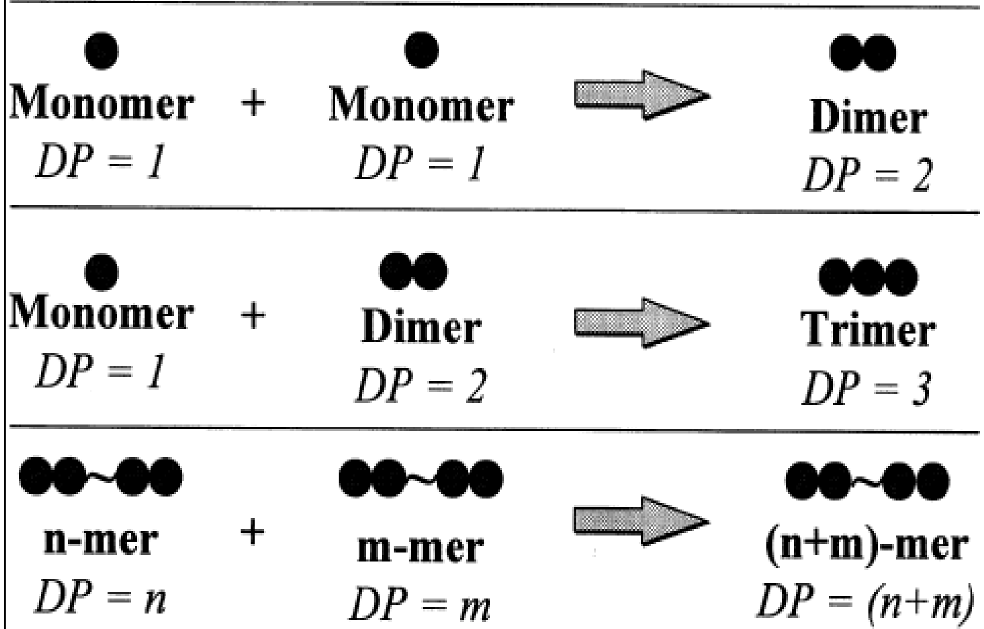
Polymers – Introduction & Classification

Contents

- ✓ Basics of polymers
- ✓ Classification criterion
- ✓ Applications

Polymer Basics

- **poly = many**
  mer = parts
- **degree of polymerization = DP**



Polymer Classification

Molecular structure

Linear
Branched
Cross-linked
Network

Thermo-physical behaviour

Thermoplastics
Thermosets

Origin

Natural
Synthetic

End use of Applications

Plastics
Elastomers
Fibres
Coatings
Adhesives
Films
Foams

Polymerization Reaction

Chain polymerization
Step polymerization

Advanced polymers

UHMWPE
Liquid Crystal polymers

Polymers

A polymer is a **large molecule** composed of many **repeated subunits**.

Natural Polymers – Shellac (bio-adhesive), cotton, silk, natural rubber, proteins, cellulose, starch, bone, leather, etc.

Synthetic polymers - Synthetic rubber, Bakelite, neoprene, nylon, polystyrene, polyethylene, polyvinyl chloride, etc.

Natural rubber

Shellac

Cellulose

Synthetic polymers

Image: Callister, 7^{th} Ed.

Cotton

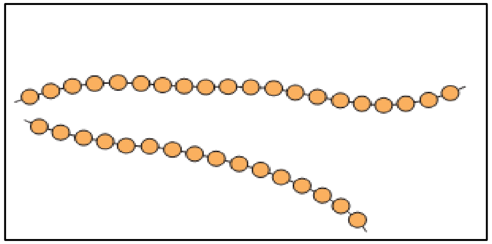
Starch

Molecular Structure

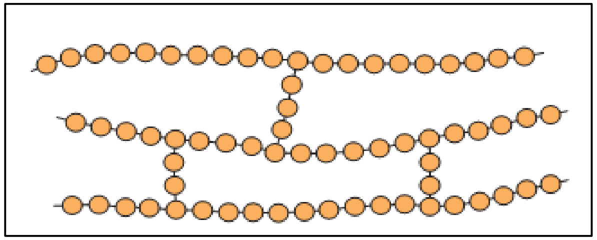
Linear Structure

- Units are joined together end to end in single chains.
- May be some weak van der Waals and hydrogen bonding between the chains.
- Soluble & Fusible

