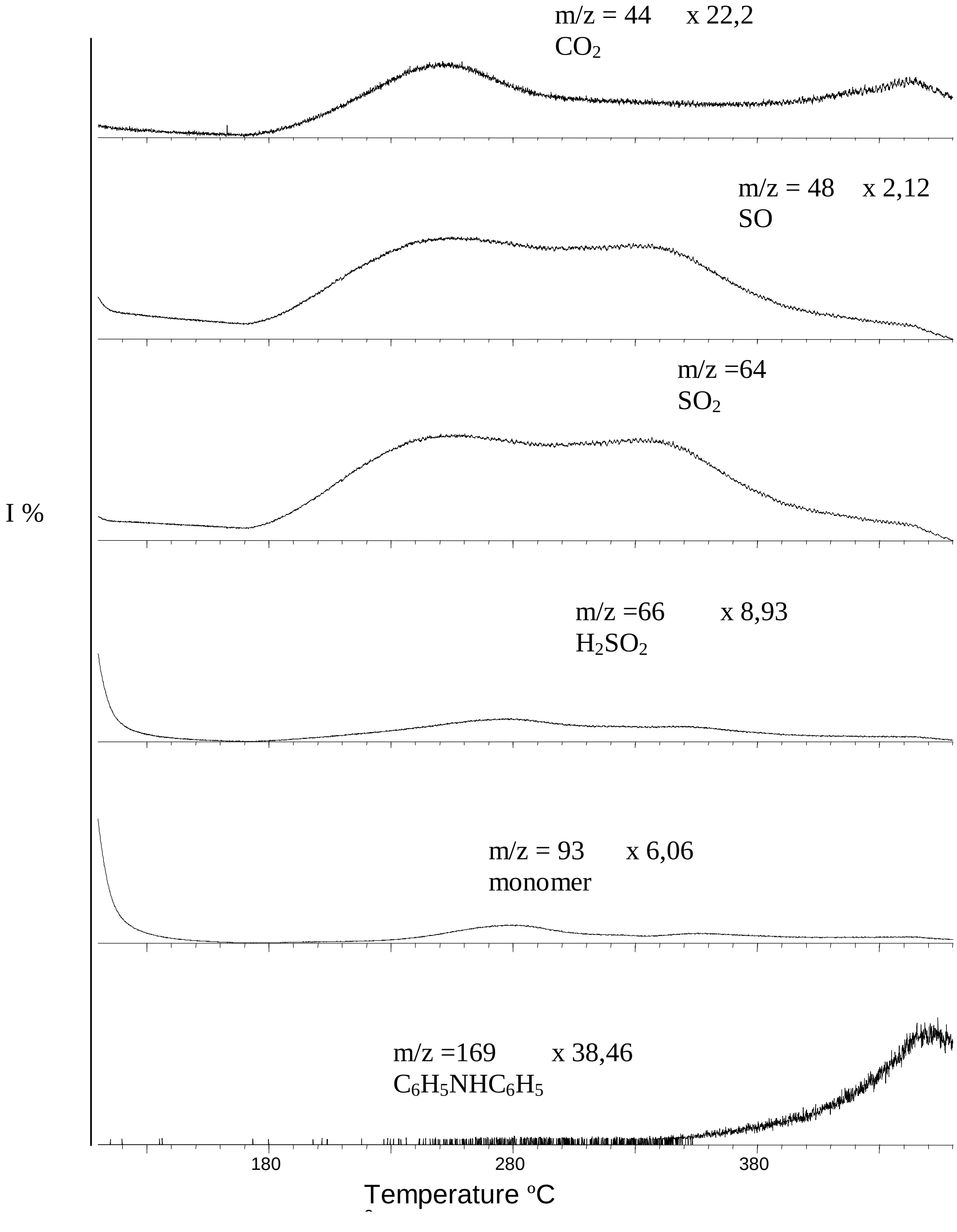


Figure 3.10: Single ion pyrograms of ions at m/z 44, 48, 66, 93, 93, 169 Da recorded during pyrolysis of 0.5 M $H_2SO_4$ doped Pure PANI.

#### 3.1.3.2 Electrochemically Prepared Pure PPy Film in 0.50 M $H_2SO_4$

The total ion current (TIC) curve recorded during the pyrolysis of 0.50M $H_2SO_4$ doped pure PPy is shown in Figure 3.11. together with the mass spectra recorded at the maxima of the TIC curve. The mass spectral data are collected in Table 3.2.

$H_2O$( m/z=17 and 18 Da) peaks were detected at moderate and elevated temperatures. It was noticed that as the temperature increased, relative yield of water showed significant increase. Evolution of water at low temperatures can directly be attributed to presence of water adsorbed on the sample. Yet, high temperature $H_2O$ evolution pointed out oxidation of pyrrole units.

Relative yield of peak at m/z=27 Da increased at elevated temperatures. According to literature results this peak belongs to HCN due to the decomposition of pyrrole ring. HCN peak is not present in the mass spectrum of pyrrole. Then, it can be concluded that generation of HCN at 445 $^{o}$C was mainly due to decomposition of polypyyrole having crosslinked structure, as a depolymerization mechanism yielding mainly the monomer can only be observed if a given polymer does not have a crosslinked structure.

Dopant based peak $SO_2$ (m/z=64 Da) have higher relative yield than monomer and oligomer based peaks. For pure PPy it was noted that the evolution of dopant based SO ( m/z=48 Da) ratherly decreased at elevated temperature Evolution profiles of some characteristic products, namely $CO_2$ (m/z =44 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO (m/z = 48 Da), HCN (m/z =27 Da) are shown in Figure 3.12.

It has been observed that the relative yield of pyrrole monomer $C_4H_4NH$ (m/z =67 Da) increased at elevated temperatures indicating that the decomposition of polypyrrole mainly occurred at elevated temperatures. Pyrrole dimer and the higher oligomers of pyrrole couldn't be seen at moderate and elevated temperatures and can again be attributed to a crosslinked structure.

The low temperature m/z =66 Da peak may be due to unreacted pyrrole adsorbed on the polymer or may be due to $H_2SO_2$ due to decompositions of $H_2SO_4$ contributing to the same peak.

Again, the evolution of $SO_2$, and $CO_2$ at the high temperature indicated that the polymers exposed to oxidation in the $H_2SO_4$ medium during the synthesis or storage conditions.

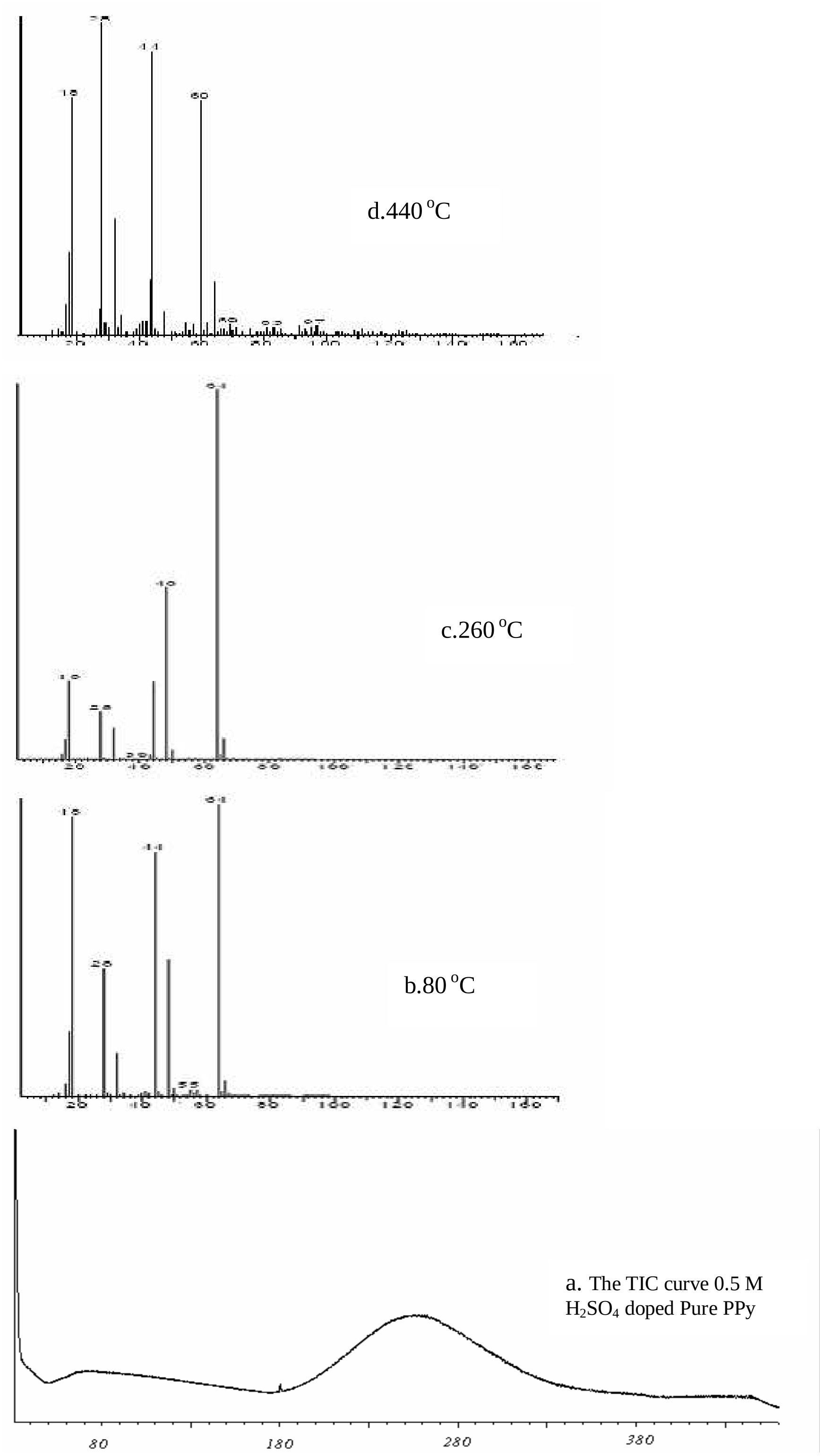


Figure 3.11: Total ion current curve of a. 0.5 M $H_2SO_4$ doped Pure PPy and the mass spectra recorded at b.80C, c. 260C, d.440C.

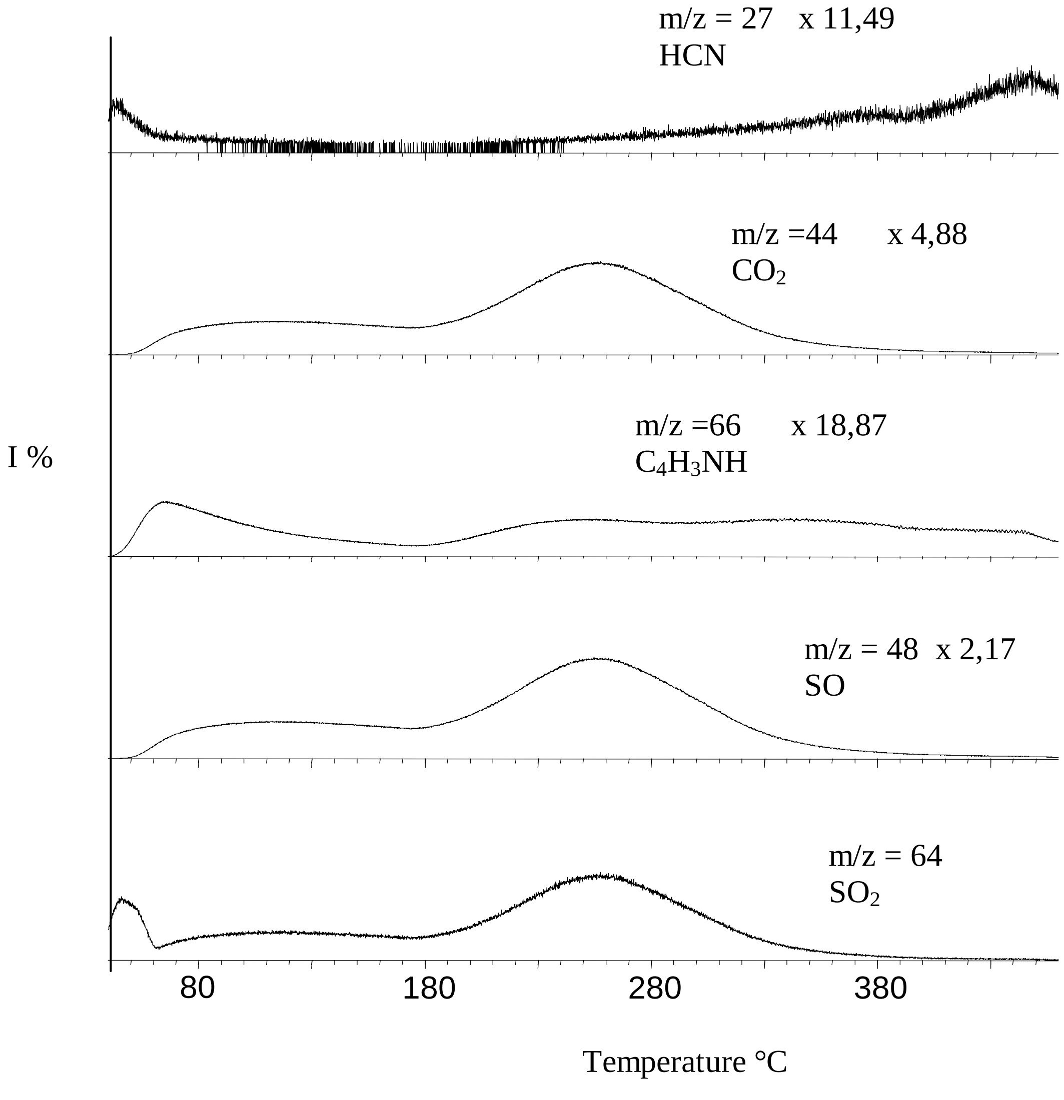


Figure 3.12: Single ion pyrograms of ions at m/z 27, 48, 64, 44, 66 Da recorded during pyrolysis of 0.5 M $H_2SO_4$ doped Pure PPy.

