

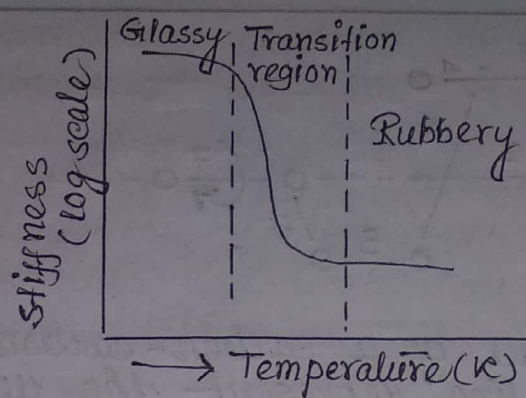
▶ ii) The Glass transition :

Amorphous polymers exist as long, randomly coiled, interpenetrating chains and the chains assume unperturbed ( $r_0$ ) dimensions. In the melt, thermal energy is sufficiently high for long segments of each polymer-chain to move in random micro-Brownian motions. As the melt is cooled, a temperature is reached at which all long-range segmental motion ceases. This characteristic temp<sup>o</sup> is called glass-transition temperature or  $T_g$ , where transition from amorphous solid state to melt state is occurred.

In other words, there is a "temp<sup>o</sup> boundary" for almost all amorphous polymers (and many crystalline polymers) only above which substance remains soft, flexible and rubbery and below which it becomes hard, brittle and glassy. This temperature below which a polymer is hard and above which it is soft, is called the "Glass transition temperature." The hard, brittle state is known as the glassy state & the soft flexible state is known as the rubbery or viscoelastic state. On further heating, the polymer (if it is uncross-linked) becomes a highly viscous liquid & start flowing; this state is termed viscofluid state, the transition taking place at its "flow temp<sup>o</sup>,"  $T_f$ .

Glassy state Brittle plastic	Rubbery or visco-elastic state Tough plastic & rubbers	Visco Fluid state Polymers melt
$T_g$		$T_f$

→ Temperature →



► **N.B**: ① The glass transition  $T_g$  is marked as an isoviscous state. This means that as a polymer is cooled from its melt state, viscosity increases rapidly to a common (maxima) value, e.g.  $10^{13}$  poise at  $T_g$ , for all glassy materials.

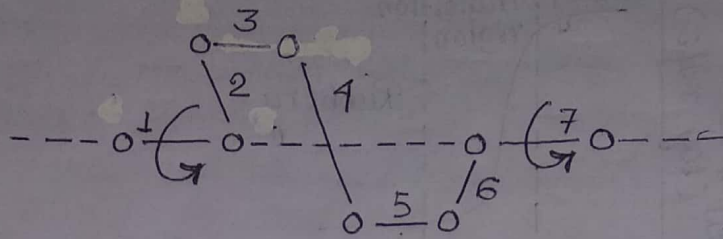
② A second view is that the glass transition represents a state of isofree volume. Free volume,  $V_f$ , may be defined as the difference between the actual ~~at~~ volume,  $V$ , of the polymer at a given temperature and its equilibrium volume at absolute zero,  $V_0$ .

$$V_f = V - V_0$$

③ A third view of the glass transition is that it represents an iscentropic state. Gibbs and Di Marzio have suggested that there is a temperature,  $T_2$ , at which ~~is~~ the conformational entropy,  $S_c$  (a measure of the total no. of ways of arranging a polymer molecule or collection of chains), goes to zero.

► (iii) Secondary - Relaxation Process:

In the amorphous glassy state, at temperature below  $T_g$ , the only molecular motions that can occur are short-range motions of several contiguous chain segments & motions of substituent groups. These processes are called secondary relaxations. These can involve limited motions of the main chain or rotations, vibrations or flips of substituent groups.



Schatzki model of a carbon-carbon backbone. The dashed line represent the virtual axis around which bonds 2-6 rotate.

## b) The crystalline state:

### ▶ i) Ordering of Polymer chains:

Under favorable conditions, some polymers cooled from the melt can organize into regular crystalline structures. Such crystalline polymers have less perfect organization than crystal of low m.w compounds / polymers. The basic units of crystalline polymers morphology are crystalline lamellae consisting of arrays of folded chains.

For some polymers crystallized from the melt or from concentrated solution, crystallites can organize into larger spherical structures called spherulites. Each spherulite contains arrays of lamellar crystallites.

