Chapter 14:
Polymer Structures

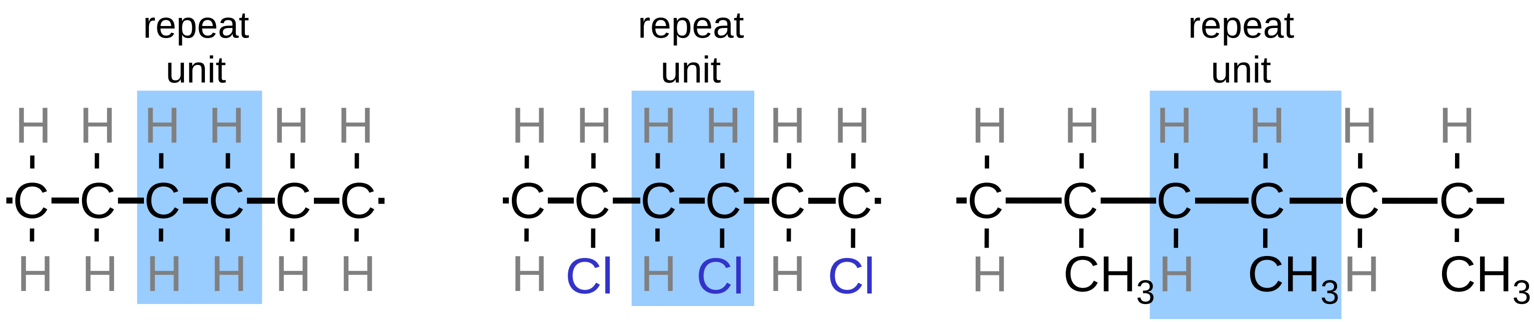
ISSUES TO ADDRESS...

- 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 ?

What is a Polymer?

Poly — many

mer — repeat unit



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

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

Natural Polymers

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

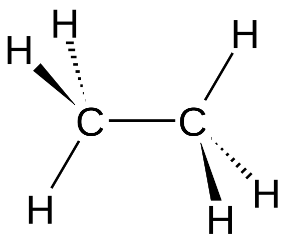
- Oldest known uses
  - Rubber balls used by Incas
  - Noah used pitch (a natural polymer) for the ark

Saturated & Unsatruated Hydrocarbons

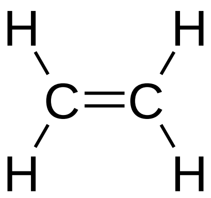
Most polymers are hydrocarbons

– i.e., made up of C and H and, maybe, other elements (O, S, N, halides, etc.)

- Saturated hydrocarbons
  - Each carbon singly bonded to four other atoms
  - Example: Ethane C_2H_6



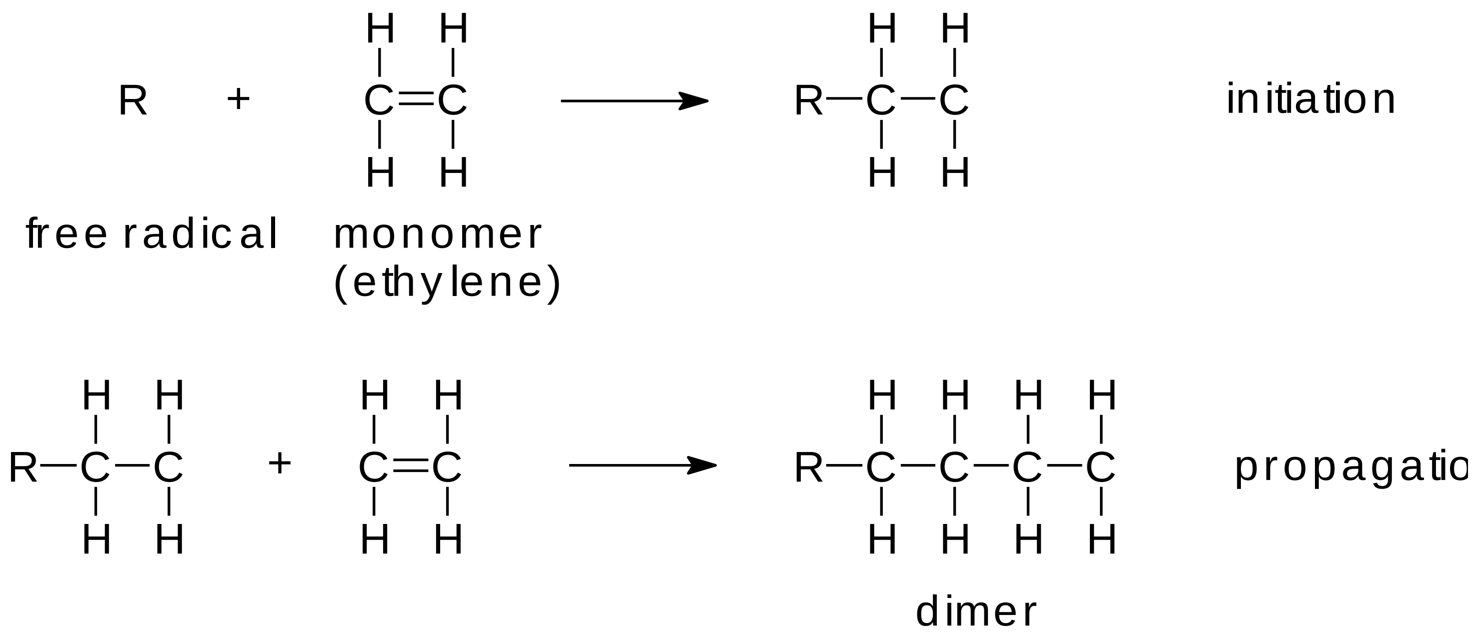
- Unsaturated hydrocarbons
  - double & triple carbon-carbon bonds exist in structure – can form new bonds
    - Double bond found in ethylene or others - C_2H_4



