Thermal Analysis

Different Techniques

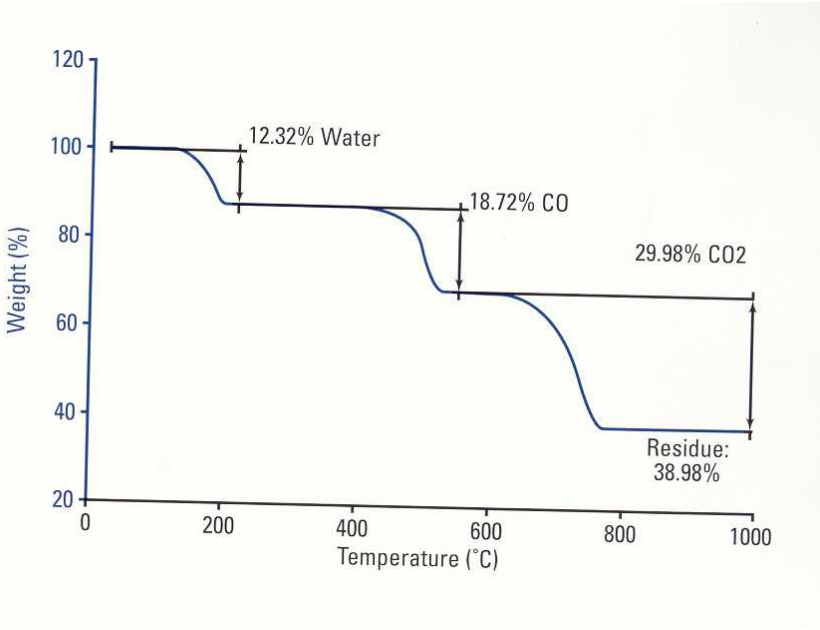
- Thermometric Titration (TT)
  - Heat of mixing
- Thermal Mechanical Analysis (TMA)
  - Thermal Expansion Coefficient
- Dynamic Mechanical Analysis (DMA)
  - Viscoelastic Properties
- Differential Scanning Calorimetric (DSC)
  - Heat flow during Transitions
- Thermal Gravimetric Analysis (TGA)
  - Weight Loss due to decomposition
  - **Derivative Thermogravimetric Analysis (DTG)**
- Differential Thermal Analysis (DTA)
  - Heat of Transitions
- Temperature Programmed Desorption (TPD)
  - Temperature at which gas is desorbed from (catalyst) surface
  - **Emission gas Thermoanalysis (EGT)**

Basic Principle

- Sample is heated at a constant heating rate
- Sample's Property Measured
  - Wt TGA
  - Size TMA
  - Heat Flow DSC
  - Temp DTA
  - Gas evolved TPD

TGA

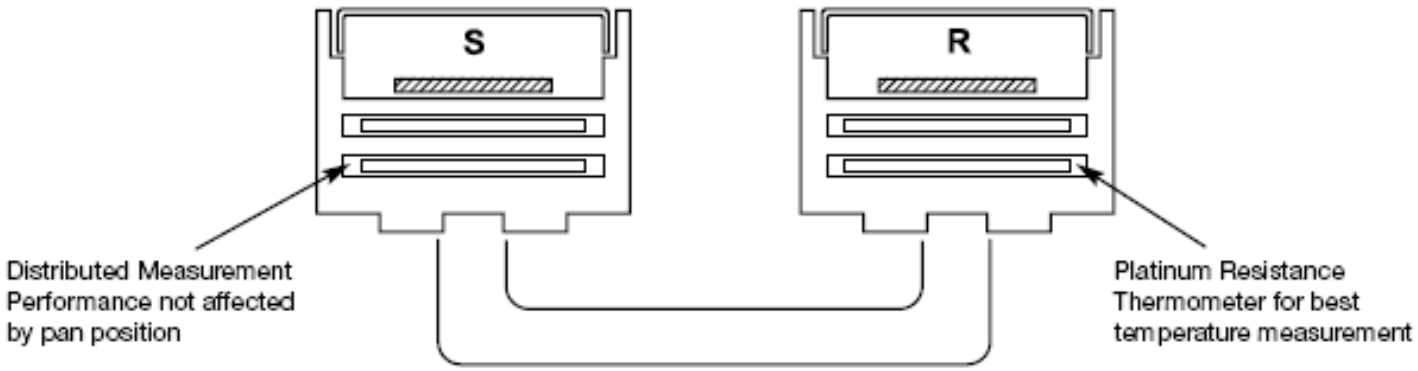
- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate (°C/min)
- Data
  - Weight vs Time
  - Weight vs Temp.
- Differential This Data (DTG)



