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Investigation of Polymers with Differential Scanning Calorimetry

Contents

1 Introduction

Differential scanning calorimetry (DSC) is a technique used to investigate the response of polymers to heating. DSC can be used to study the melting of a crystalline polymer or the glass transition.

The DSC set-up is composed of a measurement chamber and a computer. Two pans are heated in the measurement chamber. The sample pan contains the material being investigated. A second pan, which is typically empty, is used as a reference. The computer is used to monitor the temperature and regulate the rate at which the temperature of the pans changes. A typical heating rate is around $10\,°C/min$.

The rate of temperature change for a given amount of heat will differ between the two pans. This difference depends on the composition of the pan contents as well as physical changes such as phase changes. For the heat flux DSC used in this lab course, the system varies the heat provided to one of the pans in order to keep the temperature of both pans the same. The difference in heat output of the two heaters is recorded. The result is a plot of the difference in heat (q) versus temperature (T).

2 Thermal Properties of a Polymer

2.1 Heat Capacity

The heat capacity (C_p) of a system is the amount of heat needed to raise its temperature $1\,°C$. It is usually given in units of Joules/$°C$ and can be found from the heat flow and heating rate. The heat flow is the amount of heat supplied per unit time

$$\text{Heat flow} = \frac{heat}{time} = \frac{q}{t} \tag{1}$$

where t is time. The heating rate is the time rate change of temperature

$$\text{Heating rate} = \frac{\Delta T}{t} \tag{2}$$

where ΔT is the change in temperature. One can obtain the heat capacity from these quantities

$$C_p = \frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} \tag{3}$$

This means the heat capacity can be found by dividing the heat flow by the heating rate. If the C_p of a material is constant over some temperature range, then the plot of heat flow against temperature will be a line with zero slope as shown in Figure 1. If the heating rate is constant then the distance between the line and the x axis is proportional to the heat capacity. If heat is plotted against temperature then the heat capacity is found from the slope.
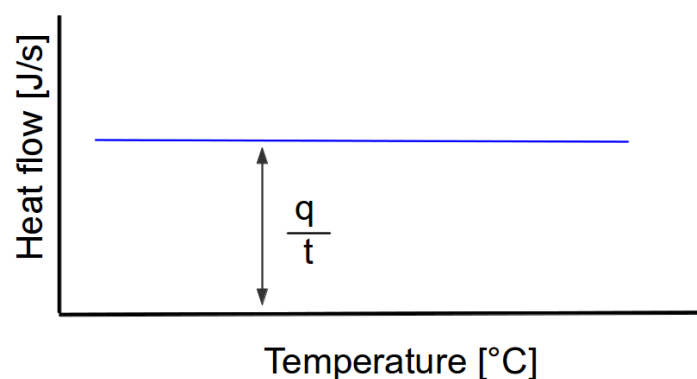
Figure 1: Example plot of heat flow versus temperature for a material that does not undergo any changes during the heating.

2.2 Glass Transition

If a polymer in its molten state is cooled it will at some point reach its glass transition temperature (T_g). At this point the mechanical properties of the polymer change from those of an elastic material to those of a brittle one due to changes in chain mobility. A typical example of a heat flow versus temperature plot at a glass transition temperature is shown in Figure 2. The heat capacity of the polymer is different before and after the glass transition temperature. The heat capacity C_p of polymers is usually higher above T_g. DSC is a valuable method to determine T_g. It is important to note that the transition does not occur suddenly at one unique temperature but rather over a range of temperatures. The temperature in the middle of the inclined region is taken as the T_g.
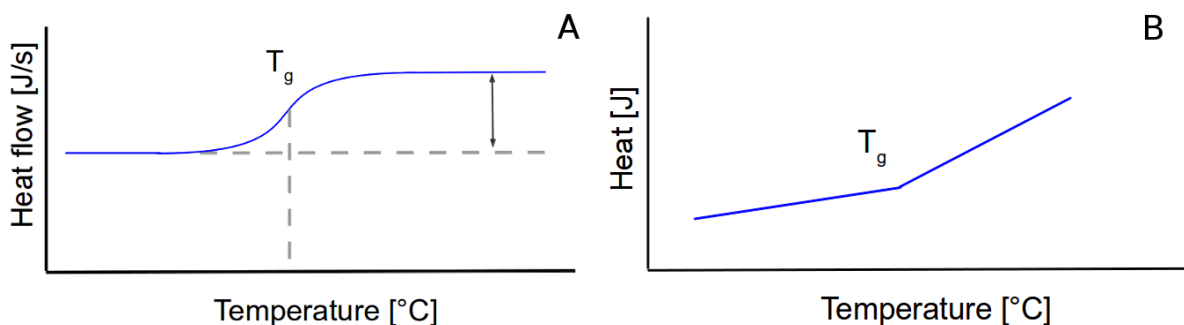

