Sumedh

- **Polymer**

$$CH_2 = CH_2 \longrightarrow \sim C - C - C - C - \sim$$

Polyethylene (PE) or

A Chain of repeated monomer is called polymer

degree of polymerization (n)

no of of monomer units in polymer

PVC - Polyvinyl Chloride

$$CH_2 = \underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow \sim CH_2 - \underset{\displaystyle Cl}{\underset{|}{C}} - C - \underset{\displaystyle Cl}{\underset{|}{C}} - C - \underset{\displaystyle Cl}{\underset{|}{C}} - \sim$$

$$\left(CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH_2}} \right)_n$$

- **Classification of polymers**

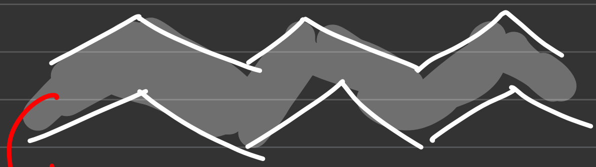
① **Based on origin**

i) Natural : rubber, protein

ii) Synthetic : Polythene, Teflon

② Based on structure

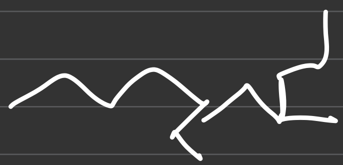
i) Linear



weak vanderwaal

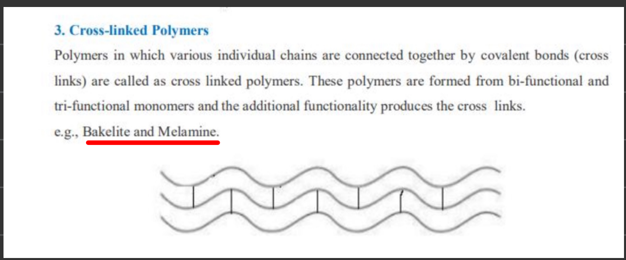
eg HDPE

ii) Branced



eg LDPE

iii) Crosslink



3. Cross-linked Polymers

Polymers in which various individual chains are connected together by covalent bonds (cross links) are called as cross linked polymers. These polymers are formed from bi-functional and tri-functional monomers and the additional functionality produces the cross links.

e.g., Bakelite and Melamine.

