Differential Scanning Calorimetry

Definitions

- **Calorimetry - The study of heat transfer during physical and chemical process.**
- **Calorimeter - A device for measuring the heat transferred.**
- **Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.**

- **It is the most widely used method of thermal analysis in pharmaceutical field.**
- **Thus, when an endothermic transition occurs, the energy absorbed by the sample is compensated by an increased energy input into the sample in order to maintain a zero temperature difference.**
- **Because this energy input is precisely equivalent magnitude of energy absorbed in transition, direct calorimetric measurement of transition is obtained from this balancing energy.**
- **On the DSC chart recording, the abscissa indicates the transition temperature and the peak measures the total energy transfer to or from the sample.**

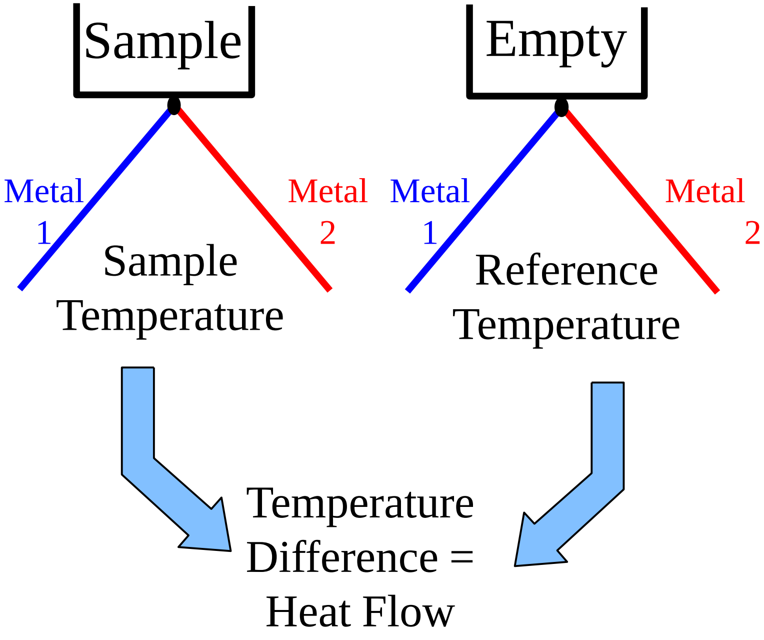
Differential scanning calorimetry

- **This technique is used to study what happens to polymers/samples upon heating**
- **It is used to study thermal transitions of a polymer/sample (the changes that take place on heating) – For example:**
  - **The melting of a crystalline polymer**
  - **The glass transition**
- **The crystallization**

Principles

- The sample and reference are maintained at the same temperature, even during a thermal event in the sample
- The energy required to maintain zero temperature difference between the sample and the reference is measured
- During a thermal event in the sample, the system will transfer heat to or from the sample pan to maintain the same temperature in reference and sample pans

Conventional DSC



Sample

Empty

Sample Temperature

Reference Temperature

Temperature Difference = Heat Flow

- A “linear” heating profile even for isothermal methods

- **Why heaters don’t heat at the same rate?**

  The simple reason is that the two pans are different. One has polymer in it, and one doesnt. The polymer sample means there is extra material in the sample pan. Having extra material means that it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan

- **So the heater underneath the sample pan has to work harder than the heater underneath the reference pan. It has to put out more heat. How much more heat it has to put out is what measured in DSC experiment?• Specifically, a plot is drawn as the temperature increases. The temperature is taken on x-axis whist the difference in heat output of the two heaters at a given temperature on y-axis**

What can DSC measures?

