

26.

BIOMOLECULES AND POLYMERS

1. INTRODUCTION

The study of chemical make-up and structure of living matter and of the chemical changes that takes place within them is called biochemistry.

The various activities of living organisms are regulated by complex organic molecules, such as carbohydrates, lipids, proteins and nucleic acids, called biomolecules.

2. CARBOHYDRATES

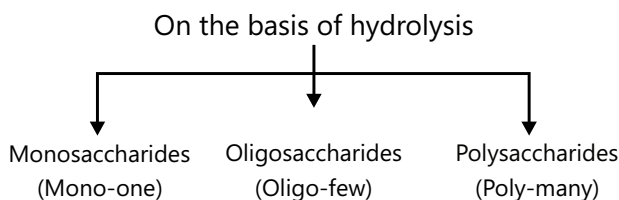
Carbohydrates are principally plants products and are a part of an extremely large group of naturally occurring organic compounds. Cane sugar, glucose, starch and so on are a few examples of carbohydrates. The general formula for carbohydrates is $C_x(H_2O)_y$. Carbohydrates are generally hydrates of carbon, which is where the name was derived. So, carbohydrates on hydrolysis produce polyhydroxy aldehydes or polyhydroxy ketones.

2.1 Classification of Carbohydrates

(a) On the basis of Physical Characteristics

- (i) **Sugar:** Characteristics of sugars are crystalline substances, taste sweet and readily water soluble. Because of their fixed molecular weight, sugars have sharp melting points. A few examples of sugars are glucose, fructose, sucrose, lactose, etc.
- (ii) **Non-Sugars:** Amorphous, Tasteless, water insoluble substances with variable melting points e.g., Starch.

(b) On the basis of Hydrolysis

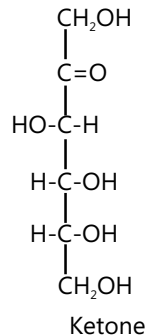
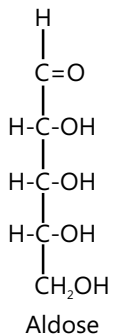


Flowchart 26.1: Classification based on Hydrolysis

Monosaccharides: A carbohydrate that can be hydrolyzed only once to break down into simpler units of polyhydroxy aldehyde or ketone is called monosaccharide. These include glucose, mannose, etc.

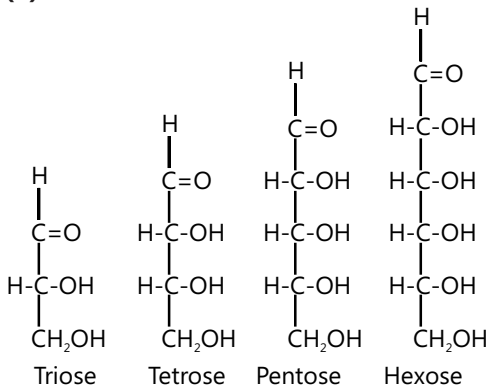
Monosaccharide classification

(i) Based on location of $\left(\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array} \right)$



Aldehyde (-CHO), ketone $\left(\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array} \right)$

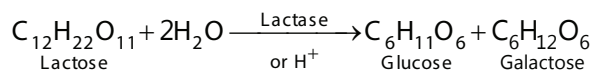
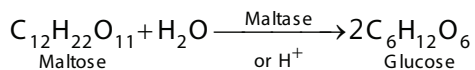
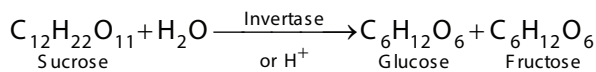
(ii) Based on number of carbon atoms in the chain



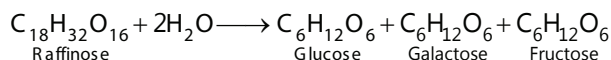
Can be either aldose or ketose sugar.

Oligosaccharides: Sugars that on hydrolysis produce two or more molecules of monosaccharides are called oligosaccharides. These are further classified as di-, tri- or tetrasaccharides, etc.

- **Disaccharides:** These are sugars that produce two molecules of the same or different monosaccharides on hydrolysis. Examples are sucrose, maltose and lactose. An example for disaccharides is sucrose: $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.



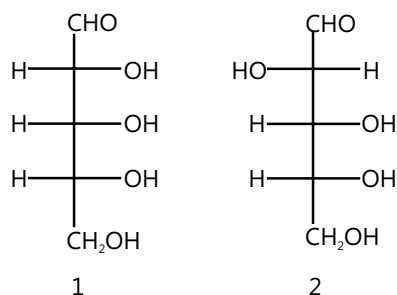
- **Trisaccharides:** Sugars that yield three molecules of the same or different monosaccharides on hydrolysis are called trisaccharides. An example of trisaccharides is Raffinose $\text{C}_{18}\text{H}_{32}\text{O}_{16}$



2.3 Epimers

Epimers are essentially diastereomers that contain multiple chiral centers that are absolutely separate from each other in configuration at only one chiral center.

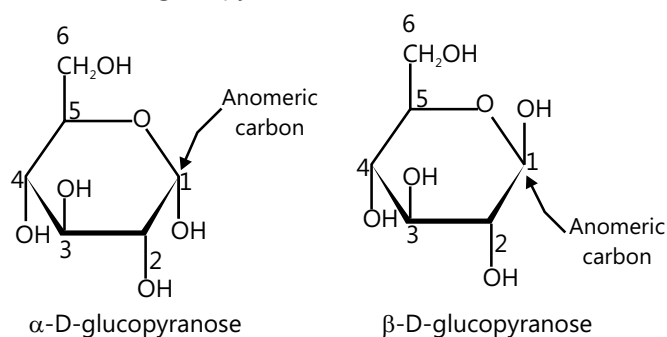
Example:



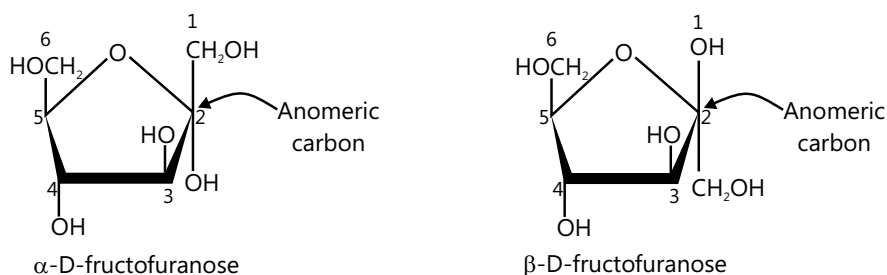
2.4 Anomers

Cyclic monosaccharides or glycosides that are epimers, differing from each other in the configuration of C-1 if they are aldoses or of C-2 if they are ketoses are called anomers. The epimeric carbon in such compounds is known as anomeric carbon or anomeric center.

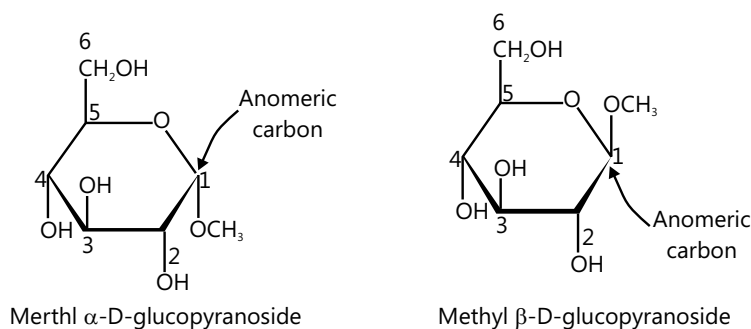
Example 1: α -D-Glucopyranose and β -D-glucopyranose are anomers.



Example 2: α -D-Fructofuranose and β -D-fructofuranose are anomers.



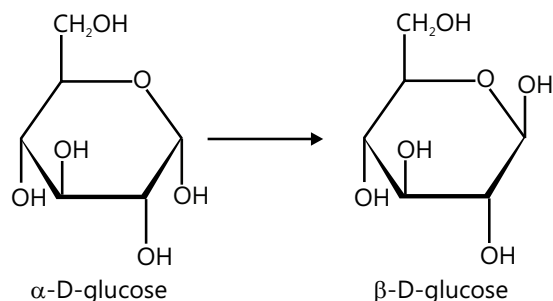
Example 3: Methyl α -D-glucopyranoside and methyl β -D-glucopyranoside are anomers.



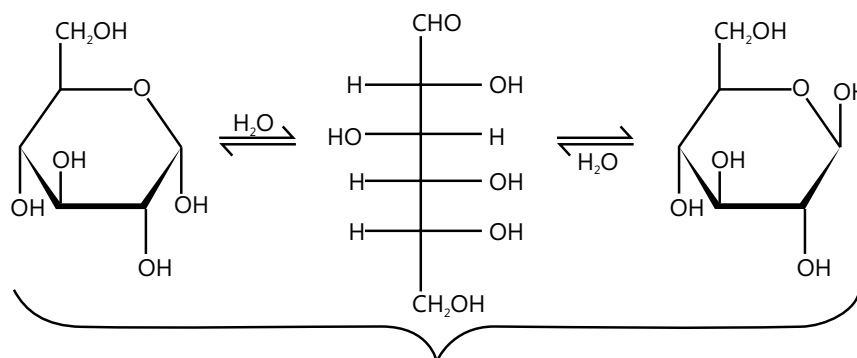
2.5 Mutarotation

Mutarotation is commonly used in carbohydrate chemistry to describe the change in specific rotation of a chiral compound due to epimerization.

For example, the monosaccharide D-glucose can be found in two cyclic forms, α -D-glucose ($[\alpha]_D^{25} = +112$) and β -D-glucose ($[\alpha]_D^{25} = +18.7$), which are epimers and are available as pure compounds.

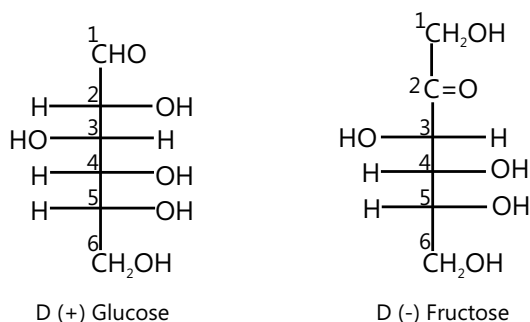


On adding water to one of the cyclic forms of D-glucose, through reversible epimerization it changes to the other via open-chain form, while the specific rotation of the solution gradually changes, until it reaches the equilibrium value $+52.7^\circ$.



