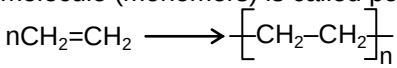
Polymers

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.



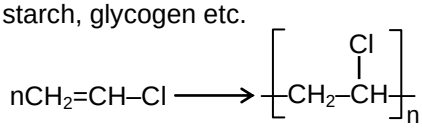
Ethene Polythene

Polymers can be classified in following ways :

(A) 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.

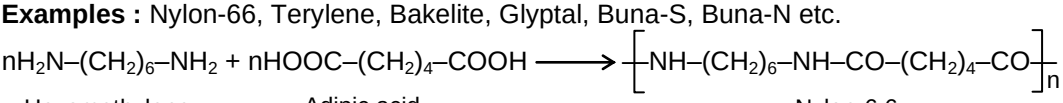
Examples: Polyethylene, polyvinyl chloride (PVC), polyisoprene, neoprene (polychloroprene) polyacrylonitrile (PAN), nylon-6, polybutadiene, teflon (polytetrafluoroethylene), cellulose, starch, glycogen etc.



Vinyl chloride Polyvinyl chloride

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

Examples : Nylon-66, Terylene, Bakelite, Glyptal, Buna-S, Buna-N etc.



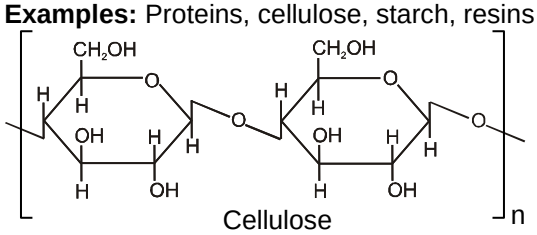
Hexamethylene diamine Adipic acid Nylon-6,6

Nylon - Polymers which have amide linkage.

(B) Classification based on source of origin :

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

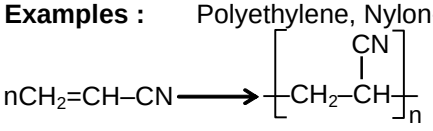
Examples: Proteins, cellulose, starch, resins and rubber.



Cellulose

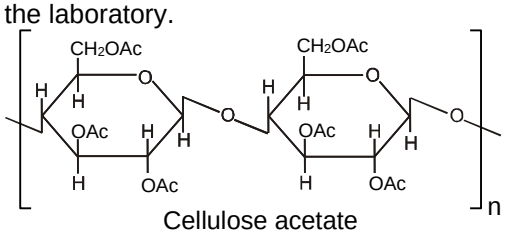
(ii) Synthetic polymers : These polymers are prepared in the laboratory.

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.

(C) Classification based on structure of polymers :

(i) Linear polymers : These polymers consist of long and straight chains.

Examples : High density polythene, Polyvinyl chloride.

$$n CH_2=CH_2 \xrightarrow[333\text{-}345\ K]{6\text{-}7\ atm} \text{High density polythene}$$

Ethene — Ziegler-Natta Catalyst

**** Ziegler Natta Catalyst :** $(C_2H_5)_3Al + TiCl_4$

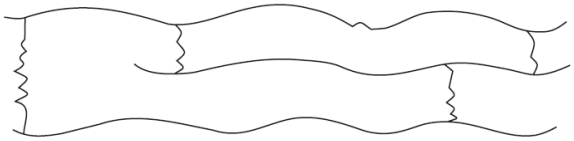
(ii) Branched chain polymers : These polymers contain linear having some branches.

Examples : Low density polythene.

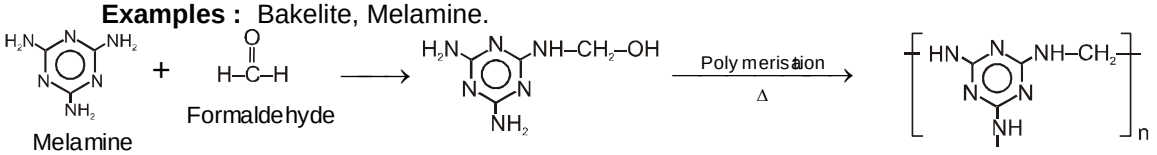
$$n CH_2=CH_2 \xrightarrow[350\text{-}570\ K]{1000\text{-}2000\ atm} \text{Low density polythene}$$

Ethene — O_2 or R_2O_2

(iii) Cross linked or Network polymers : These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chain.



