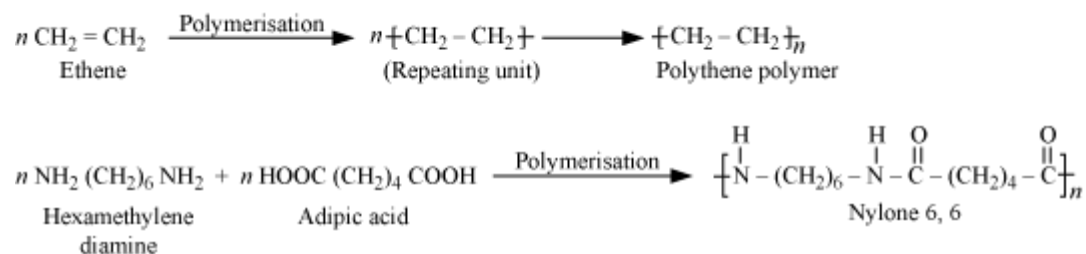


Polymers

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

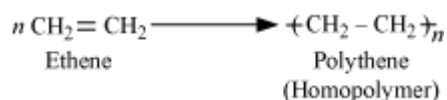


- **Cross-linked or Network polymers**
- Formed from bi-functional and tri-functional polymers
- Contain strong covalent bonds between various linear polymer chains
- Example: Bakelite, melamine, etc.
- Represented as



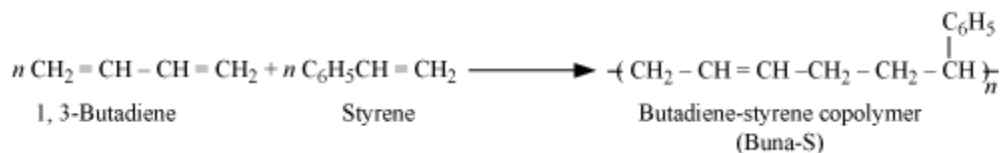
Classification Based on Mode of Polymerisation

- **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.



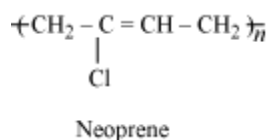
- **Condensation polymers**

- 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

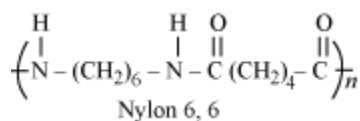


Classification Based on Molecular Forces

- **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.



- **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.



- **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 reused
- Example: Bakelite, urea-formaldehyde resins, etc.

Classification Based on Growth Polymerisation

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

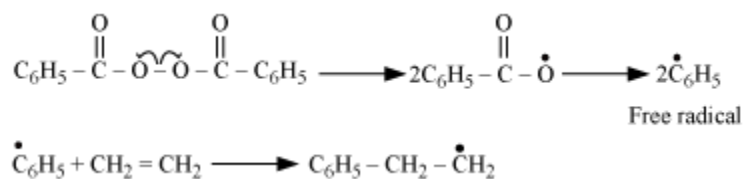
Types of Polymerisation Reactions

Addition Polymerisation or Chain-Growth Polymerisation

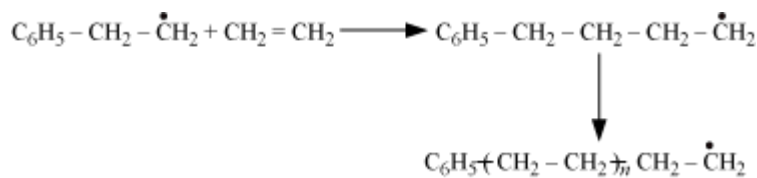
- Molecules of the same monomer or different monomers add together on a large scale to form a polymer.

