Module-7

Polymers

Contents…

- **Difference between thermoplastics and thermosetting plastics; Engineering applications of plastics - ABS, PVC, PTFE and Bakelite (1 hour)**
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- **Different moulding processes - Injection moulding (Car parts/ bottle caps), Extrusion moulding (Pipes/ Hoses), Compression moulding (Mobile Phone Cases/ Battery Trays), Transfer moulding (Fibre reinforced polymer matrix composites) and blow moulding (PET bottles) (2 hours)**
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- **Conducting polymers- Polyacetylene- Mechanism of conduction – applications (polymers in sensors, self-cleaning windows) (1 hour)**

Basic terms in polymer science

Polymer : Polymers are complex and giant molecules which are made from joining a large number of small and simple molecules by primary valency linkage.

Monomer : The individual small and simple molecules from which the polymer is formed are known as monomer.

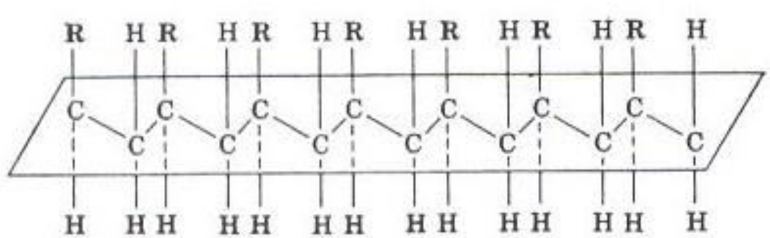
Polymerization : The process by which the monomer molecules are linked to form a big polymer molecule is called polymerization.

$$n\,CH_2 = CH_2 \xrightarrow{Catalyst} -\!\!\left(CH_2 - CH_2\right)\!\!-_n$$

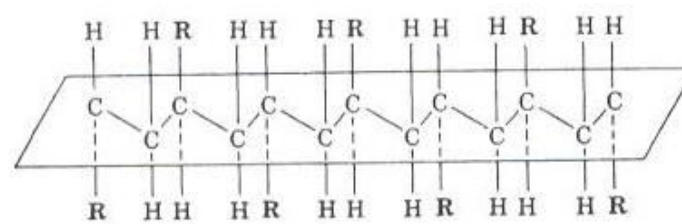
Functionality: The number of bonding sites or active sites in a monomer is called its functionality.

Degree of polymerization : The number of monomers forming the polymer chain are called its degree of polymerization

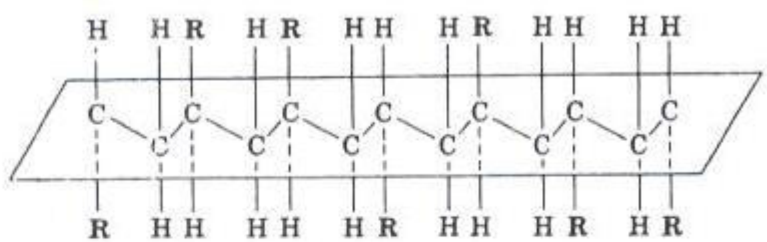
Tacticity : The spatial arrangement of pendent groups of successive stereocenters (asymmetric carbon) in the main chain is called its tacticity.



Isotactic Polymer



Syndiotactic Polymer



Atactic Polymer

Classification

One classification divides polymers in to condensation and addition polymers and the other divides them in to step and chain growth polymers.

Depending on their origin polymers are classified into **natural and synthetic polymers.**

Depending on kind of atoms constituting backbone of the polymer they are classified as **organic and inorganic polymers.**

Depending upon their ultimate use polymers are classified into **plastics, elastomers, fibres and liquid resins.**

A polymer which can be reshaped into hard and tough utility articles by applying heat, pressure or both is said to be a **plastics**.
Examples: Polystyrene, Poly(vinyl chloride), Poly(methyl methacrylate), polyester etc.

A polymer which can show good strength and elongatoan upon vulcanization is called an **elastomer.**
Examples: polyisoprene, polyisobutylene, etc.

A polymer which can be drawn into log filament like material whose length is at least 100 times at its diameter is called a **fibre.**
Examples: nylon, terylene, polyester, polyacrylonitrile, etc.

A polymer used as adhesives, potting compounds, sealants etc in a liquid form is called as **liquid resin.**
Examples: Epoxy adhesives, poly sulphides, sealants, etc.

Depending on the number of kinds of monomer used in polymerization they are classified into homopolymer and copolymer.

Homopolymers are one in which only one kind of monomer is used to prepare the polymer during polymerization.

Examples: polystyrene, polyacrylamide, etc.

Copolymer is one in which more than one kind of monomers are used to prepare the polymer during polymerization.

Examples: poly(vinylchloride-co-vinyl acetate), poly(styrene-co--butadiene).

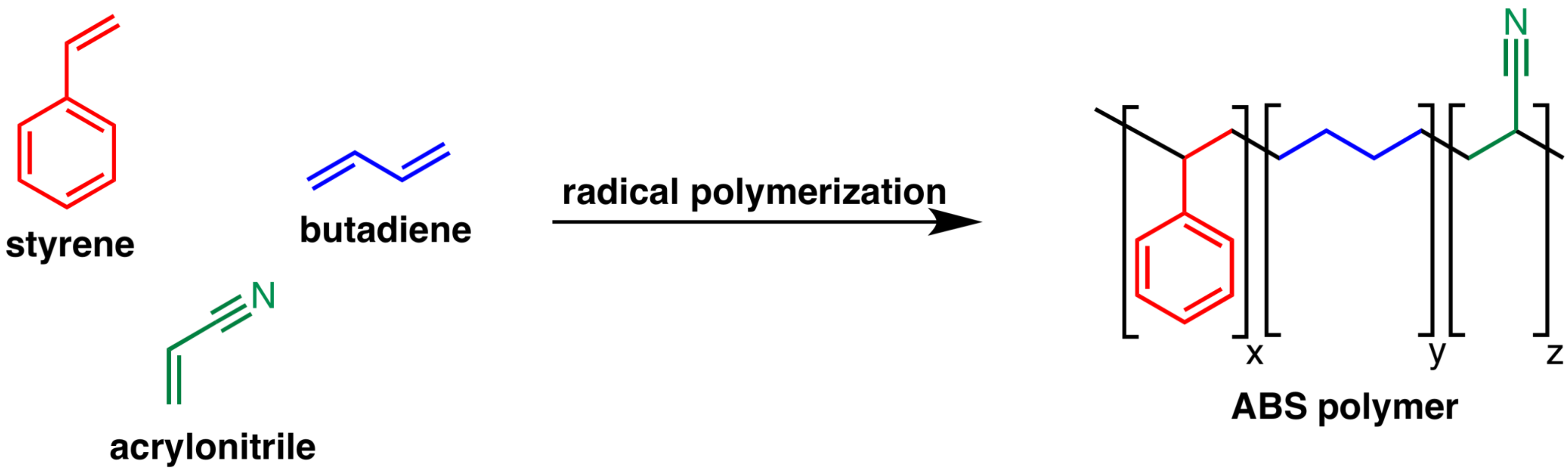
Further homopolymers are sub classified into linear, branched and crosslinked polymer based on their chain configuration (i.e. depending on their structure).

Thermoplastic	Thermosetting
They are formed by addition polymerization only.	They are formed by condensation polymerization.
They consist of long chain linear polymers with negligible cross-links.	They have three dimensional network structures, joined by strong covalent bonds.
They soften on heating readily because secondary forces between the individual chain can break easily by heat or pressure.	The cross-links and bonds retain their strength on heating and hence, they do not soften on heating on prolonged heating charring of polymers is caused.
By re-heating to a suitable temperature, they can be softened, reshaped and thus reversed.	They retain their shape and structure even on heating. Hence they cannot be reshaped and reversed.
They are usually soft, weak and less brittle.	They are usually, hand, strong and more brittle.
These can be reclaimed from wastes.	They cannot be reclaimed from wastes.
They are usually soluble in some organic solvents.	Due to storing bonds and crosslinking they are insoluble in almost all organic solvents.

