Oct. 13, 2021

Bio-integrated Materials Science (Online Lectures)

Polymer structures

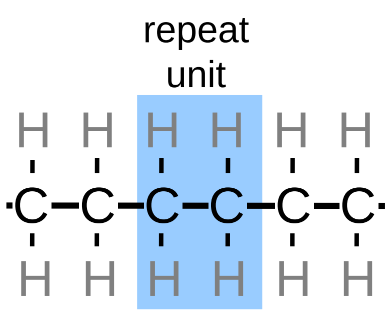
Lecture 4

Prof. Jung Heon Lee

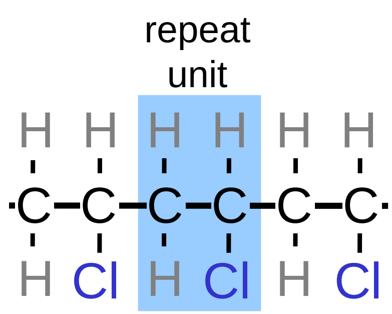
What is a Polymer?

Poly mer

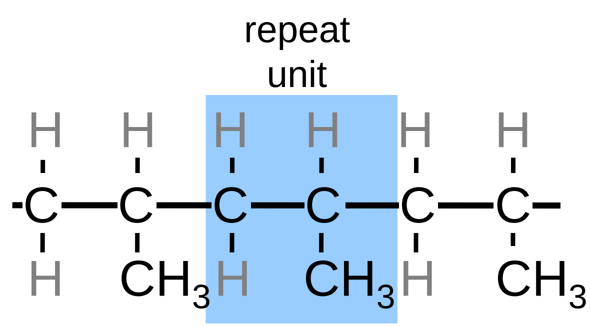
many repeat unit



Polyethylene (PE)



Poly(vinyl chloride) (PVC)



Polypropylene (PP)

Adapted from Fig. 4.2, *Callister & Rethwisch 5e.*

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

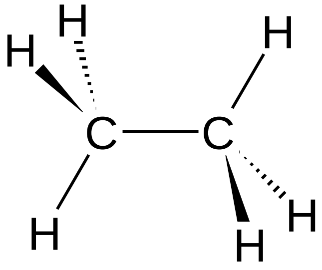


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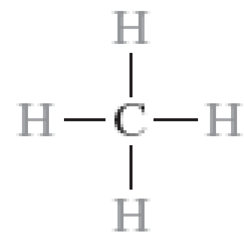
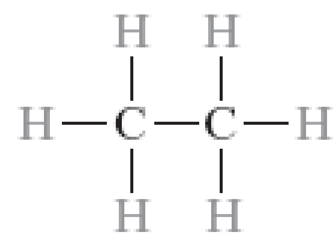
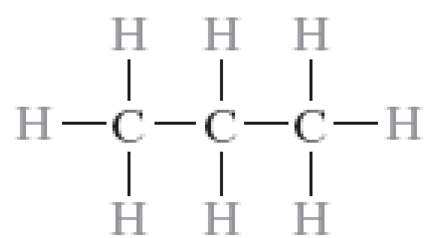
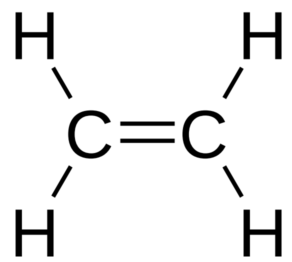
Table 4.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

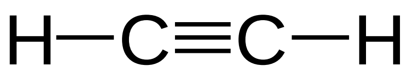
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

Unsaturated Hydrocarbons

- Double & triple bonds somewhat unstable – can form new bonds
  - Double bond found in ethylene or ethene - C_2H_4



  - Triple bond found in acetylene or ethyne - C_2H_2



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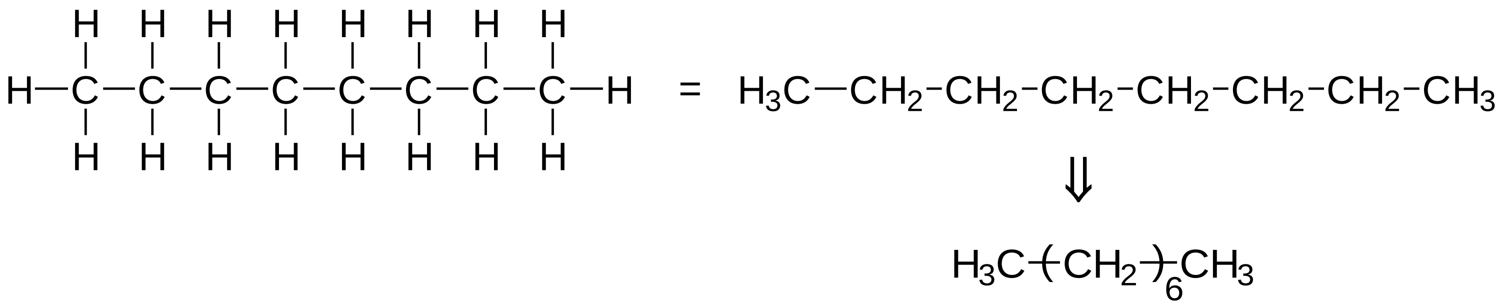
Isomerism

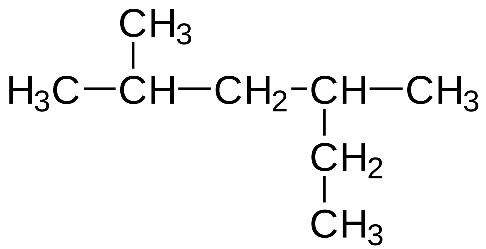
- Isomerism
  - two compounds with same chemical formula can have quite different structures

