NEET | JEE ESSENTIALS

Class XII

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Unit 8

POLYMERS CHEMISTRY IN EVERYDAY LIFE

POLYMERS

INTRODUCTION

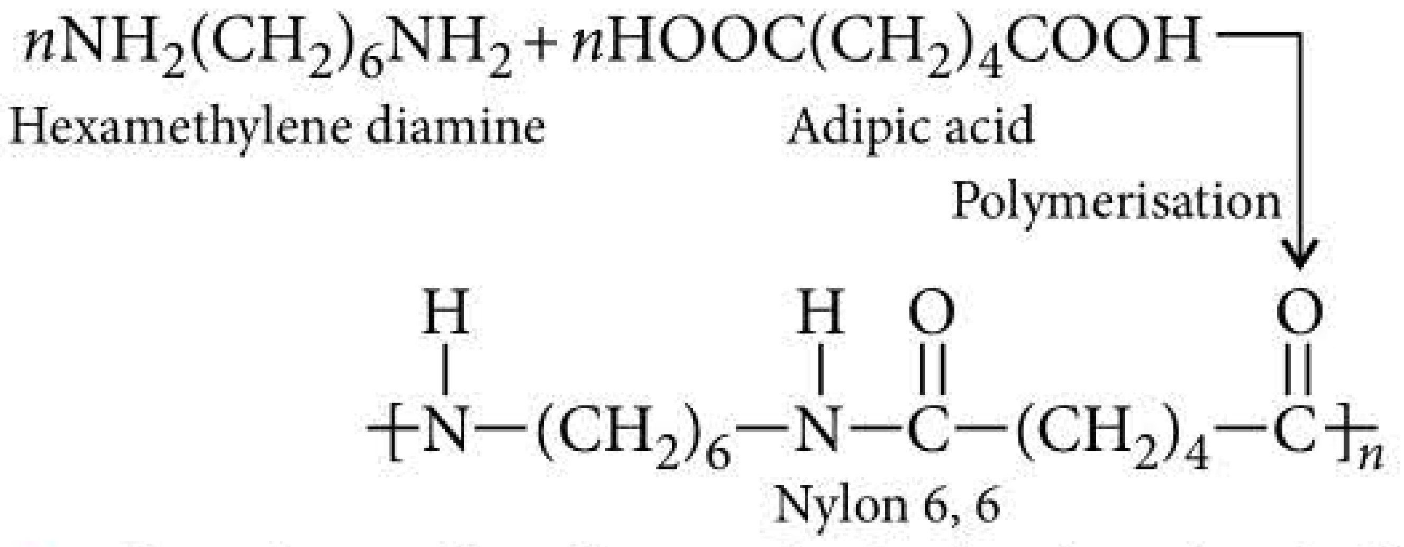
- The word 'polymer' is coined from two Greek words. *Poly* means many and *mer* means unit or part.
- Polymers are very large molecules having high molecular mass (10^3–10^7u).
- These are also referred to as *macromolecules*, which are formed by joining of repeating structural units *monomers* on a large scale.
- The process of formation of polymers from respective monomers is called *polymerisation*.
- All polymers are macromolecules but all macromolecules are not polymers.

TYPES OF POLYMERS

- **Homopolymer :** Polymer made up of only one type of monomer. *e.g.*, Polythene, Polypropylene, PVC, etc.

$$\underset{\text{Ethene}}{nCH_2{=}CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Polythene}}{\text{+}CH_2{-}CH_2\text{+}_n}$$

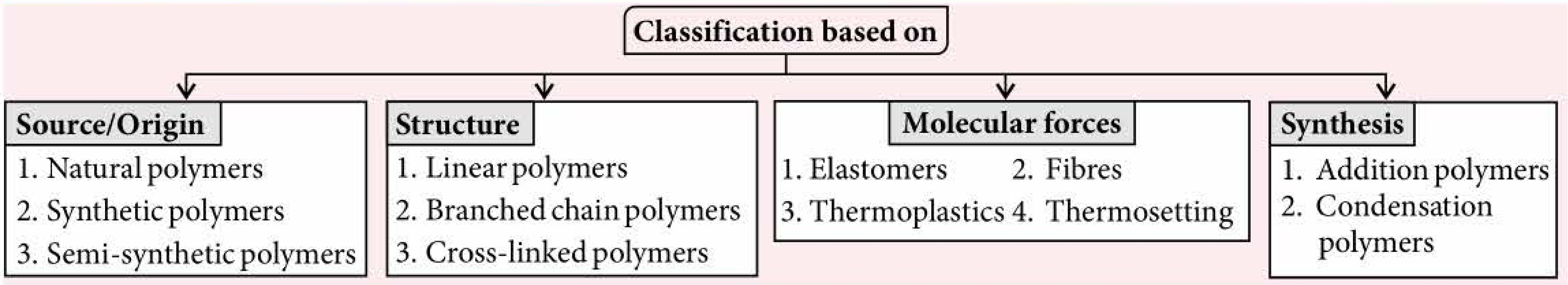
- **Copolymer :** Polymer made up of two or more types of monomers. *e.g.*, Nylon 6,6, Buna-S, Bakelite, etc. The process of formation of copolymer is called *copolymerisation*.