- Glass transitions
- Melting and boiling points
- Crystallisation time and temperature
- Percent crystallinity
- Heats of fusion and reactions
- Specific heat capacity
- Oxidative/thermal stability
- Rate and degree of cure
- Reaction kinetics
- Purity
- Enthalpy

DSC Curve

- The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment.
- This curve can be used to calculate enthalpies of transitions, which is done by integrating the peak corresponding to a given transition. The enthalpy of transition can be expressed using equation: $\Delta H = KA$

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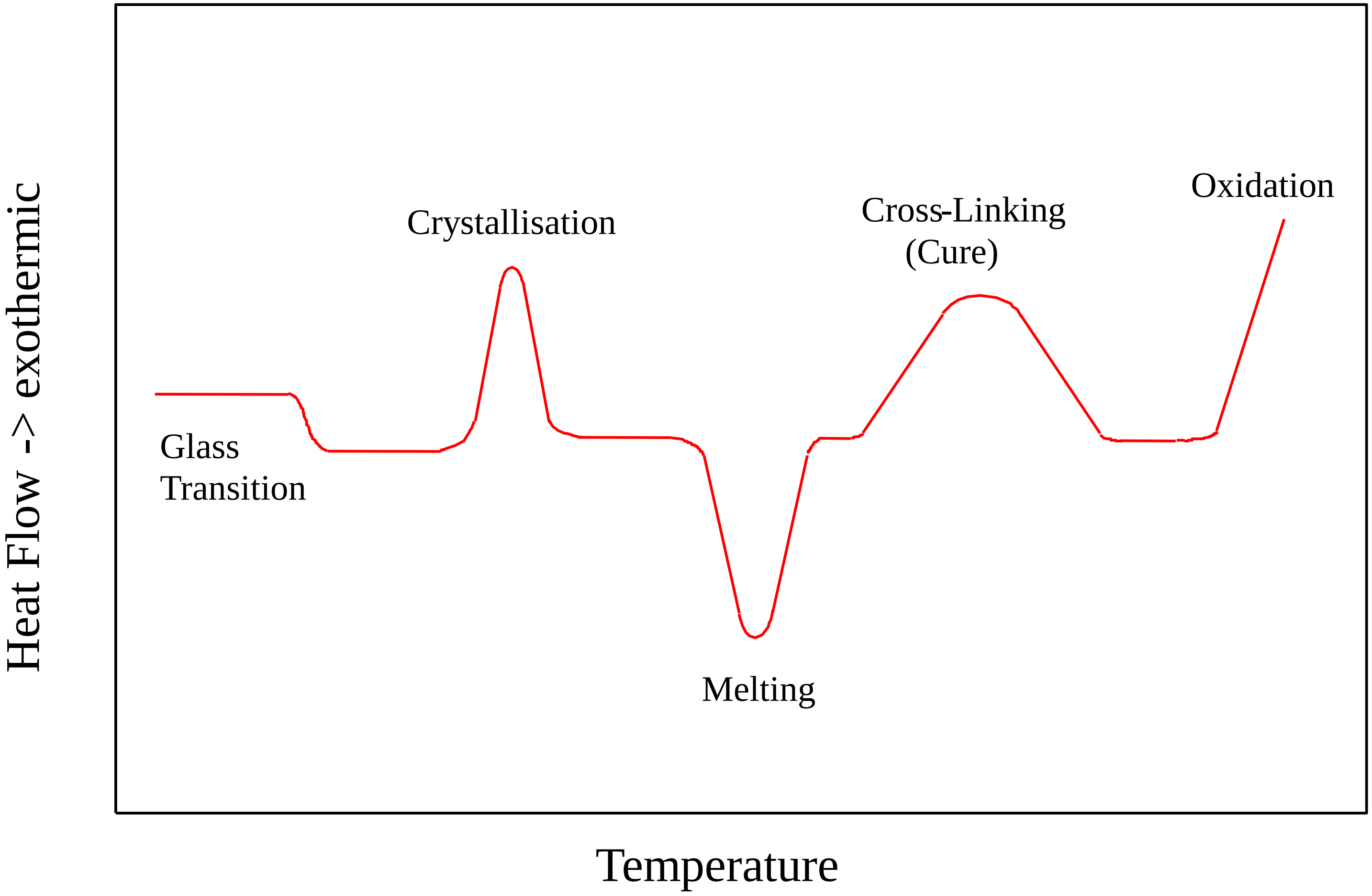
- **Where ΔH is the enthalpy of transition,**
- **K is the calorimetric constant**
- **A is the area under the peak.**
- **The calorimetric constant varies from instrument to instrument, and can be determined by analyzing a well-characterized material of known enthalpies of transition.**
- **Area under the peak is directly proportional to heat absorbed or evolved by the reaction,**
- **height of the peak is directly proportional to rate of the reaction**

