MODULE 7

Thermoplastics and thermosetting plastics;

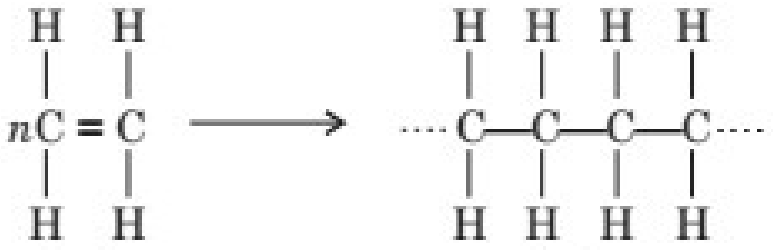
Engineering application of plastics - ABS, PVC, PTFE and Bakelite;

Compounding of plastics: moulding of plastics for Car parts, bottle caps (Injection moulding), Pipes, Hoses (Extrusion moulding), Mobile Phone Cases, Battery Trays, (Compression moulding), Fibre reinforced polymers, Composites (Transfer moulding), PET bottles (blow moulding);

Conducting polymers- Polyacetylene- Mechanism of conduction – applications (polymers in sensors, self-cleaning windows)

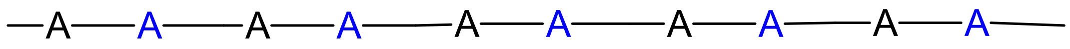
Polymer

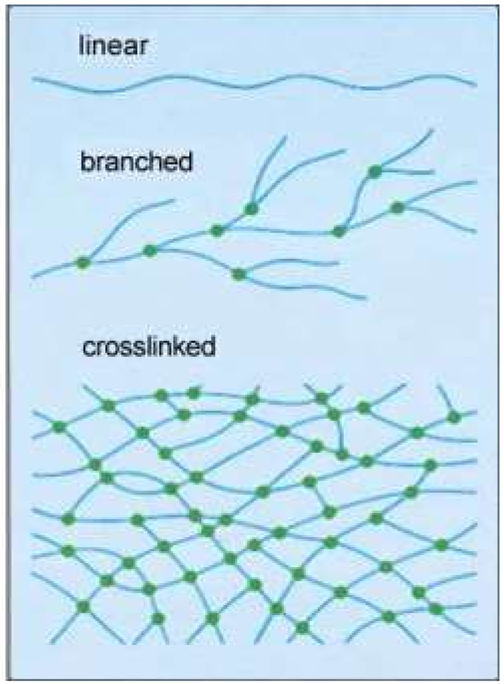
- Polymer is a generic name given to a vast number of materials of high molecular weight
- Plastic and rubber products are based on polymers mainly because of superior durability and ability to be moulded
- These are macromolecules (higher molecular weight compounds) formed by the repeated linkage of large number of small molecules called monomers.
- A polymer consists of a large number of simple monomeric structural units which are repeated over and over again to form a giant molecule called a macromolecule.
- The molecular weight of a polymer usually ranges from 5000Da to several million Dalton.



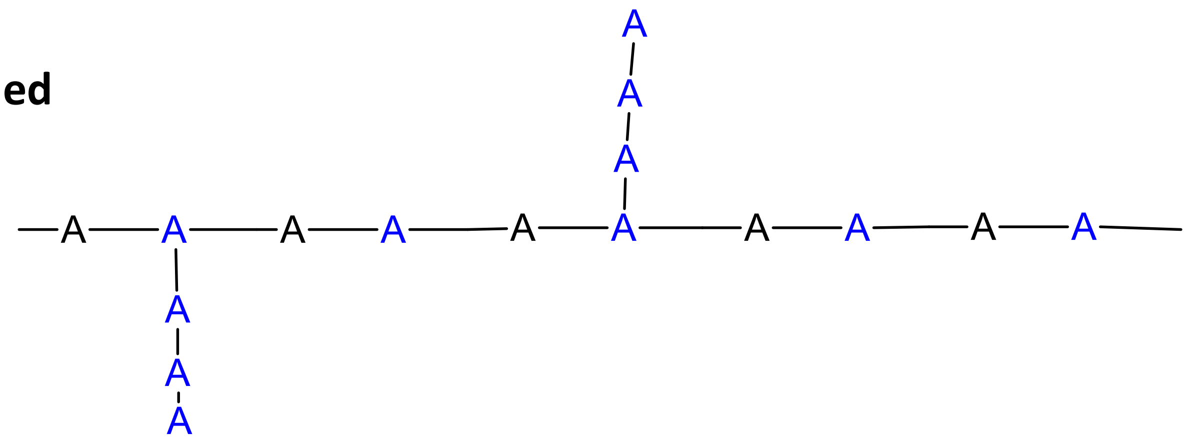
Monomers and repeating units

Linear

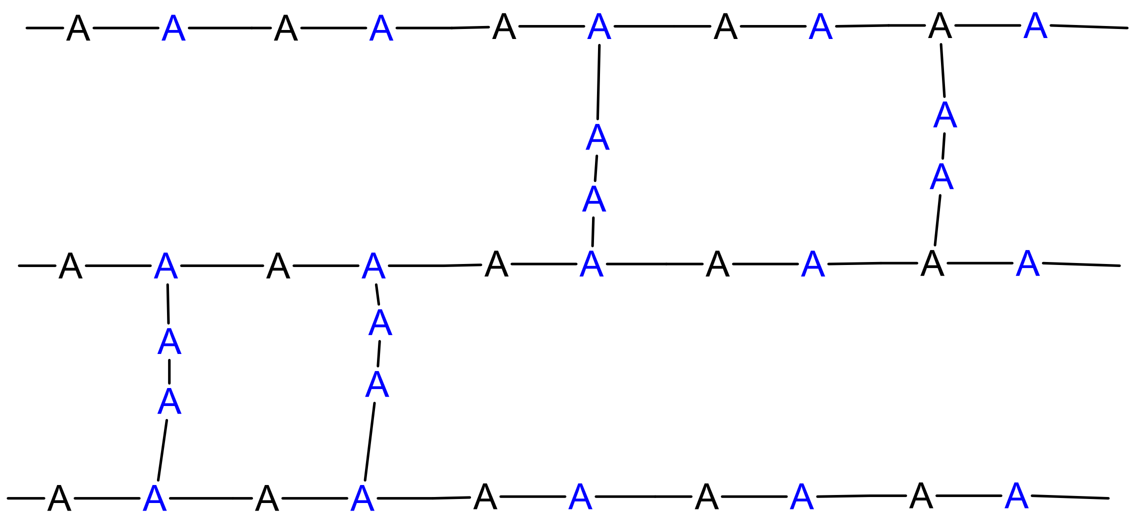




Branched



Crosslinked



Classification

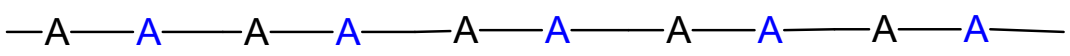
Based on origin of material	
Natural polymers	**Synthetic Polymers**
Rubber, wool, silk, cotton	Polystyrene, PTFE, rayon, terylene

Atoms composing the backbone chain	
Organic polymers	**Inorganic Polymers**
Polyethylene, pvc, nylon, terylene •Vast majority of polymers studied	Glass, silicone, clay

