

Fig.10.2

- ◀ The chemical reaction that assembles the chain from its monomers is known as polymerization (or synthesis).

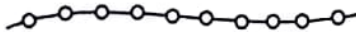
10.3 MOLECULAR STRUCTURE OF POLYMER

Physical characteristics of polymer depend not only on its molecular weight and shape but also on difference in the structure of the molecular chains.

Polymer molecules may be identified in terms of their size, shape, and structure. Molecular size means molecular weight (or degree of polymerization). Molecular shape relates to the degree of chain twisting, coiling, and bending. Molecular structure depends on the manner in which structural units are joined together. Linear, branched, crosslinked network.

(a) Linear Polymers

- ◀ In which mer units are joined together end to end in single chains. These long chains are flexible.
- ◀ For linear polymer there are extensive van der Waals and hydrogen bonding between the chains.
- ◀ Common example are polyethylene, PVC, polyethylenes, PMMA, Nylon.



(b) Branched Polymers

- ◀ Here side branches are connected to the main branch.
- ◀ These branches occur as a result of side reaction that occur during synthesis of the polymer. The Chain packing efficiency (% space occupied in unit cell) is reduced which results in lowering of polymer density.

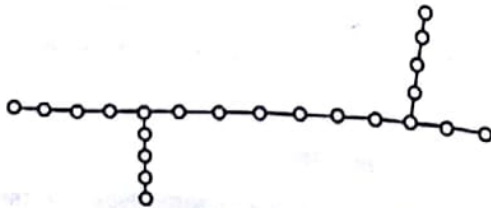


Fig.10.3

(c) Cross Linked Polymers

- ◀ Here adjacent chains are joined to one another at various positions by covalent bonds.

- ◀ The cross linking process is either achieved during synthesis or by a non reversible chemical reaction that is carried out at elevated temperature after this is accomplished by additive atoms or molecules that are covalently bonded to the chains. e.g. is vulcanization of rubber.

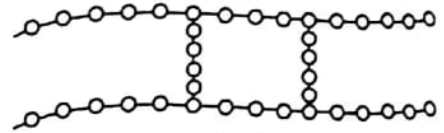


Fig.10.4

(d) Network Polymers

- ◀ A Mer unit having three or more active covalent bonds forms a 3-D network called network polymers.
- ◀ A polymer that is highly cross linked may be called network polymers. These materials have distinctive mechanical and thermal properties. Examples are epoxy and phenol formaldehyde.

10.4 STEREOISOMERISM

Stereoisomerism means the situation in which atoms are linked together in the same order (head-to-tail) but differ in their spatial arrangement. e.g. all the R groups lie on the same side of the chain as follows :

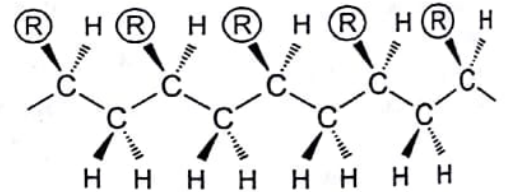


Fig.10.5

This is called an isotactic configuration. It has the zigzag pattern of the carbon chain atoms.

In a syndiotactic configuration, the R groups alternate sides of the chain:

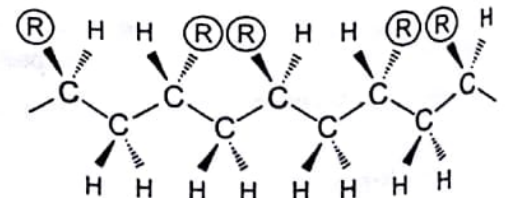


Fig.10.6

Geometrical Isomerism

Geometrical isomers, are possible within repeat units having a double bond between chain carbon atoms. Bonded to each of the carbon atoms participating in the double bond is a side group, which may be situated on one side of the chain or its opposite.

Table 1.6

S.No.	Dipole Bond	Dispersion Bond
1	Bond form on account of electrical dipole produced due to non coincidence of centers of positive and negative charge	Bond form due to attraction of fluctuating charges of adjoining atoms.
2	Secondary forces of attraction arise during bonding	Momentary polarization occurs in the molecules
3	It is a type of molecular bonding	Fluctuating and oscillating dipoles developed during bonding
4	Stronger than dispersion bond	Weak
5	Ex. Water and HF	Ex. Inert gas crystals
6	Unequal sharing of electrons	Non-symmetrical distribution of electrons around nucleus.

- Dispersion bond : Generally symmetrical molecule, electrons are distributed uniformly around the nucleus and they are constantly in motion. But in course of time the distribution of electron in molecule is not symmetrical around the nucleus. This imbalance create polarization and it is in fluctuating in nature termed as dispersion effect and bond formed is termed as dispersion bond. e.g., Argon, helium, etc.

POINTS TO BE REMEMBERED

- The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell.
- The packing of molecules in all cases is as tight as the molecular shape allows, the only exception to this being hydrogen bonded crystals which tend to have more open space in them.
- Non-polar molecules that are large and planer tend to pack face to face in layered stacks.
- Greater the difference in electronegativity, the more polar the bond will be.
- Other things being equal - polarity, hydrogen bonding - boiling point rises with increasing molecular size.
- In molecules as in isolated atoms, electrons occupy orbitals called molecular orbitals.
- Half of the molecular orbitals posses lower energies than the combining atomic orbitals known as bonding molecular orbitals and other half have higher energies than the combining

atomic orbitals known as antibonding molecular orbitals.

- The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms. Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.
- In alumina (Al_2O_3), the cation positions in neighbouring planes of octahedral voids are staggered such that the mutual repulsion of the trivalent cations is minimized. Due to multivalent ions, the bond strength in Al_2O_3 is high, producing a hard crystal with a high melting point.
- In Al_2O_3 , replacing a small fraction of Al^{3+} ions by other ions such as Cr^{3+} and Fe^{3+} results in gemstones, ruby and sapphire.
- Metal ions are bound together by the interaction of valence electron.
- CH_4 has zero dipole moment because of its symmetrical structure. While NH_3 is polar and have dipole moment due to its asymmetrical structure.
- When a solid consist of molecule held together by secondary bonds, the melting and boiling points of solid govern by strength of secondary bond between the molecule and not by primary bond within the molecule. So, molten state (sublimation) and the gaseous state are to be visualized as consisting of unit of molecule not individual atom of molecule.
e.g., SiO_2 has melting point $1723^\circ C$ while CH_4 has $-182^\circ C$. In SiO_2 , Si-O bond has bond strength $375 KJ/mol$ and CH_4 has bond strength $413 KJ/mol$. Since, SiO_2 molecule structure does not have secondary bond so melting point is high. But in CH_4 molecule have secondary weak Van-Der Waals bond. So, secondary bond will brake during melting. Same is applicable for CO_2 molecule.
- When the atoms in a solid are sepertated by their equilibrium distance the potential energy of the solid is lowest.
- Transition elements have partially filled innercell.
- Halogens have the largest Electronegativity and alkalis have the smallest.
- In periodic table chlorine has highest Electron affinity while fluorine has highest Electronegativity