

Polymer and Crystallinity

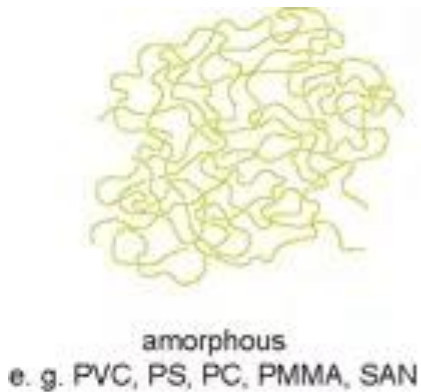
(DSE-4T)

For Semester VI

Prepared by
Dr. Subhra Mishra
Associate Professor
Department of Chemistry

Crystallinity of Polymer: The structure of a polymer is described in terms of crystallinity. Usually most of the polymers are in amorphous in nature or semicrystalline.

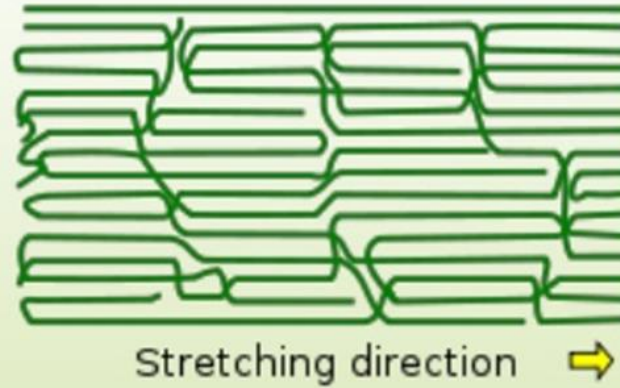
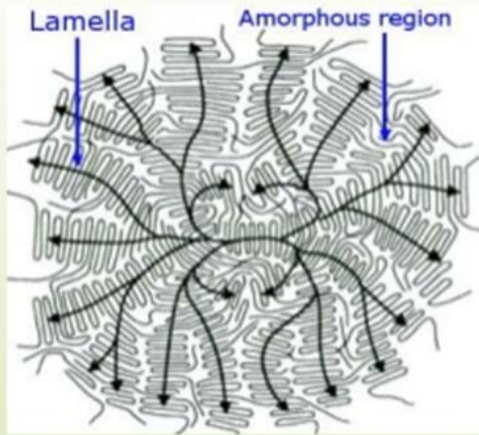
All of we know that a crystalline solid has a sharp melting point and amorphous do not have a sharp melting point.



Crystalline solids have a definite shape with orderly arranged ions, molecules or atoms in a three-dimensional pattern often termed crystal lattice with a uniform intermolecular forces.

Amorphous solids are the shapeless, disordered, and irregular arrangement of the constituent particles of a solid. Their inter-molecular forces are not the same, nor are the distances between the particles.

Polymeric material usually contains some crystalline part and some amorphous part.



The orderly stacks of folded chains are known as **Lamella**.

- Some polymers which do not crystallize from the melt, can be partially aligned by stretching.
- Some elastomers which are amorphous in the unstrained state undergo rapid crystallization upon stretching.

- The thicker the lamella the higher the melting temperature
- Semi crystalline materials display crystalline region.

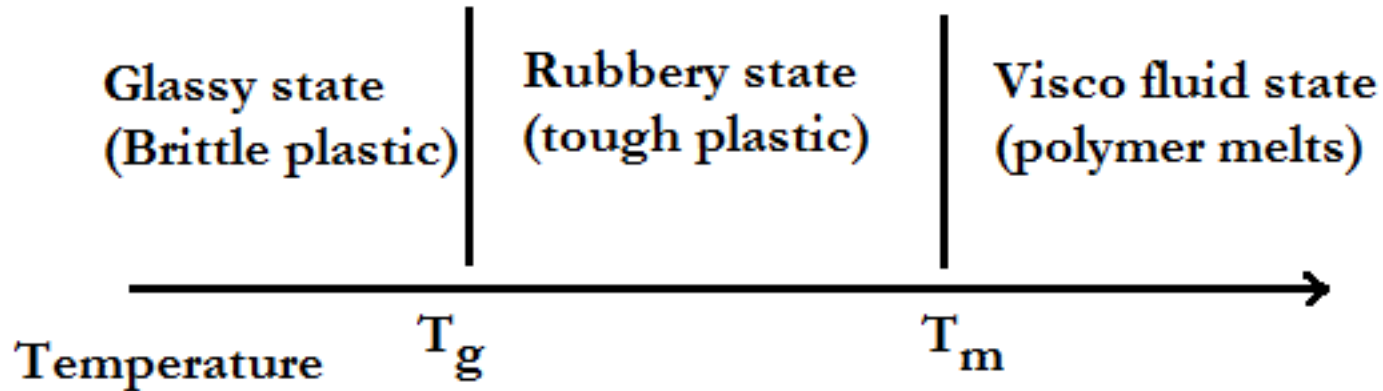
Spherulites: if the molten polymer is cooled down, then the crystalline lamellae grow in radial direction from a nucleus along the three dimensions leading to a spherical structure called spherulite.

