

# Chapter 14 & Chapter 15: Polymer Structures and Properties

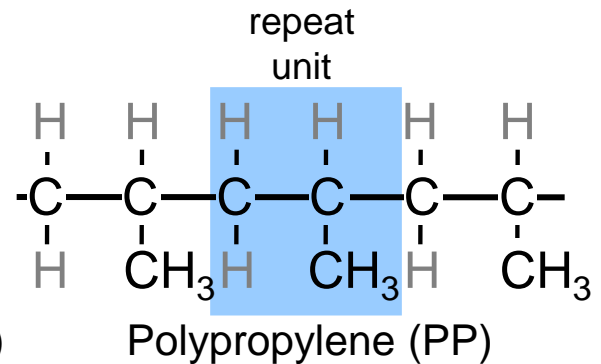
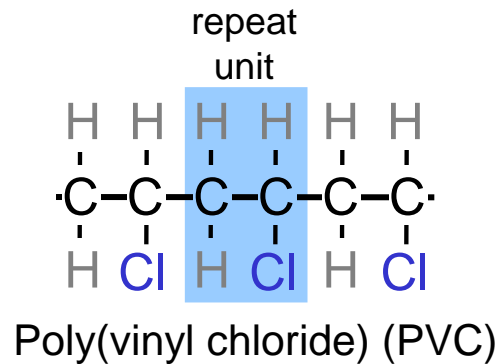
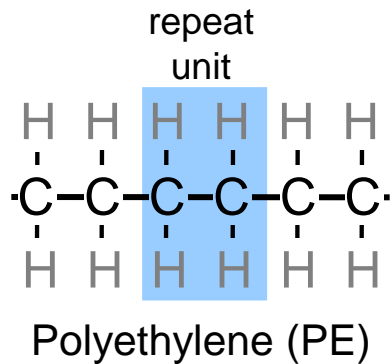
## ISSUES TO ADDRESS...

- 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**      **mer**  
many      repeat unit



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



# Ancient Polymers

- 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

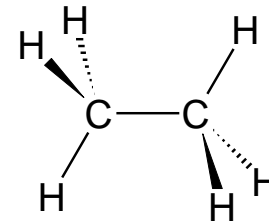
– i.e., made up of H and C

- **Saturated hydrocarbons**

- Each carbon singly bonded to four other atoms

- Example:

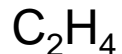
- Ethane,  $C_2H_6$



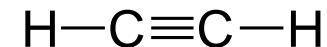
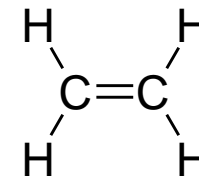
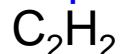
- **Unsaturated hydrocarbons**

- Double & triple bonds somewhat unstable – can form new bonds

- **Double bond** found in ethylene or ethene -

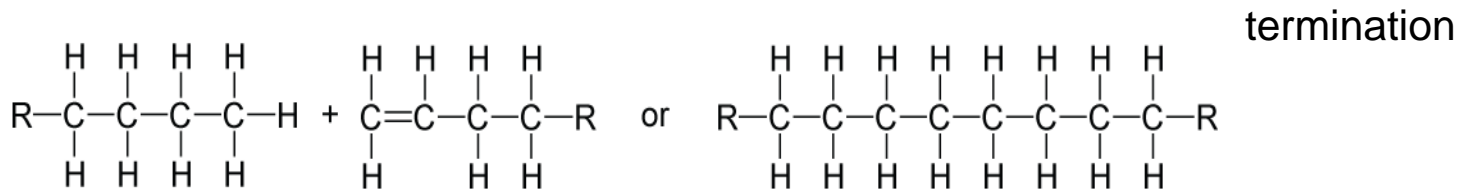
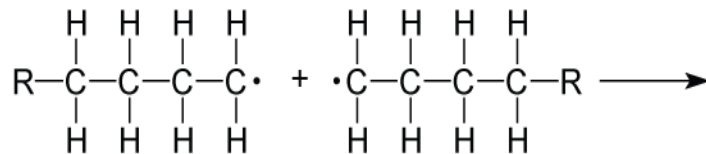
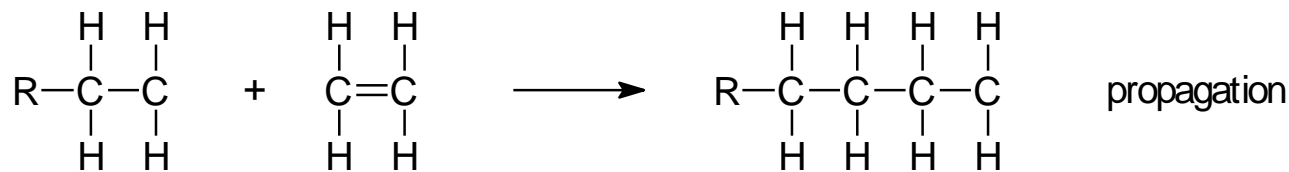
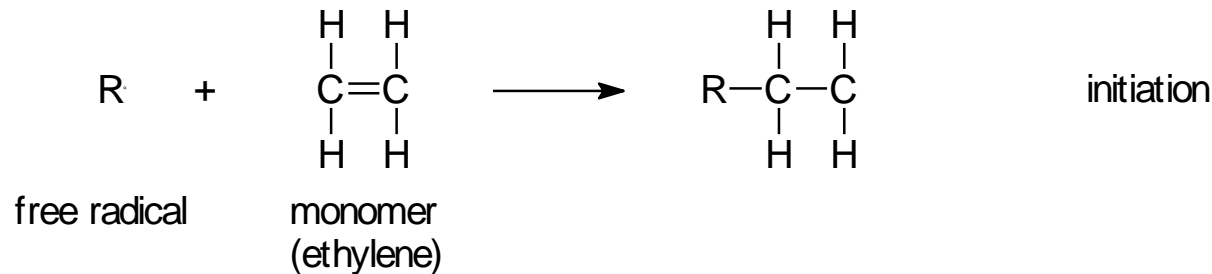


