CHAPTER 14: POLYMER STRUCTURES

ISSUES TO ADDRESS...

- What are the basic microstructural features?

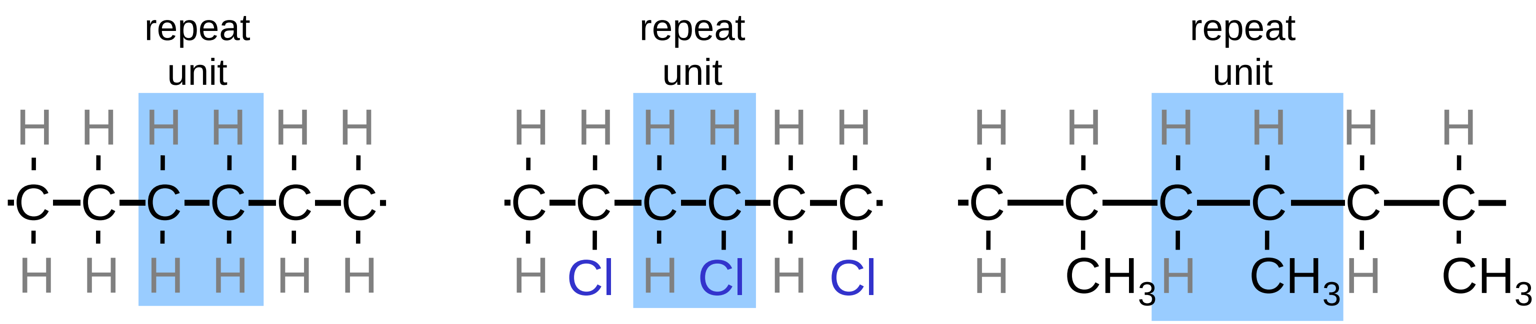
- How do polymeric crystals accommodate the polymer chain?

Chapter 14 – Polymers

What is a polymer?

Poly **mer**

many repeat unit



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

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

Ancient Polymer History

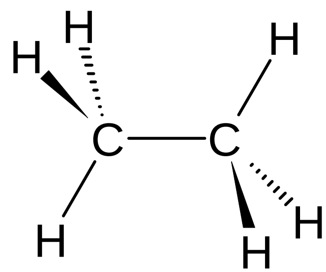
- Originally natural polymers were used
  - Wood
  - Cotton
  - Leather
  - Rubber
  - Wool
  - Silk

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

Polymer Composition

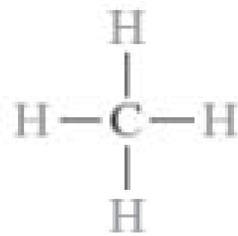
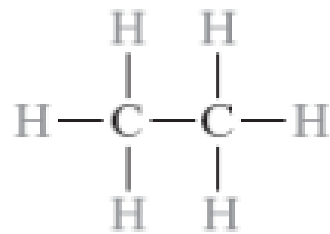
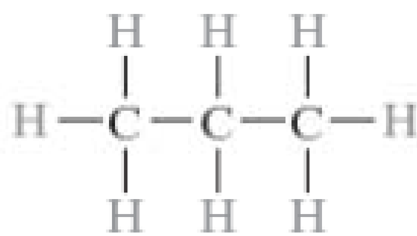
Most polymers are hydrocarbons
– i.e. made up of H and C

- Saturated hydrocarbons
  – Each carbon bonded to four other atoms



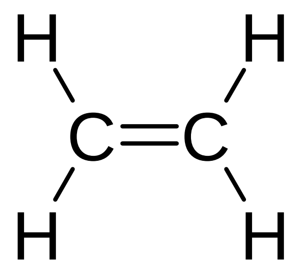
$$C_nH_{2n+2}$$

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}

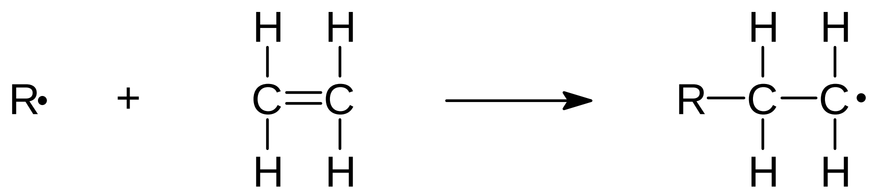


    - 4-bonds, but only 3 atoms bound to C's
  - Triple bond – acetylene or ethyne - C_nH_{2n-2}

$$H—C \equiv C—H$$

Chemistry of Polymers

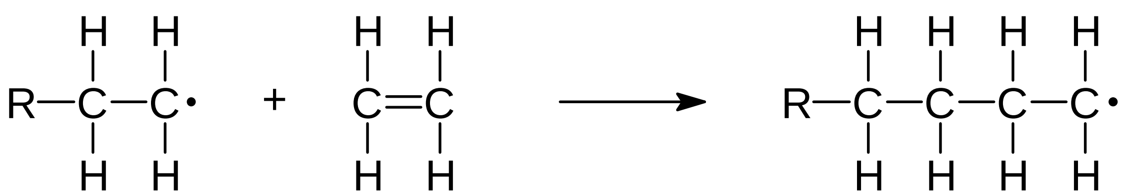
- Free radical polymerization



initiation

free radical

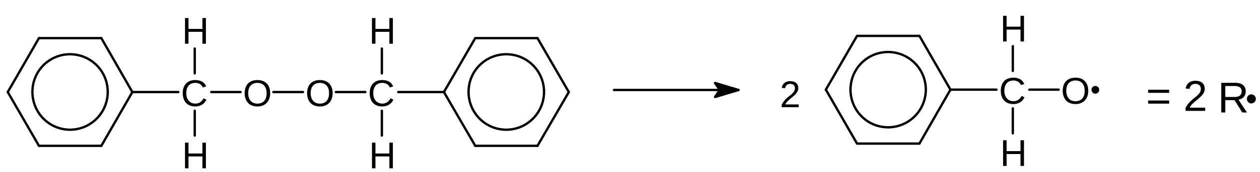
monomer (ethylene)



