

UNIT-IV

POLYMER CHEMISTRY

2.1 Introduction:

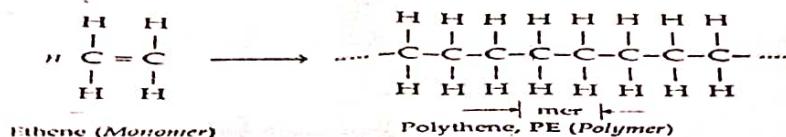
Polymers (Greek Poly=many, mers= Units or parts) are macromolecules (giant molecules of high molecular masses) build up by the linking together of a large number of small molecules (called monomers).

(or)

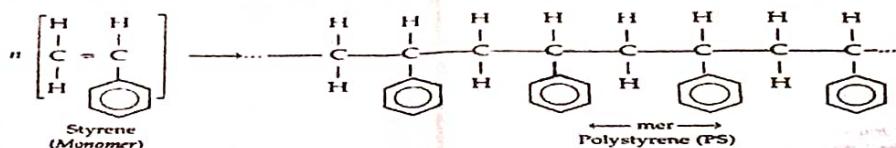
Polymer defined as a large number of small molecules (Monomers) which combine with each to form high molecular weight of the molecule is called polymer and the repeating units in a polymer are called monomers.

For example:

1. polyethene is polymer formed by linking together of a large number of ethane (C_2H_4) molecules thus:



2. polystyrene is a polymer of styrene



The number of repeating units (n) in polymer chain is known as **degree of polymerization**.

The properties of polymer and monomers are totally different.

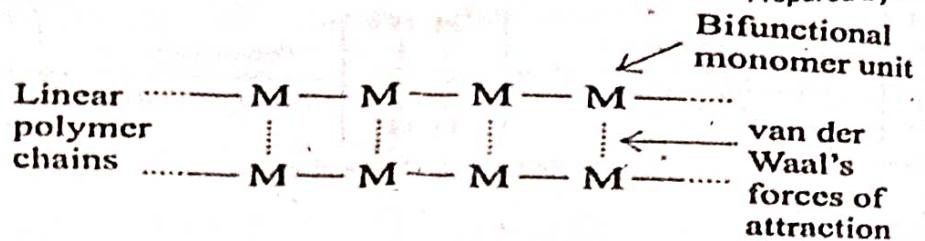
molecular weight of polymer = molecular weight of monomer X degree of polymerization

Polymers with high degree of polymerization are called high polymers, while the polymers with low degree of polymerization are called oligopolymers. The molecular weight of high polymers ranges from 5000 to 10,00,000 polymers may be natural (ex: cellulose, proteins, natural rubber, wool and silk) or synthetic (ex: polythene, PVC, Teflon, nylon and Bakelite).

Functionality: The number of bonding sites or reactive sites or functional groups present in monomer is known as **functionality**.

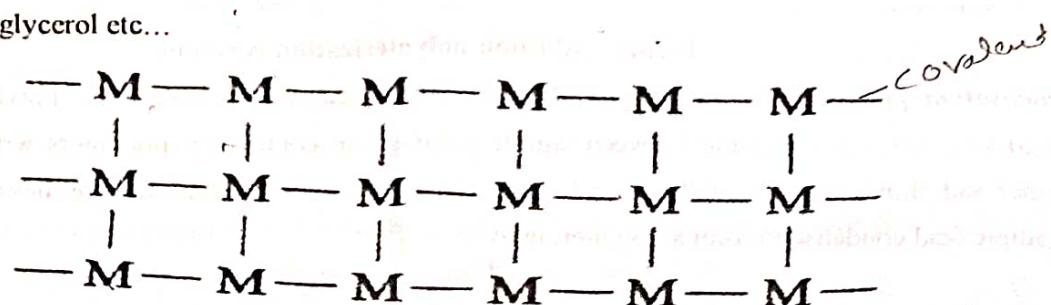
- a. **Bifunctional:** If functionality of monomer is two (bifunctional), that is two reactive groups attach side by side to each other. Hence they exhibit straight chain or linear polymers are formed. This type of polymers are soft, flexible and possess less strength. They are soluble in organic solvents.

Ex: Ethylene, styrene, vinylchloride etc....

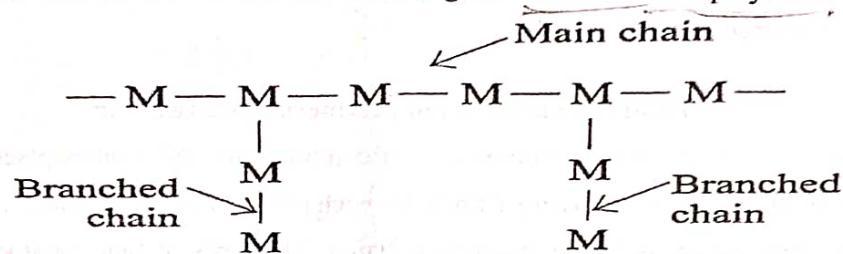


- b. **Trifunctional:** if the functionality of monomer is three, cross linked or three-dimensional network polymers are formed. The monomer molecules are joined to each other by covalent bonds and the movement of individual molecules is totally restricted

Ex: bakelite, glycerol etc...



- c. Mixture of Bifunctional and trifunctional monomers gives branched chain polymers.



2.2. Types of Polymerization:

The chemical reaction by which the monomers are combined to form polymers is called polymerization. (or) polymerization process large number of small molecules (monomers) linking together with or without elimination of small molecules (water, Ammonia, HCl) during the chemical reaction. H_2O , NH_3 , HCl

Types of polymerization: there are three types of polymerization

Addition polymerization: The number of small molecules which undergo addition chemical reaction without elimination of any byproduct if it develops polymer is known as addition polymerization. Addition polymerization is a reaction that yields a product, which is an exact multiple of the original monomeric molecule. The addition polymerization reaction must be instigated by the application of heat, light, pressure or a catalyst for breaking down the double covalent bonds of monomers. For example: Polythene, PVC, etc.

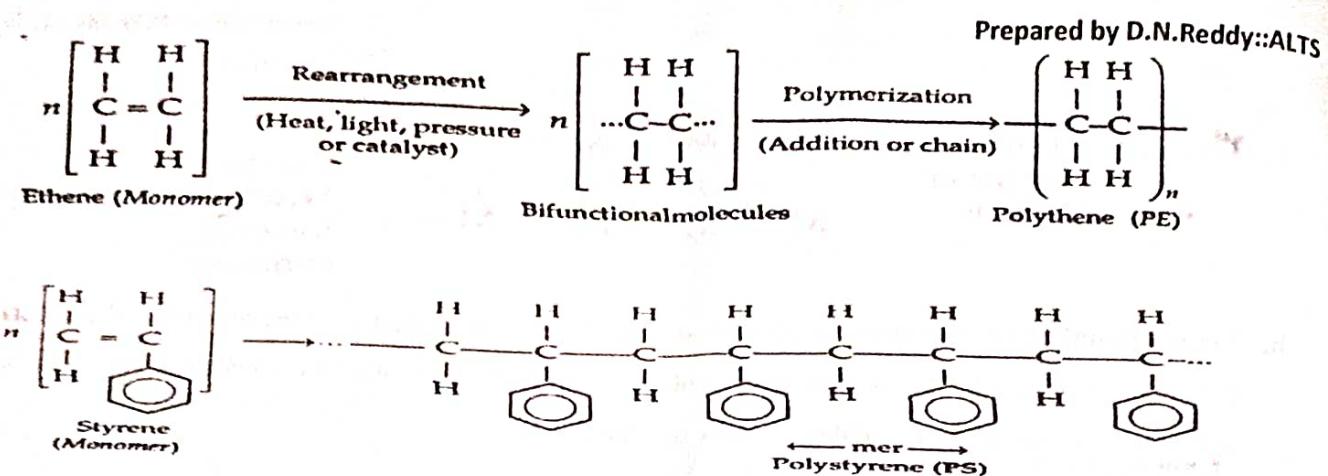


Figure: Addition polymerization reaction

Condensation polymerization or step growth polymerization reaction: Condensation polymerization may be defined as a reaction occurring between simple polar group containing monomers with the formation of polymer and elimination of small molecules like H_2O , HCl , NH_3 etc. for example: hexamethylene diamine and adipic acid condense to form a polymer, nylon 6:6.

