through a series of independent [illegible]. Each such reaction involves the condensation (bond formation) between two difunctional monomer molecules to produce dimers which, in turn, produce tetramers and so on with the loss of simple molecules like H_2O, NH_3, HCl etc. These molecules of moderate size then combine together to form the polymer. Since in this process, *the polymer is formed in a stepwise manner, it is called step-growth polymer and the process is called step-growth polymerization.*

It may be pointed out here that in contrast to chain growth polymers, the formation of step-growth polymers does not occur through chain reactions involving free radicals, carbanions or carbocations as reactive chemical species.

Some important condensation polymers, their preparation and uses are discussed below :

I. Polyesters. *Polymers which have ester linkages are called polyesters and are prepared by the condensation polymerization of diacids with diols.* Two important polyester polymers are discussed below :

1. Terylene or Dacron. It is prepared by condensation polymerization of ethylene glycol and terephthalic acid with elimination of water. The reaction is carried out at about 420 – 460 K in presence of a catalyst consisting of a mixture of zinc acetate and antimony trioxide.

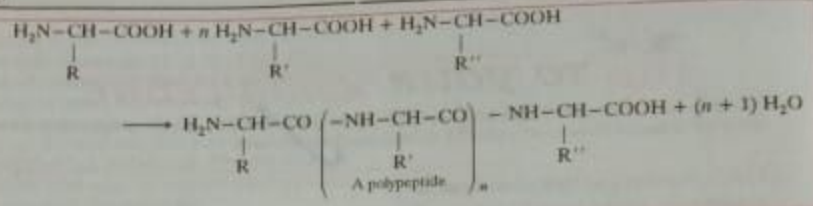
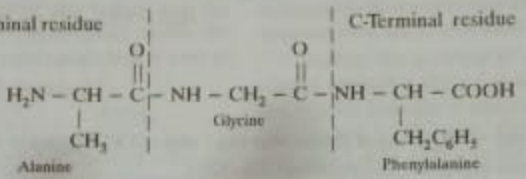


FIGURE 17.15. Formation of a polypeptide.

It is clear from the above structure that each polypeptide chain has a free amino group at one end and a free carboxyl group at the other end. These are collectively called as *end groups*. The amino acid unit having the free $-NH_2$ group is called the **N-terminal end** whereas the amino acid unit having the free $-COOH$ group is called the **C-terminal end**.

Writing and nomenclature of polypeptides As a matter of convenion, the structures of polypeptides are written in such a way that amino acid with the free amino ($-NH_2$) group is written on the left hand side of the polypeptide chain while the amino acid with the free carboxyl (–COOH) group is written in the right hand side of the cfhain. Thus a tripeptide, *alanylglycylphenylalanine* (Al-Gly-Phe) is represented as follows :



Ala – Gly – Phe or A – G – F

The name of any polypeptides is written starting from the N- terminal residue. While writing the name, the suffix *ine* in the name of the amino acid is replaced by *yl* (e.g., glycyl for glycine and alanyl for alanine etc.) for all the constituent α-amino acids except the C-terminal residue. This nomenclature is usually not used. Instead the three letter abbreviations or one letter codes for the various α-amino acids present in the chain is used. For example, the above tripeptide is named as Ala-Gly-Phe or A – G – F.

ADD TO YOUR KNOWLEDGE

1. The most widely used method for determining the **N-terminal amino acid residue** in a protein or a polypeptide molecule is called the **DNP-method or Sanger's method.** During this method, the polypeptide is treated with 1-fluoro-2, 4-dinitrobenzene (also called the **Sanger's reagent**) in presence of $NaHCO_3$ when the corresponding 2, 4-dinitrophenyl (**DNP**) derivative is formed. This upon hydrolysis gives a DNP-amino acid and a mixture of free amino acids. By identifying the DNP-amino acid, the N-terminal amino acid residue of a protein or a polypeptide can be determined.
2. The most widely used method for determining the **C-terminal amino acid** residue in a protein or a polypeptide is **hydrazinolysis.** In this method, the polypeptide is treated with anhydrous hydrazine at 373 K when all amino acid residues except the C-terminal one is converted into amino-acid hydrazides ($H_2NCHRCONHNH_2$). The mixture of products thus obtained is subjected to chromatography over a column of strong cation exchange resin. On elution, the strongly basic hydrazides are retained, but the free amino acid is eluted. By identifying the free amino acid, the C-terminal amino acid residue of a protein or a polypeptide can be determined.

