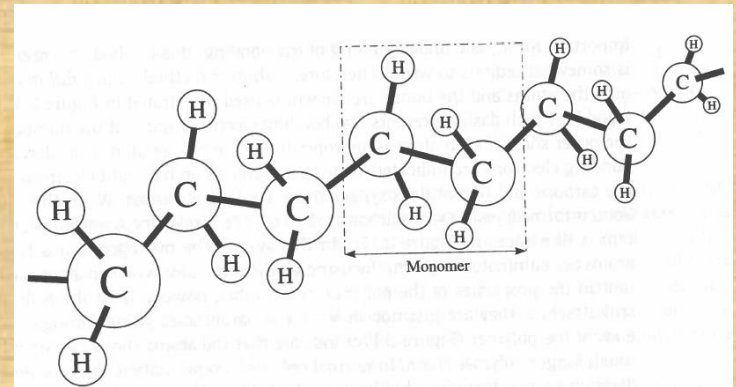


Structure and Properties of Engineering Polymers

Lecture: **Polymeric Materials: Molecular Viewpoint**

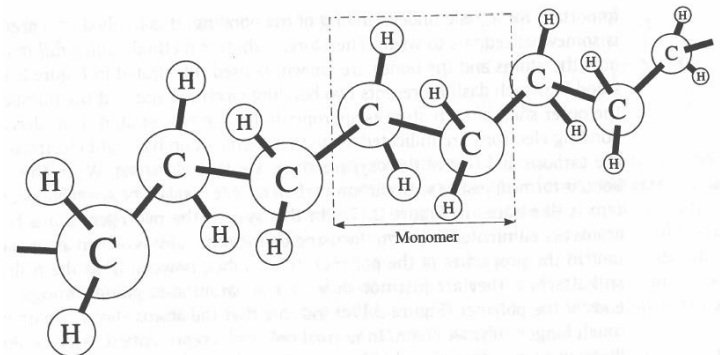
Nikolai V. Priezjev



Textbook: *Plastics: Materials and Processing* (Third Edition), by A. Brent Young (Pearson, NJ, 2006).

Polymeric Materials: Molecular Viewpoint

- Periodic table of elements, number of protons, electrons, neutrons; atomic weight, electron orbitals, and octet rule
- Covalent bonding, bond energy, carbon atom bonding, hybridization
- Secondary Bonding: dipole hydrogen bonds, van der Waals forces
- Ionic and Metallic bonding
- Functional groups, formation of polymers
- Thermoplastics and thermosets
- Copolymers



Reading: Chapter 2 of *Plastics: Materials and Processing* by A. Brent Strong

Periodic Table of the Elements																	18
1 IA 1A																	2 VIII 8A
1 H Hydrogen 1.008	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIII 8A
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIII 8A
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Dmitri Mendeleev
published the first
periodic table in
1869.

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide
-----------------	-------------------	---------------------	----------------	-----------	----------	---------	--------------	------------	----------

19	Atomic number (a.n.)
K	symbol
Potassium	
39	Atomic mass (a.m.)

Neutron = $1.6749286 \cdot 10^{-27}$ kg
Proton = $1.6726231 \cdot 10^{-27}$ kg
Electron = $9.1093897 \cdot 10^{-31}$ kg
M proton = 1837 M electron

For K: 19 protons = number of electrons
19 electrons
20 neutrons (39 – 19)

Carbon Atom

protons = 6
neutrons = 6

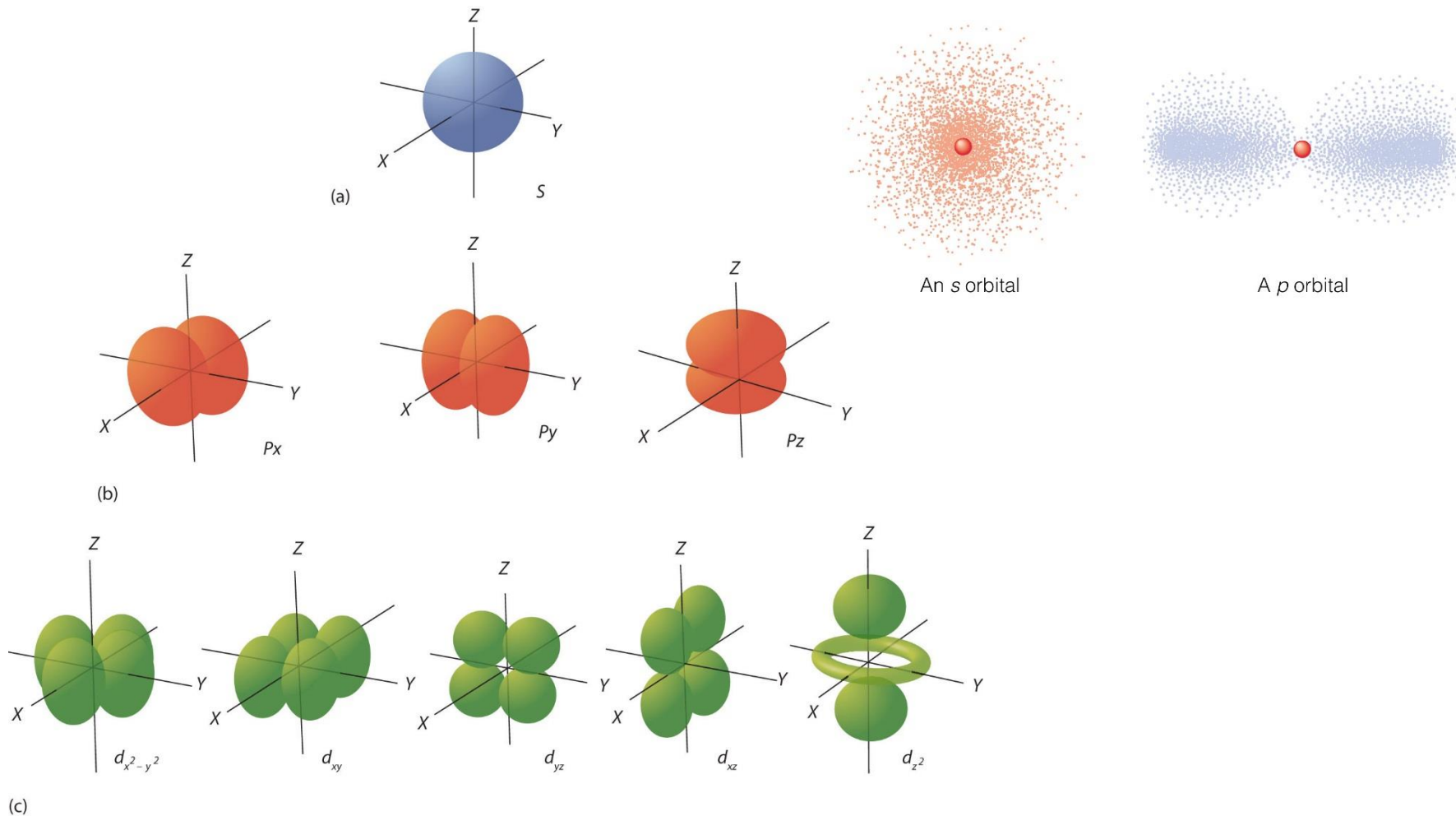
$6 + 6 = 12$

Atomic Mass = 12

● - neutron
● - proton
● - electron

A.N. – number of protons or electrons
A.M. – number of protons and neutrons
(neutron number = A.M. – A.N.)

Electron Configuration: Electron Orbitals



(a) The lone s orbital is spherical in distribution. (b) The three p orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five d orbitals are rosette in shape, except for the d_{z^2} orbital, which is a “dumbbell + torus” combination. They are all oriented in different directions.

Heisenberg principle and Schrödinger cat experiment

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

Heisenberg and Schrödinger get pulled over for speeding.

The cop asks Heisenberg "Do you know how fast you were going?"

Heisenberg replies, "No, but we know exactly where we are!"

The officer looks at him confused and says "you were going 108 miles per hour!"

Heisenberg throws his arms up and cries, "Great! Now we're lost!"

The officer looks over the car and asks Schrödinger if the two men have anything in the trunk.

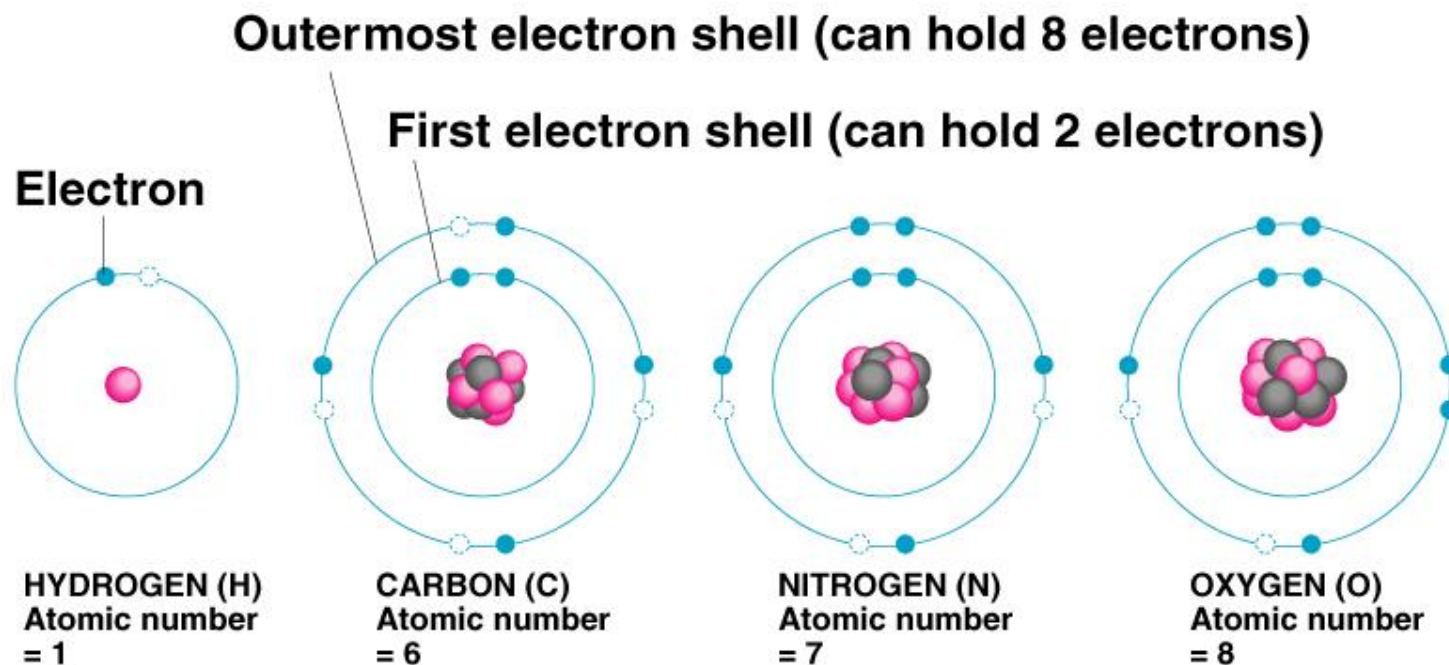
"A cat," Schrödinger replies.

The cop opens the trunk and yells "Hey! This cat is dead."

Schrödinger angrily replies, "Well he is now."



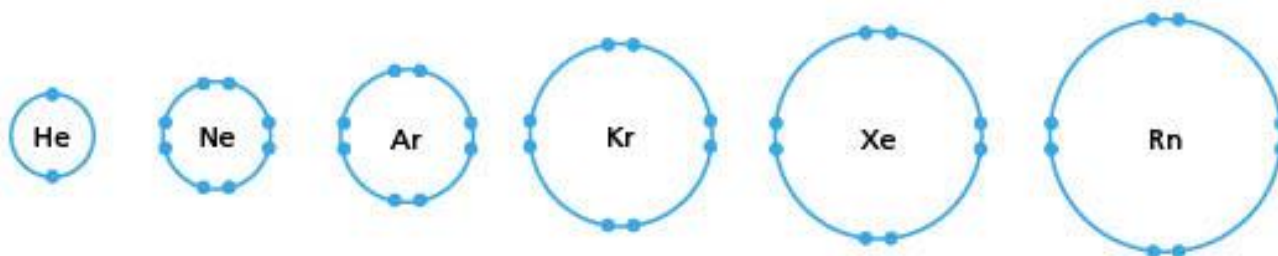
Octet Rule = atoms tend to gain, lose or share electrons so as to have 8 electrons



C would like to
gain 4 electrons

N would like to
gain 3 electrons

O would like to
gain 2 electrons



Each noble gas has a **fully filled valence shell**.

What is chemical bonding?

Chemical Bonding is the way in which atoms join together with each other.



sodium metal

+



chlorine gas

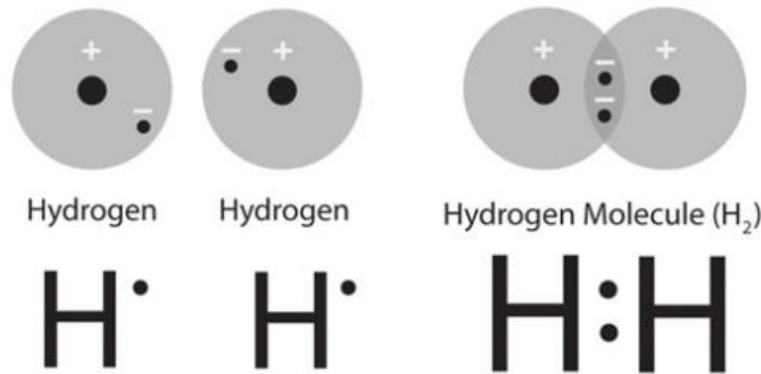
→



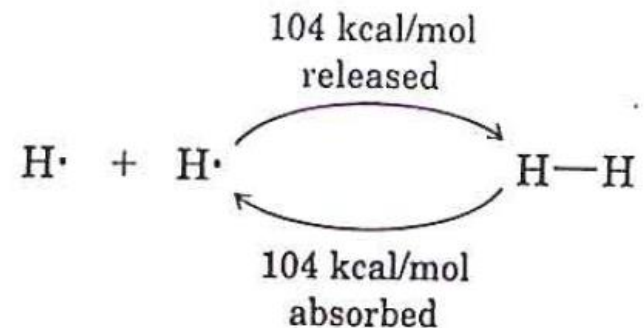
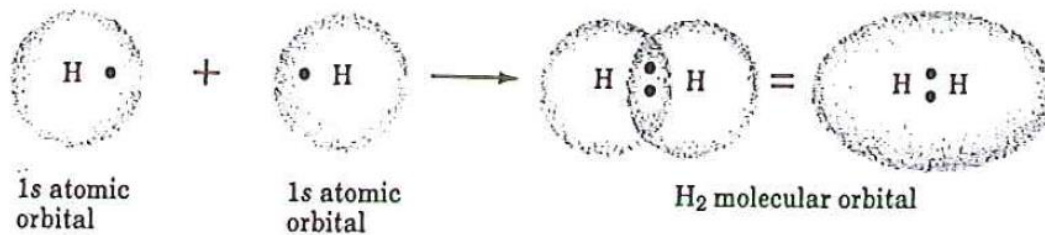
table salt

Formation of Covalent Bonds (between non-metals)

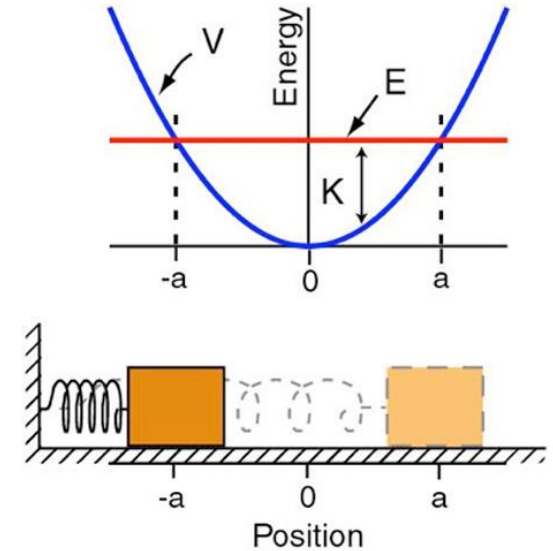
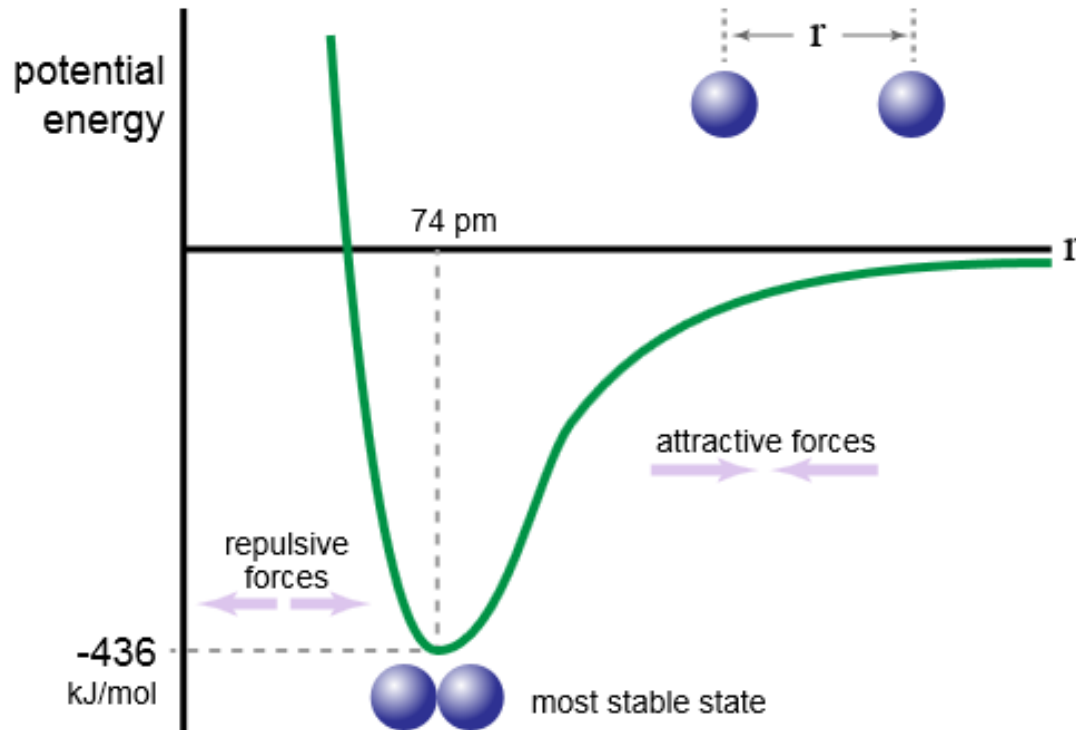
Consider hydrogen, H_2 , the simplest molecule. A hydrogen atom has a single valence electron. A **single covalent bond** is formed when a pair of electrons is shared between two, usually **nonmetal**, atoms.



Bond strength =
Amount of energy
needed to break the
bond



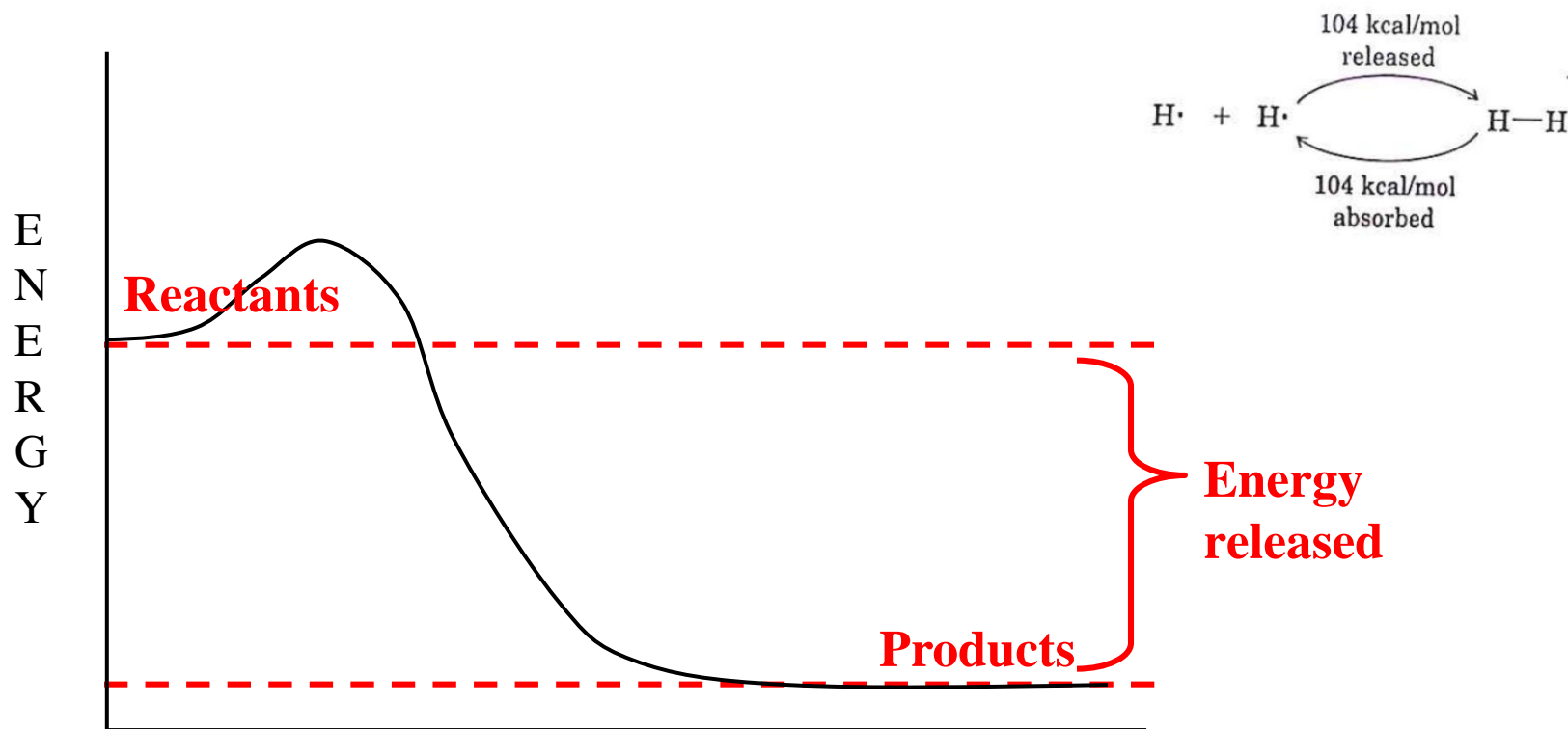
Bond energy as a function of distance between atoms



The diagram shows the energy for two hydrogen atoms. There is a clear **minimum** at 74 pm (0.74 \AA). Therefore one can say that the *bond length* is 74 pm. The bond strength is the **depth of this "well"** which is 436 kJ mol^{-1} . That is the amount of energy the H_2 molecule would need to gain to break the bond and end up as two separate H atoms.

Bond Formation Process

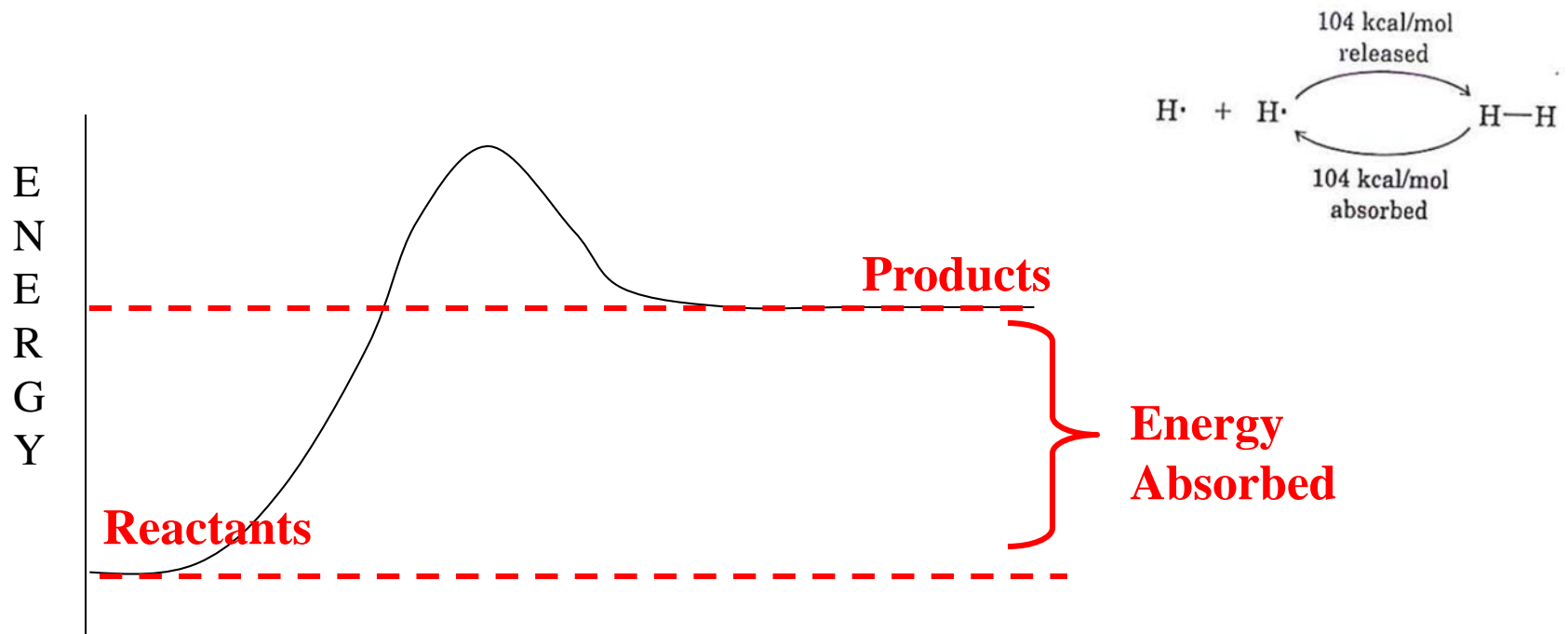
- It is an exothermic process (energy released in a form of heat)



- Strong, STABLE bonds require lots of energy to be formed or broken
- Weak bonds require little energy

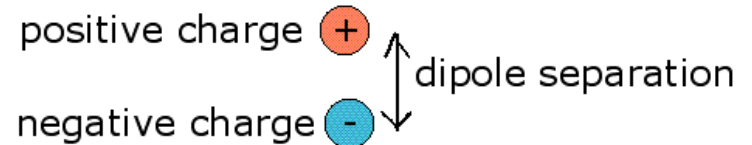
Bond Breaking Process

- Endothermic reaction
 - energy must be put into the bond in order to break it

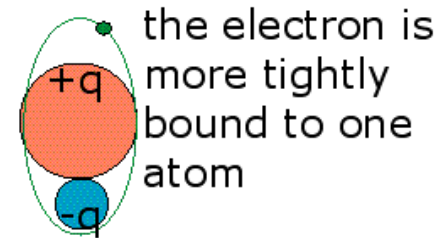


Secondary Bonding: Electric Dipoles

An electric dipole is basically a pair of equal positive and negative charges separated by a small distance.



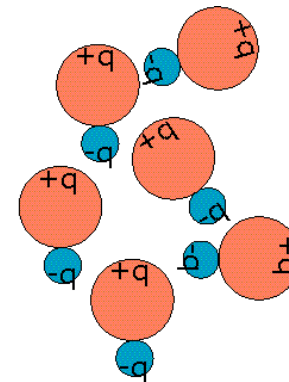
These dipoles will arise, for example, in a molecule, where atoms share an electron, but the electron spends more time with one atom, because it is bigger, and less time with the smaller atom.



The effective charge separation may be only a fraction (perhaps a tenth) of the electron's charge.

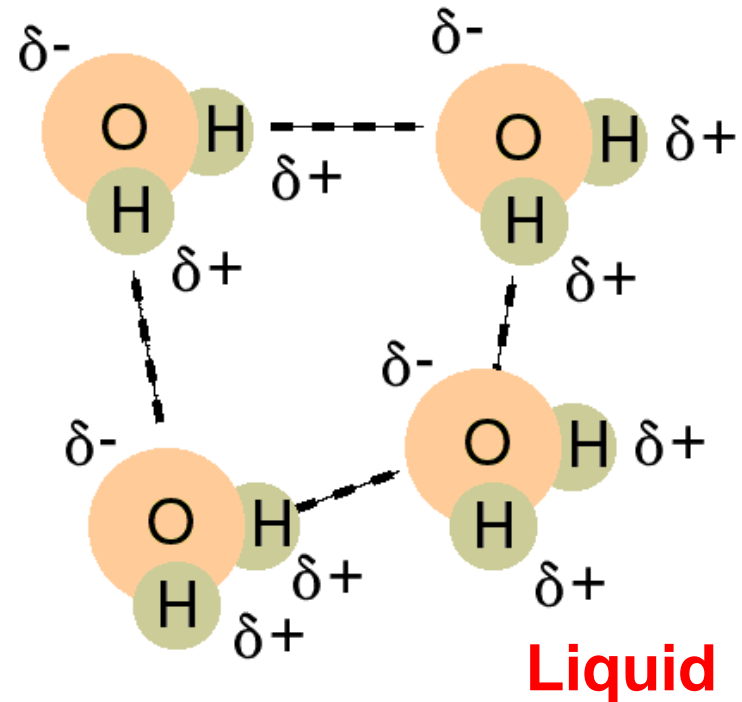
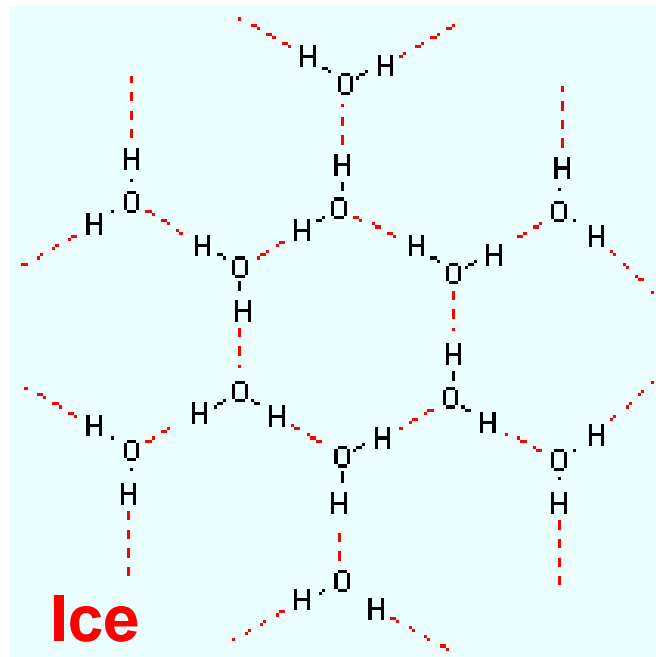
Bonding between dipoles happens when the positive end of one dipole is attracted to the negative end of another.

Since the effective charges are small compared with those involved in primary bonding, secondary bonding is about one tenth of primary bond strengths.



Secondary Bonding: dipole hydrogen bonds

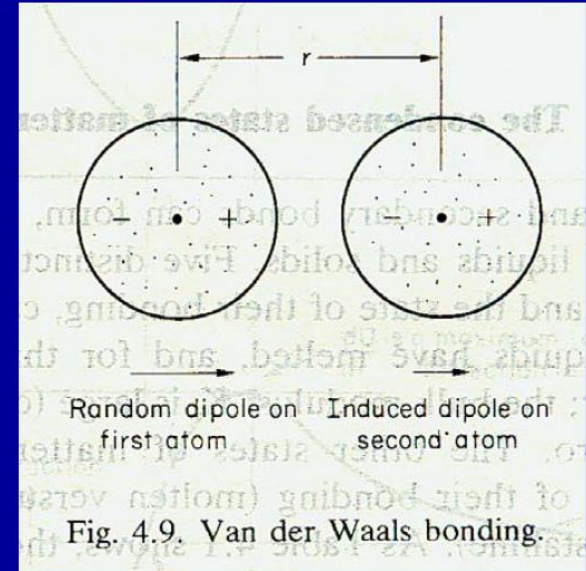
A special type of dipole-dipole attraction bonds form due to the polarity of water.



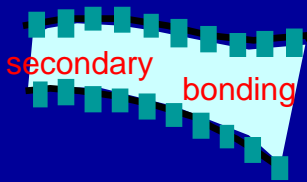
Hydrogen bonds keep water in the liquid phase over a wider range of temperatures than is found for any other molecule of its size. Permanent dipole is created due to asymmetrical arrangement of hydrogen atoms.

Secondary Bonding: van der Waals forces

- Fluctuation-induced dipole bonds
 - Charge on atom in motion being re-distributed
 - Electric dipole
 - Induced electric dipole
- Polar molecule induced dipole bonds
 - Neutral atoms form dipole
- Permanent dipole bonds: HCl



Van der Waal bonds



Linear chains

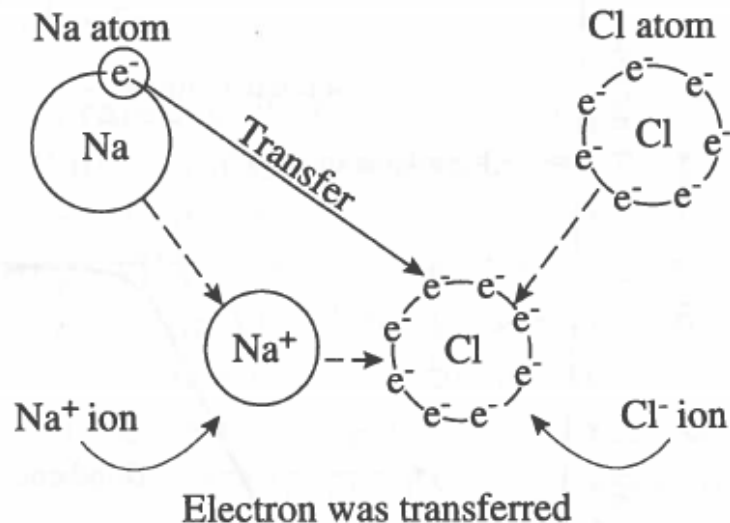
$$U_N = -\frac{A}{r^6} + \frac{B}{r^n} \quad n \approx 12$$

Attraction
Energy

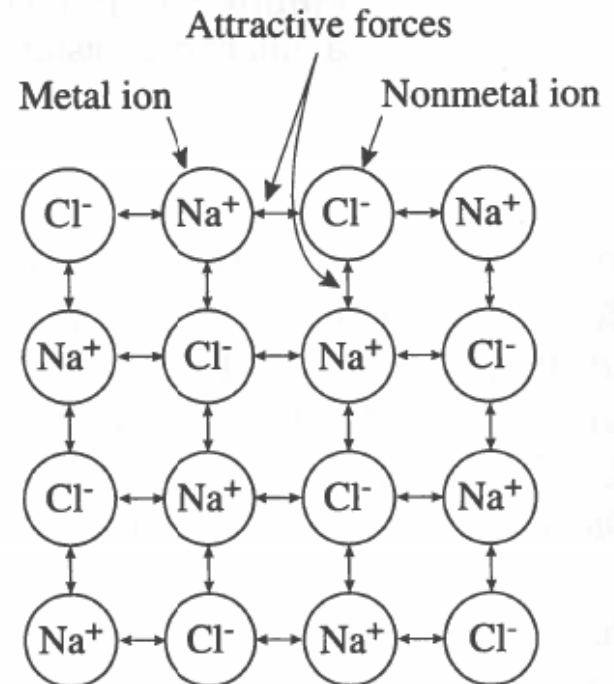
Repulsion
Energy

Ionic bonding: Me + non Me

Ionic bonds are formed when an atom that has a strong tendency to give up electrons (a metal) is in close proximity to an atom that has a strong tendency to accept electrons (a nonmetal). This nearness of the atoms allows a *transfer of one or more electrons*



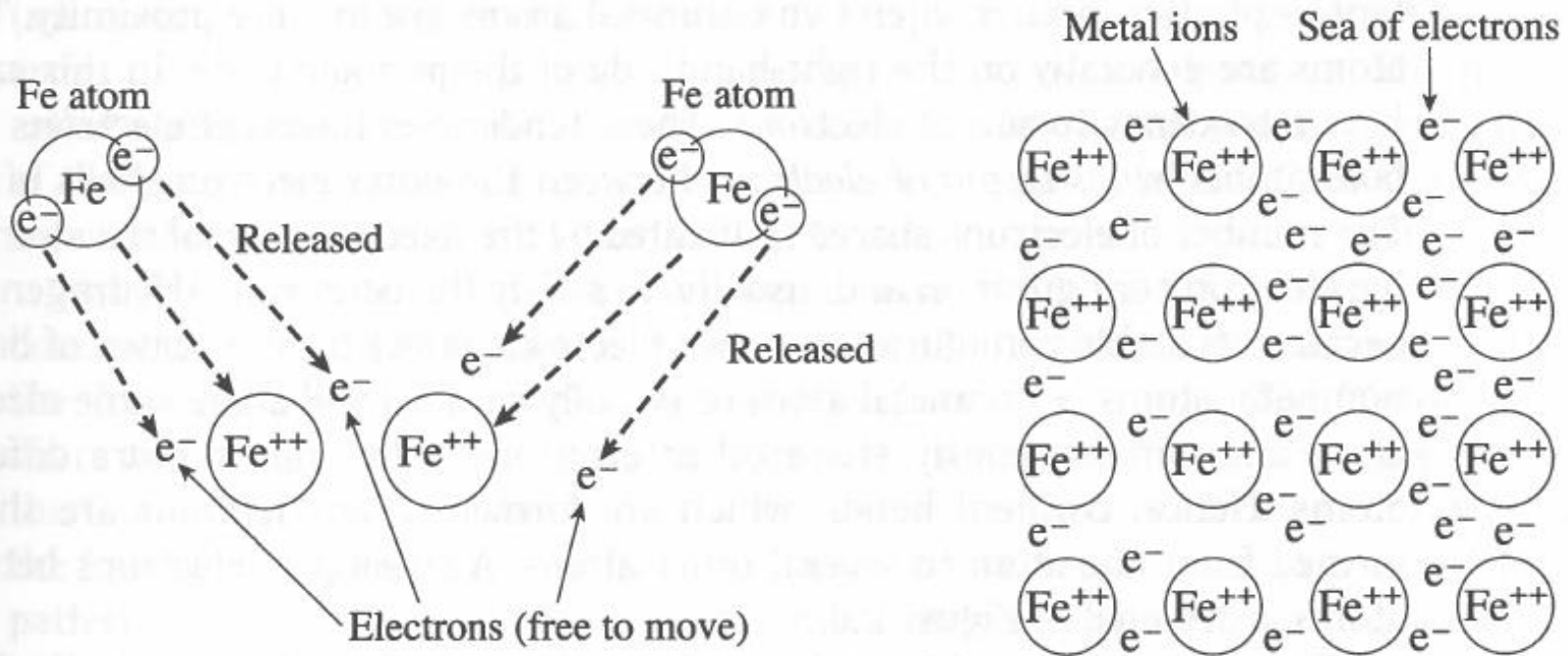
(a) Formation of a metal (Na^+) ion and a nonmetal (Cl^-) ion as a metal atom and a nonmetal atom approach each other



(b) Many metal (Na^+) ions and nonmetal (Cl^-) ions in a crystal structure showing attractive forces between oppositely charged ions

Figure 2.4 Ionic bonding and the resulting crystal structure.

Metallic Bonding: Me in the sea of electrons



(a) Formation of metal (Fe^{++}) ions and sea of electrons as metal atoms approach each other

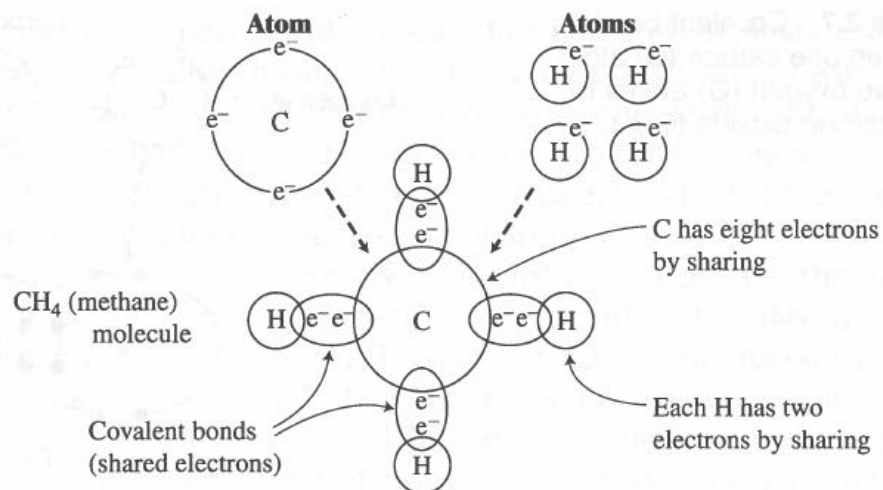
(b) Many metal (Fe^{++}) ions in a crystal structure surrounded with a sea of electrons

Figure 2.5 Metallic bonding of iron and the resulting crystal structure.

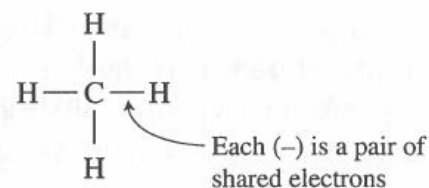
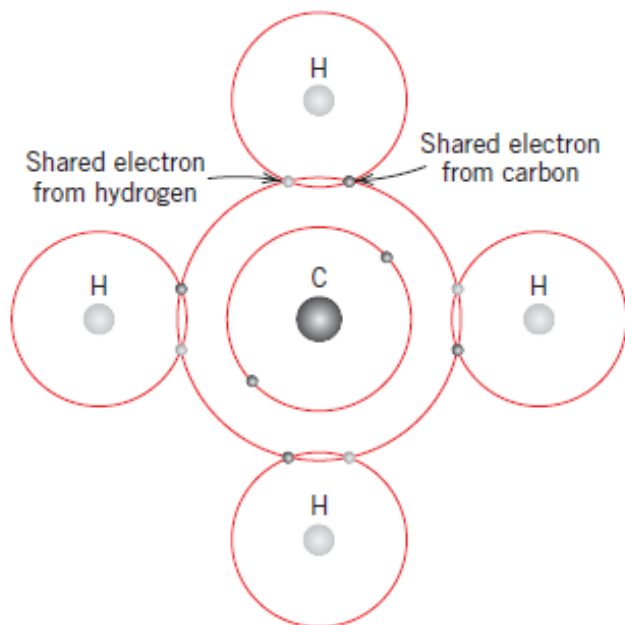
Covalent Bonding

Figure 2.6 Covalent bonding between one carbon (C) and four hydrogens (H) to form methane (CH_4).

One bond = 2 shared electrons

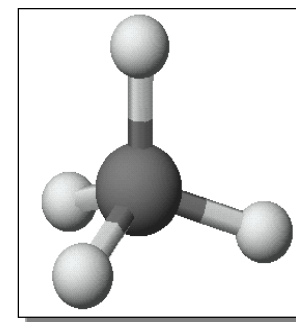


(a) Formation of covalent bonds between nonmetal atoms (one C and four H atoms)



(b) Representation of the resulting CH_4 molecule using conventional chemistry notation

Three dimensional structure?



Carbon Atom Bonding

CH₄

- The number of valence electrons attempts to satisfy the octet rule.
- Each bond has two electrons.
- Each bonding orbital moves as far away from all other orbitals as possible. Repulsion between orbitals containing electrons.

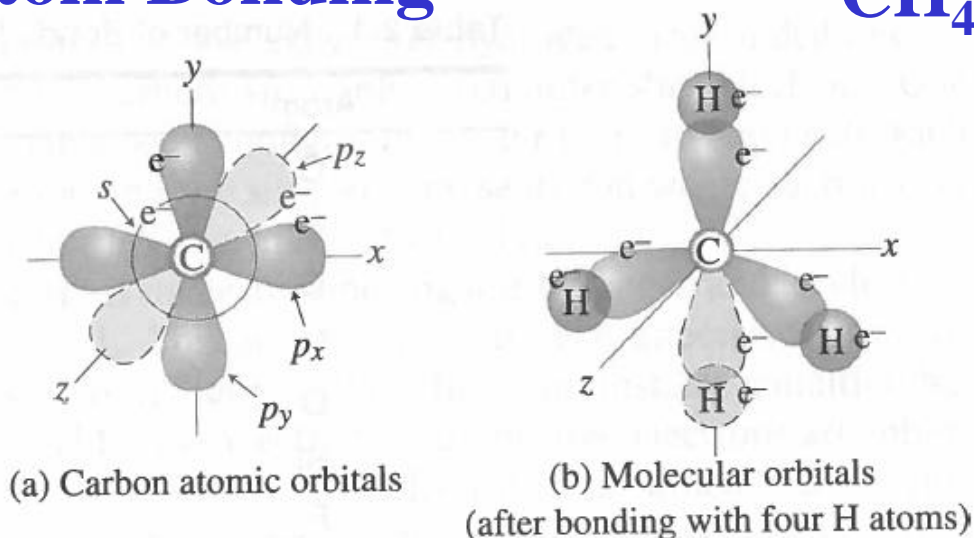
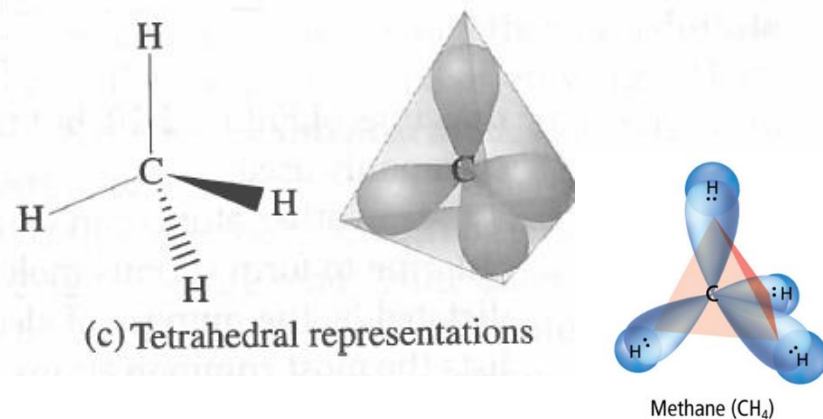
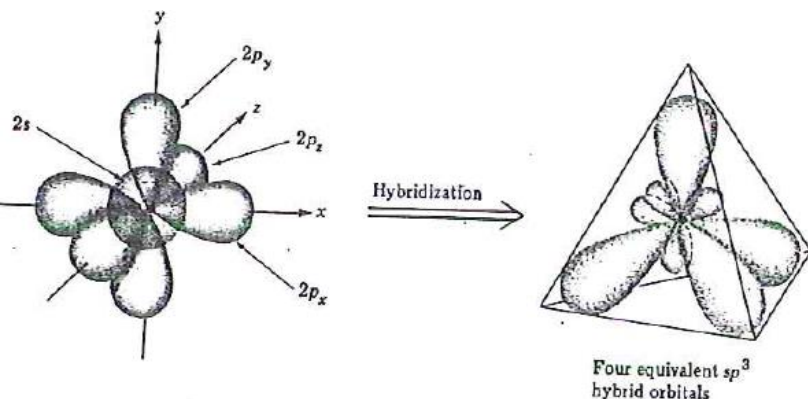
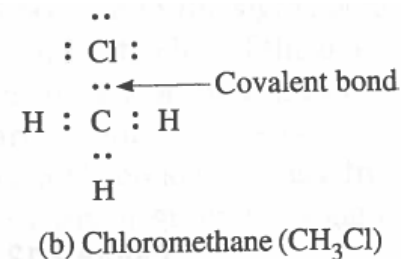
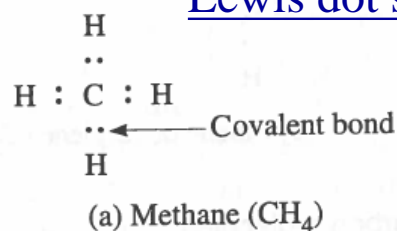


Figure 2.10 Carbon atom bonding with four hydrogen atoms to form CH₄.

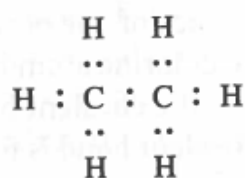
Hybridization: Formation of sp³ orbitals



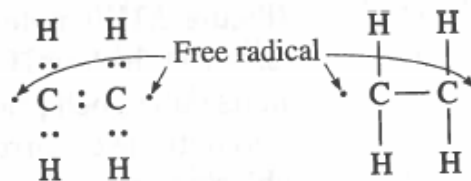
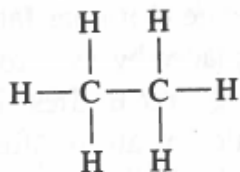
Lewis dot structures:



Carbon-Carbon Molecular Orbitals: Structure of Ethane



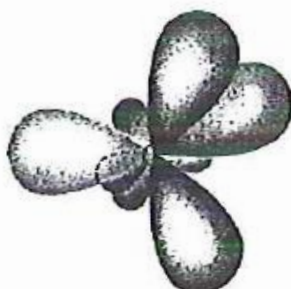
(a) Ethane (C_2H_6)



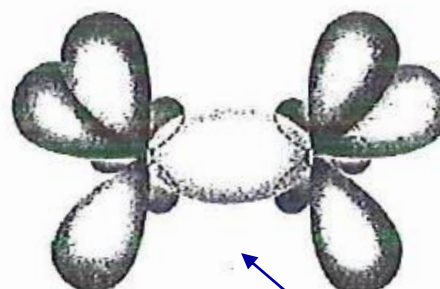
(b) Unstable configuration



sp^3 carbon



sp^3 carbon



sp^3-sp^3 sigma bond

Sigma bond

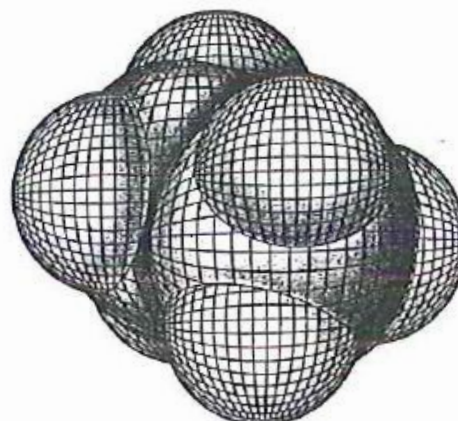
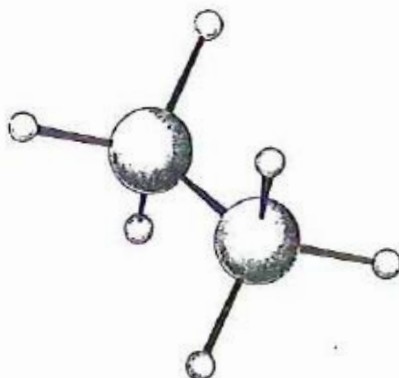
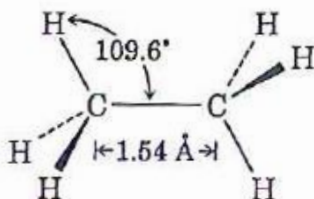
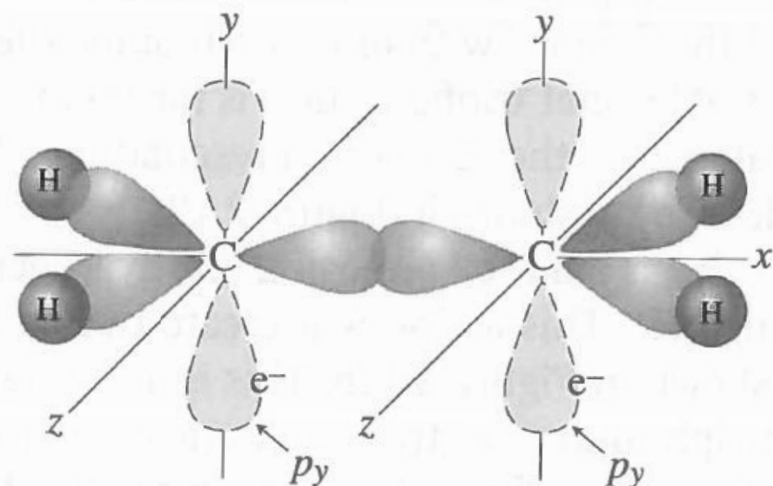
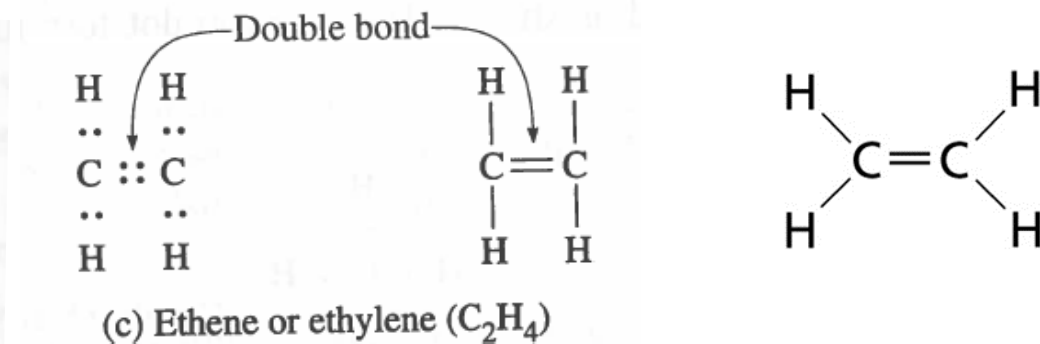
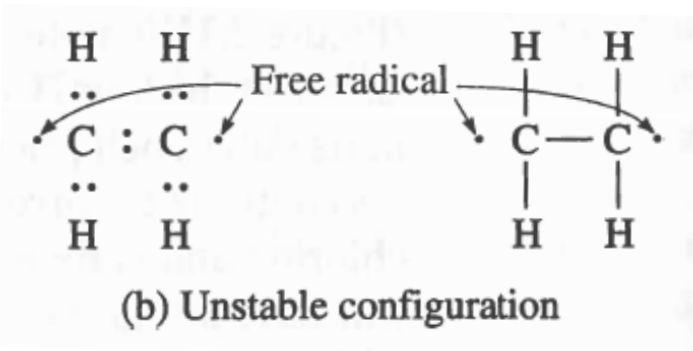
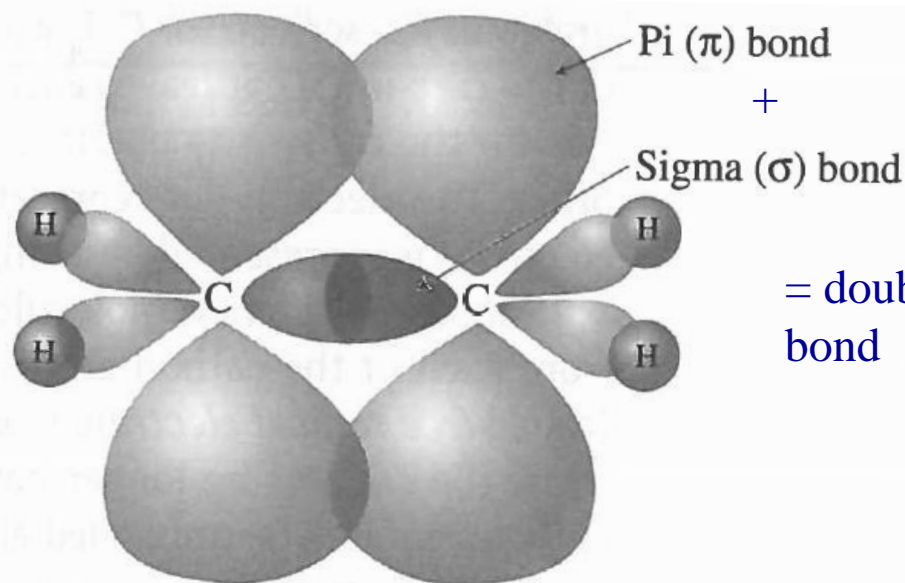


FIGURE 1.10 The structure of ethane. The carbon-carbon bond is formed by sigma overlap of two carbon sp^3 hybrid orbitals.

Carbon-Carbon Molecular Orbitals: Structure of Ethylene



(a) Prior to overlap of p_y orbitals



= double bond

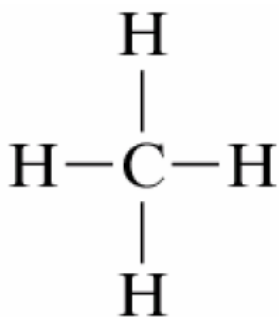
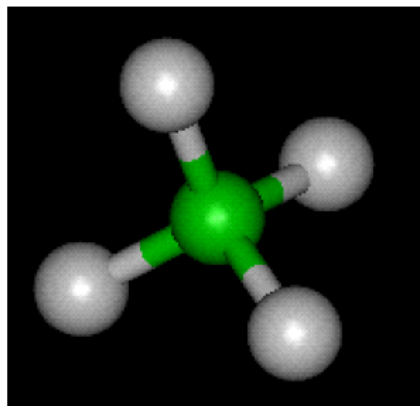
(b) After overlap of p_y orbitals to form a π -bond



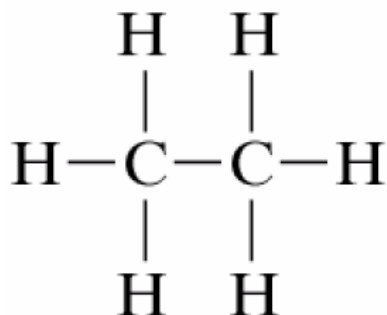
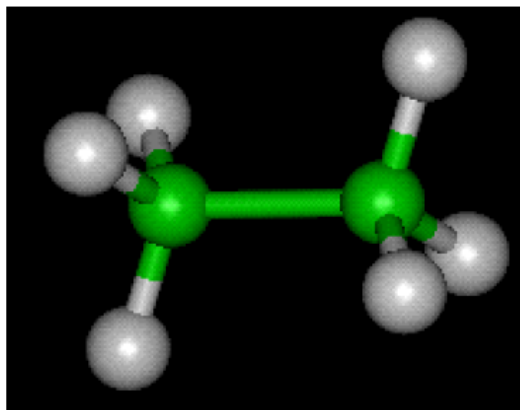
Figure 2.13 Types of bonding in double bonds (ethylene).

Hydrocarbon Molecules

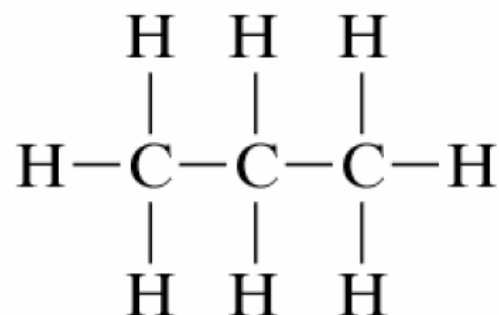
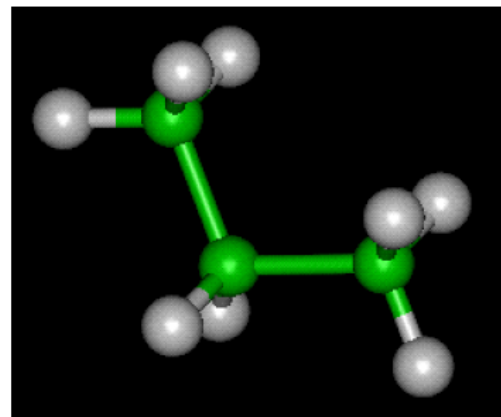
Examples of *saturated* (all bonds are single ones) hydrocarbon molecules:



Methane, CH₄



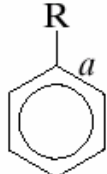
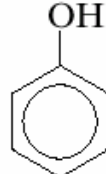
Ethane, C₂H₆



Propane, C₃H₈

Hydrocarbon Molecules

In table below R represents a [radical](#), an organic group of atoms that remains as a unit and maintains their identity during chemical reactions (e.g. CH_3 , C_2H_5 , C_6H_5).

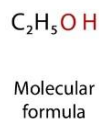
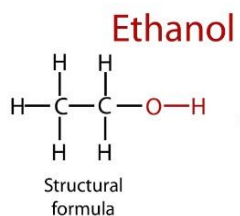
<i>Family</i>	<i>Characteristic Unit</i>	<i>Representative Compound</i>
Alcohols	$\text{R}-\text{OH}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$ Methyl alcohol
Ethers	$\text{R}-\text{O}-\text{R}'$	$\begin{array}{c} \text{H} \qquad \text{H} \\ \qquad \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{H}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

Methanol,
“wood alcohol”
toxic, chemical
manufacturing,
fuel

Vinegar smell

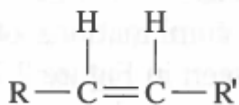
Functional Groups:

R represent a radical

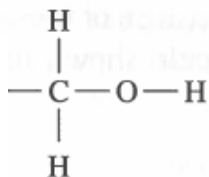


Functional Group

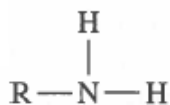
Name



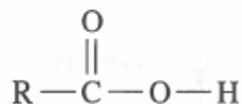
Alkene



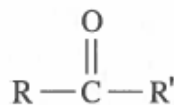
Alcohol



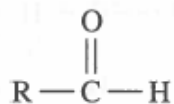
Amine



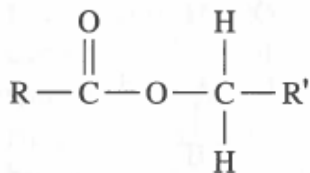
Acid



Ketone



Aldehyde



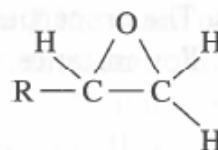
Ester

Functional Group

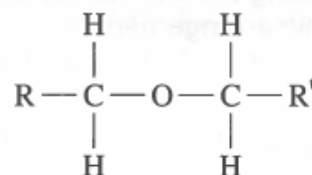
Name



Amide



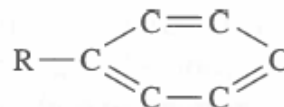
Epoxy



Ether



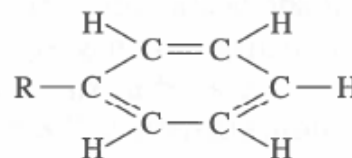
Isocyanate



Aromatic



Aromatic



Aromatic

Benzene ring

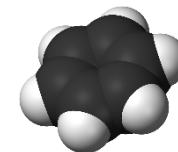
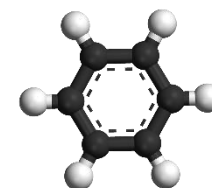
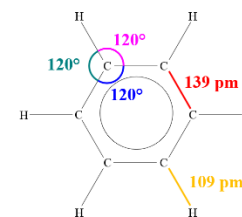


Figure 2.14 Functional groups in organic chemistry. (Some hydrogen atoms have been omitted for simplicity and ease of focusing on key atoms in the functional group. The R can be any organic group.)

Aroma around petrol stations

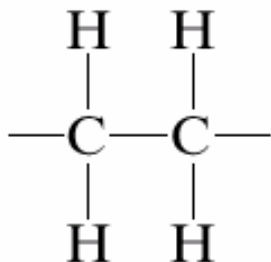
Chemistry of Polymer Molecules

When all mers are the same, the molecule is called a **homopolymer**

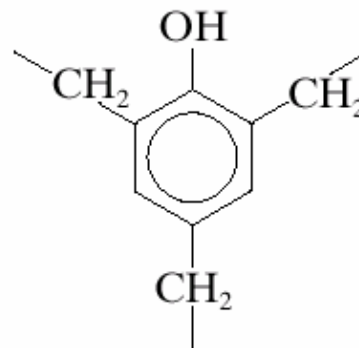
When there is more than one type of mer present, the molecule is a **copolymer**

Mer units that have 2 active bonds to connect with other mers are called **bifunctional**

Mer units that have 3 active bonds to connect with other mers are called **trifunctional**. They form three-dimensional molecular network structures



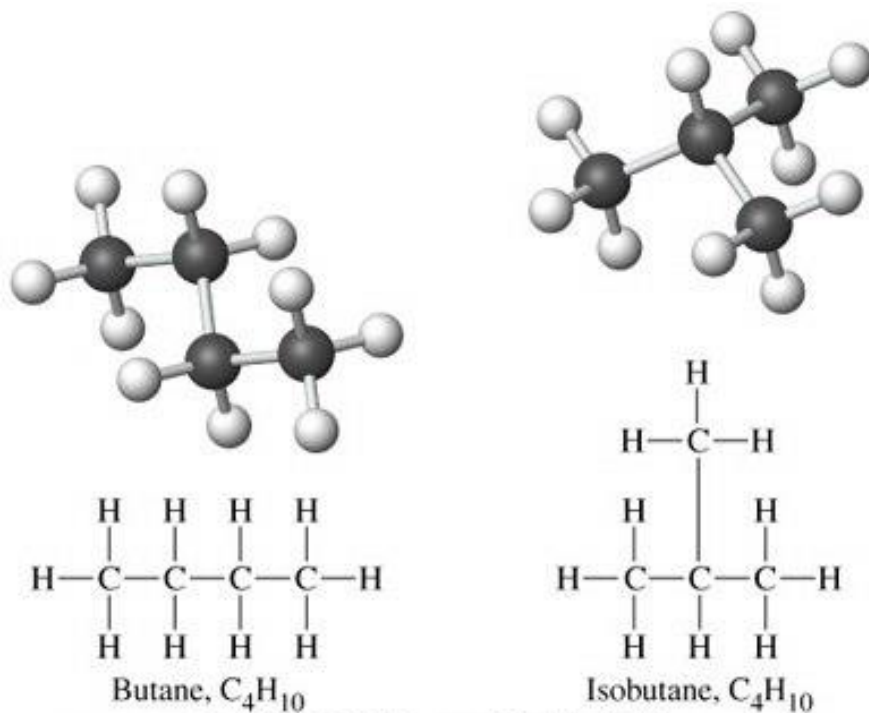
Polyethylene
(bifunctional)



Phenol-formaldehyde
(trifunctional)

Isomers

Isomers are molecules that have the same composition (contain the same atoms) but have different atomic arrangement. An example is butane and isobutane:



Physical properties and chemical reactivity depend on the isomeric state. The melting and boiling points of isobutane are lower than that of n-butane due to branching in isobutane.

More the number of branches, lower is the melting and boiling point.



Butane is suited for use as a fuel for cigarette lighters and torches, whereas isobutane is best used as a refrigerant and a propellant in spray cans.

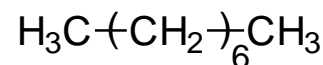
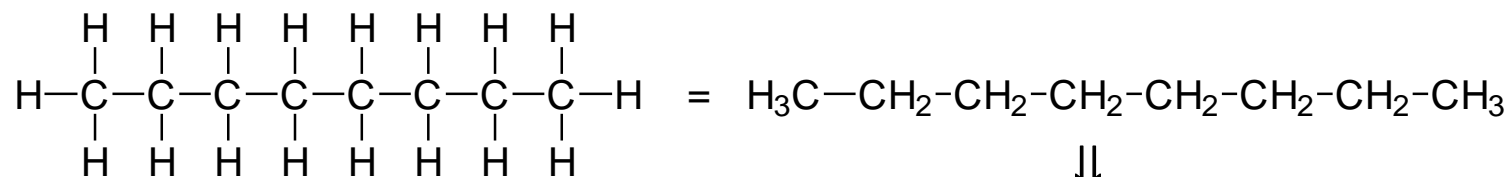
Isomers (cont.)

- Isomerism

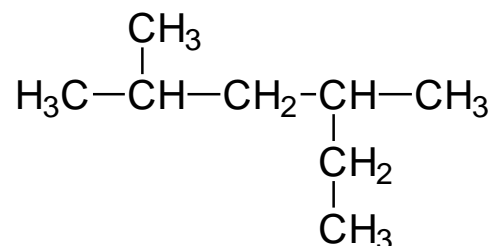
- two compounds with same chemical formula can have quite different structures

Ex: C_8H_{18}

- n-octane

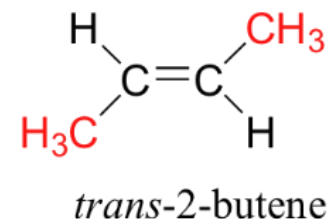
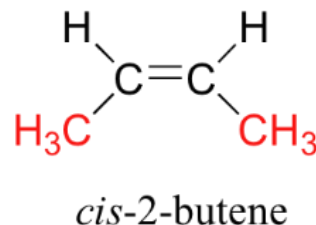
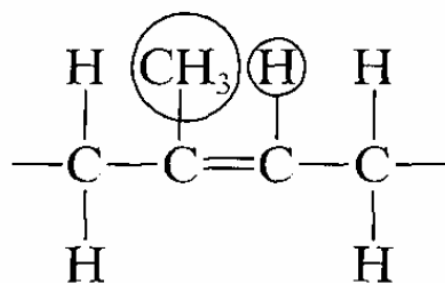


- 2-methyl-4-ethyl pentane (isooctane)

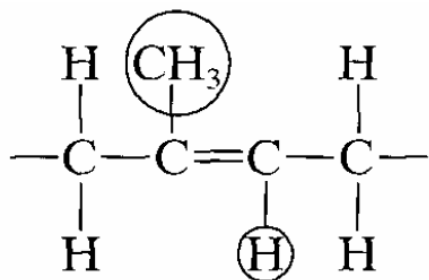


Geometric (cis / trans) Isomerism

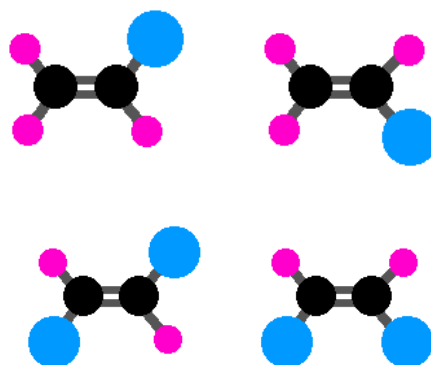
Isomers are molecules that have the same composition (contain the same atoms) but have different atomic arrangement. **Geometrical isomerism**: consider two carbon atoms bonded by a double bond in a chain. H atom or radical R bonded to these two atoms can be on the same side of the chain (**cis** structure) or on opposite sides of the chain (**trans** structure).



Cis-polyisoprene



Trans-polyisoprene



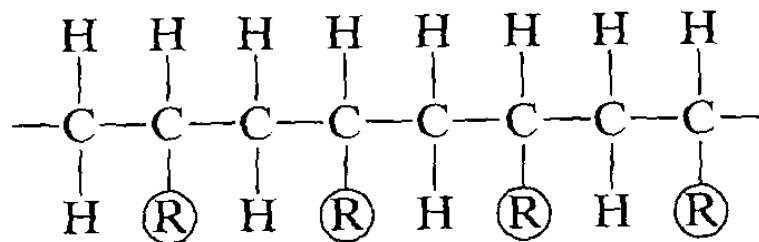
The same molecule!

Trans/cis structure

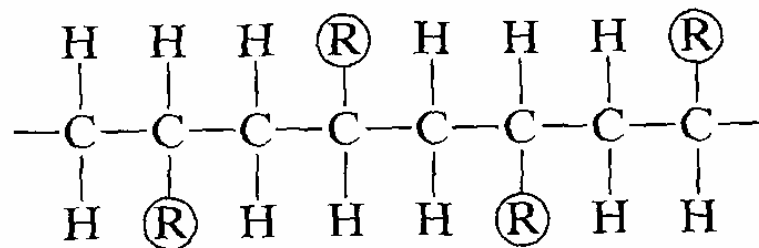
Stereoisomerism

Stereoisomerism: atoms are linked together in the same order, but can have different spatial arrangement

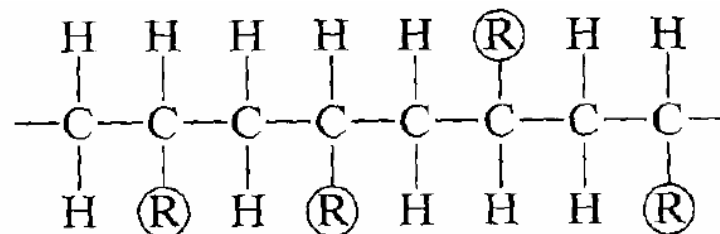
Isotactic configuration: all side groups R are on the same side of the chain.



Syndiotactic configuration: side groups R alternate sides of the chain.

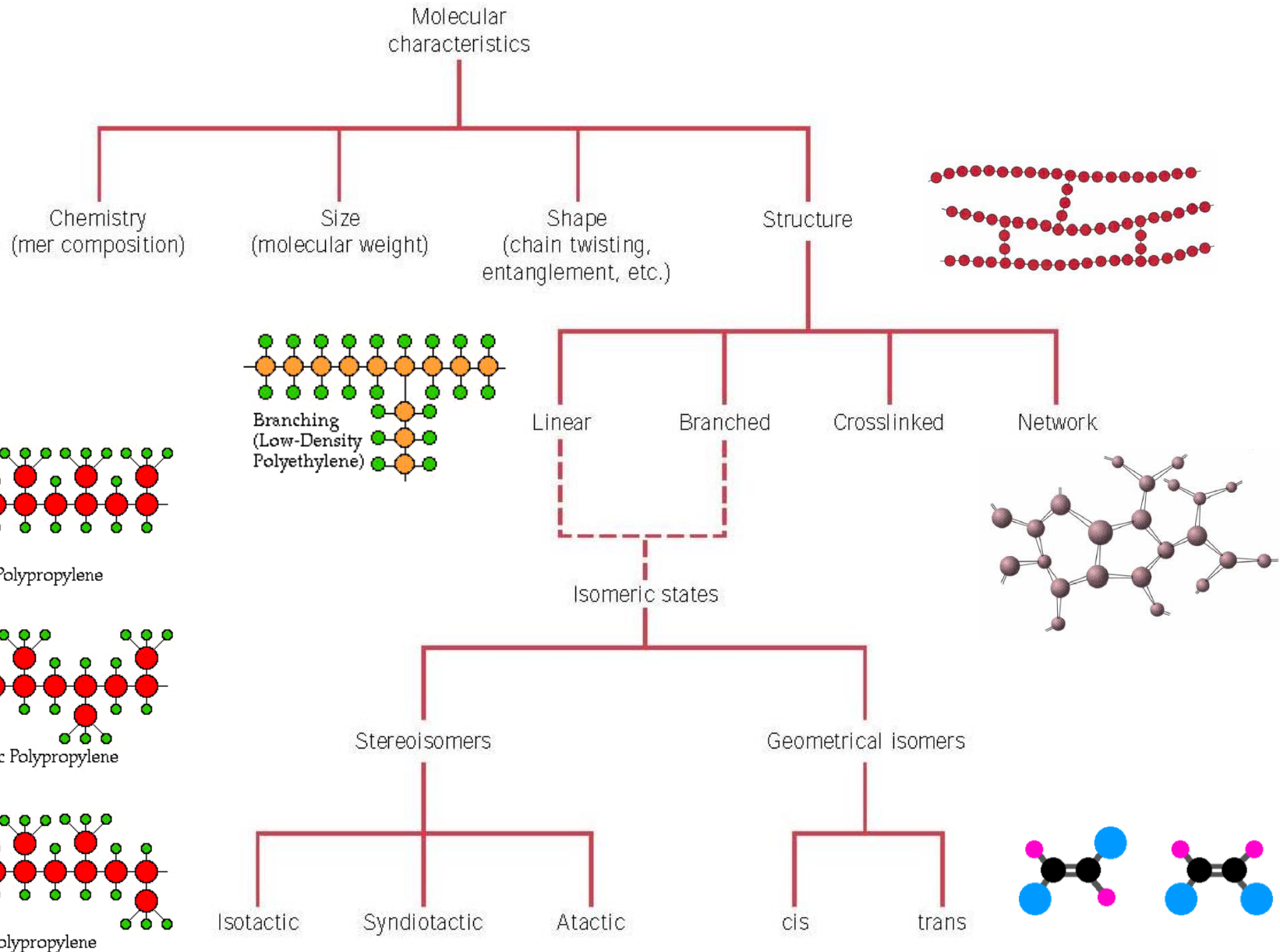


Atactic configuration: random orientations of groups R along the chain.



Can't Crystallize

Size – Shape – Structure Classification



Quiz

1. Every covalent bond is made up of how many electrons?

- a) one
- b) two
- c) three
- d) eight

b) two

2. Most polymers in use today are molecules with a backbone consisting primarily of which basic element?

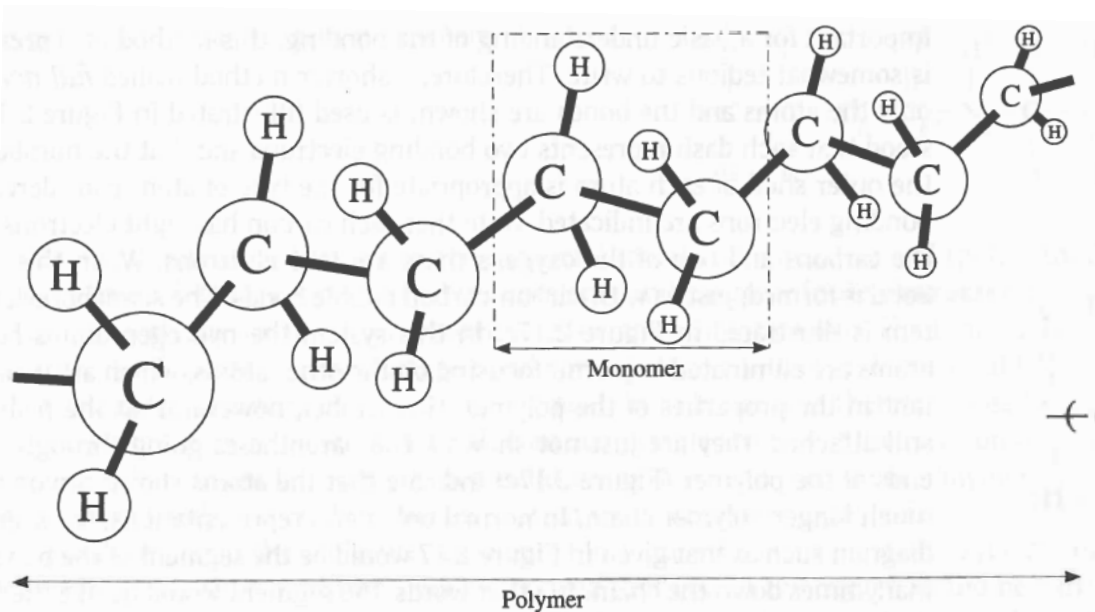
a. Silicon b. Nitrogen c. Hydrogen d. Carbon

(a) carbon

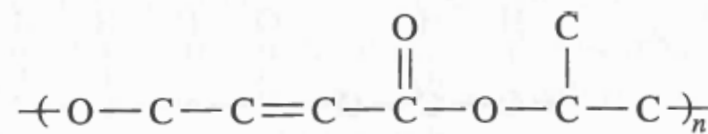
3. When naming organic compounds, the prefix but- (or buta-) is used to indicate which quantity?

- a) four
- b) five
- c) six
- d) seven

Polymer chains: how to assemble?

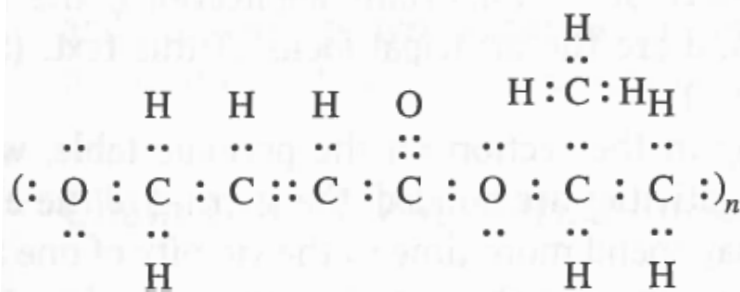


4 bonds for
each carbon
atom

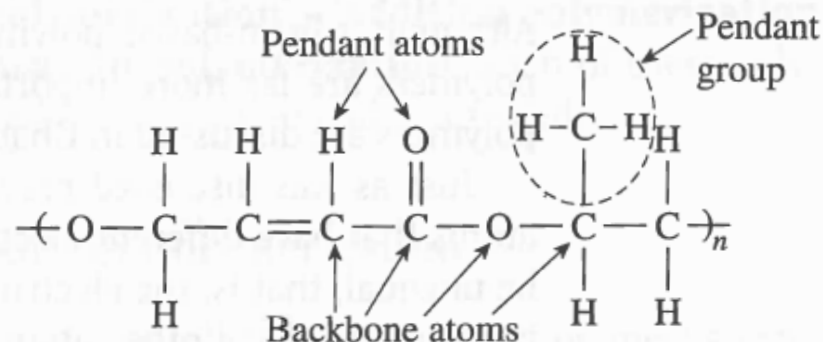


(c) Semiabbreviated notation

Figure 2.16 Three-dimensional perspective representation of ethylene monomers built into a polymer chain (polyethylene).

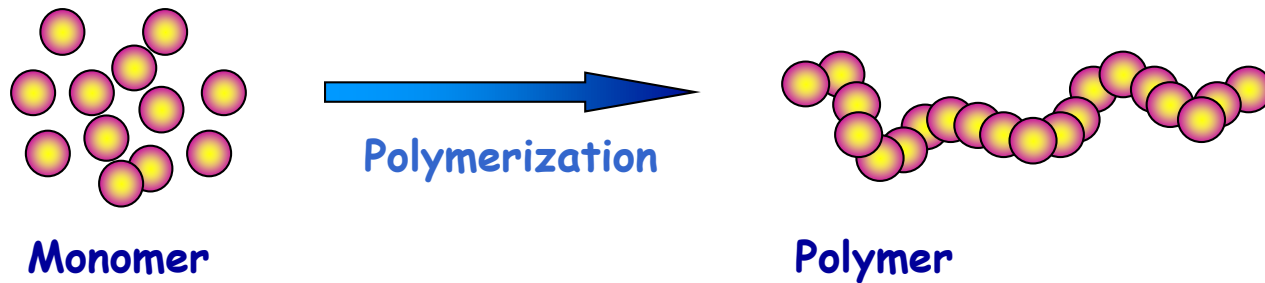


(a) Electron-dot notation



(b) Full notation

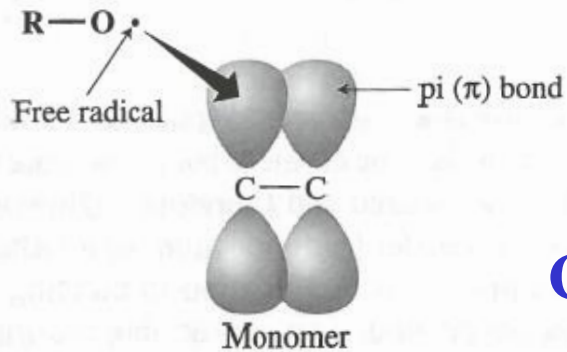
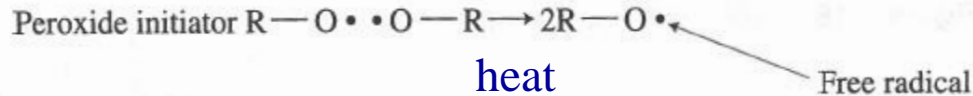
Polymerization mechanisms



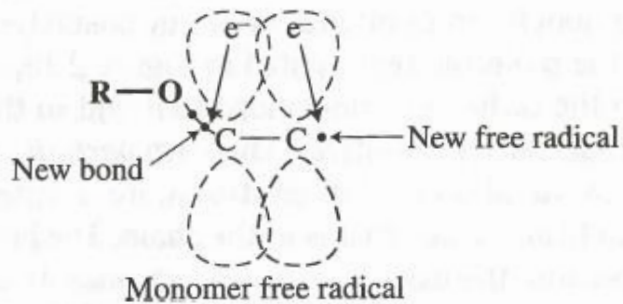
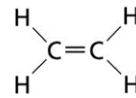
Formation of polymers: Chain-Growth polymerization

Step-growth polymerization or condensation polymerization

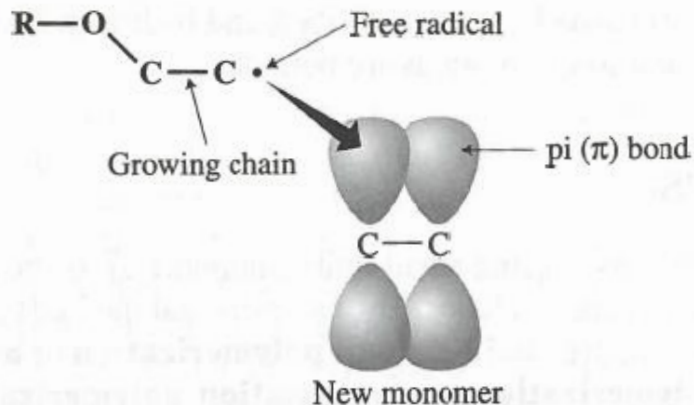
Formation of polymers: Chain-Growth polymerization



(a) Peroxide free radical interaction with monomer π -bond



(b) Peroxide-carbon bond formed and transfer of free radical to distant carbon

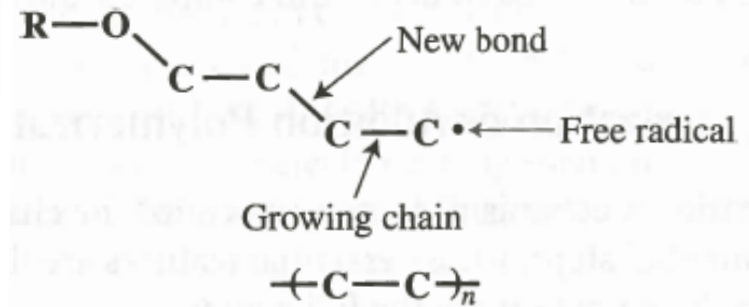


(c) Carbon free radical interaction with π -bond in new monomer

Additional polymerization:

Initiators: part of the chain end

Catalysts are not “used up”, Me



(d) Chain-lengthening (propagation) step

(e) Polymer representation (repeating unit only)

Several thousand units in a chain!

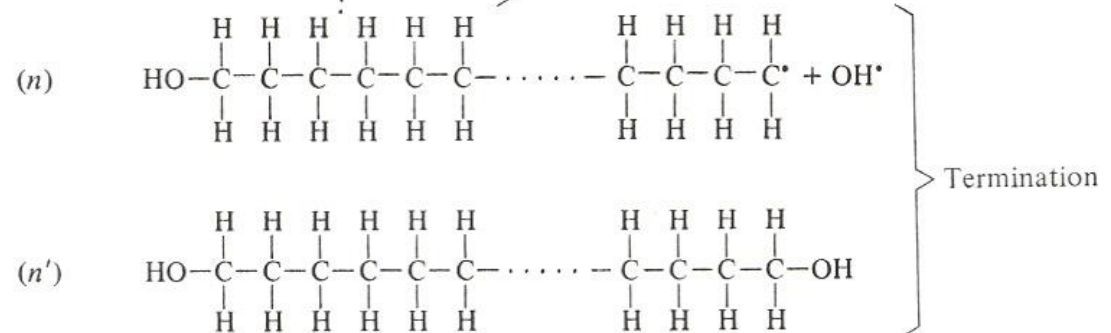
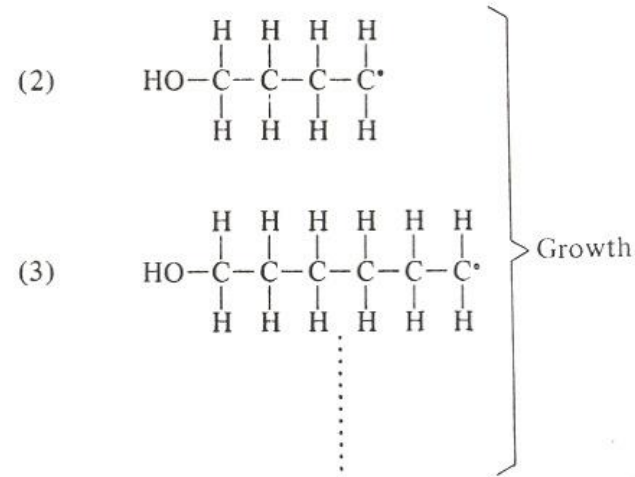
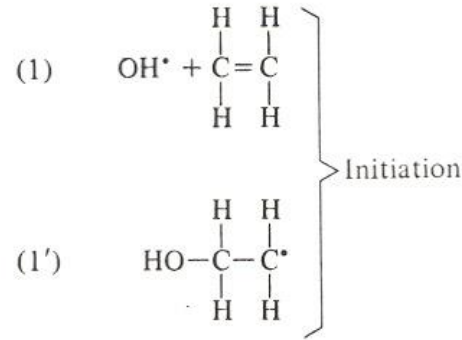
Formation of polymers: Chain-Growth polymerization

Addition

in which one “mer” is added to the structure at a time.

This process is begun by an **initiator** that "opens up" a C=C double bond, attaches itself to one of the resulting single bonds, & leaves the second one dangling to repeat the process.

Termination when two active chain ends meet each other or active chain end meet with initiator or other species with single active bond:



Rapid propagation
~1000 mer units in
1-10 ms:

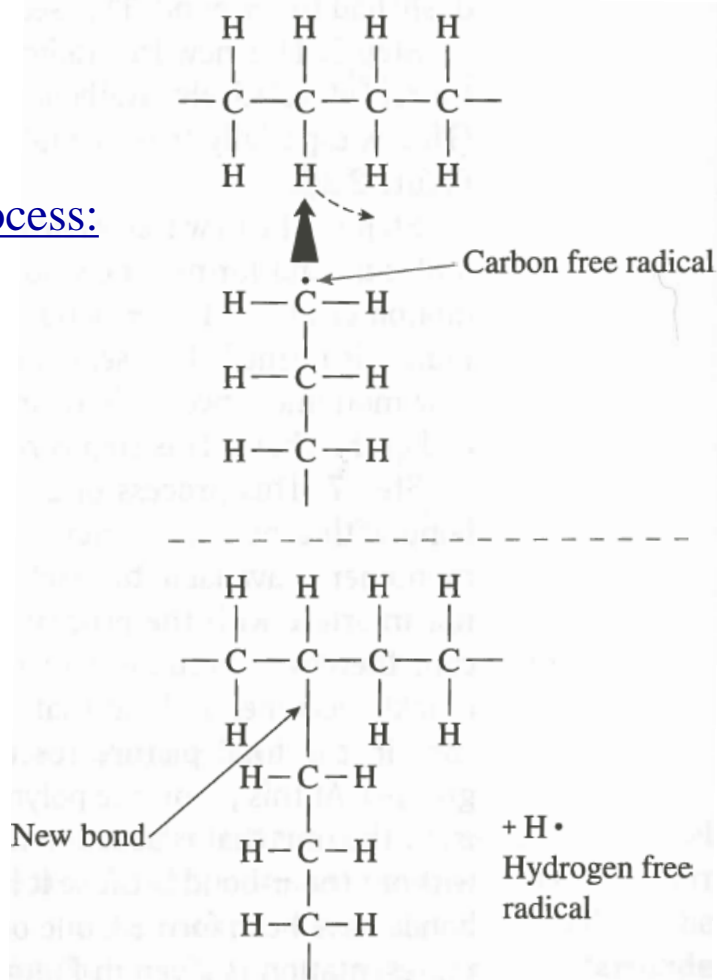
Formation of polymers: Chain-Growth polymerization (cont.)

How to end the polymer chain?

Another radical at the chain end

Two half-chains meet and form one chain

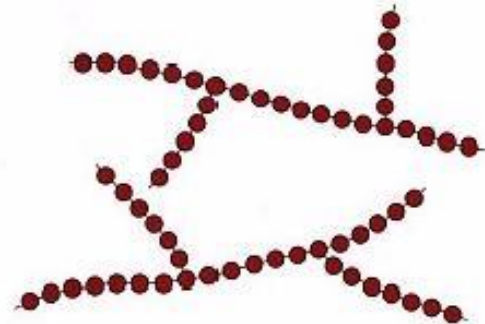
Branching process:



Additional polymerization:

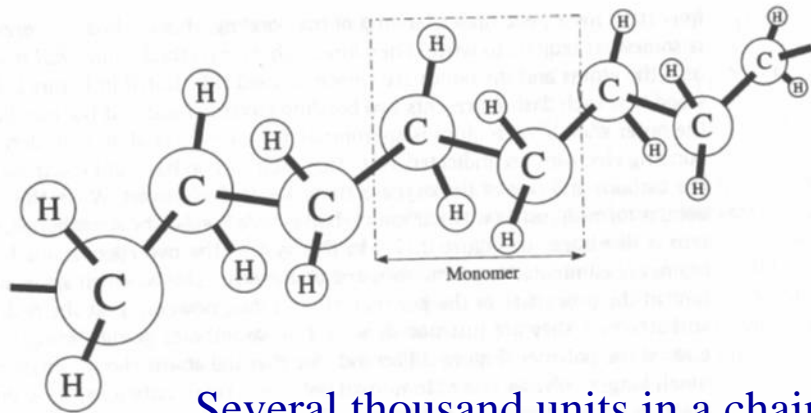
Initiators: part of the chain end

Catalysts are not “used up”, Me



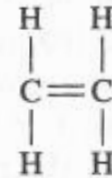
Formation of polymers: Chain-Growth polymerization (cont.)

Figure 2.22 Common monomers that polymerize using addition polymerization.



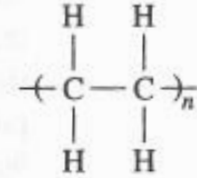
Several thousand units in a chain!

Monomer

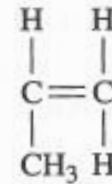


Ethylene

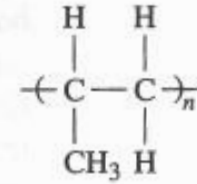
Polymer



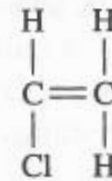
Polyethylene



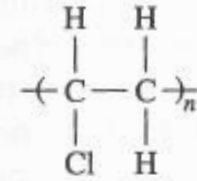
Propylene



Polypropylene

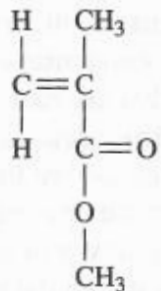


Vinyl chloride



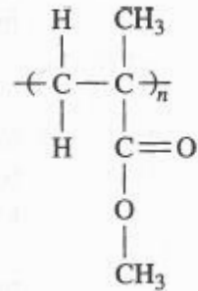
Polyvinylchloride

Monomer

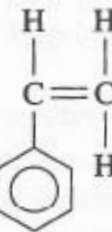


Methyl methacrylate

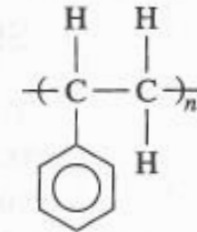
Polymer



Polymethylmethacrylate

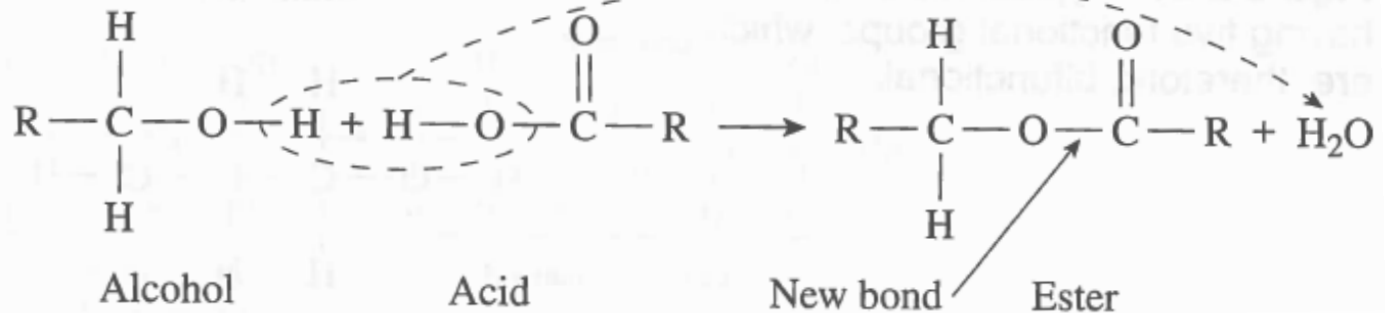


Styrene

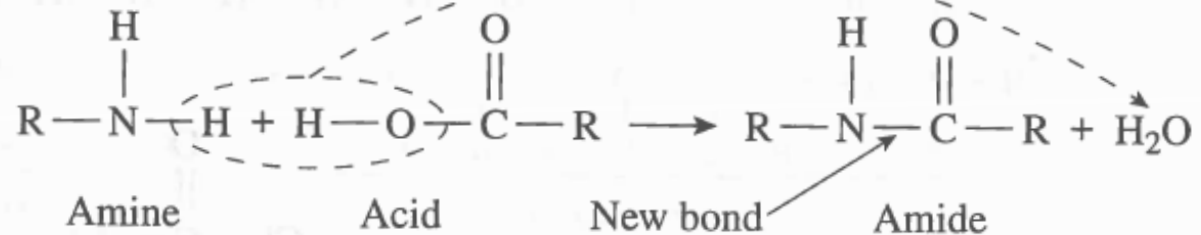


Polystyrene

Step-growth polymerization or condensation polymerization



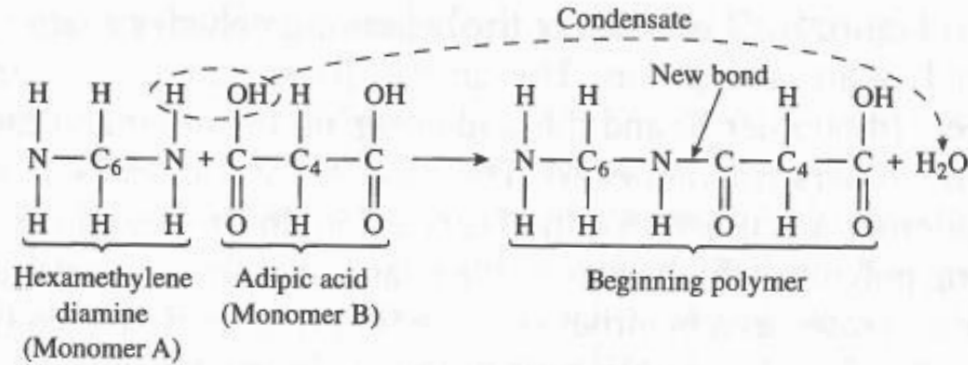
(a) Reaction of an alcohol and an acid to make an ester and water



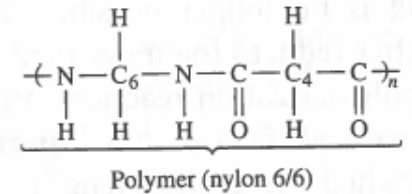
(b) Reaction of an amine and an acid to make an amide and water

Figure 2.23 Reaction between dissimilar functional groups, which is the basis of condensation or step-growth polymerization reactions.

Step-growth polymerization or condensation polymerization

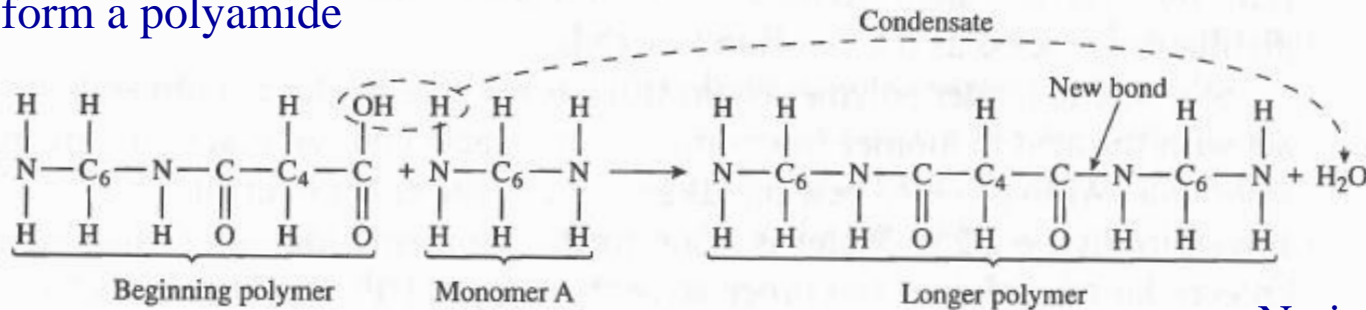


(a) Monomers react



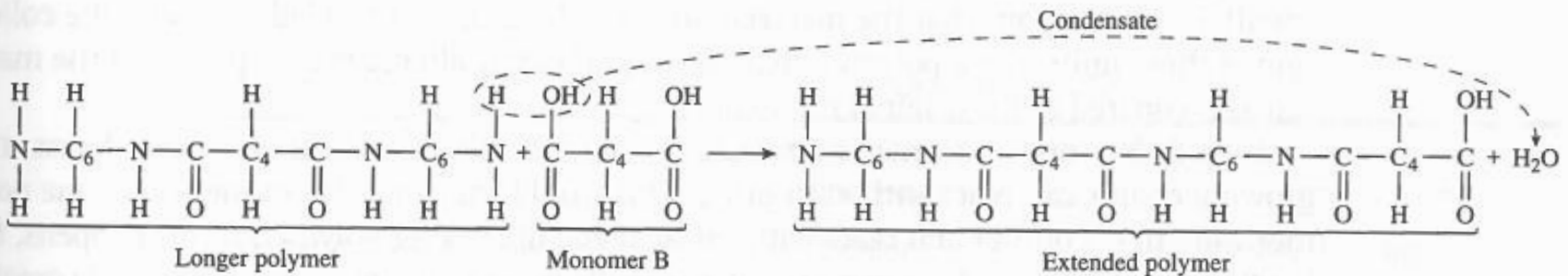
(d) Polymer representation (repeating group)

Condensation reaction
steps to form a polyamide



(b) Reaction of chain with diamine monomer (A)

No initiator or catalyst
just heat and stir



(c) Reaction of chain with diacid monomer (B)

Cool down or end-caps

Comparison of Addition and Condensation Polymers

Table 2.3 Characteristics of Addition and Condensation Polymerization Methods

	Addition or Chain-Growth Polymerization	Condensation or Step-Growth Polymerization
Polymer growth mechanism	Chain reaction	Step-by-step reactions
Dependence on previous step	Yes—sequential dependent events	No—-independent events
Initiator needed	Yes	No
Type of monomer	Contains carbon-carbon double bond	Bifunctional (has reacting functional groups on the ends)
Number of active sites (functional groups) per monomer	1	2
Number of different types of monomers needed to form polymer	1	2 (usually)
By-product formed	No	Yes (usually)
New type of bond formed	No	Yes
Basic representation (polymer repeat unit)	Monomer without the double bond and with bonds on either side	Two monomers joined together
Polymer chain characteristics	A few, long chains	Many, not very long chains
Branching	Possible	Unlikely
Name of polymer	Poly + name of monomer	Poly + name of new bond

Thermoplastics and Thermosets

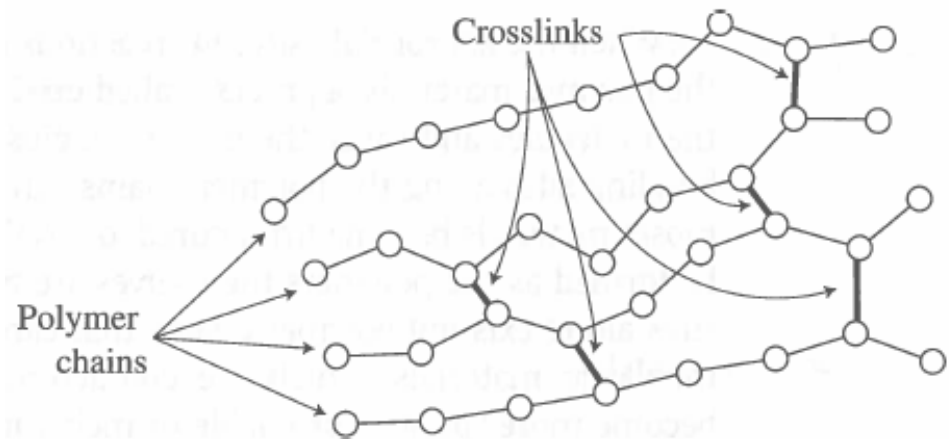
Like candy caramels: soften and melt when heated, then put in mold and cooled to take its shape; repeat many times. Solid at room T.



Thermoplastics - materials become fluid and processible upon heating, allowing them to be transformed into desired shapes that are stabilized by cooling.

-- polyethylene
polypropylene
polycarbonate
polystyrene

Thermosets cannot be reshaped; curing process.



Thermosets - initial mixture of reactive, low molar mass compounds reacts upon heating in the mold to form an insoluble, infusible network

-- vulcanized rubber, epoxies,
polyester resin, phenolic resin

Thermoplastics and Thermosetting Polymers

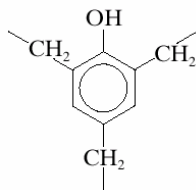
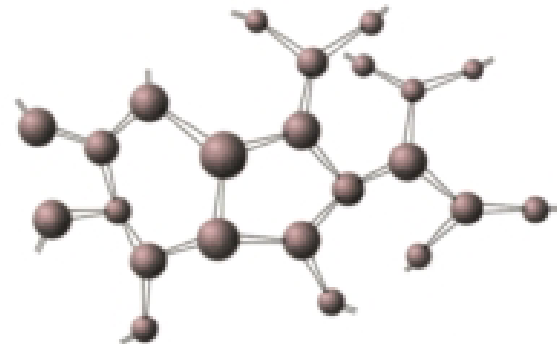
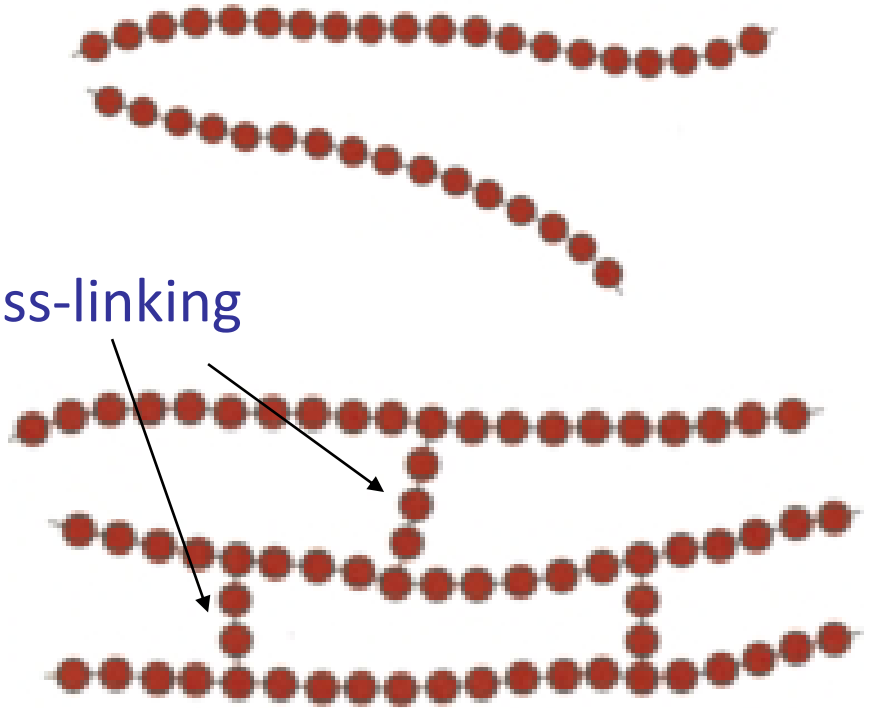
- Thermoplastics:
 - little cross-linking
 - ductile
 - soften w/heating

Ex: grocery bags, bottles

- Thermosets:
 - large cross-linking
(10 to 50% of mers)
 - hard and brittle
 - do NOT soften w/heating
 - vulcanized rubber, epoxies,
polyester resin, phenolic resin

Ex: car tires, structural plastics

cross-linking

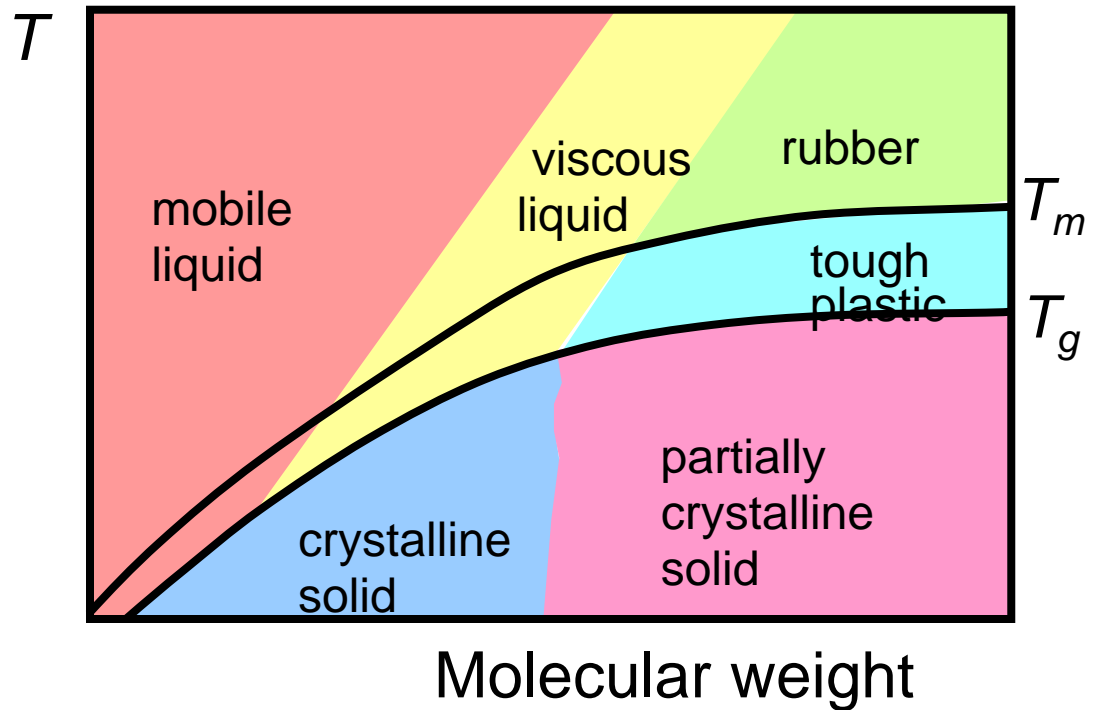


Phenol-
formaldehyde
(trifunctional)

Thermoplastics and Thermosets

- **Thermoplastics:**

- little crosslinking
- ductile
- soften w/heating
- polyethylene
- polypropylene
- polycarbonate
- polystyrene



- **Thermosets:**

- large crosslinking
(10 to 50% of mers)
- hard and brittle
- do NOT soften w/heating
- vulcanized rubber, epoxies,
polyester resin, phenolic resin

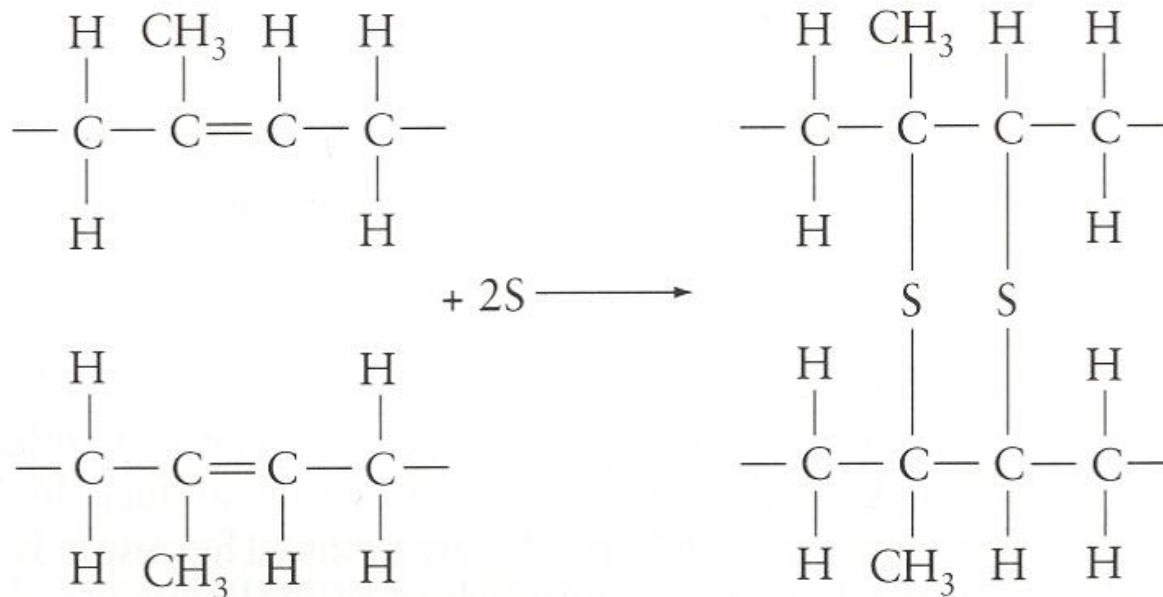
Adapted from Fig. 15.19, *Callister 7e*. (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)



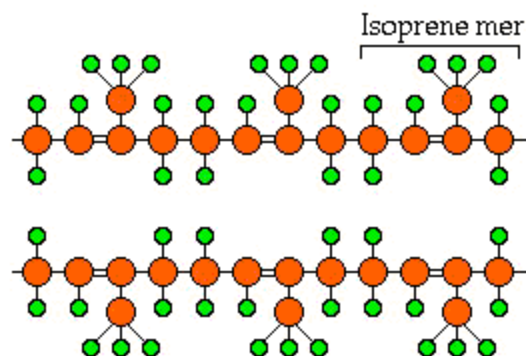
Vulcanization

In thermoset, the network is inter-connected in a non-regular fashion. Polyisoprene, the hydrocarbon that constitutes raw natural rubber, is an example. It contains unsaturated C=C bonds, and when vulcanizing rubber, sulfur is added to promote crosslinks. Two S atoms are required to fully saturate a pair of –C=C– bonds and link a pair of adjacent molecules (mers) as indicated in the reaction.

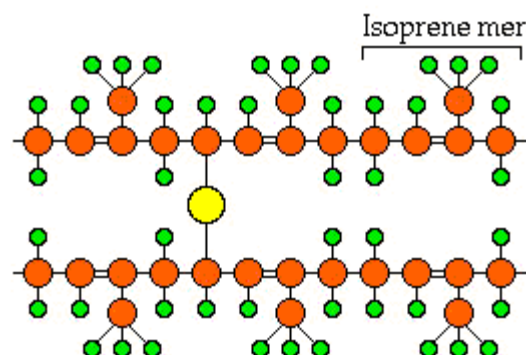
Without vulcanization, rubber is soft and sticky and flows viscously even at room temperature. By crosslinking about 10% of the sites, the rubber attains mechanical stability while preserving its flexibility. Hard rubber materials contain even greater sulfur additions.



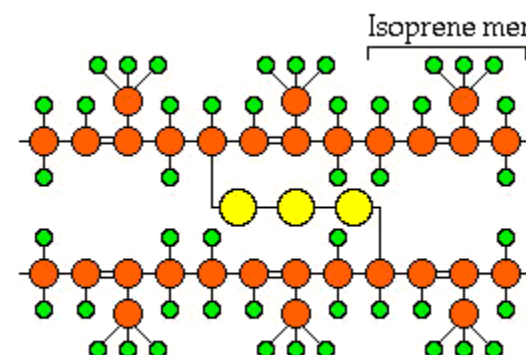
Vulcanization (cont.)



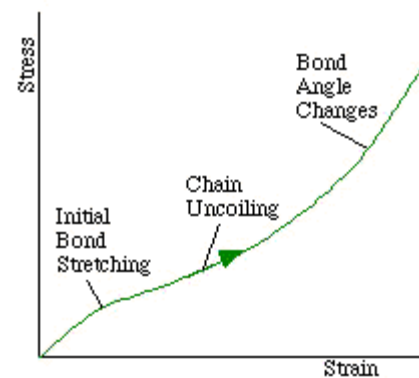
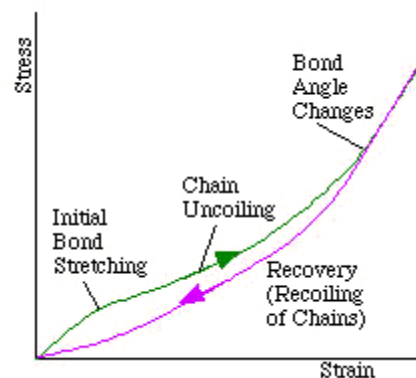
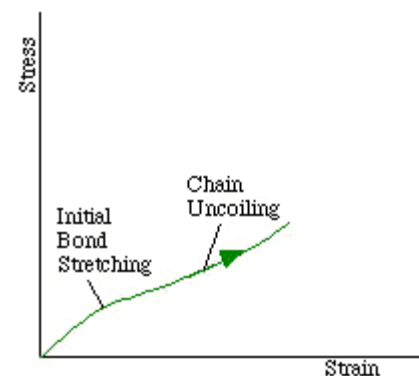
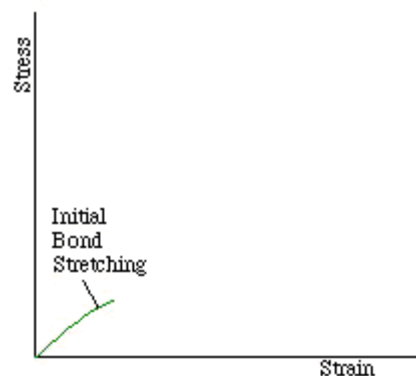
Two adjacent polyisoprene molecules...



can be joined together by a sulfur atom



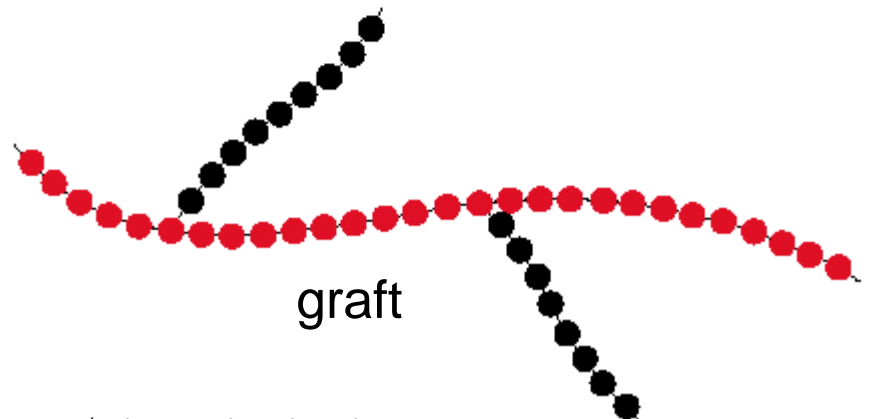
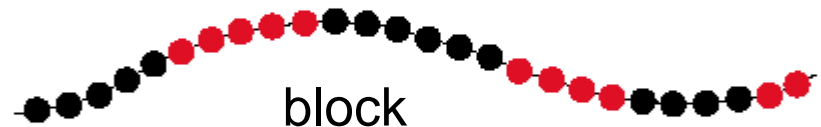
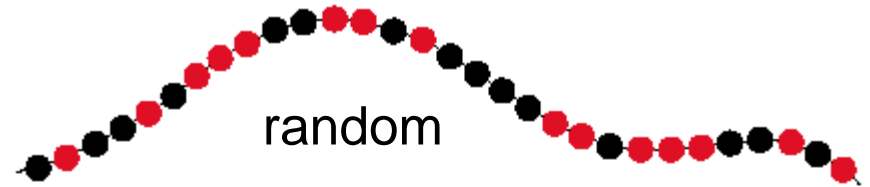
or by a series of S atoms (vulcanization).



Copolymers

**two or more monomers
polymerized together**

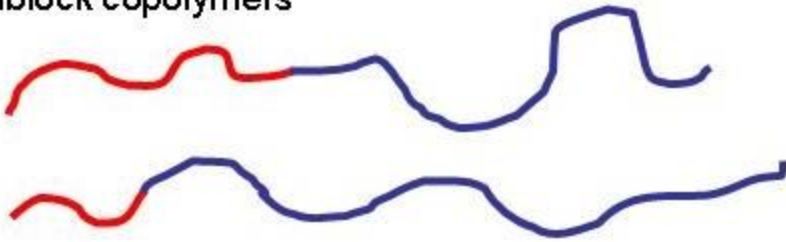
- **random** – A and B randomly vary in chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A alternate with large blocks of B
- **graft** – chains of B grafted on to A backbone



Block Copolymer Microstructures

Linear

diblock copolymers



triblock copolymers

ABA type

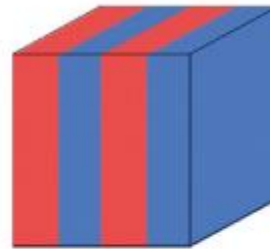


ABC type

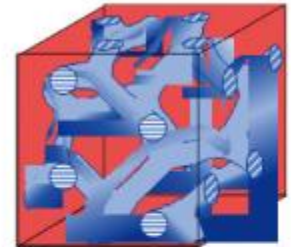
(ABCD, ...)



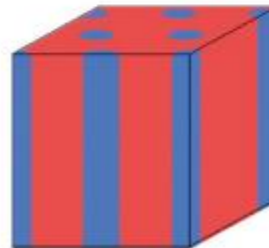
(a)



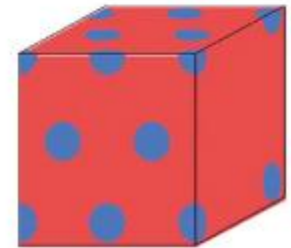
(b)



(c)



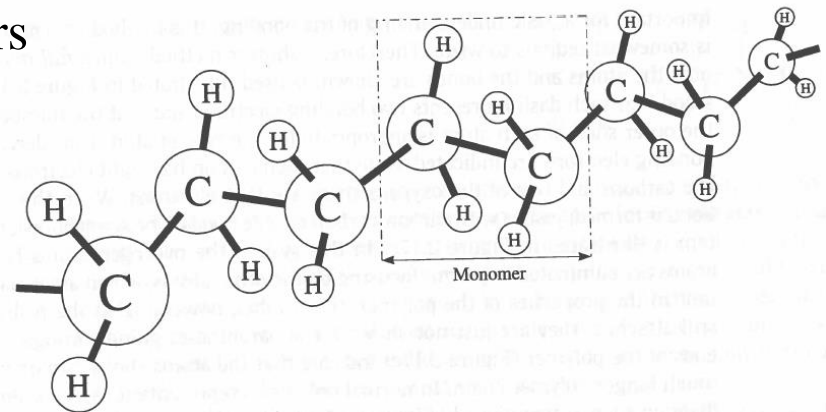
(d)



a Lamella structure. **b** Double gyroid (bicontinuous) structure. **c** Cylindrical dispersion structure. **d** Spherical dispersion structure.

Summary

- Periodic table of elements, number of protons, electrons, neutrons; atomic weight, electron orbitals, and octet rule
- Covalent bonding, bond energy, carbon atom bonding, hybridization
- Secondary Bonding: dipole hydrogen bonds, van der Waals forces
- Ionic and Metallic bonding
- Functional groups, formation of polymers
- Thermoplastics and thermosets
- Copolymers



Reading: Chapter 2 of *Plastics: Materials and Processing* by A. Brent Strong