

Chapter 14: Polymer Structures

ISSUES TO ADDRESS...

- What are the general structural and chemical characteristics of polymer molecules?
- What are some of the common polymeric materials, and how do they differ chemically?
- How is the crystalline state in polymers different from that in metals and ceramics ?



Ancient Polymers

Originally natural polymers were used

Wood	– Rubber
Cotton	– Wool
Leather	– Silk

Oldest known uses

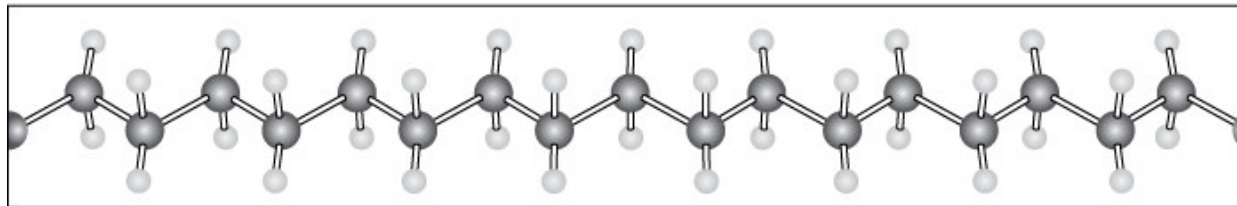
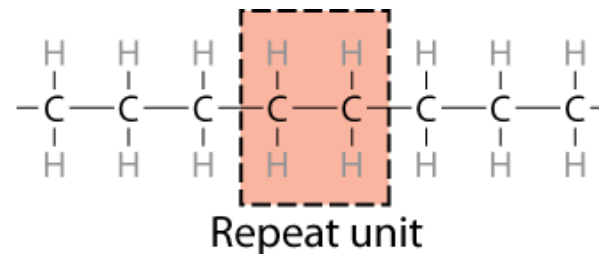
Rubber balls used by Incas

Noah used pitch (a natural polymer)
for the ark



What is a Polymer?

Most polymers are hydrocarbons (made up of H and C)



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

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

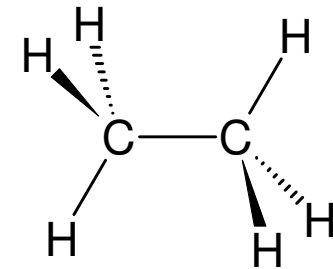


Polymer Composition

Saturated hydrocarbons

Each carbon singly bonded to four other atoms

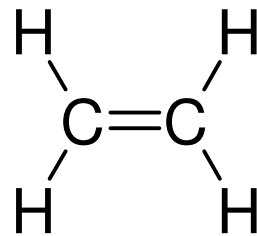
Example: Ethane, C_2H_6 or C_nH_{2n+2}



Unsaturated hydrocarbons

Double & triple bonds somewhat unstable – can form new bonds

– **Double bond** found in ethylene or ethene - C_2H_4 or C_nH_{2n}



– **Triple bond** found in acetylene or ethyne - C_2H_2 or C_nH_{2n-2}

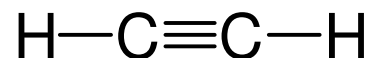


Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

<i>Name</i>	<i>Composition</i>	<i>Structure</i>	<i>Boiling Point (°C)</i>
Methane	CH ₄	$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array} $	-164
Ethane	C ₂ H ₆	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	-88.6
Propane	C ₃ H ₈	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	-42.1
Butane	C ₄ H ₁₀		-0.5
Pentane	C ₅ H ₁₂		36.1
Hexane	C ₆ H ₁₄		69.0



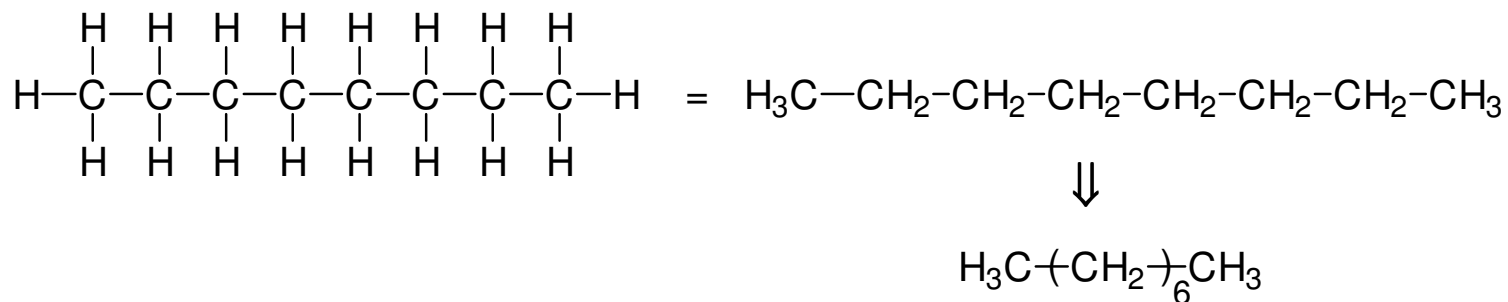
Isomerism

- Isomerism

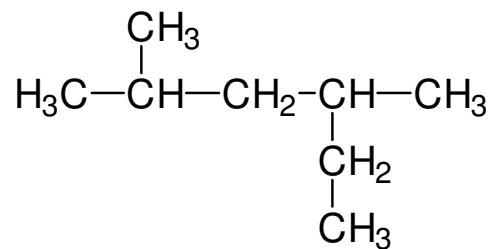
- two compounds with same chemical formula can have quite different structures

- for example: C_8H_{18}

- normal-octane



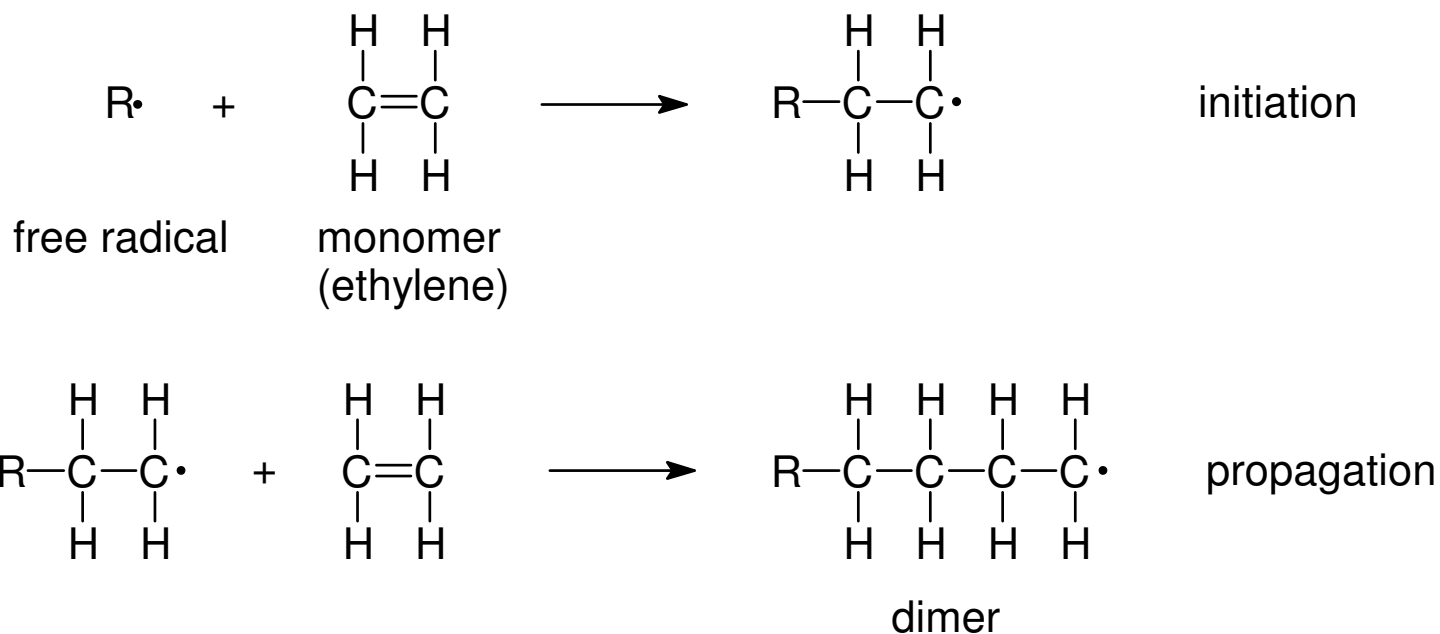
- 2,4-dimethylhexane



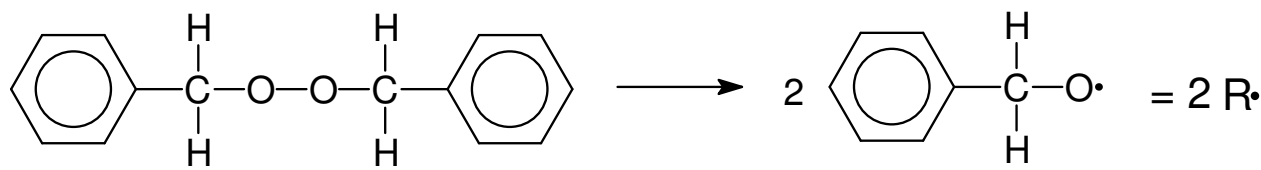
Chemistry of polymer molecules

- Free radical polymerization

R=CH₃, CH₂H₅, C₆H₅.....




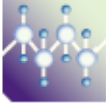
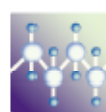


- Initiator: example - benzoyl peroxide



Bulk or Commodity Polymers

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

<i>Polymer</i>	<i>Repeat Unit</i>
 Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array}$
 Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array}$
 Polytetrafluoroethylene (PTFE)	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array}$
 Polypropylene (PP)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$
 Polystyrene (PS)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$



MOLECULAR WEIGHT

- **Molecular weight, M** : Mass of a mole of chains.



