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CHAPTER 14

MACROMOLECULES

INTRODUCTION

"The large size molecules with are formed by the combination of small repeating units called monomers are called macromolecules or polymers".

The idea of macromolecules was given by Staudinger in 1920. He proposed the long chain formula for polystyrene rubber and polyoxymethylene.

Polymerization:

"The process in which smaller molecules or monomers combine together to form bigger molecules is called polymerization".

The word "poly" means "many" and "mer" means "unit" or "parts".

Polymers are largely used in our daily life. Artificial fiber, (Nylon, polyester, orlon, dacron, rubber, plastic are all polymers. The world would be totally different without plastic or artificial fibers.

The natural materials have been replaced by the polymers. For exampole, wood and cotton have been replaced by the plastic and synthetic fibers. It is better or worse but we are living in "plastic society". If we see the things which are present in out room, we can say we cannot live without plastic. Many things like TV set, telephone set, electrical wires insulation cussion, mat, curtains, switches, plastic basket, etc are all polymers.

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CLASSIFICATION OF MACROMOLECULES

Macromolecules can be classified in the following ways:

- Macromolecuels
  - Inorganic
    - Giant molecules (Diamond, Graphite, silicones and Sand)
  - Organic
    - Biopolymers: Lipids, Proteins. Carbohydrates and Nucleic acids, etc
    - Synthetic polymers: Plastics, synthetic fibers, Rubber, etc

STRUCTURE OF POLYMERS

A polymers is a large molecule build up by the repetition of small and simple chemical units known as monomers. On the basis of structure, there are three types of polymers.

Linear Polymers

(1) Linear Polymers

If monomer combine along one direction only, they from straight chain polymer or linear polymers. e.g., polyethylene.

$$CH_2 = CH_2 \longrightarrow —CH_2—CH_2— [CH_2—CH_2]—CH_2—CH_2—$$

Ethylene — Monomer of Ethylene

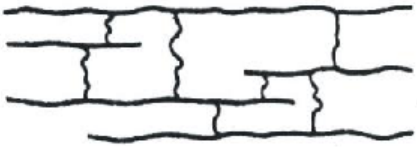
(2) Branched Polymers:

"Polymers with branches at irregular intervals along the polymer chain are called branched-polymers". Due to branches, polymer does not have a proper arrangement and it is less crystalline in nature.

Branched Polymers

(3) Cross-linked Polymers:

If chains of the polymers are connected themselves by small branches (as shown in figure) are called cross-linked polymers.



Cross-linked Polymers

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Degree of Polymerization:

"The length of the polymer chain is specified by the number of repeating units in the chain known as the degree of polymerization (DP)." For example, in linear polythene.

$$—CH_2—CH_2—CH_2—CH_2—CH_2—$$

The repeating units is $—(CH_2—CH_2)_n—$ where n is a large number and it is degree of polymerization.

Molecular Mass of Polymers:

"The molecular mass of the polymers is the product of the molecular mass of the repeating unit and the DP." For example, polyvinyl chloride, a polymer of DP 1000 = Mol . mass of the molecular mass.

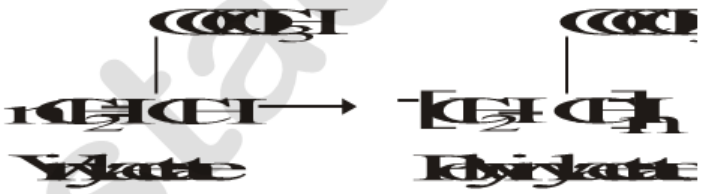
$$—(CH_2—CH_2)_n—$$
$$|$$
$$Cl \qquad 63 \times 1000 = 63000$$

Most high molecular mass polymers are useful for making plastics, rubbers or fibers, etc and have molecular masses between 10,000 to 1,000,000. The properties of polymeric materials vary widely, depending upon the chemical compositi0n, structure of the macromolecule and degree of polymerization.

TYPES OF POLYMERS ON THE BASIS OF NATURE OF MONOMERS

(1) Homopolymers:

"If a polymers is formed by the single type of monomers, it is called homopolymer." For example, polyethylene, polyvinyl chloride polyvinyl acetate polystyrene etc. Structure of polyvinyl acetate is given below.



Homopolymers my also be represented as:

$$[\ .....—A—A—A—A—A—A—A—.....]$$

(2) Copolymers:

"A polymer which is formed by the combination of two types of monomers is called copolymer." For example, vinyl acetate and Butyl maleate combine together to give copolymer.

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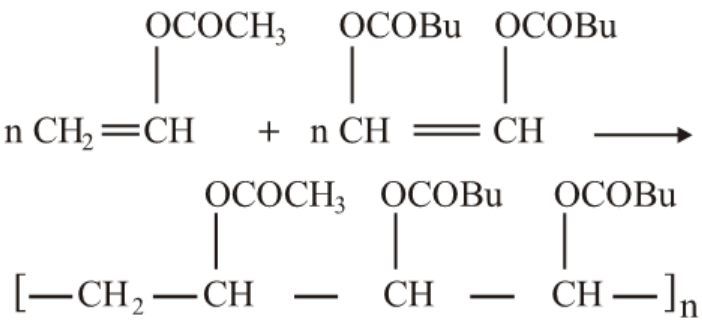

(Where Bu is abbreviation of butyl C_4H_9—)

A regular copolymer may be represented as:

[.....—A—B—A—B—A—B—A— B—.....]

(3) Terpolymer:

In terpolymer, three different monomers are polymerized and the polymerization reaction is carefully controlled. For example, combination of butyl acrylate, methacrylate and acrylic acid monomers gives a highly tough polymer which serves as a weather-resistant paint.

[.....—A—B—C—A—B—C—A—B—C— .....]

(i) Thermoplastic Polymers:

"A plastic which can be softened repeatedly when heated and hardened on cooling with a little change in properties are called thermoplastics" e.g.,

Polyvinyl chloride, polyethlene, etc, linear and branched polymers form a class of material called thermoplastics, these materials can be molded and remolded.

Other examples are Nylon, Polystyrene.

(ii) Thermosetting Plastic Polymer:

"The polymers which become hard on heating and cannot be softened again are called thermosetting polymers. A thermosetting polymer, on varnish, epoxy resins, bakelite." etc.

Thermosetting plastic are usually cross-linked polymers. Once cross-links forms, these polymers take the shape that cannot be changed without destroying the plastic.

POLYMERIZATION PROCESS

The process of forming polymers from monomers is known as polymerization. They are two mode of polymerization given by W.H Carothers in 1929.

(i) Additional polymerization

(ii) Condensational polymerization

(i) Additional polymerization:

"The polymers which are formed by the repeated addition of monomers is called addition polymer." Monomers are unsaturated compounds and commonly derivatives of ethene.

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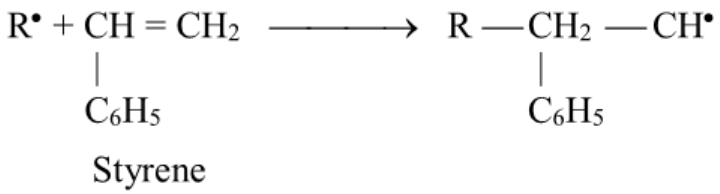
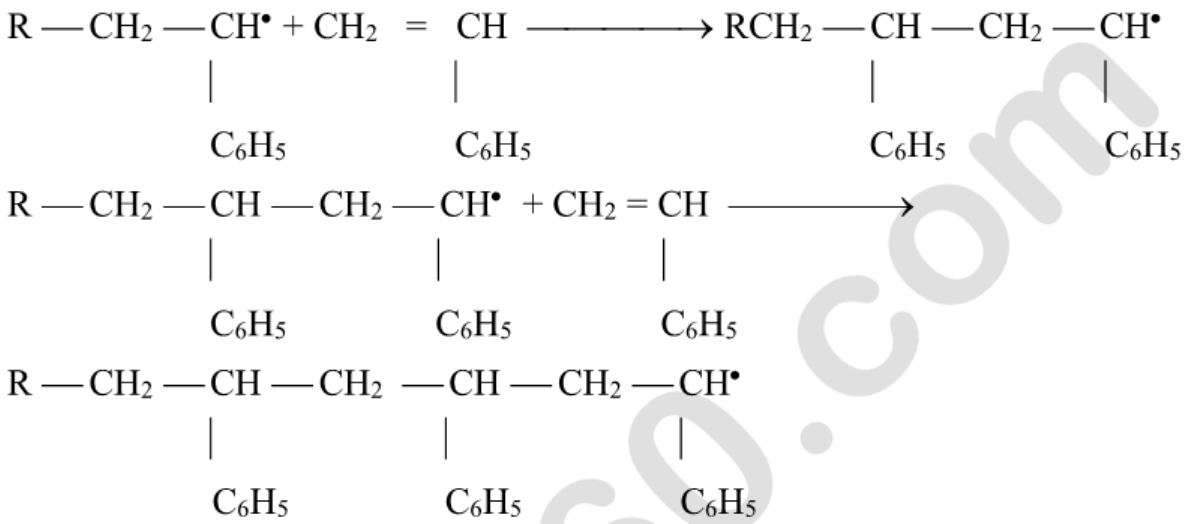
Addition polymerization have chain reaction free radical mechanism. This mechanism have three steps; initiation, propagation and termination. Polyethylene, polyvinyl chloride, polyvinyl acetate or polystyrene are example of additional polymerization. Mechanism of polystyrene formation below.

Initiation:

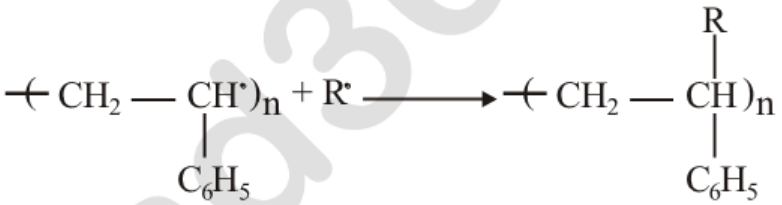


Styrene

Propagation:



Termination:



Additional polymers have same empirical formula as their monomers. They are linear or branched and are thermoplastic.

(ii) Condensational Polymerization:

"The polymer which is formed by the reactions of different types of monomers with the elimination of H_2O or other smaller molecule like NH_3, HCl or CH_3OH is called condensational polymer."

Condensation takes place at the both ends of the growing chain. For example; polyester, Bakelite, Nylon 66, etc. are examples of condensational polymers.

Terephthalic acid reacts with ethylene glycol and they form a polyester called Dacron.

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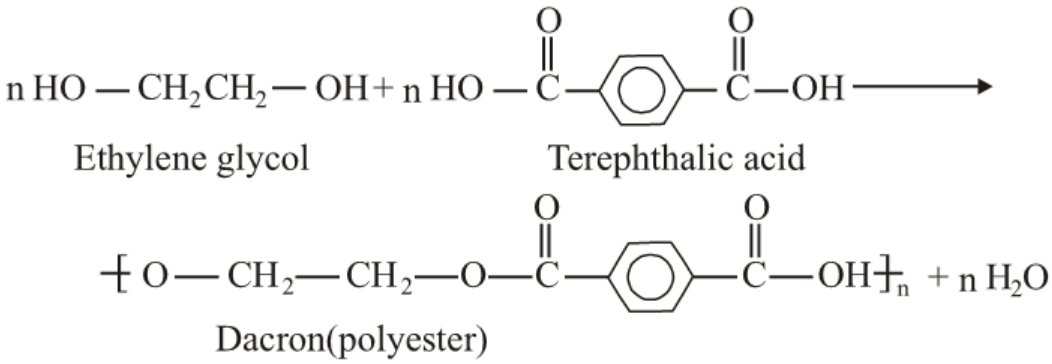
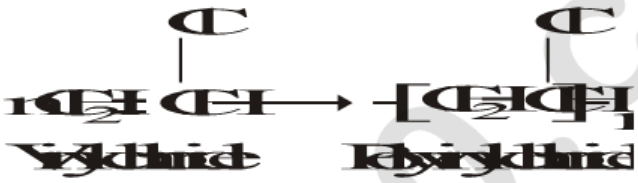


Water molecules are formed bye reacting hydroxyl group of glycol and hydrogen of terephthalic acid. Condensattional polymers are usually cross linked and thermosetting in nature.

