



Notes

33

POLYMERS

*I*n the previous lesson you have studied about petrochemicals, and their importance. You also studied about the uses of petrochemicals. In this lesson we continue with a detailed study of another vast area i.e. polymers. Today polymers have influenced our life style to the extent that it would not be wrong to say that we are in polymer age. Now-a-days polymers find wide range of uses starting from common household utensils, automobiles, clothes, furniture, etc., to space-aircraft and biomedical and surgical components.

Polymeric materials are light weight but can possess excellent mechanical properties and can be easily processed by different methods. In this lesson you would learn more about polymers, their types and some important-synthetic and natural polymers. In the next lesson you would learn about the colouring materials like dyes, paints and pigments.



Objectives

After reading this lesson, you will be able to :

- define the terms like monomers, polymer, homopolymer, copolymer and polymerization;
- classify polymers on the basis of their source, molecular forces and method of preparation;
- list the monomers of the polymers like natural and synthetic rubber;
- list the monomer of the polymer like polythene, polystyrene, Buna- S, PMMA, PVC, teflon, polyester, Nylon 66 and Nylon 6;
- define biodegradable polymers and
- cite examples of some biopolymers.

33.1 What are Polymers

A Polymer is a giant molecule formed by inter molecular linkage between same or different types of smaller molecules called **monomers**. If a large number of monomers (A) are linked together then the polymer is represented as $(-A_n-)_n$ or $(-A-A-A-A-A)_n$ is a polymer of the monomer of (A). For example, polyethene



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$-(\text{CH}_2 - \text{CH}_2)_n$ is a polymer of the monomer ethylene ($\text{CH}_2 = \text{CH}_2$).

Polymer is a high molecular mass molecule formed by linking up of two or more small molecules called monomers.

Monomers are the small molecule which are capable of linking amongst themselves to form big molecules called polymers.

In some polymers more than one type of monomers combine with each other to give the polymer. For example, a polymer may be obtained from two monomers (A) and (B) viz,



33.1.1 Types of Polymers

Depending upon the nature of the repeating structural units (monomers), polymers are divided into two broad categories viz., homopolymers and copolymers

(a) Homopolymer

A polymer formed from only one kind of monomers is called homopolymer. Polyethene $-(\text{CH}_2 - \text{CH}_2)_n$ is an example of homopolymer.

(b) Copolymer

A polymer formed from more than one kind of monomer units is called **copolymer or mixed polymer**. For example, Buna-S rubber which is formed from 1, 3-butadiene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$) and styrene ($\text{C}_6\text{H}_5\text{CH} = \text{CH}_2$) is an example of copolymer.

33.2 Polymerization

The process by which the monomers get linked up is called **polymerization**.

Polymerization is represented as :



where M stands for the monomer

33.2.1 Types of Polymerization

Depending upon the mode of reaction, polymerisation is classified as :

(a) addition polymerization and

(b) condensation polymerization.

(a) Addition Polymerization : This process involves the addition of monomer units to themselves to form a growing chain by a chain reaction mechanism. It is for this reason that the process is also known as **chain growth polymerization**.

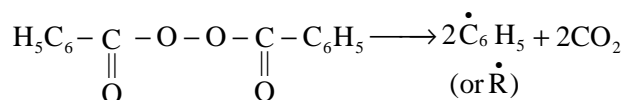
Addition polymerization is achieved by adding a catalyst (known as initiator), which provides some reactive species like free radicals.

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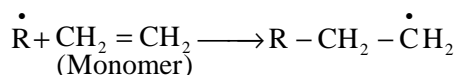


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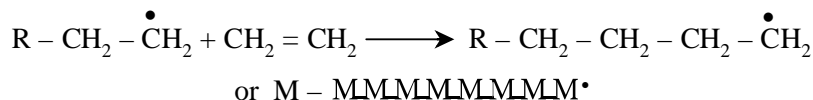
For example benzoyl peroxide provides free radical 'benzyl' to initiate the chain polymerization reaction.



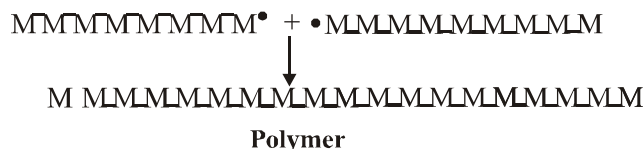
Initiation



These free radicals ($\text{R}\cdot$) then attack the unsaturated monomer and form a new free radical which goes on successively adding monomers and thus grows the chain, this is called **Chain propagation** :



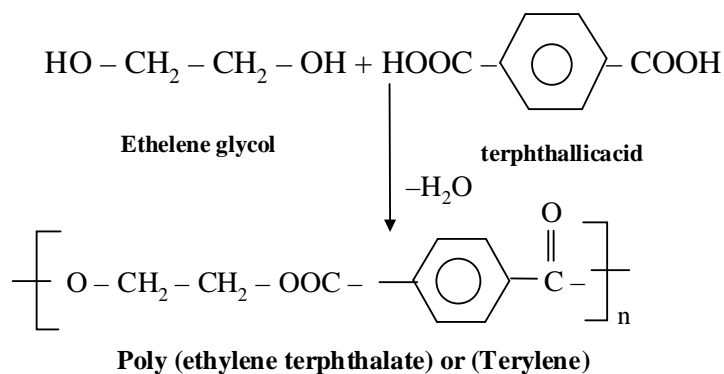
The final **termination** of the two growing chains leads to a polymer. This is called **chain termination** :



Condensation Polymerization : In this, the monomers combine with the elimination of a small molecule like H_2O , ROH or NH_3 , etc. The reaction is called (step growth) condensation polymerization and the product formed is called condensation polymer.

The process involves the elimination of by product molecules, therefore, the molecular mass of the polymer is not the integral multiple of the monomer units.

For example polyester or Terylene is a condensation polymer of ethylene glycol and terphthallic acid.



These two processes of making polymers have several characteristics which distinguish them from each other. These are shown in (Table 33.1).

Table 33.1 : Some differences between addition polymerization and condensation polymerization

Addition Polymerization	Condensation polymerization (Polycondensation)
1. Involves unsaturated monomers like ethylene, vinyl chloride, styrene etc.	1. Involves substances with at least 2 functional groups like ethylene glycol (2-OH groups), adipic acid (2-COOH groups).
2. Fast addition of monomers.	2. Step-wise slow addition.
3. At any instant, only monomer and polymers are present.	3. No monomer. Mixtures of dimers, trimers and tetramers etc. are present
4. Initiator is necessary to catalyse the polymerization.	4. Catalyst is not necessary.
5. No small molecules are eliminated.	5. Small molecules like H_2O , HCl , CO_2 , CH_3OH are often eliminated.
6. Polymers made are, for example, polyethene, polypropylene, polybutadiene, polyvinylchloride.	6. Polymer made are, for example, terylene, nylon, Formaldehyde-resins, silicones.