DSC Thermogram



Factors affecting DSC curve

- **Two types of factors effect the DSC curve**

1-Instrumental factors

A- Furnace heating rate

B- Recording or chart speed

C- Furnace atmosphere

D-Geometry of sample holder/location of sensors

E- Sensitivity of the recoding system

F- Composition of sample containers

Factors affecting DSC curve

- **2-Sample characteristics**

A- Amount of sample

B- Nature of sample

C- Sample packing

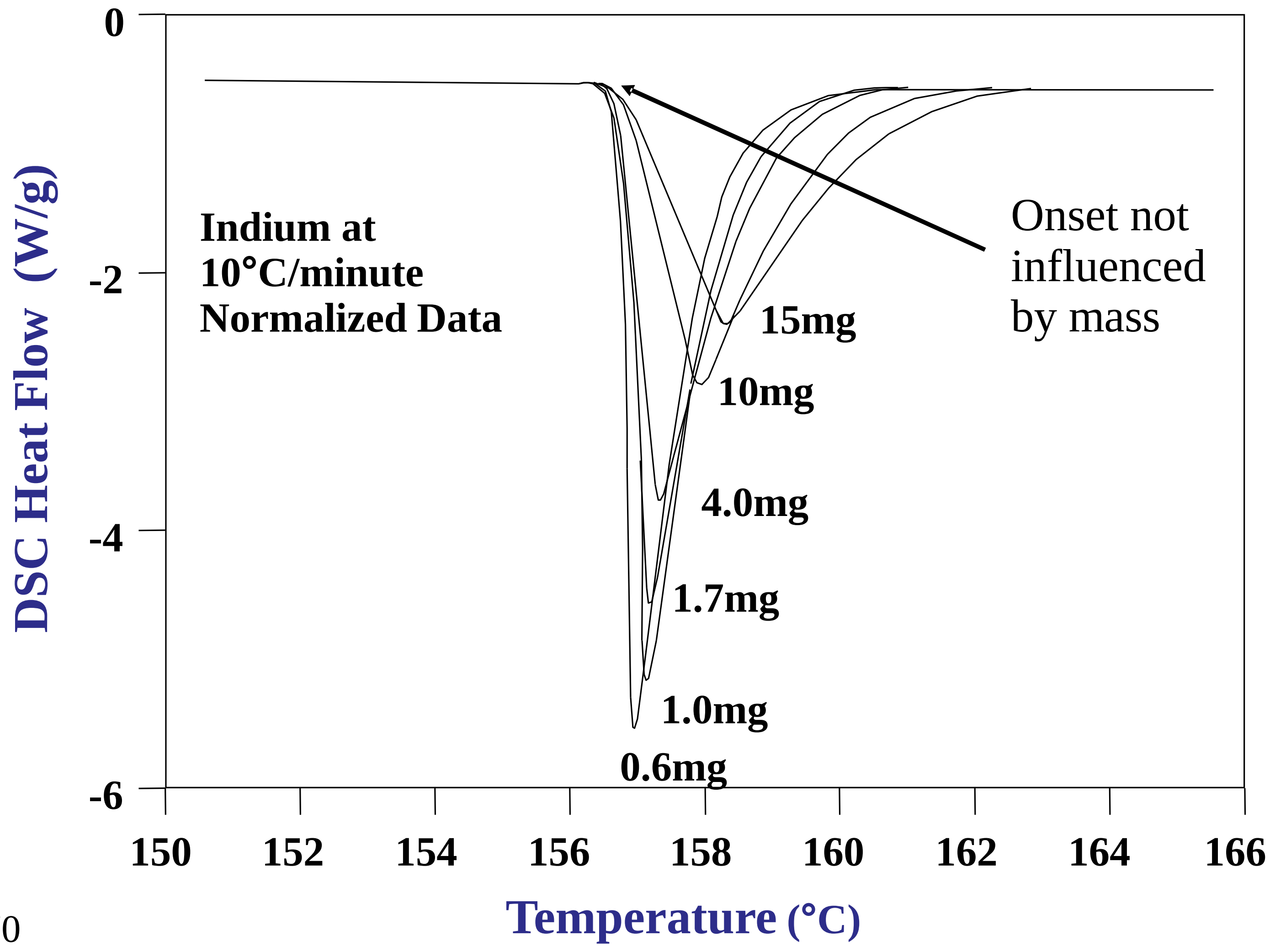
D- Solubility of evolved gases in the sample

