HUMBOLDT-UNIVERSITÄT ZU BERLIN
MATHEMATISCH-NATURWISSENSCHAFTLICHE FAKULTÄT I

INSTITUT FÜR PHYSIK . Physik von Makromolekülen

Differential scanning calorimetry investigation of polymers

Persons in charge: See announcement in guidelines

Table of contents

Topic
In this experiment, the thermal properties of different synthetic polymers are investigated. The different transitions such as glass transition, melting and crystallization will be determined. This DSC study will make it possible also to evaluate the heat capacity of a polymer in a well defined range of temperatures.

Duration
The protocol is due after one week at latest !

1. Introduction

Differential scanning calorimetry (DSC) is a technique which allows to explore the thermal behavior of polymers, namely the changes that take place in a polymer upon heating, i.e. themelting of a crystalline polymer or the glass transition.
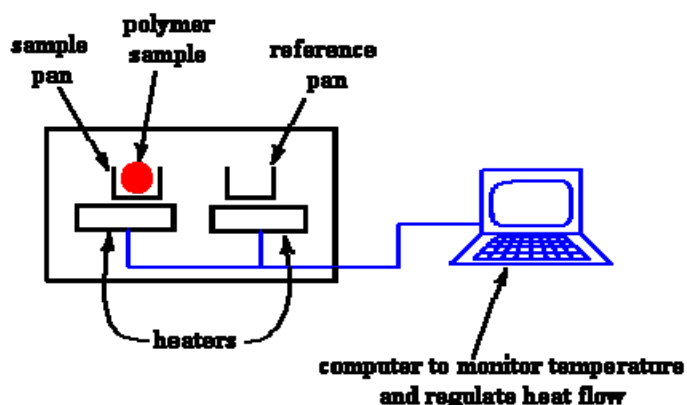
The DSC set-up is composed of two essential parts: a measurement chamber and a computer which allows to monitor the temperature and to regulate the heat flow. In the measurement chamber are placed two pans:
The sample pan, where the sample under investigation is located.
The reference pan, which normally is left empty.
Each pan is positioned on the top of a heater. Via a computer interface, it is possible select the rate of the heating of the two pans; usually it is set to ca. 10 °C/min.

The adsorption of heat will be different in the two pans due to the different composition in the pan. In order to keep the temperature of the two pans constant during the experiment, the system needs to provide more or less heat to one of the two pans. The output of the DSC experiment is the additional quantity of heat which is given to the pan in order to keep the temperature of the two pans equal. In other words, the output of the DSC is a plot of the difference in heat output of the two heaters vs. temperature (T).

2. Thermal properties of a polymer

2.1 Heat Capacity

The heat capacity (C_P) of a system is the quantity of heat needed to raise the temperature of the system of 1 °C. It is usually given in units of Joules/°C. It can be derived introducing two parameters, namely the heat flow and heating rate. Whilst the heat flow is the heat (q) supplied per unit time (t), the heating rate is variation of temperature (ΔT) per unit time (t), namely:

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

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

Dividing the heat flow by the heating rate, one obtains the heat capacity:

$$\frac{\dfrac{q}{t}}{\dfrac{\Delta T}{t}} = \frac{q}{\Delta T} = C_P = heat \quad capacity$$

In Figure 2 it is shown a simple plot (q/t) vs. T, that is the heat absorbed (q) by the polymer in a unit of time vs. temperature (T).
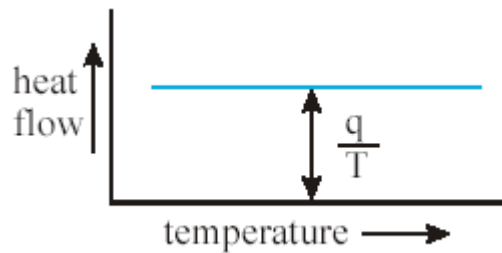

Figure 2: q/t vs. T plot.

2.2 Glass Transition

Decreasing the temperature on a polymer which is in its molten state, the polymer reaches the glass transition temperature (T_g). At this point the mechanical properties of the polymer change from those of a rubber (elastic) to those of a glass (brittle). Below the glass transition temperature, the available polymer motions are limited, but above the glass transition more motions are accessible. A typical (q/t) vs. T plot of a glass transition is shown in Figure 3. In the two regimes, before and after the T_g, the polymers have different heat capacities: Usually polymers have a higher C_p above the T_g. Due to this difference in C_p, the DSC is a valuable method to determine the T_g. It is important to note that the transition does not occur suddenly, but usually takes place over a temperature range. To overcome this problem the temperature in the middle of the inclined part of the graph is by definition the T_g.
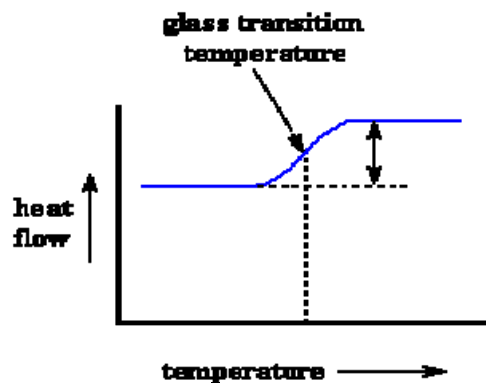

Figure 3: Typical (q/t) vs. T plot of a glass transition in a polymer.

