→ Synthetic polymers:→

→ Introduction:→

- Polymer (Greek, poly → many and meros → parts or units)
- Polymers are large molecules which are made by linking together many repeating units of small molecules in a regular fashion.
- These units of small molecules are called monomers.
- The process of transformation of monomers into polymers is known as polymerisation.

Example:- Polyethylene or polythene.

$$\underset{\text{ethene}}{n\,CH_2=CH_2} \xrightarrow{\Delta,\text{ high pressure}} \underset{\text{Polythene (polymer)}}{-(CH_2)_n-}$$

- Plastics or resins are the most widely used polymers. The first plastic, celluloid was invented by Alexander Parke (1856). It was mixture of nitrocellulose and camphor and was was used for the manfacture of billiard balls and piano keys in place of ivory.
- Plastics are glassy, hard or horny materials which are not readily undergo deformation at the temperature at which they are used.
- Elastomers or rubbers are readily undergo deformation and return to their original shapes afterwards.
- Plastics are classified into two categories- Thermoplastic and Thermosetting.
- Thermoplastic plastic soften on heating and harden again on cooling without change in their properties.

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- Thermosetting plastic undergo chemical change on heating and on cooling set to hard masses. The change is irreversible and so the polymer cannot be melted again.
- Several polymers posses fibre formation properties. The first synthetic fibre, rayon, was accidentally discovered by Louis Chardonnet (1865).
- Syntheic fibres have high tensile strength.
- Fibres are made by a process called melt spining. The molten mass is forced to pass through a number of fine holes and then allowed to cool rapidly.
- The first synthetic rubber was synthesised by German chemists during world war I.

→ Homopolymers and copolymers :→

(i) Homopolymers :→

- In these polymers repeating unit is derived from only one type of monomers.

Example:- Polythene, polypropylene, poly vinyl chloride (PVC), Poly acrylic nitrile (PAN), teflon, cellulose, nylon-6 etc.

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(2) Copolymers :→

- In these polymers repeating unit is derived from two or more types of monomers.

Example:- Nylon-66 (hexamethylene amine and adipic acid)
Buna-S (1,3-Butadiene and styrene)

→ Polymers and Macromolecules :→

- Polymer is obtained by polymerisation of hundreds to thousands of repeating units while a macromolecule may or may not contain repeating units.

Example:- Chlorophyll is a macromolecule but not a polymer. similarly proteins and nucleic acids are macromolecules not polymers because their molecule do not contain only one repeating unit.

However, polythene may be regarded as both a macromolecules as well as a polymer as it contains large number of repeating structural units. Therefore, all polymers are macromolecules but all macromolecules may not be polymers.

- Although proteins and nucleic acids are macromolecules and are usually called polymers because proteins consist of a large number of chemically similar α-amino acids and nucleic acids consist of nucleotides which are also chemically similar.

→ Classification of polymers:→

- On the basis of source

(1) Natural polymers:-

- These are found in nature (animals and plants).

e.g. proteins, nucleic acids, cellulose, rubber etc.

2. Synthetic polymers:→

— These are man made polymers.

e.g. Nylon, plastics, synthetic rubbers etc.

3. Semisynthetic polymers:→

- These are generally derived from naturally occuring polymers by chemical modifications.

Example → Vulcanised rubber

Cellulose diacetate (acetylation of cellulose with acetic anhydride in the presence of H_2SO_4).

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→ Polymerisation:→

- The process of transformation of monomers into polymers is known as polymerisation.

→ Types of polymerisation:→

- Polymerisation are of two types-

(1) Addition polymerisation or chain growth polymerisation.

(2) Condensation polymerisation or step growth polymerisation.

(1) Addition polymerisation or chain growth polymerisation:→

- In this type of polymerisation there is successive addition of monomers to the growing chain having a free radical, a carbocationic or a carboanionic terminal.
- In this types of polymerisation the empirical formula of polymer is the same as that of monomer from which it is derived.

$$\underset{\text{Ethene}}{n\ CH_2{=}CH_2} \xrightarrow[\text{Traces of } O_2]{473\,k,\ 150\,atm} \underset{\text{Low density polythene}}{-(CH_2-CH_2)_n}$$

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- Most of the commercially important polymers prepared via addition or chain growth polymerisation through monomers having carbon-carbon double bond.

(2) Condensation polymerisation or step growth polymerisation:→

- This type of polymerisation involves a repetitive condensation reaction between two bi-functional monomers.

- These polymerisation reactions may result in the loss of some simple molecule as water, alcohol, HCl, CO_2 or NH_3 and leads to formation of high molecular mass condensation polymers.
- Such reactions do not depend on chain containing free radicals or ions.

$$\underset{\text{hexamethylene diamine}}{n\,H_2N(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{n\,HOOC(CH_2)_4COOH}$$

$$\longrightarrow \underset{\text{Nylon 6,6}}{\left[NH(CH_2)_6NHCO(CH_2)_4CO\right]_n} + n\,H_2O$$

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- The main points of difference between chain growth and step growth polymerisations are as under-

(1) In chain growth polymer the molecular formula of the repeating monomer unit is the same as that of the monomer whereas in step growth polymer the molecular formula of repeating monomer unit is usually not the same as that of the monomer.

(2) Unlike chain growth polymerisation, step growth polymerisations do not depend on chain carring free radicals or ions.

→ Addition or chain growth polymerisation: →

- In this type of polymerisation there is successive addition of monomers to the growing chain having a free radical, a carbocationic or a carboanionic terminal.
- Mostly the polymerisation of alkenes occurs by chain mechanism.
- Depending upon the nature of monomer, reaction conditions and types of catalyst(initiator) used, addition or chain growth polymerisation may be classified into following two categories-

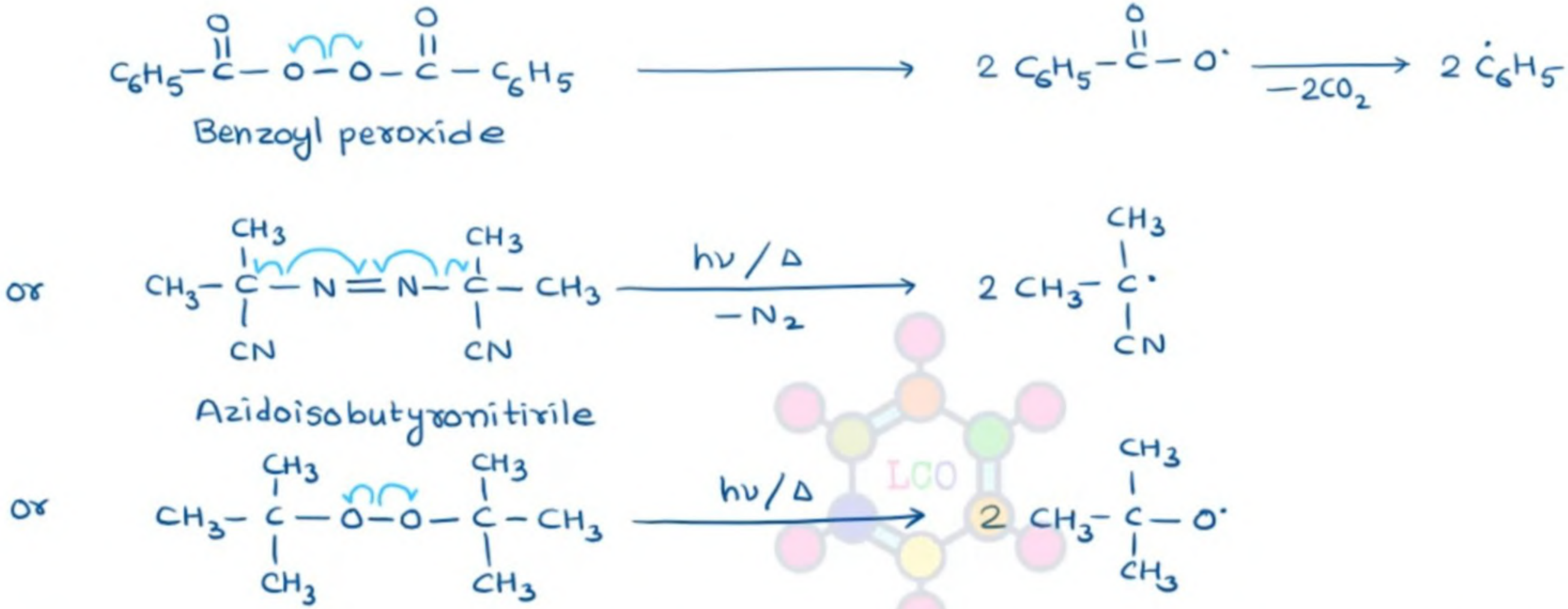
(i) Free radical vinyl polymerisation (ii) Ionic vinyl polymerisation

(i) Free radical vinyl polymerisation: →

- Monomers used in this process are usually monosubstituted ethylenes such as vinyl chloride, acrylonitrile and styrene.
- This polymerisation proceeds under pressure or in the presence of a small amount of peroxides.
- like other radical reactions, free radical vinyl polymerisation proceeds in three steps-

Step-I Chain initiation:-

- It involves the formation of free radical from a radical initiator such as benzoyl peroxide, tert-butyl peroxide and azidoisobutyronitrile or other material that can generate free radicals.
- The chain is initiated by the homolytic cleavage of the peroxide to form free radicals.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2\,C_6H_5-\overset{O}{\overset{\|}{C}}-O^{\cdot} \xrightarrow[-2CO_2]{} 2\,\dot{C}_6H_5$$

Benzoyl peroxide

or

$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-N_2]{h\nu/\Delta} 2\,CH_3-\underset{CN}{\overset{CH_3}{C^{\cdot}}}$$

Azidoisobutyronitirile

or

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{h\nu/\Delta} 2\,CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\cdot}$$

- The radical, say $R^{\cdot}$, so generated then adds to a molecule of alkene monomer, converting it into a radical.

$[\dot{R} \rightarrow \dot{C}_6H_5$ or $(CH_3)_2\dot{C}CN$ or $(CH_3)_3C\dot{O}]$

$$\dot{R} + CH_2=\underset{X}{CH} \longrightarrow R-CH_2-\underset{X}{\dot{C}H}$$

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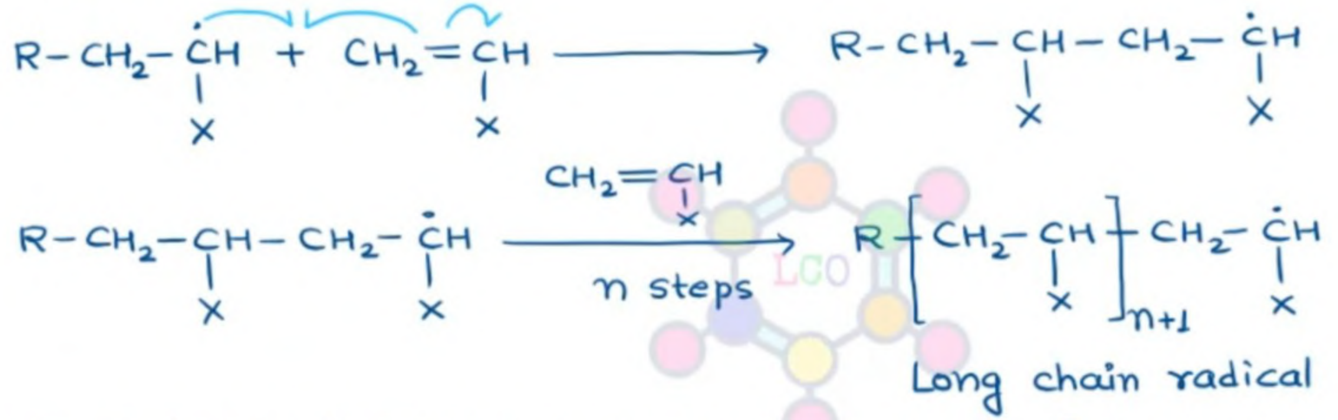
Step II Chain propagation :-

- The free radical generated in step I adds to another monomer alkene forming another radical.
- Successive addition of this radical to monomer molecules results in the formation of long chain radicals.



$$R-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

$$R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}} \xrightarrow[n\ \text{steps}]{CH_2=\underset{X}{\underset{|}{CH}}} R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

- In this step, radical attacts on methylene group of monomer due to less steric hindrance and producing a more stable secondary radical. This is called "head to tail" addition.

Step III chain termination:-

- Termination of chain usually occurs by radical coupling reaction or a disproportionation reaction of polymeric radical.

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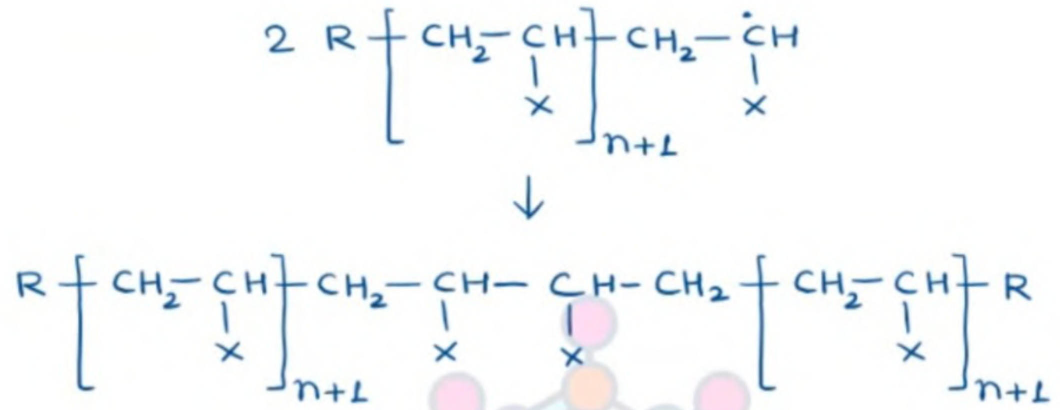
Coupling:-

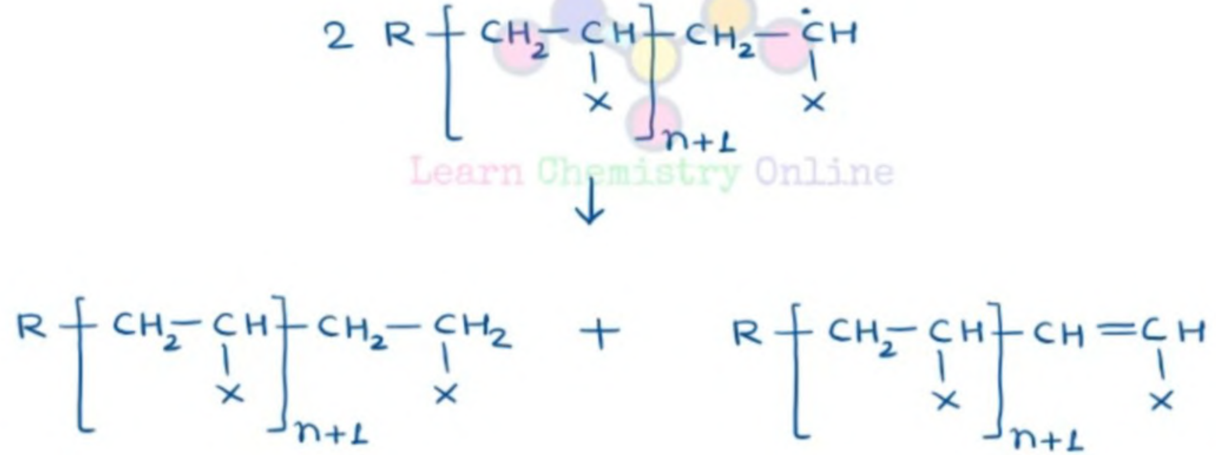


$$2\ R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

$$\downarrow$$

$$R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}CH_2-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-CH_2\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}R$$

Disproportionation:-



$$2\ R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

$$\downarrow$$

$$R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}CH_2-\underset{X}{\underset{|}{CH_2}} + R\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_{n+1}CH=\underset{X}{\underset{|}{CH}}$$

→ Chain inhibitors:→

- There are many substances which reduce the rate of polymerisation by terminating reaction chains. Such substances are called inhibitors or retarders.
- Many phenols, amines and quinones act as inhibitors.
- Inhibitors such as hydroquinone, are often used to stabilize monomers against spontaneous polymerisation when they are kept in storage.

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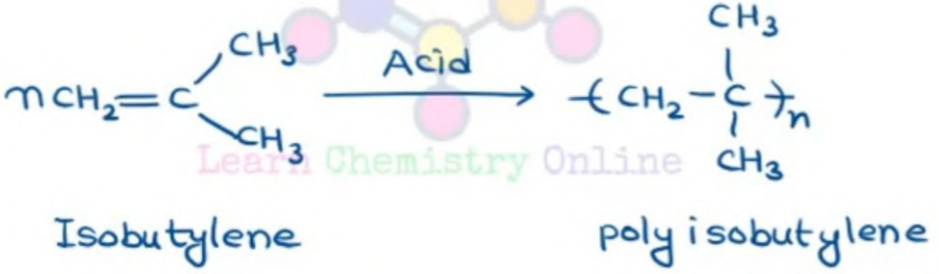
→ Ionic vinyl polymerisation:→

(i) Cationic vinyl polymerisation:→

- Cationic polymerisation takes place in the presence of an electrophile as an initiator.
- This electrophile reacts with alkene to produce cation.
- Most commonly used electrophiles are Lewis acids such as $AlCl_3$ or BF_3.
- These initiators are preferred over proton acids because they do not have any accompanying nucleophile which may terminate the chain as would be the case with acids such as H_2SO_4 or HCl.
- The monomer must have an electron releasing group such as alkyl, alkoxy or aryl groups.

Example:-



$$n\,CH_2{=}C(CH_3)_2 \xrightarrow{\text{Acid}} \left(CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_n$$

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- The pure polyisobutylene is a rubber-like substance and is used in pressure-sensitive adhesives.
- Polymerisation of isobutylene with isoprene gives a polymer which is used as synthetic rubber.

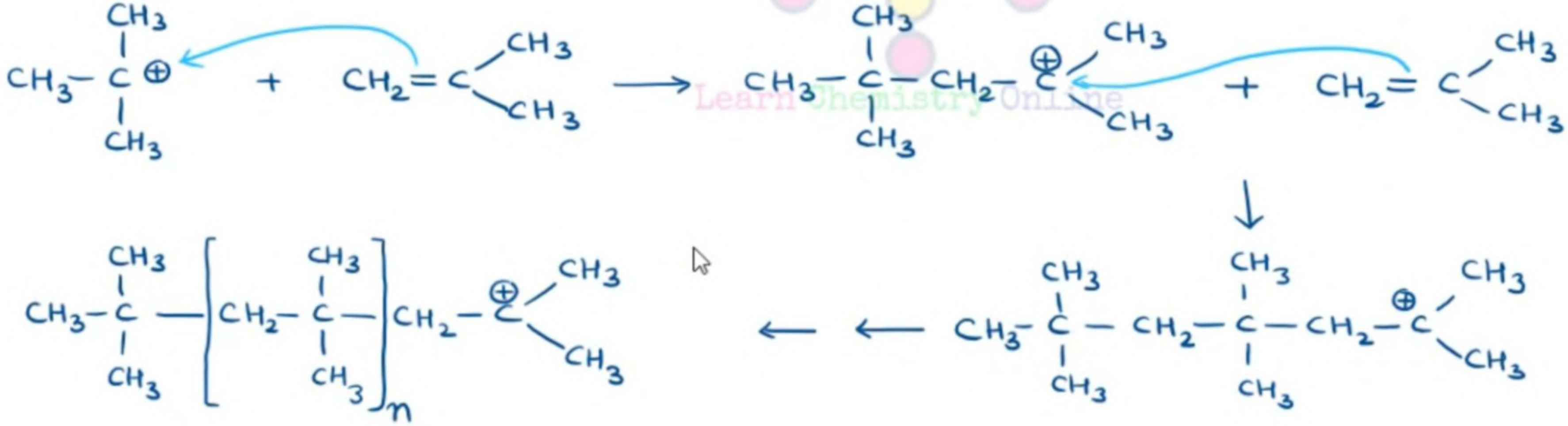
- Mechanism:→

Step-I chain initiation:-

- Protonation or addition of Lewis acid to alkene to produce a carbocation.

Step-II Chain propagation:-

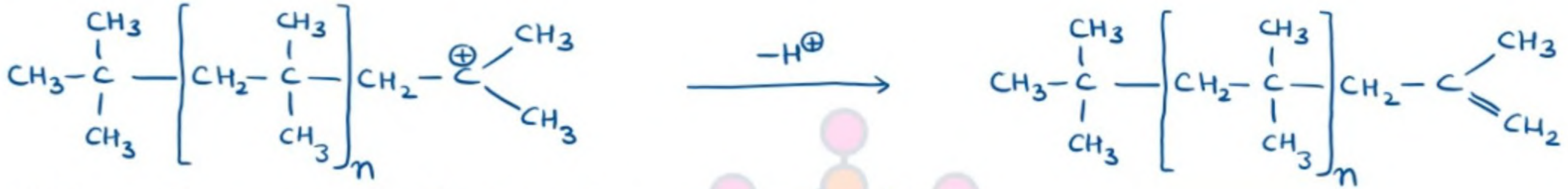
- Addition of carbocation to carbon-carbon double bond of second monomer producing a larger carbocation and so on.



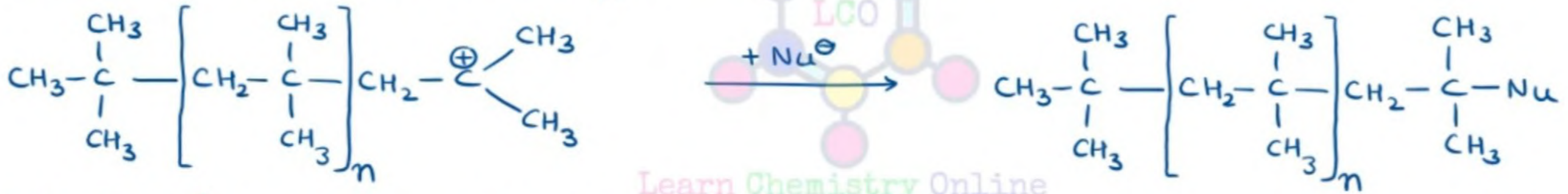
Step III Chain termination:→

- The termination of growing chain may involve any of the following reactions-

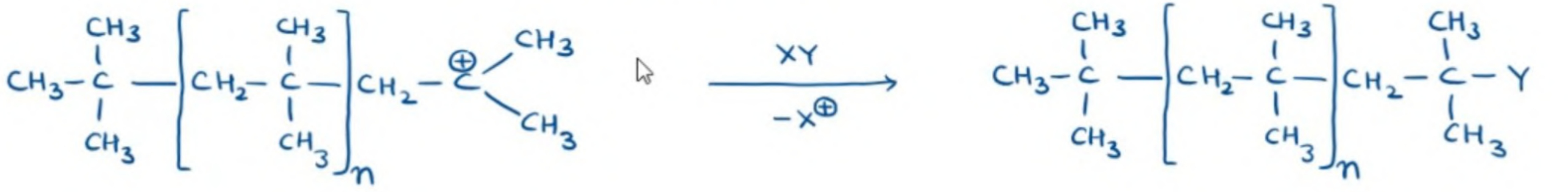
(a) Elimination of proton from polymeric terminal carbocation producing a polymer with a terminal C=C bond



(b) Addition of a nucleophile to polymer carbocation.



(c) Chain transfer reaction with solvent (XY)



- In the presence of H_2SO_4, isobutylene forms a mixture of two dimers namely 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.

This is an industrially important reaction because catalytic hydrogenation of this mixture gives isooctane, which is used to improve upon octane number of gasolene.

(ii) Anionic vinyl polymerisation :→

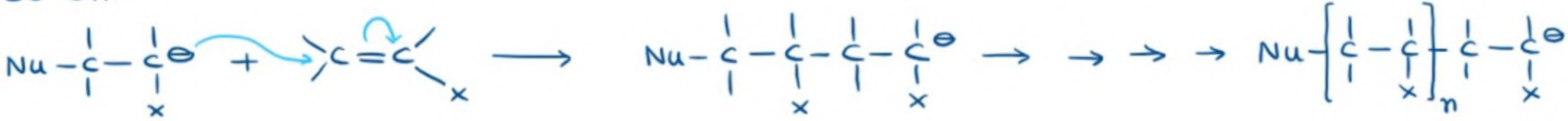
- This process is initiated by the addition of a powerful nucleophile ($-\overset{\ominus}{N}H_2$) to alkene produce the corresponding carbanion.
- The monomer must possesses an electron withdrawing substituent such as nitrile, phenyl or carbonyl in order to stabilise the propagating species.
- Mechanism: -

Step-I chain initiation.

- Addition of strong nucleophile to carbon-carbon double bond to produce a carbanion.

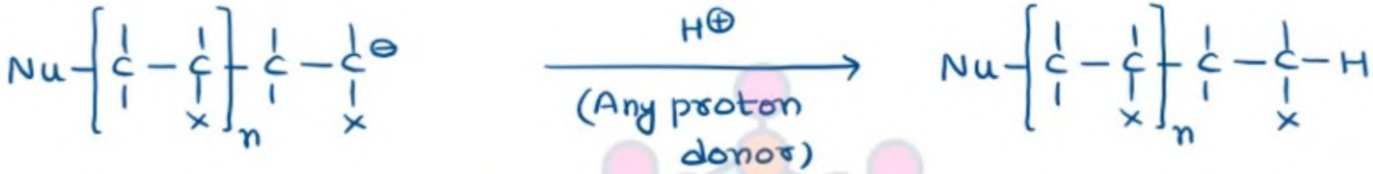
Step-II chain propagation

- Addition of the above carbanion to another molecule of alkene producing a larger carbanion and so on.



step III - chain termination

- The growing chain terminates by abstraction of a proton from any proton donor.
- chain termination by coupling and disproportionation reaction cannot takes place in ionic polymerisation. However, termination, occurs by hydride transfer, or by the action of reactive centers with solvent, or with functional group of the monomer.



- A number of reagents are used to bring initiation, the most important are n-butyllithium and lithium amide
- Some alkenes polymerises even in presence of weak base. For e.g., methyl α-cyanoacrylate having strong electron withdrawing groups (-CN and -COOH) polymerises in presence of basic impurities such as metal oxide.

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→ Condensation or step growth polymerisation:→

- This type of polymerisation involves a repetitive condensation reaction between two bi-functional monomers.
- These polymerisation reactions may result in the loss of some simple molecule of water, alcohol, HCl, CO_2 or NH_3 and leads to formation of high molecular mass condensation polymer.
- Such reactions do not depend on chain containing free radicals or ions.
- Depending on the types of monomers, the step growth polymers fall in the following two categories:-

— Category I:

- They are formed from a single bifunctional monomer having two different functional groups

New functional group of polymer.

$$X-(C)_n-Y + X-(C)_n-Y \xrightarrow{-XY} \underbrace{X-(C)_n-[A]-(C)_n-Y}_{\text{polymer}}$$

$$X \neq Y$$

— Category II:

- They are formed by two different bifunctional monomers and both the functional groups of the monomer being same.

New functional group of polymer.

$$X-(C)_n-X + Y-(C)_n-Y \xrightarrow{-XY} \underbrace{X-(C)_n-[A]-(C)_n-Y}_{\text{polymer}}$$

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→ Zeigler-Natta Polymerisation :→

- In 1953 Karl Zeigler and Guilio Natta discovered aluminium-titanium initiators, called Zeigler-Natta catalysts.
- These catatysts catalyse a smooth polymerisation of alkenes with the following advantages:-

(i) The polymerisation occurs under relatively milder conditions.

(ii) The polymerisation is stereospecific.

(iii) The polymer formed is linear with no branching.

- A Zeigler-Natta catalyst is a heterogeneous organometallic compound containing titanium and aluminium. It is made by treating $TiCl_4$ with Al_2Et_6 in heptane. This mixture is heated for about one hour.
- Besides the active catalyst the mixture also contains alkylated aluminium (Et_2AlCl) which acts as co-catalyst.
- The precise structure of active catalyst is not known but it contains partially alkylated titanium having "free coordination site" due to which it can form a complex with the both growing polymer chain and monomeric alkene.

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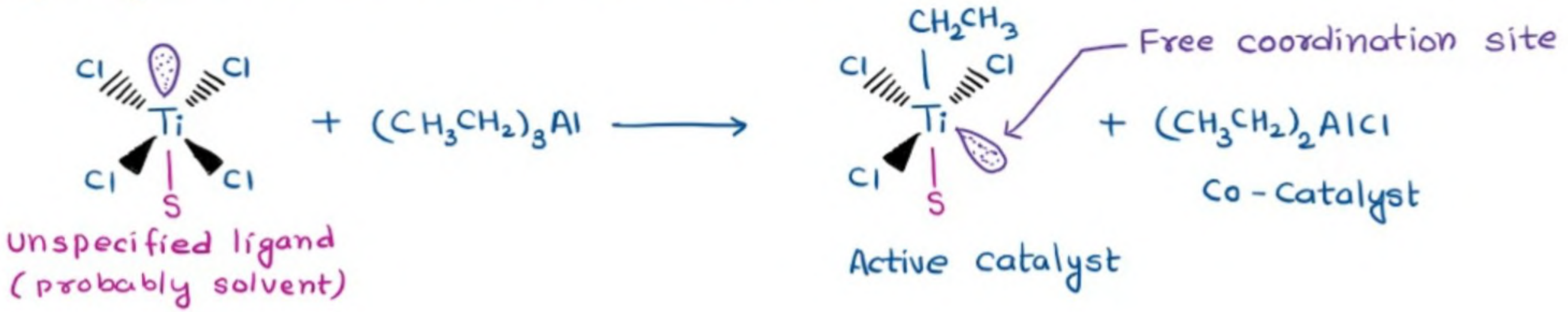
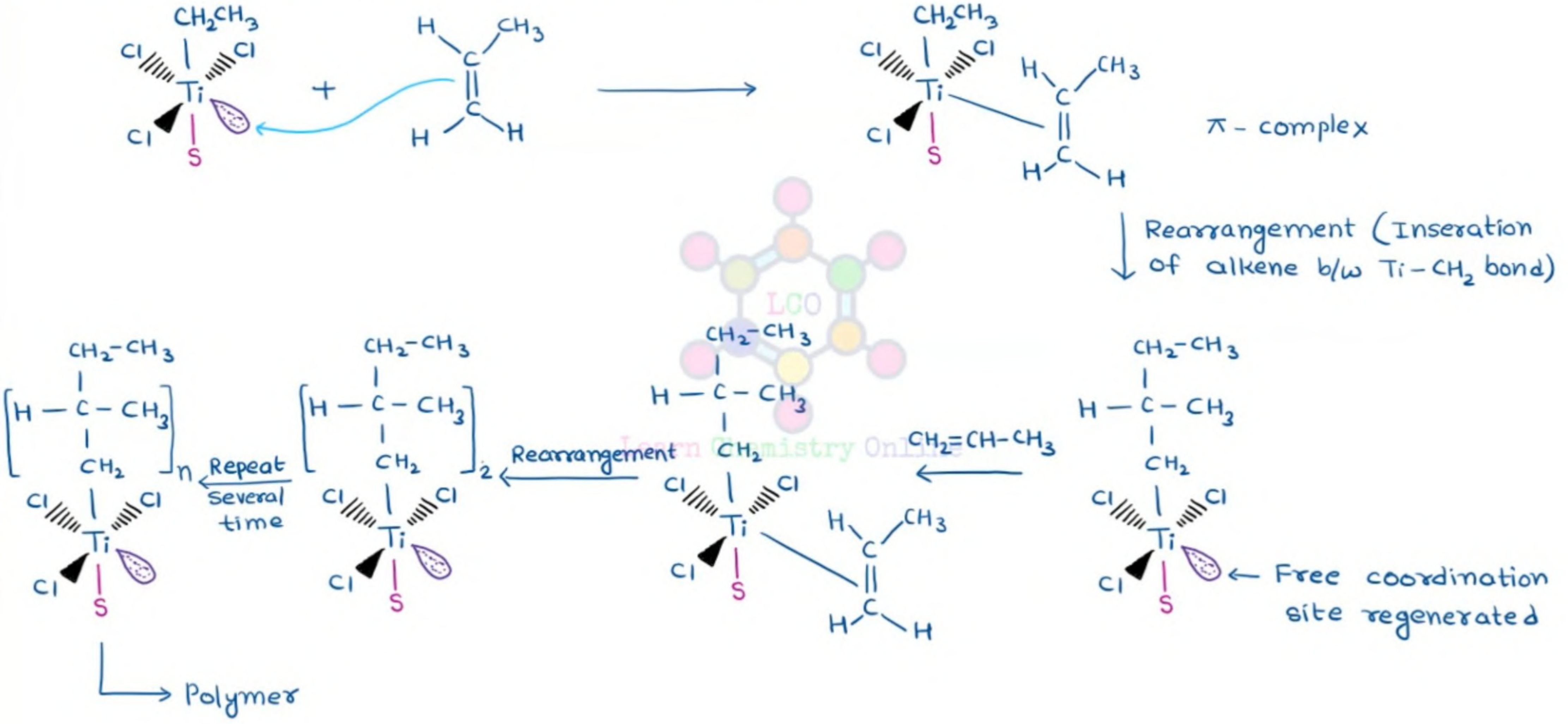


- The exact mechanism of Zeigler-Natta catalyst has not been fully worked out.
- Most probable mechanism is described below-



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→ Vinyl polymers :→

1. Polythene :→

- Polymerisation of ethylene (or ethene) gives rise to the following two types of polyethenes (polyethylenes) depending upon the reaction conditions and catalysts used. However, both have the same repeating unit.

(a) Low density polyethene :-

- This polymerisation involves free radical mechanism which is initiated by oxygen.

$$\underset{\text{Ethene}}{n\,CH_2=CH_2} \xrightarrow[\text{Trace of oxygen}]{473\text{ K},\ 150\text{ atm.}} \underset{\text{Low density polyethene}}{-\!\!\left(CH_2-CH_2\right)\!\!-_n}$$

- The polythene produced by this procedure has a molecular weight of approx. 20,000 and possesses a brached structure. Due to this branching the molecules of polythene do not pack closely and hence, the density of this type of polythenes is as low as 0·92 g/cm³.

→ Properties :-

- m.p. 384 K
- Transparent
- Moderate tensile strength & flexible
- chemically inert and a poor conductor of electricity.

→ Uses :→

- Manufacture of packing material and as insulating material for electrical wires and cables.

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(b) High density polyethene :→

- This polymerisation involves condensation polymerisation in the presence of Zieglar - Natta catalyst.

$$\underset{\text{Ethene}}{n\ CH_2=CH_2} \xrightarrow[(CH_3CH_2)_3Al\ +\ TiCl_4]{333-343K\ ,\ 6\text{-}7\ atm} \underset{\text{High density polythene}}{\left(CH_2-CH_2 \right)_n}$$

- The polymer so obtained consist of linear chains of polymer molecules. Thus, these molecules pack closely and hence, the density of this type of polyethene is as high as 0.95 gm/cm³.

→ Properties:-

- m.p. 403 K
- Translucent
- Chemically inert
- It has high toughness, hardness and tensile strength than the low density polythene.

→ Uses:-

- It is used in manufactre of buckets, tubes, house wares, pipes, bottles, toys etc.

2. Polystyrene or styron:-

$$n\ \underset{\substack{|\\C_6H_5}}{CH_2=CH} \xrightarrow{\text{Peroxide}} \left(CH_2-\underset{\substack{|\\C_6H_5}}{CH} \right)_n$$

styrene Polystyrene

- Uses:-

- Polystyrene is a transparent polymer and use for making plastic toys, household wares, telephone, radio and television bodies, refigerator linings etc.

3. Poly vinyl acetate (PVA).

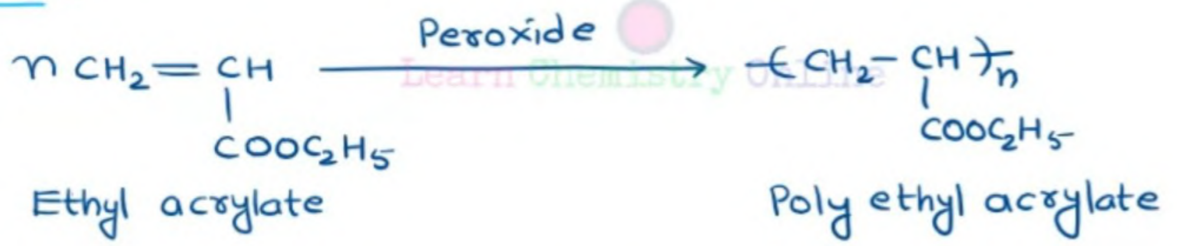
$$n\,CH_2{=}\underset{\displaystyle OCOCH_3}{\underset{|}{CH}} \xrightarrow{\text{Peroxide}} \left(CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}\right)_n$$

Vinyl acetate — Poly vinyl acetate

- Uses:-

- It is a soft rubber like polymer and is used for making plastic emulsion paints, adhesive and Grease proof paper.

4. Poly ethyl acrylate :→



$$n\,CH_2{=}\underset{\displaystyle COOC_2H_5}{\underset{|}{CH}} \xrightarrow{\text{Peroxide}} \left(CH_2-\underset{\displaystyle COOC_2H_5}{\underset{|}{CH}}\right)_n$$

Ethyl acrylate — Poly ethyl acrylate

- Uses:-

- It is a tough rubber like polymer and is used for making blankets, carpets and clothes.

5. Poly methyl methacrylate :→ (PMMA)

$$n\ CH_2=\underset{\displaystyle COOCH_3}{\underset{|}{C}}-CH_3 \xrightarrow{\text{Peroxide}} -\!\!\left(CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle COOCH_3}{\underset{|}{C}}}}\right)\!\!-_n$$

Methyl methacrylate   Poly methyl methacrylate

- Uses :-

- It is a tough rubber like polymer and is used for manufacture of blankets, carpets and clothes.

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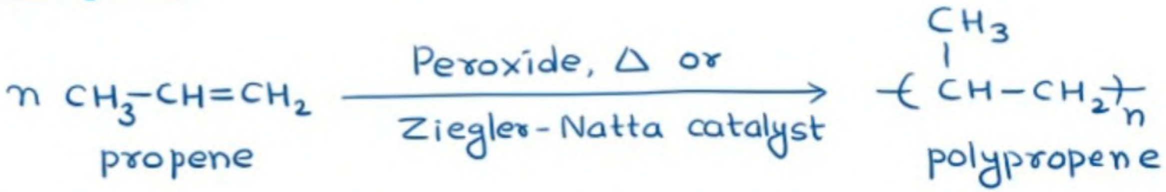
→ Vinyl polymers :→ (Part-2)

6. Polypropene or polypropylene :→



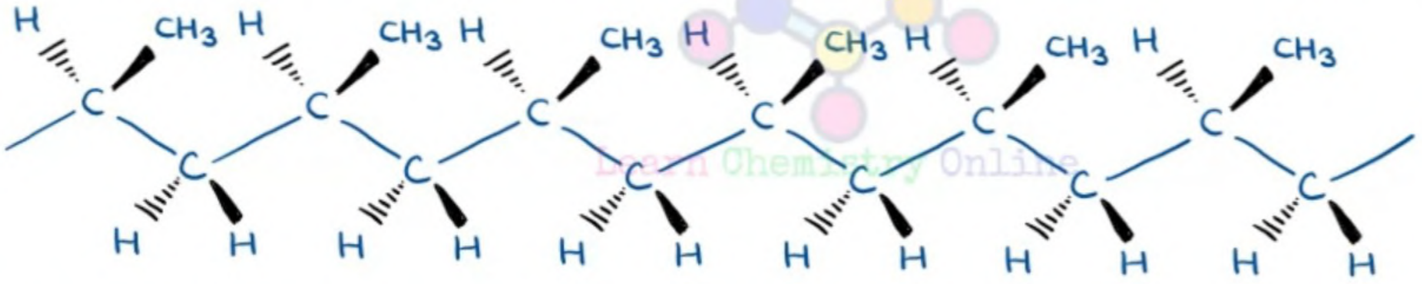
$$n\,CH_3-CH=CH_2 \xrightarrow[\text{Ziegler-Natta catalyst}]{\text{Peroxide, }\Delta\text{ or}} -\!\!\left(\overset{\overset{CH_3}{|}}{C}H-CH_2\right)\!\!-_n$$

propene → polypropene

- In the presence of Zieglar-Natta catalyst, three different stereochemical forms of polypropene are formed-

(a) Isotactic (Greek meaning "same order"):-

- In which all carbon atoms having a methyl group have identical configuration.



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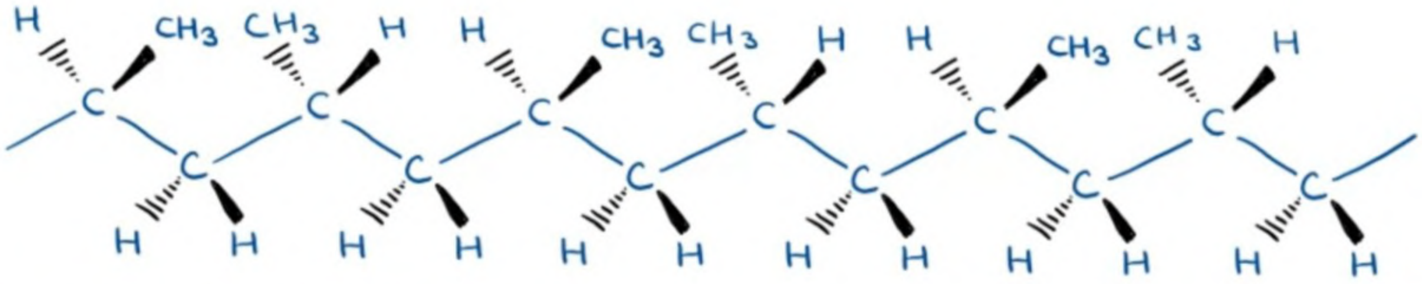
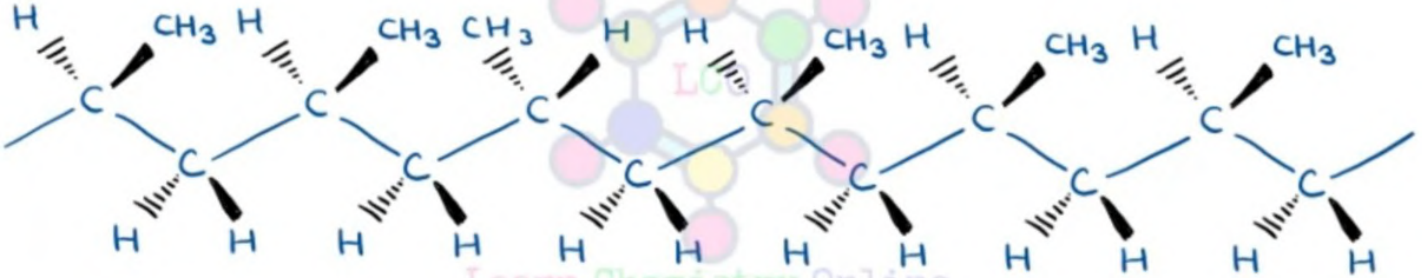
(b) Syndiotactic (Greek meaning "alternating order"):-

- In which the configuration of carbon atom having methyl group alternate regularly.



(c) Atactic (Greek meaning "no order") :-

- In which the random stereochemical distribution.



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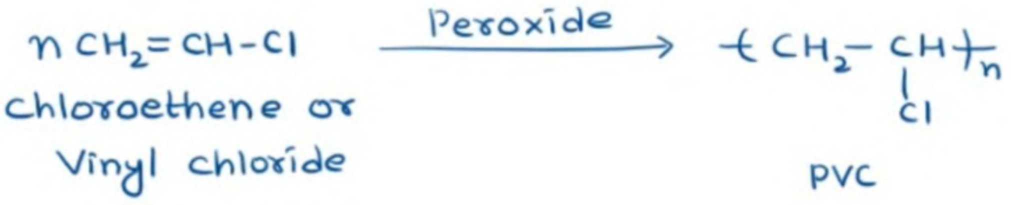
- Uses:-
- In the manufacture of stronger pipes and bottles.
- For making automobile mouldings, seat covers, carpets, ropes etc.
- For paking of foods and textiles
- For making liners of bags and heat shrinkable wraps for records and other articles.

7. Polyvinyl chloride:→ (PVC)



$$n\,CH_2=CH-Cl \xrightarrow{Peroxide} -\!\!\left(CH_2-\underset{\underset{Cl}{|}}{CH}\right)\!\!-_n$$

Chloroethene or Vinyl chloride

PVC

- Uses:-

- It has good flame resistance and electrical insulation and is used for coating wires, cables and other electrical goods.
- In making gramophone records and hose pipes.
- When mixed with high boiling esters such as di-n-butyl phthalote (plasticizer), it is used for making rain coats, hand bags, plastic dolls, shower curtains, upholestery, fabrics, shoe soles and viny flooring. Since, di-n-butylphthalate is slightly volatile, it evaporate slowly. As a result, soft plasticized vinyl polymer loses its plasticizer property and becomes hard and brittle.

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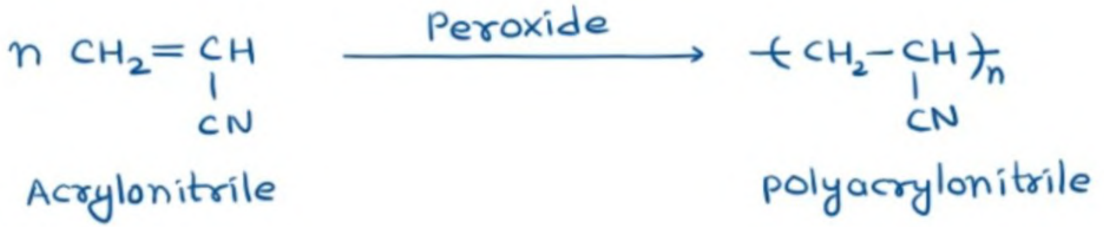
8. Polyacrylonitrile,(PAN):→



$$n\,\underset{\underset{CN}{|}}{CH_2=CH} \xrightarrow{Peroxide} -\!\!\left(CH_2-\underset{\underset{CN}{|}}{CH}\right)\!\!-_n$$

Acrylonitrile

polyacrylonitrile

- Uses:-

- It is tough and high melting polymer. If forms quick drying and water resistant fibre which is used for the manfacturing of Orlon and Acrilon fibres.
- These are used for making blankets, carpets and water proof clothes.
- The fibre can be knitted and can also blended with wool.

9. Polytetrafluoroethylene (PTFE):→

$$n\ CF_2 = CF_2 \xrightarrow{O_2} \left(CF_2 - CF_2 \right)_n$$

Tetrafluoroethylene Teflon (PTFE)

- Uses:→

- Teflon is a flexible polymer which is highly resistant to the action of acids (even boiling aqua regia), solvent and other chemicals. Therefore it is used for making pipes and surgical tubes.
- Because of its thermal stability (upto 598K) and resistance to chemicals, teflon is used for making nonstick utensil and electrical press.
- Teflon is also used for making gaskets, pump packing valves, seals, non-lubricated bearings, filter clothes etc.
- Teflon stopcocks are used in burettes and dropping funnels due to its resistance towards chemicals.

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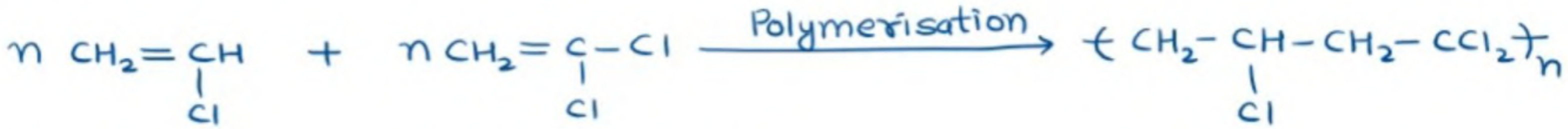
10. Saran:→

- Made by copolymerisation of vinyl chloride and Vinylidene chloride.



$$n\,CH_2=\underset{|\atop Cl}{CH} + n\,CH_2=\underset{|\atop Cl}{C}-Cl \xrightarrow{\text{Polymerisation}} \left(CH_2-\underset{|\atop Cl}{CH}-CH_2-CCl_2\right)_n$$

Vinyl chloride Vinylidene chloride Saran

Uses:-

- For making film for wrapping food and seat covers.

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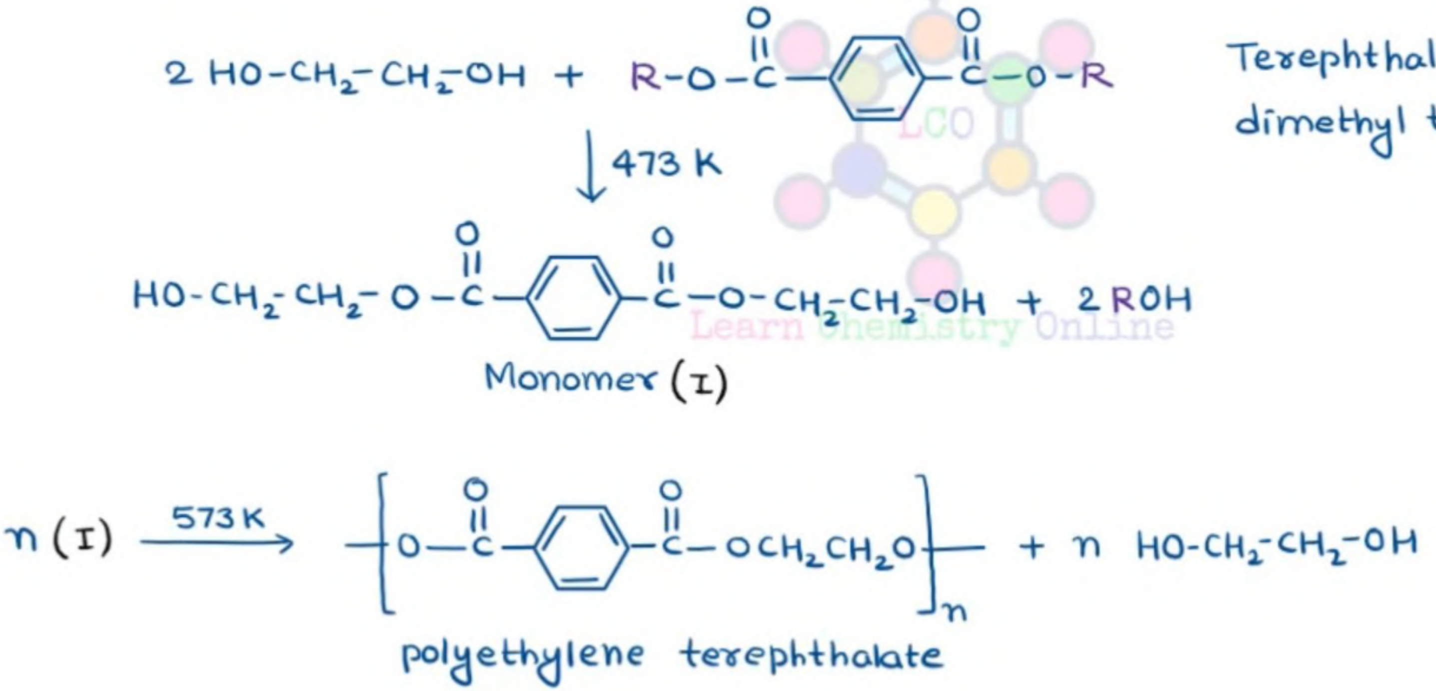
→ Polyesters:→

- Polyesters are the polymers having ester linkage and these are formed as a result of condensation reaction between polyols and polybasic acids.

(a) Poly ethylene terephthalate (PET, TERYLENE, DACRON, MYLAR):-

- It is prepared by the reaction of terephthalic acid/dimethyl terephthalate with ethylene glycol.
- The reaction takes place in two steps.



Terephthalic acid → R → H

dimethyl terephthalate → R → CH_3

→ Properties:→

- The polymer can be converted into fibre and is extensively used in the textile industry.
- The molecule of Dacron and all of the other fibre-forming materials are long, thin and thread like structure.
- There are strong intermolecular attractions which prevent the molecules from returning to random looping and coiling.
- In polyesters, this intermolecular force is provided by the presence of the polar carbonyl groups which lead to powerful dipole-dipole attractions.

– Uses:–

- Manfacturing of fabrics, tyre cords, seat belts and sails.
- Making MYLAR films used as magnetic recording tapes which are highly flexible, tear resistant and resistant to UV degradation.

(b) Poly ethylene phthalate, GLYPTAL or ALKYD RESIN :-

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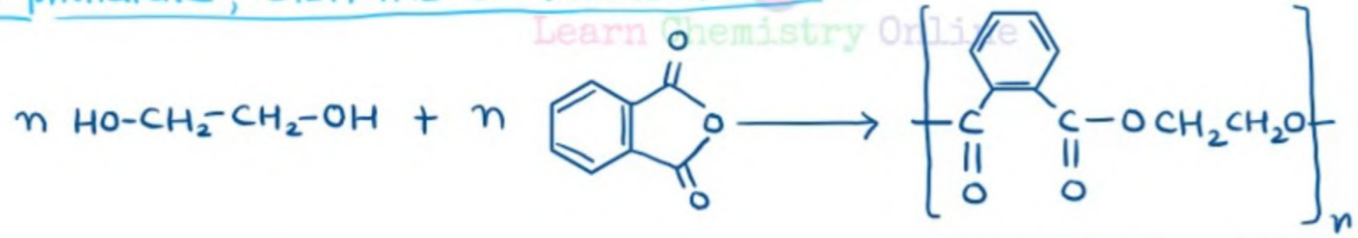


poly ethylene phthalate

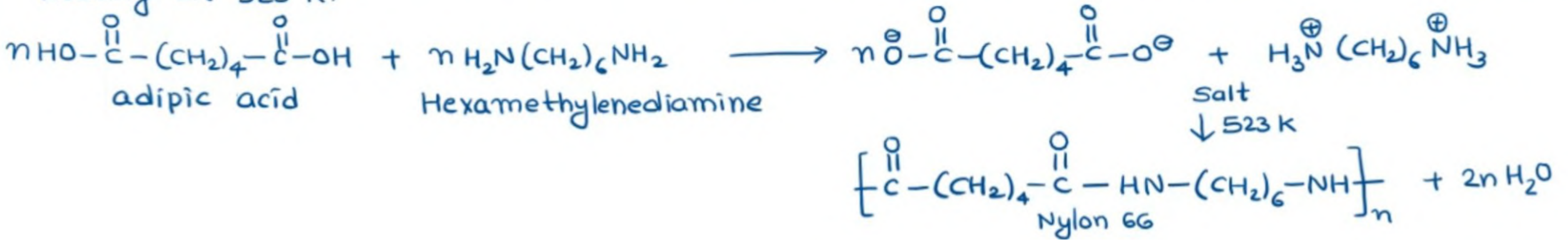
- It is a thermoplastic molding resin. It dissolves in suitable solvents and the solution on evaporation leaves a tough and non flexible material.
- Use:– Manufacutring of paints and lacquers.

→ Polyamides:→

- Polyamides are formed by the thermal decomposition of salt of diamines and dicarboxylic acids.
- The driving force for polymerisation is the elimination of water between an acid and an amine resulting in the formation of an amide linkage (–CO–NH–).
- These polymers are called Nylon (Ny → New York and lon → London) because the most common nylon polymer (nylon 66) was synthesized simultaneously in New York and London.
- Among polymers of this type, nylon 66 and nylon 6 are by far the most important products. System of numbering indicates from which type of monomers a particular nylon is made. For nylon 66, the first 6 stands for the number of carbon atoms in the amine and the second 6 for the number of carbon atom in the acid, whereas nylon 6 is made from one monomer containing six carbon atoms.

(a) Nylon 66 :→

- It is produced from hexamethylenediamine and adipic acid in two steps.
- The first step is the preparation and purification of the salt which is then polymerized by heating at 523 K.



$$\underset{\text{adipic acid}}{n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Hexamethylenediamine}}{n\,H_2N(CH_2)_6NH_2} \longrightarrow n\,\overset{\ominus}{O}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O^{\ominus} + \underset{\text{Salt}}{H_3\overset{\oplus}{N}(CH_2)_6\overset{\oplus}{N}H_3}$$

$$\downarrow 523\text{ K}$$

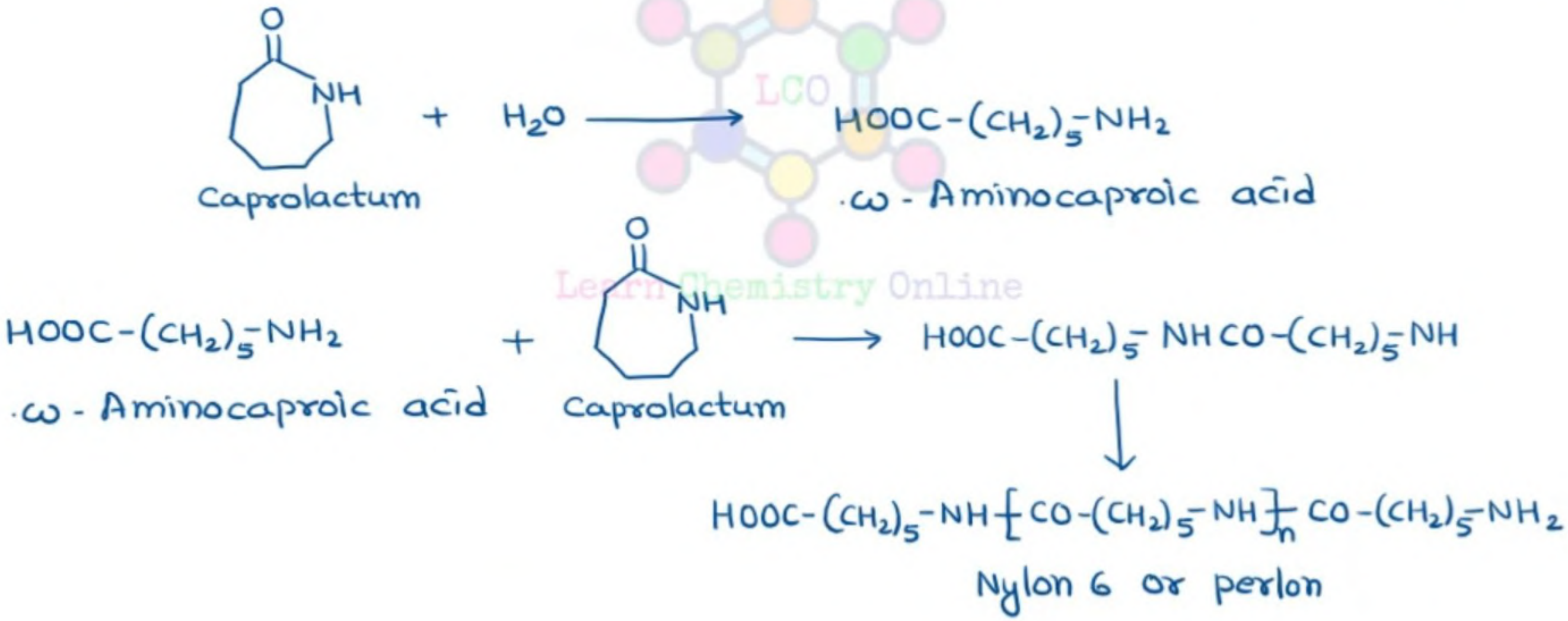
$$\underset{\text{Nylon 66}}{\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-HN-(CH_2)_6-NH\right]_n} + 2n\,H_2O$$

→ Uses:→

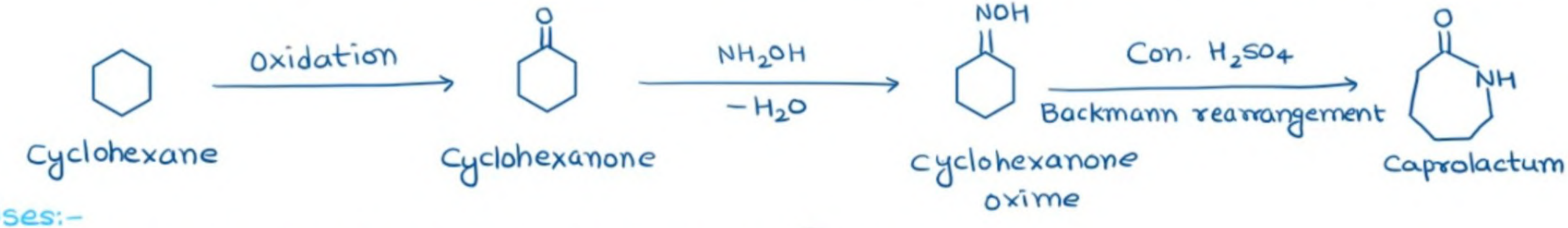
- Used as a fibre for fabrics, ropes, tyre cords as well as for molded products.
- Being tough enough it substitutes metal in bearing and gears.

(b) Nylon 6 or Perlon:→

- It is produced from caprolactum. The reaction is initiated by the hydrolysis of caprolactum to ω- aminocaproic acid whose amino group reacts with the other molecule of caprolactum and the continuation of the process results in the formation of a polymer of high mol-weight.



- Caprolactum required for this purpose is obtained from cyclohexane as shown below:-



→ Uses:-

- It is used in manfacturing of tyre cords and ropes.

✱ In nylon 66 and nylon 6, molecular chains are held together by intermolecular hydrogen bonding

(c) Nylon 610 :-

$$\underset{\text{Hexamethylenediamine}}{n\ H_2N-(CH_2)_6-NH_2} + \underset{\text{Sebacic acid}}{n\ HOOC-(CH_2)_8-COOH} \xrightarrow[-H_2O]{\Delta} \underset{\text{Nylon 610}}{\left[NH-(CH_2)_6-NH-CO-(CH_2)_8-CO\right]_n}$$

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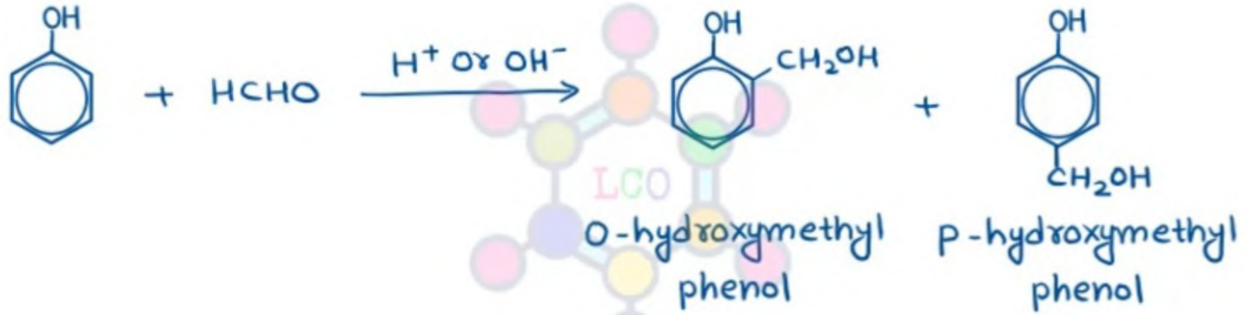
→ Phenol - formaldehyde resin: →

- Phenol and formaldehyde are used for the manufacturing of phenol-formaldehyde resin.
- Phenol and formaldehyde react to form o- and p- hydroxymethylphenol derivatives.
- lower ratio of formaldehyde to phenol gives low molecular weight branched polymer known as Novolak (Novolac) while molar ratio of formaldehyde to phenol of one or more gives three dimentional network polymer known as Bakelite.



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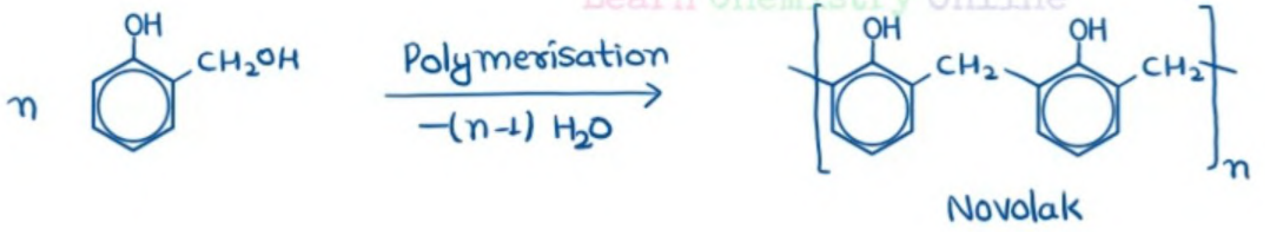
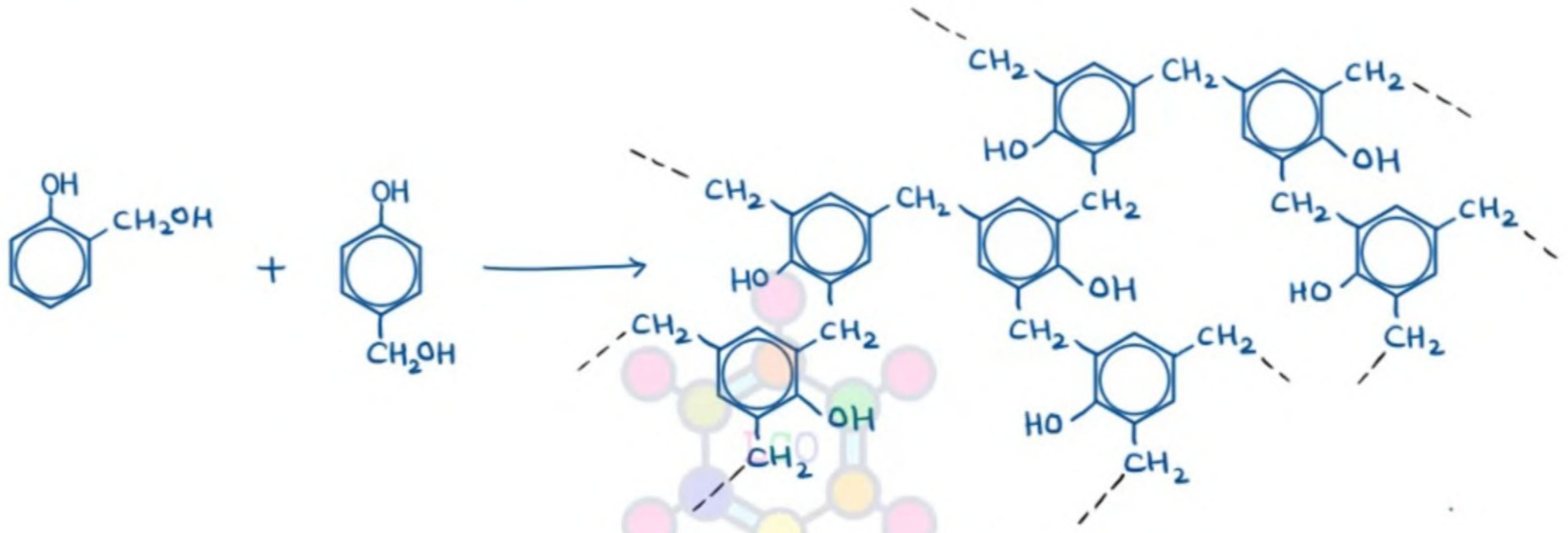


- Bakelite is a very useful thermosetting phenol-formaldehyde resin.



Bakelite

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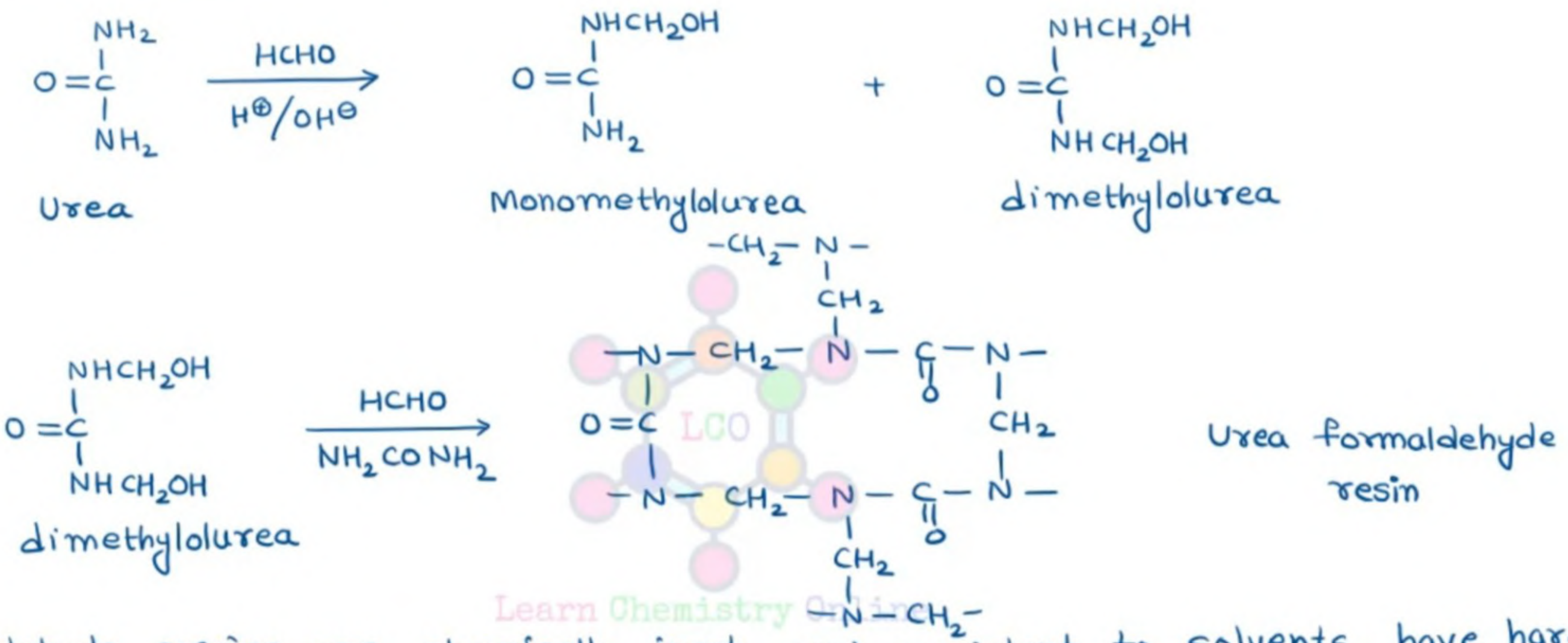
→ Uses:-

- Used for manufacture of electrical appliances such as electrical switches and plug due to its high electrical insulation.
- This polymer is water and scratch resistant and hence is used for the manufacture of combs, formica table-tops, fountain pen barrels, gramophone record etc.
- Sulphonated bakelite is used as ion exchanger.

→ Urea-formaldehyde resin:→



- Urea-formaldehyde resins are chemically inert and resistant to solvents, have hard surface and are thermosetting.
- These resins are superior to phenol-formaldehyde resins as they are colourless and do not discolour on exposure to light.

→ Uses:-

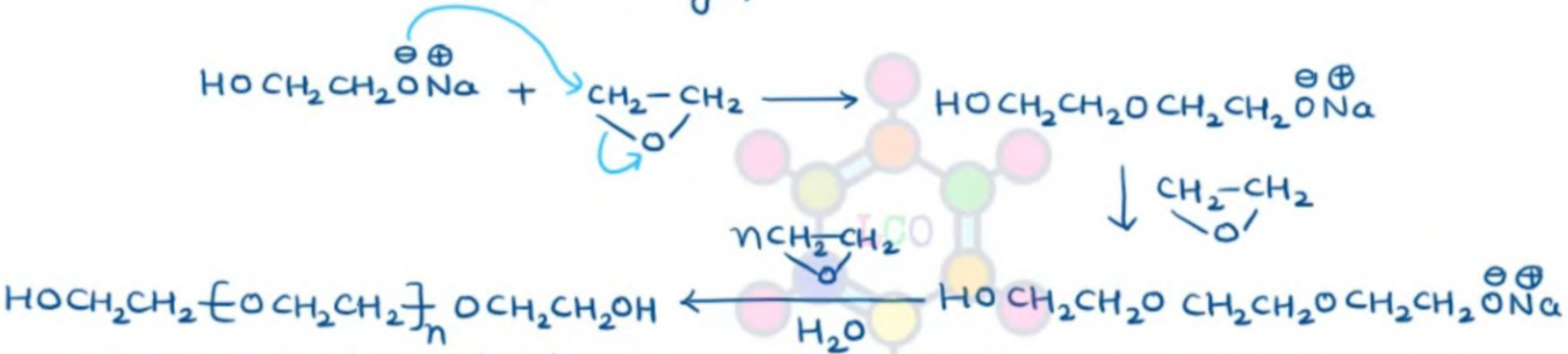
- In the manufacutring of kitchenware.
- In the manufacutring of laminates such as formica and as adhesive.
- In solution form, they are used to increase shrink-resistance of cotton and wood.

→ **Epoxy resin:→**

- 1,2-epoxides, such as ethylene oxide, are used as starting material for epoxy resin.

(i) **Poly oxyethylene glycols:→**

$$HOCH_2CH_2OH + \underset{\text{(as catalyst)}}{NaOH} \rightleftharpoons HOCH_2CH_2\overset{\ominus\oplus}{ONa} + H_2O$$



Poly oxyethylene glycol

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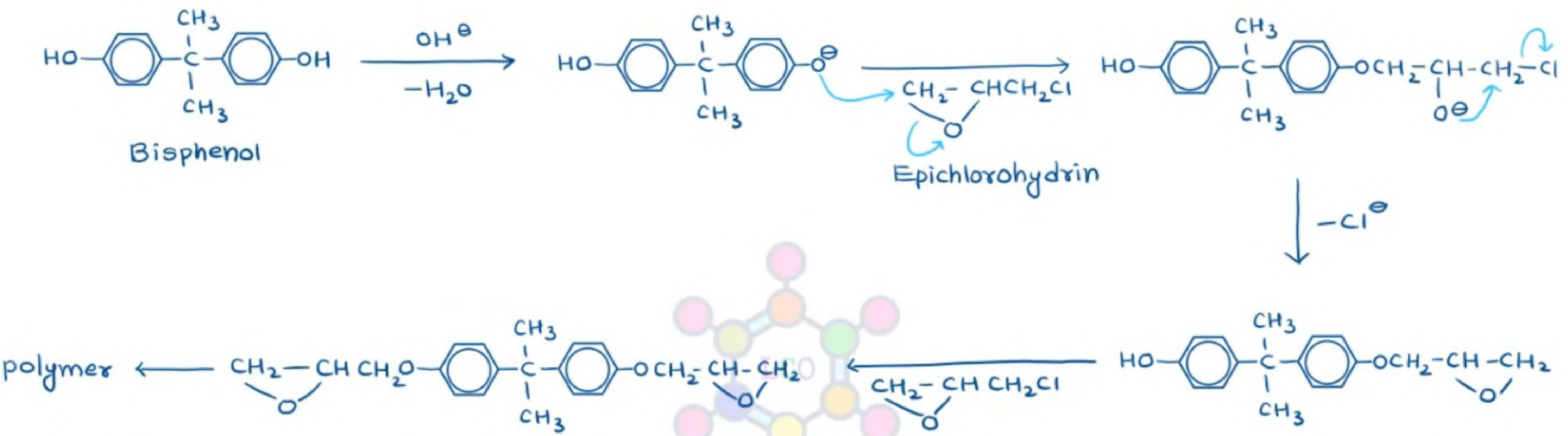
- **Uses:-**
- These are soluble in water and used in cosmetics, pharmaceutical and as lubricants.

(ii) **Epoxy resin:→**

- Most of the epoxy resins (thermosetting polymers) are made by the reaction of epichlorohydrin and bisphenol in the presence of base.



- Since there are two epoxy groups per molecule, further polymerisation initiated by both cationic and anionic initiators.

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- The low molecular mass linear polymer obtained above is converted into a cross-linked polymer by the action of a cross linking agent such as dimethylenetriamine. $(NH_2CH_2CH_2NH_2CH_2CH_2NH_2)$

- Uses:-

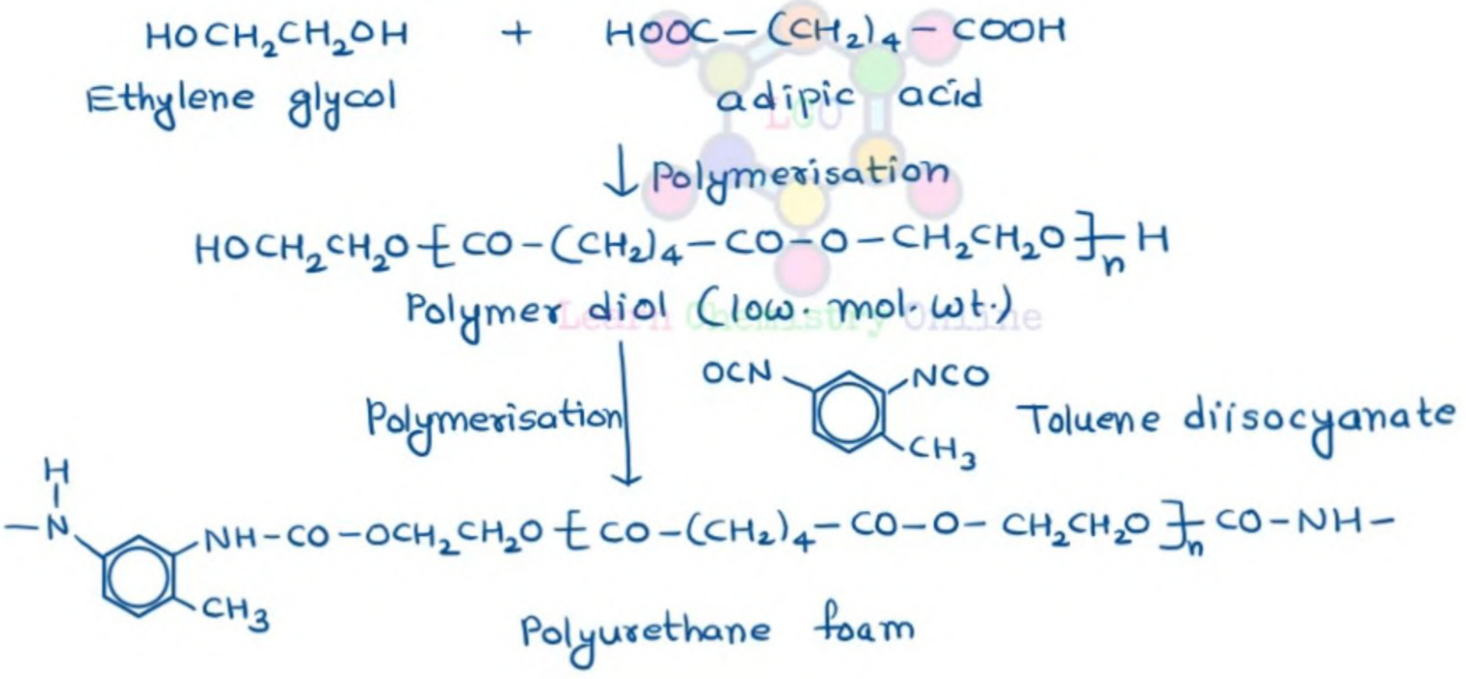
- Manufacturing of electrical equipments and in laminating materials and flooring.

→ Polyureathanes :→

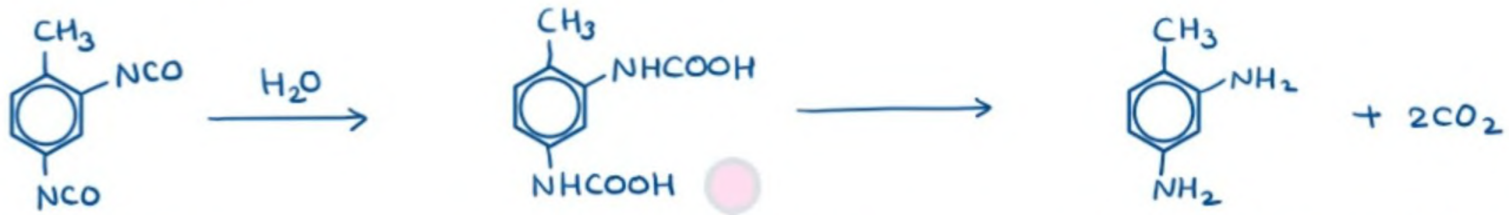
- Polyureathanes are obtained by treatment of diisocyanates with a wide variety of diols.
- The process is based on the fact that isocyanates react with substance containing active hydrogen (e.g. alcohol) to give Ureathanes.

$$\underset{\text{An isocyanate}}{R-N=C=O} + R'OH \longrightarrow \underset{\text{A Urethane}}{RNHCOOR'}$$

→ Synthesis :→



- Carbon dioxide is a foaming agent which is made available by the reaction of water with isocyanate group. The substituted carbamic acid, thus produced, immediately loses carbon dioxide to form primary amines.



diisocyanate Carbamic acid A primary amine

- There is further reaction of amino group with more isocyanate resulting in the formation of urea linkage.

$$-NH_2 + O=C=N- \longrightarrow -NH-CO-NH-$$

- Alternatively, the low boiling liquids such as freon-11 is used as foaming agent which is added to the reaction mixture. The heat of reaction vaporizes the volatile liquid producing bubbles which convert the viscous liquid polymer to frothy mass of polyureathane foam.
- Polyureathanes are long linear molecules without linkage interconnecting the individual strands.

→ Uses:→

- Manufacturing of flexible foams, foam fabrics, car seats etc.
- Used as surface coatings, fibres and insulating foams.

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→ Natural rubber :→

- Natural rubber is isolated from latex (a suspension of rubber particle in water) which is a white milky fluid exuding from the cuts made in the bark of South American rubber tree (*Hevea brasiliensis*).
- The term rubber was discovered by J. Priestley (the discoverer of oxygen) who found that the crude material was good for "rubbing" (erasing) the pencil marks. Later on, Mecintosh (scotland) found that the natural rubber being water proof can act as good coating on raincoats.
- chemically natural rubber is a polyterpenoid composed of isoprene (2-methyl-1,3-butadiene) molecules joined together in cis-1,4 fashion or head-to-tail fashion.

Natural rubber

Polyisoprene (cis-1,4-fashion)

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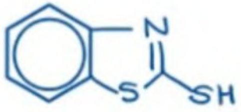
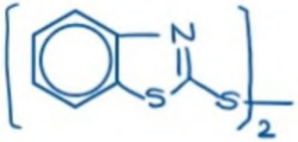
→ Vulcanisation of rubber:→

- Natural rubber is very soft and sticky at moderate temp. and hardens quickly to a brittle substance
- In 1839, Charles Goodyear found that if the the natural rubber is heated with sulphur, it attain greater toughness and elasticity campared to raw material. It does not soften at high temperatures. It remains elastic and flexible when cold. It also has resistance to heat, low water absorption tendency and resistance to organic solvents and oxidising agent. This process is called Vulcanisation.

- Vulcanisation is carried out in the presence of some vulcanisation accelerators such as 2-mercaptobenzothiazole and 2,2' – dithiobisbenzothiazole.

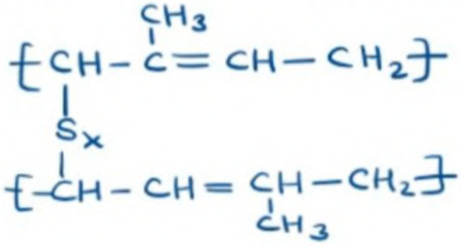


2-Mercaptobenzothiazole



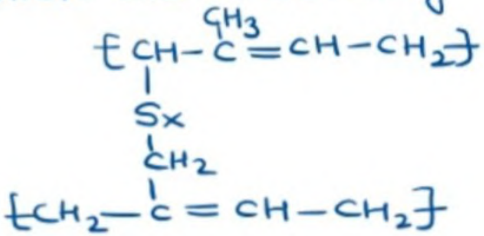
2,2'- Dithiobisbenzothiazole

- Vulcanisation causes cross-linking of the polyisoprene chains through –S–S– (disulphide) bond at carbon atoms adjacent to double bond.
- To make rubber more useful it is important to control the extent of cross-linking. Thus, 5% sulphur is used for making tyre rubber, 20-25% sulphur for making ebonite and 30% sulphur for making battery case rubber.
- Rubber is typical example of elastomeric polymer. The cis configuration of natural rubber does not allow the polymer chains to come closer enough for effective interactions. Thus, cis-polyisoprene does not have a straight chain but is coiled due to which it behave like spring. The molecules are long and thin and they become lined up when the material is stretched, but return back to original when the stretching force is removed.



$$\left[\underset{\substack{|\\ S_x \\ |}}{CH}-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right] \quad \left[-CH-CH=\underset{\substack{|\\CH_3}}{CH}-CH_2\right]$$

and/or



$$\left[\underset{\substack{|\\ S_x \\ |\\ CH_2}}{CH}-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right] \quad \left[CH_2-\overset{|}{C}=CH-CH_2\right]$$

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- Gutta-percha (Malaysian → getah → gum and parcha → tree) is a natural occuring isomer of rubber having all the double bonds in trans configuration.

Gutta-percha (trans-1,4-fashion)

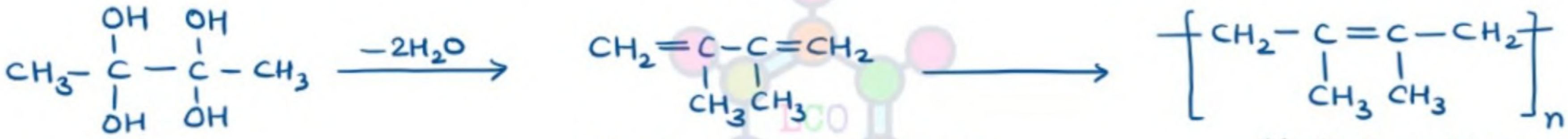
- It is also exuded by certain tree. It is harder and less elastomeric natural polymer compared to common rubber.
- It is used as a filling material for canals and also for casting golf balls.

→ Synthetic rubber:→

- Natural rubbers have limited properties. To improve the quality of rubber and to meet the ever increasing demand, a large variety of synthetic rubbers have been prepared.
- Synthetic rubbers are either homopolymers of 1,3-butadiene or its derivatives or copolymers in which one of the monomer is 1,3-butadiene.

(i) Methyl rubber:→

- First synthetic rubber, was produced by Germany during first world war.



$$CH_3-C(OH)_2-C(OH)_2-CH_3 \xrightarrow{-2H_2O} CH_2=C(CH_3)-C(CH_3)=CH_2 \longrightarrow \left[CH_2-C(CH_3)=C(CH_3)-CH_2\right]_n$$

Pinacol

2,3-dimethylbutadiene

Methyl rubber

(ii) Neoprene (Polychloroprene):→

$$CH_2=C(H)-C(Cl)=CH_2 \longrightarrow \left[CH_2-C(H)=C(Cl)-CH_2\right]_n$$

Chloroprene
(2-Chloro-1,3-butadiene)

Neoprene

- Neoprene is much more oil resistance than natural rubber. It is not oxidised by air.
- Used in making of hoses, shoe heels, stoppers, insulators and for printing rollers and conveyer belts.

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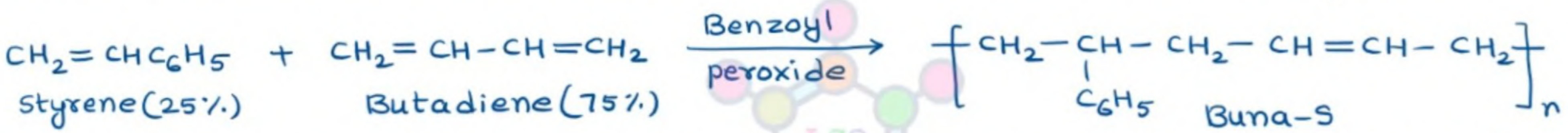
(iii) Buna-S (Styrene-butadiene rubber, SBR):→

- It is a copolymer of butadiene (75%) and styrene (25%) and is produced by free-radical polymerisation.
- It is called Buna-S (Bu → Butadiene, Na → Natrium, S → styrene) because it was originally prepared by anionic polymerisation of butadiene with styrene in the presence of sodium.
- Due to presence of double bonds, its properties can be improved by vulcanisation.



$$\underset{\text{Styrene}(25\%)}{CH_2=CHC_6H_5} + \underset{\text{Butadiene}(75\%)}{CH_2=CH-CH=CH_2} \xrightarrow[\text{peroxide}]{\text{Benzoyl}} \underset{\text{Buna-S}}{\left[CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-CH=CH-CH_2\right]_n}$$

- SBR prepared at 255-278 K is known as cold rubber while that produced at higher temperature is called regular SBR.
- Buna-S possesses high abrasion resistance, high load bearing capacity and more toughness than natural rubber.
- Used in making light duty tyres, floor tiles, footwear components and cable insulators.

(iv) Buna-N (Nitrile rubber):→

- It is a copolymer of butadiene and acrylonitrile and is produced by free-radical polymerisation.
- It properties like abrasion and mechanical strength can be improved by vulcanisation.
- Used in making oil seals, hoses and tank lining.

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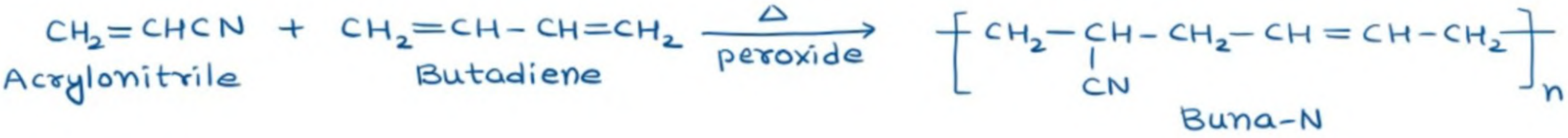
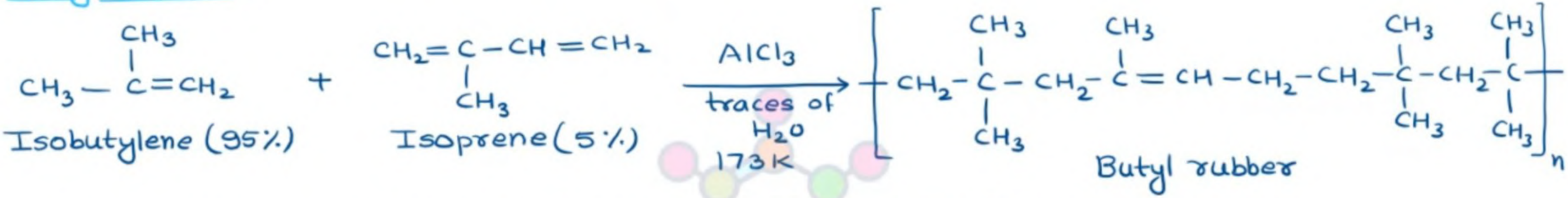


$$\underset{\text{Acrylonitrile}}{CH_2{=}CHCN} + \underset{\text{Butadiene}}{CH_2{=}CH-CH{=}CH_2} \xrightarrow[\text{peroxide}]{\Delta} \underset{\text{Buna-N}}{\left[CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2-CH{=}CH-CH_2 \right]_n}$$

(v) Butyl rubber:→



$$\underset{\text{Isobutylene (95\%)}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2} + \underset{\text{Isoprene(5\%)}}{CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-CH{=}CH_2} \xrightarrow[\substack{\text{traces of}\\ H_2O \\ 173\,K}]{AlCl_3} \underset{\text{Butyl rubber}}{\left[CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-CH_2-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} \right]_n}$$

- Used in making automobile inner tubes and tyre liners.

(vi) cis- Polybutadiene:→

- It has properties similar to those of natural rubber and is obtained by Ziegler-Natta polymerisation of butadiene.

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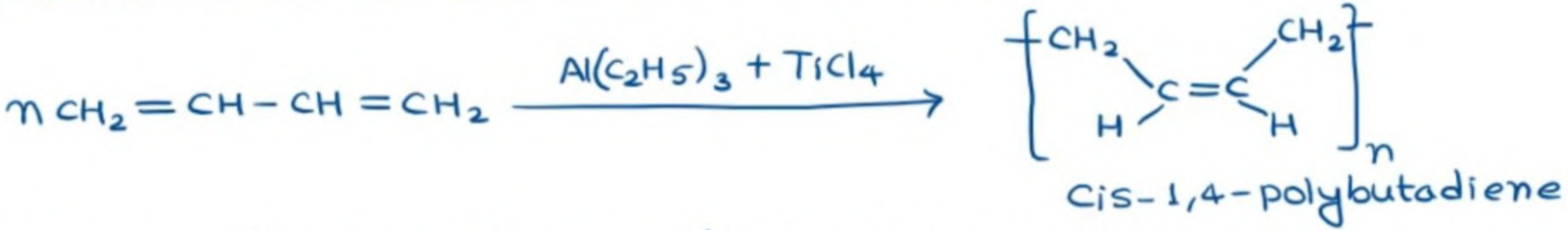

$$n\,CH_2{=}CH-CH{=}CH_2 \xrightarrow{Al(C_2H_5)_3 + TiCl_4}$$

Cis-1,4-polybutadiene

- In the same way all cis polyisoprene (isotactic) can be prepared.