③ Based on type of monomer

i) Homopolymer : Only one type of monomer chain

eg PE, PVC, PP, etc

ii) Copolymer

1] alternate copolymer

eg ~ A - B - A - B - A ~

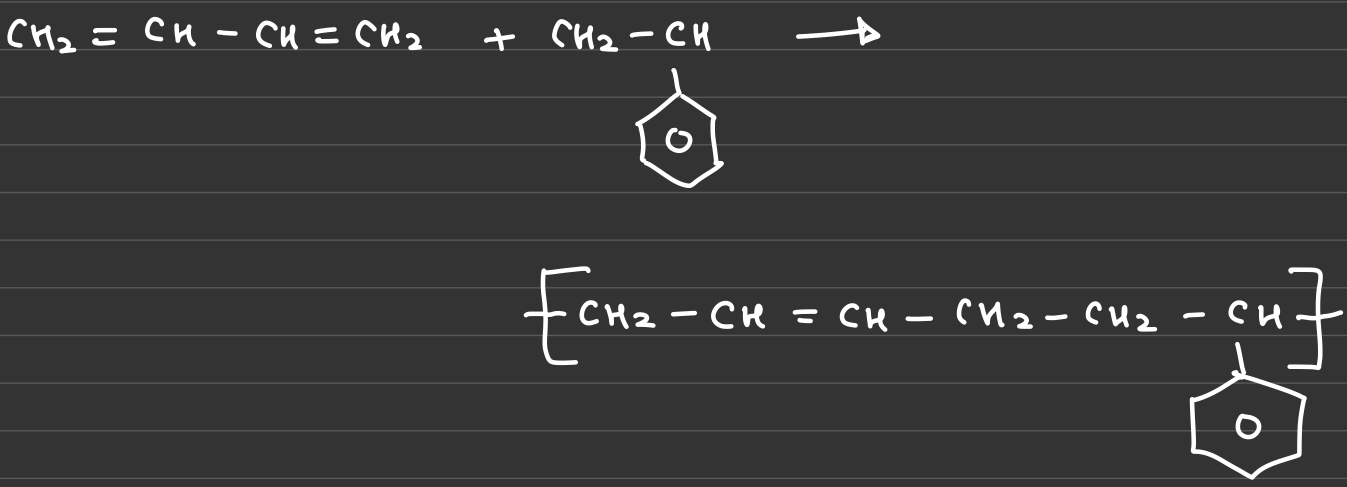
2] block

~ A-A-A-B-B-A-A-B-B-B-A ~

3] graft

~ A-A-A-A-A-A-A...
   |
   B
   |
   B
   |
   B

eg: Styrene - butadiene rubber



④ Based on synthesis

i) Addition : no loss of molecule
no change in chem comp
Mw = n (unit)
Linear
Recycalable

ii) Condensation

$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\boxed{OH + H}-\overset{H}{\overset{|}{N}}-(CH_2)_6-NH_2$$

$$\downarrow$$

$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH_2$$

Nylon (66)

⑤ Based on Thermal behaviour

i) Thermoplastic

When heated & cool can retain C, becomes soft

Linear poly, Addⁿ

ii) Thermoset

Cross link

When heated & then cooled, process is irreversible

Covalent bond breaks

Condensation

Thermoplastic	Thermoset
1. Formed by **addition** polymerization	1. Formed by **condensation** reaction
2. **No crosslinking** in structure	2. **cross-linked 3D** structure
3. **Soften on reheating** because of weak secondary forces	3. Softening on reheating **not possible** because of strong covalent bonds
4. **Can be recycled** from waste	4. **Can not be recycled** from waste
5. **soft, weak and less brittle**	5. **hard, strong and more brittle**
6. **Dissolve** in organic solvents	6. **Not soluble** in organic solvents
7. e.g. PE, PVC	7. e.g. bakelite, urea formaldehyde

Polymer types & Examples

	Type	Example
Origin :-	Natural	Rubber, protein
	Synthetic	Polythene, teflon
Structure :-	Linear	HDPE
	Branched	LDPE
	Cross - link	Bakelite, Melamine
Monomer :-	Homopolymer	PVC, PE, Nylon-6
	Copolymer	Nylon-66, Terylene
Synthesis :-	Addition	PVC, Teflon, PE
	Condensation	Nylon-66
Thermal :-	Thermoplastic	Addition, linear (PE, PVC)
	Thermoset	Condensation, cross link (Bakelite)
	Elastomer	Rubbers
	Fibres	Nylon, Terylene

Functionality of monomer :-

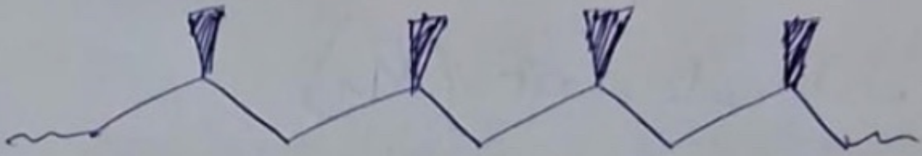
$-X, -OH, -\overset{O}{\overset{\|}{C}}-OH, -NH_2$

- Defined as the no. of active sites or reactive sites per monomer unit.
- Minimum no. of functional group per monomer is two.
- $>C=C<$ is functionality 2.
- $-C\equiv C-$ is functionality 3.
- Funtionality 2 ⇒ linear polymer
  " 3 ⇒ branched / cross linked polymer

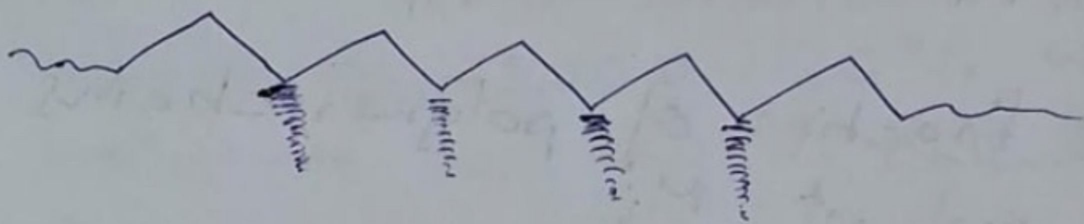
Tacticity of polymer :-

- Defined as the spatial arrangement of monomer units in a polymer chain is known as tactic.

