

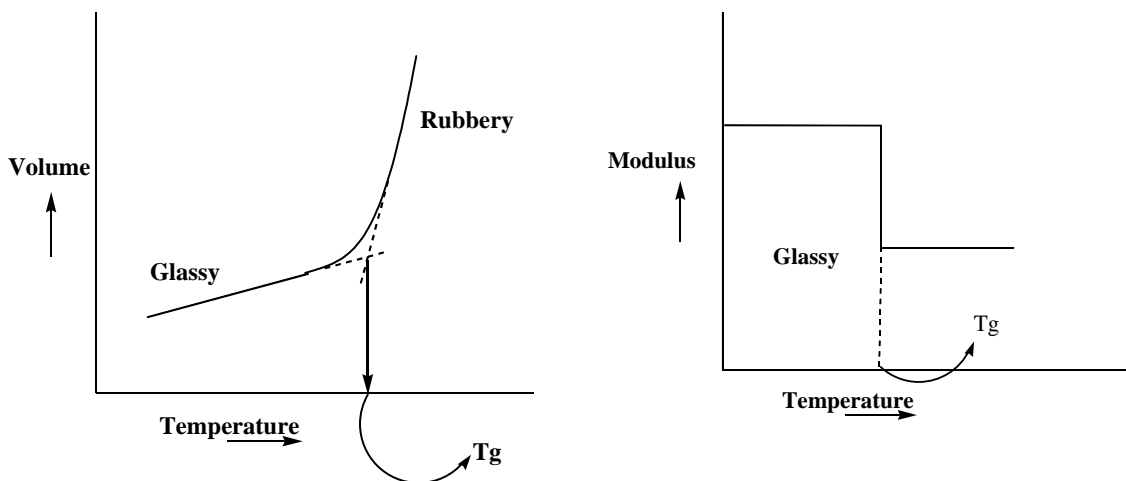
Thermal Behavior of Polymers

Glass Transition Temperature (T_g)

- At low temperatures, all amorphous polymers are stiff and glassy, sometimes called as the Vitreous State, especially for inorganic polymers.
- On Warming, polymers soften in a characteristic temperature range known as the glass-rubber transition region.
- The glass transition temperature (T_g), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states.
- T_g constitutes the most important mechanical property for all polymers. In fact, upon synthesis of a new polymer, the glass transition temperature is among the first properties measured.

The following physical properties undergo a drastic change at the glass transition temperature of any polymer:

- a) hardness
- b) volume
- c) modulus (Young's module)
- d) percent elongation-to-break



Young's Modulus E may be written as:

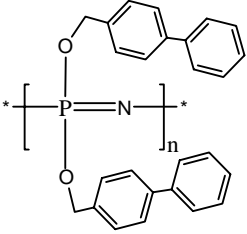
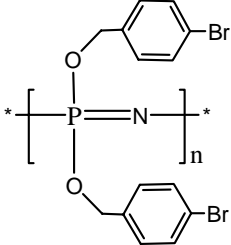
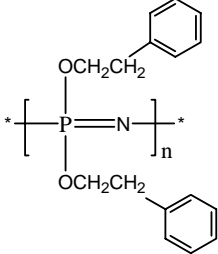
$$\sigma = E\varepsilon$$

σ = Tensile stress; ε = Tensile strain

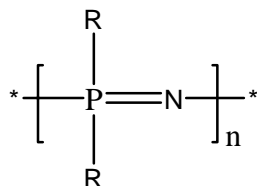
Young's modulus is a fundamental measure of the stiffness of the material. The higher its value, the more resistant the material is to being stretched.

Unit of E: dynes/cm² (10 dynes/cm² = 1 Pascal)

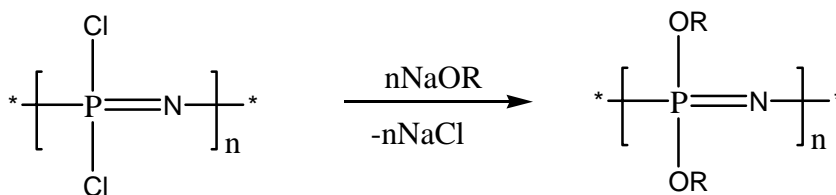
Polymer	Tg(°C)
Nylon 66	45
Polyacrylonitrile	85
Polystyrene	100
Polyethylene	-20
$\left[\begin{array}{c} \text{Cl} \\ \\ * - \text{P} = \text{N} - * \\ \\ \text{Cl} \end{array} \right]_n$	-66
$\left[\begin{array}{c} \text{Br} \\ \\ * - \text{P} = \text{N} - * \\ \\ \text{Br} \end{array} \right]_n$	-8
$\left[\begin{array}{c} \text{F} \\ \\ * - \text{P} = \text{N} - * \\ \\ \text{F} \end{array} \right]_n$	-96
$\left[\begin{array}{c} \text{OCH}_2\text{CF}_3 \\ \\ * - \text{P} = \text{N} - * \\ \\ \text{OCH}_2\text{CF}_3 \end{array} \right]_n$	-66
$\left[\begin{array}{c} \text{OCH}_3 \\ \\ * - \text{P} = \text{N} - * \\ \\ \text{OCH}_3 \end{array} \right]_n$	-74
$\left[\begin{array}{c} \text{OCH}_2\text{C}_6\text{H}_5 \\ \\ * - \text{P} = \text{N} - * \\ \\ \text{OCH}_2\text{C}_6\text{H}_5 \end{array} \right]_n$	-31.4

$\left[\begin{array}{c} \text{OC}_6\text{H}_5 \\ \\ * \text{---} \text{P} = \text{N} \text{---} * \\ \\ \text{OC}_6\text{H}_5 \end{array} \right]_n$	-8
$\left[\begin{array}{c} \text{OCH}_2\text{CH}_3 \\ \\ * \text{---} \text{P} = \text{N} \text{---} * \\ \\ \text{OCH}_2\text{CH}_3 \end{array} \right]_n$	-84
$\left[\begin{array}{c} \text{OCH}_2\text{CH}_2\text{C}_6\text{H}_5 \\ \\ * \text{---} \text{P} = \text{N} \text{---} * \\ \\ \text{OCH}_2\text{CH}_2\text{C}_6\text{H}_5 \end{array} \right]_n$	-32.7
	44
	-0.8
$\left[\begin{array}{c} \text{OCH}_2\text{CH}_2\text{CH}_3 \\ \\ * \text{---} \text{P} = \text{N} \text{---} * \\ \\ \text{OCH}_2\text{CH}_2\text{CH}_3 \end{array} \right]_n$	-100
	-47

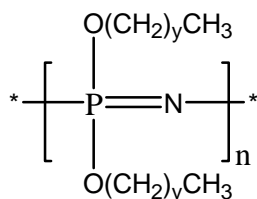
Variation in “Tg” with Phosphazene Polymer Side Group Structure:



R may be $-\text{CH}_3$, $-\text{C}_6\text{H}_5$, $-\text{OCH}_3$, $-\text{OC}_6\text{H}_5$, $-\text{NR}_2$



Examples:



$$y = 3; T_g = -105^{\circ} \text{C}$$

$$y = 4; T_g = -104^{\circ} \text{C}$$

$$y = 5; T_g = -104^{\circ} \text{C}$$

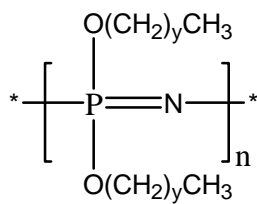
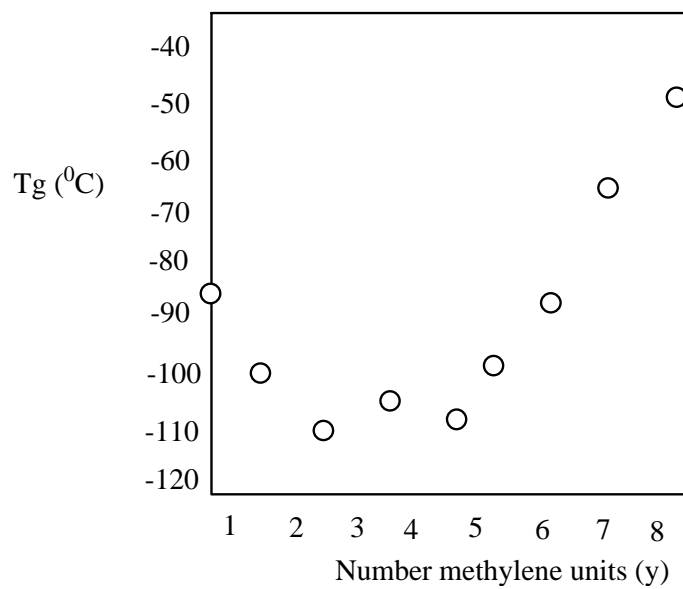
$$y = 6; T_g = -94^{\circ} \text{C}$$