SOME EXAMPLES OF SYNTHETIC POLYMERS

(1) Polyvinyl Chloride (PVC):

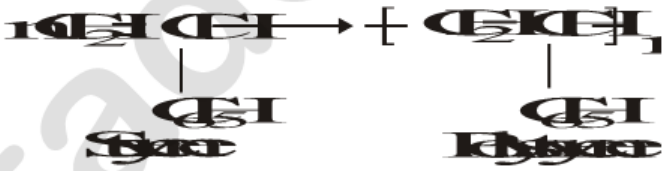
It is an additional polymer, obtained by polymerization of vinyl chloride at 52°C and 9 atmospheric pressure.



PVC is used for insulation of electric wires, floor tiles, PVC pipes plastic wrap, in gramophone recorders. If we add some plasticizer in it, its flexibility increases.

(2) Polystyrene:

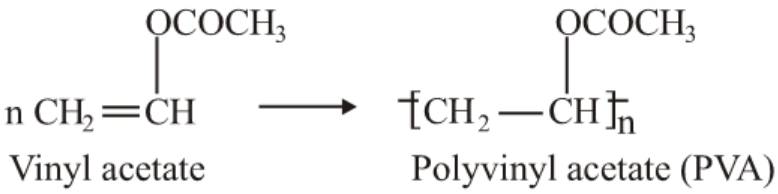
Polystyrene is made by the addition polymerization of styrene.



Polystyrene is used for preparation of food container, cosmetic bottles, toys, packing materials, styrofoam, insulation etc.

(3) Polyvinyl Acetate:

It is a polymer of vinyl acetate.



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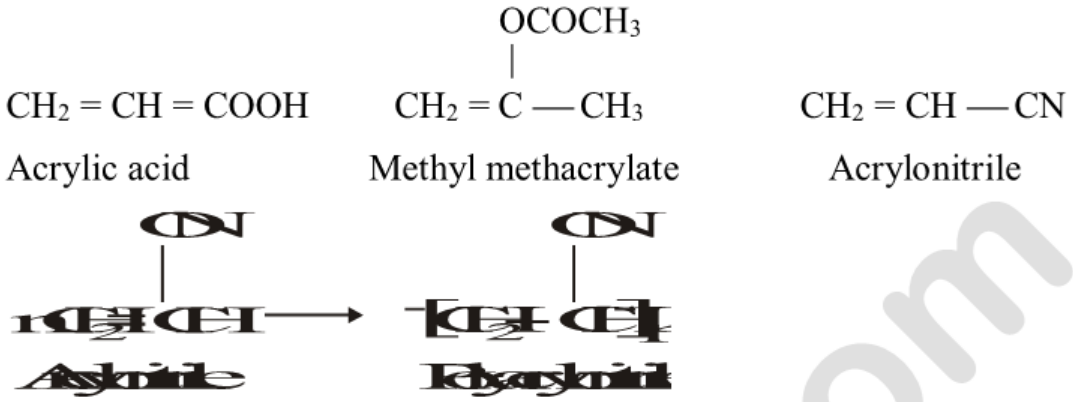
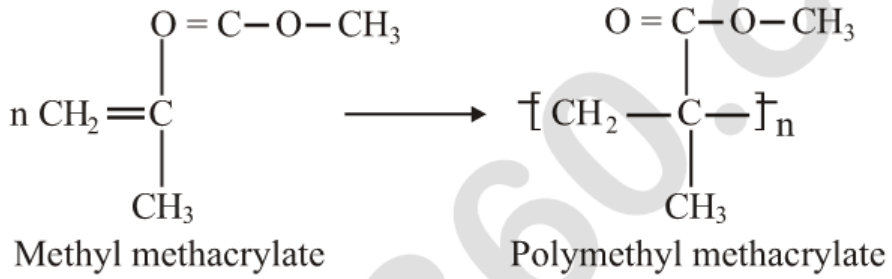
PVA (polyvinl acetate) is non-toxic and colourless material. It is supplied in number of grades, depending upon the degree of polymerization. It has a characteristic odour. It is mostly used as adhesive material, textile coating, chewing gum, resin, and as binder for emulsion paints.

(4) Acrylic Resins (Polyvinylnitrile called Orlon/Acrilon):

These are closely related to vinyl resins. Monomers may be acrylonitrile, methyl methacrylate or acrylic acid.



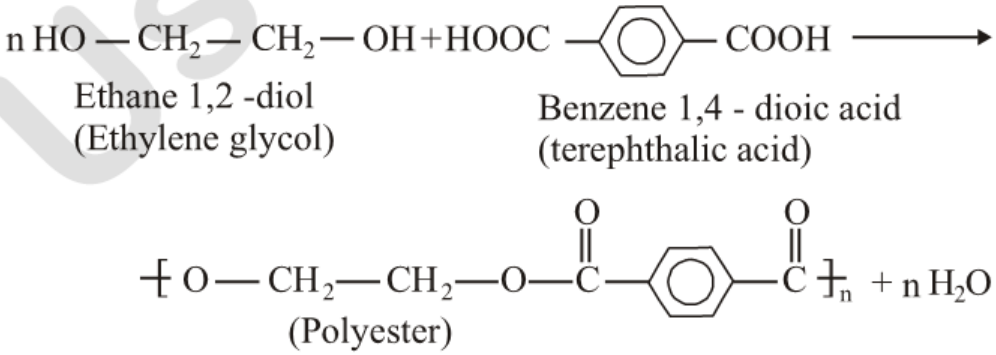
Polyacrylonitrile is used for pains, plastics and water bases resistant paints.



It is used to prepare **Lucite of Plexiglass**. It is a glass substitute and also used to prepare bowling glass.

(5) Polyester Resins:

Polyester resins are the product of the reaction of an alcohol (ethane 1,2 diol) and aromatic bi-functional acids (benzene 1,4 dicarboxylic acid). This product has a large number of uses in clothing. Polyester is often blended with cotton or wool for summer and winter clothing. Polyester resins are also used for making water tanks.



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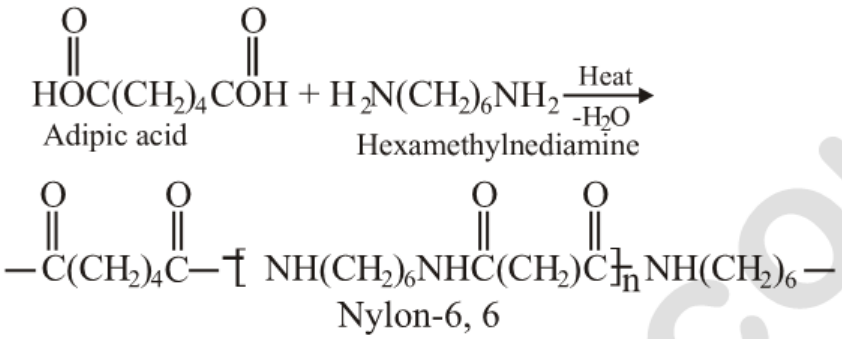
(6) Polyamide Resins (Nylon 6, 6):

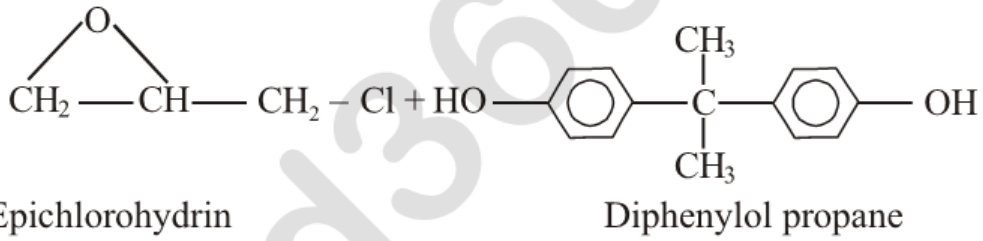
These resins are formed by the condensation of polyamines with aliphatic dicarboxylic acids. One of the most famous condensation polymers discovered is Nylon. The word Nylon has been accepted as a generic name for synthetic. Polyamides. Nylon —6, 6 is the most important polyamide. It is obtained by heating adipic acid (hexanedioic acid) with hexamethylene diamne. Nylon 6, 6 derives its name form its starting materials adipic acids and hexamethylene diamine, both of which have six carbon atoms.

Nylon is mainly used as a textile fiber. It has a combination of high strength, elasticity, toughness and abrasion resistance.

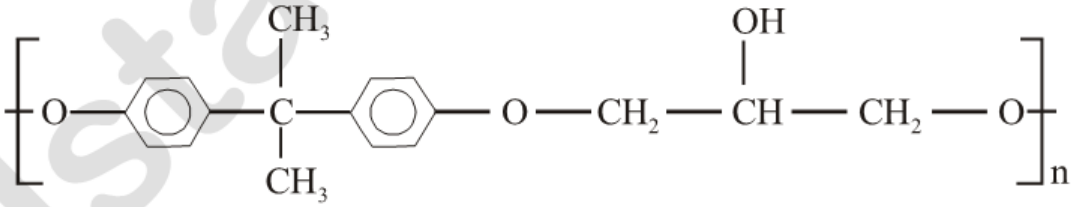


(7) Epoxy Resin:

Epoxy resin is made by condensing epichlorohydrin with diphenylol propane.



The typical repeating unit is given below.



Epoxy adhesives have two components that are mixed before they are used. The polymer chain cross linked and bonding become extremely strong.

The major use of epoxy resins is in coating materials which give toughness flexibility, adhesion and chemical resistance. Industrial materials are coated with epoxy paints, Dams, bridges, floors, etc.

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BIOPOLYMERS

"The polymers found in living things are called biopolymers". There are four main classes of biopolymers, i.e. carbohydrates, proteins, lipids and nucleic acids."

CARBOHDRATES

"The substance in living organisms consisting of polyhdroxy aldehyde or polyhydroxy ketone or its condensational polymer is called carbohydrate."

The chemical analysis indicates that carbohydrates have C, H and O in them. Carbohydrates are commonly called sugars.

Empirical Formula:

The empirical formula of carbohydrates is $C_x(H_2O)_y$. Where x and y are not less than three x and y may or may not be equal. For example, formula of glucose is $C_6H_{12}O_6$ and can also be written as $C_6(H_2O)_6$.

Carbohydrates are the most abundant biomolecules on the earth. Sucrose, starch, cellulose, glucose, fructose are common carbohydrates. Sugar and starch is found in food products, cellulose is found in wood and cotton. Sugar is found in plants etc. the most abundant carbohydrate is cellulose.

CLASSIFICATION OF CARBOHYDRATES

Carbohydrates are divided into three classes:

(1) Monosaccharides

(2) Oilgosaccharides

(3) Polysaccharides

(1) Monosaocharides:

"A carbohydrate that cannot be acid hydrolysed is called monosaccharide".

Monosaccharides have empirical formula $(CH_2O)_n$. Where n is form three to nine. The suffix –ose is commonly used to designate these simple sugars. The monosaccharides with threem four, five, six ..... carbon atoms are classified as triose, tetrose, pentose, hexose.....

In monosaccharides all carbon atoms have hydroxyl group — OH except one, which has aldehyde or ketone group in it.

Sugars with five carbon atoms (pentoses) or six carbon atoms (hexoses) are more stable as cyclic structures than as open chain structures. Glucose and fructose are very common examples of hexoses, both of which have molecular formula, $C_6H_{12}O_6$.

