

UNIT-1

INTRODUCTION TO MOLECULAR ELECTRONICS.

INTRODUCTION TO MOLECULAR ELECTRONICS Introduction: Charge transport carriers: Soliton - Polaron and bipolaron. Conducting polymers: Polyacetylene - Polyaniline. Applications of conducting polymers. Polymer Structures for LEDs: Polyphenylenes - Polythiophene. Photoresists for electronics. Molecular devices based on conducting polymers.

1.1 Introduction

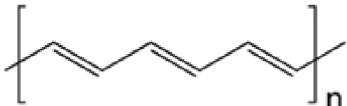
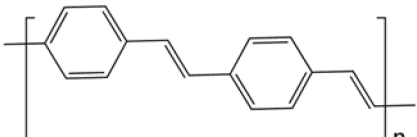
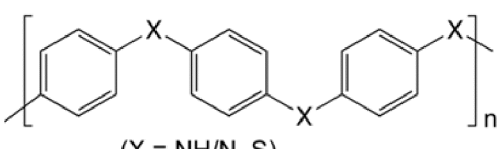
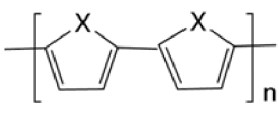
Molecular electronics, also called as molelectronics, involves the use of single or small group of molecules in device-based structures which forms the fundamental unit for electronics such as wires, switches and memory. It is an interdisciplinary study which comprises physics, chemistry, biology, electronics and information technology. Molecular electronics has evolved as a platform technology where almost all electronic devices are generated or fabricated. It is regarded as an alternative to semiconductor silicon based electronic technology. In silicon semiconductor, even the advanced silicon chip can store million bytes of information in less than 1cm^2 area. Even the Pentium 4 chip contains 42 million bytes in less than 1cm^2 area. The silicon chip suffers from a major limitation in storing the density of information. If the size of the chip is reduced, there may be an increase in capacity but other limitation like over-heating and increase Signal/Noise ratio affects its performance. In order to overcome the present scenario, organic materials like proteins, pigments, polymers are used to replace the semiconductor devices since a single mole of an organic molecule contains 6×10^{23} molecules. In a molecular circuit, every single molecule is connected to a power supply an extremely large number of switches are available in a small mass so that molecular electronics can be a powerful tool in future electronics.

Among different organic materials, conducting polymers is attracted for fabricating molecular devices due to their unique properties and versatility. These polymers possess delocalized π - electronic structure and undergoes geometrical modification during electronic excitation. These polymers can be tuned from insulating to semiconducting regime by chemical modification. Besides, these polymers offers other advantages of light weight, flexible, high chemical inertness, electrical insulation and the ease of processing. Owing to their unique electrical, electronic and optical properties several technological and commercial devices such as optical, memory, electronic, biosensing and display units have been developed.

1.2 CONDUCTING POLYMERS

Conductive polymers are polyconjugated organic polymers that conduct electricity because of their conjugated π -bonds. Such compounds can have either 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 and by advanced dispersion techniques.

Some examples of conducting polymers are:

Conducting Polymer	Structure	Conductivity (S/cm)
Polyacetylene		$10^3 - 1.7 \times 10^5$
Polyphenylene vinylene		$3 - 5 \times 10^3$
Polyaniline (X = NH/N) Polyphenylene sulfide (X = S)	 (X = NH/N, S)	30 - 200
Polypyrrole (X = NH), Polythiophene (X = S)	 (X = NH, S)	$10^2 - 7.5 \times 10^3$

In pure form (undoped or pristine state), conducting polymers have low electrical conductivity and behaves like an insulator or as a semiconductor. These polymers can be converted to polymer salts having electrical conductivities comparable to that of metals by treating with suitable oxidizing or reducing agents. These types of doped polymers having high electrical conductivities are called synthetic metals.

The electrical conductivities of undoped conjugated polymers have the range in the order of 10^{-10} S/cm from those of the typical insulators and in the range of 10^{-5} S/cm from those of the semiconductors.

1.3 Molecular Basis of Electrical Conductivity

In traditional polymers such as polyethylenes, the covalent bonds are formed as a result of sp^3 hybridization. Such sigma bonds have low mobility and do not contribute to the electrical conductivity of the material. But, in conjugated polymers, the covalent bonds are formed as a result of sp^2 hybridization. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. All the p_z orbitals combine with each other to a set of delocalized orbitals. Hence the electrons are delocalized over the entire molecule rather than residing at one particular carbon atom. The electrons in these delocalized orbitals have high mobility when the polymer is doped by oxidizing or reducing agents, which donate or removes some of the delocalized electrons respectively.

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 of 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" of conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

Undoped conjugated polymers state 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 polyactetylene are delocalized along the chain, pristine polyacetylene is not a metal.

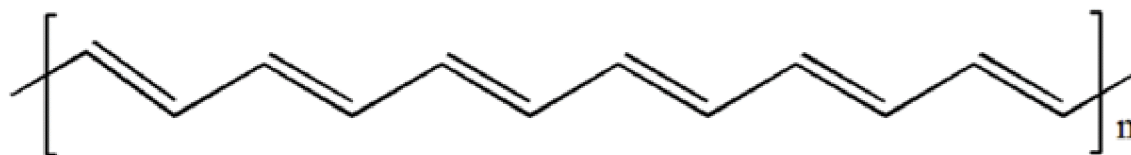
1.4 Polyacetylene

It is the first conducting polymer to be synthesized. Poly(acetylene) is the simplest conjugated polymer. In its linear form it precipitates as a black, air sensitive, infusible and intractable powder out of solution and cannot be processed.

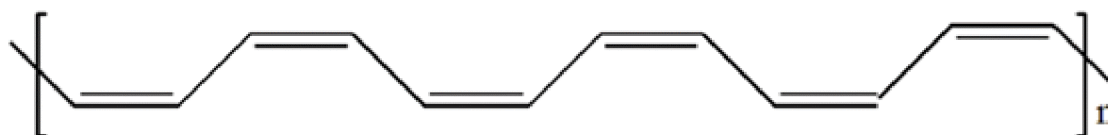
In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. For this research, they were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conducting polymers. Polyacetylene itself did not find practical applications, but drew the attention of scientists and encouraged the rapid growth of the field.

Polyacetylenes exists in isomeric forms: cis-polyacetylene and trans-polyacetylene.

In cis-configuration, the hydrogen atoms are on the same side of the carbon-carbon double bonds.



Trans polyacetylene

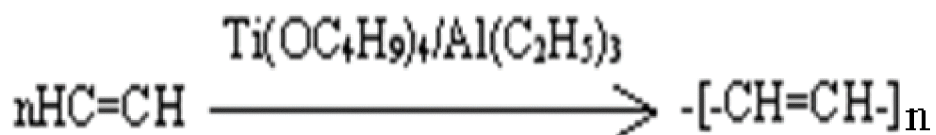


Cis polyacetylene

In trans-configuration, the hydrogen atoms are on the opposite sides of the carbon-carbon double bonds.

Synthesis

The scientist, Shirakawa, prepared poly(acetylene) by passing acetylene gas over the Zeigler-Natta catalyst. Zeigler-Natta catalyst is the coordination complex of tetra butoxy titanium, $[\text{Ti}(\text{OBu})_4]$, an organo metallic compound and triethyl aluminium, $[\text{Et}_3\text{Al}]$.



The reaction forms copper coloured cis-poly(acetylene), having conductivity in the range 10^{-8} - 10^{-7} S/cm, at low temperature (-78°C). At higher temperatures (150°C), more stable silver coloured trans-poly(acetylene), having conductivity in the range 10^{-3} - 10^{-2} S/cm is formed. Cis-poly(acetylene) can be converted to trans-poly(acetylene) by heating it at 150°C for few minutes.

1.5 Polyaniline

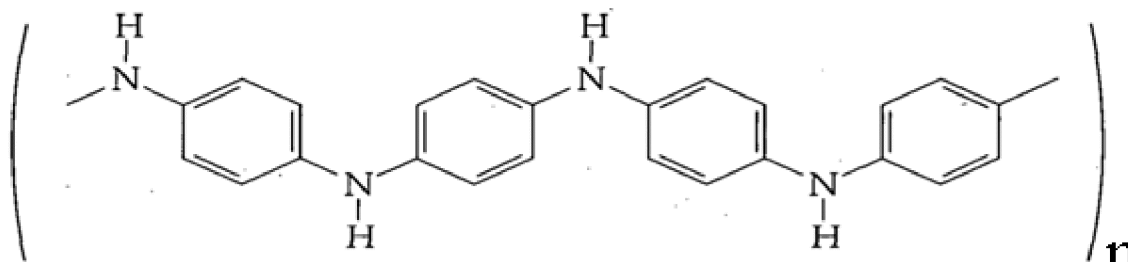
Polyaniline was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that the reduced form was colourless but the oxidized forms were deep blue.

Polyaniline consists of alternate benzenoid amine (reduced form) and quinoid imine (oxidized form) structure.

Oxidation States of Polyaniline

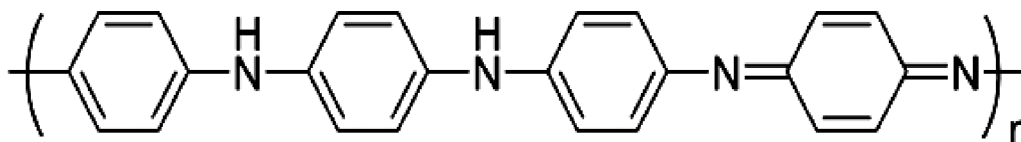
From the generalized formula of polyaniline, it is possible to have three different oxidation states.

