

UNIT 3

FUNCTIONAL MATERIALS

Introduction to conducting polymers – Charge transport carriers: Exciton formation in organic solar cells and organic light emitting diodes (principle and working) – Conduction mechanism in polymers: Soliton, polaron and bipolaron formation in polyacetylene and polyaniline – Liquid crystals: Characteristic features and phases of liquid crystals – Liquid crystal displays.

3.0 Introduction

Functional Materials comprises all materials including inorganic, organic, hybrid, nano materials, ceramics, soft materials with specific functions as

1. Adaptive Materials: Materials which response to stimuli as sensors, actuators and as energy harvesters.
2. Electronic Materials: Materials like semiconductors, dielectrics, ferroelectrics, superconductivity materials used in health care and molecular devices.
3. Magnetic Materials: Materials with spintronics, superconductivity and molecular magnets finds its application in diagnosis as body scanner as well in data storage.
4. Optical Materials: Materials like lenses, mirrors, polarizers, detectors, modulators used in photonics and in advanced optical technologies.

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Of these functional materials, electronic materials have attained a giant leap in the last few decades through the development of conducting polymers. These polymers are considered as an alternative to semiconductor silicon based electronic technology. They can be tuned from insulating to semiconducting to metallic by chemical modification and possess unique properties like light weight, flexible, easier processability and fabrication. These materials have in-filtered into our day-to-day life with a wide range of products including consumer goods like LED television, AMOLED (Active Matrix Organic Light Emitting Diode) in cell phones display to their applications in space, aeronautics and non- linear optics. Hence, the conducting polymers with wide applicability and unique properties can be regarded as "Materials of 21st century".

3.1 Conducting Polymers

Conventional Polymers like polyethylene, polypropylene, polyvinyl chloride etc., are usually characterized by their light weight, ease of fabrication, insulating nature have replaced materials in several areas of application from household water bottles to rockets. Their insulating property has been in renaissance through the invention of certain class of polymers called "Conducting Polymers." Researchers have focused for more than a decade on the synthesis of these polymers as they exhibit semiconducting properties. Conducting polymers possess unique characteristics in their structure by exhibiting conjugation (those possess an extended π bond along the polymeric back bone) and are linear in nature. The increase in conductivity in these polymers can be described as, conventional polymers usually consists of σ bonds and the charge created on any given atom in the polymeric chain is not mobile while in case of conducting polymer, the charges created on the polymeric chain are mobile due to the presence extended π conjugation.

Some of the examples of conducting polymers with their properties are given in Table 3.1

Table 3.1 Characteristics of conducting polymer

| Conducting Polymer | Structure | Band gap (eV) | Maximum Conductivity Scm^{-1} |
|------------------------|-----------|---------------|--|
| Trans Polyacetylene | | 1.5 | 1.5×10^5 |
| Polypyrrole | | 3.0 | 2000 |
| Polythiophene | | 2.0 | 100 |
| Polyaniline | | 3.6 | 10 |
| Polyphenylene | | 3.4 | 1000 |
| Polyphenylene-vinylene | | 2.32 | 1000 |

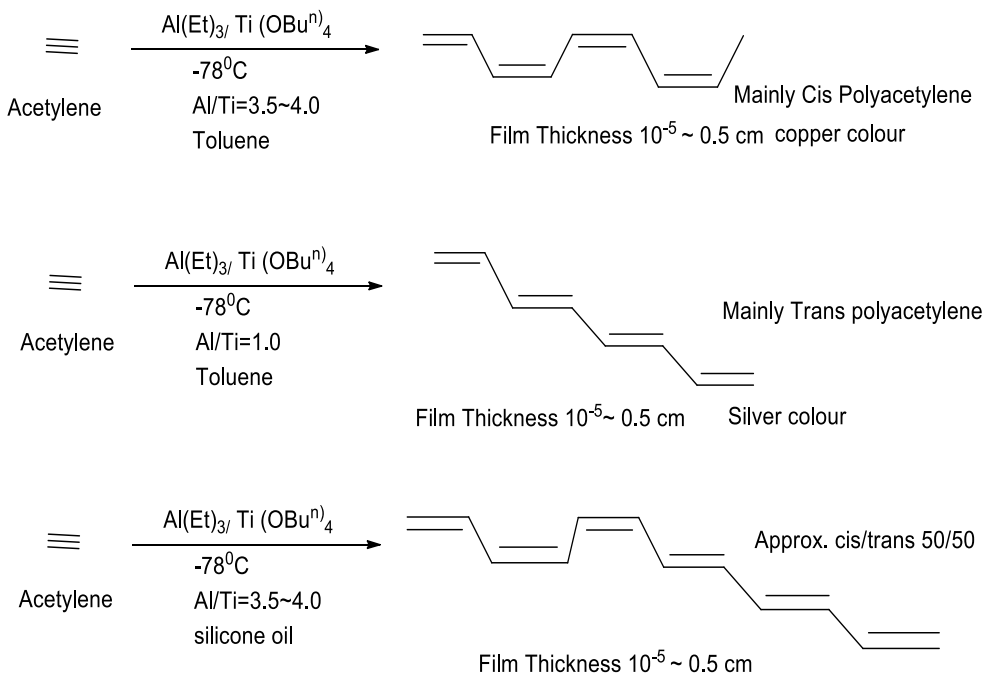
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3.2 Examples of Conducting Polymers

3.2.1 Polyacetylene (PA)

The first conducting polymer synthesized was polyacetylene which dates back to last century. Polyacetylene is the simplest molecular framework possessing conjugated polymer.

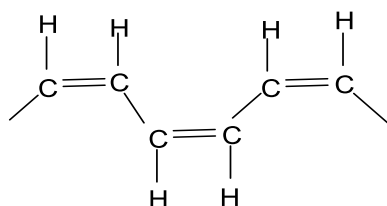
In 1977, Shirakawa and his colleagues (Japan) prepared polyacetylene as shiny metallic film by contacting acetylene gas with a soluble Ziegler-Natta catalyst and their reactions are given below.



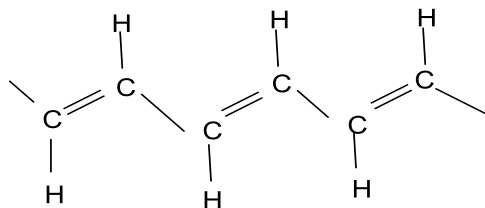
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Polyacetylene formed can exists in two isomeric forms namely

- 1) CisPolyacetylene: The hydrogen atoms are arranged on same side of C=C bond .
- 2)Trans Polyacetylene : The hydrogen bonds are arranged alternatively to C=C bond.



Cis Polyacetylene



Trans Polyacetylene

The PA films are insoluble, infusible and are unstable in nature which renders it as an unattractive material for technological applications.

The major resurgence in the discovery of PA has been made through collaboration with MacDiarmid (USA) where the conductivity of the PA is increased by 10 orders of magnitude by a process known as doping. The conduction mechanism in PA by doping was developed by Heeger.

H.Shirakawa, AG MacDiarmid and A J Heeger were awarded Nobel prize in Chemistry in the year 2000 for the discovery and development of conductive polymers. A brief biography of the Nobel laureates is given in box 3.1.

3.2.2 Polyaniline (PAni)

Polyaniline is a aromatic conjugated polymer, synthesized by electrochemical oxidation of aniline using ammonium peroxodisulphate or potassium iodate as oxidizing agent.

