UNIT 1: POLYMER CHEMISTRY

(8h)

Introduction to polymers, functionality of monomers, co-polymerization, Stereospecific polymerization with specific examples.

Plastics - Thermoplastics and Thermo settings, Preparation, Properties and Applications of – Bakelite, Urea-Formaldehyde, Nylon-6,6, Carbon fibres.

Elastomers-Buna-S, Buna-N-Preparation, Properties and Applications.

Conducting polymers - polyacetylene, polyaniline, poly pyrroles - Mechanism of conduction and Applications.

- **4 Polymers**: polymer is the word derived from two Greek words poly (= many) and meros (= parts or units).
- **4** A polymer is a macromolecule (giant molecule of high molecular weight), built up by the linking together of a large number of smaller molecules called monomers.
 - Polymers are formed by joining large number of small molecules (units) called monomers.
 - For example: vinyl chloride is the monomer of Poly Vinyl Chloride (PVC).
 - It is formed by joining large number of vinyl chloride monomers.

Types of polymerization:

i. Addition polymerization:

o In addition polymerization, the monomers are joined to each other without the formation of by products to form polymer.

ii. Condensation Polymerization:

o In condensation polymerization, the monomers are joined to each other with the formation of by products like H₂O, H₂S to form polymer.

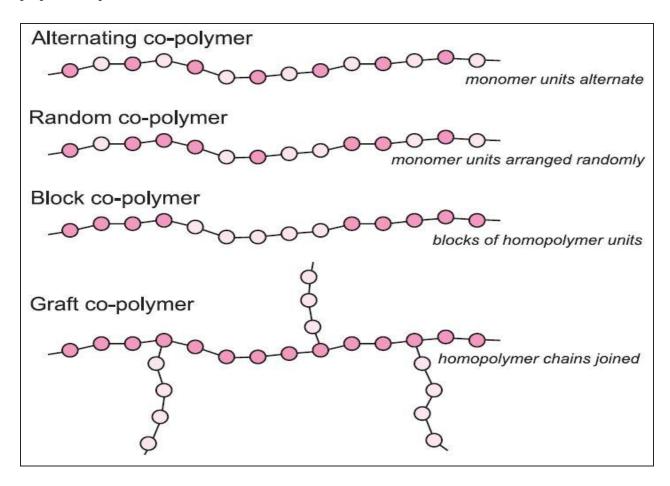
For example: Polyamides, Polyesters, Proteins etc.

o In some cases it takes place without formation of byproducts. For example: Nylon-6

	ADDITION POLYMERISATION	CONDENSATION POLYMERISATION
1.	The self addition of n- unsaturated molecules (monomers) to form a large molecule (polymer) without elimination of any byproduct by rapid chain reaction is known as addition polymerization.	1. Step wise intermolecular condensation of monomers takes place to form a large molecule (polymer) with the elimination of small molecules like H2O, HCl, NH3, etc.
2.	No byproduct is formed	2 .Byproducts are formed
3.	The molecular weight of polymer is sum of the molecular weight of all the monomers	3. The molecular weight of polymer is not identical with the sum of monomers molecular weight.
4.	Monomers with un-saturation are involoved	4. Monomers with reactive functional groups are involved.
5.	Proceeds by chain growth mechanism	5 .proceeds by step growth mechanism
6.	The polymer has same composition as that of monomer ex: polyethylene, PVC, polystyrene, etc.	6. The polymer has different composition from the monomer.Ex: polyester, Nylon, silicones, etc.

What are Copolymers?

A copolymer is a polymer that is made up of two or more monomer species. Many commercially important polymers are copolymers. Examples include polyethylene-vinyl acetate (PEVA), nitrile rubber, and acrylonitrile butadiene styrene (ABS). The process in which a copolymer is formed from multiple species of monomers is known as copolymerization. It is often used to improve or modify certain properties of plastics

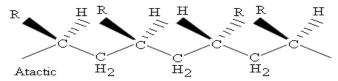


TACTICITY (STEREO SPECIFIC POLYMERS)

- **Tacticity:** The arrangement of functional groups on carbon backbone of the polymer is called Tacticity of the polymer.
 - The stereo chemical placement of the asymmetric carbons in polymer chain is called tacticity.
 - The tacticity affects physical properties like crystallinity, rigidity of the polymer.