    for example: C_8H_{18}

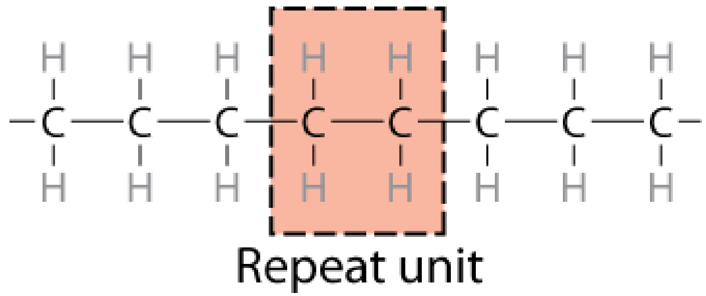
    - normal-octane



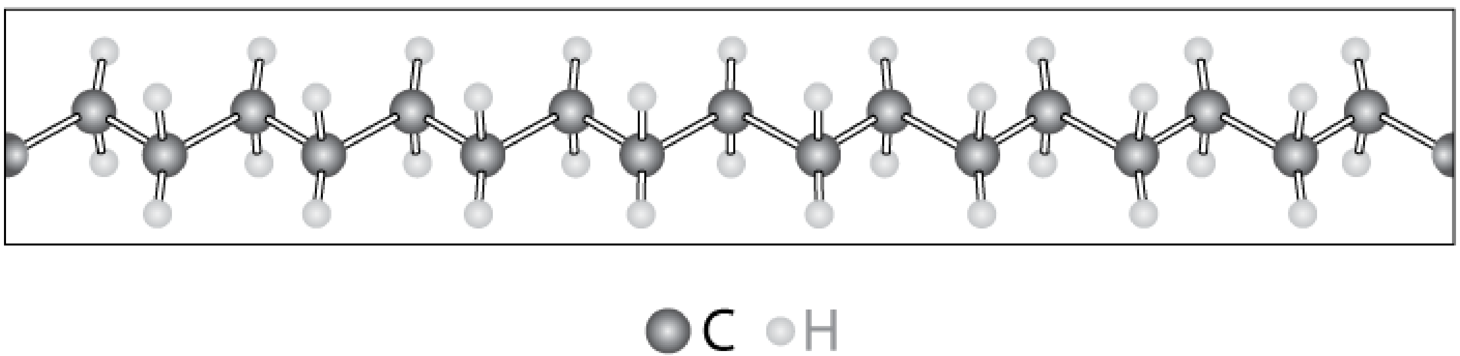
    - 2,4-dimethylhexane



Chemistry and Structure of Polyethylene



Adapted from Fig. 4.1, *Callister & Rethwisch 5e.*

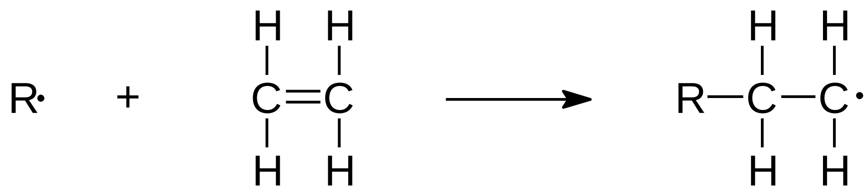


Note: polyethylene is a long-chain hydrocarbon

- paraffin wax for candles is short polyethylene

Polymerization and Polymer Chemistry

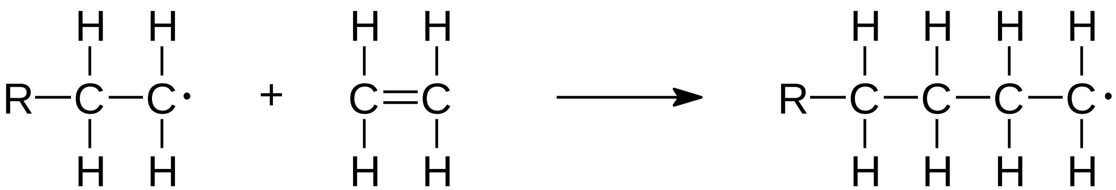
- Free radical polymerization



initiation

free radical

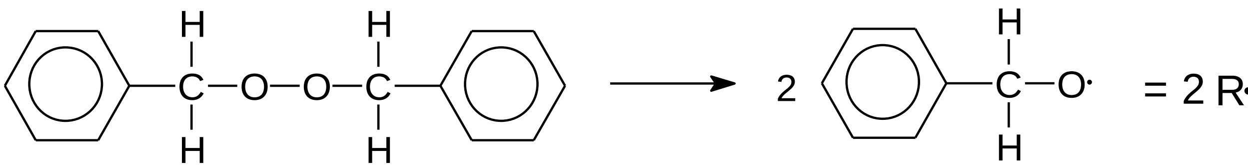
monomer (ethylene)



propagation

dimer

- Initiator: example - benzoyl peroxide



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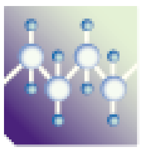
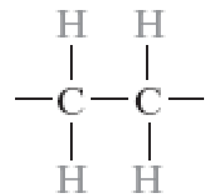
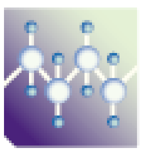
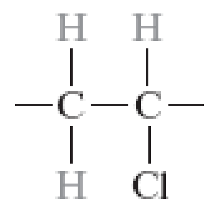
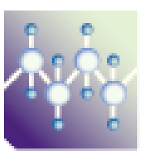
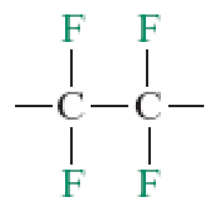
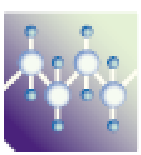
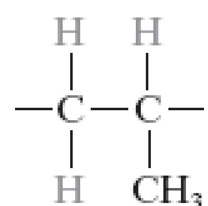
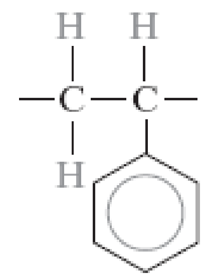
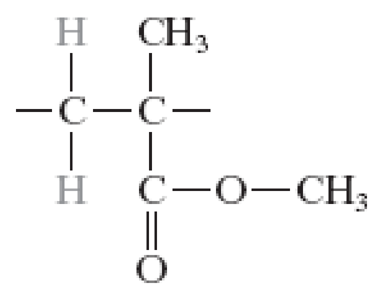
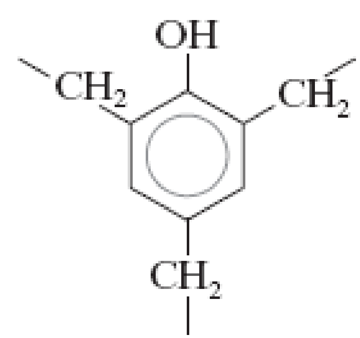
Bulk or Commodity Polymers

Table 4.3 **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)	

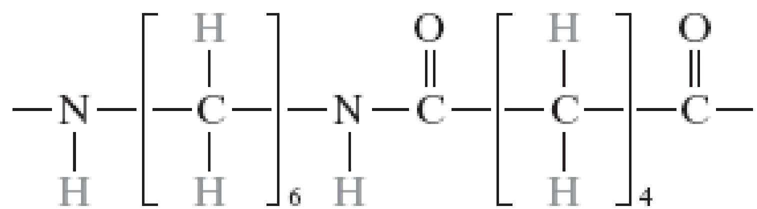
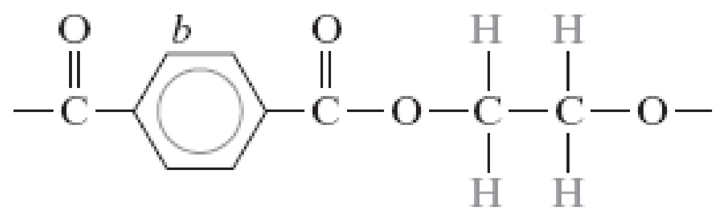
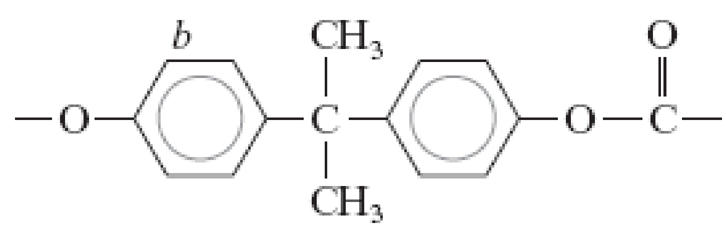
Bulk or Commodity Polymers (cont)

Table 4.3 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)	

Bulk or Commodity Polymers (cont)

Table 4.3 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)	

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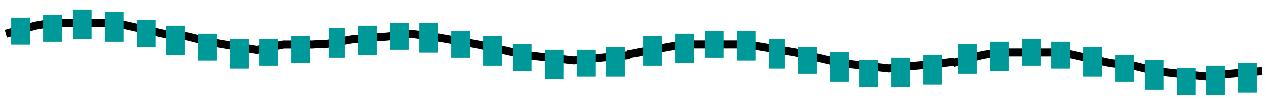
MOLECULAR WEIGHT

- 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

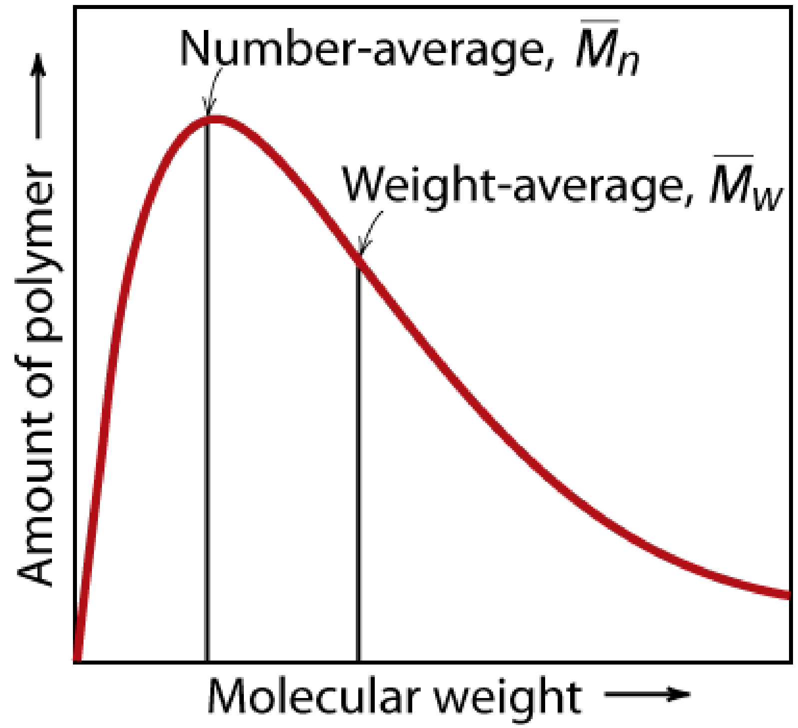
MOLECULAR WEIGHT DISTRIBUTION

Adapted from Fig. 4.4, *Callister & Rethwisch 5e.*

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

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

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



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*

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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:

a) Based on the number fraction of students in each mass range?
b) 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 mass (lb)	number of students N_i	mean weight W_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

total number → $\sum N_i$ = 10

$\sum N_i W_i$ = 1881 ← total weight

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

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

For example: for the 81-120 lb range

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

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

Molecular Weight Calculation (cont.)

weight range mass (lb)	mean weight W_i mass (lb)	number fraction x_i	weight fraction w_i
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

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

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

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

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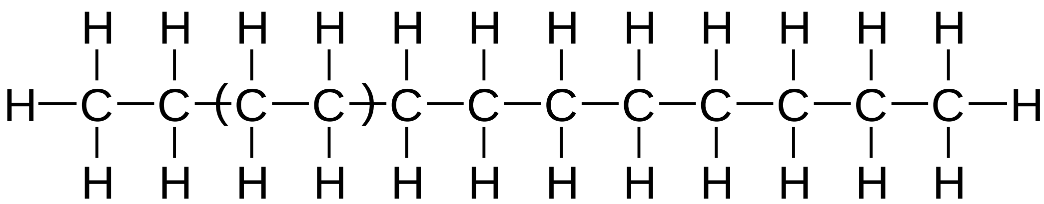
Degree of Polymerization, *DP*

DP = average number of repeat units per chain



$DP = 6$

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

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

for copolymers this is calculated as follows:

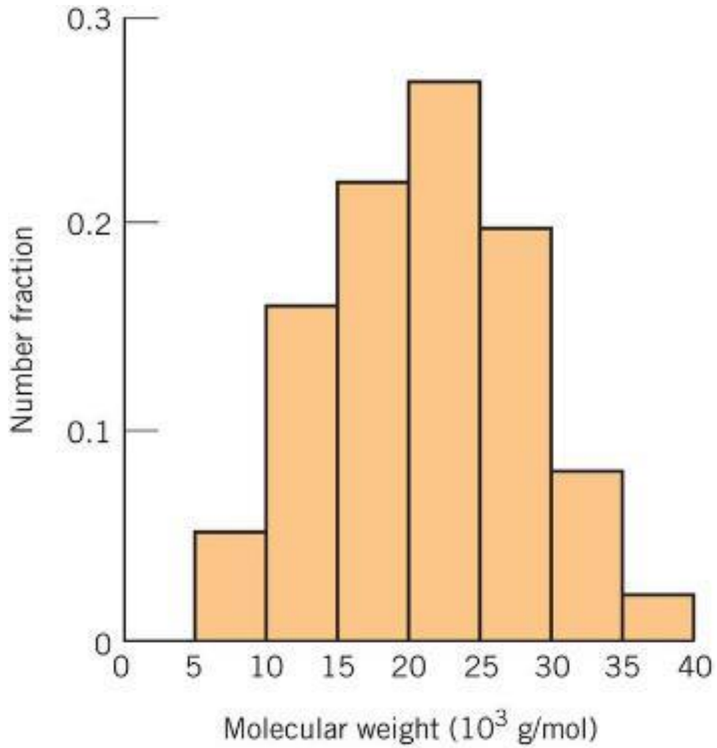
$$\bar{m} = \Sigma f_i m_i$$

Chain fraction (f_i)

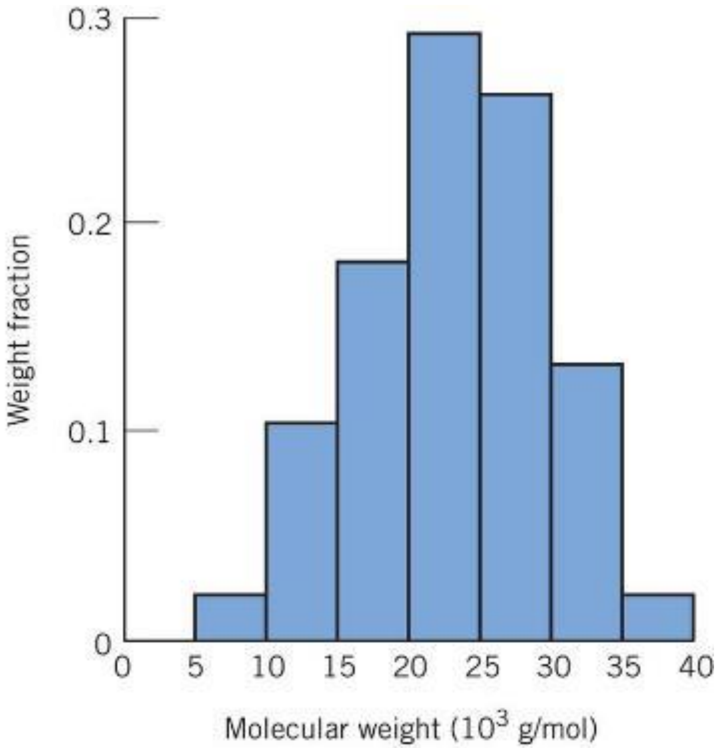
mol. wt of repeat unit *i* (m_i)

Molecular Weight Calculation

Example problem 4.1



(a)



(b)

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EXAMPLE PROBLEM 4.1

Computations of Average Molecular Weights and Degree of Polymerization

Assume that the molecular weight distributions shown in Figure 4.3 are for poly(vinyl chloride). For this material, compute **(a)** the number-average molecular weight, **(b)** the degree of polymerization, and **(c)** the weight-average molecular weight.

(a)

$$\overline{M}_n = \Sigma x_i M_i \qquad (4.5a)$$

Molecular Weight Range (g/mol)	*Mean M_i (g/mol)*	x_i	$x_i M_i$
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750
			$\overline{M}_n = 21,150$

(b)

$$DP = \frac{\overline{M}_n}{m} \qquad (4.6)$$

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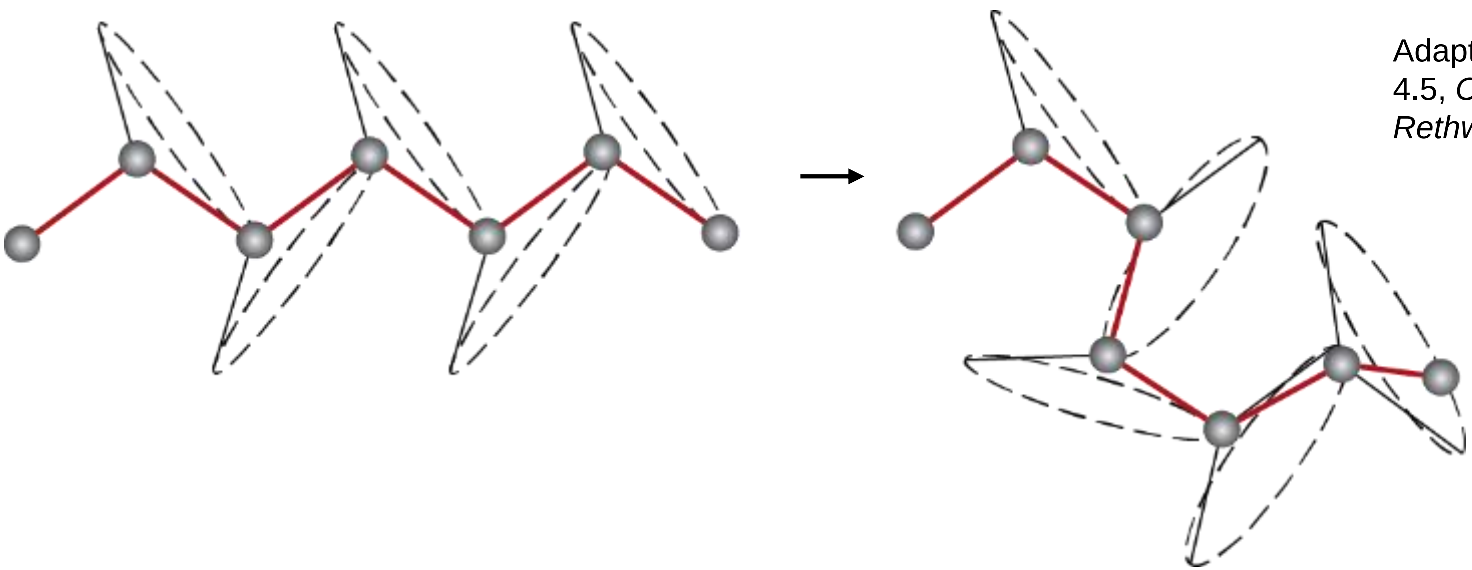
(c) $\overline{M}_w = \sum w_i M_i$ (4.5b)

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	w_i	$w_i M_i$
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750
			$\overline{M}_w = 23{,}200$

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. 4.5, *Callister & Rethwisch 5e.*

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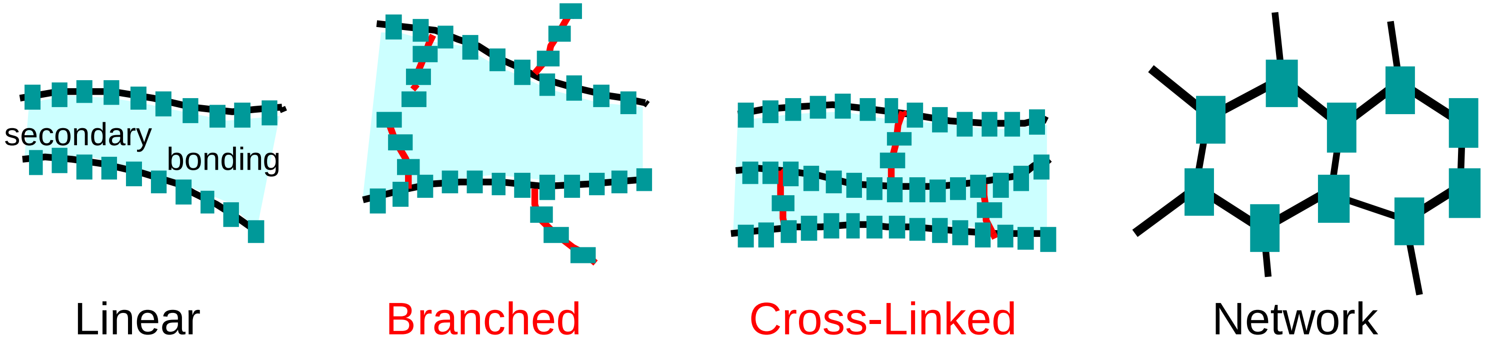
Chain End-to-End Distance, *r*

Adapted from Fig. 4.6, *Callister & Rethwisch 5e.*

Molecular Structures for Polymers

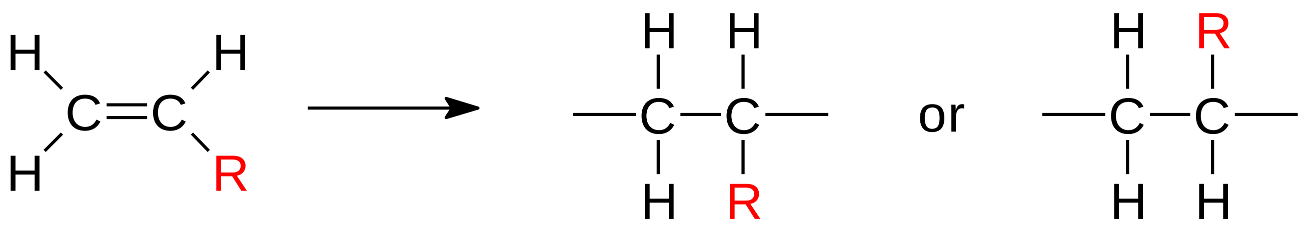


Adapted from Fig. 4.7, *Callister & Rethwisch 5e.*

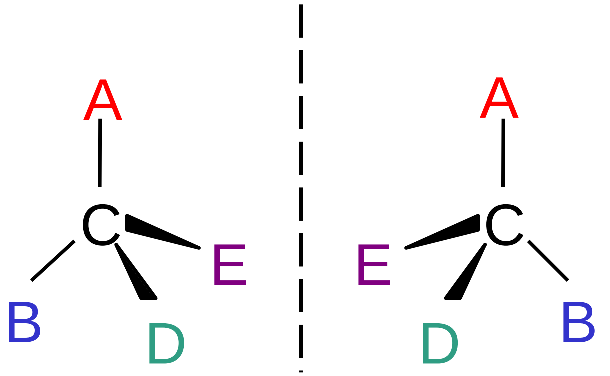
Molecular Configurations for Polymers

Configurations – to change must break bonds

- Stereoisomerism



Stereoisomers are mirror images – can't superimpose without breaking a bond

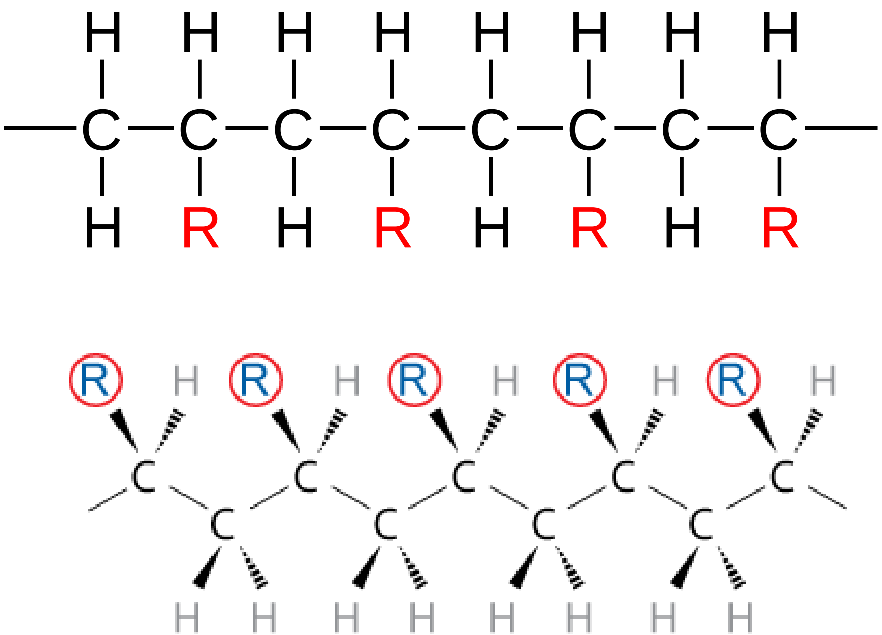


mirror plane

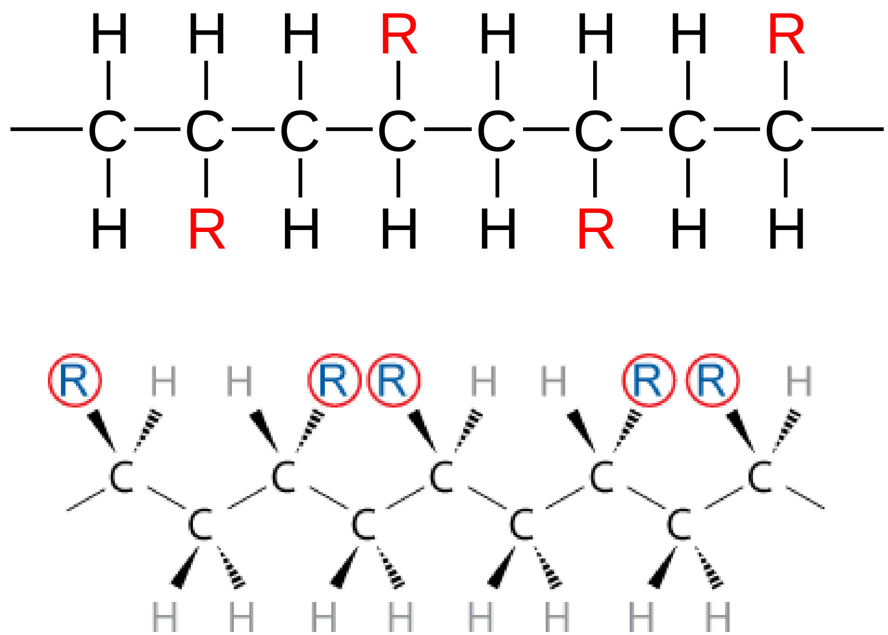
Tacticity

Tacticity – stereoregularity or spatial arrangement of R units along chain

isotactic – all R groups on same side of chain

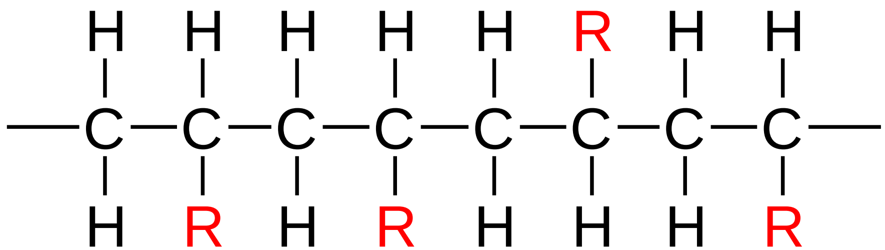


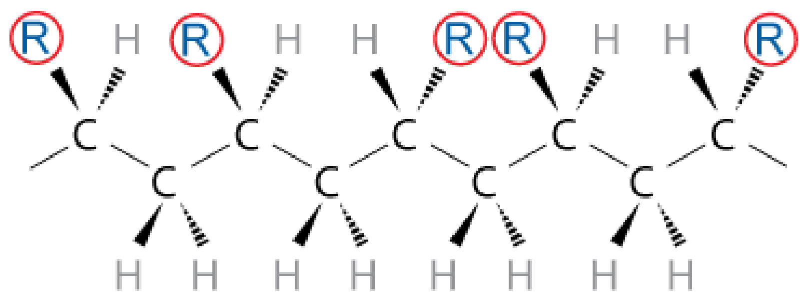
syndiotactic – R groups alternate sides



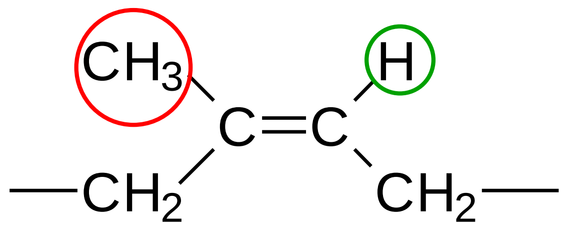
Tacticity (cont.)

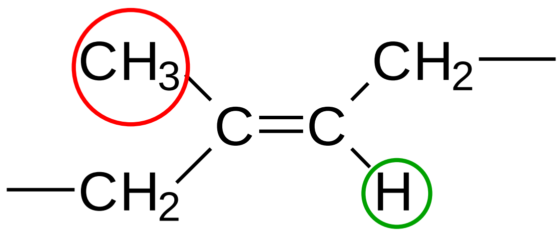
atactic – R groups randomly positioned





cis/trans Isomerism





cis

cis-isoprene
(natural rubber)

H atom and CH_3 group on same side of chain

trans

trans-isoprene
(gutta percha)

H atom and CH_3 group on opposite sides of chain

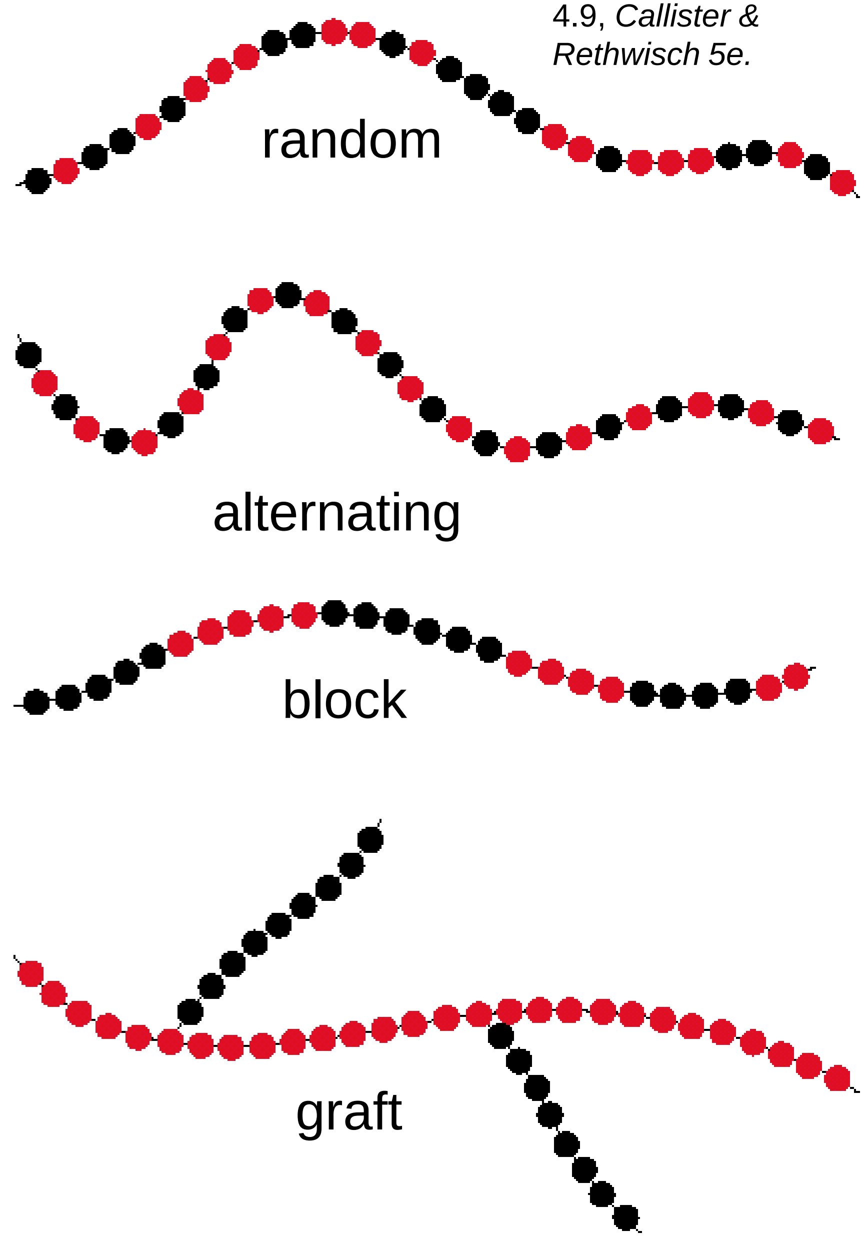
Copolymers

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 – ●

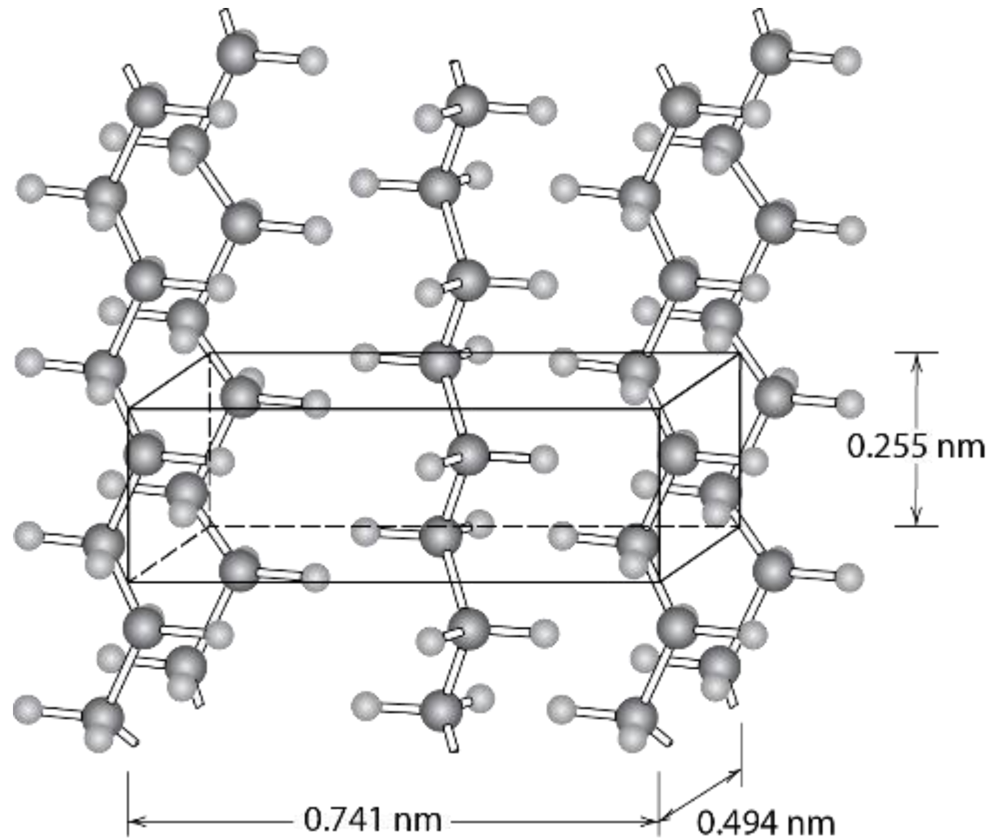
Adapted from Fig. 4.9, *Callister & Rethwisch 5e.*



Crystallinity in Polymers

Adapted from Fig. 4.10, *Callister & Rethwisch 5e.*

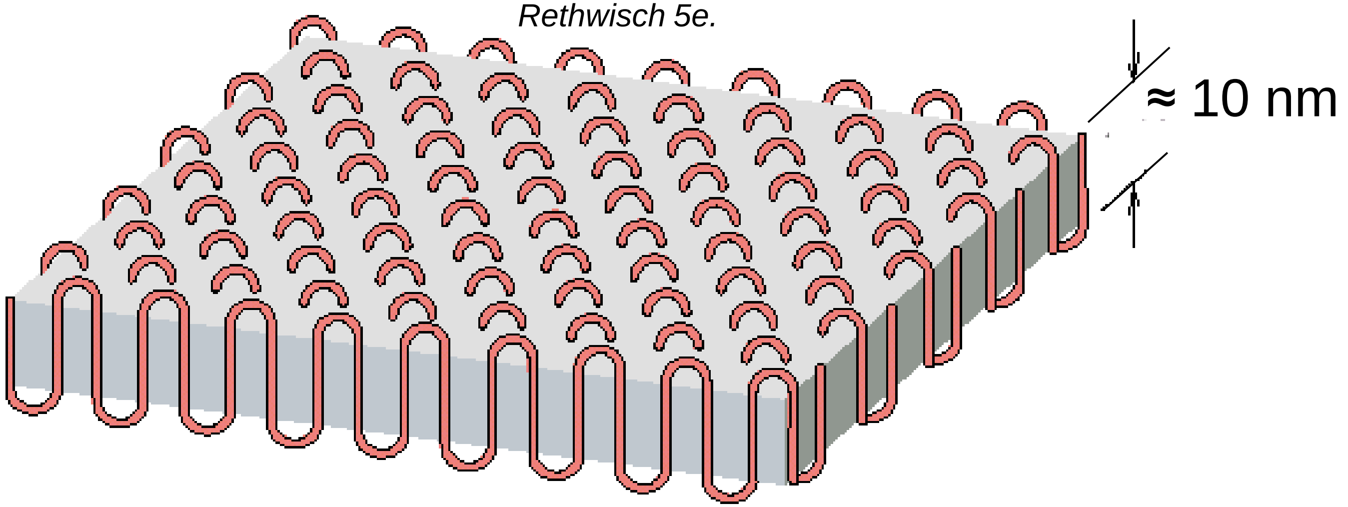
- Ordered atomic arrangements involving molecular chains
- Crystal structures in terms of unit cells
- Example shown
  - polyethylene unit cell



Polymer Crystallinity

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

Adapted from Fig. 4.12, *Callister & Rethwisch 5e.*

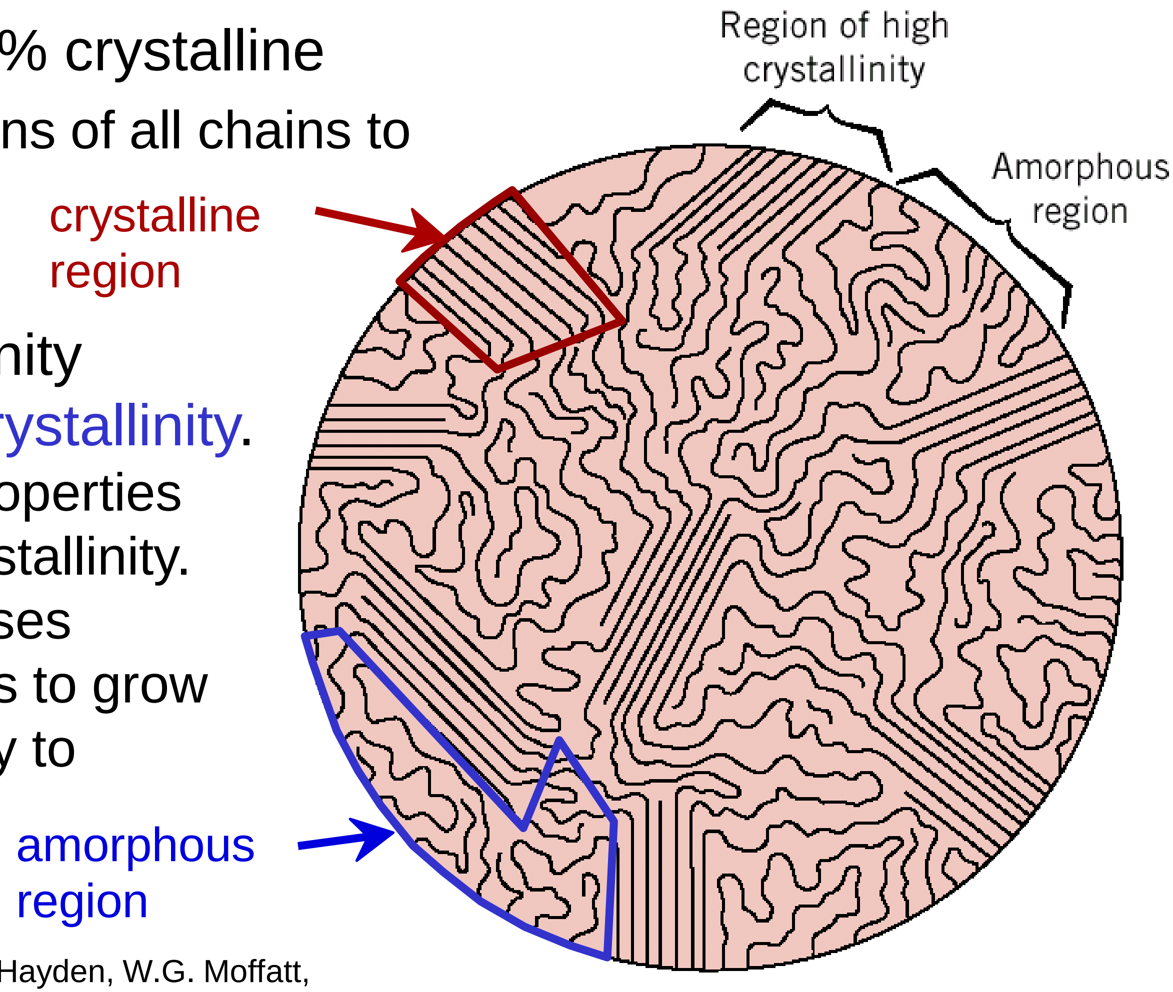


Polymer Crystallinity (cont.)

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.



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

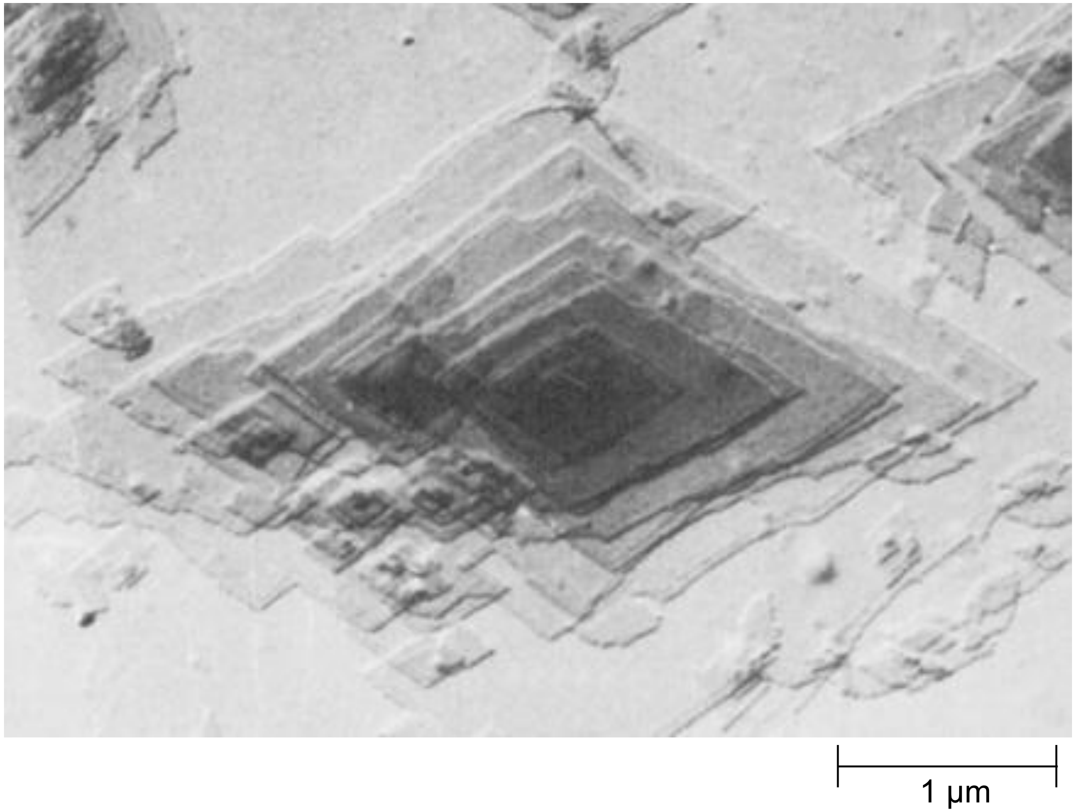
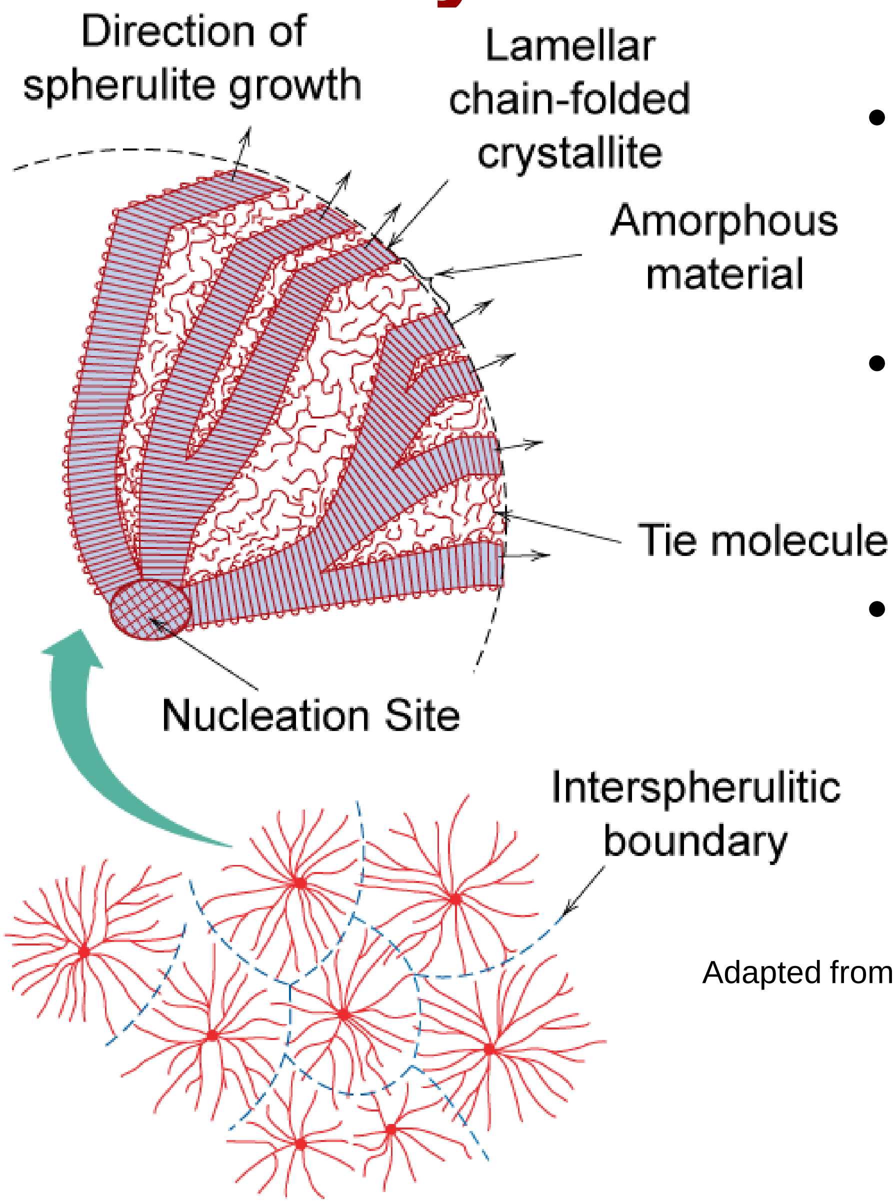


Fig. 4.11, *Callister & Rethwisch 5e.*
[From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Eds.), Growth and Perfection of Crystals. General Electric Company and John Wiley & Sons, Inc., 1958, p. 498. Reprinted with permission of John Wiley & Sons, Inc.]

Semicrystalline Polymers

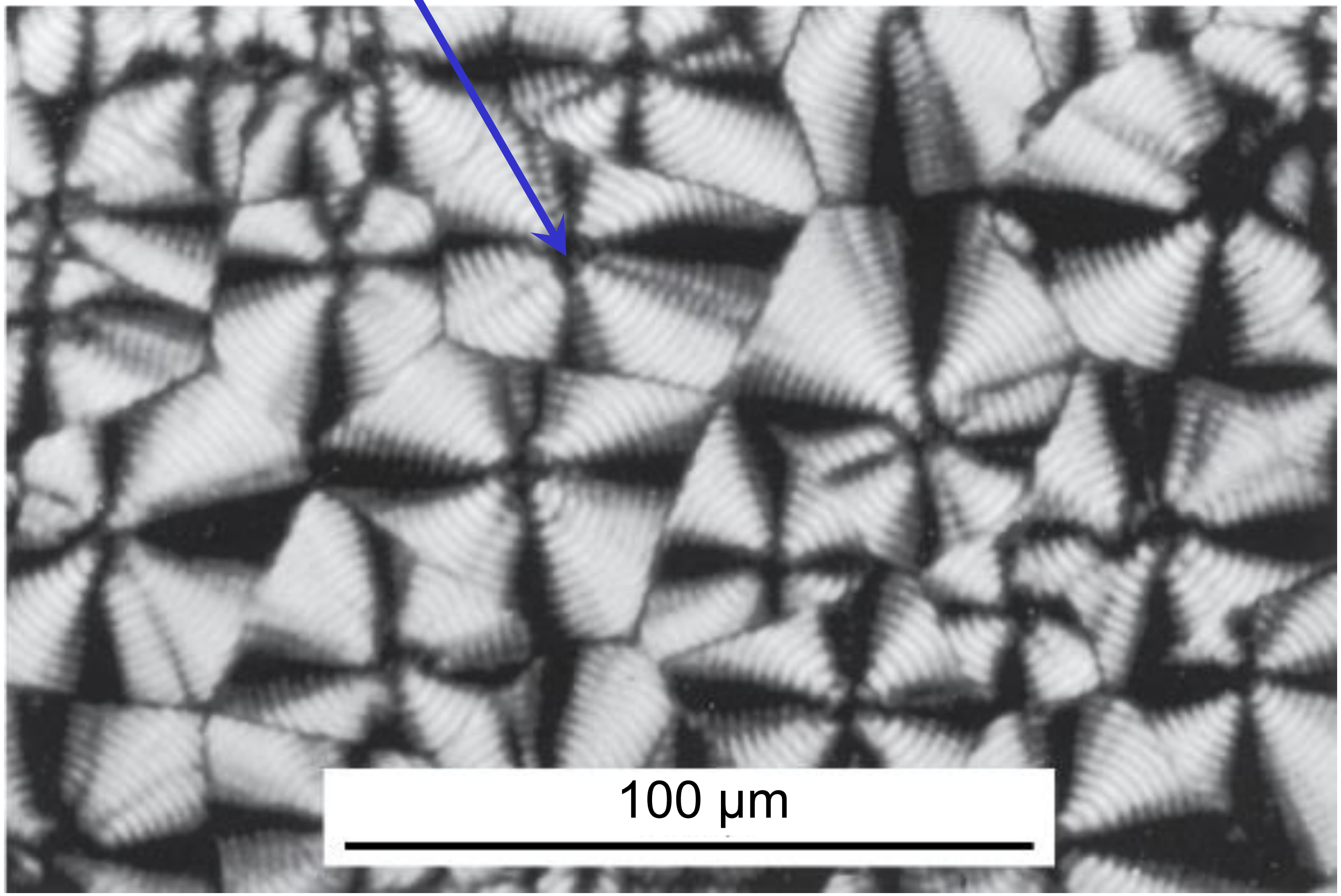


- Some semicrystalline polymers form spherulite structures
- Alternating chain-folded crystallites and amorphous regions
- Spherulite structure for relatively rapid growth rates

Adapted from Fig. 4.13, *Callister & Rethwisch 5e.*

Photomicrograph – Spherulites in Polyethylene

Cross-polarized light used
-- a maltese cross appears in each spherulite



Courtesy F. P. Price, General Electric Company

Fig. 4.14, *Callister & Rethwisch 5e.*

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