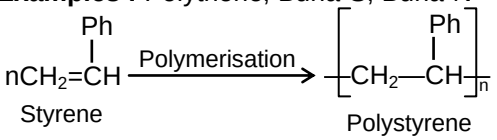
Examples : Bakelite, Melamine.



(D) Classification based on mode of Polymerisation :

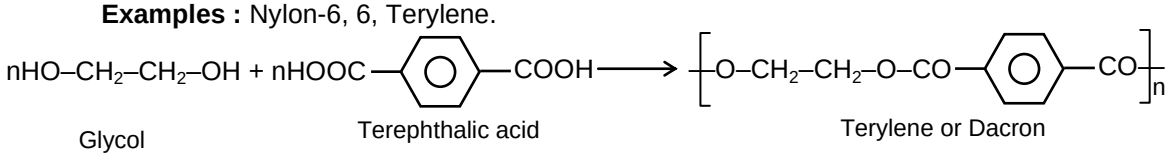
(i) Addition polymers : The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bond.

Examples : Polythene, Buna-S, Buna-N



(ii) Condensation polymers : 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.

(E) Calssification 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 ≡ 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.

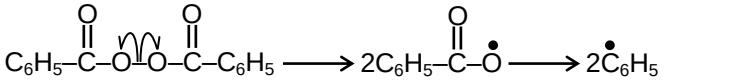
(iv) **Thermosetting polymers :** These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused.
Examples : Bakelite, urea-formaldehyde resins, etc.

(F) Classification based on Mechanism of polymerisation:

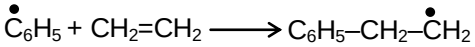
(i) **Chain growth polymerisation :** Additional polymers are chain growth polymers. Chain growth polymerisation takes place by-

(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.

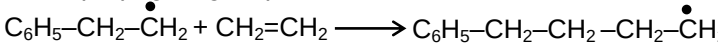
Chain initiation steps

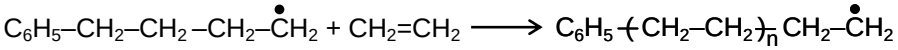


Benzoyl peroxide — Phenyl radical

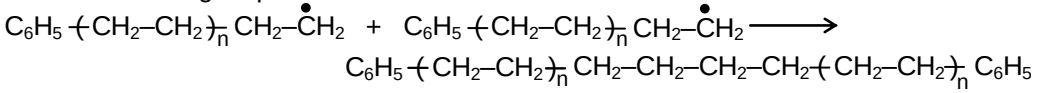


Chain propagating step





Chain terminating step



Examples : $CH_2=CH_2$, $CH_2=CH–CH_3$, $CH_2=CH–CH=CH_2$, etc.

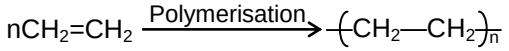
(b) Cationic mechanism : Alkenes having electron releasing group are polymerised by cationic mechanism.
Examples : $CH_2=CH–O–CH_3$

(c) Anionic mechanism : Alkenes having electron withdrawing group are polymerised by cationic mechanism.
Examples : $CH_2=CH–CN$

(ii) **Step growth polymerisation :** Condensation polymers are step growth polymer. This polymerisation progresses through step by step.
Examples : Nylon, bakelite, dacron, etc.

Examples of polymers :

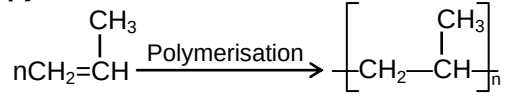
(1) **Polyethylene :**



Ethylene — 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.

