Module – 7: Polymers

- Difference between 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)

Introduction to Polymers

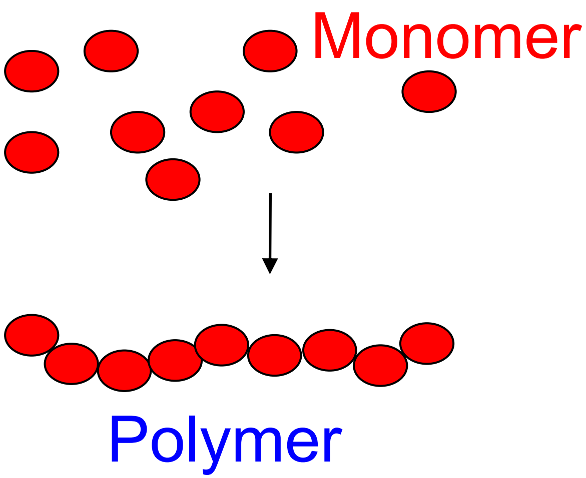
Polymers: Poly + mers

Poly means **many**

mers means **units** or **parts**

Polymers - **Many repeated parts**

- or **many repeated units**



Definition of Polymer

Polymers are macromolecules (giant molecules of higher molecular weight) formed by the repeated linking of large number of small molecules called **monomers**.

Example:

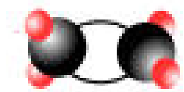
$$n\ CH_2 = CH_2 \longrightarrow \text{------}(CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-})_n\text{------}$$

Ethylene (monomer) | **Polyethylene (polymer)**

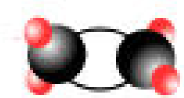
Definition

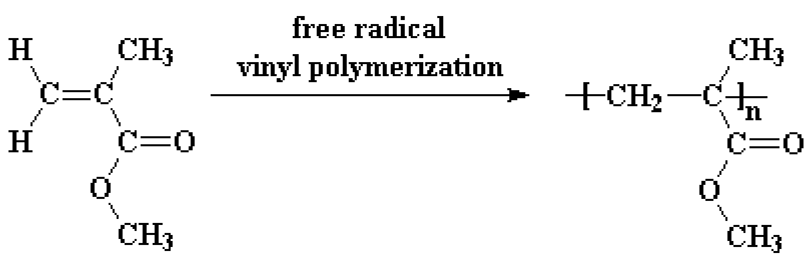
Polymers are materials made of long, repeating chains of molecules. The materials have unique properties, depending on the type of molecules being bonded and how they are bonded.

Terminology



Monomer	**: one unit**	**(A)**
Dimer	**: two units**	**(A-A)**
Trimer	**: three units**	**(A-A-A)**
Tetramer	**: four units**	**(A-A-A-A)**
Polymer	**: many units**	**$(\text{-A-A-A-A-A-A-A-A-A-A-A-})_n$**





methyl methacrylate poly(methyl methacrylate)

Polymer – Classification

Polymers are classified based on different parameters

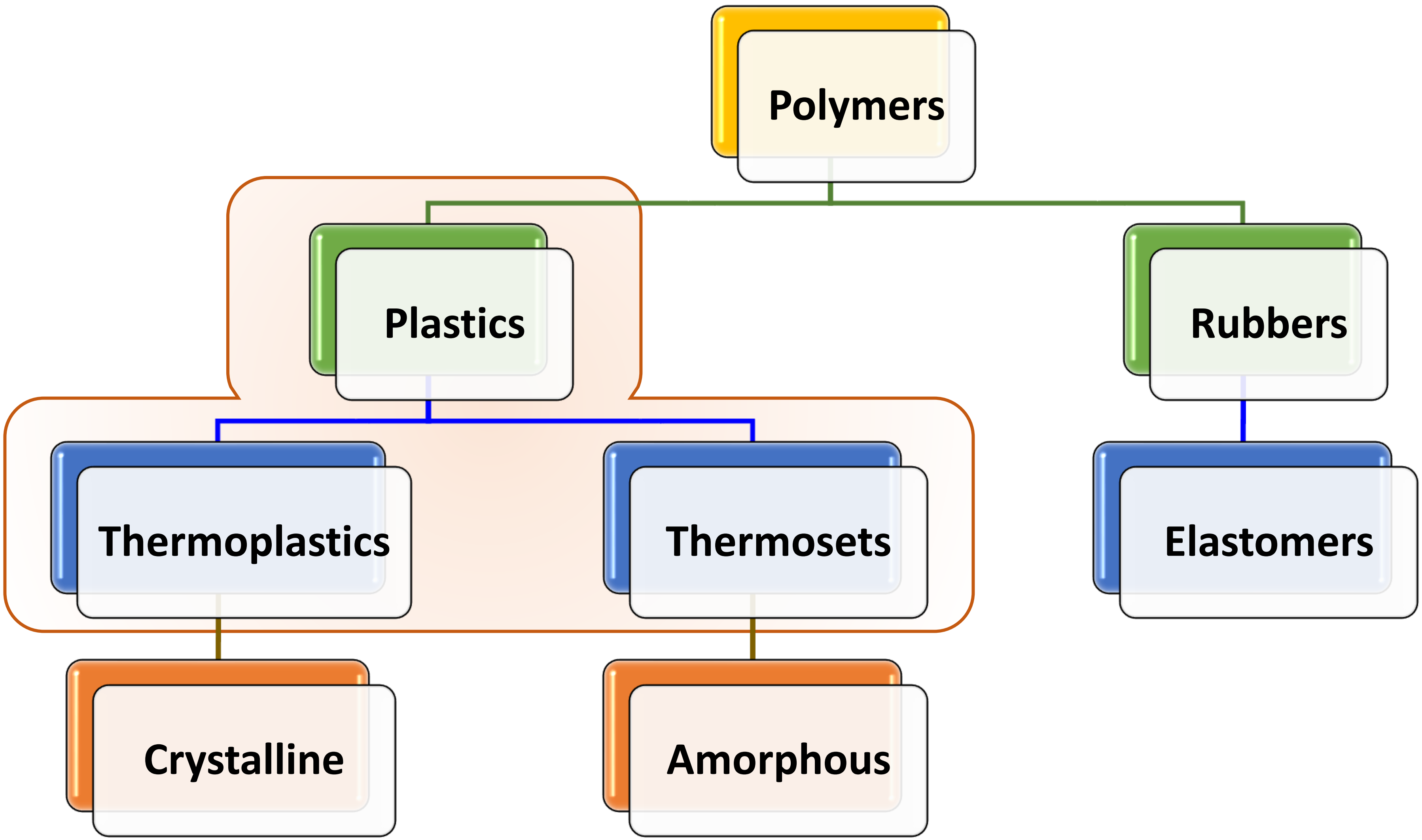
1. Based on "**Occurrence**"
   - Natural polymers (e.g. Silk)
   - Synthetic polymers (e.g. Nylon)

2. Based on "**Type of polymerization**"
   - Addition polymers (e.g. Polyethylene)
   - Condensation polymers (e.g. Polyester)

3. Based on "**Monomeric units**"
   - Homopolymers (e.g. Polypropylene)
   - Co-polymers (e.g. Styrene butadiene rubber)

4. Based on "**Thermal Effect**"
   - Plastics (e.g. Polyvinyl chloride)
   - Rubbers (e.g. Butyl rubber)

Classification – Thermal Effect



Plastics

- Plastics are high molecular weight organic polymer materials, that can be moulded into any desired shape by applying heat and pressure

- Plastics or resins are classified into two types

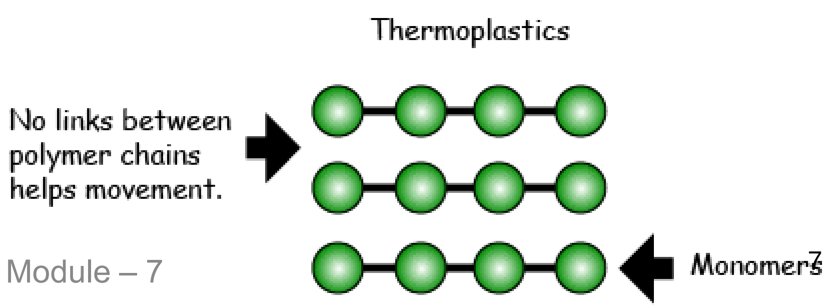
(A) Thermoplastic resins

(B) Thermosetting resins

(A) Thermoplastic resins

- They are prepared by **addition polymerisation**.
- They are straight chain (or) slightly branched polymers and various chains are held together by weak van der Waal's forces of attraction.
- Thermoplastics can be **softened on heating and hardened on cooling**.
- They are generally soluble in organic solvents

e.g. Polyethyene, Polyvinyl chloride



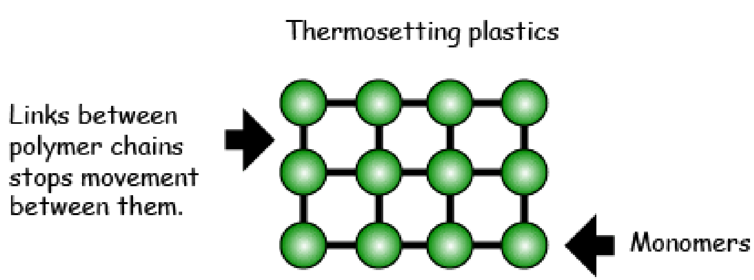
Thermoplastics

- Heated & Re-moulded 100's of times!!!
- Can also be recycles

(B) Thermosetting resins

- Thermosetting resins (or) Thermosets
- They are prepared by **condensation polymerisation**
- Various polymer chains are held together by strong covalent bonds (cross links)
- Thermosetting plastics get **harden on heating and once harden, they cannot be softened again**
- They are almost insoluble in organic solvents.