E- Particle size

F- Heat of reaction

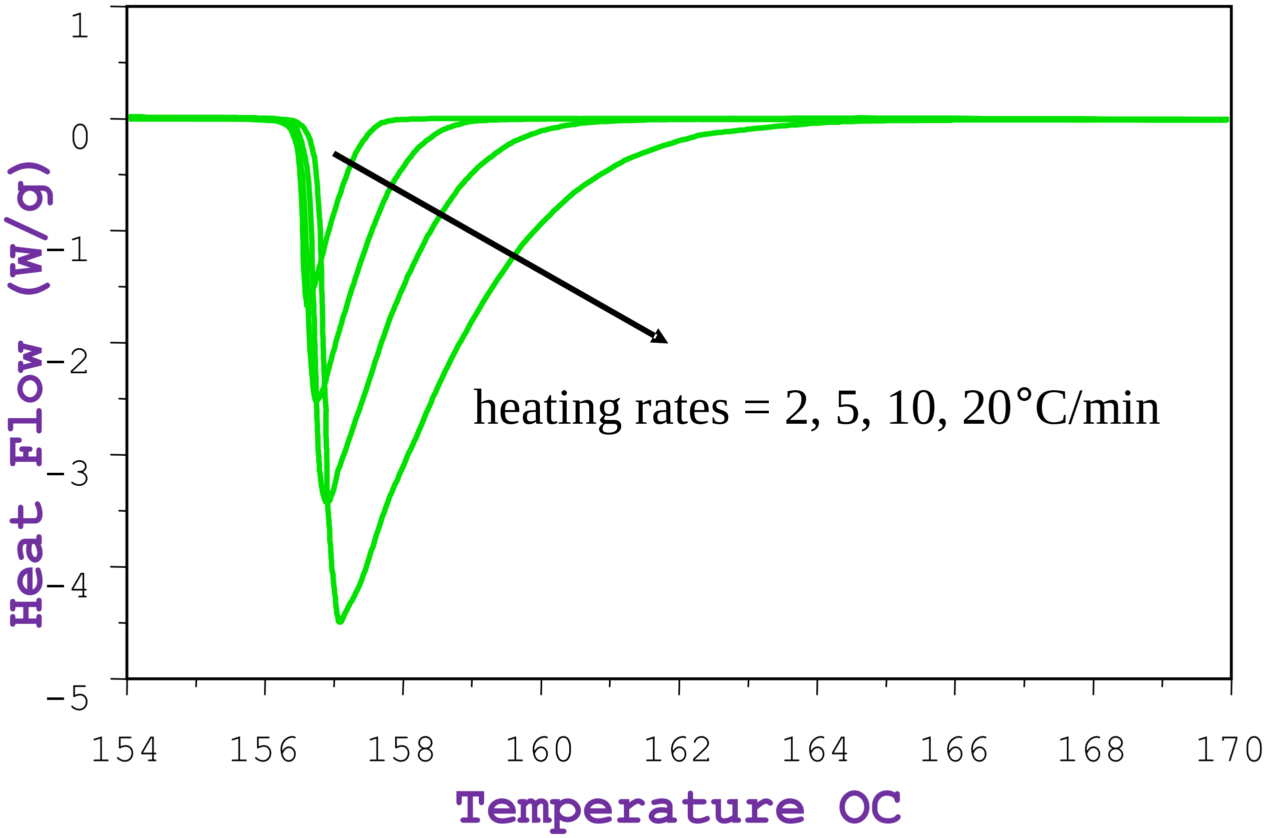
G- Thermal conductivity

Influence of Sample Mass



Effect of Heating Rate

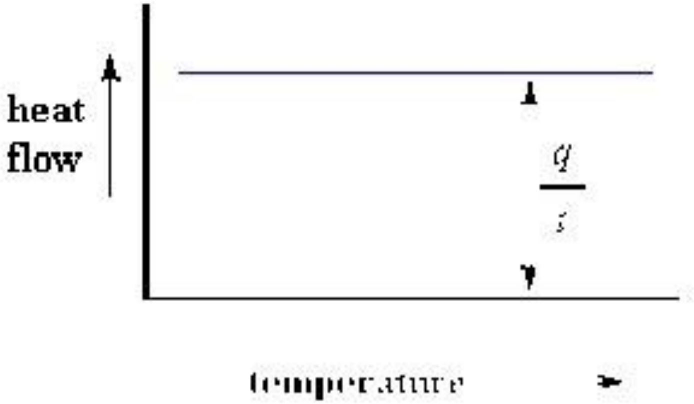
on Indium Melting Temperature



heating rates = 2, 5, 10, 20°C/min

Determination of Heat Capacity

- DSC plot can be used to determine Heat Capacity. Suppose a polymer is being heated. When we start heating two pans, the computer will plot the difference in heat output of the two heaters against temperature that is plot of heat absorbed by the polymer against temperature. The plot will look like this at first.



- The heat flow is (heat (q)) supplied per unit time (t), whereas, The heating rate is temperature increase (ΔT) per unit time (t)

$$\text{heat flow} = \frac{\text{heat}}{\text{time}} = \frac{q}{t}$$

$$\text{heating rate} = \frac{\text{temperature increase}}{\text{time}} = \frac{\Delta T}{t}$$

- By dividing heat flow (*q/t)* by the heating rate (Δ*T/t)*. It ends up with heat supplied divided by the temperature increase, which is called heat capacity.

$$\frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} = C_p = \text{heat capacity}$$

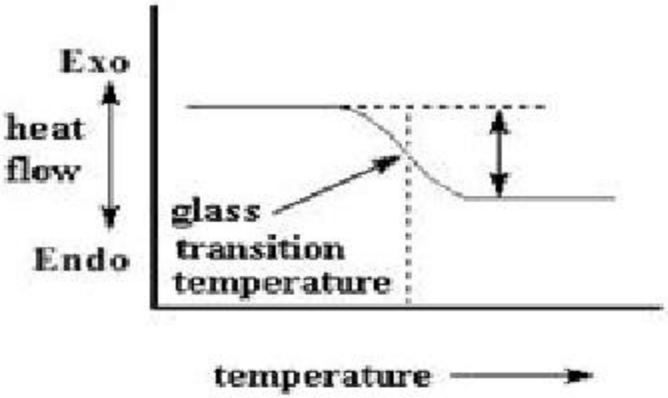
