05 Polymers

Polymers are very high molecular mass substances where each molecule is derived from very large number of simple molecules joined together in a regular way. Polymers are formed by repeated combination of simplest units called monomers and the process of formation of polymers from simple molecule (monomers) is called polymerization.

$$n CH_2 = CH_2 \longrightarrow -[CH_2-CH_2]-_n$$

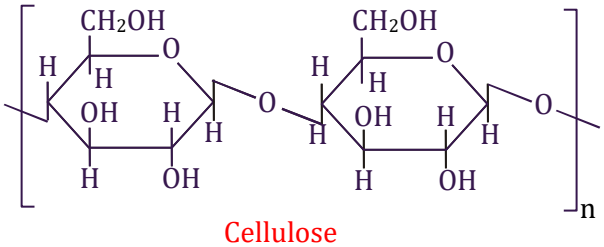
Ethene → Polythene

Classification of polymer :

1. Classification based on source of origin :

(i) Natural polymers : These polymers are found in plants and animals.

Examples: Proteins, cellulose, starch, resins and rubber.



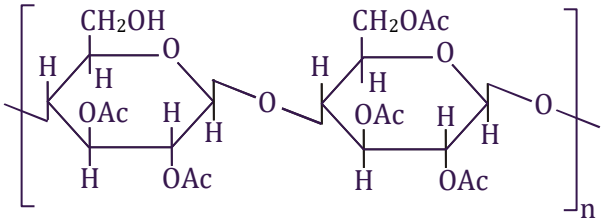
Cellulose

(ii) Synthetic polymers : These polymers are prepared in the laboratory.

Examples : Polyethylene, Nylon-6,6, Dacron & Polyacrylonitrile (PAN).

Acrylonitrile → Polyacrylonitrile

(iii) Semi-synthetic polymers : These polymers are found in plants and animals then modified in the laboratory.



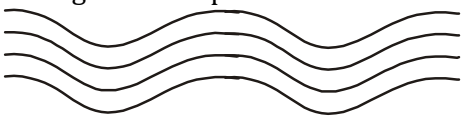
Cellulose acetate

Examples : Cellulose acetate (rayon) & Cellulose nitrate.

2. CLASSIFICATION BASED ON structure of polymer

(i) 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 fibers 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.

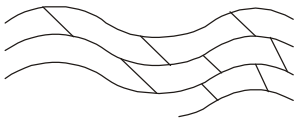
(iii) Branched chain polymers

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 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.

(iv) 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, Urea-formaldehyde resin, phenol-formaldehyde resin.



3. Classification based on type of monomer units :

(i) Homopolymers : Polymers in which repeating structural units are derived from only one type of monomer units are called homopolymers

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

(ii) Copolymers : Polymers in which repeating structural units are derived from two or more types of monomer units are called copolymers.

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

4. Classification based upon molecular force :

(i) Elastomers : These are rubber like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces.

Examples: Buna-S, Buna-N, Neoprene, etc.

(ii) Fibres : Fibres are the thread forming solids which possess high tensile strength and high modulus. Polymers in which the intermolecular forces of attraction are the strongest are called fibers. These forces are either due to H-bonding or dipole-dipole interactions. In case of nylon (polyamides), the intermolecular forces are due to H-bonding while in polyesters (terylene, dacron etc.) and polyacrylonitrile (orlon, acrylin etc.) Dipole-dipole interactions between the polar carbonyl ($>C=O$) groups and, between carbonyl and cyano ($-C\equiv N$) groups respectively.

Examples: Polyamides (Nylon 6,6), polyesters (terylene), etc.

(iii) 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 fibres.

Examples : Polythene, polystyrene, polyvinyls, etc.

(iv) Thermosetting polymers : These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused.

Examples : Bakelite, urea-formaldehyde resins, etc.

