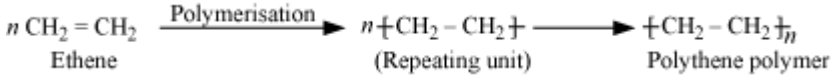
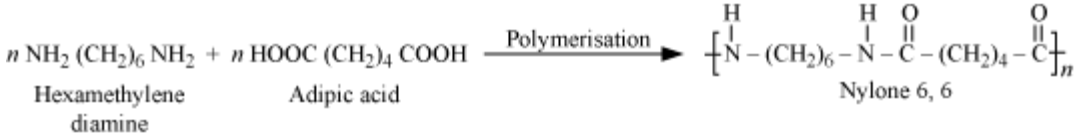
Polymers

Classification of Polymers

- **Polymers** – Large molecules having high molecular mass (10^3 – 10^7 u)
- **Polymerisation** – Process of formation of polymers from respective monomers

Example:





Classification of Polymers

Classification Based on Source

- **Natural polymers**: Found in plants and animals

  Example: Proteins, starch, cellulose, resins and rubber

- **Semi-synthetic polymers**: Cellulose derivatives

  Example: Cellulose acetate (rayon), cellulose nitrate

- **Synthetic polymers**: Man-made polymers

  Example: Plastic (polythene), synthetic fibres (nylon 6, 6) synthetic rubbers (Buna – S)

Classification Based on Structure

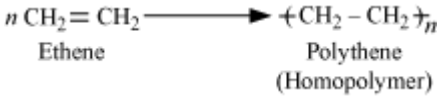
- **Linear Polymers**: Consist of long and straight chains
- Example: High density polythene, polyvinyl chloride, etc.
- Represented as

- **Branched-chain polymers**: Contain linear chains having some branches
- Example: Low density polythene
- Represented as

- **Cross-linked or Network polymers**
- Formed from bi-functional and tri-functional polymers
- Contain strong covalent bonds between various linear polymer chains
- Example: Bakelite, melamine, etc.
- Represented as

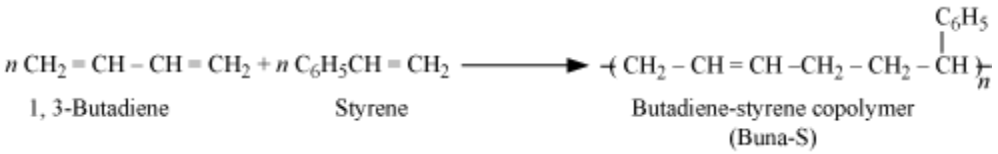
Classification Based on Mode of Polymerisation

- **Addition polymers**
- Formed by the repeated addition of monomer molecules possessing double or triple bonds
- Example: Polythene (from ethene), polypropene (from propene)
- Homopolymers − Addition polymers formed by the polymerisation of a single monomeric species



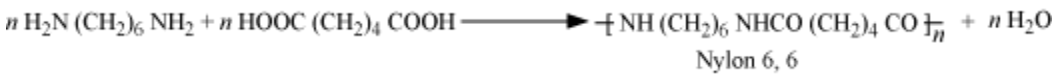
- Copolymers − Formed by the addition polymerisation from two different monomers

  Example: Buna-S, buna-N, etc.



- **Condensation polymers**

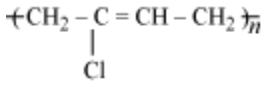
- Formed by the repeated condensation reaction between two different bi-functional or tri-functional monomeric units
- Involves elimination of small molecules such as water, alcohol, HCl, etc.
- Example: Nylon 6, 6, terylene (dacron), nylon 6, etc.
- Nylon 6, 6 – Formed by the condensation of hexamethylene diamine with adipic acid



Nylon 6, 6

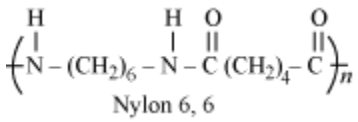
Classification Based on Molecular Forces

- **Elastomers** – Rubber-like solids with elastic properties
- Polymer chains are held together by the weakest intermolecular forces.
- Weak binding forces permit the polymer to be stretched.
- 'Cross-links' are also introduced in between the chains, which help the polymer to retract to its original position after the force is released, as in vulcanised rubber.
- Example: Buna-S, buna-N, neoprene, etc.