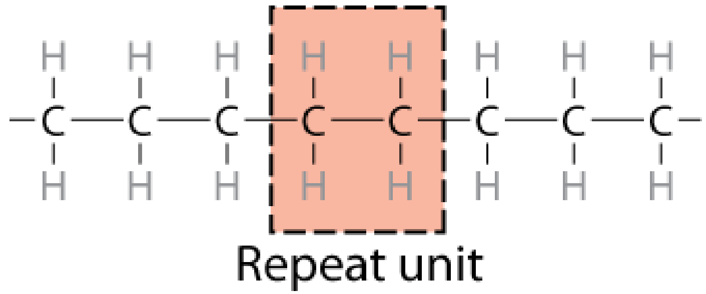
    - Triple bond found in acetylene or others - C_2H_2

Polymerization

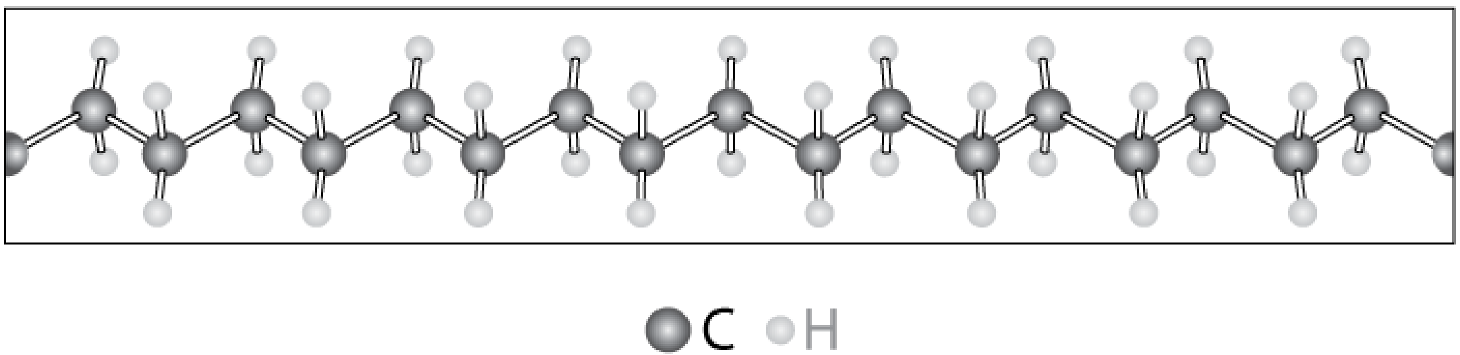
- Reaction of small molecules to form long-chain large molecules or polymers
- Example:



Example of A Polymer - Polyethylene



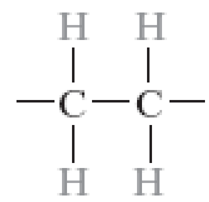
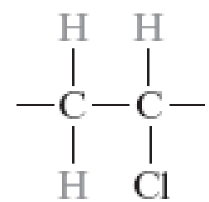
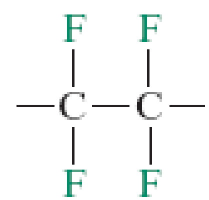
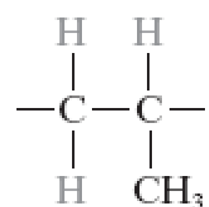
Adapted from Fig. 14.1, *Callister & Rethwisch 8e.*