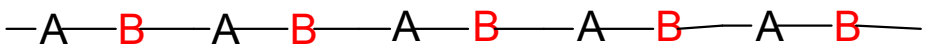
Thermal properties	
Thermoplastic polymers	**Thermosetting Polymers**
Polyethylene, PVC, nylon,	Bakelite, melamine resin

Homopolymers and copolymers

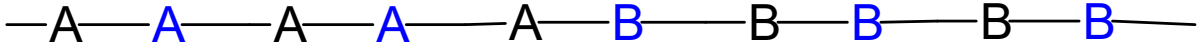
•A **Homopolymer** contains same typer of monomer



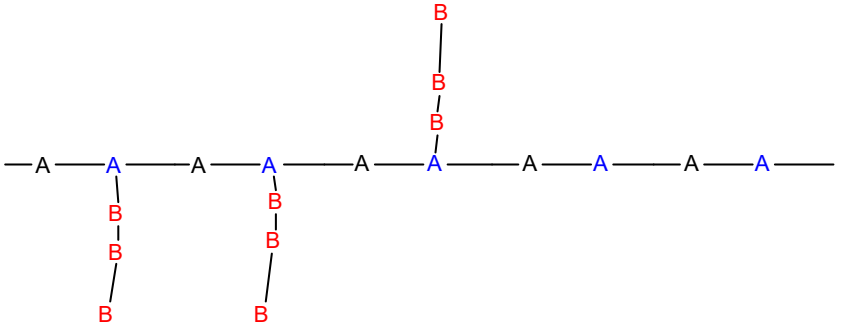
•*A **Copolymer** contains two or more different types of monomer*



•**A block Copolymer** is a linear polymer in which like/similar monomeric units occur in relatively long sequences



•*A **graft Copolymer** is a branched polymer with one kind of monomer in the main chain and a different kind in the branch or side chain*



Plastics

- Plastics are materials that show the property of plasticity ad can be moulded by the application of heat and pressure
- Resins are basic binding materials of polymer which form a major part of a plastic
- Besides resins, other additives are added in the manufacturing of plastics
- Plastics have the following advantages:
    - Light weight and high strength to weight ratio
    - Good thermal and electrical insulation
    - High corrosion resistance
    - Easy workability- casting, moulding, drilling etc
    - High chemical inertness
    - Decorative glossy surface
    - Low maintenance cost

Thermoplastics	Thermosetting plastics (thermo sets)
1. These are formed by addition polymerisation	1. These are formed by condensation polymerisation
2. Adjacent polymer chains are held together by weak vander waals force of attraction	2. Adjacent polymer chains are held together by strong covalent bonds (cross linkage)
3. These becomes soft liquid while heating and becomes stiff while cooling and hence they can be reshaped	3. These does becomes soft liquid while heating because once they are set, that becomes the permanent shape hence they cannot be reshaped
4. These are elastic, weak, soft and less brittle	4. They are strong, hard and more brittle
5. These are soluble in Organic solvents	5. These are insoluble in organic solvents
6. These are low molecular weight polymers	6. These are high molecular weight polymers
7. Example: **PVC**, polystyrene, **PTFE, ABS**	7. Example: **Bakelite**, Polyester (PET), Nylon6

Poly vinyl Chloride (PVC)

- It's a colourless odourless, non-inflamable and chemically inert polymer resistant to light, oxygen, inorganic acids and alkalis; its soluble in hot chlorinated hydrocarbons
- It is synthesised by heating a water-emulsion of vinyl chloride in the presence of a small amount for benzyl peroxide or hydrogen peroxide in a an autoclave under pressure

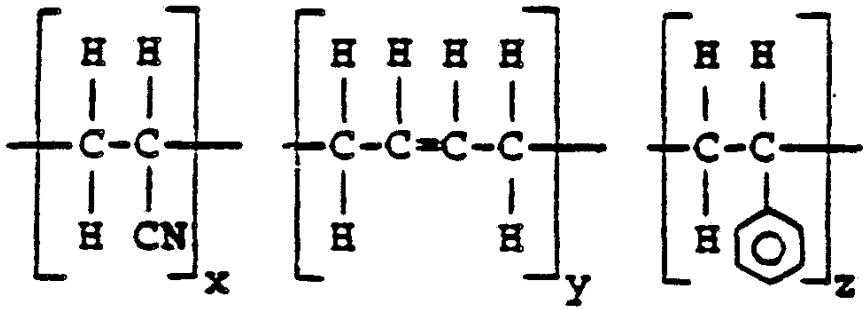
$$n\mathrm{CH_2{=}CHCl} \xrightarrow{\text{Polymerize}} \underset{\text{PVC}}{-(\mathrm{CH_2CHCl})_n-}$$

- Rigid PVC or unplasticised PVC have superior chemical resistance and high rigidity but brittle. They are used for making sheets, which are used for tank linings, light-fittings, safety helmets, refrigerator components, tyres, mudguards for motorcycles
- They are also extruded into strip and tube form for use in place of non-ferrous metals

- Plasticised PVC (obtained by adding plasticisers such as dibutyl phthalate, dioctyl phthalate, tricresyl phosphate etc) is used for making continuous sheets that are used to make raincoats, table clothes, curtains, coatings for electric wires, radio and TV components
- PVC's contain about 56% chlorine

Acrylonitrile-Butadiene-Styrene polymer (ABS)

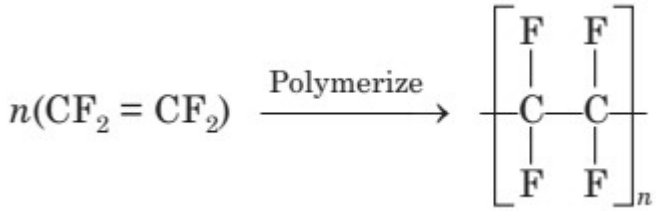
- ABS polymers are made by copolymerising acrylonitrile, butadiene and styrene



- They are structural plastics or rubber, possessing very good strength and toughness
- ABS polymers are used in telephones, pipes, moulded articles like furniture, suit-cases and packing containers

Polytetrafluoroethylene (PTFE) or TEFLON

- PTFE is obtained by polymerisation of water-emulsion of tetrafluoro ethylene under pressure in the presence of benzoyl peroxide



- The presence of highly electronegative fluorine atoms and the regular configuration of the PTFE molecules results in very strong attractive forces between the adjacent polymeric chains
- These strong attractive forces give the material extreme toughness, high softening point (above 350°C), exceptionally high chemical-resistance against almost all chemicals (except hot alkali metal and hot fluorine). High density, waxy touch, very low coefficient of friction, very good electrical and mechanical properties
- PTFE can be machined, punched, drilled

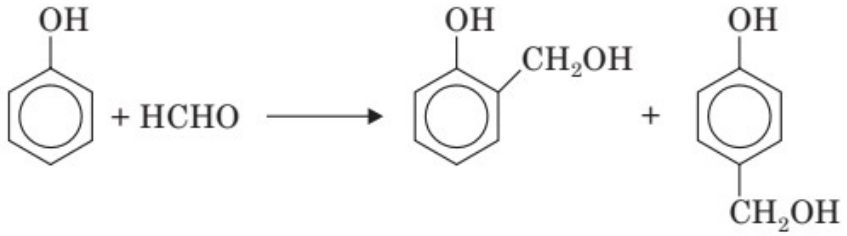
- PTFE has the disadvantage that it cannot be dissolved and cannot exist in true molten sate.
- Around 350°C, it sinters to form a very viscous opaque mass, which can be moulded into certain forms by applying high pressures
- USES: as insulating material for motors, transformers, cables etc. for making gaskets, packings, pump parts, chemical carrying tubes, pipes
- They are used for coating and impregnating glass fibres, asbestos; in non-lubricating bearings and non-sticking stop-cocks in burettes