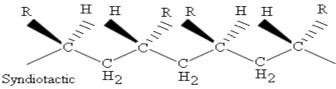
a) Atactic polymer:

- o In these polymers, groups of asymmetric carbons are placed randomly along the chain.
- When there is no regular arranagement of functional groups on the backbone of the polymer chain, these polymers are called Atactic polymers.
- The percent of **mesodiads** is in between 1 and 99%.
 For example: Polystyrene, Polyvinyl chloride etc.



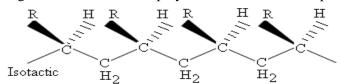
b) Syndiotactic (or syntactic) polymer:

- o In these polymers, groups of asymmetric carbon are placed in alternative positions along the polymer chain.
- The polymers with alternate arranagement of functional groups are called syndiotactic polymers.
- The percentage of **racemodiads** in these polymers is 100%. In **Recemodiads**, every two asymmetric carbons are mirror images of each other. For example:



c) Isotactic polymers:

- In these polymers, groups of asymmetric carbon are placed on the same side of the polymer chain.
- Those polymers in which the functional groups are arranged on the same side are called isotactic polymers
- The percentage of mesodiads in this polymer is 100%. For example:



Functionality:

- Ф
- ▶ The number of reactive sites or bonding sites in a monomer is called functionality of the monomer. If two reactive sites are there in a monomer, then it is called bi functional. The bi-functional monomers forms linear or straight chain molecule (Polymer)
- A tri functional monomer has three reactive sites, it gives branched chain polymer.
- A poly functional monomer contains more than three reactive sites; it gives three dimensional network polymers.

S. No.	Example	Functionality
1.	CH ₂ = CH ₂ (Ethylene)	-2 (Two bonding sites are due to the presence of one double bond in the monomer. Therefore ethylene is a bifunctional monomer).
2.	H ₂ N – (CH ₂) ₆ – NH ₂ Hexa methylene diamine	-2 (This monomer contains two functional groups, hence it is a bifunctional monomer).
3.	$\begin{array}{c} \mathrm{CH_2} - \mathrm{OH} \\ \\ \mathrm{CH} - \mathrm{OH} \\ \\ \mathrm{CH_2} - \mathrm{OH} \end{array}$	-3 (This monomer contains three functional groups, hence it is a trifunctional monomer).
	(Glycerol)	

• egree of polymerization:

▶ The number of repeating units in a polymer chain is called degree of polymerization.

PLASTICS

Pure polymers are seldom used on their own and it is when additives are present that the term plastic is applied. Hence plastics are high molecular weight materials which can be moulded or formed into stable shapes by the applications of heat and pressure.

TYPES OF PLASTIC

Plastics can be divided into two general categories from engineering point of view. They are

Thermoplastics	Thermosetting plastics
1. These are linear, long chain polymers that changes to liquid (soft) when heated and become solid (hard) when cooled. That means their hardness is not a permanent property.	1. These are highly cross connected polymers and these undergo permanent change on heating. That means once they solidified, they cannot be softened.
2. These polymers have linear and branched structures.	2.These polymers have cross linked, 3-dimensional structure
3. These are soft, weak and less hard.	3. These are hard, strong, tough and brittle (easily broken).
4. They can be amorphous (or) semi crystalline materials.	4. These are crystalline in structure
5. Neighboring polymer chains held together by the weak Vanderwaal forces of attraction (or) Dipole-Dipole interaction (or) Hydrogen bonding. There is no any cross links.	5.The polymer chains are held together by cross links (covalent bonds).
2. These are prepared by addition polymerization.	3. These are prepared by condensation polymerization.
4. These are soluble in organic solvents.	4. These are not easily soluble in organic solvents.
5. They can be got back after use and changed into other forms and reused.	5. They cannot be reused.
6. These are made in one step and changed into products in a later process.	6. These are made from low molecular mass semiliquid substances on heating.
7. Structure: Thermoplastics have long and linear chain structure. Thermoplastic	7. Structure: Thermosets have a cross connected chain structure Thermosetting
8. Examples:	8. Examples:
Polyethylene (PE)	Bakelite
Poly vinyl chloride (PVC)	Urea-formaldehyde polymer
Poly styrene (PS)	Polyesters like Nylon-6,6 and Nylon-6
Poly tetra fluoro ethylene or Teflon (PTFE)	Rubbers and poly urethanes