Eg - Isotactic
Syndiotactic
Atactic (Random)

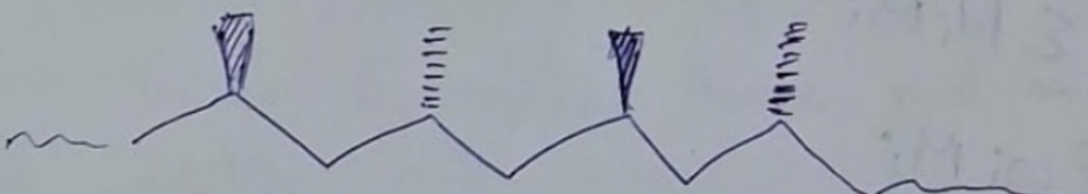


$$\sim CH_2-\underset{|}{\underset{CH_3}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-$$



Syndiotactic :

$$\sim CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}\sim$$



Atactic :

$$\sim CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}\sim$$

1) Number avg. molecular wt ($\overline{M}_n$)

$$\boxed{\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i}}$$

where N_i = no. of polymer chains having mol. wt. M_i

$$\overline{M}_n = \Sigma x_i M_i$$

x_i = mole fraction of polymer chains having mol. wt. M_i.

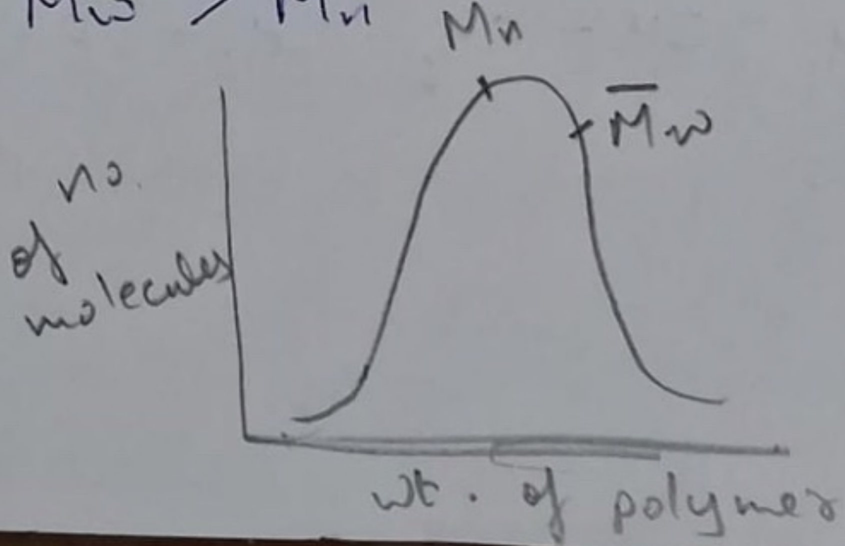
2) Weight avg. mol. wt. ($\overline{M}_w$)

$$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

$$= \Sigma w_i M_i$$

w_i = weight fraction of chains having mol. wt. M_i

* $\overline{M}_w > \overline{M}_n$



$\frac{M_w}{M_n}$ = Polydispersity index

$= 1 \Rightarrow$ monodisperse polymer

$> 1 \Rightarrow$ polydisperse "

Q) A sample of polymer contains 50% ~~molecules~~ molecules have mol. mass 15,000. 20% molecules have mol. mass 25,000. 30% with mol. mass w 10,000. Calculate $\overline{M_n}$.

$$\overline{M_n} = \frac{50 \times 15000 + 20 \times 25000 + 30 \times 10000}{50 + 20 + 30}$$

$= \cancel{16750}\ 15500$

Q) In a polymer sample,

30% molecules have mol. mass 20,000

40% - - - 30,000

the rest - - - - 60,000

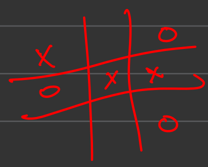
Calculate $\overline{M_w}$.

$$\overline{M_w} = \frac{30 \times (20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{30(20,000) + 40(30,000) + 60,(60,000)}$$

$= \cancel{3600000}\ 43,300$

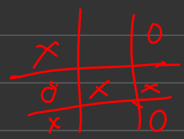
- Properties of Polymers

① Mech properties (strength)



