Lecture 25 *POLYMERS*

Wallace Carothers

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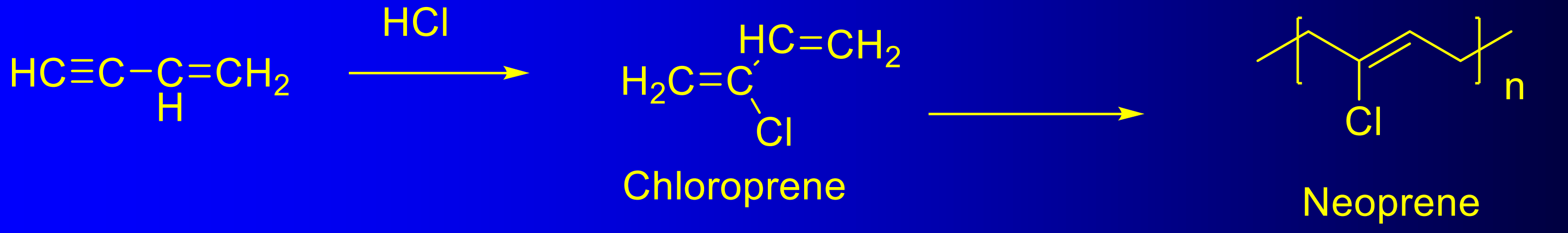
April 19, 2016

Wallace Hume Carothers 1896-1937

Carothers at Dupont



$$\text{HO-R'-OH} \; + \; \text{HOOC-R-COOH} \xrightarrow{H^+} \text{—(O - R'-OOC-R-CO)}_n\text{—}$$

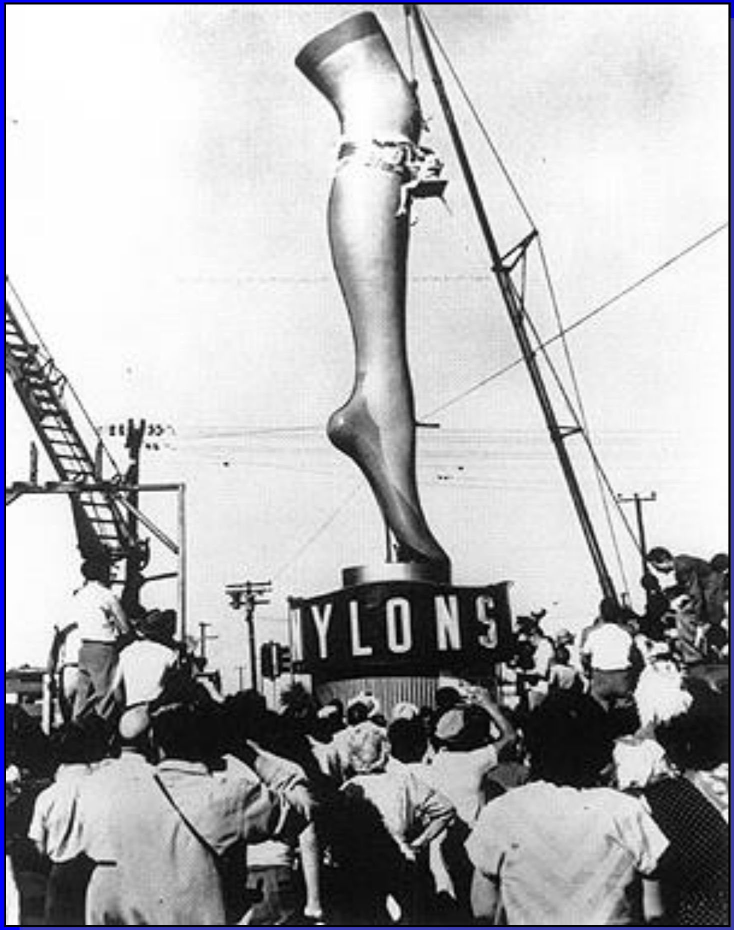
Polyesters

$$\text{H2N-R'-NH2} \; + \; \text{HOOC-R-COOH} \longrightarrow \text{—(OC-R-CONH-R-NH)}_n\text{—}$$

Polyamides

1.Commercializion of Nylon

*https://www.**chemheritage**.org/*



Nylon was first used for fishing line, surgical sutures, and toothbrush bristles. DuPont touted its new fiber as being "as strong as steel, as fine as a spider's web," and first announced and demonstrated nylon and nylon stockings to the American public at the 1939 New York World's Fair.

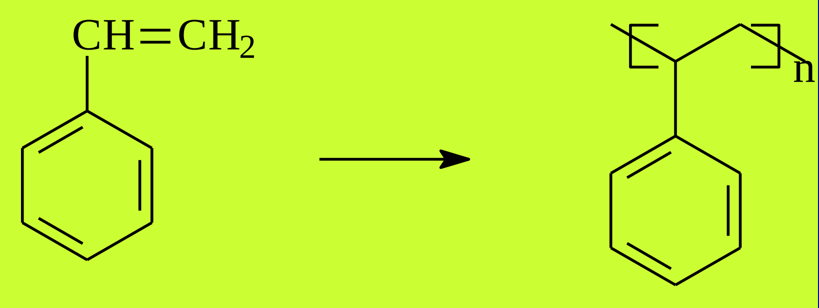
DuPont sold 5 million pairs of stockings across the U.S. on the first day they were generally available, May 15, 1940. About 63 million were sold in their first year.