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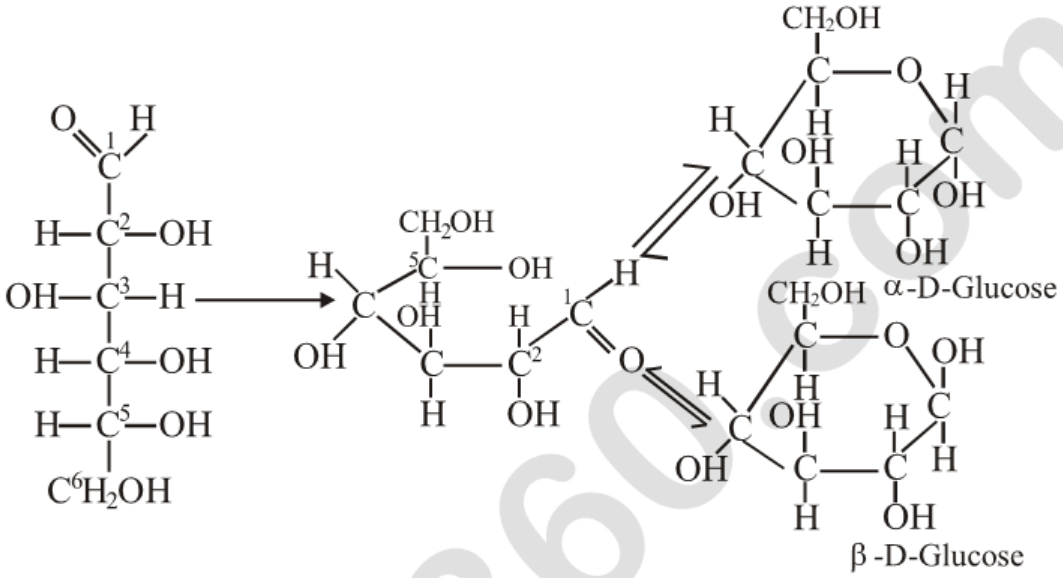
Glucose:

Glucose is also called dextrose, grape sugar or blood sugar. Open structure of glucose contains five —OH group at five carbon and one aldehyde group so it is also called aldohexose. It is found in free as well as in combined state.

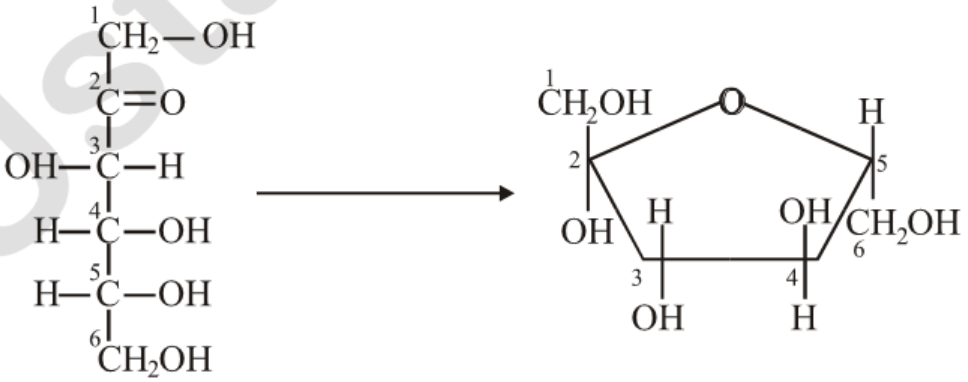
In the free state, it is preset in most sweet fruits and in honey. Small quantities of glucose are also present in human blood and urine. In the combined state it forms a major components of many disaccharides and polysaccharides. It is the cource of energy in our body. Its M.P is 146°C. It is soluble in water.

Two cyclic structures of glucose are α —D —glucose and β —D —glucose given below. In the two isomeric cyclic structures the position of —old group is different at carbon number 1.



Fructose:

Open structure of fructose contain six carbon atoms in it. Five carbon atoms have OH group and one carbon is ketone, so it is ketohexose fructose is found in combined and free state in nature. Fructose is sweetest of all sugars and used as sweetening agent in confectionary. It is substitute of cane-sugar. Open and cyclic structures of fructose are given below.



Fructose (Open chain form) Fructose (Cyclic form)

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(2) Oligosaccharides:

"The carbohydrates which give two to nine same or different monosaccharides upon hydrolysis are called oilgosaccharides."

The oilgosaccharides that give two monosaccharide units are called disaccharide. e.g., sucrose, maltose, Lactose, etc.

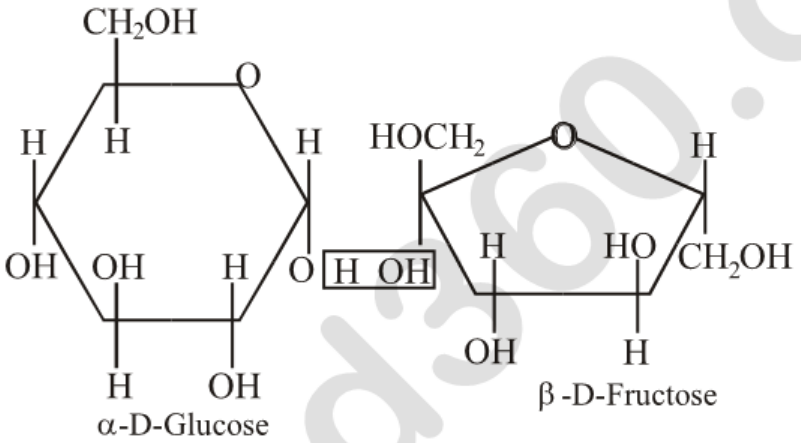
$$\text{Sucrose} + H_2O \xrightarrow{H^+} \text{glucose} + \text{fructose}$$

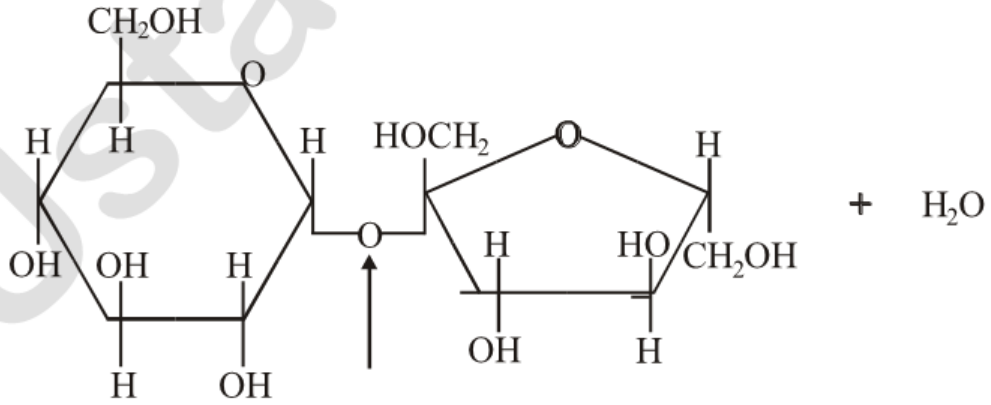
$$\text{Maltose} + H_2O \xrightarrow{H^+} \text{glucose} + \text{glucose}$$

The oilgosaccharides that give three monsaccharides units are called **trisaccharides.** e.g; raffinose, molecular formula of raffinose is $C_{18}H_{32}O_{16}$.

Sucrose:

Sucrose is a disaccharide of –D-glucose and fructose. Both the monosaccharides are linked to each other by **Glycosidic linkage.** Sucrose is also called table sugar. Sucrose occur in sugar cane, sugar beet, pineapple, apricot, mango, almond, coffee and honey. The structure of sucrose is given below:





Glycosidic linkage (1,2 linkage
Sucrose

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Lactose:

Lactose is also disaccharide. Lactose upon hydrolysis give glucose and galactose.

$$\text{Lactose} + H_2O \xrightarrow{H^+} \text{Glucose} + \text{Galactose}$$

Lactose (milk sugar) occurs in the milk of all animals. Is does not occur in platns.

(3) Polysaccharides:

"A carbohydrate that gives many simple sugar molecules upon acid hydrolysis is called polysaccharide."

Polysaccharides have usually one type of monosaccharides in it. Most of the polysaccharides are linear polymers (one main chain with no branching). e.g., starch, cellulose, Amylose, Amylopectin, glycogen, etc.

$$\text{Polysaccharide} + H_2O \xrightarrow{H^+} \text{many monosaccharides}$$

For example, starch on hydrolysis give many glucose molecules.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Polysaccharides are amorphous solids, insoluble in water, testeless and they are called **non-sugars.**

Functional of Polysaccharities:

Polysaccarides perform two main function in the animals and plants.

They are used as energy storage compounds and for building the structural elements of the cell. Plants store glucose as starch and animal store glucose as glycogen. Glycogen is highly branched polymer and it is stored in the liver and muscles of the animals.

Detail of some polysaccharides is given below:

(i) Starch:

Starch is the most important source of carbohydrates in human diet. The chief commercial sources of starch are wheat, rice, maize, potatoes and barley. Starch is a polymer of α-D-glucose. Its general formula is $(C_6H_{10}O_5)_n$.

Starch is not a pure compound. It is a **mixture** of two polysaccharides, **amylose** and **amylopectin** which can be separated from one another. Amylose is soluble in water and gives a deep blue colour with iodine while amylopectin is insoluble and gives no colour. Natural starch consists of 10 to 20% amylose and 80 to 90% amylopectin. It is used in coating and sizing of paper to improve the writing qualities.

It is also used in laundering and in the manufacture of glucose and ethyl alcohol.