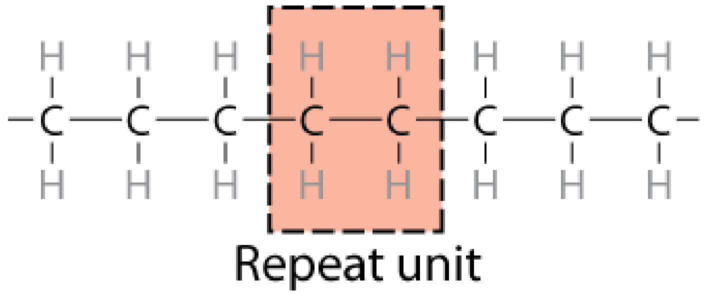
propagation

dimer

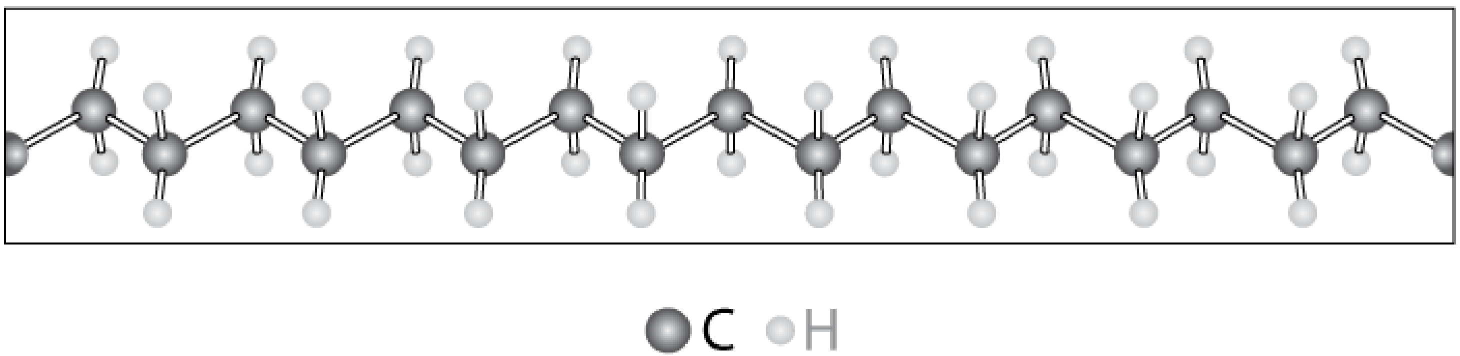
- Initiator: example - benzoyl peroxide



Chemistry of Polymers



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

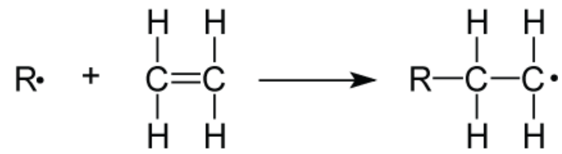


Note: polyethylene is just a long HC

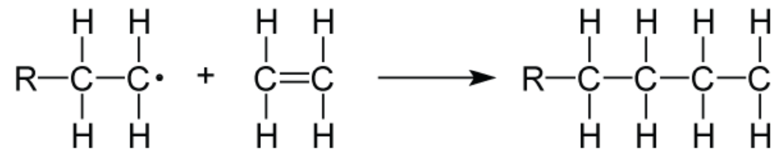
- paraffin is short polyethylene

Addition (Chain) Polymerization

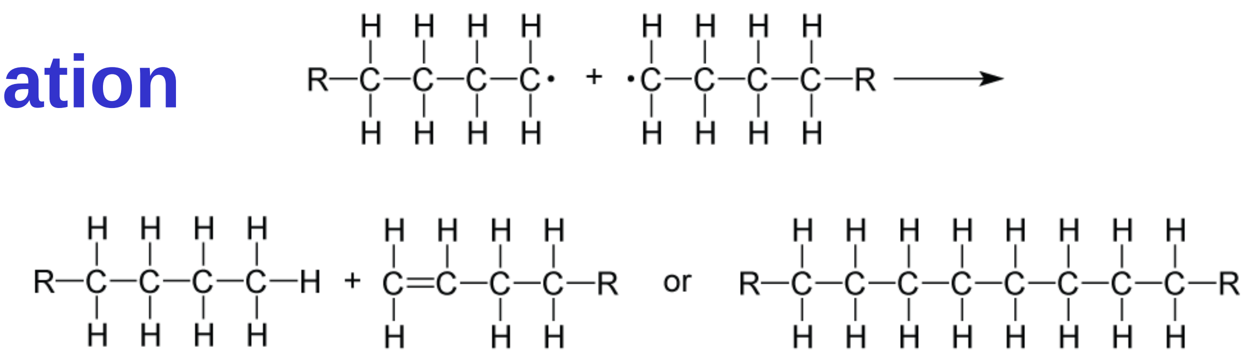
– **Initiation**



– **Propagation**



