CHAPTER 14:
POLYMER STRUCTURES

ISSUES TO ADDRESS...

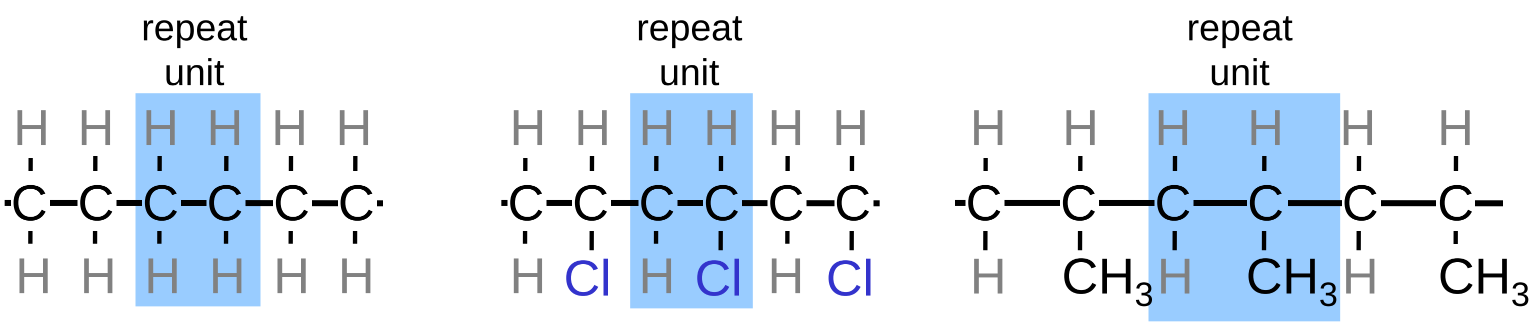
- What are the basic microstructural features?
- How are polymer properties effected by molecular weight?
- How do polymeric crystals accommodate the polymer chain?

Chapter 14 – Polymers

What is a polymer?

Poly — many

mer — repeat unit



Polyethylene (PE)   Polyvinyl chloride (PVC)   Polypropylene (PP)

Adapted from Fig. 14.2, *Callister 7e.*

Ancient Polymer History

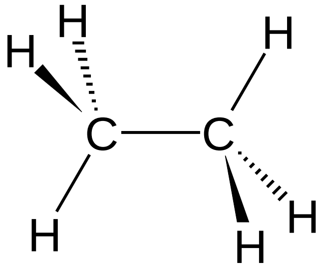
- Originally natural polymers were used
  - Wood
  - Cotton
  - Leather
  - Rubber
  - Wool
  - Silk

- Oldest known uses
  - Rubber balls used by Incas
  - Noah used pitch (a natural polymer) for the ark

Polymer Composition

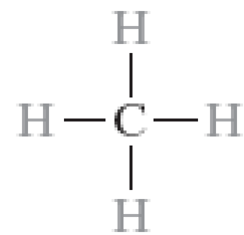
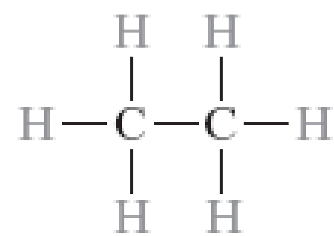
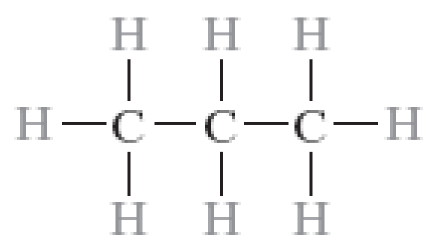
Most polymers are hydrocarbons
   – i.e. made up of H and C

- Saturated hydrocarbons
   – Each carbon bonded to four other atoms



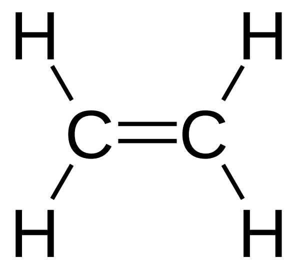
C_nH_{2n+2}

Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

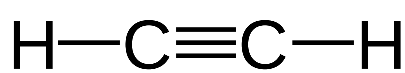
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

Unsaturated Hydrocarbons

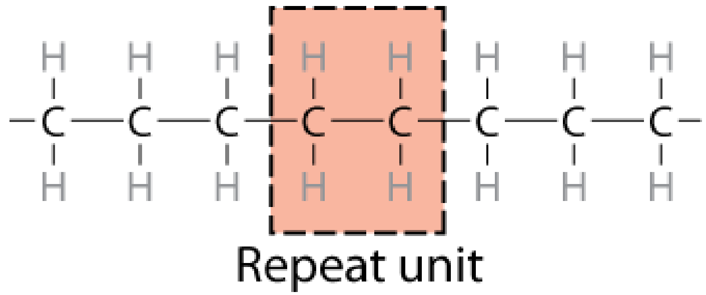
- Double & triple bonds relatively reactive – can form new bonds
  - Double bond – ethylene or ethene - C_nH_{2n}



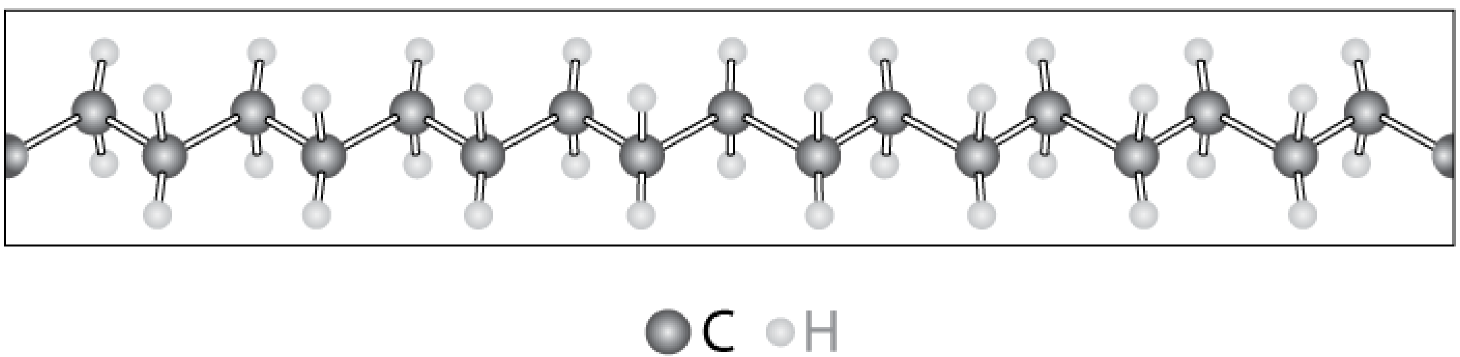
    - 4-bonds, but only 3 atoms bound to C's
  - Triple bond – acetylene or ethyne - C_nH_{2n-2}



