CONDUCTIVE AND ELECTROCHROMIC PROPERTIES OF POLY(P-PHENYLENE VINYLENE)

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CONDUCTIVE AND ELECTROCHROMIC PROPERTIES OF POLY(P-PHENYLENE VINYLENE)

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ABSTRACT

CONDUCTIVE AND ELECTROCHROMIC PROPERTIES OF POLY(P-PHENYLENE VINYLENE)

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P-xylene-bis(diethylsulphonium chloride) (PXBDC) monomer was synthesized by the reaction of α,α-dichloro-p-xylene with tetrahydrothiophene or diethyl sulphide. Electrochemical behavior of this monomer (PXBDC) was examined by cyclic voltametry. Polymerization was achieved both by using electrochemical and chemical polymerization techniques. In the electrochemical technique, PPV was synthesized by constant potential electrolysis in acetonitrile-tetrabutylammonium tetrafluoroborate (TBAFB) solvent-electrolyte couple. The polymer obtained from the electrode surface was converted to the poly(p-phenylene vinylene) (PPV) by the thermal elimination reaction of diethyl sulphide and HCl. Also, PPV was doped via electrochemical doping with ClO_4^- dopant ion.

The chemical structures were confirmed both by Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). The thermal behavior of chemically and electrochemically synthesized conducting polymers were investigated by Differential Scanning Calorimetry (DSC). Also, electrochromic and spectroelectrochemical properties of PPV was investigated by using UV-VIS spectrophotometer.

Keywords: poly(p-phenylene vinylene), conducting polymers, electrochromic properties, electrochemical doping, cyclic voltametry,

ÖZ

POLİ(P-FENİLEN VİNİLEN)'İN İLETKEN VE ELEKTROKROMİK ÖZELLİKLERİ

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p-ksilen-(bisdietilsülfonyum klorit) (PXDBC) monomeri α,α-dikloro-p-ksilenin tetrahidrotiyofen veya dietilsülfit ile reaksiyonundan sentezlendi. Bu monomerin elektrokimyasal davranışı dönüşümlü voltametri yöntemi ile incelendi. Polimerizasyon hem kimyasal hem de elektrokimyasal teknik kullanılarak gerçekleştirildi. Elektrokimyasal metotda, poli(p-fenilen vinilen) (PPV) sabit potansiyel elektrolizi ile asetonitril-tetrabutilamonyum tetrafloroborat (TBAFB) çözücü-elektrolit çifti kullanılarak elde edildi. Elektrot yüzeyinden elde edilen polimer dietilsülfit ve HCl'in termal eliminasyonu ile PPV'ye dönüştürüldü. Ayrıca, PPV elektrokimyasal doping işlemiyle ClO_4^- ile katkılandırıldı.

Kimyasal yapı NMR ve FTIR ile tayin edildi. Kimyasal ve elektrokimyasal yoldan sentezlenen iletken polimerlerin ısıl davranışı DSC yöntemiyle belirlendi. Ayrıca polimerin elektrokromik ve spektroelektrokimyasal özellikleri UV-VIS spektrofotometresiyle incelendi.

Anahtar sözcükler: Poli(p-fenilen vinilen), iletken polimerler; elektrokromik özellikler, elektrokimyasal doplama, dönüşümlü voltametre

TO MY FAMILY

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SCHEME

ABBREVIATIONS

PPV	Poly(p-phenylene vinylene)
PXBDC	p-xylene-bis(diethylsulphonium chloride)
ITO	Indiumtinoxide coated glass electrode
DMF	Dimethylformamide
TBAFB	Tetrabuthylammonium tetrafluoroborate
ACN	Acetonitrile
THT	Tetrahydrothiophene
NMR	Nuclear Magnetic Resonance Spectrometer
FT-IR	Fourier Transform Infrared Spectrometer
DSC	Differential Scanning Calorimetry
CV	Cyclic Voltametry
WE	Working electrode
RE	Reference electrode
CE	Counter electrode
CCE	Controlled current electrolysis
CPE	Controlled potential electrolysis
Pt	Platinium

CHAPTER 1

INTRODUCTION

1.1 History of Conducting Polymers

Electrically conducting polymers have attracted a huge amount of attention since their discovery. The first chemical oxidative polymerization of aniline in H_2SO_4 was taken place by Letheby in 1862. In this work, the anodic oxidation of polyaniline was achieved [1].

In recent years, a great deal of research involving conductive polymers has been carried out since the discovery of the electrical properties of doped polyacetylene. Many of these conductive polymers, however are generally difficult to process due to their non-fusibility and insolubility. This is a serious problem in the practical utilization of these compounds [2].

For many years, there has been interest in the production of electrically conductive polymers. In 1906, the photoconduction in organic solids was found for anthracene [3]. Later on, work on electrical conduction for organic solids was reported from the late 1940s to early 1950s for certain classes of organic compounds. Pthalocyanines have been found to show electrical conductivity [4]. Electrical conduction was observed for highly condensed polycyclic aromatic hydrocarbons whose molecular structure resembles that of graphite, which is known to be highly conductive [5].

In 1968 Dall'Olio and co-workers prepared pyrole black by electro-oxidation of pyrole monomer and resulting polymer was found to have an 8 S/cm electrical conductivity [6]. In 1971, H. Shirakawa and S. Ikeda discovered that polyacetylene can be made into films having metallic luster and low-level conductivity. However, the field of conductive polymers really began in 1977, when A.J. MacDiarmid and A.J. Heeger found that doping of polyacetylene with iodide demonstrated a much higher conductivity than with other dopants, with conductivities reaching as high as 10^{6} S cm^{-1} under appropriate conditions [7]. It was further found that polyacetylene could be obtained by both oxidative and reductive polymerization. Its conductivity depended on the doping ion's properties and concentration. Dopants reduce or oxidize the polymer to form p-type and n-type conductors [8].

Diaz and co-workers were able to prepare polypyrrole with a higher electrical conductivity and excellent air stability (100 S/cm) in the form of free standing and continuous films [9]. Recent reviews of conductive polymers indicate much higher conductivity and air stability and promising new developments. The most exciting developments are the prospect of a new class of semi-conducting devices and the possibility of light-emitting plastics. While it is likely to be some time before the technology is sufficiently refined to bring these applications to the market, conducting polymers have found commercial uses. These range from relatively low-tech anti-static films for textiles, to highly sophisticated chemical and biochemical sensors [10].

1.2 Types and Structures of Conductive Polymers

It has been identified that any organic polymer containing a conjugated electron system can always have metallic conductivity upon addition of electrons or holes by doping (chemically or electrochemically). Metallic conductivities have been observed in a number of conjugated systems, for instance, polyaniline, polypyrrole, polythiophene, poly(p-phenylene) and poly(p-phenylene vinylene) some of which are shown in Figure1.1.

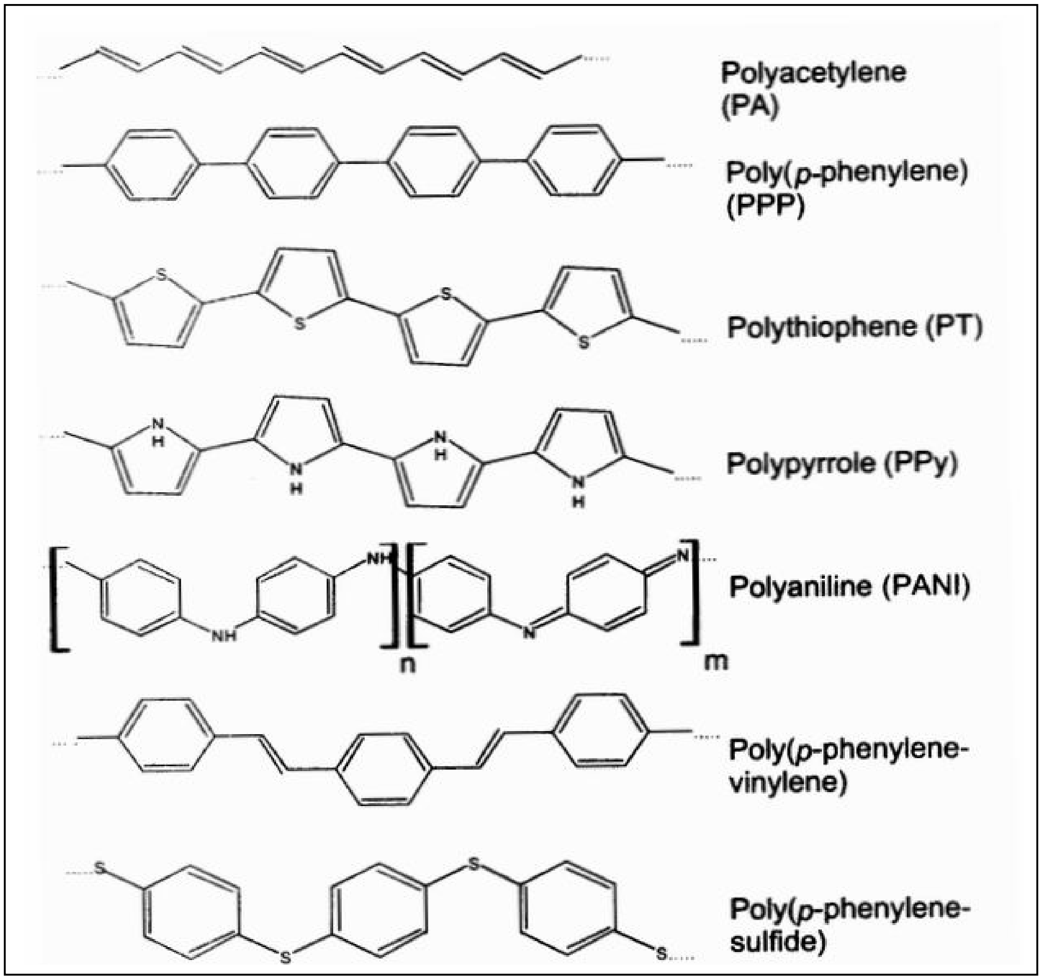


Figure 1.1 Structures of several conductive polymers

Conducting polymers can be classified into four categories from the stand point of molecular structure. The first and most commercially important are *composites*, in which the filling of an otherwise non-conducting polymer matrix with a powdered conductive medium such as metal or carbon gives rise to conductivity. These composite polymers are used as antistatic coatings, substitutes for solder and sundry other applications. The second groups of polymers are called *ionically conducting polymers,* as they are organic polymers in which electric charge is carried by ions.

Polyethylene oxide, in which lithium ion is mobile, is an example. These polymers are gaining importance in the battery industry. The third group of polymers are called *redox polymers*. These contain immobilized electroactive centers, which although not in direct contact with one an other, can exchange electrons by a hopping mechanism. The fourth type, and the type to be discussed in this thesis is *electrically conducting polymers,* or *conjugated polymers*. These polymers consist of alternating single and double bonds, creating an extended π network. Electron movement within this π-framework is the source of conductivity rather than the hopping seen in redox polymers [11].

1.3 Conductivity in Conjugated Compounds

Polymers with conjugated п-electron backbones display unusual electronic properties such as low energy optical transitions, low ionization potentials, and high electron affinities. The result is a class of polymers which can be oxidized or reduced more easily and more reversibly than conventional polymers. Charge transfer agents (dopants) affects this oxidation and reduction and in doing so convert an insulating polymer to a conducting polymer with near metallic conductivity in many cases [12].

The electrical behaviour of all solids can be described in terms of energy bands, which are the allowable energy levels for electrons in solids. These bands are composed of many very closely spaced energy levels. The bands of interest are the highest fully occupied states (valance band) and the lowest empty states (conduction band). These energy bands are separated by a range of forbidden energies that defines the band gap, eg, characteristic of a particular solid [13].Only charge carriers with energies near the top of the valence band (near so-called Fermi energy) contribute to electronic conduction by being thermally promoted to the empty conduction band where they are free to move under the influence of an applied electric field. Metallic conductors are characterized by either a partially field valance band or the presence of a marked degree of overlap between valence and conduction bands. On the other hand semiconductors and insulators are characterized by an appreciable band between the top of the valence band and the bottom of the conduction band. Hence the ease of thermally promoting electrons across the band gap to generate mobile conduction carriers in the conduction band depends on the magnitude of the band gap. In simple terms semiconductors have reasonably low band gaps, whereas the gap for insulators is rather large, this situation is shown in Figure 1.2 [14].