Bakelite

- It is a thermosetting plastic and it is prepared from phenol and formaldehyde in presence of acid catalyst.
- It was prepared by Dr. Leo Baekeland in 1907-1909.
- **Preparation:** it is prepared in three steps.

Step 1:

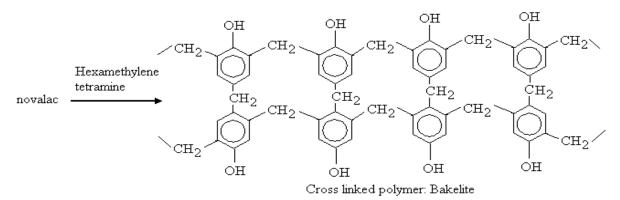
• When phenol reacts to formaldehyde, mono methylol phenol compounds are formed.

Step 2:

When mole ratio of phenol to formaldehyde is greater than 1 in presence of acid catalyst. The methylol compounds react with phenol to form Novalac.

Step 3:

When Novalac is heated with hexamethylenetetramine (HMTA), cross-connected polymer Bakelite is formed.



Properties

- o Bakelite is a pinkish brown substance.
- o It can withstand to scratching, heat, moisture and chemicals.
- o It acts as good electrical insulator.
- o Good chemical resistance
- Good adhesive
- Has very good corrosion resistance.

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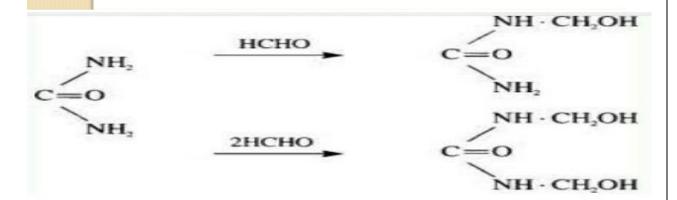
Uses

- Used for production of ion-exchange resins.
- O Used in kitchen wares, jewellary and children's toys
- Used as varnishes, electrical insulators and protective coatings.
- o Bakelite is used to make billiard balls.
- o It is used to fix metal samples in a frame to study the properties of metals.
- Used as sticky materials for grinding wheels and brake inner surface coatings.
- o For making electrical insulator parts like switches, switch boards, heater handles, etc.
- o For making moulded articles like telephone parts, cabinets for radio and television.
- o For making bearing used in paper industry and rolling mills.
- o In paints and varnishes.
- O As an adhesives (binder) for grinding wheels etc

Urea formaldehyde



- The synthesis of the urea-formaldehyde resin takes place in two stages.
- In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups.
- This is a series of reactions which can lead to the formation of mono-, di-, and trimethylolureas.
- The second stage consists of the condensation of the methylolureas to low molecular weight polymers.



Properties

Urea-formaldehyde resin's include-:

It has a very high tensile strength.

Urea formaldehyde has the property of flexural modulus.

Has the property of heat distortion temperature.

Has the capacity of low water absorption.

It has the property of mould shrinkage.

Has a property of high surface hardness.

It can be elongated at break

It is volume resistance in nature.

