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Differential Scanning Colorimetry

Summer 2021 High School Outreach Program

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Agenda

- Introduction
- Classification
- Working Process
- Pan and Lid
- Sample preparation
- Data analysis
- Example
- Factors
- Advantages/disadvantages
- Applications
- Exercise

- What is DSC?

Differential Scanning Calorimetry or DSC is a technique that is used to study what happens to polymers when they're heated.

It measures the difference in heat flow between the sample and the reference. It is used to study the thermal transitions of a polymer.

Thermal transitions are the changes that take place in a polymer when heated.

- Classification

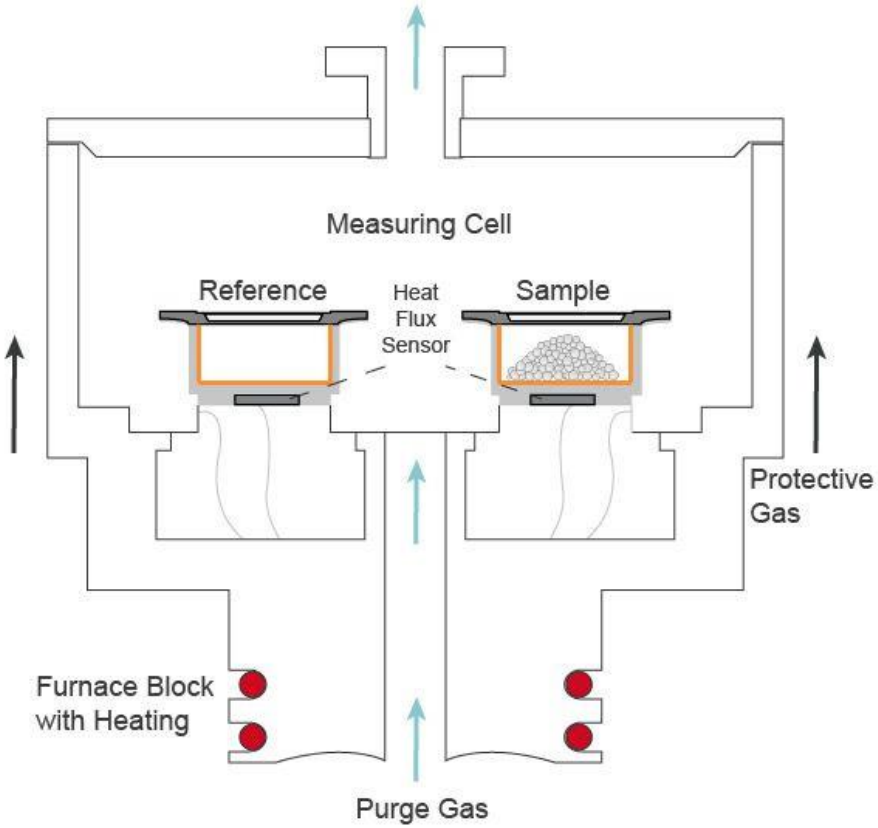
There are two different types of DSC:

1. Heat-flux DSC which measures the difference in heat flux between the sample and a reference

2. Power differential DSC which measures the difference in power supplied to the sample and a reference.

Heat-flux DSC

- There is a reference and a sample that will be both heated
- Heat flows into the sample
- The sample is measured while it is tested for temperature
- The chamber's temperature changes but the rate stays constant