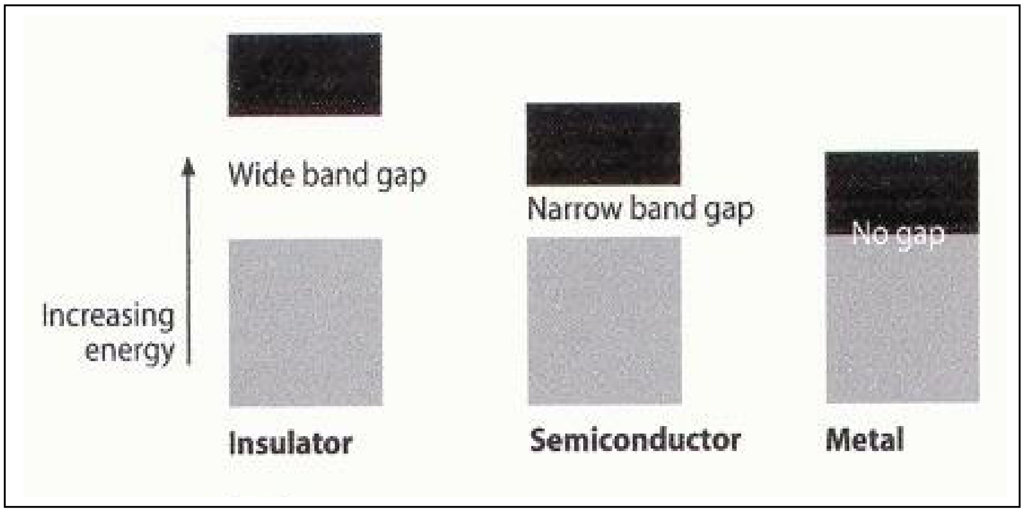


Figure 1.2 Simple band representation explaining the difference between an insulator, a semiconductor and a metal

The conductivity, σ, is proportional to the product of the free-carrier concentration, n, and the carrier mobility, μ,

$$\sigma = en\mu$$

where e is the unit electronic charge ($1.6.10^{-19}$ C). For intrinsic conductivity, the carrier concentration decreases exponentially with increasing band gap (roughly equivalent to the optical absorption threshold). Since conjugated polymers have relatively large band gaps, the concentration of free carrier is very low at normal temperatures. Therefore, even though conjugated polymers have backbone structures well suited to conduction, the low carrier concentration results in negligible conductivity.

The doping of conjugated polymers generates high conductivities primarily by increasing the carrier concentration [12]. In conventional semiconductors the concentration of dopant is very small, at the ppm level, whereas in conjugated polymers the dopant concentration or the level of the redox process is more or less stoichiometric compared with the monomer fraction. Hence, from the chemist's point of view the doped polymers are entirely different compounds, carbocations or carbanions of the parent compound. Still, even chemists are using the term p-doping for the oxidation of polymer and n-doping for the reduction [15].

1.4 Dopants and Doping Process for Conductive Polymers

In becoming electrically conductive, a polymer has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms. The first condition for this is that the polymer consists of alternating single and double bonds, called conjugated double bonds. However, it is not enough to have conjugated double bonds. To become electrically conductive, the plastic has to be disturbed - either by removing electrons from (oxidation or p-doping) or inserting them into (reduction or n-doping) the material. The process is known as doping [16].

The partial oxidation of the polymer chain is termed p-doping. The basic process involves removing electrons to form a positively charged repeat unit

$$-(P)^{x-} + xyA^{-} \rightarrow -[(P^{y+})A^{y-}]^{x-} + xy^{e-}$$

where P represents the basic monomeric repeat unit in the polymer. Furthermore, if the polymer chain is partially reduced, there is n-type doping as follows,

$$-(P)^{x-} + xy^{e-} + xyM^{+} \rightarrow -[M^{+y}(P^{y-})]^{x-}$$

It is clear that partial oxidation of the backbone can be achieved either electrochemically by applying a potential or chemically by using a gas-phase oxidizing/reducing agent. The former method is preferred due to the rigorous control that exists over the degree of doping. The need to maintain electro neutrality requires ionic transport also to be considered [14].

It is characteristic of conducting polymers that the doping process can be reversed, the conducting polymer can be rendered insulating by neutralization back to the uncharged state. This return to neutrality is referred to as compensation. Exposure of oxidatively formed polymers to electron donors or conversely of reductively doped polymers to electron acceptors affects compensation. This ability to cycle between charged and neutral states forms the basis for the application of conducting polymers in secondary (rechargeable) batteries [12].

Table 1.1 presents the list of dopant ions and their source of electrolytes which are currently being used in the electrochemical synthesis of conducting polymers. It should be noted that all of these dopant ions with the exception of last two (marked by *) are anions and refer to electrochemical oxidation of the polymers at the anode.
R = Alkyl; Et = Ethyl; But = Butyl; M = Metal (Li^+, Na^+, Ag^+, K^+). The dopant ions marked by * are not anions.

1.5 Solitons, Polarons and Bipolarons

In the oxidation of a polymer having a conjugated π backbone, one double bond is broken and a radical with a positive charge is formed on the polymer chain. The molecule formed is called polaron or radical cation. A new π bond is formed as a

Table 1.1 List of dopant ions and their source of electrolyte

Dopant ion	**Source (i.e. Supporting Electrolyte)**
BF_4^-	$R_4N^+BF_4^-$, MBF_4
PF_6^-	R_4NPF_6, MPF_6
$Cl0_4^-$	R_4NClO_4, $MClO_4$
Cl^-	R_4NCl, HCl. MCl
Br^-	R_4NBr, MBr
I^-	R_4NI, MI
AsF_6^-	$MAsF_6$
HSO_4^-	$MHSO_4/R_4NHSO_4$
$CF_3SO_3^-$	$MCF_3SO_3/R_4NCF_3SO_3$
$CH_3C_6H_4SO_3$	$MCH_3C_6H_4SO_3$
$S04^{2-}$	Na_2S04, H_2SO_4
(Et_4N^+)*	Et_4NPF_6
(Bu_4N^+)*	Bu_4NPF_6

result of the combination of the two radicals. This bond is more stable than the two radical cation bond energetically. The product is bipolaron. The mobility of charges in bipolaron is high. Thus mainly bipolarons contribute to conductivity.

Doping process causes the formation of structural defects, called solitons, in the polymer chain and these defects generates a new energy state in the midway of the energy gap. In this energy level, zero, one or two electrons can be occupied; therefore, solitons are classified as neutral, positively charged and negatively charged (Figure 1.3).

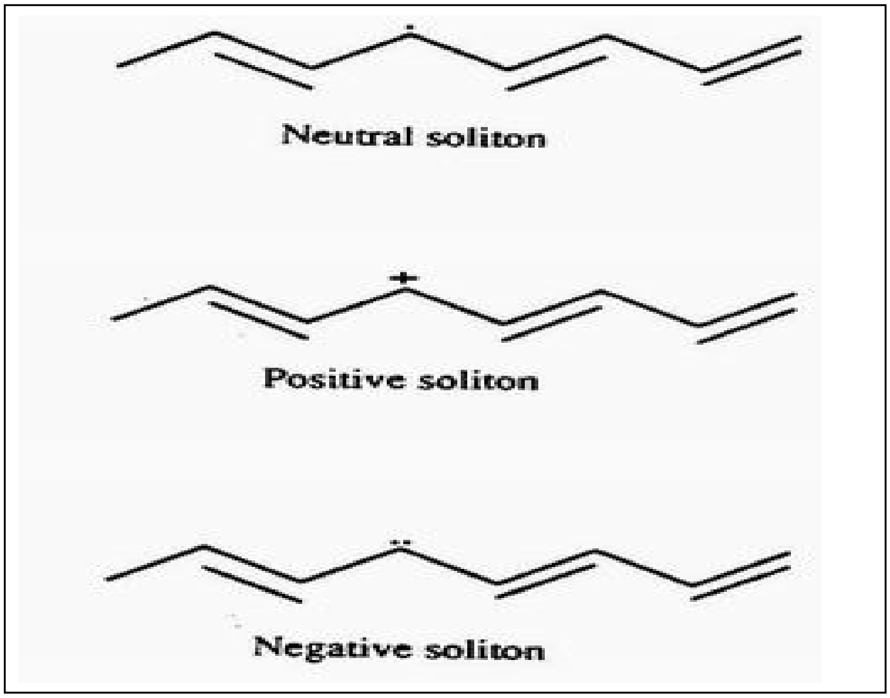


Figure 1.3 Schematic representation of soliton structures in polyacetylene

An interesting observation at this point that charged solitons have no spin; however, neutral solitons have spin but no charge [16]. When an electron is removed from localized state of a neutral soliton by oxidation (chemical or electrochemical), positively charged soliton occurs. It is same as a stabilized carbonium ion on the polyacetylene chain. Similarly, when an electron is added localized state of a neutral soliton by reduction (chemical or electrochemical) negatively charged soliton occurs.

1.6 Hopping Process

In conducting polymers the mobility of the carrier plays a more important role than the carrier concentration. The hopping process produces a generous supply of potential carriers. There are at least three ways for the carrier mobility; i.e, single chain or intra molecular transport, inter chain transport, and inter particle contact. These three elements show a complicated resistive network which determines the effective mobility of the carriers. Thus the mobility and therefore the conductivity are determined on both a microscopic (intra and inter chain) and a macroscopic (inter particle) level (Figure 1.4).

1.7 Synthesis of Conducting Polymers

Conducting polymers may be synthesized by both chemical and electrochemical ways.

1.7.1 Chemical Polymerization

It is the most useful method for preparing large amounts of conductive polymers, since it is performed without electrodes [17]. Mixing of conducting and insulating particles is a known technique to prepare conducting polymers. Thus, polymerization of a conducting polymer inside an insulating host matrix is used to improve the strength of electrically conducting polymers. The composite is expected to gain both conductivity and good mechanical properties from its components, though sacrificing some of these qualities. However, this method is limited by the requirement that various species such as neutral monomer, charged dopant and sometimes an oxidant agent, would diffuse inside the film.

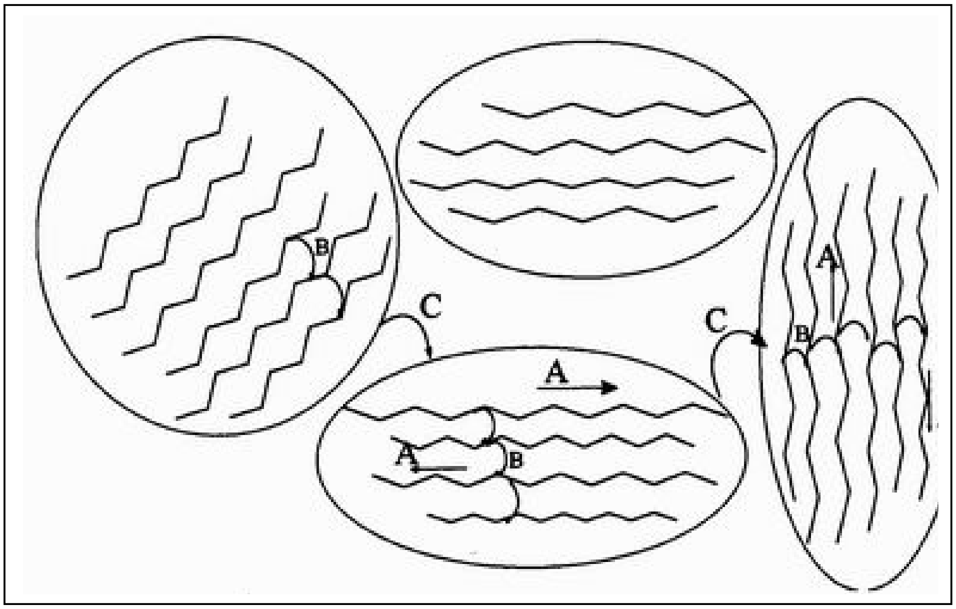


Figure 1.4 Conductivity network of a conductive polymer with [A] indicating intrachain transport of charge, [B] indicating interchain transport of charge, [C] indicating interparticle transport of charge.

1.7.2 Electrochemical Polymerization

Electrochemical synthesis remains one of the most promising areas in the research of conducting polymers. A central point of the electrochemical research is the analysis of the doping mechanism. The studies show that these processes were not comparable with the classical doping of semiconductors. Rather they correspond to oxidation in the case of p-doping or reduction in the case of n-doping. Thus, in the electrochemical terminology, the doping process corresponds to a redox reaction.

Especially for applications, it is important to know some details of such redox reactions, e.g., in which potential range the charging occurs and what is the maximum level of oxidation before the material starts degrading [1].

Advantages of electrochemical polymerization of conducting polymers are [18]

i) Reactions are done at room temperature.

ii) Thickness of films can be controlled by varying either the potential or 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 copolymers.

1.8 Electrolysis

Electroinitiated polymerization can be carried out by either constant current or constant potential electrolysis.

1.8.1 Constant Current Electrolysis (Galvanostatic)

In this method a two electrode cell is used and current is kept constant throughout the electrolysis, whereas the potential is allowed to change with time. Although application is simple, it has some disadvantages. Since potential is a variable parameter during the course of such polymerization, changes of electrochemical nature due to the involvement of undesired species, such as solvent, electrolyte, etc. are fairly high. Moreover, further oxidation or reduction of a product may also take place.