Engineering Applications of Polymers

- **Engineering applications of plastics - ABS, PVC, PTFE and Bakelite**

ABS (Acrylonitrile-Butadine-Styrene)



This material is a terpolymer of acrylonitrile, butadine and styrene.

ABS (Acrylonitrile-Butadine-Styrene)

- **ADVANTAGES:**
- Good impact resistance with toughness and rigidity
- Metal coatings have excellent adhesion to ABS
- Formed by conventional thermoplastic methods
- A light-weight plastic

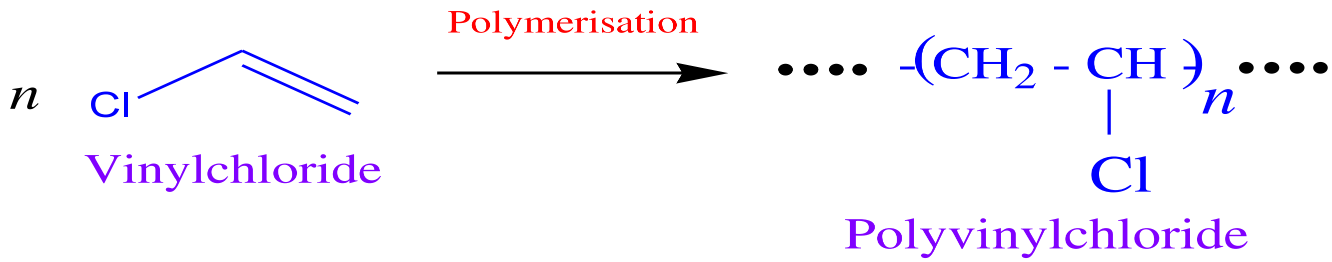
DISADVANTAGES AND LIMITATIONS:

- Poor solvent resistance
- Low dielectric strength
- Only low elongations available
- Low continuous service temperature

TYPICAL ENGINEERING APPLICATIONS:

- Automotive hardware (used in electroplated metal coatings for decorative hardware), appliance cases, pipe, plated items.

PVC (Polyvinyl Chloride)



Properties:

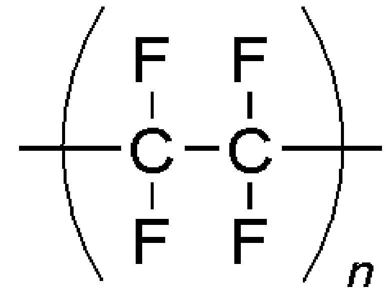
1.PVC is colourless, odourless and chemically inert powder

2. It is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons.

3. It undergoes degradation in presence of heat (or) light.

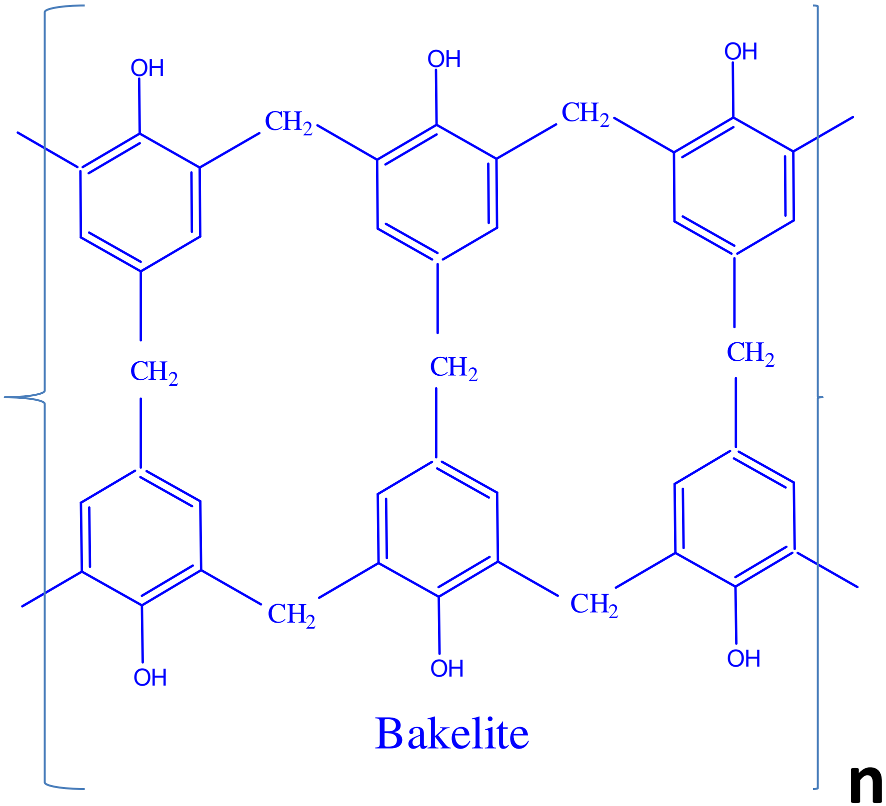
Applications: A variety of applications in the building and construction, health care, electronics, automobile and other sectors, in products ranging from piping, cable insulations, table covers and rain-coasts and siding, blood bags and tubing, to wire and cable insulation, windshield system components, tank-linings, light fittings, refrigerator components and more.

PTFE (Polytetrafluoroethylene) or Teflon



- The major applications of PTFE are found as wiring in aerospace and computer applications (*e.g.* hookup wire, coaxial cables, printed circuit boards) due to its excellent dielectric properties.
- A high-performance substitute for the weaker and lower-melting-point polymers because of its high melting temperature.
- Owing to its low friction, PTFE is used industrially for plain bearings, gears, seals, gaskets, and more applications.
- This is an ideal material for fabricating long-life electrets (a permanently polarized piece of dielectric material), the electrostatic analogues of permanent magnets based on its high bulk resistivity.
- PTFE film is also widely used in the production of carbon fiber composites as well as fiberglass composites, notably in the aerospace industry..
- PTFE is used in some aerosol lubricant sprays, and also in coating non-stick frying pans due to its high heat resistance and hydrophobic nature.

Bakelite



Cooker with **Bakelite** Handles

Properties and Applications of Bakelite

Properties

1. Bakelite is resistant to acids, salts and most organic solvents, but it is attacked by alkalis because of the presence of –OH groups
2. It possesses excellent electrical insulating property

Applications

1. Bakelite is used as an adhesive in plywood laminations, grinding wheels etc.
2. It is also widely used in paints, varnishes, decorative articles like plates, drinking glasses, dishes etc.
3. It is used for making electrical insulator parts like plugs, switches, heater handles etc.,

Moulding Processes

- **Different moulding processes - Injection moulding (Car parts/ bottle caps), Extrusion moulding (Pipes/ Hoses), Compression moulding (Mobile Phone Cases/ Battery Trays), Transfer moulding (Fibre reinforced polymer matrix composites) and blow moulding (PET bottles) (2 hours)**

Moulding Processes

This process involves fabrication of plastic material into desired shape under the influence of heat and pressure in a closed chamber.