Notation & Nomenclature

- To name a polymer, add the prefix poly to the name of the monomer from which the polymer is derived
  - if the name of the monomer is one word, no parentheses are necessary ..like polystyrene
  - for more complex monomers or where the name of the monomer is two words, enclose the name of the monomer is parenthesis, as for example poly(vinyl chloride) or poly(ethylene terephthalate)
  - Many “common” monomer names are used...

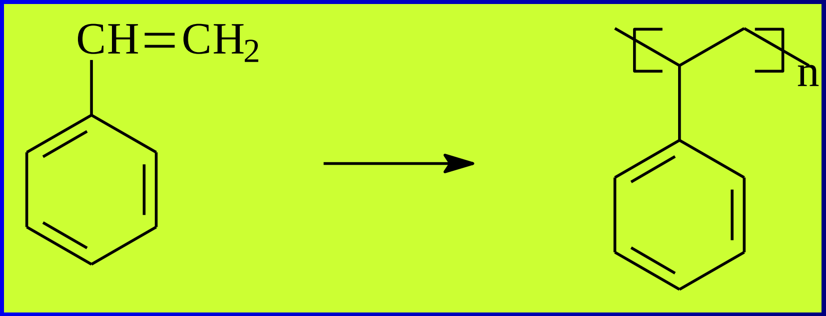
Notation & Nomenclature

- Show the structure by placing parenthesis around the repeat unit
- n = average degree of polymerization



Notation & Nomenclature

- Show the structure by placing parenthesis around the repeat unit
- n = average degree of polymerization
- Molecular weight of average chain is then n (monomer molecular wt)



Nomeclature

- First…..let's face it…..polymer nomenclature is a MESS
- There is an IUPAC formalism based on the structure of the simplest repeat using, but it generates unwieldy names and is seldom used
- "source based" nomenclature is most commonly used.

Source based Nomenclature

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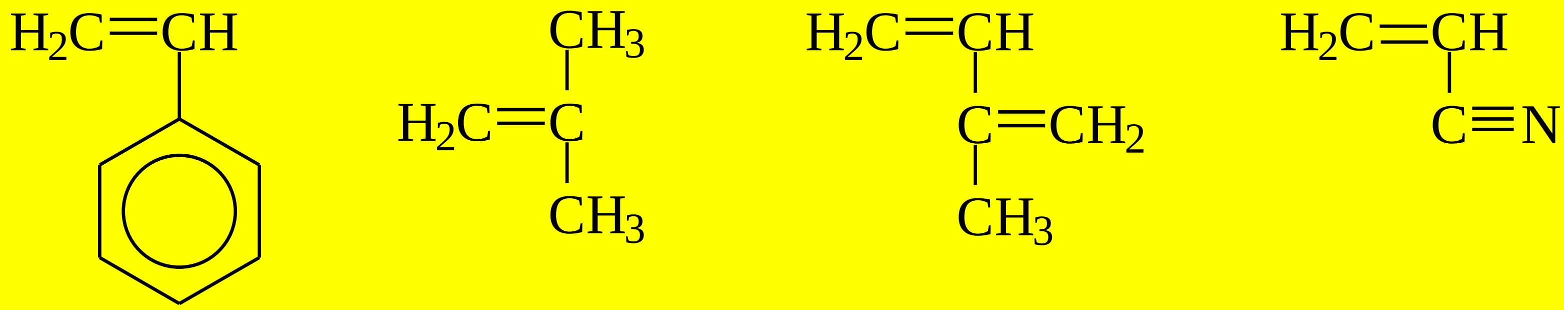
Source Based (homopolymers)

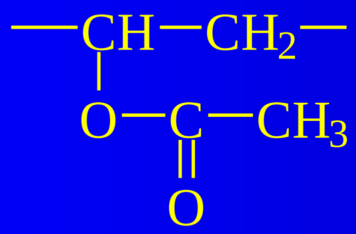
- Use name of actual monomer
  - polymonomer, i.e. polyethylene
  - Unfortunately, common names may be used for



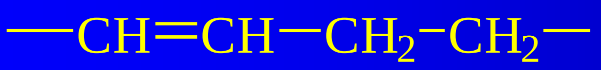
styrene isobutylene isoprene acrylonitrile

- Use ( ) when two words or substituents
  - poly(vinyl chloride), poly(1,2-difluoroethylene)