Neoprene

- **Fibres**
- Thread-forming solids which possess high tensile strength and high modulus
- Characteristics can be attributed to strong intermolecular forces like hydrogen bonding
- Strong forces lead to close packing of chains, and thus, impart crystalline nature
- Example: Polyamides (nylon 6, 6), polyesters (terylene), etc.



Nylon 6, 6

- **Thermoplastic Polymers**

- Linear or slightly branched long-chain molecules capable of repeatedly softening and hardening on cooling
- Example: Polythene, polystyrene, polyvinyls, etc.
- **Thermosetting Polymers**
- Cross-linked or heavily branched molecules, which on heating undergo extensive cross-linking in moulds and again become infusible
- Cannot be a reused
- Example: Bakelite, urea-formaldehyde resins, etc.

Classification Based on Growth Polymerisation

- Addition polymers: Chain-growth polymers
- Condensation polymers: Step-growth polymers

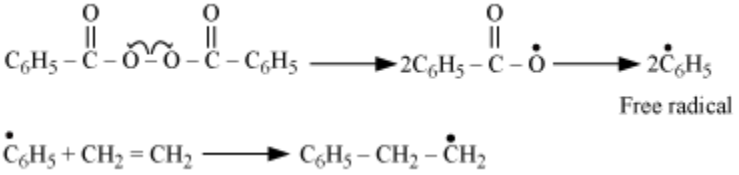
Types of Polymerisation Reactions

Addition Polymerisation or Chain-Growth Polymerisation

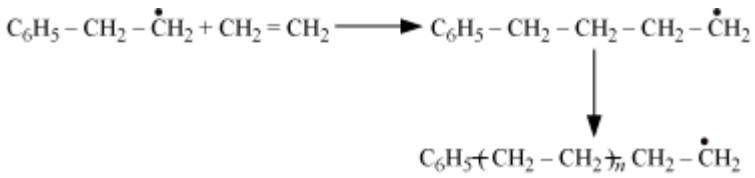
- Molecules of the same monomer or different monomers add together on a large scale to form a polymer.

Free radical mechanism

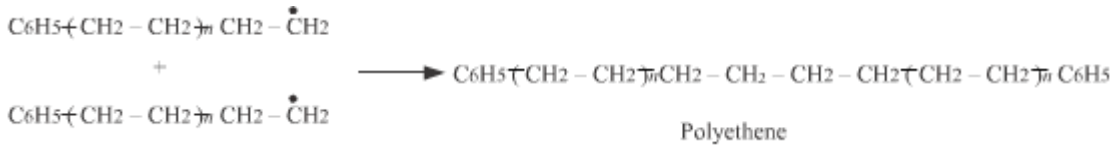
- Chain-initiation step



- Chain-propagating step



- Chain-terminating step

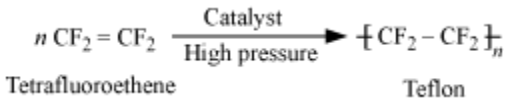


Preparation of Some Important Addition Polymers

Polythene

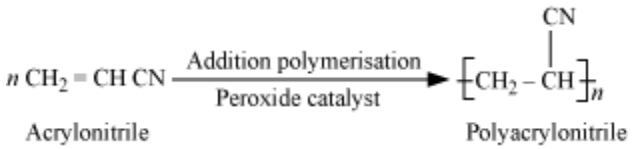
- **Low-Density Polythene**
- Obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres, and at a temperature of 350 K to 570 K, in the presence of traces of dioxygen or a peroxide initiator (catalyst)
- Chemically inert, and tough but flexible
- Poor conductor of electricity
- **High-Density Polythene**
- Formed by the addition polymerisation of ethene in a hydrocarbon solvent at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres
- Catalyst used − Triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst)
- High density is due to close-packing
- Chemically inert, and more tougher and harder than low density polythene
- Used for manufacturing buckets, dustbins, bottles, etc.

