

Polymer chemistry-Part II

(DSE-4T)

**For Semester VI
Chemistry (H)**

**by
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Determination of Tg and free volume concept:

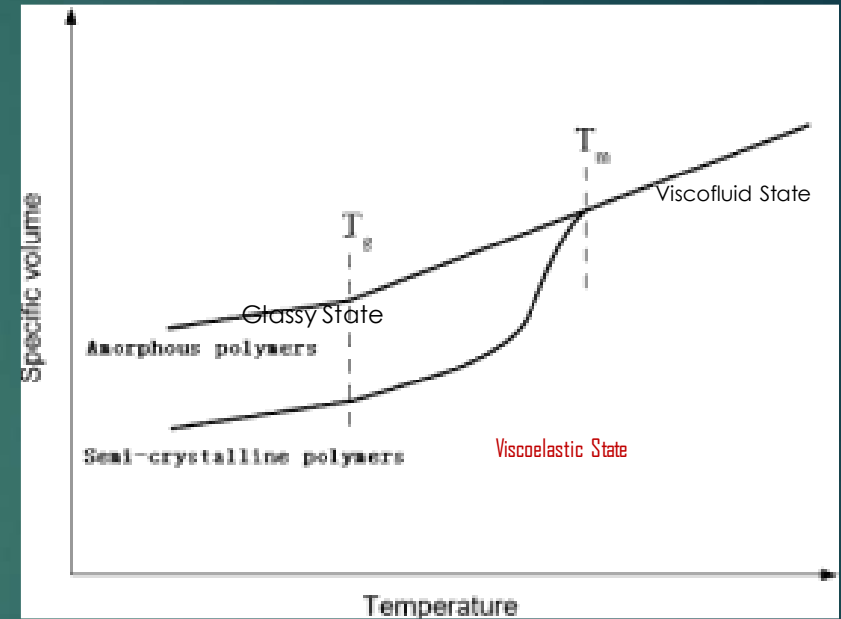
As per thermodynamic view point, T_m is a first order transition because there is an abrupt change in a fundamental property such as specific volume with temperature. However, T_g is a second order transition as only the first derivative of such properties changes. For the determination of T_g and T_m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

Crystallinity ---- Transition temperature

0%-----only T_g

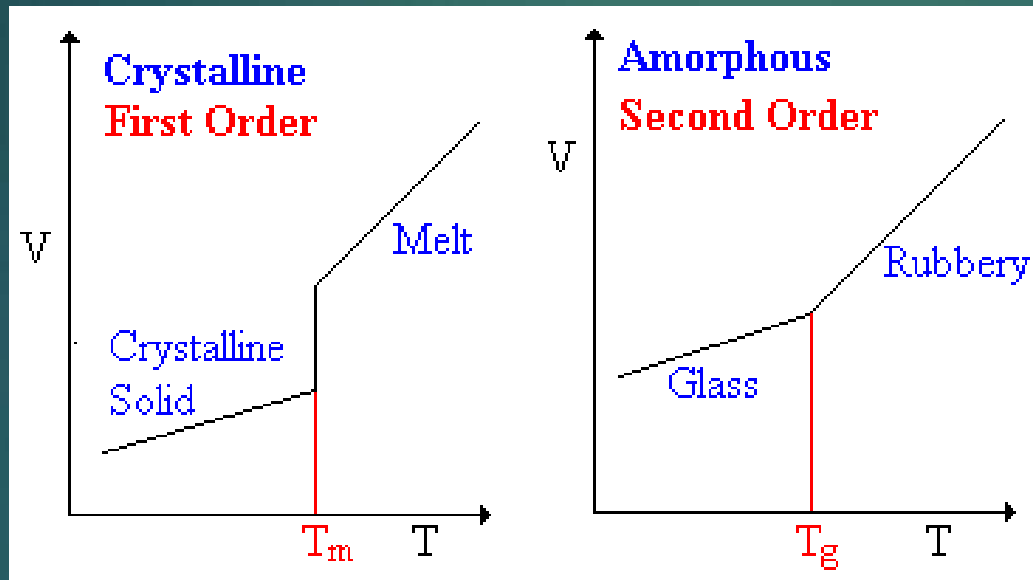
100%-----Only T_m

The plotting of data yields the curve shown in figure



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.

Thermodynamic transitions are classified as being **first-** or **second-**order. In a first-order transition there is a transfer of heat between system and surroundings and the system undergoes an abrupt volume change. In a second-order transition, there is no transfer of heat, but the heat capacity does change. The volume changes to accommodate the increased motion of the wiggling chains, but it does not change discontinuously. Illustrative plots of specific volume vs. temperature are shown at the right for amorphous and crystalline polymers.