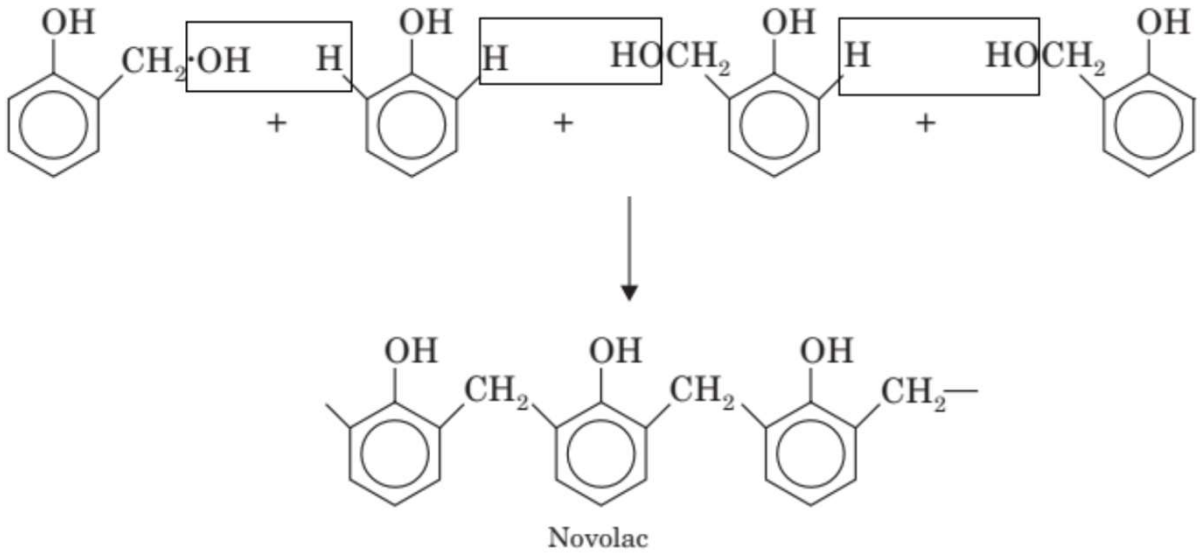



BAKELITE

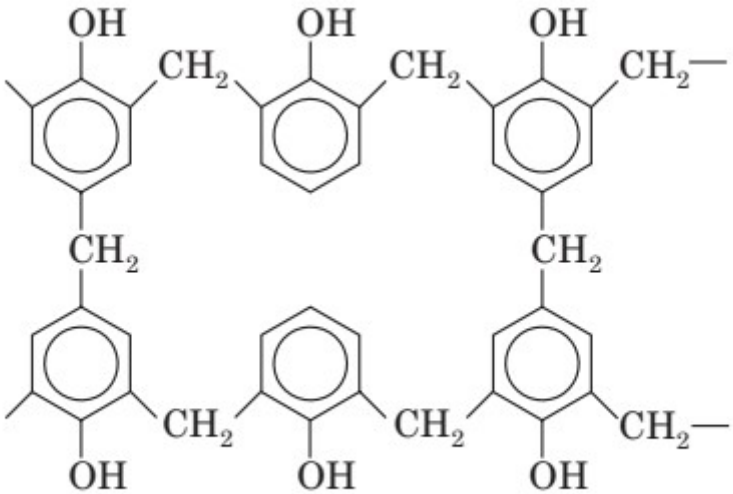
- Bakelite is an important member of a class of thermosetting resins called as phenoplasts or phenolic resins



- Bakelite is prepared by condensing phenol with formaldehyde in the presence of acidic or alkaline catalyst
- The initial reaction results in the formation of o- and p-hydroxy methyl phenol, which react to form a linear polymer known as *novolac*



- During, moulding, hexamethylene tetramine [$(CH_2)_6N_4$] is added, which provides formaldehyde, which then converts the soluble and fusible novolac into hard, infusible and insoluble solid of cross-linked structure that is Bakelite
- They are rigid, hard, scratch- resistant, water resistant and show resistance to non-oxidising acids, salts and many organic solvents, but are attacked by alkalis
- They possess excellent electrical insulation character
- They are used in making electrical insulator parts like switches, plugs
- Moulded parts like telephone parts, cabinets for radio and TV
- For impregnating fabrics, wood and paper
- In paints and varnishes
- As hydrogen-exchange resins in water softening
- For making bearings used in propeller shafts for paper industry and rolling mills



bakelite

BAKELITE - uses

Plastic processing

- Many polymers, after synthesis, exist as resins (e.g phenolic resins, amino resins, cellulose resins) which are in semi-solid form with high viscosity. To make plastic products out of these polymers, several additives need to be added before/during the moulding process.
- Some polymers like PMMA, polysterene can be moulded without any additives
- Compounding of plastics is the process of adding chemical admixtures which improves the physical properties of the resulting moulded products. Following are important additives:

1. **Resins** : Basic binding materials and holds the constituents together. These form the major part of the plastics.
    - Some resins get transformed in to cross-linked thermosetting plastics during moulding. This usually requires a catalyst during the moulding process

2. **Plasticizers:** these are chemicals that are added to resins to increase their plasticity and flexibility

   - These molecules get inside the polymer chain and neutralise the intermolecular forces of attraction between them, which facilitates greater freedom of movement of polymer chains and thereby increasing the flexibility of plastic.
   - Plasticizers , however, often reduces the plastic tensile strength and their chemical resistance
   - Vegetable oils, camphor, tricresyl phosphate, tributyl triphenyl phosphate, dibutyl phosphate are some commonly used plasticizers

3. **Fillers:** these materials are added to increase the bulk and reduce the cost as well as to impart some special property to the plastic. Some common fillers are:
    - Mica - to impart permanent electric characteristics and heat resistance
    - Graphite - self lubricating and helpful in moulding operation
    - Asbestos - Heat resistance and chemical resistance
    - Fabric scraps - impact and tensile strength
    - Sawdust, metal oxides, metal powder, wood flour, talc powder, paper pulp are also used as fillers
4. **Catalyst** : are mainly added to thermosetting plastics in order to accelerate the cross linking of the fusible resin.
    - Hydrogen peroxide, benzoyl peroxide, silver, copper, lead and metallic oxides like zinc oxide are used as catalysts

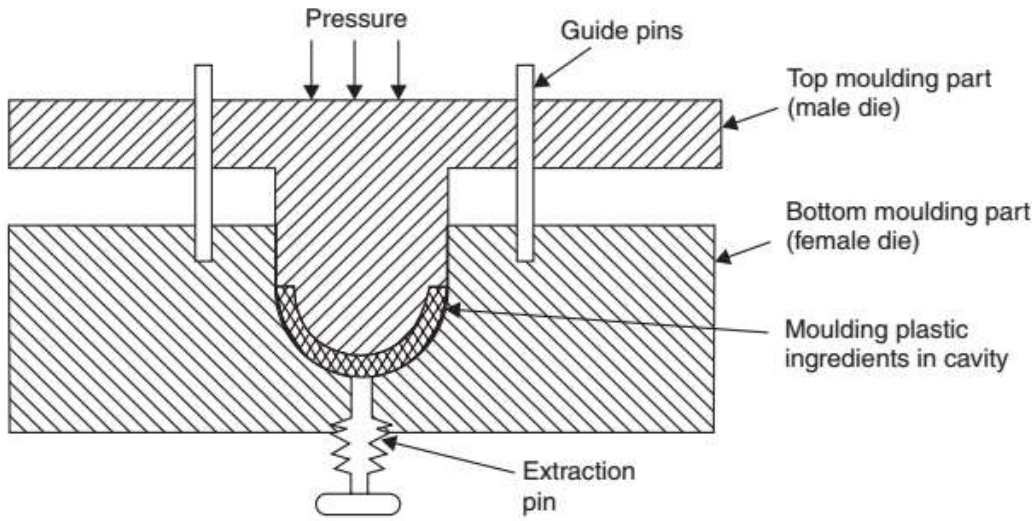
5. **Stabilizers :** are added to improve the thermal stability of plastics during processing
    - Opaque stabilizers are lead salts like lead chromate, lead naphthenate, white lead etc
    - Transparent ones are stearates of lead, barium and calcium
6. **Lubricants** : are added to make the moulding process smoother and to have a flawless glossy finished products.
    - Common lubricants are waxes, oils, stearates, oleates, soaps etc
7. **Fire retardants:** Ammonium polyphosphate, Aluminium oxide trihydrate, a mixture of 3% Sb_2O_3 and 5% Br_2, misture of borax and boric acid are some fire retardants
8. **Antioxidants:** are chemicals that prevent the oxidation reactions in polymers in the long run. E.g. diphenylamines, hindered phenols, dialkyl thiopropionates
9. **Pigments:** inorganic pigments like lead chromate (yellow), iron ferrocyanides (blue), aluminium silicates (red to blue) and organic pigments like phthalocyanins (blue to green), chlorotoluidine and sulphuric acid (red)

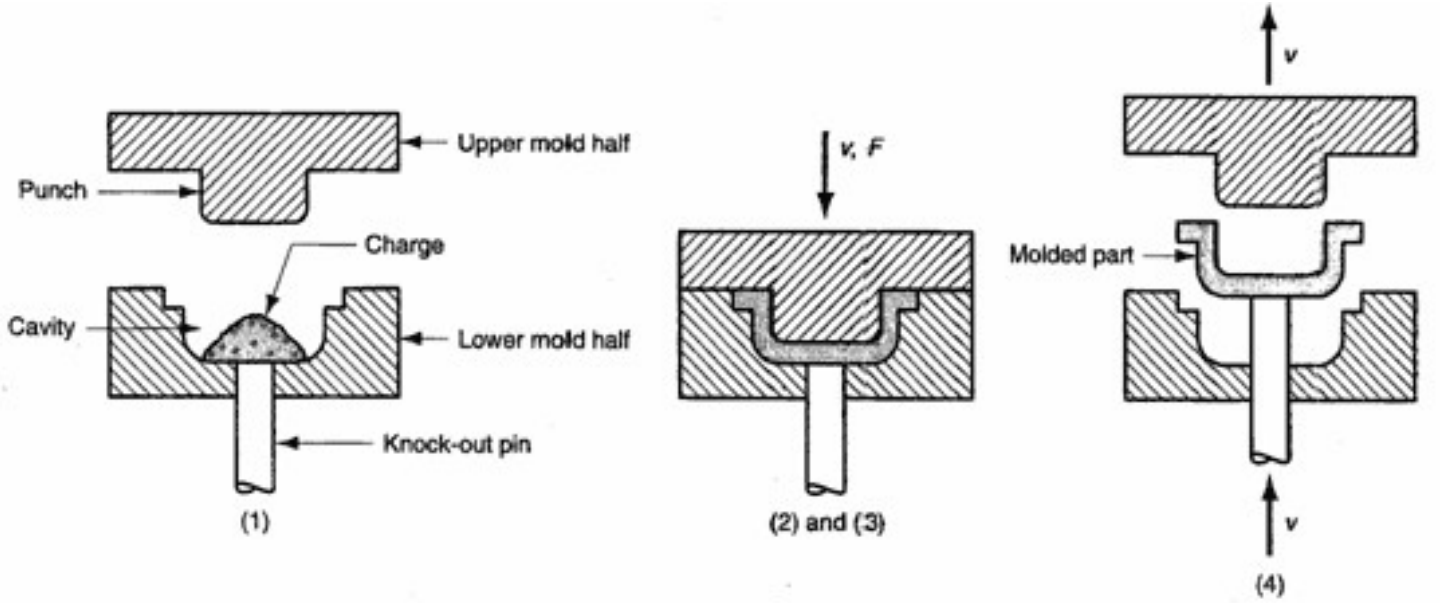
moulding

Plastic moulding methods

Compression moulding

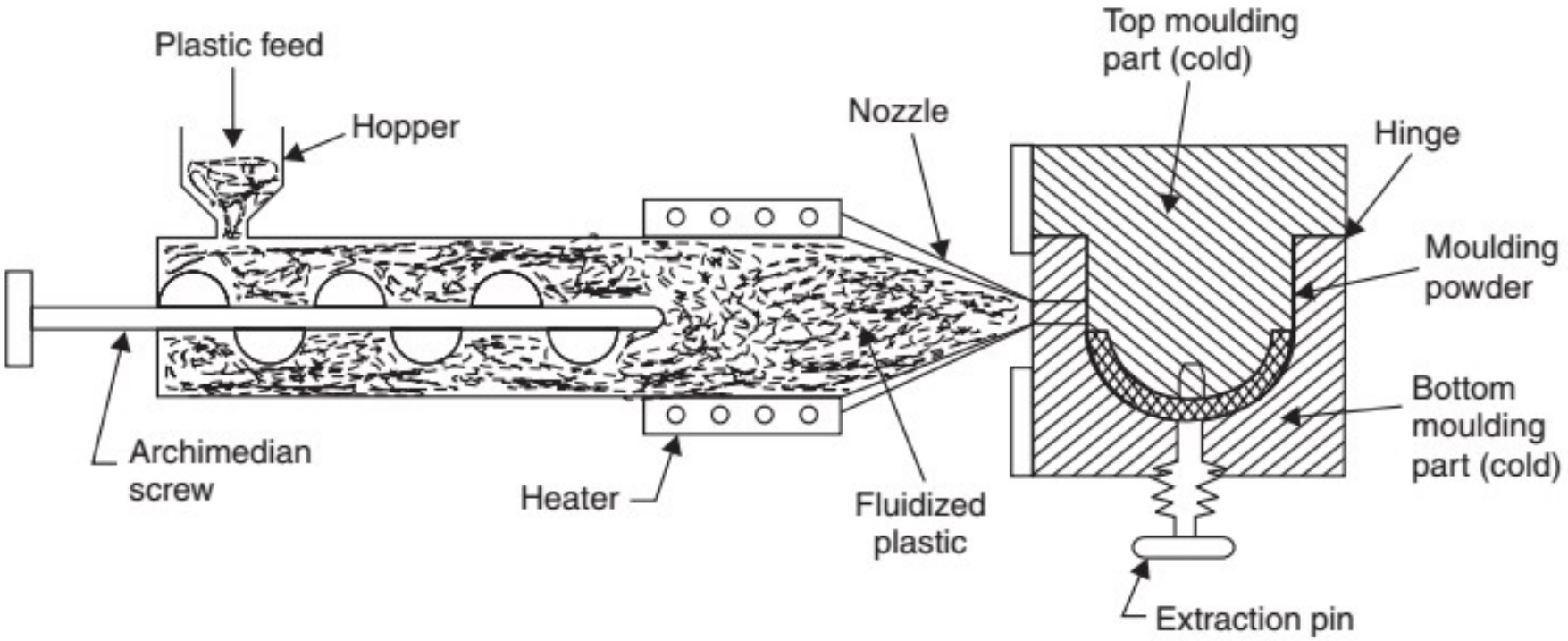
- This involves the application of heat and pressure to the mould having the compounded resin, applicable to to both thermoplastics and thermosetting plastics
- The mould is made of 2 halves, the bottom one usually has the cavity in the shape of the article to be moulded . Temperature upto 200° C and pressure of 70kg/cm^2 are applied
- The compounded plastic is placed in the bottom mould and then the top mould plunges itself into the bottom half. Any excess plastic flows out through the extrusion pin hole
- Plastic is allowed to set and then removed
- Furniture handles, telephone parts are made this way.



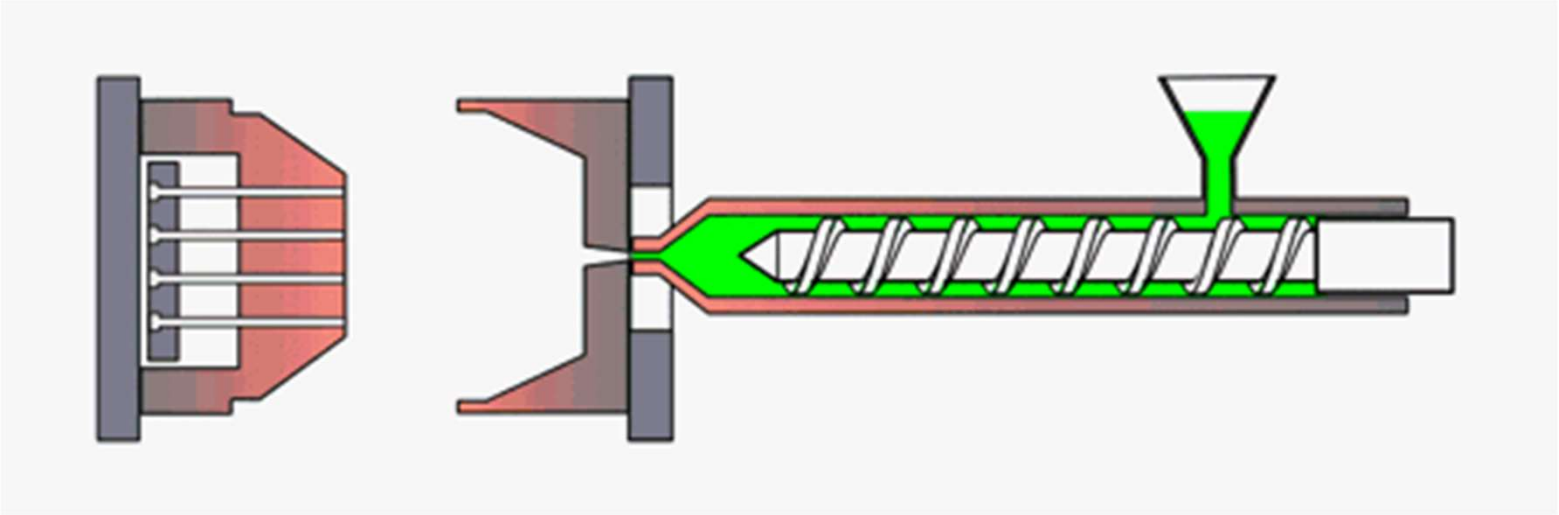

Upper mold half
Punch
Charge
Cavity
Lower mold half
Knock-out pin
(1)
v, F
(2) and (3)
v
Molded part
v
(4)

Injection moulding

- This is exclusively used for thermoplastics.
- Plastic powder is heated in a hot chamber and is injected by a piston plunger into a tight locking mould with the help of a screw arrangement.
- The mould is cooled for curing and then one half of the mould is removed to eject the moulded plastic article.
- Buckets, bowls, furniture parts are made by this method