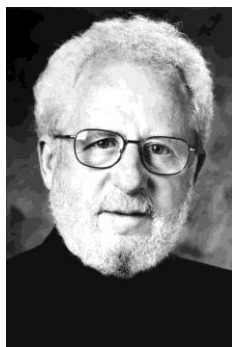
3.1 Biography of Nobel Laureates in Discovery of Polyacetylene



Alan Graham MacDiarmid was born April 14, 1927, in Masterton, New Zealand. Coming from a self-described “poor family,” he was forced to leave high school at age 16 in order to take a part-time job after his father retired. His job allowed him to apply himself as a part-time student and he was able to complete his B.Sc. in 1948. MacDiarmid then received a Fulbright fellowship to attend the University of Wisconsin, earned a Ph.D. in 1953. MacDiarmid maintained his Chair position at Penn until the end of his career, but also held positions at the University of Texas at Dallas, becoming the James Von Ehr Chair of Science and Technology and professor of

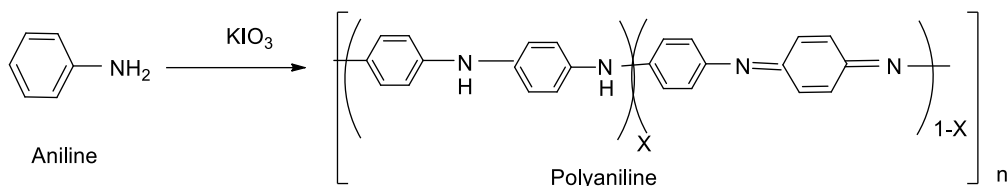
chemistry and physics there in 2002.

Hideki Shirakawa (1936-) was born August 20, 1936, in Tokyo. Spending his childhood in the small city of Takayama, he entered Tokyo Institute of Technology in April of 1957 and received a Doctor of Engineering degree in March of 1966. In 1979, he moved to the University of Tsukuba, where he was appointed associate professor. He was later promoted to full professor in 1982 and formally retired from the University of Tsukuba as professor emeritus at the end of March 2000, shortly after being awarded the Nobel Prize in Chemistry with Heeger and MacDiarmid.



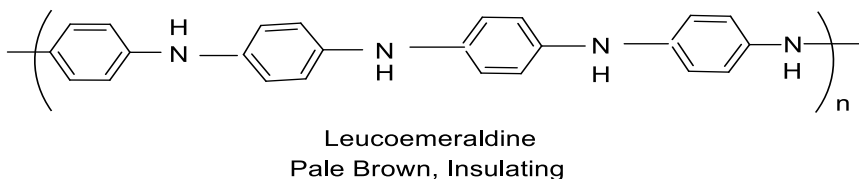
Alan Jay Heeger was born January 22, 1936, in Sioux City, Iowa. After completing his B.S. in 1957, he began graduate studies in physics at Berkeley, ultimately joining the research group of Alan Portis. After completing his Ph.D. in 1982, Heeger moved to the University of California, Santa Barbara (UCSB), where he still actively pursues research in conjugated materials. Learning that MacDiarmid had some experience with sulfur nitride chemistry, he approached him about working together on a study of this new polymer.

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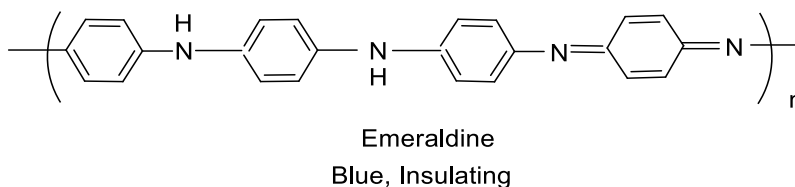


Polyaniline has a unique structure consisting of an alternating arrangement of benzene rings and nitrogen atoms. The nitrogen atoms exist either as an imine (in an sp^2 hybridized state) or as amine (in an sp^3 hybridized state). Depending on the relative concentration of nitrogen, polyaniline exists in three different oxidation state.

1. Leucoemeraldine: When $X=1$, a completely reduced state of PANi exists, consisting of only benzenoid amine structure.

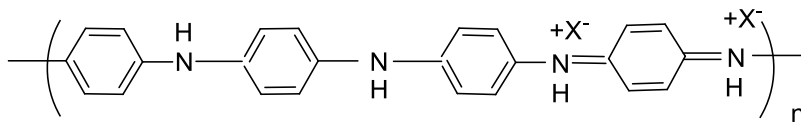


2. Emeraldine: When $X=0.5$, PANi consists of a partially reduced benzenoid amine and partially oxidized quinoid imine.



The protonated emeraldine is green in colour and is highly conductive in nature.

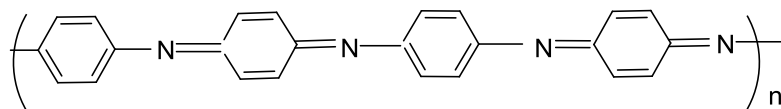
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Protonated Emeraldine

Green, Partially oxidized
conducting form

3. Pernigraniline: When $X=0$, PAni consists of a completely oxidized quinoid imine structure.



Pernigraniline

Black, Insulating

3.3 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.

3.3.1 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. a) 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.

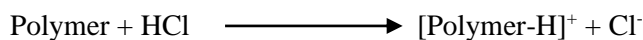
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2. n-Doping (Reduction doping): It is reduction reaction where an electron is added to the conduction band leaving the polymer with a negative charge.



- b) 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.

3.3.2 Conduction Mechanism In Polymers

The interaction of a polymer unit cell with all its neighbours in a polymeric chain leads to the formation of electronic band. 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.

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3.3.2.1 Conduction in PA

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 dimerizes, 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 produce an energy level at the centre of the band gap, known as neutral, positive or negative soliton. The neutral soliton carries a single electron which possess 1/2 spin and exhibit 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.

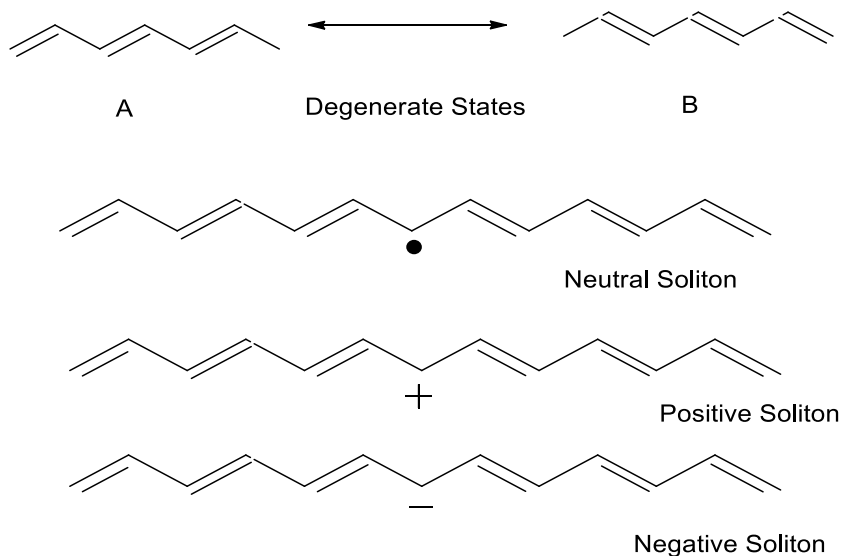


Fig 3.1 A) and B) Degenerate States of trans-PA C)PA chain with a defect (neutral, Positive and Negative soliton)

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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 and the reactions are given in Fig. 3.2

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 lower 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^{-7} to 10^3 S/cm (or by the order of 10^{10}).