Example: high density polyethylene, poly(vinyl chloride), polystyrene, nylon, poly(methyl methacrylate)



Linear Structure

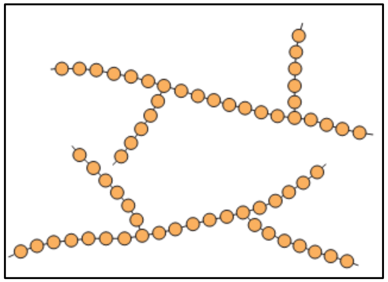


Branched Structure

Branched Structure :

- Side-branch chains are connected to the main ones
- More Soluble & Fusible

Example : low density polyethylene (LDPE)



Cross linked Structure

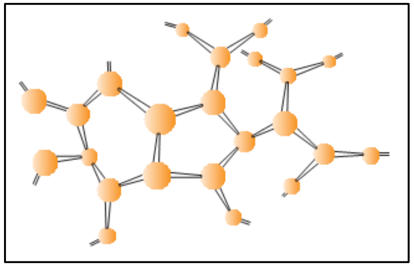
Cross linked Structure :

- Adjacent linear chains are joined one to another at various positions by covalent bonds
- Insoluble & Infusible

Network Structure :

- High cross-linking & 3D network.
- Insoluble & Infusible

Example : Rubber, polyurethanes and phenol-formaldehyde



Network Structure

Reference: W.D Callister, 7Ed.

Thermo-physical behaviour: **Thermoplastic Polymers**

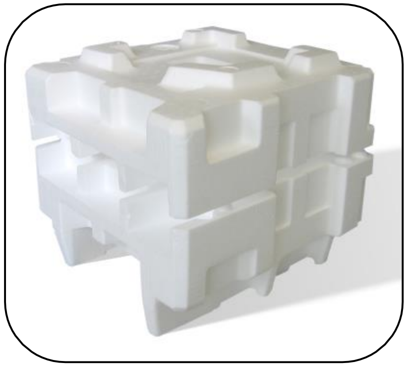
- **Heat** sensitive - soften and **flow upon heating**.
- Remain **soluble** and **fusible** under many cycles of heating and cooling, thus recyclable.
- Most linear polymers and those having some **branched structures** with flexible chains are thermoplastics.
- Individual polymer molecules are held together by weak secondary forces – **Van der Waals forces, Hydrogen bonds, dipole-dipole interactions**.
- **Easy** to **repair** by welding, solvent bonding, etc.
- **Unlimited shelf life** – won't undergo polymerization during storage or in processing unit.
- Disadvantage : prone to **creep**.

Example: Polyethylene, polystyrene, polyethylene terephthalate(PET), polyvinyl chloride (PVC), Nylon, polypropylene, polymethylmethacrylate (PMMA).

Applications

Nylon

Polyvinyl Chloride (PVC)



Polystyrene

PMMA (Queen of plastics)

Polypropylene

PET

Thermo-physical behaviour: Thermosetting Polymers

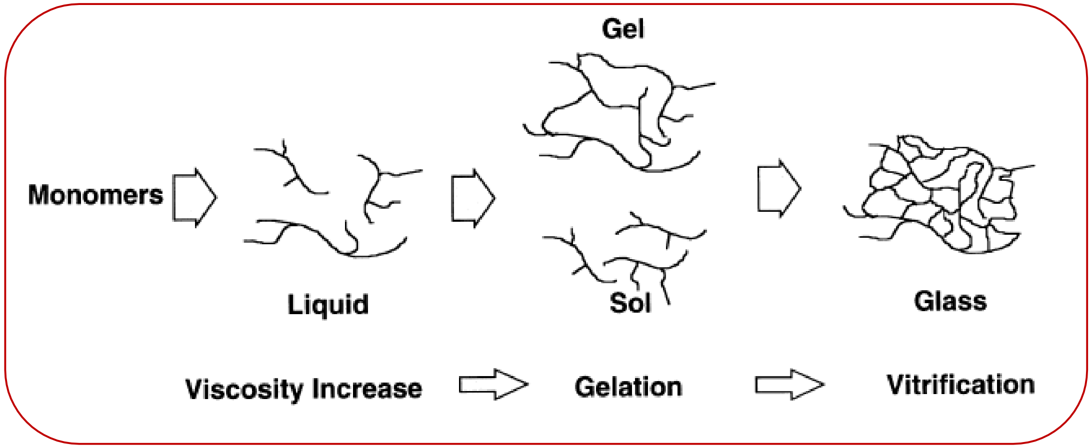
- Thermosetting polymers are **network polymers**.
- **Creep resistant** - Less sensitive to temperature.
- Attain permanent hardness due to cross-linking and then do not soften and flow upon heating.
- **Non-postformable** : Obtained in soluble or fusible stage in early or intermediate stage but once they get cured they will be infusible and insoluble.
- Excellent **thermal and chemically stable** once polymerized.
- **Disadvantage** – Brittle and non-recyclable.
- **Example** : Bakelite, epoxy, Urethane, etc.

