CRYSTALLINITY

Crystalline Polymers:

* Crystalline polymers have regular arrangement of molecules / atoms. They have high degree of folding and stacking.

* Highly crystalline polymers are rigid. They have high melting point. The flow of solvent through this type of polymer is restricted, since there is no space.

Semi-crystalline Polymers:

* Most of the polymers are semi-crystalline. They are partially regular and partially irregular.

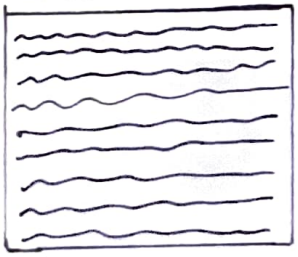
* The crystalline part of the polymer is embedded in amorphous phase.

* At a lower temperature, in the amorphous regions, molecules cannot move and rotate. It is like a frozen liquid, called glassy state.

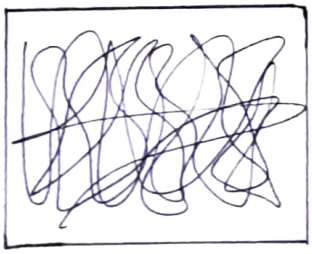
* At elevated temperature, the intermolecular forces weaker. Hence molecules are free to move and rotate (segmental motion). It becomes soft, flexible and rubbery and the volume increases.

* Intermolecular force of crystalline solid > Intermolecular force of amorphous solid.

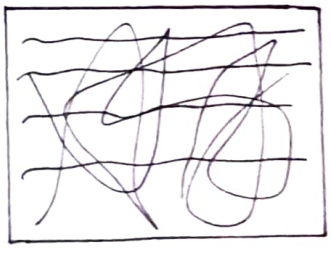
CRYSTALLINE



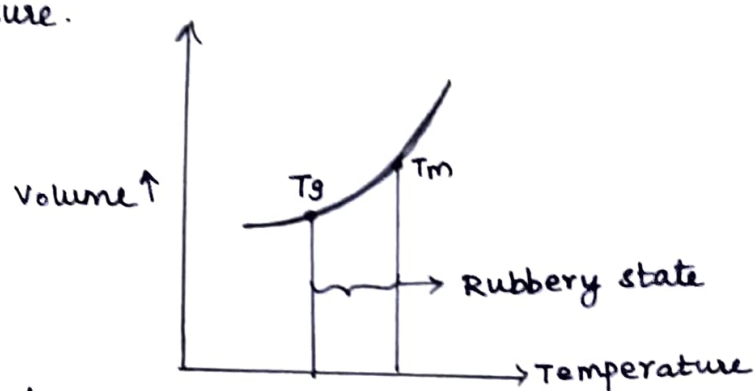
AMORPHUS



SEMI-CRYSTALLINE



* The temperature at which the polymer sample is converted into rubbery state from rigid solid state is called glass transition temperature.



* The Tg of polymer is very important as it decides its thermal properties.

* Flexibility: The property of a conducting polymer to adjust its dimensional size.

* Dimensional adjustability is an important feature in engineering applications.

* Whether the given polymer is glassy (or) rubbery, at a given temperature depends on its Tg.

B - Polystyrene: Tg = 100°C (solid)

Room Temperature

A ⇒ Rubber Tg = -20°C

* At room temperature, which is higher than the T_g of rubber, it exists as soft, rubbery polymer. However, the T_g of polystyrene is ~~less~~ higher than the room temperature.

* It is the study of property of polymer material with respect to temperature.

* The 3 most important terminologies linked with it :

ⓐ Melting point (T_m)

ⓑ Glass transition temperature (T_g)

ⓒ Crystallization temperature (T_x)