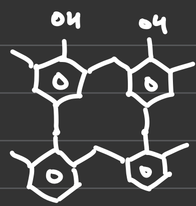
a) mol. wt ↑ St ↑

b) Polar grp (H- bond) ↑ , St ↑



c) Slip over motion ↑ , St ↓

$-(CH_2-CH_2)_n-$ > $-(CH_2-CH(Cl))_n-$ > $-(CH_2-CH(C_6H_5))_n-$ >



Strength

< < <

② Thermal bheaviour

glass Trans temp (Tg)

PE	−125°C
PP	0°C
PVC	81°C
PS	95°C

brittle — Tg — Soft, rubbery

③ Physical Phases

a) Crystalline

Crys ↑ , solub. ↓ , toughness ↑ , flexibility ↓ , shorter repeating unit , mol wt

c) Amorphous

④ Chemical resistance

Like dissolves like , i.e polar in polar , etc

factors

a) Mol. wt
b) extent of cross linking
c) Crys

} similar in Tg

- Synthesis of Polymers

① Polyethylene

$$n\, CH_2 = CH_2 \xrightarrow[\text{Poly (Benzoyl pero)}]{\text{Free rad}} -\!\!\left(CH_2 - CH_2 \right)\!\!-_n$$

Δ, high P

LDPE

Properties :- high impact strength, low brittleness, chemically inert, good resistance to acids & alkalis

Uses :- food packaging, garments, squeeze bottles, etc

HDPE :-

Properties : Better chem res than LDPE, less impact strength.

Uses : wires & cables, buckets, dust bins

② Polypropylene

$$CH_3 - CH_2 = CH_2 \xrightarrow[\text{Poly}]{\text{add}^n} -\!\!\left(CH_2 - \underset{\underset{CH_3}{|}}{CH_2} \right)\!\!-_n$$

Properties : elastic and tough, high CR to acids & alkalis, isotactic, highly flammable, white crystalline solid.

Uses : strong plastic hinges, pipes to avoid corrosion.

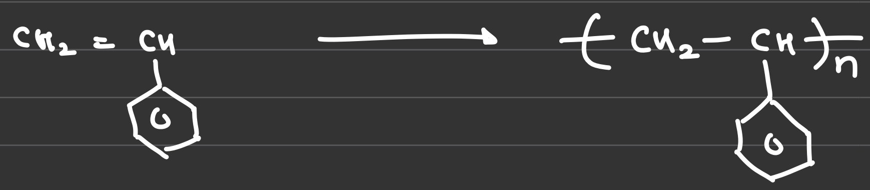
③ PVC

$$CH_2=CH(Cl) \longrightarrow \left(CH_2 - CH(Cl) \right)_n$$

Properties : colourless, odourless, non-flammable, high stiffness + rigidity, resistant to oxidation (O_2)

Uses : Building and construction materials, pipes, raincoats, film sheets

④ Poly styrene



Properties : Amorphous, high boiling point (430), non-polar, optical, hard but brittle.

Uses : Food packaging, Talcum powder, foam, combs, brush handles.

⑤ Poly tetra fluro ethylene

$$CF_2 = CF_2 \longrightarrow \left(CF_2 - CF_2 \right)_n$$

Properties : highly crystalline + CR, insoluble in all solvents, low coeff of friction

Uses : Non-stick cookware, coating medical appliances

⑥ Nylon 6,6

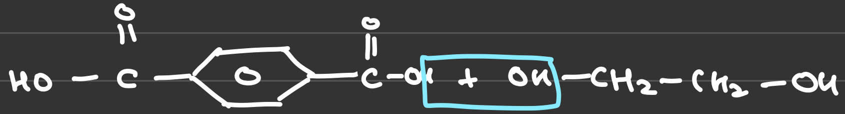
$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \;+\; H-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-H$$

adipic acid   hexamethylene diamine

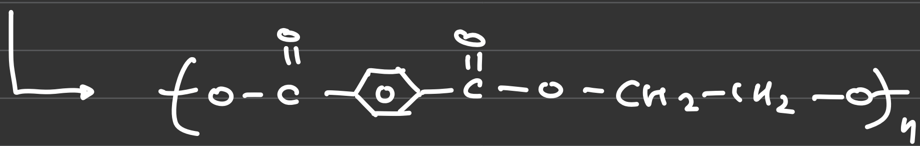
Properties : Chemically resistant, high MP, dry rapidly, durable and lightweight, fabric is tough and easy to dye

