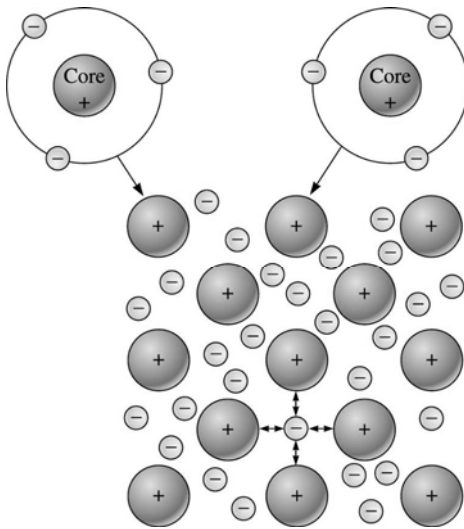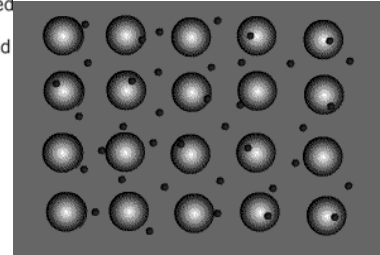# 3. The Metallic Bonding

Figure 2-9
The metallic bond forms when atoms give up their valence electrons, which then form an electron sea. The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.

Directional or Non-directional?

Core electrons are tightly held while valence electrons become delocalized

Electron mobility explains metals high electrical conductivity and thermal conductivity.
Lack of directionality explains high deformability of metals.
Homework: Investigate what the Wiedemann-Franz law is.

The Metallic Bonding (cont.)

•Delocalized electrons
•Strong Bonds
•Geometric Arrangements
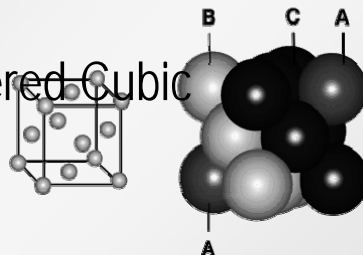•Compact Arrangements
•Deformable Solids
•Silverish Color

HCP: Compact Hexagonal
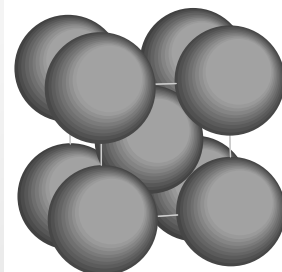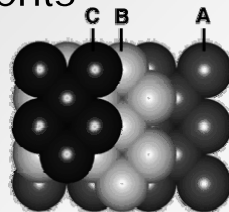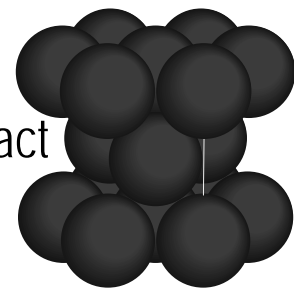
Examples:
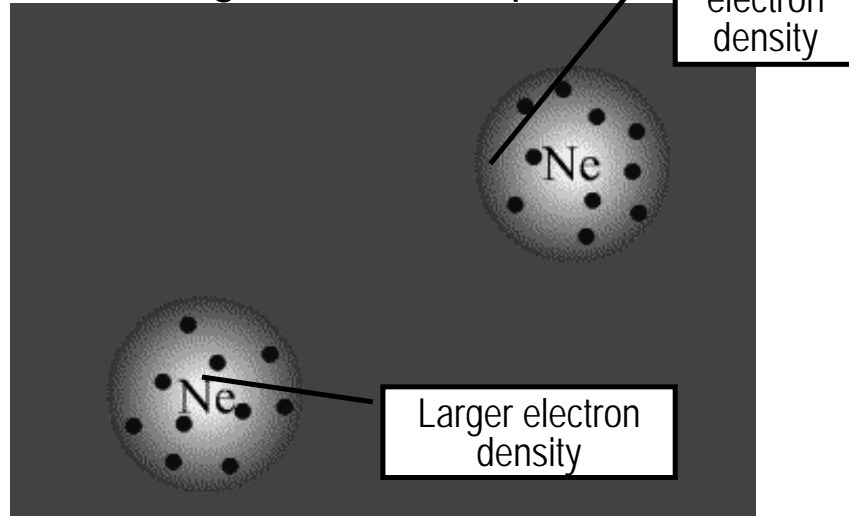**FCC**: Face-Centered Cubic