Melting

Property of the crystalline region

Below T_m : Ordered crystalline solid

Above T_m : Disordered melt

A first-order transition (see above)

Glass Transition

Property of the amorphous region

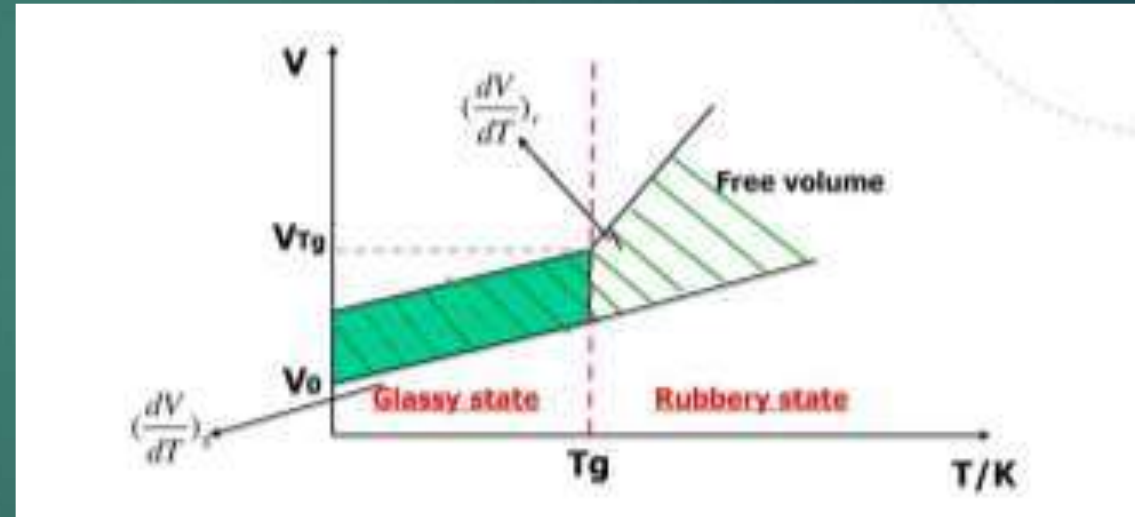
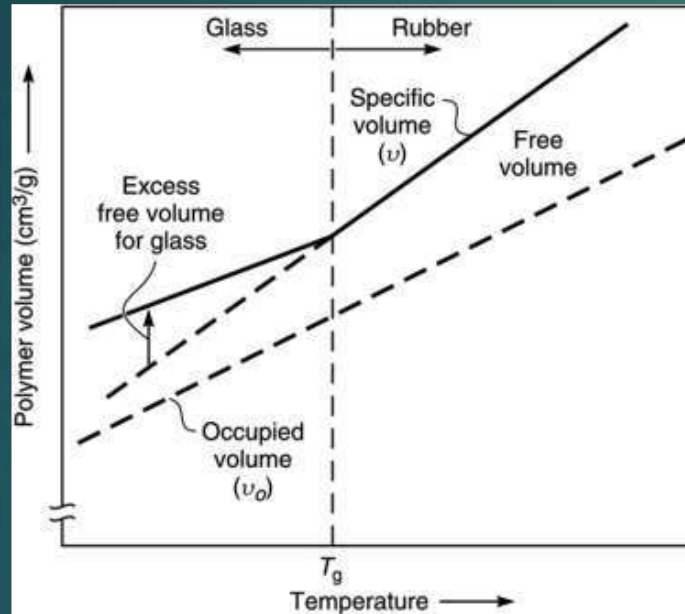
Below T_g : Disordered amorphous solid with immobile molecules

Above T_g : Disordered amorphous solid in which portions of molecules can wiggle around

A second order transition (see above)

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

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: 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

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

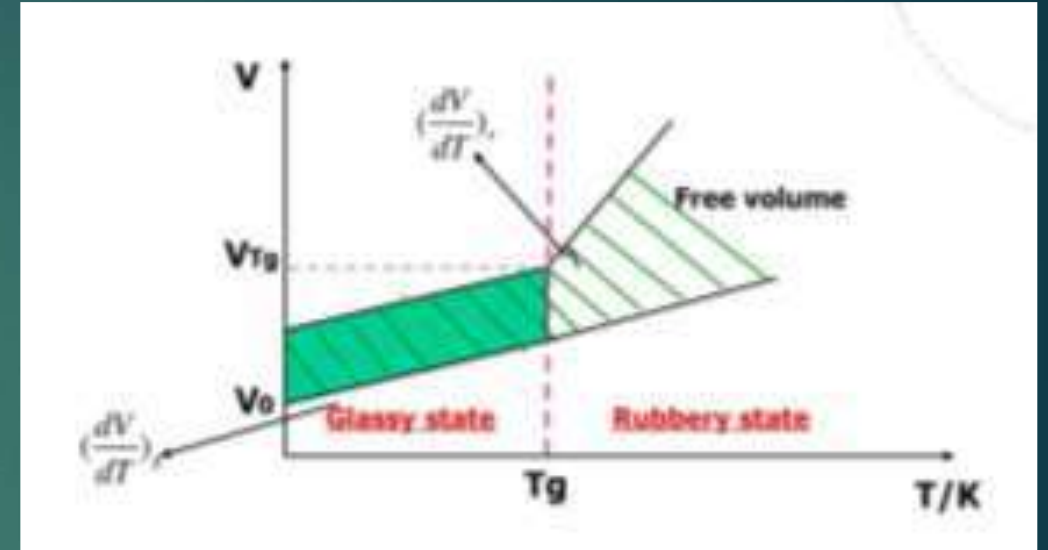
The two parameters E and A are usually determined from a plot of $\log \eta$ against $1/T$ which yields a straight line:

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

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

$$\eta = A e^{B/f(T)} \quad \longrightarrow \quad \log \eta = \log A + B / f(T)$$

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



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 .

Williams-Landel-Ferry (WLF) Equation:

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

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

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.

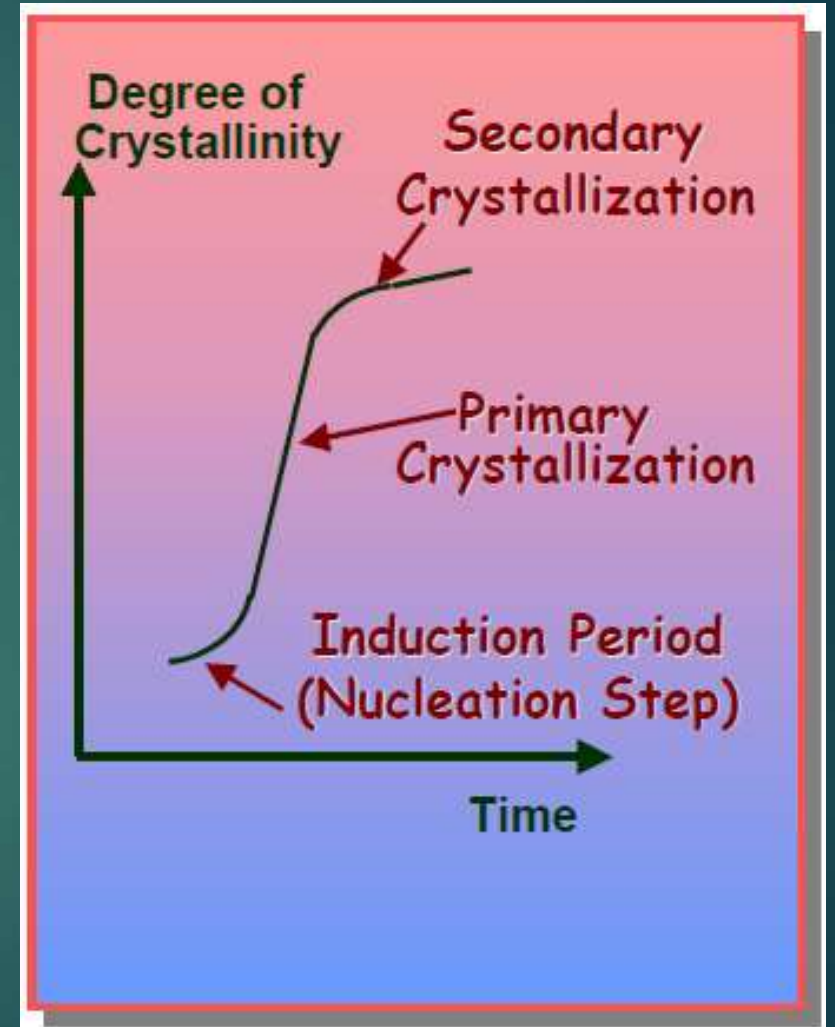
Crystallization Kinetics general Features

Crystallization kinetics are characterized in terms of two dominant processes, **nucleation kinetics** and **growth kinetics**, occurring during crystallization from solution.

Nucleation Kinetics - the rate of formation of a stable nuclei.

Growth Kinetics - the rate at which a stable nuclei grows to a macroscopic crystal.

- Induction period - formation of primary nuclei
- Primary crystallization - a period of fast spherulitic growth
- Secondary crystallization - a period of slower crystallization that occurs once the spherulites have impinged on one another