3.3.2.2 Conduction in PANi

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 as given in Fig. 3.3, 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

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resulting emeraldine salt has a conductivity of 300 S/cm, increased by the order of 10^{11} magnitude.

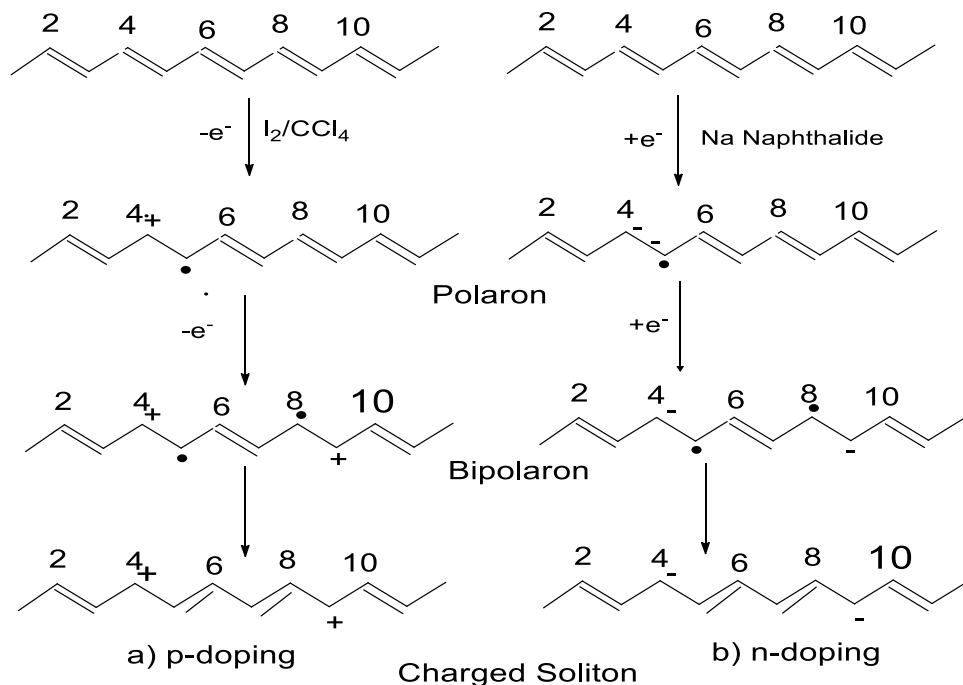


Fig 3. 2 a) p-doping b) n-doping in trans-PA

In general, polymers forming soliton energy level 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.

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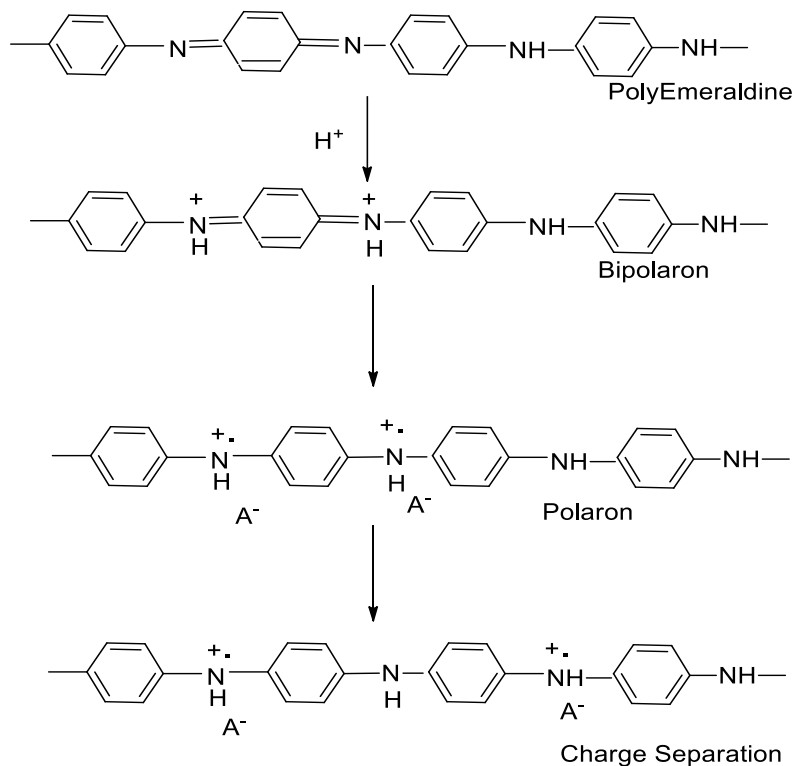


Fig3.3 Protonic acid doping in Polyaniline.

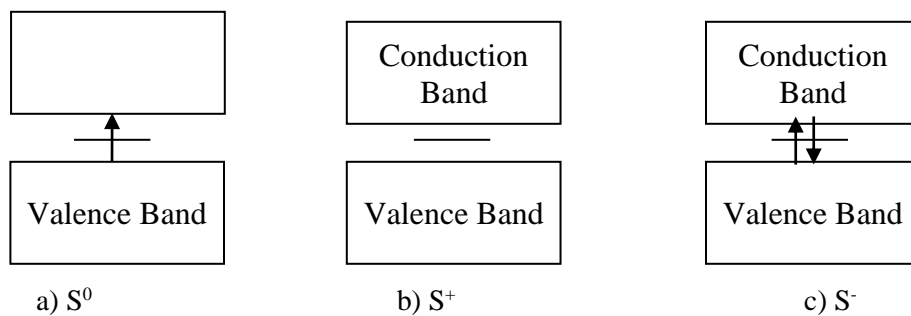


Fig 3.4 Charge and spin separation in a) Neutral Soliton (S^0), b) Positive Soliton (S^+) c) Negative Soliton (S^-)

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Factors influencing the electrical conductivity

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

1. Conjugation length: Conductivity of the polymer increases with the increase in the length of the polymer chain as well as the number of conjugation.
2. Doping level: Conductivity of the polymer increases with increase in doping level until the saturation point.
3. Temperature: Conductivity of the polymer increases with increase in temperature and becomes constant at a particular temperature.
4. Frequency: Conductivity increases with increase in frequency of current.

3.3.3 Applications of conducting polymer

- In rechargeable light weight batteries
- In optically display devices.
- In electronic devices such as diodes, transistors.
- In solar cells, drug delivery system for human body.
- In molecular wires and switches.
- In photovoltaic devices.
- In antistatic coatings for clothing.

3.4 ORGANIC SOLAR CELL (OSC)

The process by which light is converted into electricity using conducting polymers is the basis of photovoltaics. A photovoltaic cell consists of a silicon PN junction diode with a glass window at the top surface of P material with nickel plated ring act as positive terminal (anode) and a metal contact at the bottom act as cathode as shown in Fig. 3.5

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Working of Photovoltaic cell

When solar light falls on the photovoltaic cell, the photon excites some of the electrons in the semiconductor to form electron-hole (negative-positive) pairs. since there is an internal electric field (due to p-n structure) these pairs are induced to separate. As a consequence, electrons move to the negative electrode while the holes move to the positive electrode. A conducting wire connects the negative electrode, load and positive electrode in series to form a circuit. As a result, current is generated and is applied to the external load.

