Chapter- 15: Polymer

1. Polymer: Polymer is defined as a high molecular weight compound formed by the combination of a large number of one or more types of small molecules (monomers).
Molecular mass of polymer is always expressed as an average. The molecular mass of polymers can be determined by chemical and physical methods.

2. Polymerisation: The process of formation of polymers from respective monomers is called polymerisation.

3. Classification of Polymer:

(i) Classification based on source:

(a) Natural polymers: Polymers which occur in nature, i.e. in plants or animals are called natural polymers. Examples are starch, cellulose, protein, natural rubber etc.

(b) Synthetic polymers: The polymers which are prepared in the laboratory are known as synthetic polymers or man-made polymers, e.g., polythene, synthetic rubber, PVC, nylon-66, teflon, orlon etc.

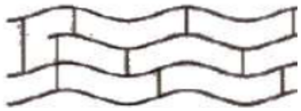
(c) Semi synthetic polymers: Polymers which obtained by making some modification in natural polymers by artificial means, are known as semi synthetic polymers, e.g., cellulose acetate (rayon), vulcanised rubber etc.

(ii) Classification based on structure of polymer:

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

(b) Branched chain polymers: These polymers contain linear chains having some branches, e.g., low density polythene. These are depicted as follows:

(c) Cross linked or Network polymers: Polymers in which monomer units are cross linked together to form a three dimensional network polymers. Examples are bakelite, melamine etc.



(iii) Classification based on mode of polymerisation:

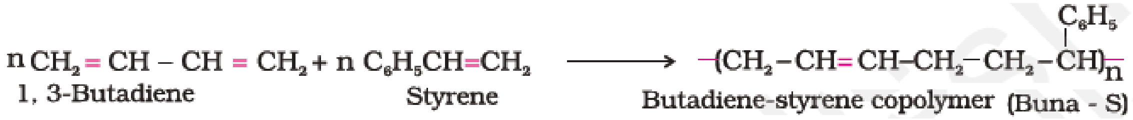
(a) Addition polymers: The polymers formed by the polymerisation of monomers containing double or triple bonds (unsaturated compounds) are called addition polymers. Addition polymers have the same empirical formula as their monomers.

Addition polymers can further be classified on the basis of the types of monomers into the following two classes:

- **Homopolymers:** The polymers which are obtained by the polymerisation of a single type of monomer are called homopolymers. Examples are polythene, polystyrene etc.

$$\underset{\text{Ethene}}{n\,CH_2=CH_2} \longrightarrow \underset{\text{Polythene}}{-\!\!\left(CH_2-CH_2\right)\!\!-_n}$$

- **Copolymers:** The polymers which are obtained by the polymerisation of two or more monomers are called copolymers. Examples are Buna-S, Buna-N etc.



$$\underset{\text{1, 3-Butadiene}}{n\,CH_2=CH-CH=CH_2} + \underset{\text{Styrene}}{n\,C_6H_5CH=CH_2} \longrightarrow \underset{\text{Butadiene-styrene copolymer (Buna - S)}}{-\!\!\left(CH_2-CH=CH-CH_2-CH_2-\overset{\overset{C_6H_5}{|}}{C}H\right)\!\!-_n}$$

(b) Condensation polymers: The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers, e.g., nylon 6,6 is formed by the condensation of hexamethylene diamine with adipic acid.

$$n\,H_2N\,(CH_2)_6\,NH_2 + n\,HOOC\,(CH_2)_4\,COOH \longrightarrow -\!\!\left[NH\,(CH_2)_6\,NHCO(CH_2)_4CO\right]\!\!-_n + n\,H_2O$$

(iv) Classification based on molecular forces:

(a) Elastomers: These are rubber like solid polymers in which the polymer chains are held together by weakest intermolecular forces. The weak binding forces permit the polymers to be stretched. Examples are natural rubber, buna-S, buna-N etc.

(b) Fibres: Fibers are thread-like and can be woven into fabrics which possess high tensile strength and strong intermolecular forces such as hydrogen bonding. Examples are nylon-66, terylene and polyacrylonitrile.

(c) Thermoplastics: These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibers. Examples are polythene, polystyrene, polyvinyl, etc.

(d) Thermosetting plastics: These polymers are cross linked or heavily branched molecules. These cannot be reused. Examples are bakelite, melamine-formaldehyde resin and urea formaldehyde resin.

Note: Correct order for intermolecular forces in various classes of polymer-

Thermosetting > Fibres > Thermoplastic > Elastomers

4. Types of Poymerisation Reactions: There are two types of polymerisation reactions:

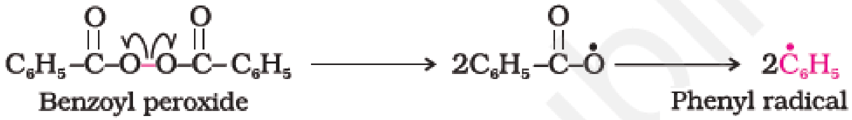
(i) Addition Polymerisation (chain growth polymerisation): It involves formation of reactive intermediate such as free radical, a carbocation or a carbanion. For this polymerisation monomers used are unsaturated compounds like alkenes; alkadienes and their derivatives. Depending upon the nature of the reactive species involved, chain growth polymerisation occurs by the following three mechanisms:

- Free radical addition polymerisation
- Cationic polymerisation
- Anionic polymerisation

Free radical addition polymerisation: The monomers used are generally mono substituted alkenes. The most commonly used catalysts are benzoyl peroxide, hydrogen peroxide or t-butyl peroxide etc.

Mechanism: The reaction involves the following steps-

Step I Chain initiation step: In this step, peroxide undergoes homolytic fission and form free radical. Example benzoyl peroxide on heating produces phenyl free radical.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow 2\dot{C}_6H_5$$

Benzoyl peroxide

Phenyl radical

$$\dot{C}_6H_5+CH_2=CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$

Step II Chain propagation step: The new free radical adds to another molecule of monomer to form a larger free radical.

$$C_6H_5-CH_2-\dot{C}H_2+CH_2=CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2 \longrightarrow C_6H_5\left(CH_2-CH_2\right)_nCH_2-\dot{C}H_2$$

Step III Chain termination step: There are three ways of chain termination: Coupling reaction, disproportionation reaction, chain transfer reaction. One mode of termination of chain is shown as under:

$$\begin{array}{c} C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2 \\ + \\ C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2 \end{array} \longrightarrow C_6H_5\left(CH_2-CH_2\right)_n CH_2-CH_2-CH_2\left(CH_2-CH_2\right)_n C_6H_5$$

Preparation of some important addition polymers:

(a) Low density polythene: This are highly branched structure polymer which is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

$$\underset{Ethene}{nCH_2=CH_2} \xrightarrow{350-570k/1000 \text{ to } 2000 \text{ atm traces of } O_2} \underset{Polythene}{(CH_2-CH_2)_n}$$

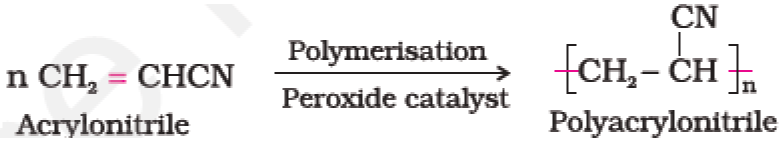
(b) High density polythene: It has high density due to close packing of monomer. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

$$nCH_2 = CH_2 \xrightarrow{333-343k/6-7 \text{ atm zieglar Natta catalyst}} (CH_2 - CH_2)_n$$

(c) Poly tetra fluoroethene (Teflon): It is used in making oil seals and gaskets and also used for non – stick surface coated utensils.

$$\underset{\text{Tetrafluoroethene}}{n\, CF_2 = CF_2} \xrightarrow[\text{High pressure}]{\text{Catalyst}} \underset{\text{Teflon}}{\left[CF_2 - CF_2 \right]_n}$$

(d) Polyacrylonitrile: Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orlon or acrilan.

