



CHEM3020: POLYMER CHEMISTRY

Unit-3: Crystallinity and Glass Transition Temperature

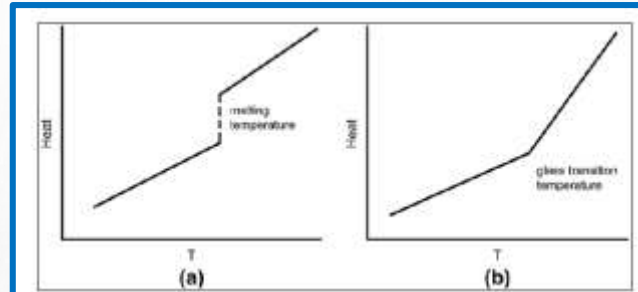
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UNIT 3 Crystallization and crystallinity

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



(a) melting point (100% Crystalline)(b) glass transition temperature (100% amorphous)

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 inter-molecular forces.

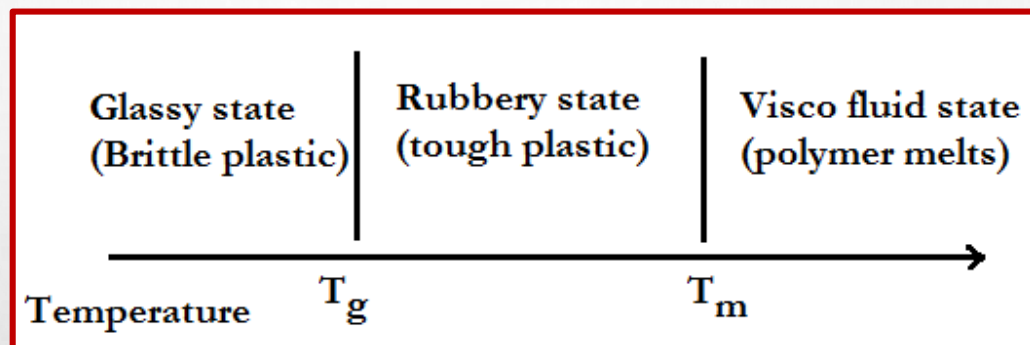
Amorphous solids are the shapeless, disordered, and irregular arrangement of the constituent particles of a solid. Their inter-molecular forces are not the same, nor are the distances between the particles.

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



UNIT 3 Crystallization and crystallinity

When we slowly heat a polymer and increase the temperature, the polymer 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)



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.

Degree of crystallinity

Degree of Crystallinity: The density of a crystalline polymer is greater than that of a non-crystalline 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.

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.

$$\text{Percentage of crystallinity} = \frac{p_c / (p_c - p_a)}{p_s / (p_s - p_a)} \times 100$$

Where, p_c - density of perfectly crystalline polymer; p_a – density of amorphous polymer;
 p_s - density of the specimen whose percentage of crystallinity is to be determined)



Degree of crystallinity

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- CH_2 - 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 $^{\circ}\text{C}$). 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 $^{\circ}\text{C}$).
- (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



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Factors affecting crystalline melting point.

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) **Cain 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 .**



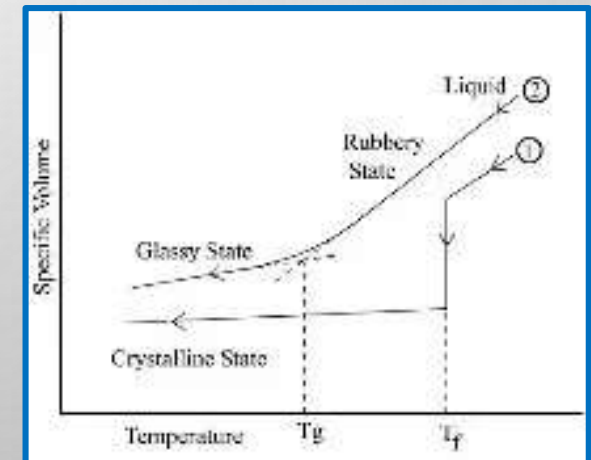
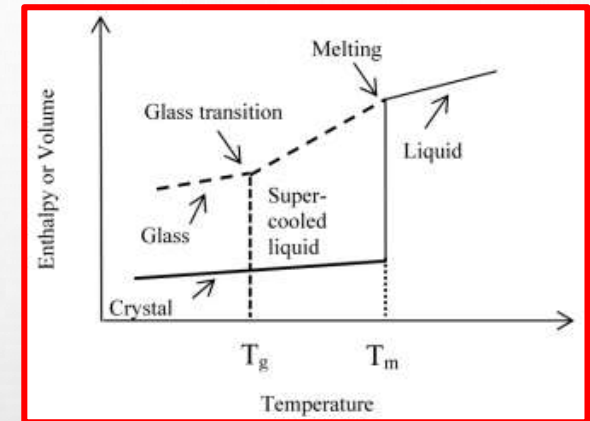
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Glass transition Temperature (T_g) of polymers

Glass transition temperature (T_g) and Factors affecting 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.

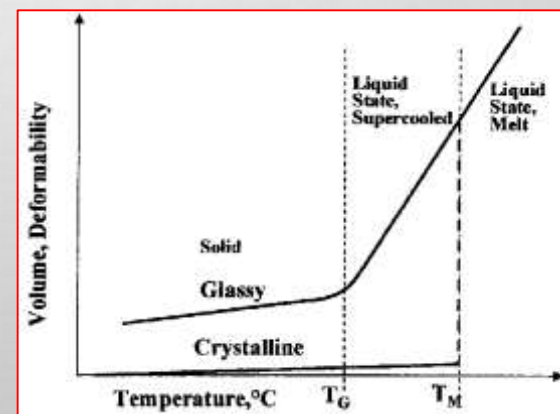
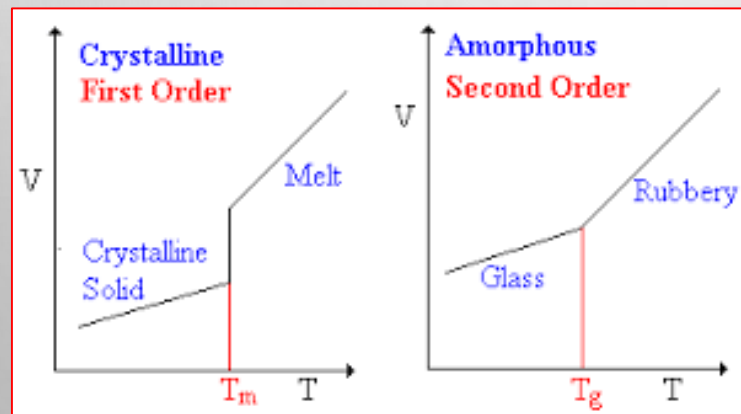
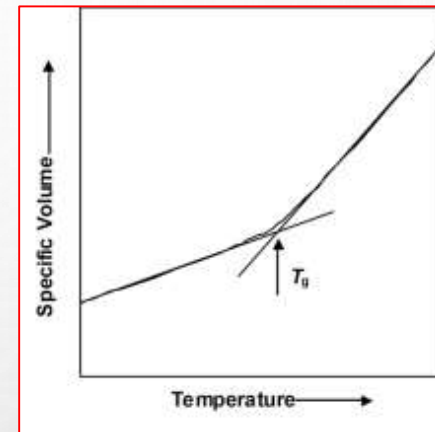
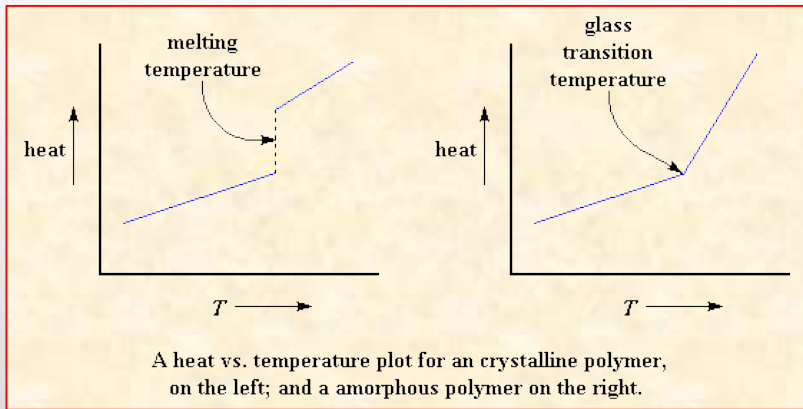




