

ELECTROCHEMICAL STUDIES OF DNA DOPED POLYPYRROLE FILMS

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TECHNOLOGY**

CERTIFICATE

This is to certify that the major project work that is being presented in this dissertation entitled “**Electrochemical Studies of DNA Doped Polypyrrole Films**” by **Priyanka Sharma** (2K11/PTE/10), a student of Delhi Technological University, is the record of her own work. This work has not been submitted in part or full for any degree or diploma of this or any other university. It is further certified that this project work was carried out and completed under my supervision. She has completed this work with utmost sincerity.

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LIST OF ABBREVAEATION

CP	Conducting Polymer
PC	Polymer Composite
PPy	Polypyrrole
DNA	Deoxyribo Nucleic Acid
PTSA	p-Toluene Sulphonic Acid
DBSA	Dodecyl Benzene Sulphonic Acid
PPV	Polyphenylene Vinylene
CV	Cyclic Voltammetry
LSV	Linear Sweep Voltammetry
PV	Pulse Voltammetry
ITO	Indium Tin Oxide
ES	Electrochemical Supercapacitor
MPS	Multi Phase System
ECP	Electrochemical Polymerization
CT	Charge Transfer
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
Nm	Nanometer
Cm	Centimeter
Ppm	Parts Per Million
eV	Electron Volt
Å	Angstroms
mA	Milliampere
V	Volt
mV/s	Millivolt/second
S/cm	Siemens/centimeter
S	Seconds
Min	Minutes

ABSTRACT

Conducting polymer polypyrrole (PPy) has been a promising candidate as electrode material in various energy applications such as energy conversion and storage. The polypyrrole doped with DNA has been shown to enhance the electrochemical performance of electrode. In this work, in order to scrutinize the electrochemical performance of PPy doped with DNA, a series of polypyrrole (PPy) films doped with different other dopants coated on ITO electrodes were prepared electrochemically and studied in detail as well. Electroactivity stability of polymer film with different dopants was then investigated using cyclic voltammetry (CV) technique. The nature of counter-ion or dopant, and the concentration of dopant, was shown to affect the morphology and electroactivity of PPy films.

The PPy films doped with different dopants were also characterized by scanning electron microscope (SEM) and fourier transform infrared spectroscopy (FTIR) and electrochemical properties were explored by means of cyclic voltammetry, linear sweep voltammetry and pulse voltammetry. Specific capacitance of PPy/DNA was found to be higher than those of PPy/PTSA and PPy/ DBSA films, foreseen from the larger area under Cyclic Voltammogram. Area of the CV for the PPy/DNA film have propensity to diminish with the increasing scan rate in the positive potential range of 0 to 1.2 V, representative of a poor capacitive behavior at high scanning rates, for the reason that PPy/DNA electrodes happen to be more resistive at more positive potential.

CHAPTER 1

INTRODUCTION

1.1 Conducting Polymers

Polymers (Plastic) shape our lives because polymers can be shaped! Is it really necessary to point this out? May be not, but it is the major driving force behind most research that tries to design plastics fit for electronic applications. Polymers have the advantage that they are so much more easily to be processed than metal for example.

Conducting polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity^[1]. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, i.e., they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis^[2] and by advanced dispersion techniques^[3]. The chemical structure of some conducting polymers is shown in the Fig 1.1.

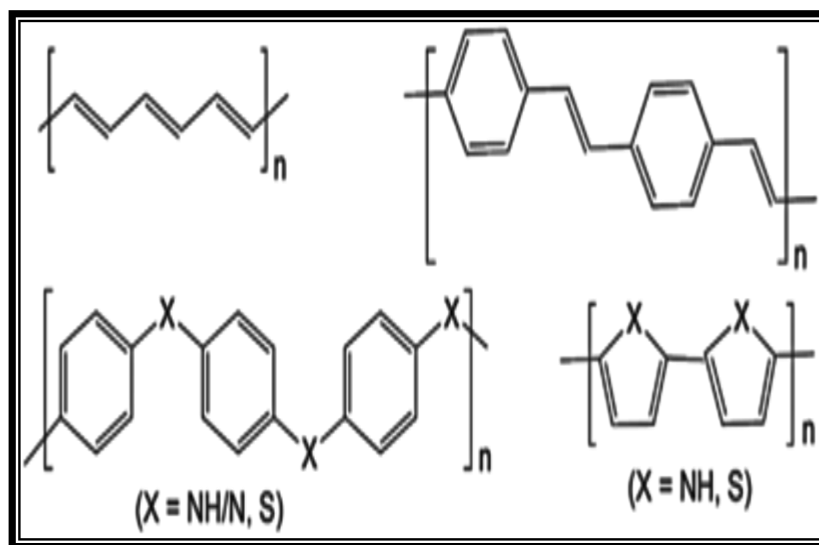


Fig.1.1. Chemical structures of some conductive polymers. From top left clockwise: polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH/N) and polyphenylene sulfide (X = S)

1.2 History

Until about 30 years ago all carbon based polymers were rigidly regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively used by the electronics industry because of this very property. They were utilized as inactive packaging and insulating material. This very narrow perspective is rapidly changing as a new class of polymer known as intrinsically conductive polymer or electroactive polymers are being discovered. Although this class is in its infancy, much like the plastic industry was in the 30's and 50's, the potential uses of these are quite significant. Polymers have long been used as insulating materials. For example, metal cables are coated in plastic to insulate them. However, there are at least four major classes of semiconducting polymers that have been developed so far. They include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers.

The conductively filled conducting polymers were first made in 1930 for the prevention of corona discharge. The potential uses for conductively filled polymers have since been multiplied due to their ease of processing, good environmental stability and wide range of electrical properties. Being a multi-phase system in nature, however, their lack of homogeneity and reproducibility has been an inherent weakness for conductively filled polymers. Therefore, controlling the quality of dispersion to obtain homogeneous conducting polymer composites is critically important.

The report of electrical conductivity in ionic polymers in 1975 (Wright, 1975) have attracted considerable interest. Since then, various ionically conducting polymers or polymer electrolytes have been prepared for a wide range of applications ranging from rechargeable batteries to smart windows. Polymer electrolytes are also highly processable. The ionic conduction mechanism requires the dissociation of opposite ionic charges and the subsequent ion migration between coordination sites, which are generated by the slow motion of polymer chain segments. Consequently, polymer electrolytes normally show a low conductivity and high sensitivity to humidity. They often become electrically non-conducting upon drying.

At the start of the 60's the research priorities at the Plastics Research Laboratory of BASF in Ludwigshafen, Germany centred on postulating new structural properties of polymers made by

oxidative coupling. Copper chloride and aluminium chloride were used to make an oligobenzene from benzene. This reaction was extended to include other aromatic compounds and heterocycles. These reaction products were characterized in terms of thermoelectric power and photo- and dark conductivities. To their surprise polyphenylene and polythiophene showed electrical conductivities up to 0.1 S cm^{-1} . Not only was this the highest value yet obtained, but it was the first capable of conducting electricity. The relative conductivities of some of the polymers synthesized are shown below^[4].

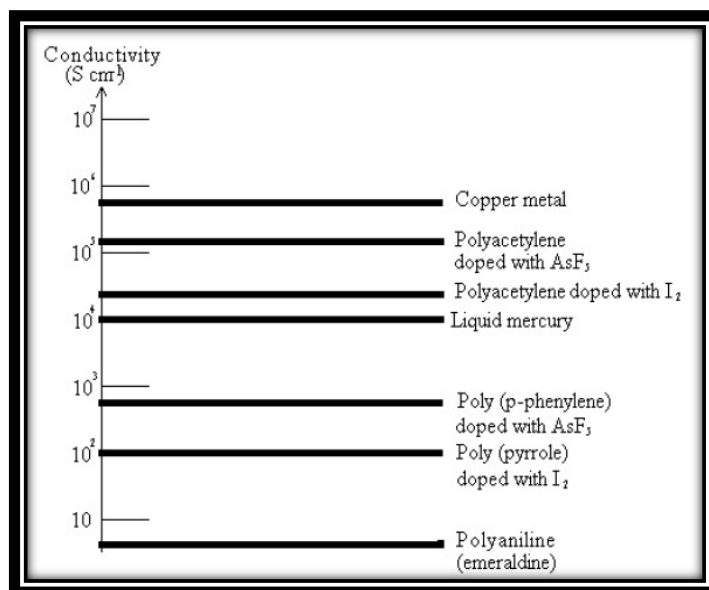


Fig.1.2. Logarithmic conductivity ladder locating some metals and conducting polymers

Since then it has been found that about a dozen different polymers and polymer derivatives undergo this transition when doped with a weak oxidation agent or reducing agent. They are all various conjugated polymers. This early work has led to an understanding of the mechanisms of charge storage and charge transfer in these systems. All have a highly conjugated electronic state.

This also causes the main problems with the use of these systems, that of processibility and stability. Most early conjugated polymers were unstable in air and were not capable of being processed. The most recent research in this has been the development of highly conducting polymers with good stability and acceptable processing attributes.

1.3 Types of Conducting Polymers

1.3.1 Organometallic Polymeric Conductors

Organometallic polymers are made of over 40 elements including main group of metals (Si or Ge), transition metals or rare earth elements in addition to the 10 elements (C, H, N, O, B, P, halides) which is found in organic polymers (Fig1.3). The variations of organometallic polymers seem endless^[5].

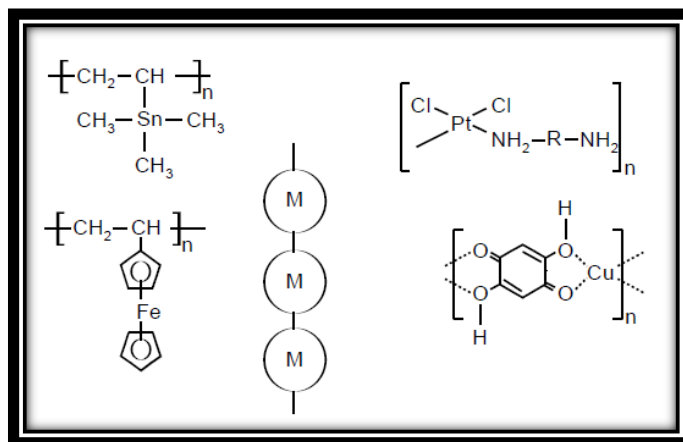


Fig.1.3. Different structures found in organometallic polymers

Organometallic polymers are new materials which combine the low density and structural variations and functional group varieties of organic materials with electrical conductivity and the high temperature stability features of inorganic compounds.

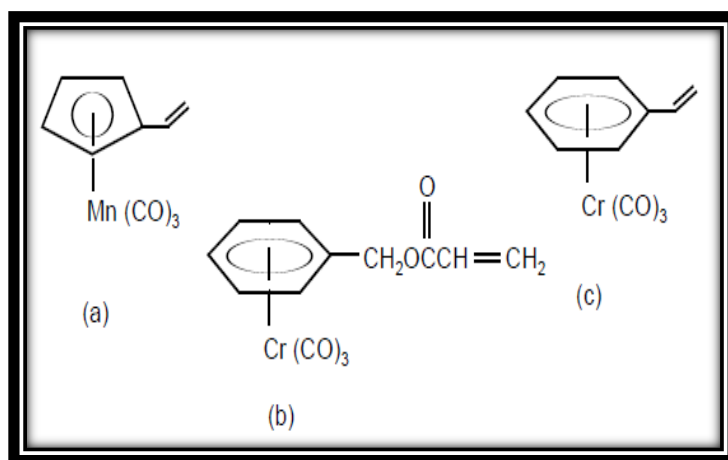


Fig.1.4. Typical organometallic polymers with metals as pendent groups

Metals may be present as in polymerization products of vinylcyclopentadienyl manganese tricarbonyl (Fig1.4 a), π -(benzylacrylate) chromium tricarbonyl (Fig1.4 b) and styrene tricarbonyl chromium (Fig1.4 c)

1.3.2 Conducting Polymer Composite

Composite materials have become common engineering materials. They are designed and manufactured for various applications including automotive components, sporting goods, aerospace parts, consumer goods, and in the marine and oil industries. Increasing awareness of product performance and competition in the global market for lightweight components also supported the growth in composite usage. Among all materials, composite materials have the potential to replace widely used steel and aluminum, and many times with better performance^[6].

Polymer composites consist of a polymer or copolymer having particles or fillers dispersed in the polymer matrix. These may be of different shape (e.g., platelets, fibers, spheroids). These systems require controlled mixing/compounding, stabilization of the achieved dispersion, orientation of the dispersed phase, and the compounding strategies for all multiphase systems (MPS), including polymer composites (PC), are similar.

Polymer material can attain electric conductivity either by the synthesis of a polymer of definite chemical structure or by the introduction of electrically conductive filler. Conductive polymer composite consists of a polymer matrix and electrically conductive particles dispersed in matrix. After introduction of conductive fillers, such as powders, flakes or fibers of different metals, graphite or carbon black, the electrical properties of composites change according to filling effect. In composite with low filler content, free charge carriers of conductive particles, which are electrons, have to pass through micro spaces between fillers, which are filled with the polymer matrix.

1.3.3 Polymeric Charge Transfer Complexes

A charge-transfer complex (CT complex) or electron-donor-acceptor complex is an association of two or more molecules, or of different parts of one large molecule in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic

attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor.

The nature of the attraction in a charge-transfer complex is not a stable chemical bond, and is thus much weaker than covalent forces. Many such complexes can undergo an transition into an excited electronic state. The excitation energy of this transition occurs very frequently in the visible region of the electro-magnetic spectrum, which produces the usually intense color characteristic for these complexes. These optical absorption bands are often referred to as charge-transfer bands (CT bands).

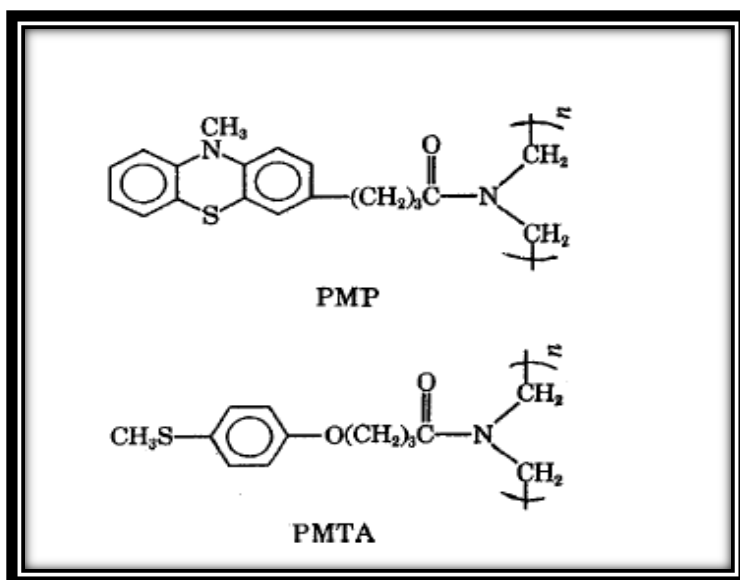


Fig.1.5. The structure of PMP and PMTA

In the CT complexes, the conductivity can be attributed to two factors: the formation of appropriate segregated stacks of donors and acceptors and a certain degree of charge transfer between the stacks. Consequently, the formation of a desired crystal structure, composed of individual donor and acceptor molecules, is essential, but it is not readily susceptible to chemical control. In this regard, organic molecules or macromolecules with D and/or A moieties separated by chemically bonded spacers have been studied. These types of molecules possess several important advantages. Firstly, the ionization potential of D, together with the electron affinity of A, can be tuned by adjusting the nature and the mode of the chemical substitution. Hence, it is

possible to prepare molecules with D and/or A in either a neutral or charged state by controlling the electron transfer from D to A. Molecules with the CT moieties in the neutral ground state should, in principle, behave like photoconductors or semiconductors, whereas their counterparts with the CT units in the charged state could be metallic conductors or superconductors. Secondly, the barrier to electron hopping along the molecules and their stacking columns may be reduced by introducing heavy atoms (*e.g.* transition metals) into the molecular spacer as certain metal atoms can overlap with the molecules through their large atomic orbitals. Finally, the incorporation of A and/or D moieties into polymer chains could increase the chances for packing segregated stacks with order and gain good processability and film-forming properties. So far, various D-and/or A-containing polymers, with the CT moieties either as pendant groups or as constituent components of the polymer backbones, have been prepared. For example, Litt and Summers (1973) reported the synthesis of poly-*N*-acylethylenimines grafted with D molecules, such as 10-methylphenothiazine (MP) and 4-(methylthio)anisole (MTA)^[7] (Fig1.5).

In these polymeric electron donors, the distance between two adjacent donors along the polymer chain allows the insertion of just one electron acceptor molecule (Fig 1.6), leading to good complexing with a stack of alternating D and A.

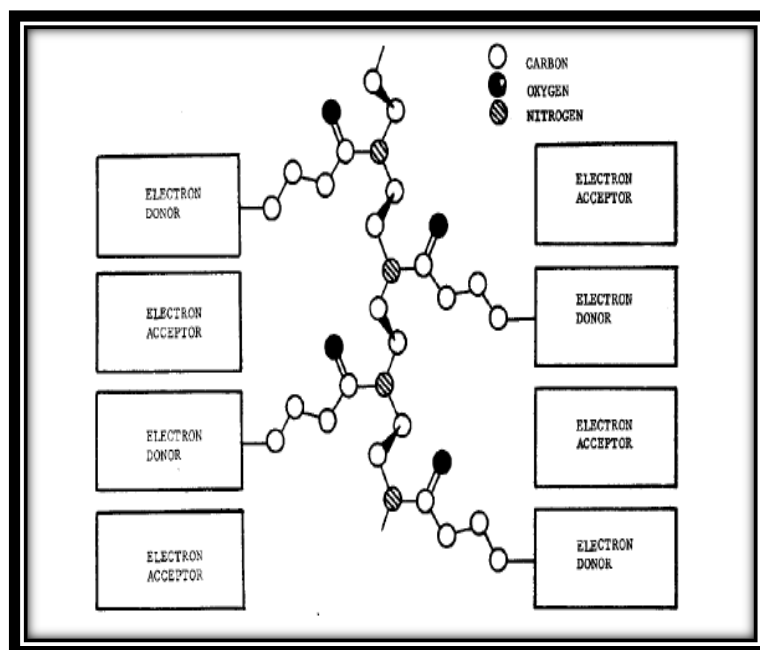


Fig.1.6. Schematic representation of the regular CT complex of polymeric electron donor with electron acceptors

1.3.4 Inherent Conducting Polymers

The linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers. Poly(p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) is the archetypical materials for solar cells and transistors. The following table presents some organic conductive polymers according to their composition.

Table 1. List of well studied conducting polymer

The main chain contains	Heteroatoms present		
	No heteroatom	Nitrogen-containing	Sulfur-containing
Aromatic cycles	<ul style="list-style-type: none"> • Poly(fluorene)s • Polyphenylenes • Polypyrenes • Polyazulenes • Polynaphthalenes 	<p>The N is in the aromatic cycle:</p> <ul style="list-style-type: none"> • Poly(pyrrole)s (PPY) • Polycarbazoles • Polyindoles • Polyazepines <p>The N is outside the aromatic cycle:</p> <ul style="list-style-type: none"> • Polyanilines (PANI) 	<p>The S is in the aromatic cycle:</p> <ul style="list-style-type: none"> • Poly(thiophene)s (PT) • poly(3,4-ethylenedioxythiophene) (PEDOT) <p>The S is outside the aromatic cycle:</p> <ul style="list-style-type: none"> • Poly(p-phenylene sulfide) (PPS)
Double bonds	<ul style="list-style-type: none"> • Poly(acetylene)s (PAC) 		
Aromatic cycles and double bonds	<ul style="list-style-type: none"> • Poly(p-phenylene vinylene) (PPV) 		

1.4 Molecular Basis of Electrical Conductivity

The conductivity of such polymers is the result of several processes. For example, in traditional polymers such as polyethylene, the valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is completely different. Conducting polymers have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band. In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction silicon atoms are replaced by electron-rich, *e.g.*, phosphorus, or electron-poor, *e.g.*, boron, atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped." Undoped conjugated polymers states are semiconductors or insulators. In such compounds, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping ($< 1\%$), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyacetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which have lengths of 1.44 and 1.36 Å, respectively. Upon doping, the bond alteration is diminished in conductivity increases. Non-doping increases in conductivity can also be accomplished in a field

effect transistor (organic FET or OFET) and by irradiation. Some materials also exhibit negative differential resistance and voltage-controlled "switching" analogous to that seen in inorganic amorphous semiconductors.