Figure 2: Schematics of a glass transition. The glass transition results in a kink in the heat versus temperature plot due to the change in heat capacity (A). In a plot of heat flow versus temperature it is a gradual transition that occurs over a range of temperatures (B). The glass transition temperature is taken to be the middle of the sloped region.

2.3 Crystallization

Above the glass transition temperature the polymer chains have high mobility. At some temperature above T_g the chains have enough energy to form ordered arrangements and undergo crystallization. Crystallization is an exothermic process, so heat is released to the surroundings. Less heat is needed to keep the heating rate of the sample pan the same as that of the reference pan. This results in a decrease in the recorded heat flow. If the convention of 'exothermic - down' is used then the result is a dip in the plot of heat flow versus temperature as seen in Figure 3.

Such a crystallization peak can be used to confirm that crystallization occurs in the sample, find the crystallization temperature (T_c) and determine the latent heat of crystallization. The crystallization temperature is defined as the lowest point of the dip. The latent heat (enthalpy) of crystallization is determined from the area under the curve.
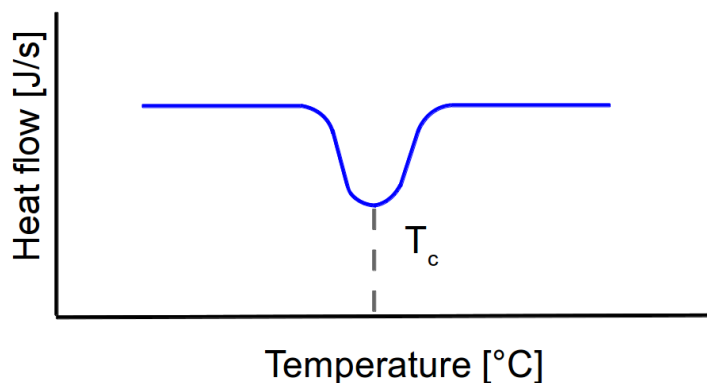

Figure 3: Example of a crystallization 'peak' in a plot of heat flow against temperature. Crystallization is an exothermic process, so the heat flow to the sample must be decreased to maintain a constant heating rate.

2.4 Melting

The polymer chains are able to move around freely at the melting temperature (T_m) and thus do not have ordered arrangements. Melting is an endothermic process, requiring the absorption of heat. The temperature remains constant during melting despite continued heating. The energy added during this time is used to melt the crystalline regions and does not increase the average kinetic energy of the chains that are already in the melt. In a plot of heat against temperature this appears as a jump discontinuity at the melting point as seen in Figure 4A. The heat added to the system during the melting process is the latent heat of melting. It can be calculated from the area of a melting peak observed in a plot of heat flow against temperature, such as the one in Figure 4B. The T_m is defined as the temperature at the peak apex. After melting the temperature again increases with heating. However, the heat capacity of a polymer in the melt is higher than that of a solid crystalline polymer. This means the temperature increases at a slower rate than before.
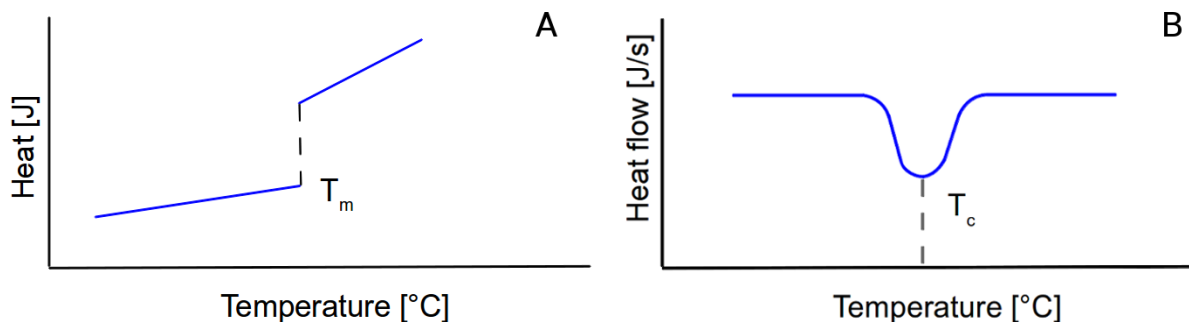
Figure 4: Melting is an endothermic process so the heat flow to the sample must be increased to keep the heating rate constant, resulting in a discontinuity in the plot of heat versus temperature (A). This appears as a peak if the heat flow is plotted against temperature (B). The area under the curve can be used to calculate the latent heat of melting.

