CHEMISTRY
FOR ENGINEERING STUDENTS

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Chapter 8
Molecules and Materials

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Chapter Objectives

- Describe the structures of graphite and diamond and explain how their properties arise from their structures.

- Describe the arrangement of atoms in the common cubic crystal lattices and calculate the packing efficiency for a lattice.

- Use band theory to describe bonding in solids.

- Draw band diagrams for metals, insulators, and semiconductors (including n- and p-type materials).

2

Chapter Objectives

- Identify a material as a metal, insulator, or semiconductor from its band diagram.

- Explain how the electrical properties of metals, insulators, and semiconductors are related to their chemical bonding.

- Identify the types of intermolecular forces likely to be most important for a particular substance.

- Explain the connection between intermolecular forces and properties such as boiling point and vapor pressure.

3

Chapter Objectives

- Describe the growth of polymers through addition and condensation reactions and predict which of these processes is likely to be important for a given monomer.

- Describe the connection between polymer properties and molecular structure.

4

Carbon

- There are three forms of the element carbon.

  - Graphite, diamond, and fullerenes.

    - Graphite and diamond have been known for a long time.

    - Fullerenes were discovered in 1985 in the form of C_{60}.

      - C_{60} was named buckminsterfullerene due to its resemblance to geodesic domes popularized by the architect Buckminster.

5

Carbon

- Carbon has long been used as material in important applications.

  - Diamond is used in drill bits and jewelry.

  - Graphite is used in pencils, as a lubricant, and as a composite material.

  - Applications for fullerenes and nanotubes are still being explored.

6

Carbon

- Phase diagrams are maps showing in which state or phase a compound or element will be most stable at a given combination of pressure and temperature.

  - The state or phase of a compound can be manipulated by changing the temperature and pressure of the compound.

7

Carbon

- Nanotubes are a type of fullerene that have remarkable properties.

  - Tensile strength significantly higher than steel.

  - Nanotubes grown with a metallic element enclosed within them show promise as wires that are one molecule wide.

- Most recently discovered form of carbon.

8

Condensed Phases - Solids

- Atoms or molecules arrange themselves into two types of solids.

  - Crystalline solids: atoms or molecules assume a regular, repeating geometric arrangement.

  - Amorphous solids: atoms or molecules assume a random arrangement.

9

Condensed Phases - Solids

- Packing efficiency in crystalline solids is the percentage of space occupied by a given arrangement.

  - The less empty space in the packing of atoms or molecules in a solid, the higher the packing efficiency.

  - The higher the packing efficiency, the higher the density of a solid.

10

Condensed Phases - Solids

- Packing of atoms into solids can be modeled with marbles.
  - Large gaps between aligned rows indicates a lower packing efficiency, 76%.
  - Smaller gaps between offset rows indicates a higher packing efficiency, 91%.

11

Condensed Phases - Solids

- Two ways to maximize packing efficiency.
  - The second layer of atoms will stack offset to the first layer of atoms to give about 74% packing efficiency.
  - The third layer can stack directly above the atoms in the first layer - hexagonal close-packing (hcp).
  - The third layer an stack directly above the hollows in the first layer - cubic close-packing (ccp).

12

2

Condensed Phases - Solids

- A unit cell is the smallest collection of atoms that displays all the features of the crystal structure.
  - Three types of cubic unit cells - simple cubic (sc) containing 1/8 each of 8 corner atoms, body-centered cubic (bcc) containing one additional atom within, and face-centered cubic (fcc) with an additional 1/2 each of 6 atoms along the faces.

Simple cubic   Body-centered cubic   Face-centered cubic
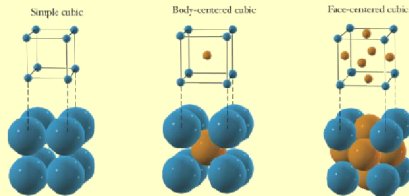
13

Calculation of Packing Efficiency

- To determine the number of complete atoms per unit cell:

$$\text{fcc} = \frac{1}{2}(\text{\# face-center atoms}) + \frac{1}{8}(\text{\# corner atoms}) = 4$$

$$\text{bcc} = (\text{\# body-center atoms}) + \frac{1}{8}(\text{\# corner atoms}) = 2$$

$$\text{sc} = \frac{1}{8}(\text{\# corner atoms}) = 1$$

- To find the total volume occupied by atoms:
  - r is the radius.

$$\text{total volume occupied by atoms} = \text{\# atoms in unit cell} \times \left(\frac{4}{3}\pi r^3\right)$$

14

Calculation of Packing Efficiency

- To find the volume of the unit cell in terms of radius:

$$V = a^3 \text{ (where } a \text{ is the edge length of the unit cell)}$$

$$a_{\text{fcc}} = \left(2\sqrt{2}\right)r; \quad a_{\text{bcc}} = \frac{4}{\sqrt{3}}r; \quad a_{\text{sc}} = 2r$$

- To calculate packing efficiency:

$$\text{Packing efficiency} = \frac{\text{volume of atoms in unit cell}}{\text{total volume of atoms in unit cell}} \times 100$$

15

Example Problem 8.1

- Show that the packing efficiency of the face-centered cubic structure is 74%.

16

Condensed Phases - Solids

- Coordination number is the number of atoms immediately adjacent to any given atom.

  - Simple cubic has a coordination number of 6.

  - Body-centered cubic has a coordination number of 8.

  - Close-packed structures have a coordination number of 12.

17

Condensed Phases - Solids

- As coordination numbers increase, each atom in the lattice interacts with more neighbor atoms.

  - The attractive forces for these interactions hold the crystal together.

  - Close-packed structure, with a coordination number of 12, is one of the most common crystal structures.

18

Condensed Phases - Solids

- Preferred crystal lattice for the solid phase of each element.
  - There is no discern-able pattern as to which crystal structure is most likely for any particular metal.

19

Condensed Phases - Solids

- The properties of a solid are related to its crystal structure.

  - Each carbon atom in diamond is covalently bonded to four neighboring atoms.

    - Diamond is an inordinately hard material.

  - The carbon atoms in graphite are covalently bonded into flat sheets.

    - Graphite sheets can slide past each other.

20

Condensed Phases - Solids

- The carbon atoms in diamond are joined by covalent bonds in a tetrahedral geometry.
  - The large number of covalent bonds in diamond explains the inordinately high strength of diamond.
- The carbon atoms in graphite are bonded together in sheets.
  - The graphite sheets are held together by much weaker forces.

21

Bonding in Solids: Metals, Insulators, and Semiconductors

- Properties of metals can be explained by bonding in metals.

- Metals are:

  - Malleable - worked into useful shapes or foils.

  - Ductile - pulled into wires

  - Good conductors of heat and electricity.

22

Models of Metallic Bonding

- The bonding in metals cannot be explained in terms of ionic or covalent bonding.

  - There is little electronegativity difference from element to element so metals and alloys do not form ionic bonds.

  - The outermost subshells are not filled, so a large number of covalent bonds would be needed to satisfy the octet rule.
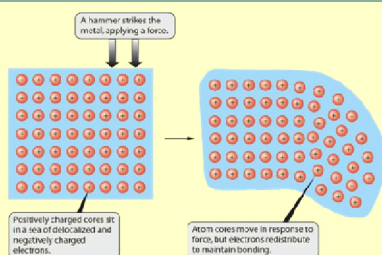
23

Models of Metallic Bonding

- The sea of electrons model is the first and simplest qualitative explanation of metallic bonding.

  - The valence electrons are delocalized and move freely throughout the solid.

  - Explains malleability, ductility, and conductivity properties of metals.

24

4

Models of Metallic Bonding

- When a force is applied to a metal, the positively charged cores respond to the stress, deforming the metal.
- The free flow of electrons maintains the bonding throughout the process.

25

Models of Metallic Bonding

- Band theory is a quantitative model of bonding in solids.

  - The wave functions of the valence electrons interact with each other.

  - Bonding molecular orbitals result from constructive interference.

  - Antibonding molecular orbitals result from destructive interference.

26

Models of Metallic Bonding

- The number of molecular orbitals formed equals the number of atomic orbitals involved.

  - For every bonding molecular orbital formed, one antibonding molecular orbital is also formed.

  - For odd number of bonding atoms, a nonbonding molecular orbital is formed.