Application

Bakelite

Curing of Thermosets

- **Curing** : Process to transform **thermosetting resin** (soft solid or viscous state) into an **infusible, insoluble polymer** network under heat and pressure.
- Viscosity of the system rises until Gelation occurs.
- At this point, two phases exist: a gel phase and a sol phase. The gel phase is the gelled part; the sol phase can be extracted with solvents.
- The amount of sol phase present decreases as the reaction progresses further.
- Upon further reaction, vitrification (hardening) occurs.



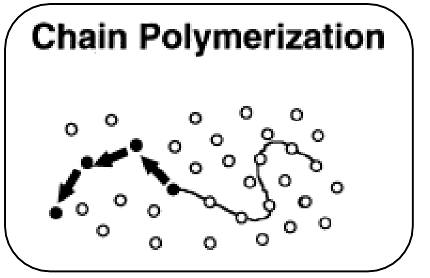
Polymerization reaction

1. Chain (addition) Polymerization
   - Monomer units are attached one at a time in chainlike fashion to form a linear macromolecule.
   - Characterized by the presence of a few active sites which react and propagate through a sea of monomers.
   - Distinct stages:
     - ✓ Initiator decomposition

$$\mathbf{I}\ \text{(catalyst)} \longrightarrow \mathbf{2R^*}\ ,\ R^* = \text{active initiator}$$

     - ✓ Chain initiation

$$\mathbf{R^* + M \longrightarrow RM_1^*}\ ,\ M = \text{monomer unit}$$



     - ✓ **Chain propagation** (linear growth - sequential addition)

$$\mathbf{RM_1^* + M \longrightarrow RM_2^*}$$

$$\mathbf{RM_{n-1}^* + M \longrightarrow RM_n^*}$$

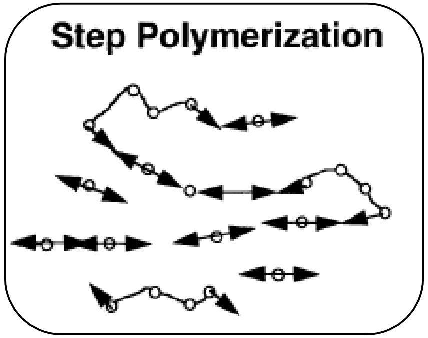
     - ✓ **Chain termination**

$$\mathbf{RM_n^* + RM_m^* \longrightarrow R - M_{m+n} - R}$$

   - Used in the **synthesis of thermoplastics.**

Polymerization reaction

2. Step (condensation) Polymerization



- Involve more than one monomer species.
- Monomers can react with any nearby monomer.
- No special activation is needed to allow a monomer to react.
- A small molecular weight **byproduct** such as water that is **eliminated** (or condensed).

Typical reaction

1st Step: HO-R-OH + HOOC-R-COOH $\longrightarrow$ HO-ROOC-R-COOH + H_2O

2nd Step: HO-ROOC-R-COOH +HO-R-OH $\longrightarrow$ HO-ROOC-R-COOR-OH + H_2O

$$\Sigma M_n + \Sigma M_m \longrightarrow \Sigma M_{m+n} + H_2O$$

- The **thermosetting** polyesters, phenol-formaldehyde, the nylons, and the polycarbonates are produced by condensation polymerization.

