The Thermal Analysis Toolkit
Seeing the Bigger Picture

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The Thermal Analysis Tools - DSC

- Differential Scanning Calorimetry
  - Measuring the heat flow into or out of a sample.

- Modulated Differential Scanning Calorimetry
  - Measuring the heat flow into or out of a sample.
  - Separating the heat flow responses due to changes in heat capacity from the kinetic events.
  - More specifically separating the heat flow events which respond to a change in the heating rate (generally Cp and some melting) from those with do not.

The Thermal Analysis Tools - DSC

- Properties measured include
  - Heat Capacity
  - Glass Transition
    - Change in Cp
  - Melting
    - Degree of crystallinity
  - Crystallisation
    - Process kinetics
  - Oxidation

The Thermal Analysis Tools - TGA

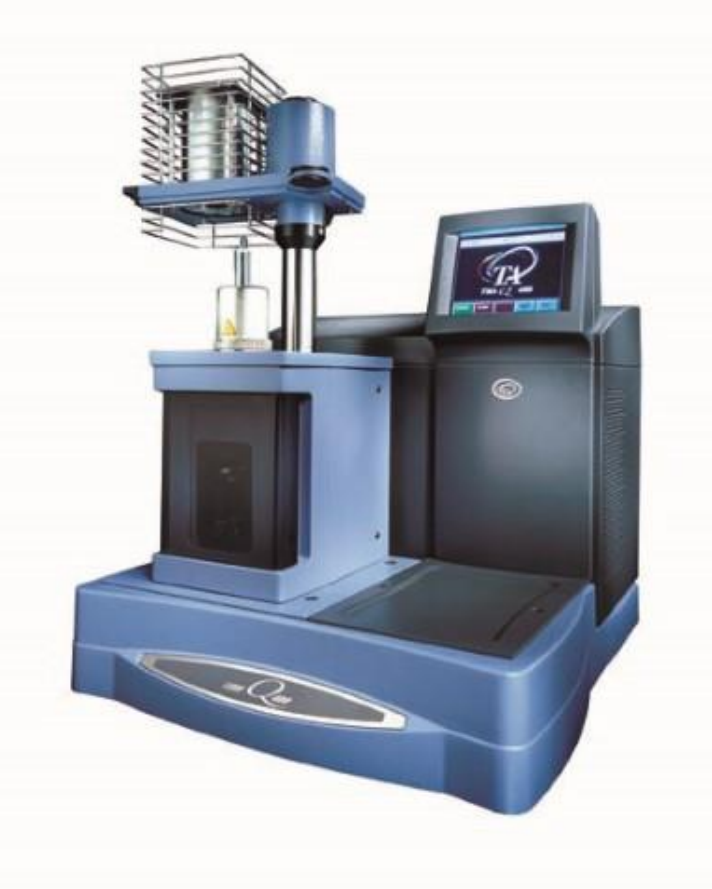
- Thermogravimetric Analysis
  - Measuring weight changes in the sample.
- Hi-Res Thermogravimetric Analysis
  - Measuring the weight changes in the sample but allowing these weight changes to control the temperature profile (sample controlled thermal analysis)

The Thermal Analysis Tools - TGA

- Composition of Multicomponent Systems
- Thermal Stability of Materials
  - Assuming volatile release is involved
- Oxidative Stability of Materials
  - Initial weight gain then volatile release
- Decomposition Kinetics of Materials
- Estimated Lifetime of a Product
- The Effect of Reactive or Corrosive Atmospheres on Materials
- Moisture and Volatile Content of Materials

The Thermal Analysis Tools - TMA

- Thermo Mechanical Analysis.
  - Measuring dimension changes as a function of temperature or time at a specific temperature.
- Modulated TMA
  - Separation of dimension changes due to CTE from dimension changes due to events such as stress relaxation.

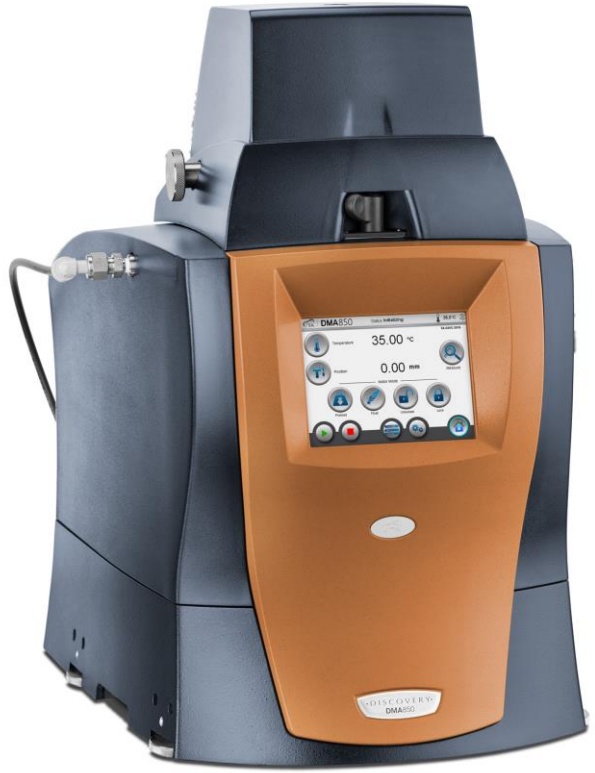


The Thermal Analysis Tools - TMA

- Coefficient of Thermal Expansion (CTE)
- Glass Transitions
- Shrinkage or Expansion due to Relaxations in Material

The Thermal Analysis Tools - DMA

- Dynamic Mechanical Analysis
  - Measuring the visco-elastic parameters of solid materials and their change as a function of temperature or time at a specific temperature.
  - The system also allows transient testing (stress relaxation and creep behaviour).



The Thermal Analysis Tools - DMA

- Glass Transitions
- Beta and Gamma relaxations
- Frequency Dependence of transitions
- Creep
- Stress Relaxation

Analysis Overview – Starting Points

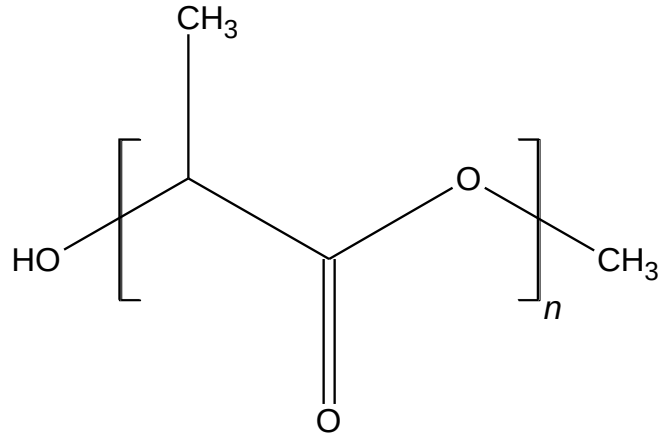
- If possible – start with TGA (ambient to 1000°C @ 10°C/min or 20°C/min.
  - Volatiles (water/solvents etc).
  - Thermal Decomposition (with volatile loss).
- DSC – Heat / Cool / Reheat @10°C/min. Stop heating before decomposition if possible (although there are exceptions).
- MDSC – If needed. Conditions can be optimised based on DSC data but:
  - ±1°C, 60 seconds period, 3°C/min is a good starting point.
  - ± 0.363°C, 60 seconds period, 3°C/min is good for polymers.
    - The amplitude here gives heat/iso conditions.

Analysis Overview – Starting Points

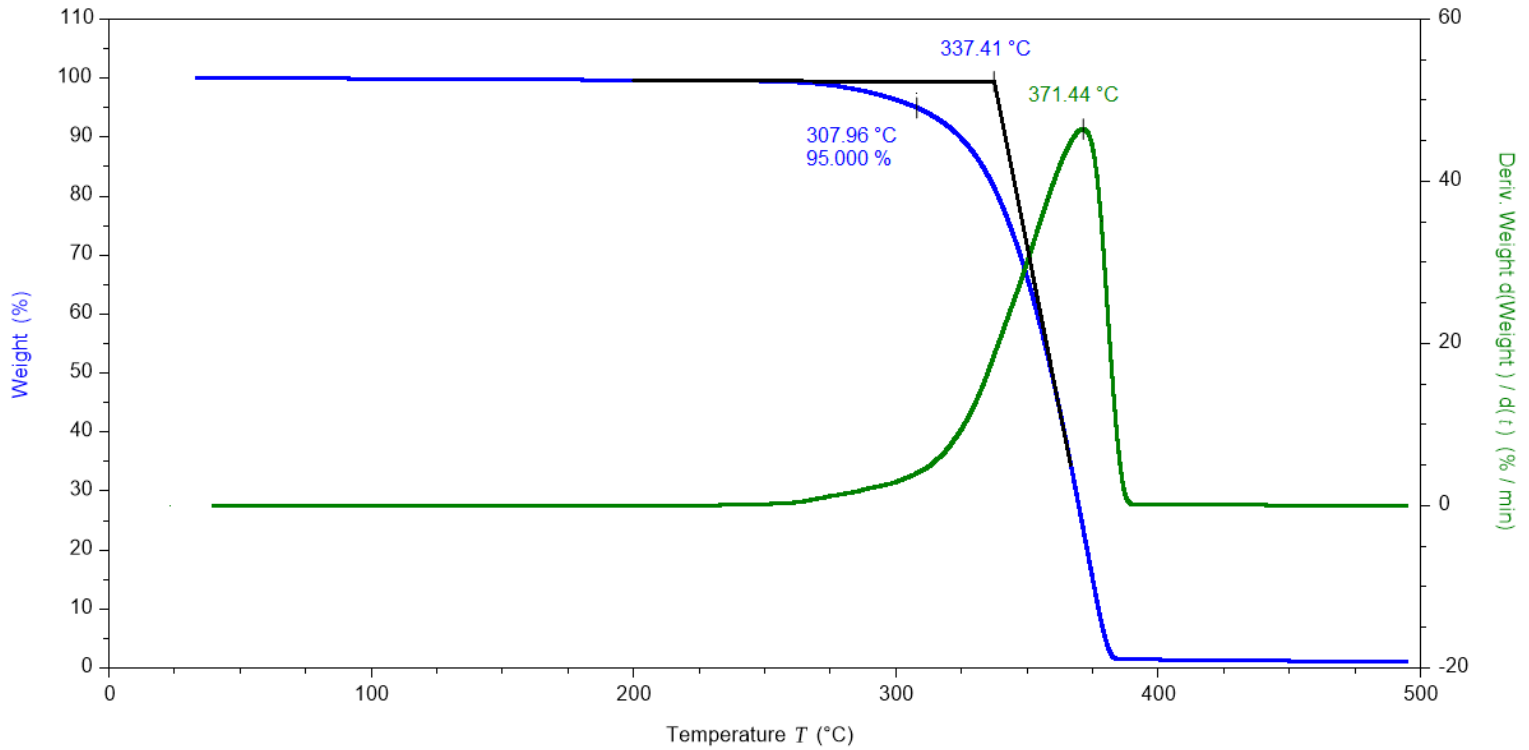
- DMA – 1Hz, 0.05% Strain (ish), 3°C/min.
  - In general you would take the sample into the rubbery region. It is unlikely you will get far into the rubbery region. The sample stiffness will limit this.
  - This is predominantly a solid rheology technique. More fluid samples will require a rheometer (the deformation mode (shear) is stiffer).
  - Creep or stress relaxation tests could also be used.
- TMA – 0.01 – 0.05N load, 3°C/min.
  - Heat – Cool – Reheat may be needed to remove relaxation events although this has the issue that the data on the second heat has a different thermal history
- MTMA - ±5°C, 300s period, 2°C/min.
  - Reversing response is CTE related.
  - Non-reversing response is relaxation related.

Example – Polylactic Acid

- Polylactic Acid (PLA) – thermoplastic aliphatic polyester.
- Feedstock for production is from renewable resources (eg corn starch / sugar cane).
- The resultant polymer can be used for wide range of applications where commodity polymers (PP, PE, PS) are typically used.
- Bioactive, therefore also has uses within medical areas.
- Biodegradable.
- Sample was an injection moulded bar.
  - Can be cut to fit the different techniques.



