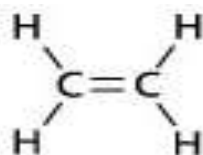


POLYMERS

Carbon-based compounds

Polymers ARE CHAINS OF
Monomers joined together.

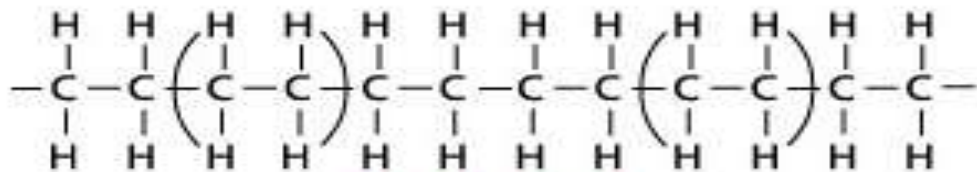


ethylene



polymerization

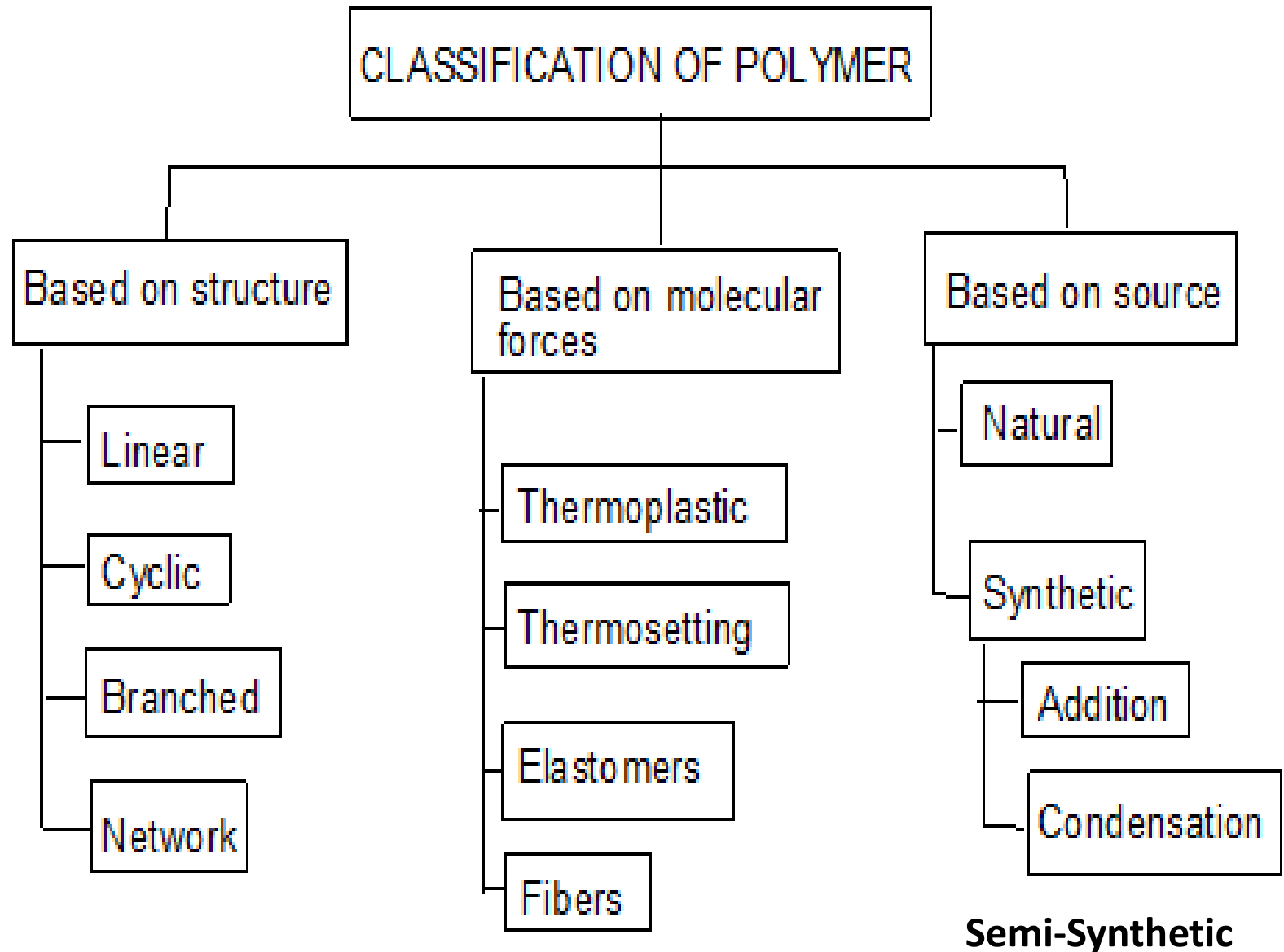
- A polymer is a macromolecule with high molecular mass ranging from 5000 to one million, which are formed by combination of one or more low molecular weight compound/ s. The unit substance from which polymer is obtained is called monomer.



polyethylene

- 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 Polymers



- 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

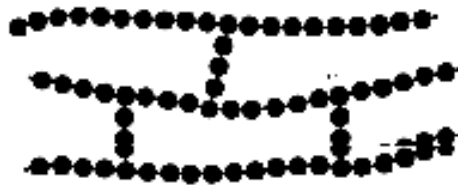
- **Linear structure** –chain-like structure Characteristic of thermoplastic polymers
- **Branched structure** –chain-like but with side branches Also found in thermoplastic polymers
- **Cross-linked structure** -Loosely cross-linked, as in an elastomer
Tightly cross-linked, as in a thermoset



(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



(a) Simple polymer

b) Copolymer



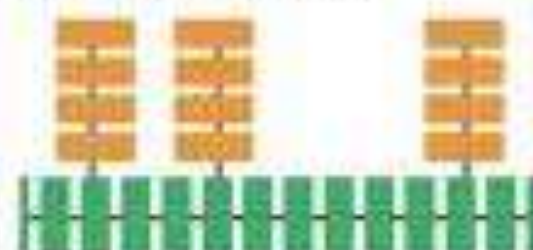
(b) Alternating copolymer

c) Block copolymer



(c) Block copolymer

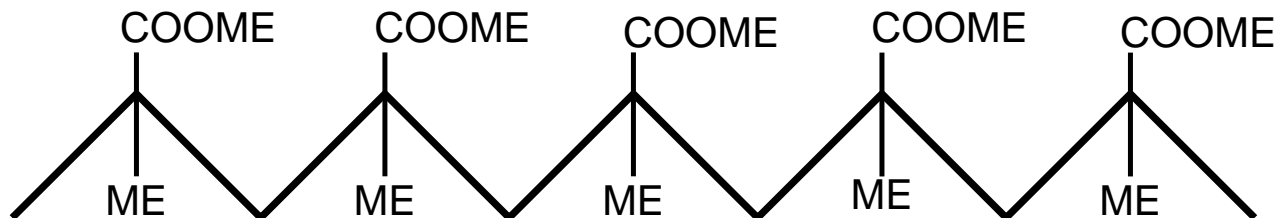
d) Graft copolymer



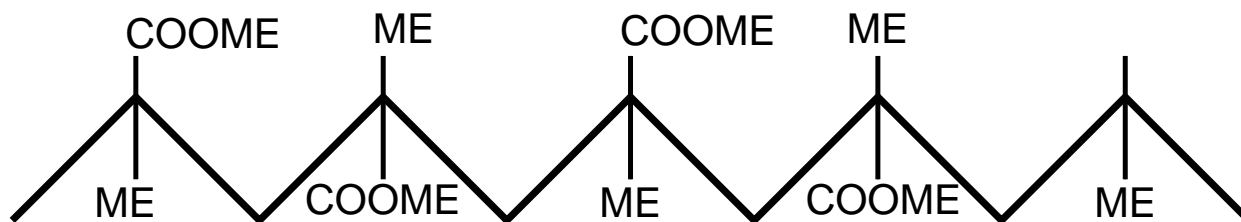
(d) Graft copolymer

- *Depending on tacticity:*

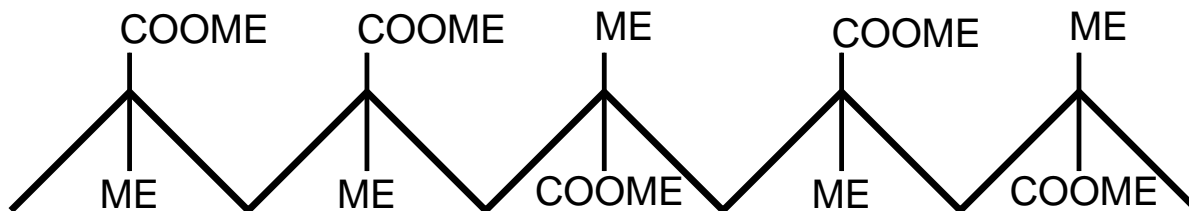
- Isotactic – similar groups on same side of chain



- Syndiotactic – two groups alternate



- Atatactic – displays no regular pattern



❖ Every other carbon in the chain is a stereocenter

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.

