Thermochemistry – physico-chemical properties of emulsions of natural compounds

Lecture 4
Differential scanning calorimetry

DSC was:

- developed by E.S. Watson and M.J. O'Neill in 1962,
- introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

The first adiabatic DSC that could be used in biochemistry was developed by P.L. Privalov and D.R. Monaselidze in 1964.

Differential scanning calorimetry (DSC) is a thermoanalytical techniue in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature or time.

the term **DSC** was coined to describe the instrument which measures energy directly and allows precise measurements of heat capacity

Important

the sample and reference are maintained at nearly the same **T** throughout the experiment

Generally,

- the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time,
- the reference sample should have a well-defined heat capacity over the range of temperature to be scanned

DSC applications

Heat of Fusion / Crystallization /
Melting Point / Glass Transition
by DSC (Differential Scanning Calorimeter)

phase transition parameters

Tg = Glass Transition Temperature = Temperature (°C) at which an amorphous polymer or an amorphous part of a crystalline polymer goes from a hard brittle state to a soft rubbery state.

Tm = melting point = Temperature (°C) at which a crystalline polymer melts.

ΔHm = the amount of energy (joules/gram) which a sample absorbs while melting.

Tc = crystallization point = Temperature at which a polymer crystallizes upon heating or cooling.

ΔHc = the amount of energy (joules/gram) a sample releases while crystallizing.

moreover to study: chemical reactions; oxidation and oxidative stability,
drug analysis,
purity analysis,
in general chemical analysis

DSC - detection of phase transitions

- the basic principle of DSC is that when the sample undergoes a physical transformation (phase transition) more or less heat will need to flow to it than the reference to maintain both at the same temperature,
- process is classified as exothermic or endothermic depending on whether less or more heat must flow to the sample comparing to the reference,

Example:
Why solid sample melting to liquid requires more heat flowing to the sample to increase its temperature to the same value as the reference?

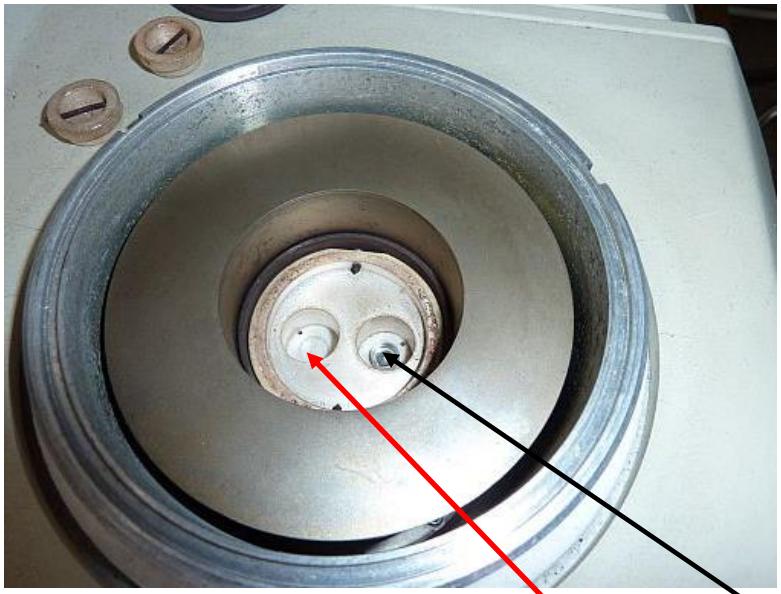
heat absorption by the sample as it undergoes the endo- phase transition solid → liquid

liquid → solid phase transition is exothermic ⟹ less heat is required to rise the same T

- the difference in heat flow between the sample and reference is detected, and differential scanning calorimeters are able to measure the amount of heat absorbed or released during phase transitions,

- DSC involve to observe more subtle physical changes: glass transitions, evaluation sample purity (polymers)