Uses : Swimmwear, sports gear, combs, fishnets, brush bristles

⑦ Polyethylene terepthalate (PET / PETE) (Terylene)



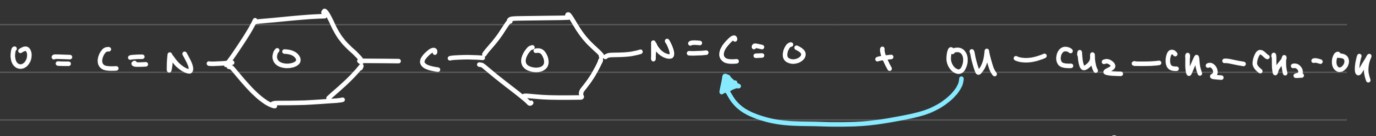
Terepthalic   ethylene gylcol



Properties : high mech strength, strong fabric, low absorption in water, elastic

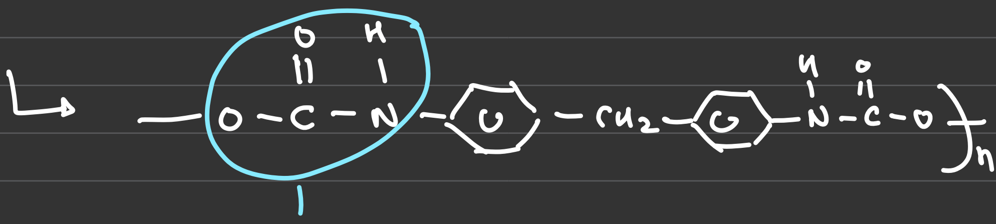
Uses : food packaging, PET sheets, plastic bottles.

② Polyurethane



diisocyanate

Polyol



urethane linkage

Properties : high cross-linking, soft & elastic if long & flexible

Uses : mattresses, cushions, couches, production of foams

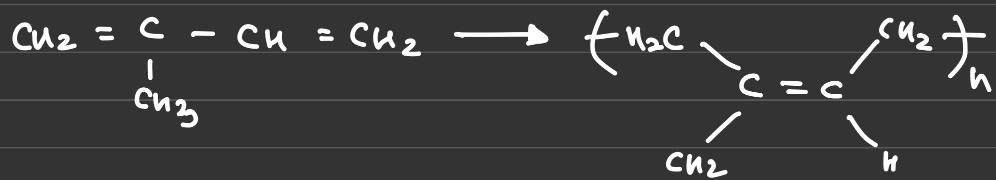
- **Rubber**

Rubber

- Natural
  - Cis-polyisoprene
  - Trans-polyisoprene (gutta-percha)
- Synthetic
  - Neoprene
  - Buna-S
  - Buna-N

· Natural rubbers

① Cis-polyisoprene



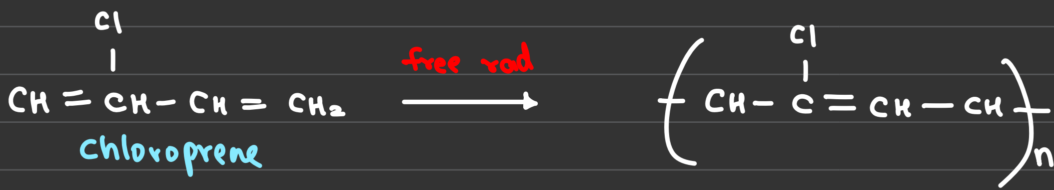
③ Trans - polyisoprene

Gutta-Percha is the trans isomer of isoprene. It is used to **fill tooth cavities** to prevent reinfection.

Properties of natural rubber:
•Soluble in non-polar solvents
•Non-resistant to attack by oxidising agents.
•High water absorption capacity.

