Chapter 14 & Chapter 15: Polymer Structures and Properties

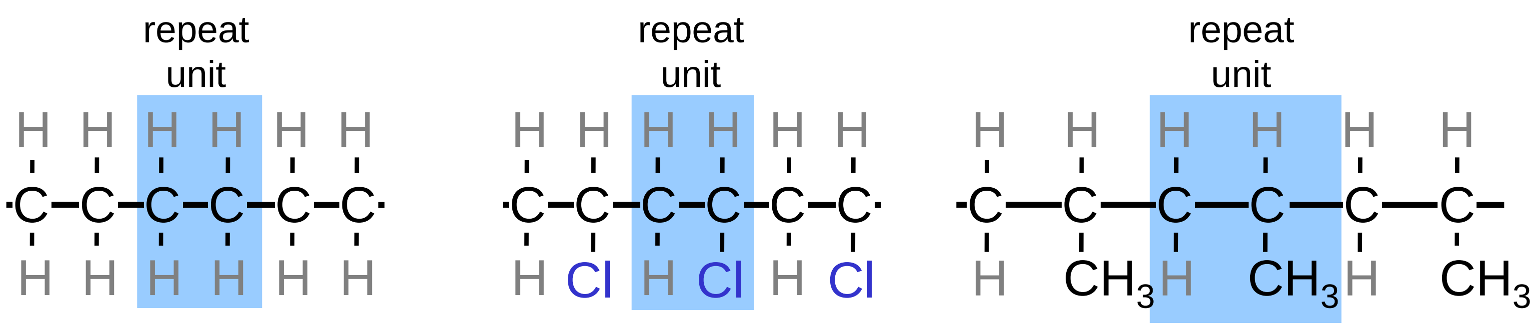
ISSUES TO ADDRESS...

- What are the general structural and chemical characteristics of polymer molecules?
- How is the crystalline state in polymers different from that in metals and ceramics ?
- What are the tensile properties of polymers and how are they affected by basic microstructural features?

What is a Polymer?

Poly — many

mer — repeat unit



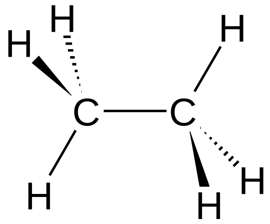
Polyethylene (PE) | Poly(vinyl chloride) (PVC) | Polypropylene (PP)

Adapted from Fig. 14.2, *Callister & Rethwisch 8e.*

Polymer Composition

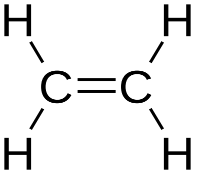
Most polymers are hydrocarbons
– i.e., made up of H and C

- Saturated hydrocarbons
  - Each carbon singly bonded to four other atoms
  - Example:
    - Ethane, C_2H_6



- Unsaturated hydrocarbons

- Double & triple bonds somewhat unstable – can form new bonds
  - Double bond –ethylene - C_2H_4

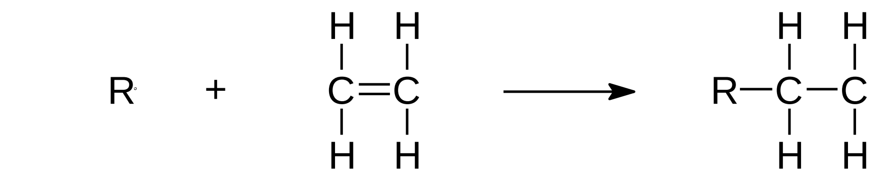


  - Triple bond – acetylene - C_2H_2

$$H-C\equiv C-H$$

Polymerization

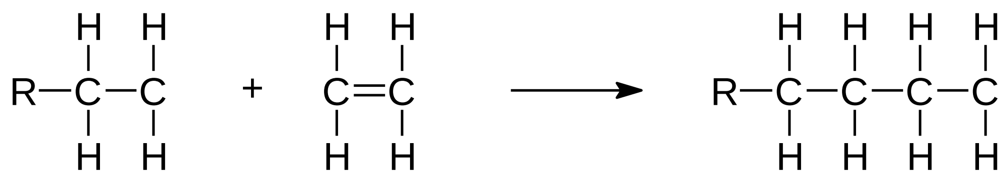
- Free radical polymerization



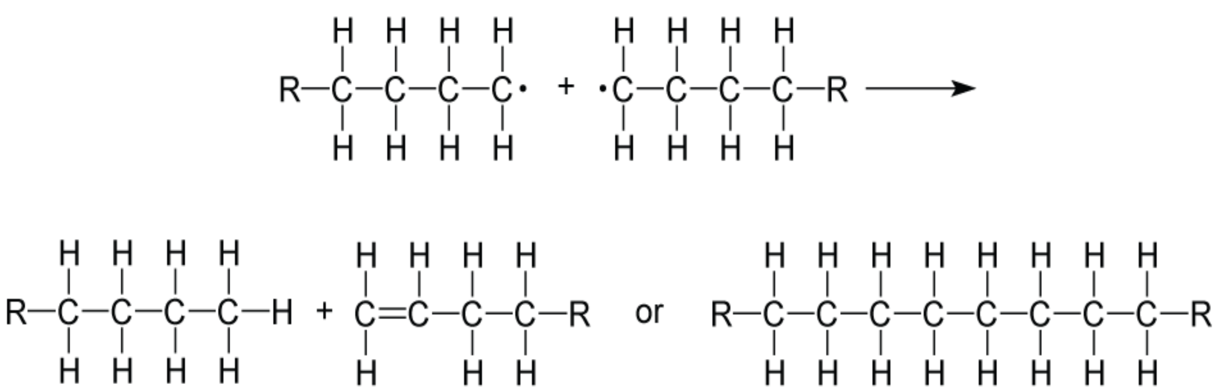
free radical

monomer (ethylene)