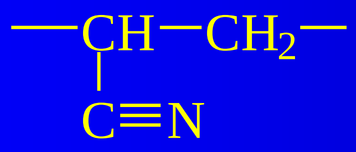
Examples



1. Poly(1-acetoxyethylene) - **structure**
2. Poly(vinyl acetate) - **source**

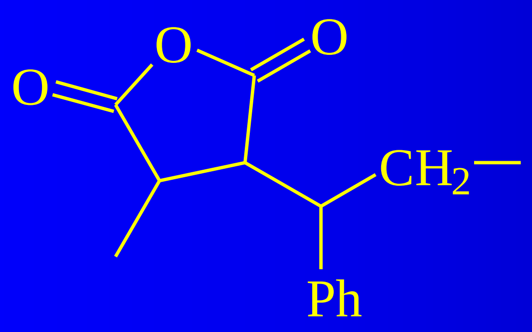


1. Poly(but-1-ene-1,4-diyl)
2. Polybutadiene



1. Poly(1-cyanoethylene)
2. Polyacrylonitrile

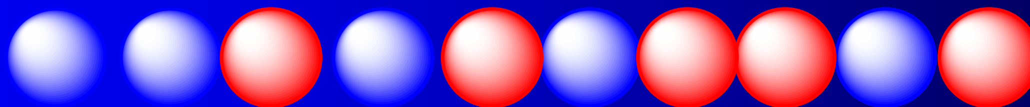
1. Poly(methylene)
2. Polyethene; polyethylene



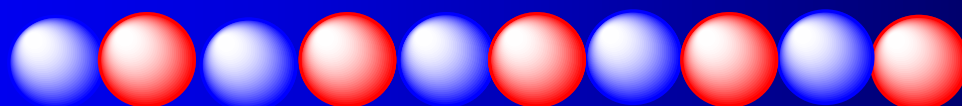
1. Poly[(2,5-dioxotetrahydrofuran-3,4-diyl)(1-phenylethylene)]
2. Poly(maleic anhydride-*alt*-styrene)

Architecture (copolymers)

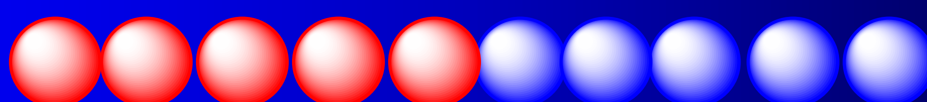
- Architecture terms
  - -*co*- (unspecified arrangement), poly(A-*co*-B)



  - -*alt*- (alternating)



  - -*block*- Polyacrylonitrile-*block*-polybutadiene



Industrial Influence: Trade Names

- PVC poly (vinylidene chloride) Saran wrap
- PVC poly (vinyl chloride) Pipe and records
- PET poly (ethylene teraphthalate) Coke bottles, Dacron
- Polystyrene Cups and packaging
- Delrin Bushings and engineering parts
- Lexan Bullet proof glass
- Teflon Non stick pans
- PVDF speakers and microphones
- Kevlar bullet proof vests
- Nylon Rope and fiber

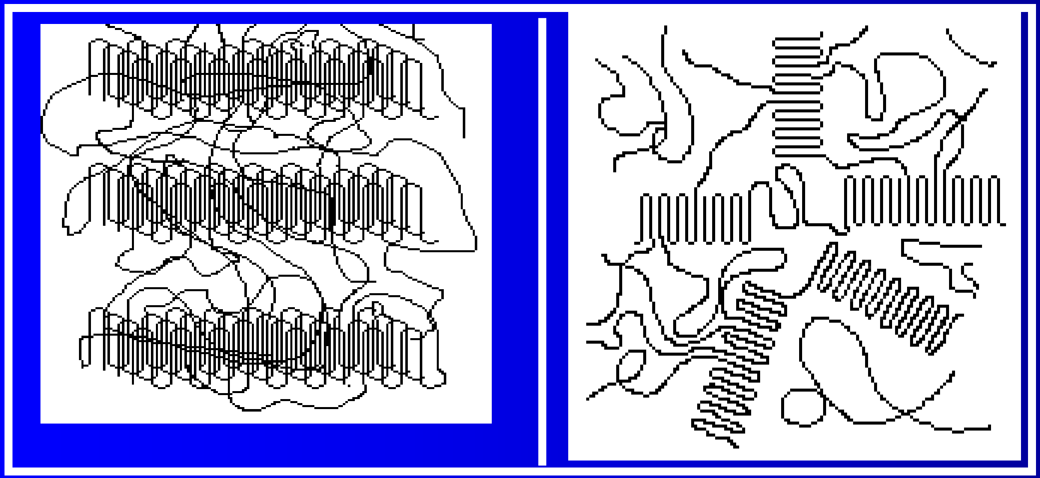
Industrial Influence...

- Poly(vinylidine chloride) Saran wrap
- Poly(vinylidne Fluoride)   Speaker membranes
- Polystyrene Packaging, etc
- Kevlar (polyamide) bullet proof vests
- Nylon (polyamide) rope and stockings
- Delrin (polyacetal) bushings
- Dacron (polyester) clothing, sails, etc.
- Lexan (polycarbonate) aircraft windows
- etc…..