– **Termination**

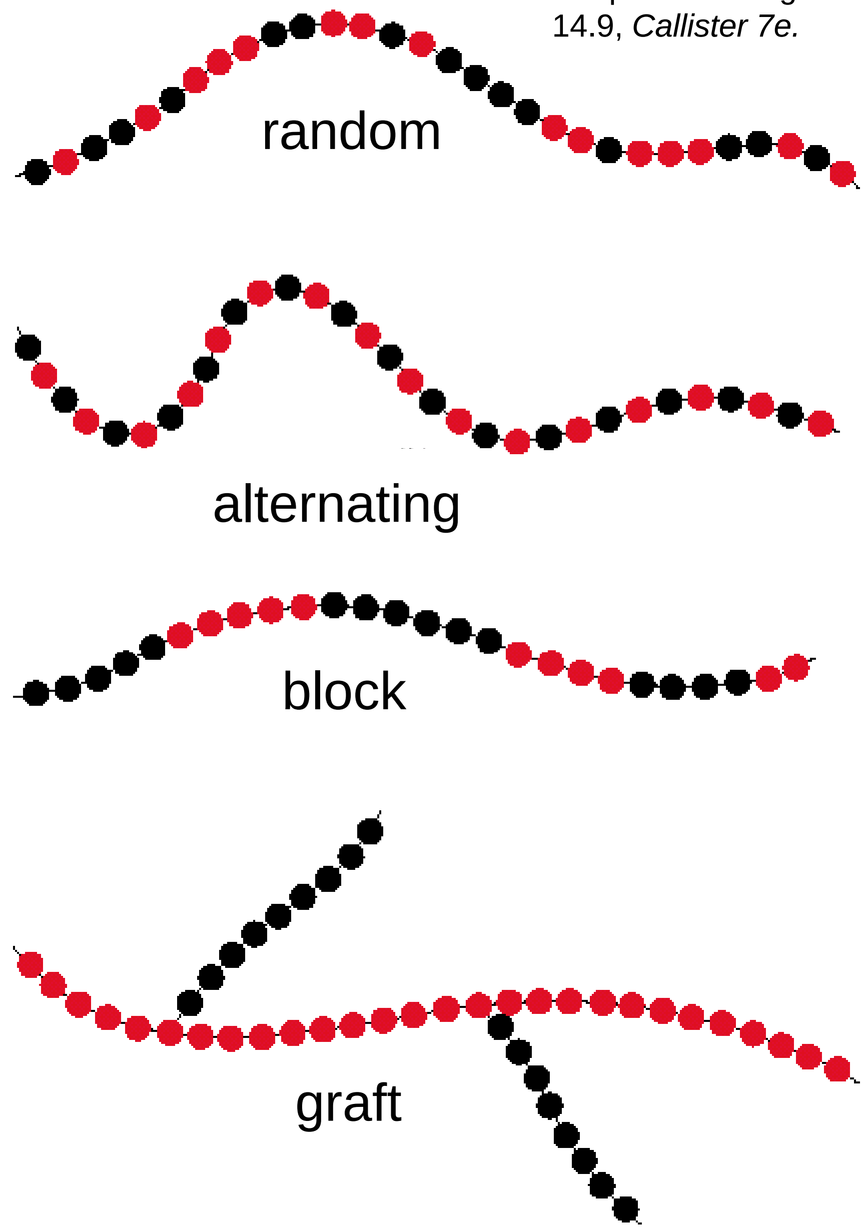


Disproportionation

Combination

Copolymers

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



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

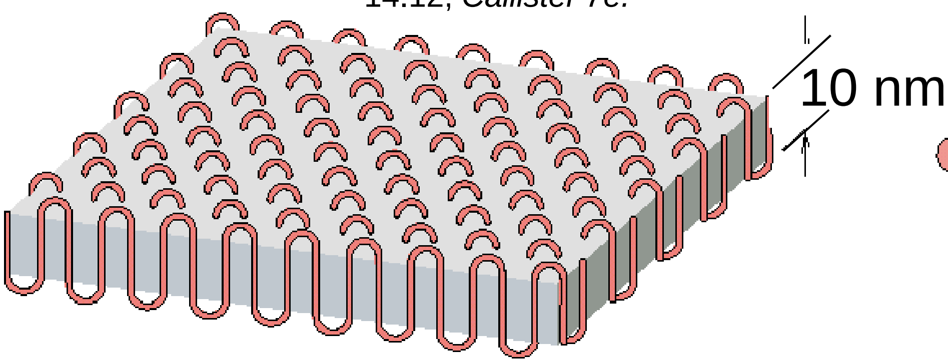
A – ●   B – ●

Polymer Crystallinity

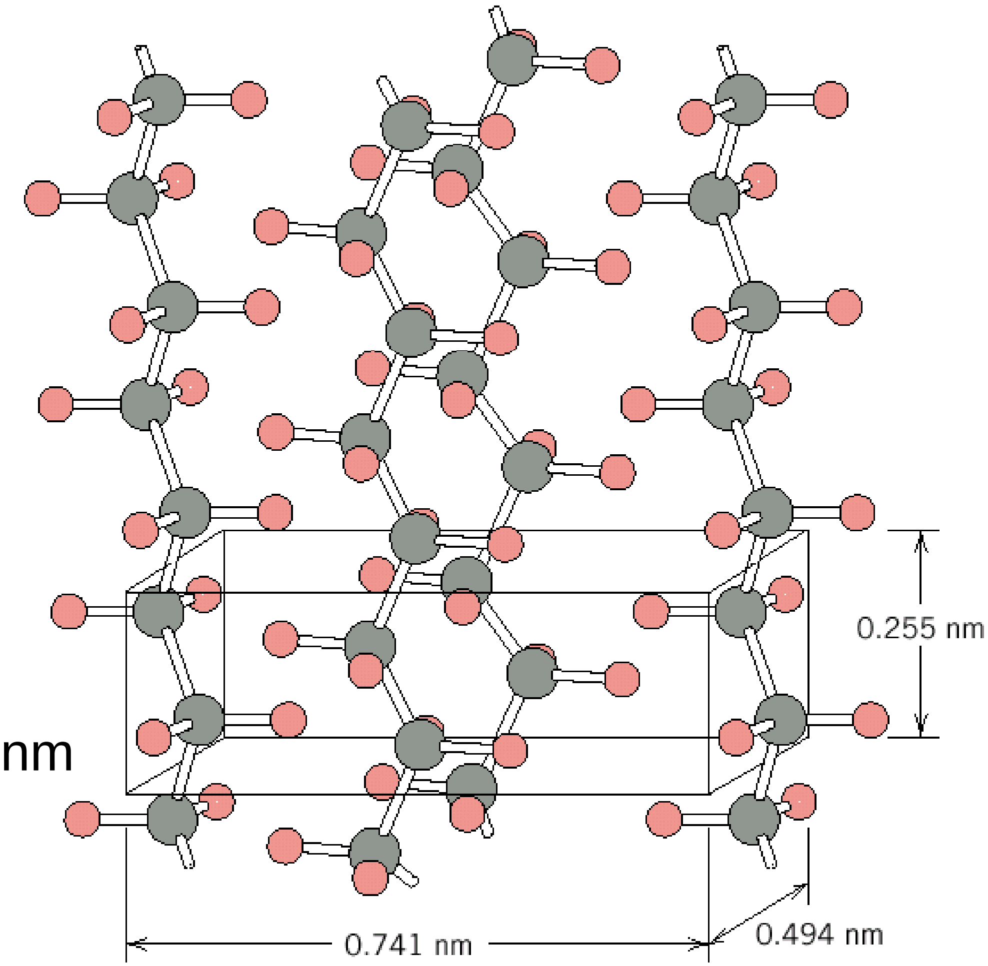
Ex: polyethylene unit cell

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

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



