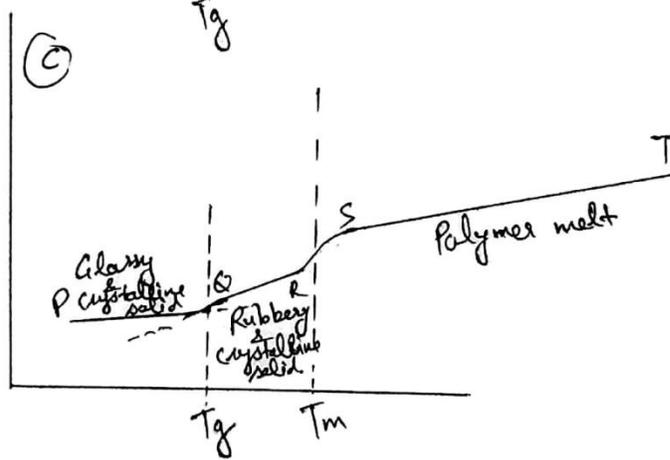
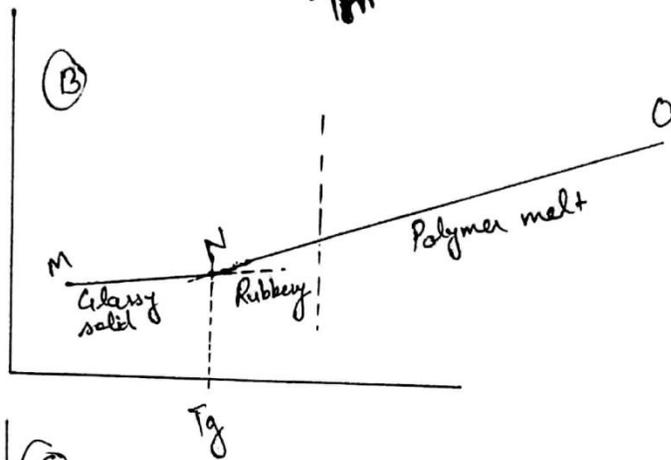
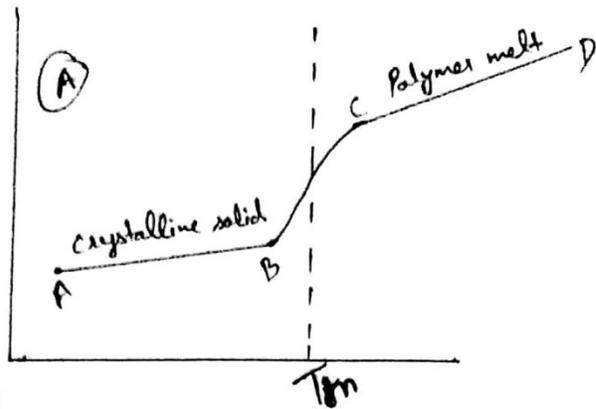


Glass Transition Temperature of Polymer

Before starting to study about glass transition temperature of polymer, we will take an overview of crystallinity of polymers. Crystallinity or degree of crystallinity of polymer is it's one of the significant characteristic. Degree of crystallinity depends on the arrangement of macromolecular chains of polymer. If the macromolecular chains are arranged in orderly fashion (Lamellae) then it is called crystalline polymer on the other hand if the chains are randomly entangled then it is called amorphous polymer. But generally no polymers are fully crystalline or we can say polymers are either semi-crystalline or amorphous. In semi-crystalline polymers, some of the macromolecular chains are arranged in orderly fashion while other are entangled randomly. Fraction of Crystalline volume and total volume of semi-crystalline polymer is known as Degree of crystallinity.

We study the variation of specific volume of polymer with the temperature then nature of curve (Specific volume versus temperature) depends whether the polymer is crystalline or not. Let we have three samples and sample 1 is crystalline, sample 2 is amorphous and sample 3 is semi-crystalline and Curve A, B and C represent V versus T behavior of respective polymers. Curve A depicts that as crystalline polymer is heated, its volume increases steadily and as the polymer melts it shows abrupt increase in volume. This concept of melting almost same as low molecular crystals only slight difference is due to polydispersity of polymers. Because of the polydispersity, curve shows a gradual band instead of sharp band. By study of Curve B we get to know that slope of curve changes gradually near the glass transition temperature and suddenly slope increases steeply and by extrapolation of this straight portions we get a point which represent the glass transition temperature (T_g). Study of Curve C reveals that volume expansion coefficient gradually changes from low value to high value corresponding to glassy state and rubbery state respectively. It can also be seen that beyond T_m , slope of curve A and B is same indicating that change in slope from rubbery state to molten state is undetectable therefore we can't observe melting point in case of amorphous polymers. In case of sample 3, which is semi-crystalline (mixture of crystalline and amorphous) shows mix behavior therefore shows change in slope at two temperatures, lower temperature range corresponds to T_g while higher one T_m .