Chemistry of Polymers



Adapted from Fig. 14.1, *Callister 7e.*



Note: polyethylene is just a long HC

- paraffin is short polyethylene

Bulk or Commodity Polymers

Table 14.3 **A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

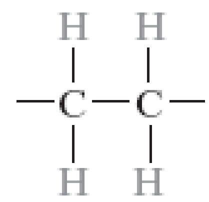
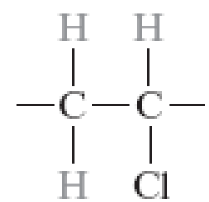
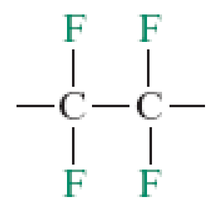
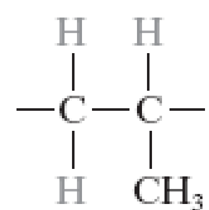
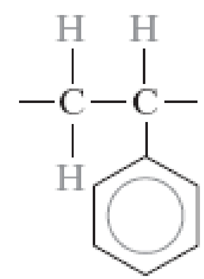
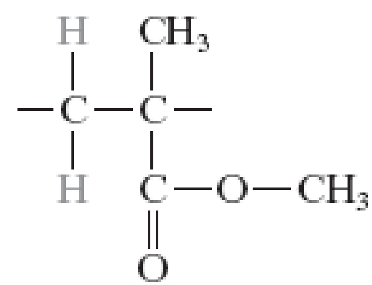
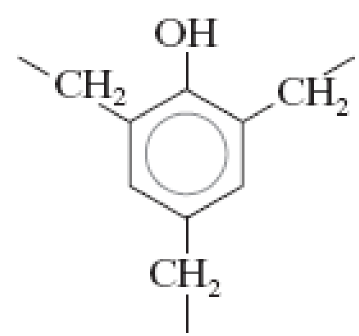
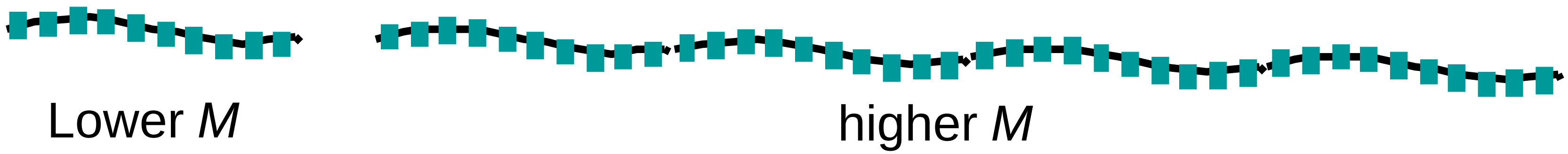
Polymer	*Repeat Unit*
Polyethylene (PE)	
Poly(vinyl chloride) (PVC)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	

Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	*Repeat Unit*
Polystyrene (PS)	
Poly(methyl methacrylate) (PMMA)	
Phenol-formaldehyde (Bakelite)	

MOLECULAR WEIGHT

- Molecular weight, M_i: Mass of a mole of chains.

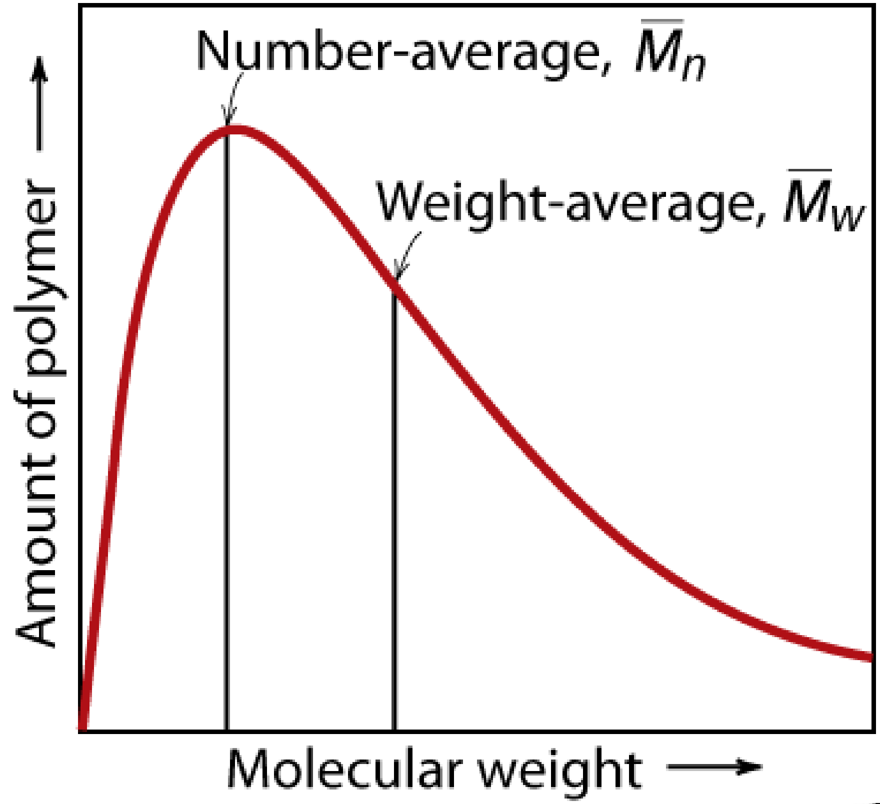


$$\bar{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

$$\bar{M}_n = \Sigma x_i M_i$$

$$\bar{M}_w = \Sigma w_i M_i$$

$\bar{M}_w$ is more sensitive to higher molecular weights



Adapted from Fig. 14.4, *Callister 7e.*

Molecular Weight Calculation

Example: average mass of a class

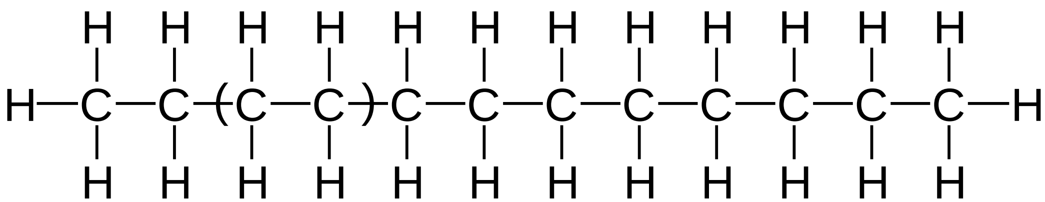
N_i	M_i	x_i	w_i
# of students	mass (lb)		
1	100	0.1	0.054
1	120	0.1	0.065
2	140	0.2	0.151
3	180	0.3	0.290
2	220	0.2	0.237
1	380	0.1	0.204
		$\overline{M}_n$	$\overline{M}_w$
		186 lb	216 lb

$$\overline{M}_n = \sum x_i M_i$$

$$\overline{M}_w = \sum w_i M_i$$

Degree of Polymerization, *n*

n = number of repeat units per chain



$n_i = 6$

$$n_n = \sum x_i n_i = \frac{\overline{M}_n}{\overline{m}} \qquad n_w = \sum w_i n_i = \frac{\overline{M}_w}{\overline{m}}$$

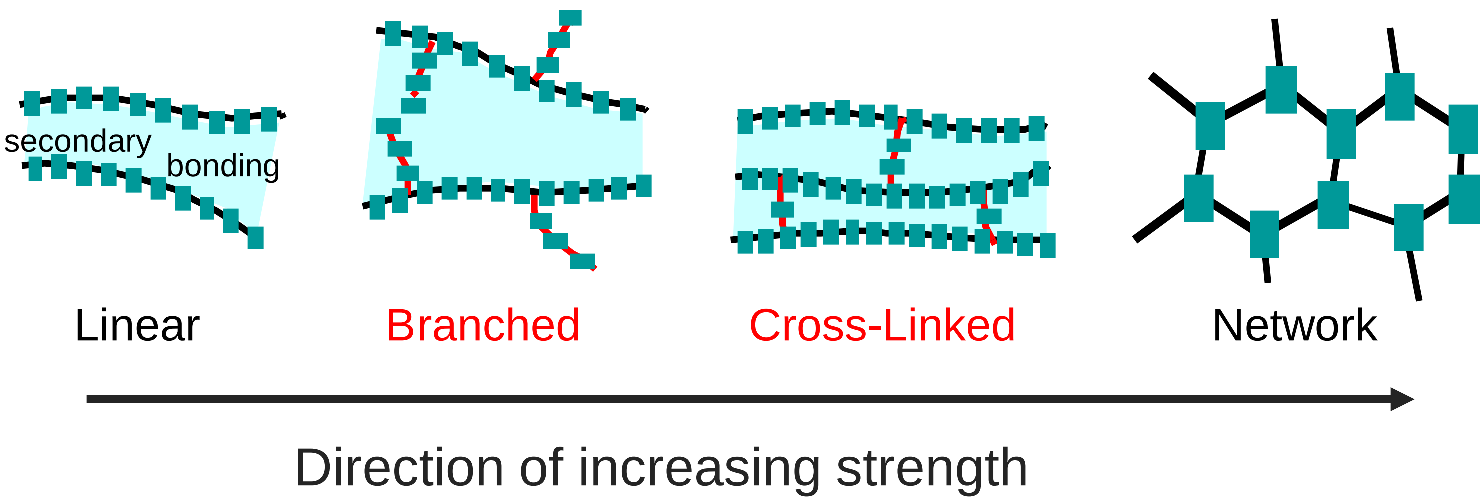
where $\overline{m} =$ average molecular weight of repeat unit

$$\overline{m} = \Sigma f_i m_i$$

Chain fraction (f_i) — mol. wt of repeat unit i (m_i)