A long-chain saturated hydrocarbon

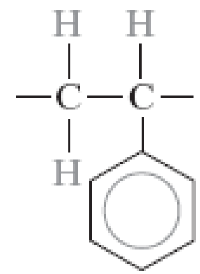
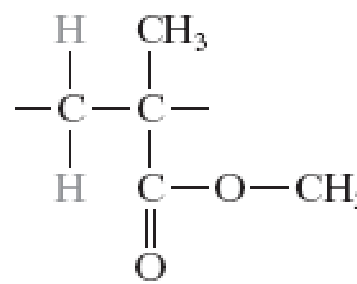
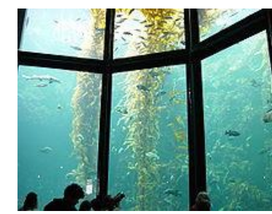
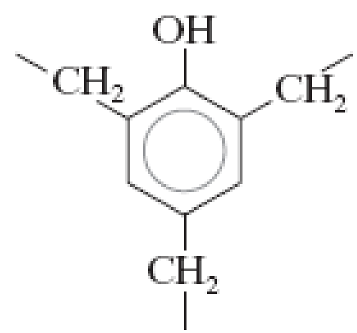
Bulk or Commodity Polymers

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)		

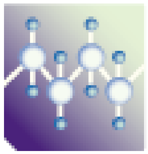
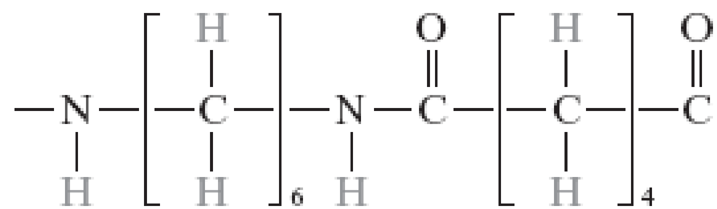
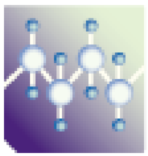
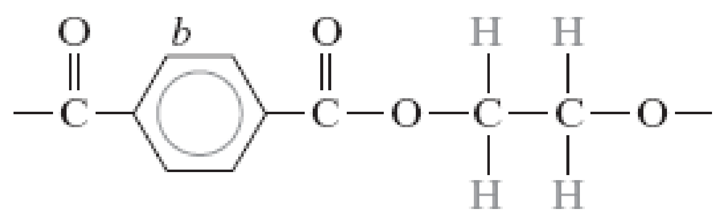
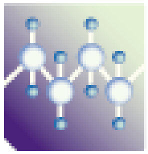
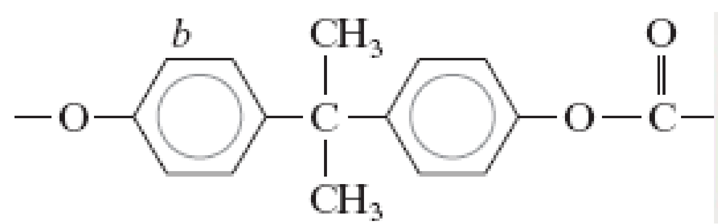
Bulk or Commodity Polymers (cont)

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)

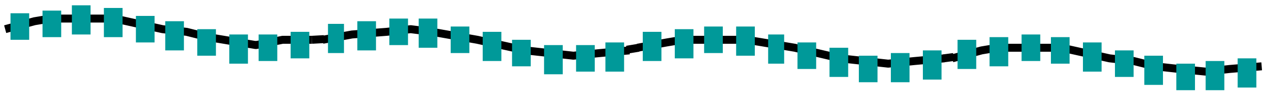
Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

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

MOLECULAR WEIGHT for Polymers

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

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

Number-average molecular weight

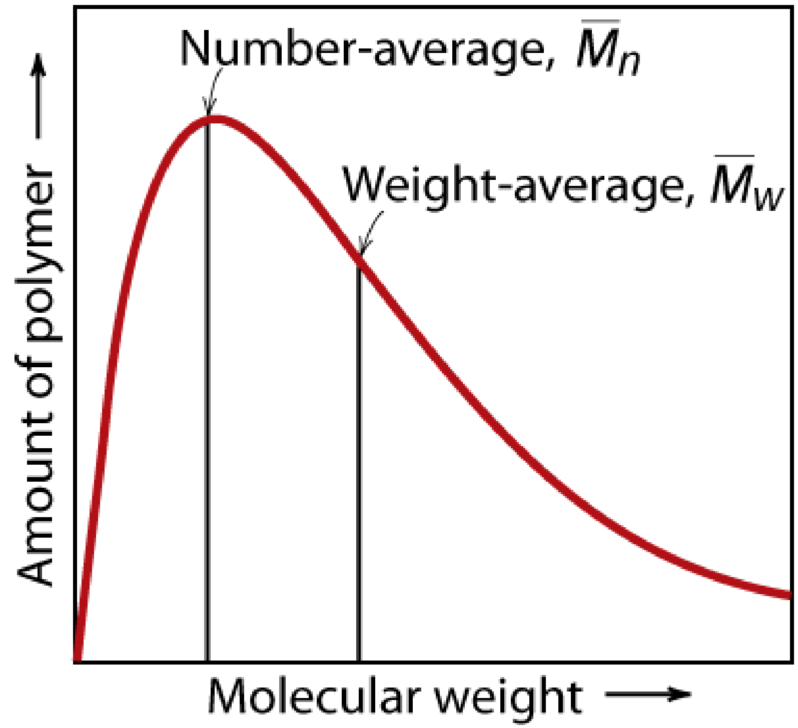
$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