Polytetrafluoroethene (Teflon)



- Catalyst used in preparation − Free radical or per-sulfate
- Chemically inert and resistant to attack by corrosive reagents
- Used for making oil seals and gaskets, and for non-stick-surface-coated utensils

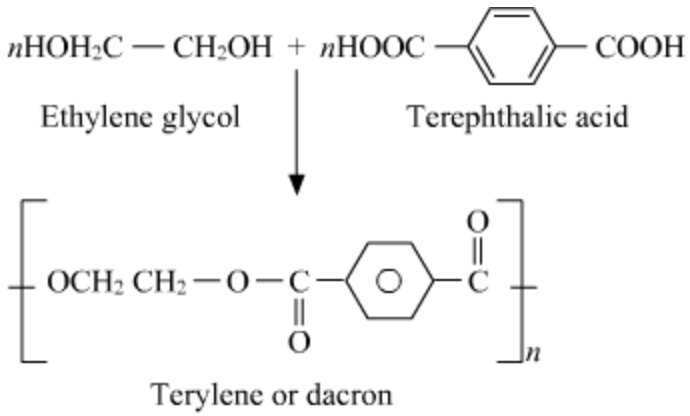
Polyacrylonitrile



- Used as a substitute for wool in making commercial fibres as orlon or acrilan

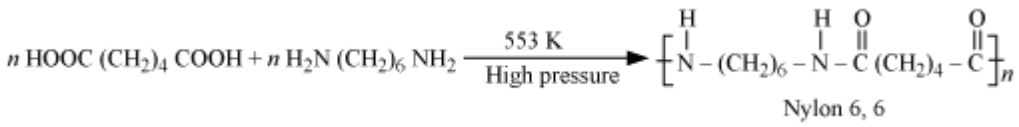
Condensation Polymerisation or Step-Growth Polymerisation

- Involves a repetitive condensation reaction between two bi-functional monomers
- Results in the loss of some simple molecules as water, alcohol, etc., and leads to the formation of high molecular mass condensation polymers
- Example: Formation of terylene or dacron by the interaction of ethylene glycol and terephthalic acid

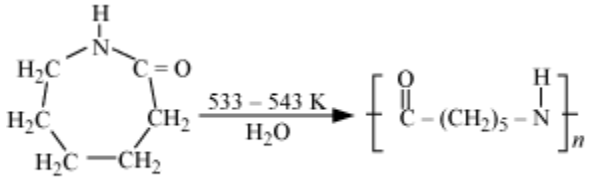


Polyamides

- Possess amide linkages
- Prepared by the condensation polymerisation of diamines with dicarboxylic acids, and also of amino acids and their lactams
- **Nylon 6, 6**



- Used in making sheets, bristles for brushes and in textile industry
- **Nylon 6**