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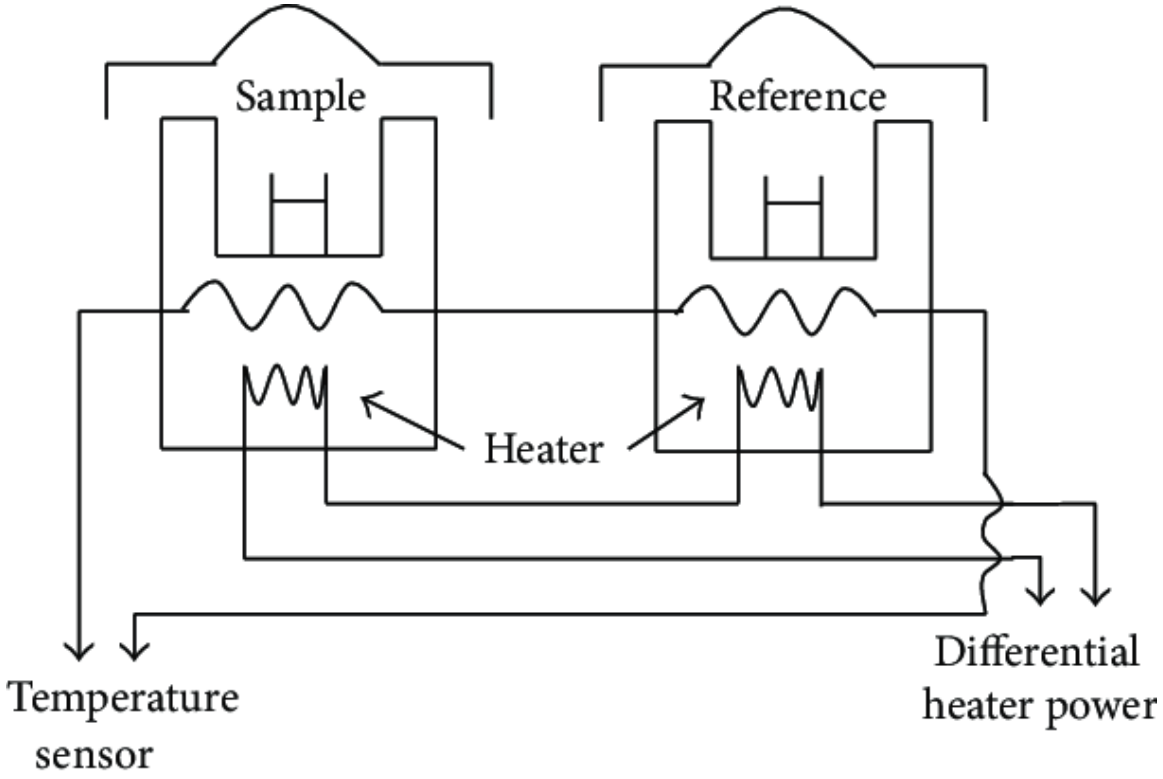
Power Compensation DSC

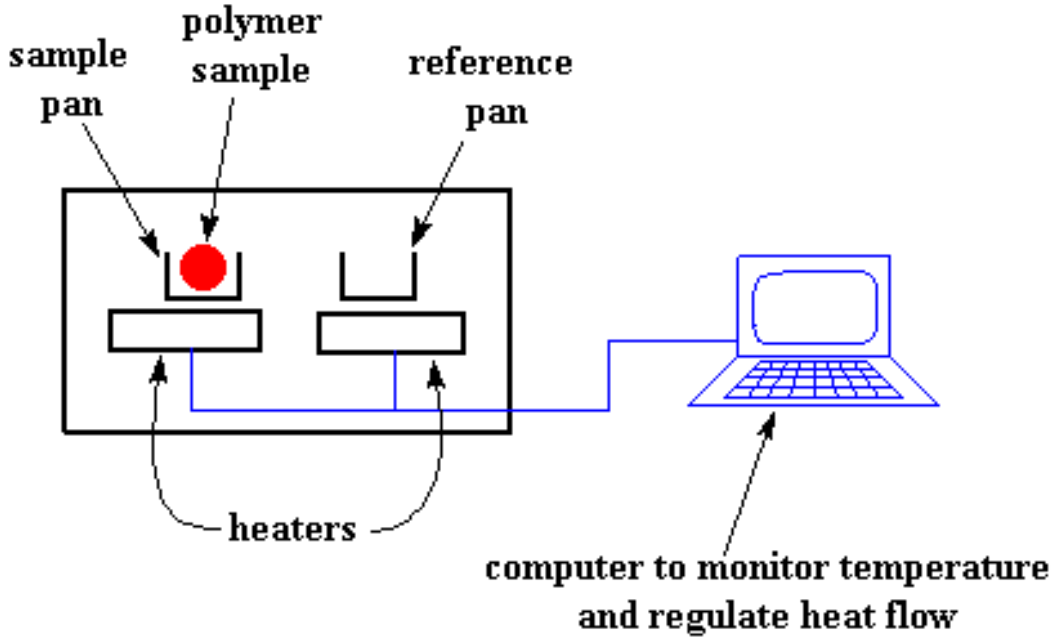
- Difference between thermal energy is applied to the sample and reference per unit is measured to equalize temperature