(*ii*) It is a good electrical insulator and hence is used for coating wires, cables and other electrical goods.

(*iii*) It is also used in making gramophone records and hose pipes.

2. Polytetrafluoroethylene (PTFE) or Teflon

Starting material. Tetrafluoroethylene ($F_2C = CF_2$).

Reaction. In presence of oxygen, tetrafluoroethylene polymerises to give polytetrafluoroethylene called *teflon*.

$$\underset{\text{Tetrafluoroethylene}}{n\ CF_2=CF_2} \xrightarrow{O_2} \underset{\text{Polytetrafluoroethylene or Teflon}}{+(CF_2-CF_2)+_n}$$

Uses. Teflon is flexible and inert to solvents and to boiling acids even to *aqua regia* and is stable upto 598 K.

(*i*) Because of its great chemical inertness and high thermal stability, teflon is used for making *non-stick utensils*. For this purpose, a thin layer of teflon is coated on the inner side of the vessel.

(*iii*) It is also used for making gaskets, pump packings, valves, seals, non-lubricated bearings, filter cloth etc.

3. Polymonoc

Starting n

ethylene (ClFC =

Reaction. N

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ethylene.

$n\ ClFC = C$

Monochloro trifluoroethyl

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FOLLOW-UP CONCEPTUAL QU

Q. 1. Free radical polymerization of styrene gives a product in which phenyl rather than on adjacent carbon atoms. Explain.

Ans. During free radical polymerization, the addition of free radicals to mon with **Markovnikov's rule** so as to give more stable free radical. For exa radical initiator) to styrene gives more stable benzylic radical (I) rather

$$\dot{R} + CH_2=CH_2 \longrightarrow \underset{\text{I}}{R-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{\dot{C}H}}} \text{ (More s}$$

$$\dot{R} + CH_2=CH_2 \longrightarrow \underset{\text{II}}{R-CH-\underset{\displaystyle C_6H_5}{\underset{|}{\dot{C}H_2}}} \text{ (Less st}$$

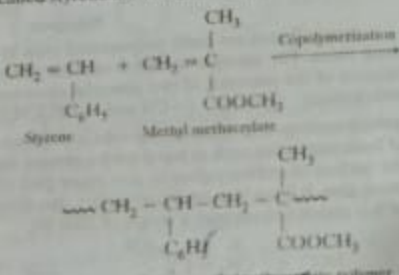
The free radical (I) then adds to another monomer molecule again giv than the less stable free radical (IV). This process continues to ultim C_6H_5 groups are on alternate carbon atoms rather than the product adjacent carbon atoms.

styrene etc. can be polymerized under anionic conditions although free radical polymerization is commercially preferred.

16.5 Copolymerization

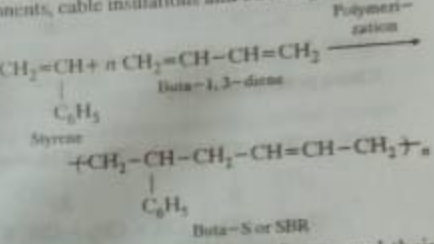
When two or more different monomers are allowed to polymerize together, the product formed is called a **copolymer** *and the process is called copolymerization.*

Thus a copolymer contains a number of units of each monomer used in the same polymeric chain. For example, the polymerization of a mixture of styrene and methyl methacrylate gives a copolymer called styrene methacrylate copolymer.



In general, the composition of the copolymer depends not only upon the proportion of the monomers but also upon their relative reactivity. *Some monomers as such do not polymerize at all but undergo copolymerization.* For example, maleic anhydride does not polymerize as such but undergoes copolymerization with styrene in a highly symmetrical manner to form styrene maleic anhydride copolymer.

The properties of copolymers are usually quite different from those of homopolymers derived from each of the combining monomers. Actually, copolymers have better physical and mechanical properties. Copolymerization is similar to alloying in metallurgy. Just like alloys, various copolymers can be synthesized having desired properties. For example, polystyrene, a homopolymer of styrene, is a good electrical insulator and can be moulded into toys, combs, radio and television parts. However, when styrene is copolymerized with 1, 3-butadiene in 1 : 3 ratio, a copolymer called Buna-S or SBR (sytrene-butadiene rubber) is obtained. It is very tough and is a good substitute for natural rubber. It possesses high abrasion resistance, high load bearing capacity and is used for the manufacture of auto tyres. It is also used for making floor tiles, footwear components, cable insulations and bubble gums.



Some other important copolymers and their uses are given in Table 16.1.

TABLE 16.1. Some common copolymers and their uses :

	Monomer name	Formula	Common name of the polymer	Uses
1.	Vinyl chloride and vinylidene chloride	$CH_2=CHCl$ $CH_2=CCl_2$	Saran	Food wrapping, fibres
2.	Styrene (25%) and butadiene (75%)	$CH_2=CHC_6H_5$ $CH_2=CH-CH=CH_2$	SBR	Tyres
3.	Acrylonitrile and butadiene	$CH_2=CHCN$ $CH_2=CH-CH=CH_2$	Nitrile rubber	Latex, adhesives, gasoline hoses
4.	Isobutylene and isoprene	$H_2C=C(CH_3)_2$ $H_2C=C(CH_3)-CH=CH_2$	Butyl rubber	Inner tubes
5.	Acrylonitrile, butadiene and styrene	$H_2C=CH-CN$ $H_2C=CH-CH=CH_2$ $H_2C=CHC_6H_5$	ABS plastic	A strong tough and resilient material used for making bumpers, crash helmets and other articles that must withstand heavy impacts.

nt polymer.
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and excellent light
even better than that

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ers, light shades,
nes and skylights,
coatings, dentures

Ethyl acrylate

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oxides

$$\left[\begin{array}{l}CH_2-CH\\ \quad\quad|\\ \quad\quad COOC_2H_5\end{array}\right]_n$$

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N)

1. Acrylonitrile

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polyacrylonitrile.

des

$$\left[\begin{array}{l}CH_2-CH\\ \quad\quad|\\ \quad\quad CN\end{array}\right]_n$$

Polyacrylonitrile

trile is itself manufac-
HCN to acetylene in
atalyst or by passing a
nonia and air over a
re of oxides of molyb-
m at 723 K.

$$\xrightarrow{-HCl} CH_2=CH-CN$$

Acrylonitrile

$$2\,CH_3CH=CH_2 + 3\,O_2 + 2\,NH_3$$

Propylene (From air)

$$\xrightarrow[\text{Mo, Co and Al, 723 K}]{\text{Oxides of}} 2\,CH_2=CH-CN + 6H_2O$$

Acrylonitrile

Uses. Polyacrylonitrile is a hard, horny and high melting material.

(*i*) It is used in the manufacture of *Orlon* and *Acrilan* fibres which are used for making clothes, carpets and blankets.

(*ii*) It is also used in the preparation of other polymers to improve their qualities.

III. Polyhalo-olefins. This class has the following three important polymers.

1. Polyvinyl chloride (PVC)

Starting material. Vinyl chloride ($CH_2=CH-Cl$).

Reaction. In presence of peroxides, vinyl chloride polymerises to form polyvinyl chloride.

$$n\,CH_2=\underset{\displaystyle Cl}{\underset{|}{CH}} \xrightarrow{\text{Peroxides}}$$

Vinyl chloride

$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

or $\left[\begin{array}{l}CH_2-CH\\ \quad\quad|\\ \quad\quad Cl\end{array}\right]_n$

Polyvinyl chloride

The monomer vinyl chloride is itself manufactured either by the addition of HCl to acetylene in presence of mercury salts as catalyst or by dehydrochlorination of ethylene dichloride.

$$\underset{\text{Acetylene}}{CH\equiv CH} + HCl \xrightarrow{Hg^{2+}} \underset{\text{Vinyl chloride}}{CH_2=CH-Cl}$$

$$\underset{\text{Ethylene dichloride}}{CH_2Cl-CH_2Cl} \xrightarrow{873-923\ K} \underset{\text{Vinyl chloride}}{CH_2=CH-Cl} + HCl$$

Uses. It is a pliable (easily moulded) polymer and thus has very wide range of applications. For example,

(*i*) When plasticized with high boiling esters such as di-*n*-butylphthalate, it is used for making raincoats, hand bags, plastic dolls, shower curtains, upholstery fabrics, shoe soles and vinyl flooring. Since dibutylphthalate is slightly volatile, it evaporates slowly. As a result, soft plasticized vinyl polymer eventually loses its plasticizer and becomes hard and brittle.

