Polymer

Poly mer

many unit or part

- Polymers are large molecules having high molecular mass ($10^3 - 10^7$ u) (macromolecule) formed by joining repeating structural units on large scale.
  - ↳ monomer
  - monomers are reactive molecules and joined by covalent bond.
- Formation of polymers from monomer is called polymerization.

eq: ethene to polythene $n\ CH_2=CH_2 \xrightarrow{\text{Polymerizn}} n[-CH_2-CH_2-] \rightarrow [-CH_2-CH_2-]_n$

Repeating unit — Polythene (polymer)

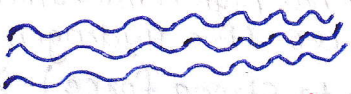
eq: Hexamethylenediamine + Adipic acid → Nylon 6,6

$n\ NH_2(CH_2)_6NH_2 + n\ COOH(CH_2)_4COOH \xrightarrow{\text{Polymerizn}}$ Nylon 6,6

Classification of Polymer

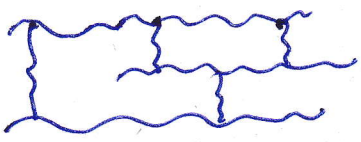
Based on Source	Based on str of Polymer	Based on mode of Polymerization	Based on molecular forces	Based on Growth polymerizn
1) Natural polymer	1) Linear polymer	1) Addition polymer	1) Elastomer	1) Chain growth polymer.
2) Semi Synthetic Polymer	2) Branched chain polymer	2) Condensation polymer	2) Fibres	2) step growth polymer.
3) Synthetic Polymer	3) Cross linked or network polymer		3) Thermoplastic polymer	
			4) Thermosetting polymer	

- Natural polymer → Found in plants & animals eg: Proteins, cellulose, Starch, Some resins & rubber
- Semi Synthetic → Derivative of natural polymer : eg: Cellulose acetate (rayon) & Cellulose nitrate
  - CAR
- Synthetic polymer → man made polymer eg: plastic (polythene), Synthetic fibre (nylon 6,6)
  - Synthetic rubber (Buna-S)
- Linear polymer : Long & Straight chains eg: High density polythene, polyvinylchloride (PVC)



- Branched chain polymer : Linear chain having some branches eg: low density polythene

- Cross linked/network : formed from bifunctional & trifunctional monomer & contain strong covalent bond b/w various linear polymer chains.
  - eg: Bakelite, melamine



Addition polymer : Repeated addition of monomer molecule having double/triple bond.

eg: polythene from ethene
polypropene from propene

Addition polymer

- Homopolymer
  polymerization of single monomer.
  eg: polythene

$$n\ CH_2=CH_2 \longrightarrow (CH_2-CH_2)_n$$

- Co-polymer
  polymerization of two different monomer.
  eg: Buna-S, Buna-N

1,3 butadiene + Styrene → Buna-S

$$n\ CH_2=CH-CH=CH_2 + n\ C_6H_5-CH=CH_2 \rightarrow \left(CH_2-CH=CH-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2\right)_n$$

Butadiene-Styrene (Buna-S)

Condensation polymer : formed by repeated condensation reaction b/w two different bifunctional or trifunctional monomers.

: Small molecules like H_2O, alcohol, HCl are eliminated.

eg: terylene (dacron), nylon 6,6, nylon 6

$$n\ NH_2(CH_2)_6NH_2 + COOH(CH_2)_4COOH \longrightarrow \left[NH(CH_2)_6NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n + n\ H_2O$$

Hexamethylenediamine + adipic acid → Nylon 6,6

Elastomer :
- Rubber like solid with elastic property.
- polymer chain are held by weak intermolecular force due to which it has stretching capability.
- few crosslinks b/w the chains help the polymer to retract its original position after external force is released.

eg: Buna-S, Buna-N, Neoprene $\longrightarrow \left(CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2\right)_n$

Fibre : Thread forming solid which has high tensile strength & high modulus due to strong intermolecular forces like Hydrogen Bond.
- crystalline nature (due to strong force) ⇒ close packing

eg: polyamides & polyesters (terylene)