Despite intensive research, the relationship between morphology, chain structure and conductivity is still poorly understood. Generally, it is assumed that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains; however this could not be confirmed for PEDOT and polyaniline, which are largely amorphous.

1.5 Charge Transport

One early explanation of conduction in conducting polymers uses band theory as a method of conduction. This says that a half filled valence band would be formed from a continuous delocalized π system. This would be an ideal condition for conduction of electricity. However, it turns out that the polymer can more efficiently lower its energy by bond alteration (alternating short and long bonds), which introduces a band width of 1.5 eV, making it a high energy gap semiconductor. The polymer is transformed into a conductor by doping it with either an electron donor or electron acceptor. This is reminiscent of doping of silicon based semiconductors where silicon is doped with either arsenic or boron. However, while the doping of silicon produces a donor energy level close to the conduction band or an acceptor level close to the valence band, this is not the case with conducting polymers. Initially, the free spins concentration increases with concentration of dopant. At larger concentrations, however, the concentration of free spins levels off at a maximum. The polymer may store charge in two ways. In an oxidation process, it could either lose an electron from one of the bands or it could localize the charge over a small section of the chain. Localizing the charge causes a local distortion due to a change in geometry, which costs the polymer some energy. However, the generation of this local geometry decreases the ionization energy of the polymer chain and increases its electron affinity making it more able to accommodate the newly formed charges. This method increases the energy of the polymer less than it would if the charge was delocalized and hence takes place in preference to charge delocalization. The combination of a charge site and a radical is called a 'polaron'. Thus, a polaron is either a positively charged hole site (radical cation) or a negatively charged electron site (radical anion). This creates new localized electronic states in the gap with the lower energy states being occupied by single unpaired electrons. Upon further oxidation, the free radical of

the polaron is removed creating a new spinless defect called ‘bipolaron’, which is a dication or a dianion,. Theoretical models demonstrate that two radical ions i.e. polarons on the same chain react exothermically to produce a bipolaron^[8]. A bipolaron has a charge = 2e and spin = 0. The polaron and bipolaron structures of pyrrole are shown in Fig. 1.7.

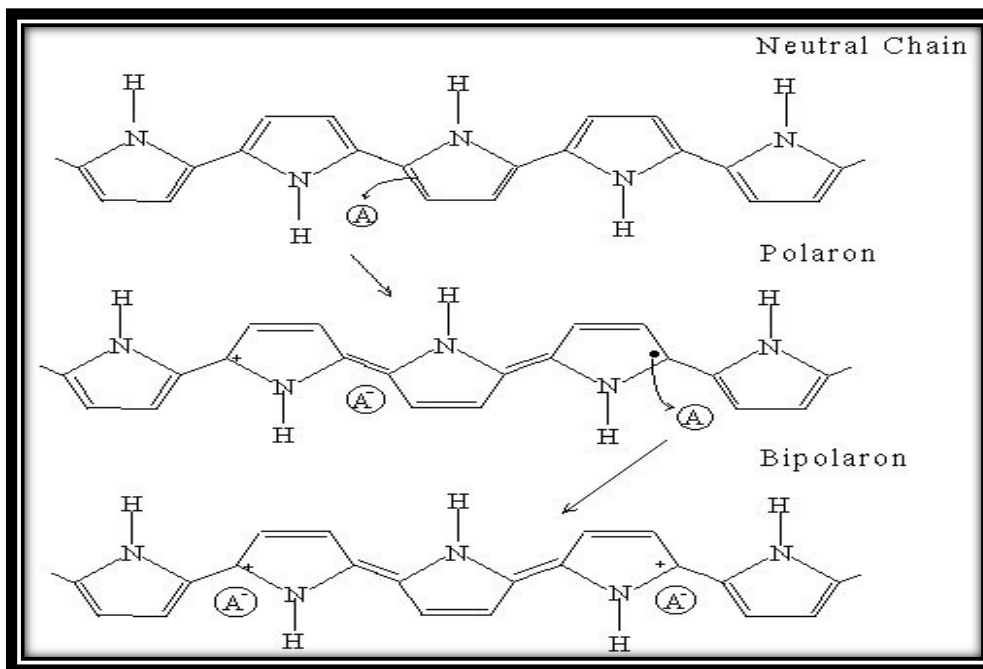


Fig.1.7. Formation of polaron and bipolaron

These test show that a variety of conduction mechanisms are used. The main mechanism used is by movement of charge carriers between localized sites or between soliton, polaron or bipolaron states. Alternatively, where inhomogeneous doping produces metallic island dispersed in an insulating matrix, conduction is by movement of charge carriers between highly conducting domains. Charge transfer between these conducting domains also occurs by thermally activated hopping or tunnelling. This is consistent with conductivity being proportional to temperature.

1.6 Polymerization Techniques

In polymer chemistry, **polymerization** is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks^[9]. In chemical compounds, polymerization occurs via a variety of reaction mechanisms that vary in complexity due to functional groups present in reacting compounds^[10]. There are many forms of

polymerization and different systems exist to categorize them e.g Chemical Polymerization and Electrochemical Polymerization.

1.6.1 Chemical Polymerization

In chemical compounds, polymerization occurs via a variety of reaction mechanisms that vary in complexity due to functional groups present in reacting compounds and their inherent steric effects. In more straightforward polymerization, alkenes, which are relatively stable due to σ bonding between carbon atoms, form polymers through relatively simple radical reactions; in contrast, more complex reactions such as those that involve substitution at the carbonyl group require more complex synthesis due to the way in which reacting molecules polymerize. Different chemical polymerization techniques are based on terms such as polymerization system, catalyst system and solvent system. These refer to the physical aspect of polymerization reactions which decide whether the monomer is polymerized in its condensed or gaseous state, whether it is polymerized as such or along with other inert components such as solvents or non solvents.

Factors such as the nature of the monomer, the type of polymerization mechanism chosen, the required physical form of the polymer and the viability of the process for industrial production are some of those dictating the physical conditions under which polymerization is to be carried out.

These varying physical conditions lead to different polymerization techniques, as enumerated below:

- ✚ Bulk Polymerization.
- ✚ Solution Polymerization.
- ✚ Suspension Polymerization.
- ✚ Emulsion Polymerization.

1.6.2 Electrochemical Polymerization Process (ECP)

Thin films of conducting polymers offer a large ratio of charge carriers to volume of active layer and can achieve high field-effect mobilities as a result of low-dimensional transport. Therefore a simple, scalable, cost-effective deposition technique for conducting polymers that produces

uniform thin film morphology reproducibly is needed. Film-forming methods for conducting polymers on the basis of solution processing, electrochemistry, and thermal annealing have been reported in the literature but suffer from a variety of problems. Another well known deposition strategy is the electrochemical growth of conducting polymer thin films via galvanostatic, potentiostatic, or voltammetric routes^[11] i.e Electrochemical Polymerization.

In the electrochemical polymerization, the initiating species are produced at the electrolytic cell containing a monomer and other suitable solvents or additives which make up the electrolyte. These species are formed by the electrode processes, involving either the monomers themselves or the additive used for the purpose. The initiating species can be a free radical, a cation or anion, produced either at the anode or at the cathode. The accepted oxidative electrochemical polymerization of Pyrrole is shown in Fig 1.8.

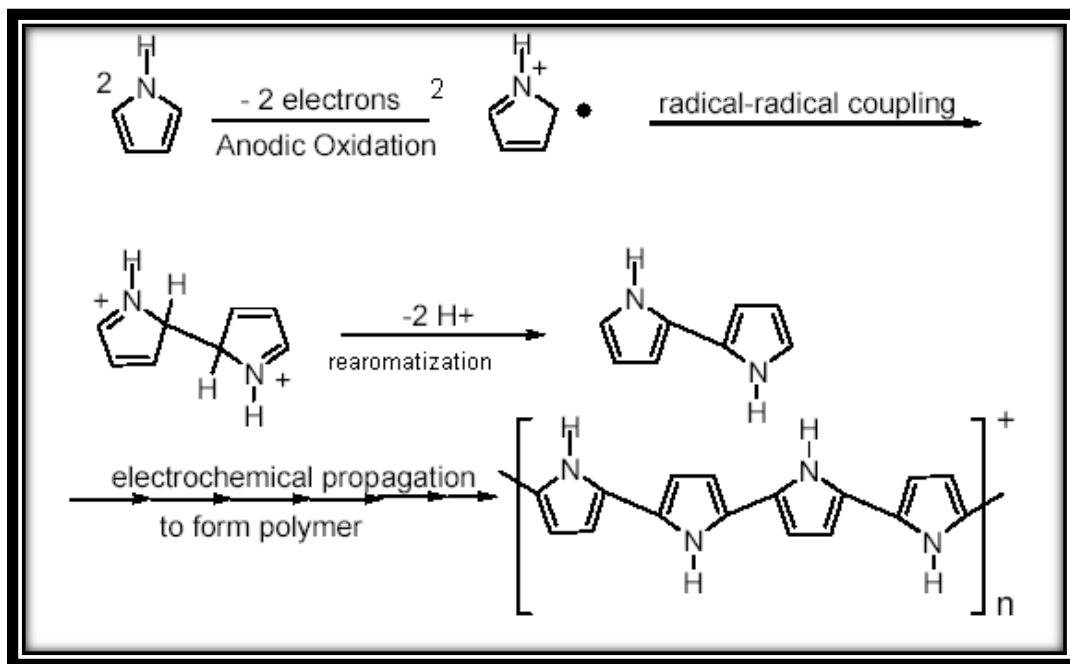


Fig.1.8. Accepted mechanism of the oxidative electrochemical polymerization of Pyrrole

1.7 Doping

Since most organic polymers do not have intrinsic charge carriers, the required charge carriers may be provided by partial oxidation (*p*-doping) of the polymer chain with electron acceptors (*e.g.* I₂, AsF₅) or by partial reduction (*n*-doping) with electron donors (*e.g.* Na, K). Through such a doping process, charged defects (*e.g.* polaron, bipolaron and soliton) are introduced, which

could then be available as the charge carriers. In fact, the insulator-to-metal transition in conjugated polymers is not so simple, and the way in which charges can be stabilized on the polymer chains and the nature of the charge transport process are still a matter of debate. Nevertheless, the simple band theory can provide some useful information about the doping-induced changes in electronic structure.

According to band theory (Harrison, 1979), the electrical properties of direct gap inorganic semiconductors are determined by their electronic structures, and the electrons move within discrete energy states called *bands*. By analogy, the bonding and antibonding π -orbitals of the sp^2 hybridized π -electron materials (*e.g.* polyenes) generate energy bands, which are fully occupied (π -band) and empty (π^* -band). The highest occupied band is called the *valence band*, and the lowest unoccupied band is the *conduction band*. The energy difference between them is called the *band gap*. Electrons must have certain energy to occupy a given band and need extra energy to move from the valence band to the conduction band. Moreover, the bands should be partially filled in order to be electrically conducting, as neither empty nor full bands can carry electricity. Owing to the presence of partially filled energy bands, metals have high conductivities (Fig 1.9(a)). The energy bands of insulators and semiconductors, however, are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap (Fig 1.9(b)). In contrast, conjugated polymers have narrower band gaps (Fig 1.9(c)) and doping can change their band structures by either taking electrons from the valence band (*p*-doping) or adding electrons to the conduction band (*n*-doping).

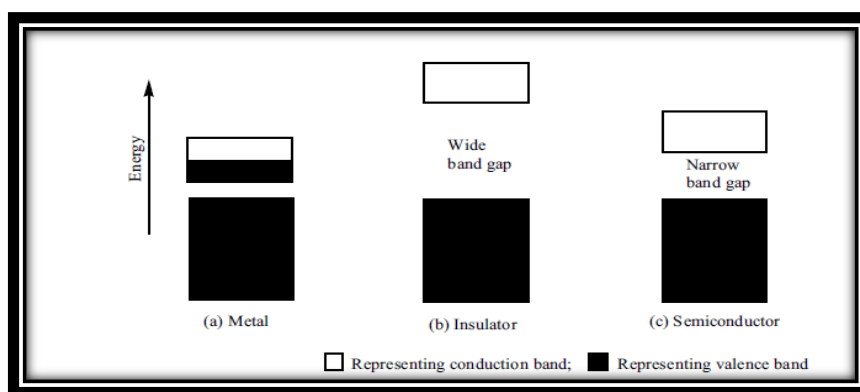


Fig.1.9. A schematic representation of energy gaps in (a) metal; (b) insulator; (c) semiconductor (After Dai, 1999, copyright 1999 Marcel Dekker, Inc.)

When an electron is added (removed) to the bottom of the conduction band (from the top of the valence band) of a conjugated polymer (Fig 1.10(a)), the conduction (valence) band ends up being partially filled and a radical anion (cation), commonly termed as a polaron (Brédas and Street, 1985), is created (Fig 1.10(b)). The formation of polarons causes the injection of states from the bottom of the conduction band and top of the valence band into the band gap. A polaron carries both spin (1/2) and charge (+ ve). Addition (removal) of a second electron on a chain already having a negative (positive) polaron results in the formation of a bipolaron (spinless) through dimerization of two polarons, which can lower the total energy (Fig 1.10(c)). In conjugated polymers with a degenerate ground state (*i.e.* two equivalent resonance forms), like *trans*-polyacetylene, the bipolarons can further lower their energy by dissociating into two spinless solitons at one-half of the gap energy (Fig 1.10(d)). Solitons do not form in conjugated polymers with nondegenerate ground states, such as in polypyrrole, polythiophene and polyaniline (Brédas and Street, 1985). The population of polarons, bipolarons, and/or solitons increases with the doping level. At high doping levels, the localized polarons, bipolarons or solitons near to individual dopant ions could overlap, leading to new energy bands between and even overlapping the valence and conduction bands, through which electrons can flow.

The bulk conductivity of conducting polymers should, in principle, consist of contributions from intra-chain, inter-chain and inter-domain electron transportations (Dai et al., 1999). While the details for each of the transporting processes and their relative importance are still not fully understood, some of the factors that influence conductivity have been recognized.

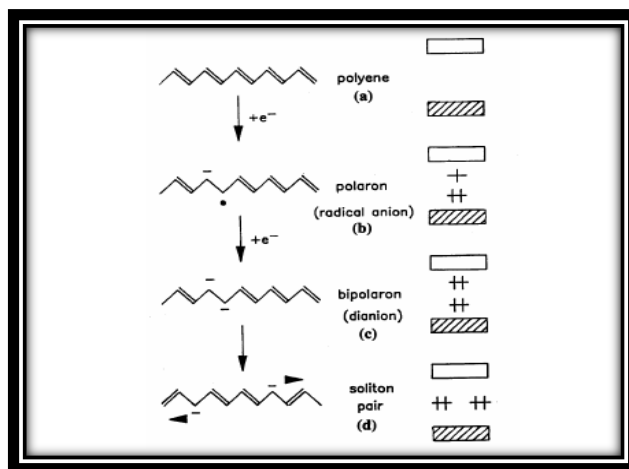


Fig.1.10. A schematic description of the formation of polaron, bipolaron, and soliton pair on a *trans*-Polyacetylene chain by doping.

As can be seen from the foregoing discussion, the doping process is the most obvious factor which influences conductivity of conjugated polymers. Other factors include the orientation, crystallinity and purity of the conjugated polymers.

1.7.1 Types of Doping

Some of the most commonly used doping methods are described below.

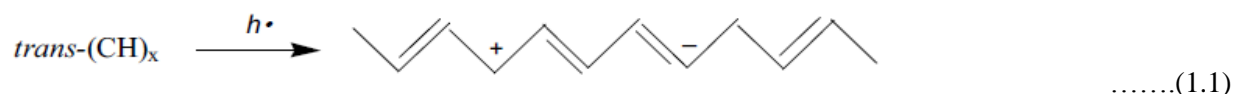
(A) Electrochemical Doping

Owing to the extensive conjugation of pi-electrons, conjugated polymers can also be easily oxidized (*p*-doping) or reduced (*n*-doping) electrochemically with the conjugated polymer acting as either an electron source or an electron sink. In particular, the doping reaction can be accomplished by applying a DC power source between a *trans*-polyacetylene-coated positive electrode and a negative electrode. Both of them are immersed in a solution of LiClO₄⁻ in propylene carbonate.

Electrochemical doping has several distinct advantages. Firstly, a precise control of the doping level can be achieved simply by monitoring the amount of current passed. Secondly, doping-undoping is highly reversible with no chemical products requiring removal. Finally, both *p*- or *n*-type doping can be achieved even with dopant species that cannot be introduced by conventional chemical means. In both cases, however, counter “dopant” ions are introduced for stabilizing the charge along the polymer backbone. The incorporation of counter ions can be both a hindrance and an advantage. While the counter ions may cause an undesirable structural distortion and a deteriorated effect on conductivity, they facilitate conjugated conducting polymers for actuation applications. In order to eliminate the incorporation of counter ions, “photo-doping” and “charge-injection doping” methods have been exploited to achieve the redox doping effects. Besides, some conjugated polymers, such as polyaniline and poly(heteroaromatic vinylenes), can also acquire high conductivities through the protonation of imine nitrogen atoms without any electron transfer between the polymer and “dopants” occurring - *i.e.* “non-redox doping” (Epstein and MacDiarmid, 1995).

(B) Photo-doping

The irradiation of a conjugated polymer (e.g. trans-polyacetylene) macromolecule with a light beam of energy greater than its band gap could promote electrons from the valence band into the conduction band, as schematically shown in Equation (1.1) (Heeger et al., 1988). Although the photogenerated charge carriers may disappear once the irradiation ceases, the application of an appropriate potential during irradiation could separate electrons from holes, leading to photoconductivity.



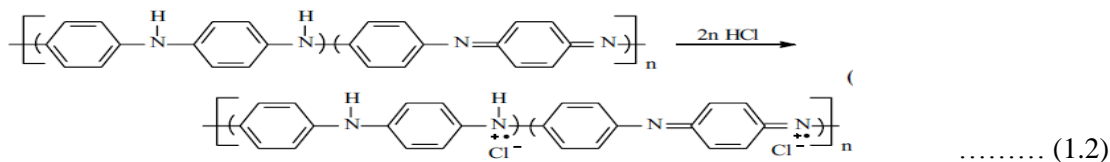
(C) Charge-injection Doping

Using a field-effect transistor (FET) geometry, charge carriers can be injected into the band gap of conjugated polymers [e.g. polyacetylene, poly(3-hexylthiophene), P3HT] by applying an appropriate potential on the metal/insulator/polymer multilayer structure (Garnier *et al.*, 1994). Just like photodoping, the charge-injection doping does not generate counter ions, allowing a systematic study of the electrical properties as a function of the charge carrier density with a minimized distortion of the material structure. Using the chargeinjection doping method, Schön *et al.* (2001) have recently demonstrated that a thin P3HT self-assembled film exhibits a metal-insulator transition with metallic-like temperature dependence. At temperatures below 235 K, these authors observed superconductivity when the charge density exceeds $2.5 \times 10^{-14} \text{ cm}^{-2}$. This observation of superconductivity appears to be closely related to two-dimensional charge transport in the self-assembled polymer film. Although much of Schön's work is currently in question (Jacoby, 2002) and the detailed superconducting mechanism remains to be found (Tinkham, 1975), the above observation may suggest that the conductivity of conjugated polymers could be tuned over the largest possible range from insulating to superconducting.