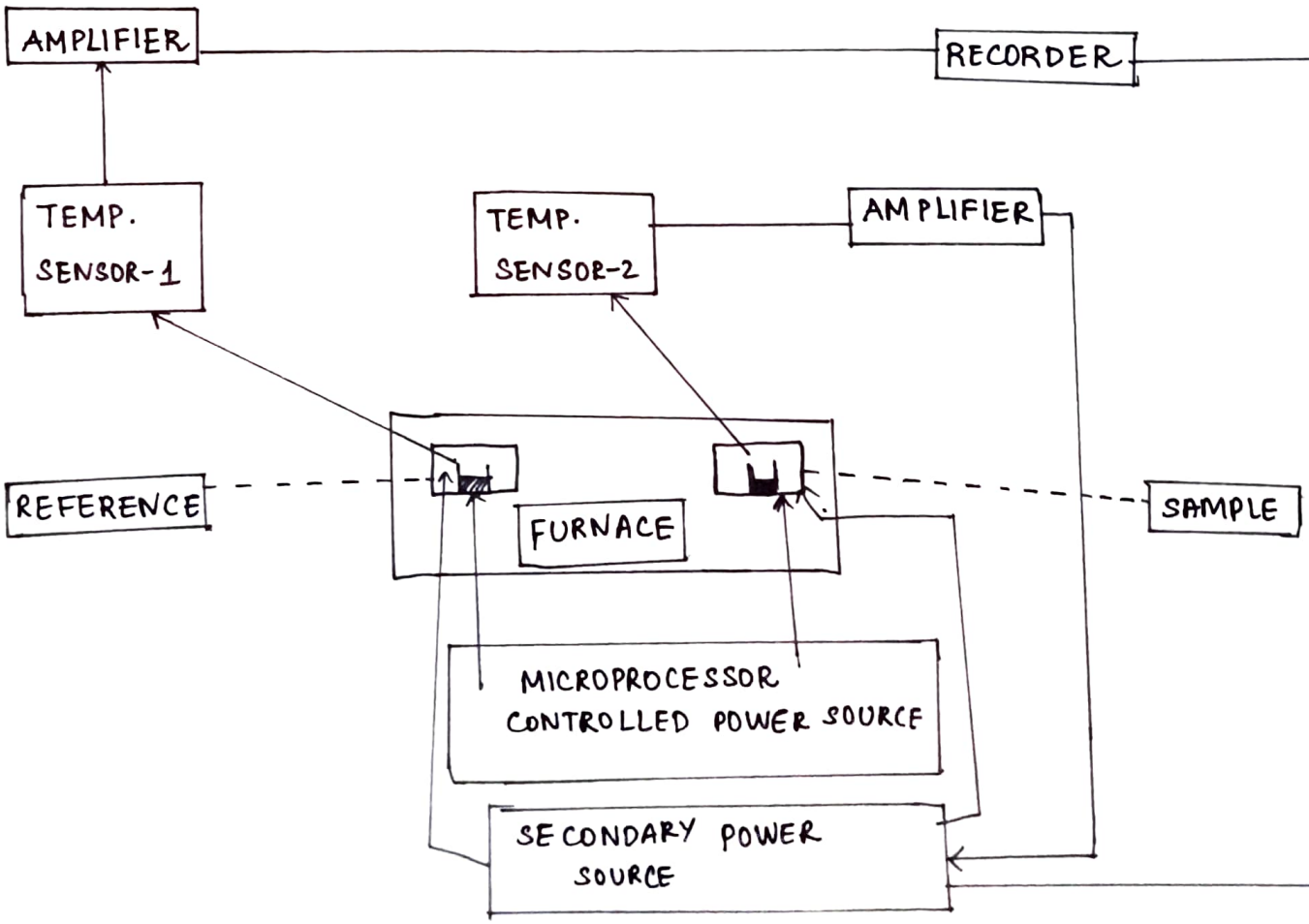
⇓

It is the temperature at which crystallization begins.

* T_m and T_g : From lower temperature → Higher temperature.

* T_x : From higher temperature → Lower temperature.

*



* The instrument consists of a furnace which is heated using computer controlled power source. The furnace consists of two chambers, which are identical and connected with temperature sensors (Thermo-couple).

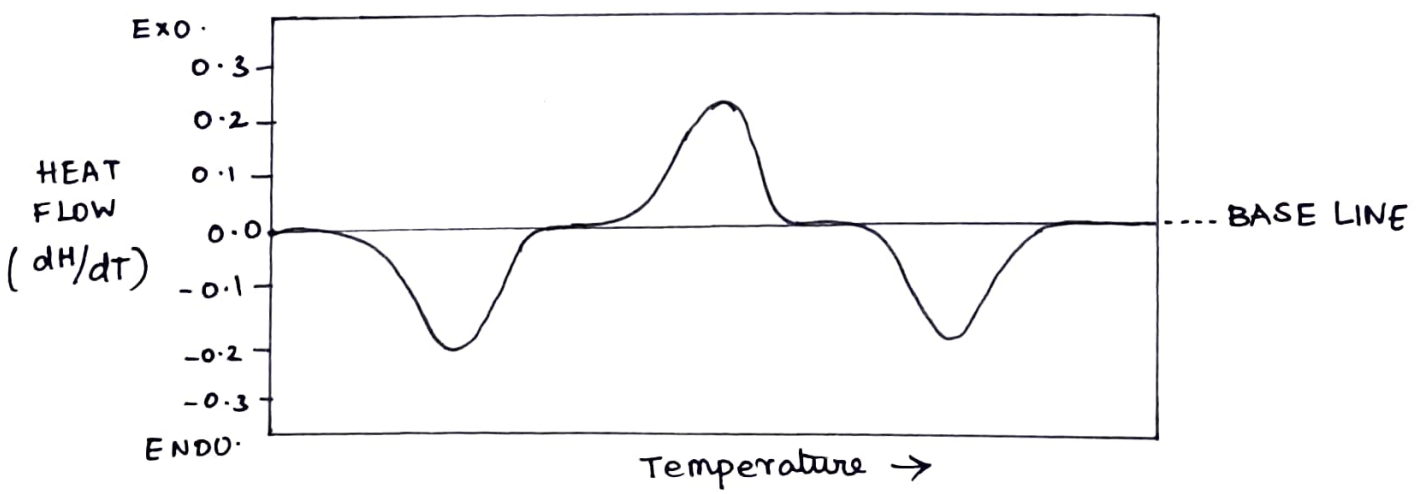
* The polymer sample is placed in one of the chambers (sample chamber) and a thermally inert material such as Al_2O_3 (alumina). is used as reference and placed in another chamber.

* Individual (separate) heaters are provided for the sample and the reference.

* T_m and T_g are endothermic change reactions.

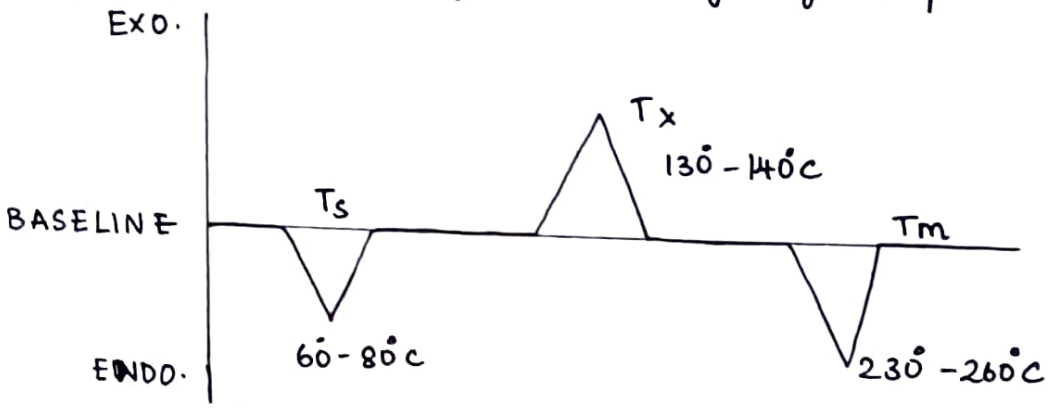
* T_x is exothermic reaction.

* Whenever, there is a difference in temperature between the sample and reference, due to the endothermic/exothermic reactions of the sample, heat is supplied from the secondary power source to the sample, so that temperature equality is restored.



* The difference in temperature between the sample and reference $\Delta T = (T_S - T_R)$ is measured with respect to reference temperature.

* A typical DSC curve for PET (Polyethyle Terp



* The inflection (changes) in the region 60°-80°C corresponds to T_g of PET.

* Since, it is a semi crystalline polymer, above its T_g the mobility of the molecules increase which leads to crystallization to some extent, which is shown in the range 130° - 140° C.

* The peak in the range of 230 - 260°C corresponds to melting temperature (T_m).

* The area (under the peak) can be directly related to enthalpy (heat) change. Hence, enthalpy of T_g, T_m and T_x can be measured.

* The % crystallinity of the polymeric material can also be determined using DSC curve.

* $$\% \text{ Crystallinity} = \frac{\Delta H_m \text{ (sample)}}{\Delta H_m \text{ (pure crystalline standard)}} \times 100$$

* Some polymers are crystalizable upon reaching its Tg by the rotation and mobility of the molecules. So, it gets crystalized to some extent after Tg that it reflects.

* T_{rg} = Reduced glass transition temperature.

$$T_{rg} = \frac{T_g}{T_m}$$

* The rate of cooling, can be found from the T_{rg} so that the crystallinity / Amorphous state can be achieved by fixing the rate of cooling.