e.g. Bakelite, Polyester



Can not be softened

Thermoplastic Vs Thermosetting plastic

Thermoplastic resins	Thermosetting resins
They are formed by **addition polymerisation**	They are formed by **condensation polymerisation**
They consists of **Linear long chain polymers**	They consists of **three dimensional network structures**
All the polymer chains are held together by **weak van der Waals forces**	All the polymer chains are linked by **strong covalent bonds**
They are **weak, soft and less brittle**	They are **strong, hard and more brittle**
They **soften on heating** and harden on cooling	They **do not soften on heating**
They **can be remoulded**	They **cannot be remoulded**
They have **low molecular weights**	They have **high molecular weights**
They are **soluble in organic solvents**	They are **insoluble in organic solvents**
e.g. PE, PVC	e.g. Bakelite, polyester

Plastics - Examples

- Properties & Engineering application of plastics

i. ABS = Acrylonitrile butadiene styrene

ii. PVC = Polyvinyl Chloride

iii. PTFE = Polytetrafuloroethylene

iv. Bakelite

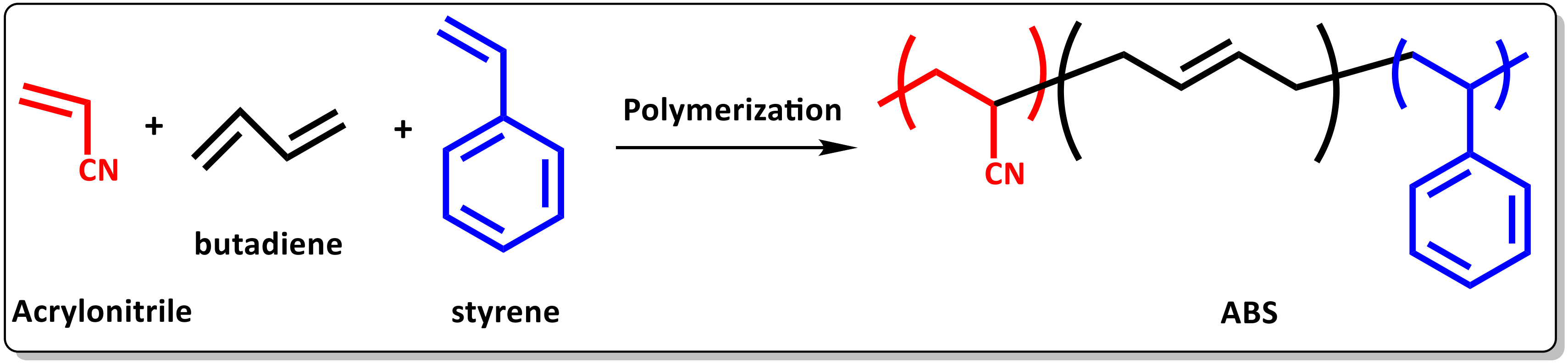
Preparation

Properties

Uses

i. ABS - Preparation

- ABS (**Acrylonitrile butadiene styrene**) is a ter-polymer
- It is polymerized by the polymerization of acrylonitrile, butadiene and styrene



- It is an amorphous and thermoplastic polymer
- Mainly ABS can be prepared in two different grades: 1. for extrusion and 2. for injection moulding.

i. ABS – Properties & Application

- **Properties of ABS**
  - Cost effective
  - Good Impact Strength
  - Good Chemical Resistance
  - High Gloss Surface Finish
  - Good Flexural Properties
  - Can prepare in different grades as per the requirement

ABS can be recycled

- **Applications of ABS**
  - musical instruments (recorders, plastic clarinets, and piano movements)
  - automotive trim components, automotive bumper bars
  - medical devices for blood access
  - White-water canoes
  - buffer edging for furniture and joinery panels
  - luggage and protective carrying cases
  - small kitchen appliances
  - Keyboard keycaps
  - toys, including Lego and Kre-O bricks
  - golf club heads (because of its good shock absorbance)
  - Household and consumer goods

i. ABS – Advantages & Limitations

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

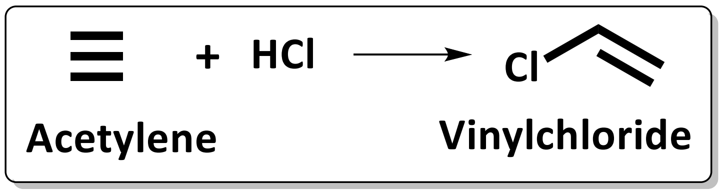
- ➢ Automotive hardware (used in electroplated metal coatings for decorative hardware), appliance cases, pipe, plated items.

ii. PVC – Preparation

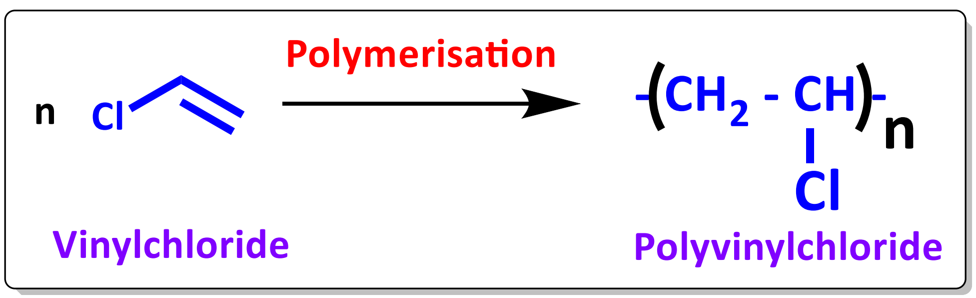
Polyvinyl Chloride (PVC)

Preparation: Preparation of PVC involves the following two steps

Step-1: Vinyl chloride is prepared by treating acetylene with hydrochloric acid at 60-80 ^{o}C in the presence of metal chloride as catalyst



Step-2: Polyvinylchloride is obtained by heating water emission of vinyl chloride in presence of benzoyl peroxide (or) hydrogen peroxide under pressure

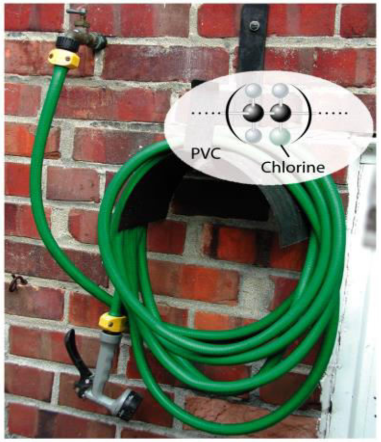


ii. PVC – Properties & Uses

Properties of PVC

1. PVC is colourless, odourless and chemically inert powder
2. It is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons such as ethyl chloride
3. It undergoes degradation in presence of heat (or) light

Polyvinylchloride (PVC)



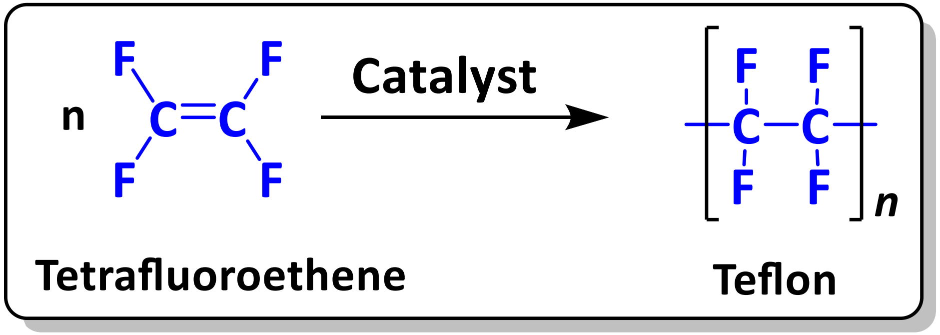
Uses of PVC

1. It is used in the production of pipes, cable insulations, table covers and rain-coats etc.
2. It is also used for making sheets, which are employed for tank-linings, light fittings, refrigerator components, etc.

iii. PTFE – Preparation & Properties

TEFLON

- **The trivial name of PTFE (polytetrafuloroethylene) is Teflon.**
- Teflon is made by the polymerization of tetrafluoroethene as shown bellow.