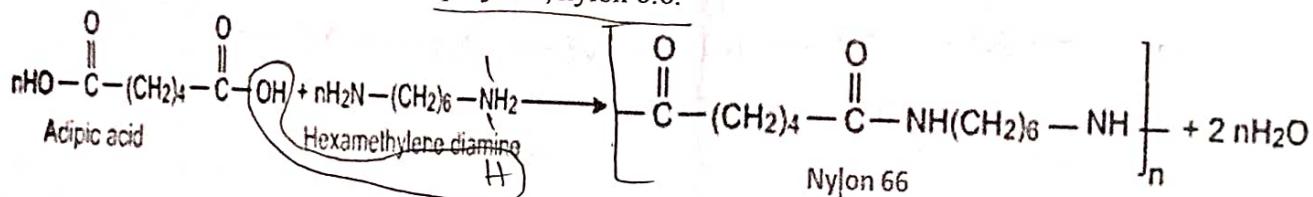
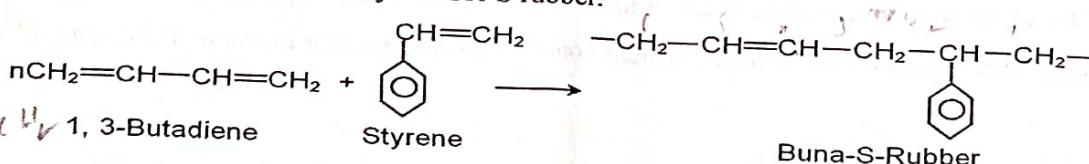


Figure: Condensation polymerization reaction

Thus condensation polymerization is an intermolecular combination, and it takes place through the different functional groups (in the monomers) having affinity for each other. When monomers contain three functional groups, it may give rise to a cross-linked structure polymer. The types of functional groups, which are most important in the condensation reactions, are.

1 st group	2 nd group	Product	Example
Hydroxyl (-OH)	Carboxyl (-COOH)	Polyester (-COO-)	Polyethylene terephthalate (terylene)
Amide(-NH ₂)	Carboxyl(-COOH)	Polyamide (-NH-CO-)	Nylon 6,6
Hydroxyl (-OH)	Isocyanate(OCN-)	Polyurethane (-OC-NH-)	Spandex fiber

Copolymerization: copolymerization is the joint polymerization of two or more monomer species. High molecular weights of the compounds obtained by copolymerization are called copolymers. For example: Butadiene and styrene copolymerize to yield GR-S rubber.



Differences between addition and condensation polymerization reaction

Addition/Chain polymerization	Condensation/step-wise polymerization
Only growth reaction adds repeating units one at a time to the chain	Any two molecular species present can react.
Number of units decreases steadily throughout the reaction.	Monomer disappears early in the reaction.
High molecular mass formed at once	Polymer molecular mass rises steadily throughout the reaction.
Longer reaction times have a little effect on molecular weight, but gives higher yields.	To obtain high molecular weight longer reaction time is essential.
The reaction mixture contains only monomers, high polymers and about 10^{-8} part of growing chains.	All types of molecular species are present at any stage
No by-products is formed	By-products are formed
Reaction proceeds chain growth mechanism	Reaction proceeds by a step growth mechanism
Examples: Polythene, PVC, Polystyrene etc.	Examples: Nylon66, Nylon 6, Terlene, Bakelite etc.

2.3. Polymerization mechanism

Polymerization reaction involves union of two or more small molecules to form a single large molecule is called polymer. Polymerization can be carried out by using different mechanism.

a. **Addition polymerization:** during the addition or chain polymerization reaction there are different types of active centers have been found to be formed polymerization.

1. **Free radical polymerization mechanism:** free radical polymerization reactions involve in following steps:

a. **Initiation step:** this step is considered to involve two reactions.

The first step is the production of free radicals, usually, by the homolytic cleavage of an inhibitor (or catalyst) to yield a pair of radicals (R^\cdot).



The second part of initiation involves the addition of this radical to do the first monomer molecule (M) to produce the chain initiating species (M_1^\cdot).



Thus the polymerization of monomer $CH_2=CHY$, takes in the form.

(the radical R^\cdot is often referred as an initiator radical or a primary radical)

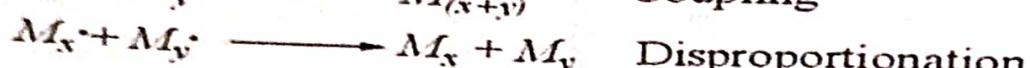
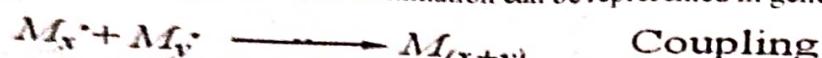
b. **Propagation step:** it consists of the growth of M_1^\cdot by successive additions of large numbers (hundreds and perhaps, thousands) of monomer molecules according to equations.



c. **Termination step:** at some point the propagating polymer chain stops growing and terminates.

1. By coupling or combination
2. More rarely, by disproportionation in which a hydrogen atom of one free radical center is transferred to another free radical center. These results in the formation of two polymer molecules, one saturated and one unsaturated.

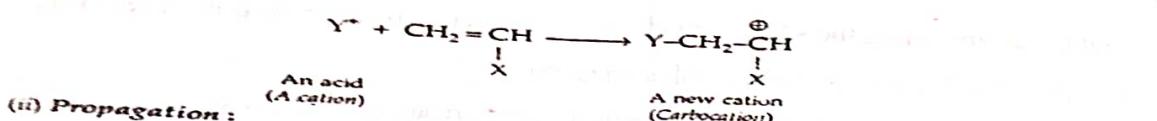
The two different modes of termination can be represented in general terms by



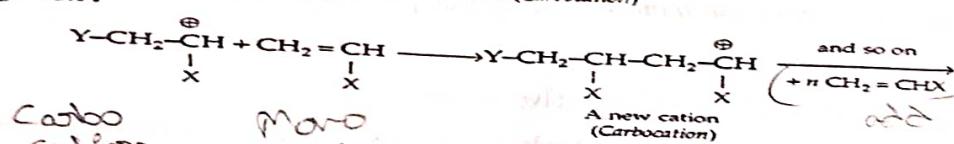
The term dead polymer signifies the cessation of the growth of the propagating radical.

