

Differential Scanning Calorimetry; First and Second Order Transitions in Polymers

Purpose: Determine the enthalpy of melting (fusion) of polyethylene and the heat capacity, glass transition temperature, and the change in heat capacity for the glass transition for polystyrene.

Introduction

Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes:

$$\left(\frac{dq}{dt}\right)_p = \frac{dH}{dt} \quad 1$$

Here dH/dt is the heat flow measured in mcal sec^{-1} . The heat flow difference between the sample and the reference is:

$$\Delta \frac{dH}{dt} = \left(\frac{dH}{dt}\right)_{\text{sample}} - \left(\frac{dH}{dt}\right)_{\text{reference}} \quad 2$$

and can be either positive or negative. In an endothermic process, 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. Other endothermic processes include helix-coil transitions in DNA, protein denaturation, dehydrations, reduction reactions, and some decomposition reactions. 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.

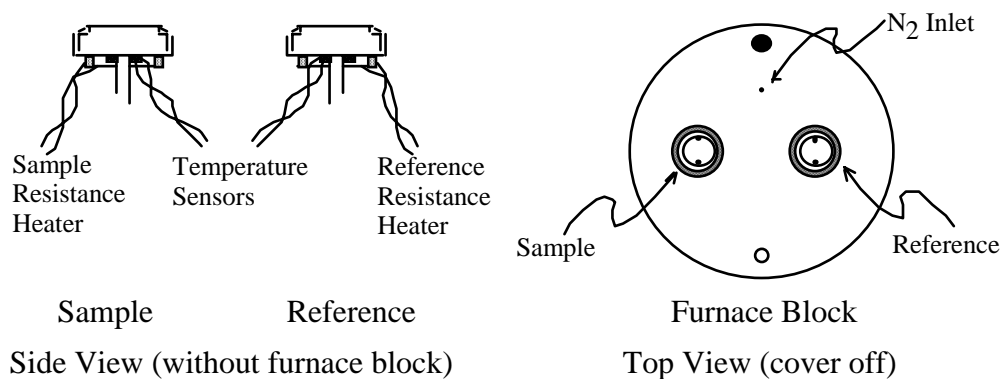


Figure 1. Differential scanning calorimeter sample and reference holder.

The calorimeter consists of a sample holder and a reference holder as shown in Figure 1. Both are constructed of platinum to allow high temperature operation. Under each holder is a resistance heater and a temperature sensor. Currents are applied to the two heaters to increase the temperature at the selected rate. The difference in the power to the two holders, necessary to

maintain the holders at the same temperature, is used to calculate $\Delta H/dt$. A schematic diagram of a DSC is shown in Figure 2. A flow of nitrogen gas is maintained over the samples to create a reproducible and dry atmosphere. The nitrogen atmosphere also eliminates air oxidation of the samples at high temperatures. The sample is sealed into a small aluminum pan. The reference is usually an empty pan and cover. The pans hold up to about 10 mg of material.