Types of copolymers. Depending upon the distribution of monomer units, the following types of copolymers are possible.

1. Random copolymer. If the *the monomer units have random distribution throughout the chain*, it *is called random copolymer.* For example, if the monomer A and monomer B undergo copolymerization, then the structure of the random copolymer is

$$n\,A + n\,B \longrightarrow -A-A-B-A-B-B-A-B-A-A-A-B-$$

Segment of random copolymer

2. Alternating copolymer. If the two monomer units occur *alternately throughout the polymer chain, it is said to be alternating copolymer.* For example,

$$n\,A + n\,B \longrightarrow A-B-A-B-A-B-A-B-$$

Segment of alternating copolymer

The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

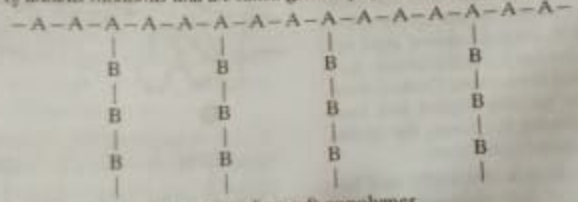
3. Block copolymer. *Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers. For example,*

$$-B-B-A-A-A-A-A-A-A-A- \qquad -B-B-B-B-B-B-B-B-A-A-$$

Segment of a block polymer

Block copolymers can be prepared by initiating the radical polymerization of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

4. Graft copolymer. *Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called* **graft copolymers.** For example,



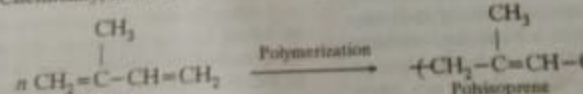
Segment of a graft copolymer

Graft copolymers are prepared by γ-irradiation of a homopolymer chain in the presence of a second monomer. The high energy radiations knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerization of the second monomer.

16.6 Natural Rubber

It is a natural polymer. It has remarkable elasticity and undergoes long range reversible extension even under relatively small applied force. It is manufactured from latex which is a colloidal solution of rubber particles in water. Latex is obtained by making incisions in the bark of rubber trees found is tropical and semitropical countries such as Southern India (Kerala, Tamil Nadu, Karnatka etc.) Indonesia, Malayasia, Sri lanka, South America etc.

Structure. Chemically, natural rubber is a 1, 4-polymer of isoprene (*i.e.* 2-methyl-1, 3-butadiene)



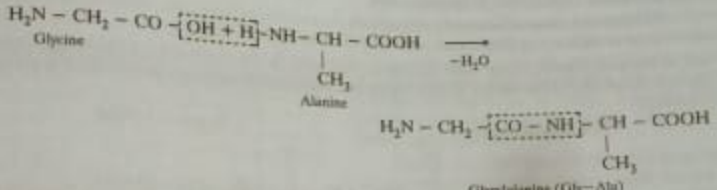
ADD TO YOUR KNOWLEDGE

All amino acids on treatment with ninhydrin (2, 2-dihydroxyindane-1, 3-dione) give purple colouration. This test is called **ninhydrin test** and is used for the detection of amino acids.

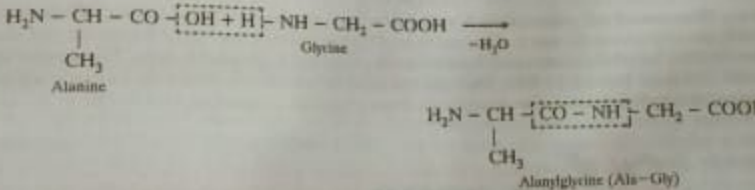
17.5.7. Peptides and their Classification.

Peptides are amides formed by the condensation of amino group of one α-amino acid with the carboxyl group of another molecule of the same or different α-amino acid with the elimination of a molecule of water. They are classified as *di-*, *tri-*, *tetra-*, *pentapeptides* etc. according as two, three, four, five etc. molecules of the same or different amino acids combine together.

For example, when –COOH group of glycine combines with the NH_2 group of alanine, we get the dipeptide, glycylalanine.



Alternatively, the $-NH_2$ group of glycine may react with –COOH group of alanine resulting in the formation of a different dipeptide, alanylglycine (Ala - Gly).



The $-\overset{O}{\overset{\|}{C}}-NH-$ *bond is called the* **peptide bond** or the *peptide linkage*.

In both the dipeptides, *i.e.*, glycylalanine and alanylglycine, there is a free amino group at one end and a free carboxyl group at the other end. These groups can further react with appropriate functional groups of other α-amino acids to form tri-, tetra-, pentapeptides etc.

17.5.8. Polypeptides

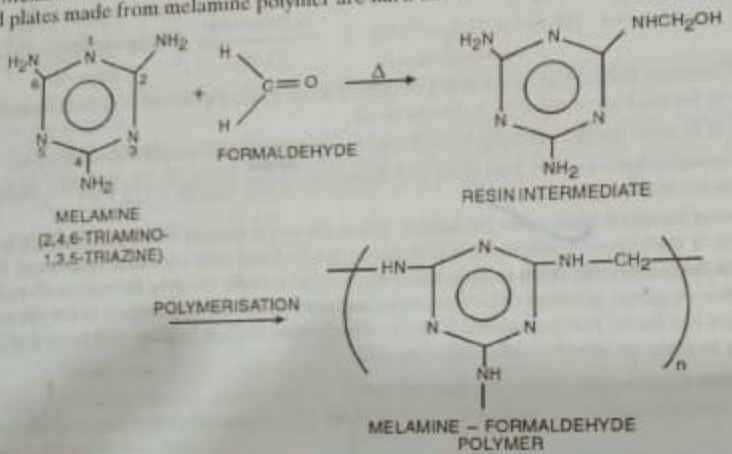
If a large number (hundreds to thousands) of α-amino acids are joined by peptide bonds, the polyamide thus formed is called a **polypeptide** Fig. 17.15.

Uses. Soft bakelites with low degree of polymerization are used as binding glue for laminated wooden planks, and in varnishes and lacquers. High degree polymerization leads to the formation of a hard bakelite which is highly cross-linked and is a *thermosetting polymer*. It is a scratch and water resistant polymer and hence is used for the manufacture of combs, formica table-tops, fountain pen barrels, gramophone records etc. It also possesses excellent electrical insulating properties and hence is widely used in making electrical goods (switches, plugs etc.). Sulphonated bakelites are used as ion exchange resins.

2. Melamine-formaldehyde resin. Melamine and formaldehyde undergo copolymerization to form melamine-formaldehyde resin.

Reaction :

Uses. Melamine-formaldehyde copolymer is widely used for making non-breakable plastic crockery *i.e.* cups and plates made from melamine polymer are hard and do not break on being dropped.



16.9 Molecular Mass of Polymers

During the process of synthesis of polymers, the degree of polymerization or the length of the polymer chain depends upon the availability of monomer molecules near the growing polymer chain. Since the number of monomer molecules differs from one place to another in the reaction mixture, therefore, a particular sample of a synthetic polymer contains a number of species of varying chain lengths. *Since each species has a different molecular mass and a given sample of a polymer contains a number of such species, therefore, the polymer as a whole has an average molecular mass. In contrast, natural polymers such as proteins, contain chains of identical length and hence have definite molecular masses.*

Types of average molecular mass. There are two types of average molecular masses of polymers, *i.e.*

(*i*) Number average molecular mass ($\overline{M}n$)

(*ii*) Weight average molecular mass ($\overline{M}w$)

(i) Number average molecular mass ($\overline{M}n$)

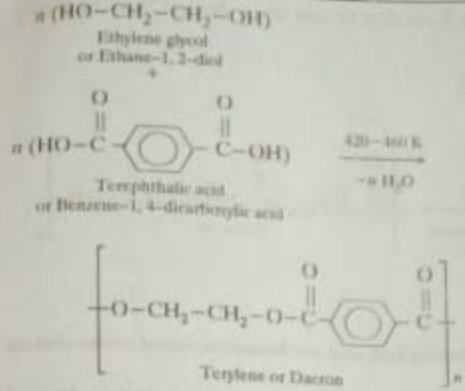
If N_1, N_2, N_3..... are the number of macromolecules with molecular masses M_1, M_2, M_3..... respectively then the number average molecular mass of the polymer is given by

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 .....}$$

$$= \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where N_i is the number of macromolecules of *i*th type with molecular mass M_i.