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Intext Questions 33.1

- Define the terms :
 (i) Polymer
 (ii) Monomer
- Write one example of each of :
 (i) Addition polymerization
 (ii) Condensation polymerization.
- Differentiate between homopolymers and copolymers.

- Write monomers of Terylene and Nylon-66.

33.3 Classification of Polymers

The polymers can be classified in a number of ways. Some of these are discussed below for a systematic investigation of their properties and uses.

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(a) Classification of Polymers on the Basis of Origin.

On the basis of origin, polymers are classified as :

1. Natural polymers
2. Synthetic polymers

1. Natural Polymers : The polymers obtained from nature (plants and animals) are called natural polymers. Starch, cellulose, natural rubber, proteins, etc. are some examples.

2. Synthetic Polymers : The polymers which are prepared in the laboratories are called **synthetic polymers**. These are also called **man-made polymers**. Polyethene, PVC, nylon, Teflon, bakelite, terylene, synthetic rubber, etc. are common examples.

(b) Classification of Polymers on the Basis of structure

On the basis of structure of polymers, these can be classified as :

1. Linear polymers
2. Branched chain polymers
3. Cross-linked polymers.

1. Linear polymers : These are polymers in which **monomeric units** are linked together to form linear chains. These linear polymers are well packed (Fig. 33.1) and therefore, have high densities, high tensile (pulling) strength and high melting points. For example, polyethelene, nylons and polyesters are examples of linear polymers.

2. Branched chain polymers : These are polymers in which the monomers are joined to form long chain with side chains or branches of different lengths [Fig. 33.2]. These branched chains polymers are irregularly packed and therefore, they have lower tensile strength and melting points than linear polymers. For example, low density polyethene, glycogen, starch, etc.

3. Cross-linked polymers : These are polymers in which long polymer chains are cross-linked together to form a three dimensional network. These polymers are hard, rigid and brittle because of the network structure. (Fig. 33.3) bakelite, melamine and formaldehyde resin are some examples of this type.

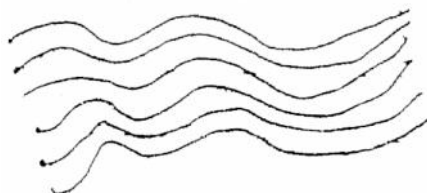


Fig. 33.1 : Linear Polymers



Fig 33.2 : Branched chain polymers

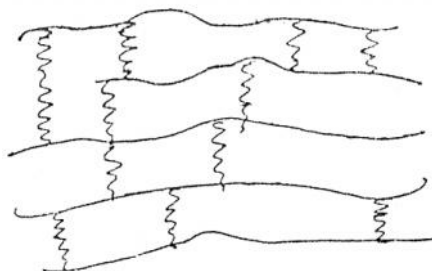


Fig. 33.3 : Cross linked polymers

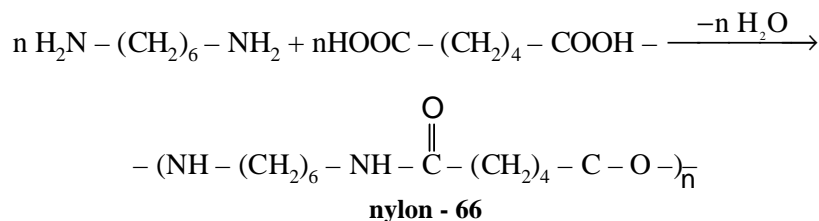


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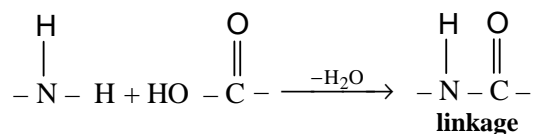
(c) Classification of Polymers on the Basis of Method of Polymerisation

On the basis of method of polymerisation the polymers are classified as :

- 1. Addition polymer :** A polymer formed by direct addition of repeated monomers without the elimination of any small molecule is called **addition polymer**. In this type, the monomers are unsaturated compounds and are generally derivatives of ethene. The addition polymers have the same empirical formula as their monomers. Examples are polyethene, polypropylene and polyvinyl chloride, etc.
- 2. Condensation polymer :** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol, etc. is called **condensation polymer**. In this type, each monomer generally contains two functional groups. For example, nylon – 66 is obtained by the condensation of two monomers; hexa methylenediamine and adipic acid with the loss of water molecules.



In this polymerization reaction $-\text{NH}_2$ group of hexamethylenediamine reacts with $-\text{COOH}$ group of adipic acid forming $-\text{NH}-\text{CO}-$ linkage with the elimination of H_2O .



Examples of condensation polymers are Nylon 66, terylene, bakelite, alkylresins, etc.

(d) Classification of Polymers on the Basis of Molecular Forces

Depending upon the intermolecular forces between monomer molecules, the polymers have been classified into four types.

1. Elastomers
2. Fibers
3. Thermoplastics
4. Thermosetting

- 1. Elastomers :** In case of elastomers the polymer chains are held together by weak **van der waals forces**. Due to weak forces, the polymers can be easily stretched on applying small stress and they regain their original shape when the stress is removed. This is due to the presence of few- 'cross links' between the chains, which help the polymer to retract to its original position after the force is removed, as in vulcanized rubber.

The most important example of elastomer is **natural rubber**.

- 2. Fibres :** These are the polymers which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interactions. Because of the strong forces, the chains are closely packed, giving them high tensile strength and less elasticity. These polymers can be drawn into long, thin and thread

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like fibres and therefore can be woven into fabrics. The common examples are nylon-66, dacron, silk, etc.

3. **Thermoplastics** : These are linear polymers with very few cross linkages or no cross linkages at all. The polymeric chains are held by weak VANDER WAAL forces and slide over one another. Due to lack of cross linkages these polymers soften on heating and harden or become rigid on cooling. Thus they can be moulded to any shape. Polythene, PVC, polystyrene are addition type thermoplastics and Terylene, nylon are condensation type thermoplastics.

Plasticizers : Certain plastics do not soften much on heating. These can be easily softened by the addition of some organic compounds which are called **plasticizers**. For example, polyvinyl chloride (PVC) is very stiff and hard but is made soft by adding di-n-butylphthalate (a plasticizer). Some other common plasticizers are dialkyl phthalates and cresyl phthalate.

