

CRYSTALLINITY IN POLYMERS

- The degree of crystallinity influences the properties, and hence applications, of polymers.
- **Crystallinity of Melt Polymer is between 0 to 100 %, It cannot be 100%.**
- **Reason:** presence of extensive chain entanglements in the melt that make it impossible for the polymer chains to be fully aligned to form a 100% crystalline polymer during solidification.
- **Measurement of Crystallinity:**
 - ❑ **Density method**
 - **Basis of Measurement:** The crystalline regions in the polymer have a higher density than the non-crystalline amorphous regions and this difference in densities, which is relatively large (up to 20%), provides basis for the determination of the degree of crystallinity
 - ❑ **Wide-Angle X-ray Scattering (WAXS) method** (Young and Lovell, 1990)
 - **Basis of Measurement:** scattering from the crystalline regions gives relatively sharp peaks compared to a broad 'hump' produced by scattering from non-crystalline areas.

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- The degree of crystallinity can, in principle, be determined from the relative areas under the crystalline peaks and the amorphous hump.

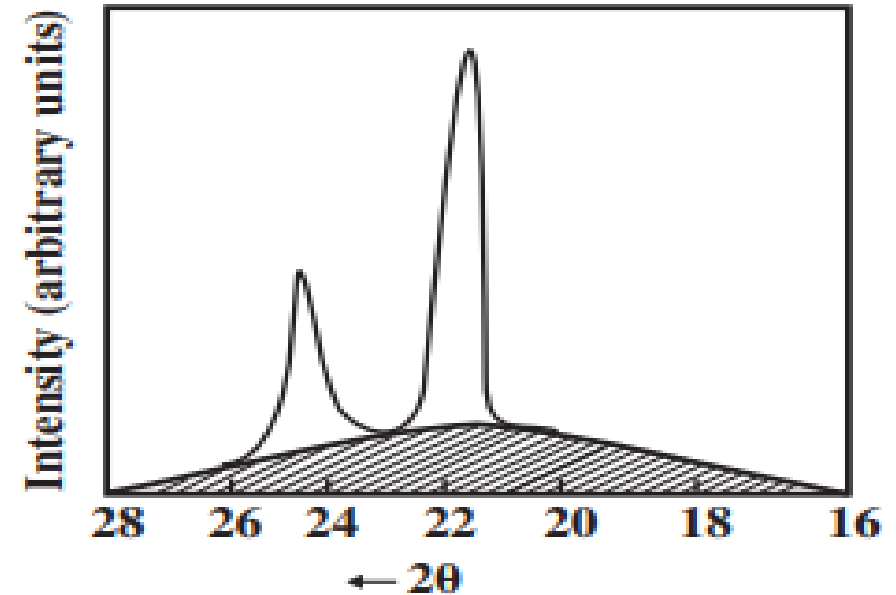
$$\diamond \text{Crystallinity} = A_c / A_T$$

Where,

A_c is the remaining area under the crystalline peaks and
 A_T is the area under the amorphous hump + Crystalline Peak Area

□ Differential Scanning Calorimetry (DSC)

- **Basis of Measurement:** comparing the enthalpy of fusion of the measured polymer matrix to the enthalpy of fusion of 100% crystalline material at the equilibrium melting point.

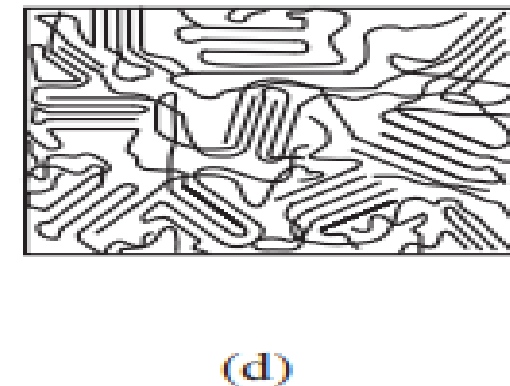
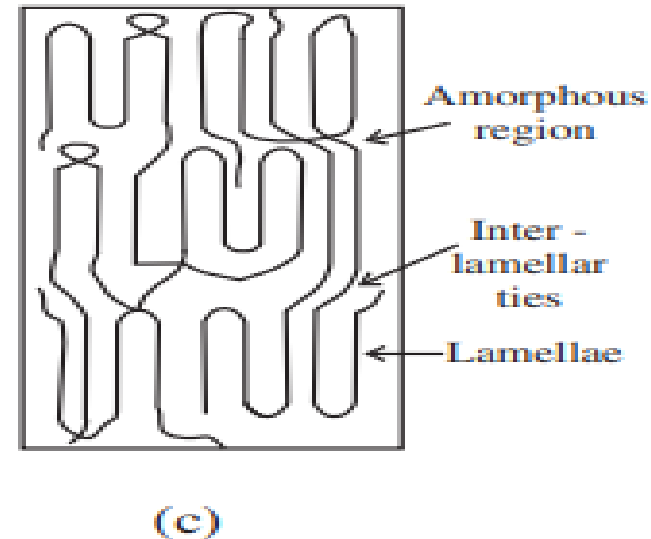
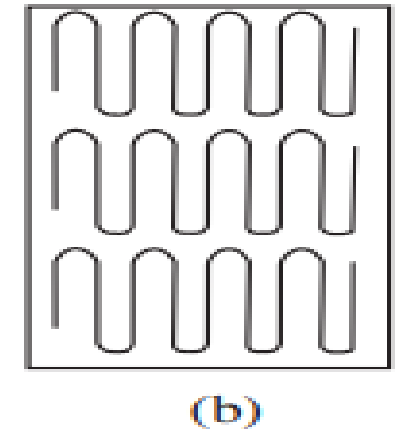
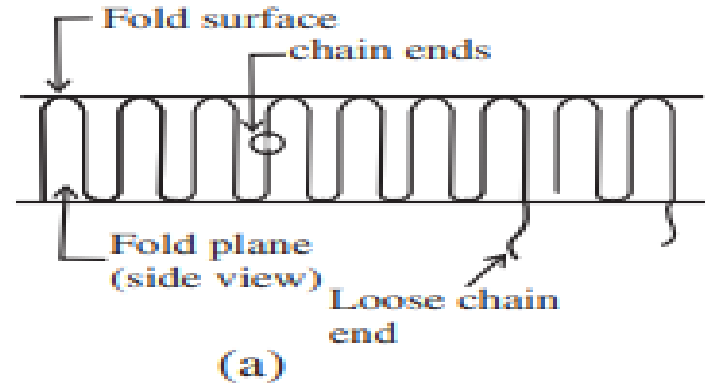