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

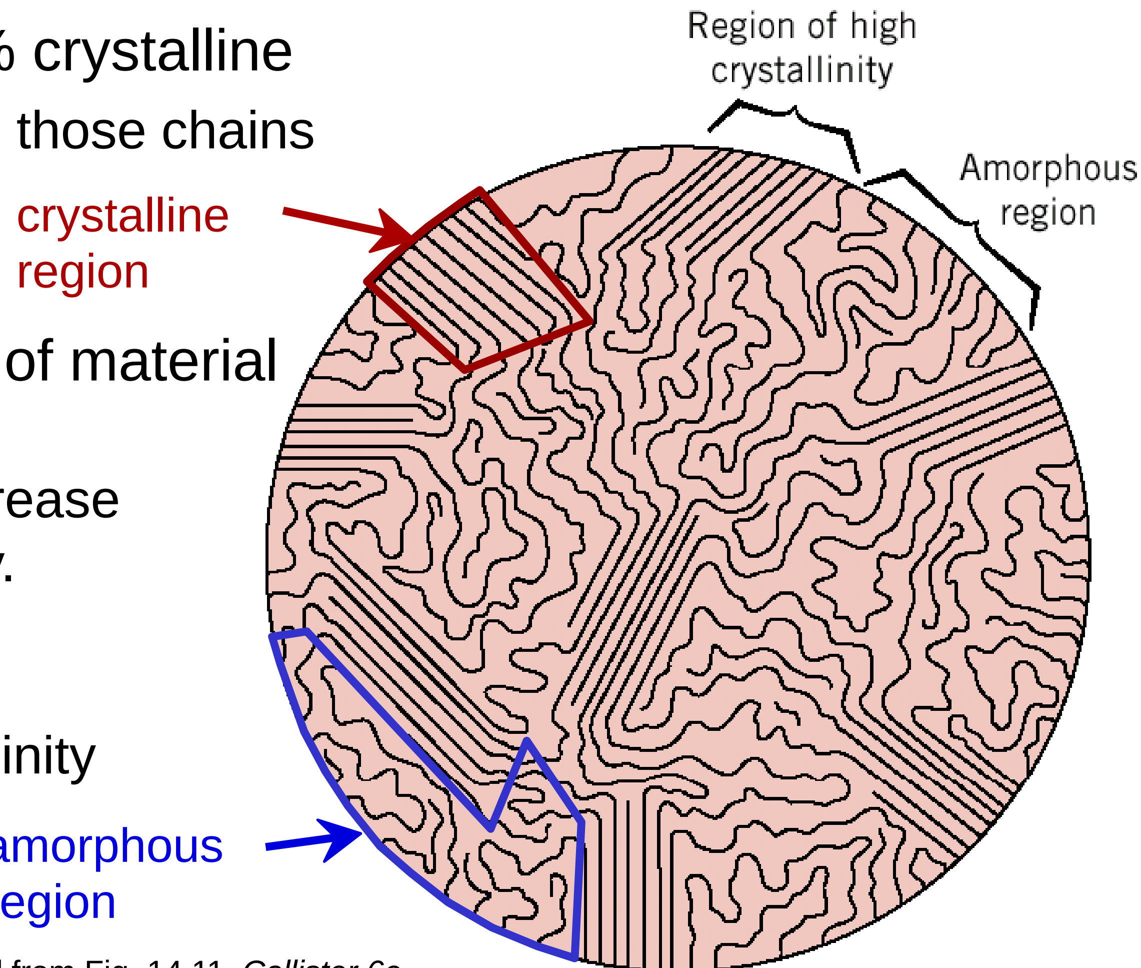


Polymer Crystallinity

Polymers rarely 100% crystalline

- Too difficult to get all those chains aligned

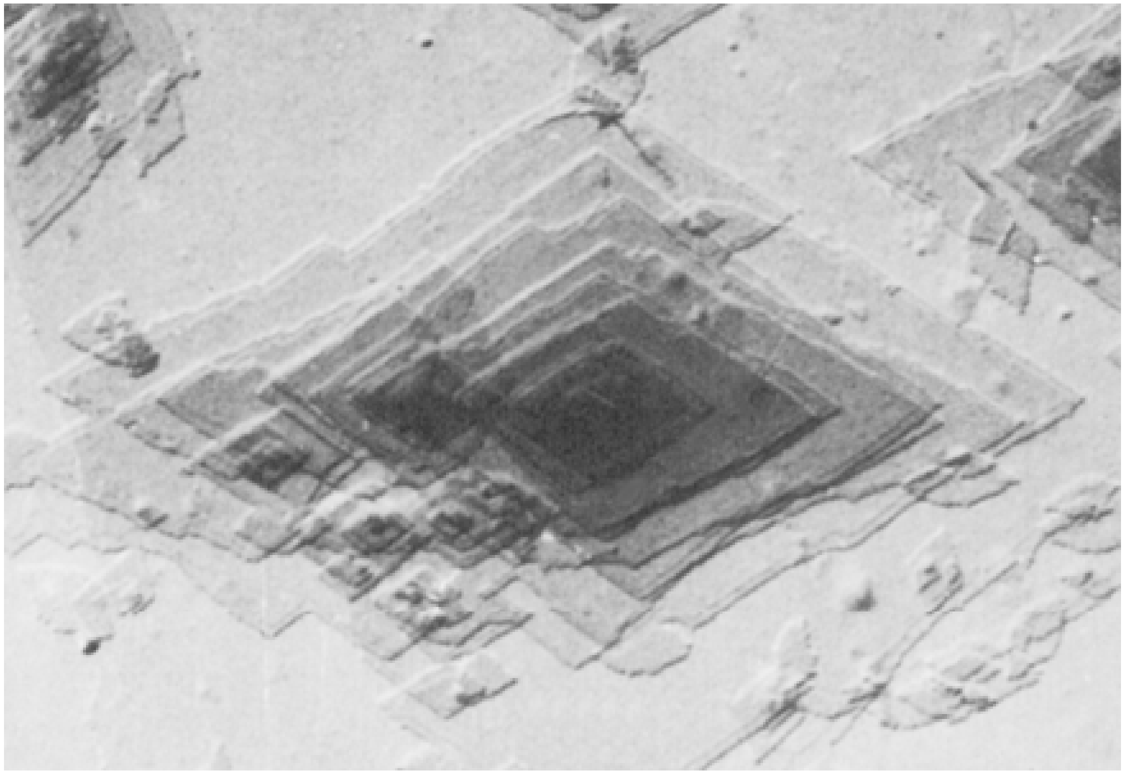
- % Crystallinity: % of material that is crystalline.
  - -- *TS* and *E* often increase with % crystallinity.
  - -- Annealing causes crystalline regions to grow. % crystallinity increases.



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.)