Uses

UF Resins

- Urea-formaldehyde (UF) resins are the main binders for wood composite boards, such as particleboards, fibreboards, or hardwood plywood.
- In the use of UF resins, water solubility, good adhesion, high curing rate, and low cost are the attractive properties.
- Their drawbacks are low water resistance and emission of formaldehyde from wood boards, resulting from the low stability of the amino- methylene bond.
- The key parameter in the decrease of formaldehyde emission is lowering the formaldehyde/urea (F/U) ratio in the synthesis of UF resins to 1.05.
- This leads to a reduction in the content of crosslinking groups in cured UF resins, lowering the strength and water resistance of adhesive joints in boards.

Ref: Structure formation in urea-formaldehyde resin synthesis, Peep Christjansona, Tõnis Pehk, and Kadri Siimer, Proc. Estonian Acad. Sci. Chem., 2006, 55, 4, 212–225

Nylon -6,6

Preparation of Nylon -6,6

Nylon -6,6 is synthesized by <u>polycondensation</u> of hexamethylenediamine and adipic acid.

Properties

- **1.**Nylon 6,6 persues excellent abrasion resistance and a high melting Point .
- 2. Nylon 6,6 has high tensile strength and exhibits only half of shrinkage in steam.
- **3.** It also provides a very good resistance to photo degradation .
- **4.**Nylon 6,6 also has good advantage over industrial products because it reduces moisture sensitivity in raw products and has a high dimensional stability and melting point.

Applications of Nylon 6,6

- 1. Nylon 66 is frequently used when high mechanical strength, rigidity, good stability under heat and/or chemical resistance are required.
- 2. It is used in fibers for textiles and carpets and molded parts.
- 3. For textiles, fibers are sold under various brands, for example <u>Nilit</u> brands or the <u>Cordura</u> brand for luggage, but it is also used in airbags, apparel, and for carpet fibres under the Ultron brand.
- 4. Nylon 66 lends itself well to make 3D structural objects, mostly by injection molding.
- 5.It has broad use in automotive applications; these include "under the hood" parts such as <u>radiator</u> end tanks, rocker covers, air intake manifolds, and oil pans, as well as numerous other structural parts such as hinges, and ball bearing cages.
- 6.Other applications include electro-insulating elements, pipes, profiles, various machine parts, <u>zip ties</u>, conveyor belts, hoses, polymer-framed weapons, and the outer layer of <u>turnout</u> blankets.
- 7. Nylon 66 is also a popular guitar nut material.
- 8.Nylon 66, especially glass fiber reinforced grades, can be effectively fire retarded with halogen-free products.

carbon fibers or carbon fibres

PREPARATION OF CARBON FIBRES

- The raw material used to make carbon fiber is called the precursor.
- About 90% of the carbon fibers produced are made from polyacrylonitrile (PAN).
- The remaining 10% are made from rayon or petroleum pitch.
- During the manufacturing process, a variety of gases and liquids are used.
- The precursor is drawn into long strands or fibers and then heated to a very high temperature without allowing it to come in contact with Oxygen. Without oxygen, the fiber can not burn.
- Instead, the high temperature causes the atoms in the fiber to vibrate violently until most of the non-carbon atoms are expelled.
- This process is called carbonization and leaves a fiber composed of long, tightly interlocked chains of carbon atoms with only a few non-carbon atoms remaining.

Characteristics and Applications of Carbon Fibers

Physical strength, specific toughness, light weight	Aerospace, road and marine transport, sporting goods
2. High dimensional stability, low coefficient of thermal expansion, and low abrasion	Missiles, aircraft brakes, aerospace antenna and support structure, large telescopes, optical benches, waveguides for stable high-frequency (GHz) precision measurement frames
3. Good vibration damping, strength, and toughness	Audio equipment, loudspeakers for Hi-fi equipment, pickup arms, robot arms
4. Electrical conductivity	Automobile hoods, novel tooling, casings and bases for electronic equipments, EMI and RF shielding, brushes
5. Biological inertness and x-ray permeability	Medical applications in prostheses, surgery and x-ray equipment, implants, tendon/ligament repair
6. Fatigue resistance, self- lubrication, high damping	Textile machinery, genera engineering
7. Chemical inertness, high corrosion resistance	Chemical industry; nuclear field; valves, seals, and pump components in process plants
8. Electromagnetic properties	Large generator retaining rings, radiological equipment