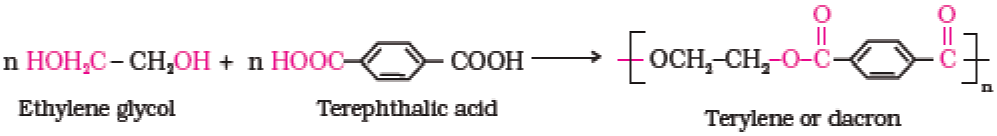


$$\underset{\text{Acrylonitrile}}{n\, CH_2 = CHCN} \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \underset{\text{Polyacrylonitrile}}{\left[CH_2 - \overset{\overset{CN}{|}}{CH} \right]_n}$$

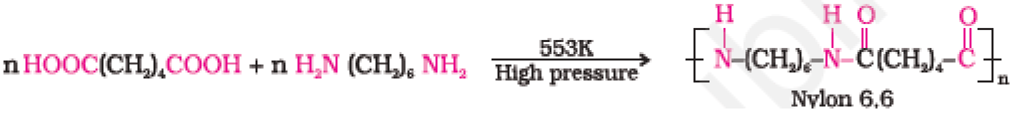
(ii) Condensation polymerisation (Step growth polymerisation): Polymerisation generally involves a repetitive condensation b/w two bi-functional monomers. In condensation polymer, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since each step produces a distinct functionalized species and is independent of each other, this process is called as step growth polymerisation.

Preparation of some important Condensation polymers:

(a) Terylene or Dacron:

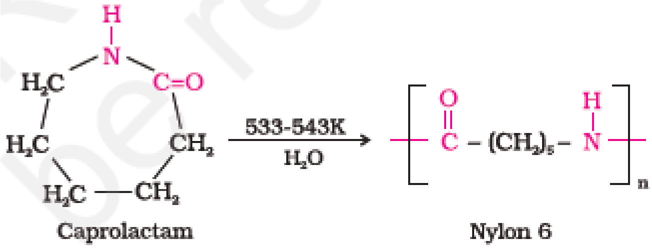


(b) Nylon 6,6: It is prepared by the condensation polymerisation of adipic acid with hexamethylenediamine. Both monomer contain six carbon atom so it's known as nylon 6,6. It uses in making sheets, bristles for brushes and in textile industry.



$$n\, HOOC(CH_2)_4COOH + n\, H_2N\,(CH_2)_6\, NH_2 \xrightarrow[\text{High pressure}]{553K} \underset{\text{Nylon 6,6}}{\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n}$$

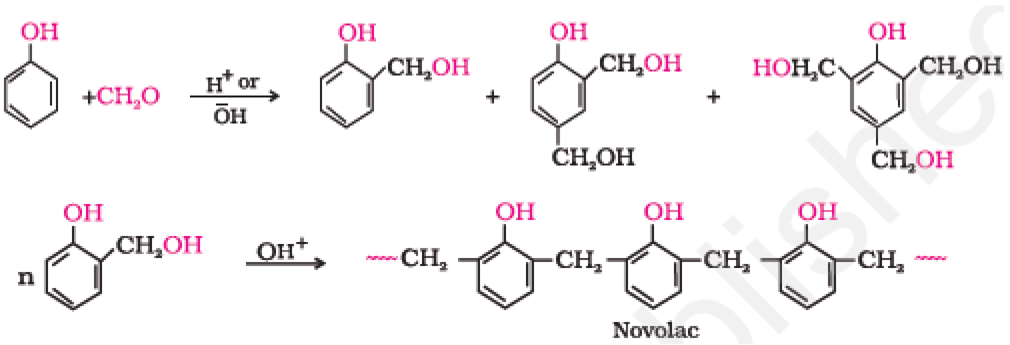
(c) Nylon 6: It is uses for manufacture of tyre cords, fabrics and ropes.



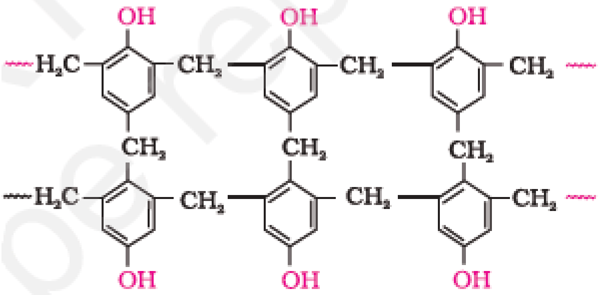
(d) Polyester:

(e) Phenol - formaldehyde polymer (Bakelite and related polymers):

Novalac: These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. The initial product could be a linear product Novolac which used in paints.

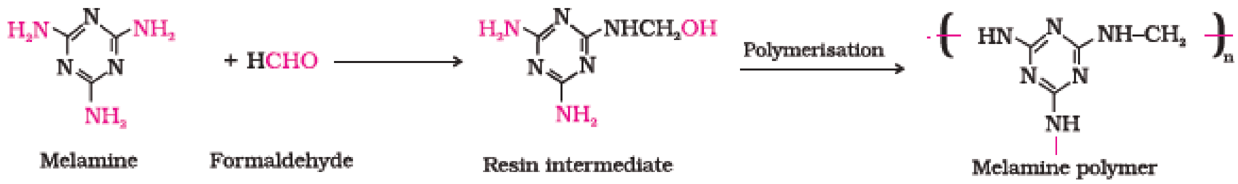


Bakelite: Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called **bakelite**. It is used for making combs, phonograph records, electrical switches and handles of various utensils.

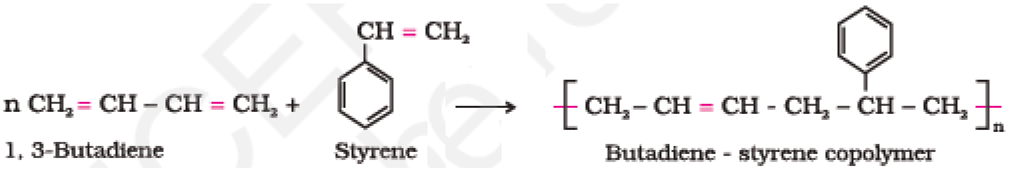


Bakelite

(f) Melamine - formaldehyde polymer: It is used in the manufacture of unbreakable crockery.

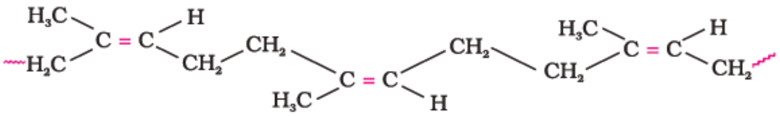


5. Copolymerisation: When two or more different monomers are allowed to polymerise together, the product formed is called a copolymer and the process is called copolymerization. Examples, butadiene-styrene copolymer (Buta-S), it is a good substitute for natural rubber and used for the manufacture of auto tyres, floortiles, footwear components, cable insulation, etc.



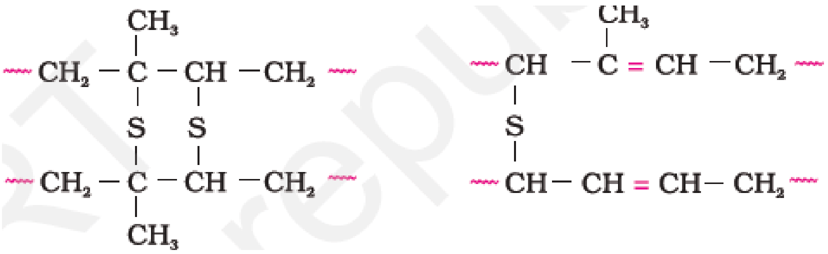
6. Types of Rubber:

(i) Natural Rubber: It is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as *cis* - 1, 4 - polyisoprene.



Vulcanisation of Rubber: The process of heating a mixture of raw rubber with sulphur and an appropriate additive in a temperature range b/w 373 K to 415 K to improve the physical properties (like elasticity, strength etc.) of natural rubber.

For example, in the manufacture of tyre rubber, 5% of sulphur is used as a crosslinking agent. The probable structures of vulcanised rubber molecules can be represent as:



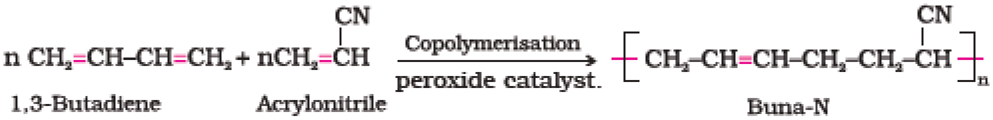
(ii) Synthetic Rubber: Synthetic rubbers are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer. Examples,

(a) Neoprene:

$$n\,CH_2=\overset{Cl}{\overset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerisation}} -\!\!\left[CH_2-\overset{Cl}{\overset{|}{C}}=CH-CH_2\right]\!\!-_n$$

Chloroprene Neoprene

(b) Buna-N:

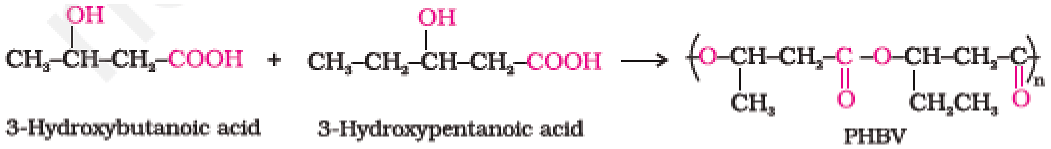


$$n\,CH_2=CH-CH=CH_2+n\,CH_2=\overset{CN}{\overset{|}{CH}} \xrightarrow[\text{peroxide catalyst}]{\text{Copolymerisation}} -\!\!\left[CH_2-CH=CH-CH_2-CH_2-\overset{CN}{\overset{|}{CH}}\right]\!\!-_n$$

1,3-Butadiene Acrylonitrile Buna-N

7. Biodegradable polymers: Polymers which are degraded by microorganisms with in a suitable period so their degraded products do not cause any serious effect on environment. Aliphatic polyesters are one of the important classes of biodegradable polymers. Some important examples are followings:

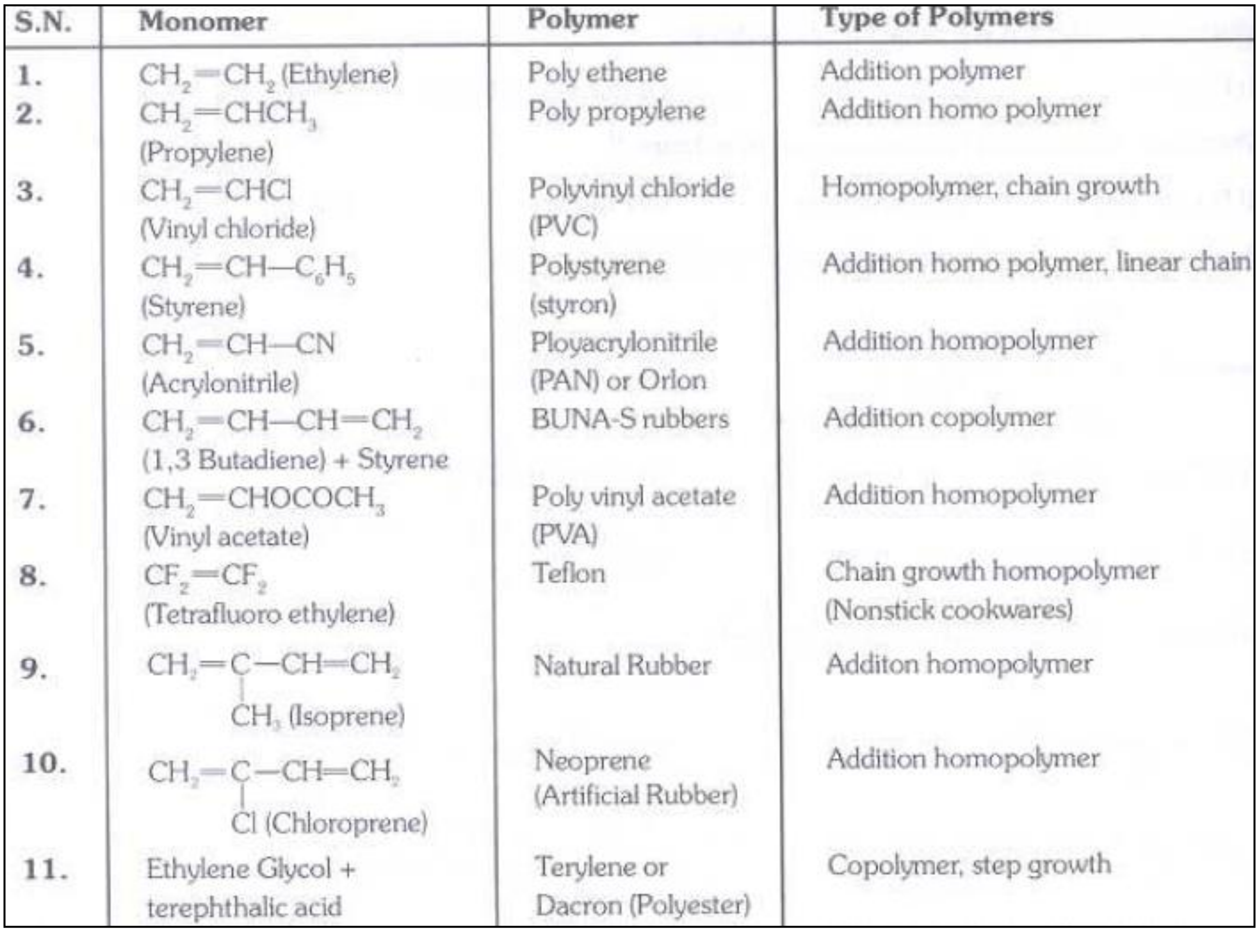
(a) Poly β-hydroxybutyrate–co-β-hydroxy valerate (PHBV): This is a copolymer of 3-hydroxybutanoic acid and 3 - hydroxypentanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs.



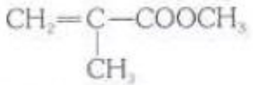
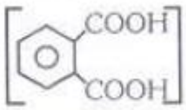
(b) Nylon 2–nylon 6: It is an alternating polyamide copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid [$H_2N\ (CH_2)_5\ COOH$] and is biodegradable.

Note: Natural polymer proteins have structural similarity with synthetic polyamides, both contain amide linkage.

8. Polymers of Commercial Importance:



S.N.	Monomer	Polymer	Type of Polymers
1.	$CH_2=CH_2$ (Ethylene)	Poly ethene	Addition polymer
2.	$CH_2=CHCH_3$ (Propylene)	Poly propylene	Addition homo polymer
3.	$CH_2=CHCl$ (Vinyl chloride)	Polyvinyl chloride (PVC)	Homopolymer, chain growth
4.	$CH_2=CH—C_6H_5$ (Styrene)	Polystyrene (styron)	Addition homo polymer, linear chain
5.	$CH_2=CH—CN$ (Acrylonitrile)	Ployacrylonitrile (PAN) or Orlon	Addition homopolymer
6.	$CH_2=CH—CH=CH_2$ (1,3 Butadiene) + Styrene	BUNA-S rubbers	Addition copolymer
7.	$CH_2=CHOCOCH_3$ (Vinyl acetate)	Poly vinyl acetate (PVA)	Addition homopolymer
8.	$CF_2=CF_2$ (Tetrafluoro ethylene)	Teflon	Chain growth homopolymer (Nonstick cookwares)
9.	$CH_2=\underset{CH_3}{C}—CH=CH_2$ (Isoprene)	Natural Rubber	Additon homopolymer
10.	$CH_2=\underset{Cl}{C}—CH=CH_2$ (Chloroprene)	Neoprene (Artificial Rubber)	Addition homopolymer
11.	Ethylene Glycol + terephthalic acid	Terylene or Dacron (Polyester)	Copolymer, step growth

12.	Hexamethylene diamine + adipic acid	Nylon-6,6 (Polyamide)	Copolymer, step growth linear
13.	Formaldehyde + urea	Urea formaldehyde resin	Copolymer, step growth
14.	Formaldehyde + Phenol	Bakelite	Copolymer, step growth
15.	Methyl methacrylate  $CH_2=\underset{CH_3}{\underset{\mid}{C}}-COOCH_3$	Poly methyl meth acrylate (PMMA)	Addition homopolymer
16.	Ethylene Glycol + Phthalic acid 	Glyptal or alkyd resin	Copolymer, linear step growth, thermo plastic
17.	Melamine + formaldehyde	Melamine formaldehyde resin	Copolymer, step growth thermosetting polymer
18.	Hexamethylene diamine + sebasic acid	Nylon - 6,10	Copolymer, step growth linear
19.	Caprolactam	Nylon - 6	Homopolymer, step growth linear