CHAPTER 14: POLYMER STRUCTURES

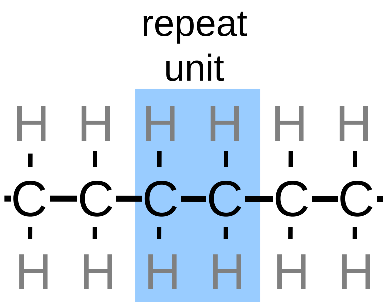
ISSUES TO ADDRESS...

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

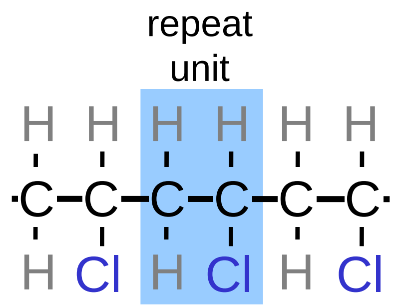
Chapter 14 – Polymers

What is a polymer?

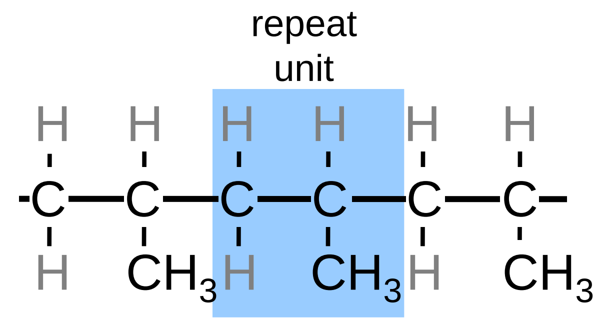
Poly — many   **mer** — repeat unit



Polyethylene (PE)



Polyvinyl chloride (PVC)



Polypropylene (PP)

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

Ancient Polymer History

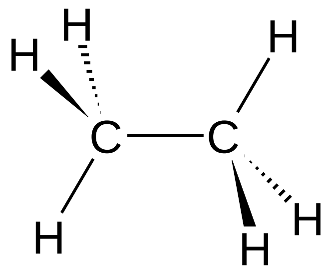
- Originally natural polymers were used
  - Wood
  - Cotton
  - Leather
  - Rubber
  - Wool
  - Silk

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

Polymer Composition

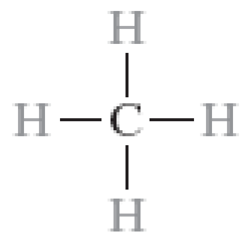
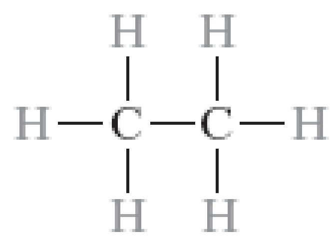
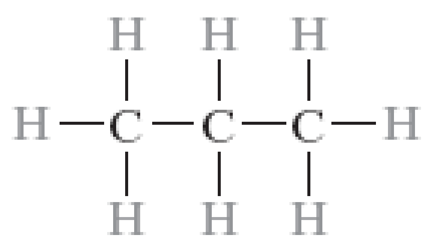
Most polymers are hydrocarbons
– i.e. made up of H and C

- Saturated hydrocarbons
  – Each carbon bonded to four other atoms



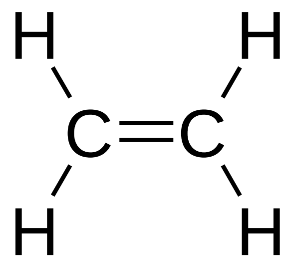
$$C_nH_{2n+2}$$

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

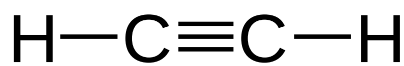
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

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}

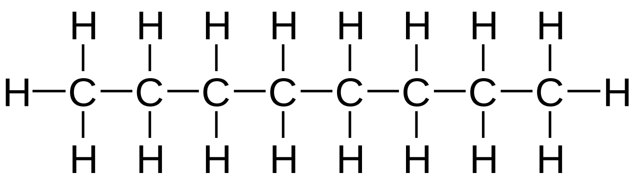


Isomerism

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

    Ex: C_8H_{18}

    - n-octane

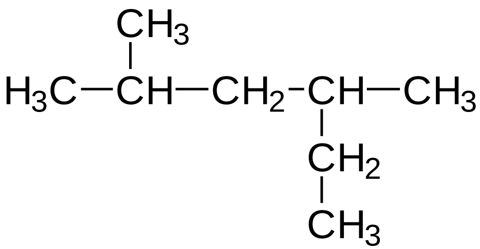


$$= H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

$$\Downarrow$$

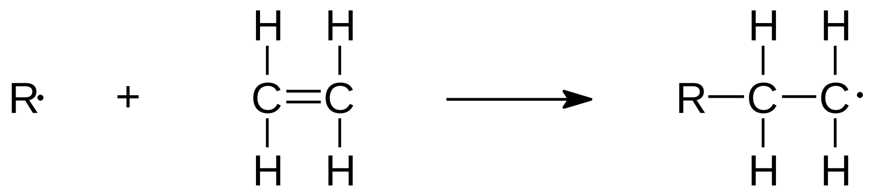
$$H_3C-(CH_2)_6-CH_3$$

- 2-methyl-4-ethyl pentane (isooctane)



Chemistry of Polymers

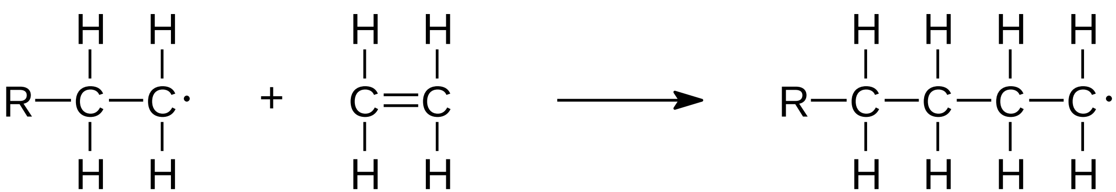
- Free radical polymerization



initiation

free radical

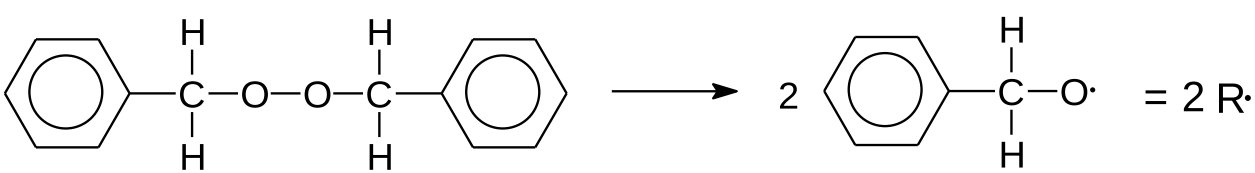
monomer (ethylene)