$$y = 7; T_g = -84^{\circ} \text{C}$$

$$y = 8; T_g = -56^{\circ} \text{C}$$

$$y = 9; T_g = -44^{\circ} \text{C}$$

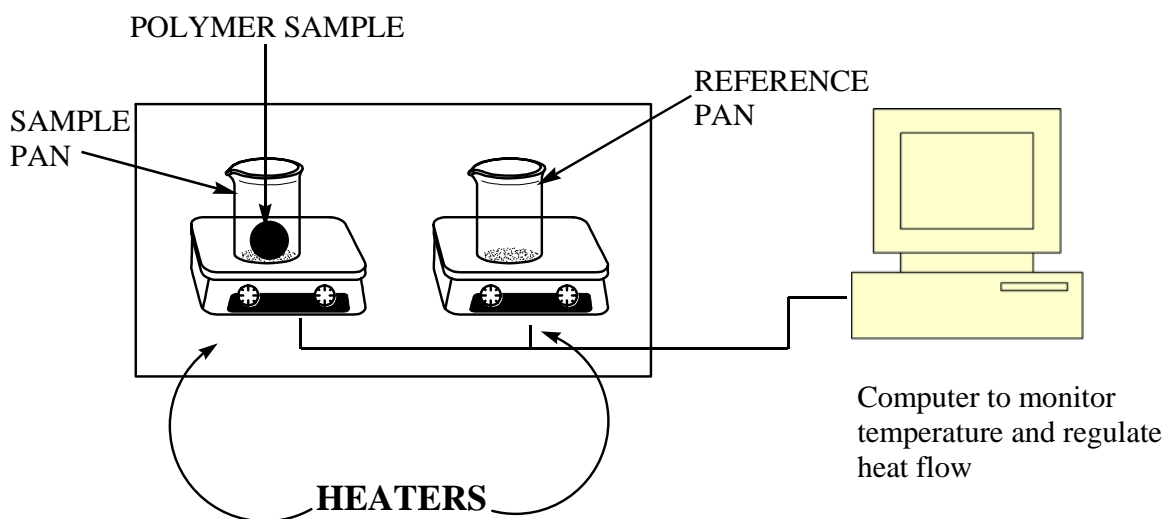
Influence of Alkyl Chain length on Tg



DSC – Degree of Crystallinity –TGA

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a technique that is used to study the thermal transition of a polymer. Thermal transitions are the changes that take place when a polymer is heated. The melting of a crystalline polymer and the glass transition (T_g) are examples of thermal transitions.

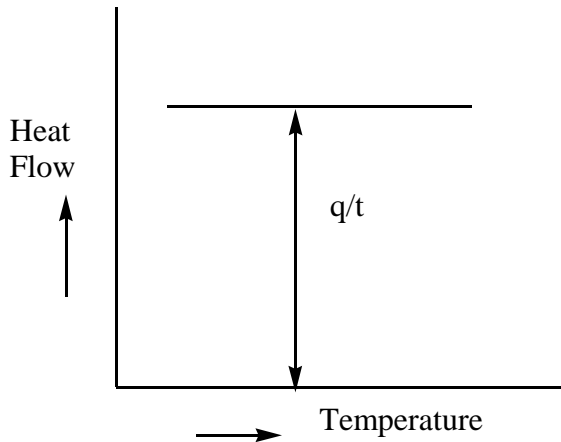


The device that is used to measure T_g and other thermal transitions (such as the melting and crystallization temperatures) is shown in the Figure.

This device consists of two pans. In one pan, the polymer sample is loaded. The other pan is the reference pan and is normally left empty. These two pans are located on top of a heater. The computer assembly will turn on the heaters and the heating rates (q/t) of the two pans are accurately controlled (about 10 C per minute). The computer programs the heating rate to stay exactly the same through out the experiment. It is also important to note that the two separate pans, with their heaters are heated at the same rate as each other.

The presence of polymer material in the sample pan results in an uptake of more heat in order to keep the temperature of the sample pan increasing at the same rate as the reference pan. This means that the heater underneath the sample pan will provide more heat energy than the heater under the reference pan. The DSC experiment is all about the measurement of HOW MUCH heat that the sample pan heater has to put out as compared to the reference pan heater. In DSC experiments the data of temperature increase (T) are plotted against the difference in heat output of the two heaters at a given temperature.

Mathematically,



The computer will provide plots of the difference in heat output of the two heaters against temperature. This means that the above plot is the heat absorbed by the polymer against temperature.

$$\text{Heat / time} = q / t = \text{heat flow}$$

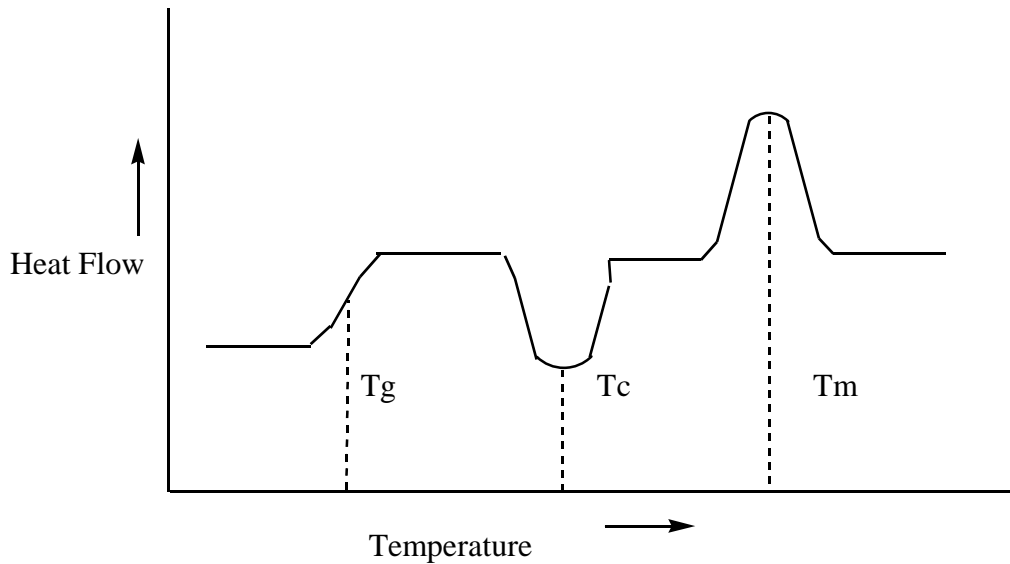
$$\text{Temperature increase / time} = \Delta T / t = \text{heating rate}$$

When we divide the heat flow q/t by the rate of heating $\Delta T/t$. We obtain:

$$(q/t) / (\Delta T/t) = q / \Delta T = C_p = \text{Heat Capacity}$$

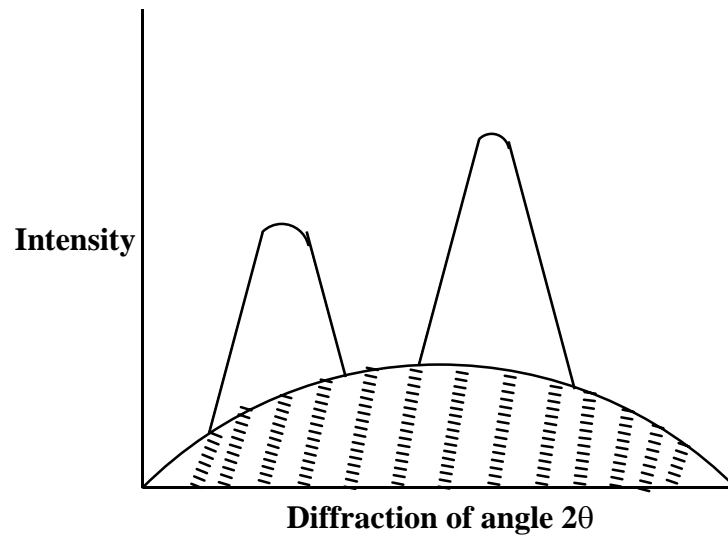
The amount of heat it takes to get a certain temperature increase in a material is called *heat capacity*, or C_p . Heat capacity is obtained by dividing the heat supplied by the temperature increase. Therefore DSC plot gives C_p .

A typical DSC plot of a polymer will look like:



It is important to recognize that not all polymers will show T_c and T_m . T_m and T_c will only show up for polymers that can form crystals. Completely amorphous polymers exhibit only T_g . However, polymers with both crystalline and amorphous domains, will show all the features as shown above.

Crystallinity of Polymers from Wide-Angle X-ray Scattering (WAXS)



$$\text{Degree of Crystallinity} = A_c / (A_a + A_c)$$

A_a = Area under the amorphous hump

A_c = Area under the crystalline peaks