- b. **Cationic mechanism of polymerization:** cationic mechanism of polymerization involves in the following steps:

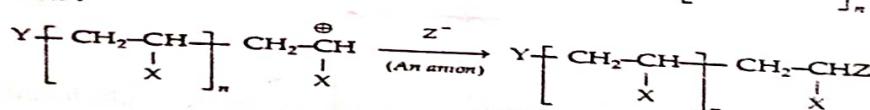
(i) **Initiation:**



(ii) **Propagation:**



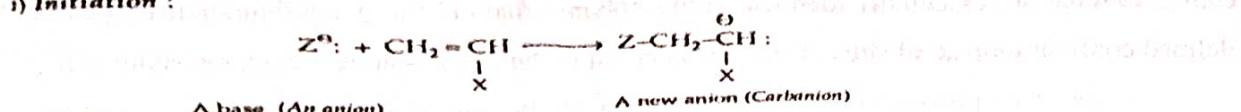
(iii) **Termination:**



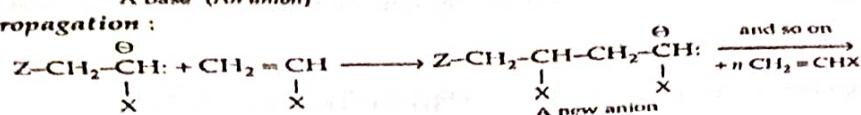
- c. **Anionic mechanism of polymerization:** Anionic mechanism of polymerization involves the following steps:

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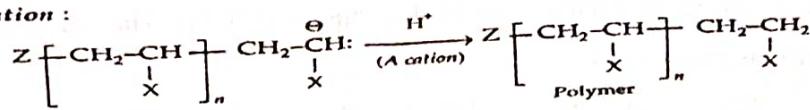
i) Initiation :



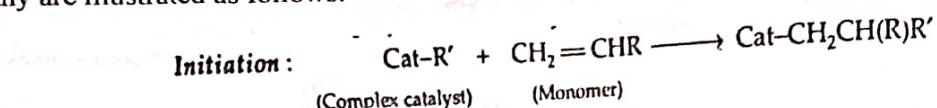
ii) Propagation :



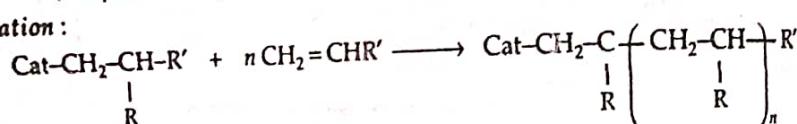
iii) Termination :



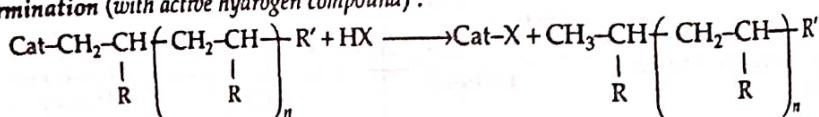
Co-ordination polymerization (or) Ziegler-Natta Polymerization: Ziegler (1953) and Natta (1955) discovered that the presence of a combination of a transition-metal halide like ($TiCl_4$ or $TiCl_3$, $ZrBr_3$, $TiCl_2$, halides of V, Zr, Cr, Mo, and W) with an organo-metallic compounds (like triethyl aluminum, trimethyl aluminum), stereospecific polymerization can be carried out. Mechanism of co-ordination polymerization many are illustrated as follows:



Propagation :



Termination (with active hydrogen compound) :



Ziegler-Natta polymerization is used to prepare polypropylene, polyethylene, polydiene etc. the importance of this method lies in the fact that stereospecific polymers are obtained. Thus during polymerization of propylene, using the conventional catalysts, normally random or Atactic polymer is obtained. By using suitable catalyst, solvent and temperature, it is possible to produce desired type (Atactic or isotactic or syndiotactic) of stereoisomers. The Atactic polymers are soft and elastic; while the other two are dense.

Stereospecific polymerization:

Plastics (or) Plastomers:

Plastics are high molecular weight organic molecules that can be moulded into desired shape by the applications of heat and pressure in the presence of catalyst.

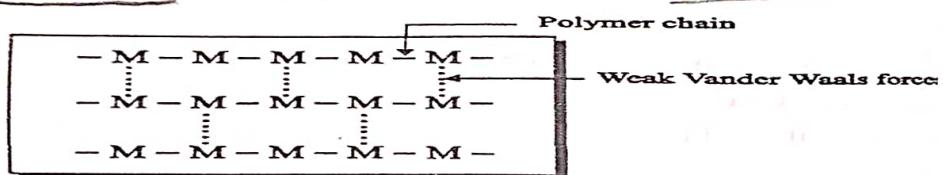
Classification of Plastics:

Plastics are classified in two types

1. Thermoplastics
2. Thermosetting plastics

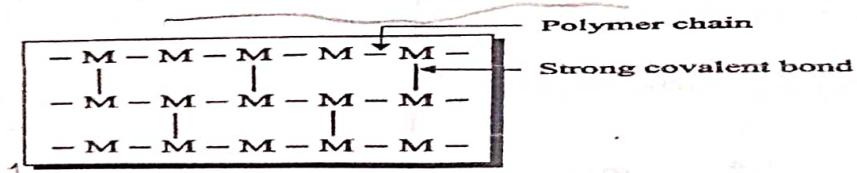
Thermoplastics: thermoplastics polymers are prepared by addition polymerization, they are linear (or) straight chain polymers and slightly branched chain polymers and they have weak vanderwaals forces of attraction.

Thermoplastics can be softened on heating and hardened on cooling. These polymers reheated they become soft again and can be reshaped or remolded to any shape. During reshaped or remolded does not change the chemical properties of polymer. These polymers are soluble in most all organic solvents.



Thermosetting plastics: thermosetting polymers are prepared by condensation polymerization. Various polymer chains are held together by strong covalent bonds (called cross linked).

Thermosetting polymers are initial heating fusible and further increasing the temperature plastics become harden, rigid and develop three dimensional structures and does not softened again. They cannot be reshaped again and again. They are almost insoluble in organic solvents.

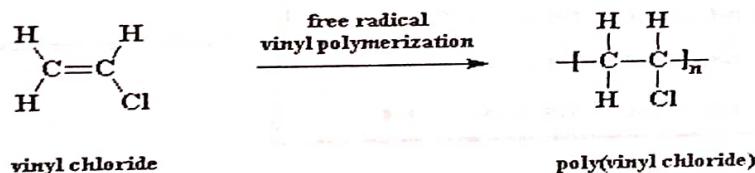


Differences between thermoplastic and thermosetting polymers

Thermoplastic polymer	Thermosetting polymer
They soften on heating and hardening on cooling	They do not soften on heating. On further heating, they become hard, rigid and infusible products.
They consist of long chain linear and branched chain polymers	Their consist of three dimensional or network polymers, joined by strong covalent bonds.
They are formed mostly by addition or condensation polymerization	They are formed by only condensation polymers
By reheating at suitable temperature, they can be softened, reshaped and thus reused.	They retain their shape and structure, even on heating. Hence they cannot be reshaped and reused.
They are usually soft, weak and less brittle	They are usually, hard, strong and more brittle.
All the polymer chains are held together by weak vanderwaals forces	All the polymer chains are linked by strong covalent bond.
They have less molecular weight	They have high molecular weight
They can be reclaimed from wastes	They cannot be reclaimed from wastes.
They are usually soluble in some organic solvents	They are insoluble in almost all organic solvents, due to strong bonds and crosslinking.
During heating there is no change in their chemical composition.	They undergo chemical changes such as, further polymerization and cross-linking during moulding process.
Examples: polythene, polypropylene, Polystyrene, PVC, nylons, etc.	Examples: Bakelite, epoxy resin, urea-formaldehyde resin.

