

POLYMERS

1. Introduction

The term polymer is used to describe a very large molecule that is made up of many repeating small molecular units. These small molecular units from which the polymer is formed are called monomers. The chemical reaction that joins the monomers together is called polymerisation. Starting from n molecules of a compound M , linking in a linear manner will form polymer $x-M-(M)_{n-2}-M-y$. The nature of linkages at the terminal units i.e. $M-x$ and $M-y$ depends upon the mode of reaction used in making the polymers.

Polymer chemistry is part of material science which involves creation of new materials to replace metal, glass, ceramics, wood, cardboard and paper.

2. Homopolymers and Copolymers

Polymers which are formed by only one type of monomer are called **Homopolymers**. Some examples of homopolymers and their monomers are given below:

Homopolymer	Monomer	Homopolymer	Monomer
Starch	Glucose	Teflon	Tetrafluoro ethylene
Cellulose	Glucose	Nylon-6	Caprolactam
Glycogen	Glucose	Polystyrene	Styrene
Dextrin	Glucose	Orlon (Acrilan)	Acrylonitrile
Inulin	Fructose	Plexiglas (Lucite)	Methyl methacrylate
Polyethylene	Ethylene	Polyvinyl acetate	Vinyl acetate
Polyvinyl chloride	Vinyl chloride		

POLYMERS

Polymers, which are formed by more than one type of monomers are known as **copolymers**. Some examples are given below in the table:

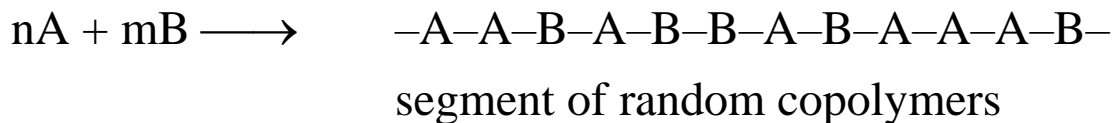
Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna-S, SBR	Styrene and Butadiene
Buna-N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylenediamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

2.1 Types of Copolymers

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

Random Copolymer

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



POLYMERS

Alternating Copolymer

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



segment of alternating copolymer

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

Block Copolymer

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers.

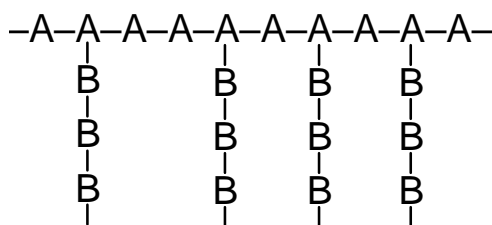
For example: $-B-B-A-A-A-A-A-A-B-B-B-B-B-B-A-A-$

Segment of a block polymer

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

Graft Copolymer

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co-polymers. For example:



Segment of a graft

POLYMERS

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

Illustration 1.

Is $[\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)]_n$, a homopolymer or a copolymer?

Solution:

It is a homopolymer and the monomer from which it is obtained is styrene, $\text{Ph}-\text{CH}=\text{CH}_2$.

3. Classification of Polymers

Polymers are classified in following ways:

3.1 Classification Based Upon Source

Natural Polymers

Polymers which are obtained from animals and plants are known as natural polymers. Examples of natural polymers are given below:

Natural polymer	Monomers
Polysaccharide	Monosaccharide
Proteins	α -L-Amino acids
Nucleic acid	Nucleotide
Silk	Amino acids
Natural Rubber (cis polyisoprene)	Isoprene(2-Methyl-1, 3 butadiene)
Gutta purcha (trans polyisoprene)	Isoprene

POLYMERS

Natural polymers which take part in metabolic processes are known as **biopolymers**. Examples are polysaccharides, proteins, RNA and DNA.

Semi-Synthetic polymers

Polymers which are prepared from natural polymers are known as semi-synthetic polymers. Most of the semi-synthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Kayon.

Synthetic Polymers

Man-made polymers, i.e., polymers prepared in laboratory are known as synthetic polymers. Example: PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

3.2 Classification Based Upon Shape

Linear Polymers

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

Note :

- (i) All fibres are linear polymers. Examples are cellulose, silk, nylon, terylene etc.
- (ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

POLYMERS

Branched chain Polymers

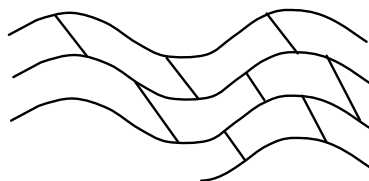
Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and low tensile strength as compared to linear polymers.

Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene and all vulcanised rubbers.



Cross-linked or Three Dimensional network Polymers

In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers.



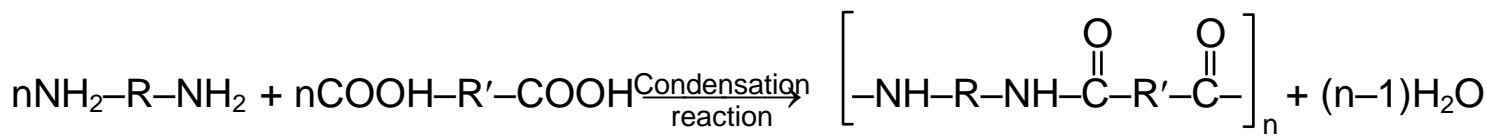
3.3 Classification Based Upon Synthesis

Condensation polymerisation

- (i) Condensation polymerisation is also known as step polymerisation.
- (ii) For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different.
- (iii) Monomers having only two functional group always give linear polymer.

POLYMERS

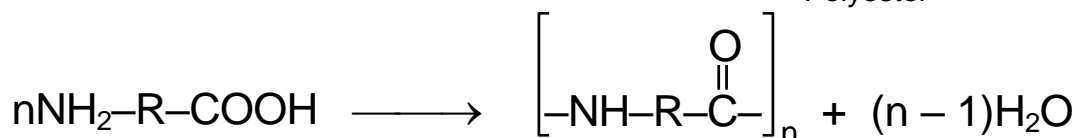
For example,



Polyamide



Polyester

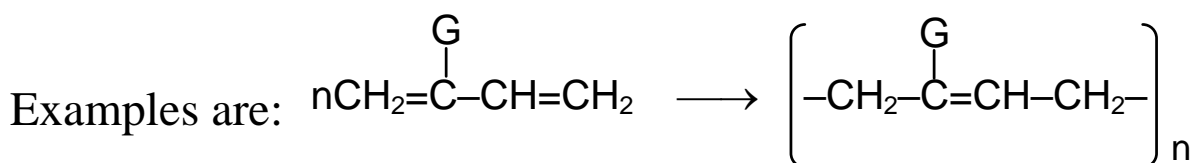


Polyamide

- (iv) Condensation polymers do not contain all the atoms initially present in the monomers. Some atoms are lost in the form of small molecules.
- (v) Monomer having three functional groups always gives cross-linked polymer. Examples are: Urea-formaldehyde resin, phenol-formaldehyde resin.

Addition polymerisation

- (i) Polymers which are formed by addition reaction are known as addition polymers.
- (ii) If monomer is ethylene or its derivative, then addition polymer is either linear polymer or branch-chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc.
- (iii) If monomer is 1,3-butadiene or 2-substituted-1,3-butadiene $\left[\text{CH}_2=\underset{\text{G}}{\text{C}}-\text{CH}=\text{CH}_2 \right]$, then polymer is always branched chain polymer.