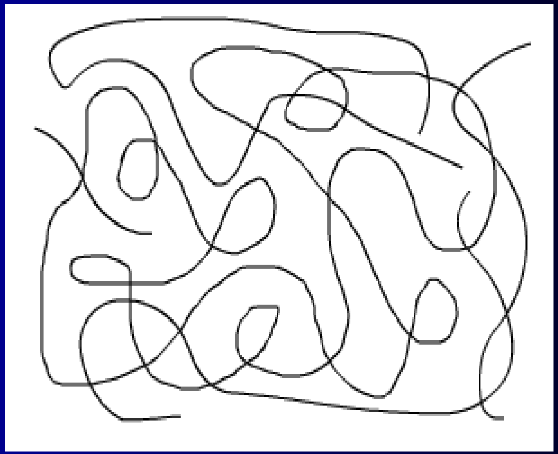
Morphology

- Many polymers tend to crystallize as they precipitate or are cooled from a melt
- But, they are very large molecules, often with complicated and irregular shapes, which inhibits crystallization and tends to prevent efficient packing into exactly ordered structures
- As a result, polymers in the solid state tend to be composed of ordered crystalline domains and disordered amorphous domains

Polymer Morphology



Crystalline and semi crystalline

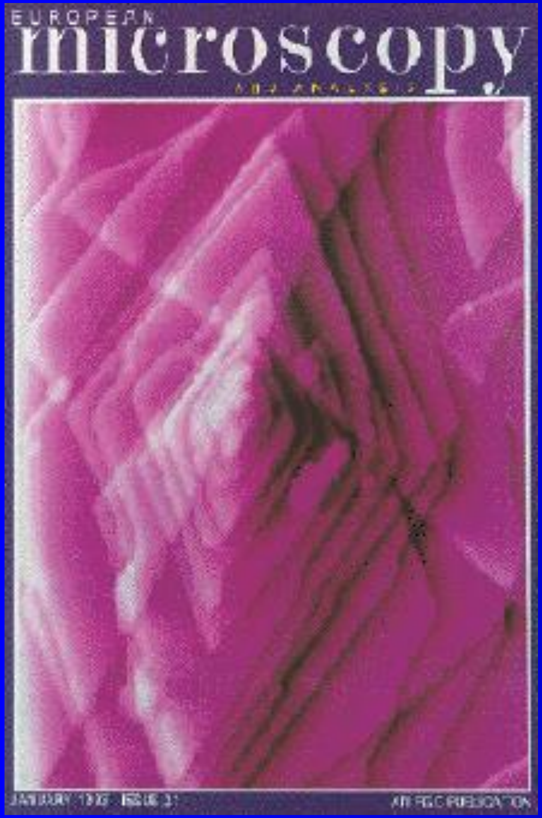


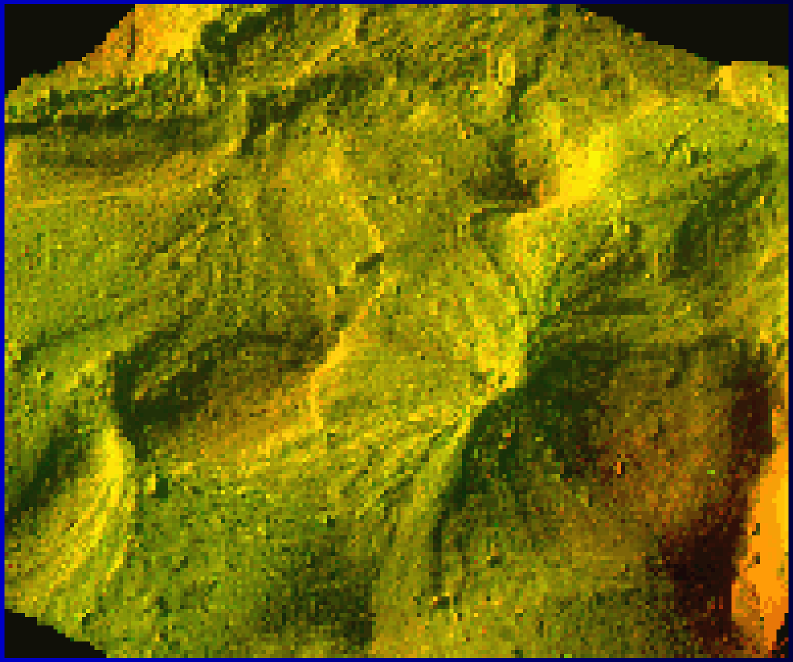
Amorphous

Morphology

- Polymers with regular, compact structures and strong intermolecular forces, such as hydrogen bonds have high degrees of crystallinity.
  - as crystallinity increases, the polymer becomes more opaque due to scattering of light by the crystalline regions…for example, teflon -(CF_2CF_2)-"looks" white
- Melt transition temperature, T_m: the temperature at which crystalline regions melt
  - as the degree of crystallinity increases, T_m increases

