# Polymers

## Definition

- Polymer is a high molecular weight substance formed by joining a large number of small repeating units called Monomers.
- In Greek language poly means many & mer means units
- Polymers form very important components in our daily life. The polymers are highly useful in domestic industrial & medical fields.
- Examples:  Rubber • Polyethene, • Polypropylene • Teflon nCH2=CH2 polymerization (CH2 – $CH_2)_n$

**Reasons for extensive usage**

- Most of the polymers are non-toxic & safe to use.
- They have low densities (light in weight) so transportation polymers will be easy.
- They possess good mechanical strength.
- These are resistant to corrosion and will not absorb moisture when exposed to the atmosphere.
- These can function as good thermal & electrical insulators.
- These can be moulded and fabricated easily.
- They possess aesthetic colours.

**Limitations for the use of polymers**

- Some polymers are combustible.
- The properties of polymers are time dependent
- Some of them cannot withstand high temperatures.

## Classification of polymers

A) Based on source: natural, synthetic, semi synthetic
B) Based on Physical State: Amorphous and semi crystalline
C) Based on Thermal Behavior or Response to Heat: thermosets and thermoplasts
D) Based on end use.- Fibres, Plastics, Elastomers, Films, Paints, Adhesives
E) Based on Origin: Natural and Synthetic
F) Based on Tacticity Classification of polymers : Atactic, Isotactic, Syndiotactic
G) Based on Conductance : Conducting non conducting
H) Based on Environment Friendly Nature
I) Based on the type of monomers : homopolymeric, copolymeric
J) Based on Number of Monomers
K) Based on Chemical Nature
L) Based on Growth Mechanism of Polymerization

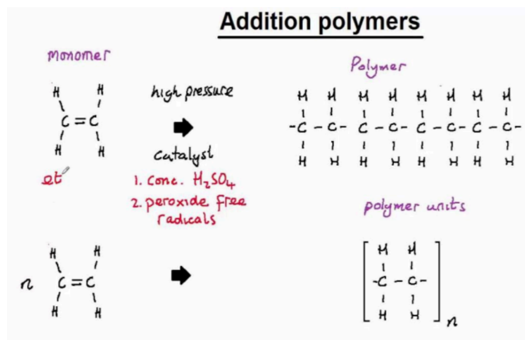
**F) Based on Tacticity:**

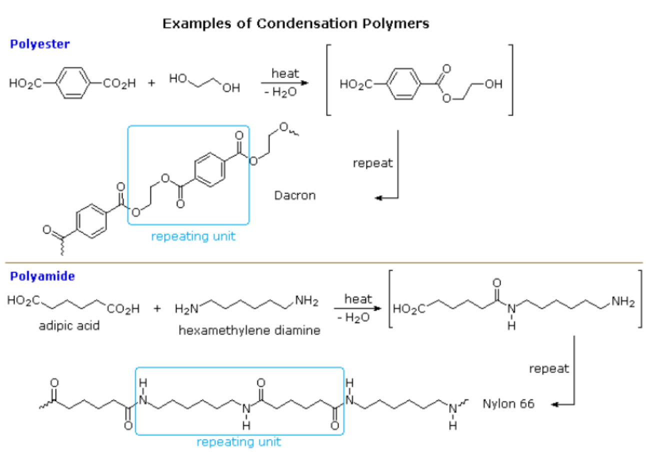
The arrangement of functional groups on the carbon backbone of the polymer is called tacticity. It is mainly divided into 3 types:

1. **Isotactic polymers:** Those polymers in which the functional groups are arranged on the same side are called Isotactic polymers. E.g.:- polypropylene (PP)
2. **Atactic polymers:** When there is no regular arrangement of functional groups on the back bone of the polymer chain these polymers are called atactic polymers. E.g.: PVC (Poly Vinyl chloride)
3. **Syndiotactic Polymers:** The polymers with alternate arrangement of functional groups are called syndiotactic polymers for e.g.:- Syndiotactic polystyrene, Gutta percha

