

MSE-S310 Lecture 3A

Differential Scanning Calorimetry (DSC)

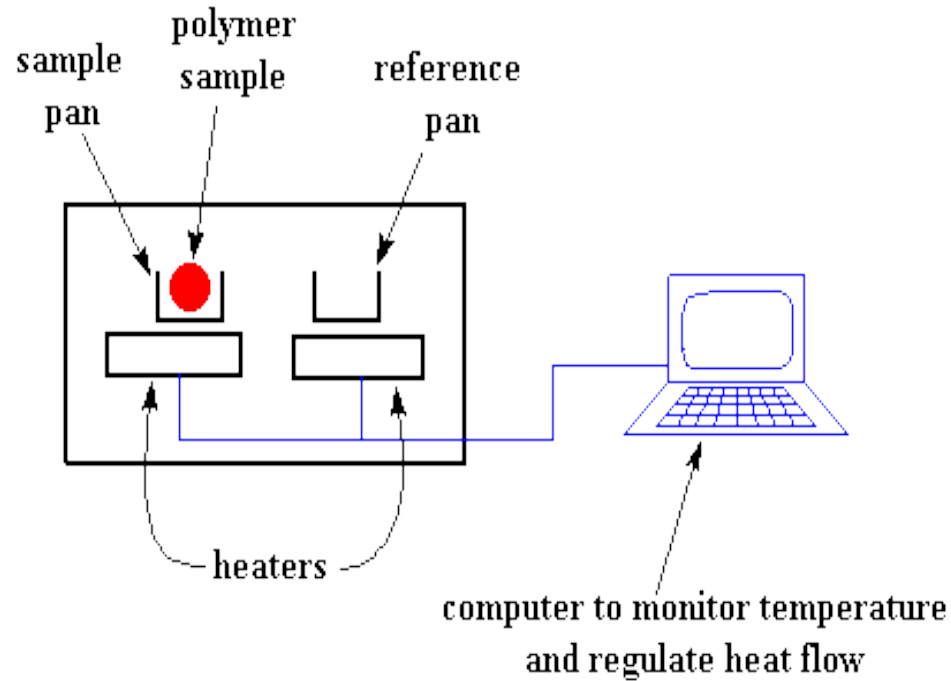
Recap

Differential Scanning Calorimetry (DSC) is a thermal analysis technique in which the heat flow into or out of a sample is measured as a function of temperature or time, while the sample is exposed to a controlled temperature program.

It is a very powerful technique to evaluate material properties such as glass transition temperature, melting, crystallization, specific heat capacity, cure process, purity, oxidation behavior, and thermal stability.

Differential Scanning Calorimeter measures the energy absorbed or released from a sample as a function of time or a temperature profile.

DSC of Polymer sample



The sample is sealed in an aluminum pan. The reference is an inert material such as alumina, or just an empty aluminum pan.

DSC of Polymer sample

- There are two pans. In one pan, the sample pan, you put your polymer or any other sample. The other one is the reference pan. You leave it empty. Each pan sits on top of a heater.
- Then you tell the computer to turn on the heaters. So the computer turns on the heaters, and tells it to heat the two pans at a specific rate, usually something like 10 °C per minute. The computer makes absolutely sure that the heating the rate stays exactly the same throughout the experiment.
- But more importantly, it makes sure that the two separate pans, with their two separate heaters, heat at the same rate as each other.

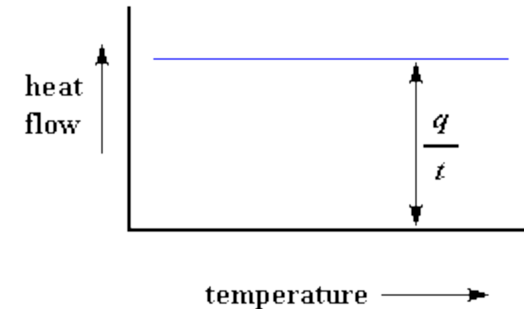
DSC of Polymer sample

- Why wouldn't they heat at the same rate? The simple reason is that the two pans are different. One has polymer in it, and one doesn't. 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. By measuring just *how much* more heat it has to put out is what we measure in a DSC experiment.

Specifically what we do is this: We make a plot as the temperature increases. On the *x*-axis we plot the temperature. On the *y*-axis we plot difference in heat output of the two heaters at a given temperature.

Heat Capacity

When we start heating our two pans, the computer will plot the difference in heat output of the two heaters against temperature. That is to say, we're plotting the heat absorbed by the polymer against temperature.



The heat flow at a given temperature can tell us something. The heat flow is going to be shown in units of heat, q supplied per unit time, t . The heating rate is temperature increase T per unit time, t .

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

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

Heat Capacity

Let's say now that we divide the heat flow q/t by the heating rate T/t . We end up with heat supplied, divided by the temperature increase.