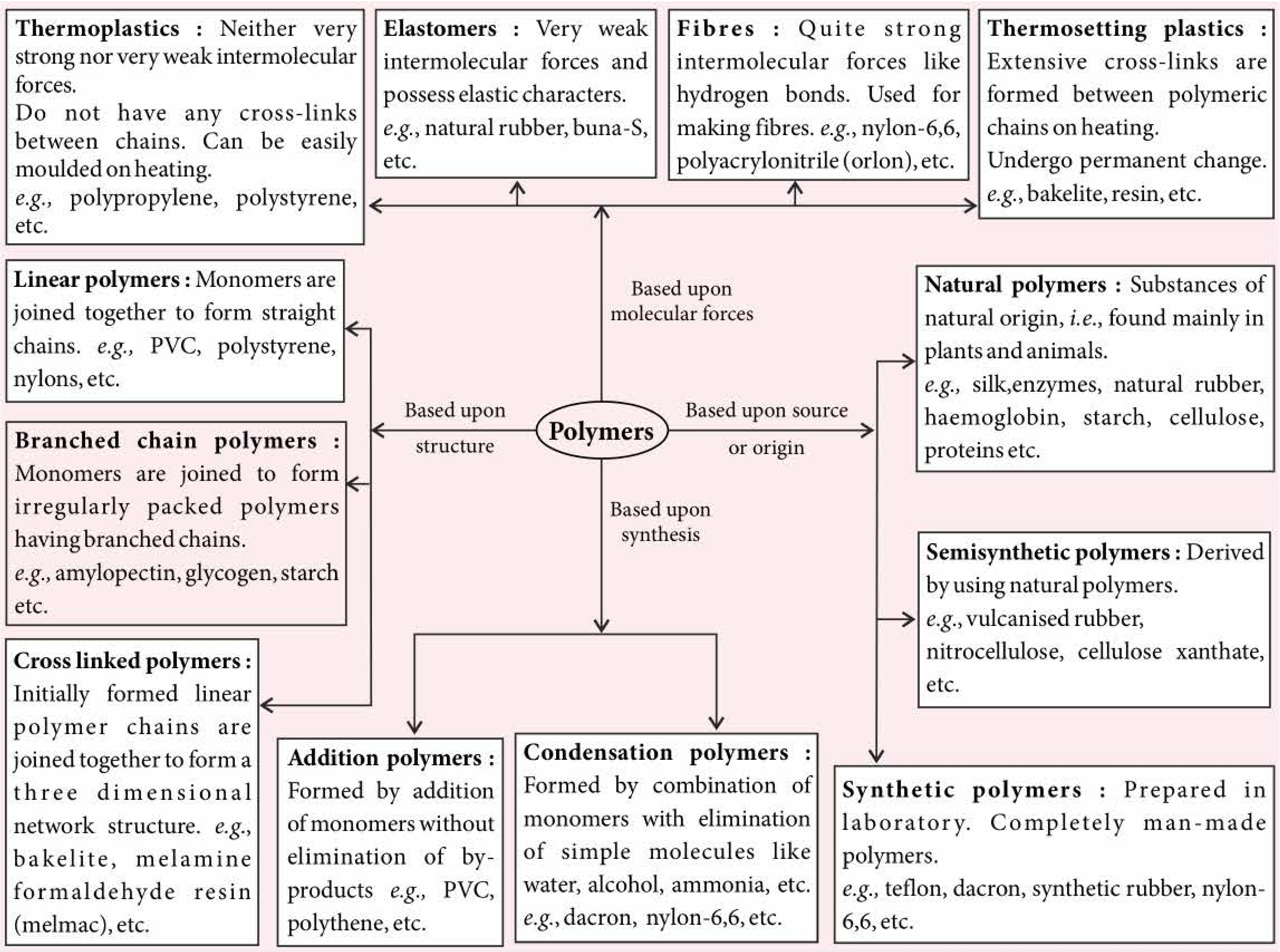


$$\underset{\text{Hexamethylene diamine}}{nNH_2(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} \xrightarrow{\text{Polymerisation}} \underset{\text{Nylon 6, 6}}{\text{+}\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}\text{+}_n}$$

- Copolymers have better physical and mechanical properties. The properties of copolymers could be changed by varying the amount of each monomer.

CLASSIFICATION OF POLYMERS





Thermoplastics : Neither very strong nor very weak intermolecular forces.
Do not have any cross-links between chains. Can be easily moulded on heating.
e.g., polypropylene, polystyrene, etc.

Elastomers : Very weak intermolecular forces and possess elastic characters.
e.g., natural rubber, buna-S, etc.

Fibres : Quite strong intermolecular forces like hydrogen bonds. Used for making fibres. *e.g.,* nylon-6,6, polyacrylonitrile (orlon), etc.

Thermosetting plastics : Extensive cross-links are formed between polymeric chains on heating.
Undergo permanent change.
e.g., bakelite, resin, etc.

Linear polymers : Monomers are joined together to form straight chains. *e.g.,* PVC, polystyrene, nylons, etc.

Branched chain polymers : Monomers are joined to form irregularly packed polymers having branched chains.
e.g., amylopectin, glycogen, starch etc.

Cross linked polymers : Initially formed linear polymer chains are joined together to form a three dimensional network structure. *e.g.,* bakelite, melamine formaldehyde resin (melmac), etc.

Natural polymers : Substances of natural origin, *i.e.,* found mainly in plants and animals.
e.g., silk, enzymes, natural rubber, haemoglobin, starch, cellulose, proteins etc.

Semisynthetic polymers : Derived by using natural polymers.
e.g., vulcanised rubber, nitrocellulose, cellulose xanthate, etc.

Addition polymers : Formed by addition of monomers without elimination of by-products *e.g.,* PVC, polythene, etc.

Condensation polymers : Formed by combination of monomers with elimination of simple molecules like water, alcohol, ammonia, etc. *e.g.,* dacron, nylon-6,6, etc.

Synthetic polymers : Prepared in laboratory. Completely man-made polymers.
e.g., teflon, dacron, synthetic rubber, nylon-6,6, etc.