Low M



high M

Not all chains in a polymer are of the same length
— i.e., there is a **distribution of molecular weights**

$$\overline{M}_n = \sum x_i M_i \rightarrow \text{Number average molecular weight}$$

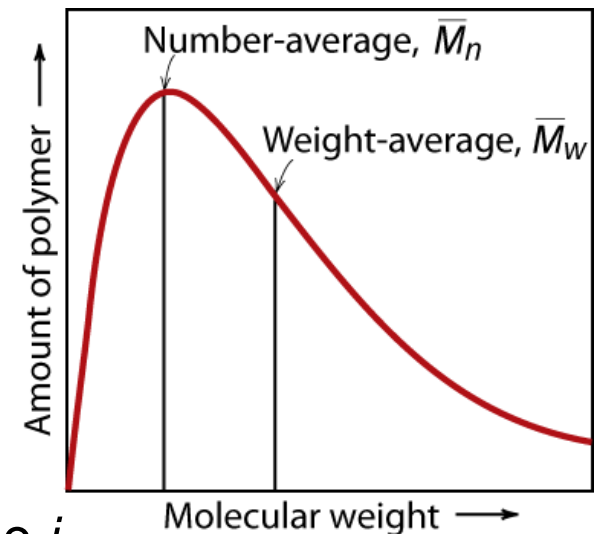
$$\overline{M}_w = \sum w_i M_i \rightarrow \text{Weight average molecular weight}$$

$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}} \quad x_i = \frac{N_i}{\sum N_i} \quad w_i = \frac{N_i W_i}{\sum N_i W_i}$$

M_i = mean (middle) molecular weight of size range i

x_i = number fraction of chains in size range i

w_i = weight fraction of chains in size range i



Adapted from Fig. 14.4, *Callister & Rethwisch 8e*.



Molecular Weight Calculation

Example: average mass of a class

Student	Weight
	mass (lb)
1	104
2	116
3	140
4	143
5	180
6	182
7	191
8	220
9	225
10	380

What is the average weight of the students in this class:

- Based on the number fraction of students in each mass range?
- Based on the weight fraction of students in each mass range?



Molecular Weight Calculation (cont.)

Solution: The first step is to sort the students into weight ranges.
Using 40 lb ranges gives the following table:

weight range	number of students	mean weight
mass (lb)	N_i	mass (lb)
81-120	2	110
121-160	2	142
161-200	3	184
201-240	2	223
241-280	0	-
281-320	0	-
321-360	0	-
361-400	1	380

Calculate the number and weight fraction of students in each weight range as follows:

$$x_i = \frac{N_i}{\sum N_i} \quad w_i = \frac{N_i W_i}{\sum N_i W_i}$$

For example: for the 81-120 lb range

$$x_{81-120} = \frac{2}{10} = 0.2$$

$$w_{81-120} = \frac{2 \times 110}{1881} = 0.117$$

total number $\rightarrow \sum N_i$
10

$\sum N_i W_i$ \leftarrow total weight
1881



Molecular Weight Calculation (cont.)

weight range	mean weight W_i	number fraction x_i	weight fraction w_i
mass (lb)	mass (lb)		
81-120	110	0.2	0.117
121-160	142	0.2	0.150
161-200	184	0.3	0.294
201-240	223	0.2	0.237
241-280	-	0	0.000
281-320	-	0	0.000
321-360	-	0	0.000
361-400	380	0.1	0.202

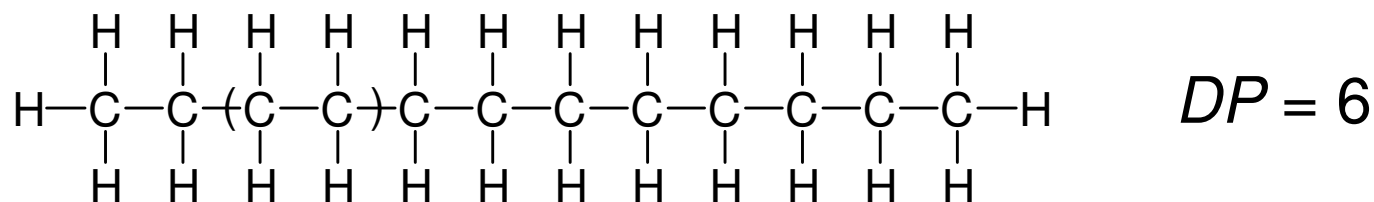
$$\bar{M}_n = \sum x_i M_i = (0.2 \times 110 + 0.2 \times 142 + 0.3 \times 184 + 0.2 \times 223 + 0.1 \times 380) = 188 \text{ lb}$$

$$\bar{M}_w = \sum w_i M_i = (0.117 \times 110 + 0.150 \times 142 + 0.294 \times 184 + 0.237 \times 223 + 0.202 \times 380) = 218 \text{ lb}$$

$$\bar{M}_w = \sum w_i M_i = 218 \text{ lb}$$

Degree of Polymerization, DP

DP = average number of repeat units per chain



$$DP = \frac{\overline{M}_n}{\overline{m}}$$

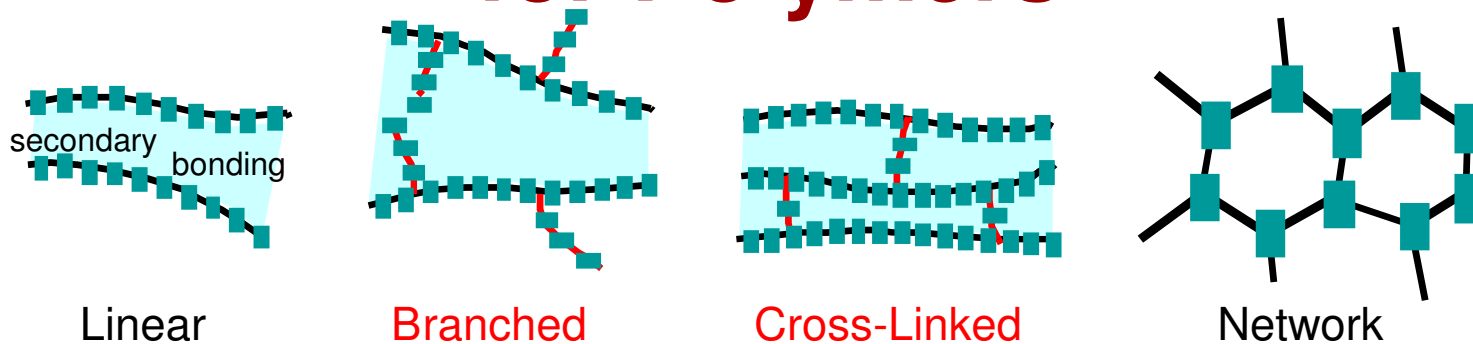
where \overline{m} = average molecular weight of repeat unit
for copolymers this is calculated as follows:

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

Chain fraction f_i mol. wt of repeat unit i



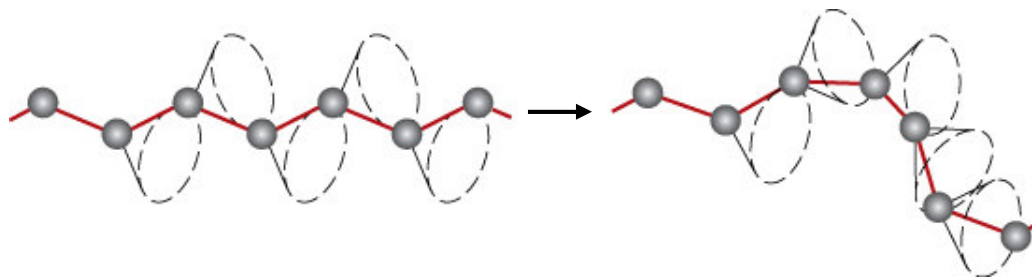
Molecular Structures and shape for Polymers



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

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



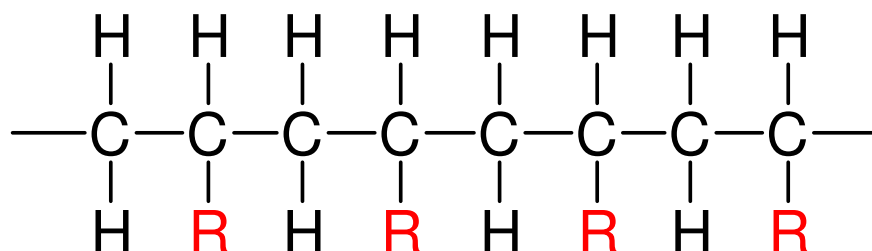
Adapted from Fig. 14.5, *Callister & Rethwisch 8e*.



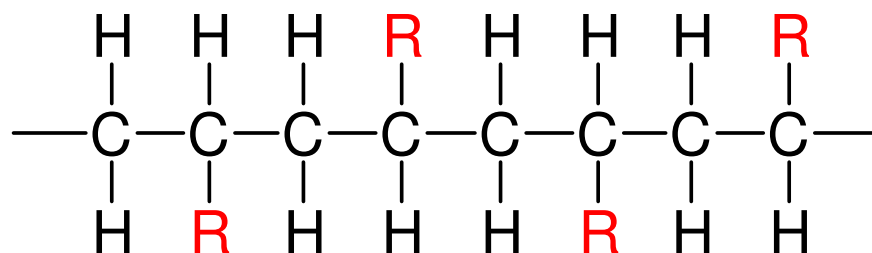
Molecular Configurations for Polymers: Tacticity

Tacticity – stereoregularity or spatial arrangement of **R** units along chain

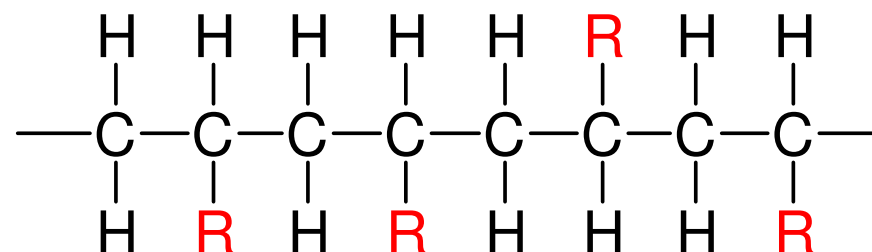
isotactic – all **R** groups on same side of chain