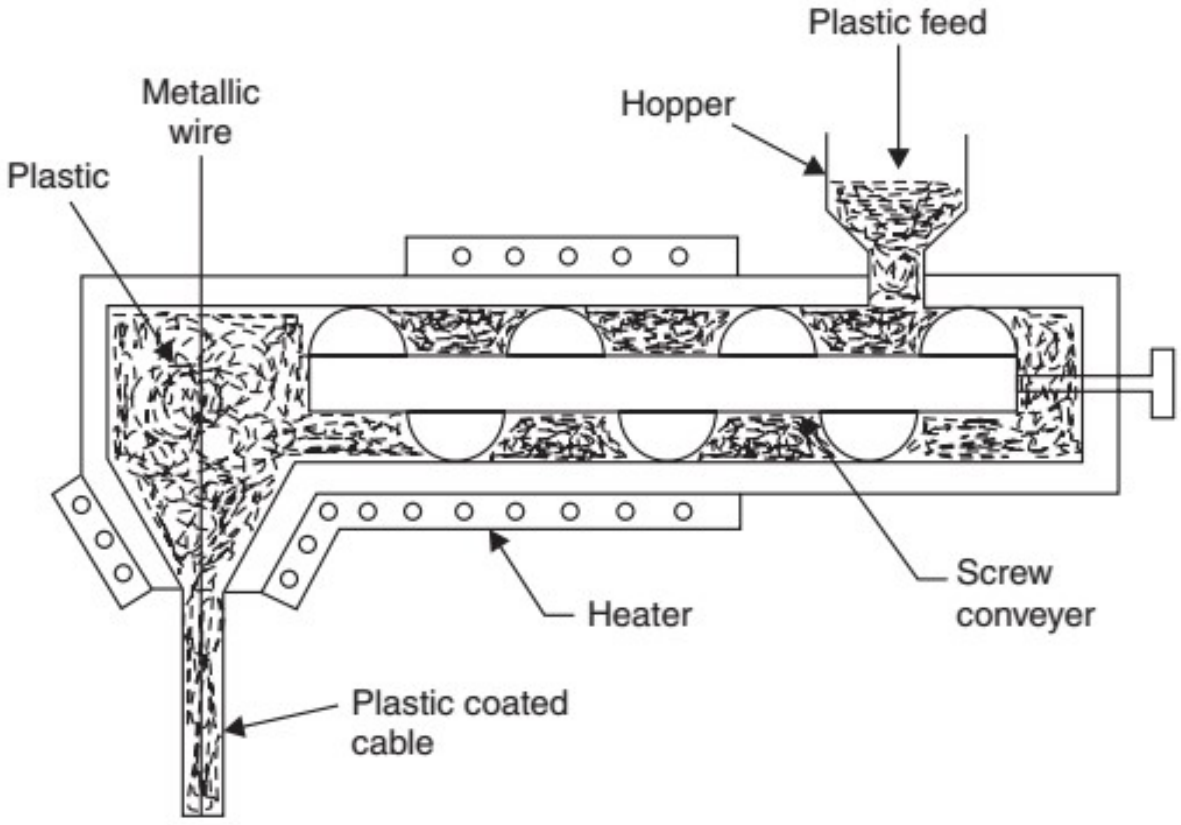


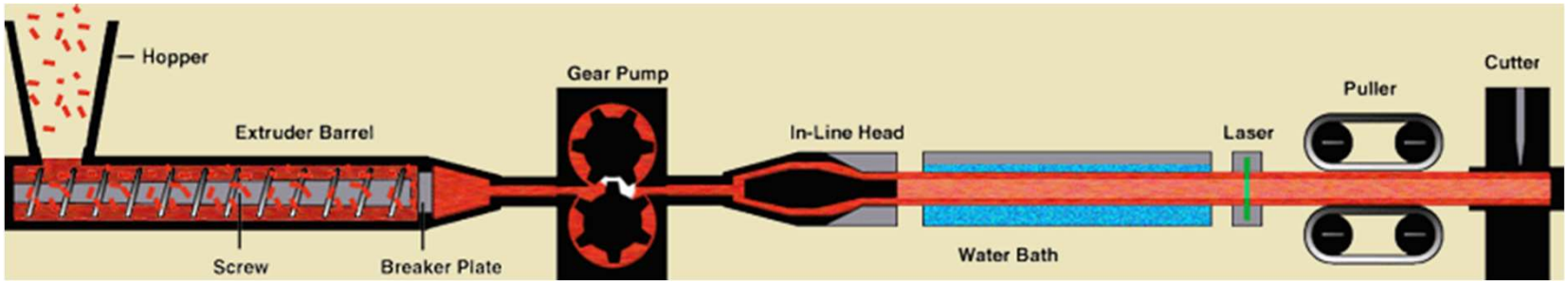
Injection moulding in action!



Extrusion moulding

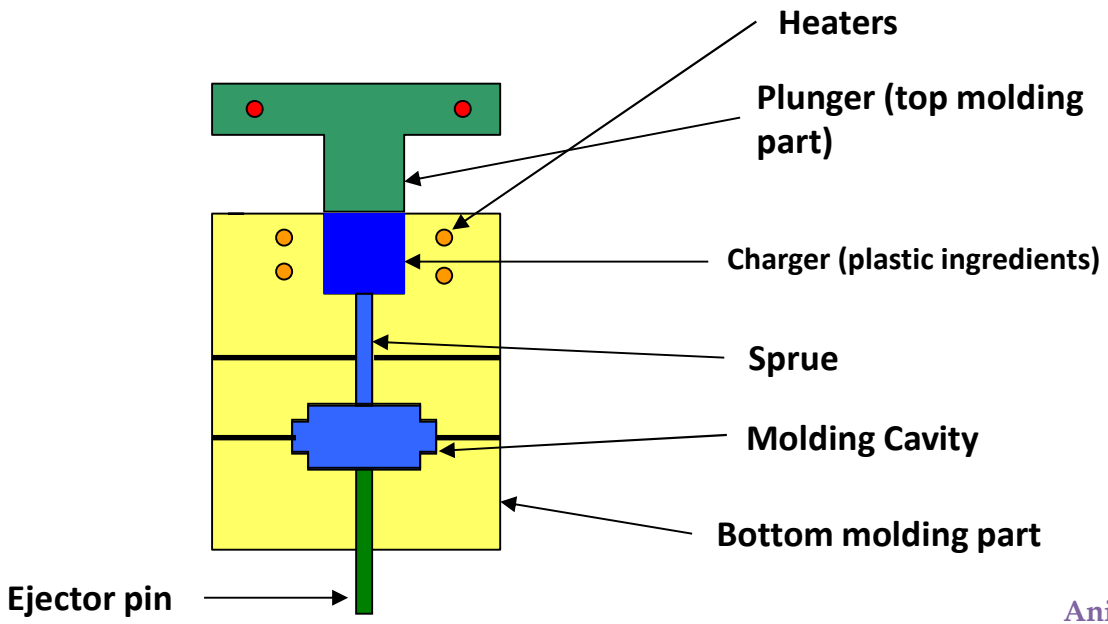
- Mainly for continuous moulding of thermoplastic materials into articles of uniform corss-section like tubes, rods, strips, insulated electric cables.
- The ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to be manufactured
- The plastic mass gets cooled by atmospheric exposure of by cooling air jets




Hopper
Extruder Barrel
Screw
Breaker Plate
Gear Pump
In-Line Head
Water Bath
Laser
Puller
Cutter

Transfer moulding

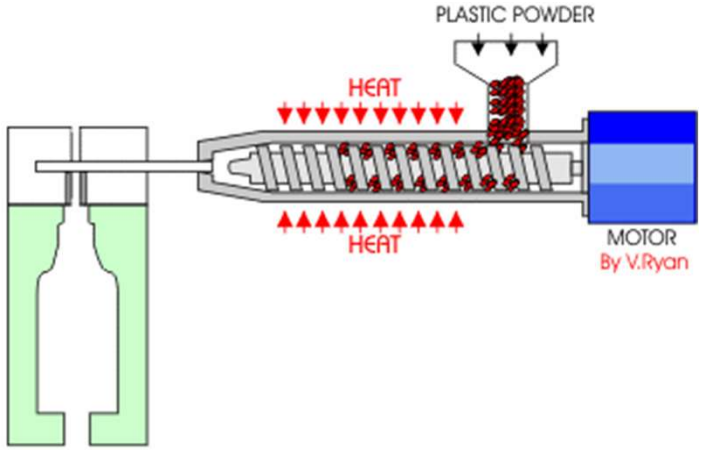
- This method uses the principle of injection moulding for thermosetting plastics.
- The moulding powder is placed in a heated chamber, to make them become plastic
- The material is then injected through an orifice into the mould by a plunger, working at a high pressure.
- The moulded article is then ejected mechanically
- Very delicate articles can be moulded, without distortion and displacement. Fine wires and glass fibres can be inserted into the mould. Articles moulded are free from flow marks

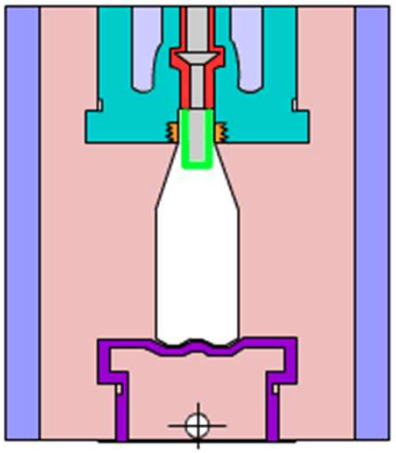


Animation courtesy: Dr. Arockiasamy

Blow moulding

- Blow molding is a manufacturing process by which hollow plastic parts are formed and can be joined together: It is also used for forming glass bottles or other hollow shapes.
- It involves the process of forming a molten tube (referred to as the parison or preform) of thermoplastic material (polymer or resin) ; The parison is a tube-like piece of plastic with a hole in one end through which compressed air can pass.
- The parison is then clamped into a mold and air is blown into it.
- The air pressure then pushes the plastic out to match the mold.
- Once the plastic has cooled and hardened the mold opens up and the part is ejected.





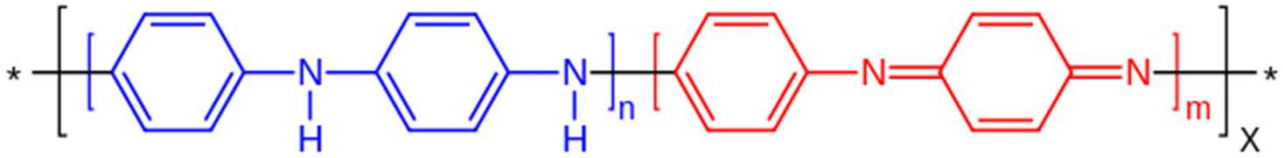
Conducting polymers

- Most polymeric materials are poor conductor of electricity, due to non availability of large number of free electrons in the conduction process
- In the past several years, polymeric materials have been synthesized which possess electrical conductivities as high as that of metallic conductors. These are called conducting polymers
- Conductivities as high as 1.5×10^7 $ohm^{-1}m^{-1}$ have been achieved. On a volume basis , this value is one-fourth the conductivity of Copper, but on a weight basis, it double the value for copper!

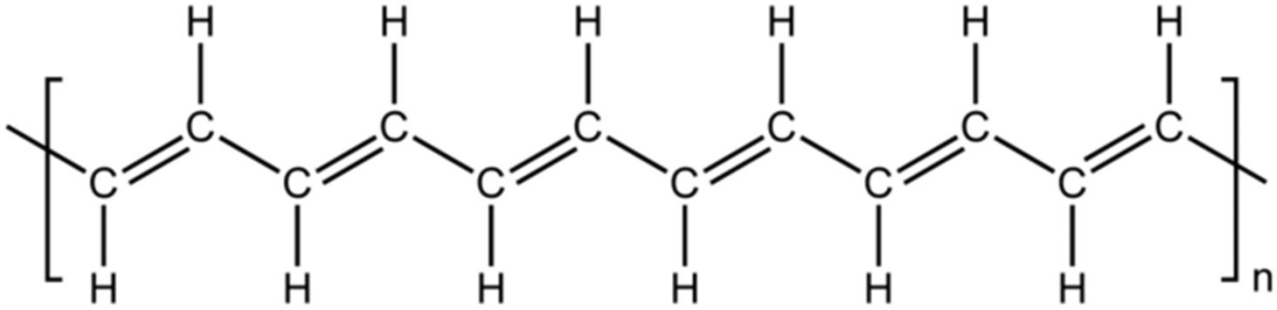
Types of conducting polymers

1. Intrinsically conducting polymers (ICP)
2. Doped conducting polymers
3. Extrinsically conducting polymers
4. Coordination conducting polymer (inorganic polymer)

Poly aniline and polyacetylene



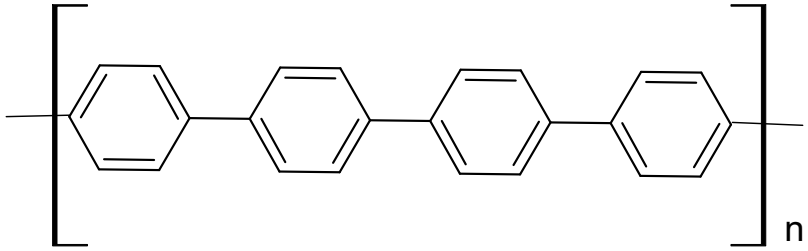
Poly aniline or PANI



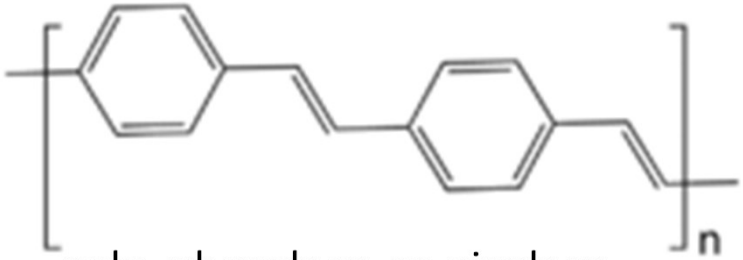
polyacetylene

Intrinsically conducting polymers (ICP)

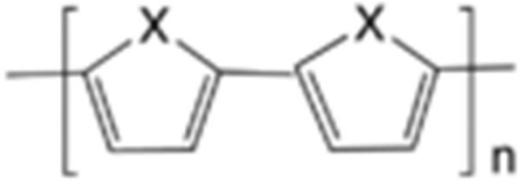
- Also known as conjugated π-electron conducting polymers, these are polymers whose backbone consists of delocalised electrons or residual charge
- They essentially contain conjugated π-electron backbone ie presence of alternate single and double bonds throughout the polymer backbone
- In an electric field, the conjugated π-electrons of the polymers get excited, thereby can be transported through the solid polymeric material through orbital overlapping
- This results in the formation of valence bands and conduction bands over the entire polymer molecule.
- Commercially important ICP's are:
- Polyacetylene polymers such as poly-p-phenylene, poly-quinoline, poly- phenylene-co-vinylene
- With condensed aromatic rings such as polyaniline, polyanthrylene
- With aromatic heteroatomic and conjugated aliphatic units such as polypyrrole, polythiophene, polybutadienylene



poly-p-phenylene



poly- phenylene-co-vinylene



(X = NH, S)

Polypyrrole & polythiophene

Doped conducting polymers

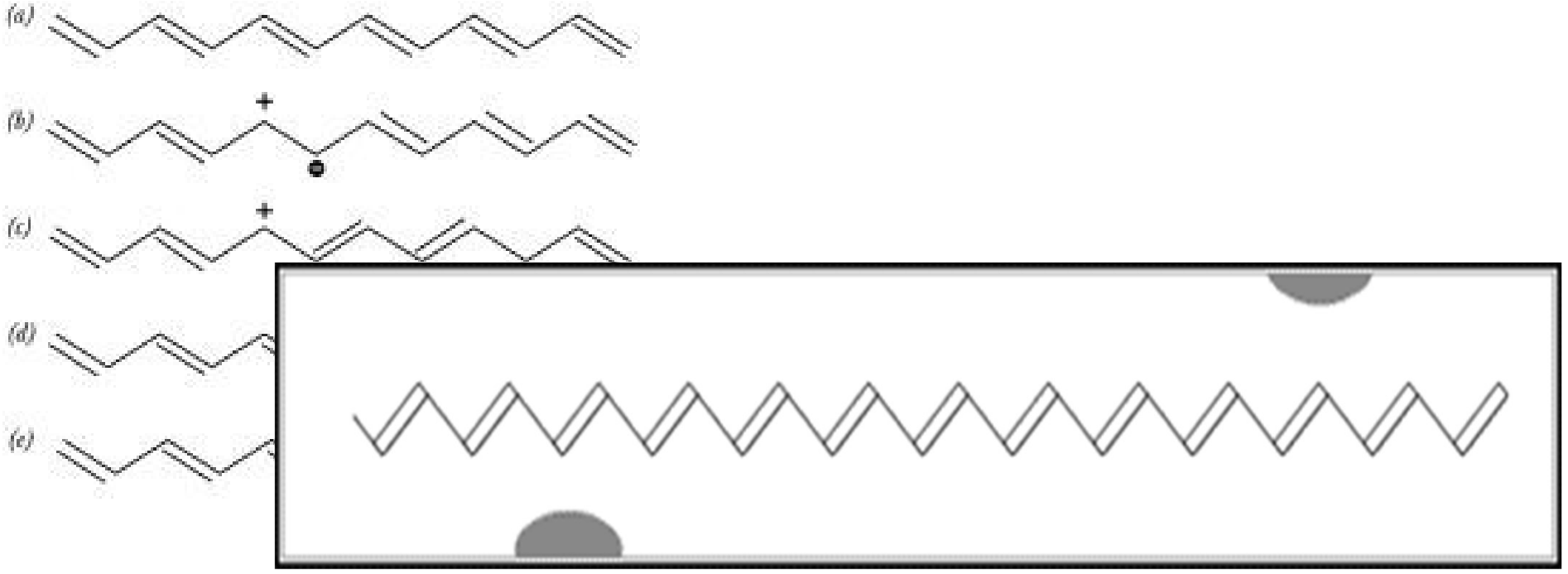
- These are obtained by exposing a polymers to a charge transfer agent in gas or in solution phase
- ICP possess low conductivity (10-10 Ω^{-1} cm^{-1}) but due to their low ionization potential and high electron affinities they can be easily oxidized or reduced
- Conductivity of ICP can be increased by creating either positive or negative charges on the polymer backbone by oxidation or reduction