Molecular Structures

- Covalent chain configurations and strength:

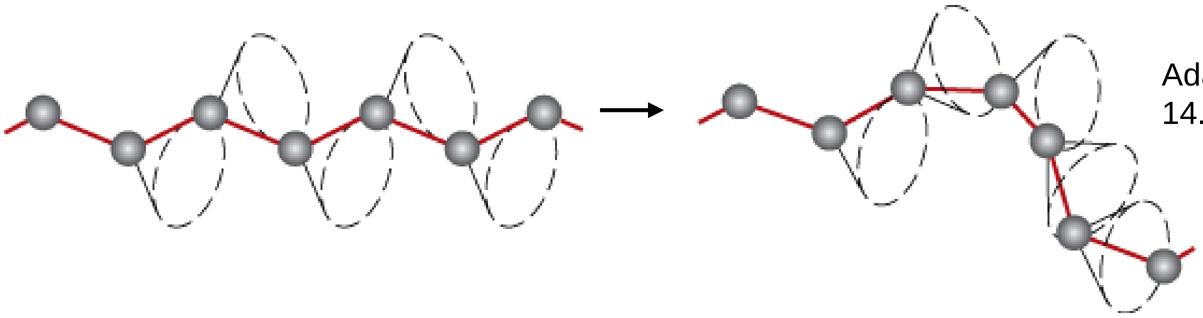


Adapted from Fig. 14.7, *Callister 7e.*

Polymers – Molecular Shape

Conformation – Molecular orientation can be changed by rotation around the bonds

– note: no bond breaking needed



Adapted from Fig. 14.5, *Callister 7e.*

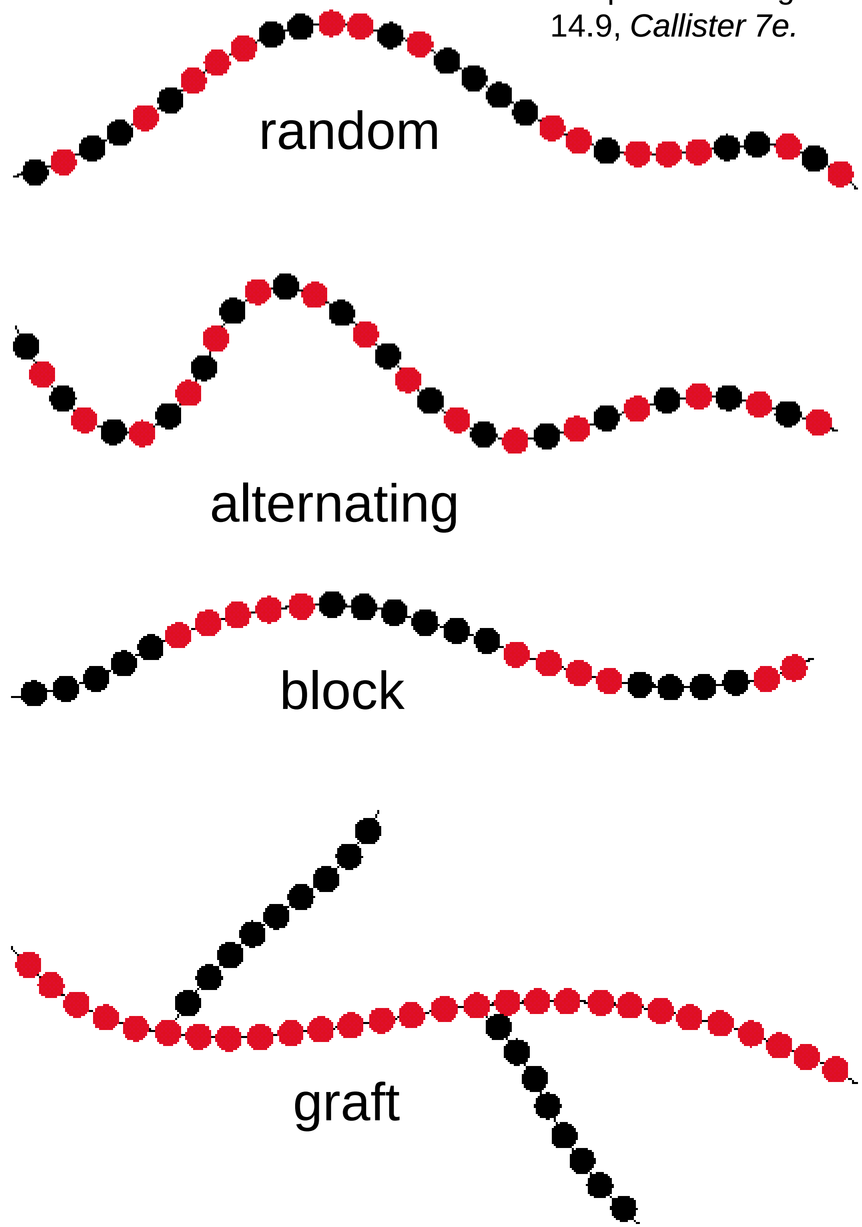
Copolymers

two or more monomers polymerized together

- random – A and B randomly vary in chain
- alternating – A and B alternate in polymer chain
- block – large blocks of A alternate with large blocks of B
- graft – chains of B grafted on to A backbone