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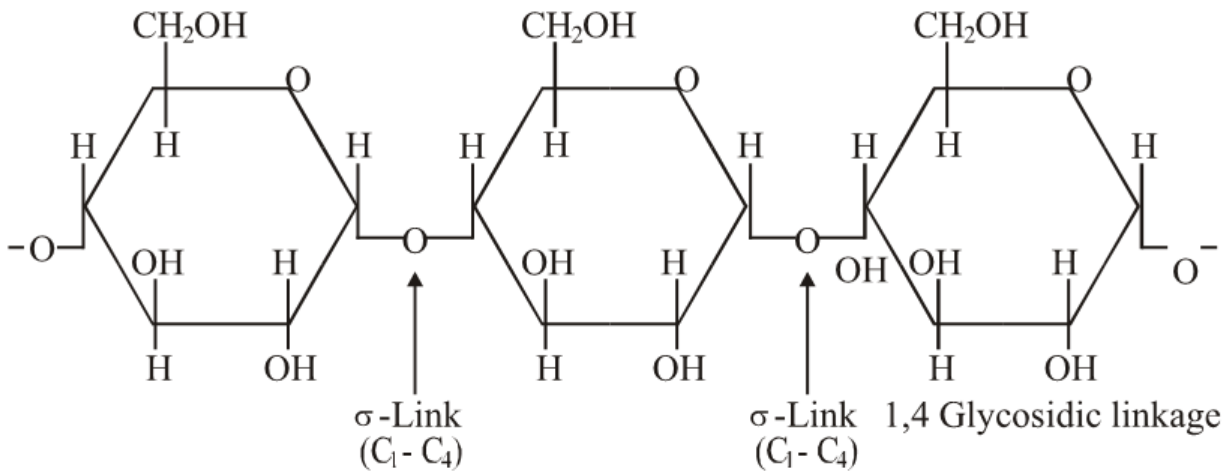
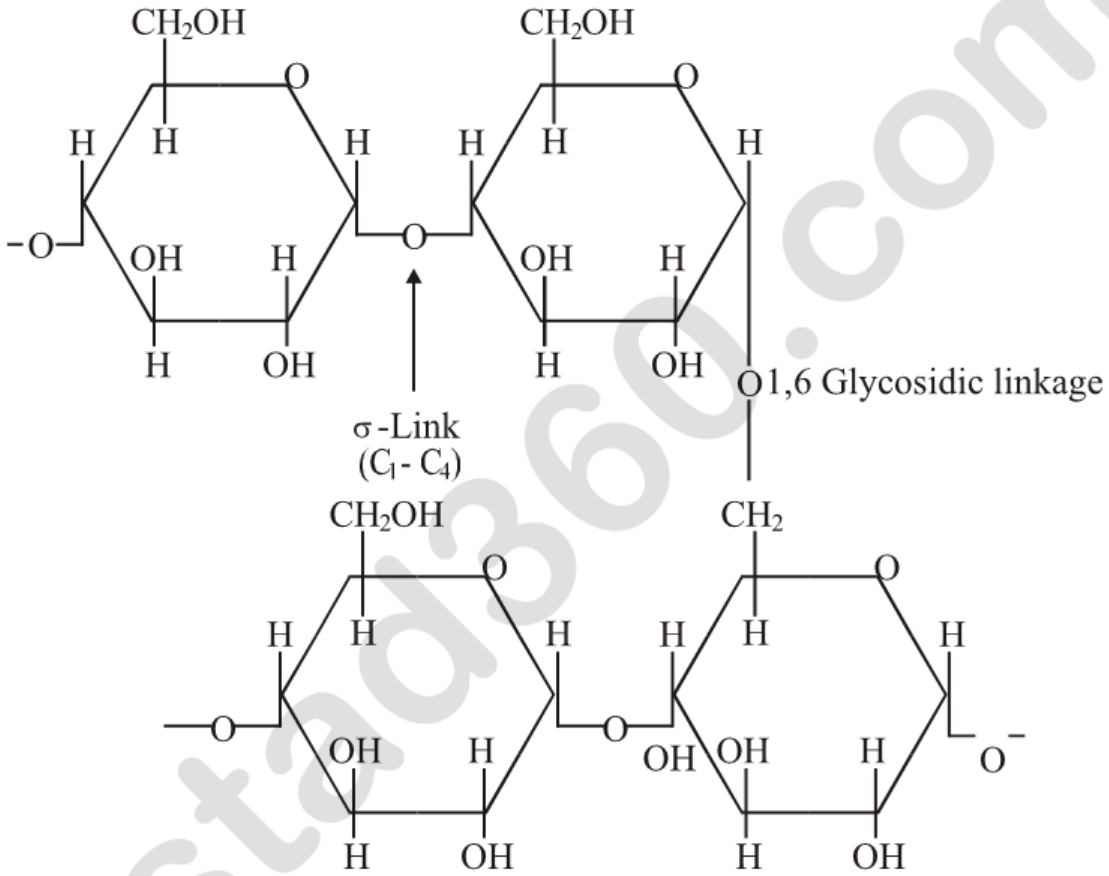


Structure of Amylose (polymer of σ-D-glucose)



Structure of Amylopectin

Amylose is linear polymer while amylopectin is a branched polysaccharide.

(ii) Cellulose:

Most abundant structural **polysaccharide** is cellulose. Approximately 100 billion of cellulose are produced each year by plants. For example, **cotton is 99% cellulose** and the woody parts of trees are generally more than 50% cellulose. It is a

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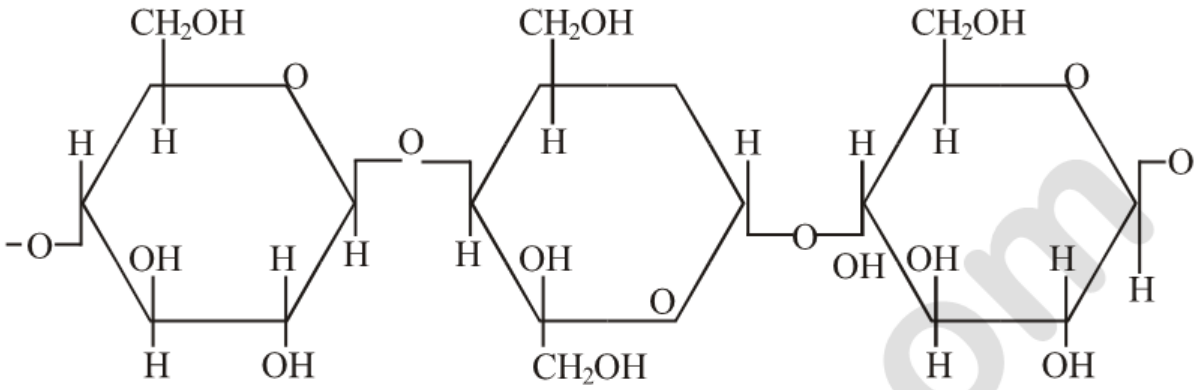
polymer of **β-D-glucose.** It is present mainly in the plant kingdom but also occurs in some marine animals. It is an un-branched polymer consisting of a large number (upto 2500) of glucose residues joined to each other through β-1→4 linkages.

Its chief importance in human nutrition is that it provides fiber and bulk to the food. This serves to satisfy the appetite and, in addition, it stimulates intestinal peristalsis. It is not digested in the human gastrointestinal track because human being lacks the enzyme cellulose which breaks the cellulose molecules.

Human enzymes can digest only α-D-glucose and not to β-D-glucose polymer.



Cellulose (polymer of β-D-glucose)

(iii) Glycogen:

Animals store sugar in the form of a polysaccharide called glycogen. It is also called animal starch. On hydrolysis it also gives many glucose units.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$

Structure of glycogen is very closely related with the amylopectin having 1→4 linkage 1 → 6 glycosidic linkage. Human is much more branched molecule as compared to amylopectin.

PROTEINS

Proteins are polymer of small building blocks called amino acids.

The molecular masses of different protein ranges from 6000 to millions. The human probably contains at least 10,000 different kinds of proteins. The name protein is derived from the Greek word "Proteins" meaning "Prime importance".

Proteins are present in all living organisms and without proteins life would not be possible. There are present in muscles, skin, hair and other tissues that make up the bulk of the body's non-bony structure.

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All proteins contain the elements carbon, hydrogen, oxygen and nitrogen. In some proteins sulphur is also present. They may also contain phosphorus and traces of other elements like iron, copper, iodine, manganese and zinc. Proteins are very high molecular masses macromolecules. All proteins yield amino acids upon complete hydrolysis.

"Proteins may be defined as the organic polymers which upon hydrolysis yield amino acids".

CLASSIFICATION OF PROTEINS

Based on physico-chemical properties, proteins may be classified into three types:

(1) Simple proteins

(2) Compound or conjugated proteins

(3) Derived proteins

(1) Simple Proteins:

"The proteins which after hydrolysis gives amino acids or their derivatives are called simple protein."

Example:

Albumin, globulins, collagen, legumin, etc.

Globulins are insoluble in water but soluble in dilute salt solutions. They are found in animals, e.g., lactoglobulin is found in muscles and also in plants. **Legumin and collagen** proteins are present in the connective tissues throughout the body. They are the most abundant proteins in the animal kingdom forming some 25 to 35% of body protein.

(2) Compound or Conjugate Protein:

*"If protein molecule is attached with some non-protein, it is called compound or conjugate protein. Non-protein attached with protein is called **prosthetic group**."* Conjugated proteins on hydrolysis give carbohydrate, fat or nucleic acid in addition to amino acids. For example, **phosphoproteins** are conjugates with phosphoric acid, **Lipoproteins** are conjugated with lipids like lecithin, cholesterol and fatty acids.

(3) Derived Proteins:

"The proteins which are derived from simple and conjugate proteins are called derived proteins."

For example, proteoses enzymes, peptones, oilgopeptides, **polypeptides** are derived proteins.

On the basis of function, proteins are classified as regulatory or **hormonal** proteins, **structural proteins, transport proteins, genetic protein,** etc.

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STRUCTURE OF PROTEINS

The proteins are the polymer of amino acids and from a longer chains. These chains of polypeptides are three dimensional and highly convoluted (coiled). Protein structure are divided into four levels called primary secondary, tertiary and Quaternary.

(1) Primary Structure:

"The sequence of amino acids in a protein is called primary structure."

The number and variety of amino acids in a protein can be determined by hydrolysis. For this purpose protein is heated with a dilute acid like HCl. Amino acids are separated by chromatography and visualized by ninhydrin.

For a protein having five amino acids units, gylcine, alanine, valine, histidine and serine, there are 120 ways in which these amino acids can be ordered to make a polypeptide.

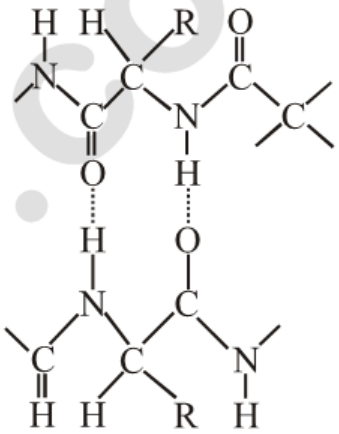
Every protein has its own sequence of amino acids.

(2) Secondary Structure:

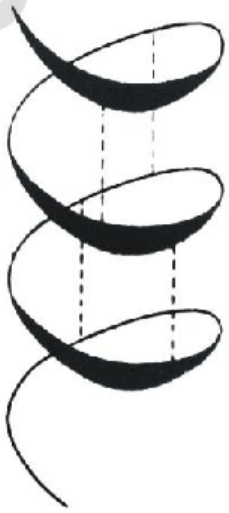
The structure describes that how segments of peptide backbone orient into a regular pattern.

Polypeptides are oriented due to intermolecular forces (hydrogen bonding) between NH and C = O groups of amino acids.

Due to hydrogen bonding, peptide chain acquire a spiral shape. This spiral shape is called α-helix contains 3.6 amino acids and the distance between coils (repeated distance) is 5.4A°.



Hydrogen bonding between carboxyl and amino groups



α-Helix

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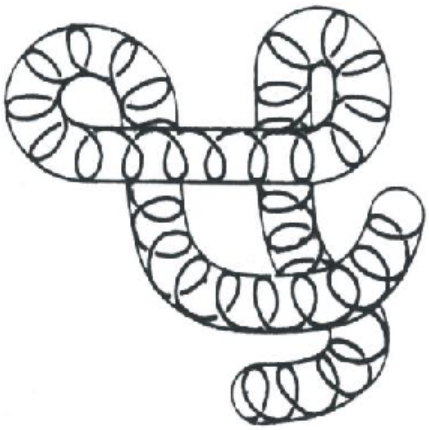
Tertiary Structures:

"The three dimensional twisting and folding of the peptide chain is called tertiary structure."

The tertiary structure is due to the cross linking between parts of the polypeptide chain. This cross-linking is due to bonding and interaction of side chains of the amino acid residues. Different polypeptide chains have their specific tertiary structures.



Folding of the α-helix

Quaternary Structures:

This describes that how individual proteins or polypeptide chains come close together and yield large aggregate structures. The polypeptide chains may be similar or dissimilar.

DENATURING OF PROTEINS

"The change in the structure of protein form normal pattern is called denaturing of proteins."