5. On the basis of degradation

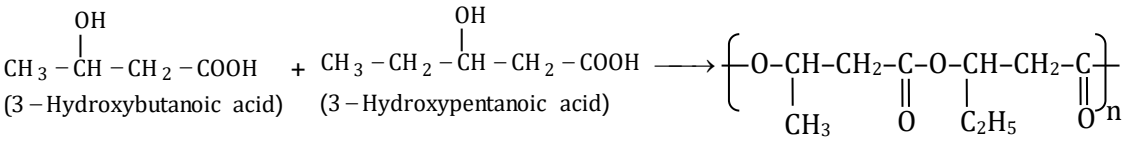
(i) Biodegradable polymers

This polymers can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms

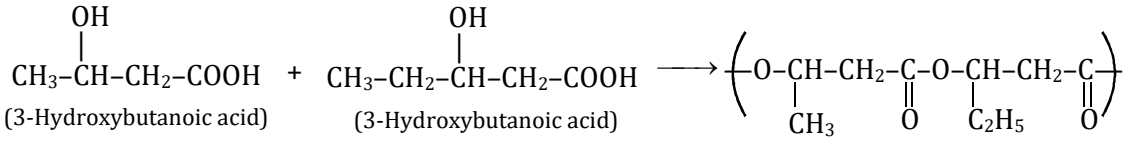
Aliphatic polyesters is an important class of biodegradable polymers.

Example

(1) Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV)



PHBV



PHBV

(2) Nylon-2 Nylon-6

(ii) Non-biodegradable polymers

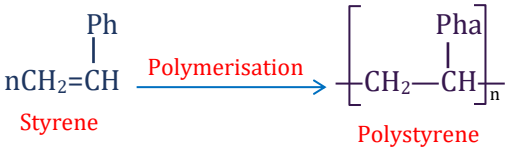
Plastics such as polyethylene, polypropylene, polystyrene & polyvinyl chloride are non-biodegradable polymer.

Their increased accumulation in the environment has been a threat to the planet.

6. Classification based on mode of Polymerisation :

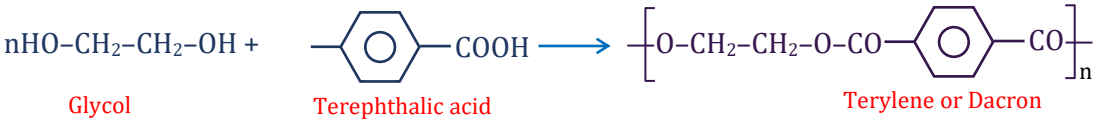
(i) Addition polymers or chain growth polymer : The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bond.

Examples : Polythene, Buna-S, Buna-N



(ii) Condensation polymers or step growth polymer : The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water. alcohol, hydrogen chloride. etc.

Examples : Nylon-6, 6, Terylene.



Polyester – Polymers which have ester linkage.

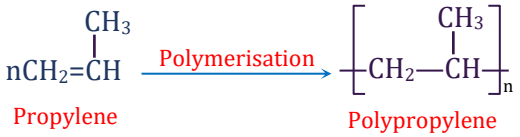
Examples of Addition polymerisation or chain growth polymerisation :

(1) Polyethylene :

Low density polythene is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

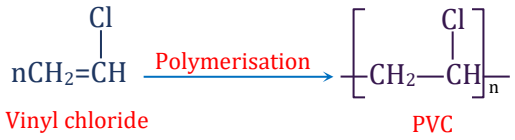
High density polythene is used for manufacturing buckets, dustbins, bottles, pipes, etc.

(2) Polypropylene :



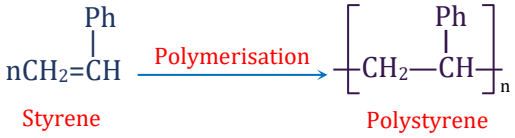
Polypropylene is used for manufacture of ropes, toys, pipes, fibres, etc.

(3) Polyvinyl Chloride (PVC) :



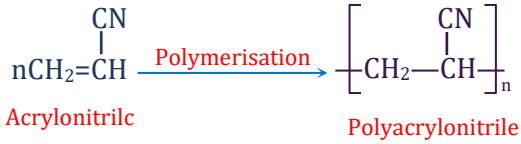
PVC is used in the manufacturing of rain coats, hand bags, vinyl flooring, water pipes, imitation leather, floor covering and gramophone records.