Free radical mechanism

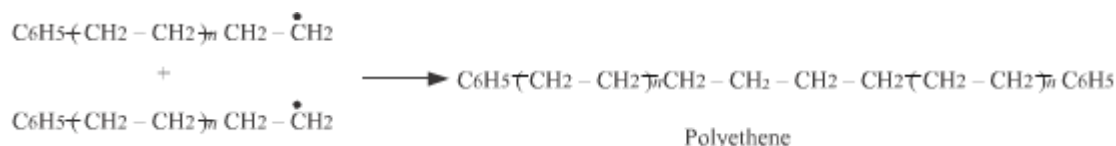
- Chain-initiation step



- Chain-propagating step



- Chain-terminating step

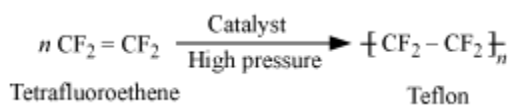


Preparation of Some Important Addition Polymers

Polythene

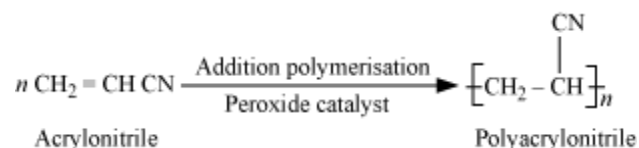
- Low-Density Polythene**
 - Obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres, and at a temperature of 350 K to 570 K, in the presence of traces of dioxygen or a peroxide initiator (catalyst)
 - Chemically inert, and tough but flexible
 - Poor conductor of electricity
- 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

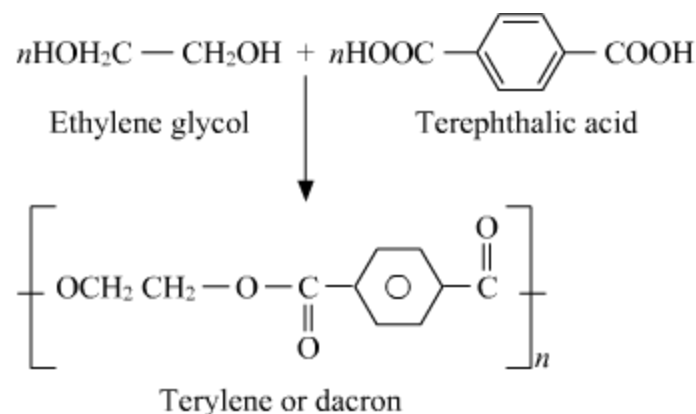
Polyacrylonitrile



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

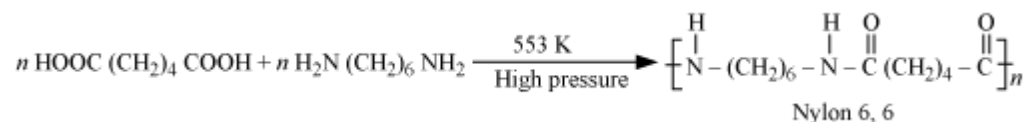
Condensation Polymerisation or Step-Growth Polymerisation

- 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

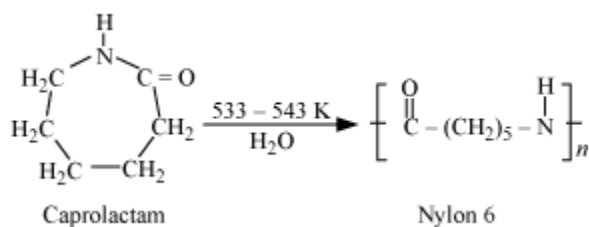


Polyamides

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



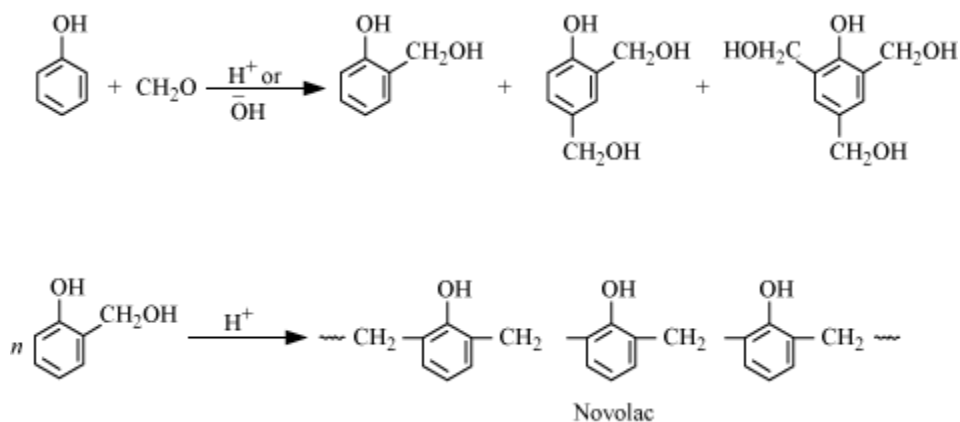
- Used in making sheets, bristles for brushes and in textile industry
- **Nylon 6**