- **Triple bond** found in acetylene or ethyne -



# Polymerization and Polymer Chemistry

- Free radical polymerization

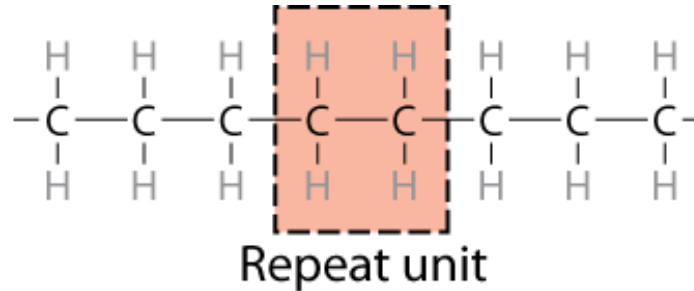


Disproportionation

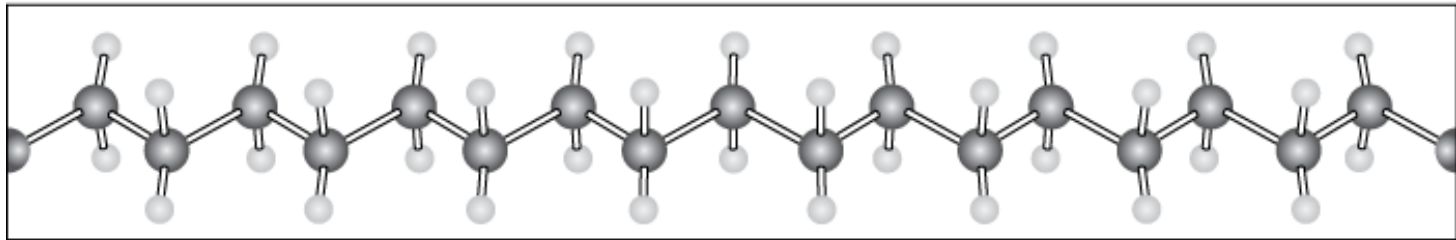
Combination



# Chemistry and Structure of Polyethylene

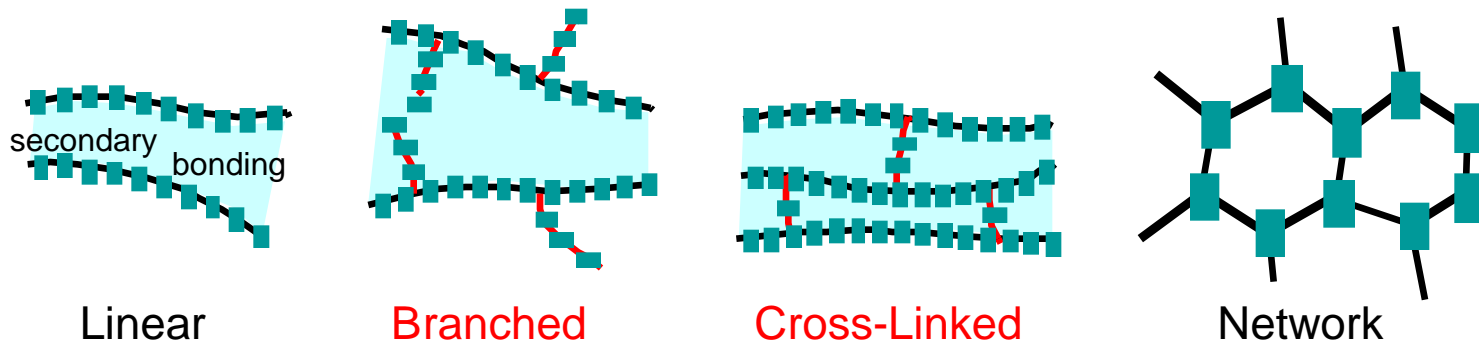


Adapted from Fig. 14.1, *Callister & Rethwisch 8e.*



Note: polyethylene is a long-chain hydrocarbon  
- paraffin wax for candles is short polyethylene