METHODS OF POLYMERISATION

- **Addition (chain-growth) polymerisation :** This involves a number of steps, in each step a reactive particle is consumed and the similar one is produced. The monomers used are unsaturated compounds such as alkenes and their derivatives. Depending upon the reactive particles formed these are of three types, free radical, cationic and anionic polymerisation.
  - *Mechanism of free radical polymerisation* : This is initiated by organic peroxides or by light. Steps involved are :
    - *Chain initiation :*

$$\underset{\text{(Alkyl peroxide)}}{(RCOO)_2} \longrightarrow 2RCOO^{\bullet} \xrightarrow{\text{heat}} \underset{\text{(Radical)}}{2\dot{R}} + 2CO_2$$

    - *Chain propagation :*

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

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

$$R{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2 \longrightarrow\longrightarrow\longrightarrow R\left(CH_2{-}CH_2\right)_n CH_2{-}\dot{C}H_2$$

    - *Chain termination* :
      Combination :

$$2R\left(CH_2{-}CH_2\right)_n CH_2{-}\dot{C}H_2 \longrightarrow R\left(CH_2CH_2\right)_n CH_2CH_2{-}CH_2CH_2\left(CH_2CH_2\right)_n R$$

      Disproportionation :

$$2R\left(CH_2{-}CH_2\right)_n CH_2{-}\dot{C}H_2 \longrightarrow \underset{\text{Alkene}}{R\left(CH_2{-}CH_2\right)_n CH{=}CH_2} + \underset{\text{Alkane}}{R\left(CH_2{-}CH_2\right)_n CH_2{-}CH_3}$$

      e.g., polythene, polystyrene
  - *Mechanism of cationic addition polymerisation* **:** Initiated by the use of strong Lewis acids such as HF, $AlCl_3$, H_2SO_4, etc.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$H^+ + CH_2{=}CH_2 \longrightarrow CH_3{-}CH_2^+$$

- The carbocation thus formed undergoes addition with several monomers and finally the chain is terminated by combination with a negative ion or loss of a proton. *e.g.*, polyvinyl ether, polyisobutylene, polystyrene, etc.

- *Mechanism of anionic addition polymerisation*: Initiated by strong bases such as $Na^-NH_2^+$, C_4H_9Li and Grignard reagent, etc.

$$B\!: + CH_2{=}CH_2 \longrightarrow B{-}CH_2{-}\underset{\text{Carbanion}}{CH_2^-}$$

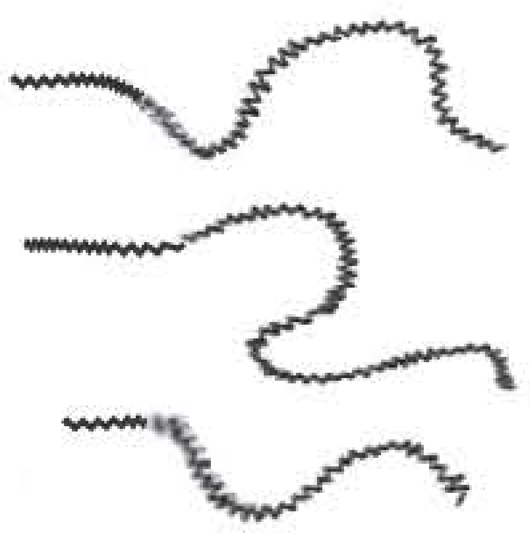
The carbanion thus so formed undergoes addition with number of monomers and finally terminates. *e.g.*, polymerisation of acrylonitrile, vinyl chloride and methyl methacrylate, etc.

- **Condensation (step-growth) polymerisation :** These are formed by the condensation of two or more bifunctional monomer units with the elimination of simple molecules like H_2O, NH_3, CO_2, etc, *e.g.*, formation of nylon, terylene and bakelite, etc.