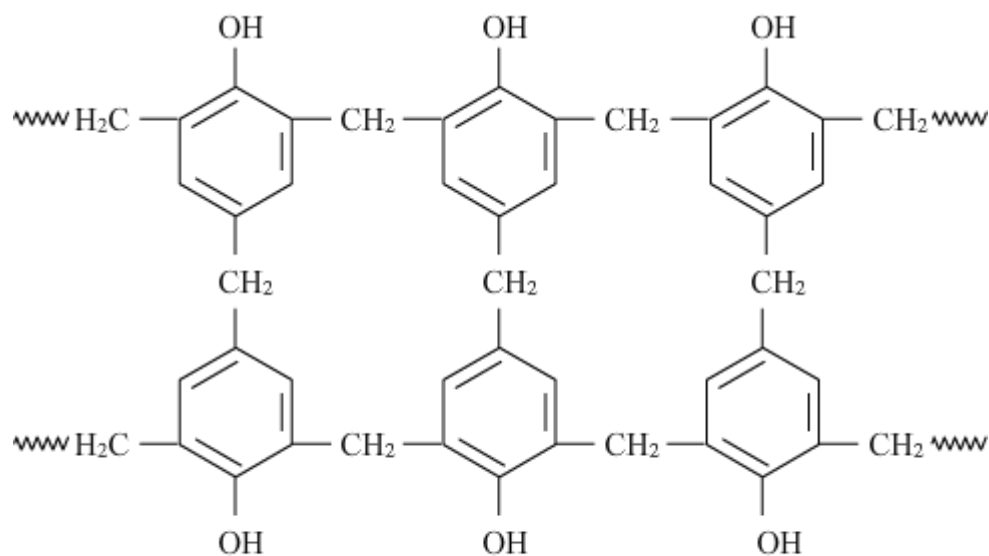
- Used for the manufacture of tyre cords, fabrics and ropes

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)**

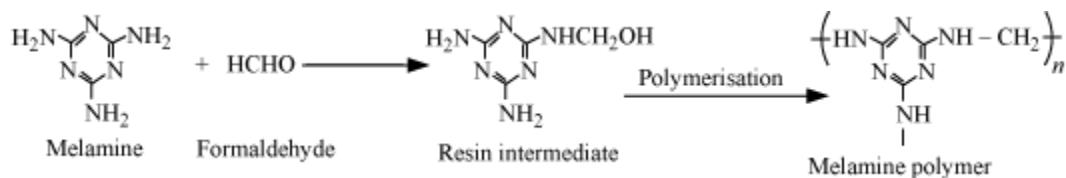


- Novolac, obtained on heating with formaldehyde, undergoes cross- linking to form an infusible solid mass called bakelite.