# Molecular Structures for Polymers



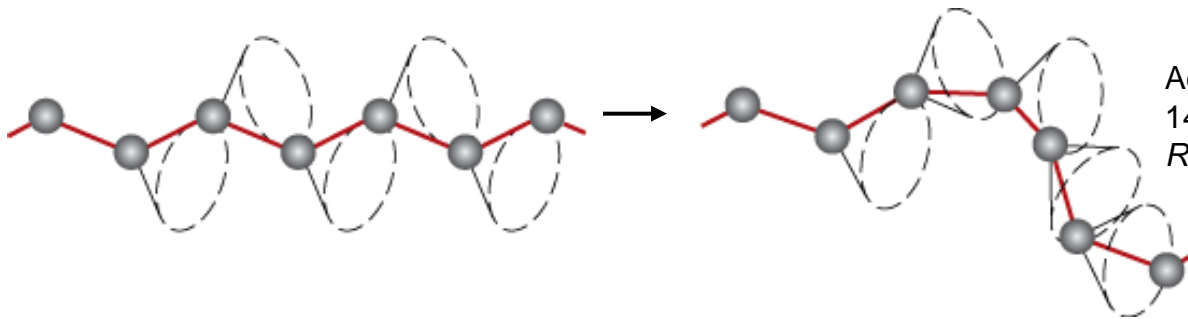
Adapted from Fig. 14.7, *Callister & Rethwisch 8e*.



# 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.*





# Copolymers

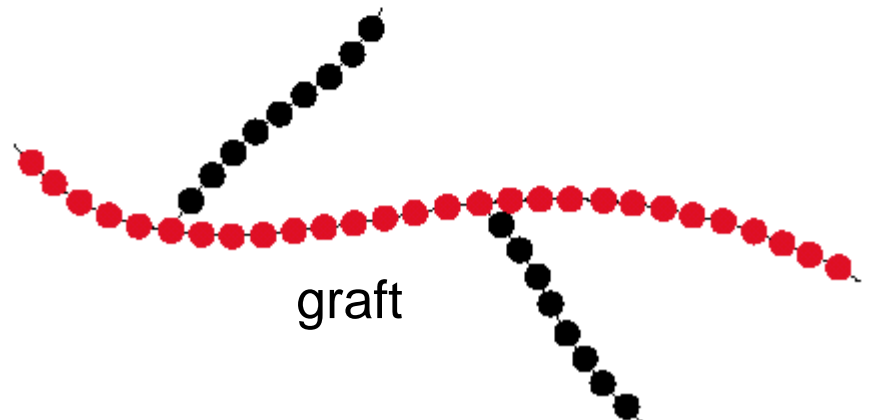
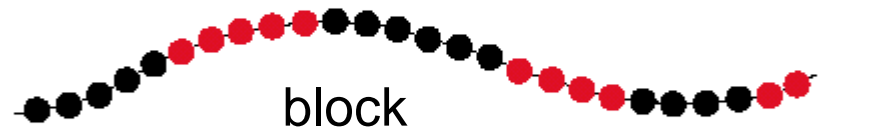
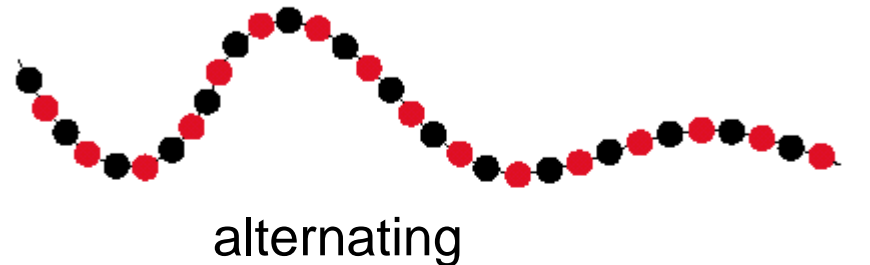
two or more monomers  
polymerized together