(4) Polystyrene :



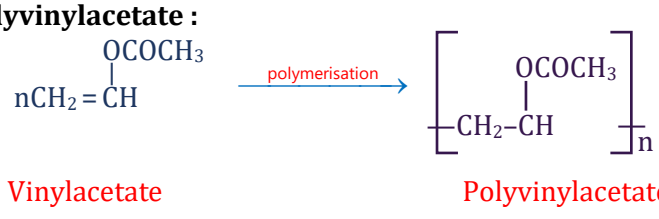
Polystyrene is used as insulator, wrapping material, manufacture of toys, radio and television cabinets.

(5) Polyacrylonitrile :

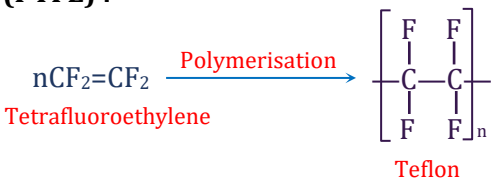


Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orlon or acrilan.

(6) Polyvinylacetate :

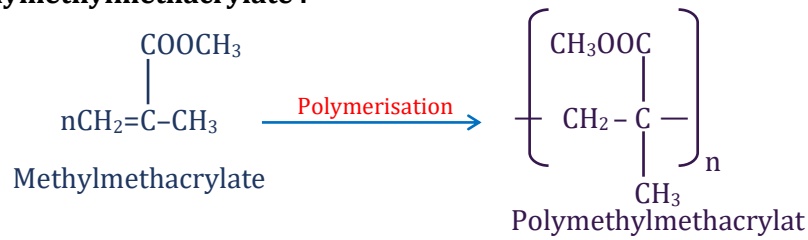


(7) Teflon (PTFE) :

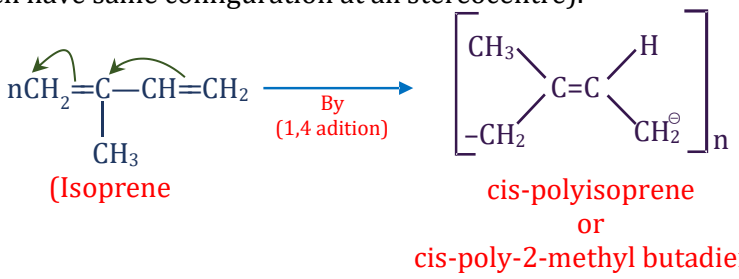


Teflon is used in making oil seals, valves and gaskets and it is also used for non-stick surface coated utensils. Because of its low chemical reactivity, excellent toughness, electrical and heat resistance, teflon is used as insulation for electrical items.

(8) Polymethylmethacrylate :

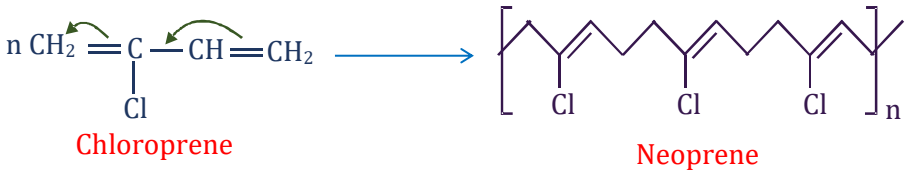


(9) Natural Rubber : Rubber is a natural polymer and possesses elastic properties. It is also termed as elastomer and has a variety of uses. It is manufactured from rubber latex which is a colloidal dispersion of rubber in water. This latex is obtained from the bark of rubber tree and is found in India, Srilanka, Indonesia, Malaysia and South America. Natural rubber is a linear polymer of isoprene (2-methyl-1,3-butadiene) and is also called as cis-1, 4-polyisoprene. Natural Ruber is isotactic polymer (polymers which have same configuration at all stereocentre).