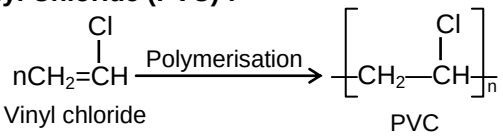
(2) **Polypropylene :**



Propylene — Polypropylene

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

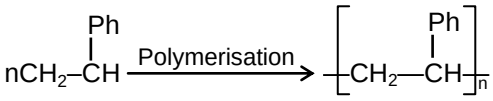
(3) Polyvinyl Chloride (PVC) :



Vinyl chloride PVC

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

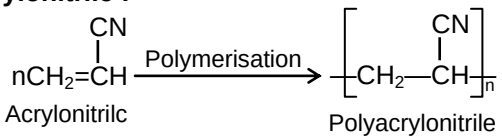
(4) Polystyrene :



Styrene Polystyrene

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

(5) Polyacrylonitrile :



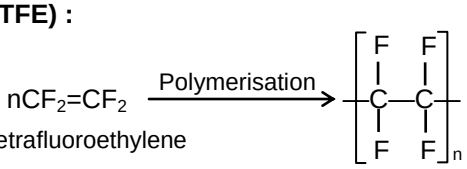
Acrylonitrilc Polyacrylonitrile

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

(6) Polyvinylacetate :

Vinylacetate Polyvinylacetate

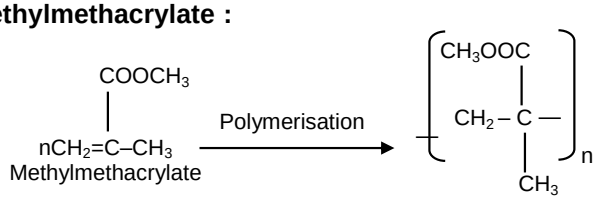
(7) Teflon (PTFE) :



Tetrafluoroethylene Teflon

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.

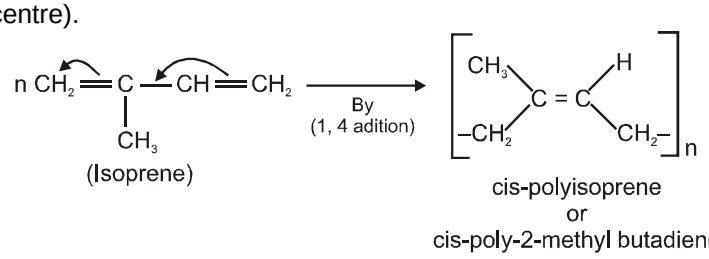
(8) Polymethylmethacrylate :



Methylmethacrylate Polymethylmethacrylate

(9) Rubbers :

(a) 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).

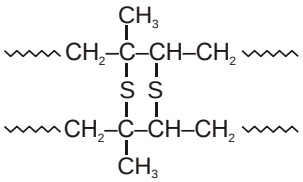


(Isoprene)

cis-polyisoprene
or
cis-poly-2-methyl butadiene

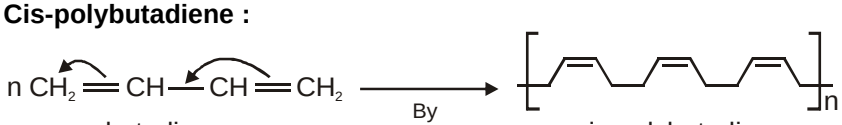
*** Gutta parcha**, has isoprene unit in trans-form (dentist used it in the filling of teeth).

Vulcanization : .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.



(b) Synthetic Rubber : Synthetic rubber is rubber like polymers, which is capable of getting stretched to twice its length. However, it returns to its original shape and size as soon as the external stretching force is released. Thus, synthetic rubbers are either homopolymers of 1,3-butadiene derivatives or copolymers of 1, 3-butadiene or its derivatives with another unsaturated monomers.

