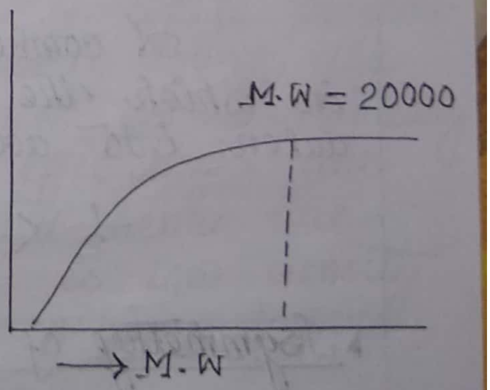
N.B : A different trend in the effect of substituent side chains on T_g is seen if we examine the T_g - values of methyl, ethyl and butyl polyacrylates. In this series, the T_g values get reduced as the length of the side chain increases (e.g 10°c, −24°c and −54°c for methyl, ethyl and butyl, respectively). Here also, the presence of the side chain, no doubt, hinders the free rotation of the c—c bond of the main chain, but this effect is ~~ab~~ almost the same in all the three acrylates. The side chains, nevertheless (তবুও), due to the presence of c—c and c—o linkages, are themselves flexible. As the side chain length increases from methyl to butyl, their freedom of flexibility increases and they also tend to push the neighbouring main chains further apart, increasing thereby the free volume and hence, the chain mobility.

N.B : Highly crystalline polymers possessing a regular chain geometry show a high T_g.

- The glass transition temperature of a polymer is influenced by its m.w, at least up to ~ 20000. We know that polymer chains made of hundreds of monomeric units comprise several segments, each made of a few tens of monomeric units. The two end segments containing the chain ends, have more freedom for motion. For a low M.W polymer, there will be more chain end segments, hence larger effective motion. Thus, the T_g will be lower for a low m.w polymer.



- Plasticisers are low M.W. non-volatile substances, which when added to a polymer, improve its flexibility, processibility and hence utility. It reduces brittleness because its addition markedly reduces the T_g of the polymer. This effect is due to a reduction in cohesive ~~form~~/forces of attraction between polymer chains, as happens due to polar attractive forces between chain segments and plasticisers. This leads to increase in segmental mobility, thereby reducing the T_g - value.

Many Plasticisers such as dibutyl phthalate, diisooctyl phthalate etc. are used to decrease the T_g value of PVC considering various factors such as compatibility, efficiency, migration effect and cost.

▸ T_g and T_m Relationship :

Based on experimental observations, T_g and T_m have been shown to be interconnected as —

$$T_g = \frac{1}{2} T_m \text{ (for symmetrical polymer)}$$
$$T_g = \frac{2}{3} T_m \text{ (for unsymmetrical polymer)}$$

[T is in degree Kelvin]

For unsymmetrical polymer, additional restriction to rotation causes T_g to increase.

A combined version of these two equations, in which the effect of molecular symmetry is not taken into account, is shown below —

$$\frac{1}{2} < \frac{T_g}{T_m} < \frac{2}{3}$$

▸ Importance of T_g :

The glass transition temperature is an important parameter of a polymeric material. It is used as a measure for evaluating the flexibility of a polymer molecule and the type response the polymeric material would exhibit the mechanical stress. The T_g value of a polymer, therefore ~~describes~~ decides whether a polymer at the 'use temperature' will behave like rubber or plastic. Polymers above their T_g will be soft and flexible and exhibit a delayed elastic response (viscoelastisity), while those below their T_g will hard & brittle and will possess dimensional stability.

▸ Factor effecting T_m :

$$\Delta G_m = \Delta H_m - T_m \Delta S_m = 0 \text{ at } T_m$$

$$\therefore T_m = \Delta H_m / \Delta S_m$$

Thus, a high melting point can be the result of a high value of enthalpy change and/or a small value of entropy change in melting. The polymer former corresponds to stronger binding in the polymer lattice and thus to higher degree of crystallinity. The factors that affects crystallinity and hence T_m can be classified as symmetry, intermolecular bonding, tacticity, branching and molecular weight.

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 lower the value of T_m. Also, 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.

N.B : In a perfectly crystalline polymer, all the chains would be contained in regions of three-dimensional order, called crystallites, and glass transition would be observed. Such a polymer would follow the curve G - F - H, meling at T_m° to become a viscous liquid.