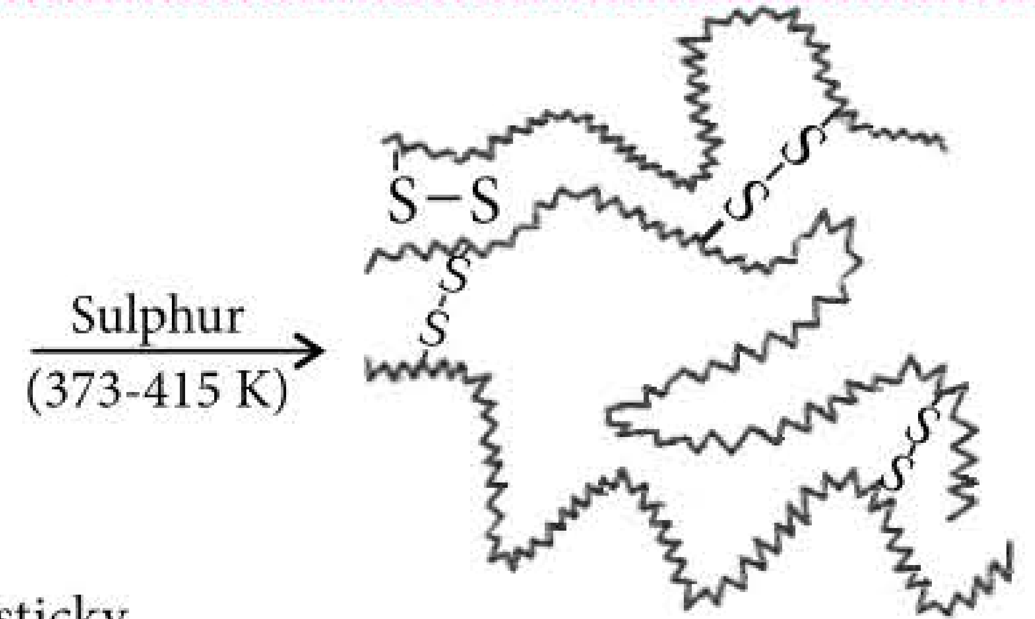
RUBBER

Vulcanisation of rubber

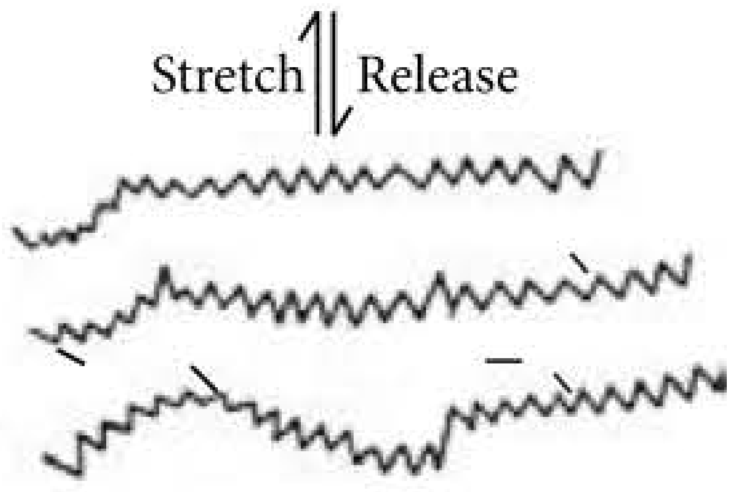
It is the process of heating natural rubber with sulphur at a temperature of 373-415 K. Sulphur cross-links makes the rubber hard, tough with greater tensile strength.
Some additives like carbon black, zinc oxide etc are used to improve wearing properties.



Natural rubber, soft and sticky No cross-links between the polymeric chains.



Vulcanised rubber: The hydrocarbon chains are held together by cross-linking chains of sulphur atoms.



When stretched, the chains are straighten out, but they cannot slip past each other because of polysulphide bridges. Thus, rubber can be stretched only to a limited extent. When the tension is removed, the chains tend to coil up again and the rubber resumes its original shape.

Natural rubber

It is a linear 1, 4-addition polymer of isoprene and have *cis*-configuration of all double bonds thus, known as *cis*-1, 4-polyisoprene.

- It is insoluble in water, dilute acids and alkalies but soluble in organic solvents like benzene, petrol etc.
- It has low elasticity and tensile strength.
- It has weak intermolecular van der Waals' forces.
- Its natural *trans*-isomer is *gutta-percha* which is non-elastic.

Rubber

Synthetic rubber

It is obtained by polymerising certain organic compounds which may have properties similar to rubber and some additional desirable properties. Most of these polymers are derived from butadiene derivatives. These are also vulcanised. For example, neoprene, styrene butadiene rubber (SBR), thiokol, silicones, polyurethane rubber.

Styrene Butadiene Rubber (SBR) or Buna-S

It is a polymer of buta-1,3-diene and styrene. It has less tensile strength than natural rubber.