Denaturing of proteins can takes place by the following ways:

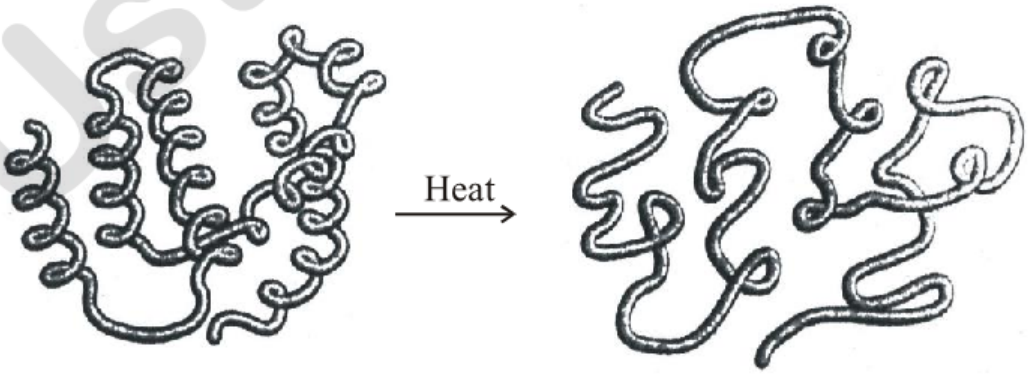
(1) Heating

(2) Changing in pH

(3) Addition of strong oxidixing or reducing agent.

(4) By adding detergents.

(5) By adding reagents like urea. In denaturing, the primary structure remain intact but the tertiary structure unfolds from a specific shape to randomly looped chain.



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For example, when albumin of the egg is cooked, it is coagulated and the tertiary structure of protein in unfolded as shown in above figure, it is an irreversible change. Most enzyme lose all catalytic activities when denatured.

IMPORTANCE OF PROTEINS

(1) Protein is essential for the formation of protoplasm and the structural material for the organism.

(2) Nucleoproteins which are complexes of proteins with nucleic acids serve as carriers of heredity from one generation to the other.

(3) Enzymes which are biological catalysts are protein in nature. Without them life is not possible.

(4) Many proteins have specialized functions. Hemoglobin acts as a carrier of oxygen. Some proteins act as hormones which have regulatory functional, for example; insulin, thyroxin etc.

(5) Industrially proteins have great importance.

- (i) We are familiar with the use of leather made by tanning of hides. This is essentially precipitation of the proteins with tannic acid.
- (ii) Gelatin is obtained by heating bones, skin and tendons in water. It is used in bakery goods.
- (iii) Causein is another protein used in the manufacture of buttons and buckles.

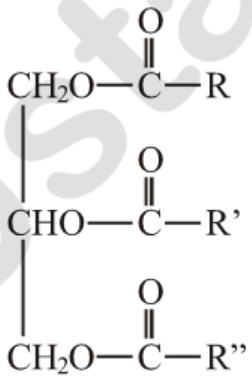
LIPIDS

"Lipids are the naturally occurring organic molecules isolated from cells and tissues by extraction with non polar organic solvents."

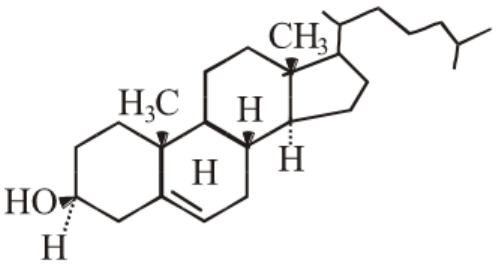
Lipids are classified into two general types:

(a) Those like fats and waxes which contain ester linkage and can be hydrolyzed.

(b) Those like cholesterols and other steroids which do not has ester linkage and cannot by hydrolyzed.



Animal fat- an ester
(R,R',R" = C_{11}- C_{19}chains)



Cholesterol

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General Properties of Lipids:

(1) They are insoluble in water and soluble in non polar organic solvents like ether, chloroform, benzene, etc.

(2) Their primary building blocks are fatty acids, glycerol and sterols.

(3 They are utilized by the living organisms.

(a) Fats and Oils:

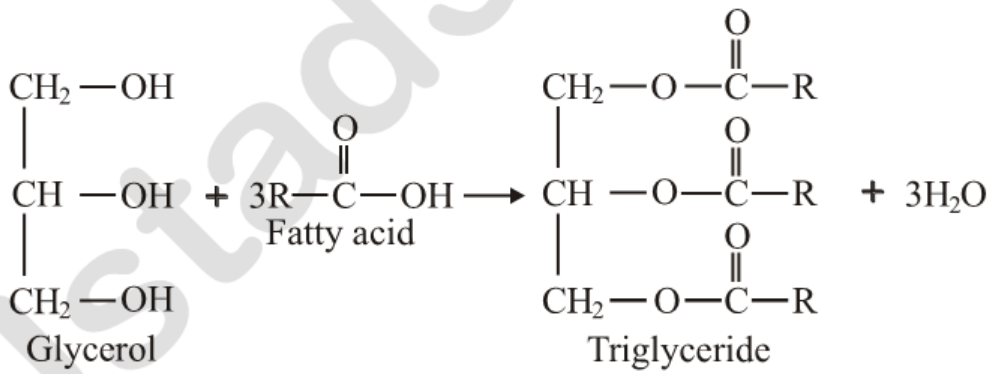
Fats and oils are the most important lipids found in nature. They are one of the three major "food factor" needed for human body, the other two being proteins and carbohydrates. Fats and oils occupy a place of pride in human diet but they also find use as raw materials for the manufacture of soaps and detergents, paints, varnishes, cosmetics, printing inks and pharmaceuticals.

Sources of Fats and Oils:

Fats and oils come from a variety of natural sources like animals, plants and marine organisms. Animals fats are located particularly in adipose tissue cells. Butter and ghee are a special type of animal fats which are made from milk. Vegetable oils are chiefly present in seeds and nuts of plants. Marine oils are obtained form sea animal like salmons and wales, etc.

Structure and Composition of Fats and Oils:

Animal and vegetable fats and oil have similar chemical structures. They are triesters formed glycerol and long chain acids called fatty acids.



A triester of glycerol is called a triglyceride or glyceride. The degree of unsaturation of the constituent fatty acid determines whether a triglyceride will be a solid or a liquid. The glycerides in which long-chain saturated acid components predominate tend to be solid or semi-solid and are termed as fats. On the hand, oils are glycerol esters which contain higher proportion of unsaturated fatty acid components.

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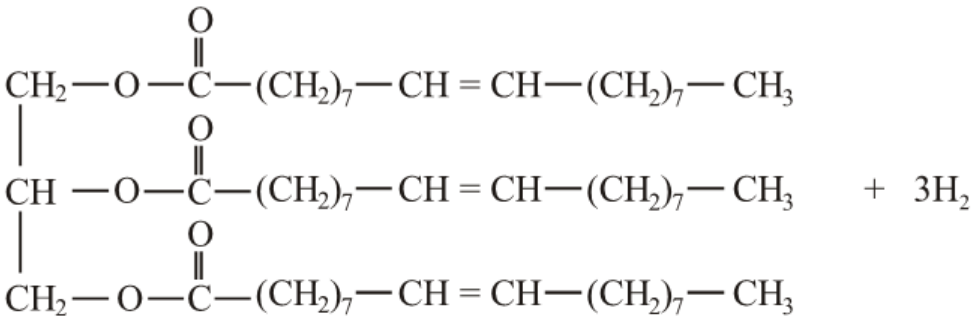
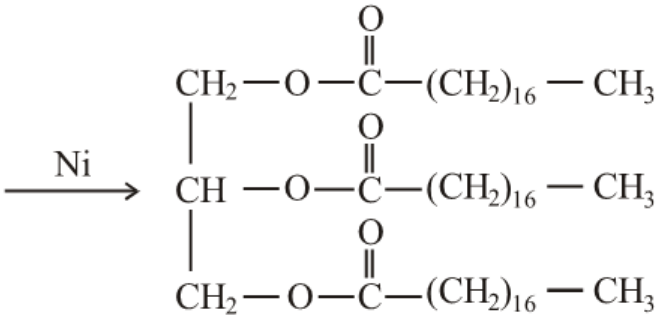


Glyceryl trioleate (An oil) M.P = $-5^{o}C$



A fat (Glyceryl tristearate) M.P = $71^{o}C$

The melting point of mixed glycerides would depend on the extent of unsaturated fatty acid components in the molecules. The polyunsaturated glycerides therefore, have very low melting points and are liquids (oils). Chemically common oils and fats are the mixture of saturated and unsaturated triglycerides, present in various ratios.

PHYSICAL PROPERTIES OF FATS AND OILS

(1) Oils and fats may either be liquid or non-crystalline solids at room temperature.

(2) When pure, they are colourless, odourless and tasteless.

(3) They are insoluble in water and readily soluble in organic solvents like diethyl ether, acetone, carbon tetrachloride and carbon disulphide.

(4) They readily form emulsion when agitated with H_2O in the presence of soap or other emulsifiers. (A colloid composed of liquid droplets dispersed in another liquid is called emulsion).

(5) They are poor conductors of heat and electricity and therefore serve as excellent insulators for the animal body.

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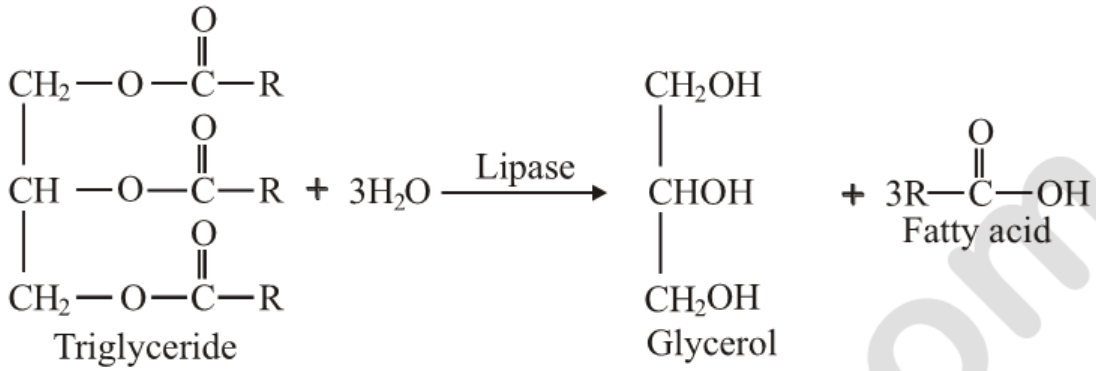
CHEMICAL PROPERTIES OF FATS AND OILS

Some chemical properties of fats and oils are given below.

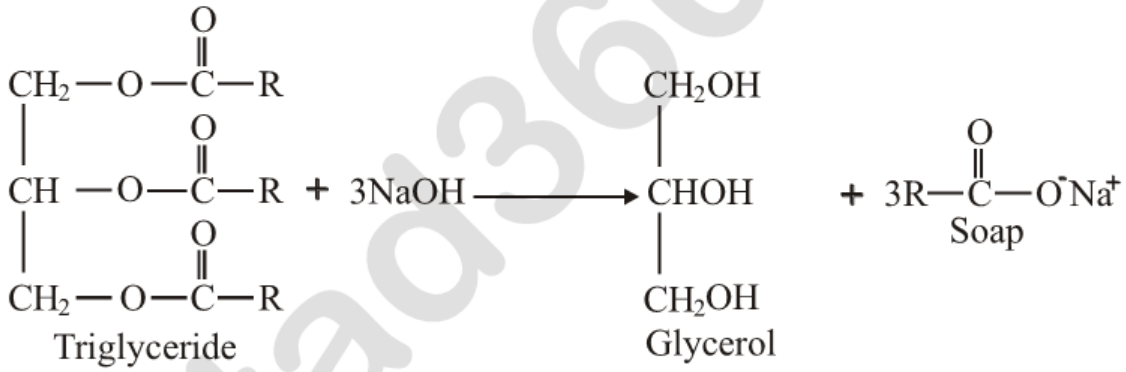
(1) Hydrolysis:

Trigylcerides are easily hydrolyzed by enzymes called lipases to fatty acids and glycerol.



(2) Saponification:

It is the hydrolysis of a fat or an oil with an alkali to form some (salt of fatty acid) and glycerol.



(3) Hydrogenation (Hardening of Oil):

Unsaturated glycerides react with hydrogen in the presence of a metal catalyst to give saturated glycerides. The results is the conversion of a liquid glyceride (an oil) into a semi-solid glyceride (a fat).