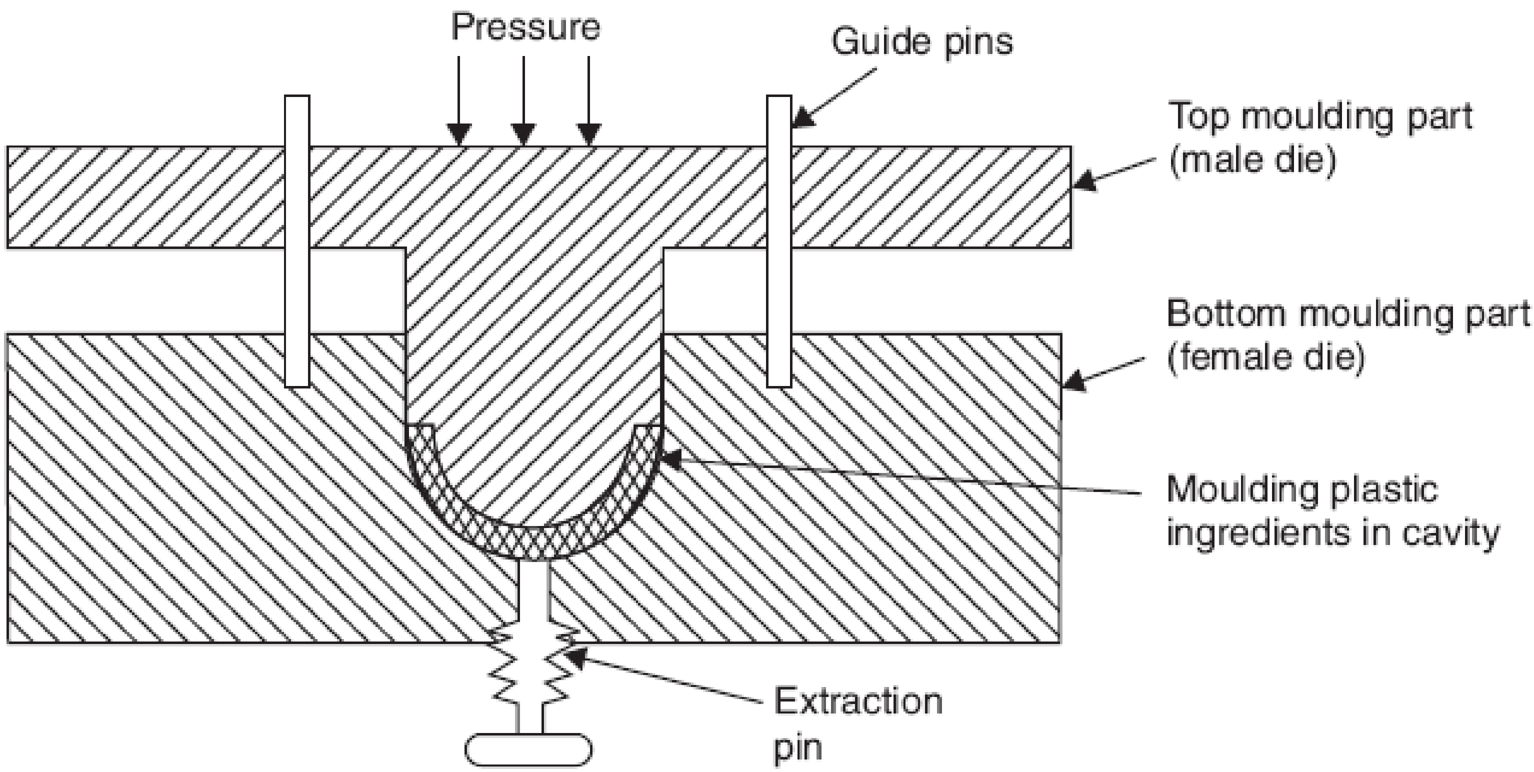
Types of Moulding:

1. **Compression Moulding**
2. **Injection Moulding**
3. **Transfer Moulding**
4. **Extrusion Moulding**
5. **Blow Moulding**

Compression Moulding

- This method is applied to both thermoplastics and thermosetting plastics
- Figure shows a typical method used for compression moulding
- The mould is made up of two halves, the upper and the lower halves.
- The lower half usually contains a cavity in the shape of the article to be moulded.
- The upper half has a projection, which fits into the cavity when the mould is closed.
- The material to be moulded is placed in the cavity of the mould. Then the mould is closed carefully under low pressure
- Finally the mould is heated to 100-200^{o} C and simultaneously high pressure (100-500 kg/cm^2) is applied on the top of the mould.
- Curing is done either by heating or cooling. After curing the moulded article is taken out by opening the mould parts.

Compression Moulding



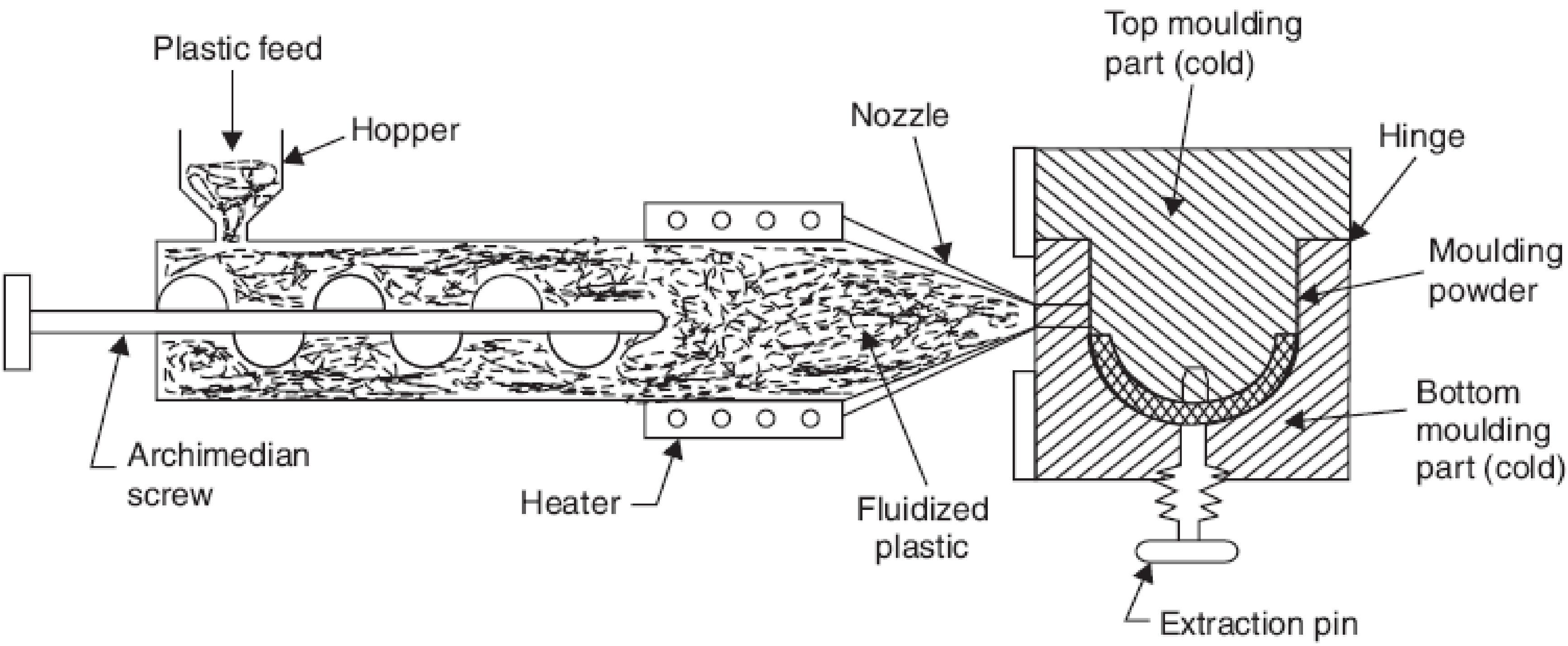
Injection Moulding

1. This method is mainly applicable to thermoplastics.
2. The powdered plastics material is fed into a heated cylinder through they hopper (Fig).
3. The plastic material melts under the influence of heat and becomes fluid.
4. The hot fluid is injected at a controlled rate into a tightly locked mould by means of a screw arrangement or by a piston
5. The mould is kept cold to allow the hot plastic to cure and becomes rigid. After curing the mould is opened and the object is ejected.
6. Telephones, buckets etc., are made by this method.