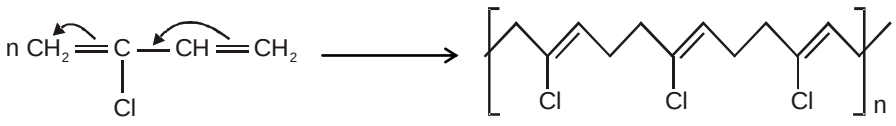
(i) Cis-polybutadiene :



butadiene

cis-polybutadiene

(ii) Neoprene :

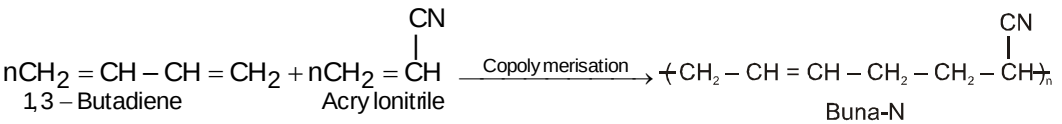


Chloroprene

Neoprene

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

(iii) Buna-N :



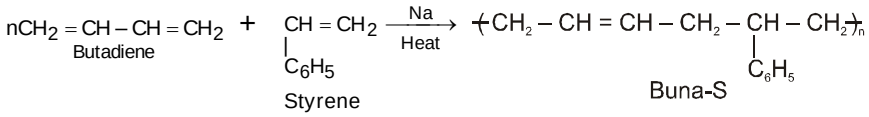
1,3 – Butadiene

Acrylonitrile

Buna-N

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

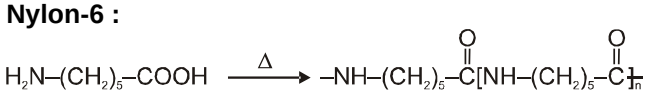
(iv) **Buna-S :** It is obtained by the polymerization of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium. It is also known as styrene butadinene rubber (SBR).



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

(10) Polyamides :

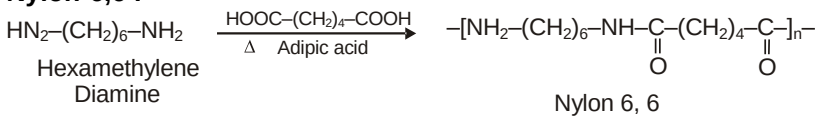
(a) Nylon-6 :



6-Aminohexanoic acid Nylon-6

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

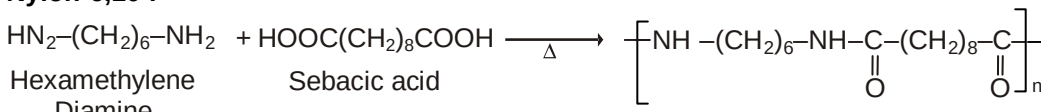
(b) Nylon-6,6 :



Nylon 6, 6

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

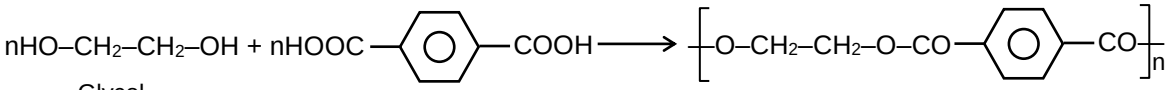
(c) Nylon-6,10 :



Nylon 6, 10

(11) Polyesters :

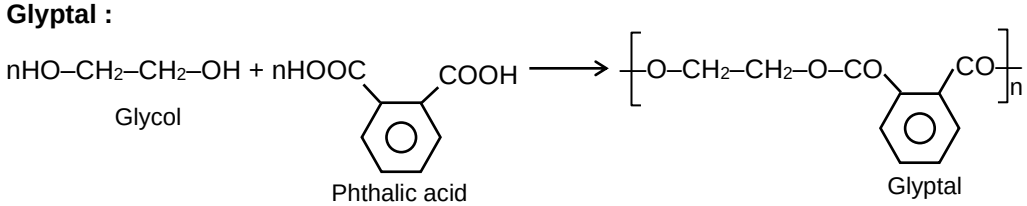
(a) Dacron :



Terylene or 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.

