Chapter 14: Polymer Structures

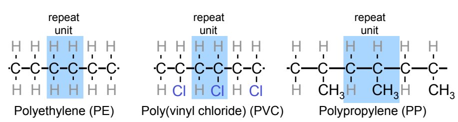
ISSUES TO ADDRESS...

- What are the general ___________________ characteristics of polymer molecules?
- What are some of the __________________ materials, and how do they differ _________?
- How is the ________ state in polymers different from that in metals and ceramics ?

What is a Polymer?

Poly — many

mer — repeat unit



Adapted from Fig. 14.2, *Callister & Rethwisch 8e.*

Ancient Polymers

- Originally ________________ were used
  - Wood
  - Cotton
  - _________
  - _________
  - Wool
  - Silk
- Oldest known uses
  - Rubber balls _____________
  - Noah used _______ (a natural polymer) for the ark

Polymer Composition

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

- Saturated hydrocarbons
  – Each _______ singly bonded to four other atoms
  – Example:
    - Ethane, C_2H_6

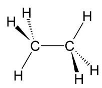


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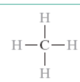
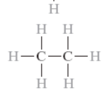
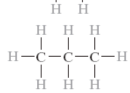
Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

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

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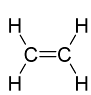
Unsaturated Hydrocarbons

- _______________ somewhat unstable – can form new bonds
  – _______ bond found in ethylene or ethene - C_2H_4



  – ______ bond found in acetylene or ethyne - C_2H_2

H—C≡C—H

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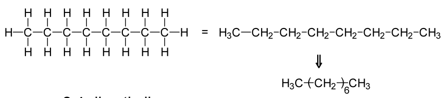
Isomerism

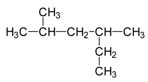
- ____________
  - two ________ with same _____________ can have quite different structures

    for example: C_8H_{18}

    - normal-octane



  - 2,4-dimethylhexane



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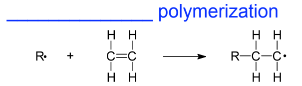
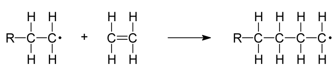
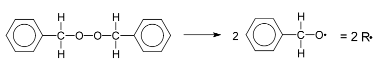
Polymerization and Polymer Chemistry

- ____________ polymerization





- _______: example - benzoyl peroxide



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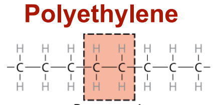
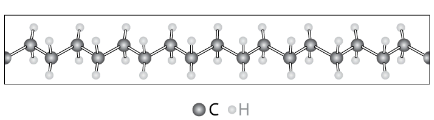
Chemistry and Structure of Polyethylene



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



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

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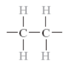
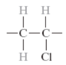
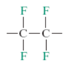
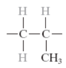
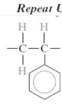
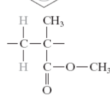
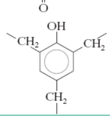
Bulk or Commodity Polymers

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)	

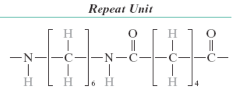
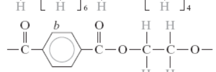
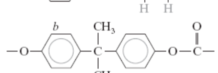
Bulk or Commodity Polymers (cont)

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

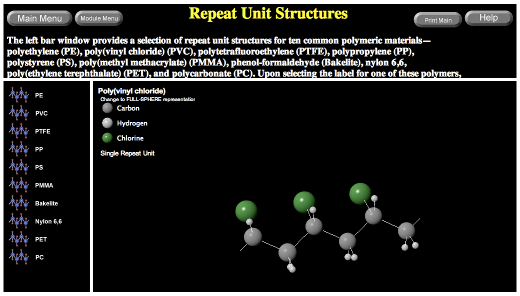
Polymer	*Repeat Unit*
Polystyrene (PS)	
Poly(methyl methacrylate) (PMMA)	
Phenol-formaldehyde (Bakelite)	

Bulk or Commodity Polymers (cont)

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)	

VMSE: Polymer Repeat Unit Structures



Manipulate and rotate polymer structures in 3-dimensions

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MOLECULAR WEIGHT

- Molecular weight, M: ________________________.