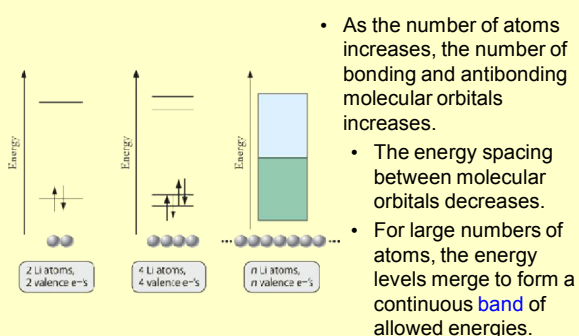 - The molecular orbitals formed belong to the entire set of atoms

27

Models of Metallic Bonding

- Energies of the molecular orbitals are related to the energy of the original atomic orbitals.

  - Bonding molecular orbitals are lower energy.

  - Antibonding molecular orbitals are higher energy.

28

Models of Metallic Bonding

- As the number of atoms increases, the number of bonding and antibonding molecular orbitals increases.
  - The energy spacing between molecular orbitals decreases.
  - For large numbers of atoms, the energy levels merge to form a continuous band of allowed energies.

29

Band Theory and Conductivity

- Electrons fill the lowest energy band first.

- The energy difference between the filled and empty bands determines the electrical properties of the bulk material.

- The band populated by valence electrons is the valence band.

- The empty band above the valence band is the conduction band.

- The energy difference between the valence and conduction band is the band gap.

30

5

Band Theory and Conductivity

- Current flows when electrons move from the valence band to the conduction band.

  - Conductors have small band gaps. A very small amount of energy is required to move electrons to the conduction band.

  - Insulators have large band gaps. A large amount of energy is required to move electrons to the conduction band.

  - Semiconductors have band gap intermediate of conductors and insulators.

31

Band Theory and Conductivity

- Band gap diagrams of a conductor, semiconductor, and insulator.

32

Semiconductors

- Electrical conductivity of semiconductors can be modified via doping.

  - Doping - adding trace amounts of an element to a substance to modify its properties.

    - n-type: prepared by doping with a valence electron rich element; "negative"

    - p-type: prepared by doping with a valence electron deficient element; "positive"

33

Semiconductors

- n-type semiconductors
  - The extra valence electron fills the donor level, which is just below the conduction band.
  - Little energy is required to promote the donor level electron to the conduction band.
- p-type semiconductors
  - The lack of valence electrons creates an acceptor level, just above the valence band.
  - Little energy is required to promote a valence band electron to the acceptor level.
  - The vacancies in the valence band are referred to as holes.

34

Semiconductors

- Formation of n-type doped silicon.
  - Doping with phosphorus introduces an extra valence electron.
  - The extra electron fills the donor level, which lies close to the conduction band.

35

Semiconductors

- Formation of a p-type doped silicon.
  - The dopant has fewer than 4 valence electrons.
  - An acceptor level slightly higher than the valence band is created.
  - Aluminum is a common p-type dopant.

36

Example Problem 8.2

- Which kind of material (n- or p-type) would result if pure germanium was doped with:
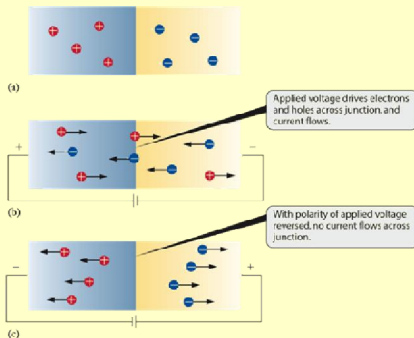
  - gallium

  - arsenic

  - phosphorus

37

Semiconductors

- A p-n junction can be constructed from p-type and n-type material.

  - The flow of electrons across the junction is easily regulated by applying voltage.

  - Current flows across the junction when the negative pole of a battery is connected to the n-type material.

  - Current does not flow across the junction when the negative pole is connected to the p-type material.

  - Important in solid state electronics.

38

Semiconductors

Applied voltage drives electrons and holes across junction and current flows.

With polarity of applied voltage reversed, no current flows across junction.

- A p-n junction can act as a simple switch when the correct voltage polarity is applied.

39

Intermolecular Forces

- Intermolecular forces - the attractive and repulsive forces between molecules.

  - The attractive and repulsive intermolecular forces are weak in comparison to bonding forces.

  - Intermolecular forces are largely responsible for determining the structure and properties of condensed phases.

