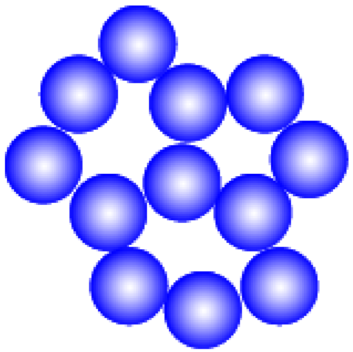
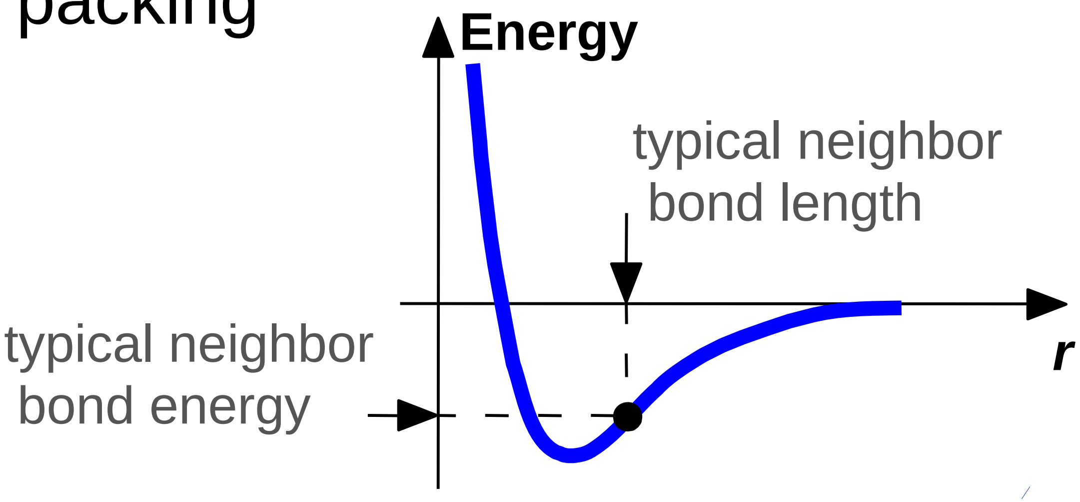
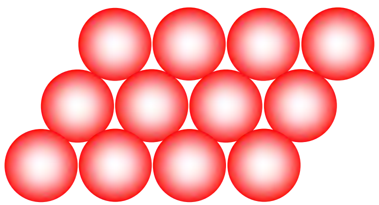
Packing of Atoms in Solids [5]

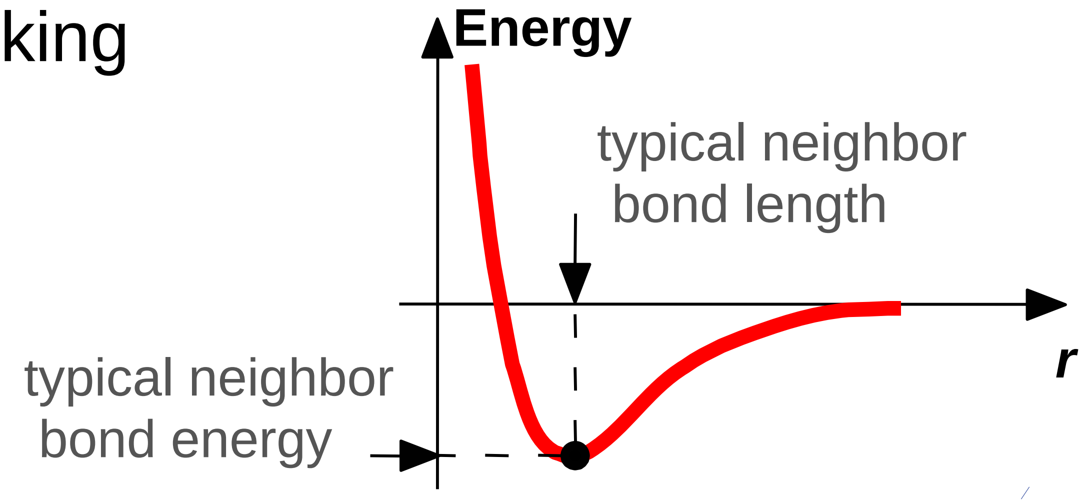
- Non dense, random packing





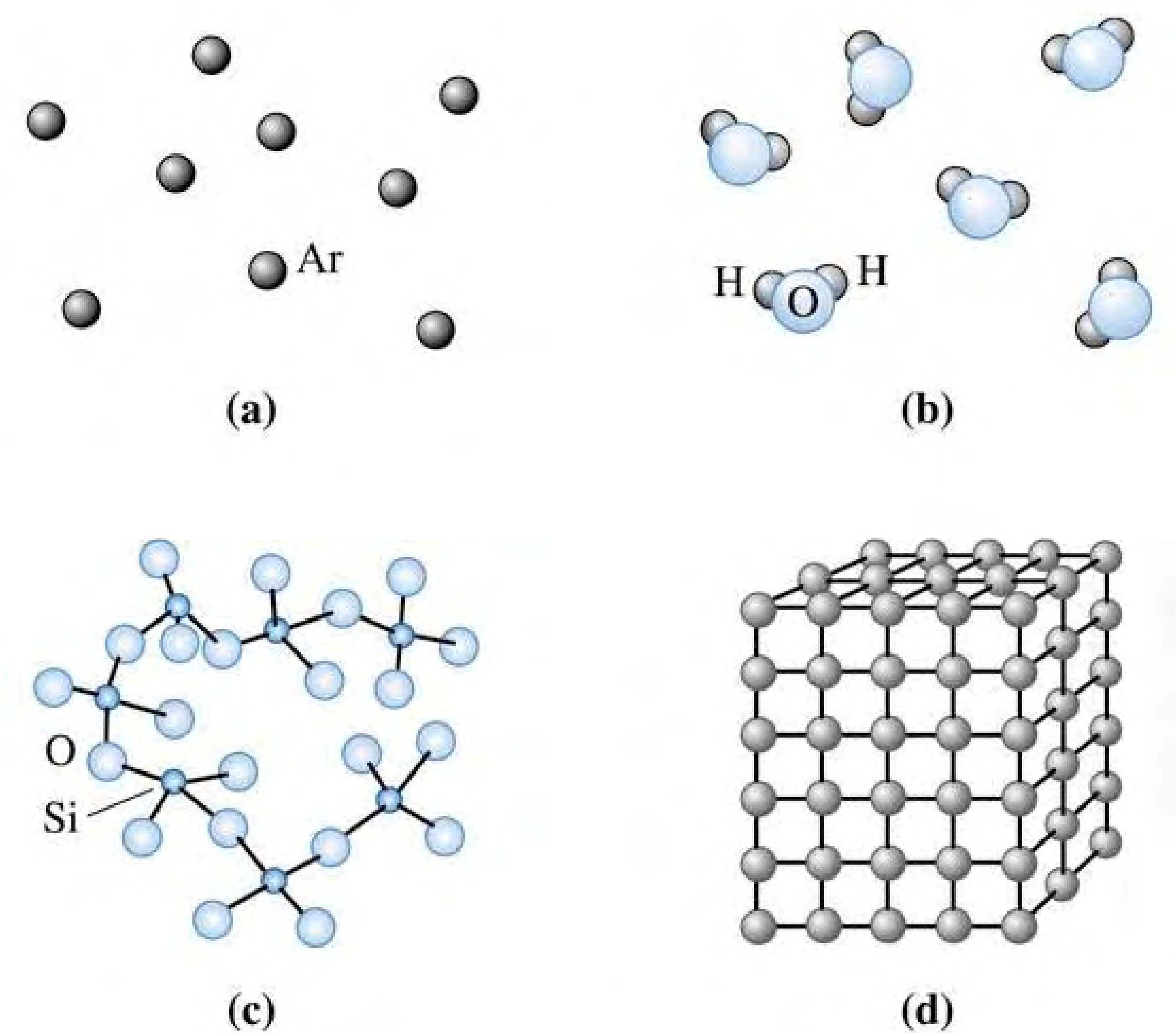
- Dense, ordered packing





Dense, ordered packed structures tend to have lower energies.

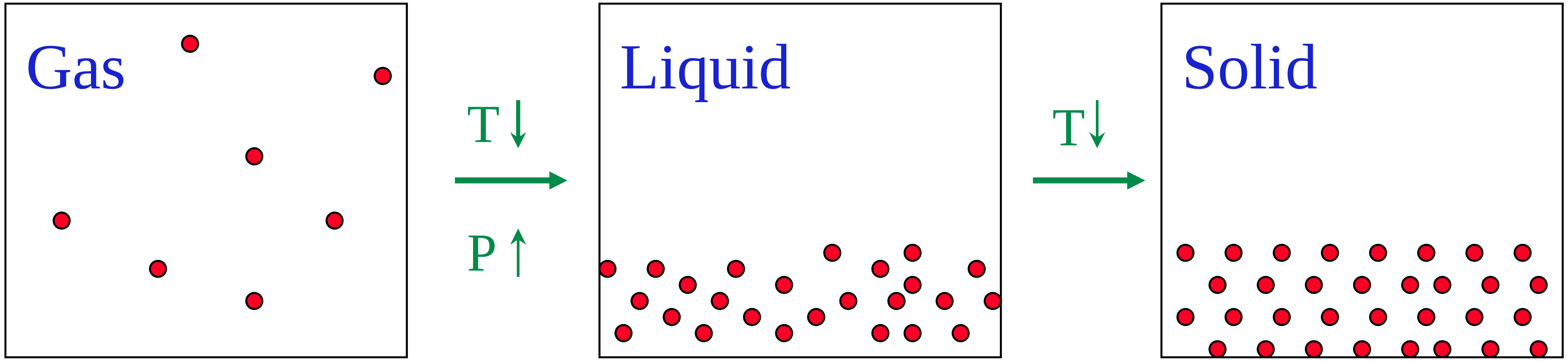
Packing of Atoms



short-range order (SRO) ~ nm

long-range order (LRO) > 100nm

States of Aggregation



- **Gas**
  - Assume volume and shape of the container
  - Low density, very compressible, free motion
- **Liquid**
  - Has definite volume, assume shape of the container
  - High density, slightly compressible, flow readily
- **Solid**
  - Definite volume, definite shape
  - High density, incompressible

Gas State

- Each individual molecule of a gas has an order. However, the overall structure has no order.

- Intermolecular bonding in gases is built by Van der Waals bonding which is a weak bond.

- Atoms are in continuous motion at high speeds which prevents them of having a fixed shape.

- The random movement of atoms will lead the gas to fill any container into which it is introduced.

Liquid State

- Liquids have more orderly structure than gases. However, this order is short ranged.

- The bond between atoms/molecules is weak and limited. So, liquids can take the shape of the container easily.

- The thermal expansion of liquids is less than that of gases.

Solid State

- **Solid materials** are classified according to the regularity with which atoms, ions or molecules are arranged with respect to one another.

  - **Crystalline Solids (ordered and periodic)**
  - **Quasicrystals (ordered no periodic)**
  - **Amorphous Solids (no ordered, no periodic)**

- In **crystalline materials** atoms are situated in an ordered periodic array over large atomic distances. (long range order)

- In **amorphous materials** are neither ordered nor periodic over long range distances

Solid State

- Upon solidification of a liquid the atoms will position themselves in a repetitive 3-D pattern in which each atom is bonded to its nearest atoms.

- Therefore, speed of solidification has a great effect on the type of solid.