Properties of TEFLON

- This polymer is a hard, strong, chemically resistant compound with a high melting point and very low surface friction.
- Hydrophobic polymer
- Lowest coefficient of friction against any solids

iii. PTFE – Uses

Uses of TEFLON

- In motors, transformers coils, capacitors, pipes, tanks and storage of chemicals
- Non-stick appliances
- Where TEFLON is used as a lubricant, it reduces friction, wear and energy consumption of machinery.

iv. Bakelite – Preparation

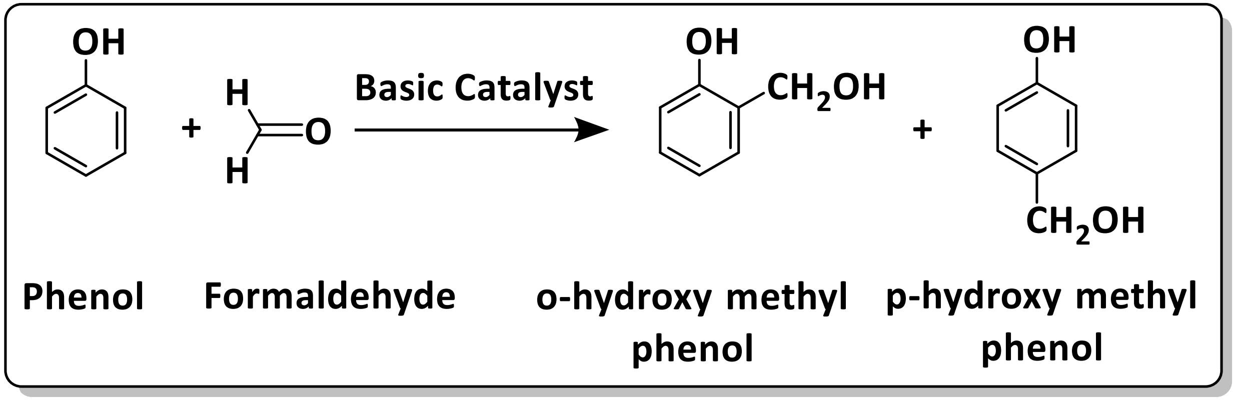
Bekalite is obtained by the condensation polymerisation of phenol and formaldehyde in the presence of acid or alkali catalyst

Preparation

The reaction involves the following **3 steps**

Step-1

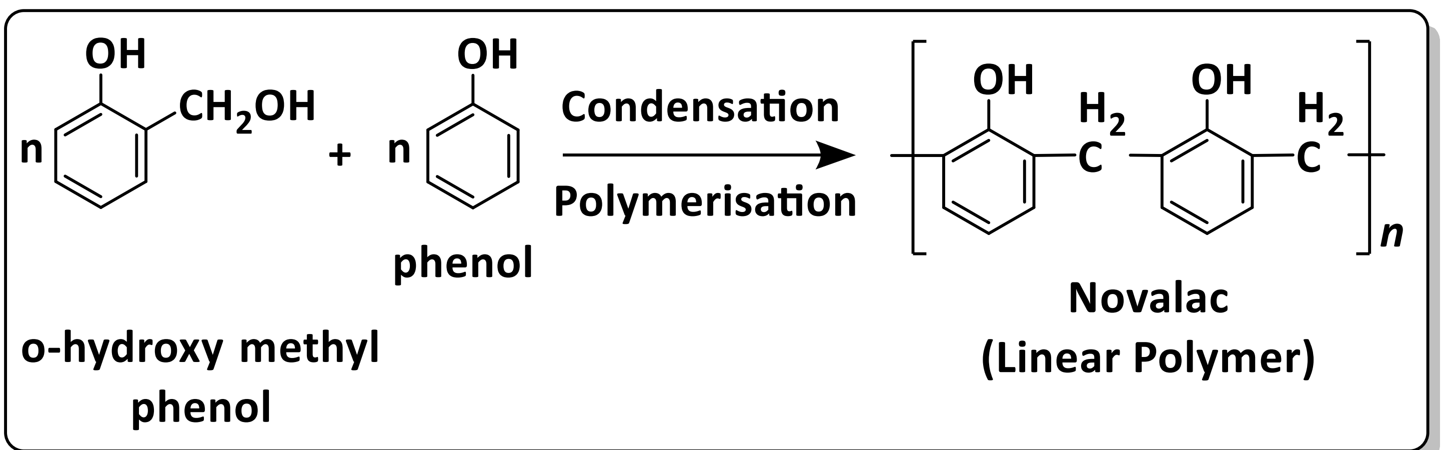
The first step is the reaction between phenol and formaldehyde to produce methylol phenols (mono, di and tri-methylol phenols)



iv. Bakelite – Preparation

Step-2: Synthesis of linear polymer Novolac

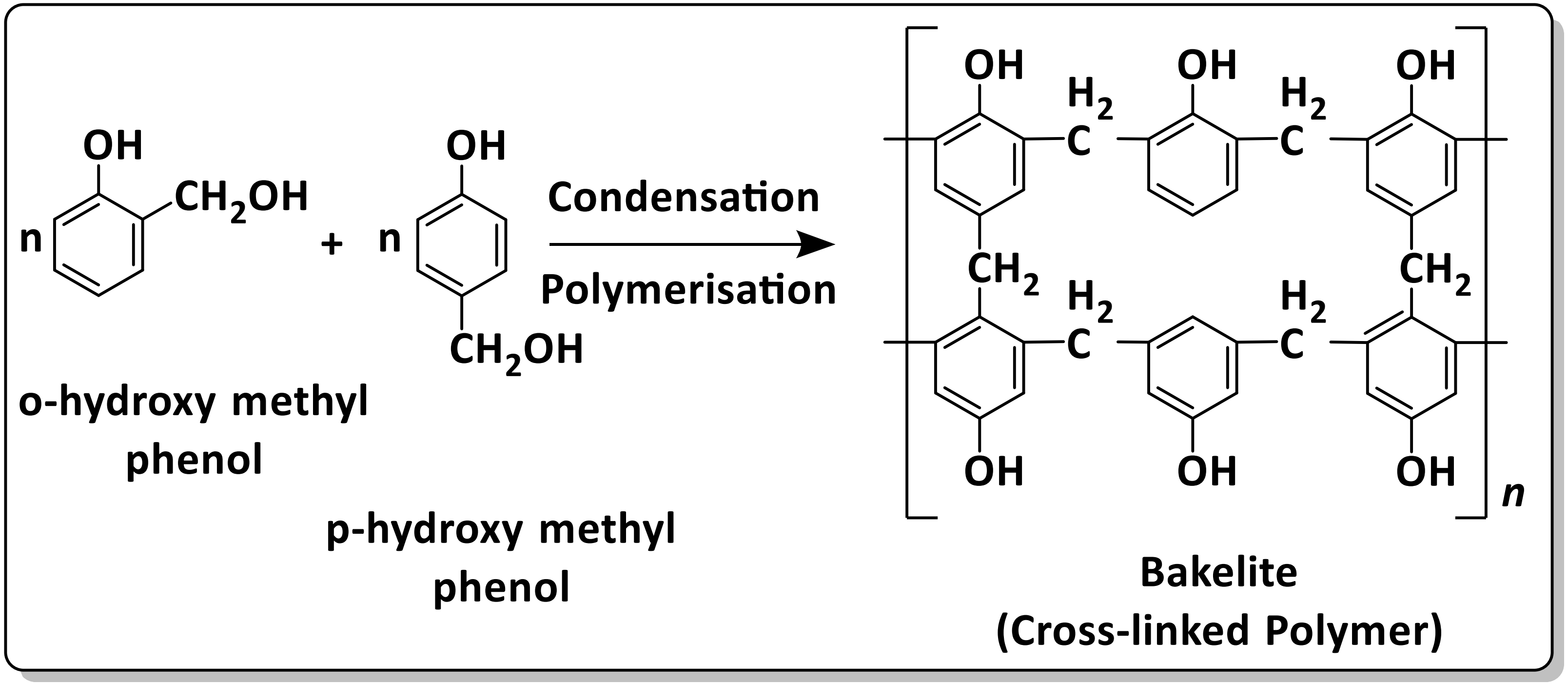
- When methylol phenols are heated with excess of phenol in presence of alkaline catalyst. The methylol phenols condense either through methylene linkages or through ether linkages to form resoles.
- Resole is a low molecular weight linear polymer. It is completely soluble in alkaline solution



iv. Bakelite – Preparation

Step-3: Synthesis of cross linked polymer Bakelite or phenol formaldehyde resin

- By reacting the methylol pheonls in the presence of a curing agent (hexamethylene tetramine) produces hard, rigid, infusible, cross-linked polymer called **bakelite**



iv. Bakelite – Properties & Uses

Properties of Bakelite

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

Uses of Bakelite

- Bakelite is used as an adhesive in plywood laminations & grinding wheels, etc.
- It is also widely used in paints, varnishes
- Cooker with **Bakelite** Handles
- It is used for making electrical insulator parts like plugs, switches, heater handles, etc.

Plastic compounding

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

Synthetic/recycled plastic material

Moulding

Temperature

Pressure

Useful plastic products

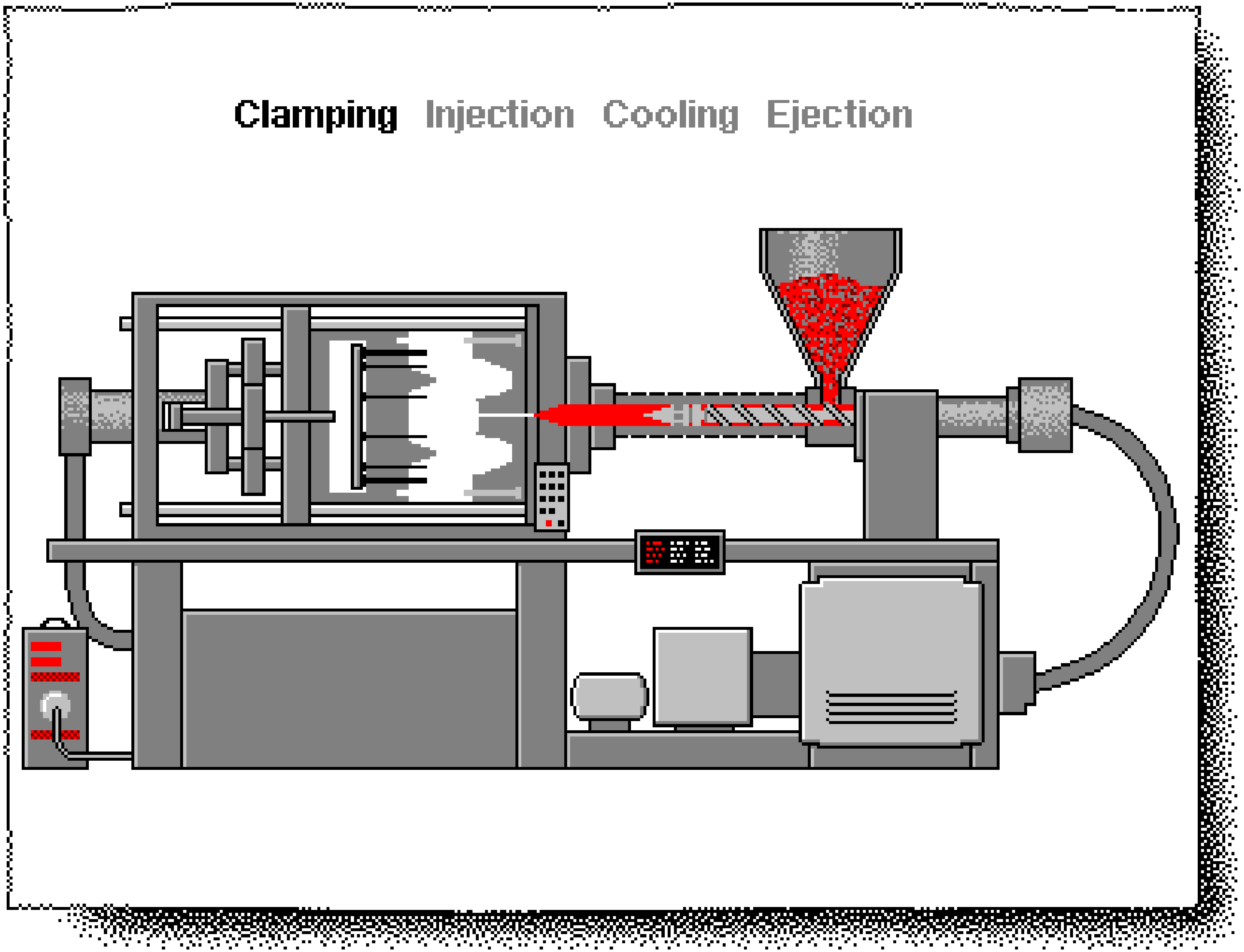
Plastics - Moulding

- Some moulding processes are

Moulding Type	-	Uses
(a) Injection moulding	-	Car parts, bottle caps
(b) Extrusion moulding	-	Pipes, Hoses
(c) Compression moulding	-	Mobile Phone Cases, Battery Trays
(d) Transfer moulding	-	Fibre reinforced polymers, Composites
(e) Blow moulding	-	PET bottles

(a) Injection moulding

35.Plastic CompoundingModule_7_(ii)



(a) Injection moulding

Process

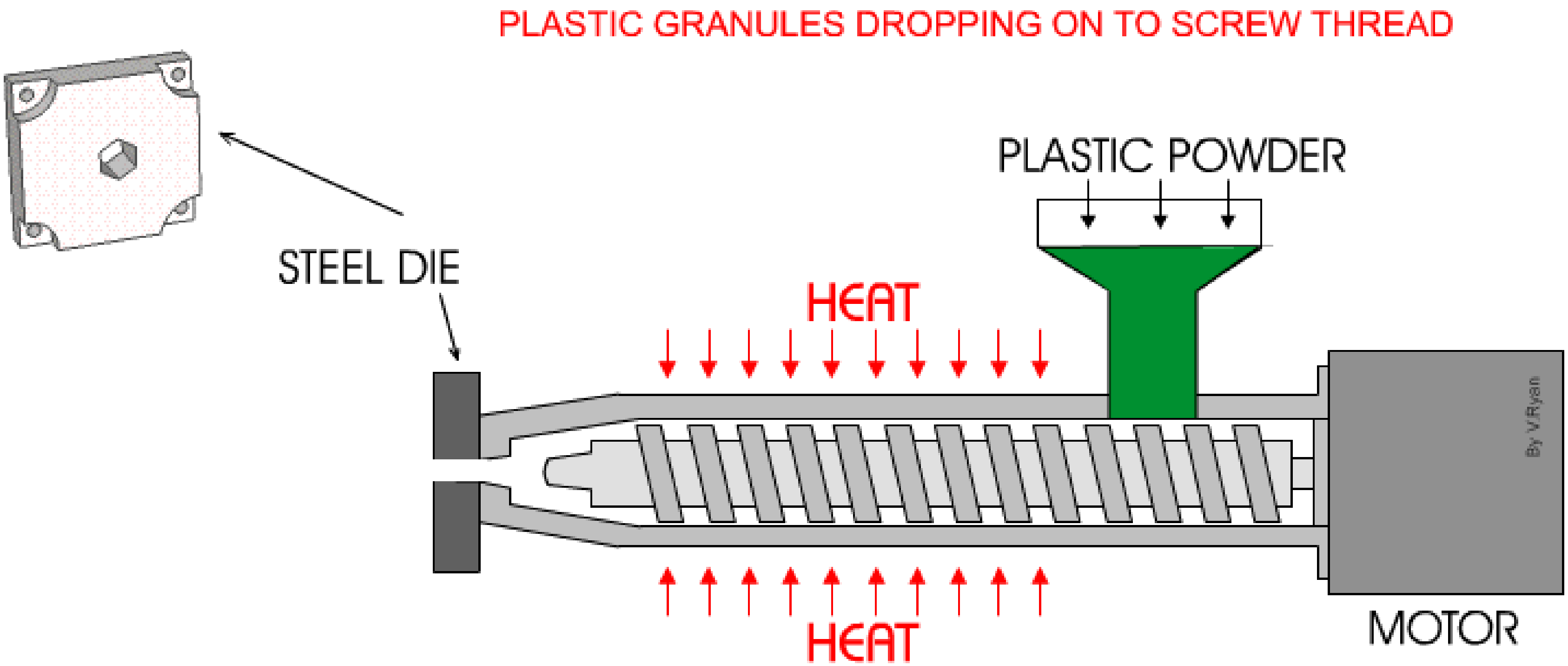
- This method is mainly applicable to thermoplastics.
- The powdered plastics material is fed into a heated cylinder through the hopper.
- The plastic material melts under the influence of heat and becomes fluid.
- The hot fluid is injected at a controlled rate into a tightly locked mould by means of a screw arrangement or by a piston
- 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.
- 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

(b) Extrusion moulding

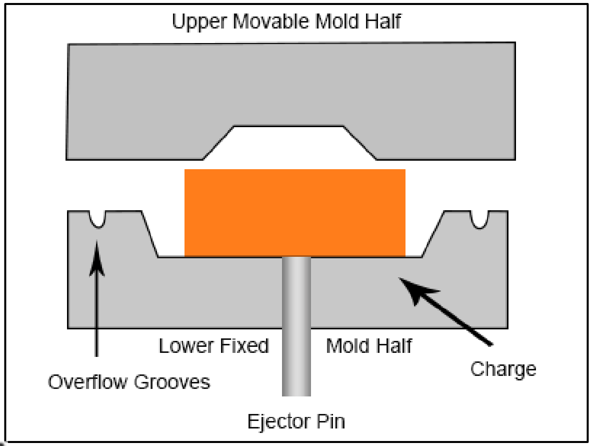
35.Plastic CompoundingModule_7_(ii)

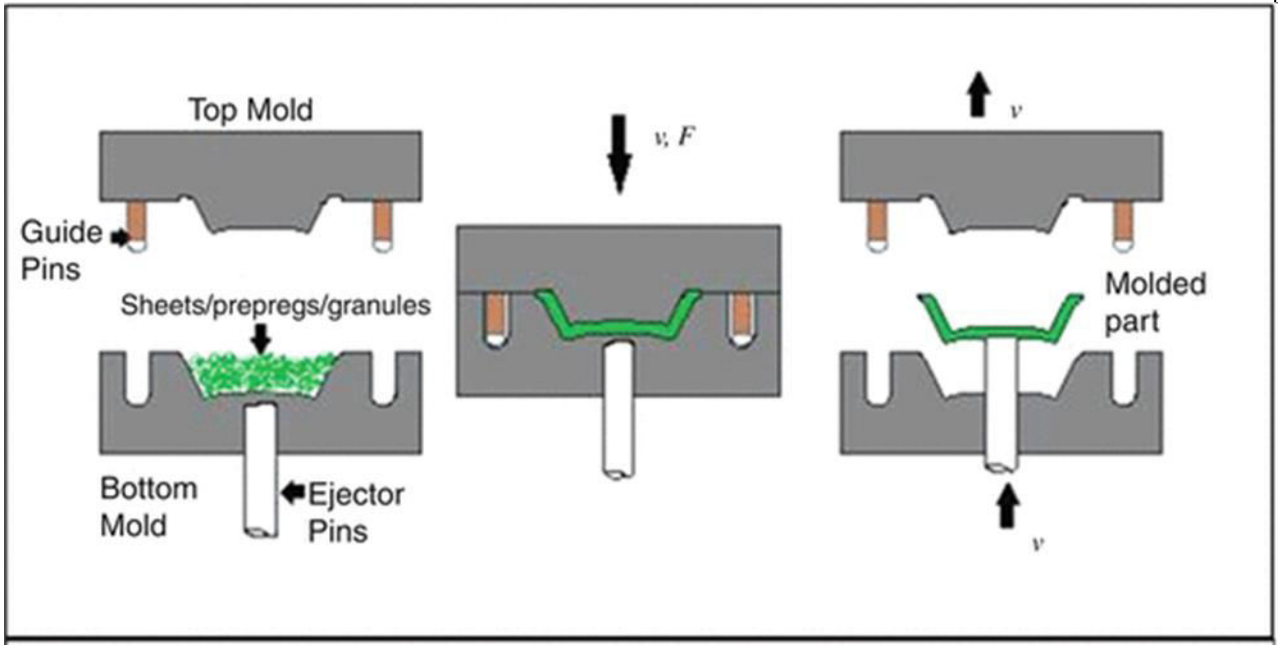


(b) Extrusion moulding

- 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.

(c) Compression moulding

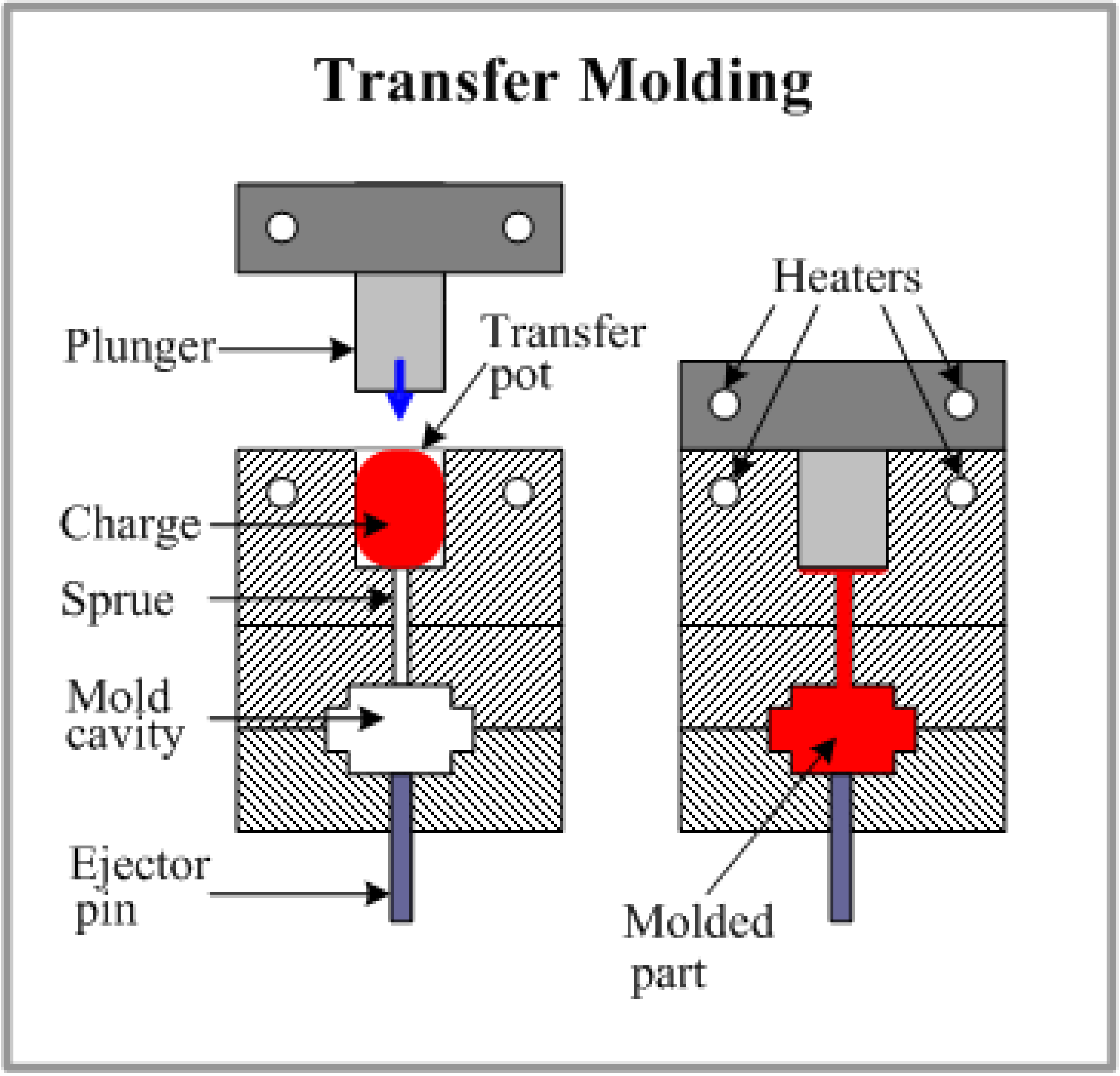




(c) Compression moulding

- This method is applied to both thermoplastics and thermosetting plastics
- 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.

(d) Transfer moulding



(d) Transfer moulding

- This method is used for thermosetting plastics
- The principle is same as that of the injection moulding
- The powdered moulding materials is taken in a heated chamber, maintained at low temperature, at which the material just begins to become plastic. This plastic is then injected through an orifice into the mould by a plunger working at high pressure
- 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.
- Then the mould is heated up to the curing temperature required for setting. Finally the moulded article is ejected from the mould

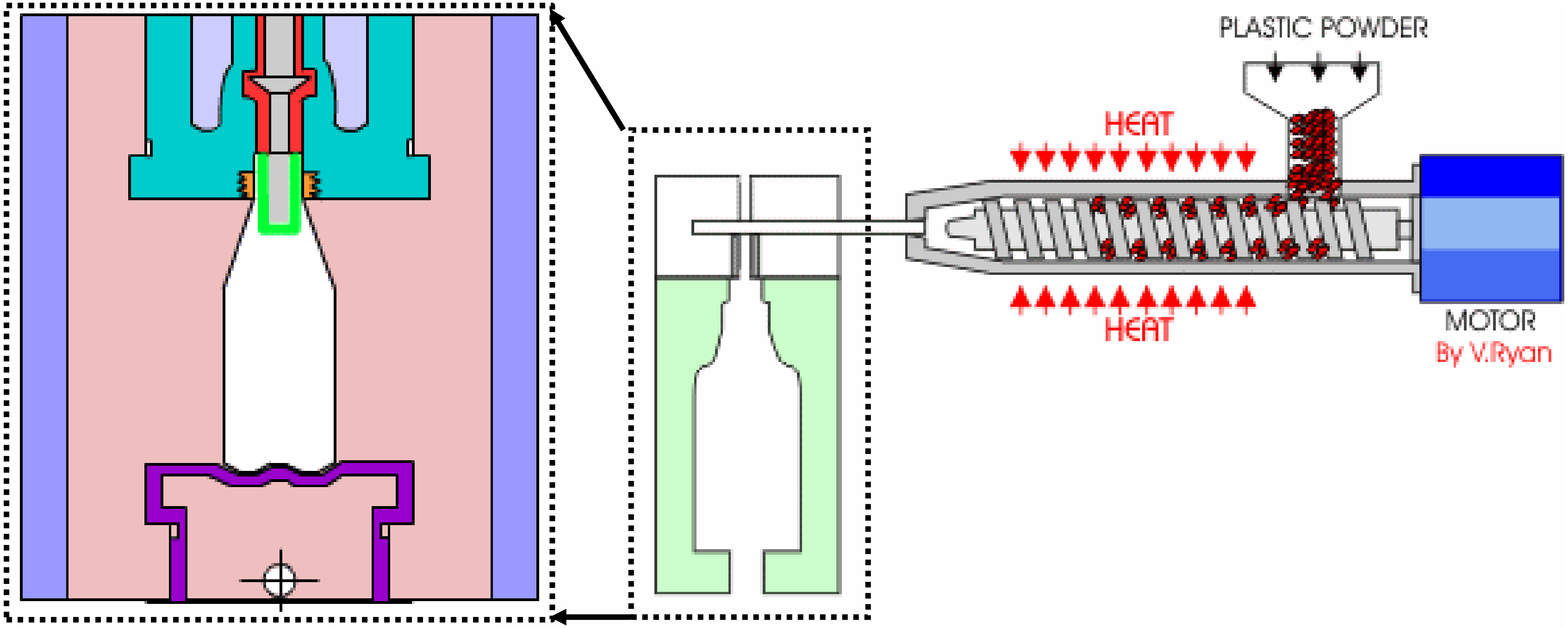
(d) Transfer moulding

Advantages

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

(e) Blow moulding

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.



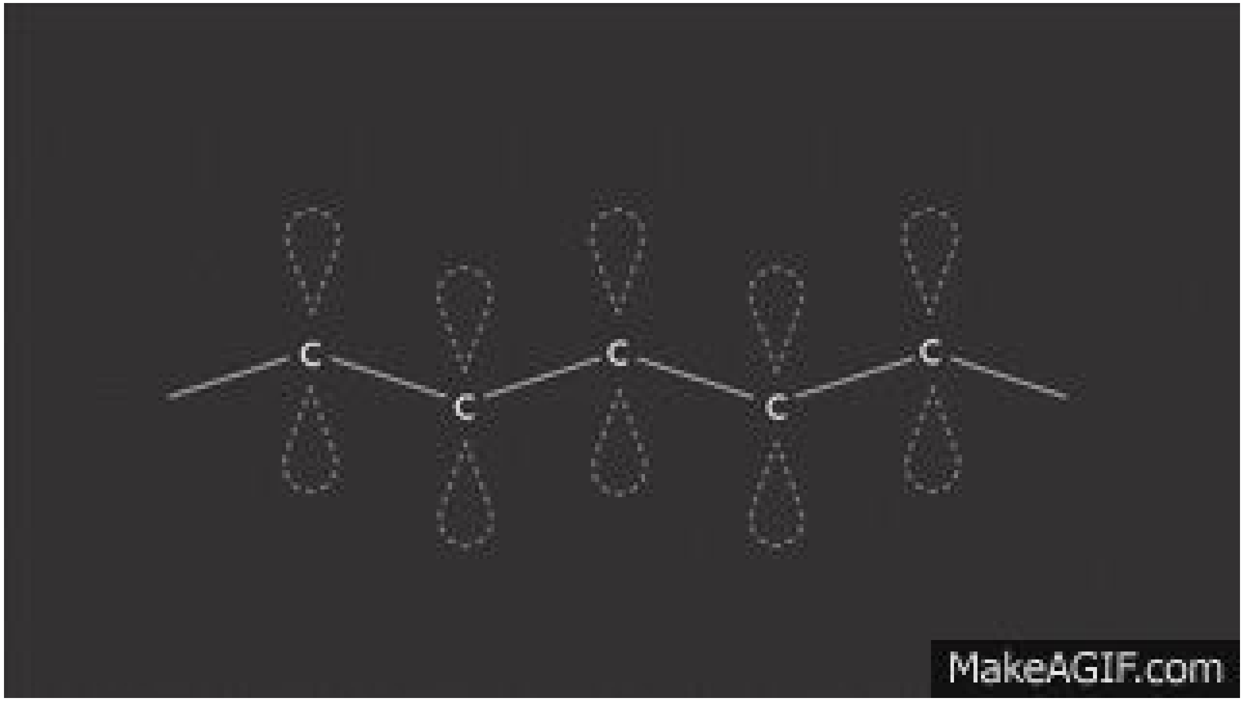
(e) Blow moulding

- 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 mould **costs** in this blow moulding are lower as compared to injection moulding and the machinery **costs** are **low** as well.

Conducting Polymers

Conducting Molecules



Electrical conduction is the movement of electrically charged particles through a transmission medium

Electrical Conduction

- Electrical conduction of a material can be calculated by

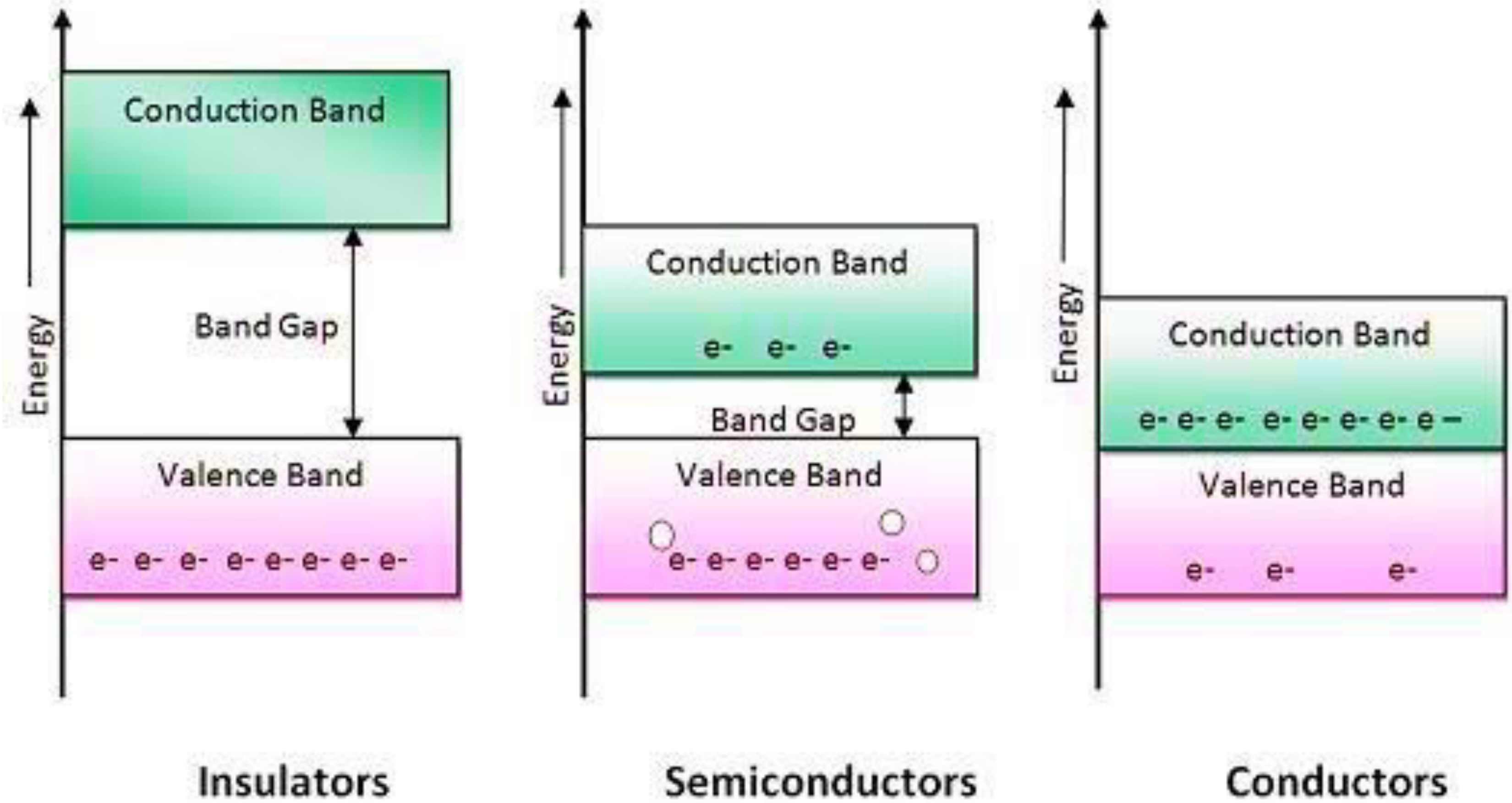
$$\mathbf{J} = \sigma\mathbf{E} \rightarrow \mathbf{E} = \rho\boldsymbol{J}$$

$$R = \rho\frac{l}{a};\ \sigma = \frac{1}{\rho}$$

$$\sigma = ne\mu$$

n – Charge carrier concentration
μ – charge carrier mobility
e – charge of the carrier

Classification of materials based on conductivity



Polymers??