J/K joule per Kelvin

- $\Delta H = KA$ ($KJ.mol^{-1}$)
- K = Constant of the instrument DSC
- $\Delta H = q$ Area under peak from DSC curve
- $\Delta S = \Delta H / T$ or
- $\Delta S = q / T$ ($j.mol^{-1}.K^{-1}$)

- When a certain amount of heat is transferred to the sample, its temperature increases by a certain amount, and the amount of heat it takes to get a certain temperature increase is called the heat capacity, or Cp, it can be figured up from the DSC plot

The Glass Transition Temperature (Tg)

- On further heating the polymer to a certain temperature, plot will shift downward suddenly, like this:

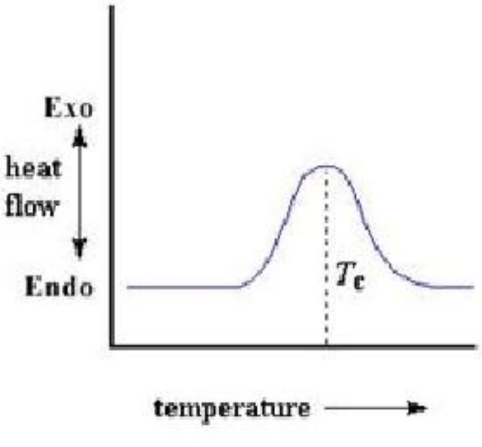


- This means there is more heat flow. There is an increase in the heat capacity of the polymer. This happens because the polymer has just gone through the glass transition. Because of this change in heat capacity that occurs at the glass transition, we can use DSC to measure a polymers glass transition temperature.• Take note that this change doesn't occur suddenly, but takes place over a temperature range. This makes picking one discreet Tg a kind of tricky matter, but we usually just take the middle of the incline to be the Tg.