Elastomers

- Rubber is an Elastomer.
- Rubber is a polymer that has the ability to get back its original shape after being spoiled its shape. Elastomers are two types
 - Naturally available polymers like natural rubber
 - Laboratory made polymers like butyl rubber, Thiokol or neoprene.
- Elastomers have high molecular weight and its polymer chain can be able to bend without breaking.
- <u>Definition:</u> Elastomer can be defined as the long chain polymers which undergo elongation under stress and regain its original shape when stress is released.
- ▶ Long flexible chains, weak intermolecular forces and occasional cross linking are the three essential requirements of elastomer. Elastomers have high molecular weight and its polymer chain can be able to bend without breaking.

Properties:

- 1. It has a linear but highly coiled structure.
- 2. It has negligible inter chain sticking forces.
- 3. It absorbs water and it becomes sticky at higher temperature.
- 4. It is decomposed in presence of chemicals.

Rubbers are two types.

- 1. Natural Rubber
- 2. Synthetic (laboratory made) Rubber

• Natural Rubber and its Structure:

- The chemical name of natural rubber is cis-polyisoprene
- Natural rubber is made from the joining of isoprene (2-methyl-1, 3-butadiene) units by an enzymatic hydrolysis.
- The molecular weight of natural rubber molecule is in between 50,000-3,000,000.

Draw backs of natural rubber

- 1. It is soft at high temperature and hard; easily broken at low temperature. Its usage temperature range is very limited. It becomes hard and brittle during winter. It becomes soft and sticky during summer.
- 2. Weak and low tensile (means extension) strength (200 Kg/Cm²).
- **3.** It absorbs more water.
- **4.** It is not stable in mineral oils, solvents and oxidizing agents. It swells up in oils.
- **5.** Its shape is completely spoiled under outside force.
- **6.** When stretched to greater extent, it suffers from permanent deformation.
- 7. It is not durable
- **8.** It possesses tackiness (under pressure two sheets becomes one)
- **9.** The properties of natural rubber are improved by Vulcanization.
- **10.** Chemicals easily affect natural rubber.

Vulcanization of rubber

- ➤ This method was developed by Charles Goodyear in 1939
- > The **vulcanization** changes natural rubber into a heavily cross-connected and hard thermosetting polymer.
- ➤ When raw rubber is heated with sulfur at 140-180°C, it becomes high quality rubber. This process is called vulcanization. The suphur forms cross links between the chains of the rubber molecules.
- > Vulcanization brings the stiffening of the rubber.
- > Vulcanization process is the improvement of the undesirable properties of rubber.
- ➤ The **vulcanization** changes natural rubber into a heavily cross-connected and hard thermosetting polymer.

 Natural rubber is mixed with other substances (called additives) along with sulfur then vulcanized to get required properties and shape.

Advantages of vulcanization:

- 1) The working temperature range is -40 to 100° C.
- 2) Tensile (means extension) strength increases (2000 Kg/Cm²)
- 3) Vulcanized rubber absorbs very less water.
- 4) It can withstand strong force many times compared to natural rubber.
- 5) It can withstand to organic solvents like benzene, carbon tetrachloride, fats and oils.
- 6) It can withstand scratching
- 7) It is stable in light, atmospheric oxygen and ozone and not affected by atmosphere.
- 8) It has high elasticity and tensile strength.
- 9) Corrosive chemicals and oils do not affect it.
- **10**) Vulcanization process is the improvement of the undesirable properties of rubber.

Buna-S

Preparation:

- It is made from monomers 1,3-butadiene and styrene in the presence of a catalyst, cumene-hydroperoxide.
- This copolymer contains about 75% 1,3-butadiene and 25% styrene.