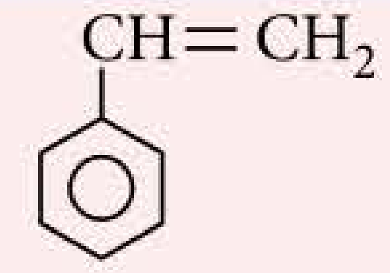
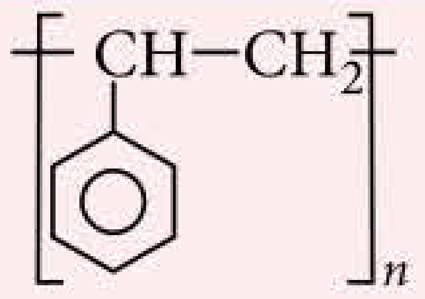
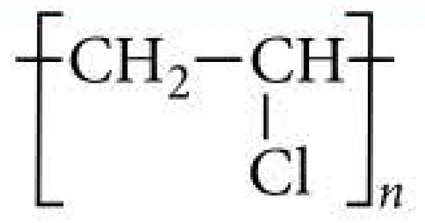
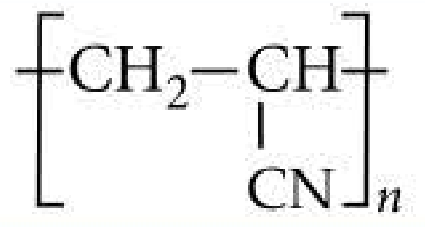
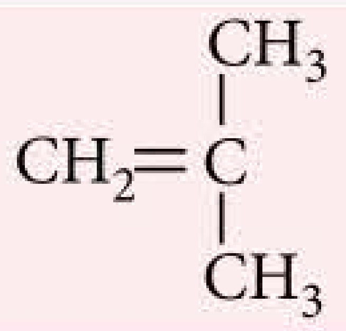
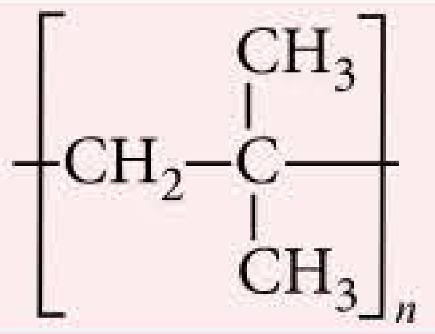
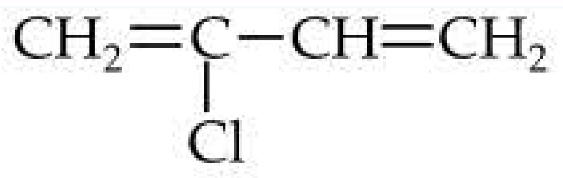
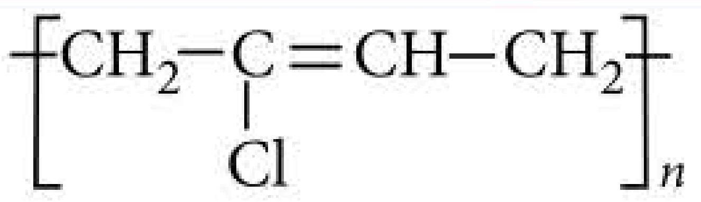
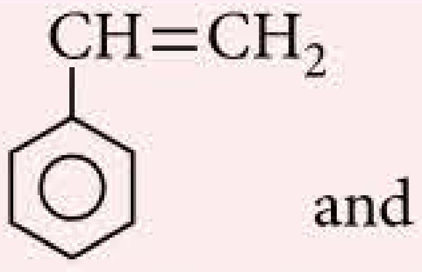
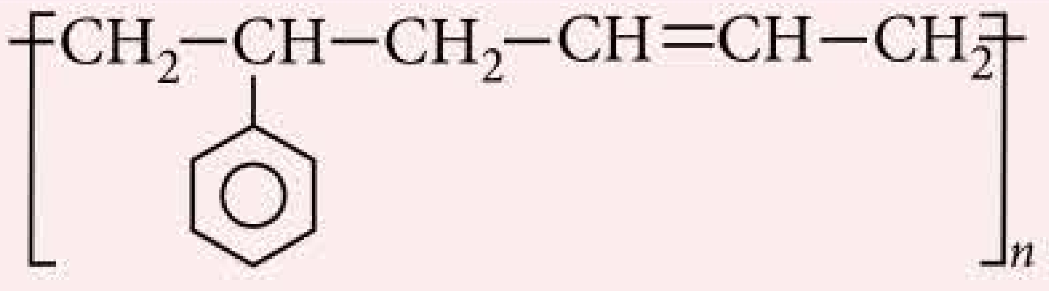
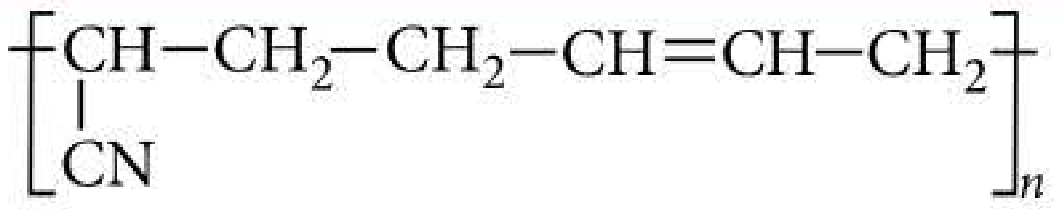
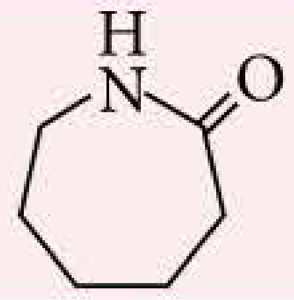
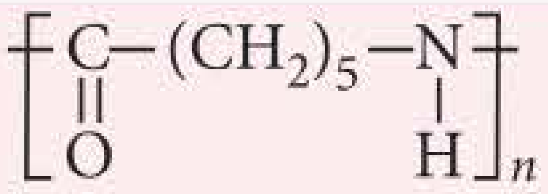
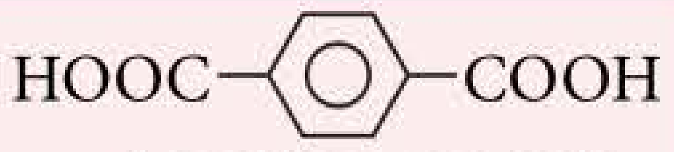
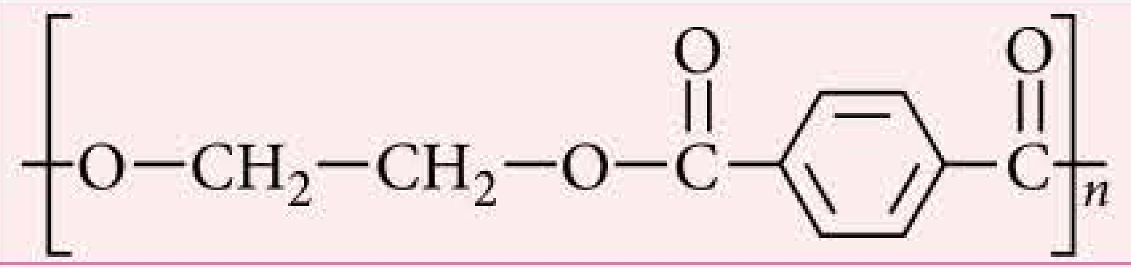
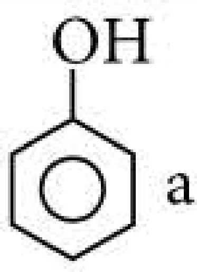
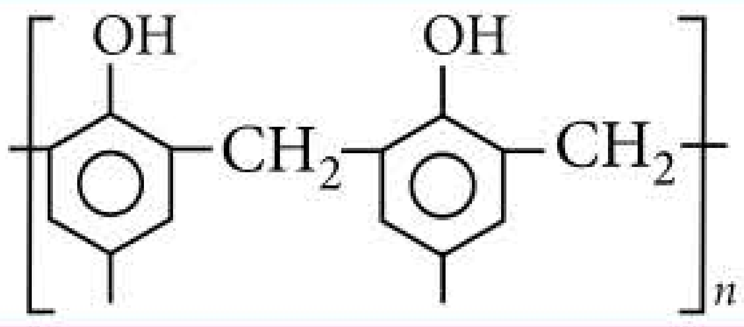
Nitrile rubber or Buna-N

It is a polymer of buta-1,3-diene and acrylonitrile. It is resistant to the action of petrol, lubricating organic solvents, etc.

Neoprene rubber

It is prepared by polymerisation of chloroprene. Neoprene is superior to natural rubber in its stability to aerial oxidation and its resistance to solvents.