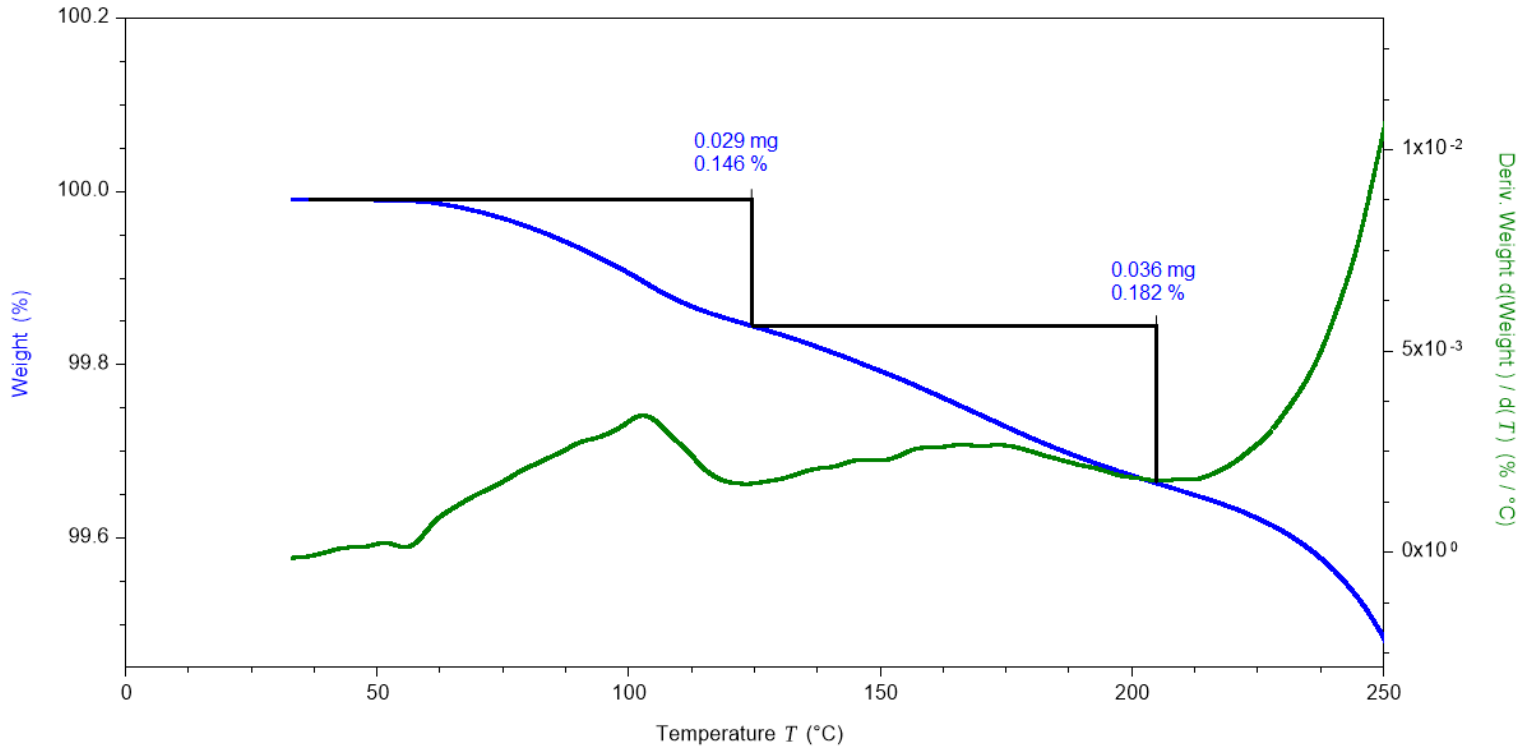
First Step - TGA



- Decomposition extrapolated onset 338°C.
- Maximum mass loss rate at 371°C
- Temperature at 95% residue 308°C.

- As a general rule DSC runs have no major benefit where the sample has lost more than 5% due to decomposition.

First Step - TGA

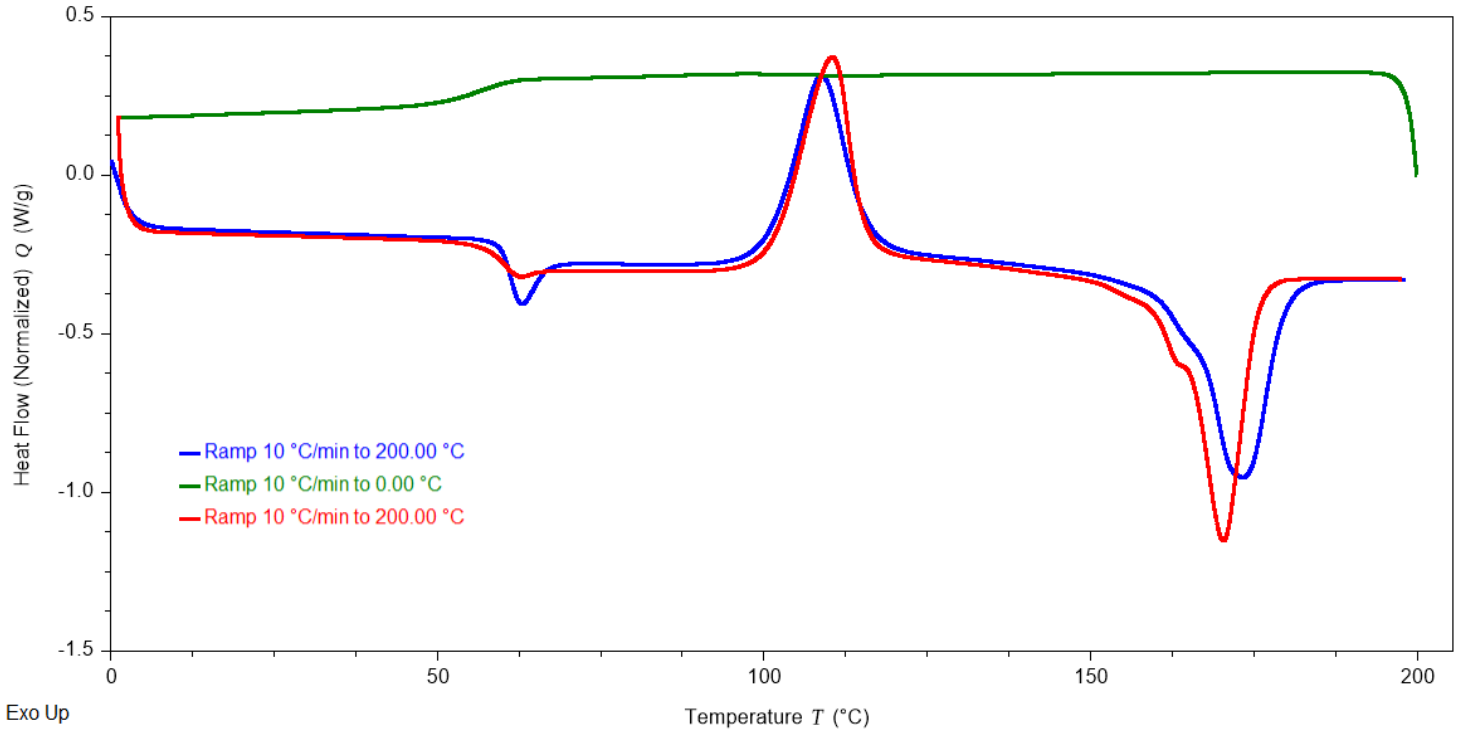


- Zoom into lower temperature range.
- Some volatiles released very early on.
- Very low quantities.
- Probably moisture related.
- May be important in material behaviour.

TGA

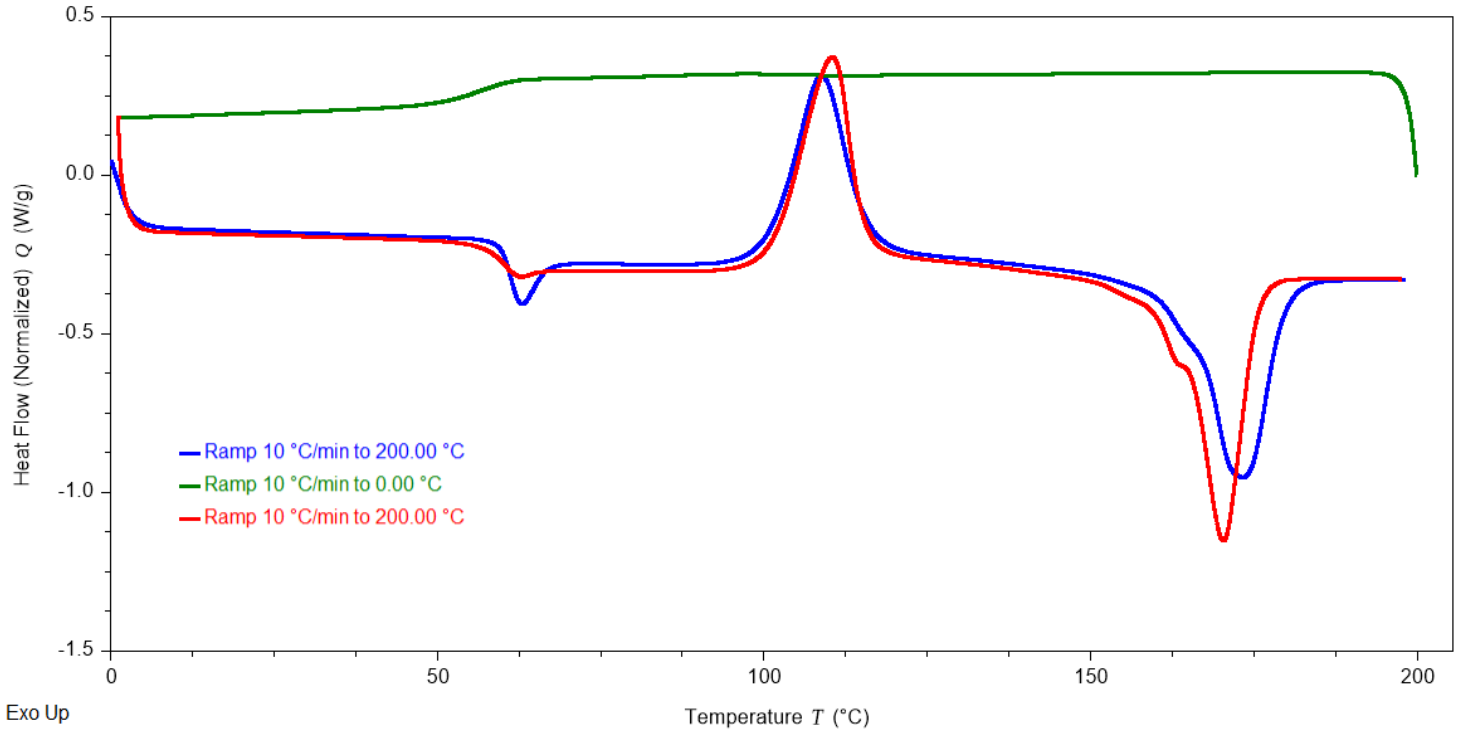
- Very small amount of moisture (possibly).
- If our material has amorphous content and is susceptible to moisture then this may affect properties.
- Sample lost 5% mass around 300°C. Unless there is good reason to run DSC to higher temperatures then this would be our maximum upper limit.

DSC – Heat-Cool-Reheat @ 10°C/min



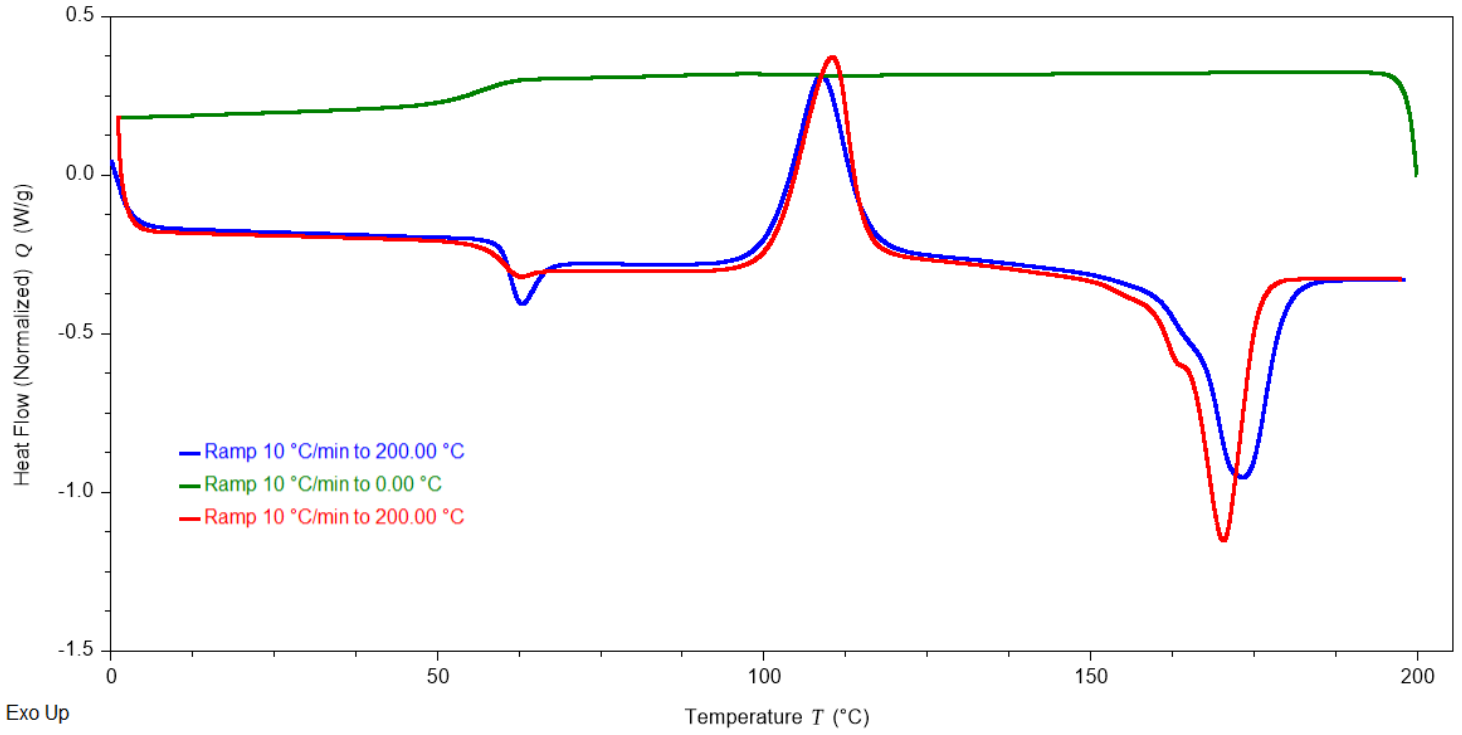
- First heat
  - Glass transition (with enthalpic recovery).
  - Cold Crystallisation
  - Melting