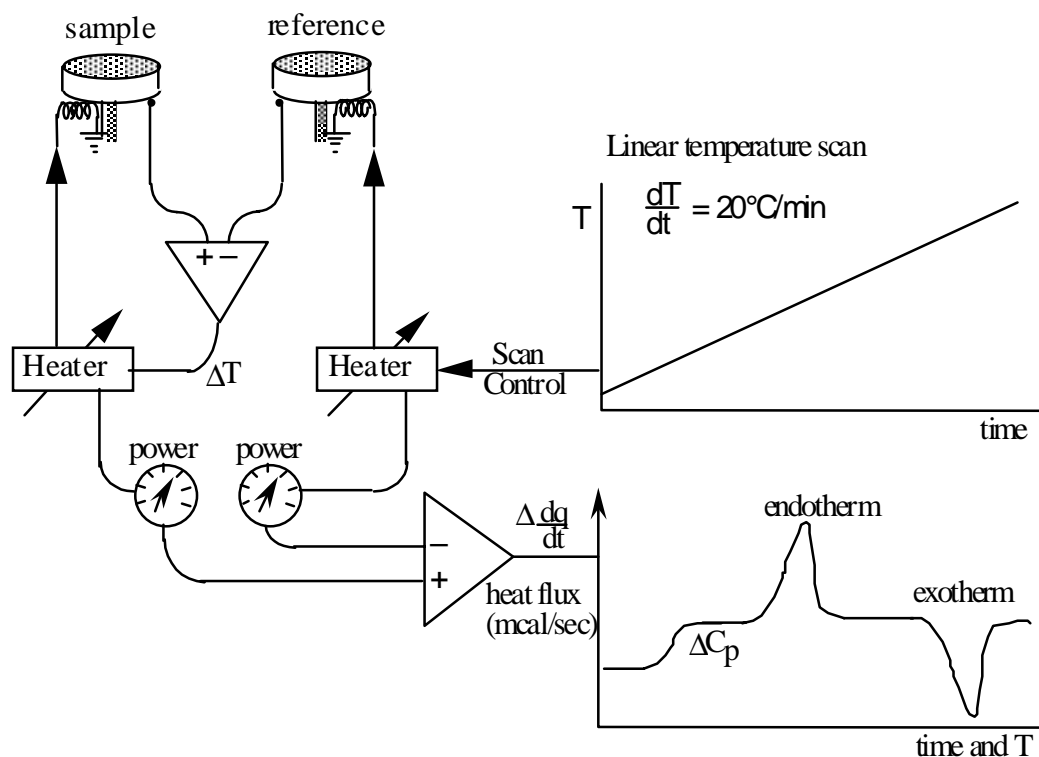


Figure 2. Schematic of a DSC. You choose the linear temperature scan rate. The triangles are amplifiers that determine the difference in the two input signals. The sample heater power is adjusted to keep the sample and reference at the same temperature during the scan.

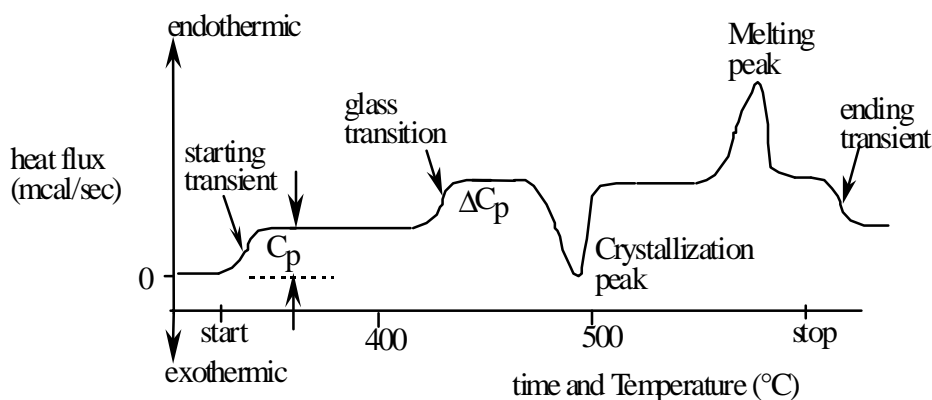


Figure 3. Typical DSC scan. The heat capacity of the sample is calculated from the shift in the baseline at the starting transient. Glass transitions cause a baseline shift. Crystallization is a typical exothermic process and melting a typical endothermic process, $\Delta_{tr}H$ is calculated from the area under the peaks. Few samples show all the features shown in this thermogram.

During the heating of a sample, for example, from room temperature to its decomposition temperature, peaks with positive and negative $\Delta H/dt$ may be recorded; each peak corresponds to a heat effect associated with a specific process, such as crystallization or melting (Fig. 3).

The question arises as to what kind of information is obtainable from a DSC curve. The first and most direct information is the temperature at which a certain process occurs, for example, the melting point of a polymer. The temperature at which a reaction, such as decomposition, may start is another important parameter. The peak temperature is associated with the temperature at which maximum reaction rate occurs.

