

Analysis of the Thermal Properties of Ammonium Nitrate and Polystyrene by Differential Scanning Calorimetry (DSC)

Introduction

In this experiment record the thermal properties of an ionic solid (ammonium nitrate) and an organic polymer (polystyrene) by differential scanning calorimetry (DSC). Analysis of the data provides insight to the types of phase transitions involved and the nature of the compounds themselves.

Background: Differential Scanning Calorimetry¹

Differential Scanning Calorimetry is a technique that allows us to determine the enthalpies associated with different types of phase transitions or other physical processes. An experimental sample contained in pan and a reference empty pan are placed in a thermally controlled chamber (Fig. 1) whose temperature is raised at a constant rate (e.g. 10°C/min), while the amount of heat flowing in and out of the two pans is monitored and compared.

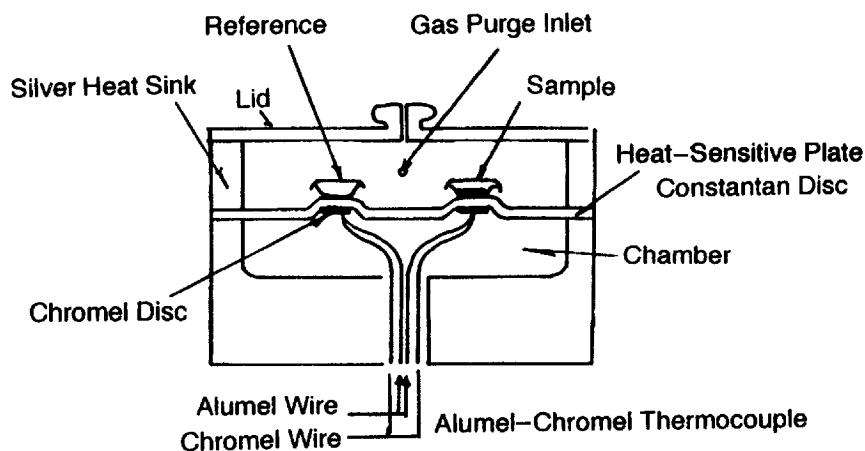


Fig. 1. Schematic of DSC Sample Chamber (TA Instruments design)²

It is important that there be good thermal contact between the sample and the pan. As the sample pan reaches a temperature where a phase transition (melting, for instance) occurs, it requires more heat than the reference pan in order to maintain the specified temperature gradient; some heat is required to bring about the phase transition itself. Similarly, upon cooling, the sample gives off heat during recrystallization, while the reference does not. The DSC therefore measures heat flow in and out of a sample as a function of temperature, giving precise measurement of phase transition temperatures. There are many types of phase transitions that can be monitored by DSC (Table 1), some examples of which are observed in this laboratory.

Table 1 Phase Transitions that may be monitored by DSC

melting	crystalline solid \Rightarrow liquid
recrystallization	isotropic liquid \Rightarrow crystalline solid
vitrification	fluid \Rightarrow amorphous solid (glassy polymer)
clearing	liquid crystal \Rightarrow isotropic liquid
glass transition	amorphous solid (glassy polymer) \Rightarrow fluid

A sample may also exhibit more complex morphology within a single phase – that is, some materials exhibit multiple solid or liquid crystalline phases. Transitions among these morphologies can also be studied. Enthalpy changes for other types of reactions and processes, such as protein folding and unfolding, can also be studied³. An example of a material that exhibits a more complex morphological behavior is poly(ethyleneterephthalate) (Fig. 2), where the DSC scan depends on the thermal history of the material. Note the quenched (heated to the melt, then cooled very quickly) sample of poly(ethyleneterephthalate) (Fig. 2, curve IV). Because the polymer has been quenched, it has been cooled without having sufficient time to recrystallize, and is therefore not at thermodynamic equilibrium. Upon heating, the first transition observed is the glass transition temperature (called T_g), the point at which the amorphous solid begins to flow. Further heating then leads to an *exothermic* peak, a crystallization (called T_c), as the entangled polymer chains now have sufficient kinetic energy to attain some degree of intermolecular order. Finally, the polymer undergoes a true melting transition, as evidenced by a large endothermic peak (called T_m).