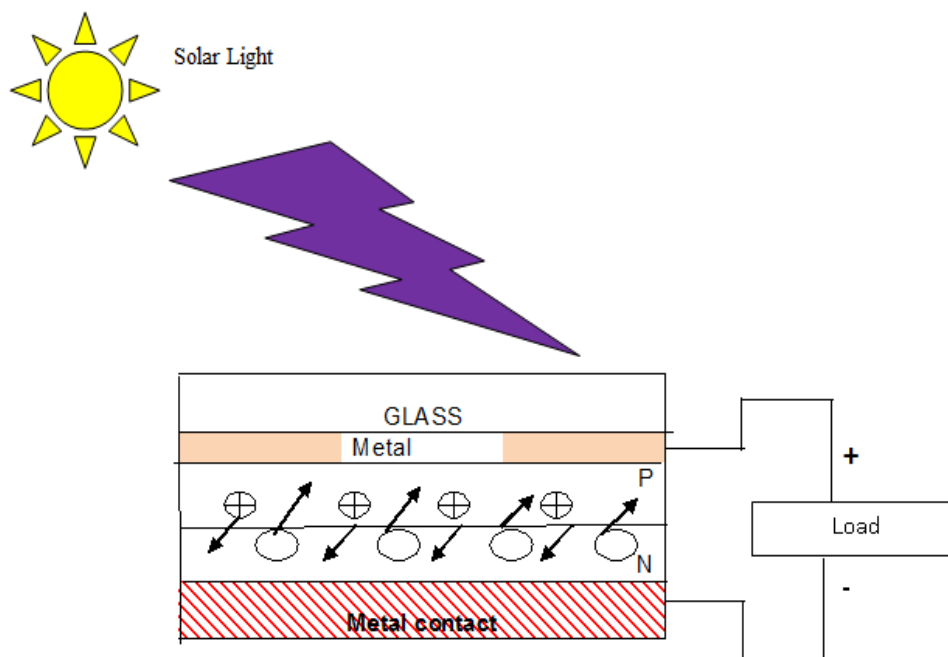


Fig. 3.5 Structure and working of Solar photovoltaic cell

Organic solar cell (OSC) possess same architecture as photovoltaic cell except the PN junction diode is replaced by the doped conducting polymer. The

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advantages of organic solar cell (OSCs) are it offers low cost solution processing, flexible substrates and high speed processing. The major disadvantage of OSC is the low power conversion efficiency.

3.4.1 Structure of OSC

All organic solar cells have a planar layered structure where the organic active layer is sandwiched between two different electrodes, one of them is transparent conductive Indium tin oxide (ITO) and the other electrode is aluminium. The polymer solar cells have different architectures.

1. ***Single layer cell***: An organic polymer is sandwiched between two electrodes. The photoactive region is very thin and the positive and negative photoexcited charges travel through the same material where recombination losses are high.

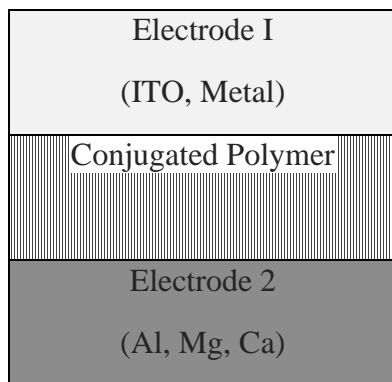


Fig 3.6 Single Layer organic solar cell.

2. ***Bi-layer cell***: The sandwiched organic polymer consists of two constituents, electron donor and electron acceptor layer at ITO and Al electrodes respectively. The donor constituents are conjugated polymers of PPV, polythiophene and their derivatives with low band gap energy. The electron acceptor materials are C60 and conjugated polymer with cyano group having strong electron affinity. The lowest

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occupied molecular orbital (LUMO) level of donor material should be 0.3 -0.4 eV higher than that of acceptor.

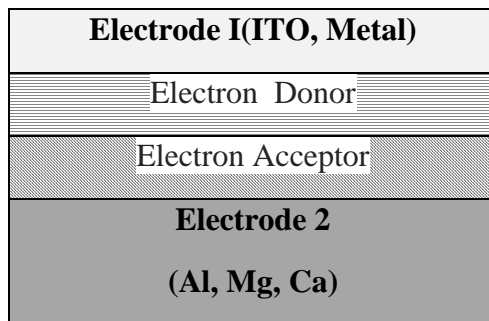


Fig 3.7 Bi Layer organic solar cell.

3. ***Bulk heterojunction***: The organic polymer consists of a nanoscale blend of donor and acceptor materials. The size of the blend is of nms allowing excitons to dissociate at the interface. It requires a percolating network that allows charge separation to occur. It has an advantage over other structures as they can be made thick enough for effective photon absorption.

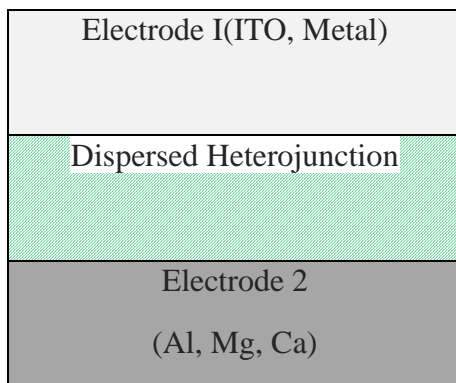


Fig 3.8 Dispersed heterojunction organic solar cell.

3.4.2 Principle and Working of OSC

The process of conversion of light into electricity by organic polymers takes place in following steps:

1. Exciton generation
2. Exciton diffusion
3. Exciton dissociation
4. Charge transport.

1. Exciton Generation: Absorption of photon from the solar spectrum by organic conducting polymers with bandgap energy 1.1eV - 2.0 eV produces electrostatically coupled electron-hole pairs called excitons.

2. Exciton diffusion: The photogenerated excitons are characterized by small life time of few picoseconds which limits the mobility of excitons to 5-10nm called exciton diffusion length. As the excitons are dissociated within this range, exciton diffusion length play a crucial role in the performance of the OSCs.

3. Exciton dissociation: It refers to splitting of electrostatically bounded electron-hole pair into free charges. The dissociation of excitons occurs at the donor-acceptor interfaces or junctions. The donor and acceptor materials are designed in such a way that there exists a difference in LUMO levels of the donor and acceptor materials. For efficient dissociation, the difference in energy level of LUMO of donor and acceptor should be higher than that of exciton binding energy.

$$\Delta(\text{LUMO}_D - \text{LUMO}_A) > \text{exciton binding energy}.$$

4. Charge transport: The charges produced travel through specific electrode materials which are connected to external circuit. The donor material serves to transport holes while the electrons travel within the acceptor material.

