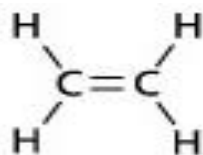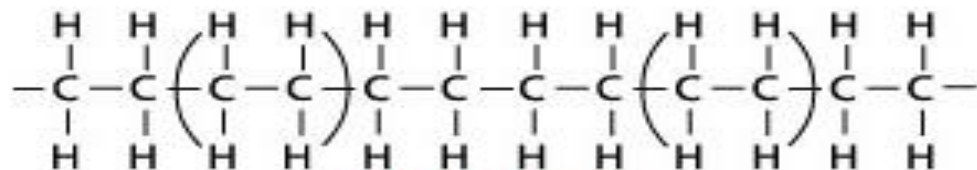# POLYMERS

Carbon-based compounds

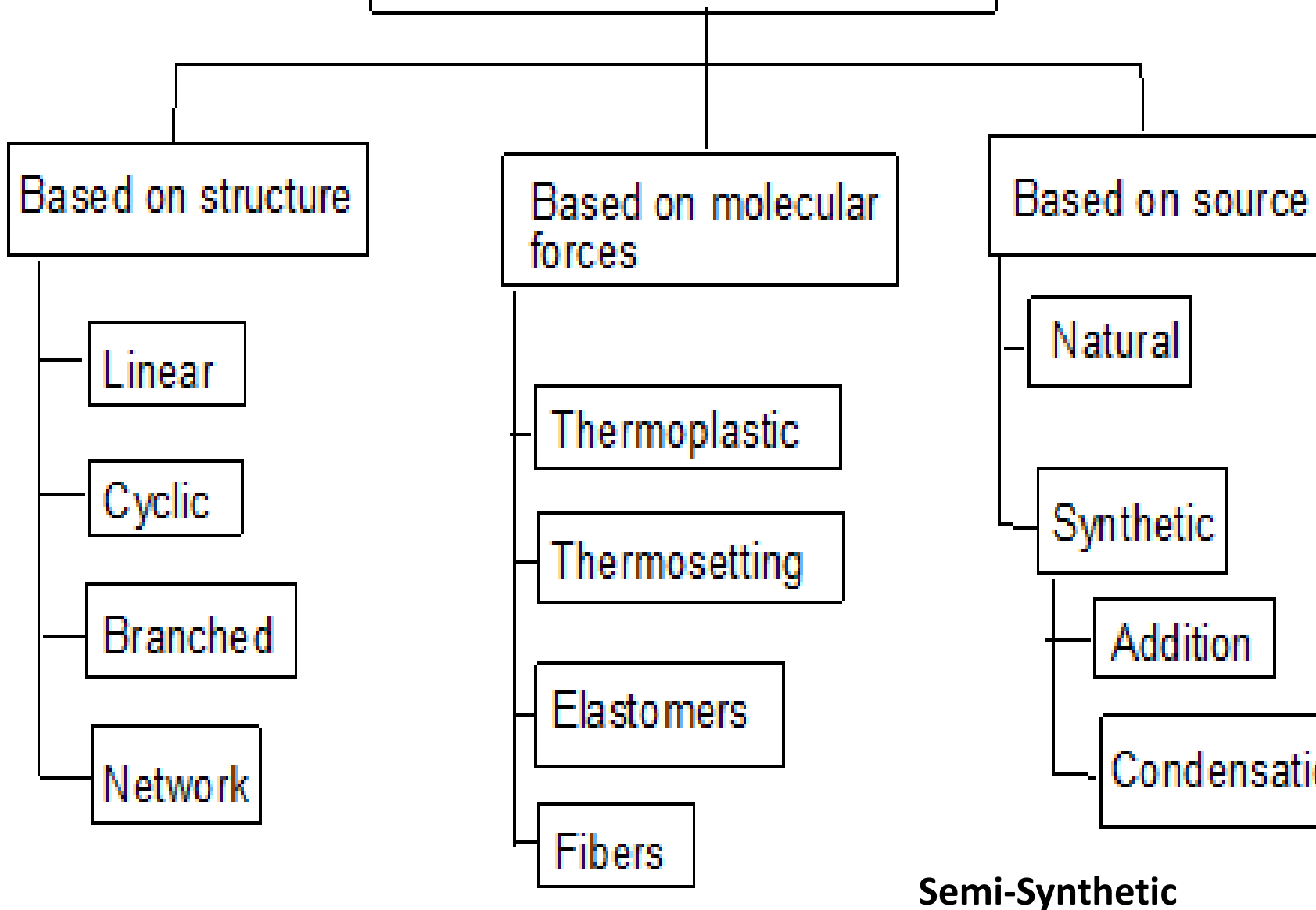## Polymers ARE CHAINS OF Monomers joined together.

ethylene

polymerization

polyethylene

- A polymer is a macromolecule with high molecular mass ranging from 5000 to one million, which are formed by combination of one or more low molecular weight compound/ s. The unit substance from which polymer is obtained is called monomer.

- The process by which polymers are obtained is called polymerization

- For e.g. polyethylene is obtained by repeating ethylene unit as a result of polymerization.

CLASSIFICATION OF POLYMER

Based on structure
- Linear
- Cyclic
- Branched
- Network

Based on molecular forces
- Thermoplastic
- Thermosetting
- Elastomers
- Fibers

Based on source
- Natural
- Synthetic
  - Addition
  - Condensation

Semi-Synthetic

• Polymers can be separated into plastics and rubbers (fibres not included here)

• As engineering materials, it is appropriate to divide them into the following three categories:

1. Thermoplastic polymers
2. Thermosetting polymers
3. Elastomers where (1) and (2) are plastics and (3) are rubbers

Thermoplastic Polymers - Thermoplastics (TP)

- Solid materials at room temperature but viscous liquids when heated to temperatures of only a few hundred degrees
- This characteristic allows them to be easily and economically shaped into products
- They can be subjected to heating and cooling cycles repeatedly without significant degradation

Thermosetting Polymers - Thermosets (TS)

•Cannot tolerate repeated heating cycles as thermoplastics can

When initially heated, they soften and flow for molding

But elevated temperatures also produce a chemical reaction that hardens the material into an infusible solid

If reheated, thermosets degrade and char rather than soften

Elastomers: Polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress

• Also known as rubber

• Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape

• Although their properties are quite different from thermosets, they share a similar molecular structure that is different from the thermoplastics

Examples of Polymers

- **Thermoplastics:** Polyethylene, polyvinylchloride, polypropylene, polystyrene, etc.
- **Thermosets:** Phenolics, epoxides, and certain polyesters
- **Elastomers:** Natural rubber, (vulcanized) Synthetic rubbers, which exceed the tonnage of natural rubber
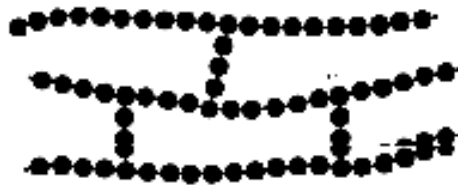
Linear, Branched, and Cross-linked Polymers

•Linear structure –chain-like structure Characteristic of thermoplastic polymers

•Branched structure –chain-like but with side branches Also found in thermoplastic polymers

•Cross-linked structure -Loosely cross-linked, as in an elastomer Tightly cross-linked, as in a thermoset

(a)

(b)

(c)

(d)

ii) On the basis of nature of monomer

- Homopolymers (comprise of monomers of the same type)
  - Linear (homochain or heterochain)
  - Branched
  - Cross-linked
- Heteropolymers/ Copolymers (Different repeating units)
  - Linear; Branched; Graft (regular/irregular); Block (regular/irregular)

iii) On the basis of chemical nature

- Organic (polymer backbone chain made up of carbon atom)
- Inorganic (No carbon atoms in the backbone chain, eg., Silicone rubbers)
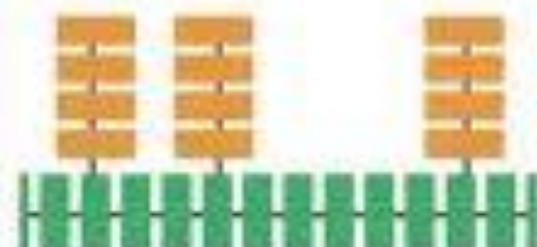
a)Homopolymer

b)Copolymer

c) Block copolymer

d) Graft copolymer

(a) Simple polymer

(b) Alternating copolymer

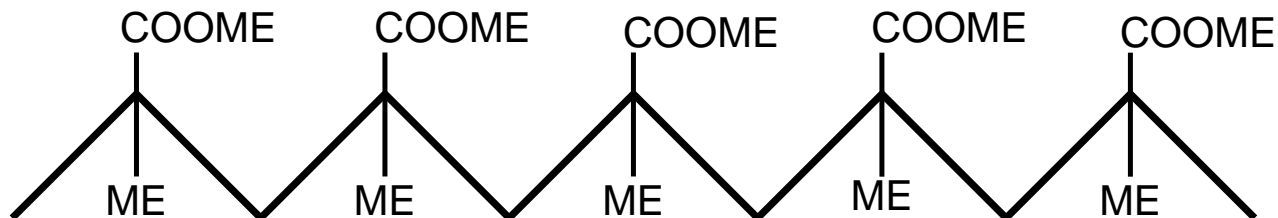(c) Block copolymer

(d) Graft copolymer

- *Depending on tacticity:*
- Isotactic – similar groups on same side of chain
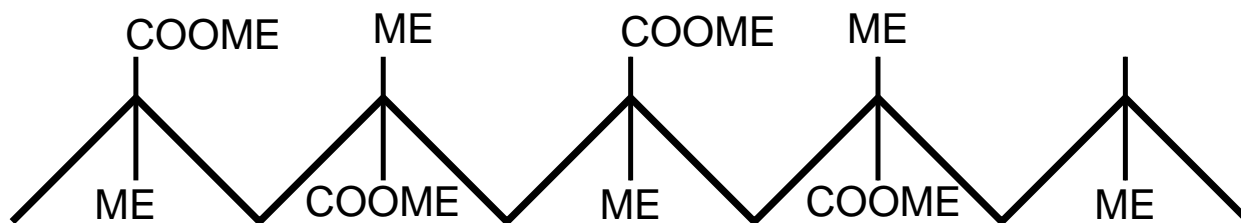
COOME   COOME   COOME   COOME   COOME

ME   ME   ME   ME   ME

- Syndiotactic – two groups alternate

COOME   ME   COOME   ME

ME   COOME   ME   COOME   ME

- Atatactic – displays no regular pattern

COOME   COOME   ME   COOME   ME

ME   ME   COOME   ME   COOME
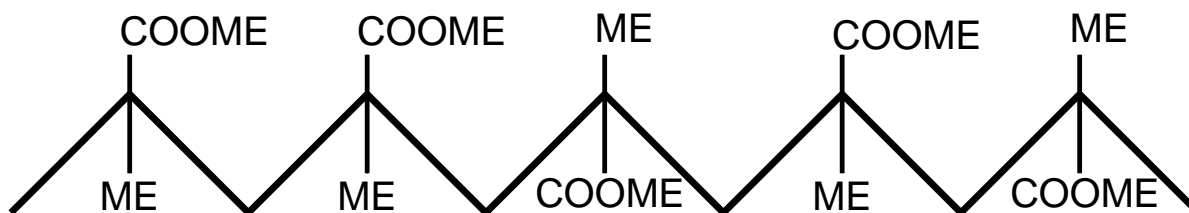
❖ Every other carbon in the chain is a steriocenter

Classification based Polymerization

- **Addition Polymerization:** A polymer formed by direct repeated addition of monomers is called addition polymerization. In this types of polymers monomers are unsaturated compounds or derivatives of alkenes.
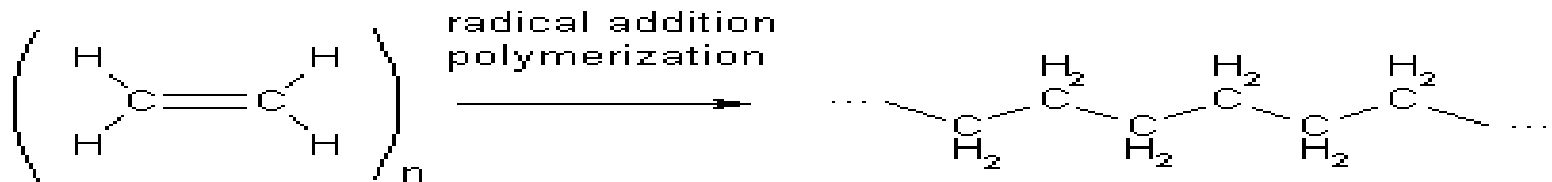

Fig 1: The polymerisation of ethene in to poly(ethene)

- **Condensation Polymerization:** Condensation polymerization involves condensation of two different monomers which are normally bi functional group. During the process there is loss of small molecule such as water
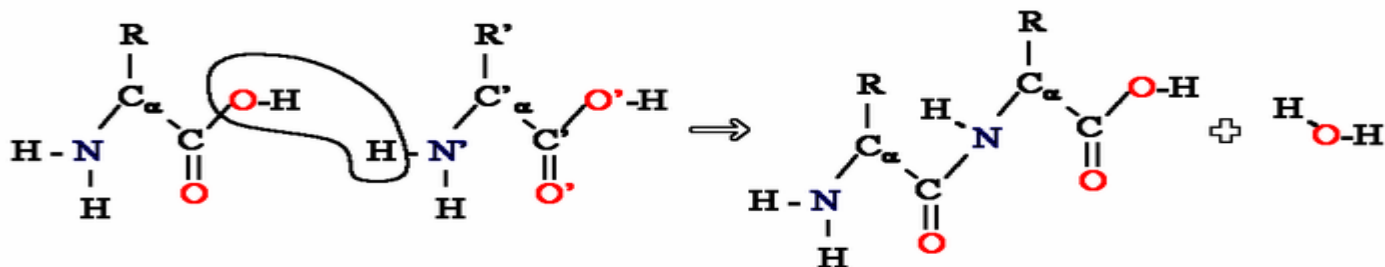
- Effect of Branching on Properties
  •Thermoplastic polymers always possess linear or branched structures, or a mixture of the two
- •Branches increase entanglement among the molecules, which makes the polymer: Stronger in the solid state. More viscous at a given temperature in the plastic or liquid state

- Effect of Cross-Linking on Properties
- •Thermosets possess a high degree of cross-linking, while elastomers possess a low degree of cross-linking
- •Thermosets are hard and brittle, while elastomers are elastic and resilient
- •Cross-linking causes the polymer to become chemically set The reaction cannot be reversed The polymer structure is permanently changed; if heated, it degrades or burns rather than melt

- Mechanical Properties of Thermoplastics
- •Low modulus of elasticity (stiffness) E is two or three orders of magnitude lower than metals and ceramics
- •Low tensile strength TS is about 10% of the metal
- •Much lower hardness than metals or ceramics
- •Greater ductility on average Tremendous range of values, from 1% elongation for polystyrene to 500% or more for polypropylene

- **Physical Properties of Thermoplastics**
- •Lower densities than metals or ceramics Typical specific gravity for polymers are 1.2 Ceramics specific gravity = 2.5 Metals specific gravity = 7.0
- •Much higher coefficient of thermal expansion Roughly five times the value for metals and 10 times the value for ceramics
- •Much lower melting temperatures
- •Specific heats two to four times those of metals and ceramics
- •Thermal conductivities about three orders of magnitude lower than those of metals
- •Insulating electrical properties

- General Properties and Characteristics of Thermosets
- •Rigid - modulus of elasticity is two to three times greater than TP
- •Brittle, virtually no ductility
- •Less soluble than TP in common solvents
- •Capable of higher service temperatures than TP
- •Cannot be remelted - instead they degrade or burn

CHARACTERISTICS OF IDEAL POLYMER

- *Should be inert and compatible with the environment.*
- *Should be non-toxic.*
- *Should be easily administered.*
- *Should be easy and inexpensive to fabricate.*
- *Should have good mechanical strength.*

Why are polymers/ plastics extensively used-

- Plastics are strong, light weight, flexible and durable.
- Plastics show superior optical properties (clarity, gloss and color).
- Plastics can be easily moulded into a variety of shapes and sizes.
- Plastics have excellent mechanical strength (tensile properties, tear resistance and impact resistance).