https://www.researchgate.net/profile/Weilun-Wang-3/publication/258397106/figure/fig5/AS:459649817288708@1486600464631/Power-compensation-DSC.png

- How is it used?

The first step of DSC would be to heat it. The polymer is heated in a device that looks like this:



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Working Process

For the sake of clarity this is the process of specifically a power differential DSC.

There are two pans, one will have a polymer sample and the other will serve as a reference pan and is empty. Each pan sits on a heater and when the process begins, it is heated at a rate of about ten Celsius per minute.

Throughout the experiment it is important to have the heating rates the same for both pans. This allows for consistent results when they come out of the DSC.

Working Process

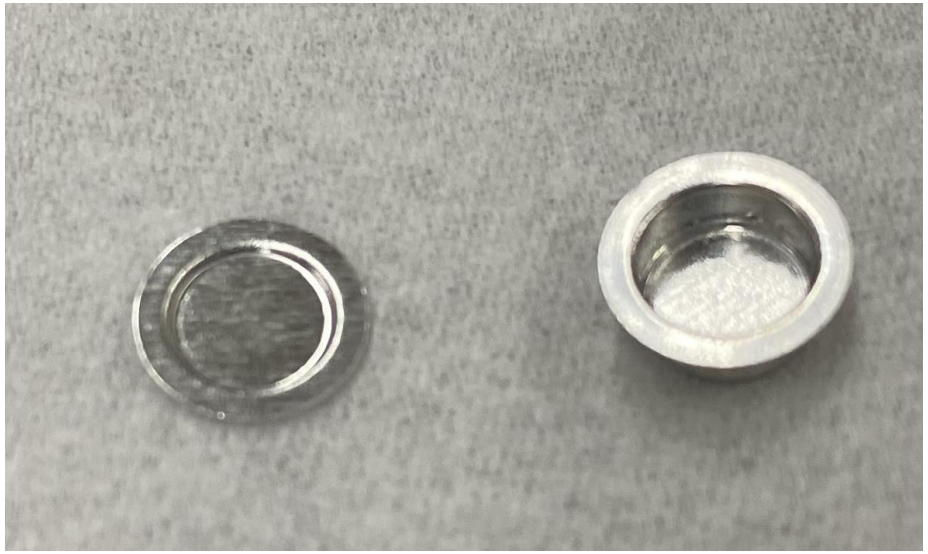
Having constant rate of heating in both chambers is usually difficult to maintain because when one pan is empty and the other has the sample, there is more to heat in the pan with the sample than the one without the sample making the process of keeping the temperature the same in both heaters super important which may require the need to increase temperature in the chamber with the sample.

And in fact, the different in the temperature that was needed to heat the reference pan versus the pan with the sample is exactly what is being measured.

Working Process

The working process of Heat flux DSC is similar, the difference is that there is one heater with both pans on it. Attached to the pans will be sensors that will produce the same outcome as the ones shown in the power differential DSC.