DSC head view

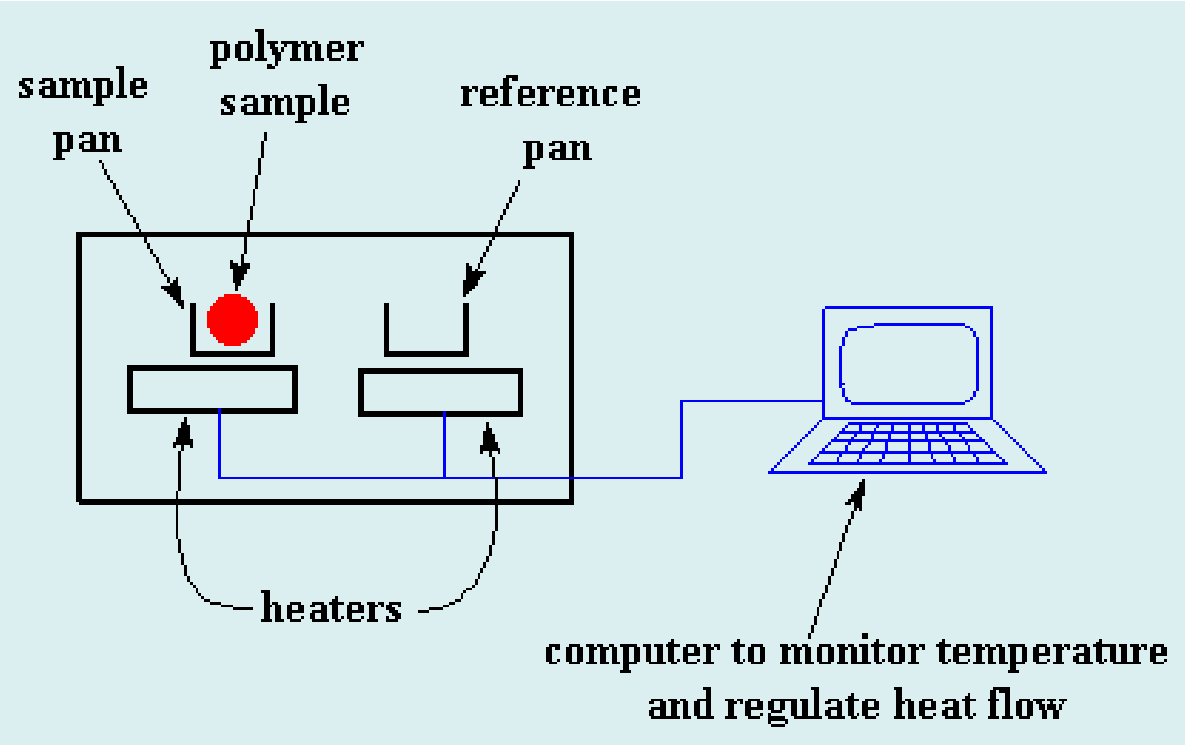


the **DSC head** contains equivalent **sample** and **reference** compartments located adjacent to each other

sample compartment contains an encapsulated sample of 10÷15mg for testing

reference compartment contains an empty aluminum pan and cover equivalent to those used to encapsulate a test sample

DSC system


sample
pan
polymer
sample
reference
pan
heaters
computer to monitor temperature
and regulate heat flow

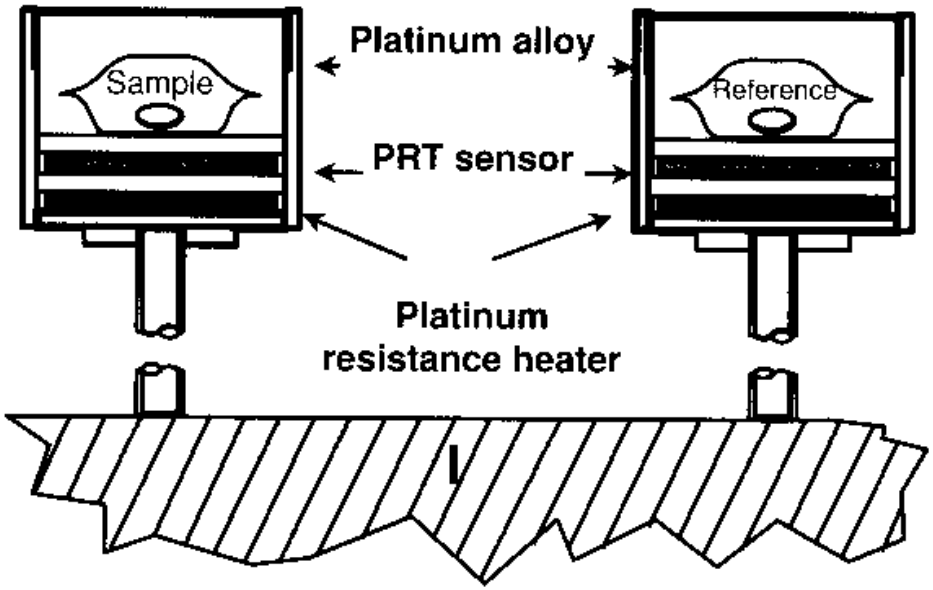
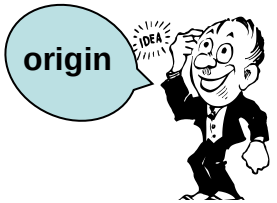


Figure 1.25 Diagram of a power compensation DSC. In this system, both the sample and reference furnaces are heated at a programmed heating/cooling rate. In order to maintain this rate when transitions occur in the sample, a power compensation circuit increases or reduces power to either furnace as required in order to maintain the heating rate. The power compensation circuit therefore reflects the energy changes occurring in the sample and is presented on the screen as a function of temperature or time. This technique measures energy changes directly.

„Principles and applications of thermal analysis" page 47

Measurement procedure



- the sample is weighted and encapsulated in an aluminum/platinum pan,
- the sample weight: of 10 to 15mg
- the sample is heated at a controlled rate and a plot of heat flow versus T/time is registered, as the result a thermal scan is obtained

heating rates: 10^{o}C/min for melting points (T_m) measurement,
20^{o}C/min for glass transition (T_g) investigations

depending upon the sample material type a thermal scan can provide: T_g, T_m, ΔH_m and ΔH_c

DSC experiment results

- the curve of heat flux versus temperature or time is recorded,
- two different conventions: positive or negative peak for exothermic reaction in the sample depend on the kind of technology used in the experiment,
- the curve can be used to calculate enthalpies of transitions (this is done by integrating the peak corresponding to a given transition) using the following equation:

$$\Delta H = K * A$$

the area under the curve

enthalpy of transition

the calorimetric constant

K is characteristic for a given instrument

Glass transition

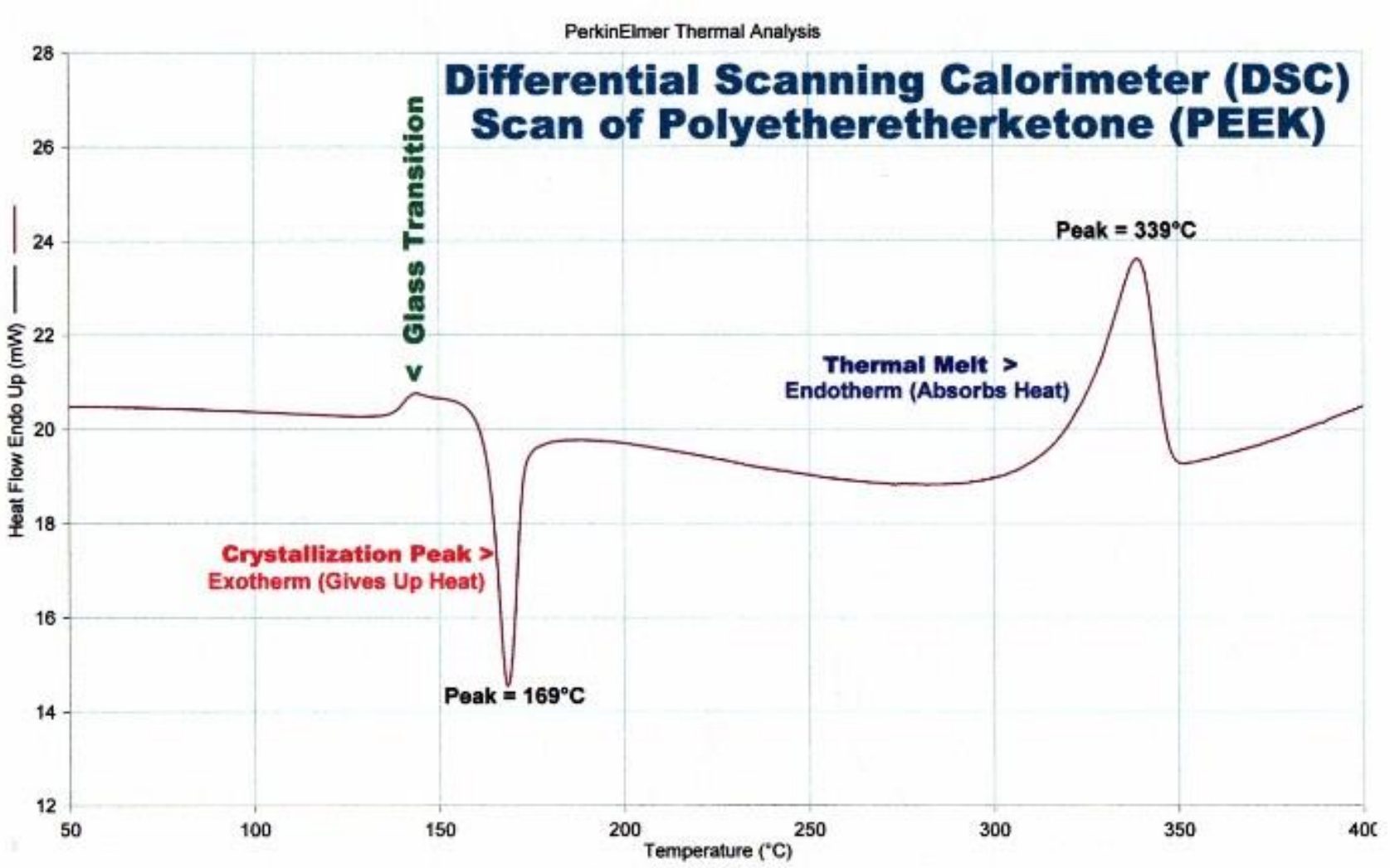
physical process occurring as T of an amorphous solid material is increase,
at some T point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This T is T_c,

- glass transition is an exothermic process,
- melting process is endothermic,
- crystallization is an exothermic process