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Glass transition Temperature(T_g) of polymers

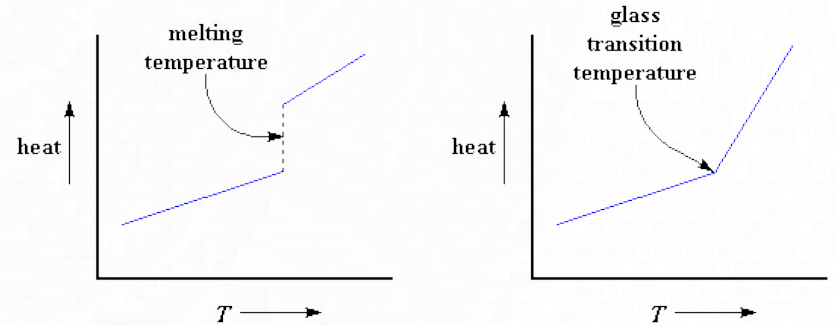
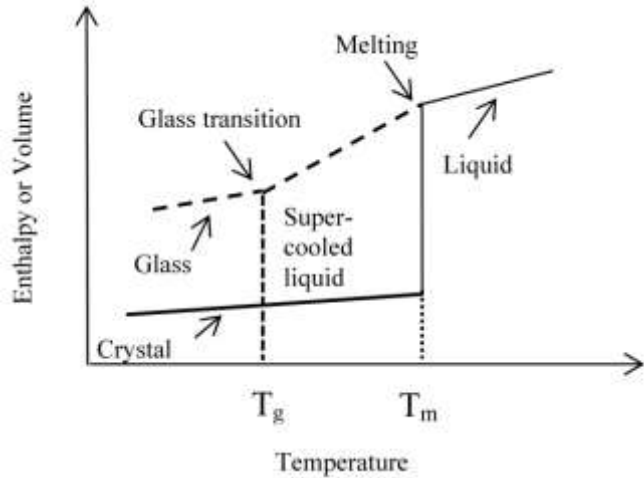
Glass transition temperature (T_g) and Factors affecting glass transition temperature (T_g)



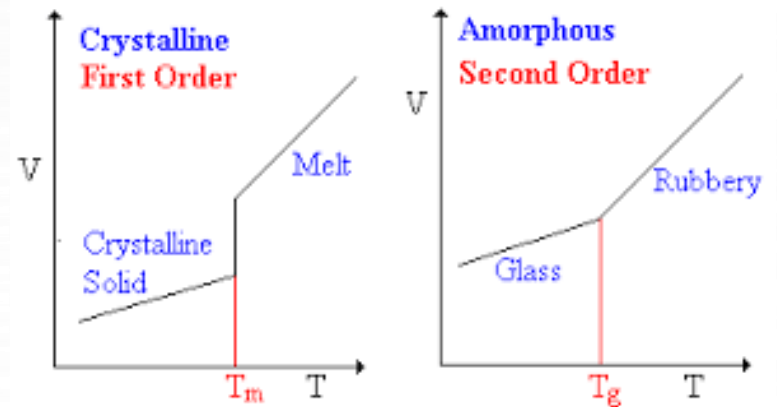
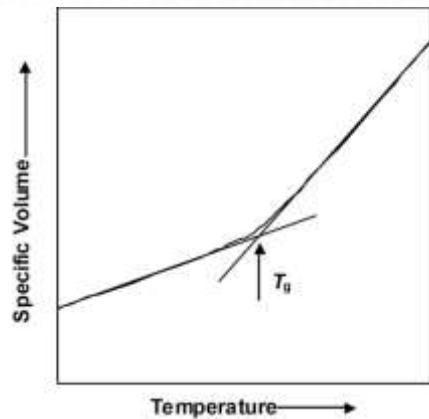


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Glass transition Temperature (T_g) of polymers



A heat vs. temperature plot for a crystalline polymer, on the left; and an amorphous polymer on the right.