  - The principle of minimization of energy applies here as well.

40

Dispersion Forces

- Dispersion forces are common to all molecules.

  - Also called London forces.

  - Also referred to as instantaneous dipole-induced dipole forces.

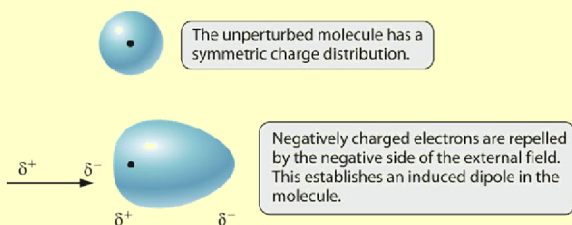 - Dipoles exist for two oppositely charged points separated by some distance.

41

Dispersion Forces

- An instantaneous dipole occurs when a fluctuation in electron density for an atom or molecule produces a dipole.

  - Instantaneous dipoles are short-lived and constantly forming and disappearing.

- An induced dipole is created when an external electric field forces a dipole to exist.

  - A permanent dipole or an instantaneous dipole is the source of the external electric field.

42

Dispersion Forces

The unperturbed molecule has a symmetric charge distribution.

δ^+ — δ^-

Negatively charged electrons are repelled by the negative side of the external field. This establishes an induced dipole in the molecule.

δ^+ δ^-

- An external electric field distorts the electron density around an atom or dipole, inducing a dipole.

43

Dispersion Forces

- Individual dispersion forces are very weak.

  - The sum of dispersion forces over an Avogadro's number of atoms results in a significant amount of energy.
  - Dispersion forces hold many liquids and solids together.

- The strength of a dispersion force can be estimated from the polarizability of a molecule.
  - Polarizability is a measure of how susceptible a molecule's electron density is to perturbation by external electric fields.
  - Large molecules are more polarizable than smaller molecules and experience stronger dispersion forces.

44

Dipole-Dipole Forces

- Dipole-dipole forces are the attractive and repulsive forces for molecules with a permanent dipole.

  - The charge at the poles of a dipole is seldom more than a fraction of the charge on an electron, making these forces weaker than a chemical bond.

  - Molecules with larger dipoles have stronger dipole-dipole forces.

  - Dipole-dipole forces are typically stronger than dispersion forces.

45

Dipole-Dipole Forces

Attractive interactions

Repulsive interactions
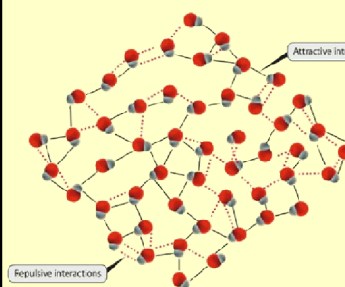
- Dipole-dipole forces for 50 polar molecules.

  - At any given time, the number of attractive interactions is greater than the number of repulsive interactions.

46

Hydrogen Bonding

- Hydrogen bonds are a special case of dipole-dipole forces.

  - Hydrogen bonds are especially strong compared to dipole-dipole forces.

  - Hydrogen bonds occur only in compounds containing hydrogen covalently bonded to the highly electronegative elements F, O, or N.

    - The strong dipole created in these types of covalent bonds creates a strong dipole-dipole interaction with similar bonds.

47

Intermolecular Forces

- Intermolecular forces are weak compared to the average covalent bond.

- The large number of intermolecular forces make intermolecular forces a key factor in determining the bulk properties of materials.
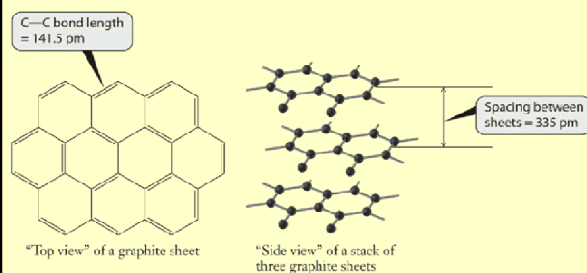
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8

Example Problem 8.3

- Which type(s) of intermolecular forces need to be overcome to convert each of the following liquids to gases?

    - CH_4

    - CH_3F

    - CH_3OH

49

Intermolecular Forces

- Carbon atoms <u>within</u> a graphite sheet held together by covalent bonds.
- Intermolecular forces hold graphite sheets together.