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

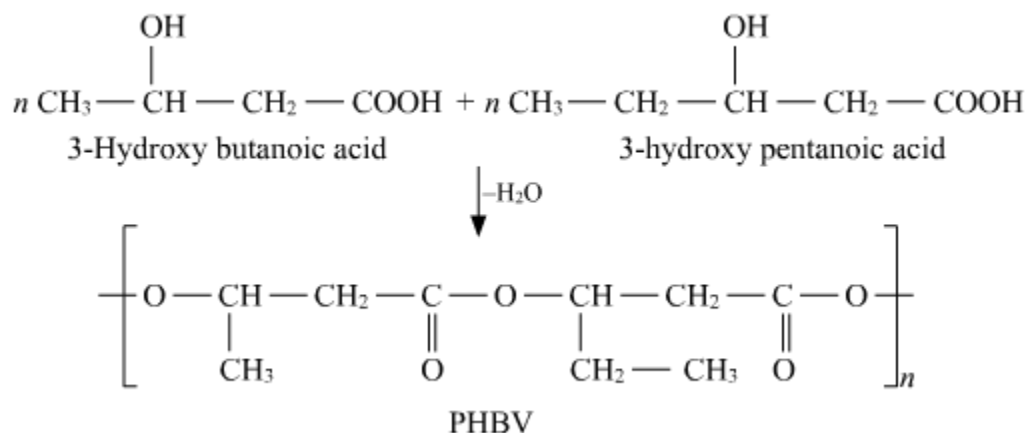
Biodegradable and Non-biodegradable Polymers

- 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:

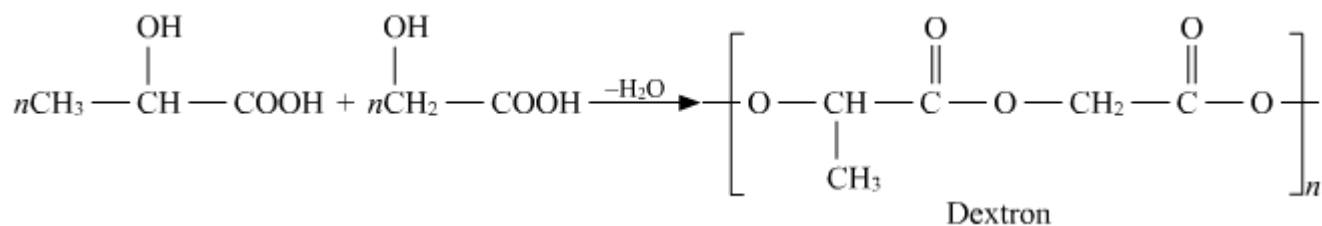
PHBV Polymer (Polyhydroxy butyrate-co- β -hydroxy valerate)

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



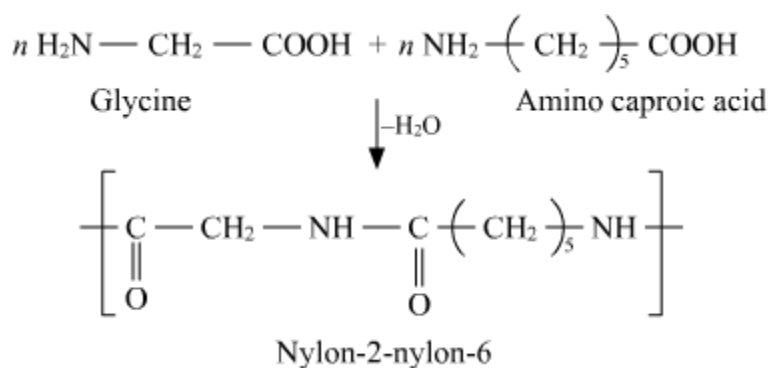
Dextron

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



Nylon-2-nylon-6

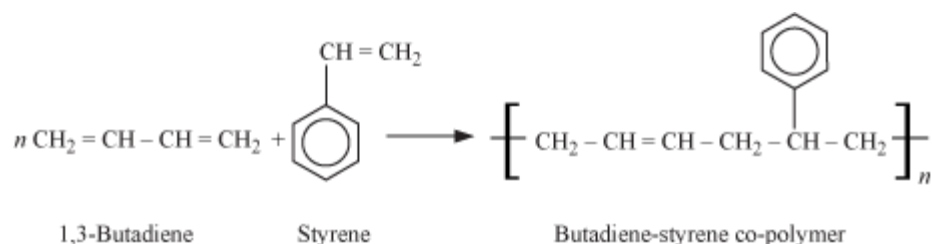
- It is copolymer containing polyamide linkages.
- Monomers are glycine and aminocaproic acid.