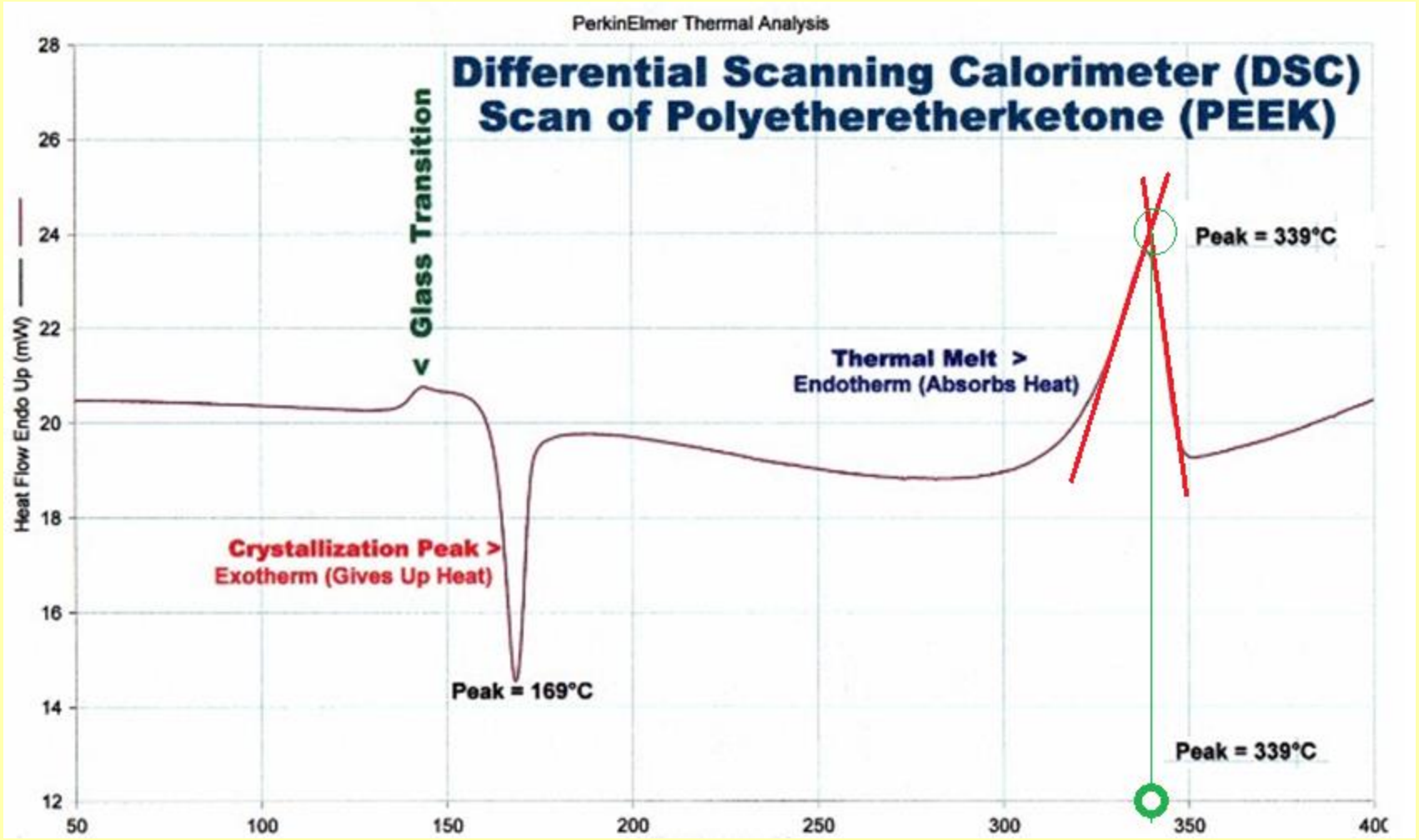
} phase diagram

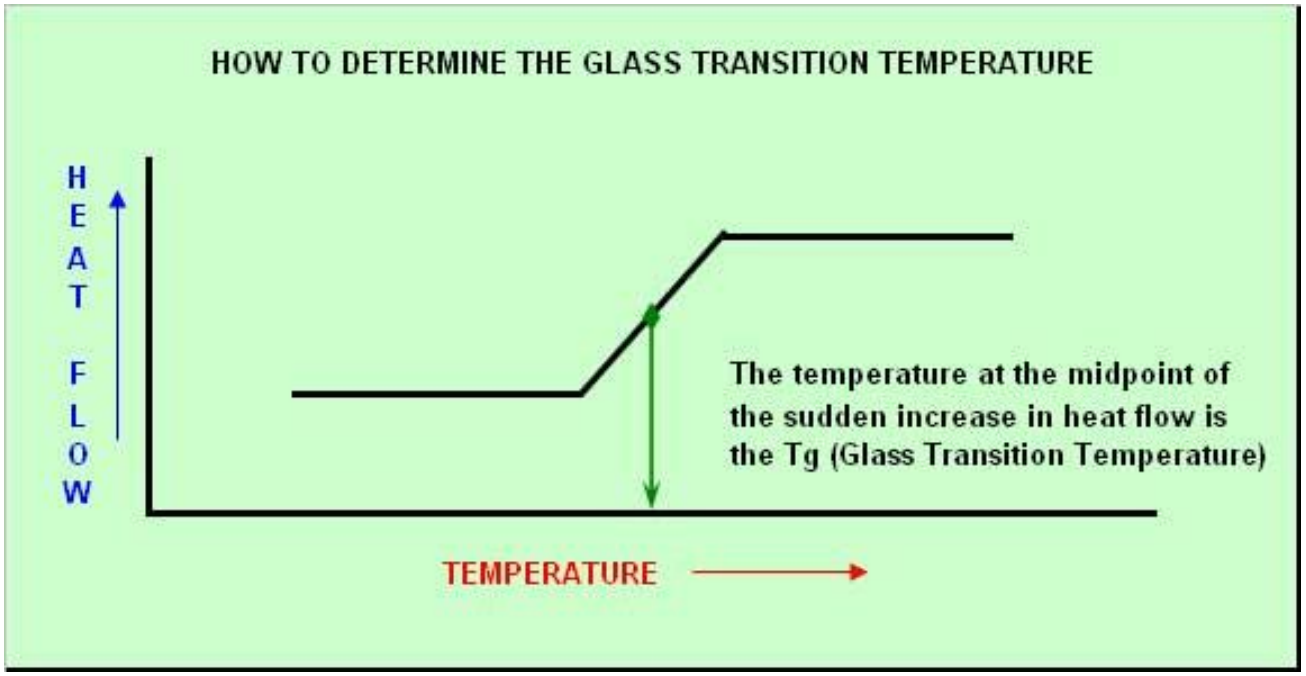
Typical DSC Thermal Scan of a PEEK Material

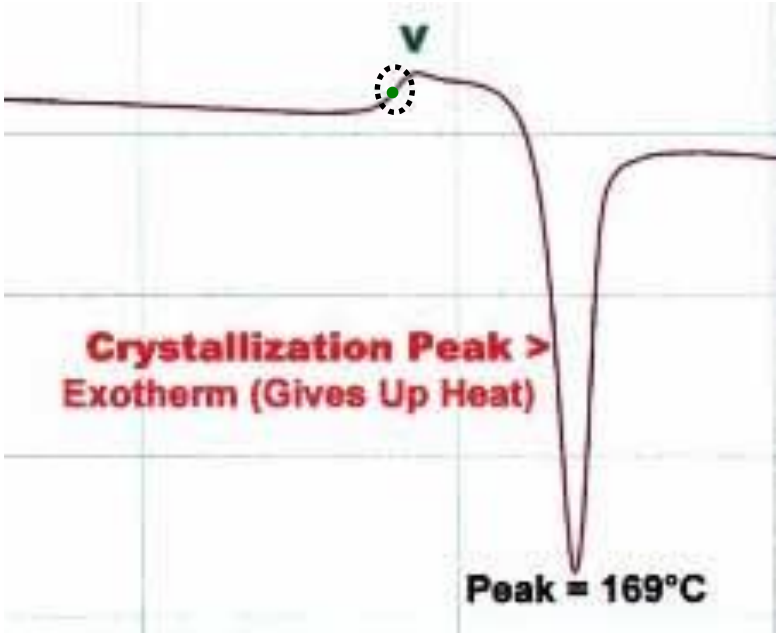
T_g a T_c and a T_m

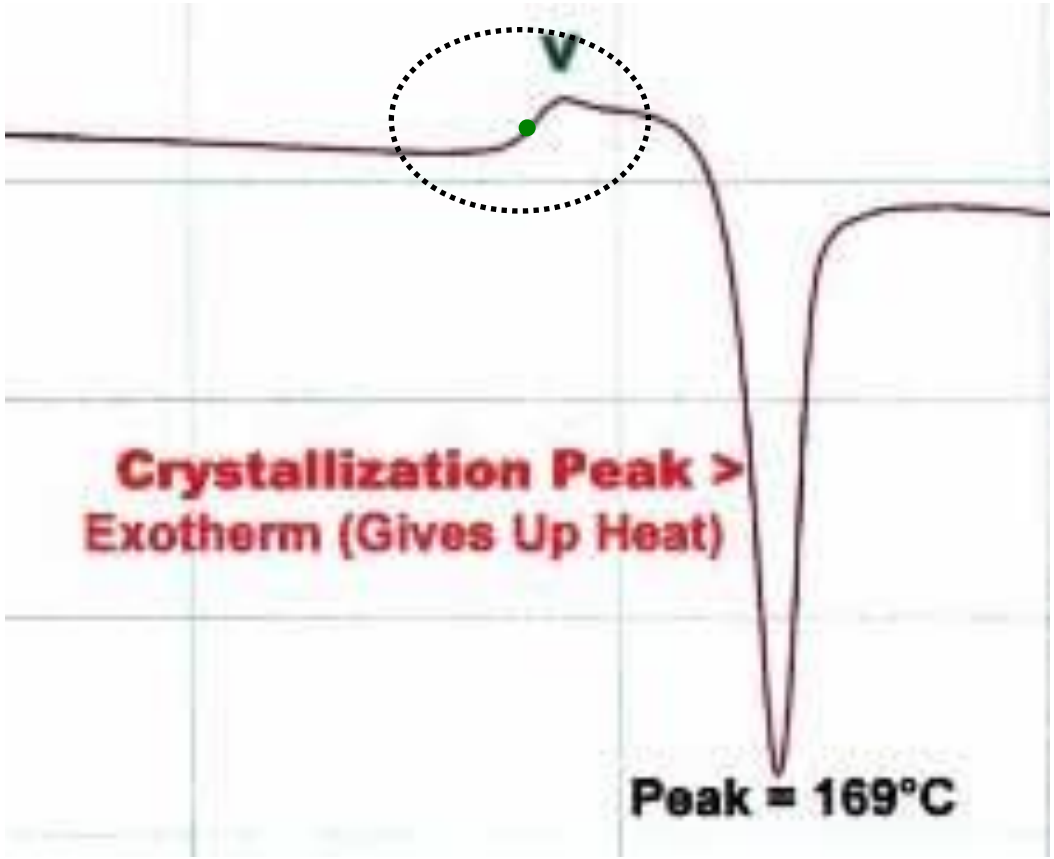


the sudden increase in heat flow is caused by the polymer having a higher heat capacity above the T_g than below it


PerkinElmer Thermal Analysis
Differential Scanning Calorimeter (DSC)
Scan of Polyetheretherketone (PEEK)
Heat Flow Endo Up (mW)
28
26
24
22
20
18
16
14
12
50
100
150
200
250
300
350
400
Glass Transition
Crystallization Peak >
Exotherm (Gives Up Heat)
Peak = 169°C
Thermal Melt >
Endotherm (Absorbs Heat)
Peak = 339°C
Peak = 339°C


HOW TO DETERMINE THE GLASS TRANSITION TEMPERATURE
HEAT FLOW
The temperature at the midpoint of the sudden increase in heat flow is the Tg (Glass Transition Temperature)
TEMPERATURE


V
Crystallization Peak >
Exotherm (Gives Up Heat)
Peak = 169°C


V
Crystallization Peak >
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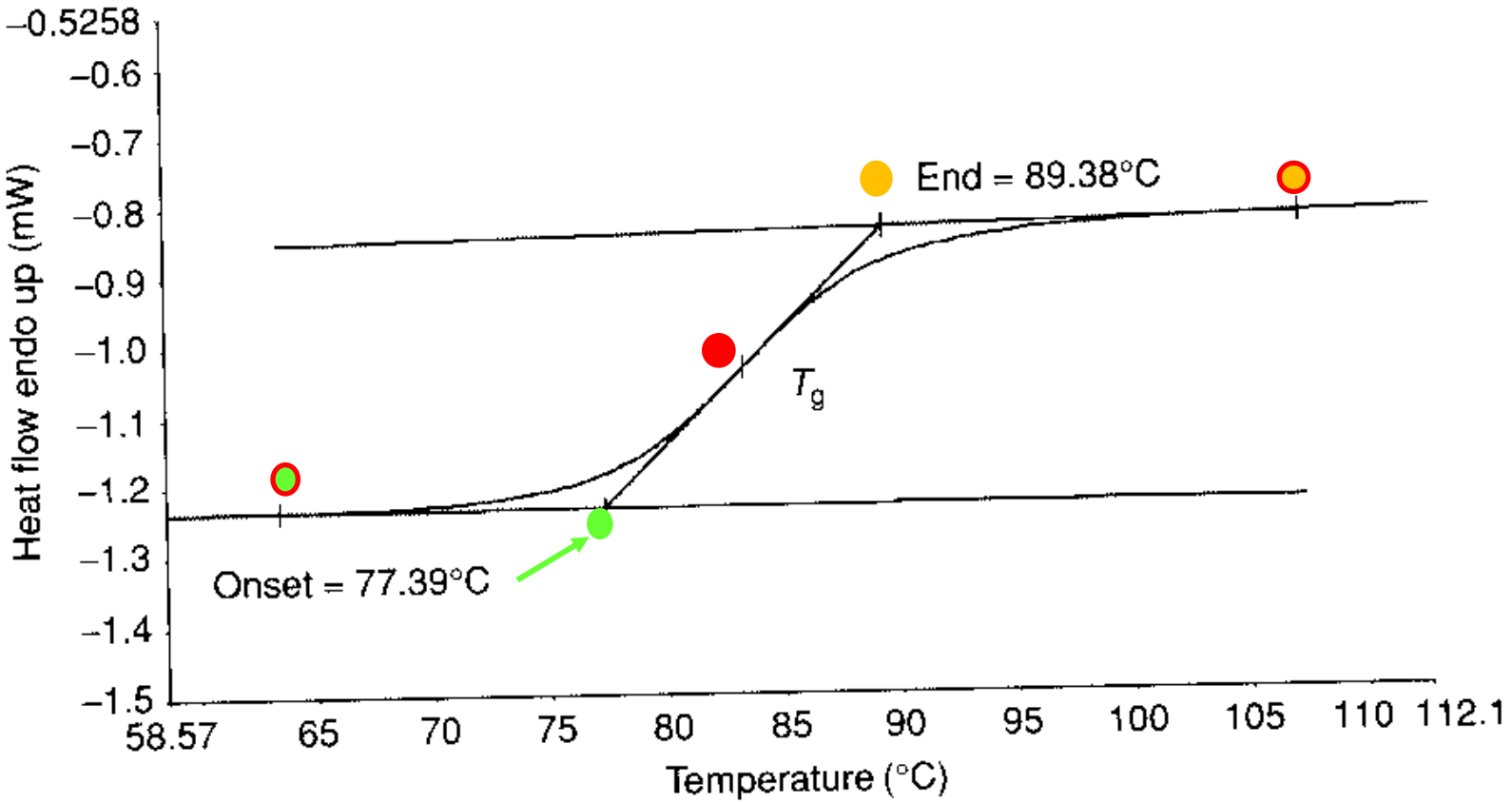
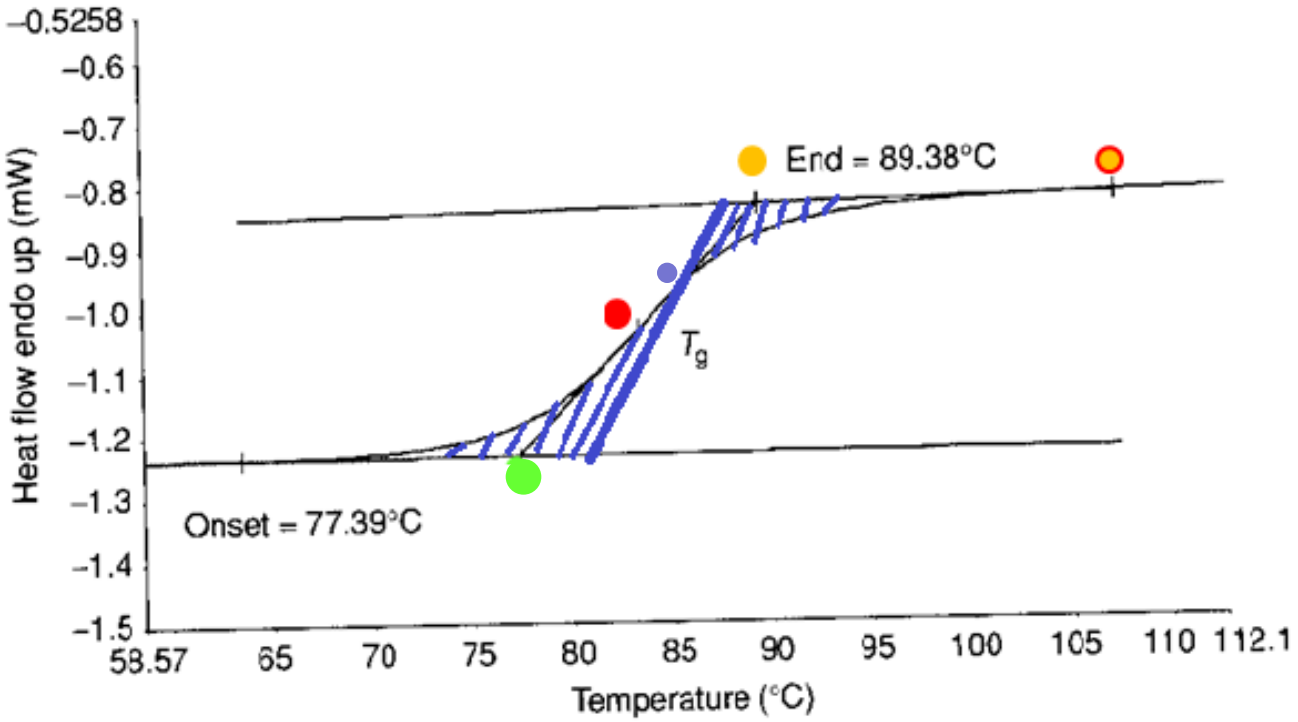


T_g calculation. The onset, midpoint and endpoint.

„Principles and applications of thermal analysis" page 26

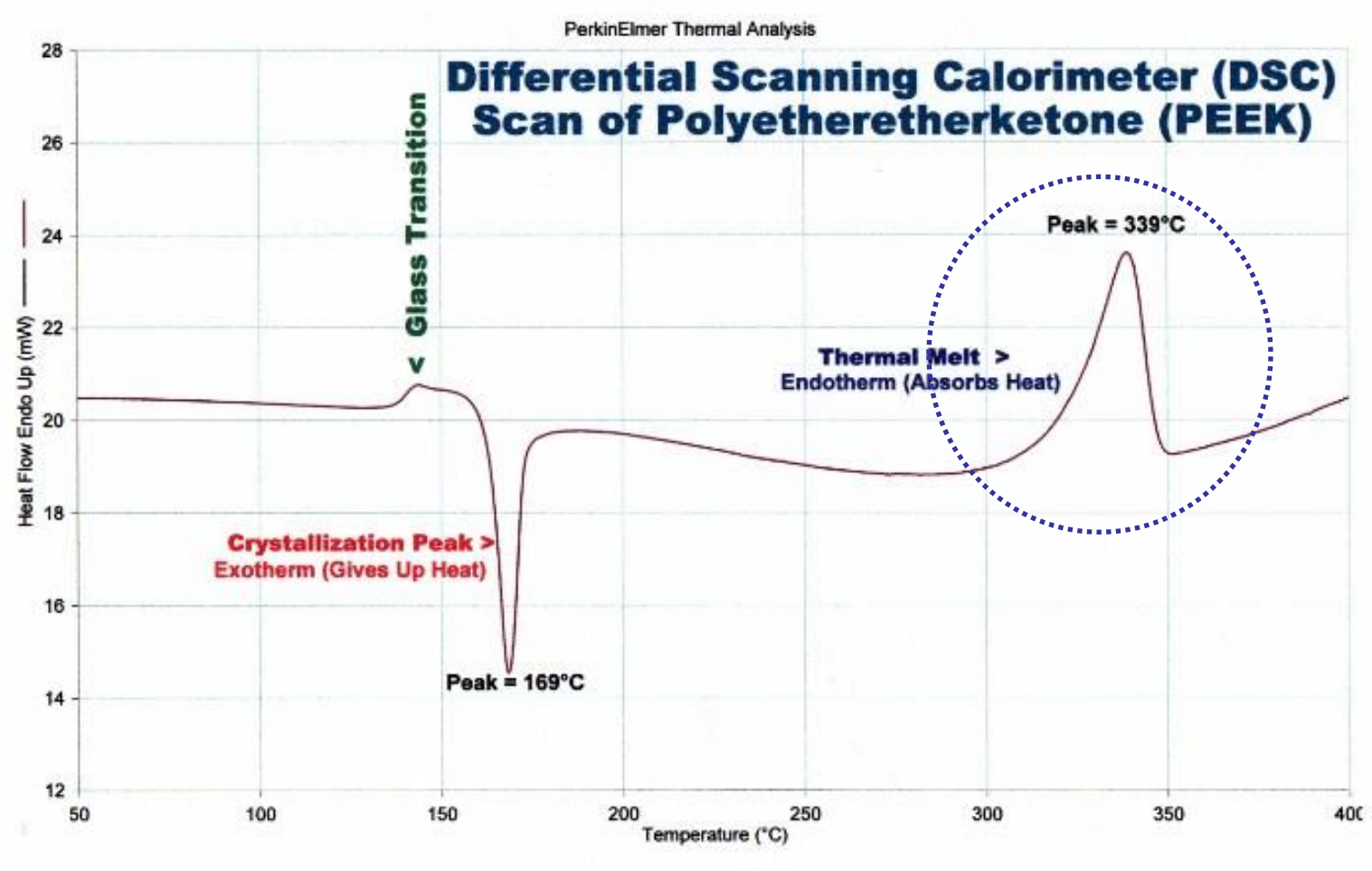


T_g calculation. The onset, midpoint and endpoint.

„Principles and applications of thermal analysis" page 26

16

T_m is defined as the temperature at which a crystalline polymer or material melts



Melting Points (T_m) coupled with an FTIR Analysis is useful for further sample identification

T_m combined with an FTIR analysis, can help differentiate between such materials as:

Nylons (Nylon 6 and Nylon 6/6);

Polyesters (Polybutylene Terephthalate (PBT) and Polyethylene Terephthalate (PET));

Polyethylenes (some high and a low density materials);

or Acetals (copolymer or homopolymer).

the DSC can help to further identify some polymers by determining their melting point:

Polypropylene (Homopolymer or Copolymer)
Nylon (6, 6/6, 10, 12)
Polyethylene (LDPE, MDPE, HDPE)