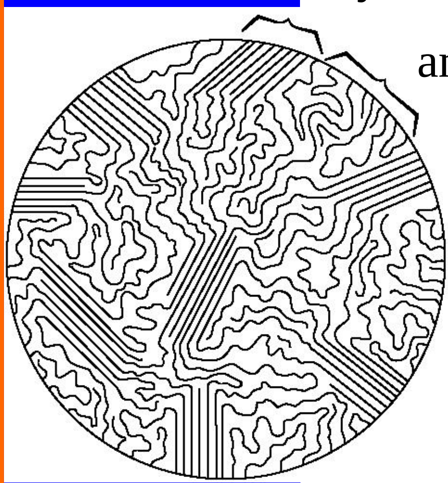
Polymer Crystals

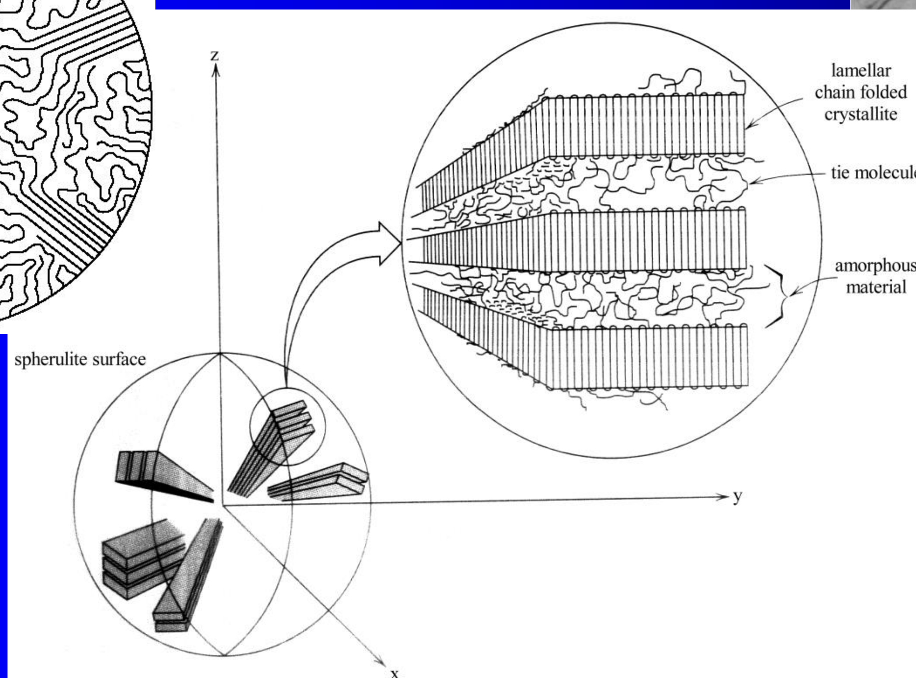


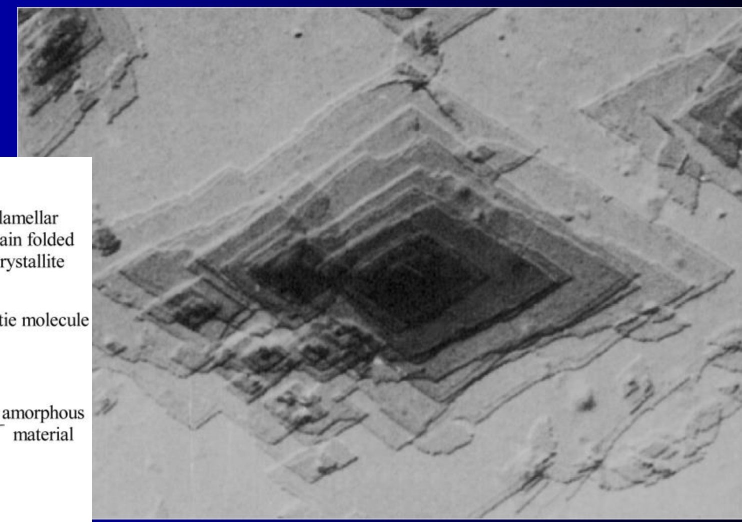


Crystallinity

some spontaneously form crystalline regions (micelles)







proportion of crystalline / amorphous strong influence on properties

PE carrier bag - amorphous, toughened pipe 95% crystalline

Property	Change with Increasing Degree of Crystallinity
Strength	Generally increases with degree of crystallinity
Stiffness	Generally increases with degree of crystallinity
Toughness	Generally decreases with degree of crystallinity
Optical Clarity	Generally decreases with increasing degree of crystallinity.Semi-crystalline polymers usually appear opaque because of the difference in refractive index of the amorphous and crystalline domains, which leads to scattering. Will depend upon crystallite size.
Barrier Properties	Small molecules usually cannot penetrate or diffuse through the crystalline domains, hence "barrier properties", which make a polymer useful for things like food wrap, increase with degree of crystallinity
Solubility	Similarly, solvent molecules cannot penetrate the crystalline domains, which must be melted before the polymer will dissolve. Solvent resistance increases with degree of crystallinity