4. **Thermosetting polymers** : Usually thermosetting polymer can be heated only once when it permanently sets into a solid which can not be remelted and remoulded. Thermosetting polymers are produced from relatively low molecular mass semi fluid polymers (called polymers) which on heating develop extensive cross-linking by themselves or by adding some cross-linking agents and become infusible and insoluble hard mass. The cross links hold the molecules in place so that heating does not allow them to move freely. Therefore, a thermosetting plastic is cross linked and is permanently rigid. The common example are bakelite, melamine, formaldehyde resin, etc.

Some important differences in the properties of thermosetting and thermoplastic polymers are summerized in Table 32.2.

Table 33.2 : Distinction between Thermoplastic and Thermosetting polymers

Thermoplastic	Thermosetting polymers
1. Linear Polymers.	1. Cross-linked polymers.
2. Weak van der Waals intermolecular forces and thus soften/melt on heating.	2. Chemical cross-linking make them infusible materials. Do not melt on heating.
3. Molten polymer can be moulded in desired shape. It can be remoulded by heating again.	3. Cross-linking is usually developed at the time of moulding where they harden irreversibly.
4. Examples are polystyrene, PVC, SBR, Teflon, PMMA terylene.	4. Examples are Glyptals, epoxy polymers, formaldehyde resins.



Intext Questions 33.2

1. Define natural and synthetic polymers with examples?

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2. What are cross linked polymers? Give one example of this type.

.....



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3. How do thermoplastic differ from thermosetting polymers?

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4. Arrange the following polymers in the increasing order of their intermolecular forces. Also classify them as addition and condensation polymers.

Nylon – 66, Buna-S, Polyethene.

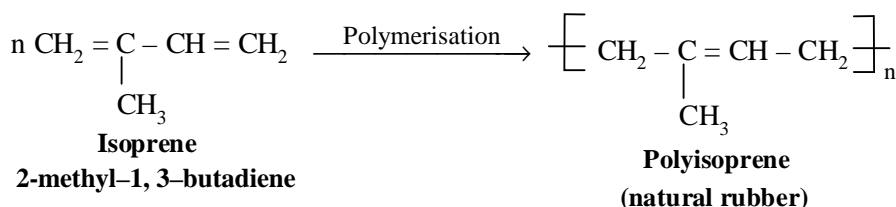
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33.4 Some Commercially Important Polymers

33.4.1 Polydiens

These polymers are obtained when an unsaturated hydrocarbon with two double bonds or when a diene (2 double bond compound) is polymerized with a substituted alkene (you have studied in lesson 32 that these alkenes and diens are petrochemicals). The polymers belonging to this class are rubbers or elastomer. They can be natural or artificial. Consequently we have natural rubber and synthetic rubber.

(1) Natural Rubber : It is a polymer of unsaturated hydrocarbon, 2-methyl-1, 3-butadiene also called isoprene. It is obtained from the latex of rubber trees found in tropical and semi-tropical countries such as India (southern part), Indonesia, Malayasia, Ceylon, South America, etc. The latex contains about 25-40% of rubber hydrocarbons dispersed in water alongwith stabilizer proteins and some fattyacids. It is a natural polymer and possess remarkable elasticity. It undergoes long range reversible extension under relatively small applied force. This elasticity makes it valuable for a variety of uses.



In natural rubber 10,000 to 20,000 isoprene units are linked together.

Drawbacks of raw rubber.

Raw natural rubber has a number of drawbacks. For example :

1. Rubber is brittle at low temperature and becomes very soft at high temperatures. Thus it can be used only in the limited temperature range of 10-60°C
2. It is too soft to be used for heavy duty operation. Its tensile strength is only 200 Kg/cm².
3. On stretching, it undergoes permanent deformation.
4. Not resistant to mineral oils, organic solvents and even action of water. It has large water absorption capacity.

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5. On exposure to air, it undergoes peroxidation. As a result, its durability is considerably decreased.

The desired valuable properties of plasticity, elasticity, toughness, hardness, softness, abrasion, resistance, impermeability, etc. are achieved by the process of Vulcanization.

Vulcanization of Rubber :

The wide applications of rubber are due to its property called elasticity and that is why rubber is said to be an **elastoplastic** or **elastomer**. Accidentally, in 1893, Charles Goodyears discovered that addition of sulphur to hot rubber cause changes that improve its physical properties in a spectacular manner. This process is called **vulcanization**. It is carried out by heating crude rubber in presence of sulphur or dipping it in a solution of S_2Cl_2 in CS_2 .

Vulcanisation depends upon :

- (i) The amount of sulphur used : by increasing the amount of sulphur rubber can be hardened
- (ii) Temperature
- (iii) Duration of heating.

Crude rubber is intimately mixed with about 3% ground sulphur, an accelerator and activator and then heated to about $150^\circ C$ (for tyres it is $153^\circ C$). Vulcanisation is a progressive reaction and is allowed to a definite stage. The detailed mode of vulcanization process may be difficult to visualize, but probable structure of vulcanized rubber is depicted below (Fig. 33.4).

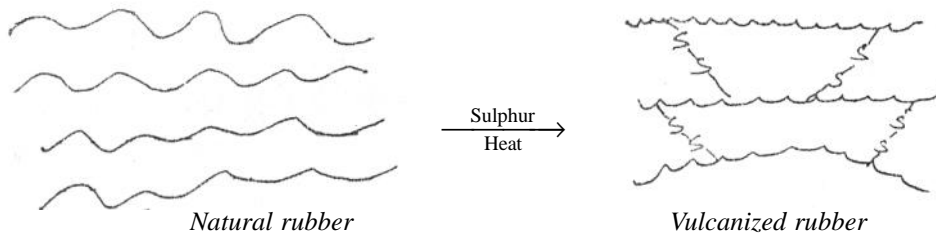


Fig. 33.4 : Process of vulcanization of rubber

Table 33.3 Comparison of some properties of natural rubber and vulcanized rubber :

Natural Rubber	Vulcanised rubber
1. Natural rubber is soft and sticky.	1. Vulcanized rubber is hard and non-sticky.
2. It has low tensile strength.	2. It has high tensile strength.
3. It has low elasticity.	3. It has high elasticity.
4. It can be used over a narrow range of temperature (from 10° to $60^\circ C$).	4. It can be used over a wide range of temperature (-40° to $100^\circ C$).
5. It has low wear and tear resistance.	5. It has high wear and tear resistance.
6. It is soluble in solvents like ether, carbon tetrachloride, petrol, etc.	6. It is insoluble in most of the common solvents.