Crystallization

- **After glass transition, the polymers have a lot of mobility. They wiggle and squirm, and never stay in one position for very long time. But when they reach the right temperature, they will give off enough energy to move into very ordered arrangements, which is called crystals.**

- When polymers fall into these crystalline arrangements, they give off heat. When this heat is dumped out, it makes the little computer-controlled heater under the sample pan really happy. Its happy because it doesnt have to put out much heat to keep the temperature of the sample pan rising. You can see this drop in the heat flow as a big peak in the plot of heat flow versus temperature



The temperature at the highest point in the peak is usually considered to be the polymers crystallization temperature, or Tc

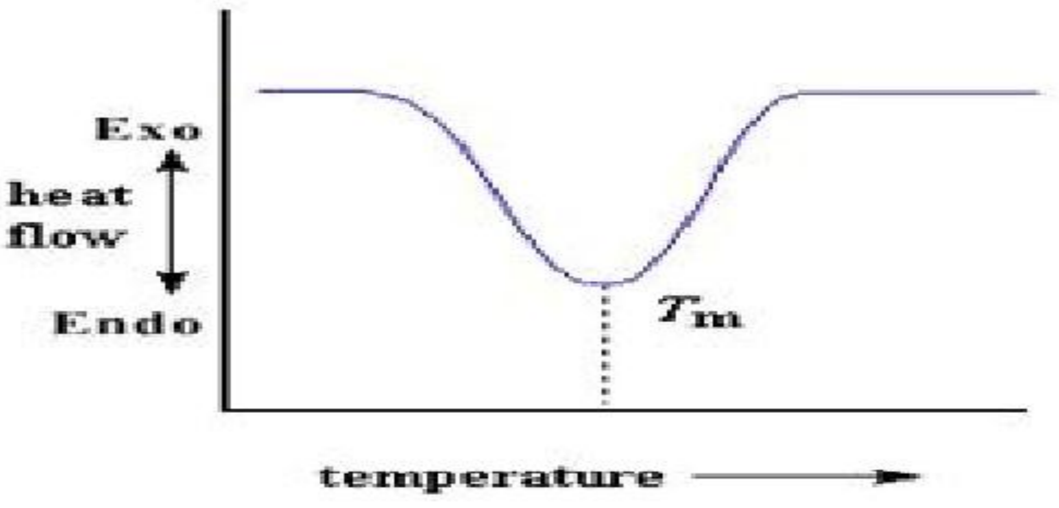
- Also, we can measure the area of the peak, which tells us the latent energy of crystallization of the polymer
- But most importantly, this peak tells us that the polymer can in fact crystallize• If you analyze a 100% amorphous polymer, like polystyrene, you wouldn’t get this peak, because such materials don’t crystallize
- Also, because the polymer gives off heat when it crystallizes, we call crystallization is an exothermic transition

Melting

- If we heat our polymer past its Tc, eventually well reach another thermal transition, called melting. When we reach the polymers melting temperature, Tm, the polymer crystals begin to fall apart, that is they melt. It comes out of their ordered arrangements, and begin to move around freely that can be spotted on a DSC plot

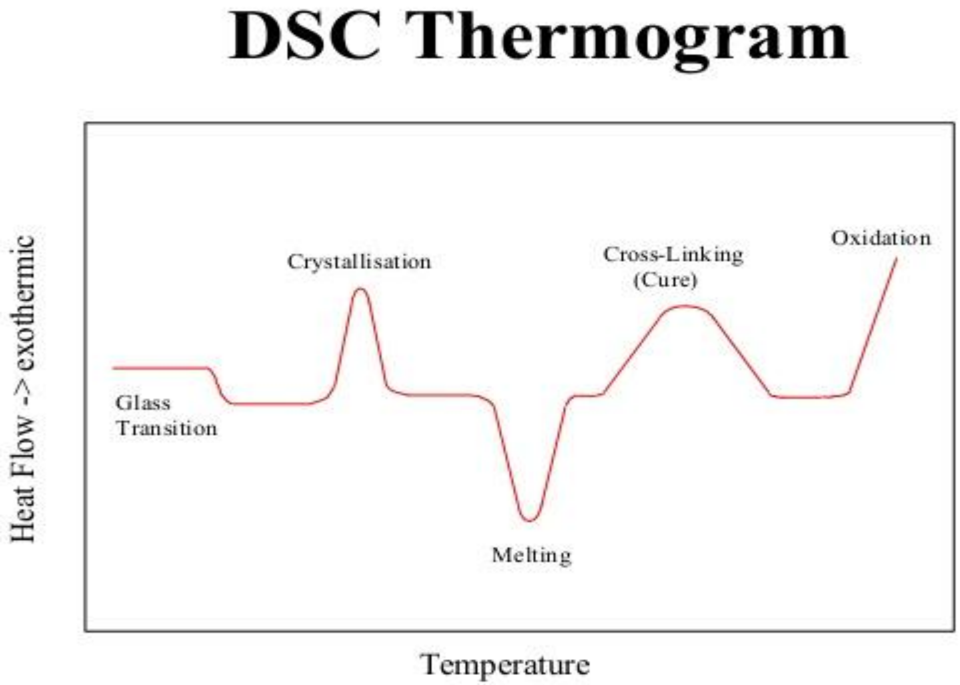
- Remember, the heat which polymer give off when crystallized is absorbed when reached at Tm. That is a latent heat of melting like latent heat of crystallization. When the polymer crystals melt, they must absorb heat in order to do so.
- Remember melting is a first order transition. This means that at the melting temperature, the polymers temperature wont rise until all the crystals have melted.

This means that the little heater under the sample pan has to put a lot of heat into the polymer in order to both melt the crystals and keep the temperature rising at the same rate as that of the reference pan. This extra heat flow during melting shows up as a big dip on DSC plot, like this:



Putting It All Together

- we saw a step in the plot when the polymer was heated past its glass transition temperature. Then we saw a big peak when the polymer reached its crystallization temperature. Then finally we saw a big dip when the polymer reached its melting temperature. To put them all together, a whole plot will often look something like this:



- Of course, not everything you see here will be on every DSC plot. The crystallization peak and the melting dip will only show up for polymers that can form crystals and melts.
- Completely amorphous polymers wont show any crystallization, or any melting either. But polymers with both crystalline and amorphous domains, will show all the features

- From DSC plot you can see a big difference between the glass transition and the other two thermal transitions, crystallization and melting. For the glass transition, there is no dip, and theres no peak, either. This is because there is no latent heat given off, or absorbed, by the polymer during the glass transition. Both melting and crystallization involve giving off or absorbing heat.

- The only thing we do see at the glass transition temperature is a change in the heat capacity of the polymer.
- Because there is a change in heat capacity, but there is no latent heat involved with the glass transition, we call the glass transition a second order transition. However, transitions like melting and crystallization, which do have latent heats, are called first order transitions

- How much crystallinity?
- DSC can also tell us how much of a polymer is crystalline and how much is amorphous?
- If we know the latent heat of melting, ΔHm, we can figure out the answer.
- The first thing we have to do is to measure the peak area for the melting of a polymer. Since, DSC curve is a plot of heat flow per gram of material, versus temperature.
- Heat flow (heat given off per second), so the area of the peak is given in units of heat x temperature x time-1 x mass-1 (joules x kelvins x (seconds)-1 x (grams)-1

It can get simpler. We usually divide the area by the heating rate of dsc experiment. The heating rate is in units of K/s. So the expression becomes simpler:

DSC: Main Sources of Errors

- Calibration
- Contamination
- Sample preparation – how sample is loaded into a pan
- Residual solvents and moisture.
- Thermal lag
  - Heating/Cooling rates
  - Sample mass
- Processing errors

• Modulated DSC

Reversible Transitions (All physical changes)

- Glass Transition
- Melting

Non-reversible (Chemical Reactions)

- Curing
- Oxidation/degradation
- Evaporation

THANK YOU FOR YOUR ATTENTION