- Spherulite formation and its diameter depend on various parameters such as the number of nucleation sites, polymer molecule structure and rate of cooling.
- Due to highly ordered lamellae in the spherulite it shows higher density, hardness, tensile strength.

Difference between Amorphous and Crystalline Polymer:

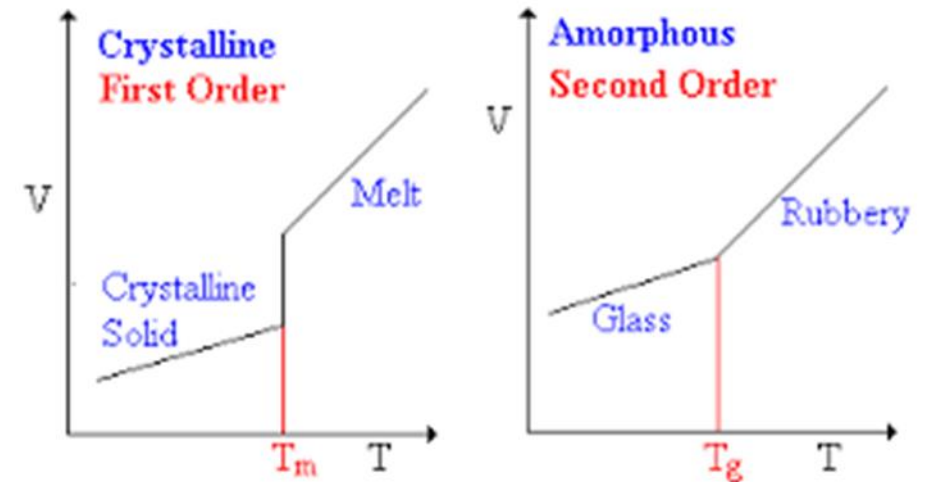
- Amorphous polymer do not have uniformly packed molecules, Crystalline polymers have uniformly packed molecules.
- Amorphous polymer do not have sharp melting point, but crystalline polymers have sharp melting pt.
- Amorphous polymers are transparent, whereas, crystalline polymers are opaque or translucent.
- Amorphous polymers have poor chemical resistance, but crystalline polymers have good chemical resistance.
- Amorphous are soft but crystalline polymers are hard in nature.

When we slowly heat a polymer and increase the temperature, the polymers changes from the glassy state to rubbery state and finally to the viscous state as they are semi-crystalline (amorphous with some percentage of crystalline)

