

POLYMERS / MACROMOLECULES

PART- III

Brotati Chakraborty
Department of Chemistry
Bejoy Narayan Mahavidyalaya, Itachuna, Hooghly

Sem V Honours

Summary of Polymer (Parts I & II)

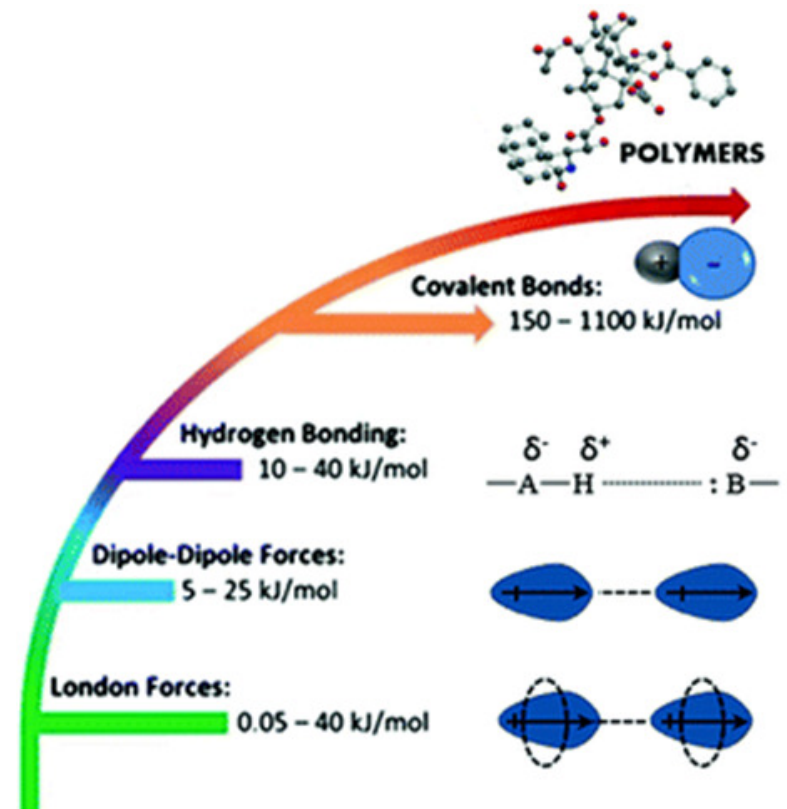
- General discussion and fundamentals of polymer
- Classification of polymers
- Carothers' equation
- Kinetics of condensation polymerization reaction
- Kinetics of copolymerization reaction

Intermolecular forces in polymers

Chain segments not connected by covalent bonds are held together by secondary forces.

Types of forces involved in the secondary forces:

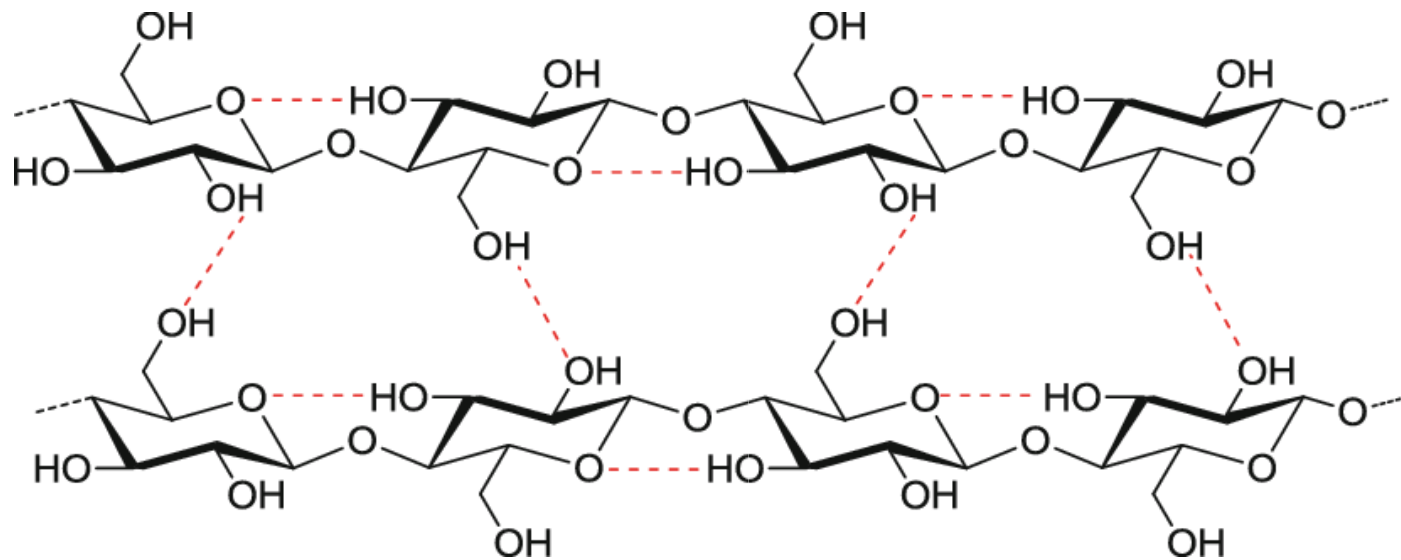
1. H-bonding (10 – 40 kJ/mol)
2. dipole-dipole forces (5 – 25 kJ/mol)
3. London dispersive force (0.05 – 40 kJ/mol)