↓

nylon 6,6

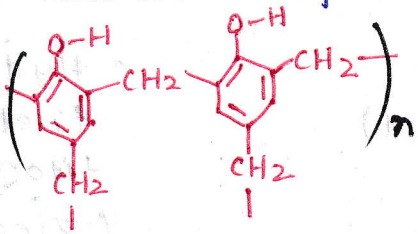
$$\left(NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right)_n$$

Thermoplastic polymer → linear or slightly branched long chain capable of repeatedly softening on heating and hardening on cooling.
→ intermolecular force : intermediate b/w elastomer & fibre.

eg: polythene, polystyrene, polyvinyl etc.
↳ PVC ↳ $\left(CH_2-\underset{Cl}{CH}\right)_n$

Thermosetting polymer → polymers are cross linked or heavily branched molecules. on heating it undergoes extensive cross linking & become infusible.

eg: Bakelite, Urea formaldehyde resins



→ Bakelite

intermolecular force : Thermosetting polymer > fibre > Thermoplastic > Elastomer

Based on Growth polymerization :- addition & condensation polymer now-a-days are also refered as chain growth polymer and step growth polymer.

Types of polymerization Reaction

- Addition or chain growth polymerization.
- Condensation or Step growth polymerization.

Addition/chain growth polymerization

- molecules of same monomer or different monomer add togather on large scale to form polymer.
- monomers used are alkenes, alkadienes & its derivatives.
- Polymerization takes place via free radical or ionic mechanism.
  ↳ most common

Free Radical Mechanism

- free radical generating initiator (catalyst) is used.
  eg: Benzoyl peroxide, acetyl peroxide, tert-butyl peroxide

eg:- • Polymerization of ethene to polythene
• Free radical mechanism involves 3 steps.

① chain initiation : $C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \rightarrow 2\,C_6H_5-\overset{O}{\overset{\|}{C}}-O^{\bullet} \rightarrow 2\,C_6H_5^{\bullet}$

② chain propagation $C_6H_5^{\bullet} + CH_2=CH_2 \rightarrow C_6H_5-CH_2-\dot{C}H_2$

$C_6H_5-CH_2-\dot{C}H_2 + CH_2=CH_2 \rightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$

$\downarrow$

$C_6H_5-(CH_2-CH_2)_n-CH_2-\dot{C}H_2$

③ chain termination

$C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2$ + $C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2$

$\rightarrow C_6H_5\left(CH_2-CH_2\right)_n CH_2-CH_2-CH_2-CH_2\left(CH_2-CH_2\right)_n C_6H_5$

Preparation of Some Imp addition polymer

1. polythene
2. polytetrafluoroethene (Teflon)
3. polyacrylonitrile

Polythene is of two types

Low density polythene

- High T, High P
  (350-570K) → (1000-2000 atm)
- Traces of dioxygen (O_2) or a peroxide initiator (catalyst) is used.
- Free radical mechanism
  Highly branched str.
- chemically inert
  tough, flexible, poor conductor of electricity
- manufacture of squeeze bottles, toys, flexible pipe, insulation of electric wire.

High density polythene

- Low T, Low P
  (333K-343K) → (6-7) atm
- Hydrocarbon solvent with triethyl Aluminium & titanium tetrachloride is used.
  (Zieglar-Natta Catalyst)
  ↓
  $Al(C_2H_5)_3 + TiCl_4$
- Linear molecule & high density due to close packing
- Chemically inert
  (more tough & hard)
- manufacture of bucket, dustbin, bottles, pipes.

Polytetrafluoro ethene (Teflon)

$$n\ CF_2=CF_2 \xrightarrow[\text{catalyst}]{\text{High P}} -(CF_2-CF_2)_n-$$

tetrafloroethene → Teflon

- Catalyst: free Radical or persulphate
- Chemically Inert
- manufacture of oil seals & gaskets, non-sticky coated utensils.