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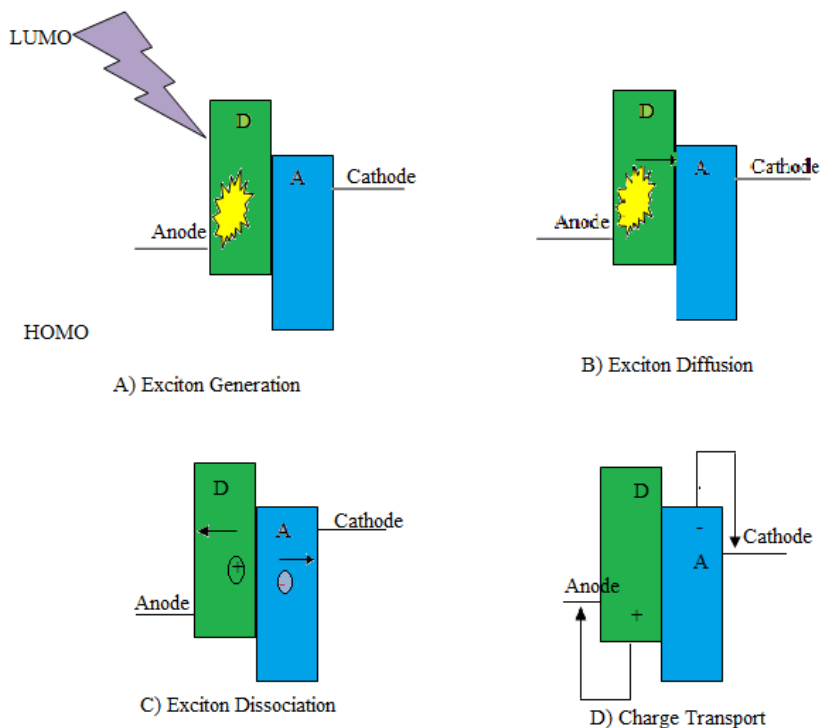


Fig. 3.9 : Principle and Working of Organic solar cell.

Advantages of OSC

- The cells are light in weight, flexible and semi-transparent in nature.
- They are 1000 times thinner than silicon solar cells.
- They are easy to integrate and offers short energy payback time.

Disadvantages of OSC

- Low efficiency compare to silicon solar cells.
- They are stable in dark but degrade in light conditions.
- Lifetime is less compare to silicon cells as they degrade rapidly in moisture and air.

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3.4.3 Applications of OSC

- Portable power supply.
- Emergency power source.
- Electric Fences.
- Toys, calculator and watches.

3.5 ORGANIC LIGHT EMITTING DIODE(OLED)

Light Emitting Diode (LED) works on the principle of electroluminescence (The process of converting electricity to light energy is known as electroluminescence.) An electroluminescent structure presented in Fig. 3.10 consists of 4 layers, two inorganic electroluminescent material (doped semiconductor) capable of emitting electrons and holes with two electrodes.

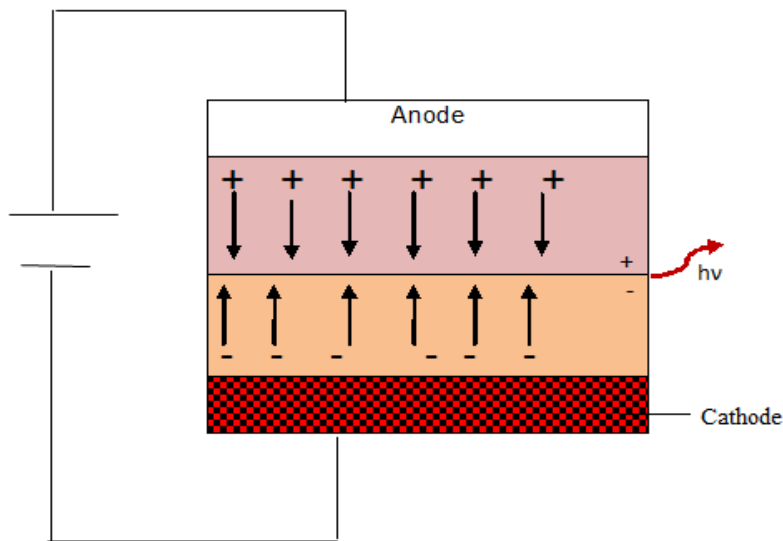


Fig. 3.10 : Structure of Electroluminescent Cell

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One of the electrode, anode is Indium Tin oxide (ITO) and the other is a metallic layer act as cathode. On applying voltage, holes and electrons are created on the luminescent material connected to anode and cathode respectively. The emission of light occurs by radiative combination of electron-hole pair to form exciton. The relaxation of excess exciton energy occurs by the emission of monochromatic light. When the electroluminescent doped semiconductor is substituted by conjugated polymer with same functionality, the LED is referred as organic light emitted diode (OLED).

3.5.1 Structure of OLED

An OLED is a light emitting diode consists of emissive electroluminescent organic film which emits light in response to electric current. The construction of single layer OLED is represented in Fig.3.11. An OLED consists of a glass substrate which is coated by a transparent ITO, act as anode. A conjugated polymer (Poly phenylenevinylene (PPV) or Poly alkyl thiophene (PAT) or Poly ethylene dioxythiophene(PEDOT)) is deposited onto the substrate by spin coating technique. On the top of the polymer layer, a metallic layer of Al or Ca is deposited by vacuum evaporation, forms the cathode. By applying bias voltage at the electrodes, emission of light is obtained through the transparent electrode.

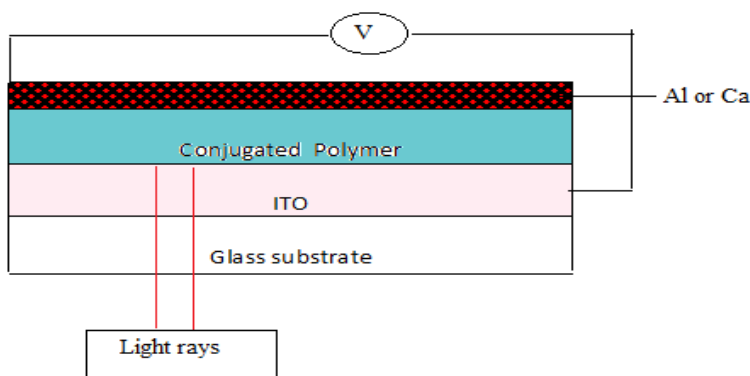


Fig. 3.11 : Structure of single layer Organic Light Emitting Diode.

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Components of OLED

The components of OLED consists of

1. Substrate : It may be plastic, glass which holds the OLED.
2. Transparent Anode: It is a transparent material of ITO which injects holes to the polymeric material .
3. Conjugated Polymer: It is an emissive layer where light is emitted. eg: PPV, PAT, PEDOT.
4. Hole transport layer: It is placed between anode and emissive layer in order to increase the hole transport. eg: Triphenyl amine derivatives.
5. Electron Transport layer: It is placed between cathode and emissive layer and act as hole blocking layer. eg: 1,3,4-Oxadiazole derivatives.
6. Cathode: A metallic layer of Al or Ca which injects electrons to the polymeric material.

3.5.2 Working of OLED

According to Su, Schrieffer and Heeger theory, electron-electron interactions are neglected and the electroluminescent properties of polymeric substances are based on strong electron-phonon interactions. Based on this theory, for non-degenerate ground state polymers, injection of charges leads to the formation of either singly or doubly charged polarons. Neutral species, excitons can be generated either by the fusion of two polarons with opposite charges or by photoexcitation due to electron-hole separation. The steps involved in the operation of OLED is as follows and is illustrated in Fig.3.12

- 1) By applying bias voltage, charges of opposite sign are injected into the active polymeric material to form positive and negative polarons (P⁺ and P⁻).