A special case in which the temperature of a phase transformation is of great importance in polymers is the glass transition temperature, T_g . This is the temperature at which amorphous (noncrystalline) polymers are converted from a brittle, glasslike form to a rubbery, flexible form. This is not a true phase transition but one that involves a change in the local degrees of freedom. Above the glass transition temperature certain segmental motions of the polymer are comparatively unhindered by the interaction with neighboring chains. Below the glass transition temperature, such motions are hindered greatly, and the relaxation times associated with such hindered motions are usually long compared to the duration of the experiment.

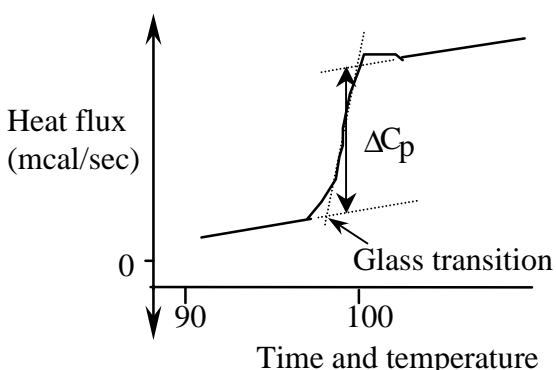


Figure 4. Glass transition. If there are sloping baselines before and after the glass transition, extrapolate the baselines forwards and backwards (as shown by dotted lines) and take the baseline shift when the transition is about 63% complete (as shown by arrows).

The operative definition of glass transition temperature is that at this temperature, or within a few degrees, the specific heat, the coefficient of thermal expansion, the free volume, and the dielectric constant (in the case of a polar polymer) all change rapidly.

Since the mechanical behavior of polymers changes markedly at the glass transition temperature, it is an important characteristic of every polymer. In the DSC experiment, T_g is manifested by a drastic change in the base line, indicating a change in the heat capacity of the polymer (Fig.4). No enthalpy is associated with such transition (for which reason it is also called a second order transition); therefore, the effect in a DSC curve is slight and is observable only if the instrument is sensitive enough.

The second direct information obtainable from DSC curves is the enthalpy associated with certain processes.

Theory

The integral under the DSC peak, above the baseline, gives the total enthalpy change for the process:

$$\int \left(\frac{dH}{dt} \right)_{\text{sample}} dt = \Delta H_{\text{sample}}$$

Assuming that the heat capacity of the reference is constant over the temperature range covered by the peak, $\Delta H_{\text{reference}}$ will cancel out because the integral above the baseline is taken. Therefore, equation 2 is also valid when the integral is taken from the DCS plot of $\Delta dH/dt$.

Heat capacities and changes in heat capacity can be determined from the shift in the baseline of the thermogram. The heat capacity is defined as:

$$C_p = \left(\frac{dq}{dT} \right)_p = \left(\frac{dH}{dT} \right)_p \quad 3$$

The temperature scan rate is:

$$\text{scan rate} = \frac{dT}{dt} \quad 4$$

Using the chain rule:

$$C_p = \left(\frac{dH}{dT} \right) = \frac{dH}{dt} \frac{dt}{dT} \quad 5$$

where dH/dt is the shift in the baseline of the thermogram (Figure 3-4) and the last derivative is just the inverse of the scan rate. For differential measurements, we determine the difference in the heat capacity of the sample and the reference:

$$\Delta C_p = C_p(\text{sample}) - C_p(\text{reference}) \quad 6$$

$$\Delta C_p = \Delta \left(\frac{dH}{dT} \right) = \Delta \frac{dH}{dt} \frac{dt}{dT} \quad 7$$

The units of the heat flow are mcal sec^{-1} and the temperature scan rate is usually expressed as $^{\circ}\text{C min}^{-1}$. So to be consistent with units you must multiply by 60 sec min^{-1} :

$$\Delta C_p = \left(\frac{\text{mcal}}{\text{sec}} \right) \left(\frac{\text{min}}{^{\circ}\text{C}} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) \quad 8$$

Procedure

Energy (Ordinate) Calibration

In practice, the measurement of energy flow will necessarily involve an instrument calibration constant, the recorder chart speed, the sensitivity used, the units employed for area measurement, etc. The RANGE switch on the instrument control panel gives nominal values for the rate of energy change, in millicalories per second, for a full scale displacement, to within $\pm 5\%$.