Low M

high M

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

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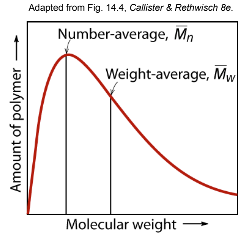
MOLECULAR WEIGHT DISTRIBUTION

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

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

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

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



M_i = ___________ molecular weight of size range i

x_i = __________________ of chains in size range i

w_i = __________________ 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?

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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 N_i	mean weight W_i
mass (lb)		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 →	ΣN_i 10	$\Sigma N_i W_i$ 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

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

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

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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

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

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

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

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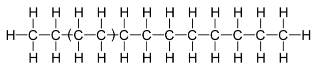
Degree of Polymerization, *DP*

DP = average number of ___________ per chain



DP = 6

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

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

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

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

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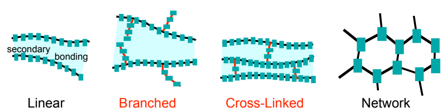
Molecular Structures for Polymers



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

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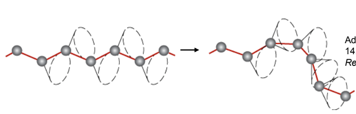
Polymers – Molecular Shape

Molecular Shape (or ________________) – chain bending and twisting are possible by rotation of carbon atoms ________________________

– note: not necessary to _________________ to alter molecular shape



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

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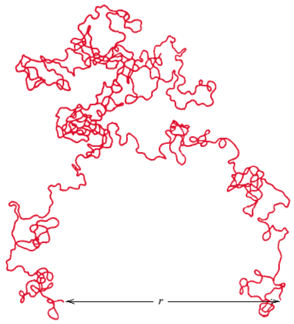
Chain End-to-End Distance, *r*



Adapted from Fig. 14.6, *Callister & Rethwisch 8e.*

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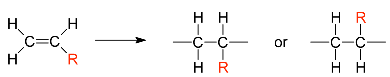
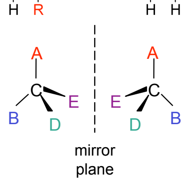
Molecular Configurations for Polymers

____________– to change must break bonds

- _______________



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



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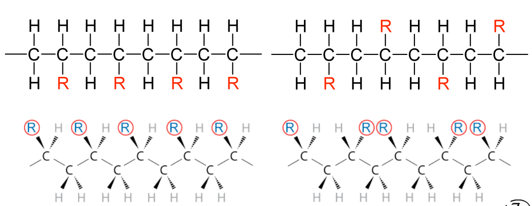
Tacticity

________ – ___________ or spatial arrangement of R units along chain

________ – all R groups on same side of chain

_________ – R groups alternate sides



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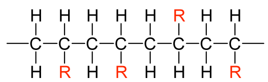
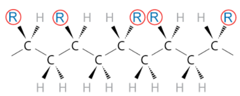
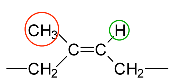
Tacticity (cont.)

_____ – R groups randomly positioned





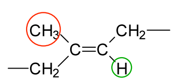
cis/trans Isomerism



cis

cis-isoprene
(natural rubber)

H atom and CH_3 group on ______ side of chain

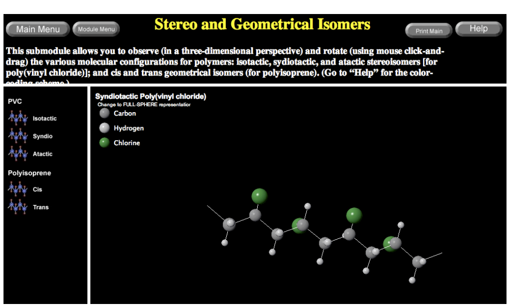


trans

trans-isoprene
(gutta percha)

