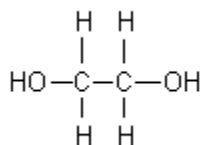


It is the presence of two functional groups that allow such molecules to behave as monomer giving them ability to form chains and polymerize.

Classify the following on the basis of their functionality:

- a. Ethylene glycol: Its chemical formula is:

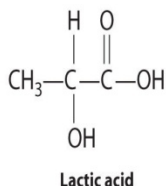


Functional groups present are 2 hydroxyl groups. Hence it is bifunctional.

- b. Vinyl chloride. Its chemical formula is $\text{CH}_2=\text{CHCl}$

Number of double bonds is one. Hence it is bifunctional.

- c. Lactic acid: Chemical formula is



Functional groups present are 1 hydroxyl group and 1 carboxylic acid group. Hence it is bifunctional.

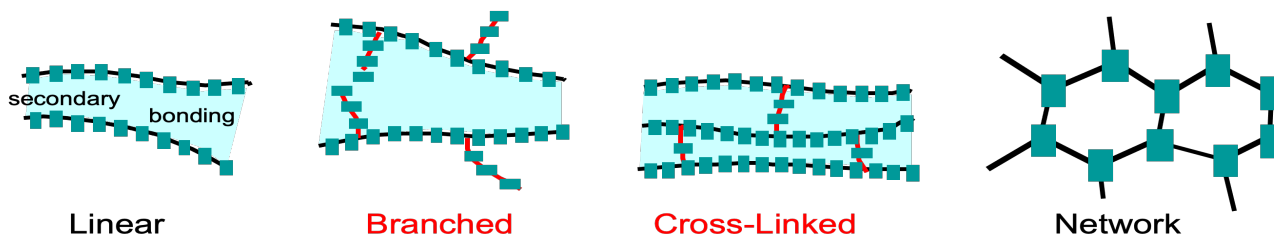
Significance of functionality:

1. When the functionality of monomer is two, linear or straight chain polymer molecule is formed. Example of bifunctional monomer is vinyl monomers, adipic acid, ethylene glycol, amino acid, hexamethylene diamine etc.
2. When the functionality of monomer is three, a three dimensional network polymer is formed. Example is phenol, melamine etc.
3. When a trifunctional monomer is mixed with a bifunctional monomer, a branched chain polymer is formed.
4. When a bifunctional monomer is mixed with a trifunctional monomer, a three dimensional network polymer is formed.

Classification of Polymers

1. Based on Structure/Shape of polymer

Polymers can be linear, branched, cross linked or networked.



- Linear polymers have monomeric units joined end to end in single chains. There may be extensive van der Waals and hydrogen bonding between the chains. Examples: polyethylene, PVC, nylon.
- In branched polymers, side-branch chains are connected to main chains. HDPE – high density polyethylene is primarily a linear polymer with minor branching, while LDPE – low density polyethylene contains numerous short chain branches. Greater chain linearity and chain length tend to increase the melting point and improve the physical and mechanical properties of the polymer due to greater crystallinity.
- In cross-linked polymers, adjacent linear chains are joined to one another at various positions by covalent bonding of atoms. Examples are the rubber elastic materials.
- Small molecules that form 3 or more active covalent bonds create structures called network polymers. Examples are the epoxies and polyurethanes.

2. Based on number of monomers:

Polymers can be homopolymers when only one type of monomer is present (eg: polyethylene, polypropylene, polyvinyl chloride).

Polymers can be co-polymer when two or more types of monomeric units are present (eg: styrene, acrylonitrile etc)

Homopolymers – only one monomer (repeating unit): - A – A – A – A – A – A – A -

Copolymer – more than one monomer

Statistical Copolymers Also called random copolymers. Here the monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain: ~ABBAABAABBBABAABA~.

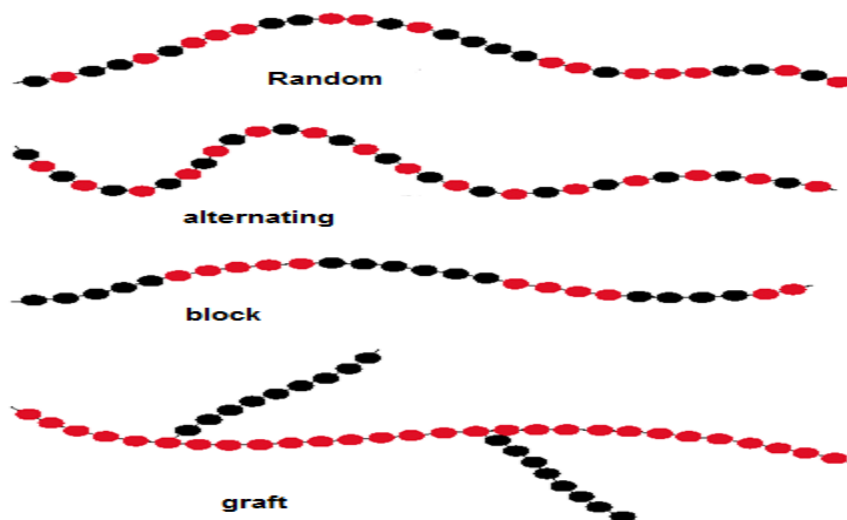
Alternating Copolymers Here the monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain: ~ABABABABABABABAB~.

Block Copolymers

Instead of a mixed distribution of monomeric units, a long sequence or block of one monomer is joined to a block of the second monomer: $\sim\text{AAAAA}-\text{BBBBBB}\sim\text{AAAAAA}\sim\text{BBB}\sim$.

Graft Copolymers

As the name suggests, side chains of a given monomer are attached to the main chain of the second monomer: $\sim\text{AAAAAAA}(\text{BBBBBB})\sim\text{AAAAAA}(\text{BBBB})\sim\text{AAA}\sim$.