2.5 Combining T_g, T_c, and T_m

An example of a DSC plot showing a glass transition, crystallization peak and melting peak is shown in Figure 5.
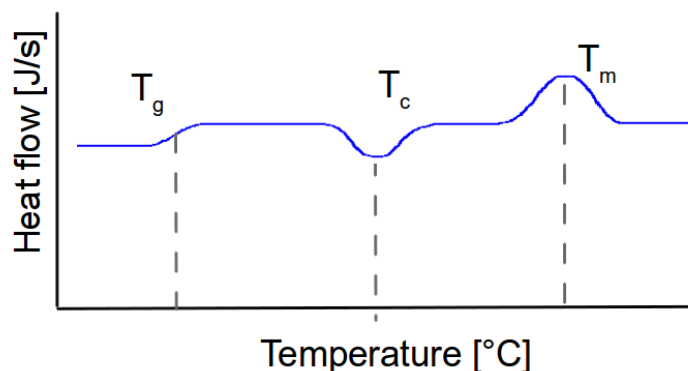

Figure 5: Example plot of a heat flow versus temperature plot for a polymer that undergoes a glass transition, crystallization and melting.

It is worth noting that not all polymers undergo all three transitions during heating. The crystallization and melting peaks are only observed for polymers that can form crystals. While purely amorphous polymers will only undergo a glass transition, crystalline polymers typically possess amorphous domains and will also exhibit a glass transition as seen in Figure 5. The amorphous portion only undergoes the glass transition while the crystalline regions only undergo melting.

The exact temperatures at which the polymer chains undergo these transitions depend on the structure of the polymer. Subtle changes in polymer structure can result in huge changes in T_g.
The difference between the glass transition and melting point is illustrated in Figure ??. In the case of a perfectly crystalline polymer the plot of heat against temperature has a jump discontinuity at the melting point. The plot of heat against temperature is

continuous for the glass transition, but plot is not smooth (the slope at T_g is different depending on if you approach the point from the right or the left). The slope gives the heat capacity. The slope increases after T_g and T_m since the heat capacity is higher.

Note: the Y axis can be set to show exothermic processes as peaks or valleys. All of the above plots use the 'exothermic down' convention.

3 DSC Instructions

Two types of DSC instruments are widely used: the heat flux DSC (eg. TA DSC and Mettler DSC) and the power compensated DSC (Perkin-Elmer system).

3.1 Heat Flux DSC

In a heat flux DSC system the sample and reference are heated at the same rate from a single heating source as shown in Figure 6. The temperature difference between the pans is recorded and converted to a power difference. This power difference gives the difference in heat flow.

$$\Delta P = \frac{\Delta Q}{dt} \tag{4}$$

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.
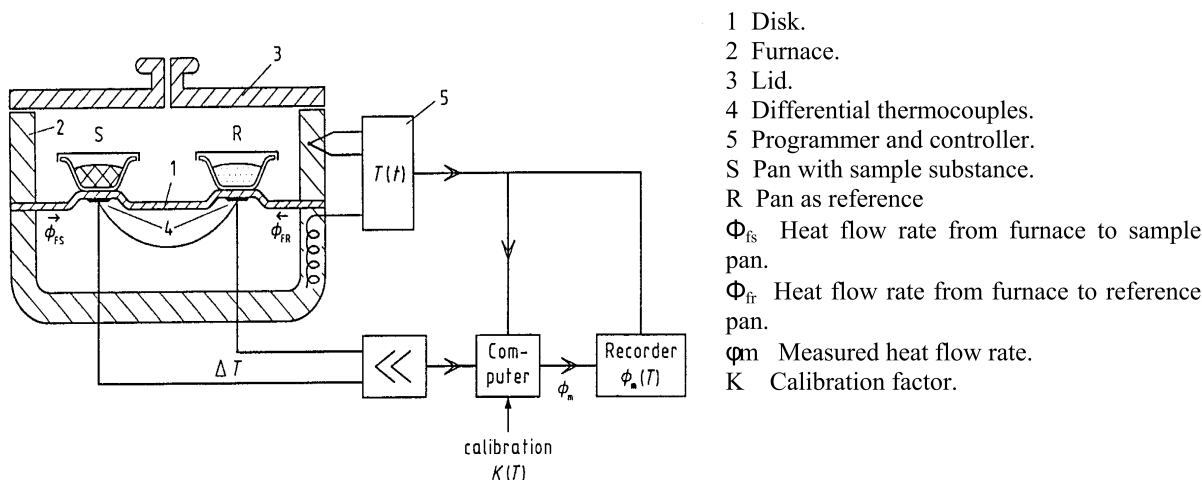φ_m Measured heat flow rate.
K Calibration factor.