There are two methods which may be used to calibrate the ordinate on the Model DSC-4. We will use "automatic" ordinate calibration, to yield an overall accuracy of $\pm 1\%$ in our results. In this method, the instrument will electronically generate a 10 mCal/Sec calibration signal, which

will be used to check the mV output at full scale. Set the Range setting on the DSC to 10 mcal/sec. Depress the black rocker switch. The output voltage for the 10 mCal/Sec calibration should give 10.0 mV. The Range setting gives the mCal/Sec value that corresponds to 10 mV output. The calibration constant, which should be close to 1.00, is then:

$$\text{Calibration constant} = \frac{\text{expected output}}{\text{actual output}} = \frac{10 \text{ mV}}{\text{full scale deflection for 10 mcal/Sec}} \quad 9$$

Make sure to turn off the Calibrate rocker switch. "Manual" calibration using a substance with a known enthalpy change is much more accurate, but will not be necessary for this laboratory.

Heat Capacity Determination Use a #2 cork borer to cut a thin disk from a sheet of polystyrene. The sample should weigh between 7 and 10 mg. Weigh an empty sample pan and cover. Add the sample and reweigh. Use an analytical balance or micro-balance with an accuracy of at least ± 0.02 mg. Crimp the pan. If any aluminum is lost during crimping, reweigh the crimped sample-pan-lid. An empty pan and lid are always kept in the reference holder. Sometime during the lab, also weigh the reference pan and lid.

Obtain the thermogram over the temperature range 25-60°C, with a 20°C min⁻¹ scan rate. Choose a scan RANGE setting so that the baseline before and after the starting transient are both between 0 and 10 mV (see Figure 3). Use the "DSCdelaystart.cmb1" Logger Pro analysis file so that you can see the baseline before the temperature scan begins.

Glass Transition Using the same sample, determine the glass transition temperature and the change in the heat capacity during the phase transition. Obtain the thermogram at the same scan rate as above but over the temperature range 30-130°C. Use the "DSCautostart.cmb1" Logger Pro analysis file. Choose a RANGE setting so that the change in heat capacity is well resolved on the chart (try 2 mCal sec⁻¹). On the first run through the glass transition a large maximum may be observed, which is much diminished on successive runs. This is probably due to the release of strains, frozen into the sample during fabrication. To avoid this effect, run at least two thermograms on your sample.

Heat a water bath to the glass transition temperature that you determined. Immerse a sample of polystyrene in the bath and play around a bit. What do you expect to happen to the properties of the plastic above the glass transition temperature? Record your observations.

Enthalpy of Fusion Commercial polystyrene is amorphous and does not exhibit a noticeable melting transition. Therefore, we will use a sample of polyethylene for this determination, instead. There are two types of polyethylene in common use, high density (HDPE) and low density (LDPE). These types can be distinguished by their density. Place a sample of the polyethylene you are going to use in a 50:50 solution of methanol and water. Tap the sample to break the surface tension and dislodge any air bubbles. HDPE will sink and LDPE will float.

Cut a sample of either crystalline polystyrene or polyethylene weighing about 2.5 mg, to the same accuracy as before. (The sample pan and cover weights are not important for this determination). Obtain the thermogram over the temperature range 50-200°C for polyethylene. Try a RANGE of 10 mCal sec⁻¹.

Calculations

Heat Capacity Determination The starting transient rarely looks like Figure 3, because of electronic overshoot caused by the sudden increase in temperature at the start of the run. Rather, a typical starting transient has sharp peaks, one negative and one positive, at the start. The baseline shift is measured before and after these overshoots, Figure 5.

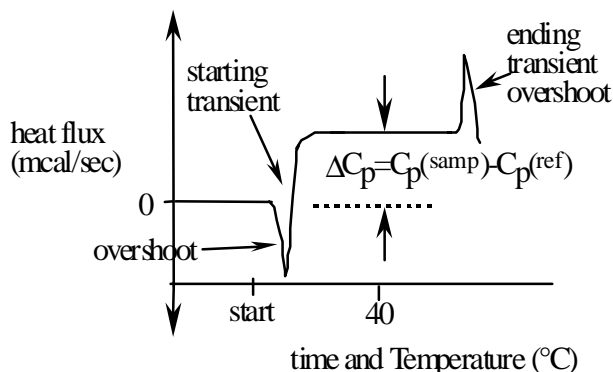


Figure 5. Ignore the electronic overshoot at the starting transient. The idealized starting transient is shown as the dotted curve.