(D) Non-redox Doping

Unlike redox doping, the non-redox doping does not cause any change in the number of electrons associated with the polymer backbone, but merely a rearrangement of the energy levels. The most studied doping process of this type is the protonic doping of polyaniline emeraldine base

(PANI-EB) with aqueous protonic acids, such as HCl, *d,l*-camphorsulfonic acid (HCSA), *p*-CH₃-(C₆H₄)SO₃H and (C₆H₅)SO₃H, to produce conducting polysemiquinone radical cations via the reaction shown in Equation (1.2) (Dai *et al.*, 1998a).



1.8 Few Important Conducting Polymers

Polyacetylene, in view of possessing the simplest molecular framework, has attracted the most attention, especially of physicists, with an emphasis on understanding the mechanism of conduction. However, its insolubility, infusibility and poor environmental stability has rendered it rather unattractive for technological applications. The technologically relevant front runners belong to essentially four families: polyaniline (PAn), polypyrroles (PPy), polythiophenes (PT) and polyphenylene vinylenes (PPV). Polyaniline is rather unique as it is the only polymer that can be doped by a protic acid and can exist in different forms depending upon the pH of the medium. While polyaniline is soluble in the neutral emeraldine form in highly polar aprotic solvents like, N-methyl pyrrolidone (NMP), all other polymers are insoluble. However, as mentioned earlier, laterally substituted derivatives of the remaining three classes are soluble in pristine form and are solution processable. A typical example of a laterally substituted conjugated polymer which has been extensively investigated is poly(3-hexyl thiophene) (P3-HT) (see PAn, PPy and PT can be prepared either by chemical or electrochemical oxidation, the latter approach being often preferred as they result in polymeric films deposited on the anode surface, which can be removed to give free-standing films. The electrochemical method, in addition, may also be well suited for fabrication of microelectronic devices in which polymer films are directly deposited on to metal contacts. Although chemical oxidation yields powders, the reaction when done in the presence of surfactants, in some cases, permits the preparation of emulsions, which upon drying form coherent films. In the case of the substituted derivatives, however, the chemical method is often preferred, as the resulting polymers are soluble, and hence can be purified and solution processed.

1.8.1 Polypyrrole

Among the conjugated polymers, polypyrrole (PPy) is the most representative one for its easy polymerization and wide application in gas sensors, electrochromic devices and batteries. Polypyrrole can be produced in the form of powders, coatings, or films. It is intrinsically conductive, stable and can be quite easily produced also continuously. The preparation of polypyrrole by oxidation of pyrrole dates back to 1888 and by electrochemical polymerization to 1957. However, this organic p-system attracted general interest and was found to be electrically conductive in 1963.

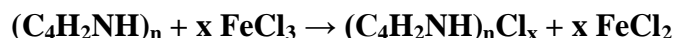
Polypyrrole (PPy) is a chemical compound formed from a number of connected pyrrole ring structures. For example a tetrapyrrole is a compound with four pyrrole rings connected. Methine-bridged cyclic tetrapyrroles are called porphyrins. Polypyrroles are conducting polymers, related members being polythiophene, polyaniline, and polyacetylene. The Nobel Prize in Chemistry was awarded in 2000 for work on conductive polymers including polypyrrole.

Some of the first examples of polypyrroles were reported in 1963 by Weiss and coworkers. These workers described the pyrolysis of tetraiodopyrrole to produce highly conductive materials. Most commonly Ppy is prepared by oxidation of pyrrole, which can be achieved using ferric chloride in methanol:



Polymerization is thought to occur via the formation of the pi-radical cation $\text{C}_4\text{H}_4\text{NH}^+$. This electrophile attacks the C-2 carbon of an unoxidized molecule of pyrrole to give a dimeric radical $(\text{C}_4\text{H}_4\text{NH})_2^+$.

Conductive forms of PPy are prepared by oxidation ("p-doping") of the polymer:



The polymerization and p-doping can also be effected electrochemically. The resulting conductive polymers are peeled off of the anode.

1.8.2 Synthesis of Polypyrrole

Polypyrrole and many of its derivatives can be synthesized via simple chemical or electrochemical methods. Photochemically initiated and enzyme-catalyzed polymerization routes

have also been described but less developed. Different synthesis routes produce polypyrrole with different forms; chemical oxidations generally produce powders, while electrochemical synthesis leads to films deposited on the working electrode and enzymatic polymerization gives aqueous dispersions. As mentioned above the electrochemical polymerization method is utilized extensively for production of electroactive/conductive films. The film properties can be easily controlled by simply varying the electrolysis conditions such as electrode potential, current density, solvent, and electrolyte. It also enables control of thickness of the polymers. Electrochemical synthesis of polymers is a complex process and various factors such as the nature and concentration of monomer/electrolyte, cell conditions, the solvent, electrode, applied potential and temperature, pH affects the yield and the quality of the film. Thus, optimization of all of the parameters in one experiment is difficult. In contrast, chemical polymerization does not require any special instruments; it is a rather simple and fast process. Chemical polymerization method involves oxidative polymerization of pyrrole monomer by chemical oxidants either in aqueous or non-aqueous solvents or oxidation by chemical vapour deposition in order to produce bulk polypyrrole as fine powders. Iron (III) chloride and water are found to be the best oxidant and solvent for chemical polymerization of pyrrole respectively regarding desirable conductivity characteristics^[12].

1.8.3 Electrochemical Polymerisation of Pyrrole

Electrochemical oxidation of pyrrole forms a film of conducting polymer at the electrode surface. The electrochemical polymerisation of pyrrole to polypyrrole precedes as follows, Fig 1.11: shows three steps of polymerization.

Initiation-Formation of monomer radical cation by electrochemical oxidation. **Propagation**-Combination of two radical cation monomers (or oligomers) followed by loss of two hydrogen ions. The linkage formed is at the 2 position of the pyrrole ring, forming 2,2'-bipyrrole. 2,5-disubstituted pyrrole do not polymerize and 2-monosubstituted pyrroles only form dimmers. Propagation continues by re-oxidation of the bipyrrole and further combination of radicals. **Termination**- Occurs when no further monomer is present for oxidative polymerization or side reactions terminate the PPy chain. An example of a termination reaction is the reaction with water to form the amide group.

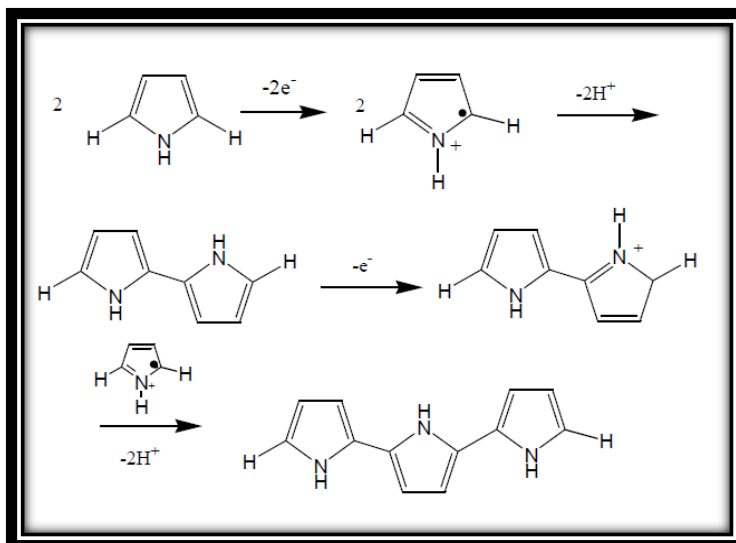


Fig.1.11. Mechanism of electrochemical polymerization of pyrrole to polypyrrole

The success of electrochemical polymerization of pyrrole is due to the stability of the radical through charge delocalization, and the ease of electro-oxidation. The loss of the hydrogen ions makes the dimer (oligomer) formation irreversible so proton acceptors, such as water, pyridine and bases, enhance electrochemical polymerization. Good solvents for electrochemical polymerization include water, acetonitrile, butanone, propylene carbonate, dimethylformamide (DMF) and ethanol though the presence of a bit of water enhances the polymer formation. Water can also result in chain termination.

Potentiostatic, potential cycling, and galvanostatic methods can be used to electropolymerize pyrrole. Potentiostatic methods (constant potential) and cycling the potential yield the most consistent films of about the same quality. Galvanostatic deposition (constant current), does not produce as good a quality film as the other methods, but is useful for controlling film thickness.

1.9 Novel Dopants

The properties like structure, surface morphology, electrical conductivity and air stability of the polymers depend upon the nature and extent of doping. It should be recalled that the concept of doping in polymers is rather different from that in traditional inorganic. Quite advantageously, the electrochemical polymerization method offers a wide choice of 'dopant' ions which are taken from the supporting electrolyte added in the electrolyte bath. Scheme of electrochemical n-

doping (reduction) and p-doping (oxidation) processes of selected conducting polymers is shown in Fig.1.12.

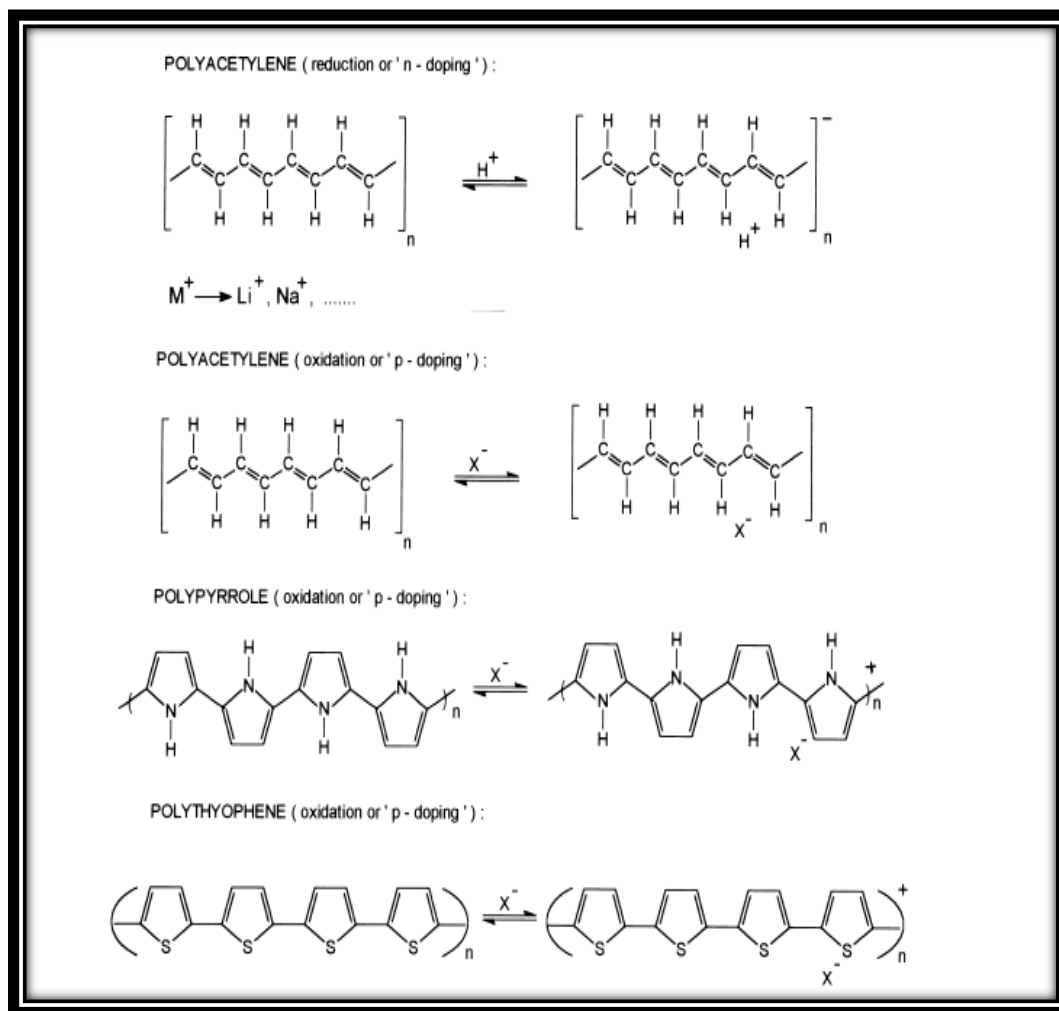


Fig.1.12. Schemes of electrochemical n-doping (reduction) and p-doping (oxidation) processes of selected conducting polymers

This is in contrast with the conventional methods of synthesizing conducting polymers where the neutral polymer is first synthesized and subsequently treated with a strong oxidant/reductant in order to produce the conducting form of the polymer. With this approach, the variety of anions/cations that can be used is more limited since it must be generated from the chemical oxidants/reductants^[13].

Table 2 represents the list of dopant ions and their source 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.

Table 2. List of dopant ions and their source of electrolyte

Dopant ion	Source (i.e. supporting electrolyte)
BF_4^-	RN^+BF_4^- , MBF_4
PF_6^-	R_4NPF_6 , MPF_6
ClO_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^-	$\text{MHSO}_4/\text{R}_4\text{NHSO}_4$
CF_3SO_3^-	$\text{MCF}_3\text{SO}_3/\text{R}_4\text{NCF}_3\text{SO}_3$
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	$\text{MCH}_3\text{C}_6\text{H}_4\text{SO}_3$
SO_4^{2-}	Na_2SO_4 , H_2SO_4
$(\text{Et}_4\text{N}^+)^*$	Et_4NPF_6
$(\text{Bu}_4\text{N}^+)^*$	Bu_4NPF_6

R = Alkyl; Et = Ethyl; But = Butyl; M = Metal (Li^+ , Na^+ , Ag^+ , K^+). The dopant ions marked by * are not anions.

1.9.1 Polyelectrolyte Dopant: DNA

DNA is a long polymer made from repeating units called nucleotides^[14]. DNA was first identified and isolated by Friedrich Miescher and the double helix structure of DNA was first discovered by James Watson and Francis Crick. The structure of DNA of all species comprises two helical chains each coiled round the same axis, and each with a pitch of 34 Å (3.4 nm) and a radius of 10 Å (1.0 nm)^[15]. According to another study, when measured in a particular solution, the DNA chain measured 22 to 26 Å wide (2.2 to 2.6 nm), and one nucleotide unit measured 3.3 Å (0.33 nm) long^[16]. Although each individual repeating unit is very small, DNA polymers can be very large molecules containing millions of nucleotides. For instance, the largest human chromosome, chromosome number 1, consists of approximately 220 million base pairs^[17] and is 85 mm long. In living organisms DNA does not usually exist as a single molecule, but instead as a pair of molecules that are held tightly together^{[18][19]}. These two long strands entwine like vines,

in the shape of a double helix. The nucleotide repeats contain both the segment of the backbone of the molecule, which holds the chain together, and a nucleobase, which interacts with the other DNA strand in the helix. A nucleobase linked to a sugar is called a nucleoside and a base linked to a sugar and one or more phosphate groups is called a nucleotide. A polymer comprising multiple linked nucleotides (as in DNA) is called a polynucleotide.

The backbone of the DNA strand is made from alternating phosphate and sugar residues^[20]. The sugar in DNA is 2-deoxyribose, which is a pentose (five-carbon) sugar. The sugars are joined together by phosphate groups that form phosphodiester bonds between the third and fifth carbon atoms of adjacent sugar rings.

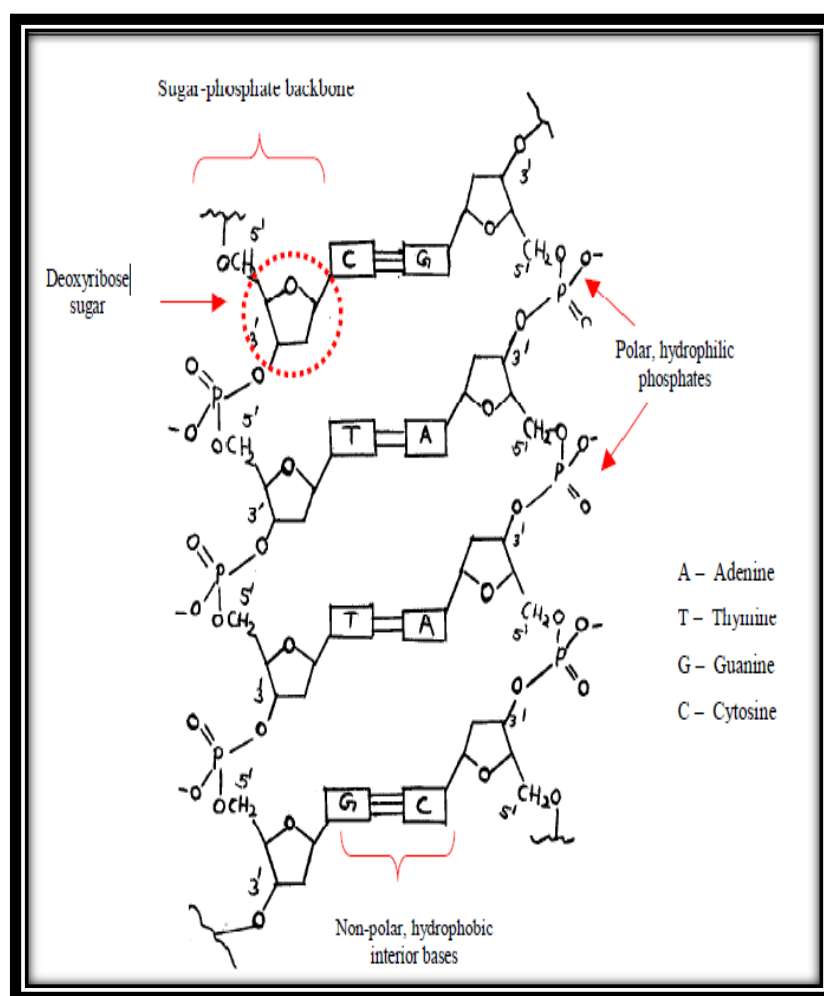


Fig.1.13.Primary structure of DNA

Deoxyribonucleic acids (DNAs) are a group of vital biomolecules that are crucial for many biological and biochemical processes. DNAs possess the following basic structural features:

- ✚ Two anti parallel and complementary strands.
- ✚ Hydrophilic polar external sugar-phosphate backbone.
- ✚ Hydrophobic core of bases: Adenine, Thymine, Guanine, and Cytosine.
- ✚ Significant secondary structure.

❖ Sugar-Phosphate Backbone

The basic structure of DNA (as shown in Fig 1.13) can be divided into two portions:

- (a) External sugar-phosphate backbone
- (b) Internal bases

The sugar-phosphate backbone, as its name implies, is the major structural component of the DNA molecule. The backbone is constructed from alternating ribose sugar and phosphate molecules, which are highly polar. Because the backbone is polar, it is hydrophilic which means that it likes to be immersed in water^[21].

1.10 Properties of Conducting Polymers

Films of PPy are yellow but darken in air due to some oxidation. Doped films are blue or black depending on the degree of polymerization and film thickness. They are amorphous, showing only weak diffraction. PPy is described as "quasi-unidimensional" vs one-dimensional since there is some crosslinking and chain hopping. Undoped and doped films are insoluble in solvents but swellable. Doping makes the materials brittle. They are air stable in air to 150 °C at which temperatures the dopant starts to evolve (e.g., as HCl). PPy is an insulator, but its oxidized derivatives are good electrical conductors. The conductivity of the material depends on the conditions and reagents used in the oxidation. Conductivities range from 2 to 100 S/cm. Higher conductivities are associated with larger anions, such as tosylate. Doping the polymer requires that the material swell to accommodate the charge-compensating anions. The physical changes associated with this charging and discharging has been discussed as a form of artificial muscle.