Plot showing variation of specific volume with temperature for A) highly crystalline. B) Amorphous and C) semi-crystalline polymer.

From the above study, it can be concluded that crystalline polymers have melting point while amorphous polymers have glass transition temperature and semi-crystalline polymers can have both melting point and glass transition temperature. Glass transition temperature (T_g) is the temperature of transition from glassy state to rubbery state or we can say below which polymer behave as a glassy material and above which it behave as a rubbery material. Glassy state is hard and brittle while rubbery state is soft and flexible. According the end use application some of the polymers are used above T_g and some are used below.

Factors affecting glass transition temperature

State of polymer (solid, rubbery or molten) depends on the presence and absence of segmental and molecular movements and in turn these movements depends on size, geometry,

- 1. Chain flexibility:** Chain flexibility is one of the important factor, which affects T_g . Intrinsic chain flexibility is determined by the nature of polymer backbone and groups directly attached to it. Aliphatic C-C and C-O bonds show quite flexibility while introduction of ringed structures causes stiffening of chain. Stiffening of chain causes increase in glass transition temperature therefore glass transition temperature of polyethylene terephthalate is higher than their aliphatic counterparts. Bulky group attached to polymer backbone also reduces flexibility of chain backbone therefore polypropylene has higher T_g than polyethylene. Polytetrafluoroethylene has high T_g than polyethylene as size of fluorine atom is large and it requires the molecule to take zig-zag configuration in which fluorine atoms are packed tightly and chain gets stiffened. Introduction of double bond also causes stiffening of chain alongwith this it may increase flexibility of adjacent bonds therefore it causes decrease in T_g and explains the low T_g of cis-1,4-polybutadiene is lower than polyethylene.
- 2. Intermolecular interactions:** Segmental rotations are also affected by intermolecular interactions or secondary bonding such as dipole-dipole interaction, induction forces, van der waals forces and hydrogen bonding etc. These types of interactions increase the rigidity of polymeric material therefore increase the glass transition temperature. Polyvinyl chloride has higher T_g than polyethylene and Nylon-6 also has higher transition point than polyolefin. Polyvinylidene chloride has lower transition point than

polyvinylchloride because of the reduction in dipole moment due to symmetry of substitution.

- 3. Molecular weight:** Polymer having low molecular weight has more number of chain ends in compare of polymer having high molecular weight. Chain ends have less strain and become more active than the chain backbone and causes greater molecular mobility. Therefore increase in molecular weight decreases the glass transition temperature of polymer and it is reasonable to assume that with increase of chain-end concentration glass transition temperature increases linearly on the other hand we can say that glass transition temperature decreases linearly with increase of molecular weight of polymer. Equation given below relates the glass transition temperature of polymer with its molecular weight,

$$T_g = T_g^\infty - K(1/M_n)$$

T_g^∞ is the glass transition temperature of sample having infinite molecular weight, K is positive constant and M_n is number average molecular weight.

- 4. Co-polymerization:** Random co-polymerization causes disorder and reduces molecular packing therefore glass transition temperature is often lower. Glass transition temperature of random copolymer depends on composition of two monomeric components and their individual value of T_g . The following relation gives the glass transition temperature of a random polymer:

$$1/T_{g(A,B)} = W_A/T_{g(A)} + W_B/T_{g(B)}$$

Where $T_{g(A,B)}$, $T_{g(A)}$ and $T_{g(B)}$ are glass transition temperature of copolymer AB and homopolymer A and B respectively. W_A and W_B are the weight fraction of monomer A and monomer B in the copolymer AB.

Syndio-tactic and iso-tactic polymers have symmetry so can be explained as linear polymers. Effect of Block co-polymerization will depend on type of block present in the polymer system. In some cases, Block-copolymers show two transitions corresponding to each block while in some cases, only single transition is observed and this transition is close to the value predicted by linear relationship. This is because random polymers causes more disorder in polymer system in compare of block copolymer as there is less contact of dissimilar comonomer units.

5. **Cross-linking:** Cross-linking introduces restriction and stiffness in the polymer therefore causes the increase in glass transition temperature.
6. **Plasticizer:** Plasticizers are generally low molecular weight substances and when added to polymer, cause separation of polymer chains, reduction of co-hesive forces and overall increase molecular mobility. Plasticizers reduces brittleness of polymers and reduces glass transition temperature

References: **Polymer science.** [V R Gowariker; N V Viswanathan; Jayadev Sreedhar]

Introduction to polymers [Robert J. Young, Peter A. Lovell. Taylor & Francis,]