DSC – Heat-Cool-Reheat @ 10°C/min



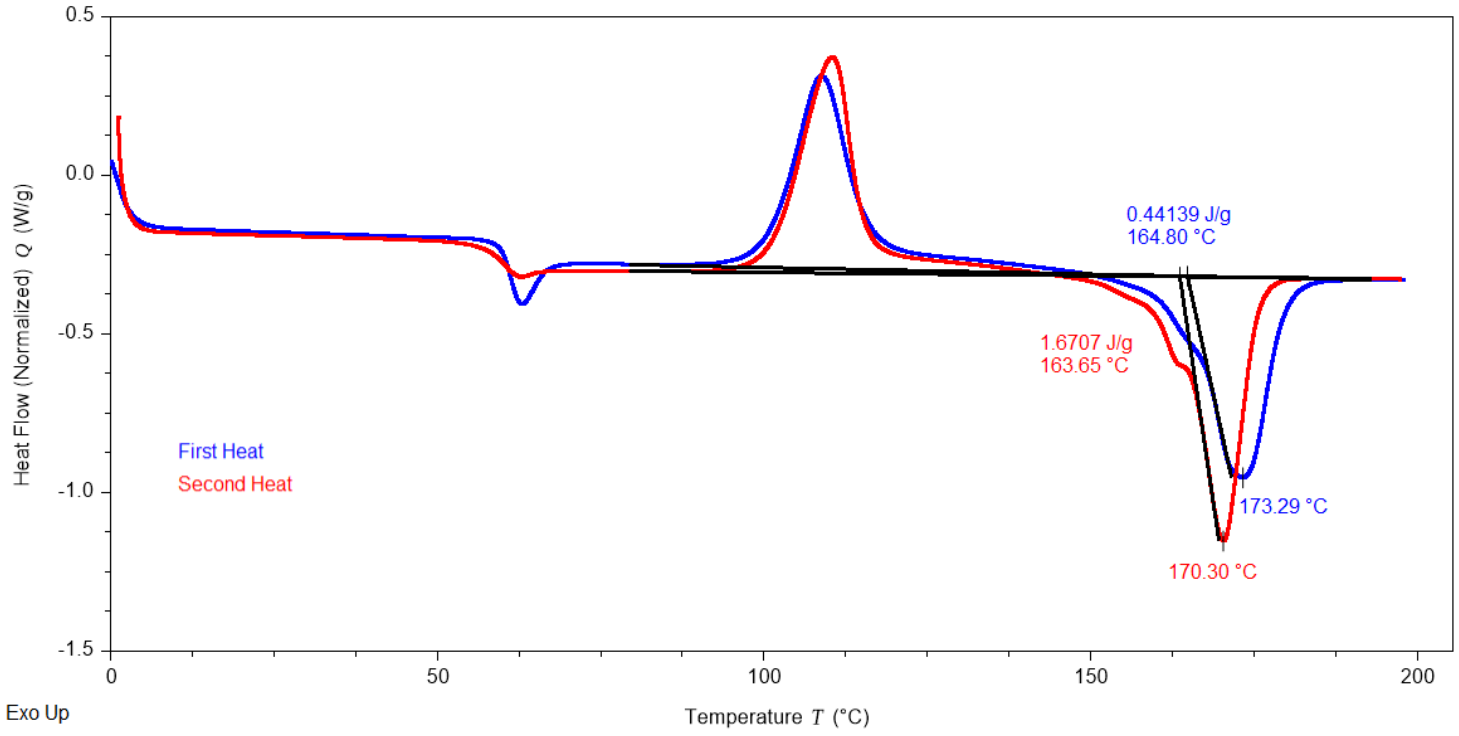
- Cool
  - Apparently just a glass transition.
  - The crystallisation kinetics are slow enough that even at 10°C/min recrystallisation is not favoured.

DSC – Heat-Cool-Reheat @ 10°C/min



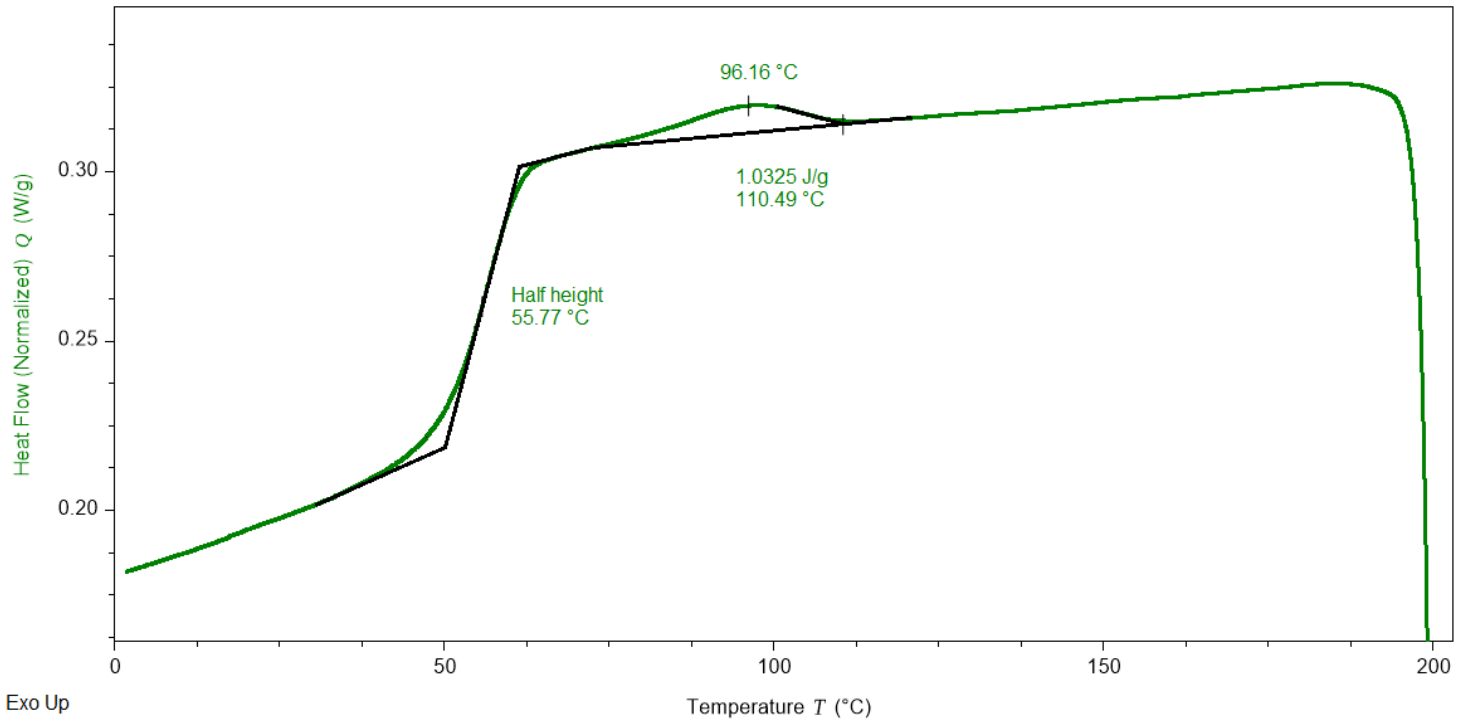
- Second heat
  - Glass transition
  - Cold Crystallisation
  - Melting

DSC - Heating Curves



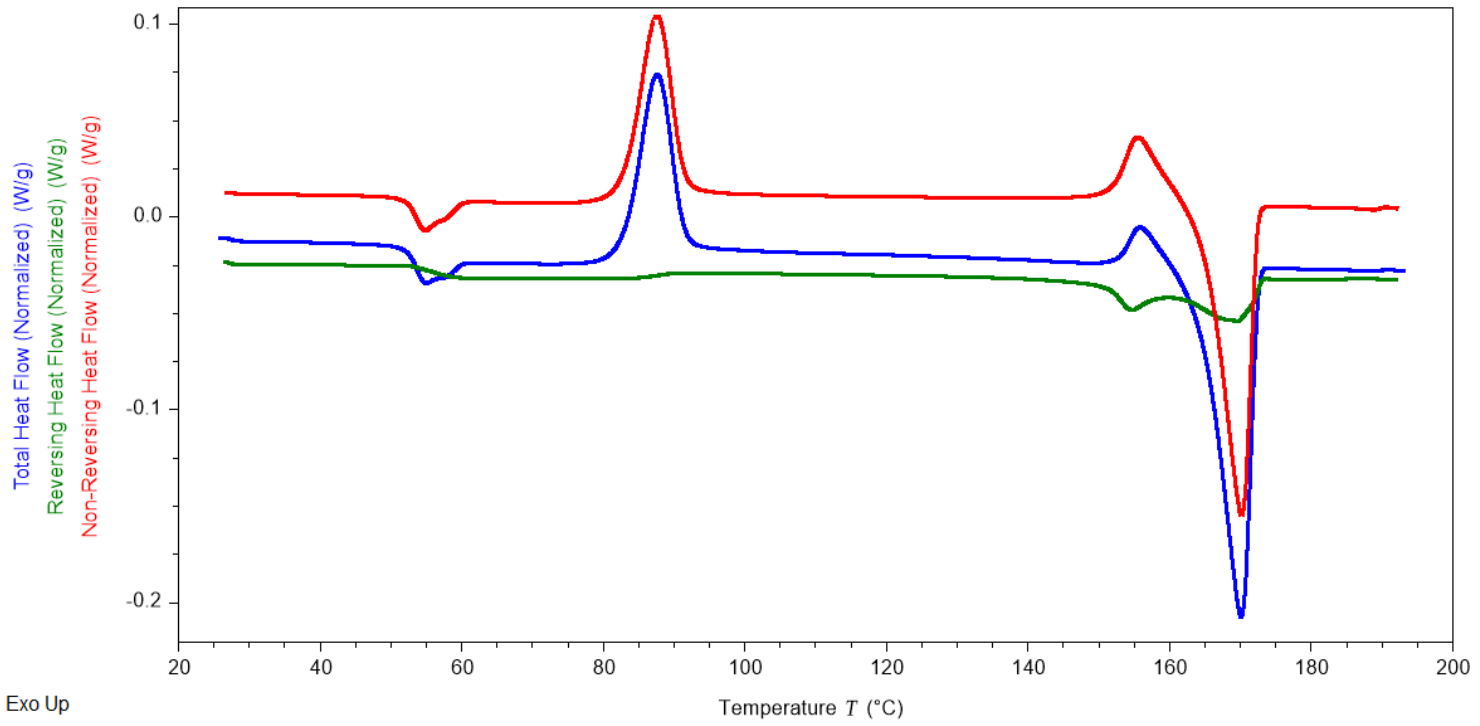
- Integration from below cold crystallisation to above the melt gives the total change in enthalpy between those two points.
- First heat shows a change of 0.5J/g so very close to totally amorphous.
- Second heat shows a change of 1.8J/g so you could still very amorphous but possible crystal formation has occurred.