The number average molecular mass ($\overline{M}n$) is determined by using methods which depend upon the number of molecules present in the polymer sample, *viz*, colligative properties such as osmotic pressure, depression in freezing points and eleva-



In practice, a better product is obtained by using a *trans- esterification process*. The dimethyl ester of terephthalic acid is heated to about 475 K with ethylene glycol. Methanol is evolved as a gas driving the reaction to completion. The molten product thus obtained is spun into Dacron or cast into a *film* called *Mylar*.

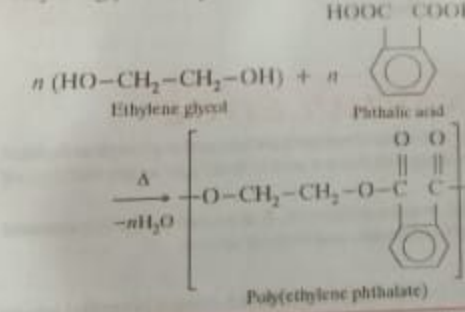
Uses. (*i*) The fibre of terylene is highly crease-resistant, durable and has low moisture content. It is also not damaged by pests like moths and mildew. It is, therefore, used for the manufacture of wash and wear fabrics, tyre cords, seat belts and sails. It is also blended with cotton and wool to increase their resistance to wear and tear.

(*ii*) The Mylar film is extremely flexible, tear-resistant and resistant to ultraviolet degradation. It is, therefore, used for making magnetic recording tapes.

ADD TO YOUR KNOWLEDGE

1. **Bubble gum** contains styrene-butadiene rubber.
2. **Lexan** is a polycarbonate (or a polyester) and is obtained by condensation polymerization of diethyl carbonate and bisphenol A. *It has unusually high impact strength and is used for making bullet proof windows and safety or crash helmets.*

2. Glyptal or Alkyd resin*. Glyptal is the general name for all the polymers obtained by the condensation of dibasic acids or their anhydrides with polyhydric alcohols such as ethylene glycol, glycerol etc. The simplest glyptal *i.e.* poly(ethylene phthalate) is formed by the condensation of ethylene glycol and phthalic acid.



Uses. Poly(ethylene phthalate) is a thermoplastic. It dissolves in suitable solvents and the solution on evaporation leaves a tough but not flexible film. It is, therefore, used in the manufacture of paints and lacquers.

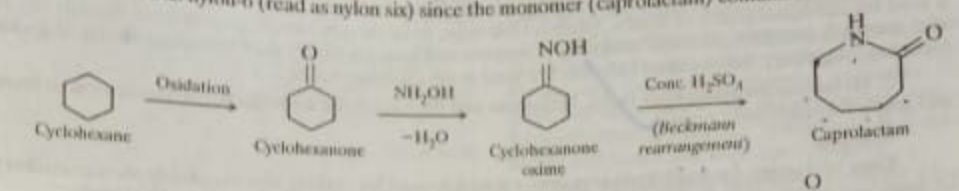
II. Polyamides. *Polymers which have amide linkages are called polyamides. These are prepared by the condensation polymerization of dibasic acids with diamines or their equivalents.* These polymers are commonly called *nylons*. The name nylon (*ny* = New York and lon = London) is given to these fibres since the most common nylon *i.e.* nylon-66 was simultaneously prepared in New York and London.

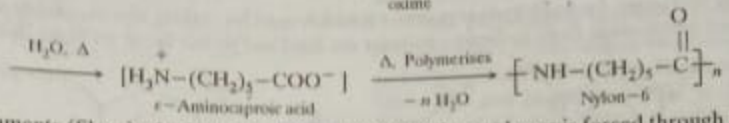
1. Nylon-66. It is manufactured by the condensation polymerization of adipic acid and hexamethylenediamine. The acid and the amine first react to form a salt which when heated to 525 K under pressure undergoes polymerization with elimination of water as

*Resins are amorphous organic solids or semisolids which usually have a typical lustre and are often transparent or translucent. For example, shellac secreted by the lac insect.