A – ● B – ●

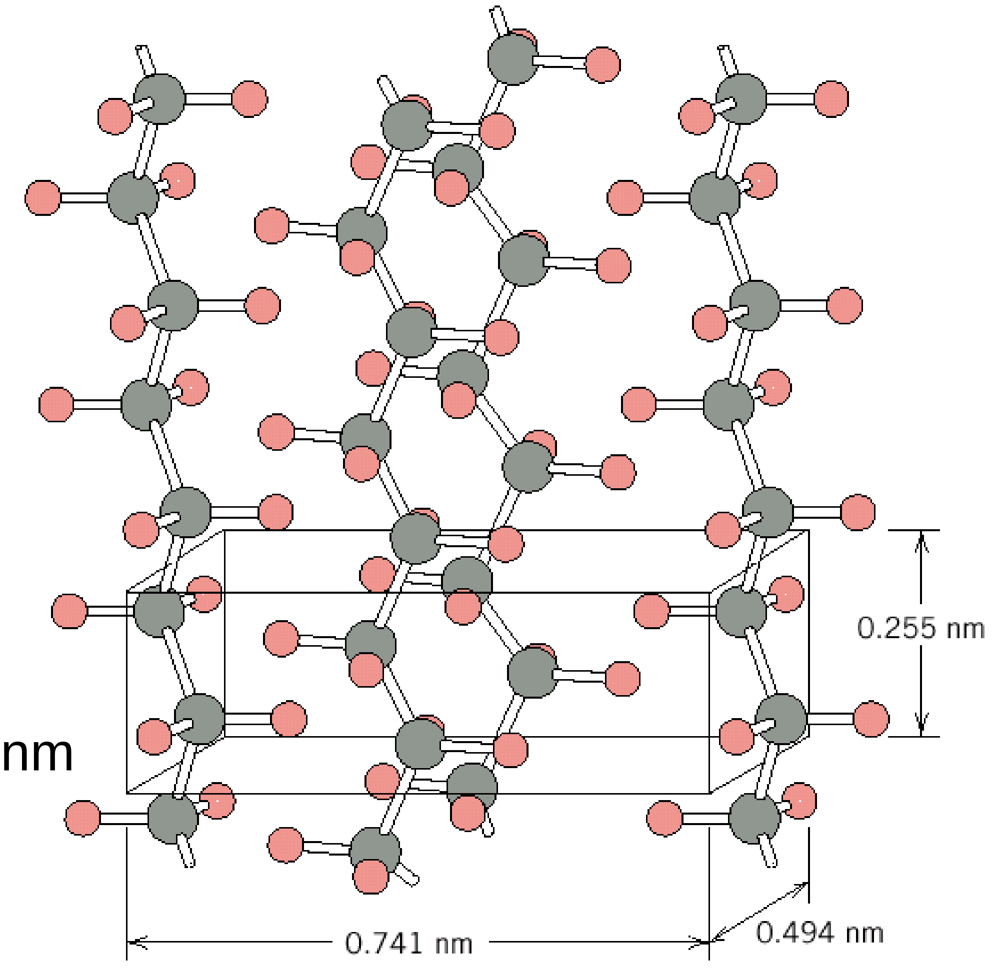
Adapted from Fig. 14.9, *Callister 7e.*



Polymer Crystallinity

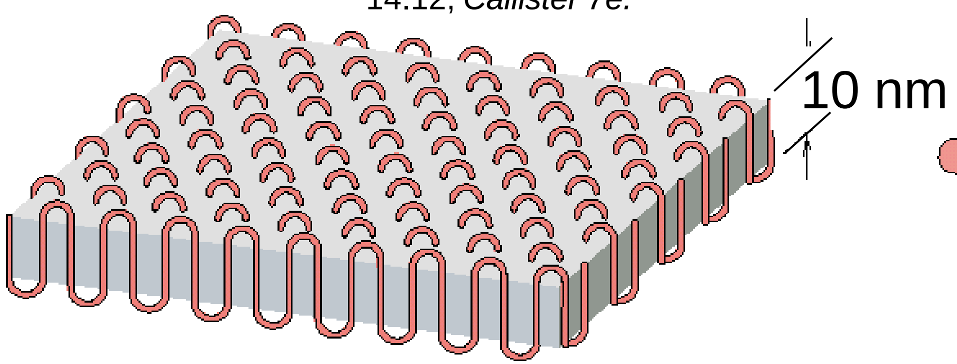
Adapted from Fig. 14.10, *Callister 7e.*

Ex: polyethylene unit cell



- Crystals must contain the polymer chains in some way
  - Chain folded structure

Adapted from Fig. 14.12, *Callister 7e.*

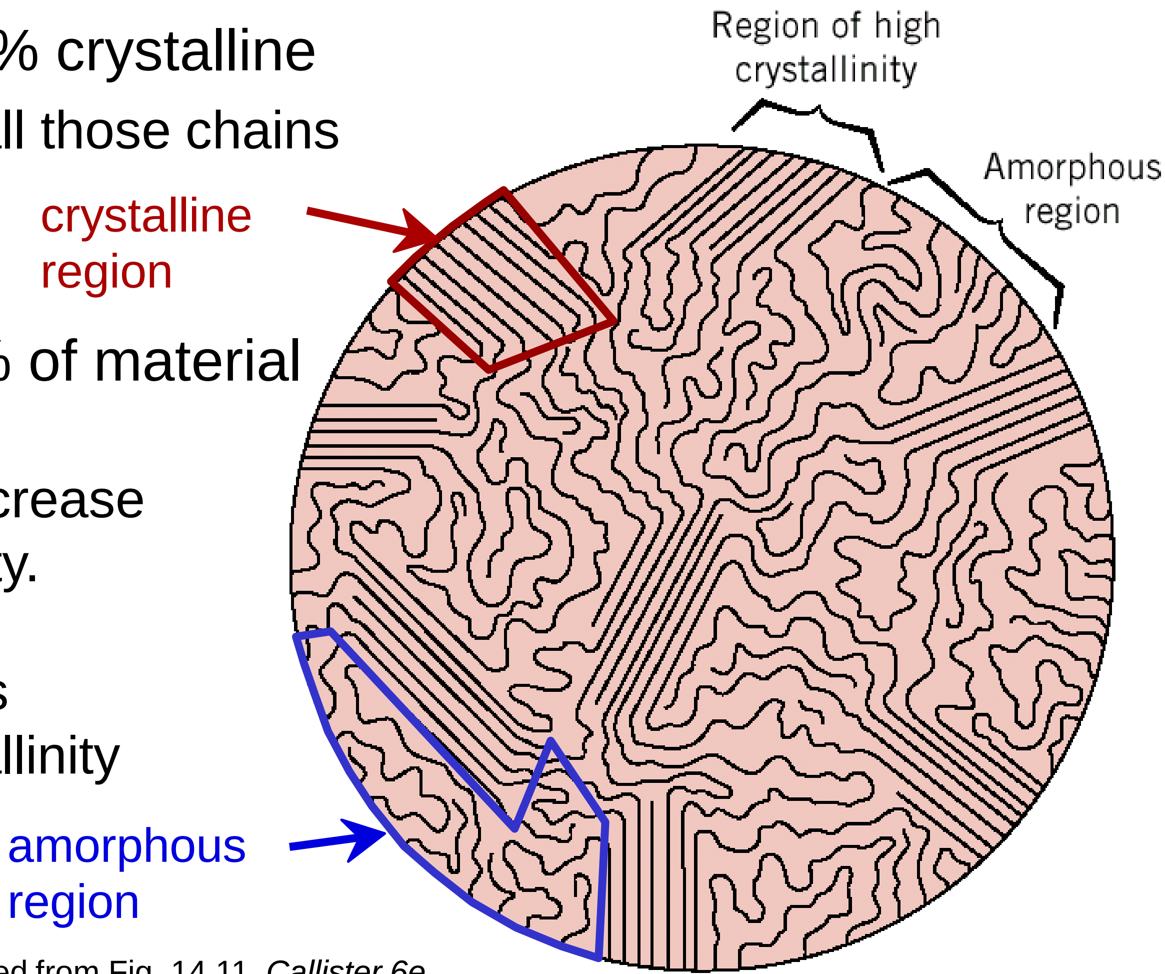


Polymer Crystallinity

Polymers rarely 100% crystalline

- Too difficult to get all those chains aligned

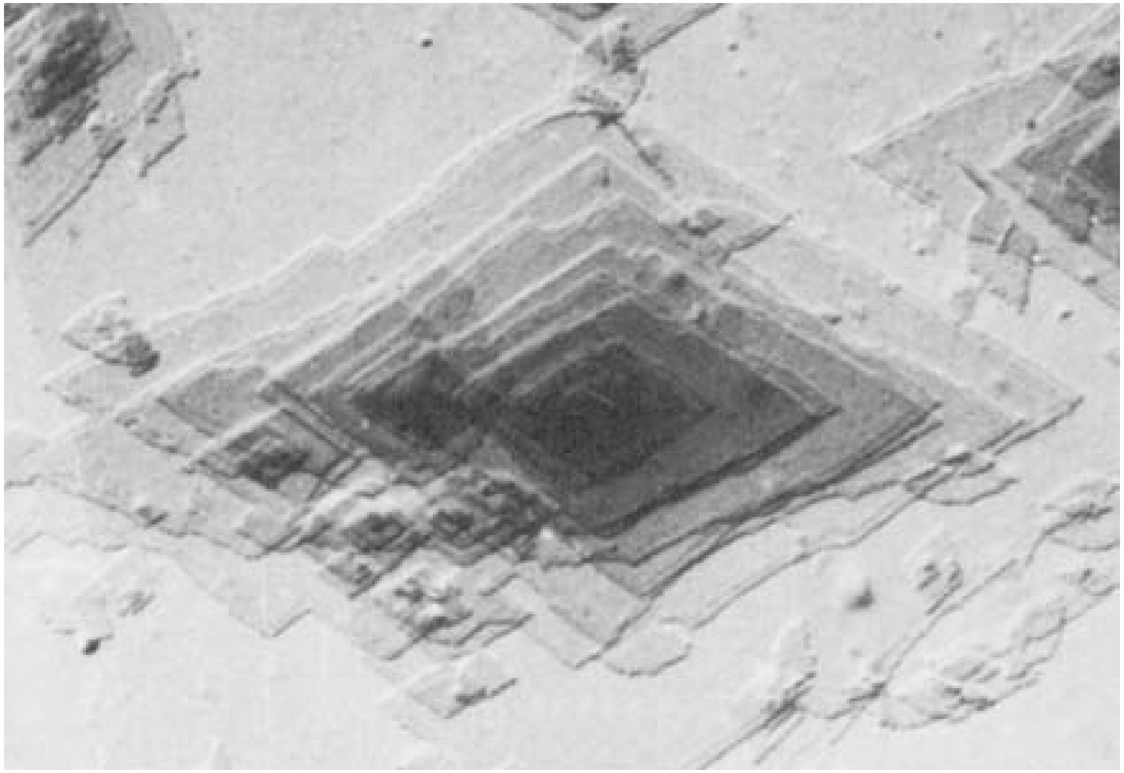
- % Crystallinity: % of material that is crystalline.
  -- *TS* and *E* often increase with % crystallinity.
  -- Annealing causes crystalline regions to grow. % crystallinity increases.



