



Polymers

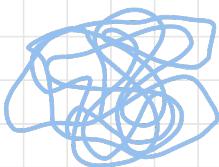
- Hitesh Pranav



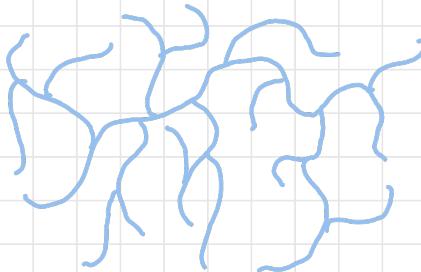
POLYMERS

- Polymer

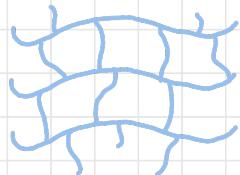
- A Giant molecule formed by repeated joining of several monomers
- Polymers can be linear, branched (or) cross-linked



Linear Polymer



Branched Polymer



Cross-Linked Polymer

- Monomer

- A simple molecule having 2 or more binding sites which can be linked together to form a giant molecule

Molecule	Structure	Monomer (Yes/No)
Ethylene	$\text{CH}_2=\text{CH}_2$	Yes
Acetic Acid	CH_3-COOH	
Ethane	CH_3-CH_3	
Ethylene Glycol	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \qquad \\ \text{OH} \qquad \text{OH} \end{array}$	
Adipic acid	$\begin{array}{c} \text{HO} \qquad \qquad \qquad \text{O} \\ \qquad \qquad \qquad \\ \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 \end{array}$	
Amino Acid	$\begin{array}{c} \text{H}_2\text{N}-\text{C}(=\text{O})-\text{R}-\text{C}(=\text{O})-\text{OH} \\ \qquad \qquad \qquad \qquad \qquad \\ \text{H} \qquad \qquad \qquad \qquad \qquad \text{OH} \end{array}$	
Styrene		

• Polymerization

- Process by which monomers of low molecular weight are converted into polymers of high molecular weight

- **Functionality**

- Total no. of functional groups or bonding sites

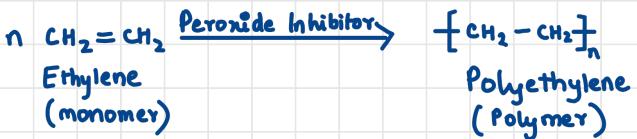
Monomer	Structure	Functionality
Ethene	$\text{CH}_2 = \text{CH}_2$	Bi functional
Ethylene Glycol	$\begin{matrix} \text{CH}_2 - \text{CH}_2 \\ & \\ \text{OH} & \text{OH} \end{matrix}$	Bi functional
Glycerol	$\begin{matrix} \text{OH} & \text{OH} & \text{OH} \\ & & \\ \text{CH}_2 - \text{CH} - \text{CH}_2 \end{matrix}$	Tri functional
Amino Acid	$\begin{matrix} \text{R} & \text{O} \\ & \\ \text{H}_2\text{N} - \text{C} - \text{C} - \text{OH} \\ & \text{H} \end{matrix}$	Bi functional

Degree of Polymerisation

- Total no. of repeat units in a polymer chain
 - $$DP = \frac{M_w \cdot wt\ of\ polymer}{M_w \cdot wt\ of\ monomer}$$

- Can be used in:

- Determining length of polymer chain
 - M.wt of polymer

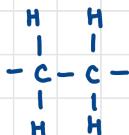


• Types of Polymerisation

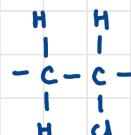
• Addition

- Self addition of unsaturated monomers to each other without elimination of byproducts

ex: PVC, polystyrene, Teflon, Polyethylene



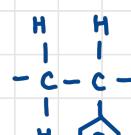
Polyethylene
(PE)



Poly Vinyl Chloride
PVC



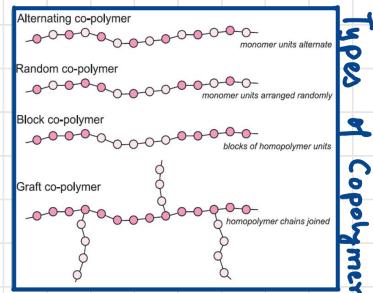
Poly Tetra Fluoro Ethylene
(PTFE)



Poly Styrene
(PS)

• Salient Features

- Linear / Branched Polymers are formed
- Rapid Self Addition
- No elimination of Products
- Can take place by:
 - Free radical mechanism
 - Cationic mechanism
 - Anionic mechanism
 - Coordination mechanism
- Molecular wt is an integral multiple of monomer's.