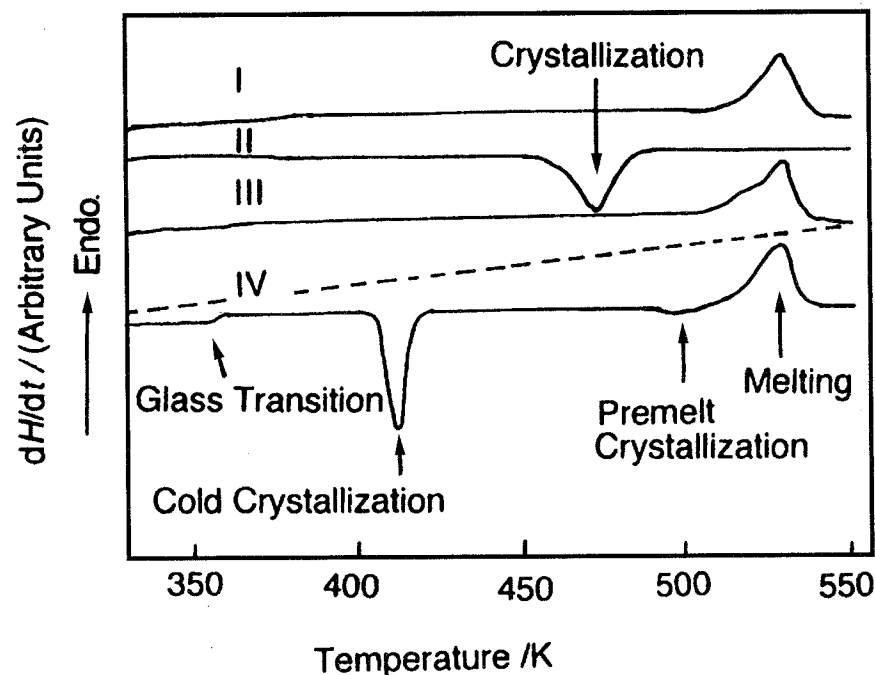


Fig. 2. DSC Curves of poly(ethyleneterephthalate): (I) as received sample, (II) cooled at 10 C/min., (III) heated at 10 C/min., (IV) heated at 10 C/min. following quenching⁴

In addition to phase transition temperatures, DSC can be used to obtain information about purity and/or the morphological composition of a sample. There are many materials for which "purity" is not clearly defined. For instance, a polymer sample may be 100% polystyrene, but is certainly not "pure" by a traditional definition since it contains individual macromolecules of many different lengths. Such a polymer sample, while macroscopically homogeneous, may contain microscopic crystalline domains that are interspersed with amorphous domains. Depending on how the polystyrene was prepared it may be a highly crystalline "isotactic" polystyrene in which the phenyl groups alternate along the polymer's backbone chain. Or, it may have a more random structure that will not crystallize regardless of its thermal history. The specifics of morphological composition can have a profound impact on a range of physical properties of a polymer or solid sample; the composition of a material determines how easy is to process (machine, mold, extrude, spin...) into a desired shape, as well as how resistant it is to environmental degradation (by exposure to light, oxygen, heat...). While morphologically mixed compositions are thermodynamically disfavored, they can be prepared through the manipulation of kinetic factors. DSC is an important technique in

determining the morphological composition of a sample as well as identifying the appropriate conditions for obtaining a sample of specific desired composition.

The transitions involving ammonium nitrate are particularly interesting; it may undergo up to 5 transitions between -20°C and its melting point (Fig. 3) ⁵.

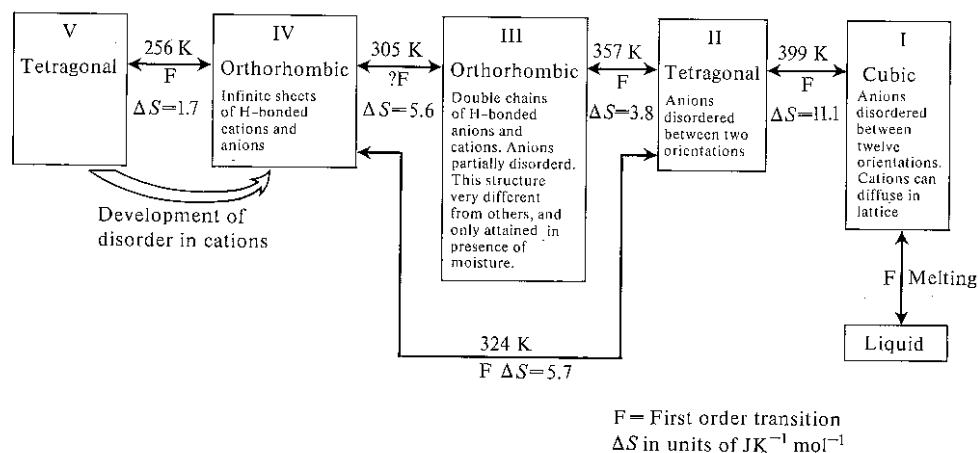


Fig. 3. Phase transitions in Ammonium Nitrate⁶

Experimental

Below are the details for preparing the two samples and the corresponding heating/cooling cycles for each compound. Prepare and run the polystyrene sample first. While the polystyrene sample is running prepare the ammonium nitrate sample. While the ammonium nitrate sample is running analyze the data you've collected for the polystyrene. Finally, when the ammonium nitrate run is complete analyze that data. Instructions for operation of the DSC instrument are in the following sections.