Properties:

- Good abrasion resistance (It can with stand scratching) and high load bearing capacity
- o It is decomposed in oil, waste water and ozone.
- o It cannot with stand strong force.
- o It acts as an electrical insulator.
- o Poorer resilience (rebounding)
- Strong and tough polymer
- Chemical resistance.

Uses:

- It is used to
- Make tyres that filled with compressed air.
- Make rubber sealing joints between metal parts, chewing gums and coated papers.
- Insulate electrical wires. Used for making wires and cable insulations.
- It is used in the foot wear industry for making shoe soles and footwear components. Make under surface of foot in shoe and heel of shoe
- Used as tank linings in chemical industries and as an adhesive.

Buna-N (NBR or Nitrile rubber)

Preparation:

- o The Nitrile rubber is made from monomers 1,3-butadiene and acrylonitrile in the presence of catalyst, cumene-hydroperoxide.
- o This copolymer contains about 75% 1,3-butadiene and 25% styrene.

Properties:

- Nitrile rubbers are stable in oil, heat, sunlight and acids.
- o It can withstand scratching and it has good tensile (extension) strength.
- o It is not stable in alkalis because of cyano groups.

Engineering applications:

- o They are used to
 - Make Fuel tanks, petrol carrying pipes, rubber sealing joints between metal parts and air craft parts.
 - Saturate paper, cloth and leather.
 - Make tyres along with vulcanized rubber.
 - Used in making of automobile parts, hoses, gaskets, printing rollers.
 - Used as blend component in tyre manufacture

Note; Buna-S & Buna-N synthetic rubbers gives Vulcanized rubbers.

Engineering applications of Elastomers

• Natural Rubber (an Elastomer) is the basic part of many products used in transportation, industrial, consumer, and medical sectors.

1. Transportation Sector:

- It is used to make
 - Tires that are filled with compressed air.
 - Rubber cloths that can withstand fire.
 - Inner rubber tubes
 - Belts that are used in cars etc.

2. Industrial Sector:

- Rubbers are used in
 - o Products for material carrying like
 - Material carrying belts
 - Tires for lift trucks
 - Small wheels on a leg of furniture
 - Earth quake related materials
 - o Other industrial items like
 - Liquid carrying pipes, belts and plates
 - Packing and sealing devices
 - Industrial gloves and car mats

3. Consumer Sector:

- These are used in
 - Rubber clothing (like Gloves) and Foot wear
 - Other consumer products like threads, erasers, golf balls, mats, articles, etc.

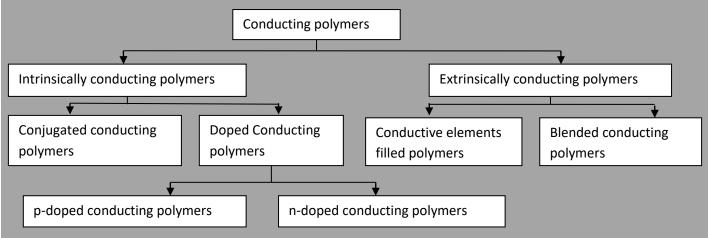
4. Medical sector:

- These are used in
 - Surgical gloves
 - Blood bags
 - Syringes
 - Tools inserted in the body (implantable devices)

7. What are conducting polymers? Explain the different types?

Conducting polymers:

• Conducting polymers have electrical conductivity in between a standard polymer and a metal.



Intrinsically conducting polymers:

- In this type of polymers, the electrical conductivity is due to repeated double bonds.
- These are two types.

i. Conjugated conducting polymers:

- O When bonding and non-bonding orbitals are overlapping over the complete chain of polymer, valence and conduction bands are formed with some band gap.
- When electric field is applied, the electrons from valence band jumps to conduction band.

ii. Doped Conducting polymers:

- The conductivities of general polymers can be increased by inserting either positive or negative charge on the polymer chain with charge transfer agents.
- There are two types of doping conducting polymers.

a. p-doped conducting polymers:

- These can be gotten by inserting a positive charge on the conducting polymer using an oxidizing agent.
- Two positive charges are formed in the polymer chain from the first and second oxidations by the removal of electrons.
- These positive charges travel to the nearby carbon atoms along the polymer chain in opposite direction to conduct electricity.

b. n-doped conducting polymers:

- These can be gotten by inserting a negative charge on the conducting polymer using a reducing agent.
- Two negative charges are formed in the polymer chain from the first and second reductions by the addition of electrons.
- O These negative charges travel to the nearby carbon atoms along the polymer chain in opposite direction to conduct electricity.