Polypyrrole has a high mechanical and chemical stability and can be produced continuously as flexible film (thickness 80 nm; trade name: Lutamer, BASF) by electrochemical techniques. Conductive polypyrrole films are obtained directly by anodic polymerization of pyrrole in aqueous or organic electrolytes.

1.11 Processibility

Table 3. Stability and Processing Attributes of Some Conducting Polymers

POLYMER	CONDUCTIVITY ($\Omega^{-1} \text{ cm}^{-1}$)	STABILITY (doped state)	PROCESSING POSSIBILITIES
Polyacetylene	$10^3 - 10^5$	poor	limited
Polyphenylene	1000	poor	limited
PPS	100	poor	excellent
PPV	1000	poor	limited
Polypyrroles	100	good	good
Polythiophenes	100	good	excellent
Polyaniline	10	good	good

Conjugated polymers may be made by a variety of techniques, including cationic, anionic, radical chain growth, co-ordination polymerization, step growth polymerization or electrochemical polymerization. Electrochemical polymerization occurs by suitable monomers which are electrochemically oxidized to create an active monomeric and dimeric species which react to form a conjugated polymer backbone. The main problem with electrically conductive plastics stems from the very property that gives it its conductivity, namely the conjugated backbone. This causes many such polymers to be intractable, insoluble films or powders that cannot melt. There are two main strategies to overcoming these problems. There are to either modify the polymer so that it may be more easily processed, or to manufacture the polymer in its desired shape and form. There are, at this time, four main methods used to achieve these aims. The first method is to manufacture a malleable polymer that can be easily converted into a conjugated polymer. This is done when the initial polymer is in the desired form and then, after conversion, is treated so that it becomes a conductor. The treatment used is most often thermal treatment. The precursor polymer used is often made to produce highly aligned polymer chain which is retained upon conversion. These are used for highly orientated thin films and fibers. Such films and fibers are highly anisotropic, with maximum conductivity along the stretch direction.

The second method is the synthesis of copolymers or derivatives of a parent conjugated polymer with more desirable properties. This method is the more traditional one for making

improvements to a polymer. What is done is to try to modify the structure of the polymer to increase its processibility without compromising its conductivity or its optical properties. All attempts to do this on polyacetylene have failed as they always significantly reduced its conductivity. However, such attempts on polythiophenes and polypyrroles proved more fruitful. The hydrogen on carbon 3 on the thiophene or the pyrrole ring was replaced with an alkyl group with at least four carbon atoms in it. The resulting polymer, when doped, has a comparable conductivity to its parent polymer whilst be able to melt and it is soluble. A water soluble version of these polymers has been produced by placing carboxylic acid group or sulphonic acid group on the alkyl chains. If sulphonic acid groups are used along with built-in ionizable groups, then such system can maintain charge neutrality in its oxidized state and so they effectively dope themselves. Such polymers are referred to as "self-doped" polymers. One of the most highly conductive derivatives of polythiophene is made by replacing the hydrogen on carbon three with a $-\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_3$. This is soluble and reaches a conductivity of about 1000 S cm^{-1} upon doping. The third method is to grow the polymer into its desired shape and form. An insulating polymer impregnated with a catalyst system is fabricated into its desired form. This is then exposed to the monomer, usually a gas or a vapour.

The monomer then polymerizes on the surface of the insulating plastic producing a thin film or a fibre. This is then doped in the usual manner. A variation of this technique is electrochemical polymerization with the conducting polymer being deposited on an electrode either the polymerization stage or before the electrochemical polymerization. This cast may be used for further processing of the conducting polymer. For instance, by stretching aligned bends of polyacetylene/polybutadiene the conductivity increase 10 fold, due to the higher state of order produced by this deformation. The final method is the use of Langmuir-Blodgett trough to manipulate the surface active molecules into a highly ordered thin films whose structure and thickness which are controllable at the molecular layer. Amphiphilic molecules with hydrophilic and hydrophobic groups produce monolayers at the air-water surface interface of a Langmuir-Blodgett trough. This is then transferred to a substrate creating a multilayer structure comprised of molecular stacks which are normal about 2.5 nm thick. This is a development from the creation of insulating films by the same technique. The main advantage of this technique is its unique ability to allow control over the molecular architecture of the conducting films produced. It can be used to create complex multilayer structures of functionally different molecular layers as determined by the chemist. By producing alternating layers of conductor and insulator it is

possible to produce highly anisotropic film which is conducting within the plane of the film, but insulating across it.

1.12 Applications of Conducting Polymers

Due to their poor processability, conductive polymers have few large-scale applications. They have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors,^[22] flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide.

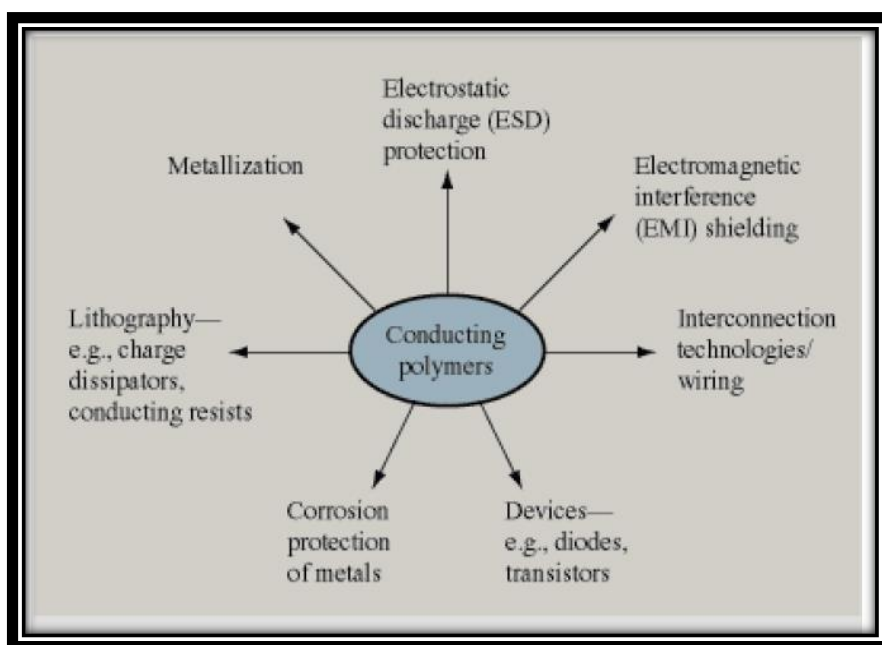


Fig.1.14. Some of the potential application of conducting polymers in microelectronics

1.12.1 Polymeric Batteries

One of the first applications of conducting polymers, that was the focus of attention world-wide, was that of light-weight batteries. While a lot of the conjugated polymers were tried most of

them failed to exhibit the desired properties, specifically with respect to stability. However, batteries made using either polypyrrole or polyaniline as the positive electrode (cathode) and lithium– aluminium alloy as the negative electrode (anode) exhibited much more respectable properties. The electrolytes in these cases were either LiClO_4 or LiBF_4 in propylene carbonate (a highly polar aprotic solvent, which is also fairly resistant to oxidation). During the battery discharge, electrons move from the lithium alloy (which gets oxidized) to the polyaniline cathode (which gets reduced), as Li^+ from the anode and BF_4^- from the cathode enter the electrolyte. One major drawback of this battery is that the energy density or energy storage capacity is low and its recyclability (charging– discharging cycles) is relatively poor. More recently, however, some composites of an alkali metal alloy and polyphenylene have been very effectively used as anode materials in batteries that exhibit much higher energy densities, of around 65mWH/g (compare with standard nickel–cadmium batteries which have about 39mWH/g). In these cases, the conducting polymer serves as a binder for the alkali metal alloy, forming a multiply connected electronically and ionically conductive network within which the alloy particles are held. The mixed ionic and electronic conductivity of the conducting polymer binder allows the alloy particles to continue the electronic and ionic processes associated with the charge-discharge cycles, consequently extending the battery cycle life. Thus, the prospect of a polymeric battery is still alive and is awaiting further technological refinement.

1.12.2 Electrochromic Displays

Electrochromic display is another interesting application which utilizes the electrochemical doping and undoping of conducting polymers. The basic idea, in such devices, is to effect a significant change in the colour (both the wavelength of absorption and its intensity) upon application of an electric potential. Depending on the conducting polymer chosen, either the doped or undoped state can be essentially colourless or intensely coloured. In general, the absorption of the doped state is dramatically red-shifted (moves to longer wavelength) from that of the undoped state. Because of their very high absorption coefficients (ca. 10^5 cm^{-1}) in the visible range of the electromagnetic spectrum, only very thin films are required to provide display devices with high contrast and a very broad viewing angle. Polyaniline, polypyrrole, polythiophene and their derivatives have been successfully used to prepare prototypes of such display devices. However, for successful commercial utilization of these materials in display devices, one important aspect is again the cycle life, which should be $> 10^7$. A maximum of

about 106 cycles has been achieved using 50 nm thick polyaniline films, wherein the switching occurs between transparent yellow and green in less than 100ms. Thus, while these materials are yet to achieve the set target (in terms of their life cycle) for use as electrochromic displays, other interesting and innovative applications, such as electrochromic windows and other applications in the automotive industry are being actively pursued. Electro-chromic windows in buildings/automobiles which can be made to go from low transmitting (during the day) to high transmitting (during the night); the switching in such systems occurs upon application of an electric potential.

1.12.3 Light Emitting Diodes

Other exciting phenomena, that have caught the imagination of both scientists and technologists alike, are the phenomena of photoluminescence and electroluminescence in conjugated polymers. Emission of light upon irradiation is termed as photoluminescence, while the emission on application of a voltage is termed electroluminescence. Light emitting diode is an example of utilization of the latter phenomenon. It was recently demonstrated that PPV films can be used as the emissive layer in electroluminescent devices. Structures for electroluminescent devices are fabricated with the polymer film formed on a bottom electrode, which is deposited on a suitable substrate (such as glass), and the top electrode is deposited on the fully converted PPV film (i.e., after thermal elimination of the precursor). Electrode materials are chosen with a low work function for use as negative, electron-injecting contact, and with a high work function as the positive hole-injecting contact. At least one of these layers must be semi-transparent for light emission normal to the plane of the device.

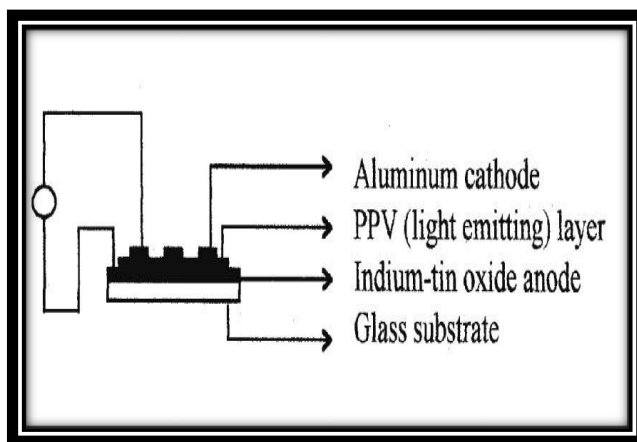


Fig.1.15. A typical LED device construction.

Both indium-tin oxide and thin aluminium films (7–15 nm) have been used as the transparent electrode. For polymer films, of about 100 nm, the forward voltages were as low as 10 V. Further improvements, using soluble PPV derivatives such as 2,5-dialkoxy PPV's and lower work function metals, particularly calcium, as the electron- injecting contact layer, have resulted in a further drop in forward voltage to about 5 V, and an increase in the efficiency to about 1% (photons per electron injected). These devices are believed to operate by double charge injection of electrons and holes from the negative and positive electrodes, respectively.

These singly charged excitations combine to form excitons which can then decay by photoemission. Changing the band-gap of these conjugated polymers, by appropriate chemical modification, can result in a change in the wavelength of the photoemission: red-shifted upon reduction of band-gap and blue-shifted upon increasing the band-gap. Enhancement of the photoemission efficiency and further lowering of forward operating voltage are two of the primary areas of current activity that is expected to lead to improved devices of greater technological relevance^[23].

Objective

Our aim is to develop an electrode material using ultrathin films of the conducting polymer (Polypyrrole) doped with a polyelectrolyte dopant like DNA. In this work a new material, DNA doped conducting polymer (PPy) films have been reported and thought of as a promising candidate for electrode material of electrochemical supercapacitor.

The advantages associated with the electrochemical polymerization and polyelectrolyte nature of DNA were the motivation for this work. In this work, an attempt has been made to utilize the several interesting properties such as electroactivity, redox & acid –base chemistry, ionic exchange properties of PPy compared to other conducting polymers. These attractive properties together with the ease of electrochemical synthesis made it a suitable absorbent for DNA.

Recently electrochemical methods were employed for investigation of interaction of small molecules with DNA. In addition, CPs are suitable substrate for immobilization of biological molecules such as DNA, proteins etc. CPs, like PPy, after immobilization of biomaterials was used as modified electrode in the field of electrochemical biosensors. Herein we report the template polymerization of Polypyrrole using a biomacromolecule, DNA, as the polyelectrolyte.

Plan of Work

In this report we plan to investigate the electrochemical doping of conducting polymer like PPy with several macromolecular dopants like DNA, PTSA and DBSA.

Firstly, we will electropolymerize the pyrrole monomer in presence of aforementioned dopants, via two methods i.e by constant voltage (Potentiostatic method) and by cyclic voltage (Cyclic Voltammetric Technique). After then we have successfully prepared PPy films doped with the dopants viz DNA, PTSA and DBSA. We moved on to characterize the films obtained using SEM, FTIR, CV, LSV and Pulse Voltammetry for its quantification and relevance to be utilized as an electrode material in electrochemical supercapacitors. We also plan to evaluate the effect of the dopant concentration on the redox behavior of the PPy films.

CHAPTER 2

EXPERIMENTAL WORK

2.1 Materials

The chemical used and their sources are given in following table. All chemicals were of Analytical Grade and they were used without any further purification.

Table 4.Name of chemicals used and their sources

CHEMICAL	ACRONYMES	SOURCES
Pyrrole	Py	Sisco research laboratories (P) Ltd.
Deoxyribo nucleic acid	DNA	Sisco research laboratories (P) Ltd.
p-toluene sulphonic acid	PTSA	Sisco research laboratories (P) Ltd.
Dodecyl benzene sulphonic acid sodium salt	DBSA	Himedia Laboratories (P) Ltd
Potassium chloride	KCl	Chemical Drug House

Indium tin oxide (ITO) glass was used as the working electrode. The ITO glasses were cleaned by ultrasonicing in soap solution, distilled water, acetone, and isopropanol successively for 15 min. Platinum wire was used as the counter electrode while Ag/AgCl served as the reference electrode. The temperature was maintained at $24 \pm 1^\circ\text{C}$.

2.2 Preparation of Precursor Solution

Pyrrole monomer used for the film formation, was distilled and stored at 0 to 4°C. The precursor solution for Ppy/DNA film was made by dissolving 1000 ppm of DNA in 100 ml of distilled water by means of sonication. Then 0.2 M Pyrrole monomer was added to this solution and again sonicated for 15 min. The other two polymerizing solutions of Ppy/PTSA and Ppy/DBSA were also prepared in the same manner as explained above by replacing the DNA dopant with PTSA and DBSA, respectively.

2.3 Preparation of PPy/DNA Film

PPy/DNA films were obtained through electropolymerization of pyrrole on suitable substrates/working electrodes such as ITO by using different electrochemical techniques such as cyclic voltammetry (CV) and potential static (constant voltage) deposition methods. To carry out the electropolymerization of pyrrole, a three-electrode one-compartment cell was employed, and Ag/AgCl (saturated KCl) as reference electrode, platinum and ITO as the counter and working electrode dipped respectively in the polymerization solution. Power supply provided either constant (potentiostatic) or reversing variable voltage (CV) for electrodeposition.

A constant potential of 1.2 V was applied for potentiostatic deposition by using potentiostat for a deposition time of 1000 s. The accumulation of charge vs. time curve was constantly monitored to ensure identical film produced in each preparation. And for cyclic voltammetry deposition the potential was switched between -1.2 V and +1.2 V at a scan rate of 50 mV/s for 10 cycles.

Under these conditions, well adherent PPy/DNA film was formed on the surface of the ITO working electrode. The salient feature of PPy electrodeposition is that polymerization, doping and film processing take place simultaneously. The PPy films were then thoroughly washed with water, dried at 50⁰C overnight. PPy-DBSA and PPy-PTSA films were also prepared via similar method, for comparative study. Effect of dopant concentrations were also evaluated in detail.

These three films viz PPy/DNA, PPy/PTSA, PPy/DBSA were also formed by changing the concentration of the dopants for comparative electrochemical studies. Morphology of the electrochemically polymerized films was studied by means of SEM and the electrochemical properties of DNA-PPy were explored as well.

Conducting polymers PPy prepared is in the film form on glass substrate and characterized by different analytical techniques. The basic principles and instrumentations of these techniques have been discussed in this chapter.

2.4 Potentiostat/Galvanostat

Electrochemical analyses can be thought of in terms of two broad classes of measurement, one in which the potential that develops between two electrodes is measured (potentiometry) and another in which the current that flows between two electrodes is measured (amperometry).

Potentiometry is the measurement of the potential between an electrode which responds to the analyte (called an ion selective or indicator electrode) and a reference electrode in an electrically conductive solution. Because the reference electrode has, by design, a constant potential, the measured potential depends on the activity of analyte. Potentiometry is the field of electroanalytical chemistry in which potential is measured under the conditions of no current flow. The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the analytic solution. The potential that develops in the electrochemical cell is the result of the free energy change that would occur if the chemical phenomena were to proceed until the equilibrium condition has been satisfied. The potential depends on the activity of the analyte, however concentration of analyte is normally the question of interest. In solutions with low (near zero) ionic strength, the activity coefficient approaches unity and concentration is equivalent to activity.

Chronoamperometry is an important and useful experimental technique. By stepping the potential from one point on a voltammetric wave to another and monitoring the current response, diffusion coefficients can be determined without knowing the concentration of electroactive species or the number of electrons transferred^[24].

2.5 Cyclic Voltammetry

Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time like linear sweep voltammetry. Cyclic voltammetry takes the experiment a step further than linear sweep voltammetry which ends when it reaches a set potential. When cyclic voltammetry reaches a set potential, the working electrode's potential ramp is inverted. This inversion can happen multiple times during a single experiment. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution^{[25][26]}

The utility of cyclic voltammetry is highly dependent on the analyte being studied. The analyte has to be redox active within the experimental potential window. It is also highly desirable for the analyte to display a reversible wave. A reversible wave is when an analyte is reduced or oxidized on a forward scan and is then reoxidized or rereduced in a predictable way on the return scan as shown in the first Fig 2.1.