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- 2) The charges (P^+ or P^-) move in the polymer towards oppositely charged electrode, driven by electric field.
- 3) Polarons of opposite sign combine to generate excitons.
- 4) The excitons undergoes radiative combination by the emission of monochromatic light.

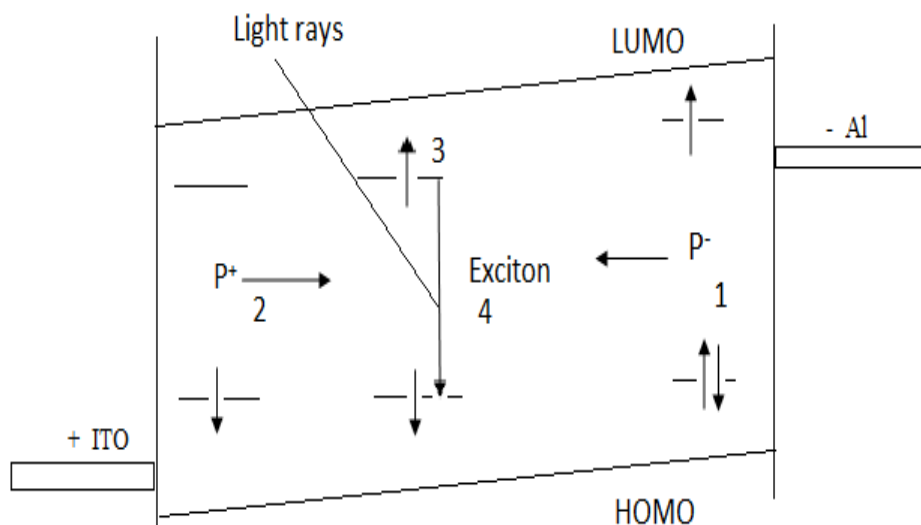


Fig. 3.12 : Working of Organic Light Emitting Diode.

The factors controlling the polymeric structures are as follows and it plays a significant role in the development of OLEDs.

1. The band gap of the conducting polymer should be in the range of 2.0- 3.0 eV, is responsible for electroluminescence.
2. The electron affinity and ionization potential of the polymer strongly affects the injection of charges into the electrode.

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3. The solid state packing of the polymer influences the stability and emission efficiencies of the polymer.
4. The surface polarity of the polymer is responsible for the adhesion between the active polymer and the electrodes, an important factor in charge injection.
5. The active polymeric layer is resistant to oxidation and temperature for the lifetime of the device.

Advantages of OLED

- Light weight, flexible and can be easily processed.
- High Resolution and high reliability.
- Consumes less power.
- Highly energy efficient.
- High levels of brightness and intensity.

Disadvantages of OLED

- OLEDs exhibit colour imbalance on long usage due to the lifetime of the organic materials.
- Expensive in nature.
- Poor resistance to water and moisture.

3.5.3 Applications of OLED

- Used in flat panel display screen such as cell phones, laptops, digital cameras.
- Used in remote controls, indicator lights.
- Used in fibre data communication.

3.6 LIQUID CRYSTALS

Liquid crystals possess unique properties and play an important role in modern technology. In 1988, an Austrian botanist, Friedrich Reinitzer observed that a material, Cholesteryl benzoate shows two melting points. On heating the solid benzoate, it changes into a hazy liquid which on further heating becomes a clear transparent material. Liquid crystals are characterized by rod-like molecular structure with strong dipole and rigidity along the molecular axis. The tendency of the molecules (mesogens) in liquid crystal points to a common axis, called director leads to a condition called anisotropy.

Liquid crystals are highly anisotropic fluids which exist between the boundaries of a solid phase and conventional liquid phase. The structure of the liquid crystal is described by the following parameters:

1. **Positional Order:** The average molecules or group of molecules exhibits translational symmetry.
2. **Orientalional Order:** The molecules align along the director axis on a long-range basis.
3. **Bond orientational order:** The adjacent molecules are joined by the line without regular spacing.

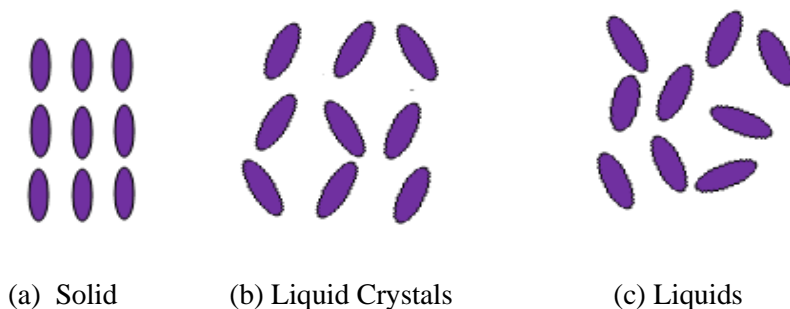
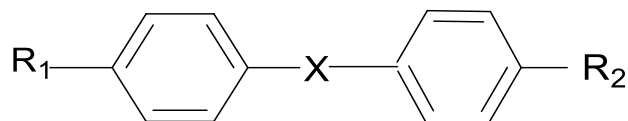


Fig. 3.13 : Molecular orientations in different States of matter.

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The chemical structure of the liquid crystal consists of

1. Long, narrow elongated molecules with molecular interaction leading to attraction between the molecules. The most common liquid crystal molecule are of the type:



A central core of benzene rings is linked by X, may be diazo, azoxy, nitrones, esters or Schiff bases. The end groups R₁ and R₂ may be alkyl, alkoxy or acyl group.

2. Presence of unsaturation in their structure increases the polarizability as well as intermolecular attractions for the formation of mesophase.
3. Presence of carboxylic groups at the end of the chain and the absence of bulky functional groups are responsible for the stability of the liquid crystal.

3.6.1 Thermography

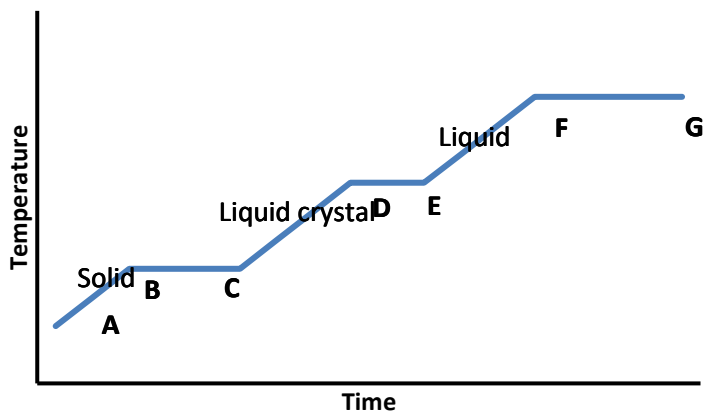


Fig 3.14 Thermographic behaviour of a solid showing mesomorphism

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The phase change observed on heating a solid showing mesomorphic behaviour is represented in the form of temperature-time graph known as thermography. On heating a solid, its temperature starts rising until it changes to liquid crystal as shown by the curve AB in Fig .3.14.

The temperature now remains constant as long as both the phases (solid and Liquid crystal) are present as presented by the curve BC. When the solid completely changes to liquid crystal, the temperature again starts rising as seen in curve CD until the liquid crystal changes to liquid. The temperature remains constant as long as the two phases (liquid crystal and liquid) are present together as seen in curve DE. When the liquid crystal completely changes to liquid, the temperature again starts rising (curve EF) and continues till it reaches a vapour state. The temperature again becomes constant as long as the liquid and vapour are present together (Curve FG).

