Characterization of Polymers and Soft Materials

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Advanced Materials Characterization Workshop
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ILLINOIS
Materials Research Laboratory
GRAINGER COLLEGE OF ENGINEERING

Center for Excellence in Soft Materials

Thermal Analysis

- Thermogravimetric Analysis – TA Q50 TGA
- TGA-Mass Spectrometry – Netzsch TG309/QMS403 ← **Coming Soon !!**
- Differential Scanning Calorimetry – TA DSC 2500
- Differential Thermal Analysis – Shimadzu DTA-50

Mechanical Analysis

- Dynamic Mechanical Analysis – TA Q800 DMA
- Rheology – TA DHR-3

Nanoparticle Analysis

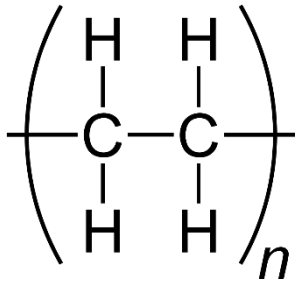
- Malvern Zetasizer Nano ZS
- Malvern NanoSight NS300

Complementary Techniques

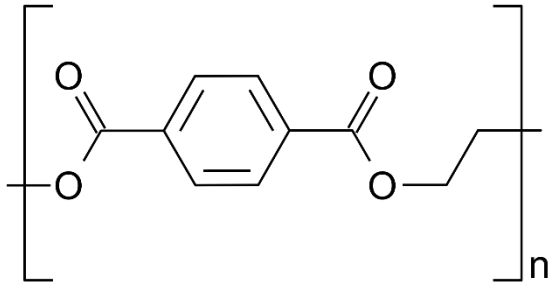
- Gel Permeation Chromatography – Tosoh EcoSEC 8320
- Dielectric Analysis – Novocontrol Concept 47
- Karl Fischer Titration – Metrohm 915 (volumetric) + 917 (coulometric)

What is a Polymer??

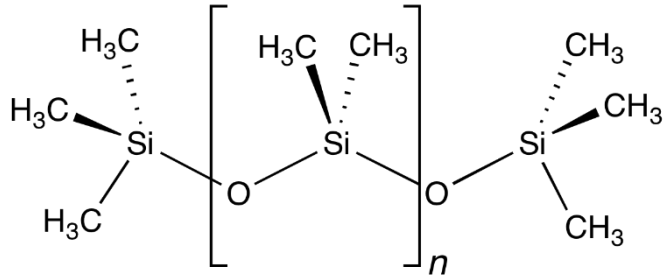
- Comes from the latin words *poly* and *meros* meaning “many parts”
- A polymer is made up of covalently linked molecules called “monomers”
- Monomers can be identical (homopolymer) or different (copolymer, terpolymer, etc.)



Polyethylene



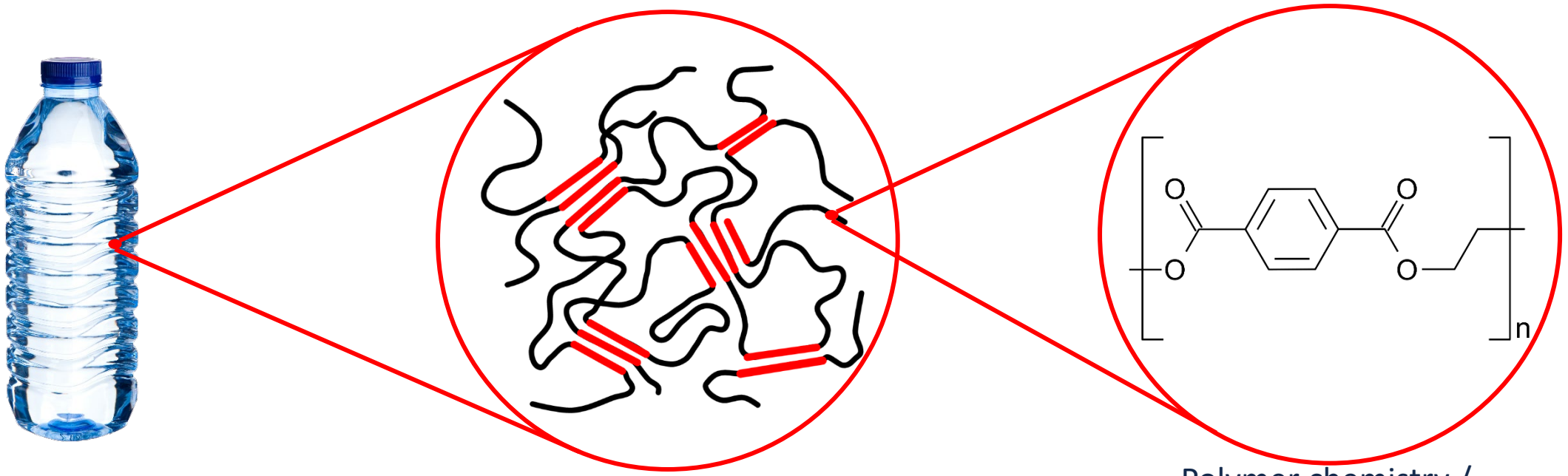
Polyethylene terephthalate



Polydimethylsiloxane

- Many polymers are known best by their trade names or abbreviations (e.g. Kevlar®, Plexiglas®, Mylar®, Teflon®, PVC, ABS, PDMS)

Zoom into Plastics



"Plastic" bottle

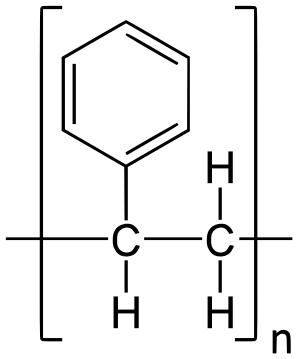
Polymer chains
Structure/behavior

Polymer chemistry /
molecular structure

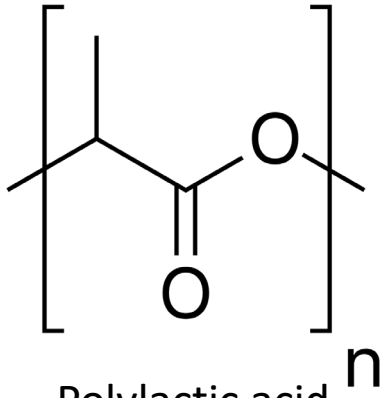
It's important to characterize materials at multiple length scales to fully understand its properties.

Case Study

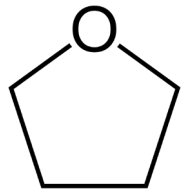
- Polystyrene (PS) – Many uses, cheap
- Polylactic acid (PLA) – Naturally derived, degradable



Polystyrene



Polylactic acid



Tetrahydrofuran (THF)

- Both materials dissolved in THF to make the blend. Solution was drop cast onto a glass slide. Left to dry overnight under vacuum.

Questions…

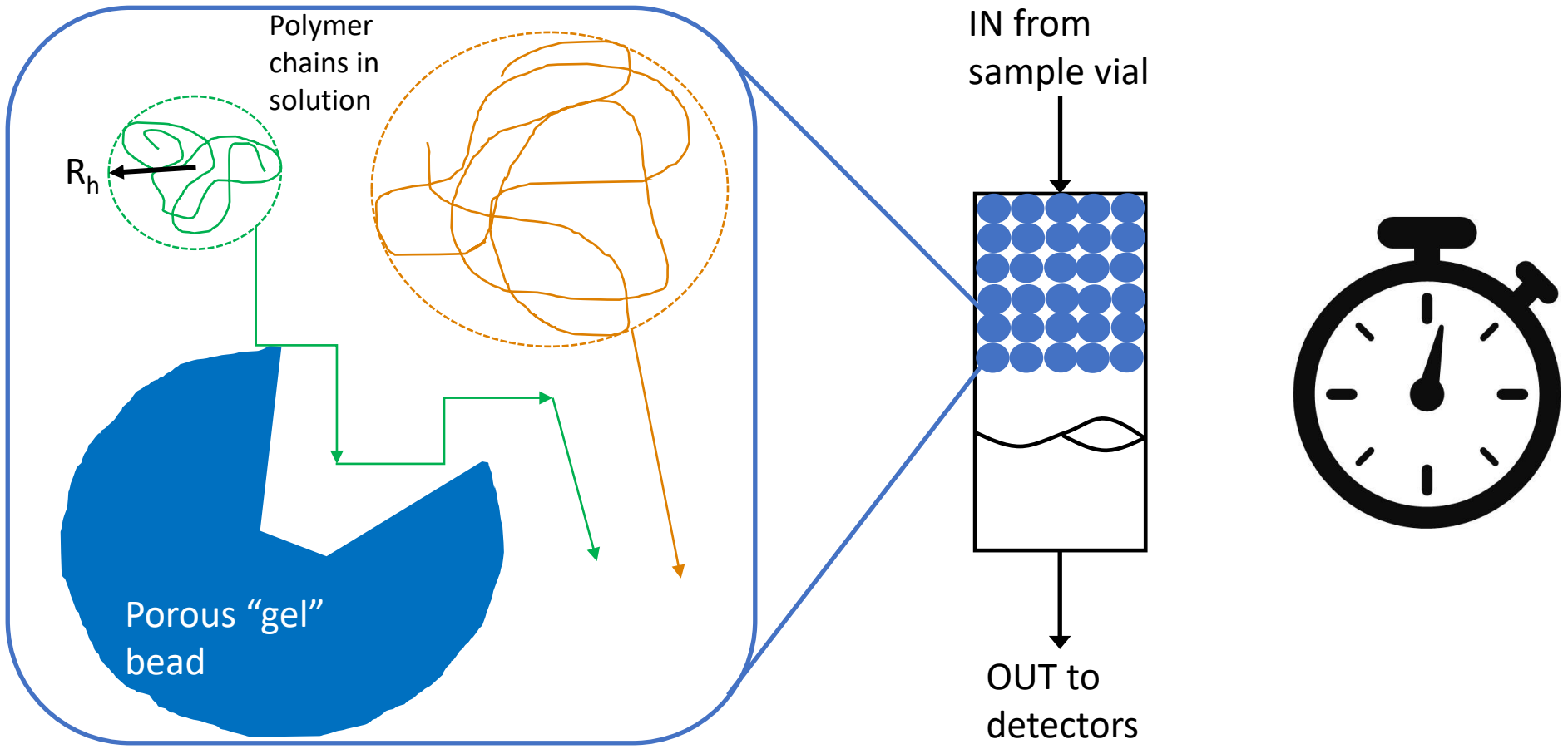
How do you know you made/have a polymer?