Typical WAXS curve for semicrystalline polyethylene where the intensity of scattering is plotted against diffraction angle 2θ . The amorphous hump is shown shaded.

STRUCTURE OF BULK POLYMERS

□ Lamellae:

- These are thin, flat platelets on the **order of 100 to 200 Å (0.01-0.02 micron) thick and several microns in lateral dimensions**, while polymer molecules are generally on the order of 1000 to 10,000 Å (Angstrom) long.
- Polymer chain axis is perpendicular to the plane of the lamellae (**revealed by:** electron diffraction).
- Therefore polymer molecules must therefore be folded back and forth within the crystal.
- This arrangement has been shown to be sterically possible.

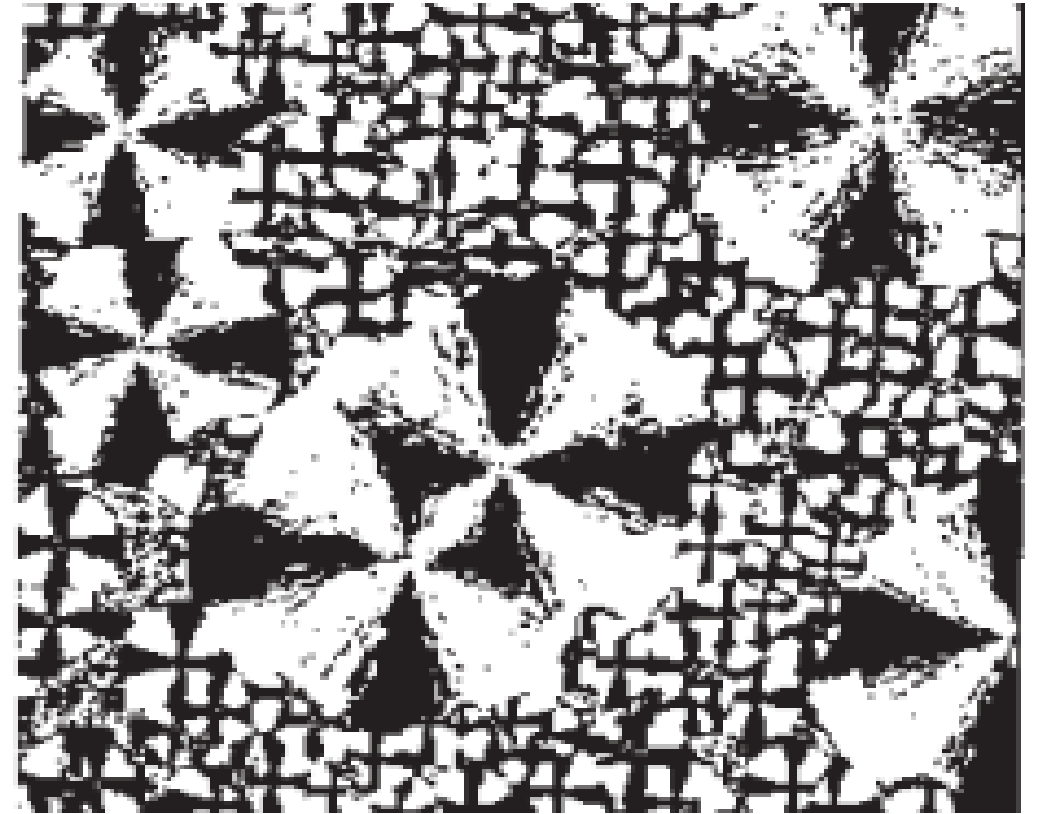


Schematic representation of (a) fold plane showing regular chain folding, (b) ideal stacking of lamellar crystals, (c) inter lamellar amorphous model, and (d) fringed micelle model of randomly distributed crystallites.

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❑ Spherulites:

- Prominent structural entity in a material crystallized from a polymer melt is the spherulite.
- Spherulites are aggregates of lamellar crystallites and the lamellar structure persists throughout the body of spherulites (**revealed by:** electron microscope).
- Spherulites are spherical aggregates, their sizes ranging from **microscopic to a few millimeters** in diameter.
- They are recognized by their characteristic appearance in the polarizing microscope (Price, 1958), seen as **circularly birefringent areas possessing characteristic Maltese cross optical patterns.**



Spherulites in a silicone like polymer, observed in the optical microscope between crossed polarizer. The large and small spherulites were grown by crystallization at different temperatures. (Adapted from Price, 1958.)

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The Avrami equation: $\theta = \exp(-Zt^n)$ or $\ln(-\ln \theta) = \ln Z + n \ln t$ (Taking logarithm twice)

- Derived in the general context of phase changes in metallurgy, has provided the starting point for many studies of polymer crystallization and spherulitic growth.
- The equation relates the fraction of a sample still molten (θ), to the time, t , which has elapsed since crystallization began, the temperature being held constant.
- For a given system under specified conditions, Z and n are constants and, in theory, they provide information about the nature of the crystallization process.