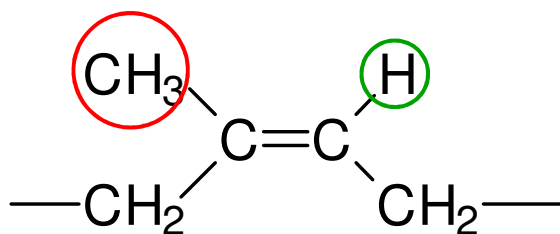
syndiotactic – **R** groups alternate sides



atactic – **R** groups randomly positioned



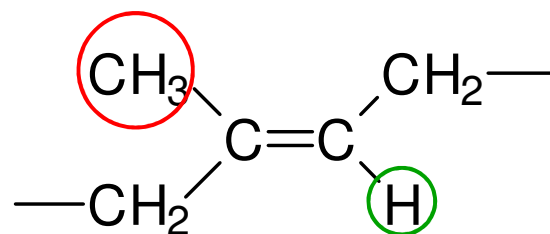
Geometrical isomer cis/trans Isomerism



cis

cis-isoprene
(natural rubber)

H atom and CH₃ group on
same side of chain



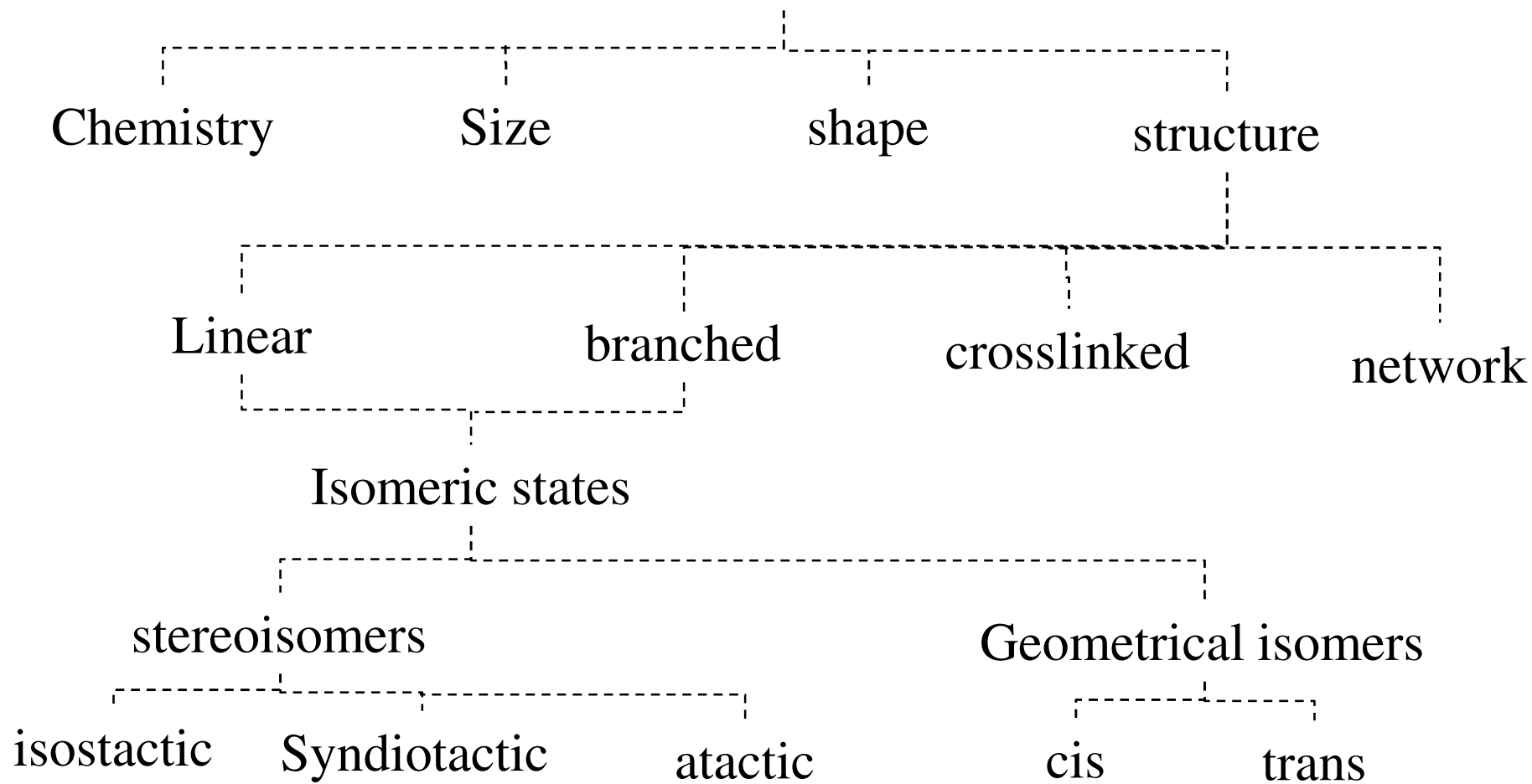
trans

trans-isoprene
(gutta percha)

H atom and CH₃ group on
opposite sides of chain



Molecular characteristics



Copolymers

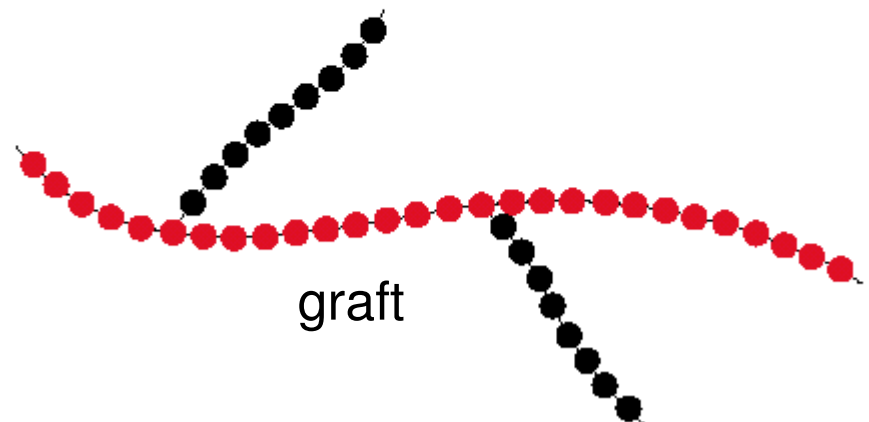
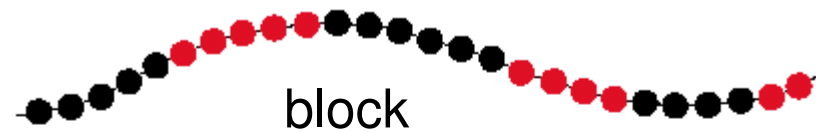
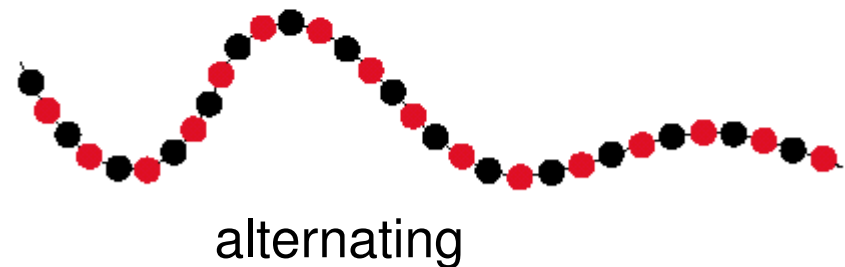
two or more monomers
polymerized together

- **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 – ●

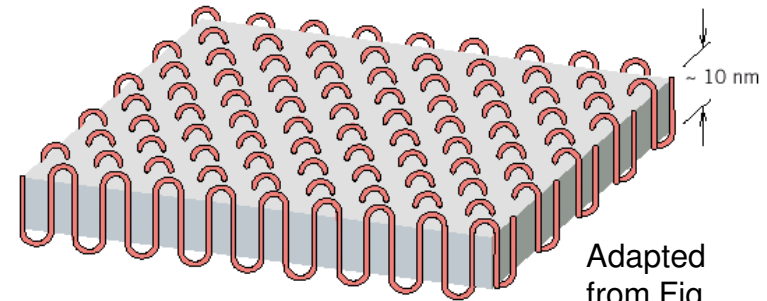
B – ●

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



Polymer Crystallinity

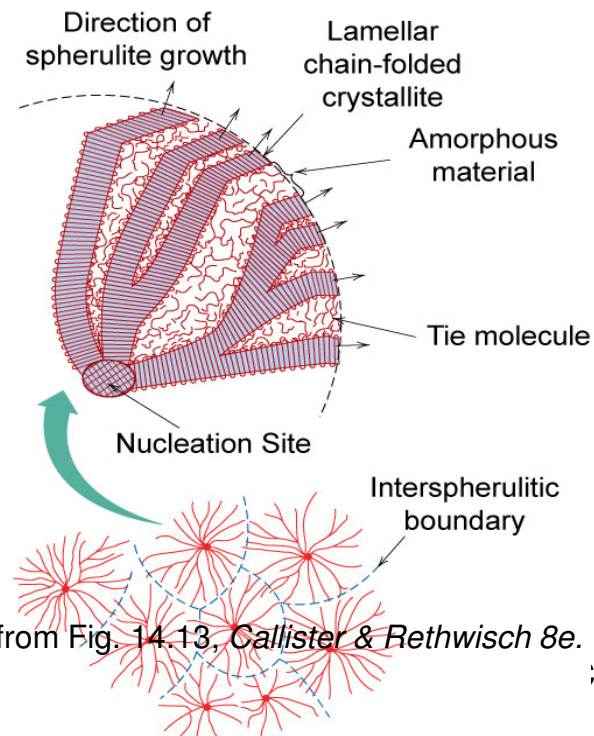
- Crystallite (small crystalline region)
- Chain folded structure



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

- Spherulite (semicrystalline)

Alternating chain-folded crystallites and amorphous regions
Spherulite structure for relatively rapid growth rates



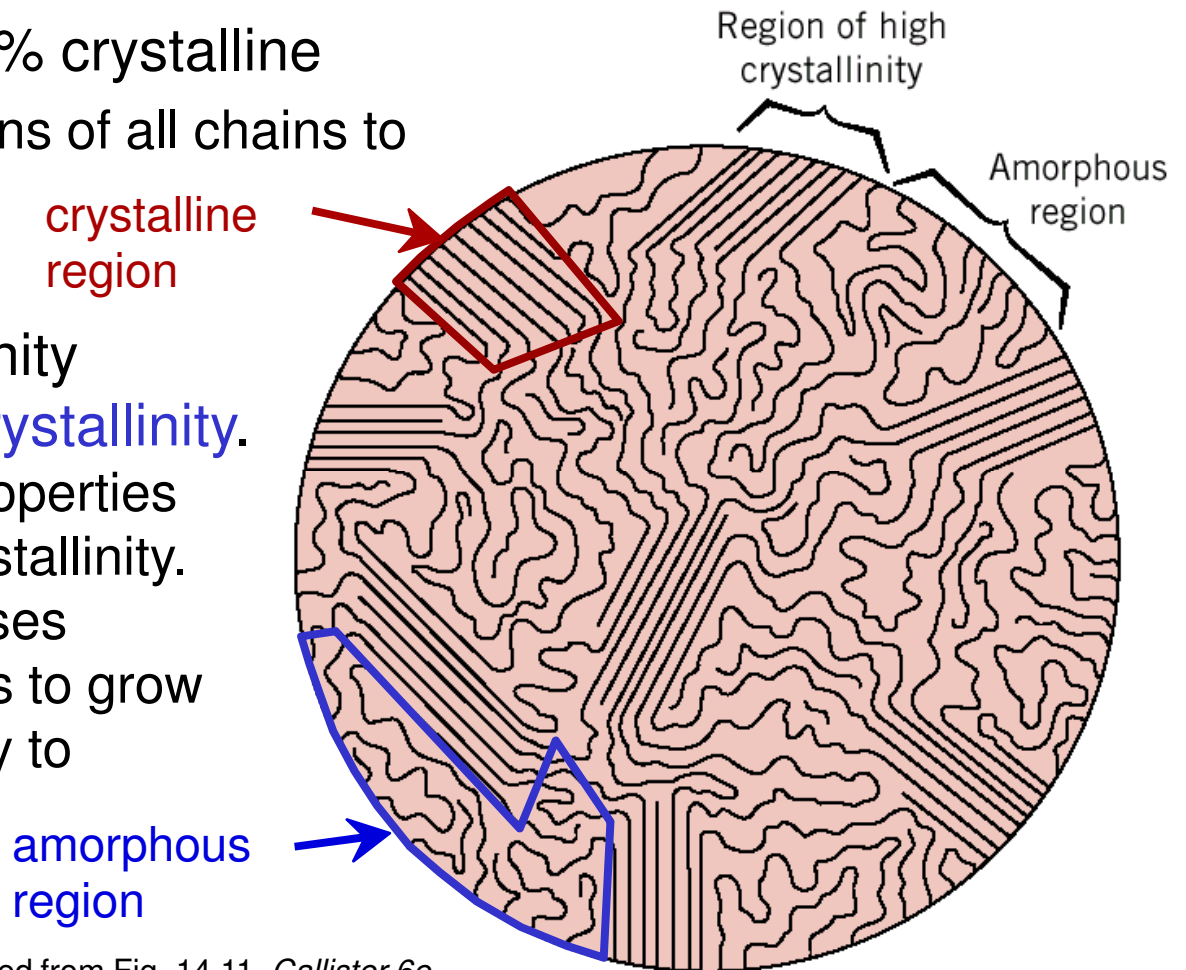
Adapted from Fig. 14.13, *Callister & Rethwisch 8e.*



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.



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.)



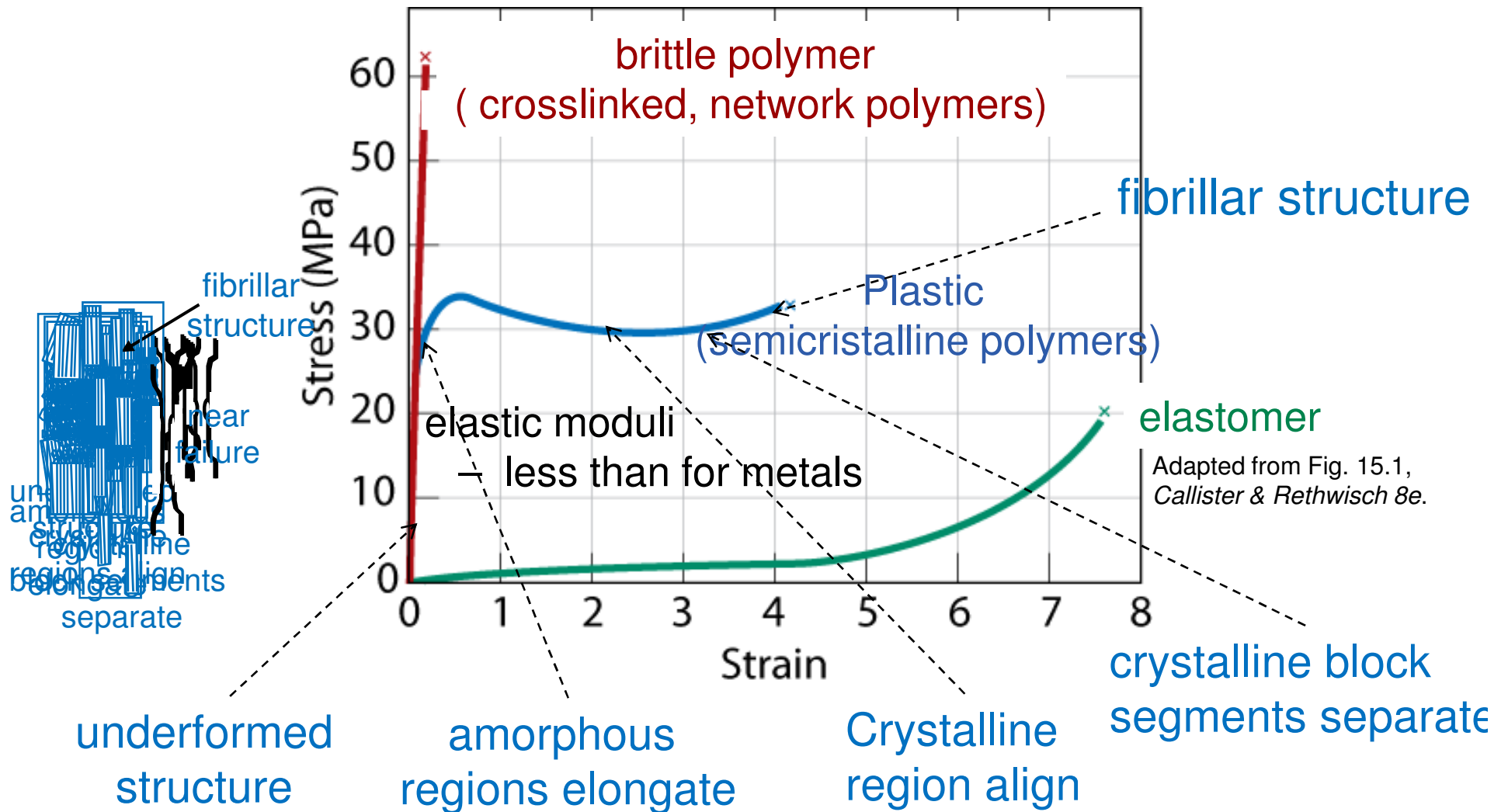
Chapter 15: Characteristics, Applications & Processing of Polymers

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?

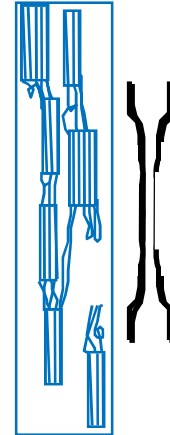


Mechanical Properties of Polymers – Stress-Strain Behavior



Predeformation by Drawing

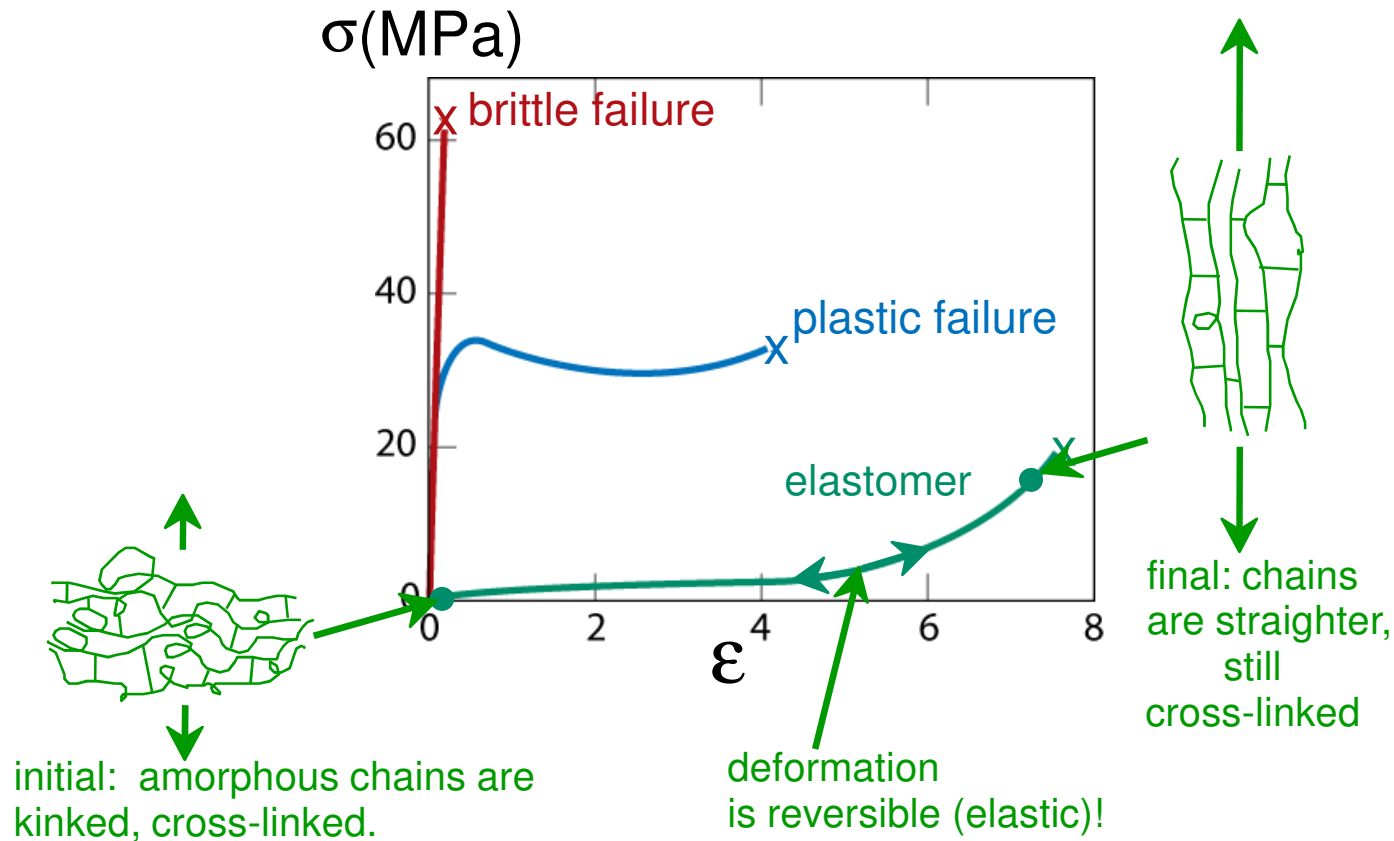
- **Drawing**... (ex: monofilament fishline)
 - stretches the polymer prior to use
 - aligns chains in the stretching direction
- Results of drawing:
 - increases the elastic modulus (E) in the stretching direction
 - increases the tensile strength (TS) in the stretching direction
 - decreases ductility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



Adapted from Fig. 15.13, *Callister & Rethwisch 8e*. (Fig. 15.13 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)



Mechanisms of Deformation— Elastomers



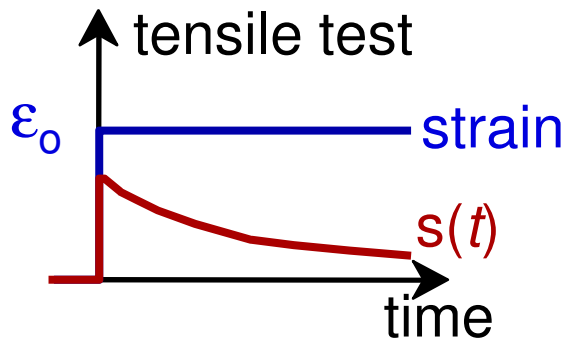
Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 8e*. Inset figures along elastomer curve (green) adapted from Fig. 15.15, *Callister & Rethwisch 8e*. (Fig. 15.15 is from Z.D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd ed., John Wiley and Sons, 1987.)

- 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)



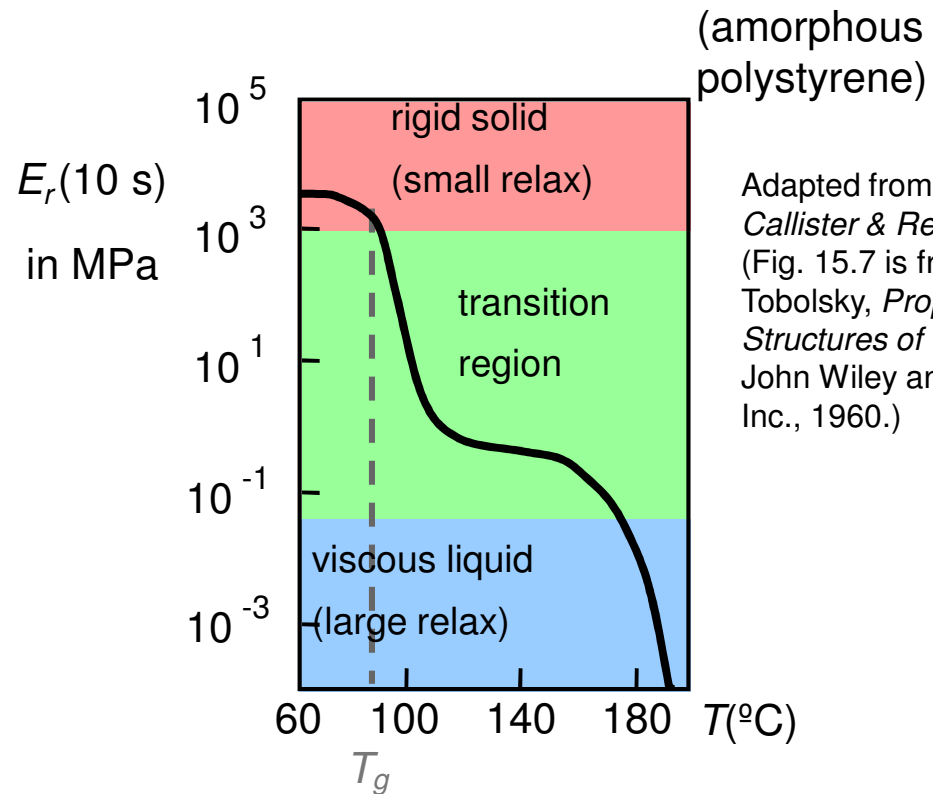
Time-Dependent Deformation

- **Stress relaxation test:**
 - strain in tension to ϵ_0 and hold.
 - observe decrease in stress with time.
- There is a large decrease in E_r for $T > T_g$.



- **Relaxation modulus:**

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0}$$



Adapted from Fig. 15.7, Callister & Rethwisch 8e. (Fig. 15.7 is from A.V. Tobolsky, *Properties and Structures of Polymers*, John Wiley and Sons, Inc., 1960.)



Time-Dependent Deformation

- Creep test:

- stress σ_0 is apply and hold.
- observe the strain evolution with time

Many material can be subject to time dependant deformation when the stress level is maintained constant.

- Creep modulus:

$$E_c(t) = \frac{\sigma_0}{\varepsilon(t)}$$

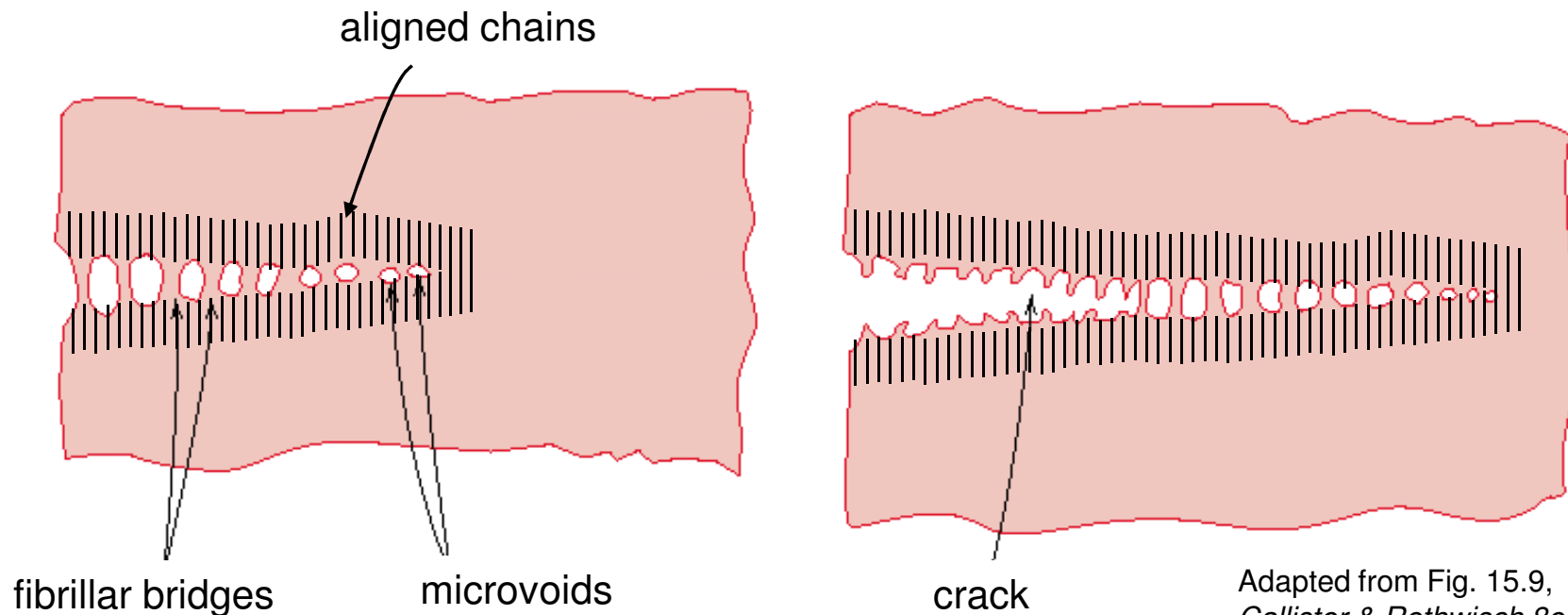
Viscoelastic creep can be really important even at room temperature. (example tires may develop flat spots if they parked for prolonged time period)



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.



Thermoplastic/Thermosetting

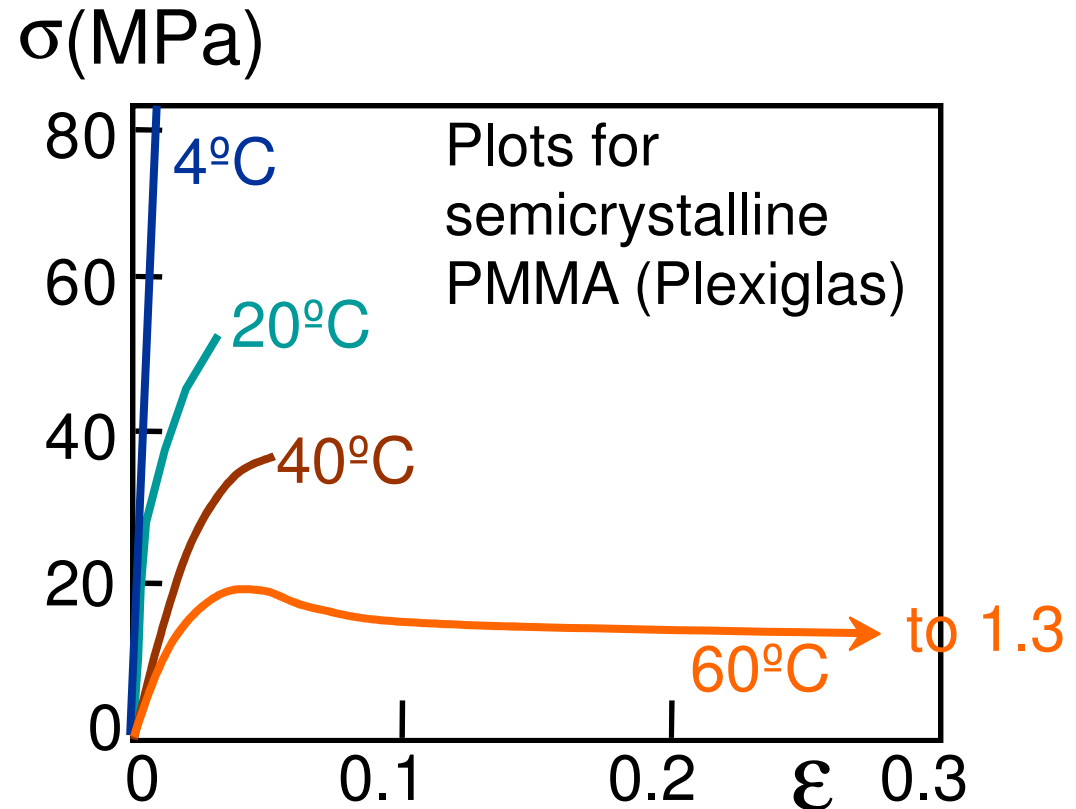
Classification of polymers according to their behavior with rising the temperature

- Thermoplastic polymer soften when you rise the temperature (eventually liquefy) and harden when you cooled reversible irreversible if molten and raised at too high temperature. (little crosslinking, ductile, soften w/heating, polyethylene, polypropylene, polycarbonate, polystyrene.)
- Thermosetting (network polymers) they become permanently hard during their formation and don't soften during heating bonds (network or cross linked) will resist to the vibration and rotation induced by the temperature. Thermosetting material are harder and stronger than thermoplastic. (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 .



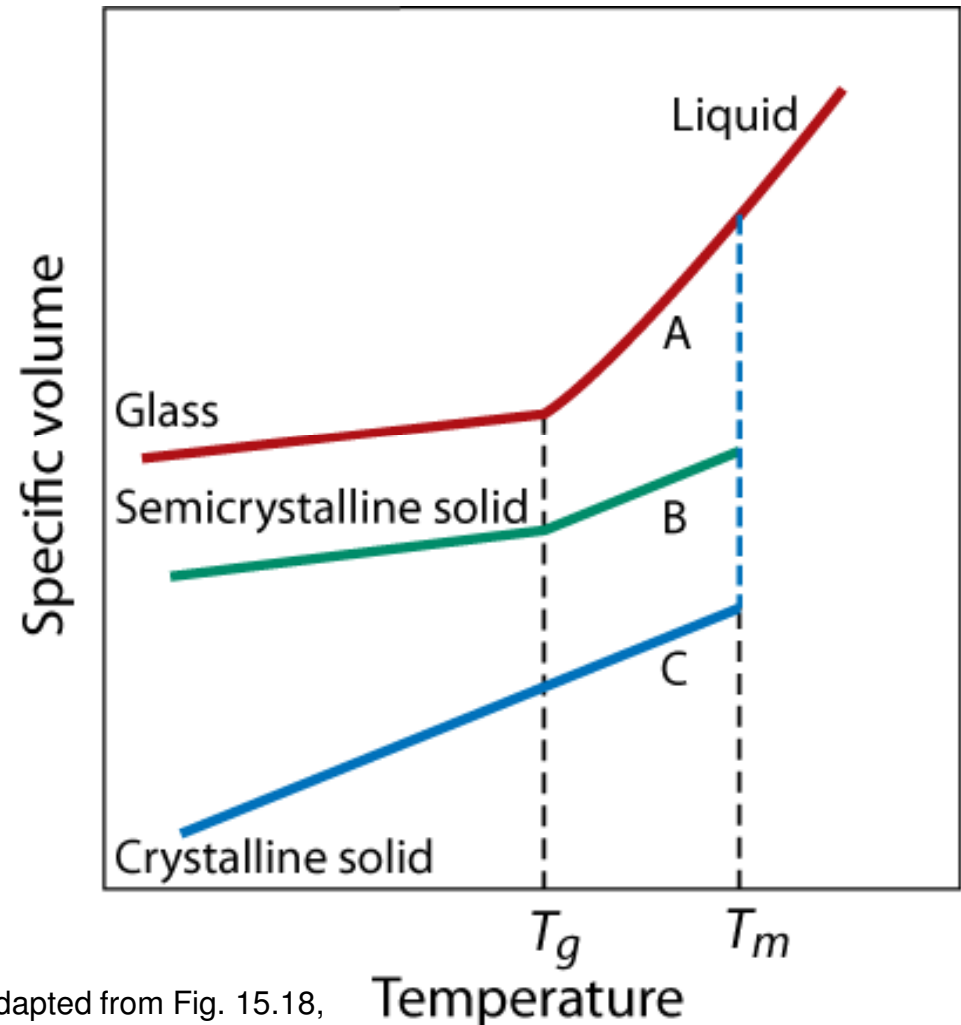
Adapted from Fig. 15.3, *Callister & Rethwisch 8e*. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics', *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)



Melting & Glass Transition Temps.

What factors affect T_m and T_g ?

- Both T_m and T_g increase with increasing chain stiffness
- Chain stiffness increased by presence of
 1. Bulky sidegroups
 2. Polar groups or sidegroups
 3. Chain double bonds and aromatic chain groups
- Regularity of repeat unit arrangements – affects T_m only



Adapted from Fig. 15.18,
Callister & Rethwisch 8e.

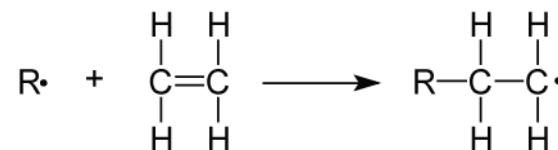


Polymer Formation

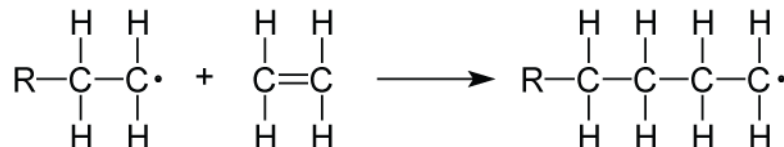
- There are two types of polymerization
 - Addition (or chain) polymerization
 - Condensation (step) polymerization

Addition (Chain) Polymerization

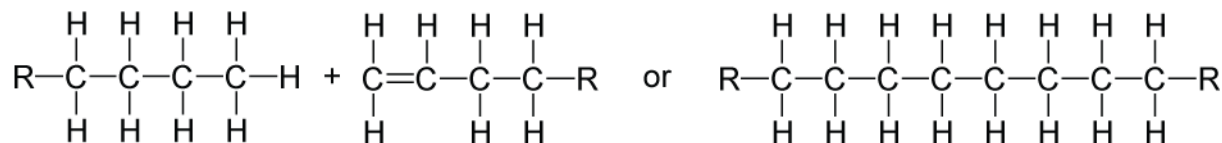
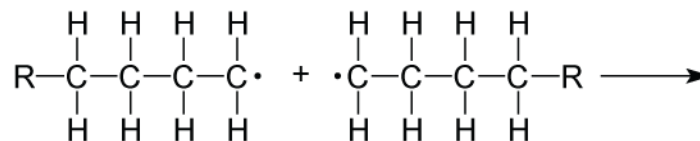
– Initiation



– Propagation



– Termination

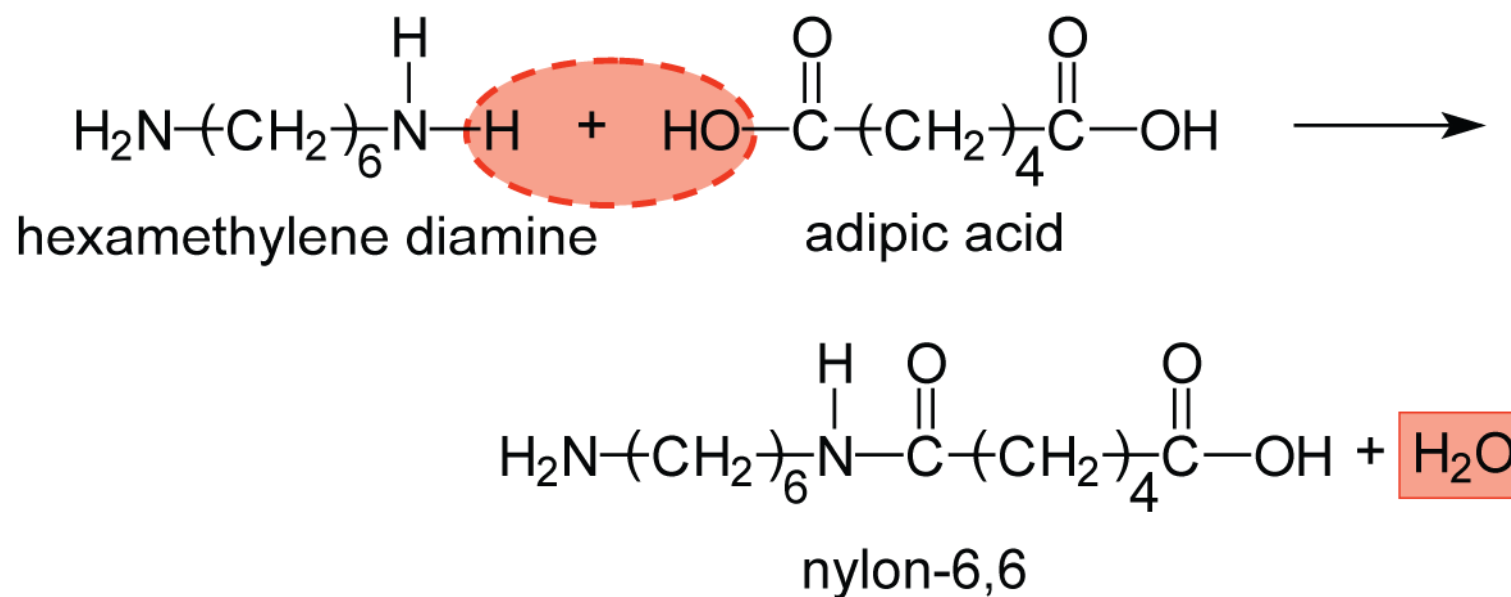


Disproportionation

Combination



Condensation (Step) Polymerization



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 below room temperature
- Presence of plasticizer transforms brittle polymer to a ductile one
- Commonly added to PVC - otherwise it is brittle



Polymer Additives (cont.)

- Stabilizers
 - Antioxidants
 - UV protectants
- Lubricants
 - Added to allow easier processing
 - polymer “slides” through dies easier
 - ex: sodium stearate
- Colorants
 - Dyes and pigments
- Flame Retardants
 - Substances containing chlorine, fluorine, and boron



Processing Plastics – Compression Molding

Thermoplastics and thermosets

- polymer and additives placed in mold cavity
- mold heated and pressure applied
- fluid polymer assumes shape of mold

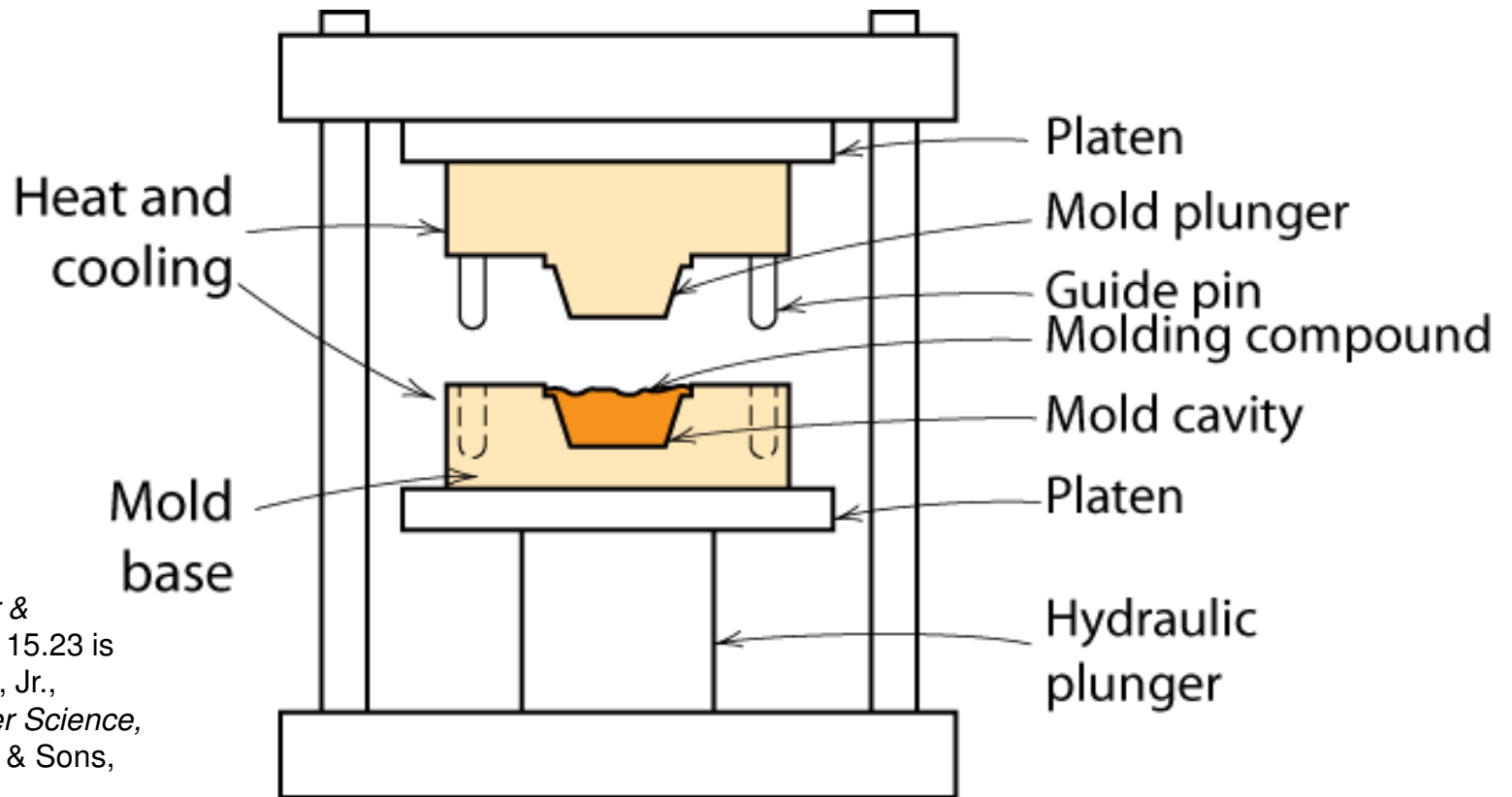


Fig. 15.23, Callister & Rethwisch 8e. (Fig. 15.23 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley & Sons, 1984.)

Processing Plastics – Injection Molding

Thermoplastics and some thermosets

- when **ram** retracts, plastic pellets drop from **hopper** into barrel
- ram forces plastic into the **heating chamber** (around the **spreader**) where the plastic melts as it moves forward
- molten plastic is forced under pressure (injected) into the mold cavity where it assumes the shape of the mold

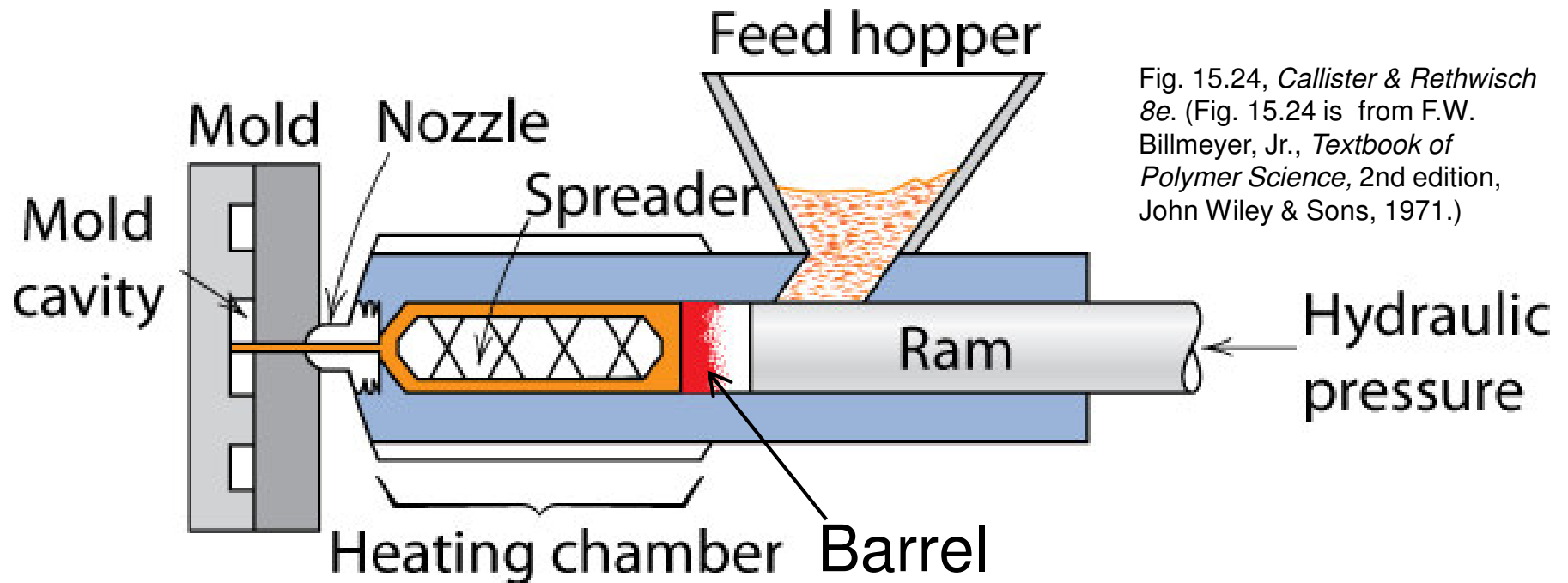


Fig. 15.24, Callister & Rethwisch 8e. (Fig. 15.24 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd edition, John Wiley & Sons, 1971.)