Pan and Lid



Standard Aluminum Pan and lid

- How to prepare samples?
  - First decide on the lid sizes that are being used for the sample and find the
  - corresponding pan and platform
  - Find the mass of only the pan and lid
  - Once the mass is recorded, press it down and set it aside as a reference
  - Grab a new pan and lid to measure the mass
  - Once the new mass is recorded, put a small amount of sample into the pan and lid

Sample Preparation

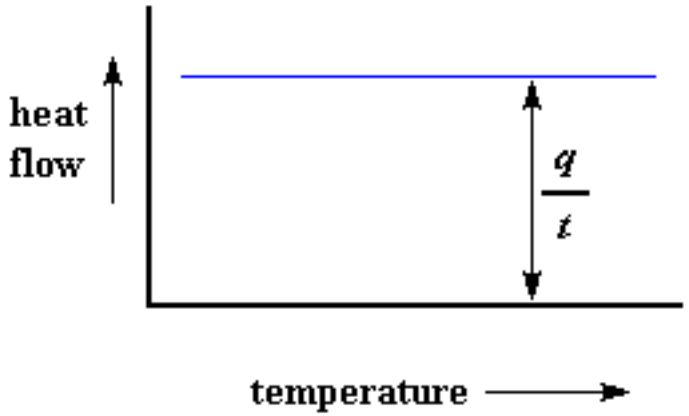
- Find the mass of the sample along with the pan and lid
- Place the sample with the pan and lid into a platform and press down
- Once the sample is pressed it is ready to be placed in the DSC

- Data Analysis

There are three things usually analyzed in a DSC graph:

1. The glass transition temperature
2. Crystallization
3. Melting

During heating a polymer, when the two pans start heating, the difference in the heat output of the two pans will be plotted as shown below.



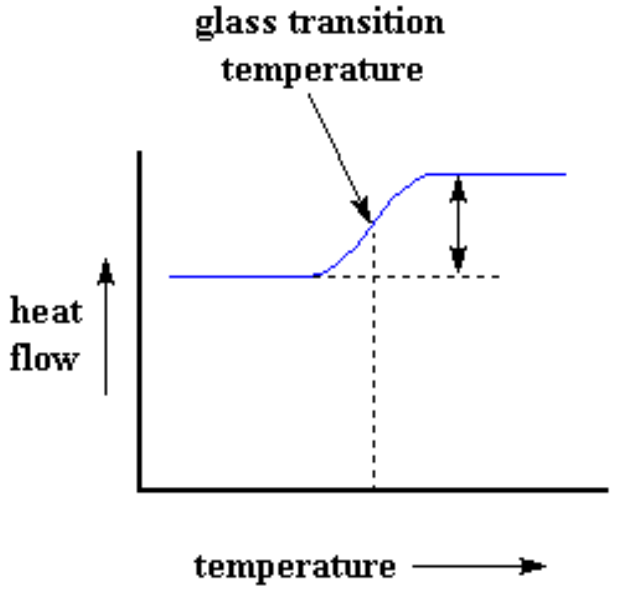
https://www.pslc.ws/welcome/tour/macrog/dsc2.htm

The Glass Transition Temperature

At some point the graph shifts upwards because of heat flow and that our polymer has an increase in heat capacity since the polymer just went through a glass transition phase

When polymers are above the glass transition temperature, they have a higher heat capacity than when they are below the glass transition temperature. Because of this, this allows us to use DSC to measure a polymer's glass transition temperature.

But the change doesn't occur suddenly, making it hard to pinpoint the true glass transition temperature. To solve this, the estimate is usually the middle of the slope of the glass transition.



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Crystallization

Once above the glass transition temperature, the polymers start moving around due to an increase of mobility since the heat has increased. Because of this, polymers will move around a lot and rarely stay in one position. Once the correct temperature is reached, polymers reach a stable arrangement called a crystalline arrangement.