Red Dot: A; Black Dot: B

3. Based on Origin:

Synthetic organic polymers

Biopolymers (proteins, polypeptides, polynucleotide, polysaccharides, natural rubber)

Semi-synthetic polymers (chemically modified synthetic polymers)

Inorganic polymers (siloxanes, silanes, phosphazenes)

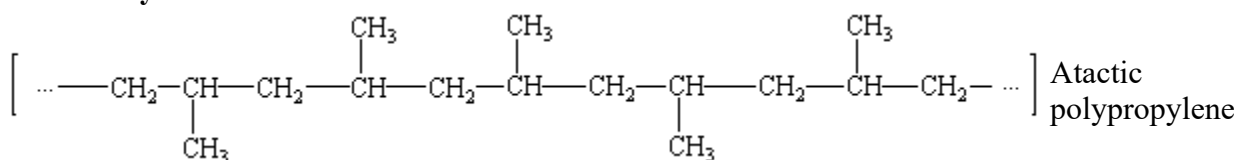
4. Based on Tacticity:

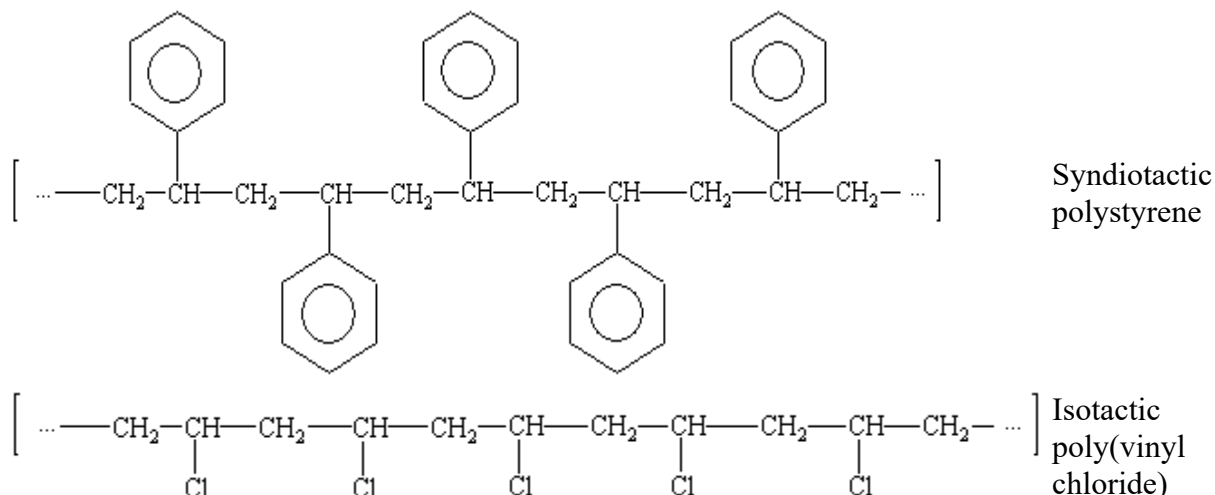
Polymers with regular substituents on the polymer chain possess a property known as **tacticity**. Tacticity results from the different ways in which the substituents can be arranged on the polymer backbone.

When the substituents are arranged in an irregular, random fashion, the polymer is **atactic** (literally, no arrangement).

When the substituents are all on the same side of the chain, the polymer is **isotactic** (literally, the same arrangement).

If the substituents alternate regularly from one side of the chain to the other, the polymer is **syndiotactic**.





5. Based on its behavior to heat

Polymers may be classified according to the mechanical response at elevated temperatures: Thermoplasts and Thermosets.

Difference b/w thermoplast and thermoset polymer

	Thermoplastic polymer	Thermoset polymer
1.	They are low molecular weight and are soluble in suitable solvent	They are high molecular weight and are insoluble in any solvent.
	Linear and branched polymer are thermoplastics	They have three dimensional, cross-linked structures.
2	Adjacent polymer chains are held together by either Van-der-Waals forces or by dipole-dipole forces or by H-bonds	Adjacent polymer chains are held together by strong covalent bonds or cross-links.
3	They are formed by either addition or by condensation polymerization reactions.	They are formed by condensation polymerization reactions.
4.	They soften on heating and stiffen on cooling	They do not soften on heating
5.	They can be remoulded, reshaped and reused	They cannot be reused.
6.	They can be recycled	They cannot be recycled
7.	They are tough	They are brittle
8.	There is no change of chemical composition during remoulding	There is change of chemical composition during remoulding
9	Thermoplastics are very soft and ductile	Thermoset polymers are harder, stronger, more brittle and have better dimensional stability.
10.	Example: PE, PP, PVC, PMMA, PS, PTFE, Nylon, Polyester	Example: vulcanized rubber, Epoxy, phenolic resins, XLPE etc.

Addition and Condensation Polymerization:

Addition Polymerization: Addition polymers are formed when an unsaturated organic compound (presence of double/triple bond) react to form long chain polymer molecule and when no small molecules are eliminated during the reaction.

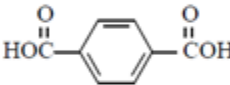
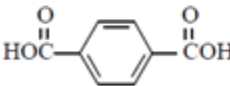
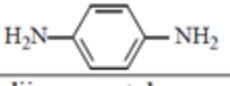
Some Common Addition Polymers

Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation bottles, toys
Poly(vinyl chloride) (PVC)	$-(CH_2-CHCl)_n-$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Polystyrene (PS)	$-[CH_2-CH(C_6H_5)]_n-$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$-(CH_2-CHCN)_n-$	acrylonitrile $CH_2=CHCN$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$-(CF_2-CF_2)_n-$	tetrafluoroethylene $CF_2=CF_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$-[CH_2-C(CH_3)(CO_2CH_3)]_n-$	methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$-(CH_2-CHOCOCH_3)_n-$	vinyl acetate $CH_2=CHOCOCH_3$	soft, sticky solid	latex paints, adhesives

Condensation Polymerization: The process of formation of polymer via condensation of two different bi-or poly functional monomers having functional groups which have affinity to each other. Condensation polymers form when:

- bifunctional monomers combine to form a long chain polymer molecule.
- small molecules like water is eliminated during the reaction.

Some Common Condensation Polymers and Their Monomers

Monomers Names and Formulas	Polymer Name and formula	Typical Uses
1,6-diaminohexane $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ hexandioic acid (adipic acid) $\text{ClC}(\text{O})(\text{CH}_2)_4\text{CCl}$	Nylon 66, a polyamide $\text{---N---}\left(\text{C}(=\text{O})\text{---}(\text{CH}_2)_4\text{---C}(=\text{O})\text{---N---}(\text{CH}_2)_6\text{---N---}\right)_n\text{C}(=\text{O})\text{---}$	Women hose, rope, fabric carpeting
Terephthalic acid  Ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$	Dacron or Mylar (polyesters) $\text{---O---}\left(\text{C}(=\text{O})\text{---}\text{C}_6\text{H}_4\text{---C}(=\text{O})\text{---O---CH}_2\text{CH}_2\text{---O---}\right)_n\text{C}(=\text{O})\text{---}$	Clothing, films, tapes
Terephthalic acid  1,4-diaminobenzene 	Kevlar, a polyamide $\text{---N---}\left(\text{C}(=\text{O})\text{---}\text{C}_6\text{H}_4\text{---C}(=\text{O})\text{---N---}\text{C}_6\text{H}_4\text{---N---}\right)_n\text{C}(=\text{O})\text{---}$	Bullet proof vests
diisocyanatobenzene $\text{O}=\text{C}=\text{N---C}_6\text{H}_4\text{---N}=\text{C}=\text{O}$ Ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$	Polyurethane $\text{---O---}\left(\text{C}(=\text{O})\text{---N---}\text{C}_6\text{H}_4\text{---N---C}(=\text{O})\text{---O---CH}_2\text{CH}_2\text{---O---}\right)_n\text{C}(=\text{O})\text{---N---}$	foams