1. When $x=1$, completely reduced form of the polymer consisting of only benzenoid amine structure is obtained. This type of polyaniline is called "Leucoemeraldine". This form undergoes easy oxidation when exposed to air. Therefore it is less stable.

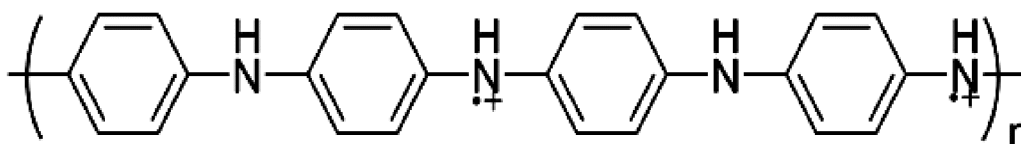
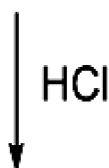


Leucoemeraldine

2. When $x=0.5$, the polymer consisting of partially oxidized quinoid imine structure and partially reduced benzenoid amine structure called "emeraldine" is obtained.



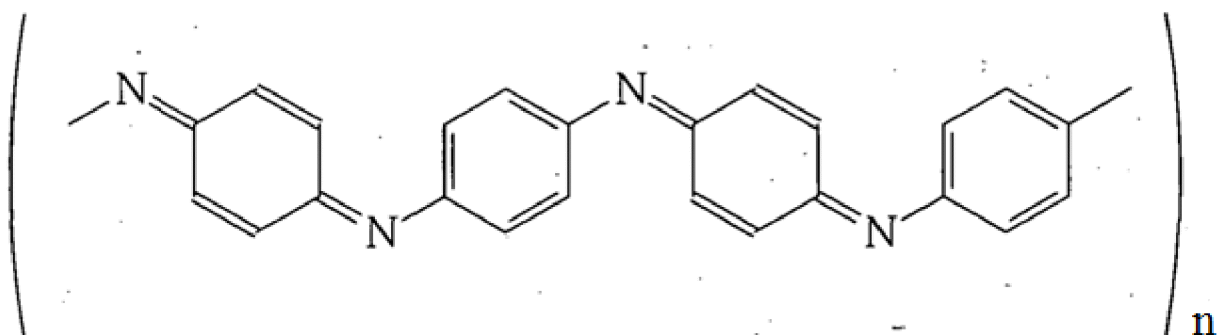
Polyaniline (Emeraldine Base)



Polyaniline (Emeraldine Salt)

The emeraldine base form is the most stable form.

3. When $x=0$, completely oxidized state of the polymer consisting of quinoid imine structure called "permigraniline" is obtained. This form undergoes degradation easily.



Pernigraniline

1.6 Electrical Conductivity In Conjugated Conducting Polymers

The electrical conducting in conducting polymers is different from inorganic semiconductors in two aspects:

1. Polymers are macromolecular in nature and lack long range of orderliness.
2. Doping in a polymer is a charge-transfer process.

Doping:

Doping involves a partial redox or non-redox reaction (acid reaction) occurring at the polymeric chain. It is carried out by exposing the polymeric film or powder to dopants. Dopants are chemical species or agents which are used in doping process. Redox doping is of two types

1. p-Doping (oxidation Doping): It is an oxidation reaction where an electron is removed from the valence band leaving the polymer with a positive charge.



2. n-Doping (Reduction doping): It is reduction reaction where an electron is added to the conduction band leaving the polymer with a negative charge.



Non-Redox doping (Protonic acid): It is an acidic reaction where a proton is added to the polymeric chain leaving the polymer with a positive charge.



These doping reactions occur in conjugated polymers with π electrons, since the electrons can be easily added or removed from the polymeric chain to form polyions which exhibit high electrical conductivity.

Nature of charge carriers in Conducting Polymers:

The interaction of a polymer unit cell with all its neighbours in a polymeric chain leads to the formation of electronic band as explained in section 1.3 . The highest occupied electronic levels or molecular orbitals constitute the valence band(VB) and the lowest unoccupied levels

represent the conduction band (CB). The difference in energy between the VB and CB is known as band gap energy which determines the intrinsic electrical property of polymers. On doping, the electrical conductivity of the polymer is increased due to the formation of self-localized excitations such as solitons, polaron and bipolaron (quasi-particles). These particles arise from strong interaction between the charge on the polymeric chain (electron or hole) acquired as a result of doping and the molecular structure. Thus, the charge carrying species in doped conjugated polymers are not free electrons or holes but quasi-particles which move relatively free through the polymeric chain.

The nature of charge carriers and the mechanism of doping in trans-polyacetylene (PA) is explained as follows;

The trans-PA exists in two alternate structures (A and B) with same ground state energies known as degenerate state. When these two degenerate states dimerize, a structural defect (kink) occurs in the chain with a change in bond alternation. A single unpaired electron exists where the structural defect occurs and it produces an energy level at the centre of the band gap, known as neutral soliton. The neutral soliton carries a single electron which possesses $1/2$ spin and exhibits paramagnetic behaviour. It can move along the chain without any distortion. In a pure (undoped) trans PA, there are only neutral solitons which are on an average of 1 in every 3000 CH units.

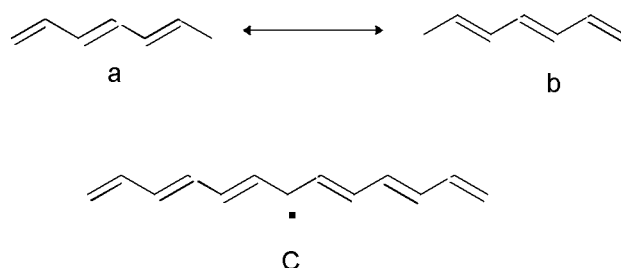


Fig 1.1 a) and b) Degenerate States of trans-PA

c) PA chain with a defect (neutral soliton)

When trans-PA is doped a number of neutral solitons is used (at very low doping level) to form charged solitons. In some cases, a charge transfer can occur directly between a doping agent and VB or CB to produce an ion radical in the chain (i.e a defect pair). The mechanism of p and n-doping in trans-PA is as follows:

During doping, an electron is added (or removed) to the bottom of the conduction band (or from the top of the valence band) of trans-PA, the conduction (valence) band is partially filled and a radical anion (or cation), polaron is formed. The formation of polaron causes the injection of states from the bottom of the CB and top of the VB into the band gap. The polaron carries both charge and spin exhibiting paramagnetic behaviour. The addition (or removal) of second electron on the chain with a negative (positive) polaron results in bipolaron (spinless). The bipolaron further lowers their energy by dissociating into two spinless charged soliton (positive charge in p-doping and negative charge in n-doping) which occupies at one-half of the band gap energy. The number of polaron, bipolaron and soliton formed increases with the doping level. At high doping, polaron, bipolaron and soliton near to the individual dopant ions could overlap leading to new band between (or even overlapping) the VB and CB through which electrons can

flow. Doping of trans-PA by I_2/CCl_4 introduces positive charges which is delocalized over 12-15 CH units to give positive soliton thereby the conductivity increases from 10^{-5} to 10^2 S/cm (or by the order of 10^7).

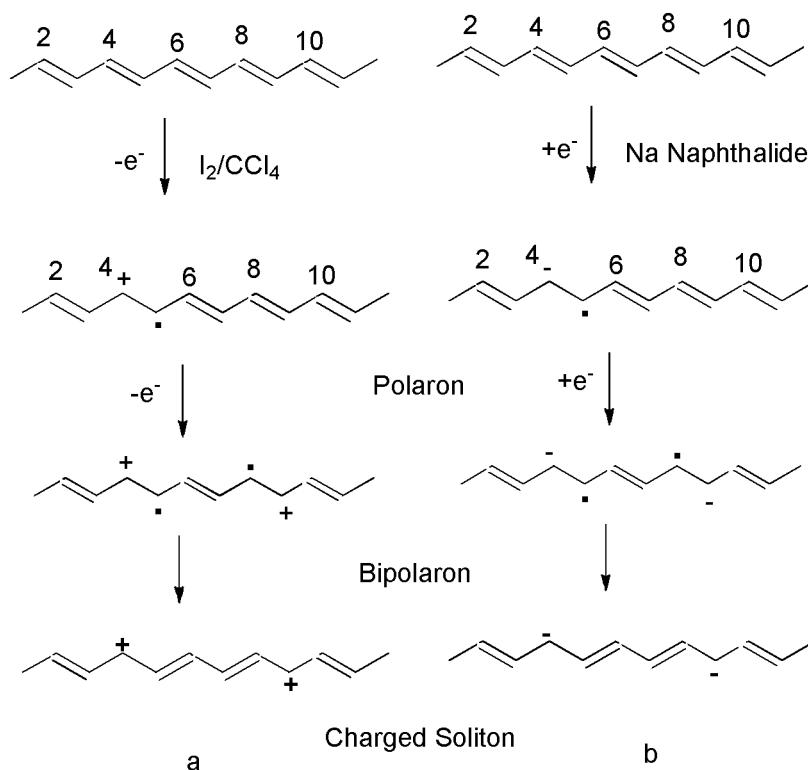


Fig1. 2 a) p-doping b)n-doping in trans-PA

In general, trans-PA forms soliton energy level which can accommodate either 0, 1 or 2 electrons with unusual spin and charge property. When the electrons are removed (i.e) Zero, a positive soliton of zero spin results. When two electrons are accommodated, a negative soliton of zero spin is observed. Both these charged solitons are non-magnetic. A neutral soliton carries a single electron and exhibits paramagnetic behaviour.