2.3 Crystallization

Above the glass transition, the polymer chains posses a notable mobility. They wiggle and squirm, and never remain 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. When polymers fall into these crystalline arrangements, they give off heat to the system, thus the process is exothermic. In fact the heat flow drops as one can note from the big dip in the plot of (q/t) vs. T:
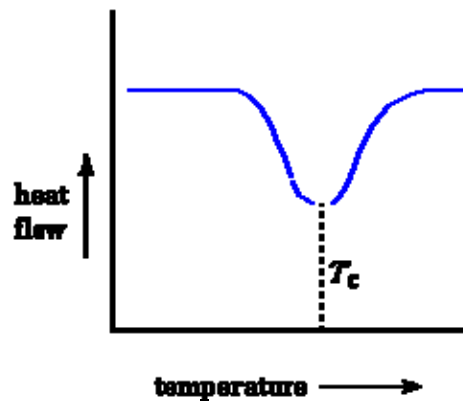

Figure 4: Typical (q/t) vs. T plot of a crystallization transition in a polymer.

From the plot in Figure 4 one can:
- have confirmation of the occurrence of the crystallization;
- determine the polymer's crystallization temperature (T_c) as the lowest point of the dip;
- gain insight into the latent energy of crystallization for the polymer by observing the area of the dip.

2.4 Melting

At the melting temperature (T_m) the chains are allowed to move around freely, thus they do not possess an ordered arrangements. Upon melting the polymers absorb heat, thus melting is an endothermic transition. The melting is a first order transition since when the melting temperature is reached; the polymer's temperature does not rise until all the crystals have completely melted.
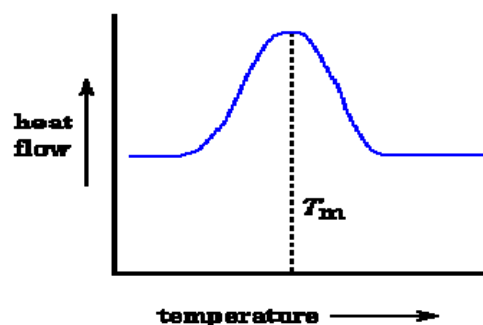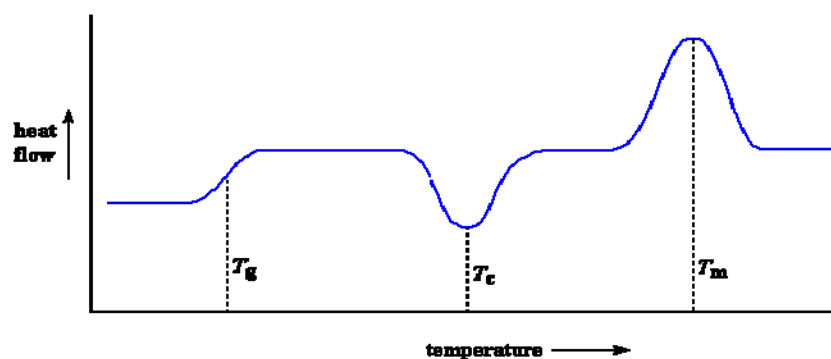

Figure 5: Typical (q/t) vs. T plot of a melting transition in a polymer.

Also in this case, the latent heat of melting can be measured from the area of the peak in Figure 5. The T_m is the temperature of the peak.

2.5 Combining T_g, T_c and T_m

Figure 6 shows a DSC plot which includes all these three types of transitions.

The entire DSC plot, right before your very eyes!
Figure 6: Typical (q/t) vs. T plot of both glass,
crystallization and melting transitions in a polymer.

Noteworthy, not all the polymers exhibit all these three transitions. The crystallization dip and the melting peak will only show up for polymers that can form crystals. Completely amorphous polymers will not show any crystallization, or any melting either. But crystalline polymers frequently posses amorphous domains. This is the reason why a polymer can exhibit both a glass transition temperature and a melting temperature as in Figure 6. One could therefore point out that the amorphous portion undergoes the glass transition only, and the crystalline portion undergoes melting only.

Comparing the different transitions in the DSC plot one can note an essential 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. In the glass transition it is just possible to observe a change in the heat capacity of the polymer but there is no latent heat involved: consequently it can be defined as a second order transition. Differently, both melting and crystallization involve giving off or absorbing heat. Since they do have latent heats, they can be defined as first order transitions.

The exact temperatures at which the polymer chains undergo these transitions depend on the structure of the polymer. Subtle changes in polymer structure can induce huge changes in T_g.

3. Glass Transition vs. Melting

To avoid any misunderstanding it is of prime importance to distinguish the glass transition from the melting one. As mentioned above, melting occurs only in a crystalline polymer, while the glass transition takes place to just to polymers in the amorphous state.

There is another notable difference between melting and the glass transition. Upon heating a crystalline polymer at a constant rate, the temperature increases at a constant rate. The temperature continues to increase until the polymer reaches its melting point. When this happens, the temperature will hold steady for a while, even though the system keeps adding heat to the polymer. It will hold steady until the polymer has completely melted. Then the temperature of the polymer will begin to increase once again. The temperature rising stops because melting requires energy. All the energy added to a crystalline polymer at its melting point goes into melting, and none of it goes into raising the temperature. This heat is called the latent heat of melting.

After melting the temperature begins to rise again, but at a slower rate. This is due to the higher heat capacity of the molten polymer than the solid crystalline polymer.

The case of the glass transition is different. When an amorphous polymer is heated, first the temperature rises at a rate determined by the polymer's heat capacity, just as for a crystalline polymer. When the T_g is reached the temperature does not stop rising. There is no latent heat of glass transition. But the temperature rising rate above the T_g changes, namely the polymer undergoes an increase in its heat capacity.

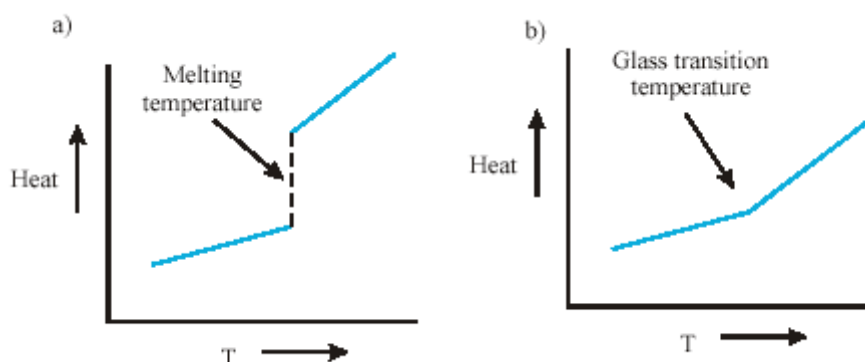In Figure 7 are shown the plots q vs. T.

Figure 7: Plot of q vs. T for (a) a crystalline polymer and (b) an amorphous polymer.

The plot in Figure 7a, which depicts the case of a 100% crystalline polymer, is discontinuous. The break is the melting temperature, where an amount of heat is added to the system without any temperature increase. The slope, which in this kind of plot corresponds to the heat capacity, gets steeper on the high side of the break.

On the other hand, the graph in Figure 7b, which shows the behavior of a 100% amorphous polymer, does not exhibit a break. The only change that can be observed at the glass transition temperature is an increase in the slope, which is due to an increase in heat capacity.

Note: The dip or peak on curve depends on you choose exothermic peak up or down on Y axis. All the plots above are exothermic down mode.

4. DSC Instruments

Two types of DSC instrument have been widely used: the heat flux DSC (e.g., TA DSC and Mettler DSC) and the power compensational DSC (Perkin-Elmer system)

4.1 Heat flux DSC:

1 Disk.
2 Furnace.
3 Lid.
4 Differential thermocouples.
5 Programmer and controller.
S Pan with sample substance.
R Pan as reference
Φ_{fs} Heat flow rate from furnace to sample pan.
Φ_{fr} Heat flow rate from furnace to reference pan.
ϕm Measured heat flow rate.
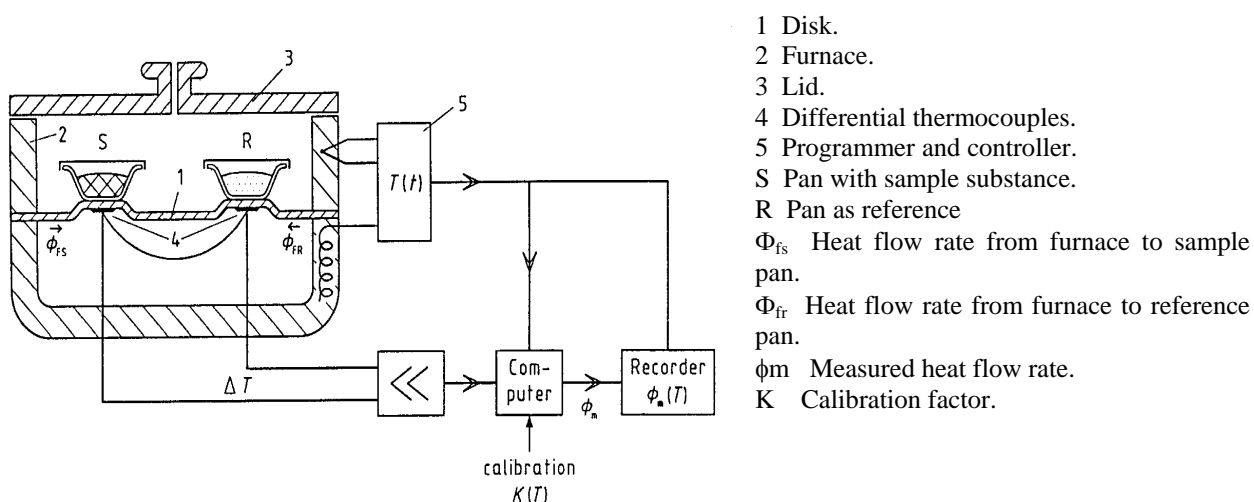K Calibration factor.