Hydrogen bonds: Present in polar molecules containing fluorine, chlorine, oxygen and nitrogen atoms. Cumulative effect of hydrogen bond network throughout the polymer structure is so pronounced that the polymer becomes inherently crystalline and resistant to heat and solvents.

Eg: cellulose, polyamides etc.

The exact nature of the hydrogen bond depends on the chemical nature and environment of the concerned polar groups.



Dipole-dipole interaction: This depends on the natural alignment of the interacting dipoles. As molecular alignments are opposed by thermal agitations, the dipole forces are very much dependent on temperature.

Ion-induced dipole/ dipole-induced dipole: Another kind of intermolecular interaction is that induced by polar molecules or segments through the dipoles on surrounding molecules that do not have permanent dipoles. The cohesive energy corresponding to induction force is small and is independent of temperature.

Dispersion forces: They are not dependent on polarity or permanent dipole but are consequences of different instantaneous configurations of electrons and nuclei of all kind of molecules, resulting in time-varying dipole moments that average out to zero. The dispersion forces exist in all molecular systems, polar or non-polar and constitute a major part of the cohesive forces except in systems having strong dipoles. In non-polar materials the molar cohesion is due only to the dispersion forces which are independent of temperature.

CONDUCTING POLYMERS

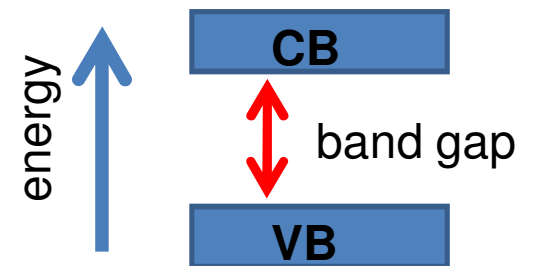
- Polymers in general are poor conductors of electricity due to non-availability of large number of free electrons.
- A polymer which can conduct electricity is termed as conducting polymer.
- A polymer which has electrical, electronic, magnetic and optical properties as that of metal but the mechanical properties, processing etc. is same as that of a conventional polymer is termed as **Intrinsically Conducting Polymer** (ICP) more commonly known as 'synthetic metal'. For example polysulphur nitride $(SN)_x$.
- Now the question arises, how does the electric current pass through the conducting polymer. The conduction in polymer is due to the presence of conjugated π -electron system. However, this alone does not contribute to high conductivity. The enhancement can be brought about through doping.

Intrinsically Conducting Polymer

Polymers with conjugated π -electrons are conducting. The conduction of such polymers is due to overlapping of the orbitals of conjugating π -electrons over the entire backbone of the polymer, resulting the formation of valence band (VB) and conduction band (CB) throughout the polymer matrix.

The energy spacing between VB and CB i.e. the band gap is not neither too high nor too narrow and the electrical conduction occurs only after thermal or photolytic activation of electrons to acquire sufficient energy to jump from VB to CB.

The common examples are polyacetylene and polyaniline.

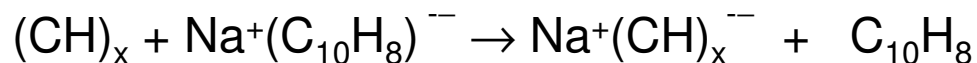


Doped Conducting Polymer

- (i) **p-doping through oxidation:** Doping through oxidation removes some electrons from π -bond, creating holes (delocalised radical cation) called polaron. The polarons are mobile and can move along the polymer chain by rearrangement of double and single bonds and the polymer becomes conducting. The oxidation process is generally carried out by Lewis acids such as FeCl_3 .



- (ii) **n-doping through reduction:** In this type of doping, electrons are introduced into a polymer chain having conjugated double bonds. This process is brought about by treating the corresponding compound with a Lewis Base, like sodium naphthalide.