Polyacrylonitrile

$$n\ CH_2=\underset{\underset{CN}{|}}{CH} \xrightarrow{\text{Peroxide Catalyst}} -\left[CH_2-\underset{\underset{CN}{|}}{CH}\right]_n-$$

{ acrylonitrile } → polyacrylonitrile

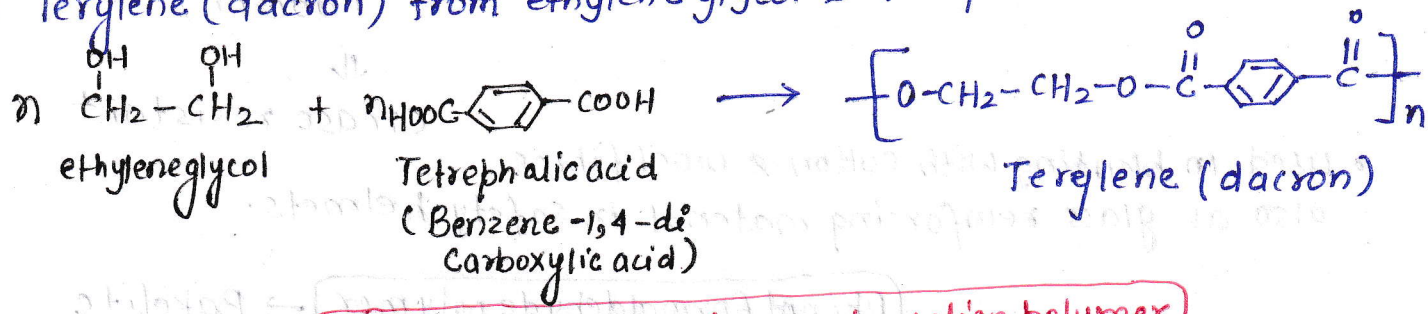
PAN

- PAN is a good substitute for wool in making commercial fibre.
  eg: orlon, acrilan

Condensation polymerization or Step growth polymerization (3)

- Repeatative condensation b/w two bifunctional monomers.
  H_2O, alcohol, HCl etc are eliminated.

eg: Terylene (dacron) from ethylene glycol & terepthalic acid



Preparation of some Imp condensation polymer

① polyamides → Polymer containing amide linkage eg → Nylon → Prepared by condensation polymerzⁿ of diamines with dicarboxylic acid & also of amino acid & their lactum.
↓
Compd containing $-NH-\overset{O}{\overset{\|}{C}}-$

Nylon → Nylon-6,6.
Nylon 6.

② polyester
③ phenol formaldehyde polymer
④ Melamine formaldehyde polymer

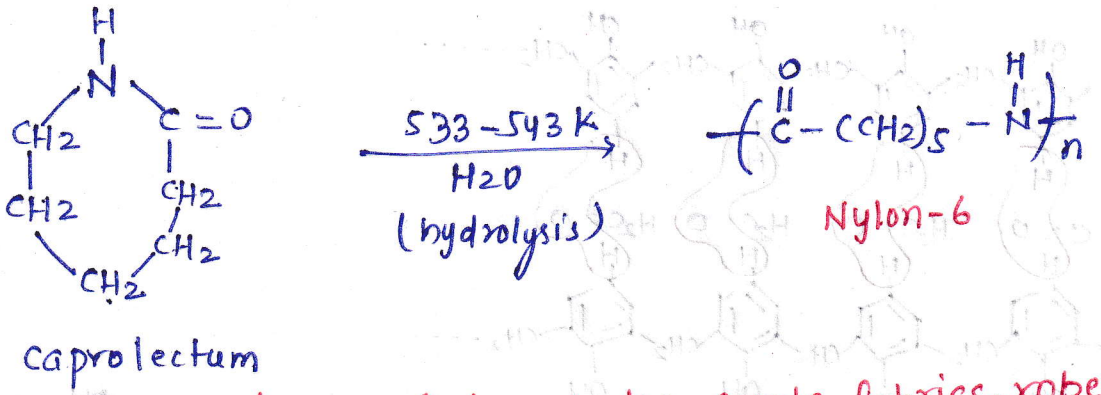
Preparation of Nylon 6,6 : Condensation polymerization of hexamethylene diamine with adipic ~~acid~~ acid.

$$NH_2(CH_2)_6NH_2 + COOH(CH_2)_4COOH \xrightarrow[\text{high P}]{553K} \left\{NH(CH_2)_6NH-\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}\right\}_n$$

Nylon 6,6

- used in making sheet, bristles for brushes.