  - Solidification occurs gradually → **Crystalline**

  - Solidification occurs suddenly → **Amorphous**

  - The type of bond also affects the type of solid

    - Ionic and Metallic Bonds → **Crystalline**

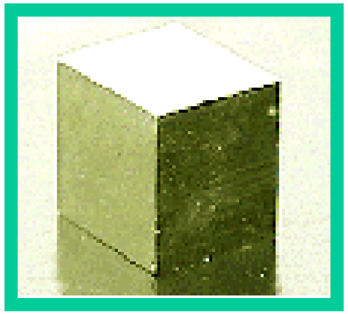
    - Covalent Bonds → **Amorphous**

Solid State

SOLID MATERIALS

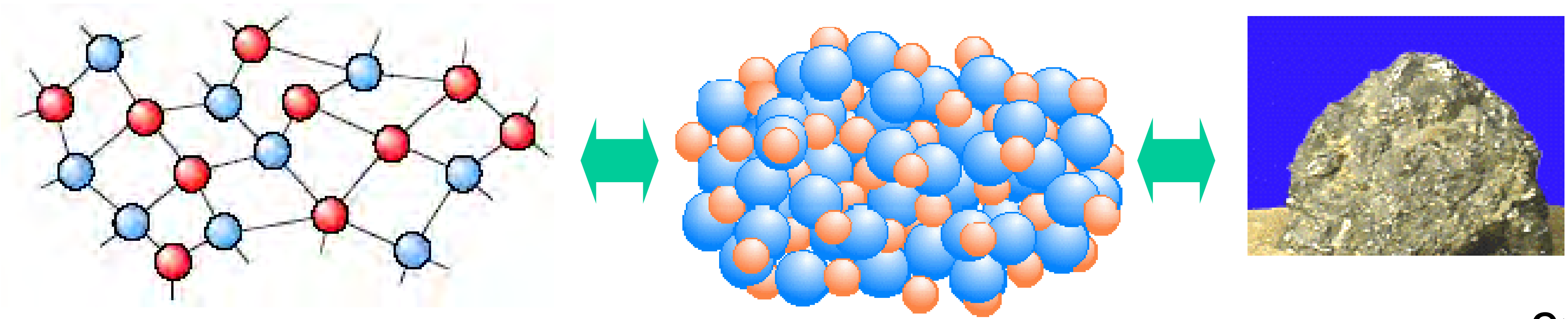
- CRYSTALLINE
  - Single Crystal
- POLYCRYSTALLINE
- AMORPHOUS (Non-crystalline)

QUASICRYSTALS



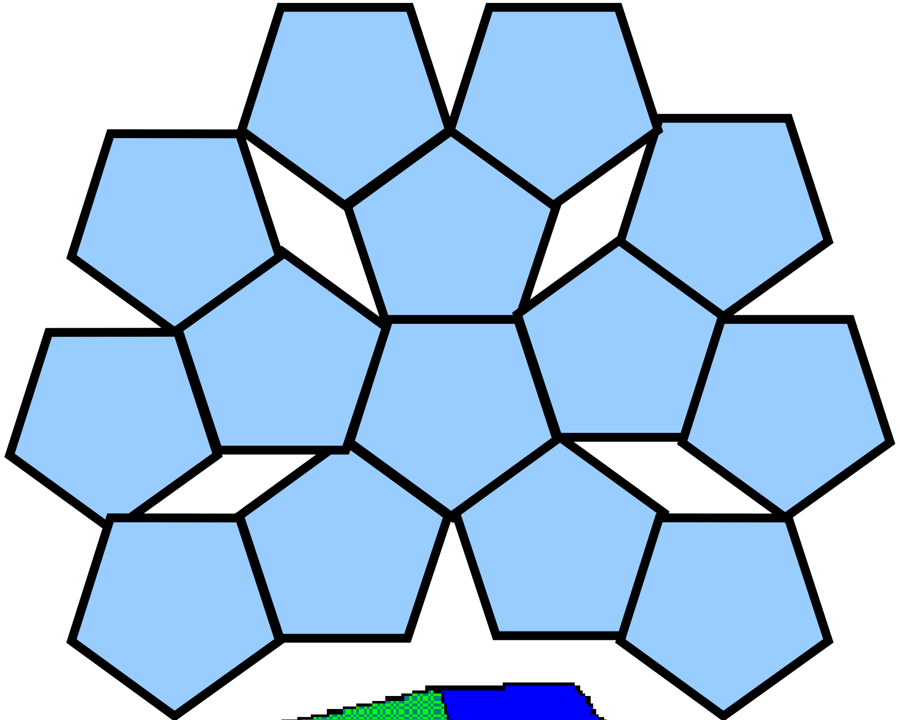
Amorphous Solid

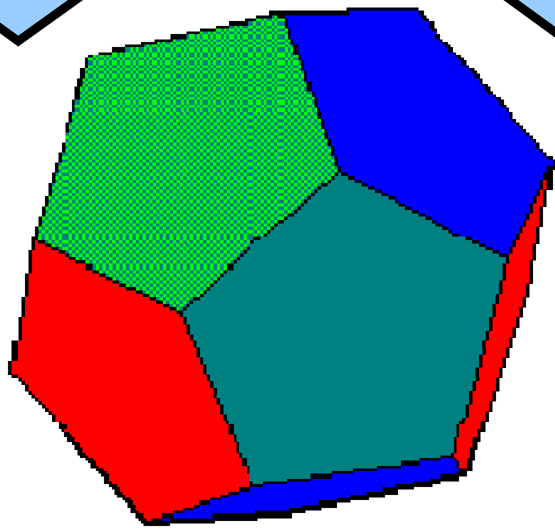
- **Amorphous (Non-crystalline) Solid** is composed of randomly orientated atoms , ions, or molecules that do not form defined patterns or lattice structures**.**
- Amorphous materials have order only within a few atomic or molecular dimensions.
- Amorphous materials do not have any long-range order, but they have varying degrees of short-range order.
- Examples to amorphous materials include amorphous silicon, plastics, and glasses.
- Amorphous silicon can be used in solar cells and thin film transistors.



Quasicrystalline Solid

- Discovered by Dan Shechtman, Nobel Prize 2011.

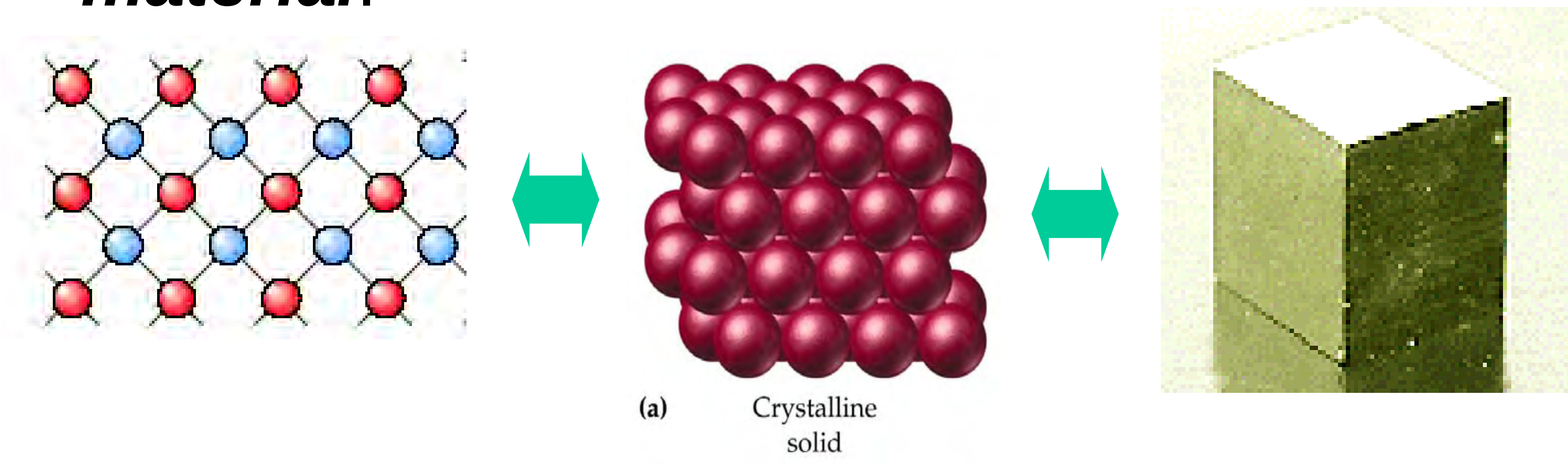




Regular pentagons cannot tile D2 space

Crystalline Solid

- **Crystalline Solid** is the solid form of a substance in which the ***atoms or molecules*** are arranged in a definite, repeating pattern in three dimension.
- Single crystals, ideally have a high degree of order, or regular geometric periodicity, throughout the ***entire volume of the material***.



Amorphous x Crystalline Solid

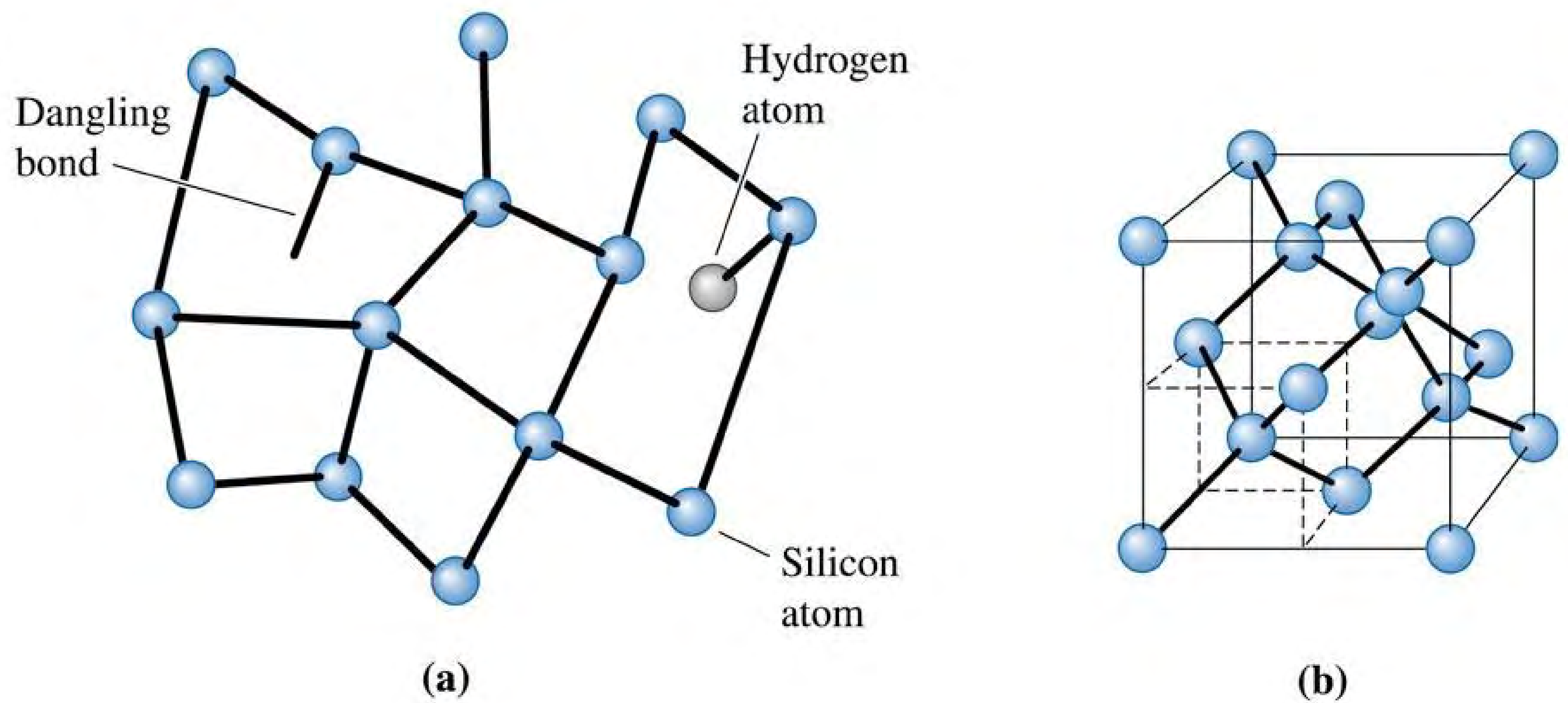


Figure 3.10 Atomic arrangements in crystalline silicon and amorphous silicon. (a) Amorphous silicon. (b) Crystalline silicon. Note the variation in the inter-atomic distance for amorphous silicon.

Polycrystalline Solid

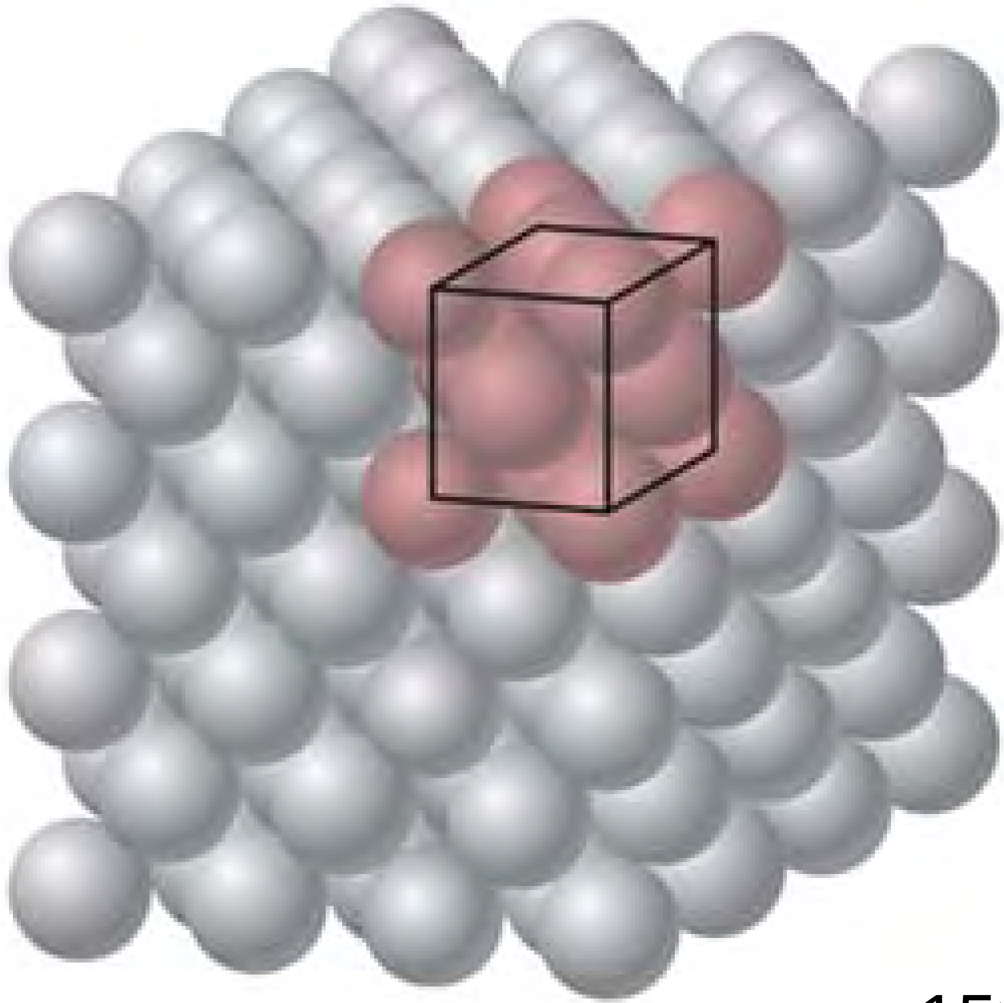
- **Polycrystal** is a material made up of an aggregate of ***many small single crystals*** (also called crystallites or grains).
- Polycrystalline material have a high degree of order over many atomic or molecular dimensions.
- These ***ordered regions,*** or single crystal regions, vary in size and orientation with one another.
- These regions are called as ***grains (domain)*** and are separated from one another by ***grain boundaries.*** *The atomic order can vary from one domain to the next.*
- The grains are usually ***100 nm - 100 microns in diameter***. Polycrystals with grains that are <10 nm in diameter are called nanocrystalline.

