



Polymers Unit 4

Chemistry (SRM Institute of Science and Technology)



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Module 4 - Polymers

Salient Features of Macromolecules

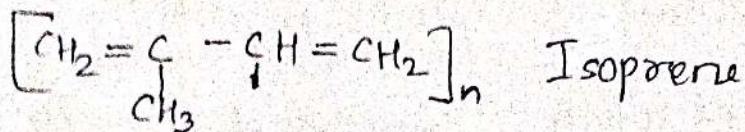
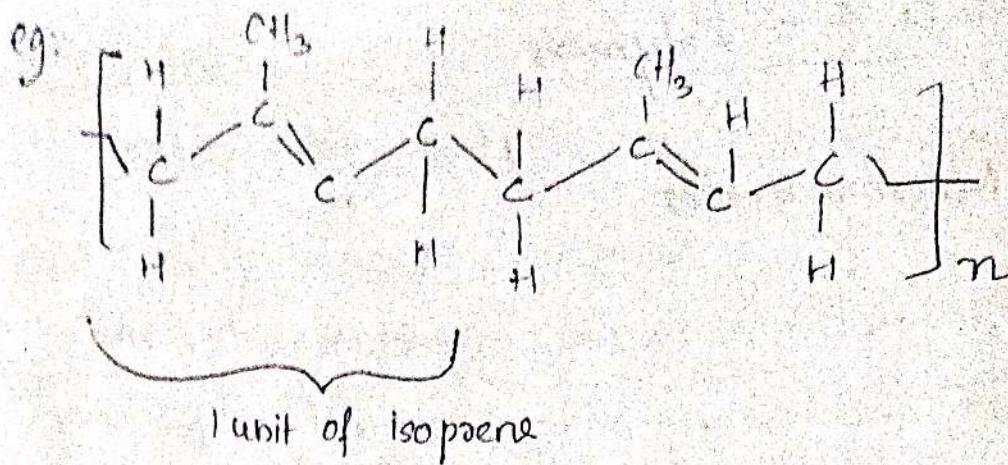
- ⇒ They are big/giant molecules having larger molecular mass. High molecular mass and corresponding structural complexity of macromolecules are the cause of specific properties.
- ⇒ A polymer is a material which is composed of macromolecules of the same kind. If there is addition of some other substance, it undergoes polymerization resulting in branched chain macromolecules.
- ⇒ When bifunctional monomers combine with n no. of same bifunctional monomers, then this would result in linear, straight chain macromolecules.
- ⇒ If monomers have 2 double bond (or) more than 2 functional groups, then it undergoes polycondensation resulting in branched chain macromolecules.

Tacticity

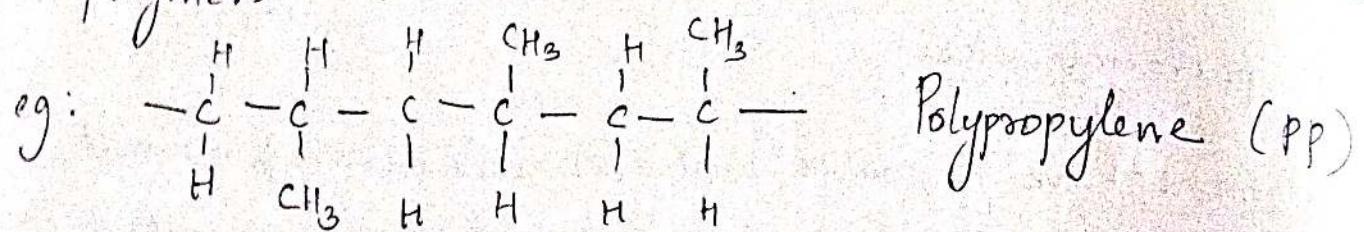
The orientation of monomeric units in a polymer molecule can take place in an orderly (or) disorderly fashion w.r.t the main chain chain.

There are 3 types

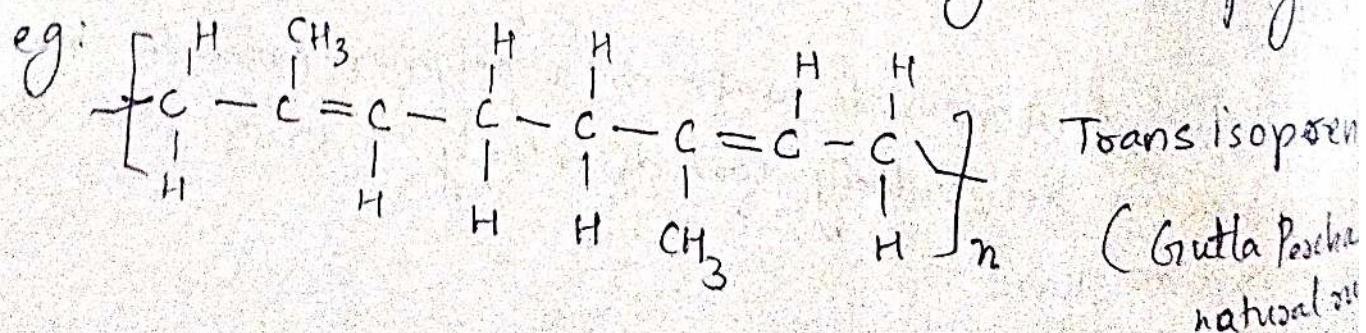
- (a) Isotactic polymers: The head-to-tail configuration in which the functional groups are all on the same side of the chains called isotactic polymers.



3) Atactic polymers: If the arrangement of functional groups at random around the main chain, it is called "atactic polymers".

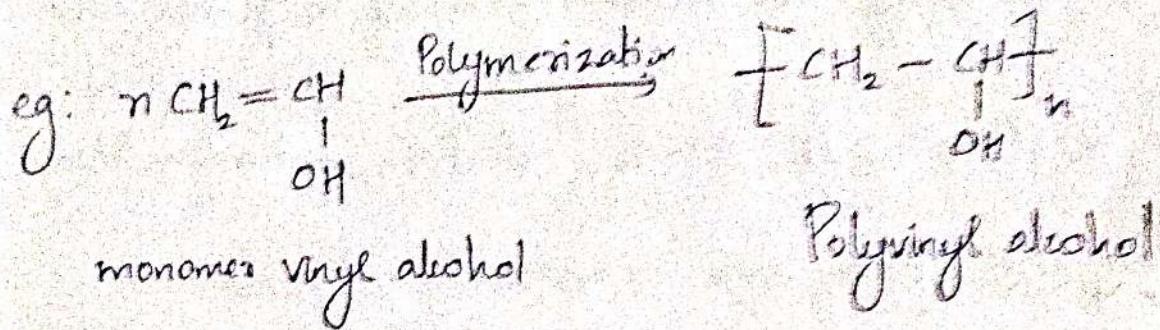


4) Syndiotactic Polymer: If the arrangement of side groups in alternating fashion, it is called syndiotactic polymer.



Polymer

They are high molecular weight organic compounds in which a large number of simple units repeat themselves in a regular fashion. These single repeating units are monomers.



Functionality

The reactive sites (or) reactive group present in a molecule is called functionality.

- (i) CH_3OH one functional group ($-\text{OH}$) Monofunctional

(ii) $\text{CH}_2=\text{CH}_2$ one functional site ($=\text{bond}$) Bifunctional
Because 2 atoms can join to 2 atoms by breaking double bond

Classification of Polymers

Polymers are classified on the basis of

- (i) origin / source
 - (ii) Nomenclature (or) nature of monomers
 - (iii) Based on structure
 - (iv) Thermal Characteristic
 - (v) Degree of polymerization
 - (vi) based on synthesis

(i) Based on origin / source

Polymers are classified as

① Natural Polymers

② Artificial Polymers

③ Natural Polymers: They are found naturally in plants, animals.

e.g.: Proteins, nucleic acids, starch, cellulose, natural...

④ Synthetic Polymers: These are man-made polymers

e.g.: Plastics, Nylons, Synthetic rubbers etc

(ii) Based on structure

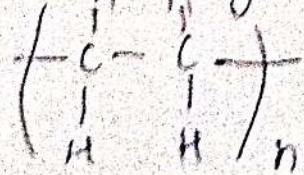
Polymers are classified as

① Linear polymers ② Branched-chain polymers

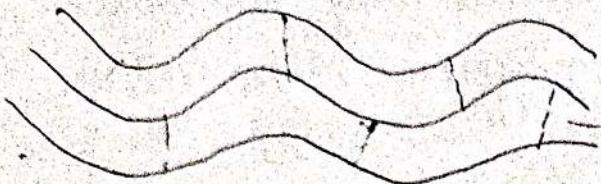
③ Cross-linked polymers

a) Linear Polymers: Polymers consisting of long and straight chains are called linear (or) straight chain polymers

e.g.: HDPE (High density polyethylene)



Note: All bifunctional monomers combine to give linear polymers. Movement of these chains are not restricted. Held by van der waal's forces. Soft, weak, remoulded many times.