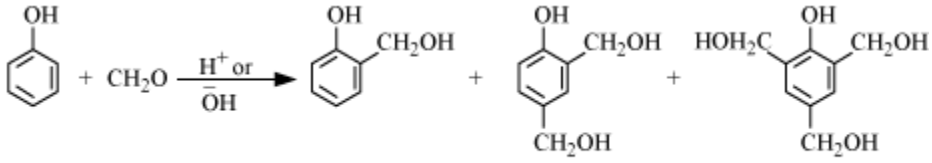


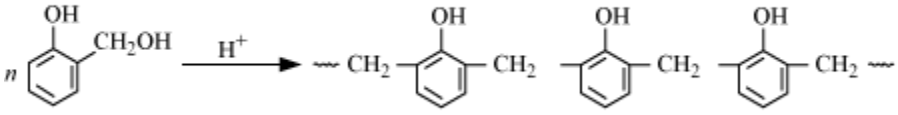
Caprolactam Nylon 6

- Used for the manufacture of tyre cords, fabrics and ropes

Polysters

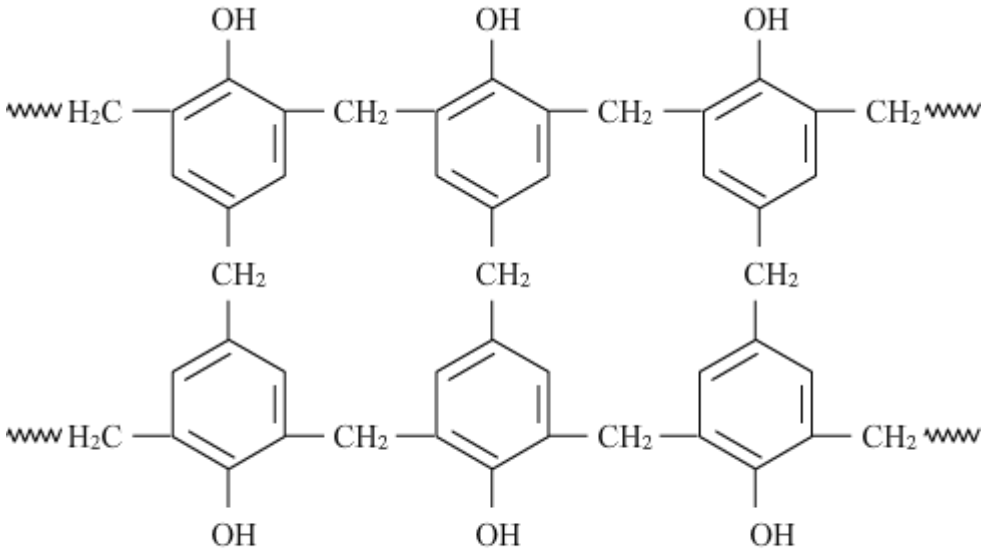
- Polycondensation products of dicarboxylic acids and diols
- Example: Dacron or terylene – manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K.
- Catalyst used: Zinc acetate-antimony trioxide
- Dacron fibre is –
- Crease resistant
- Used in blending with cotton and wool fibres
- As glass-reinforcing materials in safety helmets
- **Phenol-Formaldehyde polymer (Bakelite and related polymers)**





Novolac

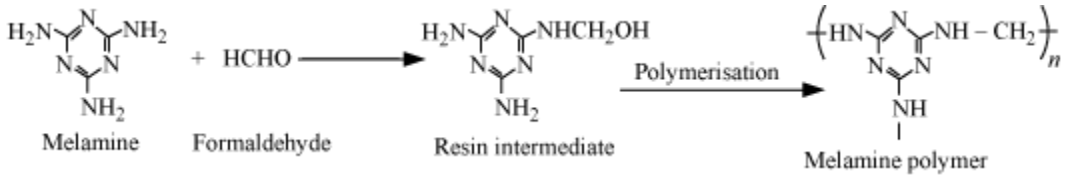
- Novolac, obtained on heating with formaldehyde, undergoes cross- linking to form an infusible solid mass called bakelite.



Bakelite

- Bakelite – Used for making combs, phonograph records, electrical switches and handles of various utensils

- **Melamine-Formaldehyde polymer**



  - Used in the manufacture of unbreakable crockery

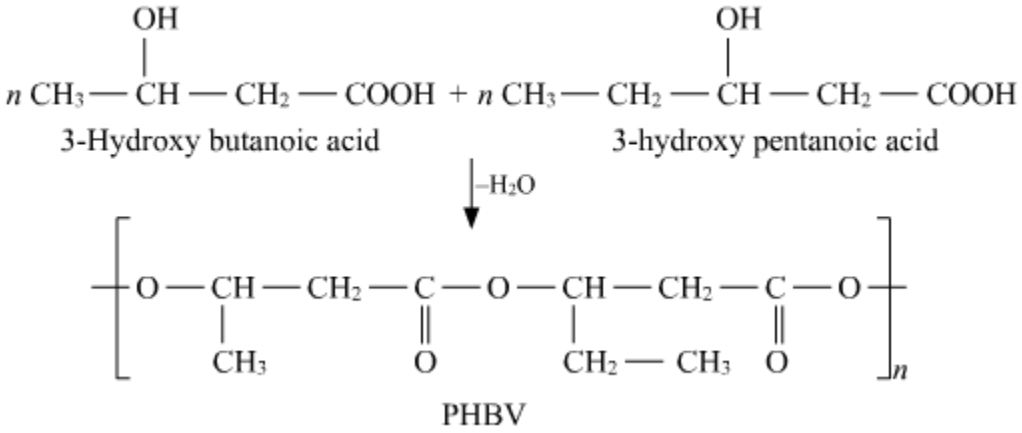
Biodegradable and Non-biodegradable Polymers

- Natural polymers degrade on their own with time but synthetic polymers do not.
- The non-biodegradable polymers do not undergo the environmental degradation processes and get accumulated as harmful solid waste materials.
- As a result efforts have been made to synthesise biodegradable polymers which are environment friendly and get degraded by natural processes with time.