BCC: Body-Centered Cubic

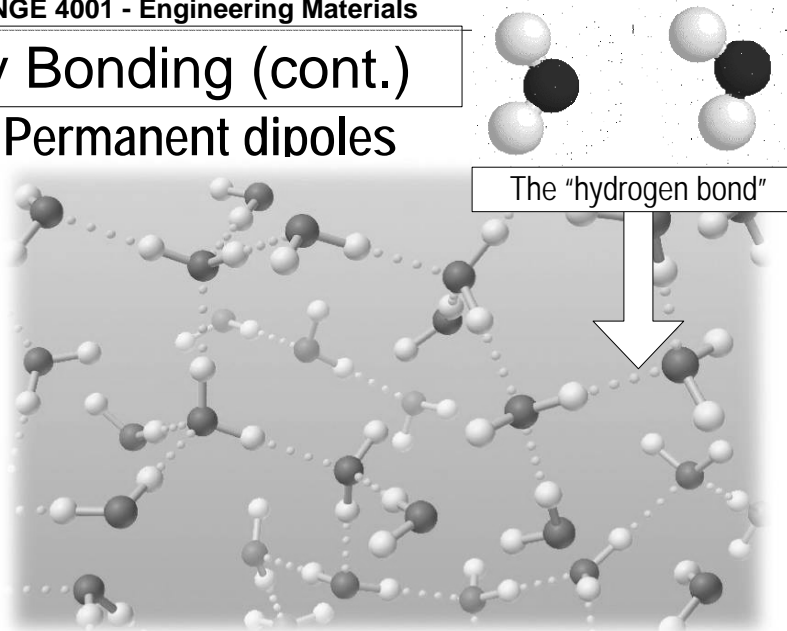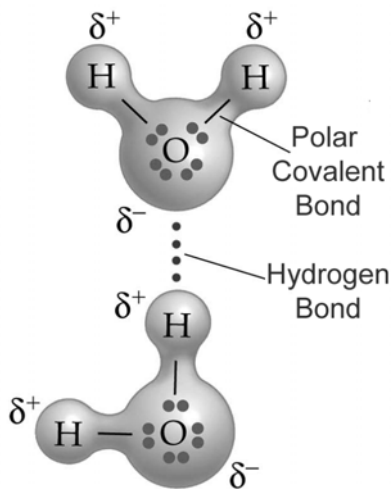# 4. Secondary Bonding (van der Waals)

Fluctuating (induced) dipoles

The van der Waals force is electrostatic

Bonding result from small quantum fluctuations in the charge which induce electric dipole moments.

Question: How would the atomic number of an inert gas affect the strength of the bond (or E_{bond})?

Smaller electron density

•Ne

Ne•

Larger electron density

Secondary Bonding (cont.)

Permanent dipoles

δ^+ δ^+

H   H

O

Polar Covalent Bond

δ^-

Hydrogen Bond

δ^+ H

δ^+ H — :O:

δ^-

The "hydrogen bond"

Strong covalent bonds bind two atoms of hydrogen (white balls) to an atom of oxygen (red balls) to form a molecule of H_2O. Hydrogen bond, glues groups of water molecules together. Hydrogen bonds are principally the electrical attractions between a positively charged hydrogen atom--which readily gives up its electron in water--and a negatively charged oxygen atom--which receives these electrons--in a neighboring molecule.

Secondary Bonding (cont.)
Permanent dipoles

Recent Discovery
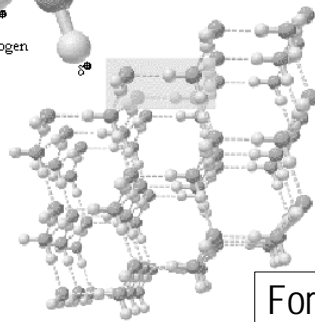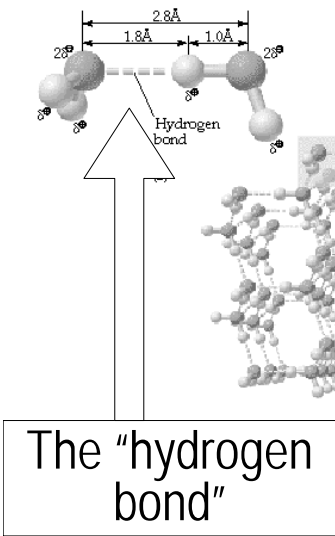
The "hydrogen bond"