The balance for weighing samples and the press for crimping samples are located across the hall in Room 148 MSL. This is Prof. Park's research lab. We are guests. Please treat all equipment with respect and leave the lab as clean or cleaner than you find it.

Sample Preparation of Polystyrene

Using the analytic balance, weigh out one small polystyrene pellet (10-20 mg). The sample will be analyzed directly on an open sample pan. For the polystyrene experiments, the reference is an empty pan.

Heating/cooling Cycle for Polystyrene

- 1) External event on
- 2) Equilibrate at 25°C
- 3) Mark end cycle 1
- 4) Ramp $15^{\circ}\text{C}/\text{min.}$ to 280°C
- 5) Mark end cycle 2
- 6) Isothermal 5 min.
- 7) Ramp $15^{\circ}\text{C}/\text{min.}$ to 25°C
- 8) Isothermal 5 min.
- 9) Mark end cycle 3
- 10) Ramp $15^{\circ}\text{C}/\text{min.}$ to 280°C
- 11) Mark end cycle 4
- 12) Isothermal 5 min.
- 13) Ramp $15^{\circ}\text{C}/\text{min.}$ to 25°C
- 14) Isothermal 5 min.

15) Mark end cycle 5

Sample Preparation of Ammonium Nitrate

Using a small mortar and pestle, grind several ammonium nitrate pills into a fine powder. Transfer a ~10-mg portion to a sample pan and record its mass. Tap the sample pan and/or spread the sample out evenly using a spatula, being careful not spill any sample. Place a pan cover evenly over the sample and place the sample in the press. Pull the press lever down to crimp the sample pan/cover. Clean up the mortar and pestle with water and a Kimwipe. For the ammonium nitrate sample, the reference is an empty pan with a crimped cover.

Heating/Cooling Cycle for Ammonium Nitrate

Caution! The b.p. of ammonium nitrate is slightly higher than 200°C. Be sure you do not enter higher temperatures than suggested for the heating/cooling cycle.

- 1) External event on
- 2) Equilibrate at -35°C
- 3) Isothermal 3 min.
- 4) Mark end cycle 1
- 5) Ramp 10°C/min to 185°C
- 6) Mark end cycle 2
- 7) Isothermal 5 min
- 8) Ramp 10°C/min. to -35°C
- 9) Mark end cycle 3
- 10) Isothermal 5 min.
- 11) Ramp 20°C/ to 25°C
- 12) Mark end cycle 4

Report

In lieu of a formal lab report answer the following questions:

1. What are the literature values of T_m and T_g for polystyrene?
2. Did you observe any transitions that correspond to either of the above values?
3. Above what temperature would you expect the polystyrene that you examined to become less brittle?
4. On the basis of your results, were you given an isotactic polystyrene sample or a polystyrene sample in which the phenyl side chains were randomly oriented (e.g. atactic polystyrene)?
5. Construct a table listing the phase transitions that you observed for ammonium nitrate. Include columns for a) the onset temperature of the transition, b) the temperature of the transition at its peak, c) the magnitude of the transition in J/g, and 4) an assignment for each transition which relates to those given in Fig. 3.
6. What are the ΔS values for each transition you listed in your table? How well do these compare with the literature values?

References

1. The background section is a modified version taken from: *Laboratory Manual CHEM 304 Instrumental Methods of Analysis*, Expt. H. (Williams College, Williamstown MA, 2002).
2. Figure adapted from: *Thermal Analysis, Fundamentals and Applications to Polymer Science 2nd Ed.*, Hatakeyama, T. and Quinn, F.X. (John Wiley and Sons: New York, 1999), pg. 9.
3. Reference 2 and *Polymer Characterization*, Hunt, J. B. and James, M. I. Eds. (Blackie Academic and Professional, Glasgow, 1999) Chap. 7 provide suitable background reading for the thermal analysis of polymers.
4. Figure adapted from Ref. 2 pg.107.
5. *Disorder in Crystals*, Parsonage, N.G. and Staveley, L. A. K. (Clarendon Press: Oxford, 1978), pp.338-350.
6. Figure adapted from: *Experimental Physical Chemistry*, Matthews, G. Peter (Clarendon Press: Oxford, 1985), pg. 61.

