Chapter 5:
Structures of Polymers

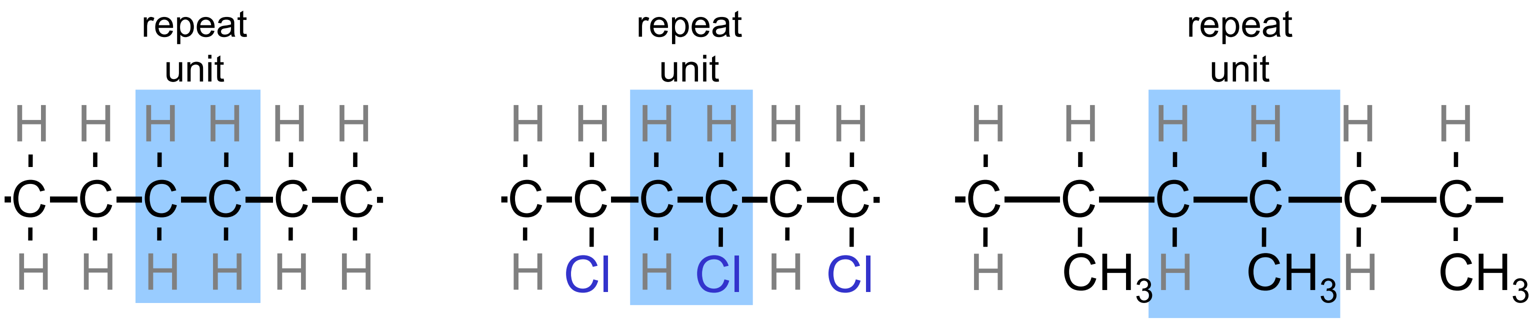
ISSUES TO ADDRESS...

- 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 ?

What is a Polymer?

Poly — many

mer — repeat unit



Polyethylene (PE) Poly(vinyl chloride) (PVC) Polypropylene (PP)

Adapted from Fig. 5.2, *Callister & Rethwisch 9e.*

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

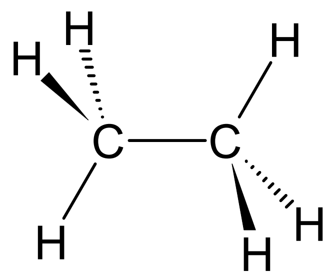
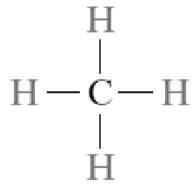
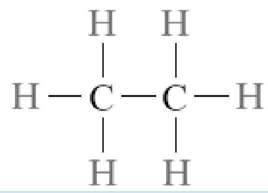
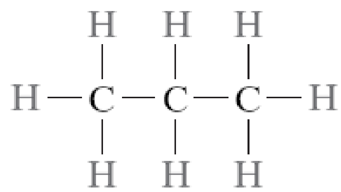
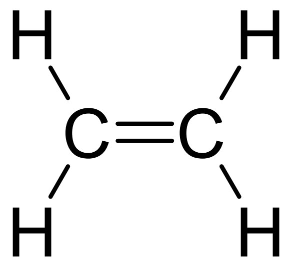


Table 5.1
Compositions and Molecular Structures for Some Paraffin Compounds: C_nH_{2n+2}

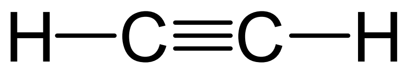
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

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

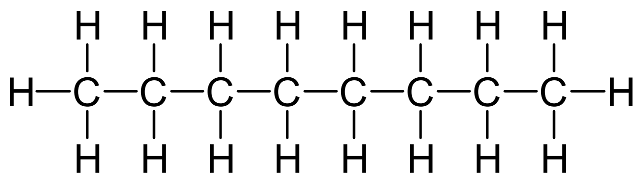


Isomerism

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

    for example: C_8H_{18}

    - normal-octane

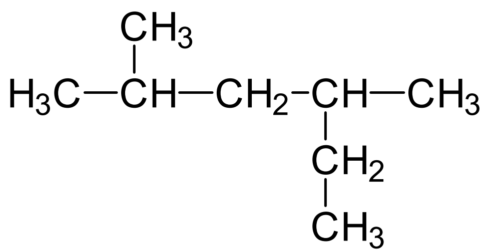


$$= H_3C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

$$\Downarrow$$

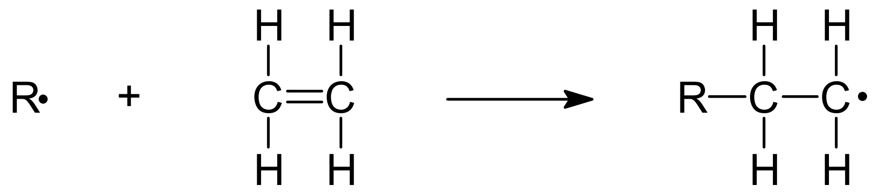
$$H_3C{-}(CH_2)_6{-}CH_3$$

    - 2,4-dimethylhexane



Polymerization and Polymer Chemistry

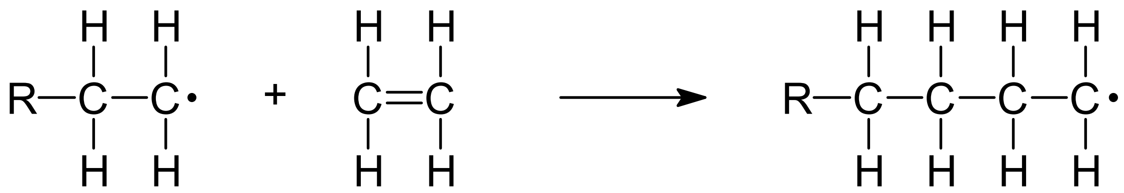
- Free radical polymerization



free radical

monomer (ethylene)