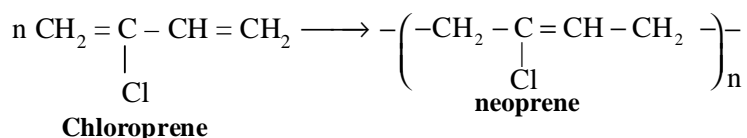
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(2) Synthetic Rubbers :

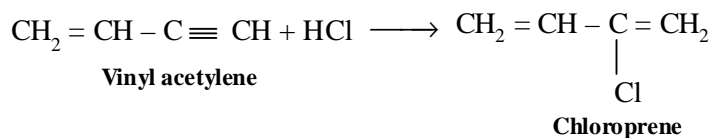
Synthetic high polymers possessing similar physical properties as that of natural rubber are called **synthetic rubber**. Usually synthetic rubber is an improvement over natural rubber, specially with respect to its resistance to oils, gas, solvents, etc. Attempts to find a synthetic substitute for natural rubber began very early. **Faraday**, in 1826 concluded that natural rubber was a hydrocarbon (C_5H_8 or $C_{10}H_{16}$). Greville William (1860), obtained isoprene, a liquid from rubber. He considered rubber as a polymer of isoprene. **Fritz Hofmann** (1909), synthesized rubber first of all by the polymerization of 2, 3-dimethyl butadiene. Synthetic rubber has been produced by the polymerization of a large number of conjugated dienes resembling to isoprene. The Buna Rubber (polymers of butadiene) was prepared by Germans by the action of sodium on butadiene and that is why such synthetic rubber is known as “Buna” rubber (“Bu” from butadiene and “na” from the symbol of sodium Na). Similarly Americans made S.B.R (styrene butadiene rubber) usually known as G.R.S. Since then the synthetic rubber industry has survived along with the natural rubber production.

Some synthetic rubbers are made by polymerization of only one monomer, for example Neoprene is made by polymerization of chloroprene, while synthetic rubbers like Buna-S, Buna N and Butyl rubber etc. are copolymers as these have more than one monomer.

Neoprene : This synthetic rubber resembles natural rubber in its properties. It is obtained by polymerization of chloroprene.



Chloroprene is obtained by the reaction of HCl with vinylacetylene



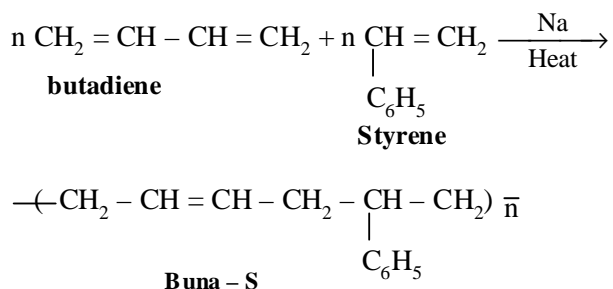
Neoprene is superior to natural rubber in its stability to aerial oxidation and its resistance to oils, gasoline and other solvents

Neoprene is used for

- (i) making belts, hoses, shoe heels, stoppers, etc. and
- (ii) manufacture of containers for storing petrol, oil and other solvents.

Buna – S:

It is obtained by polymerization of butadiene and styrene in presence of sodium metal.



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In Buna – S, Bu stands for butadiene, Na for sodium and S stands for styrene. It is also called S.B.R. (Styrene Butadiene Rubber). It has slightly less tensile strength than natural rubber.

Buna-S is used for

- (i) making automobile tyres.
- (ii) rubber soles, belts and hoses etc.

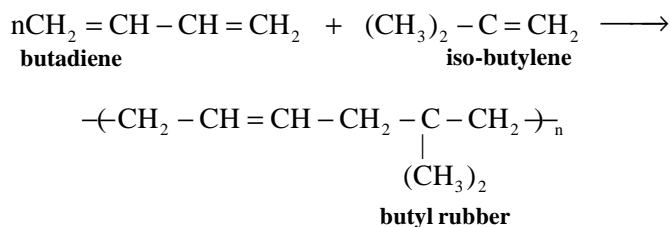
Buna – N : It is obtained by copolymerization of two parts of butadiene and one part of acrylonitrile in presence of sodium metal.

Buna – N is hard and extremely resistant to the swelling action by oils (petrol), solvents and is resistant to heat, etc.

Uses :

- (i) It is used for the manufacture of storage tanks for solvents and
- (ii) For making oil seals.

Butyl Rubber : This is obtained as a result of co-polymerization of butadiene and isobutylene. It is generally carried out in the presence of small quantity of isoprene. The function of isoprene is not exactly known.



Butyl rubbers are inert towards acids and alkalies, but have poor resistance towards petroleum products.

Uses :

- (i) It is used for making inner tubes of tyres and
- (ii) For making conveyor belts, tank linings and insulation of high voltage wires and cables etc.



Intext Question 33.3

1. Write the IUPAC names and structures of monomers of the following polymers :
 - (i) Natural rubber
 - (ii) Neoprene

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2. What is the function of sulphur in the vulcanization of rubber?

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3. What is Buna – S? How is it synthesized?

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4. Compare the properties (at least three) of natural rubber and vulcanized rubber?

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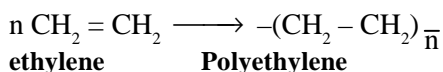
After the detailed discussion of rubbers, we shall now discuss some other commercially important polymers.

34.4.2 Polyolefins

Polyolefins is a major class of synthetic polymers made by the polymerization of an olefin (alkene) or its suitable derivative. Most of these are obtained from petro chemical industry. Polyethylene, polypropylene, PVC, Teflon, etc. belong to the class of polyolefins. Some important members of this class are discussed here with.

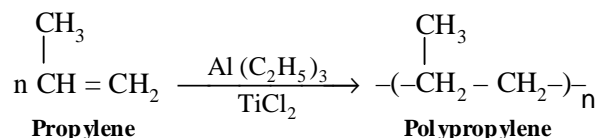
(1) Polyethylene or polyethene is formed by polymerization of ethylene ($\text{CH}_2 = \text{CH}_2$). It is manufactured in large quantities and is the most common polymer which you find almost every where.

Polyethene is of two types Low Density Polyethene (LDPE) and High Density Polyethene (HDPE) depending upon the nature of has branching in polymer chain and is not compact in polymer molecules. Low density polyethene has branching in polymer chains and is not compact in packing. While high density polyethere has linear chain of molecules which are packed in a more compact fashion (Fig. 33.1 and Fig. 33.2).