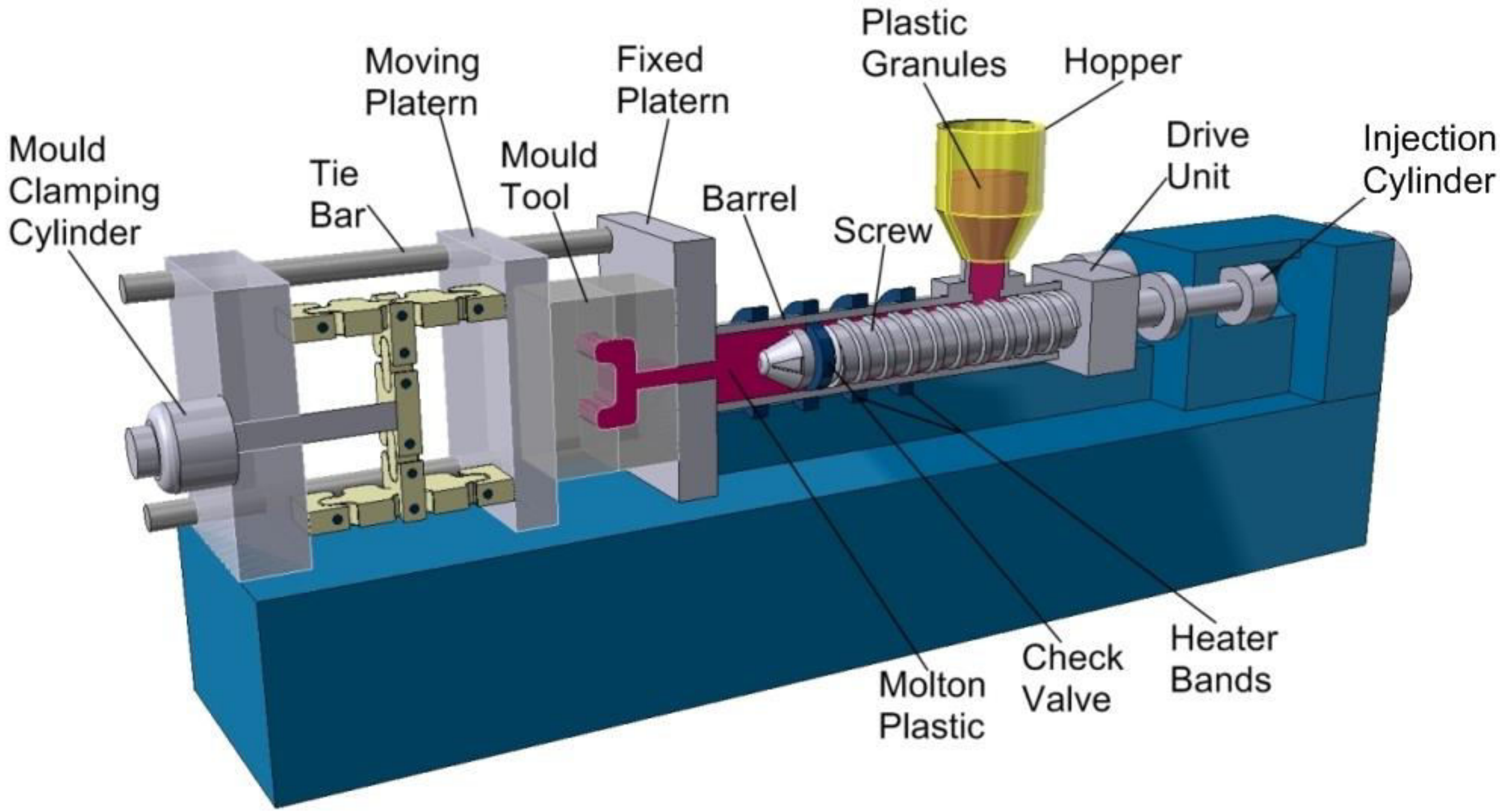
Advantages

1. Low mould cost
2. Low finishing cost
3. Low loss of materials
4. High speed production

Injection Moulding



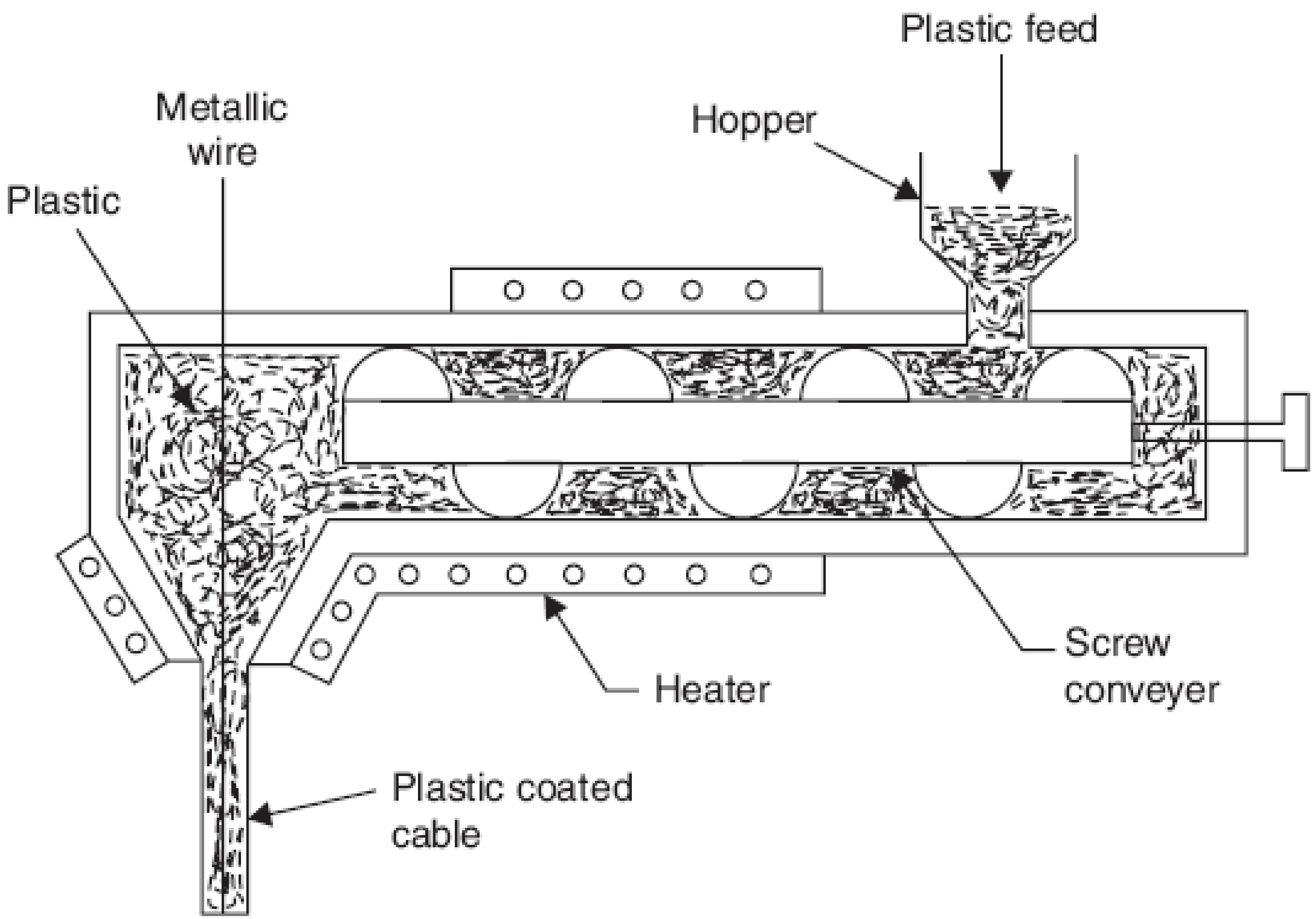
Injection Moulding Machine



Extrusion Moulding

- This method is mainly used for continuous moulding of thermoplastic materials into articles of uniform cross section like rods, tubes etc.
- In this method, the powdered plastic material is fed into the heated cylinder through the hopper.
- The molten plastic material is then pushed by means of a revolving screw conveyor into a die having the required shape of the object to be manufactured. The finished product that extrudes out is cooled by atmospheric air. A long conveyor carries away the cooled product.