TYPES OF ADDITION POLYMER

Homopolymer

PVC, PE, Teflon

Copolymer

Styrene - Butadiene Rubber

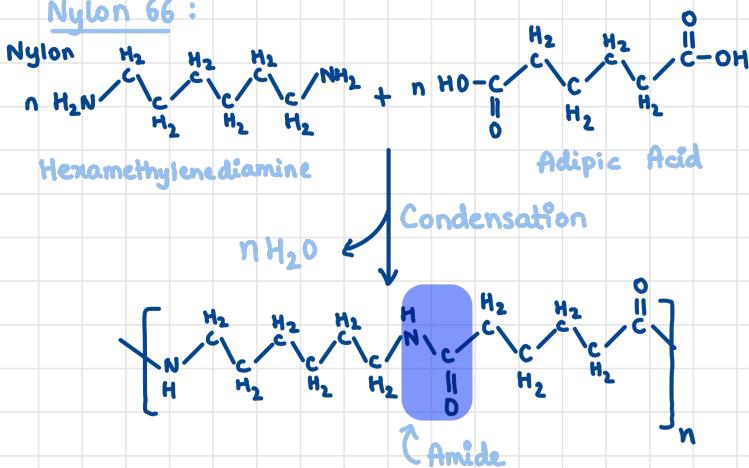
Alternating Random Block Graft

• Condensation

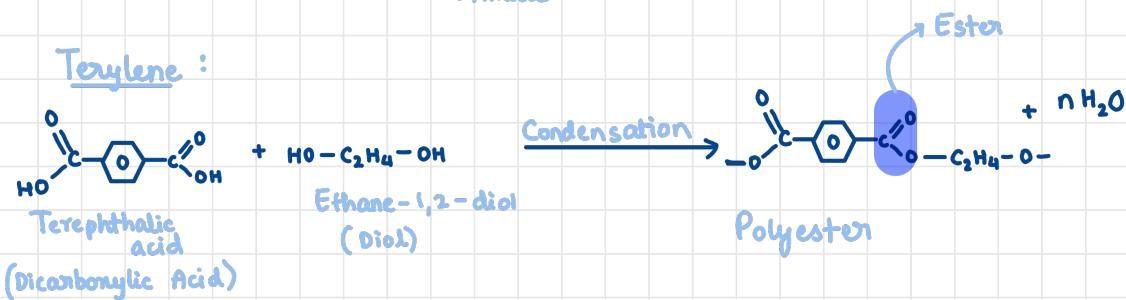
- Intermolecular condensation through functional groups of monomers with continuous elimination by products

ex: Nylons, Polyesters, Phenol-formaldehyde resin

Nylon 66 :



Terylene :



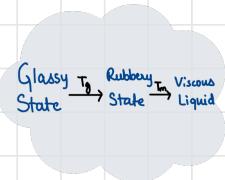
• Salient Features

- Catalysed by acids (or) alkali
- Continuous elimination of by-products
- Linear, Branched (or) Cross-Linked Polymers are formed
- Chain build-up is stepwise
- Molecular weight of polymer isn't integral multiple of monomer

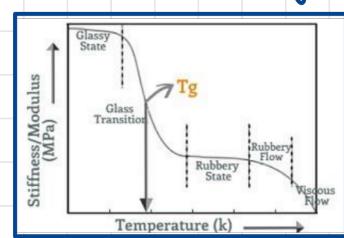
Addition Polymerization	Condensation Polymerization
No elimination of small molecule	Elimination of small molecules (H_2O, NH_3 etc)
Inhibitors are required	Catalyst is required
Linear (or) Branch polymer formed	Linear, Branch (or) cross-linked are formed
Molecular wt. is integral multiple of monomer's molecular weight	Molecular wt. isn't integral multiple of monomer's molecular weight
Monomers are unsaturated molecules	Monomer unit must have 2 active functional groups

GLASS TRANSITION TEMPERATURE (T_g)

- All amorphous polymers,
- cooled below certain temp - stiff, hard, brittle and glassy
- heated above certain temp - Soft, flexible & rubbery
- The transition temperature of a polymer from glassy state to rubbery state is called Glass Transition Temperature (T_g)
- Temp at which it is at Rubbery state and starts flowing is called melting point (T_m)



Polymer	T_g	T_m
Polyethylene	-125	137
Polyisopropene	-73	28
Polystyrene	100	240
Poly methyl methacrylate	105	200
Poly terefluoroethylene	127	327



- T_g is the measure of flexibility of polymer & predicts response to mechanical stress

STRUCTURE

- Polymers are very versatile in terms of properties
- Their properties depends on structure

Crystallinity

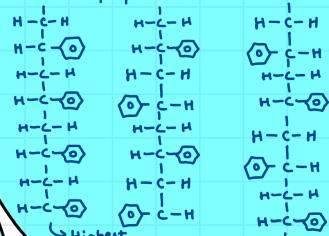
- Degree of Crystallinity depends on Structure and configuration
- Polymers can have both amorphous & crystalline structure
- Crystalline regions occur when polymer chains are arranged in an orderly fashion, parallel & close to each other

Structure

- Polymers made of linear chains w/o bulky pendant groups, are more crystalline
ex: Polyethylene more crystalline than Polyvinyl acetate
- Polymers containing polar groups are more crystalline
- Close packing b/w polymeric chains due to strong dipole-dipole interactions / H bonding \Rightarrow high D.O.C
ex: PVC $>$ PE (D.O.C)