Extrinsically Conducting Polymer

These polymers are actually insulators or have negligible conductivity and conductivity is achieved through incorporating ingredients externally. They are of two types:

- (i) **Conductive element filled polymers:** They are filled with conducting elements such as carbon black, metallic fibres, metal oxides etc. These polymers have reasonably good conductivity, low in cost, light in weight and mechanically durable and strong. Carbon black which is used as a filler is of special conducting grade having large surface area with high porosity. Carbon black having low particle size and forming fibrous aggregates can promote formation of conducting networks. The electrical conductivity of a conductive composite depends on intrinsic properties of the filler material as well as matrix-filler interactions and processing conditions. The minimum concentration of conductive filler required to start the conduction process is called percolation threshold. If excess amount of filler is incorporated in the polymer then the properties of the polymer are greatly affected. Metals may be used in the form of powders, flakes, filaments wires, wire mesh as filler in a polymer matrix. The polymer matrix should not oxidise the surface of metal fillers. Metals of importance in this respect are copper, aluminum, iron, nickel, silver etc. Sometimes, matrix polymer may generate heat due to passage of electricity. Accumulation of heat and consequent rise in temperature and thermal expansion cause the conducting filler particles move apart, leading to decrease in conductivity with time of passage of electricity.
- (ii) **Blended conducting polymer:** They are obtained by blending conventional polymers with conducting polymers. They have better physical, chemical and mechanical properties.

Coordination Conducting Polymer

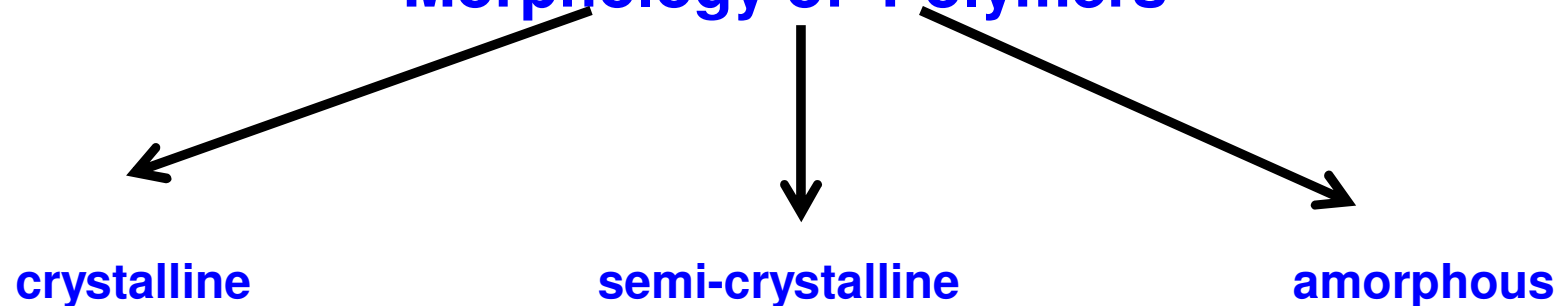
These are charge transfer complex containing polymers obtained through combination of metal atoms with polydentate ligands.

Photoconducting Polymer

Inducement or enhancement of electrical conductivity on exposure to light or irradiation is called photoconductivity. Photoconductive polymers are commonly insulators in dark and behave as semiconductors when exposed to light. Genuine photoconductors do not contain free charge carriers. The charge carriers are generated in them by the action of light. The electrical charge carriers may also be photogenerated extrinsically in an adjacent photoconductor and then transferred to the polymer that would act as a charge transporting medium.

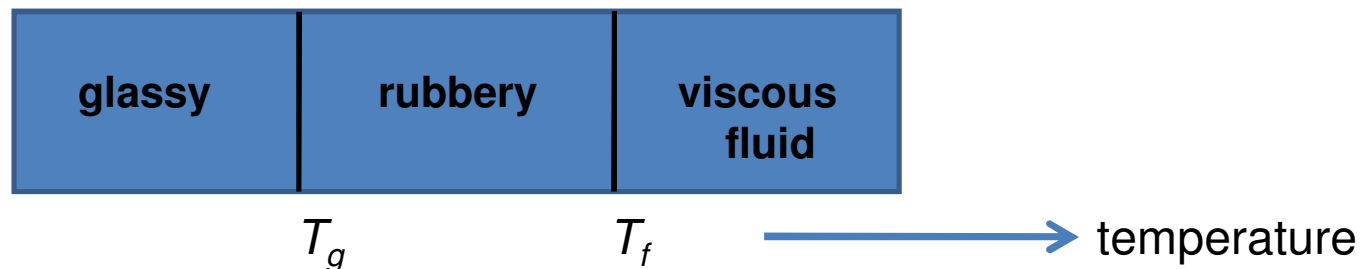
Poly(N-vinyl carbazole) (PNVC) exhibits high level of photoconductivity when sensitized with suitable electron acceptors.