$\text{[CH}_2 - \text{CH}_2]_n$

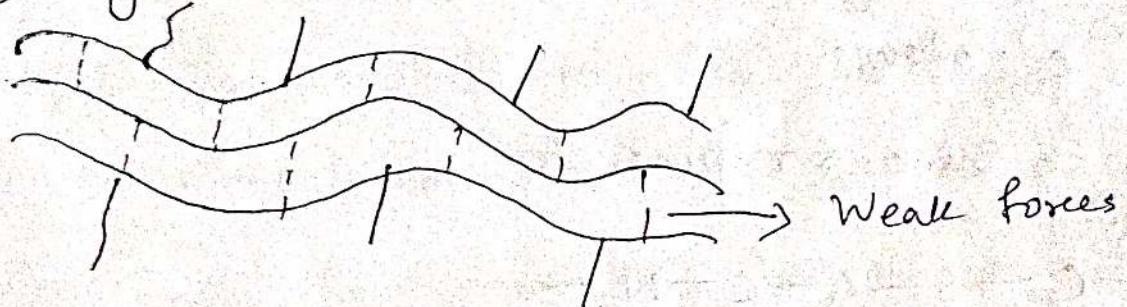
Weak vanderwaal's force

b) Branched chain polymers: Polymers comprising of linear chains with branches are called branched chain polymers.

e.g.: Low density polyethylene.

Note: When bifunctional and trifunctional combine, it would result in branched polymers. Movement of chains is partially restricted.

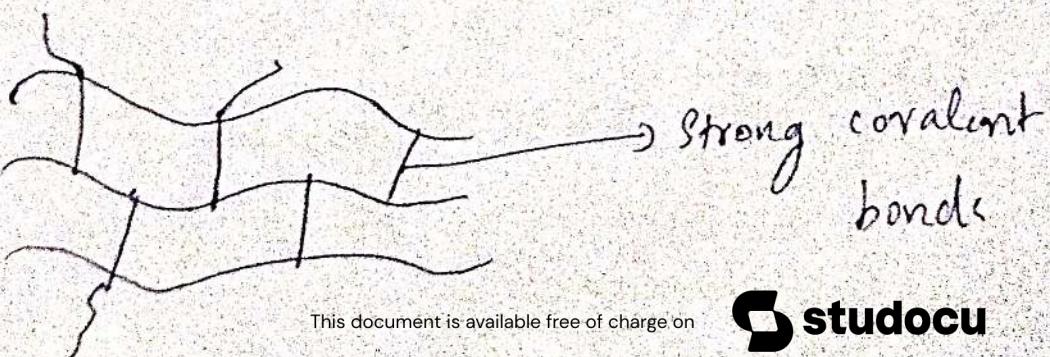
e.g.: Nylon-6



c) Cross-linked Polymers: Polymers in which various individual chains are connected together by strong covalent bonds are called cross linked polymers.

They are from poly & tri-functionality monomers & because of additional functionality they result in cross links.

e.g.: Bakelite, Melamine.

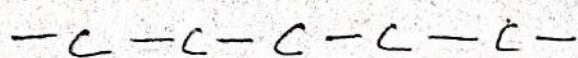


Note: When trifunctional monomers combine with trifunctional others crosslinked, hard, strong polymers. Movement is totally restricted

(iii) Based on nomenclature

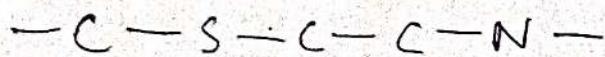
a) Homo-chain Polymers: Comprises of only 'c' atoms in the main skeletal chain

eg: Polyethylene



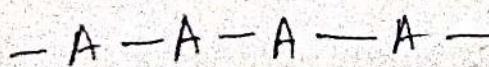
b) Hetero-chain Polymers: Comprises of diff. atoms other than 'c' atoms.

eg: Nylon-66, Buna-S rubber etc



c) Homo polymers: Comprises of one type of monomers only.

eg: Polyethylene, PVC etc



d) Co-Polymers (or) Heteropolymers: Comprises of more than one types of monomers

eg: Nylon-66, Bakelite etc.

(iv) Based on Thermal Characteristics

a) Thermoplastics: They are the polymers formed by weak forces of attractions b/w the chains. Hence can be reheated, remoulded many no: of times. Physical chains are reversible. They are recyclable.

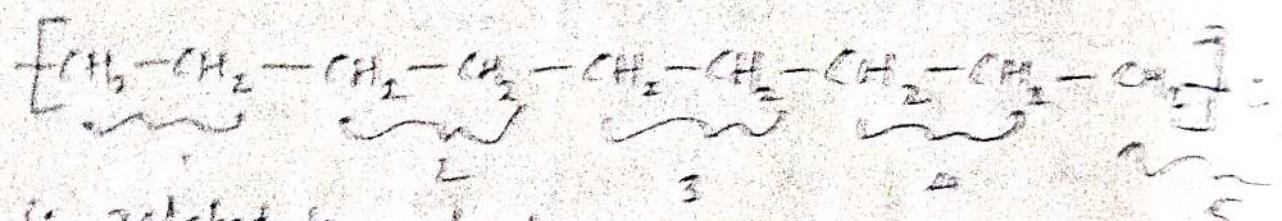
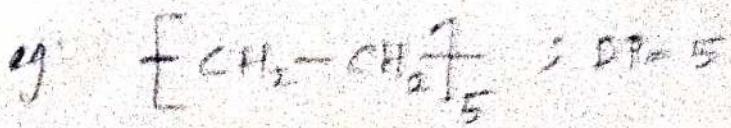
eg: PE, PVC, Polypropylene (PP)

b) Thermosetting Plastics: They have extensive crosslinking i.e, the bonds b/w the chains are strong covalent bonds & hence can't be broken easily. Once they attain a shape, they can't be remoulded. On heating becomes soft & on cooling becomes hard & attains the shape, but "once only". As the crosslinks are broken, they can't be retained back. It is purely a chemical change & is irreversible. Hence these polymers are non-recyclable. They improve the mechanical properties of a material.

eg: Bakelite, Epoxy resins etc.

(v) Based on degree of Polymerization (DP)

DP is defined as no: of repeating units in a polymer. Say, for a polymer if $DP=5$, then no: of monomeric units repeated is 5 times.



It is related to molecular weight of polymer & monomer as $\text{DP} = \frac{M}{m}$ (Mol-weight of Polymer)
 m (Mol-weight of monomer)

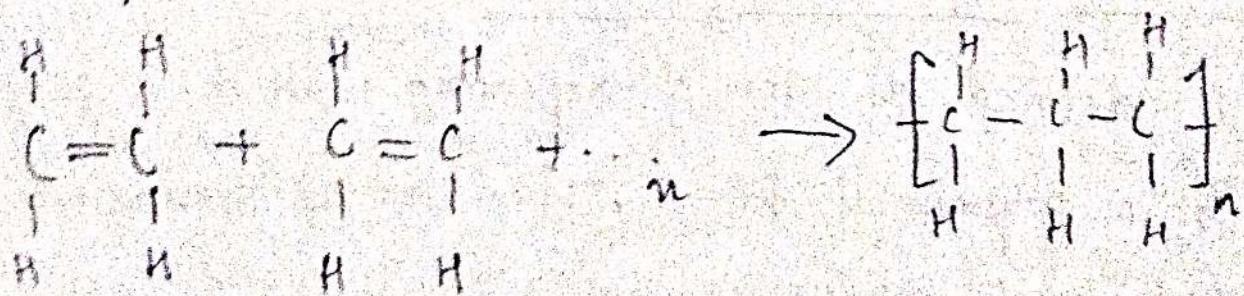
It can be classified as

- Oligomers: Formed due to polymerisation of few no. of monomers
eg: Dimers, trimers etc
- High polymers: Formed due to large no. of monomers
eg: Bakelite, PE.

(vi) Based on Synthesis

- Addition Polymers: The formation of addition polymers occurs by repeated addition of monomer molecules which possess triple or double bonds. following free radical, ionic mechanisms.

eg: PE, PP.