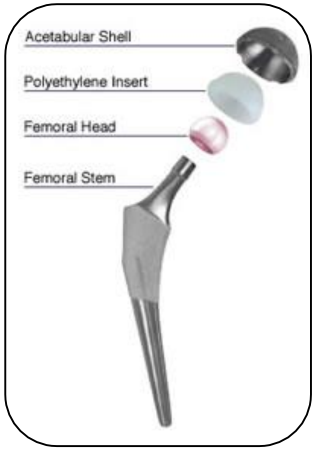
Advance Polymers

<u>UHMWPE</u> (Ultra high molecular weight polyethylene)

- Linear polyethylene that has an extremely high molecular weight (4×10^6 g/mol).
- Trade name – **Spectra** & **Dyneema**
  - ✓ An extremely high impact resistance
  - ✓ Outstanding resistance to wear and abrasion
  - ✓ A very low coefficient of friction
  - ✓ A self-lubricating and nonstick surface
  - ✓ Very good chemical resistance to normally encountered solvents
  - ✓ Excellent low-temperature properties
  - ✓ Outstanding sound damping and energy absorption characteristics

De-merit: Mechanical properties diminish rapidly with increasing temperature.

<u>Applications</u>:



Femoral implant

Pipes

Light gears

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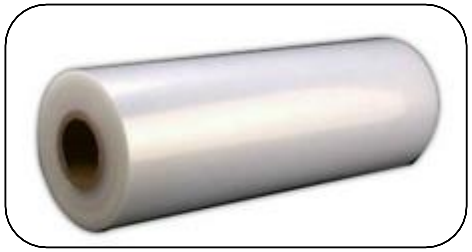
Liquid Crystal Polymer

- Aromatic polyesters based on p-hydroxybenzoic acid and related monomers.
- They are in **liquid crystalline state**, being **neither** purely crystalline nor purely liquid – considered as **new state** of matter.
- Capable of forming regions of highly ordered structure while in the liquid phase but regularity lower than solid crystal.
- **Extremely unreactive** and **inert**, and highly **resistant** to fire.
- Used in liquid crystal displays (**LCD**s) on digital watches, flat-panel computer monitors and televisions, and other **digital displays.**

End use
of
Applications

Films

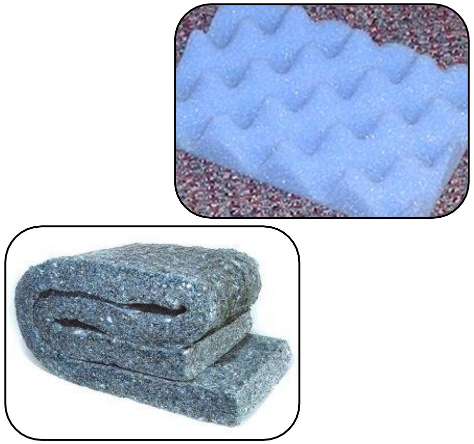
- Polymeric films having thickness between 0.025 and 0.125 mm used extensively as bags for packaging food products and other textile products.
- Important properties includes:
  - ✓ low density
  - ✓ high degree of flexibility
  - ✓ high tensile and tear strengths
  - ✓ resistance to moisture and other chemicals
- Example - Polyethylene, polypropylene, cellophane



Polymer film

Foams

- Contain a relatively **high volume** percentage of **small pores** and trapped gas bubbles.
- Commonly used as **cushions** in automobiles and furniture as well as in **packaging** and **thermal insulation**.



Polymer foam

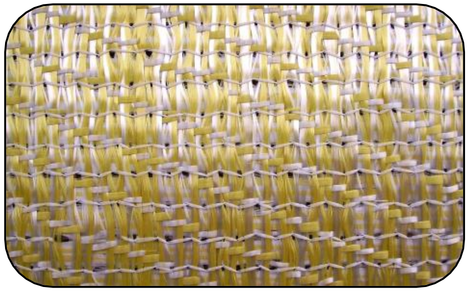
Coatings

- Ingredients in coating material are usually organic polymers which are classified as - paint, varnish, enamel, lacquer, and shellac.
- Applied to surface of materials:
  - ✓ To protect the item corrosive or deteriorative reactions.
  - ✓ To provide electrical insulation.
  - ✓ To improve the object’s appearance.