Formation of ice
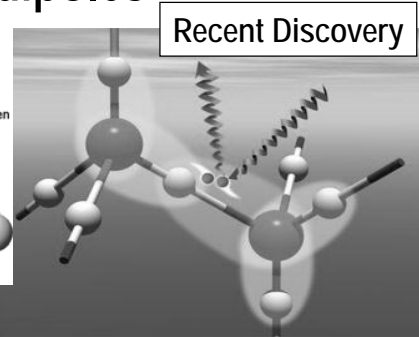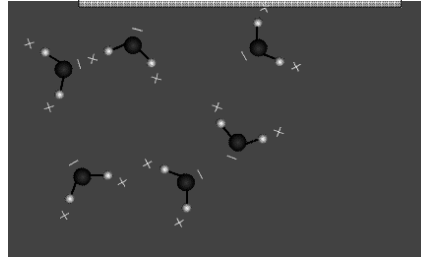
In 2001 researchers confirmed the controversial prediction of Linus Pauling that hydrogen bonds between water molecules would also be affected by the covalent bonds within the water molecules and would partially assume the identity of those bonds.

The structure of ice is regulated by the orientation of the dipoles

Ice Ih Crystal Lattice
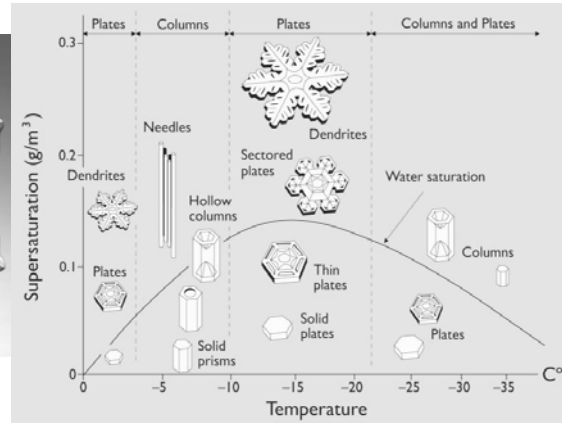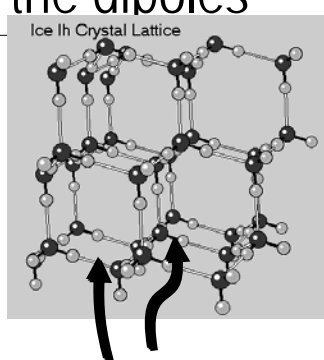
Two different types of bond intervene
This geometric pattern is due to the dipolar molecules orientation and their growth

Frost on windshields experience certain growth patterns too, called *dendrites*.

Notice the directions of ice growth. Every crystalline material tends to follow a specific spatial direction when it condenses
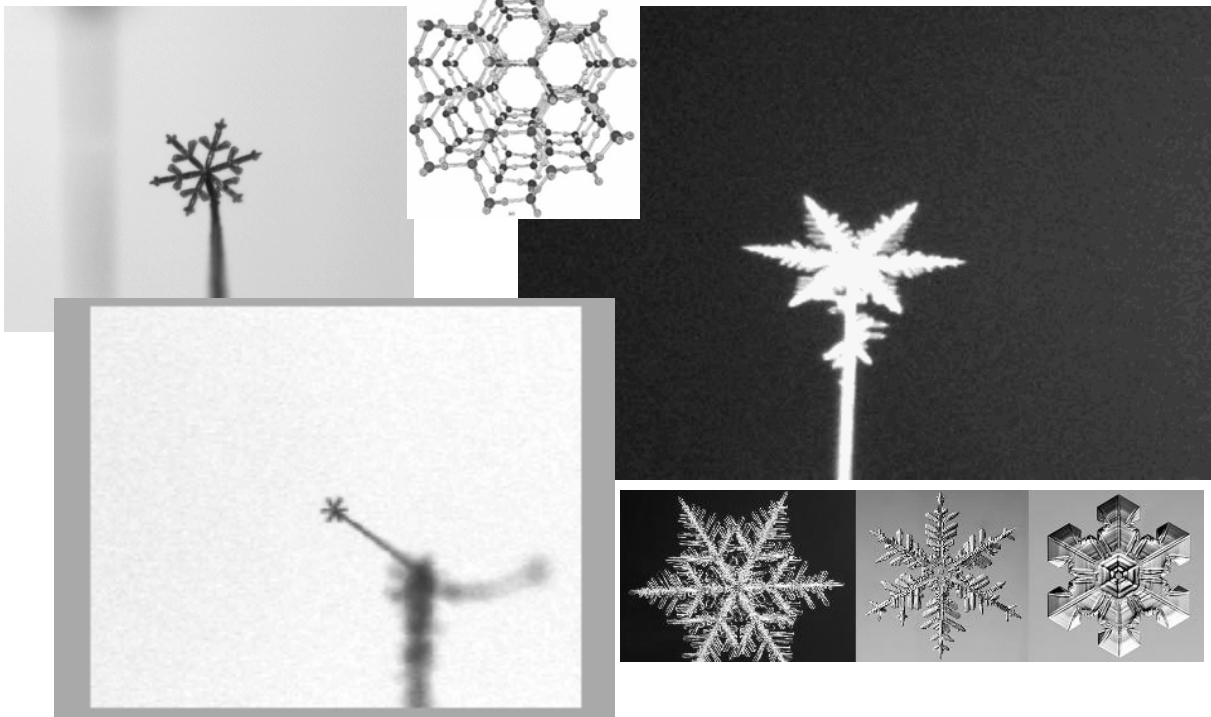

