14. POLYMERS

Synopsis:

1. Polymers are the compounds of very high molecular weight formed by combining large number of small molecules.
2. In Greek poly = many, mero's = parts
3. The simple molecule which combine to give polymer are called monomers
4. The process of conversion of monomers (simple molecule) into polymers is called polymerisation.

E.g. Polymerisation of ethylene

$$\underset{\text{ethylene (monomer)}}{nCH_2 = CH_2} \xrightarrow{\text{polymerisation}} \underset{\text{polyethylene (polymer)}}{-(-CH_2 - CH_2-)_n}$$

CLASSIFICATION OF POLYMERS:

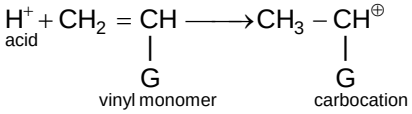
5. Polymers are classified in a number of ways as
    1) Classification based on source of availability.
    2) Classification based upon structure.
    3) Classification based upon molecular forces.
    4) Classification based upon mode of synthesis.
6. 1) Based on the source the polymers again classified as
7. a) Natural polymers b) synthetic polymers
8. The polymers obtained from nature (plants and animals) are called Natural polymers. Ex. Starch, cellulose, Natural rubbers, proteins, Nucleic acid (DNA, RNA), cotton, silk, wool)
9. The polymers which are prepared in the laboratories are called synthetic polymers
10. E.g. Poleythylene, polyvinylchloride (pvc), Nylon, Teflon, Backelite, Terylene etc.
11. 2) Based on the structure polymers are classified as (a) linear polymer (b) Branched chain polymer (c) cross–linked polymer
12. In linear polymer the monomeric units are linked together to form linear chain.
    E.g. Polyethylene, Nylon, polyester etc.
13. In branched chain polymers the monomeric units are joined to form long chains with side chains (or) Branches of different length. E.g. Glycogen, starch, L.D.P.E. etc.
14. In cross linked polymers the monomer units are cross linked together to form a three dimensional Network. E.g. Bakelite, melamine–formaldehyde Resin polystyrene–Butadiene.
15. 3) Based on the molecular forces polymers are classified as a) Thermoplastic b) Thermosetting c) Flastomers d) Fibres
16. Thermoplastics are the polymers which soften on heating and harden on cooling reversibly.
17. E.g. Polyethylene, polysterene, pvc, Teflon, Nylon, sealing wax.
18. Thermosetting plastics are the polymers which undergo permanent change on heating(irreversible)
19. E.g. Bakelite, Polyester, Polysiloxanes.
20. Elastomers are the polymers which posses elastic character.
21. E.g. Natural rubber

22. Fibres are polymers in which the chains are held by intermolecular forces like H–bond, Dipole–dipole interaction.
23. E.g. Nylon, poly Acrylonitrile
24. 4) Based on the mode of synthesis polymer are classified as
25. Addition polymers b) condensation polymers
26. A polymer formed by direct addition of repeated monomer without the elimination of by product molecules are called Addition polymer.
27. E.g. Polyethylene, polypropylene, pvc, Teflon, orlun, Neoprene, pvp (polyvinyl pyrolidone)
28. A polymer formed by the condensation of two (or) more monomers with the elimination of simple molecule like H_2O, NH_3, HCl, alcohol etc. are called condensation polymer.
29. E.g. Terylene, Bakelite, Alkyl Resin, Nylon 6, 6.
30. Leather, cellulose, Rayon etc. are the example of organic polymer and Glass (Gilicone rubber) is the example of inorganic polymers.
31. Carothers, mark and flory classified the polymers into two categories based on the mechanism of polymerisation.
    a) Addition polymerisation (or) chain growth polymerisation.
    b) Condensation polymerisation (or) step growth polymerisation.
32. Addition polymers are formed by the combination of monomers without the elimination of some byproduct molecules.
33. Alkene, Alkadienes and their derivatives are used as monomer in the formation of addition polymers.
34. Addition polymerisation can take place through the formation of either free radical (or) ions such as carbanions (or) carbocations.
35. Addition polymerisation reaction is very rapid and takes place in 3 steps (a) chain initiation (b) chain propagation (c) chain termination.
36. Addition polymerisation divided into 2 types.
    a) Ionic polymerisation
    b) free radical polymerisation.