Difference between addition and condensation polymerization

S.No	Addition Polymerization	Condensation Polymerization
1.	Requires the presence of double bond in the monomer	Requires the presence of minimum two functional groups in a single monomer which are of close proximity to each other
2.	No by product is formed	A byproduct like H ₂ O, HCl etc is formed
3.	Polymer formed is homopolymer	Polymer formed is heteropolymer
4.	Polymer is thermoplastic	Polymer formed is thermosetting
5.	Example: a. Ethylene polymerizing to polyethylene b. Vinyl chloride polymerizing to PVC c. styrene polymerizing to polystyrene	Example: a. Hexamethylene diamine and adipic acid polymerizing to nylon 66 b. Caprolactum polymerizing to Nylon 6 c. Terephthalic acid and ethylene glycol polymerizing to polyethylene terephthalate

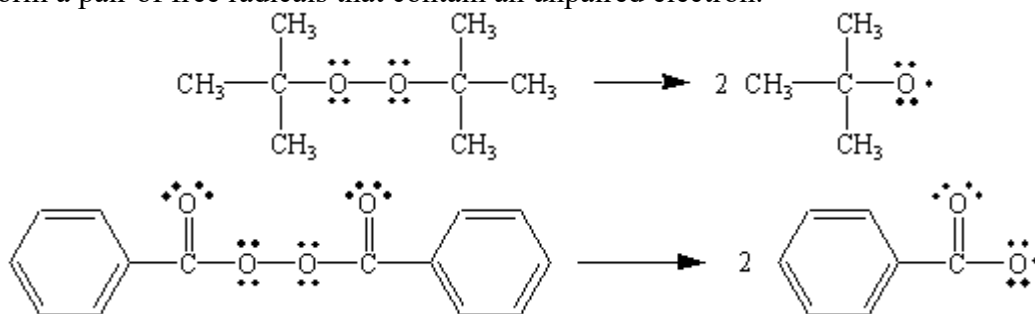
The Mechanism of Addition Polymerization

Depending on the initiator used to start the polymerization process, the mechanism can be classified as:

1. Free Radical Addition Polymerization
 2. Anionic or Carbanion Addition Polymerization
 3. Cationic or Carbonion Addition Polymerization
1. Free Radical Polymerization mechanism: The simplest way to catalyze the polymerization reaction that leads to an addition polymer is to add a source of a **free radical** to the monomer. The term *free radical* is used to describe a family of very reactive, short-lived components of a reaction that contain one or more unpaired electrons. In the presence of a free radical, addition polymers form by a chain-reaction mechanism that contains chain-initiation, chain-propagation, and chain- termination steps.

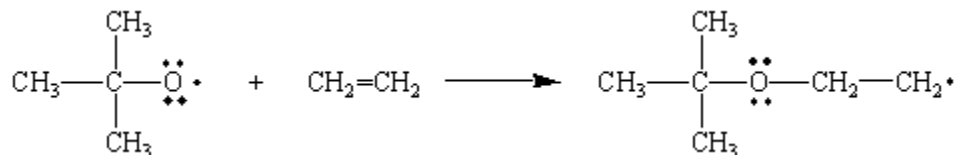
Chain Initiation

A source of free radicals is needed to initiate the chain reaction. These free radicals are usually produced by decomposing a peroxide such as di-*tert*-butyl peroxide or benzoyl peroxide, shown below. In the presence of either heat or light, these peroxides decompose to form a pair of free radicals that contain an unpaired electron.

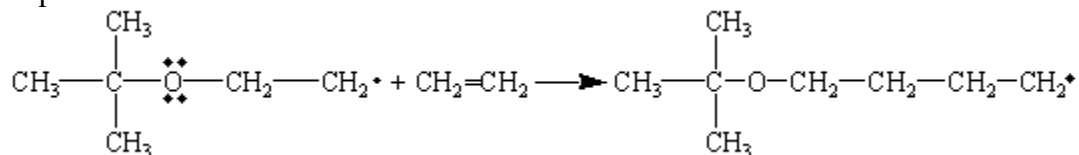


Chain Propagation

The free radical produced in the chain-initiation step adds to an alkene to form a new free radical.

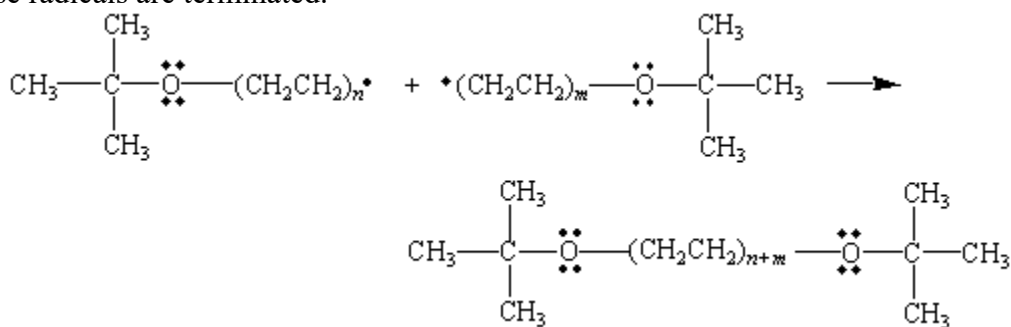


The product of this reaction can then add additional monomers in a chain reaction.



Chain Termination

Whenever pairs of radicals combine to form a covalent bond, the chain reactions carried by these radicals are terminated.