Since no polymer is completely crystalline, the polymer, therefore, may exhibit both  $T_g$  (i.e. long-range segmental motions in the amorphous region) and  $T_m$  (i.e. crystalline melting temperature, at which crystallites are destroyed and disordered melt is formed.)

### ▶ ii) Crystalline melting temperature:

A crystalline substance can exist as a "crystalline" solid (solid phase state) or as a molten liquid (liquid-phase state).

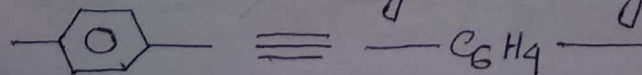
When a crystalline polymer is heated; the polymer crystal corresponds to the transformation of a solid material, having an ordered structure of aligned molecular chains, to a viscous liquid in which the structure is highly random. The temperature at which this transformation occurs, is called crystalline - melting temperature or melting temperature,  $T_m$ .

### ► Factors influencing the Glass Transition temperature

As  $T_g$  marks as the onset of molecular motion, a number of factors that effects rotation about links (necessary for movement of polymer chains) will also influence the  $T_g$  of a polymer. These include (a) chain flexibility, (b) molecular structure (steric effects), (c) molecular weight, (d) branching or cross-linking, and (e) crystallinity.

The flexibility of the chain may be considered to be the most important factor that influences the  $T_g$  of a polymer. If the chain is highly flexible,  $T_g$  will generally be low and if the chain is rigid, the  $T_g$  value will be high. The chain flexibility depends on the rotation or torsion of skeletal bonds. Chains made up of bond sequences which are able to rotate easily are flexible, and hence polymers containing  $(-CH_2-CH_2-)$ ,  $(-CH_2-O-CH_2-)$  or  $(-Si-O-Si-)$  links will have corresponding low values of  $T_g$ . For example, Poly(dimethyl siloxane), which has Si-O bonds in the backbone, has one of the lowest  $T_g$  values known ( $-123^\circ C$ )

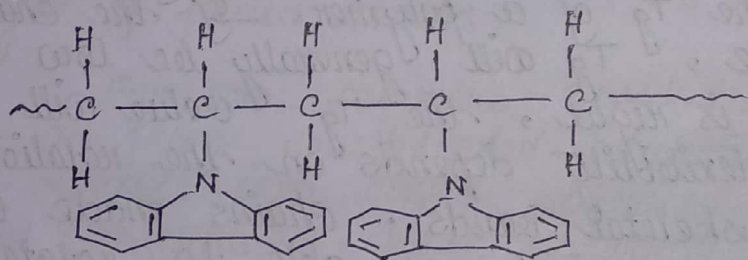
The value of  $T_g$  increases markedly with the insertion of groups that stiffen the chain by impeding rotation, since more thermal energy is then required to set the chain in motion. Particularly, effective in this respect is the p-phenylene ring.



Some example of such polymers are Poly (xylylene),  $\left[ \text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2 \right]_n$ ,  $T_g = 280^\circ\text{C}$  and Poly (Phenylene oxide),  $\left[ \text{C}_6\text{H}_4 - \text{O} \right]_n$ ,  $T_g \approx 83^\circ\text{C}$ , as compared to polyethylene  $\left[ \text{CH}_2 - \text{CH}_2 \right]_n$ ,  $T_g = -93^\circ\text{C}$  and Poly (ethylene oxide)  $\left[ \text{CH}_2 - \text{CH}_2 - \text{O} \right]_n$ ,  $T_g = -67^\circ\text{C}$ , respectively.

The effect of the side group can be appreciated by comparing the  $T_g$  of polystyrene with that of polymethylstyrene and the  $T_g$  of polymethylacrylate with that of polymethylmethacrylate. The presence of  $-\text{CH}_3$  groups hindered the chain mobility, resulting in an increase of  $\sim 70^\circ\text{C}$  and  $100^\circ\text{C}$  in their  $T_g$  values over unmethyl one, respectively.

A  $T_g$  value of  $150^\circ\text{C}$  for Polyvinyl carbazole is understandably high, as it contains bulky side groups.



► **N.B**: Polyethylene has a low  $T_g$ . But nylon 6, a polyamide, has high  $T_g$  ( $50^\circ\text{C}$ ) because of the presence of a large no of polar group in the molecules, leading to strong intermolecular H-bonding.