When polymers go in these arrangements, they release heat which causes the big dip as seen in the figure on the right and the heat flow is dramatically decreased.

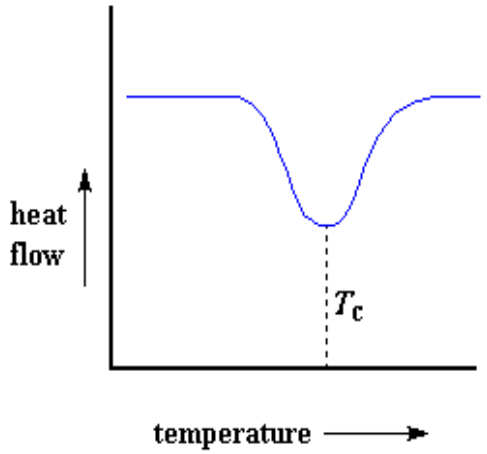
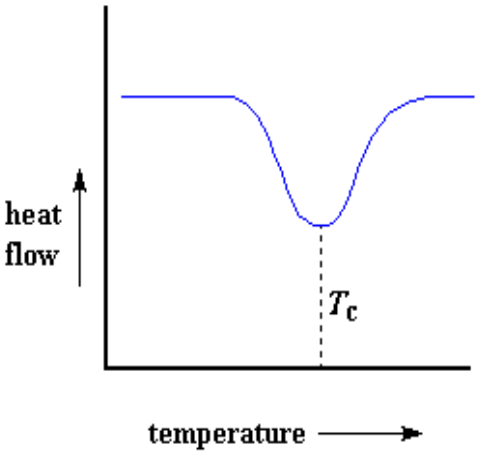


Figure-4: DSC Plot for T_C

Data Analysis - Crystallization



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Crystallization can be seen by the dip as shown on the left. As a Polymer crystalizes it releases heat which makes it an exothermic reaction which is why the lowest point can show us what the crystallization temperature is, or T_c. The dip also confirms that the polymer can crystalize, which is important because there are some that would have no dips such as the one on the left. For example, an amorphous polymer like Polybutadiene would produce no dips, because amorphous materials do not crystallize.

Melting

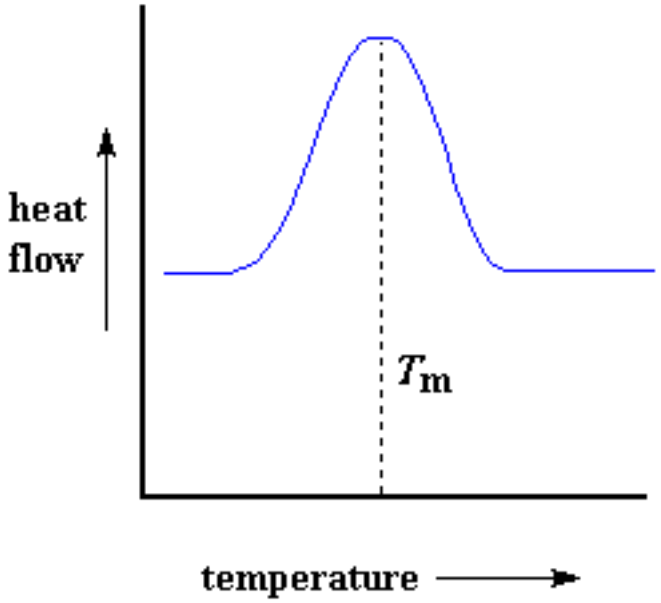
After a polymer is heated for a while, it will start melting once it passes its T_c . This results in the polymer reaching the melting temperature shown as T_m, once this is reached, the polymers that crystalized earlier will melt and fall apart. Once they leave their formation, they will move freely again

This is considered an endothermic reaction because it would have to absorb heat in order to go through the melting transition

Data Analysis - Melting

Furthermore, melting is considered a first order transition. Because of this, the polymer's temperature does not rise until the crystal structures have all melted. Thus, the heater has to raise the temperature in order to not only melt the crystals, but also keep the temperature rising at a constant rate while keeping up with the temperature for the other pan without the sample.