This reaction is used commercially to harden vegetable oils for the production of vegetable ghee or margarine. Hardened oil are also extensively used for making soaps and candles.

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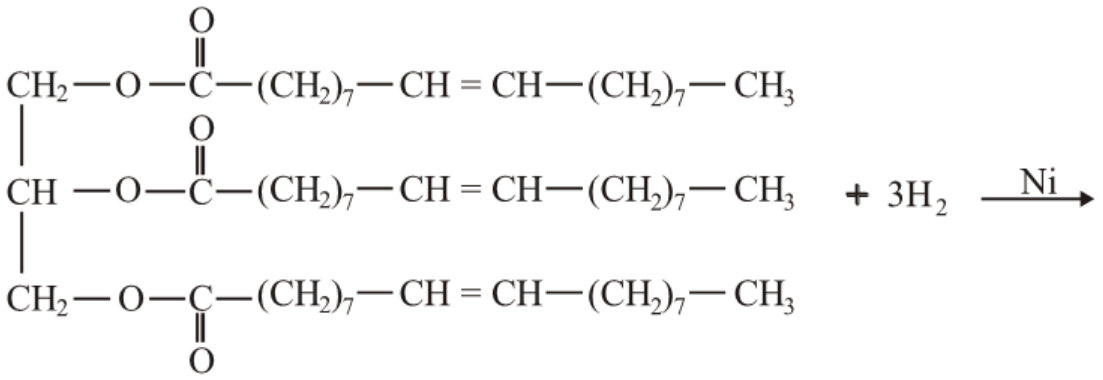
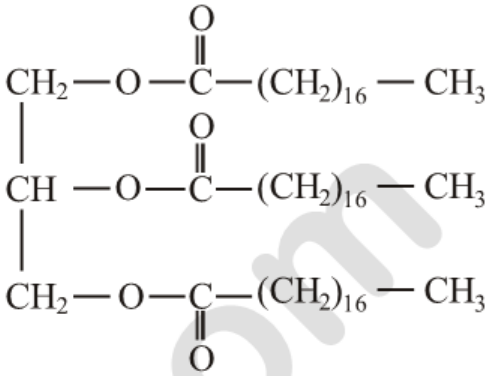


Glyceryl tristearate (an oil)



Glyceryl tristearate (a fat)

Saponification Number:

"The number of milligrams of potassium hydroxide (KOH) required to saponify one gram of fat or oil is called saponification number."

For example, one mole (806g) of glycerol tripalmitate required 168,000mg of KOH for saponification. Therefore, one gram of fat will required 168000/806mg of KOH. Hence the saponification number of glycerol tripalmitate is 208.

Rancidity of Fats or Oils:

"Fats and oils when spoiled give off an odour, it is called rancidity."

Rancidity is mainly due to hydrolytic or oxidation reaction which release foul smell of aldehydes or fatty acids. Oils obtained from sea animals have greater speed of rancidity . Sea animal oils have greater unsaturated in them.

Iodine Number:

"The number of grams of iodine which are required to react completely with 100 g of fats or oils is called iodine number."

Iodine number is used to express the degree of unsaturation of fats or oils.

The value of iodine number depends on the number of double bonds present in the acid components of the glycerides. The glycerides with no double bonds have zero iodine number.

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Acid Number:

The acid number of a fat or an oil is the amount of free fatty acids present in it. It is expressed as number of milligrams of potassium hydroxide required to neutralize one gram of fat.

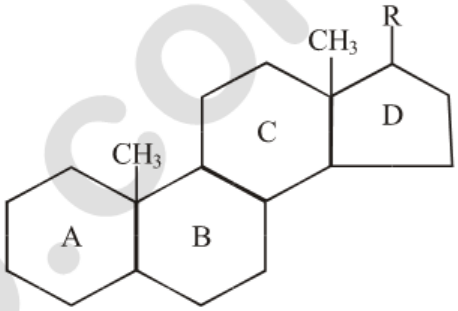
(b) Steroids:

Steroids are the second important class of lipids.

The parent nucleus of steroids has perhydrocyclopentanophenanthrene component which consists of three six membered rings. (A, B and C) and one five –membered ring(d). These rings are joined or fused to each other and have a total of 17-C atoms. Very small variations in the bonding of atoms in the ring and in the groups attached to them give rise to compounds that are remarkably diverse in their biological functions.

Examples:

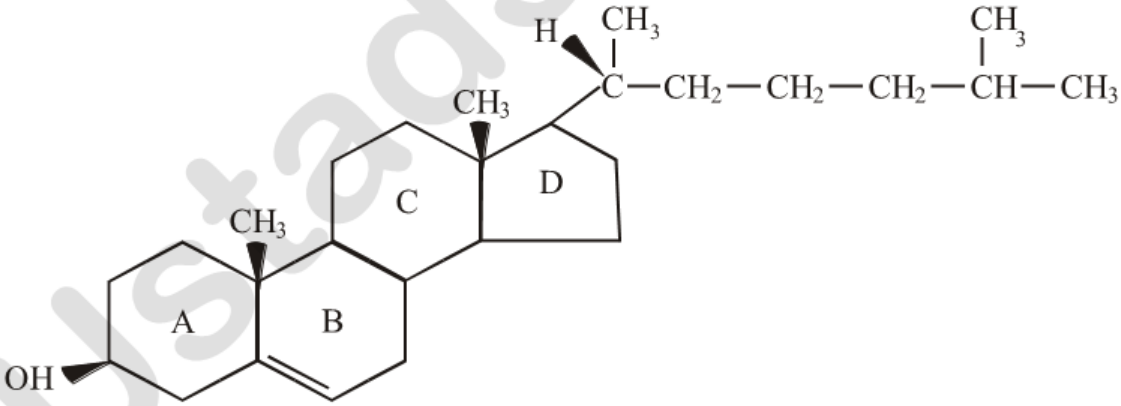
Some of the natural occurring compound belonging to steroids are cholesterol, ergosterol, male and female sex hormones and the hormones of the adrenal cortex.



Structure of Steroid Nucleus

(1) Cholesterol ($C_{27}H_{46}O$):

It is the most abundant animal sterol and occurs in all animal tissues but only in a few plants. Cholesterol is present both in the free as well as esterified formed in the blood, animal tissues, egg, yolk, various oils and fats and nerve tissues. Its increased quantities in blood makes plaque like deposits in the arteries causing blood pressure and other heart diseases.



Structure of Cholesterol

(2) Ergosterol:

It is the sterol of fungi and yeasts. When irradiated with ultraviolet rays, it is converted into ergocalciferol or vitamin D.

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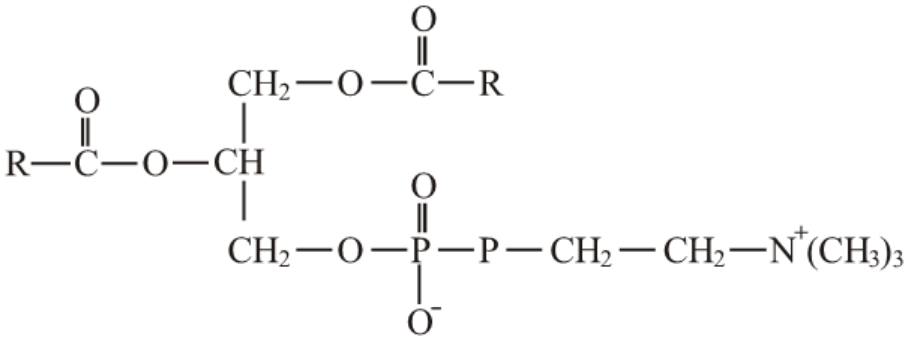
(3) Phospholipids:

Phospholipids are closely related to fats and oils. They also contain glycerol backbone. Two hydroxylic group of glycerol form ester linkage with fatty acids and third with phosphoric acid or its derivatives, for example, lecithin.



A phospholipid (Lecithin)

CLASSIFICATION OF LIPIDS

Lipids are classified as:

(1) Simple Lipids:

These are esters of fatty acids with glycerol. For example, common fats and oils.

(2) Compound Lipids:

These contain radicals in addition to fatty acids and alcohol and include glycerol phospholipids, sphingolipids, lipoproteins and lipopolysaccharides.

(3) Derived or associated lipids:

They are the hydrolytic products of above mention compounds. Sterols, vitamin D and terpenes belong to this class of lipids.

IMPORTANCE OF LIPIDS

(1) They are good source of energy and make the food more palatable.

(2) They exert an insulating effect on the nervous tissues.

(3) They are good energy reservoirs in the body.

(4) Lipids are an integral part of cell protoplasm and cell membranes.

(5) Some lipids act as precursors of very important physiological compounds. For example, cholesterol is the precursor of steroid hormones.

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ENZYMES

"The substances, usually proteins, that catalyze specific biochemical reactions are called enzymes."

Chemical Nature of Enzymes:

Enzymes are either pure proteins or contain proteins as essential components and in addition require non-protein components which are also essential for their activity. The protein component of the enzyme is called **apoenzyme** and the non-protein components is called the **co-factor or co-enzyme.** The co-factors include inorganic ions and complex organic or metallo-organic molecules, important inorganic along with their respective enzymes include Fe^{2+} (chrome oxidase) and Mg^{2+} (glucose 6-phosphatase), etc. Many enzymes contain vitamins as their co-factors, for example; nicotinamide adenine dinucleotide contains nicotinamide, vitamin and thiamine pyrophosphatase contains vitamin B_1.

Name of Enzymes:

The systematic name of enzyme has two part. First part is the name of substrate which enzyme acts and second is the suffix of enzyme "ase".

The enzyme that acts at urea are urease, which acts at cellulose is cellulase, which acts at sucrose is called sucrose, etc.

CLASSIFICATION OF ENZYMES

The commission on enzyme, appointed by the international Union of Biochemistry (IUB) classified enzymes into six main types:

(1) Oxidoreductases:

These enzymes catalyze oxidation-reduction reactions. Common examples are oxidase, dehydrogenase and peroxydase.

(2) Transferases:

These enzymes bring about an exchange of functional group such as phosphate or acryl between two compounds, for example; phospho-translterases, etc.

(3) Hydrolases:

These enzymes catalyze hydrolysis. They include proteases called protolytic enzymes.

(4) Lyases:

These enzymes catalyze the addition of small molecules like ammonia, water or carbon dioxide to double bonds or removal of these from double bonds. An example is the conversion of fumaric acid to maleic acid in the presence of fumarase enzyme.

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(5) Isomerases:

These enzymes catalyze the transfer of groups within molecules to yield isomeric forms of the substrate, for example phospho-glyceromutases.

(6) Ligases:

These enzymes link two molecules together through breaking of high energy bonds, for example; acetyl-S-COH, a corboxylase and succinic thiokinase.

Table – Classification of Enzymes

Main class	Some sub classes	Types of reaction catalyzed
Hydrolases	Lipases	Hydrolysis of ester group
	Nucleases	Hydrolysis of phosphate group
	Proteases	Hydrolysis of an amino group
Isomerases	Epimerases	Isomerization of a chirality center
Ligases	Carboxylases	Addition of CO_2
	Synthetases	Formation of new bonds
Lyases	Decarboxylases	Loss of CO_2
	Dehydrases	Loss of H_2O
Oxidoreductares	Dehydrogenases	Formation of double bond by removal of H_2
	Oxidases	Oxidation
	Reductases	Reduction
	Kinases	Transfer of a phosphate group
Transferases	Transaminases	Transfer of an amino group

PROPERTIES OF ENZYMES

(1) Specificity:

Enzyme are specific in their action. Specificity of an enzyme depends upon the active sites of the enzymes. Every enzyme has a characteristic site which combine with substrate is called active site. The substance at which enzyme acts is called substrate. In enzyme catalyse only one type or reaction and are specific in nature. For example; hexokinase catalyses the conversion of hexoses like glucose, fructose and mannose to their 6-phosphate derivatives but glucokinase is specific for glucose only.