3.6.2 Classification of Liquid Crystal

Liquid crystals are states of matter consisting of long range molecules, exhibiting optical activity, ability to form mono crystals in the presence of electric or magnetic field and are sensitive to temperature. They are broadly classified into two types:

- 1. *Thermotropic liquid crystals:*** They are formed by the variation of temperature and is of three types: a. Nematic structure b. Cholesteric structure C. Smectic

a) *Nematic Structure:* The molecules in nematic structure are arranged parallel or nearly parallel to each other along the long molecular axes. The structure is one dimensional and are mobile in three directions. It is the highest temperature mesophase in thermotropic liquid crystal. The molecules possess no translational order with rod-like molecules tend to align parallel to each other with uniaxial

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symmetry. Eg: p-methoxybenzylidene-p'-n-butyl aniline (MBRA), p-azoxyanisole (PAA), p-n-hexyl-p'-cyanobiphenyl, p-quinquephenyl.

b) Cholesteric Structure: It is composed of nematic mesogenic molecules containing a chiral centre, which produces intermolecular forces that favours alignment between molecules at a slight angle to one another. It is a stack of two-dimensional nematic -like layers forming a continuous helical pattern. A byproduct of the helical structure has the ability to selectively reflect colour light at wavelength in the visible spectrum equal to the pitch length (the distance the director takes to rotate one full turn in the helix). Eg: Cholesterylnonanoate, 2-methylbutyl-pp(p'-methoxybenzylidene-amino) cinnamate.

c) Smectic structure: The word "smectic " is derived from the Greek word for soap. The molecules show a degree of translational order and tend to align themselves in layers or planes. There are eight smectic structures observed and their properties with characteristics are given in the Table. 3.2

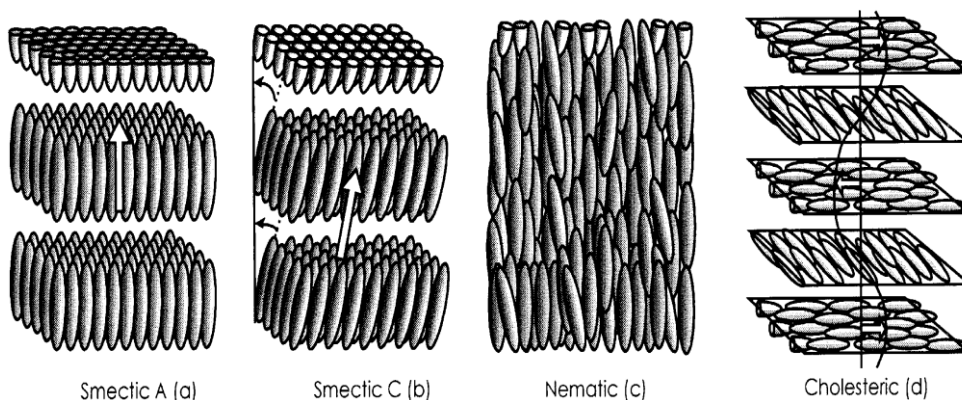


Fig. 3.15 : Molecular Orientation in Smectic, Nematic and Cholesteric phase.

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Table 3.2 Characteristic Features of Smectic A-H Liquid crystal structures.

| Unstructured Smectics | Molecular Organization | Optical Properties | |
|-----------------------|--|------------------------------|---|
| | | Optical figure | Textures |
| Smectic A | Layer structure, Molecular axes are orthogonal to the layers, Random arrangement of mesogens within the layers. Eg: ethyl p-(p'-phenylbenzal amino) benzoate | Uniaxial Positive | Focal conic (Fan shaped or polygon), Homogeneous, pseudoisotropic |
| Smectic C | Layer structure, Molecular axes are titled to the layers, Random arrangement of mesogens within the layer Eg: p-n-octyloxybenzoic acid | Biaxially positive | Broken focal conic, Homogeneous |
| Smectic D | Cubic Eg: p'-n-octadecyloxy-3'-nitrodiphenyl-p-carboxylic acid | Isotropic | Mosaic |
| Smectic F | Layer structure Eg: 2-(p-pentylphenyl)5-(p-pentyloxyphenyl) pyrimidine | Uniaxially positive | Broken focal conic with concentric axes |
| Structured Smectics | | | |
| Smectic B | Layer structure, Molecular axes are orthogonal or titled to the layers, hexagonal arrangement of mesogens within the layers. Eg: ethyl p-ethoxybenzal-p'-aminocinnamate | Uniaxial or biaxial positive | Mosaic, pseudoisotropic and Homogeneous |
| Smectic E | Layer structure, Molecular axes are orthogonal to the layers, ordered arrangement of mesogens within the layers. Eg: diethylp-terphenyl-p,p"-carboxylate | Uniaxial positive | Mosaic, pseudoisotropic |
| Smectic G | Layered structure with ordered arrangement within the layers Eg: 2-(p-pentylphenyl)-5-(p-Pentyloxyphenyl) pyrimidine | Uniaxial positive | Mosaic |
| Smectic H | Layered structure with ordered arrangement within the layers Eg: 4-butyloxybenzyl-4-ethylaniline | Uniaxial or biaxial positive | Mosaic |

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2. Lyotropic Liquid crystal: Lyotropic mesophases occur in concentrated solution of rod-like molecules in an isotropic solvent, water. They are important in soaps, gels and colloids. The amphiphilic soap molecules are arranged in bilayer structure with a minimum contact between the hydrocarbon chain and the water molecules.

There are also lamellar, cubic and hexagonal arrangement of amphiphilic molecules in water solution. Eg: sodium stearate, α -Lecithin

3.6.3 Liquid Crystal Display(LCD)

Liquid crystal technology has been applied in many areas of science and device technology. They are used as displays in digital wrist-watches, calculators, television displays and panel meters. They can be used to record, store and display images.

The liquid crystal cell design shown in Fig. 3.16 consists of a thin film of liquid crystal at room temperature which is sandwiched between two electrodes (glass coated with metal or ITO).

The thickness of the liquid crystal film is 6-25 micrometers and is controlled by a glass spacer which is chemically inert. The cell is hermetically sealed in order to eliminate oxygen and moisture both of which are chemically attacked by the liquid crystal.

3.6.3.1 Principle

A thin film of liquid crystal is placed between two sheets of glass, one of which is coated with an electrically conductive material (electrode) as shown in Fig. 3.17. When an electric current is not applied, the molecules are uniformly oriented so that the light can pass through the cell. When the current is applied, the molecular alignment changes and the cell appears opaque or dark. Hence, a number is displaced in black against a silvery background.