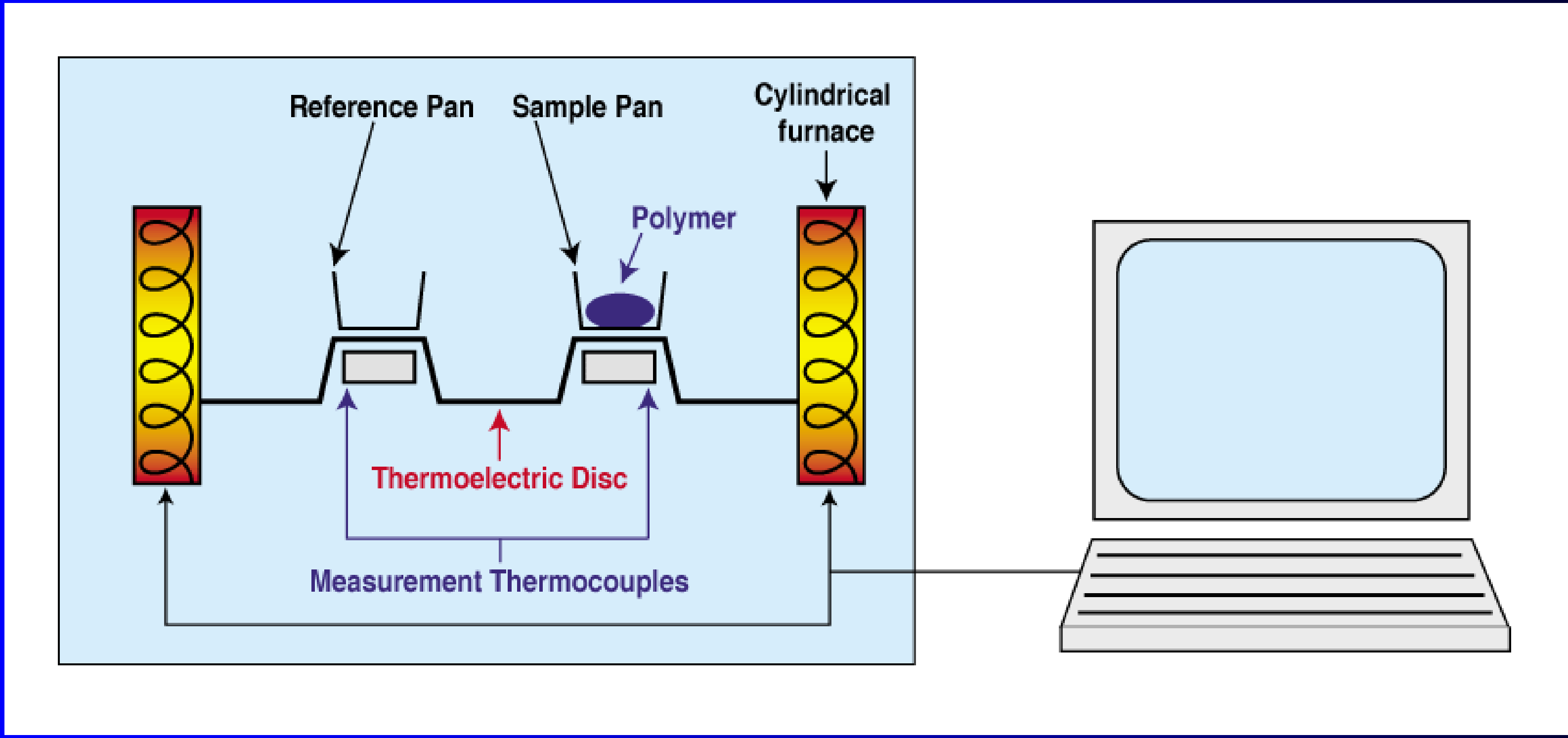
The ability to bend without breaking

Morphology

- Amorphous polymers are referred to as glassy polymers
  - they lack crystalline domains that scatter light and are transparent….Poly(methyl methacrylate)
  - they are weaker polymers and generally more flexibility
  - on heating, amorphous polymers are transformed from a hard glass to a soft, flexible, rubbery state
- Glass transition temperature, T_g: the temperature at which a polymer undergoes a transition from a hard glass to a rubbery solid (ca. 100 degrees for polystyrene)