- **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

A – ●

B – ●

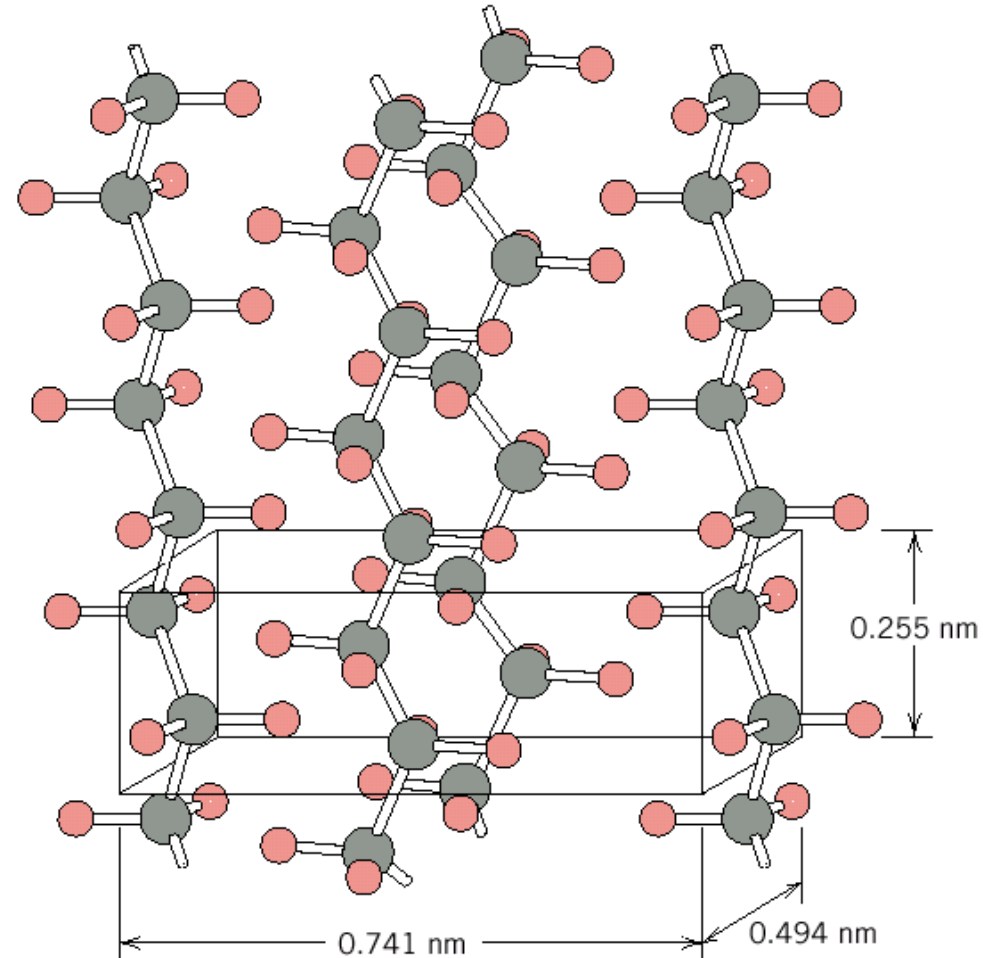
Adapted from Fig.  
14.9, Callister &  
Rethwisch 8e.



# Crystallinity in Polymers

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

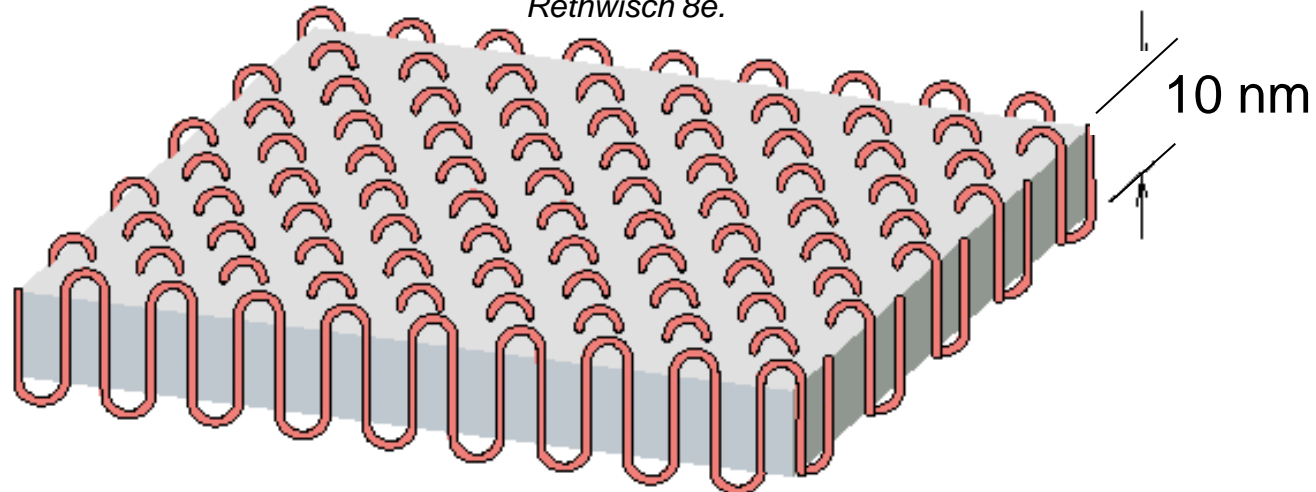
- Ordered atomic arrangements involving molecular chains
- Crystal structures in terms of unit cells
- Example shown
  - polyethylene unit cell