□ Calculation of n and Z :

- **Linearization of $\theta = \exp(-Zt^n)$:** A plot of $\ln(-\ln \theta)$ against $\ln t$ should thus be a straight line of slope n , making an intercept of $\ln Z$ with the vertical axis. In practice, this method of evaluating n and Z is very prone to error
- **Curve fitting methods using Eq. $\theta = \exp(-Zt^n)$.**
 - ✓ Avrami exponent (n) = 3 (crystallization takes the form of spherulitic growth of nuclei)
 - ✓ Avrami exponent (n) = 1-4 (other forms of nucleation and growth (Hay, 1971).)

Problem:-1

Q 1: Using the Avrami equation calculate approximately the extent of crystallization of polyethylene during cooling from the melt, if the melt is cooled in 1 s by quenching. Use $n = 3$ and $Z = 5$ (for time in seconds) as the average rate constant over the range of temperature in question.

Sol:

From Avrami equation,

$$\begin{aligned}\text{fractional completion of crystallization} &= 1 - \theta \\ &= 1 - \exp(-Zt^n) \\ &= 1 - \exp(-5) \\ &= 0.99\end{aligned}$$

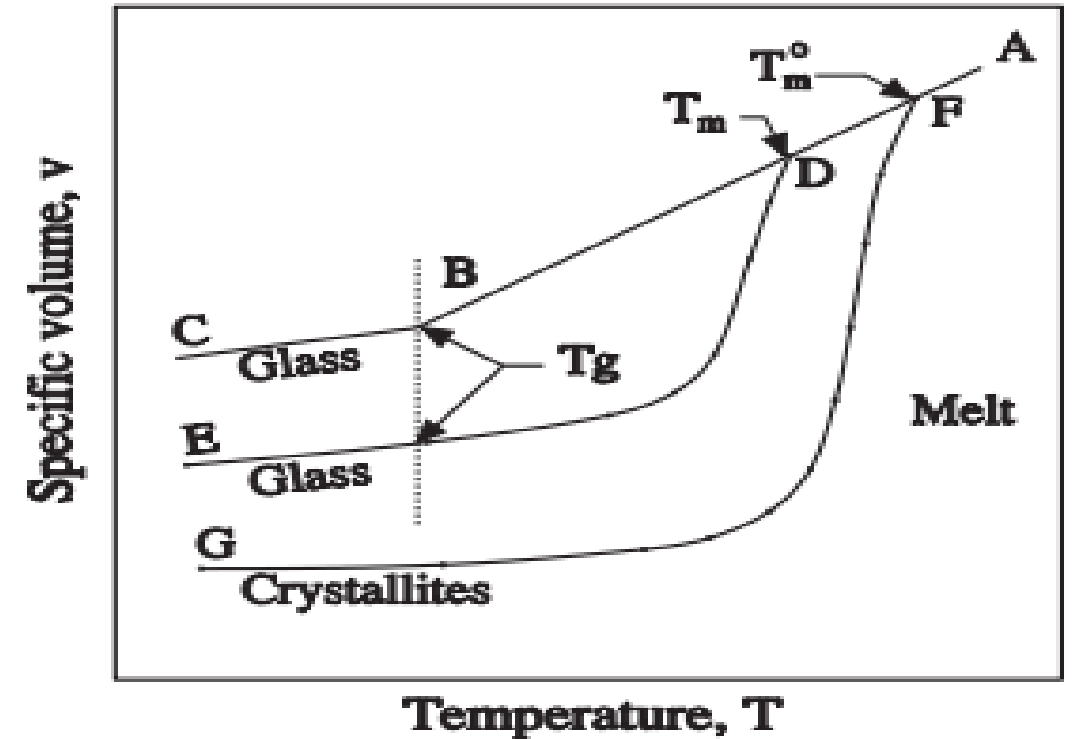
This means that crystallization occurs to 99% of its equilibrium extent (which is about 90% in high density polyethylene).

THERMAL TRANSITIONS IN POLYMERS

- The term “transition” refers to a change of state induced by changing the temperatures or pressure.
- Two major thermal transitions are the glass transition and the melting, the respective temperatures being called **T_g** and **T_m**.