To convert the output voltage difference to the corresponding mcal/Sec value, just use

$$\Delta \frac{dH}{dt} = \frac{\Delta V \text{ (in mV)}}{10 \text{ mV}} * \text{calibration constant} * \text{Range}$$

To calculate the heat capacity of the sample use equation 8. This heat capacity includes the heat capacity of the polystyrene and the heat capacity given by the difference in the mass of the sample pan and cover and the reference pan and cover. That is:

$$\Delta C_p(\text{total}) = C_p(\text{polystyrene}) + C_s (m(\text{sample pan}) - m(\text{ref pan})) \quad 10$$

where C_s is the specific heat of aluminum, $m(\text{sample pan})$ is the mass of the sample pan and cover and $m(\text{ref pan})$ is the mass of the reference pan and cover. The specific heat of aluminum is available in standard references or can be calculated from the molar heat capacity. Use equation 10 to calculate the heat capacity and specific heat of polystyrene.

Glass Transition Determine T_g . Extrapolate the baselines as shown in Figure 4. Take the baseline shift when the transition is about 63% complete (as shown by arrows). Use equation 8 to calculate the change in heat capacity and specific heat for the transition.

Enthalpy of Fusion Determine the approximate melting point of your polymer from the maximum in the melting peak. Extrapolate the baseline under the peak by connecting the flat baseline before and after the melting peak. Determine the enthalpy of the phase transition by integrating the peak above the baseline, as indicated in equation 2. If ordinate calibration was done, correct your result accordingly.

Calculate the enthalpy change that corresponds to your integral value. Given the integral value, the full scale range (Range), the nominal (expected) full scale output in mV (FS), and the ordinate calibration constant:

$$\Delta H = \text{Integral} \left(\frac{\text{Range}}{\text{FS}} \right) \text{calibration constant} \left(\frac{1 \text{ cal}}{1000 \text{ mCal}} \right)$$

For example, if the Range is 10mCal sec⁻¹, the nominal calorimeter output for full scale is 10 mV, the calibration constant is 1.064, and the integral is 112.8 mV sec:

$$\Delta H = (112.8 \text{ mV sec}) \left(\frac{10 \text{ mCal sec}^{-1} \text{ full scale}}{10 \text{ mV full scale}} \right) (1.064) \left(\frac{1 \text{ cal}}{1000 \text{ mCal}} \right) = 0.120 \text{ cal}$$

Calculate the enthalpy change per gram and the enthalpy change per mole of monomer (i.e. (-CH₂-CH₂-) for polyethylene). In calculating the molar mass of the monomer, neglect the ends of the polymer chain.

Report

In your report, give all the above results. Make sure to supply all the necessary information to repeat your calculations (e.g., sample and pan/lid weights, mcal sec⁻¹ ranges, scan rates, chart speed, calibration full scale readings, baseline shifts, masses for the integral calculations, integrals). Report the enthalpy of melting (fusion) of polyethylene and the heat capacity, glass transition temperature, and the change in heat capacity for the glass transition for polystyrene. The ordinate values are good to ±1%. Use significant figure rules to estimate the uncertainties in your final results. Compare your results to the literature values for the heat capacity and the glass transition temperature of polystyrene, and the melting points of low and high density polyethylene (try the Kirk-Othmer Encyclopedia of Science and Technology, which has chapters on polystyrene and low and high density polyethylene. You can also check the chapter on Plastics Processing and even Plastic Building Products. Note that the index to Kirk-Othmer is in the last volume.). Discuss your observations of the polystyrene sample in the hot water bath. Use the results of the floatation test and the melting temperature determination to decide whether your sample was HDPE or LDPE. Discuss the chemical significance of your observations.