2.6 Representation of Structures of Glucose and Fructose

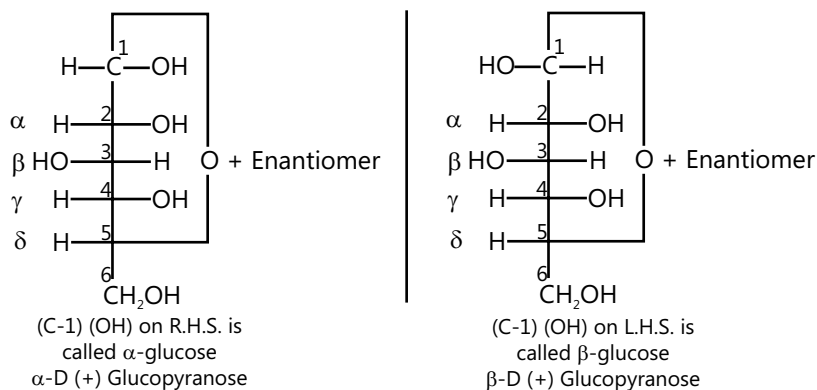
(a) Open chain structures (Fischer projection):



D symbolizes the comparative configuration of C-5 -OH group with relation to D-glyceraldehyde, which these are prepared from. Here, (+) and (-) refer to optical rotation. Naturally, D-glucose is (+) or dextrorotatory but D-fructose is (-) or laevorotatory.

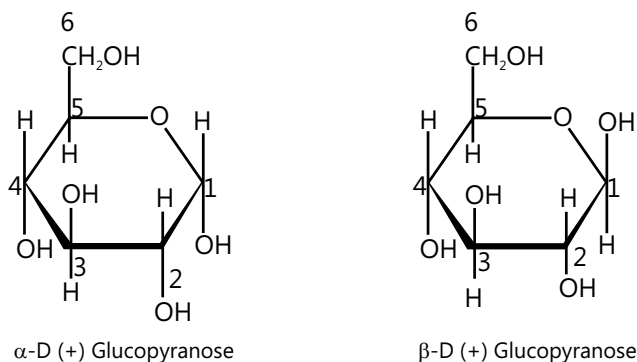
(b) Cyclic structures of glucose: The CHO group of glucose reacts with either C-5 -OH group or with C-4 -OH group to form stable six- and five-membered cyclic rings, respectively, having hemiacetalic linkage. When -CHO group reacts with C-6 -OH group, seven-membered ring is formed, or four-membered ring is formed on reaction with C-3 -OH; both are unstable.

(i) -CHO reaction with C-5 -OH group produces two anomeric glucose: In such a case, a six-membered ring, pyranose, is formed.

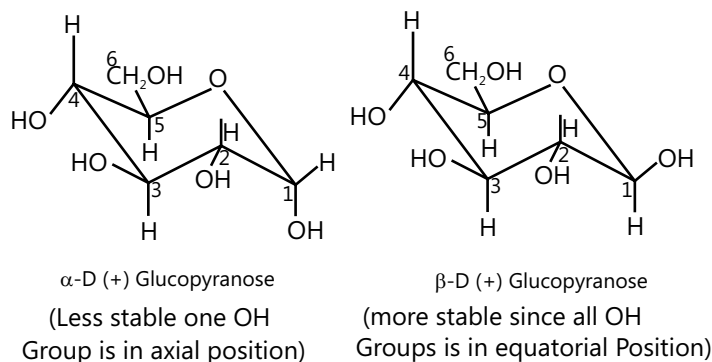


Pyranose refers to six-membered ring, like in pyran , or to δ -linkages, since there is hemiacetalic linkage is between C-1 and C-5 δ -C atom. δ -C atom is formed next to the functional group -CHO and β next to the α -C atom and so on.

- (ii) Haworth representation: English chemist W. N. Haworth (awarded the Nobel Prize in chemistry for his study of carbohydrate in 1937) established cyclic structure of glucose. Below, R.H.S. shows the -OH group above the plane of the ring in Haworth structures while as per Fischer projection, on the L.H.S., it is shown below the plane of the ring .

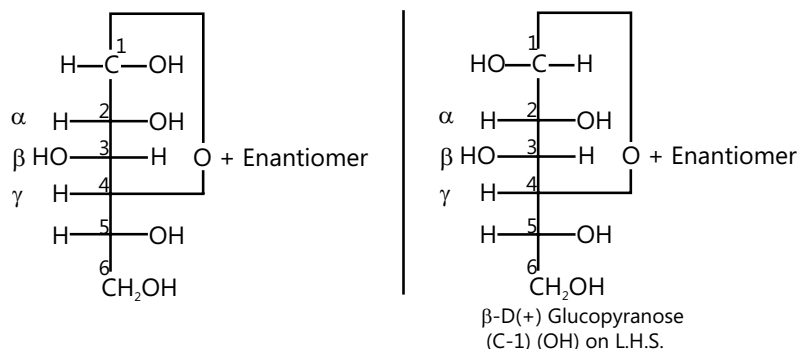


- (iii) Chair-form conformation structures: Haworth projection structures are transformed to the chair conformation. The -OH groups present below the plane of the ring in Haworth structures remain below the plane in the chair conformation as well.

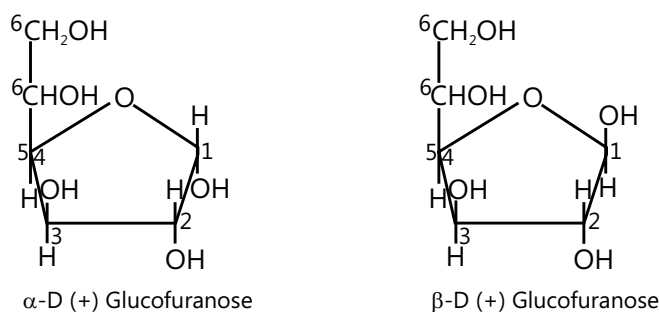


- (iv) -CHO reaction with C-4 -OH group produces two anomeric glucose: In this case, five-membered ring (furanose) is formed. Furanose refers to five-membered ring, like in furan, or to γ -linkage, as the hemiacetal linkage is between C-1 and C-4 γ -C atom. Not all carbohydrates exist in equilibrium as six-membered hemiacetal rings; in several compounds, the ring is five-membered, as in fructose. However, glucose naturally occurs

only in pyranose form (six-membered), and in small extent in furanose form, which is in equilibrium with five-membered hemiacetal ring,.

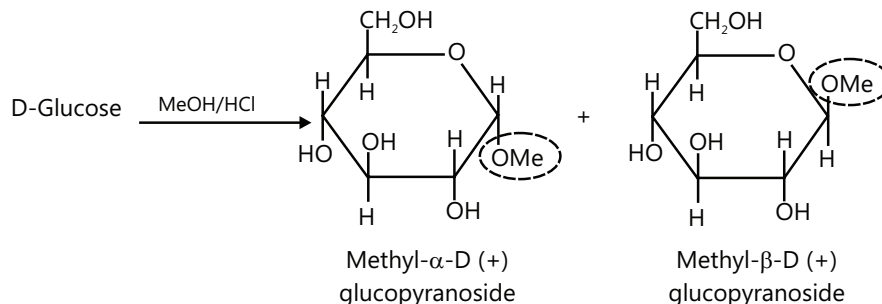


Haworth representation



Structures of Glucosides

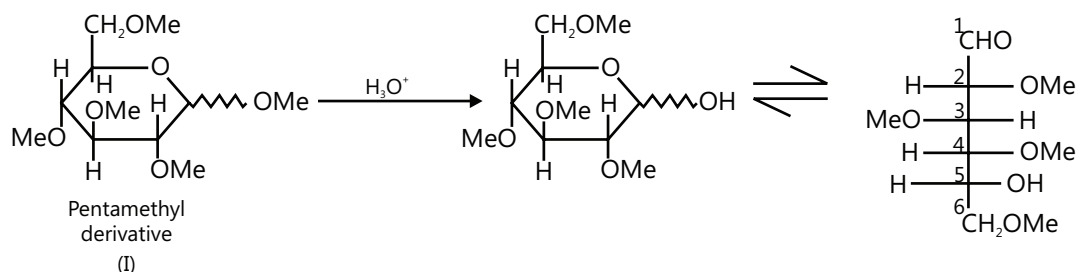
D-Glucose on reaction with MeOH + HCl gives α - and β - D-glucopyranoside.



Methyl glucoside reacts with an excess of $\text{Me}_2\text{SO}_4/\text{NaOH}$ to produce pentamethyl derivatives. Presence of many electronegative O atoms in the -OH groups of monosaccharides makes them more acidic than alcohols, and all of them exert -I effect on the nearby -OH groups. In aqueous NaOH, the -OH groups get converted to alkoxide ion (RO^-) that reacts with Me_2SO_4 by $\text{S}_{\text{N}}2$ mechanism and forms methyl ether. This process is called exhaustive methylation.

The OMe groups at C-2, C-3, C-4 and C-6 of the pentamethyl derivative are ordinary ether groups. These groups are stable in diluted aqueous acid, since ether groups are cleaved by heating with concentrated HBr or HI.

The OMe groups at C-1 are formed partly of acetal linkage (it is glucosidic) and hence are different from others.

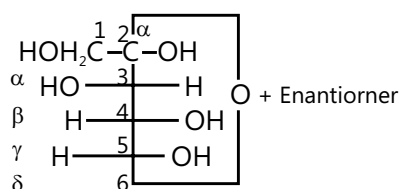
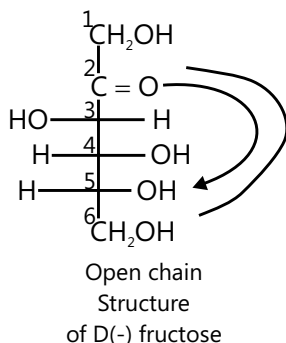


Hydrolysis of the glycosidic -OMe group occurs when pentamethyl derivatives are treated with dilute aqueous acid to give 2, 3, 4, 6-tetra-O-methyl-D-glucose. (O in the name refers that the Me groups that are attached to O atoms.)