**Difference between condensation and addition polymerisation:-**

| | Condensation polymerisation | | Addition polymerisation |
|---|---|---|---|
| (1) | It is also known as step growth polymerisation | (1) | It is also known as chain growth polymerization |
| (2) | It takes place in monomers having reactive functional groups | (2) | It takes place only in monomers having multiple bonds. |
| (3) | It takes place with elimination of simple molecule like $H_2O$,$NH_3$,HCl etc., | (3) | It takes place without elimination of simple molecule. |
| (4) | Repeat units of monomers are different | (4) | Repeat units & monomers are same. |
| (5) | The polymer is formed in gradual steps | (5) | Reaction is fast and polymer is formed at once. |
| (6) | The molecular mass of polymer increases throughout the reaction | (6) | There is very little change in the molecular mass throughout the reaction |
| (7) | Product obtained may be thermosetting/thermoplastic | (7) | Product obtained are thermoplastic |
| (8) | E.g.:- Bakelite, polyester ,polyamides etc., | (8) | E.g:-Polyethylene, PVC, poly styrene. |




**Difference between thermoplastic & thermosetting resins:-**

| | Thermoplastic resins (or) Polymers | | Thermosetting resins |
|---|---|---|---|
| (1) | These are produced by addition polymerization | (1) | These are produced by condensation polymerization. |
| (2) | The resins are made of long chains attached by weak Vander Waal's force of attraction | (2) | The resins have three dimensional network structure connected bonds. |
| (3) | On heating they soften and on cooling become stiff chemical nature won't change. | (3) | On heating they become stiff & hard. No change on cooling. Chemical nature changes. |
| (4) | They can be remoulded | (4) | They cannot be remoulded because once set means they are permanently set |
| (5) | Scrap (waste product) can be used | (5) | Scrap cannot be used |
| (6) | The resins are soft, weak and less brittle | (6) | The resins are usually hard, strong tough & more brittle |
| (7) | These are easily soluble in some organic substances E.g.:- PVC, polyethylene etc., | (7) | Resins are not soluble in organic Solvents E.g.:- Nylon, Bakelite etc., |
| (8) | Contain long chain polymer with no cross linkage. | (8) | They have 3D network structure. |

# Molecular Mass of Polymer

- The molecular mass of polymer is an important property of polymer because many important properties are influenced by the molecular mass. Polymers with higher molecular mass are tougher and more resistant. Their viscosities and softening temperature are also higher. Thus polymers with molecular mass are often required for particular purposes.

- Molecular mass of a polymer is not fixed, unlike organic compounds. Their molecular mass is controlled by polymerization reactions, which in turn depend upon availability of functional groups, charge carriers, and lifetime of charge carriers. Because of the random nature of the growth process, the product of the polymerization process is a mixture of chains of different length.
- Hence polymers are polydisperse mixtures of different polymers with varying molecular mass. Therefore the molecular mass of polymers is average molecular mass, also studied as Mn and Mw

## Average molecular mass of polymers

Represented as:

1. Number average molecular mass : Mn = $\frac{\Sigma NiMi}{\Sigma Ni} = \frac{\Sigma Wi}{\Sigma Wi/Mi}$
2. Weight average molecular mass: Mw = $\frac{\Sigma NiMi^2}{\Sigma NiMi} = \frac{\Sigma WiMi}{\Sigma Wi}$
3. Z average molecular mass = Mz = $\frac{\Sigma NiMi^3}{\Sigma NiMi^2}$
4. Viscosity average Molecular Mass (Mv)
   $$\overline{M}_v = \left[\sum_{i=1}^{\infty} w_i M_i^a\right]^{1/a}$$
   'a' is the measure of the hydrodynamic volume of the polymer.
   $W^i$ is the weight fraction, M is the molecular weight.

5. Degree of Polymerization
   a. $DP_n = \frac{Mn}{Mo}$ where M0 is the molar mass of the monomer and Mn is the number of moles of repeating units.
   b. $DP_w = \frac{Mw}{Mo}$ where M0 is the molecular weight of the monomer
6. Polydispersity Index
   a. PDI = $\frac{Mw}{Mn}$
      In case of monodisperse systems (Natural polymers and synthetic polymers made by anionic polymerization) , PDI =1 since Mn = Mw. In most other cases, PDI > 1 or Mw > Mn.

## Methods for determining the molecular weights of polymer

1. **Primary or Absolute methods:** Methods which are capable of determining molecular weights from first principles like colligative property measurements(Which gives Mn), light scattering measurements (which gives Mw).
2. **Secondary or relative methods:** Methods which require calibration with samples of known molar mass. Examples Viscosity measurements which gives Mv.

## Mark-Houwink Equation

$$[\eta] = K_m \overline{M}_v^a$$

$[\eta]$ = intrinsic viscosity
$\overline{M}_v$ = viscosity average molecular weight
$K_M$, $a$ = constants for particular polymer-solvent combination

For flexible polymeric chains, a = 0.5 to 0.8.
For stiff, rod-like chains, a = 2

## Compounding of Plastics

**Definition:** In order to impart certain definite properties to the finished products, resins are compounded with certain other substances. The process is called compounding of plastics.

### Binders or Resins

- The product of polymerization is called resins and this forms the major portion of the body of plastics.
- It is the binder which holds the different constituents together.
- Thermosetting resins are usually supplied as linear polymers of comparatively low molecular weight, because at this stage they are fusible and hence, mouldable.
- The conversion of this fusible form into cross-linked infusible form takes place, during moulding itself, in presence of catalysts etc.
- A binder may compose of 30-100% resin.
- The binders used may be natural or synthetic or cellulose derivatives.

### Fillers

- Fillers are generally added to thermosetting plastics to increase elasticity and crack resistance.
- Fillers improve thermal stability, strength, non-combustibility, water resistance, electrical insulation properties & external appearance.
- E.g. :- Mica(Hardness), cotton (Shock resistance), carbon black (electrical conductivity), graphite, $BaSO_4$ etc. asbestos (heat resistance)

### Plasticizers

- Plasticizers are substances added to enhance the plasticity of the material and to reduce the cracking on the surface.
- Plasticizers are added to the plastics to increase the flexibility & toughness.
- Plasticizers also increase the flow property of the plastics.
- Eg: vegetable oils, camphor, esters of steric, oleic acid, tributyl phosphate, triphenyl phosphate etc.

### Dyes and Pigments

- Beauty
- Eg :-Inorganic Pigments: Lead chromate (yellow), ferrocyanide (blue)
  Organic Pigments: Alizarin Red, Indigo Dye, Azo dyes

### Lubricants

- Eg: Oils, waxes and soaps.
- They help in easy moulding and glossy finish to the final product.
- The lubricant prevents the plastic materials from sticking to the mould.

### Catalysts

- They are added to plastics to accelerate polymerization reactions.
- $ZnCl_2$, CaO, ammonia, benzoyl peroxides are examples.

### Stabilisers

- They are added to improve thermal stability during processing.
- Eg. Polymers of vinyl chloride show a tendency to undergo decomposition at moulding temperatures. So during their moulding heat stabilisers are added.
- Opaque moulding stabilisers: Salts of lead, like white lead, lead chromate, red lead, lead silicate etc.
- Transparent moulding stabilisers: Stearates of Lead, chromium and barium.

In addition, small quantities of antioxidants(to prevent fading of colours), antiseptics(to avoid infection incase of injury from polymer), fungicides(prevent fungal invasion), flame retardants(prevent fires) etc. are added as ingredients of plastics.

## Fabrication of Plastics (Moulding)

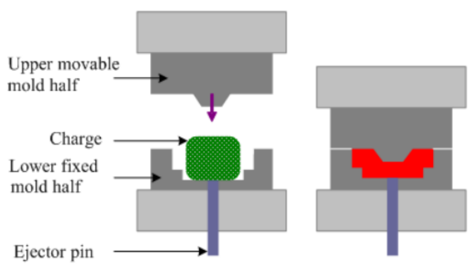
**Definition:** Giving any desired shape to plastics (granules or powders) using moulds under heat and pressure.