This leads to a large peak due to the huge increase of heat flow as shown on the graph on the right.



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Data Analysis - Melting

By calculating the area of the peak as shown in the graph in the previous slide, the latent heat can be calculated. And at the very top of the peak, there is a point that can be labeled as the melting point of the polymer.

Data Analysis - Conclusion

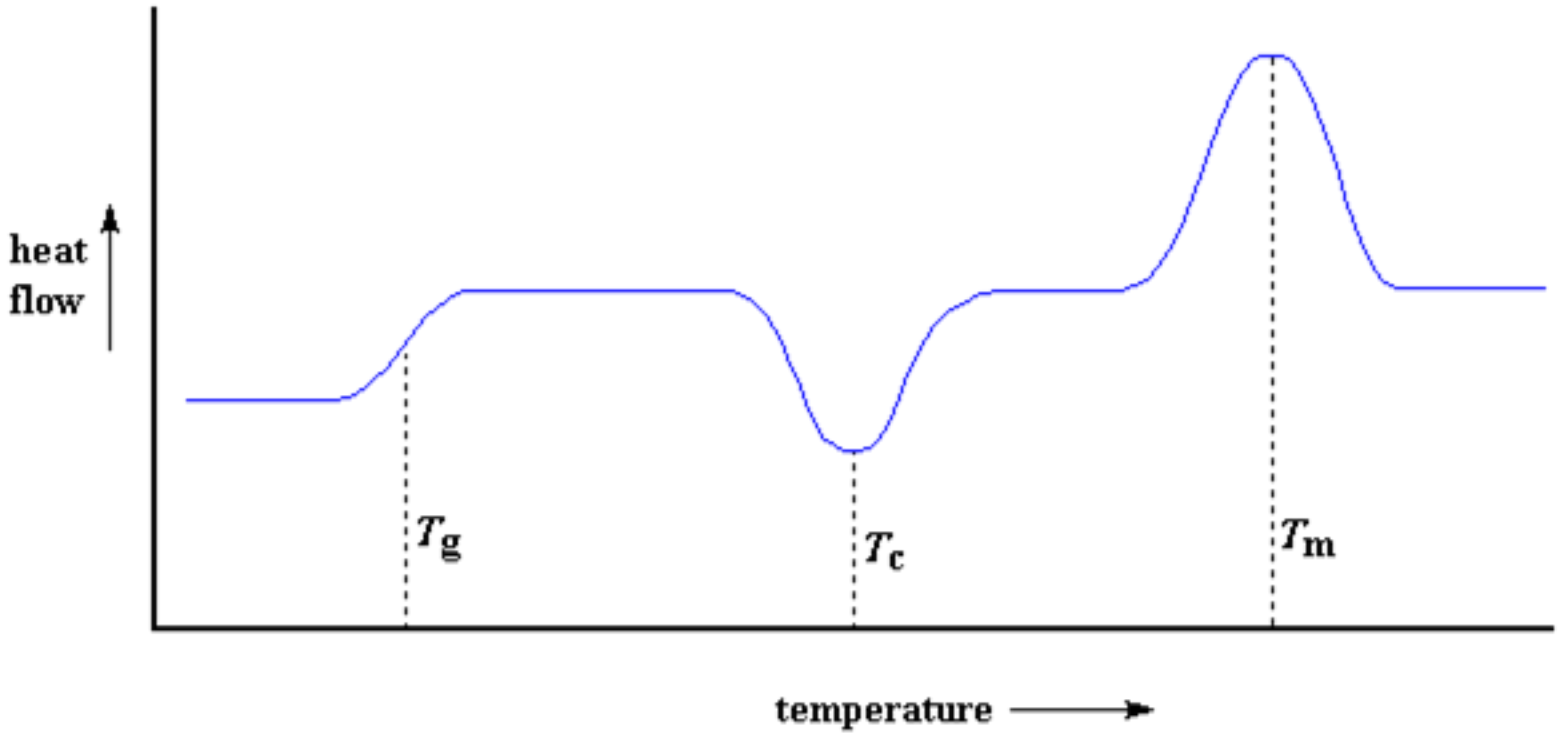
When the polymer was heated past the glass transition temperature it will have a steep slope in the plot

When there is a dip in the plot that shows the crystallization temperature

When there is a large peak it shows the melting temperature

Therefore, a whole plot will mostly look like this:

Data Analysis - Putting It All Together



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Data Analysis - Conclusion

This is only a general idea of what a DSC plot will look like, and it will change depending on different factors such as mentioned earlier that amorphous polymers will not show any sign of crystallization and it won't show any melting either. However, most polymers will show the features shown above.

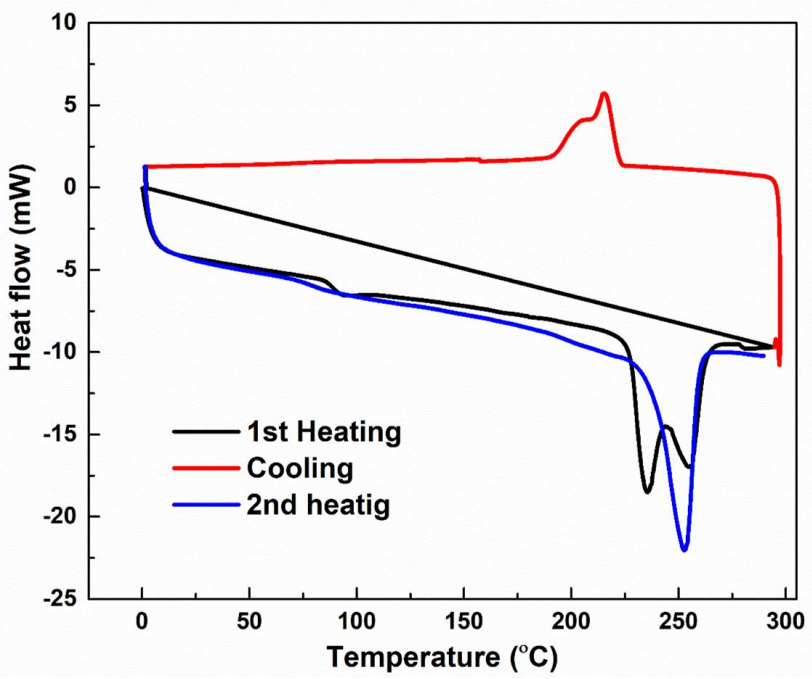
As for the differences in the way the glass transition and the other two transitions appear; there is no peak and only a slope shown for the glass transition because there is no latent heat given or absorbed by the polymer during that transition.

And because both melting and crystallization will give off and absorb heat, there is a peak in both transitions

- PET

The working principle of DSC is to do wide temperature scans in heat, cool, heat cycles. Here is a DSC heat cool heat cycle plot of PET (Polyethylene terephthalate)-

This figure shows the DSC plot of PET which was heated at a controlled rate of 30℃ per minute. Figure 7 comprises both exothermic and endothermic thermal peaks that occurred during a temperature scan within 0−300℃.



Example

The first endothermic step (i.e., glass transition) occurred in the first scan, followed by an exothermic peak because of cold crystallization, after that the endothermic peak because of melting.

For the first scanning experiment(1st heating) of PET (black line) the glass transition (T_g) was recorded at around 94℃. In addition, the doublet melting peaks (endotherms) were recorded at 235℃ and 256℃. Notably, the cold crystallization peak was not seen in the DSC plots of PET.