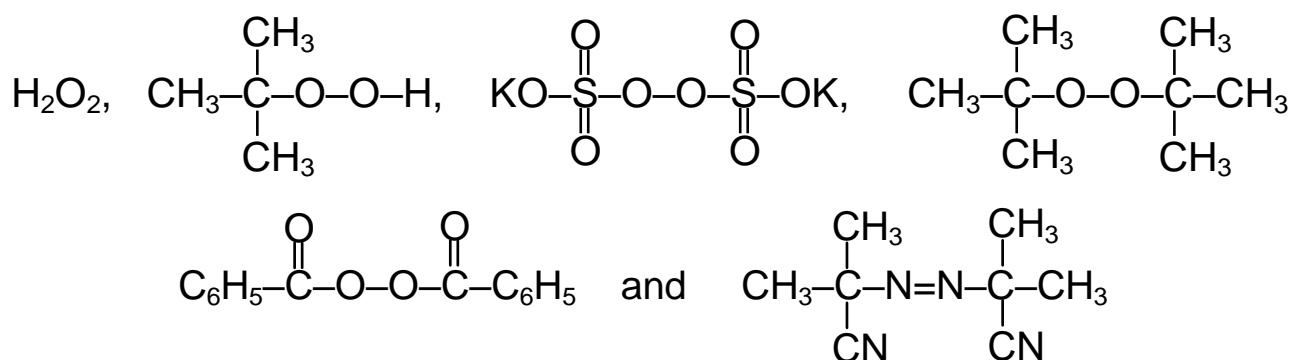
POLYMERS

- (i) $G = H$: 1,3-Butadiene gives Polybutadiene
- (ii) $G = CH_3$: 2-Methyl-1,3-butadiene gives Polyisoprene
- (iii) $G = Cl$: 2-Chloro-1,3-butadiene or chloroprene gives Polychloroprene (Neoprene)
- (iv) Addition polymers retain all the atoms of the monomer units in the polymer.
- (v) Addition polymerisation takes place in three steps:
Initiation, Chain propagation and Chain termination.

Types of Addition Polymerisation

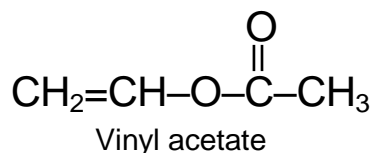
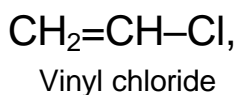
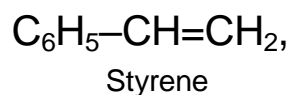
(A) Radical polymerization:

- (i) Radical polymerisation takes place in the presence of radical initiators. The radical initiator may be any of the following:

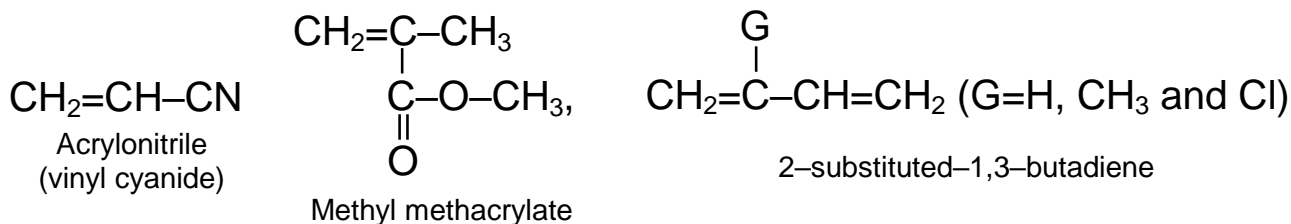


- (ii) Reaction intermediate of radical polymerization is a free radical.
- (iii) Radical polymerization is given by those monomers whose free radical is stable.

Examples are:



POLYMERS

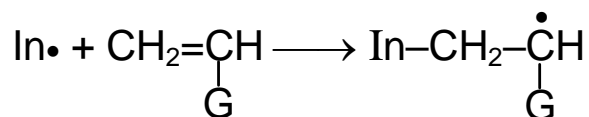
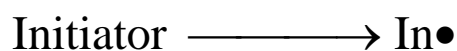


(iv) Radical polymer has linear as well as branched chain structure.

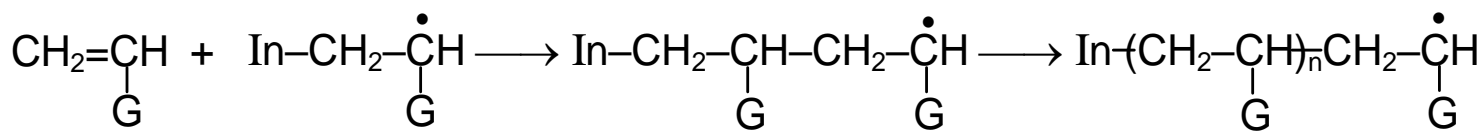
Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives $\text{CH}_2=\underset{\text{G}}{\text{CH}}$.

This type of polymerisation is performed by heating the monomer with only a very small amount of the initiator or by exposing the monomer to light. The general mode of radical polymerisation of vinyl monomers is depicted below:

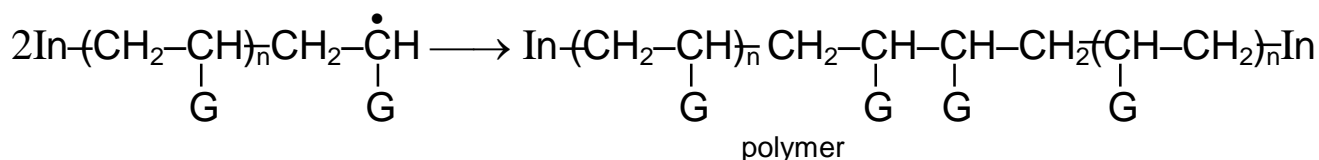
Chain initiation step:



Chain propagating step:



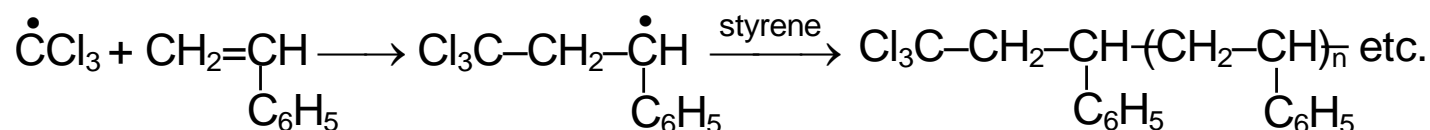
Chain terminating step:



In vinylic polymerisation, various other reactions of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can

POLYMERS

For example in the presence of CCl_4 styrene polymerises to form



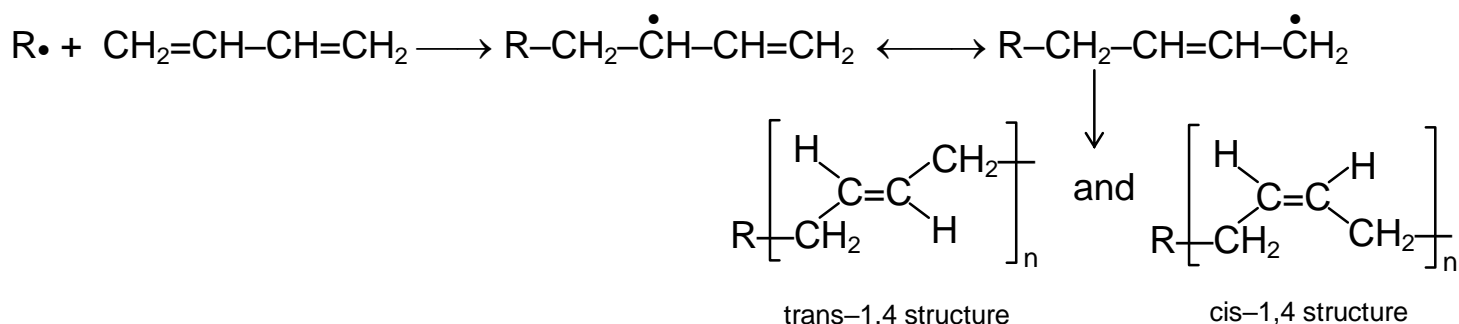
In case the alkene is a diene, the following kinds of polymerisation are

1,4-polymerization:

[illegible]

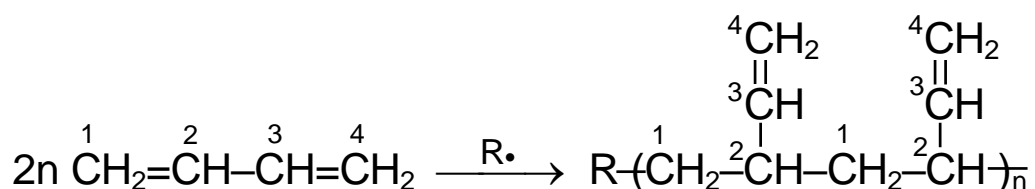
POLYMERS

substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below:



1, 2-Polymerisation:

Alternatively, 1,3-butadiene can undergo polymerisation at C₁ and C₂ to yield the polymeric product, polyvinyl polythene.