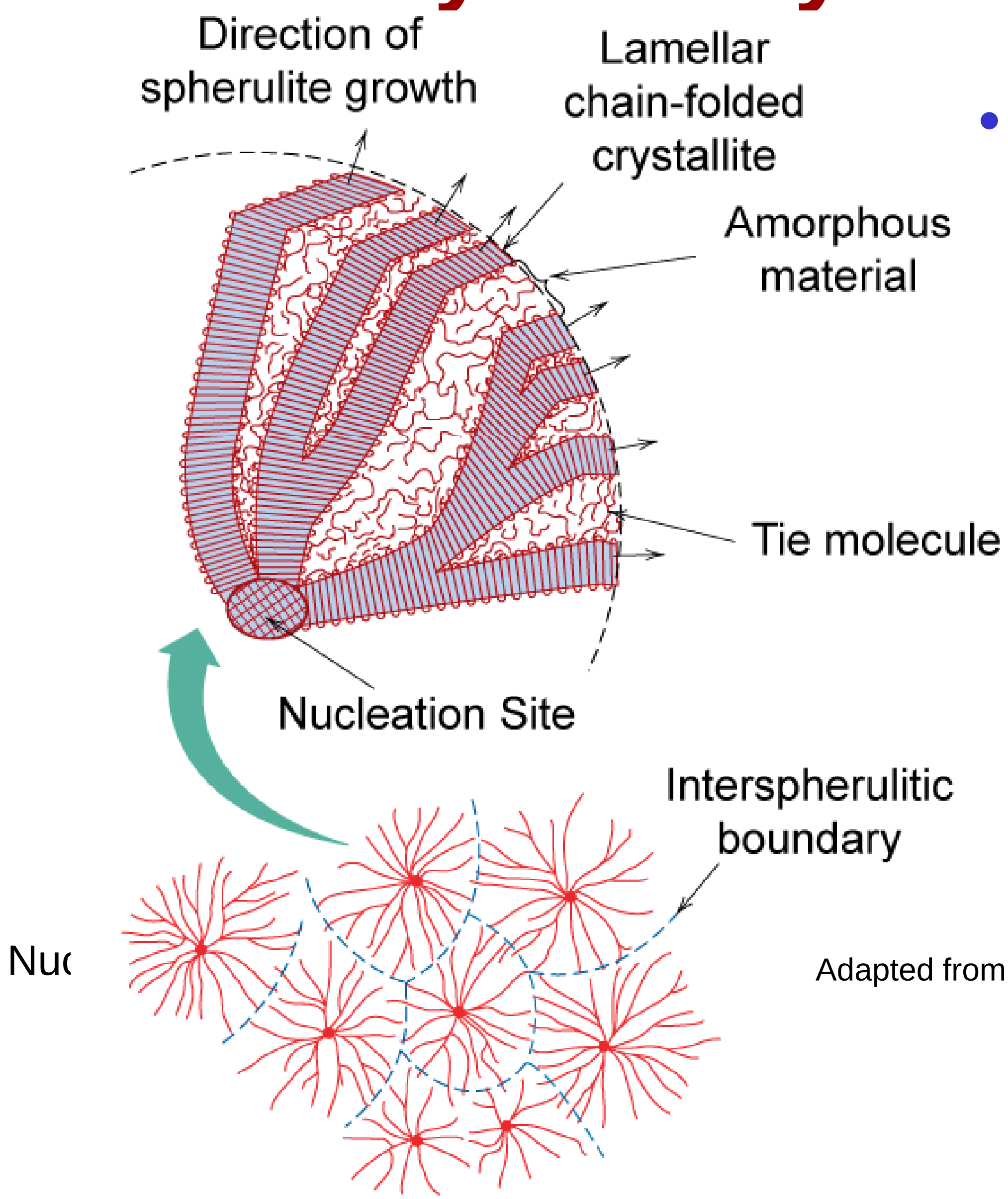
Polymer Crystal Forms

- Single crystals – only if slow careful growth



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

Polymer Crystal Forms

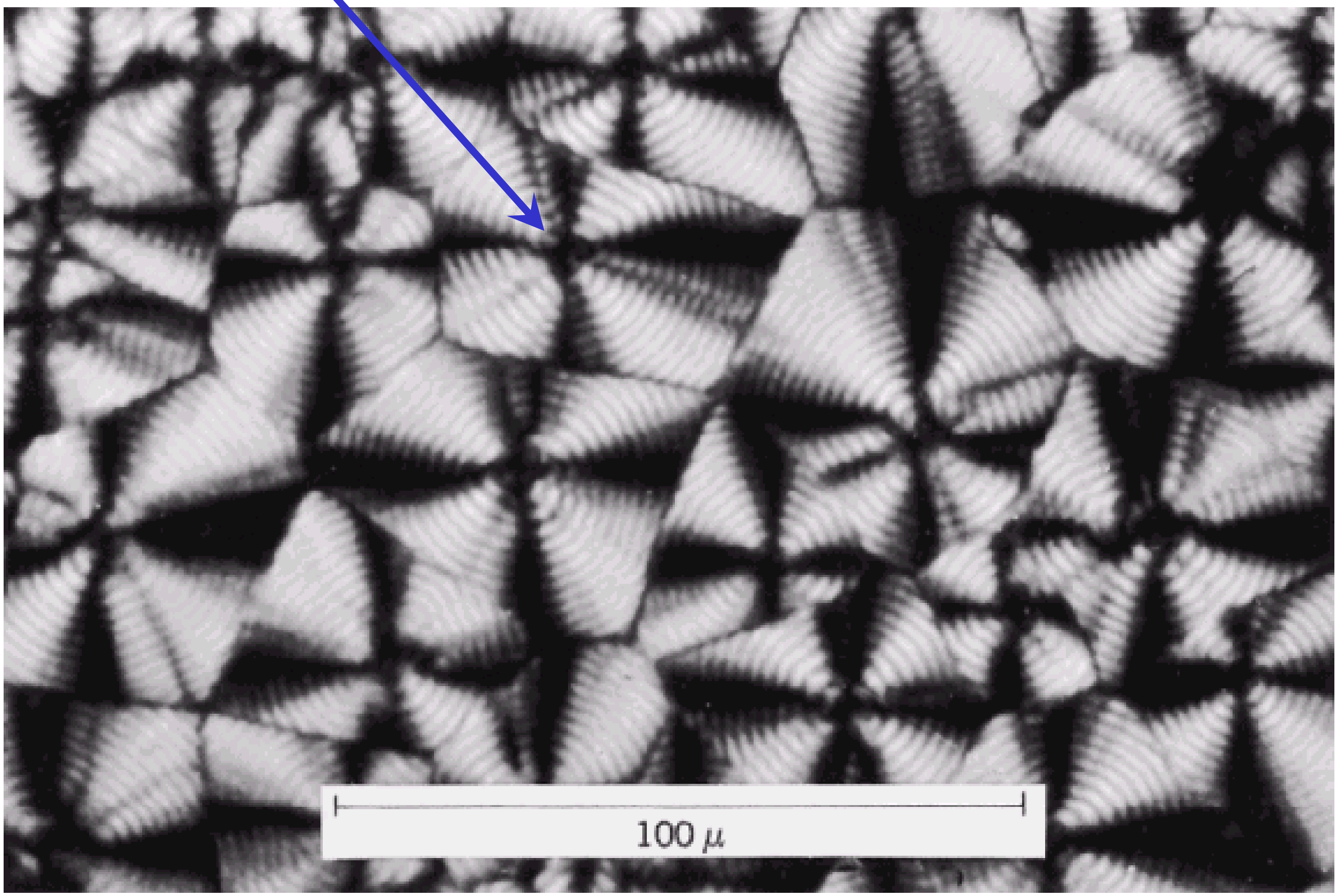


- Spherulites – fast growth – forms lamellar (layered) structures

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

Spherulites – crossed polarizers

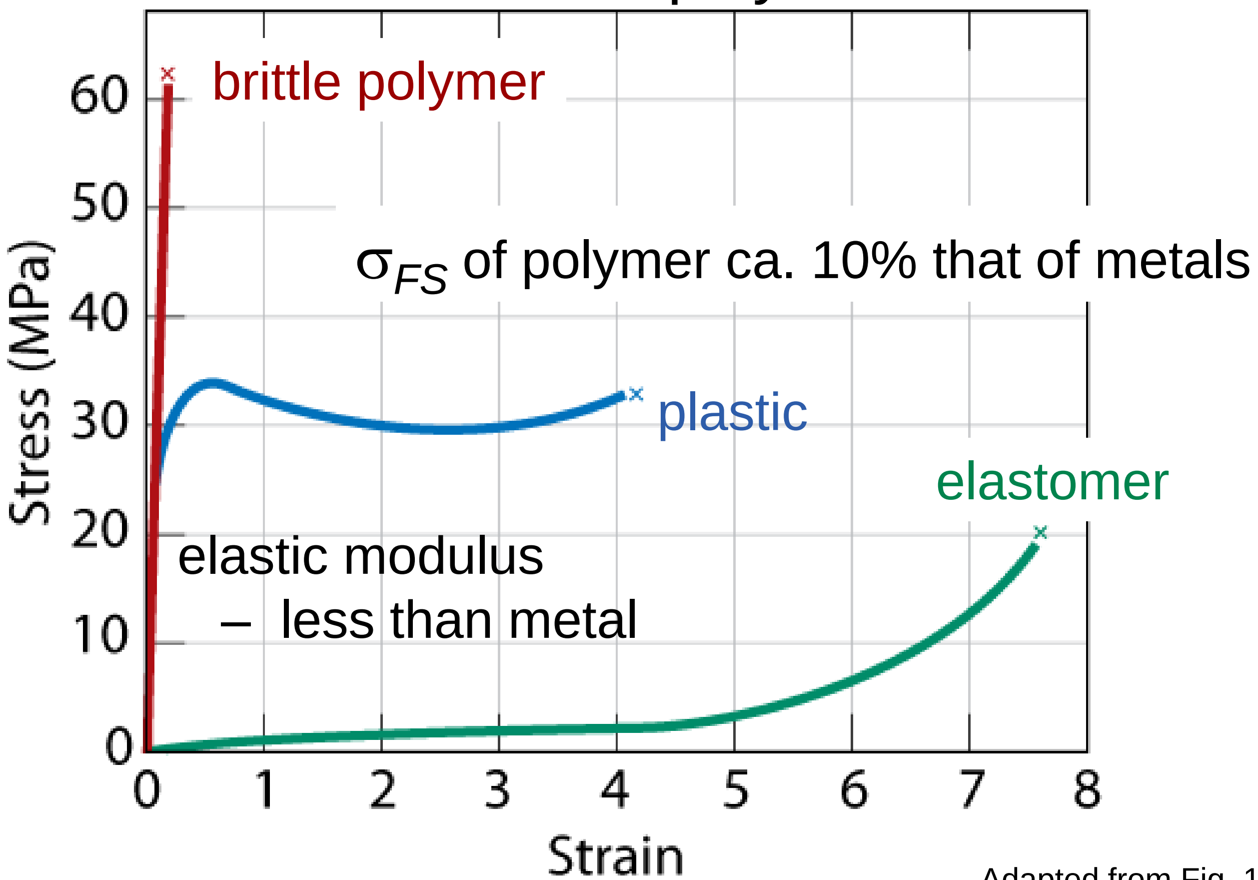