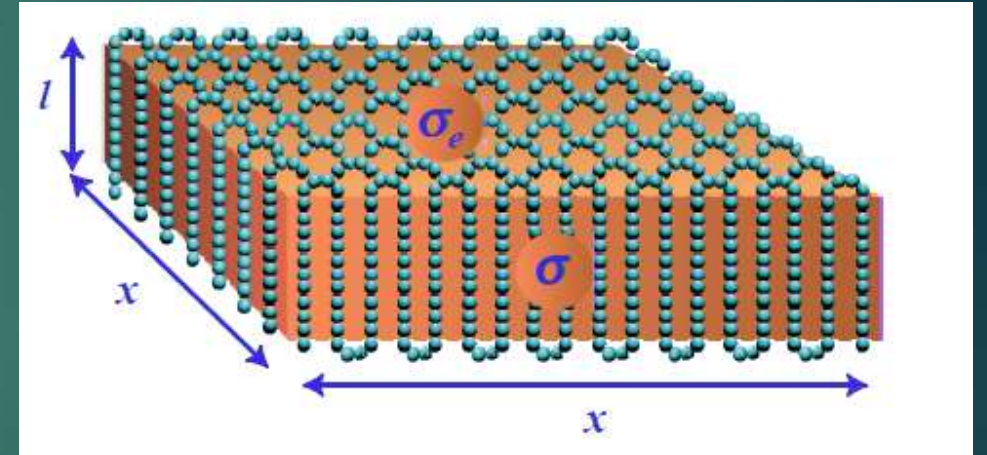
Thermodynamic Considerations

The free energy of this primary nucleus is given by

$$\Delta G_{cryst} = (4xl)\sigma + (2x^2)\sigma_e - (x^2l)\Delta g$$

The last term represents the free energy that we would obtain if all the segments were in the bulk.

- The first two terms are the excess free energy that must be “added in” to account for those segments at the surface.



Such a process involves an increase in the Gibbs free energy since the formation of a crystal results in an increase in the overall energy due to the presence of surfaces (surface energy)

Crystals irreversibly thicken on annealing - so they would like to get to the extended form

Critical Nucleus Size

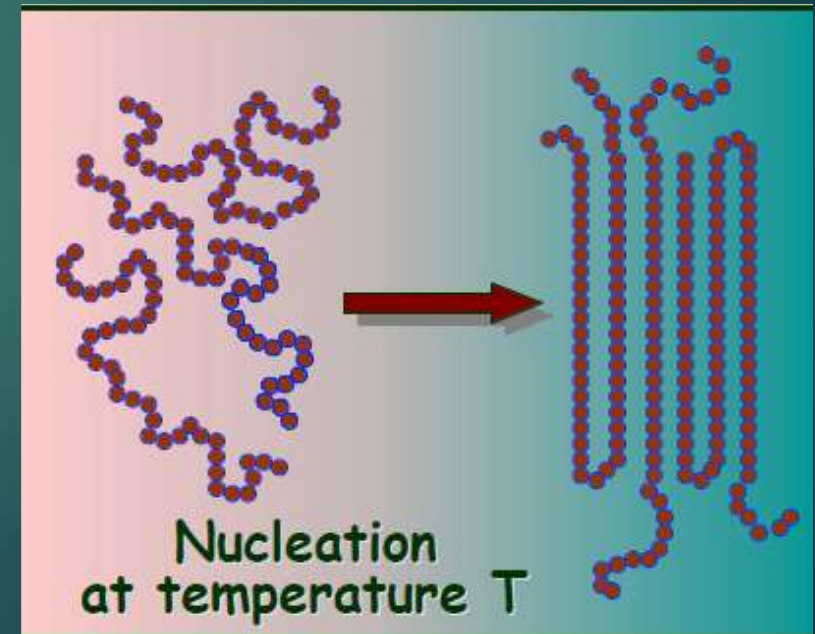
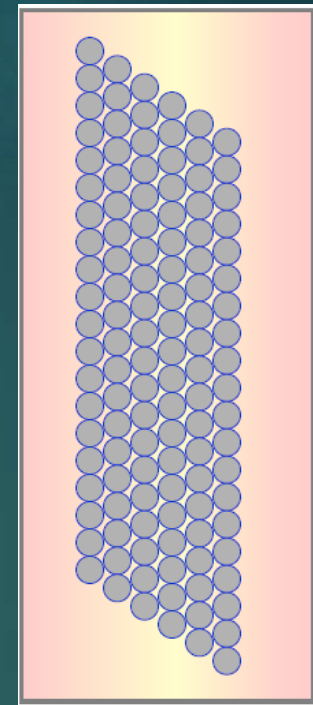
The critical nucleus size is given by the values of l and x that minimize

ΔG_{cryst} ;

$$\frac{\partial \Delta G}{\partial l} = \frac{\partial \Delta G}{\partial x} = 0$$