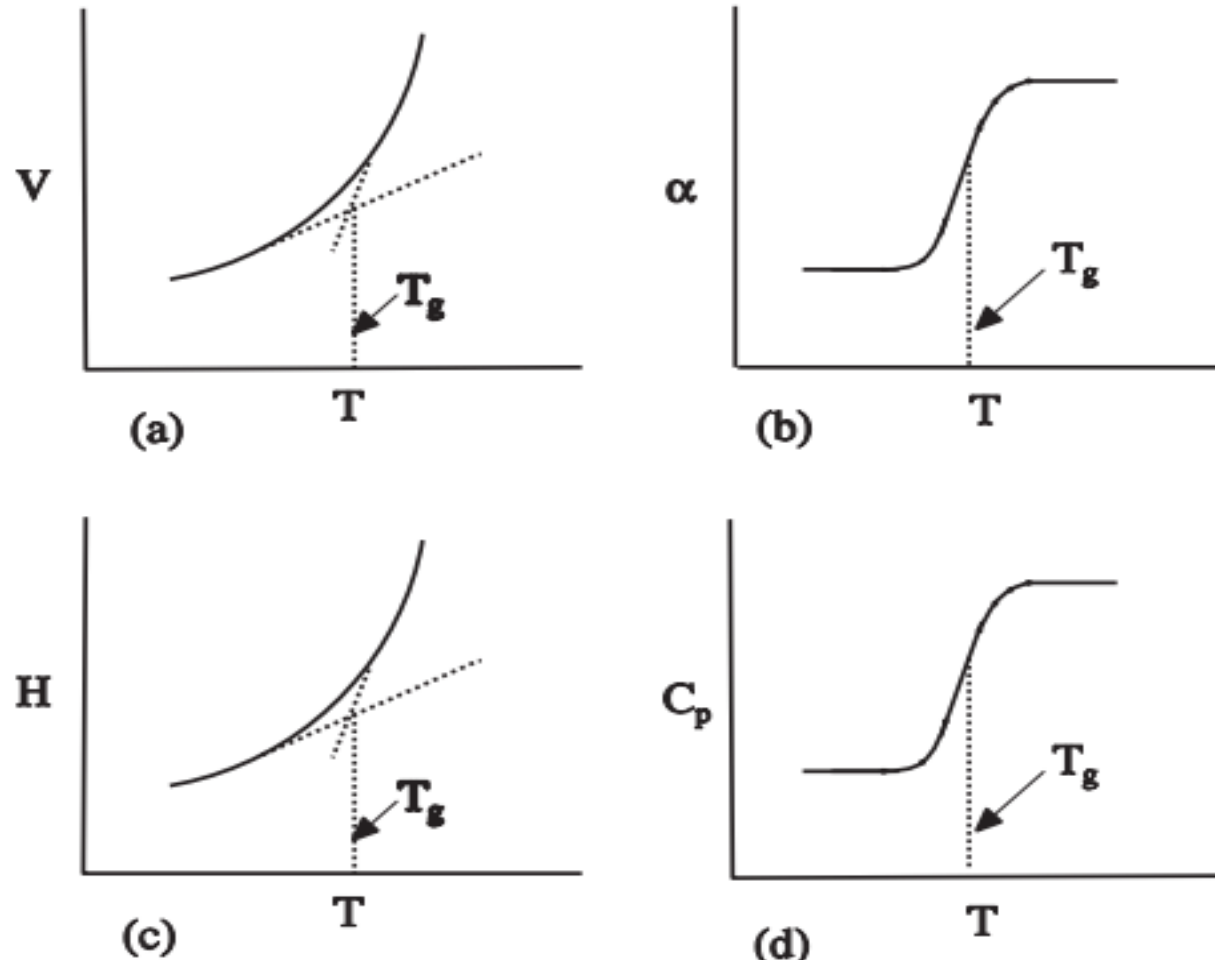
❑ **Curve ABC:** represents the volume change in amorphous polymers

- ✓ **Region C–B**, the polymer is a glassy solid and has the characteristics of a glass (including hardness, stiffness, and brittleness).
- ✓ As sample is heated, it passes through a **temperature T_g**, called the glass transition temperature, above which it softens and becomes rubberlike.
- ✓ T_g is an important temperature and **marks the beginning of movements of large segments of the polymer chain due to available thermal energy** (RT energy units/ mol)



Schematic representation of the changes of specific volume of a polymer with temperature for (a) a completely amorphous sample (A–B–C), (b) a semicrystalline sample (A– D–E), and (c) a perfectly crystalline material (A–F–G)

FIRST- AND SECOND-ORDER TRANSITIONS

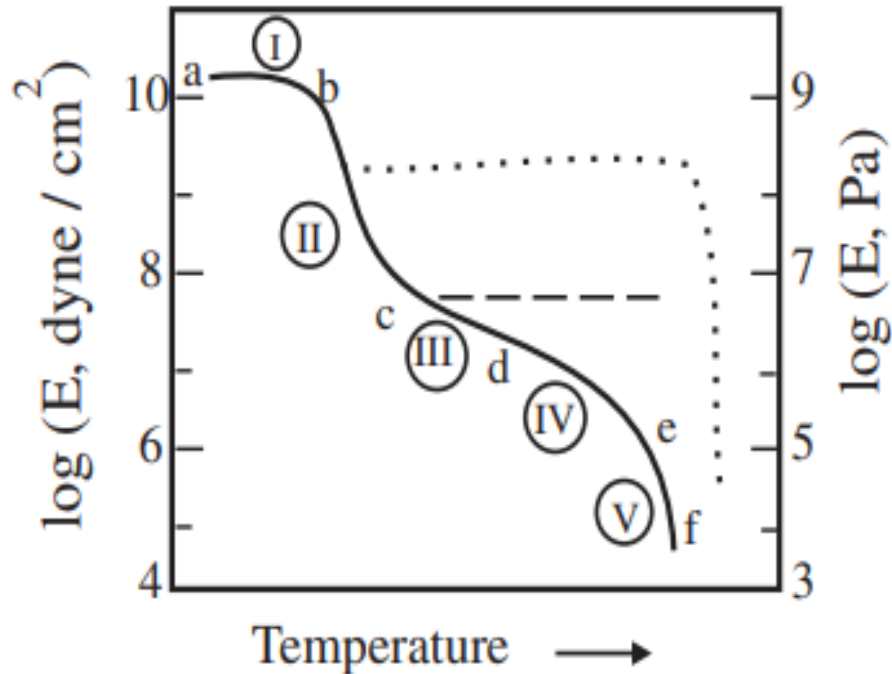


- In first order transitions, **such as melting**, there is a discontinuity in the volume-temperature plot or enthalpy-temperature plot at the transition temperature.
- In second-order transitions, only a change in slope occurs and there is thus a marked change in the first derivative or temperature coefficients, as illustrated herewith.
- For above reason T_g (glass transition temperature) is called a second-order transition.

Schematic representations of volume (V) and enthalpy (H) variations with temperature. Also shown are variations with temperature of the volume coefficient of expansion (α) and the heat capacity (C_p), which are, respectively, the first derivatives of V and H with respect to temperature (T).

REGIONS OF VISCOELASTIC BEHAVIOR

Regions of Viscoelastic Behavior



Five regions of viscoelastic behavior for a linear, amorphous polymer : I (a to b), II (b to c), III (c to d), IV (d to e), and V (e to f). Dotted line () shows the effect of crystallinity and dashed line () that of crosslinking. (After Sperling, 1986.)

Region I (a to b), described as the glassy region, the polymer is usually brittle. Common examples are polystyrene and poly(methyl methacrylate) at room temperature. Young's modulus for many polymers in this region just below the glass transition temperature is typically of the order of 3×10^{10} dyne/cm² (3109 Pa).

Region II (b to c) in Fig. 6 is the glass transition region where the modulus drops typically by a factor of about one thousand over 20-30 C. In this region, polymers exhibit tough leather-like behavior. The glass transition temperature, T_g , is often taken at the maximum rate of decline of the modulus

Region III (c to d) in Fig. 6 is described as the rubbery plateau region. The modulus after a sharp drop, as described above, again becomes nearly constant in this region with typical values of 2×10^7 dyne/cm² (2106 Pa) and polymers exhibit significant rubber-like elasticity.

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Region IV is the rubbery flow region, which is exhibited by un-crosslinked linear polymers when heated past the rubbery plateau region. In this region, the polymer exhibits both rubber elasticity and flow properties depending on the time scale of the experiment

Region V (e to f) in Fig. 6 is the liquid flow region, which is reached at still higher temperatures where the increased kinetic energy of the chains permits them to wriggle out through entanglements rapidly and move as individual molecules, often producing highly viscous flow. This is the melting temperature and it is always above the glass transition temperature.

FACTORS AFFECTING T_g

T_g marks the onset of molecular motion, a number of factors that affect rotation about links (necessary for movement of polymer chains) will also influence the T_g of a polymer which include,

- (a) chain flexibility
- (b) molecular structure (steric effects)
- (c) molecular weight
- (d) branching and crosslinking

- The flexibility of the chain is 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 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($-\text{C}_6\text{H}_4-$).

PROBLEM; Presence of flexible pendant groups reduces the glass transition of the polymer, whereas bulky or stiff side groups increase it. Why?

Answer: In general, factors that increase the energy required for the onset of molecular motion increase T_g and those that decrease the energy requirement lower T_g . Flexible pendant groups act as “inherent diluents” and lower the frictional interaction between chains, reducing the T_g thereby. Bulky or stiff side groups, on the other hand, increase interchain friction and energy requirement for molecular motion, thereby increasing T_g .

FACTORS AFFECTING T_M

Factors affecting T_m can be derived from the application of macroscopic thermodynamics

$$\Delta G_m = \Delta H_m - T_m \Delta S_m$$

At melting since change in Gibbs energy will be zero. Thus for high melting it correspond to high enthalpy or low entropy change.

- Chain flexibility has a direct bearing on the melting point. Insertion of groups that stiffen the chain increases T_m , while introducing flexible groups into the chain lowers the value of T_m (cf. Factors Affecting T_g).
- if the chain is substantially branched, reducing the packing efficiency, the crystalline content is lowered and hence the melting point. A good example is low-density polyethylene where extensive branching lowers the density and T_m of the polymer.

Table 2.2 T_m , T_g , and T_g/T_m for Some Selected Polymers

Polymer	T_m , °C	T_g , °C	T_g/T_m , °K / °K
Silicone rubber	- 58	- 123	0.70
Polyethylene	135	- 68	0.50
Polypropylene	176	- 8	0.59
Polystyrene	240	100	0.73
Poly(methyl methacrylate)	200	105	0.69
Poly(vinyl chloride)	180	82	0.78
Poly(vinylidene fluoride)	210	- 39	0.48
Polyisoprene	28	- 70	0.67
Nylon-6,6	265	50	0.60

Source: Williams, 1971.

RELATION BETWEEN T_G AND T_M

- Boyer (1954) and Beamen (1952) inspected data for a large number of semicrystalline polymers, some of which are shown in Table . They found that the **ratio T_g/T_m ranged from 0.5 to 0.75** when the temperatures are expressed in degrees Kelvin.
- The ratio is closer to **0.5 for symmetrical polymers** such as polyethylene and polybutadiene, but closer to **0.75 for unsymmetrical polymers**, such as polystyrene and polyisoprene.
- The difference in these values may be related to the fact that in unsymmetrical chains with repeat units of the type $-(CH_2-CHX)-$ — an additional restriction to rotation is imposed by steric effects causing T_g to increase, and conversely, an increase in symmetry lowers T_g .

Problem A new atactic polymer of the type $-(CH_2-CHX)-$ — has a T_m of 80°C. What is its T_g likely to be ?

Solution:

The polymer being unsymmetrical, T_g/T_m may be assumed to be about 0.75.

$$T_g/T_m = 0.75, T_m = 80^\circ\text{C} = 353\text{K}$$

$$T_g = 0.75 \times 353 = 265\text{ kelvin} = -8^\circ\text{C}.$$

THEORETICAL TREATMENT OF GLASS TRANSITION

- Molecular motion in liquids depends on the presence of holes or voids, i.e., places where there are vacancies [**Hole theory of liquids (Eyring, 1936)**]
- A similar model can also be constructed for the motion of polymer chains, the main difference being that more than one “hole” will now be required to be in the same locality for the movement of polymer chain segments.
- On this basis, the observed specific volume of a sample (v) can be described as a sum of the volume actually occupied by the polymer molecules (v_0) and the free volume or empty spaces (v_f), in the system [see Fig. 8(a)], i.e.,

$$v = v_0 + v_f$$

- Same free volume exists at the respective glass temperature (T_g) independent of molecular weight and this same free volume is retained at all temperatures below T_g . (**By iso-free-volume state theory of Fox and Flory (1950, 1954),**)
- **Reason:** Temperatures below T_g the segmental rotations become frozen and the holes that are present at the glass temperature become immobilized.

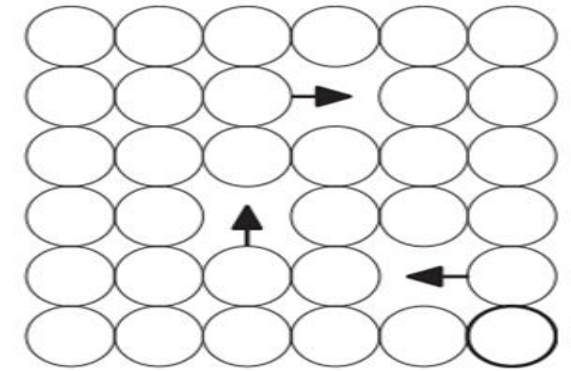


Fig. 7: Figure: A quasi-crystalline lattice of molecules (circles) exhibiting vacancies or holes. The arrow indicates molecular motion.

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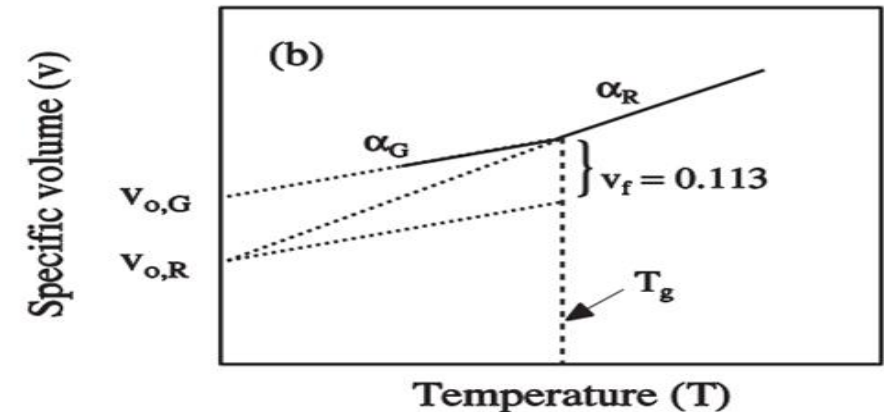
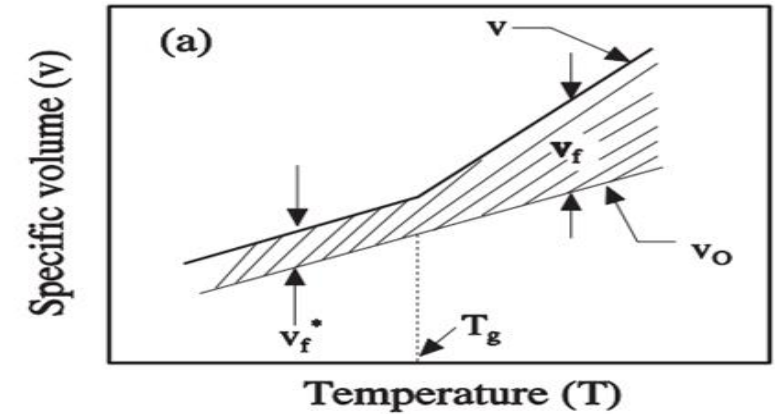
□ For $T < T_g$:

- ✓ Free volume remains nearly unchanged (Holes are no longer able to diffuse out of the structure),
- ✓ Internuclear separation can still adjust itself (thermal vibrations of the atoms become reduced)

□ For $T > T_g$:

- ✓ Both the internuclear separation between segments of neighboring chains and the number and size of holes adjust themselves continuously with changing temperature (provided sufficient time is allowed for segmental diffusion).

- ✓ The coefficient of expansion above T_g is therefore higher than that below T_g



(a) Schematic representation of the variation of specific volume with temperature. The free volume (shaded area) is assumed to be constant at v_f below T_g and to increase as the temperature is raised above T_g . (b) Schematic illustration of free volume (Simha and Boyer, 1962).

CONTINUE ...

- ❖ Simha and Boyer (1962) postulated that the free volume at $T = T_g$ should be defined as:

$$v_f = v - v_{0,R}(1 + \alpha_G T) \quad (2.14)$$

Where,

v_f = Specific free volume

$v_{0,R}$ = Extrapolated specific volume

v = Specific volume (i.e., volume per unit mass).

α_G = Expansion in the glassy state (occurs at nearly constant free volume);

$(\alpha_G)T$ is proportional to the occupied volume (Shown in Figure 2.23)

- ❖ $v_{0,R}$ and $v_{0,G}$ are the hypothetical specific volumes extrapolated from melt or rubbery state to 0°K using α_R and α_G as the coefficients of expansion. Thus at $T = T_g$,

$$v = v_{0,R}(1 + \alpha_R T) \quad (2.15)$$

CONTINUE ...

and

$$v = v_{0,G}(1 + \alpha_G T) \quad (2.16)$$

Substitution of v from Eq. (2.15) into Eq. (2.14) at $T = T_g$ leads to the following expression for free-volume fraction (Simha and Boyer, 1962)

$$(\alpha_R - \alpha_G)T_g = v_f/v_{0,R} \simeq v_f/v \quad (2.17)$$

[since $v_f \ll v_{0,R}$ and $\alpha_G T \ll 1$ in Eq. (2.14)]

- Simha and Boyer (1962) postulated that the free-volume fraction defined by Eq. (2.17) is the same for all polymers, that is,

$$(\alpha_R - \alpha_G)T_g = \text{constant} = K_1 \quad (2.18)$$

- For most of the polymers:

$$(\alpha_R - \alpha_G)T_g = 0.113 \quad (2.19)$$

CONTINUE ...

- ✓ Free volume fraction at the glass transition temperature is the same for all polymers and constitutes 11.3% of the total volume in the glassy state.
- ✓ (It is interesting to note that many simple organic compounds show a 10% volume increase on melting.)
- ✓ This is the largest of the theoretical values of free volume derived, while other early estimates yielded a value of about 2%.

A less exact but simpler relationship is:

$$\alpha_R T_g = \text{constant} = K_2 \quad (2.20)$$

The fractional free volume defined as (at $T=T_g$)

$$(v - v_{0,R})/v = \alpha_R T / (1 + \alpha_R T) = \alpha_R T + O[(\alpha_R T)^2] \quad (2.21) \quad \text{(Neglect the contribution of } \alpha_{GT} \text{ to the total expansion)}$$

From the values of α_R determined for various polymers (Simha and Boyer, 1962) Eq. (2.20) is given as

$$\alpha_R T_g = K_2 = 0.164 \quad (2.22)$$

- ✓ The quantities K_1 and K_2 provide a criterion for the glass transition temperature. They are especially useful for approximate estimation of T_g for new polymers or semicrystalline polymers, where T_g may be obscured.

Problem:-

Q: For the polymers for which $\alpha_f = 4.8 \times 10^{-4} \text{ K}^{-1}$, estimate a value of T_g , assuming that these polymers also obey the S-B relationship given by Eq. (2.19).

Answer: Since the free volume is assumed constant below T_g , the volume change with temperature in the glassy region is only due to the occupied volume, while the volume change in the rubbery region above T_g has contributions from both the occupied volume and the free volume. Therefore, one can write, approximately,

$$\alpha_R - \alpha_G \simeq \alpha_f = 4.8 \times 10^{-4} \text{ }^\circ\text{K}^{-1}$$

- Substituting this in Eq. $(\alpha_R - \alpha_G)T_g = 0.113$

$$T_g \simeq 0.113 / (4.8 \times 10^{-4} \text{ }^\circ\text{K}^{-1}) = 235 \text{ }^\circ\text{K} \equiv -38^\circ\text{C}.$$

- This value is in the range of the T_g 's observed for many polymers.

PROBLEM:-

Q : A new linear amorphous polymer is found to have glass transition at 90°C and its cubic coefficient of thermal expansion is $5.6 \times 10^{-4} \text{ K}^{-1}$ at 120°C. Can this polymer be used for an application that requires the cubic coefficient of thermal expansion to be less than $5 \times 10^{-4} \text{ K}^{-1}$ at 60°C (Sperling, 1989) ? [Assume $(\alpha_R - \alpha_G)$ to be roughly constant at $3.2 \times 10^{-4} \text{ K}^{-1}$ (Sharma et al., 1972).]

Sol: Above T_g , the expansion coefficient is α_R . Hence $\alpha_R = 5.6 \times 10^{-4} \text{ K}^{-1}$,

$$T_g = 90^\circ\text{C} \equiv 363^\circ\text{K}$$

$$\alpha_R T_g = (5.6 \times 10^{-4} \text{ }^\circ\text{K}^{-1})(363^\circ\text{K}) = 0.203$$

From Eq. : $(\alpha_R - \alpha_G)T_g = 0.113$

$$\alpha_G T_g = 0.203 - 0.113 = 0.09$$

$$\alpha_G = 0.09/(363^\circ\text{K}) = 2.5 \times 10^{-4} \text{ }^\circ\text{K}^{-1}$$

Also from the approximate relationship $\alpha_R = \alpha_G + 3.2 \times 10^{-4} \text{ K}^{-1}$. Therefore,

$$\alpha_G = 5.6 - 3.2 \times 10^{-4} = 2.4 \times 10^{-4} \text{ K}^{-1}$$

Hence the polymer is likely to satisfy the thermal expansivity requirement.

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Above T_g there is an important contribution to v_f from the expansion of the polymer in the rubbery or molten state. The free volume above T_g can thus be expressed by (from Fig. 2.23(a)) :

$$v_f = v_f^{\star} + (T - T_g)(\partial v / \partial T) \quad (2.23)$$

Dividing through by \mathcal{V} gives:

$$f_T = f_g + (T - T_g)\alpha_f \quad (2.24)$$

Williams, Landel, and Ferry (1955) proposed that the logarithm of viscosity varies linearly with $1/f$ above T_g , so that

$$\ln\left(\frac{\eta_T}{\eta_g}\right) = B\left(\frac{1}{f_T} - \frac{1}{f_g}\right) \quad (2.25)$$

where η_T and η_g are viscosities at T and T_g , respectively, and B is a constant.

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Substituting Eq. (2.23) in Eq. (2.25) gives

$$\ln\left(\frac{\eta_T}{\eta_g}\right) = B\left[\frac{1}{f_g + \alpha_f(T - T_g)} - \frac{1}{f_g}\right] \quad (2.26)$$

$$= -\frac{B\alpha_f(T - T_g)}{f_g[f_g + \alpha_f(T - T_g)]} \quad (2.27)$$

Dividing both numerator and denominator by α_f , Eq. (2.27) is rewritten as

$$\ln\left(\frac{\eta_T}{\eta_g}\right) = -\frac{(B/f_g)(T - T_g)}{(f_g/\alpha_f) + (T - T_g)} \quad (2.28)$$

This is one form of the WLF equation. Since the amount of flow is proportional to the flow time t and density P and inversely proportional to viscosity, one may write (Cowie, 1991) :

$$\frac{\rho_T \cdot t_T}{\eta_T} = \frac{\rho_g \cdot t_g}{\eta_g} \quad (2.29)$$
$$\left(\frac{\eta_T}{\eta_g}\right) = \left(\frac{\rho_T \cdot t_T}{\rho_g \cdot t_g}\right) \simeq \left(\frac{t_T}{t_g}\right)$$

CONTINUE...

Neglecting small differences in density. Substituting Eq. (2.29) in Eq. (2.28) one then obtains

$$\log_{10} \left(\frac{t_T}{t_g} \right) = \frac{-(B/2.303 f_g)(T - T_g)}{(f_g/\alpha_f) + (T - T_g)} \quad (2.30)$$

This can be compared with another form of the WLF equation written as

$$\log_{10} a_T = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (2.31)$$

Where, a_T is called the reduced variables shift factor, and
C1 and C2 are constants (can be obtained from experimental data).

✓ For many linear polymers, irrespective of chemical structure,
C1 = 17.44 and
C2 = 51.6 when T_g is the reference temperature.

The WLF equation is then written as:

$$\log_{10} a_T = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (2.32)$$

QUANTITATIVE EFFECTS OF FACTORS ON T_g

- The lower the molecular weight of a polymer sample, i.e., the greater the number of chain ends, the higher becomes the contribution to the free volume when these begin moving; consequently T_g decreases as the molecular weight of the sample is lowered.
- This behavior can be approximated to an equation of the form (Fox and Flory, 1950, 1954)

$$T_g = T_{g,\infty} - K/M$$

Where,

M = Molecular weight

$T_{g\infty}$ = Value of T_g for a polymer sample of infinite molecular weight and

K is a constant

In a polymer sample of molecular weight \overline{M}_n & density ρ ,

The number of chains per unit volume is $\rho N_{Av}/\overline{M}_n$

where, N_{Av} is Avogadro's number, and so the

The number of chain ends per unit volume is $2 \rho N_{Av}/\overline{M}_n$

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If θ is the contribution of one chain end to the free volume then the total fractional free volume due to all chain ends, f_c , will be given by

$$f_c = 2\rho N_{Av}\theta/\overline{M}_n$$

It can be argued that f_c is the extra amount of free volume in a low molecular weight compound, as compared to a polymer of infinite molecular weight, that causes lowering of the glass transition temperature from $T_{g,\infty}$ to T_g . So f_c will be equivalent to the free volume expansion between $T_{g,\infty}$ and T_g , which means that

$$f_c = \alpha_f (T_{g,\infty} - T_g)$$

where α_f is the thermal expansion coefficient of the free volume. Combining above two equations and rearranging one then gets

$$T_g = T_{g,\infty} - \frac{2\rho N_{Av}\theta}{\alpha_f \overline{M}_n}$$

which is exactly of the same form as Eq. (2.35) when $K = 2\rho N_{Av}\theta/\alpha_f$

PROBLEM:-

Problem: A polydisperse polystyrene sample was fractionated into four components of various molecular distributions and T_g of each fraction was measured:

Component	Wt. fraction (w)	\overline{M}_n	T_g ($^{\circ}\text{K}$)
1	0.05	1.5×10^6	378.9
2	0.41	4.8×10^5	378.5
3	0.39	1.2×10^5	377.2
4	0.15	3.7×10^4	373.3

- (a) Obtain a relation between T_g and molecular weight.
- (b) Calculate the T_g value of the polydisperse polystyrene.

Answer: Answer: (a) T_g is plotted against $1/\overline{M}_n$ in Fig. 2.24 according to Eq.(2.35). From the intercept and slope of the straight line plot,

$$T_{g,\infty} = 379^\circ\text{K}, \quad K = 2.1 \times 10^5 \text{ } ^\circ\text{K g mol}^{-1}$$

(b) From the definition of number average molecular weight:

$$\frac{1}{\overline{M}_n} = \frac{w_1}{M_1} + \frac{w_2}{M_2} + \frac{w_3}{M_3} + \frac{w_4}{M_4}$$

Using Eq. (2.35),

$$\begin{aligned} \frac{T_{g,\infty} - T_g}{K} &= \frac{w_1(T_{g,\infty} - T_{g,1})}{K} + \frac{w_2(T_{g,\infty} - T_{g,2})}{K} \\ &\quad + \frac{w_3(T_{g,\infty} - T_{g,3})}{K} + \frac{w_4(T_{g,\infty} - T_{g,4})}{K} \end{aligned}$$

Simplifying,

$$\begin{aligned} T_g &= w_1 T_{g,1} + w_2 T_{g,2} + w_3 T_{g,3} + w_4 T_{g,4} \\ &= (0.05)(378.9^\circ\text{K}) + (0.41)(378.5^\circ\text{K}) + (0.39)(377.2^\circ\text{K}) + (0.15)(373.3^\circ\text{K}) \\ &= 377.2^\circ\text{K} \end{aligned}$$

Therefore the T_g of unfractionated polymer sample is 104°C .

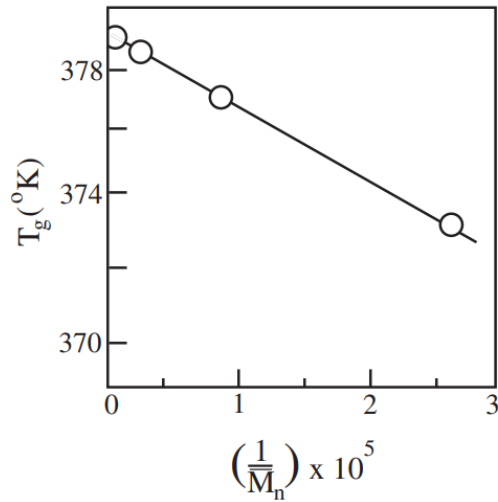


Figure Plot of T_g against reciprocal molecular weight

Branches present in small numbers on a polymer chain are known to decrease T_g . This effect also can be explained using the free volume concept. Since branches give rise to chain ends, the above analysis of the effect of molecular weight on T_g can be extended to branching. Thus, if the total number ends per chain is y , then by the analysis as given above one may write

$$T_g = T_{g, \infty} - \frac{y\rho N_{Av}\theta}{\alpha_f \bar{M}_n}$$