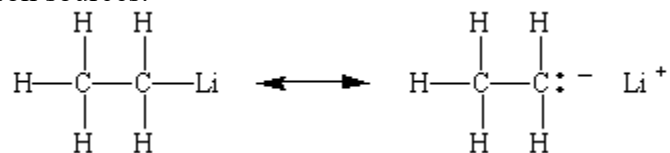


2. Anionic Polymerization

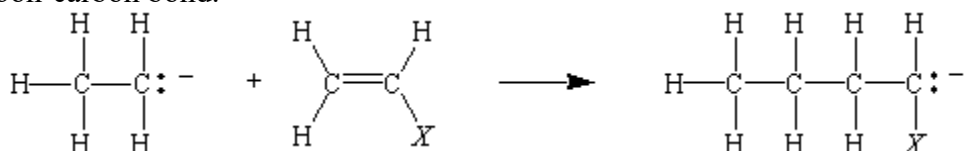
Addition polymers can also be made by chain reactions that proceed through intermediates that carry either a negative or positive charge.

When the chain reaction is initiated and carried by negatively charged intermediates, the reaction is known as **anionic polymerization**. Like free-radical polymerizations, these chain reactions take place via chain-initiation, chain-propagation, and chain-termination steps.

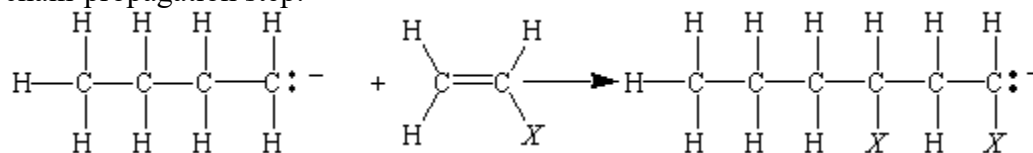
The reaction is initiated by a Grignard reagent or alkyllithium reagent, which can be thought of a source of a negatively charged CH_3^- or CH_3CH_2^- ion. Species that have been used to initiate anionic polymerization include alkali metals, alkali amides, alkyl lithium and various electron sources.



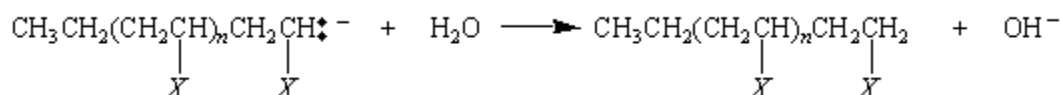
The CH_3^- or CH_3CH_2^- ion from one of these metal alkyls can attack an alkene to form a carbon-carbon bond.



The product of this chain-initiation reaction is a new carbanion that can attack another alkene in a chain-propagation step.

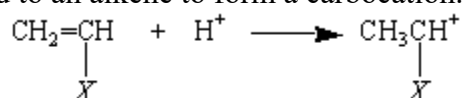


The chain reaction is terminated when the carbanion reacts with traces of water in the solvent in which the reaction is run.

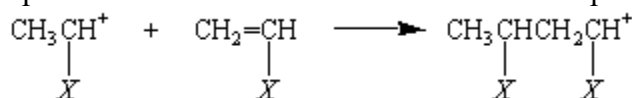


3. Cationic Polymerization

The intermediate that carries the chain reaction during polymerization can also be a positive ion, or cation. In this case, the **cationic polymerization** reaction is initiated by adding a strong acid to an alkene to form a carbocation.



The ion produced in this reaction adds monomers to produce a growing polymer chain.



The chain reaction is terminated when the carbonium ion reacts with water that contaminates the solvent in which the polymerization is run.

Monomers bearing cation stabilizing groups, such as alkyl, phenyl or vinyl can be polymerized by cationic processes. These are normally initiated at low temperature in methylene chloride solution. Strong acids, such as HClO_4 , or Lewis acids containing traces of water (as shown above) serve as initiating reagents

Difference between Mechanism of Free radical and Ionic Polymerization

	Free radical	cationic	anionic
Monomers involved	Ethylene, butadiene, isoprene, acrylates, vinyl chloride,	Monomers with electron releasing substituents like methoxy, ethoxy substituents	Monomers with electron attracting substituents like vinyl cyanide, methyl methacrylate etc
Initiator	Benzoyl peroxide	Lewis acids, Friedel Craft catalyst like AlCl_3 , BF_3 , SnCl_4 etc	Strong bases like alkali metals, sodium or potassium amide, Grignard reagent
Intermediates involved	Free radical	Carbocation intermediate	Carbanionic intermediates
Reaction conditions	Temperature $\geq 50^\circ\text{C}$	Temperature $= 0^\circ\text{C}$	
Solvent conditions	Not sensitive to polarity of solvent	Highly sensitive to changes in polarity of solvent	

PLASTICS AND FIBERS

Plastics:

- ▶ Plastics are semi-synthetic materials
- ▶ Monomers of plastics are either natural or synthetic organic compounds
- ▶ Depending on the arrangement of monomer units, plastics are classified as two types
 - Thermoplastics: linear or lightly cross linked monomers
 - Thermosetting plastics: heavily cross linked monomers

1. Thermoplastics-Polyethylene:

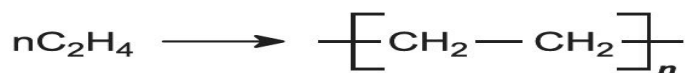
Use: Poly(ethene) is produced in two main forms: low density (LDPE) (< 0.930 g/cc) and high density (HDPE) (0.940-0.965 g/cc).

The LDPE form is preferred for film packaging and for electrical insulation.

HDPE is used to make containers for household chemicals such as washing-up liquids and drums for industrial packaging. It is also used for domestic and gas pipe.

Preparation:

LDPE is prepared from ethylene at high pressure of 1000 to 5000 atmospheres at 250°C in the presence of free radical initiator (O₂)



Two types of catalyst are used principally in the manufacture of HDPE:

- a. Using Ziegler-Natta organometallic catalyst (titanium compounds with an aluminium alkyl), ethylene is polymerized under 6-7 atmospheres at 60-70°C
- b. Using supported metal oxide catalyst like CrO₃ supported on silica-alumina, ethylene is polymerized at 35atm at 160-200°C

2. Thermoplastics-Polyvinyl chloride (PVC):

Uses:

- a. wirings and cables
- b. bottles for drinks, oils, cosmetics, detergents
- c. building and construction (window frames), floorings, pipes for drainage
- d. coated fabrics
- e. films and sheets
- f. vinyl records

Preparation: This is an example of addition polymerization. PVC is made by free-radical polymerization (in the form of emulsion) in the presence of benzoyl peroxide as catalyst under pressure.



3. Thermoplastics-PMMA:

Uses:

Poly(methyl 2-methylpropenoate) is better known as Lucite, Perspex and Altuglas (when in sheet form) and as Diakon (when in powder form).

The sheet form is used in baths and other sanitary ware. High molecular mass cast sheet (Perspex) is also used as a lightweight replacement for glass.

Lower molecular mass products, made by suspension or solution polymerization (Diakon), are used in car lights and domestic lighting.

Special grades are used in diverse applications such as false teeth and eyes and as a major component of bone cements.

The monomer is used in adhesives, surface coatings and in paints.

Preparation: PMMA is prepared by addition polymerization of methyl methacrylate in the presence of acetyl peroxide as catalyst.



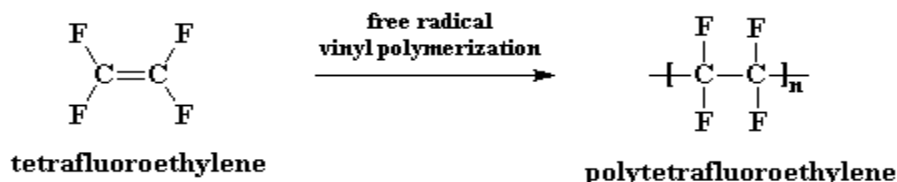
4. Thermoplastics-Teflon (Poly tetra fluoroethylene) [PTFE]

The uses of poly (tetrafluoroethylene) (PTFE) are a function of its resistance to chemical attack, unreactivity (even above 500 K), low friction, non-stick properties and high electrical resistance.

Uses of Teflon

- a. cable insulation
- b. reactor and plant equipment linings, when reactants or products are highly corrosive to ordinary materials such as steel
- c. semi-permeable membranes in chlor-alkali cells and fuel cells
- d. bearings and components in mechanical devices such as small electrical motors and pumps
- e. permeable membrane for clothing and shoes, which allows water vapor to diffuse away from the skin but prevents liquid water (rain) from soaking in
- f. non-stick domestic utensils, e.g. frying pans
- g. medical - catheter tubing
- h. hose and tubing
- i. solid lubricants

Preparation: Teflon is prepared by addition polymerization of tetrafluoroethylene in the presence of benzoyl peroxide as catalyst.



5. Thermoplastics-Polystyrene

Use: Its largest use is for packaging, particularly for foods such as poultry and eggs, for cold drinks and take-away meals.

- making audiocassettes, TV housing, refrigerators, vacuum cleaners
- talcum powder containers,
- small jars and containers for food packaging, bottle caps
- combs, brush handles

Preparation: Polystyrene is prepared by addition polymerization of styrene monomer in the presence of benzoyl peroxide as catalyst

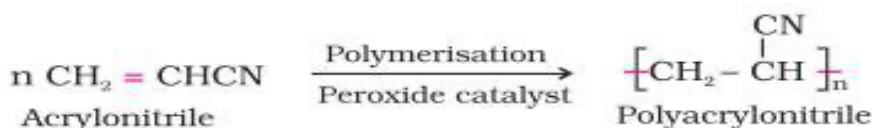


6. Thermoplastics-Polyacrylonitrile (ORLON) (PAN)

Uses:

- Used as tough fabric for example a soft top of a car or in brake linings.
- It is even used to reinforce concrete and in road construction.
- Co-polymerization of propenenitrile with ethenyl ethanoate (vinyl acetate) and propenenitrile with methyl propenoate (methyl acrylate) leads to softer variety of 'acrylic' fibers. These are often mixed with cotton fibers to produce a light fabric, used in women's clothes.

Preparation: ORLON is prepared by addition polymerization of acrylonitrile in the presence of acetyl peroxide as catalyst



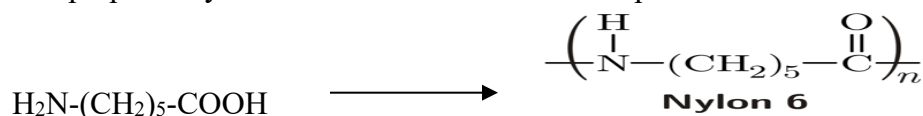
Fibers:

- ▶ Thin, long, threadlike material having high tensile strength
- ▶ High strength is due to strong intermolecular force of polymer chain
- ▶ Intermolecular forces can be Vander Waals force (polypropylene), dipole-dipole interaction (Dacron, terrylene), or hydrogen bonding (nylon, spandex)
- ▶ Example:
 (SYNTHETIC): polyamide (Nylon); polyester (polyethylene terephthalate or Terrylene or Dacron), acrylics (polyacrylonitrile), elastomeric (Spandex, Lycra)
 (NATURAL): Cellulose fiber (Cotton, linen, jute, coir), protein fiber (wool, silk), mineral fiber (asbestos)

1. Thermoset-Nylon 6: Nylon 6 is a synthetic fiber having a polyamide functional group.

Preparation:

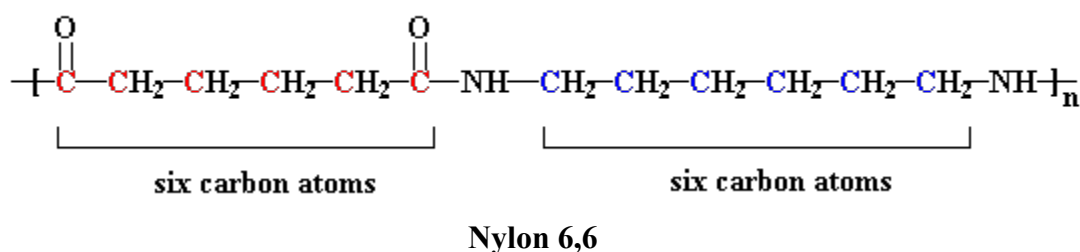
- a. It is prepared by self condensation of ϵ -amino caproic acid

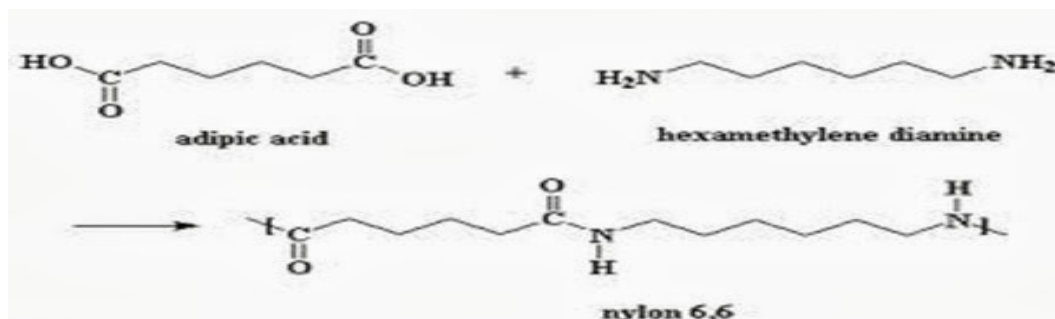


- b. or by ring opening of caprolactam



2. Thermoset-Nylon 6,6: It is made by the condensation polymerization of hexamethylene diamine and adipic acid.

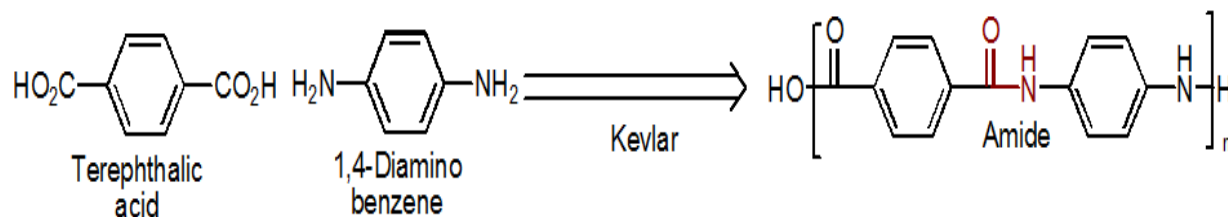




Uses:

- Nylon 6 and Nylon 6,6 are used primarily as fibres in making socks, undergarments, carpets etc.
- Used in making hair combs.
- Nylon 6 is used mainly for making tyre cords.
- Nylon 6, 6 is used in making gears, bearings etc.
- Nylon 6, 6 is used for jacketing electrical ware to provide tough abrasion resistant outer cover to protect the primary electrical insulation.

- Thermoset-Kevlar:** It is a polyamide and is prepared by condensation polymerization of Terephthalic acid and 1, 4 di-amino benzene.



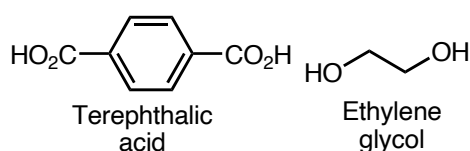
Uses:

Typically it is spun into ropes or fabric sheets that can be used as such or as an ingredient in composite material components. Currently, Kevlar has many applications, ranging from bicycle tires and racing sails to body armor because of its high tensile strength-to-weight ratio. It is also used to make modern drumheads that hold up withstanding high impact. When used as a woven material, it is suitable for mooring lines and other underwater applications.

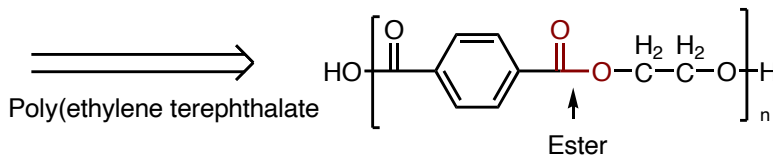
- Thermoset-Polyethylene Terephthalate (PET) (also known as Terylene or Decron)**

It is polyester, prepared by heating dimethyl terephthalate and ethylene glycol in basic medium.

Monomer



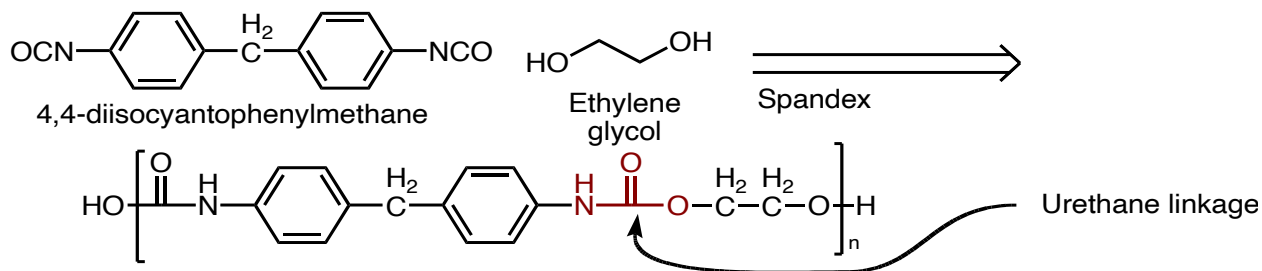
Polymer



Uses:

- It is used for making magnetic recording tapes.
- It is used for making bottles for Cola drinks, fruit juice, sauces etc.
- It is used for making wide necked jars for coffee.
- It is used for making films of overhead projector.
- Glass filled PET moldings are used for housings for toasters, coffee machines, car heaters and water meter.

5. Thermoset-Polyurethane: It has a urethane linkage and is prepared by heating 4, 4 di-isocyanato-phenylmethane and ethylene glycol

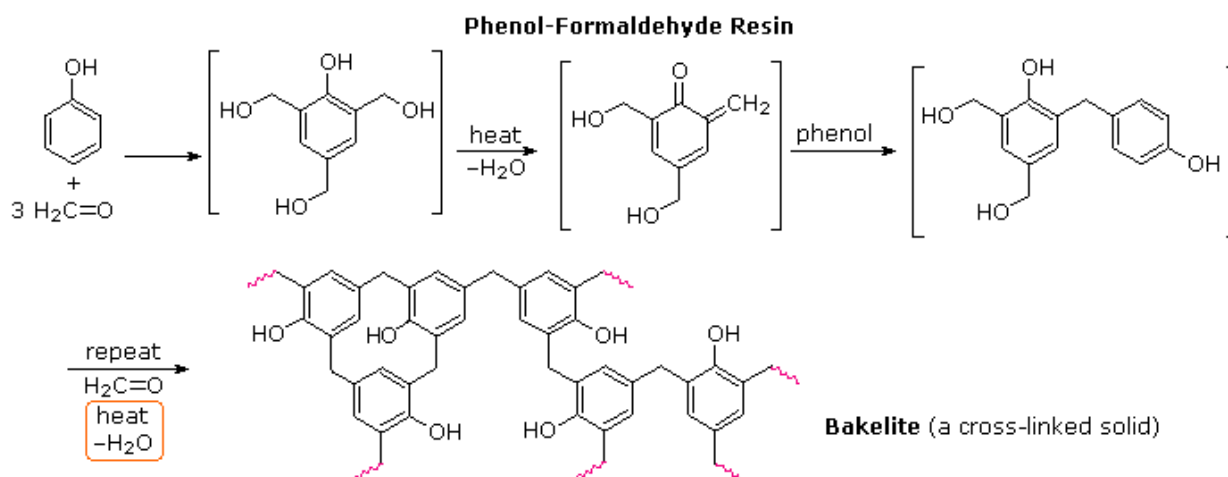


Uses:

- Apparel
- Appliances. The most common use for polyurethanes in major appliances is rigid foams for refrigerator and freezer thermal insulation systems. The good thermal insulating properties of rigid polyurethane foams result from the combination of a fine, closed-cell foam structure and cell gases that resist heat transfer.
- Automotive
Polyurethanes are used throughout cars. In addition to the foam that makes car seats comfortable, bumpers, interior “headline” ceiling sections, the car body, spoilers, doors and windows all use polyurethanes.
- Building and Construction
- Composite Wood
- Electronics
- Flooring
- Furnishings
- Medical
Polyurethanes are commonly used in a number of medical applications, including catheter and general purpose tubing, hospital bedding, surgical drapes, wound dressings and a variety of injection-molded devices.
- Packaging

6. Thermoset-Bakelite (Phenol-Formaldehyde Resin)

Preparation:

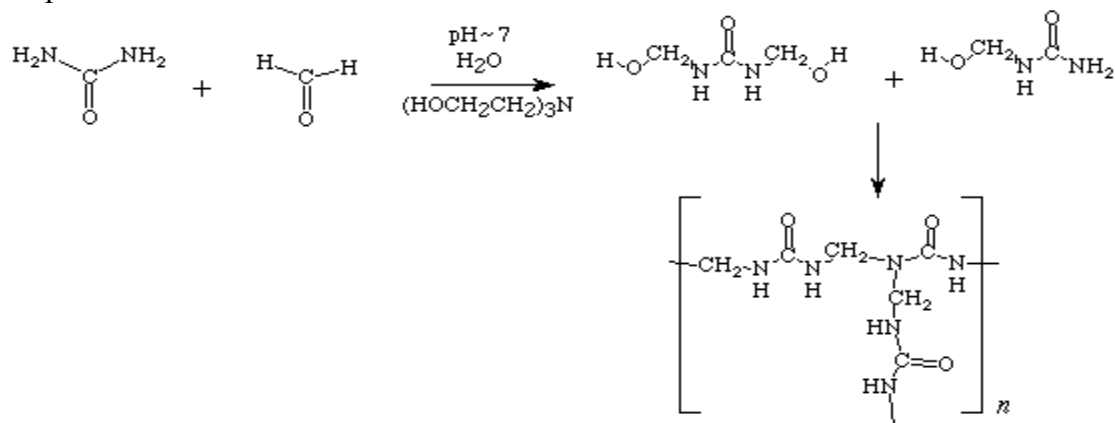


Use:

- a. Bakelite is used for the emerging electrical and automobile industries because of its extraordinarily high resistance – not only to electricity, but to heat and chemical action. It is used for all non-conducting parts of radios and other electrical devices, such as bases and sockets for light bulbs and vacuum tubes, supports for electrical components, automobile distributor caps and other insulators.
- b. Bakelite is used today for wire insulation, brake pads and related automotive components, and industrial electrical-related applications. It is used in myriad applications including saxophone mouthpieces, whistles, cameras, solid-body electric guitars, telephone housings and handsets, early machine guns, pistol grips, and appliance casings. In the pure form it was made into such articles as pipe stems, buttons, etc.

7. Thermoset-Urea-Formaldehyde Resin

Preparation:

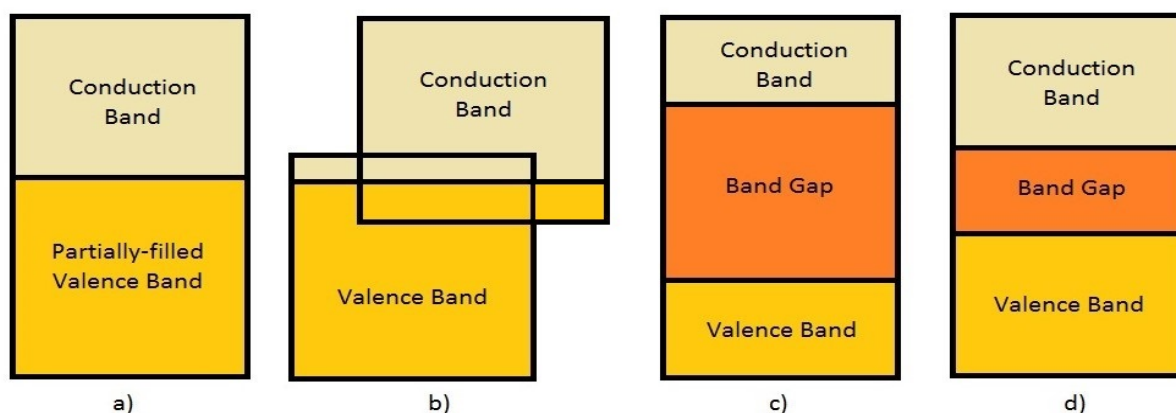


Uses:

Urea-Formaldehyde is used in many manufacturing processes due to its useful properties. Examples include decorative laminates, textiles, paper, foundry sand molds, wrinkle resistant fabrics, cotton blends, rayon, corduroy, etc. It is also used to glue wood together. Urea formaldehyde is also commonly used when producing electrical appliances casing (e.g. desk lamps).

CONDUCTING POLYMERS

Polymers are organic macromolecules, a long carbonic chain, composed by structural repeat entities, called monomer. The majority of polymers are insulators, due to an unavailability of free electrons to create conductivity. The poor conductivity of polymers is explained by the band theory. Band theory explains the existence of valence and conduction band. While valence band are continuous energy levels placing the valence electrons; conduction band are continuous higher energy levels that are empty. The band gap determines the conducting nature of materials. The Fig below shows the band structure of monovalent metallic conductors (a), for divalent metallic conductors (b) for insulators (c) and for semiconductors (d).



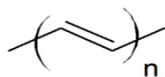
Band Structure for Conductors, Semiconductors, and Insulators: a) for monovalent metals; b) divalent metal; c) Insulators; and d) Semiconductors

Polymers were considered as insulators. But in 1970, the first intrinsic conductive polymer was discovered by Shirakawa, Heeger, and MacDiarmid, for which they were awarded the Nobel prize in 2000. The polymer was produced by the exposure of the polyacetylene to dopant compounds: oxidizing or reducing agents; electron-donor or electron-receptor of electrons.