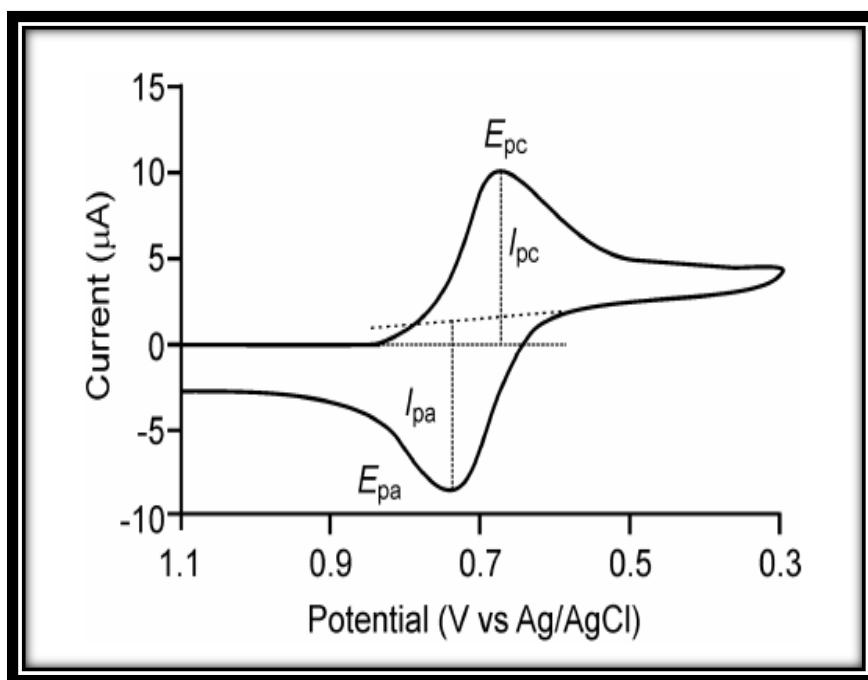


Fig.2.1. Typical cyclic voltammogram

Even reversible couples contain polarization overpotential and thus display a hysteresis between absolute potential between the reduction (E_{pc}) and oxidation peak (E_{pa}). This overpotential emerges from a combination of analyte diffusion rates and the intrinsic activation barrier of transferring electrons from an electrode to analyte. A theoretical description of polarization overpotential is in part described by the Butler-Volmer equation and Cottrell equation. Conveniently in an ideal system the relationships reduces to,

$$|E_{pc} - E_{pa}| = \frac{57 \text{ mV}}{n} ,$$

for an n electron process.

Reversible couples will display a ratio of the peak currents passed at reduction (i_{pc}) and oxidation (i_{pa}) that is near unity ($1 = i_{pa}/i_{pc}$). This ratio can be perturbed for reversible couples in the presence of a following chemical reaction, stripping wave, or nucleation event. When such reversible peaks are observed thermodynamic information in the form of half cell potential $E^0_{1/2}$ can be determined. When waves are semi-reversible such as when i_{pa}/i_{pc} is less than or greater than 1, it can be possible to determine even more information especially kinetic processes like following chemical reaction.

When waves are non-reversible it is impossible to determine what their thermodynamic $E^0_{1/2}$ is with cyclic voltammetry. This $E^0_{1/2}$ can be determined; however it often requires equal quantities of the analyte in both oxidation states. When a wave is non-reversible cyclic voltammetry cannot determine if the wave is at its thermodynamic potential or shifted to a more extreme potential by some form of over potential. The couple could be irreversible because of a following chemical process; a common example for transition metals is a shift in the geometry of the coordination sphere. If this is the case, then higher scan rates may show a reversible wave. It is also possible that the wave is irreversible due to a physical process most commonly some form of precipitation as discussed below. Some speculation can be made in regards to irreversible waves however they are generally outside the scope of cyclic voltammetry.

2.5.1 Instrument Setup for Potentiostat/Galvanostat

A CV system consists of an electrolysis cell, a potentiostat, a current-to-voltage converter, and a data acquisition system. The electrolysis cell consists of a working electrode, counter electrode, reference electrode, and electrolytic solution.

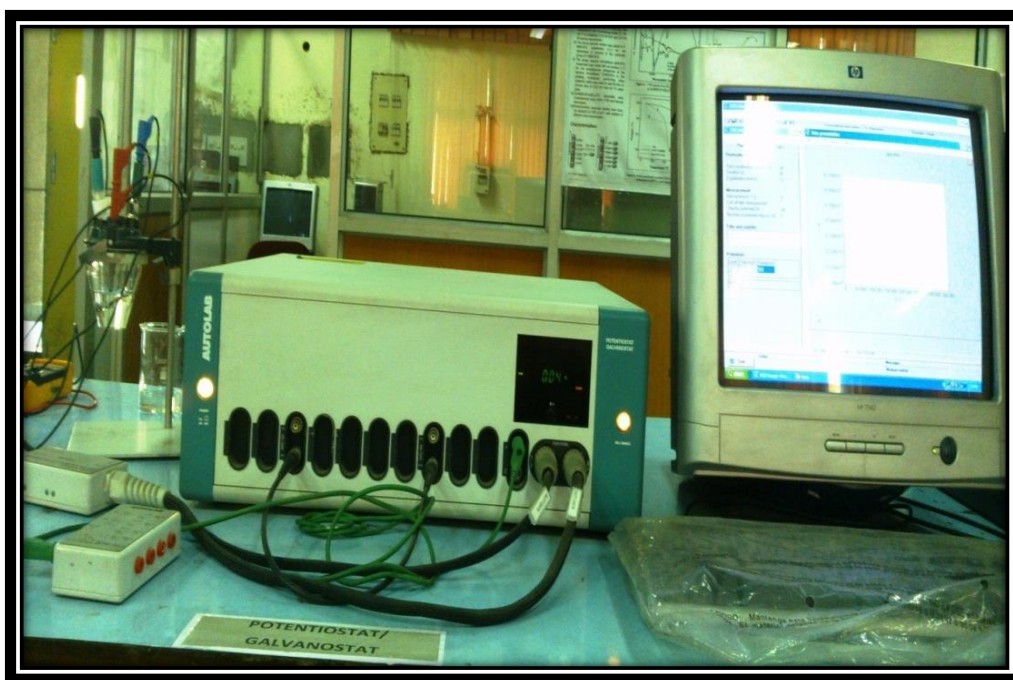


Fig.2.2. Instrument setup for potentiostat/galvanostat

The working electrode's potential is varied linearly with time, while the reference electrode maintains a constant potential. The counter electrode conducts electricity from the signal source

to the working electrode. The purpose of the electrolytic solution is to provide ions to the electrodes during oxidation and reduction. A potentiostat is an electronic device which uses a dc power source to produce a potential which can be maintained and accurately determined, while allowing small currents to be drawn into the system without changing the voltage. The current-to-voltage converter measures the resulting current, and the data acquisition system produces the resulting voltammogram.

Cyclic Voltammetry (CV) is an attractive method for the teaching of a number of concepts in electrochemistry. In brief, it is perhaps the most versatile electrochemical technique for the study of electroactive species. The effectiveness of CV results from its capability for rapidly observing the redox behaviour over a wide range of potential. The resulting voltammogram is similar to a conventional spectrum in that it conveys information as a function of an energy scan. In spite of its wide applications, this technique is not generally well understood as compared to other instrumental techniques such as spectroscopy and chromatography.

2.6 Linear Sweep Voltammetry

The simplest type of voltammetry is called Linear Sweep Voltammetry (LSV). In this technique, the potential of the working electrode is varied linearly as a function of time and the current response is recorded. The scan rates are relatively slow, i.e. less than 5 mV/s, which allows the movement of fresh analyte to reach the electrode surface, so that the electrode is always in equilibrium with the bulk solution. Consider a one electron reduction reaction.



which obeys Nernst equation.

Here, E is the potential of the working electrode, E° is the standard reduction potential of A.

If a solution containing only A is taken in a cell and an applied potential of about 200 mV is applied, then a miniscule amount of current will flow to convert a small amount of A to B so that Nernst equation is obeyed at the electrode surface. The amount of current increases as the potential approached the E° , when E becomes equal to E° , $[B] = [A]$ at the electrode surface or in other words, at E° , half of the total A reaching the electrode is converted to B, so that the current is half way to its limiting current. As E is lowered further, all the A is converted to B, as soon as it reaches the electrode.

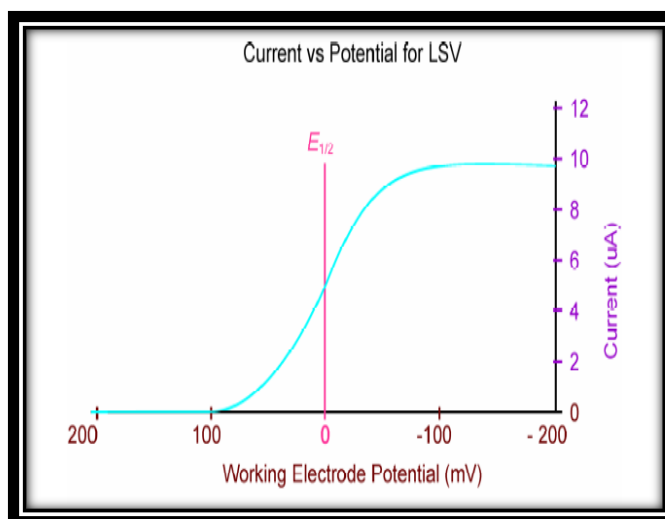


Fig.2.3. Linear sweep voltammogram

An important feature of this technique is that largest change in slope occurs around E° . The value of the potential corresponding to the point where the current is exactly half of the total current is known as half wave potential ($E_{1/2}$) and this value is used to identify the unknown species (qualitative analysis) and the difference in the value of the current from the start to the maximum value is known as limiting current, i.e. sum of migration current + residual current and diffusion current, but after elimination of the first two the diffusion current (i_d) that is directly proportional to the concentration of the analyte and is used for its analytical determination (quantitative analysis)

$$i_d = KcA \dots$$

where cA is the analyte concentration and K is a constant.

2.7 Pulse Method

Many of the limitations of traditional Linear- Scan Voltammetry were overcome by the development of Pulse methods. The idea behind all Pulse Voltammetric method is to measure the current at a time when the difference between the desired Faradaic curve and the interfering charging current is large. Pulse Voltammetry can be used with many different types of solid electrodes, the HDME, and rotating electrode.

The sensitivity of linear scan voltammetry or polarography is limited by charging current which is large initially in the drop life. The slowness, inconvenient apparatus and poor detection limits

of linear scan voltammetry or polarography were the reasons for its decline. The sensitivity of these two methods is improved by pulse methods by about 6.5 times by eliminating charging current. The current in these methods is measured at a time when the difference between the Faradaic current and the interfering charging current is large. There are four important pulse methods namely

- i) Normal pulse voltammetry/polarography
- ii) Differential pulse voltammetry/polarography
- iii) Square wave voltammetry

2.8 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, low vacuum and in environmental SEM specimens can be observed in wet conditions.

Unlike the TEM, where electrons of the high voltage beam carry the image of the specimen, the electron beam of the scanning electron microscope (SEM) does not at any time carry a complete image of the specimen. Scanning electron microscopy (SEM) uses a focused electron probe to extract structural and chemical information point-by-point from a region of interest in the sample. The high spatial resolution of an SEM makes it a powerful tool to characterise a wide range of specimens at the nanometer to micrometer length scales.

Low-temperature scanning electron microscopy is also applicable to the imaging of temperature-sensitive materials such as ice^[27]. The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE) characteristic X-rays, light (cathodoluminescence) (CL), specimen current and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron

imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen. BSE images can provide information about the distribution of different elements in the sample.

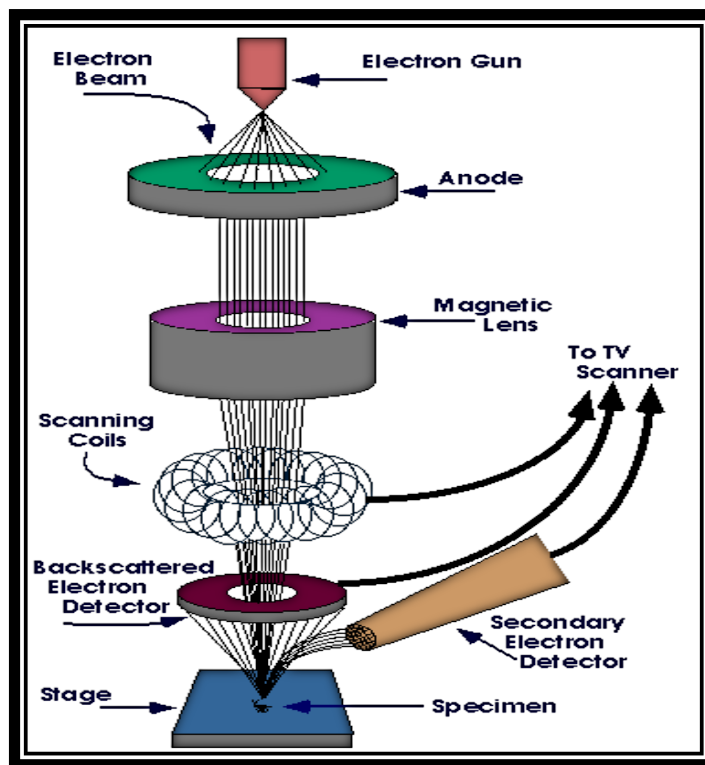


Fig.2.4. Diagrammatic representation of working of Scanning Electron Microscope

For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron

images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

2.9 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared), opening up new applications of infrared spectroscopy.

The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the "dispersive spectroscopy" technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength.

Fourier transform spectroscopy is a less intuitive way to obtain the same information. Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength.

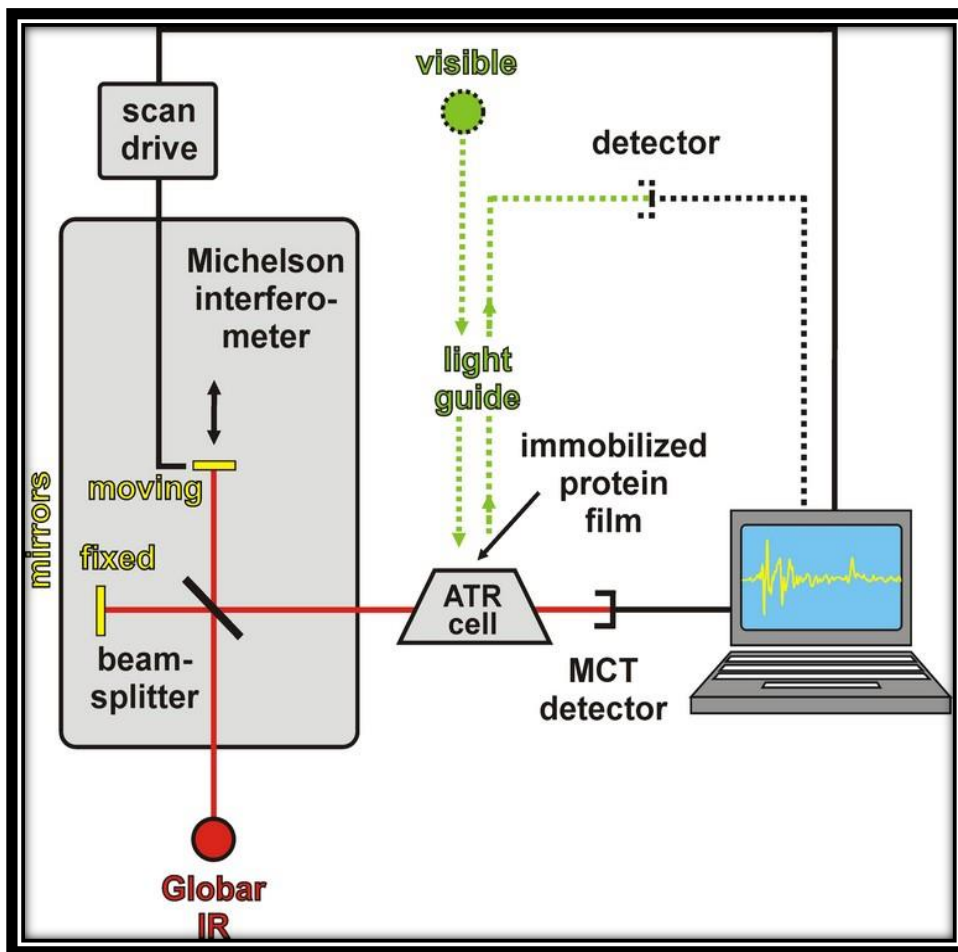


Fig.2.5. Simple working of FTIR

The beam described above is generated by starting with a broadband light source containing the full spectrum of wavelengths to be measured. The light shines into a Michelson interferometer, a certain configuration of mirrors, one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, by the interferometer, due to wave interference. Different wavelengths are modulated at different rates, so that at each moment, the beam coming out of the interferometer has a different spectrum. As mentioned, computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram".

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Electrochemical Polymerization

3.1.1 Potentiostatic Method

PPy/DNA, PPy/PTSA, and PPy/DBSA films were prepared successfully by following the method explained in the experimental section. For the film formation the ITO electrodes were scanned up to a potential range of 1.2 V for 1000 s. Fig 3.1 shows the potentiostatic response of ITO electrode in PPy/DNA solution at 1.2 V.

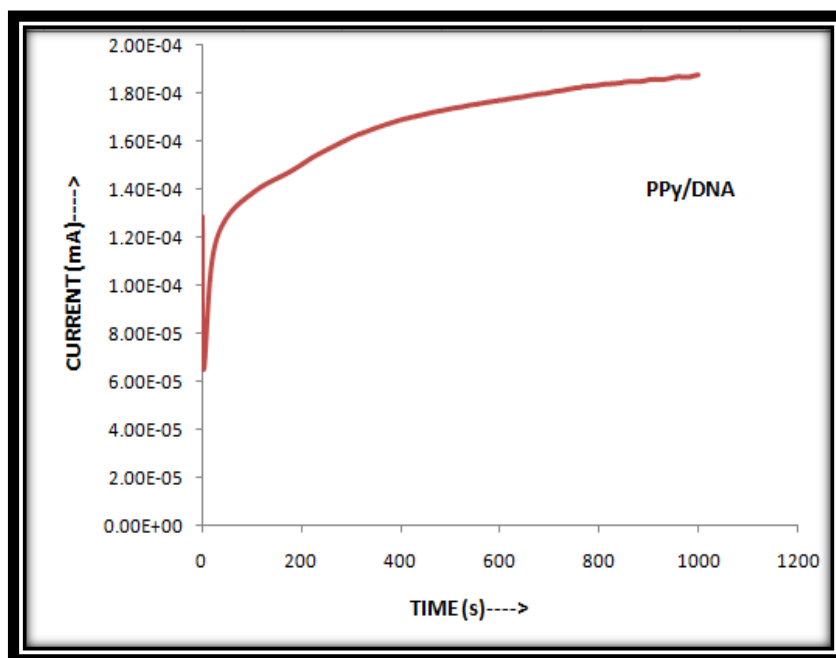
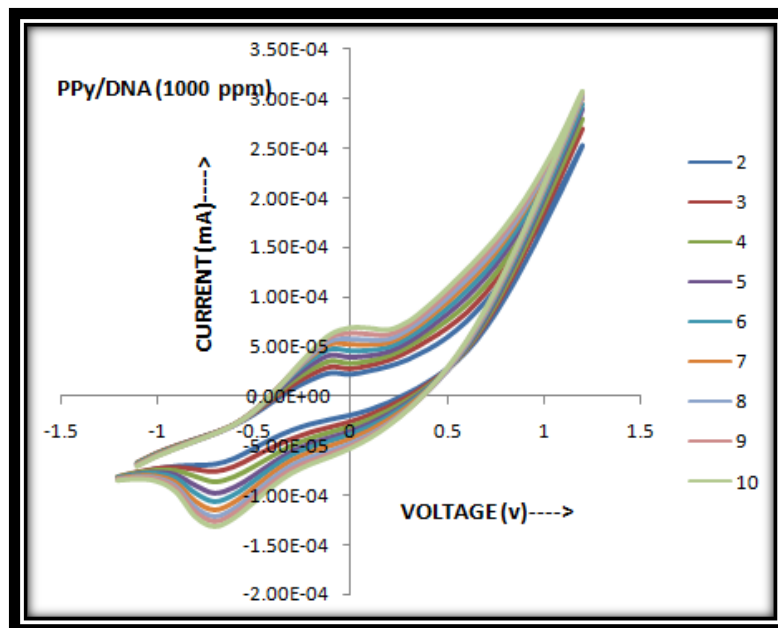


Fig.3.1. Chronopotentiogram depicting the electrochemical polymerization of pyrrole on ITO using 0.2 M pyrrole in presence of 700 ppm DNA dopant.