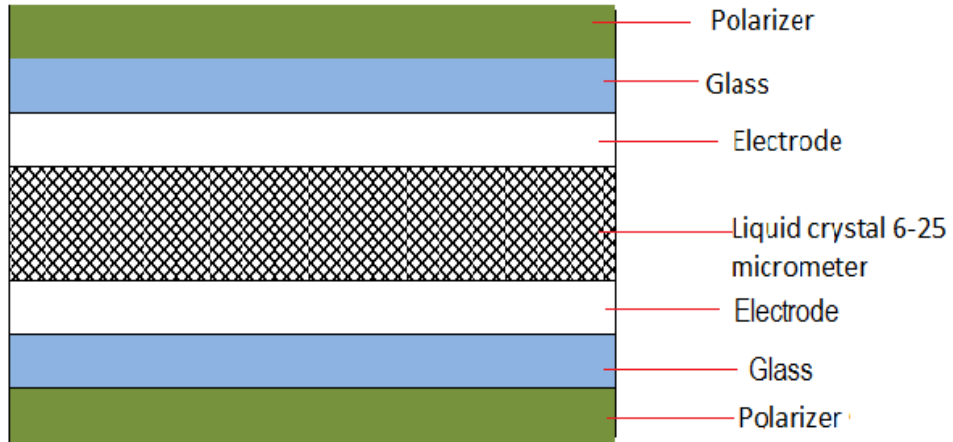


Fig. 3.16 : Design of Liquid crystal cell.

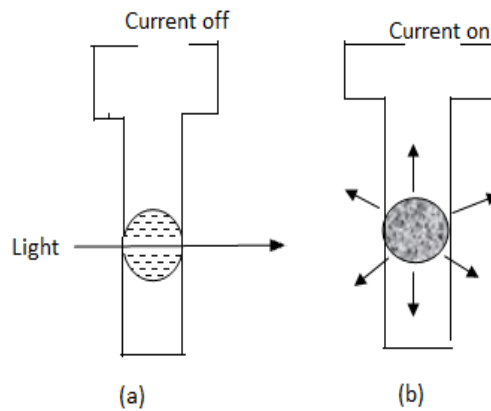
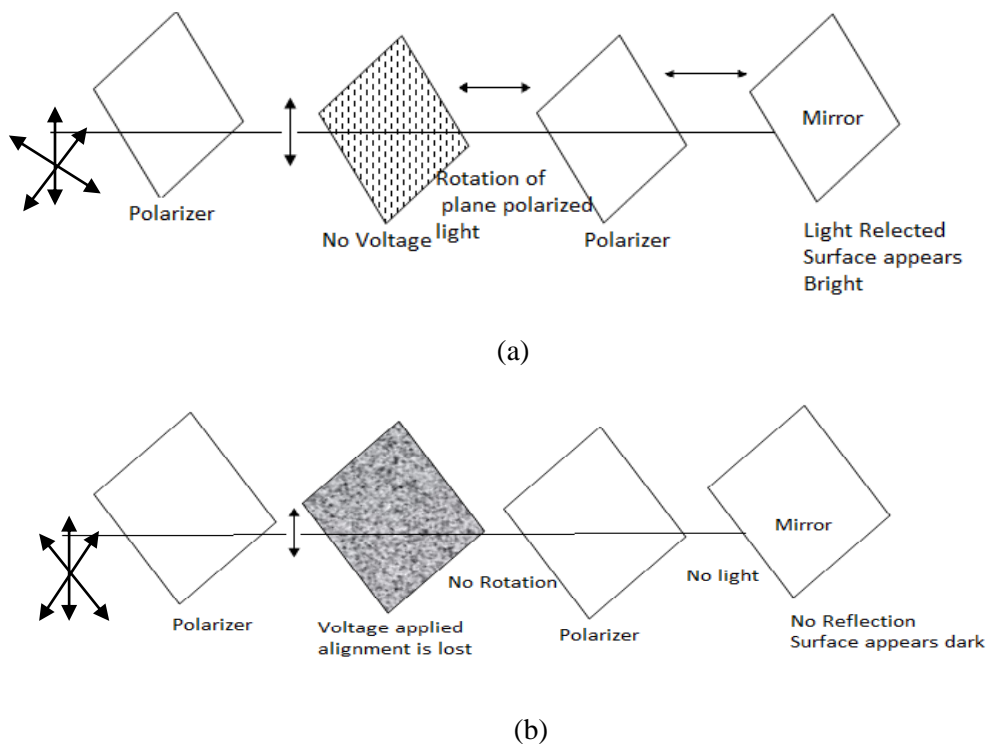


Fig. 3.17 : Principle of Liquid Crystal cell. (a) Light passes through Nematic crystal (b) Light is scattered due to disorderliness of the molecules.

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3.6.3.2 Working

The cell with the nematic liquid crystal is placed between the two crossed polarizer as shown in Fig.3.18. Polarized light entering the cell follows the twist of the nematic liquid crystal and is rotated 90° allowing the passage of light through the second polarizer. When an electric field is applied, the molecular alignment in the liquid crystal changes in such a way that polarization is not altered and no light is transmitted. Hence, if a mirror is placed behind the second polarizer it appears black or if a electrode is shaped in a numeric pattern of segment is placed, then a numeric display will appear on a black back ground on applying the current.



**Fig. 3.18 : Working of Liquid crystal display . (a) in the absence of electric field
(b) in the presence of electric field.**

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There are two modes by which liquid crystal operates namely 1) Dynamic scattering and 2) field-effect scattering. 1) In dynamic scattering, when the electric field is not applied, the cell containing twisted nematic liquid crystals is transparent. On applying the electric field, the cell becomes opaque. The cell is prepared by rubbing the glass surface directionally or by chemically treating the surface by adding a chiral compound to nematic liquid crystals. Digital display are made by photoetching a seven-segment pattern onto one of the ITO coated onto glass electrodes. 2) In Field-effect display is mostly used in watch and pocket-calculator displays. A liquid crystal watch displays hours and minutes, the quartz crystal controls the oscillating circuit with a frequency of 32,768 Hz. Each of the time pulses is decoded to give outputs that are needed for seven-segment display.

Advantages of LCD

- Less power consumption
- Better clarity even in the presence of bright light.

Disadvantages of LCD:

- LCD can be viewed up to 165^0 and the picture suffers from side.
- Non-flexible .

Compare and contrast between LCD and OLED.

- OLEDs displays are light in weight, flexible and are in deeper-blacks compare to LCD.
- OLED offers a much better viewing angle at 170^0 while LCD can be viewed up to 165^0 and the picture suffers from side.
- OLEDs offers high contrast ratio, sharper picture and fast response time compare to LCD.
- OLEDs consumes less power than LCD.

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- No geographical constraints with OLED while LCD screens lose contrast at high temperature and lose brightness and speed at low temperature environment.
- OLED consists organic compounds which emits light in response to electric field while LCD uses twist and untwist mechanism in response to electric field.
- Both OLED and LCD are vulnerable to water damage and degrades more rapidly in the presence of oxygen.
- Both OLED and LCD have poor readability and display in bright ambient light.
- Pixels get stuck in both OLED and LCD either through usage or during initial manufacturing process.

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. Define Electroluminescence.
8. Give the merits and demerits of OLED.
9. What are excitons?
10. What is an organic photovoltaics?
11. What are the advantages and limitations of OSC?
12. What are liquid crystal?
13. Classify liquid crystals.
14. Differentiate between thermotropic and lyotropic liquid crystals.
15. Compare OLED and LCD.

PART-B QUESTIONS

1. Describe the synthesis of polyacetylene and explain its isomeric forms.
2. Describe electronic conduction in conjugated conducting polymers.
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 OLED.
7. Describe the construction and working of OSC.

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- 8 Explain in detail the classification of liquid crystals with their characteristics.
9. Give a detailed account on liquid crystal display.
10. Write short note on polyaniline.

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