Application of conducting polymers

- Organic polymers are normally insulators
- It can be presumed that conducting polymers must have an unusual structure
- Polymers with conjugated π-electron (i.e. system have C=C conjugated bonds) backbones display unusual electronic properties

Application

Conducting polymers are highly useful in

- **Solar cell application**
- **Gas sensors**
- **Chemical sensors**
- **Organic Light Emitting Diodes (OLEDs)**

Conducting Polymers

Nobel Prize in Chemistry 2000

"For the Discovery and Development of Conductive Polymers"

Alan Heeger
University of California
at Santa Barbara

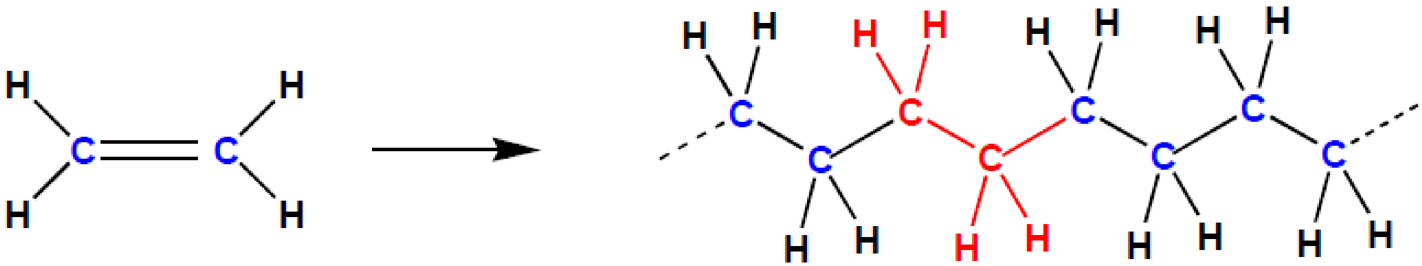
Hideki Shirakawa
University of Tsukuba

Alan MacDiarmid
University of
Pennsylvania

Polymers

- Traditional plastic : Polyethylene $\left(CH_2-CH_2\right)_n$

"Always insulator"



Ethylene

Combination of properties

Metals

High conductivity

Plastics

Lightness

Ease of processing (spin coating)

Low cost

Tailored synthesis

Conducting Polymer

- The polymeric material which possess electrical conductivity are called conducting polymer
  - e.g. Polyacetylene, Polyaniline & Polypyrrole.

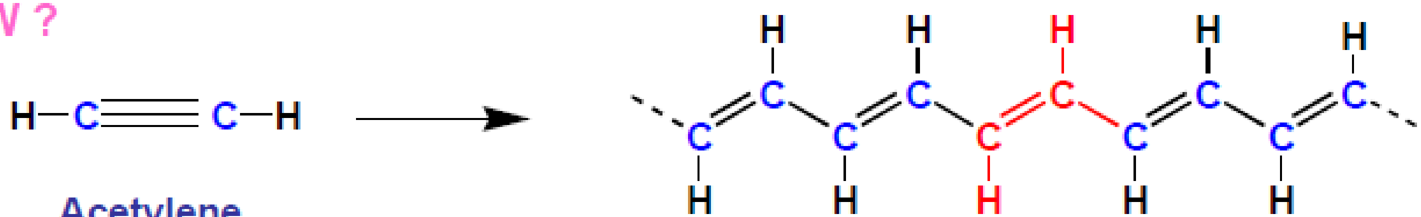
- **Intrinsically Conducting Polymer**
- **Doped Conducting Polymer**
- **Extrinsically Conducting Polymer**

Conducting Polymer

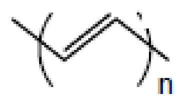
- Conjugated polymer : Trans-polyacetylene

$-\!\left(CH{=}CH\right)_n\!-$

"insulator → conducting"
HOW ?