Maltese cross



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

Mechanical Properties

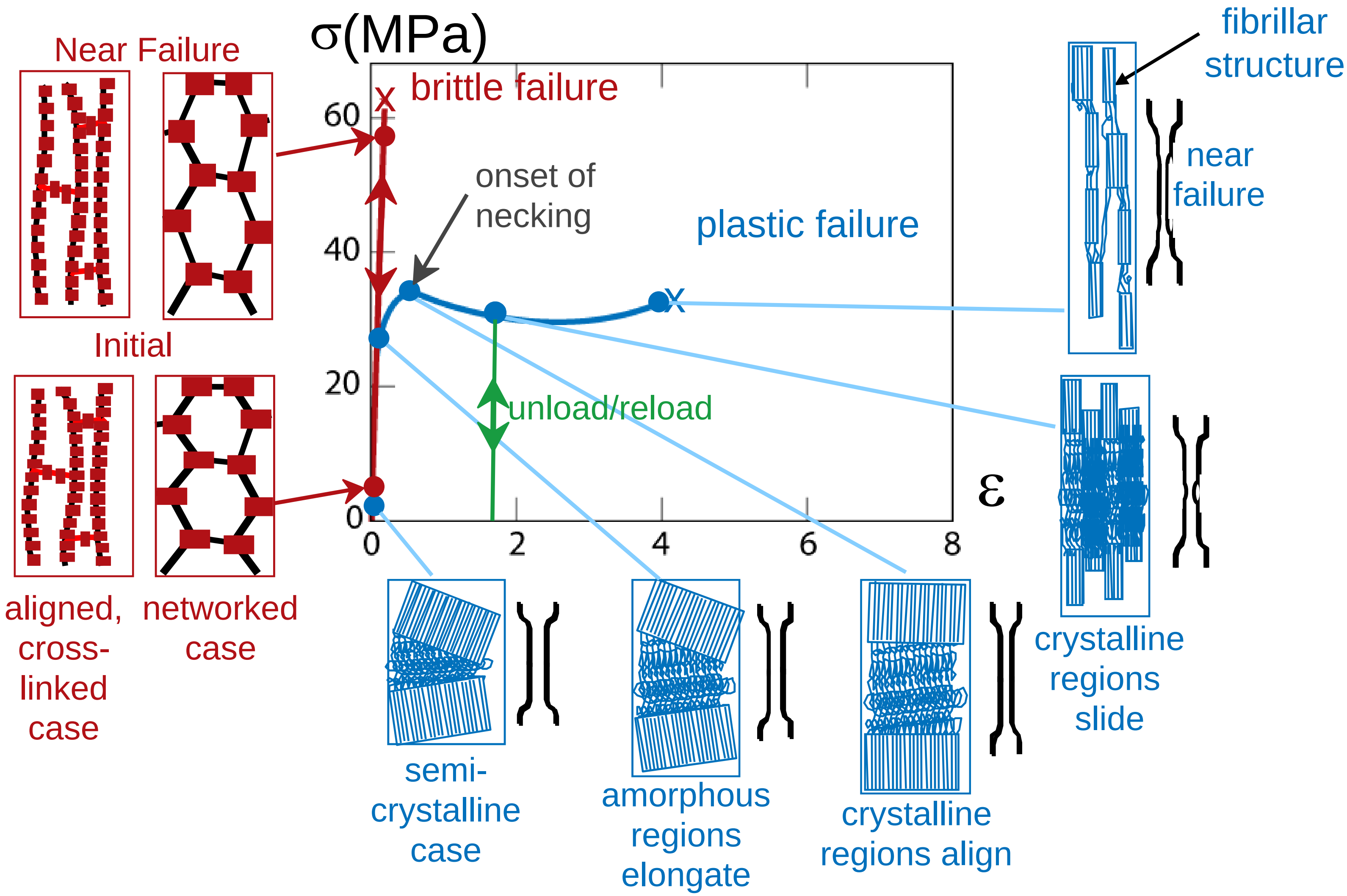
- i.e. stress-strain behavior of polymers



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

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

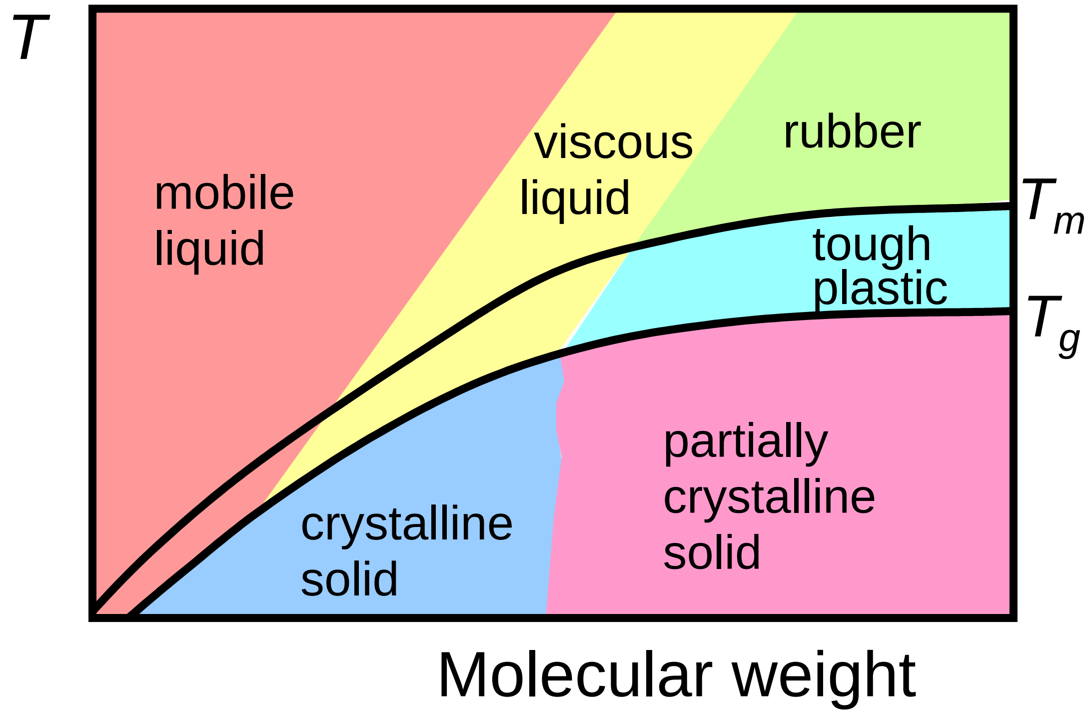
Tensile Response: Brittle & Plastic



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.)