- Plastics are relatively cheap compared to tin, glass and steel.
- Plastics are reusable and recyclable.
- Plastics have long use life.

- Plastics are good electrical / heat insulators.
- Plastics do not corrode or decay.
- Plastics are cheap and dispensable.
- Plastics are resistant to chemicals, water or grease.

- ***Compounding of polymer***
- Polymer and Additives
- ➢ Usually, polymers are mixed with added ingredients (serve a variety of purposes) •Properties of a polymer can often be beneficially changed by combining it with additives

- ➢ 2 types of additives
  - ➢ Modifying additives
  - ➢ Protective additives
- Fillers
  - – Reinforcing fillers- to toughen polymers. e.g. carbon black added to rubber; improvement in abrasion resistance
  - – Non-reinforcing fillers- are in powder, added to cheapen the mix (usually these additives do not enhance the properties). e.g. calcium carbonate.
- Plasticizer- usually non-volatile liquids, desired to increase the flexibility. e.g. flexible plasticized PVC, eg. Tricresyl phosphate, triphenyl phosphate, etc.
- Binders- Hold the constituents together. Eg. Cellulose derivatives. Influence properties of plastics.

- Types of Additives by Function
- •Resin- main constituent.
- Fillers –to strengthen polymer or reduce cost
- •Plasticizers –to soften polymer and improve flow
- •Colorants –pigments or dyes
- •Lubricants –to reduce friction and improve flow, eg. Vegetable oil, soaps, etc.
- •Flame retardents –to reduce flammability of plastic
- •Cross-linking agents –for thermosets
- Stabilizers- Ultraviolet light absorbers –to reduce degradation from sunlight, Antioxidants –to reduce oxidation damage
- Pigments- used to colour the product, eg. Titanium oxide- white color, iron oxide red color, etc.
- Catalyst- accelearate polymerisation, eg. H2O2, benzoyl peroxide, etc.

Fabrication/ Moulding

Molding or **moulding** is the process of [manufacturing](#) by shaping liquid or pliable raw material using a rigid frame called a mold or matrix. This itself may have been made using a pattern or model of the final object.

A **mold** or **mould** is a hollowed-out block that is filled with a liquid or pliable material like [plastic](#), [glass](#), [metal](#), or [ceramic](#) raw materials. The liquid hardens or sets inside the mold, adopting its shape. A mold is the counterpart to a [cast](#). The very common bi-valve molding process uses two molds, one for each half of the object.

Compression Molding is a process in which a molding polymer is squeezed into a preheated mold taking a shape of the mold cavity and performing curing due to heat and pressure applied to the material.
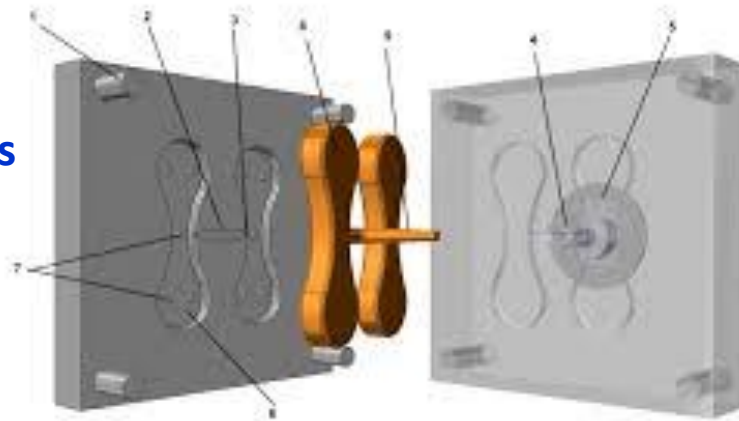
The method is used mostly for molding **thermosetting resins (thermosets)**, but some thermoplastic parts may also be produced by Compression Molding.

The method uses a split mold mounted in a hydraulic press

COMPRESSION MOLDING

UPPER MOVABLE MOLD HALF

CHARGE

LOWER FIXED MOLD HALF

EJECTOR PIN
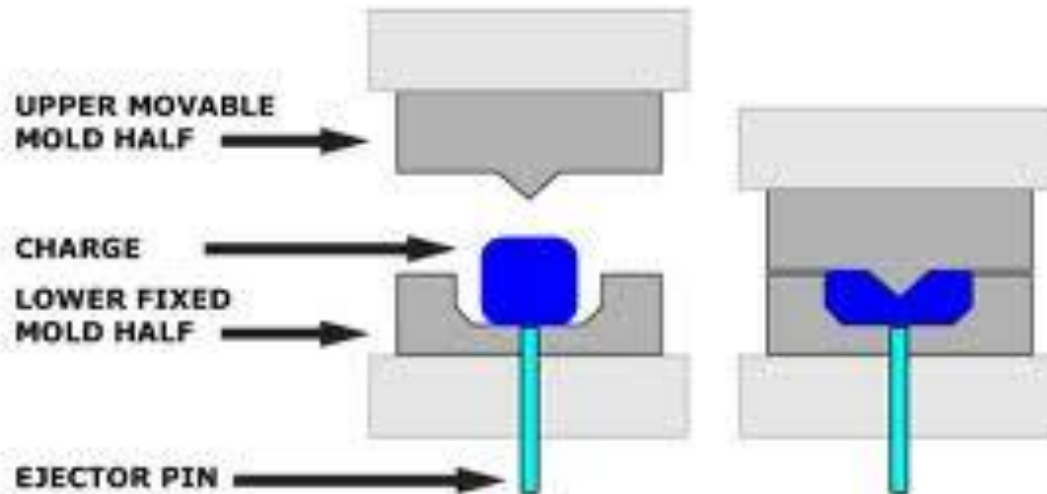
Thermoplastic and thermosets

https://www.youtube.com/watch?v=GqE93pbV_9I

Injection molding

- Injection molding is a method to obtain molded products by injecting plastic materials molten by heat into a mold, and then cooling and solidifying them.
  The method is suitable for the mass production of products with complicated shapes, and takes a large part in the area of plastic processing.

Advantages of Injection Molding

- High production rates
- Wide range of materials can be used
- Low labor costs
- Minimal scrap losses

Injection Moulding of a thermoplastic.

Thermoplastic

https://www.youtube.com/watch?v=b1U9W4iNDiQ
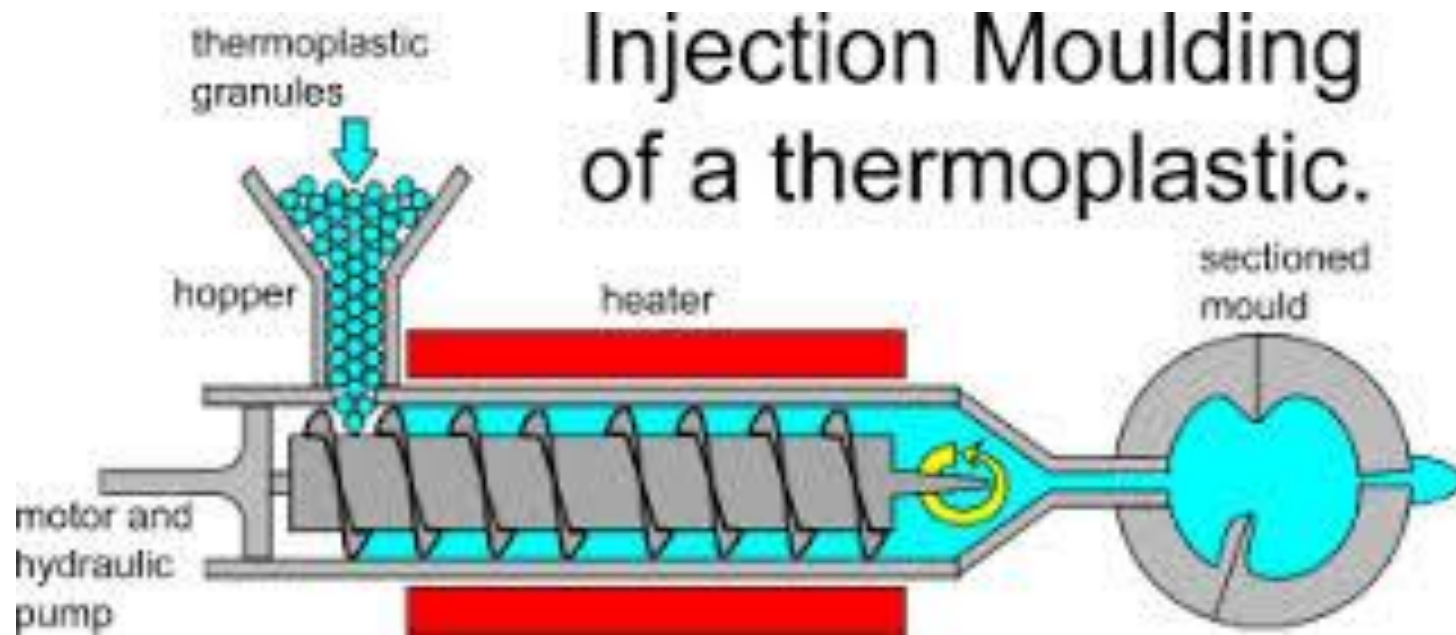
Transfer Molding

The method is used primarily for molding thermosetting resins (thermosets), but some thermoplastic parts may also be produced by Transfer Molding

The method combines features of both Compression Molding (hydraulic pressing and the same molding materials - thermosets) and Injection Molding (ram-plunger and filling the mold through a sprcue).

TS charge is loaded into a chamber immediately ahead of mold cavity, where it is heated; pressure is then applied to force soft polymer to flow into heated mold where it cures
Two variants:
    Pot transfer molding - charge is injected from a "pot" through a vertical sprue channel into cavity
    Plunger transfer molding – plunger injects charge from a heated well through channels into cavity.

Transfer Molding

Plunger

Transfer pot

Charge

Sprue

Mold cavity

Ejector pin

Heaters

Molded part
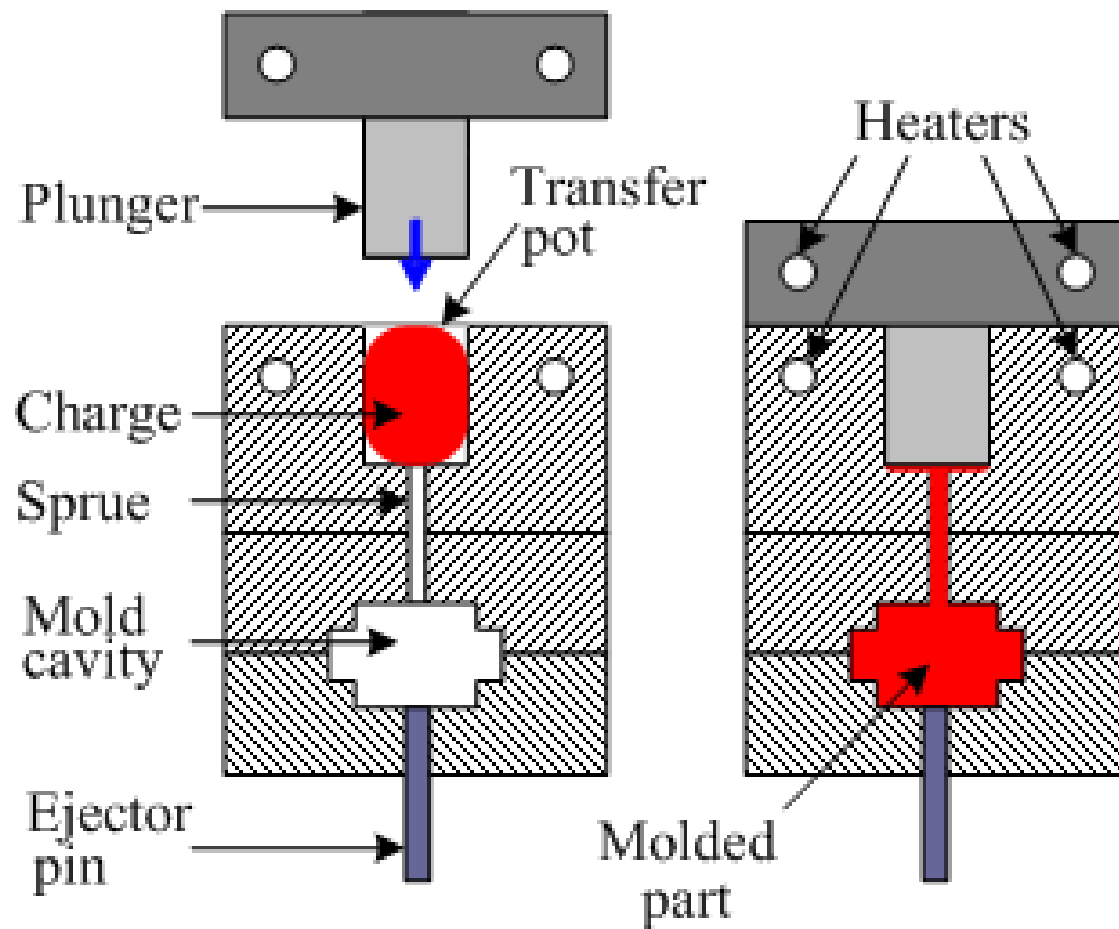
Thermosets

www.substech.com

https://www.youtube.com/watch?v=Lp7go_TMe28

Extrusion Molding-

Thermoplastic granules are fed from a hopper by a rotating screw through a heated cylinder.

The tapered shape of the screw compacts the plastic as it becomes plasticized. This part of the process is similar to the heating and compacting stages in the injection moulding process. The difference being that the softened material is allowed to flow out through a die in a continuous stream

(Extrusion moulding) rather than be pumped intermittently in measured amounts into a mould.(Injection moulding)

The die which is fitted to the end of the extruder barrel determines the cross-section of the extrusion.