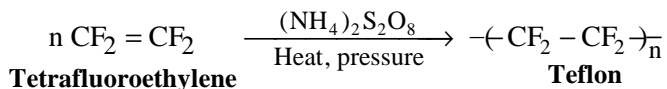
Polyethylene is used for making pipes, insulators, packing films, carry-bags, etc.

(2) Polypropylene : The monomer units are propylene molecules. It is generally manufactured by passing propylene through n-hexane (inert solvent) containing Ziegler-Natta catalyst (a mixture of triethyl aluminium and titanium chloride)



Polypropylene is harder, stronger and lighter than polyethene Polypropylene is used for packing of textile material and food, lining of bags, gramophone records, ropes, carpet fibres, etc.

(3) Teflon or Polytetrafluoro ethylene (PTFE) : The monomer unit is terafluoroethylene molecule. Teflon is prepared by heating tetra fluoroethylene under pressure in the presence of ammonium peroxosulphate. $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$.



Teflon is a very tough material and is resistant towards heat, action of acids or bases. It is

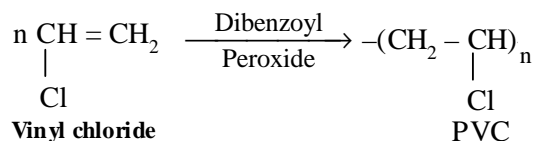
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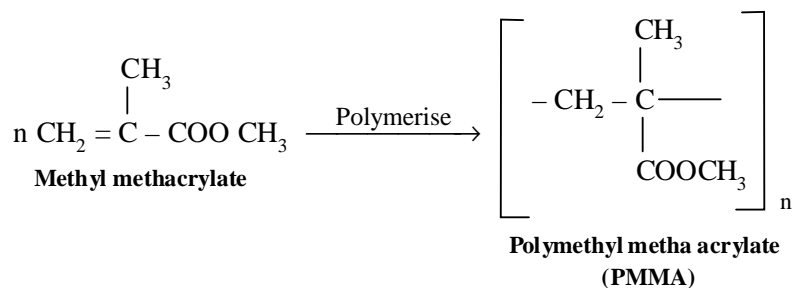
bad conductor of electricity. Teflon is used for coating utensils to make them non-sticking, making seals and gaskets which can withstand high pressures, insulation for high frequency electrical installations.

(4) Polyvinylchloride (PVC) : The monomer units are vinyl chloride molecules. PVC is prepared by heating vinyl chloride in an inert solvent in the presence of dibenzoyl peroxide.



PVC is a hard horny material. However, it can be made to acquire any degree of pliability by the addition of a plasticizer. It is resistant to chemicals as well as heat. It is used for making rain coats, hand bags, toys, hosepipes, gramophone records, electrical insulation and floor covering.

(5) Polymethyl Methacrylate (PMMA) : Its monomer unit is methyl methacrylate.



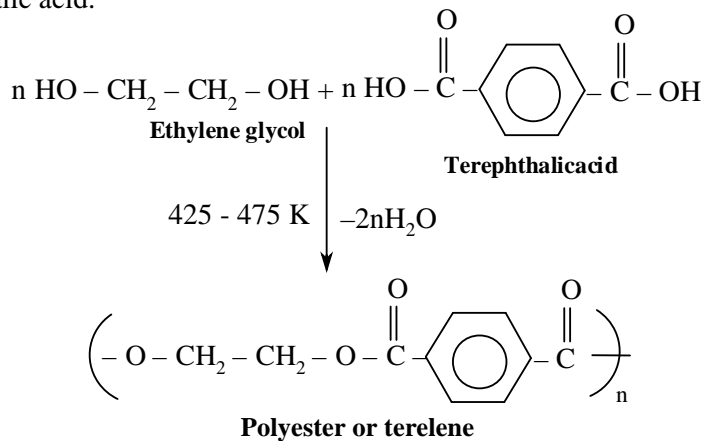
PMMA is a hard and transparent polymer and quite resistant to the effect of heat, light and ageing. It has high optical clarity. It is used in the manufacture of lenses, transparent domes and skylights, dentures, aircraft windows and protective coatings. Its commercial names are Lucite, Plexiglass, Acrylite and Perspex.

34.4.3 Polyester

Some synthetic polymers have ester group $\left(\begin{array}{c} \text{C} - \text{O} - \\ || \\ \text{O} \end{array} \right)$ in them. These are condensation

polymers. The important members of this class are polyester and glyptal resins.

Terelene : It is a polymer obtained by the condensation reaction between ethylene glycol and terephthalic acid.

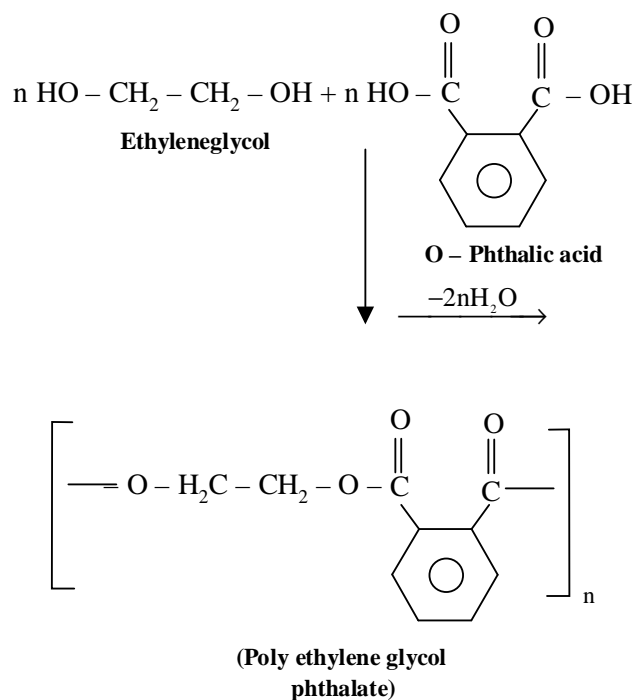




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Terelene is resistant to the action of most of the common chemicals and biological substances and also to abrasion. It has a low moisture absorbing power. As such it is widely used in making wash and wear fabrics. The polyester textile fibres made from the polymer are marketed under the trade name terelene or dacron. It is also blended with cotton and wool in clothing. It is also used in seat belts and sails. The polymer is also used in the preparation of films, magnetic recording tapes and for packing food. Dacron (and Teflon) tubes are good substitutes for human blood vessels in heart by pass operation.