# Polymer Crystallinity

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

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



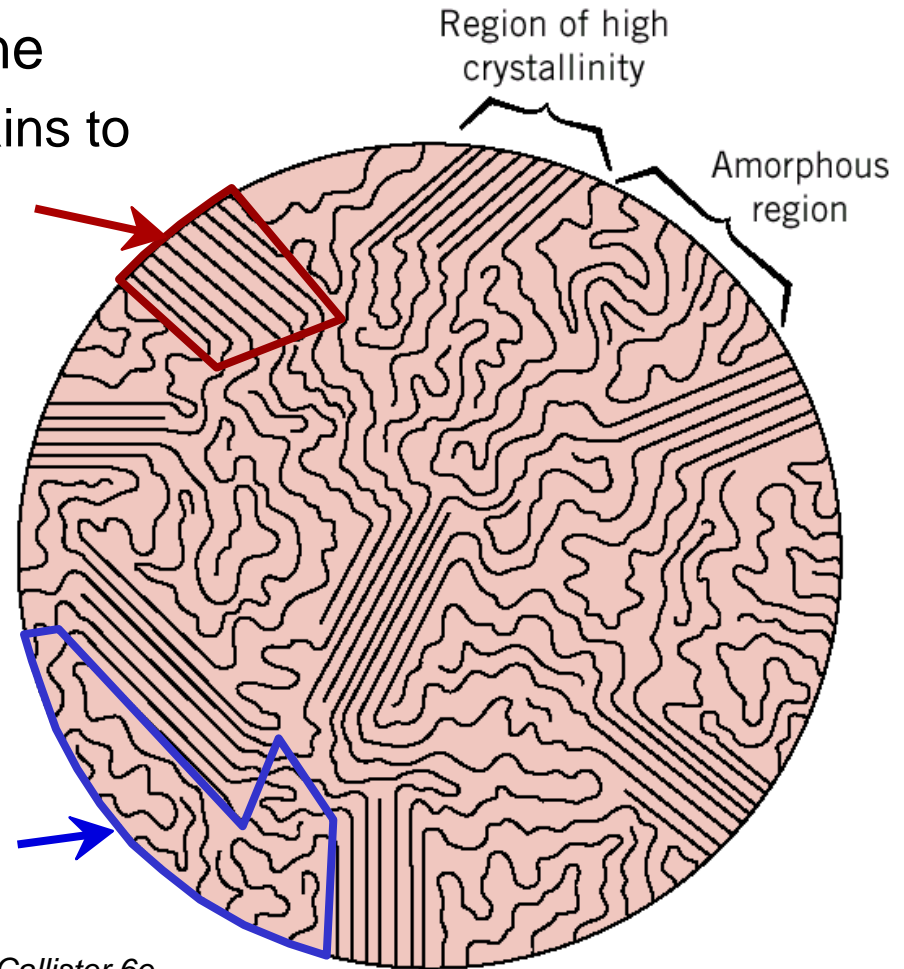
# Polymer Crystallinity (cont.)

Polymers rarely 100% crystalline

- Difficult for all regions of all chains to become aligned
- Degree of crystallinity expressed as **% crystallinity**.
  - Some physical properties depend on % crystallinity.
  - Heat treating causes crystalline regions to grow and % crystallinity to increase.

crystalline region

amorphous region

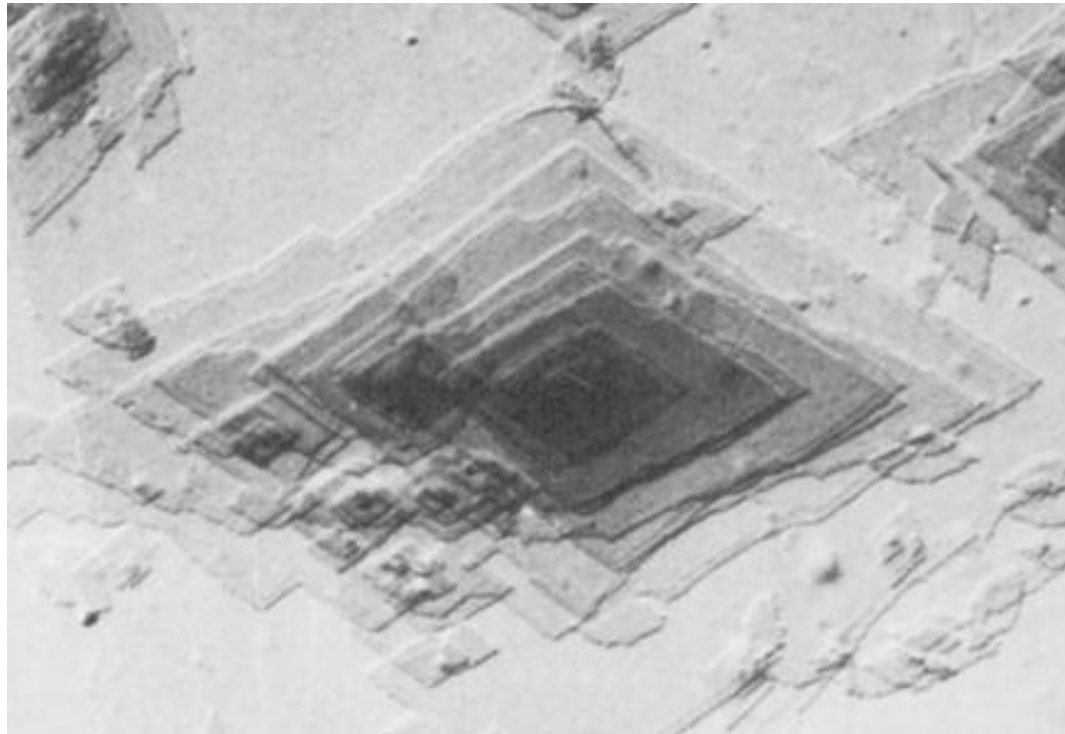


Adapted from Fig. 14.11, *Callister 6e*.  
(Fig. 14.11 is from H.W. Hayden, W.G. Moffatt,  
and J. Wulff, *The Structure and Properties of  
Materials*, Vol. III, *Mechanical Behavior*, John Wiley  
and Sons, Inc., 1965.)