Widely used for thermoplastics and elastomers to mass produce items such as tubing, pipes, hose, structural shapes, sheet and film, continuous filaments, and coated electrical wire

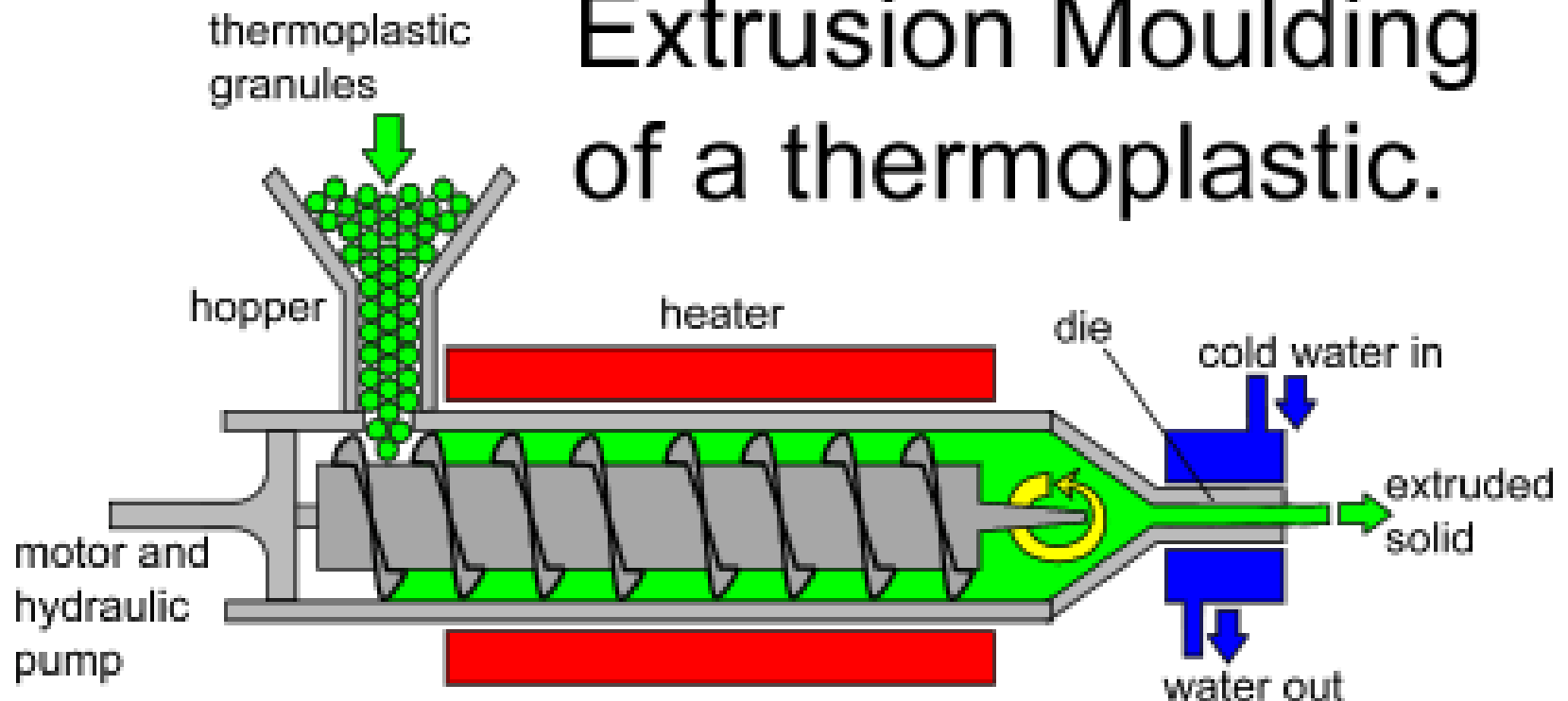Carried out as a continuous process; *extrudate* is then cut into desired lengths

Extrusion

This process can be compared to squeezing toothpaste from a tube. It is a continuous

process used to produce both solid and hollow products that have a constant

cross-section. E.g. window frames, hose pipe, curtain track, garden trellis.

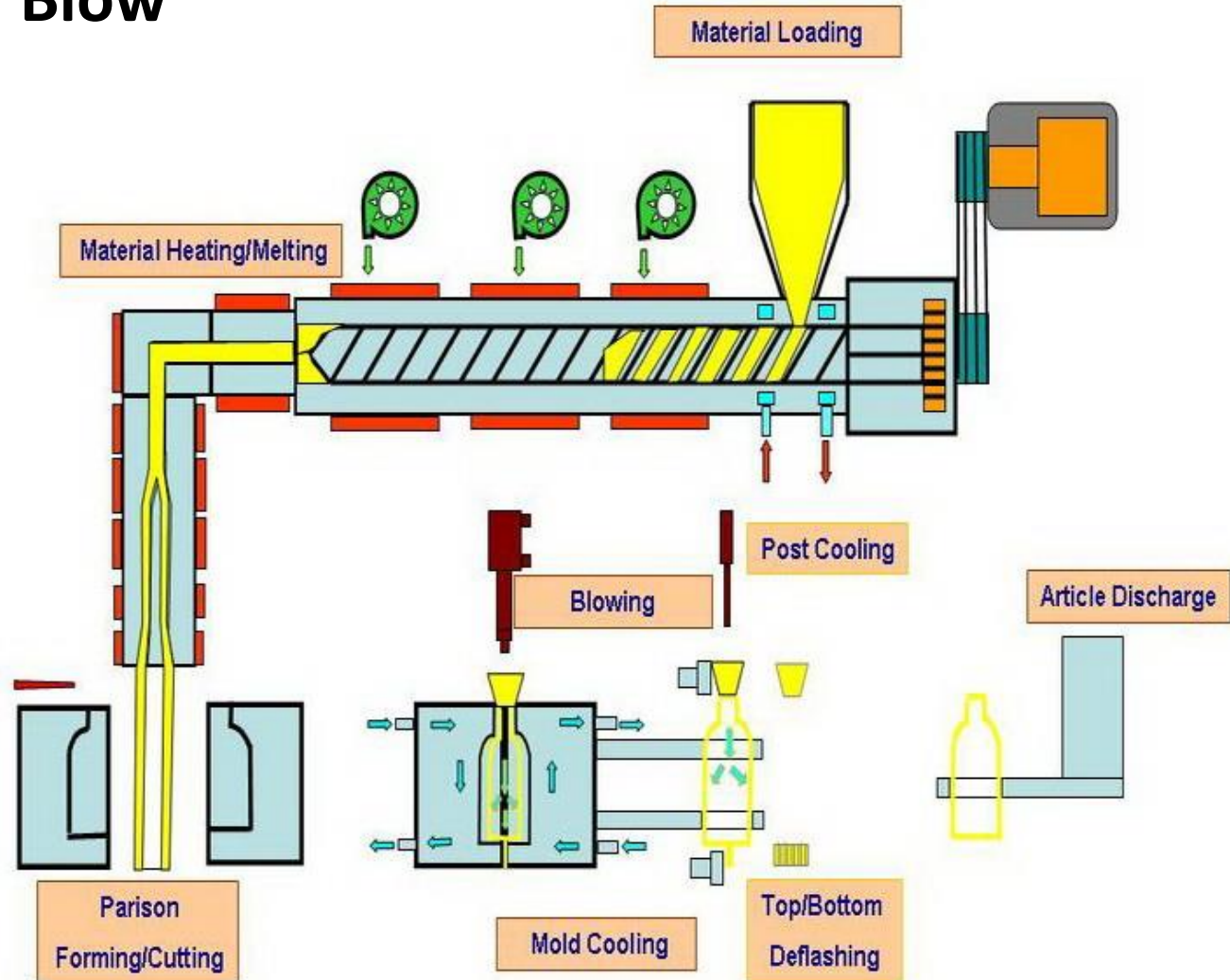Extrusion Moulding of a thermoplastic.

Thermoplastic

- *Horizontal*

https://www.youtube.com/watch?v=Tp2Rdx69SSo

Also called as 'Extrusion Blow Molding'.

Vertical

https://www.youtube.com/watch?v=xJtyn0vumQU

Synthesis of some important polymers-
Kevlar
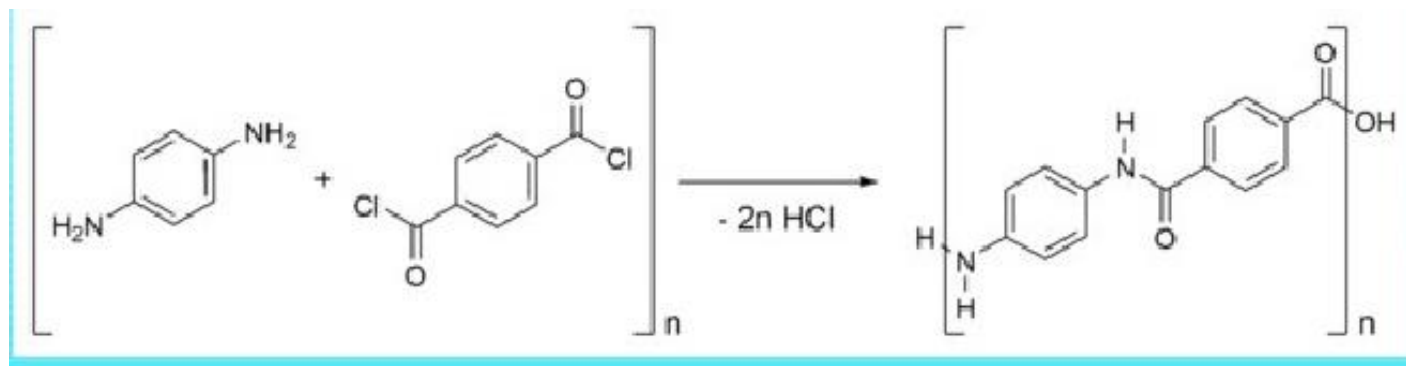
This is a amide co-polymer synthesized by condensation polymerisation of phenylene diamine and terpthaloyl chloride.

Terepthalic acid is used for manufacture of Kevlar but as terepthaloyl chloride is more active than the terephthalic acid, terepthalic aid is converted to terepthalic chloride which is used to manufacture Kevlar.

Condensation mechanism-

terephthalic acid

p-phenylenediamine
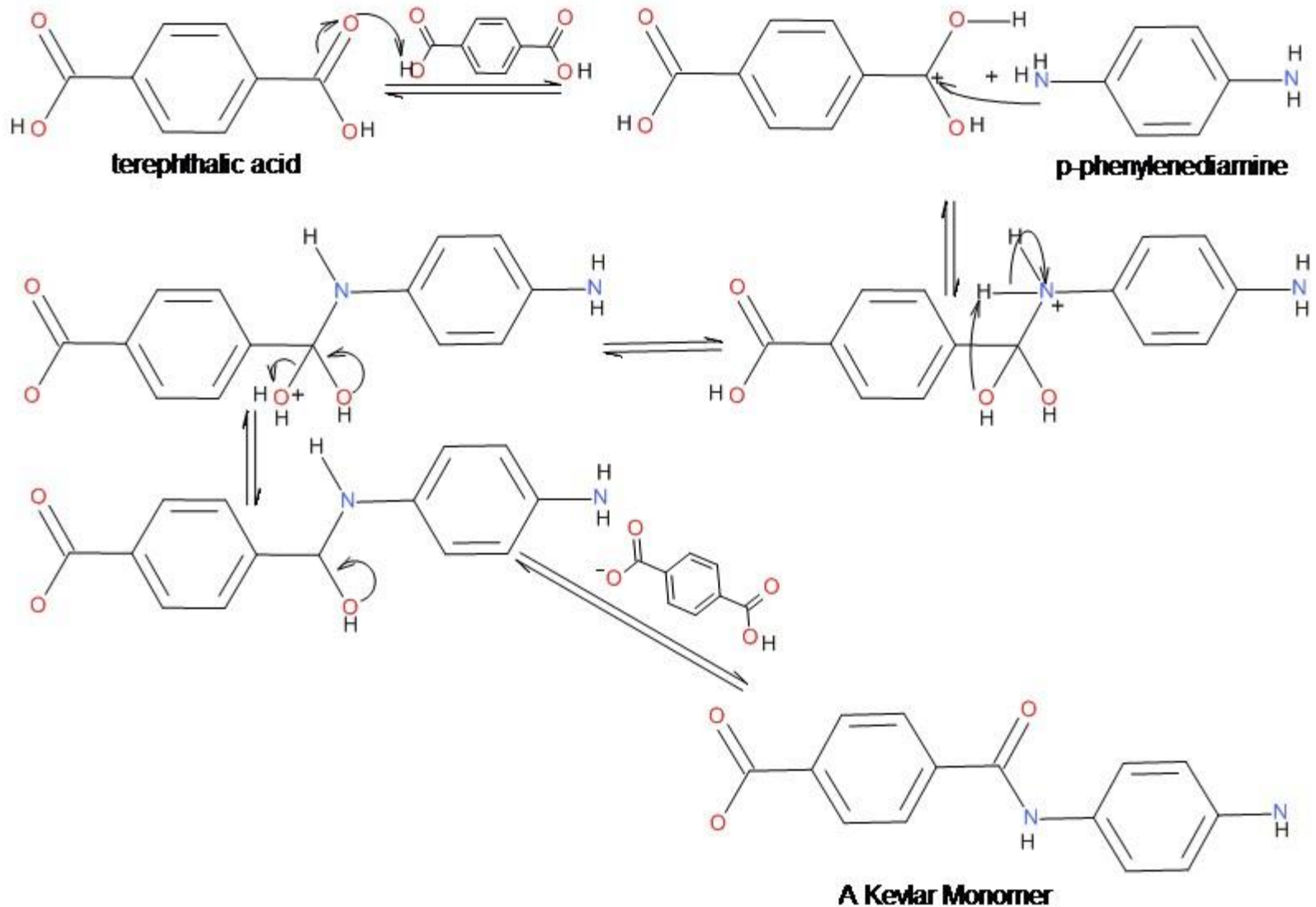
A Kevlar Monomer

Polymerisation
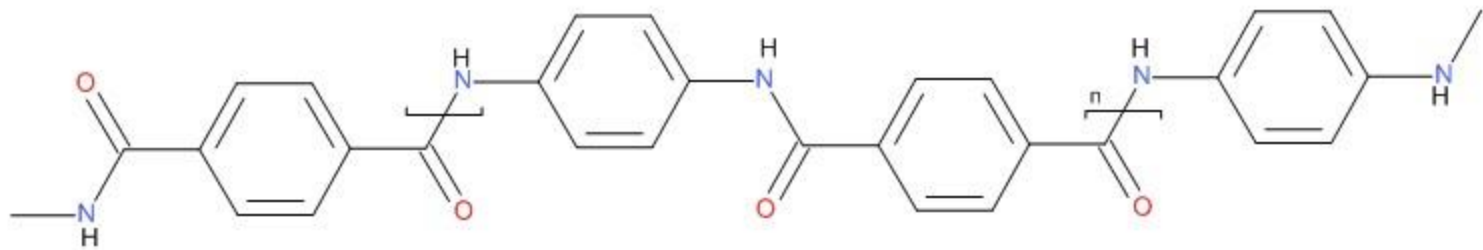
Kevlar

Basic Information

- Kevlar is a high strength material first used in the 1970's.

- It has the iupac name poly(imino-p-phenyleneimino= terephthaloyl)

- Its molecular formula is [-CO-C6H4-CO-NH-C6H4-NH-]n

- It is made up of the monomers 4-phenylene-diamine (*para*-phenylenediamine) and terephthaloyl chloride

- Kevlar's relative molecular mass is 238.241g.

- The glass transition temperature of kevlar is 170 degrees Celsius

- Kevlar is insoluble in water

Chemical Data

- Kevlar is made during a condensation reaction making hydrochloric acid as a by product.

- The production of Kevlar is extremely expensive due to the costs implicated with storing concentrated sulphuric acid.

- Kevlar when spun, has a relative density of 1.44 and has a tensile to weight ration of 5:1

- Kevlar is rarely used outdoors unprotected from sunlight as it suffers from ultra violet light degradation.
- Kevlar is very heat resistant and decomposes above 675K without melting.

Kevlar in Use

Good for its function

- Kevlar's physical hardness and tensile strength both make it very suitable for its function, in bulletproof vests, for example.

- Its hydrogen bonds give strength to the material, creating quite strong intermolecular bonds between kevlar molecules, giving it its strength and durability.