50

Condensed Phases - Liquids

- Liquids are also a condensed phase.

    - Particles in condensed phases are in constant contact.

    - Every particle in a solid vibrates around a fixed position.

    - Every particle in a liquid is free to constantly move with respect to other particles.

51

Vapor Pressure

- Vapor pressure - the gas phase pressure of a substance in dynamic equilibrium with the pure liquid in a pure substance.

    - Vapor pressure is a characteristic property of a particular substance at a particular temperature.

52

Vapor Pressure

- There is a distribution of kinetic energies for liquids at a given temperature.

    - Liquid molecules at the surface of the liquid with sufficient kinetic energy will pass into the gas phase.

    - Vapor pressure increases with temperature.
        - Liquids with strong intermolecular forces have lower vapor pressures.
        - Liquids with high vapor pressures are described as volatile.

53

Vapor Pressure

- To measure the vapor pressure of a solid or a liquid, the system must reach equilibrium.
    - The equilibrium is a dynamic equilibrium.
    - The rate of evaporation equals the rate of condensation.
    - The amount of gas and liquid does not appear to change.

54

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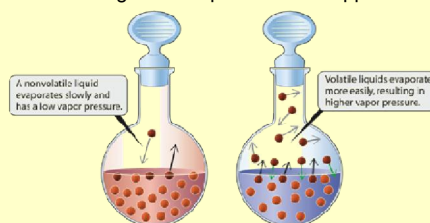
Boiling Point

- Normal boiling point - temperature where the vapor pressure of a liquid equals atmospheric pressure.
- The stronger the intermolecular forces in a liquid, the lower the vapor pressure, thus, the higher the boiling temperature.

55

Boiling Point

- Vapor pressures at 295 K for various substances.

- Substances with weaker attractive forces have higher vapor pressures and lower normal boiling points.

- At lower atmospheric pressure, such as in mountainous regions, observed boiling points are lower.

56

Surface Tension

- Liquid molecules at the surface of a liquid experience fewer attractive forces than the molecules in the bulk material.

  - Surface tension is a liquid's response to the imbalance in attractive forces and the tendency to minimize energy.

  - Liquids form spherical shapes.

  - Spherical shapes have the greatest volumes with the least amount of surface area.

  - Stronger attractive forces result in greater surface tension.

57

Surface Tension
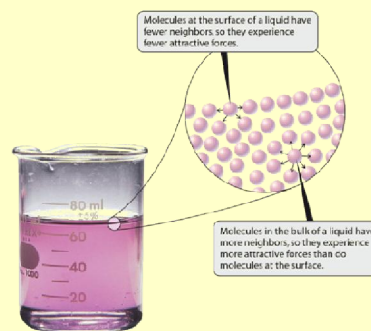
- Surface tension is the result of molecules at the surface of a liquid experiencing fewer intermolecular forces than liquid molecules inside the bulk liquid.

58

Surface Tension

- The interaction between a liquid and the surface of a solid depends on two types of attractive forces.

  - Cohesion forces are liquid-liquid interactions.
  - Adhesion forces are liquid-solid interactions.
  - The relative strengths of the two forces dictate the shape of a liquid's meniscus.
    - Strong adhesion forces and weaker cohesion forces result in a concave meniscus.
    - Weak adhesion forces and stronger cohesion forces result in a convex meniscus.

59

Surface Tension

- The concave meniscus for water results from stronger adhesive forces.

- The convex meniscus for mercury (shown in the figure) results from stronger cohesive forces.

60

10

Polymers

- **Polymers** are giant molecules constructed by sequentially stringing together smaller molecules called **monomers**.

  - Physical properties of polymers can be adjusted by modifying the monomers used, reaction types, and catalysts used to prepare the polymer.

- Monomers containing one or more double bonds undergo **free radical addition reactions** to form **addition polymers**.

  - Addition polymerization occurs through initiation, propagation, and termination steps.

61

Addition Polymers

- **Initiation**: a free radical (species with an unpaired electron) is produced.

- **Propagation**: the free radical attacks the double bond of the monomer to break the double bond, leaving a single bond; a new free radical containing the monomer results.
  - The free radical propagates itself by reacting with more monomers.

