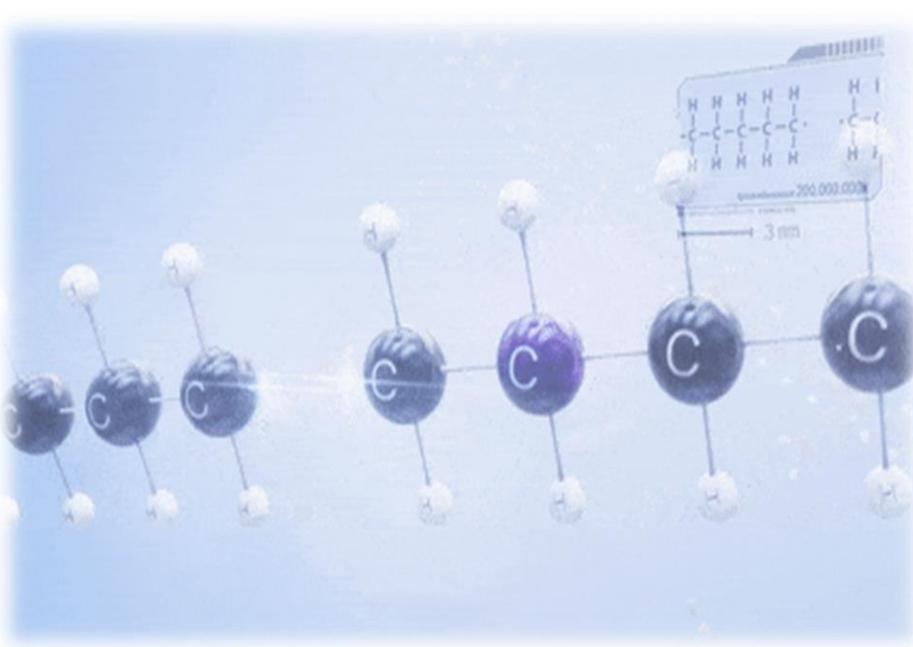


CO-4: Polymers & Plastics



K L University
(Deemed to be University estd. u/s. 3 of the UGC Act, 1956)
(NAAC Accredited "A" Grade University)
KONERU LAKSHMAIAH EDUCATION FOUNDATION



Department of Chemistry
Koneru Lakshmaiah Education Foundation (**KLEF**)

What are Polymers?

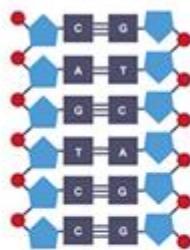
The term **polymer** refers to chemical compounds consisting of large molecules/macromolecules which are **constructed** from **repeating subunits** that are linked by numerous intertwined links.

There are two types of polymers.

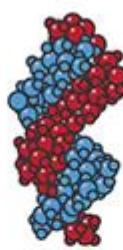
Natural Polymers: Wool, cotton, DNA, proteins.

Synthetic polymers : Teflon, Polyethylene, Nylon, polyester.

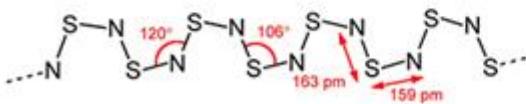
DIFFERENT TYPES OF POLYMERS



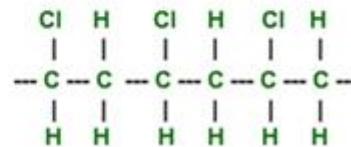
NATURAL POLYMERS



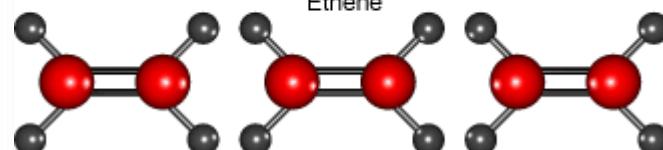
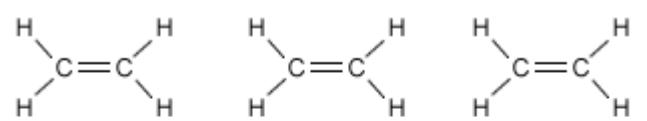
SYNTHETIC POLYMERS



INORGANIC POLYMERS



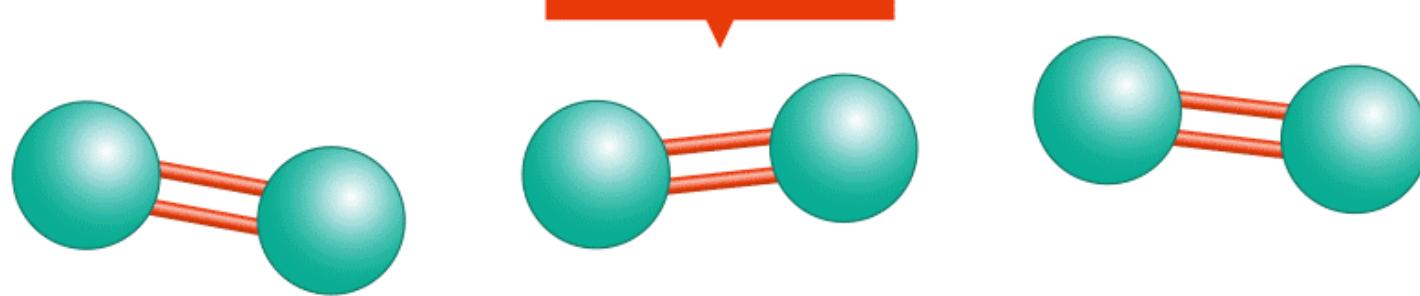
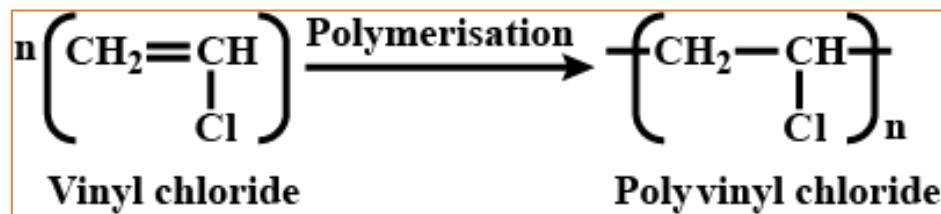
ORGANIC POLYMERS



What are Monomers?

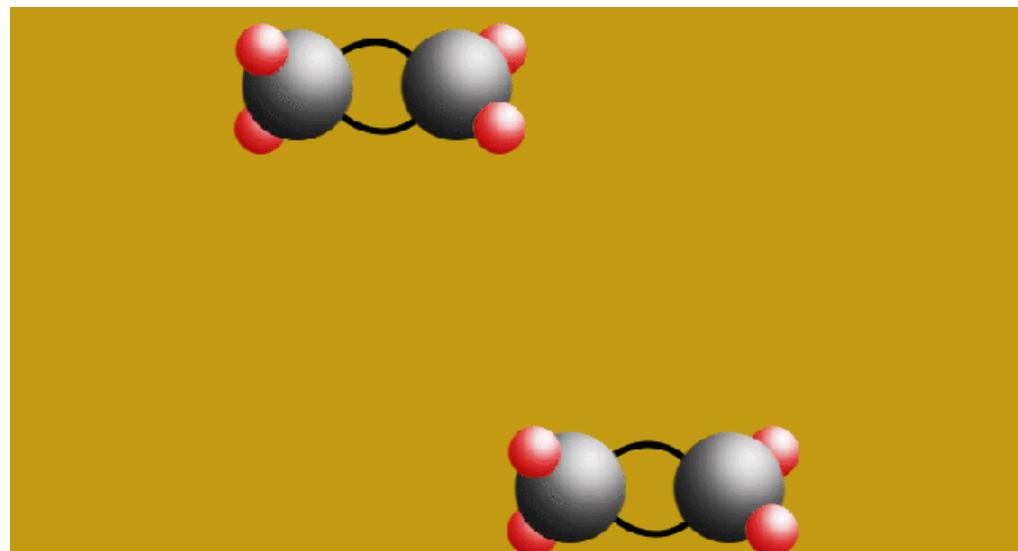
Monomers: The individual small and simple molecules from which the polymer is formed. They are joined together by chemical bonds.

Examples: Vinyl chloride, ethylene, propylene etc.



Polymerization

Polymerization is a process of reacting monomer molecules together in a **chemical reaction** to form polymer chains or three-dimensional networks.



Degree of polymerization (DP)



Degree of polymerization is 5

Classification based on DP

Oligo polymers: they have a low degree of polymerization, with mol. wt. ranging from 500-5000.

High polymers: they have a high degree of polymerization, with mol. wt. ranging from 10,000-20,000.

Basics of polymers

Polymers: Complex and giant molecules, made from joining many small and simple molecules by primary valency linkage.

Monomers: The individual small and simple molecules from which the polymer is formed.

Polymerization: The process by which monomer molecules are linked to form a big polymer molecule

Functionality: The no. of bonding sites or active sites in a monomer.

Degree of polymerization: Number of monomeric units forming the polymer chain.

Tacticity: spatial arrangement of pendant groups of successive stereocenters (asymmetric carbon) in the main chain.

Classification of polymer

Polymers can be classified into various types depending on their category.

Based on origin:

Natural & synthetic polymers.

Based on constituent groups:

Organic & inorganic polymers.

Based on applications:

Plastics, elastomers, fibres, liquids, & resins.

Based on mechanism of formation:

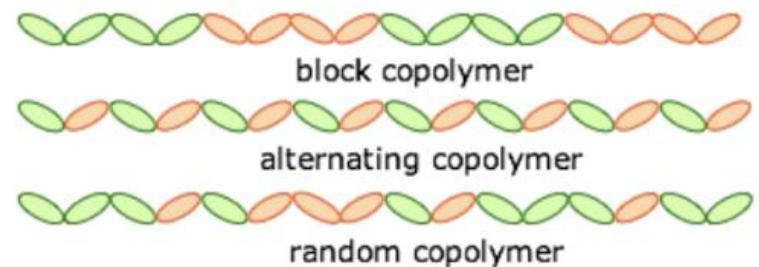
Addition
polymers.

polymers/condensation/chain-growth/step-growth

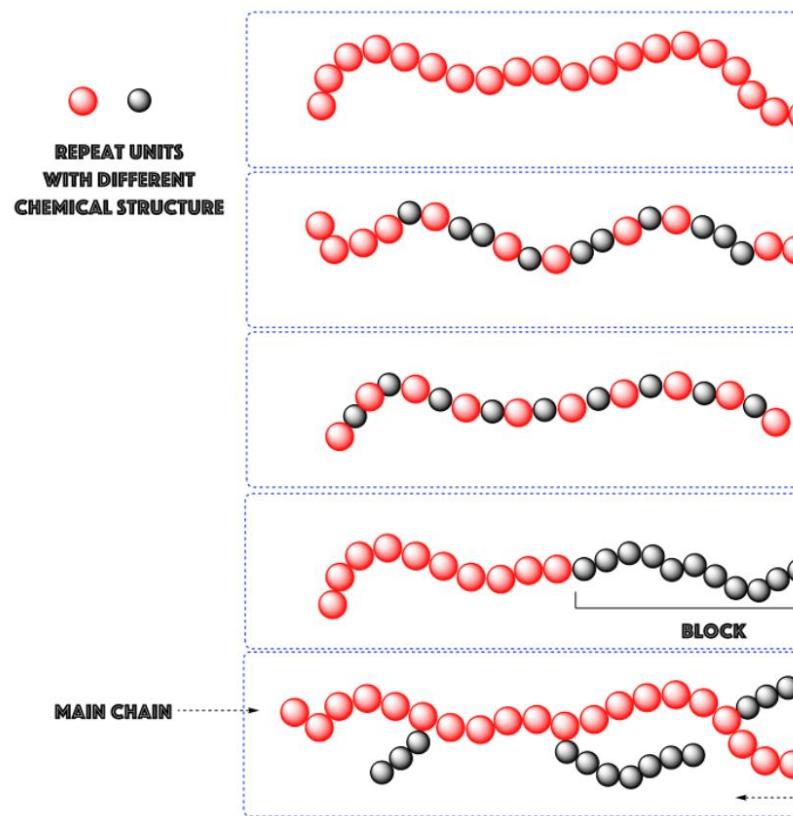
Types of polymers-based on monomer units

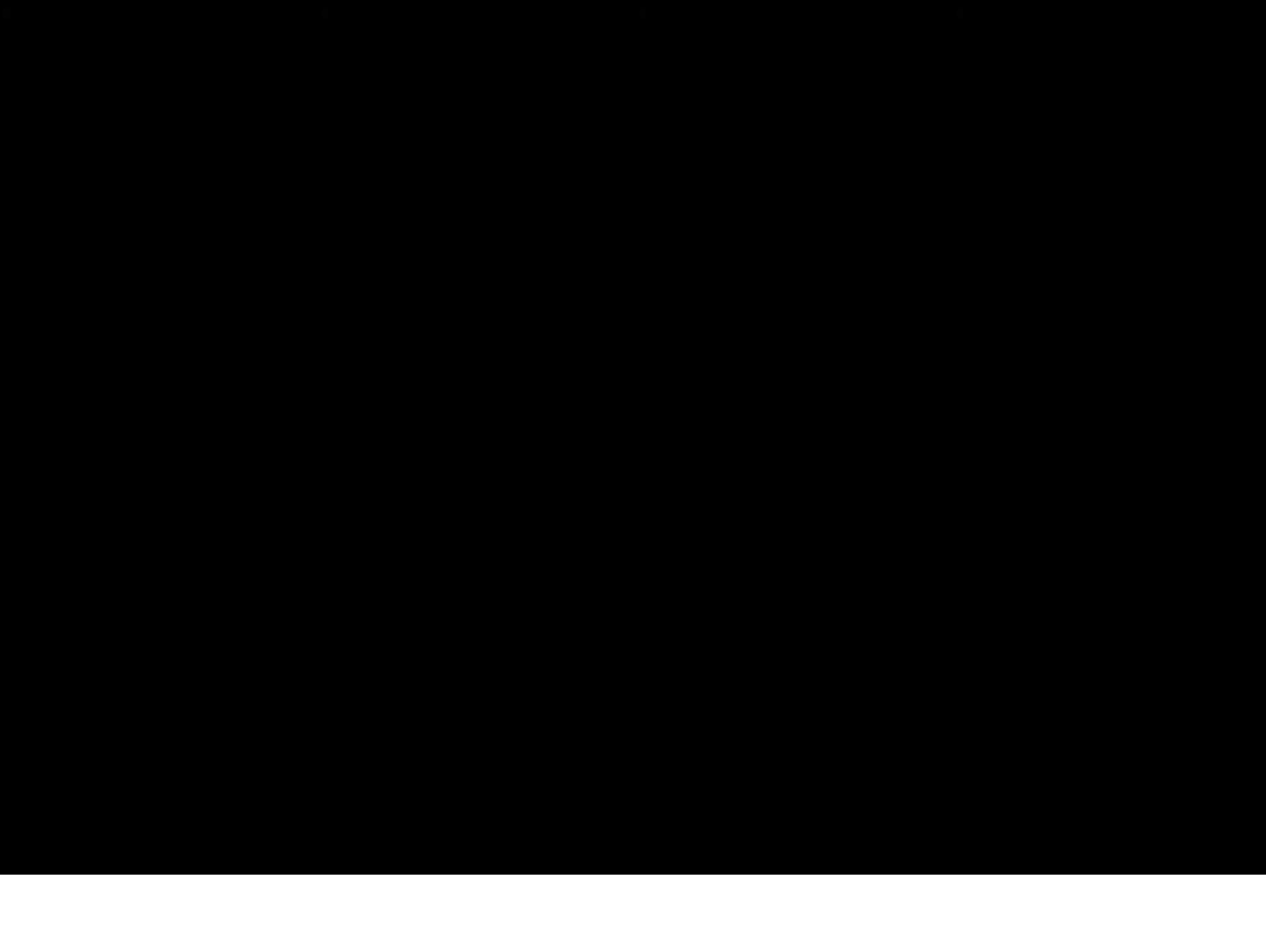


Examples: polyethylene, polystyrene, polyacrylamide, etc



Ex.; poly(vinyl chloride-co-vinyl acetate).

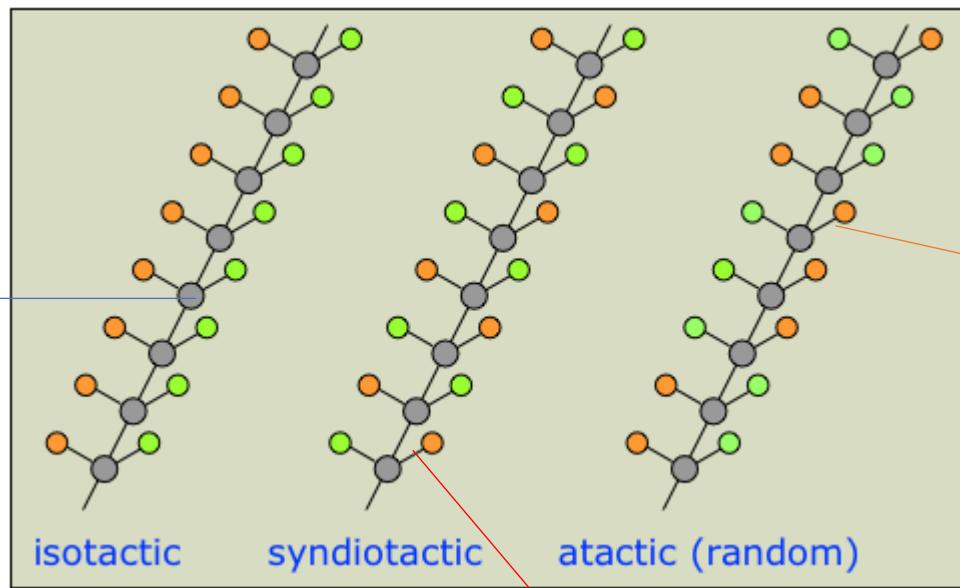




Tacticity

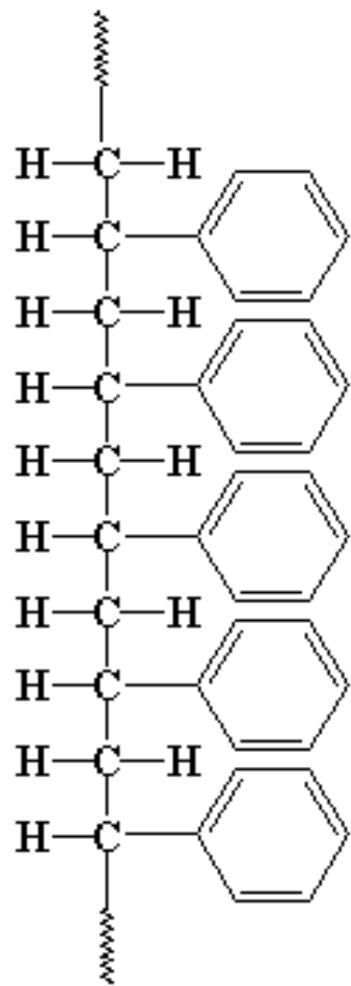
- Tacticity refers to the orientation or arrangement of functional groups in a polymer with respect to the main chain.

FG arranged on
the same side of a
polymer chain

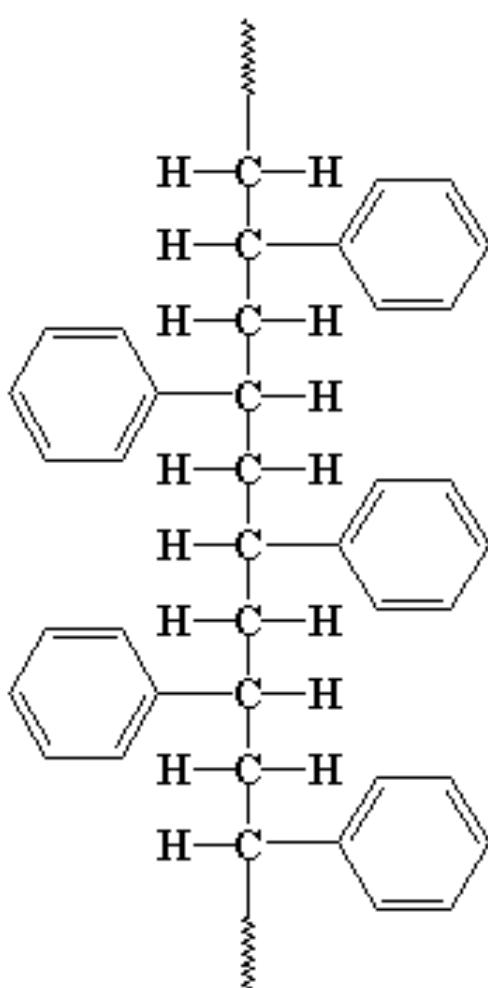


FG arranged on
the randomly of
a polymer chain

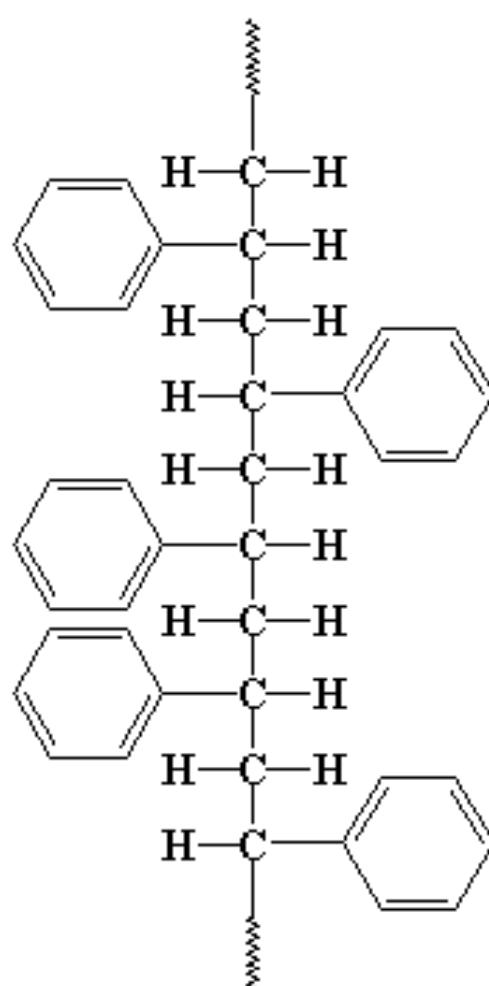
FG arranged in alternative
manner of a polymer chain



Isotactic



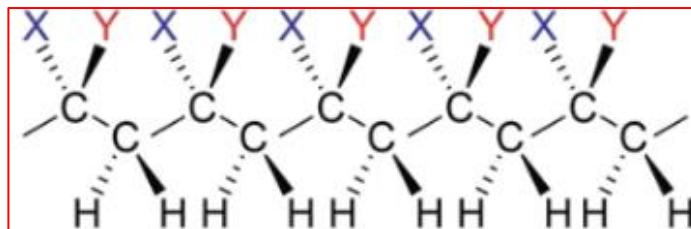
Syndiotactic



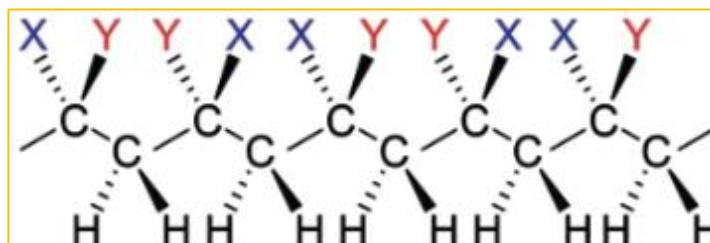
Atactic

Types of polymers-based on tacticity

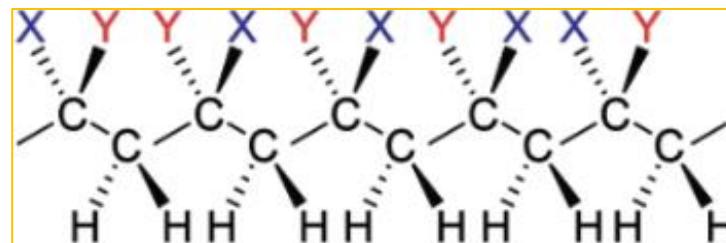
Isotactic polymer: all functional groups are on the same side of the polymer chain.



Alternating/Syndiotactic polymer: all functional groups are arranged alternatively on either side of the polymer chain in a regular fashion.



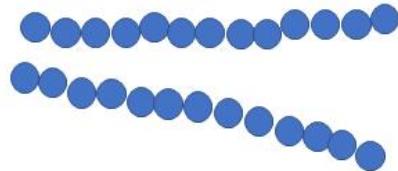
Random or Atactic polymer: all functional groups are arranged randomly on both sides of the polymer chain.



Types of polymers-based on applications

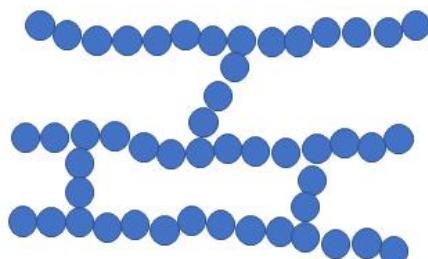
- A polymer that can be reshaped into **hard and tough utility articles** by applying heat, pressure or both is said to be a **plastic**. Ex: Polystyrene, Poly(vinyl chloride), Poly(methyl methacrylate), polyester etc.
- A polymer that shows **good strength and elongation** upon chemical treatment is called an **elastomer**. Ex: Polyisoprene, polyisobutylene, etc.
- A polymer that can be drawn into a **long filament-like material**, whose length is at least 100 times its diameter is called a **fibre**. Ex: Nylon, terylene, polyester, polyacrylonitrile, etc.
- A polymer used as **adhesives, potting compounds, sealants** etc., in a liquid form is called as **liquid resin**. Ex: Epoxy adhesives, poly sulfides, sealants, etc.

Classification of polymers-based on chain configurations

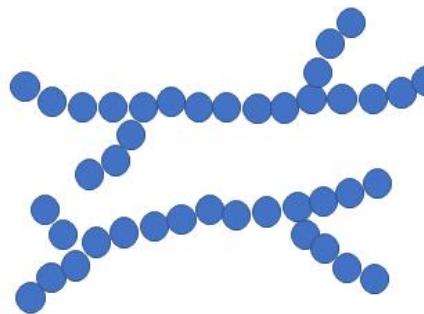


Linear Polymers

E.g., High density polyethylene, PVC.

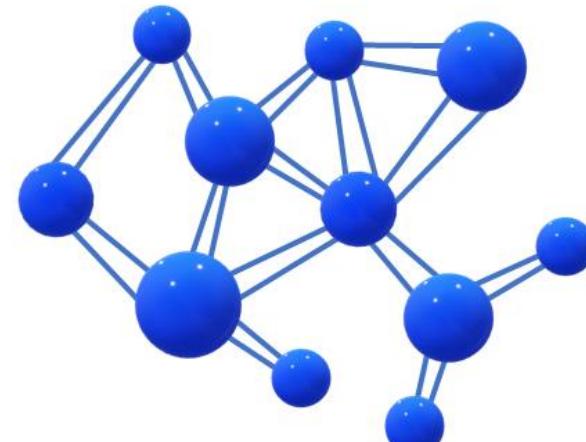


Branched Polymers



Crosslinked Polymers

E.g., Low density polyethylene.



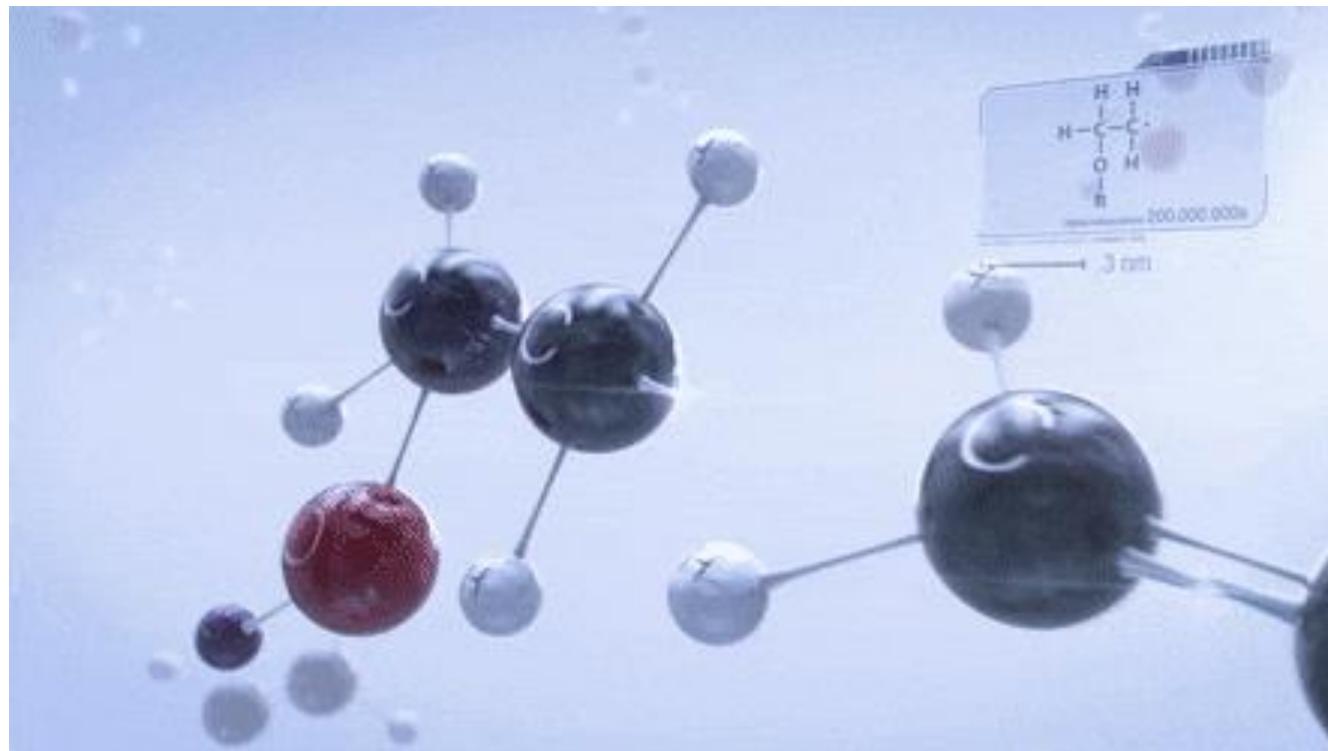
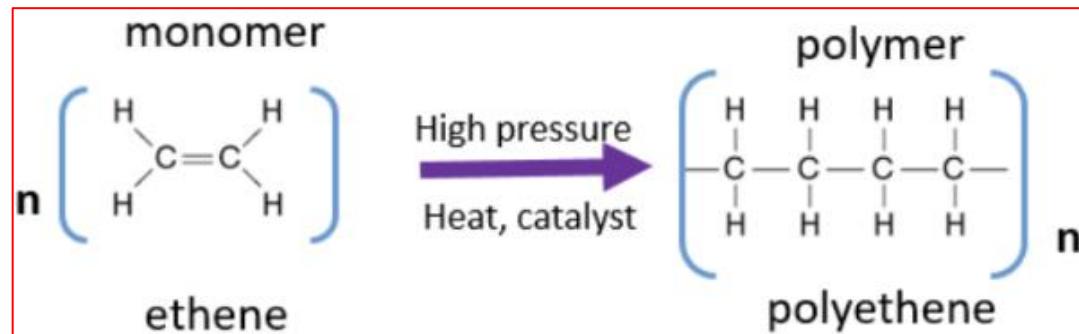
Networked Polymers

E.g., a rubber band is a collection of flexible polymer chains cross-linked with sulfur, it is a single molecule, vulcanized rubber, urea-formaldehyde resins.

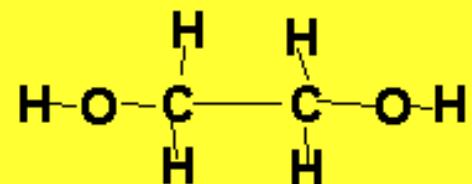
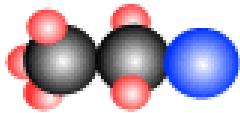
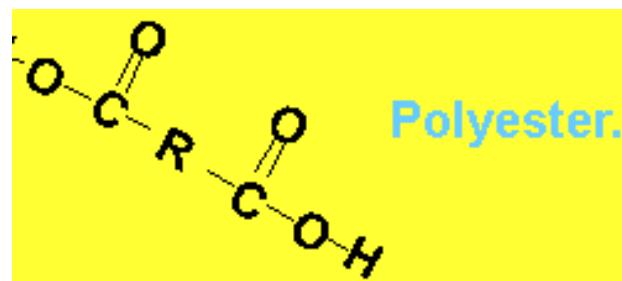
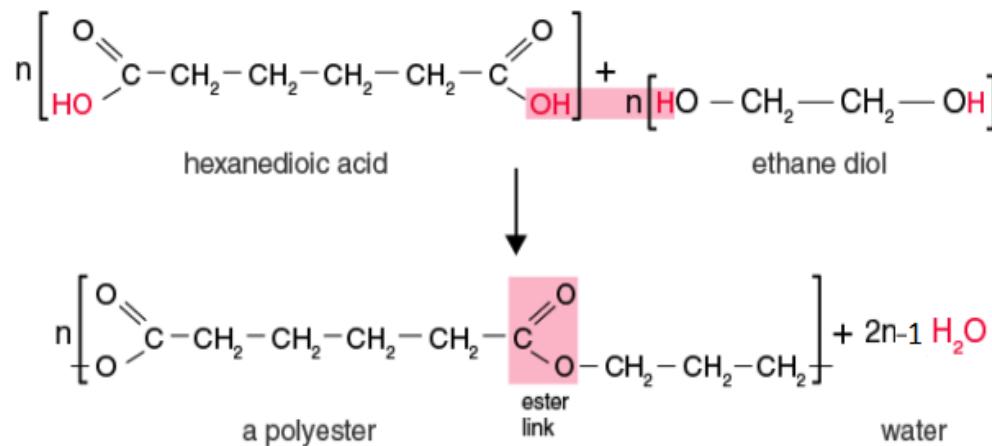
E.g., Bakelite, melamine etc.,

Classification of polymers-based on the method of synthesis

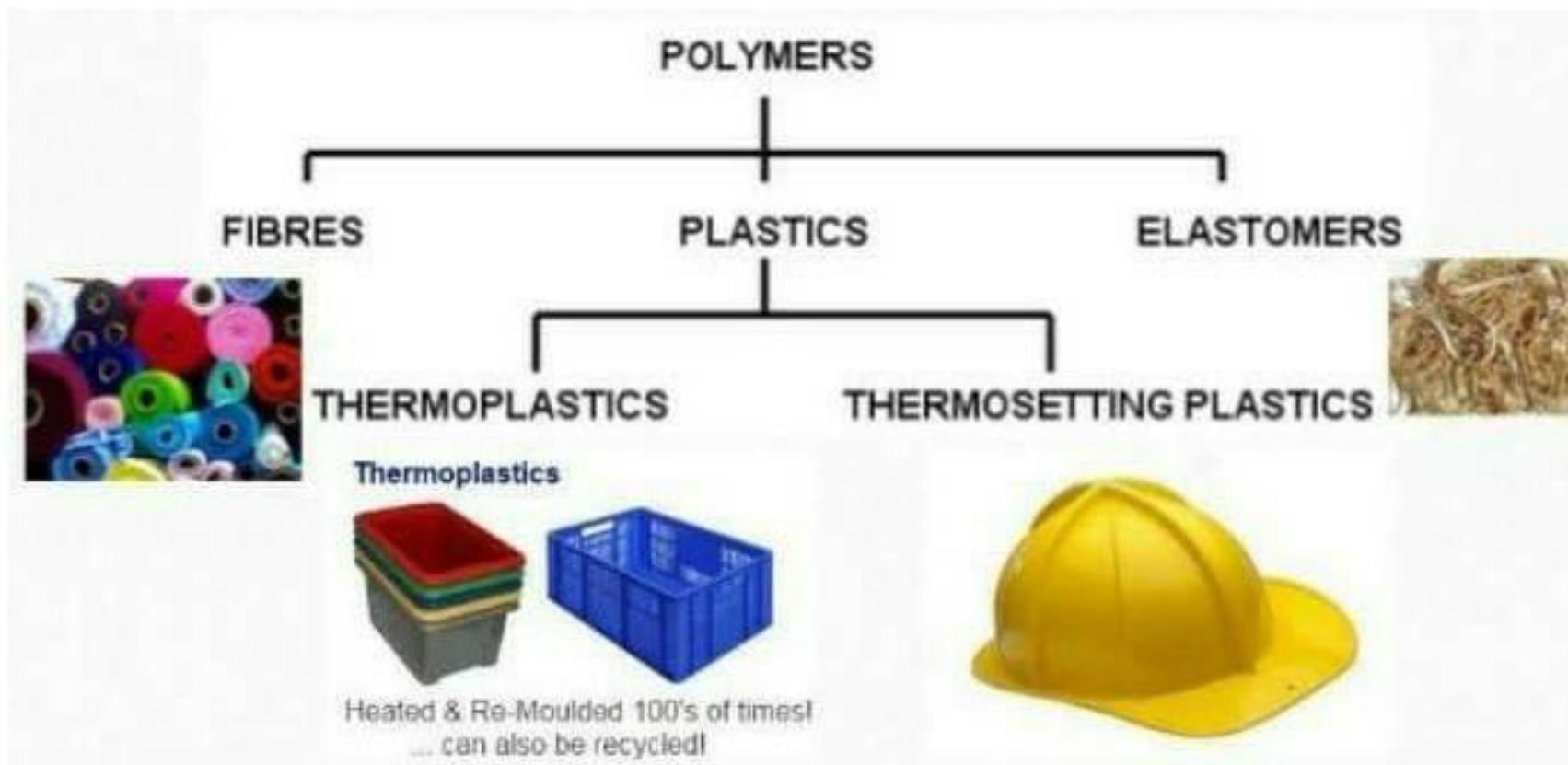
Addition Polymers



Condensation Polymers



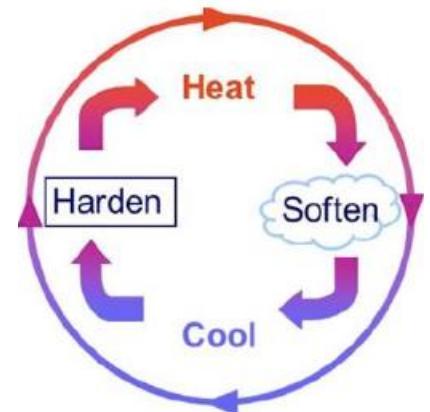
Classification of polymers-based on molecular forces



Classification of polymers-based on molecular forces

Thermoplastic polymers

- Linear polymers with long chains that **soften on heating** and **harden on cooling** reversibly.
- These are **solid at room temperatures** and **viscous liquids** when heated. So, they are shaped by extrusion, molding or pressing.
- They can be **recycled and reused** several times by heating and cooling.
- These plastics will return to its original shape, unless damaged due to overheating or overstretching; this property is called **plastic memory**. E.g., polystyrene, polyethylene, PVC, PTFE.
- Applications: Milk jugs, soft drink bottles, etc.

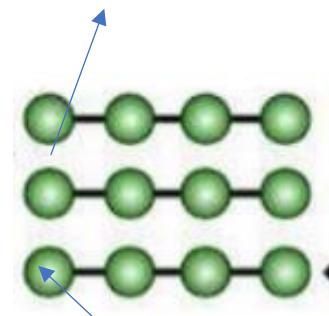


Classification of polymers-based on molecular forces

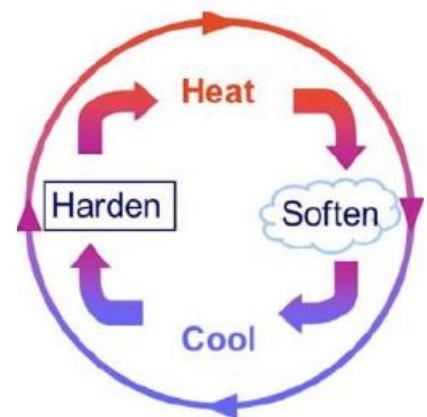
Thermoplastic polymers

- They are synthesized by **addition polymerization**
- They are straight chain or slightly branched polymers, held together by **weak van der Waal's forces of attraction**.
- Molecules of thermoplastics are **linear**, or long chains with very few entanglements.
- So, when heat is applied, molecules move apart and **disentangle**, causing them to soften, making them **malleable** to reshaping.
- On cooling, the **molecules regain their original positions**, making the plastic stiff and hard again. This process of heating and cooling can be repeated several times.
- They are generally **soluble** in **organic solvents**.

No links b/w polymers chains helps movement



Monomers

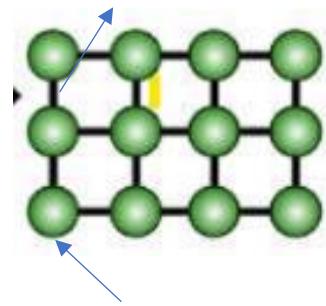


Classification of polymers-based on molecular forces

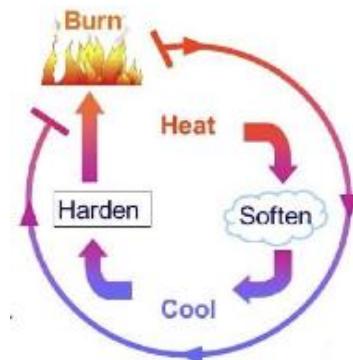
Thermosetting polymers

- Thermosetting polymer or resins, also called thermoset, is a polymer that is **irreversibly hardened** by curing from a soft solid or viscous liquid prepolymer or resin
- Various polymer chains are **cross-linked** three dimensionally using **strong covalent bonds** or cross links.
- They are prepared by **condensation polymerization**.
- They resist heat softening and solvent attack.
- Once **set after curing**, they cannot be softened and recycled. E.g., polyester resins like fiber glass; polyurethanes: mattresses, coatings, adhesives; vulcanized rubber; bakelite: phenol-formaldehyde resin.

Links b/w polymers
chains stops
movement b/w them



Monomers



Classification of polymers-based on molecular forces

Thermoplastic polymers	Thermosetting polymers
Linear, long chain polymers, held together by weak van der Waal's forces	Long chain polymers that are interlinked three dimensionally by strong covalent bonds
They are formed by addition polymerization	They are formed by condensation polymerization
They are different types of thermoplastics, some rigid, and others extremely flexible, though they are malleable and flexible at high temperatures	They are rigid and non-flexible at high temperatures, and are usually brittle and strong
Softens upon heating, and harden on cooling reversibly due to the weak interlinking forces	Upon heating and cooling, they harden irreversibly, they set permanently.
Repeated heating and cooling does not affect their structure, and the changes are purely physical	Prolonged heating causes charring of polymers
Soluble in organic solvents	Insoluble in organic solvents
E.g., Polyethylene, polyvinyl chloride	E.g., Polyester resin, bakelite

Classification of polymers-based on molecular forces

Thermoplastics

1. Soften on heating
2. Long chain linear
3. By addition polymerisation
4. Can be reshaped and reused
5. Soft weak and less brittle
6. Soluble in org. solvents
7. Reclaimed for wastes

Thermosetting polymers

1. Do not soften on heating
2. 3-D structure
3. By condensation polymerisation
4. Can not be reshaped
5. Hard and strong
6. Insoluble in org. solvents.
7. Can not be reclaimed

THERMOPLASTICS



(Can be melted repeatedly)

THERMOSETS



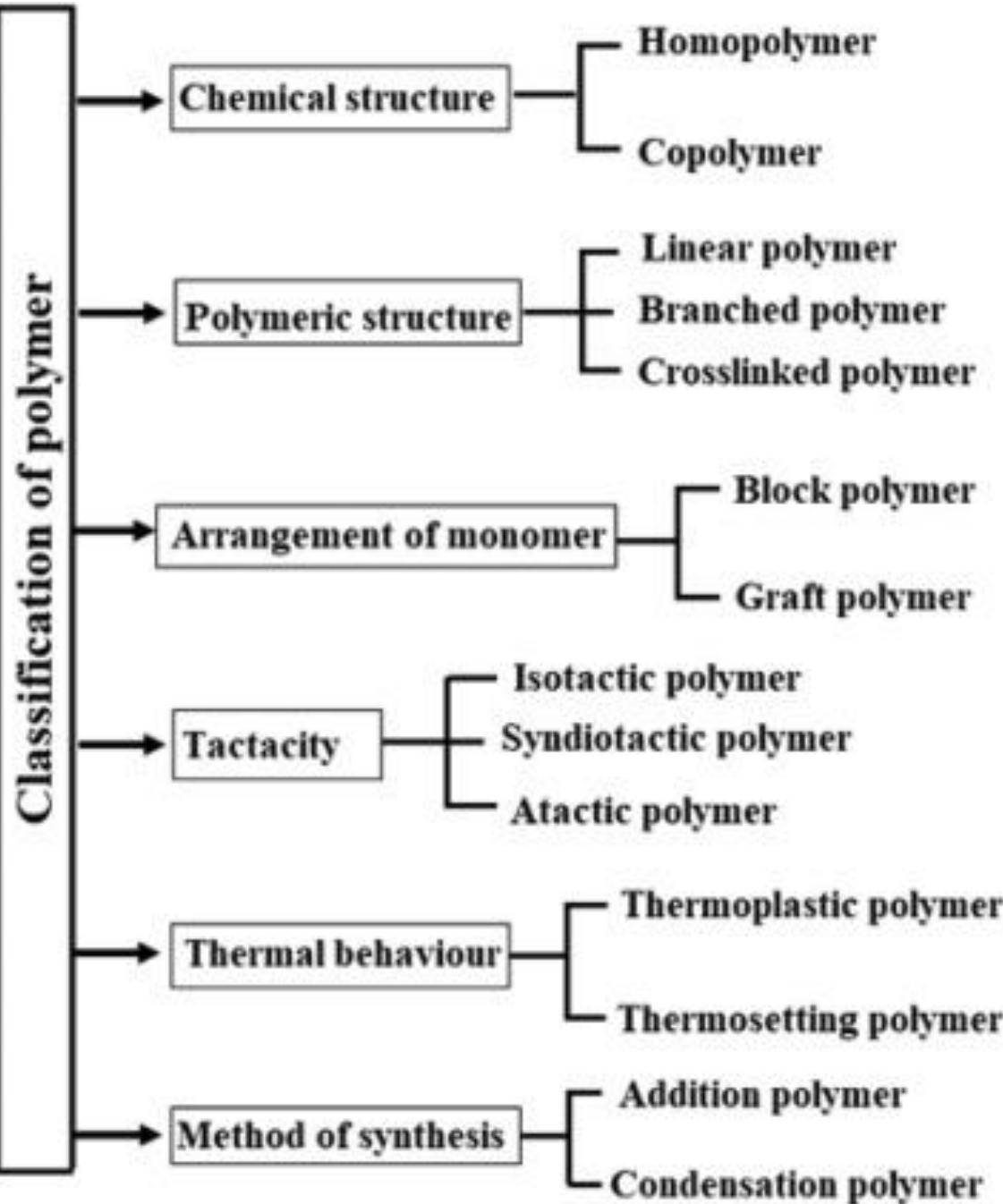
(Once shaped, cannot be melted)

Classification of polymers-based on molecular forces

Elastomers

- Elastomer is a polymer with **viscoelasticity** (i.e., both viscosity and elasticity) and weak intermolecular forces and low Young's modulus.
- Elastomers can be stretched to **at least thrice its length** but returns to its original shape and dimensions when the stretching force is released.
- They exist in the form of a **coil in the normal state**, and hence can be **stretched like a spring**.
- The elasticity is caused by **lengthening and shortening** of their polymeric chain springs. E.g., rubber, latex





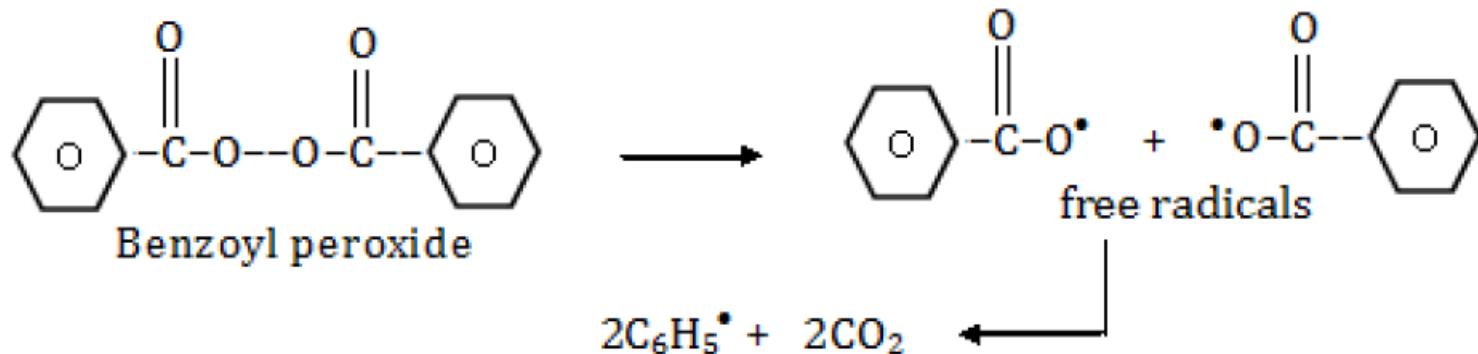
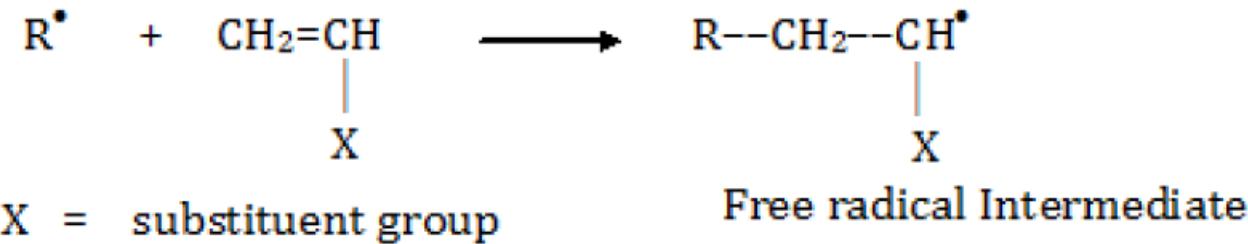
Addition Polymerization- Mechanism

1. Chain initiation:-

a) Formation of free radicals from the initiator.



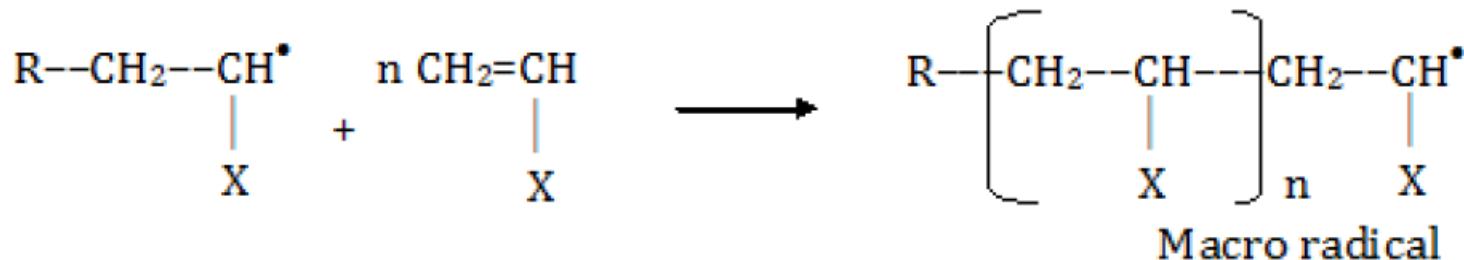
b) Addition of free radicals to monomer to form a free radical intermediate.



Addition Polymerization- Mechanism

2. Chain propagation:-

Here addition of monomer molecules to the intermediate takes place one by one leads to the formation of macro-radicals.

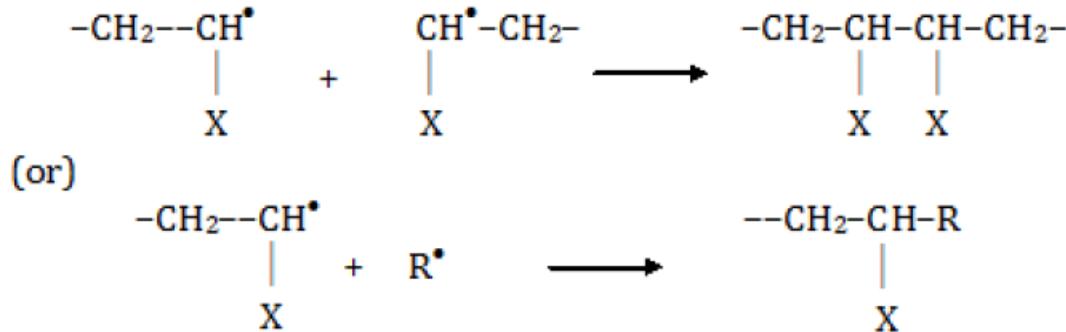


3. Chain termination:-

The growing polymer chain is terminated by many ways.

a) Recombination:-

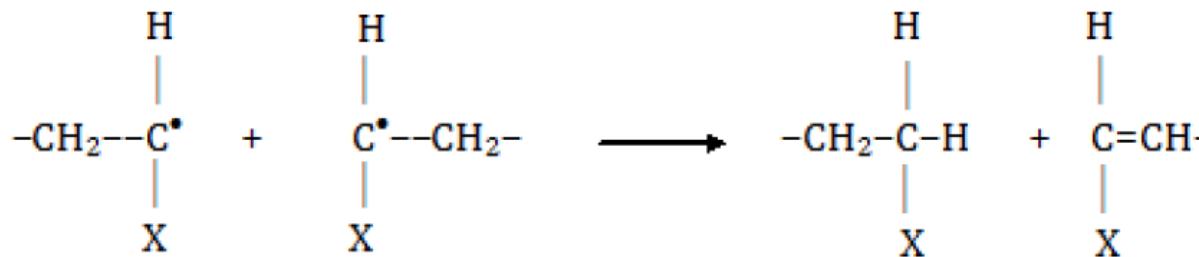
Combination of two free radicals leads to termination.



Addition Polymerization- Mechanism

b) Disproportionation:-

Transfer of 'H' atom from one radical to another leads to formation of two macro molecules, one of them with a double bond.



Ionic polymerization

Cationic polymerization

Anionic polymerization

Cationic polymerization:-

Monomers with electron releasing groups (-OCH₃, -OC₂H₅ & -C₆H₅ etc) undergo cationic polymerization in the presence of Lewis acids like AlCl₃, BF₃, SnCl₄ etc. Cationic polymerization takes place with higher rates even at low temperature.

Anionic polymerization:-

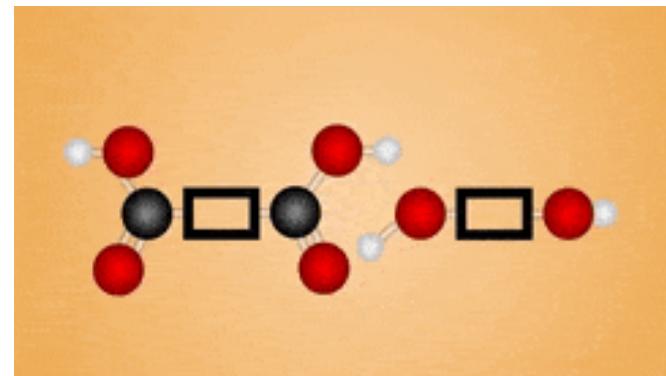
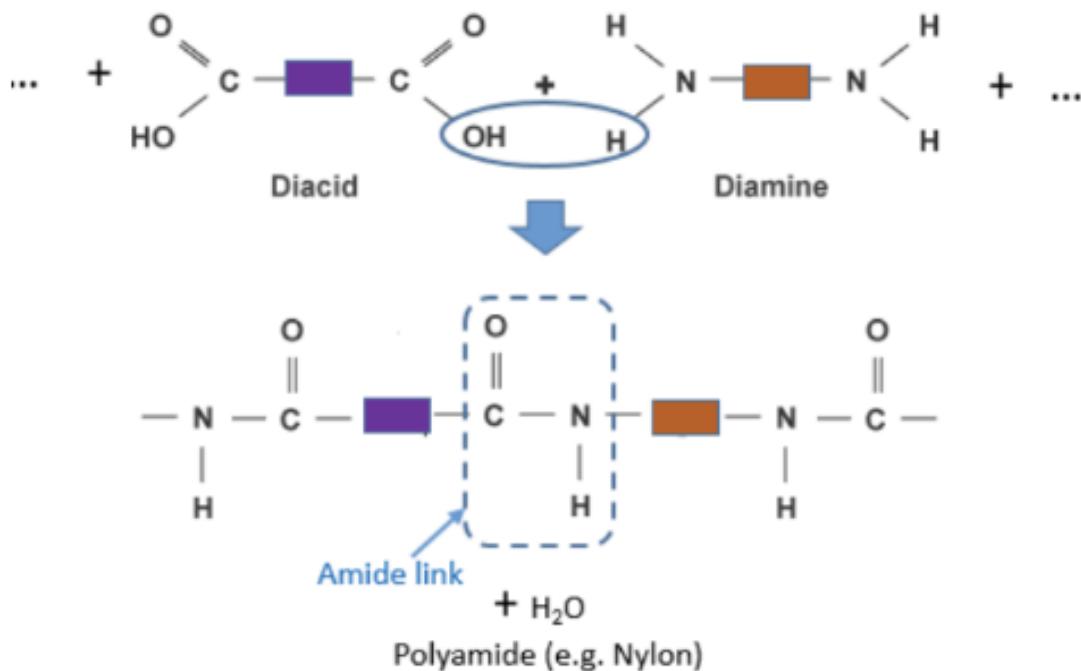
Monomers with electron withdrawing groups (-CN, CH₃COO- and C₆H₅ etc) undergo anionic polymerization in presence of sodium or potassium amide.

Classification of polymers-based on the method of synthesis

Condensation or step-growth polymerization

Polymerization occurs stepwise by reaction between reactive functional groups, followed by **elimination of small molecules** such as water, ammonia, HCl, etc.

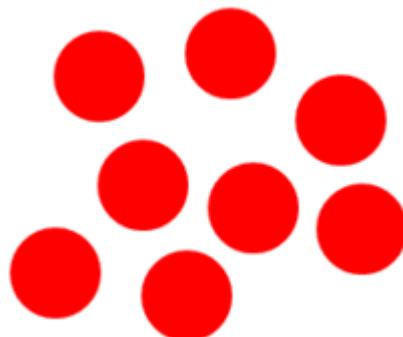
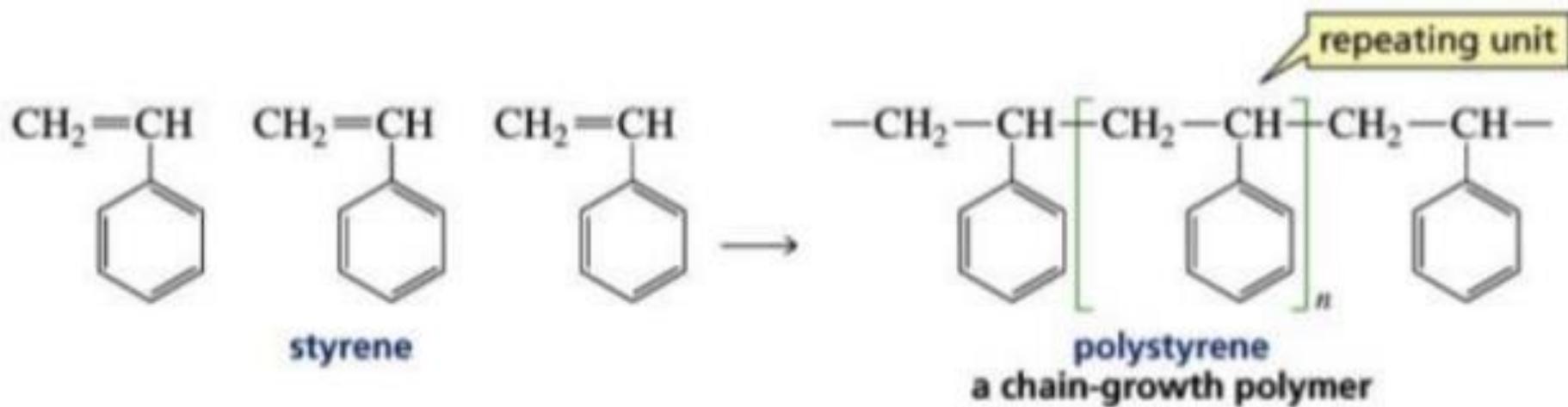
Diacid + Diamine \longrightarrow Polyamide



Classification of polymers-based on the method of synthesis

Chain growth polymers

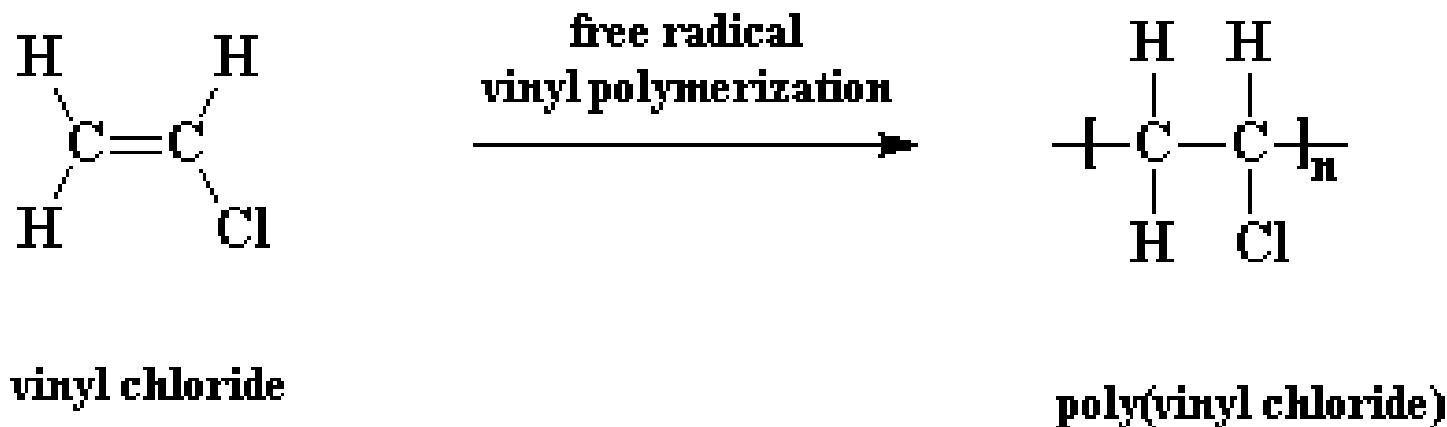
Successive addition of monomeric units to the growing chain.



Individual polymers

Preparation of Poly vinyl chloride

Polyvinyl chloride is prepared by heating a water emulsion of vinyl chloride in presence of benzyl peroxide or hydrogen peroxide in autoclave under pressure.



Properties

Polyvinyl chloride is

- Colourless
- Odourless
- Non-inflammable
- Chemically inert
- Soluble in hot ethyl chloride

Uses

Used for the preparation of

- Safety helmets



- Light fittings
- Tyres, cycles



➤ Refrigerator components



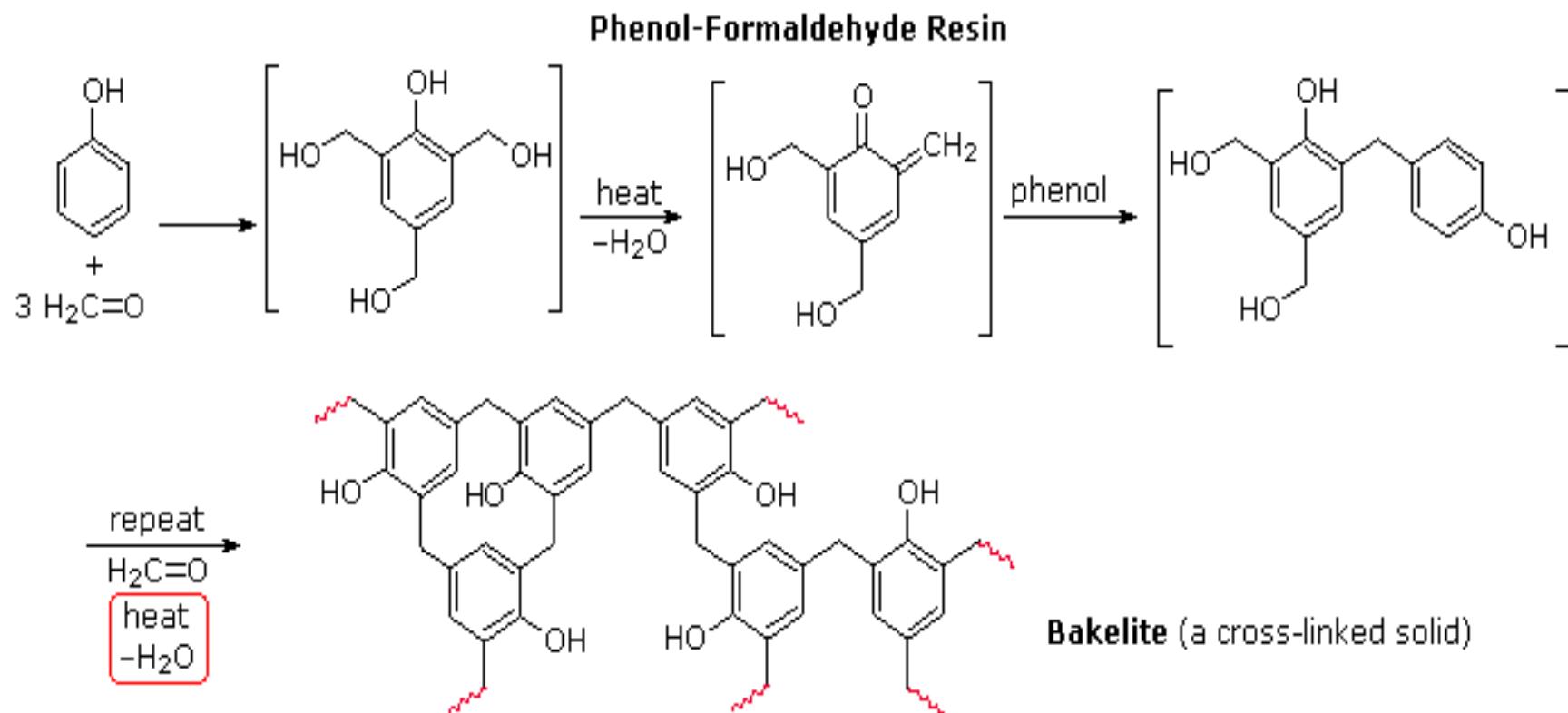
➤ Sheets, which are employed for tank linings



Phenol formaldehyde resins :Bakelite Preparation

These are formed by the poly condensation between phenol and formaldehyde.

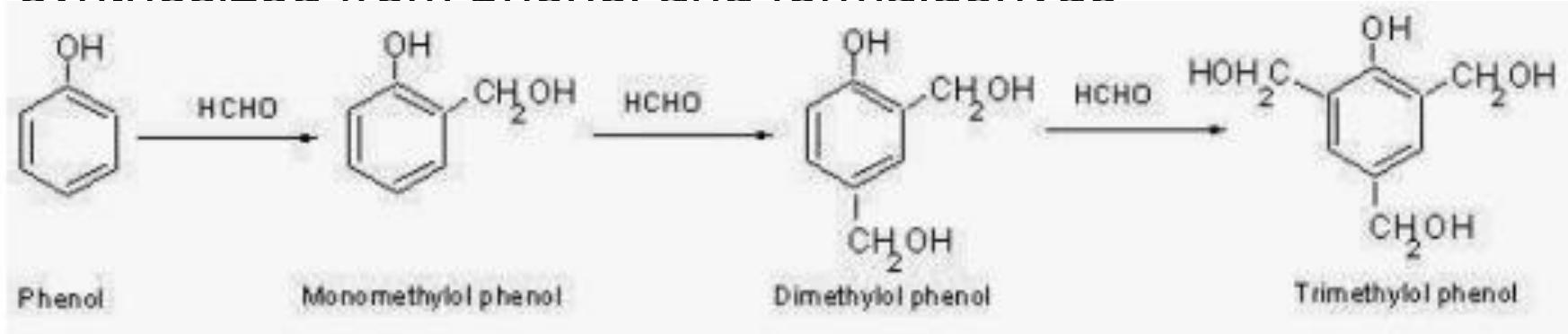
The reaction is catalysed by acid or base



Steps in synthesis of Bakelite

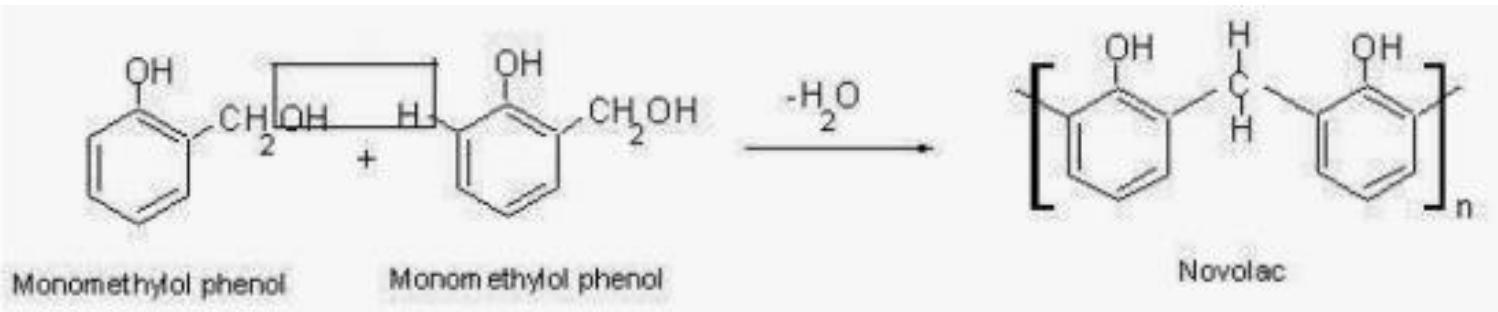
I. Methylolation

- In this step, mono, di and tri methylol phenols are synthesized from phenol and formaldehyde



II: Formation of novolac resins

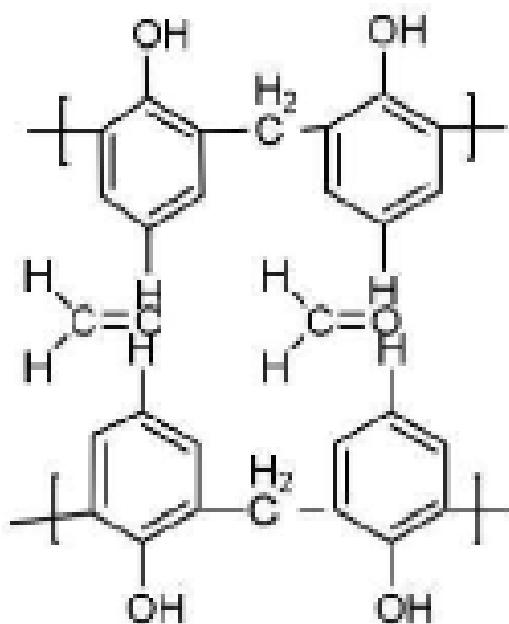
- Monomethylol phenols condense together to form novolac resins as shown below



Steps in synthesis of Bakelite

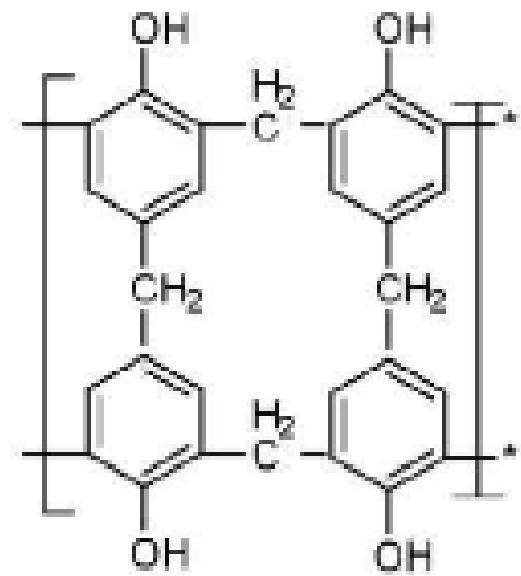
III: Formation of bakelite

- Novolac is heated further in the presence of HCHO producer, i.e., hexamethylene tetraamine (curing agent) at high temperature and pressure to form cross-linked polymers, bakelite.



Novolac

Hexamethylene Tetraamine



Bakelite

Properties of Bakelite

These are

- Rigid
- Hard , resistant to heat
- With stand to high temperature
- Good insulator

Uses of bakelite

Used for the preparation of

- Electrical insulator parts like



- Switches



➤ Plugs

➤ Handles

Moulded articles like



➤ Telephone parts



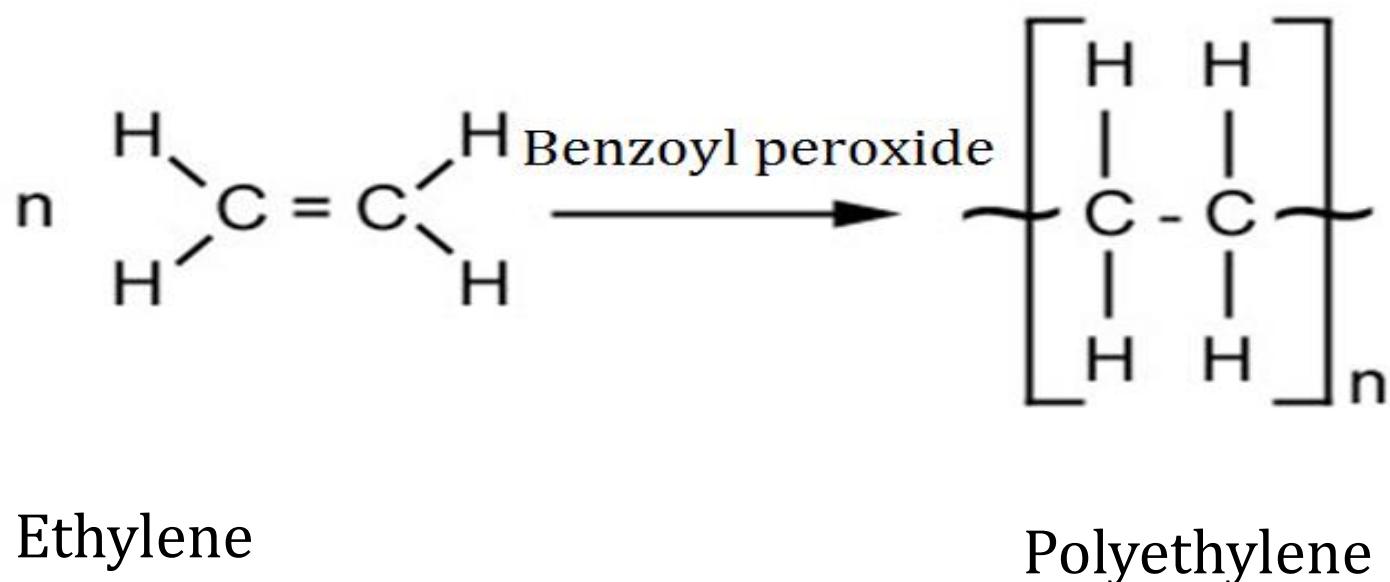
➤ Cabinets for T.V



➤ Cabinets for radio

Polyethylene Preparation of LDPE

LDPE is prepared by heating ethylene at 100°C - 300°C under high pressure 1500-3000 atm in presence of benzoyl peroxide(initiator) and benzene(solvent).



Properties

- Density range from 918-935 kg/m³
- Very tough
- Flexible

Uses



❖ Domestic ware

❖ Squeeze bottles



❖ Tubing



❖ Cold water tanks

Preparation of HDPE

HDPE is prepared by heating ethylene at 300°C under 1 atm pressure in presence of aluminum based oxide(catalyst) and paraffin (diluting agent).

Properties

- Density range from 935-965 kg/m³
- Stronger
- Stiffer

Uses

- ☒ Dustbins





☒ Bottle crates



☒ Pipes

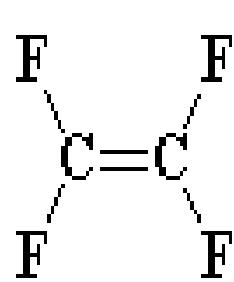


☒ Fluid containers

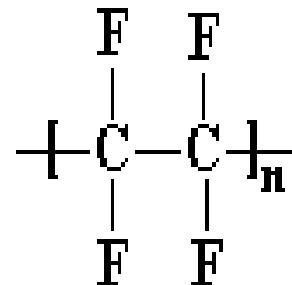
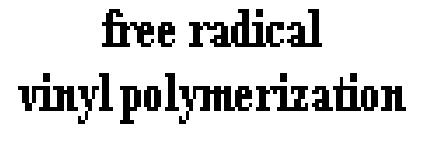
Teflon (poly tetra flouro ethylene ,PTFE) or Fluon

Preparation

Poly tetra flouro ethylene is prepared by polymerisation of a water emulsion of tetra flouro ethylene in presence of benzoyl peroxide under pressure.



tetrafluoroethylene



polytetrafluoroethylene

Properties

1. Due to presence of highly electro negative fluorine atom, very strong attractive forces between different chains.
2. Due to strong attractive forces

Teflon is extreme tough

High softening point ($>350^{\circ}$)

High chemical resistance towards all chemicals

Except hot alkali metal and hot fluorine

Uses:

Used as

- Insulating material for motors, cables



- Coatings



- Impregnating glass
- Asbestos fibre

➤ Clothes



➤ Wires

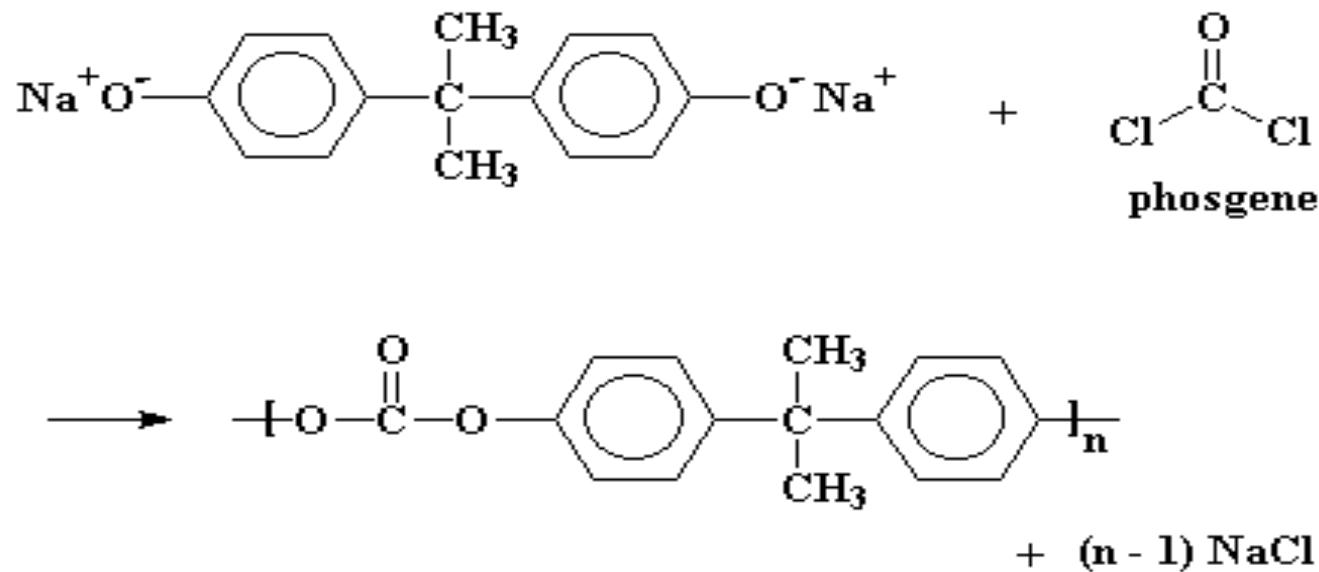
➤ Fittings



Poly Carbonates

Polymers of containing -o-co-o- functionality
Preparation

By the treatment of bisphenol-A with phosgene in presence of sodium hydroxide.



Properties

Polycarbonates

- Good electrical insulators
- Heat and flame resistance
- Easily soluble in organic solvents and alkali solvents
- Undergo large plastic deformation without cracking
- Highly transparent to visible light
- Low scratch resistance

Uses

Used in



Preparation of Compact disc, DVD'S

Construction industry



Automotive components



➤ Aircraft components



➤ Manufacture of lenses like sunglasses, eyeglasses

Conducting Polymers

- A conducting polymer is an organic based polymer that can act as a semiconductor or a conductor.
- The most widely studied organic polymers are
 - Polyacetylene
 - Polyaniline (PANI)
 - Polypyrroles
 - Polythiophenes
 - Polyphenylene vinylenes

Conducting Polymers

- Conducting polymers (CPs) are extensively conjugated molecules: they have alternating single and double bonds. In these molecules, electrons can move from one end of the polymer to the other through the extended p-orbital system.
- Hence CPs are known to be either semiconductors or conductors giving them unique optical and electrical properties.
- Most polymers are poor conductors due to non-availability of large number of free electrons in the conduction process.
- However, conducting polymers possess electrical conductivity like metalconductors

Different types

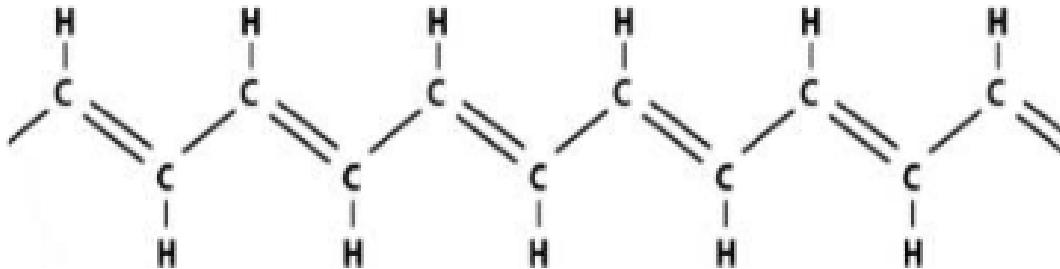
- Intrinsically conducting polymers (ICP)
- Doped conducting polymers
- Extrinsically conducting polymers (ECP)

Conducting Polymers

- Density of charge carriers
- Their mobility
- The direction
- Presence of doping materials
- Temperature

Intrinsically Conducting Polymers (ICPs)

- Alternating single and double bonds is called conjugated double bonds.
- In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized “sigma” (σ) bond which forms a strong chemical bond.
- In addition, every double bond also contains a less strongly localized “pi” (π) bond which is weaker.
- Conjugation of sigma and pi-electrons over the entire backbone, forms valence bands and conduction bands. Eg: Poly-acetylene polymers like poly-p-phenylene, polyaniline, polypyrrole.



Doped Conducting Polymers

- It is obtained by exposing a polymer to a charge transfer agent in either gas phase or in solution.
- ICPs possess low conductivity ($10^{-10}/\text{Ohm.cm}$), low ionization potential and high electron affinity.
- So, they can be easily oxidized or reduced.

Doping

The conductivity of ICP can be increased by **creating positive charges (oxidation)** or by **negative charges (reduction)** on the polymer backbone. This technique is called DOPING .

The polymer structure is disturbed - either by removing electrons from (oxidation) or inserting them into (reduction) the material.

Types of materials

- Oxidation with halogen (or p-doping).
- Reduction with alkali metal (called n-doping)

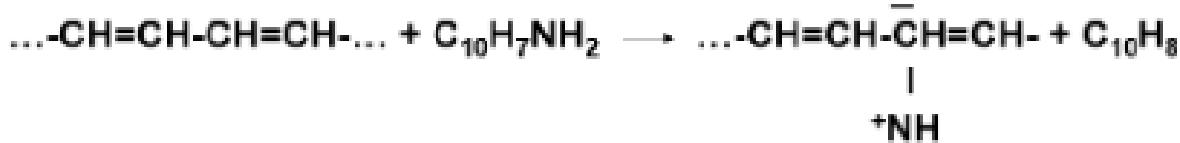
Intrinsically Conducting Polymers (ICPs)

- It involves treating an intrinsically conducting polymer with a Lewis acid which leads to oxidation process and positive charges on the polymer backbone
- Some of the p-dopants are I₂, Br₂, AsF₅, PF₅ etc.



N-doping

- It involves treating an ICP with a Lewis base which leads to reduction and negative charges on the polymer backbone.
- Some of the n-dopants are Li, Na, Ca, FeCl₃, naphthylamine etc.



Extrinsically Conducting Polymers (ICPs)

- These are those polymers whose conductivity is due to the presence of externally added ingredients in them.

(1) Conductive element filled polymer:

- It is a resin/polymer filled with carbon black, metallic fibers, metal oxides etc.
- Polymer acts as a binder to those elements.
- These have good bulk conductivity and are low in cost, light weight, strong and durable.
- They can be in different forms, shapes and sizes.

(2) Blended element filled polymer:

It is product obtained by blending a conventional polymer with a conducting polymer either by physical or by chemical change. Such polymers can be processed and possess better physical, chemical and mechanical strength.

Applications of conducting polymers

- As sensors into clothing
- Conducting polymer textiles as a camouflage for defense machinery. Since the textiles have no sharp edges, they absorb more than 50% of the incident microwave radiation.
- In LEDs
- In controlled drug release applications etc.

Applications of conducting polymers

Group 1

Electrostatic materials
Conducting adhesives
Artificial nerves
Antistatic clothing
Piezoceramics
Active electronics:

Group 2

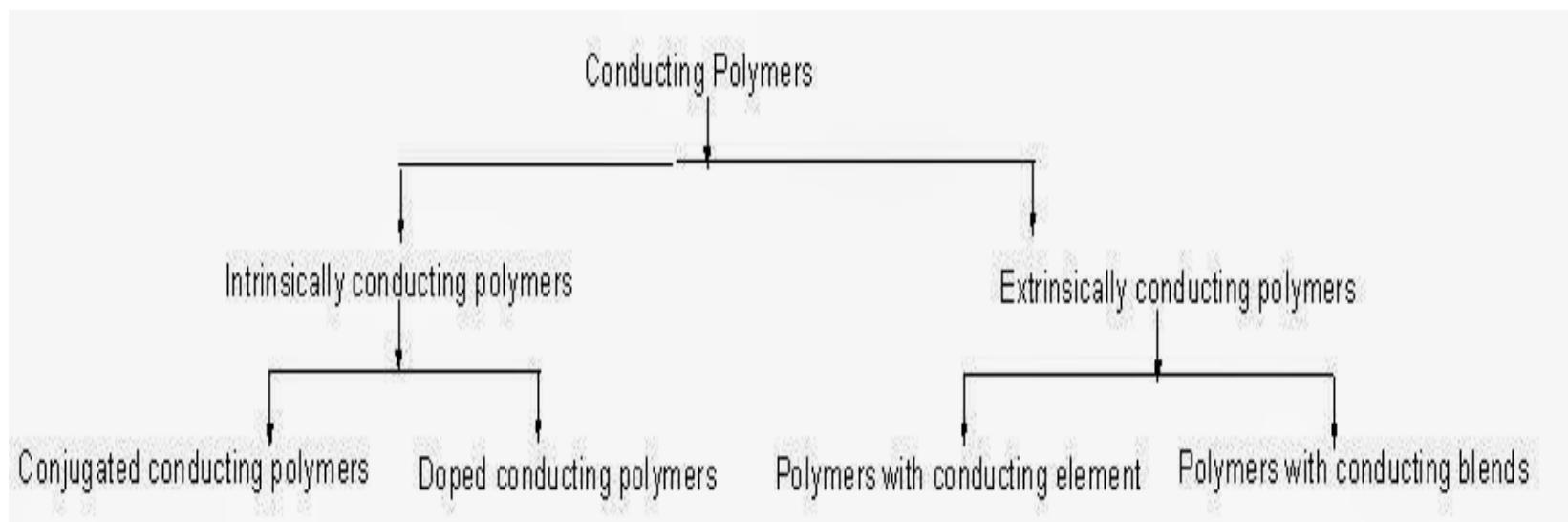
Molecular electronics
Electrical displays
Chemical & thermal sensors
Rechargeable batteries
Drug release systems
Optical computers
Ion exchange membranes
Electromechanical actuators

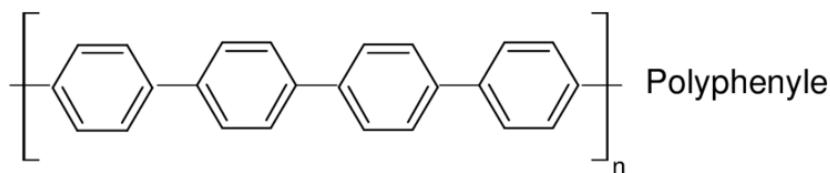
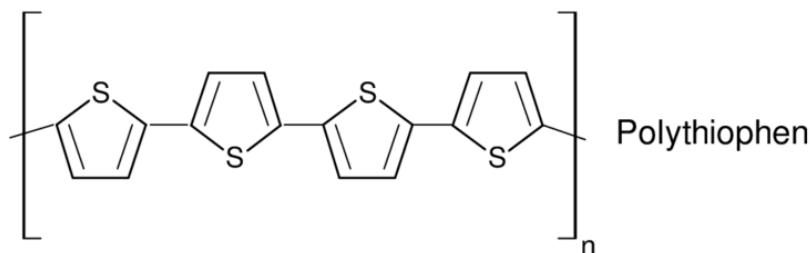
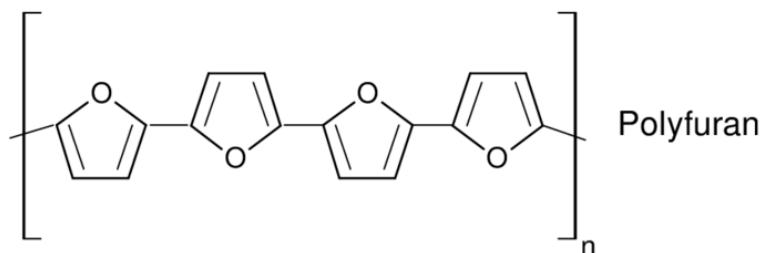
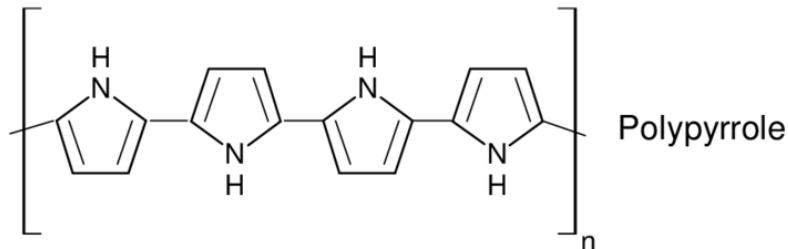
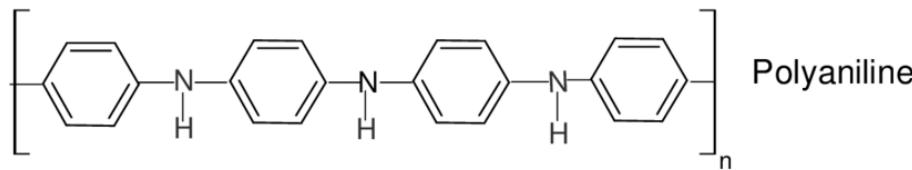
*The first group utilizes their conductivity as its main property.
The second group utilizes their electroactivity.*

Conducting Polymers

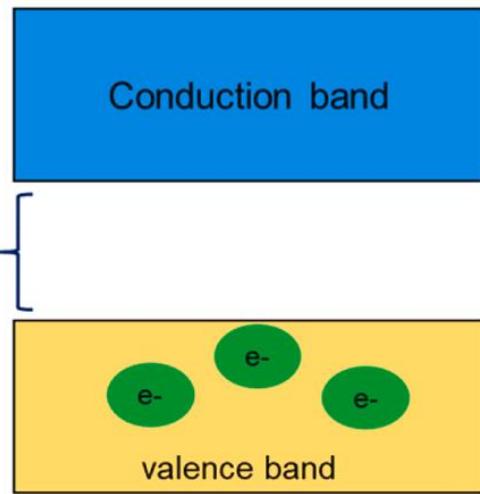
- Polymers that can conduct electricity are called conducting polymers.
Ex: Poly acetylene, poly aniline, poly pyrrole, poly thiophene, poly quinolene etc.

On the basis of their conduction properties conducting polymers are classified into two types

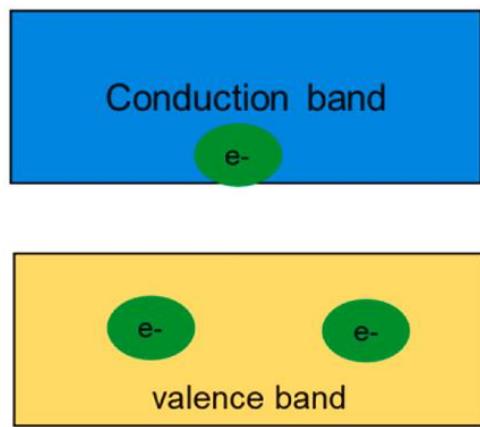




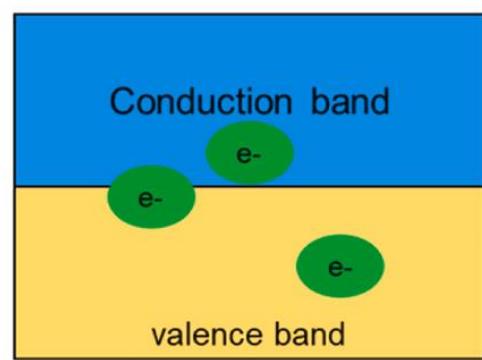
Energy



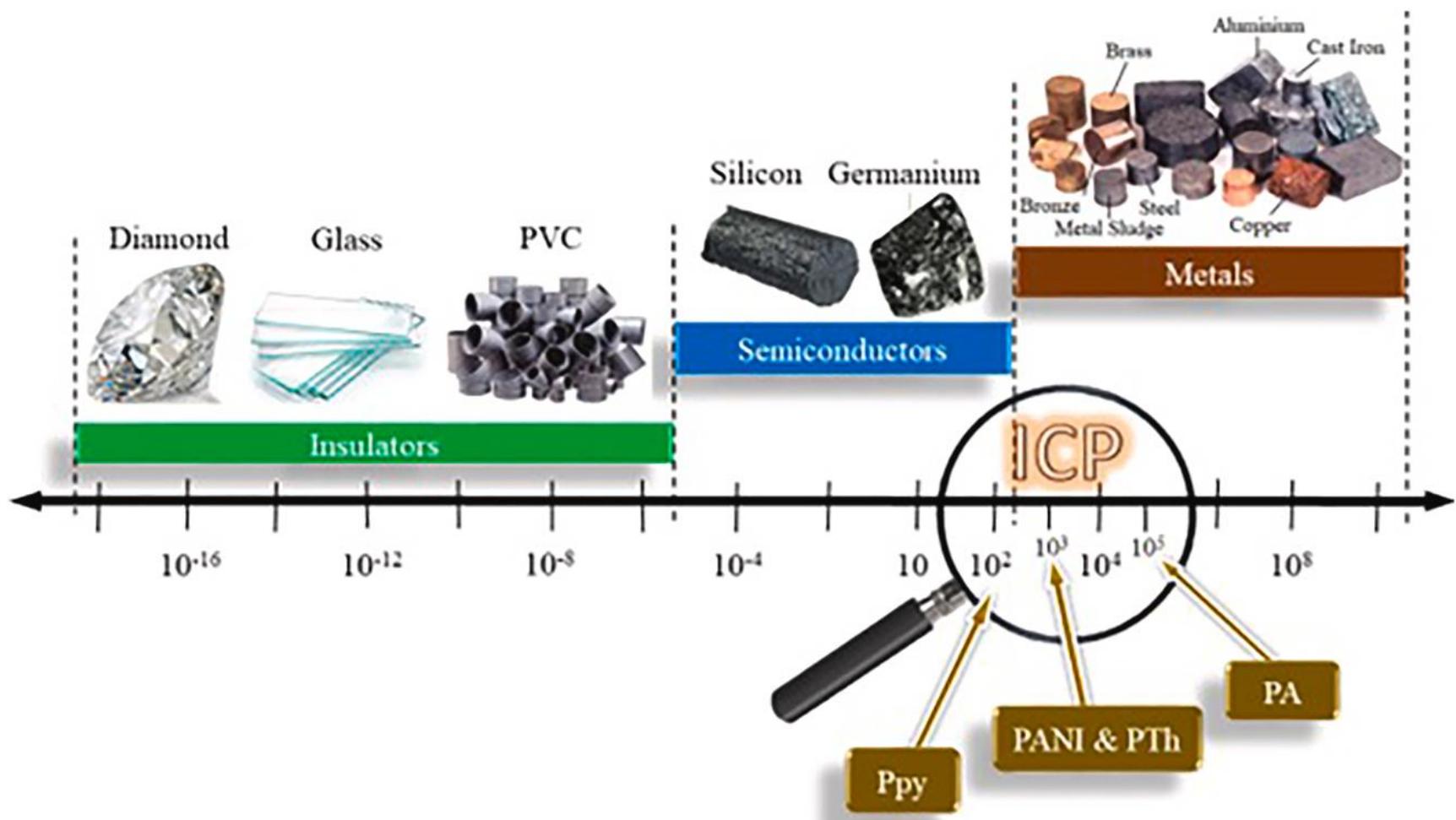
Insulator



Semiconductor



Conductor



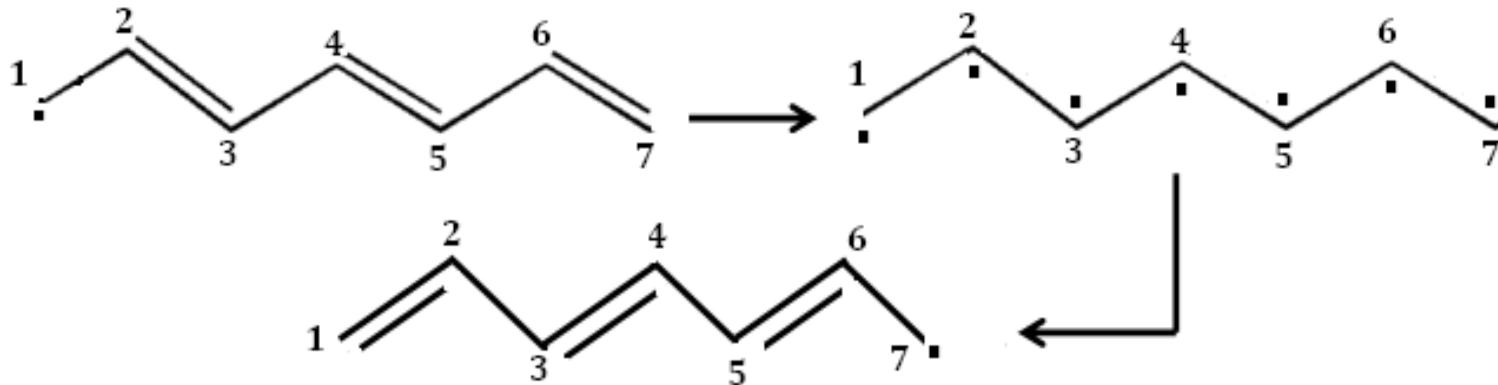
Conducting Polymers

Intrinsically Conducting Polymers

Conjugation

- These polymers contain conjugated or delocalized $\pi - e^-$ pairs in the backbone responsible for conduction.
- The orbital's of conjugated $\pi - e^-$ form valency band as well as conduction band and they are extended over the entire polymer molecule.
- When current is passed electrons enter conduction band due to shifting of $\pi - e^-$.
- Ex; Conduction of poly acetylene due to conjugation.
- When current is passed into poly acetylene, the electron enters the unhybridised P-orbital of carbon atom and moves through the C – C bonds.

Conducting Polymers



Doped conducting polymers

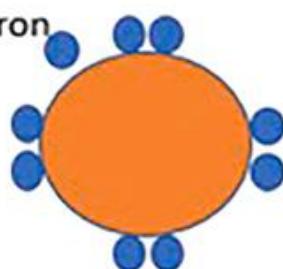
- Polymers can conduct due to doping and by using doping agents or dopants.
- Doping of conducting polymers can be two different types.
 - ♠ p-Doping (or) Oxidative Doping
 - ♠ n-Doping (or) Reductive Doping

CPs

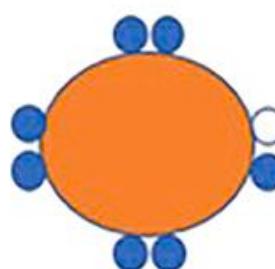
n-Doping
(additional electron)

p-Doping
(additional hole)

Extra electron



Electron hole



Dopants

Neutral

- ❖ Br₂
- ❖ I₂



CPs

Ionic

- ❖ FeClO₄
- ❖ LiClO₄



electrons

Organic

- ❖ CH₃COOH
- ❖ CF₃SO₃Na

Polymers

- ❖ PVA
- ❖ PVS

Metal oxides

- ❖ SnO₂
- ❖ TiO₂

Conducting Polymers

P-Doping (or) Oxidative Doping:

- In this method the polymer is treated with an oxidizing agent like Lewis acid which acts as a dopant.
- Examples of dopants used: FeCl_3 , I_2 etc.

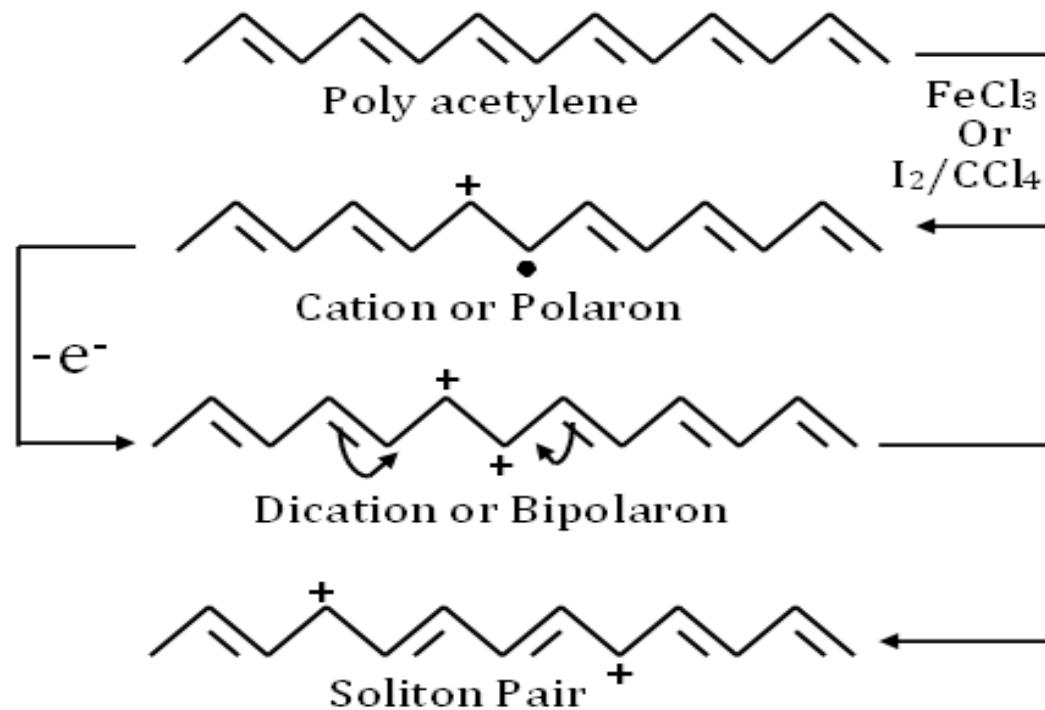


Mechanism of P-Doping:

- During this process, oxidation of polymer takes place due to dopant and forms a cation called Polaron.
- On further oxidation of polymer results in the formation of a dication or bipolaron.

Conducting Polymers

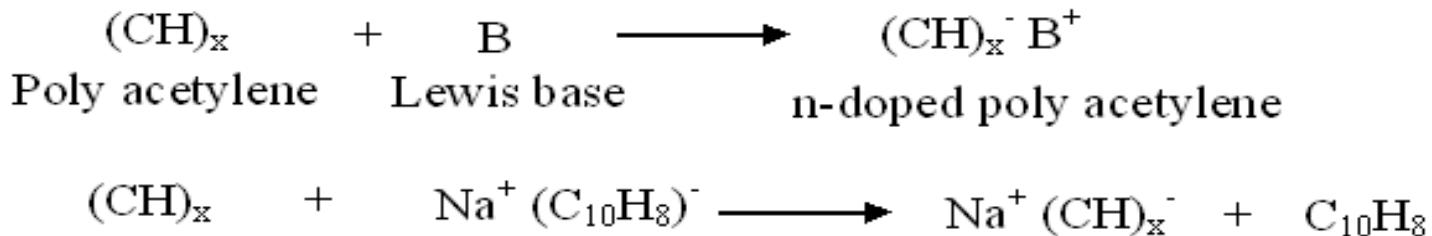
- The charges get separated by forming a soliton pair.
- The cation occupies the band gap between valency band and conduction band, thereby creating a conducting path.
- So electrons move through this path.



Conducting Polymers

n-Doping (or) Reductive Doping:

- In this method, the polymer is treated with a reducing agent like a Lewis base which acts as a dopant.
- Ex; Sodium Naphthalide $\text{Na}^+ (\text{C}_{10}\text{H}_8)^-$

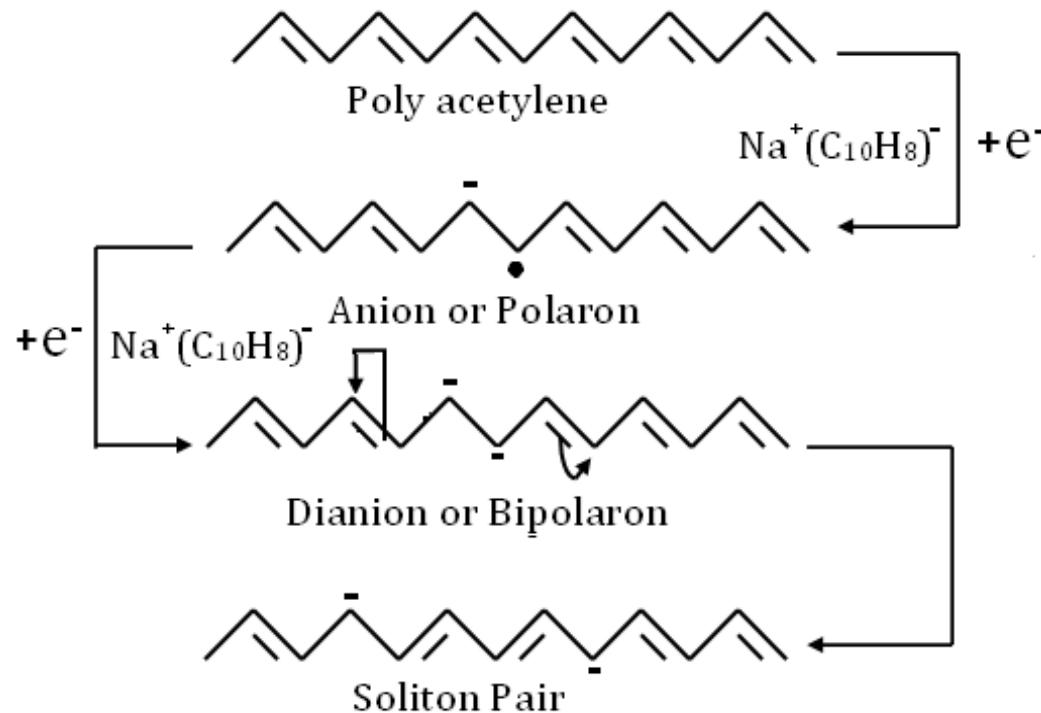


Mechanism of n-Doping:

- During this process, reduction of polymer takes place due to dopant and forms an anion called Polaron.
- On further reduction of polymer results in the formation of a dianion or bipolaron.

Conducting Polymers

- The charges get separated to form a soliton pair.
- The anions occupy the band gap between valency band and conduction band thereby creating a conducting path.
- So that electrons move through this path.



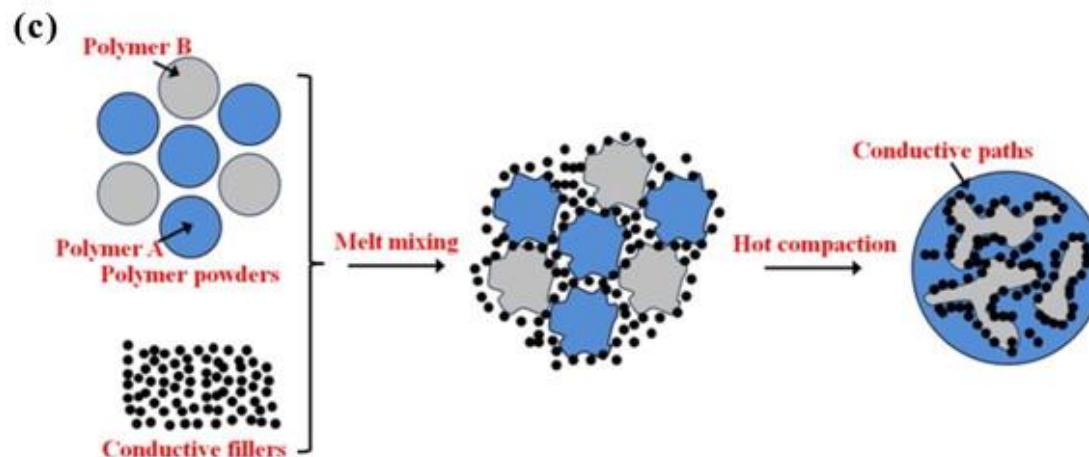
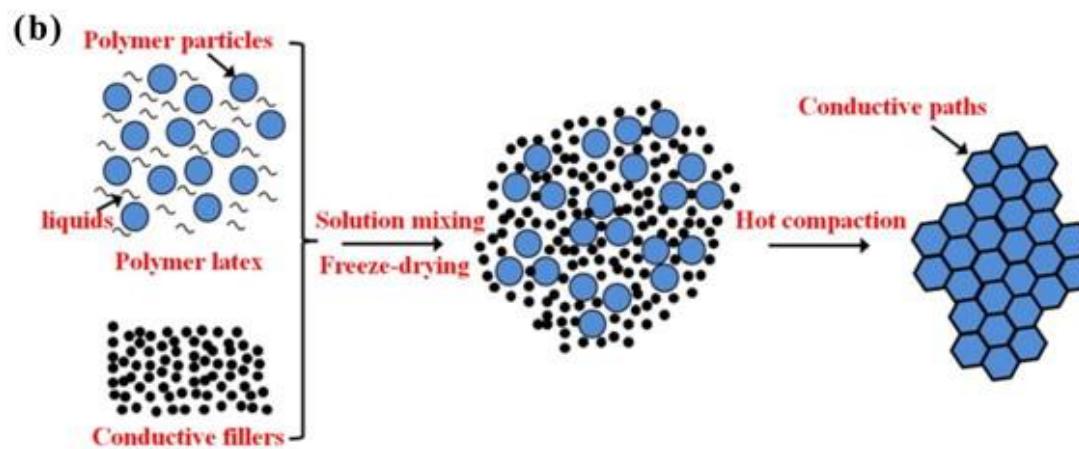
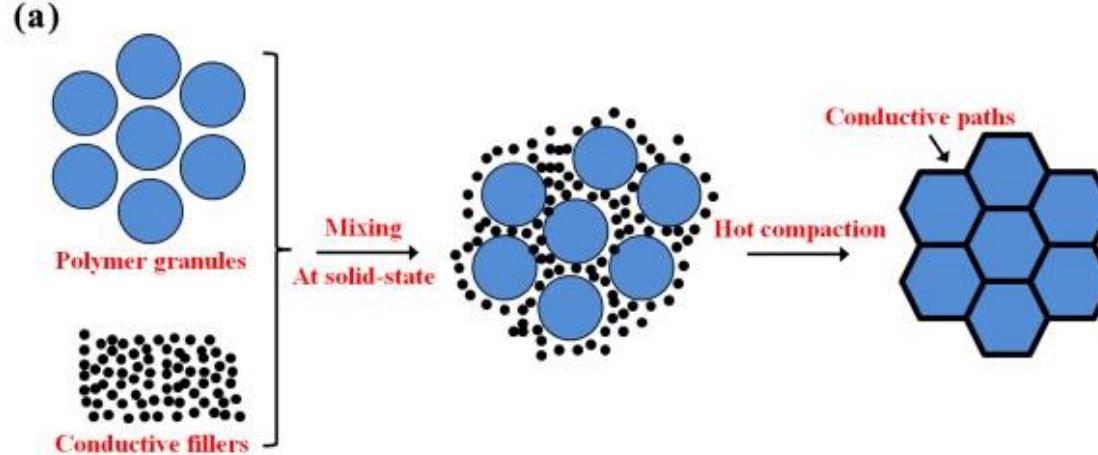
Conducting Polymers

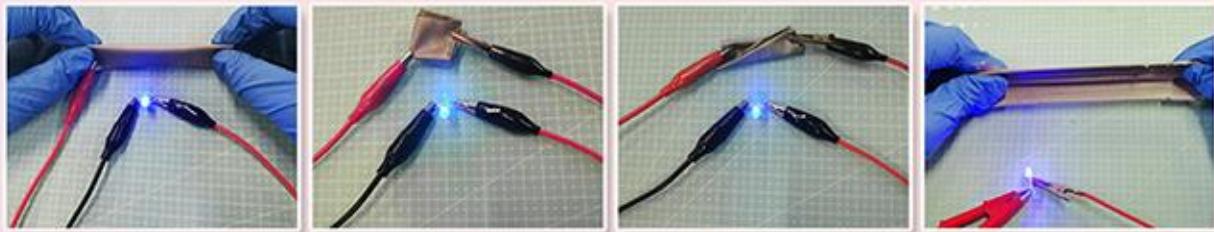
Extrinsically Conducting Polymers

- Some of the polymers conduct electricity due to externally added ingredients to them.
- They are of two types.
 - Polymers with conductive elements filled
 - Blended conducting polymers

Polymers with conductive elements filled

- In these polymers, the polymer acts as a ‘binder’ and holds the conducting element added so that the polymer becomes a conductor.
- Examples of conductive elements are carbon black, metallic fibers, metallic oxides etc.
- Minimum concentration of conductive element to be added so that the polymer becomes a conductor is called percolation threshold.
- The conductive elements added to create a conducting path in the polymer.



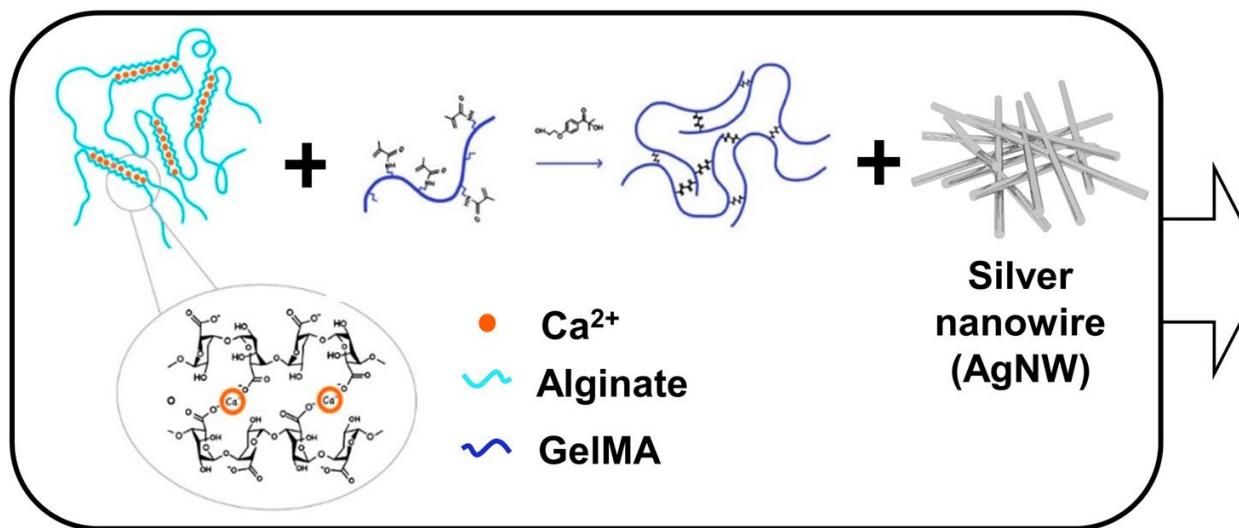


Conducting Polymers

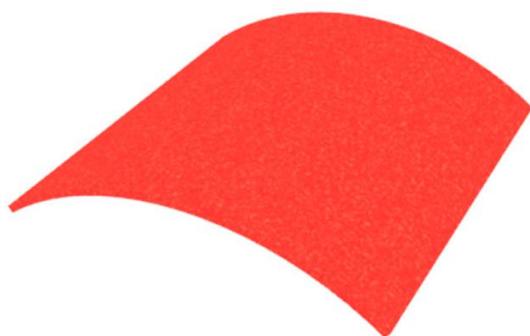
Blended conducting polymers

- These polymers are obtained by blending a conventional polymer with a conducting polymer.
- The polymer thus obtained has good chemical, physical, electrical properties and mechanical strength.

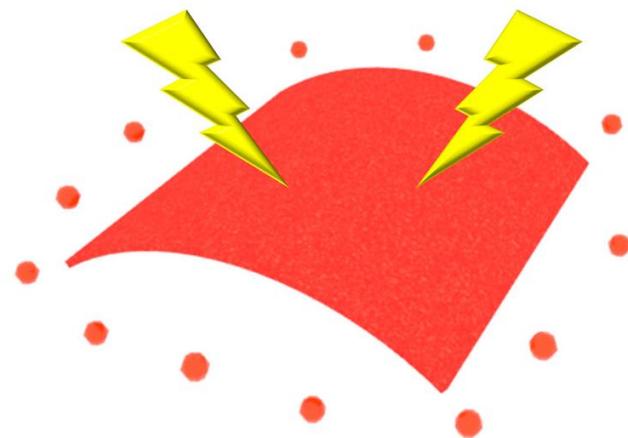
Ex; 40% pyrrole when blended with a conventional polymer, the combination gives conducting polymer with good impact strength.

A

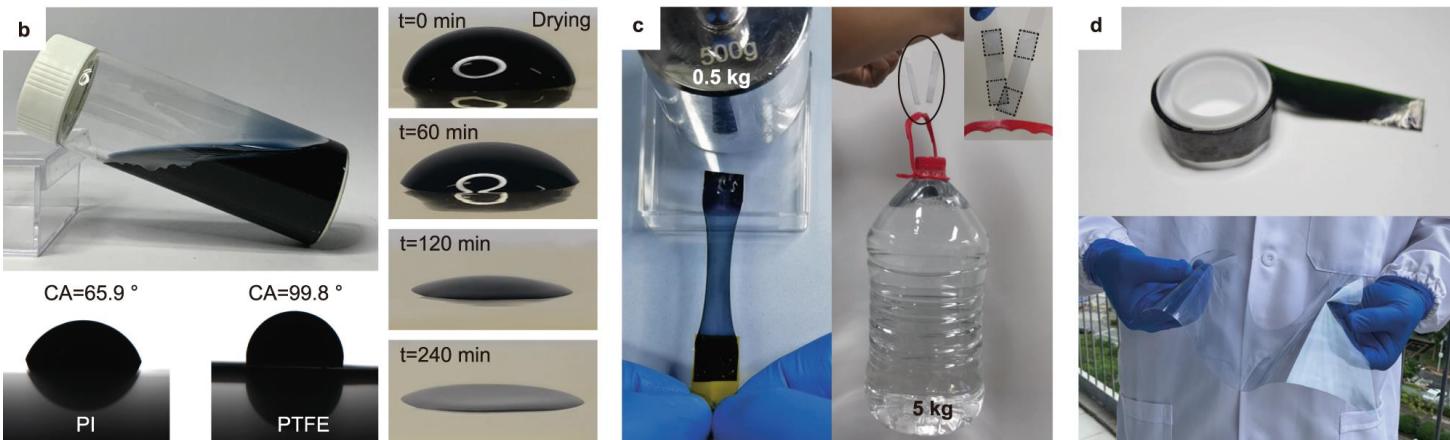
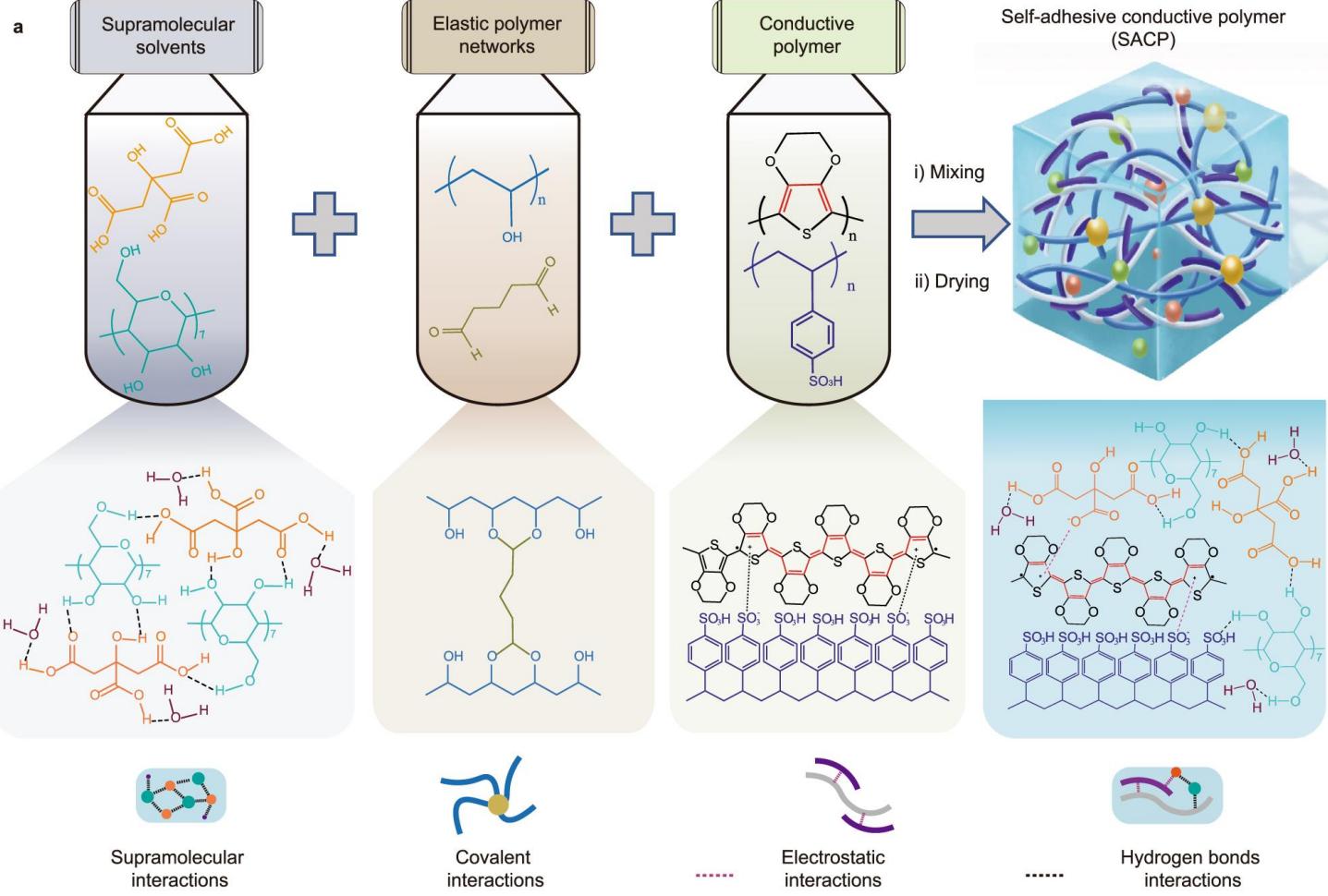
Conductive blended hydrogel patch

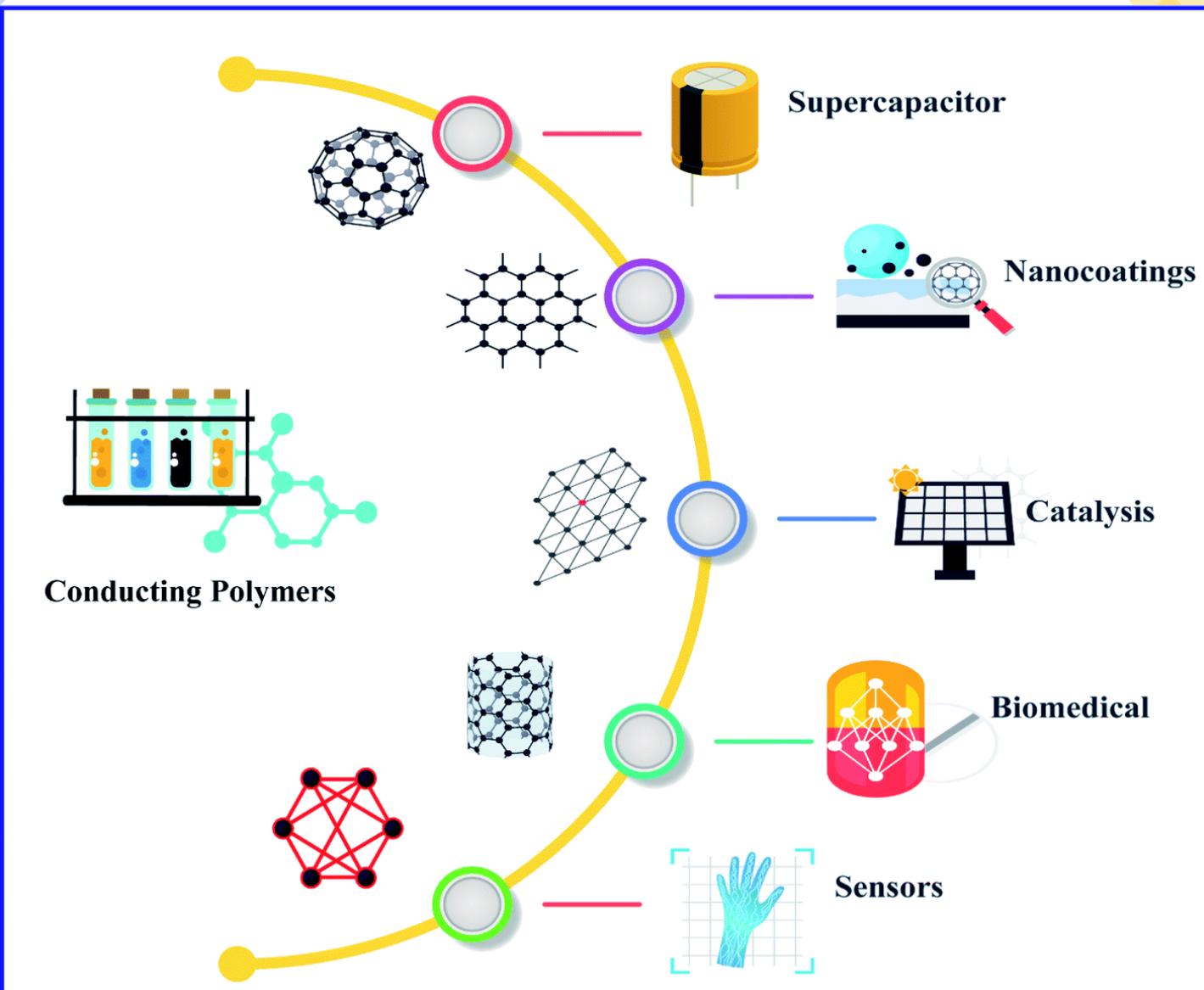
B

Electrical stimulation



DOX-loaded conductive blended hydrogel patch







Solar Cell Panel



Gas Sensor



Electronic Devices



Anticorrosive Coating

Hybrid Conducting Polymers

Inorganic compounds

- MWNT
- MnO_2
- V_2O_5

Organic Compounds

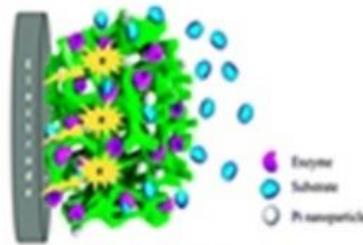
- Polyacetylene (PA)
- Polythiophene (PTh)
- Polypyrrole (PPy)
- Polyaniline (PANI)

Graphene

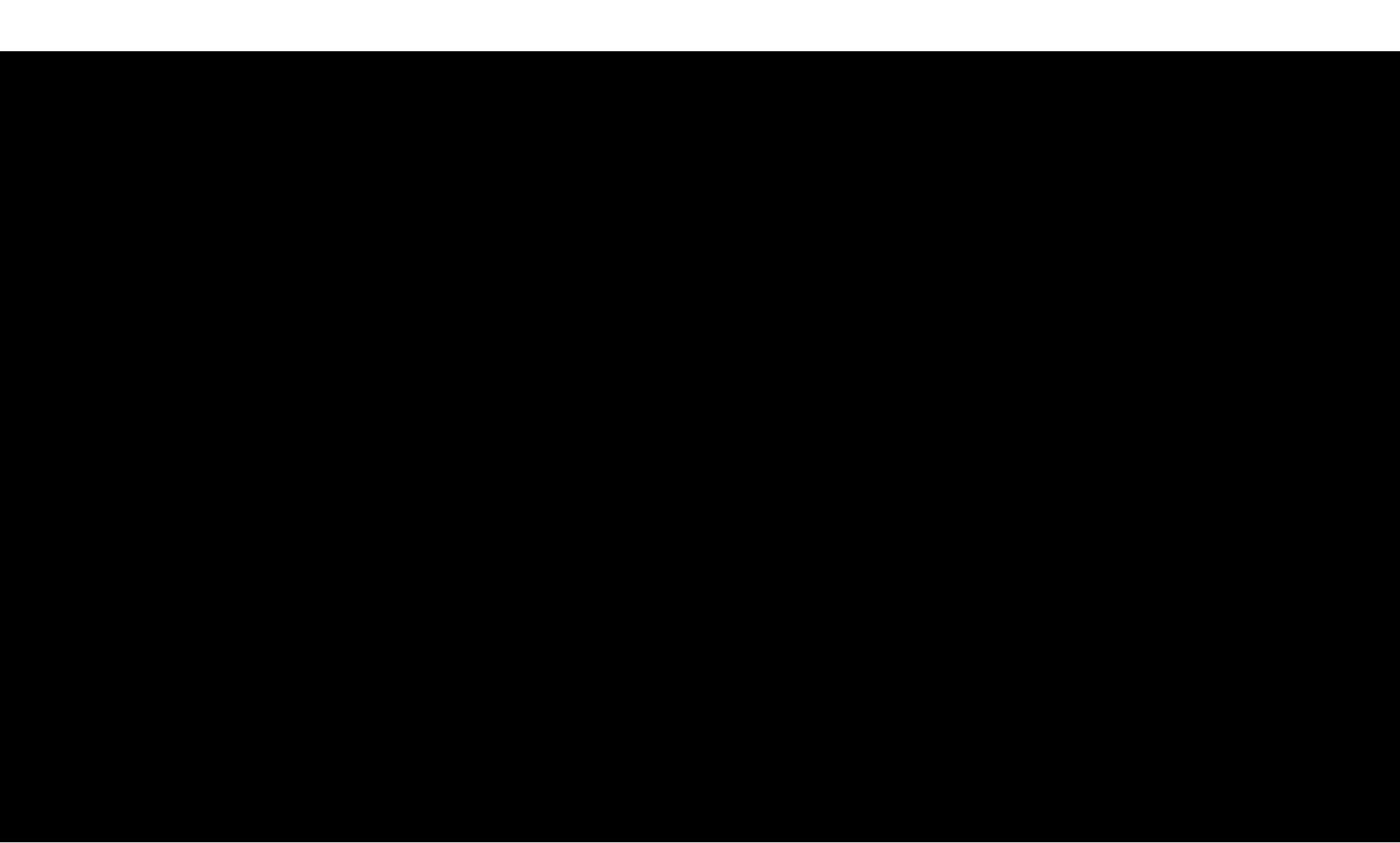
Hybrid Conducting Polymers



Tissue Engineering



Biosensor



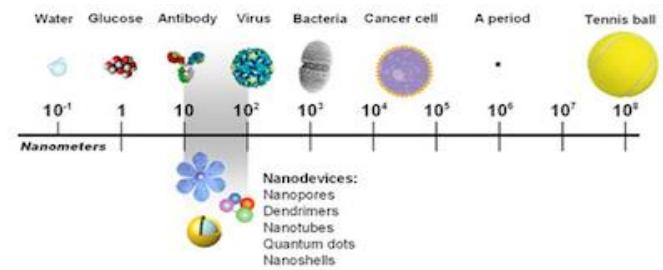
What is nano?