Nylon 6 : Heating caprolactum with water at high temp. (Hydrolysis rxⁿ)



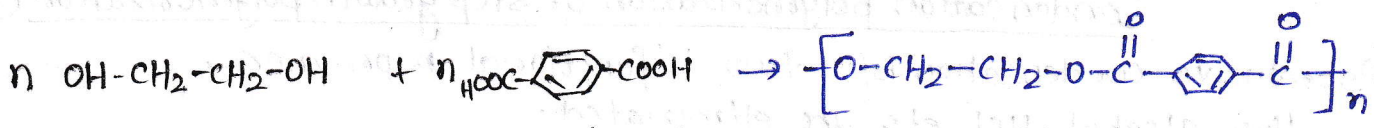
caprolectum

- used in manufacture of tyre cords, fabrics, rope

Polyester → condensation product of dicarboxylic acid & di-ols.

eg: dacron or terylene
⇓
ethylene glycol + Terephalic acid (420K – 460K)

Catalyst ← { (zinc acetate, → $Zn(CH_3COO)_2$
antimony trioxide)
↳ Sb_2O_3



ethylene glycol — terephalic acid — Terylene (dacron)

⇓

Crease resistant

- used in blending with cotton & wool fibres also as glass reinforcing material in safety helmets.

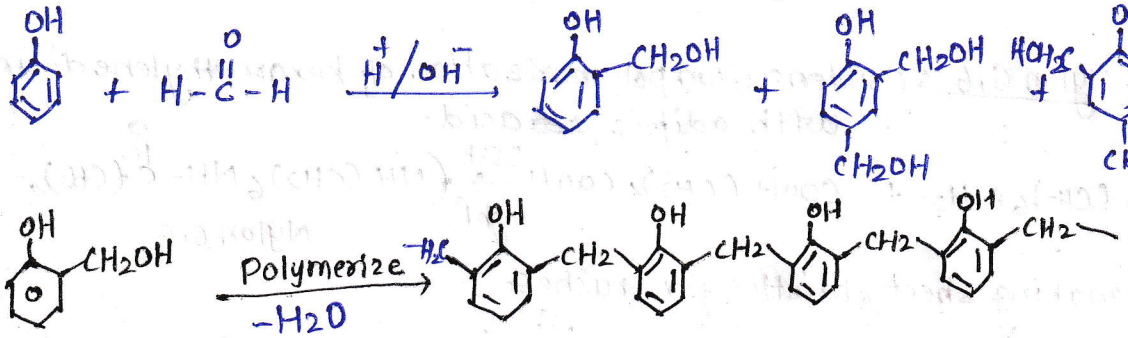
Phenol formaldehyde polymer → Bakelite

- Oldest synthetic polymer.
- Condensation reaction b/w phenol & formaldehyde in presence of either an acid or base catalyst.

Initial product → Novolac (linear polymer used in paints)

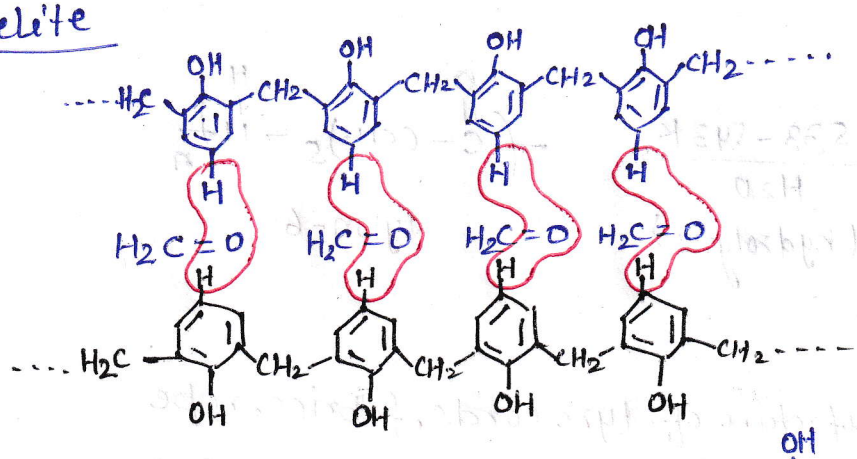
↓

on heating with formaldehyde undergoes cross linking to form Bakelite (infusible solid mass)

