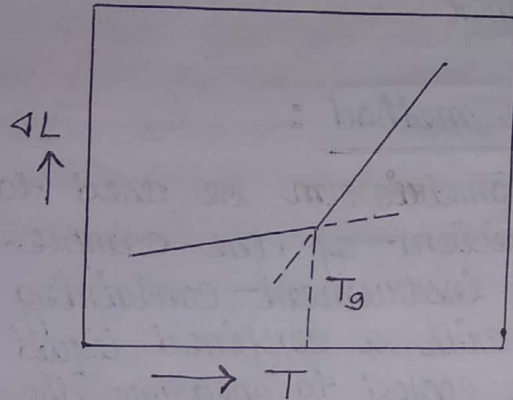
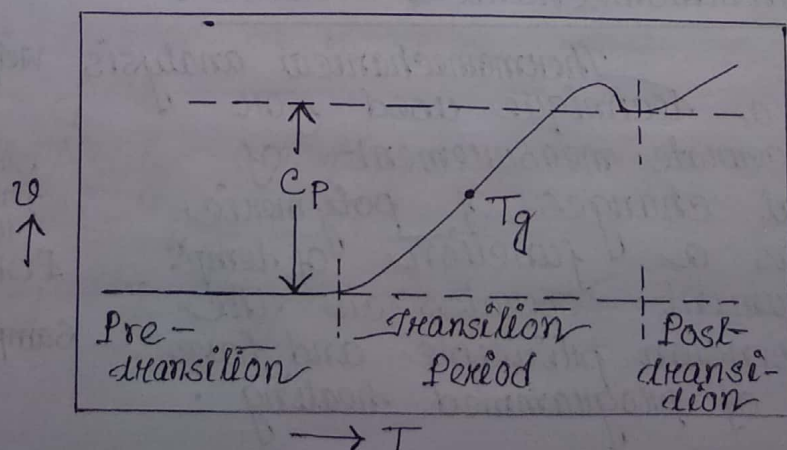


As the material expands with increase in temperature, it accumulates an expansion probe and the change in dimension ΔL is directly recorded against temperature T . The T_g value can be determined from the sudden change in the plot.



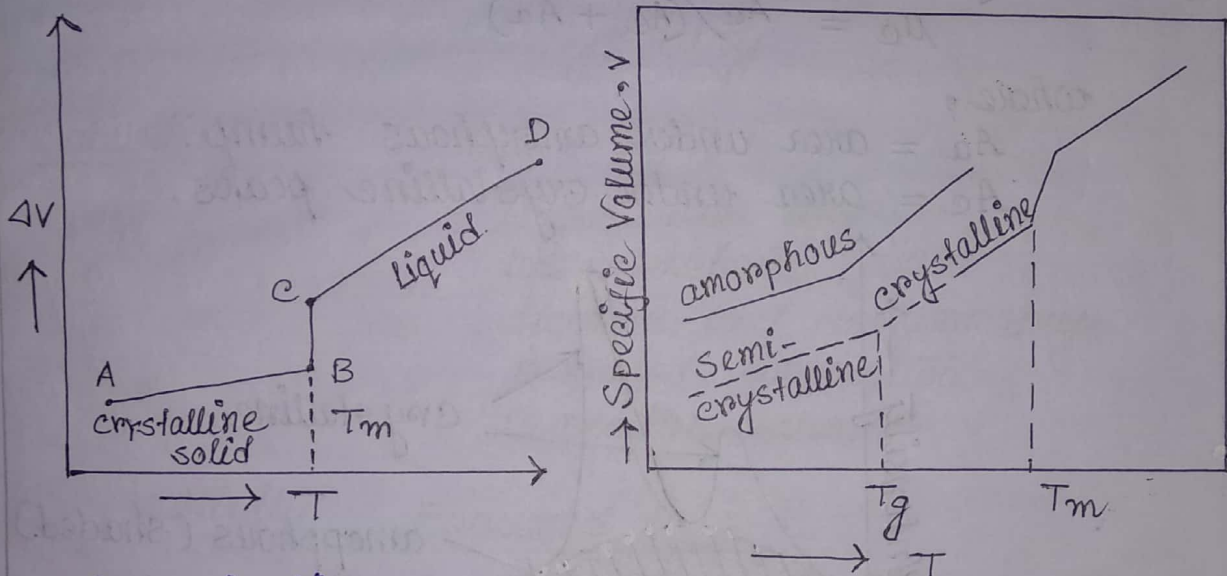
© Calorimetric method :

The calorimetric method is used to measure the heat capacity of the polymer as a function of temperature. In an instrument called the differential scanning calorimeter, the sample and a reference material are heated at a programmed rate of heating and the heat capacity of the sample is measured as a function of the differential heat flow rate between the sample and the reference material. The instrument directly gives a recording of heat flow rate (C_p) against temperature (T). The T_g value can be obtained from the change in the curve during transition.



► Determination of T_m :

A dilatometer is used to measure the T_m of a sample based on the measurement of the expansion coefficient of the sample. The bulb of the instrument containing the sample along with a confined liquid can be heated/cooled to measure the change in volume of the sample with temperature. The expansion/contraction of the sample is measured by displacement of the liquid through a graduated capillary tube. From the plot of ΔV against temp^o T , the T_m can be determined. At the T_m , there is an abrupt jump in the volume change of the material.



► Determination of Degree of Crystallinity :

Three major methods of determining crystallinity are based on specific volume, x-ray diffraction, and infrared spectroscopy.

@ Specific Volume : The crystallinity of a material is given in terms of the specific volumes of the specimen (v), the pure crystals (v_c) and the completely amorphous material (v_a) as

$$w_c \text{ or } W_c = \frac{v_a - v}{v_a - v_c}$$

The v_c is determined from x-ray unit cell dimensions, while v_a is usually determined by extrapolation of the specific volumes of the polymer melts.

⑥ X-ray diffraction :

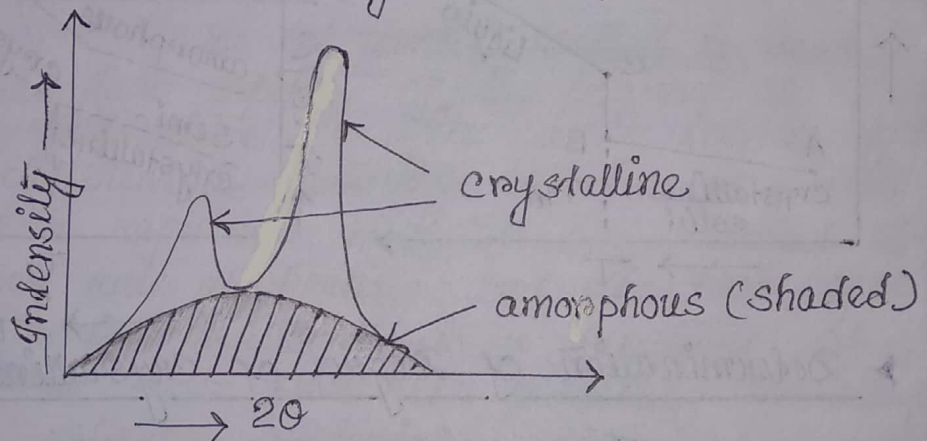
Wide-angle X-ray scattering (WAXS) method is a powerful technique for determination of degree of crystallinity. Since the scattering from the crystalline regions gives relatively sharp peaks compared to a broad 'hump' produced by scattering from noncrystalline areas, the degree of crystallinity can be determined from the relative areas (or relative heights) under the crystalline peaks and the amorphous hump. The mass fraction of crystalline region, μ_c , is given by

$$\mu_c = A_c / (A_c + A_a)$$

where,

A_a = area under amorphous hump.

A_c = area under crystalline peaks.



WAXS curve for a semicrystalline material.

⑦ Infrared absorption :

Suitable infrared absorption bands can be used as primary measures of crystallinity. The application requires that the band bear a simple and unambiguous relationship to the crystalline or amorphous character of the polymer, and that absorption data can be obtained on infrared for the pure crystalline and amorphous polymers.

▶ selected property - structure Relationships :

Glass transition temperature

Increases with the presence of :

bulky pendant groups
stiffening groups
chain symmetry
Polar groups
cross-linking

Decreases with the presence of :

additives like plasticizers
flexible main chain groups
non-polar groups
dissymmetry

Solubility

Favoured by :

longer chain lengths
low interchain forces
disorder and dissymmetry
increased temperature
Compatible solvent

Crystallinity

Favoured by :

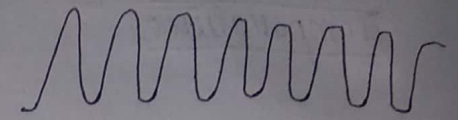
high interchain forces
regular structure, high symmetry
decrease in volume
increased stress
slow cooling from melt
homogeneous chain length.

▶ Morphology of crystalline polymers :

Lamellae :

The folded-chain lamellae theory arose in 1950s when polymer single crystals in the form of thin platelets termed lamellae, measuring $\sim 10,000 \text{ \AA} \times 100 \text{ \AA}$, were grown from polymer solutions. They are usually thickened by the spiral growth of additional lamellae from screw dislocations. The size, shape & regularity of the crystals depends on their growth conditions

such as solvents, temperature & growth rate. The thickness of the lamellae depends on the crystallization tempⁿ and subsequent annealing treatment. Folded chain lamellae represents the morphology not only for single crystals grown from the solution, but also polymers crystallized from the melt.



Model of the sharp fold surface in the lamellae.

Free Volume theory and WLF Equation

It is important to know how a material will behave (e.g. creep or stress relaxation) at a fixed temperature but over a long time period.

Fortunately, long-term behavior can be evaluated by measuring stress-relaxation or creep data over a shorter period of time at several different temperatures. Curves may then be combined to yield a master curve at a single temperature by horizontally shifting each curve along the 'log' time scale. This technique is called "time-temperature superposition." In this procedure, the master curve is plotted as stress-relaxation modulus or creep compliance vs reduced time, t/a_T .

The 'shift factor' a_T , is defined as the ratio of (real) time to reach a particular value of modulus at some temperature to the reference-scale time coordinate, t_{r0} , corresponding to the same value of modulus in the master curve at the reference temperature, T_{r0} .

$$a_T = \frac{t}{t_{r0}} \quad \text{--- (1)}$$

The dependence of the shift-factor, a_T , on temperature is given by the Williams-Landel-Ferry (WLF) relationship

$$\log a_T = \frac{-c_1 (T - T_{r0})}{c_2 + T - T_{r0}} \quad \text{--- (2)}$$