Solving the two simultaneous equations

$$l^* = \frac{4\sigma_e}{\Delta g}$$



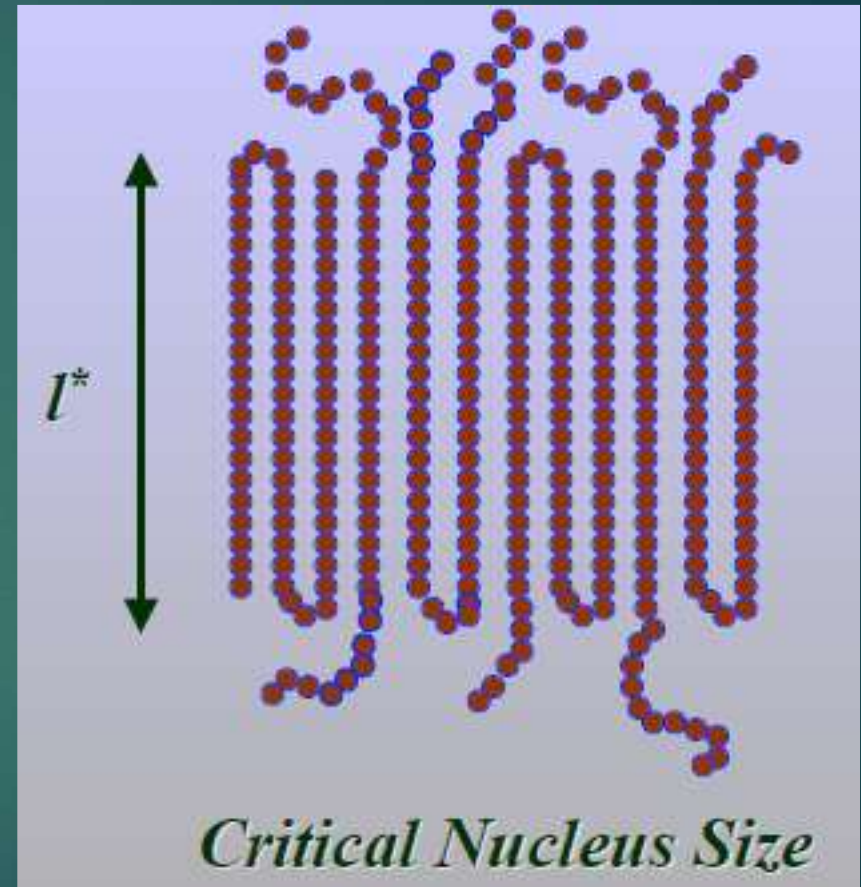
Substituting for Δg ;

$$l^* = \frac{4\sigma_e T_m^0}{\Delta h_f \Delta T}$$

where ΔT is the undercooling;

Note the inverse dependence of fold period on ΔT .

$$\Delta T = T_m^0 - T_c$$



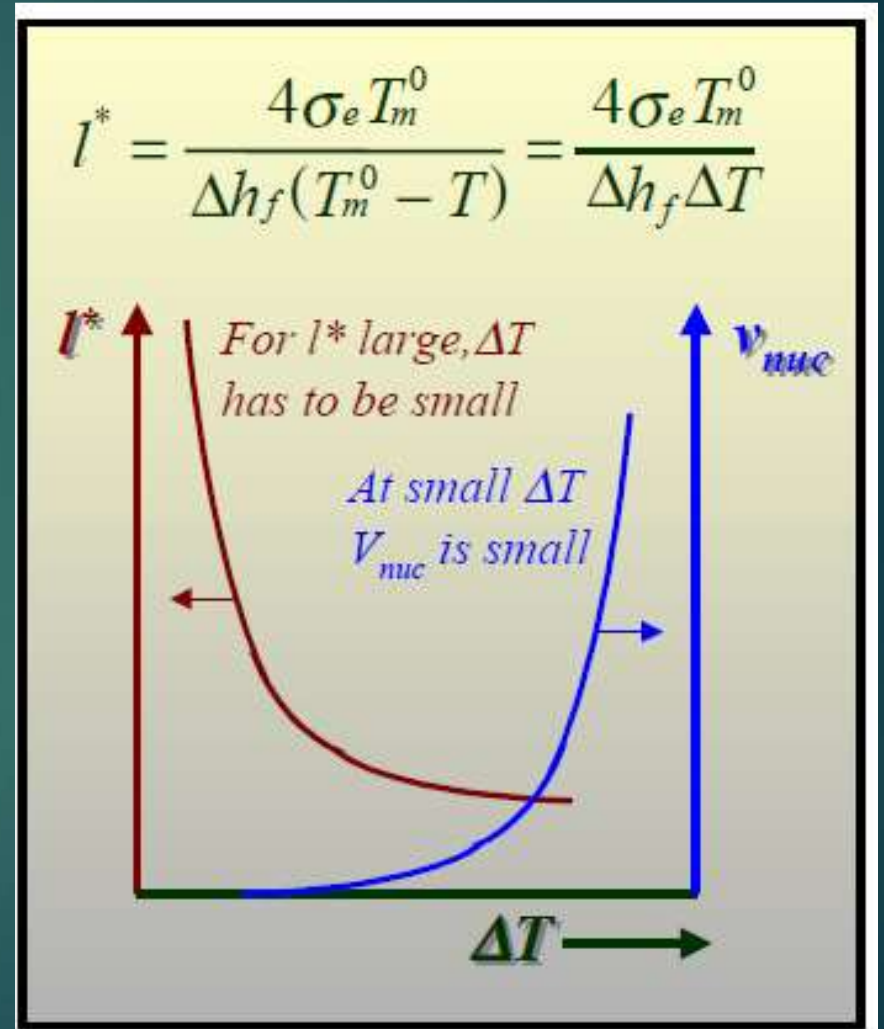
Also, at the equilibrium melting temperature, $T_c = T_m^0$ and only lamellae with infinite fold periods could grow.