- P-doping: this involves treating an ICP with a Lewis acid, thereby oxidation process takes place and positive charges on the polymer backbone are created
- Common p-dopants are I_2, Br_2, AsF_5, PF_6

$$2(C_2H_2)_n + 3I_2 \rightarrow 2(C_2H_2)_n^{+} I_3^{-}$$

Mechanism of conduction

- The iodine molecule attracts an electron from the polyacetylene chain and becomes I_3^-
- The polyacetylene molecule, now positively charged, is termed a radical cation, or polaron.
- The lonely electron of the double bond, from which an electron was removed, can move easily
- As a consequence, the double bond successively moves along the molecule
- The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily.



- N-doping: this involves treating an ICP with a Lewis base, thereby reduction process takes place and negative charges on the polymer backbone are created
- Common N-dopants are Li, Na, Ca, $FeCl_3$

$$\left(CH_n\right) + xNa \rightarrow \left(CH_n\right)^{x-} + xNa^{+}$$

Extrinsically conducting polymers

- Conductive element-filled polymer is a resin or polymer filled with materials such as carbon black, metallic fibres, metal oxides.
- The polymer acts as binder to hold the conducting elements together.
- They possess reasonably good bulk conductivity and are low in cost and light in weight.

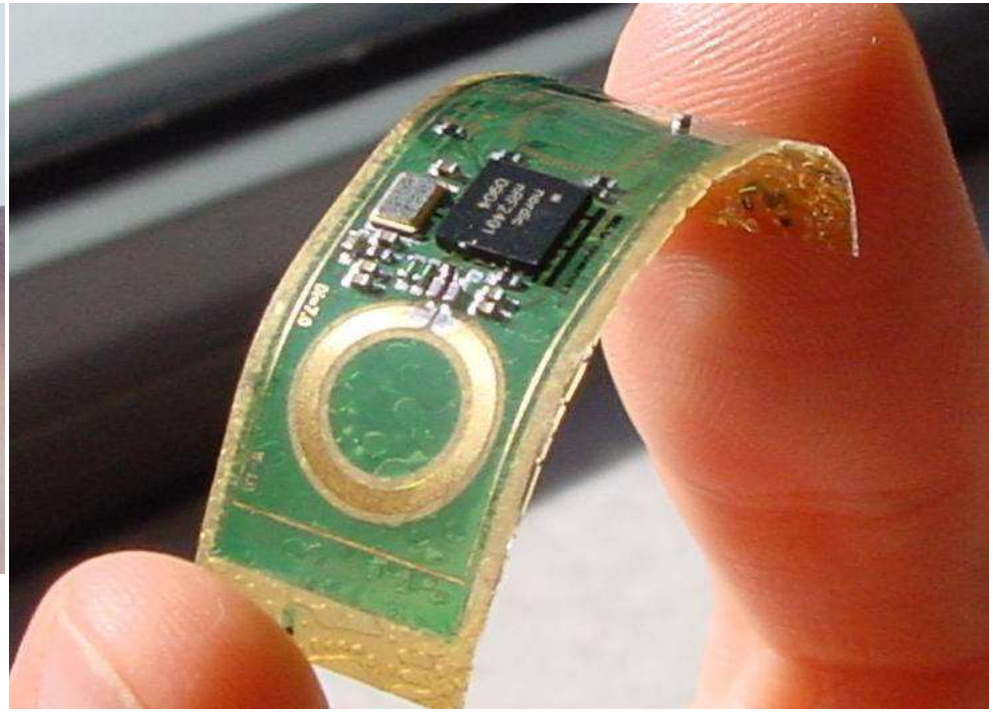
- Blended conducting polymer is a product obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change
- Such polymers are easily processed and possess goo physical, chemical and mechanical properties

Coordination conducting polymers

- A Charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand

Advantages

- A big advantage of conducting polymers over metals is that they serve as conducting materials that combine advantages of polymers such as light weight, greater workability, resistance to corrosion and chemical attack and very low cost of production
- Unlike metals, conducting polymers can be solubilised and cast as films or wires and so can be incorporated into flexible electronics such as flexible displays
- Their properties (bandgap, conductivity, mechanical properties etc)can be easily tuned by substituents on the polymer backbone



Applications

1. Conducting polymers are useful in discharging large quantities of static electricity in computer industries and in chemical industries. This can be accomplished by coating the conducting polymer over an insulating surface. Hence conducting polymers are used as **antistatics.**

2.Conducting polymers can absorb harmful electromagnetic radiation. So these can be used to coat on the cases of computer monitors and cell phones.

3. **Printed circuit boards** are used in electrical and electronic instruments. They contain copper coated epoxy resins which are expensive and have less adhesive nature. But polymer sheets coated with conducting polymers are inexpensive and have better adhesive properties.

4. These are useful in the preparation of artificial nerves i.e., biocompatible conductive polymers can be used for transmitting electrical signals in the body.

5. Conducting polymers can undergo oxidation and reduction depending upon the reagent with which they react. This property can be utilized in detecting gases. For example, the resistance of poly pyrrole increases on contact with NH_3 (reducing gas) while the resistance decreases in presence of NO_2(oxidizing gas).

6. **Polymer rechargeable batteries**: Repeated oxidation and reduction of polymeric back bone constitutes the principle of polymer rechargeable batteries. For example, in poly pyrrole lithium cell is useful rechargeable battery compared to conventional Ni-Cd cell. So, these are environmentally safe and non toxic.

7. These are useful as corrosion inhibitors.
8. These can applied in Flat Panel Displays (less than 2 mm thick) which are thinner than liquid crystals displays or plasma displays

9.These are also useful as Flexible Display Devices for mobile phones.

Conducting polymers have many uses. The most documented are as follows

- Corrosion Inhibitors
- Compact Capacitors
- Anti Static Coating
- Electromagnetic shielding for computers
- "Smart Windows"

A second generation of conducting polymers have been developed these have industrial uses like,

- Transistors
- Light Emitting Diodes (LEDs)
- Lasers used in flat televisions
- Solar cells