Polycrystalline Solid from Liquid

Crystalline Model

A hard sphere model is the atomic arrangement of some common elemental metals shown below.

- **In this example:**
- All atoms are identical.
- Sometimes the term "lattice" is used in the context of crystal structures.
- **Space-Lattice:** 3-D arrays of points in space coinciding with atom positions.



Classification of Solid Materials

- **Metals**: Materials that have metallic bonding and generally good ductility, strength, and electrical conductivity.

- **Ceramics**: Inorganic materials characterized by good strength in compression, and high melting temperatures. Many ceramics are very good electrical insulators and have good thermal insulation behavior.

- **Polymers**: Materials normally obtained by joining organic molecules into giant molecular chains or networks. Polymers are characterized by low strengths, low melting temperatures, and poor electrical conductivity.

- **Composites**: A group of materials formed from metals, ceramics, or polymers in such a manner that unusual combinations of properties are obtained.

Density of Solid Materials

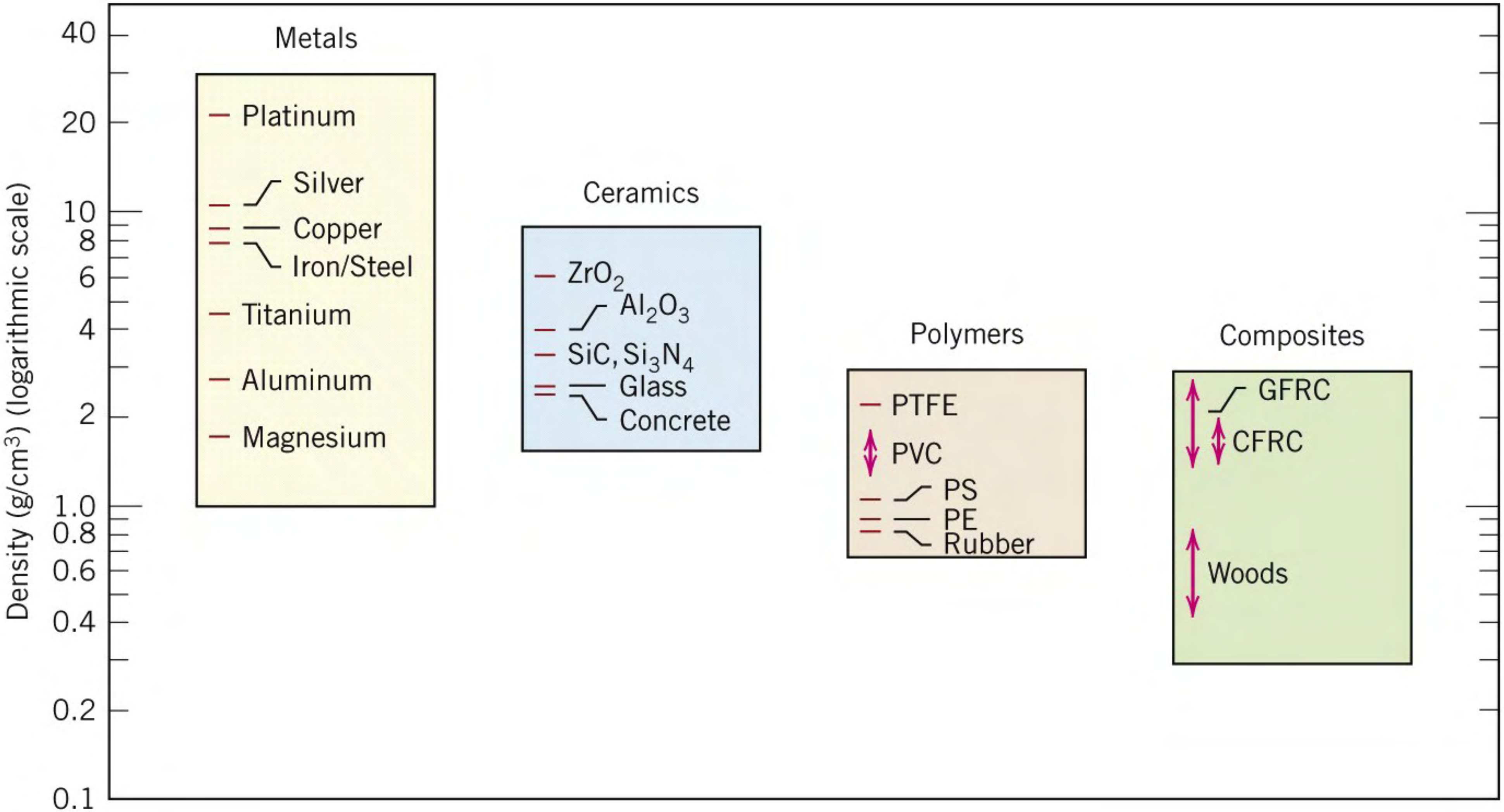


Figure 1.3

Strength of Solid Materials

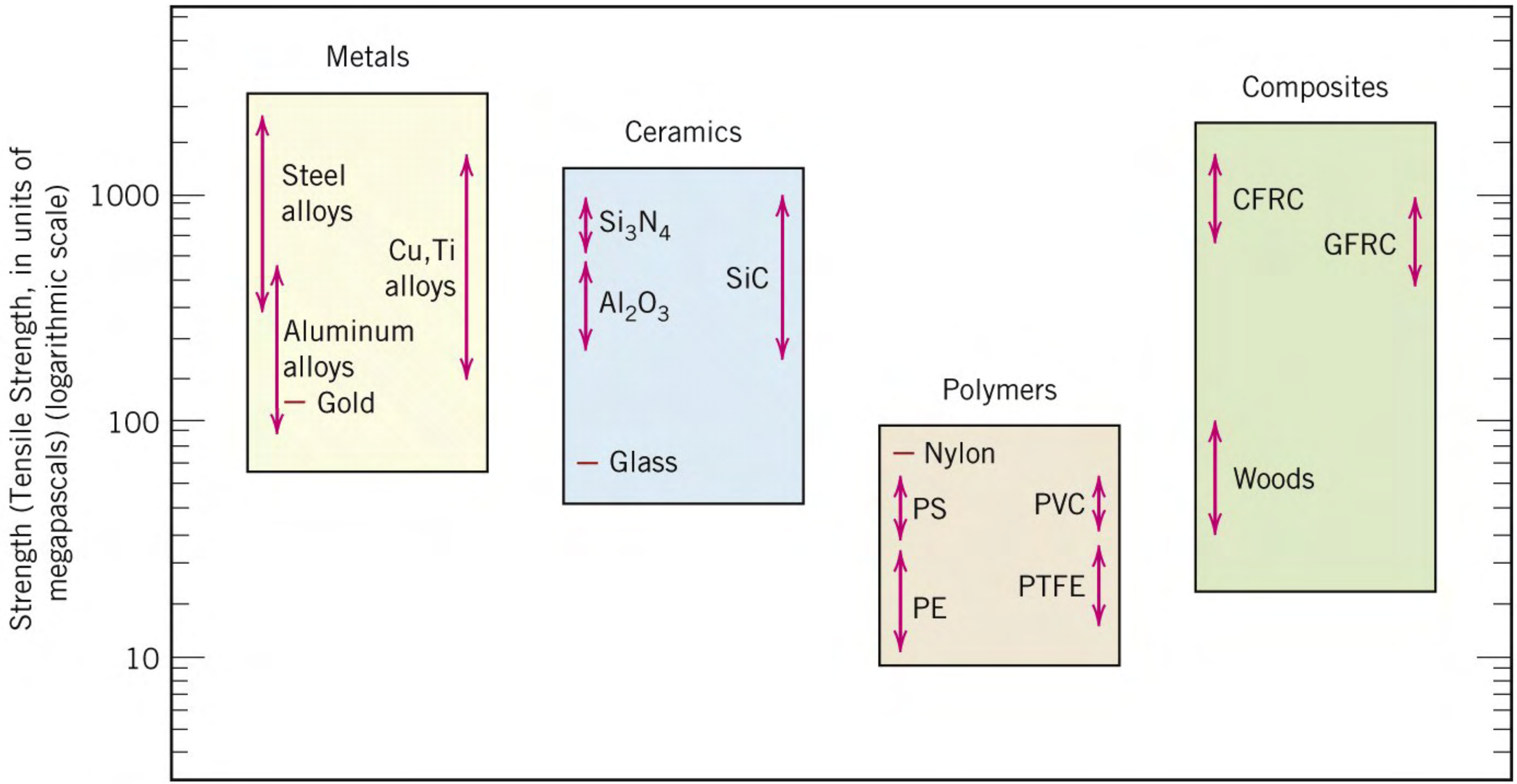


Figure 1.5

Fracture Toughness of Solid Materials

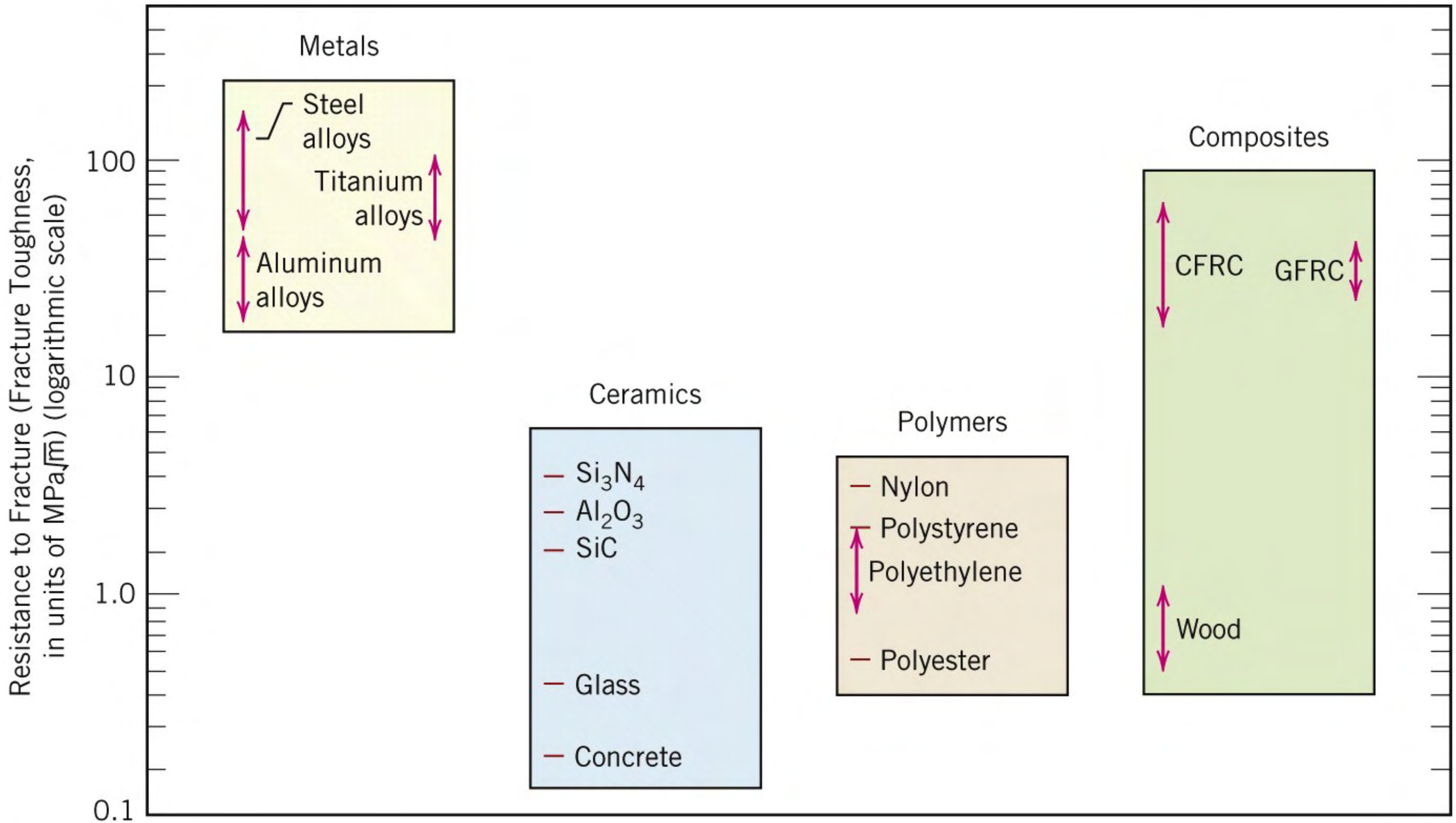
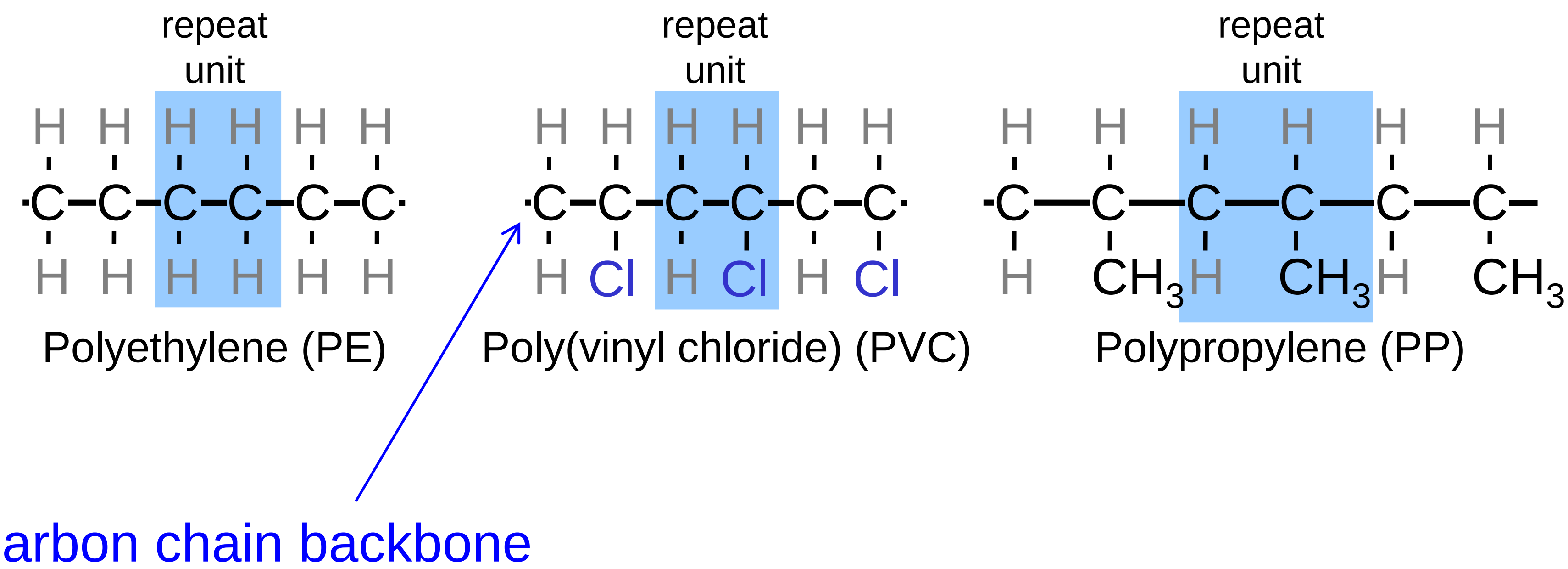


Figure 1.6

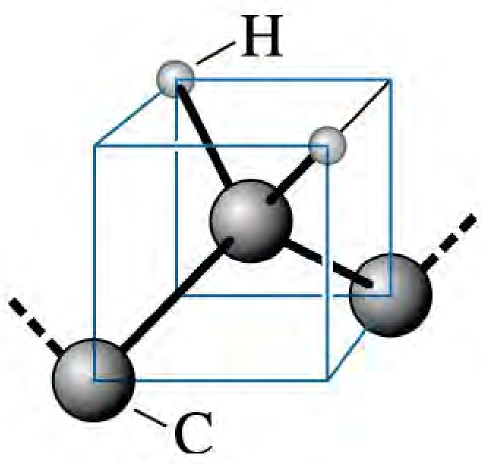
Polymers

POLY + **MER**

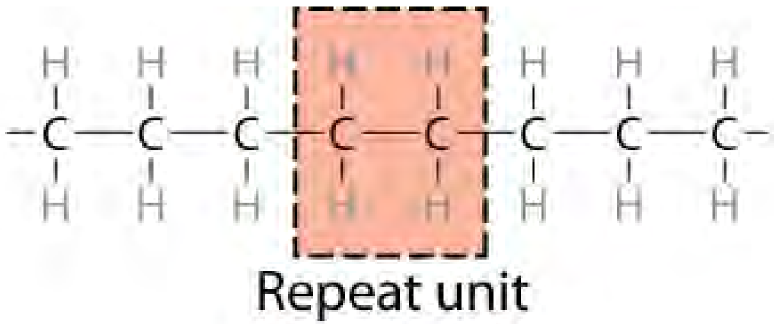
many — **repeat unit (building blocks)**

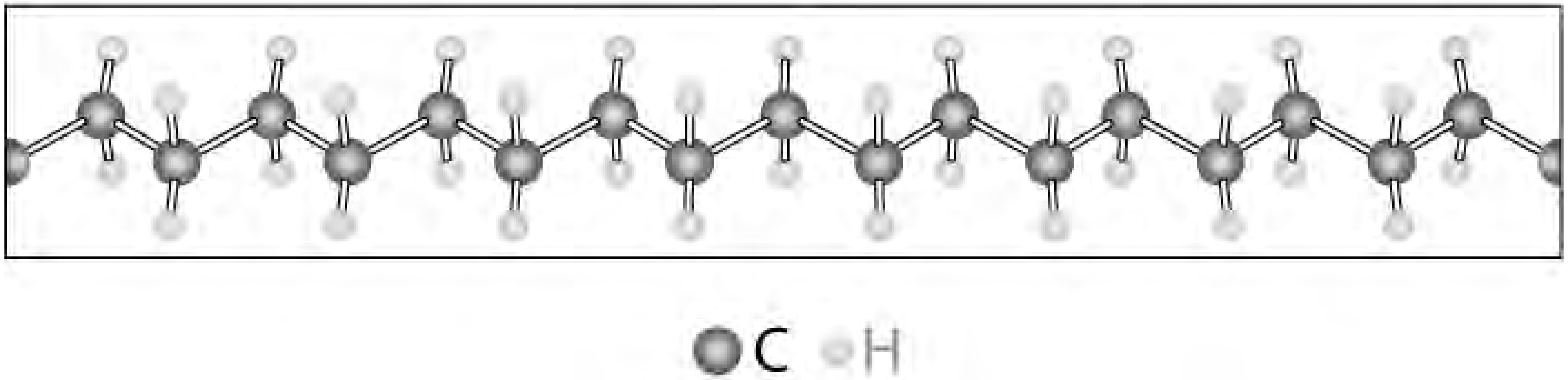


Chemistry and Structure of Polyethylene



Tetrahedral arrangement of C-H





- Polyethylene is a long-chain hydrocarbon.
- Top figure shows repeat unit and chain structures.
- Other figure shows zigzag backbone structure.

Ancient Polymers

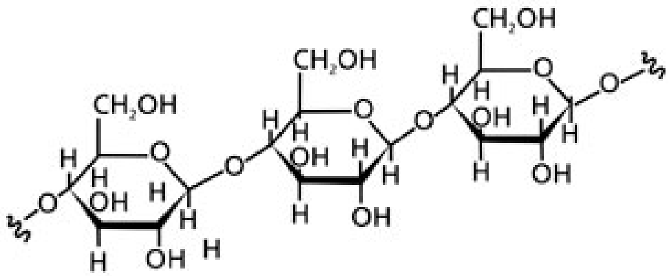
- **Naturally occurring polymers (those derived from plants and animals) have been used for centuries.**
  - **Wood**
  - **Rubber**
  - **Cotton**
  - **Wool**
  - **Leather**