Morphology of Polymers



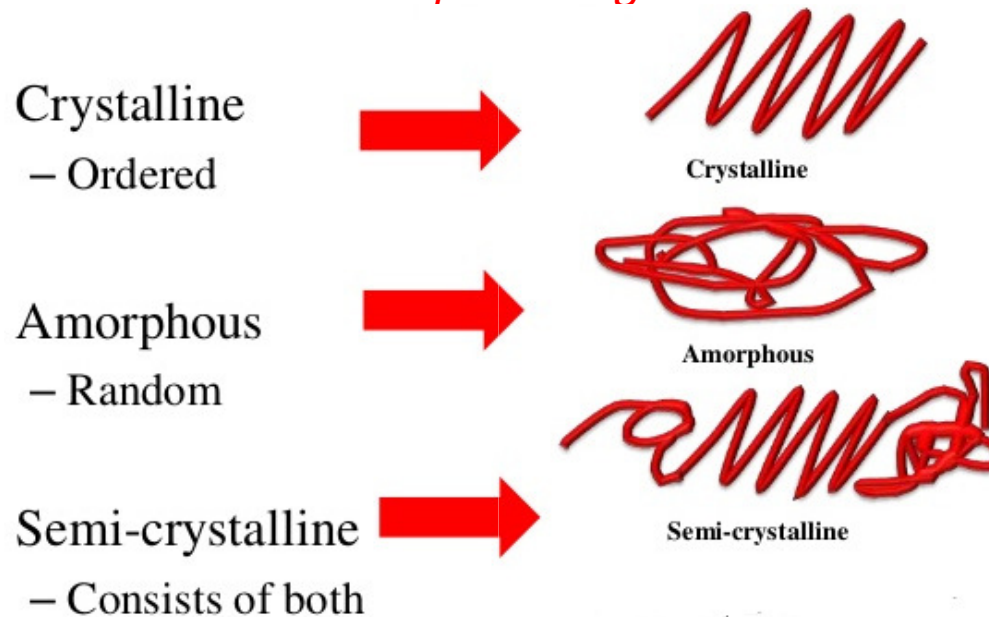
- A polymer capable of exhibiting long-range order is called a crystalline polymer.
- A polymer which does not possess long range order cannot exist in crystalline state. They exist in amorphous state.
- It is difficult to attain 100% crystallinity in bulk polymers.
- It is difficult to obtain solid amorphous polymer completely devoid of crystallinity.
- Polymers having *crystallites* in excess of 50% are generally recognized to be crystalline.

- Crystalline and amorphous regions can co-exist in a polymer.
- The orderly regions in a polymer are known as *crystallites*.
- A partially crystalline polymer consists of several crystallites co existing with amorphous regions of disorderly arranged chain segments. There is no sharp boundary between crystallites and amorphous regions.
- Degree of crystallinity = $(d-d_a)/(d_c-d_a)$, where d , d_a and d_c are densities of the sample, fully amorphous and fully crystalline components respectively.
- Amorphous polymers can exist in exist in glassy, rubbery or liquid states.



T_g is Glass Transition Temperature and is T_f is flow temperature.
 There is nothing called melting point (T_m) associated with a amorphous polymer.

- For crystalline polymers, at sufficiently high temperature, molecular mobility (segmental mobility) sets in almost abruptly, making the long-range order lose simultaneously. The polymer now passes from crystalline state directly to the liquid state. The temperature at which this transition takes place is known the melting temperature (T_m).
- A crystalline polymer can be made to exist in a glassy state by rapidly cooling its melt to a very low temperature without allowing enough time for the molecules to orient and form crystallites. This is called *quenching*.



• Partially crystalline polymers possess both T_g and T_m . Below T_g , the amorphous regions of the polymer exist in the glassy state and the crystalline region in the crystalline state. At T_g , the amorphous region passes on to the rubbery state, while the crystalline region continues to be in the crystalline state. At T_m , the crystalline regions melt and pass on to the liquid state. Beyond T_m , the amorphous and crystalline regions become one and the polymer as a whole is in a liquid state.

Polymer	T_g (°C)	T_m (°C)
Nylon 6,6	50	270
Natural rubber	-73	36
PVC	81	310
Polystyrene	100	250