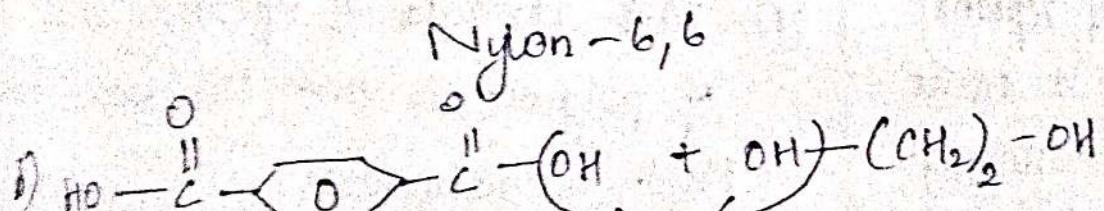
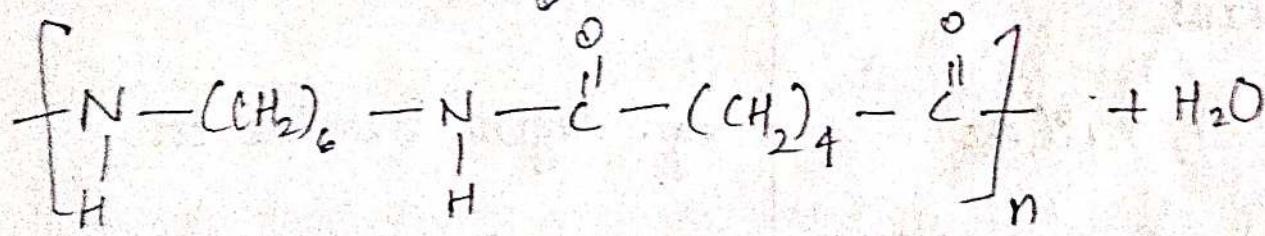
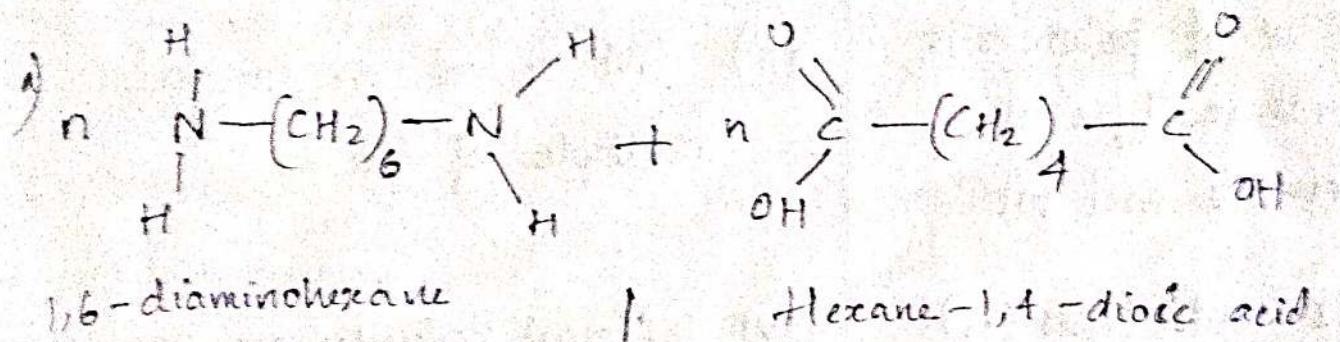


Polyethylene

Note: Monomers must be "saturated". Once initiated can't be terminated.

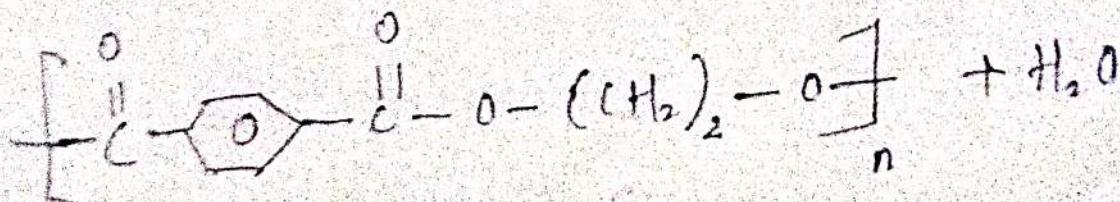
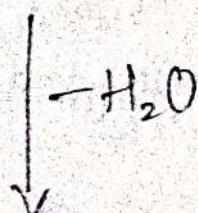
b) Condensation Polymers: It is form of step growth polymerization where smaller molecules or monomers react with each other to form larger structural units (polymers) while releasing by-products such as H_2O or methanol molecule.

e.g.: Nylon, Bakelite



Terephthalic acid

Ethylene Glycol.



PET (or) Terylene.

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Difference b/w Addition & Condensation Reaction

Addition

- (i) Monomers must have either double (or) triple bond
- (ii) No by-products
- (iii) Mol. wt of polymers is integral multiple of monomer's mol. wt
- (iv) Lewis acids, bases (or) initiators are catalysts in rens.
eg: PE, PP, PVC etc
- (v) Mol. formula of repeating unit in polymer is same as that of monomer
- (vi) Formed by chain growth polymerisation

Condensation

- (i) Must have 2 similar (or) different functional groups
- (ii) By products such as NH_3 , H_2O , CH_3OH , HCl etc.
- (iii) 'M' is not an integral multiple of 'm'.
- (iv) Different molecules are used as catalysts.
eg: Nylon, Bakelite etc
- (v) Mol. Formula of repeating unit of polymer is not the same as that of monomer
- (vi) Formed by step-growth polymerization

Difference btw Thermoplastics & Thermo setting Plastics

Thermoplastics

- (i) Soften on heating, less brittle
- (ii) Long, straight, chained 'C' compds.
- (iii) Held by weak Van der Waal's forces
- (iv) Formed by addition polymerisation
- (v) Can be reshaped and reused many times.
- (vi) Soluble in org. solvents
- (vii) Reclaimed from wastes
- (viii) Expensive
eg: PE, PP etc

Thermosetting

- (i) Do not soften on heating.
Hard & strong.
- (ii) Cross linked compds
- (iii) Held by strong covalent bond.
- (iv) Formed by condensation polymerization
- * (v) Can't be reshaped.
- (vi) Insoluble in org. solvents.
- (vii) Can't be reclaimed.
(vii) Cheap
eg: Bakelite, PET etc

Comparison - Properties of Thermoplastics, Thermosetting & Elastomers

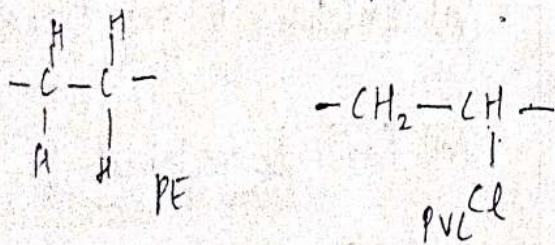
(A) Mechanical Properties:

Under mechanical properties strength of polymers are greatly influenced by their structure. Three parameter that decide the strength of polymers are

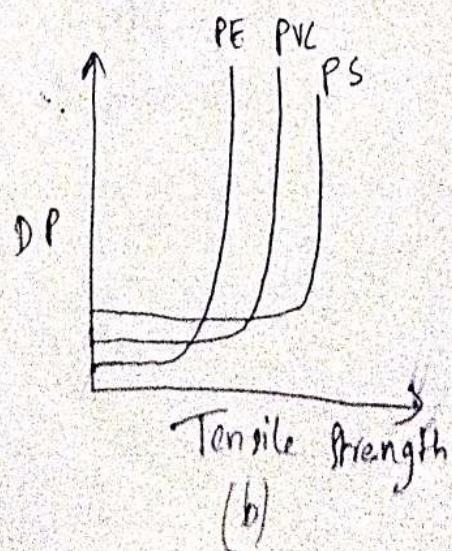
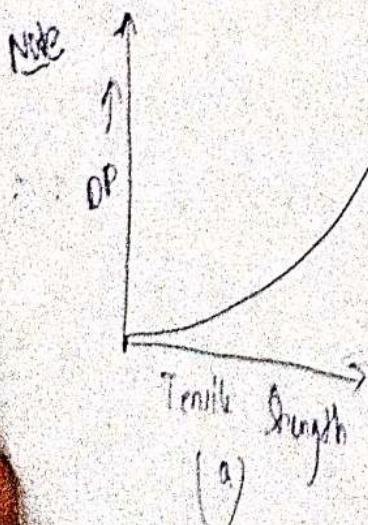
(i) Molecular Weight: In general, strength \uparrow as mol. wt \uparrow .
Mol. wt depends on DP.

(ii) Molecular Shape: Straight chain (e.g.) branched chain are held by weak van der waal's forces. Hence strength is less. By introducing polar gaps (i.e.) side substitution strength \uparrow .

Eg: PE is weak when compare to PVC



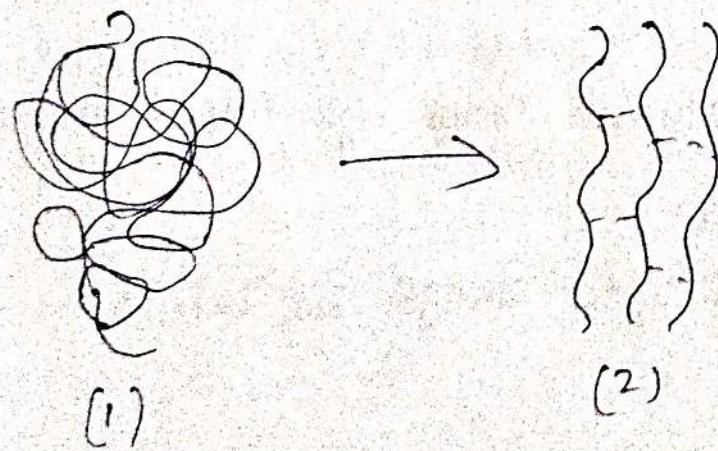
PVC has large no: of Cl atoms that \uparrow intermolecular forces of attraction \rightarrow \uparrow strength.



crosslinking: Here there are only covalent bonds & hence they are most strong & tough materials.
eg. Thermosetting plastics

(B) Elastic character:

This property of polymer has special property "elasticity" which retains its original shape after stress is released. It is seen in "rubbers". Rubbers under unstressed conditions attains a configuration of highly coiled & entangled snails. They are held by weakest internal forces, free rotating groups that under stressed conditions gets elongated.