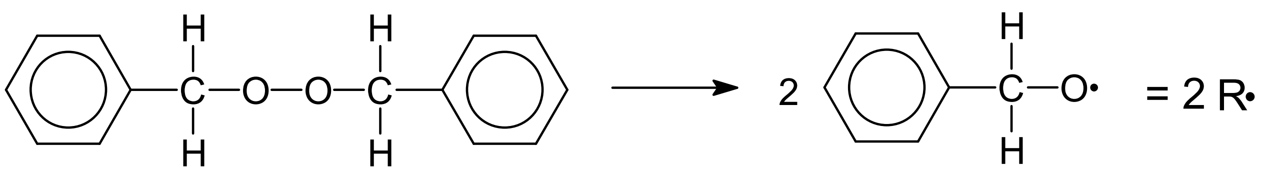
initiation



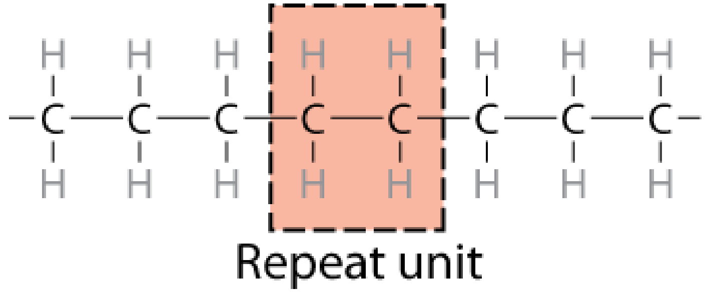
propagation

dimer

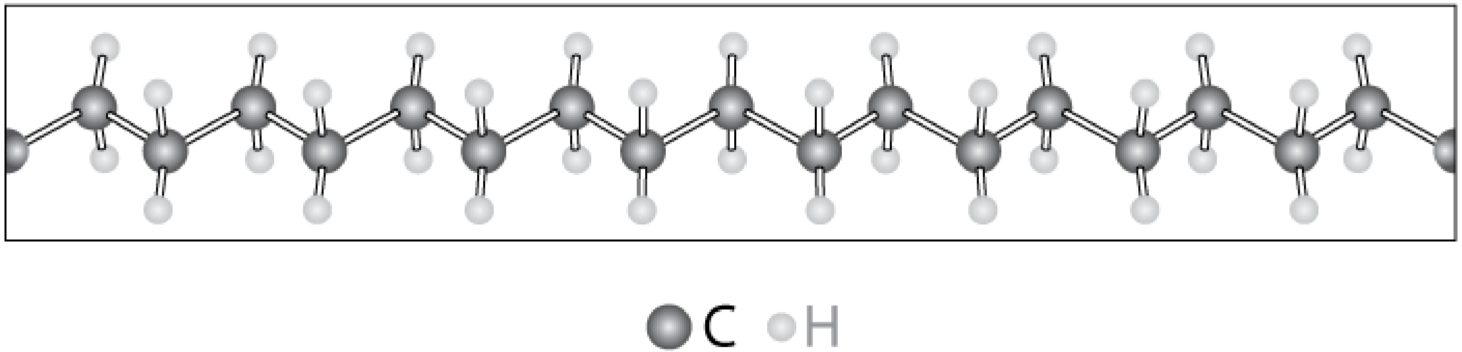
- Initiator: example - benzoyl peroxide



Chemistry and Structure of Polyethylene



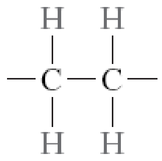
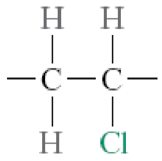
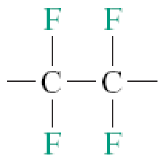
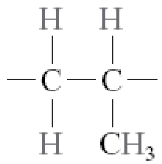
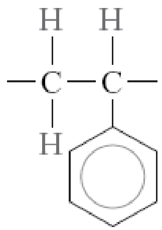
Adapted from Fig. 5.1, *Callister & Rethwisch 9e.*



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

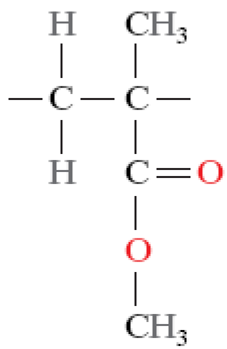
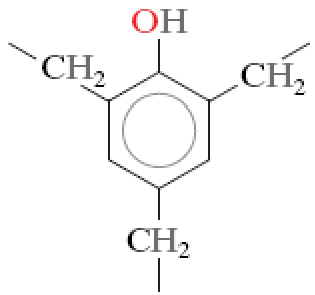
Bulk or Commodity Polymers

Table 5.3 Repeat Units for Ten of the More Common Polymeric Materials

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

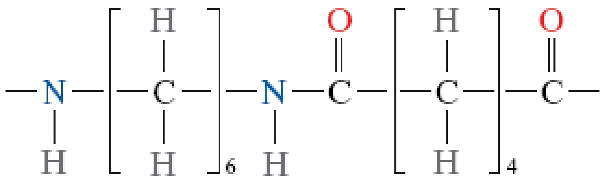
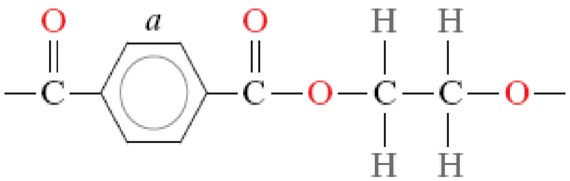
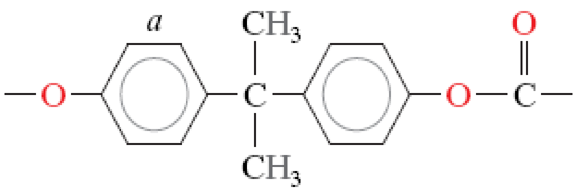
Bulk or Commodity Polymers (cont)

Table 5.3 (Continued)

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

Bulk or Commodity Polymers (cont)

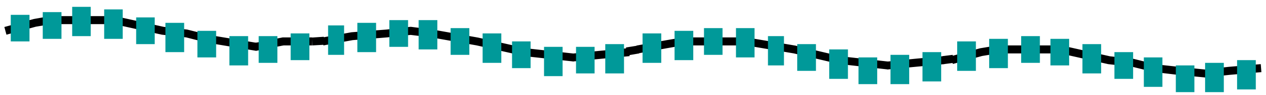
Table 5.3 (Continued)