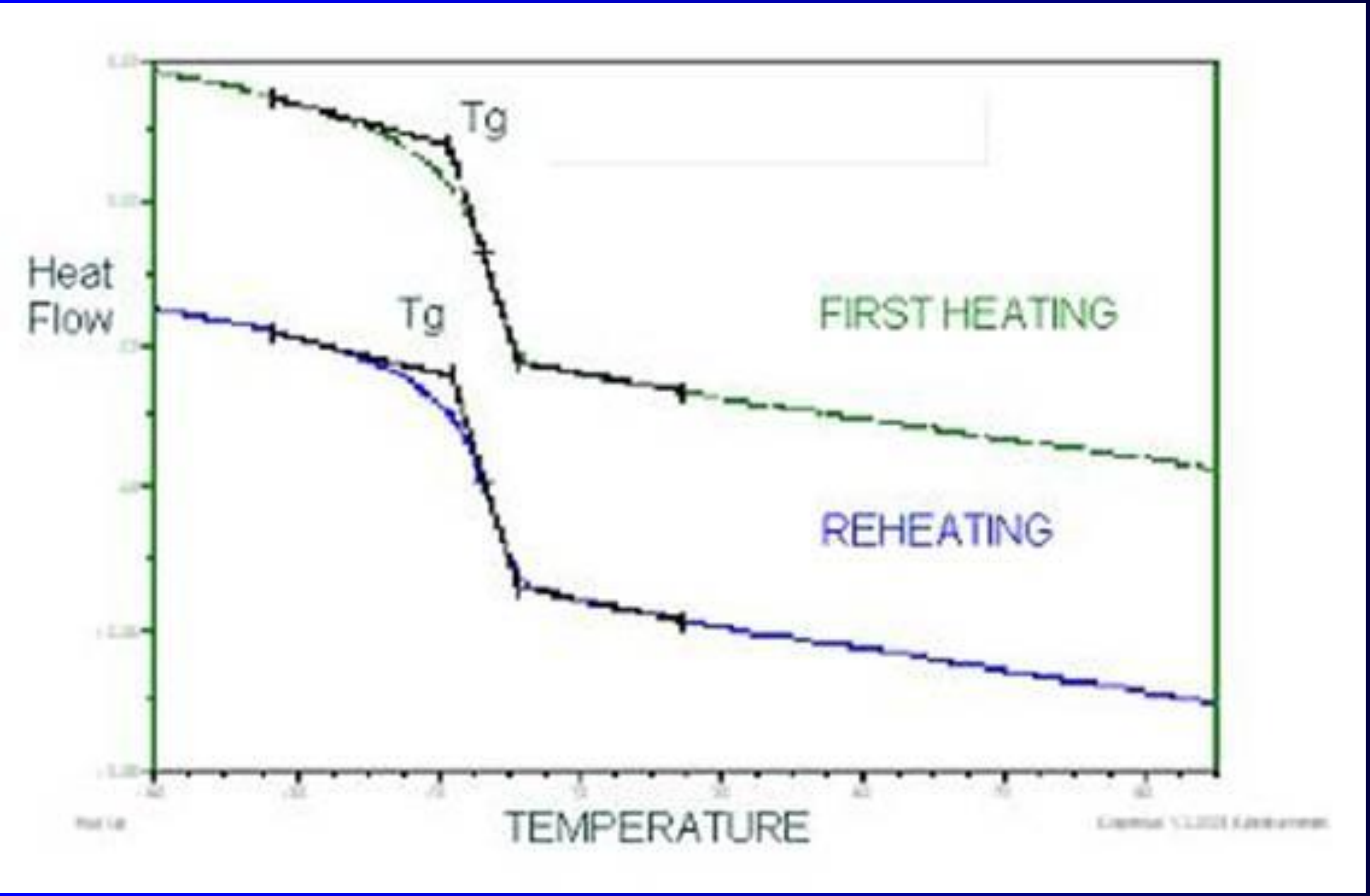
Changing Rubber into Glass!!