Acetylene



Clue: alternate single-double bonds

c-PA : 10^{-7} Sm^{-1}
t-PA : 10^{-3} Sm^{-1}

Conduction → alternate single and double bond

Factors affecting the conductivity of the polymer

1) Density of charge carriers

2) Their mobility

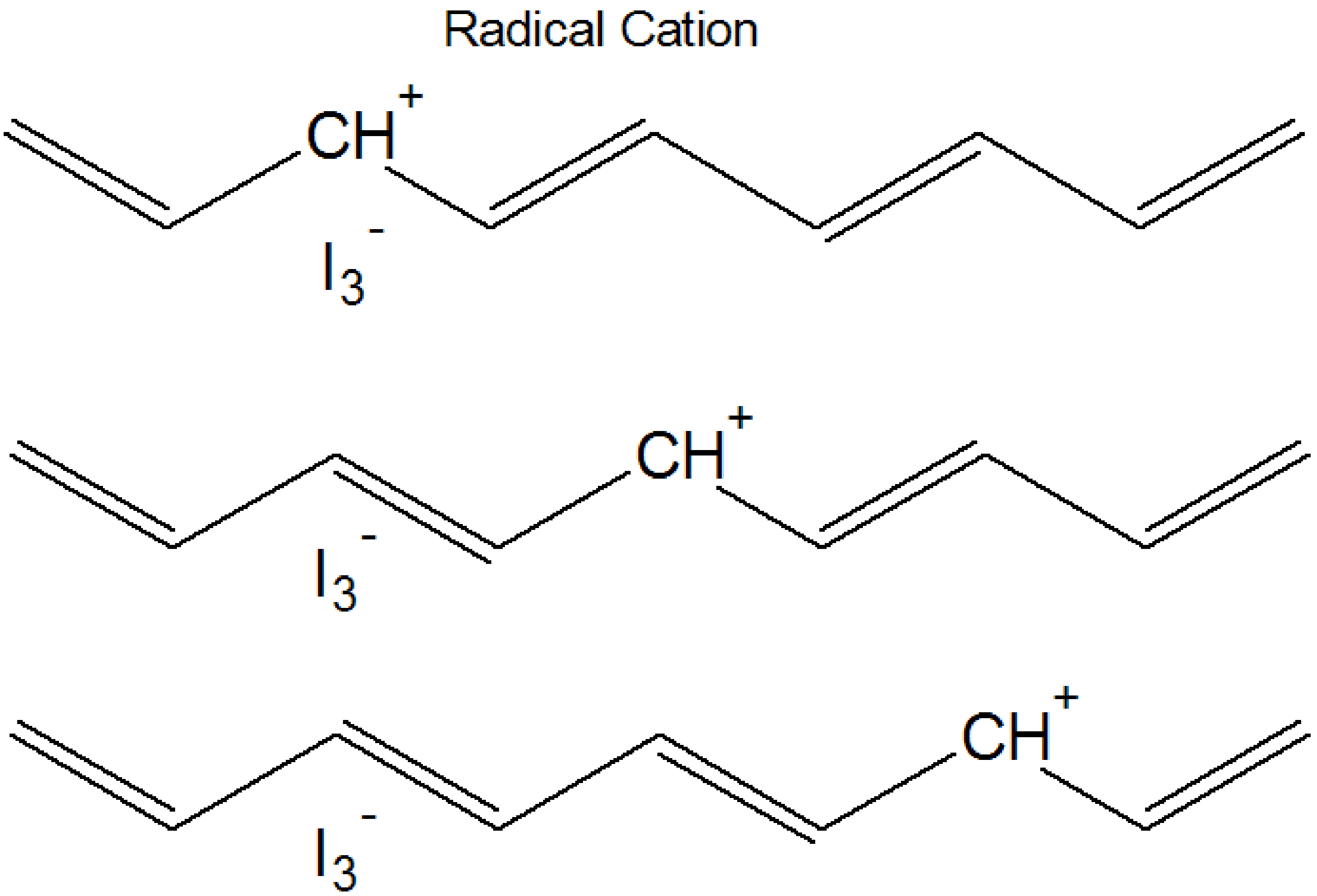
3) The direction

4) Presence of doping materials

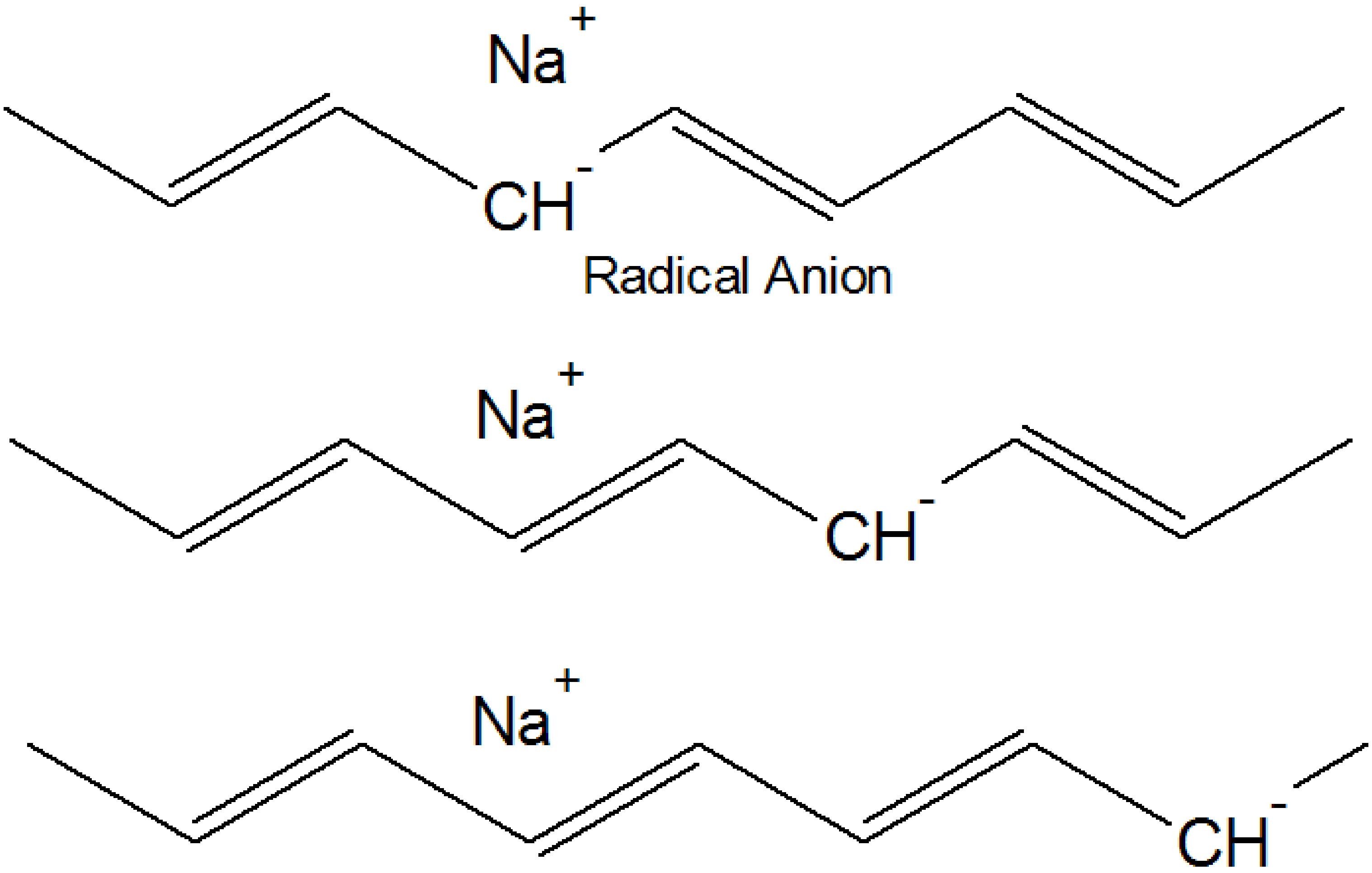
   (additives that facilitate the polymer conductivity)

5) Temperature

Doping with Iodine



Doping with Na (*n* type)



Doping in elemental semiconductor and conducting polymer

- Differences between doping in elemental semiconductor and conducting polymer

- Significant doping **levels** (until 10 mole %)

- There is a ***charge transfer*** between the incorporated dopant atom and the polymer chain ➔ the lattice is partially **oxidized or reduced**

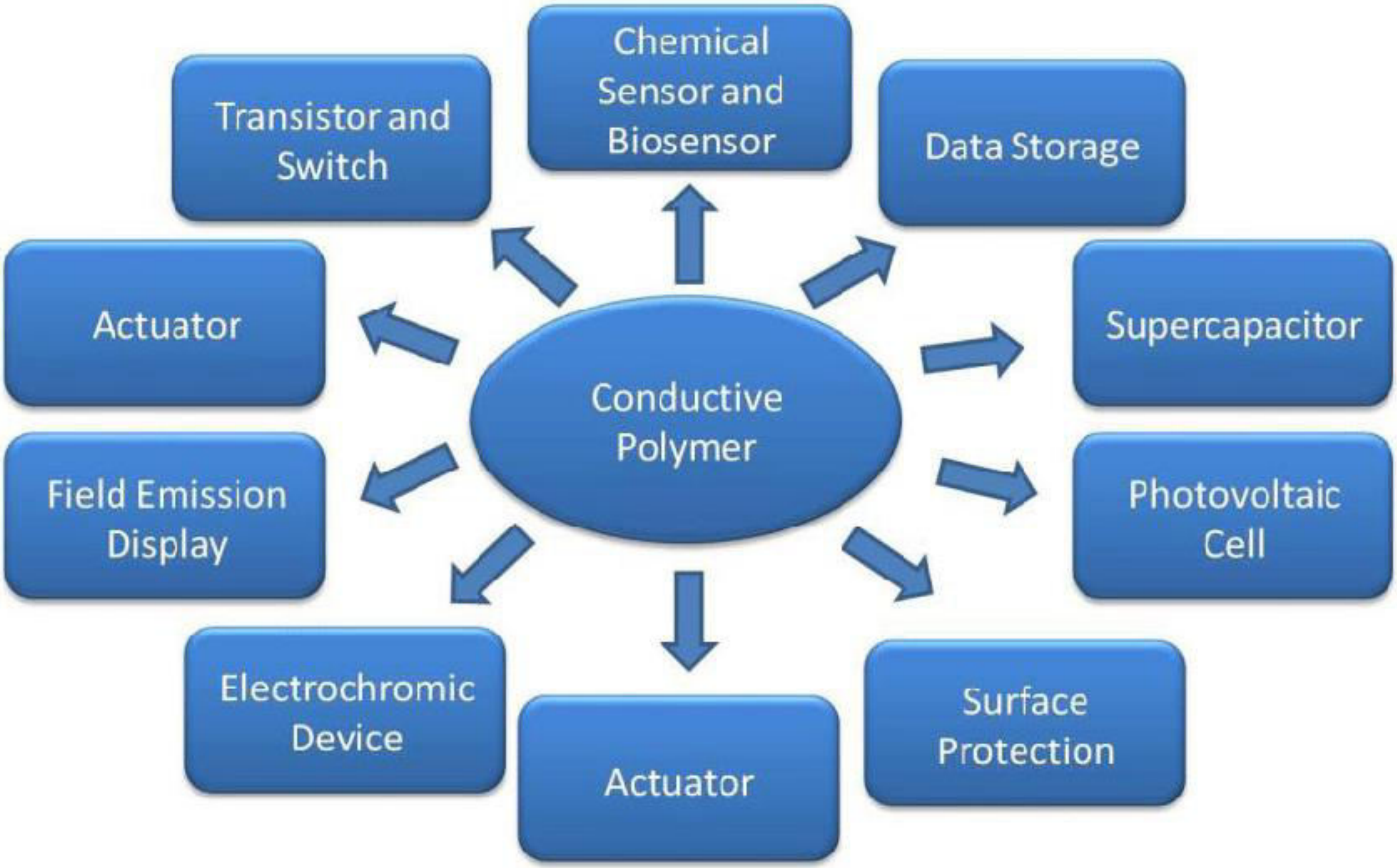
Conducting Polymers

- Resin or polymer filled with conductive elements such as carbon black, metallic fibers, metal oxides
- Polymer acts as binder to hold the conducting elements together in the solid entity.
- These polymers possess reasonably good bulk conductivity

Advantages:

1. **Low cost**
2. **Light in weight, mechanically durable and strong**
3. **Easily processable in different forms, shapes and sizes**

Application of Conducting Polymers



Gas Sensors based on conducting polymers

- This type of sensors can measure the change in the resistance of an electrically active sensitive material
- Compared with standard electrochemical sensors, polymer-based sensors do not require liquid electrolyte to work properly.