Co-polymerisation & Rubber

Co-polymerisation

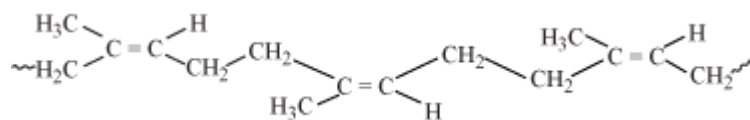
- A polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a co-polymer
- Can be made not only by chain-growth polymerisation, but also by step- growth polymerisation
- Contains multiple units of each monomer used in the same polymeric chain
-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

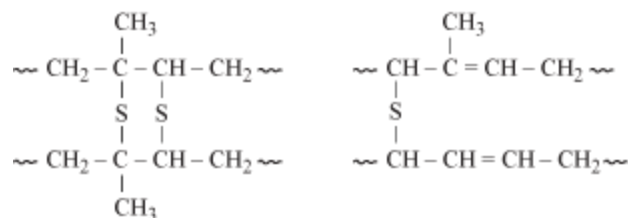
- A natural polymer which possesses elastic properties
- Also termed as elastomer
- Manufactured from rubber latex
- A linear polymer of isoprene (2-methyl -1, 3-butadiene)



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

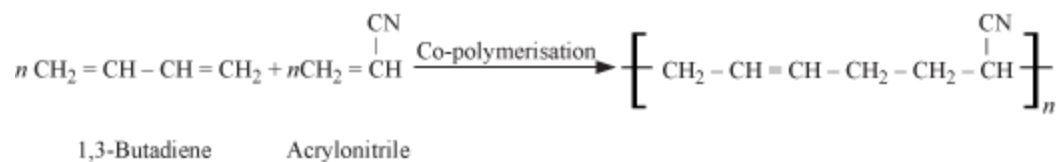
Either homopolymers of 1, 3-butadiene derivatives, co-polymers of 1, 3-butadiene or its derivatives with another unsaturated monomer

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

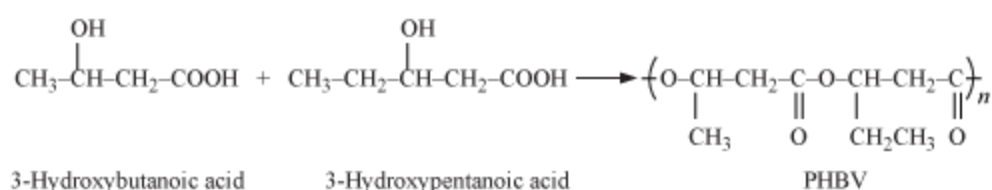
- Always expressed as an average
- Can be determined by chemical and physical methods

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-hydroxypentanoic acid



- 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 ($\text{H}_2\text{N-CH}_2\text{-COOH}$) and amino caproic acid [$\text{H}_2\text{N(CH}_2)_5\text{COOH}$]
- Biodegradable

Some Other Commercially Important Polymers with Their Use

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left(\text{CH}_2 - \underset{\text{CH}_3}{\underset{ }{\text{CH}}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.

Polystyrene	Styrene	$\left(\text{CH}_2 - \overset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}} \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets
Polyvinyl chloride(PVC)	Vinyl chloride	$\left(\text{CH}_2 - \overset{\text{Cl}}{\underset{ }{\text{CH}}} \right)_n$	Manufacture of raincoats, hand bags, vinyl flooring, water pipes
Urea-formaldehyde resin	(a) Urea (b) Formaldehyde	$\left(\text{NH} - \text{CO} - \text{NH} - \text{CH}_2 \right)_n$	For making un-breakable cups and laminated sheets
Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left(\text{OCH}_2 - \text{CH}_2\text{OOC} \begin{array}{c} \diagup \diagdown \\ \text{C} \\ \diagdown \diagup \end{array} \text{CO} \right)_n$	Manufacture of paints and lacquers
Bakelite	(a) Phenol (b) Formaldehyde	$\left(\begin{array}{c} \text{O-H} \\ \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2 - \begin{array}{c} \text{O-H} \\ \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2 \right)_n$	For making combs, electrical switches, handles of utensils and computer discs