Differential Scanning Calorimetry

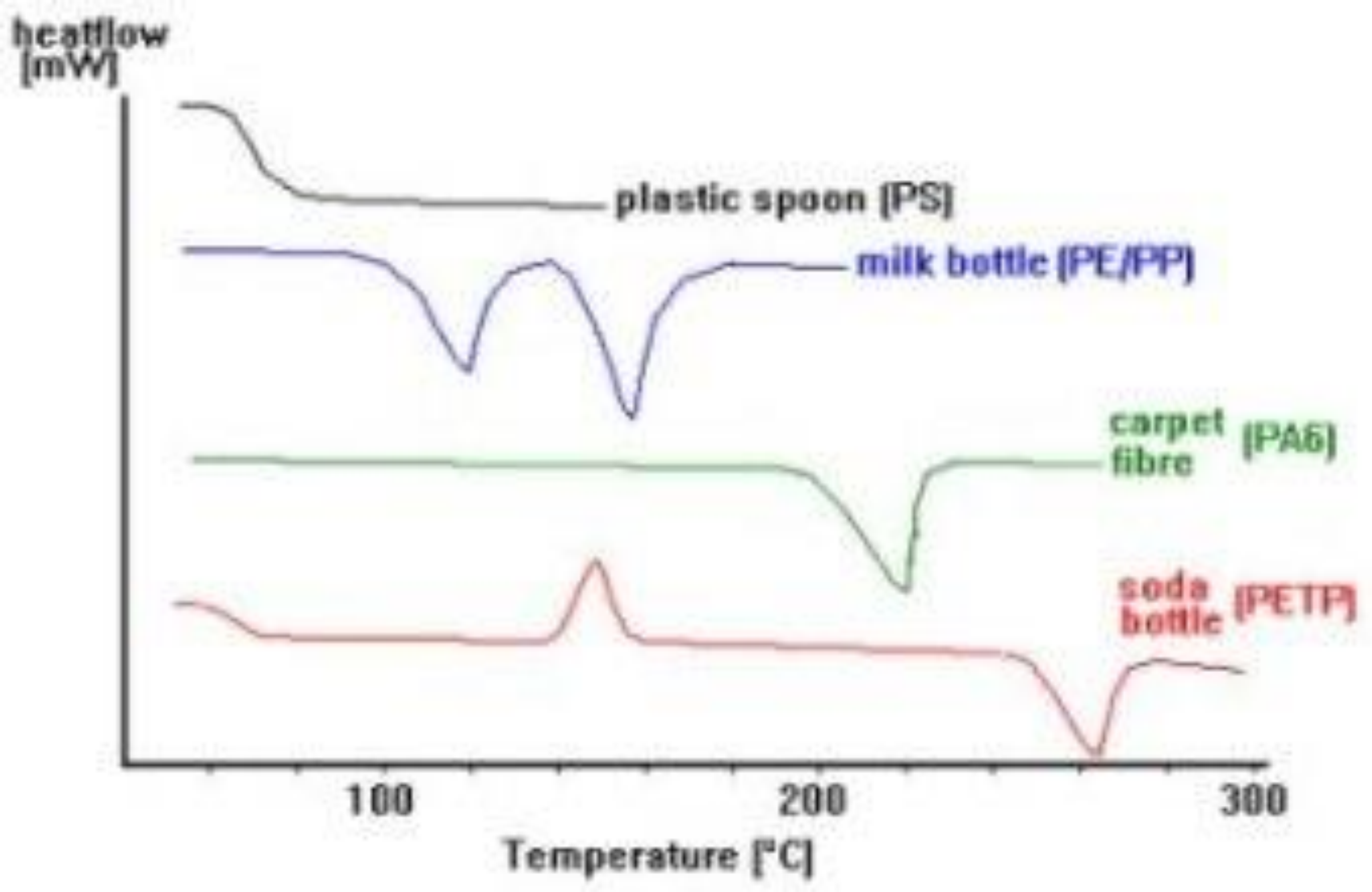


Differential Scanning Calorimeter

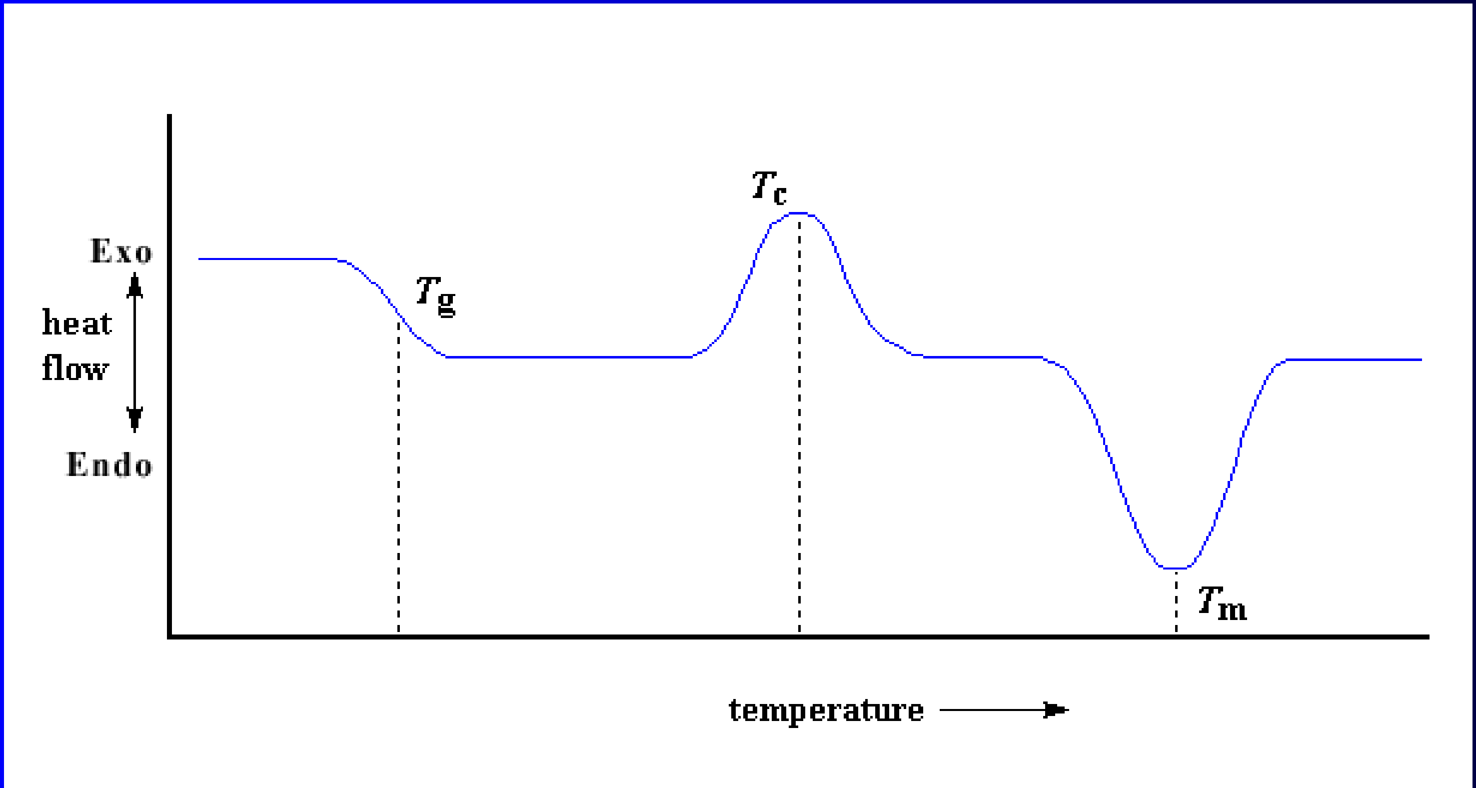
Heating a glass



DSC Data


heatflow [mW]
plastic spoon (PS)
milk bottle (PE/PP)
carpet fibre (PA6)
soda bottle (PETP)
100
200
300
Temperature [°C]

A DSC Plot for PET



Morphology

- Amorphous PET is formed by cooling the melt quickly
  - plastic beverage bottles are PET with a low degree of crystallinity
- By cooling slowly, more molecular diffusion occurs, chains become more ordered and crystalline domains form
  - PET with a high degree of crystallinity can be drawn into textile fibers and tire cords (dacron)