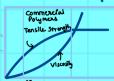
Configuration

• Crystallinity also depends on stereoregularity of polymers as isotactic, syndiotactic & atactic



Tensile Strength

- Amount of Stress object can handle before permanent deformation
- Tensile strength depends on:
 - molecular mass \propto T.S
 - Polar groups increase T.S
 - Cross linking \propto T.S
 - Force of attraction b/w chains \propto T.S
(as M.wt \uparrow , melt viscosity gradually increases then increases steeply)



FACTORS INFLUENCING POLYMERS

Chemical Resistance

- Resistance to swell, dissolve & get degraded is presence of chemical
- Depends on nature & molecular arrangement of monomers
- \Rightarrow Polymer w/ Polar grps are attacked by polar liquids
- \Rightarrow Polymer w/ non-polar grps aren't attacked but swell easily & dissolve in non-polar solvents
- \Rightarrow Residual Degradation \Rightarrow Polymers w/ Residual double bonds get attacked & degrade in air & UV light
- \Rightarrow Dense packing increases resistance for a solvent to penetrate in between the layers
- \Rightarrow Swelling \downarrow as Molecular wt \uparrow
- \Rightarrow Solubility \downarrow as Degree of cross linking

Plastic Deformation

- Application of heat \Rightarrow soft & flexible
- Application of cooling \Rightarrow Back to Original Shape
- Thermoplastic \rightarrow Polymer that becomes soft on heating & hard on cooling & can be remolded
- Thermosetting \rightarrow Polymer that becomes hard on heating & can't be remolded. Even total degradation
- This is because, \nwarrow Weak VdW force, H-Bonding
 \uparrow Dipole-Dipole interaction
- Thermoplastic have weak force of attraction which are overcome on heating
- Thermosetting have cross linked covalent bonds which can't be broken easily. Strong heating leads to degrading

Elasticity

- Property by which it deforms on applying force & regains original shape on release of force
- Elastomers have long coiled & entangled chains which straighten themselves on stretching
- When stress is removed, they go back to coiled form
- Bulky, aromatic & cyclic groups decrease elasticity of polymer
- Non-polar have weak VdW forces, so more elastic

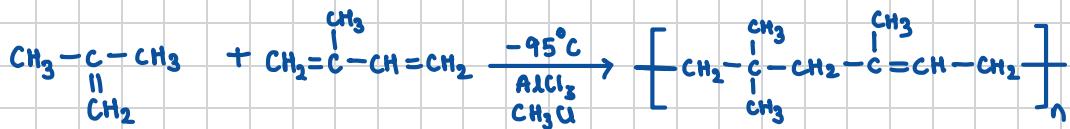
In non-elastic, plasticizers are used like Ph_2PO_4 which enter b/w polymer chains & make hard polymers flexible

• ELASTOMERS

- Property of polymers by which it deforms on applying force & regains original shape on release of force is called elasticity
- Elastomer have :
 - long, chained & tangled chains → straighten & orient themselves on stretching
 - Go back to normal → When Stress is Removed

• BUTYL RUBBER

- Synthetic Rubber with many applications
- Better than natural rubber in some cases
- Synthesis :
 - Copolymerisation of isobutylene & isoprene dissolved in CH_3Cl (at low temp)



• Process :

- isobutylene mixed with isoprene is dissolved in CH_3Cl
- Anhyd. AlCl_3 dissolved in CH_3Cl added & r/n is carried out at -95°C
- Finely powdered butyl rubber is obtained
- Isoprene introduces unsaturation to polymer chain 1% & helps in vulcanisation
- This product is mixed with antioxidants & dried to prevent degrading

• Properties :

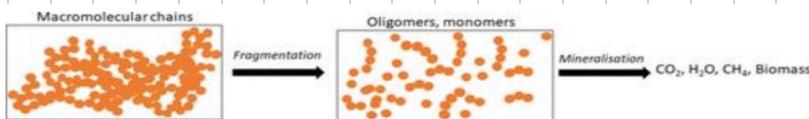
- Good Resistance towards gas & moisture permeation
- Good Chemical inertness
- Excellent electrical insulation

• Applications :