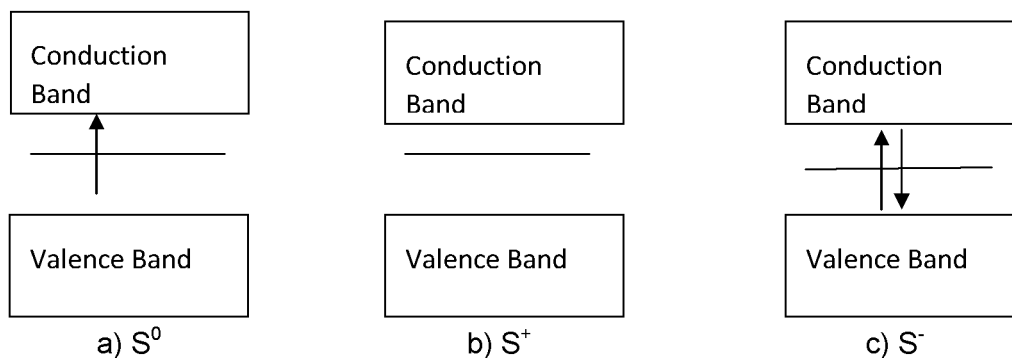


Fig 1.3 Charge and spin separation in a) Neutral Soliton (S^0), b) Positive Soliton (S^+) c) Negative Soliton (S^-)

Mechanism of doping polyaniline:

The emeraldine base of polyaniline consists of equal proportion of amino (-NH-) and imine (=N-) sites. On doping with acids like HCl, dl-camphor sulphonic acid the imino nitrogen are protonated to form bication salt, bipolaron. It is highly unstable due to the presence of C=N bonds of quinoid imine which dissociates to form polaron. The positive charges on the polaron are delocalized over the entire polymeric chain which are stabilized by resonance. The resulting emeraldine salt has a conductivity of 300 S/cm , increased by the order of 10^{11} magnitude.

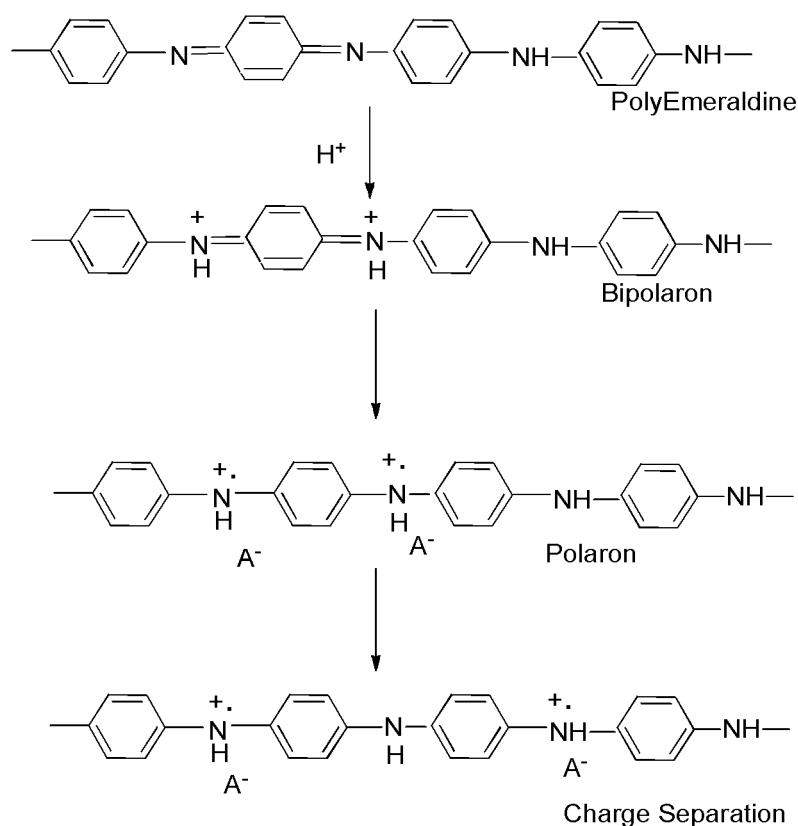


Fig1. 4 Protonic acid doping in Polyaniline.

1.7 Factors Influencing the Conductivity of Polymers

The conductivity of organic polymers is influenced by the following factors:

- 1) **Conjugation length**: The conductivity of a polymer increases with the increase in the length of the polymer chain and increase in the number of conjugation
- 2) **Doping level**: The conductivity of a polymer increases with the increase in doping level till the saturation point is reached
- 3) **Temperature**: Conductivity of a polymer increases with increase in temperature. Sometimes, the conductivity becomes constant at a particular temperature

4) **Frequency of current:** Conductivity of a polymer depends on the frequency of current as doping is the transport mechanism in these materials

1.8 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, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide.
- It is used for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft.

Applications of conducting polymers are grouped into two types based on their conductivity and electroactivity. The first group utilizes their conductivity as its main property because of their light weight, biological compatibility for ease of manufacturing or cost. The second group utilizes their electroactivity. The extended π -systems of the conjugated polymers are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. It is even possible to switch from a conducting state to an insulating state. The two groups of applications are given below:

Group 1	Group 2
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical, biochemical and thermal sensors
Printed circuit boards	Rechargeable batteries and solid electrolytes
Artificial nerves	Drug release systems
Antistatic clothing	Optical computers
Piezoceramics	Ion exchange membranes
Active electronics (diodes, transistors)	Electromechanical actuators
Aircraft structures	'Smart' structures switches

Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability. With the availability of stable and reproducible dispersions, PEDOT (poly(3,4-ethylenedioxythiophene)) and polyaniline have gained some large scale applications. While PEDOT is mainly used in antistatic applications and as a transparent conductive layer in the form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

1.8.1 Conducting polymers - Device applications

(A) **Polyaniline and substituted polyaniline** are used as : (1) Electrochromic display (2) Photolithography (3) Rechargeable battery (4) Electrochemical capacitors (5) Corrosion inhibitors (6) Sensors

(B) **Polypyrrole and substituted polypyrrole** has applications in : (1) Electrochromic display (2) Light weight battery (3) Sensors (4) Solar energy cells

(C) **Polythiophene and substituted Polythiophene** are used in : (1) Electroluminescence (2) Electrochemical capacitors (3) Cathode materials for battery (4) Microlithography (5) Corrosion inhibitors

(D) **Poly-p-phenylene (PPP) p-phenylene vinylene (PPV)** find application in (1) Electroluminescence (2) Photoconductors (3) Solar energy cells (4) Laser materials

Barriers to Applications

Most conductive polymers require oxidative doping in which the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Also, the charged organic backbone is often unstable towards atmospheric moisture. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis. Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion.

1.9 Polymer structure for LEDs

Conjugated polymers possess strongly anisotropic electrical and optical properties since the π -electron delocalisation occurs along the chain direction. An ideal conjugated polymer chain possesses a one-dimensional structure which leads to the electronic structure of a monodimensional semiconductor with an energy gap in the 1.5 – 3.5 eV range. According to Su, Schrieffer and Heeger theory, electron –electron interactions are neglected and describes the properties of the polymeric semiconductors by introducing a strong electron-phonon interaction. Based on this theory, for non degenerate ground state polymers, injection of charges leads to the formation of singly charged polarons or doubly charged bipolarons. Neutral species (exciton-polarons) can be generated by photoexcitation via e-h separation or by the fusion of two polarons with opposite charges, obtained via charge injection from the electrodes, and are

responsible for photoluminescence and electroluminescence respectively. Both the charged and the neutral excitations are stabilized through a local modification of the bond alternation. This produces two localized electronic states within the forbidden energy gap. The energy position of these levels, which are symmetrically displaced from the midgap, depends on the spatial extent of the defect. The more extended the defect, the closer the levels to the midgap. The optical transitions occurring between these levels and the conduction and the valence bands account for the sub-gap optical absorption bands observed by chemical doping, by photoinduced absorption, and by charge injection.