A plastic, on the other hand, is a substance which is capable of being moulded whereas a resin lacks this property. Typical plastics on heating become soft but do not give mobile melts. In contrast, resins on heating give mobile melts. Plastics usually have much higher molecular mass than resins. Nevertheless, this differentiation is not very clear and the two terms are often used interchangeably.

When caprolactam is heated with a trace of water, it hydrolyses to ∈-aminocaproic acid which upon continued heating undergoes polymerization to give nylon-6. It is manufactured by most of the industries in India. It is called as nylon-6 (read as nylon six) since the monomer (caprolactam) contains six carbon atoms.





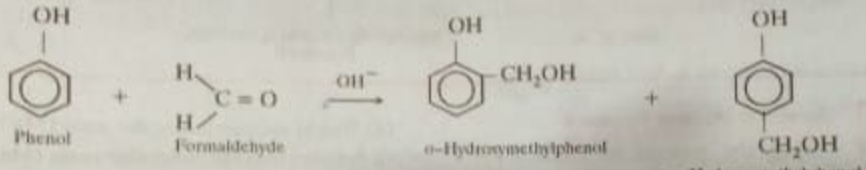
The filaments (fibres) of nylon-6 are obtained when molten polymer is forced through a spinneret and the fibres formed are cooled by a stream of air.

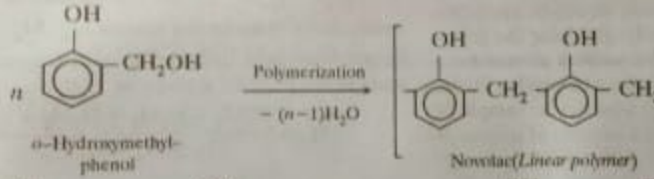
Uses. It is used for the manufacture of tyre cords, fabrics and mountaineering ropes.

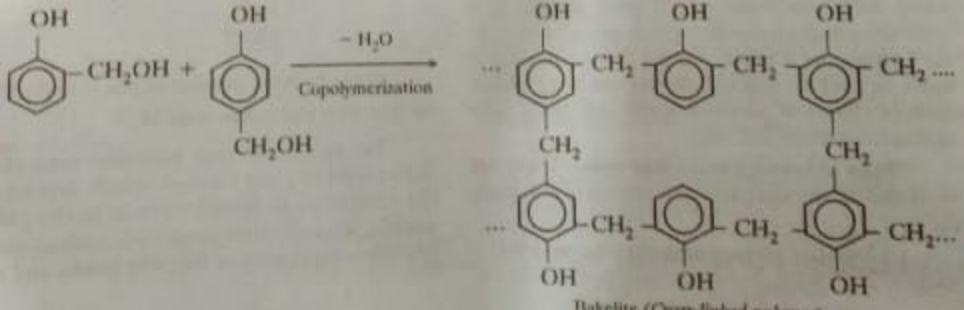
III. Formaldehyde resins. This class of polymers contains polymers like bakelite, melamine-formaldehyde, urea-formaldehyde etc.

1. Phenol formaldehyde resin (Bakelite). When phenol is treated with formaldehyde in presence of a basic catalyst, it undergoes condensation polymerization to form either a linear or a cross- linked polymer called **Phenol-formaldehyde resin or bakelite**. The process actually involves formation of methylene bridges either at *ortho*- or *para*- position or both at *ortho*- and *para*-positions with respect to the phenolic group. The initial product is a linear polymer called *Novolac* which upon further heating with formaldehyde undergoes cross-linking to form an infusible solid called *bakelite*.

Reaction :

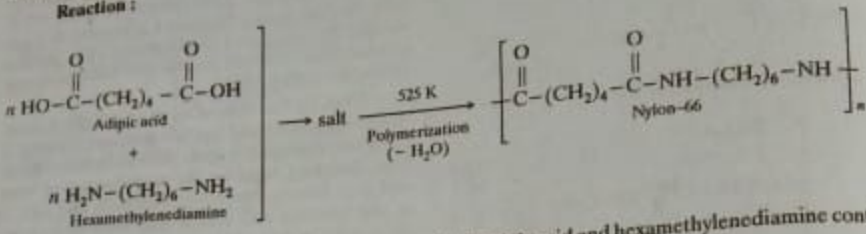






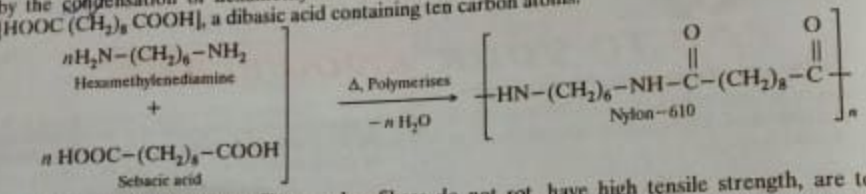
steam and the nylon is produced in the molten state. It can then be cast into a sheet or fibres by passing through a spinneret*.

Reaction :



It is called nylon-66 (read as nylon six, six) since both adipic acid and hexamethylenediamine contain six carbon atoms each.

2. Nylon-610. Another commoly used nylon is nylon-610 (read as nylon six, ten) which is obtained by the condensation of hexamethylene-diamine (containing six carbon atoms) and sebacic acid [$HOOC(CH_2)_8COOH$], a dibasic acid containing ten carbon atoms.



Uses. (*i*) Unlike cotton fibres, nylon fibres do not rot, have high tensile strength, are tough, abrasion-resistant and somewhat elastic. These are, therefore, used in the manufacture of carpets, textile fibres and bristles for brushes.

Further, nylon fibres are so much stronger than the natural materials that these can be made much thinner. The availability of such a strong thin thread made possible nearly invisible women's stockings called '*nylons*'.

(*ii*) Being tough nylon is used as a substitute for metals in bearings and gears.

(*iii*) Crinkled nylon fibres are used for making elastic hoisery.

ADD TO YOUR KNOWLEDGE

1. **Kevlar** is a polyamide obtained by condensation copolymerization of terephthalic acid and *p*- phenylenediamine (1, 4-diaminobenzene). *The fibres of this polymer are so strong that they are used to make light weight bullet-proof vests.*
2. **Nomex** is a polyamide made from *m*-phthalic acid and *m*-diaminobenzene. It is known for its fire-resistant properties and *is used in protectic clothing for firefighters, astronauts, and race-car drivers.*

3. Nylon-6 or Perlon. Nylons can also be prepared from a single monomer having a potential amino group at one end and a potential carboxyl group at the other. For example, the monomer caprolactam on polymerization gives nylon-6.

Caprolactam needed for the purpose is manufactured from cyclohexane (a petrochemical) as described below :

*Spinneret literally means spinning organ of insects but here it implies some spinning device.

their resistance to wear and tear.

(*ii*) The Mylar film is extremely flexible, tear-resistant and resistant to ultraviolet degradation. It is, therefore, used for making magnetic recording tapes.

OUR KNOWLEDGE

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er) and is obtained by condensation polymerization of diethyl carbonate
impact strength and is used for making bullet proof windows and safety

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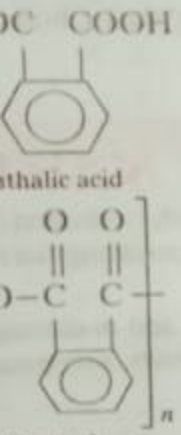

thalic acid

hthalate)

Uses. Poly(ethylene phthalate) is a thermoplastic. It dissolves in suitable solvents and the solution on evaporation leaves a tough but not flexible film. It is, therefore, used in the manufacture of paints and lacquers.

II. Polyamides. *Polymers which have amide linkages are called polyamides. These are prepared by the condensation polymerization of dibasic acids with diamines or their equivalents.* These polymers are commonly called *nylons*. The name nylon (*ny* = New York and lon = London) is given to these fibres since the most common nylon *i.e.* nylon-66 was simultaneously prepared in New York and London.

1. Nylon-66. It is manufactured by the condensation polymerization of adipic acid and hexamethylenediamine. The acid and the amine first react to form a salt which when heated to 525 K under pressure undergoes polymerization with elimination of water as

or semisolids which usually have a typical lustre and are often transparent or
ne lac insect.

nce which is capable of being moulded whereas a resin lacks this property. Typical
mobile melts. In contrast, resins on heating give mobile melts. Plastics usually have
vertheless, this differentiation is not very clear and the two terms are often used