Random arrangement
under non-stressed condition
(amorphous)

Alignment of
chain under stressed
condition
[crystalline]

(Elongated,
stretched)

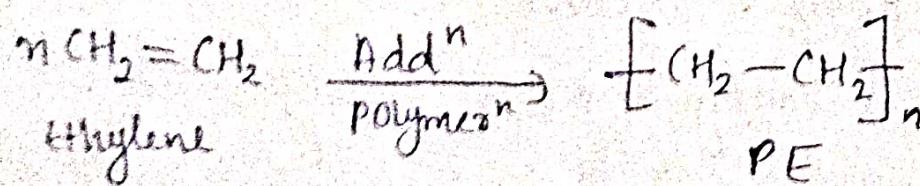
(C) Thermal Properties (Plastic Deformation):

• Between thermoplastics & thermosetting plastics

Synthesis, Properties of Addition Polymers and its Applications

① POLYETHYLENE: It is homopolymer & its monomer is ethylene.

The rexn is as follows:



$$P = 1500 \text{ atm}$$

$$T = 150 - 250^\circ \text{C}$$

H_2O_2 — catalyst

PE $\xrightarrow{\hspace{1cm}}$ LDPE

$\xrightarrow{\hspace{1cm}}$ HDPE

Properties: LDPE is waxy translucent, shows high impact strength, outstanding insulating properties.

HDPE is opaque less impact strength but barriers properties are excellent.

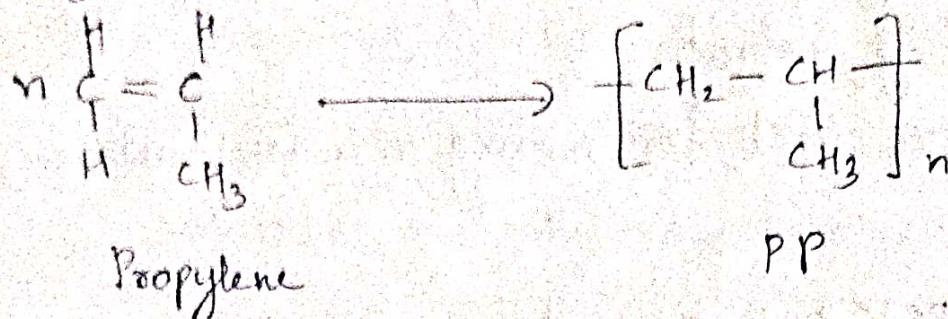
LDPE has good chemical resistance when compared to HDPE.

HDPE is tough, good tensile strength but LDPE is flexible over wider range.

Applications: LDPE — packaging materials for food, garments etc, to produce squeeze bottle and insulating wires.

HDPE — used in manufacturing dust bins, fuel tankit

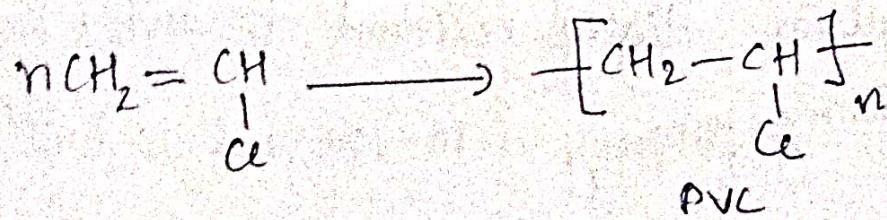
② POLYPROPYLENE: Polymerizes in the presence of Zeigler-Natta catalyst ($\text{AlR}_3 - \text{AlCl}_3$)



Properties: It is stereoregular (isotactic) & highly crystalline polymer. Melting point ($160-170^\circ\text{C}$). It possesses better hardness, strength, & stiffness than PE. It is more resistant than PE.

Uses: In producing moulded parts & fibres. It is also used in making carpets, ropes, handbags, apparels etc.

③ POLY VINYL CHLORIDE: It is prepared by Δ ing water emulsion of vinyl chloride in the presence of small amt of H_2O_2 in an autoclave under pressure

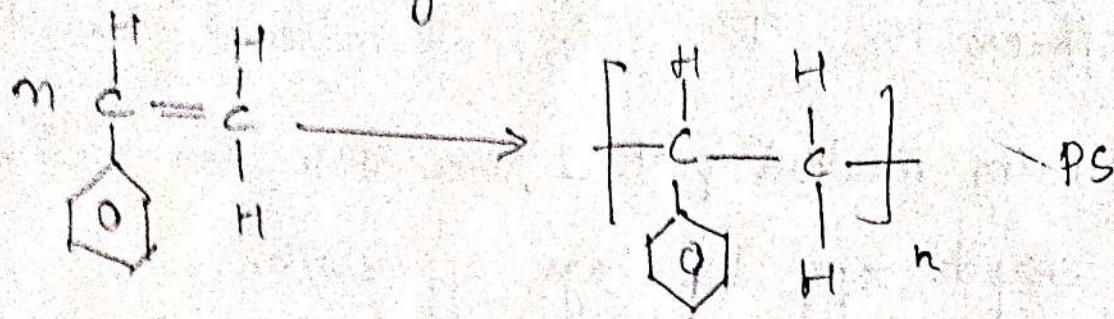


Properties: Colourless, non-inflammable, chemically most powder, resistant to atm. O_2 , inorganic acids & alkalis. Soluble in hot chlorinated HC such as ethyl chloride. High stiffening point (148°C). Great stiffness & is brittle.

Uses: Rigid (or) unplasticized PVC has superior chemical resistance & high rigidity. Used in making sheets, for tank linings, safety helmets

Plasticized PVC used for making raincoats, curtains, bags etc.

④ POLYSTYRENE (PS): It is prepared by polyⁿ of styrenes (dissolved in ethyl benzene) in the presence of benzoyl peroxide catalyst.



Properties: Transparent, excellent moisture resistant. Nitrated by fuming nitric acid & sulphonated by conc. H_2SO_4 . At 100°C , it yields water soluble emulsion. Highly resistant to acids. Low softening property ($90^\circ\text{-}100^\circ\text{C}$) & is brittle.

Uses: In moulding articles like toys, combs, buttons, radio & TV parts, battery cases, lenses etc.

⑤ Polytetrafluoroethylene (TEFLON) (or) PTFE: It is obtained by polymerization of water-emulsion of TFE, under pressure in presence of benzoyl peroxide as catalyst.



TEFLON

Properties: Since there is high electro-ve nature of F atoms & regular configⁿ, which would result in strong attractive b/w the chains. These strong forces gives the material extreme toughness, high softening point (350°C), high chem resistance (except hot alkalis & fluorine), high density, good electrical & mechanical properties. It can be machined & drilled. At 350°C it sinters to form very viscous opaque mass.

Uses: As insulating material (transformers, cables, wires etc) & for making gaskets, pump parts, non-lubricating bearings etc.

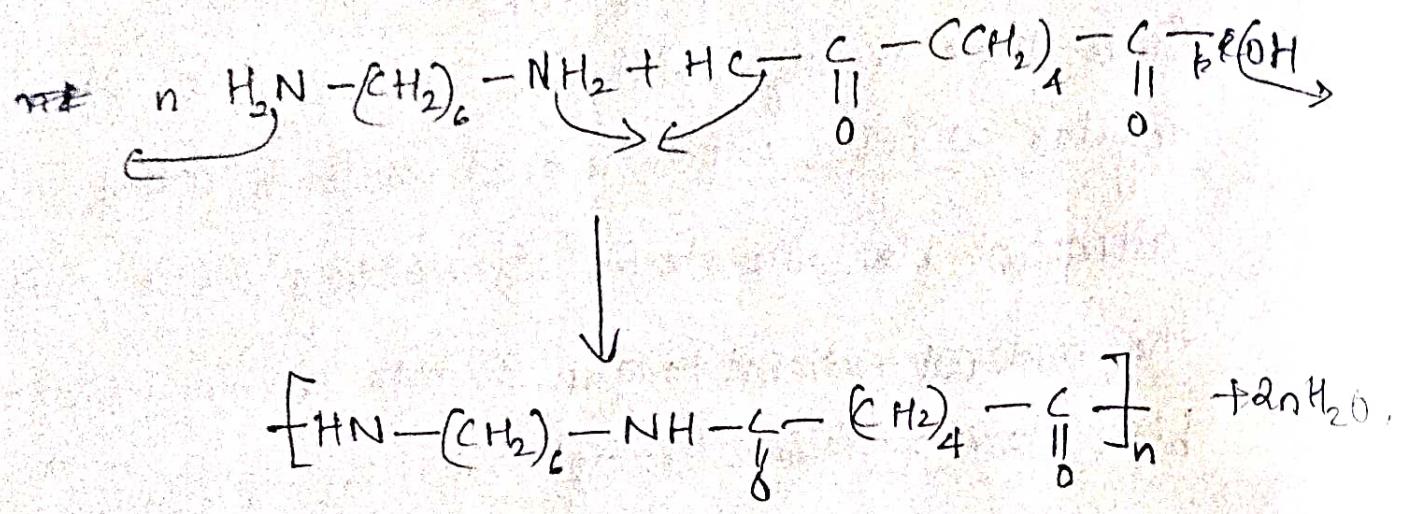
Synthesis of Condensation Polymers, Properties and Uses

(A) POLYAMIDE FIBRES:

- ① Nylon - 6, 6; ② Nylon - 6, ③ Nylon - 11

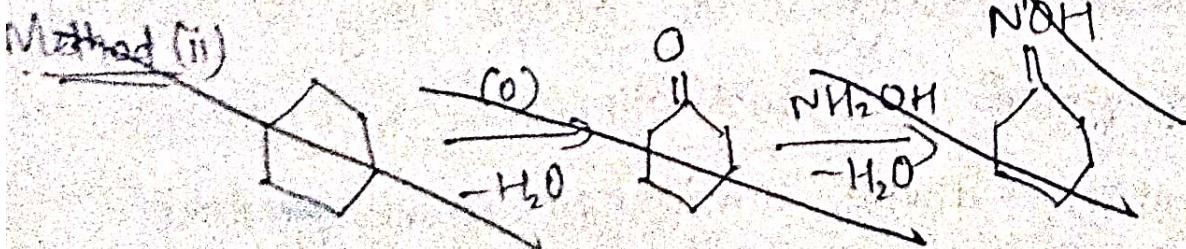
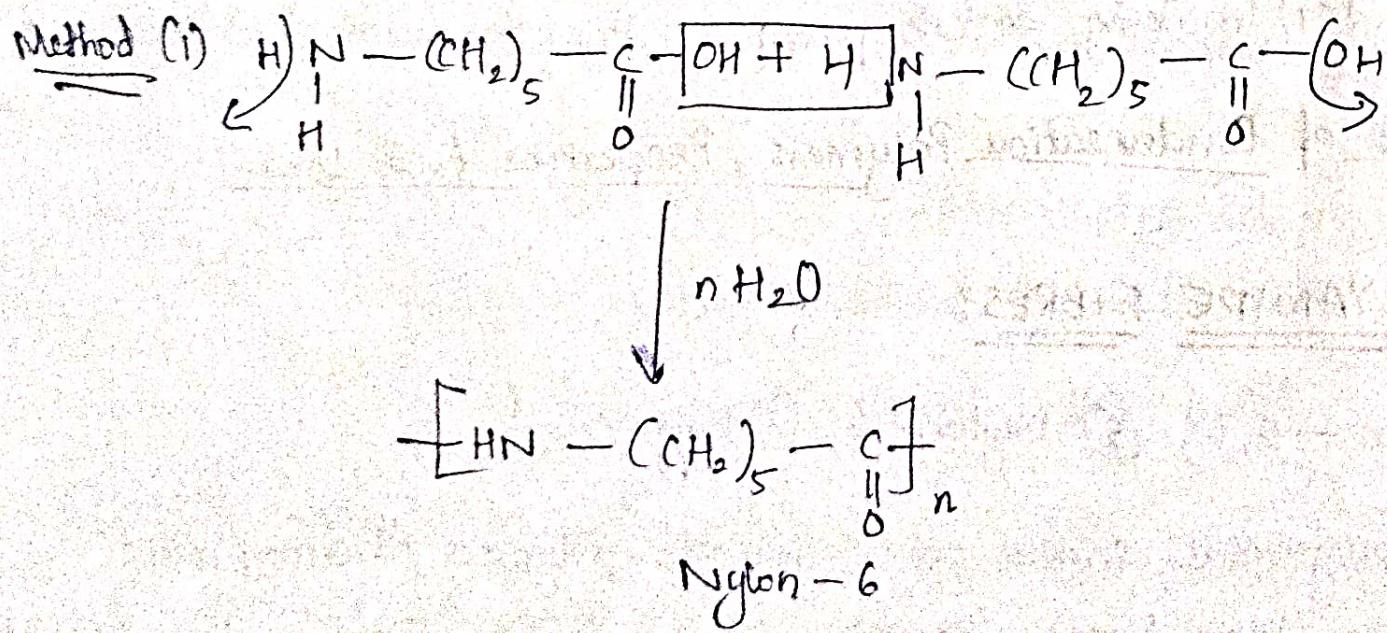
All polyamide fibres are synthetic polymers, thermoplastic oligooy which have recurring amide groups. They are prepared by condensation polymerization with elimination of by products or by self condensation without elimination of by-products.

① Nylon-6,6: Obtained by polyimr of adipic acid and hexamethylene diamine.

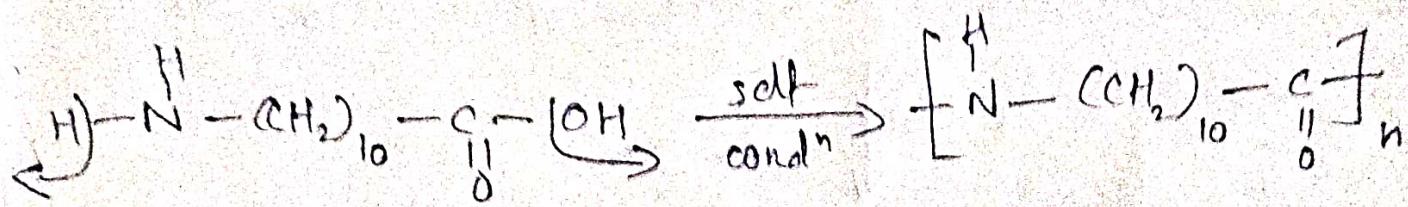


Polyhexamethylene adipate (o) Nylon-6,6

⑤ Nylon-6: Self condensation of E-amino caproic acid and by ring opening (oo) scission reaction of caprolactum.



③ Nylon - II: Prepared by self condensation of ω -amino undecanoic acid.



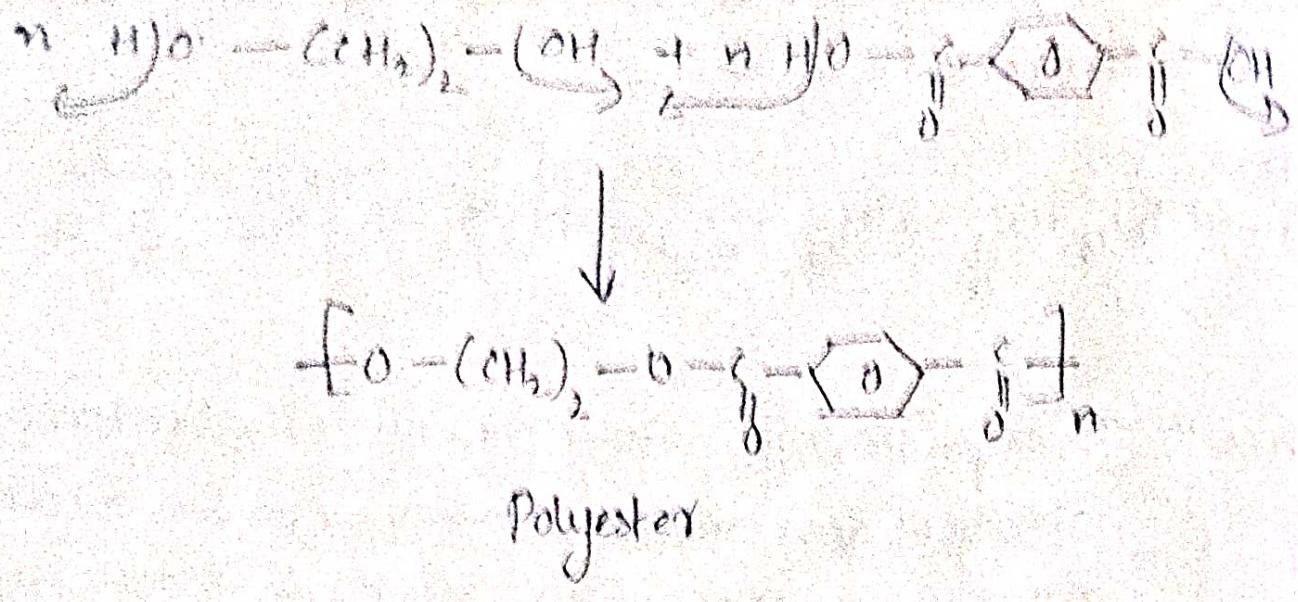
Properties: Transparent, high m.pt (160 - 240°C), high temp stability, good abrasion resistance. Insoluble in certain org solvents but soluble in phenol & HCOOH . High impact strength & self-lubricating properties. Absorb little moisture & thus 'drip-dry' in nature. On blending with wool, the strength & abrasion resistance of wool ↑.

Uses : Nylon - 6/6 \Rightarrow fibre-making socks, garments, carpets etc

Nylon - 6 & II \Rightarrow making gears, electrical components etc, ropes, bristles for tooth brushes etc.

(B) PET - Polyethylene Terephthalate:

This polymer is category of thermosetting plastic. It is prepared by condensation reacn of dicarboxylic acid (Terephthalic acid) and dihydroxy alcohol (Ethylene glycol). It is saturated fiber. Also known as DACRON, Texylene.

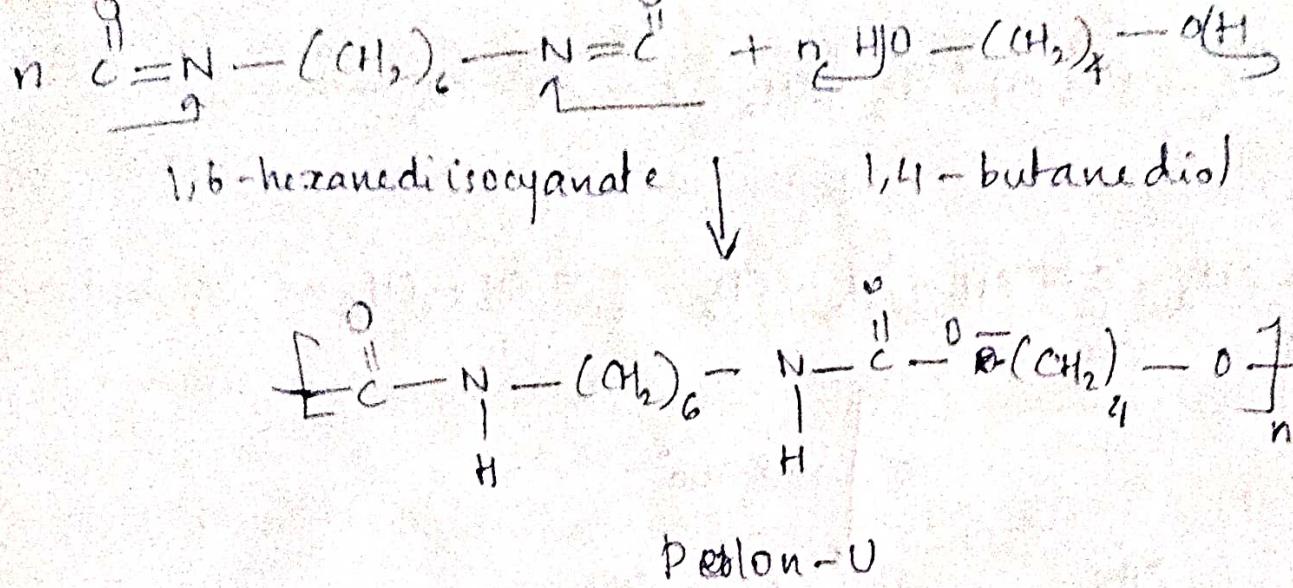


Properties: Since it has symmetrical structure, presence of numerous polar groups, it is converted to commercial fibres. Those fibres have high stretch-resistance (due to high stiffness of polymer chains). High crease & wrinkle resistance. Resistant to mineral & organic acids but less resistant to alkalis.

- Uses :**
- Manufacturing synthetic fibres
 - Blended with wool
 - As glass reinforcing material in safety helmet

(C) POLYURETHANES (PU): It can be thermoplastic (i) thermosets by varying the quantities of basic components, the properties of PU can be changed. It is prepared by condensation of di-isocyanate & diol. Ex.

Eg. Perlon - O



Properties: They are less stable than polyamides at elevated temp.
Excellent resistance towards abrasion & solvents.

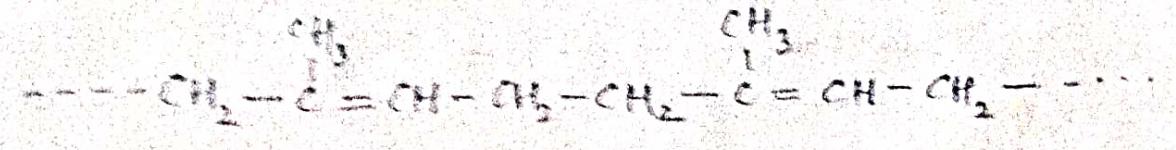
Uses : Making foams, adhesive & elastomers. Resilient
PU fibres (Spandex) are used for swimsuits.

(D) Synthetic Rubbers (or) Elastomers

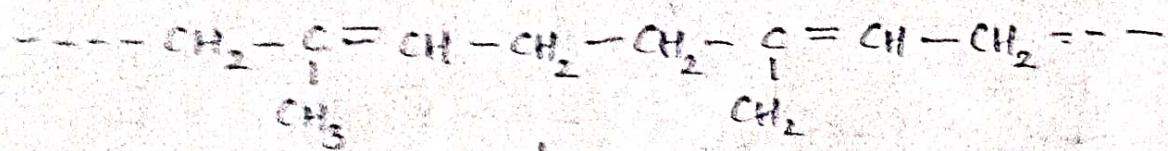
Natural (Raw) rubber has some demerits such as soft at high temp & too brittle at low 'T'. Large H_2O absorption capacity & non-resistant to non-polar solvents. Easily gets attacked by oxidising agents. When stretched to greater extent, it suffers permanent deformation because of sliding (or) slippage of molecular chains.

Hence raw rubber has to be compounded with chem like S , H_2S , benzoyl chloride etc. Most important addition is 'S'.

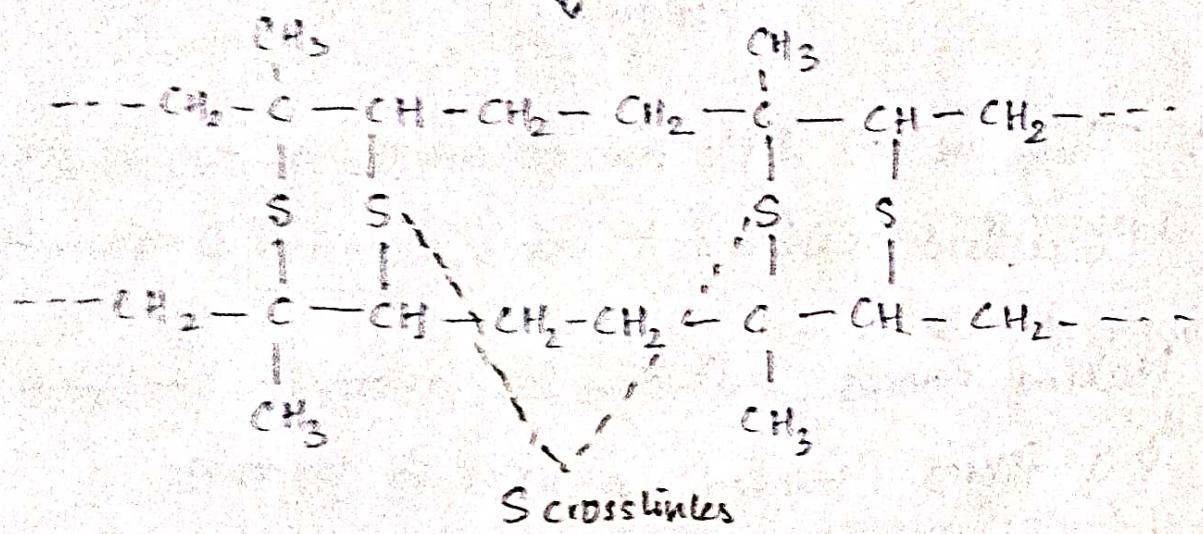
On heating raw rubber with sulphur to $100-140^\circ\text{C}$, it combines at = bonds chemically & hence becomes stiff due to restriction in movement of chains.



+



$\downarrow \text{S} \quad | \quad 100-140^\circ$



vulcanized rubber



Raw rubber



Vulcanized rubber

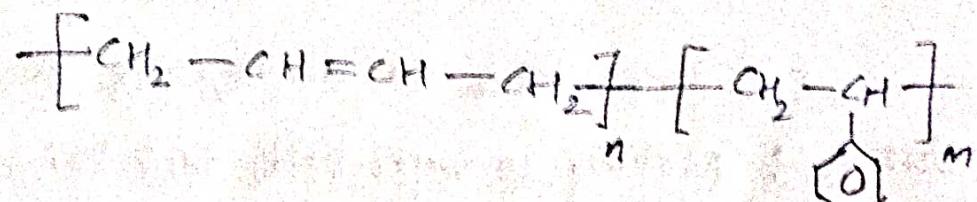
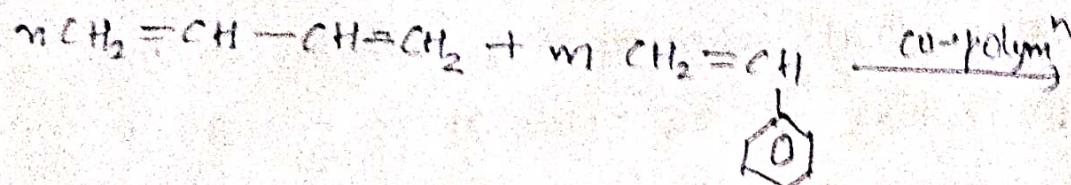
Synthetic rubbers are vulcanizable man-made rubbers like polymer, which can be stretched to atleast twice its length, but returns to its original form once stress is released.

It is also called as "misnomer" as it is not (purely) derived from natural rubber.

Example ① : STYRENE RUBBER (GR-S (or) BUNA-S)

(BU - Butadiene ; NA is for Na (catalyst) & S for styrene)

Reaction is co-polymerization. The reactants are butadiene (75% taken by weight) & styrene (25% taken by weight)



Polybutadiene - Co - styrene
(or)

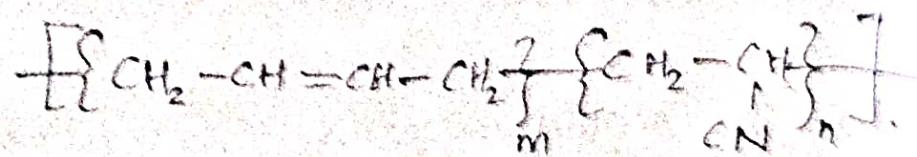
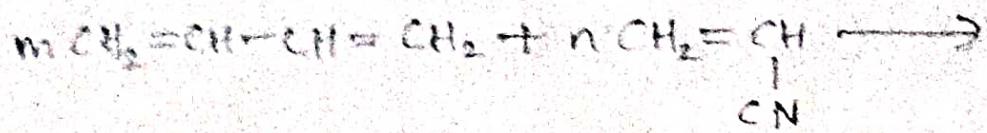
Styrene butadiene rubber, SBR

Properties: SBR possess high abrasion resistance, high load-bearing capacity & resilience. It gets readily oxidised in the presence of O_3 . It swells in oils & solvents.

Uses : Used in manufacture of motor tyres. They are used in floor tiles, gaskets, wire & cable, insulations, adhesives etc.

Example ② : Nitrile rubber (GR-N (or) BUNA-N)

It is co-polymer of butadiene & acrylonitrile



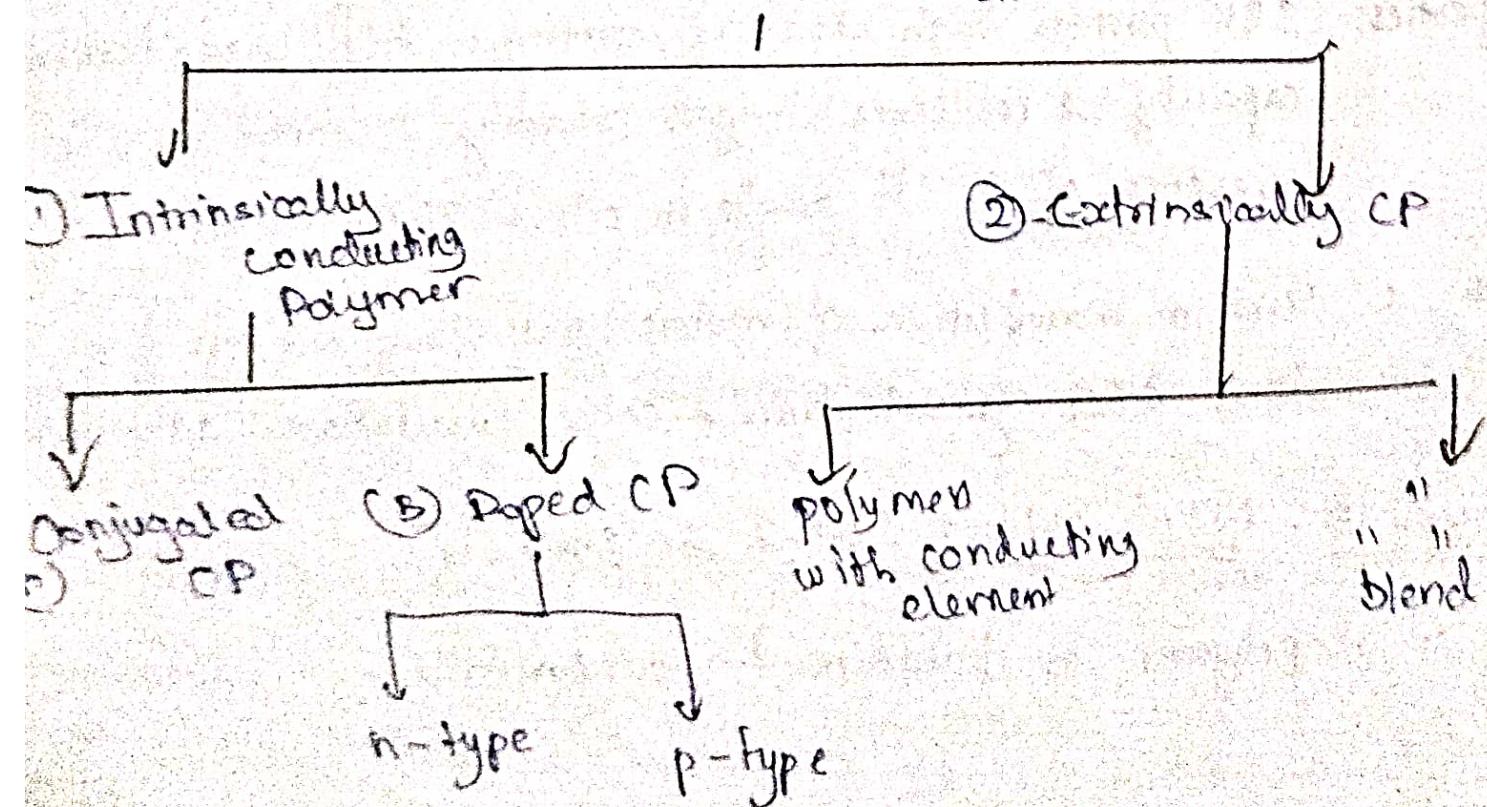
Selby Nitrile rubber

Properties : Possess excellent resistance to Δ , sunlight, oils and acids. Because of the cyano groups presence, it is less resistant to alkalis. As % of acrylonitrile \uparrow resistance to acids, oils \uparrow .

Uses : Making conveyors belts, tank-linings, gaskets, adhesives etc.

CLASSIFICATION OF CONDUCTING POLYMERS

CONDUCTING POLYMER



The conduction of electricity is due to conjugation of πe^- cloud in delocalized state. This conjugation due to either πe^- 's (or) due to doped ingredients.

conducting Polymers

Introduction: Most polymers are poor conductors of electricity, because of the non-availability of large no. of free e^- in the conduction process.

Hence polymeric materials are synthesized which possess electrical conductivities on par with metallic conductors. Such polymers are called "conducting polymers". These CP have sp^2 hybridised carbon centres.

Types of Conducting Polymers:

① Intrinsically CP: ② Conjugated $\pi - e^-$ CP

⇒ It is a polymer whose skeleton (or) groups attached consists of πe^- cloud (delocalized) or residual charge. These polymers have "conjugated $\pi - e^-$ pairs" for conducting electricity.

⇒ In the presence of electric field, the conjugated $\pi - e^-$ of the polymer gets excited & transported through the solid polymeric material.

⇒ Doping of conjugated π -bonded overlap over the entire
station of the polymer results in the form of valence band
as well as conduction bands, that spreads over the
material.

e.g. (i) Polyacetylene polymer (ii) poly- η -ethylenne
(iii) Polyacridine (iv) Poly phenylene-co-vinylene

(B) Condensed aromatic rings:-

e.g. Polyparaphenylene, poly Octamethylene etc.

It said in following conjugated π cloud & presence of lone pair of δ s help in conduction.



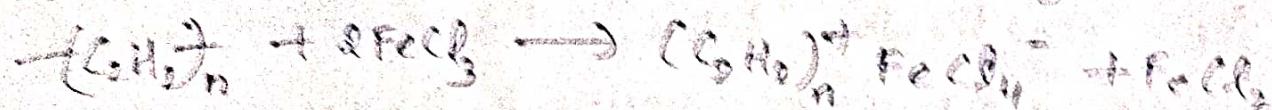
Polyacetylene

(C) Doped Conducting polymers:

This is done by treating with charge neutralizing agent in either
gas (e.g.) in O_2^+ . As O_2^+ possess low conductivity, but
high δ affinity & low Ionization potential favour O_2^+ (or)
 NO_3^- & hence increases conductivity as $+\text{ve}$ COO^- ($-$) charges
are added to the polymeric chain. This technique by addition of
charges in polymeric chains bring its conduction by creating (i) or
(ii) charge carriers called "Doping".

(i) P-doping: ICPs with Lewis acid, thereby extra π delocalized plane & one charges are created on the backbone of the chain
Dopants \rightarrow T_2 , Ba_2 , Pb etc.

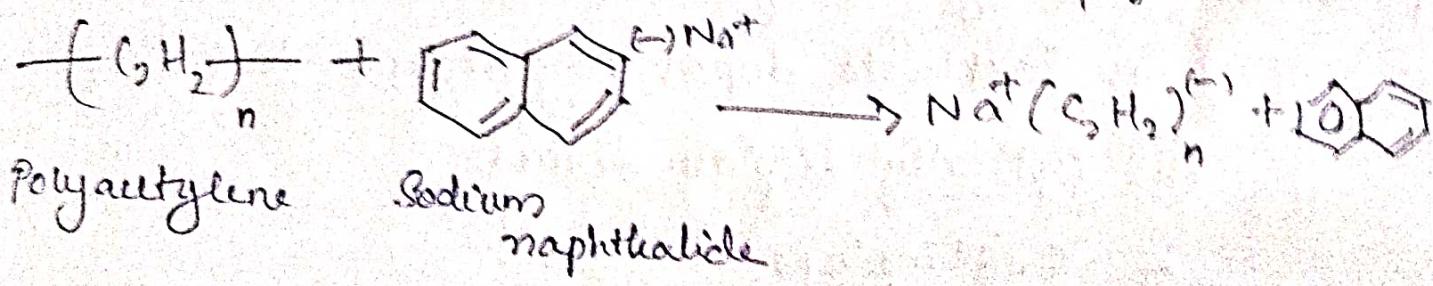
Polymer + Lewis acid \rightarrow p-doped polymer



Free delocalization of lone charge causes electrical conduction

(ii) N-doping: ICPs with Lewis bases undergoes redⁿ & creates -ve charges on the back bone resulting in conduction.

Polymer + Lewis base \rightarrow N-doped polymer



Properties:

ICPs has good electrical conductivity, capable to store charge, capacity to exchange ions, ability to absorb visible radiation thereby yielding the coloured compds. These are also X-ray transparent.

② Electrically conducting Polymers:

- ⇒ These polymers conduct electricity which is due to presence externally added ingredient in them.
- ⇒ When carbon black (or) metal oxide (or) metallic fibres are added the polymer becomes conductive.
- ⇒ The ingredient (fillers) that penetrate have more surface area, more porosity & filamentous nature due to which they can enhance the conducting properties.
- ⇒ Low in cost, light wt, durable & strong.

e.g.: Polyaniline, polythiophene.

Applications:

- (i) Rechargeable light wt batteries

e.g.: Perchlorate doped polyacetylene - Li batteries

- (ii) Optically display devices

e.g.: Polythiophene

- (iii) Anti- static coatings for clothing.

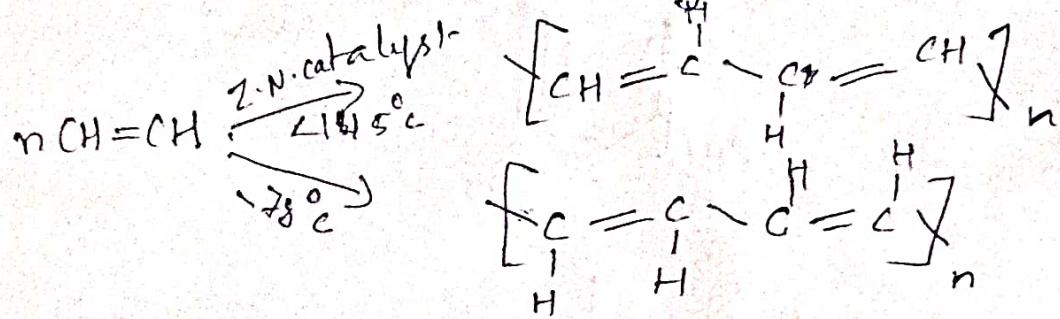
- (iv) Photovoltaic cells

e.g. Al/polymer/Ag photovoltaic cell.

- (v) Non-linear optical material.

I POLYACETYLENE

Preparation: Acetylene can be polymerized to polyacetylene via addition polymⁿ using Zeigler-Natta catalyst.

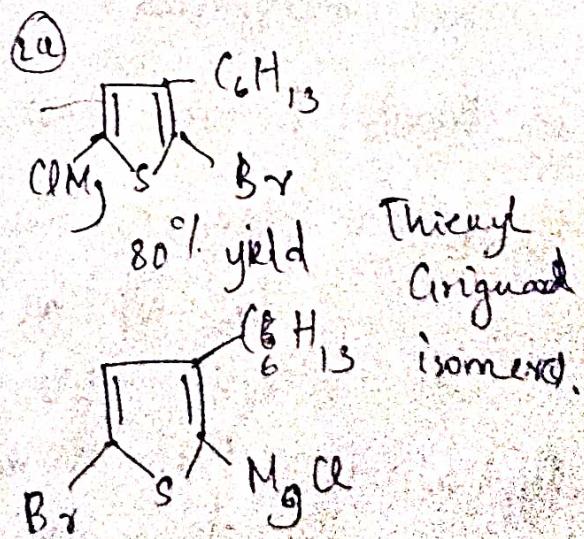
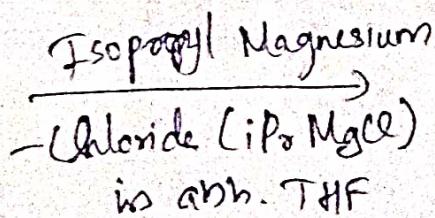
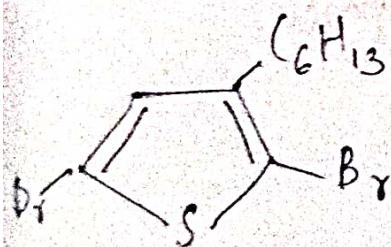
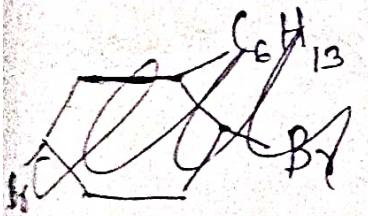


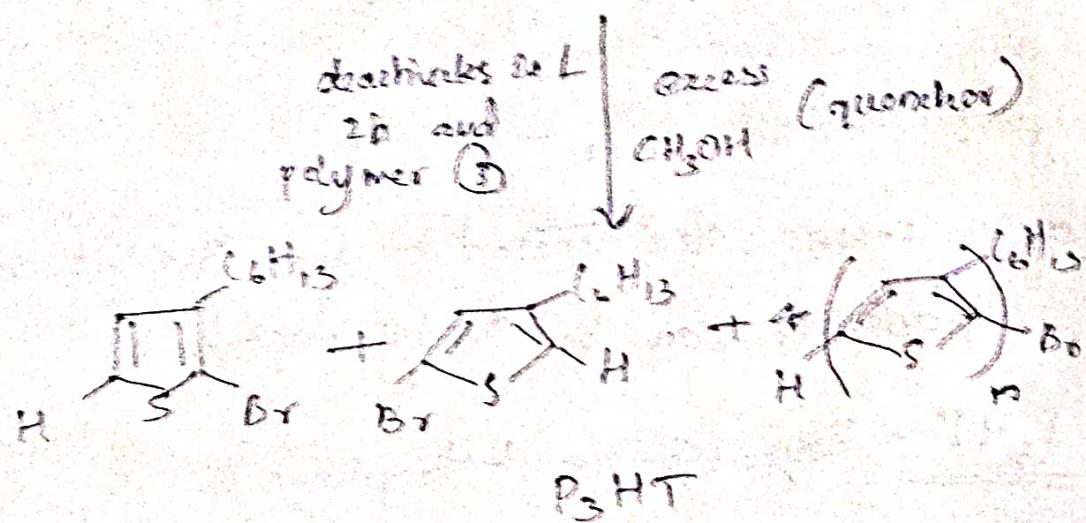
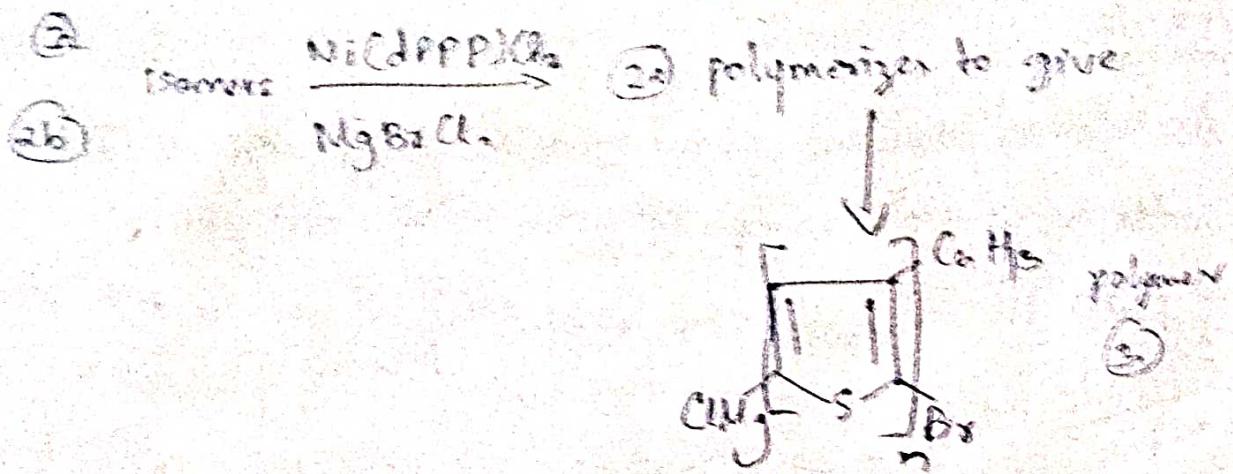
ZN catalyst: $\text{Ti}^\circ(\text{O}-\text{nBu})_4 - \text{Et}_3\text{Al}$

Properties: Unstable when exposed to air. But its conducting properties can be ↑ by doping.

II P₃HT - Poly (3-hexylthiophene)

Preparation: (i) Synthesis by Grignard ~~reac~~ metathesis polymⁿ followed by quenching reac using methanol to terminate the reac.





→ It is organic solar cell aim to provide an earth-abundant & low energy production photo voltaic cell. These provide electricity at low cost than classic (inorganic) solar cells. The organic polymer absorbs light & charges are transferred.

→ Merits: Flexible, low cost, light wt, Semitransparent

→ Demerits: low efficiency (5%)
 low lifetime
 a) yield

Applications: (i) Personal mobile phone charge
 (ii) clothes with embedded cells
 (iii) Organic photovoltaics
 etc.