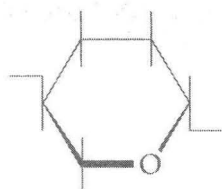


7

NATURAL POLYMER

PROLOGUE

- Polysaccharides and Lignin
- Reactions of Cellulose
- Starch
- Lignin
- Glycogen
- Proteins
- Nucleic Acids
- Bases
- Segments of RNA and DNA Polymers



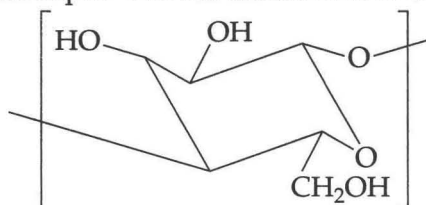
Polymers are the major components of all living matter, whether it is animal or vegetable. The naturally occurring polymers are carbohydrates, proteins, nucleic acids, natural rubber etc.

Carbohydrates are one of the major constituents of plant kingdom. These are generally made up of cellulose, starch and lignin. Besides of it, protein is also a main constituent of both plants and animals, contains a complex nitrogenous material. Nucleic acids, *i.e.*, RNA and DNA, form part of all living cells. Another example, natural rubber, *Hevea brasiliensis* species of tree, is an important product for the various industries.

▶ POLYSACCHARIDES AND LIGNIN

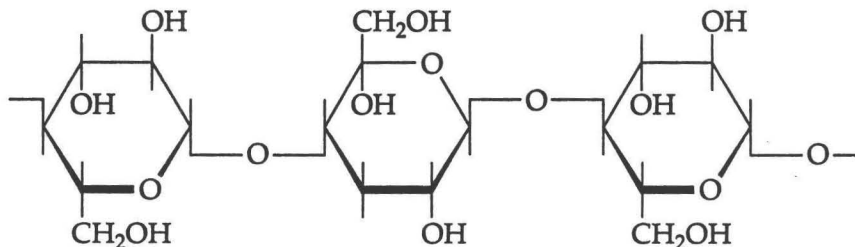
Cellulose and starch are naturally occurring polymers. These are carbohydrates and known as polysaccharides, while lignin is a non-carbohydrate natural polymer of living cells. The brief discussion of these polymers is as follows :

(1) **Cellulose** : Cellulose is a linear polysaccharide and its empirical formula is $C_6H_{10}O_5$. It is a polyanhydroglucose. On hydrolysis, cellulose gives D-glucose monomers. Between the glucose molecules, the linkage is $\beta - 1 \rightarrow 4$ (glucosidic linkage). Cellulose is a major constituent of paper and ropes. Various derivatives of cellulose, *e.g.*, cellulose nitrate,



cellulose acetate and ethyl cellulose are used widely in plastic industry. Regenerated cellulose in the form of rayon is an important fiber.

In above structure, the hydroxyl groups, the hydroxy methyl group and the ether linkages are all in equatorial positions.

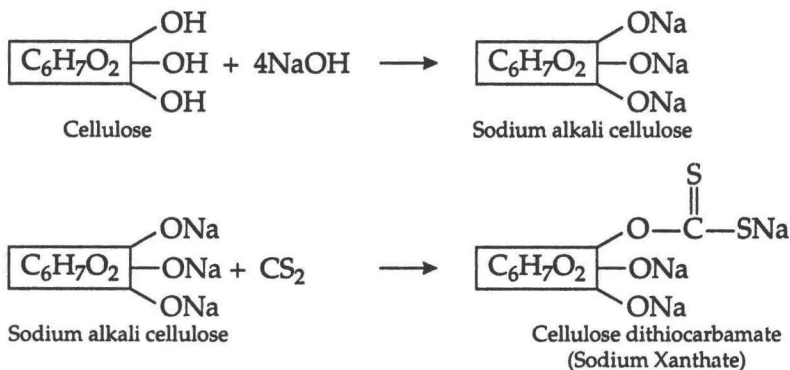


Linear-chain of cellulose polymer
(β -1, 4-linkage)

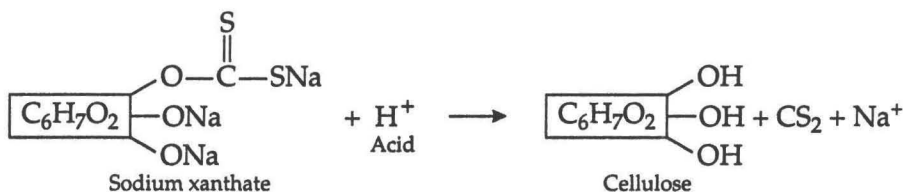
♦ REACTIONS OF CELLULOSE

(1) **Formation of Rayon Viscose :** In the formation of rayon viscose, high quality wood pulp or cotton linters or a mixture is used. It is treated with 18% caustic soda at 18°C for 30 – 90 minutes. After formation of alkali cellulose, it is treated with carbon disulphide at $25 - 30^\circ\text{C}$ for 4 hours. Thus thiocarbamate of cellulose (xanthate) is formed. It is then allowed to react with dilute NaOH at 17°C , the orange coloured liquid is resulted, which is known as 'viscose'.

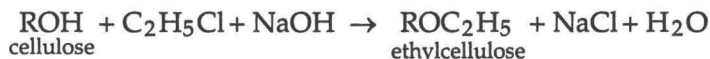
The viscose solution is filtered, and extruded by pressure in a precipitation bath. This bath contains an aqueous solution of sulphuric acid, sodium sulphate, zinc sulphate and glucose. The acid in the coagulating and regenerating bath precipitates the cellulose xanthate and further breaks down the xanthate, releasing cellulose. This cellulose is known as the 'regenerated cellulose'. The entire reactions are as :



Regeneration of cellulose by the action of acid :



(2) **Formation of Ethyl Cellulose :** When cellulose, alkali and ethyl chloride react together at 100°C, ethyl cellulose is formed.



Ethyl cellulose is a tough and flexible polymer. It contains high impact strength. It is less inflammable. The main disadvantage of ethyl cellulose is that it has low softening temperature and low moisture resistance capacity.

(3) **Formation of Cellophane :** For the preparation of cellophane, cellulose is first converted into viscose. The viscose solution is then extruded in the form of a film, which is precipitated from a bath containing sodium and ammonium sulphates and sulphuric acid. The film, which is in the form of regenerated cellulose is washed, bleached and desulphurized. Finally, it is passed through a bath of glycerol, which also acts as a plasticizer and then dried.

Cellophane films are very thin, however, these are widely used as a wrapping and packing material.

(4) **Formation of Cellulose Acetate Plastics :** Cellulose acetate can be prepared by cellulose. The cellulose acetate, used for injection moulding contains about 50 – 55% acetyl by weight, corresponding between a diacetate and triacetate. It is plasticized with a phthalate plasticizer such as dibutyl phthalate.

For the preparation of rods and tubes injection, extrusion and compression mouldings, can be used. The cellulose acetate sheets are cast from solution onto highly polished metal surfaces. These are used for making photographic, x-ray films, bags and boxes for packing.

(5) **Formation of Cellulose Nitrate :** For the preparation of cellulose nitrate, the purified cotton linters are reacted with a nitrating mixture (25% HNO₃ + 55% H₂SO₄) and 20% water, at the temperature 95 – 105°F for 20 minutes. During the reaction, the cellulose nitrate is partially hydrolyzed to dinitrate stage.

(6) **Formation of Cellulose Acetate—Butyrate :** The cellulose ester contains 13% acetyl and 37% butyral content. It is an excellent injection moulding material. It can be quite rapidly plasticized than cellulose acetate. It has high impact strength, higher moisture resistance and good stability. It is soluble in various organic solvents.

It is widely used in the preparation of films for motion pictures, and also used in the automobile parts.

▶ STARCH

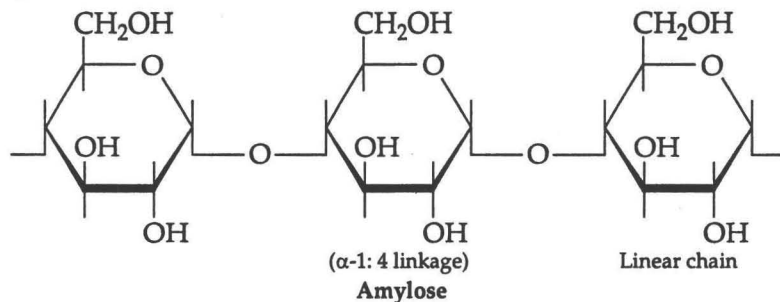
Starch is a branched polysaccharide. It is the reserve food material of plants. Starch is mainly found in potato and grains.

Starch possesses two types of polymers. Both types differ in their molecular weights and structures as :

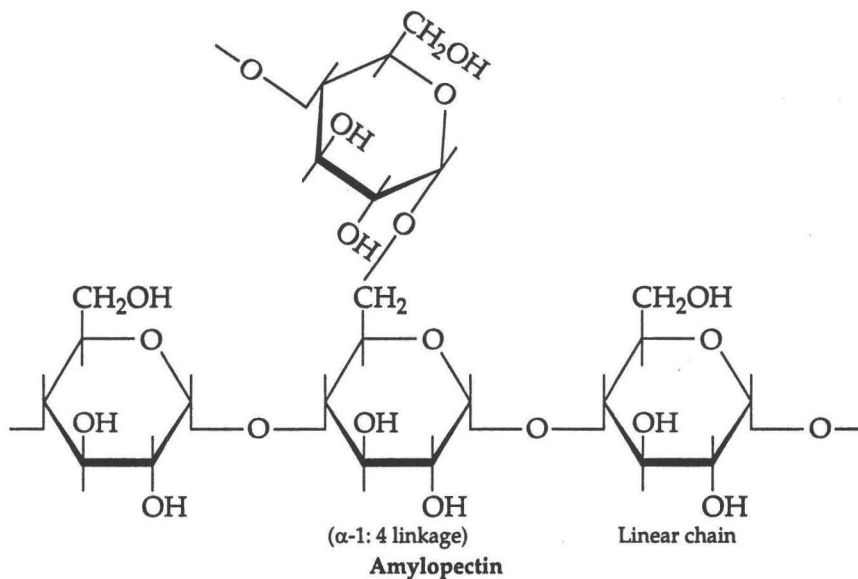
- (a) amylose (b) amylopectin

(a) **Amylose :** Amylose is a linear polyanhydroglucose. In this moiety of starch, the glucose units are joined by α-1, 4 linkages. This linkage provides high flexibility to the chain, which can adopt a coil configuration.

The molecular weight of amylose moiety can ranging from 10,000 to 4,00,000. The structure of amylose is as :



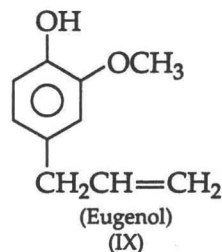
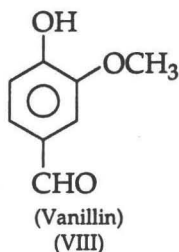
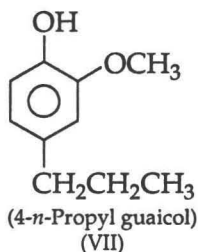
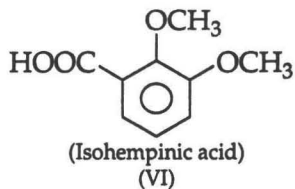
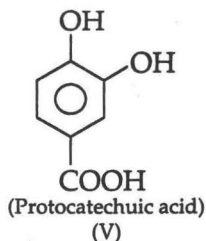
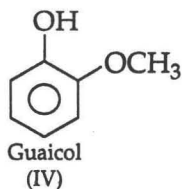
(b) **Amylopectin** : The amylopectin is the other fraction of starch. It contains a chain of linear α -1, 4 linked glucose units. It is a branched poly (anhydroglucose) unit, which is joined to the main linear chain by both α -1, 4 and α -1, 6 linkages. The molecular weight of the amylopectin is about 10,000. The structure of amylopectin is as :



Starch is used in textile, paper and laundry industry. It is also used in the various industries for the manufacturing of paper boards, adhesives for paper in brewery as the raw material and also in food industry. It finds use as a thickener and gelling agent for soaps and many desserts.

♦ LIGNIN

Lignin is a non-carbohydrate polymer. It is generally found in wood. It is the structural support and adhesive material in plants. It constitutes about 25% of wood. The structure of lignin is too complex. By oxidative cleavage, zinc dust distillation and dry distillation process, the lignin forms various degradative products, such as guaicol and its derivatives as :



Degradative products of lignin

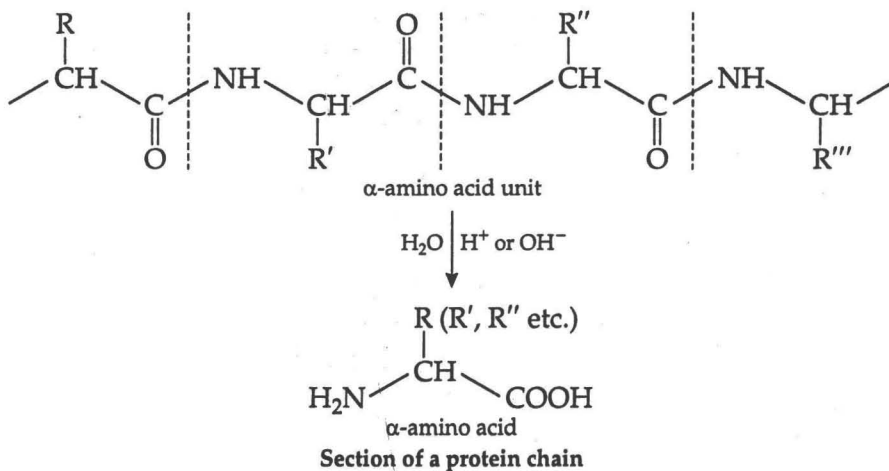
The lignin is used in the industrial preparation of vanillin. Lignin also finds numerous uses, as a dispersant and wetting agent used in oil well digging muds, in road binders, adhesives, leather tanning and industrial cleaners.

▶ GLYCOGEN

Glycogen is another reserve carbohydrate food material of living cells. It is a polysaccharide and contains highly branched poly(an hydroglucose). Its structure is almost similar to that of amylopectin. It consists of a chain length of about 10–14 units of glucose monomers. It is found in almost all animal cells and some plants.

▶ PROTEINS

Proteins are the naturally occurring condensation polymers. It contain α -amino acid monomer units; which are linked together by peptide linkages, *i.e.*, ($-\text{CO}-\text{NH}-$). Hydrolysis of proteins can be occurred by acid, base and enzymes, and consequently it forms a mixture of α -amino acids.



where, R, R', R'', etc. Can be either hydrogen or an organic group. Molecules which consist of only a small sequences of α -amino acids are known as polypeptides.

There are about 20 amino acids present in naturally occurring proteins. The amino acids can be obtained from the hydrolysis of proteins, and separated by chromatography techniques. The amino acids produce violet colour with ninhydrin reagent.

The sequence of amino acids in a protein can be achieved by carrying out reactions with the amino or carboxyl end group, followed by controlled hydrolysis.

The amino acids and proteins also can be separated by electrophoresis. The α -amino acids are dipolar ions and do not migrate to the poles at their isoelectric points, since they migrate to the opposite poles at different pH values.

The simple proteins can be divided into (a) fibrous and (b) globular proteins.

(a) The fibrous proteins contain high intermolecular hydrogen bonding. Fibrous proteins include those obtained from silk, wool, hides and hooves.

(b) Globular proteins are those, which contain intramolecular hydrogen bonding. It becomes insoluble and denatured on heating. The examples are egg albumins, globulins and glutelins.

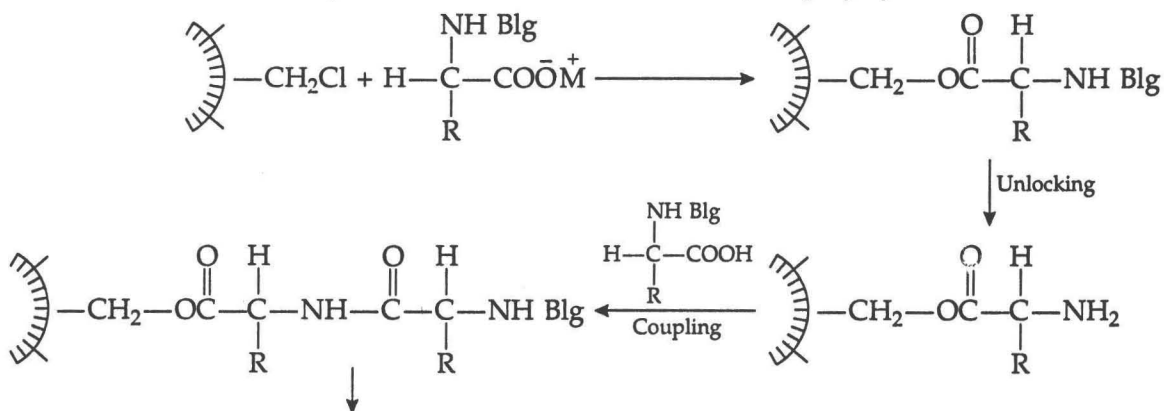
The *primary structure* of a protein describes the sequence of a α -amino acids in polypeptide chain or its configuration.

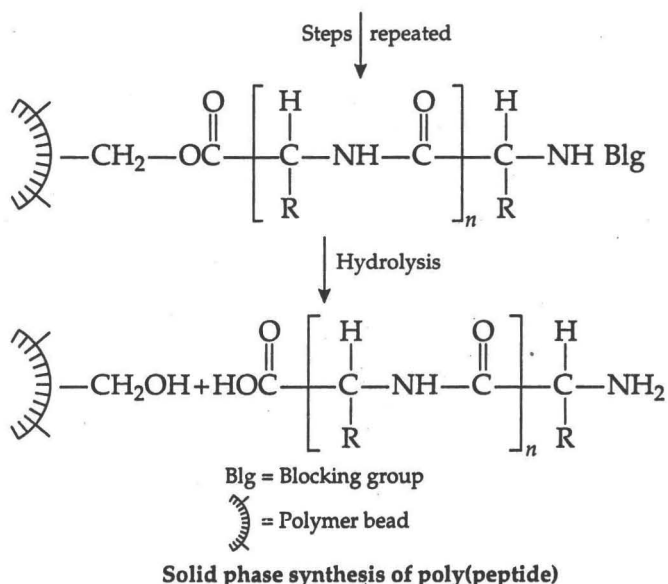
The *secondary structure* of protein describes its conformation or molecular shape. It has been shown that the polypeptide chain may have helical conformations in their crystal lattices. These helices are highly stable, even in the dissolved state, being stabilized by intramolecular hydrogen bonds involving —NHCO— groups. This arrangement may be depicted by a right handed α -helix conformation of a polypeptide.

The proteins also contain a *tertiary structure*. This structure describes the shape or folding, which are due to the presence of sulphur-sulphur (S—S) cross-links between the polymer chains.

Synthesis : The polypeptides can be synthesized by the classical methods of **Emil Fischer**. In this method, one of the groups, —NH_2 or —COOH , an amino acid is protected before condensing it with another amino acid.

Recently, **Merifield** has given a method, known as solid phase synthesis of peptides, where the reaction takes place on the surface of a cross-linked polystyrene bead.





♦ NUCLEIC ACIDS

The nucleic acids are the condensation products of nucleoside triphosphates, and it contains heterocyclic bases. The nucleic acids are of two types : (a) DNA and (b) RNA.

DNA is deoxyribose nucleic acid. It contains the heterocyclic bases; such as adenine, guanine, thymine, and cytosine.

RNA is the ribose nucleic acid. It contains adenine, guanine, uracil and cytosine. In DNA, thymine is present, while in RNA, uracil is present, *i.e.*, only one of the heterocyclic bases is different.

The names of the two nucleic acids are based on the sugar moiety present in them. Thus, DNA and RNA differ in that one contains the carbohydrate D-2-deoxyribose, and the other contains D-ribose.

The early work on the separation of nucleic acids from the human cells was initiated by Miescher in 1868. In 1930, it was recognized that there were two types of these acids. During 1940s and 1950s, special techniques of separation, namely, paper and ion-exchange chromatography were discovered, and this provided the progress in the chemistry of nucleic acids.