Extrinsically conducting polymers:

- The polymers show the conductivity due to outside addition of elements into them.
- There are two types of polymers in this.
 - i. Conductive elements filled polymers.
 - ii. Blended conducting polymers

i. Conductive elements filled polymers:

- It is a polymer gotten by filling conducting elements like carbon block, metallic fibers, metal oxides etc.
- o The polymer acts as binder to join the conducting elements.
- A polymer starts to show the conductivity at minimum concentration of conductive element added. The minimum concentration of this is called Percolation threshold.

Disadvantages:

- Decrease in the tensile (means extension) strength.
 - Breaks easily after a fixed length.

ii. Blended conducting polymers:

- These are gotten by chemical or physical mixing of a general polymer with conducting polymer.
- The blended conducting polymers have good physical, chemical and mechanical properties and they can be easily processed.
- **2. Doped Conducting Polymers**: ICP posses low conductivity, but their conductivity can be improved by creating positive or negative charges on the polymer chain by oxidation or reduction. This technique is called as Doping.
- It includes doping of ICP with a Lewis acid. Oxidation takes place & positive charge is developed on polymer chain increasing conductivity.
- Lewis acids like I₂, Br₂, FeCl₃, PF₆, AsF₆ can be used as p-dopants.
- e.g. doping of FeCl₃ in (C₂H₂)_n to form (C₂H₂)_n⁺ FeCl₄⁻ + FeCl₂ by oxidation.
- It includes doping of ICP with a Lewis base. Reduction takes place & negative charge is developed on polymer chain increasing conductivity.
- Lewis acids like lithium, sodium metals, naphthyl amines can be used as n-dopants.
- e.g. doping of Sodium in (C₂H₂)_n to form (C₂H₂)_n Na⁺ by Reduction.

Application of conducting polymers:

There are many applications of conducting polymers which is given as:

- 1. Used as anti-static subsances for photographic films.
- 2. Used as corrosion inhibitors.
- 3. Used in compact capacitors.
- 4. Used in transistors.
- 5. Used in light emiting diodes.
- 6. Used in sensors.
- 7. Used in solar cells.
- 8. Used in display screen of mobile and mini format television screen.



Polyaniline (PANI)



- Oxidation of aniline was studied from 19 century
 - Fritzsche in 1840 observed the appearance of a blue color during the aniline oxidation
 - Aniline means "indigo", "deep-blue"
 - First conductivity report by Buvet in 1967
- From mid-1980s most studied among the conducting polymers
- Easy synthesis in aqueous media, in a variety of different morphologies
- Many applications:
 - Molecular sensors
 - Rechargeable batteries
 - Antistatic coating
 - Non-volitale memory

Applications of Conducting Polyaniline

1.Used as biosensors, humidity sensors, gas sensors and

radiation sensors since

oxidised and reduced forms of polyaniline have different colours

- 2.Used as electrode material for rechargeable batteries.
- 3.Used as conductive track in PCBs.
- 4.Use d in anodic passivation of metals to control corrosion

Applications of PPY

- Polypyrrole (PPy), one of the important conducting polymers, have potential applications in drug delivery, sensors and corrosion protection.
- Based on its semiconductor properties PPy has been exploited as the electronic component in electronic devices, e.g., photoelectrochemical devices, organic light-emitting diodes and rectifying devices.
- PPy also shows physicochemical properties which impart to various applications in DNA sensors, actuator, and immunosensors.