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

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

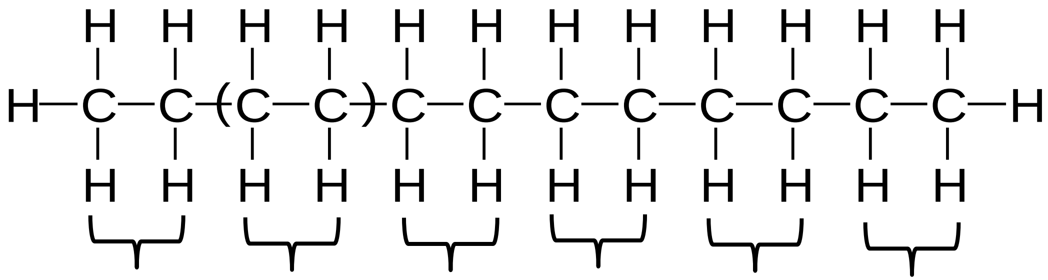
x_i = number fraction of chains in size range *i*

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



Degree of Polymerization, *DP*

DP = average number of repeat units per chain



$DP = 6$

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

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

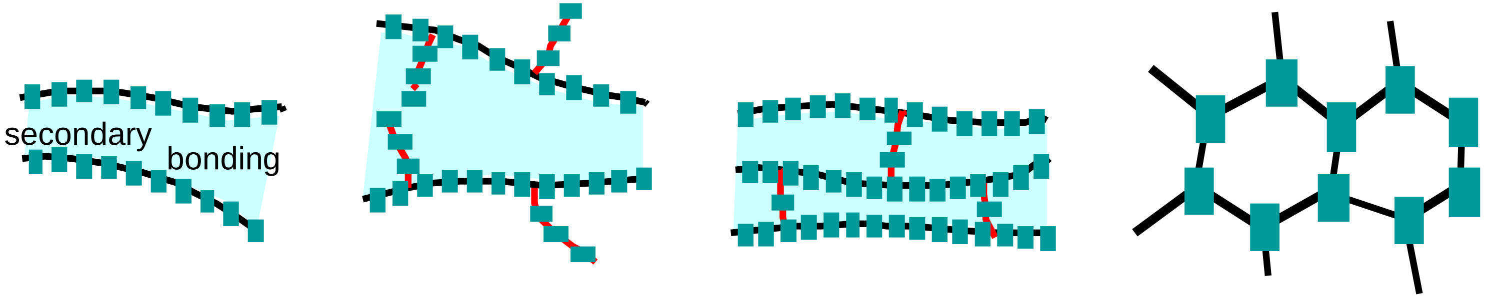
for copolymers this is calculated as follows:

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

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

Molecular Structures for Polymers

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

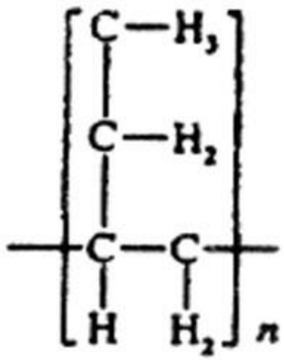


Linear	**Branched**	**Cross-Linked**	**Network**
e.g., PE, PVC, PMMA, PTFE	e.g., LDPE	e.g., Cross-linked rubber	e.g., Epoxy, phenolic resin

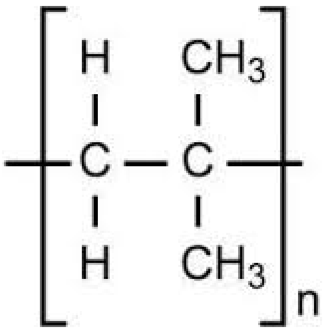
Polymers – Molecular Shape & Structure

Molecular structure (or Configuration) – Geometric arrangement of side groups/side chains; Can be complex

