

CHAPTER 14:

POLYMER STRUCTURES

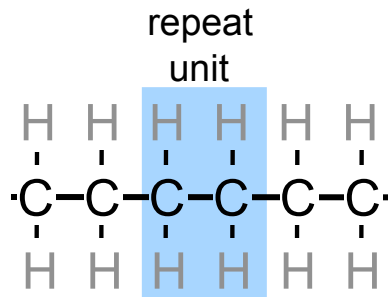
- What are the basic microstructural features?
- How are polymer properties effected by molecular weight?
- How do polymeric crystals accommodate the polymer chain?



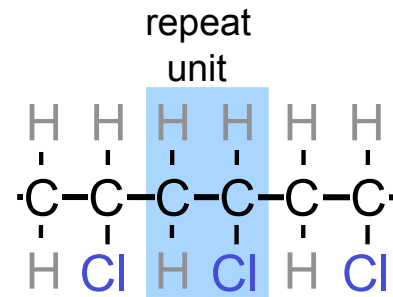
Chapter 14 – Polymers

What is a polymer?

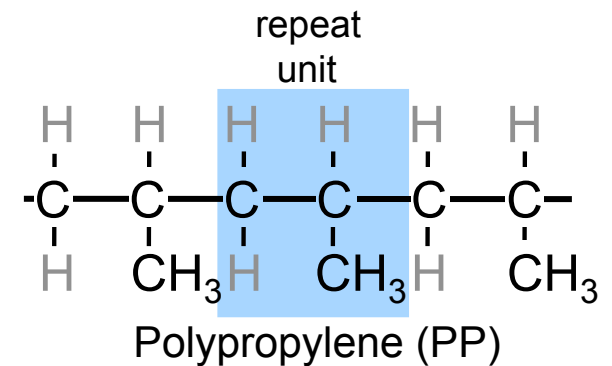
Poly **mer**
many repeat unit



Polyethylene (PE)



Polyvinyl chloride (PVC)



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



Polymer Composition

Most polymers are hydrocarbons

– i.e. made up of H and C

- Saturated hydrocarbons

– Each carbon bonded to four other atoms

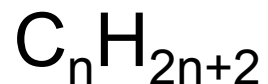
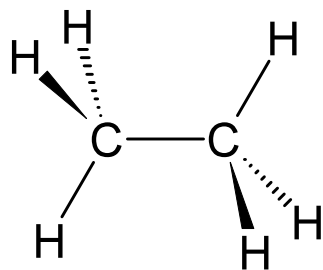


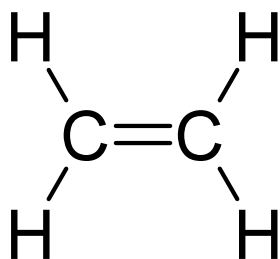
Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

<i>Name</i>	<i>Composition</i>	<i>Structure</i>	<i>Boiling Point (°C)</i>
Methane	CH_4	$ \begin{array}{c} H \\ \\ H - C - H \\ \\ H \end{array} $	-164
Ethane	C_2H_6	$ \begin{array}{c} H \quad H \\ \quad \\ H - C - C - H \\ \quad \\ H \quad H \end{array} $	-88.6
Propane	C_3H_8	$ \begin{array}{c} H \quad H \quad H \\ \quad \quad \\ H - C - C - C - H \\ \quad \quad \\ H \quad H \quad H \end{array} $	-42.1
Butane	C_4H_{10}		-0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

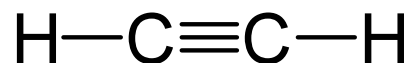


Unsaturated Hydrocarbons

- Double & triple bonds relatively reactive – can form new bonds
 - Double bond – ethylene or ethene - C_nH_{2n}



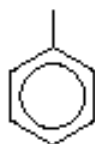
- 4-bonds, but only 3 atoms bound to C's
 - Triple bond – acetylene or ethyne - C_nH_{2n-2}



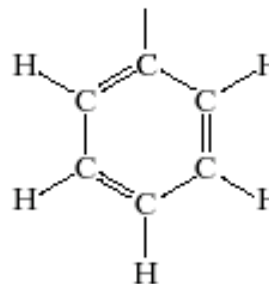
Some common hydrocarbon groups

<i>Family</i>	<i>Characteristic Unit</i>	<i>Representative Compound</i>	
Alcohols	$R-OH$	$\begin{array}{c} H \\ \\ H-C-OH \\ \\ H \end{array}$	Methyl alcohol
Ethers	$R-O-R'$	$\begin{array}{c} H & H \\ & \\ H-C-O-C-H \\ & \\ H & H \end{array}$	Dimethyl ether
Acids	$\begin{array}{c} OH \\ \\ R-C \\ \\ O \end{array}$	$\begin{array}{c} H & OH \\ & \\ H-C-C \\ & \\ H & O \end{array}$	Acetic acid
Aldehydes	$\begin{array}{c} R \\ \\ C=O \\ \\ H \end{array}$	$\begin{array}{c} H \\ \\ C=O \\ \\ H \end{array}$	Formaldehyde
Aromatic hydrocarbons	$\begin{array}{c} R \\ \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{c} OH \\ \\ \text{C}_6\text{H}_5 \end{array}$	Phenol