Thermoplastics vs. Thermosets

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



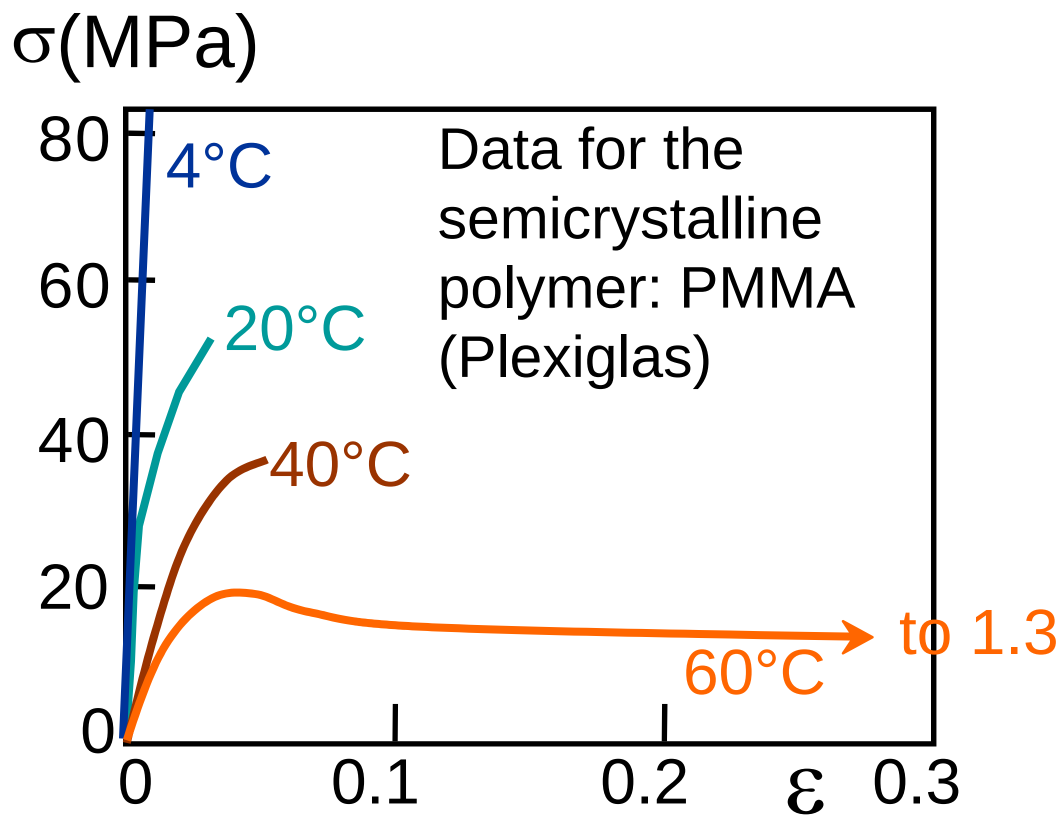
Adapted from Fig. 15.19, *Callister 7e*. (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

- 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.)

Polymer Additives

Improve mechanical properties, processability, durability, etc.

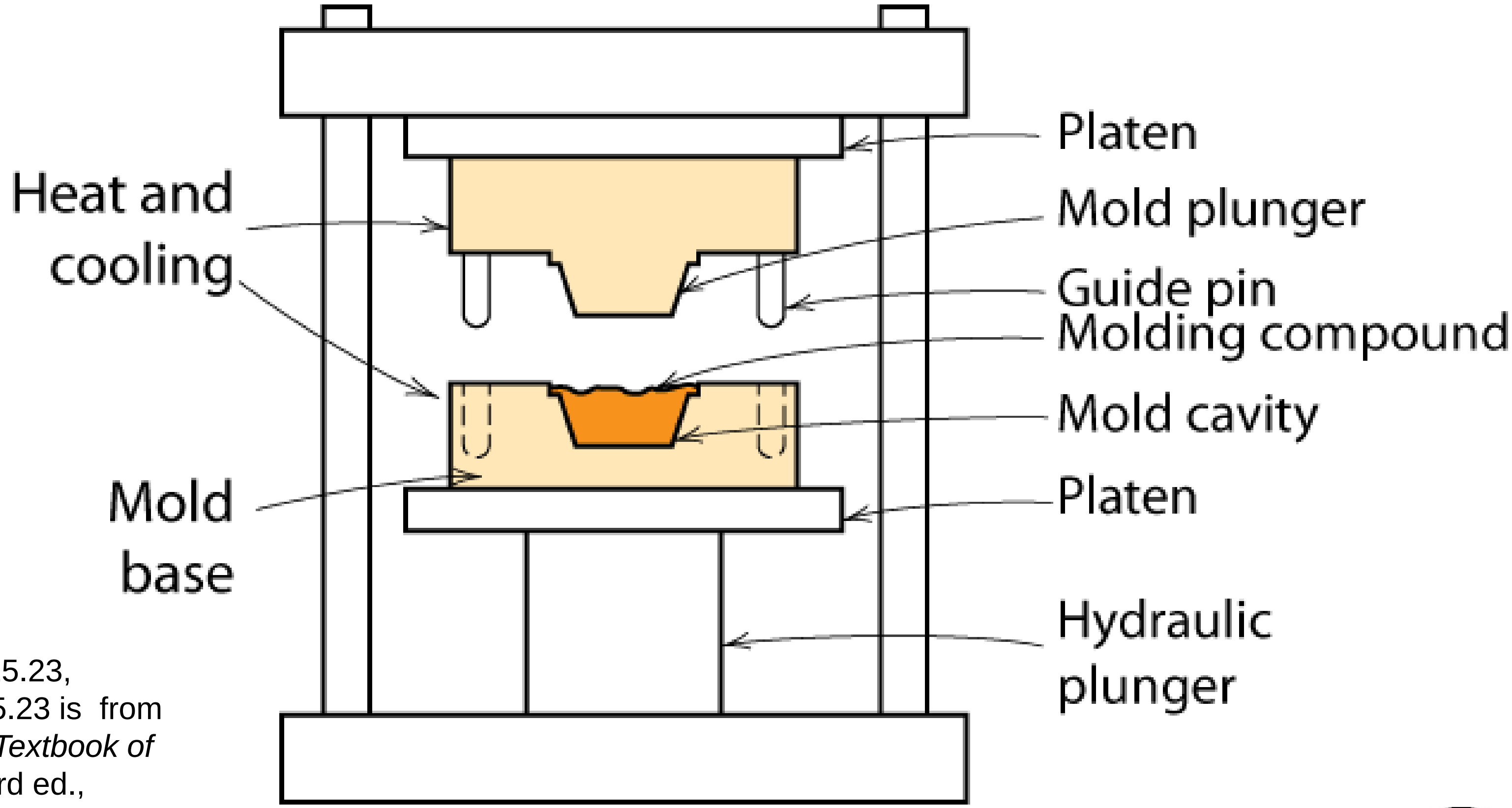
- Fillers
  - Added to improve tensile strength & abrasion resistance, toughness & decrease cost
  - ex: carbon black, silica gel, wood flour, glass, limestone, talc, etc.
- Plasticizers
  - Added to reduce the glass transition temperature T_g
  - commonly added to PVC - otherwise it is brittle