Glass transition temperature (T_g) and Factors affecting glass transition temperature (T_g)



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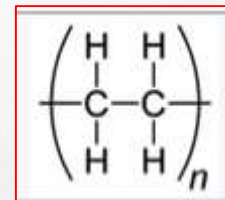
Glass transition Temperature(T_g) of polymers

Factors affecting glass transition temperature (T_g)

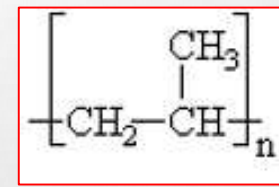
1) **Chain Flexibility and Rigidity:** Stiffening groups in the polymer chain reduce the flexibility of the chain and raise the value of T_g. In other words, greater the intrinsic chain flexibility, smaller will be the T_g.

Example: T_g (PP) T_g (PE)

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



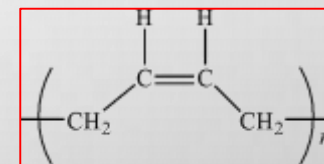
Polyethylene (PE)



Polypropylene (PP)

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

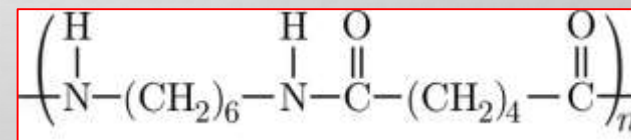
Because inclusion of a double bonds stiffen the chain at the point of inclusion but at the same time increases the flexibility of the adjacent bonds.



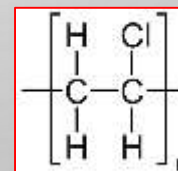
Cis-1,4-polybutadiene

2) Intermolecular Forces: T_g (PE) < T_g (PVC) or T_g (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)



Glass transition Temperature(T_g) of polymers

Factors affecting glass transition temperature (T_g)

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.**

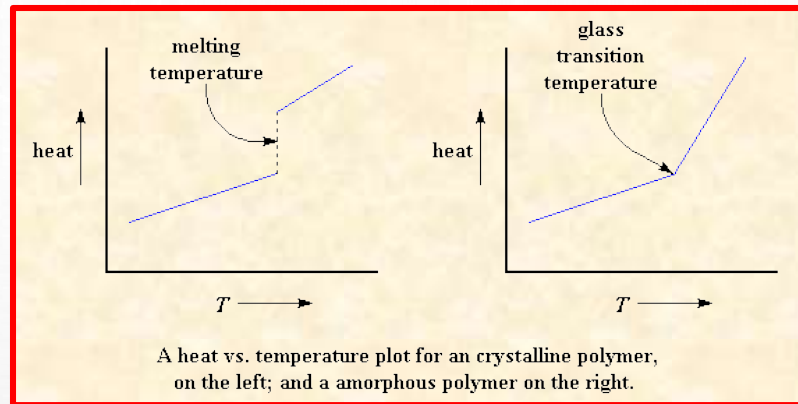
7) Copolymerization: **Random copolymers have lower T_g's** since it tends to promote the disorder, reduce molecular packing and reduces the inter chain forces of attraction.



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Factors affecting glass transition temperature

Significance of T_g



Glass transition temperature

directly proportional to molecular weight of polymer.

directly proportional to degree of cross links

directly proportional to intermolecular force.

directly proportional to number of side groups

inversely proportional to flexibility.

inversely proportional to plasticization.



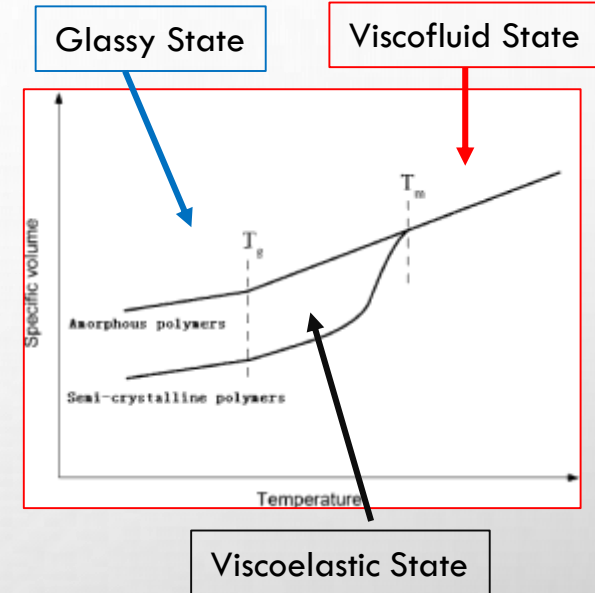
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Glass transition Temperature (T_g) of polymers