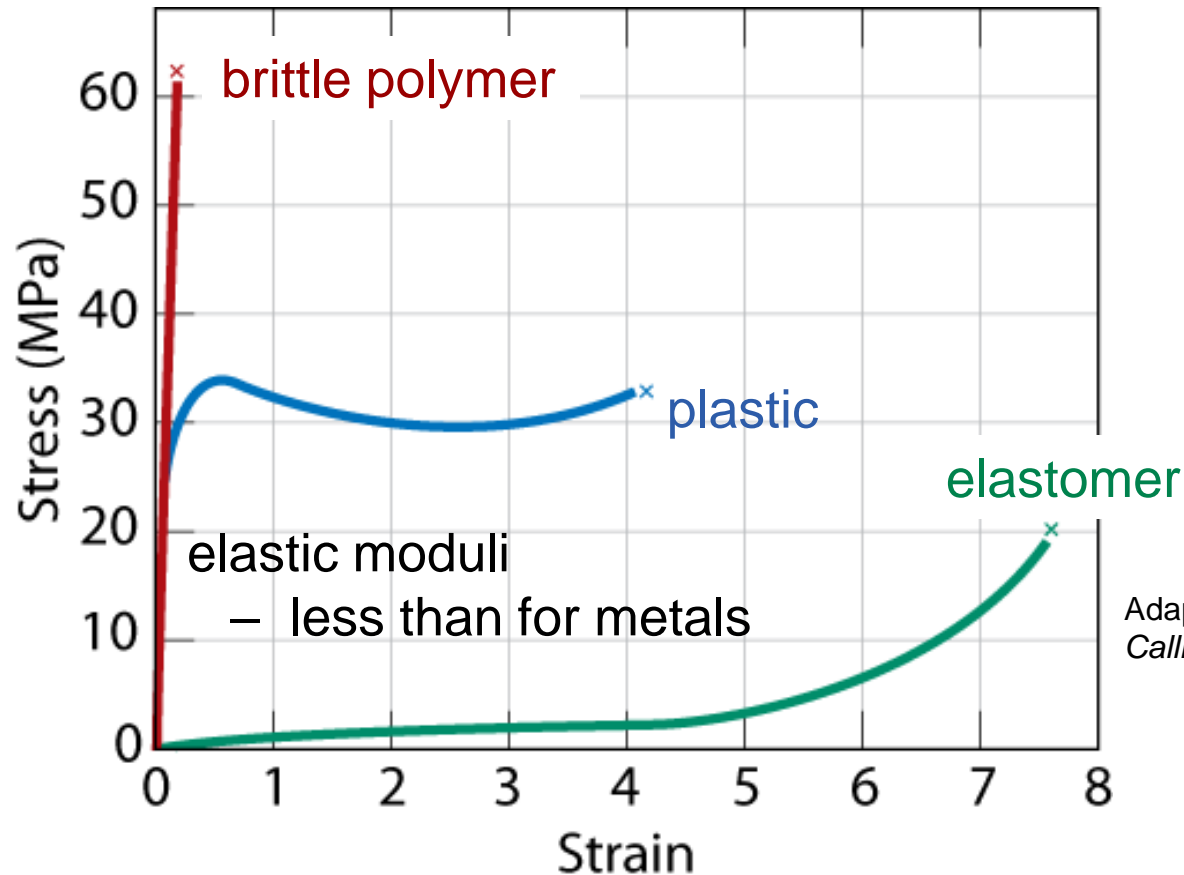
# Polymer Single Crystals

- 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*.

# Mechanical Properties of Polymers – Stress-Strain Behavior

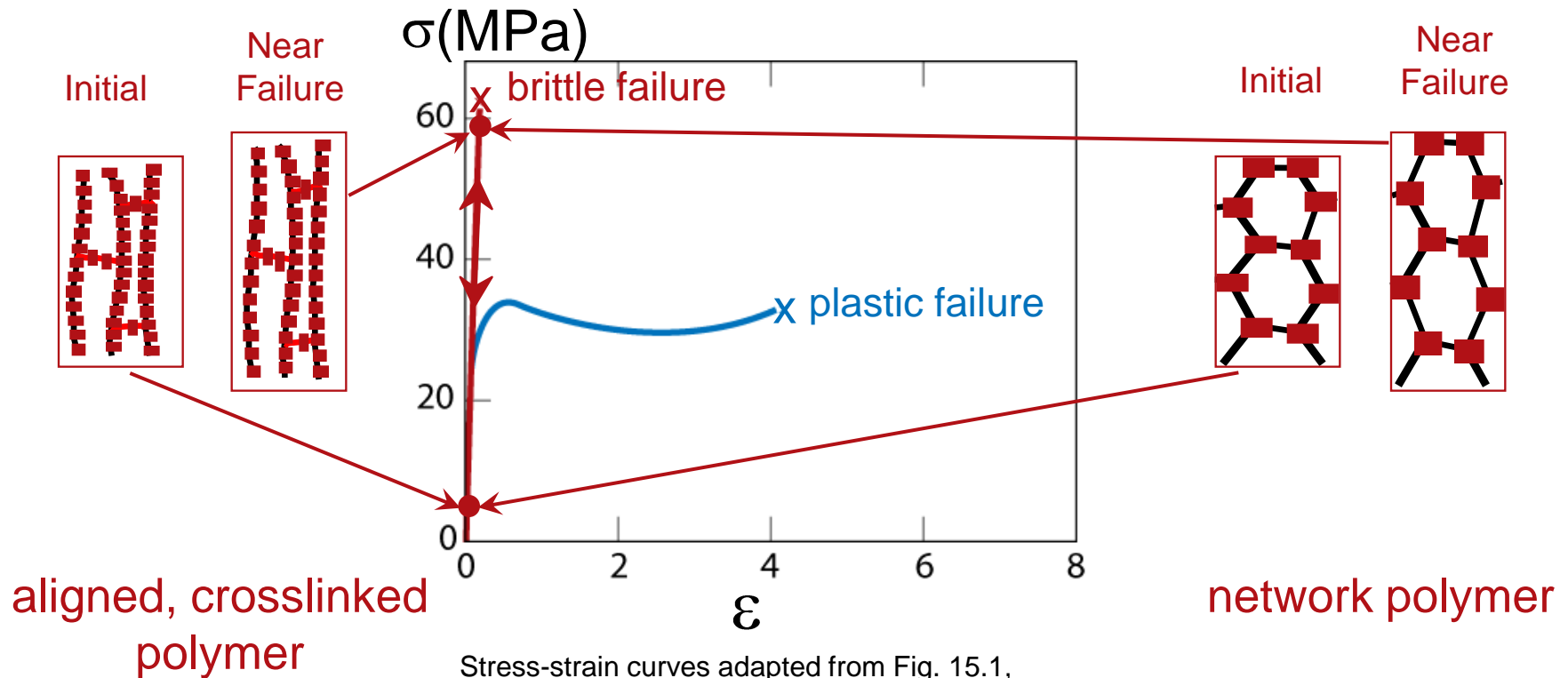


Adapted from Fig. 15.1,  
*Callister & Rethwisch 8e.*

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



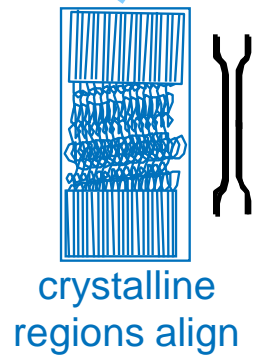
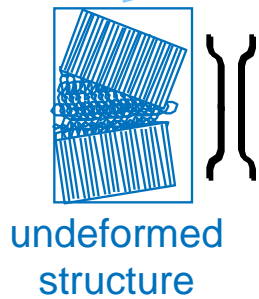
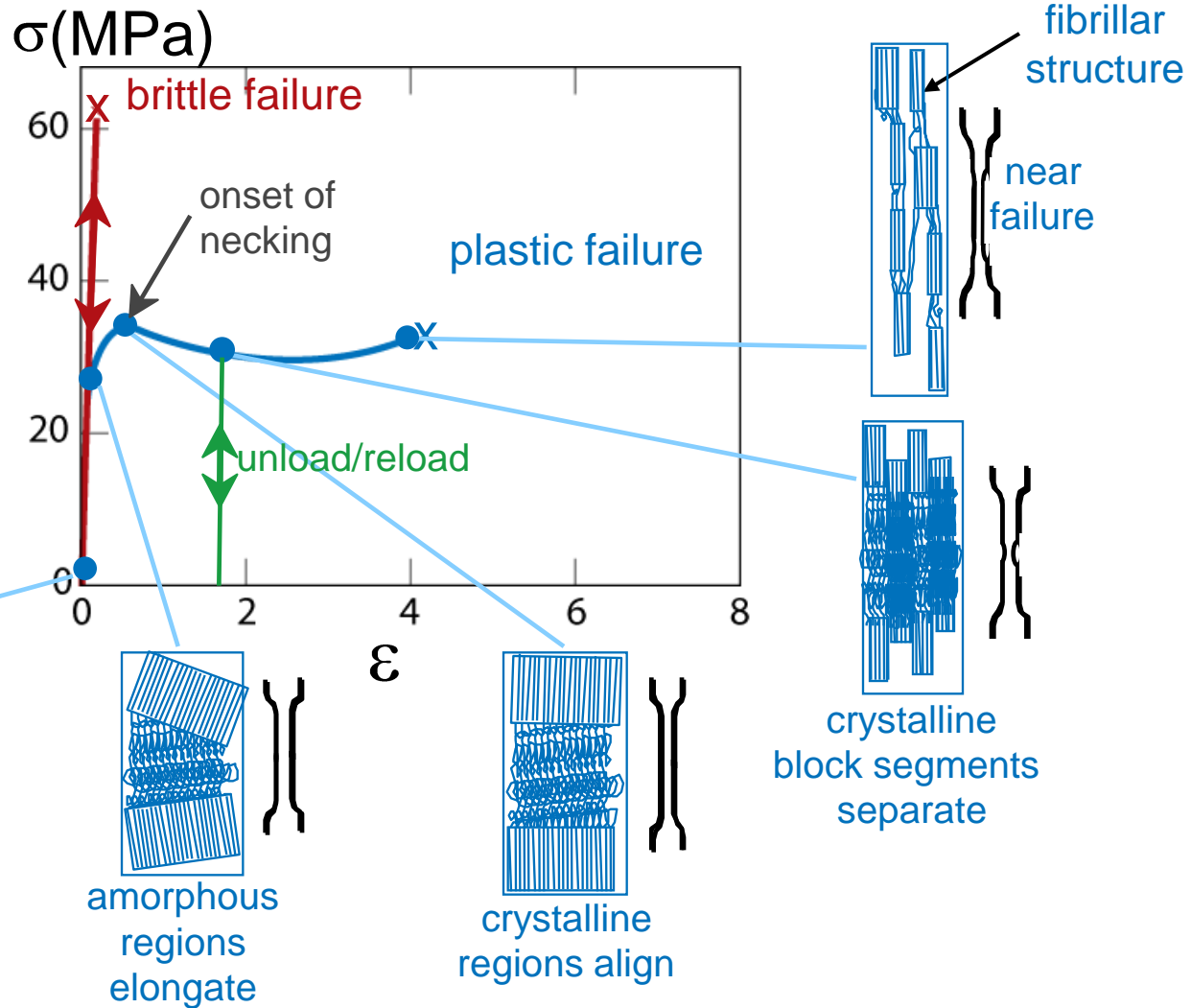
# Mechanisms of Deformation—Brittle Crosslinked and Network Polymers