37. Ionic polymerisation:

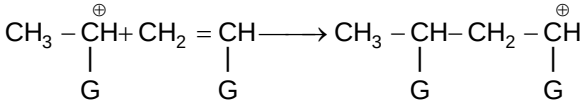
38. The Addition polymerisation that takes place due to Ionic intermediate is called Ionic Addition polymerisation.
39. Based on the nature of ions used for the initiation process Ionic polymerisation classified into 2 types
    a) Cationic polymerisation
    b) Anionic polymerisation
40. Cationic polymerisation is initiated by an acid (Lewis acids such as BF_3, $AlCl_3$, $FeCl_3$, $SnCl_4$, H_2SO_4, HF in presence of small amount of H_2O.
41. E.g. Isobutylene – Butyl rubber, polystyrene. Polyvinyl ether.
42. $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$
43. $HF \rightleftharpoons H^+ + F^-$
44. $BF_3 + H_2O \rightleftharpoons H^+ + BF_3(OH^-)$

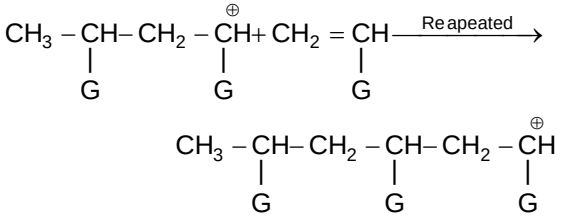
a) **Chain initiation:** Proton (H^+) add to C – C double bond of alkene to form stable carbocation.

45. 

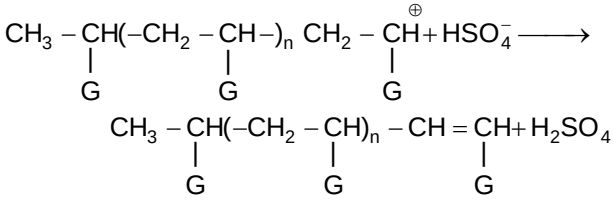
46. (G = e^- donating group, + I effect)

47. **b) Chain propagation:** Carbocation add to the C – C double bond of another monomer molecule to from new carbocation.

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50. **c) Termination:** Reaction is terminated by combination of carbocation with negative ion (or) by loss of proton

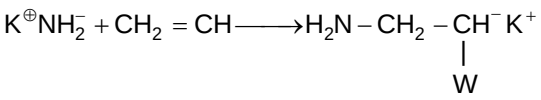
51. 

52. Anionic polymerisation is initiated by anion (may be base (or) nucleophiles such as n-butyl lithium (or) Potassium amide)

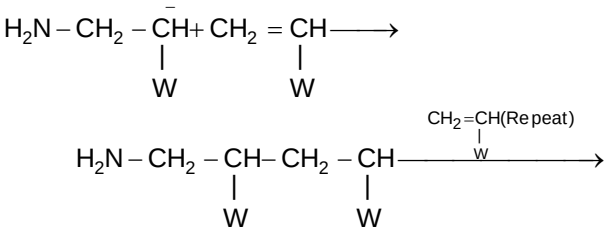
53. Monomer, containing e^- withdrawing groups like phenyl ($–C_6H_5$). Nitrile (–CN) etc. undergo anionic addition polymerisation.

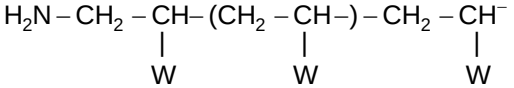
54. E.g. Polystyrene, Poly acylonitrile

55. Chain initiation:

56. 

57. Chain propagation:

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59. 

60. Anionic polymerisation has no chain termination reaction.
61. Polymer formed from one type of monomer is homopolymer.
62. E.g. Polystyrene, Polyethene, PVC, Neoprene
63. Polymer formed from two or more different monomers is copolymer (or) mixed polymer.
64. E.g. **Buna s-rubber** (Polymer of styrene and butadiene)
65. **Nylon 6,6** (Polymer of hexametheledene diamine and adipic acid)
66. Copolymers are classified into 4 types
67. i) Random co-polymer: In this monomer units are arranged randomly.
68. ii) Alternating co-polymer: In this monomer units are arranged alternatively.
69. iii) Block co-polymer: In this monomer units are arranged as lengthy block.
70. iv) Graft co-polymer: In this polymer main chain is made of one type of monomer and branches are made of another type of monomer.
71. **Natural rubber:** Rubber is a naturally occurring polymer. It is obtained as latex from rubber tree, shaubs and vines.
72. Latex is a emulsion of polyhydrocarbon droplets in a aq. solution. Latex contain 35% rubber.
73. Rubber present in latex is coagulated by the addition of CH_3COOH (or) HCOOH
74. Rubber trees are found in India, Malaysia, Indonesia, Ceylon, South America.
75. **Structure rubber:** E.F of rubber C_5H_8
76. On strong heating it gives Co_2, H_2O, SO it contain C, H.
77. When heated in absence of air (or) O_2 gives isoprene ($CH_2 = \underset{\displaystyle CH_3}{\overset{\displaystyle CH_2}{\overset{\|}{\underset{|}{C}}}} - CH$). So natural rubber is the polymer of isoprene.
78. It is a linear polymer, isoprene unit are joined head to – tail by 1, 4 links.