Figure 6: Schematic diagram of a heat flux DSC system. The sample and reference are heated at the same rate and the temperature difference is measured.

3.2 Power Compensated DSC

The sample and reference are heated separately in power compensated DSC, as shown in Figure 7. The pan temperatures are monitored using thermocouples attached to the disk platforms. The thermocouples are connected in series and measure the differential heat flow using the thermal equivalent of Ohm's Law

$$\frac{dq}{dt} = \frac{\Delta T}{R_D} \tag{5}$$

where $\frac{dq}{dt}$ is the heat flow, ΔT is the temperature difference between the reference and sample, and R_D is the thermal resistance of the disk platform. The heat flow to each pan is adjusted to keep their temperature difference close to zero while the furnance temperature is increased linearly.

The DSC 2920 Differential Scanning Calorimeter (TA Instruments) used in the PMM laboratory is a typical heat flux DSC (Figure 8). It is used to obtain qualitative and quantitative information about the physical and chemical changes that materials undergo during heating. It is also capable of modulated heating, the advantages of which will be explained in the section on modulated differential scanning calorimetry (see Section 4).
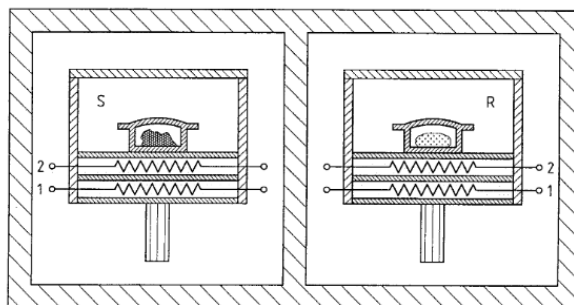

Figure 7: Schematic of a power compensated DSC system. The sample and reference pans are heated separately. The heat flow to each pan is adjusted to keep their temperature difference close to zero. The difference in heat flow is recorded.
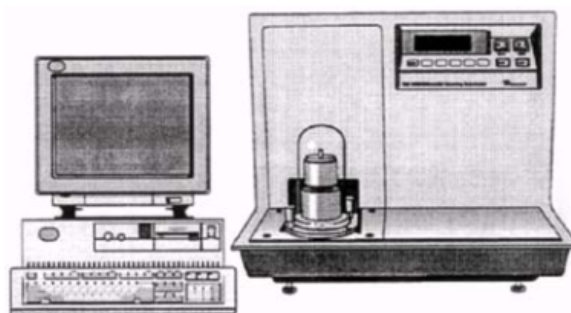

Figure 8: The DSC 2920 used in the PMM laboratory.

4 Modulated DSC

Modulated temperature DSC (MDSC) is an extension of DSC. The same heat flux DSC cell is used for MDSC, but a sinusoidal temperature oscillation (modulation) is overlaid on the conventional linear temperature ramp. This results in the heating rate at times being

faster or slower than the underlying linear heating rate. This variation in instantanous heating is illustrated in Figure 9. The actual heating rate depends on three experimental variables: the underlying heating rate, the amplitude of modulation and the period (frequency) of modulation. Typical values for these parameters are a heating rate of 1 to $5\,°C/min$, an amplitude of ± 0.5 to $\pm 1\,°C$, and an oscillation period of 40 to $60\,s$. Higher resolution can be achieved by decreasing the heating rate, increasing the amplitude, and decreasing the oscillation period.
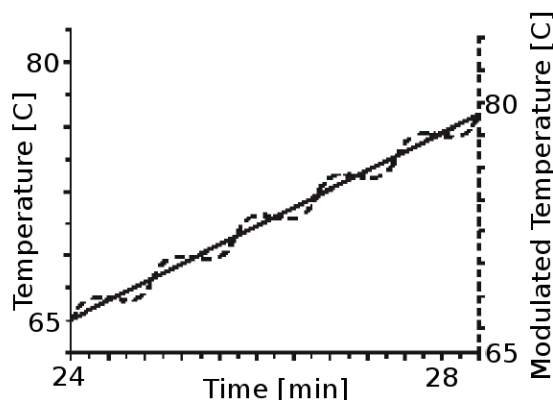

Figure 9: Typical modulated temperature versus time plot for MDSC. A sinusoidal temperature variation is overlaid on a linear heating.