#### 3.1.3.3 Electrochemically Prepared 0.50 M $H_2SO_4$ doped PANI and 0.50M $H_2SO_4$ doped PPy physical blend

The total ion current (TIC) curve recorded during the pyrolysis of 0.50M $H_2SO_4$ doped PANI/PPy physical blend is shown in Figure 3.13 together with the mass spectra recorded at the maxima of the TIC curve. The mass spectral data are also included in Table 3.2.

For the physical blend, weak $H_2O$ (m/z=17 and 18 Da) peaks were detected in pyrolysis mass spectra recorded at 265 $^oC$ and 445 $^oC$. Although, pure PANI and pure PPy samples showed intense $H_2O$ ( m/z=17 and 18 Da) peaks, PANI/PPy physical blend which was prepared by using these pure samples didn't show intense $H_2O$( m/z=17 and 18 Da) peaks. Thus, it can be concluded that presence of water was mainly due to storage conditions. Adsorption of water is very effective due to effective H bonding in the presence of $H_2SO_4$ and aniline.

Dopant based peak $SO_2$ (m/z=64 Da) have the highest intensity for PANI/PPy physical blend as in pure PANI and PPy at high temperatures. It was also noticed that evolution of $CO_2$ was diminished at the high temperatures in contrast to pure PPy samples.

Evolution of water, $CO_2$ and dopant based products at elevated temperatures were attributed to reactions of dopant with the polymer samples. However, decrease in the intensity of these peaks at the high temperatures pyrolysis mass spectra of physical blend indicates that the reactions of dopant with the polymer films were not occured during the synthesis processes but most probably has taken place during storage conditions.

Evolution profiles of some characteristic products, namely $CO_2$ (m/z =44 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO (m/z = 48 Da), $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z =93 Da) are shown in Figure 3.14.

It was also noticable that in contrast to pure PANI and pure PPy, the peak at m/z=28 Da had high intensity in PANI/PPy physical blend. According to literature we can say that the peak at m/z=28 Da may be due to CO, or CH=NH. However, as $CO_2$ yield was quiet low evolution of CO should also be unlikely. Thus, the peak at m/z=28 Da was assigned to CH=NH fragment and associated with the cleavage of the pyrrole ring.

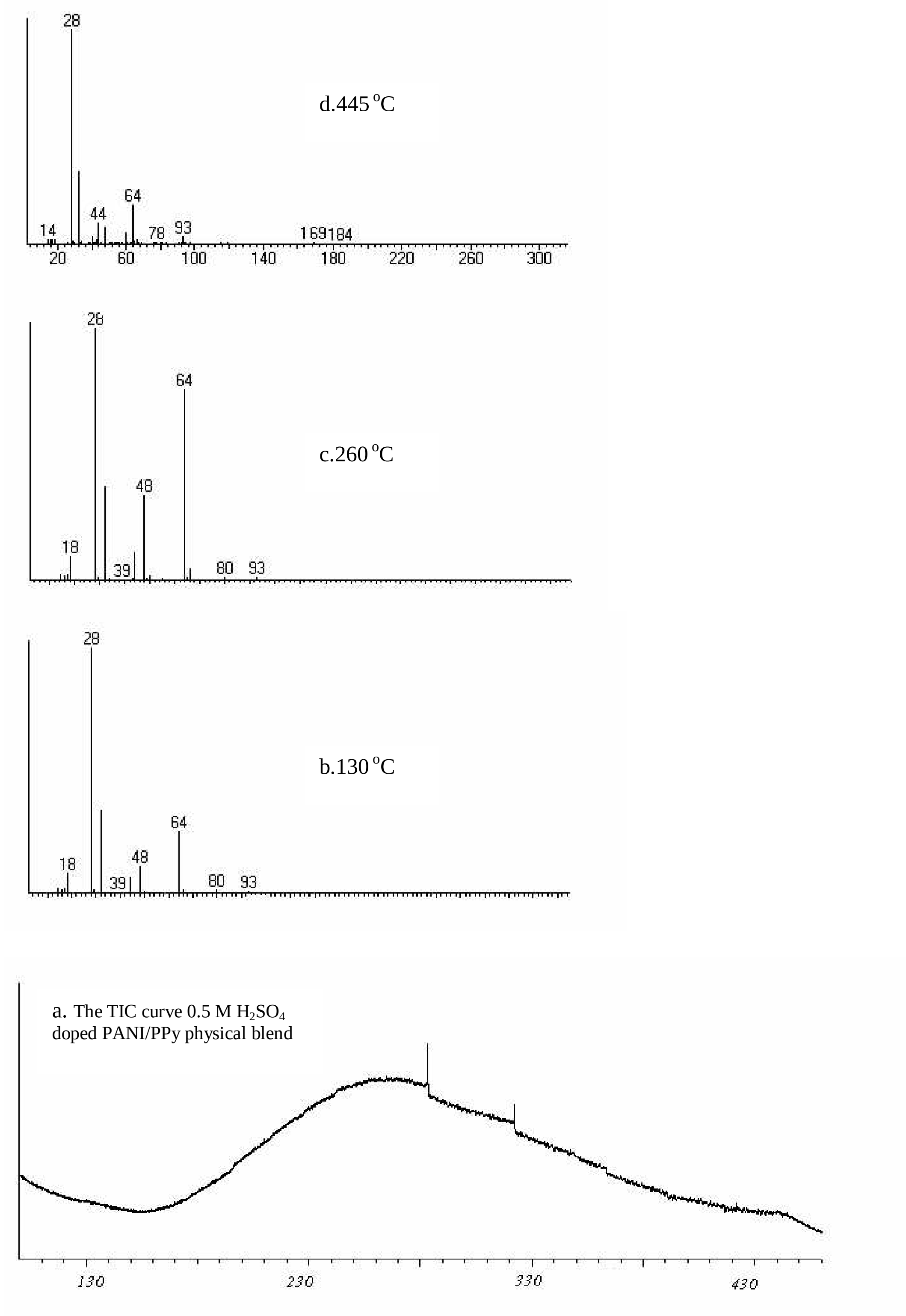


Figure 3.13: Total ion current curve of a. 0.5 M $H_2SO_4$ doped PANI/PPy physical blend and the mass spectra recorded at b.130C, c. 260C, d.445C.

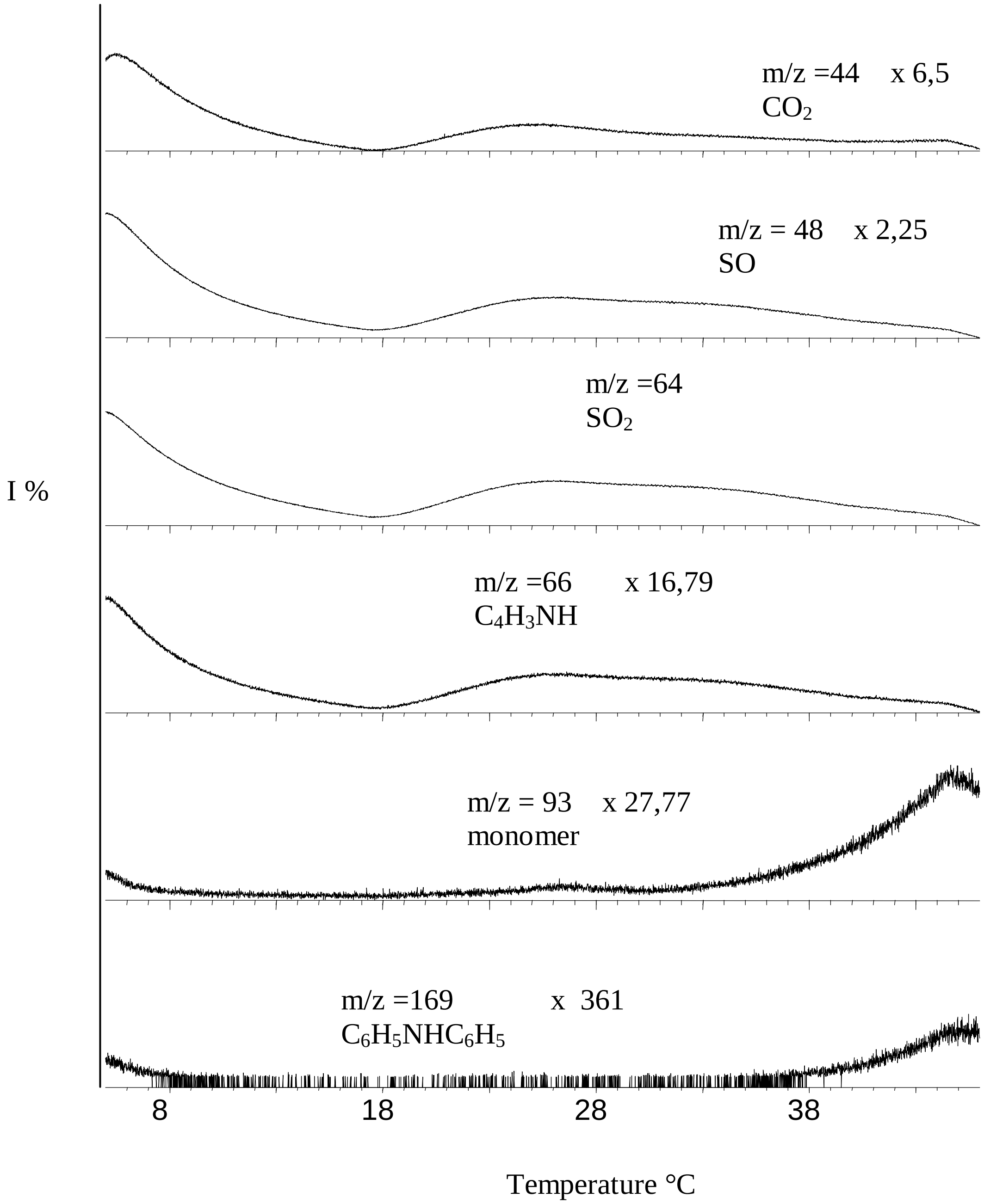


Figure 3.14: Single ion pyrograms of ions at m/z 44, 48, 64, 66, 93, 169 Da recorded during pyrolysis of 0.5 M $H_2SO_4$ doped PANI/PPy physical blend.

#### 3.1.3.4 Electrochemically Prepared PANI/PPy Film

In Figure 3.15. the total ion current (the variation of ion yield as a function of temperature) curves (TIC) of 0.25 M, O.50M and 1.0 M $H_2SO_4$ doped PANI/PPy films prepared by passing current for 30 minutes are shown. Although all the samples showed mainly three degradation stages the trends observed in the TIC curves above 100 $^oC$ are significantly different.

For all samples studied, three main thermal degradation stages have been recorded. Evolution of low molecular weight species around 50-60 $^oC$, just above 100$^oC$ evolution of dopant based products and at moderate and elevated temperatures evolution of degradation products of the polymer occurred.