Figure 8: Scheme of a heat flux DSC system.

Figure 8 shows a schematic diagram of Heat DSC system, where the sample and reference are heated from the same source and the temperature difference ΔT is measured. This signal is converted to a power difference $\Delta P(\Delta P = \Delta Q/dt$) using the calorimetric sensitivity.

4.2 Power compensated DSC

S Sample measuring system with pan microfurnace and lid.

R Sample measuring (analogous to S).
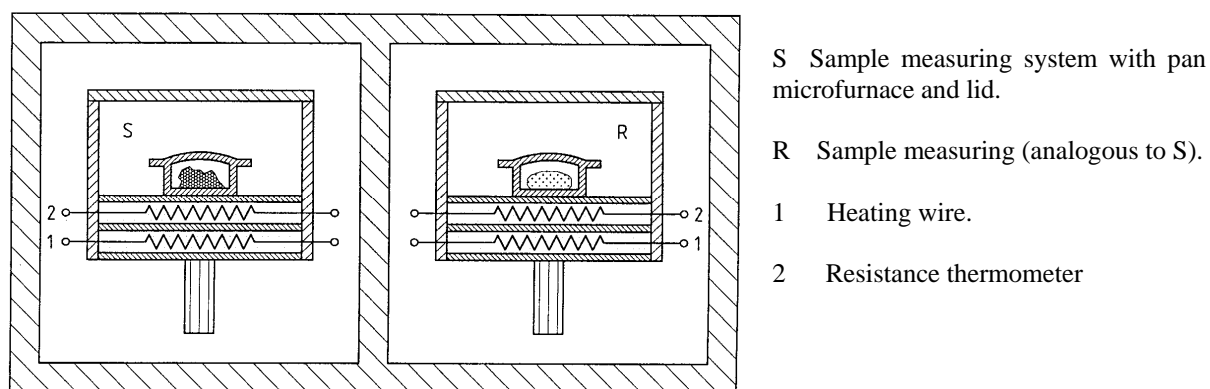
1 Heating wire.

2 Resistance thermometer

Figure 9: Scheme of a power-compensated DSC.

Figure 9 shows a schematic diagram of Power-compensated DSC, where the sample and reference are heated by separate, individual heaters, and the temperature difference is kept

close to zero, while the difference in the electrical power needed to maintain equal temperatures ($\Delta P = \Delta Q/dt$) is measured.

To be more precise, the temperature of the furnace is raised or lowered in a linear fashion, and the resultant differential heat flow to the sample and reference is monitored by area thermocouples fixed to the underside of the disk platforms. These thermocouples are connected in series and measure the differential heat flow using the thermal equivalent of Ohm's Law: $\dfrac{dq}{dt} = \dfrac{\Delta T}{R_D}$, where dq/dt= heat flow, _T=temperature difference between reference and sample and R_D=thermal resistance of the disk.

The DSC 2920 Differential Scanning Calorimeter (TA Instruments) (Figure 10), which will be used in the PMM laboratories, is indeed a typical heat flux DSC. It can provide qualitative and quantitative measurements about physical and chemical changes that involve endothermic and exothermic processes, or changes in heat capacity, and also get the benefits of MDSC.
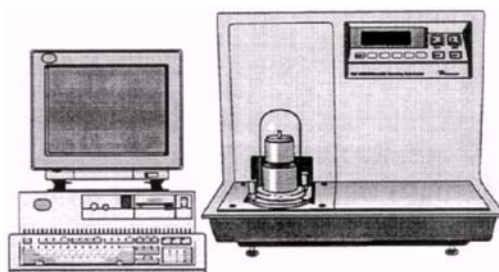

Figure 10: DSC-2920 which is the set-up available in PMM labs.

5. Modulated DSC

Traditional Differential Scanning Calorimetry (DSC) is a well-accepted technique for analyzing thermal transitions in materials. It provides information on the temperature at which transition occurs as well as quantitative measurement of the heat associated with the event.
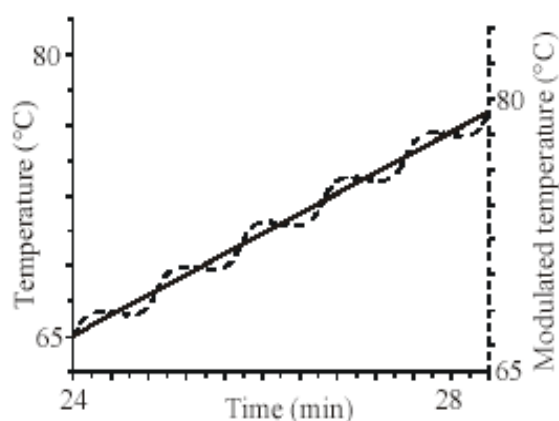

Figure 11: Typical Modulated T vs. time plot for a MDSC.