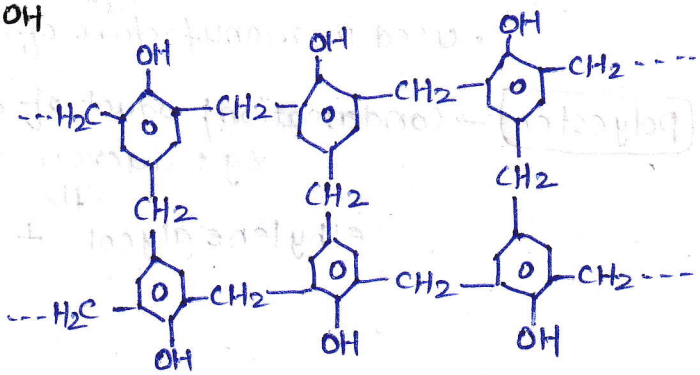


Novolac

Bakelite



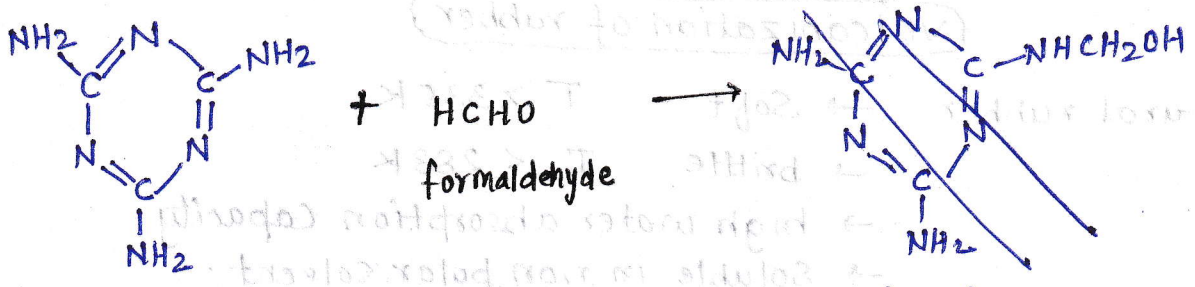
- manufacture of combs, phonograph records, electric switch handles of utensils.



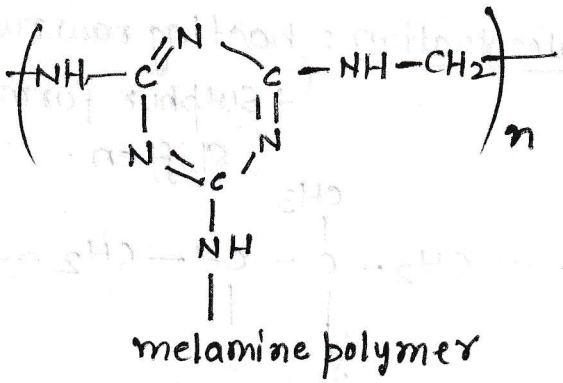
Bakelite

Melamine Formaldehyde polymer

Condensation polymer of melamine & formaldehyde.



- manufacture of unbreakable crockery.

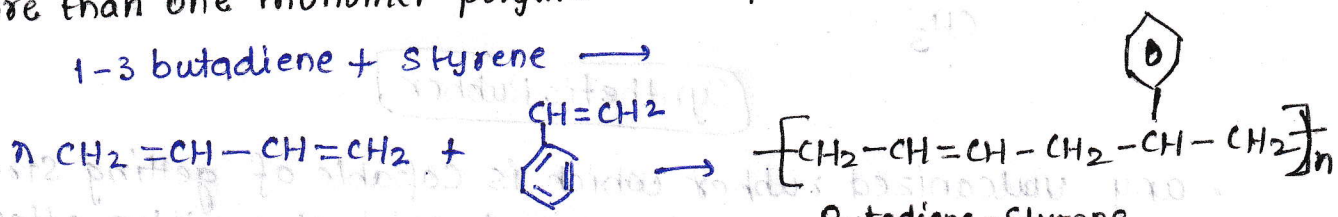


melamine polymer

(3) Copolymerization

- more than one monomer polymerize to form a copolymer.