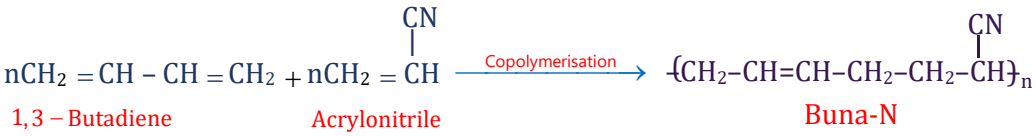
* Gutta parcha, has isoprene unit in trans-form (dentist used it in the filling of teeth).

(10) Neoprene :



Neoprene has superior resistance to vegetable and mineral oils. It is used for manufacturing conveyor belts, gaskets and hoses.

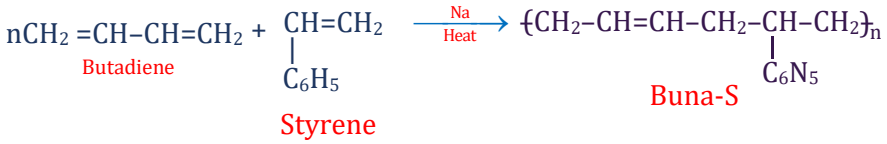
(11) Buna-N :



Buna-N is resistant to the lubricating oil and organic solvents. It is used in making oil seals, tank lining etc.

(12) Buna-S :

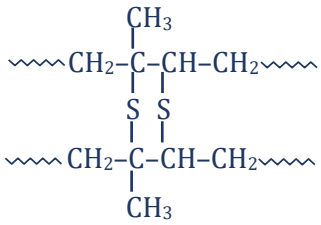
It is obtained by the polymerization of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium. It is also known as styrene butadinene rubber (SBR).



Buna-S is used for the manufacture of autotyres, floortiles, footwear components, cable insulation, etc.

Vulcanization of Rubber:

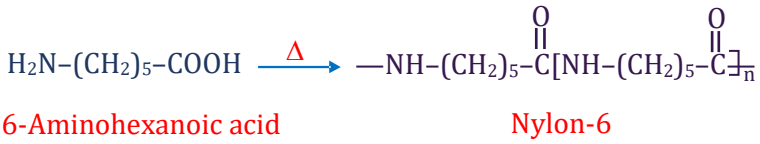
Raw rubber does not posses the characteristic of the rubber with which we are familar. In order to give it strength & elasticity it is vulcanised. In the vulcanization process, raw rubber is mixed with small amount of sulphur and heated. Use of external sulpher increases the cross-linking and toughness.1-3 % S is used in rubber bands and 5% S is used in tyre rubber.



Example of condensation polymer or step growth polymerization :

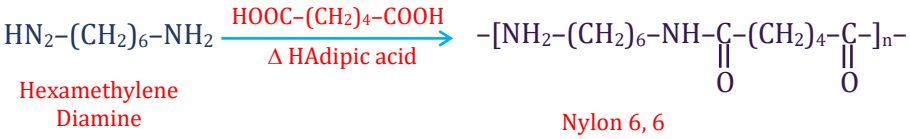
1. Polyamides :

(a) Nylon-6 :



Nylon-6 is used for the manufacture of tyre cords, fabrics and ropes.

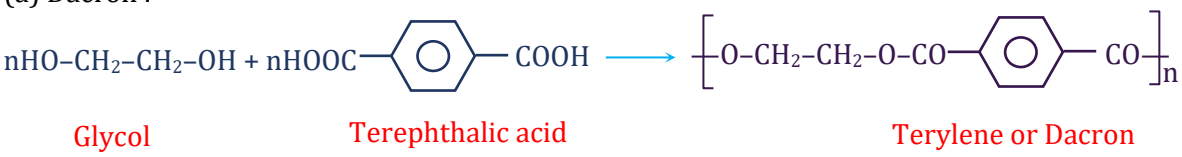
(b) Nylon-6,6 :



Nylon-6, 6 is used in making sheets, bristles for brushes and in textile industry.