^aThe simplified structure

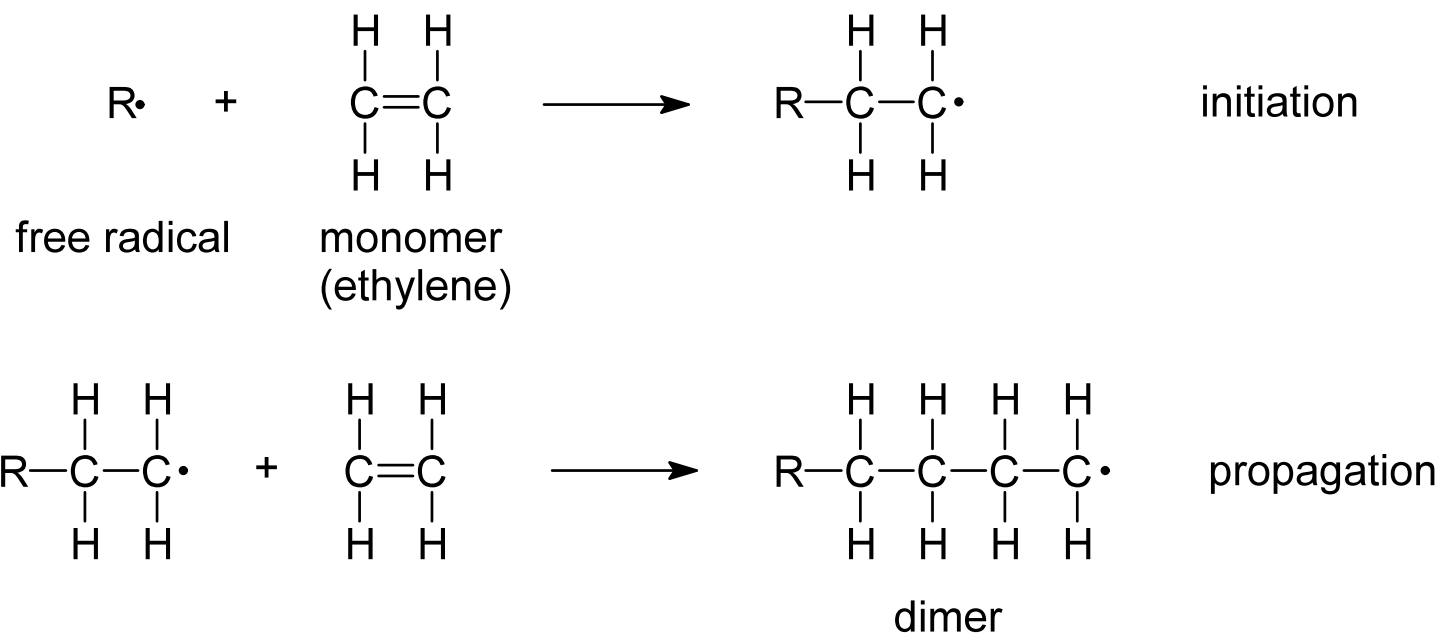


denotes a phenyl group,

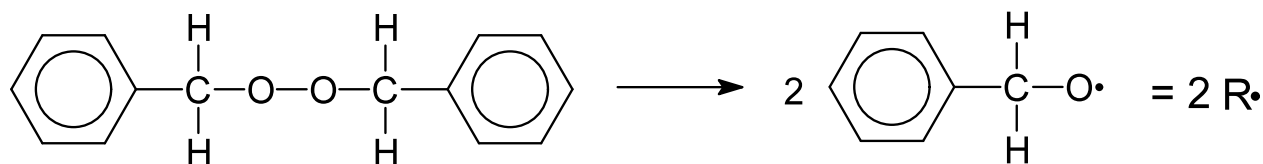


Chemistry of Polymers

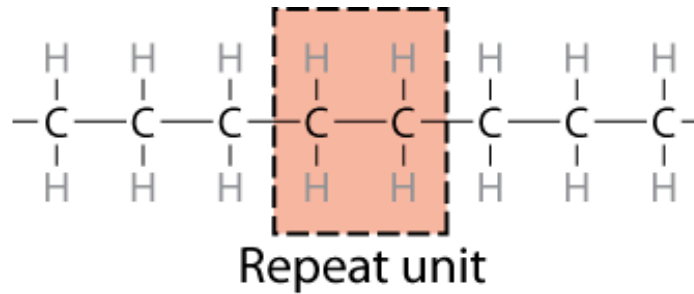
- Free radical polymerization



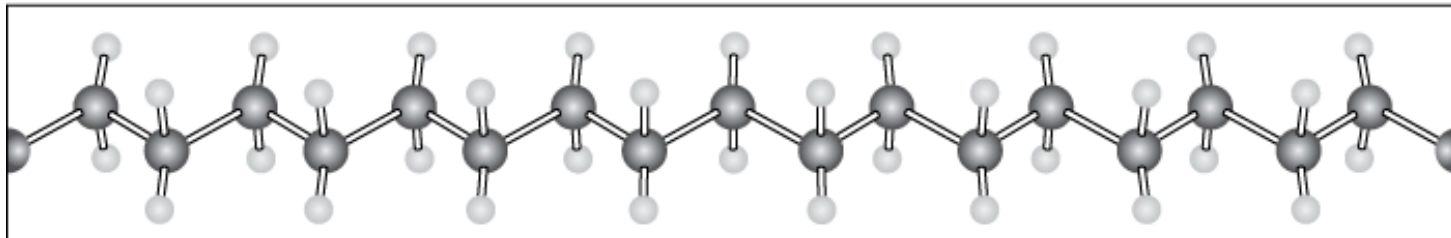
- Initiator: example - benzoyl peroxide



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

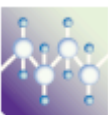
<i>Polymer</i>	<i>Repeat Unit</i>
 Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array}$
 Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array}$
 Polytetrafluoroethylene (PTFE)	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array}$
 Polypropylene (PP)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$



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

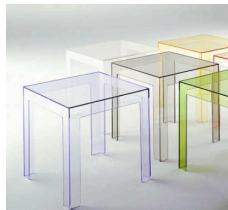
<i>Polymer</i>	<i>Repeat Unit</i>	
Polystyrene (PS)	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} $	
Poly(methyl methacrylate) (PMMA)	$ \begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}(=\text{O})\text{OCH}_3 \end{array} $	
Phenol-formaldehyde (Bakelite)	$ \begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{C}_6\text{H}_2-\text{CH}_2 \\ \\ \text{CH}_2 \end{array} $	