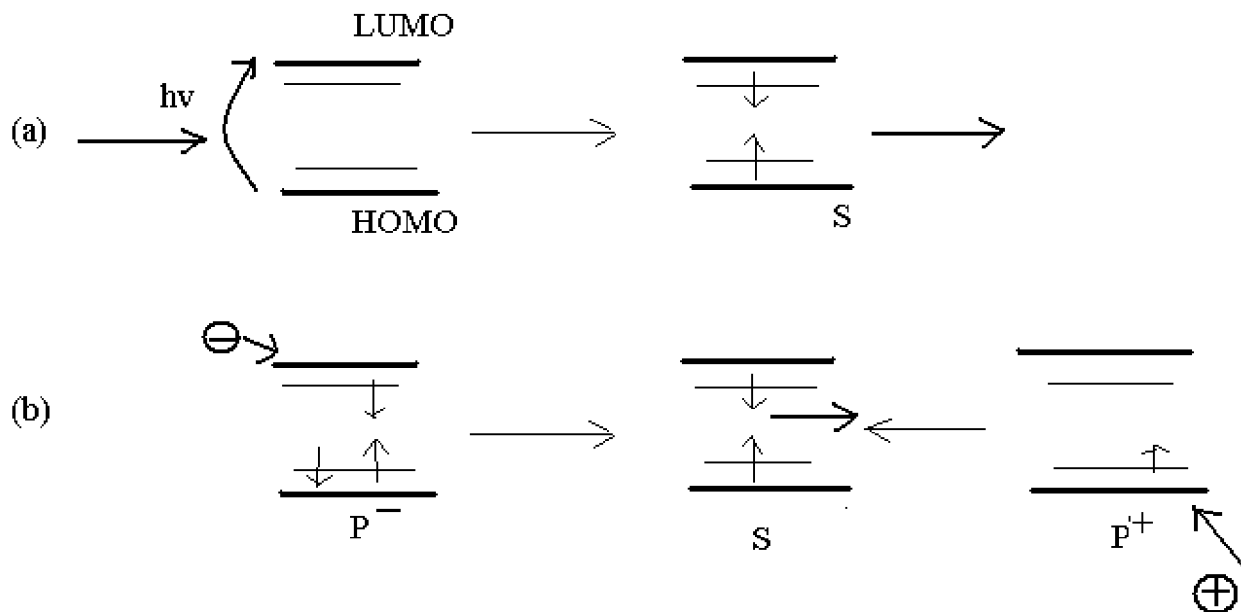


Fig 1.5: Scheme of the generation and radiative recombination of the singlet exciton S by photoexcitation (a), and by charge injection (b) mechanisms

The tailoring of polymeric structures play a significant role in the development of LEDs. The structural control can be extended to several physicochemical parameters:

- 1) The band gap of a conjugated polymer is responsible for the photoluminescence and electroluminescence peak positions
- 2) The electron affinity and ionization potential of the polymer strongly affect the charge injections from the electrodes into the polymers which is related to the photoluminescence and electroluminescence efficiency
- 3) The solid state packing of the macromolecules influences the stability and the emission efficiencies
- 4) The surface polarity of the polymer is responsible for the adhesion between the active polymer and the electrodes which is an important factor in charge injection
- 5) Resistance to oxidation and to temperature of the active polymeric layer are fundamental to the lifetime of the device.

1.9.1 Electroluminescence

Electroluminescence is light emission stimulated by electric current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers

first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

Electroluminescent materials for various colours

Colour of the emission light	Luminescent material
Red	Cyano-derivative of PPV, POPT
Yellow	Poly(2,5-bis(cholestanoxo)-1,4 phenylene vinylene and poly(3-cyclohexane thiophene) (PCHT)
Orange	MEH-PPV
Green	Poly(p-phenylene vinylene) (PPV)
Blue	Poly(3,4 ethylene-dioxy thiophene) (PEDOT), Poly(3-methyl-4,cyclo-hexane thiophene) (PCHMT)

Another favourable aspect of the polymer LED is that it is possible to cover the spectral range from blue to near infrared, even within a single family of conductive polymers such as polythiophene. The recent demonstration of voltage-controlled electroluminescence colours from polymer blends in LEDs as well as the possibility of obtaining polarised light from oriented polymers in LED devices extend the possibilities of fabricating 'exotic' polymer devices. Polymer LEDs are constructed by sandwiching a layer of conjugated polymer between a pair of electrodes.

1.9.2 Preparation of LEDs

LEDs are devices that transform electrical signals into optical signals. The typical structure of a single-layer polymeric LED is shown the figure below. A glass substrate coated by indium-tin-oxide (ITO) is used as a transparent (positive) electrode. A polymer layer is deposited onto the substrate by a spin coating technique. On the polymer is deposited a metallic layer by vacuum

evaporation which forms the negative electrode. By applying a bias voltage at the electrodes, light emission is obtained through the transparent electrode.

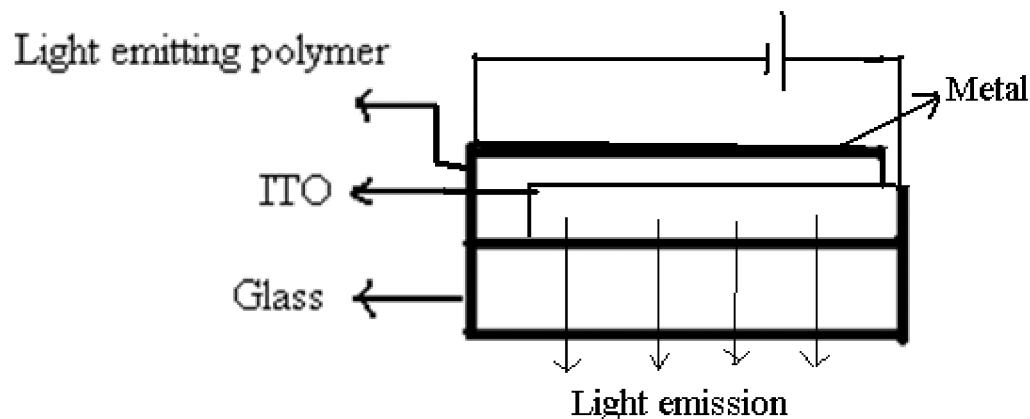


Fig1. 6 : Scheme of a single layer LED

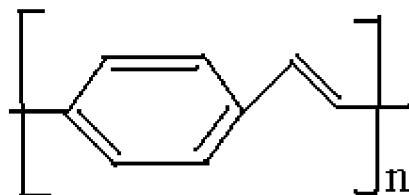
One of the advantages with polymer LEDs is the possibility to choose size and geometry freely. So far, this has mainly been exploited in making large (several square centimeters) LEDs. Granstrom and Inganäs have shown that it is possible to go in the other direction and make the light source very much smaller if the micrometer and nanometer sized polymeric LEDs are fabricated. In gold coated glass, PEDOT is deposited as a hole injecting electrode and PTOPT is deposited on PEDOT as an electroluminescent polymer. Two different conjugated polymers have been used in making these small LEDs. The first one poly(3,4-ethylene dioxy thiophene) (PEDOT) was used as the hole injecting contact; the other poly(3-(4-octyl phenyl) 2,20 - bithiophene) (PTOPT) was used as the electroluminescent layer. Electroluminescence from substituted polythiophene polymer covers the full visible spectrum, from the blue into the near infra-red. The substituted polythiophenes have all been designed to give varying degrees of main chain planarity. In this way, the conjugation length and band gap are controlled in a systematic manner. The extended family of substituents include alkyl± alkyl, cyclo-alkyl and alkyl±phenylene group. These four different polythiophene derivatives with band gaps varying by 2.0 eV display electroluminescence from blue into the infrared. It is possible to achieve a colour spectrum in the whole visible region simply by substituting an appropriate functional group in a luminescent polymer. For example, moieties like pyrazoloquinoline (PAQ) and bispyrazolopyridone (PAPI) derivatives have been incorporated in luminescent polymeric system to get full visible spectrum.

1.9.3 Poly(*p*-phenylene vinylene or polyphenylene vinylene) - PPV

It is a conducting polymer of the rigid-rod polymer family. PPV is the only polymer of this type that can be processed into a highly ordered crystalline thin film. PPV and its derivatives are electrically conducting upon doping. Although insoluble in water, its precursors can be manipulated in aqueous solution. The small optical band gap and its bright yellow fluorescence makes PPV a candidate in applications such as light-emitting diodes (LED) and photovoltaic devices. Moreover, PPV can be doped to form electrically conductive materials. Its physical and

electronic properties can be altered by the inclusion of functional side groups. PPV was one of the first polymers studied, for its good photoluminescence (PL) and electroluminescence (EL) efficiencies. Several synthetic routes have been reported for the preparation of this polymer. Its insolubility is a great problem in the preparation of high molecular weight materials.

The structure and EL spectrum of an LED prepared with PPV is shown below:

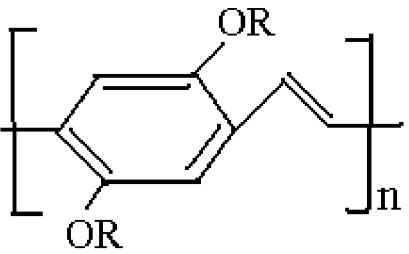
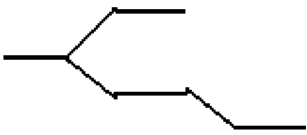
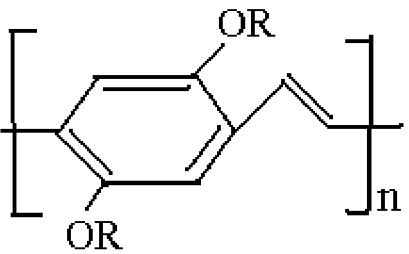


Structure of PPV

Figure1.7: Electroluminescence spectrum of PPV

The figure shows an emission centered at 525 nm corresponding to yellow-green light. The first EL from PPV stimulated the work of chemists to develop new alternative routes to improve the preparation of this polymer. The idea of having a polymer soluble in organic solvent in its conjugated form led to the introduction of solubilizing groups in the PPV backbone which also has the effect of modulating the gap, resulting in a change in color emission. As most of the semiconducting polymers are easily p-doped and not n-doped, the increase of the electron affinity through the introduction of suitable electron withdrawing substituents has been found to be very promising. Some of the most studied structures that were developed are given in the following table.