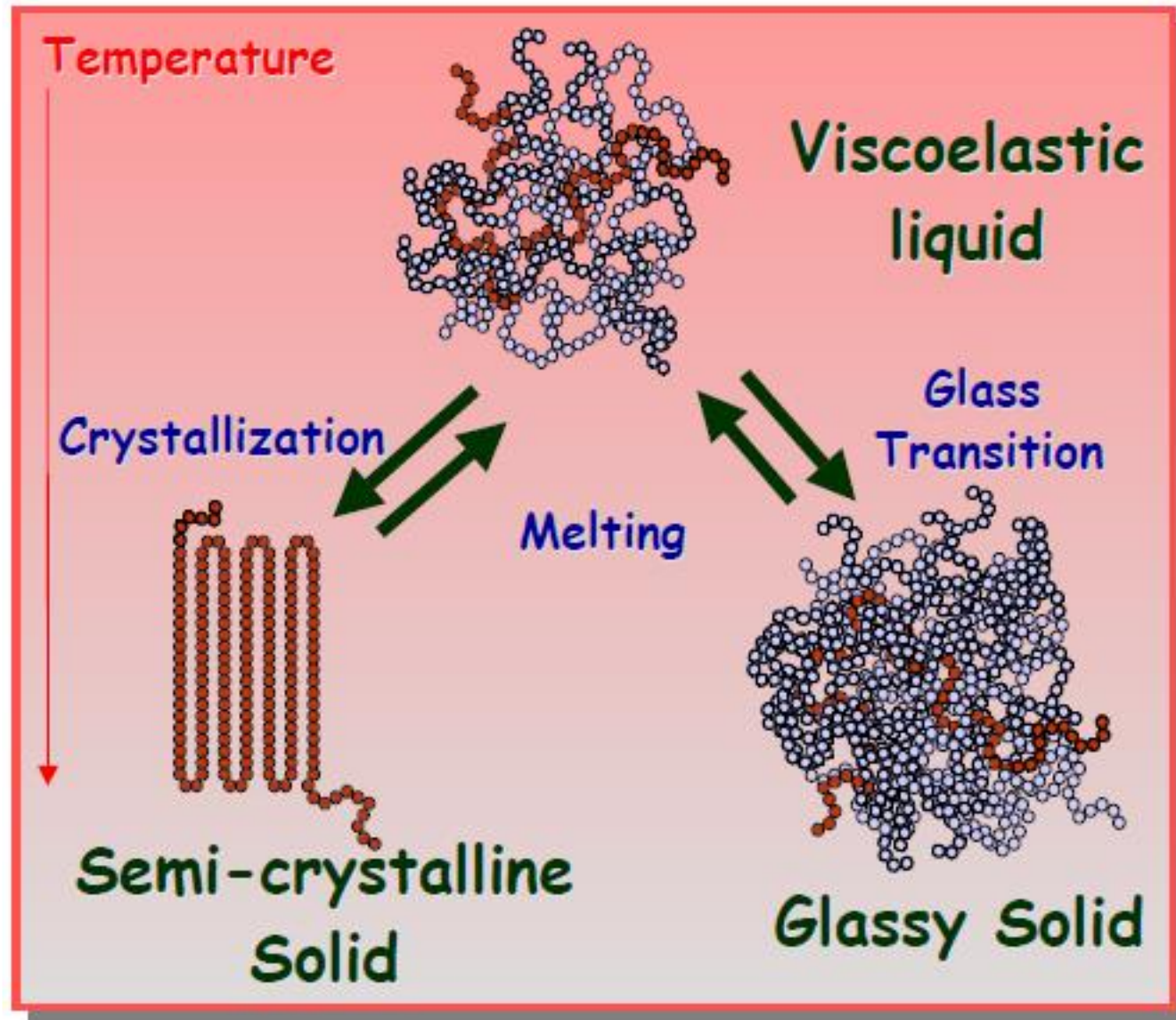


Melting Temperature: The temperature at which polymer changes from a viscous liquid to a micro-crystalline solid is the crystalline melting point of the polymer. T_m is not as sharp as melting point of other solids but is analogous to it. Accompanied by changes in density, refractive index, heat capacity, etc.

- Melting of a polymer occurs over a temperature range



Melting of a polymer crystal corresponds to the transformation of a solid material having an ordered structure of aligned molecular chains to a viscous liquid where the structure is highly random



Factors affecting Melting Temperature (T_m):

Molecular mass: Polymers are composed of long macromolecular chains. For a specific polymer, longer chains and larger Molecular mass results in higher T_m .

Chemical structure: T_m highly depends on the chemical structure of polymer. For instance, presence of H-bonding (for instance, in cellulose, Nylons and PET), polar elements (like, $-\text{Cl}$ in PVC) and polar groups (like $-\text{CN}$ in polyacrylonitril PAN) dramatically increase T_m .

Back bone / Main chain elements: The back bone / main chain of a polymer contains methylene groups, bulky benzene rings, other elements like oxygen, nitrogen depending on the polymer. The polymer with methylene groups have very low T_m as methylene groups are very light and flexible elements so very less thermal energy is required to make the chain move but polymers with bulky benzene groups require very high energy to make the chain move.

Melting point of LDPE is $\sim 118^\circ\text{C}$ whereas melting point of PEEK is $\sim 343^\circ\text{C}$

Primary Bonding: Polymers are made by primary bonds (covalent bond) between the individual monomer units. If two polymer chains are connected with a primary bond it is known as cross linking. Cross linking restricts the mobility of a chain as it is attached to another chain by means of a primary bond. When a polymer is highly cross linked then it becomes non-melting thermoset.