SOME IMPORTANT POLYMERS

Polymer	Structure of monomer	Structure of polymer	Uses
Polythene	$CH_2{=}CH_2$	$\left[CH_2-CH_2 \right]_n$	As insulator, packing material, household and laboratory ware.
Polystyrene			As insulator, wrapping material, household articles and toys maker.
Polyvinyl chloride (PVC)	$CH_2{=}CHCl$	 $\left[CH_2-\underset{\mid \atop Cl}{CH} \right]_n$	In manufacture of raincoats, hand bags, leather clothes and vinyl flooring.
Polytetrafluoro - ethylene (PTFE) or Teflon	$CF_2{=}CF_2$	$\left[CF_2-CF_2 \right]_n$	As lubricant, insulator and making cooking wares.
Polyacrylonitrile (PAN) or Orlon	$CH_2{=}CH-CN$	 $\left[CH_2-\underset{\mid \atop CN}{CH} \right]_n$	In making synthetic fibres and wool.
Butyl rubber	 $CH_2{=}\overset{CH_3 \atop \mid}{\underset{\mid \atop CH_3}{C}}$	 $\left[CH_2-\overset{CH_3 \atop \mid}{\underset{\mid \atop CH_3}{C}} \right]_n$	Used in place of natural rubber in industry.
Neoprene	 $CH_2{=}\underset{\mid \atop Cl}{C}-CH{=}CH_2$	 $\left[CH_2-\underset{\mid \atop Cl}{C}{=}CH-CH_2 \right]_n$	As insulator, making conveyor belts and printing rollers.
Styrene Butadiene Rubber (SBR) or (Buna-S)	 and $CH_2{=}CH-CH{=}CH_2$		In making automobile tyres, floor tiles, cable insulation and footwear.
Nitrile rubber (Buna-N)	$CH_2{=}CHCN$ and $CH_2{=}CH-CH{=}CH_2$	 $\left[\underset{\mid \atop CN}{CH}-CH_2-CH_2-CH{=}CH-CH_2 \right]_n$	In making oil seals, hose-pipes and tank linings.
Nylon-6 (Perlon-L)		 $\left[\underset{\| \atop O}{C}-(CH_2)_5-\underset{\mid \atop H}{N} \right]_n$	In making carpets, ropes and tyre cords.
Nylon-6, 6	$HOOC-(CH_2)_4-COOH$ and $H_2N-(CH_2)_6-NH_2$	$\left[CO-(CH_2)_4-CONH-(CH_2)_6-NH \right]_n$	Synthetic fibres, fishing nets, ropes and tyre industries.
Terylene (Dacron)	 and $HOCH_2CH_2OH$		Synthetic fibres, safety belts, tyre cords and tents.
Bakelite (Phenol-formaldehyde resin)	 and HCHO		In making gears, protective coatings and electric fittings.

POLYETHYLENES

Polyethylene

Low density polyethylene (LDPE)

- Addition or chain growth homopolymer.
- By heating ethylene under high pressure (1000-2000 atm) at temperature of 350-570 K in presence of traces of oxygen or peroxide.
- Free radical addition polymerisation.
- Highly branched polymer.
- Low density (0.92 g/cm^3), low melting point (384 K).
- Transparent, moderate tensile strength.
- Chemically inert, tough but flexible.
- Used for packaging, insulation and manufacturing squeeze bottles, pipes, toys, etc.

High density polyethylene (HDPE)

- Linear addition or chain growth homopolymer.
- By heating ethylene at 333-343 K and 6-7 atm in presence of Ziegler-Natta catalyst.
- Coordination polymerisation
- Linear molecules, closely packed.
- High density (0.97 g/cm^3), high melting point (403 K).
- Translucent
- Chemically inert, quite harder, greater tensile strength.
- Used for manufacturing containers, housewares and pipes, etc.

MOLECULAR MASS OF POLYMER

- Number average molecular mass, $\bar{M}_n = \dfrac{\sum N_i M_i}{\sum N_i}$
- Weight average molecular mass, $\bar{M}_w = \dfrac{\sum N_i M_i^2}{\sum N_i M_i}$
- The ratio of weight average molecular mass to number average molecular mass is called *polydispersity index* (PDI).
- Natural fibres usually have PDI equal to 1 while synthetic fibres usually have PDI > 1

INFO SHOTS

Macromolecules: Light to design precision polymers

Chemists of Karlsruhe Institute of Technology (KIT) have succeeded in specifically controlling the setup of precision polymers by light-induced chemical reactions. The new method allows for the precise, planned arrangement of the chain links, *i.e.* monomers, along polymer chains of standard length. The precisely structured macromolecules develop defined properties and may possibly be suited for use as storage systems of information or synthetic biomolecules. Chemical reactions may be triggered by light at room temperature. This effect was used by KIT scientists to specifically linked molecules to defined polymer chains under light. In many conventional processes, polymer chains of variable length are produced. The building blocks are arranged randomly along the chain, they wanted to develop a light-induced method for polymer structuring, which reaches the precision of nature. The models in nature, *e.g.* proteins, have an exactly defined structure. The new, light-induced synthesis method allows for customised molecule design, with the building blocks being arranged at the positions desired similar to a string of coloured pearls. By controlling the structure of the molecule, the so-called sequence, properties of macromolecules can be controlled. Sequence-defined polymers might also be used as molecular data and information storage systems. Information might be encoded by the sequence of monomers, similar to the genetic information of the DNA.

The developers expect the fundamental method to become a tool for chemists, biologists, and material scientists and to be the key to future macromolecular chemistry.

CHEMISTRY IN EVERYDAY LIFE

CHEMICALS IN MEDICINES

- Contribution of chemistry over the last two centuries towards the eradication of diseases forms perhaps the most interesting and useful era in the history of mankind. The substances used in the prevention, treatment or alleviation of diseases are called *drugs* or *medicines*.
- The use of these chemicals (drugs) to injure or destroy infectious micro-organisms without causing any injury to the host is known as *chemotherapy*.

CLASSIFICATION OF DRUGS

Drugs

On the basis of pharmacological effect : It is useful for doctors because it provides them the whole range of drugs available for the treatment of a particular type of problem. Like analgesics (pain killing effect), antiseptics (kill or capture the growth of microorganisms).