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

MOLECULAR WEIGHT

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

Low *M*



high *M*

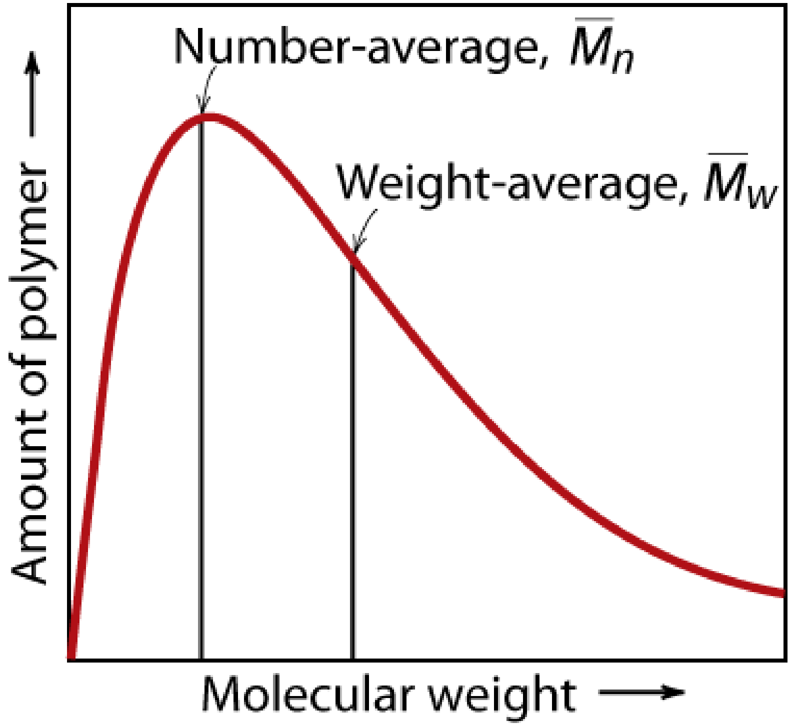
Not all chains in a polymer are of the same length
— i.e., there is a distribution of molecular weights

MOLECULAR WEIGHT DISTRIBUTION

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

$$\boxed{\begin{aligned} \bar{M}_n &= \Sigma x_i M_i \\ \bar{M}_w &= \Sigma w_i M_i \end{aligned}}$$

Fig. 5.4, *Callister & Rethwisch 9e.*



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*

Molecular Weight Calculation

Example: average mass of a class

# of Students	Weight mass (lb)
1	104
1	116
2	140
1	143
4	180
5	182
2	191
2	220
1	225
1	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.)

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

$$x_i = \frac{N_i}{\underbrace{\sum N_i}_{\text{total number} = 20}} \qquad w_i = \frac{N_i W_i}{\underbrace{\sum N_i W_i}_{\text{total weight} = 3{,}700 \text{ lb}}}$$

For example: for the 180 lb students

$$x_{180} = \frac{4}{20} = 0.2$$

$$w_{180} = \frac{4 \text{ x } 180}{3700} = 0.195$$

Molecular Weight Calculation (cont.)

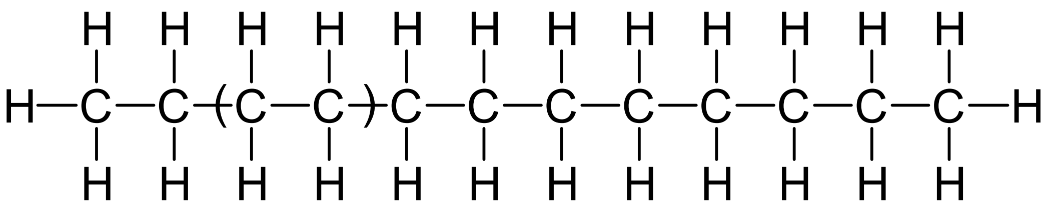
# of Students	Weight mass (lb)	Number Fractions (x_i)	Weight Fractions (w_i)	$x_i\ M_i$	$w_i\ M_i$
1	104	1/20=0.05	(104x1)/3,700= 0.028	0.05x104=5.2	0.028x104=2.912
1	116	1/20=0.05	(116x1)/3,700=0.031	0.05x116=5.8	0.031x116=3.596
2	140	2/20=0.10	(140x2)/3,700=0.076	0.10x140=14.0	0.076x140=10.64
1	143	1/20=0.05	(143x1)/3,700=0.039	0.05x143=7.15	0.039x143=5.577
4	180	4/20=0.20	(180x4)/3,700=0.195	0.20x180=36.0	0.195x180=35.10
5	182	5/20=0.25	(182x5)/3,700=0.246	0.25x182=45.5	0.246x182=44.772
2	191	2/20=0.10	(191x2)/3,700=0.103	0.10x191=19.1	0.103x191=19.673
2	220	2/20=0.10	(220x2)/3,700=0.119	0.10x220=22.0	0.119x220=26.18
1	225	1/20=0.05	(225x1)/3,700=0.061	0.05x225=11.25	0.061x225=13.725
1	380	1/20=0.05	(380x1)/3,700=0.103	0.05x380=19.0	0.103x380=39.14
Total # 20	**Total weight 3,700 lb**			$\overline{M}_n = \sum x_i M_i$ = 185 lb	$\overline{M}_w = \sum w_i M_i$ = 201 lb

$$\overline{M}_n = \sum x_i M_i = \boxed{185\ lb}$$

$$\overline{M}_w = \sum w_i M_i = \boxed{201\ lb}$$

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

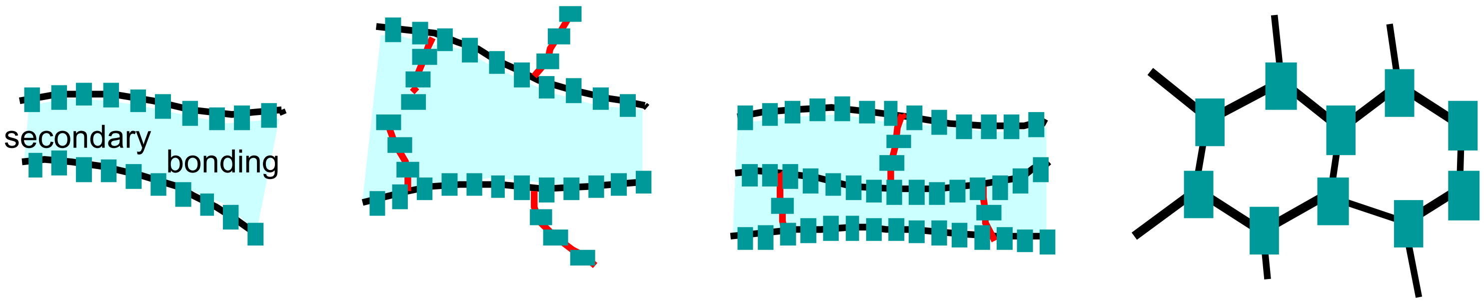
for copolymers this is calculated as follows:

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

Chain fraction

mol. wt of repeat unit *i*

Molecular Structures for Polymers



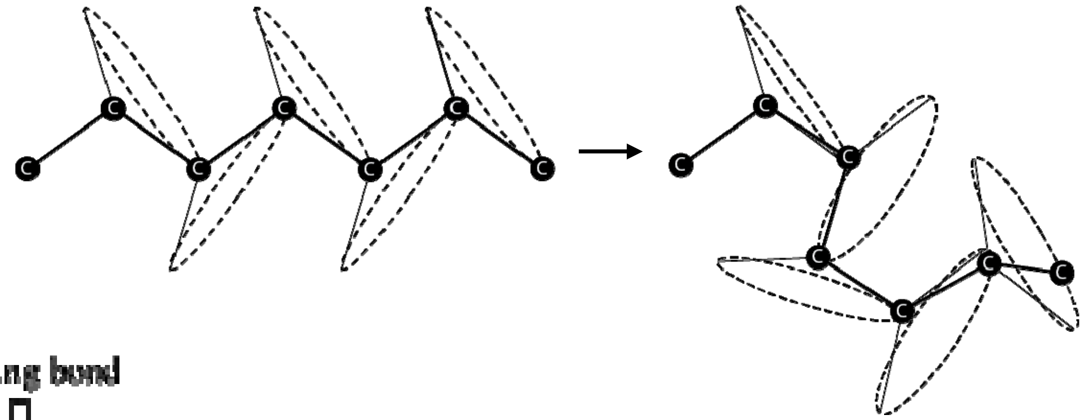
Linear Branched Cross-Linked Network

Adapted from Fig. 5.7, *Callister & Rethwisch 9e.*

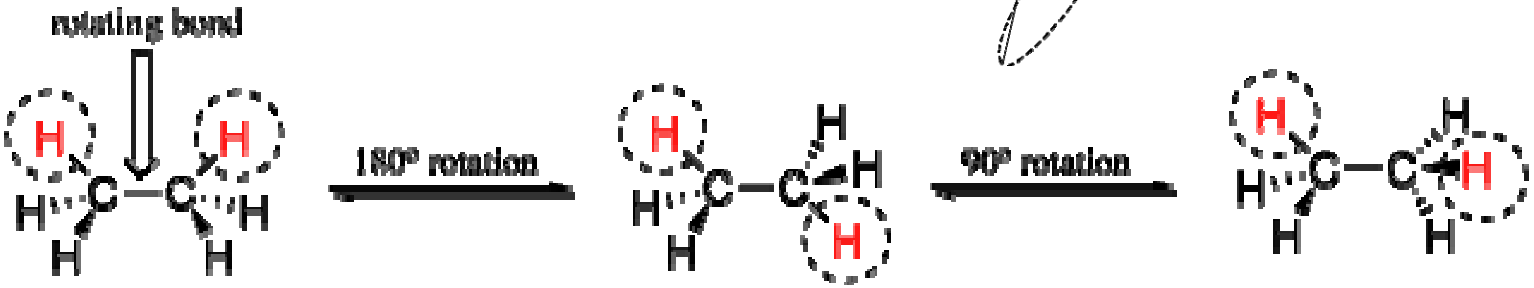
Polymers – Molecular Shape

Conformation – chain bending and twisting are possible by rotation of carbon atoms around their chain bonds, conformation encompasses portions of a molecule which are not directly linked to the same atom

note: not necessary to break chain bonds to alter molecular shape



Adapted from Fig. 5.5, *Callister & Rethwisch 9e.*

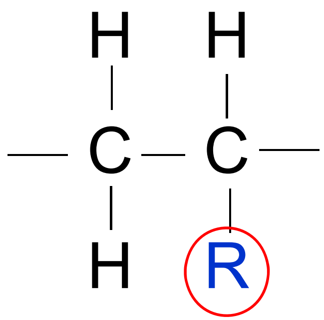


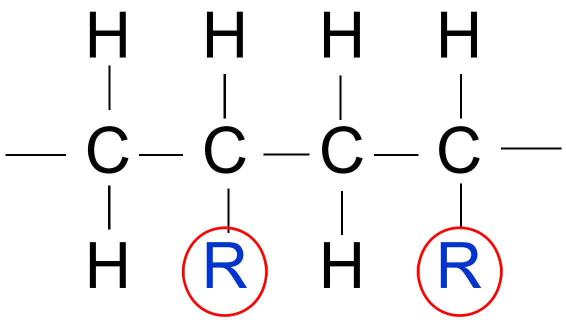
Thermal energy at room temperature is sufficient to rotate some simple covalent bonds.

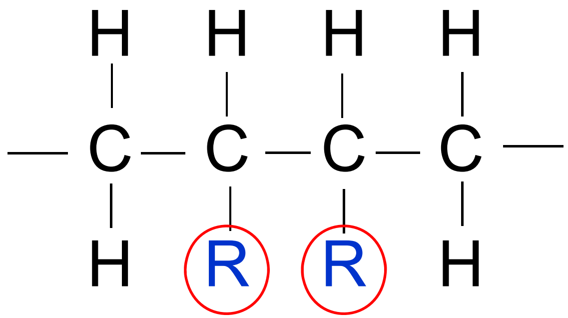
Molecular Configurations for Polymers

Configurations – arrangements of units along the axis of the chain.

Atom positions are not alterable except by breaking and re-forming primary bonds. ***This costs a lot of energy!!***







*R: atom or side group other than H (Cl, CH_3 etc.)

Isomerism

Different atomic configurations are possible for polymers with the same composition

Stereoisomerism: Atoms are linked together in the spatial arrangement in the same order but differ in their spatial arrangement.

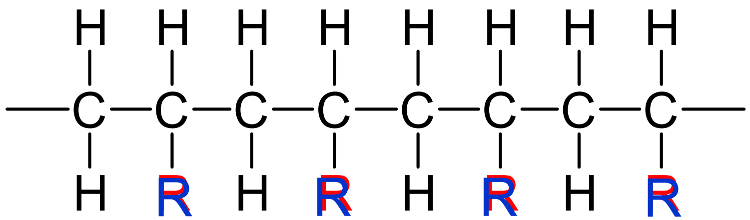
- -R groups* are situated on the same side of the chain (isotactic configuration)
- -R groups alternate sides of the chain (syndiotactic configuration)
- -R groups randomly position (atactic configuration)

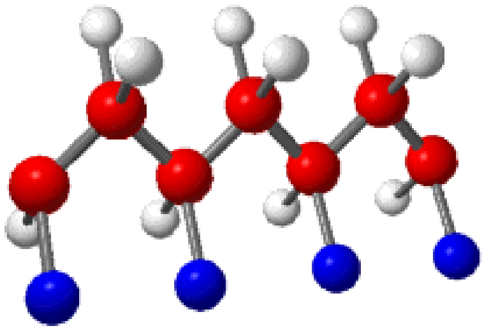
Geometrical Isomerism: Repeat units have a carbon double bond. A side group is bonded to each of the carbon atoms participating in the double bond, which may be situated on one side of the chain (cis) or its opposite (trans).