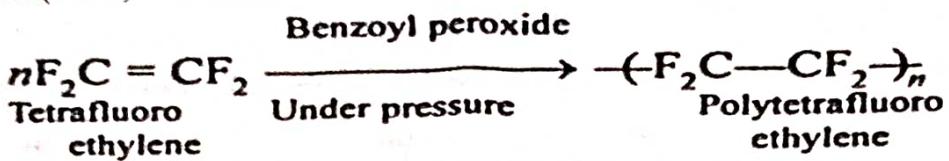
Polyvinyl chloride (PVC):

Vinyl chloride used as a monomer for preparation of poly vinyl chloride (PVC). PVC is prepared by heating a water emulsion of vinyl chloride in presence benzoyl peroxide or hydrogen peroxide in a autoclave under pressure.



Properties	Applications
It is colorless	It is used in table cloths, rain coats,
It is odour less powder	It is used in electric wires and cables
It is non-inflammable and chemically inert	It is used in toilet articals
It is soluble in chlorinated compounds like ethyl chloride and ketones	It is used in pipes, couplings, valves, TVs and radio components etc.
It is high resistance to atmospheric oxygen	Rigid PVC is used in refrigerator components, cycle, motor cycle guards, tubes and pipes etc.
It is chemically inert like inorganic acids, alkali etc.	

Teflon: Teflon is obtained by the polymerization of water emulsion of tetrafluoro ethylene under pressure in the presence of benzoyl peroxide as catalyst. Tetrafluoro ethylene (TFE) undergoes polymerization, poly tetrafluoro ethylene (PTFE) is obtained.

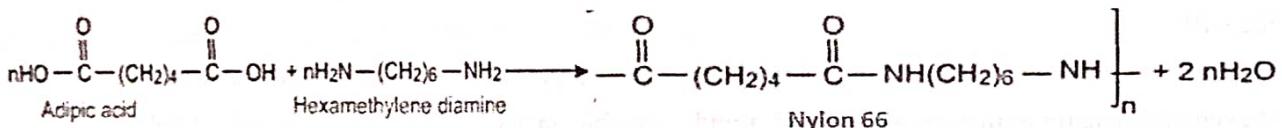


Properties	Applications
It is high crystalline nature (93-98%)	It is used as insulators of motors, generators, capacitors, transformers etc.
It is soluble in most of the solvents	It is used for making stopcocks for burettes
It exhibits high melting point (around 300°C)	It is used in non-lubricating bearings
It is good chemically inert	It is used for chemical storage, transporting tanks and carrying pipes
It exhibits high density	It is used in frying pans
It exhibits good mechanical properties	It is used in coating materials like bakery trays etc.
It exhibits good electrical properties	
It exhibits excellent thermal stability	

Condensation polymerisation

Nylons: Nylons are polyamides, which are synthetic polymers having amide groups. Nylons used mostly for making fibers, belong to this class.

Nylon-6:6:- it is obtained by the polymerization of adipic acid with hexamethylene diamine.



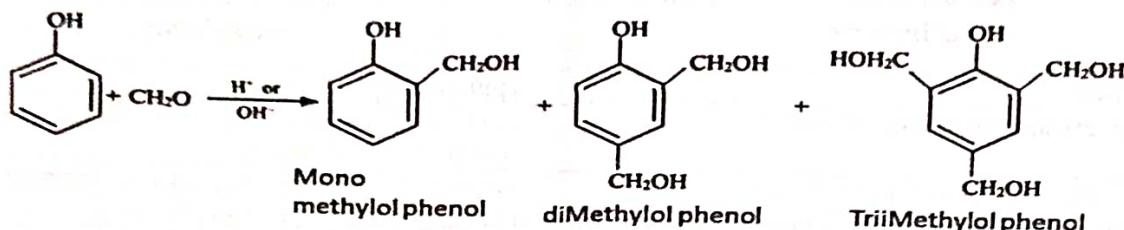
Properties	Applications
<ol style="list-style-type: none"> They are light, horny and have high melting point They are insoluble in common solvents They have good strength They absorb little moisture in nature They are very flexible and retain original shape after use. They are resistant to abrasion They have high strength and abrasive resistance 	<ol style="list-style-type: none"> Nylon 6:6 is primarily used for fibers It is used in making socks, ladies' hose, undergarments, dresses, carpets, etc. Nylon-6 and Nylon-11 are mainly used for moulding purposes for gears, bearings, electrical mountings, etc. Nylon bearings and gears work quietly without any lubrication They are also used for making filaments for ropes, bristles for tooth-brushes and films, tyre-cords etc.

Bakelite: it is one type of thermosetting resins. These are condensation polymerization products of phenolic derivatives (like phenol) with aldehydes (like formaldehyde). Most important member of this class is bakelite or phenol-formaldehyde resin.

It is prepared by condensing with phenol and formaldehyde in presence of acidic/alkaline catalyst. The initial reaction results in the formation of ortho-and para-hydroxy methyl phenol, which reacts to form linear polymer, novolac. Thus

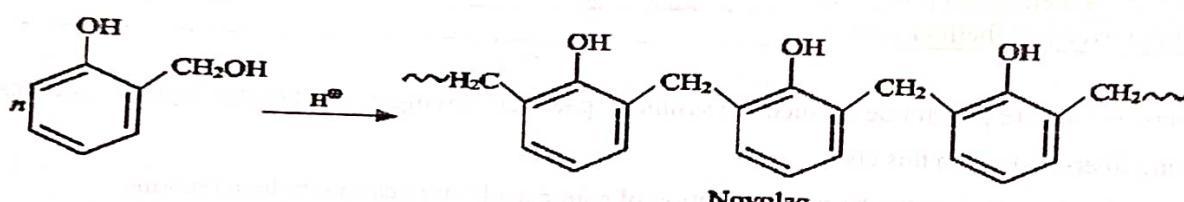
Step-1

The first step is reaction between phenol and formaldehyde, forms mono, di and tri-methylol phenols.



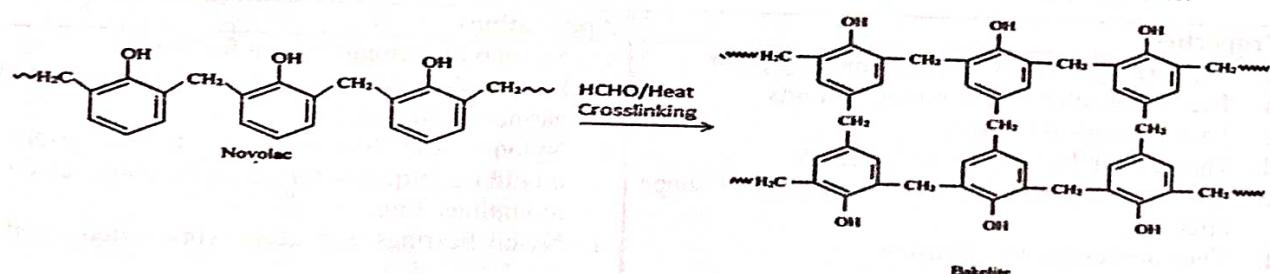
Step-II

When methylol phenols are heated with excess of phenol in presence of acid catalyst, the methylol phenols condense with phenol through methylene linkages to from novolacs.