1. **Method Selection**
   - A proper method should be selected depending on the shape and type of resin used.
2. **Process Overview**
   - The methods involve partial melting of the resinous mass by heating.
3. **Thermoplastics**
   - Molten resin is introduced into a die/mould.
   - Desired shape is achieved by compression and further cooling.
   - **Curing Temperature:** Curing is done at room temperature (low temperature) to avoid burning of thermoplastic. During compression, friction will produce heat inevitably and therefore, curing should be done with sufficient margin.

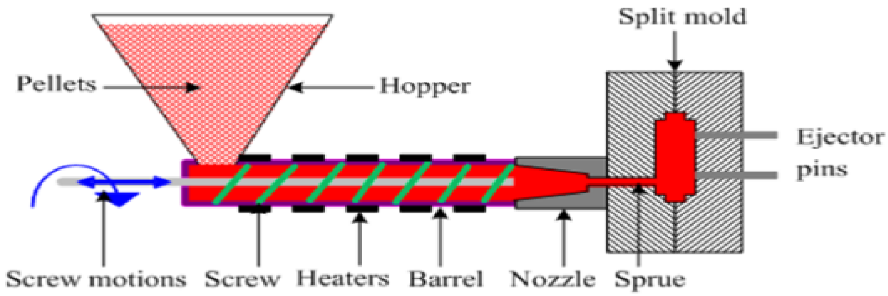
4. **Thermosets**
    - Partially polymerized mass or raw materials are introduced into the die/mould.
    - The material is further cured at high temperatures in the mould to achieve the desired shape.
    - **Curing Temperature:** Curing is done at high temperature to obtain the desired cross-linking.

# Types of Fabrication/Moulding

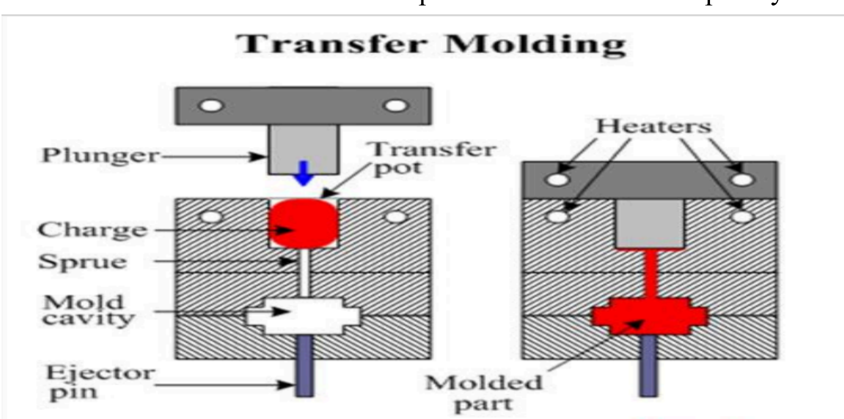
1. **Compression Moulding - Thermoplasts & Thermosets**
    - Common and oldest method for moulding thermosetting / thermoplastic materials.
    - Compression of raw materials or soften resinous mass is done in the mould /die under heat and pressure
    - Predetermined quantity of raw materials is introduced carefully in the mould, further compressed by hydraulic pressure (2000 to 10000 psi).
    - Molten or soften resinous mass gets filled in the cavity of mould.
    - Curing is done by heating (Thermosetting) or by cooling (Thermoplastics).
    - Finally, the moulded article is separated from the mould by opening the mould apart.
    - Applications: Electric switch boxes, ash trays, cabinets for radio, television, computers, etc.




2. **Injection Moulding  - Thermoplastics**
    - This method is especially used for thermoplastic materials.
    - Powder or granular resin is heated in a cylinder and injected at a controlled rate in a mould with the help of a piston plunger or screw.
    - Piston plunger or screw is used to force the material into the mould.
    - Pressure up to 2000 kg/cm² (100 psi) is used.
    - Once the article is formed, mould is cooled and half mould is opened to remove the finished article.
    - Disadvantage of the method is formation of **air bubbles or cavities** in the articles.
    - Applications: Smaller but large volume articles such as pen caps, bottle caps, cups, containers, mechanical parts.