Modulated temperature DSC is an extension of DSC, in MDSC, the same heat flux DSC cell is used, but a sinusoidal temperature oscillation (modulation) is overlaid on the conventional

linear temperature ramp, resulting heating rate is sometimes faster than the underlying linear heating rate, and sometimes slower than the underlying rate. (See Figure 11)

The actual variation in heating rate depends on three experimental variables: the underlying heating rate, the amplitude of modulation, and the period (frequency) of modulation. In normal MDSC experiment, we set Amplitude ranging from +/-0.5°C to +/-1°C, an oscillation period ranging from 40 to 60 seconds, the heat rate from 1 to 5 °C/min. Employing larger amplitudes, shorter oscillation periods, and slower rate, one can achieve higher resolution.

MDSC is exploited to study the same material properties as conventional DSC including: transition temperatures, melting and crystallization, and heat capacity. However, MDSC also provides unique capabilities that increase the amount of information that can be obtained from a single DSC experiment, thereby improving the quality of interpretation. These capabilities include:

- Measured of heat capacity and heat flow in a single experiment
- Separation of complex transition into more easily interpreted components
- Increased sensitivity for detection of weak transitions
- Increased resolution of transitions without loss of sensitivity
- Increased accuracy in the measurement of polymer crystallinity
- Direct determination of thermal conductivity

The need for extending the capabilities of traditional DSC, via MDSC, is obvious from the review of the limitations of traditional DSC. MDSC overcomes all of these limitations and is therefore the technique of choice when they are observed in traditional DSC experiments.

Problems associated with DSC measurements fall into three general categories:

- Analysis of Complex Transitions

  Most transitions are complex due to the fact that they involve multiple processes. Examples would include the enthalpic relaxation that occurs at the glass transition and crystallization of amorphous or metastable crystalline structures prior to or during melting. Enthalpic relaxation is an endothermic process that can vary in magnitude depending on the thermal history of the material. Under some circumstance it can make the glass appear to be a melting transition. Simultaneous crystallization and melting make it nearly impossible to determine the real crystallinity of the sample prior to the DSC experiment. These problems are compounded further when analyzing blends of materials.

  This significant limitation in traditional DSC is due to the fact that DSC measures only the sum of all thermal events in the sample. When multiple transitions occur in the same temperature range, results are often confusing and misinterpreted. MDSC eliminates this problem by separating the total heat flow signal into its heat capacity and kinetic components.

- Need for Increased Sensitivity

  The ability of DSC to detect weak transitions is dependent on both short-term (seconds) noise in the heat flow signal and long-term (minutes) variations in the shape of the heat flow baseline. However, since short-term noise can be effectively eliminated by signal averaging, the real limitation for reproducibly detecting weak transitions is variation in baseline linearity. Because of the need to use different materials in the construction of DSC cells and because of changes in properties of these materials and the purge gas with temperature, all commercial DSC instruments have varying degrees of baseline drift and related effects. MDSC eliminates this

problem by using the ratio of two signals to calculate real changes in the sample heat capacity rather than just the absolute value of the heat flow signal.

- Need for Increased Resolution
  High resolution, or ability to separate transitions that are only a few degrees apart, requires the use of small samples and low heating rates. However, the size of the heat flow signal decreases with reduced sample size and heating rate. This means that any improvement in resolution results in a reduction in sensitivity and vice versa. Conventional DSC results are always a compromise between sensitivity and resolution.
  MDSC solves this problem by having effectively two heating rates. The average heating rate can be as low as needed to achieve the desired resolution while the instantaneous heating rate can be as high as needed to create a large heat flow signal.

To be more precise, the impact that each variable can have on the heat flow results obtained, the general equation describing calorimetric response needs to be examined. One way to mathematically represent DSC heat flow is:

$$\frac{dq}{dt} = C_p \frac{dT}{dt} + f(t,T)$$

where dq/dt= heat flow, dT/dt= heating rate, C_p=sample heat capacity, t=time, f(t,T)=function of time and temperature which govern the kinetic response and any physical or chemical transition observed in the DSC.

This equation shows that the total DSC heat flow is comprisef of two components, one which is heating rate dependent ($C_p(dT/dt)$), and another which is dependent only on absolute temperature [f(t,T)]. In other words, there is a component which directly follows the modulated heating rate and one component which does not follow heating rate (kinetic component). The MDSC measures the total ehat flow and separates it into these two components.

The signal convolution in the process of separating the raw data signals (Modulated temperature and Modulated Heat Flow) into the average and amplitude (total change in temperature and heat flow values). In MDSC, this signal separation is accomplished by a mathematical technique known as Discrete Fourier Transformation (DFT).
The DFT technique is employed to determine the measured amplitude of the sample temperature and heat flow modulation by comparing the raw modulated data to a reference sine wave of the same frequency. The DFT software in the DSC instrument continually measures the amplitude of the sine wave modulation in the raw sample temperature and raw heat flow signal. Using these amplitudes, the Heat capacity signal is calculated by the following equation:

$$C_p = K_{Cp} \cdot \frac{q_{amp}}{T_{amp}} \cdot \frac{Period}{2\pi}$$

where C_p =heat capacity (mJ/°C), K_{Cp} =heat capacity calibration constant, Q_{amp}=heat flow amplitude (mW) , T_{amp}=temperature amplitude (°C), Period=Modulation Period (sec).

Given the Heat Capacity (C_p), the Reversing Heat Flow is calculated by multiplying the C_p by the programmed (underlying) heat rate. The minus sign simply inverts the heat flow signal so that the enothermic peaks are plotted in the downwards direction. The deconvoluted

Temperature and Total Heat Flow signals are computed over one complete cycle of the respective raw modulated signal. The Nonreversing Heat Flow is computed as the difference between the Total Heat Flow and the Reversing Heat Flow. Thus the Reversing Heat Flow signal is proportional to the amplitude of the heat flow oscillations, while the Nonreversing Heat Flow is proportional to the baseline shift of the oscillations.

(For more detail about Modulated DSC operation principle, check Appendix 1 and DSC 2920 operator's manual Appendix C

6. Set up and Experiment

Precautions: think about these things before you run the instrument
- Make sure the purge nitrogen is connected and the nitrogen tank is open
- Use clean sample pans so nothing contacts the cell surface; be sure not to let the sample you are analyzing melt and flow onto the cell!
- Never heat above 500°C with aluminum pans, and in our case, never heat the DSC-RCS cell above 400°C
- Make sure calibration has been done at your heating rate.

System start up:
- In the computer: login name: dsc – password: dsc
- Start the DSC 2920 by pressing "open" key on instrument keypad
- Make sure the purge nitrogen is connected and on at the right rate (set the flow-meter at two black mark)
- After 30 seconds machine warm up, start ***TA controller*** in the computer

7. Experiment 1: Thermal behavior of PET

The aim of this experiment is: The aim of this experiment is to:
1. Determine on the PET sample
    a. The glass transition, melting and crystallization temperature;
    b. The heat of crystrallization and melting.
2. Compare the DSC curve with the literature PET curve, and explain the differences.

Preparing sample:
- Cut a piece of PET film from the plastic bottle, clean it with water and dry it.
- Make a thin film with the weight 5-15 mg, (this is the normal sample weight in DSC experiment).
- Keep the film flat enough and with suitable size for Aluminum pan.

Encapsulating the sample: (See DSC 2920 Manual at 3-11~3-24 for more details)
- Practice making a few nonhermetic sample pans to become familiar with this procedure before encapsulating your sample.
- If the quantitative work (heat capacity and latent heat calculation) will be done, weigh the sample pan and lid.
- Place the sample in the pan, then place the lid on the pan.
- Place the sample pan in the well of the lower crimping die.
- Pull the sample Press lever forward until handle hits the stop.
- Raise the lever and remove the pan with tweezers.
- Inspect the pan. The bottom of the pan should be smooth, and the sides should appear rolled down.
- For quantitative work, weigh the crimped sample pan and lid (containing the sample) and determine the sample weight.
- Prepare an empty nonhermetic pan and lid for use as the reference pan.

Loading the sample: (See DSC 2920 Manual at 3-30 for more details)
- Use the tweezers to remove cell cover and silver lid from the cell
- Carefully place the sample pan on the front raised platform and the reference pan on the rear platform.
- Centering the pans within the grid will ensure that they are centered on the platform.
- Place the silver lid and cell cover

Setting up an experiment:
- In TA controller window, (see below), select **Experiment/Mode** from main menu, choose the "**Standard Mode**".
- Click **Experiment view** button, input the sample name, size and file name.
- Select **Ramp** from the **Test** list, then go to **Procedure Page,** enter the requested test parameters that will program the DSC to: (a)**equilibrate to 50 °C; (b)Ramp 5 °C/min to 300°C**
- Click on the **Note Page** tab. Enter/verify the requested information. (GAS 1: Nitrogen, 35ml/min, GAS 2: None)
- Click on the **Apply** button to save the experimental and sample parameters entered for this run.
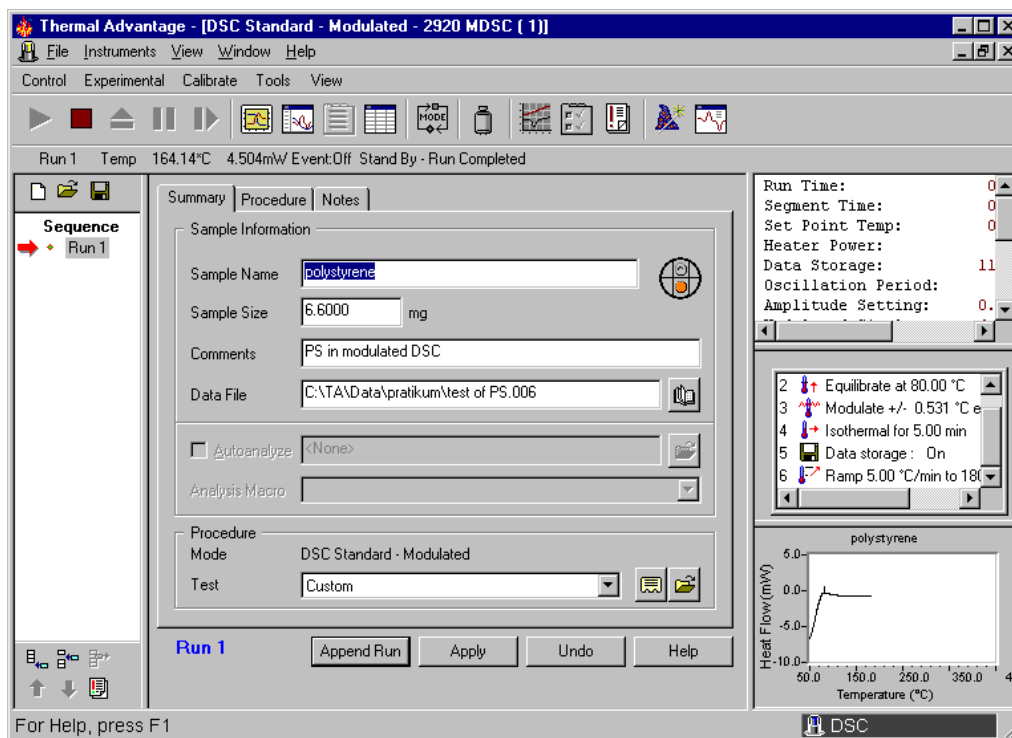
Advanced Lab: Differential scanning calorimetry investigation of polymers