DSC

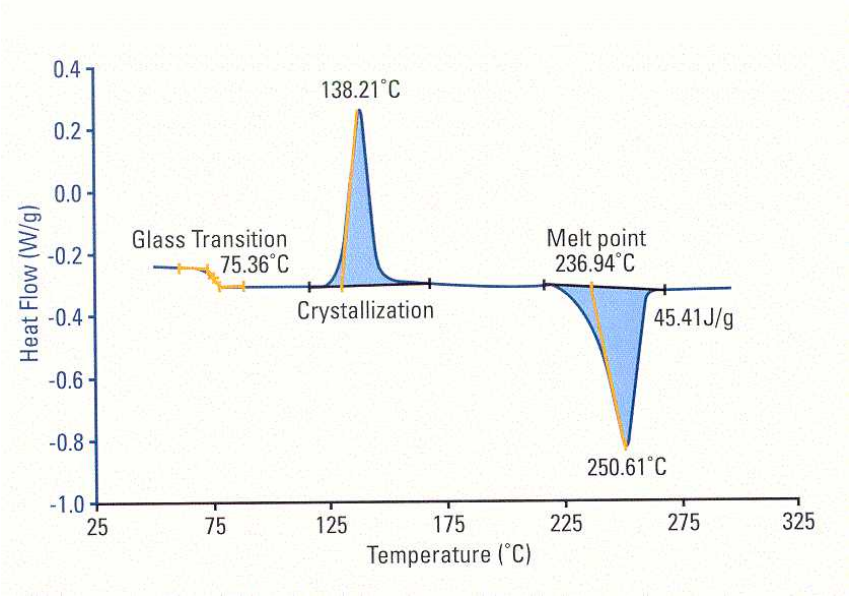
The power-compensation principle

With power-compensation DSC, the sample and the reference material are placed in independent furnaces. When the temperature rises or falls in the sample material, power (energy) is applied to or removed from the calorimeter to compensate for the sample energy. As a result, the system is maintained at a "thermal null" state at all times. The amount of power required to maintain system equilibrium is directly proportional to the energy changes occurring in the sample. No complex heat-flux equations are necessary with a power-compensation DSC because the system directly measures energy flow to and from the sample.



DSC

- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate (°C/min)
- Data
  - Heat flow to sample minus Heat flow to reference vs Time (Temp.)
- Measures heat of crystallization

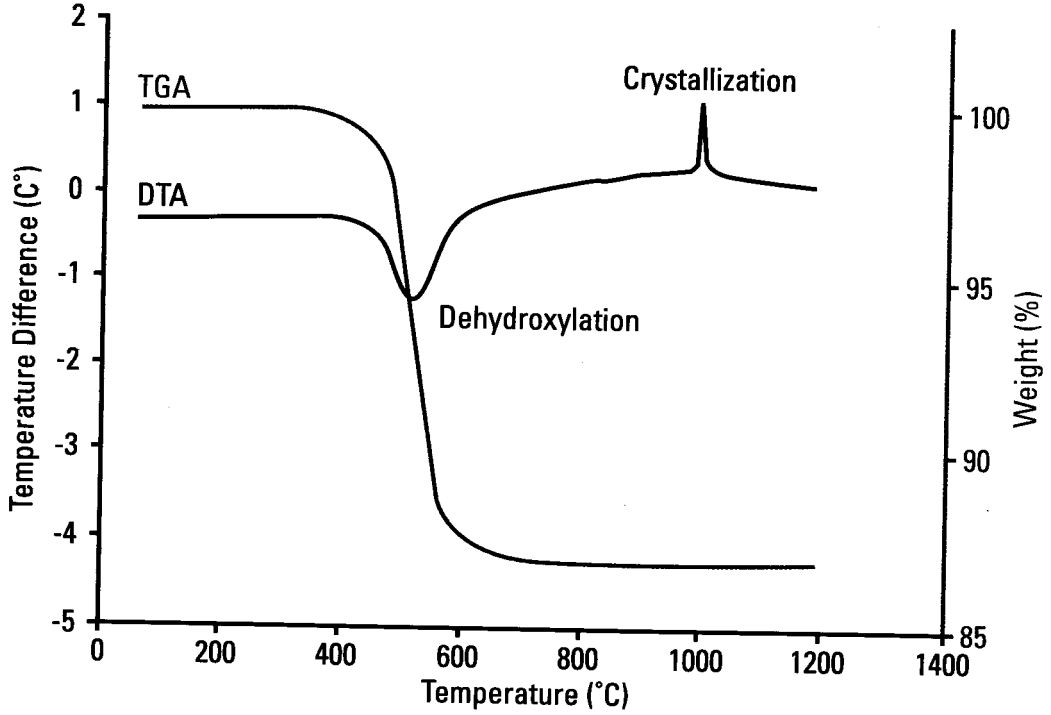


Polymer without weight change in this temperature range

DTA

- Sample and Reference Placed in Heater
- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate (°C/min)
- Data
  - Temp of Sample vs Time (or Temp)
  - Temp of Reference vs Time (or Temp)
  - Reference should be inert, e.g. nothing but latent heat
- Measures
  - Heat of crystallization
  - Glass Transition Temperature

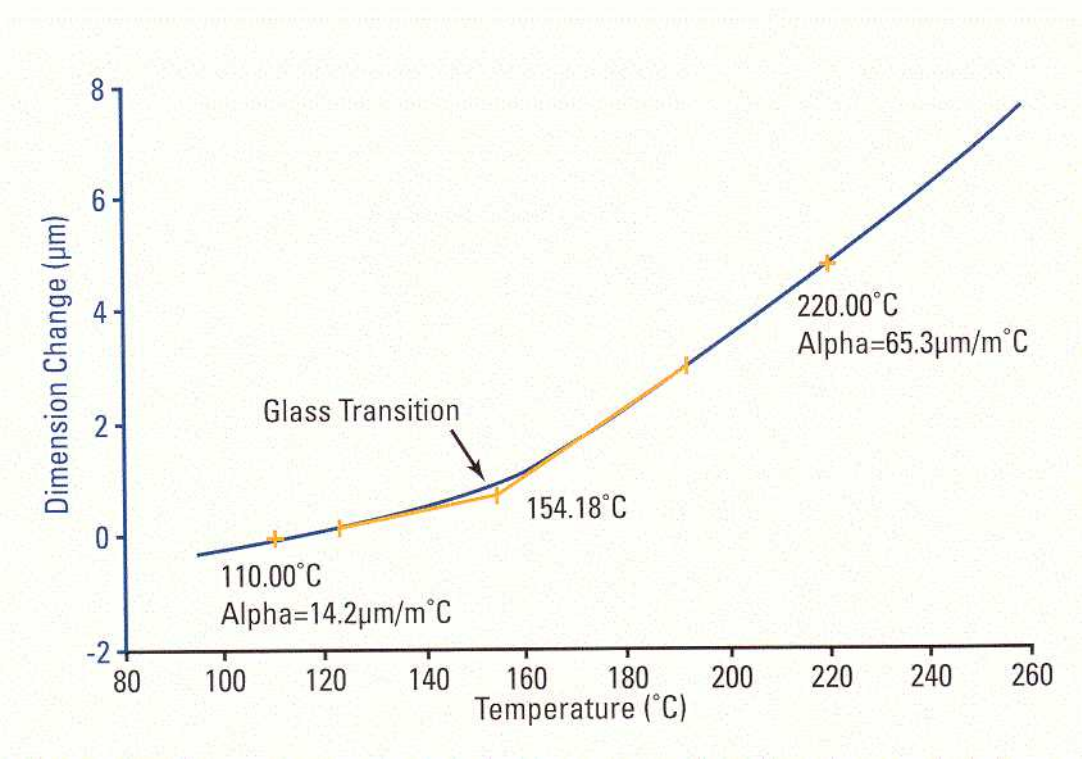
DTA + DTG


TGA
DTA
Crystallization
Dehydroxylation
Temperature Difference (C°)
Weight (%)
Temperature (°C)
2
1
0
-1
-2
-3
-4
-5
100
95
90
85
0
200
400
600
800
1000
1200
1400

TMA

- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate (°C/min)
- Data
  - Size of Sample vs Time (or Temp.)
- Measures
  - Thermal Expansion Coefficient
  - Volume change on crystalization or crystal transformations
  - Sintering
  - Glass Transitions in Polymers

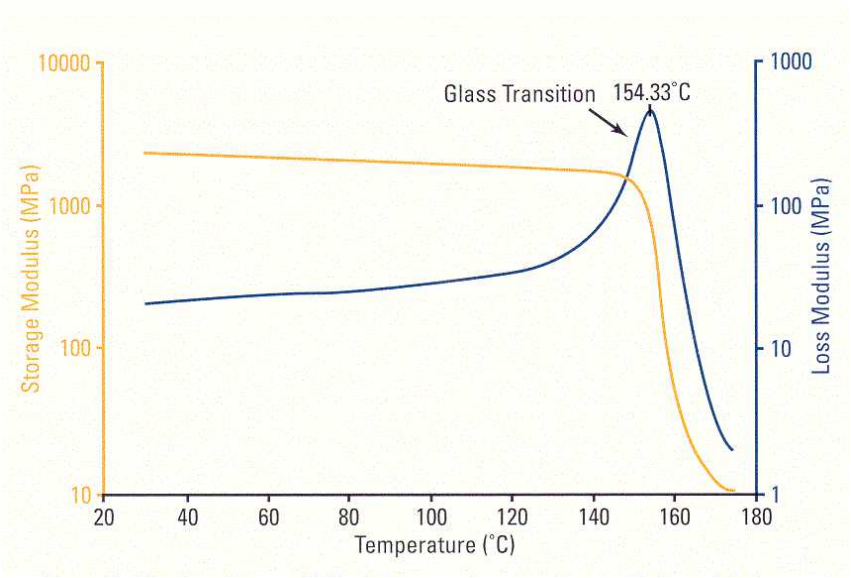
TMA



Polymer with glass transition

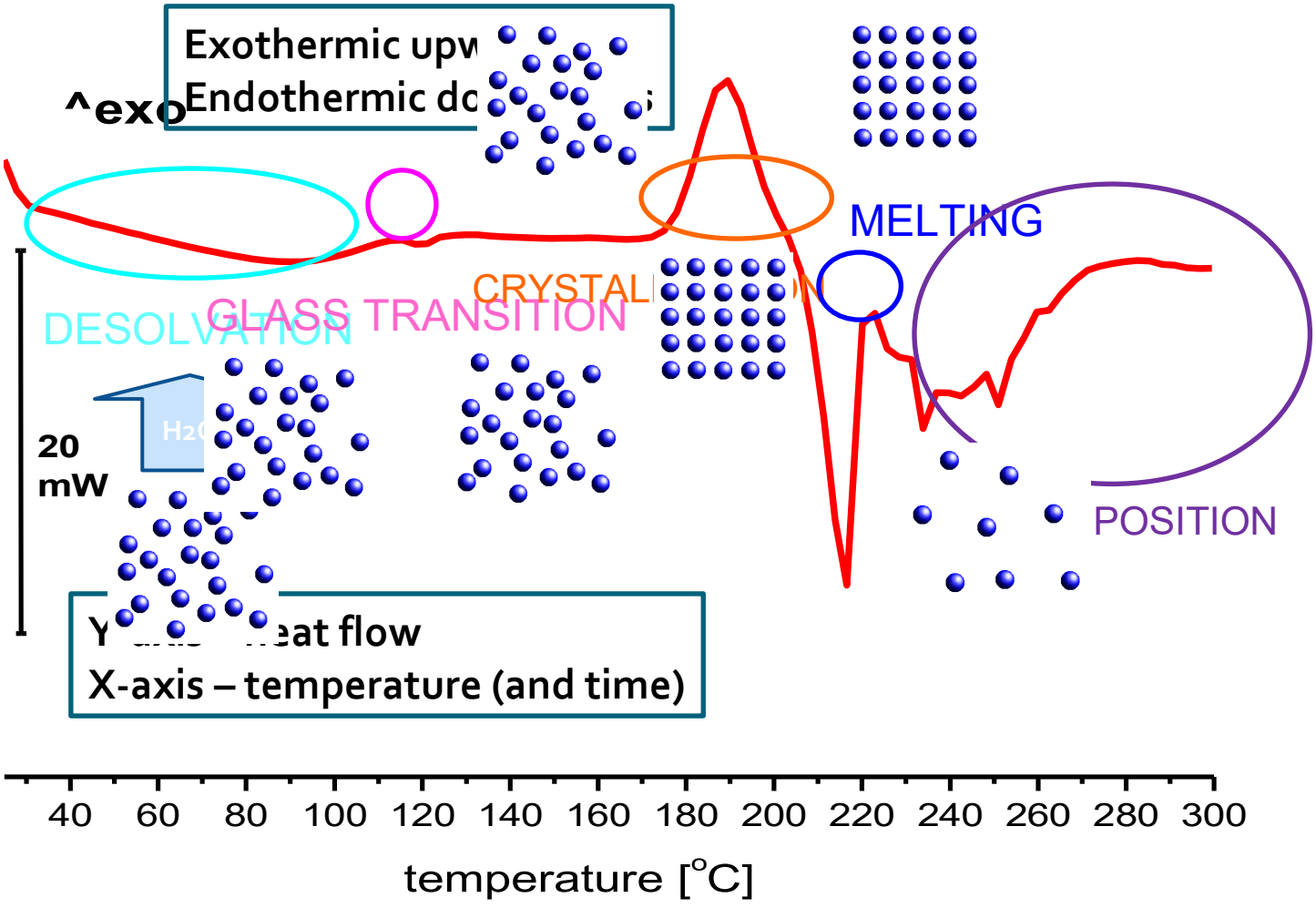
DMA

- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate (°C/min)
- Data
  - Force vs Time (or Temp.)
  - Force delay vs Time (or Temp.)
  - Viscoelastic Properties
    - Storage and Loss Modulus
- Measures
  - Glass Transition
  - Viscoelastic Properties



Polymer with Glass Transition

Typical Features of a DSC Trace

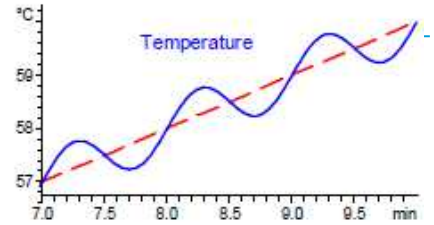


Modulated Temperature DSC (MTDSC)

- This technique uses composite heating profile: determines heat capacity and separates heat flow into the reversible and non-reversible components
- Benefits
  - Increased sensitivity for detecting weak transitions – especially glass transition
  - Separation of complex events into their:
    - **heat capacity** (reversible) e.g. glass transition, melting and
    - **kinetic components** (non-reversible) e.g. evaporation, crystallisation, decomposition
- Disadvantages

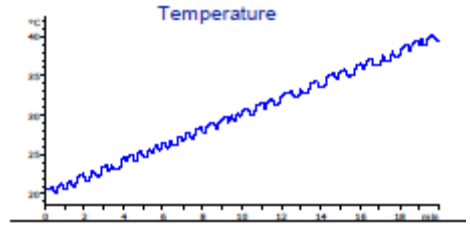
Variants of MTDSC

- **Sinusoidal** modulation (easy, only one frequency only) – TA Instruments

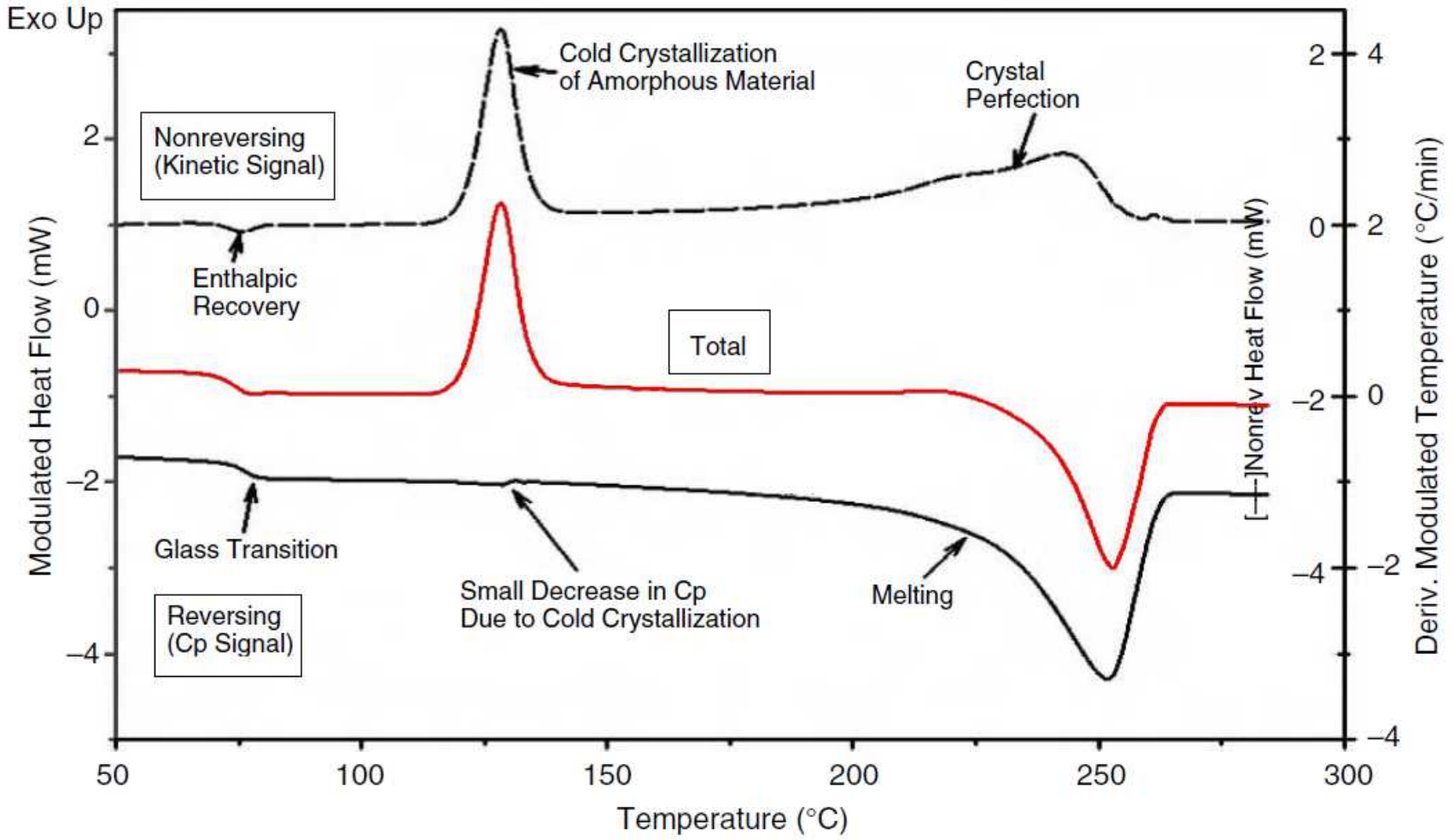


- **Step scan** modulation (easy, precise) – PerkinElmer

- **TOPEM®** modulation (stochastic modulation, complex calculations, but multiple frequency data) – Mettler Toledo



Example of a MTDSC Curve



- Polyethylene terephthalate (PET)

Source: Craig DQM and Reading M
Thermal analysis of pharmaceuticals