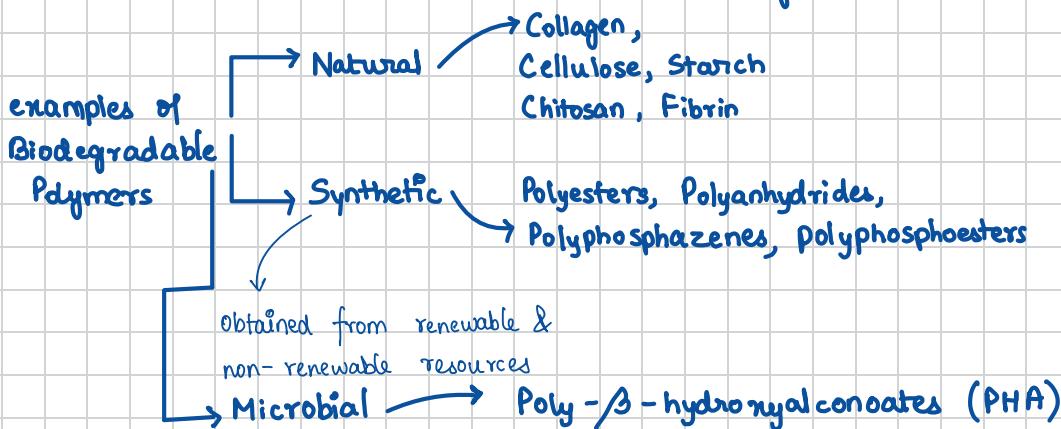
- Not allowing gas to flow
- Excellent impermeability to gas, useful in seals for vacuum operations
- Tyre inner liners & inner tubes because of gas impermeability & air retention
- Insulating high voltage wires & cables
- Hydraulic applications where Synthetic fluids are used

BIODEGRADABLE POLYMERS

- Polymers that can be decomposed by action of microorganisms into H_2O , CO_2 , CH_4 & Biomass
- It involves 2 steps:
 - Fragmentation → Polymer macromolecule is broken down into smaller chains (or) monomers by hydrolysis (or) oxidation
 - Mineralisation → Monomers get decomposed into CO_2 , H_2O , CH_4 or Biomass depending on structure of polymer & environment



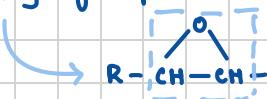
- Susceptibility of polymer to undergo degradation depends on:
 - Physical Properties like:
 - Structure of polymer
 - Molecular Weight
 - Degree of Branching
 - Crystallinity
 - Solubility
 - Environmental conditions like:
 - pH
 - availability of O_2
 - Light
 - Temp
 - Humidity
 - Microorganisms etc.,



- Advantages:
 - Reduced emission of greenhouse gases
 - Can be broken down by naturally occurring microorganisms
 - Easy usage & Recycling
 - Consume less energy to manufacture
 - No harmful products released
 - Decompose quicker
- Applications
 - Organic waste collection & diversion
 - Agriculture & Horticulture Sectors
 - Food Packing
 - Disposable Tableware
 - Drug delivery & dissolvable sutures
- **ADHESIVES**
 - They are low molecular weight polymer which bind 2 or more materials by dissolving into solvent and solidify, which is done by adding a curing agent, causing cross-linking, and forming a thermoset solid polymer
 - Natural adhesives - gum, glue, starch
Synthetic adhesives - PF, UF, epoxides
 - Adhesives → Material Used On
 - PF → Rubber
 - UF → Wood
 - Epoxy Resin → Metal, Wood, Glass, Concrete, Leather

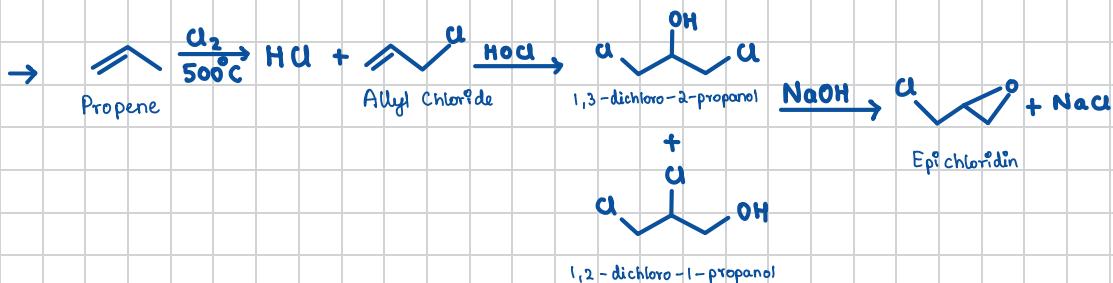
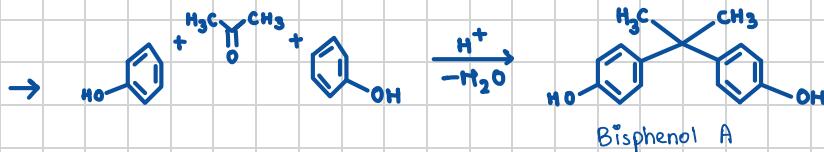
EPOXY RESIN