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)	$-\text{N}-\left[\begin{array}{c} \text{H} \\ \\ -\text{C}- \\ \\ \text{H} \end{array}\right]_6-\text{N}-\overset{\text{O}}{\parallel}\text{C}-\left[\begin{array}{c} \text{H} \\ \\ -\text{C}- \\ \\ \text{H} \end{array}\right]_4-\overset{\text{O}}{\parallel}\text{C}-$
 Poly(ethylene terephthalate) (PET, a polyester)	$-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$
 Polycarbonate (PC)	$-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-$



MOLECULAR WEIGHT

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

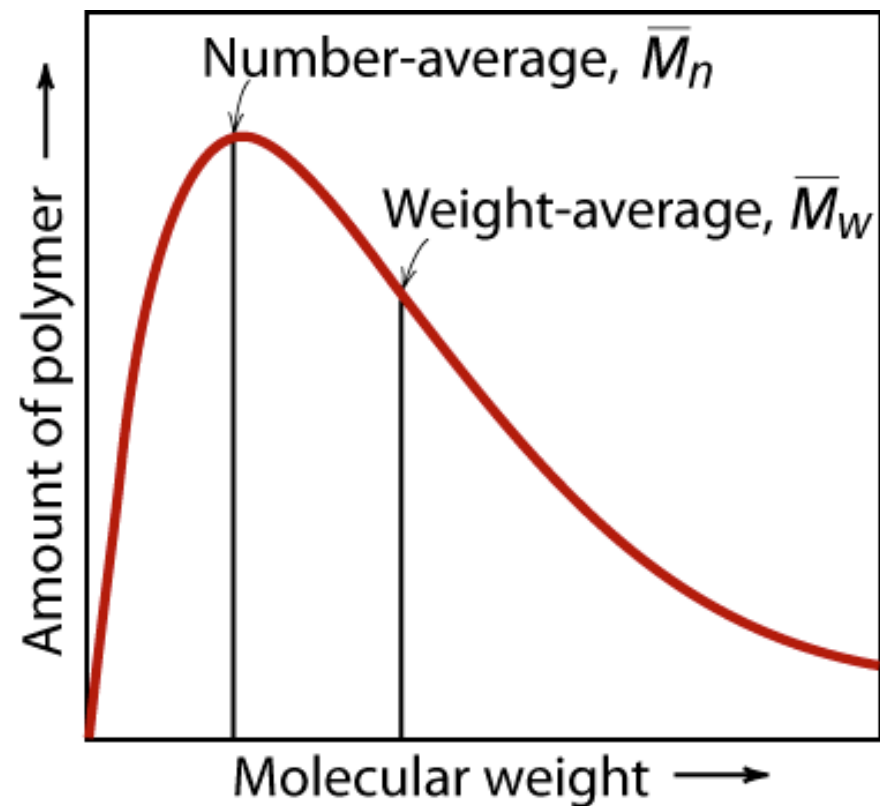


$$\bar{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

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

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

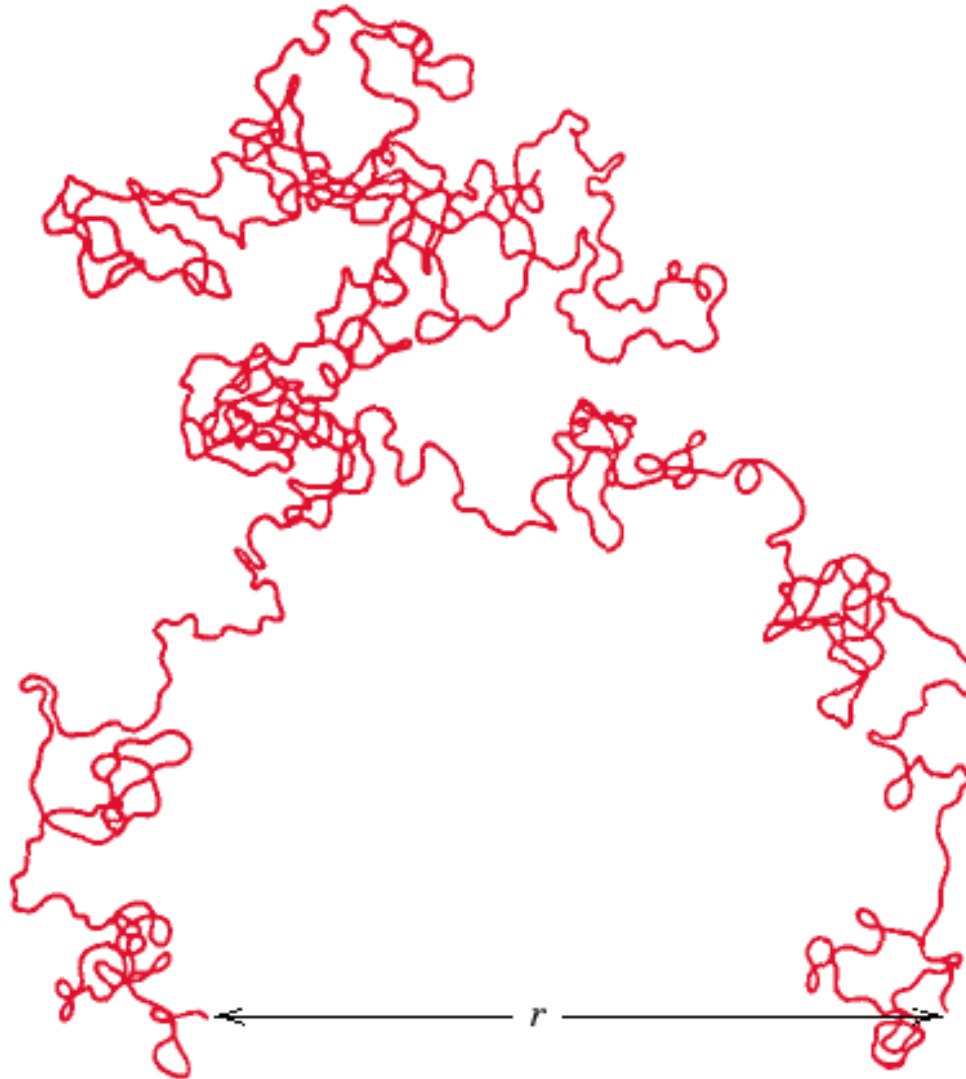
$\bar{M}_w$ is more sensitive to higher molecular weights



Adapted from Fig. 14.4, Callister 7e.