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

Endothermic and Exothermic Process

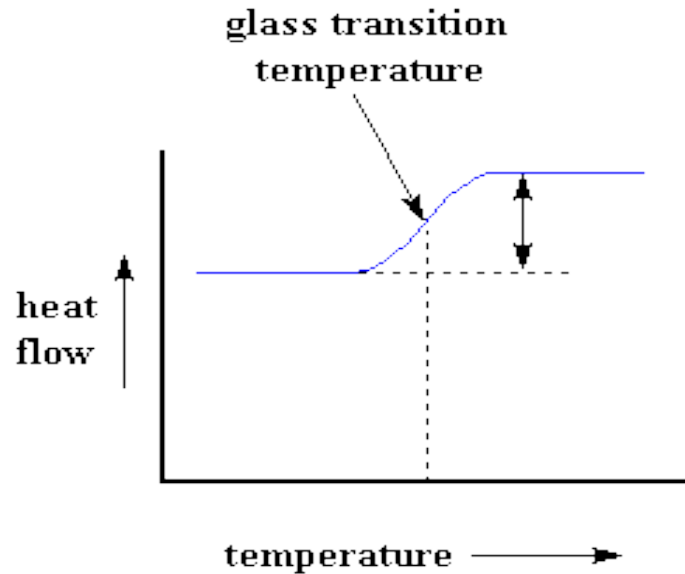
Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes: $dq_p / dt = dH / dt$. Here dH/dt is the heat flow measured in mW or equivalently $mJ s^{-1}$.

The heat flow difference between the sample and the reference:

$$\Delta dH/dt = dH/dt_{\text{sample}} - dH/dt_{\text{reference}}$$

and can be either positive or negative. In an endothermic process (in case of polymers) such as most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence $\Delta dH/dt$ is positive.. In an exothermic process, such as crystallization, some cross-linking processes, oxidation reactions, and some decomposition reactions, the opposite is true and $\Delta dH/dt$ is negative.

The Glass Transition Temperature



When we heat the polymer a little more. After a certain temperature, our plot will shift upward suddenly, like this. This means we're now getting more heat flow. This means we've also got an increase in the heat capacity of our polymer.

This happens because the polymer has just gone through the glass transition. And as polymers have a higher heat capacity above the glass transition temperature than they do below it.

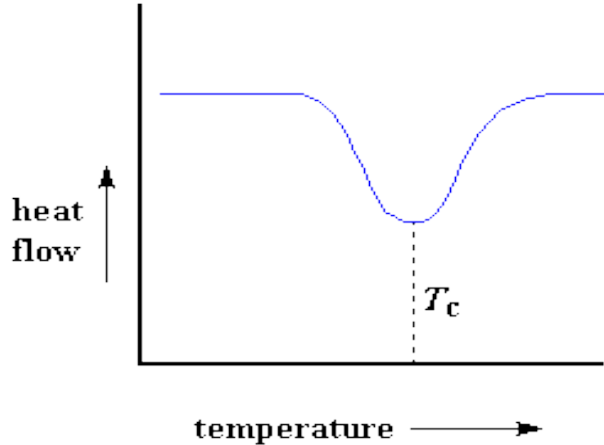
The Glass Transition Temperature

- Because of this change in heat capacity that occurs at the glass transition, we can use DSC to measure a polymer's glass transition temperature.
- We may notice that the change doesn't occur suddenly, but takes place over a temperature range. This makes picking one discrete T_g kind of tricky, but we usually just take the middle of the incline to be the T_g .

Crystallization

- Above the glass transition, the polymers have a lot of mobility. They wiggle and squirm, and never stay in one position for very long. When they reach the right temperature, they will have gained enough energy to move into very ordered arrangements, which we call crystals, of course.
- When polymers fall into these crystalline arrangements, they give off heat. When this heat is dumped out, We can see this drop in the heat flow as a big dip in the plot of heat flow versus temperature:

Crystallization



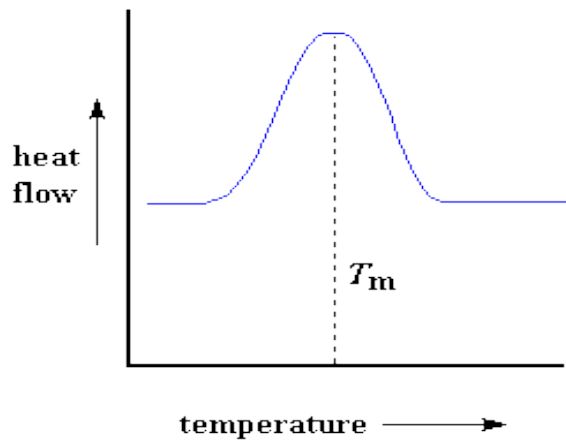
Also, because the polymer gives off heat when it crystallizes, we call crystallization an *exothermic* transition.