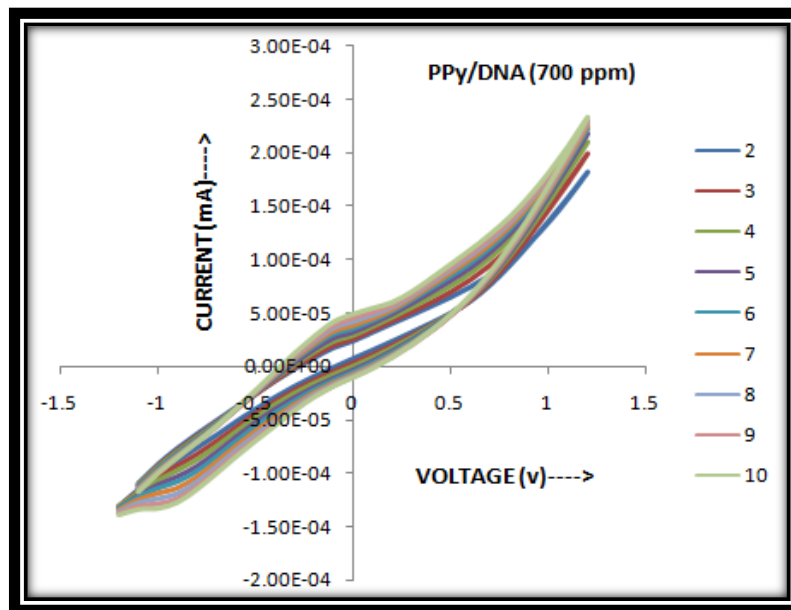
From Fig 3.1, it can be seen that the current is increasing with time which confirms polymerization and deposition of PPy/DNA over the ITO electrode.

3.1.2 Cyclic Voltammetric Method

PPy/DNA, PPy/PTSA, and PPy/DBSA films were also prepared via Cyclic voltammetry by scanning the electrode up to 10 scans between potential -1.2 to +1.2 V. Fig.3.2 shows the cyclic voltammograms of ITO over 10 scans in PPy/DNA solution.



(a)



(b)

Fig.3.2. Cyclic voltammograms of PPy/DNA at (a) 1000 ppm and (b) 700 ppm.

Fig 3.2 shows repetitive cyclic voltammograms recorded during electropolymerisation of PPy on ITO surface in the presence of 1000 ppm DNA (Fig. 3.2 (a)) and 700 ppm (Fig. 3.2 (b)). The increasing current response observed in the electrolyte-free DNA solution upon repetitive cycling suggests an efficient film growth. Such a profile indicates that the anionic DNAs are

effectively incorporated within the growing film for maintaining its electrical neutrality in a manner analogous to the doping of PPy by other anionic macromolecules. In addition, the growth of the polypyrrole continues with the number of sweepings and in the course of successive cycles monomer oxidation occurs at less and less positive potential.

This change might contribute to the fact that there was gradual decrease in the nucleation and growth energy for PPy polymerization as the PPy/DNA nanocomposite gradually formed per cycle. PPy/DNA film shows prominent redox peaks which confirm the better electropolymerization and electrochemical activity of the film formed. Greater the dopant concentration more outstanding the redox activity, pertinent to increased doping and conductivity of PPy with DNA incorporation was perceived by comparing Fig.3.3 & 3.4.

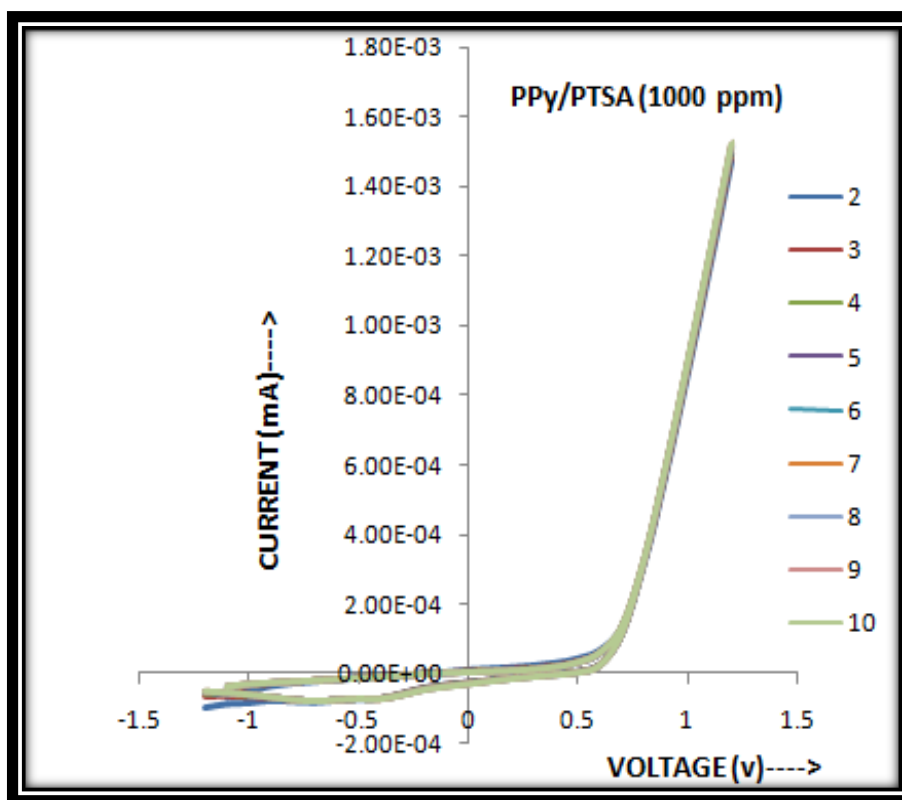


Fig.3.3. Cyclic voltammogram of PPy/PTSA at 1000 ppm

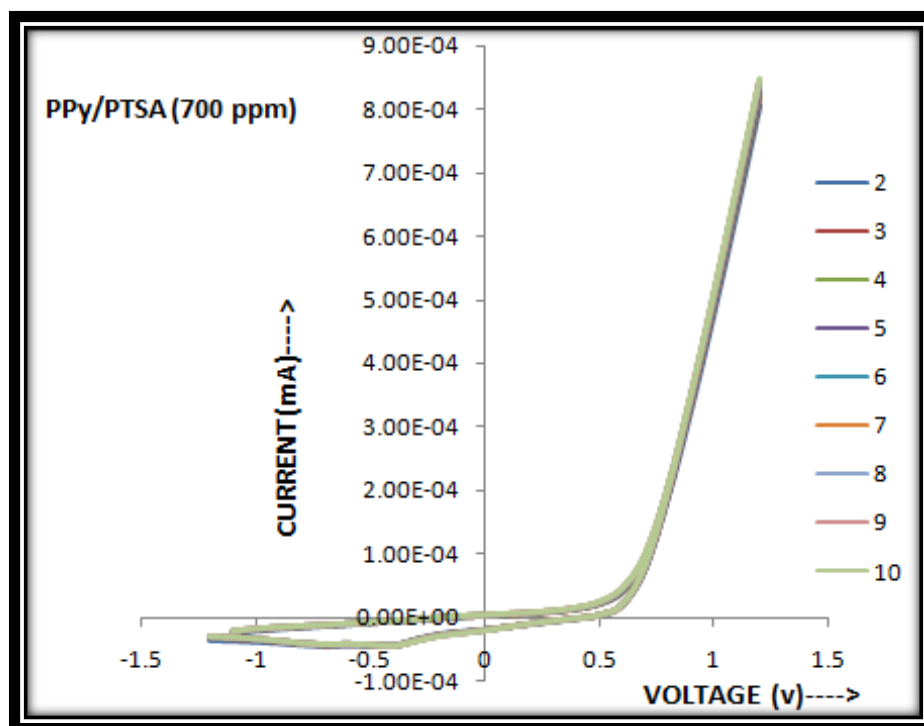
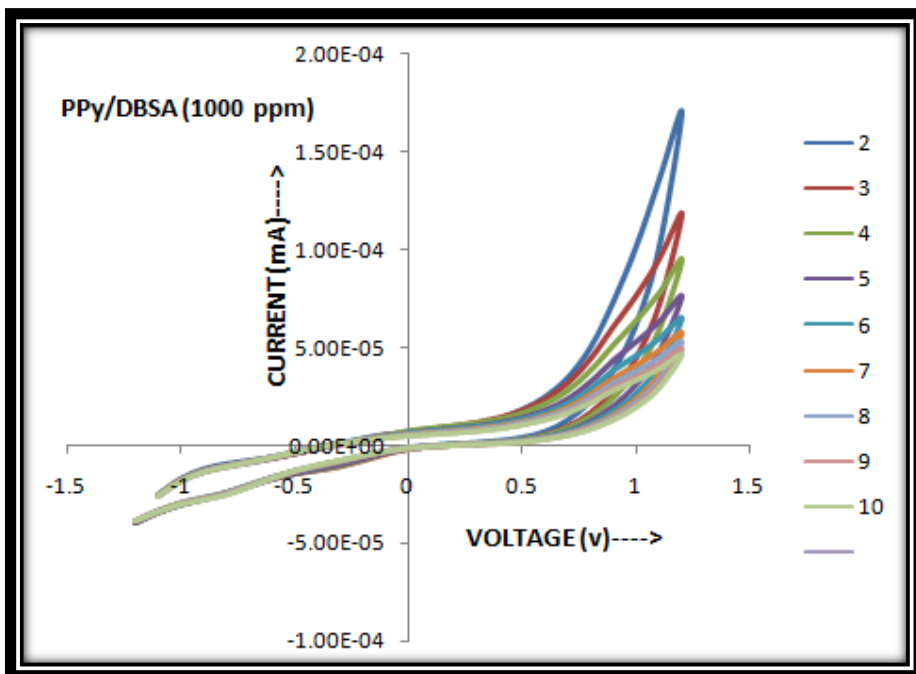


Fig.3.4. Cyclic voltammogram of PPy/PTSA at 700 ppm.

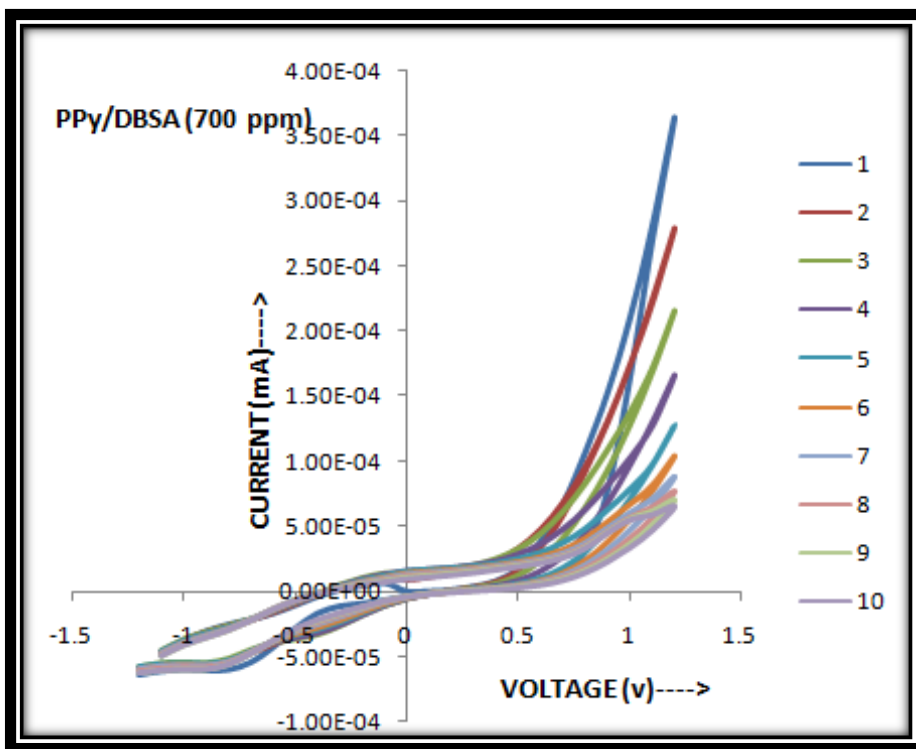
The basic CV curve of the PPy/DNA shows the reversible current response. The important parameters of a cyclic voltammogram are the peak potentials ($E_{pc} = 4.237 \times 10^{-3} \text{C}$, $E_{pa} = -2.101 \times 10^{-3} \text{C}$) and peak currents ($i_{pc} = 2.523 \times 10^{-4} \text{mV}$, $i_{pa} = -8.365 \times 10^{-5} \text{mV}$) of the cathodic and anodic peaks, respectively. The Cyclic Voltammograms of PPy/PTSA, and PPy/DBSA at 1000 ppm and 700 ppm concentrations are also shown in Fig 4.3 and 4.4 respectively. However current response difference between 1st and subsequent cycles was not great and almost similar response was seen unlike the PPy electropolymerized with DNA.

As can be seen from Fig 3.3 & 3.4, a small current increase with increase in the number of scans for PPy/PTSA, implies that the PPy/PTSA is also well polymerized on ITO electrode and stable like PPy/DNA film.

However in case of PPy/DBSA film current decreases with increase in the number of scans implying that PPy/DBSA film is unstable and fully reversible current response was not seen. Fig 4.5 shows the variation in the cyclic voltammograms of PPy film electropolymerized with different dopants DNA, PTSA, and DBSA (10th scan).



(a)



(b)

Fig.3.5.Cyclic voltammograms of PPy/DBSA at (a) 1000 ppm and (b) 700 ppm.

In a cyclic voltammogram (CV), the higher the redox peaks, the greater the electrochemical reaction activity^[28]. From Fig 3.6, it can be seen that PPy/DNA film shows prominent redox peaks which confirms the better electropolymerization and electrochemical activity of the film. The charge retention after 10 cycles is good in the PPy/DNA and PPy/PTSA film as compared to the PPy/DBSA film. Highest current response was seen for PPy-PTSA but PPy-DNA also portrayed excellent redox behavior with well defined redox peaks. The area under the CV curve for PPy-DNA is the largest among the three illustrating the superior ion-exchanging kinetics of DNA doped PPy.

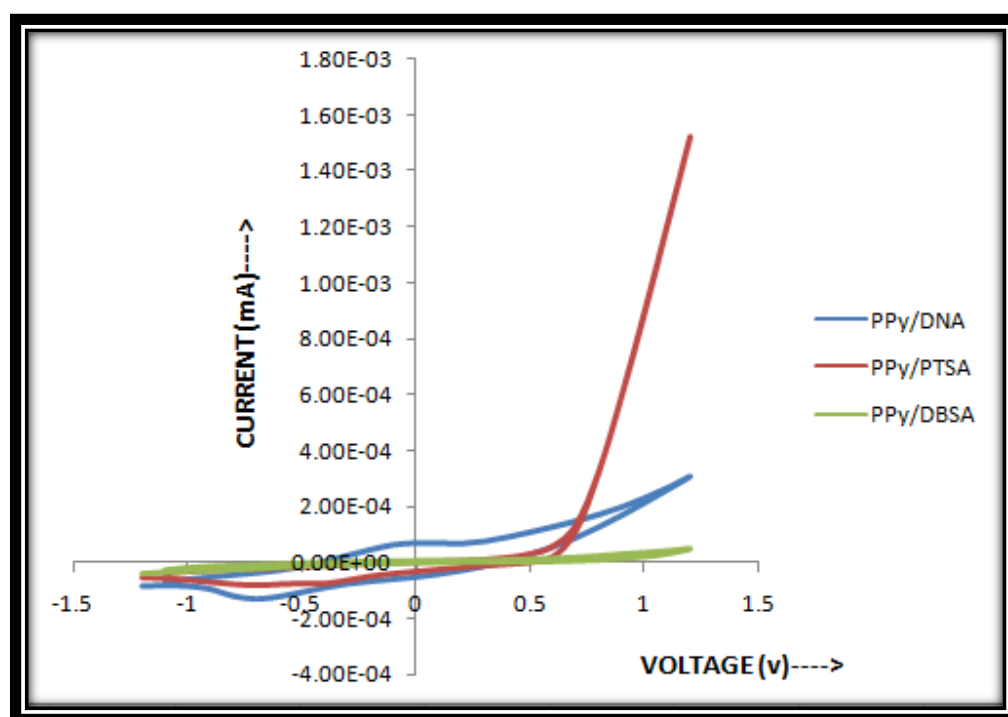


Fig.3.6.A comparative Cyclic voltammogram of PPy/DNA, PPy/PTSA, and PPy/DBSA films at 10th scan

3.2 Characterization

PPy/DNA, PPy/PTSA, and PPy/DBSA films were prepared successfully via CV technique and potentiostatic method. A detailed study of the as prepared films was carried out. Optical characterization was carried out using a ThermoScientific Nicolet 380 series Fourier Transform

Infrared Spectrometer. Morphological studies were carried out using a HITACHI S-3700 N scanning electron microscope. All the electrochemical studies of prepared films were monitored using an Autolab Potentiostat/Glavanostat.

3.2.1 Scanning Electron Microscopy

Fig 3.7 and 3.8 shows the effect of dopants on the morphology of the prepared films. The SEM image of the PPy/DNA film shows the fiber like morphology, while the PPy/PTSA and PPy/DBSA films show the rod like and spherical structure as shown in the Fig 3.7 & 3.8 Unlike PPy/DBSA film, in PPy/DNA, and PPy/PTSA film the PPy particles were distributed homogeneously.

Apart from the fact that it is a renewable resource and abundantly available, DNA offers many features which makes it an ideal candidate for use as a polyelectrolyte for template synthesis. It has optical transparency (otherwise it would negate one of the major intended uses of such systems, namely optically transparent conductors). Thus from Fig 3.7 we can see that DNA is effective for giving the fiber like morphology to PPy.