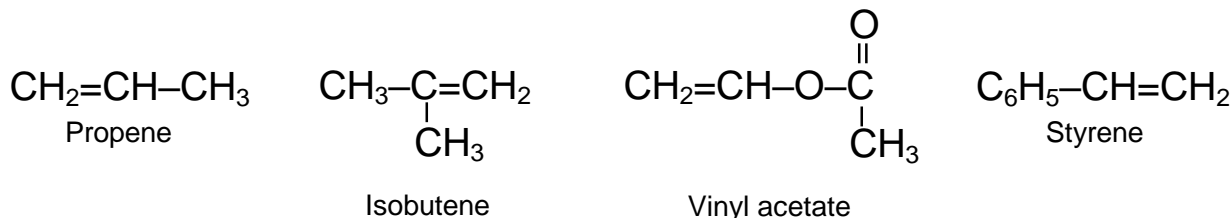


The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubbers.

(B) Cationic Polymerisation:

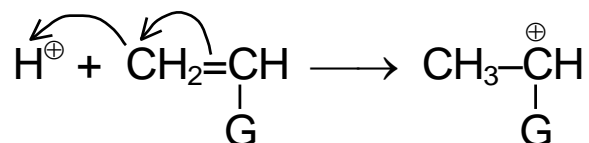
- (i) Polymerisation which is initiated by an electrophile is known as cationic polymerisation.
- (ii) Reaction intermediate of cationic polymerisation is a carbocation.
- (iii) Carbocations can undergo rearrangement leading to the formation of a more stable carbocation.
- (iv) The electrophile commonly used for initiation is BF₃.OEt₂.
- (v) Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron-donating substituents that can stabilise the carbocation. Some examples are:

POLYMERS

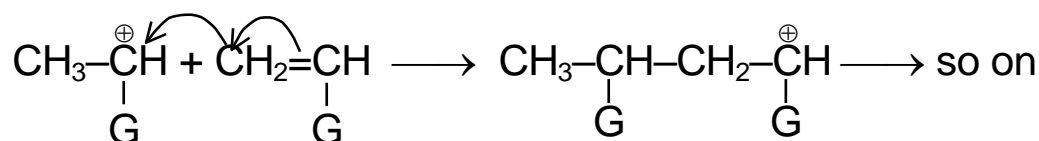


Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below:

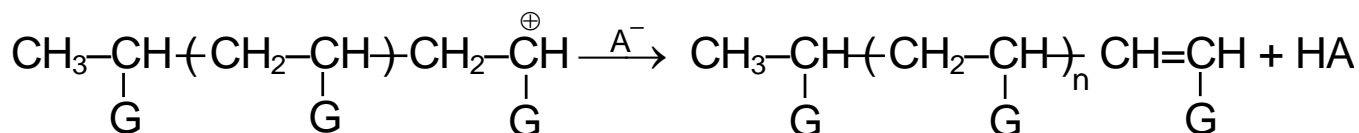
Chain initiation step:



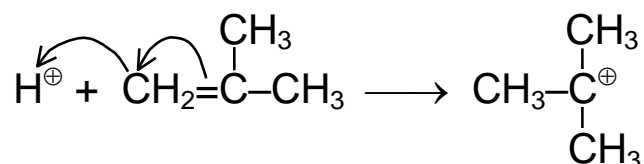
Chain propagating step:



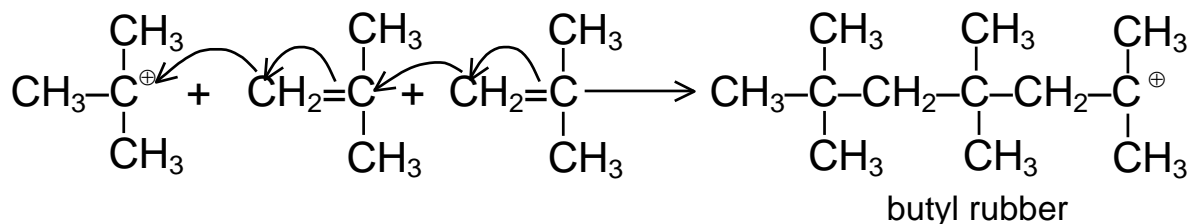
Chain terminating step:



Cationic polymerisation is facilitated in monomers containing electron-releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing $-\text{CH}_3$ groups that will stabilize the intermediate cation.

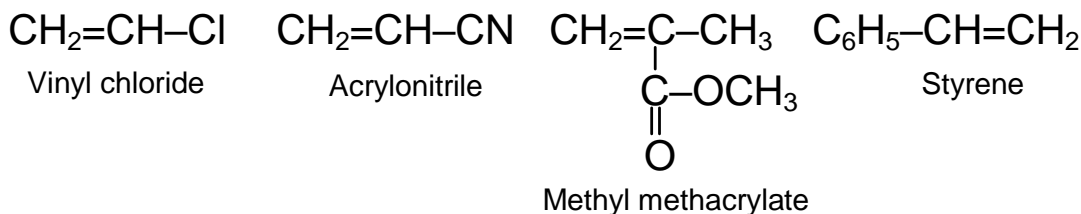


POLYMERS



(C) Anionic Polymerisation:

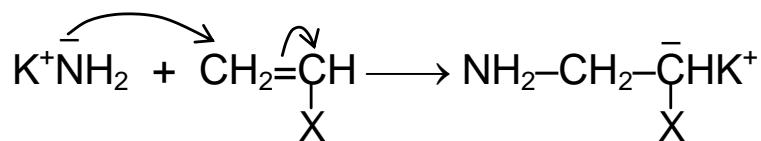
- (i) Anionic polymerisation takes place in the presence of nucleophile, which is initiator in this polymerization.
- (ii) Reaction intermediate in first propagation step is carbanion.
- (iii) The suitable initiator can be NaNH_2 or RLi .
- (iv) Those monomers undergo anionic polymerisation reaction whose anion is stable. Example of monomers are:



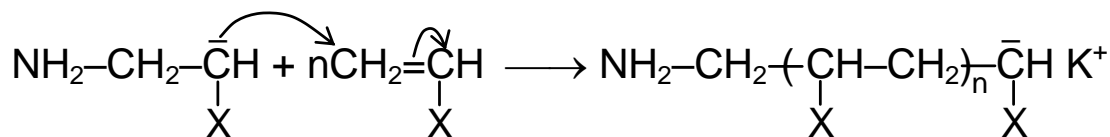
- (v) Anionic polymerisation always gives linear polymer.

The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below:

Chain initiation step:

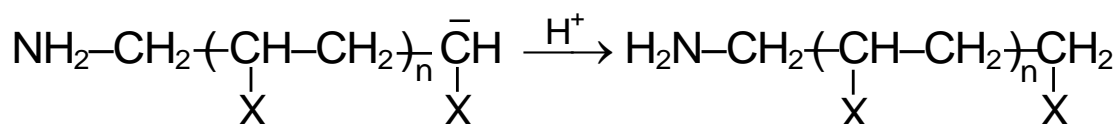


Chain propagating step:



POLYMERS

Chain terminating step:



(D) Ziegler–Natta polymerisation:

- (i) Addition polymerisation which takes place in the presence of Ziegler–Natta catalyst $[(\text{C}_2\text{H}_5)_3\text{Al}$ and $\text{TiCl}_4]$ is known as Ziegler–Natta polymerisation or Coordination polymerisation.
- (ii) Ziegler–Natta polymerisation always gives linear, stereo–regular polymers.
- (iii) Ziegler–Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat. High density polyethylene is prepared using a Ziegler–Natta catalyst.