You need to measure its molecular weight.

How do you measure polymer molecular weight?

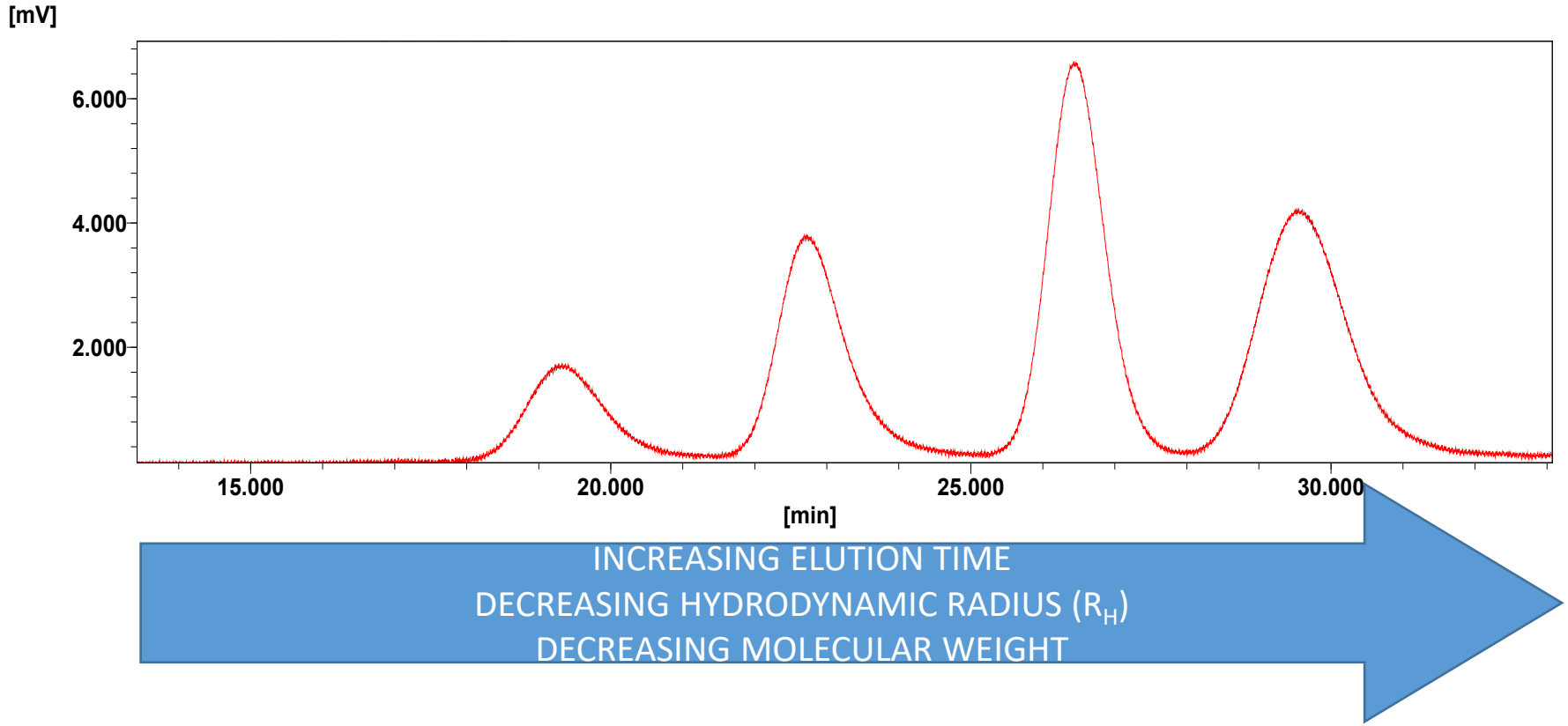
SEC/GPC.

Gel Permeation Chromatography



Gel Permeation Chromatography

- Poly(methyl methacrylate) multi-point calibration standard
- 2mg/mL in Dimethylformamide (DMF)



Gel Permeation Chromatography

Tosoh EcoSEC 8320 with LenS3

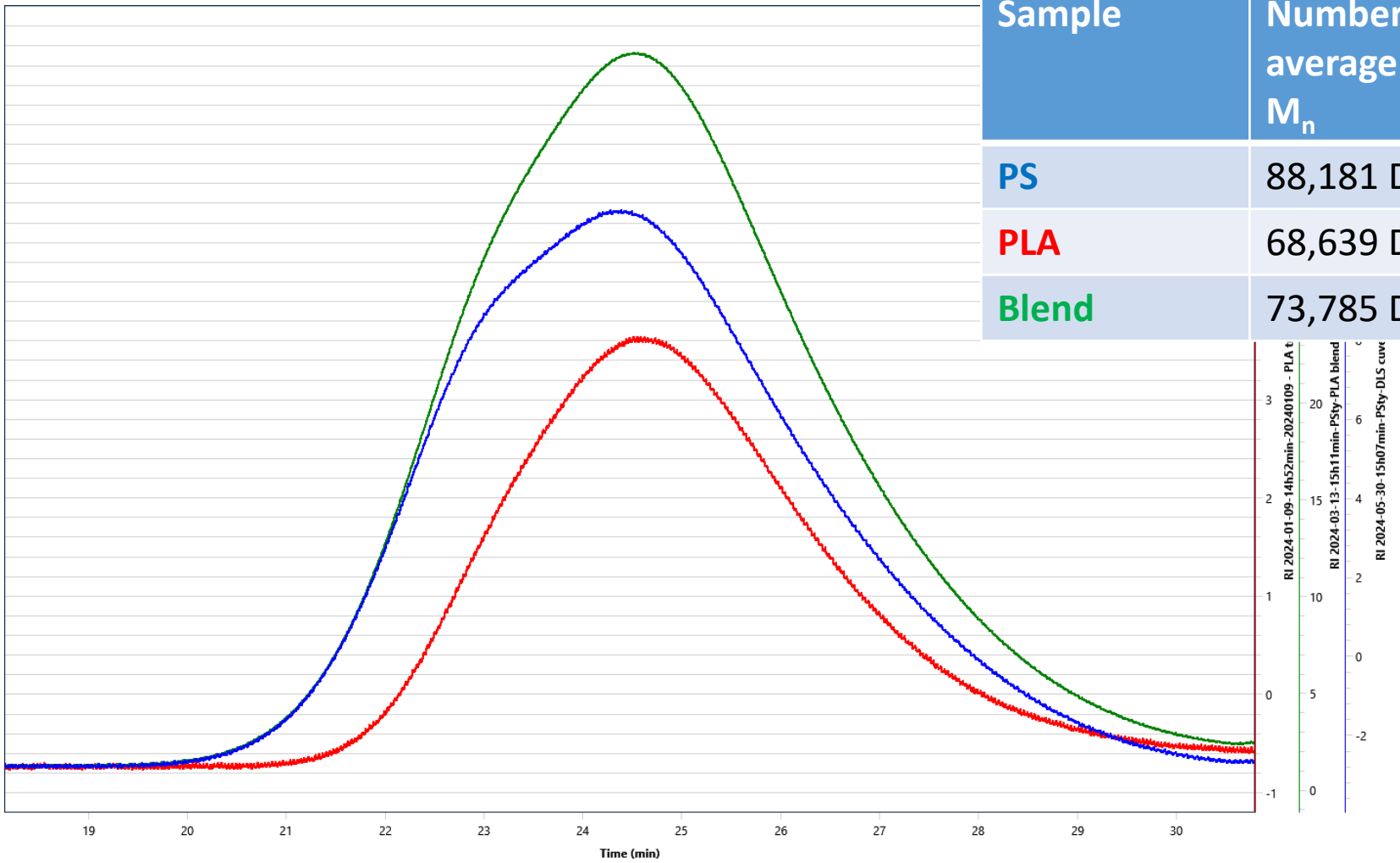
Typical experimental conditions:

- Solvent choice – THF, Chloroform, DMF, DMSO, Water….
- Column materials – Poly(styrene-co-divinylbenzene), Polymethacrylate, Silica
- Detectors – Refractive index (RI), Ultraviolet (UV), Light Scattering (LS), Viscometry
- Sample amount – < 5 mg/mL solution (must be filtered!!)