  - **Silk**

- **Oldest known uses: Rubber balls used by Incas**

http://anthropology.msu.edu/anp264-us13/2013/08/06/mesoamerican-technologies/

Cellulose

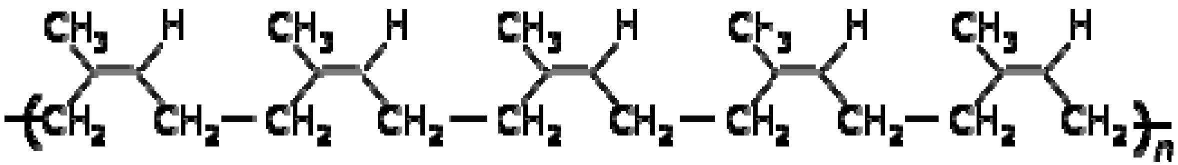
- **Cellulose is a highly abundant organic compound. Extensive hydrogen bonding between the chains causes native cellulose to be roughly 70% crystalline. It also raises the melting point (>280°C) to above its combustion temperature.**
- **Cellulose serves as the principal structural component of green plants and wood.**
- **Cotton is one of the purest forms of cellulose and has been cultivated since ancient times.**



Cellulose molecule

Rubber

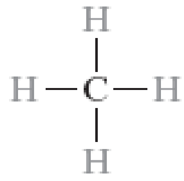
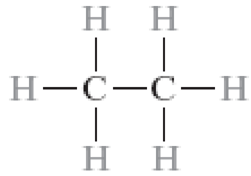
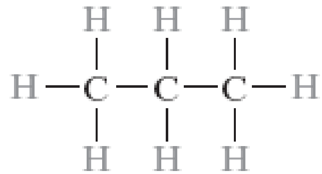
- A variety of plants produce a sap consisting of a colloidal dispersion of *cis*-polyisoprene. This milky fluid is especially abundant in the rubber tree (*Hevea*); it drips when the bark is wounded.
- After collection, the latex is coagulated to obtain the solid rubber. Natural rubber is thermoplastic, with a glass transition temperature of –70°C.
- Raw natural rubber tends to be sticky when warm and brittle when cold, so it was little more than a novelty material when first introduced in Europe around 1770.
- It did not become generally useful until the mid-nineteenth century when Charles Goodyear found that heating it with sulfur — a process he called *vulcanization* — could greatly improve its properties.



cis-polyisoprene

Saturated Hydrocarbons

- **Each carbon has a single bond to 4 other atoms; the 4 valence electrons are bonded, the molecule is stable. Examples are seen in the table.**
- **The covalent bonds in each molecule are strong, but only weak hydrogen and van der Waals bonds exist between the molecules.**

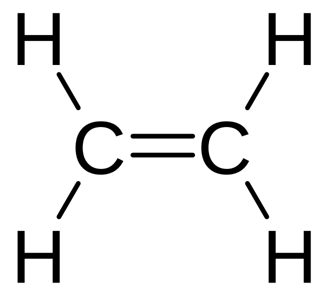
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

- Most of these hydrocarbons have relatively low melting and boiling points.
- However, boiling temperatures rise with increasing molecular weight.