Adapted from Fig. 14.11, *Callister 6e.* (Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

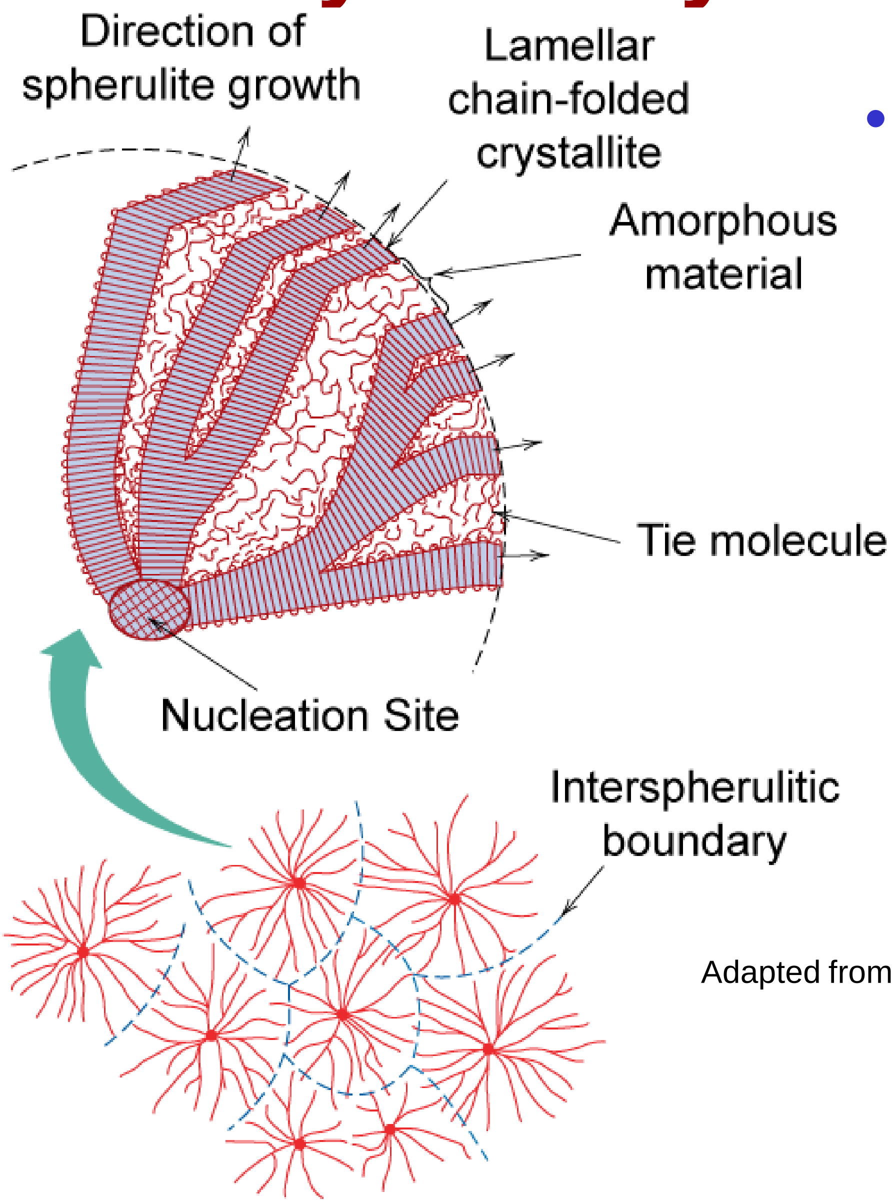
Polymer Crystal Forms

- Single crystals – only if slow careful growth



Adapted from Fig. 14.11, *Callister 7e.*

Polymer Crystal Forms

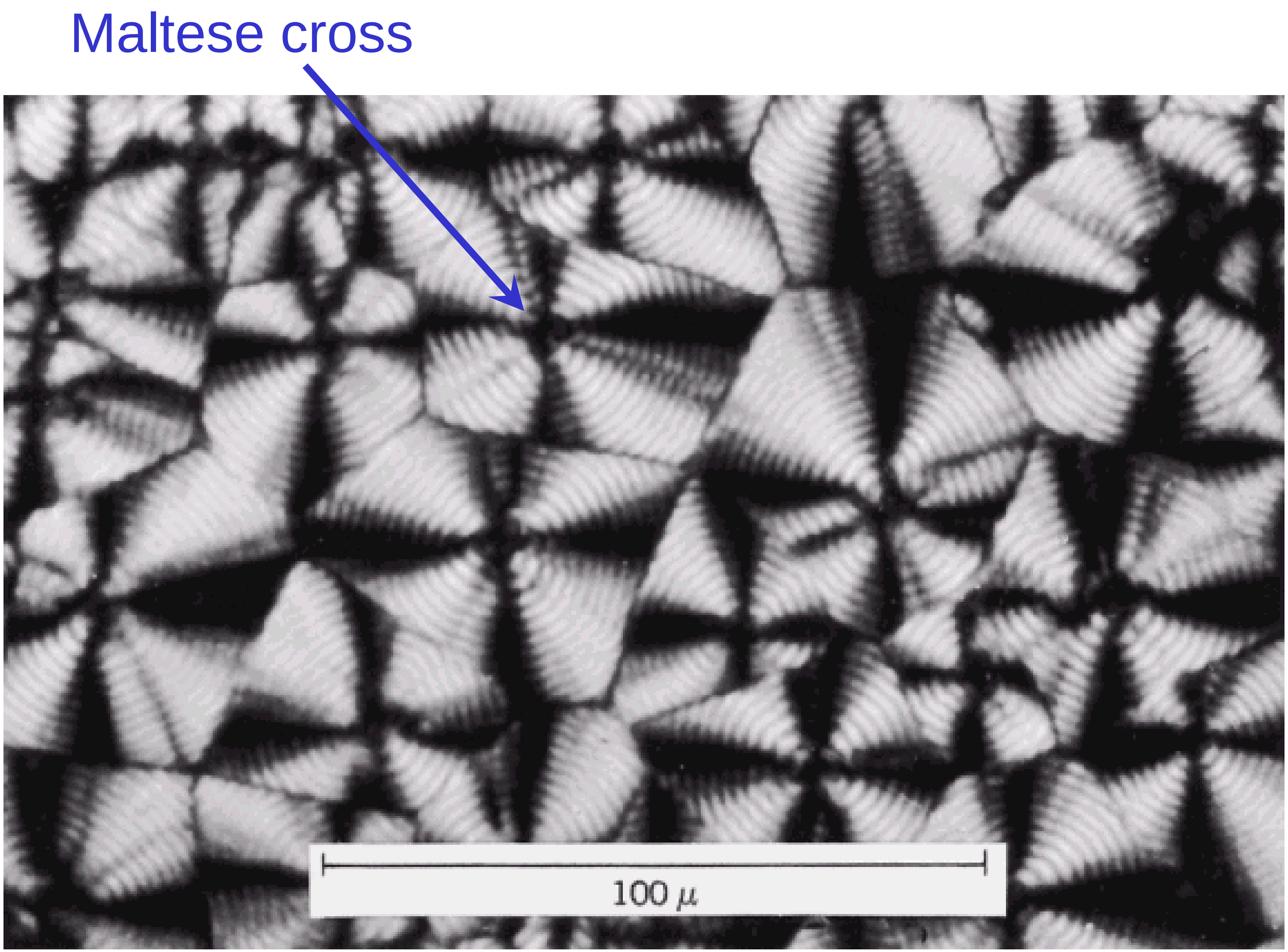


Nuc

- Spherulites – fast growth – forms lamellar (layered) structures

Adapted from Fig. 14.13, *Callister 7e.*

Spherulites – crossed polarizers



Adapted from Fig. 14.14, *Callister 7e.*

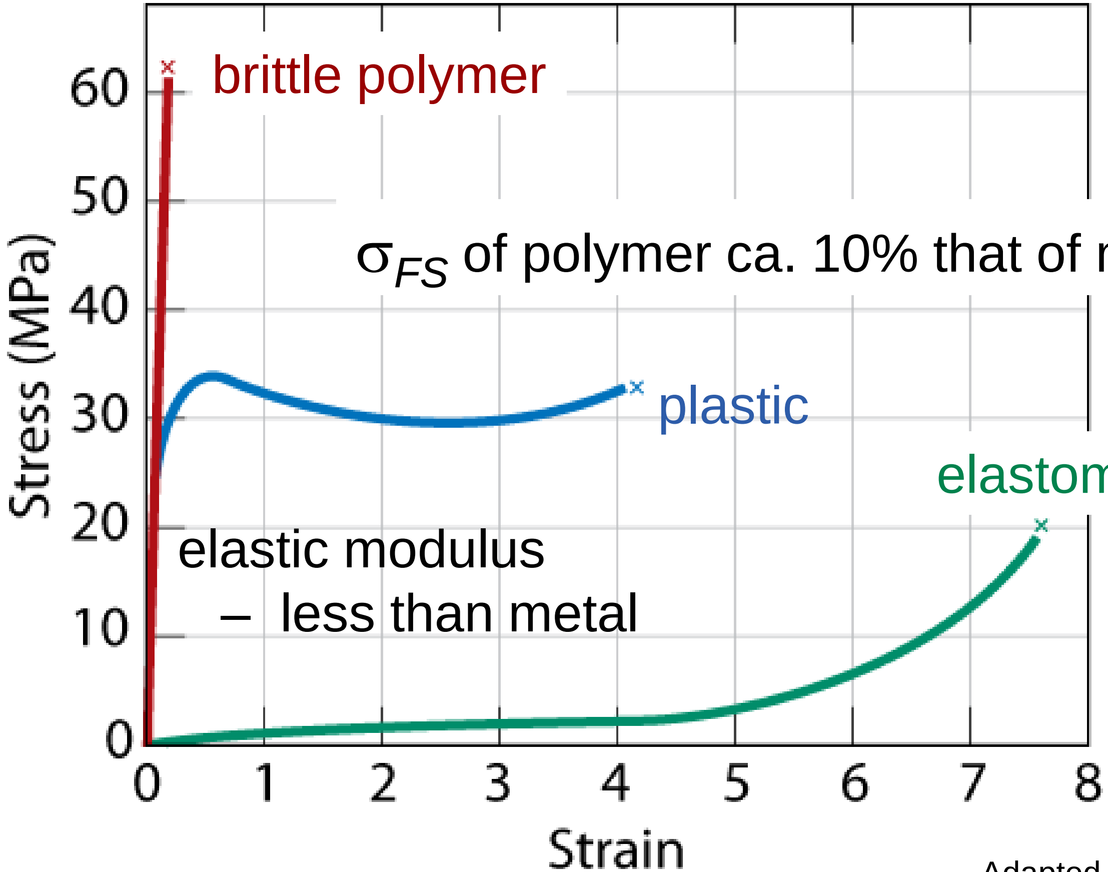
Characteristics, Applications & Processing of Polymers

ISSUES TO ADDRESS...

- What are the tensile properties of polymers and how are they affected by basic microstructural features?
- Hardening, anisotropy, and annealing in polymers.
- How does the elevated temperature mechanical response of polymers compare to ceramics and metals?
- What are the primary polymer processing methods?

Mechanical Properties

- i.e. stress-strain behavior of polymers



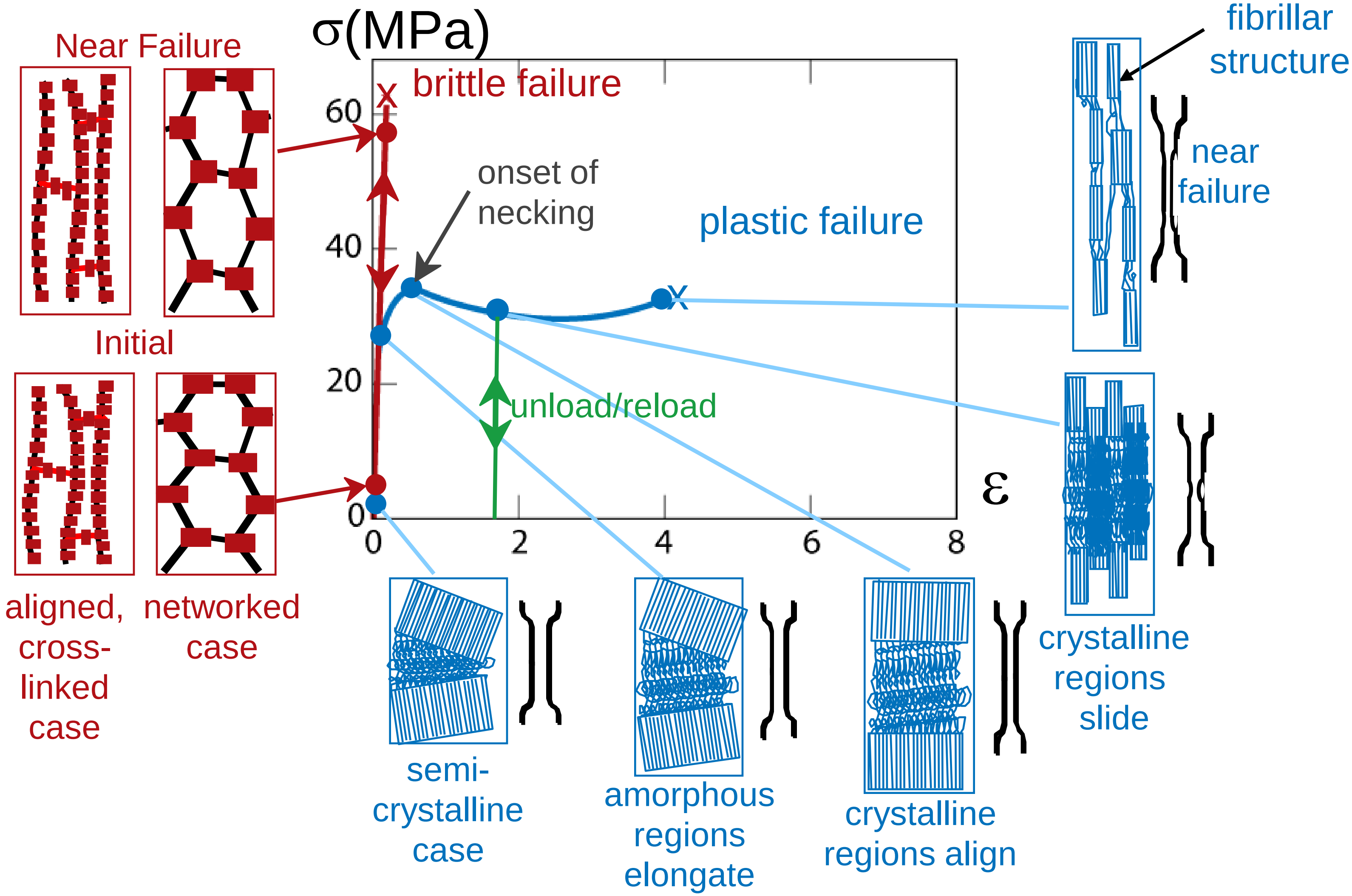
σ_{FS} of polymer ca. 10% that of metals

elastic modulus
– less than metal

Adapted from Fig. 15.1, *Callister 7e*.

Strains – deformations > 1000% possible
(for metals, maximum strain ca. 10% or less)

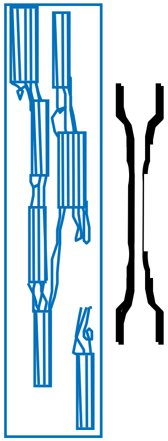
Tensile Response: Brittle & Plastic



Stress-strain curves adapted from Fig. 15.1, *Callister 7e.* Inset figures along plastic response curve adapted from Figs. 15.12 & 15.13, *Callister 7e*. (Figs. 15.12 & 15.13 are from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

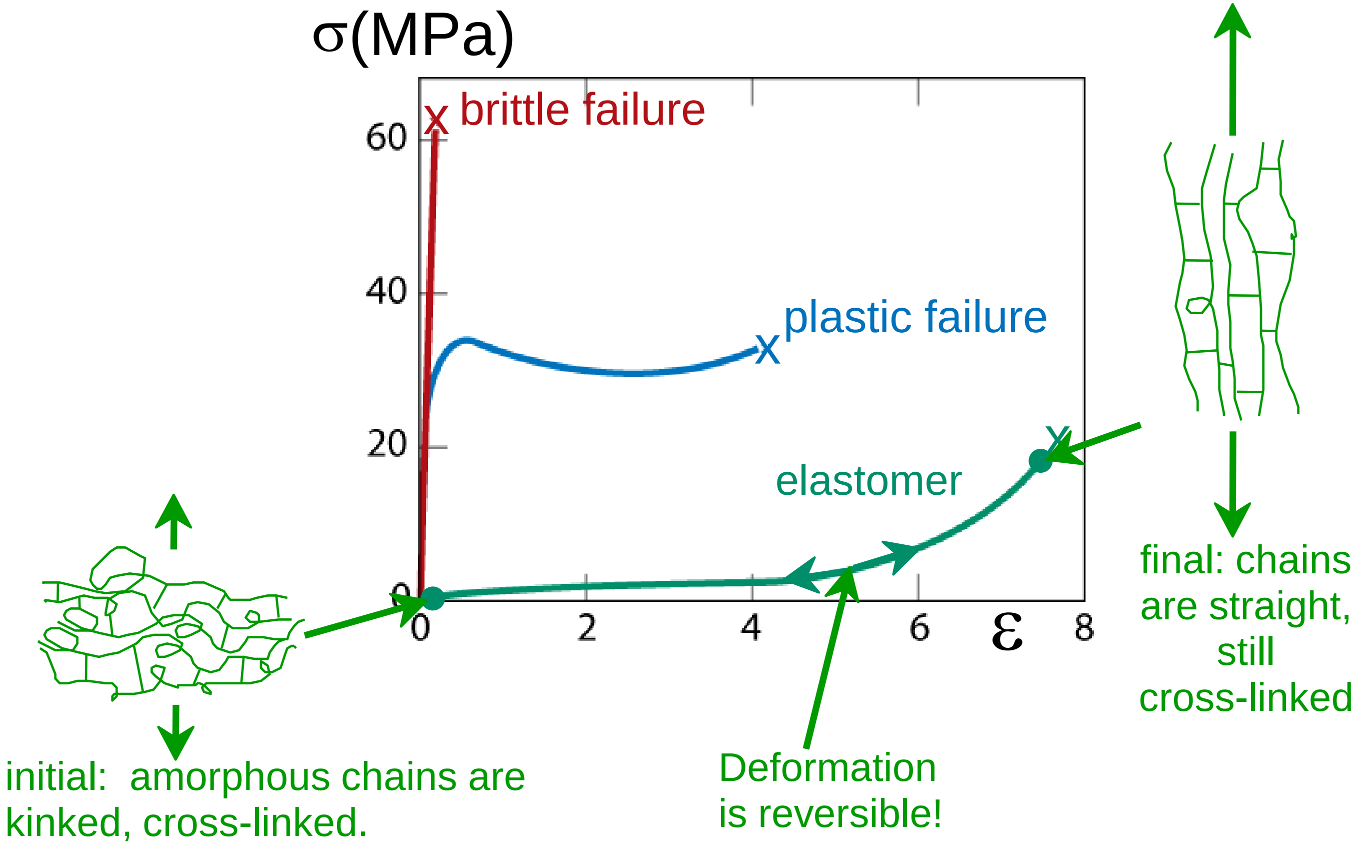
Predeformation by Drawing

- Drawing…(ex: monofilament fishline)
  -- stretches the polymer prior to use
  -- aligns chains in the stretching direction
- Results of drawing:
  -- increases the elastic modulus (*E*) in the stretching direction
  -- increases the tensile strength (*TS*) in the stretching direction
  -- decreases ductility (%*EL*)
- Annealing after drawing...
  -- decreases alignment
  -- reverses effects of drawing.
- Compare to cold working in metals!



Adapted from Fig. 15.13, *Callister 7e*. (Fig. 15.13 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

Tensile Response: Elastomer Case

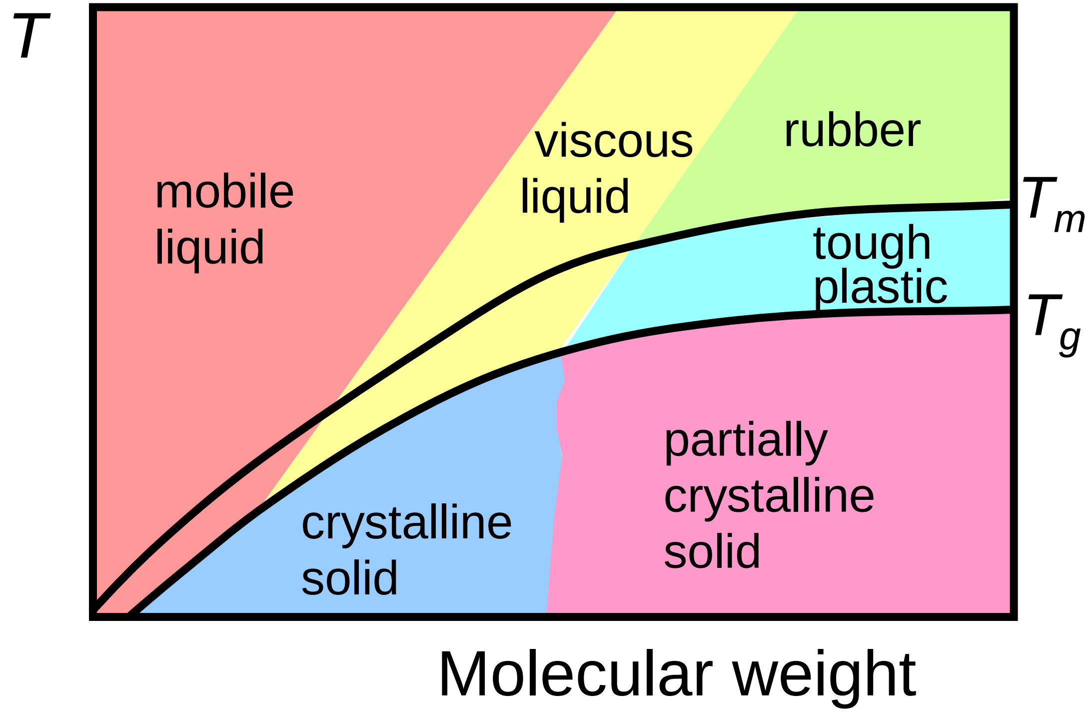


Stress-strain curves adapted from Fig. 15.1, *Callister 7e.* Inset figures along elastomer curve (green) adapted from Fig. 15.15, *Callister 7e*. (Fig. 15.15 is from Z.D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd ed., John Wiley and Sons, 1987.)