Important Points:

- Solvent choice is dependent on sample solubility, column tolerance and refractive index (sometimes)
- Column specifications determine MW resolution and range
- Different detectors give slightly different results – choose wisely
- **It's all about the polymer-solvent-instrument combination**

Gel Permeation Chromatography



Sample	Number average MW, M_n	Weight average MW, M_w	Polydispersity index, PDI (M_w/M_n)
PS	88,181 Da	214,085 Da	2.43
PLA	68,639 Da	166,071 Da	2.42
Blend	73,785 Da	197,379 Da	2.68

* 1 Da = 1 g/mol

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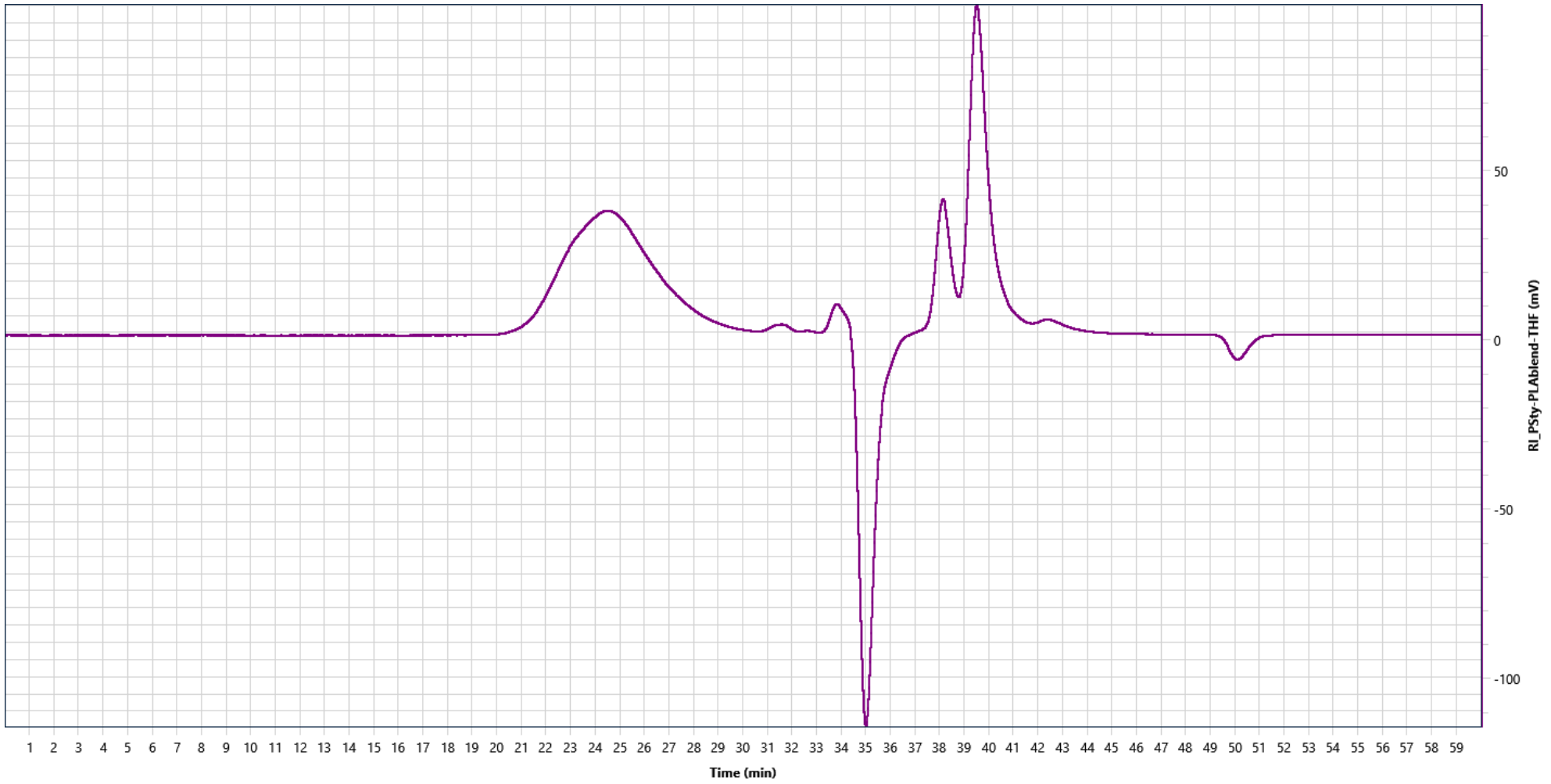
Gel Permeation Chromatography

Results of PS-PLA blend in THF
0.6 mL/min, 35 °C



Gel Permeation Chromatography

Results of PS-PLA blend in THF.
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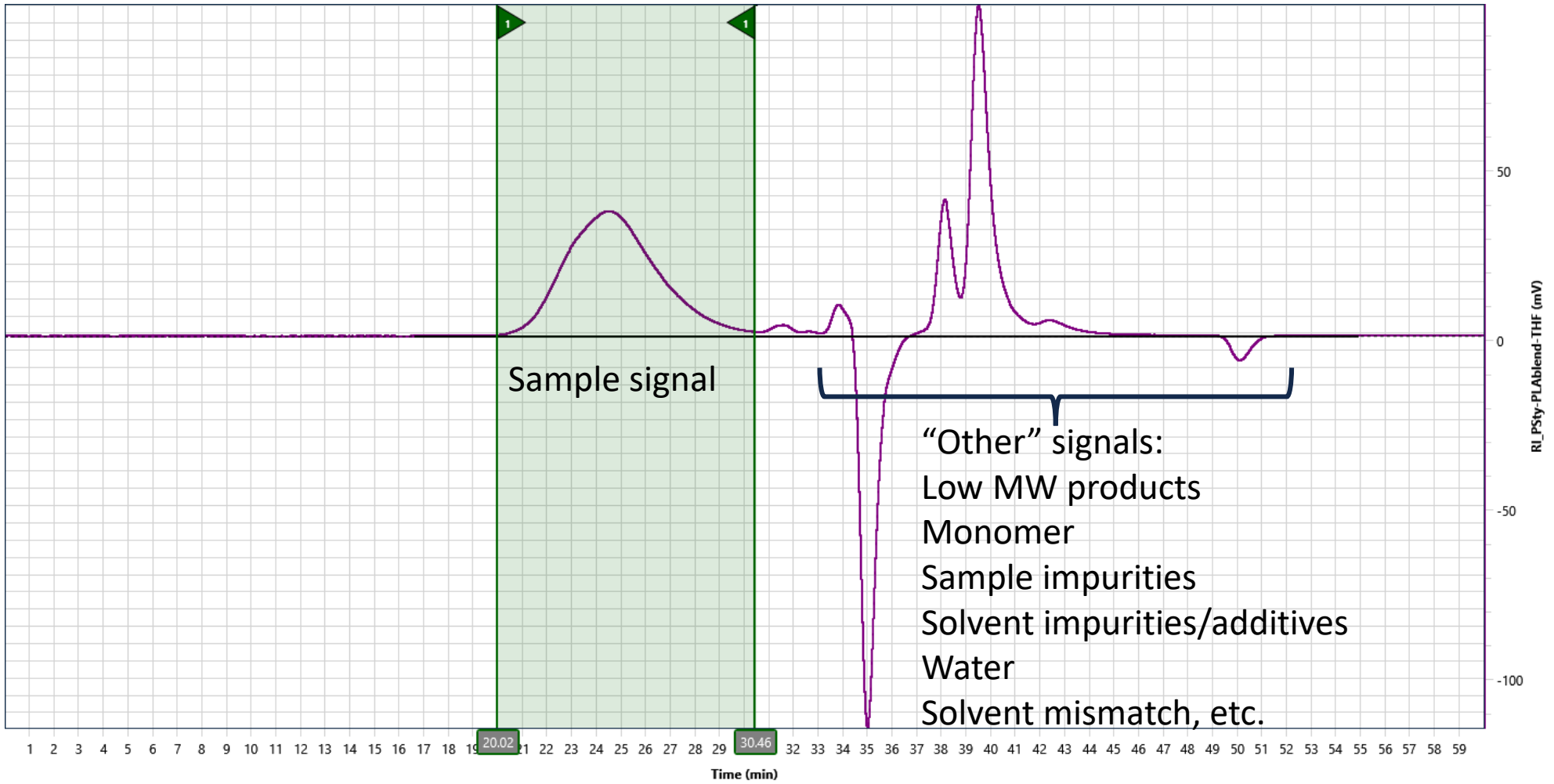


Questions…

Is the polymer stable?

When does it soften/crystallize/degrade?

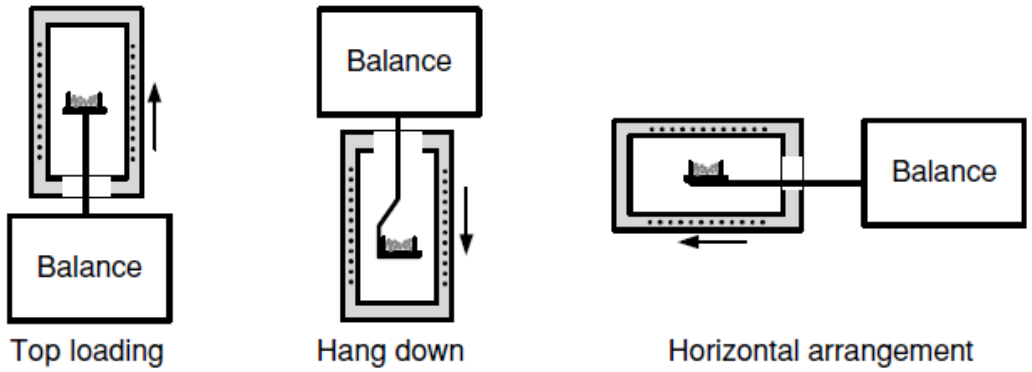
You need to measure its thermal properties.

How do you measure thermal properties?