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 Plastics - Molding

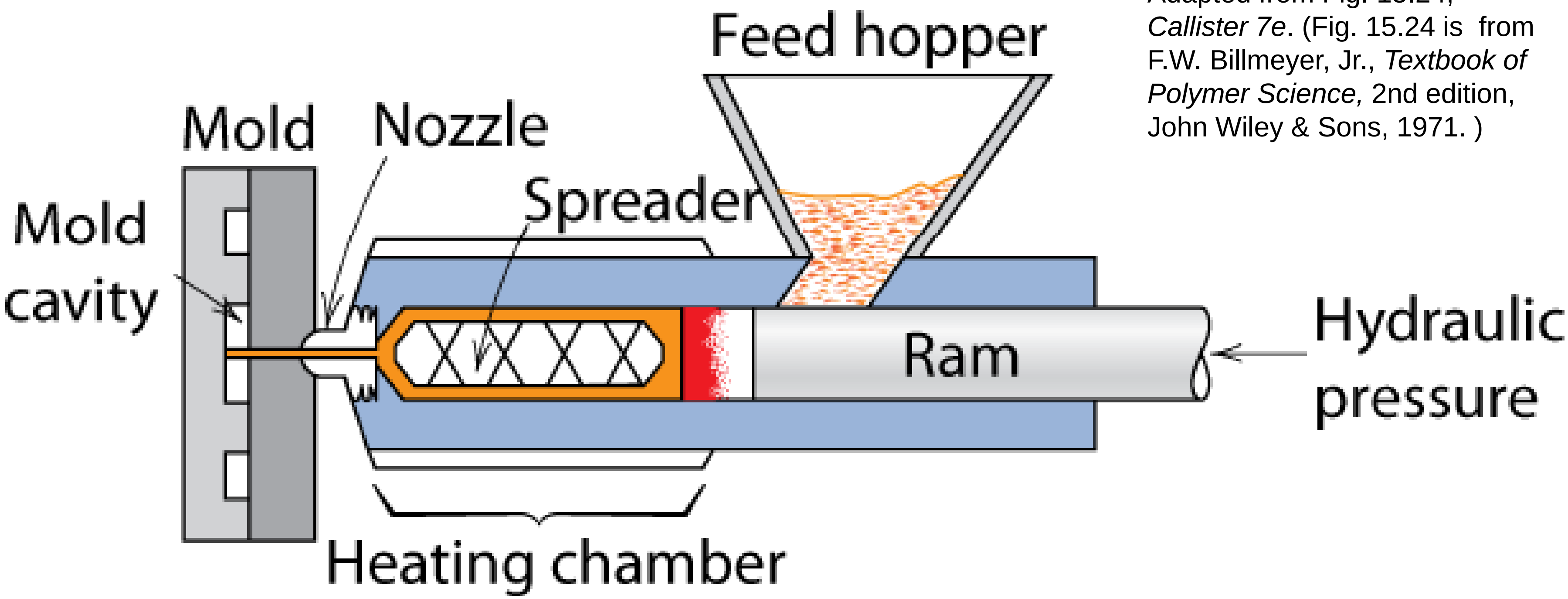
- Compression and transfer molding
  - thermoplastic or thermoset



Adapted from Fig. 15.23, *Callister 7e*. (Fig. 15.23 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science,* 3rd ed., John Wiley & Sons, 1984.)

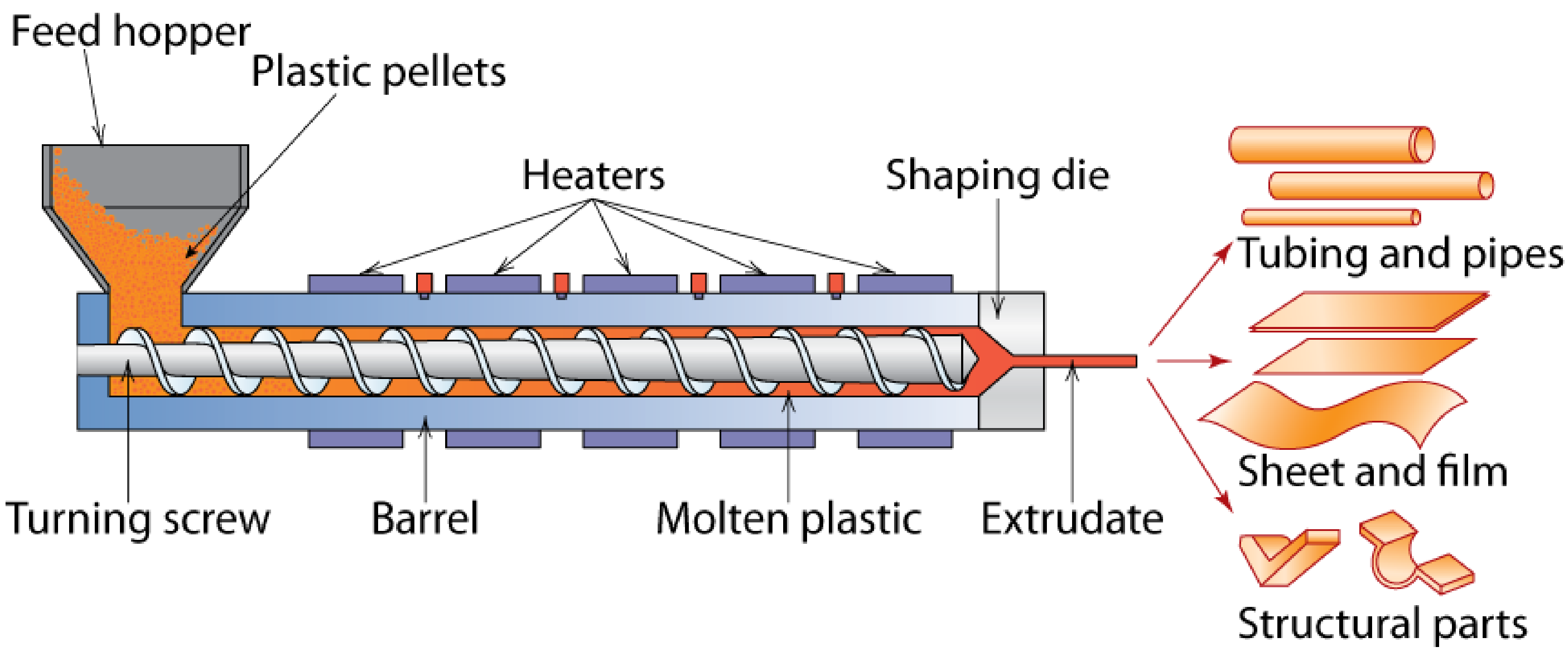
Processing Plastics - Molding

- Injection molding
  - – thermoplastic & some thermosets



Adapted from Fig. 15.24, *Callister 7e*. (Fig. 15.24 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science,* 2nd edition, John Wiley & Sons, 1971.)

Processing Plastics – Extrusion



Adapted from Fig. 15.25, *Callister 7e*. (Fig. 15.25 is from *Encyclopædia Britannica,* 1997.)