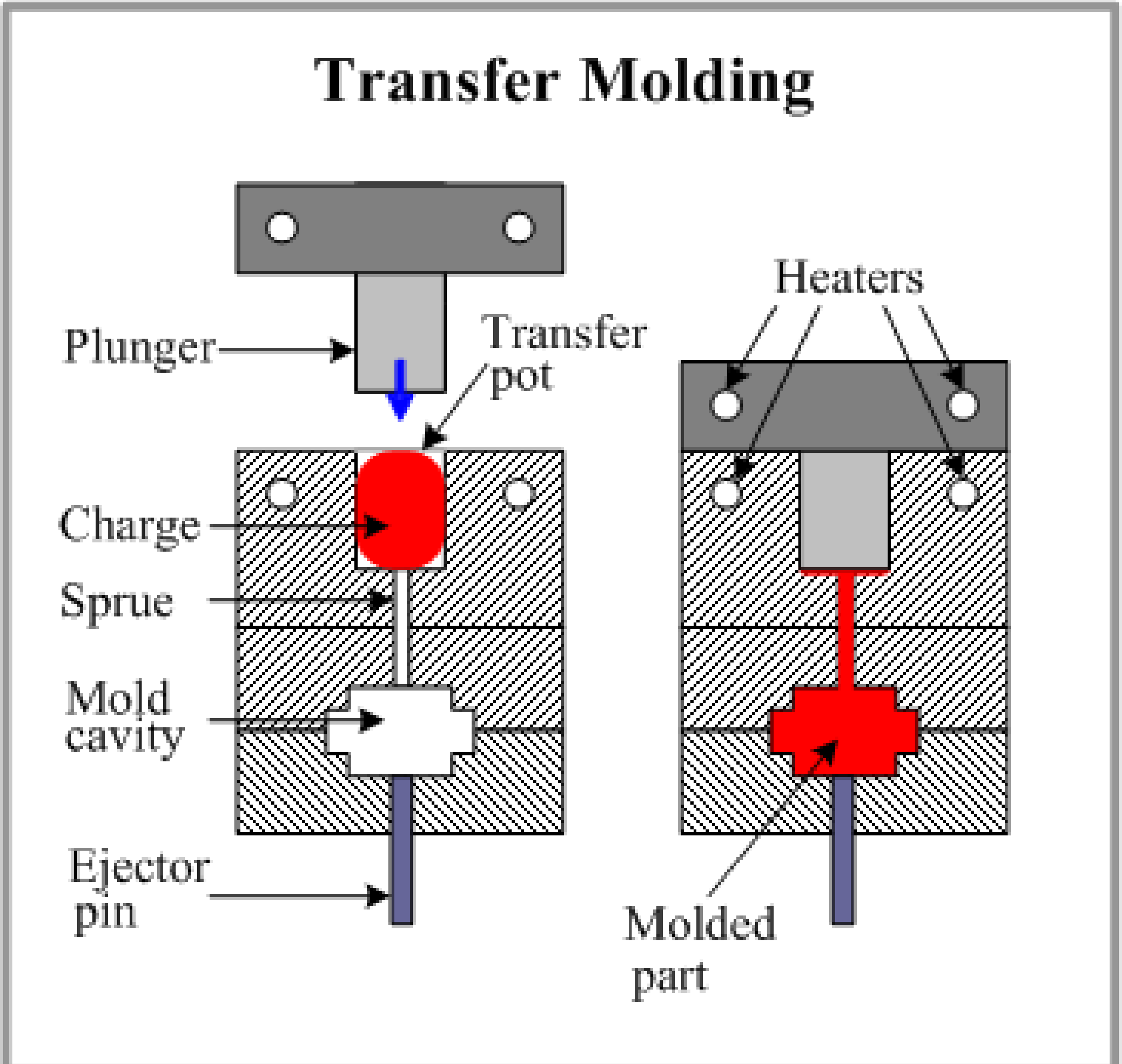
Extrusion Moulding



Extrusion Moulding Machine

Transfer Moulding

1. This method is used for thermosetting plastics
2. The principle is same as that of the injection moulding
3. The powdered moulding materials is taken in a heated chamber, maintained at low temperature, at which the material just begins to become plastic.
4. This plastic is then injected through an orifice into the mould by a plunger working at high pressure (Fig)
5. Due to the great friction developed at the orifice during ejection, the temperature of the material rises to such an extent that the moulding powder becomes almost liquid. So that it flows quickly and easily into the mould.
6. Then the mould is heated upto the curing temperature required for setting. Finally the moulded article is ejected from the mould.


Transfer Molding
Plunger
Transfer pot
Charge
Sprue
Mold cavity
Ejector pin
Heaters
Molded part