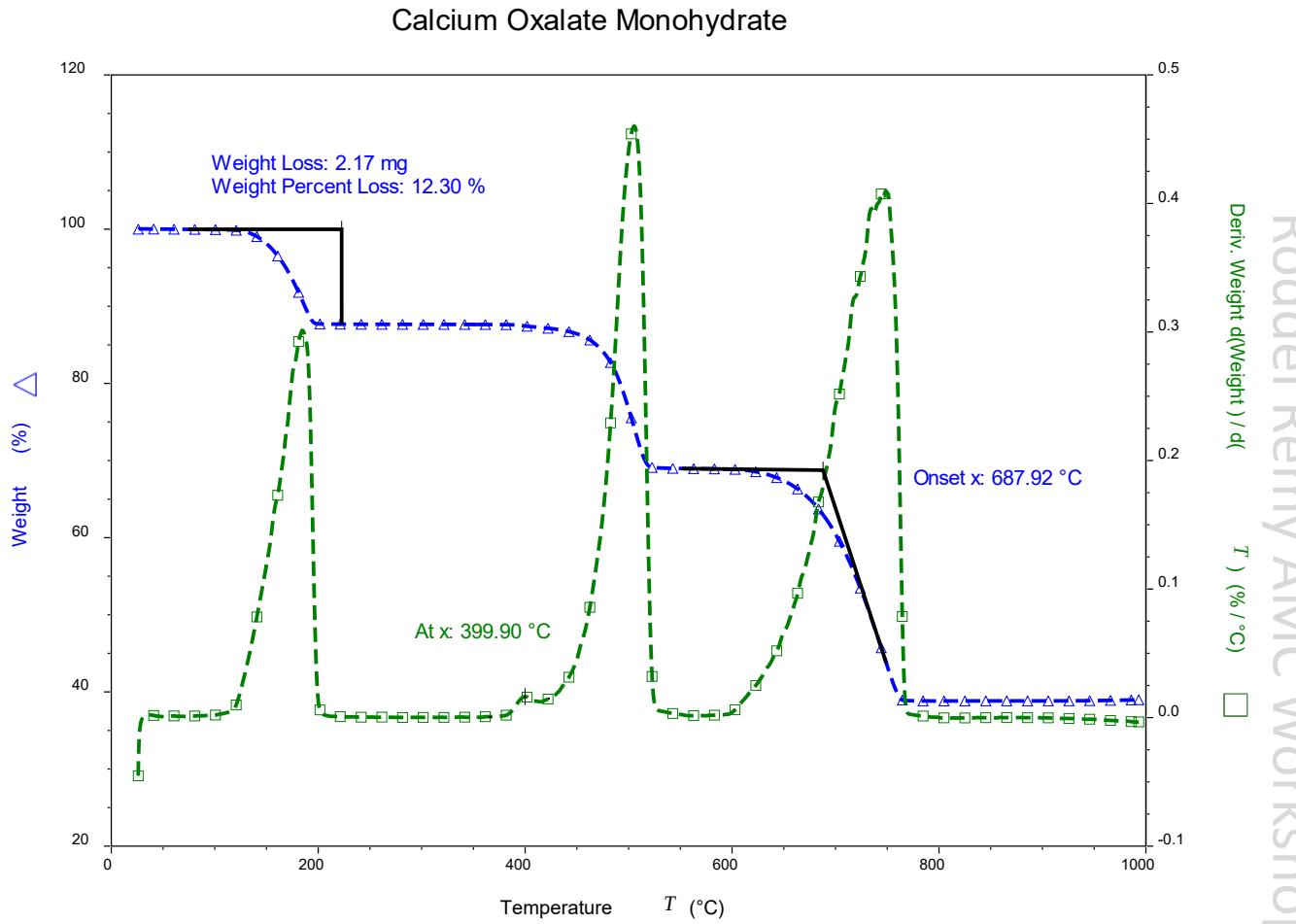
TGA and DSC.

Thermogravimetric Analysis

- Measures the change in mass of materials as a function of temperature and time.



Different TGA configurations



Thermogravimetric Analysis (TGA)

Typical experimental conditions:

- Temperature range – ambient to ≥ 1000°C
- Heating rate – 10, 20°C/min
- Atmosphere – inert (N_2, argon, He), oxidizing (air, O_2) or reducing ($5\%H_2/95\%N_2$) gases
- Sample pan type – Pt or Al_2O_3
- Sample mass – 10 mg → 50 mg **with µg resolution**

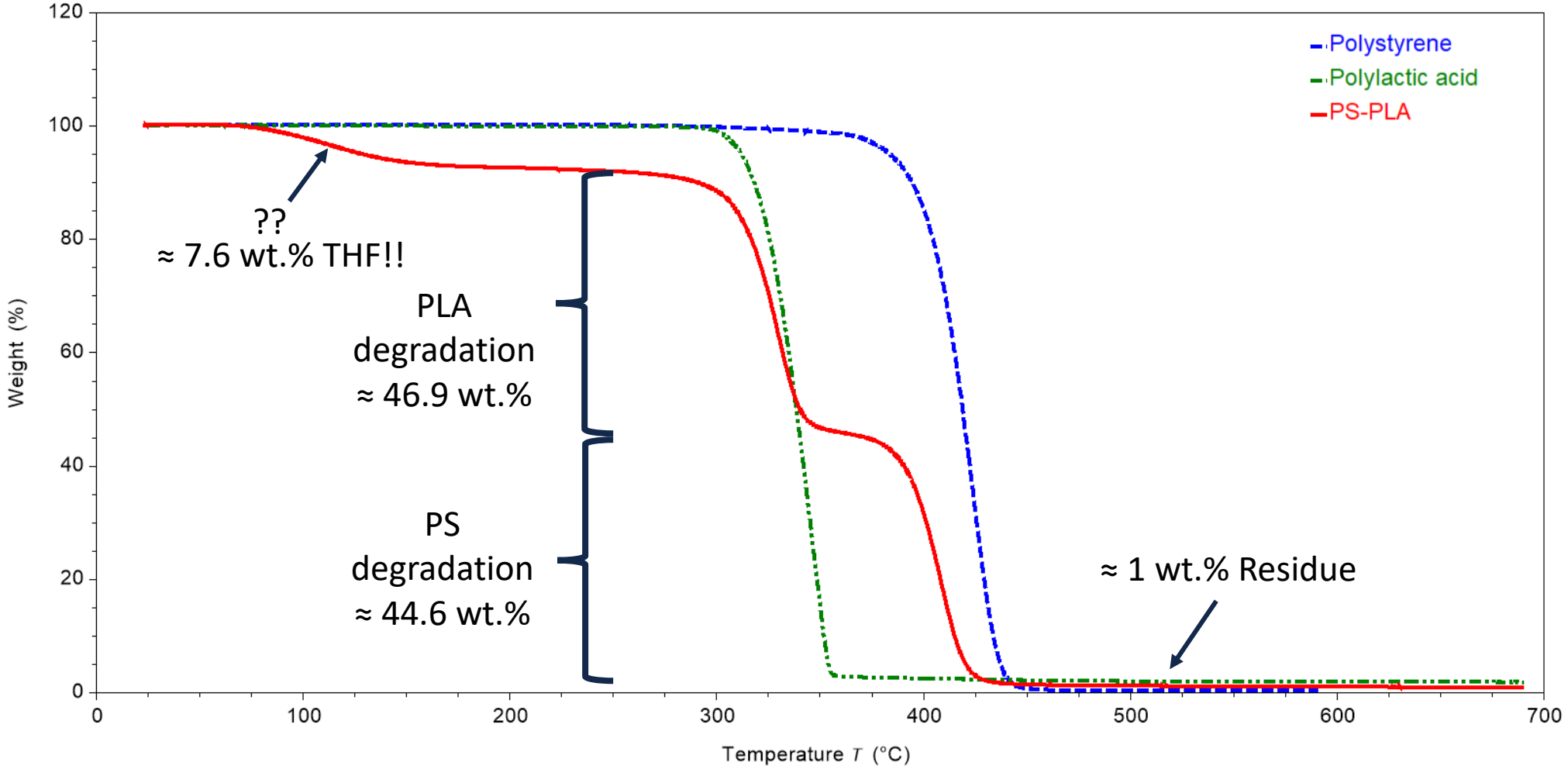
TA Instruments Q50 TGA

What can you measure?

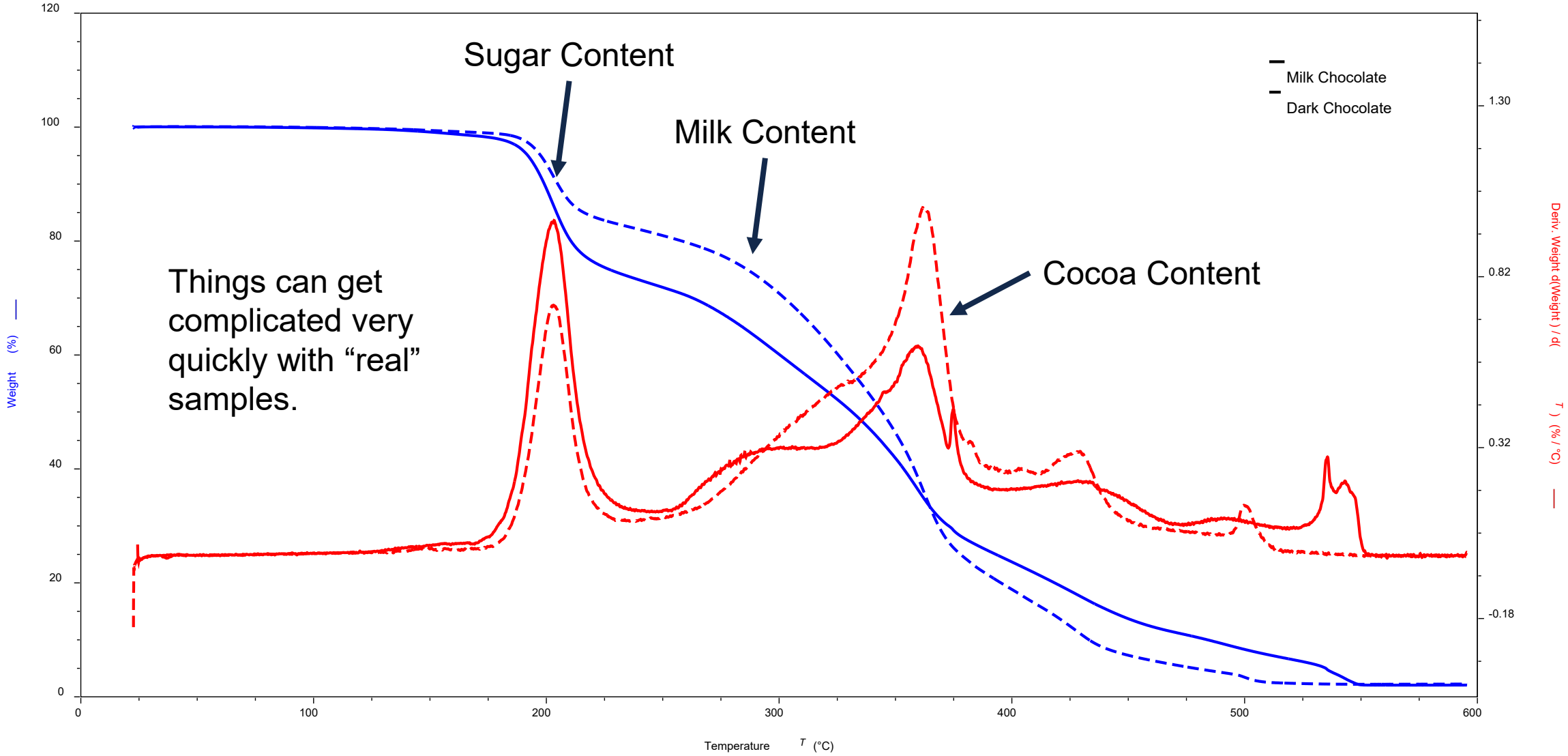
- Sample degradation
- Residual solvent or monomer
- Solute/particle concentration
- Surface area coverage
- Absorption/desorption
- Curie Temperature
- Hi-resolution TGA
- Temperature modulated TGA