Perfectly crystalline polymers are, however, rarely seen in practice and real polymers may instead contain varying ~~properties~~ proportions of ordered & disordered regions in the sample. These semicrystalline polymers usually exhibits both T_g and T_m (not T_m°) corresponding to the disordered and ordered regions, respectively, ~~m~~ and follow curves E - H - D - A. T_m is ~~to~~ lower than T_m° and more often represents a melting range, because the semicrystalline polymer contains crystallites of various sizes with many defects which act to depress the melting temperature.

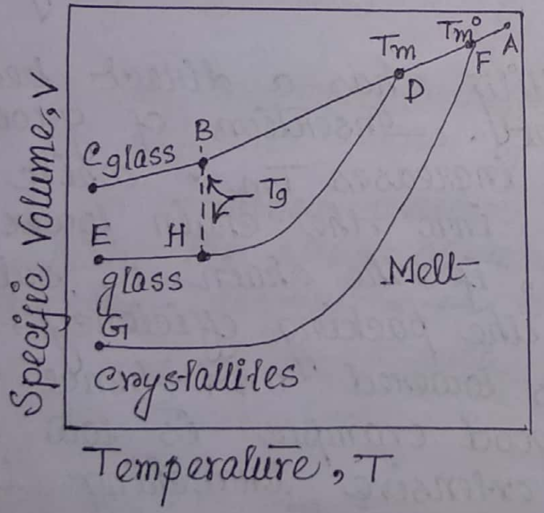


Figure : Change in specific volume with temperature for ——

ⓐ a completely amorphous sample (A — B — C),

ⓑ a semi-crystalline sample (A — D — E), and

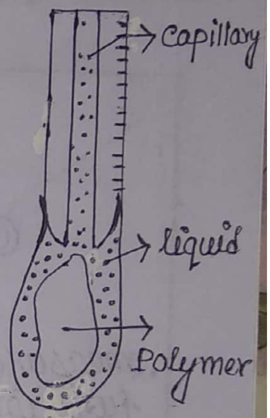
ⓒ a perfectly crystalline sample (A — F — G).

Determination of glass transition temperature

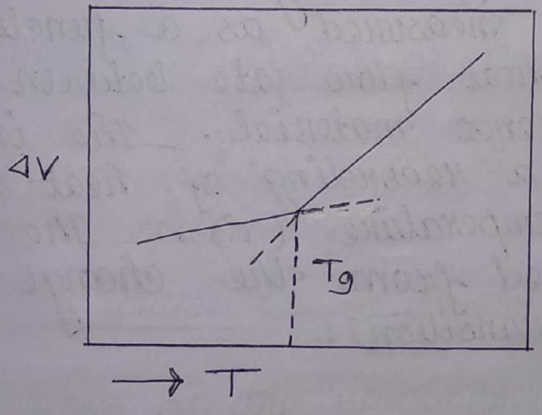
Near the glass-transition region, the polymeric materials undergoes a change in many properties such as coefficient of expansion and heat capacity. By measuring one of these properties as a function of temperature, we can determine the T_g of polymer.

ⓐ Dilatometric method :

A dilatometer can be used to measure the expansion of coefficient of the sample. The bulb of the instrument containing the sample along with a confined liquid can be heated or cooled to measure the change in volume of the sample with temperature. The expansion or contraction of sample is measured by displacement of the liquid through a graduated capillary tube. From a plot of ΔV against temperature T, the T_g can be determined.

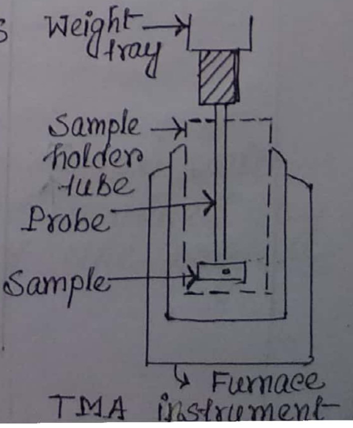


Dilatometer



ⓑ Thermomechanical method :

Thermomechanical analysis (TMA) is a technique used for making accurate measurement of dimensional changes of polymeric samples as a function of temp^{r}. TMA instrument operates on the float suspension principle and have provision of programmed heating.



TMA instrument