initiation



propagation

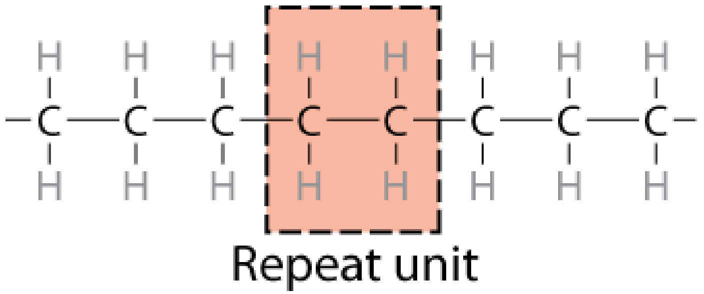


termination

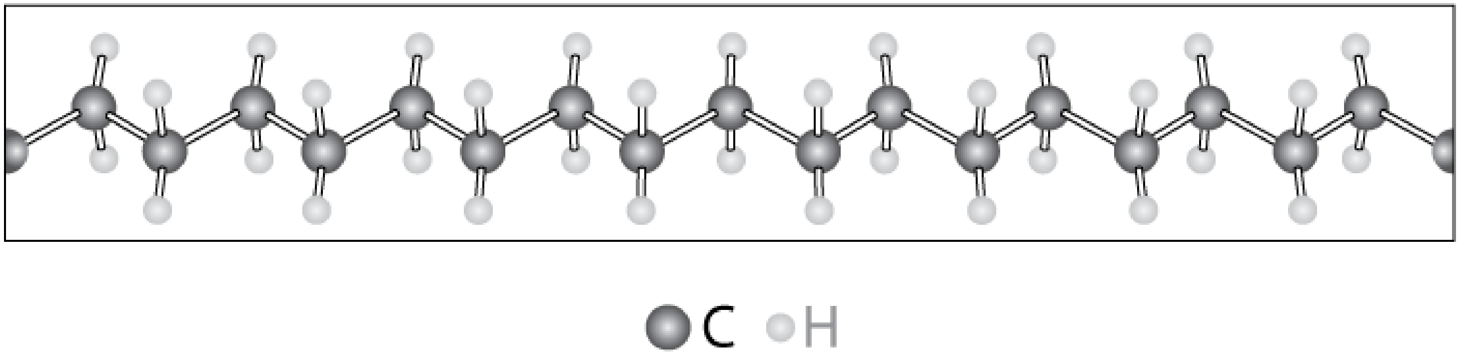
Disproportionation

Combination

Structure of Polyethylene



Adapted from Fig. 14.1, *Callister & Rethwisch 8e.*



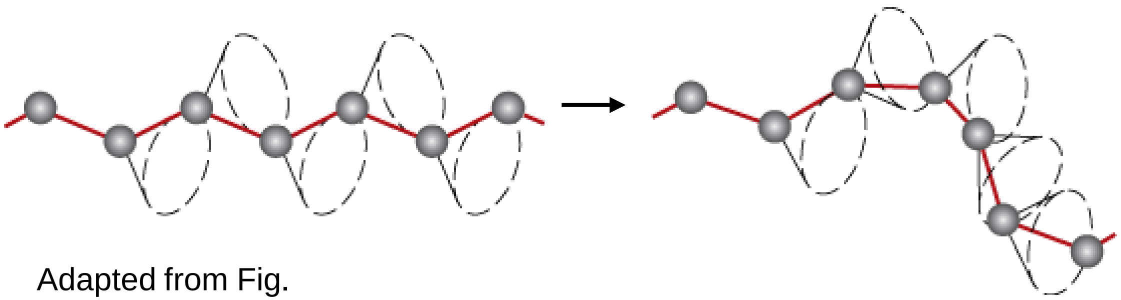
Note: polyethylene is a long-chain hydrocarbon

- paraffin wax for candles is short polyethylene

Polymers – Molecular Shape

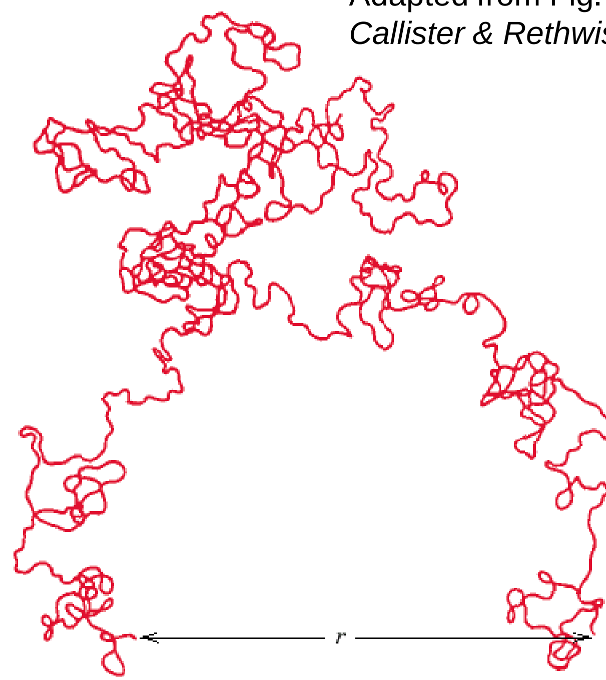
Molecular Shape (or Conformation) – chain bending and twisting are possible by rotation of carbon atoms around their chain bonds

– note: not necessary to break chain bonds to alter molecular shape

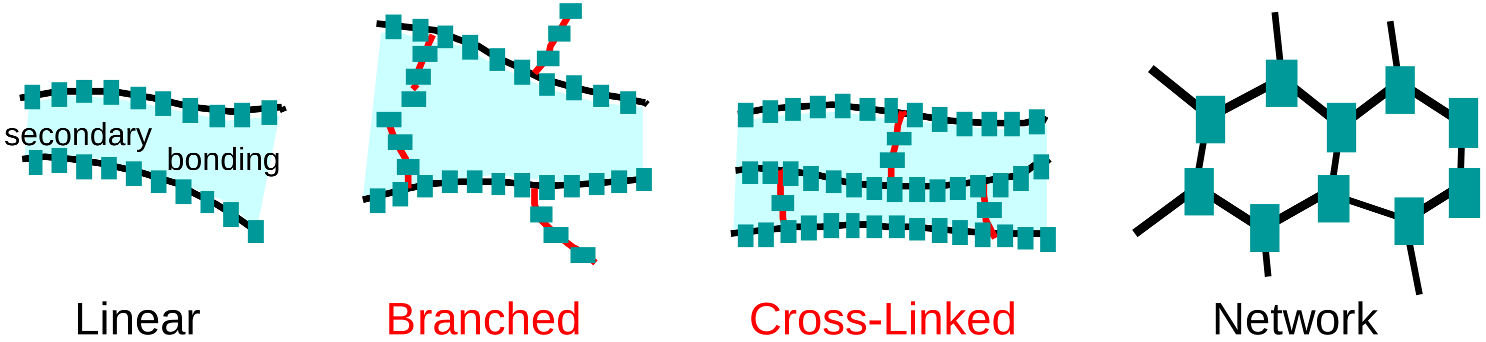


Adapted from Fig. 14.5, *Callister & Rethwisch 8e.*

Adapted from Fig. 14.6, *Callister & Rethwisch 8e.*



Polymers : Molecular Structures



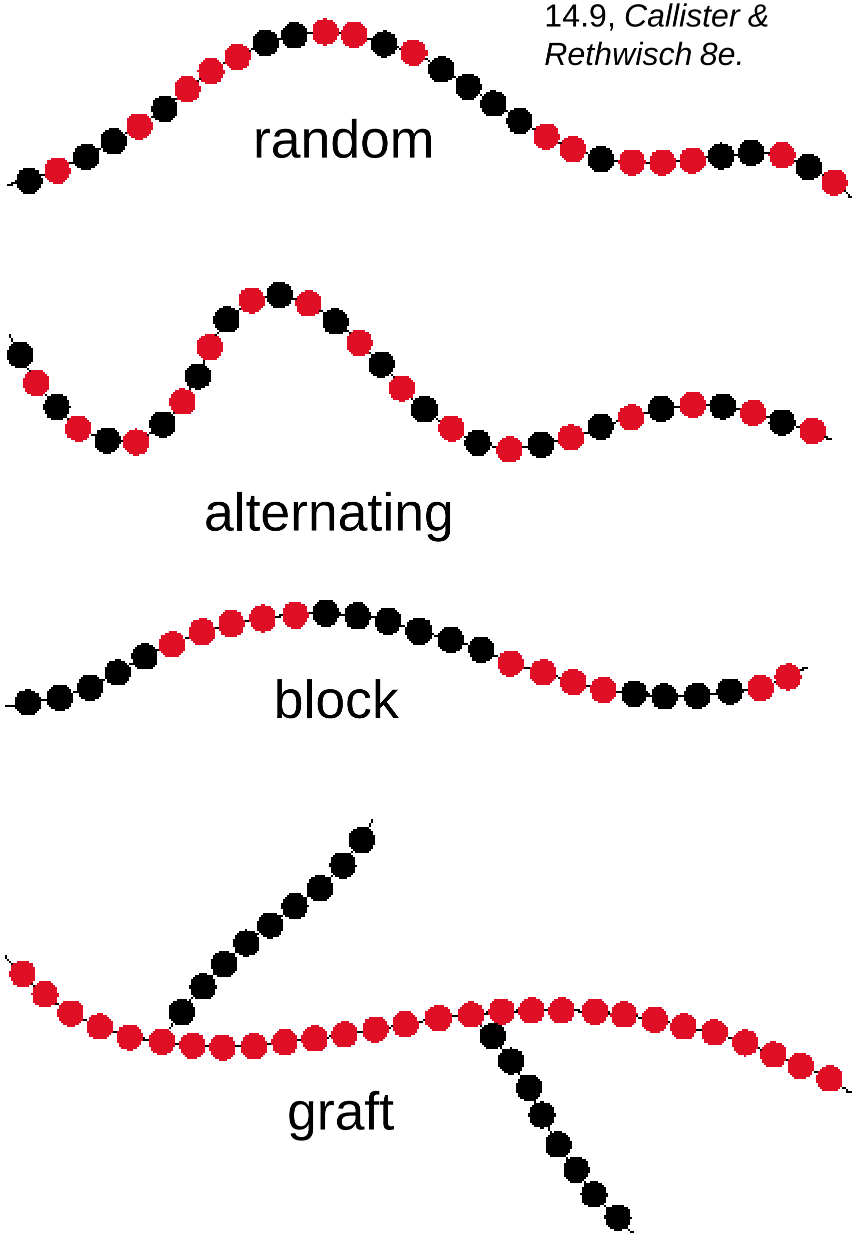
Adapted from Fig. 14.7, *Callister & Rethwisch 8e.*

Copolymers

Adapted from Fig. 14.9, *Callister & Rethwisch 8e.*

two or more monomers polymerized together

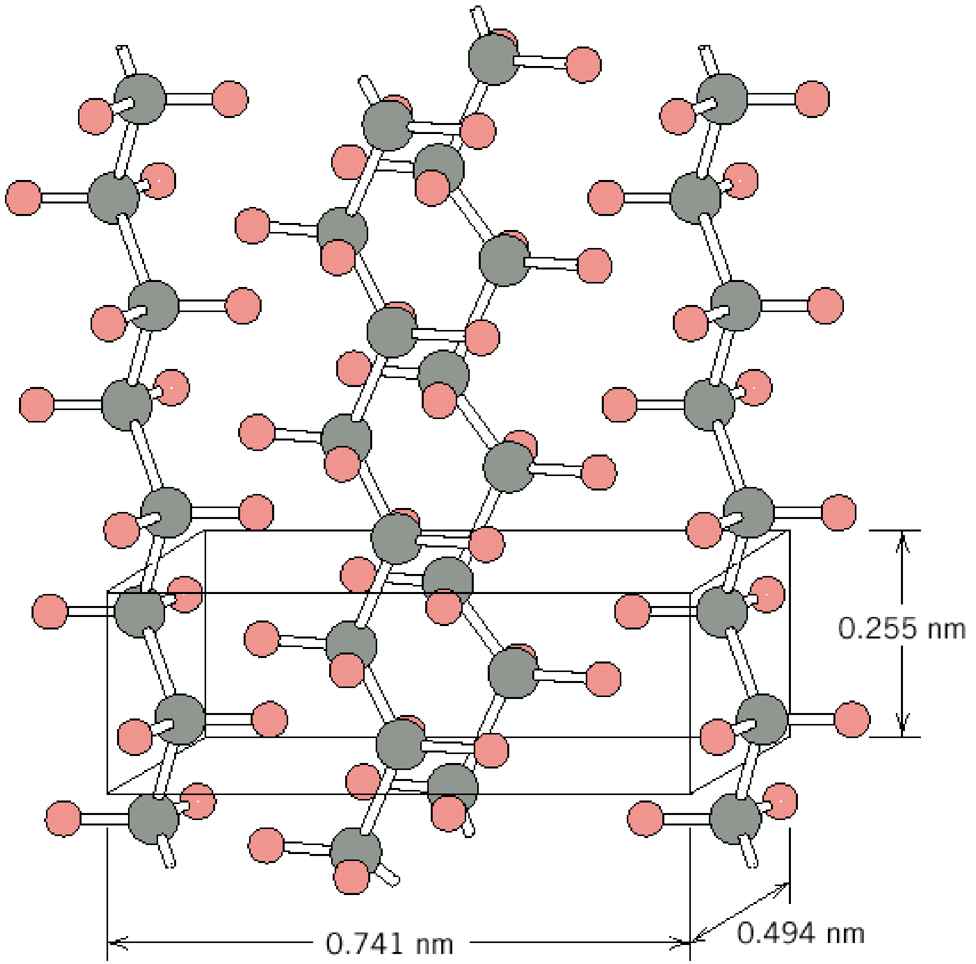
- random – A and B randomly positioned along chain
- alternating – A and B alternate in polymer chain
- block – large blocks of A units alternate with large blocks of B units
- graft – chains of B units grafted onto A backbone