A disposable nitrile rubber glove.

Fibers

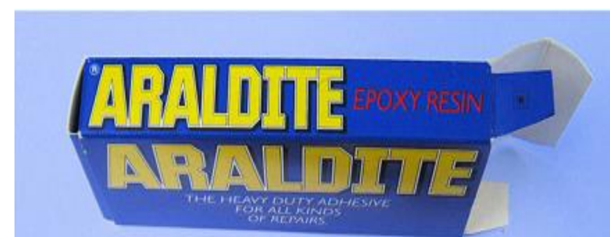
- Long filaments having at least 100:1 length-to-diameter ratio.
- Subjected to **mechanical deformations**—stretching, twisting, shearing, and abrasion.
- Widely used in **textile industry** for being woven into fabric/cloth.



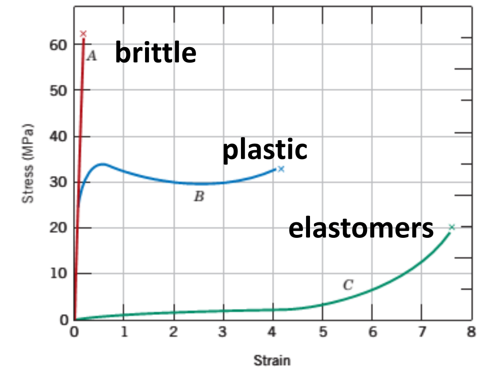
Aramid fiber

Adhesives

- Used to join a large variety of materials—viz. metals, ceramics, polymers, composites.
- Advantages
  - ✓ lighter weight.
  - ✓ Ability to join dissimilar materials and thin components.
  - ✓ Better fatigue resistance.
  - ✓ Lower manufacturing costs.
- Limitation – High temperature
- Examples - **Natural adhesives**: animal glue, casein (protein), starch (carbohydrate), and rosin (pine tree).
  Artificial adhesives: epoxy, polyurethane, cyanoacrylate and acrylic polymers.
- Applications – Aerospace, automobiles, stick-notes, etc.

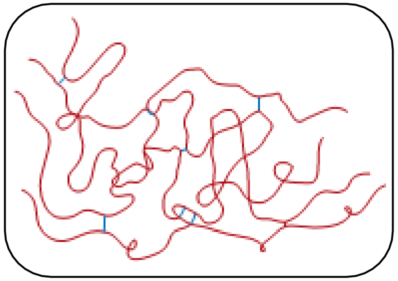


Elastomers (Elastic polymer)

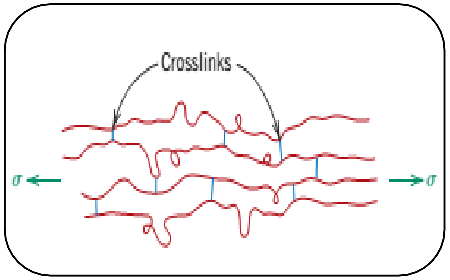


- **Amorphous polymer** with viscoelasticity (viscosity + elasticity), very **weak inter-molecular forces**, **low Young's modulus** and **high failure strain** compared with other materials.

- For a polymer to be an elastomer-
  - ✓ It must not easily crystallize - molecular chains should remain naturally coiled in the unstressed state.
  - ✓ Chain bond rotations must be free to readily respond to an applied force.
  - ✓ Delayed plastic deformation.



Unstressed state



Elastic deformation

- **Examples** - Silicone rubber, Butyl rubber, Nitrile rubber, polychloroprene, Neoprene

- **Applications**
  - ✓ Gasket seals (fill the space between imperfect mating surfaces – prevent leakages)
  - ✓ Noise and vibration dampers
  - ✓ Car door seals, etc.

Gaskets

Reference: W.D Callister, 7Ed.