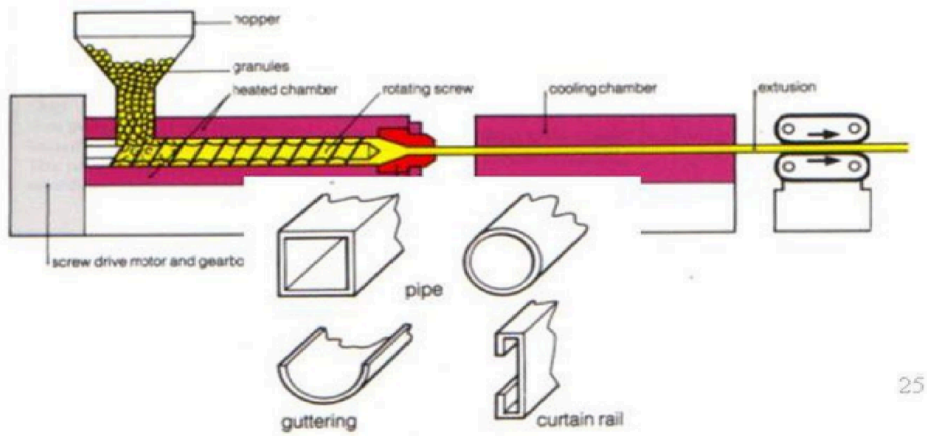

3. **Transfer Moulding - Thermosets**
    - The method combines features of both Compression Molding (hydraulic pressing of moulding materials - thermosets) and Injection Molding (ram-plunger and filling the mould through a sprue).
    - The method is used especially for moulding thermosetting resins (thermosets).
    - Products with **relatively intricate designs** could be fabricated with this method.
    - Powdered raw materials are heated at a certain low temperature to soften and then introduced through an orifice or sprue in the mould.
    - Then it is cured in the mould at high temperature for a certain time.
    - Finally, the moulded article is removed by separation of mould.
    - **Advantages:**
        - Articles with intricate shapes could be designed.
        - Aerospace and automobile parts, car body, helmets.
        - The articles produced are **blister-free, no air bubbles.**
        - Fine wires and glass fibres can be inserted in the mould.
        - Even thick pieces can be cured completely and uniformly.




4. **Extrusion Moulding - Thermoplasts**

- Whenever continuous moulding of material like wires, cables, and sheets is required, extrusion moulding is used.
- The thermoplastic materials are moulded by this method.
- They undergo continuous moulding to form articles of uniform cross-section.

- In this method, the thermoplastic material is heated to a plastic condition and pushed by means of a screw conveyor into a mould cavity having the required outer shape of the articles to be manufactured.
- Here, the plastic mass gets cooled due to atmospheric exposure.
- A long conveyor carries away the cooled products continuously.



Some common extrusions

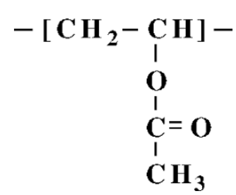
## Polymerisation

**Definition: The synthesis of polymers from monomeric units.**

1. **Condensation Polymerization:** The molecules have acidic and basic functional groups. These undergo reactions to join together and form by-products of water, etc.
2. **Addition Polymerisation:** Unsaturated molecules are capable of undergoing addition polymerisation. The pi bonds can break to free electrons and make new bonds. The reaction proceeds without any by-product. An initiator is to be added to initiate the reaction. At the beginning, only polymers with a high molecular weight are formed. Even after some time, change in molecular weight is negligible.

# Preparation, Properties, and Uses of Important Polymers

## Polyvinyl Acetate (PVAC):



**Method of Preparation:** By reacting ethylene with acetic acid and oxygen over a palladium catalyst. CH3COOH (acetic acid) ka H when replaced with ethylene gives vinyl acetate ($CH_3COO\text{-}CH{=}CH_2$). The polymerisation of vinyl acetate into poly vinyl acetate is "free radical polymerization". Thus, in this process, a catalyst (peroxide) is needed. The three stages are Initiation, Propagation, and Termination. The pi bonds of PVAC are broken to facilitate polymerization.