· Synthetic rubbers

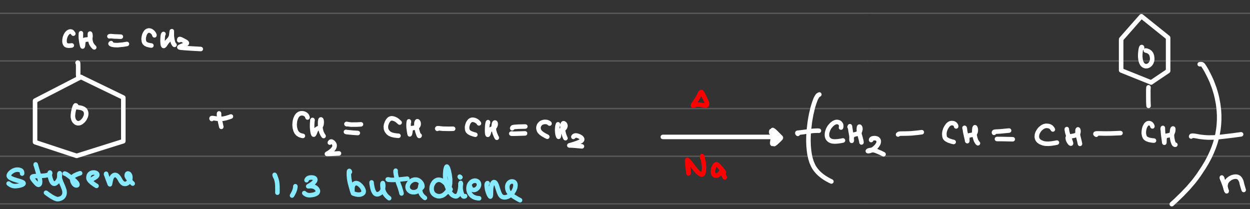
① Neoprene



Properties : Stability to aerial oxidation, resistant to oil, gasoline

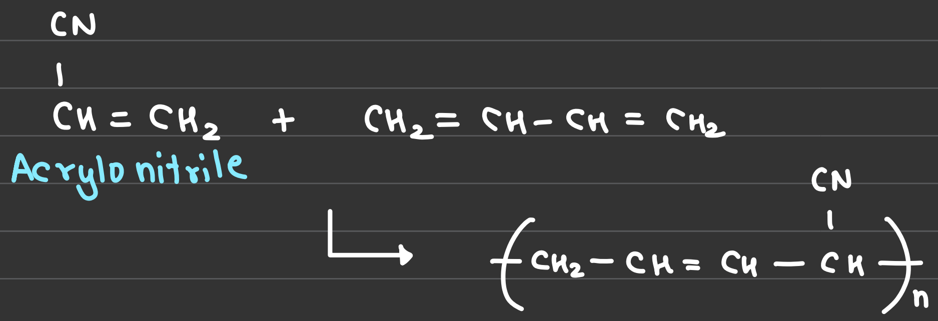
Uses : shoe heels, surgical instruments, hoses, etc.

② Buna - S



Uses : Tyres + Waterproof shoes

③ Buna-N



Properties : rigid, resistant to swealing action of petrol & oil

Uses : oil seals, tank linings.

• general properties of all three above

Properties : low temp heat resistance, heat ageing

Uses : automobile industry, wetsuits, elevator belts, footwear

Formation of Buna-N

•In the automobile industry for making **seats, airbags, padding in brakes** etc.
•In the clothing industry to produce **expandable clothes** like- cycling shorts, wetsuits etc.
•In the construction industry in the form of **tubes, elevator belts** etc.
•In the manufacturing of consumer goods like- **footwear, eraser** etc.

CONDUCTING POLYMERS

- Conducting polymers are organic polymers that conduct electricity. Until 1970, all organic polymers were used in electrical, electronic and other applications as insulators, taking advantage of their excellent insulation properties.
- Thus, organic polymers having electrical conductance of the order of conductors are now called as conducting polymers.
- Conducting polymers have been classified into two types:

1. ExtrinsicallyConducting Polymers 2. Intrinsically Conducting Polymers

1. Extrinsically Conducting Polymers

- They are prepared by mixing **conducting fillers like metal fibres , metal oxides or carbon black** with insulating polymers.
- These are also called as conductive element filled polymers.
- Here, insulating **polymer forms the continuous phase and added fillers form the conducting network**. A minimum concentration of conducting filler has to be added so that the polymer starts conducting.
- The **conductivity in this type of polymer is not due to the matrix polymer but due to conducting fillers** which are added.

2. Intrinsically Conducting Polymers

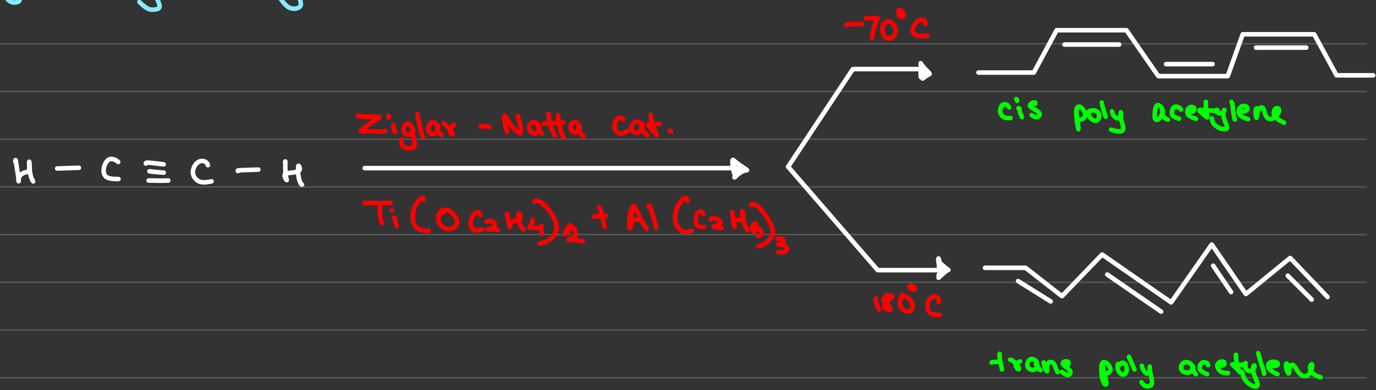
- In these type of polymers, **conductivity is due to the organic polymers themselves.**
- They conduct electricity **when doped with oxidizing or reducing agents or protonic acids**.
- The factor responsible for conductance in these polymers are **conjugated electrons.**
- Organic polymers with highly de-localized π-electrons having electrical conductance of the order of conductors are called as inherently or intrinsically conducting polymers or synthetic metals.

- Conducting Polymers

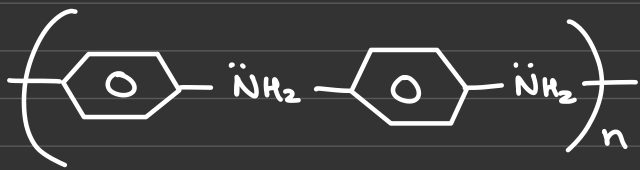
Types

- **Extrinsic**: Poly itself is insulator and mixed with conducting materials such as carbon fibres, thin metals, etc
- **Intrinsic**: The poly itself show conductometry

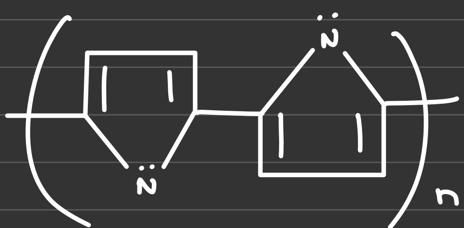
eg) Poly acetylene



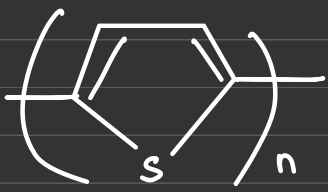
eg Poly anniline



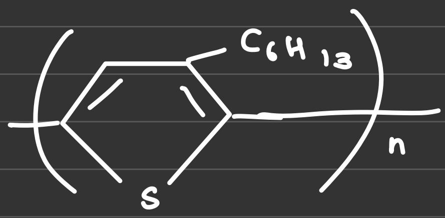
eg Polypyrole



eg Polythiophene



eg P3HT (Poly-3 thio phene)

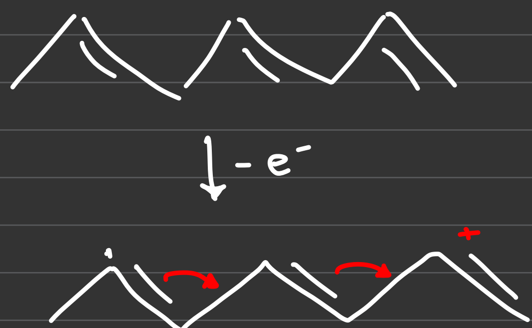


Note :- All the poly show conductance at $10^{-3} - 10^{-5}$ $ohm^{-1} cm^{-1}$

doping is done to vary conductance

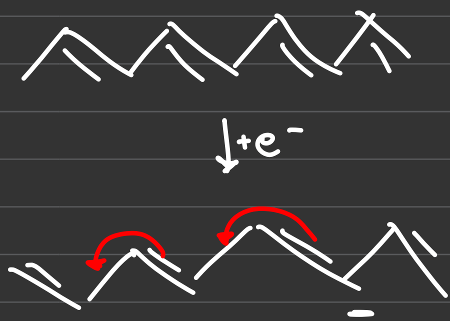
P- doping (Oxidative)

I_2 , SbF_5, AsF_5



N- doping (Reductive)

Na , K , Cs, Rb , etc



Conjugated organic polys are insulators or semi-conductors in their pure state. The $\pi - e^-$ are localized & they do not take part in conductivity. On doping they become delocalised & conduct electricity. The dopant may be oxidising or reducing agent.

p-doping poly   n-doping poly.