Step-III

Further heating methylol phenol and phenol (or) Resole and Phenol both in the presence of a curing agent (hexamethylene tetramine) products hard, rigid, infusible, cross linked polymer is called bakelite.



During moulding, hexamethylene tetramine $[(\text{CH}_2)_6\text{N}_4]$ are added. The addition of hexamethylene tetramine provides formaldehyde, which converts the soluble and fusible novolac into a hard, infusible and insoluble solid of cross-linked structure.

Properties	Applications
<ol style="list-style-type: none"> Phenolic resins are hard, rigid and strong materials They have excellent heat and moisture 	<ol style="list-style-type: none"> It is used in domestic plugs and switches It is used for moulded articles like telephone parts, cabinets for radio and television.

<ul style="list-style-type: none"> - resistance c. They have good chemical resistance d. They have good abrasion resistance e. They have good electrical insulation characteristics f. They are usually dark colored pinkish brown g. Low molecular weight grades have excellent bonding strength and adhesive properties 	<ul style="list-style-type: none"> c. Handles for cookers and saucepans d. Distributor heads of cars e. Adhesives for grinding wheels and brake linings f. For impregnating fabrics, wood and paper. g. It is used in paints, varnishes, electrical insulators and protective coatings. h. It is used as hydrogen-exchanger resins in water softening
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Carbon fibers:

Carbon fibers (alternatively carbon fibers and graphite fiber) are fibers about 5-10 micrometers in diameter and composed mostly carbon atoms. Carbon fibers are usually combined with other materials to form a composite. Carbon fibers are new breed of high strength materials consisting of extremely thin fibers about 0.005-0.010mm in diameter. Carbon fibers containing 90% of carbon obtained by the controlled pyrolysis of appropriate fibers. Carbon fiber strong material that's also extremely lightweight. Five times stronger than steel, Two times stiffer, and about Two-Third times less in weight and also Carbon fibers have several advantages including high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion.

Preparation: majority of carbon fibers are synthesized from polyacrylonitrile (PAN) method and very less percent (10%) made from rayon or the petroleum pitch process. The synthesis of carbon fibers involves two kinds of processes like chemical and mechanical in nature.

Synthesis of Carbon fibers from polyacrylonitrile shown below

1. Spinning:

Acrylonitrile plastic powder mixed with methyl acrylate or methyl methacrylate (MMA) reacted in presence of catalyst to form polyacrylonitrile plastic during polymerization process.

The plastic is mixed with certain chemicals and pumped through tiny jets into a chemical bath or quench chamber resulting plastic coagulates and solidifies into fibers. The spinning step is very important to develop internal atomic structure of the fiber is formed during the process.

The fibers are cleaned and stretched to the suitable fiber diameter. This stretching helps to align the molecules within the fiber and provides the basis for the formation of the tightly bonded carbon crystals after carbonization.

2. Stabilizing:

Before carbonization process, fibers are need to be chemically altered to convert their linear atomic structure to a more thermally stable branched structures. This is achieved by heating the fibers in air about

200 - 300°C for 30-120 minutes. As a result, the fibers are interacting with oxygen molecules from air and rearrange their atomic structure.

3. Carbonization:

After stabilizing the fibers, they are heated about 1000-3000°C for several minutes in a furnace filled with glass mixture without oxygen, which prevents the fibers burning in the very high temperatures. The gas pressure inside the furnace is maintained higher than the outside atmospheric pressure. The point of exit and enter the fibers into the furnace are completely closed without enter the oxygen. Resulting fibers began to lose non-carbon atoms like O, H, N and very less carbon atoms, in the form of various gasses like water, ammonia, carbon monoxide, carbon dioxide, H, N, and others. The remaining carbon atoms are tightly bonded carbon crystals that are aligned more or less parallel to the long axis of the fiber.

4. Treating the surface:

Fibers surface does not active with composite materials such as epoxies and other materials. To improve the bonding properties of fiber surface is slightly oxidized. The addition of oxygen atoms to the surface of fibers provides better bonding properties and also etches, rough surface for better mechanical bonding properties. Oxidation is carried out, fibers are mixing with different gasses like air, carbon dioxide or ozone or various liquids such as sodium hypochlorite or nitric acid. The surface treatment process must be very carefully and controlled to avoid formation of tiny surface.

5. Sizing:

After surface treatment, the fibers are coated to protect them from damage during winding or weaving and process is called as sizing. Coating materials are opted which is compatible with the adhesive employed to form composite materials. Ex: coating materials epoxy, polyesters, nylon, urethane etc..

The coated materials are wound onto cylinders called bobbins. The bobbins are loaded into a spinning machine and the fibers are twisted into yarns or various sizes.

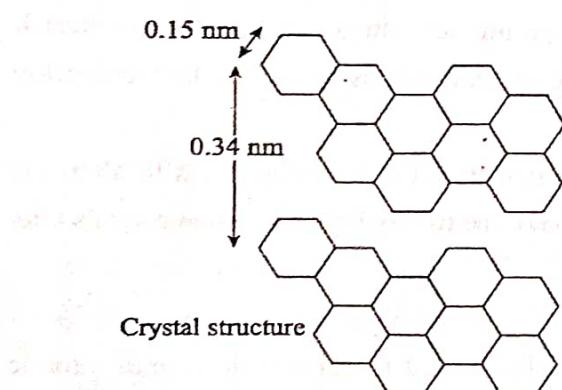


Fig: turbo static carbon crystal structure

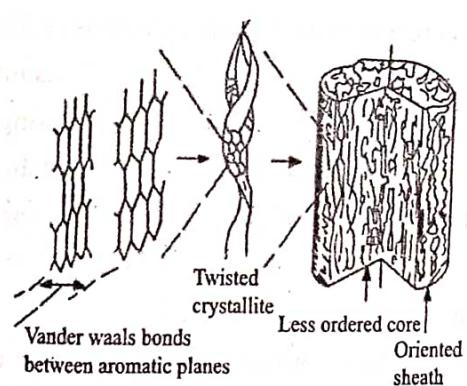


Fig: Carbon fiber schematic diagram

The crystal structure of turbo static carbon with a distance of 0.34 nm between the layers of planes is higher than that in the graphite. Wide angle X-ray diffraction has been used to obtain the characteristic parameters for carbon fibers.