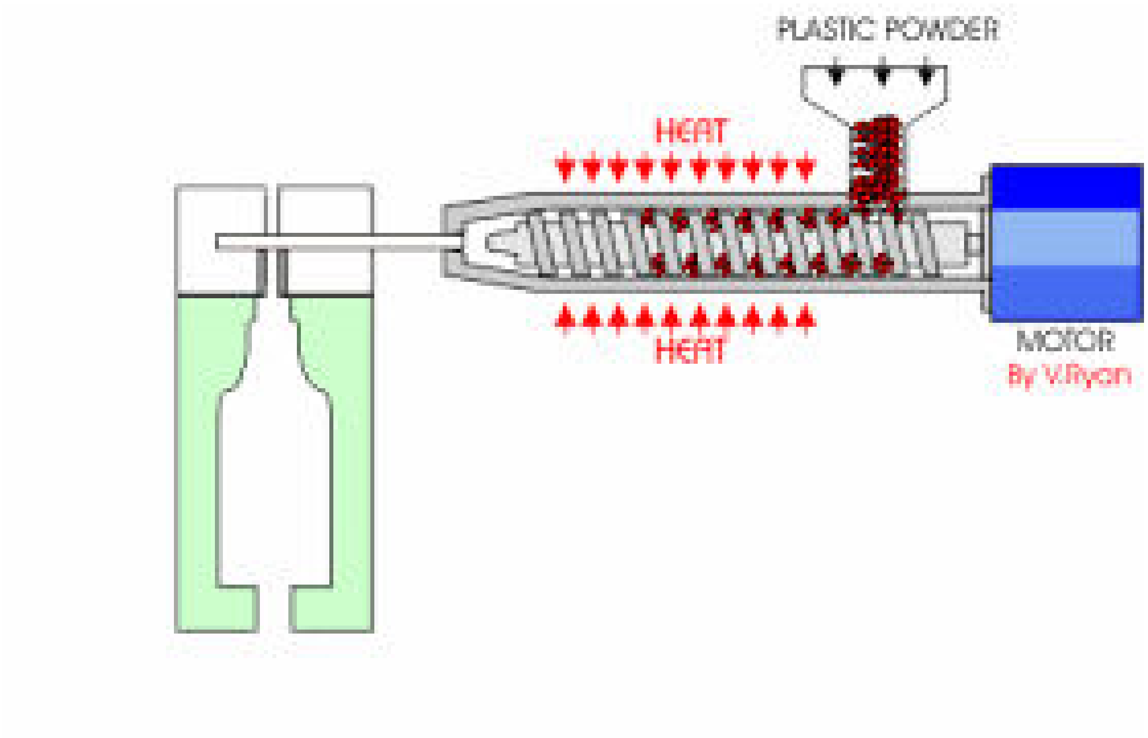
Transfer Moulding Machine

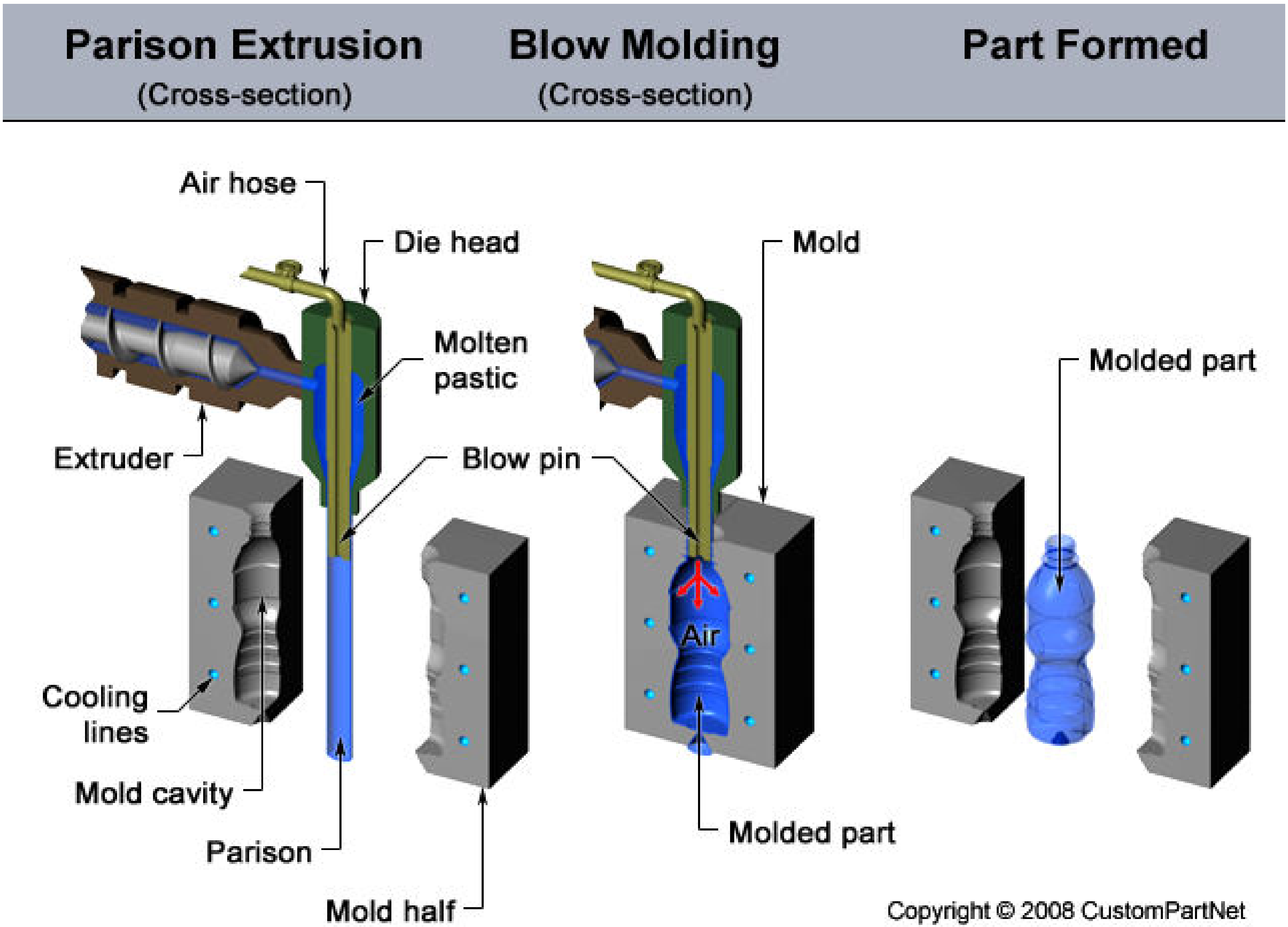
Advantages of Transfer Moulding

1. More complicated shapes can be fabricated by this method
2. Less expensive
3. Blisters can be eliminated
4. Shrinkage and distortion are minimum
5. Very delicate articles can be made by this method

Blow moulding for plastic bottles

- Blow moulding is the process of forming a molten tube (preform) of thermoplastic material (polymer or resin) and placing the preform within a mould cavity and inflating the tube with compressed air, to take the shape of the cavity and cool the part before removing from the mould.





Parison Extrusion
(Cross-section)
Blow Molding
(Cross-section)
Part Formed
Air hose
Die head
Molten
pastic
Extruder
Blow pin
Cooling
lines
Mold cavity
Parison
Mold half
Mold
Air
Molded part
Molded part
Copyright © 2008 CustomPartNet

- The major **difference between injection moulding and blow moulding** is the kind of product produced. Typically, **blow moulding** is designed to produce hollow, singular containers, such as bottles. On the other hand, **injection moulding** is used to produce solid pieces, such as plastic products.

- **Advantages:** Because of lower pressure, the mold **costs** in this blow molding are lower as compared to injection molding and the machinery **costs** are **low** as well.

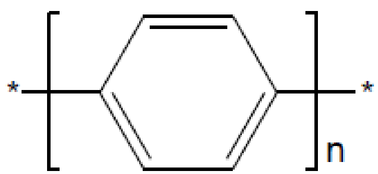
Conducting Polymers

- **Polyacetylene- Mechanism of conduction – applications (polymers in sensors, self-cleaning windows) (1 hour)**

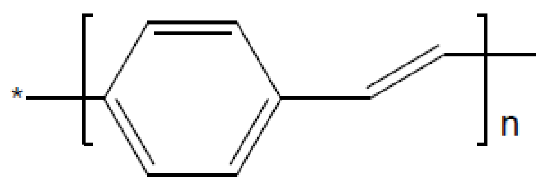
Conducting Polymers

A conducting polymer is an organic based polymer that can act as a semiconductor or a conductor.

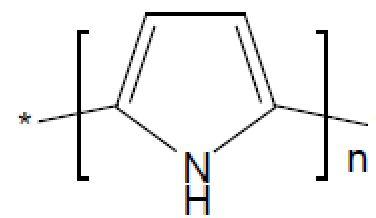
The most widely studied organic polymers are Polyacetylene, polyaniline (PANI), polypyrroles, polythiophenes, and polyphenylene vinylenes.



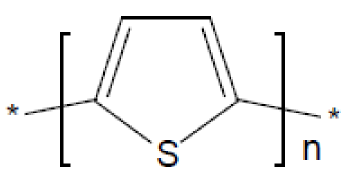
Poly (p-phenylene)



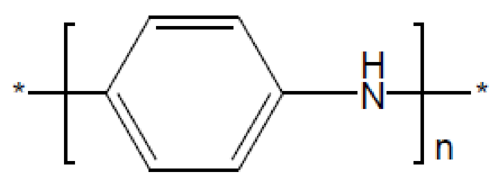
Polyphenylene vinylene



Polypyrrole



Polythiophene



Polyaniline

Conducting polymers (CPs) are extensively conjugated molecules: they have alternating single and double bonds. In these molecules, electrons are able to move from one end of the polymer to the other through the extended p-orbital system.