Examples of some biodegradable polymers:

PHBV Polymer (Polyhydroxy butyrate-co- β-hydroxy valerate)

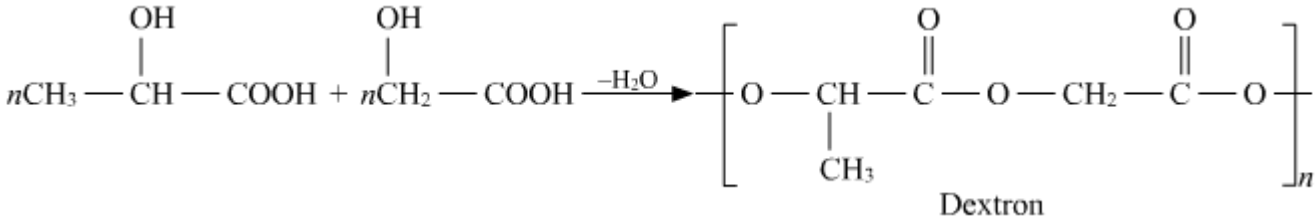
- It is a copolymer with an ester linkage.
- Monomers are 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



PHBV

Dextron

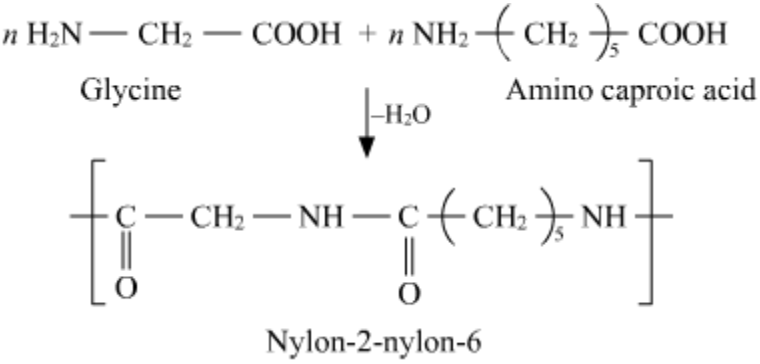
- It is also a copolymer with an ester linkage.
- Monomers are glycolic acid and lactic acid.



Dextron

Nylon-2-nylon-6

- It is copolymer containing polyamide linkages.
- Monomers are glycine and aminocaproic acid.

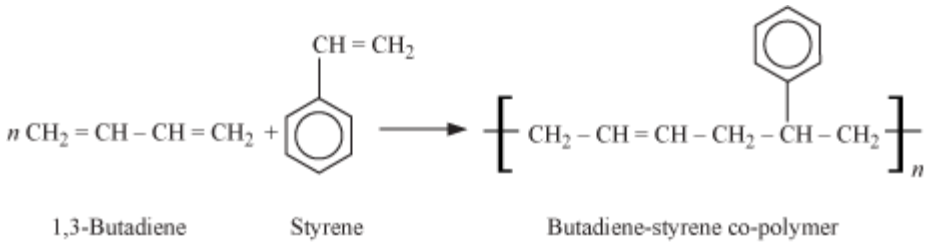


Nylon-2-nylon-6

Co-polymerisation & Rubber

Co-polymerisation

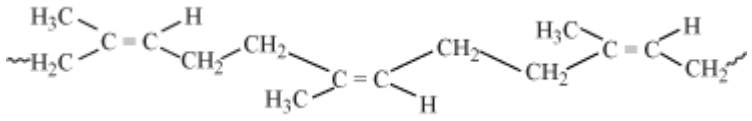
- A polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a co-polymer
- Can be made not only by chain-growth polymerisation, but also by step- growth polymerisation
- Contains multiple units of each monomer used in the same polymeric chain
- Example: Butadiene–Styrene co-polymer



- Butadiene–styrene co-polymer is quite tough.
- Used for the manufacture of auto tyres, floor tiles, footwear components, cable insulation, etc.

Rubber (Natural Rubber)

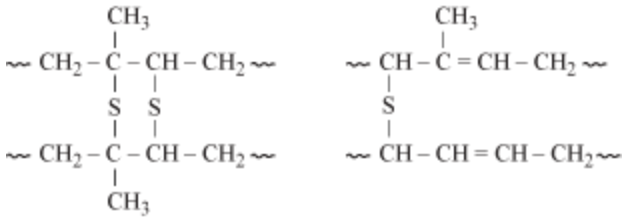
- A natural polymer which possesses elastic properties
- Also termed as elastomer
- Manufactured from rubber latex
- A linear polymer of isoprene (2-methyl -1, 3-butadiene)



Vulcanisation of rubber

- Natural rubber becomes soft at high temperatures (> 335 K) and brittle at low temperatures (< 283 K); shows high water-absorption capacity; is soluble in non-polar solvents; is non-resistant to attack by oxidising agents.
- To improve the physical properties of natural rubber, the process of vulcanisation is carried out.
- In this process, raw rubber is heated with a mixture of sulphur and an appropriate additive, at a temperature range of 373 K to 415 K.