Processing Plastics – Extrusion

thermoplastics

- plastic pellets drop from hopper onto the turning screw
- plastic pellets melt as the turning screw pushes them forward by the heaters
- molten polymer is forced under pressure through the shaping die to form the final product (extrudate)

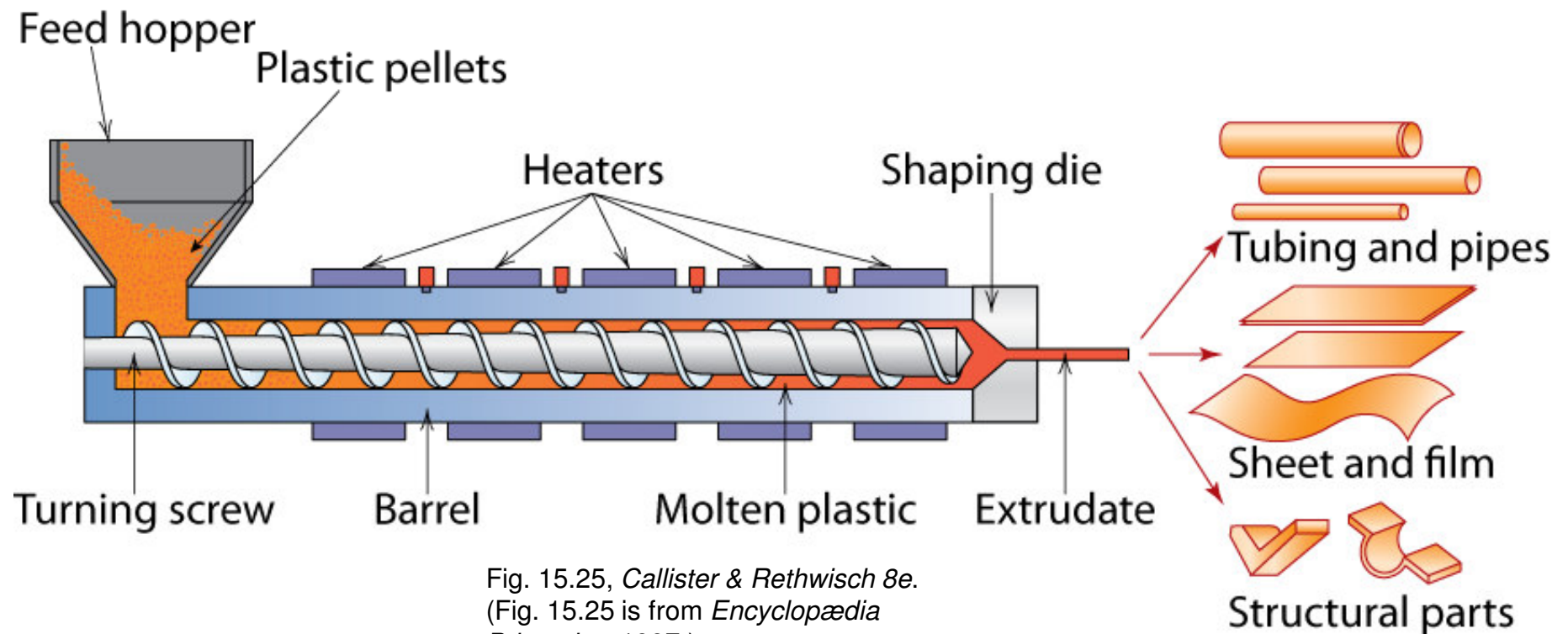


Fig. 15.25, *Callister & Rethwisch 8e.*
(Fig. 15.25 is from *Encyclopædia Britannica*, 1997.)



Processing Plastics – Blown-Film Extrusion

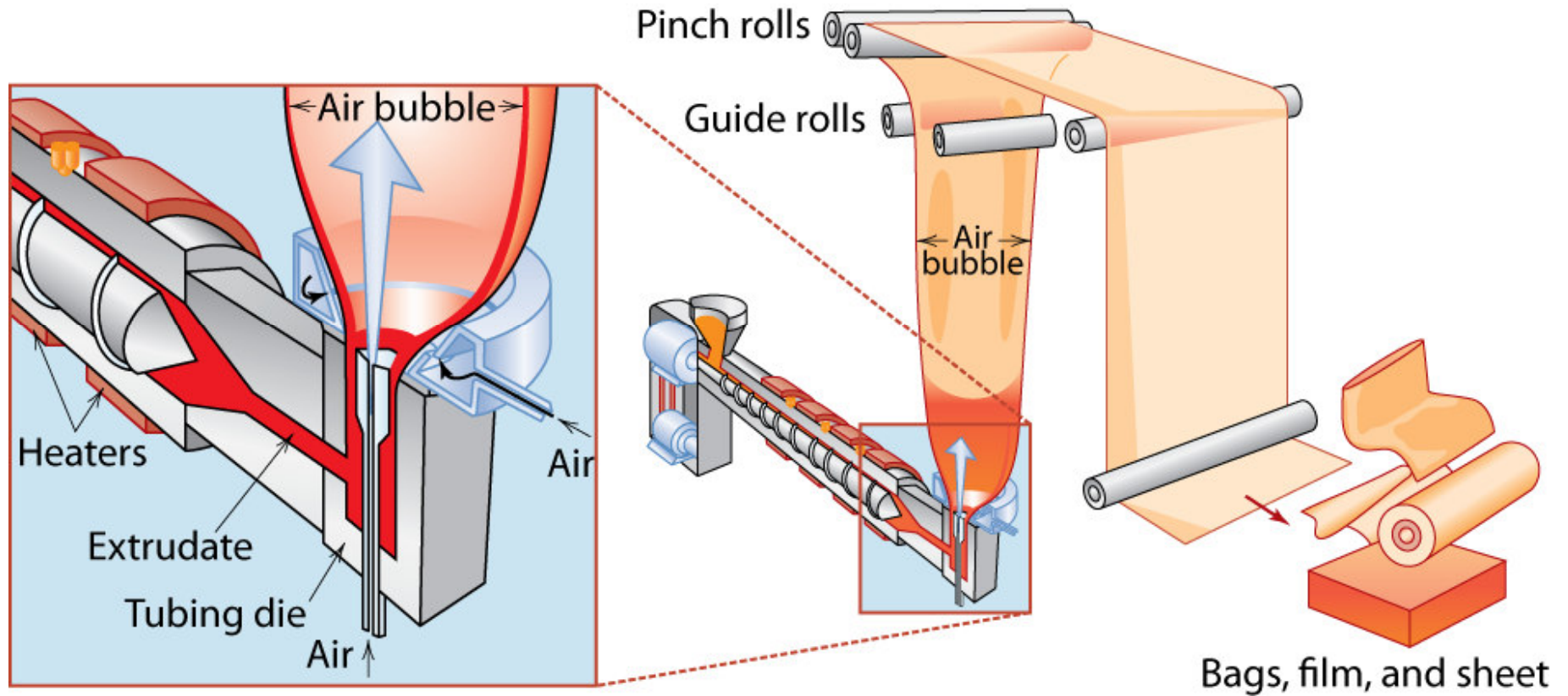


Fig. 15.26, *Callister & Rethwisch 8e*.
(Fig. 15.26 is from *Encyclopædia Britannica*, 1997.)



Polymer Types – Fibers

Fibers - length/diameter >100

- Primary use is in **textiles**.
- Fiber characteristics:
 - high tensile strengths
 - high degrees of crystallinity
 - structures containing polar groups
- Formed by **spinning**
 - extrude polymer through a spinneret (a die containing many small orifices)
 - the spun fibers are drawn under tension
 - leads to highly aligned chains - fibrillar structure



Polymer Types – Miscellaneous

- **Coatings** – thin polymer films applied to surfaces – i.e., paints, varnishes
 - protects from corrosion/degradation
 - decorative – improves appearance
 - can provide electrical insulation
- **Adhesives** – bonds two solid materials (**adherands**)
 - bonding types:
 1. Secondary – van der Waals forces
 2. Mechanical – penetration into pores/crevices
- **Films** – produced by blown film extrusion
- **Foams** – gas bubbles incorporated into plastic



Summary

- Limitations of polymers:
 - E , σ_y , K_c , $T_{\text{application}}$ are generally small.
 - Deformation is often time and temperature dependent.
- **Thermoplastics** (PE, PS, PP, PC):
 - Smaller E , σ_y , $T_{\text{application}}$
 - Larger K_c
 - Easier to form and recycle
- **Elastomers** (rubber):
 - Large reversible strains!
- **Thermosets** (epoxies, polyesters):
 - Larger E , σ_y , $T_{\text{application}}$
 - Smaller K_c

Table 15.3 *Callister & Rethwisch 8e:*

Good overview of applications and trade names of polymers.



Summary

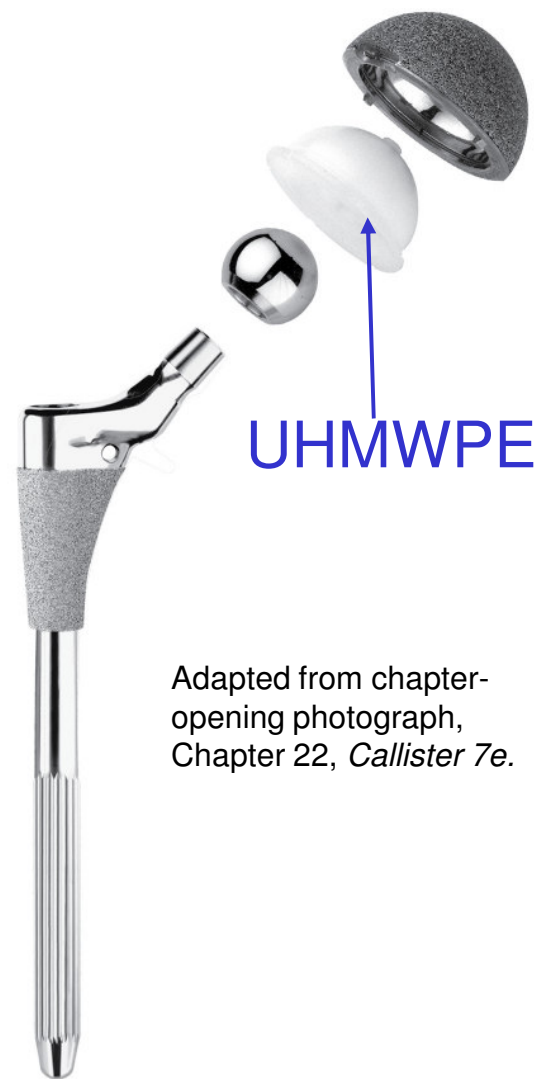
- Polymer Processing
 - compression and injection molding, extrusion, blown film extrusion
- Polymer melting and glass transition temperatures
- Polymer applications
 - elastomers
 - coatings
 - films
 - advanced polymeric materials
 - fibers
 - adhesives
 - foams



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*.