Glyptal or Alkyl resin : Glyptal is a general name of all polymers obtained by condensation of di-basic acids, and polyhydroxy alcohols. The simplest glyptal is (poly ethylene glycol phthalate) which is obtained by a condensation reaction between ethylene glycol and ortho-phthalic acid.



Glyptal resins are three dimensional cross-linked polymers. Poly (ethylene glycol phthalate) dissolves in suitable solvents and the solution on evaporation leaves a tough and non-flexible film. Thus, it is used in adherent paints and lacquers.

34.4.4 Polyamide

Polyamides are the polymers having amide group $\left(\text{---} \overset{\text{O}}{\parallel} \text{C} - \text{NH} \text{---} \right)$ in them. The important

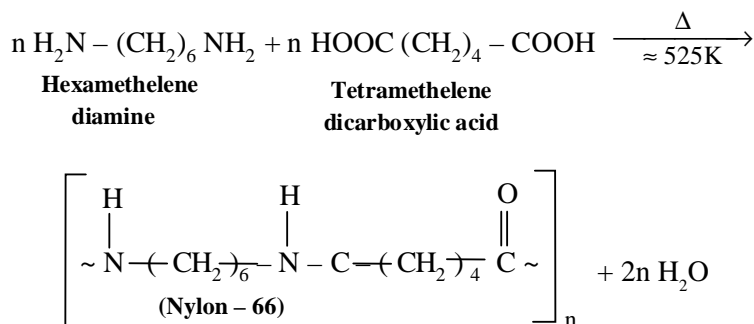
polyamide is Nylon-66 which is a synthetic polymer. In nature also the polymer have amide linkages in their molecules.

Nylon – 66 : It is a polymer of adipic acid (tetra methylene dicarboxylic acid) and hexamethylene diamine

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Nylon – 66 (read as nylon – six-six) can be cast into a sheet or fibres by spinning devices. Nylon fibres have high tensile strength. They are tough and resistant to abrasion. They are also somewhat elastic in nature.

Nylon finds use in making bristles and brushes, carpets and fabrics in textile industry, elastic hosiery in the form of crinkled nylon.



Intext Questions 33.4

- What does PMMA represent?
.....
- Write the names of monomers of terylene?
.....
- How is nylon - 66 synthesised?
.....
- Write equations for the synthesis of the following polymers :
(i) glyptal (ii) Teflon
.....

In this section we shall discuss about Biopolymers. (Natural Polymers)

33.5 Biopolymers

Many polymers which are present in plants and animals such as polysaccharides (starch, cellulose), proteins and nucleic acids etc. which control various life processes in plants and animals are called **biopolymers**.

- Starch** : It is polymer of glucose. It is a chief food reserve of plants.
- Cellulose** : It is also a polymer of glucose. It is a chief structural material of the plants. Both starch and cellulose are made by plants from glucose produced during photosynthesis.
- Proteins** : These are polymers of **amino acids**. They have generally 20 to 1000 amino acids joined together in a highly organized arrangement. These are building blocks of animals and constitute an essential part of our food.
- Nucleic acids** : These are polymers of various nucleotides. For example, RNA and DNA are common nucleotides. These biopolymers are very essential for our life.

33.6 Environmental Problems and Biodegradable Polymers

In this section we shall discuss those polymers which will not cause any environmental pollution.

With the increasing use of polymers, the problem of disposal of waste of these products is posing alarming curse. Since most of the synthetic polymers are in the form of plastics, it is frequently used in abundance in the form of packing material and throw away bags. Since ordinary polymers do not degrade naturally by light, oxygen, water or micro-organisms, there is a serious problem of their disposal. The environmental problems caused by careless use of non-biodegradable polymers can be reduced by proper disposal of these materials and reusing them and remoulding them for other uses. Another way is to collect them and depolymerise them back to monomers. Though it has a limited application.

Another option is to produce biodegradable polymers which can be broken into small segments by enzyme-catalysed reactions. The required enzymes are produced by micro-organisms. It is a known fact that the carbon-carbon bonds of chain growth polymers are inert to enzyme catalysed reactions, and hence they are non-biodegradable. To make such polymers biodegradable we have to insert certain bonds in the chains so that these can be easily broken by the enzymes. When such polymers are buried as waste, micro organisms present in the soil can degrade the polymer, so that they do not cause any serious affects on the environment.

One of the best method of making a polymer biodegradable is by inserting hydrolysable ester group into the polymer.

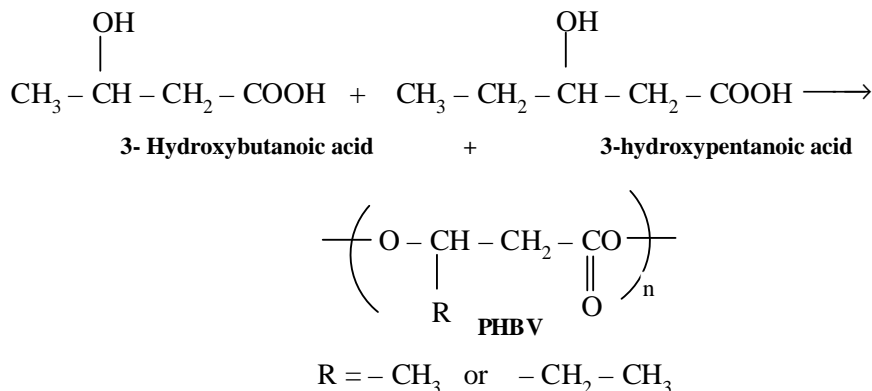
33.6.1 Some Biodegradable Polymers

A large number of bio degradable polymers are now available and more are being added to the list. However, these are expensive, therefore, these find use in special situations where cost factor can be ignored. In future, as their cost reduces these will find greater use in daily life and will replace non-bio-degradable polymers.

Some important biodegradable polymers are PHBV, PGA, PLA and PCL.

(PHBV) Poly-Hydroxybutyrate – co – S - Hydroxyvalerte

PHBV is a copolymer of 3 – hydroxy butanoic acid, and (3 – hydroxypentanoic acid), in which, the monomer units are connected by ester linkages.



The properties of PHBV vary according to the ratio of both the acids. 3 – Hydroxybutanoic acid provides stiffness and 3 – hydroxypentanoic acid imparts flexibility to the copolymer.