- **Termination**: a free radical reacts with another free radical.
  - Also called chain termination.
  - Termination is a random event, not all polymer chains will have the same length.

62

Addition Polymers

- Initiators, such as an organic peroxide, produce free radicals upon heating.

- Each propagation step adds another monomer to the chain.

- Termination occurs when two radicals combine and polymer chain growth ends.

63

Addition Polymers

- The distribution of polymer lengths and molar masses are described in terms of degree of polymerization.

  - Average number of repeating units in the polymer.

$$\text{Degree of polymerization} \ = \ \frac{\text{molar mass of polymer}}{\text{molar mass of monomer}}$$

64

Addition Polymers

- Polymer properties can be tailored.

  - Choose appropriate monomer.

  - Modify degree of polymerization.

  - Control the linking of monomers.

65

Addition Polymers

- The choice of propylene gives rise to different types of polypropylene.

  - Polypropylene resembles ethylene, but one H has been replaced with a methyl ($-CH_3$) group.

  - The methyl group attaches to the carbon backbone in three different ways.

66

Addition Polymers

- Isotactic - all methyl groups are arranged on the same side of the polymer chain.

- Syndiotactic - methyl groups alternate systematically from one side of the polymer chain to the other.

- Atactic - methyl groups are arranged randomly along the polymer chain.

- Arrangement of methyl groups impacts the properties of the polymer.

67

Addition Polymers

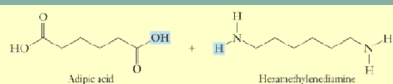- Monomers can link together in different ways.
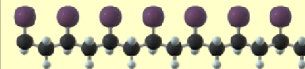
  - Isotactic

  - Syndotactic

  - Atactic

- Isotactic and syndiotactic polymers generally lead to more predictable and controllable properties.

68

Condensation Polymers

- Condensation polymers are formed when functional groups on the monomers react, linking the monomers together and producing water or another small molecule.
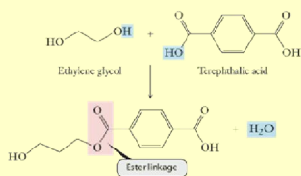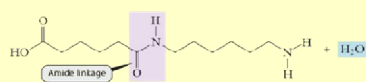
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Example Problem 8.4

- Each of the following monomers or pairs of monomers can undergo condensation polymerization reactions. Draw the structures showing the repeat units and linkages in each of the resulting polymers.
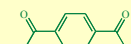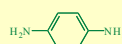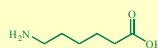
70

Copolymers

- Copolymers are made up of more than one type of monomer.
  - Nylon and Dacron are examples.
  - The order in which the monomers are arranged impacts the properties of a polymer.

  - Alternating copolymers - monomers arranged in a regular, alternating series.
  - Block copolymer - regions where a single monomer is repeated, interspersed with other regions where a different monomer is repeated.
  - Random copolymers - monomers are arranged randomly
  - Graft copolymer - monomers of different polymers are branched from a backbone of a different polymer.

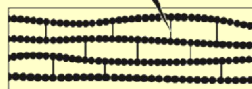71

Copolymers

- The four types of copolymers.

72

12

Physical Properties

- Thermoplastic polymers melt or deform on heating.

- Thermosetting polymers maintain their shape and strength when heated.

In a thermoplastic polymer, chains interact only through intermolecular forces.

In thermosetting polymers, chains are tied together by actual chemical bonds.

73

Polymers and Additives

- Additives are added to polymers to modify polymer properties.

  - Pigment to impart color.

  - Plasticizers to increase flexibility.

 - Antistatic agents, fillers, fire retardants, and light and heat stabilizers.

74

The Invention of New Materials

- New materials are created through a systematic approach and good fortune.

  - Fullerenes were discovered as an unusual result from an experiment with small atom clusters.

  - High temperature superconductivity was discovered using the heat-and-beat method of synthesis.

  - Conducting polymers can be designed with a polymer backbone of alternating single and double bonds.

75

The Invention of New Materials
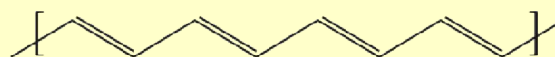
- Poly(acetylene), a prototypical example of a conducting polymer.

  - Conductivity arises from the alternating single and double bonds.

  - Conductivity can be enhanced via doping.

76