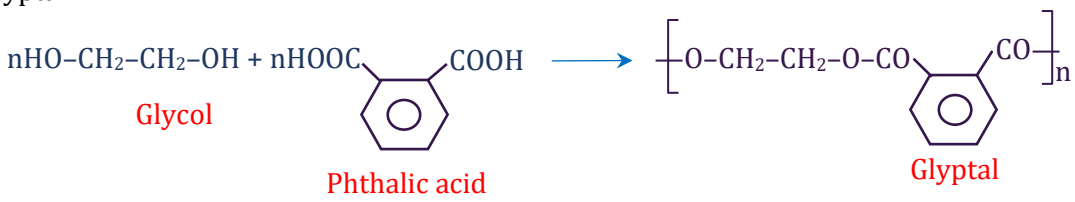
2. Polyesters :

(a) Dacron :



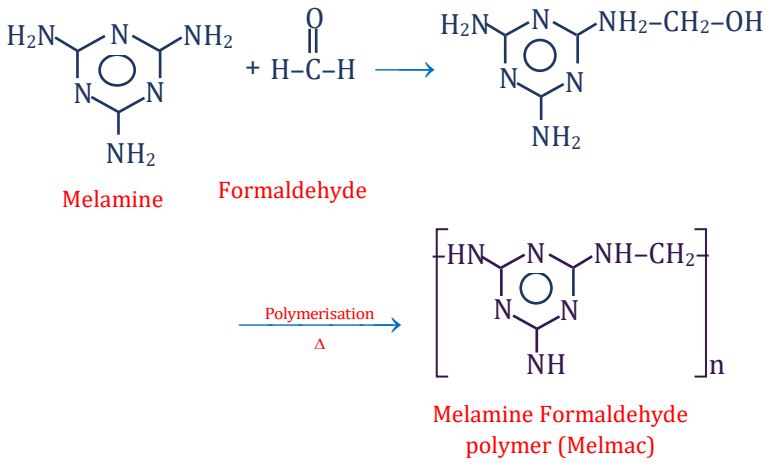
Dacron fibre (terylene) is crease resistant and is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.

(b) Glyptal :



Glyptal is used as manufacture of paints and lacquers.

3. Melamine formaldehyde Resin :

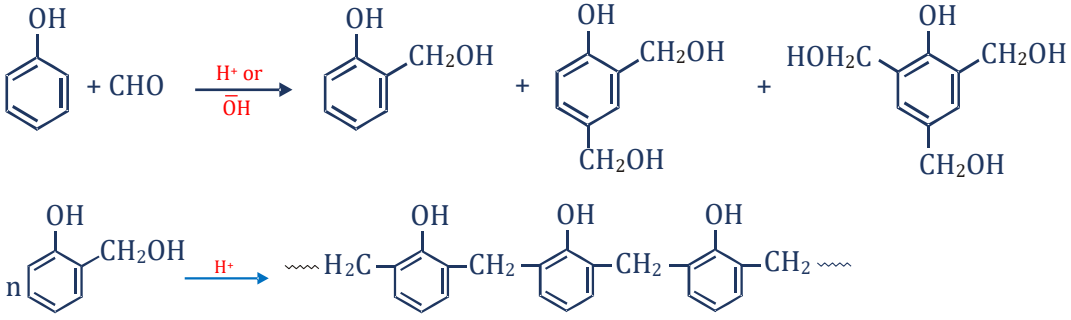


Melamine formaldehyde resin is used in the manufacture of unbreakable crockery.

4. Phenol formaldehyde polymers :

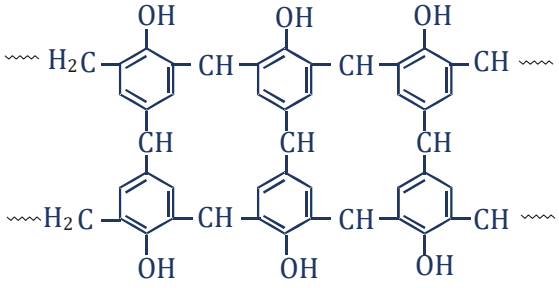
Phenol formaldehyde polymers are the oldest synthetic polymers. These are obtained by the condensation reaction of phenol with formaldehyde the presence of either an acid or a base catalyst.

