



ÇANKAYA UNIVERSITY

POLYMERS-Part 1

Structure and Properties

MSE 206-Materials Characterization I
Lecture-11

Natural and Synthetic Polymers

Natural Polymers

- Derived from plants and animals
- Rubber, cotton, wool, leather, silk



Synthetic Polymers

- Synthesized from small organic molecules
- PP, PS, PVC, PE



What is Polymer ?

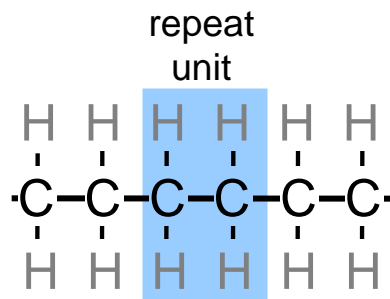
Poly

mer

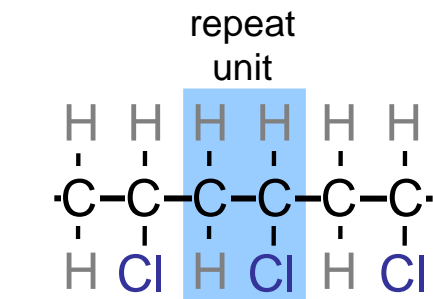
many

repeat unit

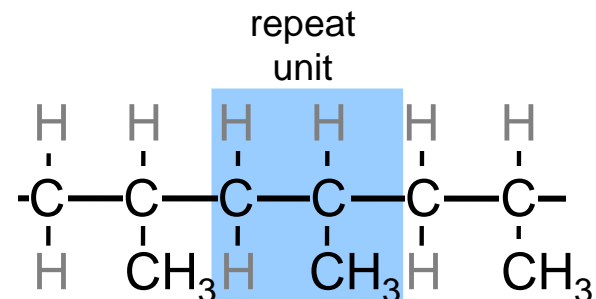
- Compounds of usually high molecular weight consisting of up to millions of repeated linked units



Polyethylene (PE)



Polyvinyl chloride (PVC)



Polypropylene (PP)

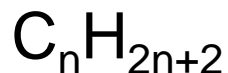
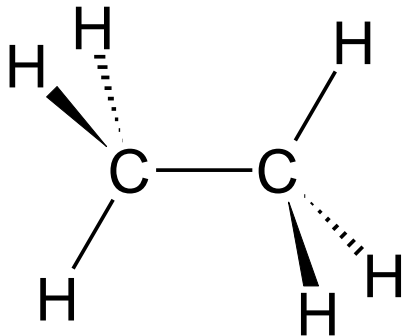
Adapted from Fig. 14.2, Callister 7e.

Polymer Composition

- Most polymers are hydrocarbons (derived from hydrocarbons)
 - i.e. made up of H and C

Saturated hydrocarbons

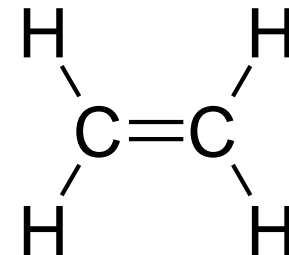
- Each carbon bonded to four other atoms



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

Polymer Composition

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

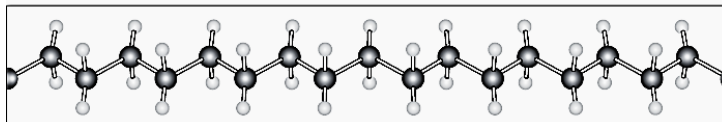
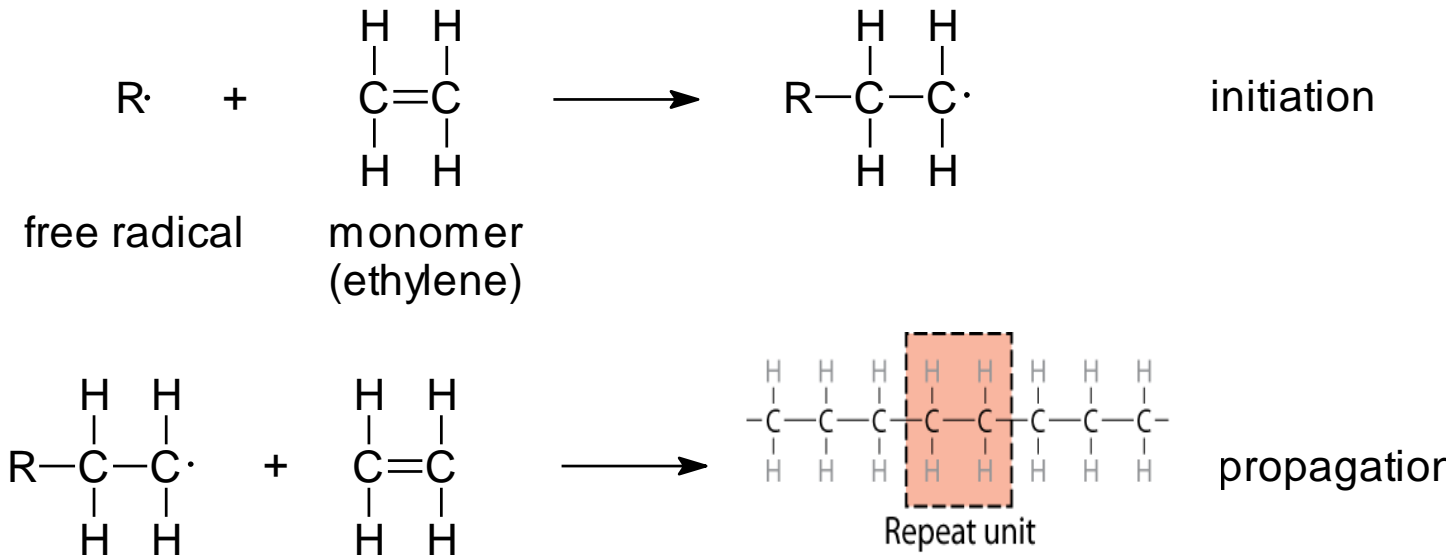
<i>Name</i>	<i>Composition</i>	<i>Structure</i>	<i>Boiling Point (°C)</i>
Methane	CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	-164
Ethane	C ₂ H ₆	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	-88.6
Propane	C ₃ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	-42.1
Butane	C ₄ H ₁₀		-0.5
Pentane	C ₅ H ₁₂		36.1
Hexane	C ₆ H ₁₄		69.0

Chemistry of Polymers

Derivation of polyethylene (-CH₂-CH₂-)_n from ethylene (an unsaturated hydrocarbon)

- When ethylene gas is reacted under appropriate conditions (initiator or catalyst, R, is added) it will transform to polyethylene




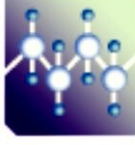
Free radical polymerization



● C ○ H

Bulk or Commodity of 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)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$

Bulk or Commodity of Polymers

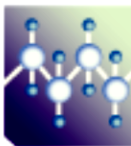
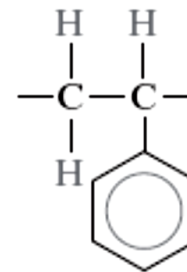
Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer

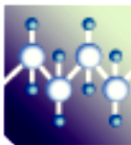
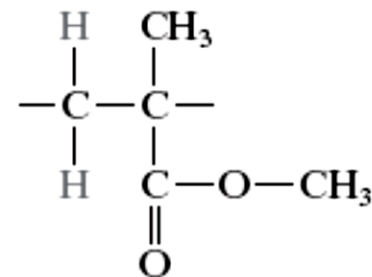
Repeat Unit



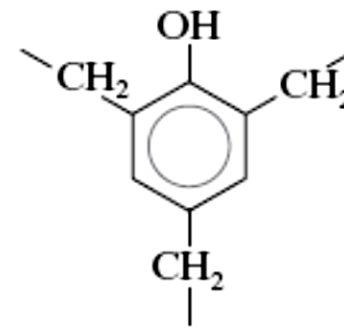
Polystyrene (PS)



Poly(methyl methacrylate) (PMMA)






Phenol-formaldehyde (Bakelite)



Bulk or Commodity of Polymers

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

<i>Polymer</i>	<i>Repeat Unit</i>
 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)	$\overset{\text{O}}{\parallel}\text{C---}\overset{b}{\text{C}_6\text{H}_4}\text{---}\overset{\text{O}}{\parallel}\text{C---O---}\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{H} \end{array}\text{---O---}$
 Polycarbonate (PC)	$\text{---O---}\overset{b}{\text{C}_6\text{H}_4}\text{---}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{---}\text{C}_6\text{H}_4\text{---O---}\overset{\text{O}}{\parallel}\text{C---}$

NOTE: See Table 15.3 for commercially important polymers – including trade names

Molecular Weight of Polymers

- During polymerization not all polymer chains will grow to the same length (results in distribution of chain lengths or molecular weights)

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

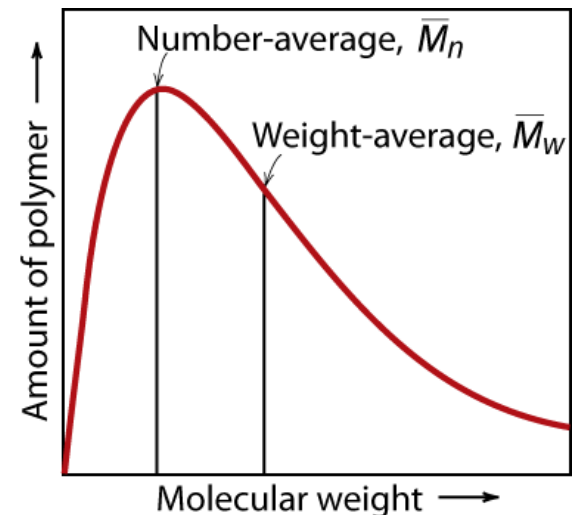


Defining Molecular Weight:

$$\bar{M}_n = \sum x_i M_i \quad \text{The number-average MW}$$
$$\bar{M}_w = \sum w_i M_i \quad \text{The weight-average MW}$$

x_i : fraction of total number of chains corresponding size range
 w_i : weight fraction of molecules within the same size interval

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



Adapted from Fig. 14.4, Callister 7e.

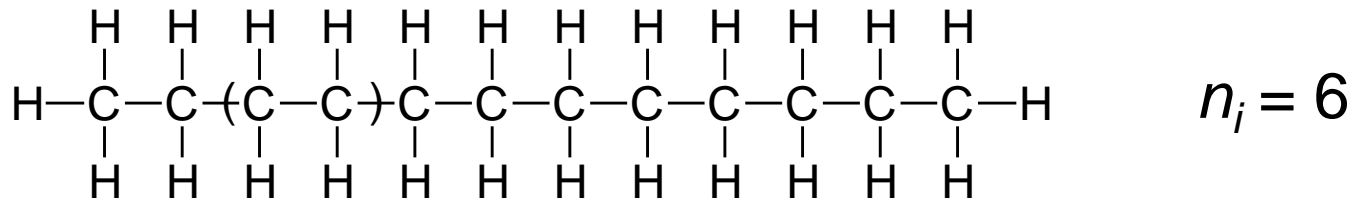
Property vs. Molecular Weight

- ❑ Depending on the molecular weight polymers can have quite different properties
- ❑ Melting and softening temperature increases with increasing molecular weight (MW) (up to 100,000 g/mol)
- ❑ Polymers at room temperature are
 - liquid and gases if MW is around 100 g/mol (short chains)
 - waxy solid (paraffin wax) if molecular weight is around 1000 g/mol
 - solid polymer if molecular weight is around 10,000-several million g/mol