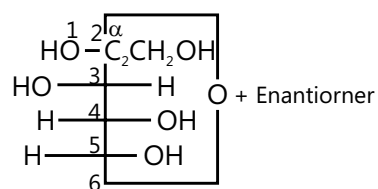
In the open-chain structure, absence of Me group at C-5 because it was originally a part of the cyclic hemiacetal linkage of D-glucose.

Representation of Structure of Fructose

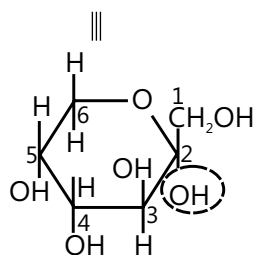
1. Haworth representation



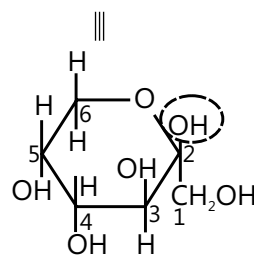
α -D(-) Fructopyranose
(C=O) reacts with C-6 OH
Six-membered pyranose
Ring of δ -linkage
OH group on R.H.S. is α



β -D(-) Fructopyranose
OH group on L.H.S. is β

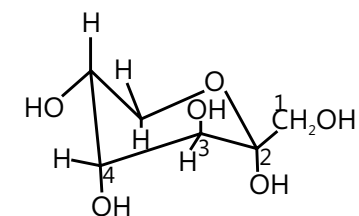


α -D (-) Fructopyranose

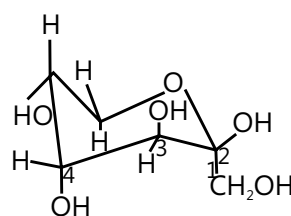


β -D (-) Fructopyranose

2. Chair-form conformational structures



α -D(-) Fructopyranose
More stable, since
bulky (CH₂OH) group
on equatorial position



β -D(-) Fructopyranose
Less stable, since
bulky (CH₂OH) group
on axial position

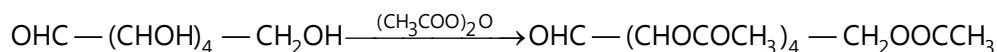
MASTERJEE CONCEPTS

- (a) **Carbohydrates:** Polyhydroxy aldehydes or ketones with general formula $C_x(H_2O)_y$.
- (b) Classification based on hydrolysis:
- (i) **Monosaccharides:** Simplest carbohydrates that cannot be hydrolyzed any further.
 - (ii) **Oligosaccharides:** On hydrolysis gives two to nine units of monosaccharides.
 - (iii) **Polysaccharides:** On hydrolysis gives many units of monosaccharides.
- (c) **Reducing sugar:** Sugars that reduce Fehling's and Tollen's solutions.
- (d) **D-L configuration:** Refers to relative configuration of the (-OH) group with respect to glyceraldehydes.
- (e) **Epimers:** Have more than one stereocenter but differ in configuration about only stereocenter.
- (f) **Anomers:** Differ in configuration about the acetal or hemiacetal carbon.
- (g) All anomers are epimers but the reverse is not true.
- (h) **Mutarotation:** Change in specific rotation of an optically active compound when dissolved in solution is called mutarotation.
- (i) β -D glucose is more stable compared to α -D glucose, since all -OH groups are in equatorial position.
- (j) In solution, β -D glucose and α -glucose are both in equilibrium.
- (k) Fructose being a polyhydroxy ketone still gives positive test for Tollen's, Benedict's and Fehling's reagent and thus is a reducing sugar.

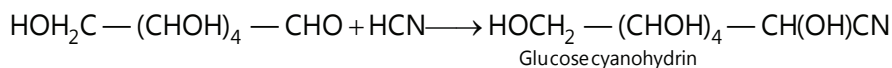
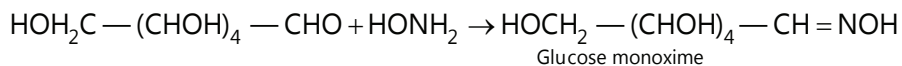
Vaibhav Krishnan (JEE 2009, AIR 22)

Chemical Reactions: Glucose has one aldehyde group, one primary ($-\text{CH}_2\text{OH}$) group and four secondary ($-\text{CHOH}$) hydroxyl groups, and gives the following reactions:

- (a) Acetylation of glucose with acetic anhydride forms a penta-acetate, proving the presence of five hydroxyl groups in glucose.

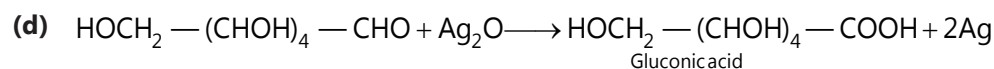


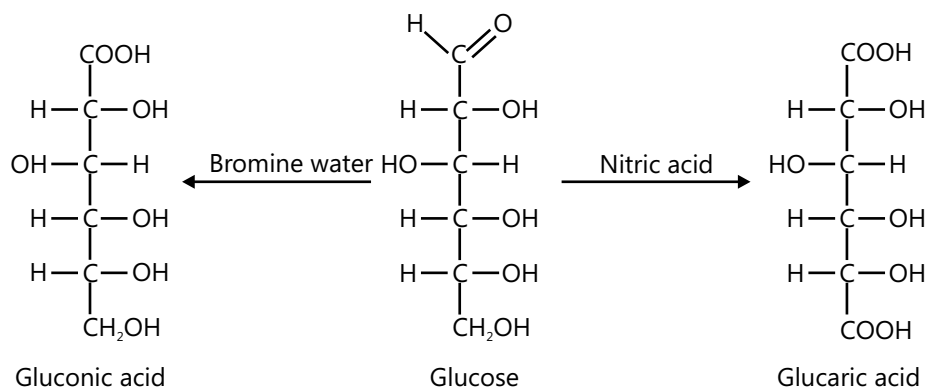
- (b) Glucose reacts with hydroxylamine to form monoxime and adds up a molecule of hydrogen cyanide to form a cyanohydrin.



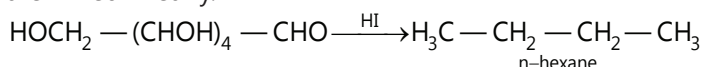
The above reactions validate the occurrence of a carbonyl group in glucose.

- (c) Ammonical silver nitrate solution (Tollen's reagent) is a reducing sugar reducing to metallic silver. Similarly, Fehling's solution is reduced to reddish brown cuprous oxide. On the other hand, it itself gets oxidized to gluconic acid. This proves the presence of an aldehydic group in glucose.

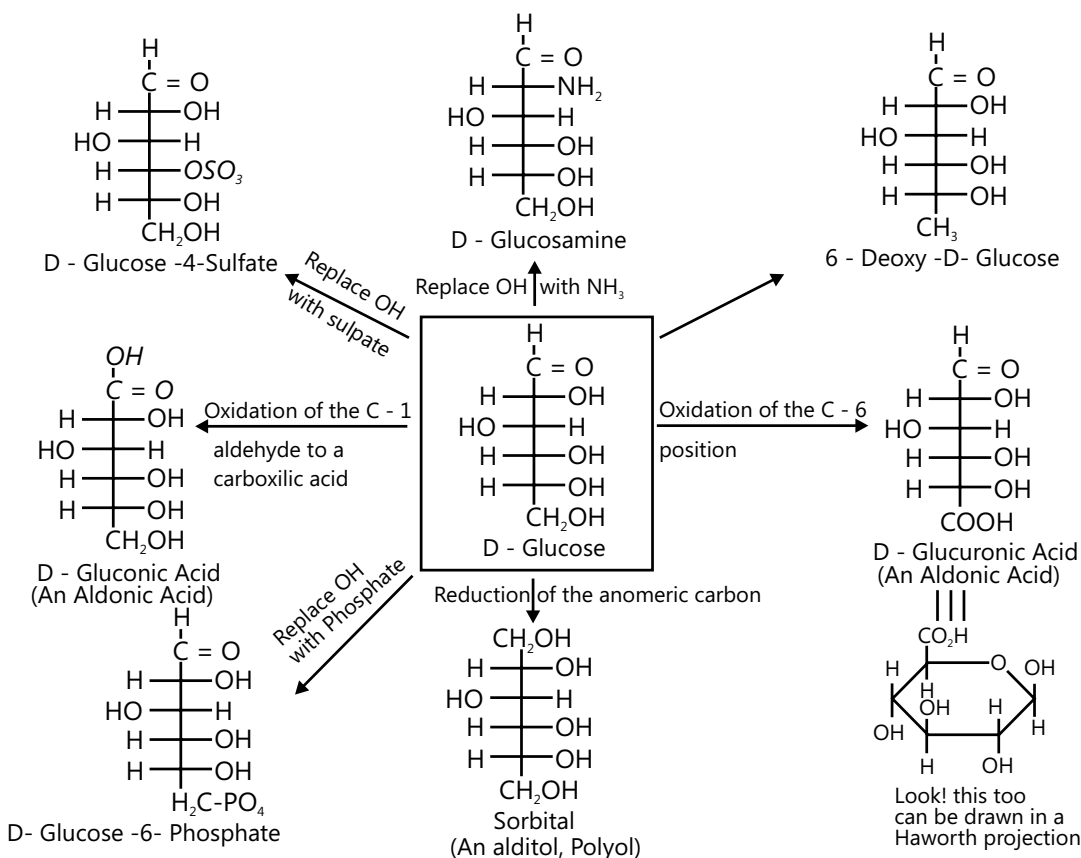
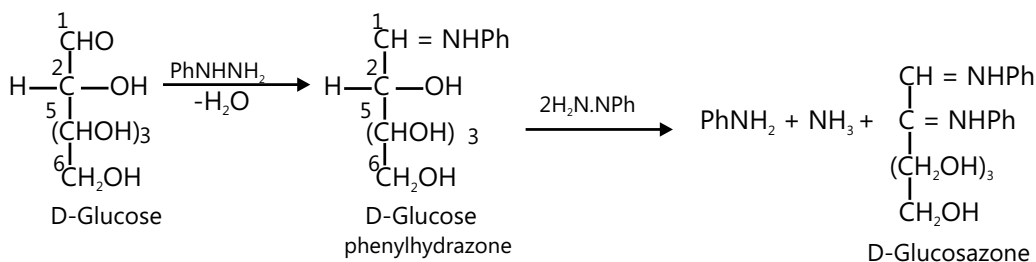




- (e) On prolonged heating with HI, glucose forms n-hexane, indicating that all the six carbon atoms in glucose are linked linearly.