Thermogravimetric Analysis (TGA)

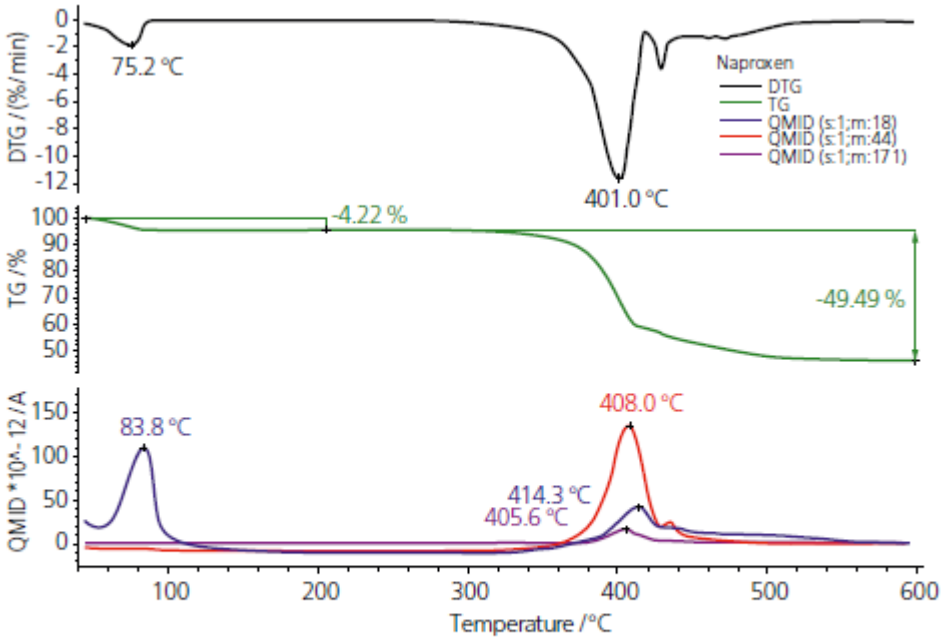
Tested @ 20 °C/min in N_2 atmosphere



TGA Example: Chocolate!!



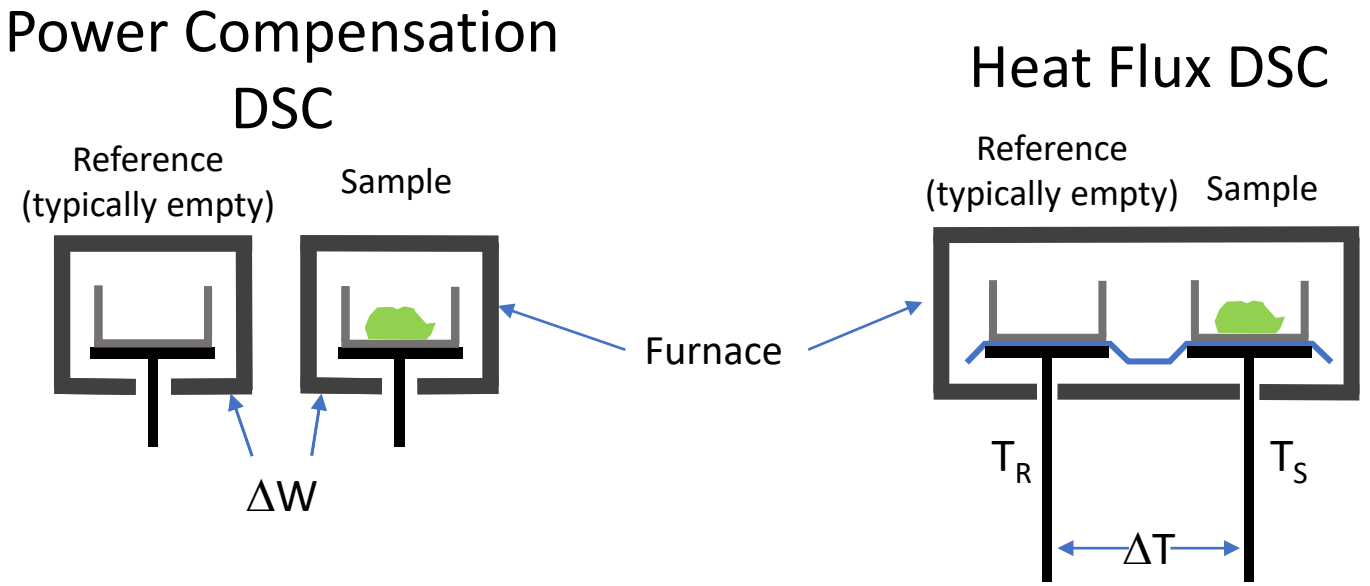
COMING SOON!! TGA – Mass Spectrometry



TGA-MS measurement on naproxen in an inert atmosphere, heating rate 10 K/min, sample mass 10 mg, TGA curve (green), DTG (black), ion current of masses m/z 18, 44 and 171

2025

Differential Scanning Calorimetry (DSC)



- Power compensation DSC measures heat flow directly (original DSC) whereas heat flux DSC converts ΔT into heat flow. However, heat flux DSC is much more common.

Differential Scanning Calorimetry (DSC)

Typical experimental conditions:

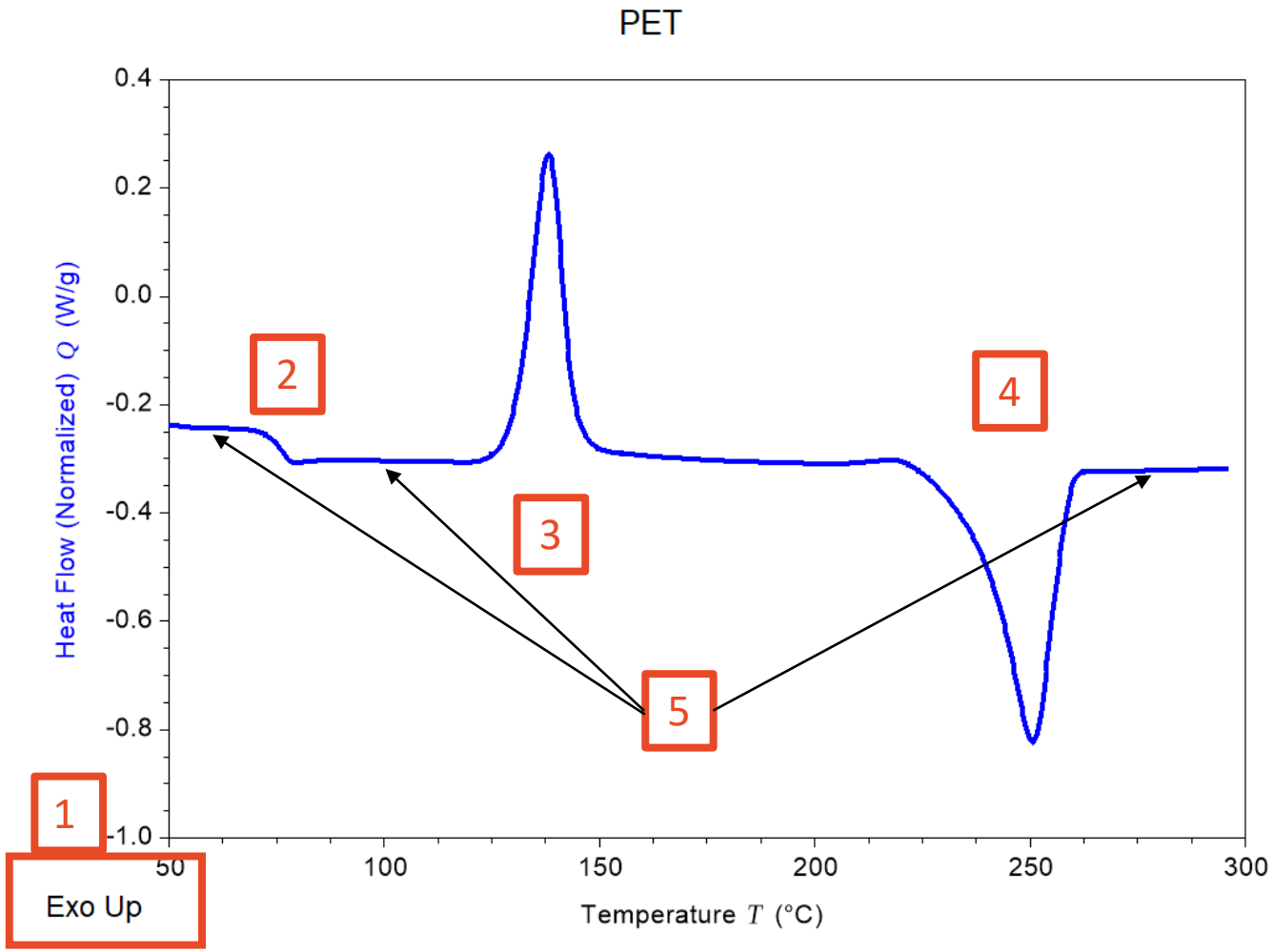
- Temperature range – -180 to 400°C
- Heating rate – 5, 10 or 20°C/min
- Atmosphere – inert (N_2, argon, He) or oxidizing (air, O_2)
- Sample pan type – Aluminum
- Sample mass – 5 → 10 mg

TA Instruments DSC 2500

What can you measure?