The Rate of Primary Nucleation

An expression for the rate of nucleation can also be obtained:

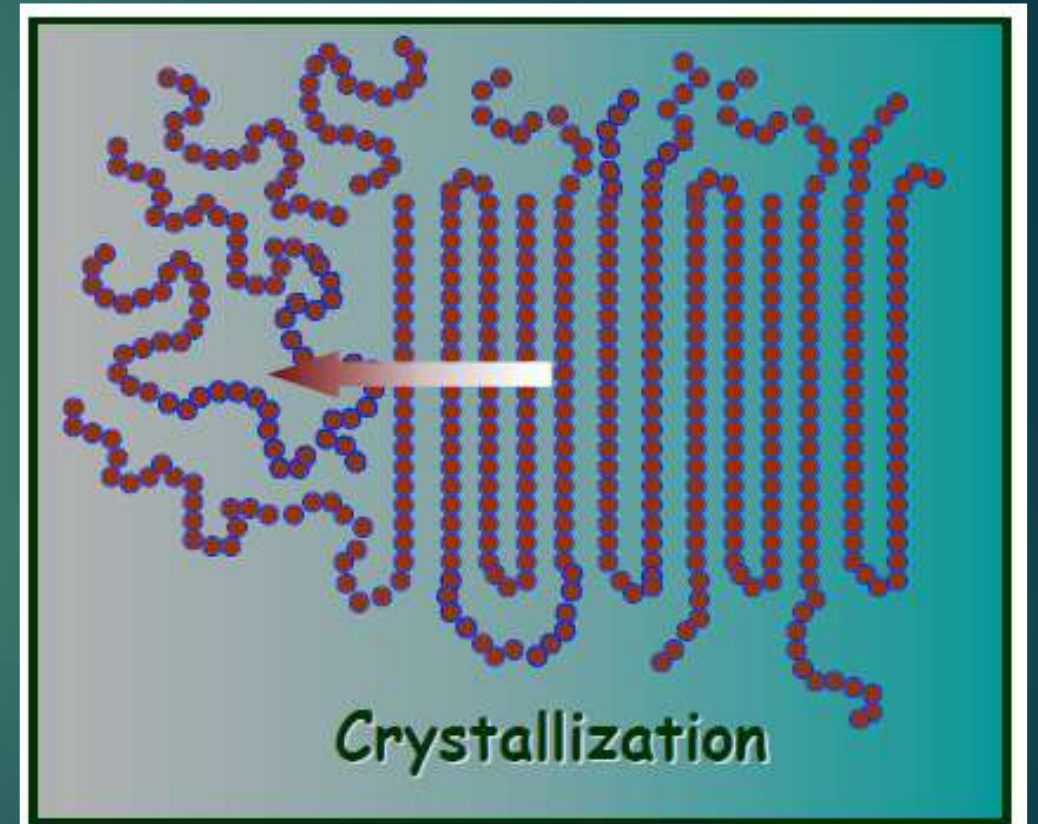
$$v_{nuc} \sim \exp\left[-\frac{\text{const.} \sigma^2 \sigma_e [T_m^0]^2}{\Delta h_f^2 k T_c [\Delta T]^2}\right]$$

Note that the rate of nucleation is vanishingly small at low undercoolings. Only nuclei with relatively short fold periods (compared to chain length) form at an appreciable rate.