DSC - Cooling Curve



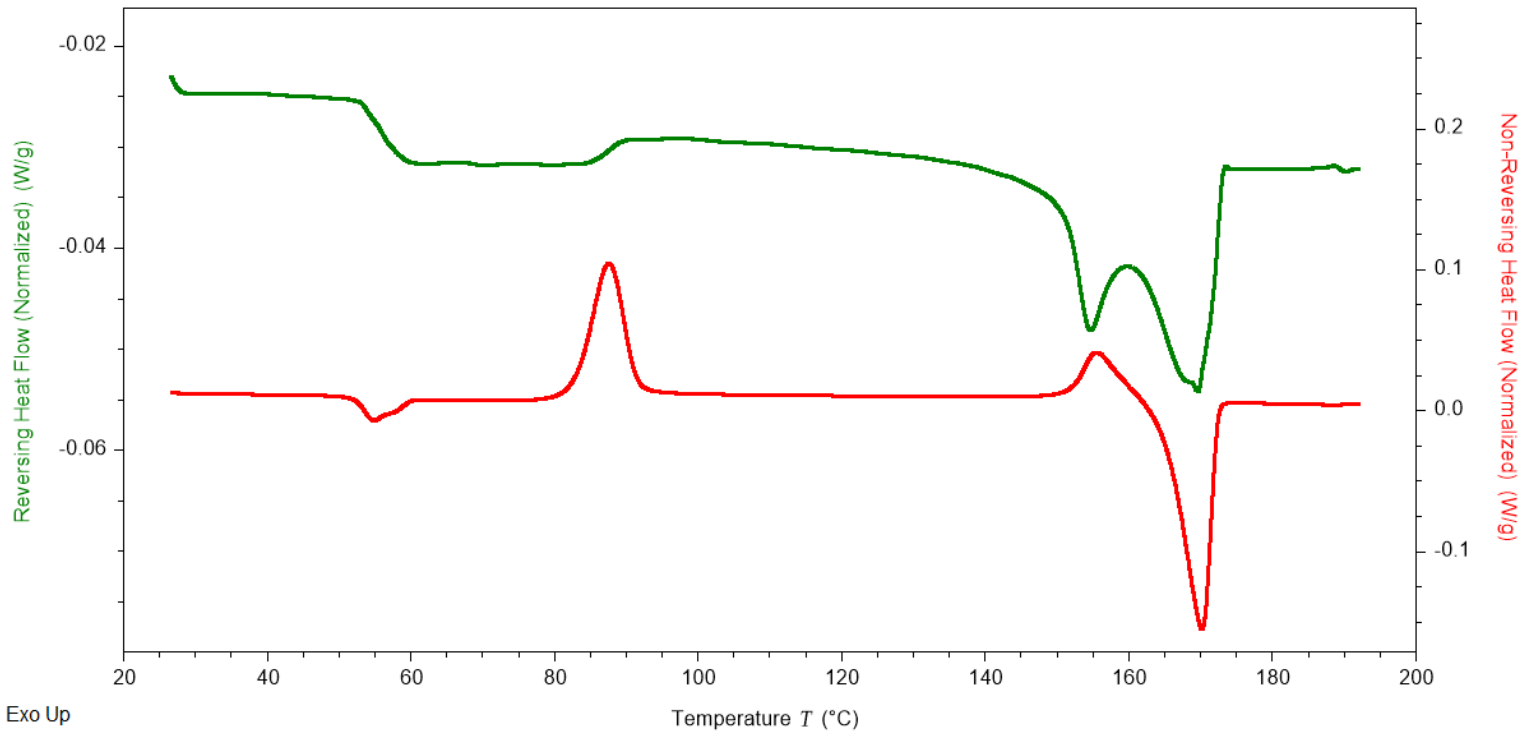
- If we look more closely at the cooling curve we can see a small exotherm suggesting that some crystal did form – but only a very small amount.
- Note – the glass transition does not have any relaxation/recovery events when studied in cooling (move from equilibrium to non-equilibrium). Ideal analysis but presents some issues with thermal history of the material.

Modulated DSC – Heat-Iso (±0.16°C, 60s, 1°C/min).



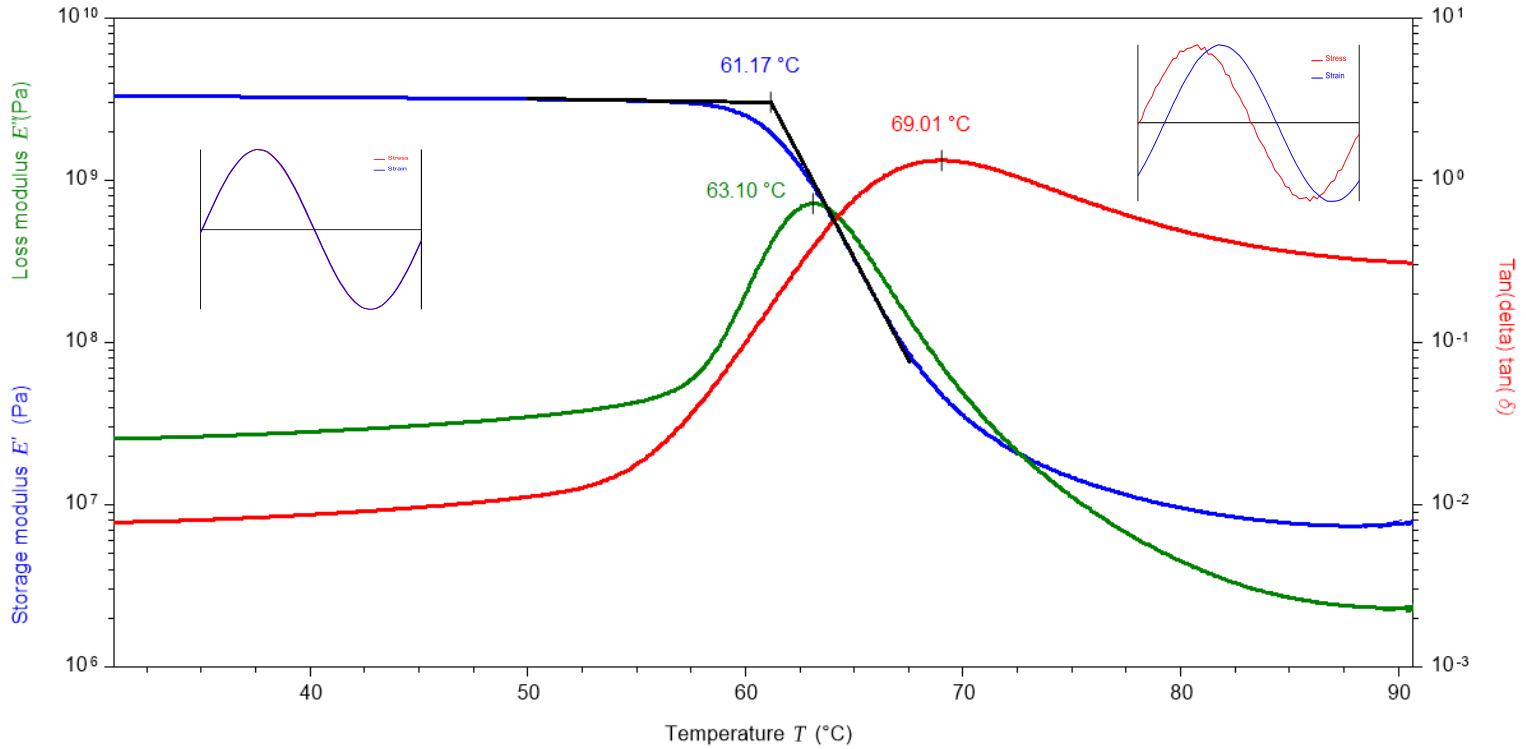
- All same scale (good to see relative response)
- Reversing signal showing Cp changes and some melting.
- Non-Reversing signal showing relaxation/recover events, crystallisations, some melting.

Modulated DSC – Heat-Iso (±0.16°C, 60s, 1°C/min).



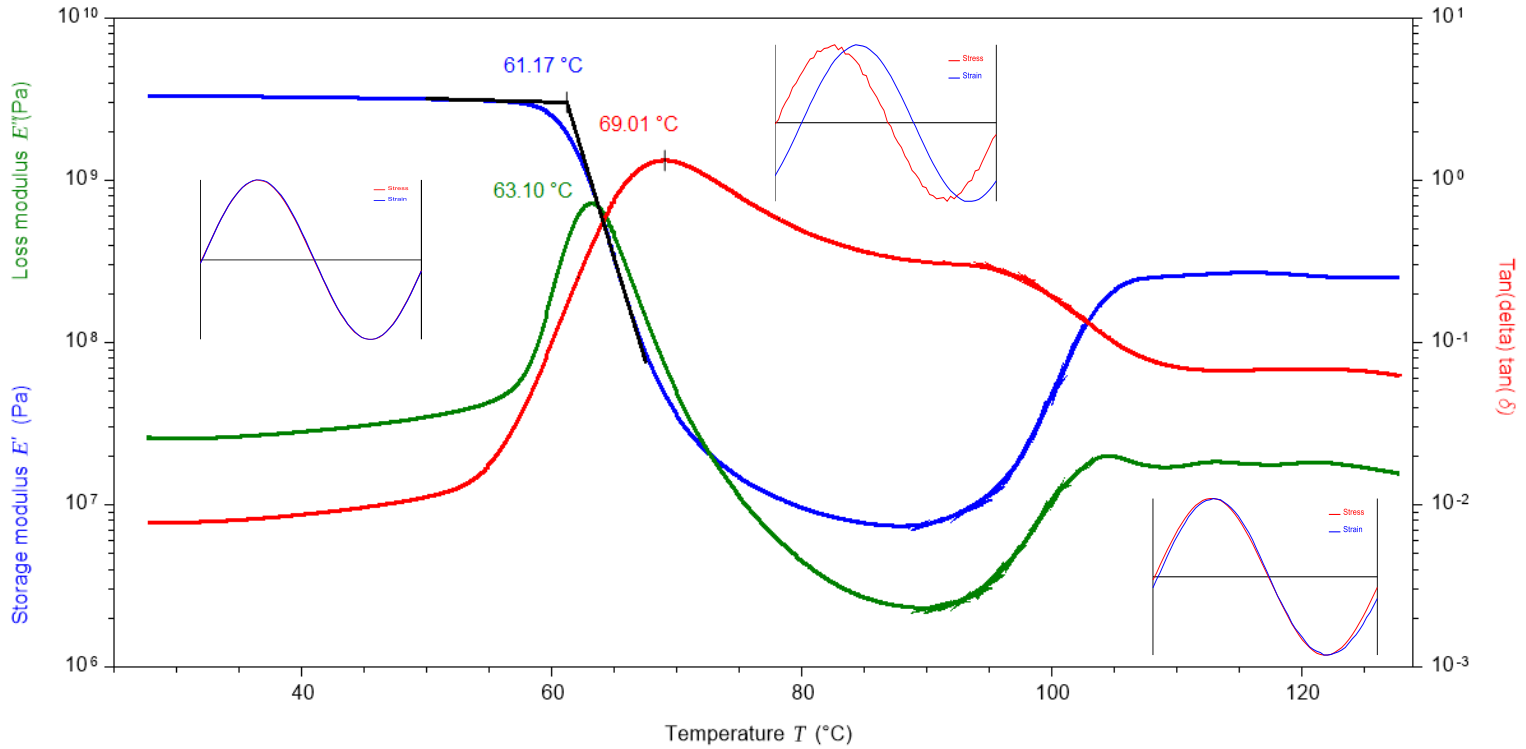
- Note – scaling difference in two signals.
- Tg is clear, reduction in Cp due to crystallisation also seen.

DMA – 1Hz, 0.05% Strain, 2°C/min to 130°C.