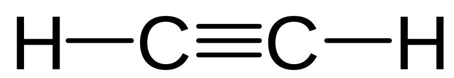
Unsaturated Hydrocarbons

- **Double & triple bonds are somewhat unstable – involve sharing 2 or 3 pairs of electrons, respectively. They can also form new bonds.**

  - **Double bond found in ethylene - C_2H_4**



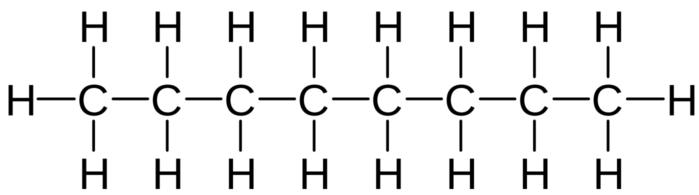
  - **Triple bond found in acetylene - C_2H_2**



Isomerism

- **Two compounds with same chemical formula can have different structures (atomic arrangements).**
- **for example: C_8H_{18}**

- **normal-octane**

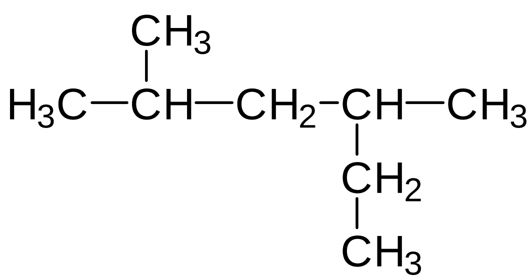


$$= H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

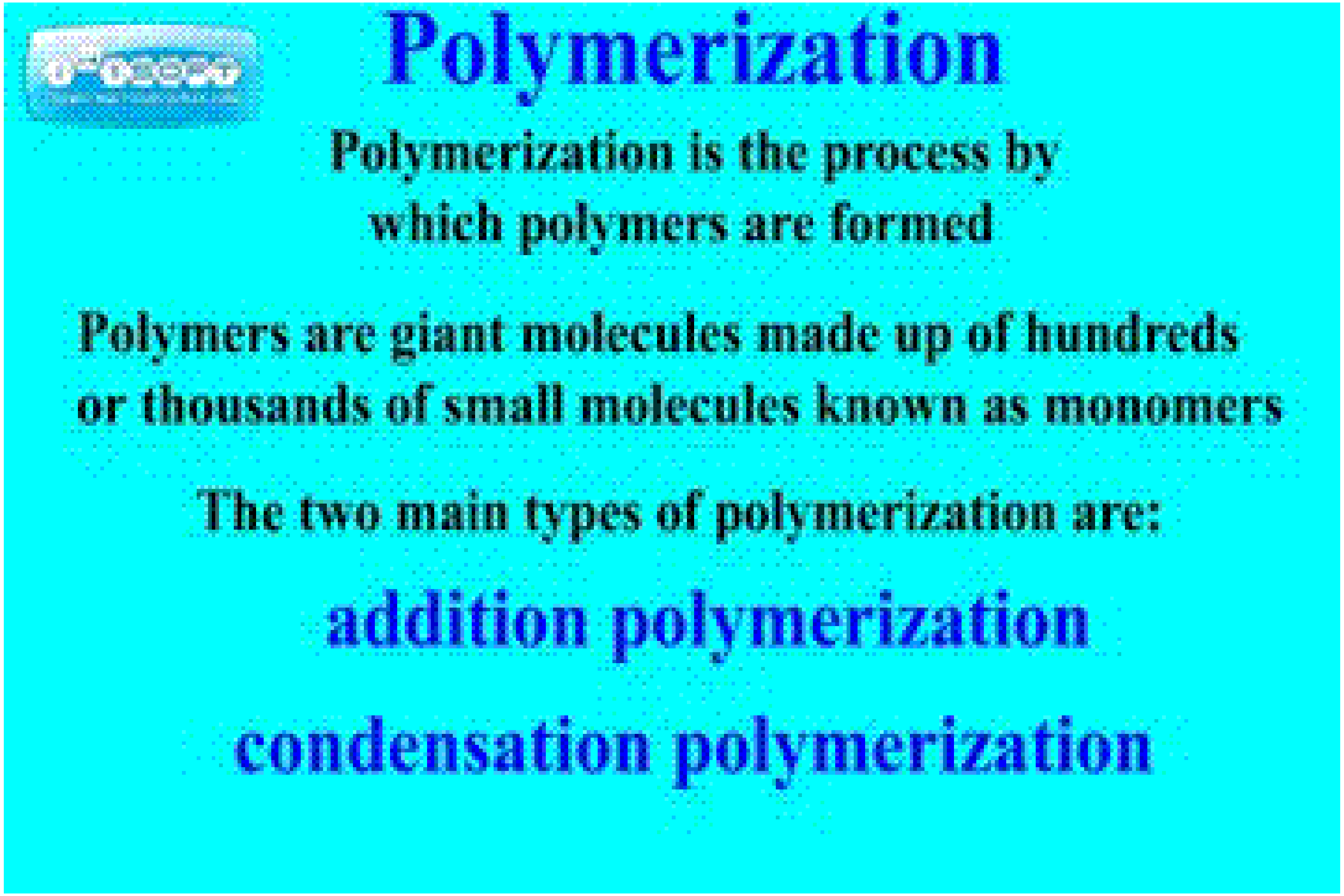
$$\Downarrow$$

$$H_3C\!-\!(CH_2)_6\!-\!CH_3$$

- **2,4-dimethylhexane**

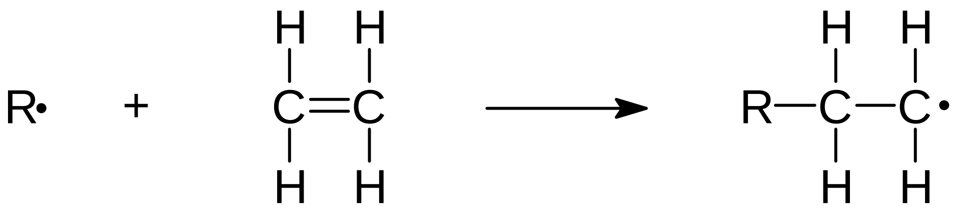


Types of Polymerization



https://www.youtube.com/watch?v=YzGZl-J0wWQ

Addition (Chain) Polymerization

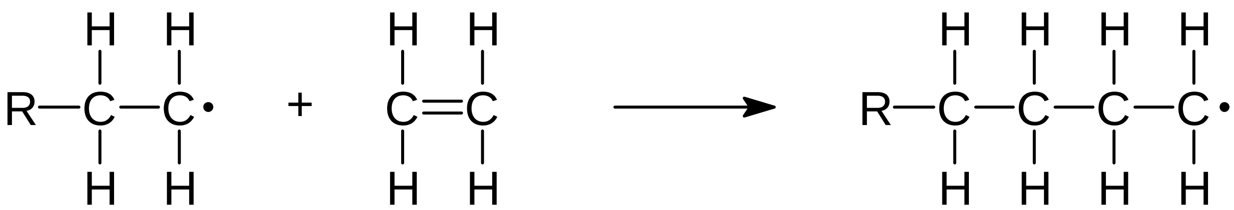


initiation

free radical

monomer
(ethylene)

Monomer refers to the small molecule from which a polymer is synthesized.



propagation

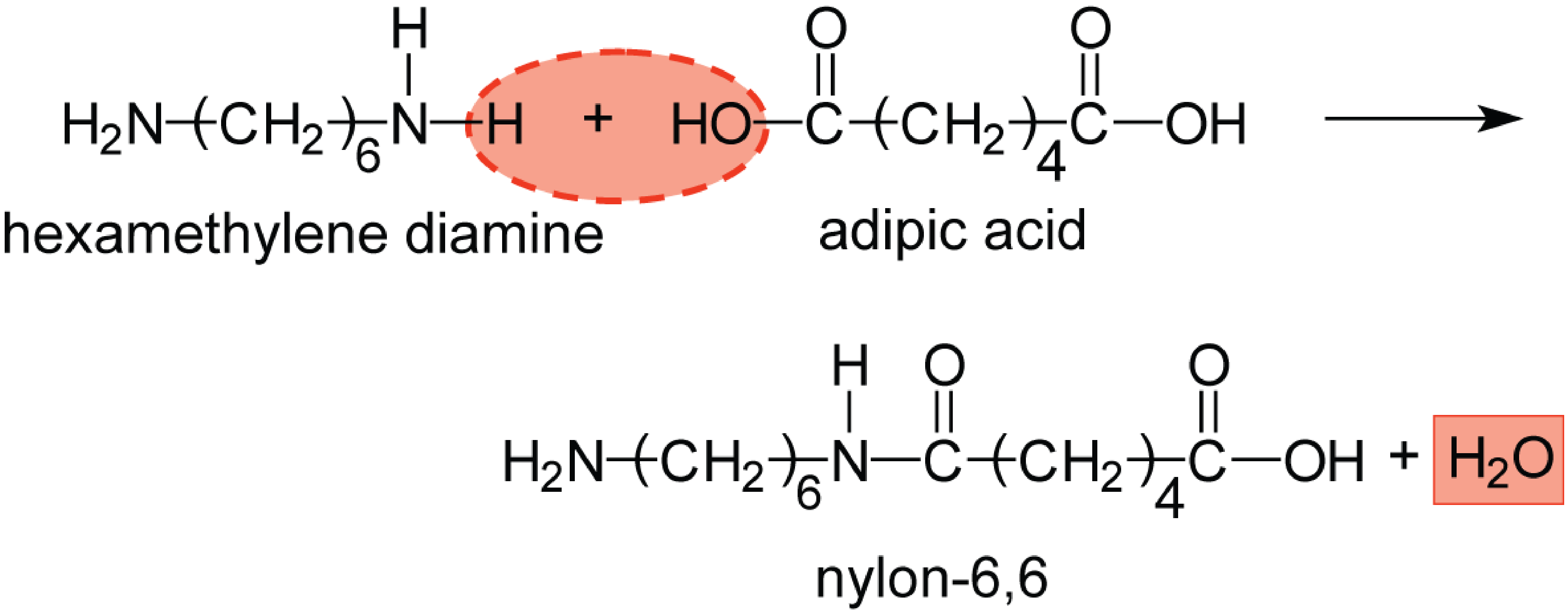
dimer

- R = metal chlorides or metal oxides

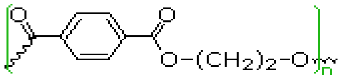
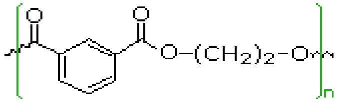
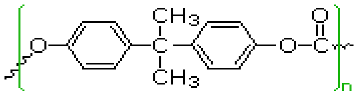
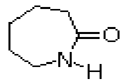
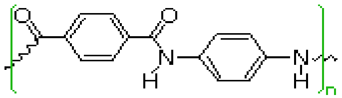
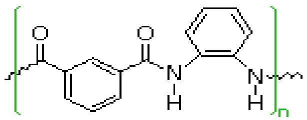
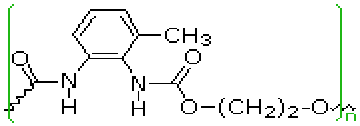
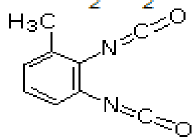
Some Addition Polymers

Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$–(CH_2-CH_2)_n–$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$–(CH_2-CH_2)_n–$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$–[CH_2-CH(CH_3)]_n–$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$–(CH_2-CHCl)_n–$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$–(CH_2-CCl_2)_n–$	vinylidene chloride $CH_2=CCl_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$–[CH_2-CH(C_6H_5)]_n–$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$–(CH_2-CHCN)_n–$	acrylonitrile $CH_2=CHCN$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$–(CF_2-CF_2)_n–$	tetrafluoroethylene $CF_2=CF_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$–[CH_2-C(CH_3)CO_2CH_3]_n–$	methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$–(CH_2-CHOCOCH_3)_n–$	vinyl acetate $CH_2=CHOCOCH_3$	soft, sticky solid	latex paints, adhesives
cis-Polyisoprene natural rubber	$–[CH_2-CH=C(CH_3)-CH_2]_n–$	isoprene $CH_2=CH-C(CH_3)=CH_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$–[CH_2-CH=CCl-CH_2]_n–$	chloroprene $CH_2=CH-CCl=CH_2$	tough, rubbery solid	synthetic rubber oil resistant

Condensation Polymerization



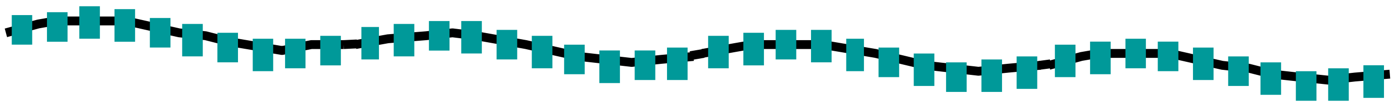
Some Condensation Polymers

Formula	Type	Components	T_g °C	T_m °C
~$[CO(CH_2)_4CO\text{-}OCH_2CH_2O]_n$~	**polyester**	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	< 0	50
	**polyester** Dacron Mylar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	70	265
	**polyester**	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	50	240
	**polycarbonate** Lexan	$(HO\text{-}C_6H_4\text{-})_2C(CH_3)_2$ (Bisphenol A) $X_2C=O$ ($X = OCH_3$ or Cl)	150	267
~$[CO(CH_2)_4CO\text{-}NH(CH_2)_6NH]_n$~	**polyamide** Nylon 66	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $H_2N\text{-}(CH_2)_6\text{-}NH_2$	45	265
~$[CO(CH_2)_5NH]_n$~	**polyamide** Nylon 6 Perlon		53	223
	**polyamide** Kevlar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ para $H_2N\text{-}C_6H_4\text{-}NH_2$	---	500
	**polyamide** Nomex	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ meta $H_2N\text{-}C_6H_4\text{-}NH_2$	273	390
	**polyurethane** Spandex	$HOCH_2CH_2OH$ 	52	---

Molecular Weight

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

- Low *M*



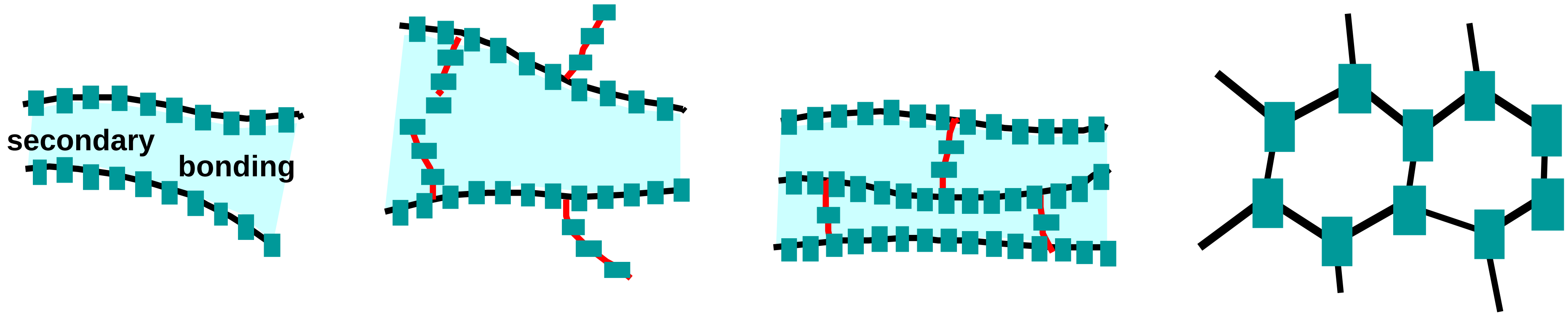
- high *M*

- Polymers can have various lengths depending on the number of repeat units.
- During the polymerization process not all chains in a polymer grow to the same length, so there is a distribution of molecular weights. There are several ways of defining an average molecular weight.
- The molecular weight distribution in a polymer describes the relationship between the number of moles of each polymer species and the molar mass of that species.

Polymer Chain Lengths

- Many polymer properties are affected by the length of the polymer chains. For example, the melting temperature increases with increasing molecular weight.
- At room temp, polymers with very short chains (roughly 100 g/mol) will exist as liquids.
- Those with weights of 1000 g/mol are typically waxy solids and soft resins.
- Solid polymers range between 10,000 and several million g/mol.
- The molecular weight affects the polymer’s properties (examples: elastic modulus & strength).

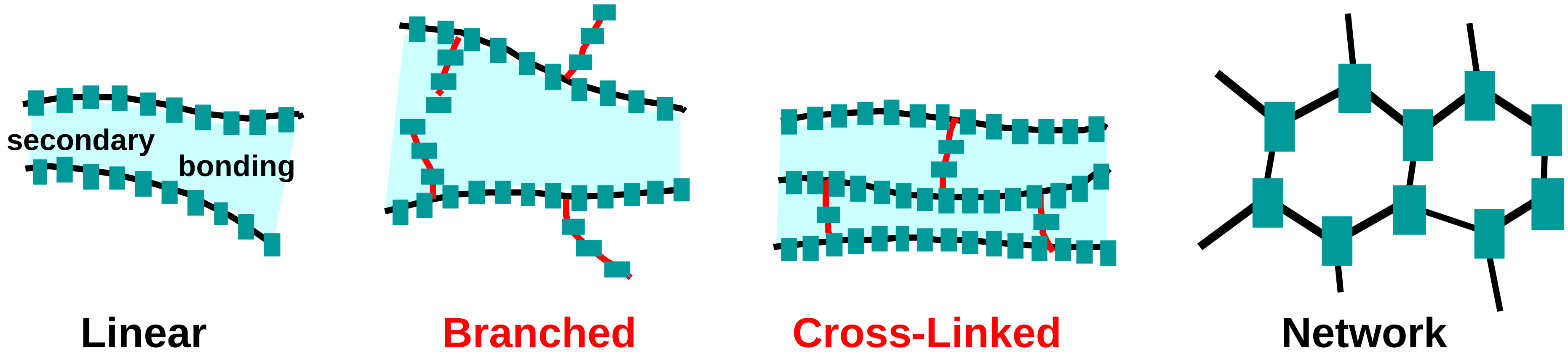
Molecular Structures for Polymers



Linear | Branched | Cross-Linked | Network

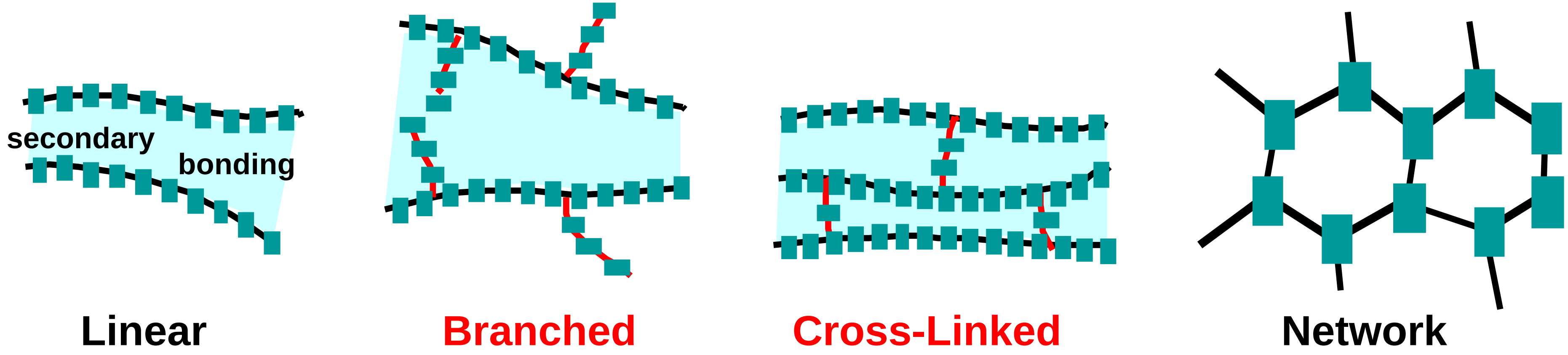
- **The physical characteristics of a polymer depend also on differences in the structure of the molecular chains (other variables are shape and weight).**
- **Linear polymers have repeat units joined end to end in single chains. There may be extensive van der Waals and hydrogen bonding between the chains. Examples: polyethylene, PVC, nylon.**

Molecular Structures for Polymers



- Where side-branch chains have connected to main chains, these are termed **branched polymers.** Linear structures may have side-branching.
- HDPE – high density polyethylene is primarily a linear polymer with minor branching, while LDPE – low density polyethylene contains numerous short chain branches.
- Greater chain linearity and chain length tend to increase the melting point and improve the physical and mechanical properties of the polymer due to greater crystallinity.

Molecular Structures for Polymers



- In **cross-linked** polymers, adjacent linear chains are joined to one another at various positions by covalent bonding of atoms. Examples are the rubber elastic materials.

- Small molecules that form 3 or more active covalent bonds create structures called **network polymers**. Examples are the epoxies and polyurethanes.

Thermoplastics and Thermosets

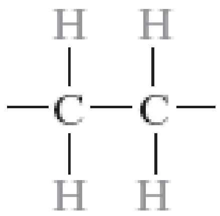
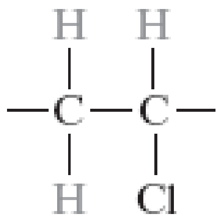
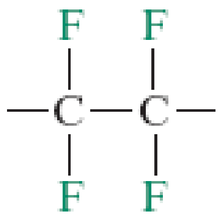
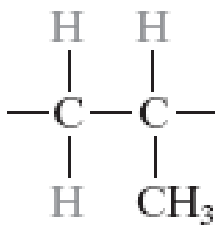
- **The response of a polymer to mechanical forces at elevated temperature is related to its dominant molecular structure.**
- **One classification of polymers is according to its behavior and rising temperature. Thermoplastics and Thermosets are the 2 categories.**
- **A thermoplastic is a polymer that turns to a liquid when heated and freezes to a very glassy state when cooled sufficiently.**
- **Most thermoplastics are high-molecular-weight polymers whose chains associate through weak Van der Waals forces (polyethylene); stronger dipole-dipole interactions and hydrogen bonding (nylon).**

Thermoplastics and Thermosets

- Thermoplastic polymers differ from thermosetting polymers (Bakelite, vulcanized rubber) since thermoplastics can be remelted and remolded.
- Thermosetting plastics when heated, will chemically decompose, so they can not be recycled. Yet, once a thermoset is cured it tends to be stronger than a thermoplastic.
- Typically, linear polymers with minor branched structures (and flexible chains) are thermoplastics. The networked structures are thermosets.

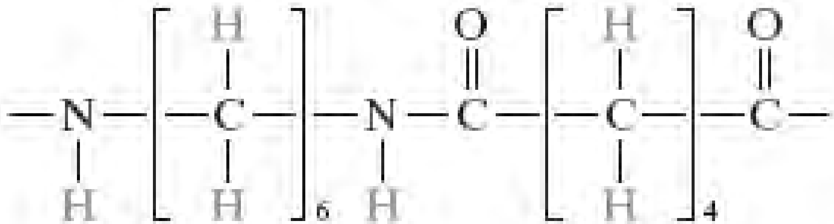
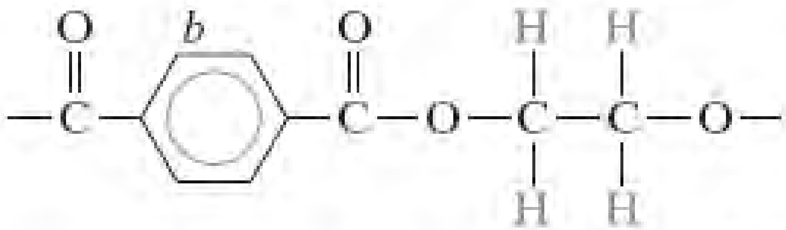
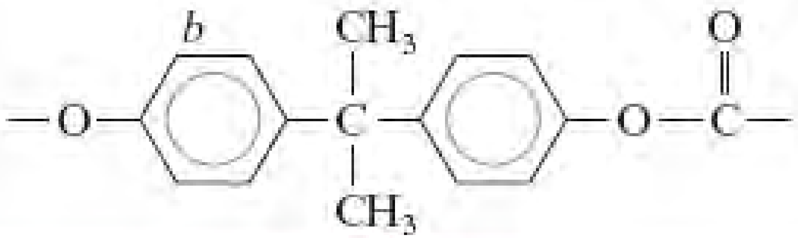
Examples of Thermoplastics

Table 4.3 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)	

Examples of Thermoplastics

Table 4.3 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)	

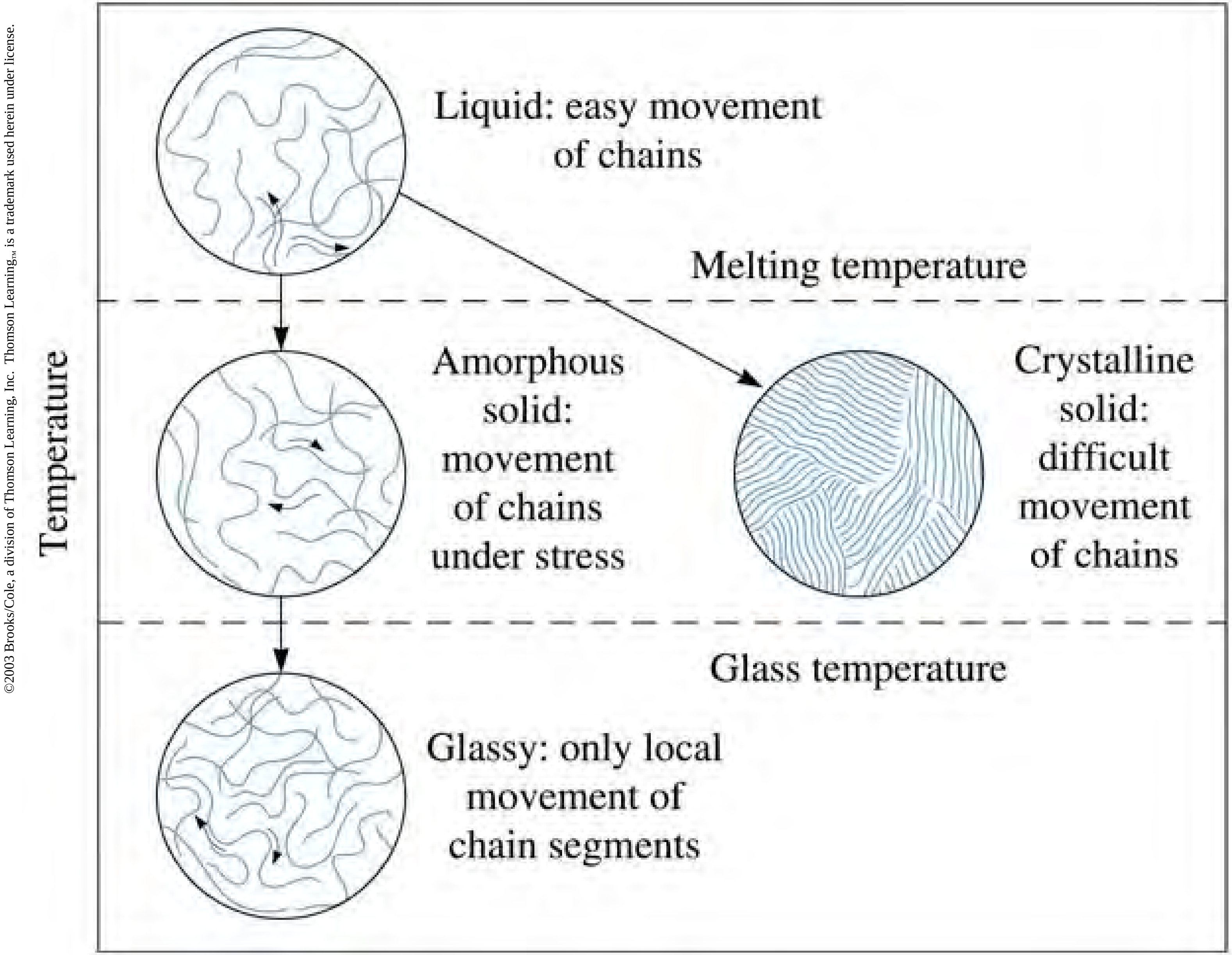
Specific Thermoplastic Properties

	Tensile Strength (psi)	% Elongation	Elastic Modulus (psi)	Density (g/cm^3)	Izod Impact (ft lb/in.)
Polyethylene (PE):					
Low-density	3,000	800	40,000	0.92	9.0
High-density	5,500	130	180,000	0.96	4.0
Ultrahigh molecular weight	7,000	350	100,000	0.934	30.0
Polyvinyl chloride (PVC)	9,000	100	600,000	1.40	
Polypropylene (PP)	6,000	700	220,000	0.90	1.0
Polystyrene (PS)	8,000	60	450,000	1.06	0.4
Polyacrylonitrile (PAN)	9,000	4	580,000	1.15	4.8
Polymethyl methacrylate (PMMA) (acrylic, Plexiglas)	12,000	5	450,000	1.22	0.5
Polychlorotrifluoroethylene	6,000	250	300,000	2.15	2.6
Polytetrafluoroethylene (PTFE, Teflon)	7,000	400	80,000	2.17	3.0
Polyoxymethylene (POM) (acetal)	12,000	75	520,000	1.42	2.3
Polyamide (PA) (nylon)	12,000	300	500,000	1.14	2.1
Polyester (PET)	10,500	300	600,000	1.36	0.6
Polycarbonate (PC)	11,000	130	400,000	1.20	16.0
Polyimide (PI)	17,000	10	300,000	1.39	1.5
Polyetheretherketone (PEEK)	10,200	150	550,000	1.31	1.6
Polyphenylene sulfide (PPS)	9,500	2	480,000	1.30	0.5
Polyether sulfone (PES)	12,200	80	350,000	1.37	1.6
Polyamide-imide (PAI)	27,000	15	730,000	1.39	4.0

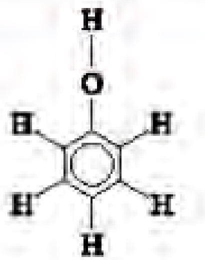
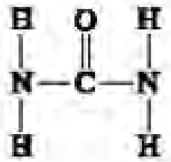
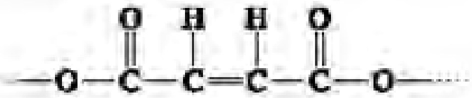
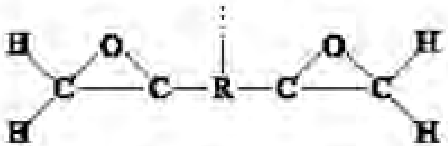
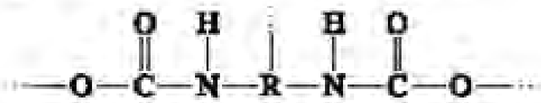
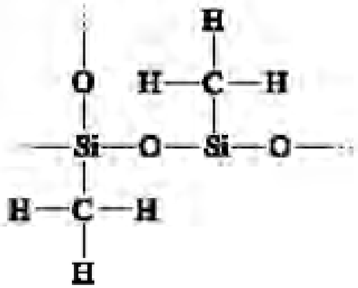
1 ksi ≅ 6.9 MPa

Behavior of Thermoplastics

- **The effect of temperature on the structure:**



Examples of Thermoset

Polymer	Functional Units	Typical Applications
Phenolics		Adhesives, coatings, laminates
Amines		Adhesives, cookware, electrical moldings
Polyesters		Electrical moldings, decorative laminates, polymer matrix in fiberglass
Epoxies		Adhesives, electrical moldings, matrix for composites
Urethanes		Fibers, coatings, foams, insulation
Silicone		Adhesives, gaskets, sealants

Thermoset Properties

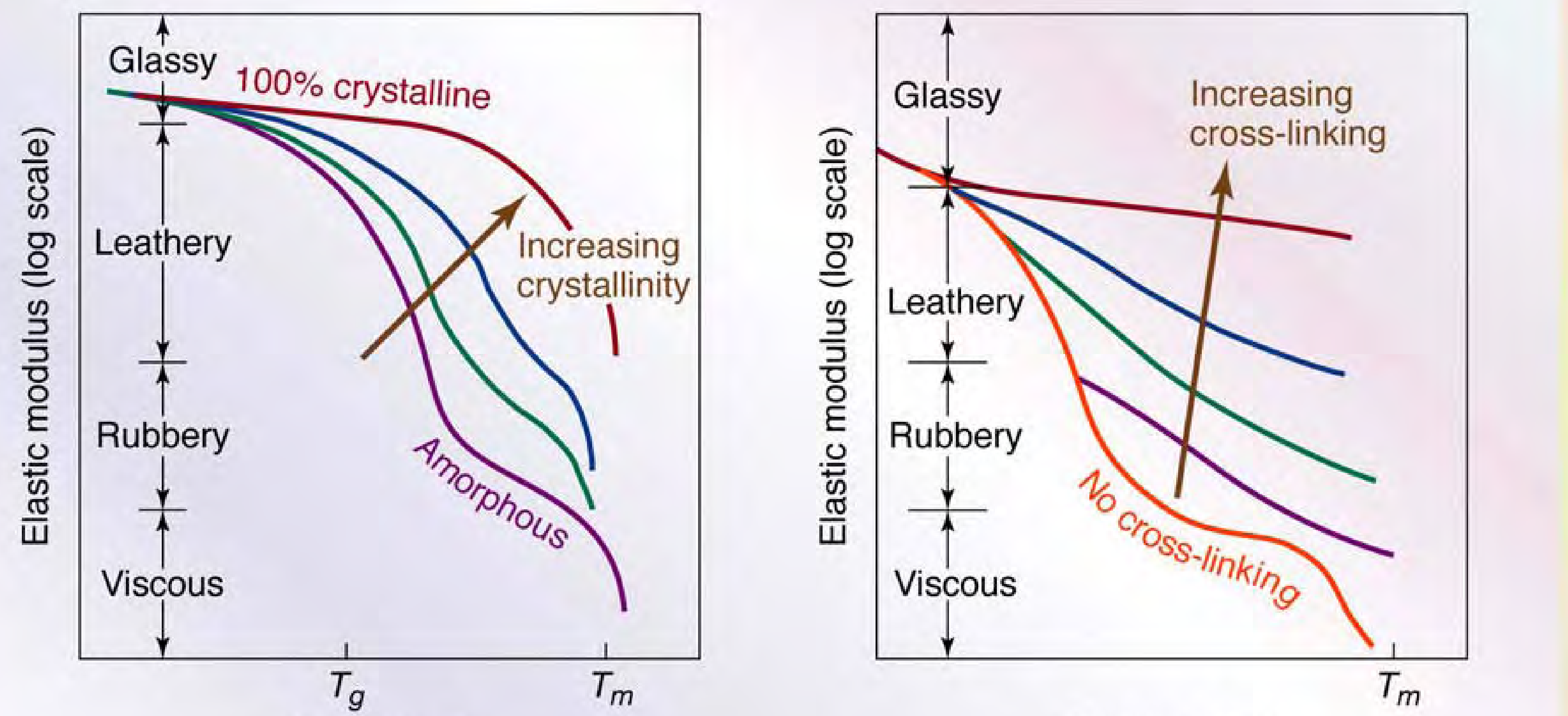
	Tensile Strength (psi)	% Elongation	Elastic Modulus (psi)	Density (g/cm^3)
Phenolics	9,000	2	1300	1.27
Amines	10,000	1	1600	1.50
Polyesters	13,000	3	650	1.28
Epoxies	15,000	6	500	1.25
Urethanes	10,000	6		1.30
Silicone	4,000	0	1200	1.55

Specific Elastomeric Properties

➢ **Elastomers**, often referred to as rubber, can be a thermoplastic or a thermoset depending on the structure. They are excellent for parts requiring flexibility, strength and durability.

	Tensile Strength (psi)	% Elongation	Density (g/cm^3)
Polyisoprene	3000	800	0.93
Polybutadiene	3500		0.94
Polyisobutylene	4000	350	0.92
Polychloroprene (Neoprene)	3500	800	1.24
Butadiene-styrene (BS or SBR rubber)	3000	2000	1.0
Butadiene-acrylonitrile	700	400	1.0
Silicones	1000	700	1.5
Thermoplastic elastomers	5000	1300	1.06

Thermoplastic vs Thermoset

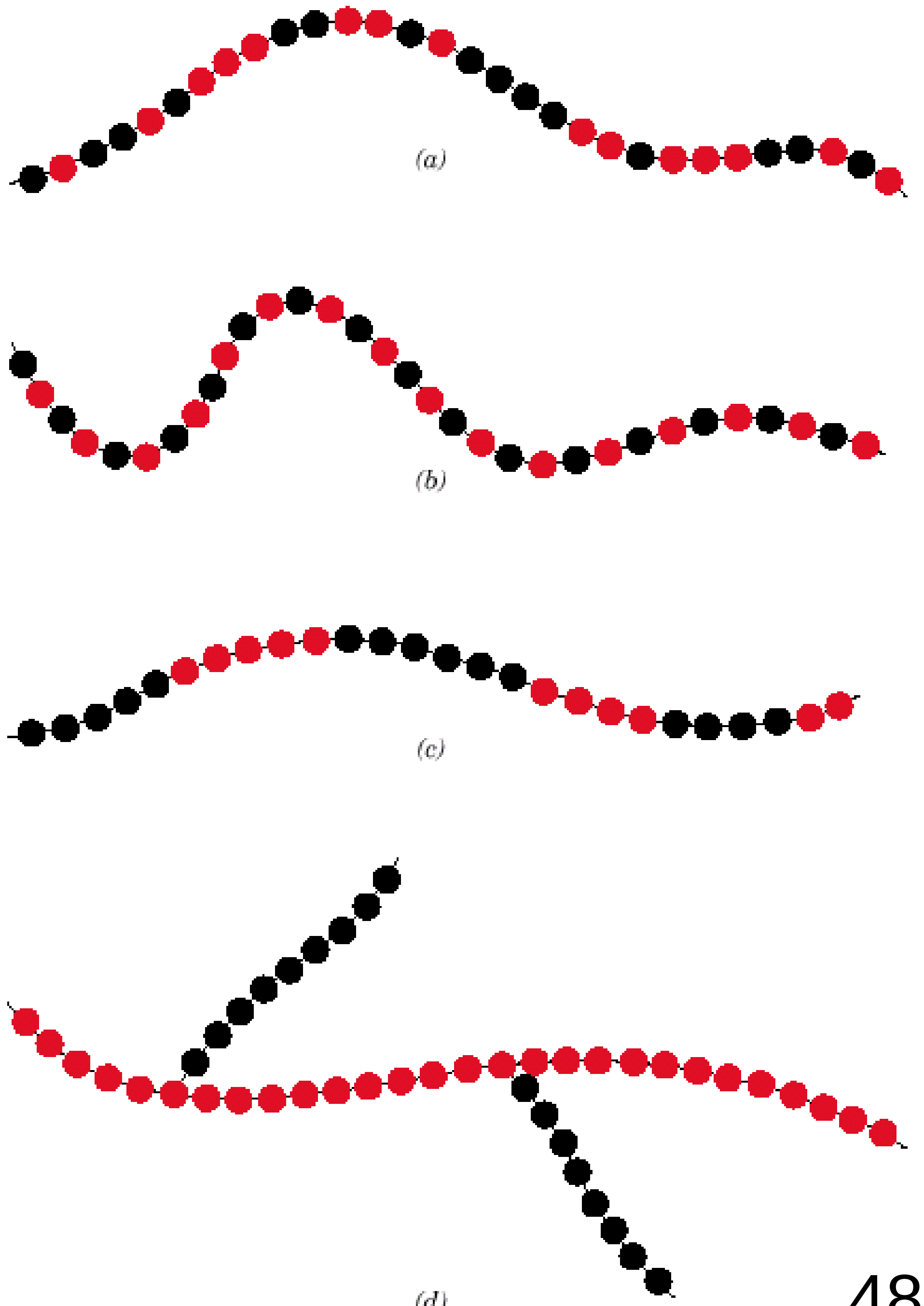


- **Thermoplastics**:
- <u>little cross linking, </u>ductile, soften with heating (PE, PP, PC, PS).
- **Thermosets**:
- <u>large cross linking</u> (10 to 50% of mers)
- hard and brittle, do NOT soften with heating
- vulcanized rubber, epoxies, polyester resin, phenolic resin

Copolymers

two or more monomers polymerized together

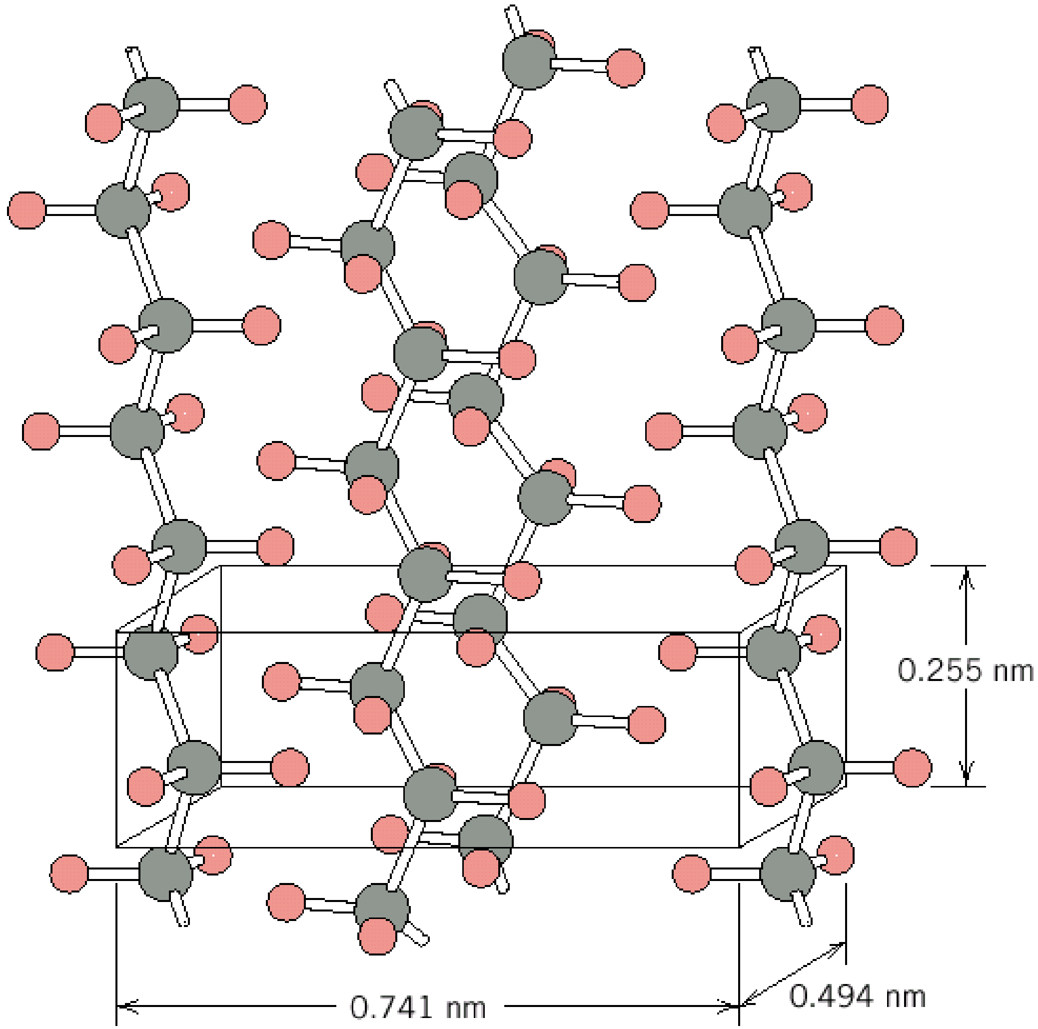
- **random – A and B randomly positioned along chain**
- **alternating – A and B alternate in polymer chain**
- **block – large blocks of A units alternate with large blocks of B units**
- **graft – chains of B units grafted onto A backbone**



A – ● **B – ●**

Crystallinity in Polymers

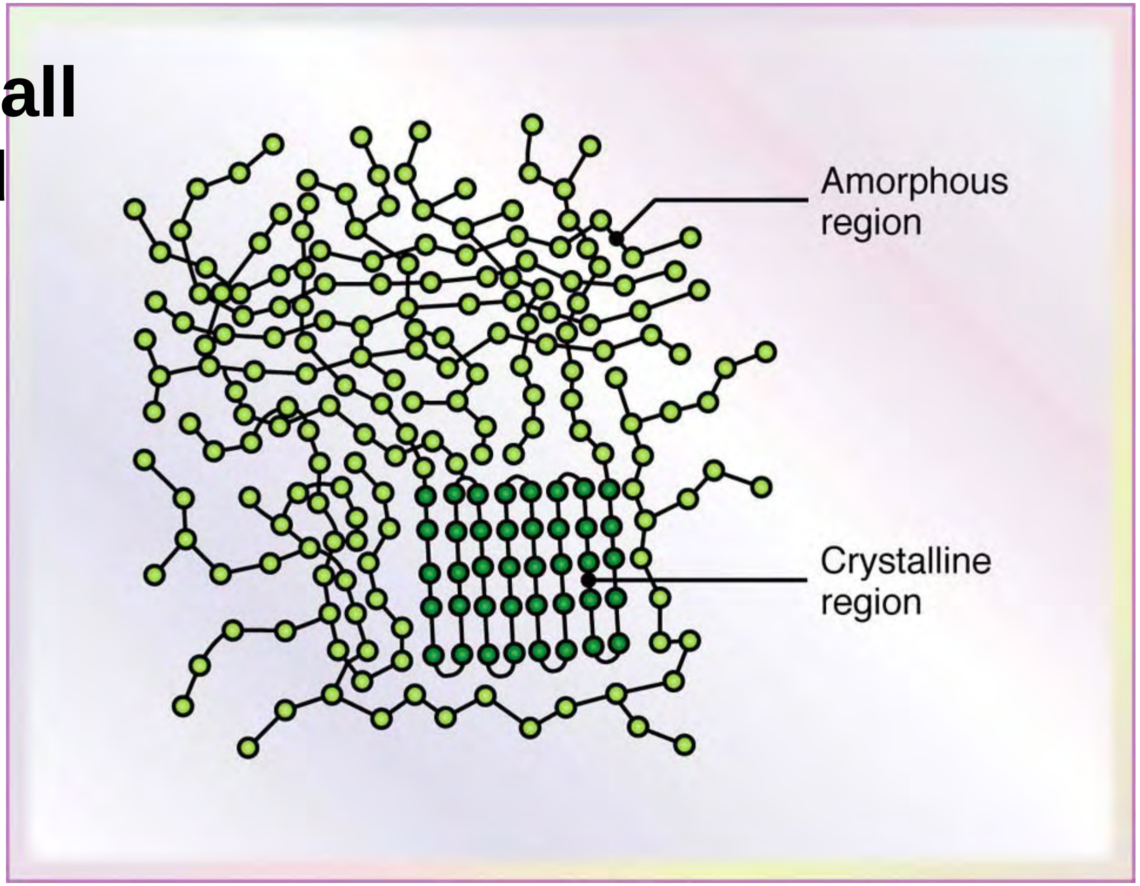
- **The crystalline state may exist in polymeric materials.**
- **However, since it involves molecules instead of just atoms or ions, as with metals or ceramics, the atomic arrangement will be more complex for polymers.**
- **There are ordered atomic arrangements involving molecular chains.**
- **Example shown is a polyethylene unit cell** (orthorhombic).



Polymer Crystallinity

Polymers are rarely 100% crystalline

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



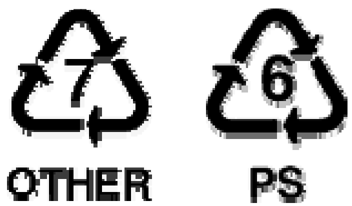
- **Degree of crystallinity expressed as % crystallinity.**
  - **-- Some physical properties depend on % crystallinity.**
  - **-- Heat treating causes crystalline regions to grow and % crystallinity to increase.**

Plastic Recycling Symbols

In 1988 the Society of the Plastics Industry developed a numeric code to provide a uniform convention for different types of plastic containers.

These numbers can be found on the underside of containers:

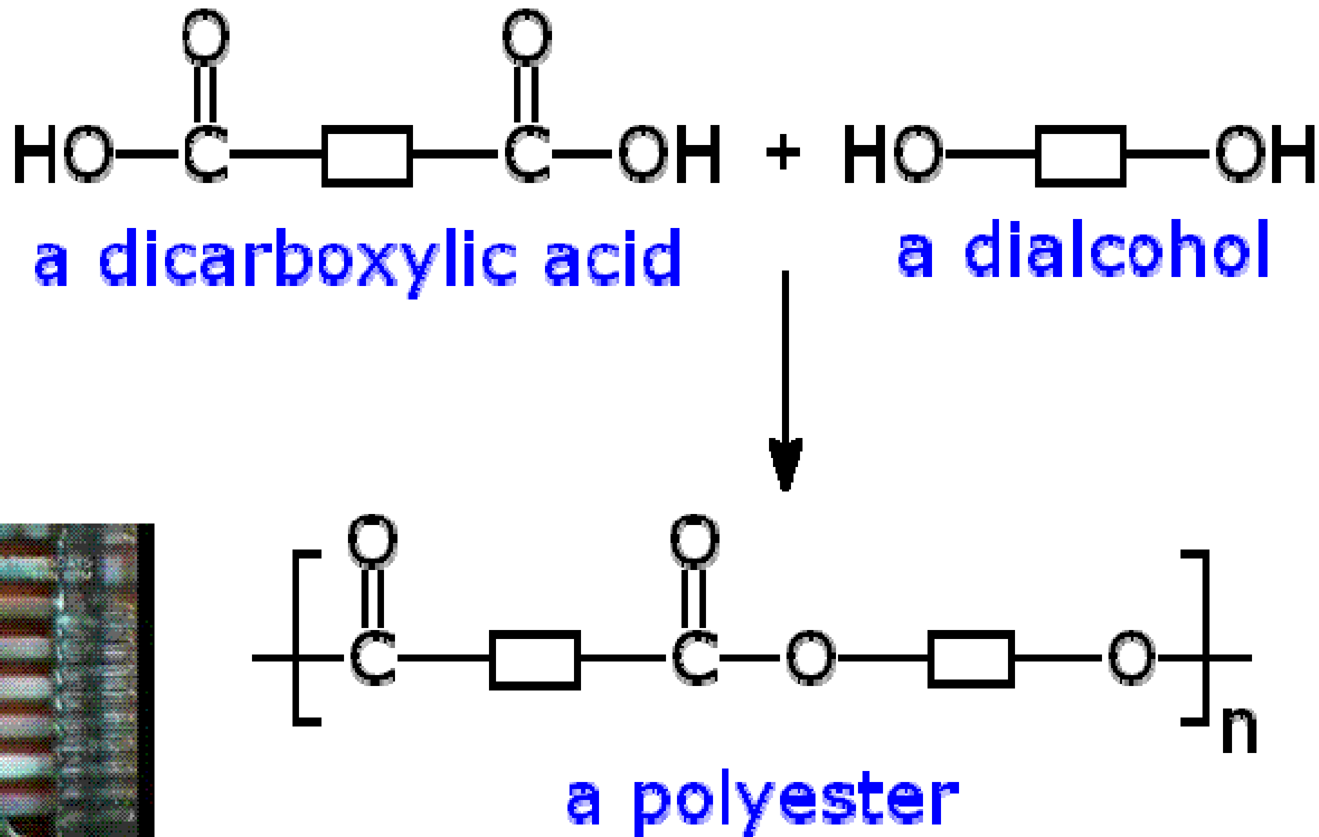
1. **PET; PETE (polyethylene terephthalate): plastic water and soda bottles.**
2. **HDPE (high density polyethylene): laundry/dish detergent**
3. **V (Vinyl) or PVC: Pipes, shower curtains**
4. **LDPE (low density polyethylene): grocery bags, sandwich bags**
5. **PP (polypropylene): Tupperware®, syrup bottles, yogurt cups,**
6. **PS (polystyrene): Coffee cups, disposable cutlery**
7. **Miscellaneous: any combination of 1-6 plastics**



How Plastic Bottles Are Recycled Into Polyester

1

PETE



https://www.youtube.com/watch?v=zyF9MxlcItw

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