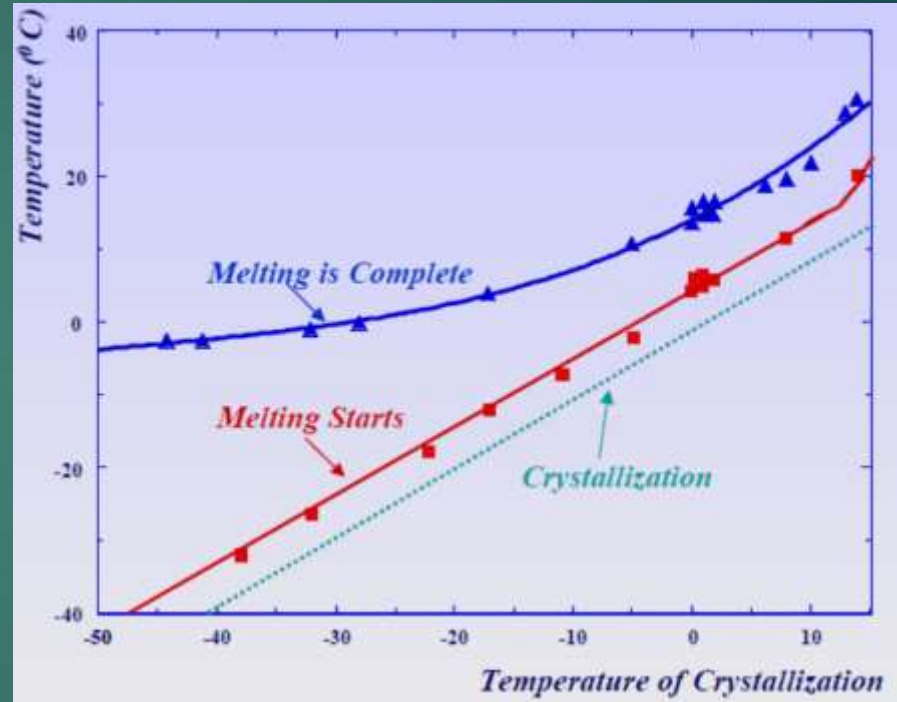
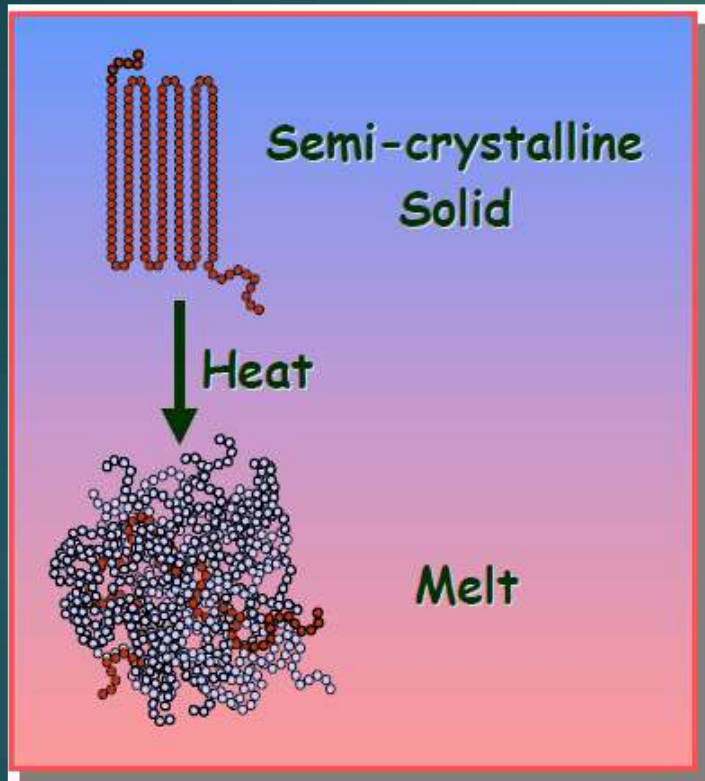


Primary Crystallization:

- Once a nucleus has been formed growth is predominantly in the lateral direction.
- There is a considerable increase in the fold period behind the lamellar front during crystallization from the melt



The Crystalline Melting Temperature



The Effect of Chemical Structure

Factors that Affect the Melting Temperature of Polymer Crystals

Polymer structure on melting temperatures has been obtained by considering the enthalpies and entropies of fusion. The relationship between free energy change ΔG with change in enthalpy content ΔH and entropy change ΔS at constant temperature is given by Eqn-----

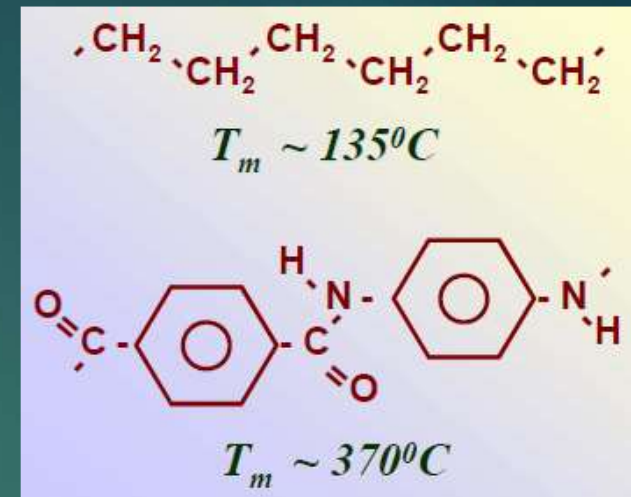
$$\Delta G_f = \Delta H_f - T\Delta S_f$$