Polybutylene

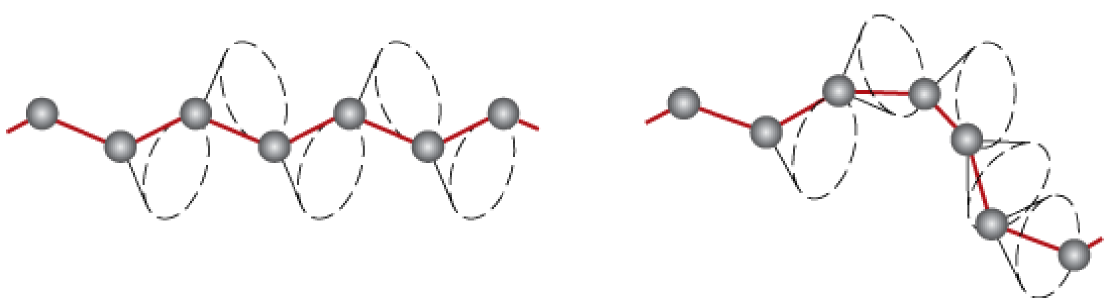


Poly isobutylene



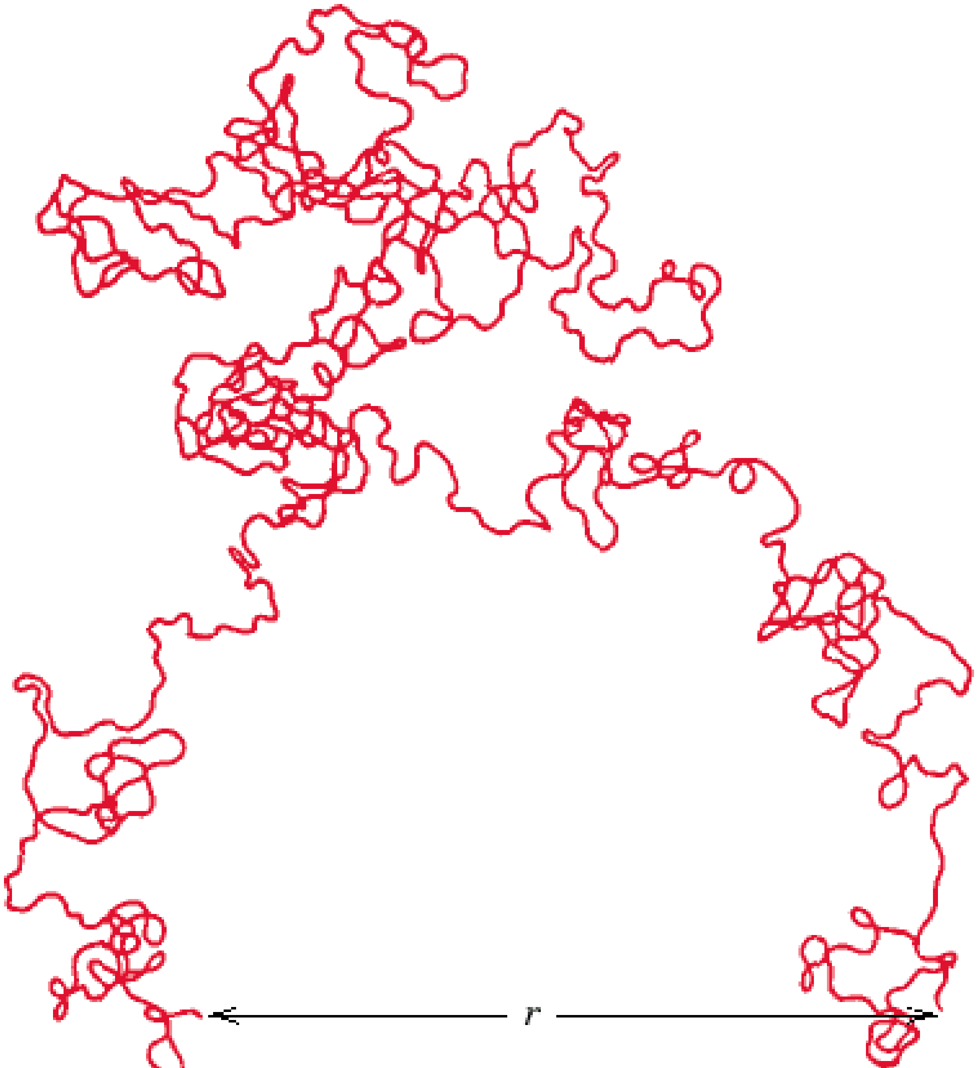
http://www.niir.org/books/book/complete-technology-book-on-industrial-polymers-additives-colourants-fillers-niir-board-consultants-engineers/isbn-8178330091/zb,,108,a,18,0,3e8/index.html

Molecular Shape (or Conformation) – chain bending and twisting are possible by rotation of carbon atoms around their chain bonds, which change molecule structures