Illustration 2.

Write the structure of the monomer of the following polymer.



Solution:

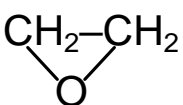
Ethylene oxide is the monomer and its structure is 

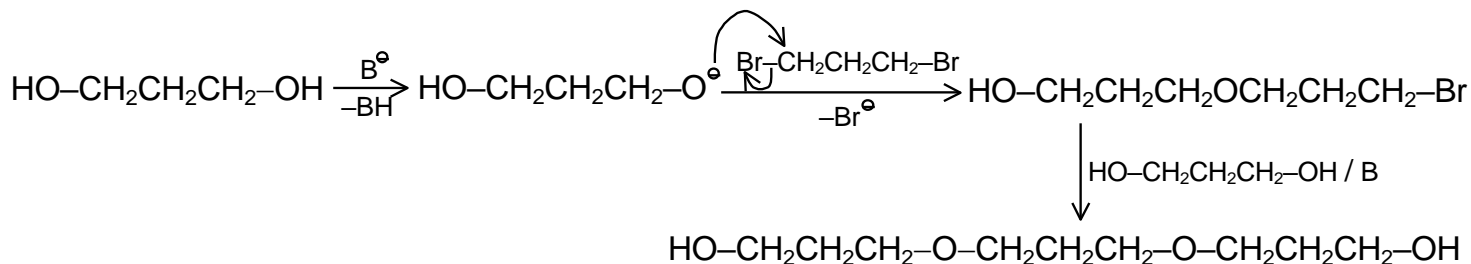
Illustration 3:

When the following reaction occurs, what is the repeating unit of the polymer formed?



Solution:

POLYMERS



The repeating unit of the polymer formed is $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$.

3.4 Classification Based On Inter-Molecular Forces (Secondary Forces)

- (i) Intermolecular forces present between polymeric chains are (a) Van der Waals forces (b) Hydrogen bonds and (c) Dipole-dipole attractions.
- (ii) Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains.
- (iii) Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains.

Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following *five categories*.

Elastomers

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Van der Waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Van der Waal forces to maintain them in that configuration

POLYMERS

and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length. Important examples are vulcanized rubbers.

Note: Addition polymers obtained from butadiene and its derivatives are elastomers.

Fibres

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds and/or dipole–dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another.

Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. They have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

Note:

- (i) Condensation polymers formed from bifunctional monomers are fibres in character.
- (ii) Addition polymers of alkene derivatives having strong – I group are fibres in character.

Thermoplastic Polymers

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non-crystalline regions (the regions of the polymer in which the chains are randomly oriented).

The intermolecular forces of attraction are in between elastomers and fibres. There are no cross–links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscous. This soft and viscous material becomes rigid on

POLYMERS

cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are: polyethene polypropylene, polystyrene, polyvinyl chloride, teflon etc. Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

Thermosetting polymers

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating.

Thermosetting polymers are cross-linked polymers. Greater the degree of cross-linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. The hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are: phenol-formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin.

Difference between Thermoplastic and Thermosetting polymers

Thermoplastic Polymers	Thermosetting Polymers
Soften and melt on heating and become hard on cooling i.e. process is reversible.	Become hard on heating and process is irreversible.
Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped.
They are addition polymers.	They are condensation polymers.

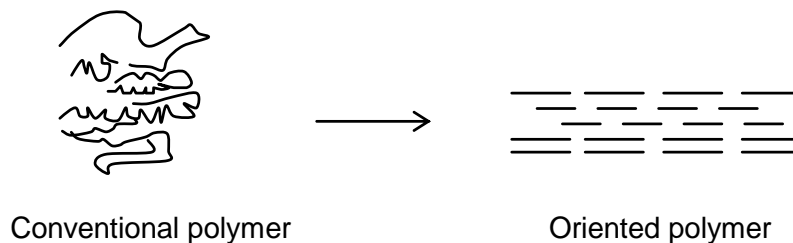
POLYMERS

Structure is generally linear.

Structure is cross-linked.

Oriented Polymers

Oriented polymers can be made by taking the polymer chains obtained by conventional polymerisation, stretching them out and putting them back together in a parallel fashion.



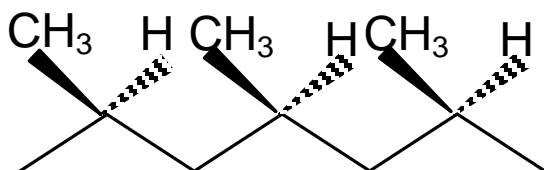
Oriented polymers are stronger than steel and very good conductors of electricity. Conducting power of such polymers is more than that of copper.

Dyneema is the strongest commercially available fabric. It is an oriented polyethylene polymer. Its molecular weight is 100 times greater than that of high density polyethylene. It is being used to make helmet, protective fencing suits and hang gliders.

3.5 Classification Based On Stereochemistry

(i) Isotactic (Greek meaning ‘same order’)

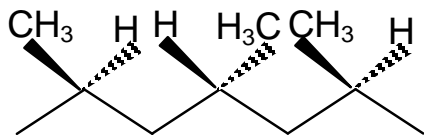
With all the methyl groups of polypropene on one side of the zig-zag backbone.



(ii) Syndiotactic (Greek meaning ‘alternating order’)

With the methyl groups of polypropene alternating regularly on the opposite sides of the zig-zag backbone.

POLYMERS



(iii) Atactic (Greek meaning ‘no order’)

With the methyl groups of polypropene randomly oriented.

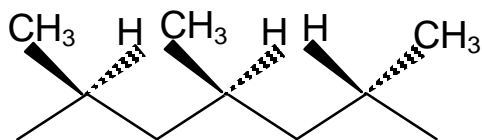


Illustration 4.

Which of the following is a natural polymer?

(1) Polythene (2) Polysaccharides (3) Nylon.

Solution:

Polysaccharides are natural polymers.

Illustration 5.

Which among the following is a synthetic polymer?

(1) Polysaccharides (2) Natural rubber (3) Phenol–formaldehyde resin.

Solution:

Phenol–formaldehyde resin is a synthetic polymer.

4. RUBBER

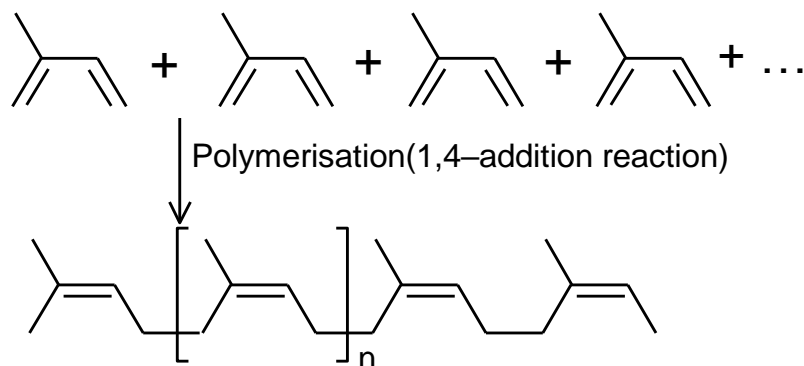
4.1 Natural Rubber

Natural rubber is obtained from nearly five hundred different plants but the main source is **Hevea brasiliensis** tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

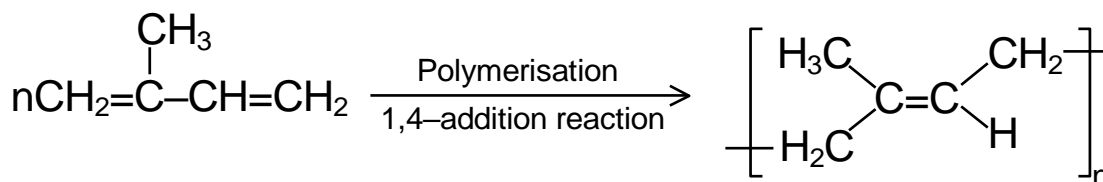
The **raw natural rubber** is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalis but soluble in non–polar solvents. It has

POLYMERS

low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1,3-butadiene (isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is **cis-polyisoprene**.