- Glass Transition (T_g)
- % Crystallinity
- Solid-solid phase transitions (polymorphism)
- Processing effects (curing, annealing, oxidation, etc.)
- Magnetic transitions (Curie, Néel temperatures)
- Temperature modulated DSC

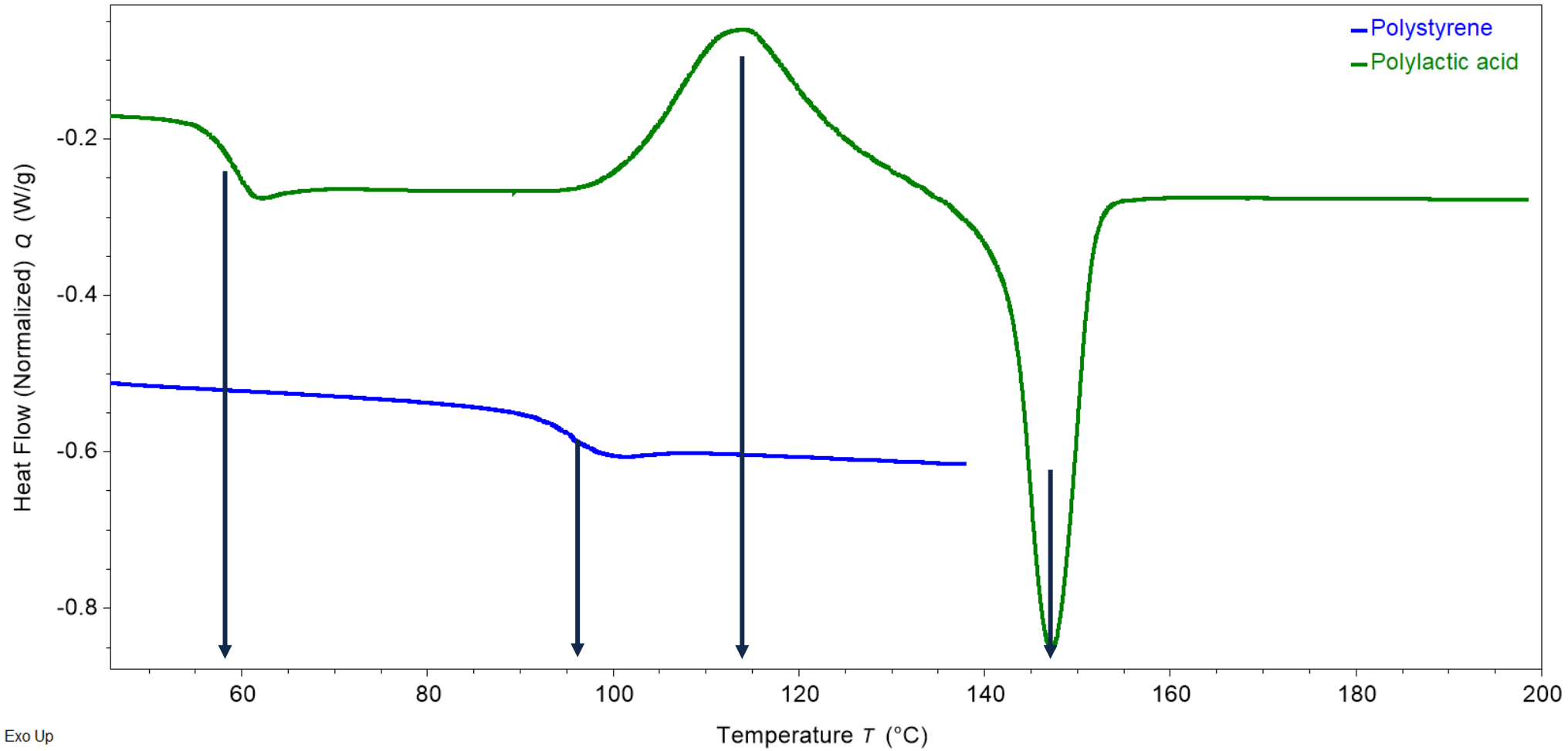
Differential Scanning Calorimetry (DSC)



1. **ALWAYS** define your heat flow direction
2. Glass Transition (T_g) – looks like a step
3. Crystallization – exothermic reaction
4. Melting – endothermic reaction
5. "Baseline" is related to the heat capacity.

Differential Scanning Calorimetry (DSC)

Tested @ 10 °C/min in N_2 atmosphere. 2nd Heat scans shown below.



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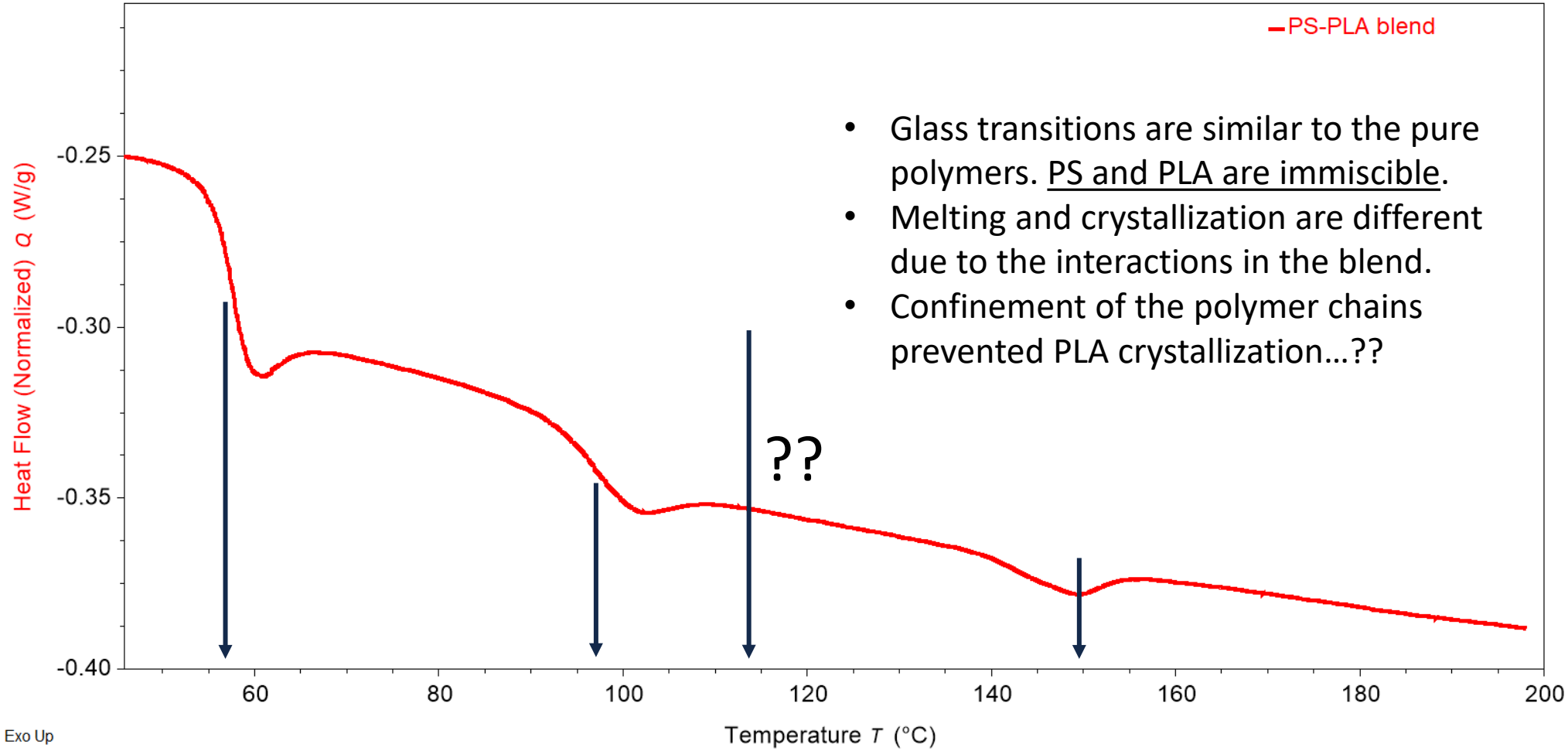
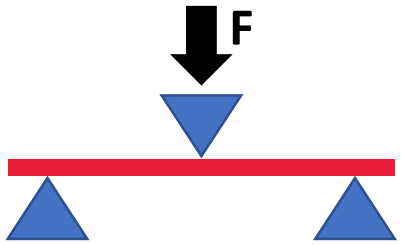


- Glass transitions are similar to the pure polymers. PS and PLA are immiscible.
- Melting and crystallization are different due to the interactions in the blend.
- Confinement of the polymer chains prevented PLA crystallization…??

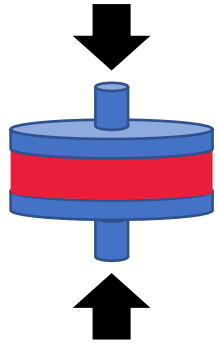
Mechanical Analysis



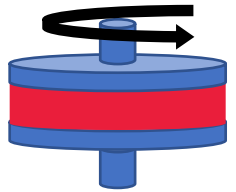
Bending:
- 3- or 4-point bending
- Single/dual cantilever

Torsion

Tension



Compression

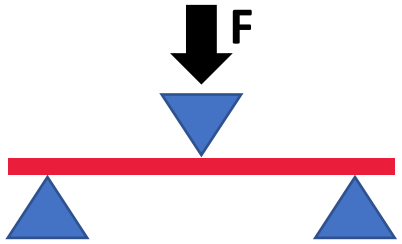


Shear (Rheometry)
- Parallel plate
- Cone & plate
- Concentric cylinders
- Capillary

DECREASING SAMPLE STIFFNESS

Choose the appropriate mechanical geometry for your application!