H atom and CH_3 group on ________ sides of chain

VMSE: Stereo and Geometrical Isomers



Manipulate and rotate polymer structures in 3-dimensions

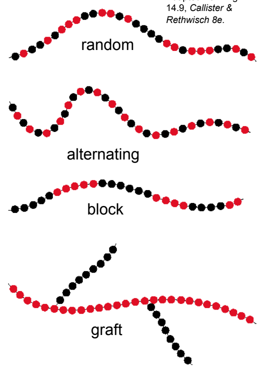
Copolymers

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

two or more monomers polymerized together

- _______ – A and B randomly positioned along chain
- ____________ – A and B alternate in polymer chain
- __________ – large blocks of A units alternate with large blocks of B units
- ________ – chains of B units grafted onto A backbone

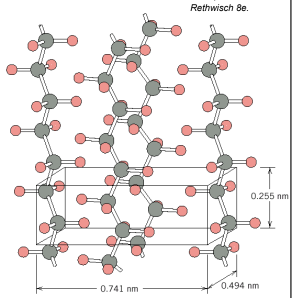
A – ● B – ●



Crystallinity in Polymers

Adapted from Fig. 14.10, *Callister & Rethwisch 8e.*

- Ordered atomic arrangements involving ____________________
- Crystal structures in terms of ____________
- Example shown
  - ____________ unit cell



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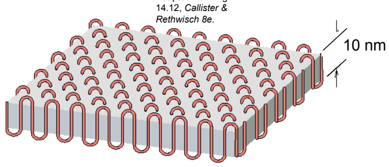
Polymer Crystallinity

- Crystalline regions
  - thin ________ with chain folds at faces
  - ______________ structure

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



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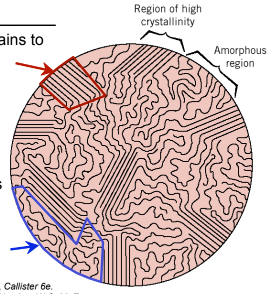
Polymer Crystallinity (cont.)

Polymers rarely ________________

- Difficult for all regions of all chains to become aligned



- Degree of crystallinity expressed as __________.
  - -- Some physical properties depend on % crystallinity.
  - -- ________________ 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.)

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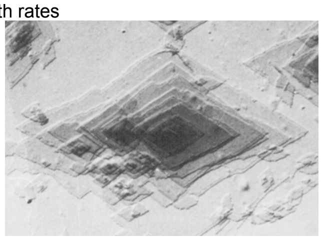
Polymer Single Crystals

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



Adapted from Fig. 14.11, *Callister & Rethwisch 8e*.

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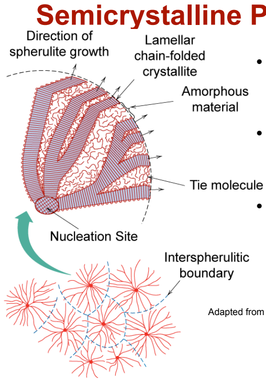
Semicrystalline Polymers



- Some semicrystalline polymers form __________ structures
- ________ chain-folded crystallites and amorphous regions
- ________ structure for relatively rapid growth rates

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

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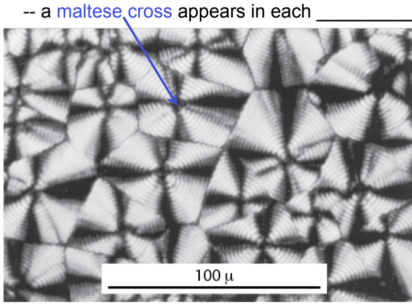
Photomicrograph – Spherulites in Polyethylene

_____________ light used

-- a maltese cross appears in each ___________



Adapted from Fig. 14.14, *Callister & Rethwisch 8e.*