On the basis of drug action : It is based on the action of a drug on a particular biochemical process. For example, all antihistamines inhibit the action of the compound, histamine which causes inflammation in the body.

On the basis of molecular targets : Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids. These are called *target molecules* or *drug targets*.

On the basis of chemical structure : Drugs classified in this way share common structural features and often have similar pharmacological activity. For example, sulphonamides.

INFO SHOTS

Artificial sweeteners can increase appetite

Researchers have revealed, for the first time, how artificial sweeteners can stimulate appetite in the brain. Billions of people worldwide consume artificial sweeteners and they are prescribed as a tool to treat obesity, despite little being known until now about their full impact on the brain and in regulating hunger. Researchers from the University of Sydney's Charles Perkins Centre and the Garvan Institute of Medical Research have identified a new system in the brain that senses and integrates the sweetness and energy content of food. After chronic exposure to a diet that contained the artificial sweetener sucralose, researcher's saw that animals began eating a lot more. Through systematic investigation of this effect, they found that inside the brain's reward centres, sweet sensation is integrated with energy content. When sweetness versus energy is out of balance for a period of time, the brain recalibrates and increases total calories consumed. When they investigated why animals were eating more even though they had enough calories, it is found that chronic consumption of this artificial sweetener actually increases the sweet intensity of real nutritive sugar, and this then increases the animal's overall motivation to eat more food. These findings further reinforce the idea that 'sugar-free' varieties of processed food and drink may not be as inert as we anticipated. Artificial sweeteners can actually change how animals perceive the sweetness of their food, with a discrepancy between sweetness and energy levels prompting an increase in caloric consumption.

DRUG-TARGET INTERACTION

- **Receptors as drug targets :** Proteins which transmit communication to the different parts of the body are called *receptors*. Receptor proteins are embedded in the cell membrane and receptor changes its shape to accommodate a chemical messenger which brings about transfer of message into the cell.
- **Drugs interact with receptors in two ways :**
  - Drugs bind to their receptor sites and inhibit its natural function **(antagonists)**. These are useful when blocking of message is required.
  - Some drugs mimic the natural messenger by switching on the receptor **(agonists)**. These are useful when there is lack of natural chemical messenger.

THERAPEUTIC ACTION OF DIFFERENT CLASSES OF DRUGS

Classes of Drugs

Antacids

Drugs which neutralise acidity or raise the pH of stomach to some appropriate level. Baking soda, metal hydroxides like $Al(OH)_3$, $Mg(OH)_2$, cimetidine, ranitidine, lansoprazole, omeprazole are few examples of antacids.

Antihistamines (anti-allergic drugs)

Drugs which interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

- Histamines are the chemicals released by mast cells during an allergic reaction.
- Diphenylhydramine (Benadryl), pheniramine maleate (avil), chlorpheniramine (zeet) are few examples of antihistamines.

Antifertility drugs

These drugs are used to reduce birth rates *e.g.*, mifepristone, silphium, etc.

Neurologically active drugs

Tranquilizers and analgesics are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.

Tranquilizers

It is a class of chemical compounds used for the treatment of stress, mild and severe mental diseases. These are commonly called *psychotherapeutic drugs*. These are the essential component of sleeping pills.

Narcotics

They reduce anxiety *e.g.*, heroin, pethidine etc.

Sedatives

They reduce the action of central nervous system. *e.g.*, valium, barbiturates.

Antidepressants (mood boosters)

They reduce depression, *e.g.*, iproniazid, phenelzine, etc.

Hypnotics (sleep producing drugs)

Barbiturates such as seconal, luminal, veronal.

Non-hypnotic drugs

Valium and serotonin.

Analgesics

Drugs which relieve pain without causing impairment of consciousness, mental confusion, paralysis.

Non-narcotics

Drugs which do not cause addiction. *e.g.*, aspirin, paracetamol are analgesics as well as antipyretics. Aspirin is also used in prevention of heart attack due to its anticlotting property.

Narcotics

Their chronic use leads to addiction. *e.g.*, morphine, codeine, etc.

Antimicrobials

Antimicrobials tend to prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (anti fungal agents), virus (antiviral agents) or other parasites (anti parasitic drugs) selectively.

Antibiotics

These are the chemicals synthesised from microbes and have either cidal (killing) effect or a static (inhibitory) effect on microbes.

Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be *broad spectrum antibiotics*. *e.g.*, ampicillin, amoxycillin, ofloxacin etc.

Antibiotics which are effective mainly against Gram-positive or Gram-negative bacteria are *narrow spectrum antibiotics* *e.g.*, penicillin.

Antiseptics

These are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. *e.g.*, furacine, soframicine, dettol (a mixture of chloroxylenol and terpineol), 0.2% solution of phenol.

Disinfectants

These substances kill or stop the growth of microorganisms but are harmful to living cells hence they are used on non-living objects like clothes, floors, utensils, etc. For example phenol, bleaching powder, H_2O_2, etc.