Figure 12 Window of the experimental view: Summary.

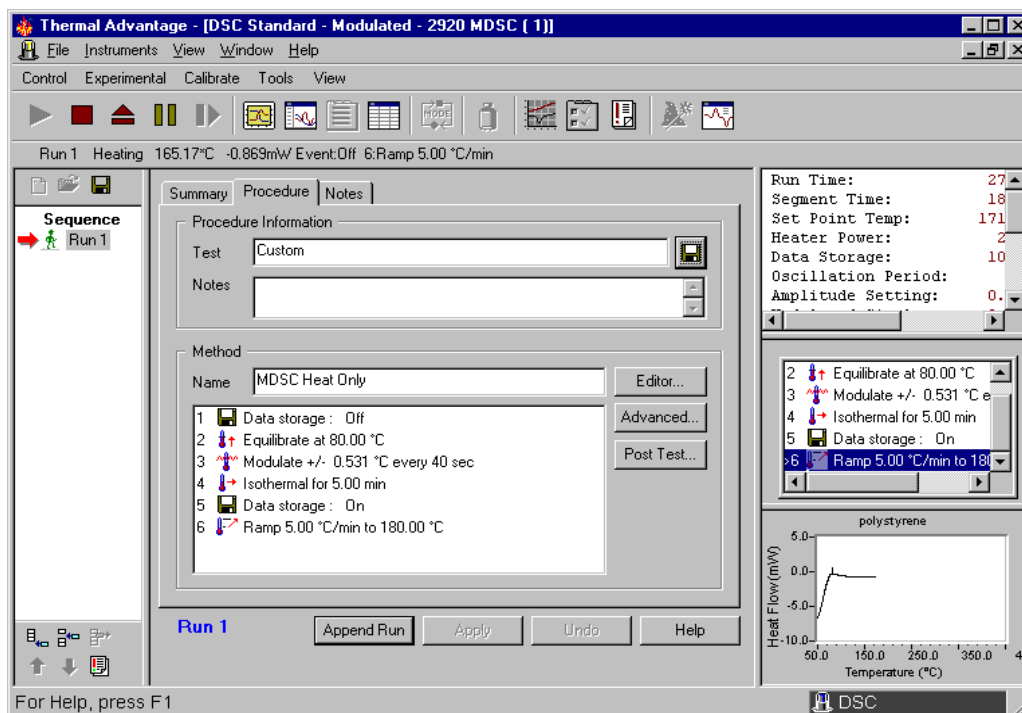**Now start the experiment by pressing START key on main menu, the window is following:**

Figure 13 Window of the experimental view: procedure.