Instructions for running the DSC

If the instrument is not turned on perform the following prior to startup. If the instrument is on, then skip to #6a:

Start up instructions (1-6)

1. Open the main valve on the N₂ tank (has red gas line attached to it). The line pressure (low pressure gauge) should be ~ 6-8 psi; do not adjust the setting on the regulator.
2. Turn on the cooling unit. (e.g. green switch, the unit is located on the floor connected to a large black hose leading to sample chamber)
3. Turn on the DSC (two red switches, only one will be lit at this point)
4. Turn on the computer, login to Novell. Be sure you know your username and password.
5. Two windows will appear, Welcome to windows and Results, close them.
6. Double click on the TA Instrument control icon.
 - a. A window will appear “**DSC-Standard Cell**”, with details of the previous run.
 - b. At this point the heater is not on but the cooling unit is (note that only one of the DSC’s red buttons is lit). To avoid condensation in the sample cell click on the **Run button** (green triangle) then the **Stop button** (red square). This will start the heater, check that both of the red switches on the DSC are now lit.
7. Select View > Exp. View and fill out the new information on the **Summary** window (Sample name, sample size, comments, data file (choose a file name and save it in the Chem 301 folder), and procedure (custom).

Note: For data file you may also type in: C:\TA\Data\DSC\Chem366\name of your file here

8. Click on the **Procedure** window. Fill out **Procedure info** test (default is custom, and can’t be changed) and notes. Below the Procedure info is the **Method info**, enter your name or initials to identify you as the operator. Below the name will be the previous run sequence. Unless you want to run the same heating/cooling cycles as the previous run click on **Editor**.
 - a. Enter your name/initials
 - b. To remove segments of the previous sequence click on the segment to highlight it then press **delete**.
 - c. To enter new segments click on the appropriate icons to the right under segment types, for some segments you may need to also enter values (i.e. temps, heating/cooling rates)
 - d. Check that you have made the changes you want then click on **O.K.**
 - e. You are now back in the **Procedure window**, click on **apply**. Check that your changes were made. Under **Post test**, make sure the instrument will return to 25-35°C and that **Event RCS control** is unchanged
9. Click on the **Notes window**. Under “Operator,” enter your name/initials. Under “Pan type,” enter aluminum (should already be aluminum). Under “Extended text,” enter any other notes you wish to make. Do not change any purge gas settings. Click on **apply**.
10. Check that the sample chamber is at or slightly above room temperature before opening. Using a pair of tweezers, remove the 3 lids on the sample chamber, place your sample pan in the closest position; place the reference pan in the rear. If you are using a crimped/capped sample the reference should be an empty crimped/capped sample pan, if you are using a sample in an open pan use an open pan for a reference.

11. To start your run go back to the **Summary window**, check that you have the proper info/run sequence, and then click the **Run button** (green triangle).
12. **Instrument shut down.** Most likely, you will leave the instrument on for the next user, or your instructor will shut the instrument off. You should, however, be aware of the shutdown procedure. When you have finished your run(s):
 - a. Turn off the cooling unit (green switch)
 - b. Wait 1/2 hour
 - c. Turn off DSC (two red switches)
 - d. Logout/turn off computer
 - e. Turn off N₂ (main valve only)

To Analyze DSC Runs

1. Click on **TA Universal Analysis** on the desktop or if you are running **TA Instrument Control** click on the top right icon from the toolbar, **WinUA**. Note that you can analyze a previous run while a current run is in progress.
2. From the **file** menu select **open**
3. Click on the **Dsc** folder
4. Click on the **Chem 366** folder
5. Click on **your file name** then click **open** or double click on **your file name**
6. Your data file info will appear, click **O.K.**
7. A trace of the run will appear (note that you can change the way the trace is presented by using the options on the tool bar)
8. To integrate peaks:
 - a. From the toolbar lick on **integrate peaks linear icon**. A pair of red crosshairs will appear.
 - b. Double click at the start, then at the end of the peak, and press **enter**. The temperature values for the start and the apex of the peak will appear as will an integration giving the area of the peak. You can move the text by dragging with the cursor.
 - c. If the integration(s) is not acceptable or if you just want to remove it, go to **edit** menu and select **delete results**. Choose **last** or **all** to delete.
 - d. Integrate any remaining peaks in a similar manner.
 - e. From the **file** menu select **print**

Acknowledgements

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