Both conventional DSC and MDSC can be used to find transition temperatures, latent heats of phase transitions and heat capacity. However, MDSC can be used to obtain more information than a single DSC run and overcomes several limitations of conventional DSC. For instance, the heat capacity and heat flow can be measured in a single experiment using MDSC. Temperature modulation also makes it possible to separate complex transitions into more easily interpreted components. MDSC has a higher sensitivity than DSC, which improves the detection of weak transitions. The resolution of these transitions can also be increased without loss of sensitivity. Finally, MDSC provides more accurate measurements of the degree of crystallinity in polymers and allows for direct determination of thermal conductivity.

One advantage of MDSC is the improved analysis of complex transitions. Many transitions are complex, meaning that they actually involve multiple processes. An example is an endothermic process known as enthalpic relaxation that can occur during the glass transition. The magnitude of enthalpic relaxations depends on the thermal history of the material. In some cases it can cause a glass transition to look like a melting peak. Another example is the melting and crystallization of a polymer. These processes can occur simultaniously, making it almost impossible to determine the true crystallinity of the sample. Conventional DSC does not help in these cases since it only measures the total heat flow from all thermal events in the sample at a given temperature. If multiple transitions occur in the same temperature range, then the results are confusing and often misinterpreted. MDSC ameliorates this problem by separating the total heat flow signal into its reversing and non-reversing components.

Conventional DSC is not well suited for the detection and accurate measurement of weak

transitions. This is due to noise in the baseline. Baseline noise that is short-term, occurring on the order of seconds, can be effectively eliminated by signal averaging. Long-term variations in the baseline are more problematic. This variation occurs on the order of minutes and is due to changes in the properties of the DSC cell materials and purge gas with temperature. The degree of baseline drift varies across commercial DSC instruments and cannot easily be corrected for. MDSC eliminates this problem by using the ratio of two signals to calculate the real changes in the sample heat capacity rather than just the absolute value of the heat flow signal.

Conventional DSC is also limited by restrictions on the possible resolution. Resolution refers to the ability to distinguish transitions that occur at similar temperatures. The resolution of DSC can be increased using smaller samples and lower heating rates. However, decreasing the sample size and heating rate also decreases the heat flow signal. This means resolution and sensitivity are inversely related for DSC. MDSC solves this problem by having two heating rates. The average heating rate can be lowered to obtain the desired resolution while the instantaneous heating rate can be raised to increase the heat flow signal.

The advantage of modulated heating can be seen clearly by considering the contributions of temperature and heating rate to the heat flow

$$\frac{dq}{dt} = C_p \frac{dT}{dt} + f(t, T) \tag{6}$$

where $\frac{dq}{dt}$ is the heat flow, $\frac{dT}{dt}$ is the heating rate, C_p is the sample heat capacity, and $f(t, T)$ is a function of time and temperature. The component of the heat flow that is dependent on the heating rate is due to thermodynamically controlled changes. This contribution follows the instantaneous heating rate and is referred to as the reversing heat flow. The kinetically controlled processes are responsible for the time and temperature dependent component. This does not follow the modulated heating rate and is referred to as the non-reversing heat flow.

The total heat flow is recorded and must be deconvoluted into the reversing and non-reversing components. The raw data signals are called the modulated temperature and modulated heat flow signals. These are separated into the average, or total heat flow, and amplitude. This separation is done using a mathematical technique known as the Discrete Fourier Transform (DFT). The DFT software continually measures the amplitudes of the sample temperature and raw heat flow signals by comparing the data to a reference sine wave of the same frequency. The sample heat capacity is calculated from these amplitudes using the relation

$$C_p = K_{Cp} \cdot \frac{q_{amp}}{T_{amp}} \cdot \frac{Period}{2\pi} \tag{7}$$

where C_p is the heat capacity, K_{Cp} is the heat capacity calibration constant, q_{amp} is the heat flow amplitude, T_{amp} is the temperature amplitude and Period is the modulation period.