eg:- 1-3 butadiene + Styrene ⟶

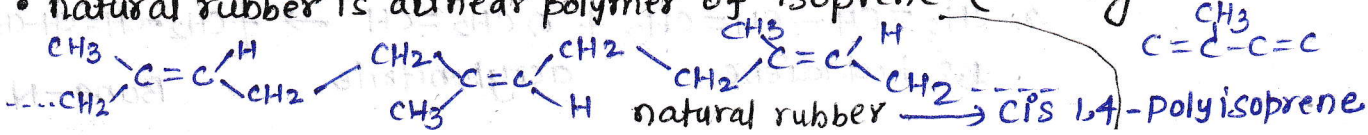


Butadiene-Styrene copolymer
↳ quite tough & it is a good substitute for natural rubber.

- autotyres, floor tiles, footwear components, cable insulators.

(4) Rubber

- has elastic properties, also k/a elastomers.
- polymer chains are held togather by weak intermolecular forces. due to which they can be stretched.
- Few crosslinks introduced b/w chains help the polymer to retract its original position after force is released.
- manufactured from rubber latex (obtained from rubber tree)
  ↓
  colloidal dispersion of rubber in water.
- natural rubber is a linear polymer of isoprene. (2-methyl-1,3-butadiene)



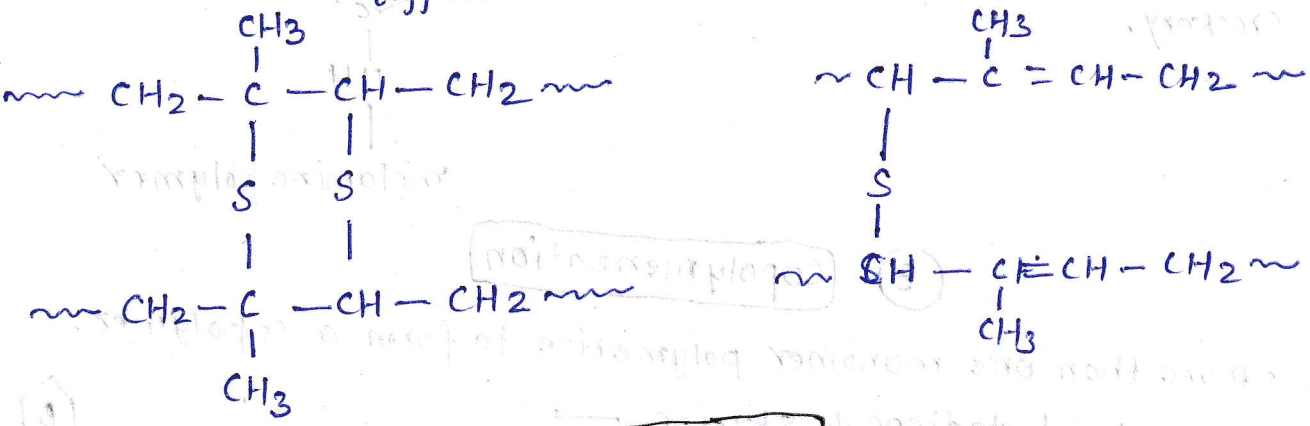
Natural rubber consists of various chains held by weak vanderwaal force & has coiled structure.

Vulcanization of rubber

Natural rubber → Soft $T > 335\,K$
→ brittle $T < 283\,K$
→ high water absorption capacity
→ Soluble in non polar solvent.

To improve physical properties of rubber vulcanization is carried out.

Vulcanization: heating raw rubber with Sulphur (373K – 415K)
↳ Sulphur forms cross link & so rubber becomes stiffen.