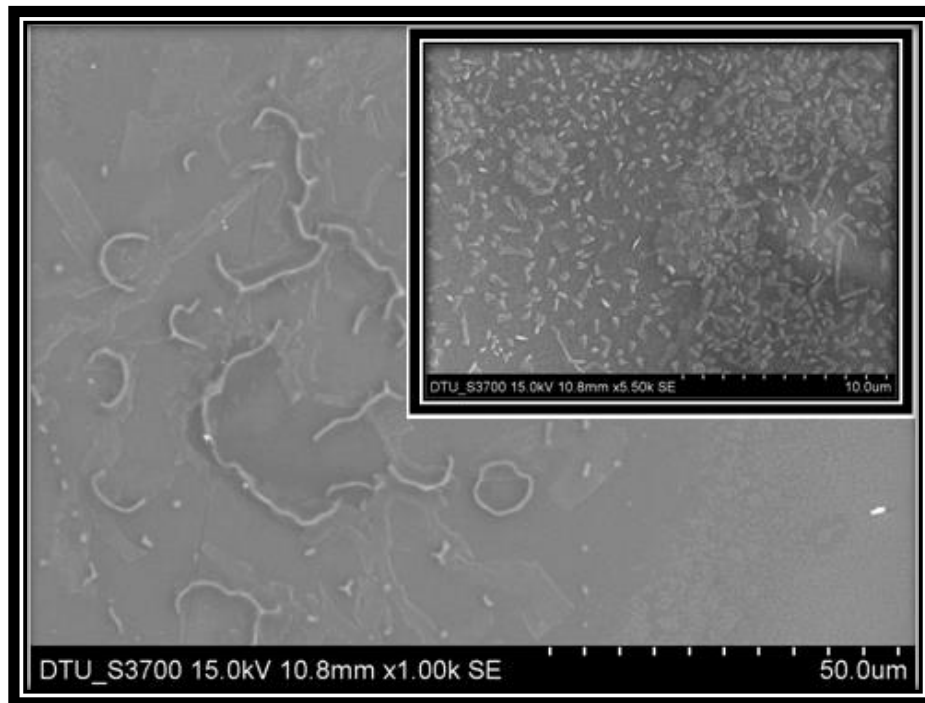
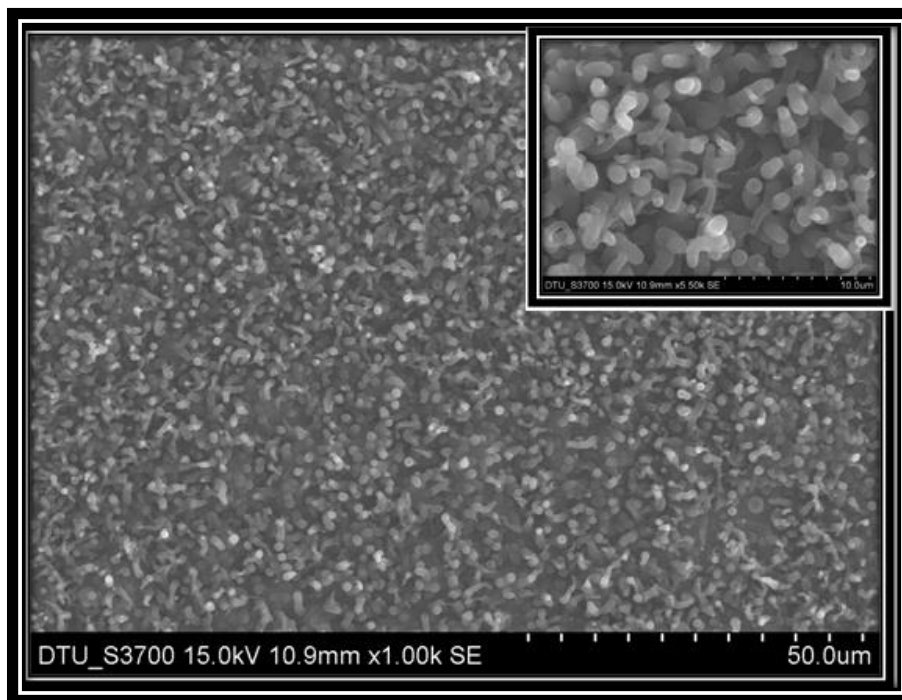
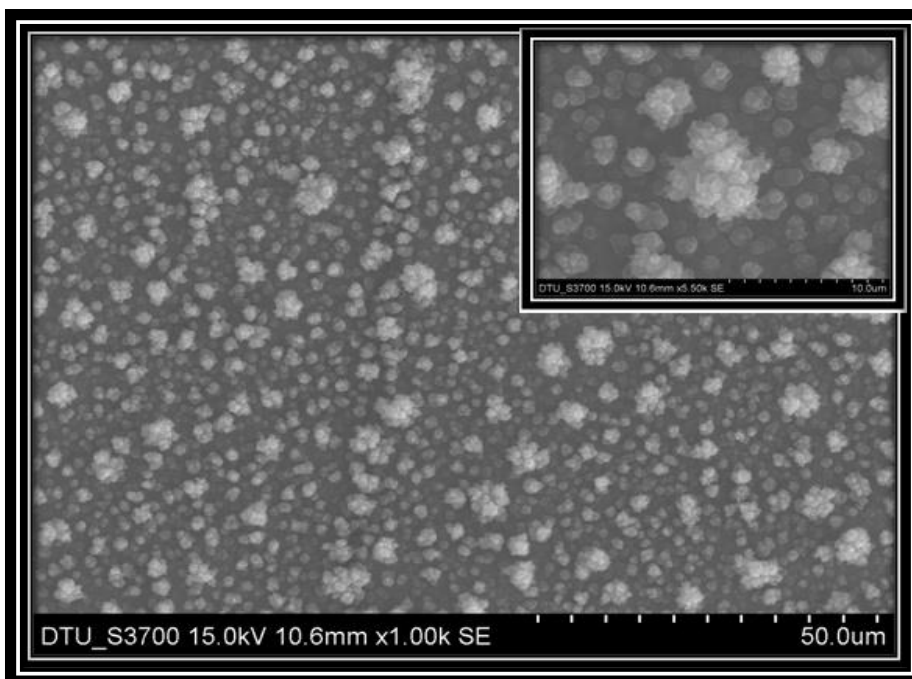


Fig.3.7.SEM micrograph of PPy/DNA film



(b)



(c)

Fig.3.8.SEM micrographs of (a) PPy/PTSA, and (b) PPy/DBSA films

3.2.2 Fourier Transform Infrared Spectra

In Fig 3.9, the spectroscopic characteristics for PPy/DNA, PPy/PTSA and PPy/DBSA are observed. The analysis of the FTIR spectra presents the increase and extension of the absorption band centered at around $\sim 3600 \text{ cm}^{-1}$ belonging to asymmetric stretching of NH groups which resulted from the covalent attachment of the DNA with NH groups of a moiety of PPy matrix. The spectrum of a PPy/DNA sample showed a continuous increase tail in absorption from ~ 3000 to $\sim 3700 \text{ cm}^{-1}$. It is the tail of the bipolaron absorption band that is the signature for electrical conductivity of conducting polymers. The wave-numbers above 1745 cm^{-1} may be caused by the conjugated molecular structure of PPy and the free charge carriers in the polymer. The bands assigned to $\nu(\text{C}=\text{C})$ stretch are observed in the region of $1459\text{-}1551 \text{ cm}^{-1}$. An intensive band at 1745 cm^{-1} vibration band due to C=N stretching and the 1551 cm^{-1} vibration band due to C=C bonds associated with C-N stretching and bending vibration.

Furthermore, due to the presence of DNA, the adsorption band expanding from $\sim 1800 \text{ cm}^{-1}$ upward that is attributed to free charge carriers, is not just split and grouped into smaller vibration bands centered at 2366 and 2854 cm^{-1} , but with higher intensity. It reveals that the imine/amine charge carriers and the conjugated structure of PPy chains may be disturbed by the interactions between them and thus limited the extent of charge delocalization along the polymer chains, leading to increase of spectral features. In the range ~ 900 to $\sim 1200 \text{ cm}^{-1}$, the increase of spectral feature of absorption bands was also observed. These bands present the relationship in population of charge carriers, amine and imine species of PPy. Without DNA strands, a sharp peak at 1174 cm^{-1} characterize C-C stretching, and a peak at 1045 cm^{-1} is attributed to C-H in plane vibration. As seen in the spectrum of PPy/DNA composite, a new sharp peak was observed at 910 cm^{-1} , corresponding to the in-plane stretching vibration of NH^+ of imine species (quinonoid structure) that was performed by protonation of PPy chains^[29].

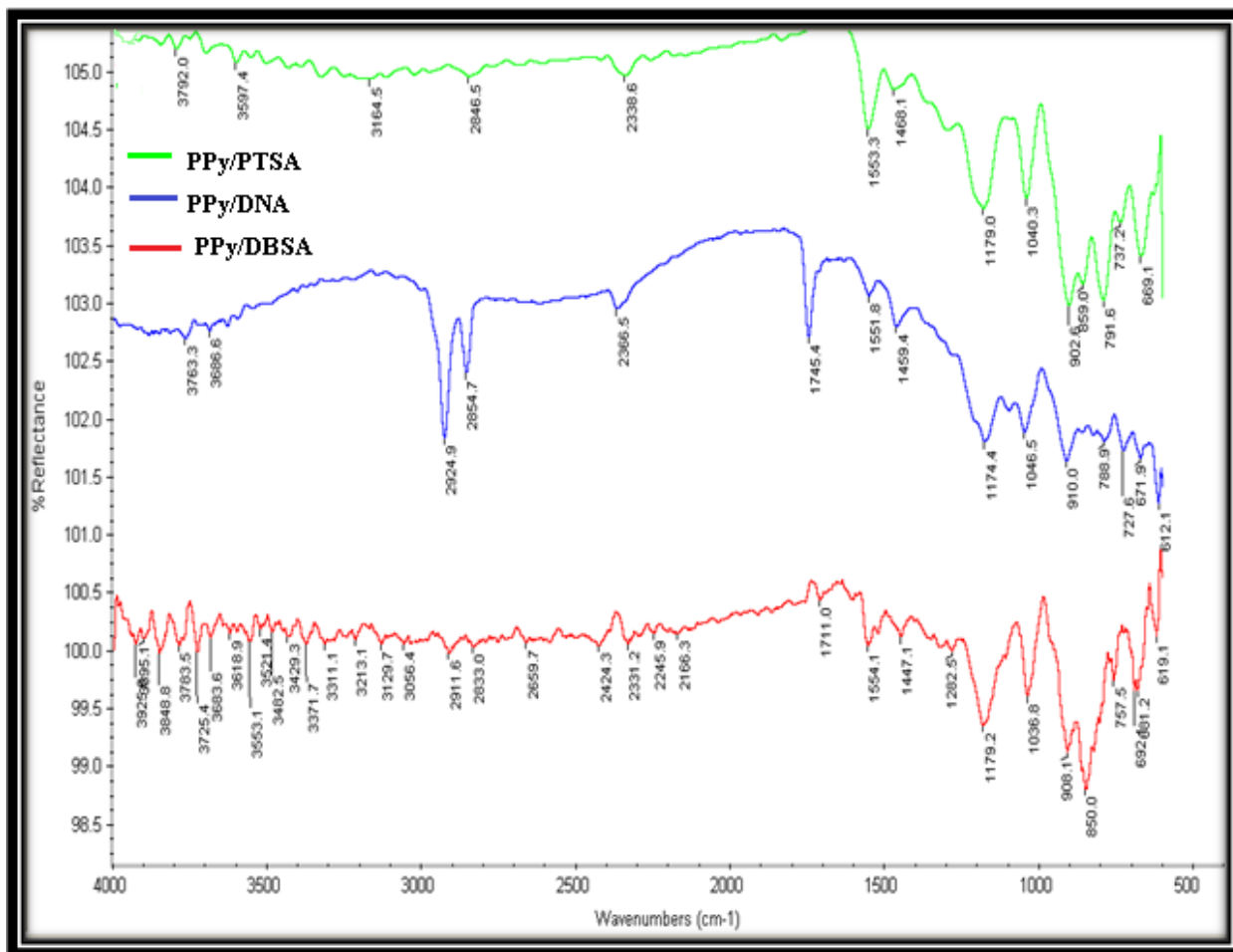


Fig.3.9.Comparative FTIR spectra of PPy/DNA, PPy/PTSA and PPy/DBSA films

In Fig 3.9 PPy/PTSA and PPy/DBSA showed the characteristic band at around 902 cm^{-1} due to C-H bending vibrations. The band at 1040 cm^{-1} corresponds to S = O stretching mode of the SO₃ group. The band at around 1179 cm^{-1} is due to SO₃ stretching.

From Fig 3.9 we can see a prominent peak at 1745 cm^{-1} . This peak is not present in the PPy films doped with PTSA and DBSA. The peak at 1745 cm^{-1} may attributed to the covalent bond formed between PPy and DNA.

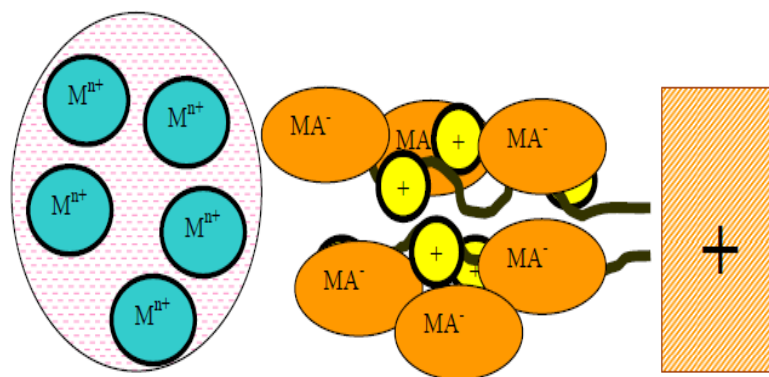
3.3 Electrochemical Studies

PPy/DNA, PPy/PTSA and PPy/DBSA films were also prepared with different concentration of dopants viz DNA, PTSA and DBSA are used for the comparative study.

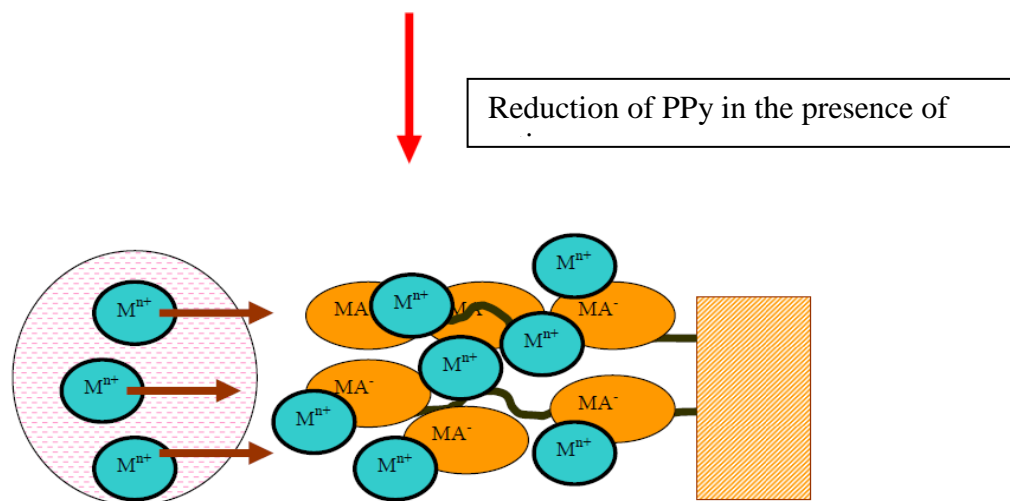
3.3.1 Cyclic Voltammetry

During the CV, the PPy film electrode-electrolyte system involves the redox couple, PPy⁺/ PPy (Kaplan & Qutubuddin, 1995), where PPy is the neutral species (associated with three to four monomer units) and PPy⁺ is the radical cationic species or polaron (one positive charge localized over three to four monomer units). At 1.2 V applications, the positive charge developed on the polymer is compensated by the movement of counter anion of DNA (anions of the pyrimidine bases). The guanine peak appeared only at a sufficiently negative switching potential (about - 2 V). The appearance of the guanine peak was conditioned by a reduction of guanine residues in the region of the switching potential and reoxidation of the reduction product in the vicinity of - 0.3 V. So, at current application potential of -1.2 V DNA structure remains intact. Redox peaks are related to the oxidation and reduction of PPy moiety.

In the oxidized state, the PPy is positively charged and so, some anions get migrated from solution into the polymer matrix so as to maintain electroneutrality. Similarly, on reduction, as electrons are injected and the positive charge on the polymer chain disappears, some anions leave the PPy matrix and enter into the solution. It may be concluded that PPy doped with large size (not releasable) are more chemically stable than those doped with easily releasable dopant anions in aqueous solutions. Therefore, anion exchange processes that would change the nature of polymer are minimized. Polymeric counterions entangle with polymer chain and stay in the polymer matrix during redox reaction (in contrast to small size mobile dopants). Fig.3.10 shows the diagrammatic representation of PPy oxidation reduction cycle in presence of polyelectrolyte like DNA.



The large ions like DNA are electrostatically attracted to the (+) charge of PPy backbone



The large ions do not move from the film, so the cations get adsorbed to the (-) charge of the macro anions (DNA)

Fig.3.10. Ion transport in PPy/MA⁻ (DNA) Film

The PPy films doped with different dopants like DNA, PTSA, and DBSA, keeping all other factors constant such as dopant concentration (1000ppm), electrolyte etc, was studied with the help of cyclic voltammetry in order to evaluate the effect of different dopants on the film's properties.

Fig 3.11 depicts the cyclic voltammogram of PPy/DNA electrode performed at various scan rates. Cyclic voltammogram of the film shows the current growth goes well with scan rate^[30]. The current growth tracks well with increased scanning rate, following the modified Randles–Sevcik equation for a film on an electrode. The shape of the CV curve changes gradually with the increased scan rates. It is understandable that entering into/ejecting and diffusion of counter ions is too slow compared to the diffusion of electrolyte in PPy matrix. Large surfactants and immobilized polymeric dopants such as polyelectrolytes counterions are not released during reduction process and become trapped within the polymer matrix due to their large size and entanglement with the PPy chain; consequently increase their solution stability.

For comparative study CV of the PPy films doped with PTSA and DBSA at different scan rates viz 20, 50 and 100 mVs⁻¹, was also carried out shown in Fig. 3.12(a) and (b). PTSA Counterion is a medium size dopant. It is more mobile than bulky dopants such as polymeric or surfactants and less mobile than small inorganic dopants such as chlorides or nitrates. PPy/PTSA showed more stability with regard to electroactivity.

The immobilized nature of the DBSA anion (due to its bulkiness) in the polymer could be a reason for its anomalous behaviour. Due to the immobility of the DBSA anions within the polymer matrix, the supporting electrolyte cations (in this experiment K^+ ions) is readily diffused in and out of the polymer during redox process in order to balance the immobilized charges of PPy/DBSA^[31]. The curve area of PPy/DNA film represents the charge storage capacity of the film. So the PPy/DNA film can be used as supercapacitors. In case of DNA doped PPy there is an increase in current with increased scan rate attributed to increased doping but there is decrease in the area under the curve with increasing scan rate and hence a decrease in charge storage capacity and capacitive performance which can be attributed to decreasing electrochemically controlled cation exchanging kinetics with increasing scan rate obviously steric effect or electrostatic system being the reason of such a discrimination. Such a decrease in the area under CV curve with increasing scan rate may also be attributed to the penetration of electrolyte in to the pores of PPy matrix and ions mobility within the pores. However in comparison a less bulky dopant like PTSA offers an equivalent increase in area under the curve as well as peak current with increasing scan rate indicating the best performance of this electrode PPy/PTSA as a supercapacitor. This relatively high capacitance of PPy/PTSA can be attributed to the uniform porous structure and small polymer particle size which determined the ability of electrolyte ions to enter and to enable local ion transfer process. DBSA dopant is however showing an anomalous behavior.

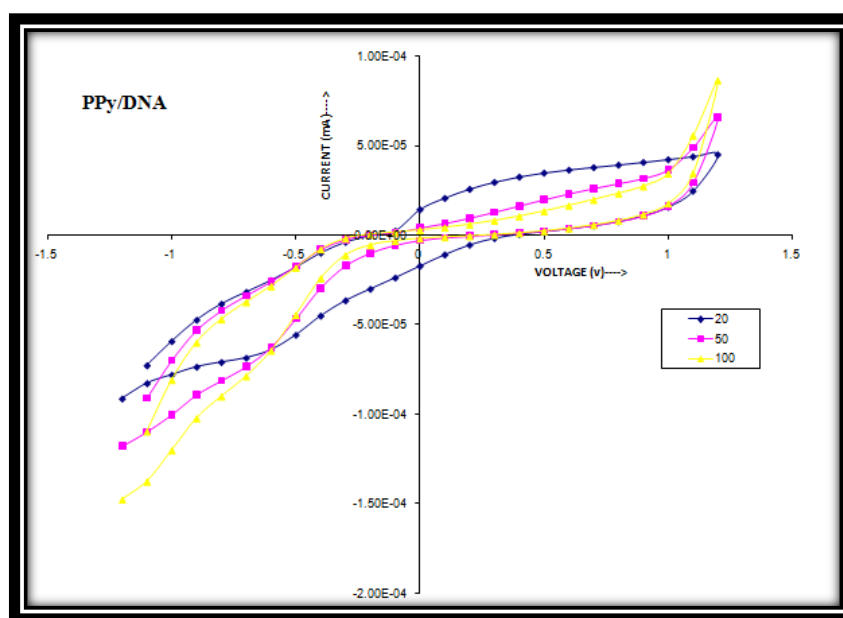
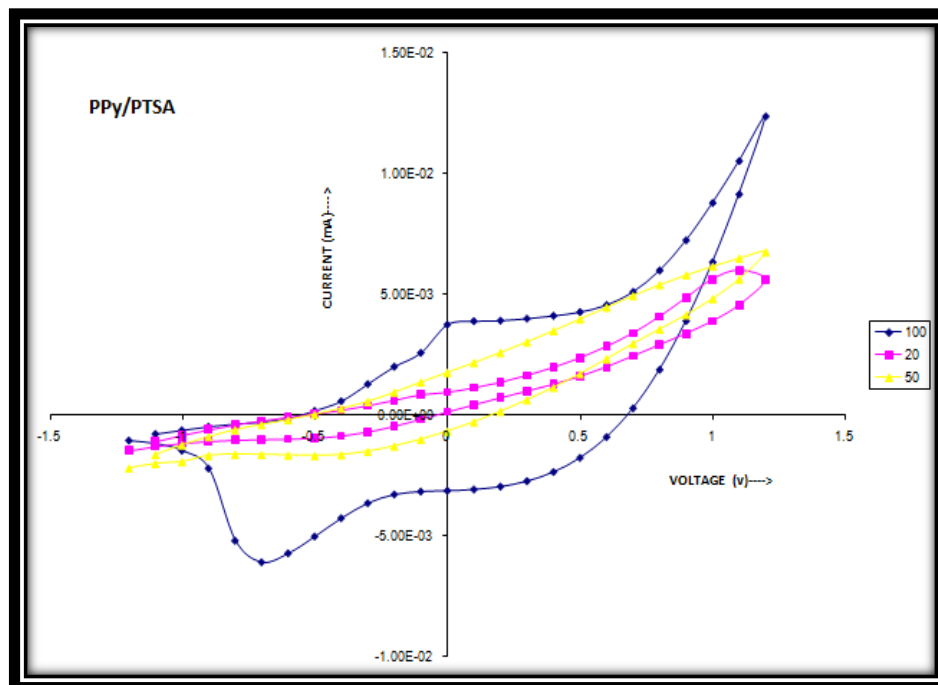
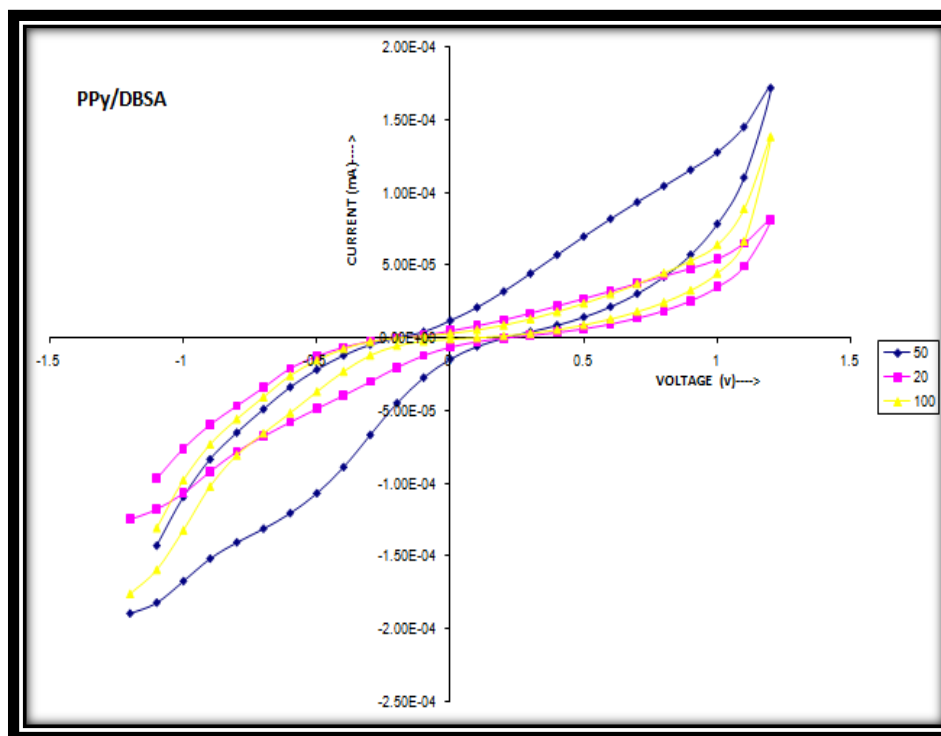


Fig.3.11.Cyclic voltammogram of PPy/DNA film at different scan rates



(a)



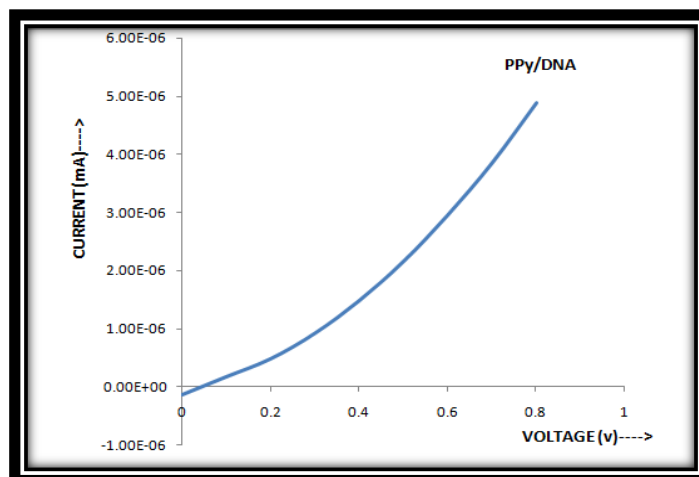
(b)

Fig.3.12 Cyclic voltammograms of (a) PPy/PTSA and (b) PPy/DBSA films at different scan rates

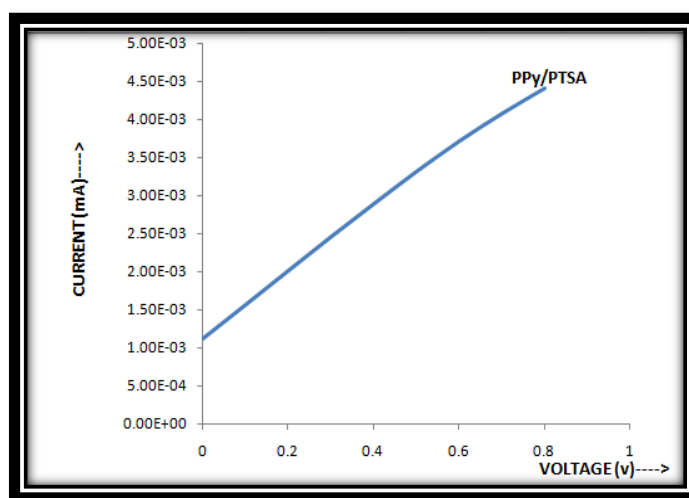
Up to a scan rate of 50 mV/s there is an increase in current as well as area under the curve however with further increase in scan rate a deteriorating effect was seen. This may be due to electrostatic interaction, decrease in PPy peak current is contributed by the increase in the resistance of electron transfer by electrostatic repulsion towards anion/cation incorporation and hence a slowdown in ion-exchanging kinetics.

3.3.2 Linear Sweep Voltammetry

Linear sweep voltammogram of PPy/DNA, PPy/PTSA, and PPy/DBSA films with 1000 ppm dopant concentration are shown in Fig 3.13 (a) & (b), and Fig 3.14 respectively. LSV of these three films represent a gradually increase in current with increase in the voltage.



(a)



(b)

Fig.3.13. Linear sweep voltammograms of (a) PPy/DNA and (b) PPy/PTSA films

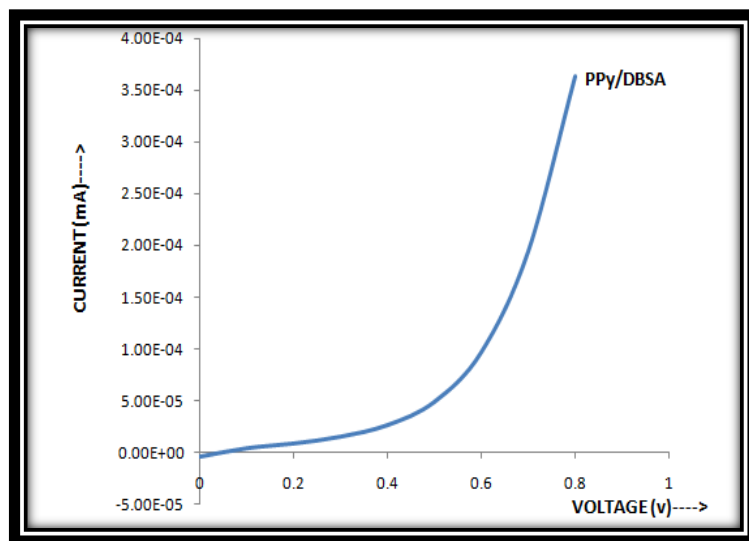


Fig.3.14. Linear sweep voltammogram of PPy/DBSA film

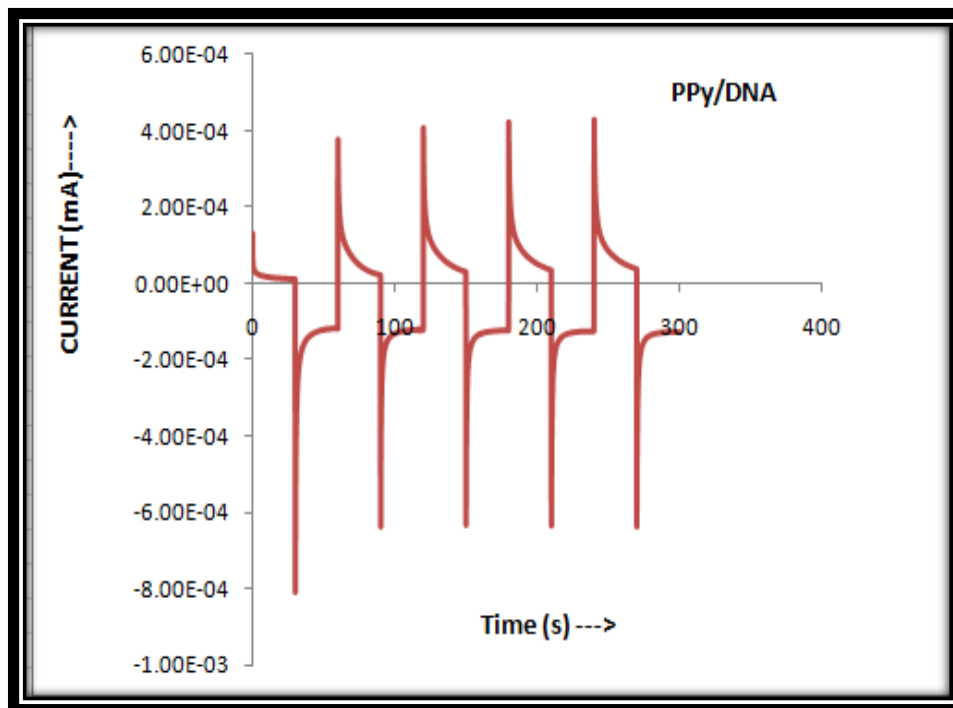
From LSV we can also calculate the conductivity of these three films. Though conductivity of the PPy/DNA film is lowest among all the three films. But still electrochemical activity and stability of the DNA doped film offers it undue advantage to be used as supercapacitor electrode. Table 5 shows the conductivity of the three films.

Table 5. Conductivity of PPy/DNA, PPy/PTSA, and PPy/DBSA films.

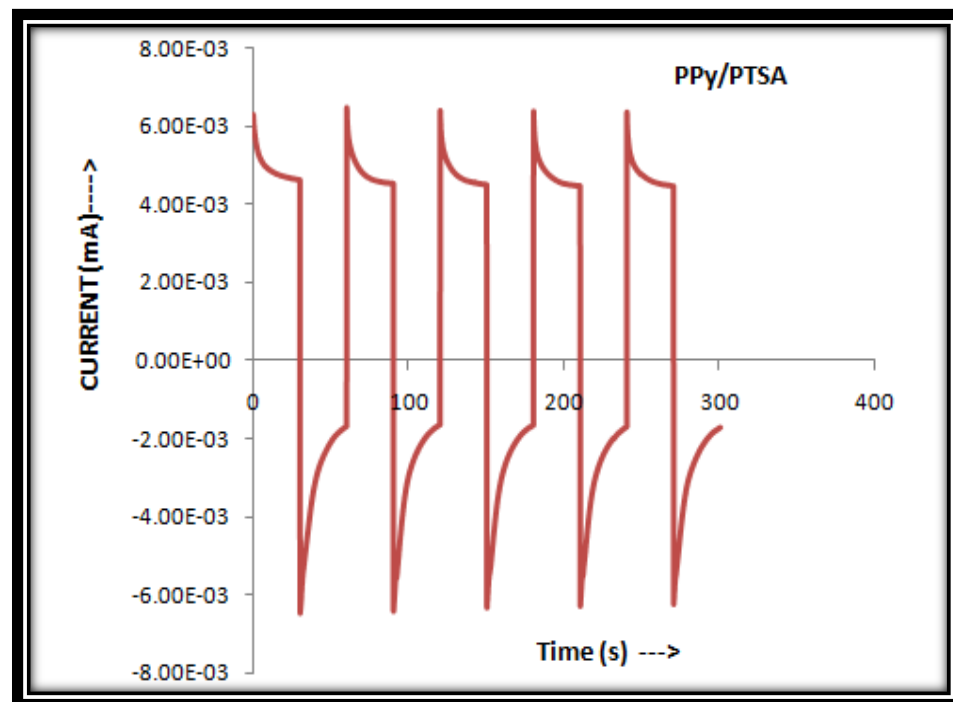
Polymeric Films	Conductivity
PPy/DNA	0.409×10^{-5} S/cm
PPy/PTSA	0.555×10^{-4} S/cm
PPy/DBSA	0.806×10^{-2} S/cm

3.3.3 Pulse Voltammetry

The ion-exchange phenomena occurring at the PPy–DNA interface could be analysed in a different way by examining switching ability using pulse voltammetric technique.

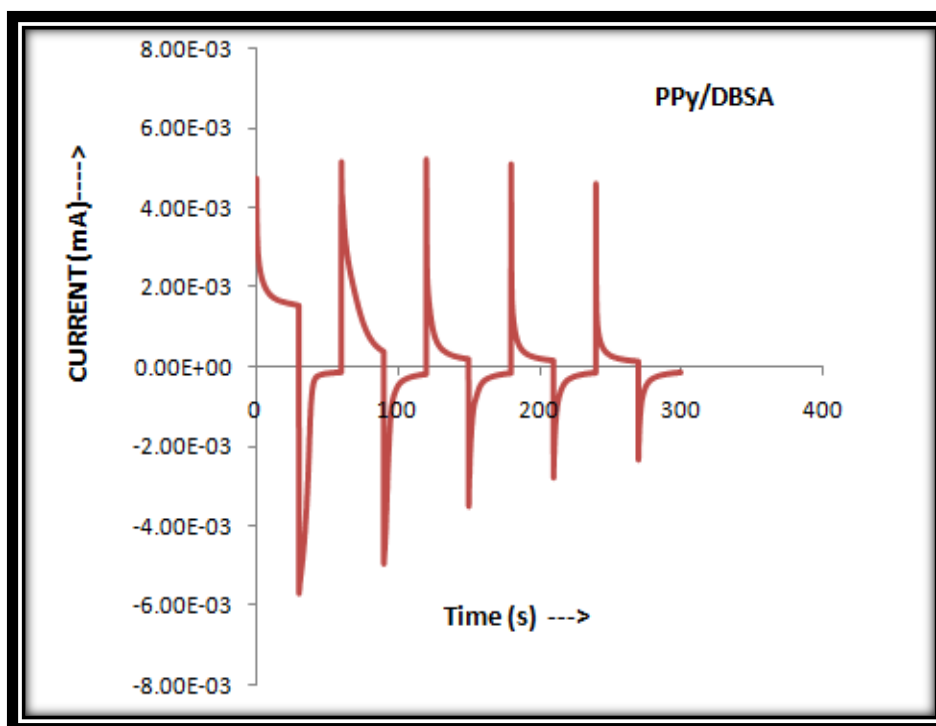


(a)



(b)

Fig.3.15. Galvanostatic charge discharge curves of (a) PPy-DNA and (b) PPy-PTSA electrodes



(c)

Fig.3.16. Galvanostatic charge discharge curve of PPy/DBSA electrode

Fast switching speeds between conductive and insulating states is an important feature, insofar the instantaneous switch between states is one of the most desirable optical properties of such materials. Pulse voltammogram of PPy/DNA film shows the good charge-discharge switching.

It is also suggested that strong charge-discharge behavior is related to cation transport properties. The changes from oxidation to reduction and vice versa occurred in less than 30 s in PPy/DNA electrode (Fig 4.12(a)) which is an essential requirement for supercapacitor applications when compared to long hours for charging/discharging required in batteries. Though the higher current response was seen in the case of other electrodes PPy/PTSA and PPy/DBSA (Fig 4.12 (b) & Fig 4.13) but switching ability between conductive and non-conductive state of PPy/DNA is comparable to conventionally synthesized PPy/PTSA and PPy/DBSA electrodes.

CHAPTER 4

CONCLUSION

The well adherent and uniform Polypyrrole films doped with DNA, PTSA and DBSA were prepared successfully by electrochemical method. SEM micrograph of PPy/DNA shows fiber like structure which indicates good diffusion of the DNA into pyrrole.

The peak at 1745 cm^{-1} may attributed to the covalent bond formed between PPy and DNA. An intensive band at 1745 cm^{-1} vibration band due to C=N stretching and the 1551 cm^{-1} vibration band due to C=C bonds associated with C-N stretching and bending vibration confirms the bonding between PPy and DNA. As seen in the spectrum of PPy/DNA composite, a new sharp peak was observed at 910 cm^{-1} , corresponding to the in-plane stretching vibration of NH^+ of imine species (quinonoid structure) that was performed by protonation of PPy chains.

Cyclic voltammetry data for the films tested in the 0.5 M KCl solutions showed a capacitive behavior in a voltage window of -1.2 to 1.2 V. Cyclic voltammogram represents the good stability of PPy/DNA film. Specific capacitance of PPy/DNA is higher than those of PPy/PTSA and PPy/DBSA films envisaging out of the larger area under CV curve.

Area of the CV curve for the PPy-DNA film tended to be smaller with the increasing scan rate in the positive potential range of 0-1.2 V, indicating a poor capacitive behavior in this range at high scanning rates, because PPy/DNA electrodes becomes more resistive at more positive potential. Counter ions of polyelectrolyte dopant DNA are not released during reduction process and become trapped within the polymer matrix due to their large size and entangle within the PPy chain.

The conductivity witnessed in case of PPy/DNA though smaller but well defined redox peaks and charge retention ability observed in the PPy/DNA film compensate for the defeat in conductivity facade. We can infer that the incorporation of DNA into the PPy films which being beneficial in providing the film finest porosity, desirable and optimum morphology and charge storage capacity and thus can be a good bet for application as electrodes of electrochemical supercapacitors (ES). Pulse Voltammogram of PPy/DNA film shows the good charge/discharge ability and switching speed of less than 30 seconds. From LSV, it is found that the conductivity of PPy/DNA is lowest among the three films.

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