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.)

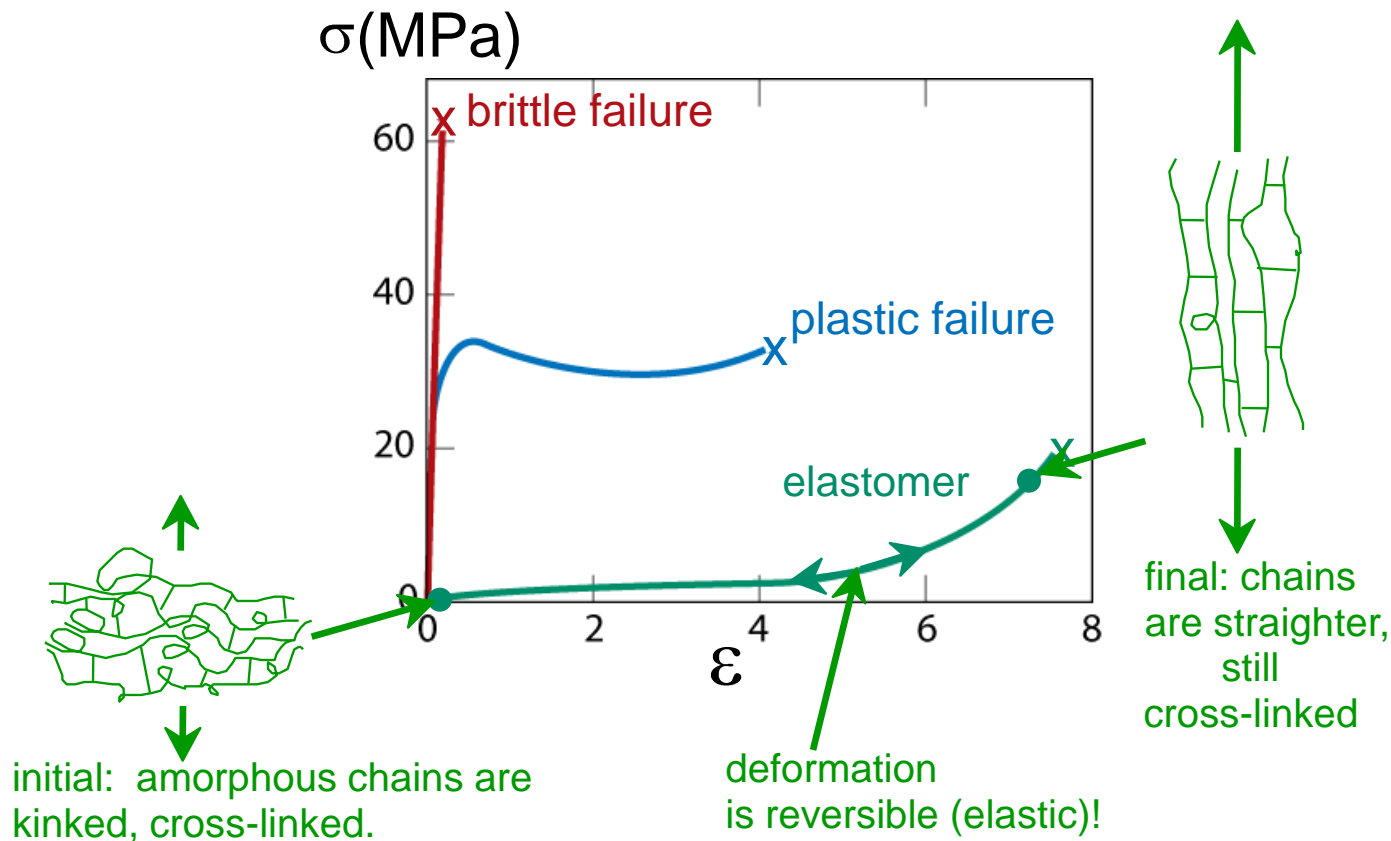


crystalline block segments separate





# 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)