Polymethyl Methacrylate

- PMMA is manufactured from Methyl methacrylate by addition poylmerisation (Free Radical Polymerization).
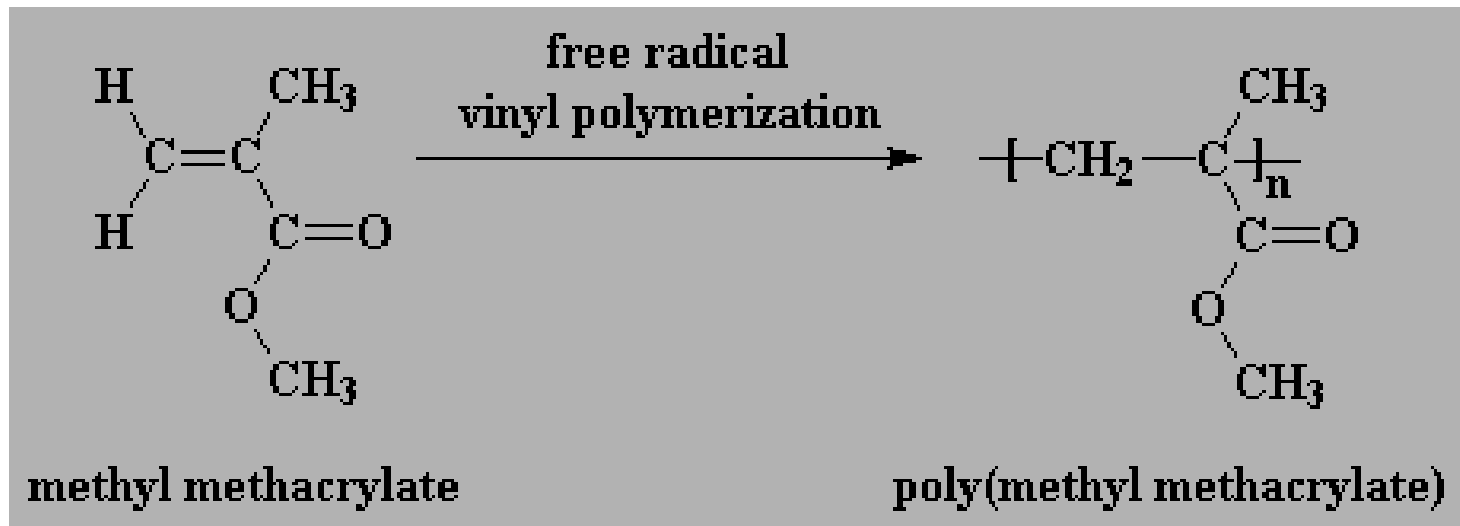
- ## Step 1 : Free radical (R*) plus methyl methacrylate
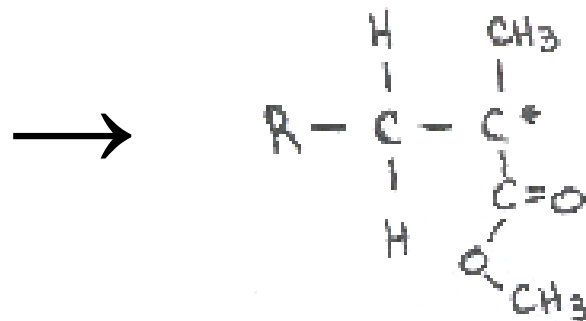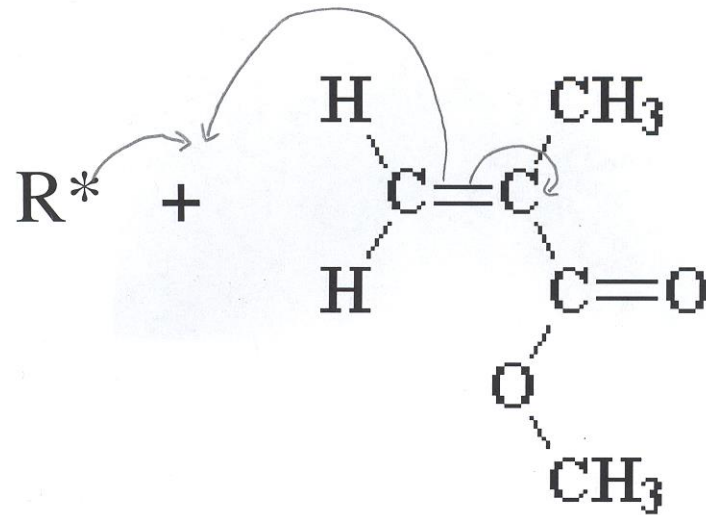
Step 2 : Polymerization - MMA radical plus MMA :repeated many, many times
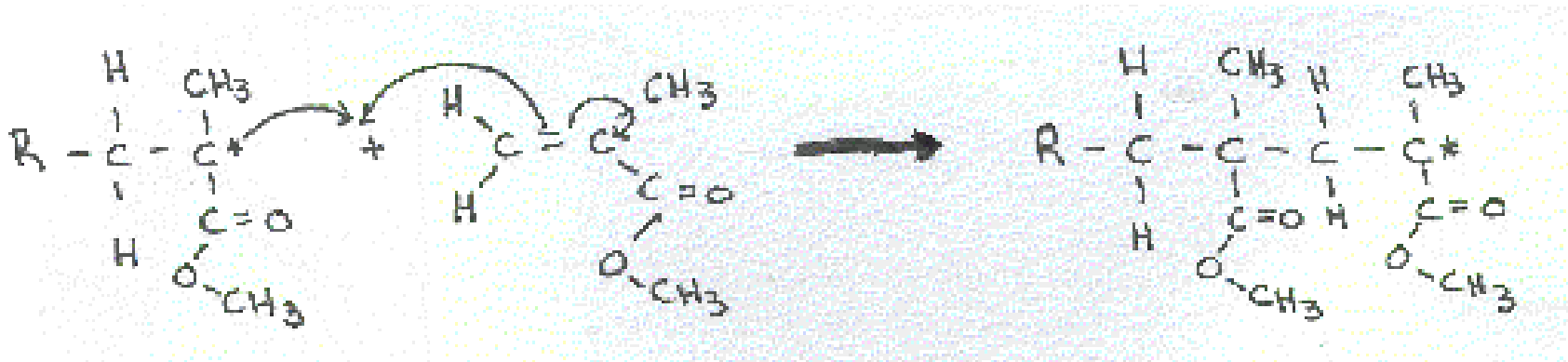
Step 3 : Termination – occurs when two radicals join
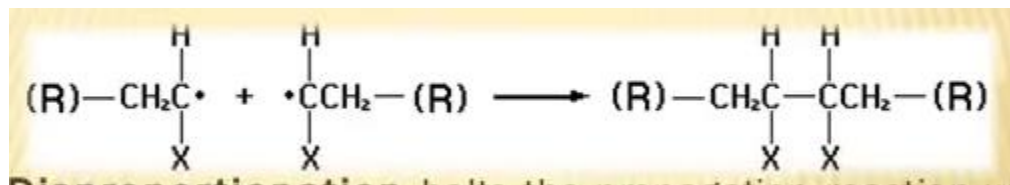
Combination

Disproportination
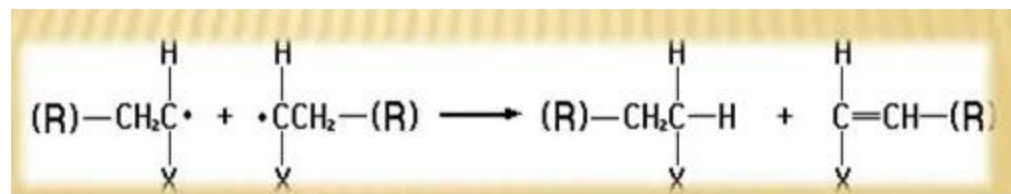
Catalysts

- Multiple catalysts can be used in production of PMMA. Some of these are:
  - Butyl Lithium
  - Highly active catalysts based on group 4 metallocenes
  - An aluminum system supported by salen ligands

Why Use Different Catalysts?

- Different catalysts result in different versions of the polymer
  - Variation is due to the placement of the ester (R-O-R) and methyl (CH$_3$) groups along the polymer backbone

- Isotactic – similar groups on same side of chain
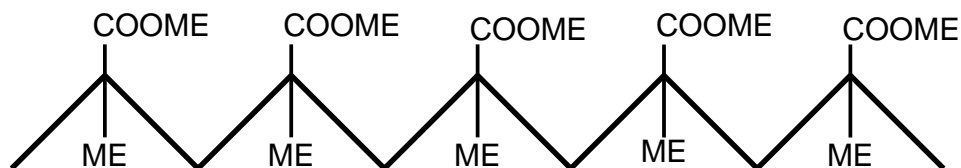
- Syndiotactic – two groups alternate
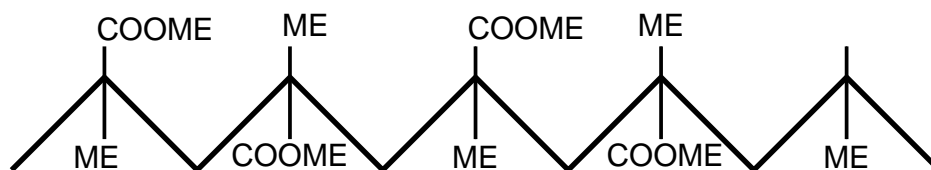
- Atatactic – displays no regular pattern
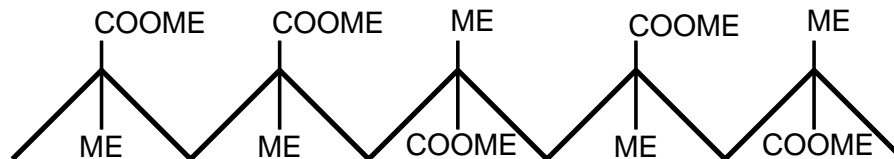
  ❖ Every other carbon in the chain is a steriocenter

Properties of PMMA

- Lighter than glass (density is about half that of glass)
- Shatter proof
- Softer and easier to scratch than glass (scratch resistant coatings may be applied)
- Transmits more light than glass (92% of visible light)
- Does not filter UV light (may be coated with UV film)
- More transparent than glass, so windows can be made thicker

Current uses for PMMA

- Include many uses similar to those for which it was first developed but include many things never imagined by the inventors! A partial list of the uses for PMMA includes:

- Safety glass such as Plexiglass and Lucite – uses range from windows for aquariums and under-water restaurants to safety shields at hockey rinks to skylights in your home to simple paperweights

Medical Uses

- Used as bone cement for use in arthroplastic procedures of the hip, knee, and other joints for the fixation of polymer or metallic prosthetic implants to living bone
- Used in Pacemakers

What are characteristics of biomedical polymers?

Polyvinyl acetate (PVAc)

- Poly(vinyl acetate) was discovered in Germany in 1912 by Fritz Klatte.

- The monomer, vinyl acetate, was first produced on an industrial scale by addition of acetic acid to acetylene with a mercury(I) salt but it is now primarily made by palladium catalyzed oxidative addition of acetic acid to ethylene.

- Polyvinyl acetate is prepared by polymerization of vinyl acetate monomer (free radical vinyl polymerization of the monomer vinyl acetate).

INITIATION

$$R - \overset{\overset{O}{\|}}{C} - O - O - \overset{\overset{O}{\|}}{C} - R \longrightarrow 2\left(R - \overset{\overset{O}{\|}}{C} - O^{\bullet}\right) \longrightarrow 2\,R^{\bullet} + 2CO_2$$

$$R^{\bullet} + \underset{\underset{CH_3}{\overset{O}{|}}}{H_2C = CH} \longrightarrow R - H_2C - \overset{\bullet}{C}H$$

(with the substituent $\begin{array}{c} O \\ | \\ C=O \\ | \\ CH_3 \end{array}$ on the CH groups)

PROPAGATION

$$R - H_2C - \overset{\bullet}{C}H + n\left(H_2C = CH\right) \longrightarrow R\left(H_2C - CH\right)_n H_2C - \overset{\bullet}{C}H$$

(with $\begin{array}{c} O \\ | \\ C=O \\ | \\ CH_3 \end{array}$ substituents)

$$R \left(H_2C - CH \right) CH_2 - \overset{\bullet}{C}H \quad + \quad \overset{\bullet}{C}H - CH_2 \left(CH - CH_2 \right)_n - R$$

with pendant groups:
- O, C=O, CH_3 (on the CH after first bracket)
- O, C=O, CH_3 (on the $\overset{\bullet}{C}H$)
- O, C=O, CH_3 (on the $\overset{\bullet}{C}H$ after +)
- O, C=O, CH_3 (on the CH inside bracket, subscript n)

↓

$$R \left(H_2C - CH \right)_n CH_2 - CH - CH - CH_2 \left(CH - CH_2 \right)_n - R$$

with pendant groups:
- O, C=O, CH_3
- O, C=O, CH_2
- O, C=O, CH_2
- O, C=O, CH_3

POLY VINYL ACETATE

PROPERTIES

✓ Under alkaline conditions, boron compounds such as boric acid or borax cause the polymer to cross-link.

✓ A number of microorganisms can degrade polyvinyl acetate(fungi and algae).

✓ Sets by the removal of water due to evaporation or absorption into a substrate.

✓ Have good weather resistance

✓ Withstand water, grease, oil, and petroleum fuels degradation.

✓ good biodegradation resistance

✓ poor resistance to creep under load.

✓ Softens at 30-45C

✓ Soluble in benzene, chloroform, methanol, acetone, butyl acetate

✓ Insoluble in ligroin, diethyl ether, butanol, turpentine, water, oils

✓ Can absorb 3-5% water when immersed for 16 hours at 60 C.

✓ Burns with a dark yellow flame that smells of acetic acid.

✓ Combustible.

Uses

- PVA water-based emulsions have been used as latex house paints.
- Making commonly used household white glues.
- Making wood glue.
- Makin paper glue.
- Adhesives.
- Glues for porous material.
- Used as a primer for drywall and other substrates.
- As a mortar additive.

PolyLactic acid (Bio-Degradable Polymer)

Lactic Acid   cyclic lactide monomer   Poly (Lactic Acid)
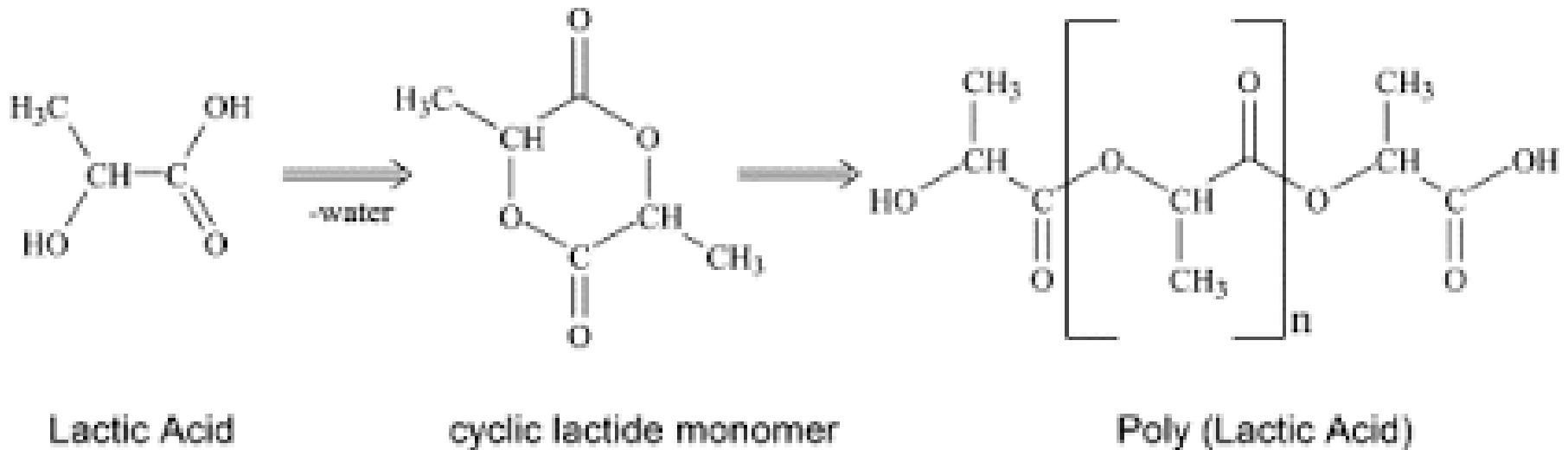
Condensation mechanism- Removal of water molecule

Polylactic acid, **PLA** is a thermoplastic polyester with backbone formula $(C_3H_4O_2)_n$ or $[-C(CH_3)HC(=O)O-]_n$, formally obtained by condensation of lactic acid $C(CH_3)(OH)HCOOH$ with loss of water. It can also be prepared by ring-opening polymerization of lactide $[-C(CH_3)HC(=O)O-]_2$, the cyclic dimer of the basic repeating unit.

The degree of crystallinity, and hence many important properties, is largely controlled by the ratio of D to L enantiomers used.

PLA has become a popular material due to it being economically produced from renewable resources. The monomer is typically made from fermented plant starch such as from corn, cassava, sugarcane or sugar beet pulp.

In 2010, PLA had the second highest consumption volume of any bioplastic of the world. Its widespread application has been hindered by numerous physical and processing shortcomings. PLA is the most widely used plastic filament material in 3D printing.