And at Equilibrium

$$\Delta G_f = 0$$

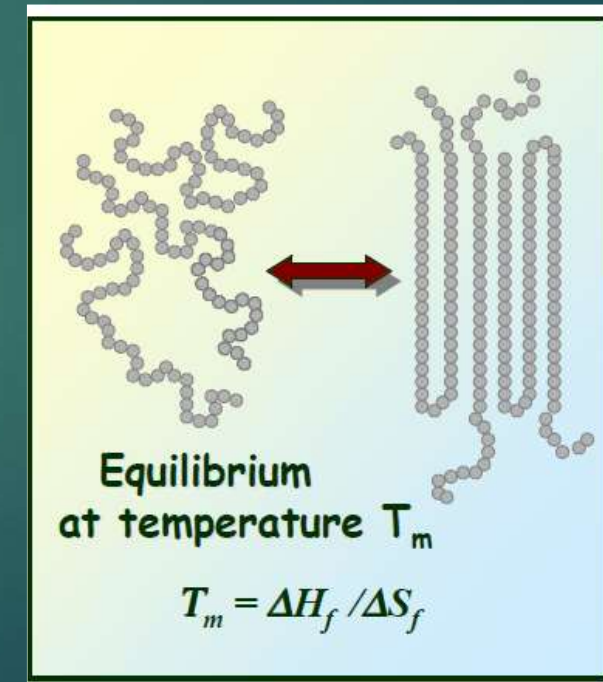
A reaction will occur if there is a decrease in the free energy, i.e., ΔG is negative. Since at the melting temperature, melting and crystallizing processes are in equilibrium ΔG is zero and the expression may be written as,

$$\text{Hence } T_m = \Delta H_f / \Delta S_f$$



Why?

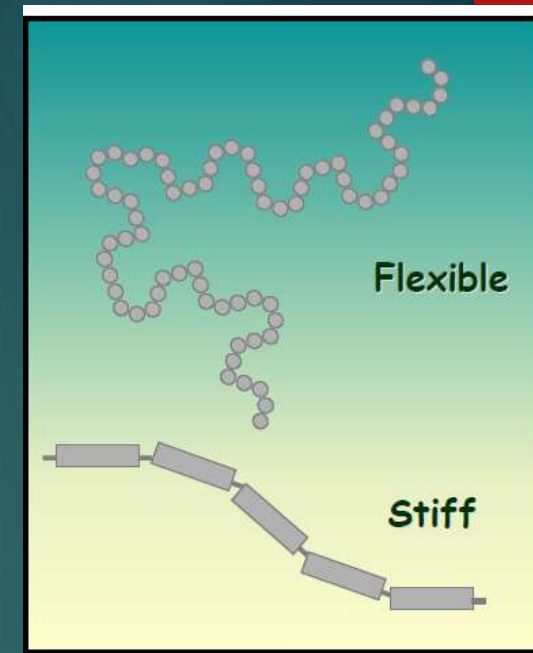
Change in disorder on melting is small because the highly crowded structure



Entropy and Chain Flexibility

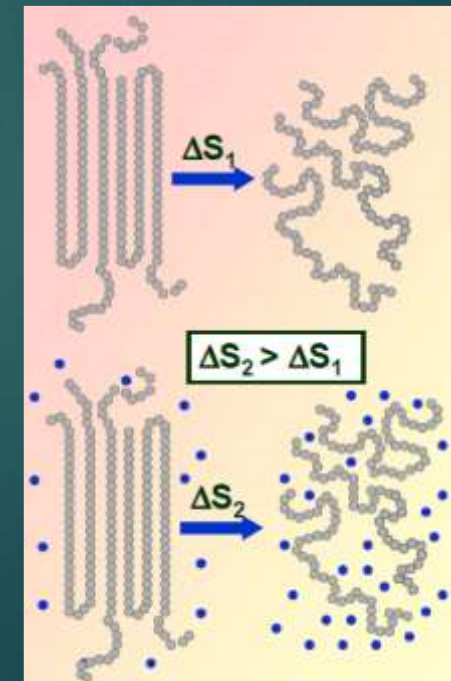
$$T_m = \Delta H_f / \Delta S_f$$

T_m decreases with increase the flexibility of a polymer



$$S = k \ln \Omega$$

$$\Delta S_f = k (\ln \Omega_{melt} - \ln \Omega_{crystal}) = \text{Large}$$



Few problems:

1. How do addition and condensation polymerization differ from each other?
2. Discuss cationic/anionic/radical mechanism of addition polymerization.
3. What are chain transfer reagent?
4. What are the assumption made during derivation of rate expression for condensation polymerization?
(Hints: Stoichiometric ratio of monomer, presence of acid catalyst)
5. Write a note on kinetic chain length and number average degree polymer.
6. Write down the different steps involved in initiation process of free radical polymerization.
7. Write down the W.L.F equation expressing the relation between viscosity and absolute temperature.
8. Explain Free Volume theory.
9. Describe the relation between entropy with chain flexibility.
10. Define primary and secondary crystallization.