**Properties (ANY 4)**

- Amorphous polymer. It does not form crystals. This is due to the branching of vinyl acetate.
- Clear, colourless, and transparent.
- Hardest polyvinyl ester is polyvinyl acetate. It offers good adhesion to most surfaces.
- Unlike some thermoplastics, this polymer does not turn yellow.
- Due to resistance to cross linkage, this polymer remains insoluble in water. It dissolves in organic solvents.
- Lower molecular weight polymers become gum like and hence used for making chewing gums. Since it harms less when taken orally.

**Uses (ANY 4)**

- Emulsified PVAC is used to make adhesives, thus used in bookbinding, glues.
- Depending on the lifetime of the book, the polymer can be copolymeric or homopolymeric.
- As a resinous component of latex paints, offering compatibility with other paint components.
- Polyvinyl acetate may be used in the lamination of metal foils. Non-emulsified, or waterless, polyvinyl acetate is useful as a thermosetting adhesive.

## Polyvinyl Alcohol (PVA): $CH_2$=CH-OH → $CH_3$CHO

Polyvinyl alcohol, also known as PVOH, PVA, or PVAL, is a synthetic polymer that is soluble in water. It is effective in film forming, emulsifying, and has an adhesive quality. It has no odor and is not toxic, and is resistant to grease, oils, and solvents. It is ductile but strong, flexible, and functions as a high oxygen and aroma barrier.

Method for preparation: Polymerisation of vinyl acetate, then via ester hydrolysis, form PVA. This is because direct polymerisation of vinyl alcohol yields only about 60% polyvinyl alcohol.

**Properties:**

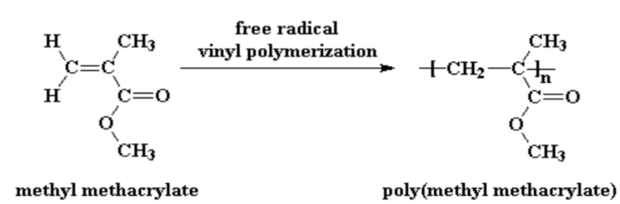
1. Atactic material(random functional group arrangement) and exhibits crystallinity due to the OH group. The OH group facilitates H-bonding and gives rigidity.
2. Excellent film forming, emulsifying, and adhesive properties.
3. Resistant to oil, grease, and solvents
4. High tensile strength and flexibility.
5. High oxygen and aroma barrier properties
6. **Properties are humidity dependent: Water absorbed acts as a plasticiser. This in turn reduces the polymer's tensile strength. But it increases the elongation and tear strength.**

**Uses (ANY 4)**

- Medical applications: Biocompatibility and low tendency for protein adhesion and toxicity, PVA is used in **cartilage replacements, eye drops, and contact lenses.**
- As an aid in **suspension polymerization**.
- Used in Additive Manufacturing: **3d printed** oral dosage forms in the pharma industry, etc.
- **Embolic agent** (substances used to block blood flow in vessels) in Uterine Fibroid Embolectomy.

## Polymethyl Methacrylate (PMMA)

**Method of Preparation:** $CH_2$=CH-COOH is acrylic acid (vinyl acetate+COOH).
Join with $CH_3$. $CH_2$=CH-$COOCH_3$



Replace H with another methyl group: $CH_2=C(CH_3)\text{-}COOCH_3$

Upon hydrolysis, COOH group is found.

Process followed is free-radical polymerization.

Poly(methyl methacrylate) (PMMA), also known as acrylic or acrylic glass as well as by the trade names Crylux, Plexiglas, Acrylite, Lucite, and Perspex among several others, is a transparent thermoplastic often used in **sheet form as a lightweight or shatter-resistant alternative to glass**. The same material can be used as a **casting resin, in inks and coatings,** and has many other uses.

**Properties:**

- PMMA is a s**trong, tough, and lightweight material.**
- It has a density of 1.17–1.20 g/cm3, which is less than half that of glass.
- It also **has good impact strengt**h, higher than both glass and polystyrene
- However, **PMMA's impact strength is still significantly lower** than polycarbonate.
- Transmits up to 92% of visible light (3 mm thickness), and gives a reflection of about 4% from each of its surfaces due to its refractive index (1.4905 at 589.3 nm).
- It filters **ultraviolet (UV) light** at wavelengths below about 300 nm
- PMMA swells and **dissolves in many organic solvents**; it also has poor resistance to many other chemicals due to its easily hydrolyzed ester.

**Uses:**

- Being transparent and durable, PMMA is a versatile material and has been used in a wide range of fields and applications such as **rear-lights and instrument clusters for vehicles, appliances, and lenses for glasses.**
- PMMA in the form of sheets affords to shatter resistant panels for building windows, skylights, bulletproof security barriers, **signs & displays, sanitary ware (bathtubs), LCD screens, furniture** and many other applications.
- It is also used for coating polymers based on PMMA and provides outstanding stability against environmental conditions with reduced emission of VOC.
- Methacrylate polymers are used extensively in **medical and dental applications** where purity and stability are critical to performance.

## Polycarbonates (PC)

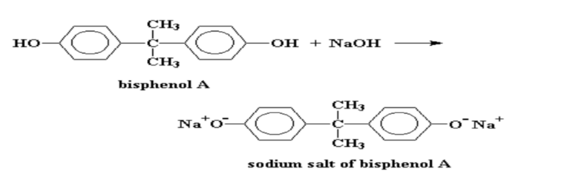
Contains carbonate groups ($CO_3$) in their chemical structures.

The method of preparation involves two steps: BPA reacts with NaOH to form sodium salt of BPA. Then with phosgene to create PC.

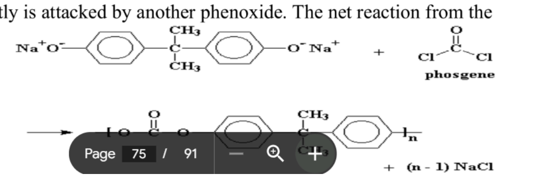
**Properties:**

- Due to BPA (bis-phenol A) in it, the plastic keeps releasing bleach into the water. This is harmful to the body.
- Durable

- The first step of the synthesis involves treatment of bisphenol A with sodium hydroxide, which deprotonates the hydroxyl groups of the bisphenol A




The diphenoxide (Na2(OC6H4)2CMe2) reacts with phosgene to give a chloroformate, which subsequently is attacked by another phenoxide. The net reaction from the diphenoxide is:



- Hard impact resistance, low scratch resistance
- Extreme temperature holdability
- Polycarbonate has a glass transition temperature of about 147 °C (297 °F; 420 K) GTT is the temperature wherein a material goes from hard and brittle to soft and flexible.
- Unlike most thermoplastics, polycarbonate can undergo large plastic deformations without cracking or breaking.

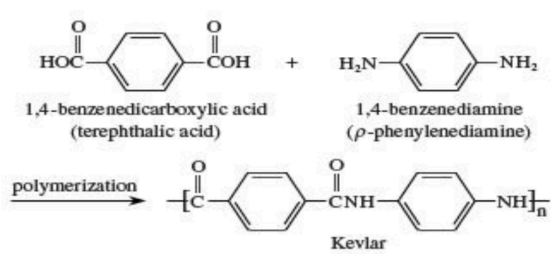
**Uses:**

- Used to make bottles, etc.
- Being a good electrical insulator and having heat-resistant and flame-retardant properties, it is used in various products associated with electrical and telecommunications hardware. It can also serve as a dielectric in high-stability capacitors
- The second largest consumer of polycarbonates is the construction industry, e.g. for domelights, flat or curved glazing, and sound walls, which all use extruded flat solid or multiwall sheet, or corrugated sheet.
- A major application of polycarbonate is the production of Compact Discs, DVDs. These discs are produced by injection molding (thermoplastic hence) polycarbonate into a mold cavity that has on one side a metal stamper containing a negative image of the disc data, while the other mold side is a mirrored surface.
- automotive headlamp lenses.

## Poly-paraphenylene Terephthalamide (KEVLAR)

Heat resistant and strong synthetic fibre.

**Method of Preparation:**




**Properties:**

- When Kevlar is spun, the resulting fiber has a tensile strength of about 3,620 MPa,[14] and a relative density of 1.44.
- Kevlar maintains its strength and resilience down to cryogenic temperatures (−196 °C); in fact, it is slightly stronger at low temperatures.
- Kevlar's structure consists of relatively rigid molecules which makes them exceptional strong
- They have high tensile strength-to-weight ratio; by this measure it is 5 times stronger than steel.

**Uses:**

- Bullet-proof jacket
- Bicycle tyres
- Racing sails

- Modern marching drumheads to withstand impact
- Personal armor such as combat helmets, ballistic face masks, and ballistic vests.
- Motorcycle safety clothing, especially in the areas featuring padding such as shoulders and elbows.

## Polyacrylamide

**Properties:**

1. Water soluble
2. Typically non-ionic but sometimes anionic

**Uses:**

1. Make clumps of solids in a liquid
2. Another common use of polyacrylamide and its derivatives is in subsurface applications such as Enhanced Oil Recovery.

## Polylactic Acid PLA

Formed by condensation of lactic acid and water loss. The monomer is typically made from fermented plant starch such as from corn, cassava, sugarcane or sugar beet pulp.

**Properties:**

1. PLA has high mechanical strength and tensile strength, comparable to petroleum-based polymers
2. PLA is resistant to weather and light.
3. PLA has a melting point of around 170°C.

**Uses:**

1. Disposable tableware, cutlery, electronics like laptop
2. PLA is used for automotive parts such as floor mats, panels, and covers
3. PLA is used for monofilament fishing line and netting for vegetation and weed prevention
4. Used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh

## Silicone Polymer

**Properties:**

1. Low thermal conductivity
2. Low chemical reactivity
3. Low toxicity
4. Thermal stability
5. Does not stick to many substrates, but adheres very well to others, e.g. glass
6. Does not support microbiological growth

**Uses:**

1. Cosmetics & Toiletries
2. Sealants in construction
3. Shaving products
4. Breast implants.

# MEMS

Microelectromechanical systems (MEMS) are devices that sense, control, and actuate at the micro-scale but create effects noticeable at the macro-scale.

MEMS works by integrating tiny components—sensors, actuators, and electronics—on a silicon chip. Here's how:

1. **Sensing**: Detects physical changes (e.g., motion, pressure, temperature).
2. **Processing**: Electronics on the chip process the sensed data.
3. **Actuation**: Tiny actuators respond (e.g., moving parts, generating forces).

This is done by precisely adding/removing material layers (micromachining) to build structures on the silicon substrate.

i) silicon is abundant, inexpensive, and can be processed to unparalleled purity
ii) silicon's ability to be deposited in thin films is very amenable to MEMS

**Biosensor**: know the concentration and composition of elements.
The ideal chemical sensor should be an inexpensive, portable, reusable, and reliable device that quickly responds with a perfect choice for a certain target analyte present in any medium, at any concentration level.

The signal strength depends on how much analyte is present. Two main detection methods are:

1. **Photochemical**: Detects light from chemical reactions.
2. **Photometric**: Measures changes in light passing through a sample.

Both give accurate results.

Applications:

- General healthcare
  - Implantable Devices: MEMS sensors monitor vital signs (like pressure, temperature, or glucose levels) inside the body and transmit data for real-time health monitoring.
  - **Lab-on-a-chip**: MEMS technology enables miniaturized systems that perform multiple diagnostic tests on a single chip, improving accuracy and speed in diagnostics
  - **Micro-pumps**: MEMS-based pumps are used in drug delivery systems to control the precise release of medication.
  - Retina wala
- Pollution control
- Agriculture