(2) Protein Nature:

Enzymes with few exceptions are protein in nature. They are produced by living cells but act in vivo as well as in vitro. Enzymes which acts in the body are vivo or outside the body are called vitro.

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(3) The Direction of Enzymes Reaction:

Most enzymatic reactions are reversible i.e. the same enzyme can catalyze reactions in both directions.

(4) Isoenzymes:

These are the enzymes from the same organisms which catalyze the same reaction but are chemically and physically distinct from each other.

(5) Efficiency of enzymes:

An enzyme lowers the energy of activation and speed up a chemical reaction. Enzymes have very amazing efficiency. Some enzymes increases the efficiency upto to 20 times.

FACTOR AFFECTING THE ACTIVITY OF ENZYMES

(1) Enzyme Concentration:

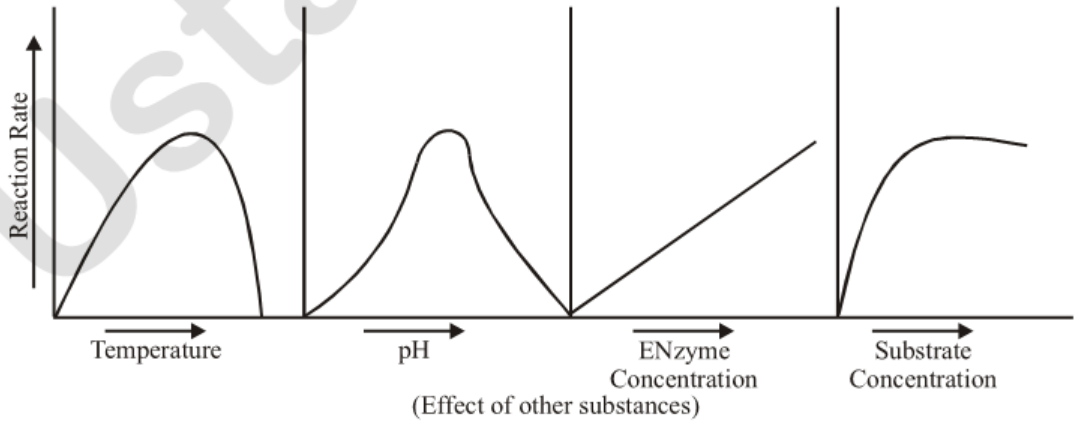
The rate of an enzymatic reaction is **directly proportional** to the concentration of the substrate. The rate of reaction is also directly proportional to the square root of the concentration of enzyme. It means that the rate of reaction also increases with the increasing concentration of enzyme.

(2) Temperature:

The enzymatic reaction occurs best at or around37°C which is the average normal body temperature. The rate of chemical reactions is increased by a rise in temperature but this is true only over limited range of temperature. The enzymes usually destroy at high temperature. The activity of enzymes is reduced at low temperature. The temperature at which an enzymes reaction occurs at the fastest rate is called its optimum temperature.

(3) Effect of pH:

Just like temperature, there is also an optimum pH at which an enzyme will catalyze will catalyze the reaction at the maximum rate. For example, the optimum pH of salivary amylase is 6.4 to 6.9.



Effect of various factors on reaction rate

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(4) Other Substances:

The enzyme action is also increased or decreased in the presence of some other substances such as **co-enzymes, activators and inhibitors.** For example, some enzymes consist of simple proteins only such as insulin. Most of the enzymes are, however, the combination of a co-enzyme and an apo-enzyme.

Activators are the inorganic substances which increase the enzyme activity. For example; Mg^{2+} ions are the activators of phosphatase and carbonic anhydrase enzymes respectively.

Inhibitors are the substances which reduce the enzyme activity.

(5) Radiations:

Generally enzymes are readily inactivated by exposure to ultra-violet light, beta rays, gamma rays and X-rays.

IMPORTANCE OF ENZYMES

(1) Enzymes are of great biological importance and are of great help in the diagnosis of certain diseases. Some examples are, alkaline phosphatase is raised in rickets and obstructive jaundice, lactic dehydrogenase or LDH-1 is raised in heart diseases.

(2) Many enzymes have proved very useful as drugs. For example; thrombin is used locally to stop bleeding.

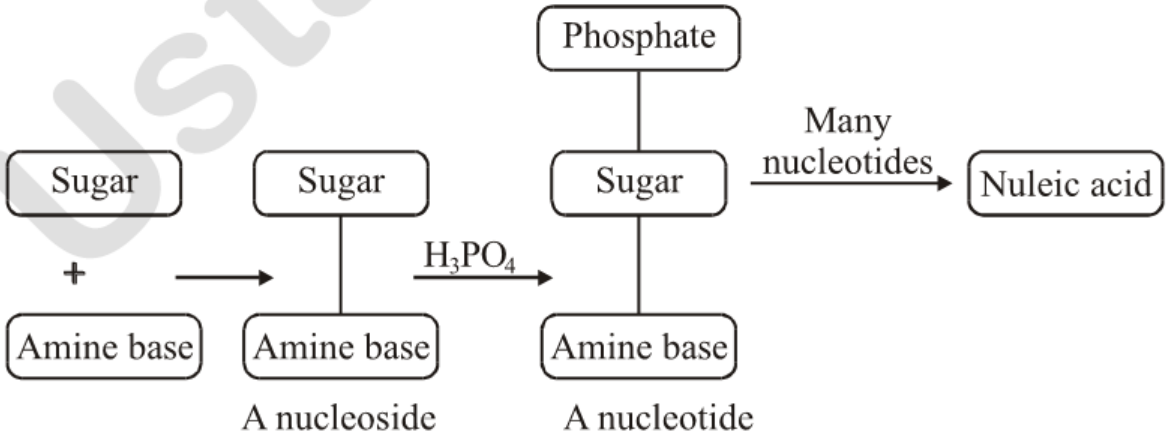
(3) Many enzymes are used for cancer treatment. For example, L-asparaginase has proved very useful of blood cancer in children.

NUCLEIC ACID

Compounds of Nuclei Acid:

Nucleic acids, deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA) are the chemical carriers of a cell genetic information.

Nucleic acids are biopolymers made up of nucleotides joins together to form a long chain. Each nucleotide is composed of nucleoside bonded to a phosphate group and each nucleoside is composed of an aldopentose sugar linked to heterocyclic purine or pyrimidine base.



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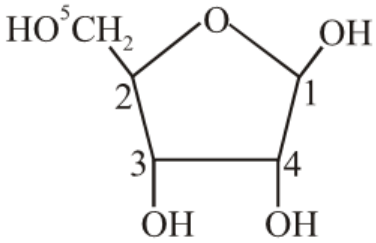
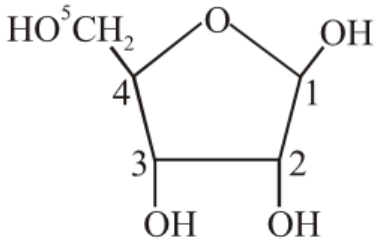
(i) The sugar component in RNA is ribose and in DNA is 2-deoxyribose.

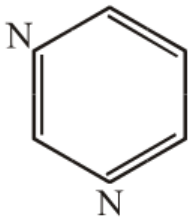


Ribose

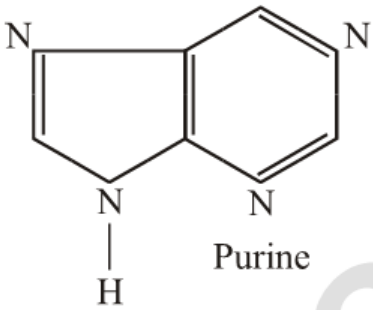


2-Deoxyribose

(ii) Amine bases of nucleotides are purines and pyrimidines.

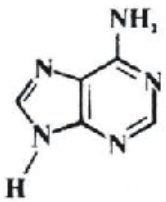


Pyrimidine

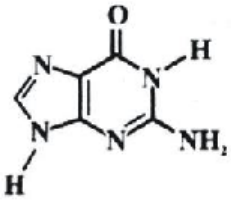


Purine

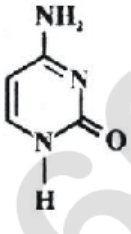
Purines are adenine and guanine while **pyrimidines** are cytocine and thymine.



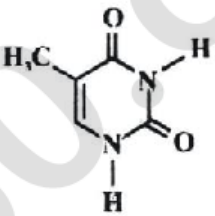
Adenine (A)
DNA
RNA



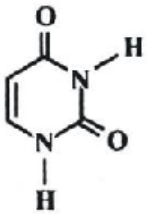
Guanine (G)
DNA
RNA



Cytosine (C)
DNA
RNA



Thymine (T)
DNA



Uracil (U)
RNA

DNA contain four bases adenine, guanine, cytosine and thymine. RNA contain adenine, guanine, cytocine and uracil instead of thymine.

Two types of nuclei acids have been discovered, deoxyribonuclec acid (DNA) and ribonucleic acid (RNA). In the body, nucleic acid occur as part of the conjugated proteins called nucleoproteins. The nucleic acids direct the synthesis of proteins. Cancer research involves an extensive study of nucleic acids.

Functions of Nucleic Acid:

Nucleic acids were first demonstrated in the nuclei of puss cells in 1868 and in sperm heads in 1872 by Friedrik Miescher. They are present in every living cell as well as in viruses and have been found to be the essential components of the normal growth and development of each and every living cell. The nucleic acids are responsible for the two fundamental functions which are common to all living organisms, there are (a) their ability to reproduce, store and transmit genetic information and (b) to undergo mutation.

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DIFFERENCE BETWEEN DNA AND RNA

DNA and RNA differs in three ways:

(1) The sugar in RNA is ribose while the sugar is DNA is 2-deoxyribose.

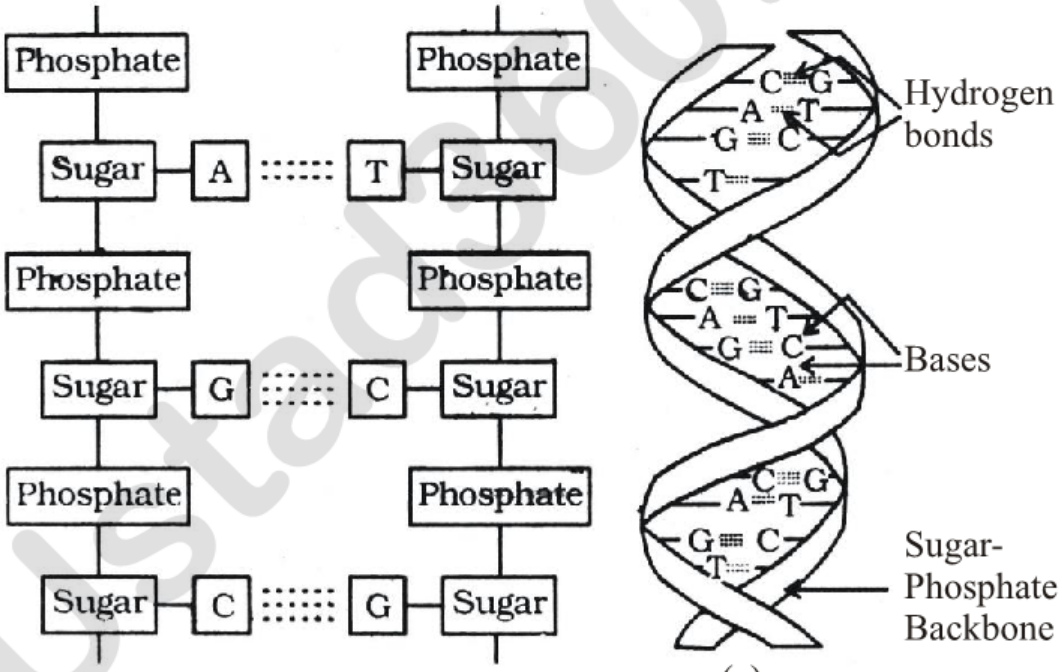
(2) Four different bases are found in DNA cytosine (C), thymine (T), adenine (A) and guanine (G). In RNA, thymine does not occur and its place is taken by uracil (U).

(3) DNA is always double stranded while RNA is usually single stranded.

REPLICATION OF DNA

DNA preserve the genetic information's and pass it from one generation to the next generation. The double stranded structure of DNA was first deduced by James Watson and Francis Crick in 1953. This was the discovery that initiated the field of molecular biology.

Replication of DNA is an enzyme catalyzed process. As the strand separate and bases are exposed, new nucleotides line up on each strand in a complementary manner, A to T and C to G and two new strand begins to grow. Each new strand is complementary to its old template strand and two new identical DNA double helices are produced. Since each of the new DNA molecules contains one strand of old DNA and one strand of new DNA. This process ids called replication.



(a)

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EXERCISE

Q.1 Fill in the blanks:

(i) Macromolecules are built up from small units called ————.

(ii) Nylon is a polyamide and terylene is a ————.

(iii) Nylon is prepared by the reaction of ———— and hexamethylenediamine.

(iv) Based on their thermal properties, plastics are divided into ———— main classes.

(v) Polyvinyl chloride is a ———— plastic.

(vi) Glucose is stored as ———— in the liver.

(vii) Glucose and fructose are water ———— carbohydrates.

(viii) Protein after digestion changes to ————.

(ix) Purine and pyrimidine are ———— of nucleic acids.

(x) Addition of a plasticizer ———— the flexibility of the polymer.

ANSWERS

(i)	monomer	**(ii)**	polyester	**(iii)**	adipic acid
(iv)	two	**(v)**	thermo	**(vi)**	glycogen
(vii)	soluble	**(viii)**	amino acid	**(ix)**	bases
(x)	increase				

Q.2 Indicate True or False:

(i) Nylon 6, 6 and terylene are condensation polymers.

(ii) The disposal of plastics does not cause any pollution problem.

(iii) Fructose is a polysaccharide carbohydrate.

(iv) Human beings get no food nutrient from cellulose.

(v) The most abundant and the most important steroid in the human body is vitamin D.

(vi) Enzymes are the compounds containing C, H and O only.

(vii) The degree of unsaturation of fats is measured by their iodine number.

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(viii) Activity of an enzyme varies with temperature and pH.

(ix) Nucleic acids are biological catalysts.

(x) The nucleic acids are responsible for protein synthesis in the human body.

ANSWERS

(i)	True	**(ii)**	False	**(iii)**	False	**(iv)**	True	**(v)**	False
(vi)	False	**(vii)**	True	**(viii)**	True	**(ix)**	False	**(x)**	True

Q.3 Multiple choice questions. Encircle the correct answer:

(i) In which of these processes are small organic molecules made into macromolecules:

(a) The cracking of petroleum fractions

(b) The fractional distillation of crude oil

(c) The polymerization of ethene

(d) The hydrolysis of proteins

(ii) Which of these polymers is an addition polymer:

(a) Nylon-6, 6 **(b)** Polystyrene

(c) Terylene **(d)** Epoxy resin

(iii) Which of these polymers is a synthetic polymer:

(a) Animal fat **(b)** Starch

(c) Cellulose **(d)** Polyester

(iv) Plastics are a pollution problem because many plastics:

(a) Are made from petroleum **(b)** Are very inflammable

(c) Burn to produce toxic fumes **(d)** Decompose to produce toxic products

(v) The fibre which is made from acrylonitrile as monomer:

(a) PVC **(b)** Rayon fibre

(c) Acrylic fibre **(d)** Polyester fibre

(vi) A polymeric substance that is formed in the liquid state and then hardened to a rigid solids is called a:

(a) Fibre **(b)** Plastic

(c) Varnish **(d)** Polyamide resin

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(vii) Vegetable oils are:

(a) Unsaturated fatty acids

(b) Glycerides of unsaturated fatty acids

(c) Glycerides of saturated fatty acids

(d) Essential oils obtained from plants

(viii) Which one of the following elements is not present in all proteins:

(a) Carbon **(b)** Hydrogen

(c) Nitrogen **(d)** Sulphur

(ix) Which one of the following is a water soluble vitamin:

(a) Niacin **(b)** Riboflavin

(c) Trypsin **(d)** Ascorbic acid

(x) Which one of the following enzymes brings about the hydrolysis of fats:

(a) Urease **(b)** Maltase

(c) Zymase **(d)** Lipase

(xi) The reaction between fat and NaOH is called:

(a) Esterification **(b)** Hydrogenolysis

(c) Fermentation **(d)** Saponification

(xii) Which one of the following statements about glucose and sucrose is incorrect:

(a) Both are soluble in water **(b)** Both are naturally occurring

(c) Both are carbohydrates **(d)** Both are disaccharides

ANSWERS

(i)	(c)	**(ii)**	(b)	**(iii)**	(d)	**(iv)**	(c)	**(v)**	(c)
(vi)	(b)	**(vii)**	(b)	**(viii)**	(d)	**(ix)**	(d)	**(x)**	(d)
(xi)	(d)	**(xii)**	(d)						

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Q.4 Explain the following terms:

(a) Addition polymer **(b) Condensation polymer**

(c) Thermoplastic **(d) Thermosetting plastic**

Ans.

(a) Addition Polymer: The polymers which are formed by the repeated addition of monomers is called addition polymer. Monomers are unsaturated compounds (derivatives of ethene). For example: PVC, PVA, Polyethylene.

(b) Condensation Polymer: When two monomers join together to produce a polymer along with the elimination of a small molecule like water then the resultant polymer is called as condensation polymer. e.g., Polyester, Bakelite.

(c) Thermoplastic: Such type of plastic which can be softened repeatedly when heated and hardened when cooled with a little change in properties. e.g., PVC pipes.

(d) Thermosetting Plastic: The polymers which become hard on heating and cannot be softened again are called thermosetting polymers. A thermosetting polymer decomposes instead of melting. e.g., Epoxy resins.

Q.5 Write notes on:

(a) Polyester resins **(b) Polyamide resine**

(c) Epoxy resins

Ans. Detailed question. See text book.

Q.6 What is the repeating unit in each of the following polymers?

(a) Polystyrene **(b) Nylon-6, 6**

(c) Teflon **(d) Orlon**

Ans.

(a) Polystyrene: In polystyrene repeating unit is styrene ($H_2C = CH\text{-}C_6H_5$)

$$nCH_2{=}\underset{\underset{C_6H_5}{|}}{CH} \longrightarrow \text{—}[CH_2\text{—}\underset{\underset{C_6H_5}{|}}{CH}]_n$$

Styrene Polystyrene

(b) Nylon-6, 6: In nylon-6, 6 repeating units are:

Adipic acid $HOOC\text{—}(CH_2)_4\text{—}COOH$

Hexamethylene diamine $H_2N\text{—}(CH_2)_6\text{—}NH_2$

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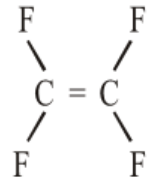
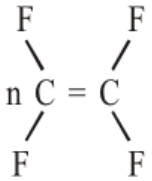
$$nHOOC—(CH_2)_4—COOH + nH_2N—(CH_2)_6—NH_2 \xrightarrow[-H_2O]{280°C}$$

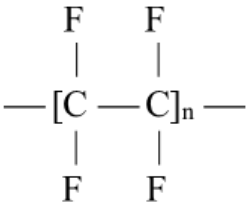
$$—\overset{O}{\overset{\|}{C}}—(CH_2)—\overset{O}{\overset{\|}{C}}—[NH(CH_2)_6NHC(CH_2)_4—\overset{O}{\overset{\|}{C}}—]_n NH(CH_2)_6NH—$$

(c) **Teflon:** In teflon repeating unit is tetrafluoro ethene





Tetrafluoro ethene



Polytetrafluoro ethene (teflon)

(d) **Orlon:** In orlon repeating unit is acrylonitrile $CH_2=CH–CN$

$$n\,CH_2 = CH—CN \longrightarrow \left[CH_2—\underset{\underset{CN}{|}}{CH}\right]_n$$

Acrylonitrile Orlon fiber or acrylic fiber

Q.7 What are carbohydrates and how are they classified?

Ans. Descriptive question. See text book for details.

Q.8 Point out one difference between the compounds in each of the following pairs:

(a) Glucose and fructose **(b) Sucrose and maltose**

(c) Cellulose and starch

Ans.

(a) Glucose is polyhydroxy aldehyde and fructose is polyhydroxy ketone.

(b) Maltose on hydrolysis give glucose:

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Maltase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose on hydrolysis gives glucose and fructose:

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Sucrase}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

(c) Starch is polymer of α-D-glucose, cellulose is polymer of β-D-glucose.

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Q.9 What are lipids? In what way fats and oils are different?

Ans. Descriptive question. See text book for details.

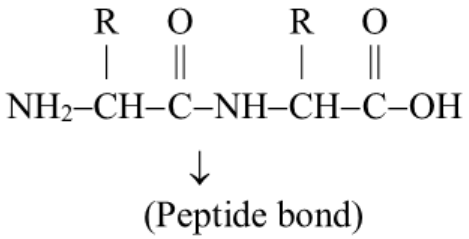
Q.10 Define saponification number and iodine number. Discuss the term rancidity.

Ans. Definitions see in text book.

Q.11 What is the difference between a glycoside linkage and a peptide linkage?

Ans. **Glycoside Linkage:** This is present in oligosaccharides and polysaccharides. Whenever monosaccharides combine together with the elimination of H_2O molecule, the resulting bond is Glycoside. e.g., In sucrose molecule.

Peptide Linkage: This linkage is present in proteins. Amino acids combine together through a peptide bond with the elimination of water molecule. e.g.,



Q.12 What is the chemical nature of enzymes? Discuss the classification of enzymes.

Ans. Detailed question. Consult text book.

Q.13 What are nucleic acids? Write down the role of DNA and RNA in life.

Ans. **Nucleic Acids:** See in text book.

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DO YOU KNOW?

(1) Satudinger (1920) gave the idea of formation of polymers.

(2) The number of repeating units which determine the length of the polymer is called degree of polymerization.

(3) The type of addition polymers which is formed by the polymerization of single type of monomer is called homopolymer.

(4) The type of polymer formed by the polymerization of two types of monomers is called copolymer.

(5) Orlon is used for the manufacture of textile fibre.

(6) Vinyl acetate is used in chewing gums.

(7) Formula of raffinose is $C_{18}H_{32}O_{16}$.

(8) Natural starch contains 10 – 20% amylose and 80 – 90% amylopectin.

(9) Amylose is water soluble but amylopectin is insoluble in water.

(10) The number of milligrams of KOH required to saponify one gram of fat or oil is called saponification number.

(11) The number of grams of iodine which will react with 100g of oil or fat is called iodine number.

(12) Glucose is stored in the liver as glycogen.

(13) Nylon is a polyamide but terylene is a polyester.

(14) Vit-A ($C_{20}H_{30}O$) is called beauty-vitamin.

(15) Deficiency disease of Vit-A is night blindness.

(16) Formula of Vit-C (Ascorbic acid) is $C_6H_8O_6$.

(17) Deficiency disease of Vit-C is scurvy.

(18) Formula of Vit-D is $C_{28}H_{44}O$.

(19) Deficiency disease of Vit-D is rickets.

(20) Formula of Vit-B_{12} $C_{63}H_{88}N_{14}O_{14}PCo$
(Cyanocobalamine)

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