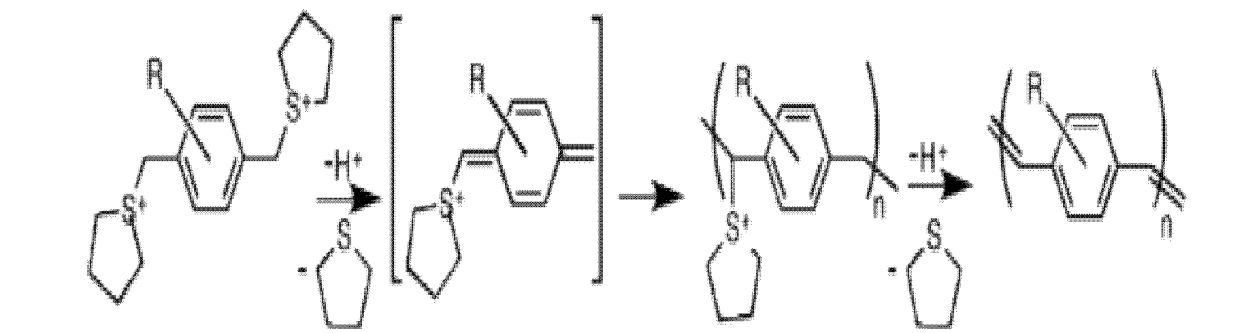
PPV derivatives used in LEDs	Substituent Groups (R)	EL wavelength/ Cathode
	<p>MEH-PPV</p>	EL= 620 nm/Ca

		EL = 560 nm
	$R = \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ $R' = \text{H}$	EL = 540 nm/Al

Highly ordered structures, packed in three dimensions, have the tendency to decrease the PL and consequently the EL efficiency. The PL efficiencies are found to be high in solution and generally decreases in the solid state.

Preparation

PPVs can be synthesized by a variety of methods, the details of which determine purity and molecular weight. The most popular methods proceed via p-xylene intermediates after a base induced elimination from α, α' -disubstituted para-xylenes.



Although xylene-based routes dominate the synthetic methodology, many other routes have been evaluated.

PPV has very low intrinsic electrical conductivity, on the order of 10^{-13} S/cm. The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals, or acids. However, the stability of these doped materials is relatively low. In general, unaligned, unsubstituted PPV presents only moderate conductivity with doping, ranging from $<<10^{-3}$ S/cm (I_2 doped) to 100 S/cm (H_2SO_4 -doped). Alkoxy-substituted PPVs are generally easier to oxidize than the parent

PPV and hence have much higher conductivities. Longer side chains lower the conductivity and hinder interchain hopping of charge carriers.

Applications

Due to its stability, processability, and electrical and optical properties, PPV has been considered for a wide variety of applications. In 1989 the first polymer-based light emitting diode (LED) was discovered using PPV as the emissive layer. Polymers are speculated to have advantages over molecular materials in LEDs, such as ease of processing, reduced tendency for crystallization, and greater thermal and mechanical stability. Ever since the first breakthrough in 1989, a large number of PPV derivatives have been synthesized and used for LED applications. Although solid-state lasing has yet to be demonstrated in an organic LED, poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) has been proven to be a promising laser dye due to its high fluorescence efficiency in solution.

Polyphenylene vinylene is capable of electroluminescence, leading to applications in polymer-based organic light emitting diodes. PPV was used as the emissive layer in the first polymer light-emitting diodes. Devices based on PPV emit yellow-green light, and derivatives of PPV obtained by substitution are often used when light of a different color is required. In the presence of even a small amount of oxygen, singlet oxygen is formed during operation, by energy transfer from the excited polymer molecules to oxygen molecules. These oxygen radicals then attack the structure of the polymer, leading to its degradation. Special precautions therefore have to be kept during manufacturing of PPV in order to prevent oxygen contamination.

PPV is also used as an electron-donating material in organic solar cells. Although PPV-based devices suffer from poor absorption and photodegradation, PPV and PPV derivatives (especially MEH-PPV and MDMO-PPV) find frequent application in research cells.

1.9.4 Polythiophene

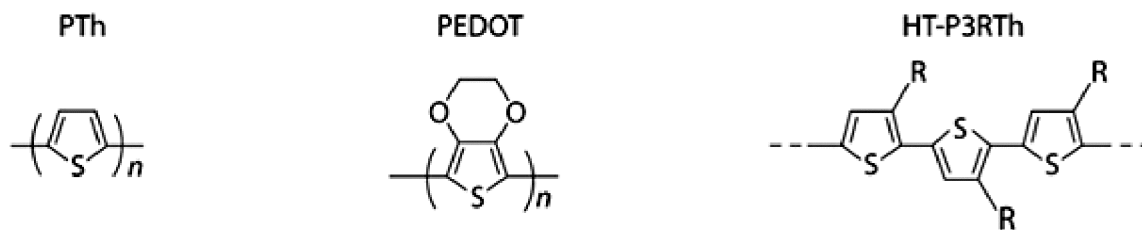
Polythiophene has been widely used as environmentally and thermally stable conjugated polymer materials, such as chemical and optical sensors, light-emitting diodes and displays, photovoltaic devices, molecular devices, DNA detection, polymer electronic interconnects, solar cells and transistors, since 1980.

Three approaches to polymerization of thiophene have been reported in the literature: (1) electropolymerization, (2) metal-catalyzed coupling reactions, and (3) chemical oxidative polymerization. Waltman et al. prepared high conductivity polythiophene films by electropolymerization in the year 1983, but it is rarely used in the preparation of electroluminescent materials. Since then various different methods of synthesis of polythiophene have been developed. Recently, Kim and his co-workers prepared polythiophene in aqueous dispersion via Fe^{3+} -catalyzed oxidative polymerization and tested its photoluminescence properties.

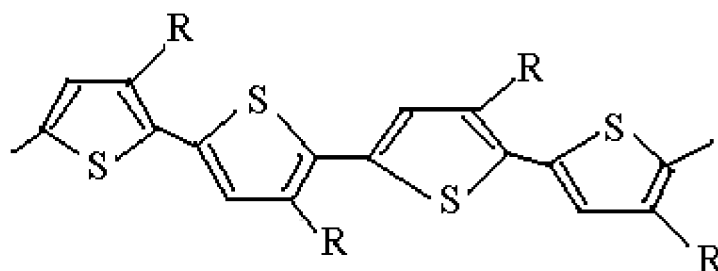
The stable morphologies, such as spherical particles, nanofibers, sphere-fiber-transition, and submicro/nanoribbons, have been obtained by controlling the ratio of the oxidant to reductant.

Polythiophene and its derivatives in particular have been the subject of many recent studies. p-Doped poly(3,4-ethylenedioxythiophene) (PEDOT) is used industrially in capacitor electrodes and as an antistatic material amongst a range of device applications, and polythiophenes with side chains bearing sulfo groups are used as antistatic materials in electron-beam lithography.

Structures of the simple and substituted polythiophenes are shown below:



Recently, PTh with long side chains (e.g. alkyl (R) side chains) and regio-regular structures along the PTh main chain have been attracting strong interest. For example, the synthesis of head-to-tail (HT) poly(3-alkylthiophene-2,5-diyl) (P3RTh) initiated active studies of the molecular assembly of the π -conjugated polymers. Poly(3-alkylthiophenes) (PATs) in a head-to-tail configuration are almost planar; the so called trans conformation minimises the steric hindrance between the adjacent monomeric units. Structure of a trans conformation of a regioregular poly(3-alkylthiophene) is shown below.



Poly(3-alkylthiophene)

By copolymerising 3,4-disubstituted thiophene and 3-alkylthiophene in different ratios, it is possible to obtain copolymers with different absorptions from 320-450 nm. A series of polymeric structures have been used to prepare LEDs covering all the visible range. By blending the different copolymers in a matrix such as PMMA, the colour emission could be varied by a proper applied voltage from orange to blue. Tuning of the EL was also obtained by preparing copolymers of 3-alkylthiophene and unsubstituted thiophenes in different molar ratios.

Various other types of thiophene (Th)-based polymers consisting of regularly repeating units also show a tendency to self-assemble. For example, Th(R)-Ar-Th(R) polythiophenes and head-to-head (HH) poly(thiophene-2,5-diyl) (HH-P3(C=C-R)Th) with $-C=C-R$ side chains form self-assembled structures in colloidal solutions and in the solid phase.

It has been reported that π -conjugated polymers with Th(R)–Ar–Th(R) repeating units (Ar, aromatic or heteroaromatic unit) produce π -stacked molecular assemblies. McCulloch and co-workers synthesized such polythiophenes with fused Th units as the central –Ar– unit, and the resulting polymer showed a large hole mobility of about $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to that of amorphous silicon. Th(R)–Ar–Th(R) polymers often form π -stacked molecular assemblies, and their applicability to polymer transistors and solar cells has been actively tested.

Through these studies, it is now recognized that self-assembled π -conjugated polymers show superior electronic and optical functionalities. π -Conjugated polymers usually respond very rapidly to light through a change in the refractive index on time scales of about 10^{-12} s . Consequently, π -conjugated polymers with large χ are considered to be important materials for future high-speed photo-communication systems.

Various π -conjugated aromatic and heterocyclic polymers have been prepared by oxidative polymerization of the corresponding monomer (e.g. pyrrole and 3,4-ethylenedioxythiophene) or by organometallic polycondensation using dihalo-aromatics and dihalo-heterocycles (e.g. *p*-dibromobenzene, 2,5-dibromothiophene, 2,5-dibromopyridine) as the monomer.