- Compare to responses of other polymers:
  - -- brittle response (aligned, crosslinked & networked polymer)
  - -- plastic response (semi-crystalline polymers)

Thermoplastics vs. Thermosets

- Thermoplastics:
  - -- little crosslinking
  - -- ductile
  - -- soften w/heating
  - -- polyethylene
    polypropylene
    polycarbonate
    polystyrene



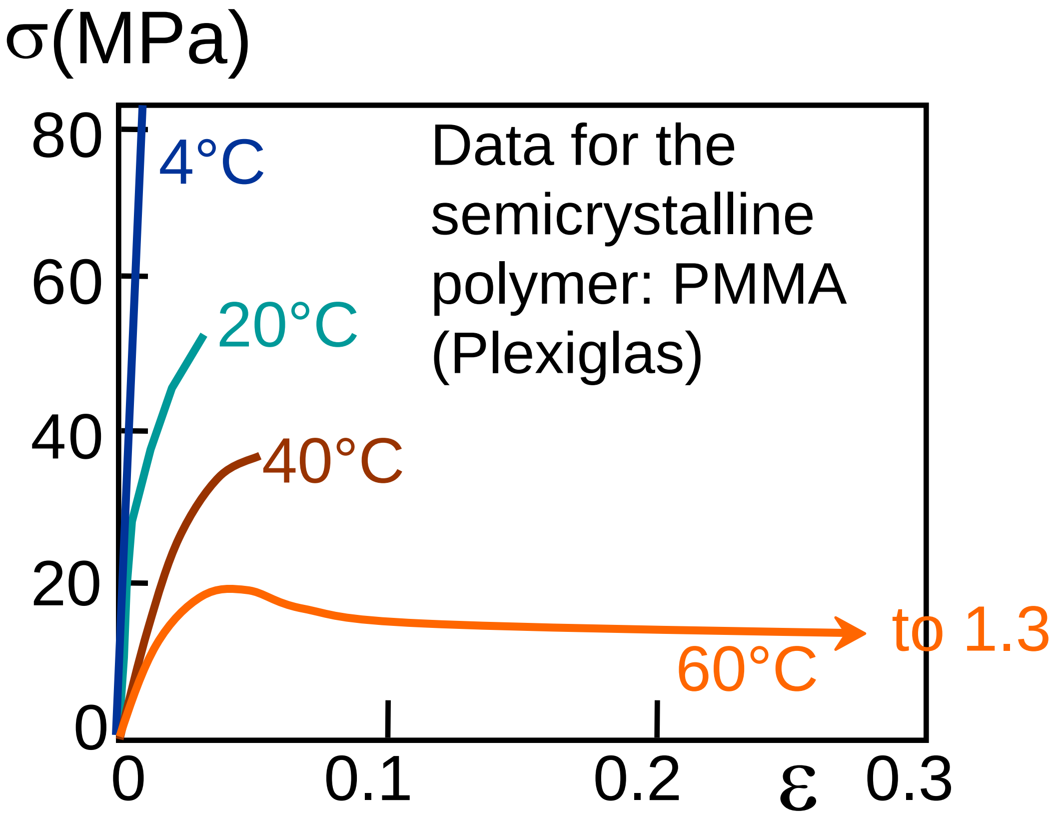
Adapted from Fig. 15.19, *Callister 7e*. (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

- Thermosets:
  - -- large crosslinking
    (10 to 50% of mers)
  - -- hard and brittle
  - -- do NOT soften w/heating
  - -- vulcanized rubber, epoxies,
    polyester resin, phenolic resin

T and Strain Rate: Thermoplastics

- Decreasing *T*...
  -- increases *E*
  -- increases *TS*
  -- decreases %*EL*

- Increasing strain rate...
  -- same effects as decreasing *T*.

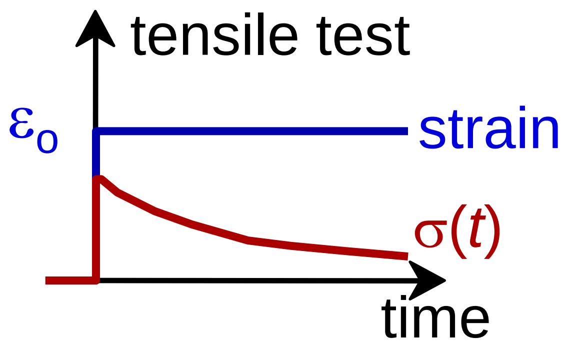


Adapted from Fig. 15.3, *Callister 7e*. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)

Time Dependent Deformation

- Stress relaxation test:

  -- strain to ε_o and hold.
  -- observe decrease in stress with time.

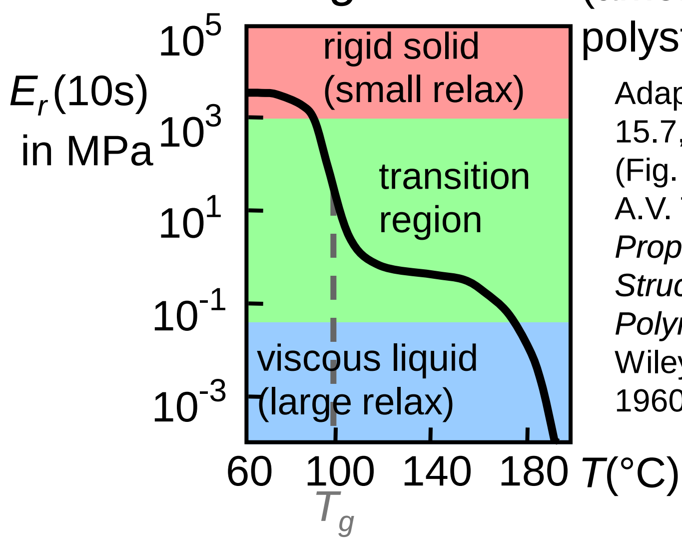


- Relaxation modulus:

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_o}$$

- Data: Large drop in E_r for $T > T_g$.

(amorphous polystyrene)



Adapted from Fig. 15.7, *Callister 7e*. (Fig. 15.7 is from A.V. Tobolsky, *Properties and Structures of Polymers*, John Wiley and Sons, Inc., 1960.)

- Sample T_g(°C) values:

PE (low density)	- 110
PE (high density)	- 90
PVC	+ 87
PS	+100
PC	+150

Selected values from Table 15.2, *Callister 7e*.

Polymer Additives

Improve mechanical properties, processability, durability, etc.

- Fillers
  - Added to improve tensile strength & abrasion resistance, toughness & decrease cost
  - ex: carbon black, silica gel, wood flour, glass, limestone, talc, etc.
- Plasticizers
  - Added to reduce the glass transition temperature T_g
  - commonly added to PVC - otherwise it is brittle

Polymer Additives

- Stabilizers
  - Antioxidants
  - UV protectants
- Lubricants
  - Added to allow easier processing
  - “slides” through dies easier – ex: Na stearate
- Colorants
  - Dyes or pigments
- Flame Retardants
  - Cl/F & B

Processing of Plastics

- Thermoplastic –
  - can be reversibly cooled & reheated, i.e. recycled
  - heat till soft, shape as desired, then cool
  - ex: polyethylene, polypropylene, polystyrene, etc.
- Thermoset
  - when heated forms a network
  - degrades (not melts) when heated
  - mold the prepolymer then allow further reaction
  - ex: urethane, epoxy

Summary

- General drawbacks to polymers:
  - -- E, σ_y, K_c, $T_{application}$ are generally small.
  - -- Deformation is often T and time dependent.
  - -- Result: polymers benefit from composite reinforcement.
- Thermoplastics (PE, PS, PP, PC):
  - -- Smaller E, σ_y, $T_{application}$
  - -- Larger K_c
  - -- Easier to form and recycle
- Elastomers (rubber):
  - -- Large reversible strains!
- Thermosets (epoxies, polyesters):
  - -- Larger E, σ_y, $T_{application}$
  - -- Smaller K_c

Table 15.3 *Callister 7e*:

Good overview of applications and trade names of polymers.