1.8.2 Constant Potential Electrolysis (Potentiostatic)

In this method three electrodes are employed in an electrolysis cell (working, counter, and reference electrodes). The potential of the working electrode relative to the reference electrode is adjusted to the desired value by a potentiostat, and the amount of current passing through the cell by using an electronic integrator can be measured. The applied potential is determined by cyclic voltametry.

1.9 Effects of Synthesis Conditions on Electropolymerization

In electrochemical polymerization two or three electrodes are amounted in an electrolysis vessel containing solvent with dissolved electrolyte and monomer. As current flows the polymer is deposited on the anode as a continuously thickening layer. After a certain time the current is switched off and either the whole anode with its polymer covered layer is used for characterization procedures, or, if the polymer is not too brittle, the layer is peeled off from the anode surfaces and used as a self supporting film.

The oxidized form of polymer contains positive charge carriers, perhaps in the form of polarons and bipolarons, but at the same time the positive charge should be compensated by a corresponding amount of negative charge. This is commonly done by incorporating of anions from the electrolyte solution during the polymerization process. The size and character of the anions may have a pronounced effect on the quality of the polymer.

1.9.1 Influence of Counterions

Oxidation and reduction introduce charges into the polymer materials, and in order to maintain electroneutrality, counter ions are incorporated. A considerable number of ions are incorporated in the polymer and their influence is not negligible. During the polymerization process, depending on the dielectric permittivity of the solvent, the cation radicals and anions form ion pairs with different readiness. The ion pairs have different reactivity from the free cation radicals. If anions have too much nucleophilicity, they may even form covalent compounds with the cation radicals, which prevents their polymerization reactions. For instance, halide ions cannot be used in connection with reactive cation radicals.

Once polymer is formed, counterions affect its properties in different ways:

Oxidation and reduction rates of the polymer are often limited by the diffusion rate of the counterions. The size and shape of the ions have a considerable effect on the diffusion rates inside the polymer matrix. Incorporation of ions into compact and hydrophobic films is more difficult than into porous, hydrophilic films.

If the counterion is very large, its mobility in the polymer matrix is nearly zero, and the only way to introduce ions into the polymer is during the growth of the polymer phase. These immobile anion centers neutralize exactly the positive charges of the oxidized polymer. When the polymer is reduced, the positive charges disappear, and the negative charge of the immobile anions should be neutralized.

The chemical structure of the counterion may have a profound influence on the morphology and conductivity of the polymer. For instance, polypyrole made in the presence of dodecyl sulfate is very smooth, dense, stable and highly conducting, whereas polypyrole made in the presence of perchlorate ion has a cauliflower morphology and its conductivity is about 100 times lower than made with dodecyl sulfate.

1.9.2 Influence of Solvent

Different monomers have different requirements for the solvent for electropolymerization.

Solvent molecules interact with cation radicals and the strength of the interaction depends on the nucleophilicity of solvent. Solvent nucleophilicity is represented by the donor number. Current efficiency increases with donor number up to a certain limit.

1.9.3 Nucleation and Film Growth

The growth of the polymer film on the electrode surface may start in principle in two different ways. Either the growth starts simultaneously from all over the surface or it starts from a number of separate sites, called nucleation sites or centers. The former case is a true one-dimentional mechanism, whereas the latter may be divided into two dimentional and three-dimentional growth mechanism.

The formation of nucleation sites may be instantaneous or progressive. In the former case the number of nucleation sites stays constant from the very beginning and the growth from these centers starts to spread either laterally from the surface or by forming three dimentional pyramids or globules around the centers. In the case of progressive nucleation, new centers are formed continuously during the growth process.

1.9.4. Cell and Electrodes

The cell maybe, a two-electrode cell with one or two compartments. If the galvonastatic method is used, two electrodes are enough unless the potential is monitored. Two compartments are needed if one wants to avoid mixing electrolysis products from counter electrode and the working electrode. Some kind of porous diaphram is used to separate the two electrodes.

A three electrode cell with one or two compartments is used in the potentiostatic method. If the potentiostatic or potentiodynamic method is used, a reference electrode is necessary, the reference electrode may be simply Ag/Ag^+ wire or SCE.

The most common electrode materials for research purposes are platinum, because of its inertness, and indium tin oxide coated glass (ITO glass) for its transparency.

1.10 Applications of Conducting Polymers

The electronic and chemical behavior of conducting polymers give rise to many attractive features which have made them potential candidates for many devices including diodes, battery electrodes, sensors, and electrochromic displays [11].

The recent developments toward the synthesis of new and processable polymers as well as discovering the broad range of physical phenomena and chemical flexibility opens up opportunities for new technological applications. The higher environmental stability and modification of properties to suit a given end use and processability achieved with the polymer derived from acetylene, pyrrole, thiophene, aniline and their derivatives, polyphenylene, poly(phenylene vinylene) and poly(p-heterocyclic vinylenes) have emerged as the materials to replace metals and semiconductors in the electrical and electronics industry, as well offering themselves as the materials for the optoelectronic industry. The specific engineering applications are charted in Figure 1.5 [19].

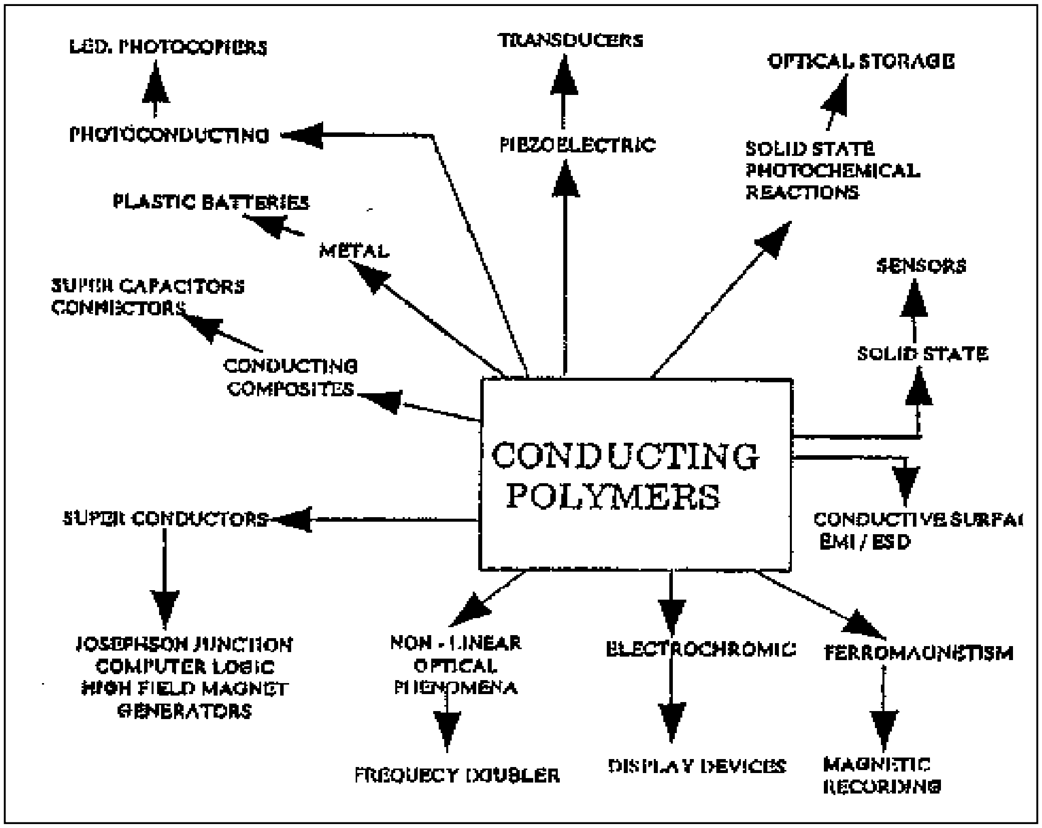


Figure 1.5 The Specific engineering applications of conducting polymers

The most advanced technical application concern the rechargeable polymer battery. Its attraction lies in the low weight of polymers as well as in environmental benefits. The active polymer electrode can be either used as a cathode, or as an anode, or as both cathode and anode [7].

Conducting polymers have filled an area of great need in the field of sensor technology. Applications range from chemical sensors for gas detection to pH electrodes to amperometric glucose electrodes [20].

Another important electrochemical application of conducting polymers may be their use as electrochromic displays. They are based on the fact that the color of a polymer changes during electrochemical charging and discharging. The use of conducting polymers as electrochromic materials is the most important aim of this thesis.

1.11 Electrochromism and Spectroelectrochemistry

The ways of producing color can be grouped into five fundamental mechanisms (Table 1.1). These five groups can be further split into what Nassau has called ‘the fifteen causes of color’.

The main Nassau grouping of i,iv,v can be considered as physical phenomena. ii is borderline between chemistry and physics and iii covers purely chemical phenomena [21].

The history of chromogenics dates back to 1704, when Diesbach discovered the chemical coloration of Prussian Blue. In the 1930s, electrochemical coloration was noted in bulk tungsten oxide. Twenty years later, Kraus observed electrochemical coloration in thin films. The first electrochromic devises were made by Deb in 1969. By the mid-1970s, electrochromic devices were being developed for displays. Electrochromics based on viologens and tugsten oxide followed in the 1980s for switchable mirrors in cars, which continues as a viable product to this day. In the 1990s, several companies began developing devices for glazing applications and the work still continues [22].

Group	Causes	Examples
i	Vibrations and simple excitations (external heat or energy transfer within molecules)	Incandescence, vapour lambs,some lasers.
ii	Ligand field effects (from unpaired electrons in transition metal ions and complexes)	Phosphoresance lasers.
iii	Transition between molecular orbitals	Absorbing dyes and pigments, both organic and inorganic, fluoresence
iv	Transition between energy bands	Metals, pure and doped semi-conductors
v	Geometrical and pysical optics	Interferance phenomena, diffraction, liquid crystals

Table 1.2 The five groupings causes of color.

The field of electrochromic devices has long been viewed as among the promising most of all CP application areas, and is basically making use of the color change associated with the redox reaction of some of the polymers, such as polyaniline. In electrochromic devices, a substance is customarily adsorbed onto a transparent conducting substrate, such as indium–tin oxide glass, or kept as a solution between transparent electrodes [11].

An electrochromic material is the one that changes color in a persistent but reversible manner by an electrochemical reaction and the phenomenon is called electrochromism. Electrochromism is the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation-reduction reaction. It results from the generation of different visible region electronic absorption band on switching between redox states [23]. Color changes are commonly between a transparent ('bleached') state, where the chromophore only absorbs in the UV region, and a colored state or between two colored states. Where more than two redox states are electrochemically accessible in a given electrolyte solution, the electrochromic material may exhibit several colors and be termed polyelectrochromic [24].

Electrochromic antiglare car rearview windows have already been commercialized, with other proposed applications of electrochromic materials including their use in controllable light-reflective or light-transmissive devices for optical information and storage, sunglasses, protective eye wear for the military, controllable aircraft canopies, glare-reduction systems for offices and smart windows for use in cars and buildings [24]. Whereas, classical research efforts focused on solid electrochromic devices using glass or transparent substrate, more recent investigations are developed to plastic substrates because of its flexibility and its potential interests for several applications such as flexible displays and switchable optical filters [25].

1.12 Poly(p-phenylene vinylene)

There has been a steadily growing interest in poly(p-phenylene vinylene) and its close derivatives [26]. In the field of polyconjugated organic polymers which show large electrical conductivities and optical non-linearities, PPV is becoming the center of interest in basic and applied material science [27, 28]. There are many reasons for this attention. PPV is easily synthesized in good purity and high molecular weight. It is relatively stable and quite insoluble, yet it can be manipulated as a water–soluble precursor polymer to form films and fibers. The optical band gap of 2.6 eV and bright yellow fluorescence make PPV a strong contender in applications such as light emitting diodes and photovoltaic devices. It can be readily doped to form electrically conductive materials and its physical and electronic properties can be varied over a wide range by the inclusion of functional side groups [26].

Conducting polymers have several advantages over metallic or mineral conductors. They are lighter, easy to work and often more resistant and less vulnerable to chemical corrosion at room temperature. Moreover their conductivity, sometimes similar to that of metals, is tuneable by adjusting the amount of doping agents [29]. Interest in conducting polymers is largely due to the wide range of possible applications because of their facile synthesis, good environmental stability and long-term stability of electrical conductivity. However they have the disadvantage of being insoluble and infusible; show poor mechanical and physical properties and poor processibilities [30].

PPV is a green emitter electroactive polymer which exhibits many optoelectronic properties such as electrical conductivity, electroluminescence, photoluminescence and photoconductivity. Like most conjugated polymers, PPV also has processibility problems because of its inherent insolubility and infusibility [31, 32].

A variety of methods to synthesize PPV has been reported over the years. The first attempt to synthesize PPV was through a direct chemical polymerization reaction. The product obtained in this way was in the form of an insoluble powder which limited the use of polymer in many applications [33]. The research interest in PPV increased considerably after the reports on electroluminescence properties of this polymer. The sulphonium precursor route, the most popular method to prepare PPV, is a base induced polymerization of sulphonium salt monomer in aqueous solution. PPV films are obtained from the precursor polymer after thermal elimination of the sulphonium groups [34]. The length of conjugation that can be achieved in the PPV material by this process largely depends on the way the thermal treatment of the precursor polymer is done. However analysis of the PPV material has shown that the polymer contains traces of both chlorine and sulfur [35].

A variety of analytical and spectroscopic techniques has been used to study PPV, commonly used techniques include FTIR spectroscopy [36], X-ray diffraction, electron diffraction, electron microscopy [38], optical spectroscopy [37], electrochemical methods [47], electron spin resonance spectroscopy [46] and NMR spectroscopy.

1.12.1 Chemical Synthesis

For the preparation of bis-sulfonium salt monomer, 10 g of α,ά-dichloro-p-xylene was dissolved in 150 mL of methanol and 15 mL of tetrahydrothiophene, THT was added. The resulting mixture was heated in a 50 °C oil bath overnight, after which the solution was concentrated, and 250 mL of acetone was poured in to precipitate the bis sulphonium salt. The mixture was stirred in an ice bath for half an hour before filtration. The white solid obtained was washed with acetone and dried under vacuum at room temperature until two sequential weightings were consistent [45].

The polymerization reaction to form the poly(p-xylylene-α-dimethylsulphonium chloride) precursor was effected in aqueous solution by the reaction of the monomer with an equimolar quantity of sodium hydroxide (0.2 M) at 0 °C for one hour under rigorous anaerobic conditions. The reaction was quenched by neutralization the solution with 1 M HCl to a slightly acidic pH (pH: 6.8) which yielded a highly viscous solution. The polyelectrolyte was separated from residual monomer and NaOH by dialysis against deionised water for 3 days. The polyelectrolyte was wet cast into free standing films by evaporation of water at or below ambient temperatures. The resulting polymer film was clear and could be redissolved in polar solvents. The solution could also be processed to yield foams or fibers [39,40]. The resulting polymer film was heated at elevated temperatures (220-300 °C) in vacuum to remove all the water, organic sulfides and HCl [45].

1.12.2 Electrochemical Synthesis

The PPV was electrochemically polymerized onto the ITO coated glass substrate (working electrode) by potential scanning between +1.3 V and -2.3 V (4 scans, scan rate 30 mV/s) in a DMF solution containing 0.05 M α,α,α′,α′-tetrabromo-p-xylene and 0.1 M TEABF with addition of 0.2 % water [41,46,47].

In the study of Win-Pin Chang et al. [38] the solution for the electropolymerization was obtained by dissolving 0.05 g p-xylenebis(tripheneyl-phosphonium bromide) in 50 ml acetonitrile. A pre-cleaned ITO conductive glass was used as a working electrode at the cathode, and a platinum plate was employed as a counter electrode at the anode. The two electrodes were separated by 2 cm. The electropolymerization reaction was carried out by a current with a fixed voltage level of 5.5 V under ambient conditions. After the electropolymerization reaction, transparent PPV was obtained by heating the electropolymerized film in a high vacuum oven at 220 °C for 2 hours.

Çırpan et al. also obtained PPV by using PXDBC monomer in ACN-TBAFB electrolyte solution at a fixed voltage of +2.5 V. At the end of the electropolymerization yellow and insulator polymer film was obtained at the surface of the counter electrode [42].

1.12.3 Synthesis on the ITO coated glass electrode

PPV, a polymer widely investigated for electroluminescent displays is made by spin coating a precursor from solution and converted thermally at 300 °C to the polymer. An alternative route to the deposition of PPV is chemical vapor deposition. In this process, chlorinated xylene condenses onto a substrate and forms a precursor polymer which is then thermally converted to PPV [43, 38].

In the study of T. Shirakawa et al. [44] PPV thin films were prepared by casting PPV precursor onto ITO coated glass electrode and heating at 250 °C for 6 hours under vacuum.

1.13 Aim of the Study

The aims of the study can be listed as follows,

1. To synthesize the p-xylene-bis(diethylsulphonium chloride) monomer.
2. To prepare chemically synthesized PPV in order to compare with the electrochemically synthesized PPV.

3. To achieve the electrochemical synthesis of PPV starting from p-xylene-bis(diethylsulphonium chloride) monomer.

4. To characterize the structure of the polymer by FTIR and DSC techniques.

5. To achieve electrochemical doping by using two different dopants (TBAFB and $LiClO_{4)}$ and investigate their conductivity by using four-probe technique.

6. To investigate electrochromic and spectroelectrochemical properties of PPV.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

-Acetonitrile (Merck): Reagent quality acetonitrile was used without any further purification.

-Diethylsulphide (Merck): Reagent quality diethylsulphide was used without any further purification.

-Tetrahydrothiphene (Merck): Reagent quality tetrahydrothiophene was used without any further purification.

-Tetrabutylamonium tetrafluoroborate (Aldrich): It was used as a dopant without any further purification.

-α,α-dichloro-p-xylene (Aldrich): It was used without any further purification.

-Methanol (Merck): Reagent quality methanol was used without any further purification.

-Acetone (Merck): Reagent quality acetone was used without any further purification.

-H_2SO_4, HCl and NaOH (Merck): They were used without any further purification.

- $LiClO_4$ (Aldrich): It was used as a dopant.

2.2 Instrumentation

2.2.1 Potentiostat

Electrolysis was carried out by using a Potentioscan MODEL PS 95D potentiostat. The function of potentiostat is to maintain the potential of the WE at an adjusted level with respect to fixed the RE. It can be used for keeping the voltage difference between the working and the reference electrodes at a constant desired value during the electrolysis. The current driven by the potentiostat can be determined by measuring the voltage drop across a small resistance R connected to the counter electrode series.

In a three electrode potentiostatic system, the major current passes only through the CE and the WE. The current amplifier supplies current to the cell, regardless of the solution resistance. By this way the purpose of maintaining potential control between the two electrodes has been accomplished.

2.2.2 Cyclic Voltametry (CV) System

The system was composed of a potentiostat, and a CV cell. The cell consist of three electrodes namely WE, CE, and RE. They were kept close to each other as much as possible to carry out the measurements with the highest possible accuracy by minimizing IR drop. In CV cell, 1 cm length platinum bead working electrode was placed next to the 3 cm length platinum spiral counter electrode. The reference electrode which was Ag/Ag^+ was separated from the others by Luggin capillary. The cell used in CV studies is shown in Figure 2.1.

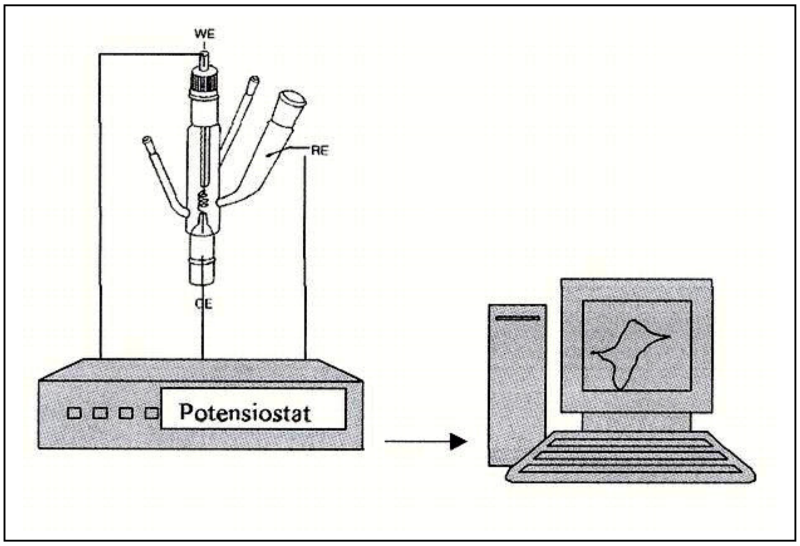


Figure 2.1 The schematic view of the CV cell used in the studies.

2.2.3. Electrolysis Cell

The polymerization reaction was carried out in an H-shaped cell that can hold 60 ml solution. The reference electrode was Ag wire, and the WE and CE electrodes were platinum with an area of 1 cm^2. The cell was divided into anolyte and catholyte compartments by a medium porosity sintered glass disc with a diameter of 2 cm. The cell was suitable for purging N_2 through the solution by glass inlets. The electrolysis cell used in the studies is shown in Figure 2.2.

2.2.4 ^{1}H and ^{13}C Nuclear Magnetic Resonance Spectrometer (^{1}H-NMR and ^{13}C-NMR)

^{1}H-^{13}C NMR spectra of monomer were taken by Bruker Instrument-NMR Spectrometer (DPX-400). The spectra were run in D_2O.

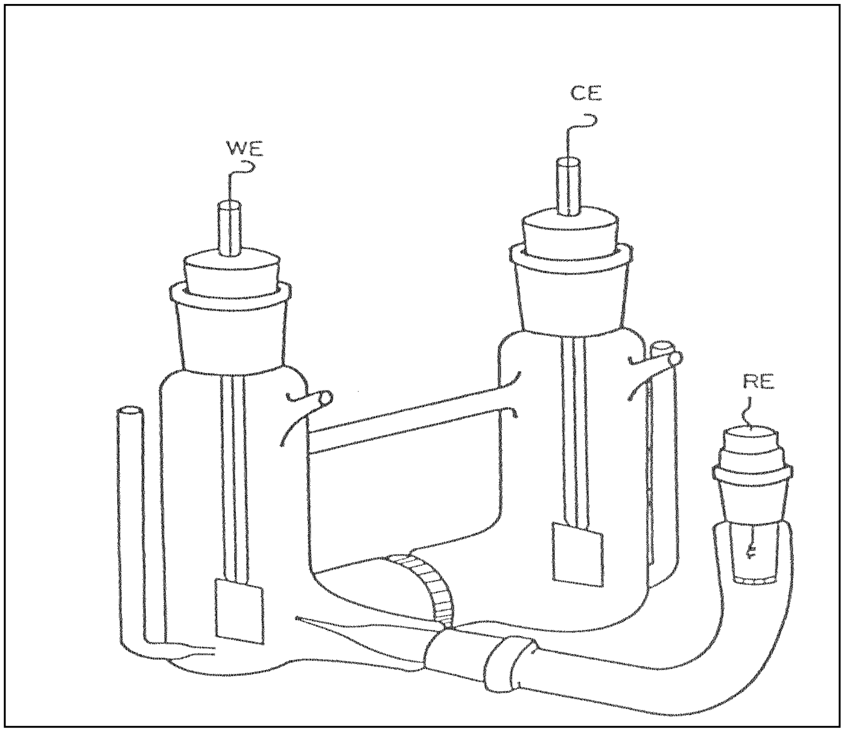


Figure 2.2 The H-shaped electrolysis cell used in electropolymerization reaction.

2.2.5 Fourier Transform Infrared Spectrophotometer (FTIR)

The spectrophotometer used in order to detect the functional groups of the polymer was a Nicolet DX 510 FTIR. The spectra were recorded by using KBr pellets.

2.2.6 Differential Scanning Calorimetry

A DSC 910/TA 2000 instrument was used to perform thermal analysis under N_2 atmosphere.

2.2.7 UV-VIS Spectroelectrophotometer

In order to carry out spectroelectrochemical studies, a HP8453A UV-VIS spectrophotometer was used. It was used to measure absorbances of the films at different potentials.

2.2.8 Conductivity Measurements

Conductivity of the polymer was measured on compressed pellets by using four probe measuring system. Figure 2.4 shows the schematic representation of four probe system.

Conductivity is given by the equation: $\sigma = (\ln 2/ \pi d) \times (i/V)$

σ: conductivity

i: current applied through the outer probes

d: sample thickness

V: voltage drop measured across the inner probes.

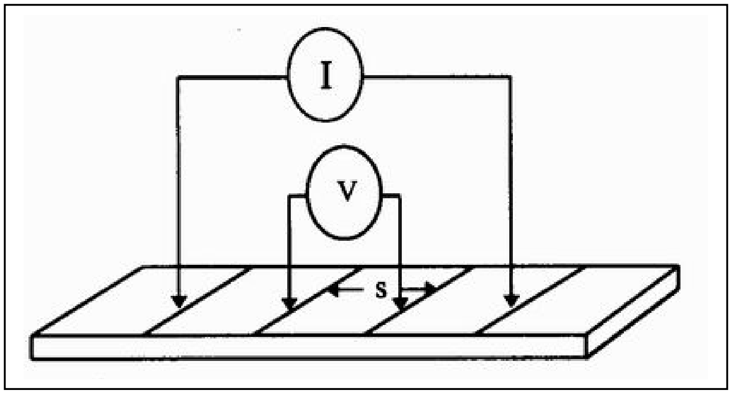


Figure 2.3 Schematic representation of four probe system.

2.3 Procedure

2.3.1 Synthesis of the p-xylene-bis(diethylsulphonium chloride) monomer

In the synthesis of monomer, 0.75 M α,α-dichloro-p-xylene was reacted with excess tetrahydrothiophene THT and/or diethyl sulphide at 50 °C in methanol:water (80:20) solution in an oil bath for 24 hours. The solution was concentrated by heating. The monomer was precipitated with cold acetone, before filtration it is stirred in an ice-bath for half an hour. The white powder was obtained by filtration, washing with acetone and vacuum drying.

2.3.2 Chemical Polymerization of PPV

The polymerization reaction was carried by mixing equal volumes of 0.5 M monomer with 0.5 M aqueous solution of NaOH at 0 °C under nitrogen with stirring in an ice-salt bath. After one hour a white precipitate was formed. The polymerization reaction was terminated by the addition of 1M aqueous solution of HCl. The resulting precursor polymer was yellow. It was dried at 30 °C under vacuum. The resulting polymer film was heated at 245 °C in vacuum to remove all the water, organic sulfides and HCl.

2.3.3. Electrochemical Polymerization of PPV

2.3.3.1 Cyclic Voltametry

Measurements were performed in ACN-TBAFB (0.1 M) solvent-electrolyte couple under N_2 atmosphere at room temperature. The WE and CE were platinum and RE was Ag/Ag^+ wire. The electroactivities of the polymer forming on the WE were investigated at potentials between 0V and 3V. The scan rate was adjusted to 50 mV/s.

2.3.3.2 Electroinitiated Polymerization

PPV was synthesized electrochemically in a three electrode cell by using Pt electrodes as WE and CE under N_2 atmosphere. Ag/Ag^+ wire was utilized as the reference electrode. Constant potential was supplied by PS 95D potentiostat.

The solution was obtained by dissolving 0.05 M PXDBC monomer in 60 ml ACN and 0.1 M supporting electrolyte, TBAFB and 0.2% water was added to the solution. Before polymerization the solution was degassed with N_2 atmosphere. The polymerization reaction was carried out by current with fixed voltage (-2.3V) at room temperature. After one hour yellow precursor polymer was obtained at the WE. It was screwed from the electrode and heated in vacuum oven at 245 °C for 6 hours in order to eliminate water and organic sulfides. The resulting polymer was brown.

2.3.4 Doping

Electrochemical doping of PPV with $LiClO_4$ was studied. The electroactivity was investigated by cyclic voltametry. For CV measurements 0.1 M $LiClO_4$ was dissolved in 25 ml ACN and 0.05 M monomer was added. The electroactivity of the polymer formed was investigated at potentials range 0-3 V.

In the electrochemical synthesis 0.1 M $LiClO_4$ was dissolved in 60 ml ACN and 0.05 M PXDBC monomer was added. The WE and CE were platinum and RE was Ag/Ag^+ wire. The solution was purged with N_2 before polymerization reaction. The potential was fixed at 1.0 V. After one hour white polymer was obtained on the WE. The polymer was screwed from electrode surface and heated at 245 °C for 6 hours in a vacuum oven. The resulting polymer was black.

2.3.5 Spectroelectrochemistry

In order to carry out spectroelectrochemical and electrochromic studies chemically synthesized PPV was dissolved in water and then cast into indium tin oxide coated glass slide (ITO) and heated at 245 °C for 3 hours in vacuum oven. The resulting polymer was yellow.

For the spectroelectrochemical studies PPV film deposited on ITO was connected to the three electrode quartz cell. UV-VIS spectra of the film was recorded at various applied potentials in ACN/TBAFB (0.1M) solution. The color change between oxidized and reduced states (green and yellow respectively) was observed.

CHAPTER3

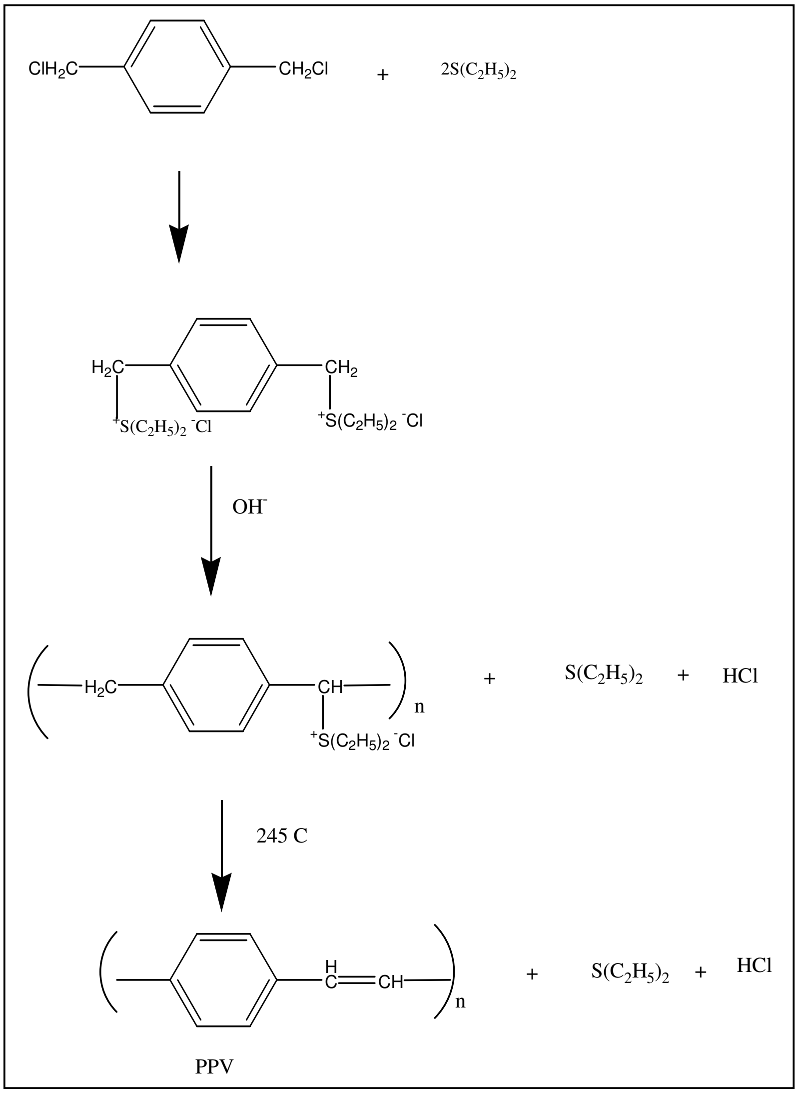
RESULTS AND DISCUSSION

3.1. Chemical Synthesis of PPV

Poly(p-phenylene vinylene) can be prepared in high molecular weight from a precursor polymer by a route originally described by Wessling and co-workers [45]. In our study we prepared the chemically synthesized polymer by the same method that Wessling and co-workers done. In Scheme 3.1 the reaction scheme is given.

Conversion of the precursor into PPV can be made by thermal elimination of the sulphonium group. This elimination reaction is a crucial step in the synthesis as defects in the system have large effects on the performance of the final material [46]. The length of the conjugation that can be achieved in the PPV material by this process largely depends on the way the thermal treatment of the precursor polymer is done [47]. By thermal treatment at 160-180 °C the soluble precursor polymer is converted to the non-soluble PPV [48].

The soluble precursor polymer was light green in color but the latter insoluble and thermally eliminated PPV was yellow.



Scheme 3.1 Processing scheme of chemically synthesized PPV

3.2 Electrochemical Synthesis of PPV

3.2.1 Cyclic Voltametry

The oxidation-reduction behavior of the PXBDC monomer has been studied by cyclic voltametry, in order to determine the voltage of electrochemical polymerization reaction. Measurements were carried out in ACN-TBAFB solvent electrolyte couple versus Ag/Ag^+ wire under N_2 atmosphere, at room temperature. In the first scan PXBDC monomer shows two irreversible oxidation peaks at 1.8 and 2.26 V respectively. After half an hour yellow precursor polymer was seen on the surface of the CE. Cyclic Voltamogram of PXBDC monomer is shown in Figure 3.1.

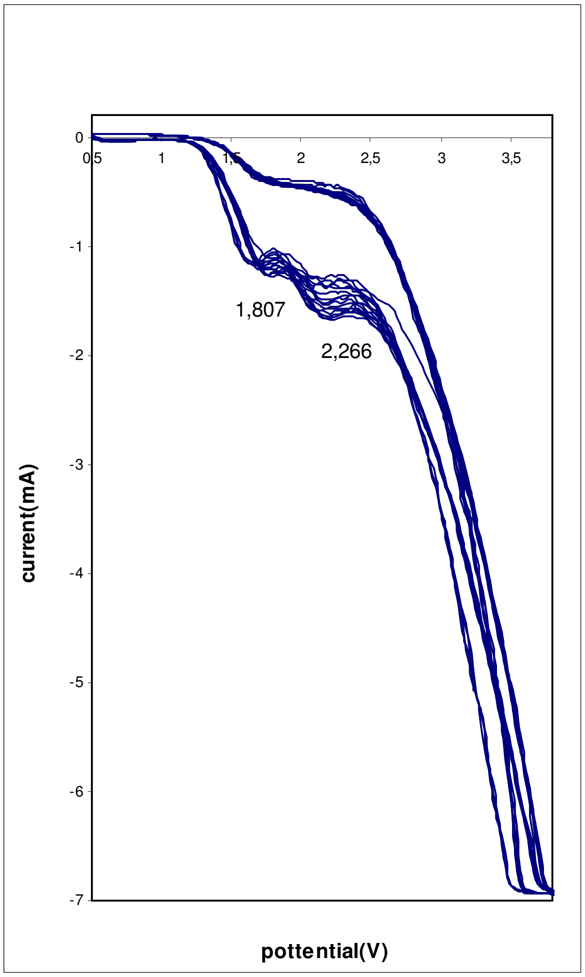


Figure 3.1 Cyclic Voltammogram of PXBDC monomer in ACN-TBAFB solution at room temperature

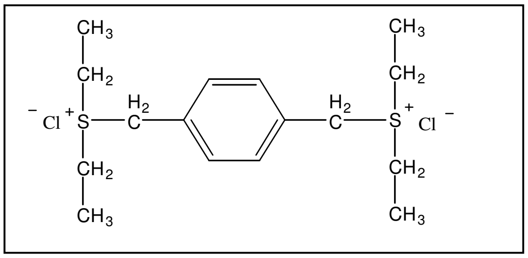
3.2.2 Electrochemical Polymerization

In order to obtain polymer on the surface of the working electrode,-2.3 V fixed voltage was used because PXBDC monomer is prone to reduction. PXBDC monomer is polymerized in ACN-TBAFB+0.2 % water solvent-electrolyte pair at -2.3 V versus Ag/Ag^+ wire at room temperature. During electrochemical polymerization the color of the solvent in the cathode compartment turned to yellow, and after one hour yellow, insoluble insulating polymer was obtained on the electrode surface. We used 0.2% water during polymerization because Damlin et al found that the addition of water in the monomer solutions used in combination with TBAFB resulted in films with adhesion [47]. We saw that water increases solubility of the monomer in ACN so polymerization was faster. The resulted yellow precursor polymer was screwed from the electrode surface and heated in vacuum oven at 245 °C for 6 hours and then insoluble brown polymer was obtained.

3.3 Characterization

3.3.1 Characterization of the monomer

3.3.1.1 ^{1}H-NMR and ^{13}C-NMR



p-xylene-bis(diethylsulphonium chloride) monomer

Figure 3.2 shows ^{1}H-NMR of the PXBDC monomer. ^{1}H-NMR (400 MHz, D_2O); δ=1.30 (t,12 H), δ=3.15 (q,8H), δ=4.60 (s, 4H), δ=4.70 (s, D_2O), δ=7.53 (s,4H).

Figure 3.3 shows ^{13}C-NMR of the PXBDC monomer. ^{13}C-NMR (400 MHz, D_2O); δ=15.77 (CH3), δ=37.0 (CH2), δ= 40.20 (CH2), δ=136.93 (C), δ=139.199 (CH).

3.3.2 Characterization of PPV

3.3.2.1 FTIR Analysis

Characterization of the chemically and electrochemically synthesized PPV was done with FTIR analysis. For this analysis chemically and electrochemically synthesized polymers were dried at 30 °C and pressed with KBr before and after heating in vacuum oven at 245 °C.

In the literature research, at 966 cm^{-1} characteristic of an out of plane bending vibration of the vinyl group in trans configuration [46,49], at 2900 cm^{-1} sp^3 C-H stretch region were seen which indicate the uneliminated units [39], the bands near 831 and 1512 cm^{-1} were assigned to para-phenylene ring C-H out of plane bending and C-C ring stretching respectively [38], in the case of treatment in air, an absorption band at 1695 cm^{-1} assigned to the carbonyl group which indicates that the polymer was oxidized thus breaking the carbonyl group was observed [2], the broad band between 1160 and 1000 cm^{-1} originates from vibrations from the anion BF_4^- introduced in the polymer during polymerization [46]. The substantial completion of the thermal conversion is clear from the absence of bands at 632, 1047, 1318, 1433 and 2998 cm^{-1} which are present in the precursor polymer. These bands are associated with diethyl sulphide moiety and correspond respectively to the C-S stretch, S-CH_3 rock, CH_3 symmetric deformation, CH_3 asymmetric deformation and CH_3 asymmetric stretch modes. Another band that is lost from the precursor spectrum following thermal conversion is that at 2913 cm^{-1} which is thought to arise from the asymmetric stretch of the R-CH_2-R unit of the precursor [36].

Figure 3.4 show the result of FTIR spectra for the chemically synthesized precursor polymer which is dried at 30°C for 3 hours. Figure 3.5 show the result of FTIR spectra for the polymer that is chemically synthesized and heated under vacuum at 245 °C for 6 hours. At 976 cm^{-1} C-H out of plane bending, characteristic peak of the trans configuration of the vinylene group was seen in both of the spectra. This proves that partial elimination of diethyl sulfide and HCl occur during the polymerization reaction. At 2900 cm^{-1} the intensity of the peak seen in the precursor polymer was increased because it indicates the uneliminated units and associated with diethyl sulphide moiety. Also intensity of the peaks seen at 500, 1049, 1260 and 1400 cm^{-1} were decreased in the eliminated polymer (Figure 3.5) because they are associated with diethyl sulphide moiety and correspond to the C-S stretch, S-CH_3 rock, CH_3 symmetric deformation, CH_3 asymmetric deformation respectively. The intensity of the absorption band near 3200 cm^{-1} was increased after the heat treatment due to the elimination of diethyl sulfide and HCl. This proves the elimination of diethyl sulfide groups but the elimination is not completed.

Figure 3.6 show the result of FTIR spectra for the electrochemically synthesized precursor polymer which is dried under vacuum at 30 °C. Figure 3.7 show the result of FTIR spectra for the electrochemically synthesized polymer heated under vacuum at 245 °C for 6 hours. At 976 cm^{-1} C-H out of plane bending peak of the trans configuration of the vinylene group was seen in both of the spectra. Peak seen at 1100 cm^{-1} originates from vibrations from the anion BF_4^- introduced in the polymer during polymerization. The intensity of this peak at Figure 3.6 is higher than the peak at Figure 3.7 which may indicate the loss of some dopant upon heating.