Mechanical Analysis



Bending:
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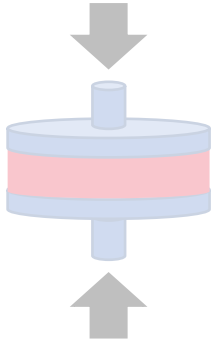
Torsion

Tension



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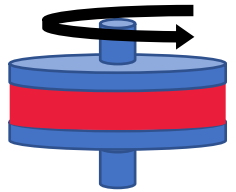
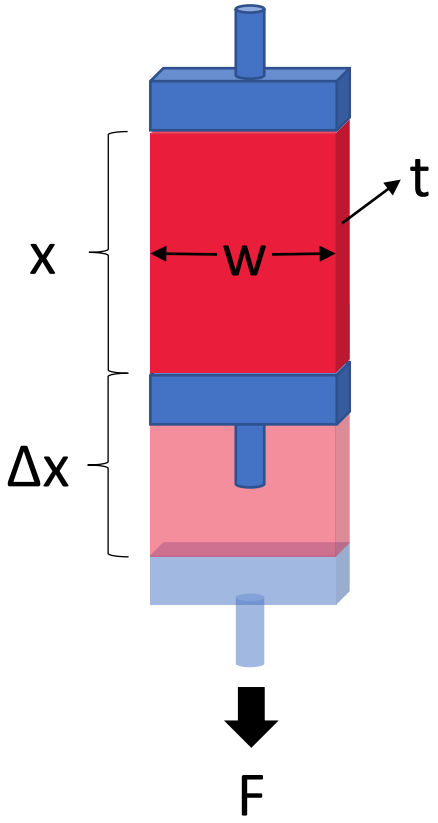


Shear (Rheometry)
- **Parallel plate**
- **Cone & plate**
- Concentric cylinders
- Capillary

TA Instruments Q800 DMA

TA Instruments DHR-3

Mechanical Analysis: Basic Calculations



In tensile mode:

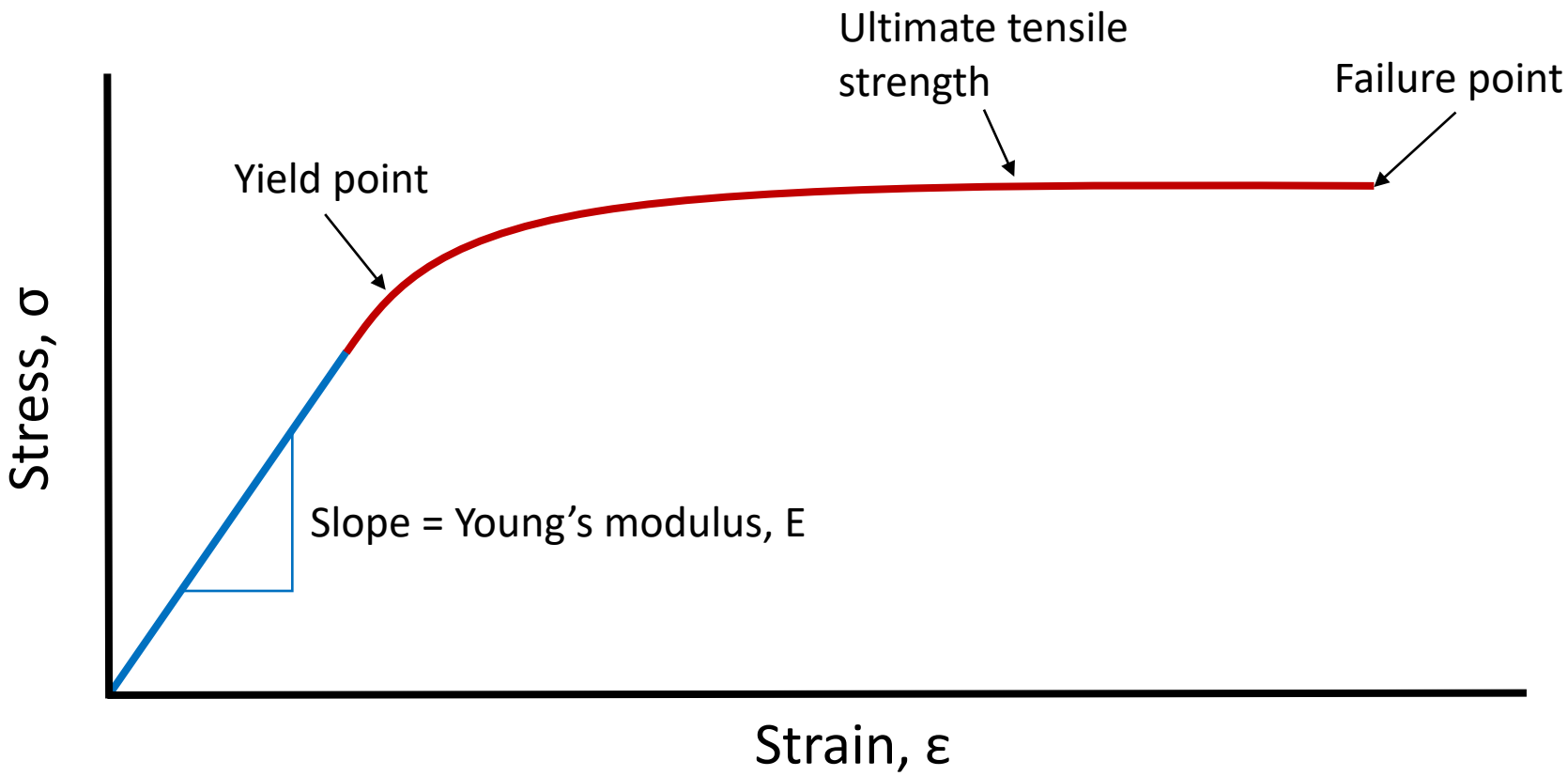
- Stress, $\sigma = \frac{F}{wt}$
- Strain, $\epsilon = \frac{\Delta x}{x}$
- Stiffness, $k = \frac{F}{\Delta x}$

Instrument may function in two ways:

- Force controlled
- Strain controlled

- Elastic (Young's) Modulus, $E = \frac{\sigma}{\epsilon}$

Mechanical Analysis: Stress-Strain

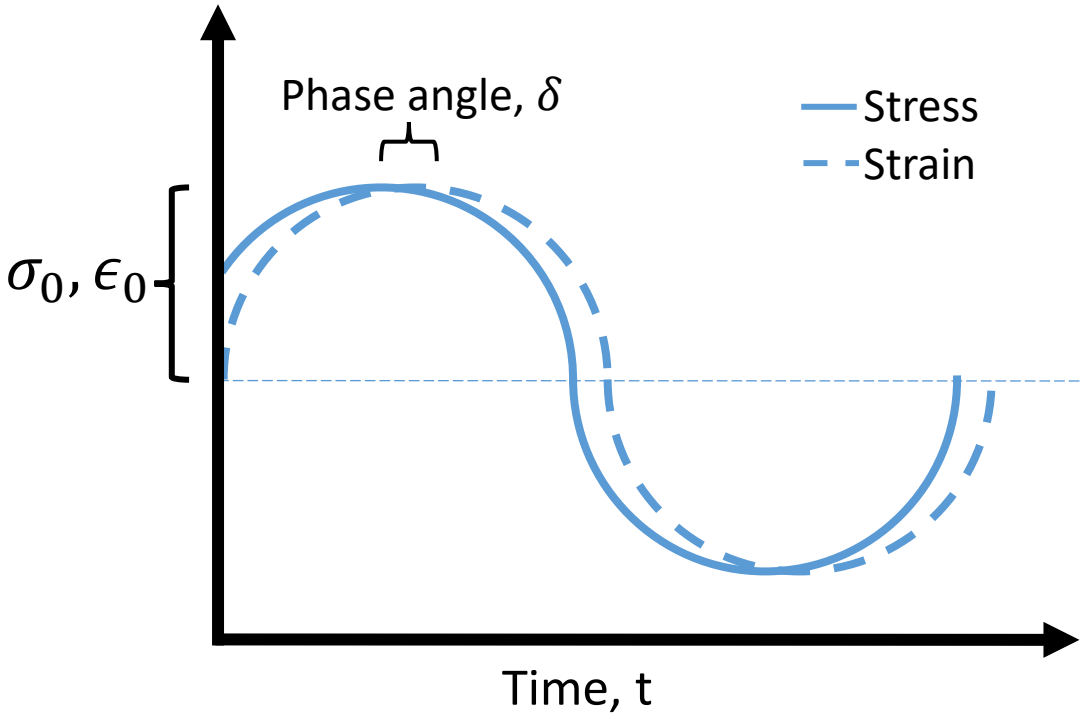


Young's modulus may be hard to find for softer materials.

- Go slow
- Take lots of data points at low strain

Dynamic Mechanical Analysis

- What if I apply an oscillating stress/strain?