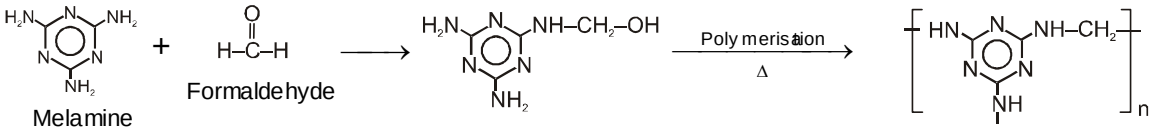
(b) Glyptal :



Glyptal

Glyptal is used as manufacture of paints and lacquers.

(12) Melamine formaldehyde Resin :



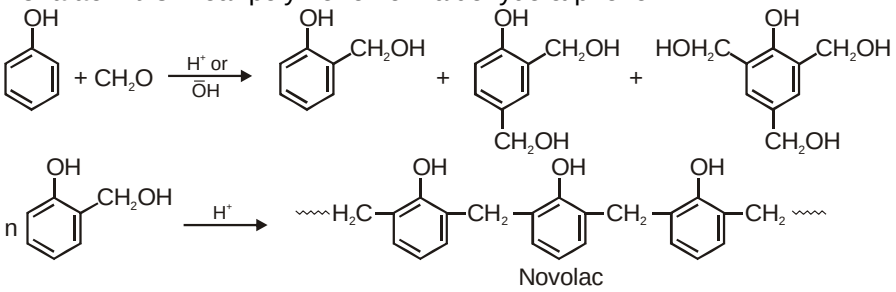
Melamine Formaldehyde polymer (Melmac)

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

(13) 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.

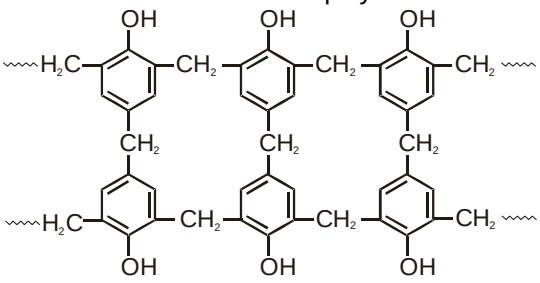
(a) Novalac : It is linear polymer of formaldehyde & phenol.



Novolac

Novalac is used in paints.

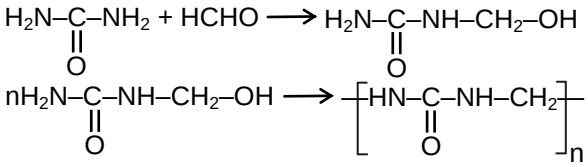
(b) Bakelite : It is cross linked polymer of formaldehyde & phenol.



Bakelite

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

(14) Urea formaldehyde Resin :



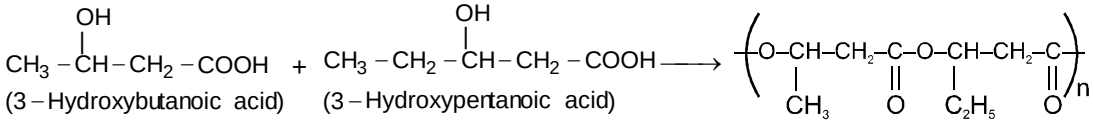
Urea formaldehyde Resin is used for making unbreakable cups and laminated sheets.