Determination of T_g and free volume concept:

As per thermodynamic view point, T_m is a first order transition because there is an abrupt change in a fundamental property such as specific volume with temperature. However, T_g is a second order transition as only the first derivative of such properties changes. For the determination of T_g and T_m , the specific volume of a semi-crystalline polymer sample is measured as a function of temperature.

The plotting of data yields the curve shown in figure.



Crystallinity ---- Transition temperature

0%-----only T_g

100%-----Only T_m

Free volume Concept: At high temperature, the semi-crystalline polymer is in fluid state and polymeric molecules adopt random configurations. As the temperature decreased, the specific volume of the polymer also linearly decreased before T_m . But after, T_m , further decrease in temperature leads to rapid decrease in specific volume. This is because crystallization occurs and crystals are significantly denser.



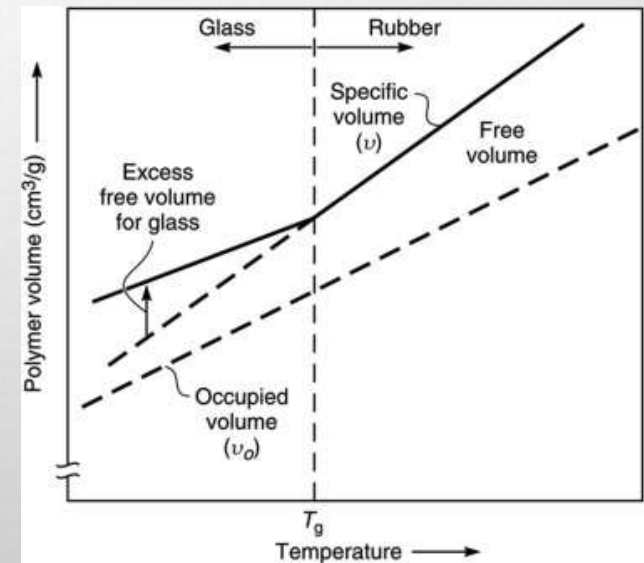
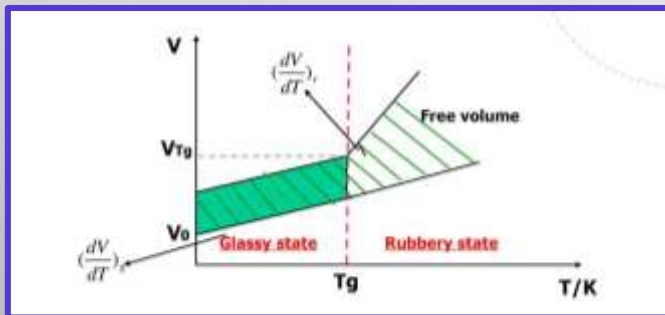
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Glass transition Temperature (T_g) of polymers

Free volume theory:

Near T_g , the slope of the curve changes, below, T_g , if the temperature is further lowered further contraction takes place through the amorphous region. Below T_g , the polymer is in solid physical state and molecules have amorphous and crystalline region. The concept of free volume can be used to analyze the glass transition. The free volume is a space in a solid or liquid sample which is not occupied by the polymer molecules, i.e. the empty space between molecules. Above T_g , the free volume is high so, polymer molecules can change conformations freely.

As the temperature of the melt lowered, the free volume will reduce eventually there will not be enough free volume to allow the molecular rotation or translation to take place. The temperature at which this happens corresponds to T_g as below this temperature, the polymer glass is effectively frozen



Below T_g - free volume is constant and above T_g - free volume increases with temperature



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Glass transition Temperature(T_g) of polymers

Williams-Landel-Ferry (WLF) Equation: A general empirical formula has been formulated and known as Williams-Landel-Ferry equation describing the dependence of molecular structure for the relation between a_T and absolute temperature- given by,

$$\log_{10} a_T = \frac{-17.44x(T - T_g)}{51.6 + (T - T_g)}$$

Where a_T is known as shift factor.