The reversing heat flow is calculated by multiplying the heat capacity by the negative of

the average heating rate. Multiplying by the negative of the heating rate inverts the heat flow signal so that endothermic processes result in valleys. The non-reversing heat flow is computed as the difference between the total heat flow and the reversing heat flow.

See Appendix C of the DSC 2920 operator's manual for more information about the principles of modulated DSC operation.

5 Set-up and Experiment

IMPORTANT:

- Make sure the nitrogen is connected and flowing.

- Use clean sample pans. Make sure nothing contacts the heater surface. Be sure the sample cannot flow out of the cell after melting!

- In general, never heat aluminum pans above $500\,°$C.

- In our case, DO NOT heat the DSC-RCS cell above $400\,°$C.

Starting the System:

- Log into the computer with the username dsc and password dsc.

- Start the DSC 2920 by pressing the power button on the instrument.

- Make sure the purge nitrogen is connected and the flow rate is correct. Set the flowmeter to match the two black marks.

- Allow the machine to warm up for 30 seconds and then start the control program by clicking the TA controller icon.

5.1 Encapsulating the Sample

See pages 3-11 to 3-24 in the DSC 2920 manual for more information.

Practice making a few nonhermetic sample pans to become familiar with the procedure before trying with your sample.

- Weigh the sample pan and lid if the heat capacity and latent heats are to be calculated.

- Place the sample in the pan, then place the lid on the pan.

- Place the pan in the well of the crimping dye.

- Pull the press lever forward until the handle hits the stop.

- Raise the lever and remove the pan with tweezers. Ask for assistance if the pan is stuck.

- Inspect the pan. The bottom should be smooth and the sides should appear rolled down.

- If quantitative work is to be done, weigh the pan with encapsulated sample to determine the sample weight.

- Prepare an empty nonhermetic pan with lid to use as a reference.

5.2 Loading the Sample

See page 3-30 in the DSC 2920 manual for more information.

- Use tweezers to remove the cell cover and silver lid from the heating chamber.

- Carefully place the sample pan on the raised platform in the front and the reference pan on the platform in the rear.

- Center to the pans on the grid to ensure they are centered on the platform.

- Replace the silver lid and cell cover.

6 Experiment 1: Thermal Behavior of PET

The aim of this experiment is to find T_g, T_c, and T_m as well of the latent heats of crystallization and melting for PET. The experimentally obtained DSC curve should be compared to a literature curve for PET and the differences should be discussed.

6.1 Sample Preparation

- Cut a piece of PET from the plastic bottle.

  - The sample should weigh between 5 and 15 mg
  - The sample must be a suitable size and shape to fit in the aluminum pan

- Clean the sample with water and dry it.

6.2 Setting up the Experiment

- Open the TA Controller window (Figure 10), select **Experiment/Mode** from the main menu, then choose **'Standard Mode'**.

- Click the button labeled **'Experimental View'** and input the sample name, size and file name.

- Select **Ramp** from the **Test** list, then go to **Procedure Page** and set the test parameters to **equilibriate to 50 °C, and ramp 5 °C/min up to 300 °C**

- Click on the **Note Page** tab and enter or verify the following information: GAS 1: Nitrogen, 35 mL/min, GAS 2: None.

- Click the **Apply** button to save the parameters entered for this run.