One word about "polar moment" in a covalent molecule

Consider that H is much less electronegative than C and N and answer the following:

What is the difference between these two molecules and the other three?

Polar   Polar

Nonpolar   Nonpolar   Polar

polar bonds

Boron Trifluoride
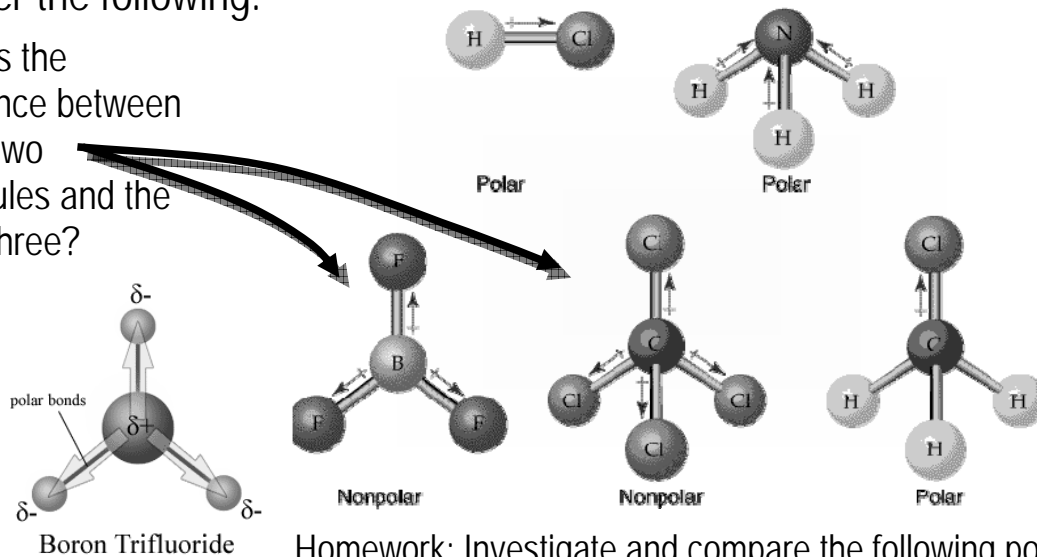
Homework: Investigate and compare the following polar molecules HF, HCl, HBr & HI

We'll use the concept of permanent dipoles to explain the diverse stregnths of polymers

Polymers (Chapter 16)

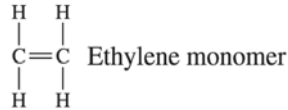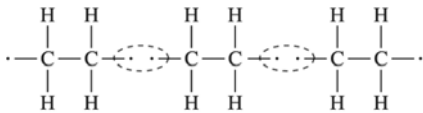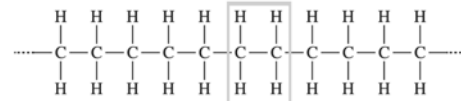- Consider the structure of ethylene with covalent π bond between C atoms:

C=C Ethylene monomer

POLYETHYLENE

- Free radical polymerization breaks the π bond to form σ bond…

109.5°

- The σ bonds link the "mer" with other "mers to form a chain.

109.5°
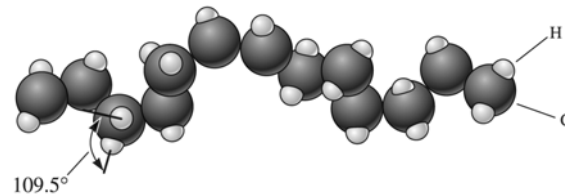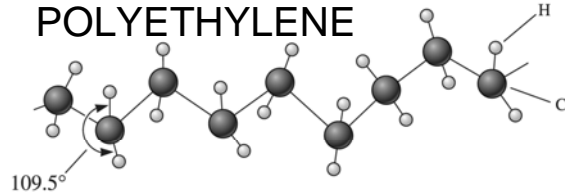
We'll use PE to define the characteristics of a THERMOPLASTIC

- The chains (macromolecules) can easily tangle up, which are somewhat untangled by applied tensile forces
- They can be amorphous (no geometric pattern) or crystalline
- They soften and melt by applying heat
- They can be easily shaped to form a part.
- They are quite recyclable
- The degree of polymerization regulates the melting point

109.5°
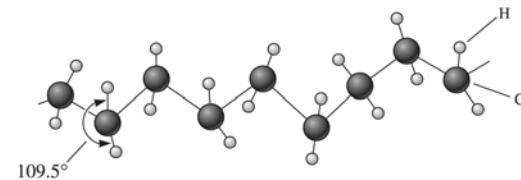
Note the formation of secondary bonds between chains

109.5°

Another examp
Polypropelene

450

(deg K)

300
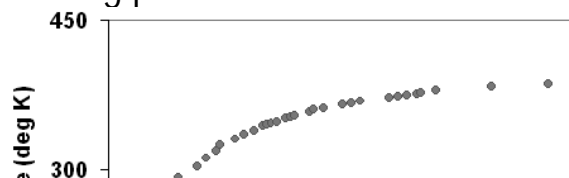
Permanent dipole concept explains the higher strength of PVC

Polyvynil Chloride (PVC) molecules

Van der Waals bonds

Note that there is an additional contribution of the stronger Van der Waals bonds to the strength of PVC compared to PE

Van der Waals bonds have to be broken

Force

As a result, PVC has a high melting point: 212°C
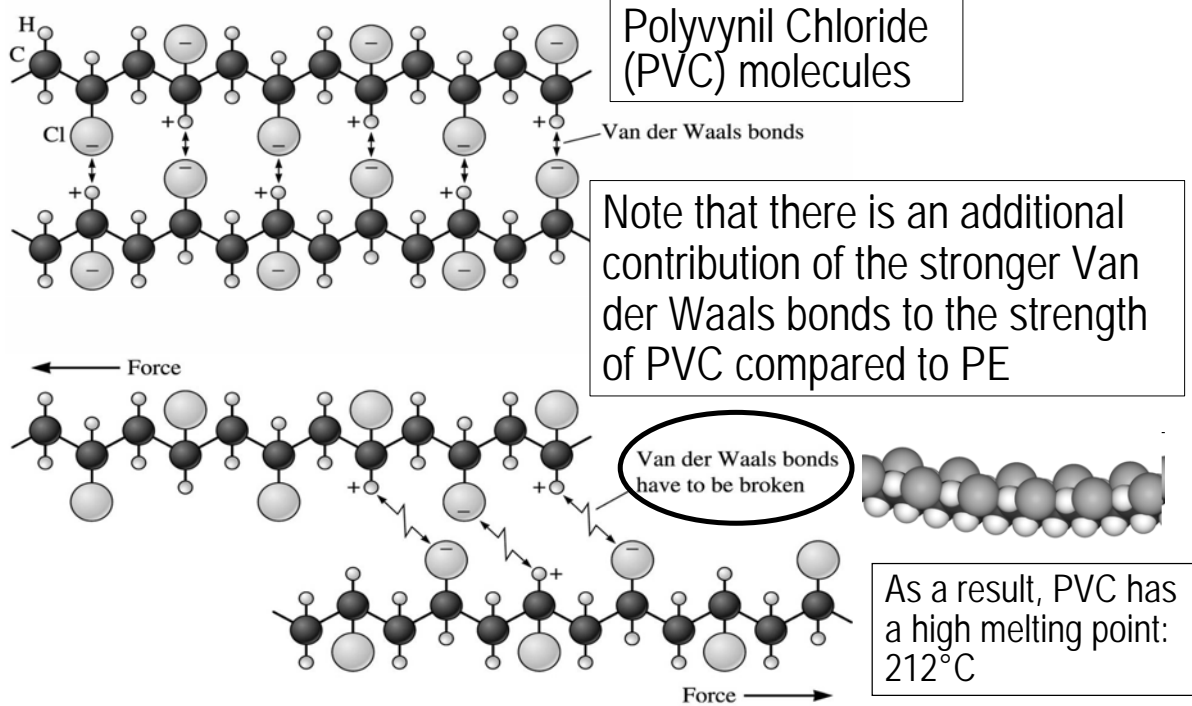
Now let's explain the main properties of a THERMOSETTING POLYMER

Consider now the hydrocarbon rubber structure

- Originally it contains double links
- Open one of them and incorporate a sulfur atom → a crosslink!

- **Now it won't melt!**
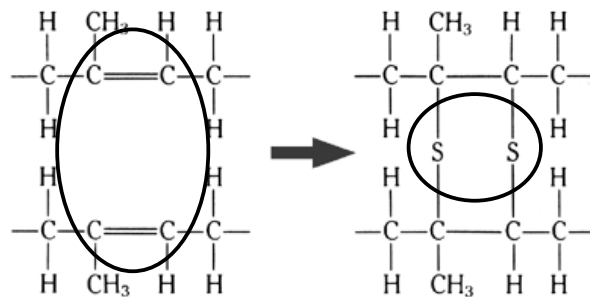
Mechanical properties of elastomers depend strongly on the nature of the crosslinks. Sec. 15.9, pages 541-543.

Stretched Rubber

More on elastomers

Vulcanization takes place simultaneously with molding. Important variables in the process:
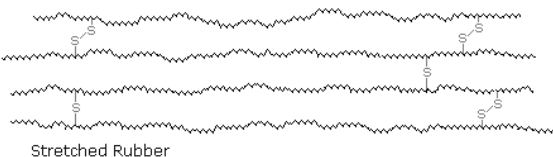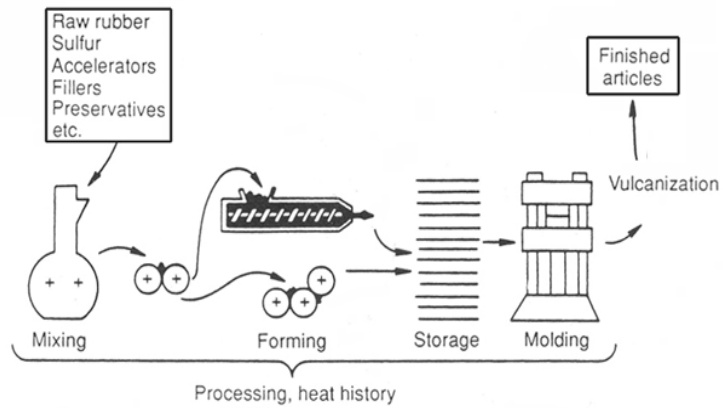- time before crosslinking starts.
- rate of crosslinking formation
- number of crosslinking formed

First, crosslinking should be retarded to give time for good mixing. Rate of crosslinking can be controlled by accelerators. Final properties depend on the number of crosslinks

Read carefully: Section 16-8 in the textbook (pages 591-596)
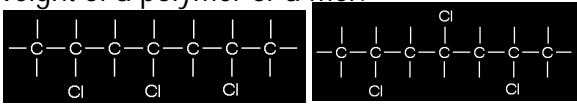
Reading Assignment 1: Polymers

Chapter 16 (pages 563-568, 572-580, 591-598)
Sections 16.1, 16.3, 16.5, 16-8 and 16.9
Solve the following example problems: 16-4 and 16-5
After reading you should be able to:

- Describe the polymerization process

- Calculate the molecular weight of a polymer or a mer.

- Define *stereoisomerism*

- Classify copolymers   Homopolymer (AAAAAAAAA); Random (CACBAABAA); Alternating (ABCABCABCA); Block (AAAABBBBCCCC); Graft

- Describe *thermoplastic elastomers.*

- Provide examples of common thermosets

- Answer the following questions (not in the book): How are melting points related to molecular weight in linear, simple polymers? Why?

Let's present a little more on the mixed nature of bonds in some metals

The strange case of the transition metals: metallic bonding + a covalent component $\rightarrow$ Look at the Melting Points!!

Remember that this tight, mixed bond is also reflected in the thermal expansion coefficients (pages 791-792)

WebElements

Melting point [K (Kelvin)] coded by intensity of red

©Mark Winter 1999 [webelements@sheffield.ac.uk]
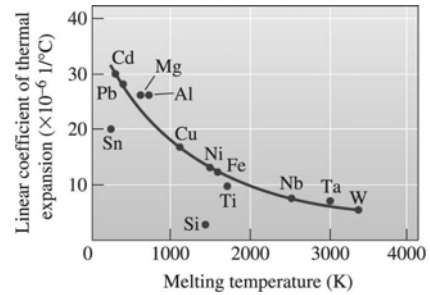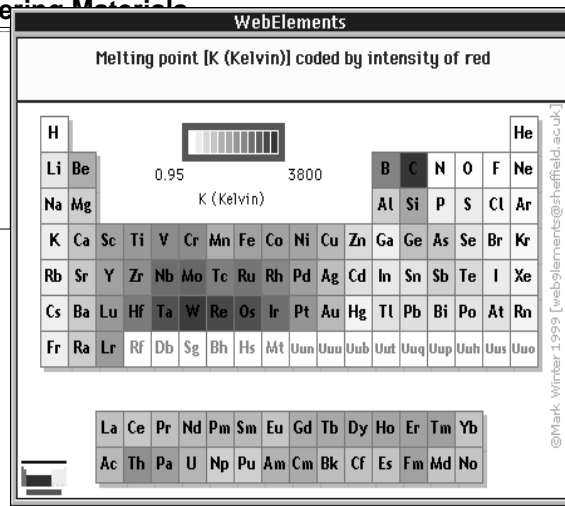
More on the mixed nature of bonds in some compounds

- Homework:

Please try to explain this image on the influence of electro-negativity difference on the percent of ionic nature of the bonds. Then find the melting points of those compounds and try to establish a trend that relates melting points and percent of ionic character
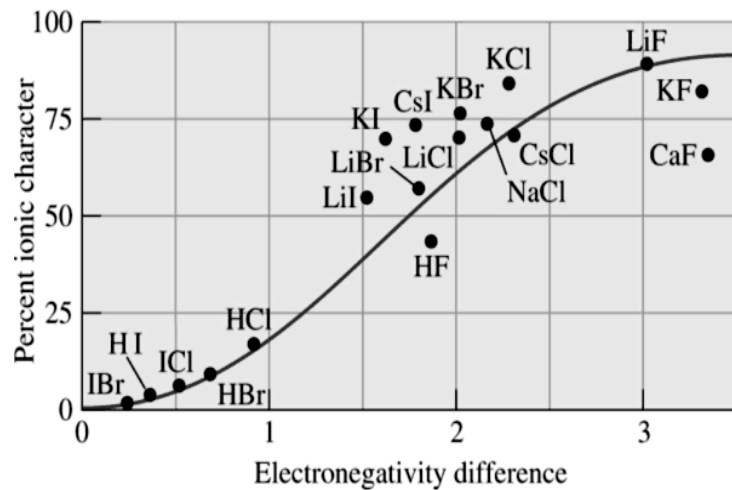
What is the nature of the rest of the bond?

Bonding energies are related not only to the nature of the bond but also to melting points of pure substances

Bonding Type	Substance	Bonding Energy		Melting Temperature (°C)
		kJ/mol (kcal/mol)	eV/Atom, Ion, Molecule	
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl_2	31 (7.4)	0.32	−101
Hydrogen	NH_3	35 (8.4)	0.36	−78
	H_2O	51 (12.2)	0.52	0

So, what does this tell us about the physical meaning of melting points?

Bonding Character of Different Engineering Materials

Material	Bonding Character	Example
Metallic	Metallic	Ferrous Alloys
Ceramics	Ionic / Covalent	Silica SiO_2
Polymers	Covalent and Secondary	Polyethylene