Date Analysis

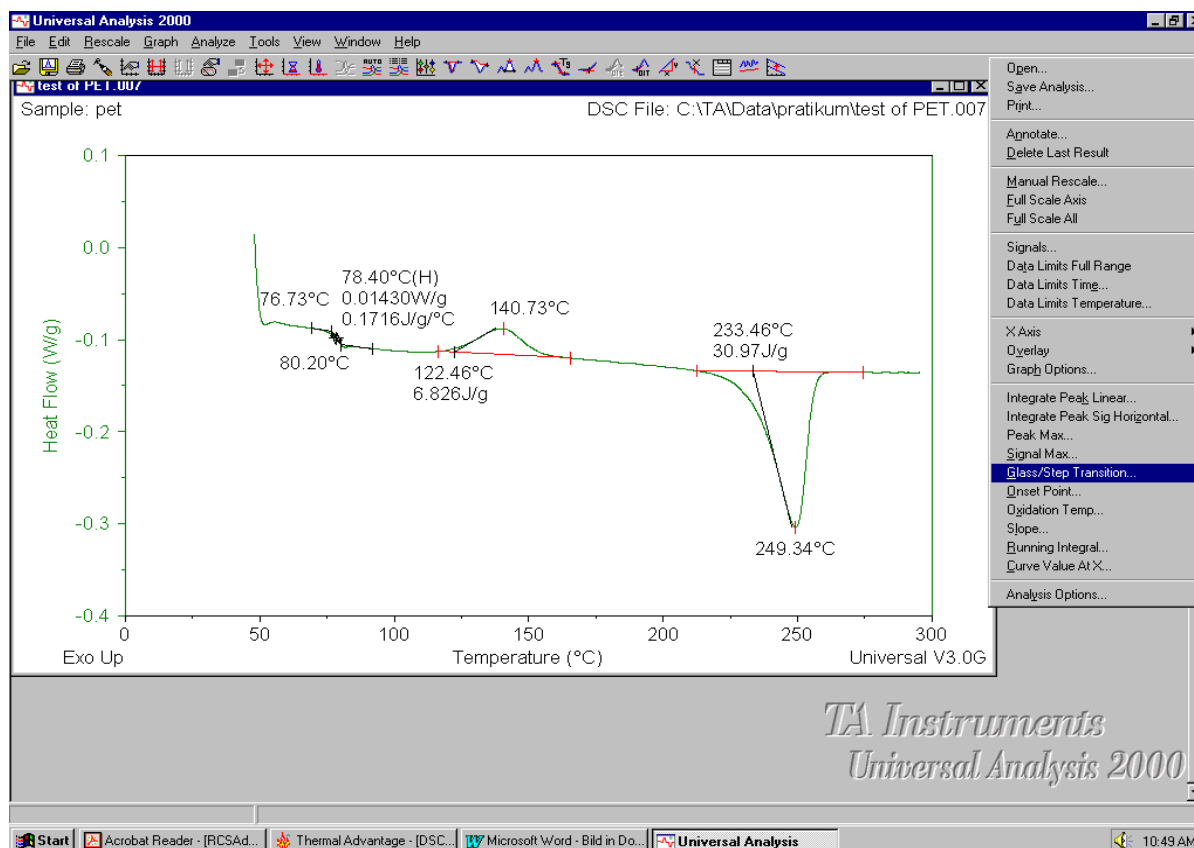Start Universal Analysis 2000 software; open the file for last experiment.

Figure 14: Analysis of the PET – DSC plot.

1) Click the right button: choose integrate peak linear: define with the mouse the starting and ending limit of the peak (for example chose the crystallization one). Right button: accept limits. As output one obtains: Tc, onset Tc and heat of crystallization (area under the curve).

2) Repeat the same procedure for the melting point (Tm) determination and heat of melting.

3) For the glass transition (Tg) determination: click the right button of the mouse: select "glass/step transition". Define starting and ending limit and accept.

One can print the obtained plot or export in a word file following these procedures:
View : custom report. Plot automatically.
New: to create a word file. Insert plot – normal or table.
At the end push the Word icon.

(See UAmanual for more details about the software)

For baseline, cell constant, heat capacity calibration details, please read Thermal Advantage User Reference Guide at 2-23~2-43

For heat capacity calibration details, please read DSC 2920 manual at C-43~C55

8. Experiment 2: Determine the Polystyrene heat capacity and weak glass transition in Modulated DSC.

- Press the PS sample to powder state before measure it.
- Weigh about 5 mg sample.
- Prepare sample pan and reference pan with same procedure.
- Set up Modulated DSC and creat a method:
    1. In TA controller window, select **Experiment/Mode** from main menu, choose the "**Modulated Mode**".
    2. Select **customer** in Test list, then in **Procedure Page** set following method:
    a) Equilibrate at 60 °C.
    b) Modulate +/-0.531°C every 40 seconds
    c) Isothermal to 5 min
    d) Ramp 5°C to 200°C
    e) Apply it

Finish running, open file in Universal Analysis.
Weak glass transition:
- Click right button, select **Signal.**
- In Y_1 list select heat flow, in Y_2 list select **non-reversing heat flow**, in Y_3 list select **reversing heat flow, Y_4** is not used.
- Return to main plot, determine the accurate T_g on reversing curve as before for Experiment 1 by defining the limits.
- Try to explain the non-reversing peak.

Open again the file in Universal Analysis.
Heat capacity data:
- Click right button , select **signal.**
- In Y_1 list select heat flow and in Y_2 list, choose **complex heat capacity. Y_3** and **Y4** is not used.
- Return to main plot, which has shown the heat capacity curve, select View.
- Select Data Table; Report.
- Enter Start: 66.85°C
        Stop:196.85
        Increment: 10°C
- Accept this form and send results to Printer
- Compare with the literature Cp value (http://web.utk.edu/~athas/databank/) or ask for the list.

9. Experiment 3: Study the glass transition of random copolymer and block copolymer (Optional)

- Follow the same procedure before to prepare a random PMMA-PS copolymer and a block PMMA-PS copolymer.
- Run 2 experiments separately with the same method:
  Equilibrate at 60 °C, Ramp 10 °C/min to 180 °C

(Before run a new experiment, it is better to let the DSC cell cool down below next experiment start temperature.)

After the running, use Universal Analysis to determine the glass transition of 2 samples, and compare 2 curves.