The carbon fibers possess the following properties:

1. Carbon fiber has very high tensile strength
2. It has low thermal expansion.
3. It is a light weight material having low density.
4. It is a good conductor of electricity.
5. It can wear a high resistance.
6. it is high specific strength and stiffness
7. it is excellent chemical inert (except high oxidizing environment)
8. it is biocompatibility

Applications:

Carbon fibers are extensively used for the replacement of metals in the most of critical applications such as

1. Aeronautical Industry: It is mostly used in the aerospace and aircraft industries.
2. Automobile Industry: Automotive body is also made up of the carbon fiber (Bonnet, bumper, engine cover, Car Body parts etc.)
3. Sports Industry: It is used in making sports equipment such as light weight badminton rackets, golf stick etc.
4. Civil Engineering: Lightweight pre-cast concrete, earthquake protection.
5. Medical Field: Robot for internal operations, Medical and bio instruments
6. Power Plant Field: Constructing up of wind mill blades, natural gas storage and transportation, fuel cells.
7. Oil exploration: deep water drilling platforms, drilling pipes
8. Other Industry: It is used for building and construction material, Rechargeable batteries and fuel cell electrodes and Portable powers.
9. Carbon nanotubes: semiconductor materials, space craft, chemical sensors and other uses.

ADVANTAGES:

- It has long working life.
- It's density is less than density of steel.
- It is insensitive to change in temperature.
- It's properties is much better than any of the other metals.
- It's compressive strength is greater than all the reinforcing material.

DISADVANTAGES:

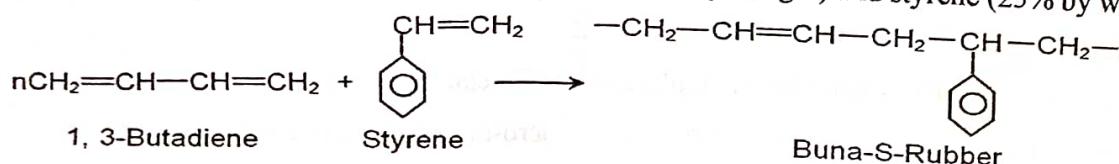
- It is very costly.
- It is little bit harmful for the human body as it cause some form of cancer of the lungs.

Synthetic rubbers (or) elastomers:

An elastomer or synthetic rubber is any vulcanisable man-made rubber-like polymer, which can be stretched to at least twice its length, but it returns to its original shape and dimensions as soon as stretching force is released.

The term synthetic rubber is misnomer, because it is not chemically identical with the natural rubber. It is thus more appropriate to use the term artificial rubber. Instead of synthetic rubber. The main types of artificial rubbers produced on large scale are:

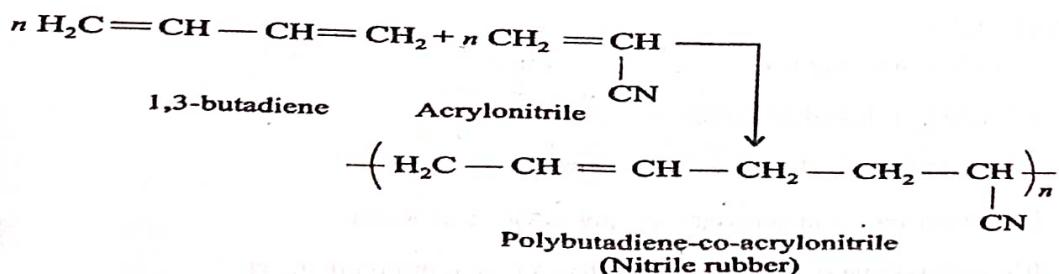
Buna-S* (or) GR-S (or) SBR (or) Styrene rubber: it is probably most important type of synthetic rubber, which is produced by copolymerization of butadiene (about 75% by weight) and styrene (25% by weight).



Since Buna-S rubber contains double bonds to vulcanization can be done in the same way as natural rubbers either by sulphur or sulphur monochloride (S_2Cl_2). Less sulphur and more accelerators are required for vulcanization. Carbon black as reinforcing filler is essential to achieve good physical properties.

Properties	Applications
<ol style="list-style-type: none"> High abrasion resistance High load-bearing capacity and resilience It swells in oils and solvents Low oxidation resistance, as it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere. 	<ol style="list-style-type: none"> It is mainly used in motor tyres It is used shoe soles, foot wear components, insulation of wire and cables It is also used in gaskets, carpet backing, adhesives and tank lining etc.

Buna-N* (or) GR-A (or) nitrile rubber: to prepare nitrile rubber, butadiene (75% by weight) and acrylonitrile (25% by weight) are mixed with water so as to get emulsion which is stabilized by adding soap (emulsifying agent). By this technique of emulsion polymerization, while nitrile rubber is manufactured.



Properties	Applications
<ul style="list-style-type: none"> a. It is excellent resistant to heat, sunlight, oils, acids and salts b. It is less resistant to alkalis (due to presence of cyano group) c. Compared to natural rubber, nitrile rubber (vulcanized) has more heat resistance and it may be exposed to high temperatures. d. It has good abrasion resistance, even after immersion in gasoline or oils. 	<ul style="list-style-type: none"> a. It is used in conveyor belts b. It is used in lining of tanks and gaskets c. It is used printing rollers d. It is used in oil resistance foams e. It is used in automobile parts and high altitude air-craft components f. It is used in oil resistance foams g. It is used in automobile parts and high altitude air-craft components

6. Conducting polymers:

Generally polymers like plastics, elastomers are regarded as electrical insulators and dielectric materials. Because of the presence of strong C-C covalent bond. But under certain circumstances, polymers with improved electrical conductivity prepared by the addition of some additives such as conducting metals like copper, silver or other materials. Thus those polymers which conduct electricity are called conducting polymers.

Organic polymers with highly delocalized π -electrons system having electrical conductance on par with metallic conductor is called a conducting polymer. The conduction in the polymers mainly due to the following reasons.

Reason for the conduction in the polymer:

- a. Presence of unsaturated conjugated double bonds in the polymer
- b. Addition or removal of electron (doping) in to the polymer.

Examples: polyaniline, Polyacetylene, polypyrrole

Synthesis of conducting polymers:

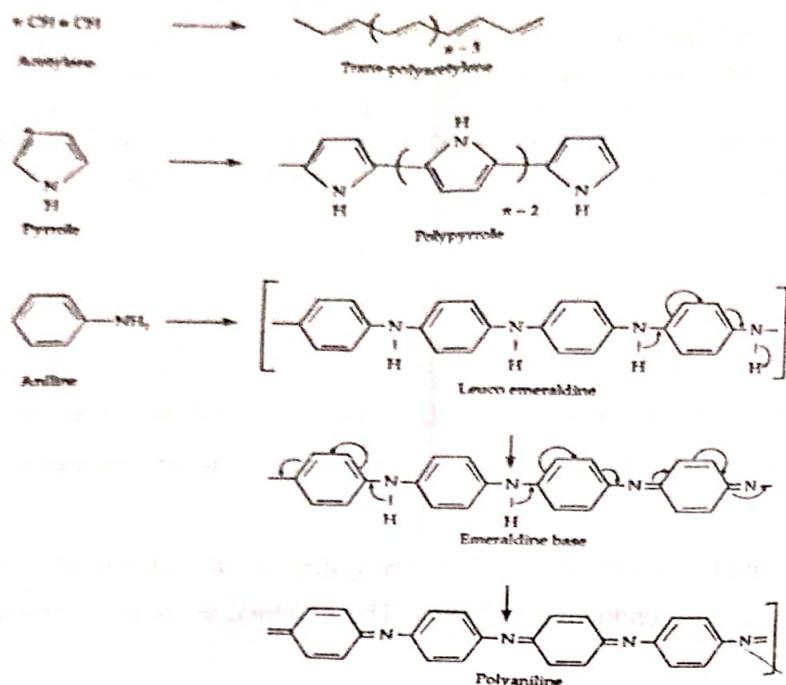
a. Conducting polymers having conjugated π -electron in the back bone.