Stereoisomerism

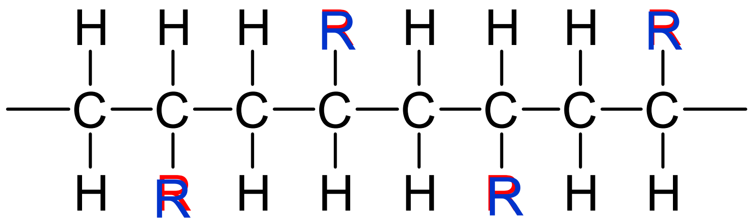
Tacticity – stereoregularity or spatial arrangement of R units along chain

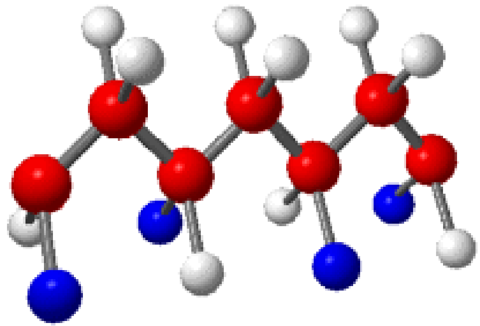
isotactic – all R groups on same side of chain





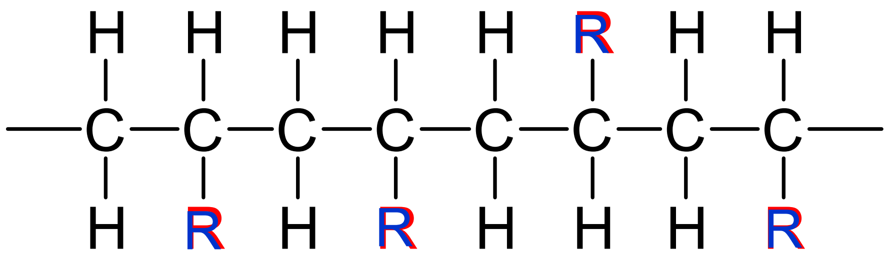
syndiotactic – R groups alternate sides

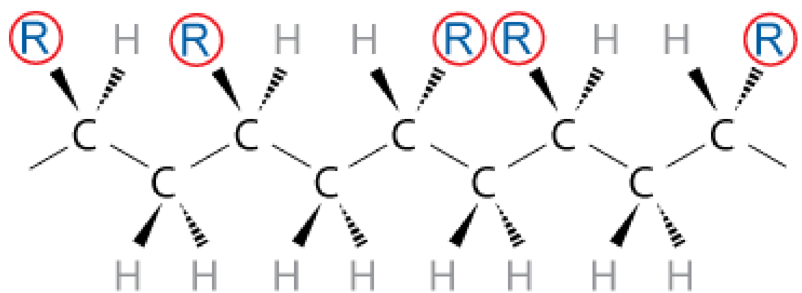




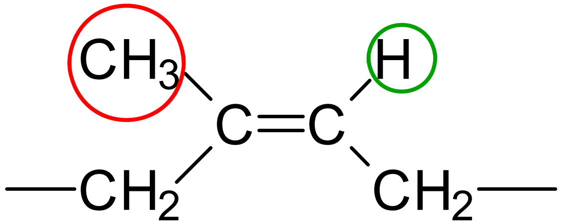
Tacticity (cont.)