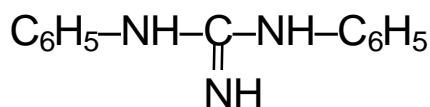
Gutta-percha is a naturally occurring isomer of rubber in which all the double bonds are trans. Thus, gutta-percha is **trans-polyisoprene**.



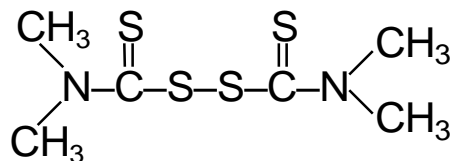
It is harder and more brittle than rubber. It is the filling material that dentists use in root canal treatment.

In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at 150°C for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerators. The common accelerators are:

POLYMERS



Diphenyl guanidine



Tetramethylthioureadisulphide

In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

Natural rubber is used for making shoes, water-proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves, tubing and car tyres.

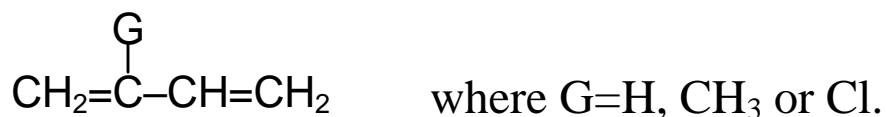
4.2 Synthetic Rubber or Polymerisation of Dienes

Polymers of 1,3-butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic.

Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

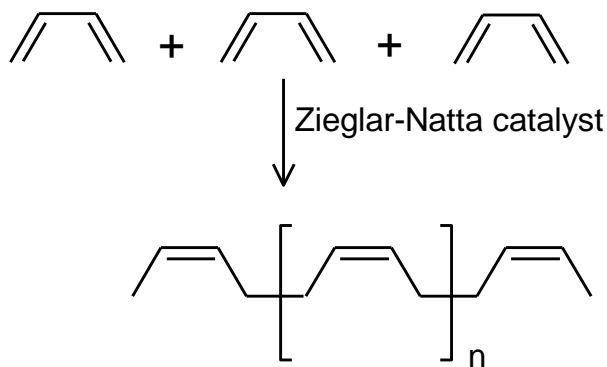
Homopolymers

Monomer of this class is 2-substituted-1,3-butadienes.



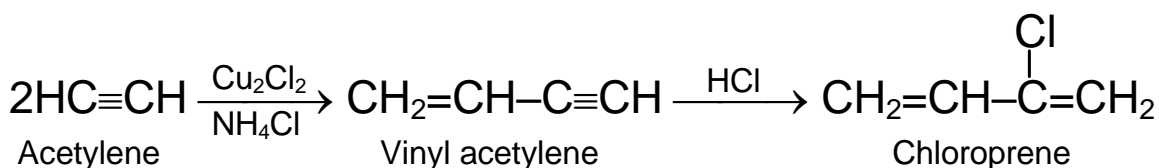
Polymerisation is always carried out in the presence of Ziegler-Natta catalyst which gives stereo regular polymers.

POLYMERS

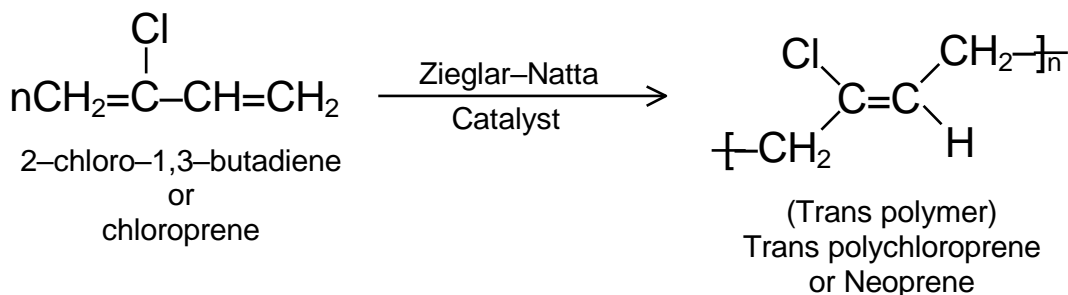


cis poly (1,3-butadiene)

Neoprene was the first synthetic rubber manufactured on large scale. It is also called **dieprene**. Its monomer, chloroprene (2-chlorobutadiene) is prepared from acetylene.



Chloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).



Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non-inflammable.

It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

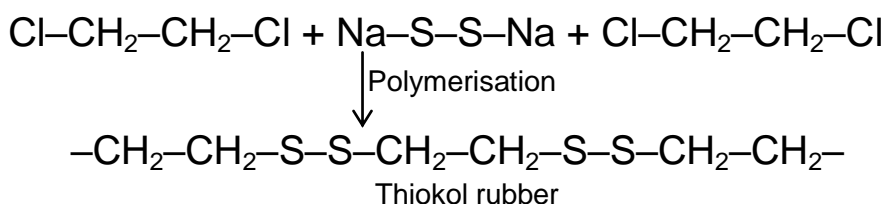
POLYMERS

Copolymers

The following synthetic rubbers are example of copolymers.

Synthetic rubber	Monomers
1. Buna–S, SBR (Styrene–Butadiene rubber)	$\text{C}_6\text{H}_5\text{--CH=CH}_2$ + $\text{CH}_2\text{=CH--CH=CH}_2$ (25%) (75%)
2. Buna–N, NBR (Nitrile–Butadiene rubber)	$\text{CH}_2\text{=CH--CN}$ + $\text{CH}_2\text{=CH--CH=CH}_2$ (25%) (75%)
3. Butyl rubber	$\text{CH}_3\text{--}\underset{\text{CH}_3}{\text{C}}\text{=CH}_2$ + Butadiene 98% 2%
4. ABS; Acrylonitrile, Butadiene, Styrene	$\text{CH}_2\text{=CH--CN}$ + $\text{CH}_2\text{=CH--CH=CH}_2$ + $\text{C}_6\text{H}_5\text{CH=CH}_2$

(a) Thiokol: Thiokol is made by polymerising ethylene chloride and sodium polysulphide.



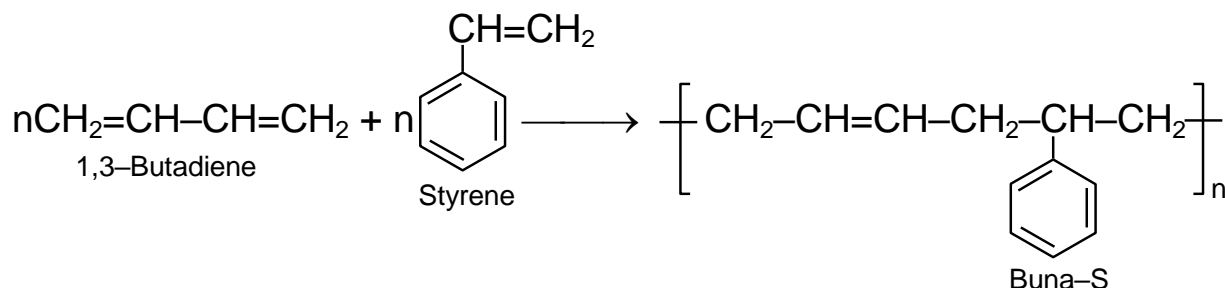
The repeating unit is $\text{--CH}_2\text{--S--S--CH}_2\text{--}$.

Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(b) Buna–S (SBR: Styrene–butadiene rubber): Buna–S rubber is a copolymer of three moles of butadiene and one mole of styrene. In Buna–S, ‘Bu’ stands for butadiene, ‘na’ for symbol of sodium (Na) which is a

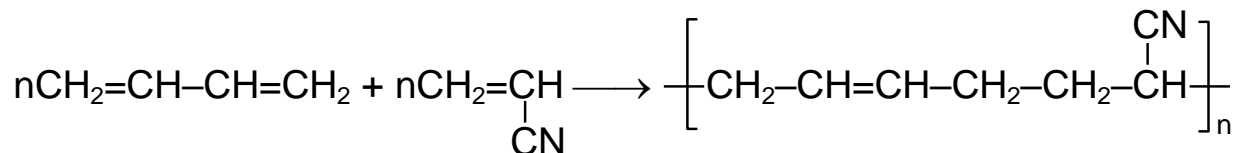
POLYMERS

polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).



Buna-S is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

(c) **Buna-N:** It is obtained by copolymerisation of butadiene and acrylonitrile (General purpose Rubber Acrylonitrile or GRA).



It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.

(d) **Cold Rubber:** Cold rubber is obtained by polymerisation of butadiene and styrene at -18° to 5°C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

Illustration 6.

Which of the following is an elastomer?

(1) Vulcanized rubber (2) Dacron (3) Polystyrene

Solution:

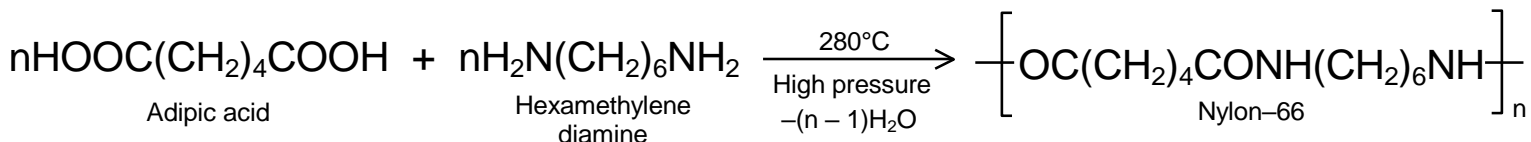
Vulcanized rubber is an elastomer.

5. Nylon

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e., having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

5.1 Nylon–66 (Read as nylon six, six)

It is obtained by the condensation polymerisation of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).



5.2 Nylon–610 (Read as nylon six, ten)

It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms).

Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes, etc.

5.3 Nylon–6 (Perlon L)

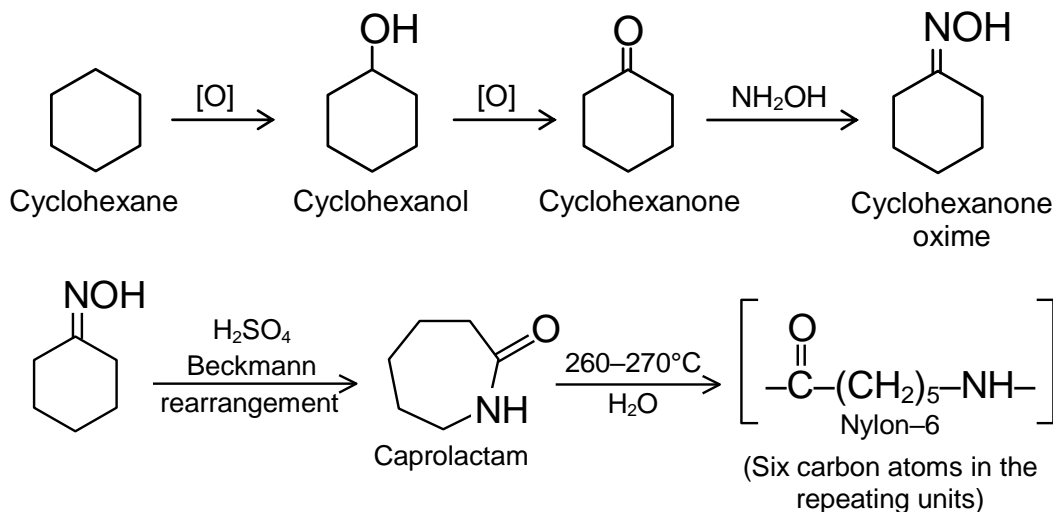
A polyamide closely related to nylon is known as perlon L (Germany) or Nylon–6 (USA).

It is prepared by prolonged heating of caprolactum at 260–270°C. It is formed by self-condensation of a large number of molecules of amino caproic acid. Since, caprolactum is more easily available, it is used for

POLYMERS

polymerization, which is carried out in the presence of H_2O that first hydrolyses the lactam to amino acid. Subsequently, the amino group of the amino acid can react with the lactam and the process goes on and onto form the polyamide polymer.

Caprolactam is obtained by Beckmann rearrangement of cyclohexanone oxime.



5.4 Nylon-2-Nylon-6

It is an alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

Illustration 7.

Nylon-66 is obtained by condensation polymerization of

- (a) Adipic acid and hexamethylene diamine
- (b) Phenol and formaldehyde
- (c) Terephthalic acid and ethylene glycol
- (d) Sebacic acid and hexamethylene diamine

POLYMERS

Solution:

(a) Adipic acid and hexamethylene diamine on condensation will generate Nylon-66

Illustration 8.

Which of the following type of forces are present in Nylon-66?

- (a) Van der Waal's forces of attraction
- (b) Hydrogen bonding
- (c) Three-dimensional network of bonds
- (d) None of these

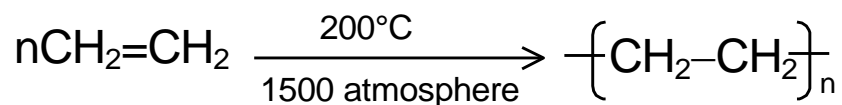
Solution:

(b) Hydrogen bonds are present in Nylon-66.

6. Polyethylene

Polyethylene is of two types:

(a) Low Density Poly Ethylene (LDPE): It is manufactured by heating ethylene at 200°C under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.



The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110°C). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

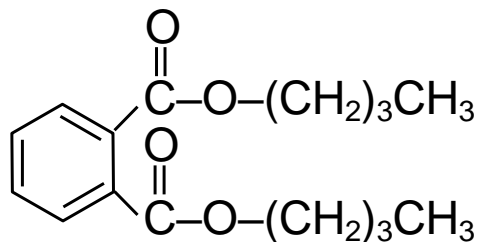
POLYMERS

(b) High Density Poly Ethylene (HDPE): It is prepared by the use of Ziegler–Natta catalyst at 160° under pressure of 6 to 7 atmosphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point (130°C). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

7. Plasticiser

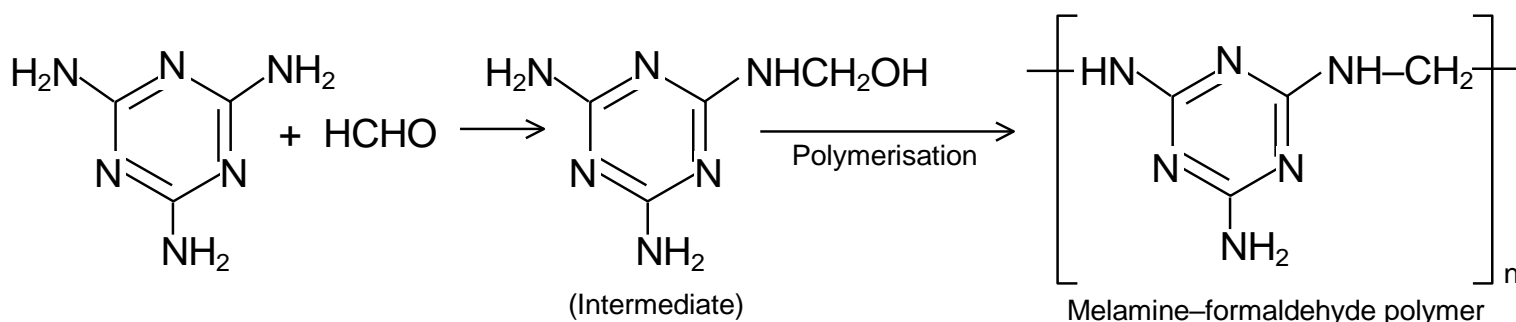
A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly used plasticiser.



Dibutylphthalate

8. Melamine–Formaldehyde Resin

This resin is formed by condensation polymerisation of melamine and formaldehyde.

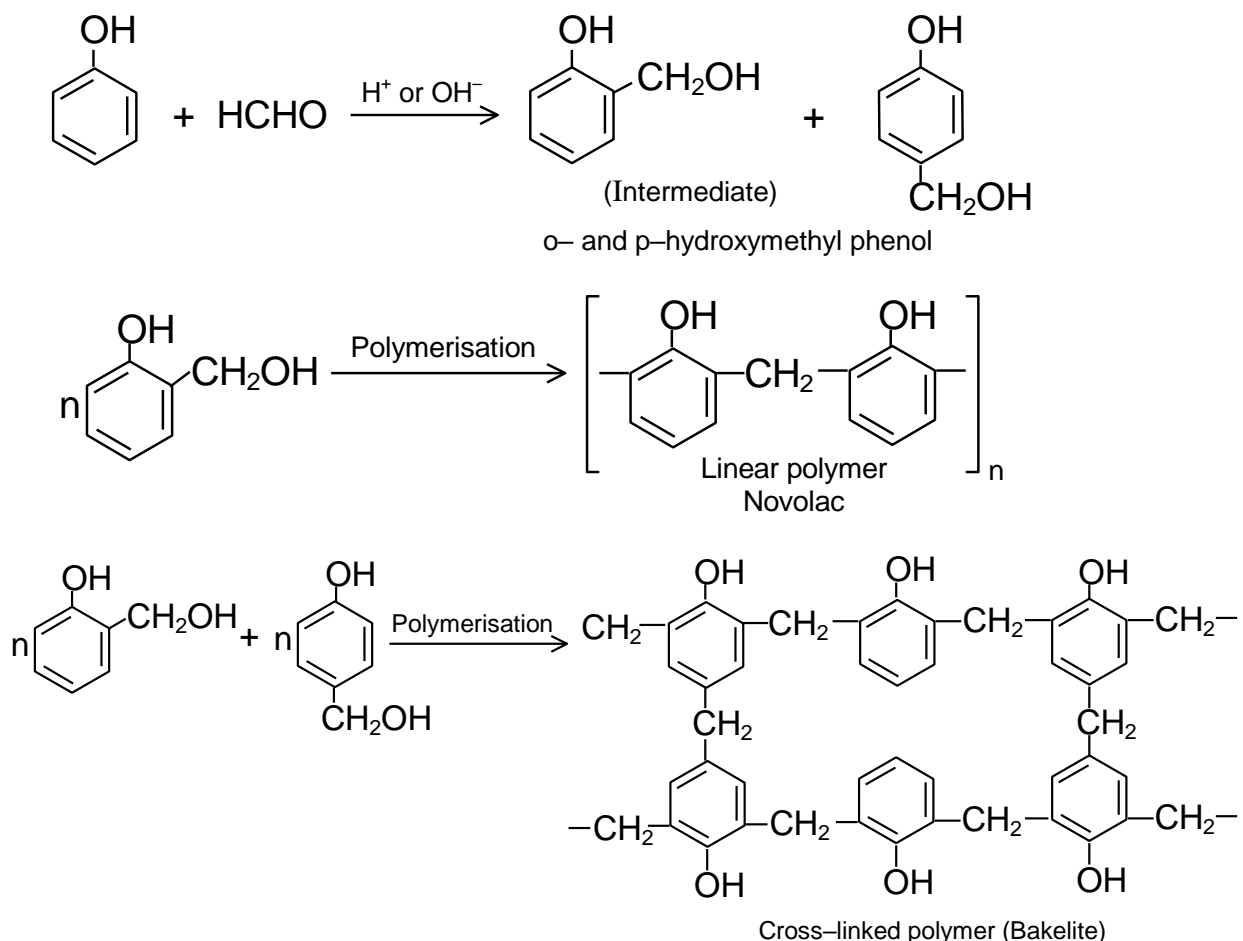


POLYMERS

It is a quite hard polymer and is used widely for making plastic crockery under the name ***melamine***. The articles made from this polymer do not break even when dropped from considerable height.

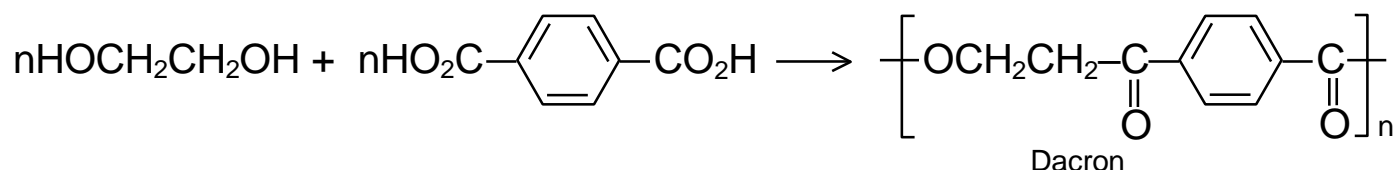
9. Bakelite

Phenol–formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para–hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $-\text{CH}_2-$ groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross–linked materials are obtained depending on the conditions of the reaction.



10. Polyesters

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140° to 180°C in the presence of zinc acetate and Sb_2O_3 as catalyst.



The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wool to provide better crease and wrinkle resistance.

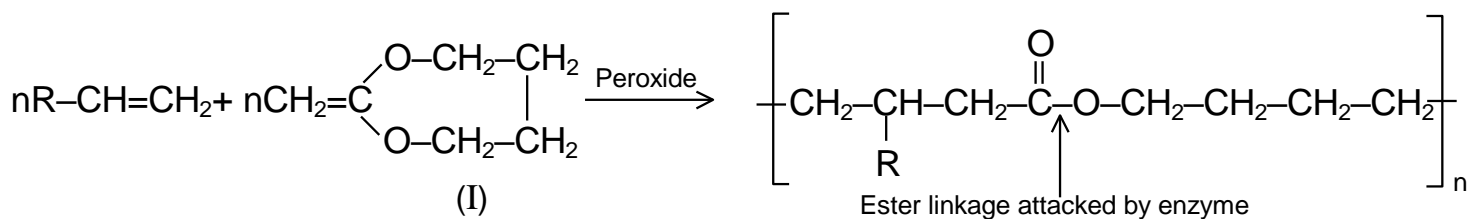
11. Biodegradable Polymers

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as **throwaway** containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non-biodegradability is due to the carbon-carbon bonds of addition polymers which are inert to enzyme catalysed reaction. These polymers create pollution problem.

Biodegradable polymers are the polymers that can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms. In biodegradable polymers, bonds that can be broken by the enzymes are inserted into the polymer. Therefore, when they are buried as waste, enzymes present in the ground can degrade the polymer.

One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.

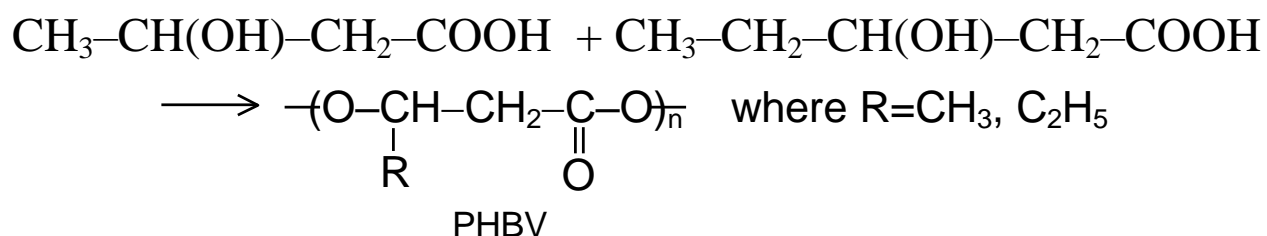
POLYMERS



Aliphatic polyesters are important class of biodegradable polymers. Some examples are described below:

11.1 Poly-Hydroxybutyrate-Co-β-Hydroxyvalerate (PHBV)

It is a copolymer of 3-hydroxybutanoic 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 co-polymer. It is used in specialty packaging, orthopaedic devices and even in controlled drug release. When a drug is put in a capsule of PHBV, it is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

11.2 Poly (Glycolic Acid) and Poly (Lactic Acid)

They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioabsorbable suture made from biodegradable polyesters for post-operative stitches.