$$\overset{1}{CH_2} = \underset{\displaystyle CH_3}{\overset{2}{\underset{|}{C}}} - \overset{3}{CH} = \overset{4}{CH_2} + \overset{4}{CH_2} - \overset{3}{CH} - \underset{\displaystyle CH_3}{\overset{2}{\underset{|}{C}}} = \overset{1}{CH_2} \longrightarrow$$

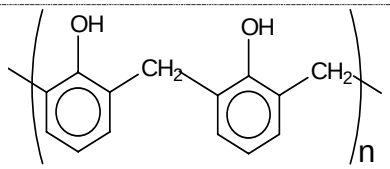
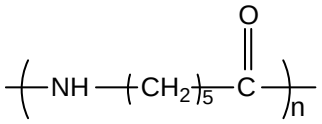
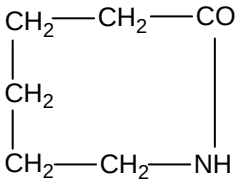
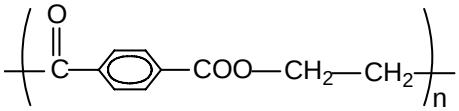
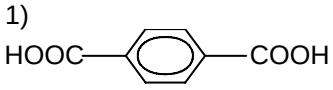
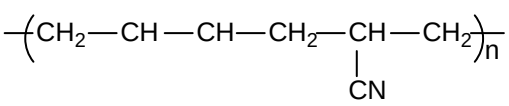
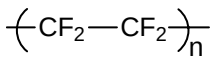
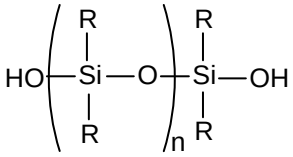
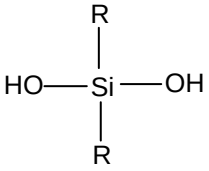
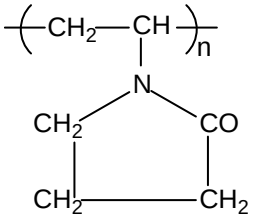
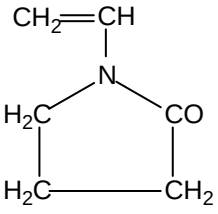
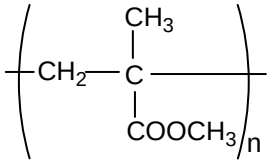
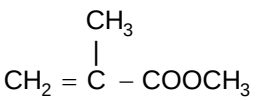
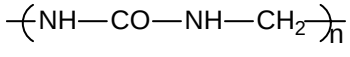
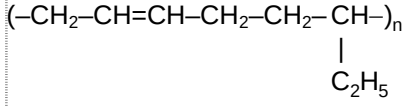
79. $$-(-CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2 - CH_2 - \underset{\displaystyle C - CH_3}{\overset{\|}{CH}} \underset{\displaystyle CH_2 \rightarrow_n}{|}$$
80. X-ray studies indicate that in natural rubber isoprene units are arranged in cis from
81. It contain 11,000 to 20,000 isoprene units with molecular wt. 13,0000 to 34,0000
82. **Vulcanisation of rubber:** Natural rubber is a thermoplastic it is soft, sticky and is not hard and tough.
83. It has low tensile strength and low elasticity due to absence of cross links between the polymer.
84. The process of heating natural rubber with sulphur to improve its properties (373-415K) is vulcanisation.
85. ZnO, Zinc stearate are used to accelerate the rate of vulcanisaion.
86. In natural rubber vulcanisation takes place at $-CH_2$ present next to double bond and s-form cross link at these centres.
87. Vulcanised rubber is hard and non sticky. It has high tensile strength, high elasticity. It is insoluble in all the common solvents. High resistance to chemical oxidation and organic solvents.

88. **Synthetic Rubber:** Synthetic polymers are either homopolymer of 1,3 butadiene (or)_ copolymer in which one of the monomer is 1,3 butadiene (or) it derivative. It undergo vulcanisation like natural rubber.
89. Some common examples of synthetic rubber. Neoprene, styrene-butadiene rubber (SBR), silicones, polyurethane rubber etc.

Properties	Natural	Polymer Synthetic polymer
Preparation	By nature (e.g. Jute, silk, wool	In the lab (e.g. Nylon, terene, decron
Length	Non uniform	uniform
Affinity for 's' vat dyes	high	low
Fixing quality	low	high

Some commercially important polymers :

S.NO.	Name of polymer	Structure	Monomer	Uses
1.	Polythene	$-(CH_2-CH_2)_n-$	$CH_2=CH_2$ (ethylene)	LDPE: Pipes in Agriculture irrigation as insulation domestic water lines HDPE: Anticorrosive, packing materials, house hold articles
2.	Polyvinyl chloride(PVC)	$-(CH_2-CH(Cl))_n-$	$CH_2=CH(Cl)$ Vinyl chloride	Manufacture raincoats, hand bags, cheap plastic for cable insulation
3.	Polystyrene	$-(CH(C_6H_5)-CH)_n-$	$CH=CH_2$ (Styrene)	As insulator, manufacture of radio TV cabinets, toys, wrapping mat
4.	Neoprene	$-(CH_2-C(Cl)=CH-CH_2)_n-$	$CH_2=C(Cl)-CH=CH_2$	As insulator making conveyor belts and printing rollers

5.	Bakelite		C_6H_5OH (phenol) HCHO (formaldehyde)	For making gears protective coating and electrical fitting
6.	Nylon-6 (or) Perlon L			For making fibres, plastics, tyre cords and ropes
7.	Polyethylene Tetra phthalate (PET) (or) Terylene (or) Dacron		1)  2) $HO-CH_2-CH_2-OH$	For making fibres safety belts, tyre cords, tents etc.
8.	Nitrite rubber (Buna–N)		1) $CH_2 = CH - CH = CH_2$ 2) 	Making oil seals, manufacture of hoses and tank lining
9.	Poly tetrafluon Ethylene (PTFE)(or) Teflon		$CF_2 = CF_2$	As lubricant insulator and making cooking wares
10.	Silicone polymers			Surface coating, as Elastomers, in aeroplanes and missiles
11.	Polyvinyl pyrrolidone		 N - vinyl pyrrolidone	Life saving sub's as blood plasma, as an additive to many basic dye composition to deepen the colour of the dye.
12.	Artificial silk or Rayon	Four different types of rayon (a) Pyroxyline (b) viscose rayon (c) Acetate rayon (d) Cupranmonium rayon		Used in packages and wrapping indestive photo films
13.	Polymethyl methacrylate (PMMA) (or) plexi glass			As substitute of glass and for making decorative articles
14.	Urea formaldehyde resin		1) HCHO (formaldehyde) 2) $H_2N - CO - NH_2$ (Urea)	For making unbreakable cups and laminated sheets
15.	Styrene butadiene rubber Buna–s		1) $CH_2 = CH - CH = CH_2$	In making Automobile tyres and footwear

	(or) SBR (or) GRA		2) $CH_2 = CH$ | C_6H_5	

MOLECULAR WEIGHTS OF POLYMERS :

- Molecular weights of polymers expressed in several methods.
  (1) Number – Average molecular weight $\bar{M}_n$
  (2) Weight – Average molecular weight $\bar{M}_w$
  (3) Z – Average molecular weight $\bar{M}_z$
  (4) Viscosity – Average molecular weight $\bar{M}_v$
- Number – Average molecular weight $(\bar{M}_n)$
- If N_1, N_2, N_3 are the number of molecules with molecular masses M_1 M_2 M_3 --- respectively. Then

  Number – Average molecular mass

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3}$$

$$\bar{M}_n = \frac{\sum N_iM_i}{\sum N_i}$$

- It is determined by

  (1) Analysis of end group

  (2) Colligative property like osmotic pressure

WEIGHT – AVERAGE MOLECULAR WEIGHT :

If m_1, m_2, m_3 are the masses of species with molecular masses M_1, M_2, M_3 respectively then the weight average molecular weight

$$\bar{m}_w = \frac{m_1M_1 + m_2M_2 + m_3M_3}{m_1 + m_2 + m_3}$$

$$\bar{m}_w = \frac{\sum m_iM_i}{\sum m_i}$$

$$\bar{m}_w = \frac{\sum N_iM_i^2}{\sum N_iM_i}$$

- $\bar{M}_w$ can be determined by light scattering and ultracentrifuge method.
- **Polydispersity Index (PDI)**

  The ratio of weight average molecular mass $(\bar{M}_w)$ and Number average mass $(\bar{M}_n)$ is called poly dispersity index (PDI)

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

  Polymers for which $\bar{M}_w = \bar{M}_n$ are called mono disperse

  Most of natural polymers are mono dispersed (PDI is unity). But synthetic polymers or poly dispersed (PDI is greater than unity)

$$\bar{M}_w > \bar{M}_n$$