Properties-

PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer with a glass transition 60–65 °C, a melting temperature 130-180 °C, and a Young's modulus 2.7–16 GPa.

Heat-resistant PLA can withstand temperatures of 110 °C.

Several technologies such as annealing, adding nucleating agents, forming composites with fibers or nano-particles, chain extending and introducing crosslink structures have been used to enhance the mechanical properties of PLA polymers. Polylactic acid can be processed like most thermoplastics into fiber and film.

The high surface energy of PLA results in good printability, making it widely used in 3D printing. PLA is used as a feedstock material in desktop fused filament fabrication by 3D printers, such as RepRap printers. PLA objects can be fabricated by 3D printing, casting, injection moulding, extrusion, machining, and solvent welding.

PLA is soluble in a range of organic solvents like ethyl acetate. PLA is also soluble in hot benzene, tetrahydrofuran, and dioxane.

PLA can be solvent welded using dichloromethane. Acetone also softens the surface of PLA, making it sticky without dissolving it, for welding to another PLA surface.

Applications-

PLA is used in disposable tableware, cutlery, housings for kitchen appliances and electronics such as laptops and handheld devices, and microwavable trays. (However, PLA is not suitable for microwavable containers because of its low glass transition temperature.

It is used for compost bags, food packaging and loose-fill packaging material that is cast, injection molded, or spun.

In the form of a film, it shrinks upon heating, allowing it to be used in shrink tunnels.

In the form of fibers, it is used for monofilament fishing line and netting.

In the form of non-woven fabrics, it is used for upholstery, disposable garments, awnings, feminine hygiene products, and diapers.

PLA has applications in engineering plastics, where the stereocomplex is blended with a rubber-like polymer such as ABS. Such blends have good form stability and visual transparency, making them useful in low-end packaging applications.

PLA is used for automotive parts such as floor mats, panels, and covers.

PLA is used for vegetation and weed prevention. It is used for sandbags, planting pots, binding tape and ropes.

Applications in the field of Medicine-

PLA can degrade into innocuous lactic acid, so it is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh.

It breaks down inside the body within 6 months to 2 years. This gradual degradation is desirable for a support structure, because it gradually transfers the load to the body (e.g. to the bone) as that area heals. PLA has high strength characteristics.

Thanks to its bio-compatibility and biodegradability, PLA has also found ample interest as a polymeric scaffold for drug delivery purposes.

The composite blend of various PLA with tricalcium phosphate (TCP) is used as scaffolds for bone engineering.

Poly-L-lactic acid (PLLA) is the main ingredient in Sculptra, a facial volume enhancer used for treating lipoatrophy of the cheeks.

PLLA is used to stimulate collagen synthesis in fibroblasts via foreign body reaction in the presence of macrophages. Macrophages act as a stimulant in secretion of cytokines and mediators such as TGF-β, which stimulate the fibroblast to secrete collagen into the surrounding tissue. Therefore, PLLA has potential applications in the dermatological studies

Degradation-

PLA is degraded abiotically by three mechanisms:[42]

1.Hydrolysis: The ester groups of the main chain are cleaved, thus reducing molecular weight.

2.Thermal degradation: A complex phenomenon leading to the appearance of different compounds such as lighter molecules and linear and cyclic oligomers with different *Mw*, and lactide.

3.Photodegradation: UV radiation induces degradation. This is a factor mainly where PLA is exposed to sunlight in its applications in plasticulture, packaging containers and films.

PLA is effectively digested in hotter industrial composts, usually degrading best at temperatures of over 60°C.

PLA samples of various molecular weights were degraded into methyl lactate (a green solvent) by using a metal complex catalyst.

PLA can also be degraded by some bacteria, such as *Amycolatopsis* and *Saccharothrix*. A purified protease from *Amycolatopsis* sp., PLA depolymerase, can also degrade PLA. Enzymes such as pronase and most effectively proteinase K from *Tritirachium album* degrade PLA.

Four possible end-of-life scenarios are the most common:
Recycling: which can be either chemical or mechanical. Currently, the SPI resin identification code 7 ("others") is applicable for PLA.

Composting: PLA is biodegradable under industrial composting conditions, starting with chemical hydrolysis process, followed by microbial digestion, to ultimately degrade the PLA. Under industrial composting conditions (58 °C), PLA can partly (about half) decompose into water and carbon dioxide in 60 days, after which the remainder decomposes much more slowly.

Incineration: PLA can be incinerated without producing chlorine-containing chemicals or heavy metals because it contains only carbon, oxygen, and hydrogen atoms. Since it does not contain chlorine it does not produce dioxins during incineration.

Landfill: the least preferable option is landfilling because PLA degrades very slowly in ambient temperatures, often as slowly as other plastics.

PolyDimethylsiloxane (Inorganic Polymer)
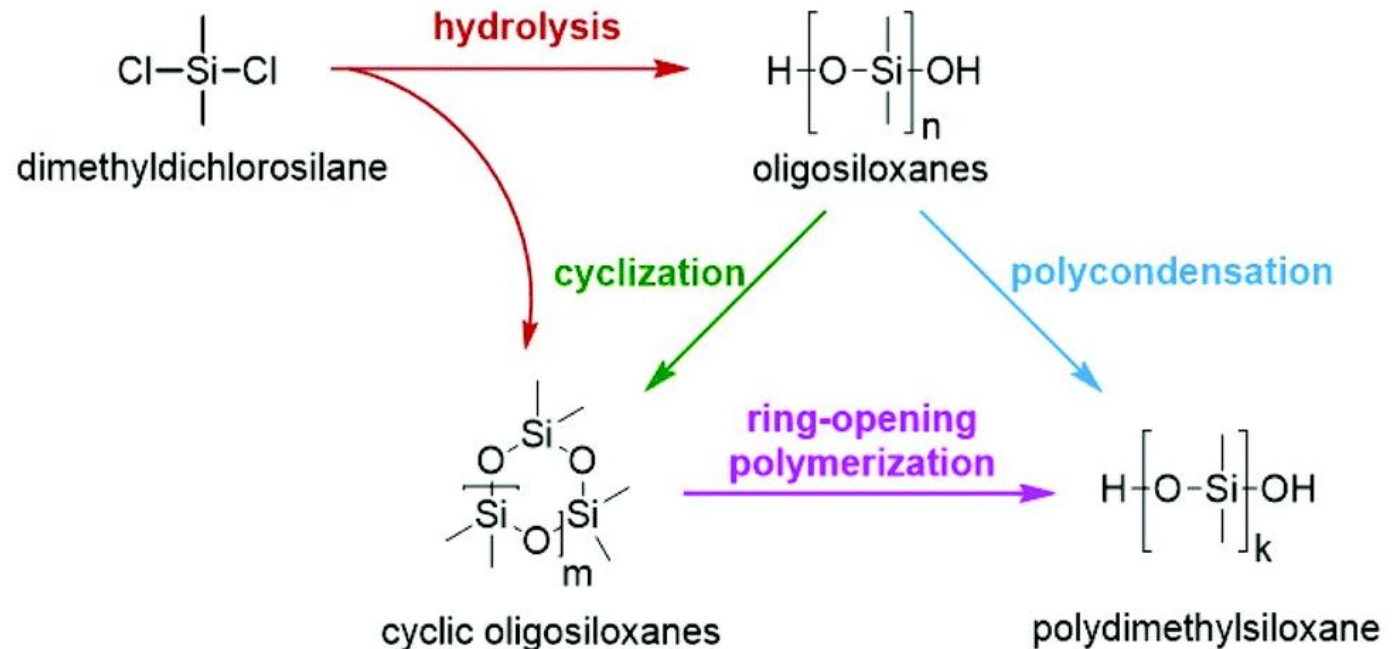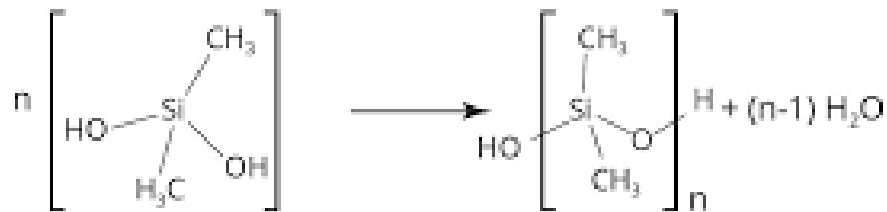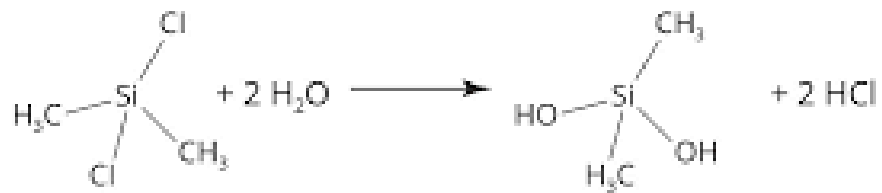
Polydimethylsiloxane (**PDMS**), also known as **dimethylpolysiloxane** or **dimethicone**, belongs to a group of polymeric organosilicon compounds that are commonly referred to as silicones.

It can be prepared by polycondensation.

Well-defined PDMS with a low polydispersity index and high homogeneity is produced by controlled anionic ring-opening polymerization of hexamethylcyclotrisiloxane. Using this methodology it is possible to synthesize linear block copolymers, heteroarm star-shaped block copolymers and many other macromolecular architectures.

PDMS is the most widely used silicon-based organic polymer, as its versatility and properties lead to many applications.

It is particularly known for its unusual rheological (or flow) properties. PDMS is optically clear and, in general, inert, non-toxic, and non-flammable.

Properties-

PDMS is viscoelastic.

this unique polymer is relatively easy to tune.

  PDMS can easily be integrated into a variety of microfluidic and microelectromechanical systems.

the cross-linked cured version of PDMS resembles rubber in a solidified form.

PDMS has a low elastic modulus.

The shear modulus of PDMS varies in the range of 100 kPa to 3 MPa. The loss tangent is very low (tan $\delta \ll 0.001$).

PDMS is hydrophobic.

Solid PDMS samples will not allow aqueous solvents to infiltrate and swell the material.

most organic solvents will diffuse into the material and cause it to swell.

  Diisopropylamine swells PDMS to the greatest extent; solvents such as chloroform, ether, and THF swell the material to a large extent. Solvents such as acetone, 1-propanol, and pyridine swell the material to a small extent. Alcohols and polar solvents such as methanol, glycerol and water do not swell the material appreciably.

Applications-

PDMS is a common [surfactant](#) and is a component of [defoamers](#). PDMS, in a modified form, is used as an [herbicide](#) [penetrant](#) and is a critical ingredient in water-repelling coatings, such as [Rain-X](#).

Dimethicone is used in the active silicone fluid in automotive viscous limited slip differentials and couplings.

PDMS is commonly used as a stamp resin in the procedure of [soft lithography](#), for flow delivery in [microfluidics](#) chips.

it possesses superior optical properties, allowing for minimal background and autofluorescence during for fluorescent imaging.

researchers can utilize various surface chemistry techniques of PDMS for different functions creating unique lab-on-a-chip devices for rapid parallel testing.

PDMS is being used in the making of synthetic [gecko adhesion](#) dry adhesive materials.

Medicine and cosmetics

Used in over-the-counter drugs as an antifoaming agent and carminative.[25][26] It has also been at least proposed for use in contact lenses.

Silicone implants used for body enhancement are made out of a PDMS elastomer shell

PDMS is useful as a lice or flea treatment because of its ability to trap insects. It also works as a moisturizer that is lighter and more breathable than typical oils.

PDMS compounds such as amodimethicone, are effective conditioners and act as surfactants.

Used in contact lenses.

PDMS is added to many cooking oils as an antifoaming agent to prevent oil splatter during the cooking process. As a result of this, PDMS can be found in trace quantities in many fast food items such as McDonald's Chicken McNuggets, french fries, hash browns, milkshakes and smoothiesand Wendy's french fries.

Polymers In Medicine

Cellophane
PGA, PLA, PLGA
Polydimethylsiloxane
Polyethylene and PMMA
Polytetrafluoroethylene
Polyurethane

What are they?

Substances other than food or drugs contained in therapeutic or diagnostic systems that are in contact with tissue or biological fluids.

Why use Biomaterials?

Improve patient's quality of life by replacing a defective body part with a substitute.

Physicians were limited to use off-the shelf supplies.

Novel biodegradable polymers and modified natural substances.

Applications of Biomaterials

Polymer	Applications	Polymer	Applications
PDMS	Catheters, heart Valves	Polytetrafluoroe thylene	Heart valves Vascular grafts Nerve repair
Polyurethane	ventricular assist Devices	Polyethylene	Catheters, hip prostheses
PGA, PLA, And PLGA	Drug delivery, devices	Polymethylmetha crylate (PMMA)	Fracture fixation
		Cellophane	Dialysis membranes

Polylactic acid, Polyglycolic cid

PGA   PLA
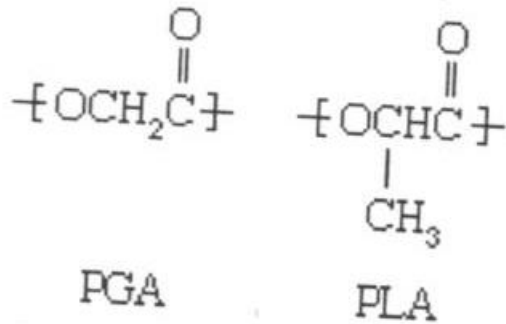
- Amorphous forms used in drug delivery systems
- Crystalline forms good for scaffolding, or sutures; stents, plastic surgery, plates rods, pins, screws.
- Two essentials in scaffolding: high surface to volume ratio, highly porous

  -Allows cells to easily proliferate
  for setup of pathways

  -Setup of pathways for nutrients

Polydimethylsiloxane

$$\text{---}\left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si---O} \\ | \\ \text{CH}_3 \end{array}\right]_n\text{---}$$
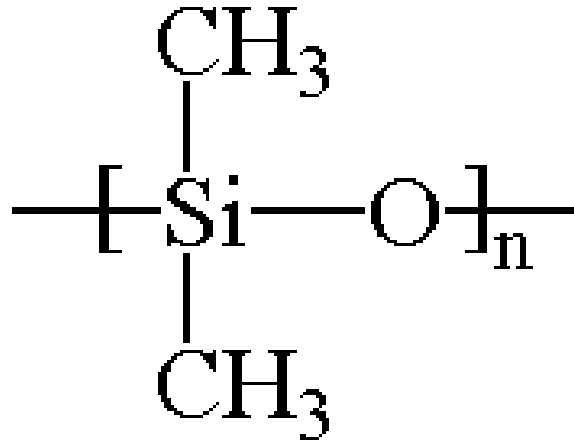
- "Silicon"

- Lubricants and Foaming agents

- Pacemakers and Vaccine Delivery systems

- Used in treatment of prostate carcinoma
- Small biodegradable pellets   (188 m) injected into area of body where needed; heart valves, blood filters, vascular tubing, artificial heart.
- Smaller doses, less toxic effects for patient

PMMA

- Thermoplastics, exhibit moderate to high tensile strength with moderate elongation
- Used for Hip replacement and Fracture Fixation
- Annual procedures approaching 5 Million
- Metal alternatives have corrosive problems

PMMA disc over femoral window during the molding process

PMMA template after polymerization, showing molded plug

Conducting polymers

Intrinsically conducting polymers (ICPs) belong to a class of organic materials with unique electronic properties such as electric conductivity, electrochromism, and electroactivity. Conjugated electrons in the backbone of their macromolecules are responsible for these properties. Due to their high electrical properties, ICPs are intensively investigated for application in electronics, microelectronics, optoelectronics mainly for areas in aerospace and automobile industries. Among the most promising applications of the ICPs are corrosion protection, solid-state charge storage devices, electromagnetic screens, antistatic coatings and gas separation coatings. However, poor mechanical properties, environmental sensitivity, moderate stability of electrical properties with temperature significantly limit the industrial applicability of ICPs.