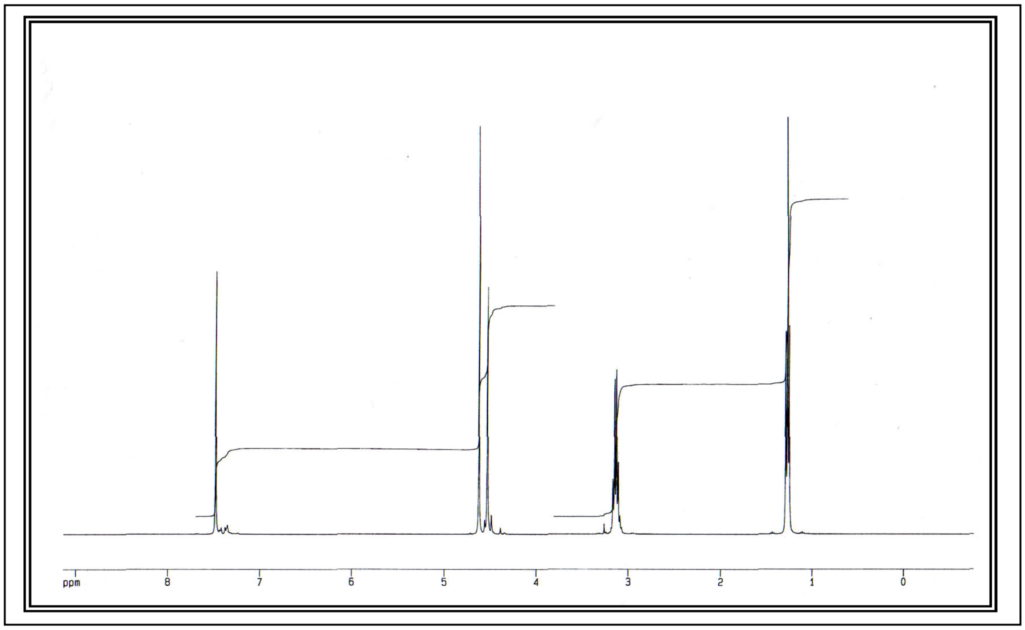


Figure 3.2 ^{1}H-NMR of the PXDBC monomer

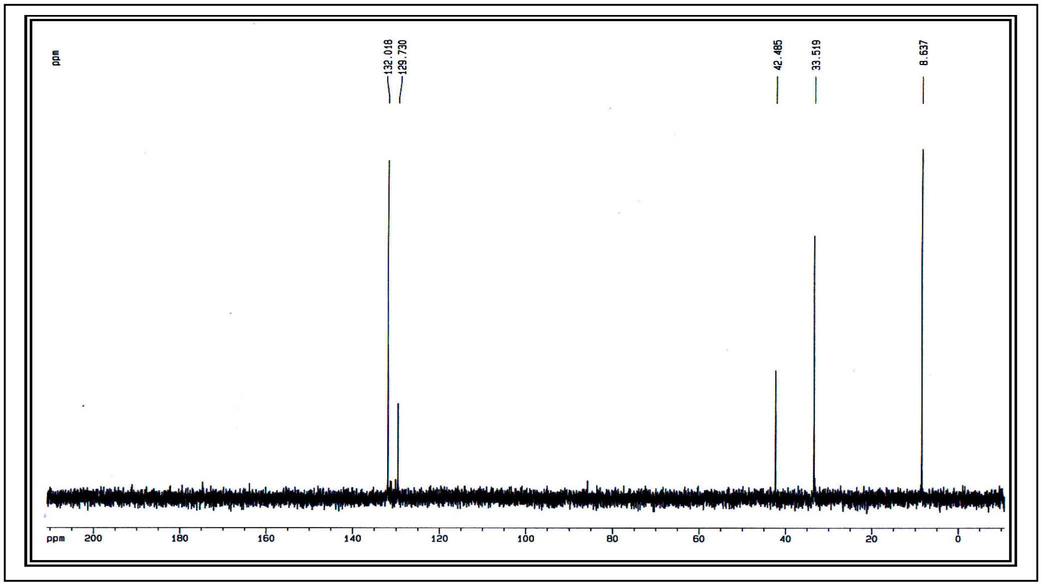


Figure 3.3 ^{13}C-NMR of the PXDBC monomer

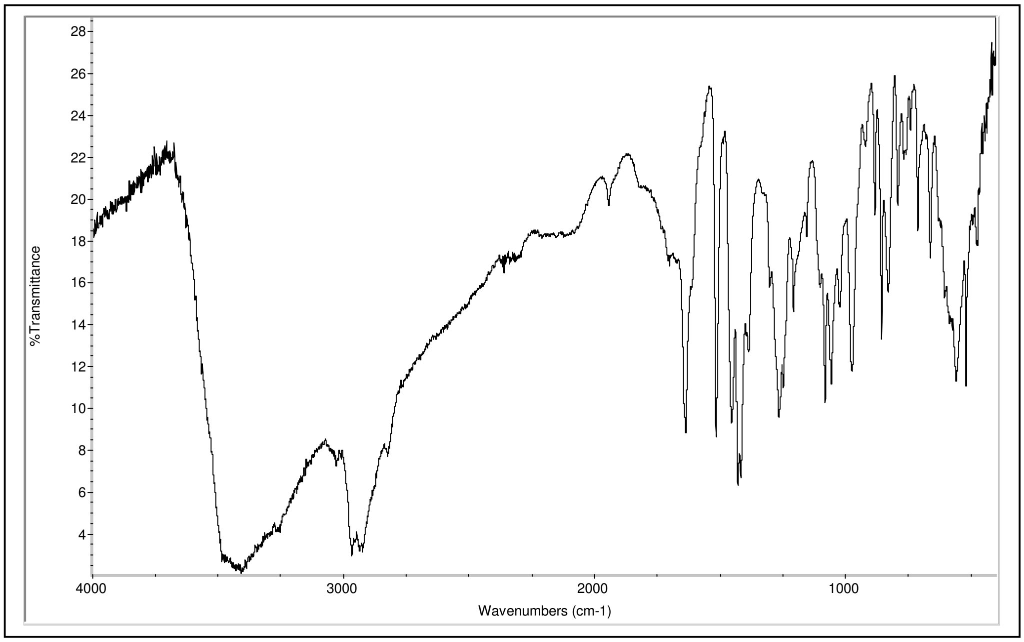


Figure 3.4 FTIR spectra of chemically synthesized precursor polymer

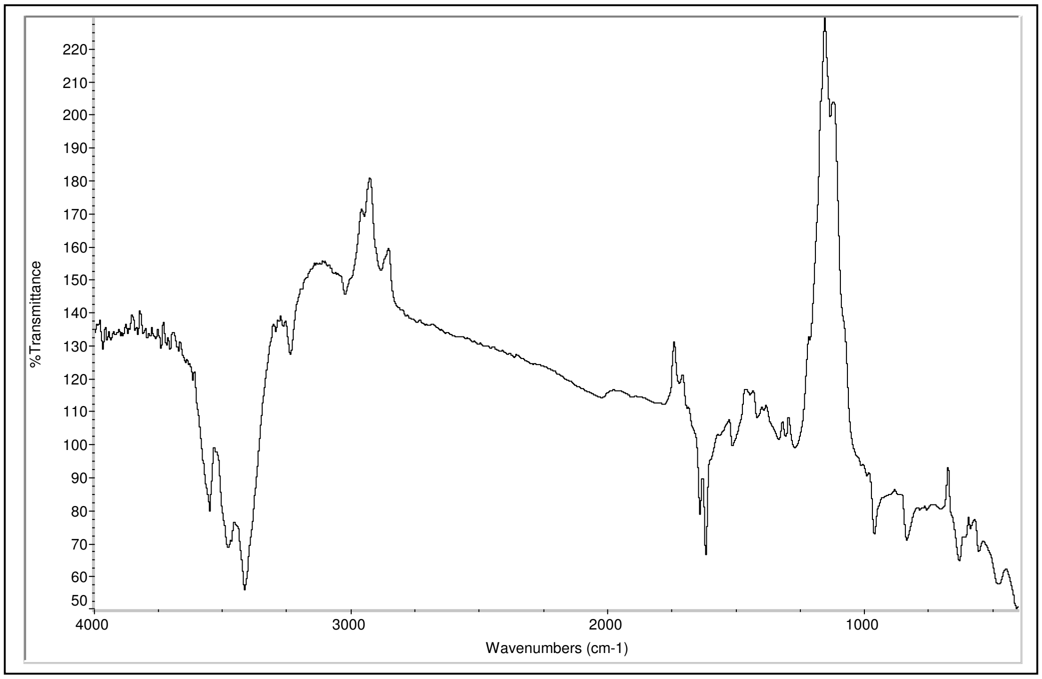


Figure 3.5 FTIR spectra of chemically synthesized PPV heated at 245 °C

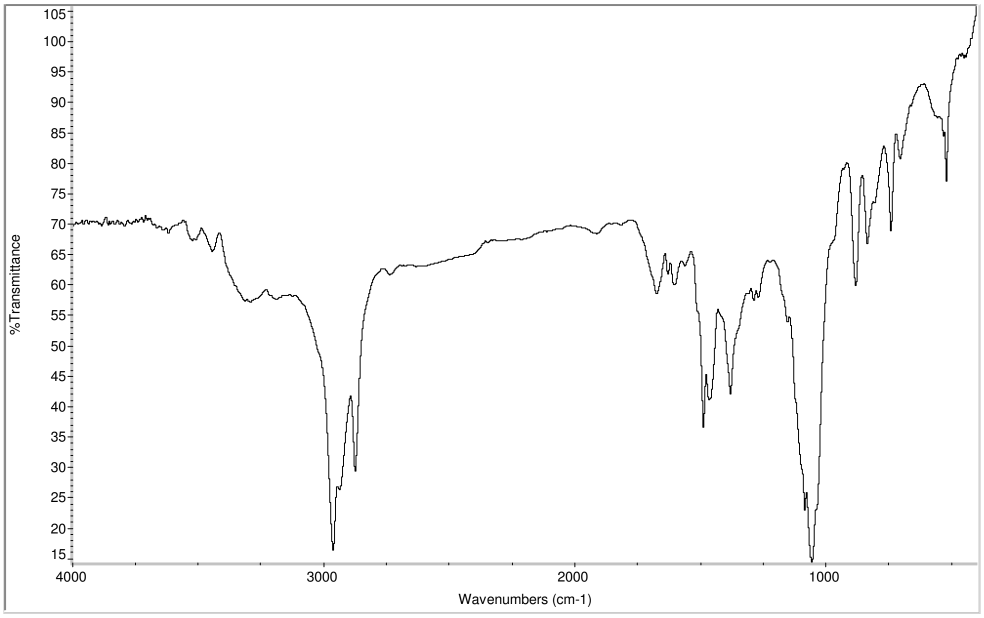


Figure 3.6 FTIR spectra of electrochemically synthesized precursor polymer

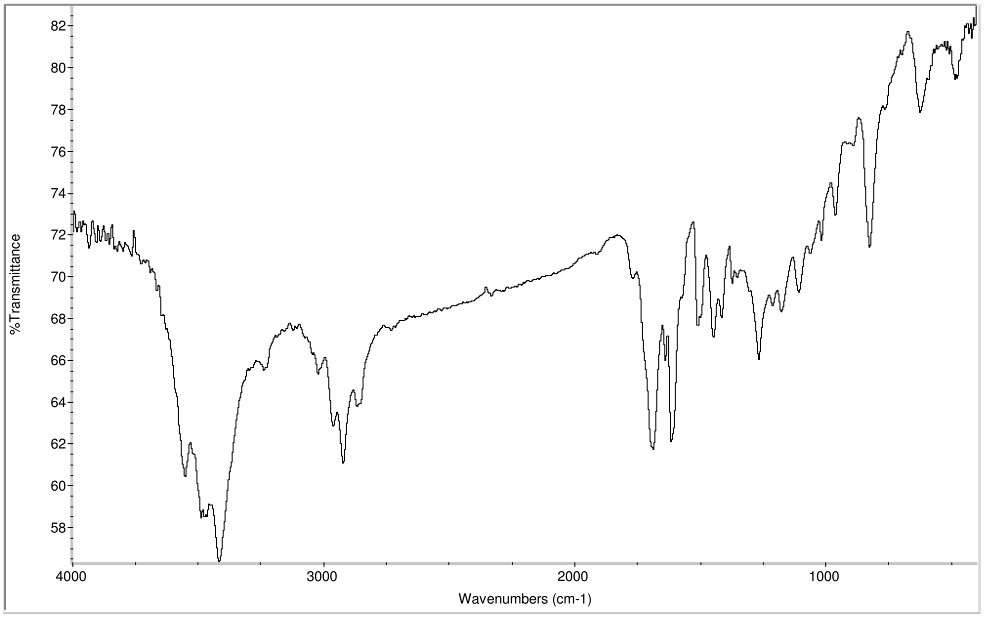


Figure 3.7 FTIR spectra of electrochemically synthesized PPV heated at 245 °C

In the FTIR spectra, at 976 cm^{-1} characteristic peak of the trans vinylene group of the PPV was seen, which indicates that PPV is synthesized successfully, and the importance of the elimination reaction was understood from the decrease of the intensity of the characteristic peaks of diethyl sulphide group.

3.3.2.2 Differential Scanning Calorimetry

Thermal behavior of the polymers was investigated by using DSC. Spectra were taken in a temperature range 25 °C to 480°C with a heating ratio of 10 °C per minute under N_2 atmosphere.

Figure 3.8 shows DSC thermogram for the chemically synthesized precursor polymer, which is dried at 30 °C. First transition is due to the removal of the solvent at 67 °C, the second one is the result of the elimination reaction and removal of diethyl sulfide and HCl at 233 °C. The third one at 370 °C is because of the decomposition of the polymer.

Figure 3.9 shows DSC thermogram for the chemically synthesized polymer, which is heated under vacuum at 245 °C for 6 hours. There was not any clear transition in the DSC spectra which proves that elimination reaction is almost complete.

Figure 3.10 shows DSC thermogram for the electrochemically synthesized precursor polymer, which is dried at 30 °C. The first peak at 121 °C is because of the removal of the solvent from the polymer. The second one between 200 and 275 °C is related to the elimination reaction yielding diethyl sulfide and HCl during the conversion of precursor polymer to PPV. Finally the endothermic transition at 357 °C is due to the degredation reaction of PPV.

Figure 3.11 shows DSC thermogram for the electrochemically synthesized polymer, which is heated under vacuum at 245 °C for 6 hours.

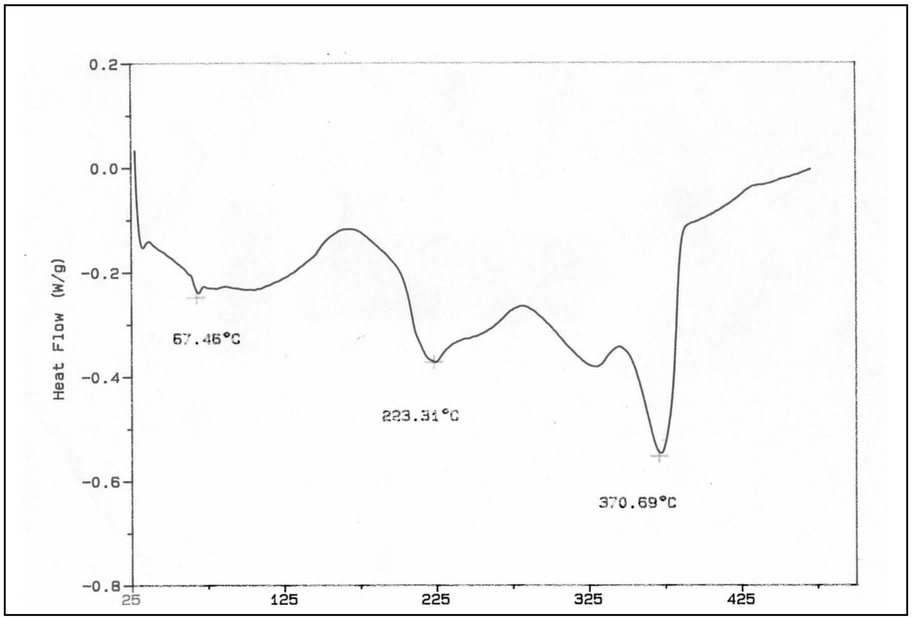


Figure 3.8 DSC thermogram of the chemically synthesized precursor polymer

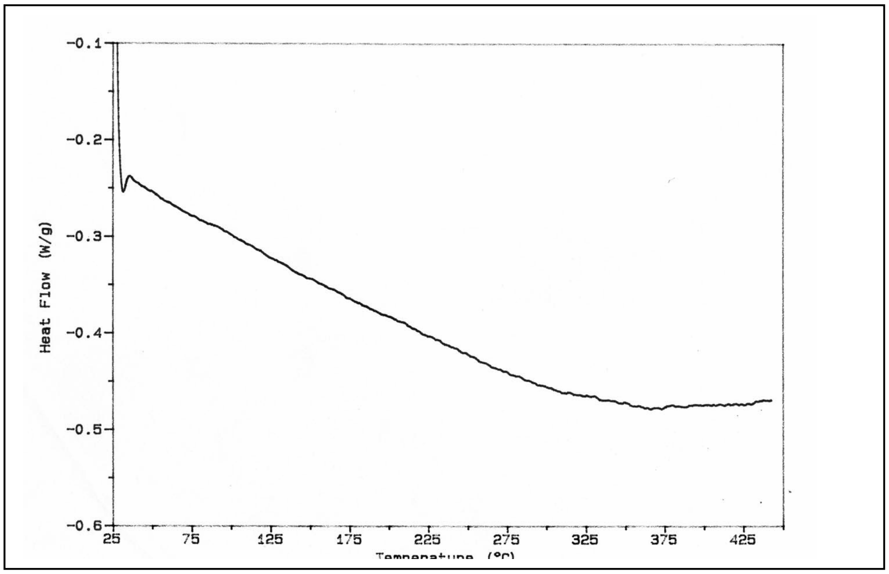


Figure 3.9 DSC thermogram of the chemically synthesized polymer heated at 245 °C

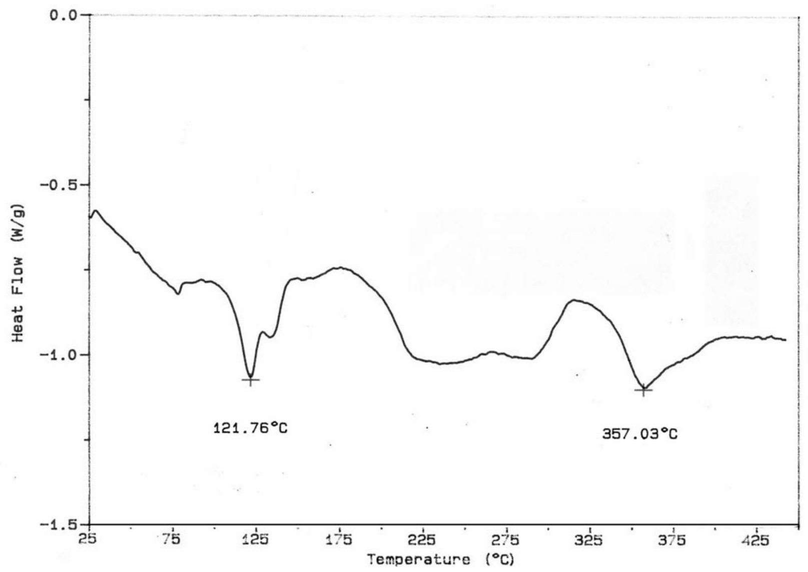


Figure 3.10 DSC spectra of the electrochemically synthesized precursor polymer

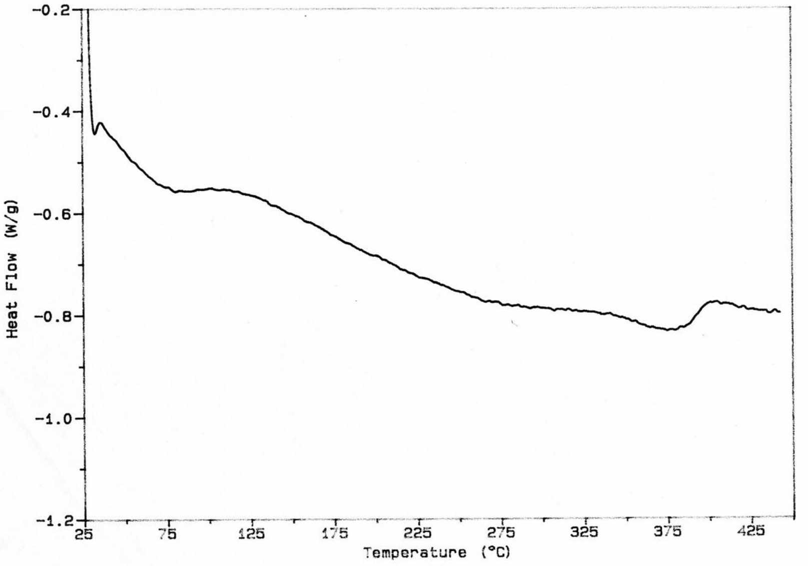


Figure 3.11 DSC spectra of the electrochemically synthesized polymer heated at 245 °C

There was not any clear transition in the DSC thermogram as in Figure 3.9 because of the elimination reaction.

3.4 Doping

Although PPV has conjugated double bonds in its structure, it isn’t conductive. It becomes electrically conductive upon the addition of electron donors and acceptors. In this study electrochemical doping technique was used. In order to investigate the effect of dopant to conductivity two dopants (TBAFB and $LiClO_4$) were used.

3.4.1 Cyclic Voltametry

The oxidation-reduction behavior of the PXDBC monomer has been studied by cyclic voltammetry, in order to determine the voltage of electrochemical polymerization reaction. Measurements were carried out in ACN-$LiClO_4$ solvent electrolyte couple versus Ag/Ag^+ wire under N_2 atmosphere, at room temperature. PXDBC monomer shows one reduction peak at 1.01 V and one oxidation peak at 1.3 V. Cyclic Voltammogram of PXDBC monomer is shown in Figure 3.12.

3.4.2 Electrochemical Polymerization

The electrochemical polymerization was achieved in ACN-$LiClO_4$ solution using Pt electrode as WE and CE under N_2 atmosphere. The potential was fixed at 1.0 V, after one hour the precursor polymer was obtained on the WE. The polymer was screwed from the electrode surface and heated under vacuum at 245 °C. The resulting polymer was black.