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

Chain End-to-End Distance, *r*



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

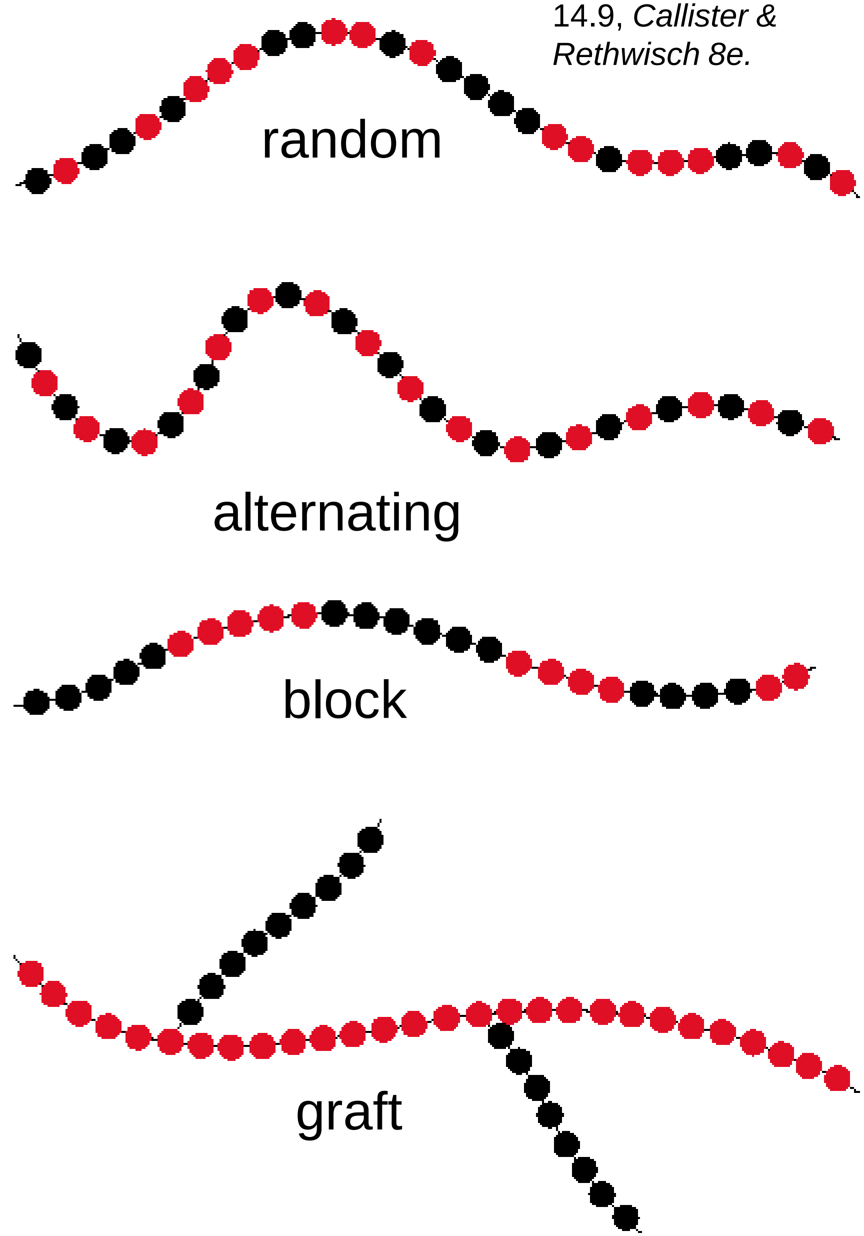
Copolymers

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.*

