CHAPTER 14: POLYMER STRUCTURES

- **Read Only:** 14.8 and 14.13-.14.14

Study Everything else.

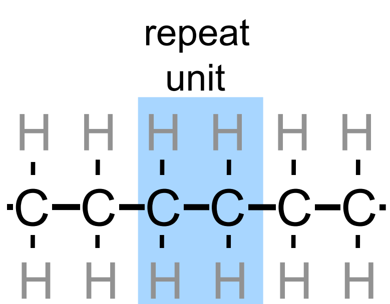
- What are the basic microstructural features?
- How are polymer properties effected by molecular weight?
- How do polymeric crystals accommodate the polymer chain?

Chapter 14 – Polymers

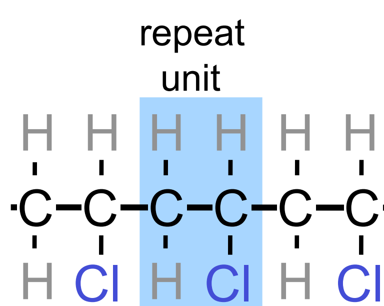
What is a polymer?

Poly **mer**

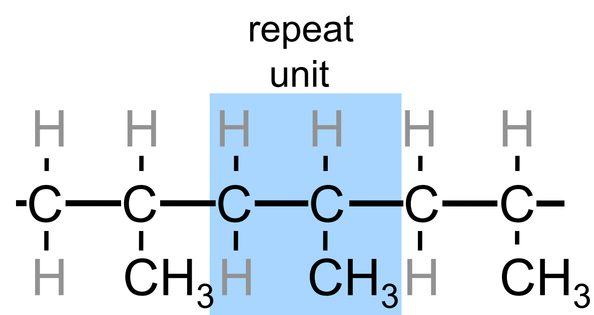
many repeat unit



Polyethylene (PE)



Polyvinyl chloride (PVC)



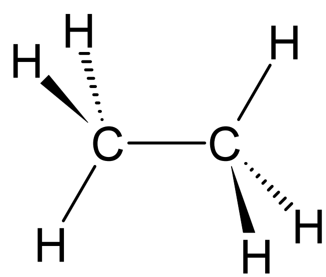
Polypropylene (PP)

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

Polymer Composition

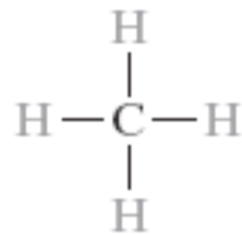
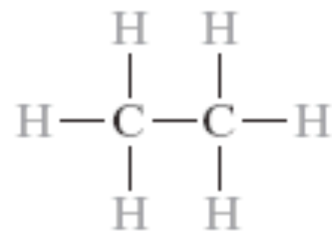
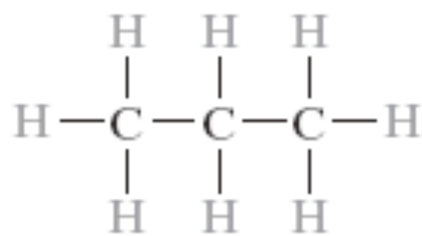
Most polymers are hydrocarbons
– i.e. made up of H and C

- Saturated hydrocarbons
  – Each carbon bonded to four other atoms

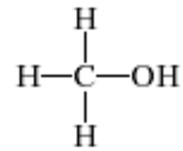
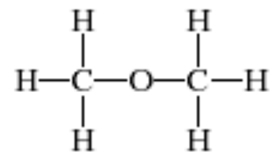
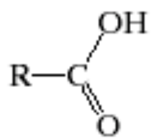
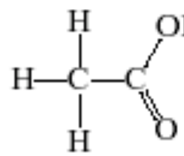
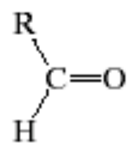
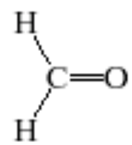
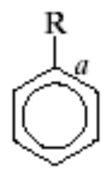
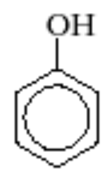


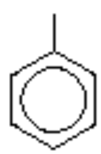
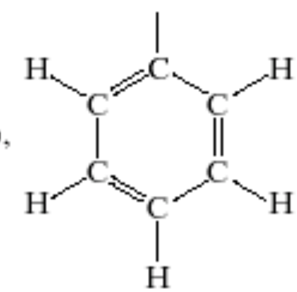
C_nH_{2n+2}

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

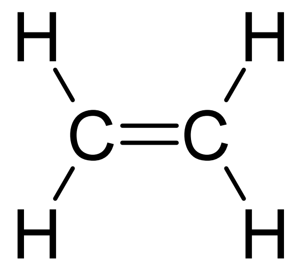
Some common hydrocarbon groups

Family	*Characteristic Unit*	*Representative Compound*	
Alcohols	R—OH		Methyl alcohol
Ethers	R—O—R′		Dimethyl ether
Acids			Acetic acid
Aldehydes			Formaldehyde
Aromatic hydrocarbons			Phenol

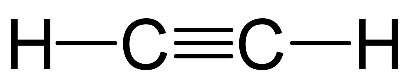
[a] The simplified structure  denotes a phenyl group, 

Unsaturated Hydrocarbons

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

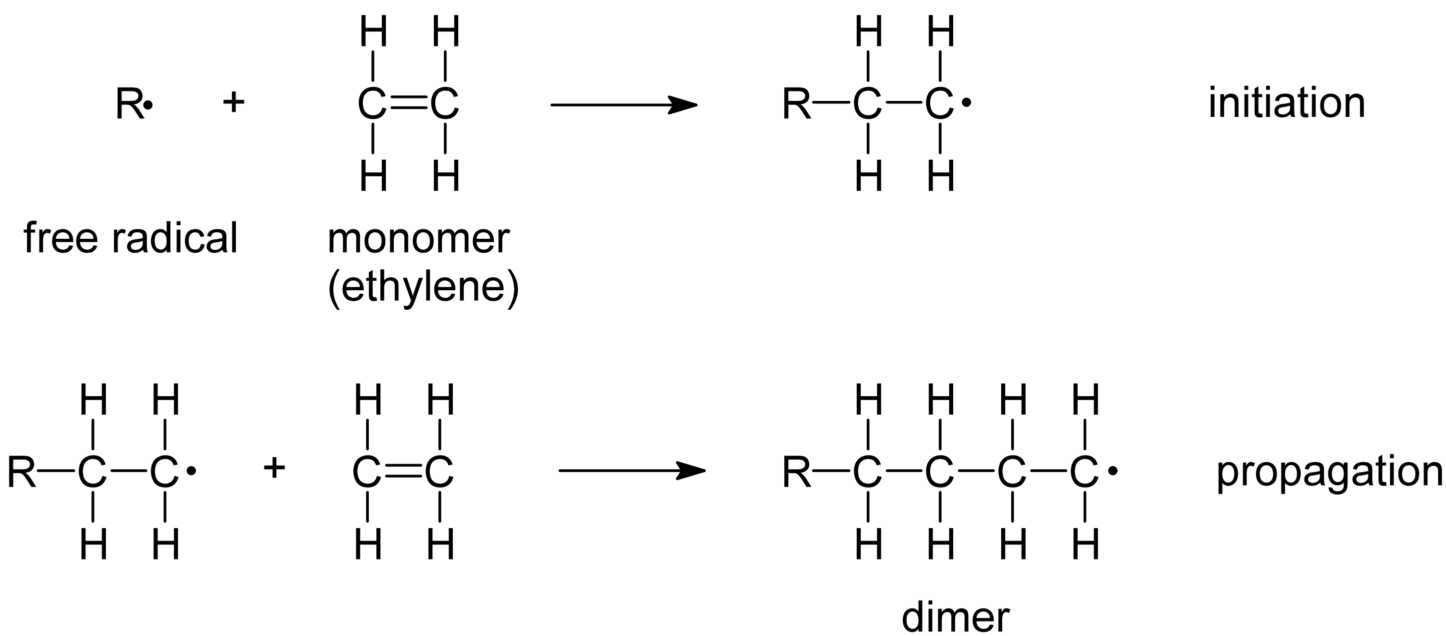


    - 4-bonds, but only 3 atoms bound to C's
  - Triple bond – acetylene or ethyne - C_nH_{2n-2}

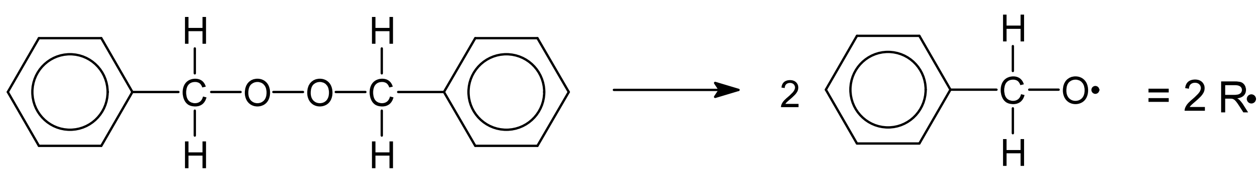


Chemistry of Polymers

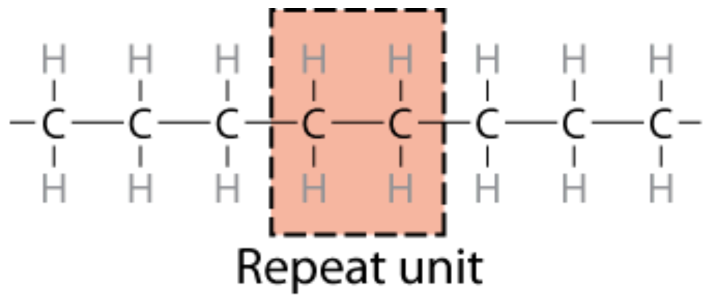
- Free radical polymerization



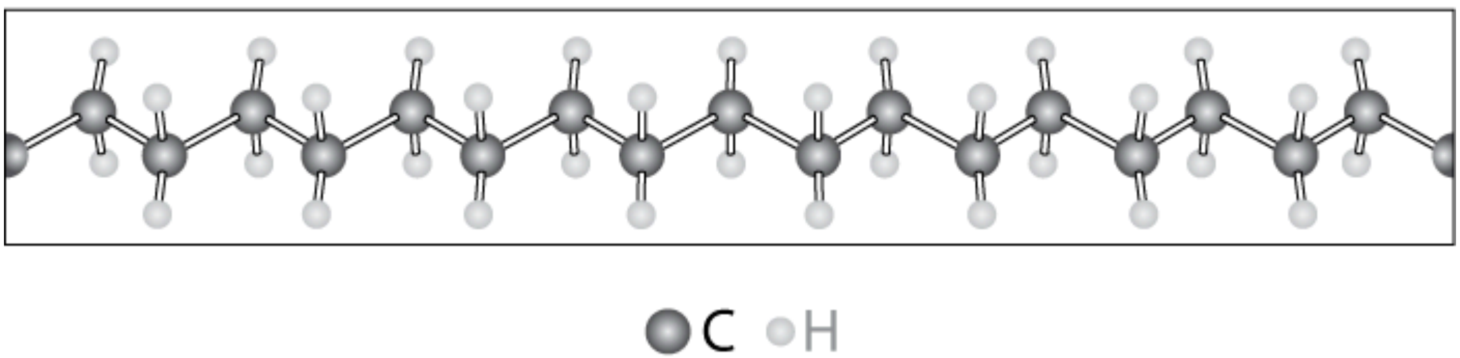
- Initiator: example - benzoyl peroxide



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

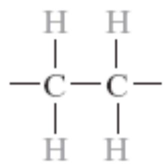
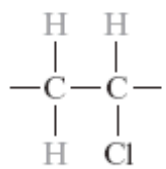
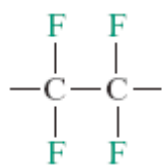
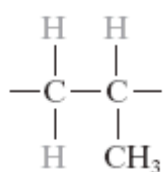
Polymer	*Repeat Unit*
Polyethylene (PE)	
Poly(vinyl chloride) (PVC)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	

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

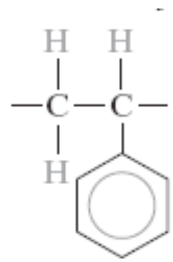
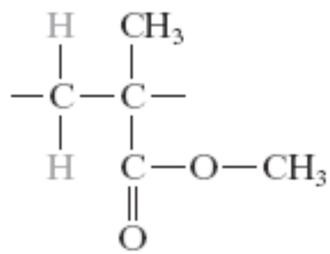
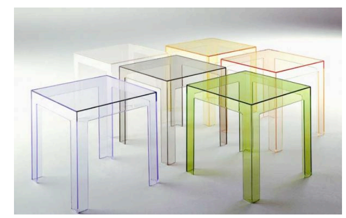
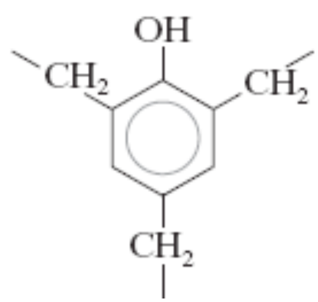
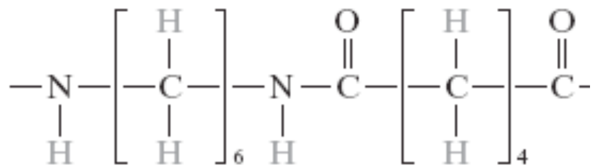
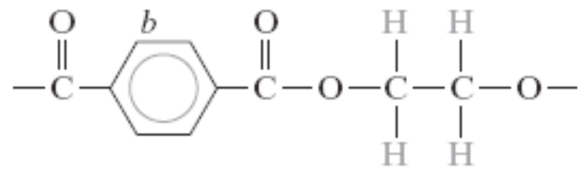
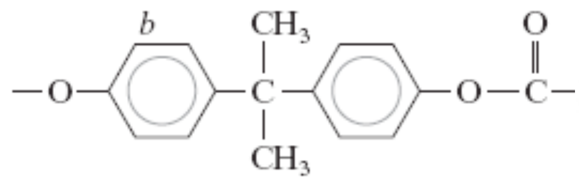
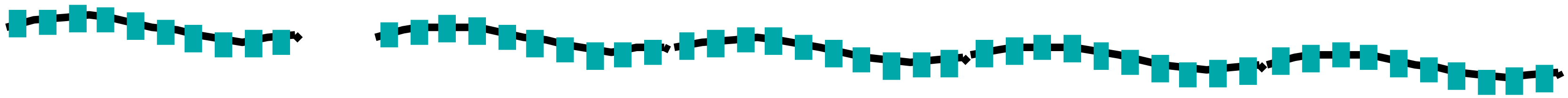
Polymer	*Repeat Unit*	
Polystyrene (PS)		
Poly(methyl methacrylate) (PMMA)		
Phenol-formaldehyde (Bakelite)		

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

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



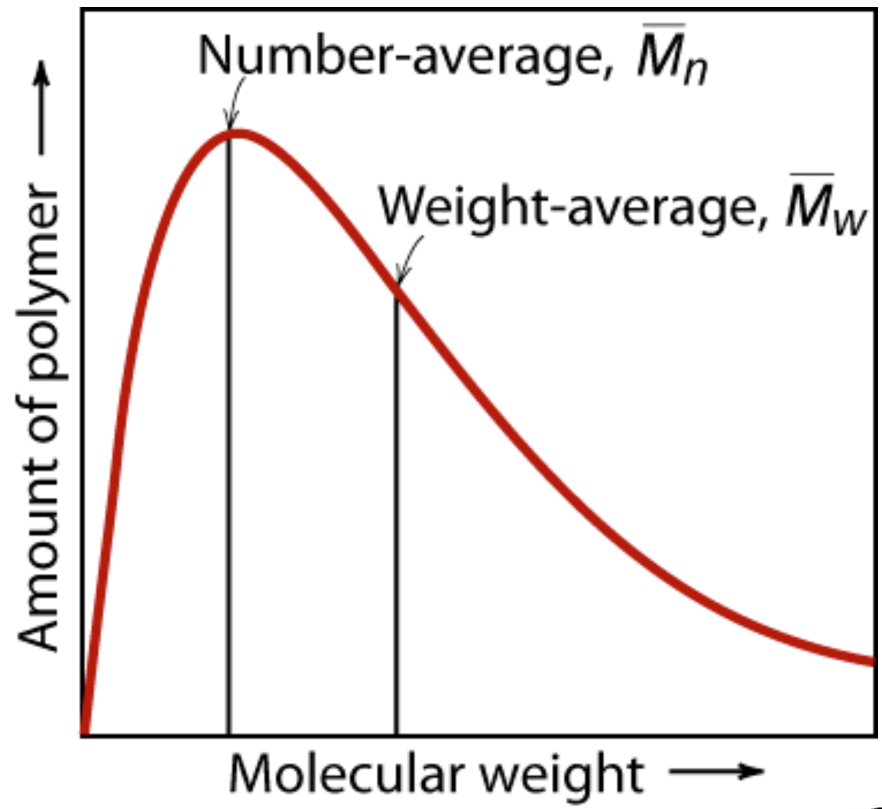
Lower M higher M

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

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

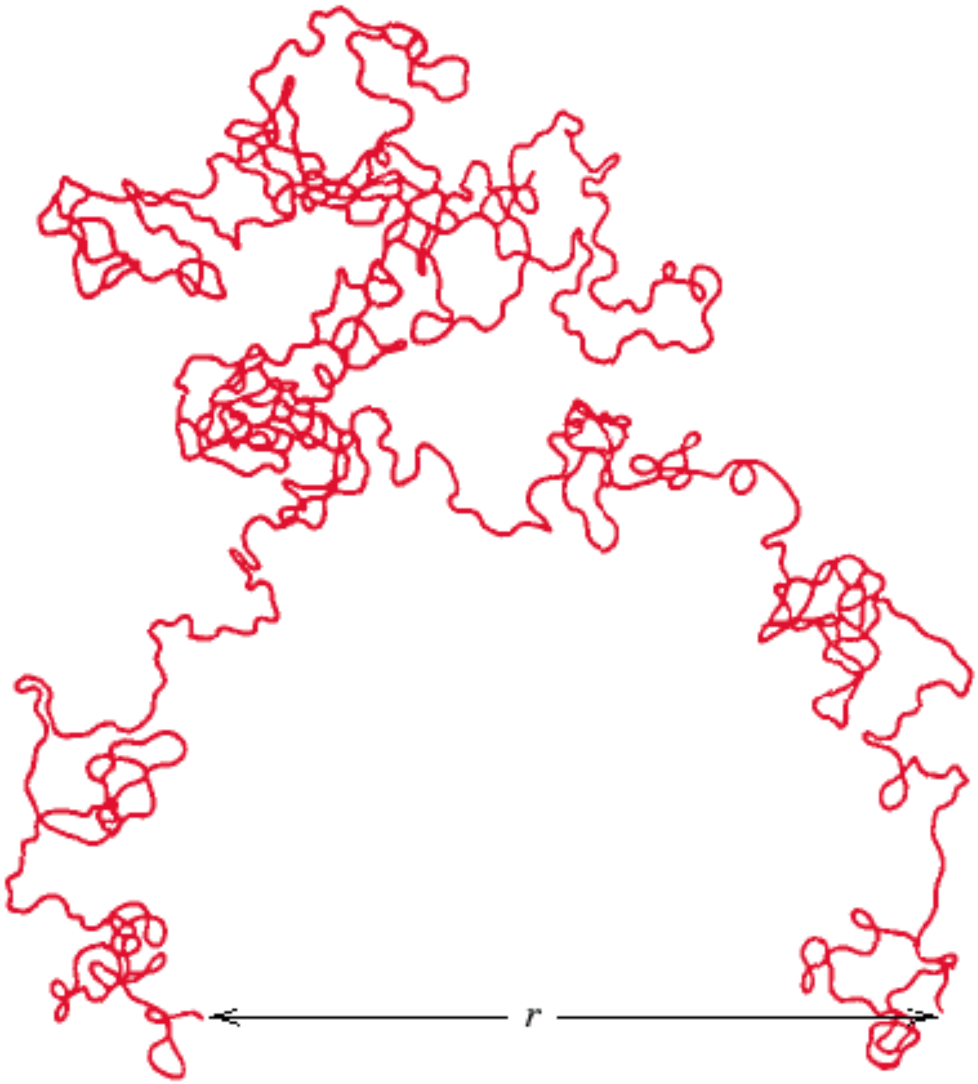
$$\overline{M}_w = \Sigma w_i M_i$$

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



Adapted from Fig. 14.4, *Callister 7e.*

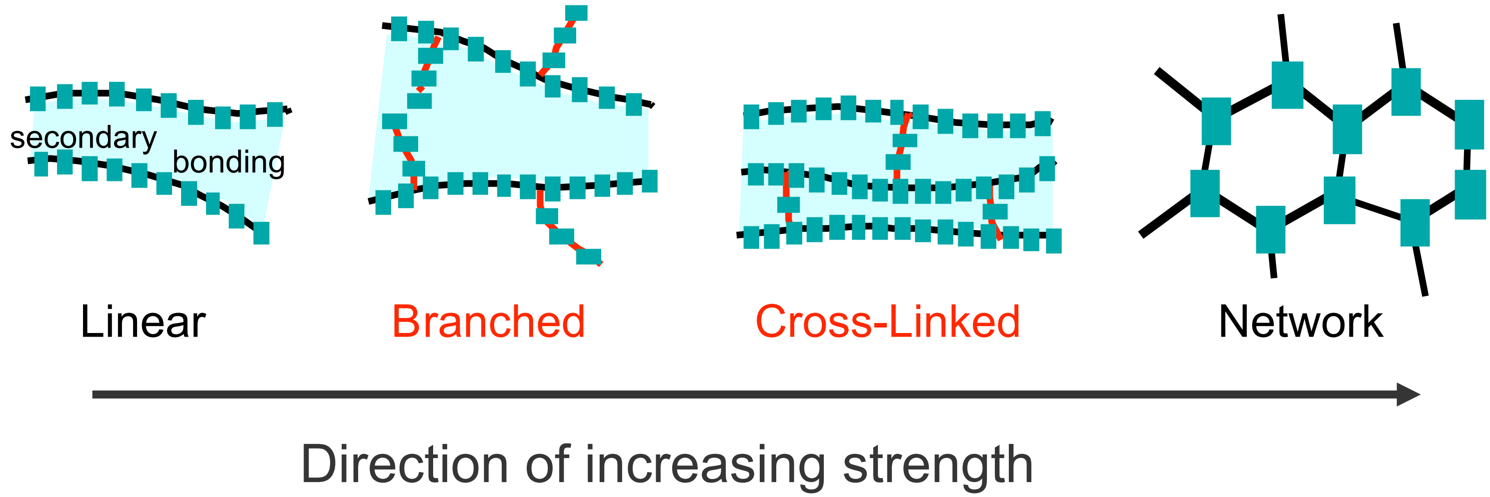
End to End Distance, *r*



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

Molecular Structures

- Covalent chain configurations and strength:

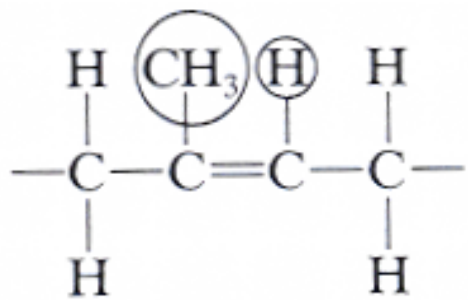


Adapted from Fig. 14.7, *Callister 7e.*

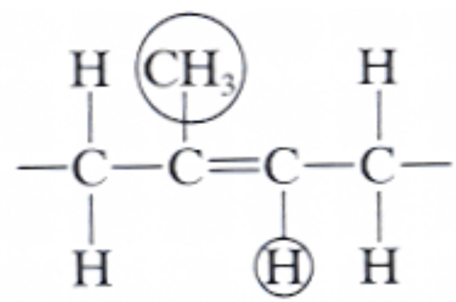
Molecular configuration

- **Geometrical isomerism**

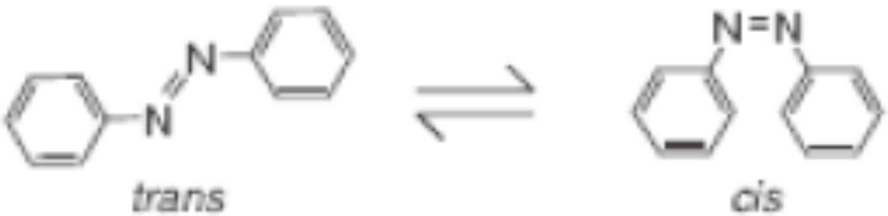
Cis

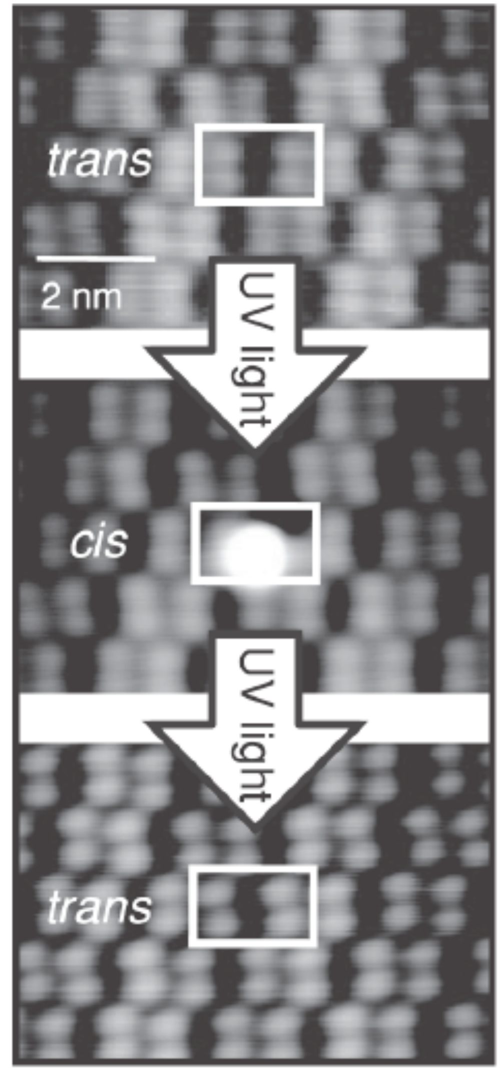


Trans



Cis-Trans Molecular Machines





azobenezene

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

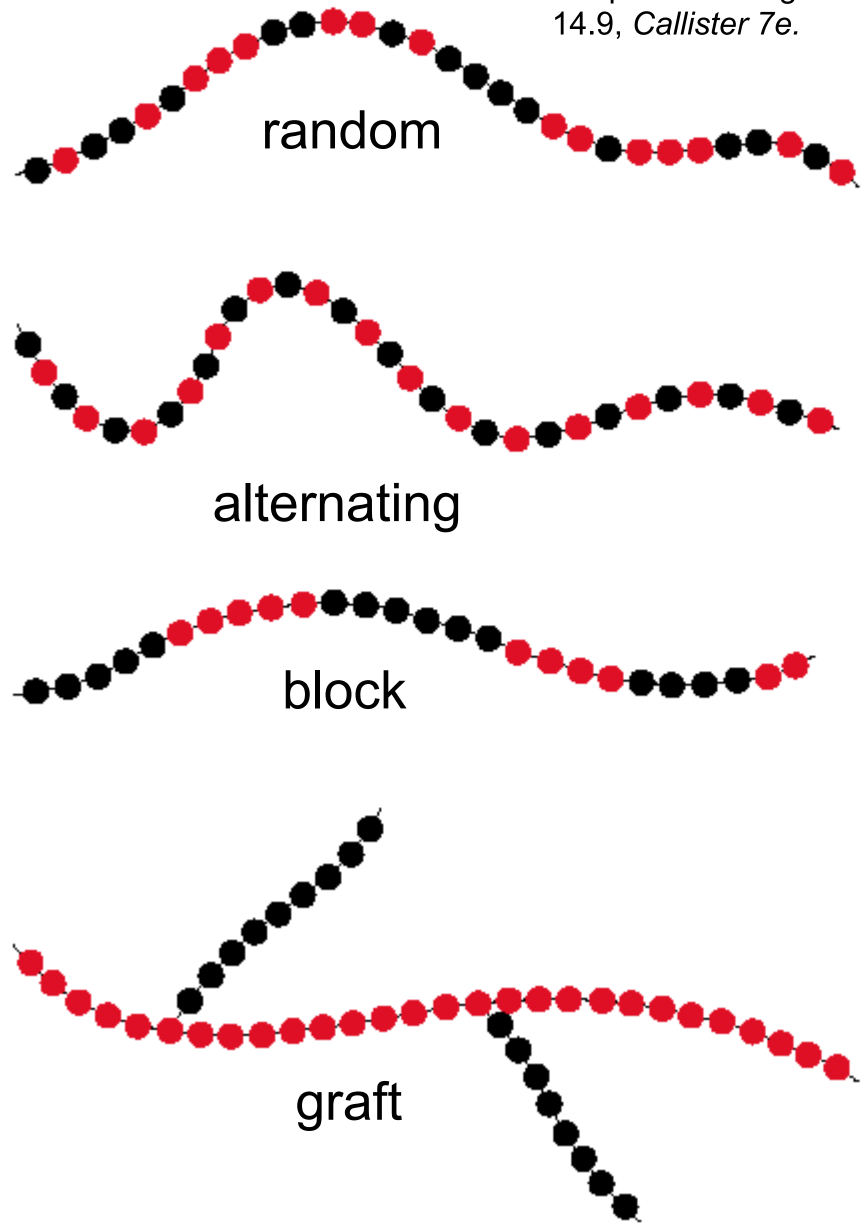
Copolymers

two or more monomers polymerized together

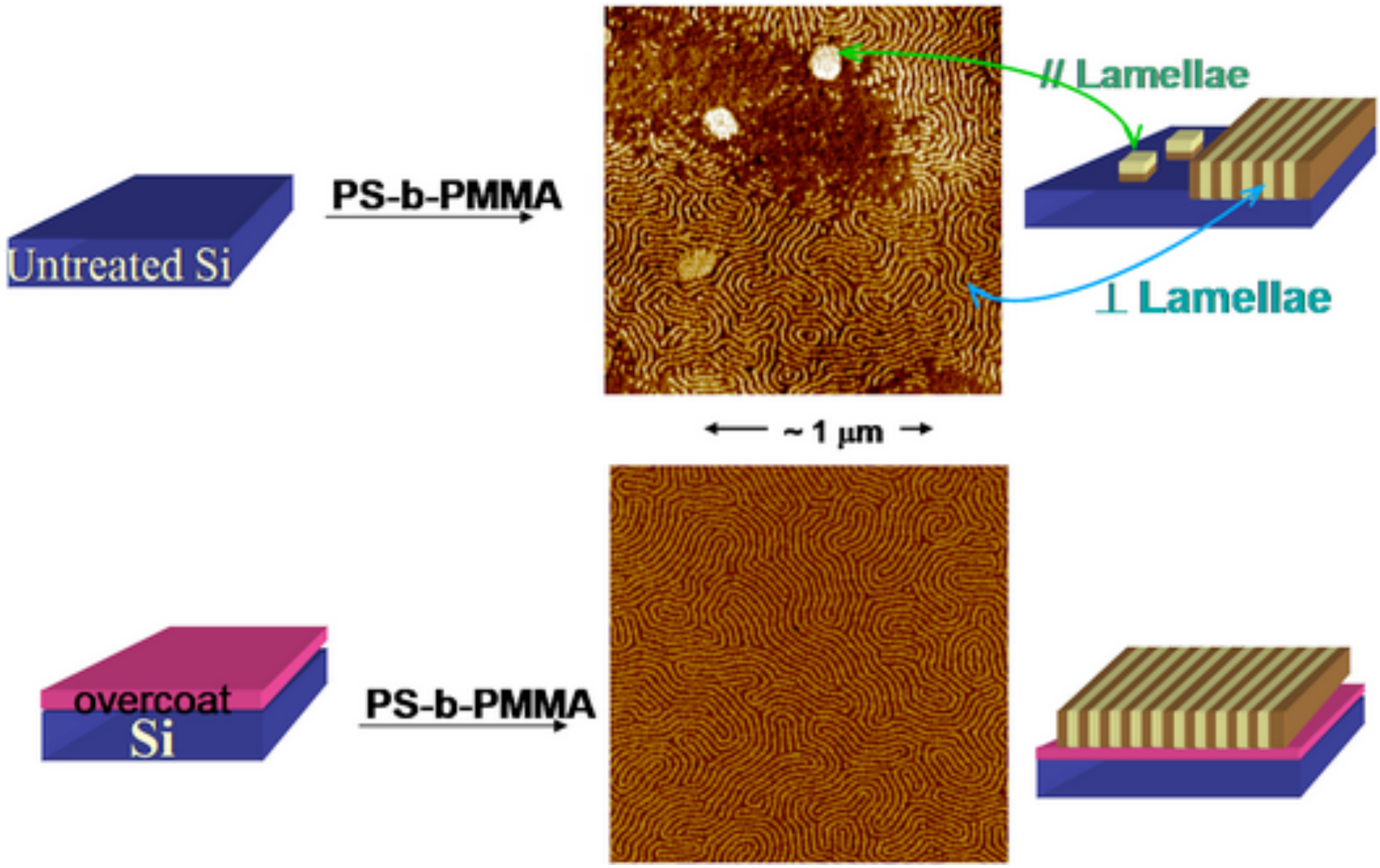
- random – A and B randomly vary in chain
- alternating – A and B alternate in polymer chain
- block – large blocks of A alternate with large blocks of B
- graft – chains of B grafted on to A backbone

A –   B –

Adapted from Fig. 14.9, *Callister 7e.*

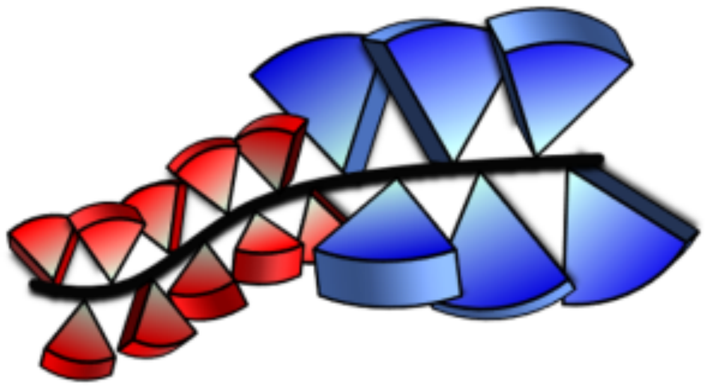


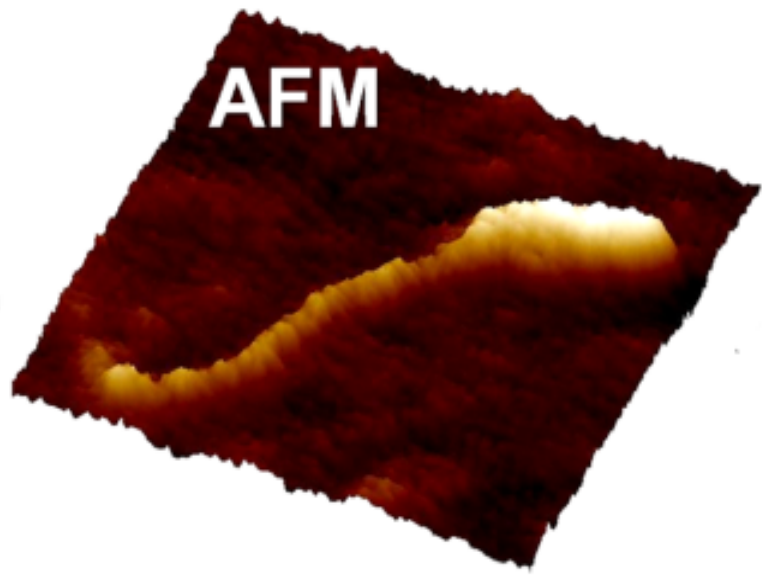
Block Copolymers



From almaden.ibm.com

Block Copolymers

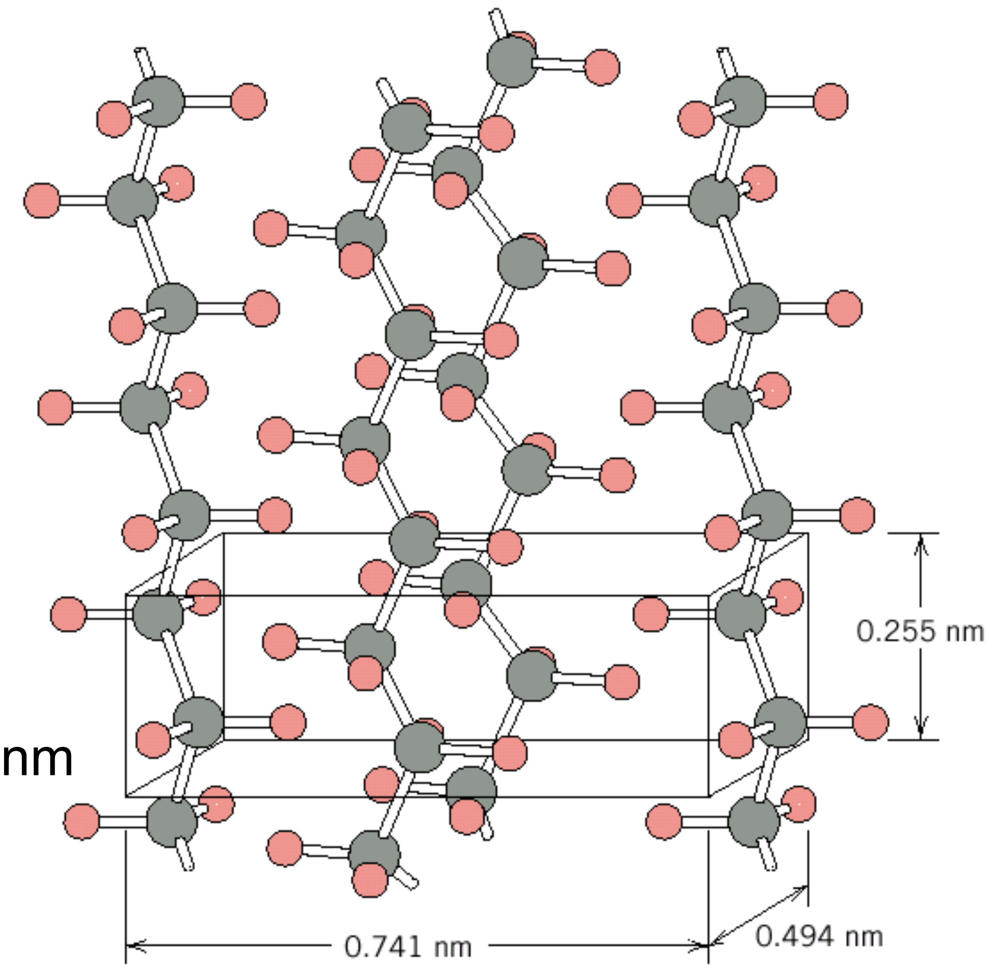




Polymer Crystallinity

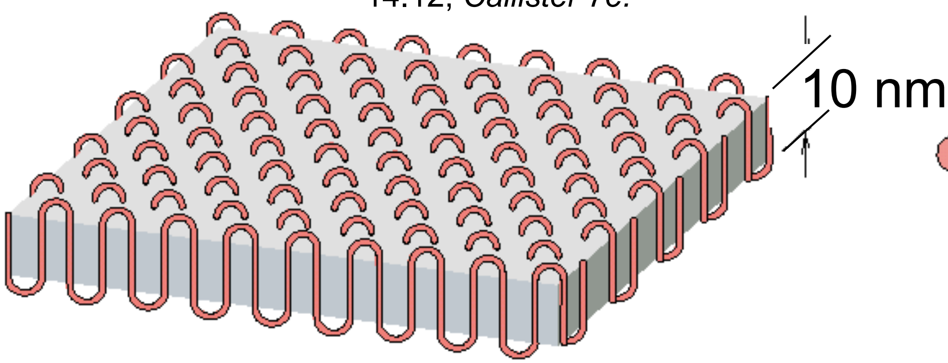
Adapted from Fig. 14.10, *Callister 7e.*

Ex: polyethylene unit cell



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

Adapted from Fig. 14.12, *Callister 7e.*

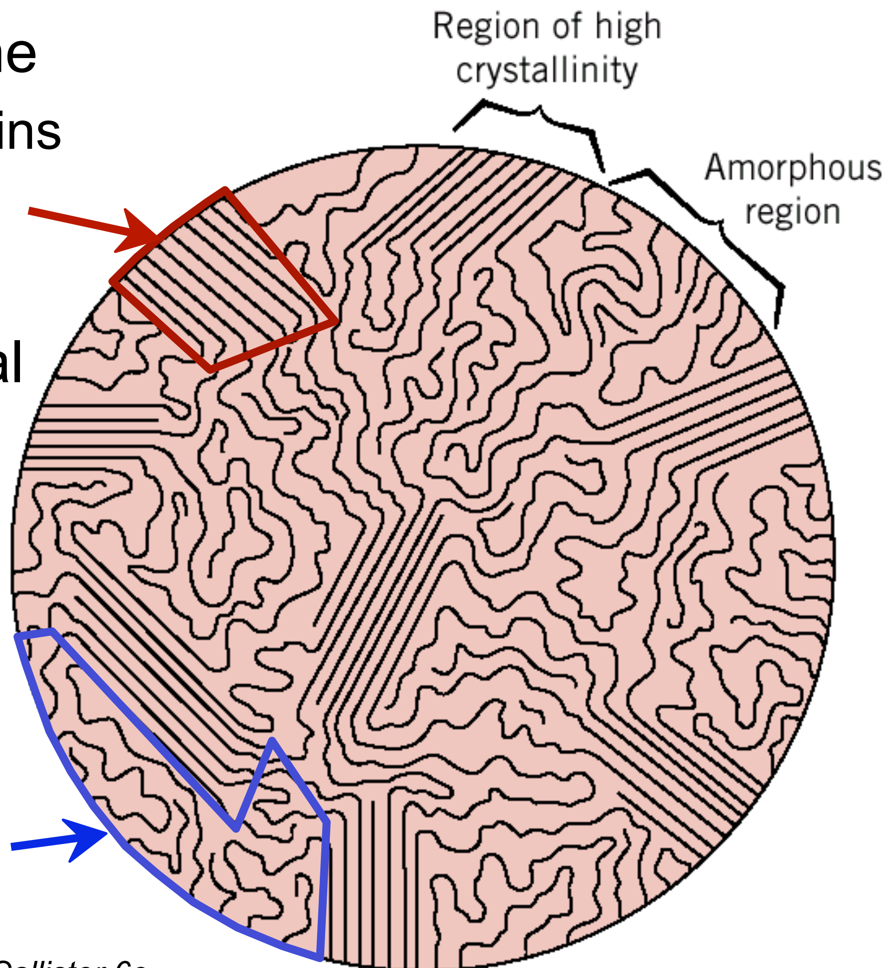


Polymer Crystallinity

Polymers rarely 100% crystalline

- Too difficult to get all those chains aligned

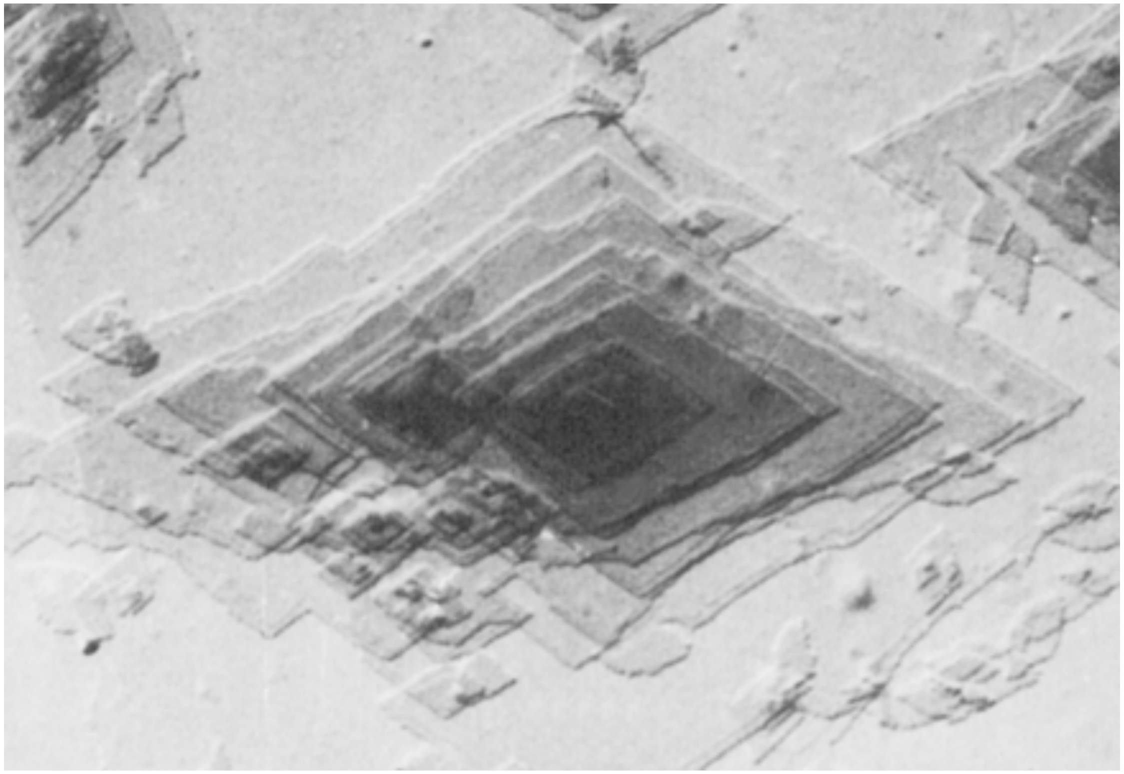
- % Crystallinity: % of material that is crystalline.
  - -- *TS* and *E* often increase with % crystallinity.
  - -- Annealing causes crystalline regions to grow. % crystallinity increases.



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.*