Hence CPs are known to be either semiconductors or conductors giving them unique optical and electrical properties.

Most polymers are poor conductors due to non-availability of large number of free electrons in the conduction process.

However, conducting polymers are synthesized which possess electrical Conductivity similar to metal conductors.

Different Types:

(1) Intrinsically conducting polymers (ICP)

(2) Doped Conducting polymers

(3) Extrinsically conducting polymers (ECP)

Factors that affect the conductivity

1. Density of charge carriers
2. Their mobility
3. The direction
4. Presence of doping materials (additives that facilitate the polymer conductivity in a better way)
5. Temperature

1. Intrinsically Conducting Polymers

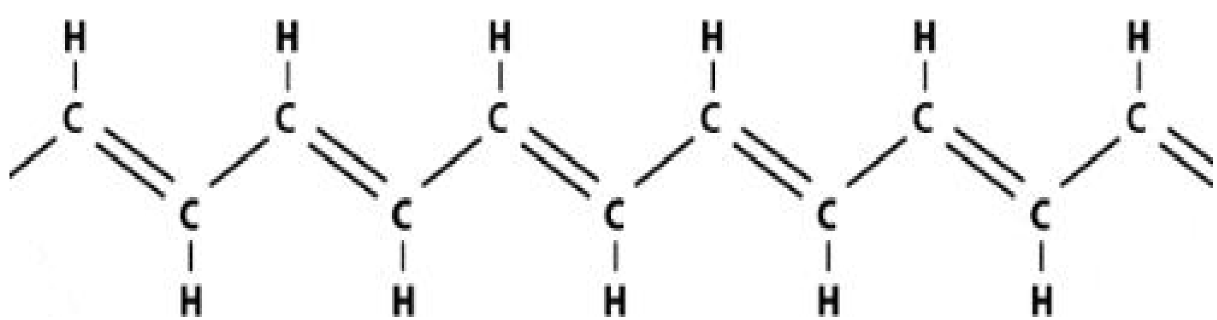
Polymer consisting of alternating single and double bonds is called conjugated double bonds.

In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond.

In addition, every double bond also contains a less strongly localised “pi” (π) bond which is weaker.

Conjugation of sigma and pi-electrons over the entire backbone, forms valence bands and conduction bands.

Eg: Poly-acetylene polymers like poly-p-phenylene, polyaniline, polypyrrole



2. Doped Conducting Polymers

It is obtained by exposing a polymer to a charge transfer agent in either gas phase or in solution. ICPs possess low conductivity (10^{-10}/Ohm.cm), but they possess low ionisation potential and high electron affinity. So they can be easily oxidised or reduced.

DOPING:

The conductivity of ICP can be increased by creating positive charges (oxidation) or by negative charges (reduction) on the polymer backbone. This technique is called **DOPING** .

In otherwords....

The polymer structure has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. The process is known as Doping.

There are two types of doping:

1. Oxidation with halogen (or *p*-doping).
2. Reduction with alkali metal (called *n*-doping).

(i) p-Doping:

It involves treating an intrinsically conducting polymer with a Lewis acid which leads to oxidation process and positive charges on the polymer backbone are created.

Some of the p-dopants are I_2, Br_2, AsF_5, PF_5 etc.

$$\underset{\text{polyacetylene}}{2(C_2H_2)_n} \quad + \quad 3I_2 \quad \longrightarrow \quad \underset{\text{Lewis acid}}{2[(C_2H_2)_n^{+}\, I_3^{-}}$$

(ii) n-Doping:

It involves treating an ICP with a Lewis base which leads to reduction process and negative charges on the polymer backbone are created.

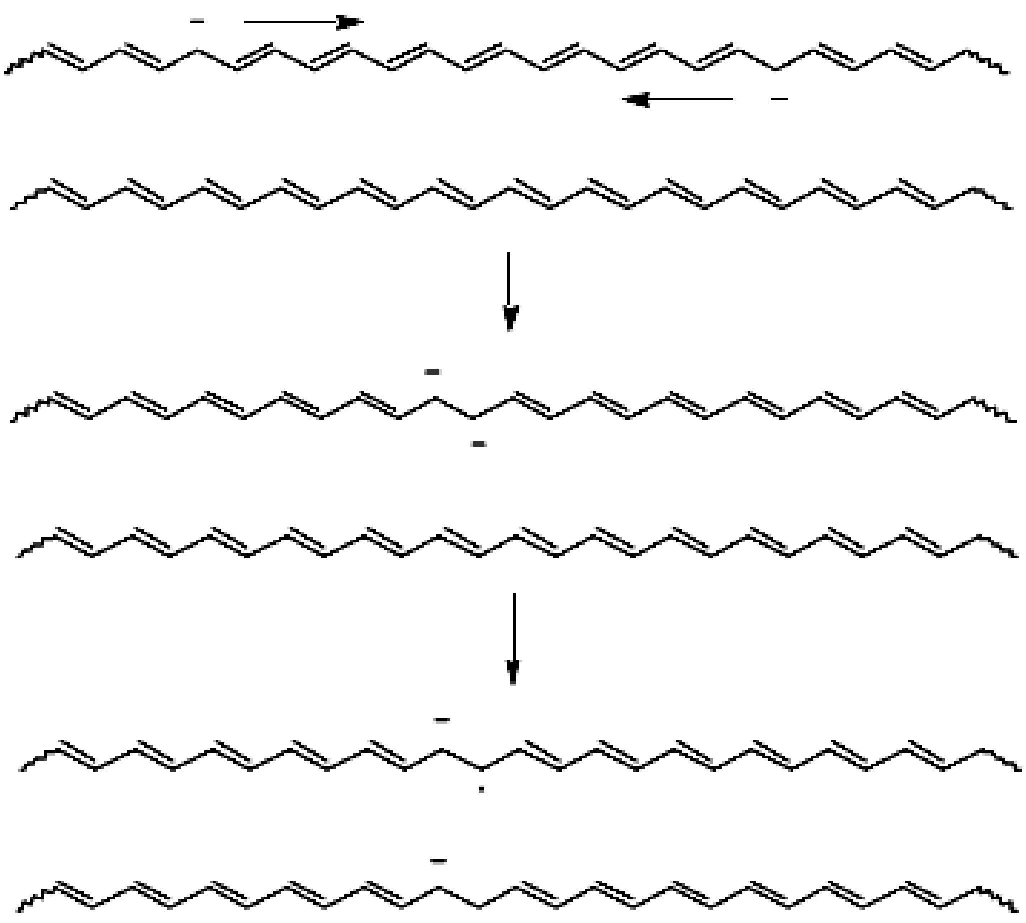
Some of the n-dopants are Li, Na, Ca, $FeCl_3$, naphthylamine etc.

$$\ldots\text{-CH=CH-CH=CH-}\ldots + C_{10}H_7NH_2 \longrightarrow \ldots\text{-CH=CH-}\underset{\underset{^{+}NH}{|}}{\overset{-}{C}}\text{H=CH-} + C_{10}H_8$$

Conductivity Mechanism in Polyacetylene:

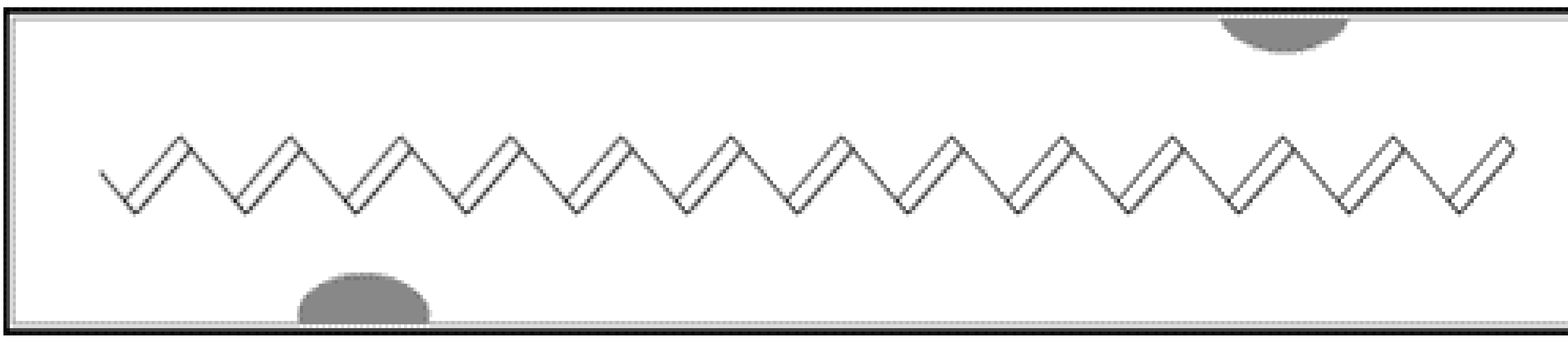
- The mechanism followed by polyacetylene for the transfer of charge from one chain to another is called **intersoliton hopping**.

- **What is a soliton?** The soliton is a charged or a neutral defect in the polyacetylene chain that propagates down the chain, thereby reducing the barrier for interconversion.



- In n-type doping (This can be done by dipping the film in THF solution of an alkali metal) soliton is a resonance-stabilized polyenyl anion of approximately 29-31 CH units in length, with highest amplitude at the centre of the defect.
- The solitons (anions) transfer electrons to a neutral soliton (radical) in a neighboring chain through an isoenergetic process.
- The charged solitons are responsible for making polyacetylene a conductor.

- In p-type doping, The dopant (Iodine, I_2) attracts an electron from the polyacetylene chain to form (I_3^-) leaving a positive soliton (carbenium ion) in the polymer chain that can move along its length.
- 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, and the polymer is stabilized by having the charge spread over the polymer chain.



3. Extrinsically Conducting Polymers

These are those polymers whose conductivity is due to the presence of externally added ingredients in them.

Two types:

(1) Conductive element filled polymer:

It is a resin/polymer filled with carbon black, metallic fibres, metal oxides etc. Polymer acts as a binder to those elements.

These have good bulk conductivity and are low in cost, light weight, strong and durable. They can be in different forms, shapes and sizes.

(2) Blended Conducting Polymers:

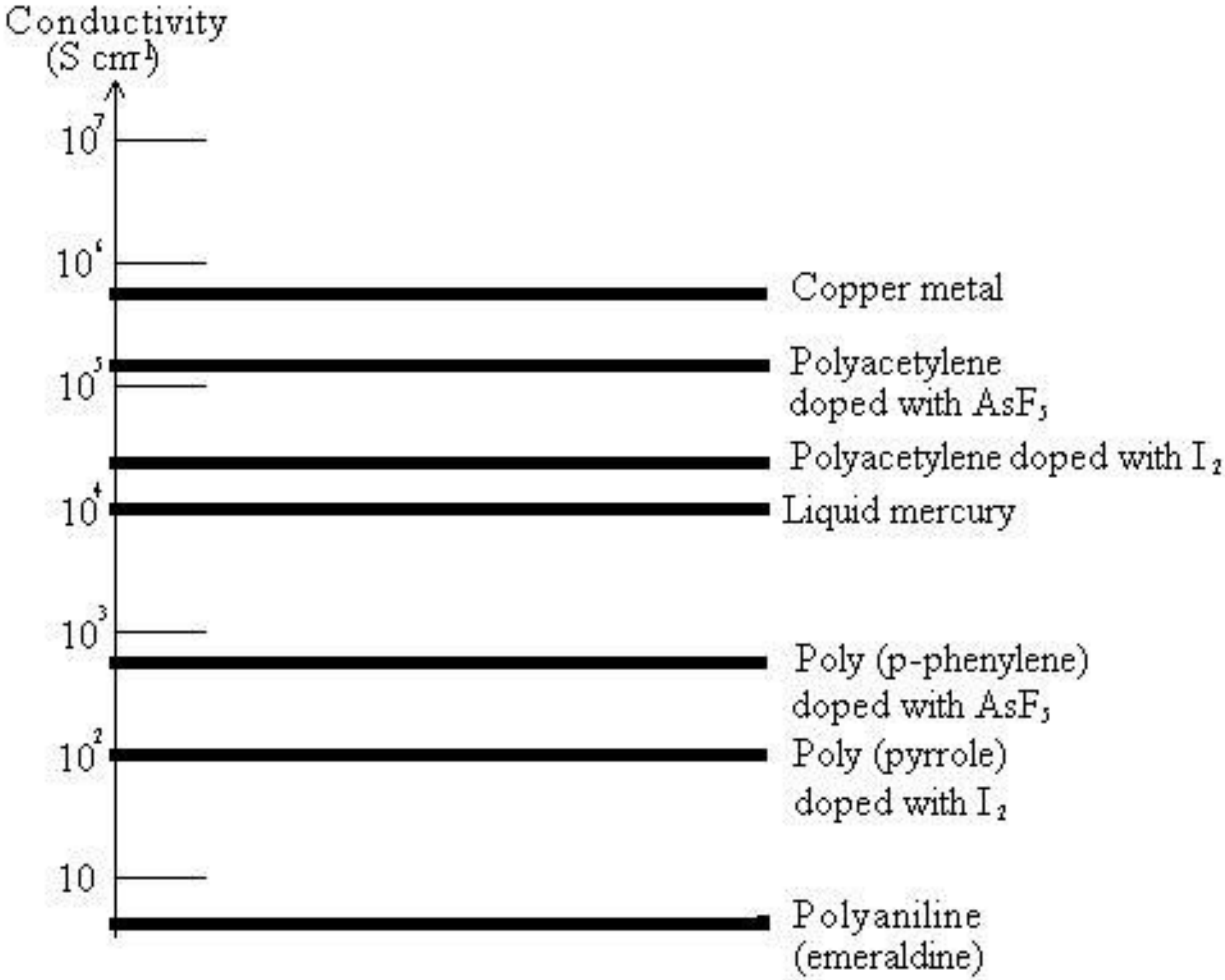
It is product obtained by blending a conventional polymer with a conducting polymer either by physical or by chemical change.

Such polymers can be processed and possess better physical, chemical and mechanical strength.

Applications of conducting polymers

1. As sensors into clothing
2. Conducting polymer textiles as a camouflage for defense machinery. Since the textiles have no sharp edges they absorb more than 50% of the incident microwave radiation.
3. In LEDs
4. In controlled drug release applications etc.

APPLICATIONS OF CONDUCTING POLYMERS



Logarithmic conductivity ladder locating some metals and conducting polymers

APPLICATIONS OF CONDUCTING POLYMERS

Group 1

Electrostatic materials
Conducting adhesives
Electromagnetic shielding
Printed circuit boards
Artificial nerves
Antistatic clothing
Piezoceramics
Active electronics:
Aircraft structures

Group 2

Molecular electronics
Electrical displays
Chemical, biochemical and thermal sensors
Rechargeable batteries and solid electrolytes
Drug release systems
Optical computers
Ion exchange membranes
Electromechanical actuators (diodes, transistors)
'Smart' structures and Switches

The first group utilizes their conductivity as its main property.
The second group utilizes their electroactivity.