1.10 Photoresist

It is a light sensitive material used in industrial processes like photolithography, etching to form a patterned coating on the surface. Photolithography uses light in the UV range for the manufacture of integrated circuit devices.

Components of Photoresist:

Photoresist consists of 3 parts:

a. Polymer b. solvent c. Photoacid generator

1. Polymer: It is a solid in its undiluted state eg: Novalac, cis-1,4 polyisoprene.

2. Solvent: Chemicals used to dissolve the polymer.

3. Photoacid Generator (PAG): It is a photo-sensitive compound brings a series of photochemical reactions which alter the solubility of the exposed region. These reactions enhances the sensitivity of the photoresist in photolithography process.

Requirements of Photoresist:

1. The photoresist must be soluble in an organic solvent.

2. It should possess good adhesion to various substrates.

3. It should possess low etching.

4. The polymer should undergo chemical modification on irradiation.

5. The polymer should be transparent at the imaging wavelength.

1.10.1 Types of Photoresist:

a. Negative Photoresist: A portion of the photoresist is exposed to UV radiation to form an insoluble cross-linked polymer. The unexposed portion is dissolved in the developer solution usually NaOH.

Mechanism:

The resist is coated onto the silicon substrate. A mask is placed between the UV source (from excimer lamps) and the substrate. The region exposed to UV light undergoes chemical reactions and becomes insoluble in NaOH solution. The unexposed areas are soluble in NaOH and the patterns formed on the substrate are reverse as in the mask.

b. Positive Photoresist: A portion of the photoresist is exposed to UV radiation becomes soluble in the developer solution. The unexposed portion remains insoluble in the developer solution.

Mechanism :

The resist is coated onto the silicon substrate. A mask is placed between the UV source and the substrate. The region exposed to UV light undergoes chemical reactions and becomes soluble in NaOH solution. The unexposed areas remains unchanged and the patterns formed on the substrate are same as in the mask.

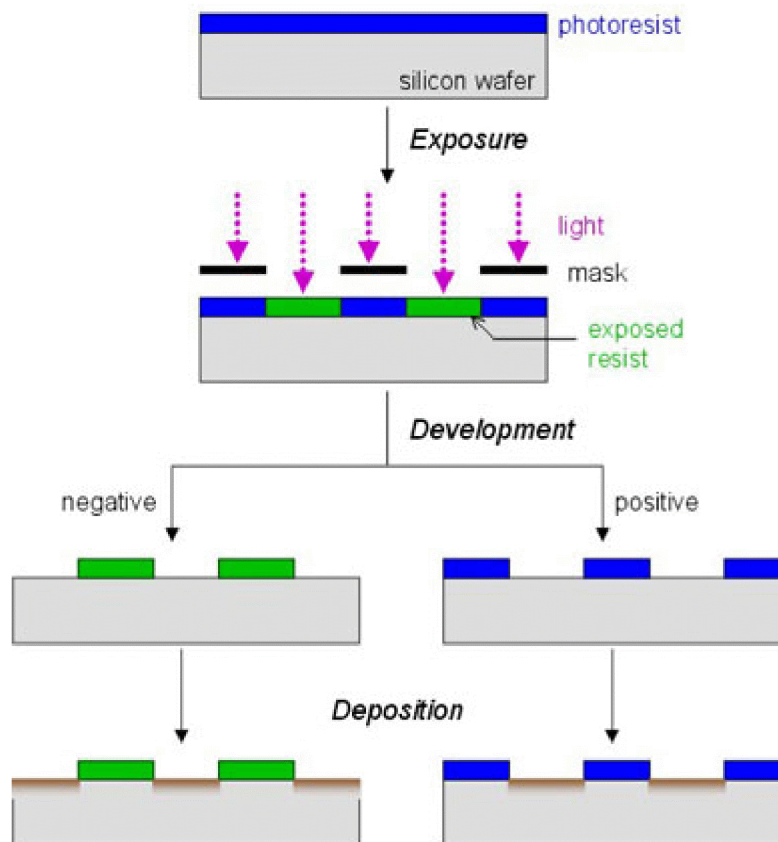


Fig 1.8 Development Mechanism of positive and negative photoresist

Positive resist are usually coloured and are soluble in strong alkaline solutions. Their chemical resistance is low and are costly to produce. The images obtained are accurate and require

minimal processing technique. Negative resist possess high chemical resistance, good image reproduction and are less in cost. Due to their high chemical resistance, they are difficult to remove and are widely used in the manufacture of circuit boards and in microelectronic devices.

1.10.2 Resist Chemistry:

Positive and Negative photoresist are classified as one and two component system. A one component system consists of a polymer which undergoes photochemical reaction while a two-component system consists of a sensitizer molecule which is dissolved in an inert polymeric matrix. The sensitizer undergoes photochemical reaction. Most of the two-component system operates at near UV region.

Positive resist : One component system- Eg: Poly Methylmethacrylate (PMMA)

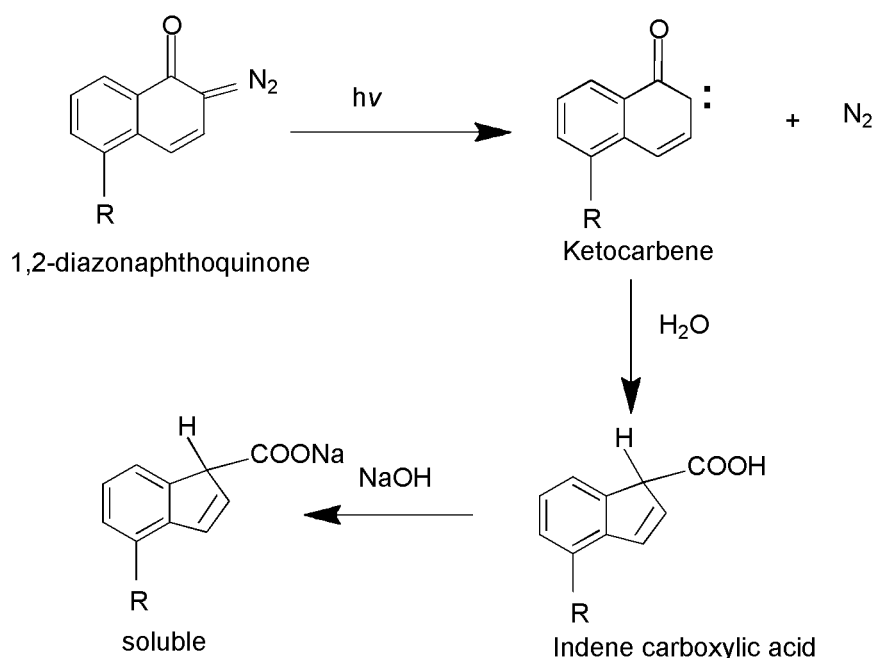
Two component system- Eg: Novolac (Phenolic resin) and diazonaphthoquinone (sensitizer)

Negative resist: One component- Eg: Co-polymer of glycidyl methacrylate and ethylacrylate

Two component- Eg: Cyclized poly cis-isoprene (polymer) and bis arylazide (sensitizer).

Reactions In Two-component Positive Photoresist:

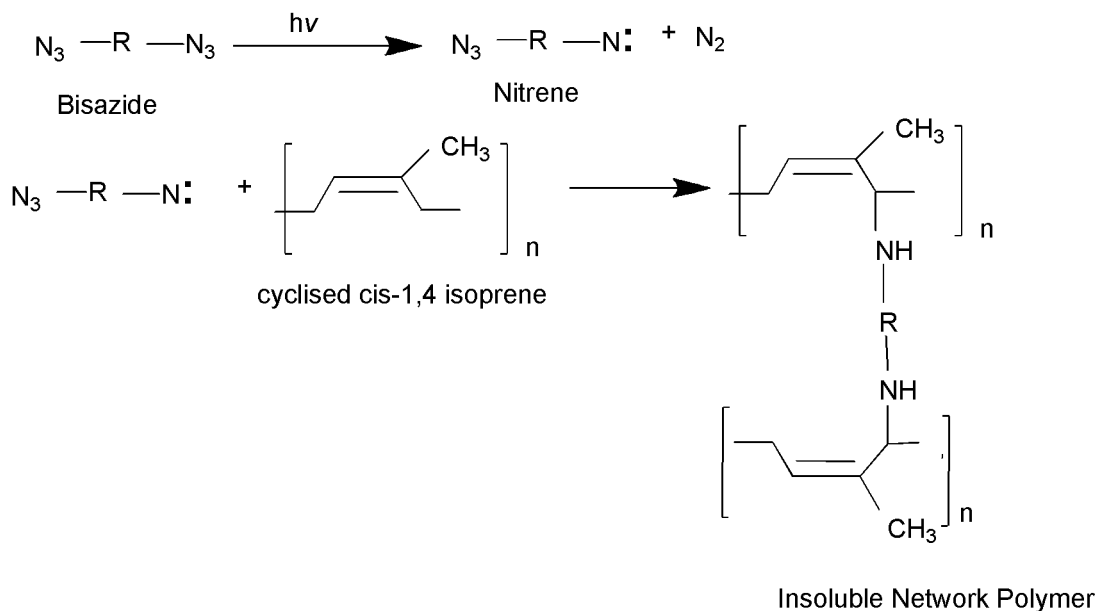
The resist operates at near UV region of 193nm. The polymeric material is a low molecular weight novolac polymer and the sensitizer is a derivative of 1,2-diazonaphthoquinone(DNQ). On exposing to UV radiation, the photosensitizer (DNQ) undergoes photodecomposition to form ketocarbene which reacts with water to form indene carboxylic acid. The acid promotes the dissolution of the novolac polymer in NaOH. The DNQ forms an insoluble complex with novolac resin at the unexposed portions of the photoresist.