Chemicals in Food

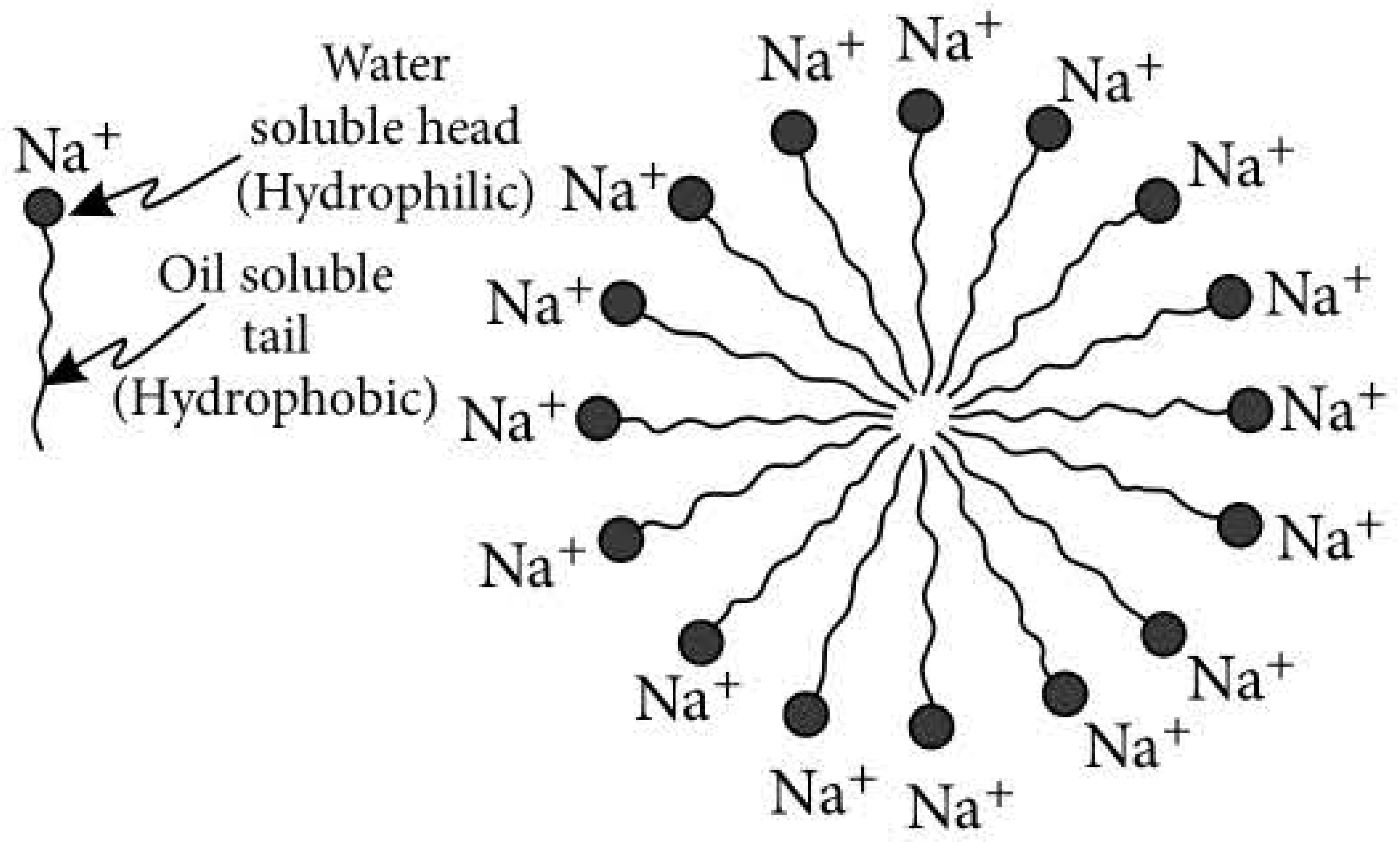
- Chemicals which are added to food for their preservation or enhancing their appeal, flavour, etc. are known as *food additives*.
- **Food preservatives :** These are the chemical substances which are added to the food materials to prevent their spoilage and to retain their nutritive value for long periods.
  - These preservatives prevent the rancidity of food and inhibit the growth or kill the microorganisms.
  - The most common preservative used is sodium benzoate (C_6H_5COONa).
- Certain food preservatives such as BHA and BHT used for edible oils also act as antioxidants.
- **Artificial sweetening agents :** These are chemical compounds which give sweetening effect to the food and enhance its odour and flavour.

Artificial sweetener	Sweetness value in comparison to cane sugar
Aspartame	100
Saccharin	550
Sucralose	600
Alitame	2000

- **Antioxidants :** These are the chemical substances which prevent oxidation and subsequent spoilage of the food by retarding the action of oxygen on food. They act as sacrificial materials as they are more reactive towards oxygen than the materials they are protecting. They also reduce the rate of involvement of free radicals in the ageing process.

Cleansing Agents

- **Soaps :** These are sodium or potassium salts of higher fatty acids (with 12-18 carbon atoms). *e.g.*, salts of $C_{15}H_{31}COOH$ (palmitic acid), $C_{17}H_{35}COOH$ (stearic acid), $C_{17}H_{33}COOH$ (oleic acid), $C_{17}H_{31}COOH$ (linoleic acid), etc.
- **Soapless soaps or synthetic detergents :** These are sodium salts of long chain alkyl hydrogen sulphates or the sodium salts of long chain benzene sulphonic acids.
  - *Cationic detergents* : These are quaternary ammonium salts of amines with acetates or halides as anions. *e.g.*, trimethylstearylammonium chloride, $CH_3(CH_2)_{17}\overset{+}{N}(CH_3)_3\overset{-}{Cl}$
  - *Anionic detergents* : These contain anionic hydrophilic groups *e.g.*, sodium lauryl sulphate, $C_{12}H_{25}OSO_3^- Na^+$
  - *Non-ionic detergents* : These are esters of high molecular mass and do not contain ions. *e.g.*, polyethyleneglycol stearate, $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$
- **Advantages of synthetic detergents over soaps :**
  - They can be used in hard water, in acidic medium while soaps get precipitated.
  - They are more soluble in water and thus, form lather more easily.
  - They are stronger cleansing agents than soaps as they decrease the surface tension to greater extent.
- **Cleansing action of soaps and detergents :**
  - The hydrophilic carboxylate group interact with water molecules while the hydrophobic long non-polar hydrocarbon chain does not interact.
  - The hydrocarbon chains cluster together forming a structure called *micelles*.
  - In the micelles, the carboxylate groups form a negatively-charged spherical surface, with the hydrocarbon chains inside the sphere.
  - Being negatively charged, soap micelles repel each other and remain dispersed in water.



Micelles