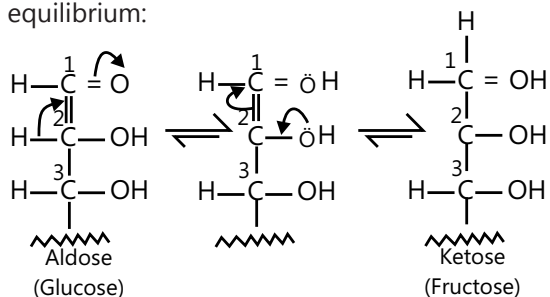
- (f) D-Glucose reacts with phenyl hydrazine and gives glucose phenylhydrazone, which is soluble. Excess use of phenylhydrazine produces, a dihydrazone, called osazone.



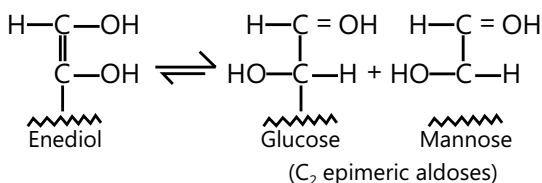
Lobry de bruyn van ekenstein rearrangement reaction

Mechanism

- (a) The ketose and aldose tautomerise in $\ddot{\text{O}}\text{H}$ to a common intermediate enediol, establishing the following equilibrium:

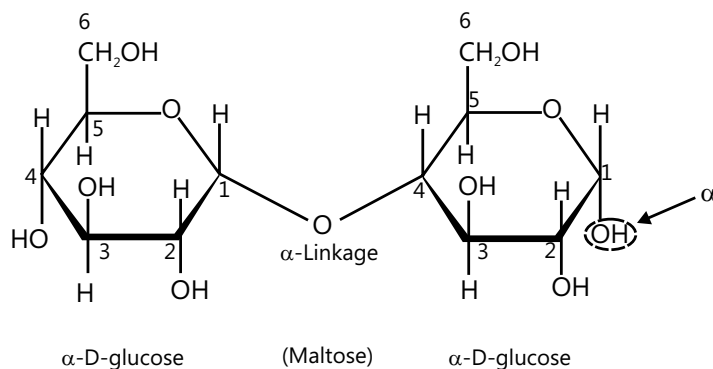
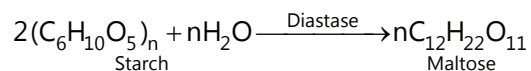


- (b) When the aldose reforms from the enediol, H^+ can add to C-2 from either face of the (C=C) to give C_2 aldohexose epimers.



2.8 Some Disaccharides

Maltose: (a) Preparation: Fractional hydrolysis of starch by enzyme diastase.



(b) **Units:** Two units of α -D glucose.

(c) Reducing sugar

(d) **Linkage:** α glycosidic linkage between C1 and C4 carbon atoms.

Sucrose: (a) Preparation: Prepared from sugarcane and beetroot

(b) **Units:** α -D glucose and α -D fructose.

(c) Non-reducing sugar

(d) **Linkage:** α glycosidic linkage with reference to glucose and β glycosidic linkage to fructose, both linked at C1 carbon.

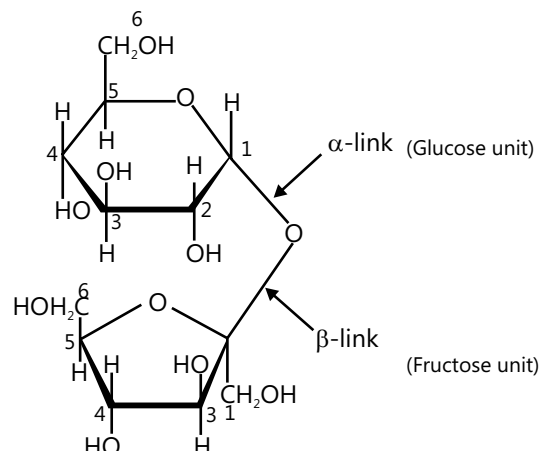
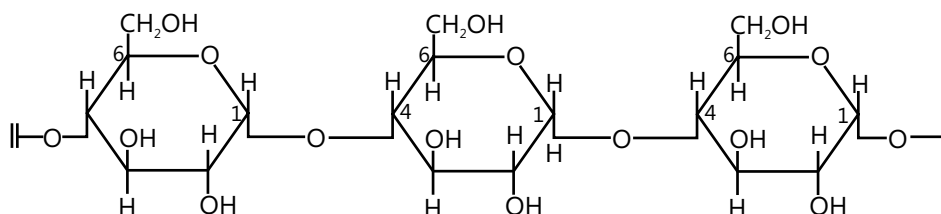


Table 26.2: Difference between Amylose and Amylopectin

| S.No. | Amylose | Amylopectin |
|-------|---|--|
| 1. | It is water soluble fraction for starch | It is water insoluble fraction of starch. |
| 2. | It is 20% of starch | It is 80% of starch. |
| 3. | It is straight chain polymer of D-glucose units. | It is branched chain polymer of D glucose units. |
| 4. | Glucose units are joined by α -1, 4 glycosidic linkage | In amylopectin, the glucose units are joined by α -1, 6 glycosidic linkage. |
| 5. | Its molecular mass lies in the range of 10,000–50,000 | Its molecular mass is in the range of 50,000–1,00,000. |

(b) It occurs exclusively in plants and is a main constituent of cell wall of plant cell. It is a linear polymer of β -D-glucose in which glucose units are linked together by C_1 - C_4 glycosidic linkage. It is a non-reducing sugar.

**Table 26.3:** Relative sweetness of sugar

| Sugar | Relative Sweetness | Sugar | Relative Sweetness |
|-----------|--------------------|--------------|--------------------|
| Sucrose | 100 (standard) | Glucose | 74 |
| Lactose | 16 | Invert sugar | 130 |
| Galactose | 32 | Fructose | 173 |
| Maltose | 33 | | |

Chemical treatment of cellulose, the most important natural polymer, gives various useful derivatives

- **Rayon:** Cellulose acetate and cellulose xanthate are used as a fibre.
- **Celluloid:** Cellulose dinitrate or pyroxylin, combined with plasticizer and alcohol, is used for the manufacturing of photographic film, spectacle frames, piano keys, etc. It is known as artificial ivory.
- **Explosive:** Cellulose trinitrate is used extensively as a blasting and propellant explosive.
- **Lacquer:** Collodion is used for manufacturing washable cellulose paints.
- **Water proofing:** Solution of cellulose acetate is used to provide anti-shrink property to textile fabric.
- **Methyl cellulose:** is used in fabric sizing, paste and cosmetics. Ethyl cellulose is used for manufacturing of rain coats and plastic films.

MASTERJEE CONCEPTS

- Both glucose and gluconic acid on oxidation with nitric acid yield a dicarboxylic acid.
- Glucose on heating with HI gives n-hexane.
- D-glucose reacts with phenylhydrazine to give glucose phenylhydrazine and excess use gives osazone. But three molecules per molecule of glucose are used for oxidation while the other two are attached to the molecule.

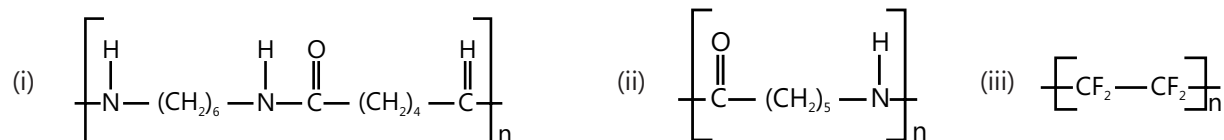
MASTERJEE CONCEPTS

- Glucose when heated with concentrated NaOH, establishes an equilibrium of D-glucose, D mannose and D-fructose.
- Sucrose on hydrolysis changes from Dextrorotatory to Levorotatory and hence is called invert sugar.
- Sucrose is a non-reducing sugar since the hemiacetal hydroxyl groups are linked by glycosidic linkage.
- Sucrose on hydrolysis gives glucose and fructose.
- Maltose is a reducing sugar that on hydrolysis gives two molecules of D-glucose.
- Starch is non-reducing polysaccharides that on hydrolysis give D-glucose.
- Starch is mixture of two polysaccharides: amylose and amylopectin.
- Amylase is straight-chain polysaccharide that is soluble in water and gives blue colour with iodine.
- Amylopectin is a branched chain polysaccharide insoluble in water and doesn't give blue colour with iodine.
- Cellulose is a straight chain polysaccharide comprising of only D-glucose units.
- The difference between starch and cellulose is that starch has α -glycosidic linkage while cellulose has β glycosidic linkage.

Nikhil Khandelwal (JEE 2009, AIR 94)

Illustration 1: Write the names of monomers of the following polymers:

(JEE MAIN)



Sol: (i) Hexamethylenediamine, $\text{H}_2\text{N---}(\text{CH}_2)_6\text{---NH}_2$ and adipic acid, $\text{HOOC---}(\text{CH}_2)_4\text{---COOH}$

(ii) Caprolactam (iii) Tetrafluoroethene, $\text{F}_2\text{C} = \text{CF}_2$.

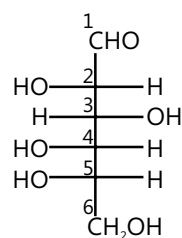
Illustration 2: Describe the term D-and L-configuration used for amino acids with examples. (JEE ADVANCED)

Sol: Consider the following configurations (I and II) of α -amino acids



NH_2 group on the α -carbon oriented toward left (as in structure I) is referred to as L-amino acid and NH_2 group oriented toward right (as in structure II) is referred to as D-amino acid.

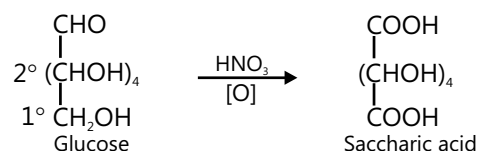
Illustration 3: The letters 'D' or 'L' before the name of a stereoisomer of a compound indicates the correlation of configuration of that particular stereoisomer. This refers to their relation with one of the isomers of glyceraldehyde. Predict whether the following compound has 'D' or 'L' configuration.



Sol: The orientation of the OH group at the penultimate chiral carbon (i.e. last but one or C₅) toward left gives the compound its L-configuration.

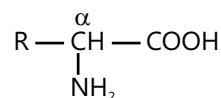
Illustration 4: How will you distinguish 1° and 2° hydroxyl groups present in glucose? Explain with reactions. **(JEE ADVANCED)**

Sol: The -OH group on the terminal carbon atom (i.e. C₆) is called the 1° hydroxyl while the rest of the four remaining OH group present on C₂, C₃, C₄ and C₅ are called 2° hydroxyl groups. While 1° Hydroxyl groups are easily oxidized to give carboxylic acids but 2° hydroxyl groups undergo oxidation only under drastic conditions. For example, glucose on oxidation with HNO₃ gives a dicarboxylic acid, saccharic acid having the same number of carbon atoms as glucose. This indicates that glucose contains one 1° hydroxyl group while the remaining four are 2° hydroxyl groups.



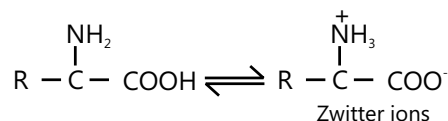
3. AMINO ACIDS

α -Amino Acids: Carboxylic acids in which one α -hydrogen atoms of alkyl group is substituted by amino (-NH₂) group are called α -Amino acids. The general formula is

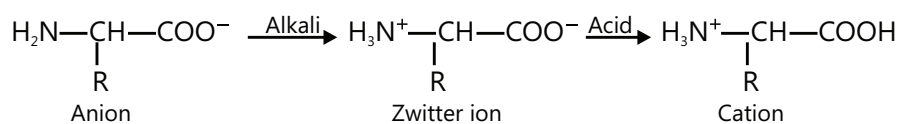


Where R = H or alkyl group

Structure of α -amino acids: The amino acids containing one carboxylic group and one amino group behave like a neutral molecule. This is because in aqueous solutions the acidic carboxylic group and basic amino group neutralize each other intramolecularly to produce an internal salt structure known as zwitter ion or dipolar ions.



However, the neutral zwitter ion (dipolar ions) changes to cation in acidic solution and exist as anion in alkaline medium. Thus amino acids exhibit amphoteric character.



Therefore, amino acid exists as zwitter ion when the solution is neutral or pH-7. The pH at which the structure of an amino acid has no net charge is called its isoelectric point.

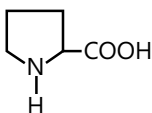
Classification of Amino Acids: Based on the relative number of -NH_2 and -COOH group, α -amino acids are classified in three main groups

- Neutral Amino acids: Amino acids containing one -NH_2 group and one -COOH group. For example, glycine, valine, alanine etc.
- Basic amino acids: These contain one -COOH group and two -NH_2 groups, such as lysine and arginine.
- Acidic amino acids: Amino acids that containing two -COOH groups and one -NH_2 group are called acidic amino acids; for example, aspartic acid and glutamic acid, etc.

Isoelectric Point: In acidic solution, an amino acid being a positive ion moves toward the cathode in an electric field. On the other hand in alkaline solution, it is available as a negative ion that migrates toward anode. At a specific hydrogen ion concentration (pH), the dipolar ion exists as neutral ion and does not show migration toward any electrode. This pH is termed as the isoelectric point of the amino acid.

The isoelectric point is dependent on other functional groups in the amino acids. Neutral amino acids have the range between pH 5.5 and 6.3. At isoelectric points, the amino acids are least soluble in water. This property is utilized in the separation of various amino acids formed by the hydrolysis of proteins.

Table 26.4: List of 20 naturally occurring α - amino acids

| Nature | α -Amino acid | Abbreviation or code | Structure |
|----------------|----------------------|----------------------|---|
| NEUTRAL | | | |
| 1. | Glycine | Gly | $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ |
| 2. | Alanine | Ala | $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}_3 \end{array}$ |
| 3. | Valine | Val | $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}(\text{CH}_3)_2 \end{array}$ |
| 4. | Proline | Pro |  |
| ACIDIC | | | |
| 5. | Serine | Ser | $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}_2-\text{OH} \end{array}$ |
| 6. | Aspartic acid | Asp | $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}_2-\text{COOH} \end{array}$ |
| 7. | Glutamic acid | Glu | $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}_2-\text{CH}_2-\text{COOH} \end{array}$ |
| BASIC | | | |
| 8. | Lysine* | Lys | $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}_2-\text{CH}_2\text{CH}_2-\text{CH}_2\text{NH}_2 \end{array}$ |
| 9. | Arginine | Arg | $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}_2(\text{CH}_2)_2\text{NH}-\text{C}-\text{NH}_2 \\ \\ \text{NH} \end{array}$ |

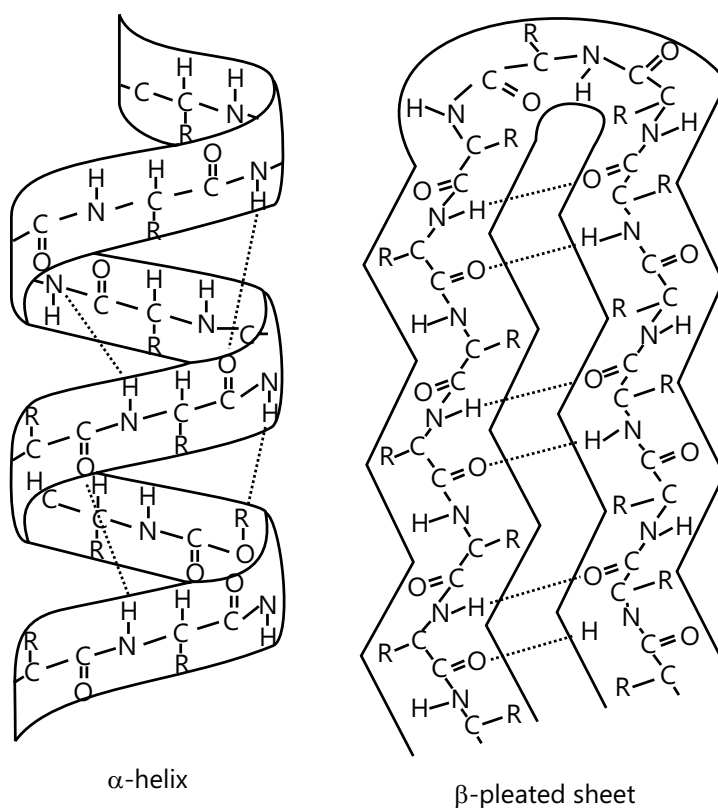
(b) Secondary structure of protein: This refers to the arrangement of polypeptide chains into a definite three-dimensional structure that protein assumes as a result of hydrogen bonding. Depending upon the size of the R-group of the amino acids in polypeptides, two different types of secondary structure are possible:

- (i) α -helix structure (ii) β -Pleated structure

(i) α -Helix structure: This type of secondary structure is possible when the alkyl groups present in amino acids are large and involved in coiling of the polypeptide chains. The intramolecular hydrogen bond between the $>C=O$ group of one amino acid and $-NH$ group of the fourth amino acid stabilizes the helical pattern in right-handed coil and the shape.

(ii) β -Pleated structure: Such secondary structure is acquired when the alkyl groups of amino acids are small. In this kind of structure, the linear polypeptide chains are arranged side by side and are held

together by intermolecular hydrogen bond between the $\left(\begin{array}{c} O \\ || \\ -C- \end{array} \right)$ and $-NH$ group.



(c) Tertiary structure of protein: The tertiary structure of protein is the most stable shape that a protein assumes under the normal temperature and pH conditions. Attractive forces between the amino acid chains are involved in acquiring tertiary structure. These attractive forces, like hydrogen bond, disulphide bonds, ionic, chemical and hydrophobic bonds, result in a complex and compact structure of protein. The two important tertiary structures of proteins are fibrous structures and globular structure. Fibrous proteins have largely helical structure and are rigid molecules of rod-like shape. Globular proteins show a polypeptide chain that consists partly of helical sections and partly β -pleated structure and remaining in random coil form. These different segments of secondary structure then fold up to give protein a spherical shape.

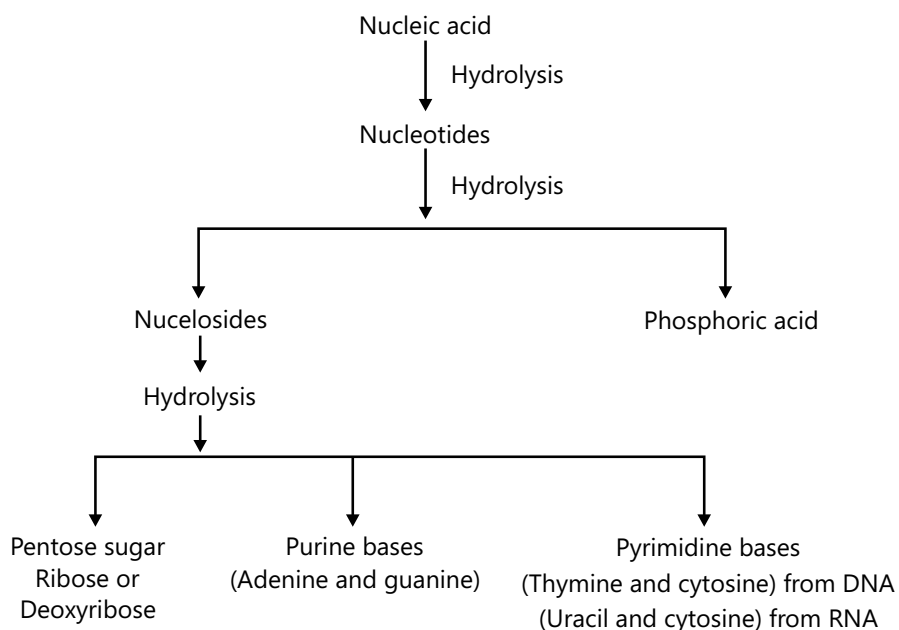
(d) Quaternary structure of proteins: The quaternary structure of proteins develops when the polypeptide chains, which may or may not be identical, are held together by hydrogen bonds. It results in the increase of molecular mass of protein greater than 50,000 amu. For example, hemoglobin contains four subunits, two identical α -chains containing 141 amino acids each and the other two identical β -chains containing 161 amino acids each.

- (e) **Denaturation of proteins:** Proteins when subjected to the action of heat, mineral acids or alkali, the water soluble form of globular protein changes to water insoluble fibrous protein resulting in the precipitation or coagulation of protein. This is called denaturation of proteins.

5. NUCLEIC ACIDS

Nucleic acids are vital biomolecules that present in the nuclei of all living cells as nucleoproteins. These are long-chain polymers with a high molecular mass. Also called biopolymer, they have nucleotide as a repeating structural unit (monomer). These play an important role in transmission of the heredity characteristics from one generation to the next and also in the biosynthesis of proteins. Therefore, the genetic information coded in nucleic acid governs the structure of protein during its biosynthesis and hence controls the metabolism in the living system.

Structure of nucleic acids: The nucleic acid is the prosthetic component of nucleoproteins. Nucleic acid on stepwise hydrolysis gives following products as shown in the chart.



Flowchart 26.1: Components of nucleic acid

Difference between DNA and RNA

The main points of difference between the two types of nucleic acids are given in the table.

Table 26.5: Difference between DNA and RNA

| | DNA | RNA |
|----|---|---|
| 1. | The pentose sugar present in it is 2- deoxy D(-) ribose. | It has D(-) ribose sugar. |
| 2. | It contains cytosine and thymine as pyrimidine bases. | It contains cytosine and uracil as pyrimidine bases. |
| 3. | DNA is double strand and pairing of bases is present throughout the molecule. | It is a single strand molecule looped back on itself. The pairing of bases is present only in helical part. |
| 4. | It occurs in the molecules of the cell. | It mainly occurs in the cytoplasm of the cell. |
| 5. | It is a very large molecule and the molecular weight varies from 6 million to 16 million amu. | It is a much smaller molecule and its molecular weight ranges from 20 thousand to 40 thousand amu. |
| 6. | It has a characteristic property of replication. | It does not replicate. |
| 7. | DNA controls the heredity character. | RNA only governs the biosynthesis of proteins. |

Ribonucleic acids

- (a) The pentose sugar in RNA is ribose.
- (b) Adenine and guanine represent the purine bases of RNA; the pyrimidine bases are uracil and cytosine.
- (c) The thymine in DNA is replaced by uracil in RNA.
- (d) RNA is single stranded, but double stranded RNA is present in Rheovirus and wound tumor virus.
- (e) There are three major classes of RNA, each with specific functions in protein synthesis

(i) mRNA

- Messenger RNA is produced by DNA; the process is called transcription.
- Messenger RNA encodes the amino acid sequence of a protein in their nucleotide base sequence.
- A triplet of nitrogenous bases specifying an amino acid in mRNA is called codon.

(ii) tRNA

- tRNA is also known as soluble RNA (sRNA) as it is soluble in 1 molar solution of sodium chloride.
- tRNA identifies amino acids in the cytoplasm and transports them to the ribosome.
- Molecules of tRNA are single-stranded and relatively very small.
- Anticodon is a three-base sequence in a tRNA molecule that forms complementary base pairs with a codon of mRNA.
- All transfer RNA possess the sequence CCA at their three ends; the amino acid is attached to the terminal as residue.

(iii) rRNA

- Ribosomal RNA is found in ribosomes of cell and is also called insoluble RNA.
- The main function of rRNA is to attract provide large surface for spreading of mRNA over ribosome's during translocation process of protein synthesis.

Table 26.6: Types of RNA

| Type | Sedimentation Coefficient | Mol. Wt. | Number of nucleotide residues | Percentage of total cell RNA |
|------|---------------------------|-----------------|-------------------------------|------------------------------|
| mRNA | 6 to 25 | 25,000-1000,000 | 75-3000 | 2 |
| tRNA | 4 | 23,000-23,000 | 75-90 | 16 |
| rRNA | 5 | 35,000 | 100 | 82 |
| | 16 | 550,000 | 1500 | |
| | 23 | 1100,000 | 3100 | |

- The relationship between the sequence of amino acids in polypeptide with base sequence of DNA or mRNA is genetic code.
- Genetic code determines the sequence of amino acids in a protein.
- A triplet would code for a given amino acid as long as three bases are present in a particular sequence.
- Later in a cell-free system. Marshall Nirenberg and Philip (1964) were able to show that GUU codes for the amino acid valine.
- The spellings of further codons were discovered by R. Holley. H. Khorana and M. Nirenberg.
- They have been awarded the Nobel Prize in 1968 for researches in genetic code.

Lipids: The term lipids represent a group of biomolecules that are insoluble in water but soluble in organic solvents of low polarity, such as chloroform, toluene, ether, carbon tetrachloride.

- (a) They serve as the energy reserve for living cell.
- (b) Lipids are classified in three groups:
- Triglyceride ester of higher fatty acids or oils and fats
 - Phospholipids
 - Waxes

MASTERJEE CONCEPTS

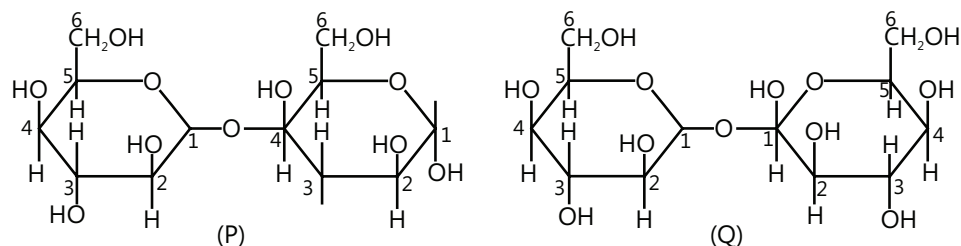
- Proteins: Complex biopolymers of amino acids. Proteins on hydrolysis give peptides that on hydrolysis give amino acids. Almost all amino acids found in our body is α -amino carboxylic acid.
- Amino acids are generally colorless, water soluble, have high melting point and are crystalline solids.
- In aqueous solutions, carboxylic group loses a proton and the amino group accepts it and thus it exists in form of dipolar ion called zwitter ion.
- At a particular pH, the dipolar ion exists as a neutral ion and does not show migration toward any electrode, and this pH is known as isoelectric point.
- At isoelectric point, the amino acids are least soluble in water and this property is used for separation of various amino acids formed by hydrolysis of proteins.
- $-\text{CO}-\text{NH}-$ bond in peptide are called the peptide linkage. There is restriction in rotation about the peptide bonds and thus free rotation is not possible.
- Test for protein:
 - Biurets' test: the blue color reagent turns violet in presence of protein.
 - Xanthoprotic test: protein + concentrated HNO_3 gives orange color in alkaline solution.
 - Millons test: protein + Million's reagent gives white precipitate that on heating gives red precipitate.
 - Ninhydrin test: proteins or amino acids in presence of Ninhydrin reagent give a colored product.

Saurabh Gupta (JEE 2010, AIR 443)

Illustration 5: Two samples of DNA, A and B have melting temperature, T_m 340 K and 350 K, respectively. Can you draw any conclusion from these data regarding their base content? **(JEE MAIN)**

Sol: We know that CG base pair has three H-bonds and AT base pair has two H-bonds; therefore, CG base pair is more stable than AT base pair. Since sample B has higher melting temperature than sample A; therefore, sample B has higher CG content as compared to sample A.

Illustration 6: Which of the following will reduce Tollens' reagent? Explain. **(JEE MAIN)**



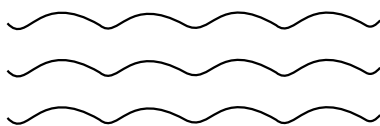
7. CLASSIFICATION OF POLYMERS

(a) On the Basis of Source

- (i) **Natural polymers:** These polymers are found in plants and animals. Examples are proteins, cellulose, starch, some resin and rubber.
- (ii) **Semi-synthetic polymers:** Cellulose derivatives as cellulose acetate (rayon), cellulose nitrate, etc. are the usual examples of this sub category.
- (iii) **Synthetic polymers:** A variety of synthetic polymers such as plastic (polythene), synthetic fibers (nylon 6,6) and synthetic rubbers (Buna -S) are examples of manmade polymers extensively used in daily life as well as in industry.

(b) On the Basis of Structure: There are three different types based on the structure of the polymers.

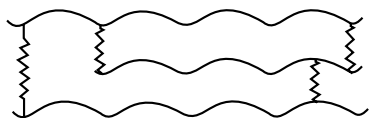
- (i) **Linear polymers:** These polymers consist of long and straight chains. The examples are high density polythene, polyvinyl chloride, etc. These are represented as:



- (ii) **Branched chain polymers:** These polymers contain linear chains having some branches, For example, low density polythene. These are depicted as follows:



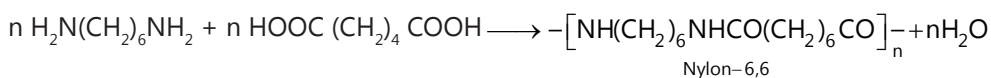
- (iii) **Cross-linked or Network polymers:** These are usually formed from bifunctional and trifunctional monomers and contain strong covalent bonds between various linear polymer chains. For example, bakelite, melamine, etc. These polymers are depicted as follows:



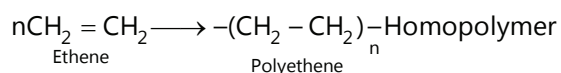
(c) On the Basis of Synthesis: These are of two types based on synthesis –

- (i) **Condensation polymerization:** In this, the monomer (same or different) units link with each other by the elimination of a small molecule (for example, water, methyl alcohol) as a byproduct. The polymer formed is known as condensation polymer. Nylon and terylene are the most common examples.

Since the condensation polymerization proceeds by a stepwise intermolecular condensation, it is also known as step polymerization and the polymer formed is known as step growth polymer.



- (ii) **Addition polymerization:** This involves self-addition of several unsaturated molecules of one or two monomers without loss of any small molecule to form a single giant molecule. The polymer formed is known as addition polymer. Polythene is the most common example. However, the addition polymers formed by the polymerization of a single monomeric species is known as homopolymers, for example, polyethene.



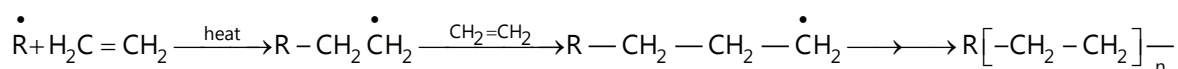
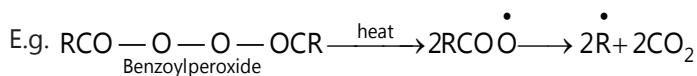
The polymers made by addition polymerization from two different monomers are termed as copolymers, for example, Buna-S, Buna-N, etc.

- (d) On the Basis of Molecular Forces:** A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, for example, van der Waals forces and hydrogen bonds.
- (i) Elastomer:** In these polymers, polymer chains are held together by the weakest intermolecular force. Weak binding forces permit the polymer to be stretched. A few "crosslinks" are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanized rubber. The examples are Buna-N, neoprene, etc.
 - (ii) Fibers:** In these polymers, polymer chain held together by strong intermolecular forces, like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. Fibers are the thread-forming solids that possess high tensile strength and high modulus. The examples are polyamides (nylon -6, 6), polyesters (terylene), etc.
 - (iii) Thermoplastic polymers:** These polymers possess intermolecular forces of attraction intermediate between elastomers and fibers. These are the linear or slightly branched long-chain molecules capable of repeatedly softening on heating and hardening on cooling. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.
 - (iv) Thermosetting polymers:** These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in molds and again become infusible. These cannot be reused. Some common example are bakelite, urea-formaldelyde resins, etc.
- (e) Classification on the Basis of Type of Polymerization:** Synthetic polymers have been classified into definite classes in various manners, for example,
- (i)** All the synthetic polymers may be classified into two groups based on of the type of the process involved during their preparation, viz. condensation or addition polymers involving condensation or addition polymerization processes, respectively, during their synthesis.
 - (ii)** A more rational method of classification is based upon the sequence of synthesis of the polymer (i.e., mode of addition of the monomer units to the growing chain).

According to this method, polymers may be of two types, viz. chain growth polymers and step growth polymers.

- Chain growth polymers (earlier called as addition polymers). These polymers are formed by the successive addition of monomer units to the growing chain having a reactive intermediate (free radical, carbocation or carbanion)

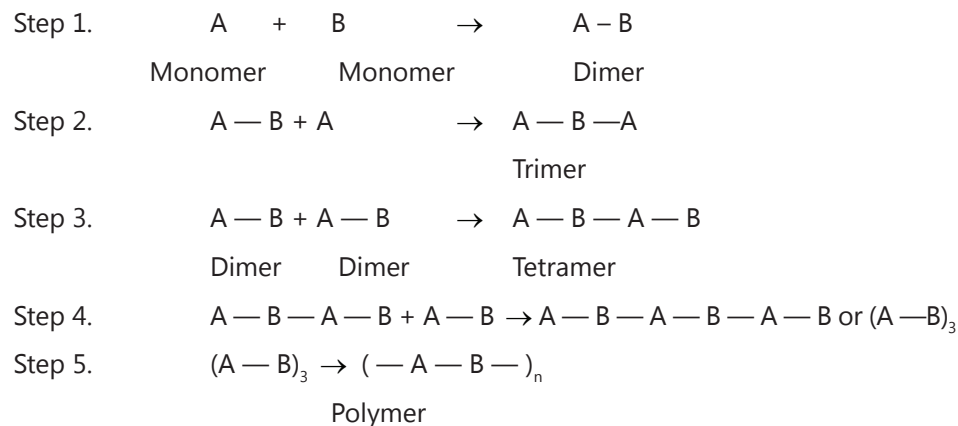
The most important free radical initiator is benzoyl peroxide.



Examples of chain growth polymers

| Monomer(s) | Polymer |
|-----------------------|--|
| Ethylene | Polyethylene |
| Propylene | Polypropylene |
| Tetrafluoroethylene | Polytetrafluoroethylene (PTFE) or Teflon |
| Vinyl chloride | Polyvinyl chloride (PVC) |
| Isoprene | Polyisoprene (Natural rubber) |
| Butadiene | Polybutadiene |
| Butadiene and styrene | Buna-S |

- Step growth polymers (earlier called as condensation polymers). These polymers are formed through a series of independent steps (reactions). Each step involves the condensation (bond formation) between two difunctional units (monomers) leading to the formation of small polymer (say dimer, trimer, tetramer, etc.)



Examples of step growth polymers

| Monomers | Polymers |
|---------------------------------------|----------|
| Adipic acid hexamethylene diamine | Nylon-66 |
| Terephthalic acid and ethylene glycol | Terylene |
| Phenol and formaldehyde | Bakelite |

(f) Based on the magnitude of molecular forces the polymers may be classified as:

(i) Elastomers

- In which the intermolecular forces of attraction are the weakest. They are amorphous and have high degree of elasticity, for example, Buna-S.

(ii) Fibers

- In which the intermolecular forces of attraction are the strongest like H bonding or dipole-dipole attraction.
- They have high tensile strength, high melting point and low solubility, for example, polyesters, polyacrylonitriles

(iii) Thermoplastics

- In which the intermolecular forces of attraction are in between those of elastomers and fibers
- They are hard at room temperature, soften on heating without any change in mechanical properties of plastic, have little or no cross links, for example, polythene, polyacrylonitrile, Teflon, etc.
- Semi-fluid substances with low molecular weight that once set into particular mold cannot be used again and again.
- This is because of extensive crosslinking between two polymer chains to give a three-dimensional network, for example, bakelite, urea-formaldehyde; melamine formaldehyde etc.

8. MOLECULAR MASS OF POLYMERS

- (a) There are two types of average molecular mass of polymers.
- (b) Number average molecular mass (\bar{M}_n): It is determined by methods depending upon the number of molecules present in the polymer sample, for example, colligative properties like ΔT_f ; ΔT_b , Osmotic pressure

$$(c) \quad \bar{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3} = \frac{\sum N_1M_1}{\sum N_1}$$

Where N_1, N_2, N_3 are the number of molecules. M_1, M_2, M_3 are the molecular masses.

Weight Average Molecular Mass: It is determined by using the methods depending upon the masses for the individual molecules like light scattering, ultracentrifugation, sedimentation, etc.

$$\bar{M}_w = \frac{\sum m_1M_1}{\sum m_1} = \frac{\sum N_1M_1^2}{\sum N_1m_1}; M- \text{ is mass of macromolecule}$$

Example in a polymer sample, 30% molecules have molecular mass 20,000; 40% have molecular mass 30,000 and the rest 30% have 60,000. Calculate the number average and mass average molecular masses.

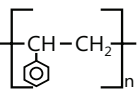
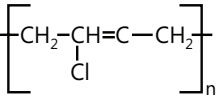
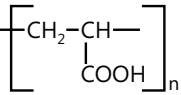
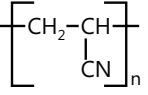
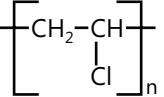
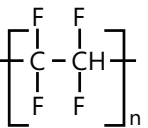
$$\bar{M}_n = \frac{30 \times 20000 + 40 \times 30,000 + 30 \times 60,000}{30 + 40 + 30} = \frac{600000 + 1200000 + 1800000}{100} = \frac{3600000}{100} = 36000$$

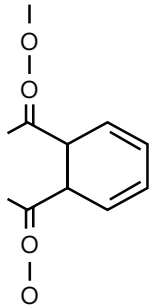
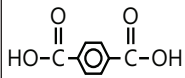
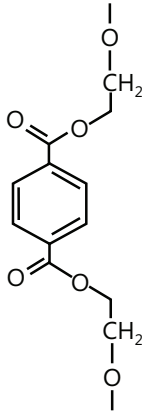
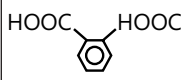

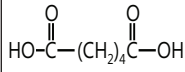
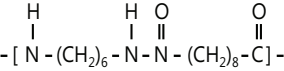
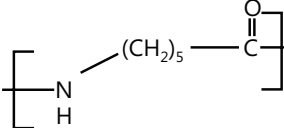
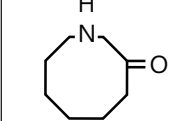
$$\bar{M}_w = \frac{30(20000)^2 + 40(30,000)^2 + 30(60,000)^2}{30 \times 20000 + 40 \times 30,000 + 30 \times 60,000} = 43,333$$

9. VARIOUS TYPES OF POLYMERS

Table 26.7: Types of polymers

| Name of the polymer along with abbreviation | Structure of monomer | Natural of polymer | Properties | Uses |
|--|------------------------------------|---|--|---|
| A. Addition Polymers | | | | |
| I. Polyolefins | | | | |
| 1. Polymers or polythome $\left[\text{CH}_2 - \text{CH}_2 \right]$ | $\text{CH}_2 = \text{CH}_2$ | (a) Low-density polyethylene (LDPE) in an addition or chain-growth homopolymer. It is a highly branched polymer and is obtained by free-radical polymerization (b) High-density polyethylene (HDPE) is obtained by coordination polymerization. It is a linear addition or chain-growth homopolymer. | Transparent, moderate tensile strength, high toughness. Translucent, chemical inert, growth toughness and tensile strength. | Packing material (plastic films, bags etc.) insulation for electrical wires and cables. Manufacture buckets, tubs, pipes, bottles and toys. |
| 2. Polypropylene or Polypropene $\left[\begin{array}{c} \text{CH} - \text{CH}_2 \\ \\ \text{CH}_3 \end{array} \right]$ | $\text{CH}_3\text{CH}=\text{CH}_2$ | Addition homopolymer linear can be obtained by free-radical or Ziegler-Natta polymerization. | Harder and stronger than polythene | Packing of textile and foods, for making liners of bags, heat shrinkable wraps, carpet fibers, ropes, automotive molding, stronger pipes and bottles. |

| Name of the polymer along with abbreviation | Structure of monomer | Natural of polymer | Properties | Uses |
|---|---|------------------------------------|--|--|
| 3. Polystyrene or Styron  | $C_6H_5CH=CH_2$ | Addition homopolymer, linear chain | Transparent | Plastic toys, household wares, radio and television bodies, refrigerator linings etc. |
| II Polydienes | | | | |
| 1. Neoprene  | $CH_2=CH-\overset{\text{Cl}}{\underset{ }{C}}=CH_2$ Chloroprene or 2-Chloro-1, 3-butadiene. | Addition homopolymer | Rubber like, inferior to natural rubber but superior in its stability to serial oxidation and its resistance to oils, gasoline, etc. | Hoses, shoe heels, stoppers etc. |
| III. Polyacrylates | | | | |
| 1. Poly (methyl methacrylate) Plexiglas, Lucise, Acrylite Perspex (PMMA) | $CH_2=\overset{\text{Cl}}{\underset{ }{C}}=COOCH_3$ Methyl methacrylate | Addition homopolymer | Hard, transparent, excellent light transmission properties, optical clarity better than glass. | Lenses, light covers, light shades, signboards, transparent domes, skylights, aircraft windows, dentures and plastic jewelry. |
| 2. Poly (ethyl acrylate)  | $CH_2=CHCOOC_2H_5$ | Addition homopolymer. | Tough, rubber like product. | — |
| 3. Polyacrylonitrile (PAN)  | $CH_2=CH-CN$ Acrylonitrile | Addition homopolymer. | Hard and has high melting material. | Manufacture of fibers, orlon, acrilon used for making clothes, carpets, blankets. |
| IV. Polyhalolefines | | | | |
| 1. Polyvinyl chloride (PVC)  | $CH_2=CH-Cl$ Vinyl chloride | Homopolymer, chain growth | Pliable (easily molded) | (i) When plasticized with high-boiling esters used in rain coats, hand bags, shower curtains, upholstery fabrics, shoe soles, vinyl flooring (ii) Good electrical insulators for wires and cables (iii) Making hose pipes. |
| 2. Polytetrafluoro ethylene of Teflon (PTFE)  | $F_2C=CF_2$ Tetrafluoroethylene | Chain growth, homopolymer | Flexible and inert to solvents, boiling acids, even aquaregia, stable up to 598 K. | (i) For making nonstick utensils coating (ii) Making baskets, pump packings, valves, seals, nonlubricated bearings. |
| Condensation Polymers | | | | |
| I. Polyesters | | | | |

| Name of the polymer along with abbreviation | Structure of monomer | Natural of polymer | Properties | Uses |
|--|--|--|--|--|
| 1. Terylene or Dacron  | HO-CH ₂ -CH ₂ -OH Ethylene glycol or Ethane-1, 2-diol and  Terephthalic acid or Benzene-1, 4-dicarboxylic acid | Copolymer, linear, step-growth. Thermoplastic, dissolves in suitable solvents and its solutions, on evaporation leaves a tough but non-flexible a film. | For making paints and lacquers. | |
| 2. Glyptal or Alkydresin  | HO-CH ₂ -CH ₂ -OH Ethylene glycol and  Phthalic acid or Benzene-1, 2-dicarboxylic acid | Copolymer, linear, step-growth. Thermoplastic, dissolves in suitable solvents and its solutions, on evaporation leaves a tough but non-flexible a film. | For making paints and lacquers. | |
| II. Polyamides | | | | |
| Nylon-6,6  |  Adipic acid and H ₂ N-(CH ₂) ₄ -NH ₂ Hexamethylene diamine | Copolymer, step, growth, linear | High tensile strength, abrasion resistant, somewhat elastic. | (i) Textile fabrics, carpets, bristles for brushes (ii) Substitute for metals in bearings and gears. (iii) Crinked nylon is used for making elastic hosiery. |
| 2. Nylon-610  | H ₂ N(CH ₂) ₆ NH ₂ Hexamethylene diamine and HOOC(CH ₂) ₈ COOH Sebacic acid | Copolymer, step- growth, linear | For making points and lacquers. | (i) Textile fabrics, carpets, bristles for brushes (ii) Substitute for metals in bearings and gears. (iii) Crimped nylon is used for making elastic hosiery. |
| 3. Nylon-6 or Parlon  |  E-Caprolactam | Homopolymer, step growth, linear | | Mountaineering ropes, tire cords and fabrics |
| III Formaldehyde resins | | | | |

| Name of the polymer along with abbreviation | Structure of monomer | Natural of polymer | Properties | Uses |
|---|-------------------------|---|------------|--|
| 1. Phenol-formaldehyde resin or Bakelite | Phenol and formaldehyde | Copolymer, step growth, highly branched thermosetting polymer | | (i) Bakelite with low degree of polymerization is used as binding glue for wooden planks and in varnishes and lacquers (ii) Bakelite with high degree of polymerization is used for making combs and micatable tops, fountain pen barrels, electrical goods (switches and plugs), gramophone records etc. |

MASTERJEE CONCEPTS

- Polymers are product of large number of small molecules, called monomers, chemically bonded to each other.
- The individual large polymer molecules are known as macromolecules.
- Polymers are characterized by the average molecular mass of the chains and the number of repeating units in such polymers is known as the degree of polymerization.
- The physical properties of a polymer are determined by such factors as the flexibility of macromolecules, the sizes and types of group attached to the polymer chains and the magnitude of intermolecular forces.
- Polymers may be linear, branched or cross linked.
- Copolymers are produced from two monomers combined randomly or in a specific manner
- To participate in polymerization, a molecule must be able to react at both ends.
- The principal types of polymerization reaction are chain reaction polymerization (initiation propagation and termination), which is undergone by monomers such as vinyl bromide and step reaction polymerization, which involves reactions between functional group on different monomer molecules like adipic acid and hexamethylene diamine to give nylon 66.

Neeraj Toshniwal (JEE 2009, AIR 21)

Illustration 9: Write the structures of the monomers of the following polymers:

(JEE MAIN)

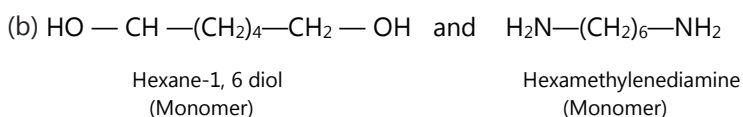
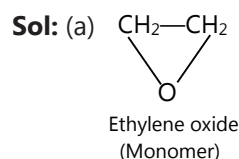
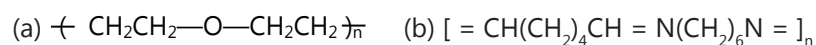


Illustration 10: (a) Can a copolymer be formed in both addition and condensation polymerization? Explain.
 (b) Can a homopolymer be formed in both addition and condensation polymerization? Explain. **(JEE MAIN)**

Sol: (a) Yes, copolymers can be formed both in addition and condensation, polymerization. For example, Buna-S is an addition copolymer of styrene and 1, 3-butadiene while nylon-6,6, bakelite and polyester are condensation copolymers.

(b) Yes, homopolymers can be formed both in addition and condensation polymerization. For example, polythene, PVC, PMMA, PAN, neoprene, etc. are example of addition homopolymers while nylon-6 is an example of condensation homopolymer.

Illustration 11: How does the presence of benzoquinone inhibit the free radical polymerization of a vinyl derivative? **(JEE ADVANCED)**

Sol: Benzoquinone react with radical of the growing polymer chain ($R\cdot$) to form a new radical (I) which is extremely uncreative, since it is highly stabilized by resonance. Because of the lack of reactivity of this new radical further growth of the polymer chain is interrupted and hence the reaction stops.

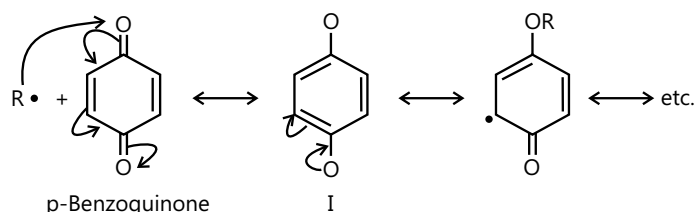
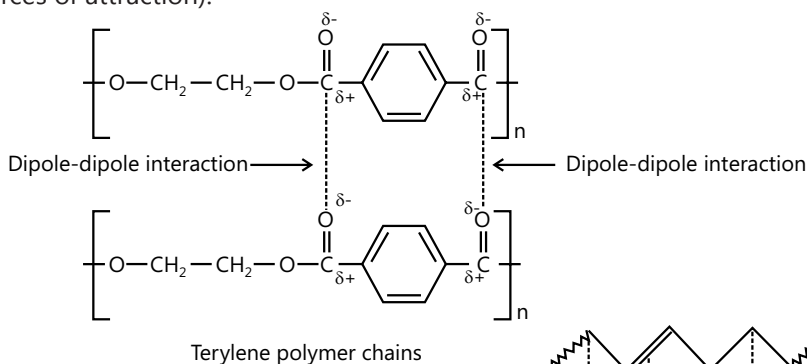


Illustration 12: Differentiate the following pairs of polymers based on the property mentioned against each. **(JEE ADVANCED)**

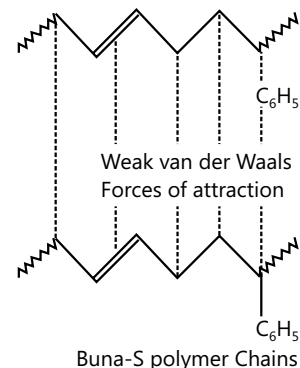
- (i) Novolac and bakelite (structure).
 (ii) Buna-S and terylene (intermolecular forces of attraction).

Sol: (i) Novolac is a linear but bakelite is a cross-linked polymer of phenol and formaldehyde.

(ii) Terylene contains ester functional groups that are polar in nature. Therefore, the intermolecular forces of attraction involved in terylene are strong dipole-dipole interaction as shown below:



Buna-S, on the other hand, does not have polar functional groups. It has only nonpolar hydrocarbon chains and hence has only weak Van Der Waals forces of attraction as shown below:



POINTS TO REMEMBER