Reactions In two-component Negative Photoresist:

Negative near UV photoresist consists of cyclized cis 1,4-isoprene polymeric resin and bisazide sensitizer. Cyclized cis 1,4-isoprene units is obtained by heating 1,4 polyisoprene in

the presence of Lewis acid like ZnO, AlCl₃ and SnCl₄. The bisazide sensitizer on irradiation by UV light forms nitrene which reacts with cyclised isoprene units to form an insoluble three-dimensional crosslinked network polymers which is insoluble in NaOH solution. The sensitizer forms an soluble complex with the polymer at the unexposed portions of the resist.



The choice of the resist depends on the needs of specific applications, resolution, ease of processing and cost. Negative photoresist is used in fabricating printed wiring boards while positive photoresist is used for patterning high resolution semiconductor device.

1.11 Molecular Devices based on conducting polymers:

1.11.1. Diode:

Diodes are basic components of electronic devices. Conducting polymers play a vital role in fabricating flexible, low-cost diodes by combining either with a semiconductor (n or p-doped semiconductor) to form a hetero junction or with a metal to form Schottky junction. Most of the conducting polymers forms a Schottky junction diode rather than a hetero junction due to their inherent difficulty in forming a conducting polymeric film onto the semiconductor. The Schottky junction diode is also referred as 'majority carrier device'. A schematic diagram of Schottky diode is shown in the Fig in which the conducting polymeric film is coated onto the SnO₂ or SnO₂ coated substrate. The polymeric film is in contact with metals like Cu, Al, Ag, Au or In. On applying temperature or light rays, the electrons are injected from the metal electrode into the conduction band of the polymer (p-doped) to form free moving electronic carriers along the polymeric chain. The diode ceases its conduction faster than p-n junction due to low or no recombination of n and p- type of charge carriers. The conducting polymers used in Schottky diode are polypyrrrole, polyaniline and poly(3-)alkyl thiophene which finds their application in photovoltaic cell. Poly alkyl based thiophenes are used as sensors for analyzing nitric oxide, ammonia in ambient air due to their high selectively, low cost and can be operated at room conditions.

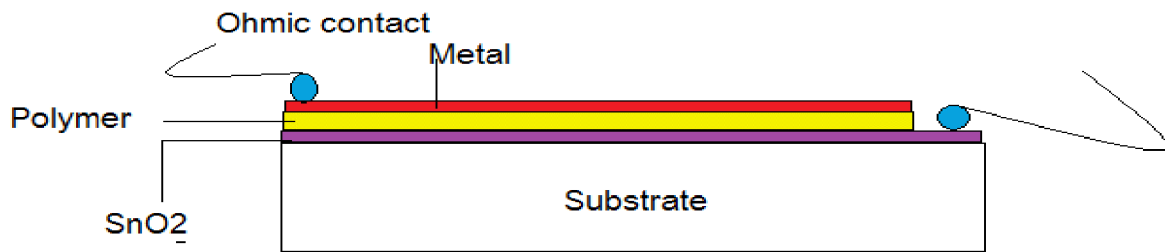


Fig 1.9 Schematic representation of Conducting polymer based Schottky diode

1.11.2. Field-Effect transistor:

FET is the basic building block for solid- state electronics. The FET consists of 3 components: 1. source 2. Drain and 3. Gate. The source and the drain operate as a conducting channel between the two ohmic contacts while the Gate controls the charge induced onto the channel. The direction and movement of carriers in the channel (electrons or holes or both) is from the source to drain. The three components are inter-related with the Gate controls the carrier movement. It acts as a molecular switch or as an amplifier where the current is controlled across the two electrodes, source and drain in response to the voltage at the third electrode, gate. There are three types of FET,

- a. Metal-Insulator semiconductor Field Effect Transistor (MISFET): The source and the drain are connected by a semiconductor and the Gate is separated from the channel by a layer of insulator.
- b. Metal-semiconductor Field Effect Transistor (MESFET): The source and the drain are connected by n-region of semiconductor.
- c. Thin-Film transistor (TFT): The source and the drain are deposited onto the conducting channel with a thin film of insulator is placed between the semiconductor and the Gate.

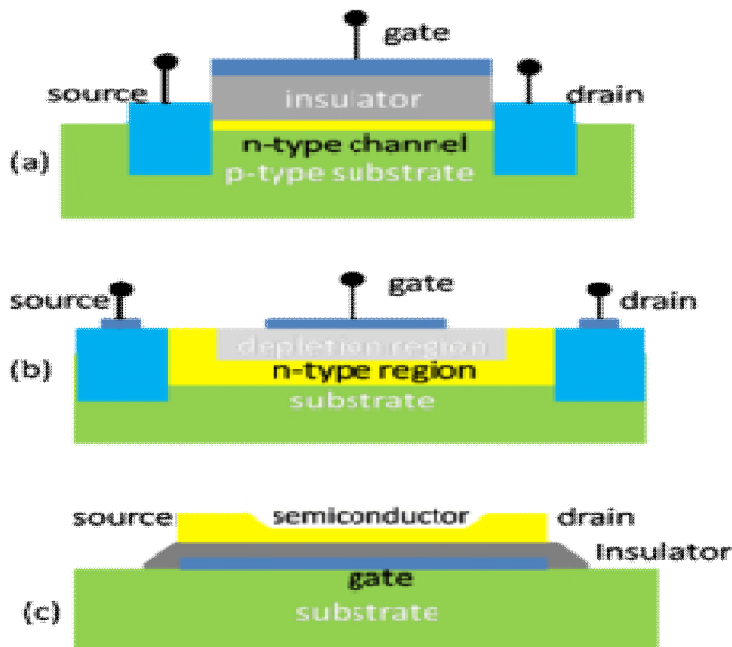


Fig1.10 Schematic representation of three types of FET a) MISFET b) MESFET c) TFT

Conducting polymers offers a promising candidate for fabricating TFT over conventional semiconductor due to their low cost and ease of processing.

Construction of Polymer field-effect Transistor (PFET):

A PFET is constructed by applying a layer of Al onto the SiO₂ wafer to form contact pads. The source, drain and the gate electrode are made of poly ethylenedioxythiophene, PEDOT. A PEDOT is coated onto the Al to form Gate electrode. An insulating polymer (polyvinyl pyrrolidone) acts as dielectric is dispersed onto the Gate. An conducting polymer (Polypyrrole or poly alkylthiophene) is dispersed onto the Gate which forms the active layer. On top of the conducting polymer, the source and drain electrodes are deposited and extended to Al contact pads. When a positive charge is applied, electrons are accumulated at the interface to form a conducting channel at the interface. The performance of PFET is slow and have limited life time with field mobilities in the range of $0.5\text{-}1 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. These polymers can be fabricated into flexible flat panel devices which opens a new era of low cost plastic electronics.

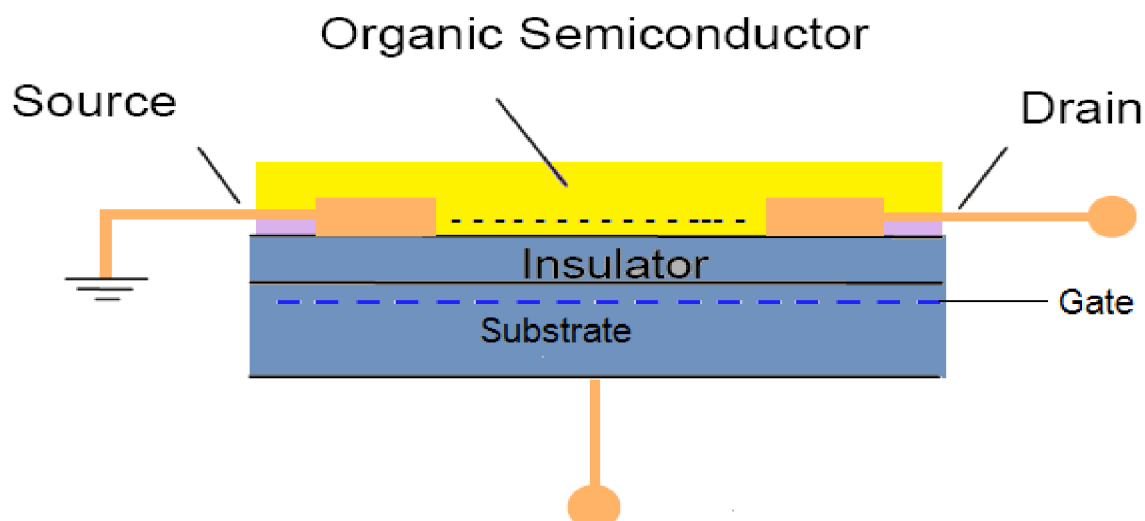


Fig 1.11 Schematic representation of PFET

1.11.3. Biosensors: A biosensor is an analytical device incorporating either a biological or biological sensing element which is integrated or intimately connected with a physicochemical transducer. The transducer can be either an electrical, optical, thermal or piezoelectric device. A biosensor is a combination of an electrochemical device and an immobilized biomolecule to measure the concentration of the analyte. A number of biomolecules such as enzymes, antibodies, organelles, cells and receptors are used as sensing probes for the fabrication of biosensor. Organic conducting polymers provides a convenient tool for immobilizing enzymes at the electrode surface and its interaction with metallic or carbon electrode surface. These conducting polymers provide a suitable matrixes for biomolecules in order to enhance stability, speed and sensitivity. Enzyme-immobilization technique plays a vital role to develop a stable and long lasting sensor. Enzymes are immobilized on to the transducer either by adsorption, covalent attachment by cross-linking and entrapment. In adsorption method, the hydrophobic or hydrophilic nature of the polymer is used to develop the enzyme electrode while in covalent attachment, the functional groups in biomolecules ($-\text{NH}_2$, $-\text{COOH}$, $-\text{SH}$) are used for binding with the conducting polymer. In the recent years, most of the enzyme electrode constructed is based on enzyme entrapment in which the polymer forms a porous, homogeneous morphology with an ideal size to entrap the enzyme molecule.