Secondary Bonding: Secondary bonding in case of polymers is hydrogen bonding and polar bonding. Hydrogen bonding is seen in nylons and polyesters polar bonding is seen in polymers like PVC. Hence to break these secondary bonds it requires more thermal energy, thus the melting point of Polyamides and Polyesters are very high compared to hydrocarbon polymers like PE.

Additives: Addition of certain additives like nucleating induces crystallization in polymers thereby increasing the melting point of the polymer and certain additives like plasticizer breaks the interaction between the chains and creates more free volume such that the polymer on very less thermal energy flows easily without any restriction.

Glass transition temperature (T_g): When plastic or rubber is cooled up to certain temperature, it becomes so hard and brittle that it breaks into pieces on application of stress. The temperature below which the polymer becomes hard, brittle and glassy and above which it is softer and flexible, is known as glass transition temperature (T_g). The glass transition is a property of only amorphous portion of a semi-crystalline solid. The crystalline portion remains crystalline during the glass transition

When a polymer is heated beyond T_g , it passes from glassy state to rubbery state. Further heating much above, causes melting of the polymer and it starts flowing. The temperature below which the polymer is in rubbery state and above which it is a liquid is called melting temperature of the polymer.

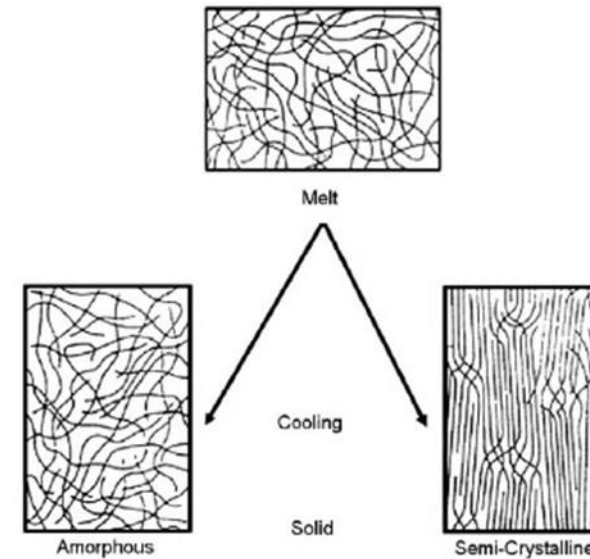
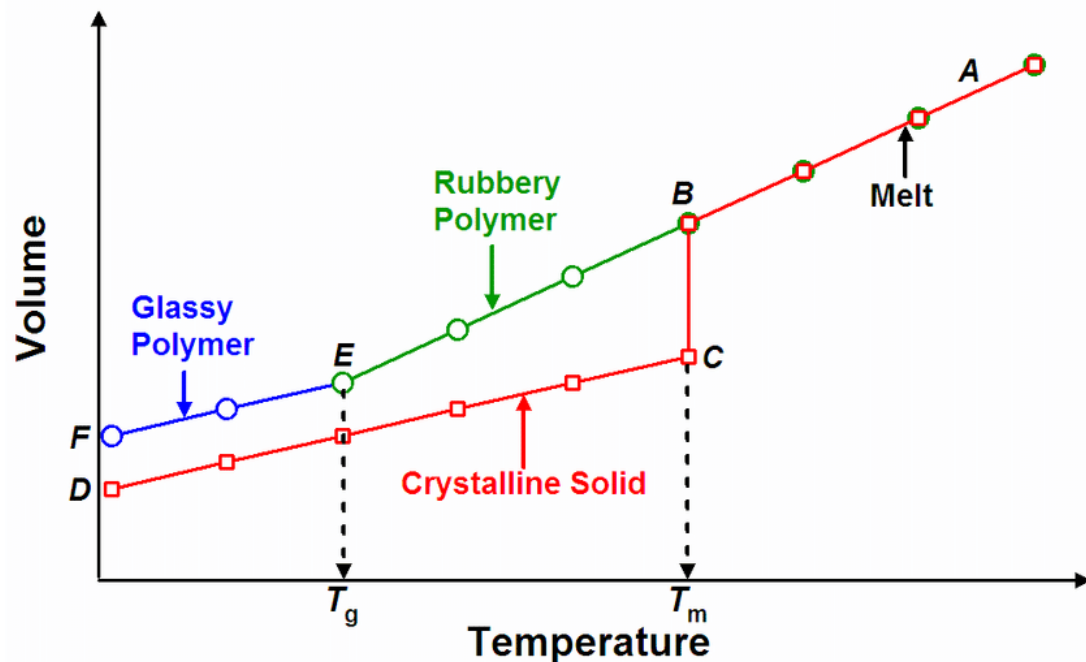


Figure 3.4 Cooling behaviour of materials

Degree of Crystallinity: The density of a crystalline polymer is greater than that of a noncrystalline polymer because of more efficient packing.

The degree of crystallinity is the measure of the amount of crystalline part in a polymeric sample.

So, degree of crystallinity is quantity which provides a measure of how much crystalline material is present in a given polymer sample.

$$\% \text{ crystallinity} = \frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \times 100$$

Where, ρ_c - density of perfectly crystalline polymer;
 ρ_a – density of amorphous polymer; ρ_s - density of the specimen whose percentage of crystallinity is to be determined)

- Polymer crystallinity can be determined with DSC by quantifying the heat associated with melting (fusion) of the polymer. This heat is reported as Percent Crystallinity by normalizing the observed heat of fusion to that of a 100 % crystalline sample of the same polymer.
- The most common method for determining the percent crystallinity of a sample involves comparing the density of the sample to the fully crystalline and fully amorphous densities.

One of the common methods for measuring the degree of crystallinity of the semi crystalline polymers is the density method. In this method the densities of the crystalline and amorphous polymer samples as well as the crystalline, as well as the semi crystalline sample their densities are used to get an estimate of the degree of crystallinity.

Degree of Crystallinity: Due to the large size, even a polymer of regularity of molecular structure does not exist entirely in crystalline form. As solidification begins, the viscosity of the polymer rises and molecules find more and more difficulty in arranging their long chain in the regular pattern required for crystal formation. In fact, polymers have regions of crystallinity called crystallinities, embedded in amorphous material.

Crystallinities provide hardness and the amorphous region provides flexibility to the polymeric material.

Crystallinity and Polymers

Question 1

The density and associated percent crystallinity for two poly(ethylene terephthalate) materials are as follows:

ρ (g/cm ³)	Crystallinity (%)
1.408	74.3
1.343	31.2

- (a) Compute the densities of totally crystalline and totally amorphous poly(ethylene terephthalate)
- (b) Determine the percent crystallinity of a specimen having a density of 1.382 g/cm³.

(5 marks)

$$\%C = \frac{\rho_c}{\rho_s} \left(\frac{\rho_s - \rho_a}{\rho_c - \rho_a} \right) \times 100$$

Factors influence Crystallinity:

- (i) **Molecular Weight:** With increase in molecular weight of a polymer, % crystallinity increases due to the large number of entanglement of chain which impose restriction for unlimited growth of a crystallite.
- (ii) **Symmetry of the repeating unit:** Symmetrical repeat unit structure like-CH₂- facilitates the formation of crystallites. Random copolymers do not crystallize because there is no regularity of the repeat unit. Geometrical regularity is also desired in a polymer for it to show crystallinity. For example, only the configurationally regular forms (isotactic and syndiotactic) of polypropylene can crystallize but atactic polypropylene is amorphous.
- (iii) **Chain Branching:** High density polypropylene has almost perfectly linear structure and therefore it can be obtained in a highly crystalline state (80-85% crystallinity) with high melting point (133-135°C). Low density polyethylene has number of short chain (ethyl and butyl) and long chain branches. So, it can not be obtained in a highly crystalline state (55% crystalline) and melting point is also low (110-115°C).
- (iv) **Cross Linking:** A polymer with high cross-linked density is devoid of crystallinity because the presence of a dense array of cross-links effectively eliminate crystallinity

Affect of Crystallinity on properties of polymer:

With increase in % crystallinity-

- (i) Strength and stiffness of polymer increases but brittleness also increases.
- (ii) Solubility and permeability of polymer decreases
- (iii) Density and melting point of polymer decreases
- (iv) Opacity of the polymer also increases.

Factors affecting Crystalline melting point T_m :

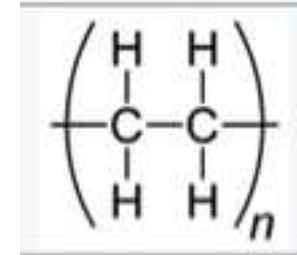
- (i) **Flexibility:** Higher flexibility, lower T_m . The presence of double bond and aromatic group in the polymeric backbone lowers the flexibility, thus increases T_m .
- (ii) **Size and type of side groups:** Bulky or large side groups tends to restrict molecular rotation and raise T_m .
- (iii) **Presence of Polar Groups:** Polar groups (Cl, OH, CN) in main chain, Hydrogen bonding within the crystal raise T_m .
- (iv) **Degree of Branching:** Side branching introduces defects into the crystalline materials, hence lowers T_m .

Factors affecting glass transition temperature (Tg):

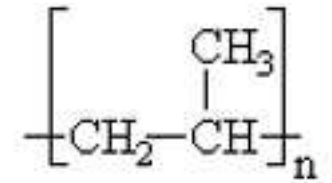
1) Chain Flexibility and Rigidity: Stiffening groups in the polymer chain reduce the flexibility of the chain and raise the value of Tg . In other words, greater the intrinsic chain flexibility, smaller will be the Tg.

Example: Tg (PP) Tg (PE)

Since substitution of H in PE by CH3 group in PP impedes the rotation about a C-C single bond. Thus, Tg is affected by the nature of substitution



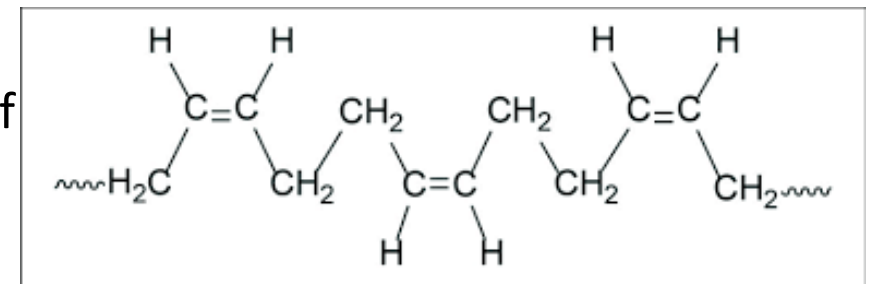
Polyethylene (PE)



Polypropylene (PP)

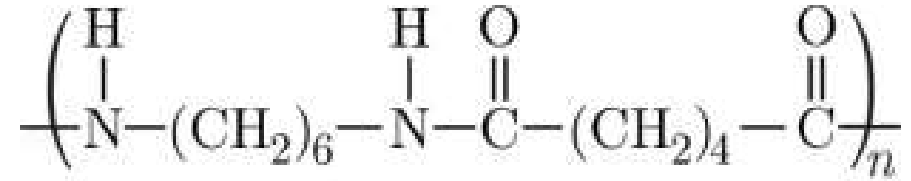
Example: Configuration, Tg (PE) Tg (Cis-1,4-polybutadiene)

Because inclusion of a double bonds stiffen the chain at the point of inclusion but at the same time increases the flexibility of the adjacent bonds

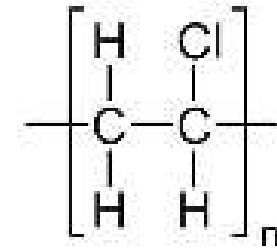


2) Intermolecular Forces: $T_g(\text{PE}) < T_g(\text{PVC}) < T_g(\text{Nylon 66})$

Stronger intermolecular forces due to dipole forces, H-bonding etc. decreases the mobility of the chain lead to a higher T_g . PVC has stronger intermolecular forces than polypropylene because of the dipole-dipole forces from the C-Cl bond.



Nylon 66



Polyvinyl chloride (PVC)

3) Molecular Weight: Glass transition temperature, T_g is directly proportional to molecular weight of the polymer.

4) Pendant Groups: The influence of pendant groups on the glass transition temperature is somewhat more complicated. Bulky pendant groups, such as a benzene ring, can catch on neighboring chains like a "fish hook" and restrict rotational freedom and can increase T_g .

5) Cross-Linking: The presence of cross-links between chains restricts rotational motion and hence, greater the degree of cross-linking, the higher the T_g .

6) Plasticizers: Plasticizers are low molecular weight compounds added to plastics to increase their flexibility and workability. They weaken the intermolecular forces between the polymer chains as it increases the mobility and decrease T_g .

7) Copolymerization: Random copolymers have lower T_g 's since it tends to promote the disorder, reduce molecular packing and reduces the inter chain forces of attraction.