12. Molecular Mass of Polymer

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contain chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

(a) Number average molecular mass (\bar{M}_n)

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Where, N_i is the number of molecules of molecular mass M_i .

(b) Weight average molecular mass (\bar{M}_w)

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Where, N_i is the number of molecules of molecular mass M_i . Methods such as light scattering and ultracentrifuge depend on the mass of the individual molecules and yield weight-average molecular masses. \bar{M}_n is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. colligative properties like osmotic pressure.

The ratio of the weight and number average molecular masses (\bar{M}_w / \bar{M}_n) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e. $\bar{M}_w = \bar{M}_n$).

In synthetic polymers, which are always polydispersed, $\text{PDI} > 1$ because \bar{M}_w is always higher than \bar{M}_n .

POLYMERS

Illustration 9.

Calculate the average molecular mass of a polymer sample in which 30% molecules have a molecular mass 20,000; 40% have 30,000; and rest have 60,000. Calculate the \bar{M}_n and \bar{M}_w of this sample. Also calculate the PDI.

Solution:

$$\bar{M}_n = \frac{\sum M_i N_i}{\sum N_i} = \frac{(30 \times 20,000) + (40 \times 30,000) + (30 \times 60,000)}{(30 + 40 + 30)} = 36,000$$

$$\bar{M}_w = \frac{\sum M_i N_i^2}{\sum N_i M_i} = \frac{30(20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{(30 \times 20,000) + (40 \times 30,000) + (30 \times 60,000)} = 43,333$$

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{43,333}{36,000} = 1.2$$

So, the given polymer is synthetic.

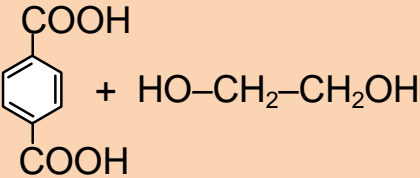
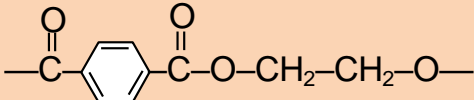
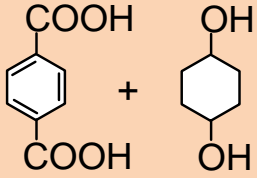
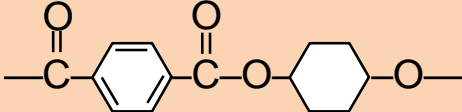
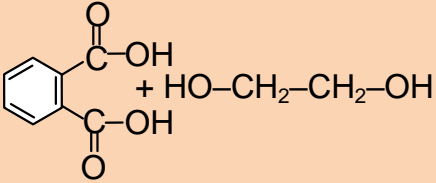
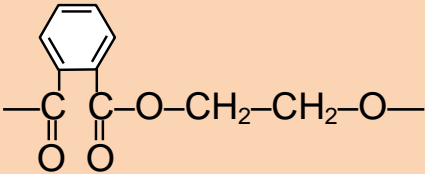
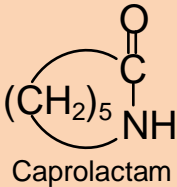
13. Common Polymers

	Monomer	Repeating unit	Polymer
1.	$\text{CH}_2=\text{CH}_2$ Ethylene	$-\text{CH}_2-\text{CH}_2-$	Polyethylene
2.	$\text{CH}_3-\text{CH}=\text{CH}_2$ Propene	$-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-$	Polypropene
3.	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ Styrene	$-\text{CH}_2-\overset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}}-$	Polystyrene

POLYMERS

4.	$\text{CF}_2=\text{CF}_2$ Tetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$	Polytetrafluoroethylene (PTFE), Teflon
5.	$\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	$-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}-$	Polyvinyl chloride (PVC)
6.	$\text{CH}_2=\text{CH}-\text{CN}$ Vinyl cyanide or Acrylonitrile	$-\text{CH}_2-\overset{\text{CN}}{\underset{ }{\text{CH}}}-$	Polyvinyl cyanide, polyacrylonitrile, Orlon.
7.	$\begin{array}{c} \text{H}_3\text{C} \quad \text{O} \\ \quad \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_3 \end{array}$ Methyl methacrylate	$-\text{CH}_2-\overset{\text{COOCH}_3}{\underset{\text{CH}_3}{\text{C}}}-$	Polymethyl methacrylate, Plexiglas, Lucite
8.	$\text{CH}_2=\text{CH}-\text{O}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_3$ Vinyl acetate	$-\text{CH}_2-\overset{\text{OCOCH}_3}{\underset{ }{\text{CH}}}-$	Polyvinyl acetate
9.	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$	Polybutadiene, Buna rubber
10.	$\begin{array}{ll} \text{CH}_2=\text{CH}-\text{Cl} & \text{(Vinyl chloride)} \\ \text{CH}_2=\overset{+}{\text{C}}\text{Cl}_2 & \text{(Vinylidene chloride)} \end{array}$	$-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}-\text{CCl}_2-\text{CH}_2-$	Saran
11.	$\begin{array}{ll} \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 & \text{(styrene)} \\ \text{CH}_2=\overset{+}{\text{C}}\text{H}-\text{CN} & \text{(acrylonitrile)} \end{array}$	$-\text{CH}_2-\overset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}}-\overset{\text{CN}}{\underset{ }{\text{CH}}}-\text{CH}_2-$	SAN
12.	$\begin{array}{c} \text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \\ + \\ \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 \end{array}$	—	ABS

POLYMERS

13.	$\text{CH}_2=\underset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CH}_3 + \text{CH}_2=\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CH}=\text{CH}_2$	—	Butyl rubber
14.	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	—	Buna-S, SBR
15.	$\text{CH}_2=\text{CH}-\text{CN} + \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$	—	Buna-N, NBR
16.	$\text{CH}_2=\overset{\text{Cl}}{\underset{ }{\text{C}}}-\text{CH}=\text{CH}_2$ Chloroprene	$-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{C}}}=\text{CH}-\text{CH}_2-$	Neoprene
17.			Poly(ethylene terephthalate) Terylene, Dacron or Mylar
18.			Kodel polyester
19.			Polyethylene phthalate, Alkyd resin (Glyptal)
20.	 Caprolactam	$-\text{NH}-(\text{CH}_2)_5-\overset{\text{O}}{\parallel}{\text{C}}-$	Nylon-6

POLYMERS

21.	$\begin{array}{c} \text{NH}_2-(\text{CH}_2)_6-\text{NH}_2 \\ \text{Hexamethylenediamine} \\ + \\ \text{HO}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-\text{OH} \\ \text{Adipic acid} \end{array}$	$-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-$	Nylon-66
22.	$\begin{array}{c} \text{NH}_2-\text{C}_6\text{H}_4-\text{NH}_2 \\ 1,4\text{-Diaminobenzene} \\ + \\ \text{Cl}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl} \\ \text{Terephthaloyl chloride} \end{array}$	$-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-$	Kelvar
23.	$\text{C}_6\text{H}_5\text{OH} + \text{HCHO}$	—	Bakelite or resol
24.	$\text{NH}_2-\text{C}(=\text{O})-\text{NH}_2 + \text{HCHO}$	—	Urea-formaldehyde resin
25.	$\begin{array}{c} \text{NH}_2 \\ \\ \text{N} \\ / \quad \backslash \\ \text{H}_2\text{N} \quad \text{N} \\ \quad \\ \text{H}_2\text{N} \quad \text{NH}_2 \end{array} + \text{HCHO}$ <p style="text-align: center;">Malamine</p>	—	Melamine-formaldehyde resin