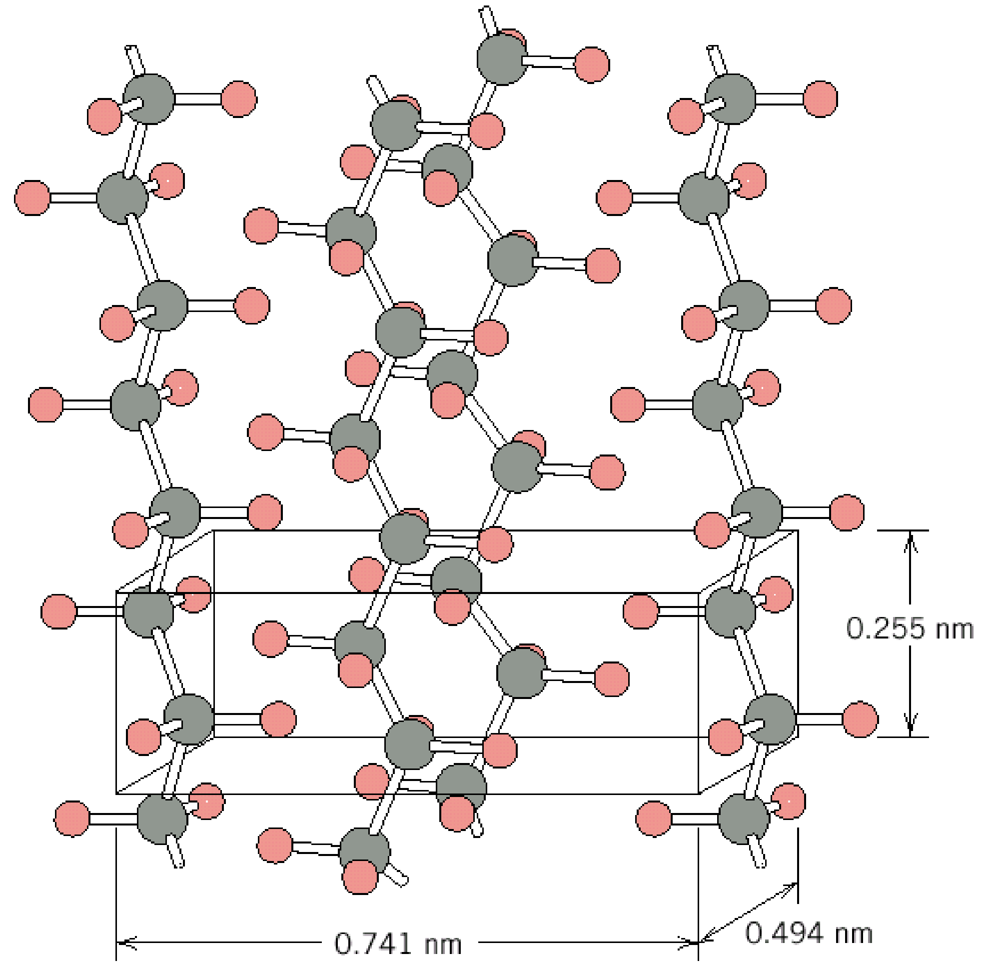


Crystallinity in Polymers

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

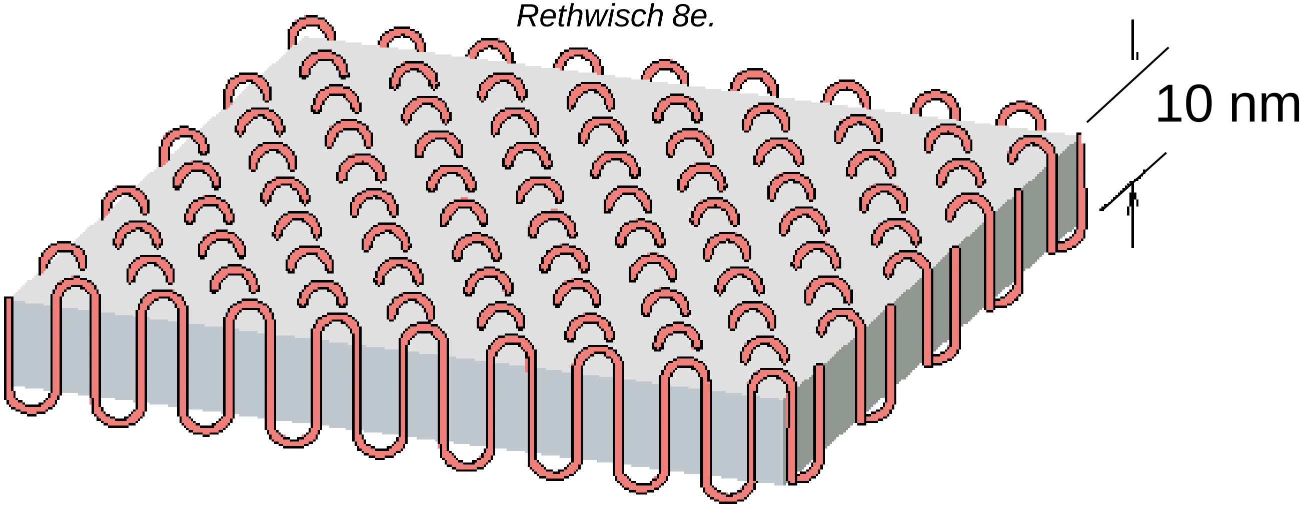
- Polymer may contain crystalline regions with ordered atomic arrangements involving molecular chains

- Example shown
  - polyethylene unit cell



Polymer Crystallinity

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

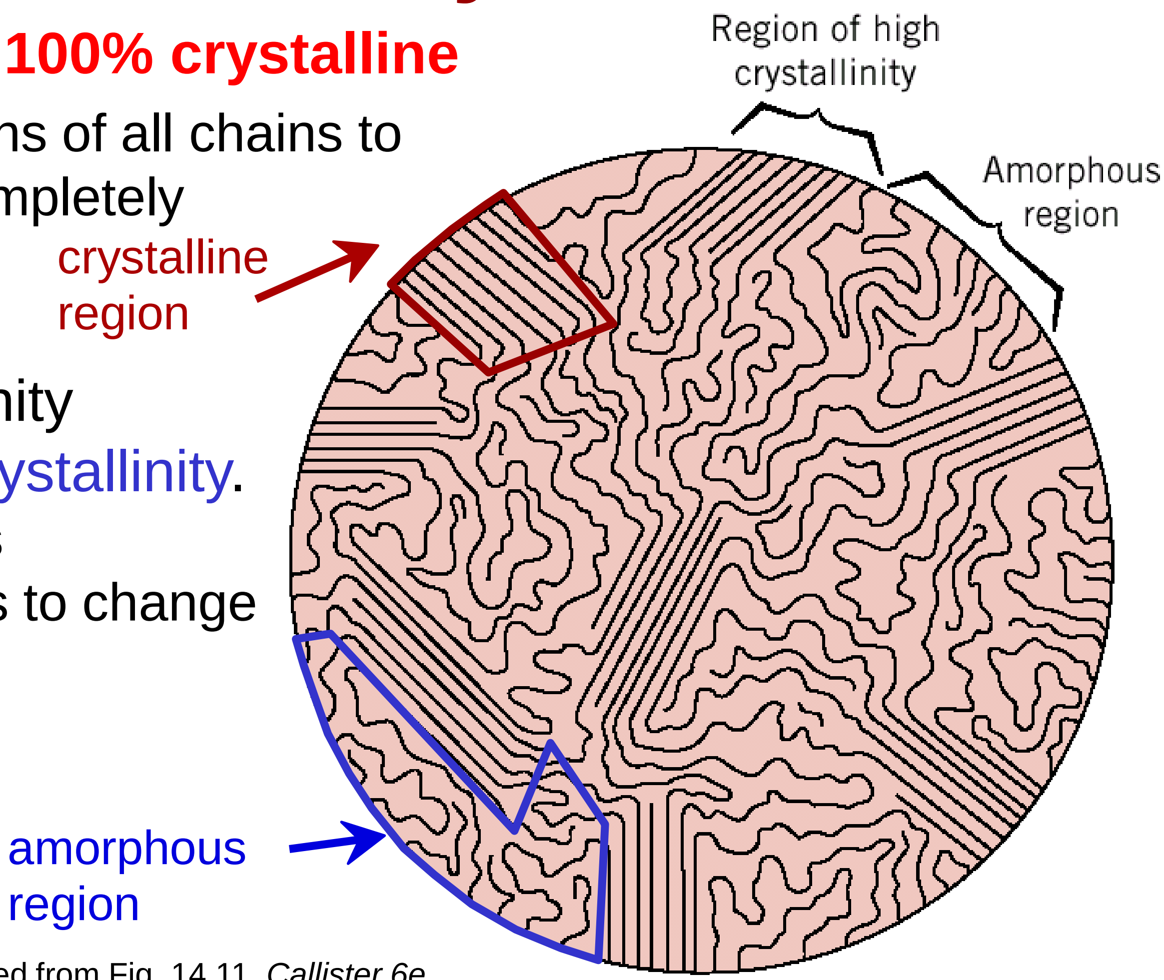


Adapted from Fig. 14.12, *Callister & Rethwisch 8e.*

Crystalline and Amorphous Regions in Polymers

Polymers are **rarely 100% crystalline**

- Difficult for all regions of all chains to become aligned completely



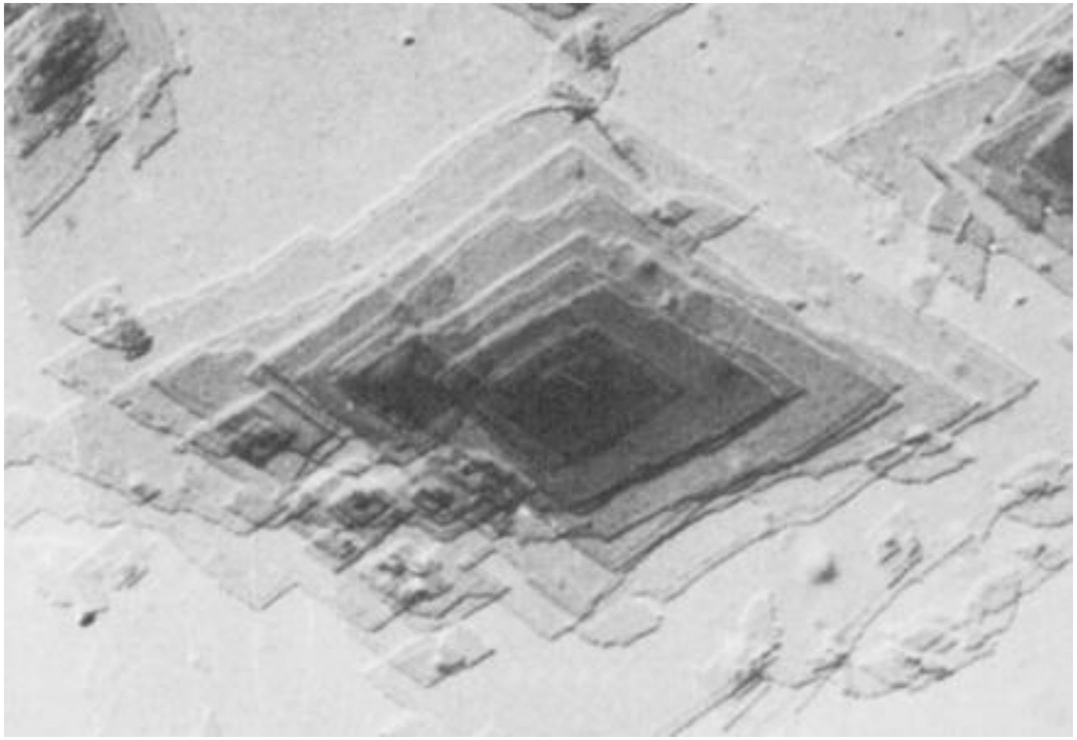
- Degree of crystallinity expressed as % crystallinity.

-- Heat treating causes crystalline regions to change

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 Single Crystals

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



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