atactic – R groups randomly positioned

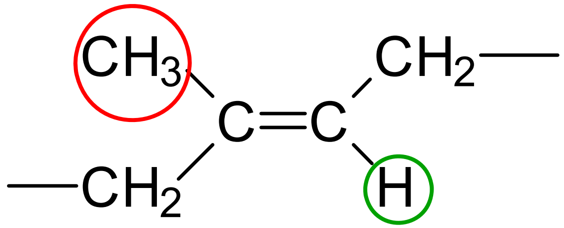




Geometrical (cis/trans) Isomerism



cis



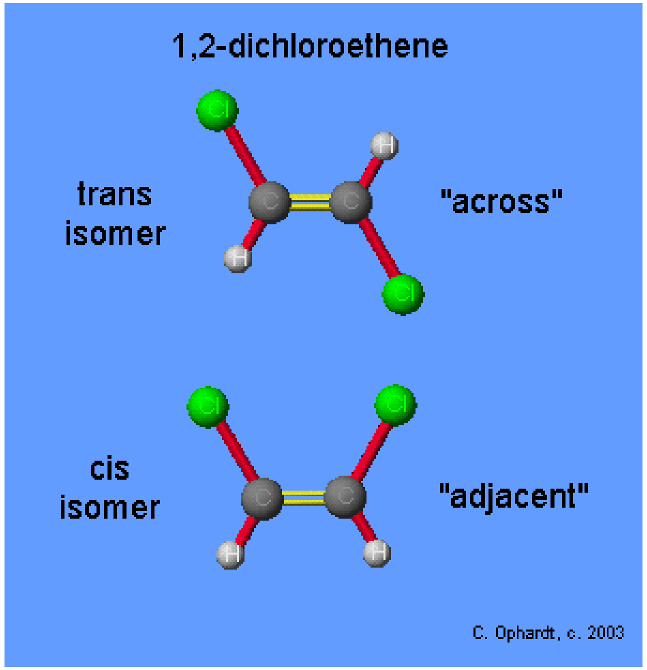
trans

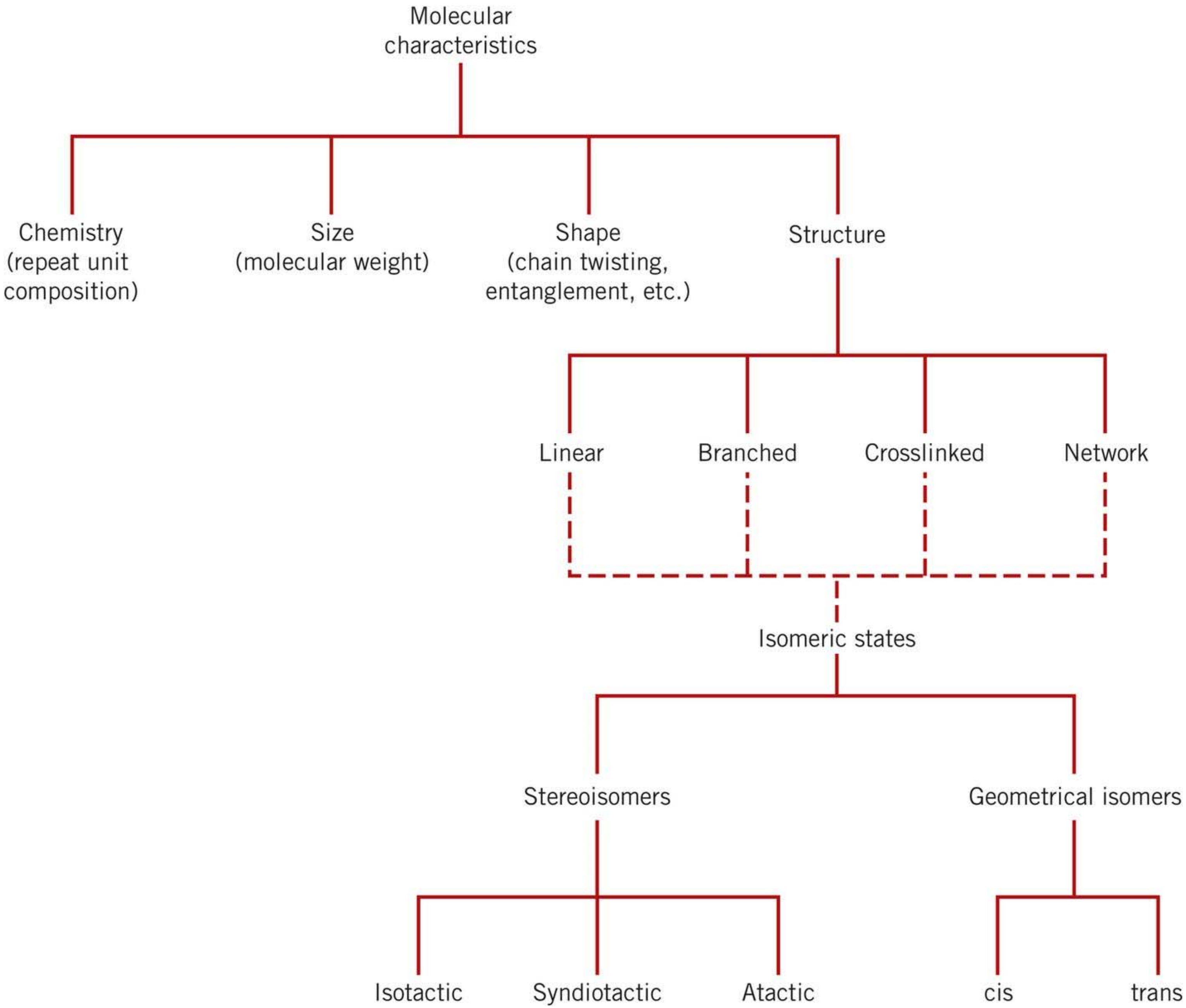
cis-isoprene (natural rubber)

H atom and CH_3 group on same side of chain

trans-isoprene (gutta percha)

H atom and CH_3 group on opposite sides of chain




Molecular characteristics
Chemistry (repeat unit composition)
Size (molecular weight)
Shape (chain twisting, entanglement, etc.)
Structure
Linear
Branched
Crosslinked
Network
Isomeric states
Stereoisomers
Geometrical isomers
Isotactic
Syndiotactic
Atactic
cis
trans