Applications:

1) In case of glucose biosensor, the glucose oxidase (GOX) enzyme is entrapped on to polypyrrole or polyaniline which is electrochemically deposited on a Pt electrode. The glucose concentration is determined either by the decrease in oxygen consumption or by generation of hydrogen peroxide.

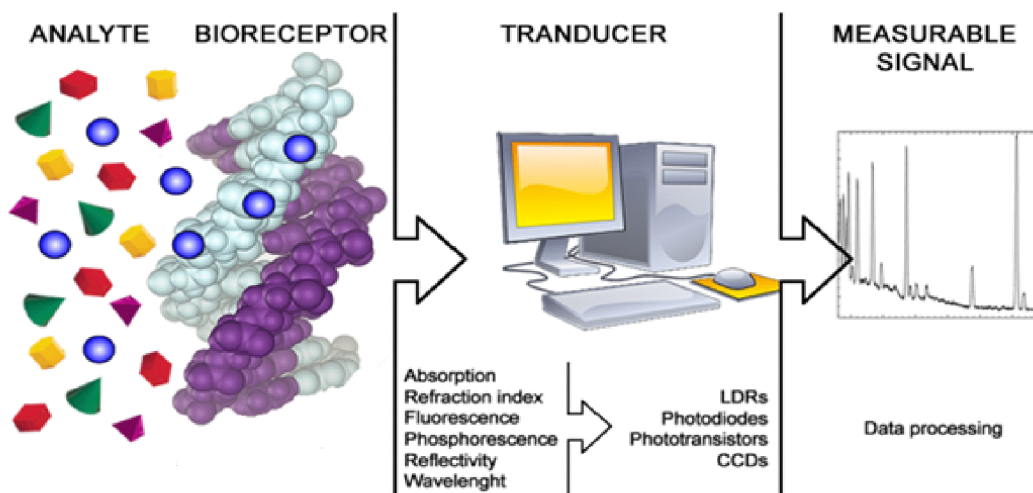


Fig 1.11 Schematic representation of a biosensor.

2) Amperometric acetylcholine esterase (AChE) biosensors are employed to analyse organophosphate pesticide. The acetylcholine esterase is immobilised on to polypyrrole and polyaniline copolymer doped in multiwalled carbon nanotubes. The copolymer provides an ideal size and biocompatible environment for enzyme molecules and it is used to analyse organophosphates.

1.11.4 Actuators:

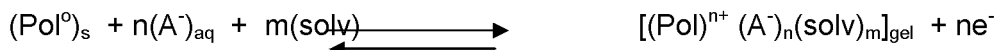
Actuators are devices which convert electrical energy to mechanical energy by undergoing volume changes during oxidation and reduction. Actuators are bilayer device consisting of a passive substrate on which the active conjugated polymer like polypyrrole, polyaniline and polythiophene is deposited by electrochemical method. During oxidation and reduction reactions, there is a change in volume in the active layer which forces the device to bend. The bilayers are few cm long and few mms wide. The volume change in conducting polymer is dominated by movement of ions in and out of the polymer takes place by oxidation and reduction reactions.

Oxidation reaction :

During p-doping, the electrons are extracted from the polymeric chain to form positive charges or holes which are compensated by ions from the electrolytic medium. The transformation from a neutral polymer to an oxidised material can occur through two different ways:

1. Anion Exchange: During oxidation, the polymeric chains generate free volume and anions penetrate from the solution to balance the positive charges along the chain. The high

concentration of charges inside the oxidised material induces the entrance of solvent from the solution required to maintain the osmotic pressure. The volume of the material increases during oxidation and decreases in the reverse reaction.



where subscript s, aq represents the solid and aqueous solution. The volume change and transition is promoted by the reaction from a packed solid state to a gel state.

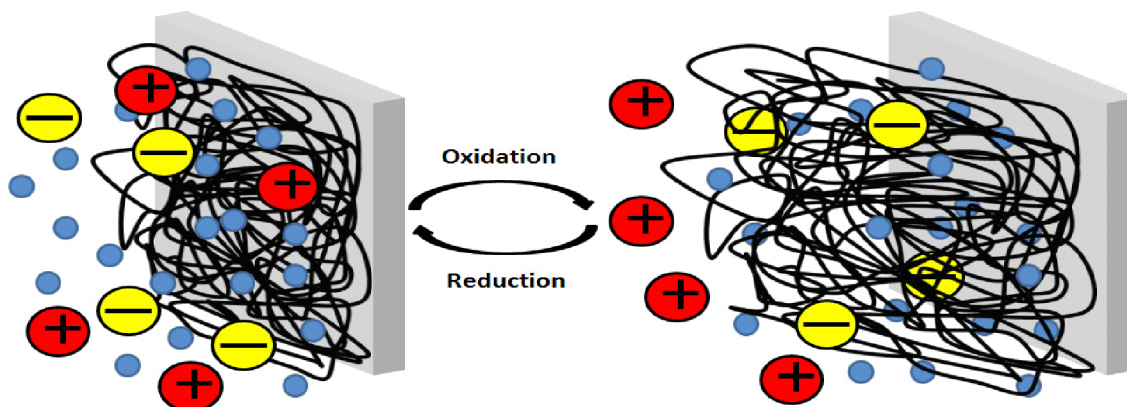


Fig1.12 Complex polymer structure, showing volume changes (swelling/shrinking) produced during p-doping of polypyrrole film. Anions go inside the film during oxidation and are released during neutralization. Blue circles represent solvent molecules.

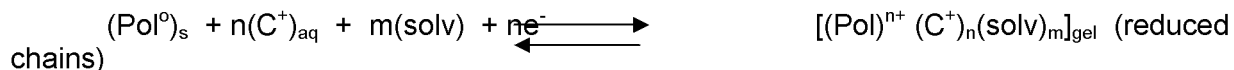
2. Cation Exchange: When the polymeric chain is oxidized in the presence of big macro anion, the anion gets trapped inside the polymeric matrix with the cations expelled. The material shrinks during oxidation and swells during reduction.



where MA represents the macroanion (organic, polymer or inorganic) trapped inside the conducting polymer and C^+ represents the cation.

n-Doping:

Conducting polymers such as PEDOT, polythiophene, polyfluorenes possessing high electron affinity are able to store negative charges on the polymeric chain during reduction. The cations, solvents enter the polymeric material which enables them to swell during reduction and shrinks during oxidation.



Applications:

1. **Micropump:** Micropumps are capable of transporting fluids at a microflow rate with high precision. These pumps are used in microfluidic systems and in biosensors. The energy consumption rate of these polymeric micropumps is lower than conventional micropumps.
2. **Steerable Microcatheters:** Two conducting films around a positive catheter and a ionic electrolyte are used to control the movement of catheter tip which bends at an angle of 20° and are used to produce high resolution 3D imaging.

Part-A Questions

1. What are conducting Polymers?
2. Define doping.
3. Give the isomeric forms of PA.
4. Draw the different oxidation states of polyaniline.
5. What are Solitons?
6. Differentiate soliton and polaron.
7. What are the applications of conducting polymers?
8. What are the factors influencing the conductivity in conducting polymers?
9. Define Electroluminescence.
10. Give the merits and demerits of PLED.
11. What are excitons?
12. What is photoresist?
13. Differentiate Negative and positive photoresist.
14. Draw the structures of polyphenylene vinylene and polyalkyl thiophene.
15. What is a Schottky diode ?
16. What is a principle in FET?
17. Define biosensor?
18. What are the advantages of conducting biosensor?
19. What are actuators?
20. What are the advantages of conducting polymers in molecular devices?

Part-B Questions

1. Describe the synthesis of polyacetylene and explain its isomeric forms.
2. Describe the electronic conduction in conjugated conducting polymer.
3. Explain in detail the mechanism of p-doping in trans-PA.
4. Explain in detail the mechanism of n-doping in trans-PA.
5. Describe the mechanism of protonic acid doping in polyaniline.
6. Explain the principle, construction and working of PLED.
7. Give the structural relationships of different PPV and polythiophene with their electroluminescence.
8. What is a photoresist? Explain the chemistry behind positive and negative photoresist.
9. Explain in detail the application of conducting polymers in molecular devices.
10. Write a short notes on polyaniline.