Crystallinity in Polymers

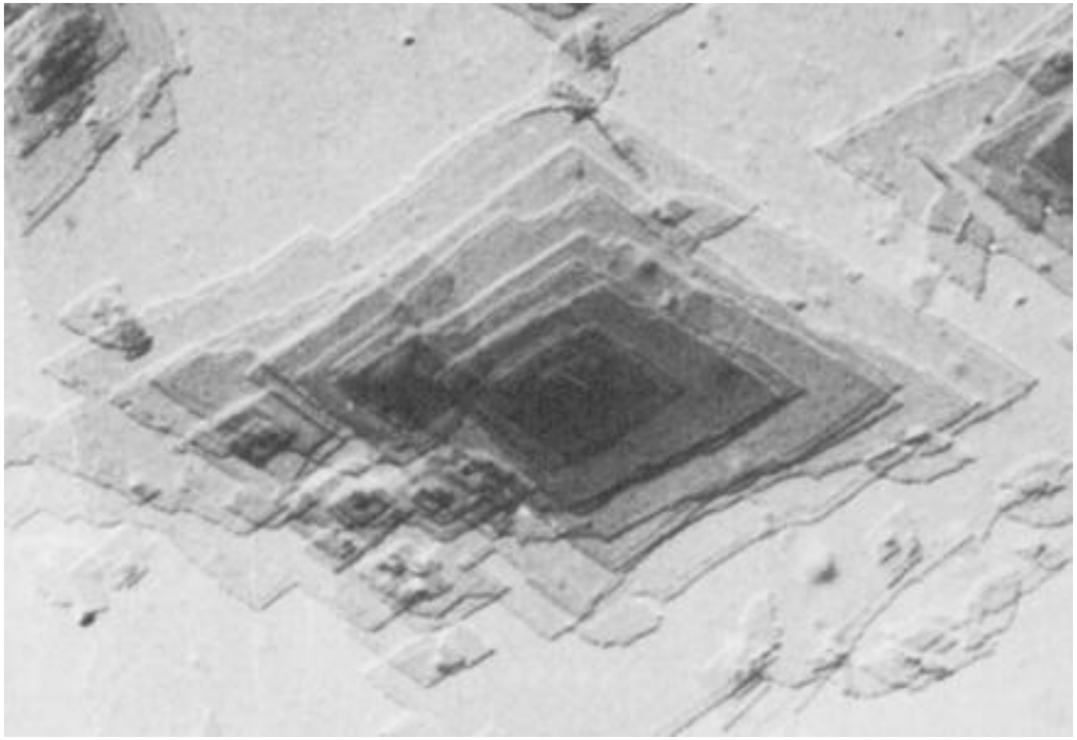
Adapted from Fig. 14.10, *Callister & Rethwisch 8e.*

- Ordered atomic arrangements involving molecular chains
- Crystal structures in terms of unit cells
- Example shown
  - polyethylene unit cell



Polymer Single Crystals

- Electron micrograph – multilayered single crystals (chain-folded layers) of polyethylene
- Single crystals – only for slow and carefully controlled growth rates

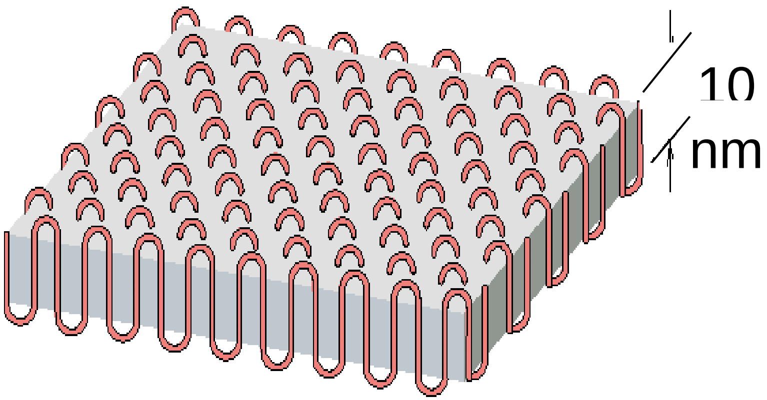


Adapted from Fig. 14.11, *Callister & Rethwisch 8e.*

Polymer Crystallinity

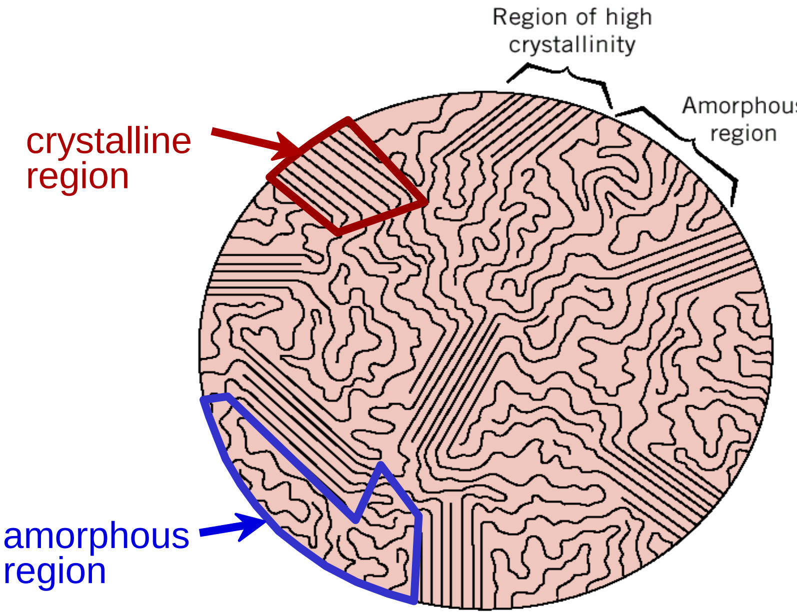
- Crystalline regions
  - thin platelets with chain folds at faces
  - Chain folded structure