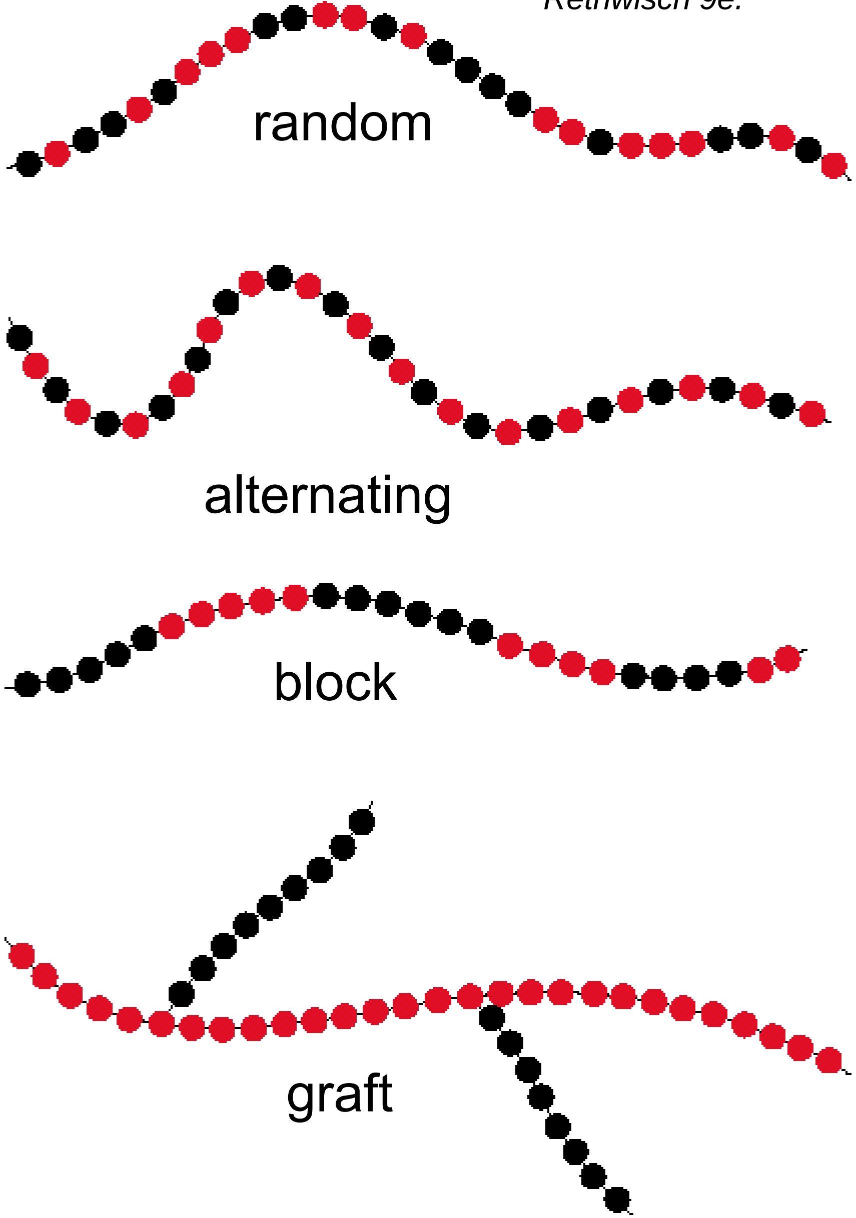
Copolymers

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 –

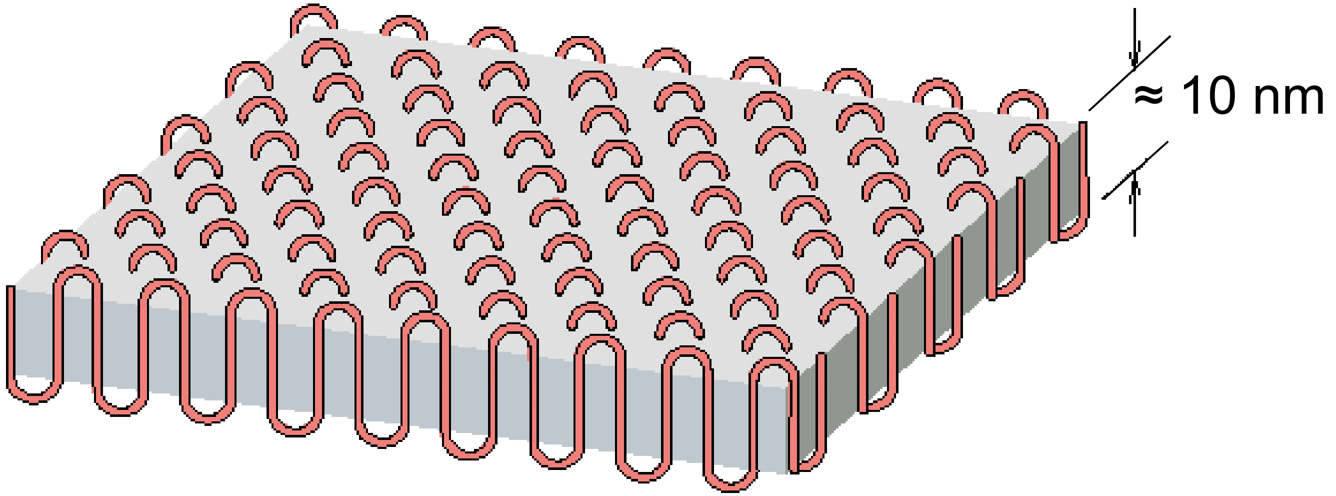
Fig. 5.9, *Callister & Rethwisch 9e.*



Polymer Crystals

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

Fig. 5.11, *Callister & Rethwisch 9e.*



Polymer Crystals (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.

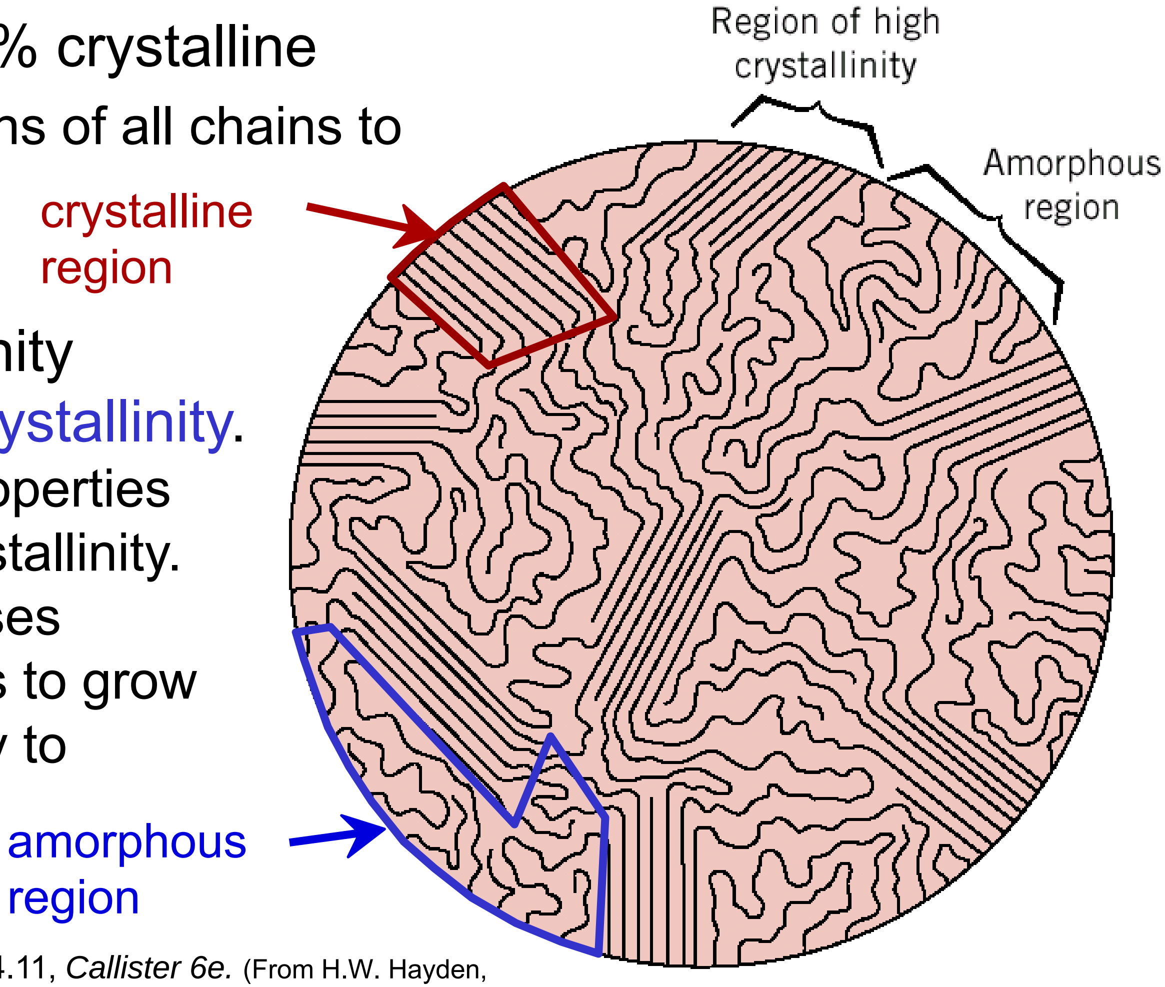
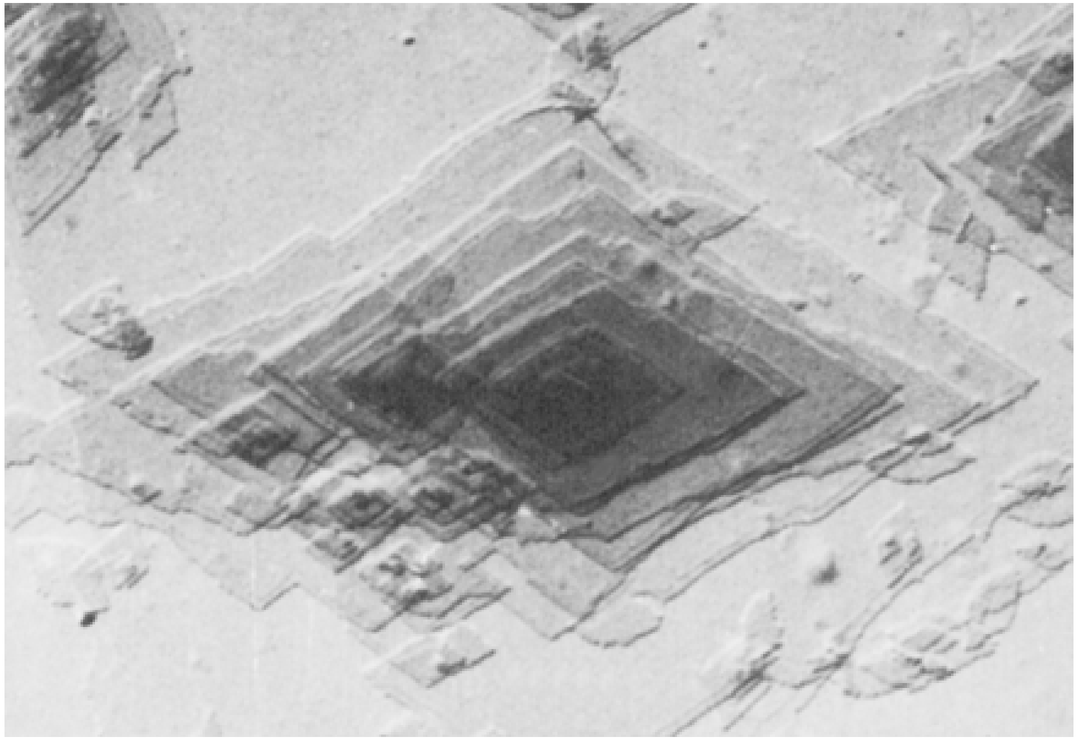


Fig. 14.11, *Callister 6e.* (From H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

Polymer Single Crystals

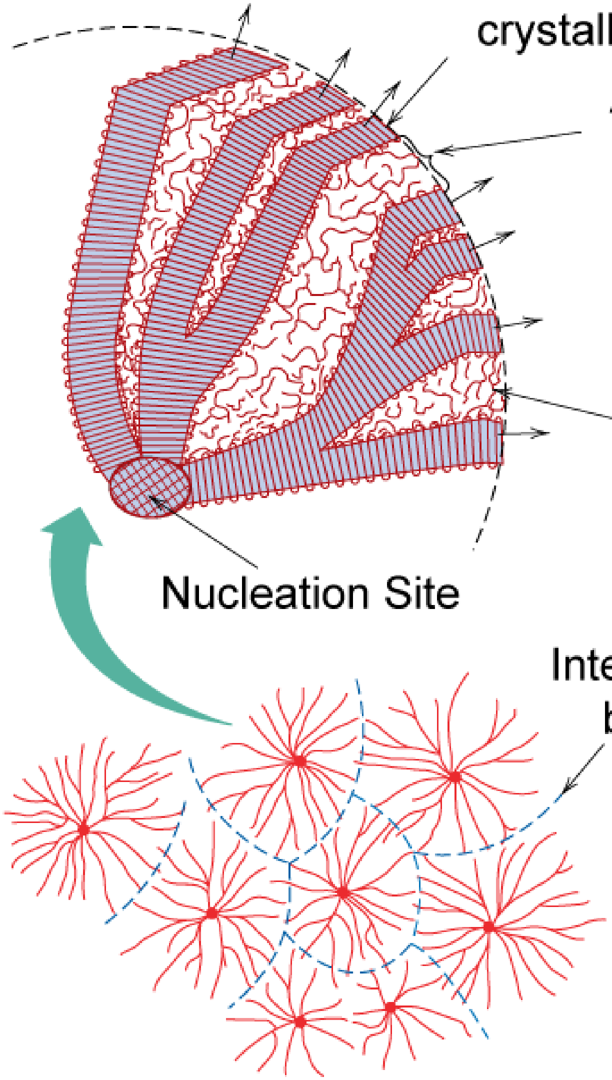
- Electron micrograph – multilayered single crystals (chain-folded layers) of polyethylene
- Single crystals – only for slow and carefully controlled growth rates



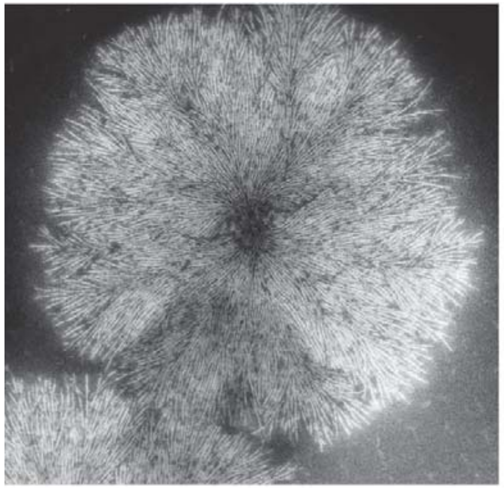
1 μm

Fig. 5.10, *Callister & Rethwisch 9e.*
[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



(d)

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Fig. 5.12, *Callister & Rethwisch 9e.*