Now start the experiment by pressing the START button on the main menu. The window should appear as shown in Figure 11.
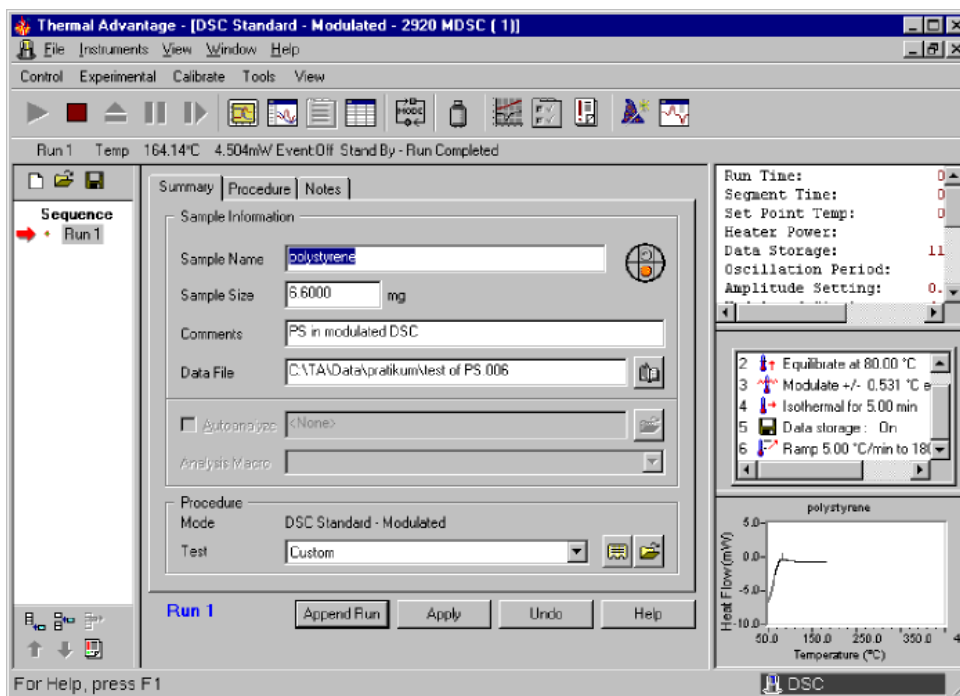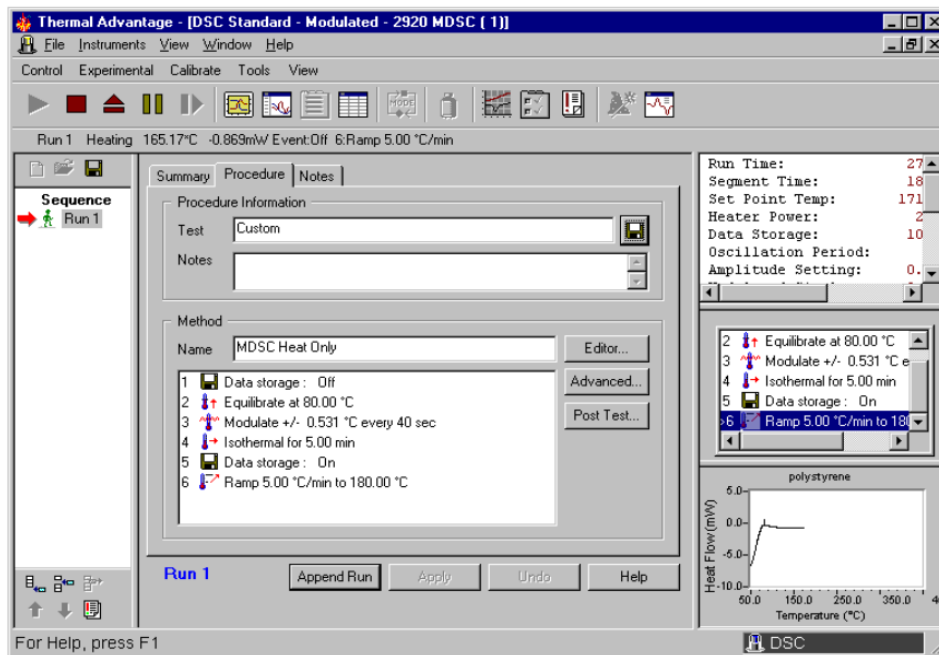
Figure 10: The 'Experimental View' summary window.

Figure 11: The 'Experimental View' procedure window

6.3 Data Analysis

See the UA manual for more information about the software.
See pages 2-23 to 2-43 of the Thermal Advantage User Reference Guide for details about baseline, cell constant and heat capacity calibration.
**See pages C-43 to C55 of the DSC 2920 manual for more information about heat capacity calibration.**

Start the Universal Analysis 2000 software and open your experiment file.

- Right mouse click, select 'Integrate peak linear', use the mouse to define the starting and ending limits of the peak, right mouse click again and click 'Accept limits'.

    - For the crystallization peak the software gives T_c, onset T_c and the heat of cyrstallization (area under the curve).

    - Repeat with the melting peak to obtain T_m and the heat of melting.

- Right mouse click, select 'Glass/step transition', define the starting and ending limits of the glass transition and accept.

The final plot can be printed or exported:

- View: custom report. Plot automatically.

- New: to create a Word file. Insert plot - normal or table

- Click the Word icon.
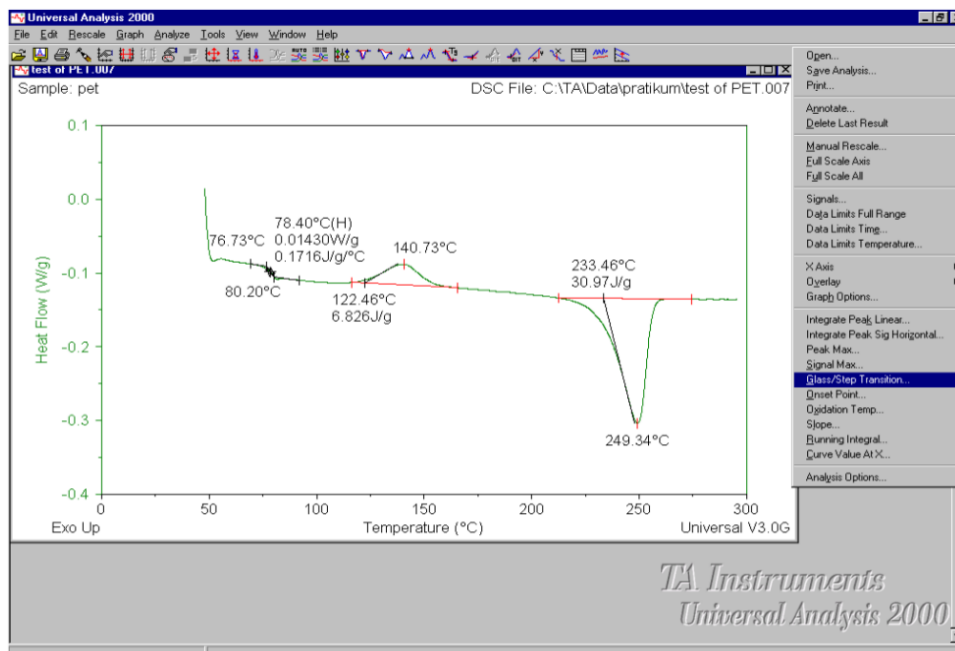
7 Experiment 2: Determination of C_p and Weak Glass Transition in PS Via Modulated DSC

7.1 Experimental Set-up

The goal of this experiment is to find the glass transition temperature of PS using modulated DSC and compare the results to literature.

- Grind the PS into a powder.

- Weigh out about 5 mg of PS powder

- Prepare the sample pan and reference pan as writen in Section 5.2.

- Select **Experiment/Mode** from the main menu in the TA controller window and choose the **Modulated Mode**.

- Select **Customer** in the **Test** list, the in the **Procedure Page** set the following parameters:

  - Equilibriate at 60 °C.
  - Modulate $\pm\, 0.531$ °C every 40 seconds.
  - 5 min isothermal.
  - Ramp 5 °C to 200 °C.

- Hit **Apply** to set the parameters.

- Start the experiment.

7.2 Data Analysis

After the experiment is done running, open the file using the Universal Analysis software.

For the weak glass transition:

- Right mouse click and select **Signal**.

- Select **heat flow** from the Y_1 list.

- Select **non-reversing heat flow** from the Y_2 list.

- Select **reversing heat flow** from the Y_3 list. Y_4 is not used.

- Return to the main plot and determine the T_g from the reversible heat flow curve as explained in Section 6.3.

- Try to explain the peak in the non-reversible heat flow curve.

For the heat capacity:

- Open the file in the Universal Analysis program again.

- Right mouse click and select **Signal**.

- Select **heat flow** from the Y_1 list.

- Select **complex heat capacity** from the Y_2 list. Y_3 and Y_4 are not used.

- Return to the main plot and select **View**.

- Select **Data Table; Report**.

- Enter the following parameters:

    - Start: 66.85 °C
    - Stop: 196.85 °C
    - Increment: 10 °C

- Accept this form and send the results to printer

- Compare the results to the literature C_p value (`http://web.utk.edu/~athas/databank/`).

8 Experiment 3: Glass Transition of a Random Copolymer and Block Copolymer (Optional)

- Follow the same procedure to prepare the random PMMA-PS copolymer and PMMA-PS block copolymer samples.

- Run the two experiments seperately using the parameters **equilibriate at 60 °C, ramp 10 °C/min to 180 °C**.

- Use the Universal Analysis software to determine the glass transition temperatures and compare the curves of the two copolymers.

NOTE: It is best to let the DSC cell cool to below the experiment start temperature before beginning a new run.