- Resins containing epoxy group

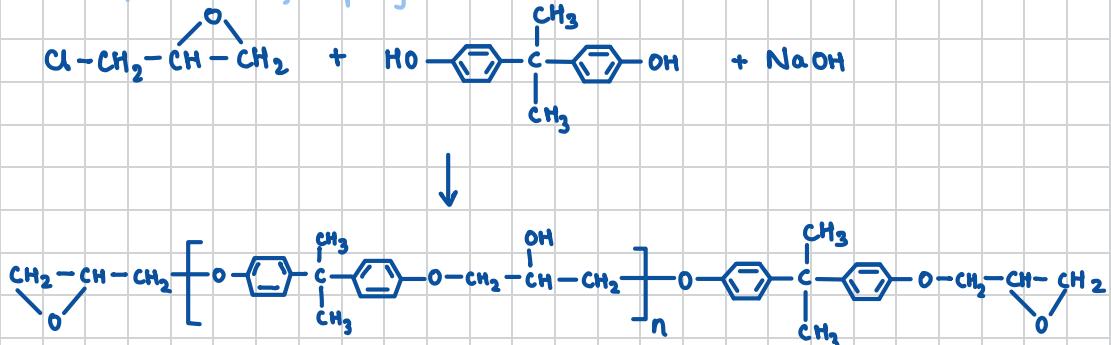


- Commercially known as Araldite (or) Epon

- They are obtained by condensation In b/w Bisphenol A & Epichlorohydrin



- Synthesis of Epoxy Resin



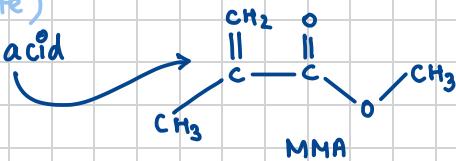
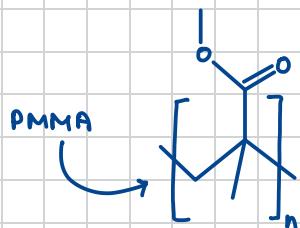
- Excess of epichlorohydrin is used so that end groups are epoxy groups which are highly active
- When curing agents are added, 3D crosslinked structure is formed
- Curing agents are diamines, dicarbonylic acids (or) acid anhydrides
- **Properties**
 - Excellent Adhesive
 - Excellent Resistance to Water, Acid, Base & corrosive chemicals
 - High Mechanical Strength
 - Absorb less moisture
 - Good insulation properties
- **Applications**
 - Cured epoxies frequently used in aerospace & defence
 - Used to bind glass, metal, leather, wood, ceramic etc.,
 - Coated on floor to give antiskid layer
 - Laminating materials
 - Crease & Shrinkage resisting fabrics

POLYMER COMPOSITES

- When 1 or more components make up and their properties aren't attainable by an individual component alone are Polymer Composites
- 2 Components are fibre & matrix
 - Matrix: Polyester, epoxy, phenolic, silicone, melamine, vinyl derivatives
 - Fibers: Glass Fiber, Boron filaments, carbon fibers, aramid, Al fiber
 - Aromatic Polyamide
- Polymer composite are produced by suitably bonding fiber material with polymer resin matrix & curing the same under pressure & heat
- Composites have high strength / unit weight

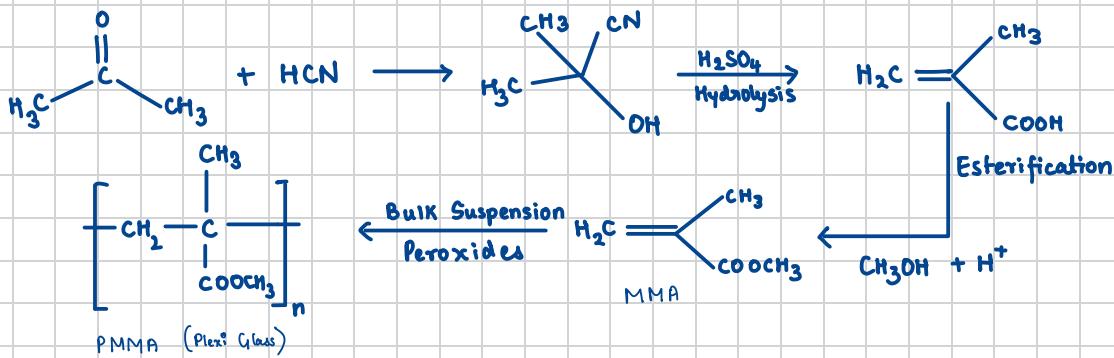
• PMMA (Poly Methyl Methacrylate)

- Vinyl polymer of methacrylic acid



(Free Radical Polymerization)

- Monomer synthesis from acetone to MMA



• Properties

- It is amorphous, thermoplastic material (moldable at 60°-80°C)
- Excellent optical properties
- Dissolves in organic solvents
- Hard & resists scratching, sun rays & weather agents
- Inert to acid environment deterioration
- Transparent & glossy finish

• Applications

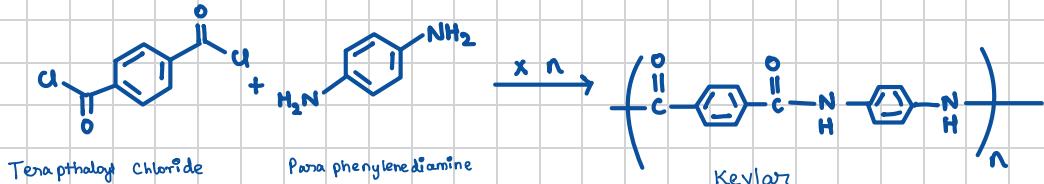
- | | |
|-------------------------|----------------------|
| • Glass Substitute | • Cosmetics |
| • Construction & Design | • Lamps & Lighting |
| • Automobile Industry | • Electronic Devices |
| • Healthcare Industry | • Solar devices |