Example

For the second heating experiment (blue line), the glass transition (T_g) region was almost vanished. In addition, the melting peaks (endotherm) were recorded at 253℃. Similar to the previous. The cold crystallization peak was not seen in the DSC plots of PET.

In the cooling experiment of PET which was cooled from a melt at an extremely low rate (i.e., 10℃ per minute). For the cooling experiment the exothermic peaks appeared at 251℃ with a shoulder at 204℃.

Factors affecting DSC curve

- Instrumental factors:
  - Furnace heating rate.
  - Recording or chart speed
  - Furnace atmosphere
  - Geometry of sample holder
  - Location of sensors
  - Sensitivity of recording mechanism
  - Composition of sample container

- Sample Characteristics:
  - Amount of sample
  - Solubility of evolved gases in sample
  - Particle size
  - Heat of reaction
  - Sample packing
  - Nature of sample
  - Thermal conductivity

Advantages & Disadvantages of DSC

Advantages

- Most popular technique
- Instruments can be used at very high temperatures
- Instruments are highly sensitive
- Flexibility in sample form
- Can be tested in variety of environments
- Flexibility in sample volume
- Stability of material

Disadvantages

- Relative low accuracy and precision.(5-10%)
- Can not be used for overlapping reactions

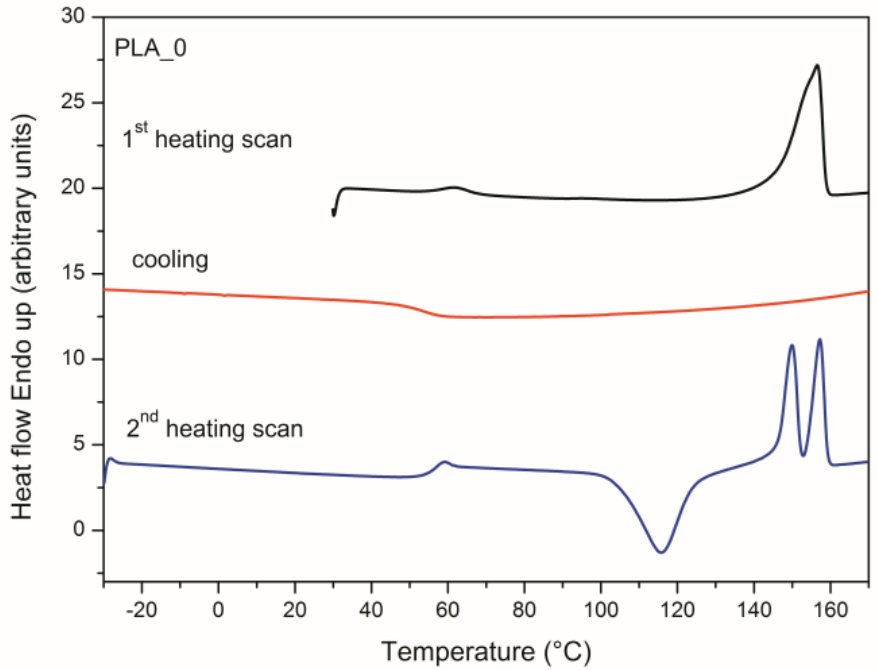
Applications of DSC

There are many applications of DSC in different sectors. Some applications of DSC in Polymer Chemistry are-

- DSC is used in characterizing materials.
- It is used to determine phase transition.
- It is used in studying heat of melting, crystallization, percentage of crystallinity, heat capacities, thermal stabilities, purities, oxidative stabilities, food science, drug analysis, and liquid crystals.
- It is also used to determine reaction kinetics.

Exercise:

1. Analyze the graph. Determine the value of T_g,T_m & T_c. Describe the whole process.



Exercise

2. Make a flowchart of the working process of the DSC machine.

3. Discuss what precautions to take during the whole process. (Sample processing, machine processing, Data analysis)

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