Degree of Polymerization

- An alternative way of expressing average chain size of a polymer

n = number of repeat units per chain



$$n_n = \sum x_i n_i = \frac{\overline{M}_n}{m} \qquad n_w = \sum w_i n_i = \frac{\overline{M}_w}{m}$$

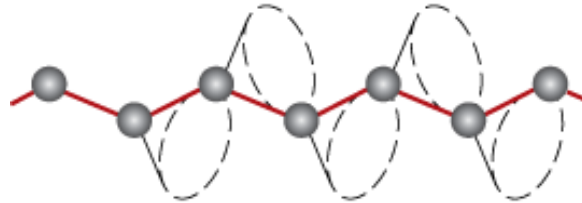
where \overline{m} = average molecularweight of repeat unit

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

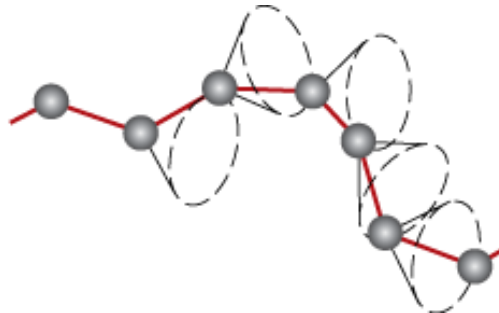
Chain fraction f_i mol. wt of repeat unit m_i

Molecular Shape

- Single chain bonds are capable of rotating and bending in three dimensions (the angle between carbon atoms is 109.5°)



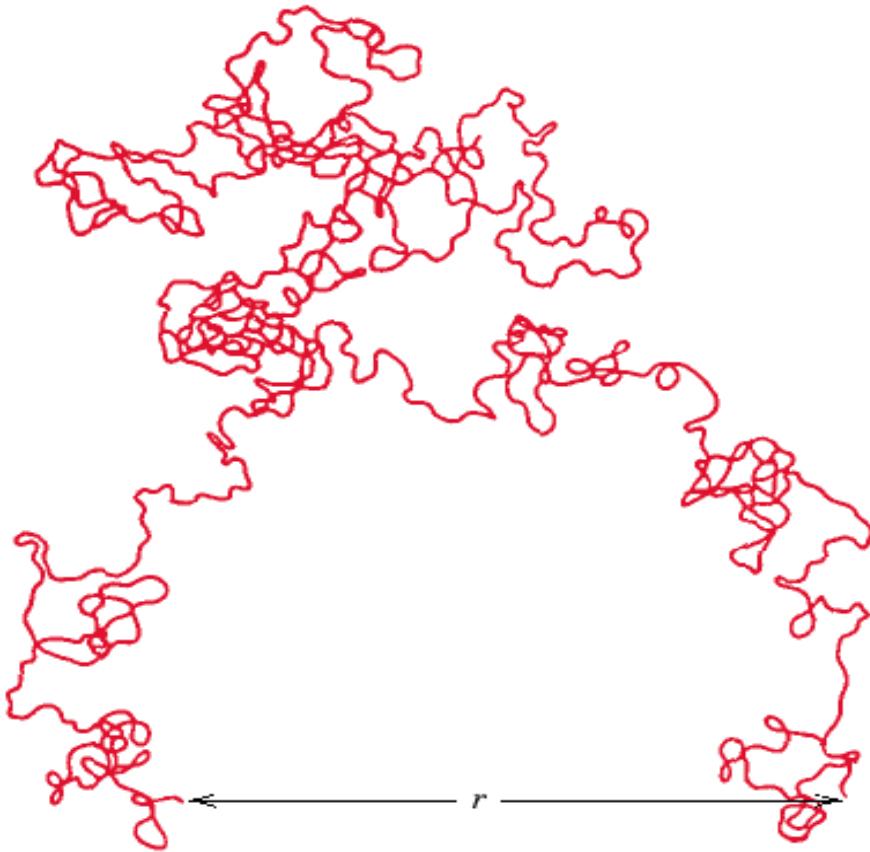
- Chain bending and twisting are possible where there is a rotation of the chain atoms
 - note: no bond breaking needed



Adapted from Fig. 14.5, *Callister 7e*.

Molecular Shape

□ A single chain might contain multitude of bends, twists.

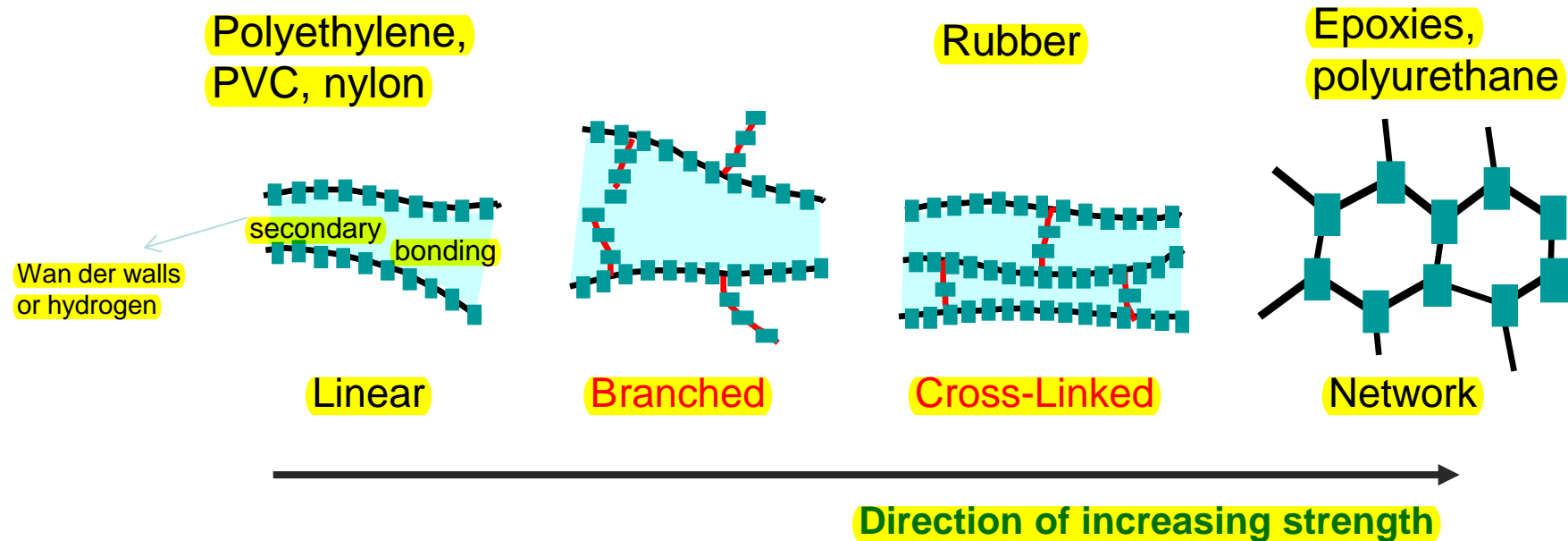


Chain End-to-End Distance, r

□ Some of the mechanical and thermal characteristics of polymers are a function of the ability of chain segments to experience rotation in response to applied stresses or thermal vibrations

Molecular Structure

- The physical properties of polymers are affected from the structure of polymer chains

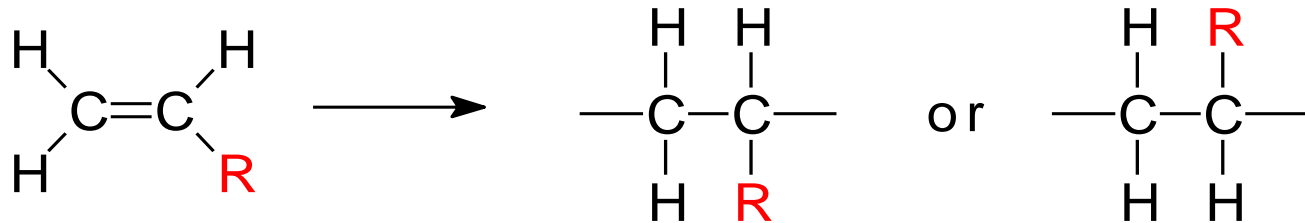


- Branches lower polymer density
 - i.e. High density polyethylene (HDPE): linear polymer
 - Low density polyethylene (LDPE) : brached polymer

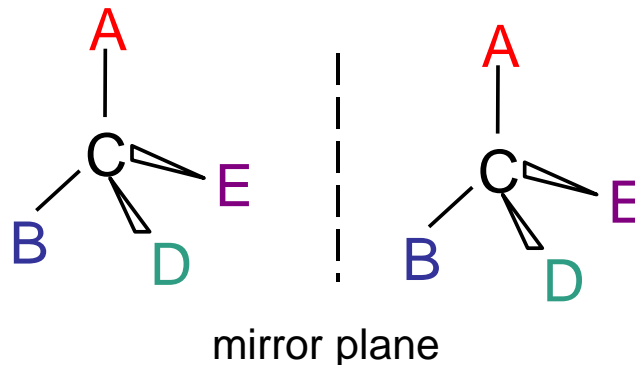
Molecular Configuration for Polymers

Configurations – to change must break bonds

- **Stereoisomerism**: denotes the situation in which atoms are linked together in the same order but differ in their spatial arrangement



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

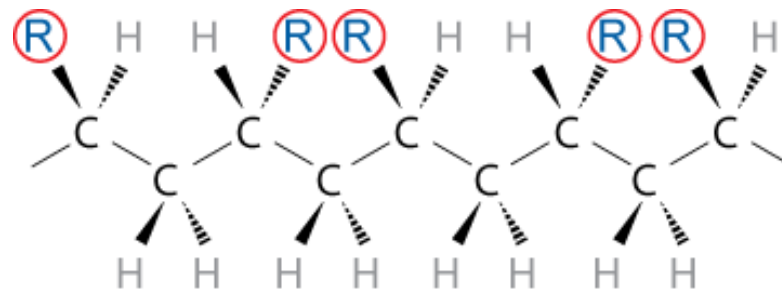
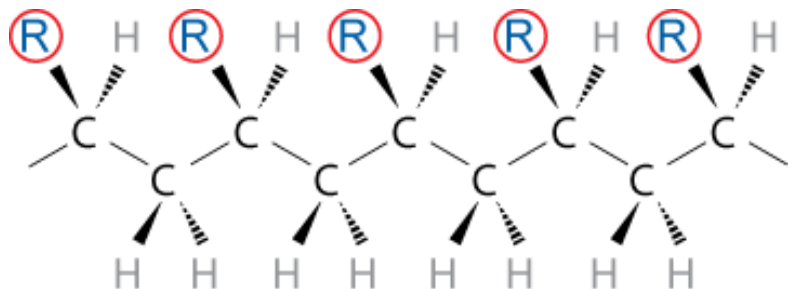
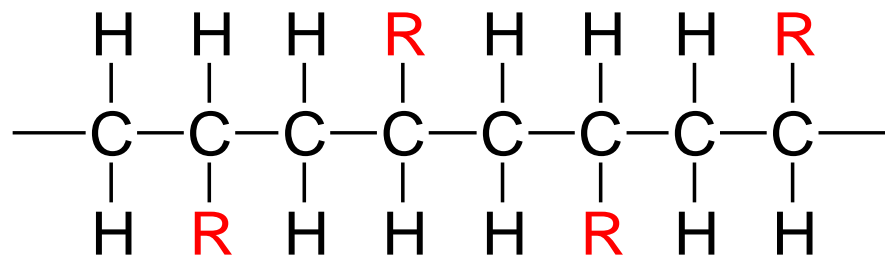
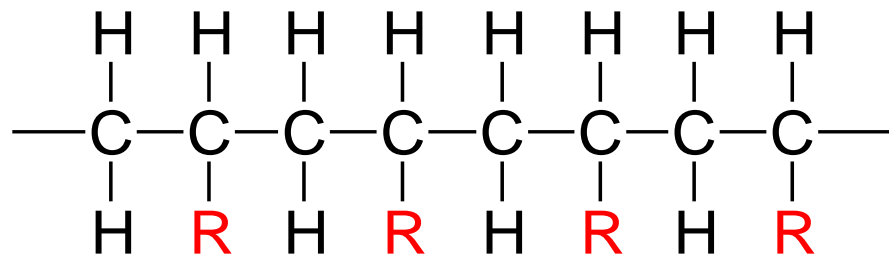


Molecular Configuration for Polymers

Tacticity — stereoregularity or spatial arrangement of **R** (side atom or group of atoms) units along chain

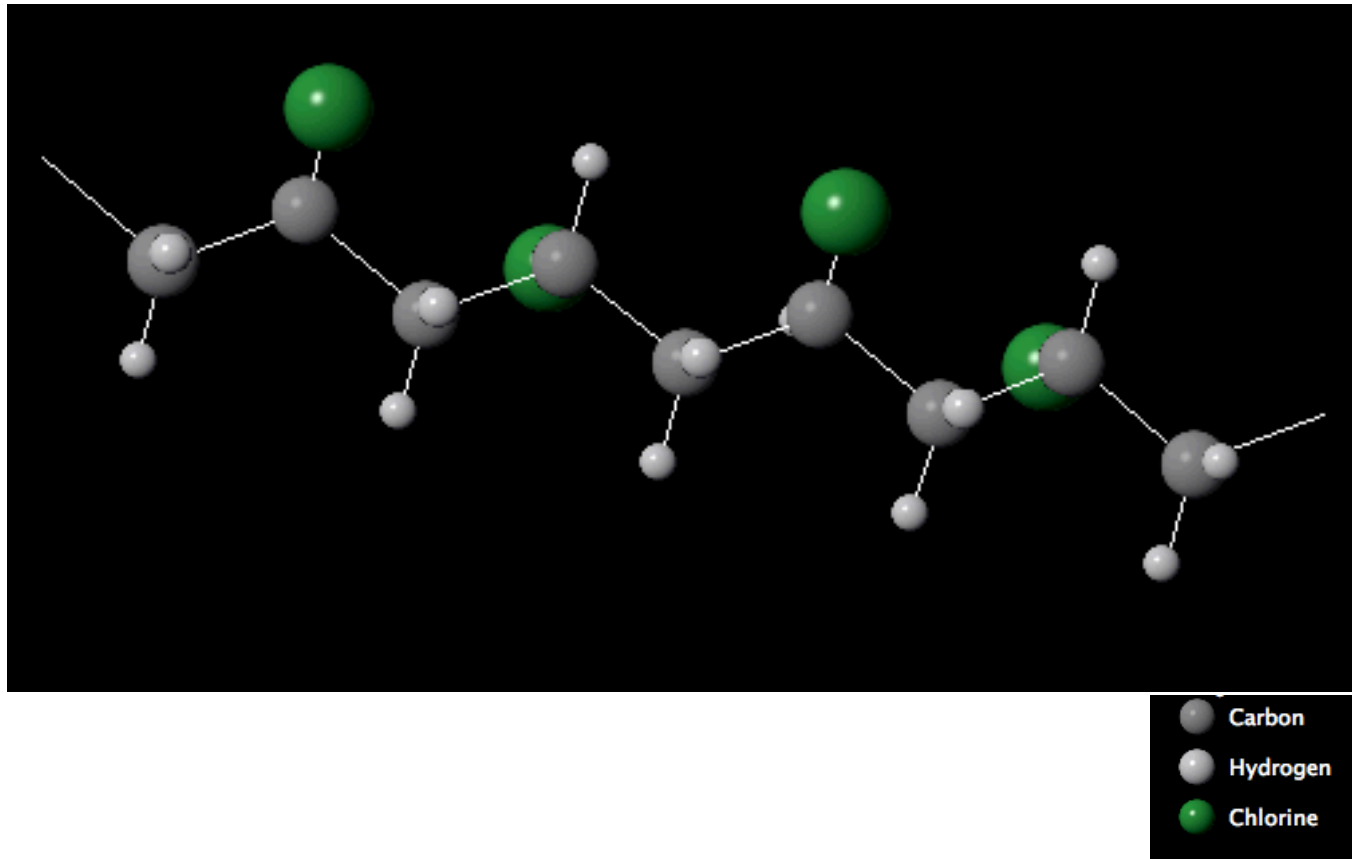
isotactic — all **R** groups on same side of chain

syndiotactic — **R** groups alternate sides



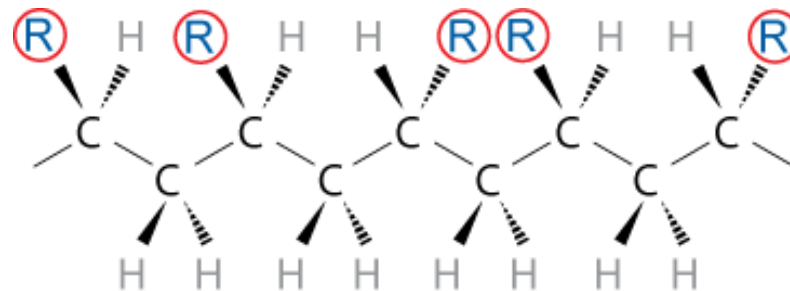
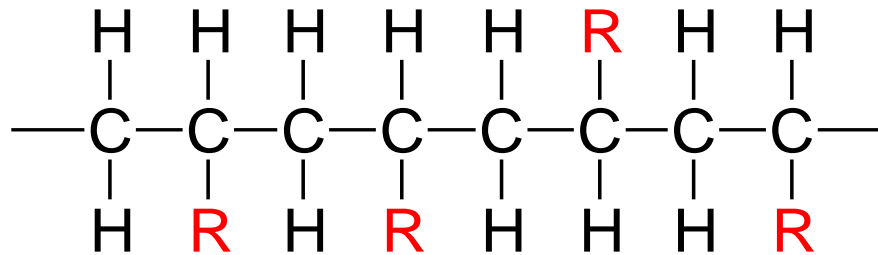
Molecular Configuration for Polymers

Syndiotactic Poly(vinyl chloride)



Molecular Configuration for Polymers

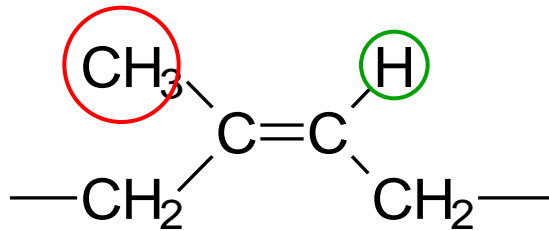
atactic – R groups randomly positioned



Molecular Configuration for Polymers

Geometrical isomerism: another chain configuration seen in repeat units that have double bond within carbon atoms

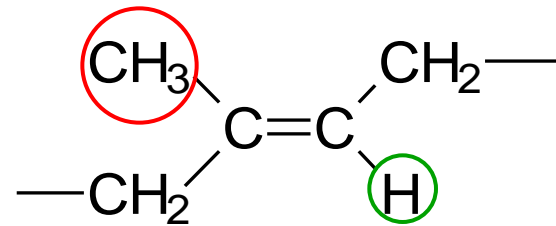
cis/trans Isomerism



cis

cis-isoprene
(natural rubber)

Side groups (H atom and CH₃) **on same side of chain**



trans

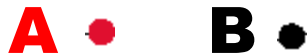
trans-isoprene
(gutta percha)

Side groups (H atom and CH₃) **on opposite sides of chain**

Copolymers

- They have improved and better properties than homopolymers
- two or more monomers polymerized together

Repeat units:



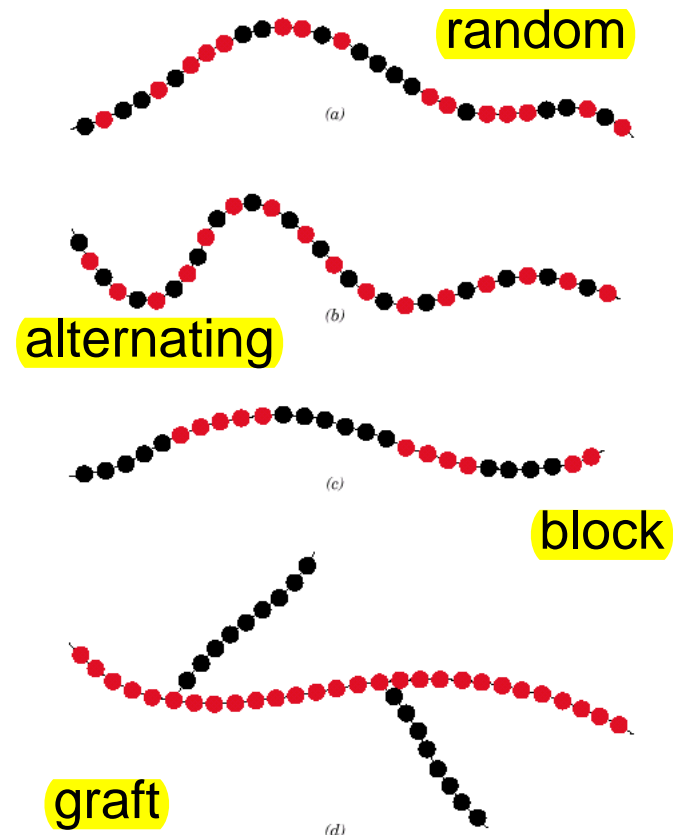
1-Random copolymer – A and B randomly vary in chain

2-Alternating copolymer – A and B alternate in polymer chain

3-Block copolymer – large blocks of A alternate with large blocks of B

4-Graft copolymer – chains of B grafted on to A backbone

Example: Styrene-butadiene rubber (SBR); random copolymer used in automobile tires

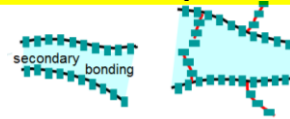


Thermoplastic and Thermosetting Polymers

- Classification is done according to behavior of polymers with rising temperature

Thermoplastics

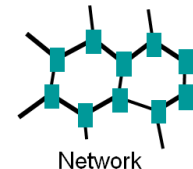
- Soften when heated (eventually liquefy) and harden when cooled. (reversible)
- Why do they soften when heated? : secondary bonding forces diminishes by increased molecular motion.



- Examples: Linear polymers and those having some branched structure
Polyethylene(PE), Polystyrene (PS), Polyvinylchloride (PVC)

Thermosets (harder and stronger than thermoplastics)

- They are network polymers
- They are permanently hard and don't soften upon heating
- Why don't they soften when heated? : covalent crosslinking between molecular chains resist motion of chains.
- Examples: vulcanized rubbers, epoxies, phenolics

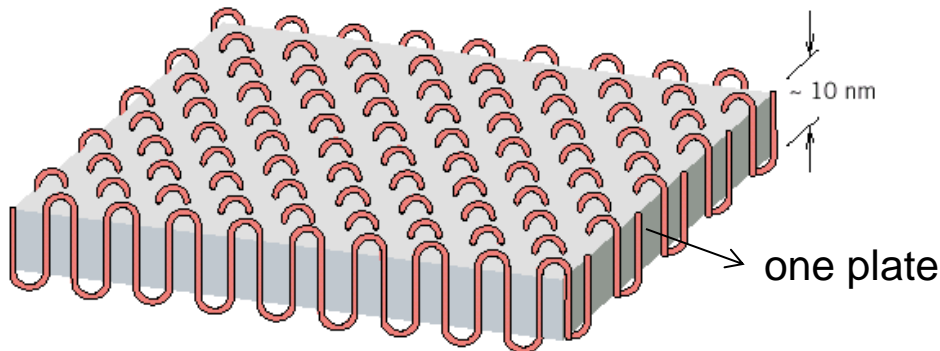


Polymer Crystallinity

- ❑ Polymers are partially crystalline (crystalline regions are dispersed within the amorphous matrix)
- ❑ We think polymer crystallinity as the packing of molecular chains to produce an ordered atomic array

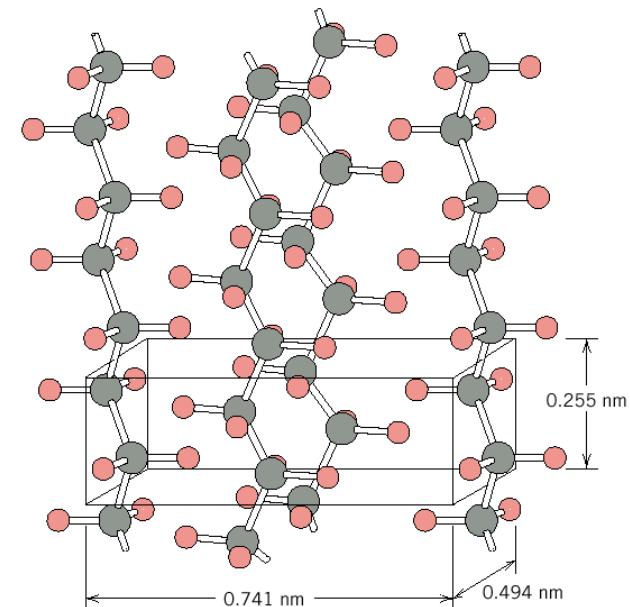
Ex: polyethylene unit cell

- Crystals must contain the polymer chains in some way
 - Chain folded structure
 - Thin plates 10 to 20 nm thick, and on the order of 10 μm long



Each plate consists of number of molecules

Adapted from Fig. 14.10, Callister 7e.

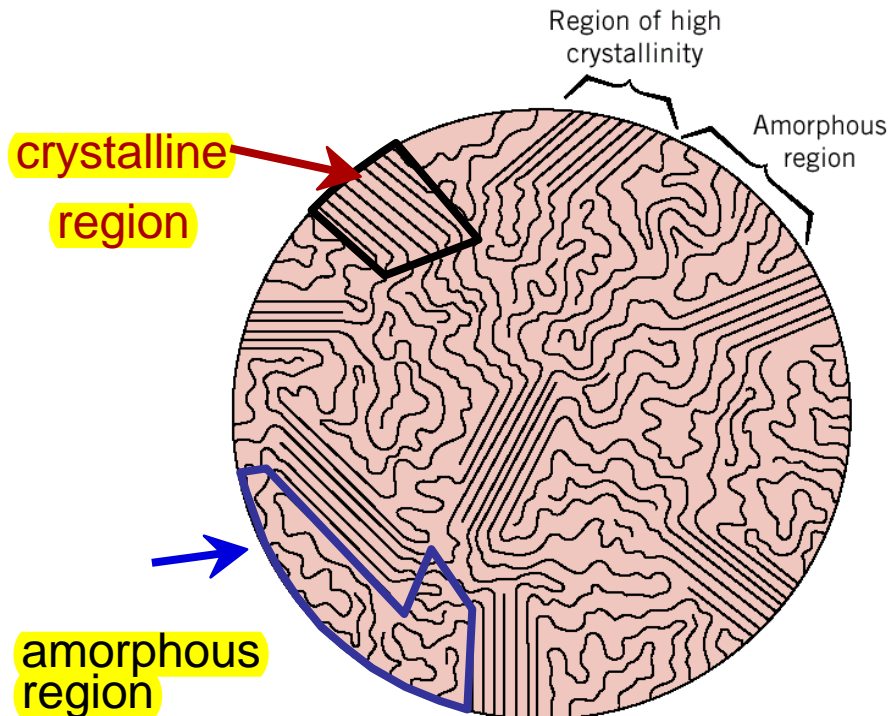


Polymer Crystallinity

❑ Polymers rarely exhibit 100% crystalline

Too difficult to get all those chains aligned

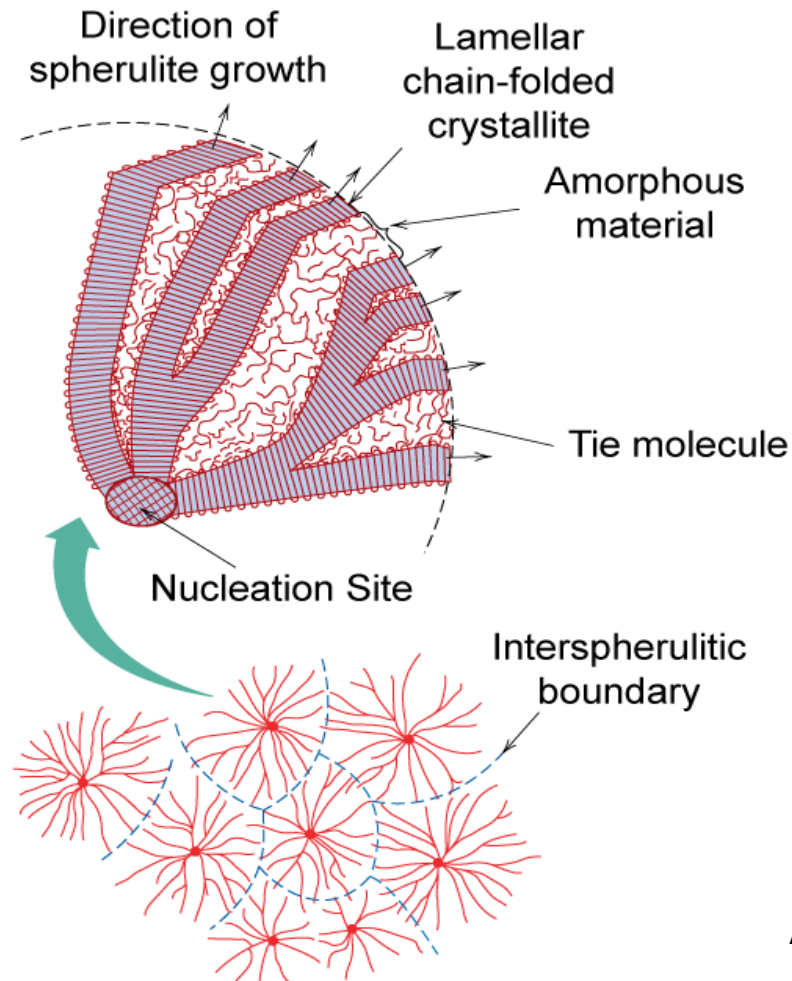
❑ Annealing causes crystalline regions to grow. % crystallinity increases.



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 Crystallinity

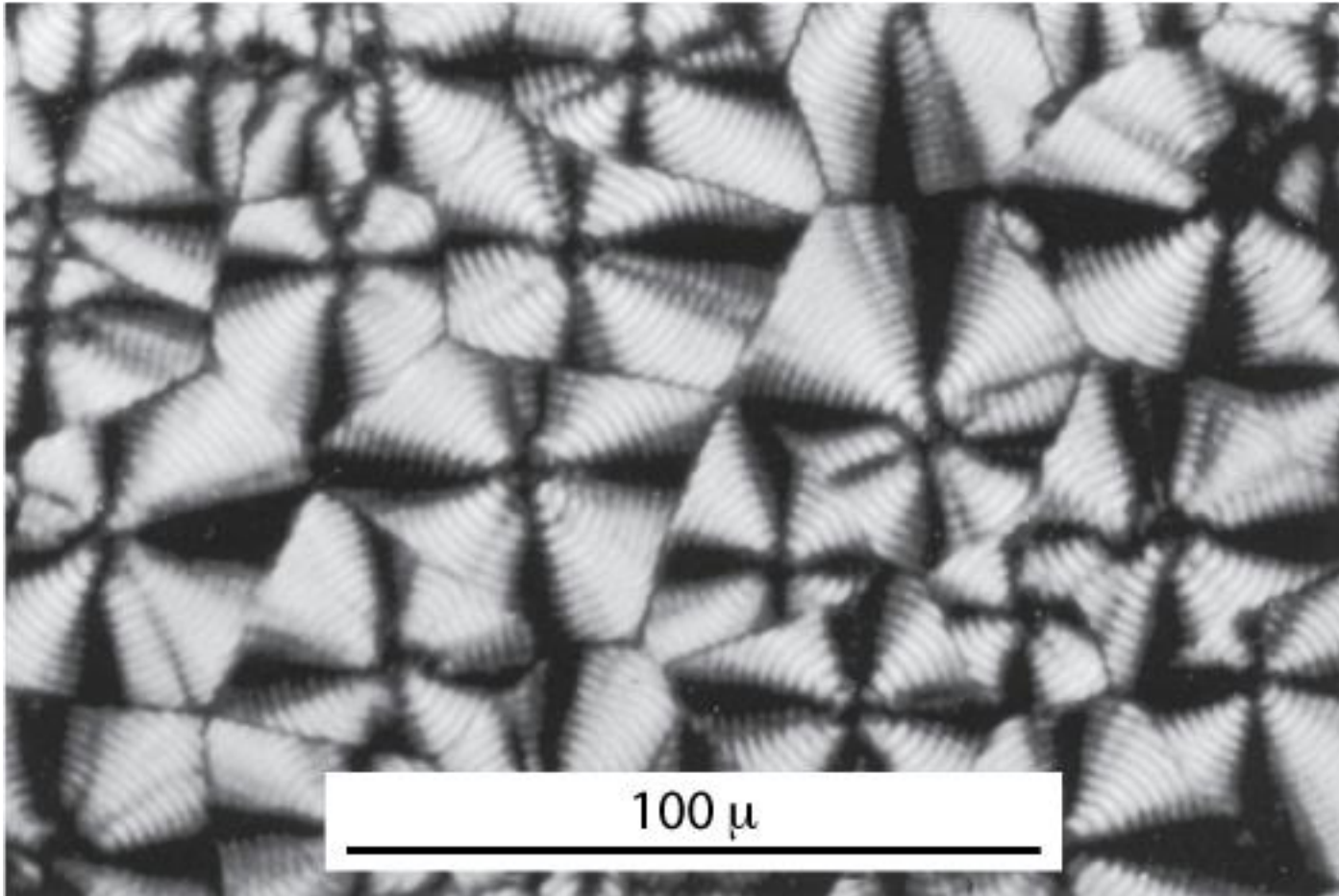
- Many bulk polymers that are crystallized from melt are semicrystalline and form a spherulite structure. (composed of lamellar crystal and amorphous material)



(Polyethylene, PVC, PP, nylon)

Polymer Crystallinity

Photomicrograph – Spherulites in Polyethylene



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

Polymer Crystallinity

- ❑ Most network and cross-linked polymers: totally amorphous because crosslinks prevent the polymer chains aligning.
- ❑ Crystallization is easier for simple polymers (polyethylene, polytetrafluoroethylene, etc.)
- ❑ Alternating and block copolymers may be crystalline
- ❑ Random and graft copolymers are amorphous

Physical Properties:

- ❑ Crystalline polymers are usually stronger and more resistance to dissolution and softening by heat.
- ❑ Density of crystalline polymers are higher than that of amorphous polymers
- ❑ *Tensile Strength* and *Elastic modulus* often increase with % crystallinity.