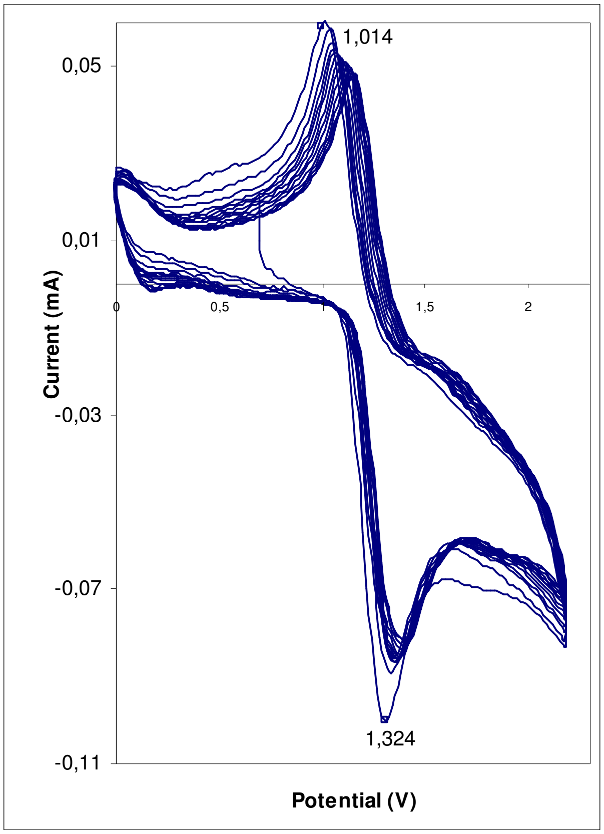


Figure 3.12 Cyclic Voltamogram of PXDBC monomer in ACN- $LiClO_4$ solution at room temperature

3.4.3 FT-IR Analysis of $LiClO_4$ doped polymer

Characterization of the doped PPV was done with FTIR analysis. For this analysis electrochemically doped polymers were pressed with KBr before and after heating in vacuum oven at 245 °C.

Figure 3.13 shows the result of the FTIR spectra for the polymer that was doped with $LiClO_4$ and dried under vacuum at 30 °C for 3 hours. Figure 3.14 shows the result of the FTIR spectra for the polymer that was doped with $LiClO_4$ and heated under vacuum at 245 °C for 6 hours.

At 976 cm^{-1} C-H out of plane bending, characteristic peak of the trans configuration of the vinylene group was seen in both of the spectra which proves that partial elimination of diethyl sulphide and HCl occur during the polymerization reaction. The peak seen at 1440 cm^{-1} originates from vibrations from the anion ClO_4^- introduced in the polymer during polymerization.

When comparing Figure 3.13 and Figure 3.14, the intensity of the peak seen at 2990 cm^{-1} which indicates the uneliminated units is decreased in the one that is heated at 245 °C for 6 hours. Another band that is decreased from the precursor spectrum following thermal conversion is that at 2913 cm^{-1} which is thought to arise from the asymmetric stretch of the R-CH_2-R unit of the precursor [36].

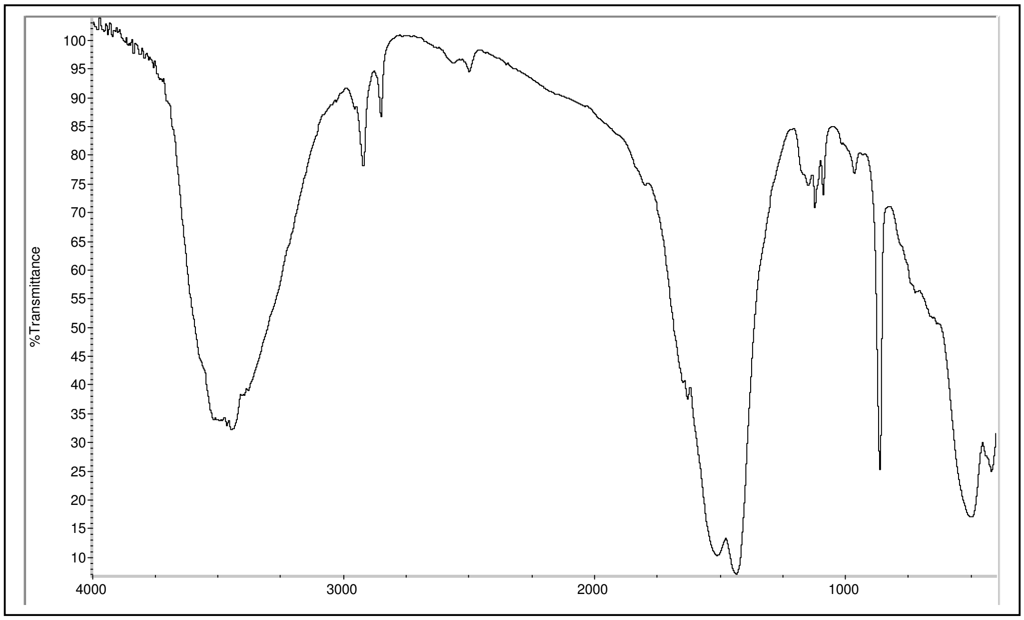


Figure 3.13 FTIR spectra of the PPV doped with $LiClO_4$ dried at 30 °C for 3 hours.

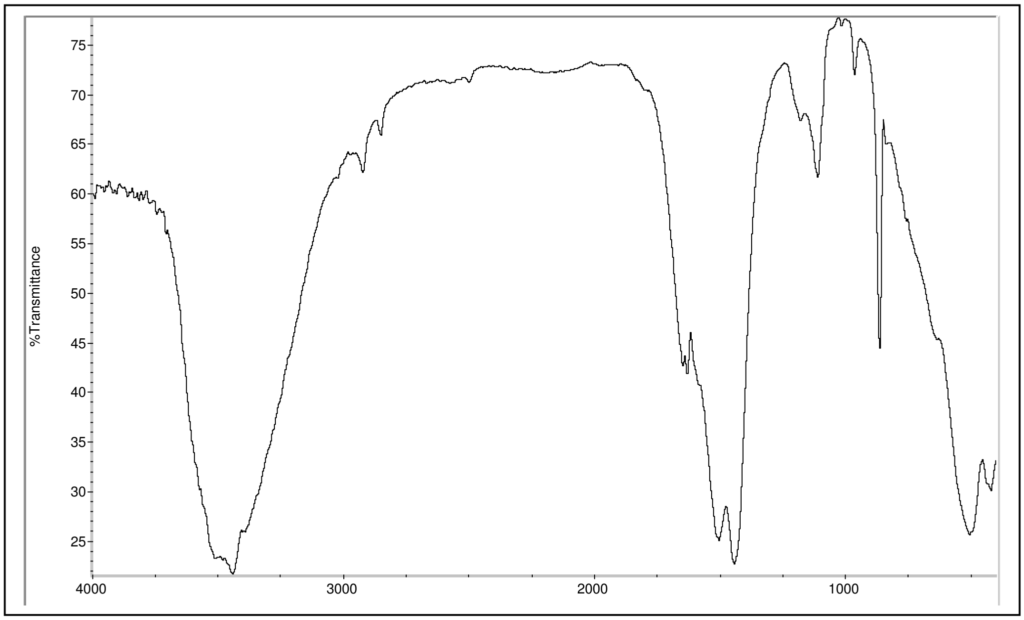


Figure 3.14 FTIR spectra of the PPV doped with $LiClO_4$ and heated at 245°C for 6 hours.

3.4.4 Electrical Conductivity

Electrical conductivity measurements were carried out by using the standard four-probe technique. For the conductivity measurements PPV was doped with TBATFB and $LiClO_4$ by the electrochemical way.

Conductivity of the polymer doped with BF_4^- was 3.5 10^{-3} $(ohm.cm)^{-1}$ and the conductivity of the polymer doped with ClO_4^- was 4.7 10^{-3} $(ohm.cm)^{-1}$.

Although the polymer doped with ClO_4^- is more conductive compared to BF_4^- doped polymer, the conductivities are in the same order of magnitude.

3.5 Spectroelectrochemical behavior of PPV

Spectroelectrochemical properties of PPV were studied in TBAFB (0.1M)/ACN electrolyte-solvent couple. For this purpose films deposited on the ITO coated glass electrode were placed in a UV cuvette for UV-VIS experiments.

After 30 seconds oxidation of the polymer film at 1.1 V a new band at 637 nm forms which indicates the formation of polarons. However during stepwise oxidation of the polymer film at 1.1 V this band and the band that appear at 490 nm start to decrease in intensity. Upon reduction of the film at 0.1 V for 60 seconds, the polaronic band completely disappears (Figure 3.15). The film is yellow colored in the reduced form and it becomes green during oxidation (Figure 3.16). The shift upon applied voltage is related to the electrochromic property of the polymer. With multiple cycles polymer tend to loose its ability to access these multicolor states.

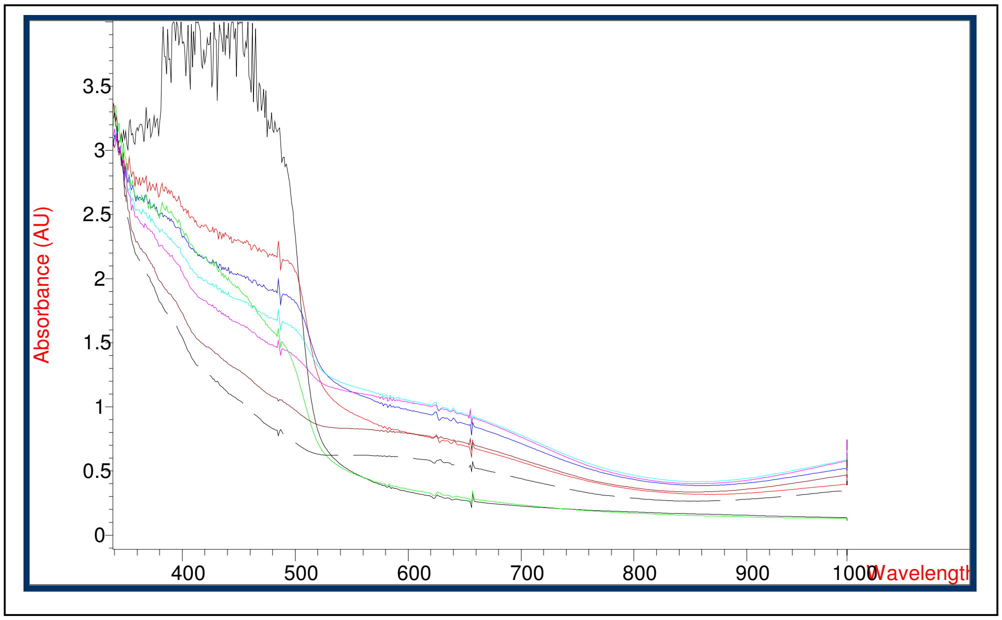
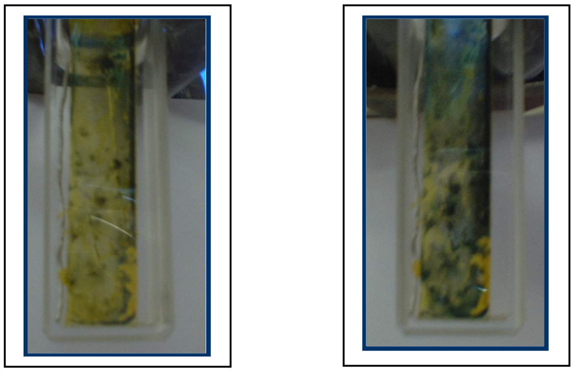


Figure 3.15 Spectroelectrochemisty of PPV.



(a) (b)

Figure 3.16 Color change of PPV film during oxidation and reduction (a) reduced (b) fully oxidized state

CHAPTER 4

CONCLUSION

PXDBC monomer was synthesized starting from α,α-dichloro-p-xylene. The polymer was synthesized both by chemical and electrochemical polymerization technique. Chemical polymerization of PPV was performed by the sulphonium precursor route which is a base induced polymerization of sulphonium salt monomer in aqueous solution. The electrochemical synthesis of the PPV was achieved by using ACN/ TBATFB solvent-electrolyte couple.

The structure of the monomer was supported by ^{1}H-NMR and ^{13}C-NMR spectroscopic analyses.

Electrochemical behavior of PXDBC monomer was investigated by cyclic voltammetry. Cyclic voltammogram of PXDBC in ACN/TBAFB system revealed first an increase in peak intensities with increasing scan number, and then loss of electroactivity was observed.

FTIR analysis support the chemical and electrochemical formation of PPV and the importance of elimination reaction was also supported by FTIR.

DSC thermogram of the chemically and electrochemically synthesized PPV showed that, after the reaction at 245°C, the elimination of HCl, diethyl sulfide and solvent were completed.

To investigate the effect of dopant PPV was also doped with $LiClO_4$ by electrochemical doping technique. The conductivity of the polymer doped with BF_4^-

and ClO_4^- was investigated with four-probe conductivity technique and it is seemed that conductivities were nearly same.

Spectroelectrochemical properties were studied in TBAFB(0.1M)/ACN electrolyte-solvent couple. Stepwise oxidation of the polymer show reduction in the absorbance throughout the visible region as the color changes from yellow (reduced state) to green (highly oxidized state). But with multiple cycles polymer tend to loose its ability to access these multicolor states.

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