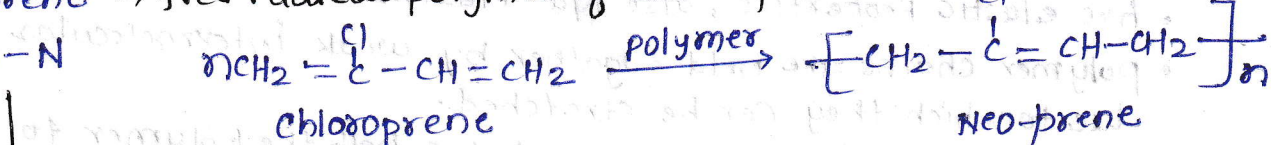


Synthetic Rubber

- any vulcanized rubber which is capable of getting stretched to twice its length. (returns to original position after external force is released).
- Synthetic rubber → either homopolymer of 1,3-butadiene
  or copolymer of 1,3-butadiene

Preparation of Synthetic Rubber

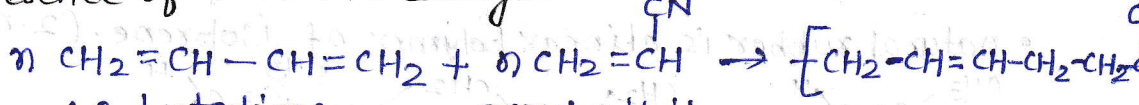
1) Neoprene → free radical polymer of chloroprene
2) Buna–N



Chloroprene
2-chloro-1,3-butadiene
Neo-prene

- Conveyor belt & gaskets manufacture.

→ Copolymerization of 1,3-butadiene & acrylonitrile in presence of peroxide catalyst.



1,3-butadiene acrylonitrile Buna–N

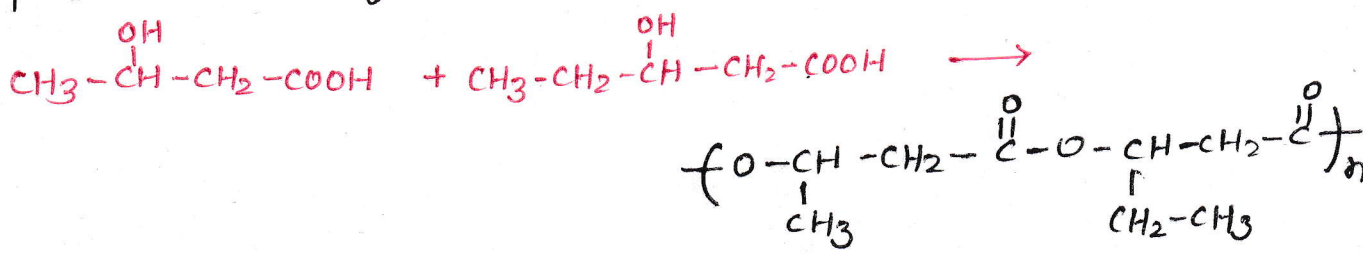
Biodegradable polymer

↓

aliphatic polyesters (PHBV, nylon-2-nylon-6)

① PHBV (poly-β-hydroxybutyrate-co-β-hydroxy valerate)

→ copolymerization of 3-hydroxybutanoic acid & 3-hydroxy Pentanoic acid

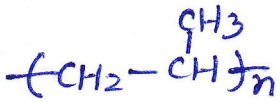
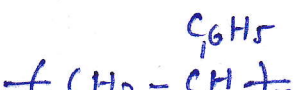
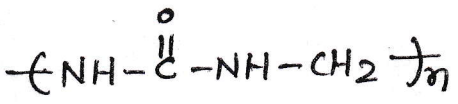
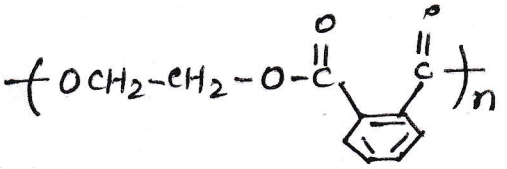


PHBV

- it undergoes backterial degradation in environment

② nylon-2-nylon 6

- copolymer of glycine (NH_2-CH_2-COOH) & amino caproic acid ($NH_2(CH_2)_5COOH$)

Name of polymer	Monomer	structure	~~Uses~~
• polypropene	propene		
• polystyrene	styrene		
• polyvinylchloride PVC	vinyl chloride		
• Urea formaldehyde Resin	a) urea b) formaldehyde		
• Glyptal	a) ethylene glycol b) pthalic acid		
• Bakelite	a) phenol b) formaldehyde