Adapted from Fig. 14.12, *Callister & Rethwisch 8e.*

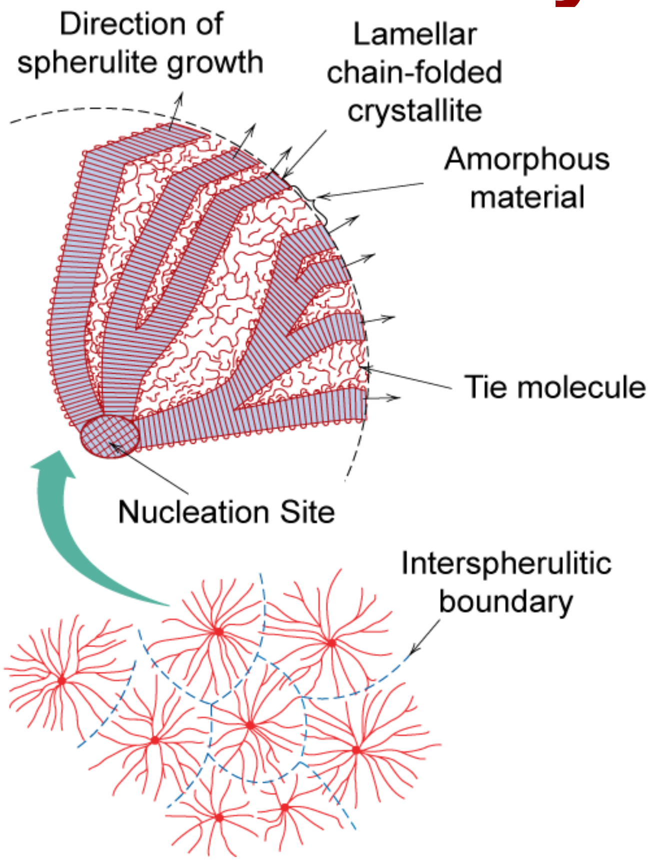


Polymers rarely 100% crystalline

- Difficult for all regions of all chains to become aligned



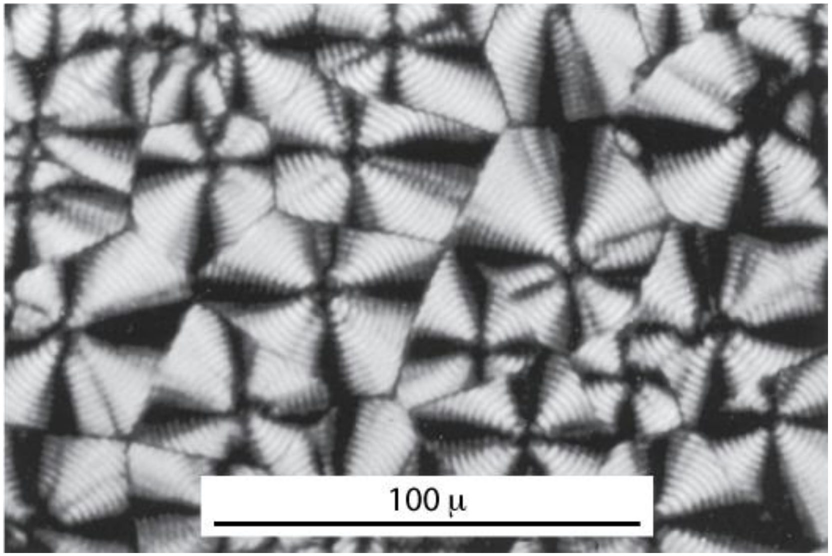
Semicrystalline Polymers



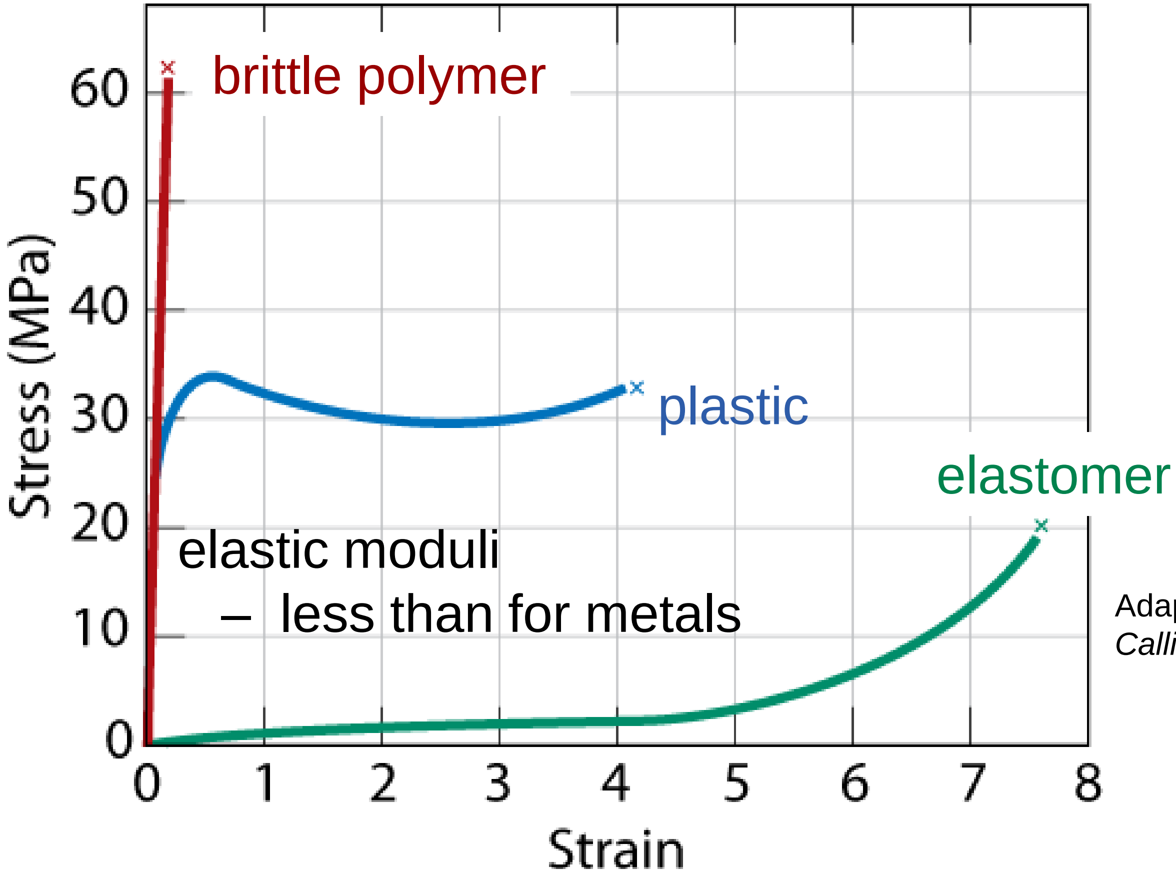
Adapted from Fig. 14.13, *Callister & Rethwisch 8e.*

- Some semicrystalline polymers form spherulite structures
- Alternating chain-folded crystallites and amorphous regions

Photomicrograph – Spherulites in Polyethylene



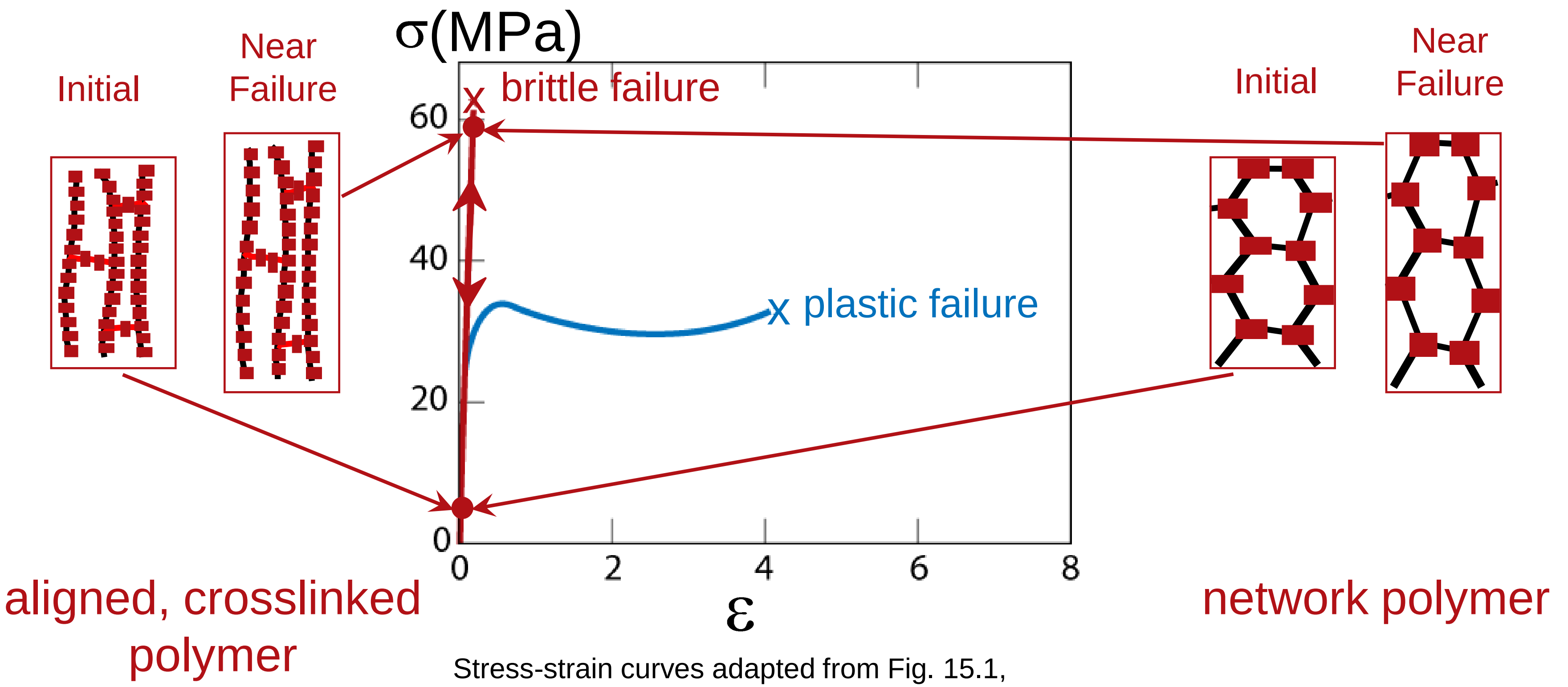
Mechanical Properties of Polymers – Stress-Strain Behavior