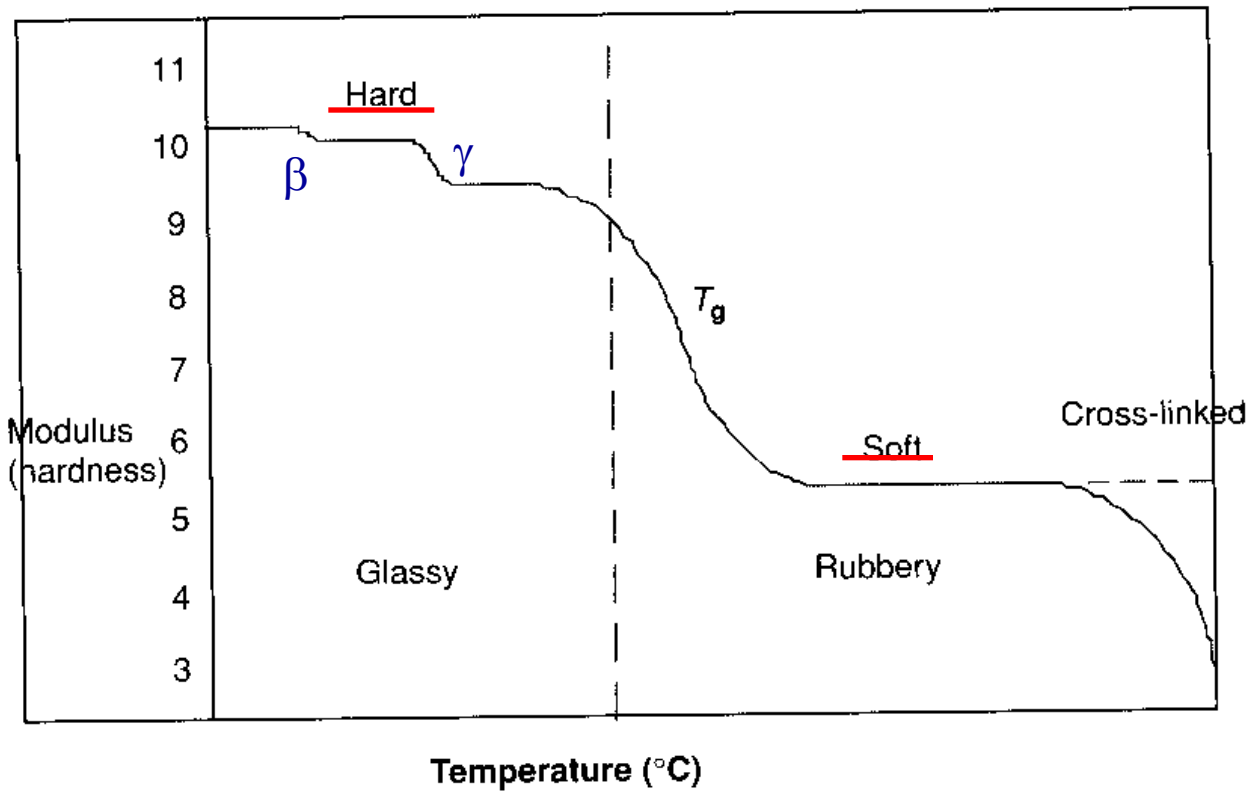


Figure 1.9 Modulus (hardness) of an amorphous polymeric material as a function of temperature showing the dramatic change in hardness that occurs in the glass transition region. Small lower temperature events are termed β- and γ-transitions.

„Principles and applications of thermal analysis" page 23

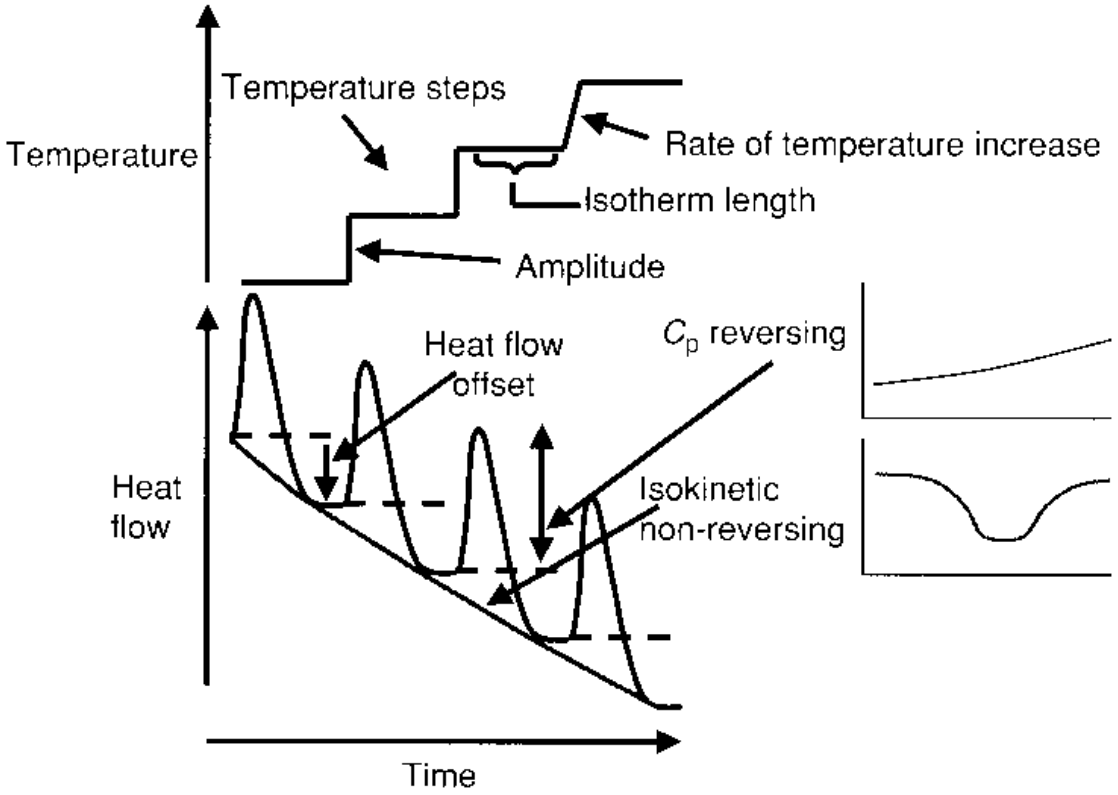


Figure 1.23 A diagram of the temperature profile used in step-based methods and the heat flow signal that results. Heat capacity is calculated either from peak height as in the classical method, or peak area of the heat flow trace. The kinetic response is obtained from the isothermal portion.

„Principles and applications of thermal analysis" page 45