End to End Distance, r

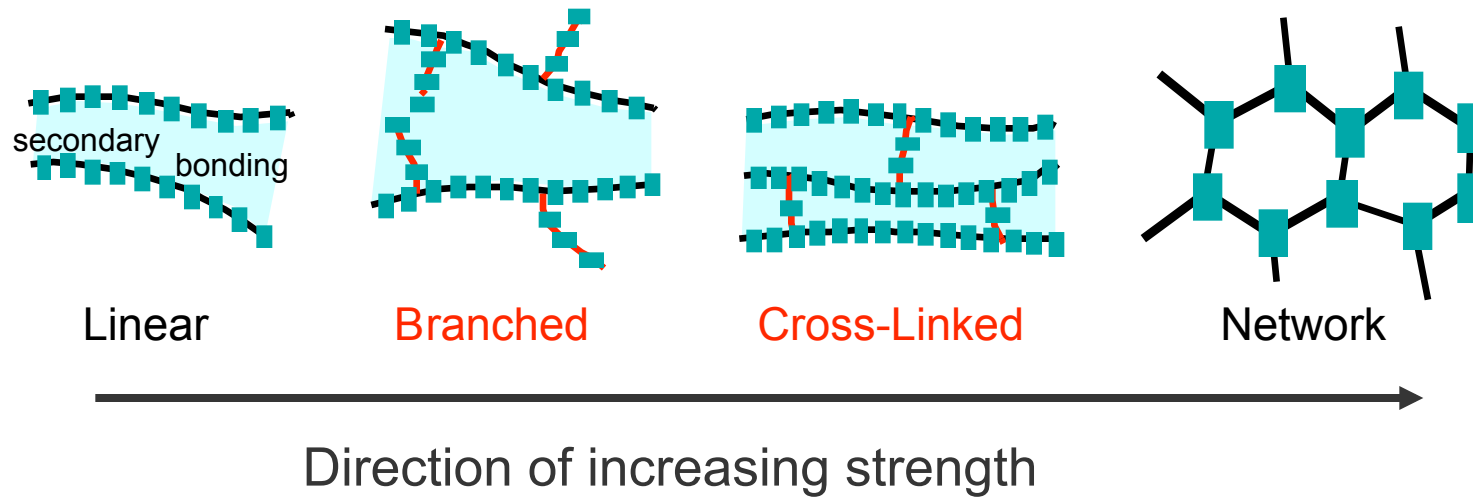


Adapted from Fig.
14.6, *Callister 7e*.



Molecular Structures

- Covalent **chain** configurations and strength:

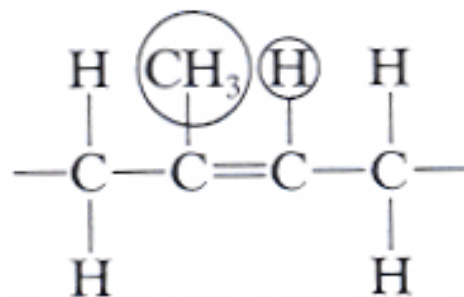


Adapted from Fig. 14.7, *Callister 7e*.

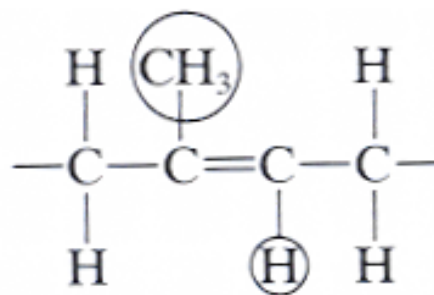
Molecular configuration

- **Geometrical isomerism**

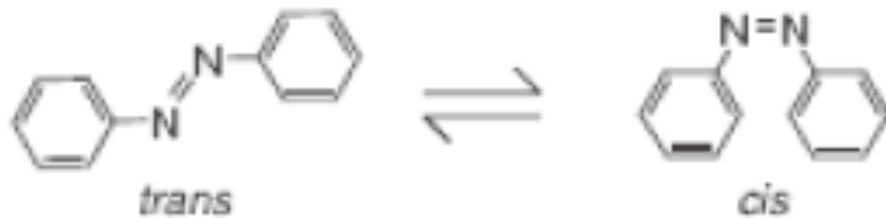
Cis



Trans

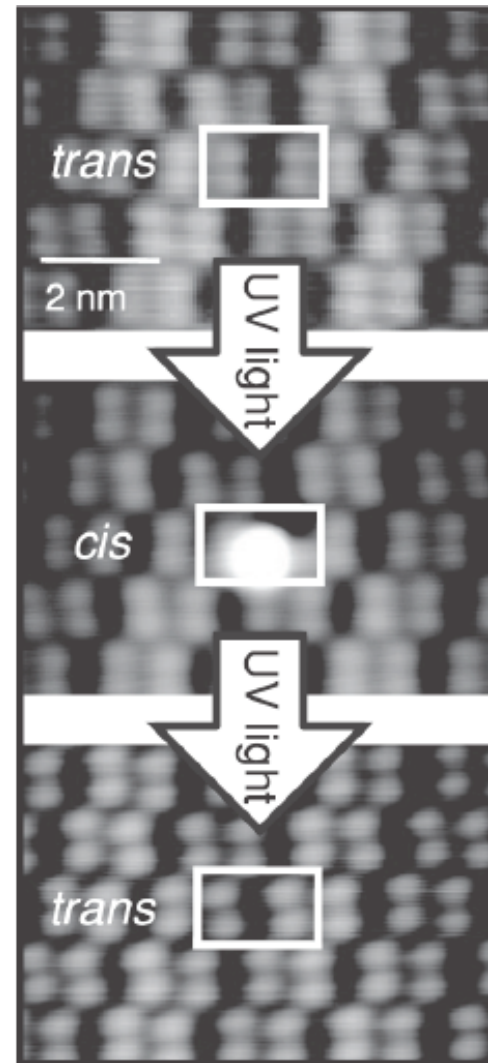


Cis-Trans Molecular Machines



azobenzene

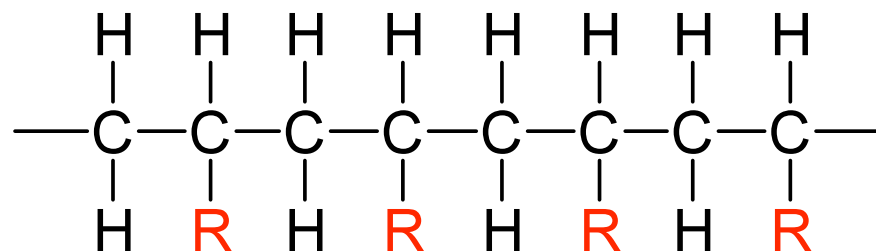
<http://www.physics.berkeley.edu/research/crommie>



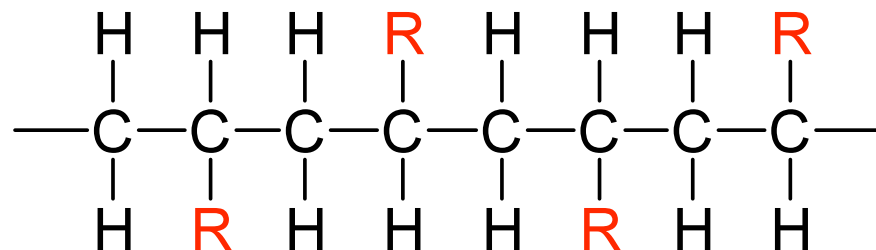
Tacticity

Tacticity – stereoregularity of chain

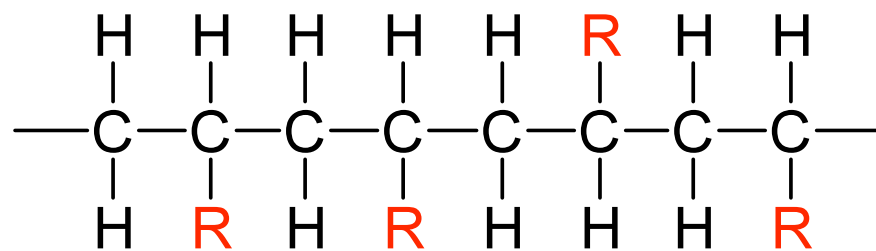
isotactic – all **R** groups on same side of chain



syndiotactic – **R** groups alternate sides



atactic – **R** groups random



Copolymers

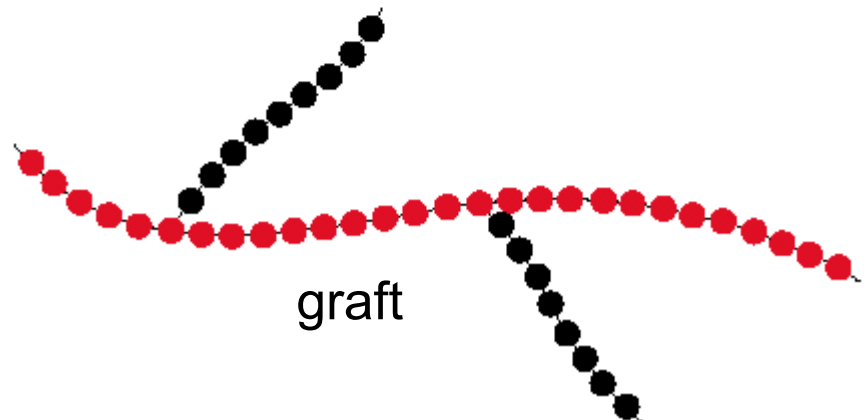
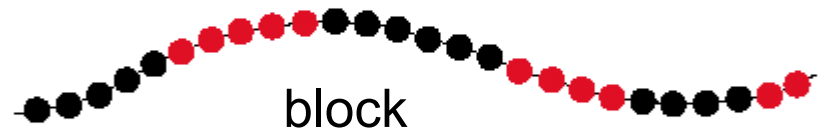
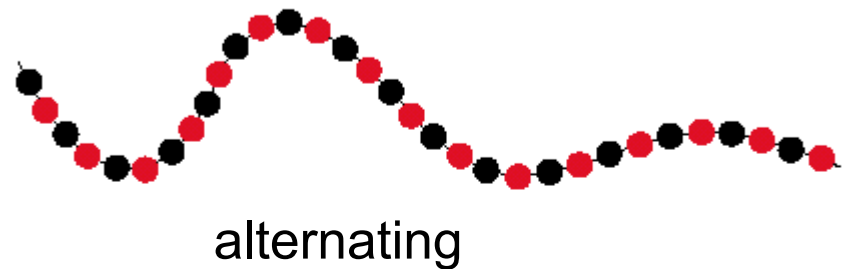
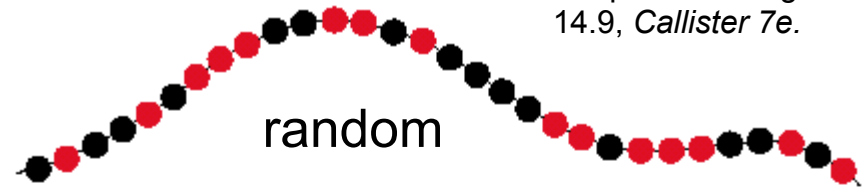
two or more monomers
polymerized together

- **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

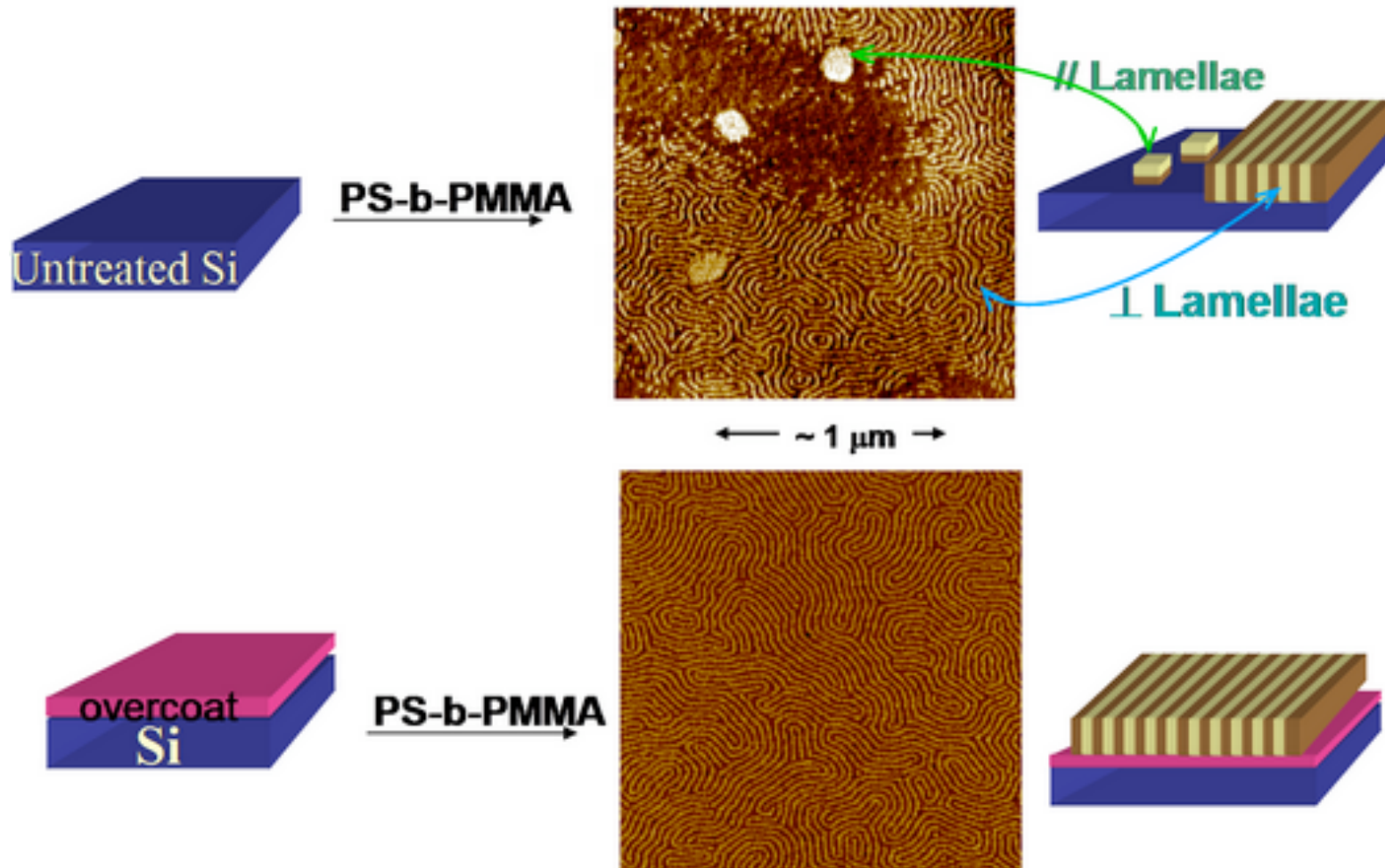
A – ●

B – ●

Adapted from Fig.
14.9, Callister 7e.

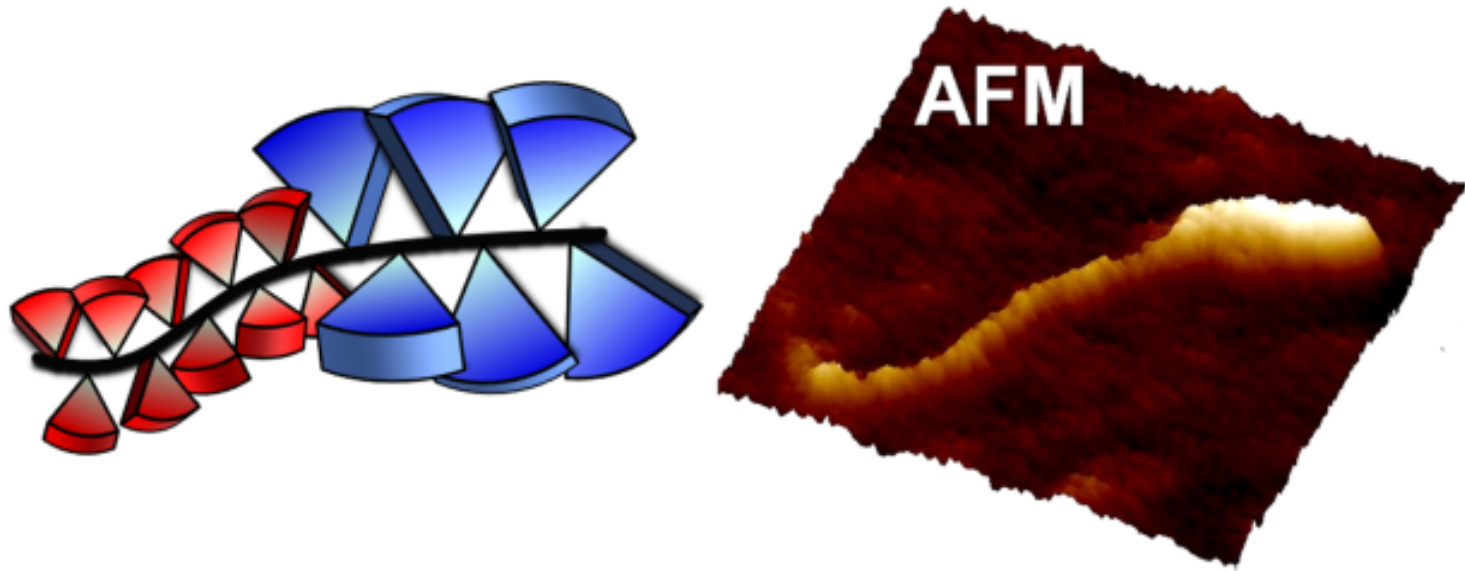


Block Copolymers



From almaden.ibm.com

Block Copolymers



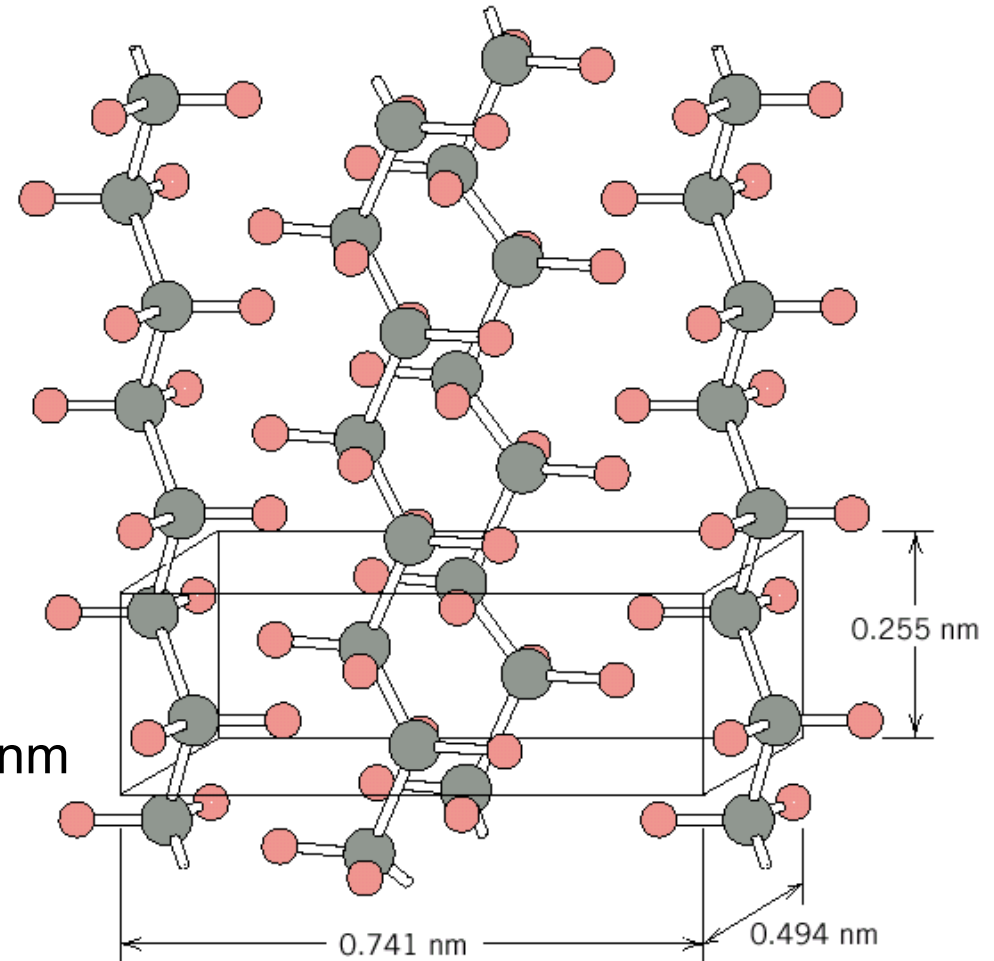
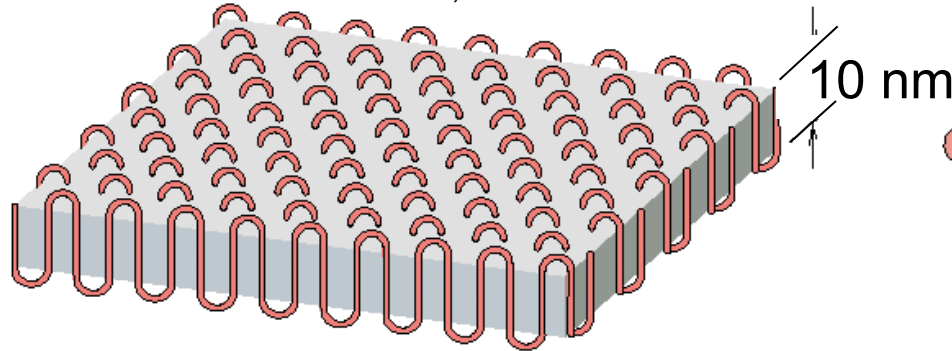
Polymer Crystallinity

Adapted from Fig.
14.10, Callister 7e.

Ex: polyethylene unit cell

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

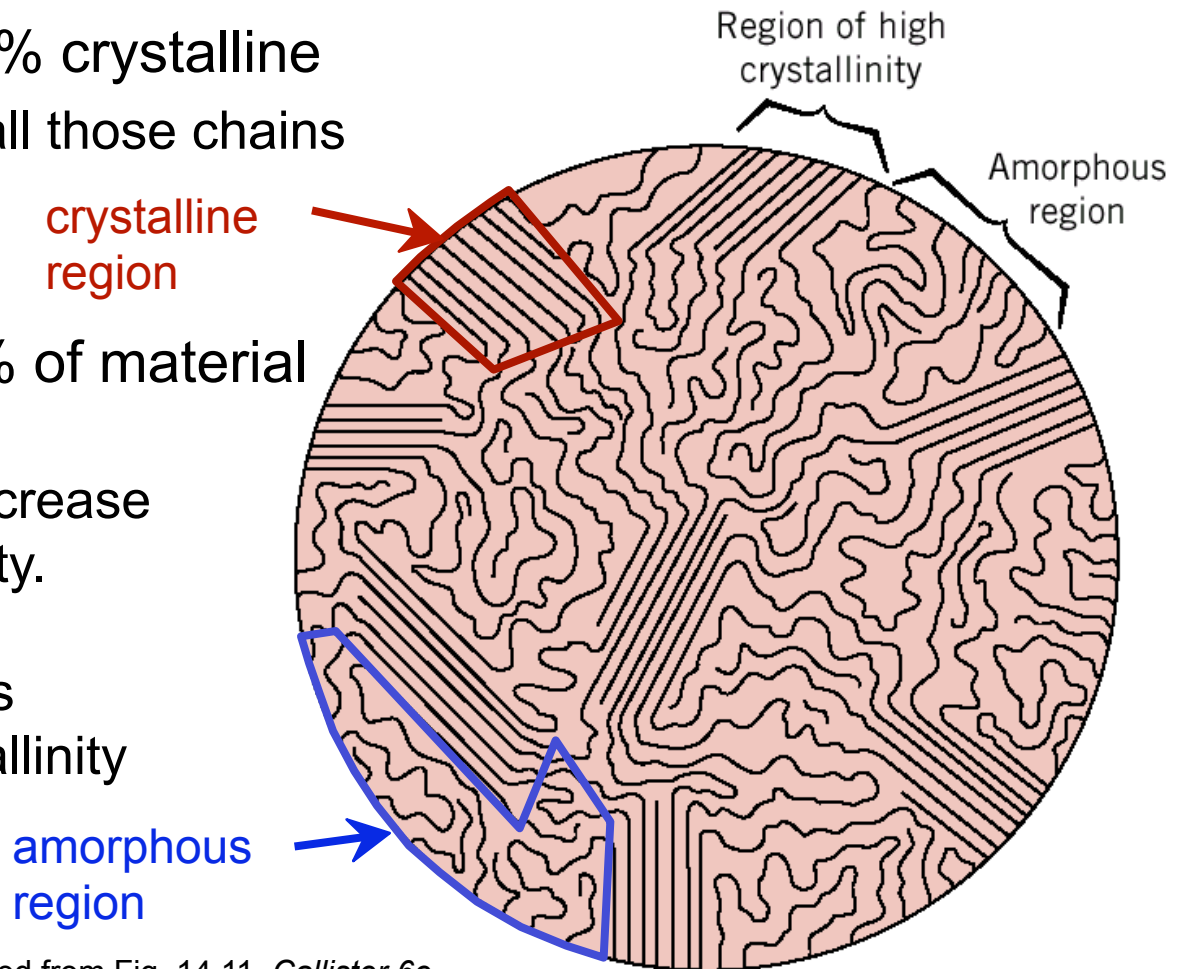
Adapted from Fig.
14.12, Callister 7e.



Polymer Crystallinity

Polymers rarely 100% crystalline

- Too difficult to get all those chains aligned
- **% Crystallinity**: % of material that is crystalline.
 - T_S and E often increase with % crystallinity.
 - Annealing causes crystalline regions to grow. % crystallinity increases.

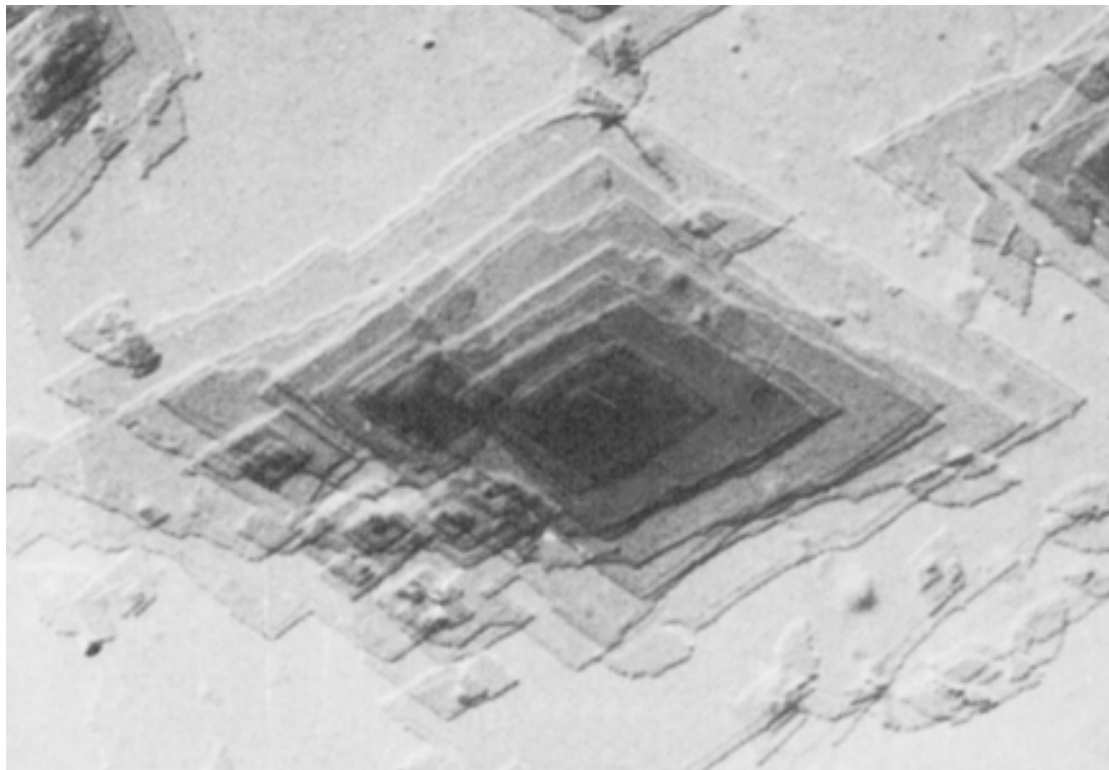


Adapted from Fig. 14.11, *Callister 6e*.
(Fig. 14.11 is from H.W. Hayden, W.G. Moffatt,
and J. Wulff, *The Structure and Properties of
Materials*, Vol. III, *Mechanical Behavior*, John Wiley
and Sons, Inc., 1965.)



Polymer Crystal Forms

- Single crystals – only if slow careful growth



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