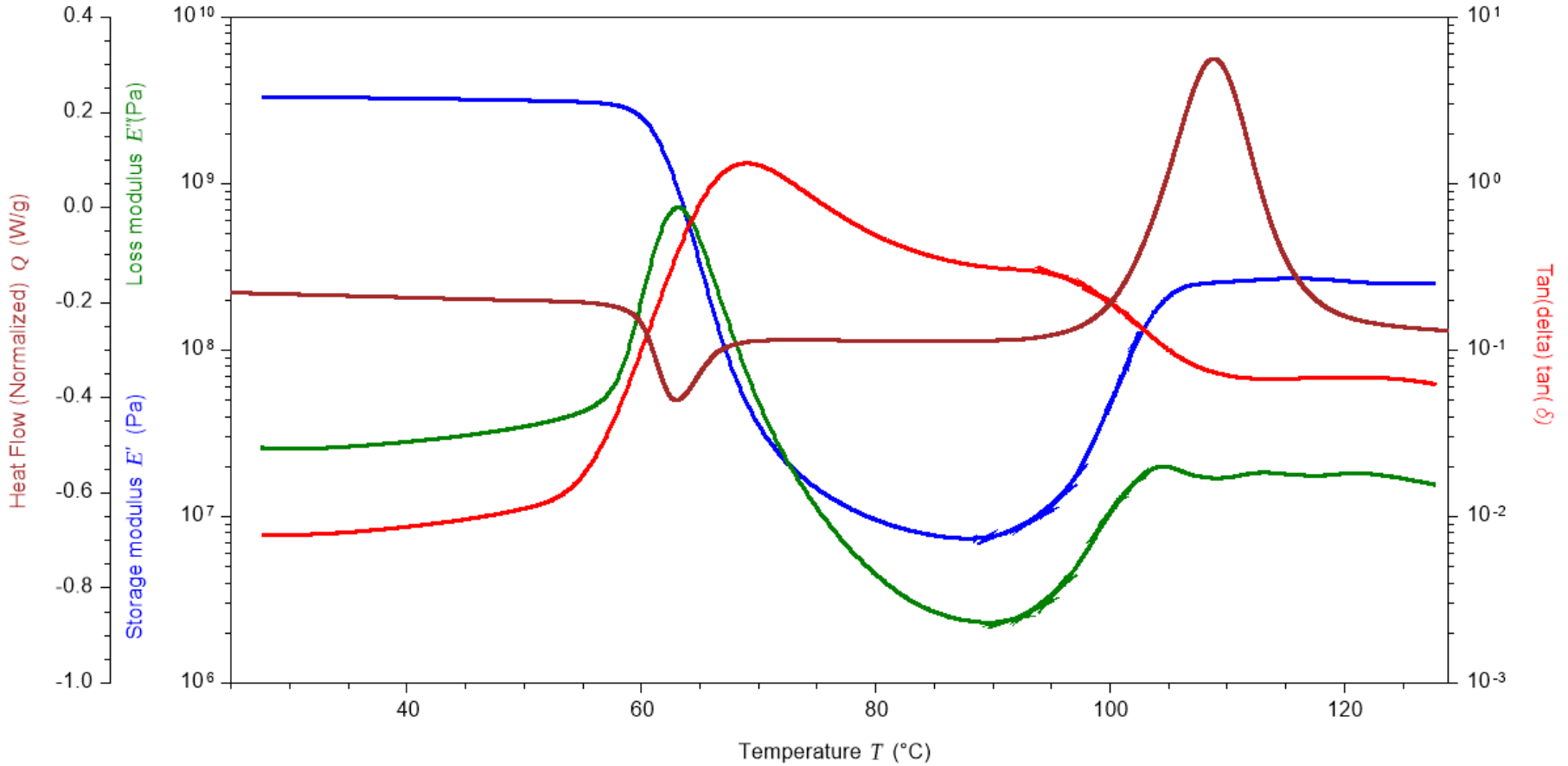
- Change in viscoelastic parameters seen as the material move through the glass transition.
- Tg analysed as the change in these viscoelastic parameters.

DMA – 1Hz, 0.05% Strain, 2°C/min to 130°C.

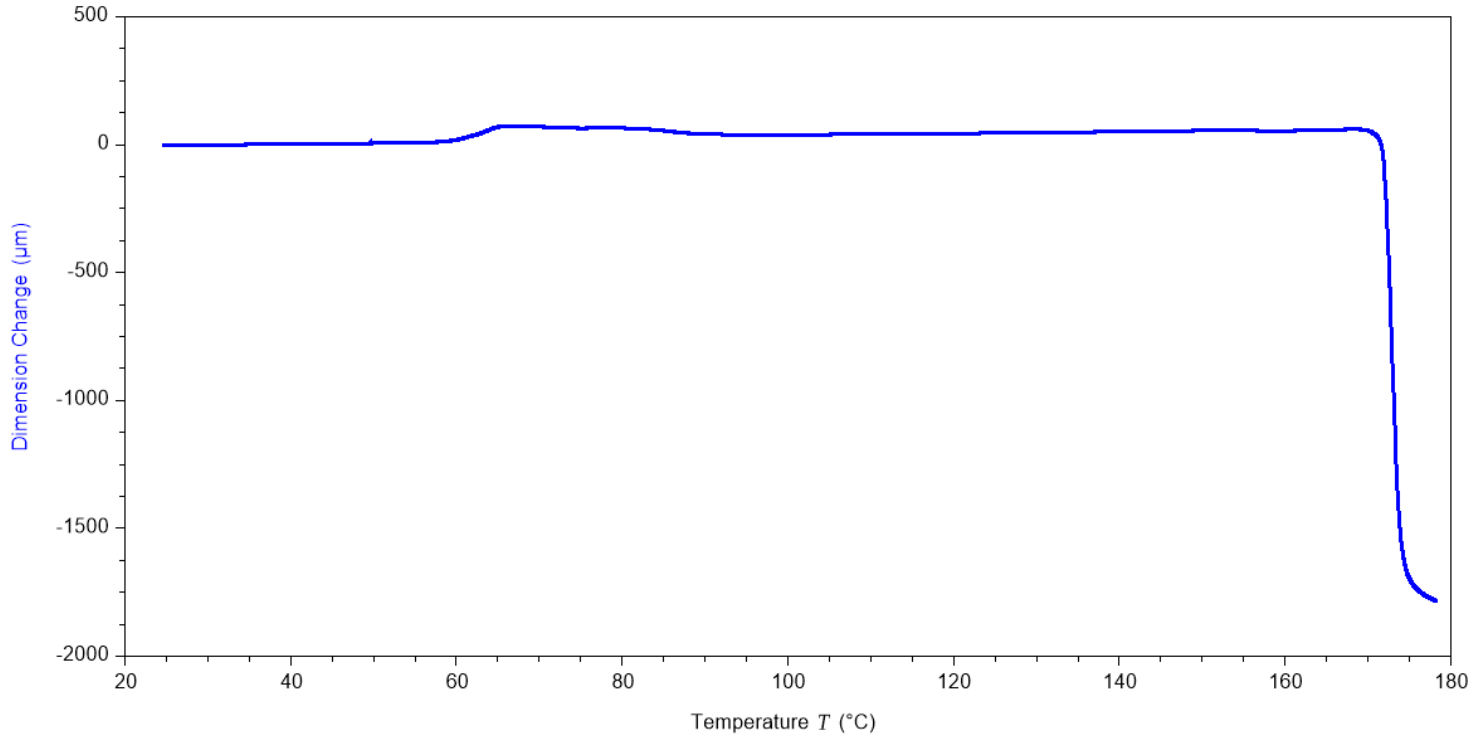


- Change in viscoelastic parameters seen as the material move through the glass transition and now through the cold crystallisation
- Test stopped before the melt.

DSC & DMA Overlay

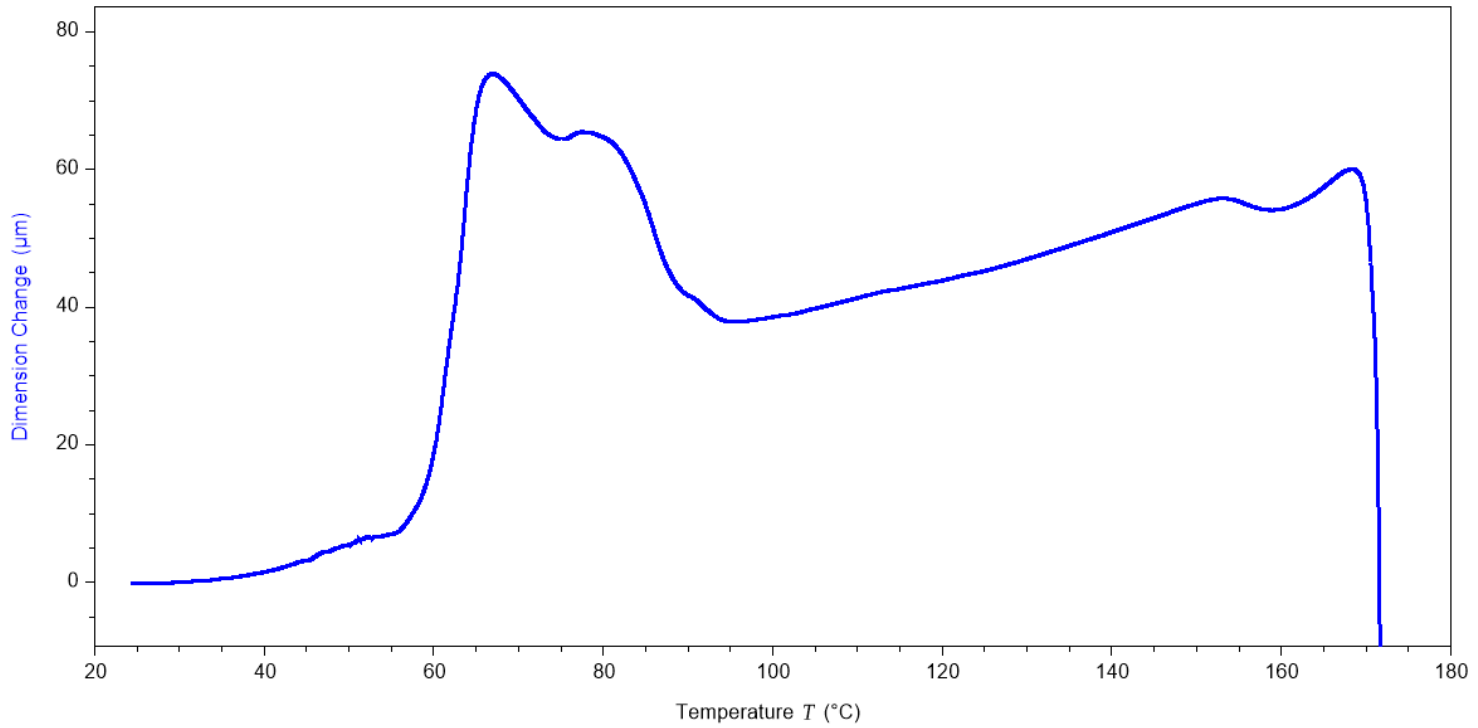


TMA



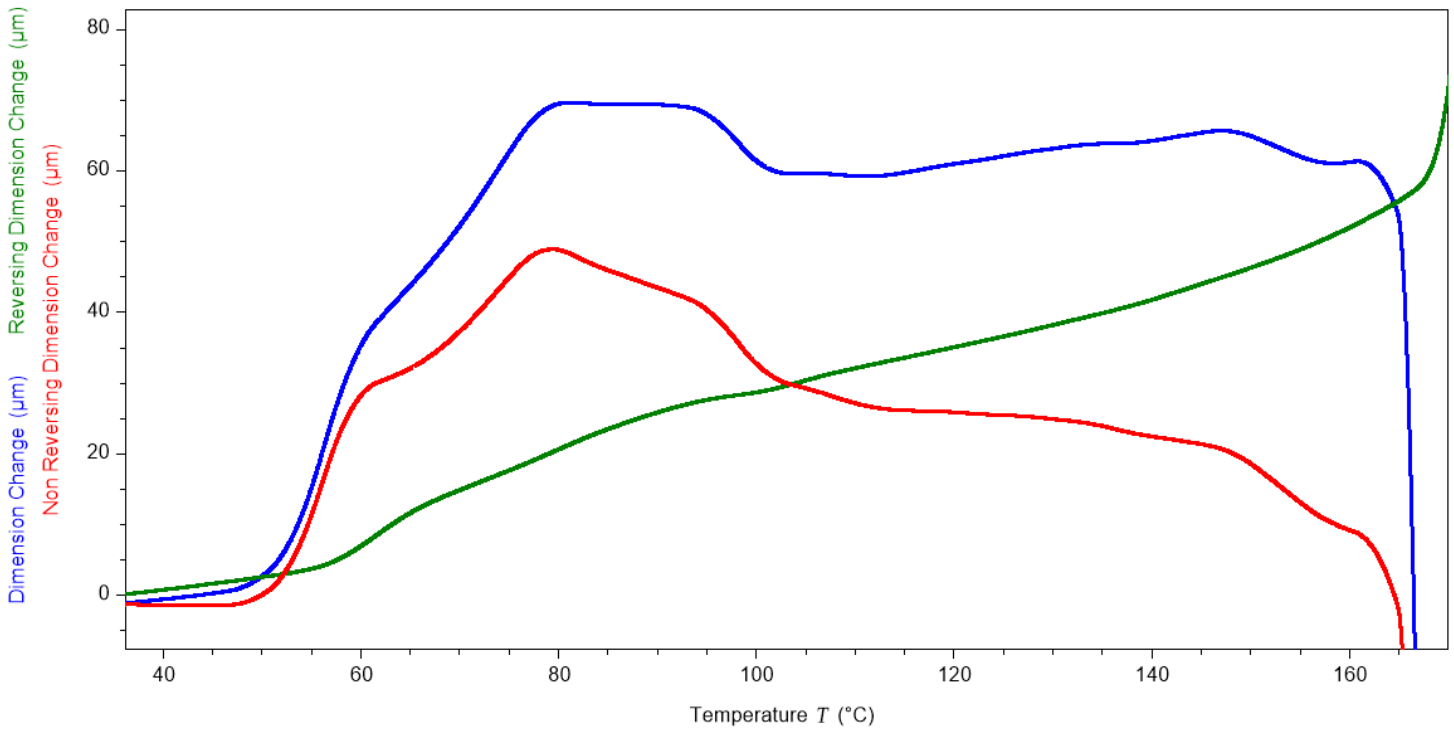
- Initial sample was about 2mm thick.
- We can see the dimension changes in the material, however, the sample was taken into the melt. This dominated the change in dimension but we can focus in on the lower temperature range.

TMA



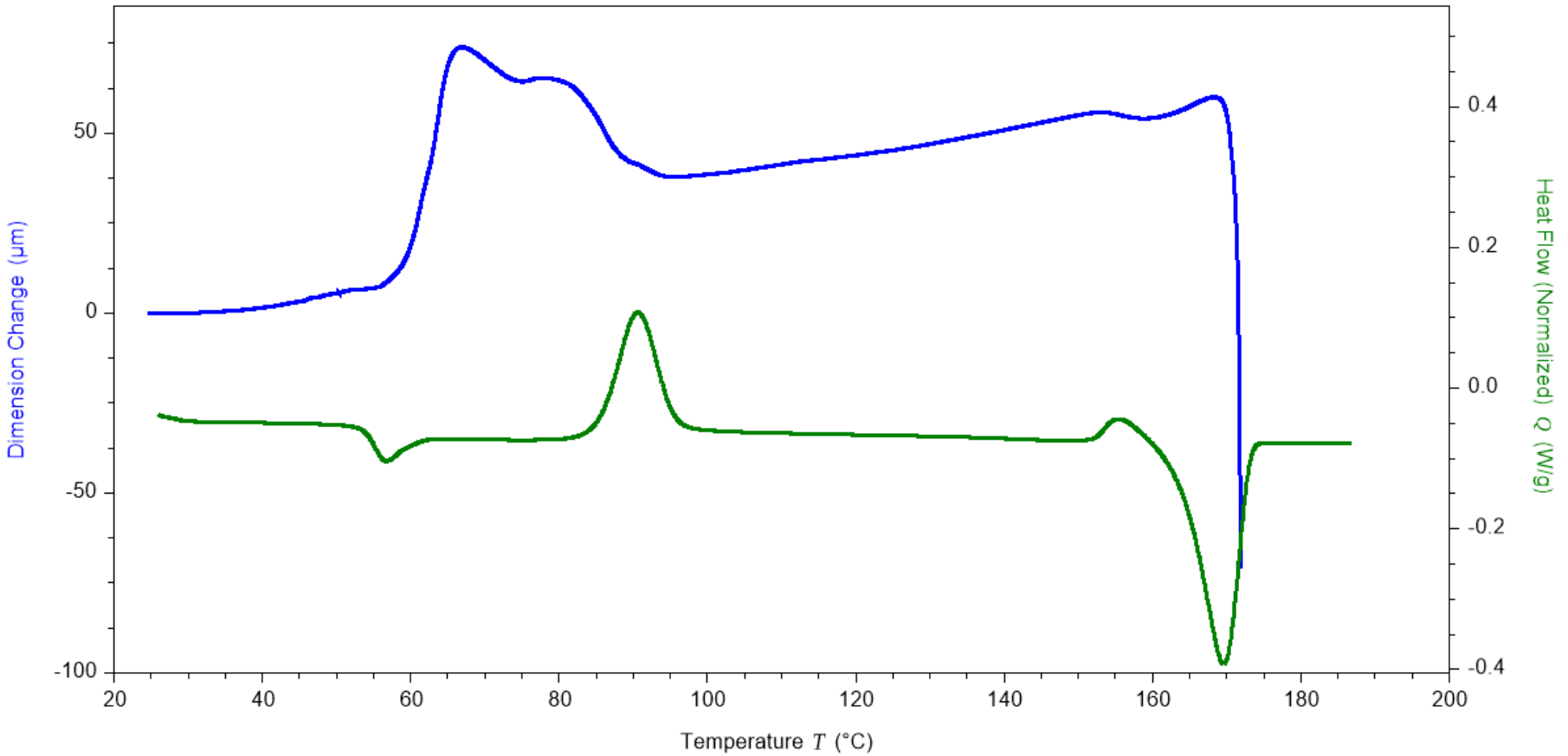
- Dimension changes seen more clearly now the melt effect has been removed.
- This is the sum of all dimension changes.
  - CTE
  - Morphology
  - Relaxations

Modulated TMA

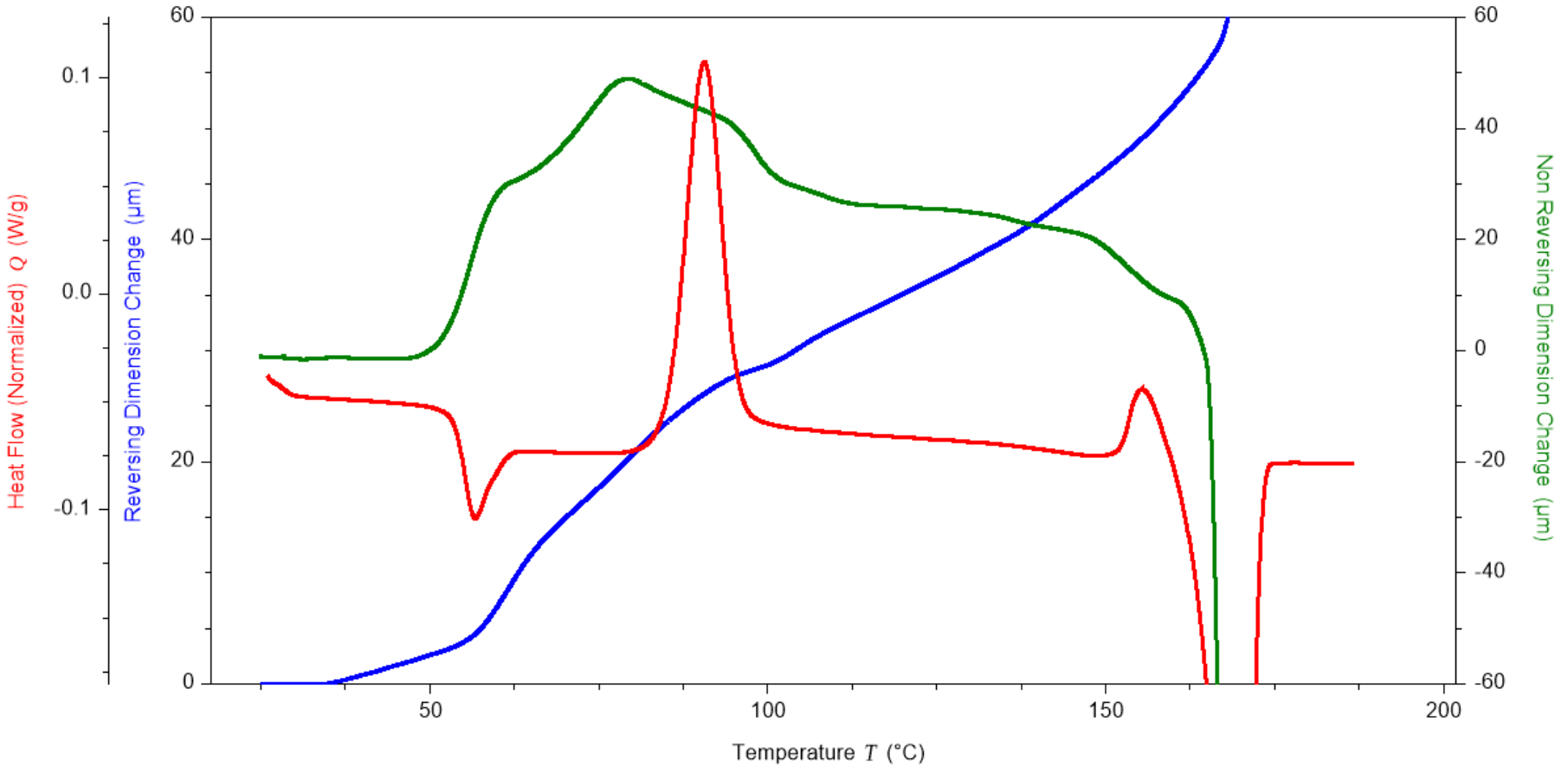


- The reversing dimension change is giving dimension changes due to the CTE of the polymer. We can see how that is changing dramatically at the glass transition.
- The non reversing dimension change is showing permanent changes in the material dimensions. You can see an expansion (stress relaxation?) at the glass transition but also shrinkage in the material during the cold crystallisation.

DSC & TMA Overlay



DSC & MTMA Overlay



Adding more visualisation to the data.

Discovery DSC Microscope Accessory

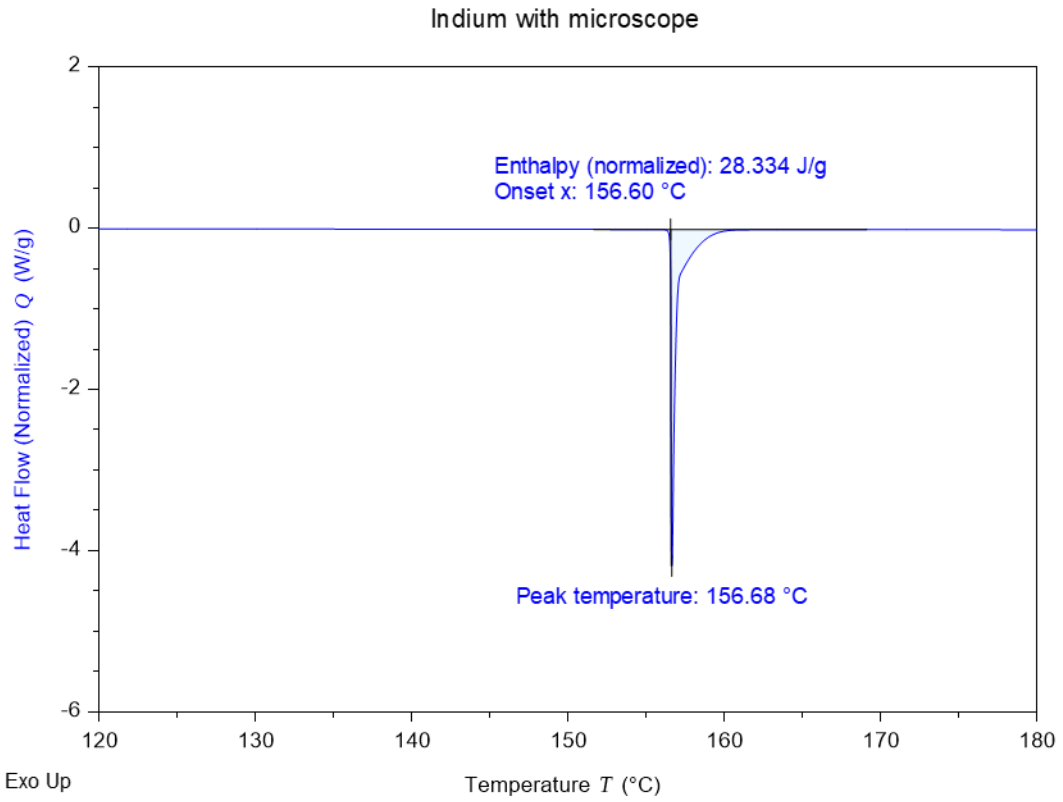
- Provides imaging and video capabilities during a DSC measurement on the Discovery DSC 2500, 250 and 25
- Includes a high resolution (1.3 MP vivid color) digital microscope camera with a long range working distance and magnification range of 10x-90x; with a typical magnification of 50-60x when focused on a sample pan in the DSC cell
- Collects individual images of up to 1 fps (frames per second) and video at 15 fps
- Illumination provided by several white light LEDs and an adjustable polarizer is included for viewing highly reflective materials and minimizing the amount of glare

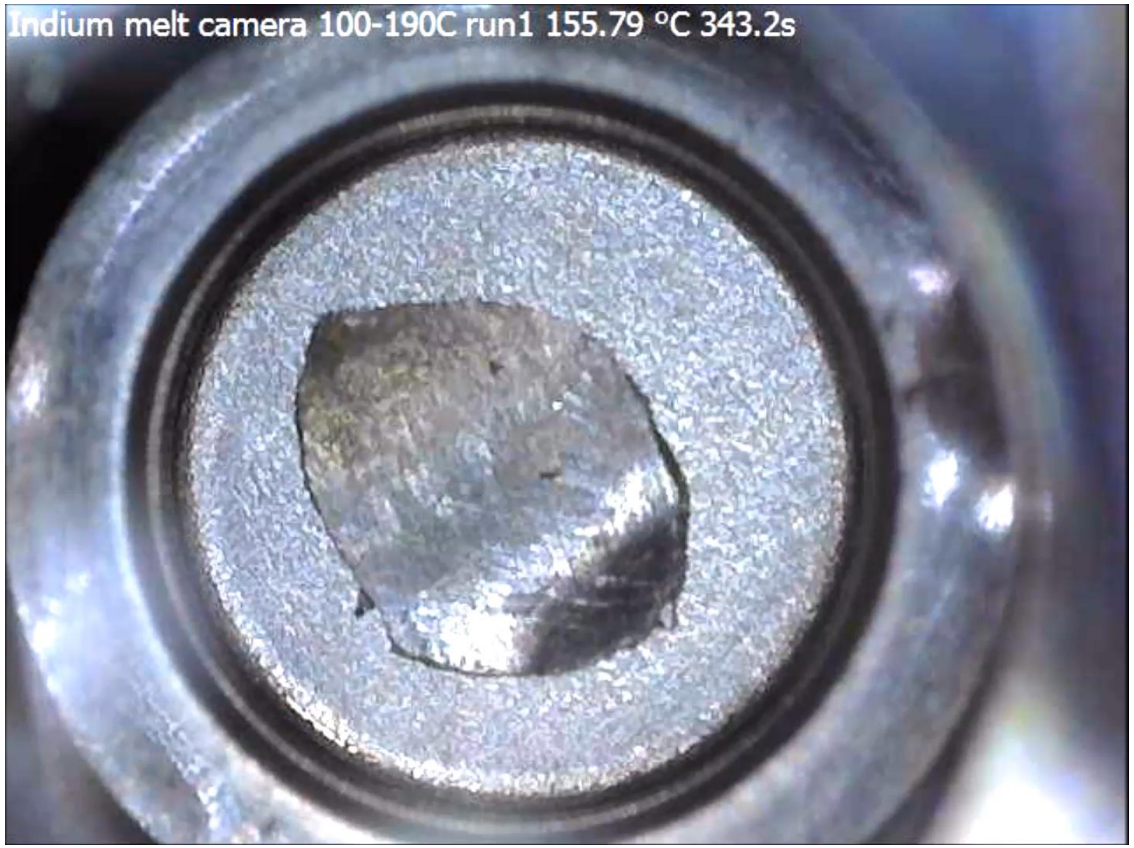
Discovery DSC Microscope Accessory

	Specifications and Requirements
Microscope Specs	Resolution 1080x1024 pixels ≥40X zoom (50X-60X optimal, 90X max) Monochrome and color still images Video with polarizer Commercial software compatibility with Windows 7, 8 and 10 USB 2.0 port connected to the computer, not instrument
Software	TRIOS software with method segments that allow for triggering the camera to take images and/or video with accurate image-time superposition Image acquisition rate of 15 frames/sec Images easily exported from data file within TRIOS

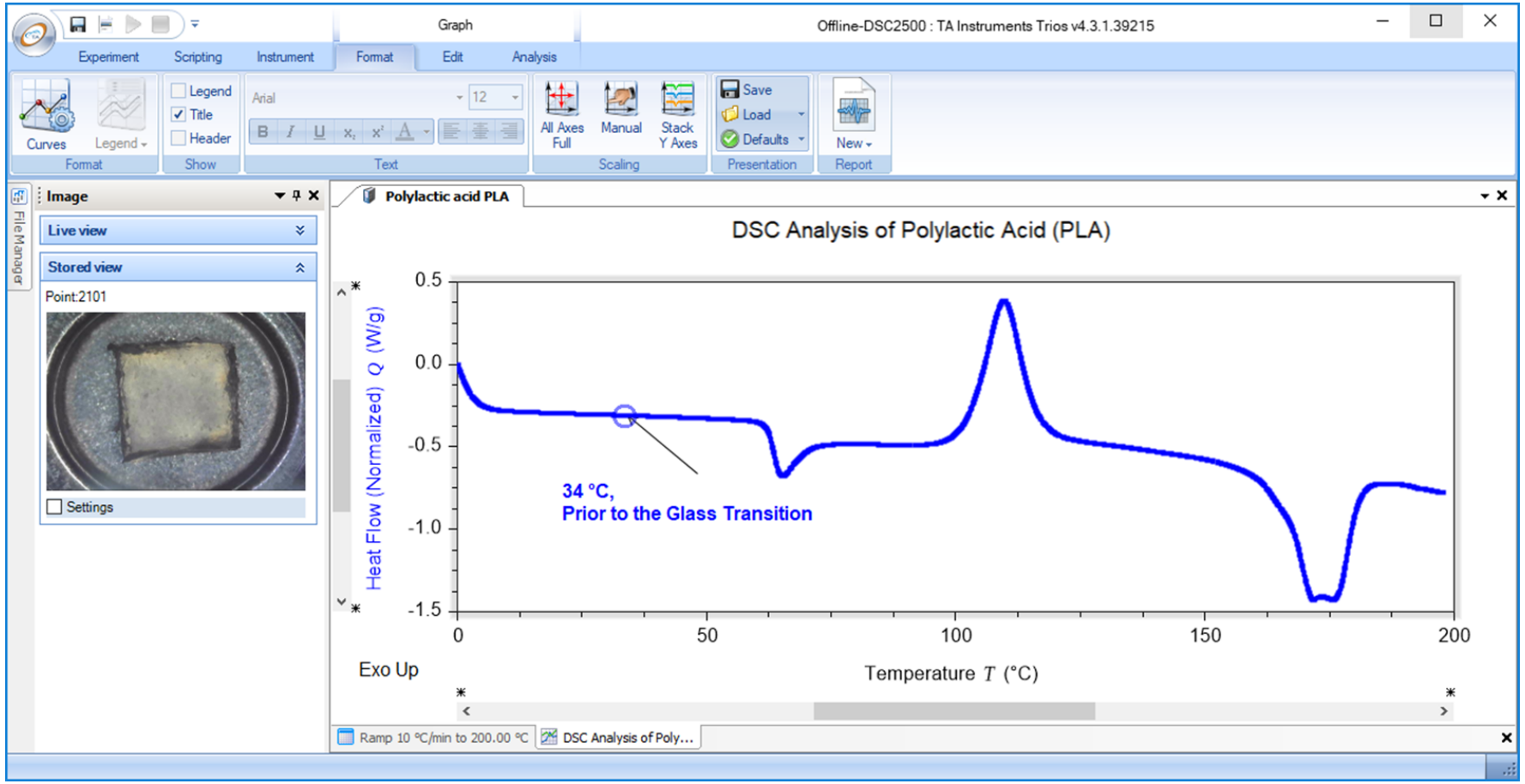
- DSC performed with the microscope accessory has several applications that may prove insightful to better understanding materials' properties and behaviors. It allows the scientist to capture images of:
- crystallization and melt transitions
- flow of materials above the glass transition and melting point
- volumetric, dimensional changes associated with a phase transition, evaporation and sublimation
- visual observations of coloration and other deviations in appearance
- DSC Microscopy can be utilized by the chemical materials, food, pharmaceutical and inorganic industries.

DSC Microscope Accessory - Indium

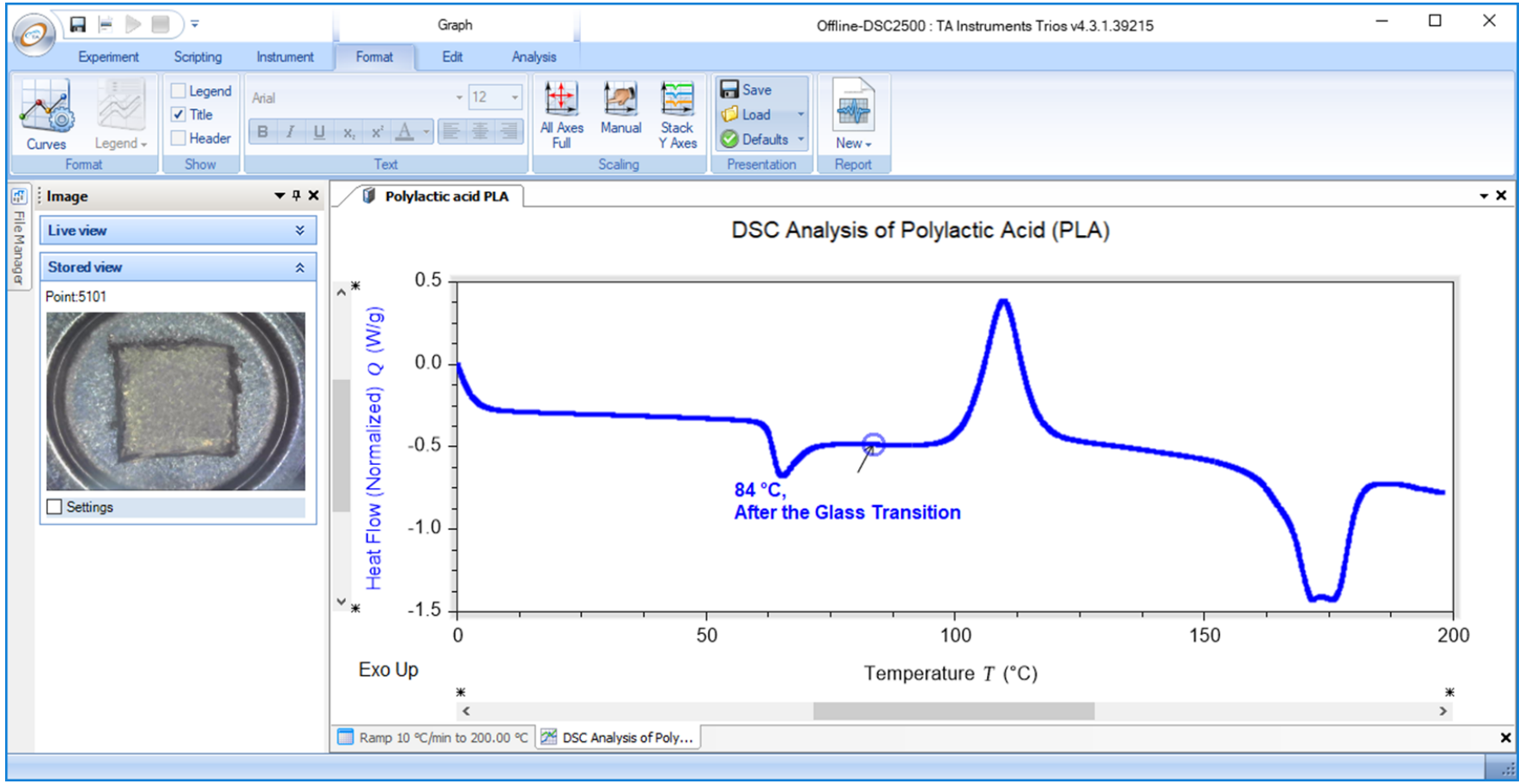




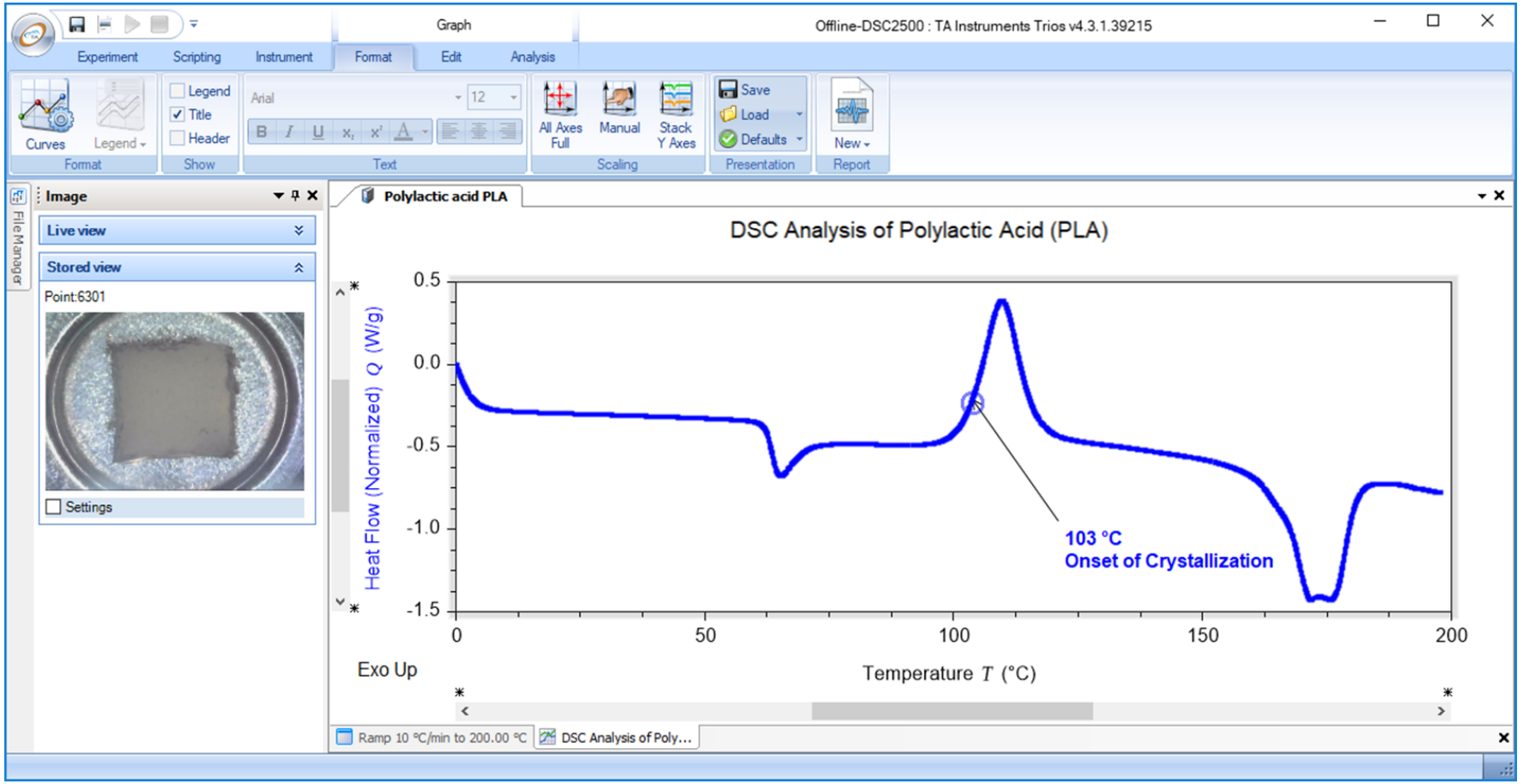
DSC Analysis of Polylactic Acid (PLA): Pre-Tg



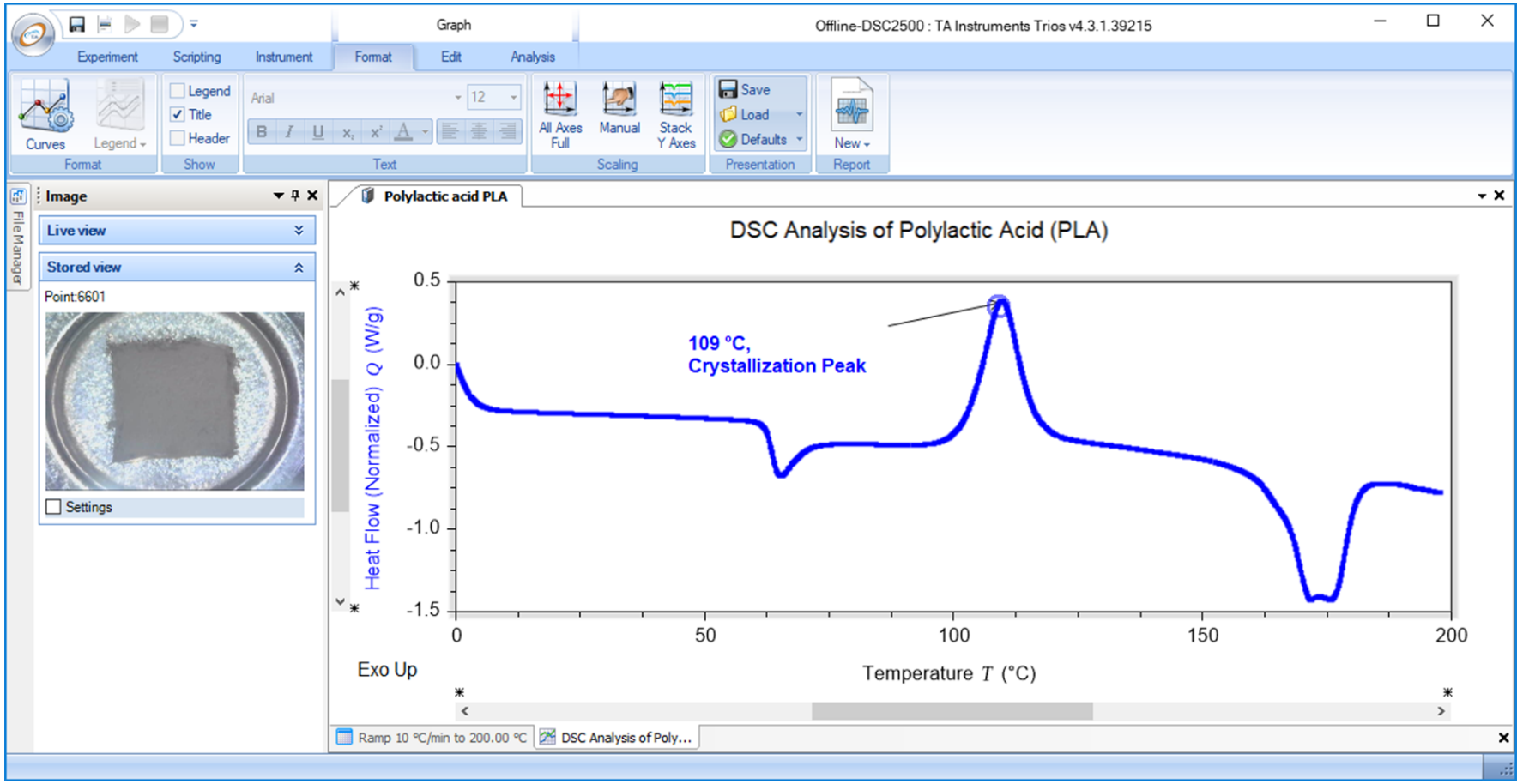
DSC Analysis of Polylactic Acid (PLA): Post-Tg



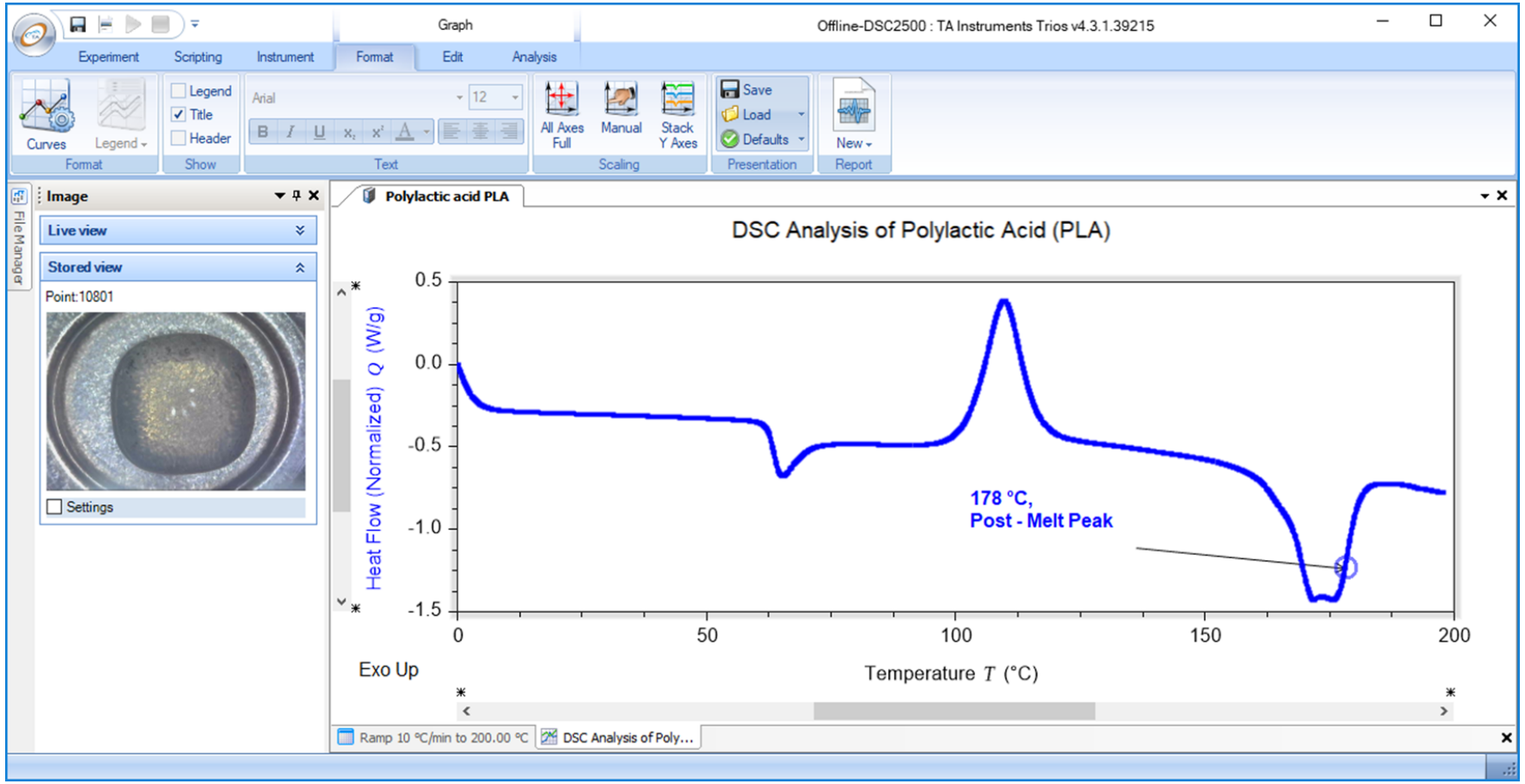
DSC Analysis of Polylactic Acid (PLA): Onset of Crystallization



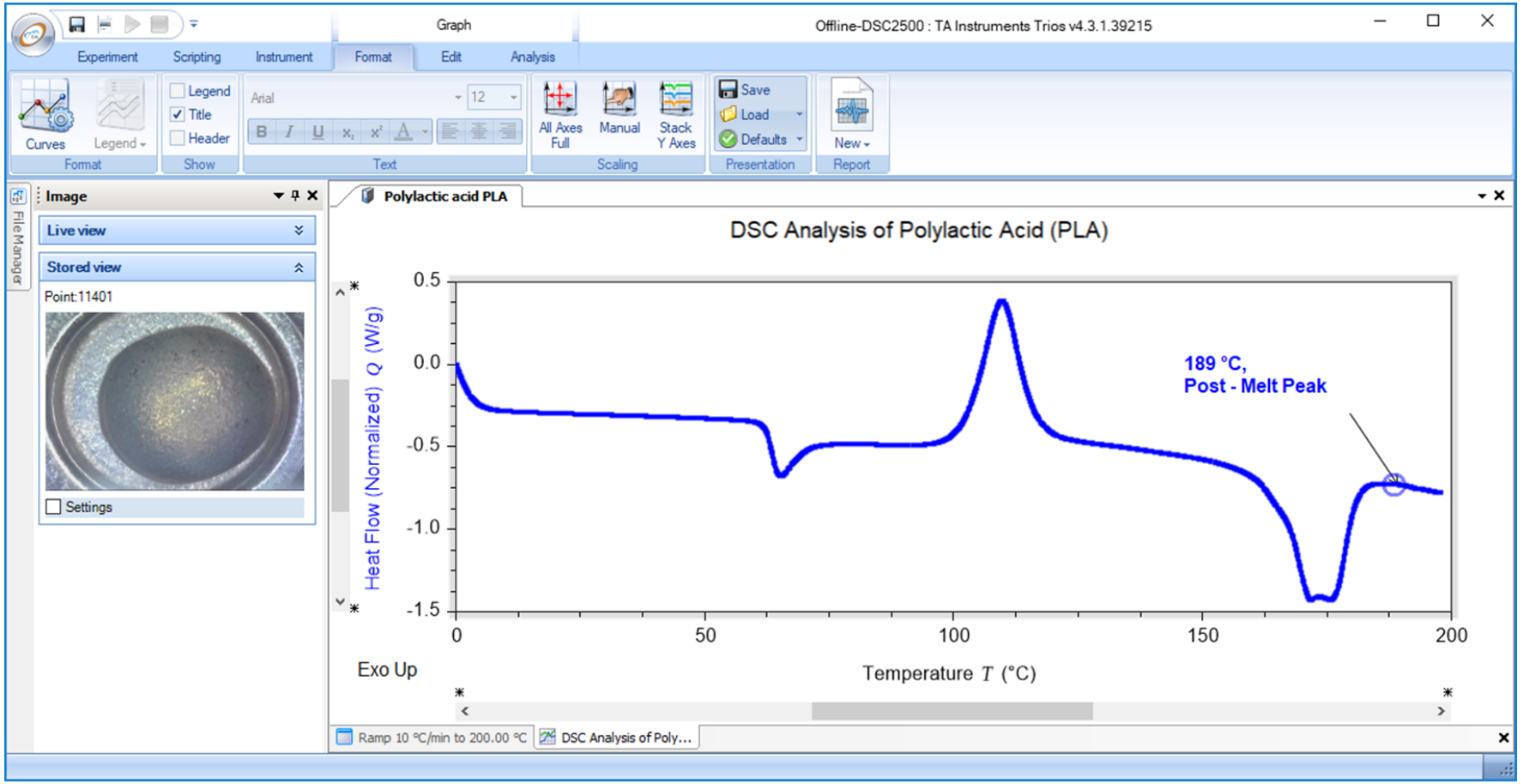
DSC Analysis of Polylactic Acid (PLA): Crystallization Peak



DSC Analysis of Polylactic Acid (PLA): Melting



DSC Analysis of Polylactic Acid (PLA): Post-Melt



Conclusions

- Multiple techniques allow us to obtain a clearer picture of what is happening in a material helping minimise the risk of misinterpreting data or helping explain events occurring during the material processing.
- Increasing that information by with other complimentary techniques (optical microscopy shown here but you could also include DSC-Raman or NIR, TGA-MS etc…) further adds to the picture giving a fuller understanding of the material being characterised.

Questions?

Thank You

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry