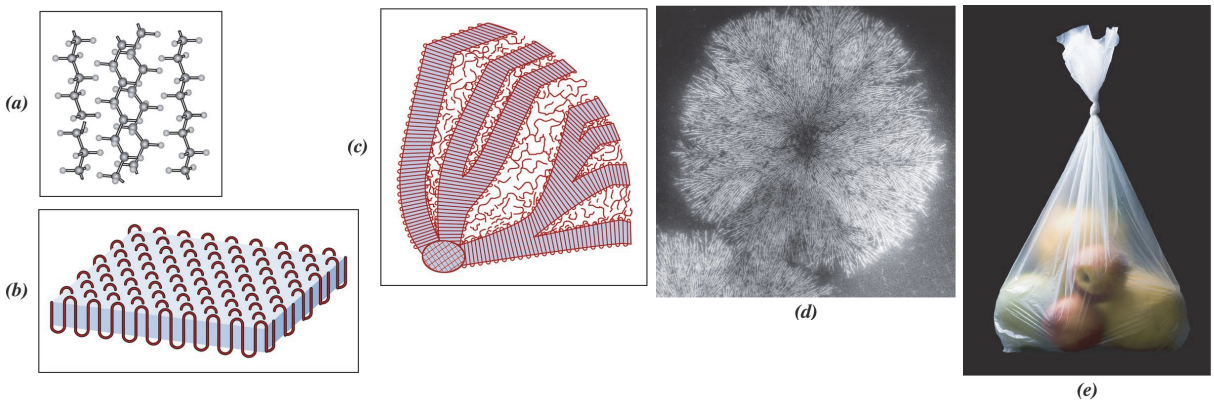
Chapter 5. Structures of Polymers

- **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?



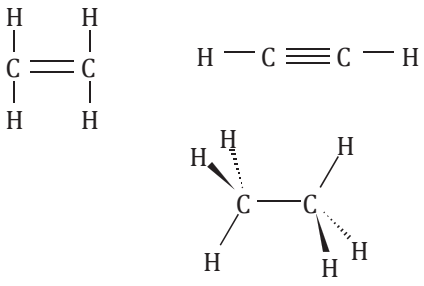
(a) Schematic representation of the arrangement of molecular chains for a crystalline region of polyethylene.
(b) Schematic diagram of a polymer chain-folded crystallite-a plate-shaped crystalline region.
(c) Structure of a spherulite found in some semicrystalline polymer (schematic).
(d) Transmission electron micrograph showing the spherulite structure.
(e) A polyethylene produce bag containing some fruit.

Polymers & Hydrocarbon Molecules

- **Naturally occurring polymers**
  - Derived from plants and animals: Wood, rubber, cotton, wool, leather, silk
  - Other natural polymers: Proteins, enzymes, starches, and cellulose
- **Synthetic polymers**
  - Plastics, rubbers, and fiber materials
  - The synthetic polymers can be produced inexpensively, and their properties may be managed to the degree that many are superior to their natural counterparts.

- **Most polymers are hydrocarbons, i.e., made up of Hydrogen and Carbon.**
- **Intramolecular bonds are covalent.**

- **Unsaturated hydrocarbons**
  - Molecules have double or triple covalent bonds.
  - Somewhat unstable – can form new bonds
  - Ex: C_2H_4 (double bond), C_2H_2 (triple bond)
- **Saturated hydrocarbons**
  - Each carbon singly bonded to four other atoms.
  - Example: Ethane, C_2H_6



Definitions

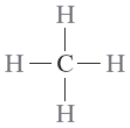
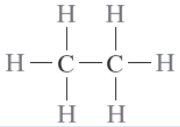
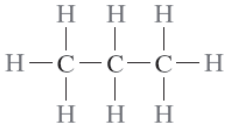
- **Term "polymer": greek poli (many) + meros (unit) = many units**
  - Polymers are a large class of materials consisting of many small molecules (called monomers) that can be linked together to form long chains, thus they are known as macromolecules (term introduced by H. Staudinger in 1920's).

- **Polymer:** Large molecule consisting of a number of repeating units with molecular weight typically several thousand or higher
- **Repeating unit:** The fundamental recurring unit of a polymer
- **Monomer:** The smaller molecule(s) that are used to prepare a polymer
- **Oligomer:** A molecule consisting of reaction of several repeat units of a monomer but not large enough to be consider a polymer
- **Single repeat unit: MONOMER**
- **Many repeat units: POLYMER**
- **Degree of polymerization:** The number of the repeating units

Hydrocarbon Molecules

- **Paraffin family**

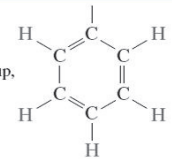
Table 5.1 Compositions and Molecular Structures for Some Paraffin Compounds: C_nH_{2n+2}

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

Hydrocarbon Groups

Table 5.2 Some Common Hydrocarbon Groups

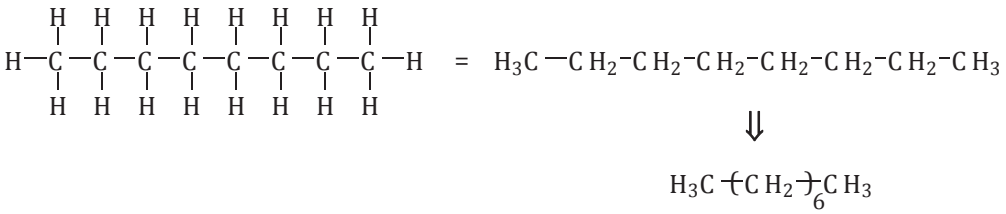
Family	*Characteristic Unit*	*Representative Compound*
Alcohols	R—OH	Methyl alcohol
Ethers	R—O—R′	Dimethyl ether
Acids	R—C(=O)—OH	Acetic acid
Aldehydes	R—C(=O)—H	Formaldehyde
Aromatic hydrocarbons[a]		Phenol

[a]The simplified structure  denotes a phenyl group, 

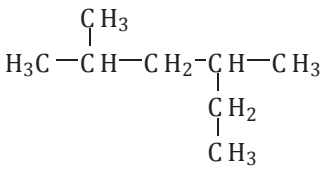
Isomerism

- **Hydrocarbon compounds with the same chemical formula can have different atomic arrangements.**

- **For example: C_4H_{10} (butane), C_8H_{18} (octane)**
  - Normal-octane



  - 2,4-dimethylhexane

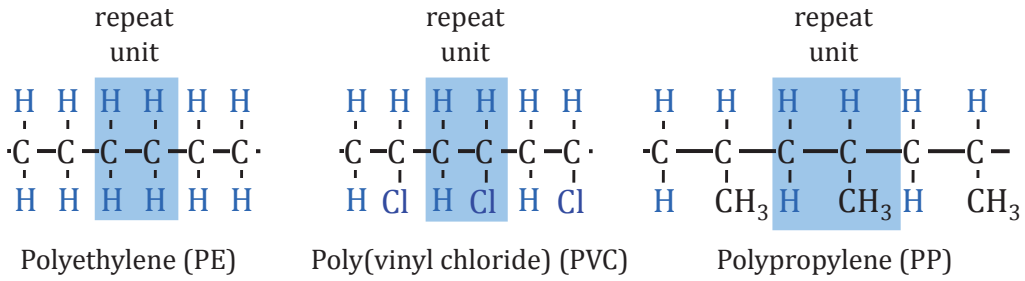


Polymer Molecules

- **Polymers = Macromolecules**
  - The backbone of each chain is a string of carbon atoms.

- **Monomer ≅ Repeat Unit**

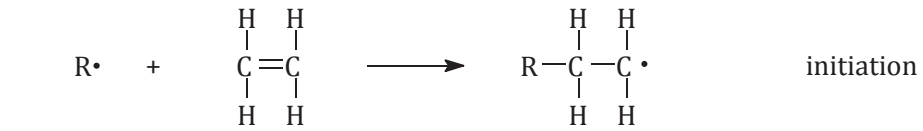
Poly **mer**
= many **= repeat unit**



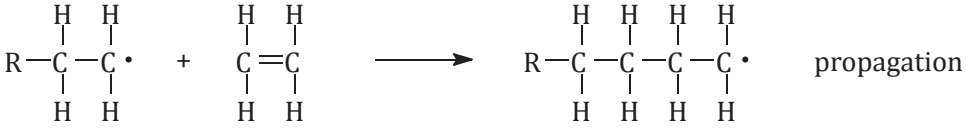
Polyethylene (PE) Poly(vinyl chloride) (PVC) Polypropylene (PP)

Polymerization and Polymer Chemistry

- **Free radical polymerization**

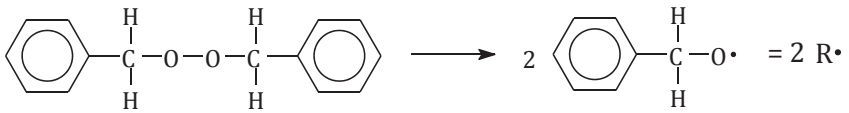


free radical monomer (ethylene)

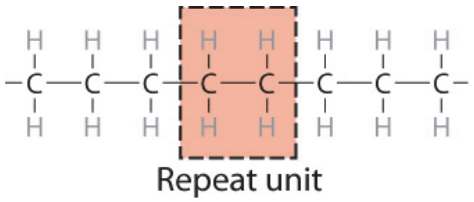


dimer

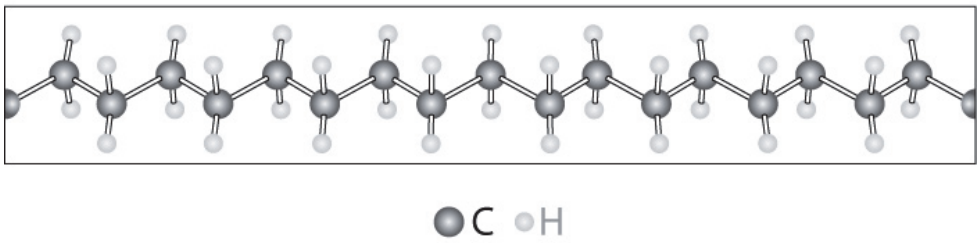
- **Initiator: example - benzoyl peroxide**



Chemistry and Structure of Polyethylene



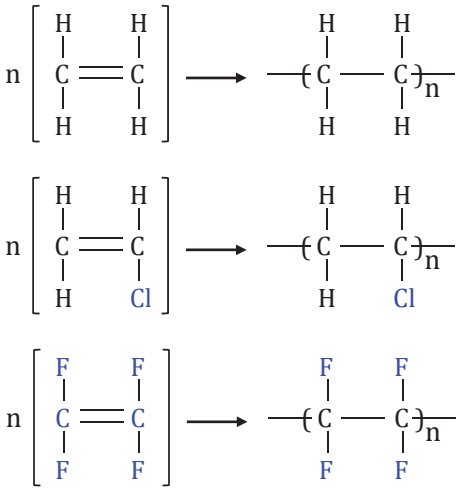
Adapted from Fig. 5.1, *Callister & Rethwisch 9e.*

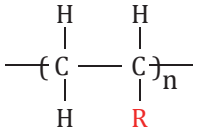


Note: - polyethylene is a long-chain hydrocarbon
- paraffin wax for candles is short polyethylene

Various Polymers

- **Homopolymer: All the repeating units along a chain are of the same type.**
- **Copolymer: Chains are composed of two different repeat units.**
- **Terpolymer: Chains are composed of three different repeat units.**



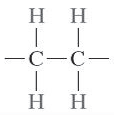
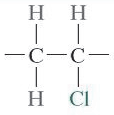
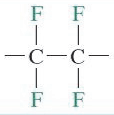
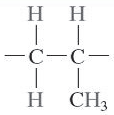
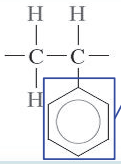


R = radical atom or group
- Atom: H, F, Cl, etc.
- Group: CH_3 (methyl), C_2H_5 (ethyl), C_6H_5 (phenyl), etc.

- **Functionality: The number of bonds that a given monomer can form**
  - Ethylene: bifunctional, phenol-formaldehyde: trifunctional

Bulk or Commodity Polymers

Table 5.3 Repeat Units for Ten of the More Common Polymeric Materials

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


WileyPLUS: VMSE
Repeat Unit Structures

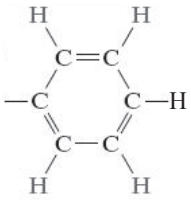

WileyPLUS: VMSE


WileyPLUS: VMSE


WileyPLUS: VMSE


WileyPLUS: VMSE

Aromatic ring (benzene ring)



Volatile Organic Compounds (VOCs): 휘발성 유기화합물

- Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room temperature. Their high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air, a trait known as volatility. For example, formaldehyde, which evaporates from paint, has a boiling point of only –19 °C.

- VOCs are numerous, varied, and ubiquitous. They include both human-made and naturally occurring chemical compounds. Most scents or odors are of VOCs. VOCs play an important role in communication between plants,[1] and messages from plants to animals. Some VOCs are dangerous to human health or cause harm to the environment. Anthropogenic VOCs are regulated by law, especially indoors, where concentrations are the highest. Harmful VOCs typically are not acutely toxic, but have compounding long-term health effects. Because the concentrations are usually low and the symptoms slow to develop, research into VOCs and their effects is difficult.

5.5 Molecular Weight

- **Molecular weight, M: Mass of a mole of chains.**
  - Not all chains in a polymer are of the same length, i.e., there is a distribution of molecular weights.

- **Molecular weight distribution**

$$\overline{M}_n = \frac{\text{total weight of polymer}}{\text{total number of molecules}}$$

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

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

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

x_i = number fraction of chains in size range i

w_i = weight fraction of chains in size range i

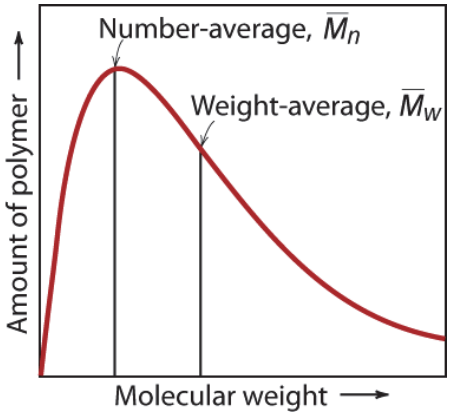


Fig. 5.4, *Callister & Rethwisch 9e.*

Degree of Polymerization, DP

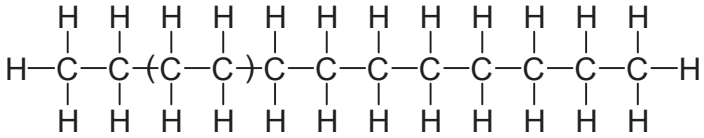
- **Degree of Polymerization (DP) = average number of repeat units per chain**
  - $DP = \overline{M}_n / \overline{m}$

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

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

f_i : Chain fraction

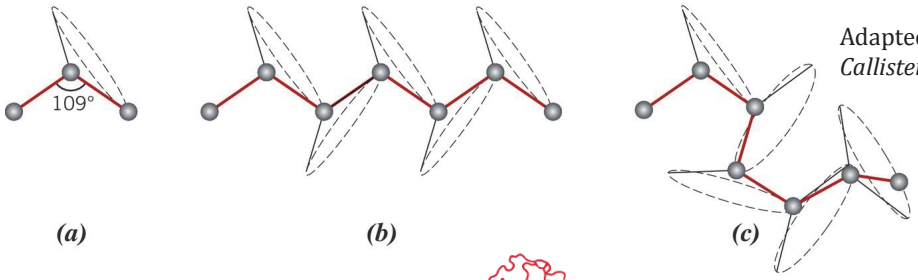
m_i : mol. wt of repeat unit i



$DP = 6$

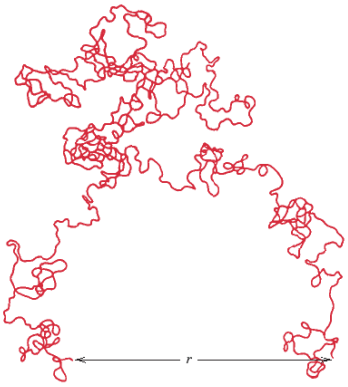
5.6 Molecular Shape

- **Molecular Shape (or Conformation) – chain bending and twisting are possible by rotation of carbon atoms around their chain bonds**
  - Note: not necessary to break chain bonds to alter molecular shape



Adapted from Fig. 5.5, *Callister & Rethwisch 9e.*

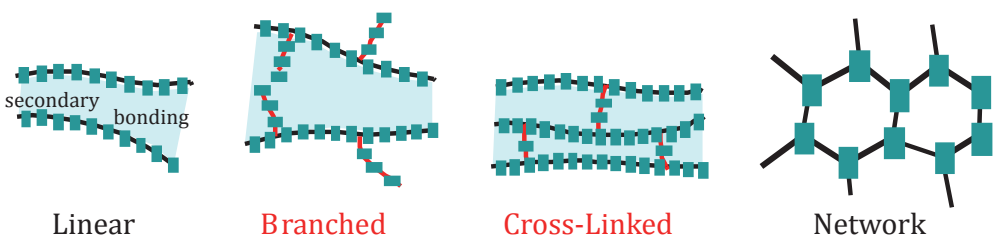
- **Chain End-to-End Distance, r**



Adapted from Fig. 5.6, Callister & Rethwisch 9e.

5.7 Molecular Structure of Polymer

- **Linear chains:** a polymer consisting of a single continuous chain of repeat units.
- **Branched chains:** a polymer that includes side chains of repeat units. connecting onto the main chain of repeat units.
- **Hyper branched polymer** consist of a constitutional repeating unit including a branching groups.
- **Cross linked polymer:** a polymer that includes interconnections between chains.
- **Net work polymer:** a cross linked polymer that includes numerous interconnections between chains.

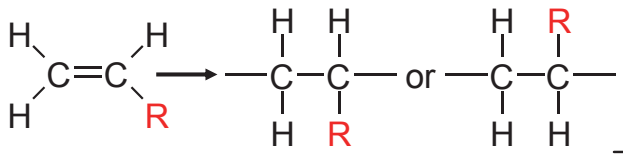


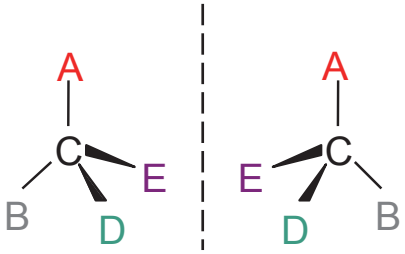
Direction of increasing strength →

Adapted from Fig. 5.7, *Callister & Rethwisch 9e.*

5.8 Molecular Configurations for Polymers

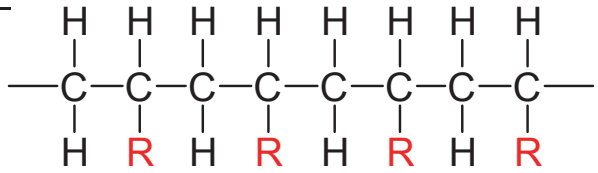
- **Stereoisomerism: Atoms are linked together in the same order (head-to-tail) but differ in their spatial arrangement.**
- **Stereoisomers are mirror images: can't superimpose without breaking a bond.**
- **Tacticity – stereoregularity or spatial arrangement of R units along chain**

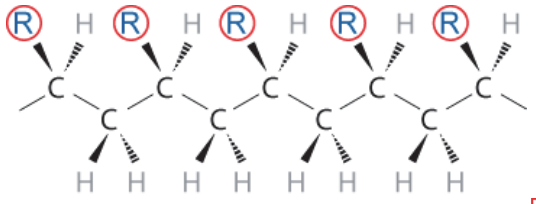




mirror plane

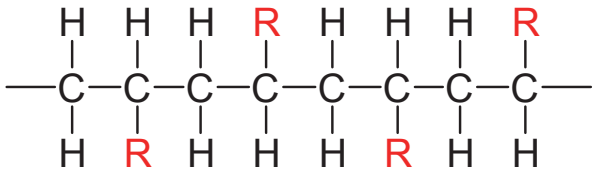
isotactic – all R groups on the same side of chain

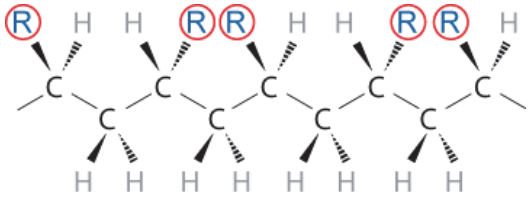




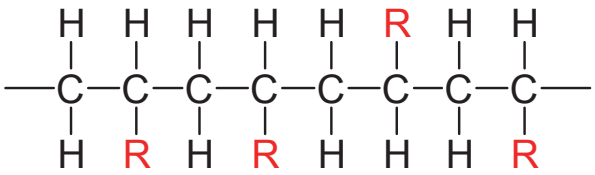
Stereoisomerism (continued)

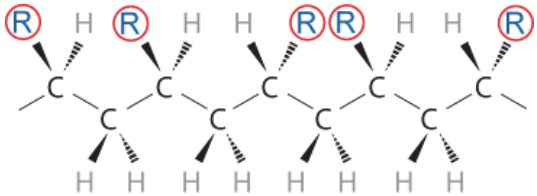
syndiotactic – R groups: alternate sides





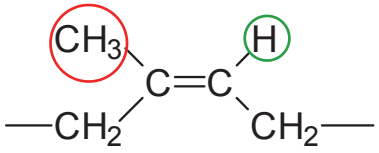
atactic – R groups randomly positioned





Geometrical Isomerism

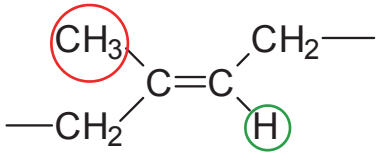
- **Cis/Trans Isomerism**



cis

cis-isoprene
(natural rubber)

H atom and CH_3 group on the same side of chain



trans

trans-isoprene
(gutta percha)

H atom and CH_3 group on opposite sides of chain

5.9 Thermoplastic and Thermosetting Polymers

- **Polymers may be classified as follows, according to the mechanical response at elevated temperatures:**
  - Thermoplasts
  - Thermosets.

a) Thermoplastics:

- Thermoplastic polymers soften when heated and harden when cooled. Simultaneous application of heat and pressure is required to fabricate these materials.
- On the molecular level, when the temperature is raised, secondary bonding forces are diminished so that the relative movement of adjacent chains is facilitated when a stress is applied.
- Most linear polymers and those having branched structures with flexible chains are thermoplastics.
- Thermoplastics are very soft and ductile.
- The commercial available thermoplasts are
  - Polyvinyl Chloride (PVC) and Polystyrene
  - Polymethyl methacrylate
  - Polystyrene

5.9 Thermoplastic and Thermosetting Polymers

b) Thermosets

- Thermosetting polymers become soft during their first heating and become permanently hard when cooled. They do not soften during subsequent heating. Hence, they cannot be remolded/reshaped by subsequent heating.
- In thermosets, during the initial heating, covalent cross-links are formed between adjacent molecular chain. These bonds anchor the chains together to resist the vibration and rotational chain motions at high temperatures. Cross linking is usually extensive in that 10 to 15% of the chain mer units are cross linked. Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation. Thermoset polymers are harder, stronger, more brittle than thermoplastics and have better dimensional stability.
- They are more usable in processes requiring high temperatures
- Most of the cross linked and network polymers, including Vulcanized rubbers, Epoxies, Phenolic, and Polyester resins, are thermosetting polymers.
- Thermosets cannot be recycled, do not melt, are usable at higher temperatures than thermoplastics, and are more chemically inert

5.10 Copolymers

- **Homopolymers:** Consist of only one type of constitutional repeating unit (A)
- **Copolymers:** Consist of two or more constitutional repeating units (A-B)
- **Several classes of copolymer are possible**
  - **Statistical copolymer (Random)**: Two or more different repeating unit are distributed randomly

    ABAABABBBAABAABB
  - **Alternating copolymer** are made of alternating sequences of the different monomers

    ABABABABABABABAB
  - **Block copolymer**: Long sequences of a monomer are followed by long sequences of another monomer

    AAAAAAAAAABBBBBBBBB
  - **Graft copolymer** consist of a chain made from one type of monomers with branches of another type

    AAAAAAAAAAAAAAAAAA

    B B B

    B B B

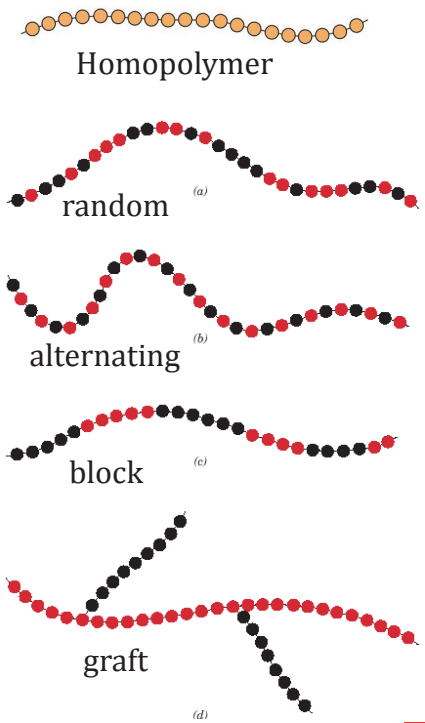


Fig. 5.9, *Callister & Rethwisch 9e.*

5.10 Polymer Crystals

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

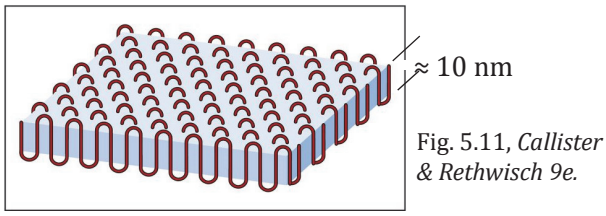


Fig. 5.11, *Callister & Rethwisch 9e.*

- **Polymers rarely 100% crystalline**
  - Difficult for all regions of all chains to become aligned
  - Degree of crystallinity expressed as % crystallinity.
  - Some physical properties depend on % crystallinity.
  - Heat treating causes crystalline regions to grow and % crystallinity to increase.

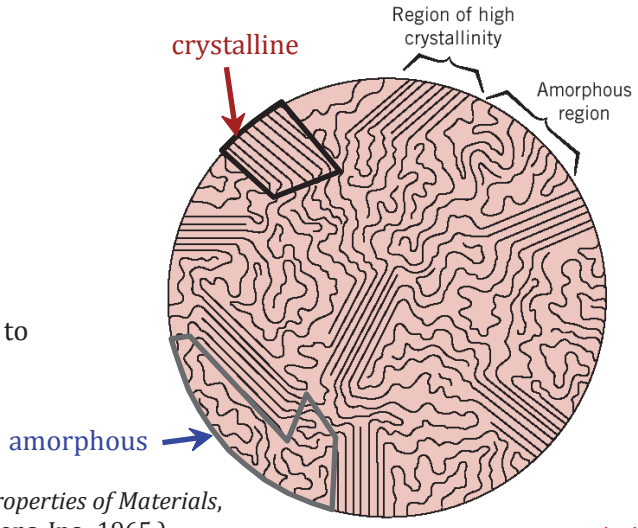


Fig. 14.11, *Callister 6e.* (From H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

Polymer Single Crystals

- **Electron micrograph– multilayered single crystals (chain-folded layers) of polyethylene**
- **Single crystals – only for slow and carefully controlled growth rates**
- **Spherulite**
  - Some semicrystalline polymers form spherulite structures
  - Alternating chain-folded crystallites and amorphous regions
  - Spherulite structure for relatively rapid growth rates