The polymer whose backbone is made up of molecules that contain conjugated π -electrons which increase their conductivity to a large extent. This is because, overlapping of conjugated π -electron over the entire back bone results in the formation of valence bands as well as conduction bands which extends over the entire polymer molecule.

Example:

1. Polyacetylene is prepared by the addition polymerization of acetylene. Acetylene gas passed over the Ziegler natta catalyst ($Ti(oBu)_4$ and $Al(C_2H_5)_3$) to get Polyacetylene.
2. Polypyrole is prepared by oxidation of pyrole with $FeCl_3$.

3. Polyaniline is prepared by the slow addition of aqueous solution of ammonium per sulphate to a solution of aniline in aqueous HCl at lower temperature ($0\text{--}5^\circ\text{C}$). the precipitate formed is separated by filtration. Which is emeraldine hydrochloride.



All the three forms of polyanilines have conductivities of the order of 10^{-10} s cm $^{-1}$. Conductivity of these polymers, having conjugated π -electrons in the back bone is not sufficient for their use in different applications.

b. Doped Conducting polymers:

In comparison of to conventional polymers, organic conjugated π -electron polymers can be easily oxidized or reduced as they have low ionization potentials and high electron affinities. Their conductivities can be increased by creating positive or negative charge on polymer back bone by oxidation or reduction.

To become electrical conductive, the electron of the polymer need to be free to move. The polymers having conjugated double bond has to be discussed either removing electron from or inserting electron into polymer by oxidation or reduction. This process is known as doping.

Types of doping

- 1. p-doping (oxidation):** it is done by oxidation process. Conducting polymers treated with lewis acids or halogens or with iodine vapour or iodine in CCl_4 .

Examples of p-dopant: I_2 , Br_2 , $AlCl_3$, AsF_5 , $FeCl_3$ etc...

2. n-doping (reduction): it is done by reduction process. Conducting polymers treated with lewis bases like sodium naphthalide or alkali metals.

Examples of n-dopant: Na, K, Lithiumnaphthalides, etc..

Example of Polyacetylene:

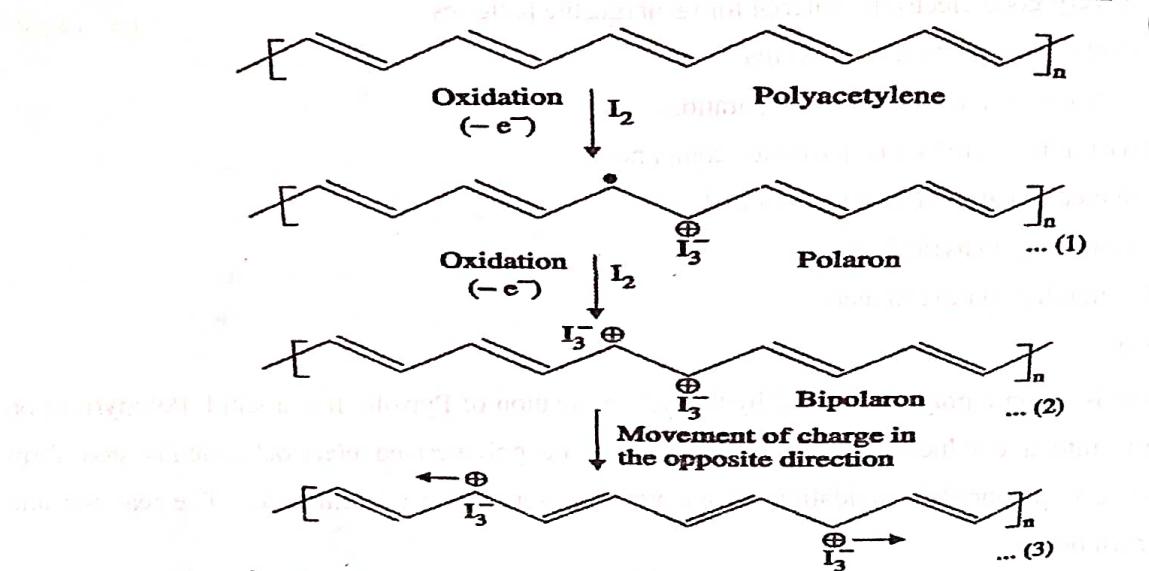
The conductivity of cis-polyacetylene is less when compare to trans Polyacetylene. The conductivity of Polyacetylene can be improved by either p-doping or n-doping.

p-Doping of polyacetylene:

It involves the following two steps.

Step-I involves the oxidation of a Polyacetylene with iodine vapor (lewis acid). During oxidation, the iodine molecule accepts an electron from Polyacetylene chain and becomes I_3^- . Now the Polyacetylene chain carrying the +ve charges is called polaron.

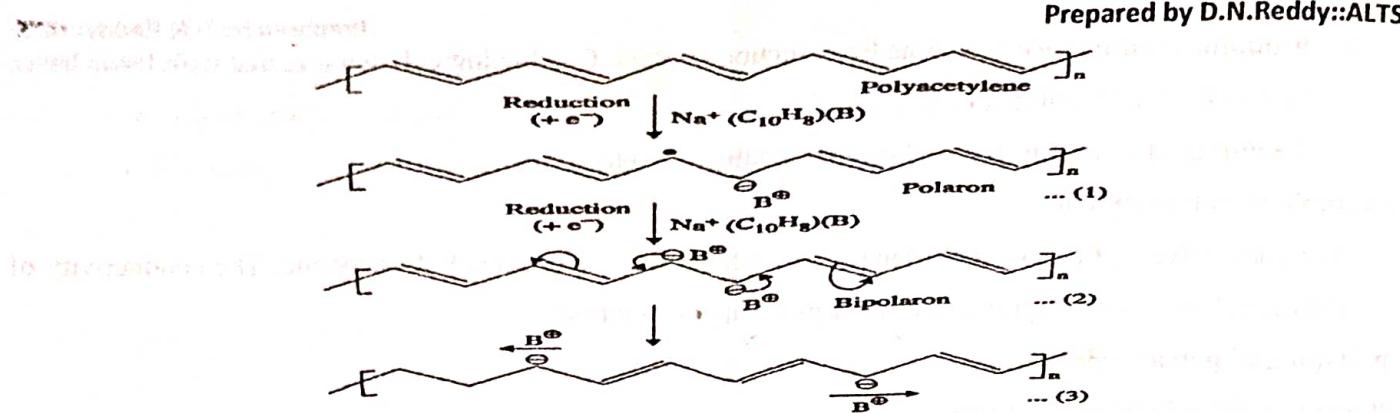
Step-II the second oxidation of polaron produces two +ve charges on the chain called bipolaron. This +ve charges are mobile because of delocalization and responsible for electrical conductance.



n-doping of Polyacetylene:

Step-1 involves reduction of Polyacetylene with sodium naphthalide ($Na^+(C_{10}H_8)^-$). During the reduction sodium naphthalide donates an electron to Polyacetylene chain. Now Polyacetylene carrying the -ve (negative) charge is called polaron.