Polyacetylene
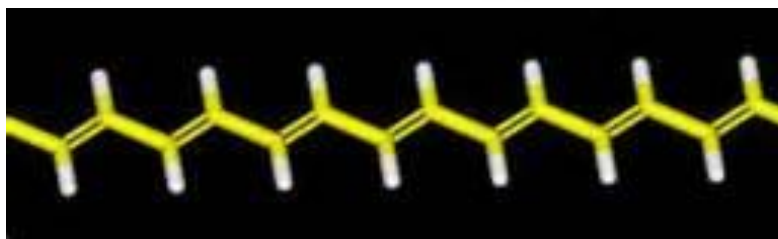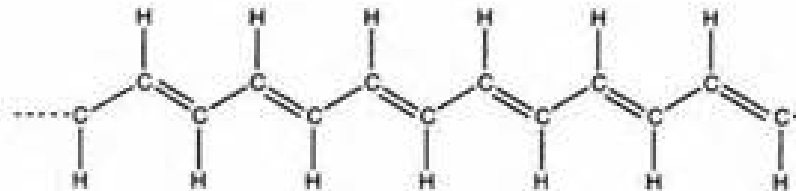
Few Common Conducting Polymers
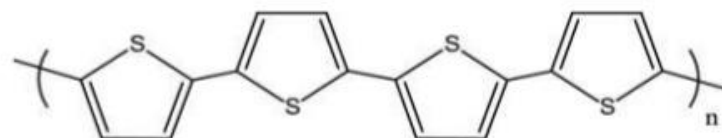
polythiophene
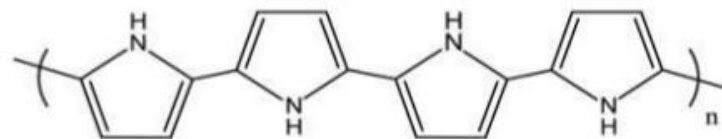
polypyrrole
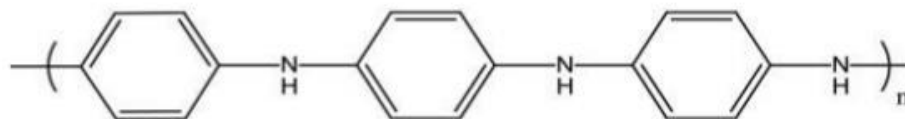
polyaniline
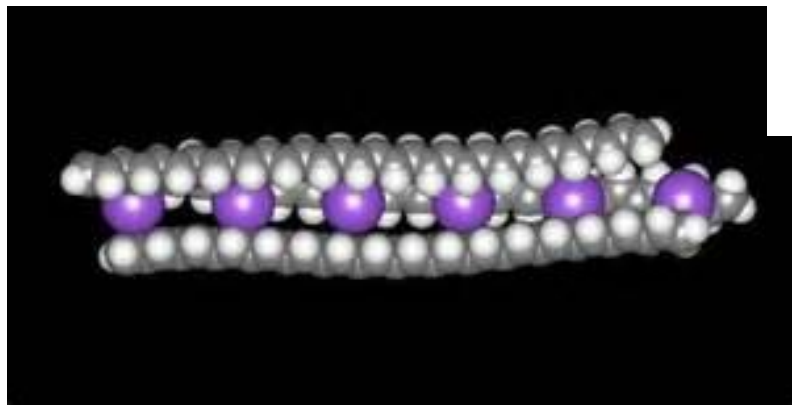
(DCP) Doped conducting polymer

While the addition of a donor or an acceptor molecule to the polymer is called "doping ", the reaction that takes place is actually a redox reaction. • The first step is the formation of a cation (or anion) radical, which is called a soliton or a polaron.

Pn ⇔ [Pn + A −] (reduction oxidation)

• As synthesized conductive polymers exhibit very low conductivities. It is not until an electron is removed from the valence band (p-doping) or added to the conduction band (n-doping, which is far less common) does a conducting polymer become highly conductive. • Doping (p or n) generates charge carriers which move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity.

(i) Oxidation process (p–doping):

$$(C_2H_2)_n + FeCl_3 \rightarrow (C_2H_2^+)_n.FeCl_4 + FeCl_2$$

Polyacetylene   lewis acid   +vely charged backbone

$$2(C_2H_2)_n + 3I_2 \rightarrow 2[(C_2H_2^+)_nI_3^-]$$
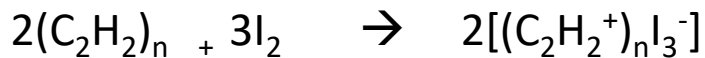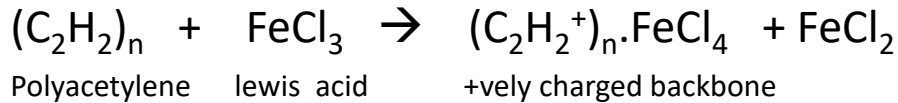
(i) Reduction process (n-doping):

$$(C_2H_2)_n + C_{10}H_7NH_2 \rightarrow [(C_2H_2^-)_nNH^+] + C_{10}H_8$$

Polyacetylene   Naphthylamine   reduction   -vly charged backbone   naphthalene
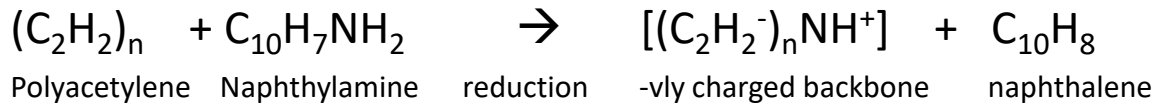
The above reactions are most likely to occur saturated polym electrons, as they can be very easily removed from the polymeric chains to form polyion therefore, these are the types of polymers, which as
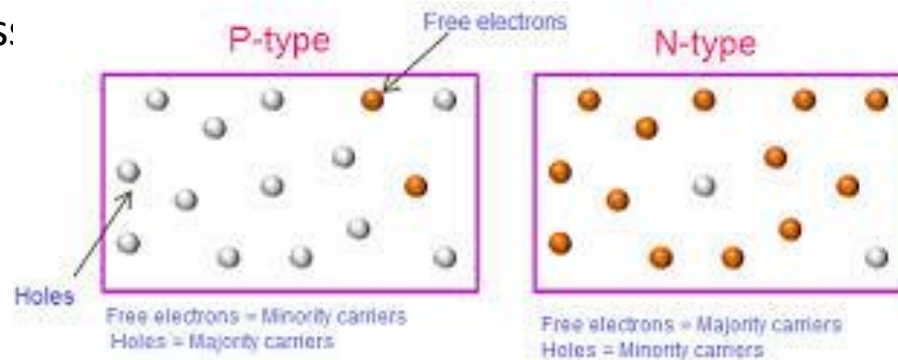
- *ECP*

➢ One type of extrinsically conducting polymer consists of a matrix of poly(ethene) with a percentage of conducting carbon black (a form of powdered graphite) incorporated (filled) in it. If the carbon black particles are close enough to be in contact with one another, the material conducts. If the particles are not in contact, it is an insulator. This means that the degree of electrical conduction depends on temperature. At high temperature, the poly(ethene) matrix expands and pulls the particles of carbon black away from each other, decreasing the conductivity. At lower temperatures the poly(ethene) contracts, the carbon black particles are closer and the material conducts well. This temperature dependence of conductivity leads to the use of this material in self-regulating heater cable and PolySwitch* re-settable circuit protection devices.
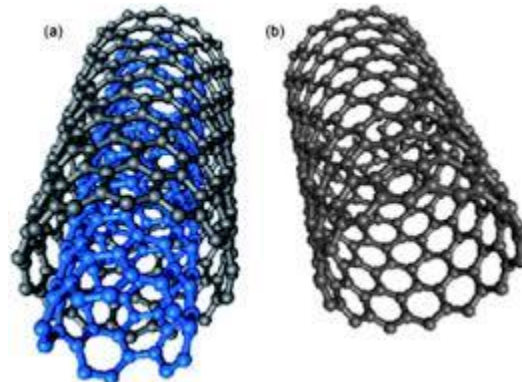
➢ Another type includes the blends
Extrinsically conductive polymers can involve a blend of conductive and nonconductive polymers.

- **Co-ordinate Conjugate Polymers (CCP)**-

- A **coordination** **polymer** is an [inorganic](#) or [organometallic](#) [polymer](#) structure containing metal cation centers linked by organic [ligands](#). More formally a coordination polymer is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.

- It can also be described as a polymer whose repeat units are [coordination complexes](#). Coordination polymers contain the subclass coordination networks that are coordination compounds extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions. A subclass of these are the [metal-organic frameworks](#), or MOFs, that are coordination networks with organic ligands containing potential voids.

Coordination polymers are relevant to many fields such as organic and inorganic chemistry, biochemistry, materials science, electrochemistry, and pharmacology, having many potential applications. This interdisciplinary nature has led to extensive study in the past few decades.

Coordination polymers can be classified in a number of different ways according to their structure and composition. One important classification is referred to as dimensionality.

One Dimension

Two Dimensions
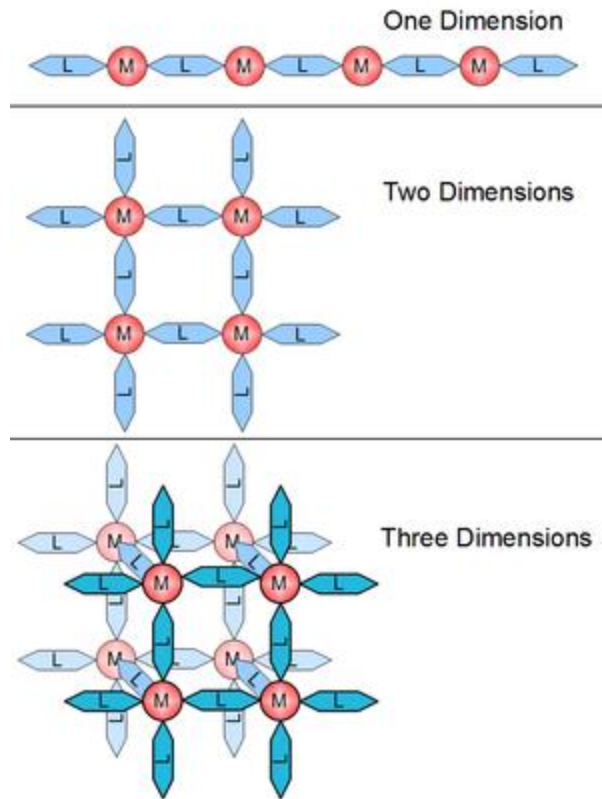
Three Dimensions

A structure can be determined to be one-, two- or three-dimensional, depending on the number of directions in space the array extends in. A one-dimensional structure extends in a straight line (along the x axis); a two-dimensional structure extends in a plane (two directions, x and y axes); and a three-dimensional structure extends in all three directions (x, y, and z axes). This is depicted in Figure

In most coordination polymers, a [ligand](atom or group of atoms) will formally donate a [lone pair] of [electrons] to a metal [cation] and form a [coordination complex] via a Lewis acid/ base relationship ([Lewis acids and bases]). Coordination polymers are formed when a ligand has the ability to form multiple coordination bonds and act as a bridge between multiple metal centers.

Polymers in industry

Type	Abbreviation	Typical Uses
Phenol-formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder
Urea-formaldehyde	UF	Similar to PF polymer; also treatment of textiles, coatings
Unsaturated polyester	UP	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tanks, etc., business equipment
Epoxy	-	Protective coatings, adhesives, electrical and electronics applications, industrial flooring highway paving materials, composites
Melamine-formaldehyde	MF	Similar to UF polymers; decorative panels, counter and table tops, dinnerware

Glass transition temperature

Collections of molecules can exist in three possible physical states: solid, liquid and gas. In polymeric materials, things are not so straightforward. For example, most polymers will decompose before they boil, and cross-linked polymers decompose before they melt. For many polymers the transition between the solid and liquid states is rather diffuse and difficult to pinpoint. Amorphous polymers are viscous liquids when they are held at temperatures above their glass transition temperature, T_g. Below T_g, the material is solid, yet has no long-range molecular order and so is non-crystalline. In other words, the material is an amorphous solid, or a glass. The glass transition temperature is different for each polymer, but many polymers are above T_g at room temperature. In many cases the polymers are at least partially crystalline at room temperature and the temperature at which the crystals melt (T_m) is above room temperature.

When an amorphous polymer is heated, the temperature at which the polymer structure turns "viscous liquid or rubbery" is called the Glass Transition Temperature, Tg. It is also defined as a temperature at which amorphous polymer takes on characteristic glassy-state properties like brittleness, **stiffness** and rigidity (upon cooling).

This temperature (measured in °C or °F) depends on the chemical structure of the polymer and can therefore be used to identify polymers.

Amorphous polymers only exhibit a Tg.
Crystalline polymers exhibit a Tm (melt temperature) and typically a Tg since there is usually an amorphous portion as well ("semi"-crystalline).

The value of Tg depends on the mobility of the polymer chain, and for most synthetic polymers lies between 170 K to 500 K.

The transition from the glass to the rubber-like state is an important feature of polymer behavior, marking a region of dramatic changes in the physical properties, such as **hardness** and elasticity.

The graph below shows how some polymers are above Tg but below Tm at room temperature. Such polymers are rubbers (so long as they are largely amorphous) at room temperature. However, the polymer may flow like a liquid over long time periods as its amorphous component relaxes under the polymer's weight.
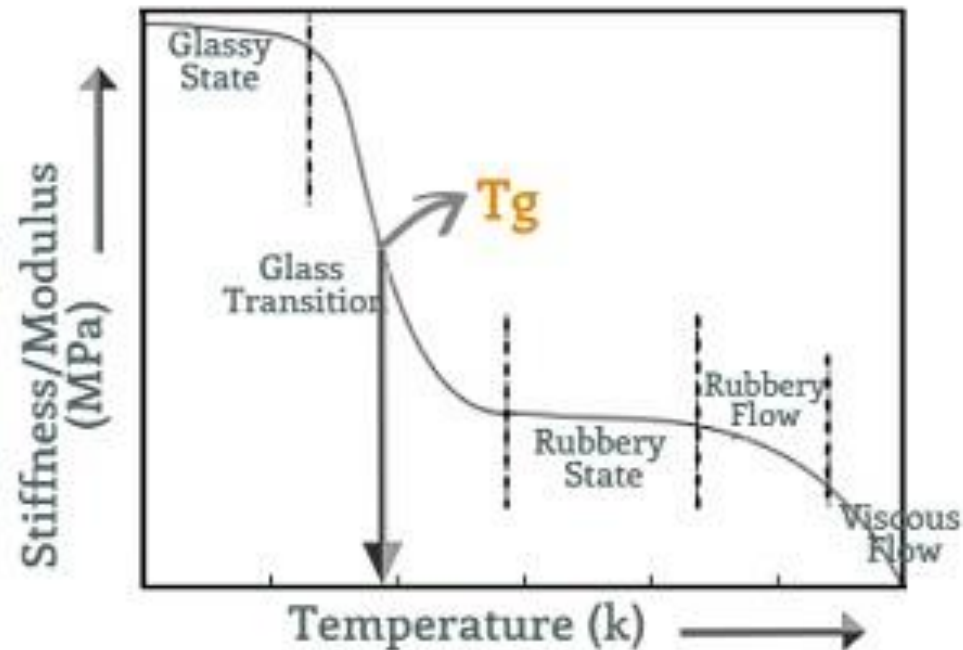
At Tg, changes in hardness, volume, percent **elongation to break** and **Young's modulus** of solids are mainly seen.

Some polymers are used below their Tg (in glassy state) like polystyrene, **poly(methyl methacrylate)** etc., which are hard and brittle. Their Tgs are higher than room temperature.

Some polymers are used above their Tg (in rubbery state), for example, rubber elastomers like polyisoprene, polyisobutylene. They are soft and flexible in nature; their Tgs are less than room temperature.

Applications include:
Identifying the Tg of polymers is often used for quality control and research and development. Also, it is an important tool used to **modify physical properties of polymer molecules.**

Further, improvement in handling characters, solubility and reproducibility in dissolution of solids can be achieved by increasing the Tg of solids.

The most usual test **method to determine Glass Transition Temperature** of plastics is **ASTM E1356**. This test method covers the assignment of the glass transition temperatures of materials using **differential scanning calorimetry** or **differential thermal analysis**.

This test method is applicable to amorphous materials or to partially crystalline materials containing amorphous regions, that are stable and do not undergo decomposition or sublimation in the glass transition region.

Both methods, DTA and DSC, yield peaks relating to endothermic and exothermic transitions with thermal input and show phase changes or occurrence of reactions.

In DTA, the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.

In DSC, the difference in heat flow to a sample and to a reference is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.
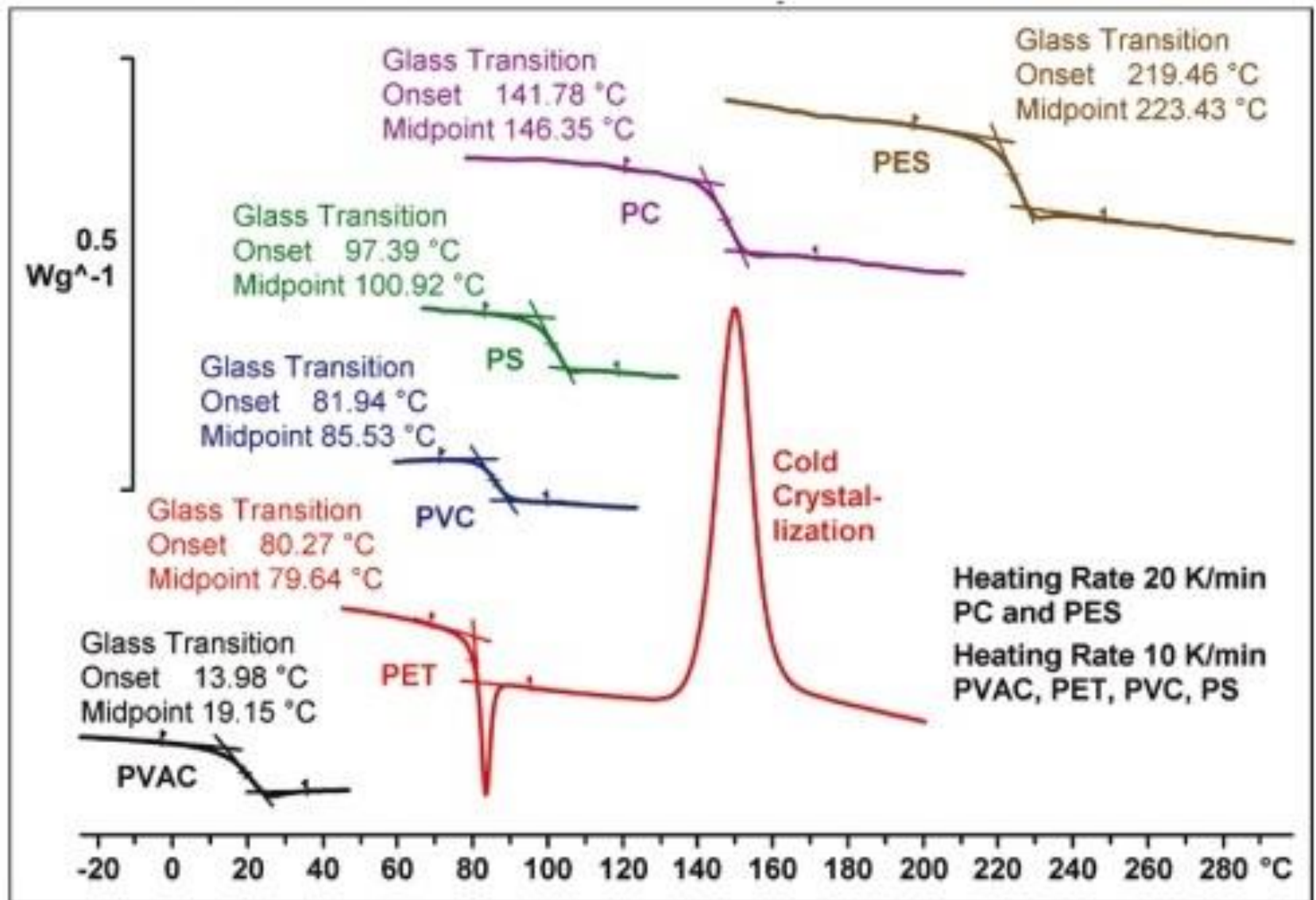
The operating temperature of polymers is defined by transition temperatures

At the molecular level, at Tg, the chains in amorphous (i.e., disordered) regions of the polymer gain enough thermal energy to begin sliding past one another at a noticeable rate. The temperature where entire chain movement occurs is called the melting point (Tm) and is greater than the Tg

Glass Transition is a property of the amorphous region while melting is the property of crystalline region

Below Tg, there exists disordered amorphous solid where chain motion is frozen and molecules start wiggling around above Tg. The more immobile the chain, the higher the value of Tg.

While, below Tm it is an ordered crystalline solid which becomes disordered melt above Tm.

The operating temperature of polymers is defined by transition temperatures

The glass transition of a polymer is related to the thermal energy required to allow changes in the conformation of the molecules at a microscopic level, and above Tg there is sufficient thermal energy for these changes to occur. However, the transition is not a sharp one, nor is it thermodynamically well defined. It is therefore different from melting a crystal. A distinct change from rubbery (above Tg) to glassy (below Tg) behaviour is readily observable in a wide range of polymers over a relatively narrow temperature range. It is necessary to explore the behaviour of polymers around the glass transition temperature and the effects of strain rate, cooling or heating rate and other factors affecting the glass transition temperature.

The temperature above which the torsion angles can change is called the glass transition temperature.

Factors affecting Tg:

- Chain Length- Each chain end has some free volume associated with it. A polymer with shorter chains will have more chain ends per unit volume, so there will be more free volume. Hence Tg' for shorter chains will be lower than Tg for long chains.

- Chain Flexibility- A polymer with a backbone that exhibits higher flexibility will have a lower Tg. This is because the activation energy for conformational changes is lower. Therefore, conformational changes can take place at lower temperatures.

- Side Groups- Larger side groups can hinder bond rotation more than smaller ones, and therefore cause an increase in Tg. Polar groups such as Cl, CN or OH have the strongest effect.

- Branching Polymers- with more branching have more chain ends, so have more free volume, which reduces Tg, but the branches also hinder rotation, like large side groups, which increases Tg. Which of these effects is greater depends on the polymer in question, but Tg may rise or fall.
- Cross-linking- reduces chain mobility, so Tg will be increased. It also affects the macroscopic viscosity of the polymer, since if there are cross-links between the chains, then they are fixed relative to each other, so will not be able to slide past each other.
- Plasticisers- Small molecules, typically esters, added to the polymer increase the chain mobility by spacing out the chains, and so reduce Tg.

- Time Effects- The properties of an amorphous polymer above Tg can change with time. At very short loading times the polymer can still be glassy because there is not time for the chains to move. At intermediate times the polymer may be rubbery- i.e. chains can uncoil and recoil between entanglements, which remain stable. At very long times, the chains can move past each other permanently, and so the polymer behaves as a viscous liquid.

Polymers-Tg

Dry Nylon-6 has a glass transition temperature of 47 °C. Nylon-6,6 in the dry state has a glass transition temperature of about 70 °C. Whereas polyethene has a glass transition range of −130 to −80°C.

It must be kept in mind that the above are only mean values, as the glass transition temperature depends on the cooling rate and molecular weight distribution and could be influenced by additives.

Note also that for a semi-crystalline material, such as polyethene that is 60–80% crystalline at room temperature, the quoted glass transition refers to what happens to the amorphous part of the material upon cooling.

Values of T_g and T_m for various polymers
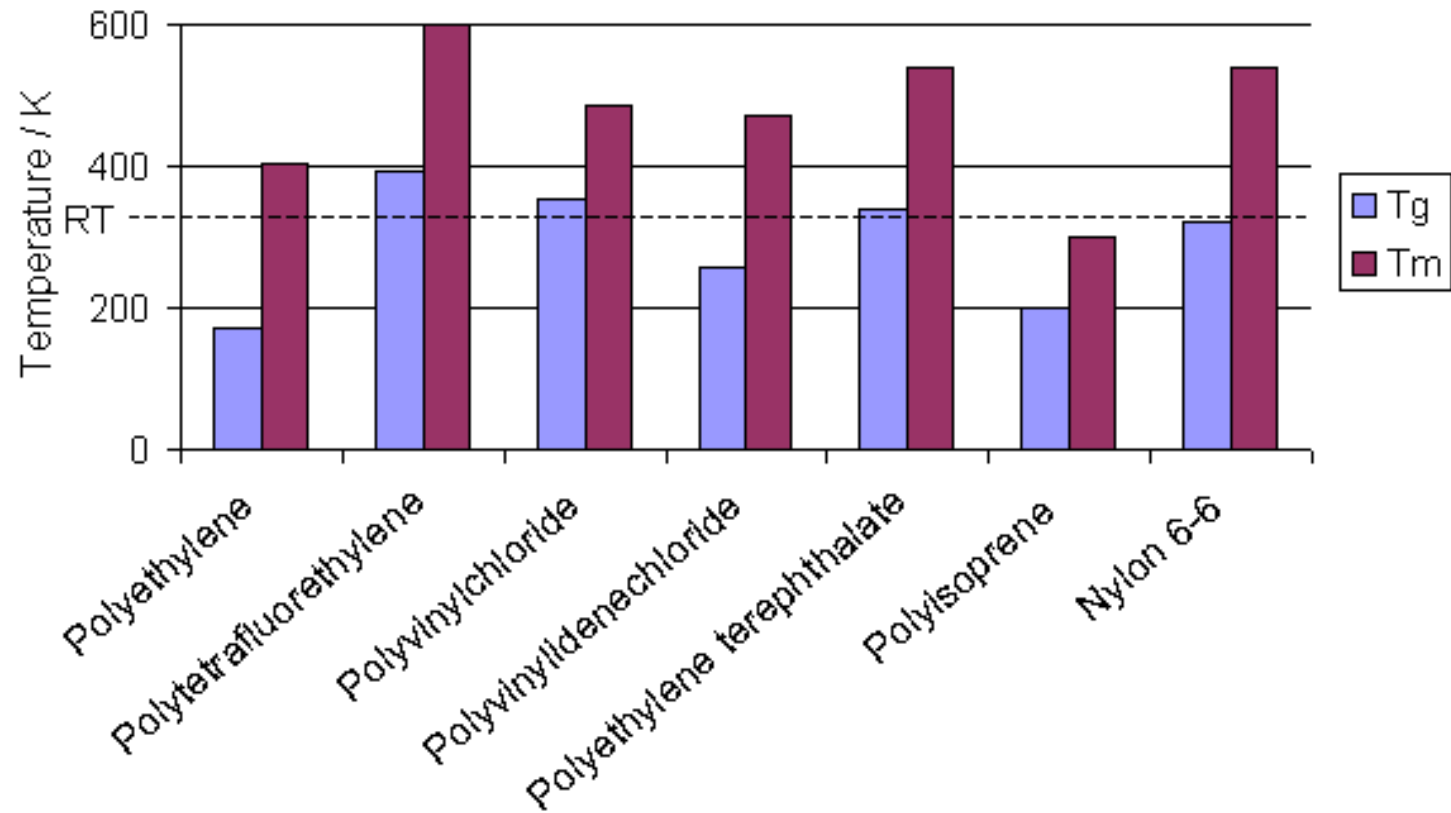
Polymer Molecular weight and its Measurement methods

<u>There are several reasons why we might want to measure polymer average molecular weight and its distribution:</u>

1. The molecular weight and its distribution determine the viscous and elastic properties of the molten polymer. This affects the processibility of the melt and also the behavior of the resulting solid material. *For example*, a resin suitable for extrusion must have a high viscosity at low shear rates so that the extrudate maintains its integrity. To be suitable for injection molding, however, the same resin must have a low viscosity at high shear rates so that the injection pressure not be excessive.

2. The molecular weight of a polymer can determine its applications. *For example*, the resin used for making polycarbonate water bottles differs significantly in molecular weight from the polycarbonate that goes into compact disks.

3. Differences in molecular weight distribution also influence the polymer properties. As a consequence, two chemically similar polymers, processed identically, that have the same molecular weight but different molecular-weight distributions may result in products that show significantly different shrinkages, tensile properties, and failure properties. For this very important reason, it is advantageous to know the molecular weight and molecular-weight distribution of the polymers used.

4. Other situations where the molecular weight and its distribution directly influence results include phase equilibrium and crystallization kinetics.

M.wt Measurement Methods

- Number average M.wt
  - END-GROUP ANALYSIS
  - COLLIGATIVE PROPERTIES
- Weight average M.wt
  - Light Scattering
- Z-average M.wt
  - Ultracentrifugation
- Viscosity average M.wt
  - Viscometry

Gel Permeation Chromatography (GPC)
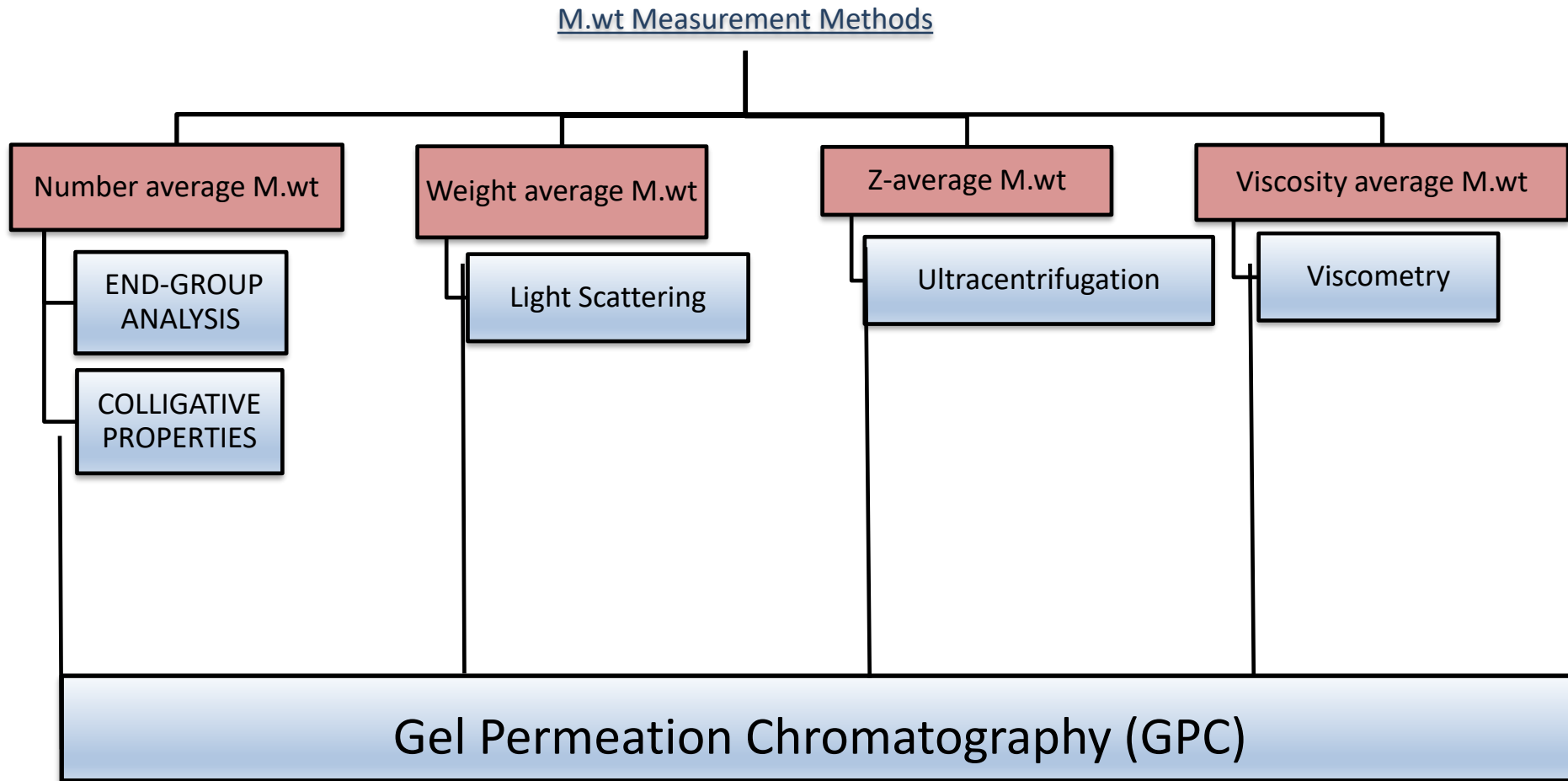
NOTE: The choice of method for polymer molecular weight determination is influenced by factors such as: (i) information required, (ii) operative region, (iii) cost effectiveness, and (iv) experimental conditions and requirements.

Molecular Weight:

Molecular weight of a chemical compound can be defined, simply, as the sum of the atomic weights of each of the atoms in the molecule.

Examples:

Water (H_2O) is 2 H (1g) and one O (16g) = 2*(1) + 1*(16)= 18 g/mol
Methane CH_4 is 1 C (12g) and 4 H (1g)= 1*(12) + 4 *(1) = 16 g/mole
Polyethylene -(C_2H_4)-$_{1000}$ = 2 C (12g) + 4H (1g) = 28g/mole * 1000 = 28,000 g/mole

Average Molecular Weight

Polymers are made up of many molecular weights or a distribution of chain lengths. In other other words, if one takes polyethylene as an example, this polymer may have chains of ethylene (C_2H_4) with different lengths; some longer than others.

Example:

Polyethylene -(C_2H_4)-$_{1000}$ has some chains with 1001 repeating ethylene units, some with 1010 ethylene units, some with 999 repeating units, and some with 990 repeating units. The average number of repeating units or chain length is 1000 repeating ethylene units for a molecular weight of 28*1000 or 28,000 g/mole .

Therefore, polymers must be represented by the value of average molecular weight.

There are four ways to represent the average molecular weight:

(1) *Number-average molecular weight (Mn)* for a discrete distribution of molecular weights is g

$$\bar{M}_n = \frac{\sum_{i=1}^{N} N_i M_i}{\sum_{i=1}^{N} N_i} = \frac{\sum_{i=1}^{N} W_i}{\sum_{i=1}^{N} (W_i / M_i)}$$

where *Ni* indicates the number of moles of molecules having a molecular weight of *Mi and Wi*, is the weight of molecules with molecular weight *Mi. Thus, Wi = Ni Mi*.

The expression for the number-average molecular weight of a continuous distribution function is:

$$\bar{M}_n = \frac{\int_0^\infty N M \, dM}{\int_0^\infty N \, dM} .$$

(2) **Weight-average molecular weight (Mw)** for a discrete distribution of molecular weights is given as:

$$\bar{M}_w = \frac{\sum_{i=1}^{N} N_i M_i^2}{\sum_{i=1}^{N} N_i M_i} = \frac{\sum_{i=1}^{N} W_i M_i}{\sum_{i=1}^{N} W_i}$$

The expression for the weight-average molecular weight of a continuous distribution function is:

$$\bar{M}_w = \frac{\int_0^\infty N M^2 dM}{\int_0^\infty N M dM}.$$

(3) **Z-average molecular weight (Mz)** for a discrete distribution of molecular weights is given as:

$$\bar{M}_z = \frac{\sum_{i=1}^{\infty} N_i M_i^3}{\sum_{i=1}^{\infty} N_i M_i^2} = \frac{\sum_{i=1}^{\infty} w_i M_i^2}{\sum_{i=1}^{\infty} w_i M_i}$$

(4) *Viscosity-average* molecular weight (*M*v) can be obtained, experimentally, from dilute-solution viscometer using Mark-Howink equation. The viscosity-average molecular weight falls between *M*n and *M*w depending upon whether the solvent is a good or poor solvent for the polymer. In the case of a good solvent, *M*v = *M*w .

- Mark-Howink-Sakurada equation:

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

$[\eta]$: intrinsic viscosity
K , a : constant for specific polymer and solvent
$\overline{M}$: average molecular weight

NOTES:

1. A measure of the breadth of the molecular-weight distribution is given by the ratios of molecular-weight averages. For this purpose, the most commonly used ratio is *M*w/*M*n ,called the *polydispersity index* or *PDI*.

$$PDI = \frac{Mw}{Mn} > 1 \; ; \; \text{polymers having PDI = 1 are called monodiseperse polymers}$$

2. Degree of Polymerization (*DP*): is the number of monomeric units in a macromolecule or **polymer** or oligomer (consists of a few repeating units Or *DP* is the number of repeat units.

$$DP_w = \frac{Mw}{Mo} \quad , DP_n = \frac{Mn}{Mo} \; ; \text{where } M_0 \text{ is the monomer molecular weight.}$$

Viscometry

A method that is widely use for routine molecular-weight determination is based on the determination of intrinsic viscosity, η, of a polymer in solution through measurements of solution viscosity.

The fundamental relationship between η and molecular-weight is given in Mark-Howink eq

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

$[\eta]$: intrinsic viscosity

K , a : constant for specific polymer and solvent

$\overline{M}$: average molecular weight

It is clear in the above equation that the value of intrinsic viscosity of the diluted polymer is needed to determine the molecular weight. To find the intrinsic viscosity, a series of experimental measurements and calculations have to be made. These steps are as follows:

1. The relative viscosity can be measured experimentally using a suitable viscometer:

Relative viscosity : $\eta_{rel} = \dfrac{\eta}{\eta_o} = \dfrac{t}{t_o}$

η : solution viscosity

η_o: solvent viscosity

t : flow time of solution

t_o: flow time of solvent

2. The intrinsic viscosity can be calculated as shown below:

Relative viscosity

$$\eta_{rel} = \frac{t}{t_0}$$

Inherent viscosity

$$\eta_{inh} = ln\frac{\frac{t}{t_0}}{c} = ln\frac{\eta_{rel}}{c}$$

Specific viscosity

$$\eta_{sp} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$

Intrinsic viscosity

$$[\eta] = \lim_{c \to 0} (\eta_{red})$$

$$[\eta]_K = \lim_{c \to 0} (\eta_{inh})$$

Reduced viscosity

$$\eta_{red} = \frac{t - t_0}{t_0 * c} = \frac{\eta_{sp}}{c}$$

Red arrows: Parameter used for intrinsic viscosity determination for multi concentration measurements

Grey arrows: Parameter used for intrinsic viscosity determination for single concentration measurements
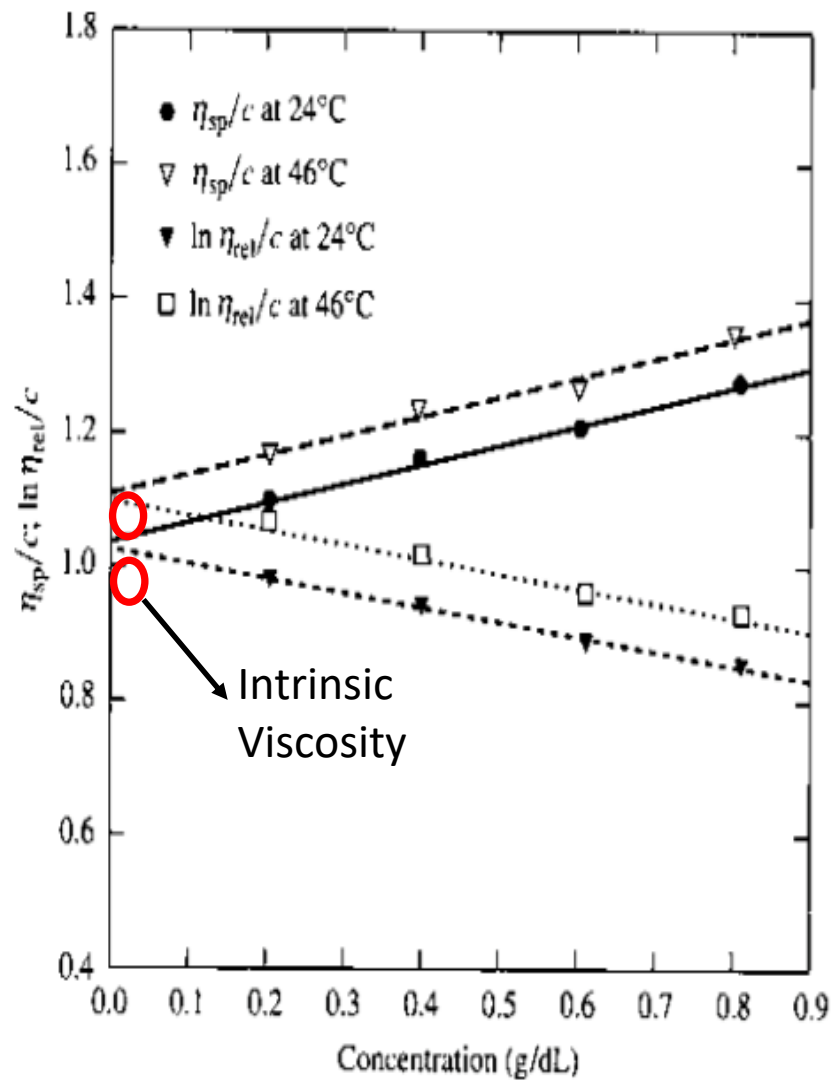
Fig. 1 Reduced viscosity and inherent viscosity of nylon 66 in 90% formic acid (Adapted from Ph.D thesis of R Walia, P. S., Chemical Engineering, West Virginia University, Morgantown, 1998).

Example 1. *A polymer sample consists of 10% by weight of macromolecules of molecular weight 10,000 and 90% by weight of macromolecules with molecular weight 100,000. Calculate* $\overline{M}_n$ *and* $\overline{M}_w$.

Solution. As $\overline{M}_n = \dfrac{\Sigma N_i M_i}{\Sigma N_i} = \dfrac{\Sigma W_i}{\Sigma N_i}$

where W_i = weight of ith constituent,

N_i = number of moles of ith constituent,

and M_i = molecular weight of ith constituent

Given $W_1 = 10$ gms. and $W_2 = 90$ gm.

∴ $\Sigma W_i = W_1 + W_2 = 10 + 90 = 100$ gm.

Since $\qquad N_i = \dfrac{W_i}{M_i}$

Hence $\qquad N_1 = \dfrac{10}{10,000}$ and $\quad N_2 = \dfrac{90}{100,000}$

Now $\qquad \overline{M}_n = \dfrac{\Sigma W_i}{\Sigma N_i} = \dfrac{W_1 + W_2}{N_1 + N_2} = \dfrac{10 + 90}{\dfrac{10}{10,000} + \dfrac{90}{100,000}} = 5.26 \times 10^4$

Similarly, $\overline{M}_w = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \dfrac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2} = \dfrac{N_1 M_1{}^2 + N_2 M_2^2}{W_1 + W_2}$

$$= \dfrac{\dfrac{10}{10,000} \times (10,000)^2 + \dfrac{90}{100,000}(100,000)^2}{10 + 90}$$

$$= 9.1 \times 10^4$$

Example 2:

A polydisperse sample of polystyrene is prepared by mixing three *monodisperse* samples in the following proportions:

1 g   10,000 molecular weight
2 g   50,000 molecular weight
2 g   100,000 molecular weight

Using this information, calculate the number-average molecular weight, weight- average molecular weight, and PDI of the mixture.

Solution:

$$\bar{M}_{n} = \frac{\sum\limits_{i=1}^{3} N_i M_i}{\sum\limits_{i=1}^{3} N_i} = \frac{\sum\limits_{i=1}^{3} W_i}{\sum\limits_{i=1}^{3} \left(W_i/M_i\right)} = \frac{1+2+2}{\dfrac{1}{10,000}+\dfrac{2}{50,000}+\dfrac{2}{100,000}} = 31,250$$

$$\bar{M}_{w} = \frac{\sum\limits_{i=1}^{3} N_i M_i^{2}}{\sum\limits_{i=1}^{3} N_i M_i} = \frac{\sum\limits_{i=1}^{3} W_i M_i}{\sum\limits_{i=1}^{3} W_i} = \frac{10,000+2\left(50,000\right)+2\left(100,000\right)}{5} = 62,000$$

$$PDI = \frac{\bar{M}_{w}}{\bar{M}_{n}} = \frac{62,000}{31,250} = 1.98$$

Example 3. *In a polymer, there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000. Find* $\overline{M}_n$, $\overline{M}_w$ *and PDI.*

Solution. $\overline{M}_n = \dfrac{\Sigma N_i M_i}{\Sigma N_i} = \dfrac{N_1 M_1 + N_2 M_2 + N_2 M_3}{N_1 + N_2 + N_3}$

$= \dfrac{100 \times 100 + 200 \times 1000 + 300 \times 10,000}{100 + 200 + 300}$

$= \dfrac{3.21 \times 10^6}{600} = 5.35 \times 10^3$

$\overline{M}_w = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \dfrac{100 \times (100)^2 + 200 \times (1000)^2 + 300 \times (10,000)^2}{100 \times 100 + 200 \times 1000 + 300 \times 10,000}$

$= 9.4 \times 10^3$

$PDI = \dfrac{\overline{M}_w}{\overline{M}_n} = 1.757$

Example 4-

In a polymer sample, 30% molecules have a molecular mass 20,000, 40% have molecular mass 30,000 and rest have 60,000. Calculate mass average and number average molecular masses.

Solution

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{(30 \times 20,000) + (40 \times 30,000) + (30 \times 60,000)}{30 + 40 + 30}$$

$$= 36000$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{30(20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{30 \times 20,000 + 40 \times 30,000 + 30 \times 60,000}$$

$$= 43333.$$

$$M_0 \qquad 104$$

Example 6. *Find $\overline{M}_w$ for PP given its degree of polymerization as 10,000.*

Solution. Since $\overline{DP}_w = \dfrac{\overline{M}_w}{M_0}$

$$\therefore \qquad \overline{M}_w = \overline{DP}_w \times M_0$$

where $\qquad \overline{DP}_w$ = Degree of Polymerization = 10,000 (given)

And $\qquad M_0$ = Molecular weight of repeat unit of PP

$$= \left(\!\!-CH_2-CH-\!\!\right) = 12 \times 3 + 6 \times 1 = 42$$
$$\Bigg|$$
$$CH_3$$

Hence, $\overline{M}_w = 10,000 \times 42$

$$\Rightarrow \qquad \overline{M}_w = 42 \times 10^4 \ gm/mol$$

Problem:

<u>Computations of Average Molecular Weights and Degree of Polymerization</u>

Assume that the molecular weight distributions shown in Figure 14.3 are for poly(vinyl chloride). For this material, compute:

(a) the number-average molecular weight,

(b) the degree of polymerization, and

(c) the weight-average molecular weight.

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	x_i	$x_i M_i$
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750

$$\overline{M}_n = 21,150 \qquad \sum x_i M_i = 21,150$$

Where, x_i: Fraction of total no. of chain within the corresponding size change

$\overline{M}_n$: Number average molecular weight

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	w_i	$w_i M_i$
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750

$$\overline{M}_w = 23{,}200 \qquad \sum x_i M_i = 23{,}200$$

Where, $\overline{M}_w$: weight average molecular weight

PVC: C_2H_3Cl

	C	H	Cl
Atomic weight (g/mol)	12.01	1.01	35.45

$\overline{m}=2(12.01)+3(1.01)+35.45$

$\overline{m}=62.50\text{g/mol}$

Number average degree of polymerization,

$$n_n = \frac{\overline{M_n}}{\overline{m}} = \frac{21,150}{62.50} = 338$$