This dip tells us a lot of things. The temperature at the lowest point of the dip is usually considered to be the polymer's crystallization temperature, or T_c . Also, we can measure the area of the dip, and that will tell us the latent energy of crystallization for the polymer.

But most importantly, this dip tells us that the polymer can in fact crystallize. If you analyzed a 100% amorphous polymer, like atactic [polystyrene](#), you wouldn't get one of these dips, because such materials don't crystallize.

Melting

- Heat may allow crystals to form in a polymer, but too much of it can be their undoing. If we keep heating our polymer past its T_c , eventually we'll reach another thermal transition, one called melting.



When we reach the polymer's melting temperature, or T_m , those polymer crystals begin to fall apart, that is they melt. The chains come out of their ordered arrangements, and begin to move around freely. And in case you were wondering, we can spot this happening on a DSC plot.

Melting

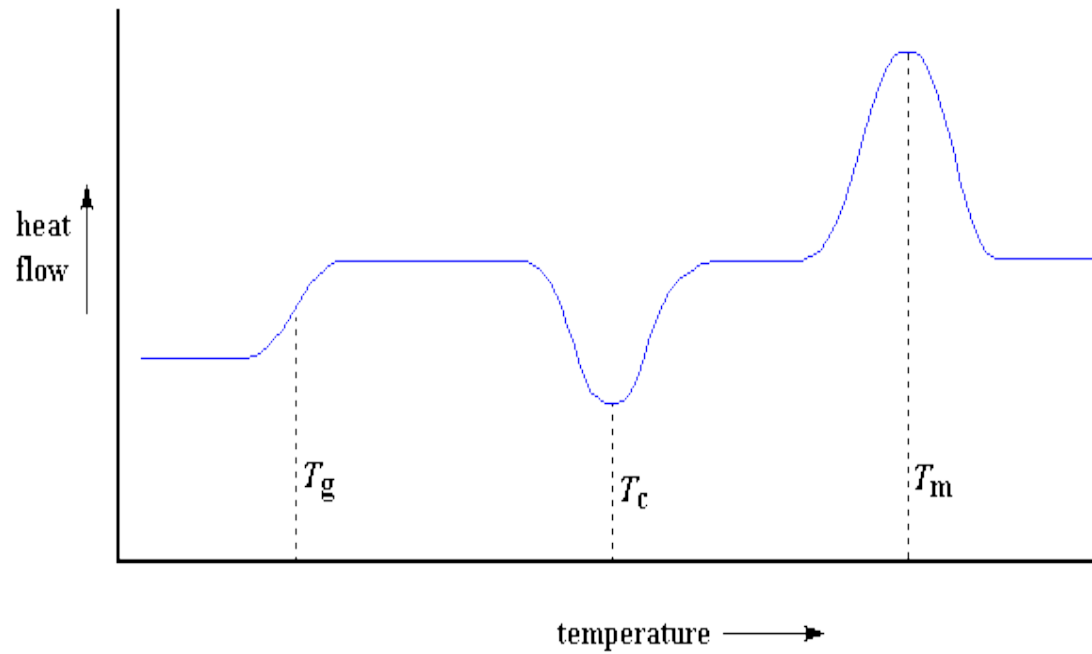
- Remember that heat that the polymer gave off when it crystallized? Well when we reach the T_m , it's payback time. There is a latent heat of melting as well as a latent heat of crystallization. When the polymer crystals melt, they must absorb heat in order to do so.
- Remember melting is a first order transition. This means that when you reach the melting temperature, the polymer's temperature won't rise until all the crystals have melted.
- This means that the little heater under the sample pan is going to have 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 peak on our DSC plot.

DSC Curve

We can measure the latent heat of melting by measuring the area of this peak. And of course, we usually take the temperature at the top of the peak to be the polymer's melting temperature, T_m . Because we have to add energy to the polymer to make it melt, we call melting an *endothermic* transition.

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

DSC Curve



The entire DSC plot, right before your very eyes!

DSC Curve

The crystallization dip and the melting peak will only show up for polymers that can form [crystals](#). Completely amorphous polymers won't show any crystallization, or any melting either. But polymers with both crystalline and amorphous domains, will show all the features you see above.

If you look at the 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 there's no peak, either. This is because there is no latent heat given off, or absorbed, by the polymer during the glass transition.

DSC Curve

➤ 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*. Transitions like melting and crystallization, which do have latent heats, are called *first order transitions*

Summary

- DSC Curve of polymer was explored.
- Three transitions were observed i.e Glass transition, Crystallization, and Melting.
- Crystallization peak was negative i.e exothermic and melting was positive i.e endothermic