Step-II involves second reduction of polaron to produce two -ve (negative) charges on the chain are called bipolaron. This -ve charges are mobile because of delocalization and responsible for electrical conductance as shown in figure.

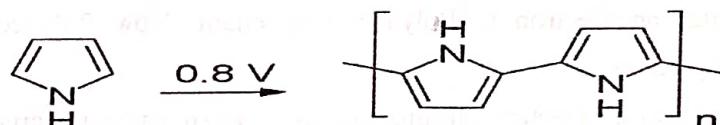


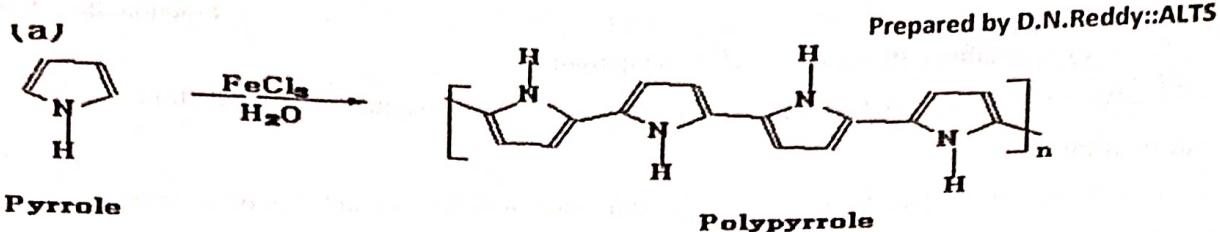
General applications of conducting polymers:

- it is used in solar cells
- it is used in telecommunication systems
- it is used in photovoltaic devices
- it is used in non-linear optical materials
- it is used in very good electrode material for rechargeable batteries
- it is used in antistatic coating for clothing
- it is used as a membrane film for gas separations
- it is used wiring in aircrafts and aerospace components
- it is used in electro catalytic materials in fuel cells
- it is used in making analytical sensors
- it is used in making ion exchangers

Polypropylene:

Polypyrrole is organic polymer formed by the polymerization of Pyrrole. It is a solid, Polypyrrole on oxidation converts into a conducting polymer. Pyrrole can be polymerized electrochemically and form Polypyrrole. Pyrrole is prepared by oxidation of pyrrole in presence of ferric chloride. The reaction and mechanism is shown below.



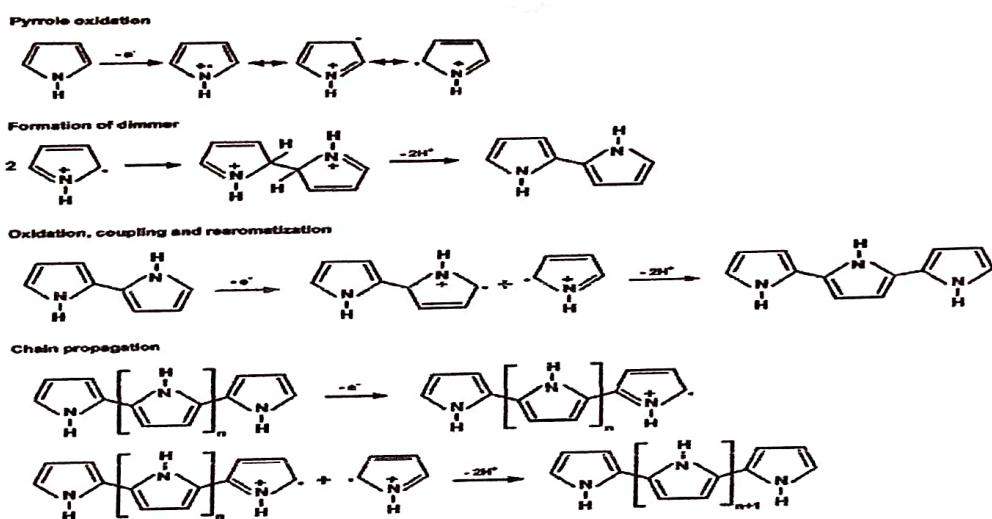


The process occurred via the formation of the pi-radical cation $C_4H_4NH^+$. The electrophile attacks on the 2nd carbon of unoxidized molecules of pyrrole to give dimeric cation $(C_4H_4NH)_2^{++}$. The same process repeats itself many times, resultant polypyrrole formed. Conductive forms of polypyrrole (PPy) are synthesized by oxidation of p-doping of the polymer.



The polymerization and p-doping can also be carried out electrochemically. The resulting conductive polymer are peeled off of the anode. Cyclic electrochemical synthesis of pyrrole is done by voltammetry and conductometric techniques.

Mechanism:



Properties:

1. Polypyrrole films are yellow but darken in presence of air
2. Doped filims are blue or black based on the degree of polymerization and film thickness
3. They are amorphous, showing only weak diffraction
4. It is usually designed as one dimensional verses quasi-unidimensional
5. Undoped and doped materials are insoluble in solvents but they swell in nature

6. They are stable with air up to 150°C temperature.

7. Polypyrrole is insulator, but its oxidized derivative are good electrical conductors.

Applications:

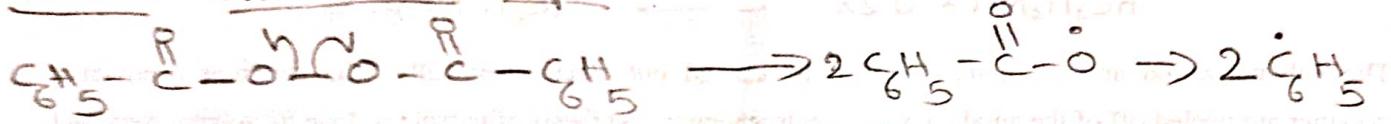
1. Polypyrrole and its derivatives are used in electrical devices and chemical sensors

2. It is used as catalyst for support for fuel cells

3. It has been used as artificial muscles

4. It is used in microwave synthesis of multi layered carbon nanotubes.

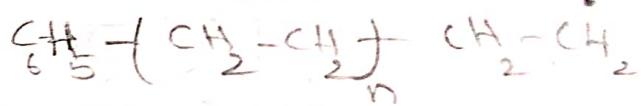
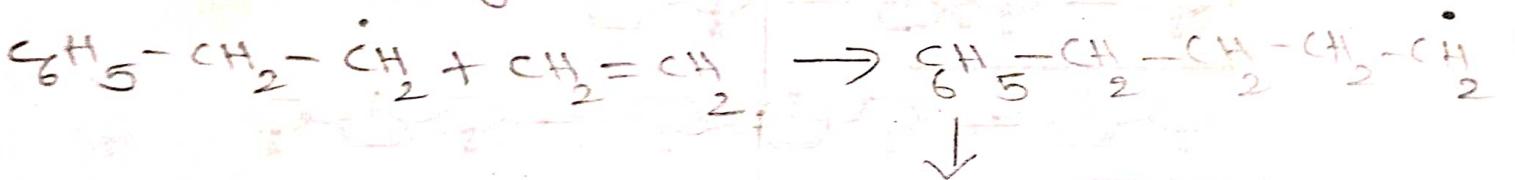
Chain initiation steps:-



Benzoyl peroxide



Chain propagation step:-



Chain termination