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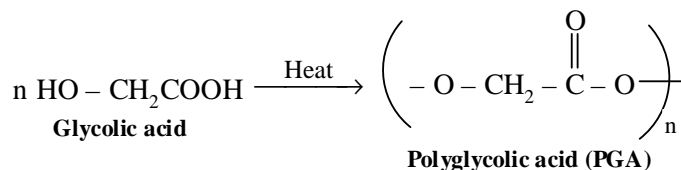


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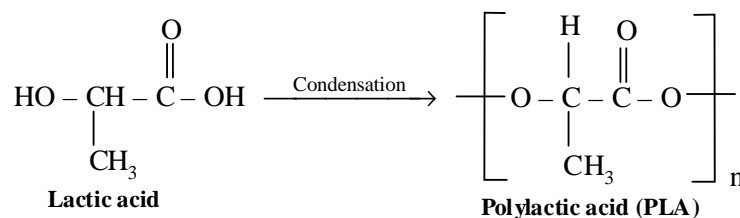
(i) PHBV is used in orthopaedic devices and

(ii) In controlled drug release. The drug put in PHBV capsule is released after this polymer is degraded by enzymatic action. It can also be degraded by bacterial action.

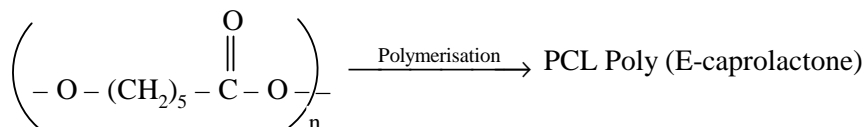
PGA Polyglycolic acid is obtained by the chain polymerization of dimer of glycolic acid, $\text{HO} - \text{CH}_2\text{COOH}$.



PLA Polyactic acid is obtained by polymerization of the dimer of lactic acid ($\text{HO} - \text{CH}(\text{CH}_3)\text{COOH}$) or by micro biological synthesis of lactic acid followed by the polycondensation and removal of water by evaporation.



PCL Poly (E-caprolactone) is obtained by chain polymerization of the lactone of 6-hydroxy hexanoic acid.



Most of the biodegradable polymers find use in stitching wounds and cuts.

1. In medical goods such as surgical sutures.
2. In agriculture materials such as films, seed coatings.
3. In food wrappers, personal hygiene products, etc.



Intext question 33.5

1. What is PHBV?

.....

2. Give two examples of biopolymers?

.....

3. Define biodegradable polymers? Give three examples?

.....

4. Which polymer is used for post-operative stitches?

.....

In the following Table 33.4 we shall now give a brief account of the various commercially important polymers alongwith their structures and uses.

Table 33.4



Notes

S. No.	Name of Polymer	Structure	Uses
1.	Polythene	$-(CH_2 - CH_2)_n-$	As Insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polystyrene	$\begin{array}{c} -(CH - CH_2)_n- \\ \\ C_6H_5 \end{array}$	As Insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinylchloride (PVC)	$\begin{array}{c} -(CH_2 - CH)_n- \\ \\ Cl \end{array}$	In manufacture or raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or Teflon	$-(CF_2 - CF_2)_n-$	As lubricant, insulator and making cooking wares.
5.	Polymethyl methacrylate (PMMA) or Flexi glass	$\begin{array}{c} CH_3 \\ \\ -(CH_2 - C)_n- \\ \\ COOCH_3 \end{array}$	As substitute of glass and making decorative materials.
6.	Polyacrylonitrile (Orlon)	$\begin{array}{c} CN \\ \\ -(CH_2 - CH)_n- \end{array}$	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or BuNa-S)	$\begin{array}{c} -(CH_2 - CH = CH - CH_2 - CH - CH_2)_n- \\ \\ C_6H_5 \end{array}$	In making automobile tyres and footwear.
8.	Nitrile rubber (Buna-N)	$\begin{array}{c} -(CH_2 - CH = CH - CH_2 - CH - CH_2)_n- \\ \\ CN \end{array}$	In making oil seals manufacture of hoses and tank linings.
9.	Neoprene	$\begin{array}{c} -(CH_2 - C = CH - CH_2)_n- \\ \\ Cl \end{array}$	As insulator, making conveyor belts and printing rollers.
10.	Poly ethyl acrylate	$\begin{array}{c} -(CH_2 - CH)_n- \\ \\ COOC_2H_5 \end{array}$	In making films, hose pipes and furnishing fabrics.
11.	Terylene (Dacron)	$-(OOC - \text{C}_6\text{H}_4 - COO - CH_2 - CH_2 - O)_n-$	For making fibres, safety belts, tyre cords, tents, etc.

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12. Glyptal	$\left(\text{OCH}_2\text{CH}_2\text{OOC} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \end{array} \text{COO} \right)_n$	As binding material in preparation of mixed plastics and paints.
13. Nylon 6	$\left(\text{NH} - (\text{CH}_2)_5 - \overset{\text{O}}{\parallel} \text{C} \right)_n$	In making fibres, plastics, tyre cords and ropes.
14. Nylon 66	$\left(\text{NH} - (\text{CH}_2)_6 - \text{NHCO} (\text{CH}_2)_4 \text{CO} \right)_n$	In making brushes synthetic fibres, parachutes, ropes and carpets.
15. Bakelite	$\left(\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_6\text{H}_4 - \text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2 \end{array} \right)_n$	For making gears, protective coating and electrical fittings.
16. Urea formaldehyde resin	$\left(\text{NH} - \text{CO} - \text{NH} - \text{CH}_2 \right)_n$	For making unbreakable cups and laminated sheets.
17. Melamine formaldehyde resin	$\left(\begin{array}{c} \text{HN} \quad \text{N} \quad \text{NH} - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} \quad \text{N} \\ \\ \text{NH}_2 \end{array} \right)_n$	Formaking plastic crockery, unbreakable cups and plates.
18. Poly-β-hydroxy butyrate-co-βhydroxy valerate (PHBV)	(a) $\left(\begin{array}{c} \text{O} - \text{CH} - \text{CH}_2 - \text{C} - \text{O} \\ \quad \quad \parallel \\ \text{R} \quad \quad \text{O} \end{array} \right)_n$ R = CH ₃ , - C ₂ H ₅	As packing, orthopaedle devices and in controlled drug release.



What You Have Learnt

- Polymers, the high molecular mass macrosized molecules consisting of repeating units of monomers of synthetic or natural origin.
- Synthetic polymers are classified with respect to their composition, mode of polymerization and nature of molecular forces.
- Polymerization is classified into two categories (i) addition polymerization (ii) condensation polymerization.
- Addition polymers are formed by addition of large number of monomers without the elimination of any smaller molecules.