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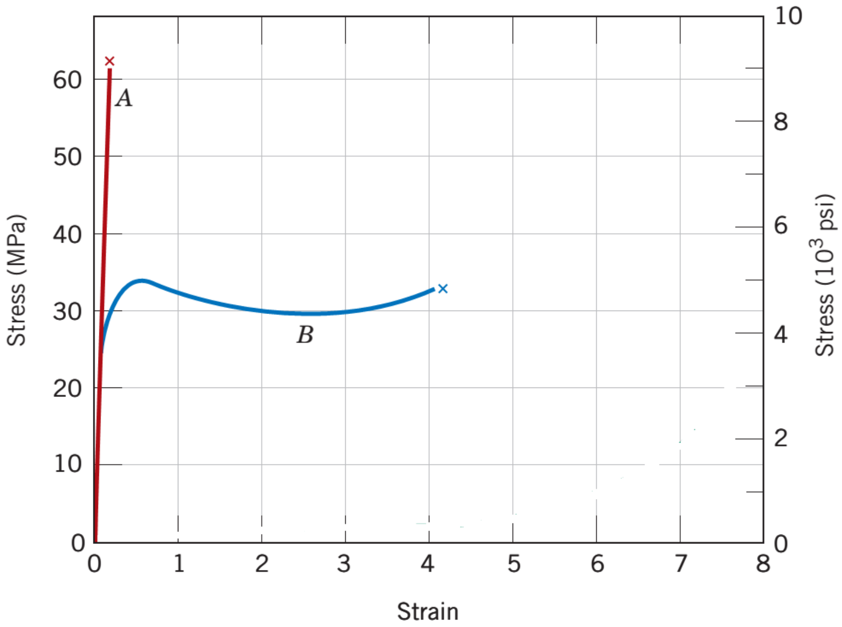
Plastics

- Malleable and can be molded into solid objects of diverse shapes.
- Some plastics are very rigid and brittle (curve A) and other are flexible (curve B).
- Used in general purpose applications.
- May be either thermoplastic or thermosetting.



Reference: W.D Callister, 7Ed.

Some Thermoplastics – for reference

Material	Trade name	Applications
Acrylonitrile-butadiene-styrene (ABS)	Abson, Cycolac, Kralastic, Lustran, Novodur, Tybrene	Refrigerator linings, lawn and garden equipment, toys, highway safety devices
Acrylics	**Acrylite**, Diakon, Lucite, Plexiglas	Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs
Fluorocarbons	**Teflon**, Fluon, Halar, Hostaflon TF, Neoflon	Anticorrosive seals, chemical pipes and valves, bearings, antiadhesive coatings, high temperature electronic parts
Polyamides	**Nylon**, Baylon, Durethan, Herox, Nomex, Ultramid, Zytel	Bearings, gears, cams, bushings, handles, and jacketing for wires and cables
Polypropylene	Herculon, Meraklon, Moplen, Poly-pro,Pro-fax,	Sterilizable bottles, packaging film, TV cabinets, luggage
Polystyrene	Carinex, Dylene, Hostyren, Lustrex, Styron, Vestyron	Wall tile, battery cases, toys, indoor lighting panels
Polyester	Celanar, **Dacron**, Eastapak, Hylar, Melinex, **Mylar**, Petra	Magnetic recording tapes, clothing, automotive tire cords, beverage containers
Polyethylene	Alathon, Alkathene, Fortiflex. Hi-fax, Petrothene, Rigidex, Rotothene, Zendel	Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials

Reference: W.D Callister, 7Ed.

Some Thermosettings – <u>for reference</u>

Material	Trade name	Applications
Phenolformaldehyde (Amorphous)	**Bakelite**, Amberol, Arofene, Durite, Resinox	Motor housings, **telephones**, auto distributors, electrical fixtures
Epoxies (Amorphous)	**Araldite**, Epikote, Epon Epi-rez, Lekutherm Lytex	Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates
Polyesters (both thermoplastics and thermosetting depending on chemical structure, i.e., linear or cross-linked) (Amorphous)	Aropol, Baygal, Derakane, Laminac, Selectron	Helmets, fiberglass boats, auto body components, chairs, fans

Reference: W.D Callister, 7Ed.

In the **next lecture**, we will learn:

- ✓ **Calculation of molecular weight in polymers**
- ✓ **Polymer Structure**
- ✓ **Tacticity**

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