- On vulcanisation, sulphur forms cross-links at the reactive sites of the double bonds, and thus, rubber gets stiffened.
- For example, in the manufacture of tyre rubber, 5% of sulphur is used as a cross-linking agent.



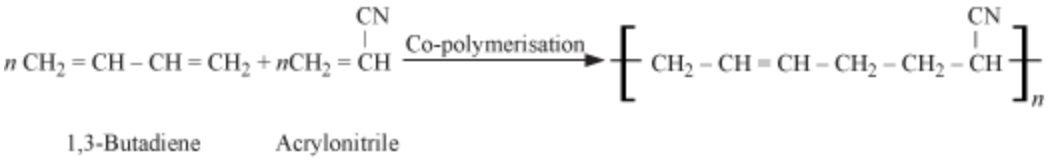
Synthetic Rubbers

Either homopolymers of 1, 3-butadiene derivatives, co-polymers of 1, 3-butadiene or its derivatives with another unsaturated monomer

Preparation of synthetic rubbers

- Neoprene

-
- Use: For manufacturing conveyer belts, gaskets and hoses
- **Buna – N**
- Obtained by the co-polymerisation of 1, 3-butadiene and acrylonitrile in the presence of peroxide catalyst



- Resistant to the action of petrol, lubricating oil and organic solvents
- Used for making oil seals, tank lining, etc.

Molecular Mass of Polymers

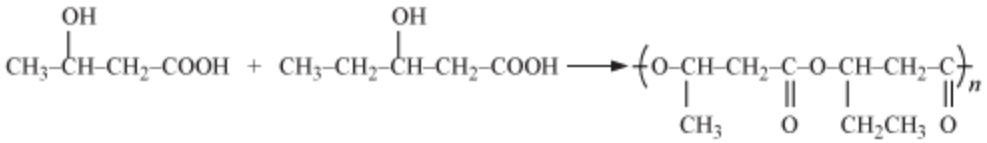
- Always expressed as an average
- Can be determined by chemical and physical methods

Biodegradable Polymers

- These polymers contain functional groups similar to the functional groups present in biopolymers.
- Example: PHBV and Nylon 2-nylon 6

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

- Obtained by the co-polymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanioic acid



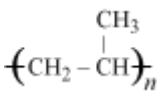
3-Hydroxybutanoic acid 3-Hydroxypentanoic acid PHBV

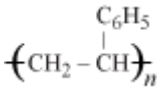
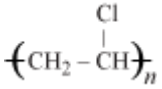
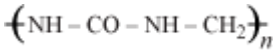
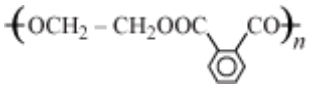
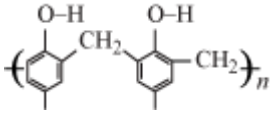
- Used in speciality packaging, orthopaedic devices and in controlled release of drugs
- Undergoes bacterial degradation in the environment

Nylon 2-nylon 6

- An alternating polyamide co-polymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid [$H_2N(CH_2)_5COOH$]
- Biodegradable

Some Other Commercially Important Polymers with Their Use

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene		Manufacture of ropes, toys, pipes, fibres, etc.

Polystyrene	Styrene		As insulator, wrapping material, manufacture of toys, radio and television cabinets
Polyvinyl chloride(PVC)	Vinyl chloride		Manufacture of raincoats, hand bags, vinyl flooring, water pipes
Urea-formaldehyde resin	(a) Urea (b) Formaldehyde		For making un-breakable cups and laminated sheets
Glyptal	(a) Ethylene glycol (b) Phthalic acid		Manufacture of paints and lacquers
Bakelite	(a) Phenol (b) Formaldehyde		For making combs, electrical switches, handles of utensils and computer discs