(a) Novalac : It is linear polymer of formaldehyde & phenol.



Novalac is used in paints.

(b) Bakelite : It is cross linked polymer of formaldehyde & phenol.



Bakelite is used for making combs, phonograph records, electrical switches, handles of various utensils & computer discs.

5. Urea formaldehyde Resin :

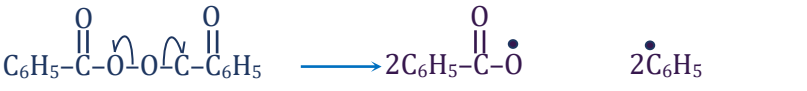
Urea formaldehyde Resin is used for making unbreakable cups and laminated sheets.

Mechanism of Addition polymerisation or chain growth polymerisation :

(i) Chain growth polymerisation : Additional polymers are chain growth polymers. Chain growth polymerisation takes place by-

(a) Free radical mechanism : A variety of alkenes, dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc.

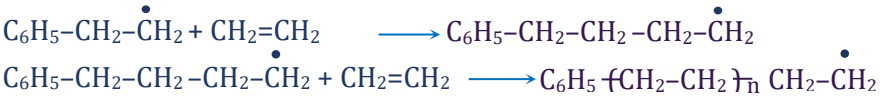
Chain initiation steps



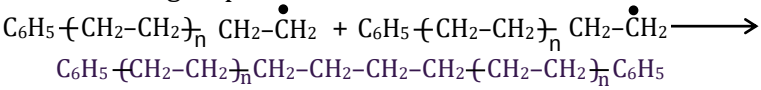
Benzoyl peroxide

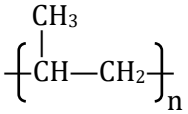
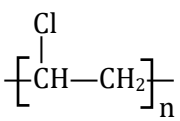
Phenyl radical

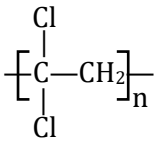
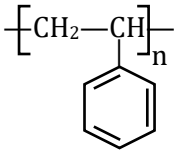
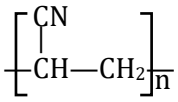
Chain propagating step

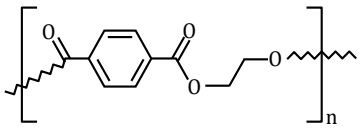
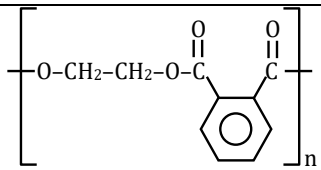
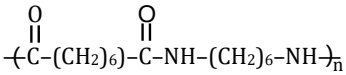
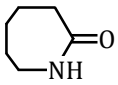
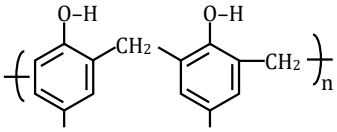
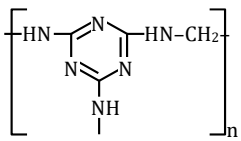
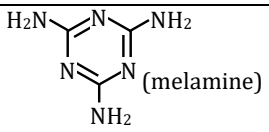


Chain terminating step



Some common addition polymers/chain growth polymer				
S. No.	**Name(s)**	**Formula**	**Monomer**	**Uses**
1.	Polyethylene (low density (LDPE))	$-(CH_2\text{-}CH_2)_n-$	$CH_2=CH_2$ (ethylene)	Film wrap, Plastic Bags
2.	Polyethylene (high density (HDPE))	$-(CH_2\text{-}CH_2)_n-$	$CH_2=CH_2$ (ethylene)	Electrical insulation bottles, toys
3.	Polypropylene (PP) different grades		$CH_2=CHCH_3$ (propylene)	Manufacture of ropes, toys, pipes, fibres etc.
4.	Poly vinyl chloride (PVC)		$CH_2=CHCl$ (vinyl chloride)	Manufacture of rain coats, hand bags, vinyl flooring, water Pipes etc.