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- Condensation polymers are formed by elimination of smaller molecules such as H_2O , NH_3 etc.
- Natural rubber is a linear polymer of isoprene, and is vulcanized by heating with sulphur, which forms cross link between different chains.
- Vulcanized rubber has much improved physical properties.
- Synthetic rubbers are usually obtained by copolymerization of an alkene and 1,3-butadiene derivatives.
- Synthetic polymers due to their inertness to degradation have created environmental problems.
- Since biopolymers degrade enzymatically, synthetic biodegradable polymers having functional groups such as ester, amide etc. have potential use as sutures, implants, drug release materials, are developed as alternatives. For example, PHBV, PLA, etc. constitute such materials.

**Terminal Exercise**

1. Explain the difference between chain growth and step growth polymerization.
2. Define the terms thermosetting and thermo-plastics. Give one example of each.
3. What is a copolymer. Give one example.
4. Differentiate between addition polymer and condensation polymer with the help of one example each.
5. What are elastomers? Give the chemical equation for the preparation of Buna-S.
6. Write the information asked for the following polymers :
 - (i) Neoprene : Materials required for preparation.
 - (ii) PVC : monomer unit.
 - (iii) Synthetic rubber : monomer units
7. What is vulcanization of rubber? What are the advantages of vulcanized rubber?
8. Give examples of two plasticizers.
9. How are polymers classified into different categories on the basis of intermolecular forces? Give one example of a polymer of each of these categories.
10. What are biodegradable polymers? Give three examples.
11. Write the names and structures of monomers of the following polymers :
 - a. Polystyrene
 - b. Teflon
 - c. PMMA
 - d. PVC



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- e. PHBV
- f. Polypropylene.
- 12. How will you prepare the following? Give chemical reaction only :
 - a. PVC
 - b. Nylon-66
 - c. PMMA



Answers to Intext Questions

33.1

1. (i) Polymer is a giant chain like molecule obtained by inter-molecular combinations of similar or different types of smaller molecules.
(ii) Monomers are the low molecular mass simple molecules capable of forming inter-molecular linkage to give giant molecules called polymers.
2. (i) Polyethene (ii) Terelene
3. (i) Homopolymers are polymers made of single monomer units, for example, polythene, polystyrene, or polybuta diene.
(ii) A copolymer is one which is formed by the co-polymerisation of two monomers. For example, Buna (or SBR, styrene - butadiene rubber)
4. (i) Ethelene glycol and terephthallic acid
(ii) Hexamethelene diamine and adipic acid.

33.2

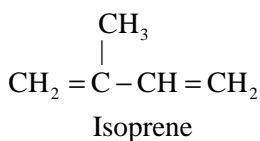
1. (i) Natural polymers are found in nature, (in animals and plants) e.g. proteins and nucleic acids.
(ii) Synthetic polymers are man-made. e.g. Nylon, polyesters and rubbers.
2. The polymers in which the linear polymer chains are cross linked to form a three-dimensional network structure are called cross-linked polymers. The common example of this type of polymer is bakelite.
3. Thermoplastics differ from thermosetting plastics in terms of mode of linkage and intermolecular forces. Thermoplastic polymer can be moulded in desired shape but thermosetting polymers set to shape on heating and can not be moulded.
4. Polyethene < Buna-S < Nylon-66
Nylon 66 : Condensation polymer
Buna-S : Addition polymer
Polyethene : Addition polymer



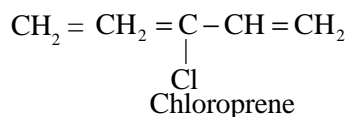
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33.3

1. (i) Monomer of natural rubber is

**2-methyl buta-1,3-diene**

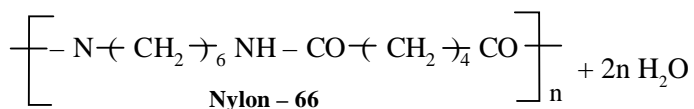
- (ii) Monomer of Neoprene is

**2-Chlorobuta – 1,3-diene**

- Sulphur makes the rubber more elastic, more ductile, less plastic and non-sticky.
- Buna-S is obtained by co-polymerization of butadiene and styrene in presence of sodium metal. Bu stands for butadiene, na for sodium and S stands for styrene, It is also called S.B.R.
1. Natural rubber is soft and sticky, but vulcanised rubber is hard and non-sticky.
 2. Natural rubber has less tensile strength while vulcanised rubber has high tensile strength.
 3. Natural rubber is soluble in solvents like ether, carbon tetrachloride, petrol etc. whereas vulcanised rubber is insoluble in all common solvents.

33.4

- Polymethyl methacrylate (PMMA)
- Ethelene glycol and terphthalic acid.
- Nylon – 6, 6 is synthesised by the polymerisation of two monomer units adipic acid and hexamethelene diamine.

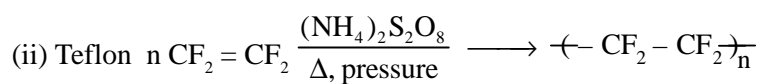
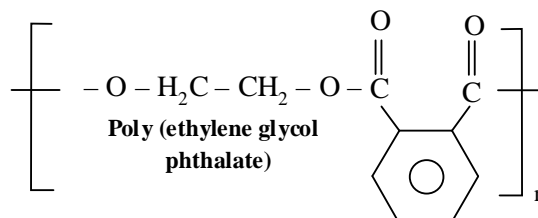
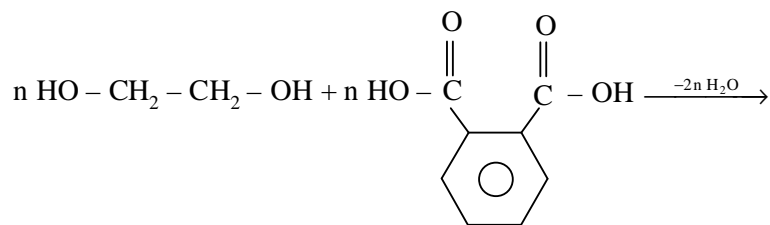


4. (i) Glyptal

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Notes



33.5

1. PHBV is a copolymer of 3 – Hydroxy butanoic acid and 3-hydroxypentanoic acid. It is used in making capsules. It is biodegradable in nature.
2. Nucleic Acids, proteins.
3. Polymers, which are degraded by microorganisations are called biodegradable polymers. For examples, PHBV, Polyglycolic acid, Polylactic acid, etc.
4. Polyglycolic acid (PGA) and poly Lactic Acid (PLA).