At small amplitudes ($\epsilon < 1\%$), the modulus can be defined in complex notation:

$$E^* = E' + iE''$$

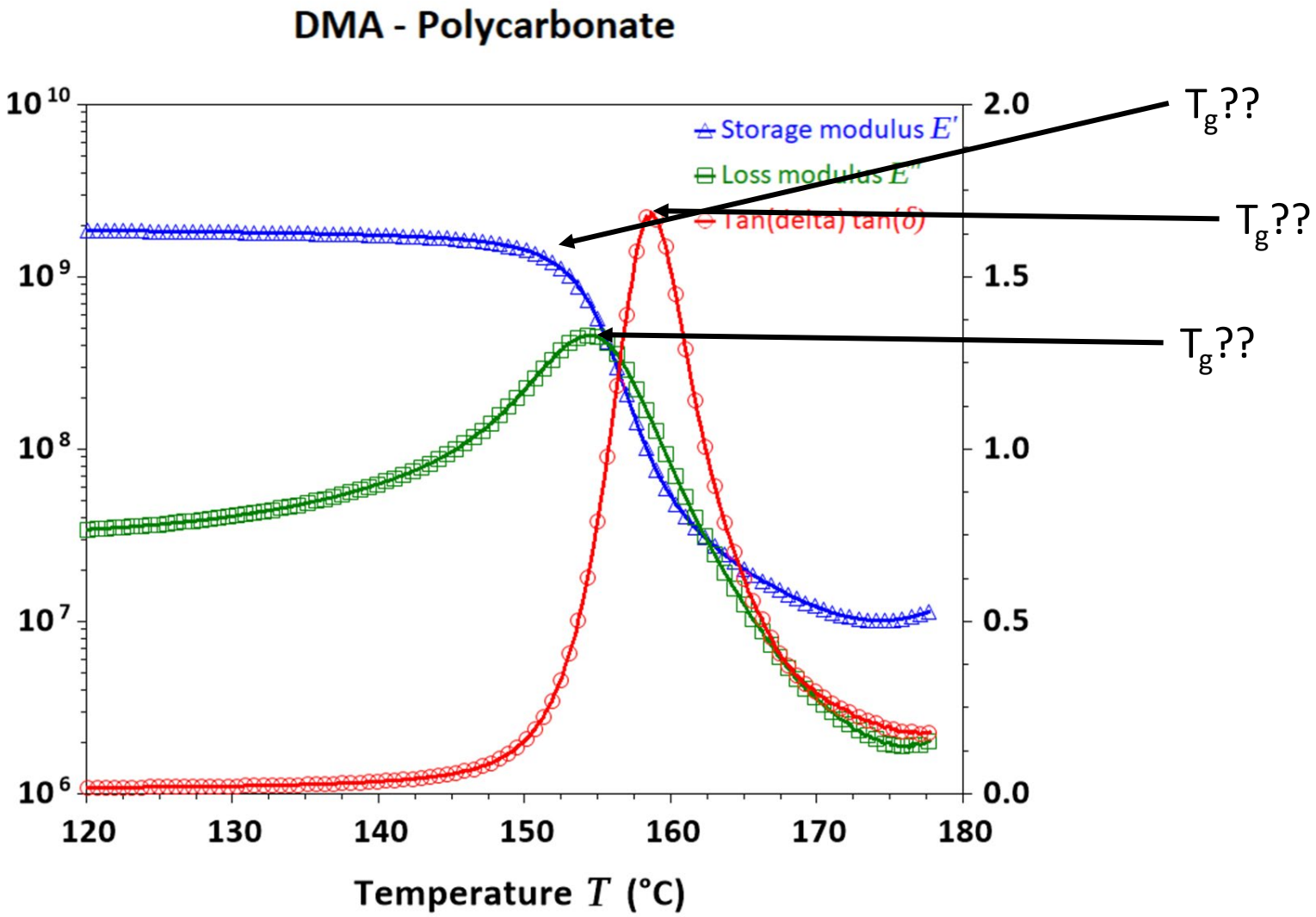
Storage modulus:
- Elastic component
- ~~"solid" like behavior~~

Loss modulus:
- Viscous component
- Damping behavior
- ~~"liquid" like behavior~~

Damping Factor,

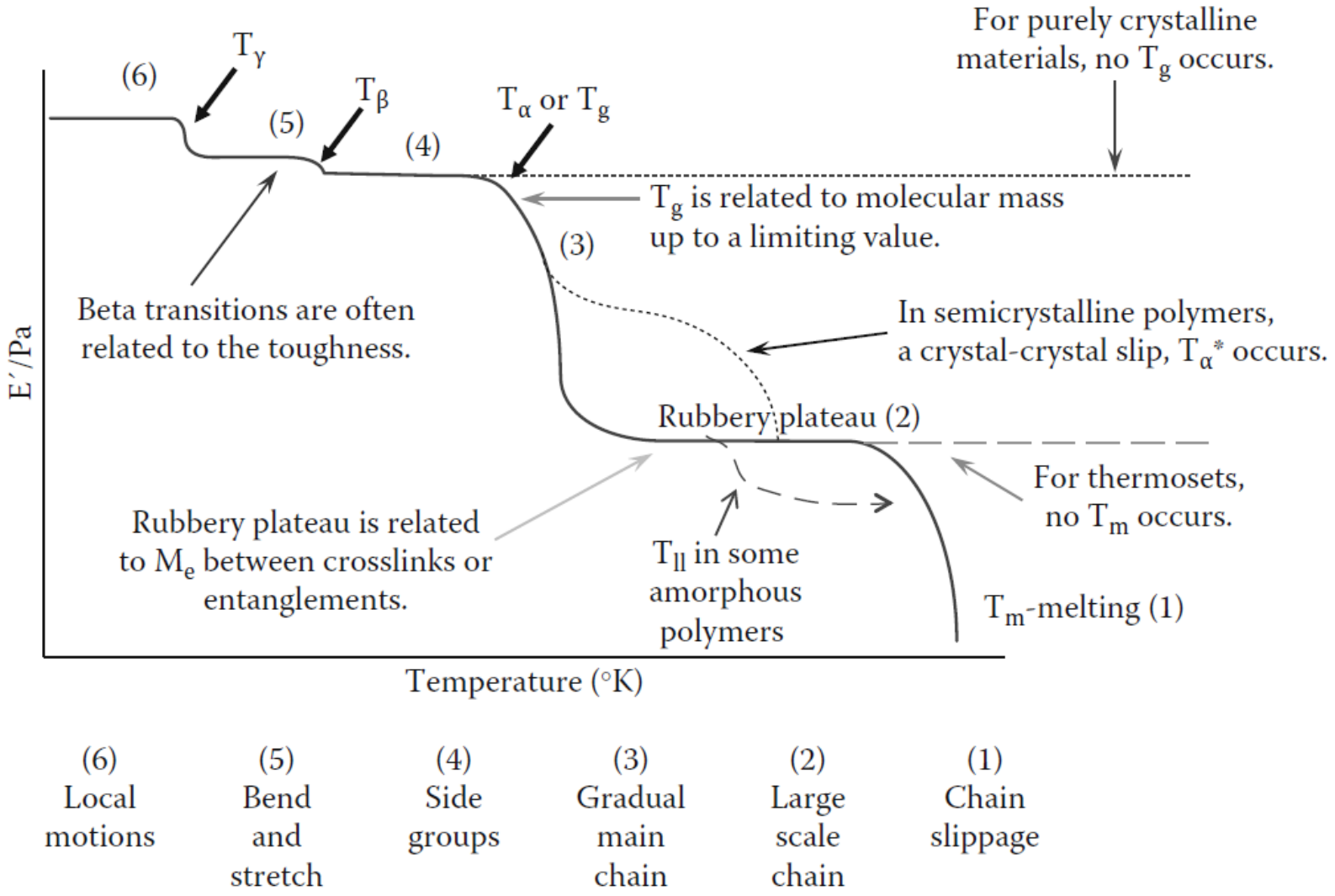
$$Tan\ \delta = \frac{E''}{E'}$$

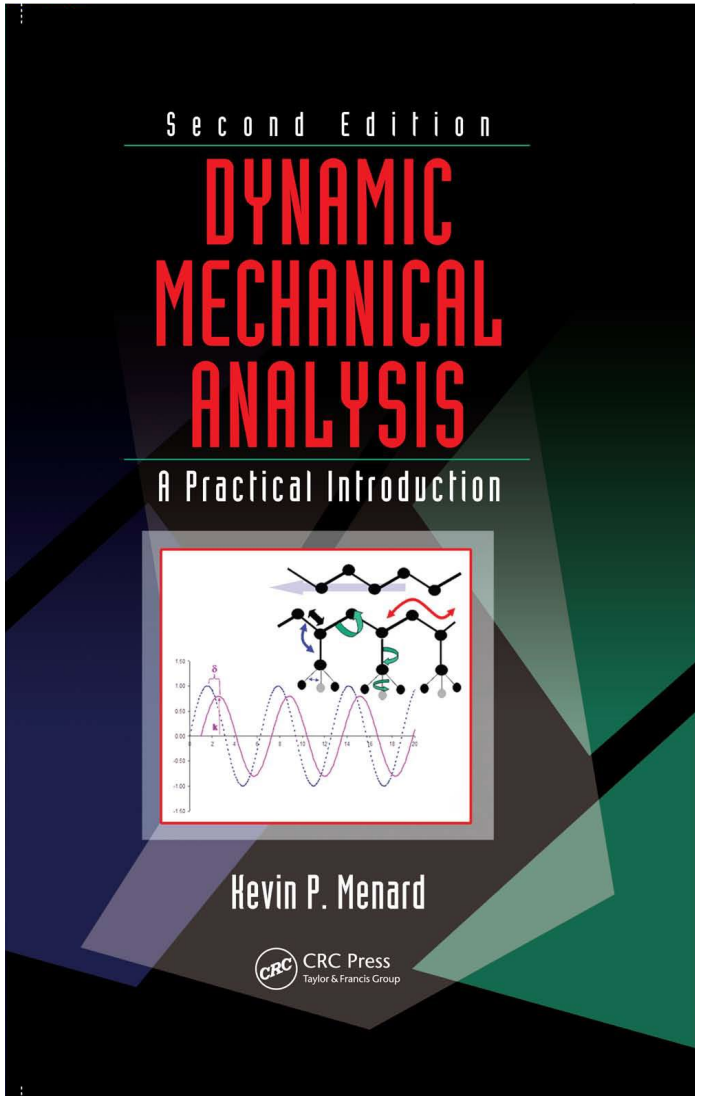
Dynamic Mechanical Analysis



- They can all be defined as the T_g….don't mix and match!!
- It's important to state:
  - Measurement Geometry
  - Experiment parameters (heating rate, frequency, strain amplitude)
  - Analysis method

Dynamic Mechanical Analysis





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