5.	Poly vinylidene chloride (Saran A)		$CH_2=CCl_2$ (vinylidene chloride)	Seat covers, films & fibers
6.	Polystyrene (Styron)		$CH_2=CHC_6H_5$ (styrene)	As insulator, wrapping material, manufactures of toys, radio and Television cabinets
7.	Polyacrylonitrile (PAN, Orlon, Acrilan)		$CH_2=CHCN$ (acrylonitrile)	Rugs, Blankets clothing
8.	Polytetrafluoroethylene (PTFE, Teflon)	$-(CF_2\text{-}CF_2)_n-$	$CF_2=CF_2$ (tetrafluoroethylene)	Non-stick surfaces electrical insulation
9.	Poly methyl methacrylate (PMMA, Lucite, Plexiglas, perspex)	$-[CH_2C(CH_3)CO_2CH_3]_n-$	$CH_2=C(CH_3)CO_2CH_3$ (methylmethacrylate)	Lighting covers, signs skylights
10.	Poly vinyl acetate (PVAc)	$-(CH_2\text{-}CHOCOCH_3)_n-$	$CH_2=CHOCOCH_3$ (vinyl acetate)	Latex paints, Adhesives
11.	Natural Rubber	$-[CH_2\text{-}CH=C(CH_3)\text{-}CH_2]_n-$ (cis)	$CH_2=CH-C(CH_3)=CH_2$ (isoprene)	Requires vulcanization for practical use
12.	Neoprene	$-[CH_2\text{-}CH=CCl\text{-}CH_2]_n-$	$CH_2=CH\text{-}CCl=CH_2$ (chloroprene)	Synthetic rubber, oil resistant seal, gaskets, hoses & conveyor belts
13.	SBR styrene butadiene rubber (Buna-S)	$-[CH_2-CH(Ph)-CH_2-CH=CH-CH_2]-$	$H_2C=CHC_6H_5$ and $H_2C=CH\text{-}CH=CH_2$	Tyres, floortiles, foot wear & cable insulation
14.	Nitrile Rubber (Buna-N)	$-[CH_2-CH(CN)-CH_2-CH=CH-CH_2]-$	$H_2C=CHCN$ and $H_2C=CH\text{-}CH=CH_2$	Making oil seals, tank lining and hoses

Some condensation polymers/step growth polymers				
S. No.	**Name(s)**	**Formula**	**Monomer**	**Uses**
1.	Polyester/Dacron /Terylene/Mylar		$HO_2C\ C_6H_4\ CO_2H$ (Terephthalic acid) $HO–CH_2CH_2–OH$ Ethylene glycol	Fabric, Tyrecord
2.	Glyptal or Alkyds resin		$HO_2C–C_6H_4–CO_2H$ (Phthalic acid) $HO–CH_2CH_2–OH$	Paints and Lacquers
3.	Polyamide (Nylon 6,6)	$\sim[CO(CH_2)_4CO–NH(CH_2)_6NH]_n\sim$	$HO_2C–(CH_2)_4–CO_2H$ $H_2N–(CH_2)_6–NH_2$	Parachutes & Clothing
4.	Nylon 6,10		$HOOC–(CH_2)_8–COOH$ $H_2N–(CH_2)_6–NH_2$	
5.	Polyamide Nylon 6, Perlon-L	$\sim[CO(CH_2)_5NH]_n\sim$	 Caprolactam	Rope & Tyrecord
6.	Bakelite		PhOH + HCHO in (excess)	Electrical Switch, combs, Handle of Utensils, computer discs and Bowling Balls
7.	Urea-formaldehyle resin	$(–NH–CO–NH–CH_2–)_n$	$H_2N–CO–NH_2$ (Urea) HCHO (Formaldehyde)	Making unbreakable cups and laminated sheets.
8.	Melamine formaldehyde resin		 (melamine) +HCHO (formaldehyde)	Unbreakable crockery