• KEVLAR

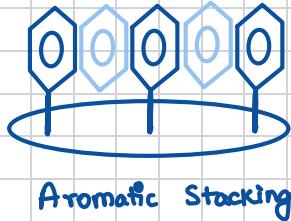
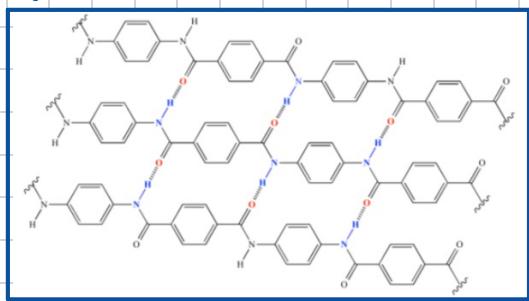
- An aramid fibre
- Chemical name \Rightarrow Poly-paraphenylene terephthalamide

• Synthesis

- Condensation of 1,4 phenylene diamine & 1,4-benzene dicarbonyl chloride



- Kevlar is about 5 times stronger than steel because:
 - Inter-molecular H-bonds formed b/w carbonyl groups & NH centers
 - Additional strength from aromatic stacking interactions b/w adjacent strands



• Properties :

- High Tensile strength, high modulus of Elasticity
- High strength : weight ratio
- High chemical inertness
- Low co-efficient of Thermal Expansion
- Flame Resistance
- High impact & cut resistance
- Textile Processibility

- Applications
 - Combat helmets, ballistic face masks, bullet proof jacket
 - Gloves, sleeves, jackets to protect users from cuts & heat
 - Inner lining in bicycle tyres
 - Light weight boat hulls, aircraft panels, race cars & bridges
 - Fibres are woven into ropes for off - shore drilling
 - Reinforcement in car-tyres & car brakes
 - Strings in archery bows

- Disadvantages :

- Special cutting scissor & drilling machines required
- Fibre is
 hygroscopic
absorbs moisture

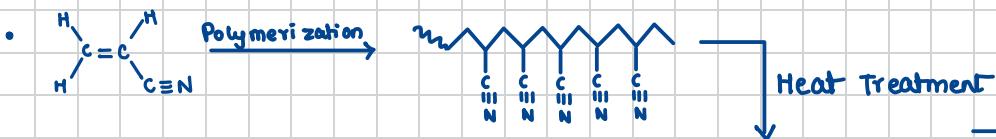
- REINFORCED KEVLAR COMPOSITES

- It is formed by combining Kevlar & Epoxy Resin
- Applications:
 - Monocoque bodies of F1 cars, helicopter rotor blades, Kayaks, tennis & squash racquets

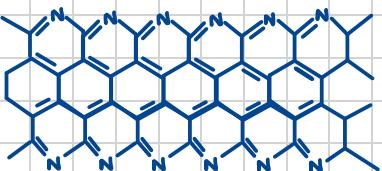
CARBON FIBRES

- Fibres about $5\text{-}10 \mu\text{m}$ in diameter and composed mainly of 'C'
- Several 1000s of these fibres are twisted together to form yarn which is used like that or woven into fabric
- Synthesis:
 - Each Carbon filament is produced from a precursor polymer like PAN, pitch blende etc.,

↳ Polyacrylonitrile



Heat Treatment
 2000°C



+ H_2

- Polymerisation
- Cyclisation (low temp)
- Oxidative treatment (high temp)
- Graphitisation (2000°C in inert atmosphere)

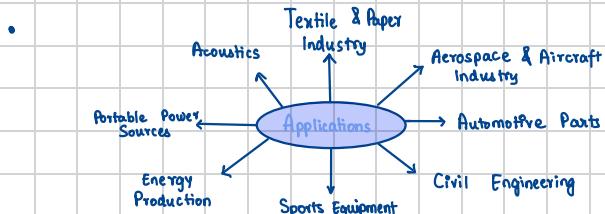
Graphitisation

- **Structure:**
 - Sheets of Carbon in regular pattern like graphite but sheets interlock
 - In Turbostratic carbon fibre, Sheets of Carbon are haphazardly folded (or) crumpled together
- **Properties:**
 - High Strength : weight ratio
 - Corrosion Resistant & Chemically Stable
 - Good Tensile Strength
 - Non-poisonous & Biologically inert
 - Low coefficient of Thermal Expansion
- **Applications :**
 - Aerospace, marine & road transport
 - Sporting goods
 - Medical equipment
 - Automobile hoods, novel tooling, casings and bases of electronics
 - Speakers, pick up arms, robot arms
- **Disadvantages :**
 - Expensive
 - Volatile by-products are formed (HCN)



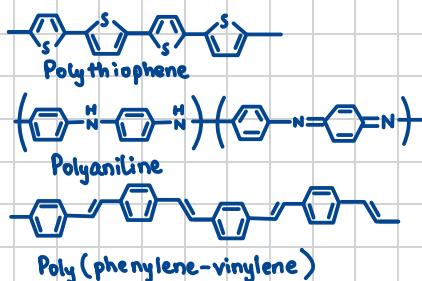
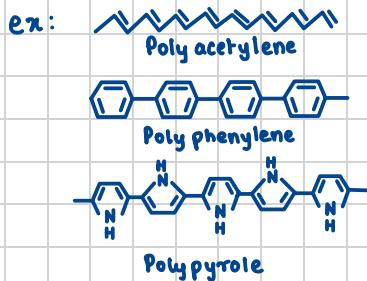
CARBON FIBRE REINFORCED POLYMER (CFRP)

- Made by reinforcing Carbon fibre & epoxy resin matrix
- Properties
 - Light weight
 - High Strength : weight ratio
 - Low coefficient of thermal expansion
 - High Electrical Conductivity

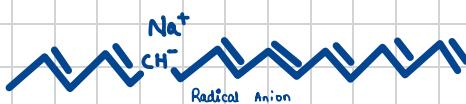
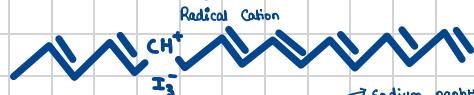


CONDUCTING POLYMERS

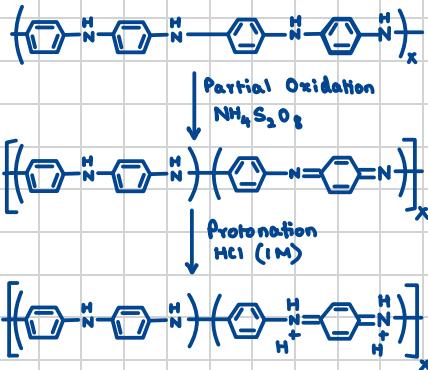
- Polymers are generally insulators because organic molecules that they consist of, don't have any free e^- to carry current
- But, If an organic polymer has highly delocalized $\pi-e^-$, has high electrical conductivity, similar to that of electrical conductors.
- They are called conducting polymers / synthetic metals
- So, if a polymer is doped with an e^- acceptor / donor , it leads to dramatic changes in electrical, electronic, magnetic & optical properties



- Conducting polymers conduct if :
 - delocalisation of $\pi-e^-$
 - linear structure
 - extensive conjugation in polymeric back bone
 - has several double bonds
- 3 Types of doping :
 - Oxidative Doping (p-doping)
 - π -backbone of polymer is partially oxidised using **oxidising agent** → Iodine in CCl_4 , $HBrO_4$ etc., which creates +vely charged sites on polymer backbone, which are current carriers for conduction.
 - Reductive Doping (n-doping)
 - π -backbone of polymer is partially reduced using **reducing agent** → Sodium naphthalide in THF which creates -vely charged sites on polymer backbone, which are current carriers for conduction.



- Protonic acid doping
 - Current carrying charged species ($\text{v}^{+}-\text{v}^{-}$) are created using a protonic acid
 - A typical example, During doping of polyaniline, charged species are created by protonation of imine nitrogen



- Applications
 - Electrode material for commercial rechargeable batteries (high power:weight)
 - Conductive tracks on printed circuit boards
 - Humidity sensor, gas sensor, radiation sensor, biosensor
 - Electrochromic display windows
 - Information storage devices
 - Film membranes for gas separation
 - In LEDs
 - Microelectronics, electrocatalysis, fuel cell electrodes, reinforced composites etc.

AVERAGE MOLECULAR WEIGHT

- Weight of polymers can't be directly measured as they are a mix of chains of different length, so we use average molecular weight instead.
- Properties like stress-strain, impact, fracture, fatigue, creep, stress relaxation & cracking are influenced by average molecular weight

Average Molecular Weight

Number Avg. M.wt

$$\cdot \bar{M}_n = \frac{\text{Total wt. of dispersed material}}{\text{Total no. of polymer units}}$$

$$= \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

$$= \frac{\sum n_i M_i}{\sum n_i}$$

- \bar{M}_n depends only on no. of polymer units & not the size

- Colligative Properties are used to determine number avg. m.wt

Weight avg. m.wt

$$\cdot \bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + \dots}{m_1 + m_2 + \dots}$$

$$= \frac{\sum m_i M_i}{\sum m_i}$$

where, $m_1, m_2, \dots \Rightarrow$ mass of polymer units

$M_1, M_2, \dots \Rightarrow$ Respective m.wt

$$\bar{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + \dots}{n_1 M_1 + n_2 M_2 + \dots}$$

$$= \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

where, $n_1, n_2, \dots \Rightarrow$ No. of polymer units

- Properties like sedimentation velocity or light scattering depend on size of particle which is used to determine weight avg. m.wt

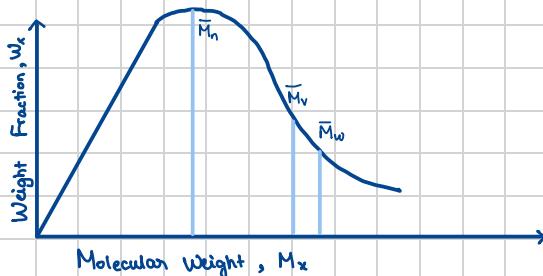
Viscosity avg. m.wt

$$\cdot \bar{M}_v = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right)^{1/a}$$

where a is Mark-Houwink Parameter

- a depends on polymer solvent system at a particular temp
- $0.5 \leq a \leq 0.9$
- \bar{M}_v is closer to \bar{M}_w as larger molecules contribute more to viscosity.

- The $\frac{\bar{M}_w}{\bar{M}_n}$ ratio is called Polydispersity Index (PDI) which measures the broadness of a m.wt distribution of polymer.
- $PDI = 1 \Rightarrow$ Monodisperse polymer, chain lengths are equal
- $PDI > 1 \Rightarrow$ Polymeric sample is less homogeneous & polydisperse



$$\bar{M}_n < \bar{M}_v < \bar{M}_w$$

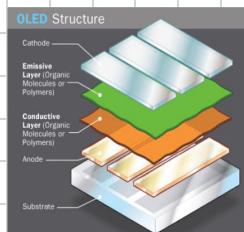
• ORGANIC LIGHT EMITTING DIODES

- OLEDs are similar to LEDs but instead of layers of p & n-type semiconductors, they use organic molecules
- OLEDs have an emissive electroluminescent layer which is filled with organic compounds that emit light on response to current

- Emerging Technology for displays
- Displays are flexible, thin & light weight

• Construction:

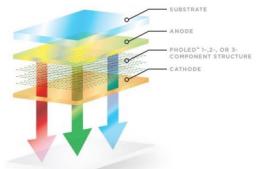
- Substrate: Glass for Support
- Anode : Transparent, usually made of Indium Tin Oxide (ITO)
- Cathode : Injects e^- . (Metals like Mg)
- Conductive Layer: Organic molecules/polymers transport holes from anode
- Emissive Layer: Organic molecules/polymers transport e^- from cathode & recombine with e^- to emit light. (Polyfluorene (aniline))



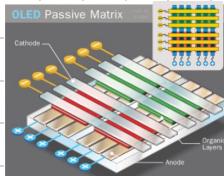
• Working:

- Voltage applied across anode & cathode of OLED
- e^- flows from cathode to anode through organic layers
- e^- are transported to emissive layer
- holes are transported to conductive layer
- e^- combine with holes & emit light
- Recombination is closer to emissive layer
- Colour of light depends on organic molecule used
- Intensity depends on current density

Passive Matrix OLED



- They have strips of cathode & anode, organic layers
- Anode strips are \perp to cathode strips
- The intersections form pixels where light is emitted
 - External circuitry determines which pixel should be on or off
 - More Power usage than other OLED
- Used for small screens



White OLED

- Emit White light brighter, uniform & energy efficient than fluorescent lights
- Have true-color qualities of incandescent lighting
- Used for large & efficient lighting Systems

Active Matrix OLED

- Have full layers of cathode, anode & organic molecules
- Anode layer has thin film transistor array back plate that forms matrix
- TFT array is the circuitry that determines which pixel gets turned on
 - AMOLED consumes less power than PMOLEDs because TFT array needs less power
 - Used for Large Display

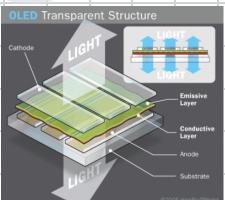
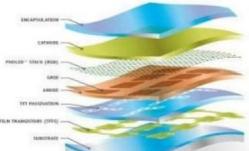
Foldable OLED

- Substrates made off very flexible metallic foils or plastics
- Very light weight, Ultra thin & reduce breakage
- Used in cell phones & PDAs

TYPES OF OLED

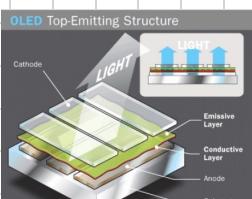
Transparent OLED

- Has transparent substrate, cathode & anode
- When it is turned on, It allows light to pass in both directions
- It can be either active or passive matrix
 - Used in transparent projector Screens & glasses



Top-Emitting OLED

- Substrate is opaque or reflective
- Suitable for Active Matrix
- Used for small card displays



- **ADVANTAGES**

- Organic layer of OLEDs are thinner, lighter, brighter & flexible than Crystalline layer of LEDs & LCDs
- Consume less power
- Easier to produce
- Have large fields of view (upto 170°)
- High color contrast & faster response time

- **DISADVANTAGES**

- Have shorter life span
- Expensive manufacturing
- Water can easily damage it

- **APPLICATIONS**

- Mobile Phones
- A/v Players
- Digital Cameras
- OLED TVs
- OLED Lamps
- Other devices (watches, infotainment system, headsets, digital photo frames etc.,)