(15) Biodegradable Polymers :

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric soild waste materials. These soild wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric soild wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable poylmers. Some examples are given below :

(a) Poly β-hydroxybutyrate-co-β-hydroxy valerate (PHBV) : It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

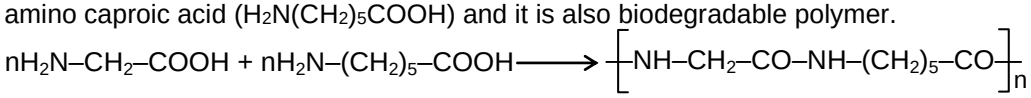


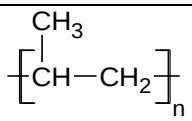
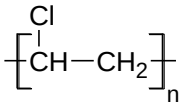
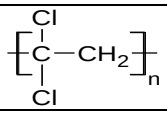
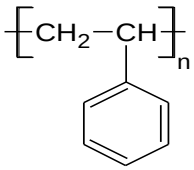
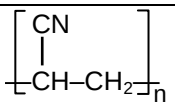
(3 – Hydroxybutanoic acid) (3 – Hydroxypentanoic acid)

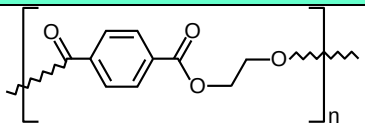
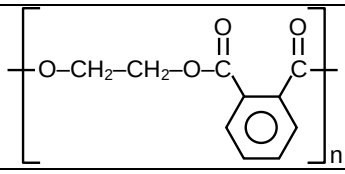
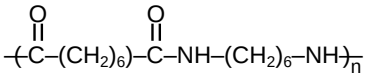
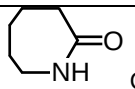
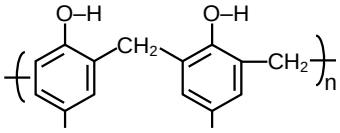
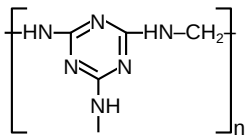
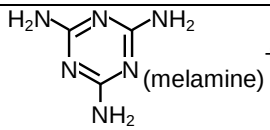
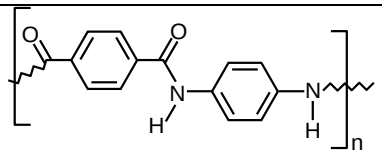
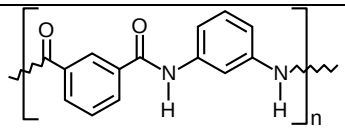
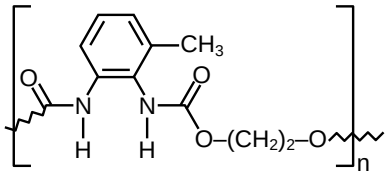
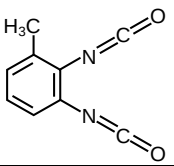
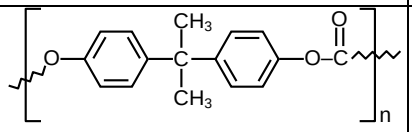
PHBV

PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

(b) Nylon-2-nylon-6 : It is an alternating polyamide copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid ($H_2N(CH_2)_5COOH$) and it is also biodegradable polymer.



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)	$\text{-}[CH_2\text{-}CH(Ph)\text{-}CH_2\text{-}CH=CH\text{-}CH_2]\text{-}$	$H_2C=CHC_6H_5$ and $H_2C=CH\text{-}CH=CH_2$	Tyres, floortiles, foot wear & cable insulation
14.	Nitrile Rubber (Buna-N)	$\text{-}[CH_2\text{-}CH(CN)\text{-}CH_2\text{-}CH=CH\text{-}CH_2]\text{-}$	$H_2C=CHCN$ 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		 +HCHO (formaldehyde)	Unbreakabl e crockery
9.	Polyamide Kevlar		Para $HO_2C–C_6H_4–CO_2H$ Para $H_2N–C_6H_4–NH_2$	Tyre
10.	Polyamide Nomex		Meta $HO_2C–C_6H_4–CO_2H$ Meta $H_2N–C_6H_4–NH_2$	
11.	Polyurethane Spandex		$HOCH_2CH_2OH$ 	Foams, Shoes, Automobile seats and components
12.	Polycarbonate Lexan		$(HO–C_6H_4–)_2C(CH_3)_2$ (Bisphenol A) $X_2C=O$ (X = OCH_3 or Cl)	Bike helmet, goggles, bullet proof glass