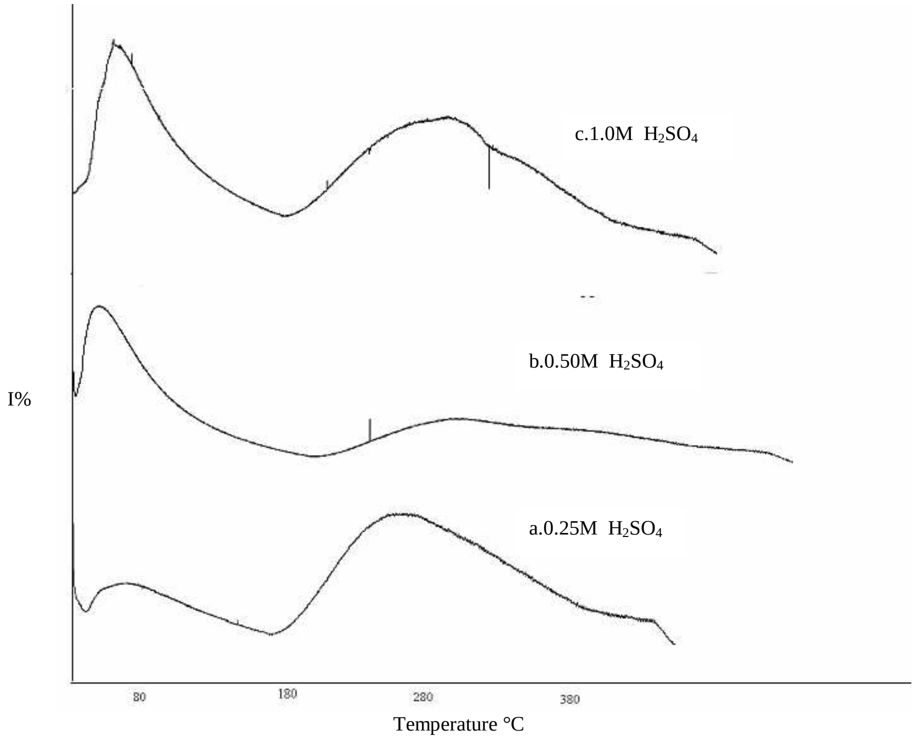


Figure 3.15: Total ion current curve of a. 0.25 M $H_2SO_4$ doped PANI/PPy b. 0.50 M $H_2SO_4$ doped PANI/PPy c. 1.0 M $H_2SO_4$ doped PANI/PPy films.

Table 3.3: The characteristic and/ or intense peaks present in the pyrolysis mass spectra at the maxima of the TIC curves of 0.25M, 0.50M, 1.0 M $H_2SO_4$ doped PANI/PPyI, PANI/PPy2, PANI/PPy3

| | PANI/PPy1<br>Relative Yield | | PANI/PPy2<br>Relative Yield | | PANI/PPy3<br>Relative Yield | | Assignment |
|---|---|---|---|---|---|---|---|
| m/z | $270^{o}$C | $445^{o}$C | $260^{o}$C | $445^{o}$C | $260^{o}$C | $445^{o}$C | |
| 18 | 160 | 445 | 154 | 164 | 155 | 344 | $H_2O$ |
| 27 | 004 | 124 | 08 | 16 | 11 | 58 | $C_2H_3$,or HCN |
| 44 | 184 | 765 | 092 | 128 | 168 | 621 | $CO_2$ |
| 48 | 485 | 437 | 445 | 435 | 492 | 445 | SO |
| 64 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | $SO_2$ |
| 65 | 13 | 32 | 11 | 14 | 13 | 19 | $C_5H_5$ |
| 66 | 63 | 86 | 55 | 57 | 64 | 64 | $C_4H_4N$ or $C_4H_3NH$ |
| 67 | 01 | 28 | 2 | 5 | 1 | 8 | $C_4H_4NH$ (monomer) |
| 80 | 0 | 7 | 8 | 4 | 0 | 8 | $C_5H_6N$ or $SO_3$ |
| 93 | 01 | 78 | 01 | 15 | 01 | 14 | $C_6H_5NH_2$ (monomer) |
| 132 | 0 | 4 | 0 | 0 | 0 | 0 | Pyrrole dimer |
| 169 | 0 | 6 | 0 | 3 | 0 | 2 | $C_6H_5NHC_6H_5$ |
| 184 | 0 | 2 | 0 | 1 | 0 | 0 | aniline dimer |

#### 3.1.3.5 Electrochemically Prepared PANI/PPy Film in 0.25 M $H_2SO_4$ (PANI/PPy1)

The total ion current (TIC) curve recorded during the pyrolysis of 0.25M $H_2SO_4$ doped PANI/PPy film is shown in Figure 3.16. together with the mass spectra recorded at the maxima of the TIC curve. The mass spectral data are summarized in Table 3.3.

At low temperatures $H_2O$ (m/z=17 and 18 Da) based peaks were much more intense than at higher temperature. Evolution of water at lower temperatures showed the presence of water adsorbed on the sample.

Dopant based peaks such as SO (m/z=48 Da) and $SO_2$ ( m/z=64 Da) were more abundant than monomer and oligomer based peaks.

Evolution profiles of some characteristic products, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z =93 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO (m/z = 48 Da), HCN (m/z = 27 Da) are shown in Figure 3.17.

Evolution of aniline and its oligomers at elevated temperatures indicated that the thermal degradation of PANI chains followed mainly a depolymerization mechanism in accordance with literature results. The trends observed in the evolution profile of pyrrole at low and moderate temperatures were almost identical to those for dopant based products. Thus, it may be thought that contribution of $H_2SO_2$ peak to pyrrole peak has occurred. The yield of products generated by decomposition of pyrrole ring, such as HCN, were comparable to that of the monomer. In the literature studies, higher yield for products generated by decomposition of pyrrole ring compared to that of monomer was noted and attributed to a crosslinked structure. Thus, the increase in monomer yield compared to that of HCN indicated that the extent of crosslinked structure was limited for the PPy chains in PANI/PPy1 films.

Evolution of $SO_2$, $CO_2$ and CO evolution at the high temperatures indicated that the polymers exposed to oxidation in the $H_2SO_4$ medium during the synthesis or storage conditions.

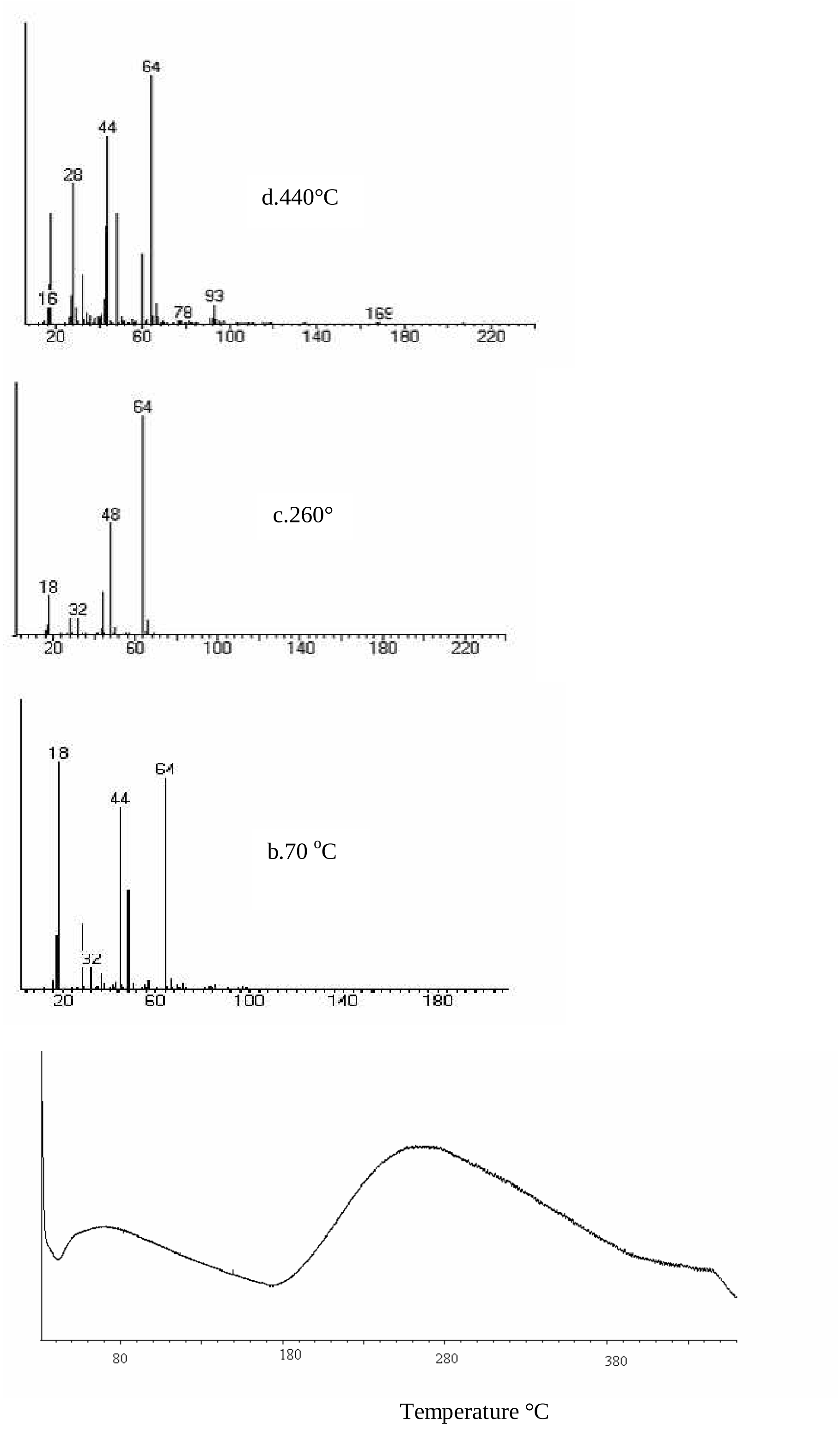


Figure 3.16: Total ion current curve of a. 0.25M $H_2SO_4$ doped PANI/PPy film and the mass spectra recorded at b.70$^o$C, c. 260C, d.440$^o$C.

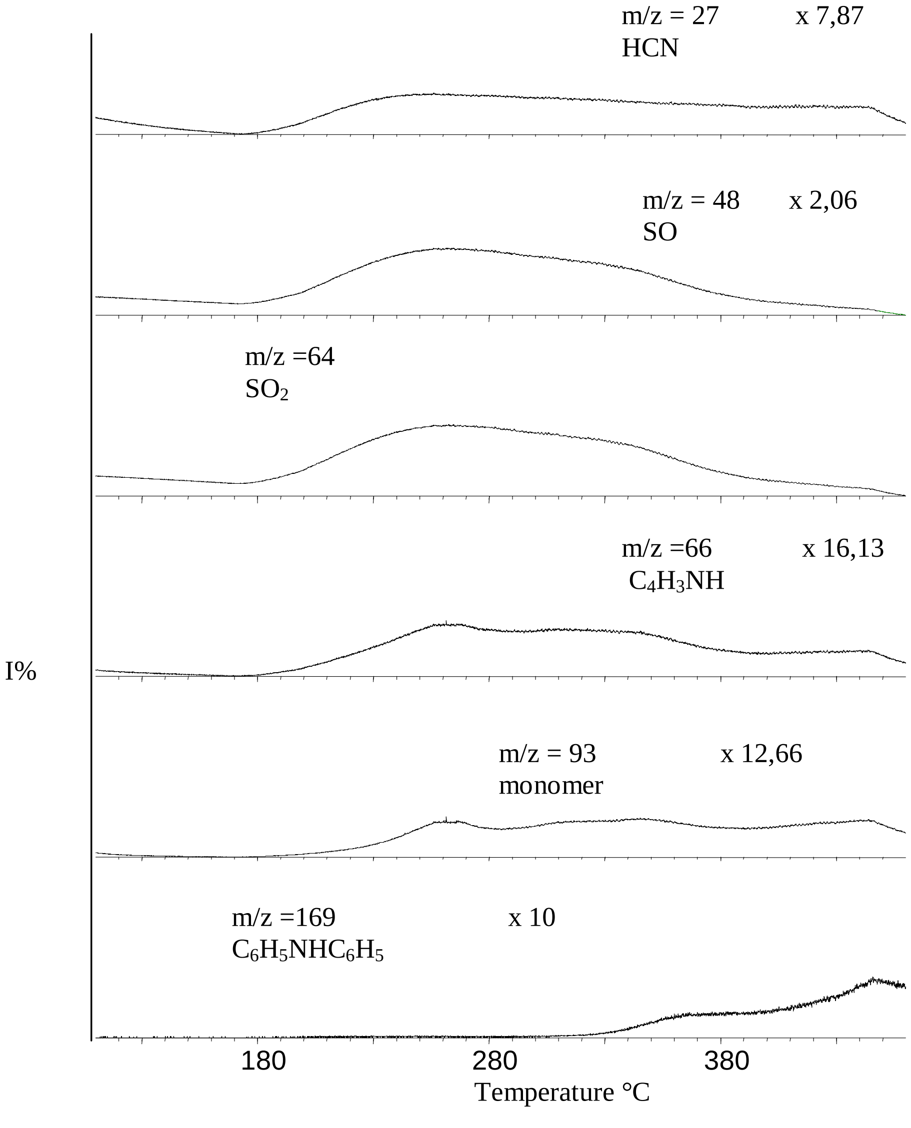


Figure 3.17: Single ion pyrograms of ions at m/z 27, 48, 64, 66, 93, 169 Da recorded during pyrolysis of. 0.25M $H_2SO_4$ doped PANI/PPy film .

#### 3.1.3.6 Electrochemically Prepared PANI/PPy Film in 0.50 M $H_2SO_4$ (PANI/PPy2)

The total ion current (TIC) curve recorded during the pyrolysis of 0.50M $H_2SO_4$ doped PANI/PPy film is shown in Figure 3.18. together with the mass spectra at the maxima of the TIC curve. The mass spectral data are summarized in Table 3.3.

The pyrolysis mass spectra were dominated with identical peaks that were detected for PANI/PPy1 but small variations in relative intensities were noted.

Evolution profiles of the same characteristic products discussed for PANI/PPy1, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z = 93 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO (m/z = 48 Da), HCN (m/z = 27 Da) are shown in Figure 3.19.

Similar trends were observed in the evolution profiles. Yet, the relative intensities of dopant based peaks were increased at initial stages of pyrolysis. On the other hand, the relative abundance of aniline monomer (m/z = 93 Da) decreased compared to that was detected for 0.25M $H_2SO_4$ doped polyaniline. But, the relative abundance of pyrrole monomer, namely $C_4H_3NH$ (m/z =66Da), didn't show any significant change.

Oligomer yields were again low. And the decreasing in abundance of polyaniline dimer, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), was detected.

Again, evolution of $SO_2$, $CO_2$ and CO at the high temperatures indicated that the polymers exposed to oxidation in the $H_2SO_4$ medium.

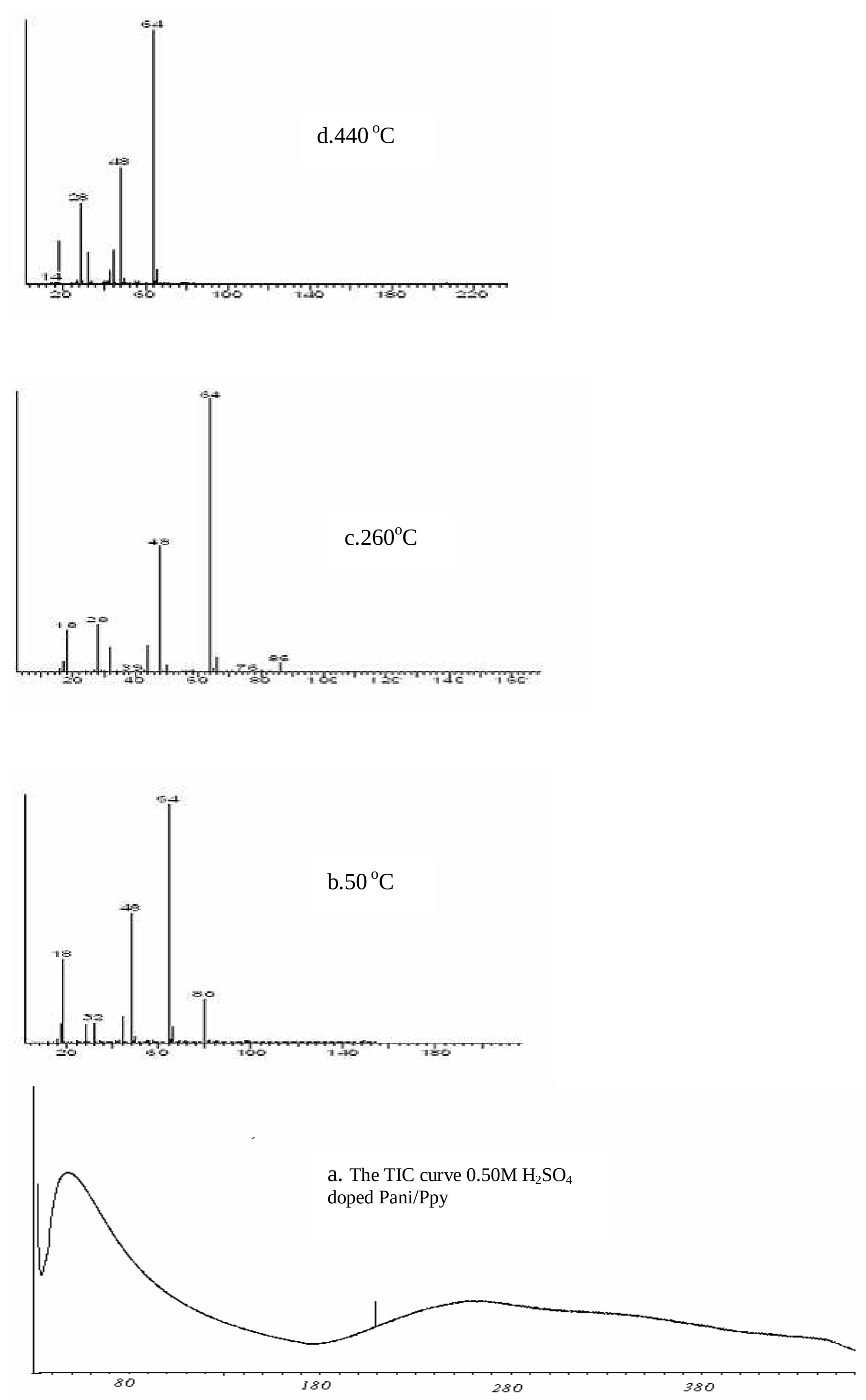


Figure 3.18: Total ion current curve of a. 0.50 M $H_2SO_4$ doped PANI/PPy film and the mass spectra recorded at b.50$^o$C, c. 260$^o$C, d.440$^o$C.

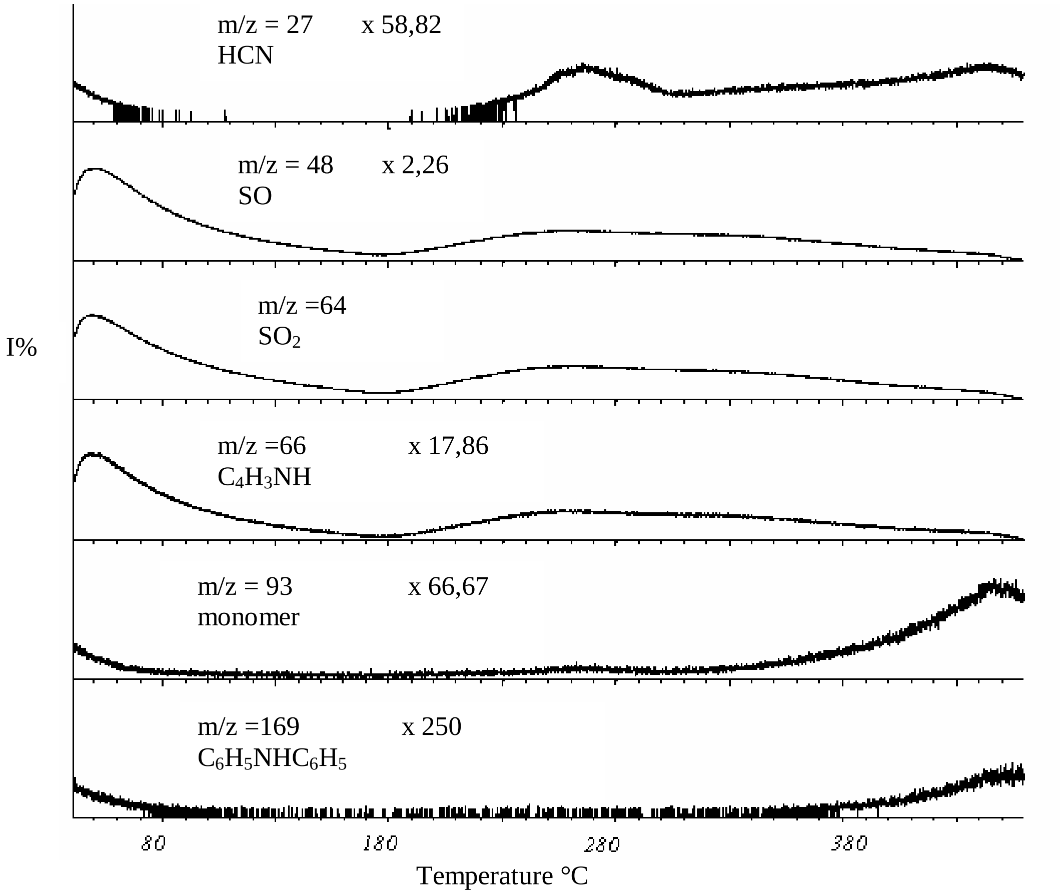


Figure 3.19: Single ion pyrograms of ions at m/z 27, 48, 64, 66, 93, 169 Da recorded during pyrolysis of. 0.50M $H_2SO_4$ doped PANI/PPy film.

#### 3.1.3.7 Electrochemically Prepared PANI/PPy Film in 1.0 M $H_2SO_4$ (PANI/PPy3)

The total ion current (TIC) curve recorded during the pyrolysis of 1.0 M $H_2SO_4$ doped PANI/PPy in Figure 3.20. together with the mass spectra at the maxima of the TIC curve. The mass spectral data are summarized in Table 3.3.

Dopant based peaks which are SO (m/z=48) and $SO_2$ (m/z=64) were again more abundant than the monomer and the oligomer peaks.

Evolution profiles of $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z = 93 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO (m/z = 48 Da), HCN (m/z = 27 Da) are shown in Figure 3.21.

It has been detected that at elevated temperatures the relative abundance of aniline monomer (m/z = 93 Da) was decreased compared to those of 0.25M and 0.50M $H_2SO_4$ doped PANI/PPy films. But the relative abundance of pyrrole monomer, namely $C_4H_3NH$ (m/z =66 Da), didn't show any noticable change. Furthermore, evolution of aniline at moderate temperatures was also noted. The detection of aniline at low temperatures indicated presence of low molecular weight PANI segments in the sample.

Oligomer yields were again low. And the relative abundance of polyaniline dimer, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), has decreased compare to that was detected for of 0.25M and 0.50M $H_2SO_4$ doped PANI/PPy films

Evolution of $SO_2$, $CO_2$ and CO evolution at the high temperature indicates that the polymers exposed to oxidation in the $H_2SO_4$ medium again.

Comparison of evolution profiles of aniline pointed out that as the concentration of dopant increased the yield of aniline at elevated temperatures was decreased. In the view of these experimental findings, it can be concluded that, as the dopant concentration increased, extent of degradation of the PANI film coated on the electrode increased during the synthesis of the copolymer.

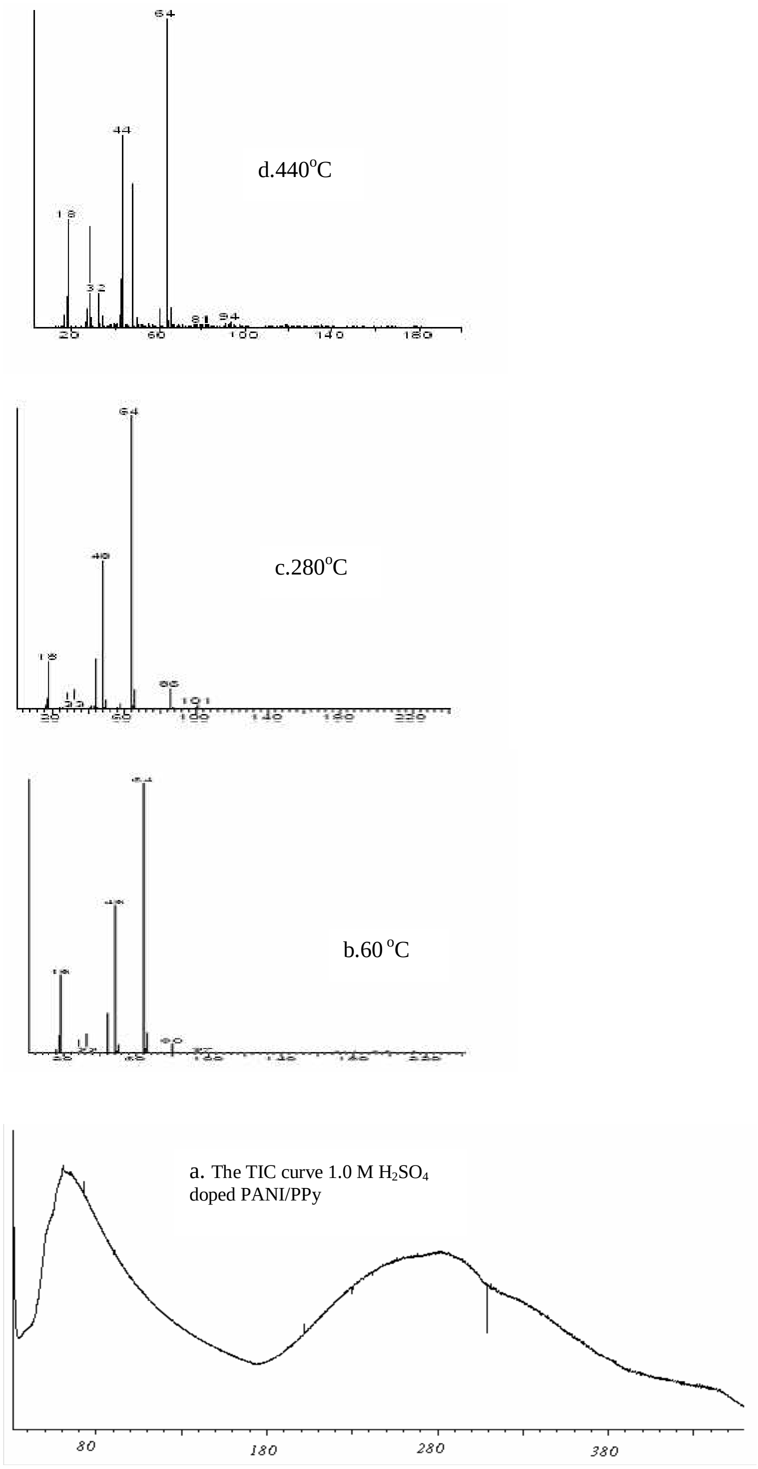


Figure 3.20: Total ion current curve of a. 1.0 M $H_2SO_4$ doped PANI/PPy film and the mass spectra recorded at b.60$^o$C, c. 280$^o$C, d.440$^o$C.

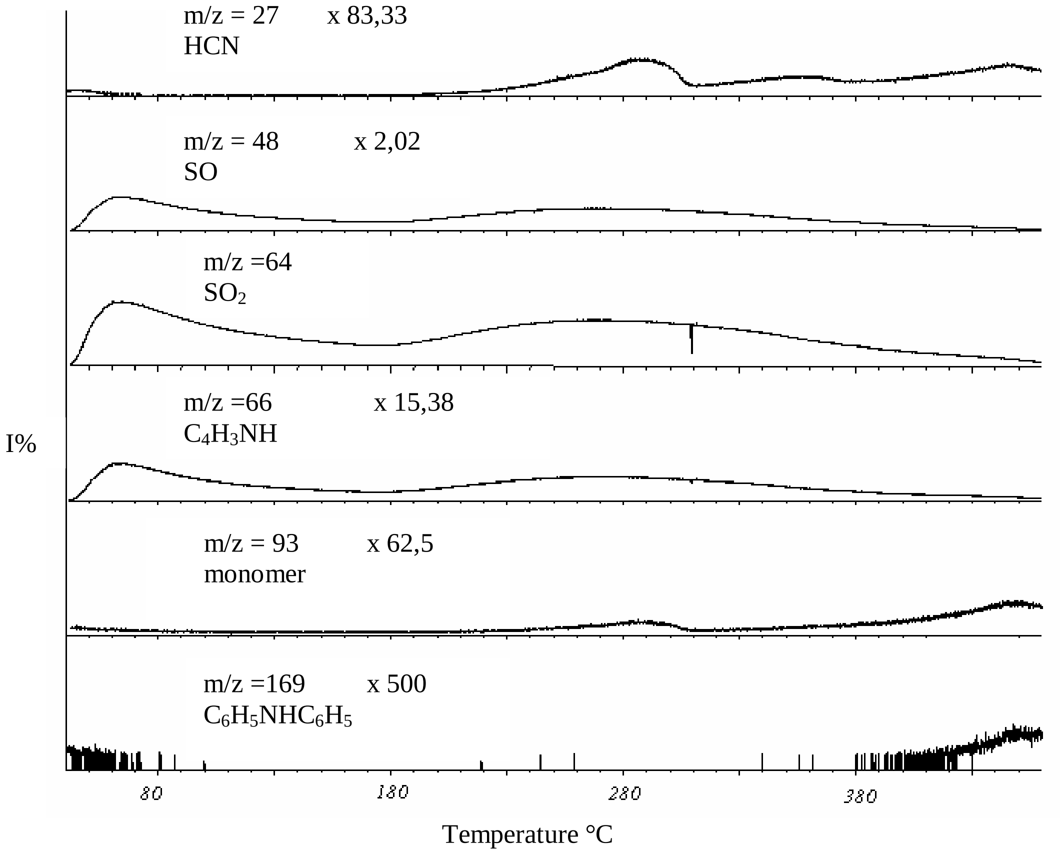


Figure 3.21: Single ion pyrograms of ions at m/z 27, 48, 64, 66, 93, 169 Da recorded during pyrolysis of. 1.0M $H_2SO_4$ doped PANI/PPy film.

#### 3.1.3.8 Electrochemically Prepared PPy/PANI Films

In this part of the study, thermal degradation behavior of PPy/PANI films and the effect of dopant ($H_2SO_4$) concentration on structural and thermal characteristics have been investigated. For all samples studied, three main thermal degradation stages have been recorded. Evolution of low molecular weight species around 50-60 $^{o}$C, just above 100$^{o}$C evolution of dopant based products and at moderate and elevated temperature evolution of degradation products of the polymer were occurred. In Figure 3.22., the total ion current curves (TIC) of 0.25 M, O.50M and 1.0 M $H_2SO_4$ doped PPy/PANI films prepared by passing current 30 minutes are shown. Although all the samples showed mainly three degradation stages the trends observed in the TIC curves have some differences.

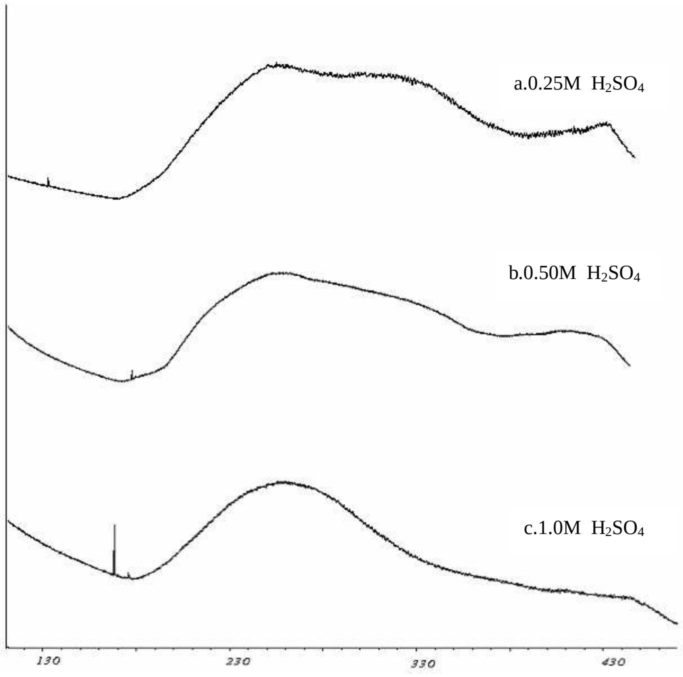


Figure 3.22: Total ion current curve of a. 0.25 M $H_2SO_4$ doped PPy/PANI b. 0.50 M $H_2SO_4$ doped PPy/PANI c. 1.0 M $H_2SO_4$ doped PPy/PANI films.

Table 3.4: The characteristic and/ or intense peaks present in the pyrolysis mass spectra at the maxima of the TIC curves of 0.25M, 0.50M, 1.0 M $H_2SO_4$ doped PPy/PANI1, PPy/PANI2, PPy/PANI3

| | PPy/PANI1 Relative Yield | | PPy/PANI2 Relative Yield | | PPy/PANI3 Relative Yield | | Assignment |
|---|---|---|---|---|---|---|---|
| m/z | 260$^o$C | 445$^o$C | 270$^o$C | 440$^o$C | 260$^o$C | 445$^o$C | |
| 18 | 158 | 288 | 118 | 133 | 142 | 475 | $H_2O$ |
| 27 | 003 | 107 | 09 | 10 | 00 | 42 | $C_2H_3$,or HCN |
| 44 | 179 | 649 | 089 | 103 | 142 | 787 | $CO_2$ |
| 48 | 461 | 409 | 470 | 432 | 445 | 418 | SO |
| 64 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | $SO_2$ |
| 65 | 034 | 145 | 061 | 106 | 11 | 29 | $C_5H_5$ |
| 66 | 095 | 266 | 129 | 194 | 56 | 84 | $C_4H_4N$ or $C_4H_3NH$ |
| 67 | 07 | 39 | 10 | 20 | 02 | 16 | $C_4H_4NH$ (monomer) |
| 80 | 13 | 37 | 139 | 049 | 0 | 0 | $C_5H_6N$ or $SO_3$ |
| 93 | 118 | 585 | 217 | 417 | 03 | 96 | $C_6H_5NH_2$ (monomer) |
| 132 | 0 | 4 | 0 | 0 | 0 | 0 | Pyrrole dimer |
| 169 | 00 | 56 | 0 | 3 | 0 | 5 | $C_6H_5NHC_6H_5$ |
| 184 | 000 | 103 | 0 | 4 | 0 | 4 | aniline dimer |

#### 3.1.3.9 Electrochemically Prepared PPy/PANI Film in 0.25 M $H_2SO_4$ (PPy/PANI1)

The total ion current (TIC) curve recorded during the pyrolysis of 0.25M $H_2SO_4$ doped PPy/PANI film prepared by 30 minutes electrolysis shown in Figure 3.23. together with the mass spectra at the maxima of the TIC curve. The mass spectral data are summarized in Table 3.4.

At low temperatures and moderate temperatures $H_2O$ (m/z=17, 18 Da) based peaks were intense. Dopant based peaks which are SO (m/z=48 Da) and $SO_2$ (m/z=64 Da) were more abundant than monomer and oligomer based peaks.

Evolution profiles of some products, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z = 93 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64Da), SO (m/z = 48 Da), $CO_2$(m/z = 44 Da) are shown in Figure 3.24.

Relative yield of HCN (m/z = 27 Da) which is the product of decomposition of pyrrole ring increased at elevated temperatures. This increase in the abundance of HCN showed the decomposition of pyrrole ring at elevated temperatures.

Presence of monomer peak at elevated temperatures has been observed. Another point that should be noticed was very low oligomer yield.

Evolution of $SO_2$, CO and $CO_2$ at elevated temperatures was again attributed to reactions of dopant with phenyl ring, and to oxidation in the $H_2SO_4$ medium.

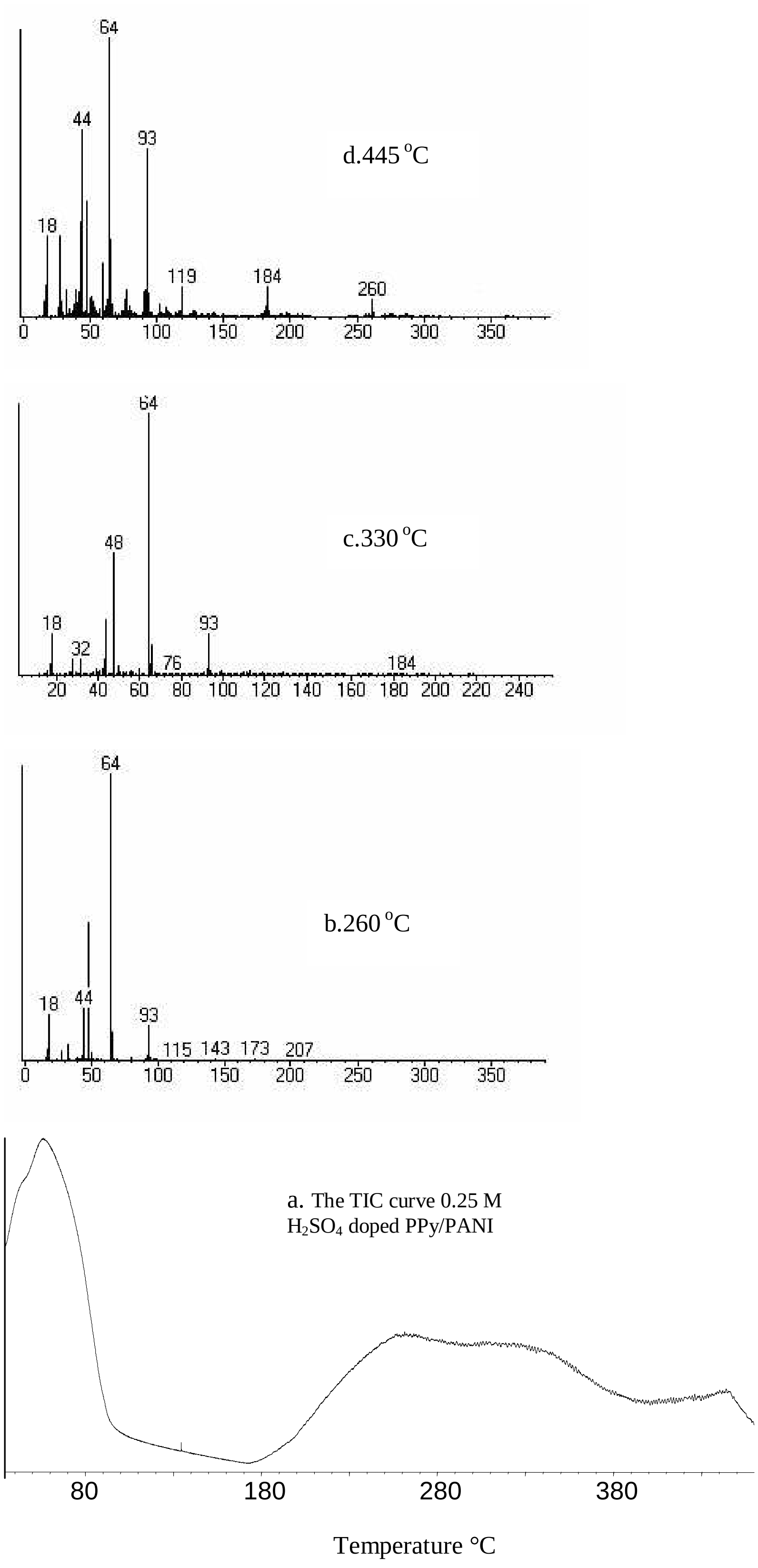


Figure 3.23: Total ion current curve of a. 0.25 M $H_2SO_4$ doped PPy/PANI film and the mass spectra recorded at b.260$^o$C, c. 330$^o$C, d.445$^o$C.

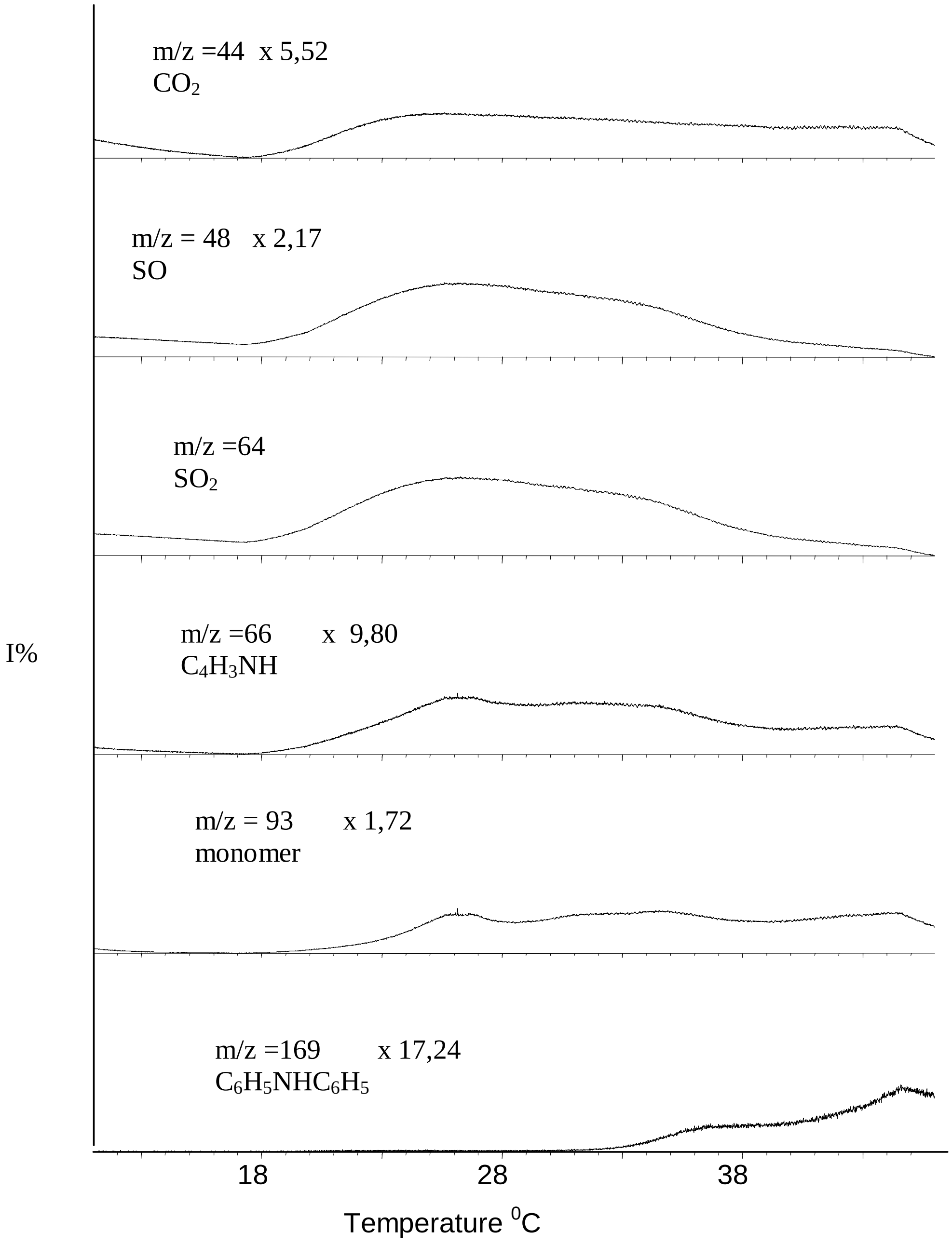


Figure 3.24: Single ion pyrograms of ions at m/z 44, 48, 64, 66, 93, 169 Da recorded during pyrolysis of 0.25 M $H_2SO_4$ doped PPy/PANI film.

#### 3.1.3.10 Electrochemically Prepared PPy/PANI Film in 0.50 M $H_2SO_4$ (PPy/PANI2)

The total ion current (TIC) curve recorded during the pyrolysis of 0.50M $H_2SO_4$ doped PPy/PANI film is shown in Figure 3.25. together with the mass spectra at the maxima of the TIC curve. The mass spectral data are summarized in Table 3.4.

Evolution profiles of some characteristic products, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z = 93 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO(m/z = 48 Da), HCN(m/z = 27 Da) are shown in Figure 3.26.

It was noticed that the abundance of pyrrole monomer (m/z = 67 Da) decreased compared to that of 0.25M $H_2SO_4$ doped PPy/PANI1.

Oligomer yield was again low. Decrease in the abundance of polyaniline dimer, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), was also observed compared to that of the sample prepared in 0.25M $H_2SO_4$ medium.

Relative yield of HCN (m/z = 27 Da) increased at elevated temperatures but formation of this product showed again a decrease compared to that of the sample PPy/PANI1 film.

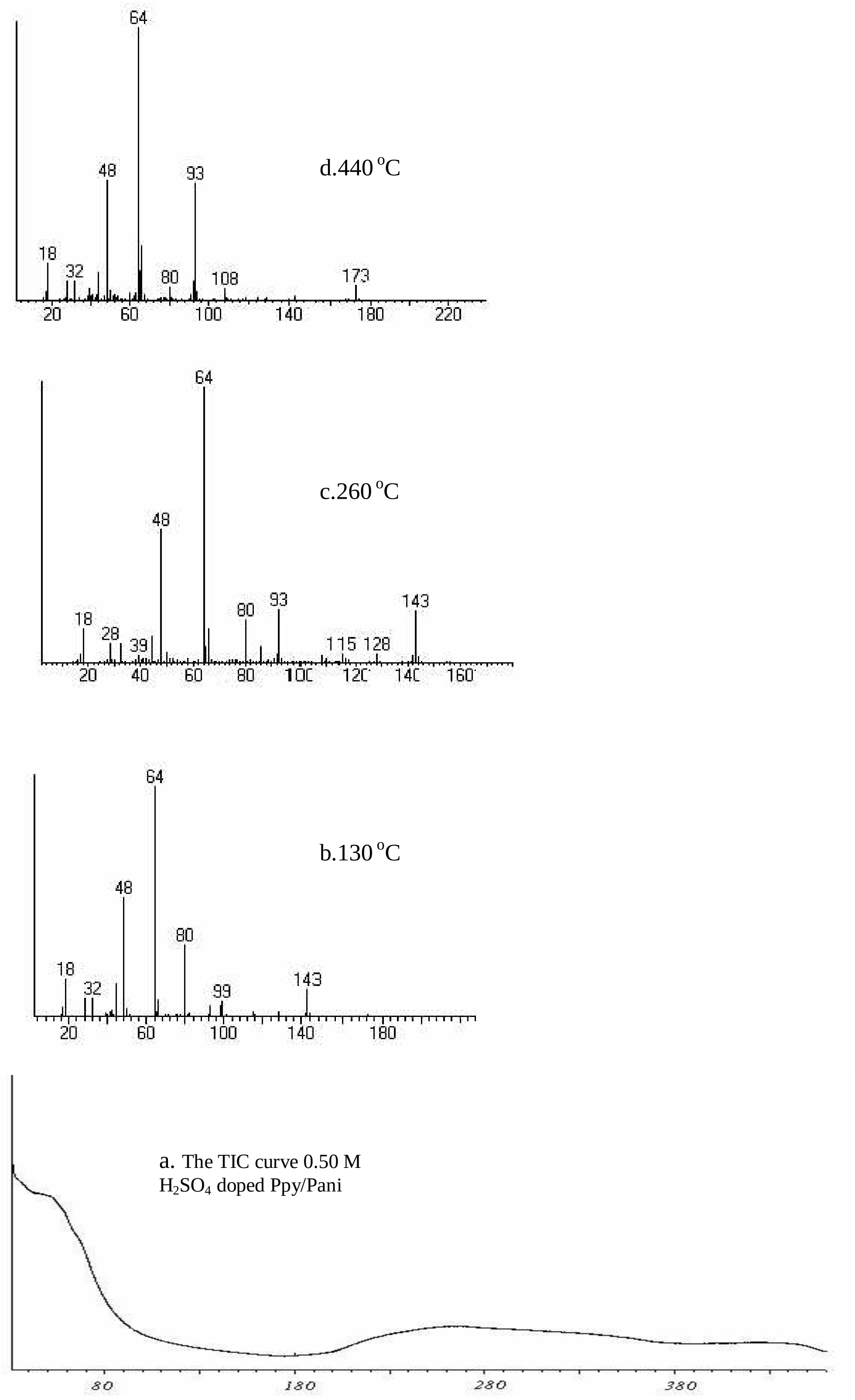


Figure 3.25: Total ion current curve of a. 0.50 M $H_2SO_4$ doped PPy/PANI film and the mass spectra recorded at b.130$^o$C, c. 260$^o$C, d.440$^o$C.

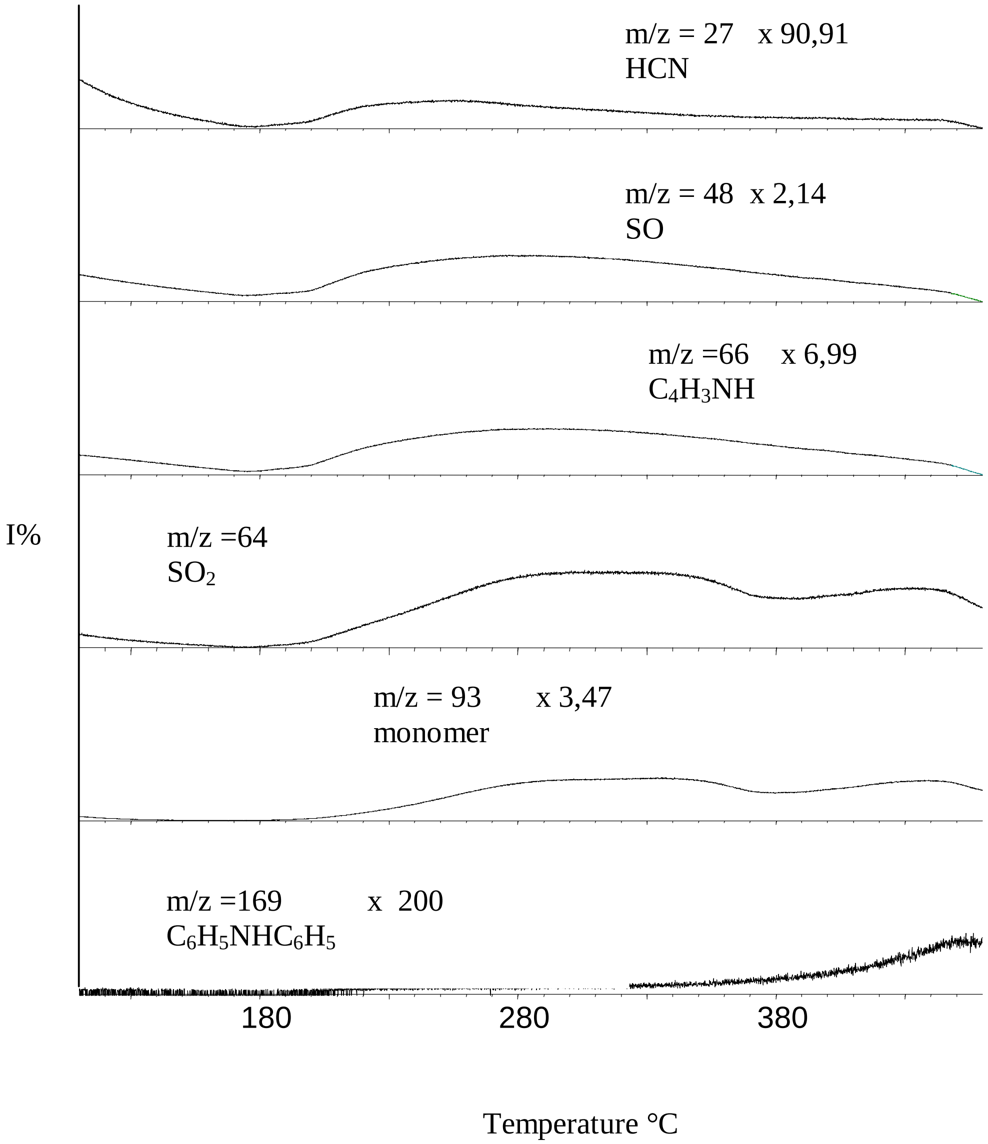


Figure 3.26: Single ion pyrograms of ions at m/z 27, 48, 64, 66, 93, 169 Da recorded during pyrolysis of. 0.50M $H_2SO_4$ doped PPy/PANI film .

#### 3.1.3.11 Electrochemically Prepared PPy/PANI Film in 1.0 M $H_2SO_4$ (PPy/PANI3)

The total ion current (TIC) curve recorded during the pyrolysis of 1.0 M $H_2SO_4$ doped PANI/PPy film is shown in Figure 3.27. together with the mass spectra at the maxima of the TIC curve. The mass spectral data are summarized in Table 3.4.

Dopant based peaks which are SO (m/z=48) and $SO_2$ (m/z=64) have approximately the same abundance as in 0.25M and 0.50M $H_2SO_4$ mediums. They are again among the most abundant.

Evolution profiles of some products, namely $C_6H_5NHC_6H_5$ (m/z =169 Da), monomer (m/z = 93 Da), $C_4H_3NH$ (m/z =66 Da), $SO_2$ (m/z =64 Da), SO (m/z = 48 Da), $CO_2$ (m/z = 44 Da) are shown in Figure 3.28.

It has been observed that at elevated temperatures relative abundance of pyrrole monomer (m/z = 67 Da) has decreased compared to that of 0.25M and 0.50M $H_2SO_4$ doped PPy/PANI films. In addition, the relative yield of aniline monomer, namely (m/z =93 Da), also showed a decrease compare to that of the samples prepared in 0.25M and 0.50M $H_2SO_4$ doped PPy/PANI films.

Oligomer yield was again low. And the abundance of polyaniline dimer (m/z =184 Da), has drastically decreased compared to that of 0.25M $H_2SO_4$ doped PANI/Ppy films.

Evolution of $SO_2$ and $CO_2$ showed the same properties as in case of 0.25M and 0.50M $H_2SO_4$ doped PPy/PANI films.

Formation of HCN at elevated temperatures shows again the decomposition of pyrrole ring. Although the relative yield of HCN is increased at elevated temperature, this increase is lower than that of in 0.25M PPy/PANI film.

It could be concluded that as the dopant concentration increased, extent of degradation of the PPy that is firstly coated on the electrode, during the synthesis of the PPy/PANI copolymer was increased. This observation is similar to what was detected for PANI/PPy samples for which increase in degradation of firstly coated PANI was detected as the concentration of dopant increased. However, for PPy/PANI samples decrease in the PANI content was also detected with the increase in dopant concentrations.

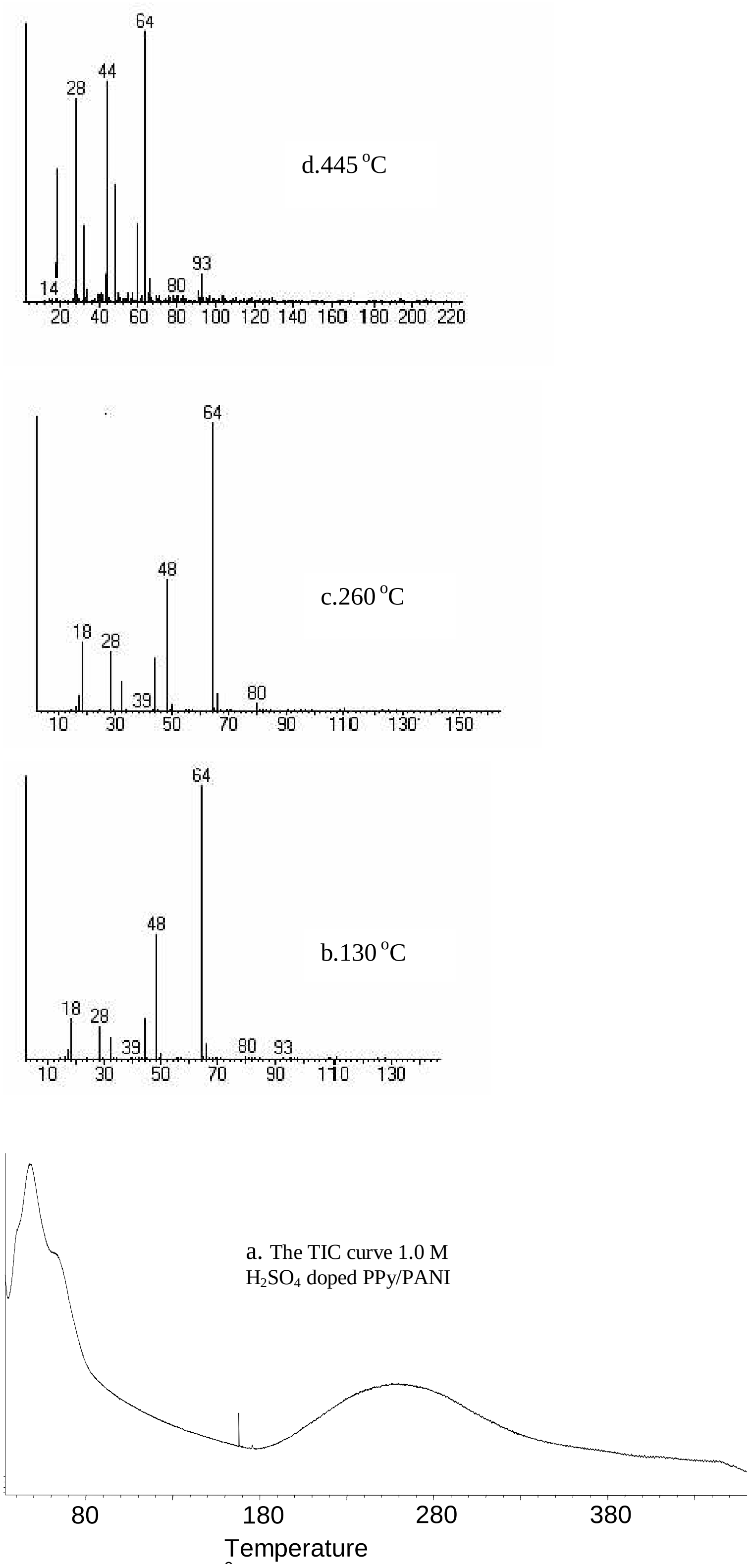


Figure 3.27: Total ion current curve of a. 1.0 M $H_2SO_4$ doped PPy/PANI film and the mass spectra recorded at b.130$^o$C, c. 260$^o$C, d.445$^o$C.

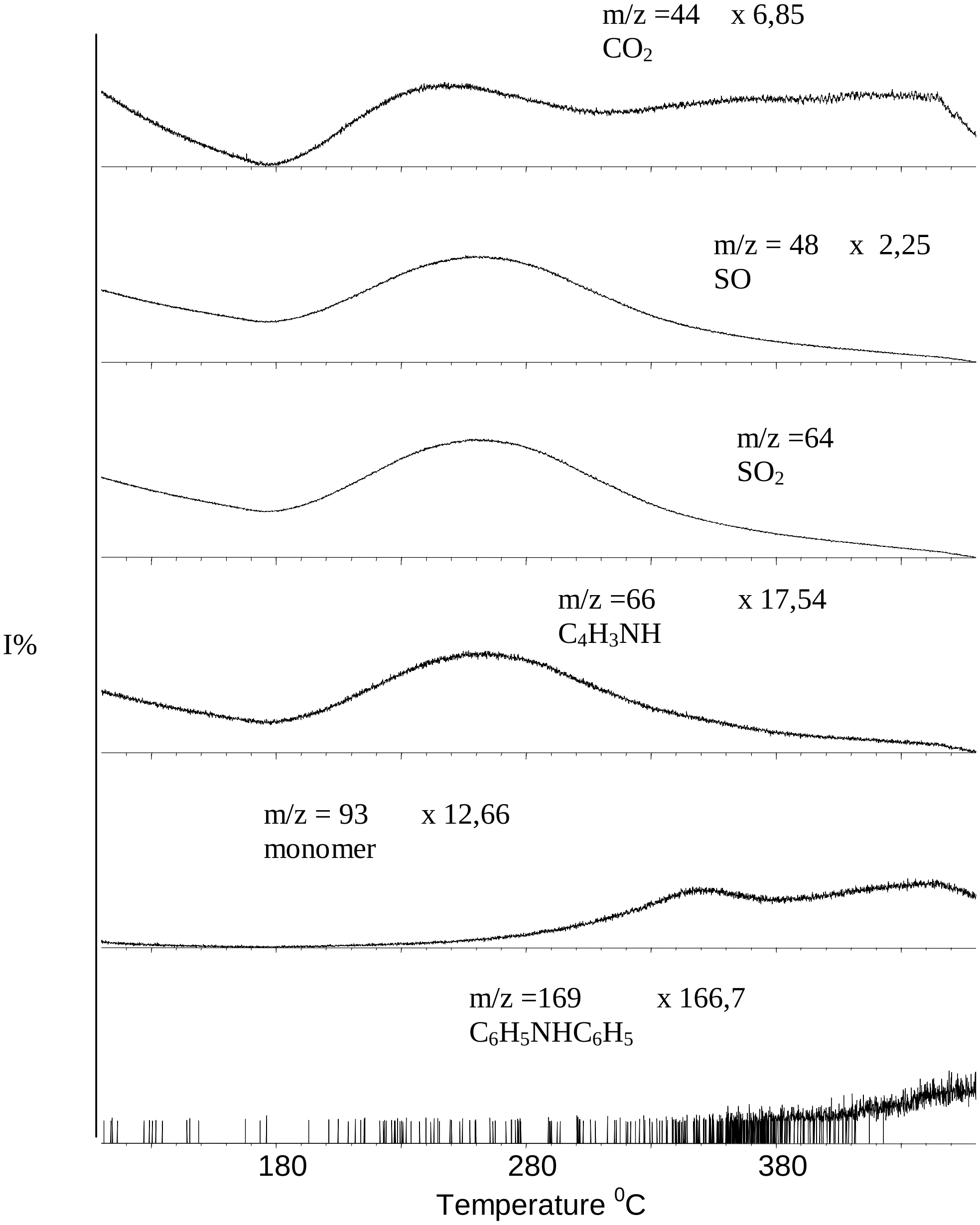


Figure 3.28: Single ion pyrograms of ions at m/z 44, 48, 64, 66, 93, 169 Da recorded during pyrolysis of 1.0 M $H_2SO_4$ doped PPy/PANI film.

# CHAPTER 4

# CONCLUSIONS

In the first part of this work, the syntheses of pure PANI, pure PPy, PANI/PPy, PPy/PANI films were achieved by electrochemical polymerization. PANI-PPy physical blend was also prepared for comparison. The supporting electrolyte used was $H_2SO_4$ and the solvent was water. In order to investigate the effect of dopant (${SO_4}^{2-}$) concentration, the supporting electrolyte concentration was varied as 0.25M, 0.50M, 1.0 M for PANI/PPy and PPy/PANI films.

In the second part of the work, thermal characteristics of homopolymers and copolymers were investigated by thermal gravimetric analysis (TGA), differential scanning calorimeter analysis (DSC) and direct insertion pyrolysis mass spectrometry techniques.

It can be concluded:

**1.** Thermal degradation of PANI, PPY and their copolymers degrade in three steps, the first being due to evolution of water and monomer adsorbed on the samples, the second being due to loss of dopant and the third being due to degradation of the polymer.

**2.** Evolution of $SO_2$, $CO_2$ and CO during the pyrolysis of homopolymers and copolymers at elevated temperatures indicated that the polymers exposed to oxidation in the $H_2SO_4$ medium. Taking into account, the trends observed in the evolution profiles of degradation products of the physical blend indicated that these reactions were mainly took place during the storage.

**3.** Adsorption of water was very effective and attributed to effective H bonding in the presence of $H_2SO_4$ and aniline. Evolution of water at low temperatures showed the presence of water adsorbed on the sample. On the other hand, its evolution at high temperatures indicated generation of water during the decomposition of the polymer pointing out oxidation of the polymer.

**4.** As the dopant concentration increased, extent of degradation of the PANI that was firstly coated on the electrode, during the synthesis of the PANI/PPY copolymer was increased. This observation is similar to what was detected for PPy/PANI samples for which the increase in extent of degradation of the firstly coated PPy was detected as the concentration of dopant increased. However, for PPy/PANI samples significant decrease in the PANI content was also detected with the increase in dopant concentrations.

# REFERENCES

[1] A.Pocchetino, Accad Lineci Rend ,15 ,(1) ,355 (1906)

[2] A.Szent- Gyorgi ,Nature , 148 , 157 (1941)

[3] H.Kallman and , M.Pape , J. Chem. Phys. , 32 , 300 (1960)

[4] H.Shirakawa and S.Ikeda , Polymer J. , 2 , 31 (1971)

[5] H.Shirakawa and S.Ikeda , J. Polym. Sci.Chem. , 12 , 929 (1974)

[6] H.Shrikawa , A.G.Mac Diarmid, C.K.Chiang and A.J.Heeger, J.Chem.Soc.Chem.Comm. , 578 (1977)

[7] J.L.Bredas , R.R.Chance and R.Silbey , Mol. Cryst. Liq. Cryst. , 77 , 319 (1981)

[8] J.L.Bredas , B.Themans, J.M.Andre , R.R.Chance, D.S.Boudreaux and R.Silbey,J.Phys. Coll., 44 ,373 (1983)

[9] W.P.Su, J.R.Shrieffer and A.J Heeger , Phy. Rev. Lett., 42 , 1698 (1979).

[10] J.A. Pople and S.H. Walmsley, Mol., Phys., 5, 15 (1982)

[11] W.P.Su and J.R. Shrieffer, Phy. Rev. B, 22 , 2099 (1980)

[12] J.C.Scott, J.L.Bredas , J.H.Kaufman , P.Pfuger, G.B.Street and K.Yakushi , Mol.Cryst.Lig. Cryst. ,118, 163 (1985).

[13] G.B.Street, T.C. Clarke , M.Krounbi , K.K. Kanazawa ,V.Lee , P. Pfluger , J.C.Scott and G.Werser , Mol. Cryst .Liq. Cryst , 83 ,253 (1982)

[14] A.I. Nazzal and G.B. Street, J. Chem. Soc., Chem. Comm., 83, (1984 )

[15] R.H. Baughman and L.W. Shacklette , Phys. Rev. B, 39 ,5872, (1989)

[16] M.Reghu and S.V. Subramanyan and S. Chatterjce, Phys. Rev., b, 43, 4236, (1991)

[17] V.Bocchi and P. Gardini , J.Chem. Soc. Chem. Comm., 148, (1986)

[18] O.Niwa and T.J. Tamamura ,J. Chem. Soc. Chem. Comm., 817, (1984)

[19] M.A. Depaoli ,R.J. Waltman , A.F. Diaz and J.J. Bragon, J.Chem. Soc. Cehm.Comm. , 1015 , (1984)

[20] H.L. Wang , L . Toppare and J.E. Fernandez, Macromolecules , 23, 1053, (1990)

[21] U. Geissler , M.L. Hallensleben and L.Toppare, Synth. Met., 40, 239, (1991)

[22] O.Niwa ,M. Kakuchi and T.Toshiaki, Macromoleculs, 20 , 749, (1987)

[23] S.Doğan ,U.Akbulut and L. Toppare , Synth. Met. , 53 , 29 , (1992)

[24] G.Çakmak, Z.Küçükyavuz, S. Küçükyavuz, Synt. Met. 151, 10-18, (2005)

[25] G.Çakmak, Z.Küçükyavuz, S. Küçükyavuz, Jour.of Appl. Poly. Sci. 93, 736-741, (2004)

[26] B.Sarı, M.Talu, Synt. Met. 94, 221-227, (1998)

[27] C.L. Gettinger, A.J. Heeger, D.J. Pine, Y.Cao, Synt. Met. 74, 81-88, (1995)

[28] E.Erdem, M.Saçak, M.Karakışla, Poly. Inter. 39, 153-159, (1996)

[29] M.Saçak, M.Karakışla, U.Akbulut, Jor.of Appl. Polym. Sci 65, 1103-1111, (1997)

[30] W.F. Focke, G.E. Wnek, Y. Wei, J.Phys. Chem., 91, 5813-5818, (1987)

[31] M.Karakışla, M.Saçak, E.Erdem, U.Akbulut, Jour. of Appl. Elect. 27, 309-316, (1997)

[32] D.M.Mohilner , R.N. Adams and W.j. Argersinger , Jr. J.Am. Chem. Soc., 84, 3618, (1962)

[33] M.Breitenbach and K.H.Heckner , J.Elechoanal. Chem., 29 , 309, (1971)

[34] Idem, Ibid., 33, 45, (1971)

[35] Idem, Ibid., 43, 267, (1973)

[36] R.L.Hand and R.F Nelson , J.Am. Chem. Soc.,96 ,850, (1974)

[37] Idem, J.Electrochem. Soc. ,125 ,1059, (1978)

[38] E.M. Genies , A.A. Syed and C.Tsintavis , Mol. Cryst. Lig. Cryst , 1985 , 121 , 181

[39] E.M. Genies , and C. Tsintavis, J. Electroanal., Chem., 195, 109, (1985)

[40] Organic electrochemistry , M.M Baizer and H.Lund (eds), Chap. 15 , Dekker ,New York, (1983)

[41] E.M. Genies ,J.F. Penneau and M. Lapkowski , J. Electranal. Chem., 260,145, (1989)

[42] E.M. Genies ,J.F. Penneau and M. Lapkowski and A.Boyle , Ibid., 269 , 63, (1989)

[43] Idem, Ibid., 200, 127,(1968)

[44] G. P. Gardini, Adv. Heterocycl. Chem. 15, 67 ,(1973)

[45] A. Angeli, Gazz. Chim. Ital. 42, 279, (1916)

[46] V. Varacco, V. Bocchi, C. R. Acad. Sci. Ser. C., 267, 433 (1968)

[47] E. Simon, E. Sable, H. Handel, M. L'Her, Electrochim Acta, 45, 855-863 (1999)

[48] H. Korri-Youssoufi, F. Garnier, P. Srivastave, P. Godillot, A. Yassar, J. Am. Chem.Soc. 119, 7388, (1997)

[49] M. Zhou, J. Heinze, Electrochim. Acta, 44, 1733, (1999)

[50] A. Dall'olio, Y. Dascola and G. P. Gradini, C. R. Acad. Sci. 267, 4336, (1969)

[51] A. F. Diaz, K.K. Kanazawa and G.P. Gradini, J. Chem. Soc. Chem. Commun. 635, (1979)

[52] M.M. Fares, T.Yalcin, J.Hacaloğlu, A. Güngor and S. Süzer, Analyst 119, 693, (1994)

[53] T. Ersen, Msc., Middle East Technical University, (1996)

[54] M.Erdoğan, T.Yalçın, T.Tinçer and S.Süzer, Eur.Polym. J., 27, 413, (1991)

[55] M.M. Fares, J.Hacaloğlu and S. Süzer, Eur.Polym. J., 30, 845,(1994)

[56] T.Uyar, L.Toppare, and J.Hacaloğlu, Synt. Met.123, 335, (2001)

[57] T.Uyar, L.Toppare, and J.Hacaloğlu, Synt. Met.119, 307, (2001)

[58] Y.P. Khanna, in ' Material Characterization and chemical Analysis' J-P. Sibilia, ed, 2nd ed. VCH Publishers, Inc, New York, NY, 261, (1996)

[59] H. Qiu , W.Wu, J. Li, K. Fang, W.Mao, Synth. Met., 155, 560, ( 2005 )

[60] M. K. Traore, W. T. K. Stevenson, B. J. Mac Cormick, R. C. Dorey, S. Wen,D. Meyers, Synth. Met., 40, 137, ( 1991 )

[61] K. G. Neoh, E. T. Kang, K. L. Tan, J. Macromol. Sci. Pure Appl. Chem., A 29, 401, (1992)

[62] K. G. Neoh, E. T. Kang, S. H. Khor, K. L. Tan, Polym. Degrad. Stab., 27, 107, (1990)

[63] S. Kim, J. M. Ko, I. J. Chung, Polym. Adv. Technol., 7, 599, (1996)P. Rannou, M. Nechtschein, Synth. Met., 84, 755, (1997)

[64] P. Rannou, M. Nechtschein, Synth. Met., 84, 755, (1997)

[65] B. Sixou, J. P. Travers, Y. F. Nicolau, Synth. Met., 84, 703, (1997)

[66] A.Wolter, P. Rannou, J.P. Travers, B.Gilles, D.Djurado, Phys. Review B, 58 (12), 7637, (1998)

[67] V. Jousseaume, M. Morsli, A. Bonnet, J Appl. Polym. Sci., 84, 1848, (2002)

[68] J.Yue, A. J. Epstein, Z. Zhong, P. K. Gallagher, A. G. MacDiarmid, Synth. Met., 41-43, 765, (1991)

[69] V. G. Kulkarni, L. D. Campbell, W. R. Mathew, Synth. Met., 30, 321, (1989)

[70] L.M. Huang, C.H. Chen, T.C. Wen, A. Gopalan, Electrochimica Acta, 51, 2756, (2006)

[71] S.B. Gomez, I. J. Folch, Anal. Appl. Pyrol, 55, 247, (2000)

[72] B. Sreedhar, M. Sairam, D.K. Chattopadhyay, P.P. Mitra, D.V.M. Rao, J Appl. Polym. Sci., 101, 499, (2006)

[73] E.S. Matveeva, R.D.Calleja, V. P. Parkhutik, Synth. Met., 72, 105, (1995)

[74] E.Argın, Msc., Middle East Technical University, (2005)

[75] T.Uyar, L.Toppare and J. Hacaloğlu, J. Anal. and Appl. Pyrol. 64(1), 1-13, (2002)

[76] T.Uyar, L.Toppare and J. Hacaloğlu, Macromolecular Rapid Communications 22, 199, (2001)

[77] T.Uyar, L.Toppare and J. Hacaloğlu, J.M.S. Pure and Appl. Chem., A38, 1141, (2001)