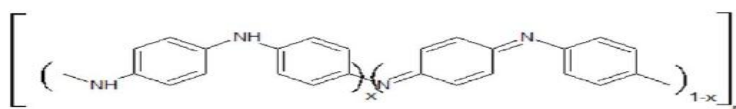
Conducting Polymers

Polymers which conduct electricity are known as conducting polymers. Conducting polymers are classified as Intrinsically and Extrinsically Conducting polymers

Intrinsically Conducting polymers have inherent double or triple bonds in conjugation. Extensive delocalization of π electrons over the entire polymeric backbone results in the formation of valence and conduction bands. Significant band gap exists in such polymers. Such polymers exhibit semiconducting properties. Electrical conductivity in such polymers results only after appropriate thermal or photolytic activation. The electrons in valence band get sufficient energy to jump the gap and reach the lower energy level of the conduction band. Examples are polyacetylene, Polyaniline and polypyrrole



Structure of a polyacetylene



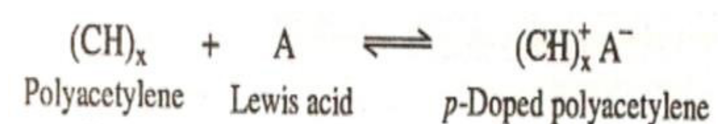
Structure of Polyaniline



Structure of polypyrrole

Doping i.e addition of external agent into the conjugated polymer can lead to a dramatic increase in electrical conductivity to values as high as 10^5 S/cm (Cu has an electrical conductivity of 10^6 S/cm). In the presence of a dopant, positive or negative charges are created on the polymer backbone as a result of oxidation or reduction. Doping is of two types: p type and n type

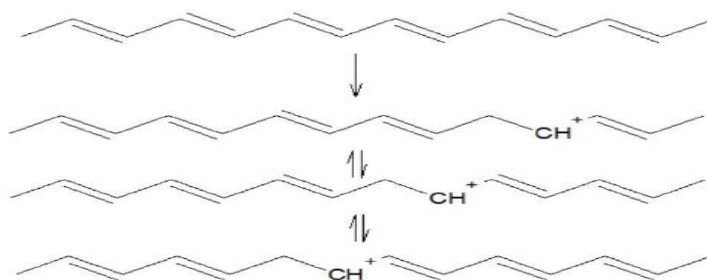
In p type, conducting polymers are exposed to Lewis acid. Oxidation occurs and positive charges are developed on polymer backbone.



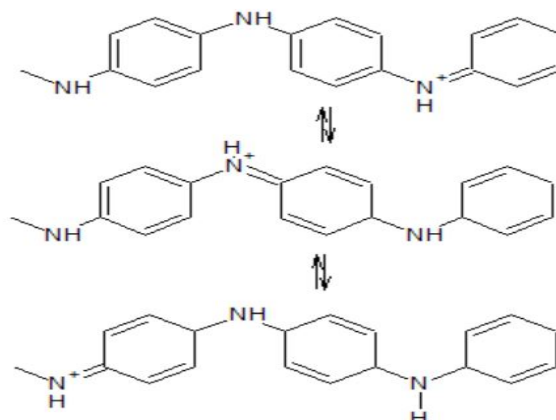
In n type, Lewis base causes reduction to occur and negative charges are developed on polymer chain.



The movement of such charges as a result of resonance in the presence of an externally applied field give rise to enhanced conductivity.



Resonance in polyacetylene in the presence of Lewis acid



Resonance in Polyaniline in the presence of Lewis base

Disadvantage of such Intrinsically Conducting Polymers is low conductivities, improcessabilities, poor mechanical strength and poor stability.

Extrinsically Conducting Polymers are of two types:

- a. Conductive element filled polymer: Conducting elements like carbon black, metallic fibers, metallic oxides etc. are filled into the polymer to form a solid entity
Such polymers are low in cost, possess high conductivity, light in weight, mechanically durable, strong and are easily processable in different forms, shapes and sizes.
Disadvantages include reduction in tensile strength
- b. Blended conducting polymer: a conventional polymer that is insulator is blended with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and can easily be processed.

Application

Conducting polymers are widely used

1. In rechargeable batteries.
2. In making analytical sensors for pH, O₂, SO₂, NH₃, glucose, etc.
3. In the preparation of ion exchangers.
4. In controlled release of drugs.
5. In optical filters.
6. In photo voltaic devices.
7. In telecommunication systems.
8. In micro-electronic devices.
9. In bio-medical applications.

Synthesis

There are three ways to produce conductive polymers: reactional chemistry, electrochemical, and photoelectrochemical, being the first one the most used, due to its high profitability and efficiency.

The chemical process consists in the union of monomers by the addition of the oxidizing or reducing agents that makes the neutral polymer to a cationic or anionic ionic complex, ending the reaction by the bonding of this complex to the counter-ion of the redox agent. This process requires a high control, since the reaction is very exothermic and emits gases, requiring proper treatment and equipment of protection.

The electrochemical method consists in the electronic deposition of the polymer in the electrode. The solution that the electrode is immersed has the monomers and the dopants. When a voltage or a current strong enough is applied, the monomers oxidize resulting in the polymerization. This process results in polymers with shape of the electrode, requiring a posterior processing to get the shape desired.

The photoelectrochemical process is based on photoexcitation of the polymer or in compounds that have catalyst properties in presence of light, oxidizing the monomers resulting in a polymerization. Even though this process is simple and environmentally friendly, the mechanical properties of the resulting polymer are not good.

BIODEGRADABLE POLYMERS

- Polymers which get degraded by the process of biodegradation
- Biodegradation is the process which involves biological organisms like fungi or bacteria for degrading or cleaving of a polymer
- Requirements for biodegradation are
 - biological organisms,
 - appropriate environmental conditions (temperature, pH, moisture, O₂, light, pressure etc.
 - Substrate i.e the polymer
- Types of Biodegradable Polymers are:
 - Natural Biodegradable Polymers: Natural Rubber, collagen, lignin
 - Synthetic Biodegradable Polymers: Polyvinyl alcohol, polyanhydrides, poly (3 hydroxy butyrate), polylactic acid, β -hydroxy butyrate- β -hydroxy valerate)
- Applications of Biodegradable Polymers
 - a. Poly (β -hydroxy butyrate) or PHB is used in the manufacture of shampoo bottles
 - b. β -hydroxy butyrate- β -hydroxy-valerate are suitable as matrices for controlled release of drugs due to their favorable biocompatibility and biodegradation properties. It is also used as a packaging material, in orthopaedic devices etc.
 - c. Poly (lactic acid) or PLA is used widely in medical applications like sutures, drug delivery systems and wound clips. It is also used in some agricultural applications like “timed-release coatings for fertilizers and pesticides”
 - d. Dextron is the 1st bioabsorbable suture made from biodegradable polyester for post operative stitches
- Need for Biodegradable polymers are
 - Environmental friendly as they do not cause solid waste and pollution problems