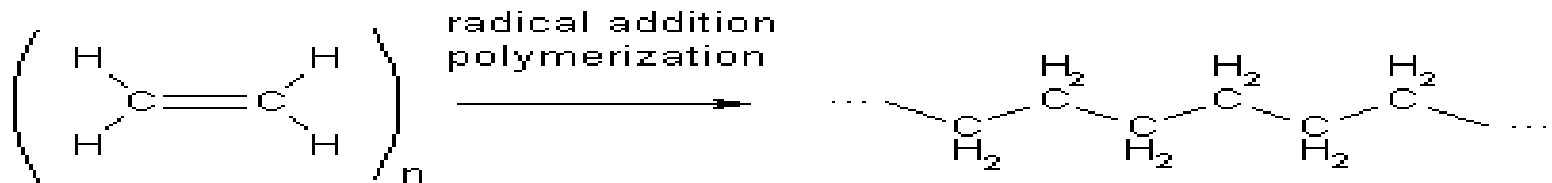
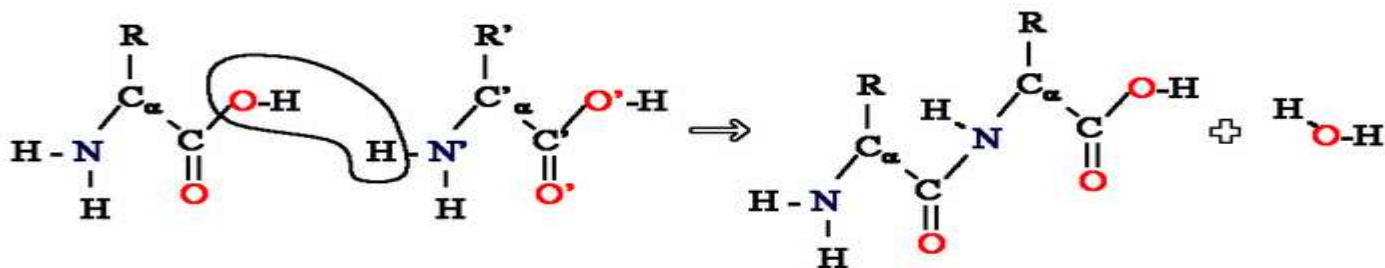


Fig 1: The polymerisation of ethene into poly(ethene)

- **Condensation Polymerization:** Condensation polymerization involves condensation of two different monomers which are normally bifunctional groups. During the process there is loss of a 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**- accelerate polymerisation, eg. H_2O_2 , 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.

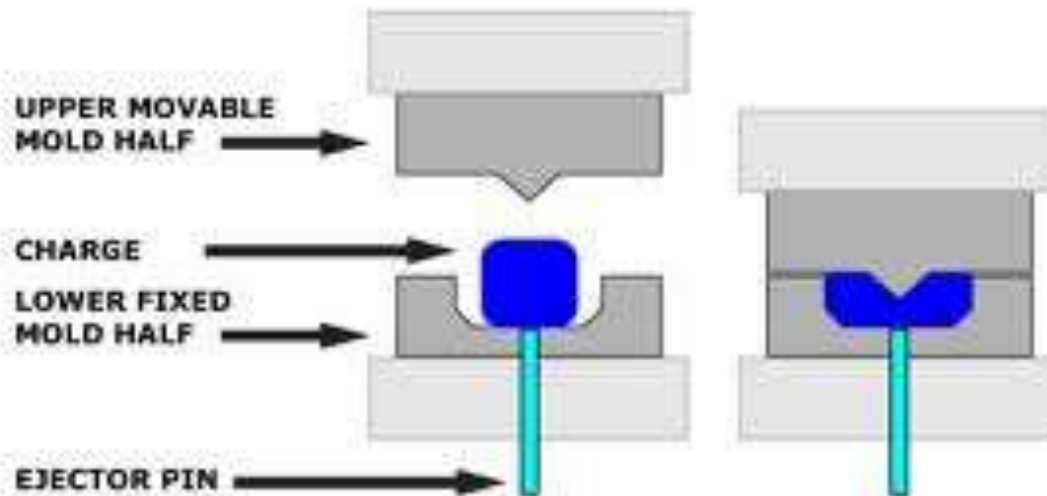
A **mold** or **mould** is a hollowed-out block that is filled with a liquid or pliable material like [plastic](#), [glass](#), [metal](#), or [ceramic](#) raw materials. The liquid hardens or sets inside the mold, adopting its shape. A mold is the counterpart to a [cast](#). The very common bi-valve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

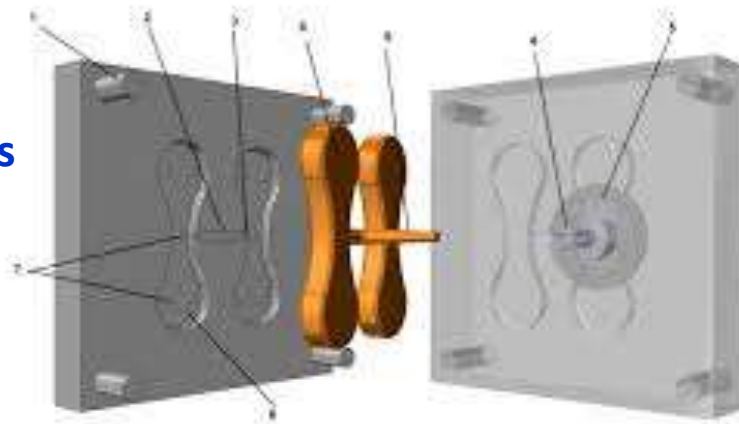
The method is used mostly for molding **thermosetting resins (thermosets)**, but some thermoplastic parts may also be produced by Compression Molding.

The method uses a split mold mounted in a hydraulic press

COMPRESSION MOLDING



Thermoplastic and thermosets



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

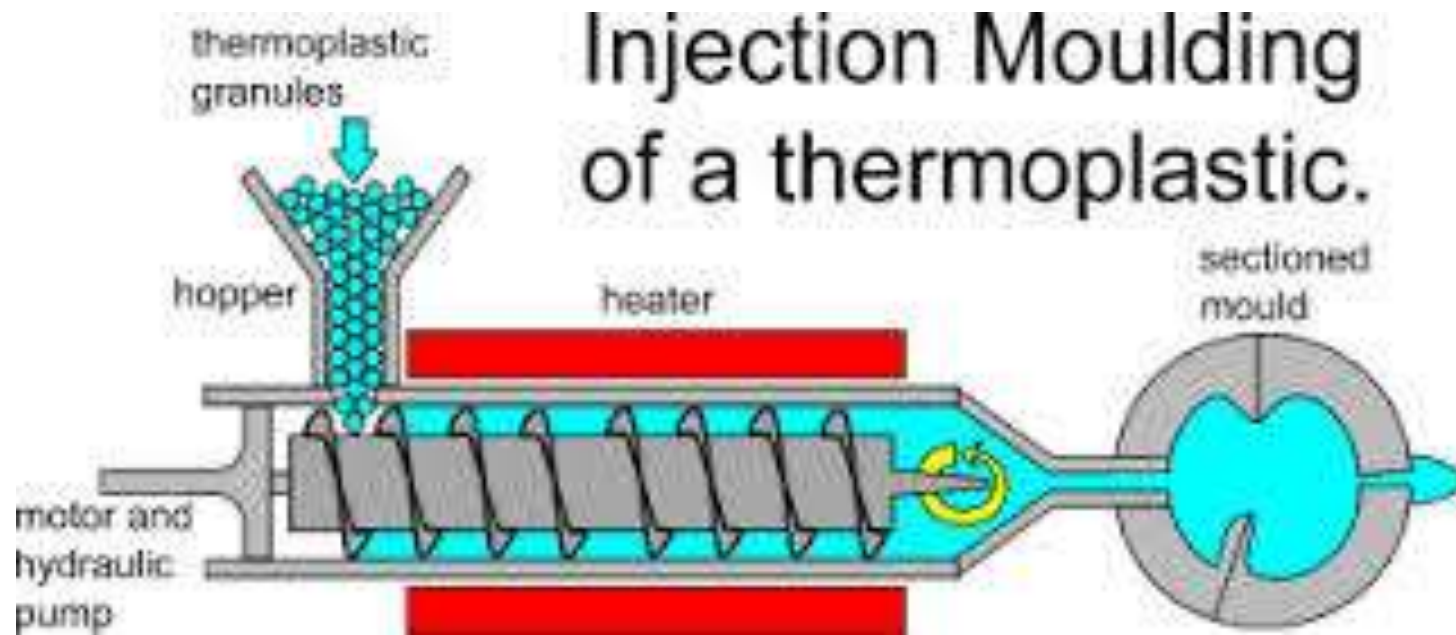
Injection molding

- 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



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 sprue).

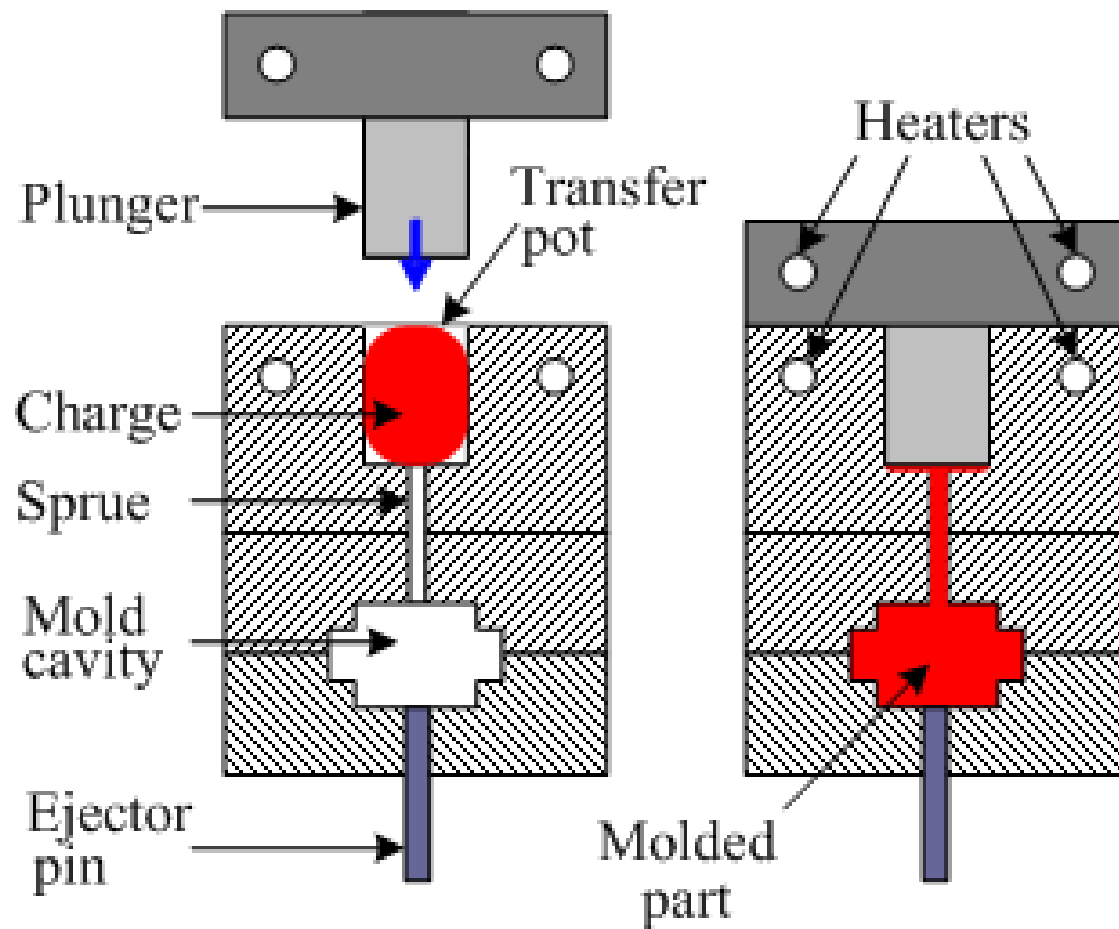
TS charge is loaded into a chamber immediately ahead of mold cavity, where it is heated; pressure is then applied to force soft polymer to flow into heated mold where it cures

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



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

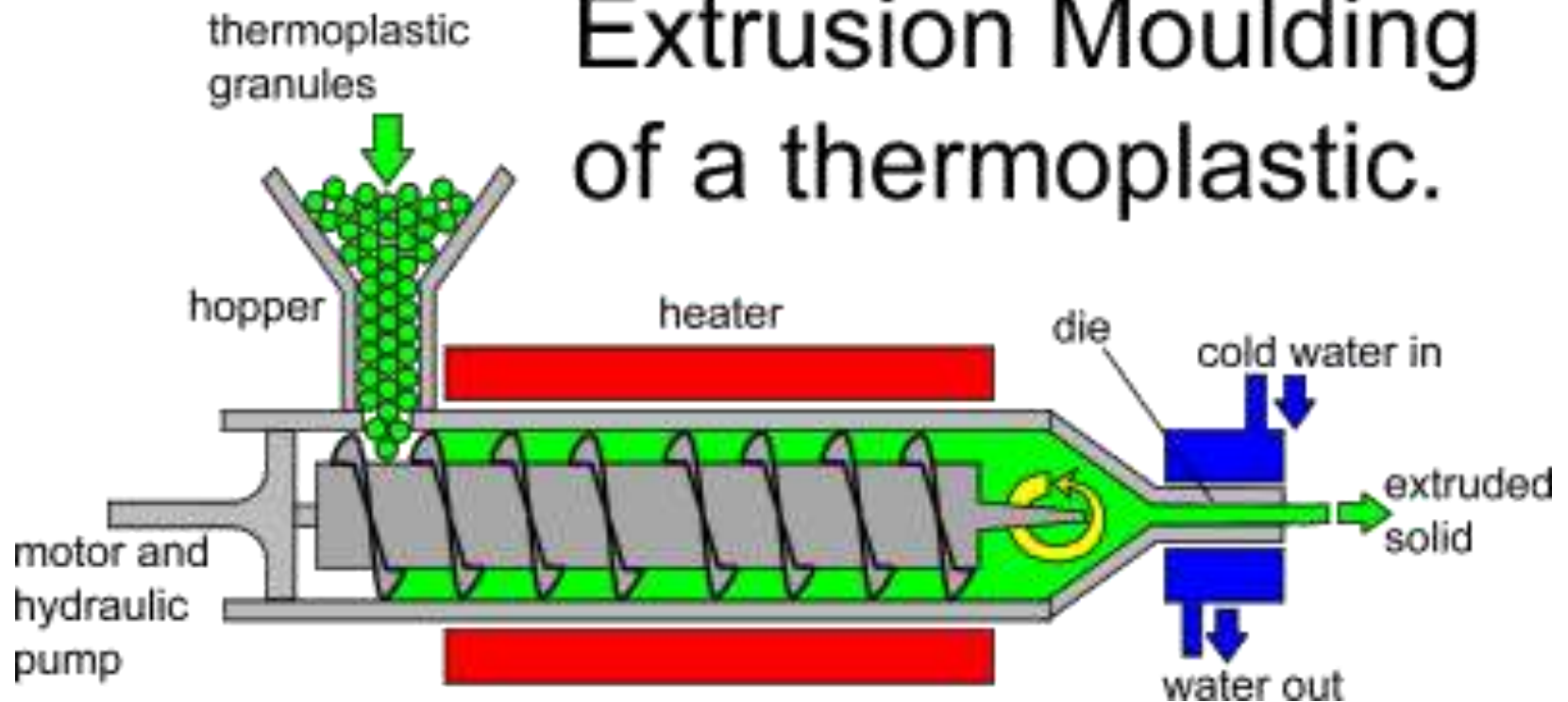
Extrusion

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.



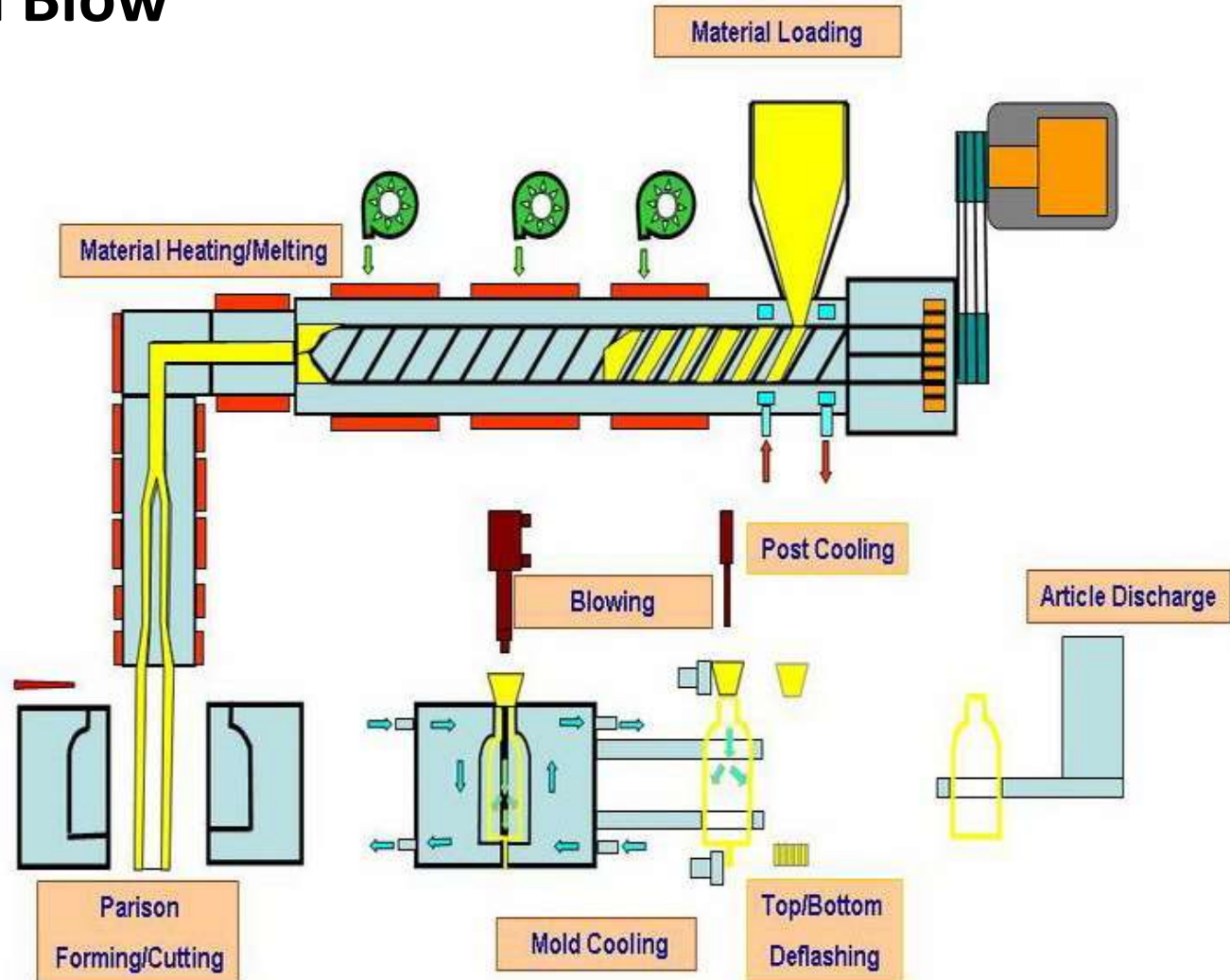
Thermoplastic

- *Horizontal*

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

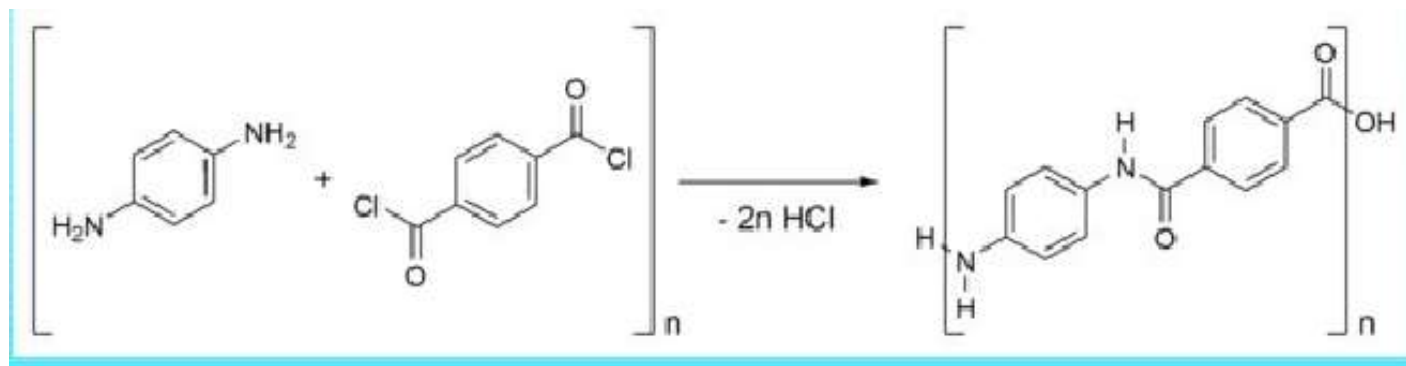
Also called as
'Extrusion Blow
Molding'.

Vertical



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

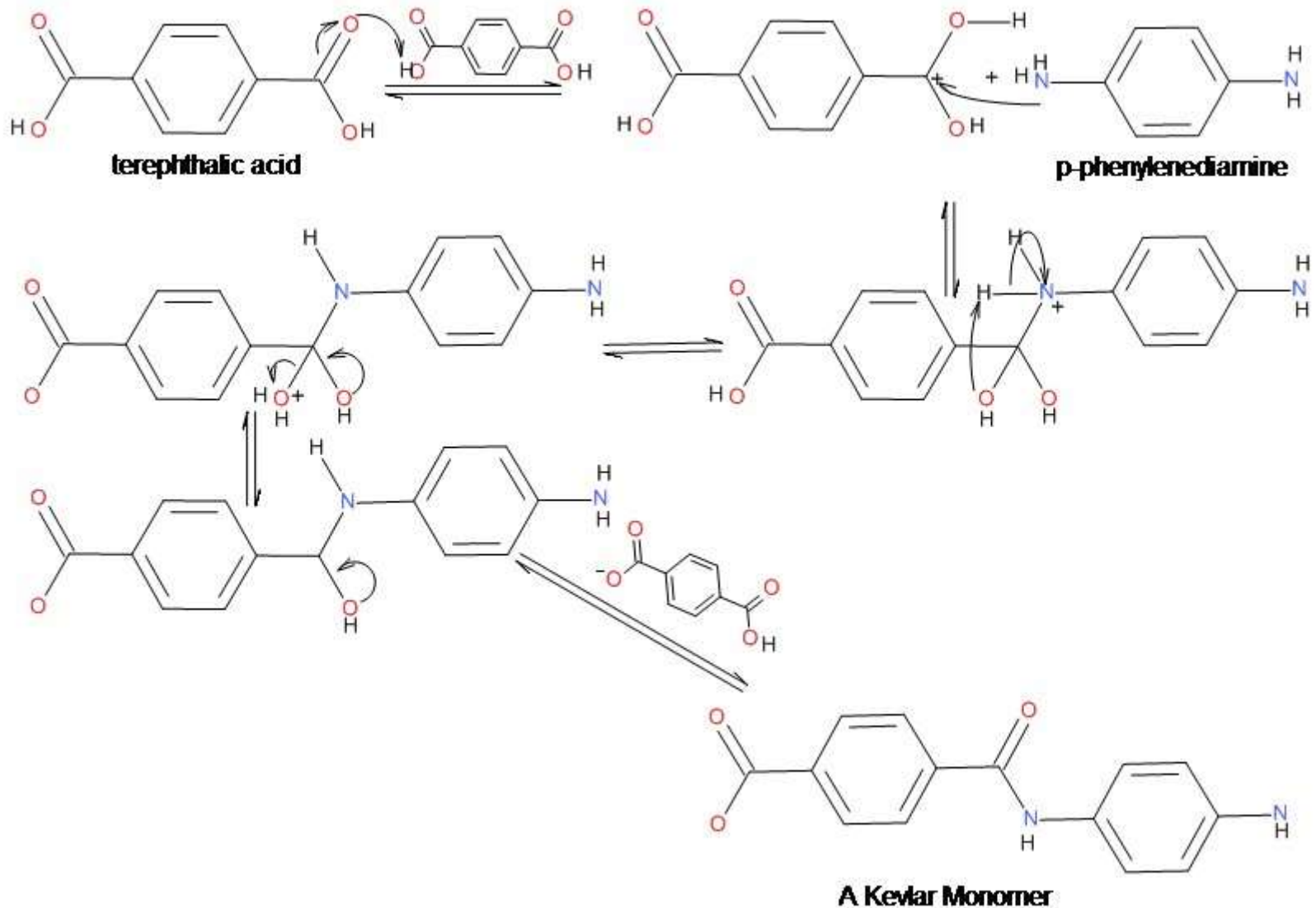
Synthesis of some important polymers- Kevlar



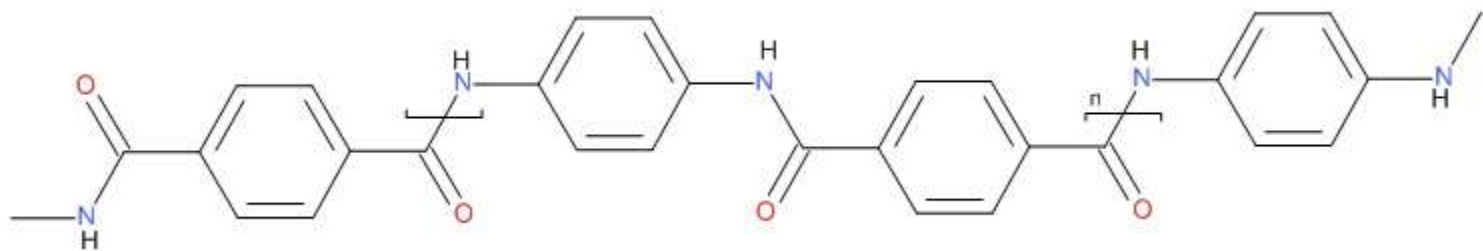
This is a amide co-polymer synthesized by condensation polymerisation of phenylene diamine and terephthaloyl chloride.

Terephthalic acid is used for manufacture of Kevlar but as terephthaloyl chloride is more active than the terephthalic acid, terephthalic acid is converted to terephthalic chloride which is used to manufacture Kevlar.

Condensation mechanism-



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 $[-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-]_n$
 - It is made up of the monomers 4-phenylenediamine (*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

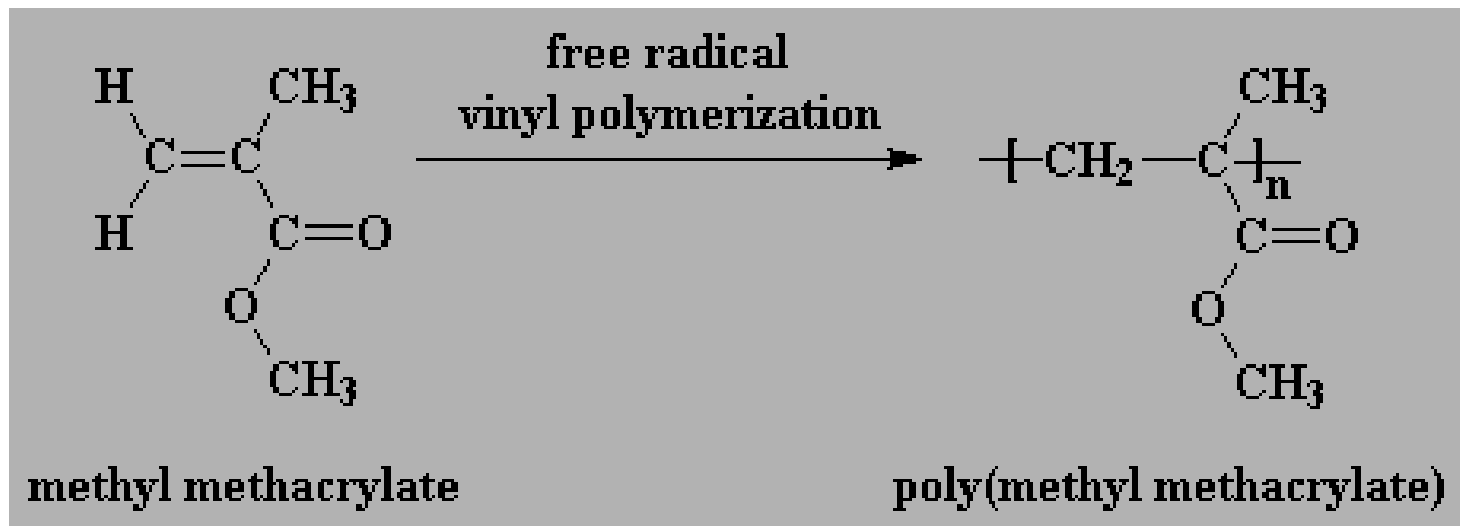


Good for its function

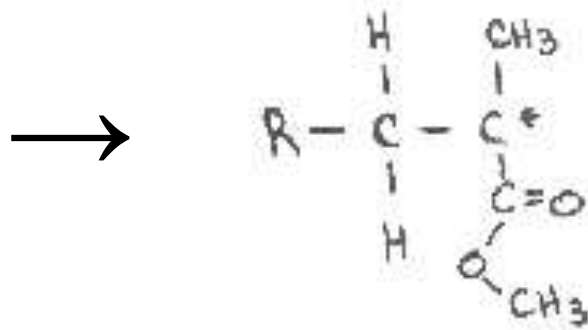
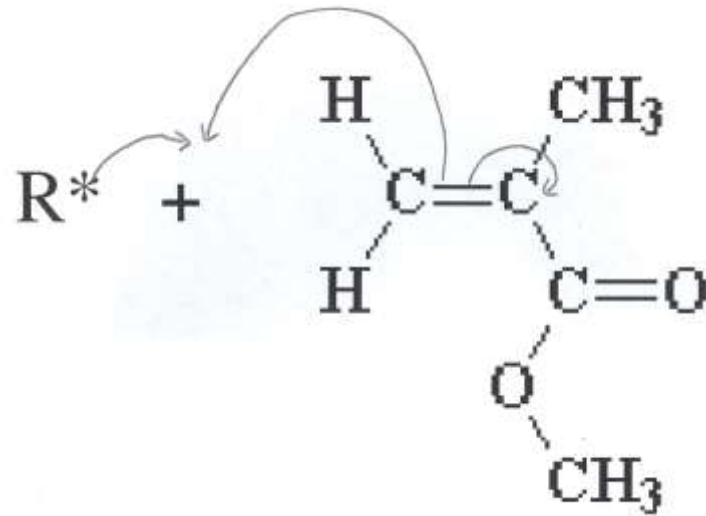
- Kevlar's physical hardness and tensile strength both make it very suitable for its function, in bulletproof vests, for example.
- Its hydrogen bonds give strength to the material, creating quite strong intermolecular bonds between kevlar molecules, giving it its strength and durability.

Polymethyl Methacrylate

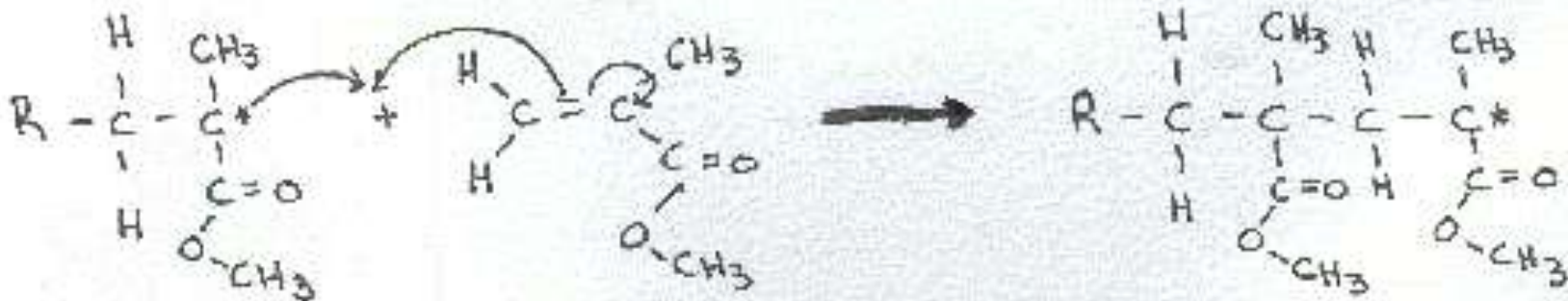
- PMMA is manufactured from Methyl methacrylate by addition polymerisation (Free Radical Polymerization).



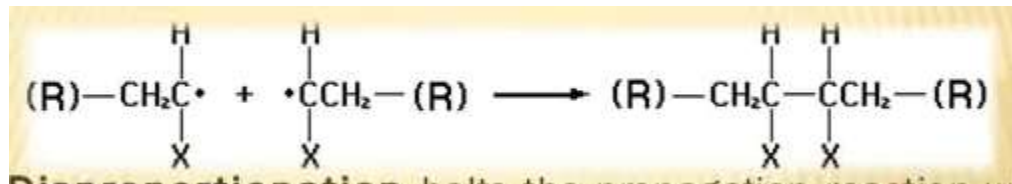
- Step 1 : Free radical (R^*) plus methyl methacrylate



Step 2 : Polymerization - MMA radical plus MMA :repeated many, many times

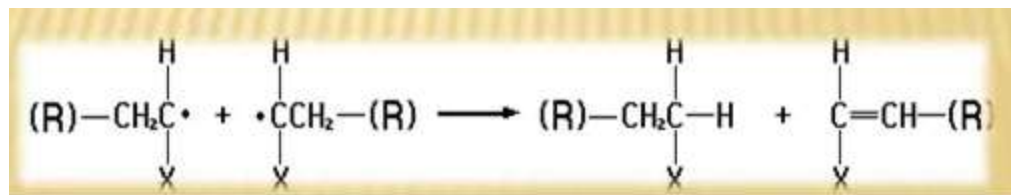


Step 3 : Termination – occurs when two radicals join



Combination

Disproportionation



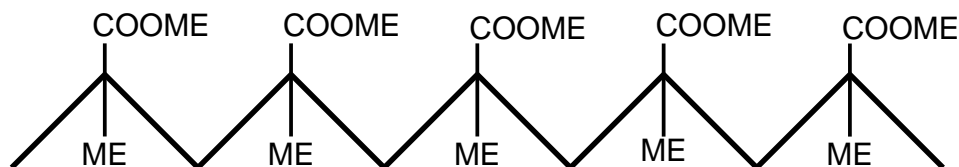
Catalysts

- 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

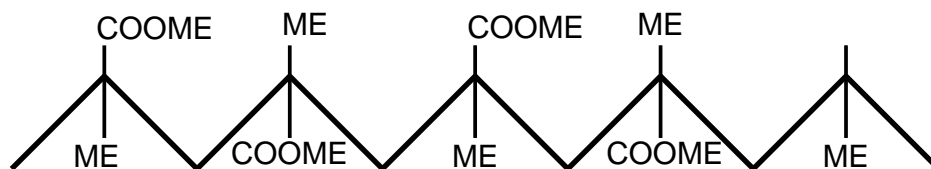
Why Use Different Catalysts?

- Different catalysts result in different versions of the polymer
 - Variation is due to the placement of the ester (R-O-R) and methyl (CH₃) groups along the polymer backbone

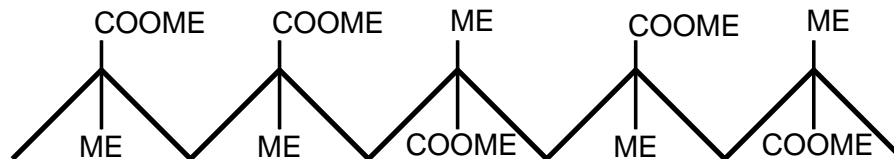
- Isotactic – similar groups on same side of chain



- Syndiotactic – two groups alternate



- Atatactic – displays no regular pattern



❖ Every other carbon in the chain is a stereocenter

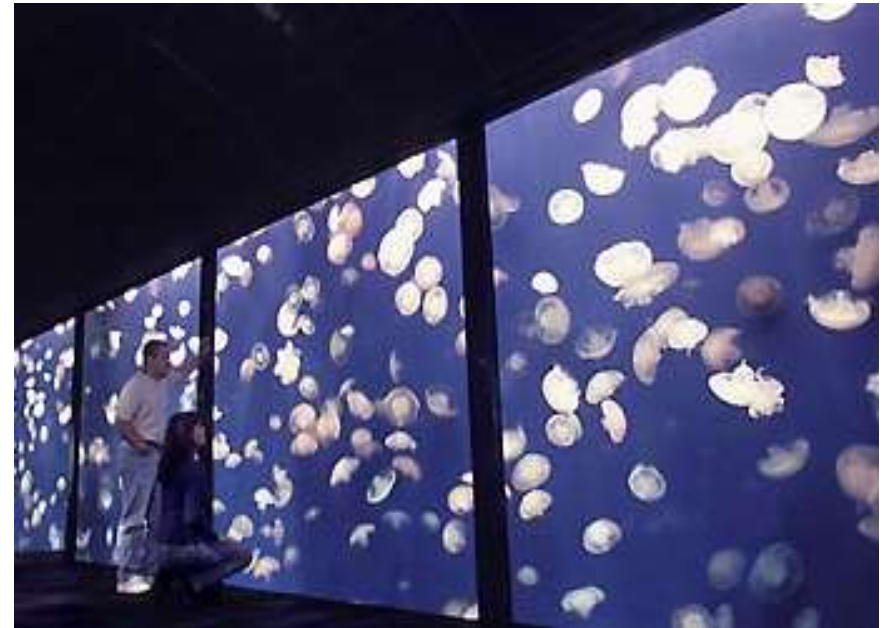
Properties of PMMA

- 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

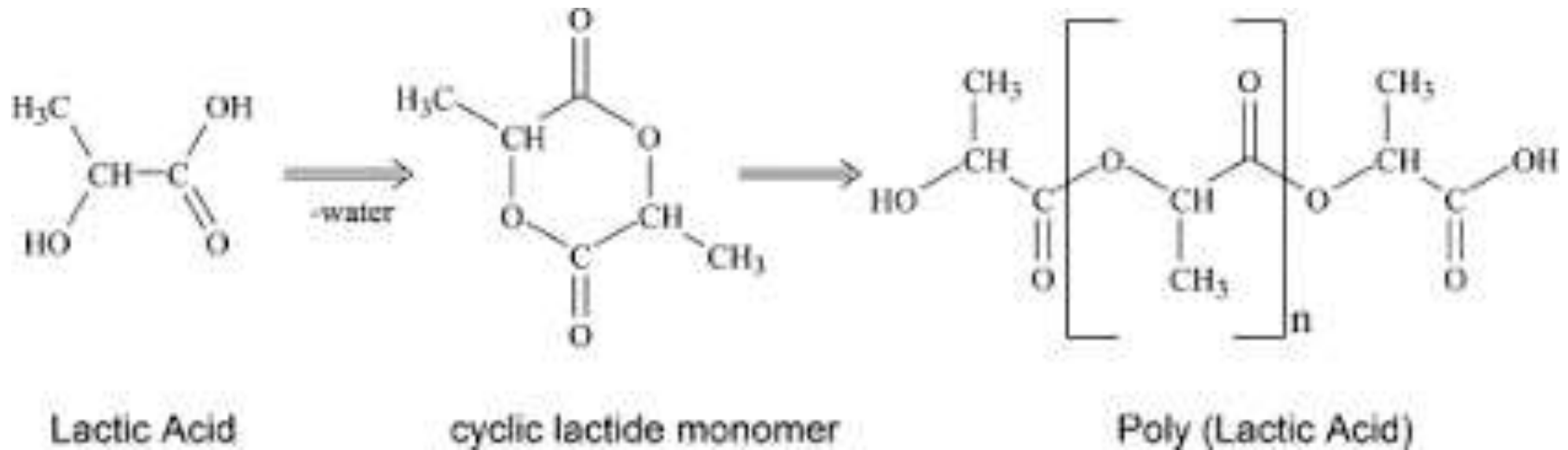


Medical Uses

- 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?

PolyLactic acid (**Bio-Degradable Polymer**)



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- \$\beta\$](#) , 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.

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?

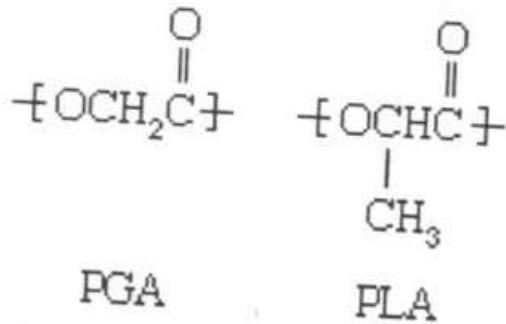
Improve patient's quality of life by replacing a defective body part with a substitute.

Physicians were limited to use off-the shelf supplies.

Novel biodegradable polymers and modified natural substances.

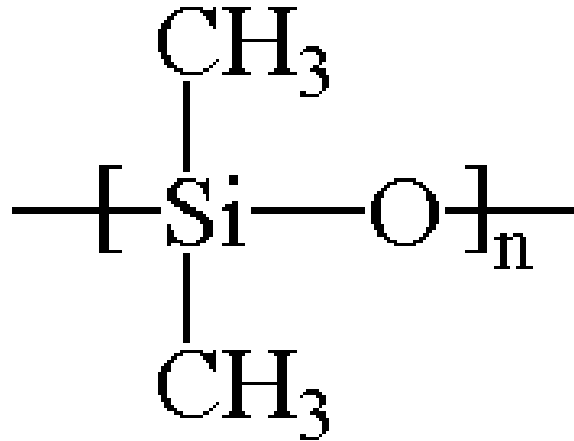
Applications of Biomaterials			
Polymer	Applications	Polymer	Applications
PDMS	Catheters, heart	Polytetrafluoroe	Heart valves
	Valves	thylene	Vascular grafts
			Nerve repair
Polyurethane	ventricular assist	Polyethylene	Catheters, hip
	Devices		prostheses
		Polymethylmetha	Fracture fixation
PGA, PLA,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

Polylactic acid, Polyglycolic acid



- 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



- “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



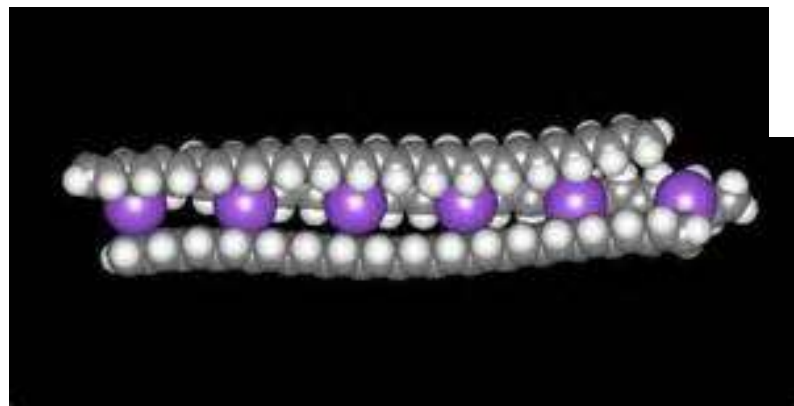
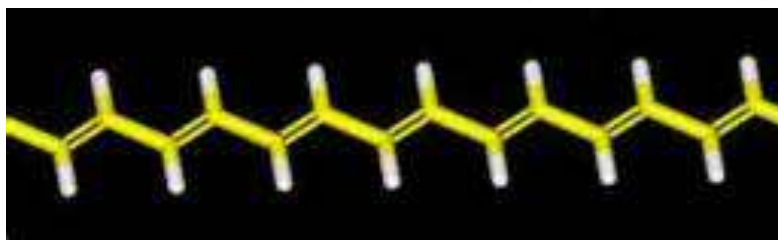
PMMA disc over femoral window during the molding process



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.

C=CC=CC=CC=CC=CC=CC=C

The chemical structure of poly(2,5-bis(4-phenyl)pyridine) (PBP) is shown. It consists of a repeating unit of a pyridine ring substituted at the 2 and 5 positions with phenyl groups, which are further substituted at the 4 position with another phenyl group. The structure is enclosed in brackets with a subscript 'n'.

$$\left(\text{—C}_6\text{H}_4\text{—NH—C}_6\text{H}_4\text{—NH—C}_6\text{H}_4\text{—NH—} \right)_n$$

polyaniline

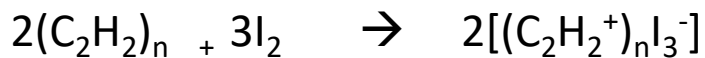
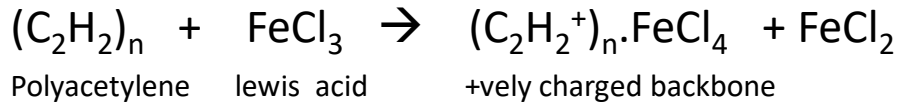
(DCP) Doped conducting polymer

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.

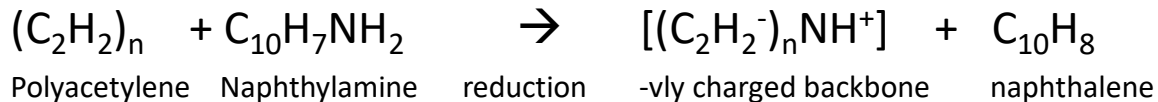


- As synthesized conductive polymers exhibit very low conductivities. It is not until an electron is removed from the valence band (**p-doping**) or added to the conduction band (**n-doping**, which is far less common) does a conducting polymer become highly conductive. • Doping (p or n) generates charge 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.

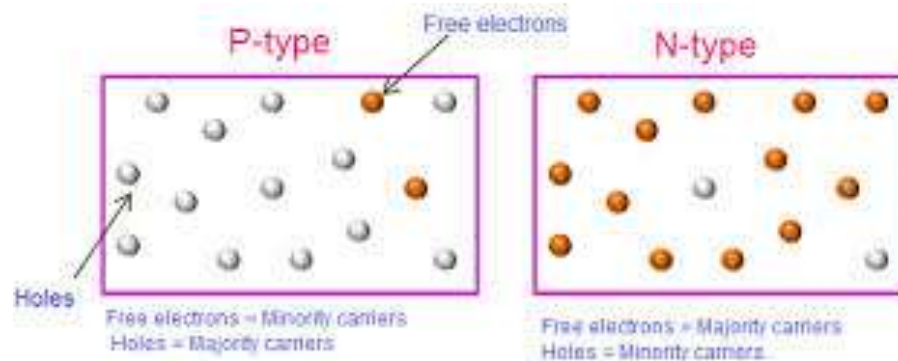
(i) Oxidation process (p-doping):



(i) Reduction process (n-doping):

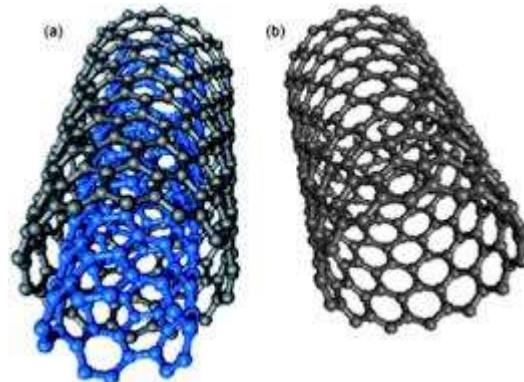


The above reactions are most likely to occur saturated polymers, as they can be very easily removed from the polymeric chains to form polyion therefore, these are the types of polymers, which assume high conductivity on doping.



- *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.



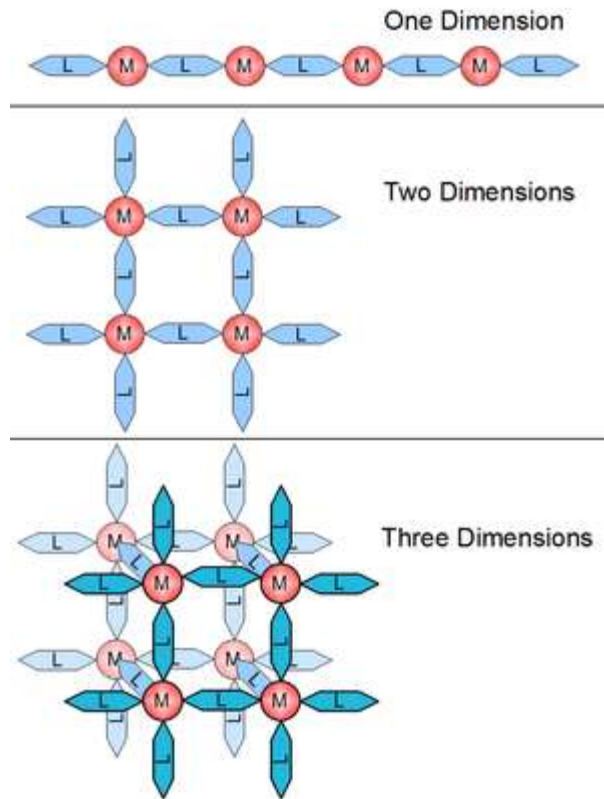
➤ Another type includes the blends
Extrinsically conductive polymers can involve a blend of conductive and nonconductive polymers.

- ***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](#).



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

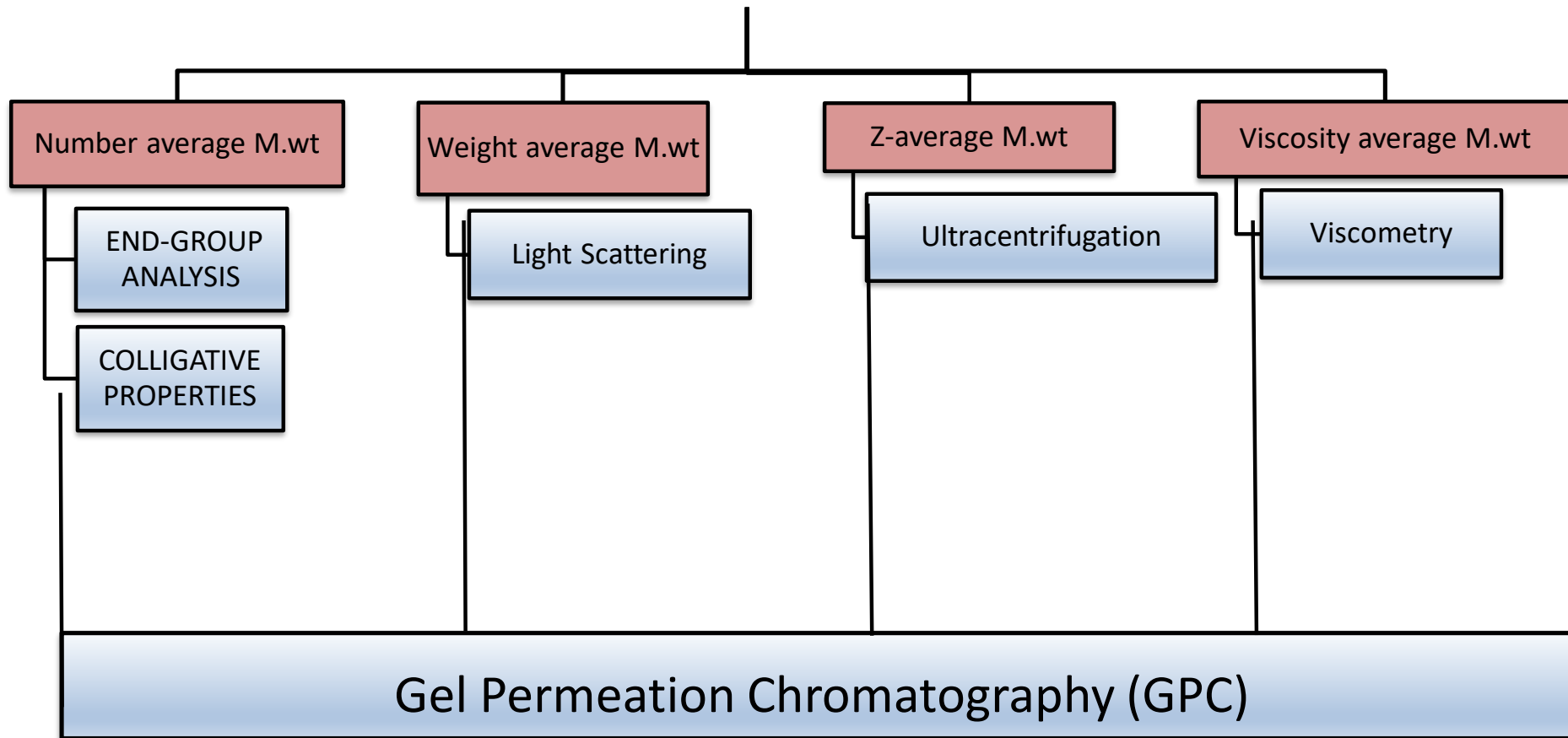
<i>Type</i>	<i>Abbreviation</i>	<i>Typical Uses</i>
Phenol-formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder
Urea-formaldehyde	UF	Similar to PF polymer; also treatment of textiles, coatings
Unsaturated polyester	UP	Construction, 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

Polymer Molecular weight and its Measurement methods

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

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



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) = $2 \times (1) + 1 \times (16) = 18 \text{ g/mol}$

Methane CH_4 is 1 C (12g) and 4 H (1g) = $1 \times (12) + 4 \times (1) = 16 \text{ g/mole}$

Polyethylene $-(\text{C}_2\text{H}_4)_{-1000}$ = 2 C (12g) + 4H (1g) = $28\text{g/mole} \times 1000 = 28,000 \text{ g/mole}$

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 $-(\text{C}_2\text{H}_4)_{-1000}$ 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.

- (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:

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

$[\eta]$: intrinsic viscosity
 K, a : constant for specific polymer and solvent
 \bar{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*.

$$PDI = \frac{M_w}{M_n} > 1 ; \text{ polymers having } PDI = 1 \text{ are called monodisperse polymers}$$

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.

$$DP_w = \frac{M_w}{M_0} , DP_n = \frac{M_n}{M_0} ; \text{ where } M_0 \text{ is the monomer molecular weight.}$$

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

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

$[\eta]$: intrinsic viscosity
 K, a : constant for specific polymer and solvent
 \bar{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 :

$$\eta_{\text{rel}} = \frac{\eta}{\eta_o} = \frac{t}{t_o}$$

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

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

Specific viscosity

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

Reduced viscosity

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

Intrinsic viscosity

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

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

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

Grey arrows: Parameter used for intrinsic viscosity determination for single concentration measurements

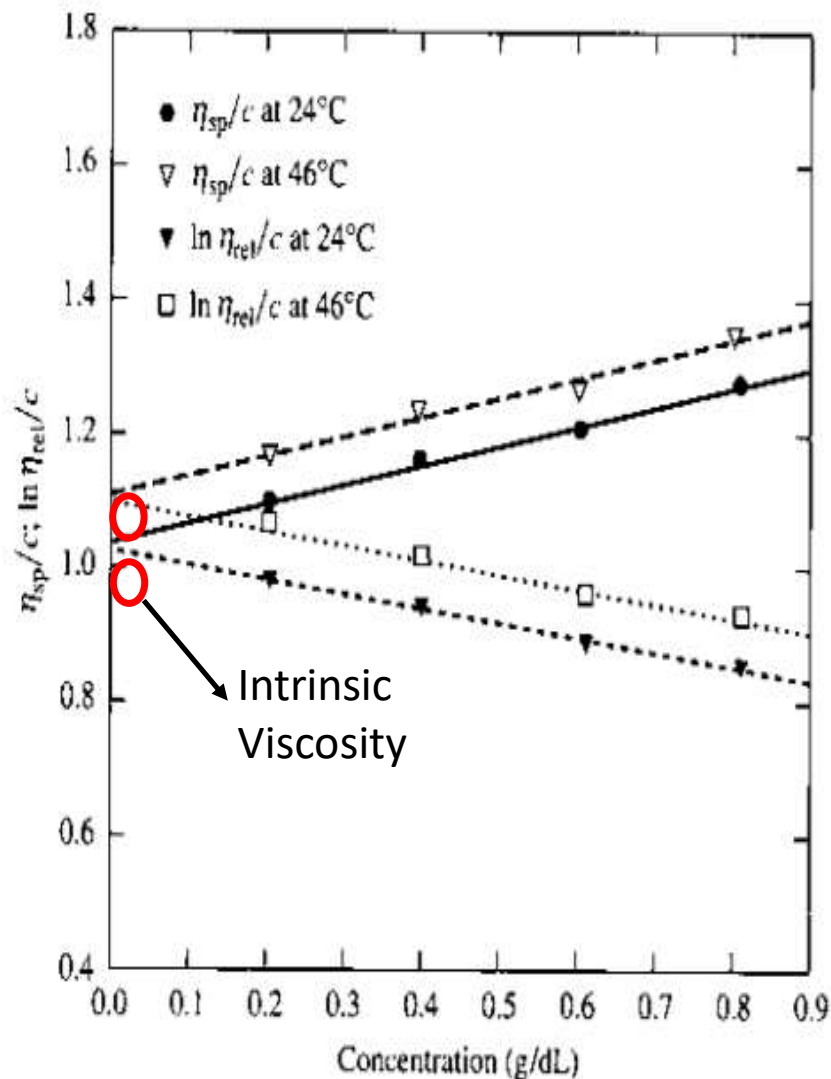


Fig. 1 Reduced viscosity and inherent viscosity of nylon 66 in 90% formic acid
 (Adapted from Ph.D thesis of R Walia, P. S., Chemical Engineering, West Virginia University, Morgantown, 1998).