Adapted from Fig. 15.1, *Callister & Rethwisch 8e*.

- Fracture strengths of polymers ~ 10% of those for metals
- Deformation strains for polymers > 1000%
  - for most metals, deformation strains < 10%

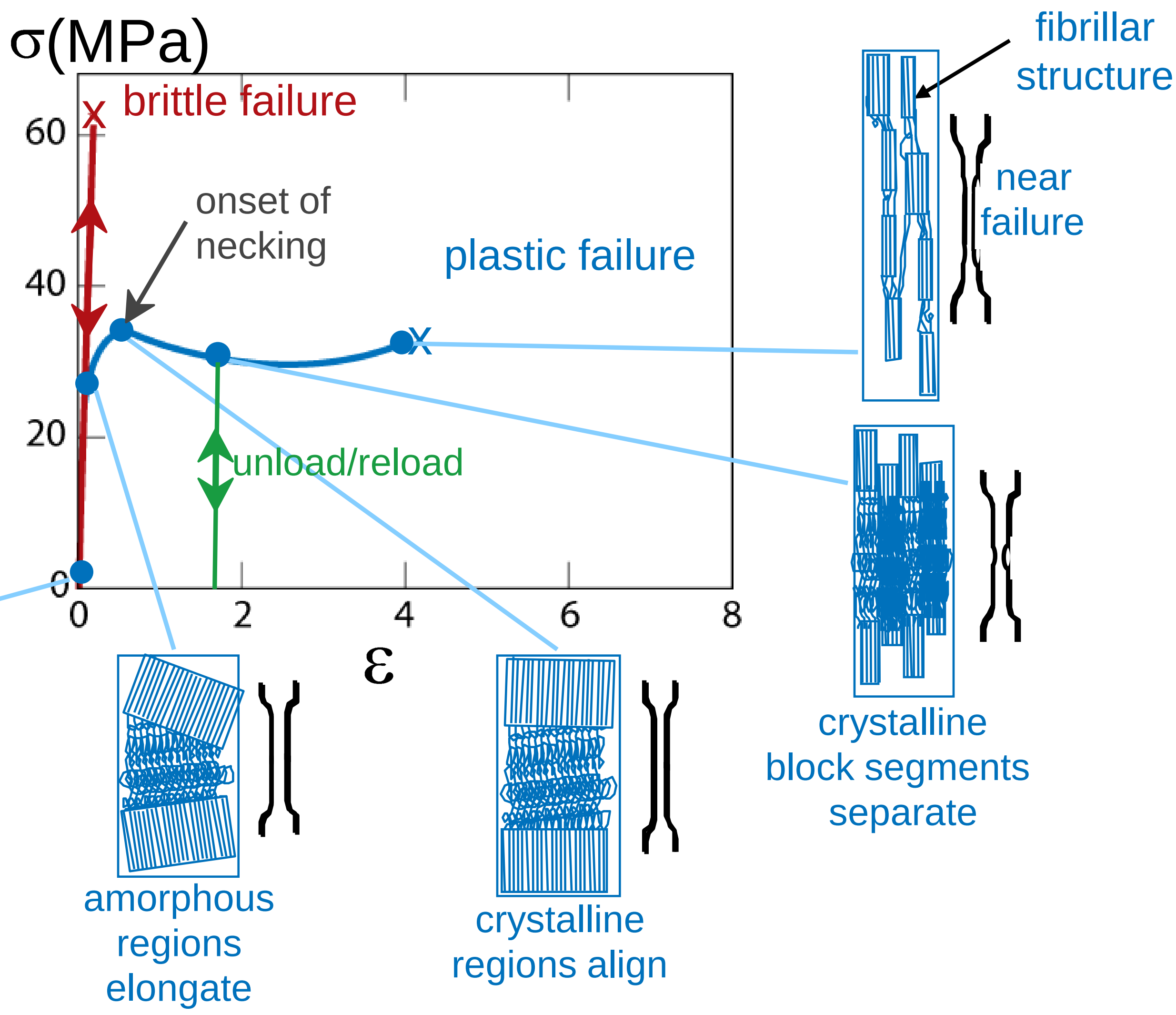
Mechanisms of Deformation—Brittle Crosslinked and Network Polymers



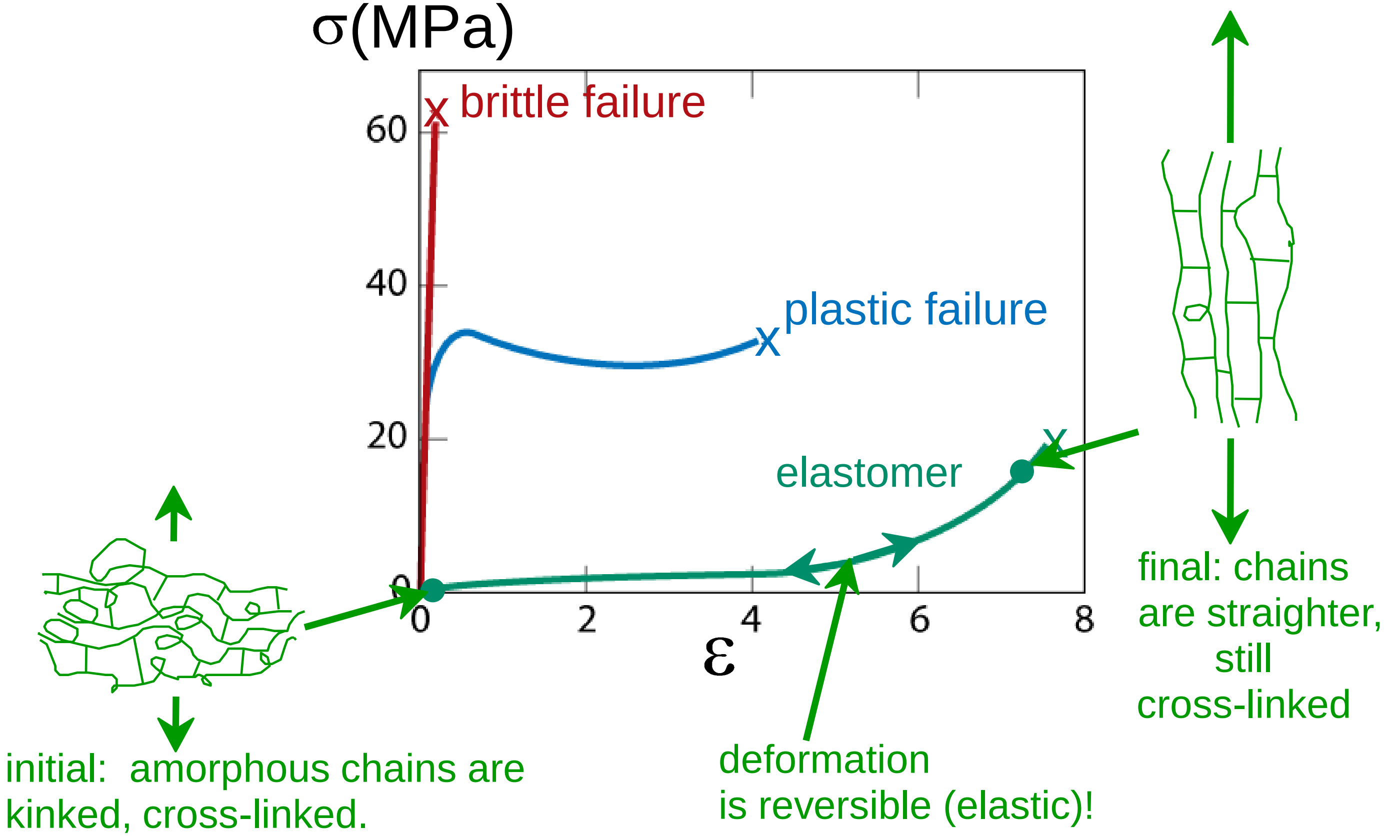
Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 8e.*

Mechanisms of Deformation — Semicrystalline (Plastic) Polymers

Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 8e.* Inset figures along plastic response curve adapted from Figs. 15.12 & 15.13, *Callister & Rethwisch 8e*. (15.12 & 15.13 are from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)



Mechanisms of Deformation—Elastomers



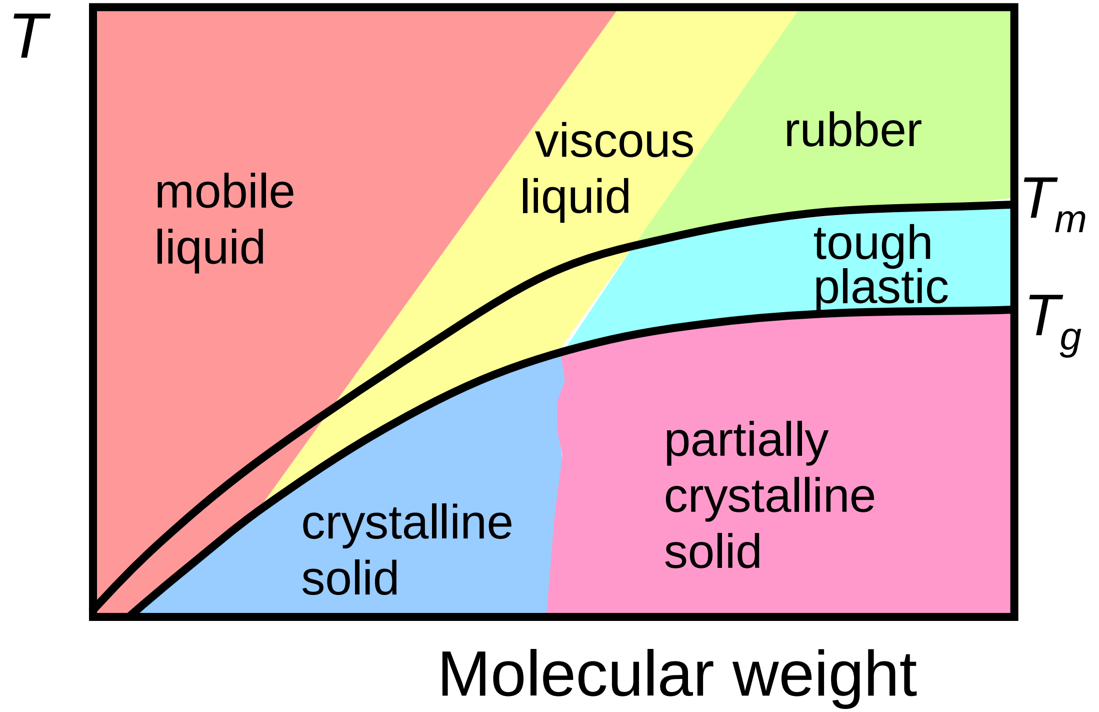
Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 8e.* Inset figures along elastomer curve (green) adapted from Fig. 15.15, *Callister & Rethwisch 8e*. (Fig. 15.15 is from Z.D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd ed., John Wiley and Sons, 1987.)

- Compare elastic behavior of elastomers with the:
  - -- brittle behavior (of aligned, crosslinked & network polymers), and
  - -- plastic behavior (of semicrystalline polymers)

  (as shown on previous slides)

Thermoplastics vs. Thermosets

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



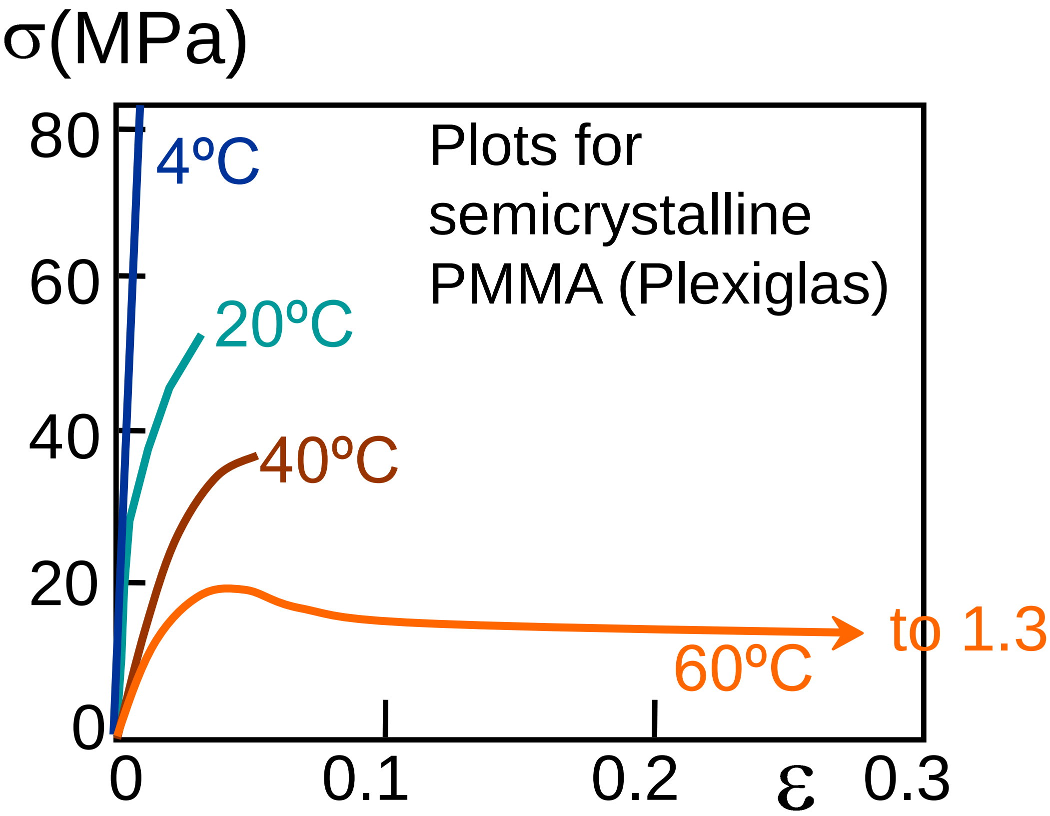
Adapted from Fig. 15.19, *Callister & Rethwisch 8e.* (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

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

Influence of *T* and Strain Rate on Thermoplastics

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

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

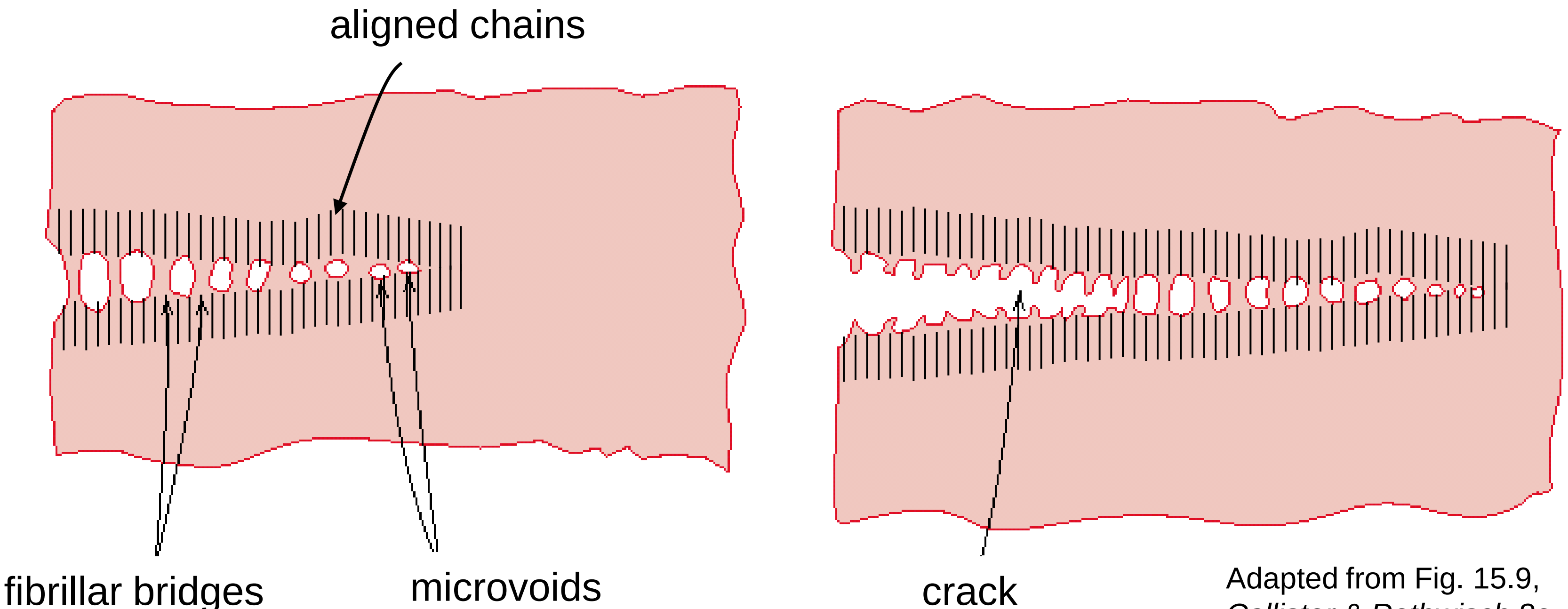


Adapted from Fig. 15.3, *Callister & Rethwisch 8e*. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)

Crazing During Fracture of Thermoplastic Polymers

Craze formation prior to cracking

– during crazing, plastic deformation of spherulites
– and formation of microvoids and fibrillar bridges

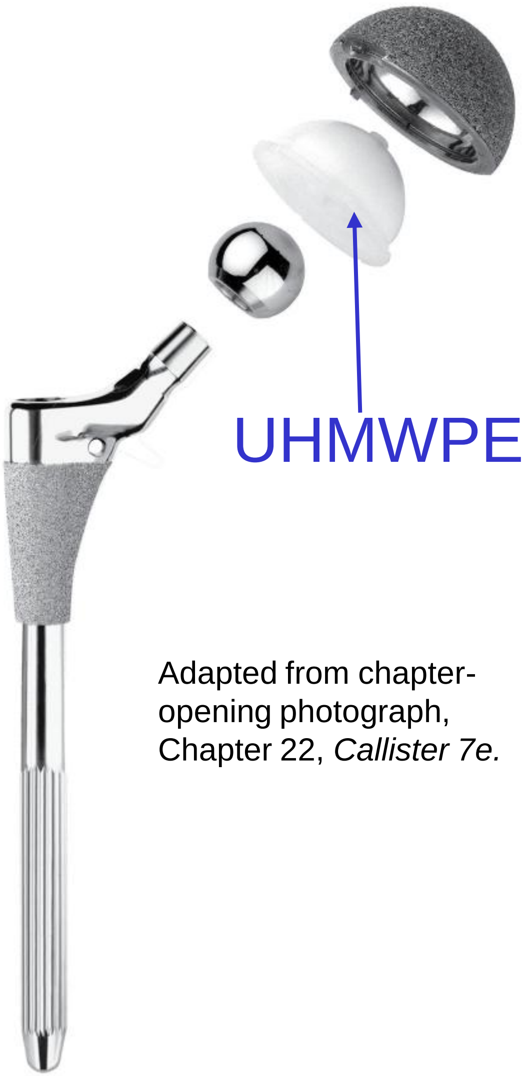


Adapted from Fig. 15.9, *Callister & Rethwisch 8e.*

Advanced Polymers

Ultrahigh Molecular Weight Polyethylene (UHMWPE)

- Molecular weight ca. 4×10^6 g/mol
- Outstanding properties
  - high impact strength
  - resistance to wear/abrasion
  - low coefficient of friction
  - self-lubricating surface
- Important applications
  - bullet-proof vests
  - golf ball covers
  - hip implants (acetabular cup)



Adapted from chapter-opening photograph, Chapter 22, *Callister 7e.*

Summary

- Limitations of polymers:
  -- E, σ_y, K_c, $T_{application}$ are generally small.
  -- Deformation is often time and temperature dependent.
- 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 & Rethwisch 8e*:

Good overview of applications and trade names of polymers.