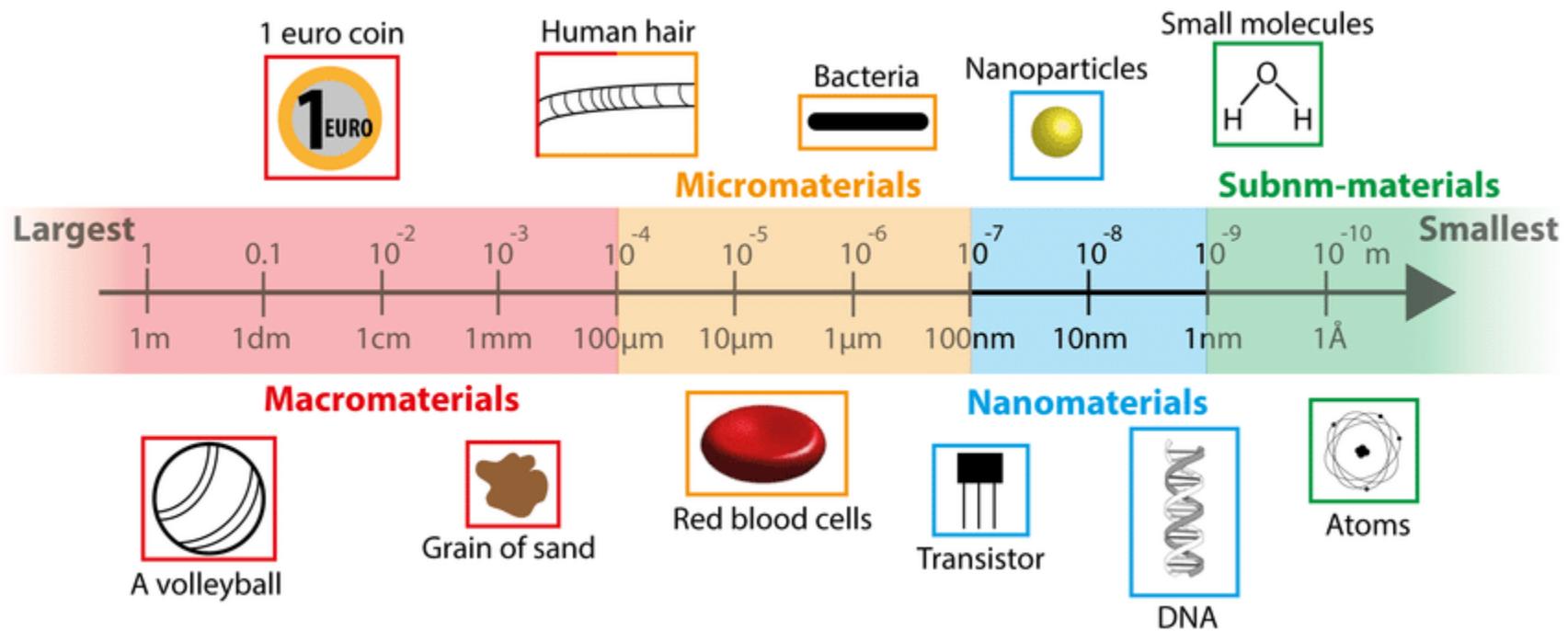
The prefix '**nano**' is derived from the Greek word for **dwarf**. One nanometre (nm) is equal to one-billionth of a metre, 10^{-9}m

Nano can refer to technologies, materials, particles, objects – we are focusing on ***nanomaterials*** as these are already being used in workplaces more widely

A sheet of paper is about **100,000 nm** thick, a human hair is around **80,000 nanometers wide**, a red blood cell approximately **7000nm** wide

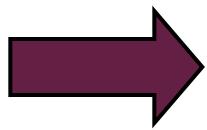
- At the nanometer scale, materials may behave differently.
- We can harness this new behavior to make new technologies.





How Big is a Nanometer?

To cover a football field with a 1nm thick layer of paint, you would need just **1 teaspoon** of paint!

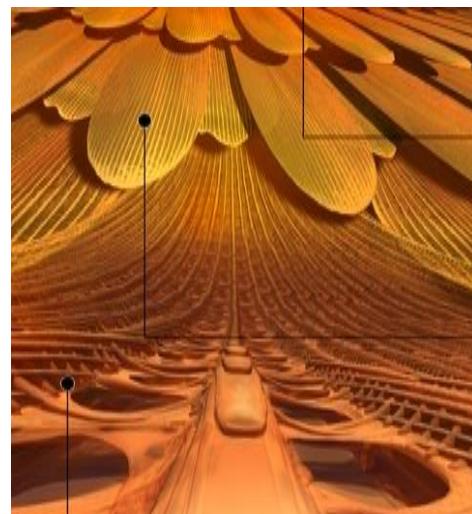


Did Scientists “Create” Nano?

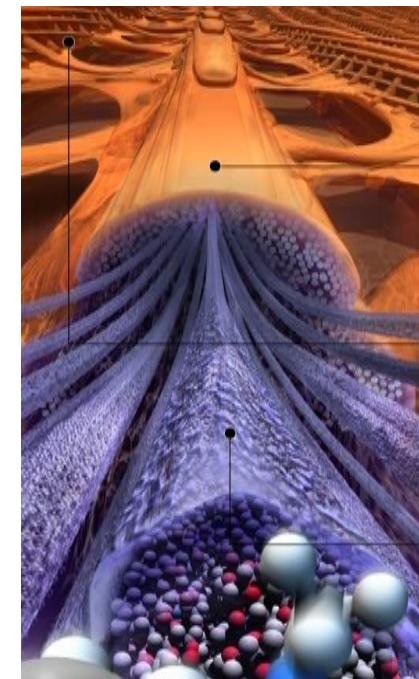
- No, it was already in nature!



centimeters to micrometers



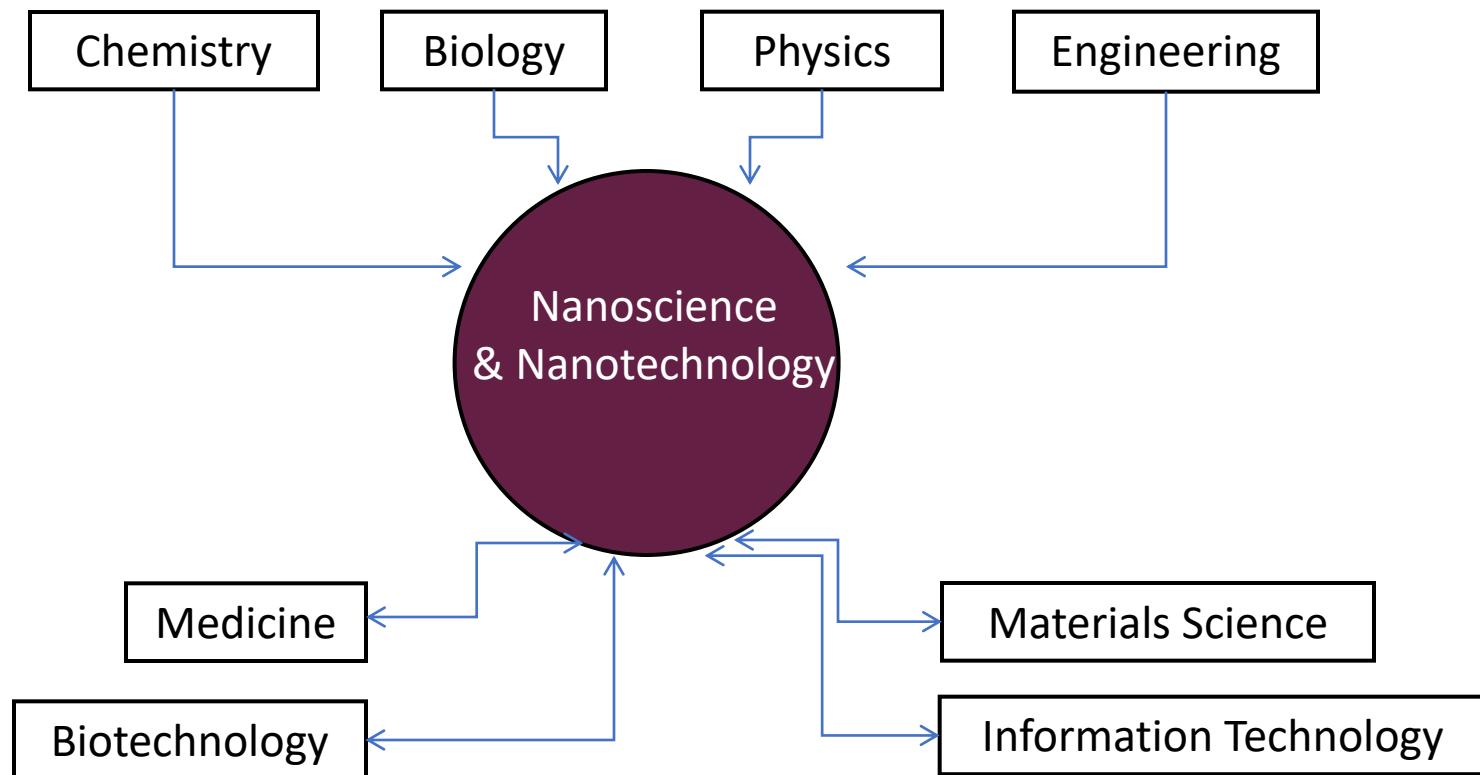
micrometers



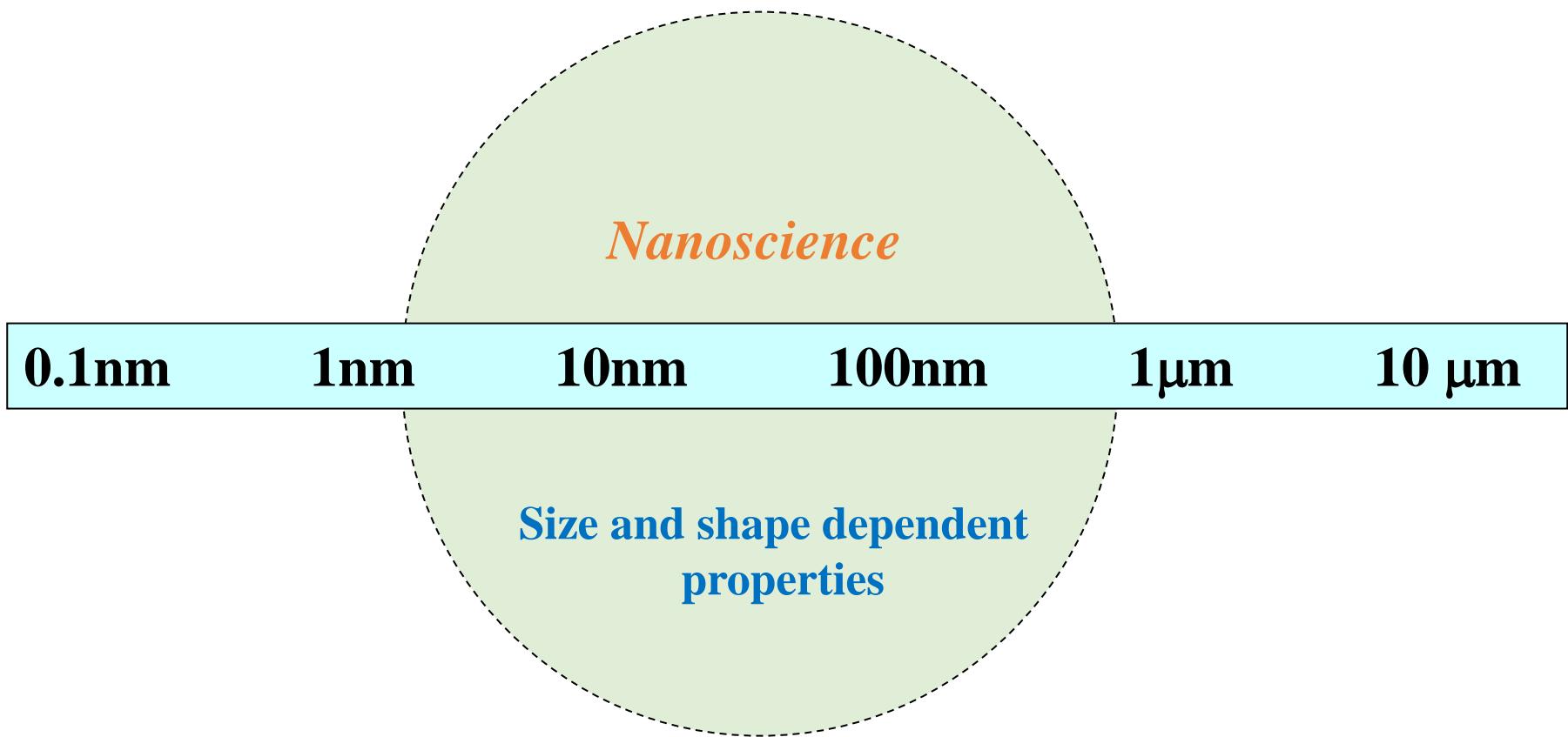
nanometers

- 1) Wing and wing scale
- 2) Wing scale
- 3) Scale ridge, ridge microrib, chitin fibrils and molecules

An Interdisciplinary Endeavor

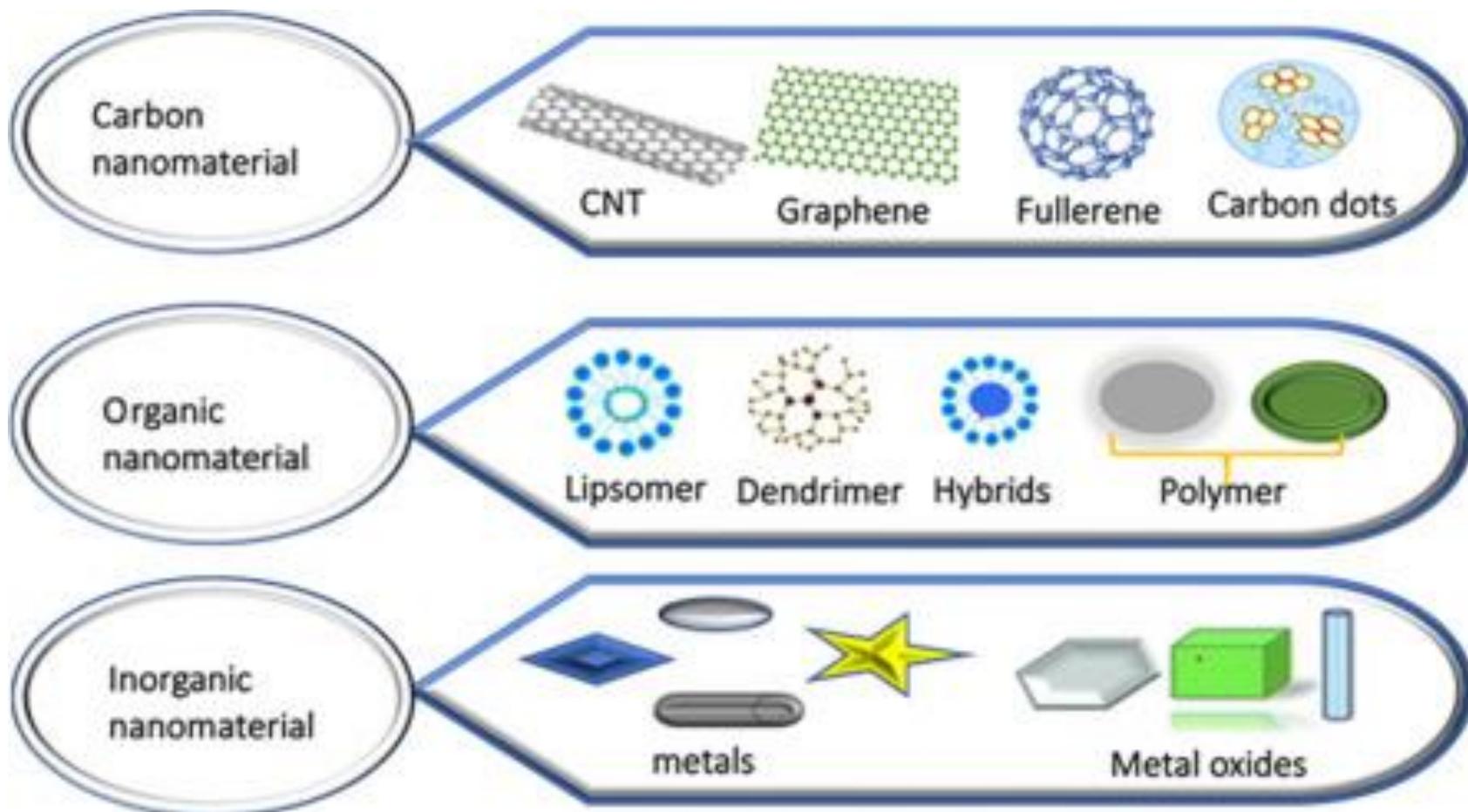


Actual physical dimensions relevant to Nanosystem

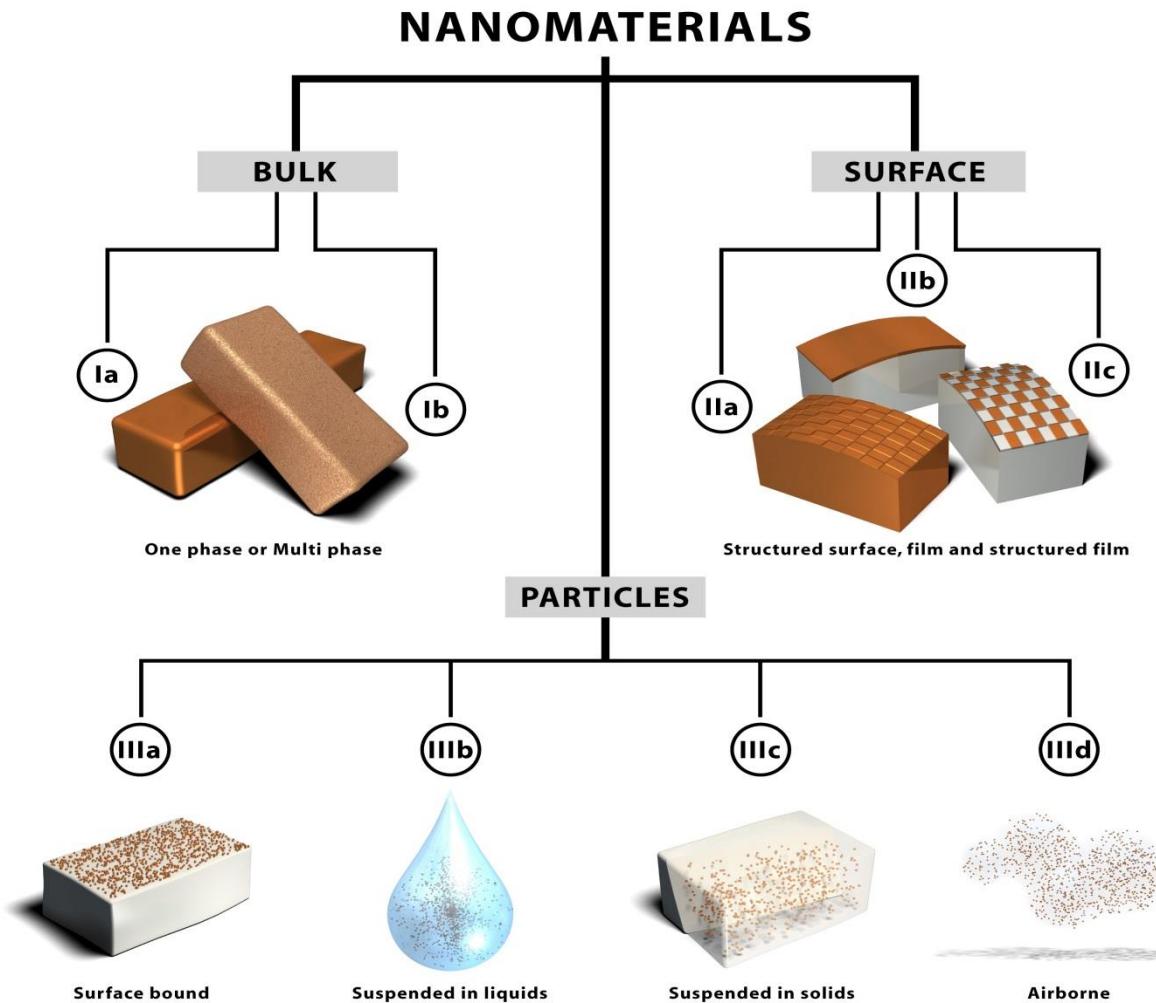


Nanometer scale : The length scale where corresponding property is size & shape dependent.

Types of nanomaterials



Classes of nanomaterials



Why are nanomaterials used?

- At nano-scale,
 - The material **properties change** - melting point, fluorescence, electrical conductivity, and chemical reactivity
 - **Surface size is larger** so a greater amount of the material comes into contact with surrounding materials and increases reactivity
- Nanomaterial properties can be '**tuned**' by varying the size of the particle (e.g. changing the fluorescence colour so a particle can be identified)
- Their **complexity** offers a variety of functions to products

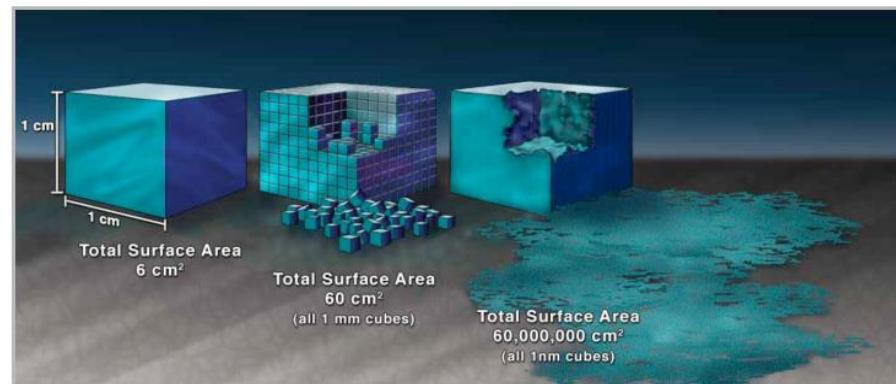
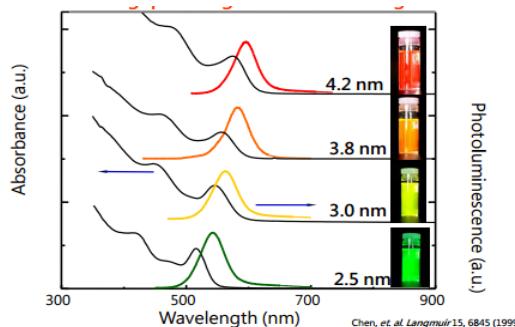
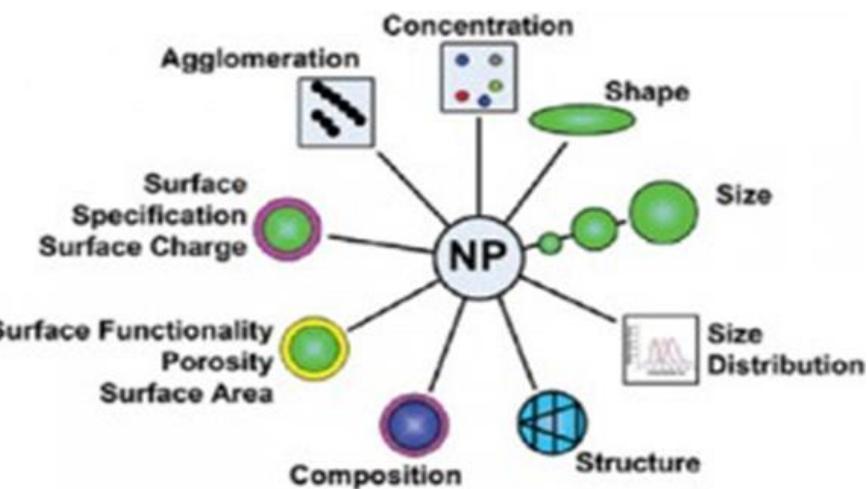


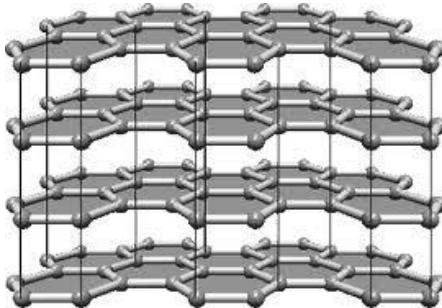
Illustration demonstrating the effect of the increased surface area provided by nanostructured materials



Introduction to Carbon Materials



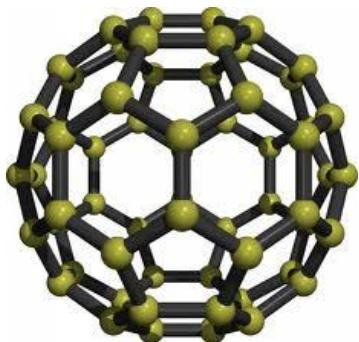
Diamond



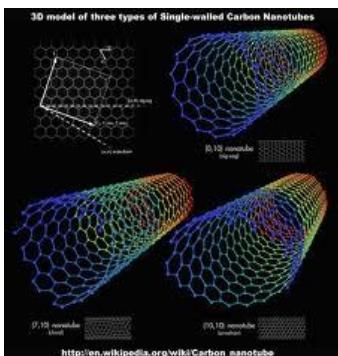
Graphite



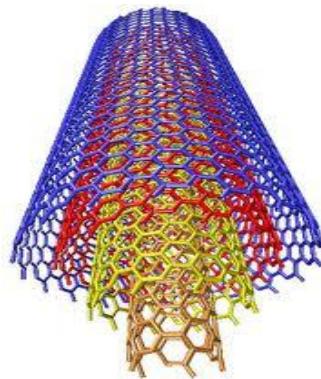
Amorphous Carbon



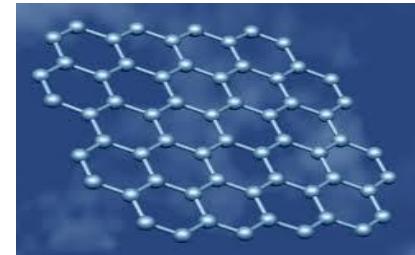
Fullerene



SWCNT



MWCNT



Graphene

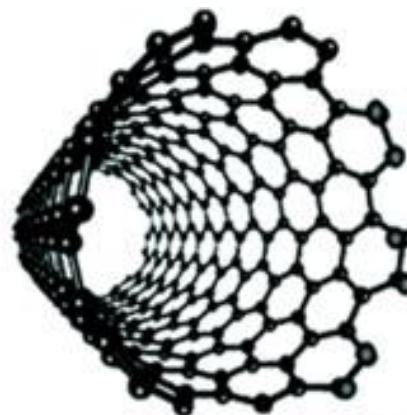
- The advantages of carbon materials include low cost, wide potential window and electrocatalytic activity for a variety of redox reactions.



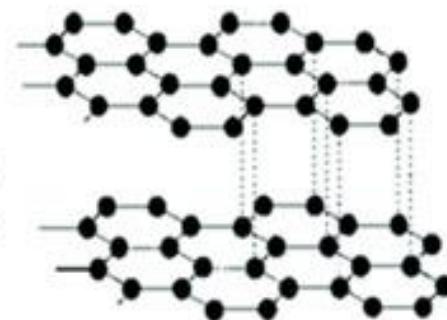
Diamond



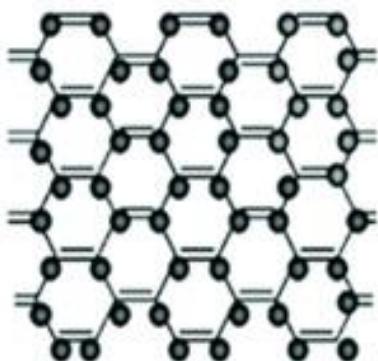
Fullerene



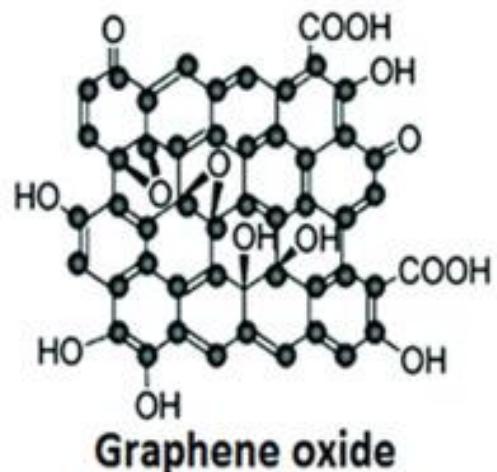
Carbon nanotube



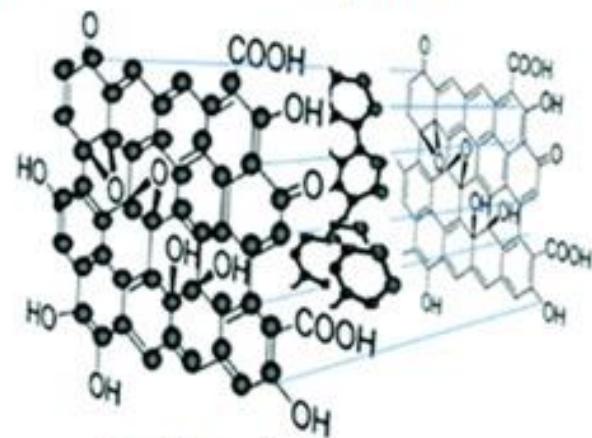
Graphite



Graphene



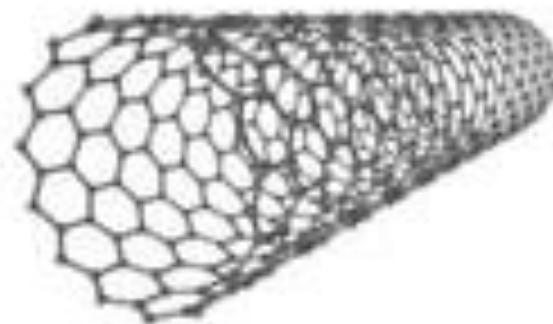
Graphene oxide



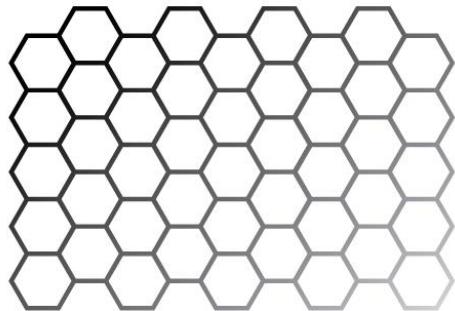
Carbon dot

WHAT ARE CARBON NANOTUBES?

- Carbon nanotubes (CNTs) are small cylindrical molecules of graphene.
- Consist of rolled-up sheets of single-layer carbon atoms (graphene).
- Have very small diameter
- (1nm-100nm).

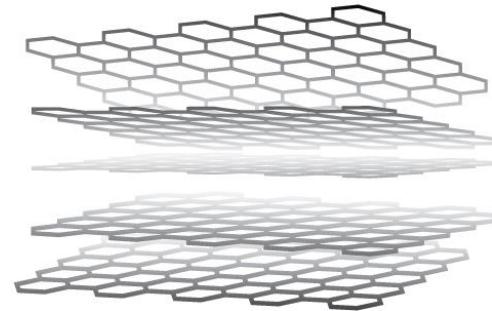


Graphene

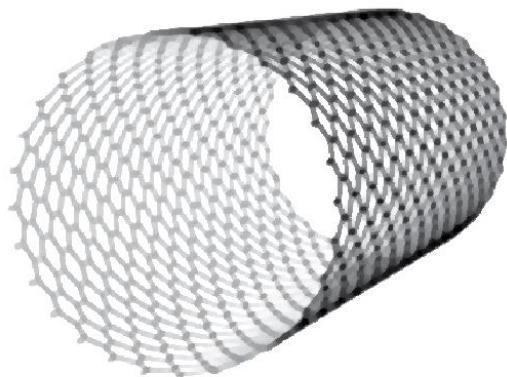


Multi-layered

Graphite

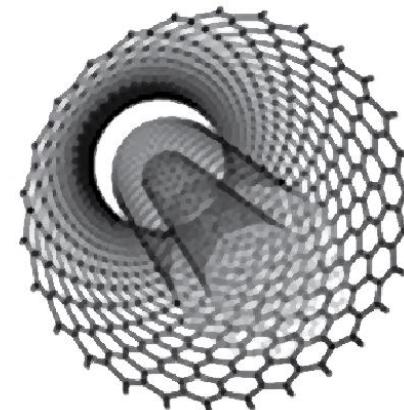


Rolled up



Multi-layered

Rolled up



**Single-walled
carbon nanotube
(SWCNT)**

**Multi-walled
carbon nanotubes
(MWCNT)**

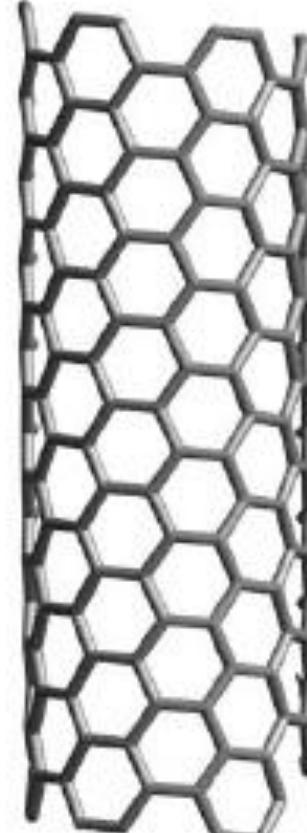
Single-Wall Nanotube (SWNT)



armchair



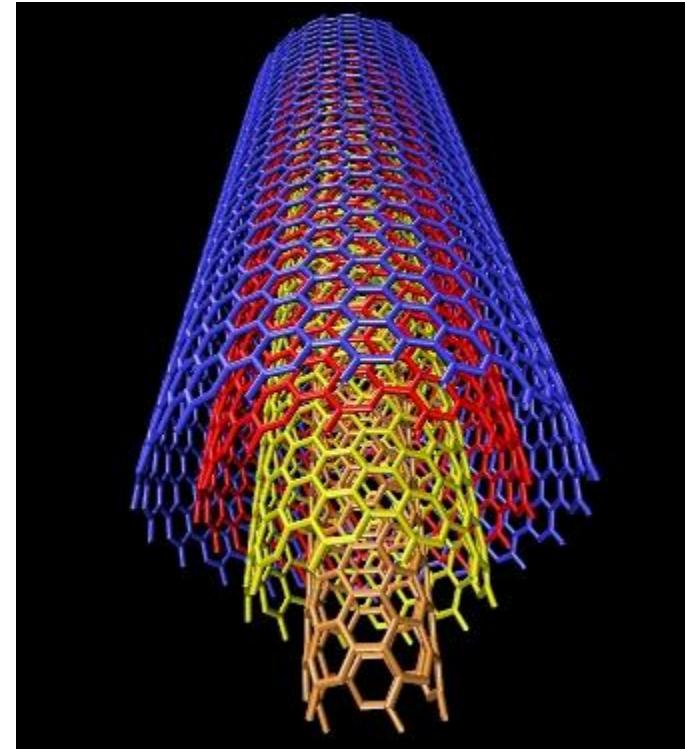
zigzag

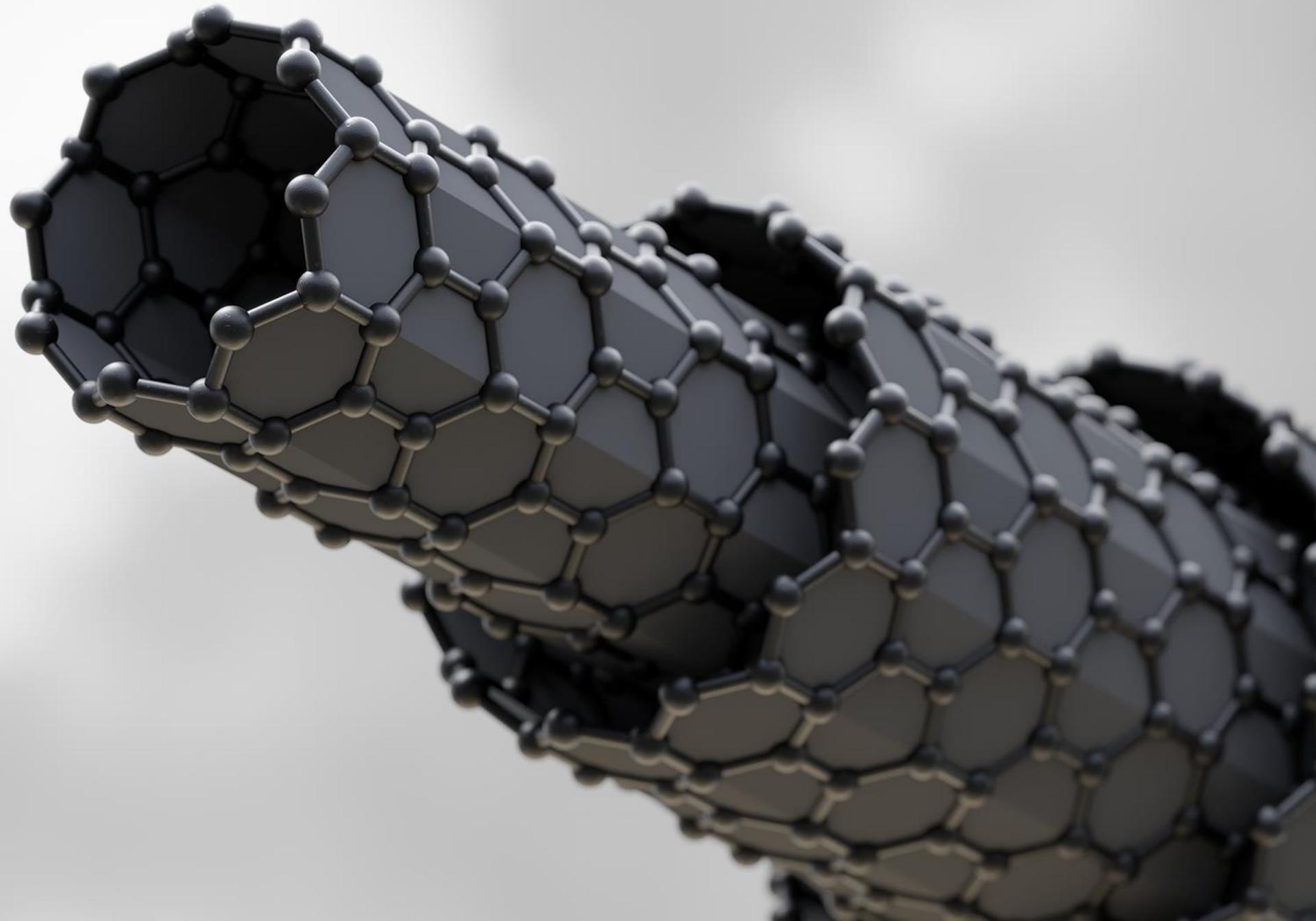


chiral

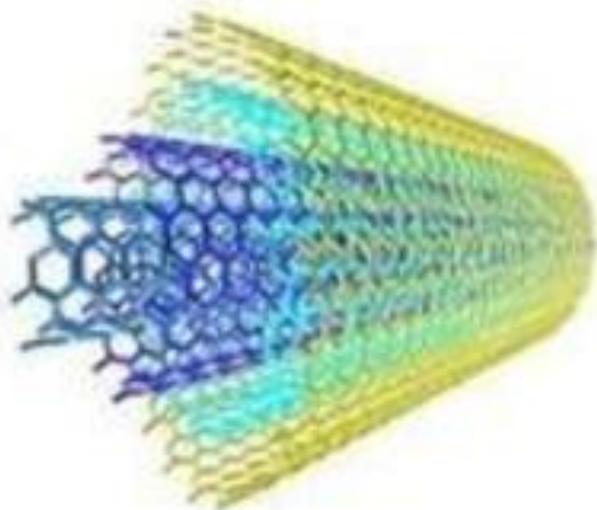
Multi-Walled Nanotubes (MWNT)

- Multiple rolled layers of SWCN sheets
- More resistant to chemical changes than SWNTs





Multi-Walled Nanotubes (MWNT)



Russian doll model
*(concentric cylindrical arrangement
of various graphite sheets)*



Parchment Model
*(single sheet of graphite is rolled
in around itself)*

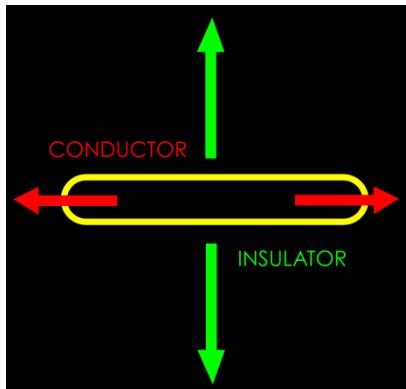
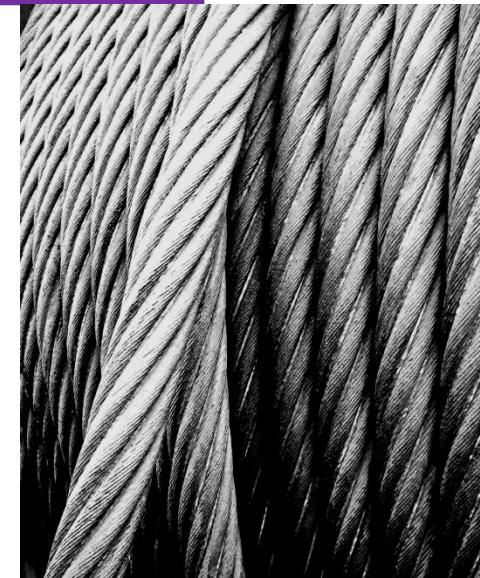
Why Should We Care of these materials ?

Thermal Properties



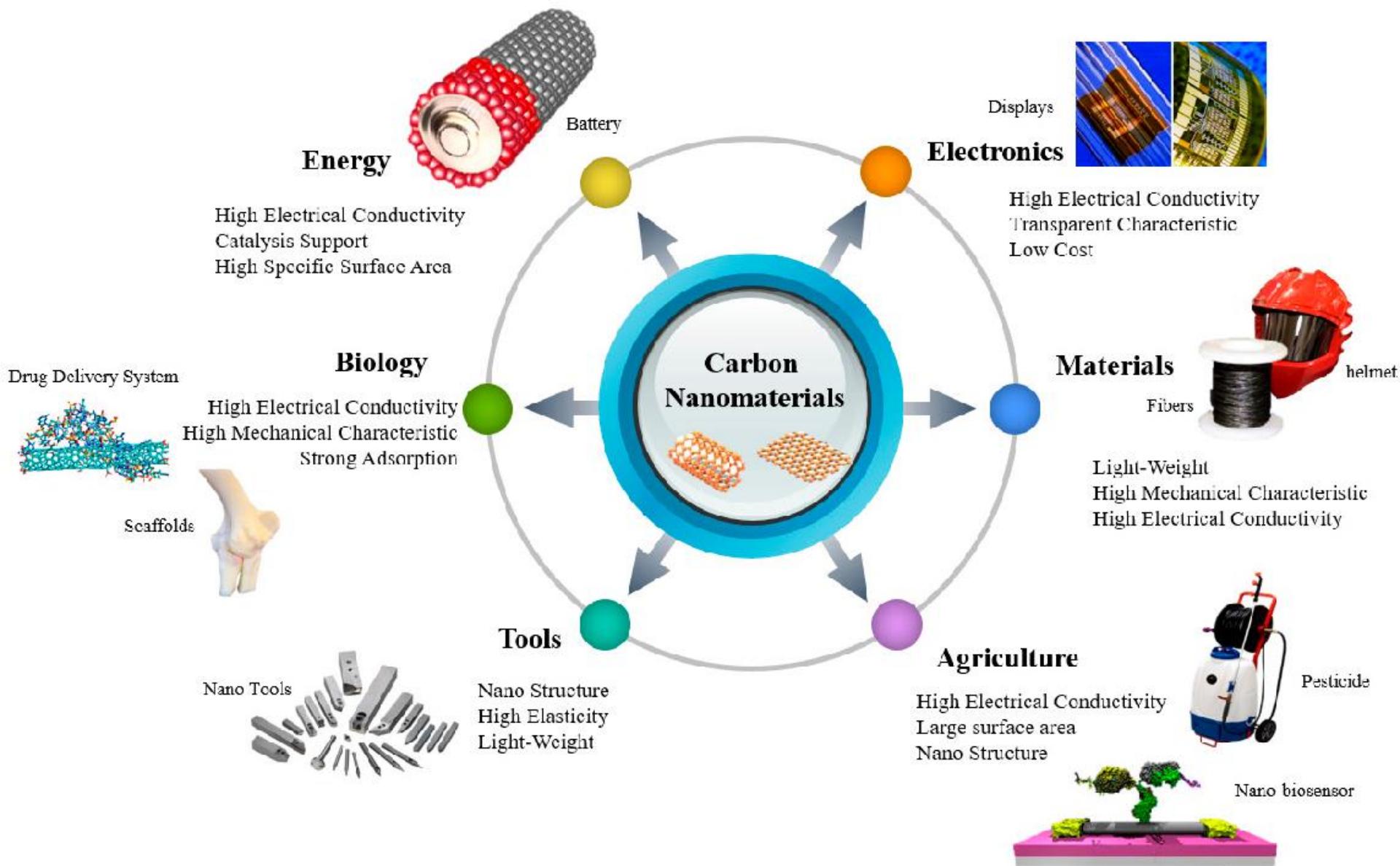
- Unique properties
- Material of the future
- Seemingly infinite applications
- Possible health issues

Mechanical Properties



- Strong Like Steel
- Light Like Aluminum
- Elastic Like Plastic

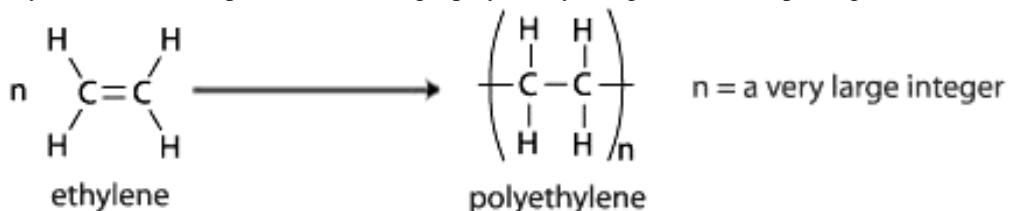




POLYMERS

Introduction

- Polymers are the macromolecules which are formed by the combination of many smaller molecules called monomers.
 - Polymerization is the process of forming a polymer by using number of repeating units.



Degree of polymerization

- It is defined as the number of monomers units in a homo polymer.
 - Most of the polymers are in the molecular mass range of 5,000 – 2, 00,000.
 - But incase of hetero polymer, degree of polymerization (D.P) is defined as the ratio of total molecular weight of a polymer to molecular weight of each repeating unit.
 - In the above equation, ‘n’ is the degree of polymerization.

$$D_p = \frac{\text{Total Molecular Weight of the Polymer}}{\text{Molecular Weight of Monomeric Unit}} = \frac{M_n}{M_0}$$

Mn = Mo , Dp

Mn = Total molecular weight of the polymer

Mo = Molecular weight of monomeric unit

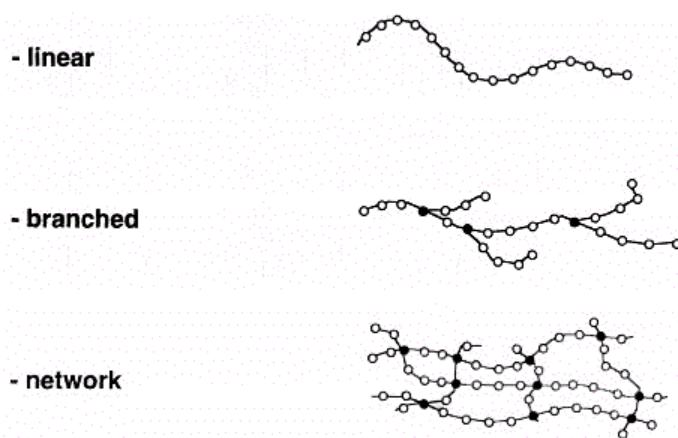
D_p = Degree of Polymerisation

Functionality

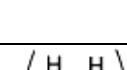
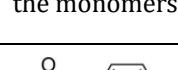
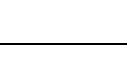
- The number of active bonding sites of a monomer is referred to as its functionality.
 - So, the monomer should have two reactive sites (or) bonding sites to form a polymer.

Different types of polymer structure can be obtained based on the functionality of monomeric units.

- Linear or straight chain molecules are formed by the combination of bifunctional monomers which contain two reactive sites
 - Branched chain polymers are obtained by the combination of trifunctional monomer and bifunctional monomers.
 - Three dimensional network polymers are obtained by the combination of polyfunctional monomers.
 - In such polymeric molecules, the movement of monomer units is prevented by strong cross links.



Differences between Addition & Condensation Polymerisation

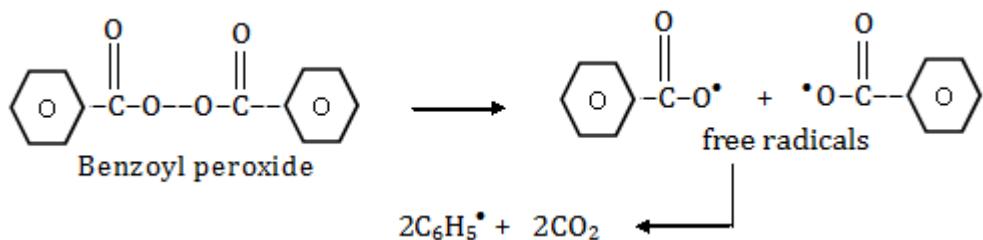
Addition Polymerisation	Condensation Polymerisation
1. Polymer is formed by addition of monomers without elimination of small molecules.	1. Polymer is formed by two or more monomers by the elimination of small molecules.
2. No by-products are formed.	2. By products are formed.
3. Homo chain polymers, generally thermo plastic is obtained.	3. Hetero chain polymer either thermo plastic or thermo setting can be obtained.
4. Proceeds by chain growth mechanism.	4. Proceeds by step growth mechanism.
5. Weight of polymer is identical with sum of the monomers.	5. Weight of polymer is not identical with sum of the monomers.
n  ethylene	 polyethylene
n  Terephthalic acid	n  Ethylene glycol

Mechanism of polymerization

Free radical polymerization

In this type of polymerization monomer is activated to free radical by any one of the following methods.

- a) Photo chemical initiation:- By exposing to sunlight free radicals are generated.
 - b) Thermal initiation:- By heating free radicals are generated.
 - c) Radiation initiation:- By exposing to α , β or γ -rays free radicals are generated.
 - d) Chemical initiation:- By using initiators like peroxides free radicals are generated. Benzoyl peroxide or Azo bis isobutyronitrile, persulphates etc are used as chemical initiators. They produce free radicals as



Mechanism of free radical polymerization involves three steps.

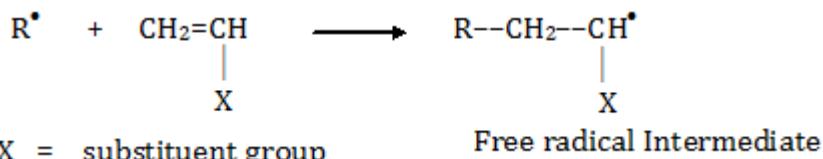
1. Chain initiation:-

It involves two steps.

- a) Formation of free radicals from the initiator.

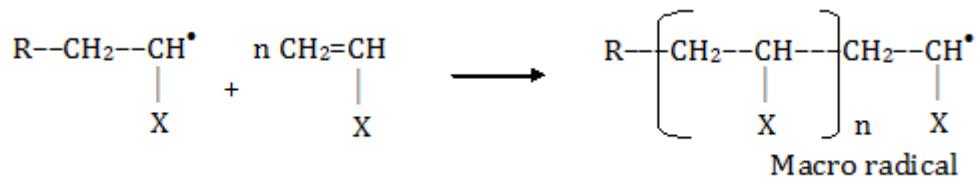


- b) Addition of free radicals to monomer to form a free radical intermediate.



2. Chain propagation:-

Here addition of monomer molecules to the intermediate takes place one by one leads to the formation of macro-radicals.

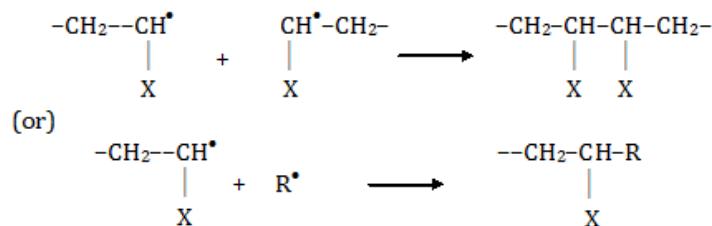


3. Chain termination:-

The growing polymer chain is terminated by many ways.

a) Recombination:-

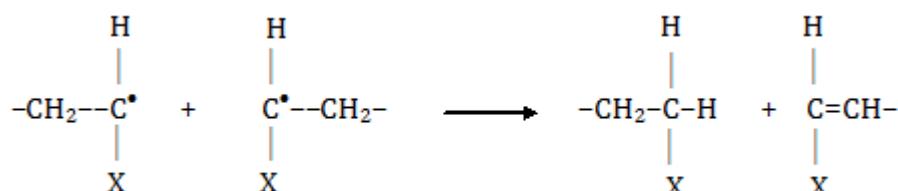
Combination of two free radicals leads to termination.



At 60°C poly styrene or Acrylonitrile chains terminate mainly by recombination.

b) Disproportionation:-

Transfer of 'H' atom from one radical to another leads to formation of two macro molecules, one of them with a double bond.



Ionic polymerization

Cationic polymerization

Anionic polymerization

Cationic polymerization:-

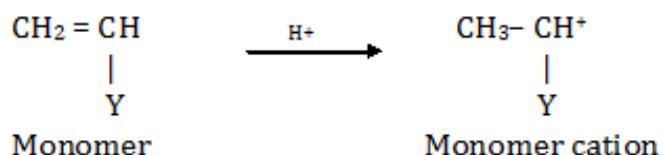
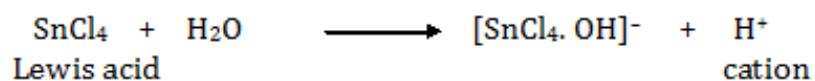
Monomers with electron releasing groups (-OCH₃, -OC₂H₅ & -C₆H₅ etc) undergo cationic polymerization in the presence of Lewis acids like AlCl₃, BF₃, SnCl₄ etc. Cationic polymerization takes place with higher rates even at low temperature.

Mechanism of cationic polymerization:-

It involves three steps.

a) Initiation:-

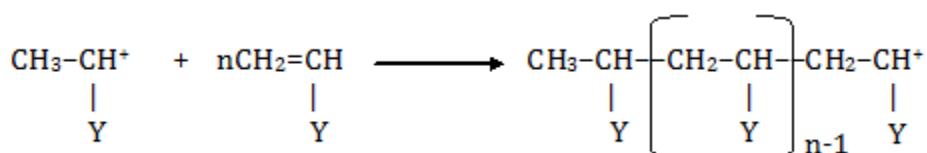
H⁺ ion is produced from Lewis acid and it forms cation with monomer.



Where, Y is electron releasing group.

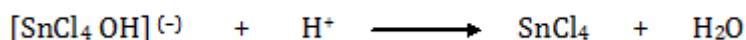
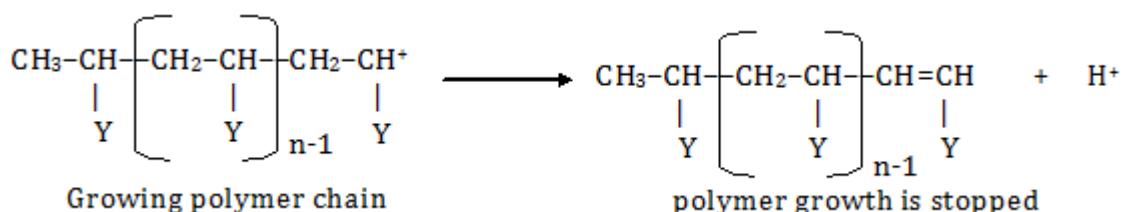
b) Propagation:-

Monomers are added to monomer cation in a sequence and length of polymer chain increases gradually.



c) Termination:-

Growing polymer chain is stopped by removing H⁺ ion from the chain.



Anionic polymerization:-

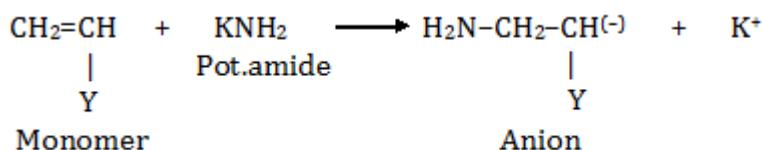
Monomers with electron withdrawing groups (-CN, CH₃COO- and C₆H₅ etc) undergo anionic polymerization in presence of sodium or potassium amide.

Mechanism of anionic polymerization:

It involves 3 stages.

a) Initiation:-

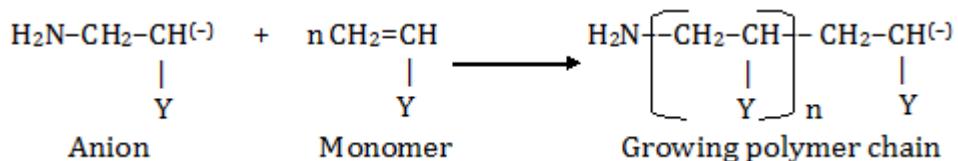
Anion is generated on reaction of potassium amide with monomer.



Y = electron withdrawing group.

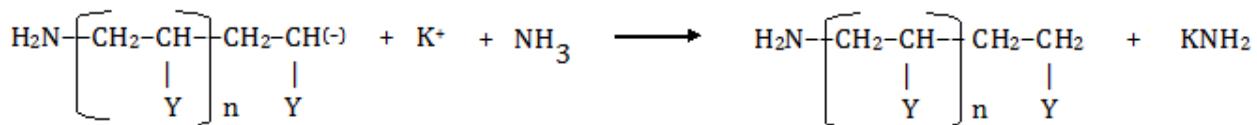
b) Propagation:-

Monomer units are added to anion one after the another and growth of polymer chain is continued.



c) Termination:-

Growing polymer chain is stopped by neutralizing the negative charge on growing chain.



Ziegler – Natta catalysis (or) Co-ordination polymerization:

- ✓ Ziegler Natta catalyst is useful in synthesizing stereo regular polymers commercially.
- ✓ This catalyst is a co-ordination catalyst, consists of two components of catalyst and co-catalyst.

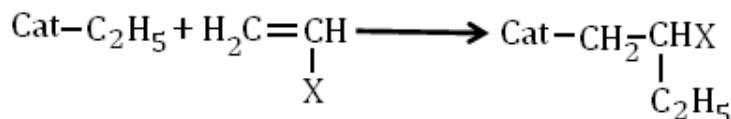
Mechanism:

❖ Preparation:

- ★ The active Ziegler – Natta catalyst is formed by chemisorption of aluminium alkyl on TiCl_4 crystal.
- ★ Heating the monomers at 100°C at 10atm in presence of Ziegler Natta catalyst forms stereo regular polymers.

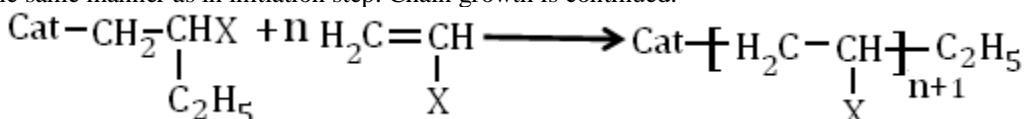
❖ Initiation:

- ★ Monomer forms π -complex with active catalyst by co-ordination bond and with empty orbital of titanium.



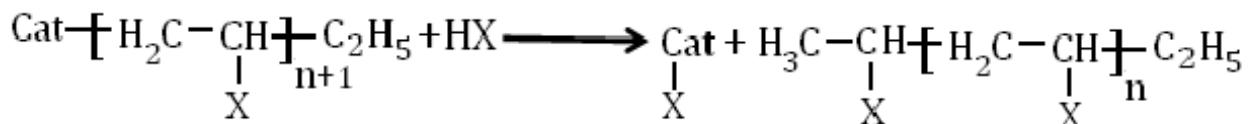
❖ Propagation:

In this step monomers are added one after another in between the metal and ethyl group in the same manner as in initiation step. Chain growth is continued.



❖ Termination:

- ★ The polymer chain is separated from the catalyst by the addition of molecules containing active hydrogen (HX). Chain growth is stopped.



❖ Applications:

- Ziegler Natta catalyst is used for synthesizing the Syndiotactic and Isotactic polymers.
- Co-polymers, like ethylene and propylene are obtained by using Ziegler Natta catalysts, which are excellent elastomers.

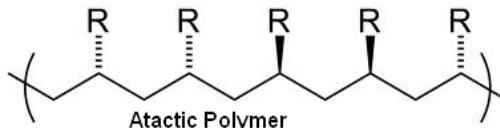
STEREO REGULAR POLYMERS

- ✓ Asymmetric alkenes linked together to form asymmetric carbon chain polymers.

- ✓ The stereo chemical placement of the asymmetric carbons in the polymer chain is called tacticity.
- ✓ Based on the stereo chemical orientation of atoms or groups at asymmetric carbons, the polymers can be classified as
 - a) Atactic
 - b) Syndiotactic (Syntactic)
 - c) Isotactic
- ✓ Tacticity helps in understanding M.P, Solubility and mechanical properties, crystallinity, rigidity of the polymer.

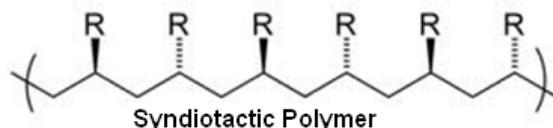
Atactic polymer:

- ▲ In these polymers, the substituents of asymmetric carbons are placed randomly along the chain.
- ▲ The percentage of mesodiads is in between 1 - 99%.
- ▲ Ex: PS, PVC etc.
- ▲ These polymers have low crystallinity, low melting point and mechanically weak due to irregular structure.



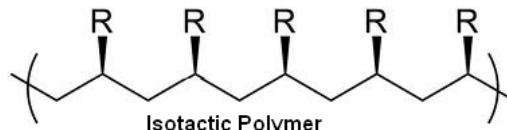
Syndiotactic polymers:

- ▲ The polymers in which the substituents of asymmetric carbon are placed in alternative positions along the macro molecule chain are known as Syndiotactic polymer.
- ▲ The percentage of racemodiads in this polymer is 100%.
- ▲ These polymers have high crystallinity, high melting point and mechanically strong due to the presence of weak interaction forces.



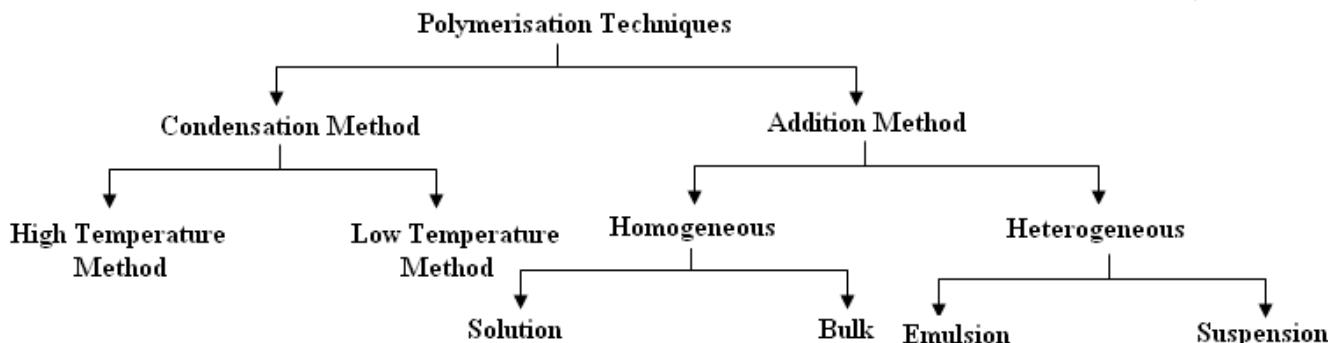
Isotactic polymer:

- ▲ The polymers composed of the substituents of asymmetric carbon on the same side of the polymer chain are known as Isotactic polymers.
- ▲ The Isotactic polymers consist of 100% mesodiads.
- ▲ These polymers have high crystallinity, high melting and mechanically strong due to the presence of weak interaction forces.



- ✓ The polymers which are having tacticity and regular order of arrangement are called stereo regular polymers.
- ✓ Syndiotactic and isotactic polymers are stereo regular polymers.

Methods of polymerization



♣ Heterogeneous polymerization:

If the polymerization reaction takes place in more than one phase, it is known as heterogeneous polymerization.

Suspension polymerization

- ❖ It is also known as pearl or bead or granular polymerization.
 - ❖ It is the polymerization process that uses mechanical agitations to mixture of monomers in liquid state.
 - ❖ In which, the monomers are dispersed as relatively large droplets (0.1 – 1 mm) in liquids.
 - ❖ A catalyst is added for initiation of polymerization process, and the suspension is stabilized by adding stabilizer agents (Al(OH)_3 , Kaolin).
 - ❖ Without adding stabilizer breaking of suspension takes place.
 - ❖ Then the polymers are obtained as pearls or spherical beads.
 - ❖ Ex: PS, PVC, PMMA
- ❖ **Advantages:**
- High purity product formed.
 - Process is more economical.
 - Efficient thermal control.
- ❖ **Disadvantages:**
- It is difficult to control the size of the particle.
 - Applicable to water insoluble monomers.

Emulsion polymerization

- ❖ The most common type of emulsion polymerization is oil – in – water emulsion.
 - ❖ In this method, the monomer is dispersed in water phase as fine droplets (10^{-5} to 10^{-6} mm) which are stabilized by adding surfactants like soap or detergents.
 - ❖ These surfactants form micelles. When their concentration exceeds critical micelle concentration.
 - ❖ The formed micelles dispersed through out the solution.
 - ❖ The addition of initiator leads to the activation of reaction in micelles.
 - ❖ Due to the formation of polymers, these micelles increase in size.
 - ❖ To continue the reaction, monomers diffuse from its droplets to micelle, then the size of the micelle increases.
 - ❖ Termination reactions are less likely as the polymerization sites are isolated from each other.
 - ❖ Here, high molecular weight polymers can be obtained.
 - ❖ Ex: PS, PVC
- ❖ **Advantages:**
- High molecular weight polymers can be prepared.
- ❖ **Disadvantages:**
- It cannot be used for condensation, ionic, Ziegler – Natta polymerization processes.
 - It is economically costly.

Properties of polymers

Physical properties:

These properties depend on average molecular weight of a polymer.

For molecular weights < 1000 - oily viscous liquids

For molecular weights 1000 – 10,000- soft, waxy solids

For molecular weights > 10,000 - hard, brittle solids or flexible solids

❖ Crystallinity:

- ✓ The orderly arrangement of polymeric molecule is known as crystallinity.
- ✓ The properties like solubility, diffusion, toughness, density and transparency depend on degree of crystallinity.
- ✓ In crystalline polymer, the polymeric molecules are packed close to each other through intermolecular forces of attraction.
- ✓ Thus, these polymers have higher and sharper melting point, greater rigidity, greater density and strength.
- ✓ A completely crystalline polymer tends to acquire brittleness.

❖ Amorphous state:

- ✓ Random arrangement of polymer molecules results amorphous state.
- ✓ The intermolecular forces between polymer chains are weak.
- ✓ So, amorphous polymers can be moulded to desired shape.
- ✓ Both thermosetting and thermoplastics are amorphous.



Mechanical properties:

- ✓ **Elasticity:** It is the ability of a material to recover to its initial shape and dimensions when applied stress is removed.
- ✓ **Hardness:** It is the ability of a material to surface deformation, indentation or abrasion.
- ✓ **Dimensional stability:** it is the ability of a polymer to withstand progressive removal of material from its surface as a result of mechanical action of rubbing, scrapping or corrosive nature.
- ✓ **Plasticity:** A material is said to exhibit plasticity if on releasing the applied stress it retains a permanent deformation.
- ✓ **Brittleness:** A brittle material shatters suddenly without noticeable plastic deformation preceding failure.
- ✓ **Ductility:** A ductile material undergoes large irrecoverable deformation before rupture.
- ✓ **Strength:** It is the ability of a material to withstand a gradually applied stress without rupture. These are of three types.
 - **Tensile strength:** It is the stress needed to break a sample.
 - **Compressive strength:** It is the ability of a material to resist crushing when a squeezing force is applied to it.
 - **Impact strength:** It measures the ability of a material to resist sharp blows or shock . or *Impact strength* is the resistance of a material to fracture under dynamic load.

PLASTICS

Introduction:

- ✓ The Word Plastics is derived from Greek Word ‘Plastikos’ meaning capable of being moulded [or] shaped.
- ✓ Plastics can be moulded [or] pressed [or] casted [or] extruded into various shapes like plates, tubes, bottle, boxes, fibers etc.
- ✓ Plastics materials have
 - Sufficient rigidity
 - Mechanical strength
 - Insulation Property
 - Low density
 - Low cost
 - Light weight
 - Resistance to chemicals, corrosion, insect abrasion etc to shape them into desired article.
- ✓ Resin is a part of plastic.
- ✓ It helps in binding the constituent together in the plastic.

Advantages:

1. Recyclable
2. It can be destroyed by burning [incineration]
3. Durable.

Disadvantages:

1. Recycling of plastic is a costly process.
2. Plastic undergo biodegradation after long time.
3. Incineration of plastic causes pollution.
4. Plastics are derived from petrochemicals and their production causes environmental pollution.

5. Plastics are low heat resistance and brittle. They undergo deformation at low temperatures.

Uses:

- **In Packaging industry:** As bags, covers and containers LDPE and HDPE are used.
- **In construction industry:** PVC, HDPE are used as drainage pipes, electrical pipes etc.
- **In automobiles:** Wipers, air intake manifolds, fuel pipe lines, bumpers, brake linings etc.
- **In electronic devices:** TV & Radio cabinets, computers, clocks produced from plastic materials.
- **In house hold purpose:** Around the house, some of the most popular uses are shower heads, dishes, food containers, tooth brushes, pens, skylights, eye glasses, toys, decorative items, carpets, piano keys, buttons, door knobs, luggage suitcases etc.

Differences between Thermo Settings and Thermo Plastics

Thermo Plastics	Thermo Settings
Formed by either addition (or) condensation polymerisation.	Formed by condensation polymerisation.
They are linear (or) branched linked structures.	They are cross linked (or) three dimensional structures.
Polymers chains are held together by weak attractive forces.	Polymers chains are held together by covalent cross links.
They soften on heating and stiffen on cooling.	They don't soften on heating.
They are soluble.	They are not soluble.
They can be remoulded, reshaped and reused.	They cannot be remoulded.
They can be recycled.	They cannot be recycled.
They are tough.	They are brittle.
They have low melting points.	They have high melting points.

Compounding of plastics

- ❖ The process of including various additives into plastic by mechanical means to get a homogeneous mixture is called compounding.
- ❖ By the addition of suitable materials, plastics get desired qualities.
- ❖ Additives are classified into various types based on their role in the plastic.
 - Binders
 - Fillers
 - Plasticizers
 - Stabilizers
 - Colorants
 - Accelerators
 - Fire retardants

Binders:

- ♣ The main purpose of binder is to hold the different constituents together in the material.
- ♣ A binder may compose of 30-100% of the plastic.
- ♣ The binders used may be natural [or] synthetic [or] cellulose derivatives.
- ♣ These are also polymeric materials.
- ♣ Resins are the basic binding materials in the plastics.
- ♣ Binders used also determine the type of process needed to mould the plastic.
- ♣ Plastic are classified based on the type of binder used.
- ♣ **Thermoplastic:**
 - These are prepared in single step process.
 - These plastic are generally amorphous (or) crystalline.

- These are linear (or) branched polymers with weak intermolecular attractive forces.
- These plastics become soft on heating and stiffen on cooling at any time.
- They may be remolded, reshaped and reused.
- They can be recycled.



Thermosettings



Thermoplastics

▲ **Thermosetting:**

- These are normally produced.
- These are cross linked, three dimensional structures.
- Once a product is prepared by heating and moulding, it can't be changed by further heating.
- On excess heating materials undergoes destruction but not become soft.

Fillers:

- ♣ Fillers are cheap organic (or) inorganic materials used to reduce cost of the material (or) to improve certain properties of it.
- ♣ These are two types.

Particulate fillers;

- ▲ They are used to lower the cost of plastic.
- ▲ They also help to increase tensile strength & retention of shape.
- ▲ Ex; Asbestos, clay, silica, talc, lime stone, mica & even wood flour.

Fibrous Fillers:

- ▲ These are mainly used to improve tensile strength, wear, tear & impact resistance.
- ▲ They act like steel in reinforced concrete.
- ▲ Ex; Cotton threads, scrap clothes, nylon poly ester fiber, fiber glass etc.

Plasticizers:

- ★ Some plastics are hard, brittle and glassy with high T_g and melt viscosity.
- ★ It is difficult to prepare products from such plastics.
- ★ Plasticizers are high molecular weight organic compounds which make the plastic soft, flexible and low melt viscosity.
- ★ Ex; Triphenyl phosphate, Phthalic esters, Fatty acid esters etc.

Stabilizers:

- ♦ Many plastics undergo thermal (or) photo chemical degradation during their processing (or) when they are put into use.
- ♦ Stabilizers protect the plastic from such degradation.
- ♦ Natural rubber, PE, esters undergo such degradation.
- ♦ It is prevented by adding anti oxidants like alkyl phenols, naphthols, phenyl salicylate etc.

Colorants:

- ★ These are inorganic (or) organic pigments used to impart pleasing colours to the plastic.
- ★ They don't cause any influence on other properties.
- ★ Ex; Carbon black, anthraquinones, azodyes, phthalocyanines, BaSO_4 , TiO_2 , PbCrO_4 , Fe_2O_3 , Zinc chromate.

Accelerators (or) Catalysts:

- These are used in the preparation of thermosetting polymers in which cross linked are produced by adding accelerators.
- Ex; H_2O_2 , Benzoyl peroxide, ZnO , NH_3 etc.

Fabrication of plastics

These are 5 methods of fabrication

Casting:

- ♠ This method is suitable for thermosetting & thermoplastics.
- ♠ Molten plastic material is poured in a suitable mould and it is subjected to curing at 70°C for several hours at atmospheric pressure.
- ♠ The products formed are free from internal stresses and can take high polish.

Blowing:

- ♠ In this process, molten plastic is blown by air (or) steam into a closed mould.

Extrusion:

- ♠ By this method, articles like sheets, pipes, rods, having uniform dimension are prepared.
- ♠ The method is used only for thermoplastics.
- ♠ The material of required composition is forced by a screw conveyor into a heated chamber. Where it softens, and then it is forced through a die having the required shape.
- ♠ The finished product extruded out is cooled by blowing air (or) spraying water.

Lamination:

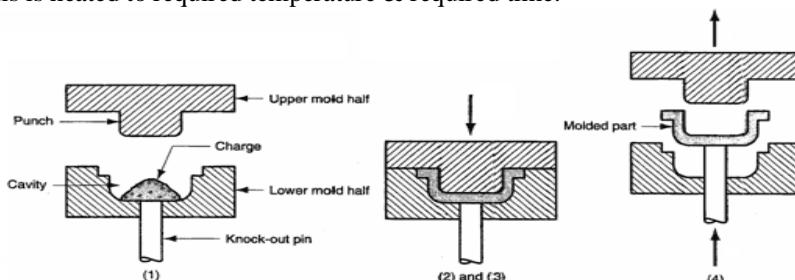
- ♠ Sheets of cloth, paper (or) wood are soaked with resin solvent solution.
- ♠ Such sheets are arranged one over the other till the required thickness is obtained and pressed together by using smooth polished metal sheets to get laminated product.
- ♠ Laminated products have high tensile strength and impact resistance.

Moulding Techniques

- ♠ Moulding is an important method of fabrication.
- ♠ There are several ways of moulding.

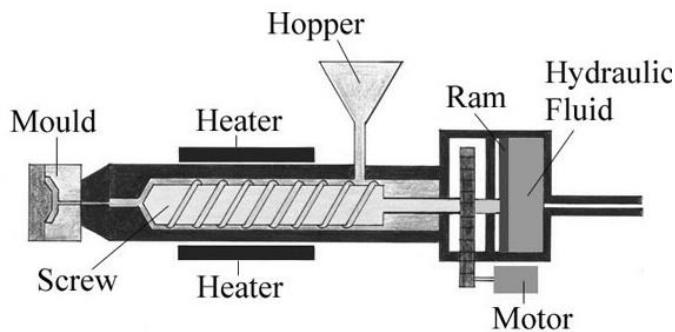
Compression moulding:

- ♦ It is the most common method used for thermosetting polymers.
- ♦ With this process, the material is squeezed into its desired shape with the help of pressure and heat.
- ♦ Plastic powder is mixed with other components & placed in the mould and closed.
- ♦ This is heated to required temperature & required time.



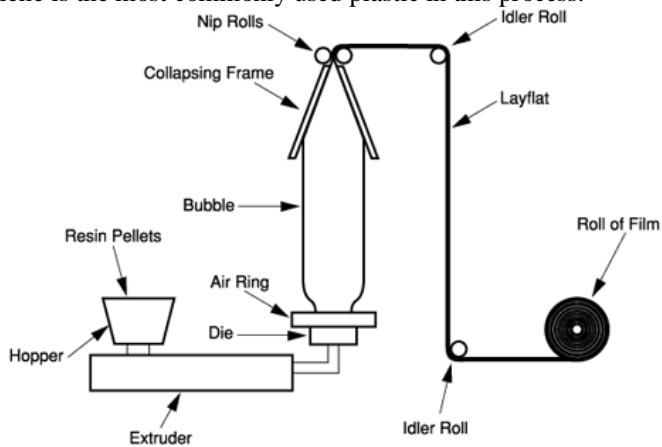
Injection moulding:

- ♦ The plastic material placed in the hopper.
- ♦ Hopper feeds the material to the heated injection unit.
- ♦ This unit is provided with a reciprocating screw.
- ♦ This screw forces the melted plastic through a nozzle into a cold mould.
- ♦ Two halves of the mould is fitted with one another through clamps.
- ♦ When the plastic is cooled and solidified, the halves are opened and plastic moulded article is ejected with the help of ejector pins.
- ♦ Thermosetting polymer can't be moulded by this method.



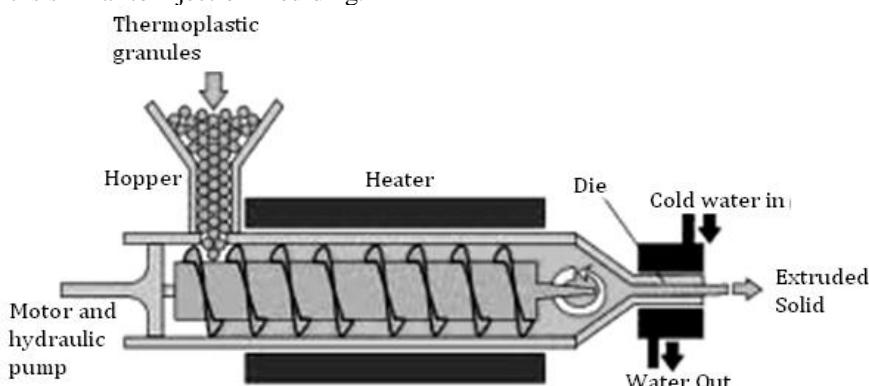
Blown film extrusion moulding:

- ◆ Plastic film is usually produced using a process called ‘blown – film’
- ◆ Molten plastic is injected into a blow film machine and blowing air through the molten plastic.
- ◆ This creates a bubble in the molten plastic.
- ◆ The bubble is blown vertically, creating a long bubble like a party balloon.
- ◆ The air is blowing into the outside of the balloon from a cooling ring at the base of the balloon blown air cools the balloon & then a thin film is produced.
- ◆ It is guided through pinched rollers which make the film flatten and it is wound on the roller.
- ◆ The flattened balloon is called lay flat tube.
- ◆ It is used to make carry bags.
- ◆ Polyethylene is the most commonly used plastic in this process.



Extrusion moulding:

- ◆ This method is used to produce continuous sheets, rods, threads, cords and cables.
- ◆ It is similar to injection moulding.



- ◆ Dry plastic material is placed into heated injection chamber.
- ◆ At the end of the chamber, the material is forced out of a small ring opening (or) a die in the shape of the desired finished product.

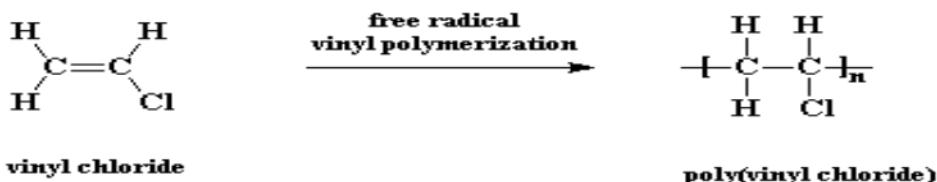
- ♦ Extruded out plastic is placed on a moving conveyor belt for uniform cooling.

Individual polymers

Poly vinyl chloride:

Preparation:

Polyvinyl chloride is prepared by heating a water emulsion of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide in autoclave under pressure.



Properties: Polyvinyl chloride is

- Colourless
 - Odourless
 - Non-inflammable
 - Chemically inert
 - Soluble in hot ethyl chloride

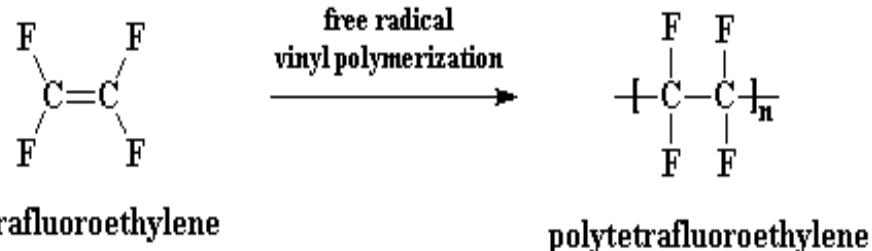
Uses: Used for the preparation of

- Safety helmets
 - Light fittings
 - Tyres, cycles
 - Refrigerator components

Teflon (poly tetra flouro ethylene ,PTFE) or Fluon:

Preparation:

Poly tetra flouro ethylene is prepared by polymerization of a water emulsion of tetra flouro ethylene in presence of Benzoyl peroxide under pressure.



Properties:

- ◆ Due to presence of highly electro negative fluorine atom, very strong attractive forces between different chains.
 - ◆ Due to strong attractive forces
 - Teflon is extreme tough
 - High softening point ($>350^{\circ}$)
 - High chemical resistance towards all chemicals except hot alkali metal and hot fluorine

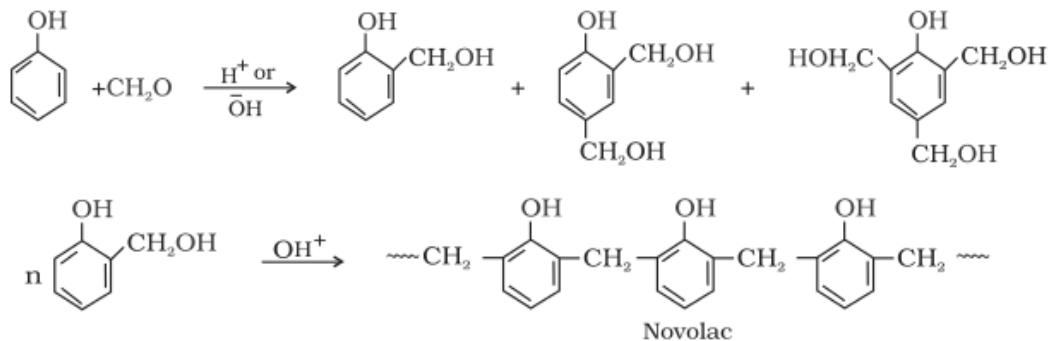
Uses: Used as

- 3. Used as
 - ▲ Insulating material for motors, cables
 - ▲ Coatings
 - ▲ Impregnating glass
 - ▲ Asbestos fibre
 - ▲ Clothes
 - ▲ Wires
 - ▲ Fittings

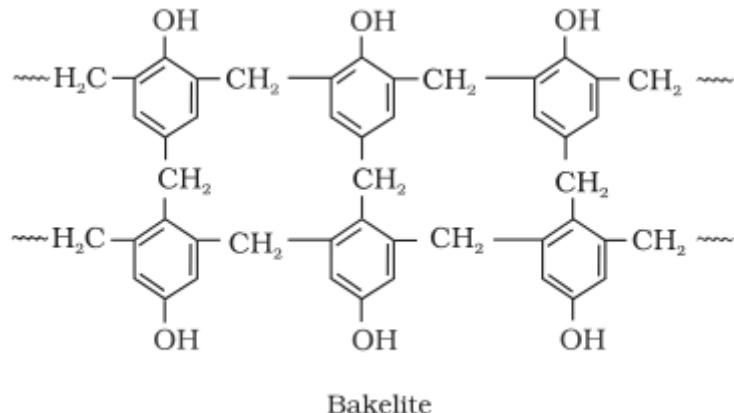
Phenol formaldehyde resins: Bakelite

Preparation:

- ↗ These are formed by the poly condensation between phenol and formaldehyde.
- ↗ The reaction is catalysed by acid or base.
- ↗ The initial product is Novalac (linear product).



- ↗ Novalac on heating with formaldehyde forms Bakelite.



Properties:

- These are
- ↗ Rigid
 - ↗ Hard, resistant to heat
 - ↗ With stand to high temperature
 - ↗ Good insulator

Uses:

Used for the preparation of
Electrical insulator parts like

- ↗ Switches
- ↗ Plugs
- ↗ Handles

Moulded articles like

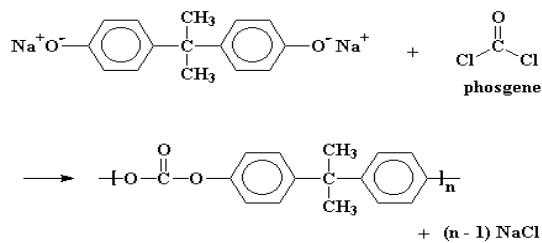
- ↗ Telephone parts
- ↗ Cabinets for T.V
- ↗ Cabinets for radio

Poly Carbonates

Polymers containing **-O-CO-O-** functionality

Preparation:

By the treatment of bisphenol-A with phosgene in presence of sodium hydroxide.



Properties: Polycarbonates

- Good electrical insulators
- Heat and flame resistance
- Easily soluble in organic solvents and alkali solvents
- Undergo large plastic deformation without cracking
- Highly transparent to visible light
- Low scratch resistance

Uses: Used in

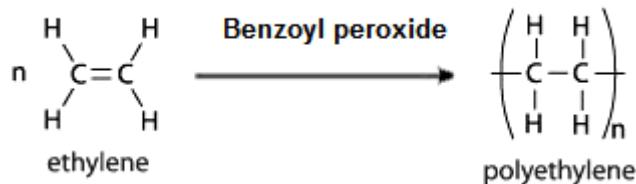
- Preparation of Compact disc, DVD'S
- Construction industry
- Automotive components
- Aircraft components
- Manufacture of lenses like sunglasses, eyeglasses

Disadvantages:

- Polycarbonate containers or bottles used for the storage of food are controversial because their hydrolysis releases bisphenol-A which causes several health hazards.

Polyethylene:**Preparation of LDPE:**

LDPE (low density polyethylene) is prepared by heating ethylene at 100-300°C under high pressure 1500 – 3000 atm in presence of benzoyl peroxide (as initiator) and benzene or chloro benzene (as solvent).

**Properties:** Density range from 918-935 Kg/m³

- Very tough
- Flexible

Uses: Used for the preparation of

- Domestic ware
- Tubing
- Squeeze bottles
- Cold water tanks

Preparation of HDPE:

HDPE (High density polyethylene) is prepared by heating ethylene at approximately 300°C under 1 atm pressure in presence of aluminium based oxide (as Catalyst) and paraffin or cyclo paraffin (as diluting agent).

Properties: Density range from 935 - 965 Kg/m³

- Stronger
- Stiffer

Uses: Used for the preparation of

- Dustbins
- Fluid containers
- Pipes
- Bottle crates
- Sheets, which are employed for tank linings

RUBBERS

- Rubber is an elastomer.
- A polymer which regains its original shape after removing applied force is called elastomer.
 - Natural rubber, Thiokol, neoprene etc.

Characteristics of Elastomers

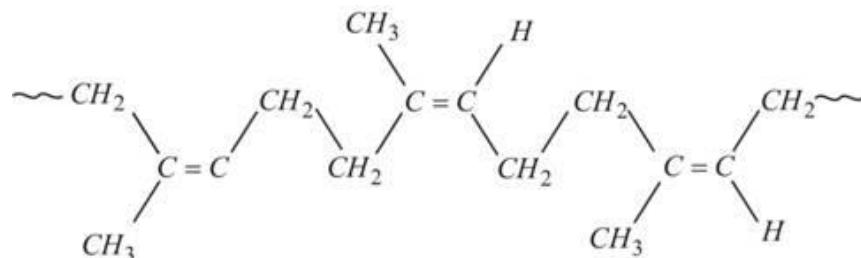
- ❖ Elastomers regain original shape after removing stress.
- ❖ Elastomers are sticky at higher temperatures.
- ❖ Elastomers exist at above glass transition (T_g) temperature.
- ❖ Elastomers absorb moisture.
- ❖ Elastomers have less chemical resistance.
- ❖ Elastomers have weak intermolecular attractions.
- ❖ Elastomers have coiled structures.

Natural Rubber

- ♣ Latex is collected from a tree known as Hevea brasiliensis.
- ♣ Latex is a water suspension.
- ♣ Rubber is coagulated by adding acetic acid or formic acid or electrophoresis of suspension.
- ♣ Separated rubber is then further processed.
- ♣ Natural rubber is Cis – poly isoprene formed from isoprene (2 – methyl 1, 3 – butadiene) by the biochemical reaction.

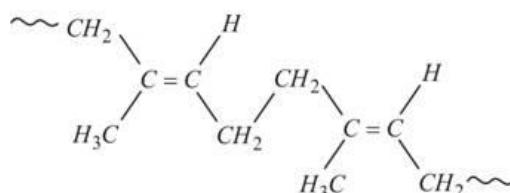


- ♣ The repeating unit is Cis configuration which is responsible for elastic property.
- ♣ The molecular weights of rubber molecules range from 50,000 to 30,00,000.
- ♣ Asia contributes 90% of rubber products. Thailand, Malaysia and Indonesia are major producers of rubber.



Gutta percha:

- It is obtained from mature leaves of dichopsis gutta and palagum gutta trees.
- Tran's polyisoprene is gutta percha.
- It is crystalline polymer & the chains are very closely packed.
- It leads to the formation of rod like structure.
- It is used to fill dental cavities and to prepare conveyor belts.

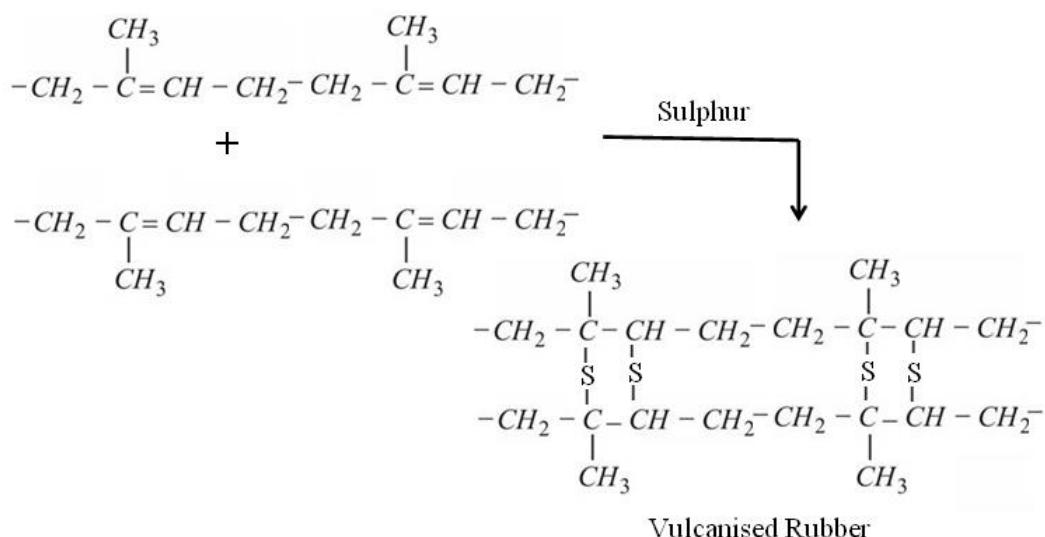


Compounding of rubber

To improve the qualities from rubber, it is mixed with various chemicals like plasticizers, stabilizers, fillers, vulcanizing agents etc is called compounding of rubber.

1) Vulcanization of rubber:

- ♣ To improve the undesirable properties of rubber, it is heated in the presence of sulphur.
- ♣ Heating of rubber in presence of sulphur is called vulcanization.
- ♣ On heating three dimensional cross linkings of the chains through sulphur atoms formed.
- ♣ Rubber becomes stiff.
- ♣ This process converts rubber into insoluble, infusible thermosetting polymer.



2) Accelerators:

- ❖ Vulcanization process is catalyzed by adding accelerators.
 - ❖ They reduce the time required for vulcanization.
 - ❖ Accelerators may be inorganic or organic.
 - **Inorganic:** Lime, Magnesia, ZnO
 - **Organic:** Aldehydes, Amines, thio carbonates
 - ❖ 0.5 to 1% of the accelerator is used.

3) Antioxidants:

- Antioxidants protect the rubber from oxidation by O_2 , ozone and light.
 - Example: Phenylnaphthylamine, Phenolic substances, Phosphate.

4) Reinforcing agents:

- They provide strength, rigidity and toughness to the rubber.
 - Example: Carbon black, ZnO, MgCO₃, CaCO₃ and clays.

5) Fillers:

- The main function of the fillers is to change the physical properties and to reduce the cost.

6) Plasticizers:

- These are added to impart greater tenacity and adhesion to the rubber.
 - Example: Vegetable oils, Waxes, Stearic acid, Rosin etc.

7) Coloring agents:

- ❖ These are added to impart the desired colour to rubber.

TiO ₂ , ZnS, BaSO ₄	- White	Sb ₂ S ₃	- Crimson red
PbCrO ₄	- Yellow		Ultramarine- Blue
Ferric Oxide	- Red	Cr ₂ O ₃	- Green

8) Miscellaneous agents:

- ❖ Baking soda is added to prepare sponge rubber.
 - ❖ Silica and pumice are added to cause abrasiveness.
 - ❖ Processed rubber is converted into various articles by calendering (or) injection moulding (or) compressed moulding.

Advantages of vulcanization:

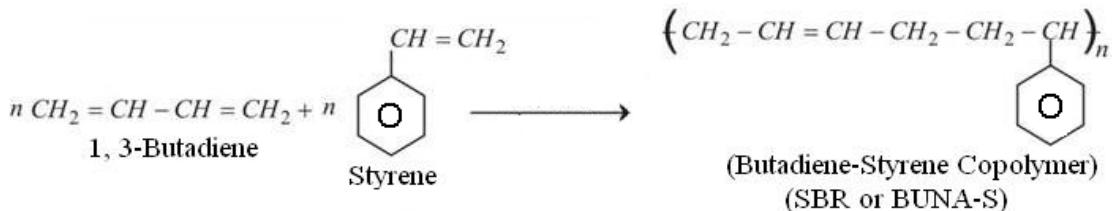
- Working temperature range is -40°C to 100°C.
 - Tensile strength increases 2000Kg/cm²
 - Water absorption capacity is reduced.

- Elasticity is reduced.
- Resilience is improved.
- Resistance to organic solvents such as benzene, CCl_4 , fats and oils.
- Resistance to abrasion, ageing and reactivity with O_2 and O_3 .

Synthetic rubber

Buna –S (or) SBR (styrene butadiene rubber):

- It is prepared by free radical polymerization in the presence of free radical initiator cumene hydrogen peroxide.
- It is a copolymer consists of 75% butadiene and 25% styrene.



Properties:

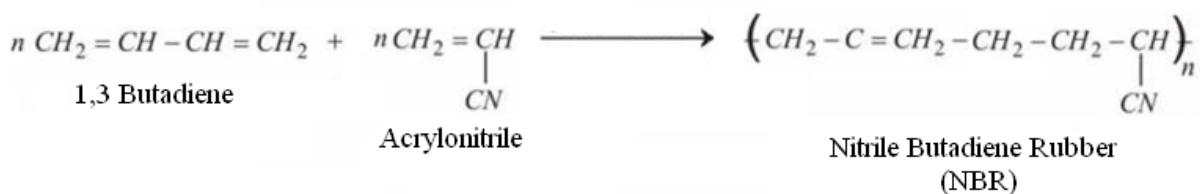
- Excellent abrasion resistance.
- Very tough.
- high load bearing capacity
- Sensitive to oil, waste water and ozone.
- Good electrical properties.
- Poorer resilience than that of natural rubber.

Uses:

- Used for the manufacture of
 - Tyres
 - Shoes heels
 - Shoe soles
 - Gaskets
 - Chewing gums
 - Electrical insulation
 - Floor tiles
 - Foot wear components

Buna –N (or) Nitrile butadiene rubber (NBR):

- It is prepared by free radical polymerization in the presence of free radical initiator cumene hydrogen peroxide.
- It is a copolymer of 75% butadiene and 25% acrylonitrile.



Properties:

- It is oil resistance. If the content of acrylonitrile more than 40% then it is extremely oil resistance.
- Resistant to heat, light and acids.
- High load bearing capacity.
- It has good tensile strength
- It has good abrasion resistance.
- It is less resilient than natural rubber.

Applications:

- Used for the manufacture of
 - Oils
 - Hoses

- Conveyer belts
 - Tank lining
 - High altitude air craft components
 - Used as latex in textile and cloth
 - Printing rollers

Polyurethane:

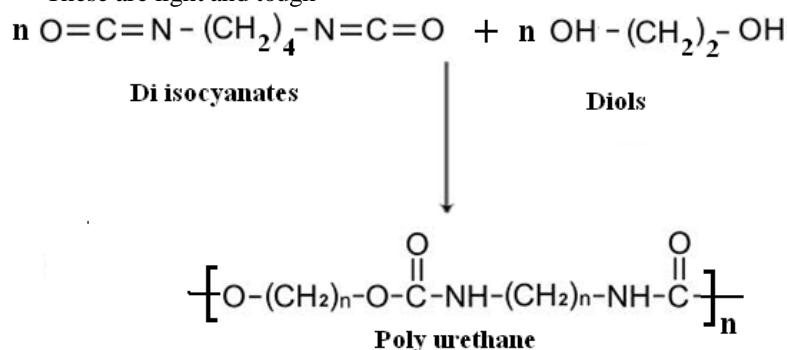
- Polyurethane polymer has urethane ($-\text{RNHCOOR}-$) linkage.

Preparation:

- Polymerization of diols and diisocyanates by addition polymerization gives polyurethane.

Properties:

- High strength
 - Good resistance to ozone, oxygen, aromatic hydrocarbons
 - These are light and tough



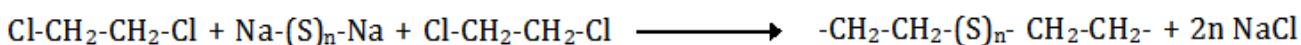
Uses:

- ❖ Used in beading and truck seating
 - ❖ Used in thermal insulation
 - ❖ Used in foot wear
 - ❖ Electronic instruments
 - ❖ Structural parts
 - ❖ Gel pads
 - ❖ Print rollers
 - ❖ Flexible plastic - straps, bands

Thiokol (Poly Sulphide rubber):

Preparation:

- ♦ It is obtained by the polymerization of ethylene dichloride with sodium poly sulphide.



Properties:

- ◆ The property of this material depends upon the length of the chain and number of sulphur atoms present in it.
 - ◆ With four sulphur atoms per monomer – the product is rubbery.
 - ◆ Where as with 2 sulphur atoms per monomer – the product do not act as rubber.
 - ◆ It can withstand cold but not heat.
 - ◆ It is unaffected by petrol, oil etc.

Uses: It is used for making

- ◆ Hose pipes
 - ◆ Linings tanks

Conducting polymers

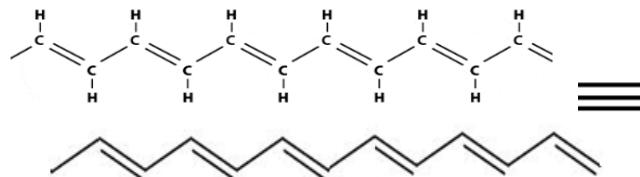
- ♣ Polymers that can conduct electricity are called conducting polymers.
Ex: Poly acetylene, poly aniline, poly pyrrole, poly thiophene, poly quinolene etc.
- ♣ On the basis of their conduction properties conducting polymers are classified into two types
 - ❖ Intrinsically Conducting Polymers
 - ❖ Extrinsically Conducting Polymers
- ❖ Intrinsically conducting polymers, which are able to conduct through either
 - ❖ Conjugation
 - ❖ Doping
- ❖ Extrinsically conducting polymers that are able to conduct through

- ☒ External Elements Filled
- ☒ Blending

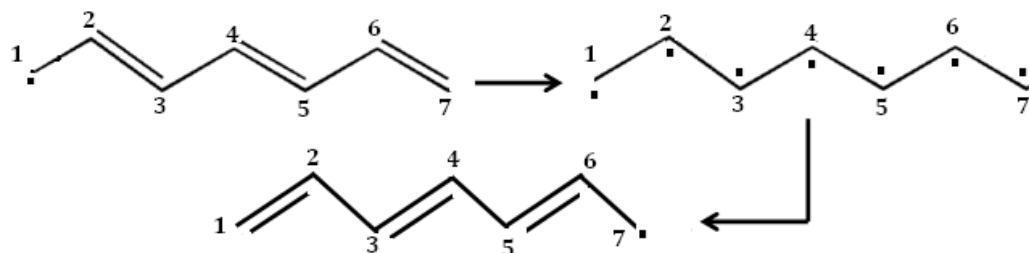
Intrinsically Conducting Polymers:

Conjugation:

- These polymers contain conjugated or delocalized $\pi - e^-$ pairs in the back bone responsible for conduction.
- The orbital's of conjugated $\pi - e^-$ form valency band as well as conduction band and they are extended over the entire polymer molecule.
- When current is passed electrons enter conduction band due to shifting of $\pi - e^-$.
- Ex; Conduction of poly acetylene due to conjugation.



- When current is passed into poly acetylene, the electron enters the unhybridised P-orbital of carbon atom and moves through the C – C bonds.



Explanation:

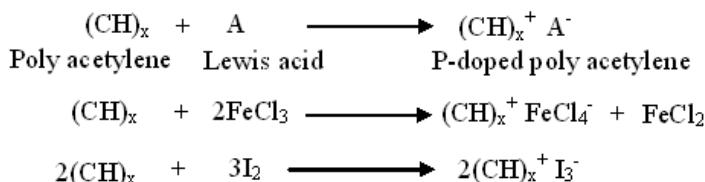
- ◆ When the electron enters the chain, breakage of $\pi -$ bond takes place and a new $\pi -$ bond is formed.
- ◆ $\pi -$ bond between 2&3 is broken and a new $\pi -$ bond is formed between 1&2.
- ◆ Similarly $\pi -$ bond between 4&5 is broken and anew $\pi -$ bond is formed between 3&4.
- ◆ $\pi -$ bond between 6&7 is broken and a new $\pi -$ bond is formed between 5&6.
- ◆ As long as current flows in to the polymer this process is continued and thereby a conducting path is created in the polymer.

Doped conducting polymers:

- ♣ Polymers can conduct due to doping and by using doping agents or dopants.
- ♣ Doping of conducting polymers can be two different types.
 - p-Doping (or) Oxidative Doping
 - n-Doping (or) Reductive Doping

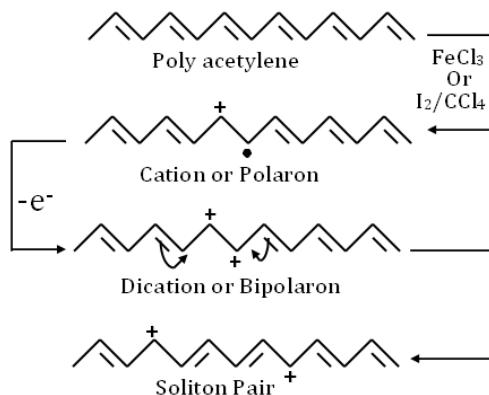
p-Doping (or) Oxidative Doping:

- In this method the polymer is treated with an oxidizing agent like Lewis acid which acts as a dopant.
- Examples of dopants used: $FeCl_3$, I_2 etc.



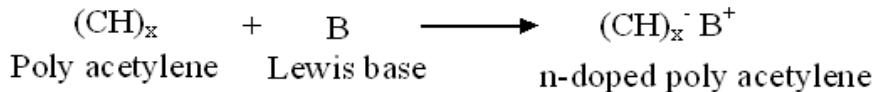
Mechanism of p-Doping:

- ▲ During this process, oxidation of polymer takes place due to dopant and forms a cation called Polaron.
- ▲ On further oxidation of polymer results in the formation of a dication or bipolaron.
- ▲ The charges get separated by forming a soliton pair.
- ▲ The cation occupies the band gap between valency band and conduction band, thereby creating a conducting path.
- ▲ So electrons move through this path.

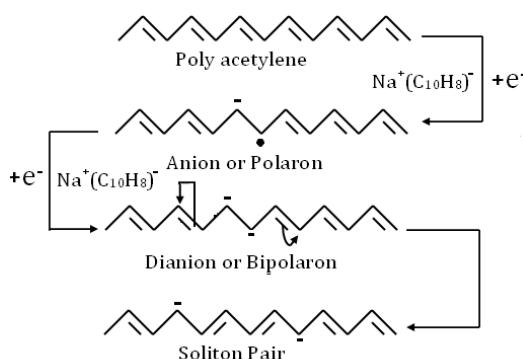


n-Doping (or) Reductive Doping:

- ▲ In this method, the polymer is treated with a reducing agent like a Lewis base which acts as a dopant.
- ▲ Ex; Sodium Naphthalide $\text{Na}^+(\text{C}_{10}\text{H}_8)^-$



Mechanism of n-doping:



- ▲ During this process, reduction of polymer takes place due to dopant and forms an anion called Polaron.
- ▲ On further reduction of polymer results in the formation of a dianion or bipolaron.
- ▲ The charges get separated to form a soliton pair.
- ▲ The anions occupy the band gap between valency band and conduction band thereby creating a conducting path.
- ▲ So that electrons move through this path.

Extrinsically Conducting Polymers:

- ▲ Some of the polymers conduct electricity due to externally added ingredients to them. They are of two types.
 - Polymers with conductive elements filled

- Blended conducting polymers

Polymers with conductive elements filled:

- ◆ In these polymers, the polymer acts as a ‘binder’ and holds the conducting element added so that the polymer becomes a conductor.
- ◆ Examples of conductive elements are carbon black, metallic fibers, metallic oxides etc.
- ◆ Minimum concentration of conductive element to be added so that the polymer becomes a conductor is called percolation threshold.
- ◆ The conductive elements added to create a conducting path in the polymer.

Blended conducting polymers:

- ◆ These polymers are obtained by blending a conventional polymer with a conducting polymer.
- ◆ The polymer thus obtained has good chemical, physical, electrical properties and mechanical strength.
- ◆ Ex; 40% pyrrole when blended with a conventional polymer, the combination gives conducting polymer with good impact strength.

Applications of conducting polymers in biomedical devices:

- ★ Conducting polymers are used in preparation of artificial devices like Heart valves, kidneys, and lungs.
- ★ Poly methyl methacrylate is used as bone cement used for some fracture repairs.
- ★ Poly methyl methacrylate is also used for artificial teeth.
- ★ Used in preparation other medical devices include sutures, pins, screws used during surgery on bones, ankles, hands etc.
- ★ They are used to prepare contact lenses which permit O₂ to the eyes. These lenses are called rigid gas permeable lenses (RGP).

Applications of conducting polymers in electronics:

- ✉ They are used in rechargeable batteries.
- ✉ They are used in analytical sensors of p^H, O₂, NO₂, SO₂, NH₃ etc.
- ✉ Used in photo voltaic cells. Ex; Al/polymer/Au.
- ✉ Used in telecommunication systems.
- ✉ Used in transistors and diodes.
- ✉ Used in solar cells.
- ✉ Used as wiring in air crafts and aerospace parts.

NANO MATERIALS

Introduction

- In recent years, nano science and technology have grown rapidly.
- Nano chemistry has wide applications in almost all the fields.
- The word “Nano” means “dwarf” in Greek language.
- Nano is one billionth parts.
- A nano second is one billionth of a second and a nano meter is one billionth of a meter. i.e., $1\text{ nm} = 10^{-9}\text{ m}$

Examples

- ▲ Size of atom is up to 10 nm.
- ▲ DNA molecules are about 2.5 nm wide.
- ▲ RBC size is 1000 nm.
- ▲ A two meter tall person is two billion nano meters tall.

NANO CHEMISTRY

It is the science of tools, technologies and methodologies for chemical synthesis, analysis and biochemical diagnostics performed in nano litre to femto litre level. i.e., Nano = 10^{-9} femto = 10^{-15}

NANO MATERIALS

Nano materials are the materials having components within size less than 100 nm.

Nano particles are the particles having size 1-50nm.

- ▲ Nano materials in one dimension are layers like thin films or surface coatings.
- ▲ Nano materials in two dimensions are tube like nano tubes and nano wires.
- ▲ Nano materials in three dimensions are particles like precipitates, colloids and quantum dots.

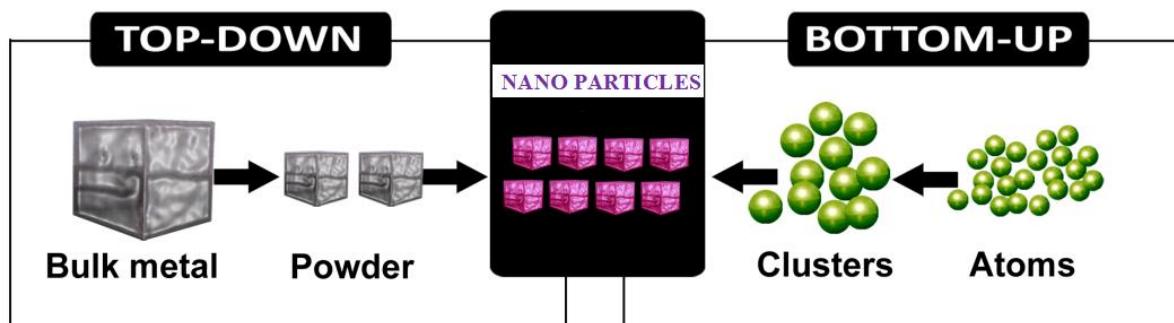
Quantum Dot (Three Dimensional Nano Materials)

- ▲ The size of the quantum dot is one billionth of a meter.
 - ▲ The key to the quantum dot is in the electrons.
 - ▲ Electrons occupy are of two bands (valency band & conduction band) in a crystal.
 - ▲ By supplying energy, an electron is excited from valency band (VB) to conduction band (CB).
 - ▲ As it moves from one band to the other, it creates a hole which is positively charged.
 - ▲ Together, the hole and the electron are referred to as an exciton.
 - ▲ The electron and the hole in the exciton normally keep their distance from each other.
 - ▲ This is called the exciton Bohr radius.
 - ▲ If the crystal is reduced in size, it crowds this gap.
 - ▲ Once that happens, it changes the crystals ability to absorb and emit energy.
 - ▲ At this point, quantum dot is created.
 - ▲ Different colours can be obtained by reducing or increasing the size of the quantum dot.
- ▲ Applications**
- ▲ Used to track trespassers in restricted areas.
 - ▲ Used as light emitting diodes in sign display
 - ▲ Used as cell staining for life science.

GENERAL METHODS OF PREPARATION OF NANO MATERIALS

There are basically two major types of approach for the preparation of nanomaterials.

- Synthesis of Nanomaterials**
- ```
graph TD; A["Synthesis of Nanomaterials"] --> B["Top-Down Method
(Destruction)"]; A --> C["Bottom-Up Method
(Construction)"]
```
1. **Top – Down Method:** In this method bulk materials are converted to nano particles by using different methods. This method is used in the microelectronic industry.
  2. **Bottom – Up Method:** in this method very small particles like individual molecules or atoms are assembled to get cluster which in turn are aggregated to get nano particles



### **SOL- GEL METHOD**

- Sol gel method is bottom up approach for the synthesis of nano materials and it is very long known since 1980.
- A colloid suspended in a liquid is called as **sol**.
- A suspension that keeps its shape is called **gel**.
- Thus sol-gel is suspensions of colloids in liquids that keep their shape.
- The sol-gel formation occurs in different stages.

**Step – I:** Precursor (metal oxide) undergoes hydrolysis by continuing stirring for 24hrs gives sol.

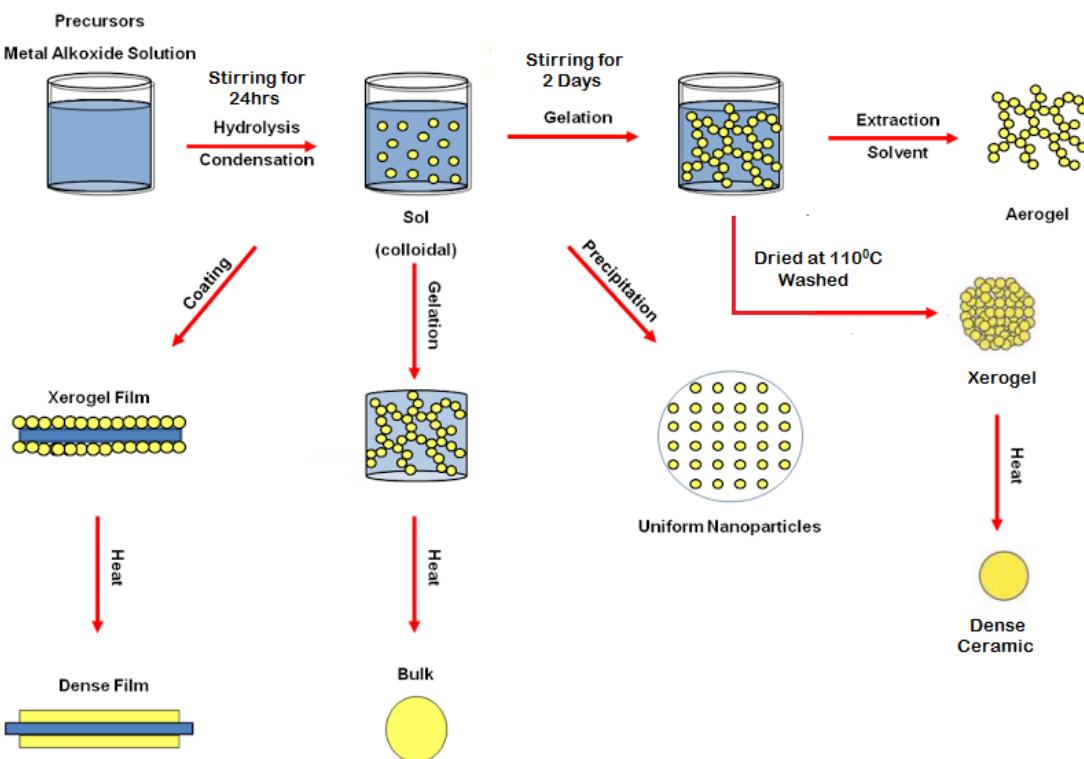
**Step – II:** On continues stirring for 2 days, sol is converted into gel. This results increase in the viscosity of solution.

**Step – III:** On drying at 110°C, gel is converted into Xerogel.

**Step – IV:** On extraction of solvent from the gel produces aerogel.

**Step – V:** Sol on precipitation uniform nano particles is formed.

**Step – VI:** Sol is coated on a material and heated, dense layer is formed.



### CHEMICAL REDUCTION METHOD

- In this method also belongs to bottom up approach.
- Metal nano particles are prepared by this method like nano silver particles, nano platinum particles etc.
- General preparation is carried out by mixing metal salt with phase transferring agents and reducing agents.
- Different types of phase transfer agents are used for the preparation of different metal nano particles.

**The method involves following steps.**

- To the metal salt solution, precursor, stabilizer and reducing agents are added.
- This mixture is allowed to stand for sometime, and then the nano particles are separated out.
- The formed nano particles are purified by centrifugation.
- A dried powder of nano particle is obtained by freeze drying.

**For example: Silver nano particles are obtained by following method.**

- Metal salt solution - silver nitrate
- Precursor and stabilizer - sodium dodecyl sulphate (SDS)
- Reducing agents – hydrazine hydrate, citrate solution
- This mixture is allowed to stand for sometime, and then the nano particles are separated out.
- The formed nano silver particles are purified by centrifugation.
- A dried powder of nano silver particle is obtained by freeze drying.

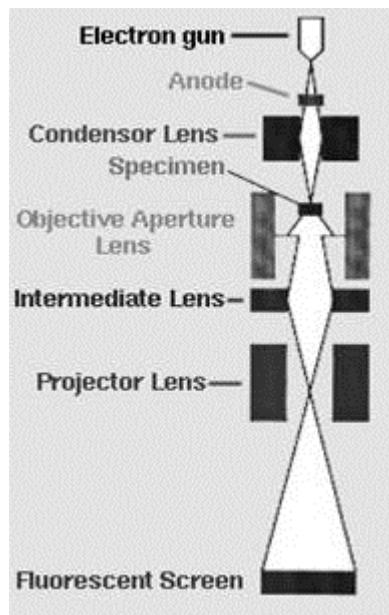
### METHODS OF CHARACTERIZATION OF NANO PARTICLES

#### TEM (Transmission Electron Microscopy)

1. TEM is used for the determination of particle size, size distribution and morphology of the nanoparticles.
2. TEM is a technique whereby a beam of electrons is transmitted through a thin specimen, interacting with the specimen as it passes.
3. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto fluorescent screen or onto

photographic film, for a record of the sample.

4. Areas of dense material (such as solid nano particles) absorb the electrons and appear as dark areas on the viewing screen.
5. Less dense material (such as coating around the nano particles) allows the electrons to pass through more freely and appear as lighter areas.
6. TEM images can also be used to judge whether good dispersion has been achieved or whether agglomeration is present in the system.



### **BET (Brunauer Emmett Teller Method)**

- ★ This method gives the information about the physical [adsorption](#) of [gas molecules](#) on a [solid surface](#).
- ★ It is an important analytical technique used for the measurement of the specific surface area of a material.
- ★ BET is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption and the BET theory refers to multi layer molecular adsorption.
- ★ The sample is weighed and placed into a vacuum chamber.
- ★ The sample is degassed and cooled down to a constant temperature by means of an external bath containing liquid nitrogen.
- ★ Other inert gases, such as Ar or Kr, can also be used.
- ★ N<sub>2</sub> gas is admitted and adsorbs on the sample surface.
- ★ The BET theory is then used to determine the amount of gas necessary to form a monolayer on the surface, also called the monolayer capacity.
- ★ From the monolayer capacity, the known surface requirement of a single adsorbate molecule and the mass of the sample, the specific surface area in m<sup>2</sup>/g can be calculated.

### **CARBON NANO TUBES (CNTS)**

- ☛ Carbon nano tubes were discovered in 1991 by Iijima.
- ☛ Carbon nano tubes are long thin cylinders of carbon.
- ☛ These are large macro molecules that are unique for their size, shape and physical properties.
- ☛ CNTs are allotropes of carbon with a nano structure having a length to diameter ratio greater than 1, 00,000.
- ☛ A sheet of graphite rolled into a cylinder. Rolled graphite sheets are called Carbon nano tubes.
- ☛ CNT have very broad range of electronic, thermal and structural properties which vary with the dimensions of tubes.

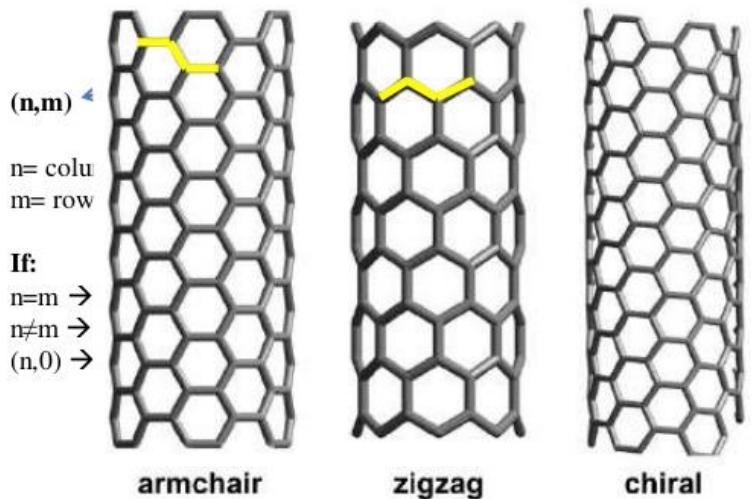
### **TYPES OF CARBON NANO TUBES**

- Carbon nano tubes are lattice structure of carbon atom.
- Each carbon atoms are covalently bonded to each other.
- Depending upon the arrangement of carbon atoms, these are classified into two types.
  - Single walled nano tubes (SWNTs)
  - Multi walled nano tubes (MWNTs)

#### **Single walled nano tubes (SWNTs)**

- ♣ SWNT have diameter close to one nano meter
- ♣ It is obtained by wrapping graphene in to seamless cylinder.

- ♣ One atom thick layer of graphite is graphene.
- ♣ One useful application of SWNT's is in the development of first intermolecular field effect transistors (FET).
- ♣ Based on the way the graphene sheet is wrapped SWNT's are three types.
  - Zig – Zag
  - Arm Chair
  - Chiral



Graphene sheet consisting of pair of indices n, m

#### Arm chair

- If  $n=m$  the nano tubes are called armchair.
- The lines of hexagons are parallel to the axis of the nano tube.

#### Zig – Zag

- If  $m=0$  the nano tube are called zig-zag.
- The lines of carbon bonds are down the centre.

#### Chiral

- Remaining all are Chiral.
- It has twist or spiral around the nano tube.

### Multi walled nano tube (MWNTs)

- ❖ It consists of multiple rolled layers of graphite.
- ❖ These are concentric tubes.
- ❖ The distance between two layers is  $3.3 \text{ \AA}$ .
- ❖ These are two models.

- Russian doll model
- Parchment model

#### Russian doll model

- ❖ Sheets of graphite are arranged in concentric cylinders.
- ❖ A tube is arranged inside the larger tube.

#### Parchment model

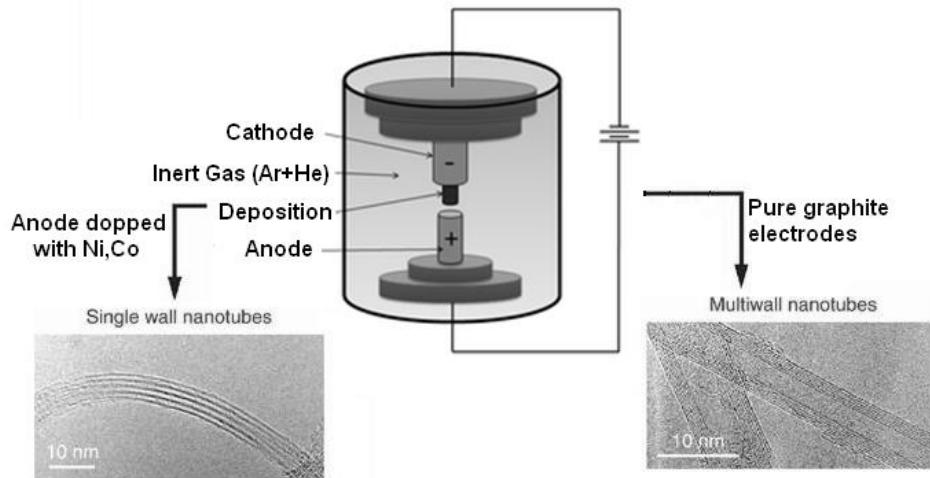
- ❖ A single sheet of graphite is rolled in around itself like a rolled News paper.



### SYNTHESIS OF CARBON NANO TUBES

Carbon nano tubes are synthesized by 3 methods.

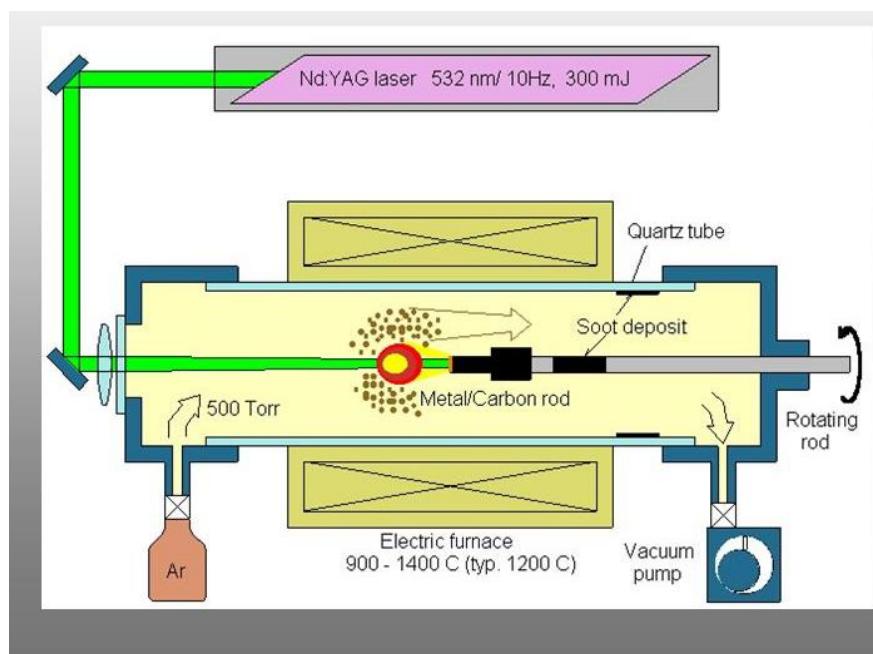
#### 1. Arc Discharge Method



- This is the most common and easiest way of producing CNT.
- This method creates nano tubes through the arc vaporization of two carbon rods placed end to end, separated by 1mm.
- A direct current of 50 to 100 Amps driven by approximately 20 V creates high temperature discharge between the two electrodes.
- The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod.
- Size of the nano tubes formed depends up on the mixture of He & Ar gas used in the discharge tube.
- This mixture shows different diffusion co-efficient and thermal conductivities which affect the size of CNTs formed.
- By this method, it is possible to produce SWNTs (or) MWNTs selectively.
- Single walled nano tubes are prepared by anode dopped with Ni, Co.

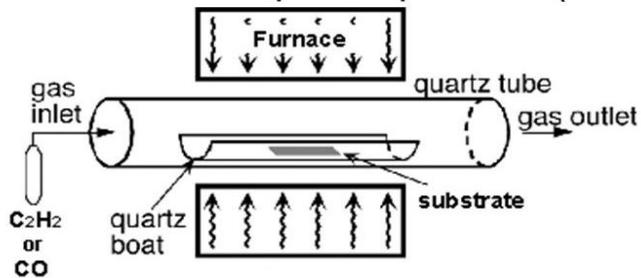
## 2. Laser Ablation Method

- In 1995, Smalley's group produced CNTs using laser ablation technique.
- In laser ablation technique a high power laser is used to vaporize carbon from a graphite target at high temperature.
- Both SWNTs and MWNTs can be produced.
- To produce SWNTs the catalyst must be added to graphite.
- The laser is focused on the carbon target containing 98.8% graphite, 1.28% cobalt (or) nickel composite placed in 1200°C quartz furnace under argon atmosphere under 500 torr pressure.
- These conditions are achieved for production of SWNTs.
- Argon gas carries the vapour from the high temperature chamber in to water cooled collector position at down stream.
- CNTs produced by this method are purity up to 90%.
- Quantity and quality of CNTs depend on laser power, wave length, temperature, pressure, type of inert gas, type of catalyst.



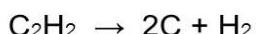
## 3. Chemical Vapour Deposition Method (CVD)

- CH<sub>4</sub>, CO and acetylene gases are used as a source for carbon atoms.
- Using heated coil, the energy is supplied to the gas molecules and carbon atoms are separated by cracking.
- Then the carbon atoms diffuse towards substrate which is heated and coated with Ni or Fe or Co where it will bind.
- By this method, alignment and position of the carbon tubes can be controlled in nano scale.
- Even length of the nano tube is also controlled.
- CVD is a two step process.
- In the first step, transition metal is coated on the substrate by sputtering.
- In the second step, nano tubes are deposited on the specified areas of substrate by thermal annealing or chemical etching of catalyst.
- NH<sub>3</sub> may be used in etching.
- The temperature maintained in this process is 650 – 900°C.
- Yield in this method is 30%.



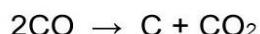
MWCNT

600-800 °



SWCNT

900-1000 °



### PROPERTIES OF CARBON NANO TUBES (NANO MATERIALS)

CNTs have unique chemical, optical, electrical and structural properties which are useful in bio sensing and drug delivery systems for treating various diseases.

#### Mechanical Properties

##### Strength:

- Carbon nano tubes are the strongest and stiffest materials.
- They possess high tensile strength and Young's modulus.
- This strength is due to  $\text{SP}^2 - \text{Sp}^2$  bonding between carbon atoms.
- CNTs are much softer in the radial direction than along the tube axis.

##### Hardness:

- Super hard material is prepared by compressing SWNTs to above 24 GPa at room temperature.
- The bulk modulus of compressed SWNT was 462 – 546 GPa.

#### Electrical Properties

- ✓ CNTs are metallic or semi conducting depending on their structure.
- ✓ If  $n=m$ , the nano tube is metallic.
- ✓ If  $n-m$  is multiple of 3, then nano tube is semi conducting.
- ✓ Some nano tubes have higher conductivities than that of copper.

#### Vibrational Properties

- ✓ Atoms in CNT are continuously vibrating back and forth.
- ✓ **A<sub>1g</sub> Mode:** It involves in and out oscillations.
- ✓ **E<sub>2g</sub> Mode:** Here squashing of the tube takes place (Oscillation between sphere and ellipse).

### APPLICATIONS OF CARBON NANO TUBES

- The small size, strength and unique properties of these nano materials found greater applications in various fields of engineering.

#### Engineering Applications

- Sensors
- Radiation sources
- Hydrogen storage media
- They are used as efficient tools for transporting therapeutic molecules.
- CNTs attached with peptides, proteins, nucleic acids, drugs are used to deliver the materials to cells or organs.
- CNTs are used in nano biotechnology and nano medicine.

#### Applications in Fuel Cell

- SWNTs are effective as a hydrogen storage material for fuel cell electric vehicles.

- ▲ Electrodes constructed with nano tubes are light weight and thin.
- ▲ They work as good as conventional electrodes.

### **Applications in Catalysis**

- ▲ A catalyst having CNT makes reaction milder, safer and more selective.
- ▲ CNTs are used as catalyst or catalyst additives or catalyst promoter.
- ▲ Oxidized CNT with phosphorous is used as a catalyst for the conversion of butane to butadiene.
- ▲ Some chemical reactions are carried out inside the nano tubes.
  - Reduction of NiO to Ni
  - Reduction of AlCl<sub>3</sub> to Al

### **Application in Medicines**

- ▲ CNTs deliver drugs in low potential to the cancer cells without damaging other healthy cells.
- ▲ CNTs are useful in selective destruction of cancer cells by IR radiation.
- ▲ A biosensor prepared from SWNT is used for the detection of DNA.