In glassy state, large scale molecular motion does not take place, rather atoms and small groups of atoms move against the local restraints of secondary bond forces, much as atoms vibrate around their equilibrium position in crystal lattice. The glass transition state corresponds to the onset of liquid like motion of much longer segments of molecules, characteristic to rubbery state. This motion requires more free volume than the short range movements of atoms in the glassy state. The rise in relative free volume with increasing temperature above T_g leads to the higher observed volume expansion coefficient in this region. Since fully extended chain is the conformations of minimum energy, it tends to be assumed more frequently as the temperature is lowered. As the molecule thus straightened out, the free volume decreases and flow becomes more difficult.



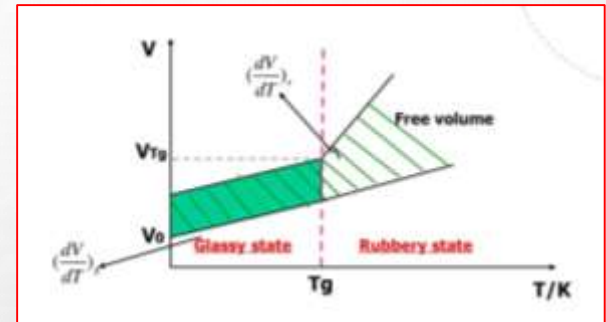
WLF equation

WLF equation: Williams-Landel-Ferry Equation-Explanation

The empirical Williams-Landel-Ferry equation describes the temperature dependence of the viscoelastic properties of polymers.

The **temperature** dependence of the **viscosity** may be described by an Arrhenius equation of the form

$$\eta = A e^{E/RT}$$



The two parameters E and A are usually determined from a plot of $\log \eta$ against $1/T$ which yields a straight line:

$$\log \eta = \log A + E / RT$$

Doolittle postulated that the **viscosity** is an exponential function of the reciprocal of the **fractional free volume f**

$$\eta = A e^{B/f(T)}$$



$$\log \eta = \log A + B / f(T)$$

where A and B are constants and f is the free volume fraction.



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Glass transition Temperature(T_g) of polymers

Williams-Landel-Ferry (WLF) Equation: The fraction of free volume f may be defined as-

$$f = f_g + (T - T_g) \Delta \alpha \quad \text{when } T \geq T_g$$

$$f = f_g \quad \text{when } T < T_g$$

Thus f is a constant at the value f_g for all temperature below T_g .

α is the expansion coefficient resulting from the increase in amplitude of molecular vibrations with temperature. Above T_g , new free volume is created as the result of an increase $\Delta \alpha$ in the expansion coefficient.

Williams, Landel and ferry proposed that \log viscosity varies linearly with $1/f$ above T_g . So,

$$\ln \left(\frac{\eta}{\eta_g} \right) = \frac{1}{f} - \frac{1}{f_g}$$

Thus the equation become-

$$\ln \left(\frac{\eta}{\eta_g} \right) = \frac{a(T - T_g)}{b + T - T_g}$$

$$\log_{10} a_T = \frac{-17.44x(T - T_g)}{51.6 + (T - T_g)}$$

The numerical constants a and b given in the equation are determined by fitting literature data on the viscosity-temperature behavior of many glass-forming substances. The shift factor a_T is just the ratio of the viscosity at T relative to that of T_g .



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WLF equation

Williams-Landel-Ferry (WLF) Equation:

$$\ln \left(\frac{\eta}{\eta_g} \right) = \frac{a(T - T_g)}{b + T - T_g}$$

$$\log_{10} a_T = \frac{-17.44x(T - T_g)}{51.6 + (T - T_g)}$$

The WLF equation finally becomes-

$$\log_{10} a_T = \log_{10} \frac{\eta(T)}{\eta(T_g)} = - \frac{17.44 (T - T_g)}{51.6 + T - T_g}$$

The above equation, the relationship between viscosity and temperature is known as WLF Equation.



References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley

2. Polymer Chemistry by Charles E Carraher, Jr., Marcel Dekker, Inc.

3. Principle of Polymerization by George Odian, Wiley

THANK YOU