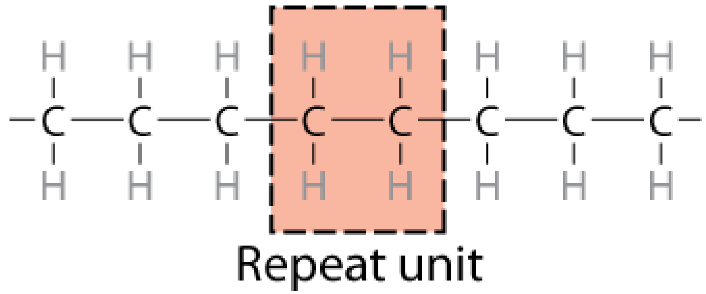
propagatior

dimer

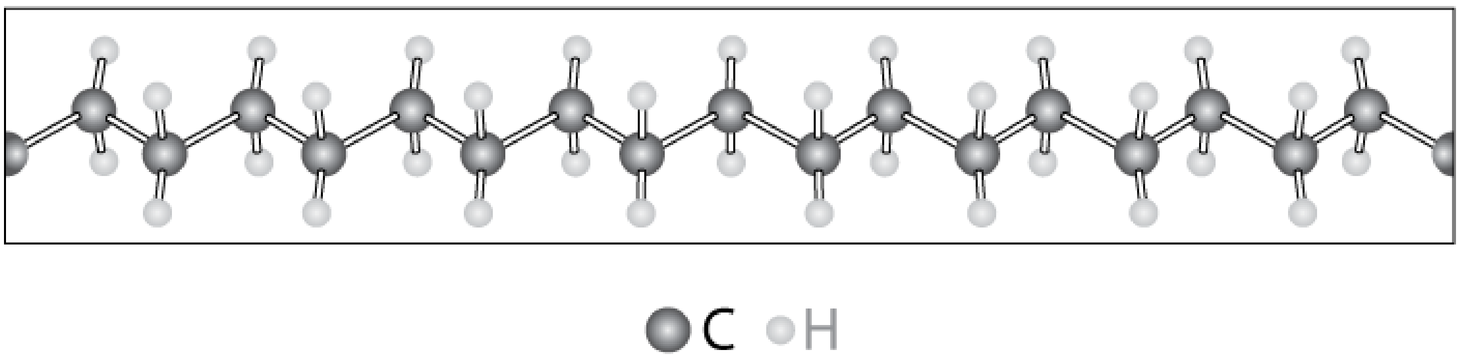
- Initiator: example - benzoyl peroxide



Chemistry of Polymers



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



Note: polyethylene is just a long HC

- paraffin is short polyethylene

Bulk or Commodity Polymers

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

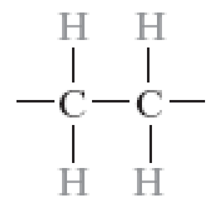
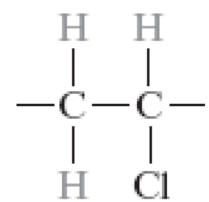
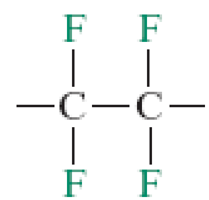
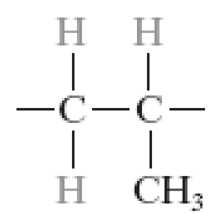
Polymer	*Repeat Unit*
Polyethylene (PE)	
Poly(vinyl chloride) (PVC)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	

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

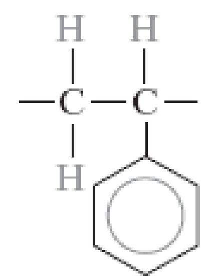
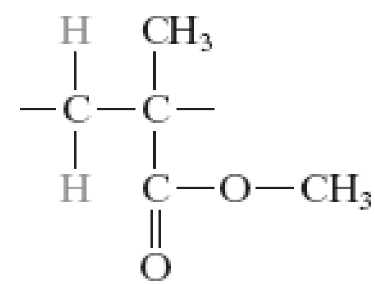
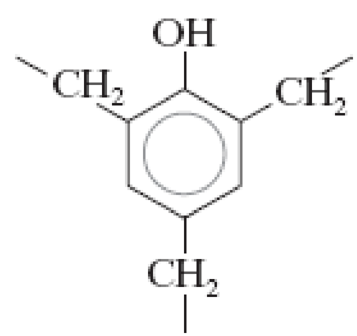
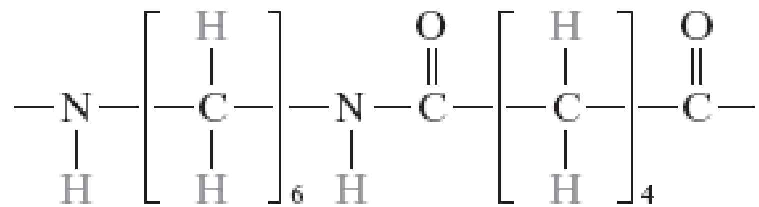
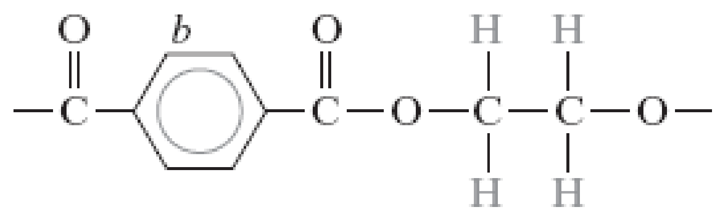
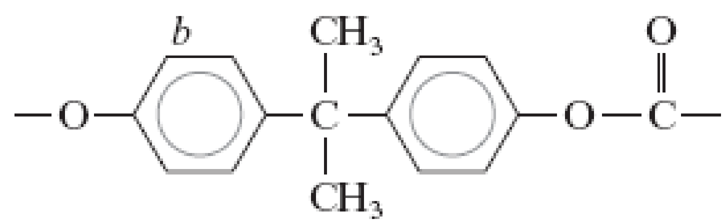
Polymer	*Repeat Unit*
Polystyrene (PS)	
Poly(methyl methacrylate) (PMMA)	
Phenol-formaldehyde (Bakelite)	

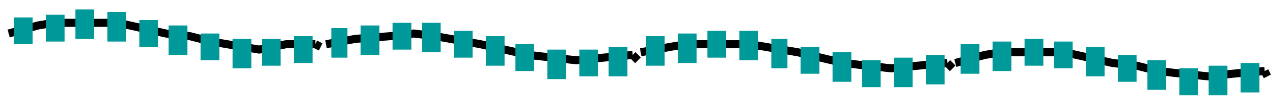
Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	*Repeat Unit*
Poly(hexamethylene adipamide) (nylon 6,6)	
Poly(ethylene terephthalate) (PET, a polyester)	
Polycarbonate (PC)	

MOLECULAR WEIGHT

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

Lower M



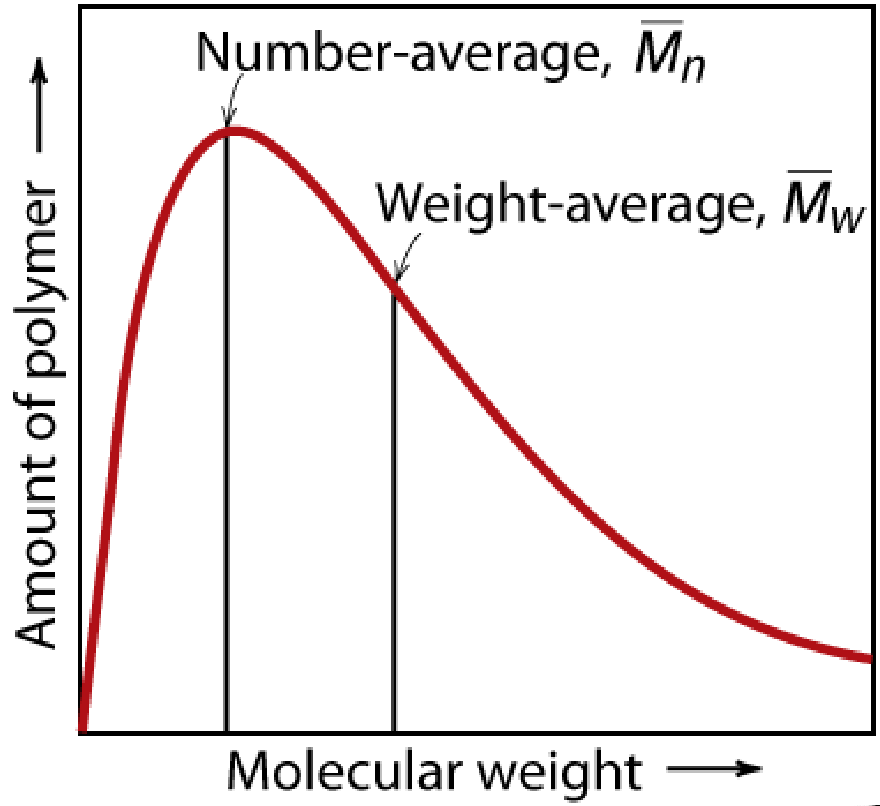
higher M

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

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

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

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



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

Molecular Weight Calculation

Example: average mass of a class

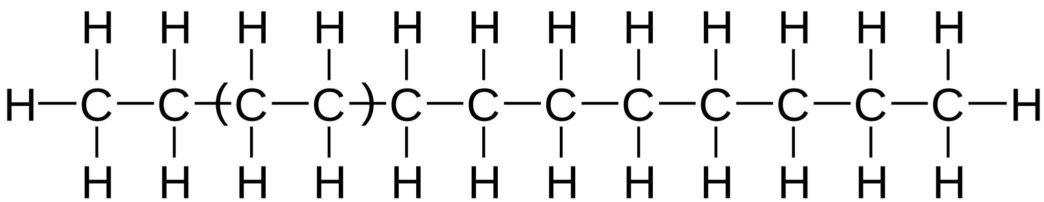
N_i	M_i	x_i	w_i
# of students	mass (lb)		
1	100	0.1	0.054
1	120	0.1	0.065
2	140	0.2	0.151
3	180	0.3	0.290
2	220	0.2	0.237
1	380	0.1	0.204
		$\overline{M}_n$	$\overline{M}_w$
		186 lb	216 lb

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

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

Degree of Polymerization, *n*

n = number of repeat units per chain



$n_i = 6$

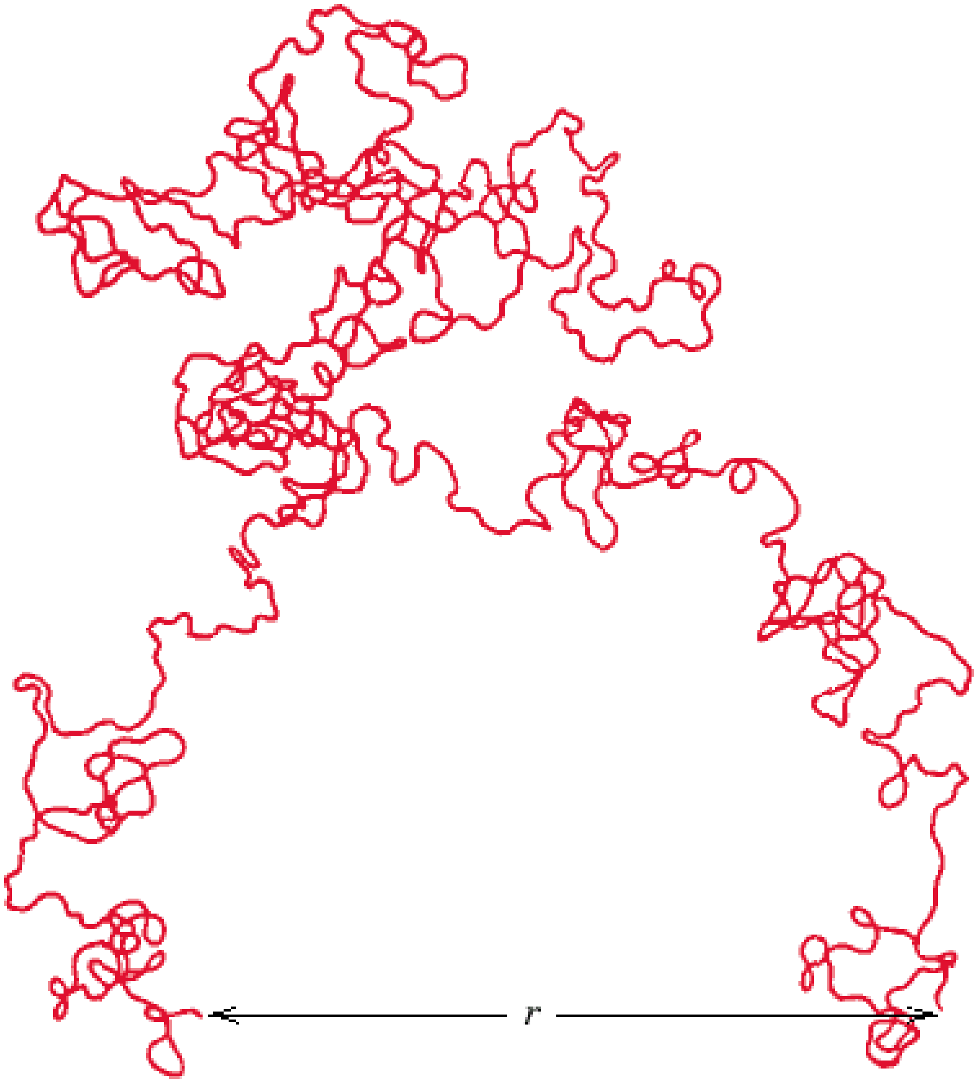
$$n_n = \sum x_i n_i = \frac{\overline{M}_n}{\overline{m}} \qquad n_w = \sum w_i n_i = \frac{\overline{M}_w}{\overline{m}}$$

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

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

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

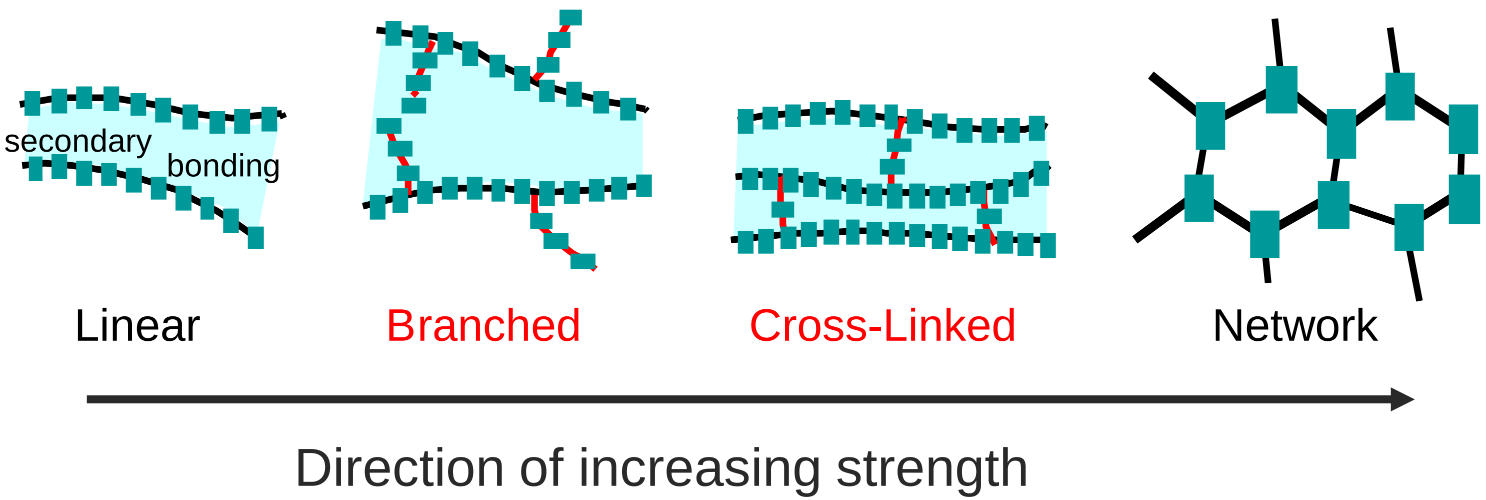
End to End Distance, *r*



Adapted from Fig. 14.6, *Callister 7e.*

Molecular Structures

- Covalent chain configurations and strength:

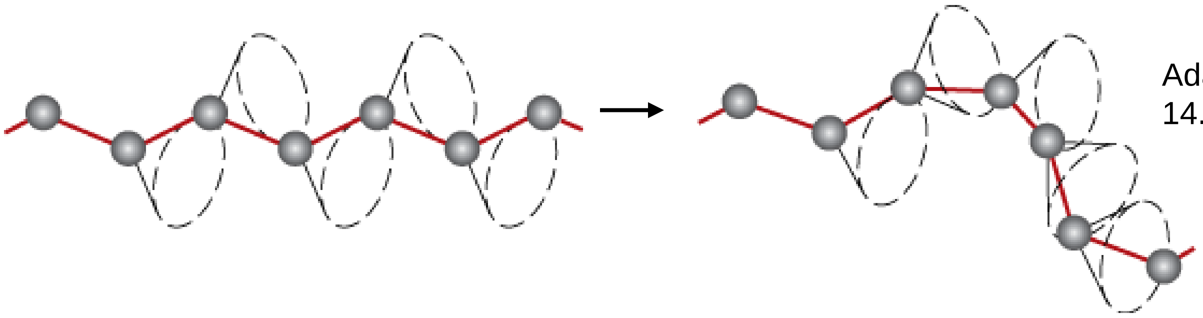


Adapted from Fig. 14.7, *Callister 7e.*

Polymers – Molecular Shape

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

– note: no bond breaking needed

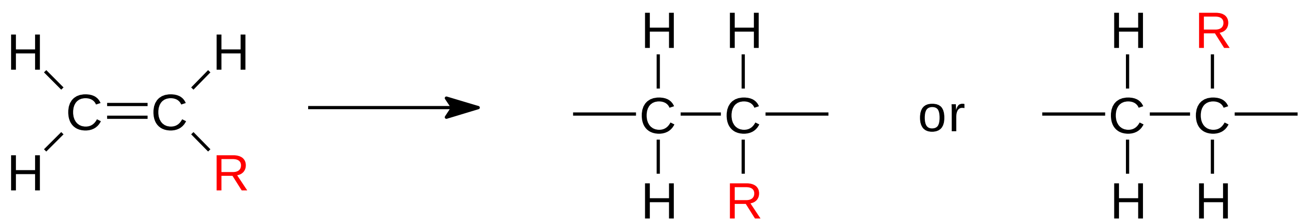


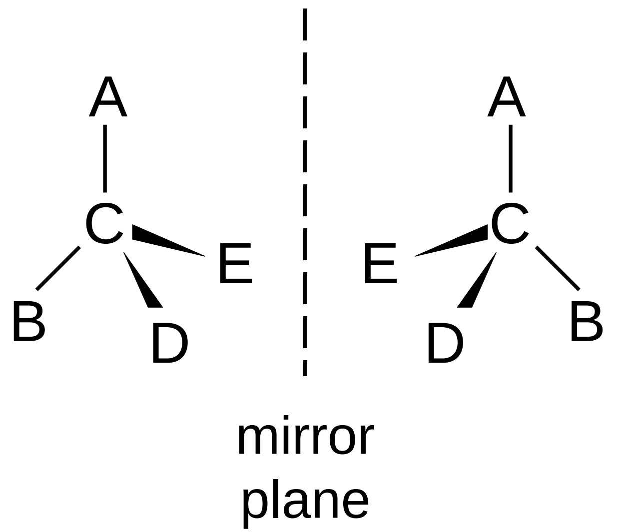
Adapted from Fig. 14.5, *Callister 7e.*

Polymers – Molecular Shape

Configurations – to change must break bonds

- Stereoisomerism

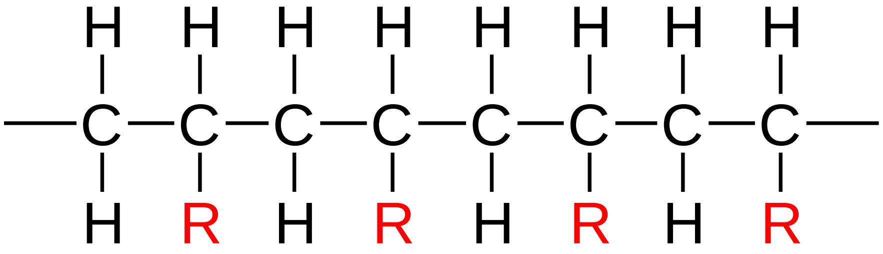




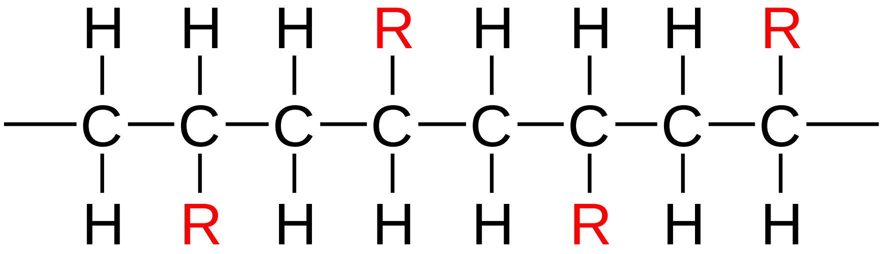
Tacticity

Tacticity – stereoregularity of chain

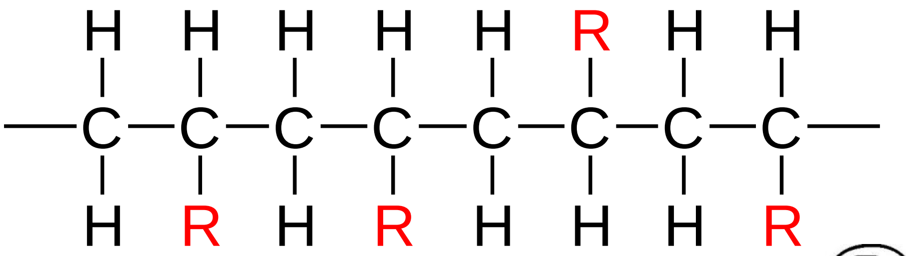
isotactic – all R groups on same side of chain



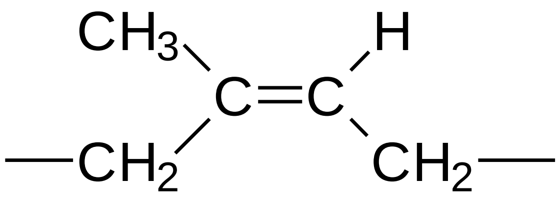
syndiotactic – R groups alternate sides



atactic – R groups random



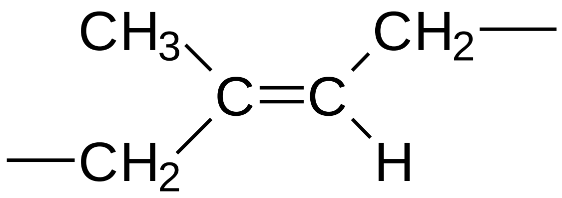
cis/trans Isomerism



cis

cis-isoprene
(natural rubber)

bulky groups on same
side of chain



trans

trans-isoprene
(gutta percha)

bulky groups on opposite
sides of chain

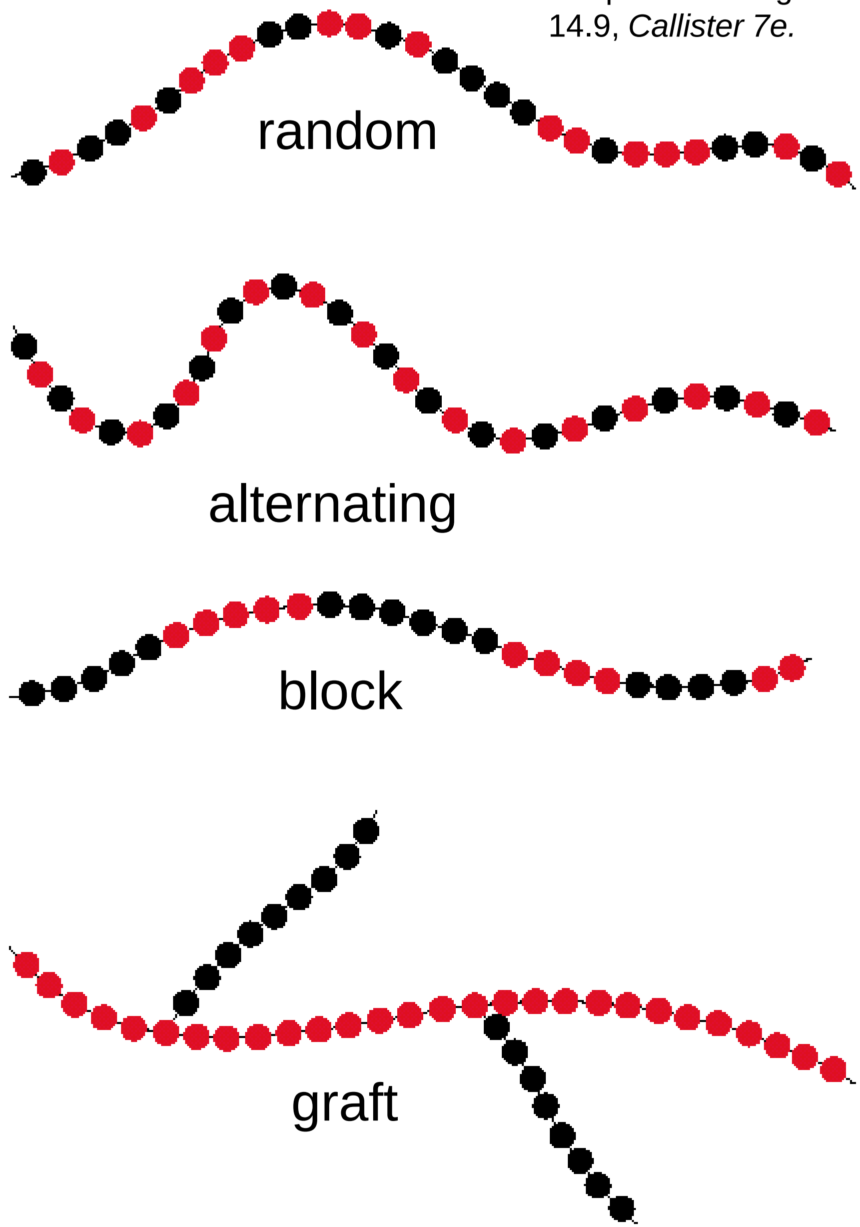
Copolymers

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 –

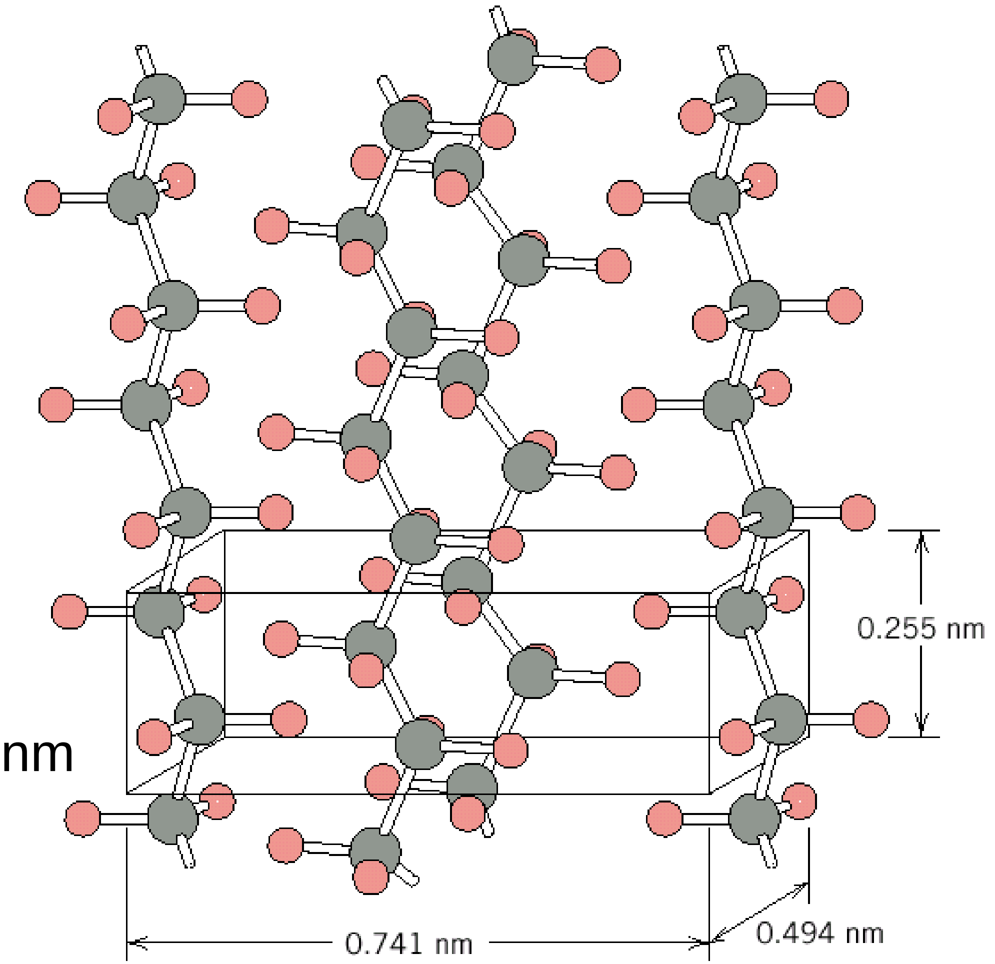
Adapted from Fig. 14.9, *Callister 7e.*



Polymer Crystallinity

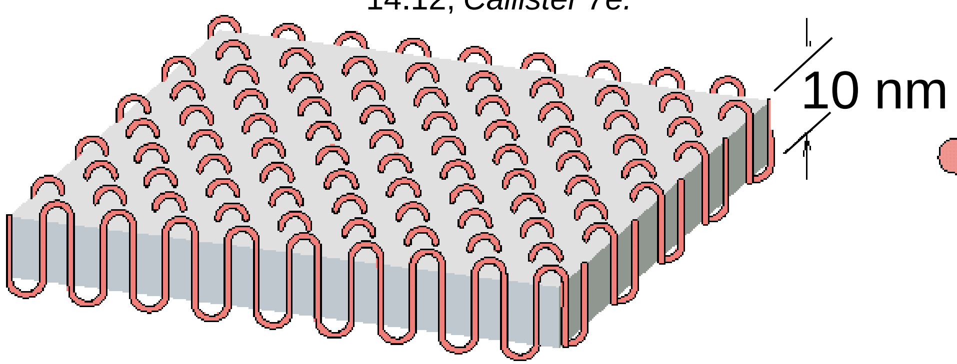
Adapted from Fig. 14.10, *Callister 7e.*

Ex: polyethylene unit cell



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

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

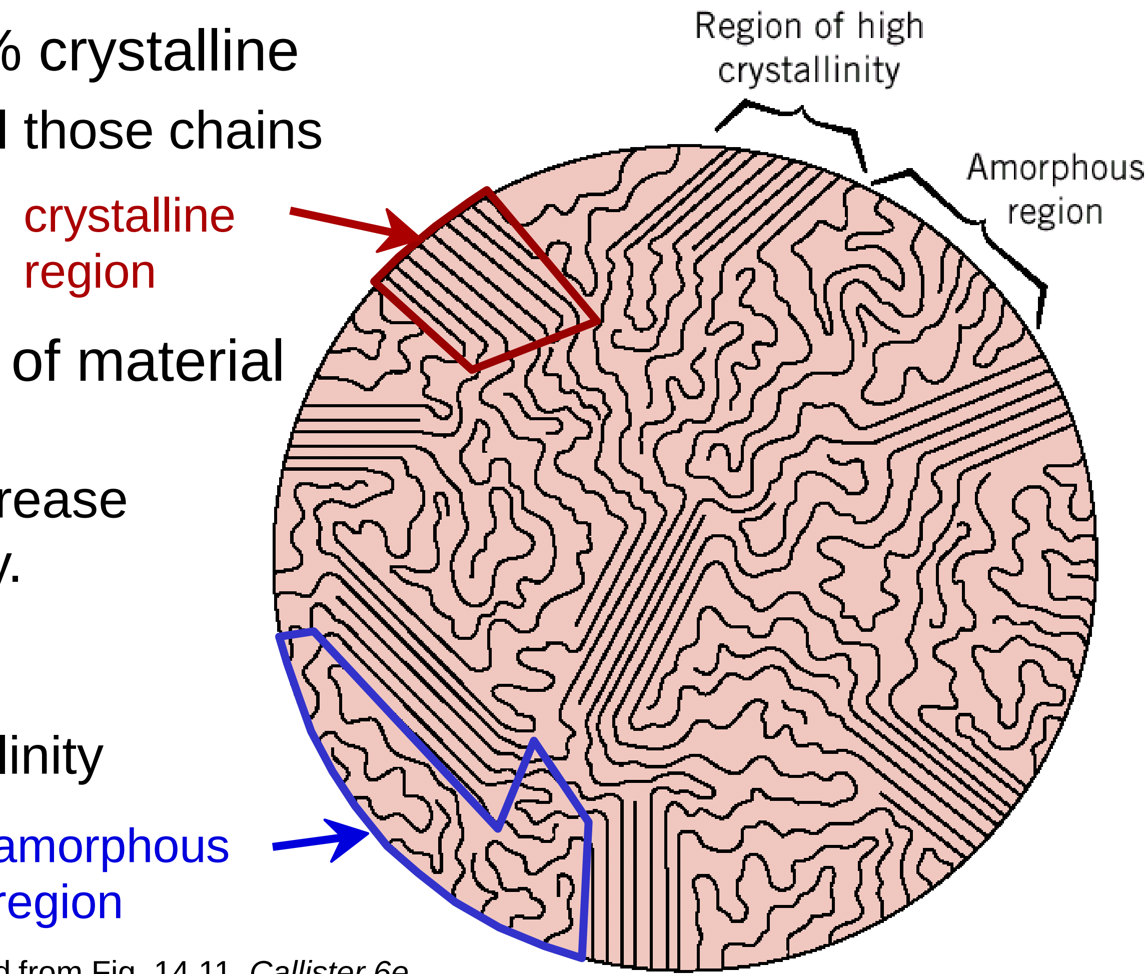


Polymer Crystallinity

Polymers rarely 100% crystalline

- Too difficult to get all those chains aligned

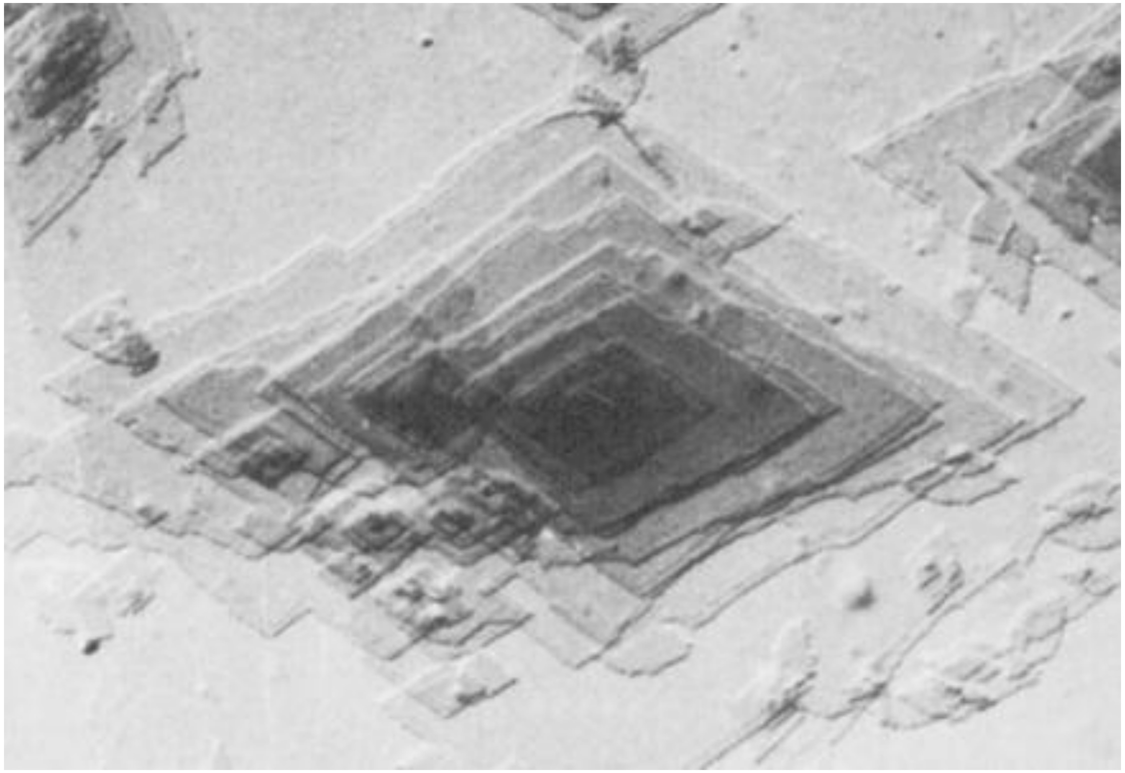
- % Crystallinity: % of material that is crystalline.
  -- *TS* and *E* often increase with % crystallinity.
  -- Annealing causes crystalline regions to grow. % crystallinity increases.



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.)

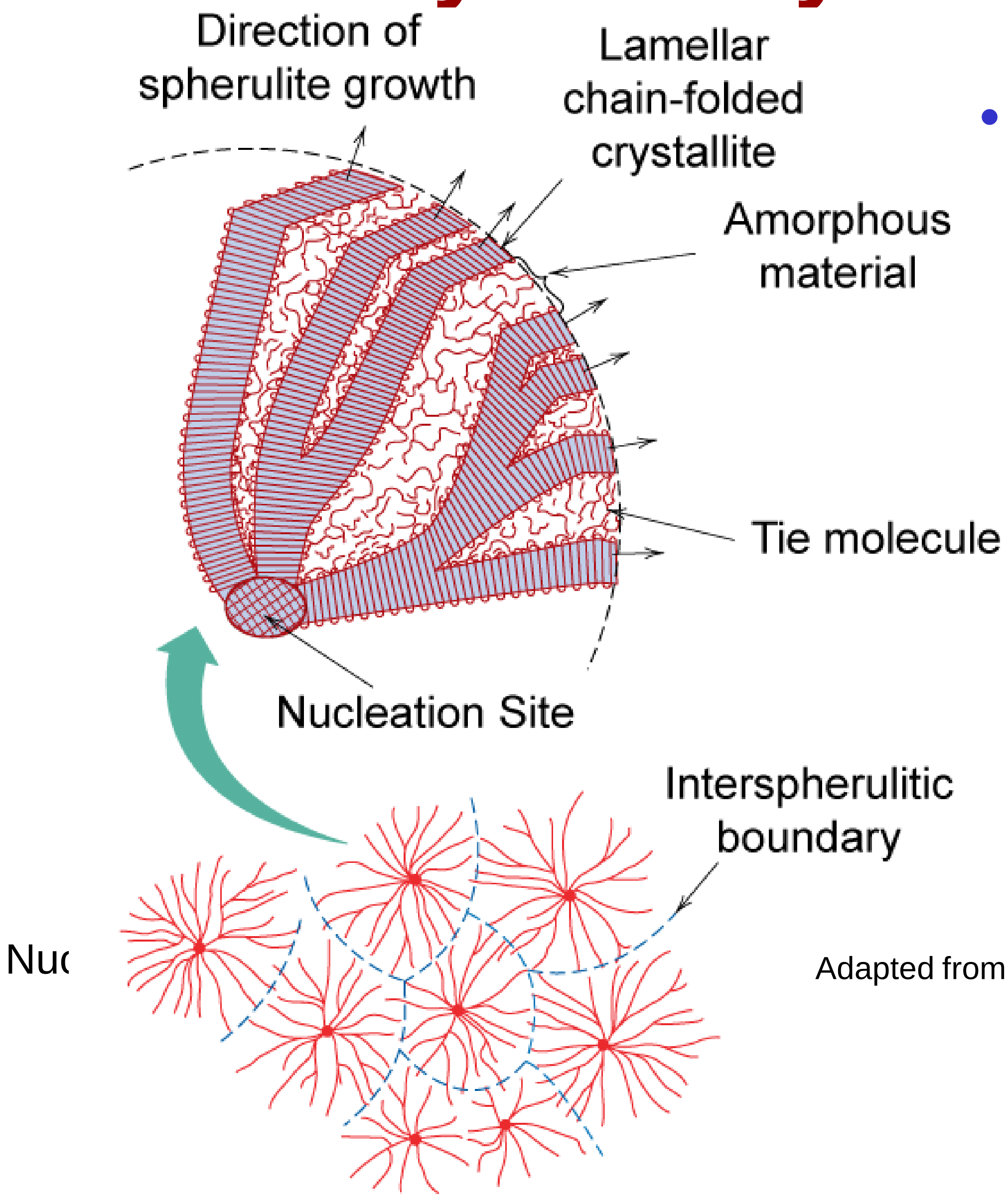
Polymer Crystal Forms

- Single crystals – only if slow careful growth



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

Polymer Crystal Forms

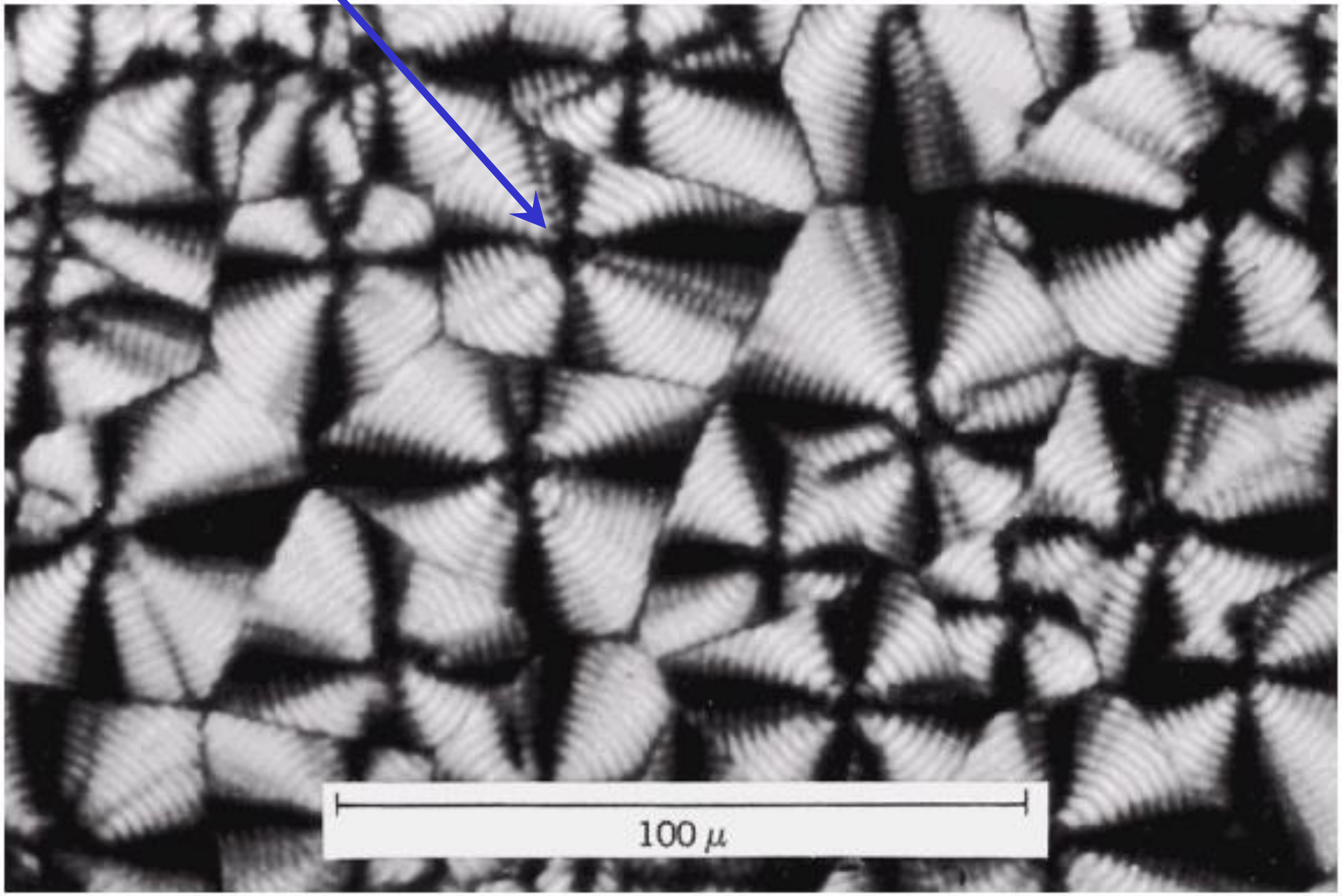


- Spherulites – fast growth – forms lamellar (layered) structures

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

Spherulites – crossed polarizers

Maltese cross



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

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: